

Electron Interactions With CF₃I

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Low-energy electron collision data for the plasma processing gas CF₃I are sparse. Limited cross section data are available only for total and differential elastic electron scattering, electron-impact ionization, and electron attachment. These data are assessed, synthesized, and discussed in this paper. There is a need for confirming measurements for some of these data, and for measurements of cross sections for the other main electron-collision processes for which no data exist. There are presently no data available for the electron transport, ionization, and attachment coefficients of this molecule. © 2001 by the U.S. Secretary of Commerce on behalf of the United States. All rights reserved. [S0047-2689(00)00504-3]

Key words: attachment; CF₃I; coefficients; cross sections; electron interactions; electron transport; ionization; scattering; trifluoriodomethane.

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TABLE I. Definition of symbols

Symbol	Definition	Common scale and units
$\sigma_{\text{pa,t}}(\lambda)$	Total photoabsorption cross section	10^{-19} cm ² ; 10^{-23} m ²
$\sigma_{\text{sc,t}}(\varepsilon)$	Total electron scattering cross section	10^{-16} cm ² ; 10^{-20} m ²
$\sigma_{\text{e,diff}}$	Elastic differential electron scattering cross section	10^{-16} cm ² sr ⁻¹
$\sigma_{\text{m}}(\varepsilon)$	Momentum transfer cross section (elastic)	10^{-16} cm ² ; 10^{-20} m ²
$\sigma_{\text{vib,diff}}(\varepsilon)$	Vibrational differential electron scattering cross section	10^{-16} cm ² sr ⁻¹
$\sigma_{\text{i,partial}}(\varepsilon)$	Partial ionization cross section	10^{-16} cm ² ; 10^{-20} m ²
$\sigma_{\text{i,t}}(\varepsilon)$	Total ionization cross section	10^{-16} cm ² ; 10^{-20} m ²
$\sigma_{\text{a,t}}(\varepsilon)$	Total electron attachment cross section	10^{-14} cm ² ; 10^{-18} m ²
$k_{\text{a,t}}(\langle\varepsilon\rangle)$	Total electron attachment rate constant	10^{-7} cm ³ s ⁻¹
$(k_{\text{a,t}})_{\text{th}}$	Thermal electron attachment rate constant	10^{-7} cm ³ s ⁻¹

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1. Introduction

Trifluoroiodomethane (CF₃I) is a potential plasma etching gas (e.g., see Refs. 1–6) that provides copious quantities of CF₃⁺ and CF₃ via dissociative electron-impact ionization and dissociative electron attachment. These reactive species play a key role in the plasma etching of Si and SiO₂. CF₃I is also an “environmentally friendly” gas as its overall atmospheric lifetime is very short (<1 to a few days).^{7–9} Consequently, its global warming potential is very low (1–5 times that of CO₂).^{7,10} This is in sharp contrast to the much higher global warming potentials of other plasma etching gases, such as

the fully fluorinated hydrocarbons and SF₆.¹⁰ Because of its short lifetime, CF₃I does not contribute significantly to ozone depletion.⁷

In this paper, as in the previous eight papers^{11–18} in this series on electron interactions with plasma processing gases, we assess and synthesize the available information on the cross sections and rate coefficients for collisional interactions of electrons with CF₃I. Definitions of the symbols used here to describe the various collision processes discussed in the paper are given in Table 1.

2. Electronic Structure and Basic Properties

The trifluoroiodomethane (CF₃I) molecule belongs to the C_{3v} point group. It is polar, and McClellan¹⁹ lists two values for its electric dipole moment: 0.92 D and (1.0 ± 0.1) D (1 D = 3.3356 × 10⁻³⁰ C m). Of its six fundamental vibrational frequencies (ν_1, \dots, ν_6), the ν_4 , ν_5 , and ν_6 are degenerate, and the ν_1 , ν_2 , and ν_4 are infrared active.²⁰ The ν_1 , ν_3 , and ν_4 frequencies have been attributed to stretching modes, ν_2 , and ν_5 to deformation modes, and ν_6 to a bending mode. The energies of the six vibrational modes of CF₃I as given by Shimanouchi²⁰ are, respectively: 1080 cm⁻¹ (0.134 eV), 742 cm⁻¹ (0.092 eV), 286 cm⁻¹ (0.035 eV), 1187 cm⁻¹ (0.147 eV), 537 cm⁻¹ (0.067 eV), and 260 cm⁻¹ (0.032 eV) (see also Bürger *et al.*²¹ for vibrational frequencies of ¹²CF₃I and ¹³CF₃I).

The CF₃I molecule has a positive (adiabatic) electron affinity. Atom-impact crossed-molecular beam studies have provided values of the electron affinity (EA) of CF₃I. These are listed in Table 2 along with other pertinent fundamental data. The lowest unoccupied molecular orbital (LUMO) of CF₃I is an antibonding σ -type orbital of *a*₁ symmetry and is almost entirely localized on the C–I bond. The small dissociation energy *D* and relatively long length of the F₃C–I⁻ bond indicate that CF₃I⁻ can be regarded as a weakly bound radical anion.²²

In Table 3 are listed the energy positions of the negative ion states of the CF₃I molecule, as they have been deter-

TABLE 2. Basic data on CF₃I and CF₃I⁻

Physical quantity	Value	Reference/method
CF₃I		
Electron affinity (adiabatic)	1.278 eV	22/Calculation
	1.29±0.1 eV	23/Charge exchange in Cs-CF ₃ I collisions
	1.4±0.2 eV	24/Charge exchange in Cs-CF ₃ I collisions
	1.54±0.2 eV	25/Charge exchange in Na-CF ₃ I collisions
	1.6±0.2 eV	25/Charge exchange in Cs-CF ₃ I collisions
	2.2±0.2 eV	26/Charge exchange in K-CF ₃ I collisions
D (CF ₃ -I)	1.9 eV	27/Electron attachment using mass spectrometry
	2.0±0.2 eV	25/Charge exchange in Na-CF ₃ I collisions
	2.05±0.2 eV	24/Charge exchange in Cs-CF ₃ I collisions
	2.2±0.2 eV	26/Charge exchange in K-CF ₃ I collisions
	2.33±0.17 eV	28/Reaction kinetics
	2.39±0.04 eV	29/Photodissociation
	2.681 eV (2.4 eV) ^a	22/Calculation
R (C-I)	2.122±0.037 Å	30/Electron diffraction
	2.134±0.02 Å	31/Microwave spectroscopy
	2.135±0.033 Å	32/Electron diffraction
	2.137±0.032 Å	32/Electron diffraction
	2.140 Å	22/Calculation
	2.1438 Å	33/Microwave spectroscopy
R (C-F)	1.328±0.026 Å	30/Electron diffraction
	1.3285 Å	33/Microwave spectroscopy
	1.334±0.015 Å	32/Electron diffraction
	1.340±0.021 Å	32/Electron diffraction
	1.343 Å	22/Calculation
∠F-C-F	108.1°	22/Calculation
	108.2°±1.6°	32/Electron diffraction
	108.3°±2°	30/Electron diffraction
	108.4°±1.9°	32/Electron diffraction
	108.42°	33/Microwave spectroscopy
CF₃I⁻		
D (CF ₃ -I ⁻)	0.29±0.2 eV	25/Charge exchange in Cs-CF ₃ I collisions
	0.35±0.2 eV	25/Charge exchange in Na-CF ₃ I collisions
	0.38±0.1 eV ^b	24/Charge exchange in Cs-CF ₃ I collisions
	0.610 eV	22/Calculation
R (C-I)	2.881 Å	22/Calculation
R (C-F)	1.367 Å	22/Calculation
∠F-C-F	106.0°	22/Calculation

^aRoszak *et al.*²² point out that the spin-orbit effect could be important in computing the bond dissociation energy and the electron affinity of the CF₃I molecule, since the ²P_{3/2}-²P_{1/2} splitting of the I atom is 0.94 eV. The value in parenthesis includes spin-orbit correction.

^bObtained using EA (I)=3.063 eV.

mined from electron scattering and electron attachment studies (see also Secs. 3 and 8). The presence of the dissociative electron attachment resonance near 0 eV indicates that the electron attachment cross section will be large at low energies, and thus suggests that the contribution of this process to the total electron scattering cross section will be substantial.

Figure 1 shows the total room-temperature photoabsorption cross section, $\sigma_{\text{pa,t}}(\lambda)$, of CF₃I as a function of the photon wavelength λ in the wavelength range 160–390 nm.^{7,9,45,46} The spectrum consists of a continuous absorption band with a local maximum cross section value of about $6.0 \times 10^{-19} \text{ cm}^2$ at 267 nm (4.64 eV). The absorption band is

TABLE 3. Energy positions of the negative ion states of the CF₃I molecule

Energy position (eV)	Reaction mechanism/Possible assignment	Reference and comments
0.0	$e + \text{CF}_3\text{I} \rightarrow \text{I}^- + \text{CF}_3^{\text{a}}$	27, Electron attachment using mass spectrometry
0.0	$e + \text{CF}_3\text{I} \rightarrow \text{I}^- + \text{CF}_3$	35-37, Dissociative attachment producing I ⁻
0.0	$e + \text{CF}_3\text{I} \rightarrow \text{I}^- + \text{CF}_3$	38, Total dissociative attachment cross section measurement ^b
~0.0	$a_1(\text{C}-\text{I}\sigma^*)$	
~0.0	$e + \text{CF}_3\text{I} \rightarrow \text{I}^- + \text{CF}_3$	39, Total dissociative attachment cross section measurement ^b
0.4	$a_1(\text{C}-\text{I}\sigma^*)$	40, Calculation
~1.0	$e + \text{CF}_3\text{I} \rightarrow \text{F}^- + \text{CF}_2\text{I}^{\text{c}}$	39, Total dissociative attachment cross section measurement
~1.5	$e + \text{CF}_3\text{I} \rightarrow \text{F}^- + \text{CF}_2\text{I}$	27, Electron attachment using mass spectrometry
1-2	$e + \text{CF}_3\text{I}^* \rightarrow \text{F}^- + \text{CF}_2\text{I}$	41, Formation of F ⁻ from CF ₃ I at 500 and 700 K ^d
3.8	$e + \text{CF}_3\text{I} \rightarrow \text{F}^- + \text{CF}_2\text{I}^{\text{e}}$	35, 36, Dissociative attachment producing F ⁻
3.8	$e + \text{CF}_3\text{I} \rightarrow \text{CF}_3^- + \text{I}$	35-37, Dissociative attachment producing CF ₃ ⁻
~4.5	$a_1(\text{C}-\text{F}\sigma^*)$	38, Total dissociative attachment cross section measurement
~4.9	$a_1(\text{C}-\text{F}\sigma^*)$ and $e(\text{C}-\text{I}\pi^*)$	40, Total electron scattering cross section measurement/Calculation
4-10	$a_1(\text{C}-\text{F}\sigma^*)$ and $e(\text{C}-\text{I}\pi^*)$	42-44, Vibrational excitation cross section function measurements

^aDibeler *et al.* in Ref. 34 give the onset of this process as ~0.0 eV, but the maximum intensity at the unacceptably high value of 1.8 eV.

^bDue almost entirely to the respective reaction shown in column 2 of this table.

^cSuggested possible reaction in Ref. 39.

^dFound to be strongly temperature dependent.

^eDibeler *et al.* in Ref. 34 give a threshold value of 3.6 ± 0.3 eV for this process, and a maximum-abundance energy of 5.6 eV.

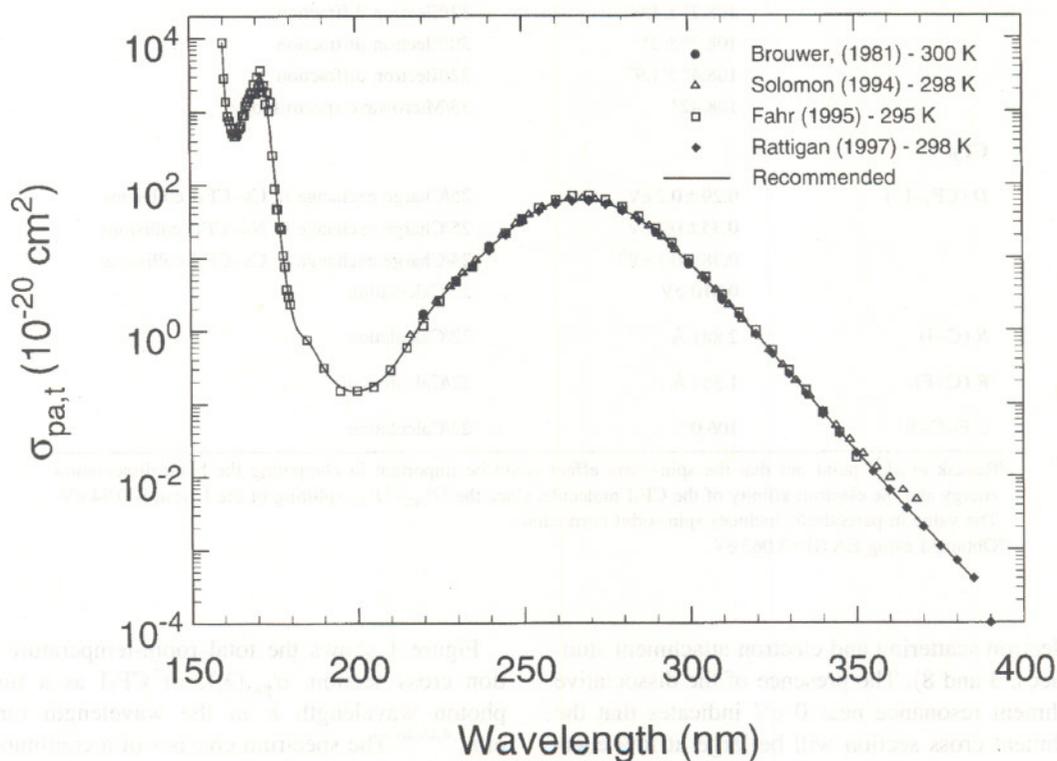


FIG. 1. Total photoabsorption cross section, $\sigma_{\text{pa,t}}(\lambda)$, as a function of the photon wavelength, λ , for CF₃I: (●) Ref. 45; (△) Ref. 7; (□) Ref. 46; (◆) Ref. 9.

TABLE 4. Recommended total photoabsorption cross section, $\sigma_{\text{pa},\text{I}}(\lambda)$, for CF₃I in the wavelength range 160 nm to 385 nm ($T=295$ K to 300 K)

Wavelength (nm)	$\sigma_{\text{pa},\text{I}}(\lambda)$ (10^{-20} cm ²)	Wavelength (nm)	$\sigma_{\text{pa},\text{I}}(\lambda)$ (10^{-20} cm ²)
160	8716	230	4.81
161	1385	240	13.4
162	764	250	32.1
164	477	260	55.5
166	886	270	61.5
168	1529	280	44.3
170	2376	290	22.3
171	2905	300	8.52
173	1806	310	2.83
175	257	320	0.885
178	10.9	330	0.262
180	2.33	340	0.0764
185	0.75	350	0.0218
190	0.31	360	0.006 51
200	0.15	370	0.002 08
210	0.29	380	0.000 67
220	1.39	385	0.000 38

due to $n \rightarrow \sigma^*$ transitions involving excitation of a nonbonding p electron on the I atom to an antibonding σ^* orbital involving the C and I atoms⁹ (see also Robin⁴⁷ and Herzberg⁴⁸). Photoabsorption measurements have also been reported as a function of temperature.^{7,9,45,46} Brouwer and Troe⁴⁵ made photoabsorption measurements at 300, 625, and 1050 K that show considerable band broadening at high temperatures. They also observed thermal decomposition of

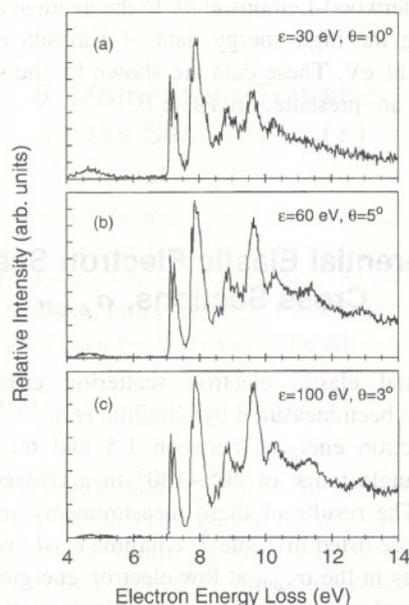


FIG. 2. Electron energy-loss spectrum of CF₃I for 30 eV (scattering angle of 10°), 60 eV (scattering angle of 5°), and 100 eV (scattering angle of 3°) incident-electron energies [data of Kitajima *et al.* from Ref. 43, as provided to the authors by Professor H. Tanaka (Ref. 44)].

TABLE 5. Threshold energies for the production of the parent and fragment positive ions by photon and electron impact on CF₃I

Positive ion	Threshold energy (eV)	Reference and method
CF ₃ I ⁺ ($X^2E_{3/2}$) ^{a,b}	10.23	50, 51, MSPI ^c
	10.29	52, 53
	10.32±0.03	54, ICR/PI ^d
	10.45	55, PES ^e
	10.61	56
	10.81	57, PES
CF ₃ I ⁺ ($X^2E_{1/2}$)	≤10.9 ^f	58, EI ^g
	10.91	52, 53
	11.18	55, PES
CF ₃ ⁺	11.37	57, PES
	10.89	50, MSPI
CF ₂ ⁺	10.91 ^h	59, DPI ⁱ
	11.36±0.03	54
	11.85 ^j	59/DPI
	≤11.7	58, EI
I ⁺ (³ P ₂)	12.70	59, DPI
	13.50	59, DPI
	13.58	59, DPI
I ⁺ (³ P ₁)	≤14.5	58, EI
	13.40	59, DPI
CF ₂ I ⁺	≤14.3	58, EI
	17.62	59, DPI

^aThe CF₃I⁺ ground state is a doublet, $X^2E_{3/2}$ and $X^2E_{1/2}$. The two states are separated by ~0.6 eV.

^bAssociated with the removal of a lone-pair electron from the I atom.

^cMSPI=mass spectrometric photoionization study.

^dICR/PI=Ion cyclotron resonance/photoionization technique.

^ePES=photoelectron spectra.

^fThe electron energy resolution was not adequate to allow separation of the $X^2E_{3/2}$ and $X^2E_{1/2}$ states of CF₃I⁺.

^gEI=electron impact.

^hFor the products CF₃⁺+I(²P_{3/2}).

ⁱDPI=dissociative photoionization.

^jFor the products CF₃⁺+I(²P_{1/2}).

CF₃I at temperatures above ~1000 K (see also Ref. 49). The solid line in Fig. 1 is a least squares fit to the four sets of "room temperature" measurements. Values from this line are listed in Table 4 as the recommended $\sigma_{\text{pa},\text{I}}(\lambda)$ for CF₃I.

Recent electron energy-loss spectra of CF₃I at 5° scattering angle and 30, 60, and 100 eV incident electrons^{43,44} are consistent with the photoabsorption results in Fig. 1. Figure 2 shows these electron energy-loss spectra, which cover the energy-loss range from 4 to 14 eV. Taken at forward scattering angles of 3°–10°, these spectra exhibit little variation with incident electron energy. They show distinct structure below the first ionization threshold energy at ~10.4 eV (see Table 5) with peaks at 4.7, 7.2, 8.1, 9.0, and 9.8 eV. The structure at 7.2 eV in the electron-energy-loss spectrum is consistent with that in the $\sigma_{\text{pa},\text{I}}(\lambda)$ around 170 nm.

Photoionization, photodissociation, and electron-impact studies have provided values of the ionization threshold en-

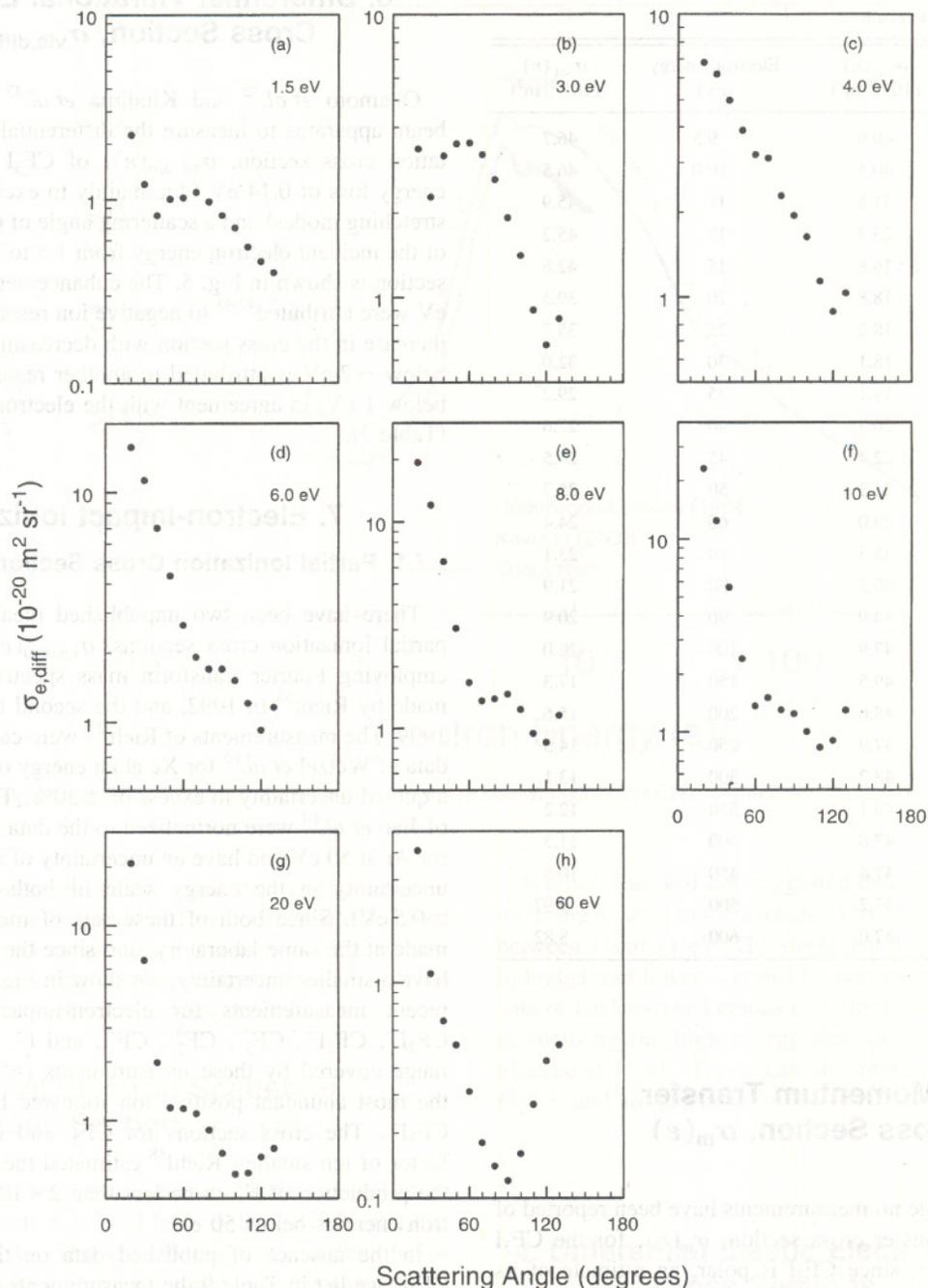


FIG. 4. Differential elastic electron scattering cross sections, $\sigma_{e,\text{diff}}$, for CF_3I at a number of incident electron energies [data of Kitajima *et al.* from Ref. 43, as provided to the authors by Professor H. Tanaka (Ref. 44)].

volving I^+ and CF_3^+ with CF_3I see Berman *et al.*,⁵⁴ and for formation of CF_3I^+ in photoinduced charge transfer at surfaces see Sun *et al.*⁶⁷.

7.2. Total Ionization Cross Section, $\sigma_{i,t}(\epsilon)$

The total ionization cross section, $\sigma_{i,t}(\epsilon)$, of CF_3I obtained by summing the partial ionization cross sections of Jiao *et al.*⁶⁴ is shown in Fig. 7. The error bar shown in the figure indicates the $\pm 22\%$ uncertainty of the partial ioniza-

tion cross sections. Also plotted in Fig. 7 is the value $[(10.9 \pm 0.48) \times 10^{-16} \text{ cm}^2]$ of $\sigma_{i,t}(\epsilon)$ of CF_3I measured by Beran and Kevan⁶⁸ for 70 eV incident electrons. The values agree within the combined uncertainty of the two measurements. The data of Jiao *et al.* are listed in Table 10 as our presently suggested values for the $\sigma_{i,t}(\epsilon)$ of CF_3I .

To our knowledge no measurements of the electron-impact ionization coefficient have been made for this molecule.

TABLE 7. Differential elastic electron scattering cross sections, $\sigma_{e,\text{diff}}$, of CF₃I (in units of $10^{-20} \text{ m}^2 \text{ sr}^{-1}$) for a number of incident electron energies (data of Kitajima *et al.* from Refs. 43 and 44)

Angle	Electron energy (eV)							
	1.5	3	4	6	8	10	20	60
20°	2.22	3.35	6.79	15.7	19.3	23.0	20.8	4.06
30°	1.21	2.27	6.16	11.2	12.0	12.4	6.62	1.10
40°	0.82	3.16	4.96	7.01	6.40	5.62	1.98	0.66
50°	1.00	3.49	3.88	4.33	3.03	2.39	1.16	0.51
60°	1.02	3.52	3.18	2.65	1.67	1.36	1.15	0.31
70°	1.09	3.20	3.10	1.92	1.36	1.50	1.08	0.18
80°	0.97	2.61	2.28	1.70	1.39	1.30	0.89	0.14
90°	0.82	1.91	1.94	1.70	1.46	1.24	0.68	0.12
100°	0.70	1.41	1.63	1.52	1.23	1.00	0.53	0.16
110°	0.55	0.90	1.14	1.21	0.94	0.82	0.54	0.27
120°	0.46	0.68	0.89	0.92	0.85	0.90	0.65	0.43
130°	0.40	0.84	1.03	1.16	1.15	1.29	0.72	0.51

8. Electron Attachment

8.1. Relative Cross Sections for the Production of the Fragment Negative Ions I⁻, F⁻, CF₃⁻, and FI⁻ by Dissociative Electron Attachment to CF₃I

There have been a number of studies of electron attachment to CF₃I. These include electron-beam measurements of the relative cross sections for the formation of the various fragment negative ions,^{27,34–37,41,69} electron-beam measurements of the total electron attachment cross section,^{38,39} electron-swarm measurements of the thermal-electron attachment rate constant,^{70–73} very-low-energy electron-beam total electron attachment cross-section measurements,⁷⁴ and measurements of the rate constant of bound-electron attachment at thermal and subthermal electron energies.^{75,76}

Based on the results of these studies, electron attachment to CF₃I produces I⁻, F⁻, CF₃⁻, and FI⁻ negative ions, mainly *via* two dissociating negative-ion states, one at ~ 0.0 eV and another near 3.8 eV. This is seen from the measurements of Oster *et al.*³⁶ shown in Fig. 8. The zero-energy process generates I⁻ *via* the reaction



and is exothermic by $-(0.67 \pm 0.1)$ eV.³⁶ The 3.8 eV process generates F⁻, CF₃⁻, and FI⁻. The fragment anions F⁻ and CF₃⁻ are generated *via* the reactions

TABLE 8. Calculated values of $\sigma_m(\varepsilon)$ for CF₃I determined via Eq. (1) and using for the dipole moment of CF₃I the value of 0.96 D

Electron energy (eV)	$\sigma_m(\varepsilon)$ (10^{-20} m^2)
0.005	902
0.01	451
0.05	90.2
0.10	45.1
0.50	9.0



Reactions (3a) and (3b) are endothermic, respectively, by $(\sim 1.5 \pm 0.3)$ eV,³⁶ and by (0.7 ± 0.3) eV.³⁶ According to Oster *et al.*,³⁶ the weak F⁻ signal near 0.0 eV does not arise from the direct dissociative electron attachment process, Eq. (3a), but rather from an ion–molecule reaction of the form $\text{I}^- + \text{CF}_3\text{I} \rightarrow \text{F}^- + \text{CF}_2\text{I}_2$.

The formation of the FI⁻ ion has an “appearance energy” of (2.2 ± 0.2) eV and requires a multiple dissociation process.³⁵ Interestingly, the complementary reaction to Eq. (3b), that is, the production of $\text{I}^- + \text{CF}_3$ was not observed from the 3.8 eV negative ion state.^{35,36}

Reactions (2) and (3b) result from breaking the C–I bond as a result of localization of the extra electron into a molecular orbital with antibonding $\sigma_{\text{C-I}}^*$ character. This is supported by theoretical calculations⁴⁰ and also by the fact that, in the formation of CF₃⁻ at threshold, the total excess energy of the transient anion appears as kinetic energy of the dissociation products.³⁵ This is also consistent with photoabsorption and photodissociation studies. For instance, Suh *et al.*⁷⁷ found

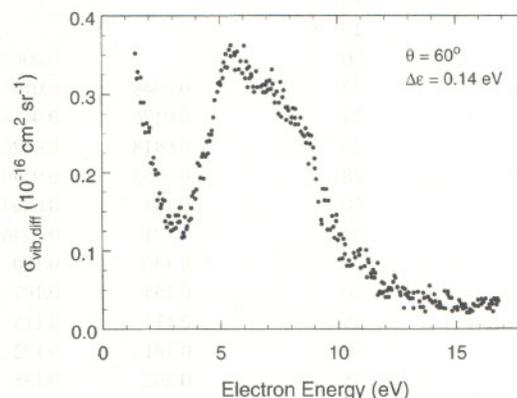


FIG. 5. Differential vibrational excitation cross section as a function of the incident electron energy, $\sigma_{\text{vib,diff}}(\varepsilon)$, for CF₃I [data of Kitajima *et al.* from Ref. 43, as provided to the authors by Professor H. Tanaka (Ref. 44)]. The measurements are for a scattering angle of 60° and an electron-energy loss of 0.14 eV.

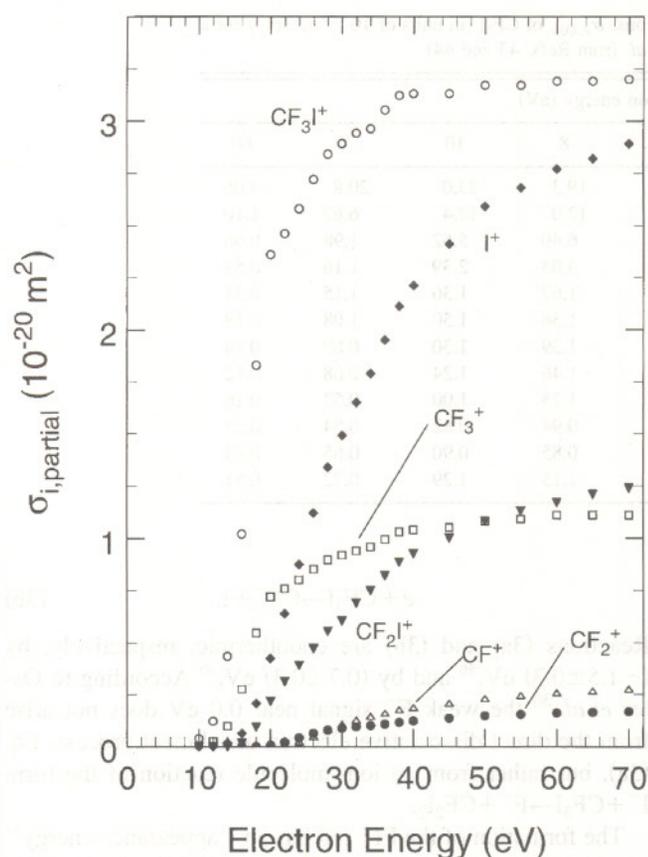


FIG. 6. Partial ionization cross sections, $\sigma_{i,\text{partial}}(\epsilon)$, for CF_3I (data of Jiao *et al.* from Ref. 64).

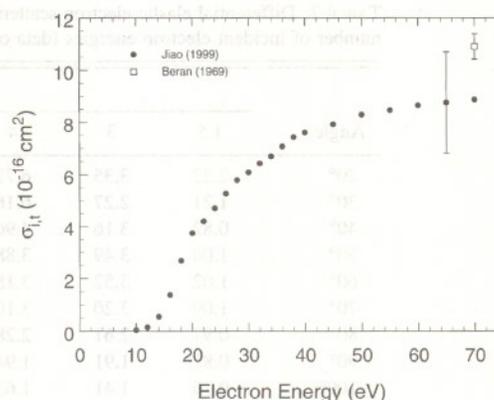


FIG. 7. Total ionization cross section, $\sigma_{i,t}(\epsilon)$, for CF_3I : (●) Ref. 64; (□) Ref. 68.

that in the photodissociation of CF_3I at 266 nm (4.66 eV), 85% of the available energy is partitioned into translational energy.

In addition to the dissociative electron attachment processes, Eqs. (2) and (3), F^- and CF_3^- ions have been observed, respectively, at energies above 12.3 and 11.8 eV,^{35,36} and their production at these energies has been attributed to the nonresonant ion-pair-formation processes

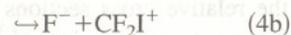
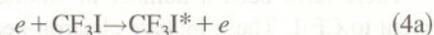


TABLE 9. Suggested values for the partial ionization cross sections, $\sigma_{i,\text{partial}}(\epsilon)$, of CF_3I (data of Jiao *et al.* from Ref. 64)

Electron energy (eV)	$\sigma_{i,\text{partial}}(\epsilon)$ (10^{-20} m^2)					
	CF^+	CF_2^+	CF_3^+	I^+	CF_2I^+	CF_3I^+
10						0.0389
12			0.0246			0.121
14			0.0978	0.0180		0.435
16			0.277	0.0629	0.0161	1.02
18			0.547	0.208	0.0929	1.83
20		0.0064	0.720	0.425	0.219	2.36
22	0.0048	0.0193	0.759	0.640	0.313	2.46
24	0.0176	0.0418	0.800	0.874	0.392	2.58
26	0.0418	0.0626	0.852	1.12	0.473	2.72
28	0.0755	0.0780	0.896	1.34	0.555	2.84
30	0.101	0.0864	0.919	1.49	0.604	2.89
32	0.121	0.0946	0.940	1.65	0.690	2.94
34	0.140	0.100	0.958	1.79	0.750	2.96
36	0.155	0.107	0.995	1.95	0.820	3.05
38	0.171	0.115	1.03	2.11	0.885	3.12
40	0.181	0.122	1.04	2.21	0.925	3.13
45	0.202	0.135	1.05	2.41	1.00	3.13
50	0.225	0.147	1.08	2.59	1.08	3.17
55	0.240	0.154	1.09	2.68	1.13	3.17
60	0.253	0.160	1.11	2.77	1.17	3.19
65	0.261	0.164	1.11	2.82	1.21	3.19
70	0.271	0.167	1.11	2.89	1.24	3.20

TABLE 10. Suggested values for the total ionization cross section, $\sigma_{it}(\epsilon)$, of CF₃I (data of Jiao *et al.* from Ref. 64)

Electron energy (eV)	$\sigma_{it}(\epsilon)$ (10^{-20} m^2)	Electron energy (eV)	$\sigma_{it}(\epsilon)$ (10^{-20} m^2)
10	0.039	32	6.44
12	0.146	34	6.70
14	0.551	36	7.08
16	1.38	38	7.43
18	2.68	40	7.61
20	3.73	45	7.93
22	4.20	50	8.29
24	4.71	55	8.46
26	5.27	60	8.65
28	5.78	65	8.76
30	6.09	70	8.88

The CF₃I⁻ parent negative ion has not been observed in any of the gas-phase electron attachment studies, however, it is known to be formed in charge-transfer reactions involving K, Na, and Cs atoms²⁴⁻²⁶ and by electron attachment to CF₃I

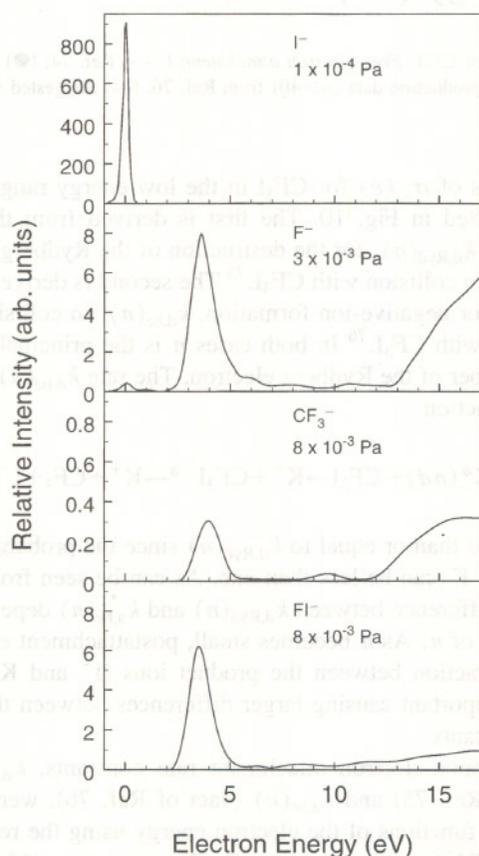


FIG. 8. Relative cross sections for the formation of I⁻, F⁻, CF₃⁻, and FI⁻ by dissociative electron attachment to CF₃I for $T=300 \text{ K}$ (data of Oster *et al.* from Ref. 36). Note the pressures in comparing the magnitudes of the relative cross sections of the various negative ions. The work of Oster *et al.* indicates possible production of I⁻ at higher energies than the zero-energy peak.

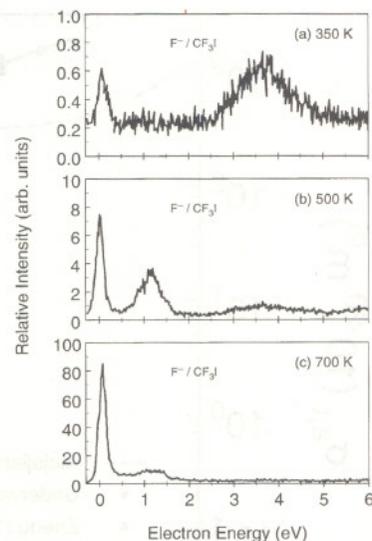


FIG. 9. Variation with gas temperature of the relative cross section for the formation of F⁻ by dissociative electron attachment to CF₃I (data of Hahndorf and Illenberger from Ref. 41).

clusters.³⁶ Interestingly, in a study of the desorption of CF₃⁻ following the interaction of low-energy (0–10 eV) electrons with a CF₃I film,³⁷ the desorption cross section was found to be more than two orders of magnitude greater than the corresponding gas-phase dissociative electron attachment cross section.

8.2. Effect of Temperature on the Production of F⁻ by Dissociative Electron Attachment to CF₃I

Figure 9 shows the relative cross section for the formation of F⁻ by dissociative electron attachment to CF₃I at three temperatures (350, 500, and 700 K) as reported by Hahndorf and Illenberger.⁴¹ The weak F⁻ signal at $\sim 0.0 \text{ eV}$ in the room temperature measurements (Fig. 8) increases substantially with increasing temperature above ambient, however, even at 700 K the relative cross section for the formation of F⁻ is small compared with that for the formation of I⁻ at this energy. Additionally, in view of the magnitude and energy dependence of the cross section for I⁻ production, it is not expected that the I⁻ signal will exhibit a significant temperature dependence.⁷⁸ Hence, for temperatures in this range, the total electron attachment cross section as measured by Underwood-Lemons *et al.*,³⁸ and the total thermal-electron attachment-rate constant as measured by various groups (see Table 13 in Sec. 8.5) should not be considerably affected by the gas temperature, as is indeed the case (see Fig. 10 in Sec. 8.3). Moreover, the data in Fig. 9 indicate that the production of F⁻ from CF₃I has another maximum between 1 and 2 eV. This is consistent with earlier observations of a negative-ion peak around 1 eV by Marriott and Craggs²⁷ and by Buchel'nikova³⁹ (see Table 3).

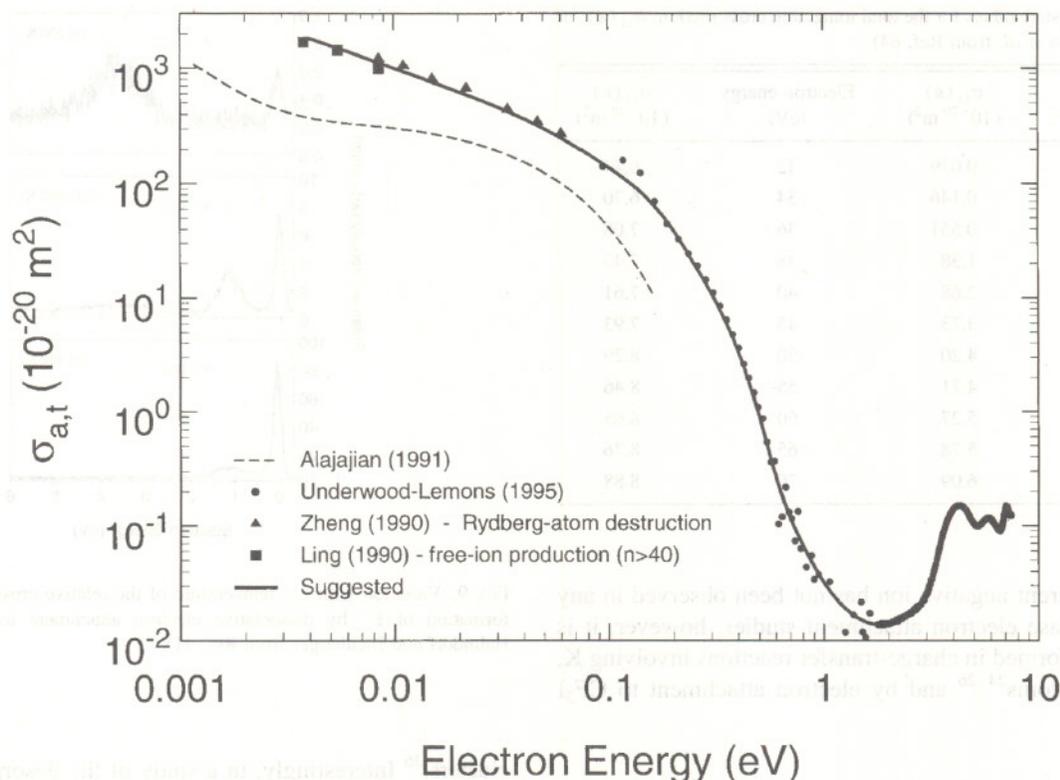


FIG. 10. Total electron attachment cross section as a function of electron energy, $\sigma_{a,t}(\varepsilon)$, for CF_3I . Free-electron attachment: (---) Ref. 74; (●) Ref. 38. Bound-electron attachment: (▲) Rydberg-atom destruction data from Ref. 75; (■) free-ion production data ($n > 40$) from Ref. 76. (—) Suggested values.

8.3. Total Electron Attachment Cross Section as a Function of Electron Energy, $\sigma_{a,t}(\varepsilon)$

The total electron attachment cross section, $\sigma_{a,t}(\varepsilon)$, of CF_3I has been measured by Underwood-Lemons^{38,79} for electron energies ≤ 7.5 eV under single-collision conditions and temperatures of 393 and 563 K. Figure 10 shows the data from the measurements made at 393 K. No significant temperature effects were observed. The peak energy and symmetry assignment of the negative-ion resonances observed in a total electron-scattering cross section study⁴⁰ are given in Table 3. The steep rise of the cross section toward zero energy is attributed to electron capture into the LUMO of CF_3I with a_1 symmetry and $\sigma^*(\text{C}-\text{I})$ bonding character. The fragment ion is thus I^- [Reaction (2)]. In contrast, the fragment negative-ion peak near 4.5 eV is associated with the next higher unoccupied orbital a_1 ($\text{C}-\text{F}\sigma^*$). The primary ion associated with this resonance is thus F^- [Reaction (3a)].

Also plotted in Fig. 10 are the total electron attachment cross sections of Alajajian *et al.*⁷⁴ determined using the Kr photoionization method for the production of monoenergetic low-energy electrons. The relative cross section values obtained by this method were put on an absolute scale by normalization to the thermal ($T = 300$ K) electron attachment-rate-constant value of Shimamori and Nakatani⁷⁰ (see Table 13 in Sec. 8.5).

In addition to the data of Alajajian *et al.*,⁷⁴ two other mea-

surements of $\sigma_{a,t}(\varepsilon)$ for CF_3I in the low-energy range have been plotted in Fig. 10. The first is derived from the rate constant, $k_{d,\text{Ryd}}(n)$, for the destruction of the Rydberg atoms $K^*(nd)$ in collision with CF_3I .⁷⁵ The second is derived from the rate for negative-ion formation, $k_{d,\text{be}}(n)$, in collisions of $K^*(nd)$ with CF_3I .⁷⁶ In both cases n is the principal quantum number of the Rydberg electron. The rate $k_{d,\text{be}}(n)$ refers to the reaction



and is less than or equal to $k_{d,\text{Ryd}}(n)$ since the probability of escape of I^- can be less than one. As can be seen from Fig. 11, the difference between $k_{d,\text{Ryd}}(n)$ and $k_{a,\text{be}}(n)$ depends on the value of n . As n becomes small, postattachment electrostatic attraction between the product ions (I^- and K^+) becomes important causing larger differences between the two rate constants.

The bound-electron attachment rate constants, $k_{d,\text{Ryd}}(n)$ (data of Ref. 75) and $k_{a,\text{be}}(n)$ (data of Ref. 76), were converted to functions of the electron energy using the relationship $\varepsilon = R/v^2$, where R is the Rydberg constant (13.6 eV). These values were then used to determine the bound-electron attachment cross section, $\sigma_{a,\text{be}}(\varepsilon)$ (and similarly $\sigma_{d,\text{Ryd}}(\varepsilon)$), from

$$\sigma_{a,\text{be}}(v) = k_{a,\text{be}}(n)/v_{\text{rms}}, \quad (6)$$

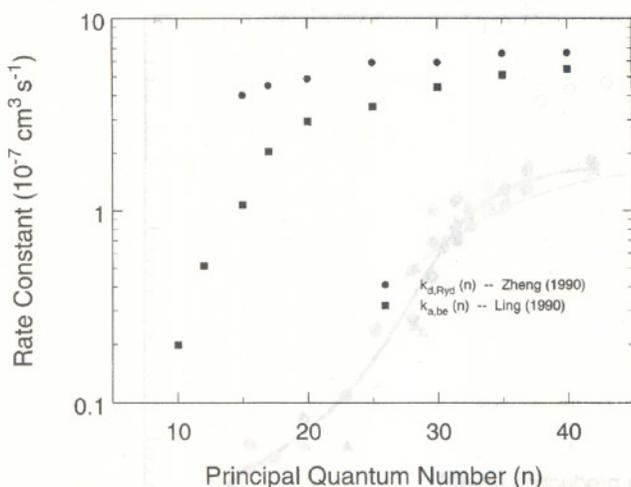


FIG. 11. Rate constants, $k_{d,Ryd}(n)$, for Rydberg-atom destruction (●, Ref. 75), and, $k_{a,be}(n)$, for negative-ion production (■, Ref. 76) in collisions of $K^*(nd)$ with CF₃I as a function of n (see text).

where v_{rms} is the root-mean-square velocity of the Rydberg electron. All values of $\sigma_{d,Ryd}(\varepsilon)$ determined this way are shown in Fig. 10, however, for $\sigma_{a,be}(\varepsilon)$ we have plotted only the data for $n \geq 40$ since a number of studies^{18,80–82} have indicated that Eq. (6) is expected to be valid only for large values of $n (> 30)$. Figure 10 shows that the low-energy bound-electron attachment data agree well with the higher-energy electron-beam measurements of Underwood-Lemons *et al.*³⁸ However, both sets of data disagree with the data of Alajajian *et al.*,⁷⁴ that were obtained by normalizing to the swarm attachment rate constant. This may indicate a difference in the magnitude of the electron attachment rate constant near thermal energies as determined by swarm methods and by techniques employing bound electron capture processes (see discussion in next section).

The data in Fig. 10 show that at thermal energy ($\varepsilon \approx 0.038$ eV, $T = 300$ K), the total electron attachment cross section exceeds 10^{-14} cm². This value is more than two orders of magnitude greater than the value of 7.8×10^{-17} cm² of the cross section measured by Buchel'nikova³⁹ at ~ 0.0 eV, which is not shown in Fig. 10.

The data of Underwood-Lemons *et al.*,³⁸ Zheng *et al.*,⁷⁵ and Ling *et al.*⁷⁶ are in agreement, and the solid line in Fig. 10 is a fit to these three sets of data. Values from this curve are listed in Table 11 as our suggested data for the $\sigma_{a,t}(\varepsilon)$ of CF₃I.

8.4. Total Electron Attachment Rate Constant as a Function of the Mean Electron Energy, $k_{a,t}(\langle \varepsilon \rangle)$

The measurements of $k_{a,t}(\langle \varepsilon \rangle)$ by Shimamori *et al.*⁷¹ and Sunagawa and Shimamori⁷³ are shown in Fig. 12. A pulse-radiolysis microwave-cavity method was employed with provisions for electron heating above thermal energies and an indirect method of determining the mean electron energy (see Ref. 71 for details). Also shown in the figure are the

TABLE 11. Suggested values for the total electron attachment cross section, $\sigma_{a,t}(\varepsilon)$, of CF₃I

Electron energy (eV)	$\sigma_{a,t}(\varepsilon)$ (10^{-20} m ²)	Electron energy (eV)	$\sigma_{a,t}(\varepsilon)$ (10^{-20} m ²)
0.004	1820	0.70	0.114
0.005	1575	0.80	0.067
0.006	1399	0.90	0.044
0.007	1265	1.00	0.032
0.008	1157	1.50	0.015
0.009	1070	2.00	0.014
0.010	997	2.50	0.017
0.015	757	3.00	0.026
0.020	623	3.50	0.070
0.025	532	4.00	0.138
0.030	464	4.25	0.148
0.040	369	4.50	0.140
0.050	302	4.75	0.122
0.060	251	5.00	0.104
0.070	212	5.25	0.100
0.080	183	5.50	0.107
0.090	158	5.75	0.115
0.10	139	6.00	0.112
0.15	76.1	6.25	0.102
0.20	39.4	6.50	0.092
0.25	19.9	6.75	0.098
0.30	11.1	7.00	0.135
0.40	3.38	7.25	0.134
0.50	0.930	7.50	0.118
0.60	0.266		

$k_{a,t}(\langle \varepsilon \rangle)$ measurements of Alajajian *et al.*⁷⁴ They used the Kr photoionization technique for the production of monoenergetic low-energy electrons and the room temperature ($T = 300$ K) thermal-electron attachment-rate constant, $(k_{a,t})_{th}$, of Shimamori and Nakatani⁷⁰ (1.7×10^{-7} cm³ s⁻¹, see Table 13 in Sec. 8.5) for normalization of their relative data. The average of the four "room temperature" values of $(k_{a,t})_{th}$ (Table 13, Sec. 8.5) is 1.9×10^{-7} cm³ s⁻¹, and this value is also plotted in Fig. 12. Additionally, we have plotted in Fig. 12 the values of $k_{d,Ryd}(n)$ measured by Zheng *et al.*⁷⁵ and the values of $k_{a,be}(n)$ for $n > 40$ measured by Ling *et al.*⁷⁶

The bound-electron attachment measurements indicate higher values of the electron attachment rate constant than the electron swarm measurements. At thermal ($T \approx 300$ K) energies the electron swarm data are lower by about a factor of 2. This difference is not understood, and complicates the determination of suggested values for the $k_{a,t}(\langle \varepsilon \rangle)$ of this molecule. Because all four independent measurements of the thermal ($T \approx 300$ K) value of $k_{a,t}(\langle \varepsilon \rangle)$ are in essential agreement (they are within the quoted or expected uncertainties), we opted to fit only the electron swarm data in Fig. 12 in an effort to determine suggested values for $k_{a,t}(\langle \varepsilon \rangle)$. Our fit to the swarm data is shown by the solid line, and values from this line are listed in Table 12 as our suggested data for $k_{a,t}(\langle \varepsilon \rangle)$ of CF₃I.

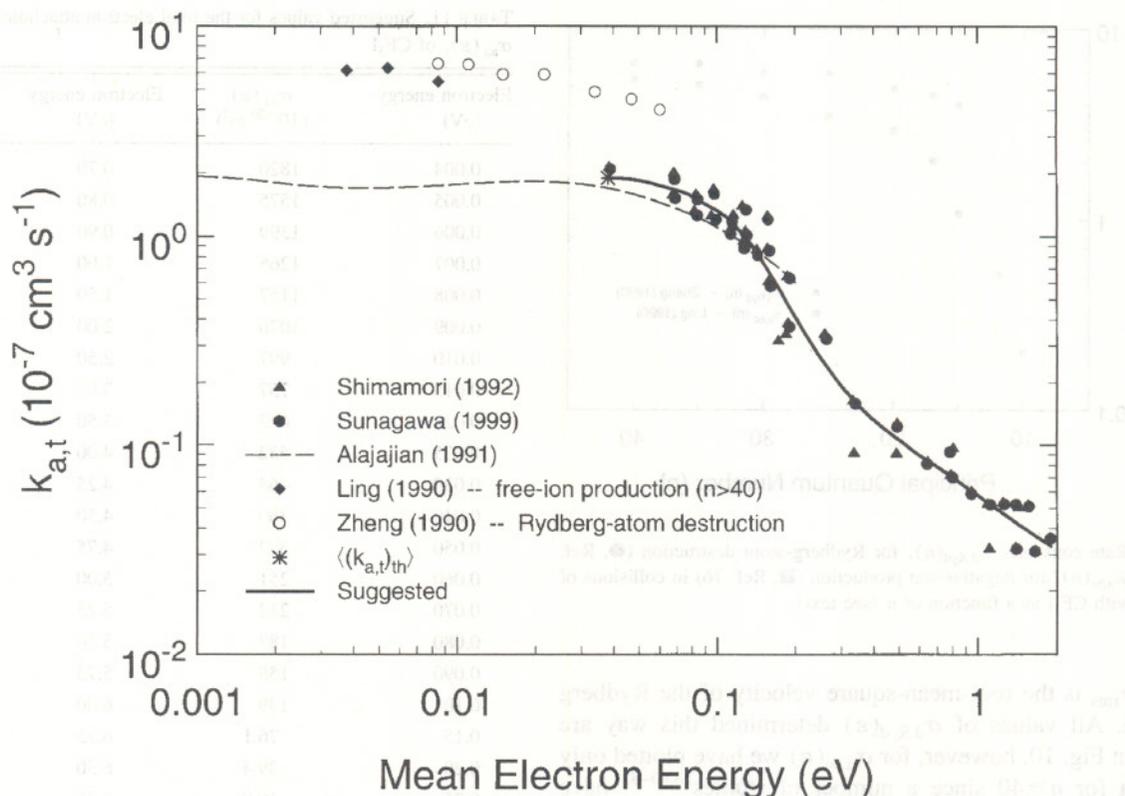


FIG. 12. Total electron attachment rate constant as a function of the mean electron energy, $k_{a,t}(\langle \epsilon \rangle)$, for CF_3I . *Swarm data*: (\blacktriangle) Ref. 71; (\bullet) Ref. 73. *Low-energy electron beam data*: (- -) Ref. 74. *Bound-electron attachment data*: (\circ) Rydberg-atom destruction data from Ref. 75; (\blacklozenge) free-ion production data ($n > 40$) from Ref. 76. (*) Average thermal value ($1.9 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$) of the room temperature swarm measurements (see text). (—), Suggested values for $k_{a,t}(\langle \epsilon \rangle)$.

8.5. Thermal Electron Attachment Rate Constant, $(k_{a,t})_{\text{th}}$

The available data on the thermal value of the electron attachment rate constant, $(k_{a,t})_{\text{th}}$, are listed in Table 13. The room-temperature values of $(k_{a,t})_{\text{th}}$ are within the combined quoted uncertainties. Their average is $1.9 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$.

Interestingly, the measurements of $(k_{a,t})_{\text{th}}$ in Fig. 13 show a small increase with increasing T from 250 to 500 K and a

TABLE 12. Suggested values for the total electron attachment rate constant, $k_{a,t}(\langle \epsilon \rangle)$, of CF_3I

Mean electron energy (eV)	$k_{a,t}(\langle \epsilon \rangle)$ ($10^{-7} \text{ cm}^3 \text{ s}^{-1}$)	Mean electron energy (eV)	$k_{a,t}(\langle \epsilon \rangle)$ ($10^{-7} \text{ cm}^3 \text{ s}^{-1}$)
0.038	1.90	0.4	0.13
0.05	1.85	0.5	0.11
0.06	1.75	0.6	0.089
0.07	1.66	0.7	0.079
0.08	1.56	0.8	0.070
0.09	1.43	0.9	0.063
0.10	1.33	1.0	0.058
0.15	0.75	1.5	0.040
0.20	0.41	1.9	0.033
0.30	0.19		

decline beyond 600 K. This is consistent with other observations⁷⁸ involving strong dissociative electron attachment processes peaking at $\sim 0 \text{ eV}$ when the potential energy curve of the dissociating negative ion state crosses that of the ground state of the neutral molecule in such a way that population of vibrational levels higher than the $\nu=0$ of the neutral molecule results in the initial state of the neutral molecule lying above the dissociating negative ion state.

TABLE 13. Thermal values, $(k_{a,t})_{\text{th}}$, of the total electron attachment rate constant of CF_3I

$(k_{a,t})_{\text{th}}$ ($10^{-7} \text{ cm}^3 \text{ s}^{-1}$)	T (K)	Reference
1.5	250	70
1.7 ± 0.2	~ 300	70
2.0	350	70
1.9 ± 0.1	300	83
2.0 ± 0.2	~ 300	71
2.2	293	72
2.4	615	72
2.2	777	72
1.5	1022 ^a	72

^aData suspected for possible error due to possible thermal decomposition of the gas.

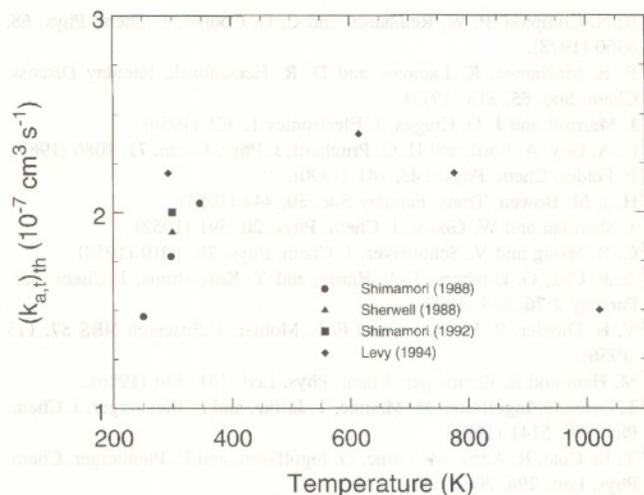


FIG. 13. Temperature dependence of the thermal electron attachment rate constant, $(k_{a,t})_{th}$, of CF₃I: (●) Ref. 70; (▲) Ref. 83; (■) Ref. 71; (◆) Ref. 72.

9. Optical Emission Under Electron Impact

Martínez *et al.*⁸⁴ performed an experimental study of the visible and ultraviolet emissions following pulsed electron-impact on CF₃I. For electron-impact energies of 100 eV, the spectra in the 200–600 nm region show a number of narrow lines superimposed on two broad bands centered at 300 and

470 nm. The emission bands were attributed⁸⁴ to the CF₃^{*} and IF^{*} species and the atomic lines to the I_I^{*} and I_{II}^{*} fragments.

10. Summary of Cross Sections

The meager data on the electron scattering cross sections for CF₃I are summarized in Fig. 14. The suggested values for $\sigma_{sc,t}(\epsilon)$ (Fig. 3; Table 6), $\sigma_{i,t}(\epsilon)$ (Fig. 7; Table 10), and $\sigma_{a,t}(\epsilon)$ (Fig. 10; Table 11) are shown by solid lines, and the calculated values of $\sigma_m(\epsilon)$ (Table 8) are shown by a dashed line.

The values of $\sigma_{pa,t}(\lambda)$ (Table 4), $\sigma_{e,diff}$ (Table 7), and $\sigma_{i,partial}(\epsilon)$ (Table 9) are also suggested but are not plotted in Fig. 14.

11. Data Needs

With the exception of the total electron scattering, electron-impact ionization, and electron attachment cross sections, measurements of the cross sections for all other electron collision processes are needed. Even the cross sections for total electron scattering, electron attachment, and electron-impact ionization need further investigation to confirm the limited data that are presently available and to extend the range of energies over which data are available.

No experimental data are available for the electron transport, ionization, and attachment coefficients of this molecule.

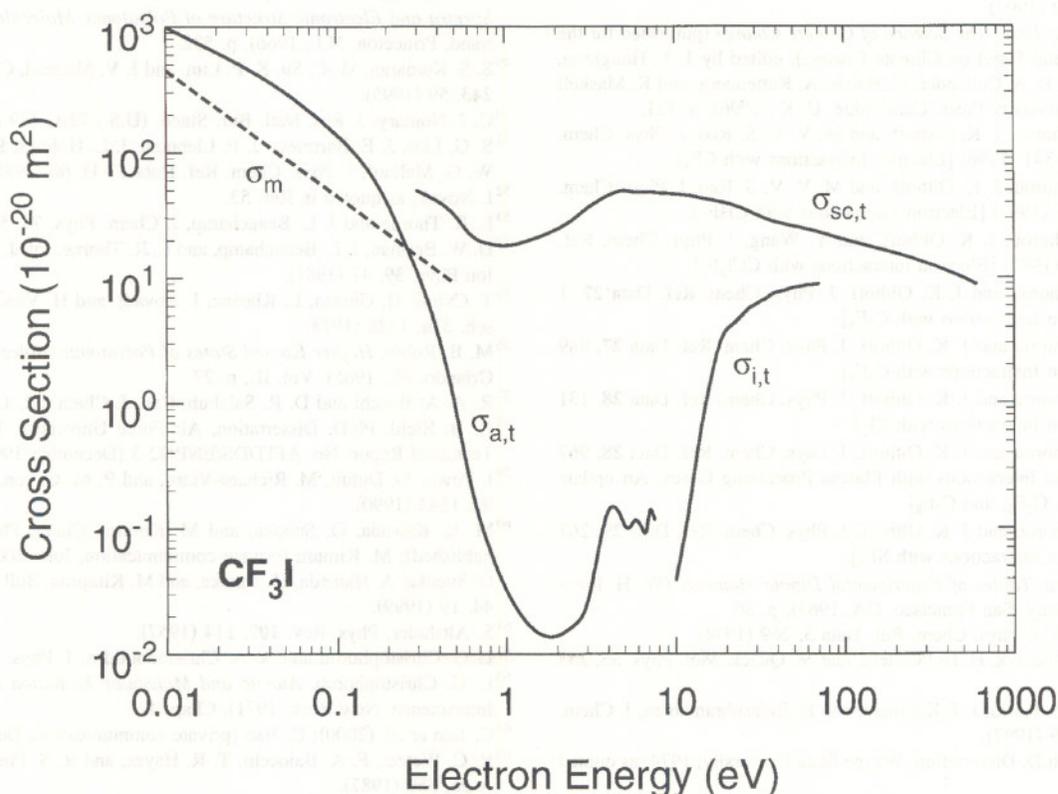


FIG. 14. Summary of suggested electron collision cross sections for CF₃I (see the text).

12. Acknowledgments

We thank Professor H. Tanaka (Sophia University) for providing us with his data on the differential electron scattering cross sections, Dr. C. Jiao (Wright Laboratory) for providing us with his measurements of the partial and total electron-impact ionization cross sections, and for bringing to our attention the earlier measurements by K. B. Riehl, Professor M. Kimura (Yamaguchi University) for providing us with a preprint of their paper on CF_3I , and Dr. P. Haaland (Mobium Enterprises) for providing parts of K. B. Riehl's dissertation.

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