Electron Interactions With Plasma Processing Gases: An Update for CF_4, CHF_3, C_2F_6, and C_3F_8

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An update of electron–collision cross sections and electron transport parameters is presented for CF_4, CHF_3, C_2F_6, and C_3F_8. © *1999 American Institute of Physics and American Chemical Society.* [S0047-2689(99)00104-X]

Key words: attachment, CF_4, C_2F_6, C_3F_8, CHF_3, cross sections, dissociation, electron interactions, ionization, scattering, transport coefficients.

Contents

List of Tables

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List of Figures

1. Introduction

In 1996, a program was begun at the National Institute of Standards and Technology (NIST) to develop a database of low-energy electron collision cross sections and transport coefficients for plasma processing gases relevant to the semiconductor industry. Since our reviews of the available data on low-energy electron interactions with CF_4,[1] CHF_3,[2] C_2F_6,[3] and C_3F_8,[4] significant new data have appeared in the literature which require updating our initial reports on these four molecules. This is done in this paper. Where necessary, new values of preferred data are presented. Only cross sections and transport coefficients for which new data have been published are discussed in this paper. For a complete review of electron interaction data for a particular gas, and for a complete listing of preferred data, this article must be used in conjunction with the original reviews.[1–4]

Our method and criteria for determining recommended data have evolved somewhat since the beginning of this effort in 1996. Most significant is the designation of two levels of preferred data, "recommended" and "suggested," which was formalized in our review paper on C_2F_6.[3] Our present protocol for determining which data are the most reliable is as follows.

For our work performed at NIST, "recommended" or "suggested" values of cross sections and transport coefficients are determined, where possible, for each type of cross section and coefficient for which data exist. These values are derived from fits to the most reliable data, as determined by the following criteria: (i) the data are published in peer reviewed literature; (ii) there is no evidence of unaddressed errors; (iii) the data are absolute determinations; (iv) multiple data sets exist and are consistent with one another within combined stated uncertainties over common energy ranges; and (v) in regions where both experimentally and theoretically derived data exist, the experimental data are preferred. Data that meet these criteria are selected for each cross section or coefficient and a fit to these data is designated as our recommended data. The recommended data represent the best current estimates for the cross sections and coefficients for each of these processes.

A cross section or coefficient may be designated as suggested, if the available data are deemed to be reasonable but do not meet all of the criteria listed above. For example, results from a single measurement may be designated as suggested if a second, independent, confirming measurement is unavailable. In cases where no reasonable data exist, or where two or more measurements are in an unresolved contradiction, the raw data are presented for information and no recommendation is made. At the present time, we make no use of data presented on the Internet unless these have been also published in the archival literature or in a formal report of a scientific institution or conference.

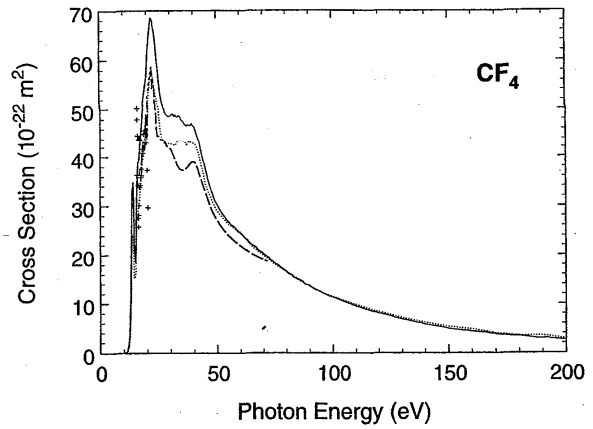

FIG. 1. Photoabsorption cross sections of CF_4: (– –, +, ▲) photoabsorption data from Refs. 1 and 7; (—, ···) differential oscillator strength measurements from Refs. 5 and 6, respectively.

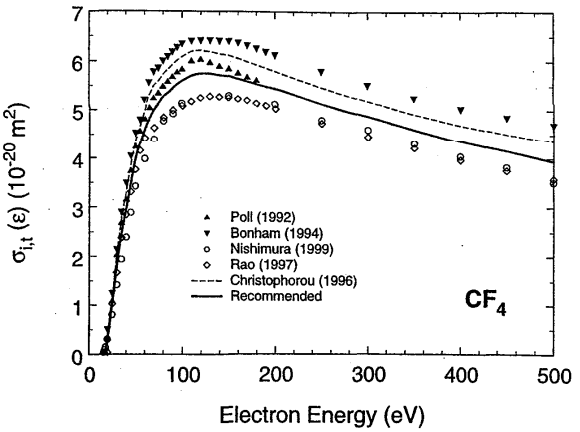

FIG. 2. Total ionization cross section, $\sigma_{i,t}(\varepsilon)$, for CF_4 updated with the inclusion of the recent data of Rao and Srivastava, Ref. 29 (◇) and Nishimura *et al.*, Ref. 30 (○). Also shown in the figure are the experimental data previously used to determine the recommended values (▲, Ref. 31; ▼, Refs. 32 and 33), and the previously recommended $\sigma_{i,t}(\varepsilon)$ from Ref. 1 (– – –). The new recommended cross section based on the four sets of experimental data is shown as the solid line.

2. Update for CF_4

The previously reported values of the recommended data for CF_4 were reasonably complete. However, significant studies of this molecule continue due to its high technological significance.

2.1. Basic Properties

Regarding the basic properties of the CF_4 molecule, absolute differential oscillator strengths, $df/d\epsilon$, for the valence–shell electronic excitation have been recently measured by Au *et al.*[5] from 10 to 200 eV. These data have been converted to photoabsorption cross sections $\sigma_{pa}(\epsilon)$ as a function of photon energy ϵ via the relationship[5]

$$\sigma_{pa}(10^{-22}\,m^2) = 109.75\, df/d\epsilon \quad (eV^{-1}),$$

and are plotted in Fig. 1 along with similar earlier data by Zhang *et al.*,[6] and earlier photoabsorption data.[7] The data of Au *et al.* and Zhang *et al.* are more detailed and cover a much broader energy range than the photoabsorption measurements. While the recent measurements by Au *et al.* lie somewhat higher than the previous data, all measurements are consistent in showing the large photoabsorption maximum around 20 eV. The significance of the data in Fig. 1 within the purpose of the present review is that $\sigma_{pa}(\epsilon)$ represents the total electron-impact excitation cross section for optically allowed transitions of this molecule and reflects the distribution of electron-energy losses for sufficiently energetic electrons.

In addition, Au *et al.*[5] reported two new values for the static electric-dipole polarizability of CF_4 equal to $28.42 \times 10^{-25}\,cm^3$ and $28.24 \times 10^{-25}\,cm^3$ (see also Ref. 8 for a recent calculation of the static and dynamic polarizabilities of CF_4).

In our earlier paper[1] we indicated that Bonham and Bruce[9] reported that the average value of the ionization threshold energy of CF_4 obtained from a number of electron-impact studies is 15.9 eV. Consistent with this high value are the results of electron impact,[10] photoelectron,[11] and photoabsorption[6] studies which give a value of 16.20 eV. It was also indicated in Ref. 1 that Bonham and Bruce[9] gave the value of 14.7 eV for the zero translational energy threshold of the reaction $CF_4 + e \rightarrow CF_3^+ + F + 2e$. Two recent studies[12,13] on the heat of formation of CF_3^+ put the threshold energy (adiabatic) for the process $CF_4 + \text{energy} \rightarrow CF_3^+ + F + e$ at 14.28 eV[13] and 14.67 ± 0.04 eV ($T = 0$ K),[12] in support of similar earlier values [14.2 ± 0.1 eV ($T = 298$ K),[14] 14.24 ± 0.07 eV ($T = 298$ K),[15] $\leq 14.7 \pm 0.3$ eV ($T = 0$ K)[16]]. These values are clearly consistent with the zero translational energy threshold of 14.7 eV, and since the threshold energy for the formation of CF_3^+ may be taken as the lower energy for ionization of CF_4, at room temperature the adiabatic and vertical ionization energies of CF_4 may be identified, respectively, with the values of 14.7 and 16.2 eV. It should be mentioned also that Jarvis and Tuckett[17] have recently put the adiabatic ionization energy of the CF_3 radical at $\leq 8.8 \pm 0.2$ eV.

It should be noted as well that while all ionization processes for the CF_4 molecule are believed to be dissociative,[1] weak metastable CF_4^+ ion signals have been observed[18–20] using mass spectrometers. The CF_4^+ ion has also been observed to be formed by collisions of electrons with CF_4 clusters.[21]

2.2. Electron Collision Cross Sections for CF_4

2.2.1. Total Electron Scattering Cross Section, $\sigma_{sc,t}(\varepsilon)$, for CF_4

In our earlier paper,[1] the recommended total electron scattering cross section $\sigma_{sc,t}(\varepsilon)$ above 1 eV was derived from three independent measurements[22–24] all of which are in good agreement, thus making $\sigma_{sc,t}(\varepsilon)$ in this energy range a well established cross section. Recent measurements of $\sigma_{sc,t}(\varepsilon)$ by Sueoka *et al.*,[25,26] in the electron energy range of

TABLE 1. Recommended and suggested cross sections for CF_4 updated from those presented in Ref. 1.

Electron energy (eV)	$\sigma_{i,t}(\varepsilon)$ (10^{-20} m^2)	$\sigma_{diss,neut,t}(\varepsilon)$ (10^{-20} m^2)	$\sigma_{vib,indir,t}(\varepsilon)$ (10^{-20} m^2)
5	-	-	0.45
6	-	-	1.65
7	-	-	4.93
8	-	-	7.00
9	-	-	6.74
10	-	-	4.95
12	-	0.025	-
14	-	0.050	-
16	0.011	0.072	-
17	0.038	-	-
18	0.084	0.095	-
19	0.159	-	-
20	0.284	0.13	-
25	1.03	0.40	-
30	1.80	0.65	-
35	2.46	0.84	-
40	2.96	0.96	-
45	3.48	1.05	-
50	3.97	1.09	-
55	4.30	1.11	-
60	4.59	1.13	-
65	4.81	1.13	-
70	5.00	1.14	-
75	5.11	1.14	-
80	5.26	1.13	-
85	5.34	1.13	-
90	5.43	1.13	-
95	5.52	1.12	-
100	5.59	1.12	-
110	5.69	1.10	-
120	5.74	1.09	-
130	5.73	1.08	-
140	5.71	1.07	-
150	5.68	1.07	-
160	5.63	1.06	-
170	5.58	1.05	-
180	5.52	1.04	-
190	5.47	1.03	-
200	5.43	1.02	-
250	5.12	0.97	-
300	4.87	0.94	-
350	4.61	0.90	-
400	4.37	0.86	-
450	4.16	0.82	-
500	3.94	0.78	-

1–400 eV are in general agreement with the recommended cross section in Ref. 1, but exhibit smaller values at the extremes of their energy range. No change to the recommended values of $\sigma_{sc,t}(\varepsilon)$ appears necessary as a result of these measurements. Additionally, since our initial review, a direct measurement of $\sigma_{sc,t}(\varepsilon)$ has been reported by Lunt *et al.*[27] [$(11.8\pm1)\times10^{-16}$ cm^2 at 0.003 eV], which confirms the value of 12.7×10^{-16} cm^2 at 0.003 eV deduced in Ref. 1.

2.2.2. Elastic Integral Cross Section, $\sigma_{e,int}(\varepsilon)$, for CF_4

Recent calculations by Isaacs *et al.*[28] confirm the energy position of the Ramsauer–Townsend minimum present in the recommended $\sigma_{e,int}(\varepsilon)$, and are in reasonable agreement with the recommended data for electron energies ranging from 0.5 to 5 eV.

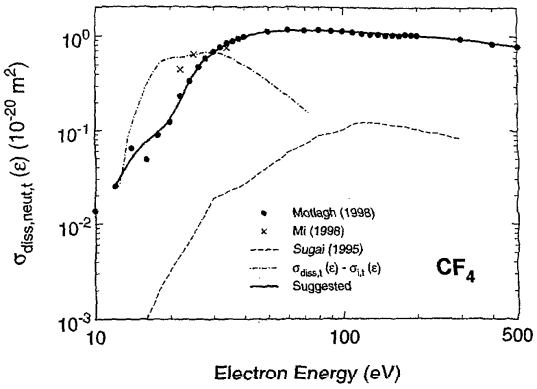

FIG. 3. Total cross section for electron-impact dissociation into neutrals, $\sigma_{diss,neut,t}(\varepsilon)$, for CF_4 based upon recent measurements from Ref. 36 (×) and Ref. 37 (●). The solid line represents the new suggested values for this cross section. For comparison, the previously recommended values, based on the measurements of Ref. 38 are shown as a dashed line. Also shown (–·–) is the value of $\sigma_{diss,t}(\varepsilon)-\sigma_{i,t}(\varepsilon)$.

2.2.3. Total Ionization Cross Section, $\sigma_{i,t}(\varepsilon)$, for CF_4

Two new measurements[29,30] of the total ionization cross section $\sigma_{i,t}(\varepsilon)$ have recently become available, which exhibit magnitudes below the two previously available measurements[31–33] that were used to derive the original recommended values of $\sigma_{i,t}(\varepsilon)$ for CF_4.[1] All four cross section measurements are shown in Fig. 2, and all four are considered to be reliable. The solid line in Fig. 2 is derived from a fit of the four measurements, and represents the updated recommended values of $\sigma_{i,t}(\varepsilon)$. These data are listed in Table 1. The magnitude of the updated cross section is 7.6% smaller than the original recommended cross section (shown in Fig. 2 as a dashed line) at the peak. Since the two recently published cross sections[29,30] are for total ionization, containing no information about the ions produced, the required modification of the partial ionization cross section for CF_4 must be estimated. In the absence of direct measurements, updated partial ionization cross sections for CF_4 may be roughly estimated by a reduction of the values presented in Ref. 1 by this same percentage (7.6%). Two recent calculations[34,35] of $\sigma_{i,t}(\varepsilon)$ fall somewhat below the new recommended value.

2.2.4. Total Cross Section for Dissociation Into Neutrals, $\sigma_{diss,neut,t}(\varepsilon)$, for CF_4

Two recent measurements[36,37] of $\sigma_{diss,neut,t}(\varepsilon)$ confirm that the earlier measurements by Sugai *et al.*[38] are too small (Fig. 3). This possibility was discussed in Ref. 1 because of the large observed inconsistencies in magnitude and shape between the data of Sugai *et al.*[38] and the difference between an independent measurement[39] of the total dissociation cross

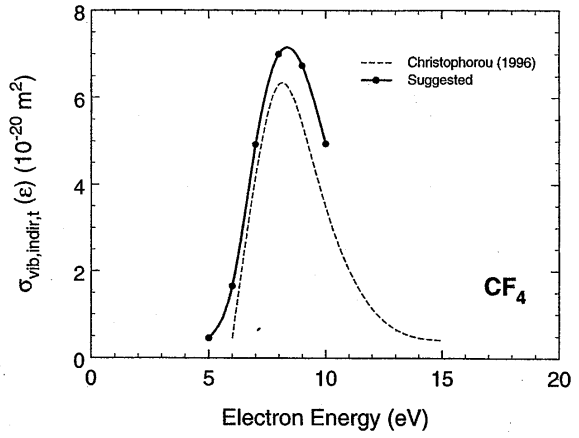

FIG. 4. Updated suggested cross section for indirect vibrational excitation, $\sigma_{vib,indir,t}(\varepsilon)$, of CF_4: Presently revised (—), previously suggested (– –).

section $\sigma_{diss,t}(\varepsilon)$ and the recommended total ionization cross section $\sigma_{i,t}(\varepsilon)$. However, the data of Sugai *et al.* were designated as recommended in Ref. 1 because theirs was the only direct measurement of $\sigma_{diss,neut,t}(\varepsilon)$ available at that time. In light of the new absolute measurements of Mi and Bonham[36] and the new relative measurements of Motlagh and Moore,[37] we suggest the solid curve in Fig. 3 as the preferred cross section for $\sigma_{diss,neut,t}(\varepsilon)$. Values from this fit to the data of Motlagh and Moore are given in Table 1. As can be seen in Fig. 3, these data still exhibit significant discrepancies when compared to the difference between the recommended values of $\sigma_{diss,t}(\varepsilon)$ and $\sigma_{i,t}(\varepsilon)$, particularly near threshold. This suggests the need for additional measurements of $\sigma_{diss,neut,t}(\varepsilon)$.

2.2.5. Indirect Vibrational Excitation Cross Section, $\sigma_{vib,indir,t}(\varepsilon)$, for CF_4

The cross section recommended in Ref. 1 for indirect (resonance enhanced) vibrational excitation, $\sigma_{vib,indir,t}(\varepsilon)$, was based on a deducement of the total inelastic electron scattering cross section by Boesten *et al.*[40] who subtracted their values for the elastic integral cross section $\sigma_{e,int}(\varepsilon)$ from the values of Jones[22] for the total scattering cross section $\sigma_{sc,t}(\varepsilon)$. While this technique is valid, a reassessment of this calculation indicated that a more reliable value of $\sigma_{vib,indir,t}(\varepsilon)$ could be derived if the values of $\sigma_{e,int}(\varepsilon)$ and $\sigma_{sc,t}(\varepsilon)$ used in the calculation were those recommended in Ref. 1 rather than the ones used by Boesten *et al.*[40] The new suggested cross section is shown in Fig. 4 as a solid line with solid dots, and is compared with the original recommended value.[1] The new suggested data for $\sigma_{vib,indir,t}(\varepsilon)$ are listed in Table 1. The peak value at 8 eV is ~11% higher than for the previous data. The difference is primarily due to the uncertainty in the measurements of $\sigma_{e,int}(\varepsilon)$ in this energy range. Additional measurements of $\sigma_{vib,indir,t}(\varepsilon)$ to reduce the uncertainty of this cross section are indicated due to its large influence on the calculated electron swarm parameters.[41] These measurements could either take the form of new mea-

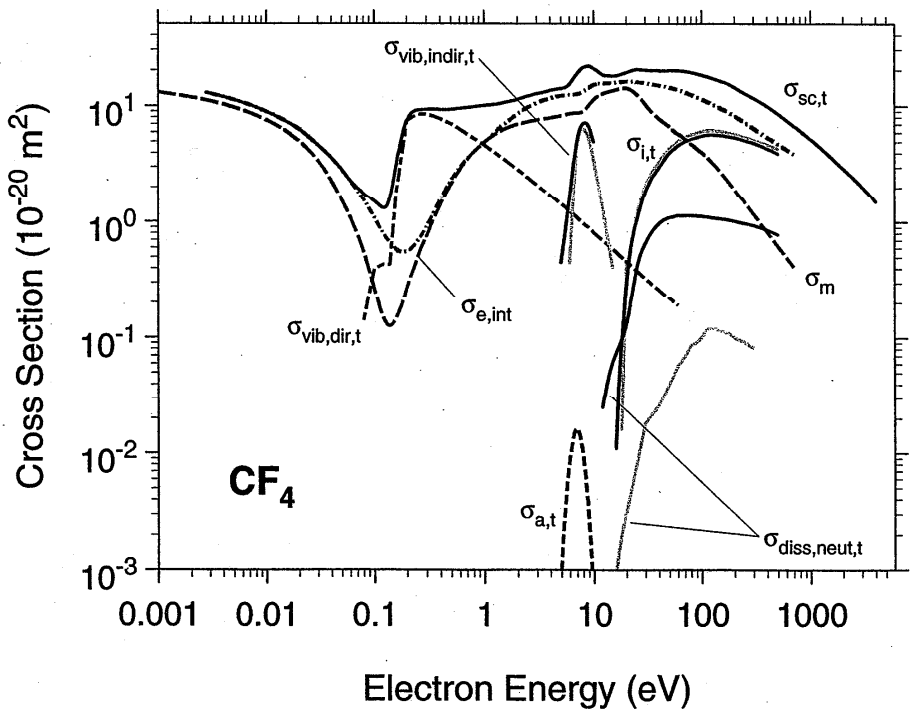

FIG. 5. Updated independently assessed cross sections for CF_4. These are as in Ref. 1, except for those cross sections which have been revised in this paper. The revised data are shown by the black lines. The gray lines are the previous recommended values for the cross sections updated here.

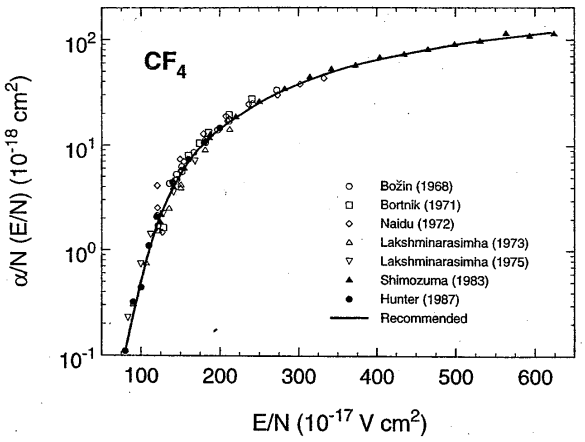

FIG. 6. Measurements of the density reduced electron-impact ionization coefficient, α/N, as a function of E/N in CF_4: (▲) Ref. 44; (●) Ref. 43; (○) Ref. 45; (□) Ref. 46; (◇) Ref. 47; (△) Ref. 48; (▽) Ref. 49. The solid line is a fit to the data of Hunter *et al.* (Ref. 43) and Shimozuma *et al.* (Ref. 44), and represents our recommended data for $\alpha/N(E/N)$.

surements of $\sigma_{e,int}(\varepsilon)$ to reduce the uncertainty of the deduced value of $\sigma_{vib,indir,t}(\varepsilon)$, or direct measurements of $\sigma_{vib,indir,t}(\varepsilon)$.

2.2.6. Assessed Cross Sections for CF_4

Figure 5 shows the updated recommended cross sections for electron interactions with CF_4. The gray lines are the previously recommended data[1] that were modified in the previous three subsections of this paper. The recommended cross sections for CF_4 from Ref. 1 were recently used in a Monte Carlo calculation[42] and were found to give calculated electron transport coefficients in agreement with their recommended experimental values. Similar conclusions were reached by Bordage *et al.*[41] who used the updated recommended cross sections in a Boltzmann code.

2.3. Ionization and Diffusion Coefficients for CF_4

2.3.1. Density-Reduced Ionization Coefficient, $\alpha/N(E/N)$

In the earlier review,[1] the recommended values of the density-reduced ionization coefficient, $\alpha/N(E/N)$, were based on the most recent measurements of Hunter *et al.*,[43] which were deemed to be the most reliable, but which only extended up to E/N values of 200×10^{-17} V cm^2 (200 Td). In fact, measurements by Shimozuma *et al.*[44] extend to much higher E/N values and are in agreement with the values of Hunter *et al.* over their common E/N range. Thus both sets of data should have been used to derive recommended data for $\alpha/N(E/N)$ extending up to 600×10^{-17} V cm^2. Figure 6 shows data from the seven measurements[43–49] of $\alpha/N(E/N)$ that are available in the literature. The measurements of Hunter *et al.*[43] and Shimozuma *et al.*[44] are shown by solid symbols. The data from these two measurements are used to derive the new recommended values of $\alpha/N(E/N)$ because of the improved experimental techniques employed as compared to the earlier measurements. The solid line shows a fit to these data from which new recommended values of $\alpha/N(E/N)$ have been derived (Table 2).

TABLE 2. Updated recommended values for the density-reduced ionization coefficient, α/N (E/N), for CF_4

E/N (10^{-17} V cm^2)	α/N (10^{-18} cm^2)	E/N (10^{-17} V cm^2)	α/N (10^{-18} cm^2)
80	0.11	360	54.2
100	0.50	380	59.3
120	1.71	400	64.2
140	3.82	420	69.1
160	6.97	440	74.0
180	10.5	460	79.1
200	14.4	480	84.3
220	18.3	500	89.7
240	22.8	520	94.8
260	27.8	540	99.3
280	32.9	560	103.5
300	38.1	580	107.9
320	43.4	600	112.4
340	48.8	620	116.9

2.3.2. Ratio of Longitudinal Electron Diffusion Coefficient D_L to Electron Mobility μ, $D_L/\mu(E/N)$, for CF_4

Hayashi and Nakamura[50] measured the product ND_L of the gas number density N and D_L for 100% CF_4 and for mixtures of 5.08% and 0.495% CF_4 in argon. These data are shown in Fig. 7(a). The data for $ND_L(E/N)$ in 100% CF_4 are listed in Table 3.

Hayashi and Nakamura[50] also measured electron drift velocities $w(E/N)$ in these systems, which are in agreement with the earlier measurements of Hunter *et al.*[51] for CF_4 and with the measurements of Christophorou *et al.*[52] and Hunter *et al.*[53] for the mixtures. We have used the measurements of Hayashi and Nakamura on $ND_L(E/N)$ and $w(E/N)$, and the relation

$$\frac{D_L}{\mu}=\frac{D_L N}{w}\times\frac{E}{N},$$

to determine the ratio D_L/μ, as a function of E/N, which is shown in Fig. 7(b) by the solid points. For comparison, the earlier $D_L/\mu(E/N)$ measurements of Schmidt and Polenz[54] are also plotted in the figure. Although the two sets of data converge to their asymptotic value as $E/N\rightarrow0$, they disagree considerably at higher E/N, stressing the need for further measurements.

In Fig. 7(b) are also plotted (broken line) the recommended[1] values of the ratio of the transverse electron diffusion coefficient D_T to electron mobility μ, $D_T/\mu(E/N)$. It is interesting to observe that the values of $D_T/\mu(E/N)$ lie above the corresponding values of $D_L/\mu(E/N)$ for the Hayashi and Nakamura data and below the Schmidt and Polenz data. Since $D_T/\mu(E/N)$ is expected[55] to be greater than or equal to $D_L/\mu(E/N)$, the data of Hayashi and Nakamura are considered to be more reliable. They are listed in Table 3 as our suggested values for the $D_L/\mu(E/N)$ of CF_4.

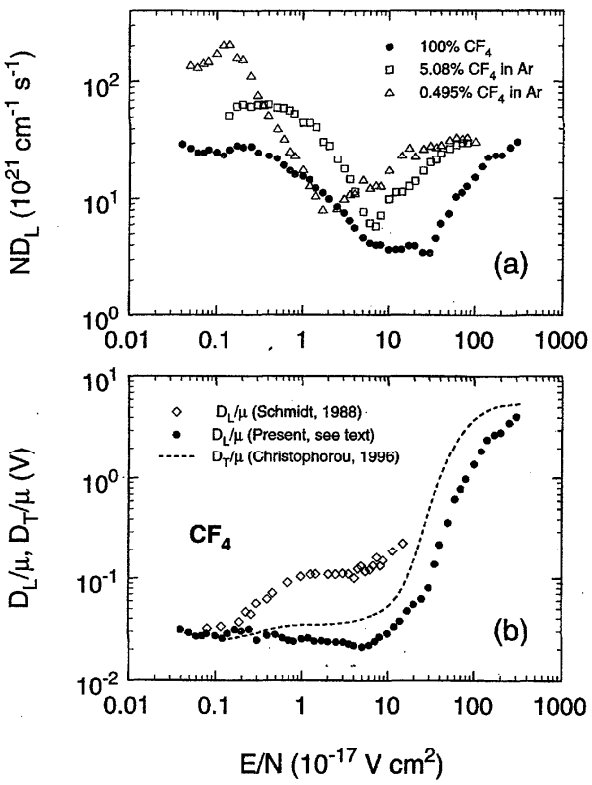

FIG. 7. (a) Measurements of the product of the longitudinal electron diffusion coefficient and the gas density, $ND_L(E/N)$, for 100% CF_4 (●), 5.08% CF_4 in Ar (□), and 0.495% CF_4 in Ar (△) from Ref. 50. (b) Measurements of the ratio of the longitudinal electron diffusion coefficient to electron mobility, $D_L/\mu(E/N)$: (◇) Ref. 54; (●) calculated from the measured values of ND_L and w presented in Ref. 50. Also shown for comparison are the recommended values of $D_T/\mu(E/N)$ from Ref. 1 (– –).

3. Update for CHF_3

When the review and assessment work on electron collisions with CHF_3 was begun about 2 years ago by Christophorou *et al.*,[2] there were no measurements of electron scattering cross sections, electron transport coefficients, or cross sections for dissociative electron attachment for CHF_3. The available cross section[38] for electron-impact dissociation into neutrals was judged to be questionable. Partly as a consequence of the discussions during the review and assessment process, measurements have since been made of the cross sections for total electron scattering, elastic differential electron scattering, electron-impact dissociation of CHF_3 into CHF_2 and CF_3 neutral fragments, and total and partial ionization. Measurements have also been reported for the electron drift velocity and the electron attachment rate constant. These new results are presented in this section.

3.1. Electron Collision Cross Sections for CHF_3

3.1.1. Total Electron Scattering Cross Section, $\sigma_{sc,t}(\varepsilon)$, for CHF_3

At the time of the initial review, the only available information on the total electron scattering cross section $\sigma_{sc,t}(\varepsilon)$ of CHF_3 was the calculation of Christophorou *et al.*[2] at low energies (<1 eV), and the unpublished measurements of Sanabia *et al.*, which have since been published.[56] Another measurement of $\sigma_{sc,t}(\varepsilon)$ has since been reported by Sueoka *et al.*[26] which extends to 500 eV. Figure 8 shows these values of the $\sigma_{sc,t}(\varepsilon)$ for CHF_3. The solid line gives our revised recommended values (listed in Table 4) that are derived by

TABLE 3. Suggested values of $ND_L(E/N)$ and $D_L/\mu(E/N)$ for CF_4 based upon measurements from Ref. 50

E/N (10^{-17} V cm^2)	ND_L (10^{21} cm^{-1} s^{-1})	D_L/μ[a] (V)
0.04	29.29	0.031
0.05	27.06	0.029
0.06	24.85	0.027
0.07	24.97	0.027
0.08	26.33	0.028
0.10	25.06	0.027
0.12	23.42	0.025
0.14	26.33	0.028
0.17	28.50	0.031
0.20	27.58	0.030
0.25	28.06	0.031
0.30	24.74	0.024
0.40	23.11	0.027
0.50	22.01	0.028
0.60	19.16	0.026
0.70	17.30	0.024
0.80	15.95	0.024
1.0	15.39	0.025
1.2	14.41	0.026
1.4	12.27	0.024
1.7	11.09	0.024
2.0	9.87	0.024
2.5	8.48	0.024
3.0	7.48	0.023
3.5	6.41	0.023
4.0	5.57	0.022
5.0	4.57	0.021
6.0	4.10	0.022
7.0	3.96	0.024
8.0	3.98	0.026
10.0	3.62	0.028
12.0	3.62	0.033
14.0	3.64	0.037
17.0	3.92	0.047
20.0	3.90	0.055
25.0	3.41	0.062
30.0	3.40	0.081
35.0	4.56	0.138
40.0	6.05	0.224
50.0	7.38	0.368
60.0	10.3	0.621
70.0	11.2	0.778
80.0	12.6	0.976
100.0	15.0	1.36
120.0	18.5	1.85
140.0	22.3	2.41
170.0	23.1	2.70
200.0	23.2	2.84
250.0	27.4	3.51
300.0	30.5	4.07

[a]Derived using the measured values of $ND_L(E/N)$ and $w(E/N)$ presented in Ref 50.

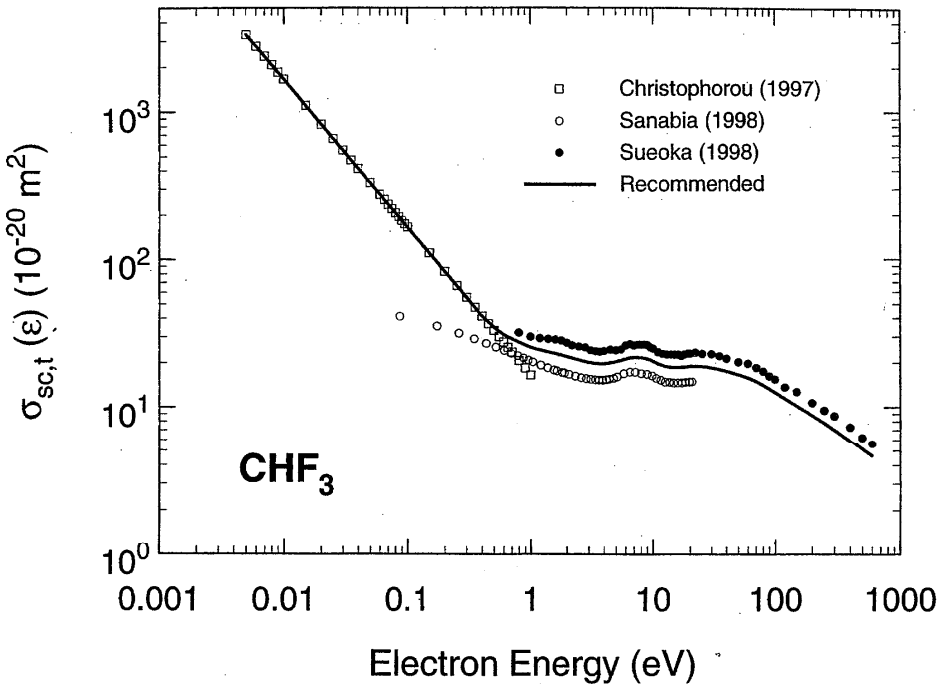

FIG. 8. Updated total electron scattering cross section, $\sigma_{sc,t}(\varepsilon)$, for CHF_3: (□) calculation from Ref. 2; (○) measurement from Ref. 56; (●) measurement from Ref. 26; (—) updated recommended values.

an average of the experimental values below 23 eV that is merged with the calculated values near 1 eV. An extrapolation of this fit is made to higher energies based upon the shape of the data of Sueoka *et al.*[26] above 23 eV. It is interesting to observe the large increase in the $\sigma_{sc,t}(\varepsilon)$ of CHF_3 as the electron energy is decreased below 1 eV. This is due to the large (5.504×10^{-30} C m=1.65 D) permanent electric dipole moment of this molecule.[57] It is also expected for other polar gases.[55]

TABLE 4. Updated recommended total electron scattering cross section, $\sigma_{sc,t}(\varepsilon)$, for CHF_3

Electron energy (eV)	$\sigma_{sc,t}(\varepsilon)$ (10^{-20} m^2)	Electron energy (eV)	$\sigma_{sc,t}(\varepsilon)$ (10^{-20} m^2)
0.005	3321.2	2.0	22.1
0.006	2767.6	3.0	20.3
0.007	2372.3	4.0	19.9
0.008	2075.8	5.0	20.5
0.009	1845.1	6.0	21.3
0.01	1660.6	7.0	21.9
0.02	830.3	8.0	21.8
0.03	553.5	9.0	21.4
0.04	415.2	10.0	20.6
0.05	332.1	15.0	18.7
0.06	276.8	20.0	19.0
0.07	237.2	30.0	18.6
0.08	207.6	40.0	17.7
0.09	184.5	50.0	16.7
0.1	166.1	60.0	15.9
0.2	82.9	70.0	15.0
0.3	55.4	80.0	14.2
0.4	41.5	90.0	13.4
0.5	35.0	100.0	12.7
0.6	31.3	200.0	8.8
0.7	29.2	300.0	7.0
0.8	27.7	400.0	5.9
0.9	26.5	500.0	5.2
1.0	25.6	600.0	4.6
1.5	23.5		

3.1.2. Elastic Differential Electron Scattering Cross Section, $\sigma_{e,diff}$, for CHF_3

Tanaka *et al.*[58,59] recently reported measurements of the elastic differential electron scattering cross section, $\sigma_{e,diff}$, of CHF_3 for incident electron energies from 1.5 to 100 eV and scattering angles between 15° and 135°. These data are reproduced in Fig. 9. The experimental errors in these measurements are reported to be between 15% and 30%.

A recent publication by Natalense *et al.*[60] presented a calculation of the $\sigma_{e,diff}$ of CHF_3 at a single electron energy of 20 eV. The result of this calculation which employed the Schwinger multichannel method is compared in Fig. 9 (solid line) with the experimental data at 20 eV, and the results are seen to be in reasonable agreement.

3.1.3. Momentum Transfer Cross Section, $\sigma_m(\varepsilon)$, for CHF_3

Natalense *et al.*[60] calculated $\sigma_m(\varepsilon)$ over a narrow range of energies from 10 and 30 eV using the Schwinger multichannel method. Their results are shown in Table 5. They are the only values presently available, and as such represent our suggested values.

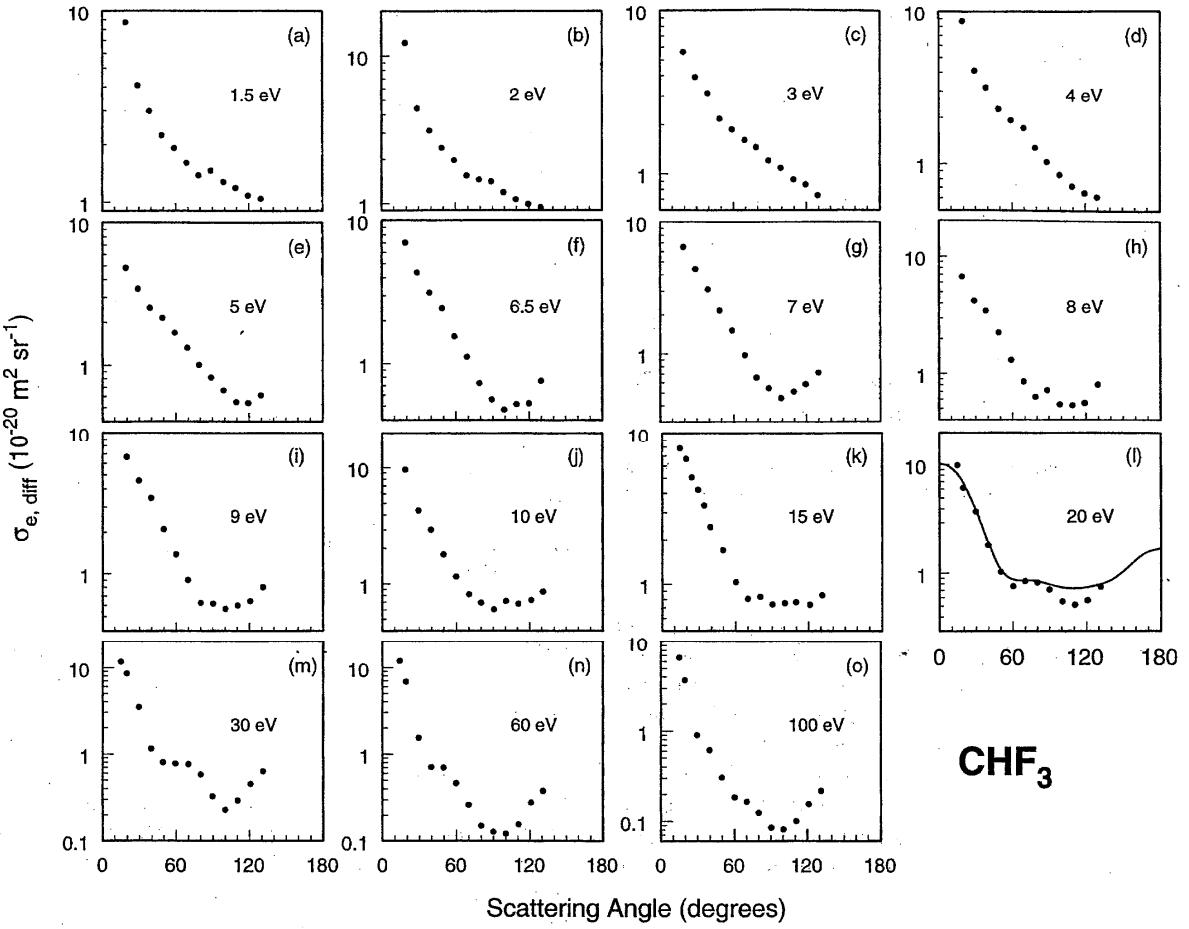

FIG. 9. Measured elastic differential electron scattering cross sections $\sigma_{e,diff}(\varepsilon)$, for CHF_3 from Refs. 58 and 59. A recent calculated result from Ref. 60 is also shown (—) for 20 eV.

3.1.4. Cross Section for Electron-Impact Dissociation of CHF_3 into CHF_2 and CF_3 Neutral Fragments

Motlagh and Moore[37] reported relative measurements of the cross section for electron-impact dissociation of CHF_3 into CHF_2 and CF_3 neutral fragments (produced by neutral dissociation and by dissociative ionization). They detected the radicals mass spectrometrically as organotellurides produced by their reaction at the surface of a tellurium mirror. Via a number of assumptions regarding calibration factors (see Ref. 37), they put their measurements on an absolute scale as shown in Fig. 10, with an estimated uncertainty of 30%. However, the sum of the cross sections in Fig. 10 is approximately a factor of four smaller than the total dissociation cross section measured by Winters and Inokuti[39] for CHF_3, even though CHF_2 and CF_3 would be expected to be the major products of dissociation. This significant discrepancy demonstrates the need for additional measurements related to this process.

Additionally, in view of the new data which confirm that the values of $\sigma_{diss,neut,t}(\varepsilon)$ derived by Sugai *et al.*[38] for CF_4 are too small (as discussed earlier in Sec. 2.2.4.), the values derived by Sugai *et al.* for CHF_3 (previously recommended in Ref. 2) must similarly be assumed to be too small. In light of the numerous discrepancies involving $\sigma_{diss,neut,t}(\varepsilon)$ for CHF_3, no data for $\sigma_{diss,neut,t}(\varepsilon)$ may be recommended or suggested at this time.

TABLE 5. Momentum transfer cross sections, $\sigma_m(\varepsilon)$, for CHF_3 calculated in Ref. 60

Electron energy (eV)	$\sigma_m(\varepsilon)$ (10^{-20} m^2)
10	15.5
15	12.4
20	11.4
25	10.5
30	10.1

3.1.5. Total, $\sigma_{i,t}(\varepsilon)$, and Partial, $\sigma_{i,part}(\varepsilon)$, Ionization Cross Sections for CHF_3

A recent study[61] of the ion chemistry in CHF_3 using Fourier-transform mass spectrometry yielded total and partial ionization cross sections for CHF_3 from threshold to 60 eV with an estimated uncertainty of $\pm 10\%$.[62] The partial

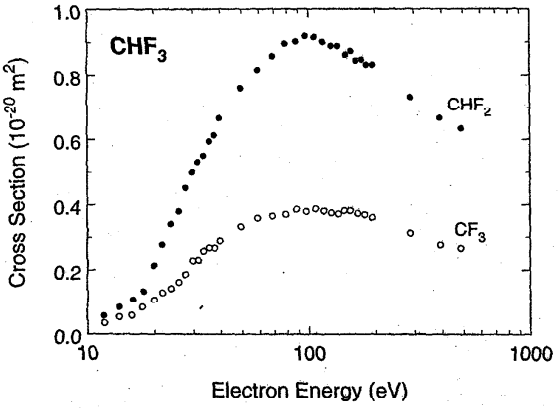

FIG. 10. Cross sections from Ref. 37 for the production of CHF_2 (●) and CF_3 (○) by neutral dissociation and dissociative ionization from electron impact on CHF_3.

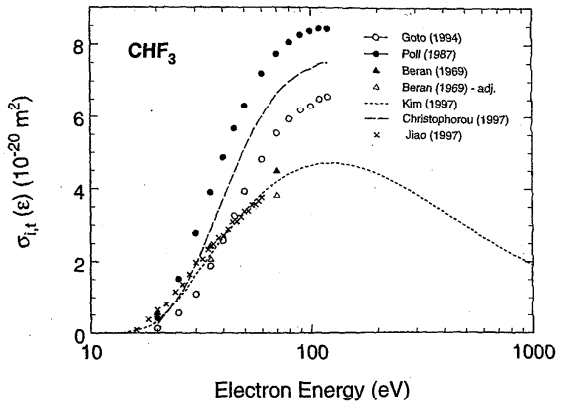

FIG. 12. Total ionization cross sections, $\sigma_{i,t}(\varepsilon)$, for CHF_3 as obtained by summing up the partial ionization cross sections, $\sigma_{i,part}(\varepsilon)$: (●) Ref. 63; (○) Ref. 64; (×) recent data from Ref. 61. Also shown are the data of Ref. 65 (▲), the adjusted data of Ref. 65 (△), the calculated values from Ref. 34 (- - -), and the previously suggested values from Ref. 2 (— —).

ionization cross sections, $\sigma_{i,part}(\varepsilon)$, for the production of CF_3^+, $CHF_2^+ + CF_2^+$, and CF^+ from this work are compared in Fig. 11 with those of two earlier mass-spectrometric studies.[63,64] Since Poll and Meichsner[63] gave only the sum of the cross sections for production of the two ions $CHF_2^+ + CF_2^+$ and not the cross section for each of these ions separately, this sum is plotted in Fig. 11(b) for comparison with its value from the other two studies. Clearly the data are inconsistent. Jiao *et al.*[61] present separate cross sections for

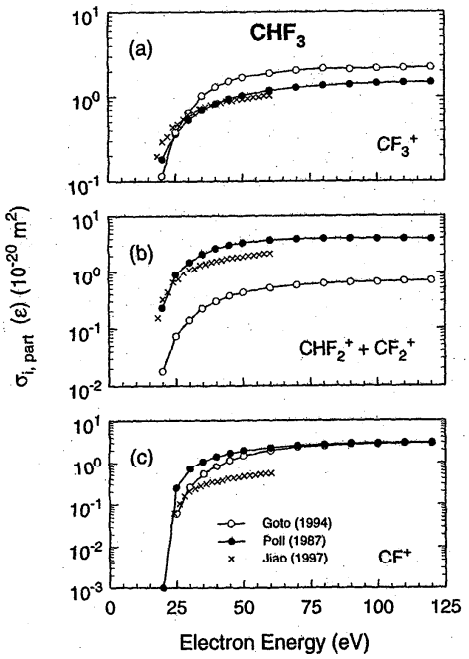

FIG. 11. Partial ionization cross sections, $\sigma_{i,part}(\varepsilon)$, for CHF_3 for the product ions indicated: (●) Ref. 63; (○) Ref. 64; (×) recent data of Ref. 61.

CHF_2^+ and CF_2^+, with the magnitude for CHF_2^+ production exceeding that of CF_2^+ by more than an order of magnitude at all energies (≤ 60 eV) investigated.

The sums of the partial ionization cross sections from the three studies, which we designate as $\sigma_{i,t}(\varepsilon)$, are shown in Fig. 12. Also shown in Fig. 12 are the earlier measurements of Beran and Kevan,[65] as originally published and adjusted for the reasons discussed in Ref. 3 (decreased by 15%). The result of a recent calculation by Kim *et al.*[34] is also shown in the figure. The differences between the data of Poll and Meichsner, Goto *et al.*, and Jiao *et al.* for $\sigma_{i,t}(\varepsilon)$ are significant and exceed the combined experimental uncertainties.

In view of the unexplained discrepancies between the measured values of $\sigma_{i,t}(\varepsilon)$, no changes in the initially recommended values (long dash curve in Fig. 12) of $\sigma_{i,t}(\varepsilon)$ are deemed advisable at this time. Further work is indicated for both the partial and the total ionization cross sections for this molecule to resolve this issue. A direct, independent measurement of $\sigma_{i,t}(\varepsilon)$ without mass analysis would be desirable. The apparent agreement between the recent data of Jiao *et al.*,[61] the adjusted data of Beran and Kevan, and the recent calculations of Kim *et al.*[34] suggests that a reduction in the recommended values of $\sigma_{i,t}(\varepsilon)$ may be justified if supported by future measurements.

3.2. Electron Drift Velocity, Electron Attachment Rate Constant, and Effective Ionization Coefficient for CHF_3

3.2.1. Electron Drift Velocity, $w(E/N)$, for CHF_3

Since the publication of our initial review for CHF_3,[2] Wang *et al.*[66] published measurements of $w(E/N)$ in CHF_3 for values of E/N ranging from 0.4×10^{-17} to 75×10^{-17} V cm^2. De Urquijo *et al.*[67] recently presented similar data for values of E/N from 8×10^{-17} to 250×10^{-17} V cm^2. Both sets of data are shown in Fig. 13(a),

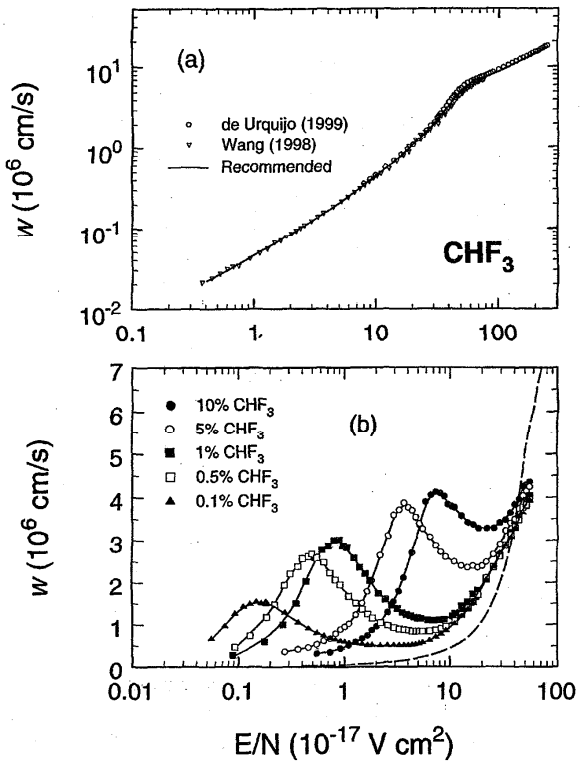

FIG. 13. (a) Measurements from Ref. 66 (▽) and Ref. 67 (○) of electron drift velocity, $w(E/N)$, as a function of E/N in CHF_3. The solid line represents the recommended values. (b) Measurements of $w(E/N)$ in mixtures of CHF_3 with argon at the indicated compositions ($T \approx 298$ K, total pressure of 1.13 kPa) from Ref. 66. The solid lines are weighted-least-squares fits to the data. The dashed curve is the recommended value of $w(E/N)$ in 100% CHF_3 from Fig. 13(a).

and are in agreement within their combined uncertainties for overlapping values of E/N. The solid line represents our recommended data for $w(E/N)$. Below 75×10^{-17} V cm^2 the line is fit to the two sets of data. An extrapolation of the fit based upon the shape of the data of de Urquijo *et al.* is used to extend the line for E/N values greater than 75×10^{-17} V cm^2. Recommended values of $w(E/N)$ from the solid line are listed in Table 6. It is interesting to observe the profound differences between the $w(E/N)$ in CF_4 and in CHF_3 due to the large permanent electric dipole moment of the latter molecule.[68]

Two sets of measurements of $w(E/N)$ have been made in mixtures of CHF_3 with argon.[66,69] The data of Wang *et al.*[66] are more extensive and are reproduced in Fig. 13(b). Comparison of the data for the mixtures from the two sources[66,69] can be made for only two common compositions (0.1% and 1%), for which they are in reasonable agreement.

3.2.2. Electron Attachment Rate Constant, $k_a(E/N)$, for CHF_3

Wang *et al.*[66] measured an electron attachment rate constant, $k_a(E/N)$, in 100% CHF_3 to be equal to 13×10^{-14} cm^3 s^{-1}, which is almost independent of E/N for

TABLE 6. Recommended values of electron drift velocities, $w(E/N)$, in CHF_3 ($T \approx 298$ K) determined from a fit to the data from Refs. 66 and 67 shown in Fig. 13(a)

E/N (10^{-17} V cm^2)	w (10^6 cm s^{-1})	E/N (10^{-17} V cm^2)	w (10^6 cm s^{-1})
0.40	0.022	9.0	0.39
0.45	0.024	10.0	0.44
0.50	0.026	15.0	0.72
0.60	0.030	20.0	1.09
0.70	0.034	25.0	1.52
0.80	0.038	30.0	2.02
0.90	0.042	40.0	3.38
1.0	0.046	50.0	4.98
1.5	0.065	60.0	6.10
2.0	0.085	70.0	6.92
2.5	0.105	80.0	7.49
3.0	0.125	90.0	8.12
4.0	0.166	100.0	8.66
5.0	0.208	150.0	11.6
6.0	0.252	200.0	14.3
7.0	0.296	250.0	16.9
8.0	0.342		

E/N values between 1.5×10^{-17} and 50×10^{-17} V cm^2. This low value is consistent with the earlier small values of $k_a(E/N)$ measured at thermal energies,[2] and also with a recent electron-swarm mass spectrometric measurement.[70] In contrast to these measurements, a ten times higher $k_a(E/N)$ is indicated by the work of Clark *et al.*[69] Wang *et al.* argued that the values of Clark *et al.* may be in error, and conjectured that the weak attachment observed in this gas below 60×10^{-17} V cm^2 may be due to traces of electronegative impurities.

3.2.3. Density-Reduced Effective Ionization Coefficient, $(\alpha-\eta)/N(E/N)$, for CHF_3

De Urquijo *et al.*[67] recently reported measurements of the density-reduced effective ionization coefficient, $(\alpha-\eta)/N$, for CHF_3 as a function of E/N. These data are shown in Fig. 14, and are listed in Table 7 as our suggested values of

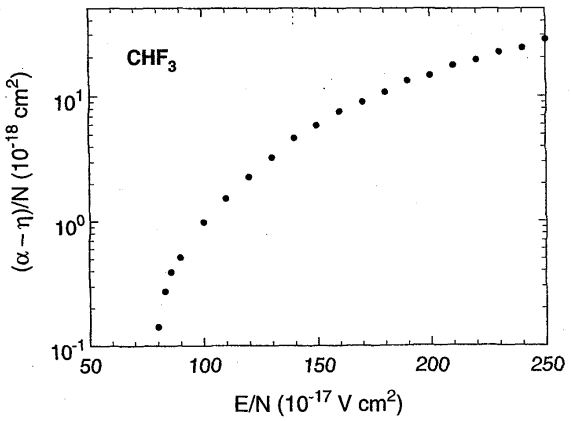

FIG. 14. Density-reduced effective ionization coefficient, $(\alpha-\eta)/N$, in CHF_3, from Ref. 67.

TABLE 7. Density-reduced effective ionization coefficients, $(\alpha-\eta)/N\,(E/N)$, for CHF_3 from Ref. 67

E/N (10^{-17} V cm^2)	$(\alpha-\eta)/N$ (10^{-18} cm^2)	E/N (10^{-17} V cm^2)	$(\alpha-\eta)/N$ (10^{-18} cm^2)
80.0	0.14	170.0	9.04
90.0	0.51	180.0	10.8
100.0	0.98	190.0	13.3
110.0	1.53	200.0	14.6
120.0	2.27	210.0	17.5
130.0	3.27	220.0	19.3
140.0	4.68	230.0	22.1
150.0	5.93	240.0	23.7
160.0	7.61	250.0	27.7

$(\alpha-\eta)/N(E/N)$ for this molecule.

4. Update for C_2F_6

4.1. Total Ionization Cross Section, $\sigma_{i,t}(\varepsilon)$, for C_2F_6

Since our original report on C_2F_6,[3] there has been one measurement of the $\sigma_{i,t}(\varepsilon)$ of this molecule by Nishimura *et al.*,[30] and one calculation by Deutsch *et al.*[71] using a modified-additivity-rule method. Both of these results are shown in Fig. 15, and are compared with the previously published data from Ref. 3. Based upon the new measurements of Nishimura *et al.*, a new recommended value of $\sigma_{i,t}(\varepsilon)$ is derived and is shown as the heavy solid line. The new recommended values are derived using a technique similar to that described in Ref. 3. Briefly, the new recommended data are derived by fitting a curve to the ionization threshold of 15.9 eV, and to the average of the four experimental measurements[30,63,65,72] at 20, 35, and 70 eV. This curve is then extended by fitting the data of Nishimura *et al.* above 70 eV. The original suggested cross section from Ref. 3 is shown as the light gray line, and the new recommended data are listed in Table 8.

TABLE 8. Recommended total ionization cross section, $\sigma_{i,t}(\varepsilon)$, for C_2F_6

Electron energy (eV)	$\sigma_{i,t}(\varepsilon)$ (10^{-20} m^2)	Electron energy (eV)	$\sigma_{i,t}(\varepsilon)$ (10^{-20} m^2)
15.9	0.00	95.0	8.29
16.0	0.014	100.0	8.37
17.0	0.15	110.0	8.52
18.0	0.30	120.0	8.62
19.0	0.47	130.0	8.69
20.0	0.67	140.0	8.73
25.0	1.76	150.0	8.75
30.0	2.85	160.0	8.74
35.0	3.84	170.0	8.72
40.0	4.71	180.0	8.68
45.0	5.44	190.0	8.63
50.0	6.06	200.0	8.58
55.0	6.57	300.0	7.63
60.0	6.99	400.0	6.56
65.0	7.31	500.0	5.78
70.0	7.56	600.0	5.18
75.0	7.77	700.0	4.66
80.0	7.93	800.0	4.25
85.0	8.07	900.0	3.96
90.0	8.19	1000.0	3.77

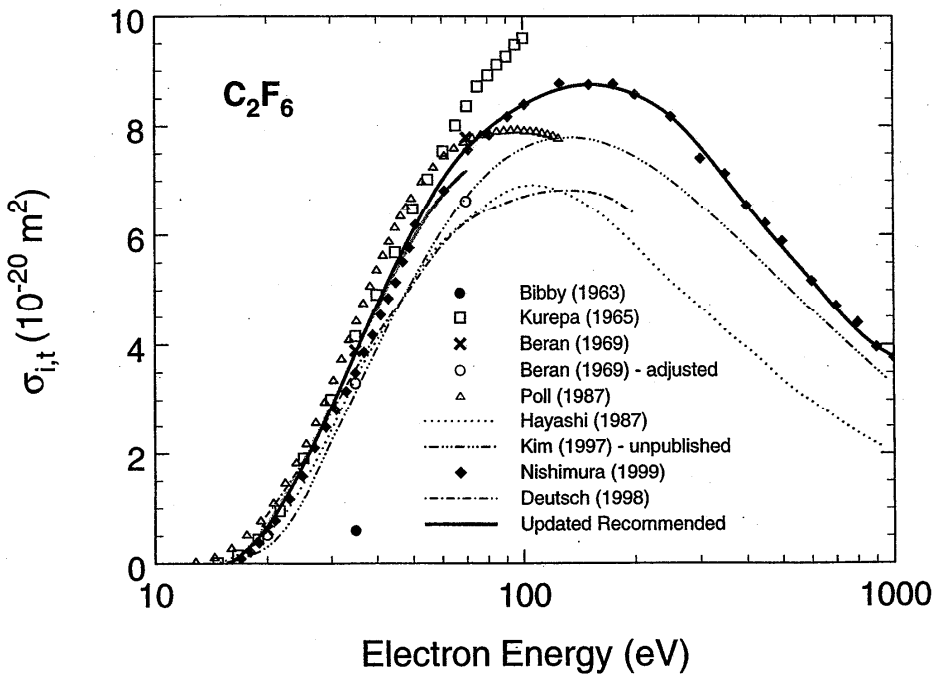

FIG. 15. Total ionization cross sections, $\sigma_{i,t}(\varepsilon)$, for C_2F_6, including the newly published experimental values from Ref. 30 (♦) and the recent modified-additivity-rule calculations of Ref. 71 (–·–). The rest of the data are as discussed in Ref. 3. The light gray line is the previously suggested $\sigma_{i,t}(\varepsilon)$ for C_2F_6 from Ref. 3, and the solid line represents the updated recommended values.

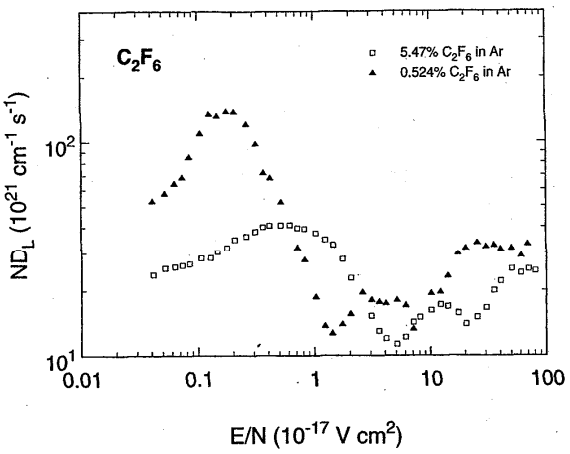

FIG. 16. Measurements of the product of the gas density and longitudinal electron diffusion coefficient, $ND_L(E/N)$, for 5.47% C_2F_6 in Ar (□) and 0.524% C_2F_6 in Ar (▲) from Ref. 73.

Note added in proof. Since the completion of this work, new measurements of the partial and total ionization cross sections of C_2F_6 to 70 eV have been reported by Jiao *et al.* [C. Q. Jiao, A. Garscadden, and P. D. Haaland, Chem. Phys. Lett. **310**, 52 (1999)]. These measurements are in general agreement with the data in Fig. 15 and the partial ionization cross sections of H. U. Poll and J. Meichsner [Contrib. Plasma Phys. **27**, 359 (1987)] (see Fig. 11 of Ref. 3).

4.2. Product, $ND_L(E/N)$, of the Gas Number Density N and the Longitudinal Electron Diffusion Coefficient D_L, as a Function of E/N, for C_2F_6

Okumo and Nakamura[73] measured $ND_L(E/N)$ for mixtures containing 0.524% and 5.47% of C_2F_6 in argon. These data are shown in Fig. 16. Their measurements on $w(E/N)$ for these mixtures are consistent with the earlier measurements of Hunter *et al.*[53]

5. Update for C_3F_8

5.1. Total Electron Scattering Cross Section, $\sigma_{sc,t}(\varepsilon)$, for C_3F_8

At the time the review of Christophorou and Olthoff[4] for C_3F_8 was completed, the only data on the total electron scattering cross section, $\sigma_{sc,t}(\varepsilon)$, for C_3F_8 were the measurements of Sanabia *et al.*,[56] which were designated as suggested in the absence of confirming measurements. Since then another set of measurements of $\sigma_{sc,t}(\varepsilon)$ has been made by Tanaka *et al.*[74] The two sets of data are shown in Fig. 17 and they agree within their combined uncertainties. The average was determined over the energy range in which the two sets of measurements overlap and is shown by the solid line in the figure. This solid line was extended to lower and to higher energies by normalization, respectively, of the measurements of Sanabia *et al.*[56] to the average value at 0.8 eV and the measurements of Tanaka *et al.*[74] to the average value

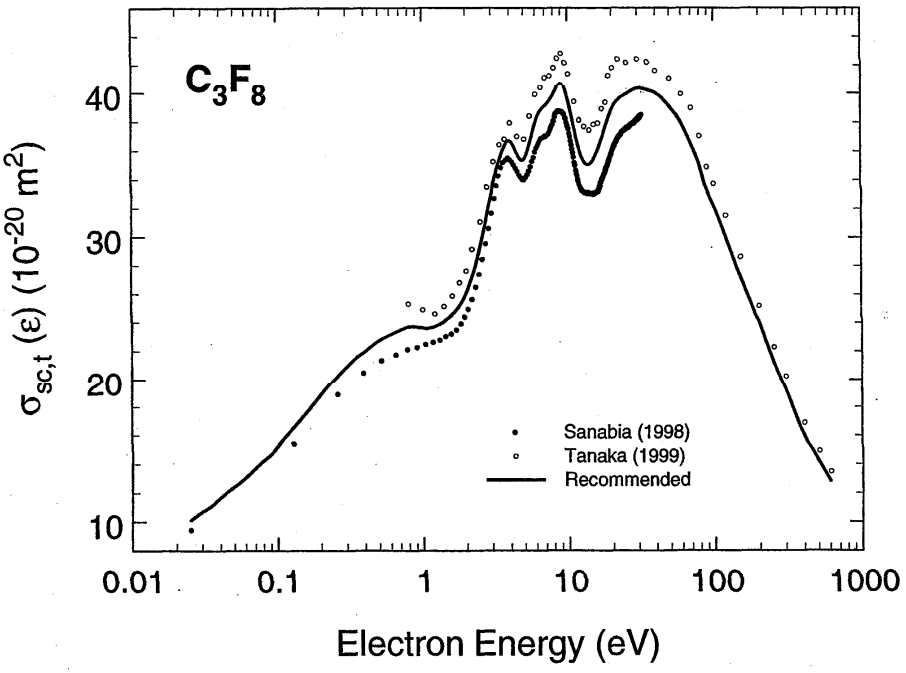

FIG. 17. Total electron scattering cross section, $\sigma_{sc,t}(\varepsilon)$, for C_3F_8: (●) measurements of Ref. 56; (○) recent measurements of Ref. 74; (—) updated recommended values.

TABLE 9. Recommended total electron scattering cross section, $\sigma_{sc,t}(\varepsilon)$, for C_3F_8

Electron energy (eV)	$\sigma_{sc,t}(\varepsilon)$ (10^{-20} m^2)	Electron energy (eV)	$\sigma_{sc,t}(\varepsilon)$ (10^{-20} m^2)
0.025	10.1	5.0	35.4
0.030	10.7	6.0	38.0
0.035	11.2	7.0	39.1
0.04	11.7	8.0	39.9
0.05	12.4	9.0	40.7
0.06	13.1	10.0	39.6
0.07	13.7	12.5	35.6
0.08	14.3	15.0	35.4
0.09	14.7	20.0	38.9
0.10	15.2	25.0	39.9
0.15	17.3	30.0	40.3
0.20	18.9	35.0	40.2
0.25	20.1	40.0	40.0
0.30	20.9	50.0	39.1
0.35	21.6	60.0	37.9
0.40	22.0	70.0	36.5
0.50	22.7	80.0	35.0
0.60	23.2	90.0	33.2
0.70	23.5	100.0	32.1
0.80	23.7	120.0	30.0
0.90	23.7	150.0	27.2
1.0	23.6	200.0	23.9
1.5	24.3	250.0	21.2
2.0	26.0	300.0	19.2
2.5	29.3	400.0	16.0
3.0	33.2	500.0	14.2
3.5	35.7	600.0	12.8
4.0	36.7		

at 23 eV. In this way the range of recommended data was extended considerably. The solid line represents our recommended $\sigma_{sc,t}(\varepsilon)$ for C_3F_8, and values taken off this line are listed in Table 9.

5.2. Density-Reduced Effective Ionization Coefficient, $(\alpha-\eta)/N(E/N)$, for C_3F_8

Values of the density-reduced effective ionization coefficient, $(\alpha-\eta)/N(E/N)$, were given in Ref. 4, for a fixed temperature (~298 K) and pressure (<1.0 kPa). Specifying the temperature and pressure is important for this molecule because electron attachment to C_3F_8 is a function of both of these experimental variables. Since Hunter *et al.*[43] reported values of the electron attachment coefficient $\eta/N(E/N)$ at "infinite" gas pressure, in this update we use the density-independent values of Hunter *et al.*[43] for $\eta/N(E/N)$ and the recommended[4] values of the density-reduced ionization coefficient $\alpha/N(E/N)$ to determine the room temperature (~298 K) density-independent $(\alpha-\eta)/N(E/N)$ of C_3F_8. This is shown in Fig. 18 and listed in Table 10.

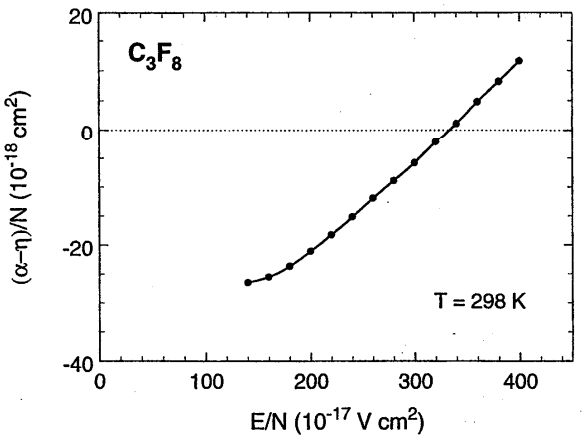

FIG. 18. Density-independent values of the effective ionization coefficient, $(\alpha-\eta)/N(E/N)$, ($T\approx298$ K) for C_3F_8.

TABLE 10. Recommended data for the density-independent effective ionization coefficient, $(\alpha-\eta)/N$ (E/N) ($T\approx298$ K), of C_3F_8

E/N (10^{-17} V cm^2)	$(\alpha-\eta)/N$ (10^{-18} cm^2)	E/N (10^{-17} V cm^2)	$(\alpha-\eta)/N$ (10^{-18} cm^2)
140	−26.5	280	−8.9
160	−25.5	300	−5.8
180	−23.7	320	−2.2
200	−21.1	340	1.1
220	−18.3	360	4.8
240	−15.2	380	8.2
260	−12.0	400	11.6

5.3. Product, $ND_L(E/N)$, of the Gas Number Density N and the Longitudinal Electron Diffusion Coefficient D_L, as a Function of E/N, for C_3F_8

Jeon and Nakamura[75] measured $ND_L(E/N)$ for mixtures containing 0.526% and 5.05% of C_3F_8 in argon. These data are shown in Fig. 19. Their measurements of $w(E/N)$ for these mixtures are consistent with the earlier measurements of Hunter *et al.*[53]

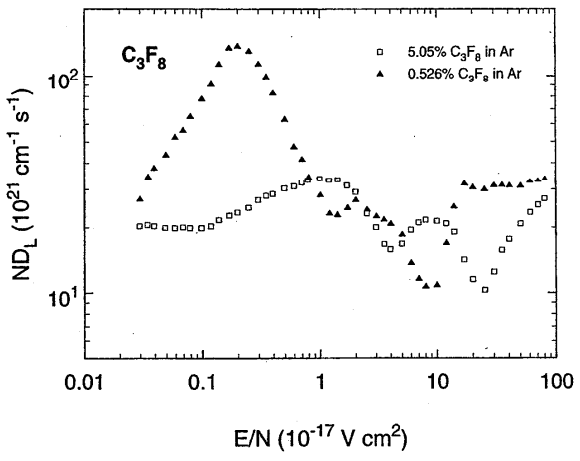

FIG. 19. Measurements of the product of the gas density and longitudinal electron diffusion coefficient, $ND_L(E/N)$, for 5.05% C_2F_6 in Ar (□) and 0.526% C_3F_8 in Ar (▲) from Ref. 75.

6. Summary

The data updates that justify a change in the recommended or suggested data values that have been published previously[1–4] are summarized here.

For CF_4, the values of $\sigma_{i,t}(\varepsilon)$, $\sigma_{diss,neut,t}(\varepsilon)$, and $\sigma_{vib,indir,t}(\varepsilon)$ have been updated as presented in Table 1 and in Figs. 2–4, respectively. The recommended values of $\alpha/N(E/N)$ for CF_4 were updated for higher values of E/N as shown in Table 2 and Fig. 6. Additionally, the recently derived values of $ND_L(E/N)$ and $D_L/\mu(E/N)$ for CF_4 listed in Table 3 and shown in Fig. 7 were designated as suggested values.

For CHF_3, the recommended total scattering cross section was updated to higher energies in Table 4 and Fig. 8. The recently calculated values of $\sigma_m(\varepsilon)$ for CHF_3 listed in Table 5 are designated as suggested since they are the only independently derived values available. Additionally, the new electron drift velocity data presented in Table 6 and Fig. 13(a) are designated as recommended, while the results of recent measurements of $(\alpha-\eta)/N(E/N)$ presented in Table 7 and Fig. 14 are suggested.

For C_2F_6, the previously suggested values of $\sigma_{i,t}(\varepsilon)$ were updated to higher electron energies, and the new recommended values are shown in Fig. 15 and listed in Table 8.

Similarly, the previously recommended total scattering cross sections, $\sigma_{sc,t}(\varepsilon)$, for C_3F_8 were updated and extended to higher energies, and are shown in Fig. 17 and Table 9. Also, the values of the density-reduced effective ionization coefficient for C_3F_8 at "infinite" pressure were derived and are presented in Fig. 18 and Table 10.

All of the updated values of these parameters are presented on the "NIST Electron Interactions with Plasma Processing Gases" website at http://www.eeel.nist.gov/811/refdata.

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