

# *ELECTRON COLLISION DATA FOR PLASMA-PROCESSING GASES*

*LOUCAS G. CHRISTOPHOROU and JAMES K. OLTHOFF*

*Electricity Division, Electronics and Electrical Engineering Laboratory,  
National Institute of Standards and Technology, Gaithersburg, Maryland 20899*

I. Introduction .....	59
II. Plasma-Processing Gases .....	60
III. Data Assessment .....	65
A. Synthesis, Assessment, and Recommendation of Data .....	65
B. Deduction of Unavailable Data and Understanding from Assessed Knowledge, New Measurements, and Data Needs .....	72
C. Dissemination and Updating of the Database .....	83
IV. Assessed Cross Sections and Coefficients .....	83
V. Boltzmann-Code-Generated Collision Cross-Section Sets .....	93
VI. Conclusions .....	95
VII. References .....	96

## **I. Introduction**

Low-temperature plasma applications require detailed understanding of the physical and chemical processes occurring in the plasmas themselves. For instance, as the push for smaller feature sizes and higher quality devices in the semiconductor industry has increased, so has the need for sophisticated models with predictive capabilities that can guide the technology, and the need for advanced diagnostics to probe the details of the plasmas used to etch features, deposit materials, or clean reactor chambers. In addition, environmental concerns have fostered the demand for the more efficient use of global warming gases used in plasma processes. Advancement in each of these areas inherently requires detailed understanding of the physics and chemistry occurring within the discharge, which itself requires knowledge of the basic collision processes taking place between the species existing in the plasma. The most fundamental of the discharge processes are collisions between electrons and atoms, radicals, or molecules. These collisions are the precursors of the ions and the radicals that drive the etching, cleaning, or deposition processes. Hence, a quantitative understanding of the fundamental electron collision processes in terms of cross sections and rate coefficients is of utmost importance.

This chapter deals with fundamental data necessary for targets of importance in the plasma etching of silicon. It draws heavily from the work we have conducted at the National Institute of Standards and Technology (NIST) over the last four years under a project aimed at building a database for electronic processes in plasma processing gases, including cross sections, and electron transport and rate coefficients. To date, this effort has yielded six comprehensive publications, each containing detailed information on and assessed values for electron-molecule interaction cross section and rate-coefficient data for an important plasma processing gas:  $\text{CF}_4$  (Christophorou *et al.*, 1996),  $\text{C}_2\text{F}_6$  (Christophorou and Olthoff, 1998a),  $\text{C}_3\text{F}_8$  (Christophorou and Olthoff, 1998b),  $\text{CHF}_3$  (Christophorou *et al.*, 1997a),  $\text{CCl}_2\text{F}_2$  (Christophorou *et al.*, 1997b), and  $\text{Cl}_2$  (Christophorou and Olthoff, 1999a). In this chapter we emphasize the methodology of the assessment adopted and its value, the assessed cross sections and coefficients derived and their significance, the differences between independently assessed cross sections and those determined as cross-section sets from Boltzmann codes and the significance of the former to guide the latter, and fundamental data needs. This effort is but one example of the many critical reviews that have been made on a number of species (e.g., see Morgan, 1992a, b). Its basic goal is to show how critically assessed data can provide recommended cross sections for the various electron collision processes from often widely differing sets of data, and how such knowledge can serve to establish correlations between the various collision cross sections and molecular physical properties. Such correlations are a prerequisite of a physical understanding of the magnitude and energy dependence of the cross sections, and provide the capability to predict these quantities for gases for which such knowledge is not available.

A list of the basic electron collision processes considered here and their respective cross sections and coefficients are given in Table I. See, also, the Introduction to this volume by Itikawa (2000), Christophorou (1971), Csanak *et al.* (1984), and Christophorou *et al.* (1996).

## II. Plasma-Processing Gases

In general, there are four groups of gases of interest to plasma processing. Those used in etching, deposition, or cleaning (e.g.,  $\text{CF}_4$ ,  $\text{CHF}_3$ ,  $\text{C}_2\text{F}_6$ ,  $\text{C}_3\text{F}_8$ , *c*- $\text{C}_4\text{F}_8$ ,  $\text{Cl}_2$ ,  $\text{SF}_6$ ,  $\text{BCl}_3$ ,  $\text{NF}_3$ ,  $\text{HBr}$ ,  $\text{HCl}$ ), those used as buffer gases (e.g.,  $\text{He}$ ,  $\text{Ar}$ ,  $\text{N}_2$ ), those used as additives (e.g.,  $\text{O}_2$ ,  $\text{CO}$ ), and those that are present in virtually all practical systems as unavoidable impurities (e.g.,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{H}_2\text{O}$ ). These gases are, of course, the gases comprising the initial gaseous media. It should be realized, however, that in a discharge a large

TABLE I

ELECTRON COLLISION PROCESSES CONSIDERED IN THIS CHAPTER, THEIR RESPECTIVE CROSS SECTIONS AND SYMBOLS, AND ELECTRON-IMPACT IONIZATION, ATTACHMENT, AND TRANSPORT COEFFICIENTS

Electron Collision Process	Respective Cross Section/Coefficient	Symbol
Electron scattering	Total electron scattering cross section	$\sigma_{sc,t}(\epsilon)$
	Differential electron scattering cross section(s) <sup>a</sup>	$\sigma_{sc,diff}(\epsilon)$
Rotational excitation	Total rotational electron scattering cross section	$\sigma_{rot,t}(\epsilon)$
Elastic electron scattering	Total elastic scattering cross section <sup>b</sup> / Total elastic integral <sup>b</sup>	$\sigma_{e,t}(\epsilon)/\sigma_{e,int}(\epsilon)$
	Momentum transfer cross section (elastic)	$\sigma_m(\epsilon)$
Vibrational excitation	Total vibrational excitation cross section	$\sigma_{vib,t}(\epsilon)$
	Total direct vibrational excitation cross section	$\sigma_{vib,dir,t}(\epsilon)$
	Total indirect vibrational excitation cross section	$\sigma_{vib,indir,t}(\epsilon)$
Electronic excitation	Electronic excitation cross section	$\sigma_{elec}(\epsilon)$
Dissociation	Total dissociation cross section	$\sigma_{diss,t}(\epsilon)$
	Total cross section for electron-impact dissociation into neutrals	$\sigma_{diss,neut,t}(\epsilon)$
Ionization	Total ionization cross section	$\sigma_{i,t}(\epsilon)$
	Partial ionization cross section	$\sigma_{i,partial}(\epsilon)$
	Multiple ionization cross section	$\sigma_{i,mult}(\epsilon)$
	Density-reduced ionization coefficient	$\alpha/N$
	Effective ionization coefficient	$(\alpha - \eta)/N$
Attachment	Total electron attachment cross section	$\sigma_{a,t}(\epsilon)$
	Total dissociative electron attachment cross section	$\sigma_{da,t}(\epsilon)$
	Density-reduced electron attachment coefficient	$\eta/N$
	Total electron attachment rate constant	$k_{a,t}$
Ion-pair formation	Cross section for ion-pair formation	$\sigma_{ip}(\epsilon)$
Electron drift	Electron drift velocity	$w$
Electron diffusion	Transverse electron diffusion coefficient to electron mobility ratio	$D_T/\mu$

<sup>a</sup> For total or for a particular electron scattering process.

<sup>b</sup> These two cross sections refer to the same quantity (see Christophorou, 1971 and Csanak, 1984).

fraction of the molecules of the initial feed gas(es) may be dissociated into atoms, radicals, and ions. Additionally, depending on the discharge conditions and the gas itself, the initial gas molecules can have considerable vibrational excitation energy and the discharge-produced species can also

be vibrationally (and/or electronically) excited. Therefore, besides the knowledge on electron-molecule interactions presented in this chapter on the initial feed gases, there is a need for basic electron-collision data for vibrationally excited molecules and radicals, and electronically excited atoms, radicals, and molecules.

Although this latter kind of knowledge is sparse, its acquisition is necessary because the cross sections for electron collisions with excited (energy-rich) targets are normally much larger than for the corresponding ground-state (unexcited) species (e.g., see Christophorou, 1991; Christophorou *et al.*, 1994) and hence a small amount of excited species can influence the behavior of electrons in a plasma and, consequently, the discharge properties. Important as these processes are, they are not dealt with here, but are presented in detail later in this volume (Christophorou and Olthoff, 2000, this volume). This chapter focuses on the fundamental primary interactions of electrons (mostly with kinetic energies below 100 eV) with the neutral, unexcited feed-gas molecules, and reviews critically the current state of our knowledge on these interactions. The practical significance of these electron-collision processes and their respective cross sections depends on the nature of the application, as illustrated by the examples that follow.

*a. Plasma Models.* Many models have been designed to emulate various aspects of reactive plasmas (see for example, Ventzek *et al.*, 1994; Lymberopoulos and Economou, 1995; Bukowski *et al.*, 1996; Meyyappan and Govindan, 1996). The fundamental parameters required for the accurate modeling of reactor plasmas are electron-energy distributions, electron densities, positive ion fluxes and energies, negative ion densities, and reactive radical densities. Knowledge of these parameters is the precursor to the calculation of other more industrially significant parameters, such as etch and deposition rates, etch profiles, and plasma uniformity. The calculation of the fundamental quantities relies heavily on knowledge of the magnitude of electron-collision cross sections, since virtually all physical processes in the discharge are determined or initiated by electron motion through the gas.

For example, the *electron-energy distributions* are determined by the elastic and inelastic electron-scattering processes. Especially significant are the latter, even when they lie at low energies such as those inelastic processes due to strong vibrational excitation of molecules. Such processes can indeed determine the probability of high-energy processes via their effect on the electron energy distribution function. The determination of these energy distribution functions for the electrons in the discharge is the initial calculation in models based upon Boltzmann or Monte Carlo techniques (see, for instance, Bordage *et al.*, 1996), and relies for its success on the

availability of detailed and accurate electron scattering and electron transport coefficient data. Similarly, electron transport parameters and rate coefficients are often the first parameters calculated by plasma models. Accurate measurements of these values are, thus, essential to validate model calculations. The transport parameters commonly calculated in such models include the electron drift velocity, the transverse (and longitudinal) electron diffusion coefficient to electron mobility ratio, the density-reduced ionization coefficient, the density-reduced electron attachment coefficient, and the total electron attachment rate constant.

The *electron density in a plasma* is primarily determined by electron-impact ionization processes (which produce free electrons), electron attachment processes (which remove free electrons by creating negative ions), and by secondary electron emission from surfaces. The first two processes are described by the ionization and the electron attachment cross sections, respectively, and the third process, while important and worthy of investigation, is a surface process and is not discussed here. Ionization and attachment cross sections are of particular importance as they determine the ionization balance within the plasma and thus influence the plasma properties. Another process of interest in this regard is the ion-electron recombination reactions, but since these are secondary processes they are not covered in the present discussion.

*Positive ion bombardment* is one of the main drivers of plasma surface reactions, and the ion flux is a direct result of electron-impact ionization. Although the final identity and magnitude of the positive ion flux may be dependent upon secondary reactions, such as ion-molecule reactions occurring as the ion travels through the discharge, the initial ion-formation process is driven by electron-impact processes. Partial ionization cross sections are required to determine the identity and quantity of the initial ions created in the plasma. Moreover, since positive ion and negative ion recombination processes influence the positive ion densities, the production of negative ions by resonant electron attachment processes also plays a critical role. Dissociative electron attachment is significant both as an efficient source of negative ions and as a source of free radicals because for many molecules the cross section for this process is very large at low electron energies ( $< 1$  eV) (Christophorou *et al.*, 1984).

*b. New Diagnostic Techniques.* The need to measure the identity and density of gas-phase plasma products, including reactive radicals, in industrial plasmas has led to the development of new diagnostic techniques such as negative-ion mass spectrometry and threshold-ion mass spectrometry. Negative-ion mass spectrometry detects gas-phase plasma products by monitoring negative ions formed by electron attachment to radicals, excited

species, and molecules formed by reactions in the plasma (Stoffels *et al.*, 1997; Rees *et al.*, 1998). Cross sections for electron attachment and dissociative electron attachment are required for the feed gas and for the species to be detected in order for this technique to be effective. Threshold-ionization mass spectrometry, on the other hand, detects radicals by monitoring positive ions generated by collisions of radicals with electrons whose kinetic energy is above the ionization threshold of the radical, but below the ionization threshold of the feed gas (Sugai *et al.*, 1995a; Nakamura *et al.*, 1997; Schwarzenback *et al.*, 1997). This allows detection of radicals even when the mass spectra of the radicals are similar to those of the feed gas. This technique, too, requires detailed electron-impact ionization cross sections for the feed gas and for the radicals at energies near threshold. This same technique can be used to detect excited species.

Additionally, *optical emission diagnostic* techniques rely on light emission from a processing plasma and are often used to monitor plasma uniformity, excited species densities, and electron-energy distributions. The latter two applications require electron-impact excitation cross sections for the feed gas and for the gas-phase products generated in the discharge.

*c. Environmental Applications.* Environmental concerns over the use of fluorinated compounds that are often global warming gases have prompted significant interest in increasing and optimizing the efficiency of plasma-assisted cleaning techniques (Sobolewski *et al.*, 1998), and in the development of post-processing emission abatement techniques (i.e., the destruction or conversion of any remaining feed gas being exhausted from the reactor). Both of these processes, cleaning and abatement, require the dissociation of the feed gas into reactive radicals by three basic processes, electron-impact dissociative ionization, where a positive ion and a radical are produced; dissociative electron attachment, where a negative ion and a radical are produced; and neutral dissociation, where two neutral fragments are produced by electron impact. Knowledge of the cross sections for electron-impact dissociation, dissociative electron attachment, and partial ionization are necessary to optimize such industrial processes.

*d. New Applications.* Fundamental research in electron collision processes involving transient species such as radicals and excited species (such as electronically excited atoms and electronically and/or vibrationally excited molecules) will undoubtedly avail new possibilities for applications. Little is known about these reactions and their effect on the plasma itself at the current time. As already indicated in this section, the data show that electron interactions with energy-rich species have large cross sections that often are orders of magnitude greater than for similar interactions with the feed gas (Christophorou and Olthoff, 2000, this volume).

### III. Data Assessment

For discharges utilized in industrial plasma processes, the most significant electron collisions occur in the electron energy range  $< 100$  eV. The generic primary processes are elastic and inelastic electron scattering, electron-impact ionization, electron-impact dissociation, and electron attachment (Table I). No discussion is given here of electron interactions with energy rich gases (vibrationally and/or electronically excited), or with discharge decomposition products such as radicals.

The three principal components of our effort to provide electron-impact reference data relevant to plasma processing are: (1) synthesis, assessment, and recommendation of electron collision data; (2) deduction of unavailable data and understanding from the assessed knowledge, including identification of new measurements and data needs; and (3) dissemination and updating of the database. We provide examples for each of these components in the following three subsections.

#### A. SYNTHESIS, ASSESSMENT, AND RECOMMENDATION OF DATA

This component begins with thorough literature searches and contacts with researchers in the field, followed by a critical review and assessment of the available data, and a recommendation of data. The critical review and assessment requires understanding of the physical processes themselves, which itself requires auxiliary and complementary information on the physical and chemical properties of the molecules under consideration.

In general, there exist three main sources of electron collision data. These are experimental measurements (obtained principally by electron beam and electron swarm techniques), calculations (of varied levels of sophistication), and Boltzmann- and Monte Carlo-based computations. The first provides directly—and at times indirectly—cross sections or coefficients for individual electron collision processes. The second gives in principle cross sections for any process, but they are in practice limited in their utility by the complexity the calculations themselves entail, especially for polyatomic molecules. The third relies on electron transport data and other inputs and yields only self-consistent sets of cross sections, not independent and unique cross sections for each individual collision process (see discussion in Section V).

Assessment of these cross sections is essential as the values determined from each of these sources are often contradictory. In addition, assessment of the cross sections from each of these sources is often difficult. The uncertainty of the measurement, the limitation of the calculation, and the

physical reasonableness of the data obtained as sets rather than for each individual reaction are the main issues.

Any assessment of data relies upon some established protocol for determining which data are the most reliable. For our work performed at NIST, "recommended" or "suggested" values of cross sections and transport coefficients are determined, where possible, for each type of cross section and coefficient for which data exist. These values are derived from fits to the most reliable data, as determined by the following criteria: (i) the data are published in peer reviewed literature; (ii) there is no evidence of unaddressed errors; (iii) the data are absolute determinations; (iv) multiple data sets exist and are consistent with one another within combined stated uncertainties over common energy ranges; and (v) in regions where both experimentally and theoretically derived data exist, the experimental data are preferred. Cross sections and coefficients for the various processes that meet these criteria are designated as "recommended" and fits to these data represent the best current estimates for the cross sections and coefficients for each of these processes. For cross sections and coefficients for which the only data that are available do not meet all of the forementioned criteria, the best available data may be used to designate a "suggested" cross section or coefficient. In cases where no reasonable data exist, or where two or more measurements are in an unresolved contradiction, the raw data are presented for information and no recommendation is made.

To identify most clearly the reliable data for electron interactions with a given gas, all published data for each cross section are considered in our assessment, even those which have been subsequently superseded. This is done in order to aid the understanding of the evolution of the data, assist in the determination of the reliability of the data, and draw attention to these changes for researchers who might have used the earlier data in their work. When possible, data are obtained from published tables. For data presented only in graphical form, the published figures are scanned and the data are digitized for use in this work. Depending on the quality of the original figure, the values of the data obtained in this manner are within 1–3% of the original values.

No uncertainty values are assigned to our recommended data since no means exist of confirming the experimental uncertainties reported by the original authors (see Christophorou *et al.* 1996, 1997a, 1997b; Christophorou and Olthoff, 1998a, 1998b, 1999a). Some measure of uncertainty can be obtained from an analysis of the combined relative uncertainties of the original data, which are fitted to derive the recommended set. It should be stressed that although for many cross sections there exist published values that differ by as much as two orders of magnitude, critical analysis of these data allows the determination of cross sections whose uncertainties

are expected to be between 10 and 20% for most cases.

We wish to illustrate this assessment process with four examples. One shows how reasonable data may be extracted from conflicting data, another shows how a recommended cross section for a particular electron collision process can be determined by considering its relationship to known cross sections for other electron collision processes, a third shows where the magnitude of electron-beam determined cross sections is adjusted based on knowledge provided by the electron swarm method, and finally, an example of the required consistency between different cross sections is provided.

*a. Determination of the Recommended Cross Section for Momentum Transfer  $\sigma_m(\epsilon)$  for  $CF_4$ .* Figure 1 shows an example of how a recommended cross section is extracted from multiple sets of experimental and theoretical data. It refers to the momentum transfer cross section  $\sigma_m(\epsilon)$  of  $CF_4$  for which some values in the literature differ by more than two orders of magnitude.

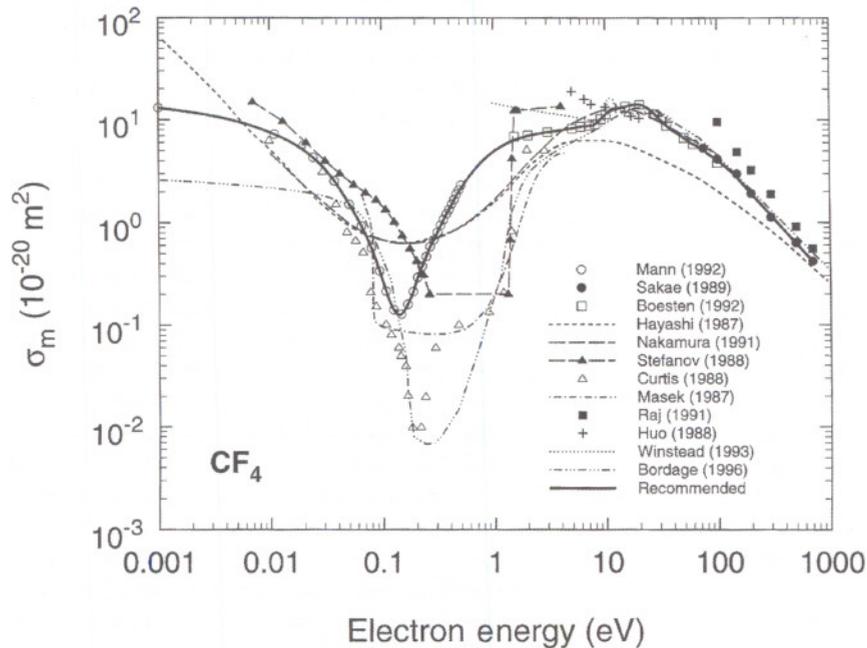


FIG. 1. Extraction of a recommended cross section for the momentum transfer cross section  $\sigma_m(\epsilon)$  of  $CF_4$  from multiple sets of experimental and theoretical data (see text and Christopherou *et al.*, 1996).

The data in Fig. 1 cover the energy range 0.001–1000 eV and come from three sources, direct measurements, calculations, and swarm-based Boltzmann codes. The  $\sigma_m(\epsilon)$  derived from direct measurements are the high-energy data of Sakae *et al.* (1989) and Boesten *et al.* (1992), which are in agreement within their combined uncertainty [ $\sim 10\%$  (Sakae *et al.*, 1989) and 15–20% (Boesten *et al.*, 1992)], and the low-energy values of Mann and Linder (1992), which were determined from their elastic differential cross-section measurements (uncertainty 20–30%) and modified effective range theory. The calculated  $\sigma_m(\epsilon)$  are the results of three investigations, one using an independent-atom model with partial waves (Raj, 1991), and the other two using the static exchange approximation (Huo, 1988; Winstead *et al.*, 1993), and agree only partially with the experimental measurements of Sakae *et al.* and Boesten *et al.* The swarm-based Boltzmann-code cross sections (Hayashi, 1987; Masek *et al.*, 1987; Nakamura, 1991; Stefanov *et al.*, 1988; Curtis *et al.*, 1988; Bordage *et al.*, 1996) are model dependent and have different degrees of uncertainty depending on the electron transport data used and on other inputs. None agrees well with the measurements. In spite of these disparities, a recommended cross section can be obtained (Christophorou *et al.*, 1996) over the energy range 0.001–700 eV (solid black line in Fig. 1) from a least squares fit to the experimental cross sections of Mann and Linder for energies  $< 0.5$  eV, those of Sakae *et al.* and Boesten *et al.*  $> 1.5$  eV, and an interpolation between 0.5–1.5 eV.

*b. Determination of the Recommended Total Electron Scattering Cross Section  $\sigma_{sc,t}(\epsilon)$  for  $CF_4$  below  $\sim 1$  eV.* A recommended value for the total electron scattering cross section  $\sigma_{sc,t}(\epsilon)$  of the  $CF_4$  molecule was derived with confidence for energies  $> 1$  eV because there exist reliable experimental measurements over wide energy ranges that agree within specified uncertainties (Christophorou *et al.*, 1996). However, for energies  $< 1$  eV this is not the case. Nonetheless, recommended values for the  $\sigma_{sc,t}(\epsilon)$  of the  $CF_4$  molecule down to 0.003 eV were determined by considering the relationships between other known types of cross sections as shown in Fig. 2. First, measurements of  $\sigma_{sc,t}(\epsilon)$  for  $\epsilon \gtrsim 0.5$  eV by Jones (1986) (solid circles) and by Szmytkowski *et al.* (1992) (open triangles) were accepted as accurate high-energy reference data points. Second, measurements of Mann and Linder (1992) for the elastic integral cross section  $\sigma_{e,int}(\epsilon)$  of  $\lesssim 2$  eV (long-dash curve in Fig. 2) were accepted because they were determined from their differential electron scattering cross-section measurements and a sound analysis. Third, below the lowest vibrational threshold of  $CF_4$  at 0.054 eV,  $\sigma_{sc,t}(\epsilon)$  was taken equal to  $\sigma_{e,int}(\epsilon)$ , that is,  $\sigma_{sc,t}(\epsilon) = \sigma_{e,int}(\epsilon)$ . Fourth, as there are no known negative ion states of  $CF_4$  for energies  $\lesssim 2$  eV (Christophorou *et al.*, 1996), it was assumed that all vibrational excitation below 2 eV is due to the direct

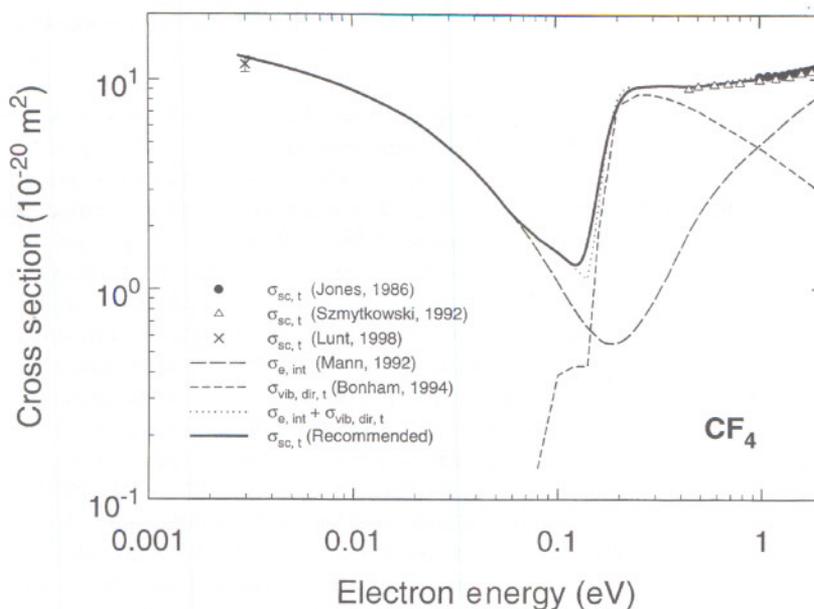


FIG. 2. Determination of the recommended total electron scattering cross section  $\sigma_{sc,t}(\epsilon)$  of  $CF_4$  below  $\sim 1$  eV (see text).

excitation by electron impact of the two modes  $\nu_3$  and  $\nu_4$  of  $CF_4$ . Furthermore, since in this energy range electronic excitation is absent and rotational excitation is negligible (the  $CF_4$  molecule has neither a dipole nor a quadrupole moment) it was assumed that between  $\sim 0.06$  eV and 2 eV,  $\sigma_{sc,t}(\epsilon) = \sigma_{e,int}(\epsilon) + \sigma_{vib,dir,t}(\epsilon)$ , where  $\sigma_{vib,dir,t}(\epsilon)$  is the sum of the cross sections for the direct excitation of the  $\nu_3$  and  $\nu_4$  infrared active modes of  $CF_4$  as calculated (Bonham, 1994) in the Born-dipole approximation (short-dash curve in Fig. 2). The dotted curve in Fig. 2 is  $\sigma_{sc,t}(\epsilon) = \sigma_{e,int}(\epsilon) + \sigma_{vib,dir,t}(\epsilon)$  and was obtained by using the recommended values of Christophorou *et al.* (1996) for  $\sigma_{e,int}(\epsilon)$  and  $\sigma_{vib,dir,t}(\epsilon)$ . The cross section  $\sigma_{sc,t}(\epsilon)$  estimated in the manner just outlined from 0.08 to 2 eV was used, along with the measurements of Jones (1986) and Szmytkowski *et al.* (1992) for  $\sigma_{sc,t}(\epsilon)$  at energies  $\geq 0.5$  eV and the  $\sigma_{e,int}(\epsilon)$  below 0.08 eV to obtain a best estimate of  $\sigma_{sc,t}(\epsilon)$  from 0.003 to  $\sim 1$  eV. This then allowed recommended values to be delineated for  $\sigma_{sc,t}(\epsilon)$  from 0.003 to 4000 eV (Christophorou *et al.*, 1996). A subsequent measurement by Lunt *et al.* (1998), shown in Fig. 2 by the cross ( $\times$ ) point, is in excellent agreement with the assessed cross section. The results of a recent *ab initio* calculation by Isaacs

*et al.* (1998) are also in general agreement with the recommended cross section.

*c. Determination of the Recommended Total Electron Attachment Cross Section  $\sigma_{a,t}(\varepsilon)$  for  $\text{Cl}_2$ .* The total electron attachment cross section of  $\text{Cl}_2$  has been measured by Kurepa and Belić (1978) using a beam experiment. From a critical assessment of the available swarm data, Christophorou and Olthoff (1999a) adjusted the Kurepa and Belić cross section upward by 30%. It is instructive to see how this adjustment was made, for it shows an example of the assessment process itself and is also an excellent example of the value of absolute electron-swarm measurements to adjust (normalize) the absolute magnitude of electron beam data. The process essentially utilizes the strength of each experimental procedure—the determination of well-resolved relative cross sections by electron beam experiments and the determination of absolute magnitude by electron swarm experiments.

Let us then first refer to the measurements of McCorkle *et al.* (1984) of the rate constant  $k_{a,t}$  of electron attachment to  $\text{Cl}_2$  in a buffer gas  $\text{N}_2$  over a wide range of density-reduced electric fields  $E/N$ . Since for these measurements the content of  $\text{Cl}_2$  in  $\text{N}_2$  was kept very small, the electron energy distribution function in the mixture is virtually the same as in the pure buffer gas  $\text{N}_2$ . Furthermore, since the electron energy distribution functions in  $\text{N}_2$  can be reliably calculated at the  $E/N$  values for which the  $k_{a,t}$  measurements were made, the  $k_{a,t}(E/N)$  data can be plotted as a function of the mean electron energy  $\langle\varepsilon\rangle$ , that is, the quantity  $k_{a,t}(\langle\varepsilon\rangle)$  was accurately determined. The  $k_{a,t}(\langle\varepsilon\rangle)$  measurements determined this way at room temperature ( $\sim 298$  K) are shown in Fig. 3a.

In Fig. 3a three sets of calculated values for  $k_{a,t}(\langle\varepsilon\rangle)$  are also plotted. One was calculated by McCorkle *et al.* using the electron energy distributions in  $\text{N}_2$  and the total electron attachment cross section of Kurepa and Belić (1978), and the other two were calculated by Kurepa *et al.* (1981) and by Chantry (1982) using the Kurepa and Belić (1978) cross section and a Maxwellian electron energy distribution function for the electron energies. Clearly, the assumption of a Maxwellian distribution function for the electron energies is unrealistic at high  $E/N$  as is shown by the large difference in the calculated rate by the last two groups and the measurements. In the low-energy region (around the  $k_{a,t}(\langle\varepsilon\rangle)$  maximum) all three calculated values of  $k_{a,t}(\langle\varepsilon\rangle)$  using the Kurepa and Belić (1978) total electron attachment cross section have an energy dependence similar to the directly measured rate constants of McCorkle *et al.* (1984). However, each of the calculated values is lower in magnitude by  $\sim 30\%$ , suggesting that the Kurepa and Belić electron attachment cross section is lower than its true value by this amount. Hence the swarm-based

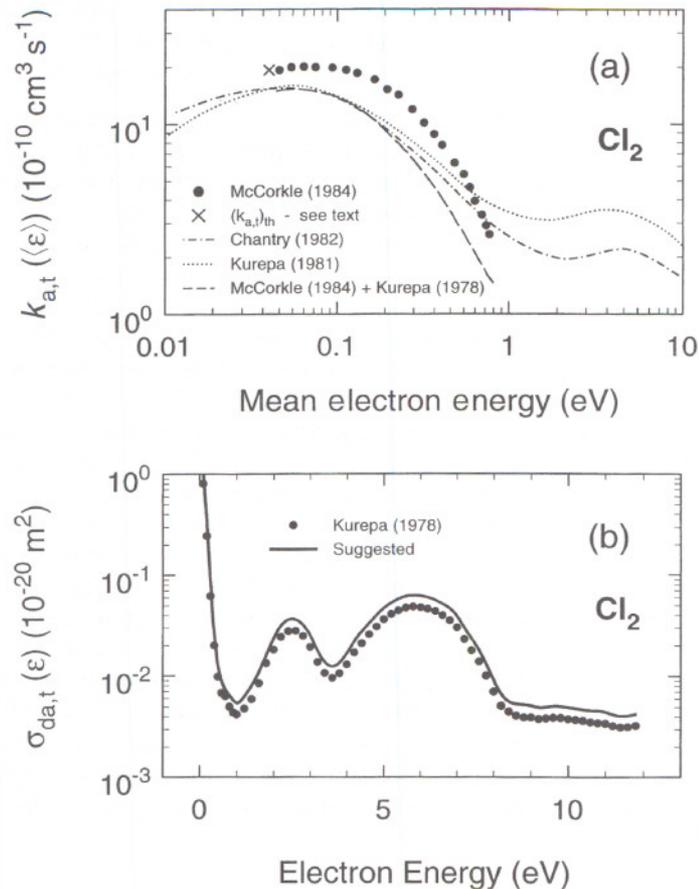


FIG. 3. (a) Total electron attachment rate constant as a function of the mean electron energy  $\langle \epsilon \rangle$ ,  $k_{a,t}(\langle \epsilon \rangle)$ , for Cl<sub>2</sub> ( $T \sim 298 \text{ K}$ ) (from Christophorou *et al.*, 1999).

●, (McCorkle *et al.*, 1984).

×,  $(k_{a,t})_{th}$  [average of the two most recent values (McCorkle *et al.*, 1984; Smith *et al.*, 1984) of the thermal ( $T \sim 300 \text{ K}$ ) electron attachment rate constant].

-.-, Chantry (1982) using the  $\sigma_{a,t}(\epsilon)$  of Kurepa and Belić (1978) and a Maxwellian distribution function for the electron energies.

...., Kurepa *et al.* (1981) using the  $\sigma_{a,t}(\epsilon)$  of Kurepa and Belić (1978) and a Maxwellian distribution function for the electron energies.

---, McCorkle *et al.* (1984) using the  $\sigma_{a,t}(\epsilon)$  of Kurepa and Belić (1978) and the electron energy distribution functions they calculated for N<sub>2</sub>.

(b) Total dissociative electron attachment,  $\sigma_{da,t}(\epsilon)$ , for Cl<sub>2</sub> (from Christophorou and Olthoff, 1999).

●, measurements of Kurepa and Belić (1978).

—, cross section of Kurepa and Belić (1978) adjusted upwards by 30% (see text).

adjustment of +30% to the electron-beam dissociative electron attachment data for  $\text{Cl}_2$  shown in Fig. 3b. A similar adjustment would be in order for the Kurepa and Belić (1978) cross section for ion-pair formation.

*d. Consistency between Assessed Cross Sections.* Finally, it is important to stress the significance of the total electron scattering cross section in efforts to establish the consistency of the independently assessed cross sections for the various electron collision processes for a given gas. This cross section is usually measured with the lowest uncertainty compared to the other cross sections. While this cross section is rarely used in plasma models, it provides a way to normalize or validate the other cross sections: the sum of the independently assessed cross sections of all possible electron-collision processes should add up to and not exceed the total electron scattering cross section. This has been nicely shown by Christophorou *et al.* (1996) for the  $\text{CF}_4$  molecule for which the sum of the independently assessed cross sections nearly adds up to the independently assessed total electron scattering cross section as can be seen from Fig. 4. The small dip around 20 eV in the sum of the independently assessed cross sections may be an artifact due to the significant discrepancy in this energy range between the two experimental measurements of  $\sigma_{e,\text{int}}(\epsilon)$  (Boesten *et al.*, 1992; Mann and Linder, 1992). Indeed, if instead of taking the average of the two sets of experimental measurements of  $\sigma_{e,\text{int}}(\epsilon)$  in this energy range, one considers only the values of Boesten *et al.* (1992), the dip in the sum of the independently assessed cross sections disappears and the sum agrees well with the assessed values of  $\sigma_{\text{sc,t}}(\epsilon)$  in this region as well. Conversely, this suggests that the cross section from Boesten *et al.* may be preferred to that of Mann and Linder in this energy range, and that further measurements of  $\sigma_{e,\text{int}}(\epsilon)$  in this energy range are needed.

## B. DEDUCTION OF UNAVAILABLE DATA AND UNDERSTANDING FROM ASSESSED KNOWLEDGE, NEW MEASUREMENTS, AND DATA NEEDS

A thorough and critical assessment of the available knowledge on electron-molecule collisions and related physical and chemical properties for each plasma processing gas often helps deduce needed data, which at the time are not otherwise available. It also enhances our understanding of the dependence of the cross sections of the various electron collision processes on the structural and electronic properties of molecules, leads to new measurements, and identifies needed critical data. Examples of these benefits are given in what follows.

*a. Deduction of Unavailable Data from Assessed Knowledge.* Two examples of cross sections deduced from critically assessed data are given in this

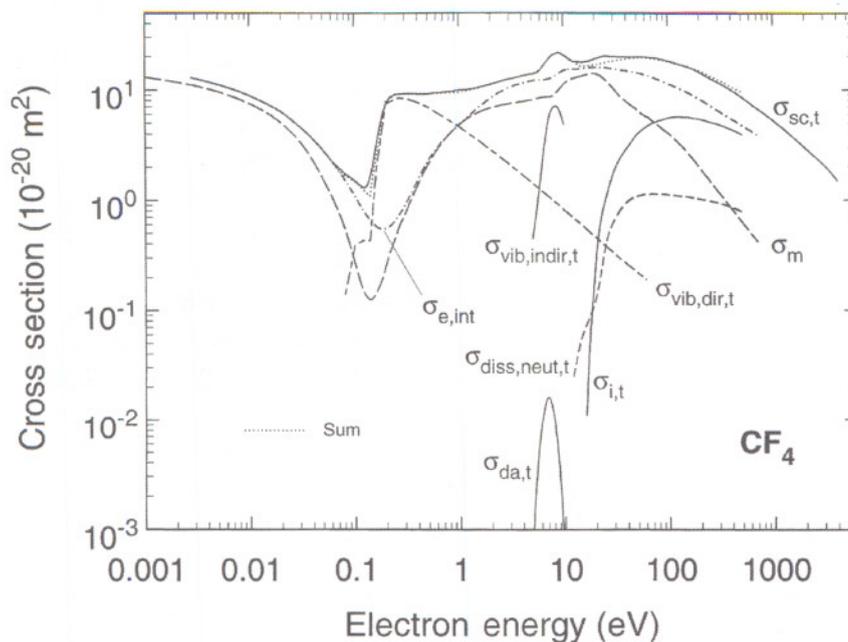


FIG. 4. Recommended and suggested electron-impact cross sections for  $\text{CF}_4$ . The data are from Christophorou *et al.* (1996) except as follows:  $\sigma_{\text{vib,indir,t}}(\epsilon)$  (Fig. 5a, Section III.B),  $\sigma_{\text{diss,neut,t}}(\epsilon)$  (Fig. 7, Section III.B), and  $\sigma_{\text{i,t}}(\epsilon)$  (Fig. 14, Section IV). Note the excellent agreement between the sum of the independently assessed cross sections (dotted curve) and the total electron scattering cross section (see text).

subsection (for other examples and additional details see Christophorou *et al.*, 1996, 1997a, 1997b; Christophorou and Olthoff, 1998a, 1998b, 1999a). The first example is the deduced cross sections for indirect (resonance enhanced) vibrational excitation cross sections for  $\text{CF}_4$  and  $\text{Cl}_2$ . Figure 5a shows the sum of the cross sections for direct vibrational excitation of the two infrared active modes  $\nu_3$  and  $\nu_4$  of  $\text{CF}_4$  as calculated in the Born-dipole approximation (Bonham, 1994). This sum is taken to give the cross section,  $\sigma_{\text{vib,dir,t}}(\epsilon)$  for total direct vibrational excitation of  $\text{CF}_4$ . This cross section is compared in Fig. 5a with the total inelastic cross section  $\sigma_{\text{inel,t}}(\epsilon)$  [which is approximately equal to  $\sigma_{\text{vib,dir,t}}(\epsilon)$  in this energy range] ( $\times$ ) measured by Mann and Linder (1992), and with the values ( $\bullet$ ,  $\circ$ ) of the total inelastic cross section  $\sigma_{\text{inel,t}}(\epsilon) = [(\sigma_{\text{sc,t}}(\epsilon) - \sigma_{\text{e,int}}(\epsilon))]$  deduced from the assessed values of Christophorou *et al.* (1996) for  $\sigma_{\text{sc,t}}(\epsilon)$  and  $\sigma_{\text{e,int}}(\epsilon)$ . Since electronic excitation is not energetically possible below the electronic excitation

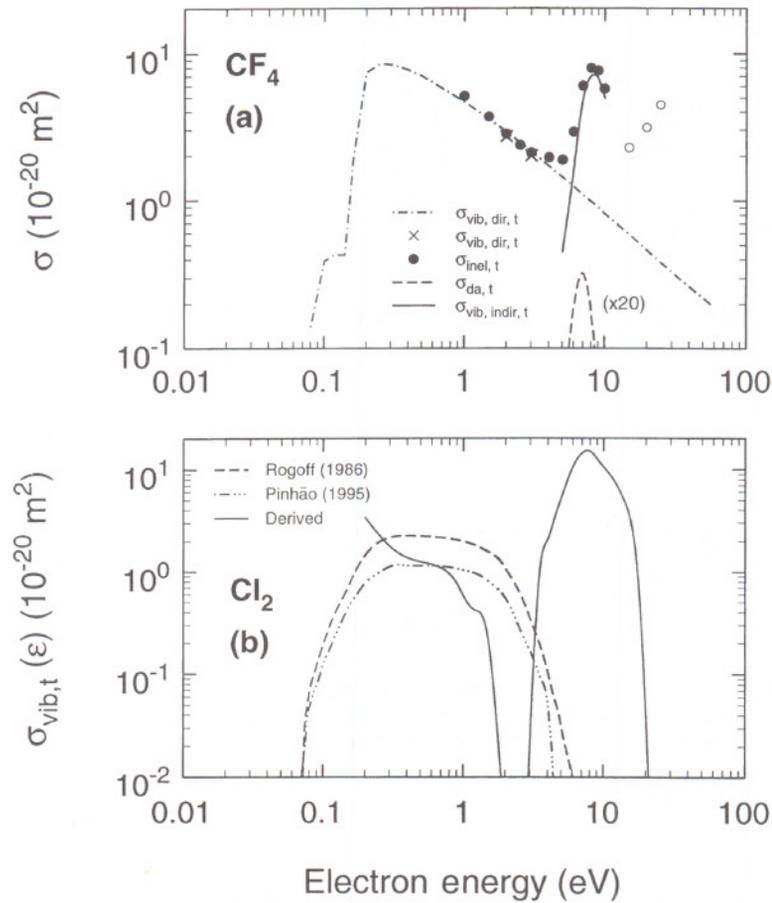


FIG. 5. (a) Total indirect vibrational excitation cross section  $\sigma_{\text{vib, indir, t}}(\epsilon)$  for  $\text{CF}_4$ .  
 (-.-) Total direct vibrational excitation cross section  $\sigma_{\text{vib, dir, t}}(\epsilon)$  for  $\text{CF}_4$  [sum of the Born-approximation calculation (Bonham, 1994) for the two infrared active modes of  $\text{CF}_4$ ].  
 x, measurements of  $\sigma_{\text{vib, dir, t}}(\epsilon) \approx \sigma_{\text{inel, t}}(\epsilon)$  by Mann and Linder (1992).  
 ●, ○,  $\sigma_{\text{sc, t}}(\epsilon) - \sigma_{\text{e, int}}(\epsilon)$ , where the values of these two cross sections are those assessed in Christophorou *et al.* (1996).  
 ---, assessed total dissociative electron attachment cross section  $\sigma_{\text{da, t}}(\epsilon)$  (Christophorou *et al.*, 1996).  
 —, Deduced  $\sigma_{\text{vib, indir, t}}(\epsilon)$  (see text).  
 (b) Total vibrational excitation cross section  $\sigma_{\text{vib, t}}(\epsilon)$  for  $\text{Cl}_2$  (from Christophorou and Olthoff, 1999).  
 Results of Boltzmann-code analyses: (----) (Rogoff *et al.*, 1986), (-.-.-) (Pinhão and Chouki, 1995); —, Deduced by Christophorou and Olthoff (1999) from assessed cross sections (see text).

threshold at 12.5 eV, the difference between  $\sigma_{\text{inel,t}}(\epsilon)$  and the Born  $\sigma_{\text{vib,dir,t}}(\epsilon)$  gives the cross section for indirect inelastic electron scattering  $\sigma_{\text{inel,indir,t}}(\epsilon)$  for  $\text{CF}_4$ . The indirect vibrational excitation cross section  $\sigma_{\text{vib,indir,t}}(\epsilon)$  can then be obtained by subtracting the assessed total dissociative electron attachment cross section  $\sigma_{\text{da,t}}(\epsilon)$  from  $\sigma_{\text{inel,indir,t}}(\epsilon)$  for energies  $< 12.5$  eV, that is,

$$\sigma_{\text{vib,indir,t}}(\epsilon) = [\sigma_{\text{sc,t}}(\epsilon) - \sigma_{\text{e,int}}(\epsilon)] - [\sigma_{\text{vib,dir,t}}(\epsilon) + \sigma_{\text{da,t}}(\epsilon)]$$

This is shown by the solid line in Fig. 5a. The data shown in the figure by the open circles were not considered in this process because the values of  $\sigma_{\text{e,int}}(\epsilon)$  are less reliable in the 10–20 eV range due to the large difference between the two experimental sets (Mann and Linder, 1992; Boesten *et al.*, 1992) of measurements used to derive the recommended values of  $\sigma_{\text{e,int}}(\epsilon)$ . The work of Boesten *et al.* (1992) did not indicate any contribution to the scattering cross section in this energy range due to the existence of negative ion resonances.

The deduced cross section clearly shows that indirect vibrational excitation is a dominant inelastic electron scattering process in the energy range from  $\sim 7$  to  $\sim 13$  eV. It plays a crucial role in the yield of the various discharge products by virtue of its effect on the electron energy distribution function. This effect results not only from the large value of the cross section  $\sigma_{\text{vib,indir,t}}(\epsilon)$ , but also from the large electron energy loss associated with indirect vibrational excitation (as compared to direct vibrational excitation) via the negative ion states of  $\text{CF}_4$  in this energy range (see further details in Christophorou *et al.*, 1996 and Bordage *et al.*, 1999).

The second example is the deduction of an estimated cross section for electron-impact vibrational excitation for the  $\text{Cl}_2$  molecule. In this case, one can use the “suggested” values (Christophorou and Olthoff, 1999a) derived from the assessment of the cross sections for total electron scattering  $\sigma_{\text{sc,t}}(\epsilon)$ , total elastic electron scattering  $\sigma_{\text{e,t}}(\epsilon)$ , total ionization  $\sigma_{\text{i,t}}(\epsilon)$ , total dissociation into neutrals  $\sigma_{\text{diss,neut,t}}(\epsilon)$ , and total dissociative electron attachment  $\sigma_{\text{da,t}}(\epsilon)$  to calculate a cross section for total vibrational excitation of  $\text{Cl}_2$  by electron impact,  $\sigma_{\text{vib,t(e),t}}(\epsilon)$ , from the expression

$$\sigma_{\text{vib,t(e),t}}(\epsilon) = \sigma_{\text{sc,t}}(\epsilon) - [\sigma_{\text{e,t}}(\epsilon) + \sigma_{\text{i,t}}(\epsilon) + \sigma_{\text{diss,neut,t}}(\epsilon) + \sigma_{\text{da,t}}(\epsilon)]$$

Moreover, since  $\text{Cl}_2$  is a homopolar molecule, direct vibrational excitation is expected to be small and the total vibrational excitation cross section can be taken to be the cross section for the total vibrational excitation  $\sigma_{\text{vib,indir,t}}(\epsilon)$ , that is,  $\sigma_{\text{vib,indir,t}}(\epsilon) \approx \sigma_{\text{vib,t}}(\epsilon)$ . The  $\sigma_{\text{vib,t}}(\epsilon)$  deduced this way is shown in Fig. 5b, where it is compared with the total vibrational

excitation cross section of  $\text{Cl}_2$  obtained from two Boltzmann-code analyses. It bears no similarity to them. In spite of the uncertainty involved in the derivation of  $\sigma_{\text{vib,indir,t}}(\epsilon)$ , the derived cross section shows that the indirect vibrational excitation cross section of  $\text{Cl}_2$  is large. In the absence of any direct measurement of  $\sigma_{\text{vib,t}}(\epsilon)$ , the cross section  $\sigma_{\text{vib,t}}(\epsilon)$  deduced from the assessed data is to be preferred to those provided by the Boltzmann codes.

*b. Better Understanding from Assessed Data.* The critical review and assessment of existing data on electron collisions with the six plasma processing gases covered in this chapter has enhanced our understanding of electron-molecule interactions in a number of ways. This is illustrated by the following two examples.

The first example pertains to the enhancement of our knowledge on the negative ion states (NIS) of these molecules, their effects on the various types of electron collision processes, and their respective cross sections. Let us then look at a specific molecule, namely,  $\text{CCl}_2\text{F}_2$ , and the number and energy positions of its negative ion states that fall below 10 eV. The available data on the number and energy positions of the negative ion states of  $\text{CCl}_2\text{F}_2$  are summarized in Fig. 6. The last column in the figure lists the assessed energies of the negative ion states of the  $\text{CCl}_2\text{F}_2$  molecule. This assessment is based on published data on the electron affinity, electron attachment using the electron swarm method, electron attachment using the electron beam method, electron scattering, electron transmission, indirect electron scattering deduced in the assessment process, and related calculations (see References in Christophorou *et al.*, 1997b). Thus, the lowest negative ion states of  $\text{CCl}_2\text{F}_2$  have been identified with the average positions as follows:  $a_1(\text{C-Cl}\sigma^*)$  at +0.4 eV and -0.9 eV,  $b_2(\text{C-Cl}\sigma^*)$  at -2.5 eV,  $a_1(\text{C-F}\sigma^*)$  at -3.5 eV, and  $b_1(\text{C-F}\sigma^*)$  at -6.2 eV. The lowest negative ion state  $a_1(\text{C-Cl}\sigma^*)$  accounts for both the production of  $\text{Cl}_2^-$  with a binding energy of +0.4 eV and the production of  $\text{Cl}^-$  via the lowest negative ion state of  $\text{Cl}_2$  at -0.9 eV. [Note that the + and - signs are used here and in Fig. 6 to indicate, respectively, a positive electron affinity and a negative electron affinity (vertical attachment energy) for the various negative ion states of  $\text{CCl}_2\text{F}_2$ .] Similar information has been obtained for other molecules (see Christophorou *et al.*, 1996, 1997a, 1997b; Christophorou and Olthoff, 1998a, 1998b, 1999a).

The second example pertains to an increased understanding of electron collisions with the perfluoroalkanes. For example, a thorough review of the literature used to determine the assessed data leads one to a rather simple picture of the collisional behavior of the  $\text{CF}_4$  molecule with low-energy electrons.

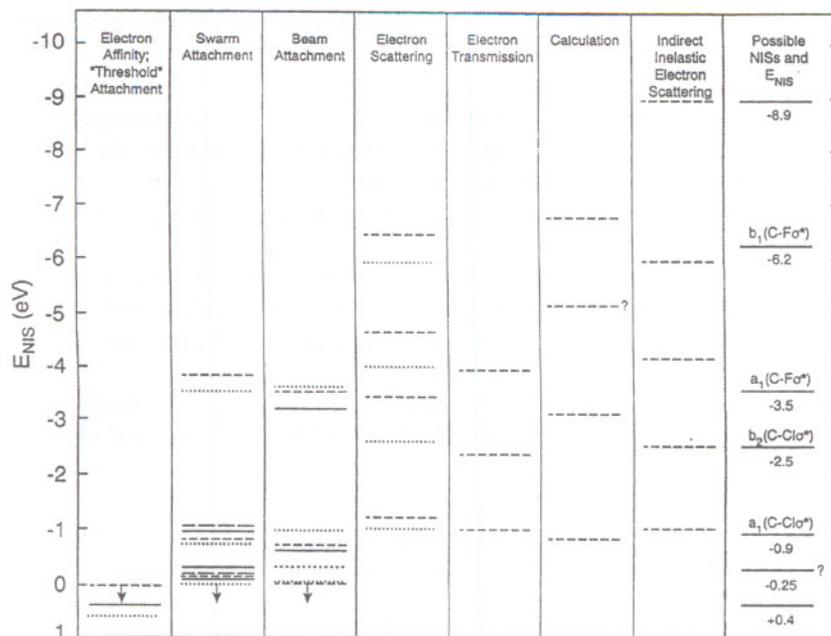


FIG. 6. Energy positions of the negative ion states of  $CCl_2F_2$   $< 10$  eV obtained from various experimental and theoretical sources. The last column gives the assessed energies of the negative ion states and their assignments [see text and Christophorou *et al.* (1997b) for original sources of data].

- Vibrational excitation is the dominant inelastic process for energies  $< 12.5$  eV, that is, below the threshold for electronic excitation. It is dominated by the excitation of the infrared active modes  $\nu_3$  and  $\nu_4$  via direct dipole scattering below the negative ion resonance region 6–8 eV, and via indirect scattering in the resonance region.
- All electronic excitations of  $CF_4$  lead to dissociation (Winters and Inokuti, 1982). Therefore, no separate cross sections for electronic excitation are required.
- Dissociation of  $CF_4$  into neutral fragments begins at  $\sim 12.5$  eV, dominates until ionization sets in, and progressively yields to dissociative ionization.
- Cross sections for positive ion-negative ion pair formation, and multiple ionization, are generally smaller than those for single ionization in the low-energy range of interest.

Similarly, a systematic review of the assessed data for all three perfluoroalkane molecules ( $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ ,  $\text{C}_3\text{F}_8$ ) reveals:

- large *direct* vibrational excitation cross sections at low energies, and very large *indirect* vibrational excitation cross sections in the energy regions of the negative ion resonances;
- maxima in the various cross sections at the location of negative ion states;
- variation of the cross sections with molecular polarizability (Table II);
- existence of a Ramsauer-Townsend (R-T) minimum in the total, elastic, and momentum scattering cross section and its dependence on the molecular polarizability (Table II); and
- dissociation of all electronic states into charged and/or neutral fragments (a property largely shared also by  $\text{CHF}_3$ ,  $\text{CCl}_2\text{F}_2$ , and  $\text{Cl}_2$ ).

TABLE II  
ELECTRON SCATTERING DATA FOR  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ , AND  $\text{C}_3\text{F}_8$

Physical Quantity	$\text{CF}_4$	$\text{C}_2\text{F}_6$	$\text{C}_3\text{F}_8$
Position of R-T minimum in eV (cross-section value at the minimum in $10^{-20} \text{ m}^2$ )	$\sigma_{\text{se,t}}(\epsilon)$ : 0.13(1.30)	<0.04 (<10.8)	<0.025 (<9.4)
	$\sigma_{\text{m}}(\epsilon)$ : 0.15(0.13)	0.15(0.32)	—
	$\sigma_{\text{e,int}}(\epsilon)$ : 0.18(0.55)	0.18(1.67)	—
Position of cross section maximum in eV (cross-section value at the maximum in units of $10^{-20} \text{ m}^2$ )	$\sigma_{\text{se,t}}(\epsilon)$ : <0.003 (>12.7)	~5.1(26.4)	9.0(38.7)
		9.0(21.8)	~9.1(28.6)
		~25(20.4)	>20 (>27.1)
	$\sigma_{\text{m}}(\epsilon)$ : <0.001 (>13.0)	<0.01 (>9.5)	~9.5(41.3)
		~20.0 (14.1)	~17.0 (22.7)
	$\sigma_{\text{e,int}}(\epsilon)$ : <0.003 (>12.7)	<0.01 (>12.2)	9.0(45.0)
		~20.0 (16.1)	~20.0(28.0)
Static polarizability ( $10^{-25} \text{ cm}^3$ ) <sup>d</sup>	$\sigma_{\text{diss,t}}(\epsilon)$ : ~120(5.6)	~120(8.6)	~120(11.8)
	$\sigma_{\text{i,t}}(\epsilon)$ : 120(5.7) <sup>a</sup>	~120 <sup>b</sup> (~8.0) <sup>b</sup>	~120 <sup>c</sup> (≥13.0) <sup>c</sup>
	$\sigma_{\text{da,t}}(\epsilon)$ : 6.9(0.016)	4.0(0.14)	2.9(0.15)
		46.0; 50.6; 65.0	64.7; 73.6; 94.0
	<31.9> <sup>e,f</sup>	<53.9>	<77.4>

<sup>a</sup> From revised data (Fig. 14, Section IV).

<sup>b</sup> Estimated from data presented in Fig. 12a of Christophorou and Olthoff (1998a).

<sup>c</sup> Estimated from data presented in Fig. 9 of Christophorou and Olthoff (1998b).

<sup>d</sup> From Beran and Kevan (1969).

<sup>e</sup> Average of three values.

<sup>f</sup> The average of two recent experimental values (Au *et al.*, 1997) for this molecule is  $28.3 \times 10^{-25} \text{ cm}^3$ .

*c. Determination of Data Needs, and New Related Measurements and Calculations.* The data assessment for each molecular species naturally identifies gaps in the database. In general, there are two types of data needs: (i) new data to replace existing data judged to be incorrect; and (ii) data that are needed, but are not available.

In connection with the first kind of data needs we give as an example the cross section for electron-impact dissociation of molecules into neutral fragments. At the time the  $\text{CF}_4$  review (Christophorou *et al.*, 1996) was performed, there was only one direct measurement (Nakano and Sugai, 1992; revised by Sugai *et al.*, 1995b) of the cross section for the production of  $\text{CF}_3$ ,  $\text{CF}_2$ , and  $\text{CF}$  radicals by electron impact on  $\text{CF}_4$ . The sum of the revised cross sections for the three radicals was determined (Christophorou *et al.*, 1996) as the recommended value of  $\sigma_{\text{diss,neut,t}}(\epsilon)$ . This previously determined cross section is plotted (short dashed curve) in Fig. 7. For comparison, the cross sections for total electron-impact dissociation  $\sigma_{\text{diss,t}}(\epsilon)$  (Winters and Inokuti, 1982) and ionization  $\sigma_{\text{i,t}}(\epsilon)$  are also plotted in the figure. An estimated value (dotted curve) of  $\sigma_{\text{diss,neut,t}}(\epsilon)$  deduced from  $\sigma_{\text{diss,t}}(\epsilon) - \sigma_{\text{i,t}}(\epsilon)$  for energies  $< 70$  eV [using the currently recommended values of  $\sigma_{\text{i,t}}(\epsilon)$  derived in Section IV], is also shown in Fig. 7. Clearly, the measurements of Sugai *et al.* (1995b) are inconsistent with the recommended values of  $\sigma_{\text{diss,t}}(\epsilon)$  and  $\sigma_{\text{i,t}}(\epsilon)$  by more than one order of magnitude. The need for more accurate measurements of the cross section for this important process led to new measurements by both Mi and Bonham (1998) and Motlagh and Moore (1998). The results of both of these groups are also shown in Fig. 7 and confirm the conclusions of the initial assessment, namely that the cross section from Sugai *et al.* (1995b) is much too small. The new suggested cross section  $\sigma_{\text{diss,neut,t}}(\epsilon)$  is shown in the figure by the solid line. The fairly large discrepancy remaining between the values of Motlagh and Moore and the values deduced from  $\sigma_{\text{diss,t}}(\epsilon) - \sigma_{\text{i,t}}(\epsilon)$  requires further investigation.

In connection with the second kind of data, we point to the situation with  $\text{CHF}_3$ , a gas used in place of  $\text{CF}_4$  because of its lower global warming potential. In this instance, when the review and assessment work was begun about 2 yr ago by Christophorou *et al.* (1997a), there were no measurements of electron scattering cross sections or electron transport coefficients. The cross section from Sugai *et al.* (1995b) for electron-impact dissociation into neutrals was judged to be incorrect, and there were no absolute cross-section measurements for dissociative electron attachment. Partly as a consequence of the discussions during the review and assessment process, measurements have since been made of the cross section for total electron scattering (Sanabia *et al.*, 1998; Sueoka *et al.*, 1998; Tanaka, 1998), dissociation into  $\text{CHF}_2$  and  $\text{CF}_3$  neutrals (Motlagh and Moore, 1998), elastic differential

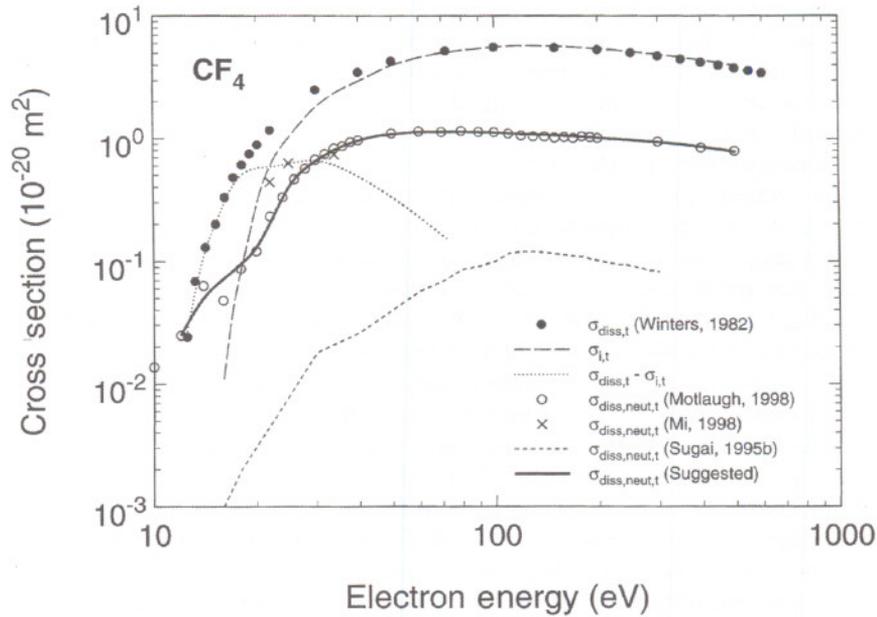


FIG. 7. Cross sections for electron-impact dissociation of  $\text{CF}_4$  into neutrals.

---,  $\sigma_{\text{diss,neut,t}}(\epsilon)$  (Sugai *et al.*, 1995b)

....,  $\sigma_{\text{diss,t}}(\epsilon) - \sigma_{\text{i,t}}(\epsilon)$

○,  $\sigma_{\text{diss,neut,t}}(\epsilon)$  (Motlaugh and Moore, 1998)

×,  $\sigma_{\text{diss,neut,t}}(\epsilon)$  (Mi and Bonham, 1998)

—, Suggested.

For comparison, the total dissociation cross section  $\sigma_{\text{diss,t}}(\epsilon)$  (●) (Winters and Inokuti, 1982) and the assessed  $\sigma_{\text{i,t}}(\epsilon)$  (---) are also plotted in the figure.

electron scattering cross section (Tanaka *et al.*, 1997; Tanaka, 1998), electron drift velocity (Wang *et al.*, 1998; Clark *et al.*, 1998), and electron attachment coefficient (Wang *et al.*, 1998; Clark *et al.*, 1998; Jarvis *et al.*, 1997). In addition, a study has been made of the ion chemistry in  $\text{CHF}_3$  using Fourier-transform mass spectrometry (Jiao *et al.*, 1997) in which it was reported that at 60 eV the total cross section for the production of  $\text{CHF}_2^+$ ,  $\text{CF}_3^+$ ,  $\text{CF}_2^+$ , and  $\text{CF}^+$  was measured to be  $(3.4 \pm 0.4) \times 10^{-16} \text{ cm}^2$ . Figure 8a shows the updated total electron scattering cross section  $\sigma_{\text{i,t}}(\epsilon)$  for  $\text{CHF}_3$  and Fig. 8b the recently measured electron drift velocities in pure  $\text{CHF}_3$  and in mixtures with argon. The small measured (Wang *et al.*, 1998) small electron attachment rate constant ( $\sim 13 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$  for  $E/N \lesssim 50 \times 10^{-17} \text{ V cm}^2$ ) is thought to be due to traces of electronegative impurities.

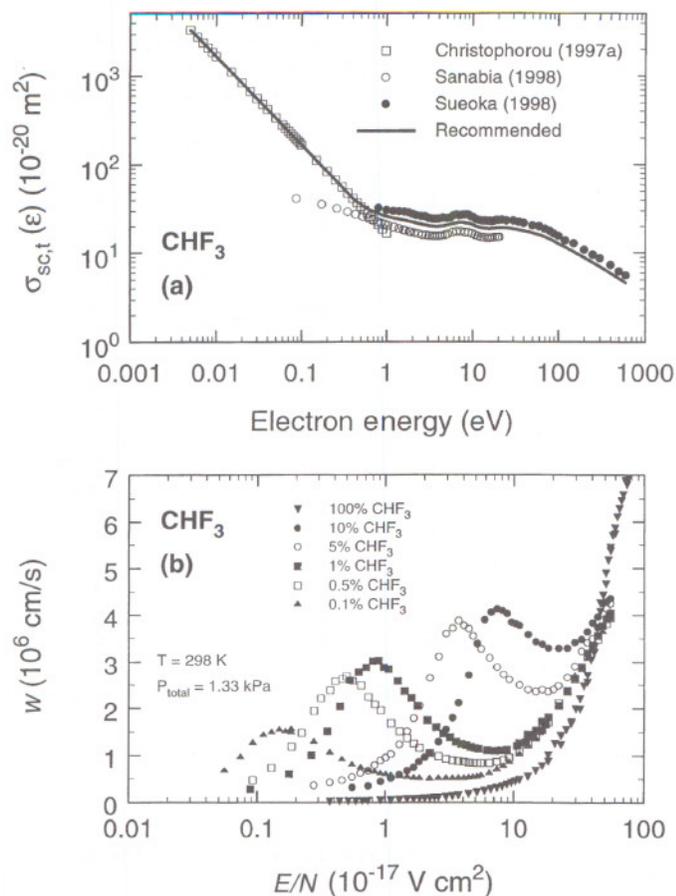


FIG. 8. (a) Updated total electron scattering cross section  $\sigma_{sc,t}(\epsilon)$  for CHF<sub>3</sub>.

□,  $\sigma_{sc,t}(\epsilon)$  [calculation, Christophorou *et al.*, 1997a]

○,  $\sigma_{sc,t}(\epsilon)$  [measurement, Sanabia *et al.*, 1998]

●,  $\sigma_{sc,t}(\epsilon)$  [measurement, Sueoka *et al.*, 1998]

—, Recommended.

(b) Electron drift velocity  $w$  as a function of  $E/N$  for CHF<sub>3</sub> and mixtures of CHF<sub>3</sub> with Ar (from Wang *et al.*, 1998).

In terms of determining remaining data needs, it is useful to review the state of our knowledge regarding electron-collision data for the six gases we have considered so far. This is summarized in Table III. In general, our knowledge is the best for CF<sub>4</sub> and the worst for CHF<sub>3</sub>. With the sole exception of CF<sub>4</sub>, the database for the other five gases needs much

TABLE III  
THE STATE OF CURRENT KNOWLEDGE ON ELECTRON-COLLISION DATA FOR  
CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, C<sub>3</sub>F<sub>8</sub>, CHF<sub>3</sub>, CCl<sub>2</sub>F<sub>2</sub>, AND Cl<sub>2</sub>

Cross Section/ Coefficient	CF <sub>4</sub>	C <sub>2</sub> F <sub>6</sub>	C <sub>3</sub> F <sub>8</sub>	CHF <sub>3</sub>	CCl <sub>2</sub> F <sub>2</sub>	Cl <sub>2</sub>
$\sigma_{sc,t}(\epsilon)$	R <sup>a</sup>	R	R	R	R	R
$\sigma_m(\epsilon)$	R	S <sup>b</sup>	S	None	C <sup>c</sup>	C
$\sigma_{e,diff}(\epsilon)$	M <sup>d</sup> /C	M/C	M	None	M/C	None
$\sigma_{e,int}(\epsilon)$	R	S	S	None	S	S
$\sigma_{vib,indir,t}(\epsilon)$	R/D <sup>e</sup>	None	None	None	D	D
$\sigma_{vib,dir,t}(\epsilon)$	R	C	None	None	R	None
$\sigma_{i,t}(\epsilon)$	R	S	R	S	S	S
$\sigma_{i,part}(\epsilon)$	M	M	M	M	M	None
$\sigma_{ip}(\epsilon)$	M	None	None	None	None	S
$\sigma_{i,mult}(\epsilon)$	M	None	None	None	M	None
$\sigma_{diss,t}(\epsilon)$	R	R	R	R	None	None
$\sigma_{diss,neut,t}(\epsilon)$	S	None	None	M	None	S
$\sigma_{a,t}(\epsilon)$	R	R	R	None	S	S
$\alpha/N(E/N)$	R	R	R	None	R	S
$\eta/N(E/N)$	R	R	R	None	R	S
$(\alpha - \eta)/N(E/N)$	R	R	R <sup>f</sup>	None	R	S
$k_{a,t}(\langle \epsilon \rangle)$	R	R	R	None	R	S
$w(E/N)$	R	R	R	S	S	M
$D_T/\mu(E/N)$	R	R	S	None	S	M

<sup>a</sup>R = Recommended.

<sup>b</sup>S = Suggested.

<sup>c</sup>C = Calculated.

<sup>d</sup>M = Measured.

<sup>e</sup>D = Deduced.

<sup>f</sup>Deduced in this work from the recommended values of  $\alpha/N(E/N)$  and the density-independent values of  $\eta/N(E/N)$ .

improvement. The cross sections for total electron scattering, elastic integral, total ionization, total dissociation, and total electron attachment are better known than the cross sections for momentum transfer, vibrational excitation, partial ionization, multiple ionization, ion-pair formation, and dissociation into neutrals. Existing data for electron transport and electron attachment and ionization rate coefficients are reliably known for CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, and C<sub>3</sub>F<sub>8</sub>, and to some degree also for CCl<sub>2</sub>F<sub>2</sub>. However, such knowledge is meager for Cl<sub>2</sub> and CHF<sub>3</sub>. For some of the molecules, the coefficients, although accurately known in a restricted  $E/N$  range, are not known or are poorly known in other or wider  $E/N$  ranges.

### C. DISSEMINATION AND UPDATING OF THE DATABASE

For the review and assessment process being performed at NIST, the end product is a comprehensive article for each gas published in the *Journal of Physical and Chemical Reference Data*. These critical reviews contain our best effort to provide a complete, yet concise, review of data relevant to electron collision cross sections for these gases.

A much briefer summary of relevant data, containing primarily the recommended and suggested cross-section data and coefficients for the plasma processing gases studied, is also available on the Worldwide Web at <http://www.eeel.nist.gov/811/refdata>. These data are updated as new measurements become available (Christophorou and Olthoff, 1999b).

## IV. Assessed Cross Sections and Coefficients

A complete assessment of data for all electron collision processes for a single gas is useful in many instances—for example, to the industry using the gas or to the modeler performing calculations on a system containing the gas—and this is the approach used in the articles resulting from our assessment process. However, the complementary approach, namely, of following the variation of the cross section for each particular electron-collision process for all gases and highlighting its dependence on molecular physical properties is also productive. It allows for the possible understanding of the physics of the collision processes themselves, from which deductions and generalizations can be inferred that can be used to deduce knowledge on collision processes for which no data exist. Thus, in this subsection we follow the latter approach and present in graphical form the recommended or suggested cross sections and coefficients for the following gases,  $\text{CF}_4$  (Christophorou *et al.*, 1996),  $\text{C}_2\text{F}_6$  (Christophorou and Olthoff, 1998a),  $\text{C}_3\text{F}_8$  (Christophorou and Olthoff, 1998b),  $\text{CHF}_3$  (Christophorou *et al.*, 1997a),  $\text{CCl}_2\text{F}_2$  (Christophorou *et al.* 1997b), and  $\text{Cl}_2$  (Christophorou and Olthoff, 1999a) (see the respective references for details and more data, and also the summary in Table III). In both subsequent sections and Figs. 9–21, all quoted assessed data are as discussed in the respective references just mentioned, and no further reference will be made to these articles. When, however, assessed cross sections are reported that incorporated new or revised data, full citation of these sources is made.

*a. Total Electron Scattering Cross Section  $\sigma_{\text{sc},t}(\epsilon)$ .* Figure 9a presents the recommended values of the total electron scattering cross section  $\sigma_{\text{sc},t}(\epsilon)$ , for  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ , and  $\text{C}_3\text{F}_8$ , and Fig. 9b gives the recommended values of  $\sigma_{\text{sc},t}(\epsilon)$

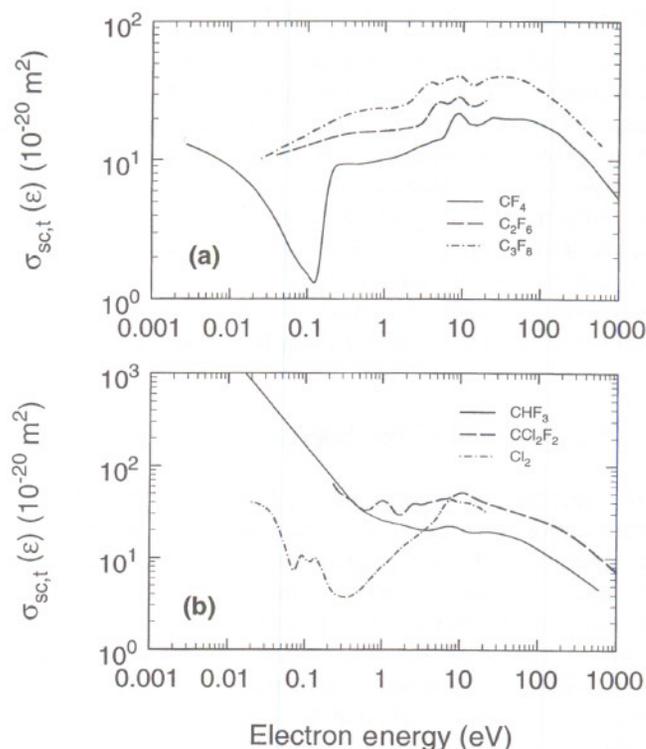


FIG. 9. Total electron scattering cross sections  $\sigma_{sc,t}(\epsilon)$ . (a) Recommended data for  $\text{CF}_4$  (—),  $\text{C}_2\text{F}_6$  (---), and  $\text{C}_3\text{F}_8$  (-.-) [as revised in this work (see text)]. (b) Recommended data for  $\text{CCl}_2\text{F}_2$  (---),  $\text{CHF}_3$  (—) [as revised in this work (see text)], and  $\text{Cl}_2$  (-.-).

for  $\text{CCl}_2\text{F}_2$ ,  $\text{CHF}_3$ , and  $\text{Cl}_2$ . The recommended cross section of Christophorou and Olthoff (1998b) for  $\text{C}_3\text{F}_8$  has been revised in this work to include the recent measurements of Tanaka *et al.* (1999). Similarly, the cross section for  $\text{CHF}_3$  of Christophorou *et al.* (1997a) has been revised in this work in view of the recent measurements discussed in the previous section (see Fig. 8a). It is interesting to note the deep Ramsauer-Townsend (R-T) minimum exhibited by the  $\sigma_{sc,t}(\epsilon)$  of  $\text{CF}_4$ . Such a minimum is expected in the  $\sigma_{sc,t}(\epsilon)$  of  $\text{C}_2\text{F}_6$  and  $\text{C}_3\text{F}_8$ , but the direct electron transmission measurements are unable to locate it possibly because of poor energy resolution in this low energy range. A new, direct, high-resolution measurement of  $\sigma_{sc,t}(\epsilon)$  has been made for  $\text{Cl}_2$  (Gulley *et al.*, 1998), which resolves such a low-lying minimum for this gas. Similar high-resolution

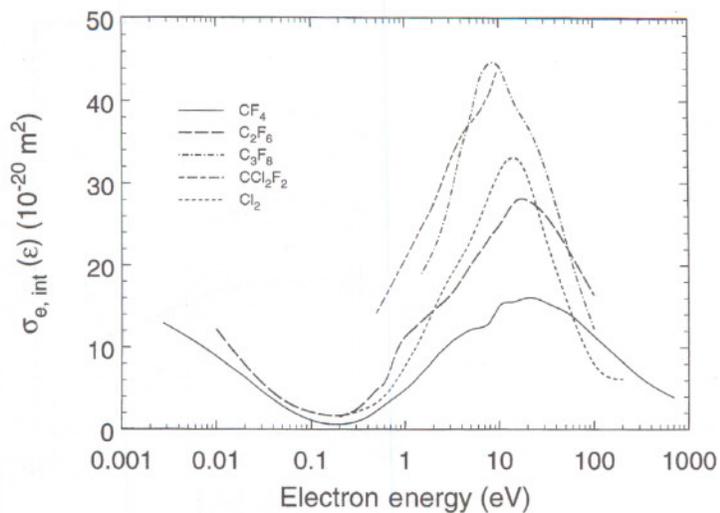


FIG. 10. Elastic integral electron scattering cross sections  $\sigma_{e,int}(\epsilon)$ . Recommended data for  $\text{CF}_4$  (—); suggested data for  $\text{C}_2\text{F}_6$  (---),  $\text{C}_3\text{F}_8$  (-.-) (Christophorou and Olthoff, 1998b; Tanaka *et al.*, 1999),  $\text{CCl}_2\text{F}_2$  (-.-) (Christophorou *et al.*, 1997b; Mann and Linder, 1992), and  $\text{Cl}_2$  (-). For  $\text{Cl}_2$  the cross section plotted is the total elastic  $\sigma_{e,t}(\epsilon)$ .

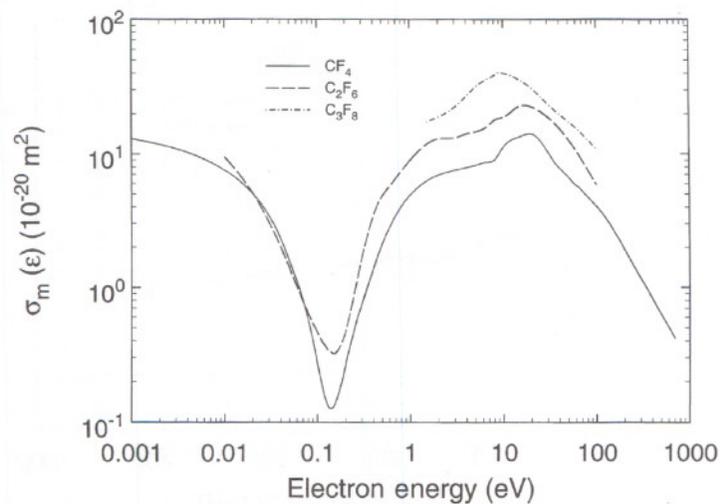


FIG. 11. Momentum transfer cross sections  $\sigma_m(\epsilon)$ . Recommended data for  $\text{CF}_4$  (—); suggested data for  $\text{C}_2\text{F}_6$  (---) and  $\text{C}_3\text{F}_8$  (-.-).

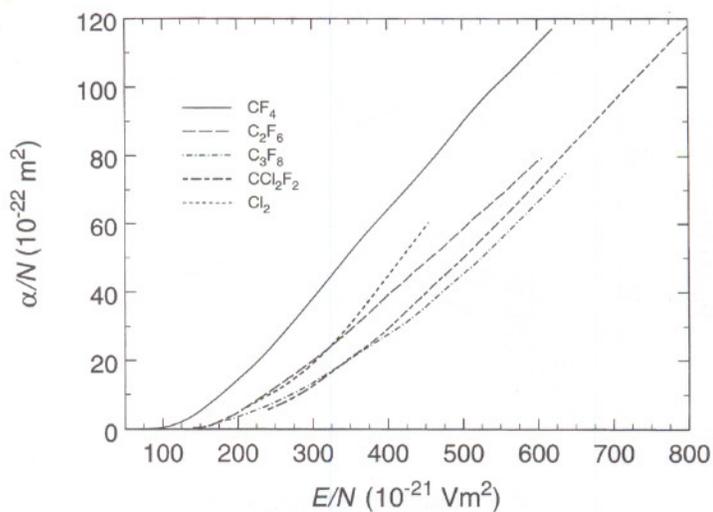


FIG. 16. Density-reduced electron-impact ionization coefficient,  $\alpha/N(E/N)$  ( $T \approx 300$  K). Recommended data for  $\text{CF}_4$  (—),  $\text{C}_2\text{F}_6$  (---),  $\text{C}_3\text{F}_8$  (-·-), and  $\text{CCl}_2\text{F}_2$  (-·-·); suggested data for  $\text{Cl}_2$  (···).

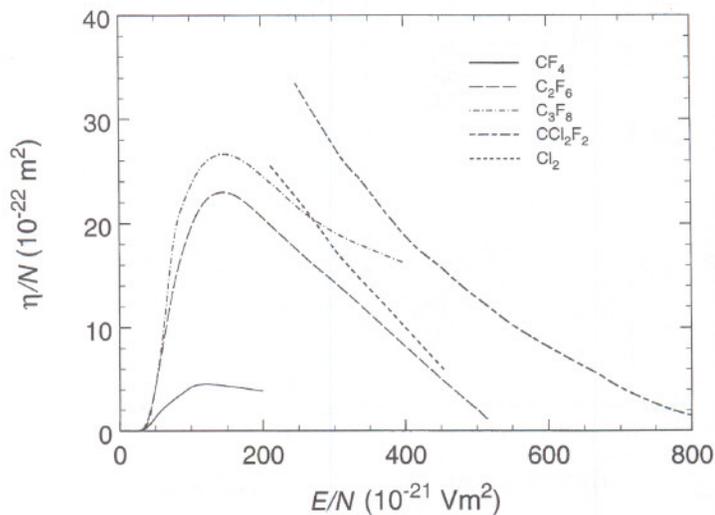


FIG. 17. Density-reduced electron attachment coefficient  $\eta/N(E/N)$  ( $T \approx 300$  K). Recommended data for  $\text{CF}_4$  (—),  $\text{C}_2\text{F}_6$  (---),  $\text{C}_3\text{F}_8$  (-·-), and  $\text{CCl}_2\text{F}_2$  (-·-·); suggested data for  $\text{Cl}_2$  (···). The  $\eta/N(E/N)$  for  $\text{C}_3\text{F}_8$  are the density-independent data of Hunter *et al.* (1987).

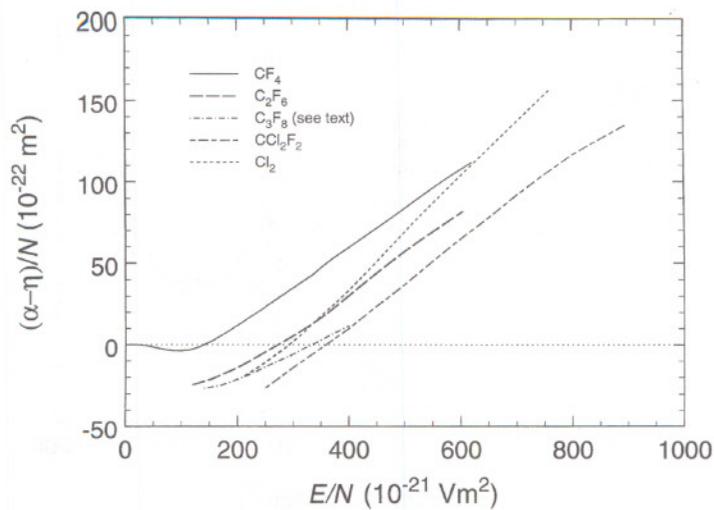


FIG. 18. Density-reduced effective ionization coefficient  $(\alpha - \eta)/N(E/N)$  ( $T \approx 300 \text{ K}$ ). Recommended data for  $\text{CF}_4$  (—),  $\text{C}_2\text{F}_6$  (— —),  $\text{C}_3\text{F}_8$  (-.-), and  $\text{CCl}_2\text{F}_2$  (-.-.); suggested data for  $\text{Cl}_2$  (---).

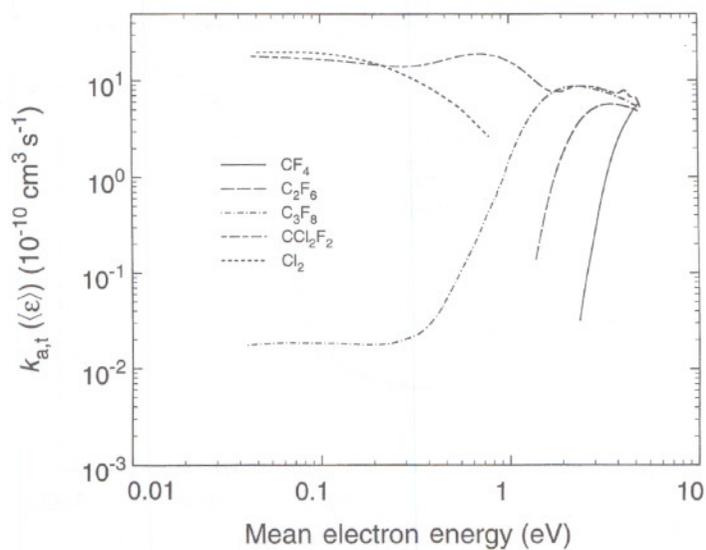


FIG. 19. Total electron attachment rate constant  $k_{a,t}(\langle \epsilon \rangle)$  ( $T = \sim 300 \text{ K}$ ). Recommended data for  $\text{CF}_4$  (—),  $\text{C}_2\text{F}_6$  (— —),  $\text{C}_3\text{F}_8$  (-.-), and  $\text{CCl}_2\text{F}_2$  (-.-.); suggested data for  $\text{Cl}_2$  (---).

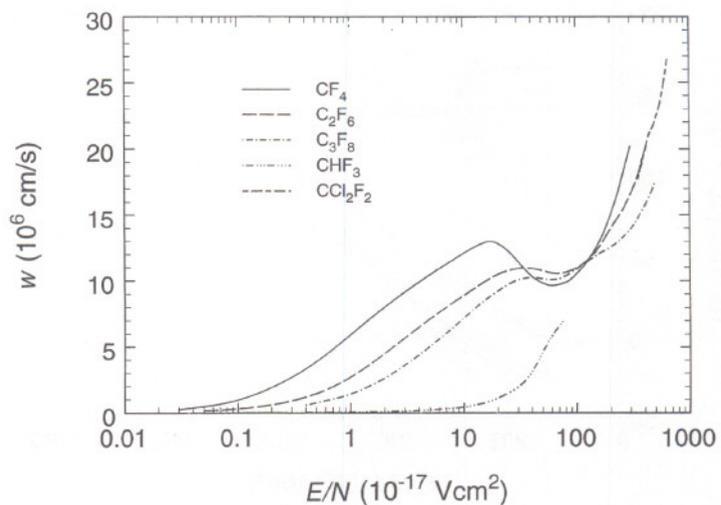


FIG. 20. Electron drift velocity  $w(E/N)$  ( $T = \sim 300$  K). Recommended data for  $\text{CF}_4$  (—),  $\text{C}_2\text{F}_6$  (---), and  $\text{C}_3\text{F}_8$  (-.-.); suggested data for  $\text{CCl}_2\text{F}_2$  (— —) and  $\text{CHF}_3$  (-...-...) (data of Wang *et al.*, 1998).

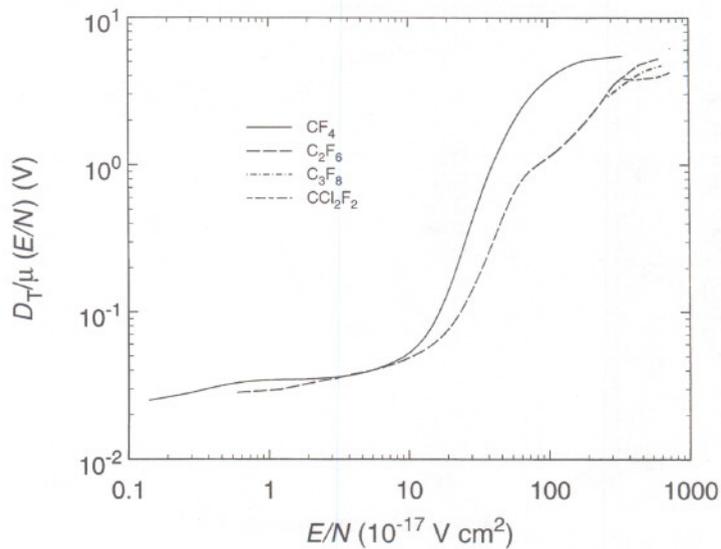


FIG. 21.  $D_T/\mu(E/N)$  ( $T = \sim 300$  K). Recommended data for  $\text{CF}_4$  (—) and  $\text{C}_2\text{F}_6$  (---); suggested data for  $\text{C}_3\text{F}_8$  (-.-.), and  $\text{CCl}_2\text{F}_2$  (- - -).

measurements for the other molecules discussed here would be useful in this regard.

The  $\sigma_{\text{sc,t}}(\epsilon)$  of  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ , and  $\text{C}_3\text{F}_8$  increase with increasing molecular dipole polarizability (Table II). It is also interesting to observe the large increase in the  $\sigma_{\text{sc,t}}(\epsilon)$  of  $\text{CHF}_3$  as the electron energy is decreased below 1 eV (Fig. 9b). This is due to the large ( $5.504 \times 10^{-30} \text{ C m} = 1.65 \text{ D}$ ) (McClellan, 1963) permanent electric dipole moment of this molecule. Similar behavior is to be expected for other polar gases (Christophorou, 1971).

*b. Elastic Integral Electron Scattering Cross Section  $\sigma_{\text{e,int}}(\epsilon)$ .* Figure 10 presents the recommended values of the elastic integral electron scattering cross section  $\sigma_{\text{e,int}}(\epsilon)$  for  $\text{CF}_4$ , and suggested data for  $\text{C}_2\text{F}_6$ ,  $\text{C}_3\text{F}_8$  (Christophorou and Olthoff, 1998b; Tanaka, 1998; Tanaka *et al.*, 1999),  $\text{CCl}_2\text{F}_2$  (Christophorou *et al.*, 1997b; Mann and Linder, 1992), and  $\text{Cl}_2$ . The R-T minimum is clearly evident in the  $\sigma_{\text{e,int}}(\epsilon)$  of both  $\text{CF}_4$  and  $\text{C}_2\text{F}_6$  and is located at about the same energy (see Table II).

*c. Momentum Transfer Cross Section  $\sigma_{\text{m}}(\epsilon)$ .* Figure 11 presents the recommended values of the momentum transfer cross section  $\sigma_{\text{m}}(\epsilon)$ , for  $\text{CF}_4$ , and suggested data for  $\text{C}_2\text{F}_6$  and  $\text{C}_3\text{F}_8$ . The cross section  $\sigma_{\text{m}}(\epsilon)$  of both  $\text{CF}_4$  and  $\text{C}_2\text{F}_6$  exhibits—as does the cross section  $\sigma_{\text{e,int}}(\epsilon)$  of both molecules—a pronounced R-T minimum located at roughly the same energy (see Table II). A similar minimum is expected for  $\text{C}_3\text{F}_8$ .

*d. Total Dissociation Cross Section  $\sigma_{\text{diss,t}}(\epsilon)$ .* Figure 12 presents the values of the total dissociation cross section  $\sigma_{\text{diss,t}}(\epsilon)$  for  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ ,  $\text{C}_3\text{F}_8$ , and  $\text{CHF}_3$ . These are measurements made by Winters and Inokuti (1982) and they are the only data available at this time. The cross section  $\sigma_{\text{diss,t}}(\epsilon)$  for  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ ,  $\text{C}_3\text{F}_8$  increases with increasing molecular dipole polarizability.

*e. Total Cross Section for Dissociation into Neutrals  $\sigma_{\text{diss,neut,t}}(\epsilon)$ .* Figure 13 shows the suggested total cross sections for electron-impact dissociation into neutrals for  $\text{CF}_4$  (from Fig. 7) and  $\text{Cl}_2$  (Cosby and Helm, 1992; Cosby, 1998). It is interesting to note the profound difference in the energy dependence of  $\sigma_{\text{diss,neut,t}}(\epsilon)$  for the two molecules. The  $\sigma_{\text{diss,neut,t}}(\epsilon)$  for  $\text{Cl}_2$  is accounted for by considering the excitation of the  $\text{Cl}_2$  molecule to its lowest five excited electronic states ( $^3\Pi_{\text{u}}$ ,  $^1\Pi_{\text{u}}$ ,  $^3\Pi_{\text{g}}$ ,  $^1\Pi_{\text{g}}$ ,  $^3\Sigma_{\text{u}}^+$ ) (Rescigno, 1994; Christophorou and Olthoff, 1999a). This would indicate that higher electronic states of the  $\text{Cl}_2$  molecule preionize with high efficiency, a conclusion consistent with the observed preponderance of  $\text{Cl}_2^+$  compared to  $\text{Cl}^+$  in electron collisions with the  $\text{Cl}_2$  molecule. In contrast, the cross section  $\sigma_{\text{diss,neut,t}}(\epsilon)$  of  $\text{CF}_4$  indicates that for this molecule dissociation into neutrals and dissociative ionization are competitive processes to high energies [ $\text{CF}_4^+$  is rarely formed for the  $\text{CF}_4$  molecule (Christophorou *et al.*, 1996)].

f. *Total Ionization Cross Section*  $\sigma_{i,t}(\epsilon)$ . Figure 14 presents the recommended values of the total ionization cross section  $\sigma_{i,t}(\epsilon)$ , for  $\text{CF}_4$ , and suggested data for  $\text{C}_2\text{F}_6$ ,  $\text{C}_3\text{F}_8$ ,  $\text{CHF}_3$ ,  $\text{CCl}_2\text{F}_2$ , and  $\text{Cl}_2$ . The recommended data for  $\text{CF}_4$  in Fig. 14 are based on the cross sections discussed in Christophorou *et al.* (1996) and two new sets of measurements (Rao and Srivastava, 1997; Nishimura *et al.*, 1999) that have appeared since.

g. *Total Electron Attachment Cross Section*  $\sigma_{a,t}(\epsilon)$ . Figure 15a,b gives the recommended values of the total electron attachment cross section  $\sigma_{a,t}(\epsilon)$  for  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ , and  $\text{C}_3\text{F}_8$ , and suggested data for  $\text{CCl}_2\text{F}_2$ , and  $\text{Cl}_2$ . These data are for  $T \approx 300$  K. It is important to specify the temperature at which the electron attachment cross sections have been measured, since both dissociative and nondissociative electron attachment processes are often strong functions of gas temperature (Christophorou, 1991; Christophorou *et al.*, 1994). With the exception of  $\text{C}_3\text{F}_8$  for which there is some evidence for parent anion formation in addition to dissociative attachment, for the rest of these molecules all electron attachment processes are dissociative. It is interesting to note (Fig. 15a) the progressive increase in the magnitude and the progressive shift to lower energy of the  $\sigma_{a,t}(\epsilon)$  of the three perfluoroalkane molecules. It is also interesting to note the increase in both the attachment cross section and the number of negative ion states of the chlorine-containing molecules compared to the perfluoroalkane molecules. For  $\text{CCl}_2\text{F}_2$ , negative ions (mostly  $\text{Cl}^-$ ) are produced via a number of negative ion states  $\lesssim 6$  eV (Christophorou *et al.*, 1997a), and for  $\text{Cl}_2$ ,  $\text{Cl}^-$  negative ions are produced at  $\sim 0$ , 2.5 eV, and 5.5 eV (Christophorou and Olthoff, 1999a). These negative ion states are also responsible for the peaks in the total electron scattering cross section around these energies.

h. *Density-Reduced Electron-Impact Ionization Coefficient*  $\alpha/N(E/N)$ . Figure 16 presents the recommended values of the density-reduced electron-impact ionization coefficient,  $\alpha/N(E/N)$  for  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ ,  $\text{C}_3\text{F}_8$ , and  $\text{CCl}_2\text{F}_2$ , and suggested data for  $\text{Cl}_2$ . These data are for temperatures of  $\sim 300$  K. The  $\alpha/N(E/N)$  for  $\text{CF}_4$  was extended here to higher  $E/N$  than in the earlier study by Christophorou *et al.* (1996).

i. *Density-Reduced Electron Attachment Coefficient*  $\eta/N(E/N)$ . Figure 17 shows the assessed values of the density-reduced electron attachment coefficient,  $\eta/N(E/N)$ : recommended data for  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ ,  $\text{C}_3\text{F}_8$ , and  $\text{CCl}_2\text{F}_2$ , and suggested data for  $\text{Cl}_2$ . These data are for temperatures of  $\sim 300$  K. The  $\eta/N$  used for  $\text{C}_3\text{F}_8$  are the density-independent values (Hunter *et al.*, 1987) because for this gas,  $\eta/N$  varies with gas pressure.

*j. Density-Reduced Effective Ionization Coefficient  $(\alpha - \eta)/N(E/N)$ .* Figure 18 presents the recommended values of the density-reduced electron-impact effective ionization coefficient,  $(\alpha - \eta)/N(E/N)$  for  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ ,  $\text{C}_3\text{F}_8$ , and  $\text{CCl}_2\text{F}_2$ , and suggested data for  $\text{Cl}_2$ . The recommended coefficient for  $\text{C}_3\text{F}_8$  was determined in this work using the recommended values of  $\alpha/N(E/N)$  in Christophorou and Olthoff (1998b) and the density-independent values of  $\eta/N(E/N)$  given by Hunter *et al.* (1987). Note the progressive increase in the value of  $E/N$  at which  $(\alpha - \eta)/N = 0$  with increasing electron attachment for the perfluoroalkanes.

*k. Total Electron Attachment Rate Constant  $k_{a,t}(\langle\varepsilon\rangle)$ .* Figure 19 presents the recommended values of the total electron attachment rate constant  $k_{a,t}(\langle\varepsilon\rangle)$  ( $T \approx 300$  K) for  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ ,  $\text{C}_3\text{F}_8$ , and  $\text{CCl}_2\text{F}_2$ , and suggested data for  $\text{Cl}_2$ . The larger electron attachment cross sections for the chlorine-containing gases ( $\text{CCl}_2\text{F}_2$  and  $\text{Cl}_2$ ) are clearly evident.

*l. Electron Drift Velocity  $w(E/N)$ .* Figure 20 shows the recommended values of the electron drift velocity  $w(E/N)$  ( $T \approx 300$  K) for  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ , and suggested data for  $\text{C}_3\text{F}_8$ ,  $\text{CCl}_2\text{F}_2$ , and  $\text{CHF}_3$ . The data for  $\text{CHF}_3$  are recent measurements by Wang *et al.* (1998). It is interesting to observe the reduction in the negative differential conductivity as the size of the perfluorocarbon molecule is increased. It is also interesting to observe the profound differences in  $w(E/N)$  between  $\text{CF}_4$  and  $\text{CHF}_3$  due to the large permanent electric dipole moment of the latter.

*m. Ratio of Lateral Electron Diffusion Coefficient to Electron Mobility  $D_T/\mu(E/N)$ .* Figure 21 shows the recommended values of  $D_T/\mu(E/N)$  ( $T \approx 300$  K) for  $\text{CF}_4$  and  $\text{C}_2\text{F}_6$ , and suggested data for  $\text{C}_3\text{F}_8$  and  $\text{CCl}_2\text{F}_2$ . Further measurements of this quantity are indicated.

## V. Boltzmann-Code-Generated Collision Cross-Section Sets

Boltzmann and Monte Carlo codes have provided useful information on electron collision cross sections for a number of gases including those discussed in this chapter. For instance, in the past decade, a number of cross-section sets for electron interactions with  $\text{CF}_4$  have been derived that are based upon Boltzmann modeling of electron swarm parameters (Hayashi, 1987; Nakamura, 1991; Bordage *et al.*, 1996; Hayashi and Nakamura, 1998; Bordage *et al.*, 1999). In these investigations a cross-section set is assumed, which is modified iteratively until the electron-transport parameters calculated using the Boltzmann equation best agree with their measured values. Such calculations rely heavily on electron swarm transport

coefficients measured over wide ranges of  $E/N$ , and on knowledge of collision cross sections from other sources used as input to the procedure. A serious difficulty of this procedure is that the derived electron-interaction cross section set is not a unique solution, and if little is known about the cross sections for the molecule under study, the Boltzmann-code-generated cross sections for individual processes may be physically unrealistic [see, for instance, in Fig. 1 the most recent values of  $\sigma_m(\varepsilon)$  calculated this way by Bordage *et al.* (1996)], or, in some cases, fictitious [e.g., the cross section for electronic excitation by Hayashi and Nakamura (1998)].

A solution to this problem is to use as inputs to such calculations the assessed data on electron-impact cross sections, to consider them as essentially invariant (within experimental uncertainties) in the iterative process, and to use the assessed electron transport coefficients as a reliable reference for their computed values. In this way, these codes can serve as a means of computing cross sections and coefficients that are not available, and/or as a means of checking the validity of questionable data.

The assessed cross sections for  $\text{CF}_4$  have indeed been used in such a manner by Bordage *et al.* (1999). That is, the assessed cross sections and coefficients for  $\text{CF}_4$  were used without modification using the solution of the Boltzmann equation under the hydrodynamic regime (Bordage *et al.*, 1996). It was found that the agreement between the calculated and the measured values of the swarm parameters was good for the drift velocity in  $\text{CF}_4$  and in its mixtures with Ar, for the transverse diffusion coefficient in  $\text{CF}_4$ , for the longitudinal coefficient in  $\text{CF}_4$  and in its mixtures with Ar, and for the attachment coefficient in  $\text{CF}_4$ . This rather satisfying agreement between the measured and the calculated electron-transport parameters using the independently assessed cross sections validates both the cross sections and the model, and removes the usual arbitrariness and lack of uniqueness that are often characteristic of cross-section sets derived from Boltzmann analyses. The agreement was, however, not as good for the ionization coefficient at low  $E/N$  values.

Analysis of the input of the different cross sections on the output of the code enables reasonable conjectures of possible reasons for the lack of agreement between the calculated and the measured values of the ionization coefficient at low  $E/N$ . For instance, it was found that the magnitude of the cross section for indirect vibrational excitation and the associated energy loss influence the calculated coefficient significantly as do also the energy thresholds for the various inelastic processes and the angular distributions of the elastically and inelastically scattered electrons. Clearly, this indicates the effect of such processes on the high-energy tail of the electron energy distribution function on which the low  $E/N$  values of the ionization coefficient critically depend. In addition, such calculations, by relying on

invariant inputs of assessed cross sections, can be employed to assess the effects of excited molecules, as well as the validity of methods used to extrapolate differential scattering cross sections to  $0^\circ$  and to  $180^\circ$  scattering angles from measurements in restricted ranges of electron scattering angles.

## VI. Conclusions

At this time a reasonably complete set of electron collision cross sections and coefficients exists only for  $\text{CF}_4$ . The assessed knowledge for this prototype of many plasma processing gases can serve as a benchmark for experimental, theoretical, and model-calculation studies. All the other gases assessed and discussed in this chapter have significant gaps in the known cross sections and coefficients. Data needs for electron interactions with plasma processing gases vary from gas to gas, as can be seen from Table III. Two nearly universal needs for these and other plasma processing gases are experimentally derived cross sections for vibrational excitation and for dissociation into neutrals. Both of these processes play a critical role in industrial plasmas and a minimal amount of data are currently available for  $\text{CF}_4$ , with virtually no data available for the other gases. To these needs must be added the need for electron-impact electronic excitation cross sections and differential elastic and inelastic cross sections. In connection with angular distribution measurements, there is a need for differential cross sections at small ( $\rightarrow 0^\circ$ ) and large ( $\rightarrow 180^\circ$ ) scattering angles. While such measurements have not been possible to perform in the past, two new recent techniques (Read and Channing, 1996; Zubek *et al.*, 1996; Trantham *et al.*, 1997) may allow such measurements over the entire scattering-angle range from near  $0^\circ$ – $180^\circ$ .

There are still some electron-collision cross sections that are nearly universally needed for all cases. Foremost among these are electron collision cross sections for radicals and excited species commonly produced in industrial plasmas. Electron-impact ionization cross sections have been measured for only some radicals produced in  $\text{CF}_4$  plasmas (Tarnovsky *et al.*, 1993).

Boltzmann-code analyses require accurate transport coefficients over wide energy ranges, angular distribution measurements that extend to  $0^\circ$  and to  $180^\circ$  scattering angles, and energy losses assigned to each particular electron-collision process. These analyses require assessed data as "invariant" inputs, and knowledge of electron scattering from and electron attachment to excited species. The effects of such processes on the electron energy distribution functions in plasmas need to be considered.

## VII. References

- Au, J. W., Burton, G. R., and Brion, C. E. (1997). *Chem. Phys.* 221: 151.
- Beran, J. A. and Kevan, L. (1969). *J. Phys. Chem.* 73: 3860.
- Boesten, L., Tanaka, H., Kobayashi, A., Dillon, M. A., and Kimura, M. (1992). *J. Phys. B* 25: 1607.
- Bonham, R. A. (1994). *Jpn. J. Appl. Phys.* 33: 4157.
- Bordage, M.-C., Ségur, P., and Chouki, A. (1996). *J. Appl. Phys.* 80: 1325.
- Bordage, M.-C., Ségur, P., Christophorou, L. G., and Olthoff, J. K. (1999). *J. Appl. Phys.* 86: 3558.
- Bukowski, J. D., Graves, D. B., and Vitello, P. (1996). *J. Appl. Phys.* 80: 2614.
- Chantry, P. J. (1982). in *Applied Atomic Collision Physics*, vol. 3, *Gas Lasers* (H. S. W. Massey, E. W. McDaniel, and B. Bederson, eds., New York: Academic Press, p. 35.
- Christophorou, L. G. (1991). in *Invited Papers, Proc. XXth Intern. Conf. on Ionization Phenomena in Gases*, V. Palleschi, D. P. Singh, and M. Vaselli, eds., Pisa, Italy: Institute of Atomic and Molecular Physics, CNR, July 8–12, 1991, p. 3.
- Christophorou, L. G. (1971). *Atomic and Molecular Radiation Physics*, New York: Wiley-Interscience, Ch. 4.
- Christophorou, L. G., McCorkle, D. L., and Christodoulides, A. A. (1984). in *Electron-Molecule Interactions and Their Applications*, L. G. Christophorou, ed., New York: Academic Press, vol. 1, Ch. 6.
- Christophorou, L. G. and Olthoff, J. K. (1998a). *J. Phys. Chem. Ref. Data* 27: 1.
- Christophorou, L. G. and Olthoff, J. K. (1998b). *J. Phys. Chem. Ref. Data* 27: 889.
- Christophorou, L. G. and Olthoff, J. K. (1999a). *J. Phys. Chem. Ref. Data* 28: 131.
- Christophorou, L. G. and Olthoff, J. K. (1999b). *J. Phys. Chem. Ref. Data* 28: 967.
- Christophorou, L. G. and Olthoff, J. K. (2000). Electron interactions with excited atoms and molecules, in *Advances in Atomic, Molecular, and Optical Physics*, B. Bederson and H. Walther, eds., Boston: Academic Press, vol. 44, p. 155.
- Christophorou, L. G., Olthoff, J. K., and Rao, M. V. V. S. (1996). *J. Phys. Chem. Ref. Data* 25: 1341.
- Christophorou, L. G., Olthoff, J. K., and Rao, M. V. V. S. (1997a). *J. Phys. Chem. Ref. Data* 26: 1.
- Christophorou, L. G., Olthoff, J. K., and Wang, Y. (1997b). *J. Phys. Chem. Ref. Data* 26: 1205.
- Christophorou, L. G., Pinnaduwa, L. A., and Datskos, P. G. (1994). in *Linking the Gaseous and the Condensed Phases of Matter, the Behavior of Slow Electrons*, L. G. Christophorou, E. Illenberger, and W. F. Schmidt, eds., New York: Plenum Press, p. 415.
- Clark, J. D., Wright, B. W., Wrbanek, J. D., and Garscadden, A. (1998). in *Gaseous Dielectrics VIII*, L. G. Christophorou, and J. K. Olthoff, eds., New York: Plenum Press, p. 23.
- Cosby, P. C. (1998). Private communication.
- Cosby, P. C. and Helm, H. (1992). *Wright Laboratory Report No. WL-TR-93-2004*, Wright Patterson AFB, OH 45433-7650.
- Csanak, G., Cartwright, D. C., Srivastava, S. K., and Trajmar, S. (1984). in *Electron-Molecule Interactions and Their Applications*, L. G. Christophorou, ed., New York: Academic Press, vol. 1, Ch. 1.
- Curtis, M. G., Walker, I. C., and Mathieson, K. J. (1988). *J. Phys. D* 21: 1271.
- Gulley, R. J., Field, T. A., Steer, W. A., Mason, N. J., Lunt, S. L., Siesel, J.-P., and Field, D. (1998). *J. Phys. B* 31: 2971.
- Hayashi, M. (1987). in *Swarm Studies and Inelastic Electron-Molecule Collisions*, L. C. Pitchford, B. V. McKoy, A. Chutjian, and S. Trajmar, eds., New York: Springer, p. 167.

- Hayashi, Y. and Nakamura, Y. (1998). in *International Conference on Atomic and Molecular Data and Their Applications*, W. L. Wiese, and P. J. Mohr, eds., *NIST Special Publication 926* (National Institute of Standards and Technology, Gaithersburg, MD), p. 248.
- Huo, W. M. (1988). *Phys. Rev. A* 38: 3303.
- Hunter, S. R., Carter, J. G., and Christophorou, L. G. (1987). *J. Chem. Phys.* 86: 693.
- Isaacs, W. A., McCurdy, C. W., and Rescigno, T. N. (1998). *Phys. Rev. A* 58: 309.
- Jarvis, G. K., Mayhew, C. A., Singleton, L., and Spyrou, S. M. (1997). *Intern. J. Mass Spectrom. and Ion Processes* 164: 207.
- Jiao, C. Q., Nagpal, R., and Haaland, P. D. (1997). *Chem. Phys. Lett.* 269: 117.
- Jones, R. K. (1986). *J. Chem. Phys.* 84: 813.
- Kurepa, M. V., and Belić, D. S. (1978). *J. Phys. B* 11: 3719.
- Kurepa, M. V., Babić, D. S., and Belić, D. S. (1981). *Chem. Phys.* 59: 125.
- Lunt, S. L., Randell, J., Ziesel, J.-P., Mrotzek, G., and Field, D. (1998). *J. Phys. B* 31: 4225.
- Lymberopoulos, D. P. and Economou, D. J. (1995). *IEEE Trans. Plasma Science* 23: 573.
- Mann, A. and Linder, F. (1992). *J. Phys. B* 25: 533.
- Masek, K., Laska, L., D'Agostino, R., and Cramarossa, F. (1987). *Contrib. Plasma Phys.* 27: 15.
- McClellan, A. L. (1963). *Tables of Experimental Dipole Moments*, San Francisco: W. H. Freeman and Company, p. 38.
- McCorkle, D. L., Christodoulides, A. A., and Christophorou, L. G. (1984). *Chem. Phys. Lett.* 109: 276.
- Meyyappan, M. and Govindan, T. R. (1996). *J. Appl. Phys.* 80: 1345.
- Mi, L. and Bonham, R. A. (1998). *J. Chem. Phys.* 108: 1910.
- Morgan, W. L. (1992a). *Plasma Chem. Plasma Proc.* 12: 449.
- Morgan, W. L. (1992b). *Plasma Chem. Plasma Proc.* 12: 477.
- Motlagh, S. and Moore, J. H. (1998). *J. Chem. Phys.*, 109: 432.
- Nakamura, Y. (1991). in *Gaseous Electronics and Their Applications*, R. W. Crompton, M. Hayashi, D. E. Boyd, and T. Makabe, eds., Tokyo, Japan: KTK Scientific, p. 178.
- Nakamura, K., Segi, K., and Sugai, H. (1997). *Jpn. J. Appl. Phys.* 36: L439.
- Nakano, T. and Sugai, H. (1992). *Jpn. J. Appl. Phys.* 31: 2919.
- Nishimura, H., Huo, W. M., Ali, M. A., and Kim, Y.-K. (1999). *J. Chem. Phys.* 110: 3811.
- Pinhão, N. and Chouki, A. (1995). in *Proceedings XXII International Conference on Phenomena in Ionized Gases*, K. H. Becker, W. E. Carr, and E. E. Kunhardt, eds., Hoboken, USA, July 31–August 4, 1995, Contributed Papers 2, p. 5.
- Raj, D. (1991). *J. Phys. B* 24: L431.
- Rao, M. V. V. S. and Srivastava, S. K. (1997). in *Proceedings XX Intern. Conf. on the Physics of Electronic and Atomic Collisions, Scientific Program and Abstracts of Contributed Papers*, F. Aumayr, G. Betz, and H. P. Winter, eds., Vienna, Austria, 23–29 July, 1997, vol. II, p. MO 150.
- Read, F. H. and Channing, J. M. (1996). *Rev. Sci. Instrum.* 67: 2372.
- Rees, J. A., Seymour, D. L., Greenwood, C. L., and Scott, A. (1998). *Nuc. Instrum. Methods in Physics Research B* 134: 73.
- Rescigno, T. N. (1994). *Phys. Rev. A* 50: 1382.
- Rogoff, G. L., Kramer, J. M., and Piejak, R. B. (1986). *IEEE Trans. Plasma Science* PS-14: 103.
- Sakae, T., Sumiyoshi, S., Murakami, E., Matsumoto, Y., Ishibashi, K., and Katase, A. (1989). *J. Phys. B* 22: 1385.
- Sanabia, J. E., Cooper, G. D., Tossell, J. A., and Moore, J. H. (1998). *J. Chem. Phys.* 108: 389.
- Schwarzenback, W., Tserepi, A., Derouard, J., and Sadeghi, N. (1997). *Jpn. J. Appl. Phys.* 36: 4644.
- Smith, D., Adams, N. G., and Alge, E. (1984). *J. Phys. B* 17: 461.
- Sobolewski, M. A., Langan, J. G., and Felker, B. S. (1998). *J. Vac. Sci. Technol. B* 16: 173.

- Stefanov, B., Popkirova, N., and Zarkova, L. (1988). *J. Phys. B* 21: 3989.
- Stoffels, W. W., Stoffels, E., and Tachibana, K. (1997). *Jpn. J. Appl. Phys.* 36: 4638.
- Sueoka, O., Takaki, H., Hamada, A., Sato, H., and Kimura, M. (1998). *Chem. Phys. Lett.* 288: 124.
- Sugai, H., Nakamura, K., Hikosaka, Y., and Nakamura, M. (1995a). *J. Vac. Sci. Technol. A* 13: 887.
- Sugai, H., Toyoda, H., Nakano, T., and Goto, M. (1995b). *Contrib. Plasma Phys.* 35: 415.
- Szymtkowski, C., Krzysztofowicz, A. M., Janicki, P., and Rosenthal, L. (1992). *Chem. Phys. Lett.* 199: 191.
- Tanaka, H. (1998). Private communication.
- Tanaka, H., Masai, T., Kimura, M., Nishimura, T., and Itikawa, Y. (1997). *Phys. Rev. A* 56: R3338.
- Tanaka, H., Tachibana, Y., Kitajima, M., Sueoka, O., Takaki, H., Hamada, A., and Kimura, M. (1999). *Phys. Rev. A* 59: 2006.
- Tarnovsky, V., Kurunczi, P., Rogozhnikov, D., and Becker, K. (1993). *Int. J. Mass Spectrom. Ion Processes* 128: 181.
- Trantham, K. W., Dedman, C. J., Gibson, J. C., and Buckman, S. J. (1997). *Bull. Amer. Phys. Soc.* 42: 1727.
- Ventzek, P. L. G., Grapperhaus, M., and Kushner, M. J. (1994). *J. Vac. Sci. Technol. B* 12: 3118.
- Wang, Y., Christophorou, L. G., Olthoff, J. K., and Verbrugge, J. K. (1998). in *Gaseous Dielectrics VIII*, L. G. Christophorou, and J. K. Olthoff, eds., New York: Plenum Press, p. 39.
- Winstead, C., Sun, Q., and McKoy, V. (1993). *J. Chem. Phys.* 98: 1105.
- Winters, H. F. and Inokuti, M. (1982). *Phys. Rev. A* 25: 1420.
- Zubek, M., Gulley, N., King, G. C., and Read F. H. (1996). *J. Phys. B* 29: L239.