

Electron Interactions with CHF₃

Cite as: Journal of Physical and Chemical Reference Data **26**, 1 (1997); <https://doi.org/10.1063/1.556004>

Submitted: 06 August 1996 . Published Online: 15 October 2009

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Electron Interactions with CHF₃

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Received August 6, 1996; revised manuscript received October 11, 1996

In this paper we assess and synthesize the available information on the cross sections and the rate coefficients for collisional interactions of trifluoromethane (CHF₃) with electrons in an effort to build a database on electronic and ionic collision processes that will aid the understanding of the behavior of CHF₃ in its use in manufacturing semiconductor devices and other applications. The limited data on the total and partial electron impact ionization cross sections, total and partial cross sections for electron impact dissociation of CHF₃ into neutral species, electron-impact induced line and continuous light emission from CHF₃, negative ion states of CHF₃, and the energetics of ionization, dissociation, and attachment are summarized and discussed. Besides some recent unpublished measurements of the total electron scattering cross section below 20 eV, to our knowledge no measurements are available of the cross sections of any of the electron scattering processes (elastic, momentum, vibrational, inelastic, etc.) or the electron transport, attachment, and ionization coefficients. While the available information is meager, the synthesis of the existing knowledge and the background information provided in the paper can be helpful for modeling plasma reactors. Clearly, more measurements and calculations are needed of the cross sections for virtually all fundamental electron impact processes for this plasma processing gas. Measurements of the transport, attachment, and ionization coefficients over wide ranges of the density reduced electric field are also needed. © 1997 American Institute of Physics and American Chemical Society. [S0047-2689(97)00201-8]

Key words: attachment; CHF₃; cross sections; dissociation; electron scattering; emission; fluoroform; ionization; transport; trifluoromethane.

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1. Introduction

Trifluoromethane or fluoroform (CHF_3) is a plasma processing gas. As a fluorohydrocarbon, it does not contain atomic chlorine and is, thus, not destructive of stratospheric ozone. Trifluoromethane is, however, a greenhouse gas. It has a global warming potential over a 100-year time horizon of 12 100 relative to the global warming potential of CO_2 over the same time period.¹ The global warming potential of CHF_3 is about twice as large as that of CF_4 , which is also used in plasma processing. However, the lifetime of CHF_3 in the atmosphere is much shorter¹ (250 years) compared to the lifetime of CF_4 (50 000 years).¹ This makes CHF_3 a desirable substitute for CF_4 in some industrial applications.

In this paper, as in a previous study² for CF_4 , we assess and synthesize the available information on the cross sections and the rate coefficients for collisional interactions of CHF_3 with electrons. Definitions of the symbols we use to describe the various collision processes discussed in this paper are given in Table 1. This study is part of an effort to build a database on electronic and ionic collision processes that will aid the understanding of the behavior of CHF_3 in its use in manufacturing semiconductor devices and other appli-

TABLE 1. Definition of symbols

Symbol	Definition	Common scale and units
$\sigma_{sc,t}(\epsilon)$	Total electron scattering cross section	10^{-20} m^2
$\sigma_{i,t}(\epsilon)$	Total electron impact ionization cross section	10^{-20} m^2
$\sigma_{i,part}(\epsilon)$	Partial dissociative ionization cross section	10^{-20} m^2
$\sigma_{diss,t}(\epsilon)$	Total electron impact dissociation cross section	10^{-20} m^2
$\sigma_{diss,n,part}(\epsilon)$	Partial cross section for electron impact dissociation into neutral fragments	10^{-20} m^2
$\sigma_{diss,n,t}(\epsilon)$	Total electron impact dissociation into neutral species	10^{-20} m^2
σ_{em}	Emission cross section	10^{-19} cm^2
$(k_a)_{th}$	Thermal electron attachment rate constant	$10^{-14} \text{ cm}^3 \text{ s}^{-1}$

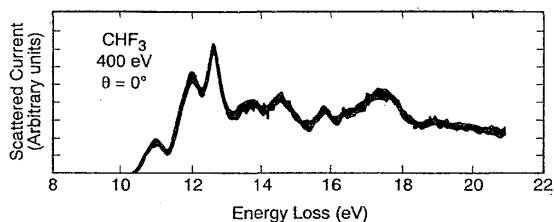


FIG. 1. Electron impact energy loss spectrum of CHF₃ obtained (Ref. 13) with 400 eV incident electrons scattered at an angle $\theta=0^\circ$.

cations. Unlike our earlier work on CF₄, however, the data on this molecule are insufficient to allow a recommendation of specific data at this time.

2. Electronic and Molecular Structure

The structure of the CHF₃ molecule is a symmetric top of the C_{3v} point group. The outer electronic orbital structure³⁻⁶ of CHF₃ is

$$\dots (4a_1)^2(5a_1)^2(3e)^4(4e)^4(5e)^4(1a_2)^2(6a_1)^2.$$

In contrast to CF₄ which is nonpolar, the CHF₃ molecule is polar. Its electric dipole moment has been reported to be 5.504×10^{-30} C m (=1.65 D).⁷⁻⁹ As a consequence of its dipole moment, CHF₃ has a strong rotational spectrum (see, e.g., Cazzoli *et al.*¹⁰). The CHF₃ molecule also has a sizeable static polarizability. Beran and Kevan¹¹ calculated the static polarizability of CHF₃ using three different methods. Their values are: 26.9×10^{-25} cm³, 27.8×10^{-25} cm³, and 35.5×10^{-25} cm³. Sutter and Cole⁹ obtained the value 35.7×10^{-25} cm³ from dielectric constant measurements (see Kobayashi *et al.*¹² for frequency-dependent polarizabilities of CHF₃).

There have been a number of electron-impact energy loss, photoelectron, and photoabsorption studies of CHF₃ and we only refer to representatives of such data below. Figure 1 shows the electron-impact energy loss spectrum¹³ of CHF₃ up to 21 eV. The spectrum was obtained using electrons with 400 eV incident energy scattered at an angle $\theta = 0^\circ$. Table 2 lists the measured vertical excitation and ionization energies of CHF₃ with assignments as given by Harshbarger *et al.*¹³ Table 2 also lists similar data⁶ derived from measurements of the generalized oscillator strengths of valence electronic transitions of CHF₃ as a function of energy loss (0 eV to 15 eV) using angle-resolved electron energy loss-spectroscopy at 2.5 keV incident electrons. A more recent *ab initio* configuration interaction calculation¹⁴ confirmed the Rydberg nature of the electronic transitions that constitute the absorption spectrum of CHF₃, but maintained that "most of the transitions correspond to relatively unlocalized charge transfers and that the distinction between types *s*, *p*, or *d* Rydberg states is difficult to establish."

The vacuum ultraviolet absorption spectrum of CHF₃ has been reported by Sauvageau *et al.*¹⁵ between 60 nm and 120 nm and by Wu *et al.*⁴ in the wavelength range of 18 nm to 72

TABLE 2. Vertical excitation and ionization energies of CHF₃ with assignments (from Harshbarger *et al.*—Ref. 13 unless otherwise noted)

Excitation energy (eV)	Ionization energy (eV)	Assignment
10.92; 11.1 ^a		6a ₁ →3s
11.95; 11.9 ^a		6a ₁ →3p
12.58; 12.7 ^a		5e→3s
13.65; 13.7 ^a		5e→3p
		4e→3s
		4e→3p
14.49	14.8	6a ₁
	15.5	1a ₂
15.76		4e→3d
	16.2	5e
16.42		3e→3s
		5a ₁ →3s
	17.24	4e
17.4		3e→3p
		5a ₁ →3p
19.14		3e→3d
		5a ₁ →3d
	20.84	3e
		5a ₁

^aReference 6.

nm using synchrotron radiation. As an example of this type of measurement we reproduce in Fig. 2 and list in Table 3 the data of Wu *et al.*⁴ Adiabatic and vertical ionization energies^{3,16-18} of CHF₃ determined from photoelectron spectra are given in Table 4 (see also a relevant review by Bieri *et al.*¹⁹). Interestingly, in optical studies, vibrational fine structure has been observed for some excited electronic states,^{4,15,16} showing that "stable" excited electronic states exist for this molecule.

The energies of the six fundamental vibrational modes^{20,21} of CHF₃ ν_1 , ν_2 , ν_3 , ν_4 , ν_5 , and ν_6 are (0.3763, 0.1415, 0.0864, 0.1708, 0.1435, and 0.063) eV, respectively.

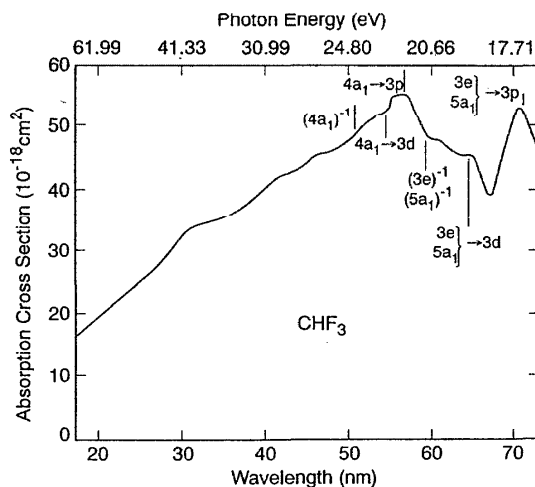


FIG. 2. Absorption cross section of CHF₃ in the wavelength range 17.5 nm to 76 nm. Indicated in the figure are the positions of the probable Rydberg states and their ion states (from Wu *et al.*—Ref. 4).

TABLE 3. Absorption cross section of CHF₃ (from Wu *et al.*—Ref. 4)

Wavelength (nm)	Cross section (10 ⁻¹⁸ cm ²)
18	17.5
20	19.6
22	21.8
24	23.9
26	26.3
28	29.0
30	32.5
32	34.6
34	35.1
36	36.3
38	38.4
40	40.4
42	42.8
44	44.0
46	45.7
48	46.6
50	48.0
52	50.2
54	52.1
56	55.3
58	52.0
60	48.3
62	46.7
64	45.6
66	42.8
68	41.7
70	53.1
72	49.3

3. Electron Scattering

The sizeable electric dipole moment of the CHF₃ molecule allows for a determination of an estimate for the momentum transfer and total electron scattering cross sections at low electron energies (thermal and near thermal). First, the Born approximation theory of Altshuler²² predicts that the momentum transfer cross section $\sigma_m(\nu)$ varies with the incident electron velocity ν as

$$\sigma_m(\nu) = 1.72D^2/\nu^2, \quad (1)$$

TABLE 4. Adiabatic and vertical ionization energies of CHF₃ determined from photoelectron spectra (from Ref. 3 unless otherwise indicated)

Orbital	Adiabatic ionization energy (eV)	Vertical ionization energy (eV)
6a ₁	≥ 13.8; 13.84; ^b 14.19; ^c 13.86 ^d	14.8; 14.77 ^d
1a ₂		15.5; 15.46 ^d
5e		16.2; 16.16 ^d
4e	17.11; 17.13 ^d	17.24; 17.26 ^d
3e	20.6 ^a ; 20.05 ^d	19.84 ^a ; ~21 ^d
5a ₁		
4a ₁	≥ 24.34	24.44

^aUnresolved blend of two or more transitions.

^bReference 16.

^cReference 17.

^dReference 18.

where the dipole moment, D , is in debye units ($1 D = 3.3356 \times 10^{-30} \text{ C m}$) and the electron velocity, ν , is in cm s^{-1} . Christophorou and Christodoulides²³ have found that for the molecules they studied with electric dipole moments in the range $2 \times 10^{-30} \text{ C m} < D < 13.68 \times 10^{-30} \text{ C m}$, the experimental cross sections for electrons having a Maxwellian energy distribution are within 50% of those calculated via Eq. (1). We employed Eq. (1) and obtained the momentum transfer cross section shown in Fig. 3 by the broken line using $5.504 \times 10^{-30} \text{ C m} (= 1.65 D)^{7-9}$ for the D of CHF₃. Second, Christophorou and Christodoulides^{23,24} approximated the total electron scattering cross section for thermal and near thermal electron scattering for strongly polar molecules as

$$\sigma_{\text{sc},t}(\nu) \approx A_I/\nu^2, \quad (2)$$

where A_I is a constant equal to $7.7574 \times 10^5 \text{ S}^{-1}$ and $S = w/(E/P)$. The slope, S , is determined in the low E/P region where the electron drift velocity, w , varies linearly with E/P (E is the applied uniform electric field and P is the total gas pressure at the temperature of the experiment). We have used the value $1.773 \times 10^7 \text{ cm}^2 \text{ Pa V}^{-1} \text{ s}^{-1} (= 13.3 \times 10^4 \text{ cm}^2 \text{ Torr V}^{-1} \text{ s}^{-1})$ of S reported by Christophorou *et al.*²⁵ for $E/N < 3.69 \times 10^{-17} \text{ V cm}^2 (E/P < 1.2 \text{ V cm}^{-1} \text{ Torr}^{-1})$ and estimated the electron scattering cross section, $\sigma_{\text{sc},t}(\nu)$, at low energies shown in Fig. 3 by the open triangle line. The total cross section we determined via Eq. (2) is ~25% higher than the momentum transfer cross section determined via Eq. (1). The cross sections determined through (1) and (2) are very large at low electron energies.

In Fig. 3 are also plotted (open circle line) recent unpublished measurements of $\sigma_{\text{sc},t}(\epsilon)$ by Sanabia and Moore²⁶ between about 0.1 eV and 20 eV. These data clearly fall below the calculated values for energies less than about 0.7 eV. In this low energy region the calculated cross sections can be useful as an estimate in the absence of accurate direct measurements. They are, however, approximate and are expected to fall below the true total electron scattering cross section values progressively by larger amounts as the energy is increased above about 1 eV, as is indeed the case (Fig. 3). For example, in the case of H₂O ($D = 6.17 \times 10^{-30} \text{ C m}$) and NH₃ ($D = 4.87 \times 10^{-30} \text{ C m}$) the total electron scattering cross sections determined via (2) are compatible with the experimental measurements below about 2 eV, but begin to fall below the experimental values progressively by larger amounts as the electron energy is increased above ~2 eV (see Fig. 3 of Ref. 25 and Fig. 4 of Ref. 27). We have determined a suggested set of values for $\sigma_{\text{sc},t}(\epsilon)$ by accepting the calculated values of $\sigma_{\text{sc},t}(\epsilon)$ below ~0.7 eV and merging these with the measured values of Sanabia and Moore²⁶ above this energy. These cross sections are shown in Fig. 3 by the solid line and are listed in Table 5 as the suggested set of values for $\sigma_{\text{sc},t}(\epsilon)$ of CHF₃ in the absence of more reliable data.

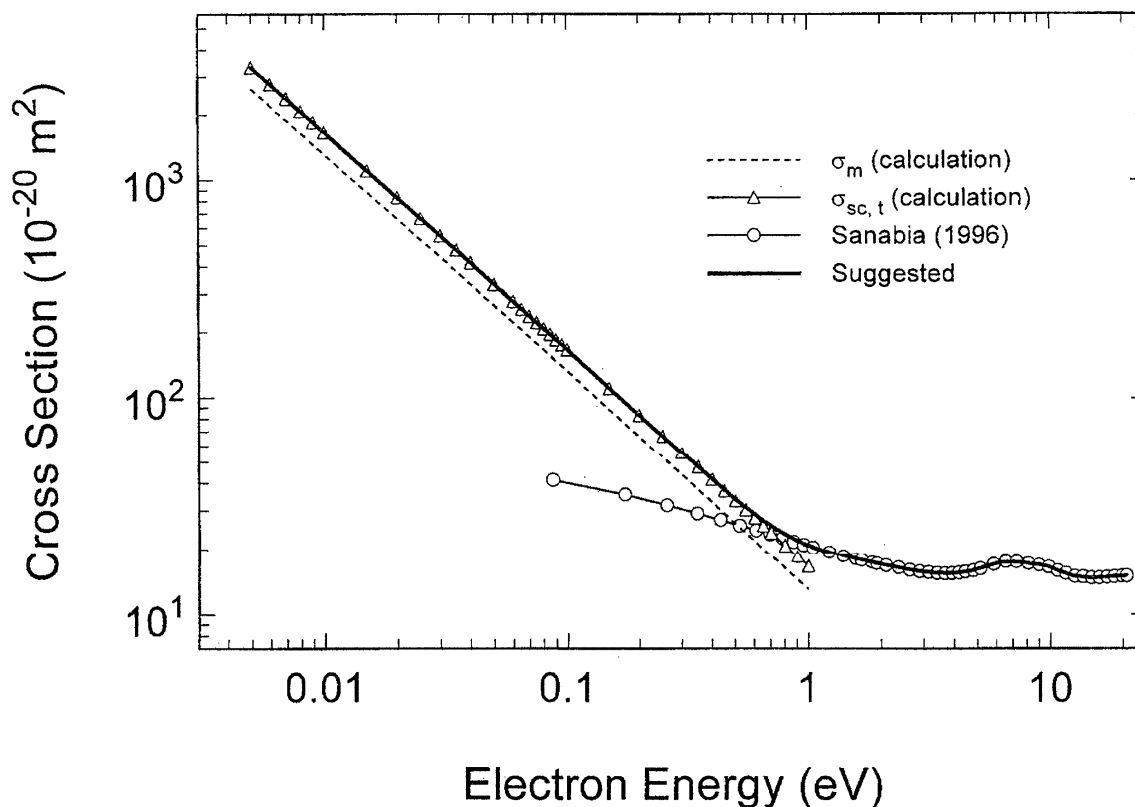


FIG. 3. Calculated momentum transfer (---) and total (Δ) electron scattering cross sections for CHF₃ at low electron energies. Measured—Ref. 26 (O) and suggested (—) total electron scattering cross sections (see the text).

4. Electron Impact Ionization

There have been few measurements of the partial and total electron impact ionization cross sections of CHF₃. Poll and Meichsner²⁸ measured the partial ionization cross sections for the following ions: CF₃⁺, CHF₂⁺ + CF₂⁺, and CF⁺, and their results (obtained from Fig. 2(j) of their paper) are listed in Table 6 and are plotted in Fig. 4. We determined the sum $\sigma_{i, \text{part}, t}(\epsilon)$ of these partial cross sections which is listed in column 5 of Table 6. A second set of measurements of the partial ionization cross sections was made by Goto *et al.*²⁹ for the following ions: CF₃⁺, CHF₂⁺, CF₂⁺, CHF⁺, CF⁺, CH⁺, and F⁺, and these are listed in Table 7 and are plotted in Fig. 5. Their sum $\sigma_{i, \text{part}, t}(\epsilon)$ is given in column 9 of Table 7.

Figure 6 compares the partial ionization cross sections, $\sigma_{i, \text{part}}(\epsilon)$, of Poll and Meichsner²⁸ on CF₃⁺, CHF₂⁺ + CF₂⁺, and CF⁺ with the respective data of Goto *et al.*²⁹ There are substantial differences in the two sets of data which depend on the particular ion; the largest difference is for the sum of the two ions CHF₂⁺ + CF₂⁺.

A comparison of the sum $\sigma_{i, \text{part}, t}(\epsilon)$ of the partial ionization cross sections, which should approximate $\sigma_{i, t}(\epsilon)$, of Poll and Meichsner²⁸ and of Goto *et al.*²⁹ is made in Fig. 7. Clearly the two sets of data differ and since we have insuff-

icient basis to judge their respective validity, we have averaged the two sets of values and have taken this average to be a "recommended" set for the total ionization cross section, $\sigma_{i, t}(\epsilon)$. The $\sigma_{i, \text{part}, t}(\epsilon)$ of the two experimental groups and their average are listed in Table 8. Table 8 also gives the early measurement of the total ionization cross section of CHF₃ made by Beran and Kevan³⁰ at three values of the incident electron energy. The three sets of values are compared in Fig. 7 with the recent unpublished results of a calculation of the total ionization cross section, $\sigma_{i, t}(\epsilon)$, of CHF₃ by Kim.³¹ The result of Kim's calculation is in reasonable agreement with the measurements below about 50 eV, but the calculated cross section is much lower than the experimental values at higher energies. Kim used a model³² which combines binary encounter theory and the Bethe theory of electron impact ionization.

Since all electronically excited states of the CHF₃ molecule dissociate or predissociate³³ (no parent CHF₃⁺ has been observed although some optical emission resulting from electron impact on CHF₃ has been attributed to CHF₃⁺, see Sec. 8), and since the electron impact dissociation cross sections of CHF₃ into neutral species are small (see Sec. 5), the total dissociation cross section should be about equal to the total dissociative ionization cross section at energies sufficiently above the ionization threshold.

TABLE 5. Total electron scattering cross section, $\sigma_{sc,t}(\epsilon)$, of CHF_3 in units of 10^{-20} m^2 (see the text)

Electron energy (eV)	$\sigma_{sc,t}(\epsilon)$ (10^{-20} m^2)
0.005	3321.2
0.006	2768.9
0.007	2373.4
0.008	2075.3
0.009	1845.2
0.01	1660.4
0.015	1107.2
0.02	830.4
0.025	664.3
0.03	553.5
0.035	474.4
0.04	415.2
0.045	369.0
0.05	332.1
0.06	276.8
0.07	237.2
0.08	207.6
0.09	184.5
0.10	166.1
0.15	110.7
0.20	83.0
0.25	66.4
0.30	55.3
0.35	47.6
0.40	41.7
0.45	37.3
0.50	33.7
0.60	28.8
0.70	25.5
0.80	23.4
0.90	21.8
1.0	20.8
1.5	18.2
2.0	16.9
2.5	16.1
3.0	15.6
3.5	15.4
4.0	15.4
4.5	15.7
5.0	16.1
6.0	17.0
7.0	17.3
8.0	17.1
9.0	16.7
10	16.3
12	15.1
14	14.7
16	14.7
18	14.8
20	14.9

Table 9 lists the energy thresholds of a number of reactions leading to positive ions by electron impact on CHF_3 (Refs. 29 and 34–36). The larger positive ions have lower energy thresholds. By selectively choosing the electron energy, one may eliminate the production of ions with higher energy onsets using the information in this table.

TABLE 6. Partial dissociative ionization cross sections, $\sigma_{i, \text{part}}(\epsilon)$, of CHF_3 in units of 10^{-20} m^2 (from Ref. 28); $\sigma_{i, \text{part}, t}(\epsilon)$ is the sum of the cross sections in columns 2–4

Energy (eV)	$\sigma_{i, \text{part}}(\epsilon)$ CF_3^+	$\sigma_{i, \text{part}}(\epsilon)$ $\text{CHF}_2^+ + \text{CF}_2^+$	$\sigma_{i, \text{part}}(\epsilon)$ CF^+	$\sigma_{i, \text{part}, t}(\epsilon)$
20	0.18	0.23	0.001	0.41
25	0.36	0.90	0.25	1.51
30	0.53	1.54	0.71	2.78
35	0.69	2.13	1.07	3.89
40	0.82	2.64	1.40	4.86
45	0.94	3.04	1.67	5.65
50	1.03	3.36	1.91	6.30
60	1.18	3.77	2.24	7.19
70	1.28	3.93	2.52	7.73
80	1.35	4.00	2.69	8.04
90	1.40	4.03	2.82	8.25
100	1.44	4.02	2.90	8.36
110	1.47	4.00	2.96	8.43
120	1.48	3.95	3.00	8.43

5. Electron Impact Dissociation Producing Neutral Species

As in the case of CF_4 , the CHF_3 molecules predominantly dissociate or predissociate upon electronic excitation. Although the observation of vibrational structure for some electronic transitions would indicate stable excited electronic states, dissociation is the dominant process that follows elec-

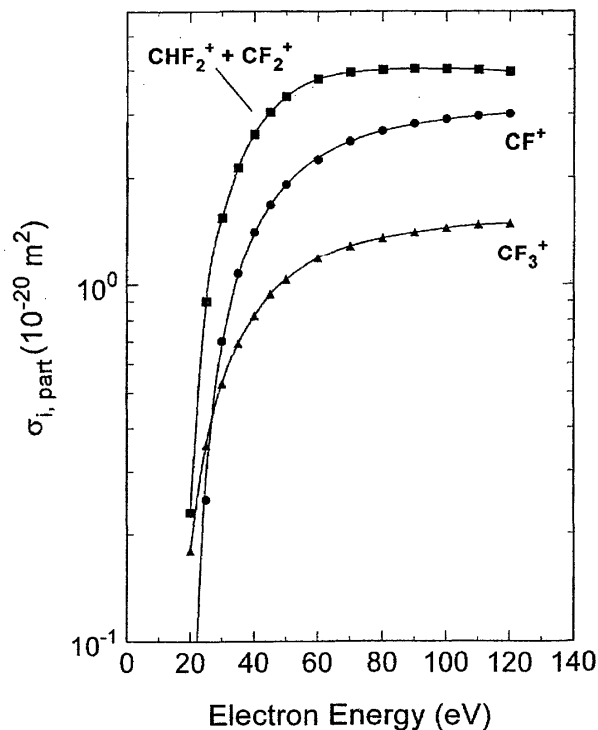


FIG. 4. Partial electron impact ionization cross sections, $\sigma_{i, \text{part}}(\epsilon)$, of CHF_3 for the production of CF_3^+ , $\text{CHF}_2^+ + \text{CF}_2^+$, and CF^+ (data of Poll and Meichsner—Ref. 28).

TABLE 7. Partial dissociative ionization cross sections, $\sigma_{i, \text{part}}(\epsilon)$, of CHF₃ in units of 10^{-20} m^2 (from Ref. 29)

Energy (eV)	$\sigma_{i, \text{part}}(\epsilon)$ CF ₃ ⁺	$\sigma_{i, \text{part}}(\epsilon)$ CHF ₂ ⁺	$\sigma_{i, \text{part}}(\epsilon)$ CF ₂ ⁺	$\sigma_{i, \text{part}}(\epsilon)$ CHF ⁺	$\sigma_{i, \text{part}}(\epsilon)$ CF ⁺	$\sigma_{i, \text{part}}(\epsilon)$ CH ⁺	$\sigma_{i, \text{part}}(\epsilon)$ F ⁺	$\sigma_{i, \text{part}}(\epsilon)^a$
20	0.12	0.01						0.13
25	0.38	0.06	0.01	0.03	0.06			0.54
30	0.64	0.12	0.02	0.05	0.26			1.09
35	1.02	0.19	0.03	0.10	0.53			1.87
40	1.30	0.25	0.05	0.15	0.81	0.01	0.01	2.58
45	1.52	0.30	0.07	0.20	1.12	0.01	0.02	3.24
50	1.70	0.34	0.09	0.26	1.46	0.02	0.04	3.91
60	1.88	0.39	0.13	0.36	1.94	0.02	0.07	4.79
70	2.04	0.41	0.17	0.42	2.35	0.02	0.10	5.52
80	2.15	0.42	0.19	0.49	2.50	0.03	0.12	5.90
90	2.12	0.43	0.21	0.53	2.71	0.03	0.13	6.16
100	2.16	0.43	0.23	0.56	2.75	0.02	0.14	6.29
110	2.18	0.44	0.24	0.58	2.87	0.02	0.15	6.48
120	2.22	0.44	0.25	0.60	2.88	0.02	0.15	6.56

^aThe sum of columns 2–8.

tronic excitation. Thus, Winters and Inokuti³³ argued that the total dissociation cross section of CHF₃ is equal to the total cross section for electronic excitation (the sum of the cross sections for excitation to all electronic and ionic states). The data of Winters and Inokuti on the total dissociation cross section of CHF₃ up to 300 eV, are listed in Table 10 and are plotted in Fig. 8.

There has been a study by Goto *et al.*²⁹ reporting partial cross sections, $\sigma_{\text{diss}, n, \text{part}}(\epsilon)$, for dissociation of CHF₃ by electron impact into the neutral fragments CF₃, CHF₂,

CF₂, CHF, and CF. The reported cross sections are listed in Table 11 and are plotted in Fig. 9. Column 7 of Table 11 gives the sum, $\sigma_{\text{diss}, n, \text{t}}(\epsilon)$, of the partial dissociation cross sections in columns 2–6.

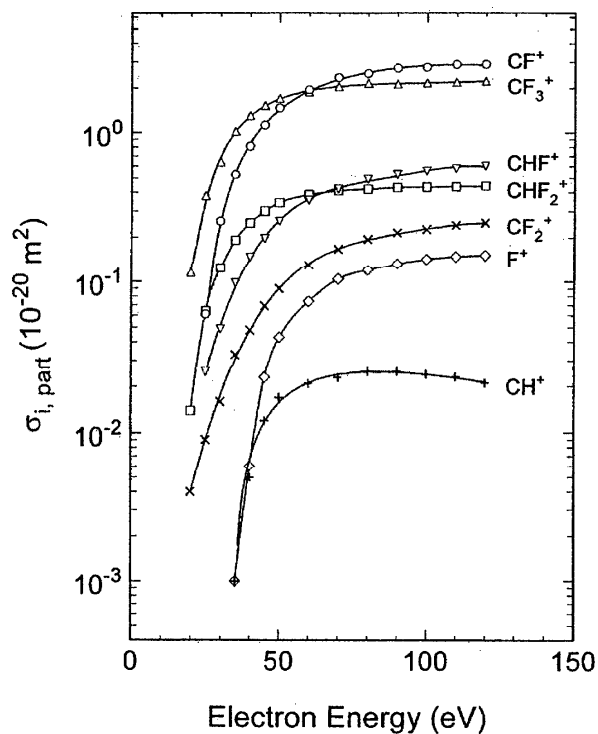


FIG. 5. Partial electron impact ionization cross sections, $\sigma_{i, \text{part}}(\epsilon)$, of CHF₃ for the production of CF₃⁺, CHF₂⁺, CF₂⁺, CHF⁺, CF⁺, CH⁺, and F⁺ (data of Goto *et al.*—Ref. 29).

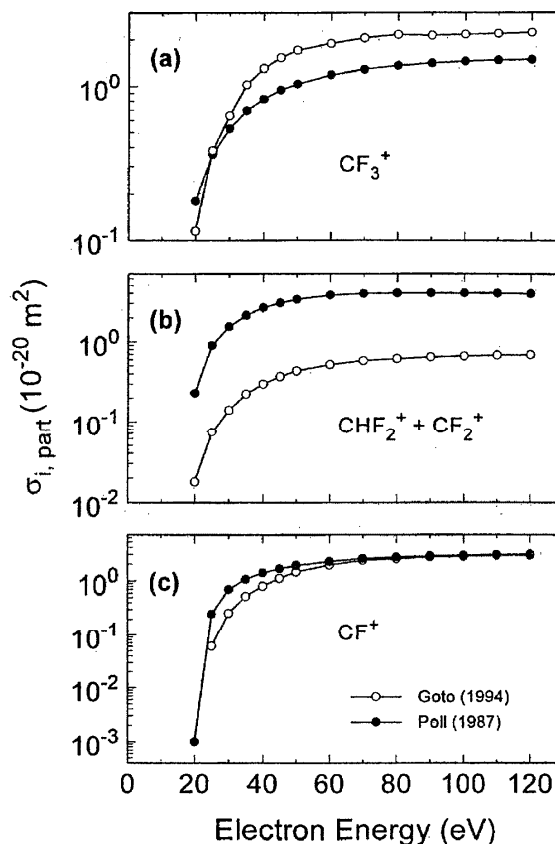


FIG. 6. Comparison of the measurements of Poll and Meichsner (Ref. 28) of the $\sigma_{i, \text{part}}(\epsilon)$ for CF₃⁺, CHF₂⁺+CF₂⁺, and CF⁺ with the measurements of Goto *et al.*—Ref. 29 for the same ions. Since Poll and Meichsner reported a cross section for the sum of CHF₂⁺ and CF₂⁺ the corresponding cross sections for the two ions reported by Goto *et al.* were summed up and plotted in (b).

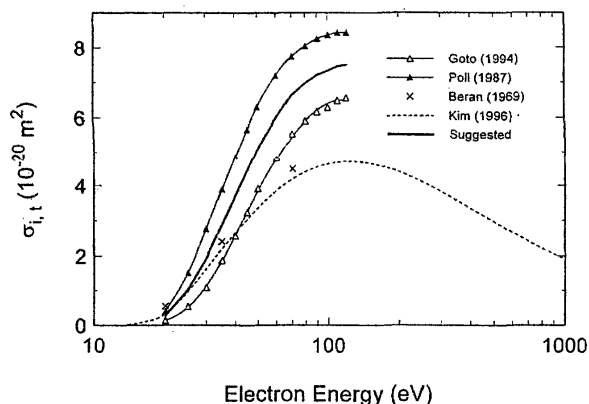


FIG. 7. Total electron impact ionization cross section, $\sigma_{i,t}(\epsilon)$, for CHF_3 (see the text). Experimental values: \times , Ref. 30; \blacktriangle , Ref. 28 (Column 5 of Table 6); \triangle , Ref. 29 (Column 9 of Table 7); —, average of data from Refs. 28 and 29 (Column 5 of Table 8). Calculated values; ---, Ref. 31.

The cross sections of Goto *et al.*²⁹ have subsequently been revised by Sugai *et al.*³⁷ using the absolute cross sections for electron impact dissociation of the CF_x ($x = 1-3$) radicals reported by Tarnovsky *et al.*^{38,39} The revised data of Sugai *et al.*³⁷ for the CF_3 , CF_2 , and CF radicals are given in Table 12 and are plotted in Fig. 10. Column 5 of Table 12 lists the sum, $\sigma_{\text{diss},n,t}(\epsilon)$, of the partial cross sections for the three neutral fragments. The revised cross sections are very small and differ from the original data (Table 11) by factors of up to 16 (see Fig. 11). The most abundant neutral fragments are the CF_3 and CF radicals.

The sum of the partial dissociation cross sections into neutrals, $\sigma_{\text{diss},n,t}(\epsilon)$, are listed in the last columns of Tables 11 and 12 and are plotted in Fig. 12. They represent an estimate of the total cross section for electron impact dissociation of the CHF_3 molecule into neutral fragments. Even though the cross sections $\sigma_{\text{diss},n,t}(\epsilon)$ in Table 12 do not include the con-

TABLE 8. Total electron impact ionization cross section, $\sigma_{i,t}(\epsilon)$, for CHF_3 in units of 10^{-20} m^2

Energy (eV)	Ref. 30	Ref. 28 ^a	Ref. 29 ^b	$\sigma_{i,t}(\epsilon)$ ^c
20	0.55	0.41	0.13	0.27
25		1.51	0.54	1.03
30		2.78	1.09	1.94
35	2.41	3.89	1.87	2.88
40		4.86	2.57	3.72
45		5.65	3.24	4.45
50		6.30	3.91	5.11
60		7.19	4.79	5.99
70	4.47	7.73	5.52	6.63
80		8.04	5.90	6.97
90		8.25	6.16	7.21
100		8.36	6.29	7.33
110		8.43	6.48	7.46
120		8.43	6.56	7.50

^a $\sigma_{i,\text{part},t}(\epsilon)$; last column of Table 6.

^b $\sigma_{i,\text{part},t}(\epsilon)$; last column of Table 7.

^c $\sigma_{i,t}(\epsilon)$; average of columns 3 and 4.

TABLE 9. Threshold energies for "appearance" of positive ions by electron impact on CHF_3

Reaction	Threshold energy (eV)	Reference
$\text{CHF}_3 + e \rightarrow \text{CF}_3^+ + \text{H}$	15.2	29
	14.67	34
	14.53	35
	14.42	36
$\text{CHF}_3 + e \rightarrow \text{CHF}_2^+ + \text{F}$	16.8	29
	16.4	34
	15.75	36
$\text{CHF}_3 + e \rightarrow \text{CF}_2^+ + \text{HF}$ $\rightarrow \text{CF}_2^+ + \text{H} + \text{F}^-$	17.6	29
	17.5	34
	20.2	36
$\text{CHF}_3 + e \rightarrow \text{CHF}^+ + \text{F}_2$	19.8	29
$\text{CHF}_3 + e \rightarrow \text{CF}^+ + \text{HF} + \text{F}$	20.9	29
	20.75	36
	20.2	34
$\text{CHF}_3 + e \rightarrow \text{CH}^+ + \text{F}_2 + \text{F}$	33.5	29
$\text{CHF}_3 + e \rightarrow \text{F}^+ + \dots$	37.0	29

TABLE 10. Total electron impact dissociation cross section, $\sigma_{\text{diss},t}(\epsilon)$, for CHF_3 in units of 10^{-20} m^2 (data of Ref. 33)

Energy (eV)	$\sigma_{\text{diss},t}(\epsilon)$
22	2.4
72	5.5
100	5.8
125	5.7
200	5.4
300	4.9

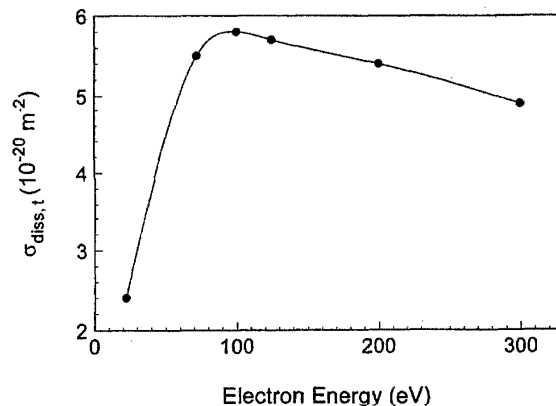


FIG. 8. Total electron impact dissociation cross section, $\sigma_{\text{diss},t}(\epsilon)$, (from Winters and Inokuti—Ref. 33).

TABLE 11. Cross sections, $\sigma_{\text{diss, n, part}}(\epsilon)$, for electron impact dissociation of CHF₃ into neutral fragments in units of 10^{-20} m^2 (from Ref. 29). The last column is the sum, $\sigma_{\text{diss, n, t}}(\epsilon)$, of the respective cross sections in columns 2-6

Energy (eV)	$\sigma_{\text{diss, n, part}}(\epsilon)$ CF ₃	$\sigma_{\text{diss, n, part}}(\epsilon)$ CHF ₂	$\sigma_{\text{diss, n, part}}(\epsilon)$ CF ₂	$\sigma_{\text{diss, n, part}}(\epsilon)$ CHF	$\sigma_{\text{diss, n, part}}(\epsilon)$ CF	$\sigma_{\text{diss, n, t}}(\epsilon)$
20	0.02	0.001			0.01	0.031
25	0.03	0.002			0.16	0.192
30	0.05	0.003	0.014		0.22	0.287
35	0.08	0.004	0.025		0.23	0.339
40	0.10	0.005	0.040		0.24	0.385
50	0.24	0.008	0.075	0.002	0.23	0.555
60	0.33	0.010	0.098	0.002	0.22	0.660
70	0.37	0.017	0.104	0.004	0.21	0.705
80	0.38	0.024	0.099	0.004	0.19	0.697
90	0.46	0.027	0.092	0.005	0.20	0.784
100	0.49	0.032	0.092	0.006	0.18	0.800
110	0.50	0.034	0.094	0.008	0.21	0.846
120	0.48	0.038	0.090	0.011	0.18	0.799
130	0.47	0.039	0.086	0.014	0.18	0.789
140	0.45	0.040	0.088	0.015	0.19	0.783
150	0.44	0.038	0.080	0.016	0.16	0.734
160	0.45	0.037	0.075	0.019	0.18	0.761
170	0.43	0.038	0.074	0.019	0.19	0.751
180	0.44	0.038	0.076	0.019	0.20	0.773
190	0.45	0.041	0.073	0.018	0.16	0.742
200	0.44	0.040	0.076	0.019	0.20	0.775

tributions from the production of the neutral species CHF₂ and CHF, the contribution to the magnitude of $\sigma_{\text{diss, n, t}}(\epsilon)$ from the cross sections for these two neutral species is small (see Table 11).

The data in Fig. 12 can be compared with the difference $\sigma_{\text{diss, t}}(\epsilon) - \sigma_{\text{i, t}}(\epsilon) \approx \sigma_{\text{diss, n, t}}(\epsilon)$. We estimated this difference using the limited measurements of $\sigma_{\text{diss, t}}(\epsilon)$ in Fig. 8 and the values of $\sigma_{\text{i, t}}(\epsilon)$ shown in Fig. 7 by the solid line. While the uncertainty of the resultant total dissociation cross section into neutral fragments is very large, the values of

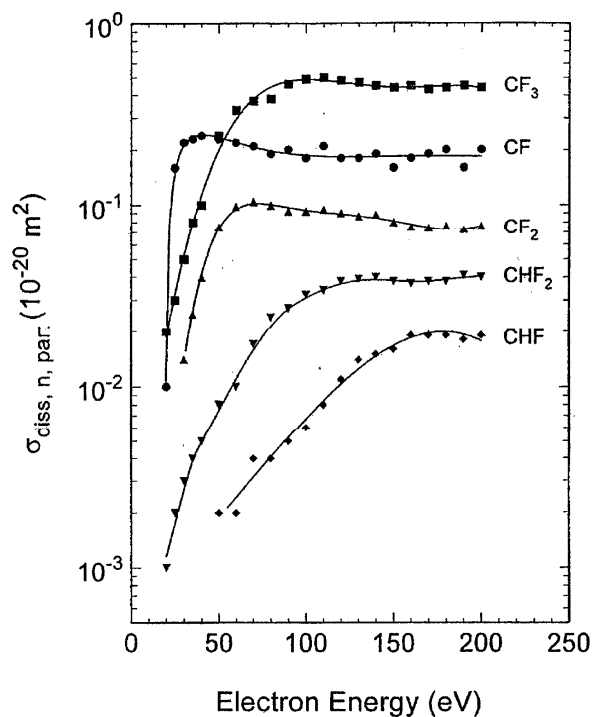


FIG. 9. Partial cross sections, $\sigma_{\text{diss, n, part}}(\epsilon)$, for electron impact dissociation of CHF₃ into the neutral fragments CF₃, CHF₂, CF₂, CHF, and CF (data of Goto *et al.*—Ref. 29).

TABLE 12. Cross sections $\sigma_{\text{diss, n, t}}(\epsilon)$ for electron impact dissociation of CHF₃ into the neutral fragments CF₃, CF₂, and CF in units of 10^{-20} m^2 (data of Goto *et al.*—Ref. 29—as revised by Sugai *et al.*—Ref. 37). The last column is the sum, $\sigma_{\text{diss, n, t}}(\epsilon)$, of the respective cross sections in columns 2-4

Energy (eV)	$\sigma_{\text{diss, n, part}}(\epsilon)$ CF ₃	$\sigma_{\text{diss, n, part}}(\epsilon)$ CF ₂	$\sigma_{\text{diss, n, part}}(\epsilon)$ CF	$\sigma_{\text{diss, n, t}}(\epsilon)$
20	0.006		0.001	0.007
25	0.009		0.012	0.021
30	0.014	0.0009	0.016	0.031
35	0.023	0.0016	0.017	0.042
40	0.030	0.0025	0.018	0.051
50	0.074	0.0047	0.017	0.096
60	0.101	0.0062	0.016	0.123
70	0.113	0.0066	0.015	0.135
80	0.116	0.0062	0.015	0.137
90	0.138	0.0058	0.015	0.159
100	0.149	0.0058	0.014	0.169
110	0.153	0.0059	0.016	0.175
120	0.145	0.0057	0.014	0.165
130	0.144	0.0054	0.014	0.163
140	0.137	0.0055	0.014	0.157
150	0.133	0.0050	0.012	0.150
160	0.137	0.0047	0.014	0.156
170	0.130	0.0046	0.015	0.150
180	0.133	0.0048	0.016	0.154
190	0.136	0.0046	0.012	0.153
200	0.135	0.0048	0.015	0.155

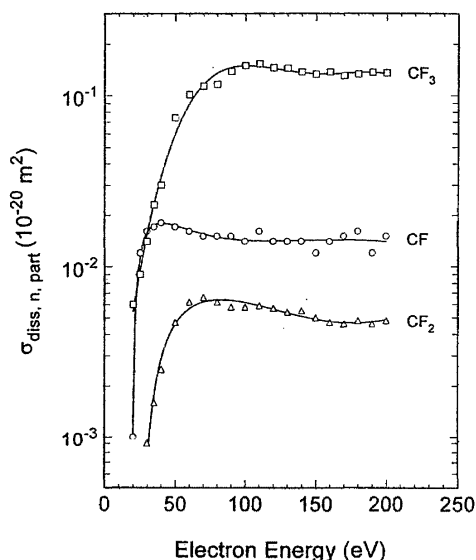


FIG. 10. Partial cross sections, $\sigma_{\text{diss, n, part}}(\epsilon)$, for electron impact dissociation of CHF_3 into the neutral fragments CF_3 , CF_2 , and CF (data of Goto *et al.*—Ref. 29 as revised by Sugai *et al.*—Ref. 37).

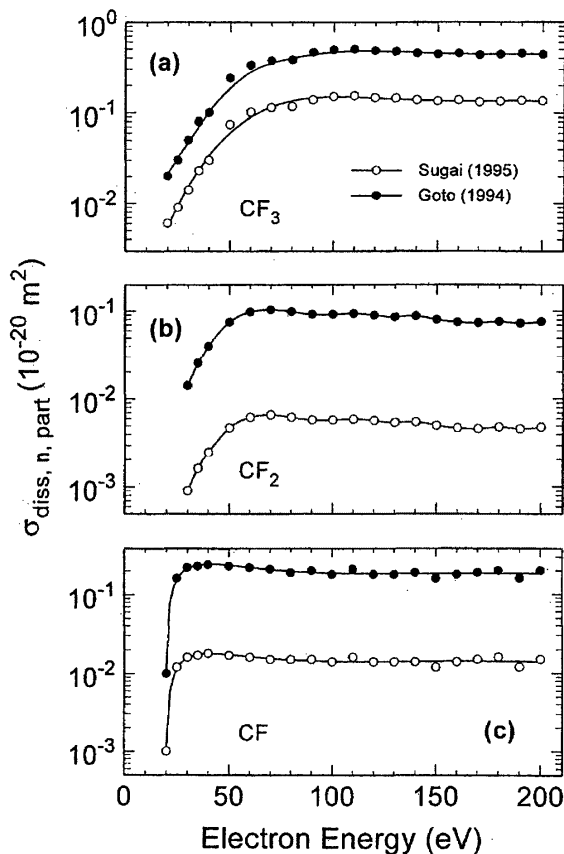


FIG. 11. Comparison of the original (Ref. 29) and the revised (Ref. 37) values of the partial cross sections, $\sigma_{\text{diss, n, part}}(\epsilon)$, for electron impact dissociation of CHF_3 into the neutral fragments CF_3 , CF_2 , and CF .

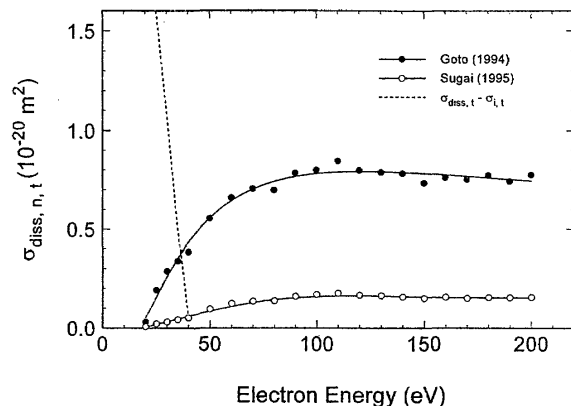


FIG. 12. Total cross section, $\sigma_{\text{diss, n, t}}(\epsilon)$, for electron impact dissociation of CHF_3 into neutral species: \circ , derived from the measurements of Goto *et al.*—Ref. 29 (column 7 of Table 11); \bullet , derived from the revised data of Sugai *et al.*—Ref. 37 (column 5 of Table 12). —, $[\sigma_{\text{diss, t}}(\epsilon) - \sigma_{i, t}(\epsilon)]$ (see the text).

$\sigma_{\text{diss, n, t}}(\epsilon)$ determined this way (dashed line in Fig. 12) clearly indicate that the data of Sugai *et al.*³⁷ may be grossly underestimating the magnitude of $\sigma_{\text{diss, n, t}}(\epsilon)$. It might, of course, be possible that the values of Tarnovsky *et al.*^{38,39} to which Sugai *et al.* normalized the Goto *et al.* data are themselves low. Clearly, more work is indicated.

Threshold energies for electron impact dissociation of CHF_3 into neutral species are listed in Table 13 as given by the authors. They help understand the energetics of the various dissociation processes leading to neutral fragments.

6. Electron Attachment

There have been a number of studies^{40–50} on electron attachment to CHF_3 , but the data are still fragmentary and no absolute cross sections as a function of electron energy have been reported for any of the negative ion fragments. The three mass spectrometric studies^{40,43,49} are in agreement that the predominant dissociative electron attachment channels

TABLE 13. Threshold energies for electron impact dissociation of CHF_3 into neutral species^a (from Goto *et al.*—Ref. 29—unless otherwise indicated)

Reaction	Threshold energy (eV)
$\text{CHF}_3 + e \rightarrow \text{CF}_3 + \text{H} + e$	11.0 ^{b,c}
$\text{CHF}_3 + e \rightarrow \text{CHF}_2 + \text{F} + e$	13.0 ^{b,c}
$\text{CHF}_3 + e \rightarrow \text{CF}_2 + \text{H} + \text{F} + e$	15.0 ^b
$\text{CHF}_3 + e \rightarrow \text{CF}_2 + \text{HF} + e$	9.1 ^b
$\text{CHF}_3 + e \rightarrow \text{CHF} + 2\text{F} + e$	16.9 ^b
$\text{CHF}_3 + e \rightarrow \text{CHF} + \text{F}_2 + e$	16.1 ^b
$\text{CHF}_3 + e \rightarrow \text{CF} + \text{H} + 2\text{F} + e$	20.5 ^b
$\text{CHF}_3 + e \rightarrow \text{CF} + \text{F}_2 + \text{H} + e$	19.7 ^b
$\text{CHF}_3 + e \rightarrow \text{CF} + \text{HF} + \text{F} + e$	14.6 ^b

^aThe CF_3 –H bond dissociation energy is 4.46 ± 0.17 eV (Ref. 35).

^bExpected value.

^cMeasured value; experimental uncertainty ± 0.5 eV.

TABLE 14. Negative ion states of CHF₃

Energy (eV)	Reference and method of observation
2.9 ^a	Dissociative electron attachment ^b
3.7 ^a	
9.3 ^a	
0.04	Electron swarm ^c
~4.5(2.2±0.3) ^d	Dissociative electron attachment ^c
10.1±0.1(8.2±0.2) ^d	
12.3±0.2(≅11) ^d	
6.3(?) ^f	Electron transmission ^e
9.3 ^f	
9.10 ^f	Multiple scattering X _α (MS-X _α) bound-state calculations ^g
10.01 ^f	
9.44 ^f	Continuum MS-X _α (CMS-X _α) method ^g
9.64 ^f	

^aThresholds of dissociative attachment processes.

^bReference 43.

^cData of Lee (Ref. 41) as analyzed by Blaunstein and Christophorou (Ref. 42).

^dThe first value is the energy position of the cross section maximum and the value in parentheses is the respective energy threshold.

^eReference 49.

^fVertical attachment energy.

^gReference 50.

are those leading to F⁻. Actually, Reese *et al.*⁴⁰ and Scheunemann *et al.*⁴⁹ observed only F⁻ while MacNeil and Thynne⁴³ reported the observation of F⁻, H⁻, C⁻, CH⁻, CF⁻, F₂⁻, CF₂⁻, and CF₃⁻, with the F⁻ being by far the most abundant negative ion. Appearance onsets and peak energies for the F⁻ negative ions from CHF₃ are given in Table 14. Table 14 also gives the vertical attachment energies measured in an electron transmission experiment⁵⁰ along with the vertical attachment energies obtained via bound and continuum multiple scattering X_α calculations.⁵⁰ Figure 13 shows⁴⁹ the yield for the formation of F⁻ from CHF₃ as a function of electron energy. Clearly at least three

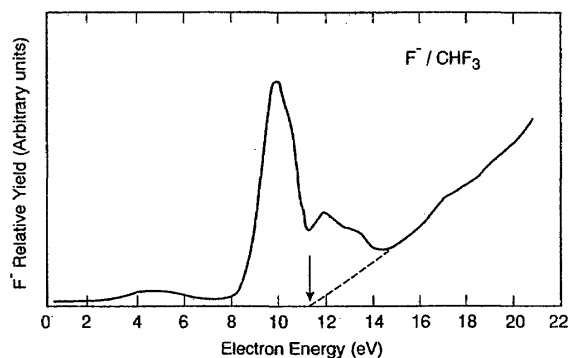
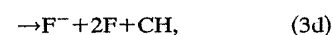
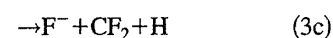
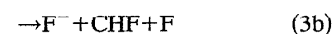


FIG. 13. Relative yield of F⁻ produced by dissociative electron attachment to CHF₃. The rising part with an apparent onset at 11.5 eV (indicated by the arrow) is attributed to the nonresonant production of F⁻ via the negative ion-positive ion pair process (from Scheunemann *et al.*—Ref. 29).

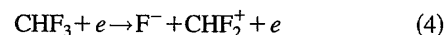
TABLE 15. Values of the thermal ($T \approx 295$ K) electron attachment rate constants, $(k_a)_{th}$, for CHF₃

$(k_a)_{th}(10^{-14} \text{ cm}^3 \text{ s}^{-1})$	Reference
4.6	44
<6.2	45
3.6	46
1.1×10^5	41, 42

negative ion resonances lead to the production of F⁻ below 14 eV. Depending on the energetics, a number of dissociative attachment processes,⁴³



can lead to the production of F⁻. According to Scheunemann *et al.*,⁴⁹ the first resonance (~5 eV) is due to reaction (3a). The higher energy resonances at about 10 eV and 12 eV can be due to a multiplicity of fragmentation channels. It is interesting to note that the cross section for the production of F⁻ via the 10 eV resonance far exceeds that from the lower lying resonance. The rise in the F⁻ yield beyond about 14 eV has been attributed⁴⁹ to the positive ion-negative ion pair process



for which Scheunemann *et al.*⁴⁹ have calculated a threshold of 11.5 eV ± 0.3 eV.

There have been a number of measurements of the thermal value of the rate constant, $(k_a)_{th}$, for electron attachment to CHF₃. These are listed in Table 15. With the exception of the earlier value based on the measurements of Lee,⁴¹ all other values indicate that the rate constant for the attachment of thermal electrons to CHF₃ is very small. To our knowledge, no measurements of the density reduced electron attachment coefficient, η/N , or the density reduced electron impact ionization coefficient, α/N , have been reported for CHF₃. They are being planned in our laboratory.

The most recent mass spectrometric measurements using a trochoidal monochromator as the electron source,⁴⁹ clearly show the existence of at least three negative-ion resonances leading to F⁻ formation located at about 4.5 eV, 10.1 eV, and 12.3 eV (see Fig. 13). On the basis of these findings, it would be expected that the electron scattering cross sections (elastic and inelastic) from CHF₃ in this energy range will exhibit structure associated with these negative ion resonances. Additionally, by comparison to the electron attachment data on CF₄ (see Refs. 2 and 48) and methane,^{47,48} the dissociative electron attachment to CHF₃ is expected to have a peak cross section value > 10⁻¹⁹ cm². Negative ions have been detected in rf plasmas of CHF₃ using a laser photodetachment method.⁵¹ It is important to note that under high gas pressure conditions, a multitude of secondary negative

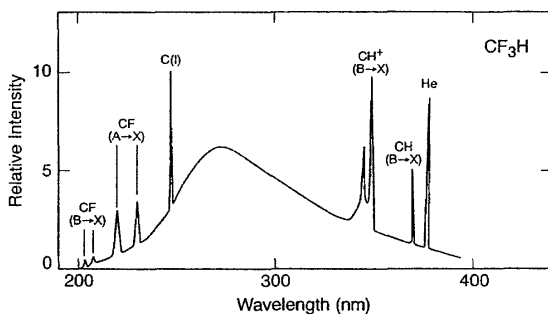


FIG. 14. Electron impact induced emission spectrum of CHF_3 in the wavelength range 200 nm to 400 nm (Ref. 57).

ions and negative ion clusters can form (see, e.g., Tiernan *et al.*⁵²). For instance, the primary negative ion F^- which is formed in the dissociative attachment of electrons to CHF_3 undergoes rapid ion molecule reactions yielding⁵² the cluster anions $(\text{HF})_n\text{F}^-$ ($n = 1-3$).

7. Electron Transport

To our knowledge, no electron transport coefficient measurements have been made for CHF_3 except for a measurement of the ratio $w/(E/P)$ of the electron drift velocity, w , in CHF_3 over the pressure-reduced electric field, E/P , in the low E/P region over which w varies linearly with E/P . The value of this ratio at $T=295$ K was reported²⁵ to be $1.773 \times 10^7 \text{ cm}^2 \text{ Pa V}^{-1} \text{ s}^{-1}$ [$= 13.3 \times 10^4 \text{ cm}^2 \text{ Torr V}^{-1} \text{ s}^{-1}$ (for $E/N < 3.69 \times 10^{-17} \text{ V cm}^2$)] and has been used to obtain an estimate of the electron scattering cross section at low energies (see Sec. 3 and Ref. 25).

The CHF_3 molecule is strongly polar^{7,25} and has been used as the buffer gas in testing mixtures of weakly electron-attaching gases with strongly electron-attaching gases for gas dielectric purposes.^{25,53-56} Mixtures of CHF_3 with electronegative gases that attach electrons over a wide range of electron energies above thermal^{25,53} have been especially studied. The uniform field dielectric strength of CHF_3 has been reported²⁵ to be 0.27 that of SF_6 , i.e., $\sim 97.5 \times 10^{-17} \text{ V cm}^2$. No measurements have been reported of the value, $(E/N)_{\text{lim}}$, of the density-reduced electric field, E/N , at which $\alpha/N = \eta/N$.

8. Electron Impact Induced Light Emission

A number of investigations have been made of light emission from CHF_3 under electron impact.⁵⁷⁻⁵⁹ The first such study was by Van Sprang *et al.*⁵⁷ who used incident electron beam energies of 100 eV. The emission spectrum they obtained in the wavelength range 200 nm to 400 nm is reproduced in Fig. 14. Table 16 lists the emission cross sections measured by Van Sprang *et al.*⁵⁷ for the various atomic F and H lines for 100 eV incident electrons. Van Sprang *et al.*⁵⁷ also reported relative cross sections for the continuous emission from CHF_3 excited by electrons having kinetic

TABLE 16. Emission cross sections, σ_{em} (100 eV), for various atomic F and H lines induced by impact of 100 eV electrons on CHF_3 (from Van Sprang *et al.*—Ref. 57)

Emission line	Wavelength (nm)	σ_{em} (10^{-19} cm^2) ^a
$\text{F(I)} \ ^2P_0 - ^2P$	703.7	1.5
	712.7	1.1
	760.7	0.7
$\text{F(I)} \ ^2D_0 - ^2P$	775.4	4.7
	780	1.9
	731.1	2.0
$\text{F(I)} \ ^2S_0 - ^2P$	731.1	2.0
$\text{F(I)} \ ^4P_0 - ^4P$	733.1	1.8
	739.8	3.9
	742.5	1.1
$\text{F(I)} \ ^4D_0 - ^4P$	677.3	2.0
	685.6	5.9
	690.2	4.8
H_α	656.2	2.7
H_β	486.1	5.7

^aQuoted uncertainty $\pm 10\%$.

energies from 20 eV to 2 000 eV. They ascribed the observed continua to the $\text{C}^2E - \text{X}^2A_1$ transition in CHF_3^+ . (Continuous emission from F_2 also occurs⁵⁷ in the wavelength range 200 nm to 400 nm, because F_2 is a dissociation product of CHF_3 .) In contrast with the Van Sprang *et al.* assignment of the continuous emission, Aarts⁵⁸ assigned the 230 nm to 350 nm emission band (the maximum intensity of this broad emission is around 270 nm) to the $\text{CF}_2 (\tilde{A} \rightarrow \text{X})$ transition and this assignment was later confirmed by Creasy *et al.*⁵⁹ The threshold for the continuum emission was found⁵⁸ to be $14.1 \text{ eV} \pm 0.5 \text{ eV}$. Aarts used electrons with incident energies of up to 1 keV, and Creasy *et al.* used electron, photon, and metastable atom impact methods. Creasy *et al.* observed fluorescence which they associated with the D^2A_1 state of CHF_3^+ (adiabatic ionization energy 20.08 eV) (See also Lee *et al.*⁶⁰ concerning observation of fluorescence from CHF_3^{+*} under photoexcitation.) Aarts and Creasy reported emission spectra similar to those in Fig. 14. The emission cross section for the 270 nm band produced by electron impact on CHF_3 has been measured as a function of electron energy⁵⁸ and is listed in Table 17 and plotted in Fig. 15. Relative cross sections as a function of electron energy have also been reported by Van Sprang *et al.*⁵⁷

Another important study dealing with light emission induced by electron impact on CHF_3 has been made by Wang and McConkey.⁶¹ These investigators measured the emission spectrum of CHF_3 in the vacuum ultraviolet range (50 nm to 130 nm) under single collision conditions for incident electron energies up to 600 eV. The spectrum showed contributions from neutral and singly ionized fluorine and carbon fragments, and also from neutral hydrogen atoms. Wang and McConkey,⁶¹ made absolute measurements of the cross sections for the F I and F II emissions in the range 75.1 nm to 97.77 nm, the C I and C II emissions in the range of 68.7 nm

TABLE 17. Cross section for the 270 nm continuous emission band produced by electron impact on CHF₃ (from Aarts—Ref. 58)

Electron energy (eV)	Cross section (10 ⁻¹⁸ cm ²) ^a
14.1	0
30	5.4
40	5.8
45	6.1
50	5.8
60	5.4
80	5.2
100	4.8
150	4.6
200	4.5
300	3.4
400	3.2
500	2.7
600	2.4
800	2.0
1000	1.7

^aThe estimated reported uncertainty is about ±15%.

to 127.7 nm, and the hydrogen atom emissions in the range of 91.46 nm to 121.6 nm following impact of 200 eV incident electrons on CHF₃. The carbon emission cross sections are generally lower than the fluorine emission cross sections. The emission spectrum is dominated by the F I and H I emissions with the strongest lines at (78, 80.8, 95.5, 97.4 and 97.6) nm for F I, and the Ly α and Ly β for H I. The cross sections at these wavelengths are 2.2×10⁻¹⁹ cm², 3.3×10⁻¹⁹ cm², 9.3×10⁻¹⁹ cm², 5.9×10⁻¹⁹ cm², 2.9×10⁻¹⁹ cm², 27.1×10⁻¹⁹ cm², and 6.5×10⁻¹⁹ cm², respectively. All the major F I lines involve transitions of a 3s or 3d electron decaying to the ground state 1s²2s²2p⁵2P_{1/2,3/2} (for further details see Ref. 61).

Danilevskii *et al.*⁶² also studied light emission from excited CHF₃ fragments formed by electron impact on CHF₃. They have reported measurements in the wavelength range of 300 nm to 850 nm for the effective excitation cross sections of excited F atoms, the Balmer series of the hydrogen

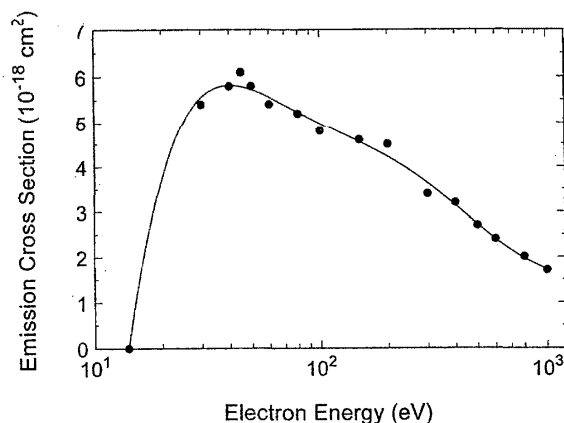


FIG. 15. Emission cross section for the 270 nm band in electron impact on CHF₃ as a function of incident electron energy (Ref. 58).

TABLE 18. Cross sections of emissions from excited F atoms, Balmer series lines of the hydrogen atom, and the CH molecular fragment (A²Δ→X²Π) formed by impact of 4 keV energy electrons on CHF₃ (from Ref. 62)

Wavelength (nm)	Transition	Cross section (10 ⁻²¹ cm ²)
F atom		
623.96	3s ⁴ P-3p ⁴ S ^o	14.2
634.85	3s ⁴ P-3p ⁴ S ^o	10.9
641.36	3s ⁴ P-3p ⁴ S ^o	10.0
669.05	3s ⁴ P-3p ² D ^o	5.4
677.4	3s ⁴ P-3p ⁴ D ^o	7.0
683.4	3s ⁴ P-3p ⁴ D ^o	6.0
685.6	3s ⁴ P-3p ⁴ D ^o	17.3
687	3s ⁴ P-3p ⁴ D ^o	7.0
690.98	3s ⁴ P-3p ⁴ D ^o	10.2
733.2	3s ⁴ P-3p ⁴ P ^o	3.9
739.86	3s ⁴ P-3p ⁴ P ^o	8.5
703.75	3s ² P-3p ² P ^o	3.1
712.79	3s ² P-3a ² P ^o	2.6
720.26	3s ² P-3p ² P ^o	1.7
731.1	3s ² P-3p ² P ^o	4.9
775.47	3s ² P-3p ² D ^o	36.2
CH(A ² Δ-X ² Π)		20.4
H _α		184.6
H _β		19.4
H _γ		17.0
H _δ		9.7

atom, and the CH molecular fragment (A²Δ→X²Π) using 0.4 keV to 6 keV incident energy electrons. This incident electron energy is much larger than those used by Van Sprang *et al.*⁵⁷ and Wang and McConkey.⁶¹ One, thus, would expect the cross sections of Danilevskii *et al.*⁶² to be smaller. Their measured emission cross sections for 4 keV incident electrons are listed in Table 18. Interestingly, Danilevskii *et al.*⁶² observed emission from only excited fragments.

The emission spectra of CF₃ radicals produced in the photolysis of CHF₃ have also been studied (see, e.g., Suto and coworkers⁶³).

9. Electron Interactions with CHF₃ Fragments

Electron impact dissociation of the CHF₃ molecule produces CF₃, CF₂, and CF radicals which are common with radicals produced by electron impact on CF₄. For these three radicals cross sections for electron impact ionization producing the respective parent positive ions have been reported^{38,39,64} and have been summarized and discussed in Ref. 2. Similarly, cross sections for electron impact dissociative ionization of these three radicals have been measured by Tarnovsky *et al.*³⁹ and have also been summarized in Ref. 2. No information exists on the other two possible fragments, CHF₂ and CHF, produced by electron impact on CHF₃.

Measurements of the concentrations of the CF₃, CF₂ and CF radicals in rf CHF₃ etching plasma have recently been made as a function of the microwave power and the gas

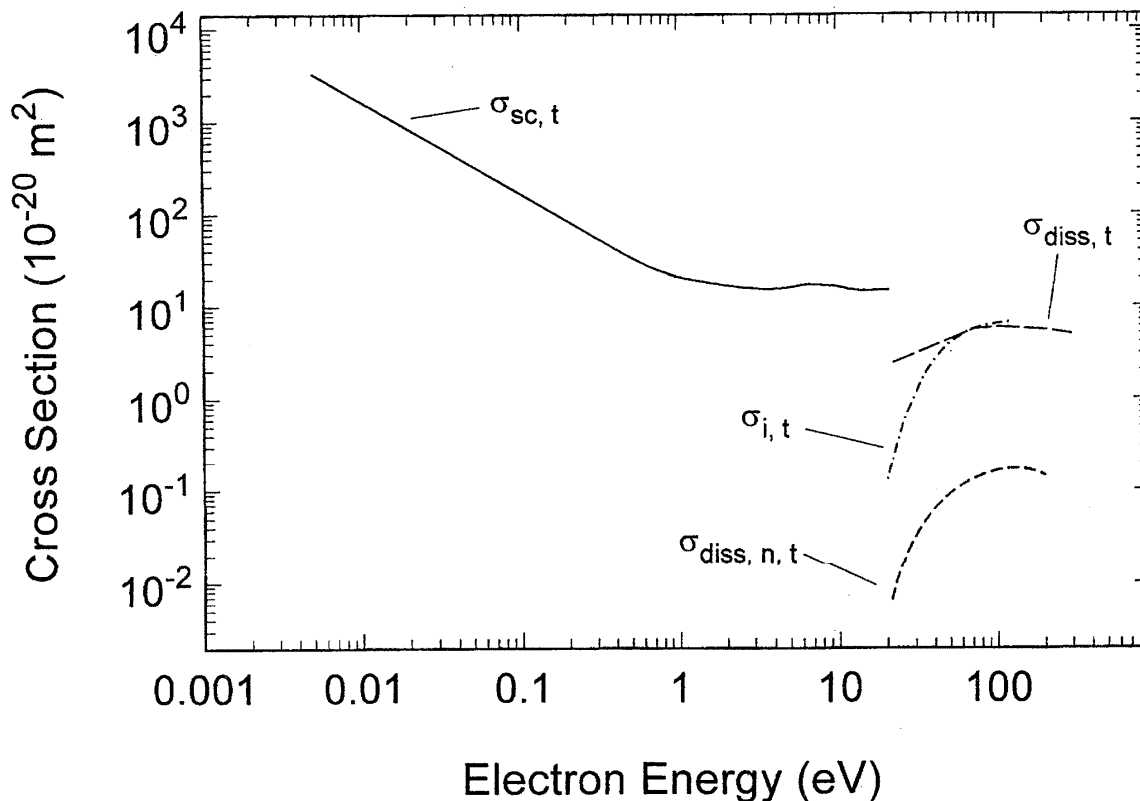


FIG. 16. Comparison of $\sigma_{sc,t}(\epsilon)$, $\sigma_{i,t}(\epsilon)$, $\sigma_{diss,t}$ and $\sigma_{diss,n,t}(\epsilon)$.

pressure using infrared diode laser absorption spectroscopy.⁶⁵ The reader is referred to this source for details.

10. Summary of Cross Sections and Transport Coefficients

Unlike the case of CF_4 where sufficient data were available that allowed the recommendation² of cross sections for a number of electron collision processes, the limited amount of data for CHF_3 makes it difficult to recommend electron collision cross sections for this molecule. However, since such data may be currently needed to model plasma processing devices, we suggest the following cross sections:

- (1) the total electron scattering cross section, $\sigma_{sc,t}(\epsilon)$, in Table 5;
- (2) the averaged total ionization cross section, $\sigma_{i,t}(\epsilon)$, in Fig. 7 (solid line) (Table 8, column 5);
- (3) the total dissociation cross section, $\sigma_{diss,t}(\epsilon)$, in Fig. 8 (Table 10);
- (4) the total cross section for dissociation into neutral fragments, $\sigma_{diss,n,t}(\epsilon)$, in Fig. 12 (open triangles) (Table 12, column 5) of Sugai *et al.*³⁷ since it is the only direct measurement of this cross section (see Sec. 5 for a discussion of possible inconsistencies regarding the Sugai *et al.* data).

The cross sections just mentioned are plotted in Fig. 16;

they are also available via the World Wide Web at <http://www.eeel.nist.gov/811/refdata>. They clearly show the limitations of the existing data and the large gap in the present database. Besides the recent unpublished measurements of Sanabia and Moore,²⁶ no cross sections of any kind exist in the important energy range between about 0.5 eV and 20 eV.

Data on electron transport coefficients for CHF_3 do not exist.

11. Needed Data

Basic measurements and calculations are needed for virtually all elastic and inelastic electron scattering processes, namely, cross sections for total, differential, and elastic electron scattering, cross section for momentum transfer, and cross sections for direct and indirect electronic, vibrational, and rotational excitation. Additional data are needed also for electron impact dissociation and ionization to resolve the apparent discrepancies between the direct measurement of $\sigma_{diss,n,t}(\epsilon)$ and $\sigma_{i,t}(\epsilon)$ and $\sigma_{diss,t}(\epsilon)$. Measurements are necessary for all electron transport, attachment, and ionization coefficients over wide ranges of E/N .

12. Acknowledgments

We wish to thank J. Vergrugge for valuable assistance with the literature, Dr. R. J. Van Brunt and Dr. Y. Wang for

valuable comments, Dr. Y.-K. Kim for his unpublished data on the total ionization cross section, and Dr. J. Moore and J. Sanabia for their unpublished data on the total electron scattering cross section. This research has been sponsored in part by the U. S. Air Force Wright Laboratory under Contract No. F3361596-C-2600 with the University of Tennessee.

13. References

- ¹The 1994 Report of the Scientific Assessment Working Group of IPCC, Intergovernmental Panel on Climate Change (unpublished), p. 28.
- ²L. G. Christophorou, J. K. Olthoff, and M. V. V. S. Rao, *J. Phys. Chem. Ref. Data* **25**, 1341 (1996).
- ³C. R. Brundle, M. B. Robin, and H. Basch, *J. Chem. Phys.* **53**, 2196 (1970).
- ⁴C. Y. R. Wu, L. C. Lee, and D. L. Judge, *J. Chem. Phys.* **71**, 5221 (1979).
- ⁵M. B. Robin, *Higher Excited States of Polyatomic Molecules* (Academic New York, 1974), Vol. I, pp. 178–191.
- ⁶J. F. Ying and K. T. Leung, *Phys. Rev. A* **53**, 1476 (1996).
- ⁷R. D. Nelson, Jr., D. R. Lide, Jr., and A. A. Maryott, *Selected Values of Electric Dipole Moments for Molecules in the Gas Phase*, NSRDS-NBS 10 (U.S. GPO, Washington, DC, 1967).
- ⁸W. L. Meerts and I. Ozier, *J. Chem. Phys.* **75**, 596 (1981).
- ⁹H. Sutter and R. H. Cole, *J. Chem. Phys.* **52**, 132 (1970).
- ¹⁰G. Cazzoli, I. Chiodi, G. Cotti, I. Dora, C. D. Esposito, M. Bellini, and P. de Natale, *J. Mol. Spectrosc.* **163**, 521 (1994).
- ¹¹J. A. Beran and L. Kevan, *J. Phys. Chem.* **73**, 3860 (1969).
- ¹²R. Kobayashi, R. D. Amos, H. Koch, and P. Jørgensen, *Chem. Phys. Lett.* **253**, 373 (1996).
- ¹³W. R. Harshbarger, M. B. Robin, and E. N. Lassette, *J. Electron Spectrosc. Relat. Phenom.* **1**, 319 (1972/1973).
- ¹⁴C. Larrieu, M. Chaillet, and A. Dargelos, *J. Chem. Phys.* **94**, 1327 (1991).
- ¹⁵P. Sauvageau, R. Gilbert, P. P. Berlow, and C. Sandorfy, *J. Chem. Phys.* **59**, 762 (1973).
- ¹⁶S. Stokes and A. B. F. Duncan, *J. Am. Chem. Soc.* **80**, 6177 (1958).
- ¹⁷F. C.-Y. Wang and G. E. Leroi, *Ann. Isr. Phys. Soc.* **6**, 210 (1983).
- ¹⁸B. P. Pullen, T. A. Carlson, W. E. Moddeman, G. K. Schweitzer, W. E. Bull, and F. A. Grimm, *J. Chem. Phys.* **53**, 768 (1970).
- ¹⁹G. Bieri, L. Asbrink, and W. von Niessen, *J. Electron Spectrosc. Relat. Phenom.* **23**, 281 (1981).
- ²⁰A. Campargue and F. Stoeckel, *J. Chem. Phys.* **85**, 1220 (1986).
- ²¹K. Kim and C. W. Park, *J. Mol. Struct.* **161**, 297 (1987); B. Galabov, T. Dudev, and W. J. Orville-Thomas, *ibid.* **145**, 1 (1986).
- ²²S. Altshuler, *Phys. Rev.* **107**, 114 (1957).
- ²³L. G. Christophorou and A. A. Christodoulides, *J. Phys. B* **2**, 71 (1969).
- ²⁴L. G. Christophorou, *Atomic and Molecular Radiation Physics* (Wiley-Interscience, London, 1971), Chap. 4.
- ²⁵L. G. Christophorou, D. R. James, and R. A. Mathis, *J. Phys. D* **14**, 675 (1981).
- ²⁶J. Sanabia and J. Moore (private communication).
- ²⁷J. A. LaVerne and A. Mozumder, *Radiat. Res.* **96**, 219 (1983).
- ²⁸H. U. Poll and J. Meichsner, *Contrib. Plasma Phys.* **27**, 359 (1987).
- ²⁹M. Goto, K. Nakamura, H. Toyoda, and H. Sugai, *Jpn. J. Appl. Phys.* **33**, 3602 (1994).
- ³⁰J. A. Beran and L. Kevan, *J. Phys. Chem.* **73**, 3866 (1969).
- ³¹Y.-K. Kim (private communication).
- ³²Y.-K. Kim and M. E. Rudd, *Phys. Rev. A* **50**, 3954 (1994); W. Hwang, Y.-K. Kim, and M. E. Rudd, *J. Chem. Phys.* **104**, 2956 (1996).
- ³³H. F. Winters and M. Inokuti, *Phys. Rev. A* **25**, 1420 (1982).
- ³⁴D. L. Hobrock and R. W. Kiser, *J. Phys. Chem.* **68**, 575 (1964).
- ³⁵J. B. Farmer, I. H. S. Henderson, F. P. Lossing, and D. G. H. Marsden, *J. Chem. Phys.* **24**, 348 (1956).
- ³⁶C. Lifshitz and F. A. Long, *J. Phys. Chem.* **69**, 3731 (1965).
- ³⁷H. Sugai, H. Toyoda, T. Nakano, and M. Goto, *Contrib. Plasma Phys.* **35**, 415 (1995).
- ³⁸V. Tarnovsky and K. Becker, *J. Chem. Phys.* **98**, 7868 (1993).
- ³⁹V. Tarnovsky, P. Kurunczi, D. Rogozhnikov, and K. Becker, *Int. J. Mass Spectrom. Ion Proc.* **128**, 181 (1993).
- ⁴⁰R. M. Reese, V. H. Dibeler, and F. L. Mohler, *J. Res. Natl. Bur. Stand.* **57**, 367 (1956).
- ⁴¹T. G. Lee, *J. Phys. Chem.* **67**, 360 (1963).
- ⁴²R. P. Blaunstein and L. G. Christophorou, *J. Chem. Phys.* **49**, 1526 (1968).
- ⁴³K. A. G. MacNeil and J. C. J. Thynne, *Int. J. Mass Spectrom. Ion Phys.* **2**, 1 (1969).
- ⁴⁴R. W. Fessenden and K. M. Bansal, *J. Chem. Phys.* **53**, 3468 (1970).
- ⁴⁵F. J. Davis, R. N. Compton, and D. R. Nelson, *J. Chem. Phys.* **59**, 2324 (1973).
- ⁴⁶A. A. Christodoulides, R. Schumacher, and R. N. Schindler, *Int. J. Chem. Kinet.* **10**, 1215 (1978).
- ⁴⁷L. G. Christophorou, D. L. McCorkle, and A. A. Christodoulides, in *Electron Molecule Interactions and Their Applications* (Academic, New York, 1984), Vol. 1, Chap. 6.
- ⁴⁸L. G. Christophorou, *Environ. Health Perspectives* **36**, 3 (1980).
- ⁴⁹H.-U. Scheunemann, M. Heni, E. Illenberger, and H. Baumgärtel, *Ber. Bunsenges. Phys. Chem.* **86**, 321 (1982).
- ⁵⁰A. Modelli, F. Scagnolai, G. Distefano, D. Jones, and M. Guerra, *J. Chem. Phys.* **96**, 2061 (1992).
- ⁵¹M. Haverlag, A. Kono, D. Passchier, G. M. W. Kroesen, W. J. Goedheer, and F. J. de Hoog, *J. Appl. Phys.* **70**, 3472 (1991).
- ⁵²T. O. Tiernan, C. Chang, and C. C. Cheng, *Environ. Health Perspectives* **36**, 47 (1980).
- ⁵³L. G. Christophorou, D. R. James, and R. Y. Pai, in *Applied Atomic Collision Physics* (Academic, New York, 1982), Vol. 5, p. 87.
- ⁵⁴L. G. Christophorou, D. R. James, I. Sauers, M. O. Pace, R. Y. Pai, and A. Fatheddin, in *Gaseous Dielectrics III* (Pergamon, New York, 1982), p. 151.
- ⁵⁵EPRI Report No. EPRI EI-2620, September 1982.
- ⁵⁶R. S. Nema, S. V. Kulkarni, and E. Husain, *IEEE Trans. Electric. Insul. EI-17*, 434 (1982).
- ⁵⁷H. A. Van Sprang, H. H. Brongersma, and F. J. De Heer, *Chem. Phys.* **35**, 51 (1978).
- ⁵⁸J. F. M. Aarts, *Chem. Phys.* **95**, 443 (1985).
- ⁵⁹J. C. Creasey, I. R. Lambert, R. P. Tuckett, and A. Hopkirk, *Mol. Phys.* **71**, 1355 (1990).
- ⁶⁰L. C. Lee, J. C. Han, C. Ye, and M. Suto, *J. Chem. Phys.* **92**, 133 (1990).
- ⁶¹S. Wang and J. W. McConkey, *Can. J. Phys.* **67**, 694 (1989).
- ⁶²N. P. Danilevskii, I. Y. Rapp, V. T. Koppe, and A. G. Koval, *Opt. Spectrosc.* **60**, 441 (1986).
- ⁶³M. Suto and N. Washida, *J. Chem. Phys.* **78**, 1007, 1012 (1983); M. Suto, N. Washida, H. Akimoto, and M. Nakamura, *ibid.* **78**, 1019 (1983); M. Suto and L. C. Lee, *ibid.* **79**, 1127 (1983).
- ⁶⁴H. Deutsch, T. D. Märk, V. Tarnovsky, K. Becker, C. Cornelissen, L. Cespiva, and V. Bonacic-Koutecky, *Int. J. Mass Spectrom. Ion Proc.* **137**, 77 (1994).
- ⁶⁵K. Takahashi, M. Hori, K. Maruyama, S. Kishimoto, and T. Goto, *Jpn. J. Appl. Phys.* **32**, L694 (1993); K. Takahashi, M. Hori, and T. Goto, *ibid.* **33**, 4745 (1994); K. Maruyama, K. Ohkouchi, Y. Ohtsu, and T. Goto, *ibid.* **33**, 4298 (1994); K. Takahashi, M. Hori, S. Kishimoto, and T. Goto, *ibid.* **33**, 4181 (1994).