Electron interactions with plasma processing gases: present status and future needs

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Abstract

The work conducted at the National Institute of Standards and Technology over the last 7 years on the systematic synthesis and assessment of fundamental knowledge on low-energy electron interactions with plasma processing gases is briefly summarized and discussed. This work deals mostly with the primary electron interaction processes. Assessed data on electron collision cross sections and rate coefficients are discussed and their multiple value is indicated. Data needs are identified for electron interactions with ground-state, excited, and transient species, and for electron energy losses. It is indicated that the currently limited knowledge on electron reactions at surfaces and interfaces can be aided by related existing knowledge on electron interactions in dense gases, liquids, clusters, and molecular layers on cold surfaces. Published by Elsevier Science B.V.

Keywords: Cross sections; Database; Data needs; Electron interactions; Plasma processing gases; Transport coefficients

1. Introduction

The study of the fundamental electron–molecule collision processes and the behavior of slow electrons in gases under an applied electric field traces back for about 100 years (e.g., see Refs. [1–5]). This basic knowledge has underpinned many technologies and is still underpinning many of today's technological advancements. For this purpose, over the last 7 years the National Institute of Standards and Technology (NIST) has undertaken a systematic synthesis and assessment of the fundamental knowledge of the interactions of low-energy electrons with a number of plasma processing gases at relatively low-energies (mostly below 100 eV). The aim of this effort is to build a database for electron interaction processes in plasma processing gases, including electron collision

cross sections and electron transport and rate coefficients. Table 1 lists the critical reviews and comprehensive assessments that have been completed to date. Other similar work has been cited by Morgan [6].

The molecules in Table 1 (CF_4, CHF_3, C_2F_6, C_3F_8, c-C_4F_8, Cl_2, SF_6, BCl_3, CF_3I, and CCl_2F_2) are commonly used in plasma etching. Similar work is needed for other groups of gases of interest to plasma processing, namely, gases used in deposition (e.g., CH_4, SiH_4, CO_2), reactor cleaning (e.g., NF_3), as buffer gases (e.g., He, Ar), as additives (e.g., O_2, CO), and also those present as unavoidable impurities in virtually all practical systems (e.g., O_2, N_2, H_2O). Furthermore, since in the discharge the "initial feed" gas may be dissociated into atoms, radicals, and ions, there is a need for information on these species as well. Additionally, depending on the discharge conditions and the gas, 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

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Table 1
Electron interactions with plasma processing gases: status of the NIST program

CF_4	J. Phys. Chem. Ref. Data 25 (1996) 1341
CHF_3	J. Phys. Chem. Ref. Data 26 (1997) 1
CCl_2F_2	J. Phys. Chem. Ref. Data 26 (1997) 1205
C_2F_6	J. Phys. Chem. Ref. Data 27 (1998) 1
C_3F_8	J. Phys. Chem. Ref. Data 27 (1998) 889
Cl_2	J. Phys. Chem. Ref. Data 28 (1999) 131
Update (CF_4, CHF_3, C_2F_6, and C_3F_8)	J. Phys. Chem. Ref. Data 28 (1999) 967
SF_6	J. Phys. Chem. Ref. Data 29 (2000) 267
CF_3I	J. Phys. Chem. Ref. Data 29 (2000) 553
$c\text{-}C_4F_8$	J. Phys. Chem. Ref. Data 30 (2001) 449
BCl_3	J. Phys. Chem. Ref. Data (in press)

the knowledge of electron–molecule interactions presented in most papers in this area which is on molecules in their ground vibrational and electronic states, there is a need for basic electron collision data for vibrationally excited molecules and radicals, and for 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 Refs. [7,8]) and hence a small amount of excited species can influence the behavior of electrons in a plasma and, consequently, the discharge properties.

2. Primary electron interactions and secondary processes

For the discharges utilized in low temperature, low density, nonequilibrium plasmas, the most significant processes occur in the energy range below about 100 eV, and can be separated into two groups: *primary* and *secondary*.

The principal generic primary processes are elastic and inelastic electron scattering. The latter include vibrational and electronic excitation, electron-impact ionization, electron-impact dissociation, and electron attachment. It is on these primary processes that we at NIST have mainly focused (Table 2). However, when possible, our work (Table 1) also provided information on the interactions of slow electrons with the products of the primary processes which include

electron interactions with transient species such as atoms and radicals and energy rich (excited) targets.
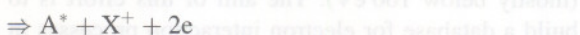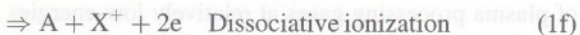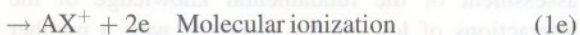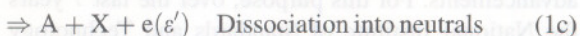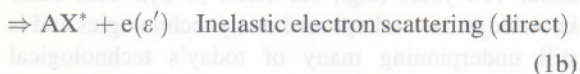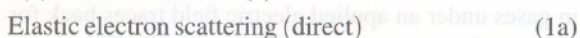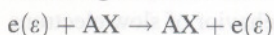
The secondary reactions are the reactions among the by-products of the primary collisions and include collisional detachment, charge transfer, ion-molecule reactions, and photophysical processes. Some information on the secondary processes has also been incorporated in our publications in an effort to provide reliable basic knowledge for better characterization of industrial plasmas.

2.1. Primary processes

These are the primary interactions of electrons with the parent gas (the initial feed gas). They are significant in that they generate the key plasma particles—electrons, positive and negative ions, radicals, excited species, and the photons which accompany their radiative decay. In the most fundamental way these electron interaction processes control the energies and the number densities of free electrons in electrically stressed gases. Knowledge of these primary electron interactions, then, can be used to control the important species in the plasmas of many of today's technologies, foremost in the microelectronics industry.

In the low electron energy range of interest here, the primary interactions of electrons with molecules are of two types: *direct* and *indirect*.

The principal direct elastic and inelastic electron scattering reactions are:

$$e(\varepsilon) + AX \rightarrow AX + e(\varepsilon)$$
Elastic electron scattering (direct)   (1a)

$$\Rightarrow AX^* + e(\varepsilon') \quad \text{Inelastic electron scattering (direct)}$$
                                        (1b)

$$\Rightarrow A + X + e(\varepsilon') \quad \text{Dissociation into neutrals} \quad (1c)$$

$$\Rightarrow A + X^* + e(\varepsilon') \quad \text{Dissociative excitation} \quad (1d)$$

$$\rightarrow AX^+ + 2e \quad \text{Molecular ionization} \quad (1e)$$

$$\Rightarrow A + X^+ + 2e \quad \text{Dissociative ionization} \quad (1f)$$

$$\Rightarrow A^* + X^+ + 2e$$
Dissociative ionization with fragment excitation (1g)

$$\rightarrow A^+ + X^- + e(\varepsilon') \quad \text{Ion-pair formation} \quad (1h)$$

In the above reactions, $e(\varepsilon)$ and $e(\varepsilon')$ represent, respectively, the incident electron with energy ε and the

Table 2
Electron collision processes normally considered in plasma processing, 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	$\sigma_{sc,t}(\varepsilon)$
	Differential electron scattering cross section(s)[a]	$\sigma_{sc,diff}(\varepsilon)$
Rotational excitation	Total rotational electron scattering cross section	$\sigma_{rot,t}(\varepsilon)$
Elastic electron scattering	Total elastic electron scattering cross section[b]/total elastic integral[b]	$\sigma_{e,t}(\varepsilon)/\sigma_{e,int}(\varepsilon)$
	Momentum transfer cross section (elastic)	$\sigma_{m}(\varepsilon)$
Vibrational excitation	Total vibrational excitation cross section	$\sigma_{vib,t}(\varepsilon)$
	Total direct vibrational excitation cross section[c]	$\sigma_{vib,dir,t}(\varepsilon)$
	Total indirect vibrational excitation cross section	$\sigma_{vib,indir,t}(\varepsilon)$
Electronic excitation	Electronic excitation cross section	$\sigma_{elec}(\varepsilon)$
Dissociation	Total dissociation cross section	$\sigma_{dis,t}(\varepsilon)$
	Total cross section for electron-impact dissociation into neutrals[d]	$\sigma_{dis,neut,t}(\varepsilon)$
Ionization	Total ionization cross section	$\sigma_{i,t}(\varepsilon)$
	Partial ionization cross section	$\sigma_{i,partial}(\varepsilon)$
	Multiple ionization cross section	$\sigma_{i,mult}(\varepsilon)$
	Density-reduced ionization coefficient	α/N
	Density-reduced effective ionization coefficient	$(\alpha - \eta)/N$
Attachment	Total electron attachment cross section	$\sigma_{a,t}(\varepsilon)$
	Total dissociative electron attachment cross section[e]	$\sigma_{da,t}(\varepsilon)$
	Density-reduced electron attachment coefficient	η/N
	Total electron attachment rate constant	$k_{a,t}$
Ion-pair formation	Cross section for ion-pair formation	$\sigma_{ip}(\varepsilon)$
Electron drift	Electron drift velocity	w
Electron diffusion	Transverse electron diffusion coefficient to electron mobility ratio	D_T/μ
	Longitudinal electron diffusion coefficient to electron mobility ratio	D_L/μ

[a] For total or for a particular electron scattering process.
[b] These two cross sections refer to the same quantity (see Refs. [2,9]).
[c] Also, for specific vibrational excitations.
[d] Also, for specific neutral fragments.
[e] Also, for specific negative ion fragments.

scattered electron with energy ε'. The notation AX, AX*, and AX$^+$ represents, respectively, ground-state, excited, and ionized molecules. Similarly, the notation A and X, X*, X$^+$ and A$^+$, and X$^-$ represents, respectively, ground-state fragments, excited fragments, positive ion fragments, and stable negative ion fragments. The asterisk denotes an excited species and the double arrow indicates multiple reaction pathways which normally occur for polyatomic molecules.

The probability of occurrence of the various reactions represented by the reaction channels (1a)–(1h) is described by the corresponding cross sections, $\sigma(\varepsilon)$, for these reactions. The cross sections of these direct

electron collision channels extend over a range of incident electron energies which depends on the process itself. Fig. 1 shows an example of the assessed cross sections for some of these processes for the case of the plasma processing gas CF$_4$. With the exception of elastic electron scattering, the cross sections for the other processes have an energy threshold which depends on the physical inelastic process involved. The thresholds for molecular dissociation and ionization, for instance, are much higher than those for direct vibrational excitation (Fig. 1). On the other hand, elastic electron scattering is seen to be large over a wide range of electron energies.
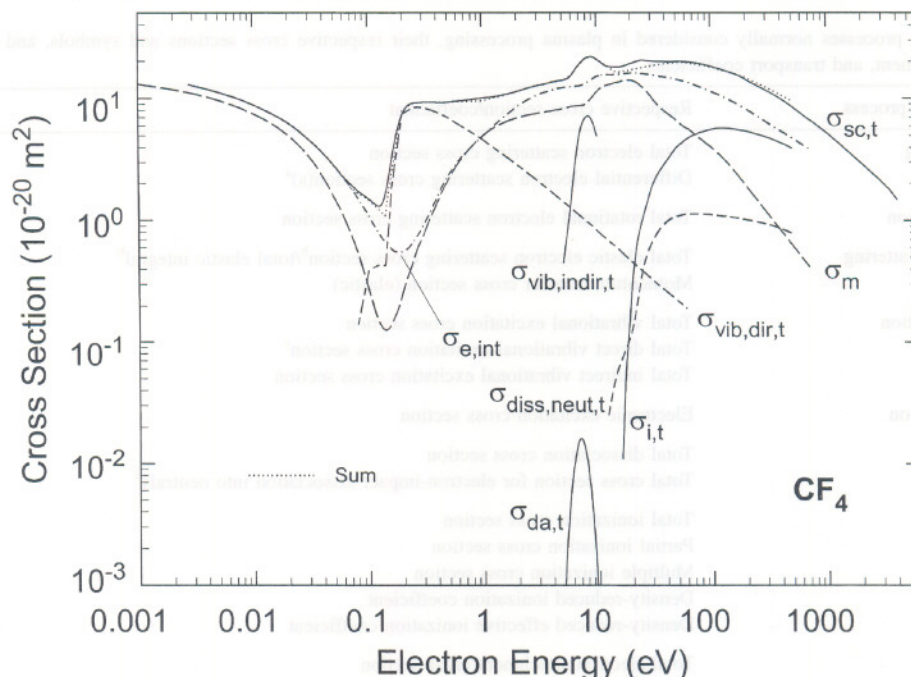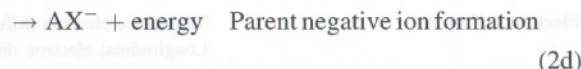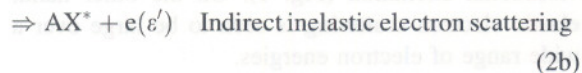
Fig. 1. Assessed cross sections for direct and indirect electron collision processes for the case of the plasma processing gas CF$_4$ (Refs. [10,11]).

In contrast with the direct collision processes (1a)–(1h) for which the cross sections are substantial over a large electron energy range, in the low-energy region ($\lesssim 20$ eV) electrons with certain energies can be selectively captured by the molecules AX to form transient negative ions AX^{-*}. These indirect—electron capturing—collisions are resonant, that is, they occur only for limited ranges of electron energy which are characteristic of the molecules themselves. The transient negative ions AX^{-*} have lifetimes ranging from $\sim 10^{-15}$ to $>10^{-2}$ s (Refs. [2,12,13]) and decay by autoionization leaving the neutral molecule with or without excess internal energy. Alternatively, AX^{-*} can decay via the processes of dissociative electron attachment, or can form stable parent negative ions if the electron affinity of AX is positive. These indirect collision channels are represented as

$$e(\varepsilon) + AX \rightarrow AX^{-*} \rightarrow AX + e(\varepsilon)$$

Indirect elastic electron scattering   (2a)

$$\Rightarrow AX^* + e(\varepsilon') \quad \text{Indirect inelastic electron scattering}$$
(2b)

$$\Rightarrow A + X^- \quad \text{Dissociative electron attachment} \quad (2c)$$

$$\rightarrow AX^- + energy \quad \text{Parent negative ion formation}$$
(2d)

Reactions (1a)–(1h) and (2a)–(2d) crucially determine the energies and the number densities of the free electrons present in electrically stressed gaseous matter. The energies of the free electrons are a function of the amount of energy they receive from the applied electric field and the energy they lose through these elastic and inelastic collisions with the atoms and molecules making up the gaseous medium. The low-energy indirect scattering process (2b) can constitute the most effective way of transferring energy from the electrons to molecular vibrational excitation and thus can crucially influence the distribution of electron energies in electrically stressed gases and plasmas. The large cross sections for direct and indirect vibration excitation can be seen from the data in Fig. 2 on the vibrational excitation of CF$_4$.

Similarly, the electron number density controlling reactions principally consist of the electron generating processes (1e)–(1g) and the electron-depleting
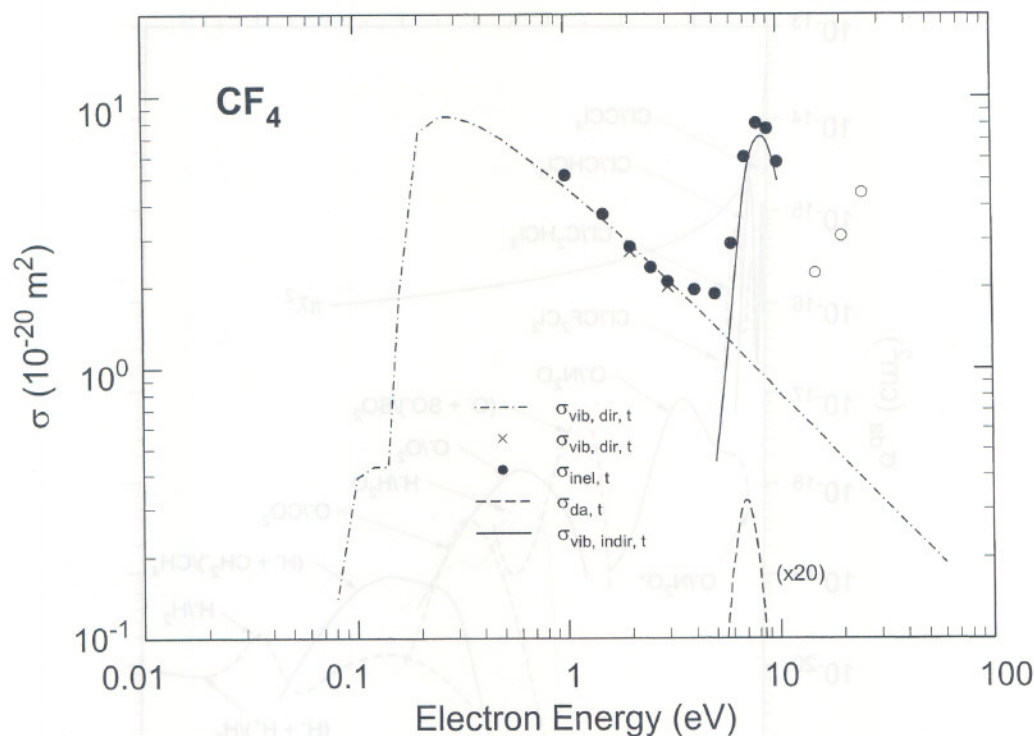
Fig. 2. Cross sections for vibrational excitation of CF_4 by electron-impact. (– · –) Born approximation calculation [14] of $\sigma_{vib,dir,t}(\varepsilon) = \sigma_{v_3}(\varepsilon) + \sigma_{v_4}(\varepsilon)$; (×) measurements [15] of $\sigma_{vib,dir,t}(\varepsilon)$; (●) measurements [16] of $\sigma_{inel,t}(\varepsilon)$; (–) total indirect vibrational excitation cross section, $\sigma_{vib,indir,t}(\varepsilon)$, obtained from assessed cross sections (see text and Refs. [10,11]).

processes (2c) and (2d). The former are direct (non-resonant) and the latter are indirect (resonant). Other processes (secondary, see Section 2.2) such as electron detachment may also affect the electron number densities. In assessing the effect of electron attachment processes on free electron number densities in plasmas, it is important to recognize the strong dependence of the magnitude of the electron attachment cross section on the energy position of the negative ion states (NISs) (Fig. 3). It is also important to recognize that the effectiveness of a given electron attachment process to control the free electron number density in a plasma is a function of the electron scattering processes which determine the electron energy distribution function.

2.2. Secondary processes

The initial products of the primary electron–molecule interactions undergo subsequent collisions and react with the plasma constituents (neutral species, excited species, positive and negative ions, photons). Via these secondary reactions the initial electron generated products are transformed, often very efficiently, into other species. There is a multiplicity of secondary reactions which affect the identity and the number density of the "final" species in weakly ionized, low temperature plasmas. In Table 3 are listed a number of photon-induced, ion-induced, and neutral species-induced secondary reactions (see also Ref. [17]). Depending on the gaseous medium, some of these reactions can be significant both in determining the densities of the desirable species in the plasma and also in the plasma diagnostics. For instance, the secondary processes of electron-ion recombination can be significant in determining the overall electron number density and the negative ion destruction processes can similarly deplete the negative ions; ion-molecule reactions can change the identity of the ionic species in the discharge, and Penning ionization
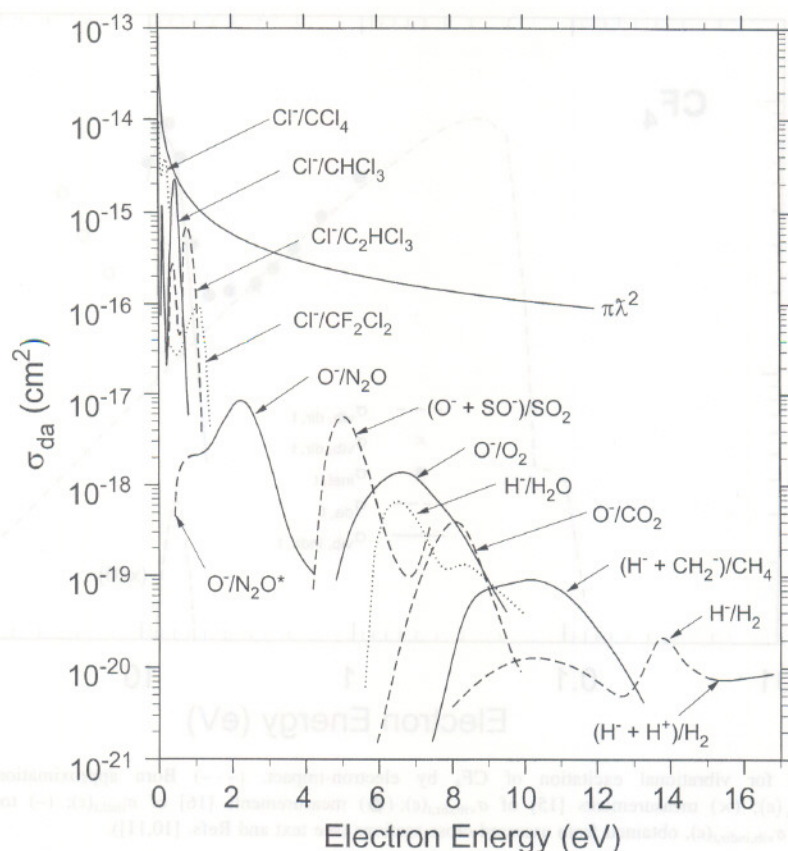
Fig. 3. Dissociative electron attachment cross sections as a function of electron energy for a number of molecules. The line designated by $\pi(\lambda/2\pi)^2$ is the s-wave capture cross section (from Ref. [13]).

processes may be significant for mixtures containing, for instance, rare gas atoms. Similarly, charge-exchange reactions influence the identity of the dominant ion(s) in the discharge. Via the secondary reactions, also, energy is exchanged between charged and neutral species and between excited and unexcited species.

Our knowledge on the secondary reactions both in terms of data and in terms of critical assessment and synthesis is limited.

3. Assessed data on electron collision cross sections and rate coefficients

The three principal components of the NIST 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; (3) dissemination and updating of the database. Elements of these three components are listed below (for a fuller discussion see the publications listed in Table 1 and Ref. [18]).

3.1. Sources of data

In general, there exist three main sources of electron collision data: 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 provide directly—and at times indirectly— cross sections or coefficients for individual electron

Table 3
Photon-induced, ion-induced, and neutral species-induced secondary reactions

Process representation[a]	Process description
Photon-induced reactions	
$hv + AX \rightarrow AX^*$	Photoabsorption
$hv + AX \rightarrow AX^+ + e$	Photoionization
$\Rightarrow A + X^+ + e$	Dissociative photoionization
$hv + AX \Rightarrow A + X$	Photodissociation
$hv + AX^-(X^-) \rightarrow AX(X) + e$	Photodetachment
$hv + AX^- \rightarrow A + X^-$	Negative ion photodissociation
Ion-induced reactions	
$AX^+ + C \rightarrow AX(AX^*)$	Electron recombination
$\Rightarrow A + X^{(*)}$	Dissociative recombination with/without excitation
$\rightarrow AX + hv$	Radiative recombination
$A^+ + X^- \rightarrow AX(AX^*)[AX^+ + C^- \rightarrow \text{products}]$	Positive ion-negative ion recombination
$AX^- + C \rightarrow AX + C + e$	Collisional detachment
$AX^- + C \rightarrow AXC + e$	Associative detachment
$AX^+ (X^+) + CD(C) \Rightarrow \text{products}$	Positive ion-molecule (atom) reactions[b]
$AX^- (X^-) + CD(C) \Rightarrow \text{products}$	Negative ion-molecule (atom) reactions[b]
$AX^+ + nC \rightarrow AX^+nC, n \geq 1$	Cluster formation involving positive ions
$AX^- + nC \rightarrow AX^-nC, n \geq 1$	Cluster formation involving negative ions
Neutral species-induced reactions	
$AX^* + C \rightarrow AX + C^*$	Energy transfer
$AX^* (X^*) + C \rightarrow AX(X) + C^+ + e$	Penning ionization
$A + BC(B) \Rightarrow \text{products}$	Chemical reactions involving neutral species[c]

[a] AX represents an unexcited and AX* represents an excited diatomic or polyatomic molecule. The double arrow indicates that the reaction can generate a multiplicity of products.

[b] A multiplicity of reactions and products are possible depending on the type and state of the reactants.

[c] These may include radical recombination $(2A \rightarrow A_2)$, addition $(A + AX \rightarrow A_2X)$, or abstraction $(A + AX \rightarrow A_2 + X)$ reactions.

collision processes. The second give, in principle, cross sections for any process, but are, in practice, limited in their utility by the complexity the calculations themselves entail, especially for polyatomic molecules. One exception might be semiempirical calculations that have been rather successful in determining the total electron-impact ionization cross section for a number of atoms, molecules, and radicals (e.g., see Refs. [19,20]). The third rely on electron transport data and other inputs and yield only self-consistent sets of cross sections, not independent and unique cross sections for each individual collision process.

3.2. Assessment process

Any assessment of data relies upon some established protocol for determining which data are the most reliable. For the work performed at NIST, "recommended" or "suggested" values of cross sec-

tions 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; (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 above 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. Although for many cross sections there exist published values that differ by as much as two orders of magnitude, critical analysis of these data often allows the determination of cross sections whose uncertainties are expected to be between 10 and 20% for most cases.

3.3. Assessed cross sections

Independently assessed cross sections for a number of electron collision processes are given in Fig. 1 for CF_4. Similarly, assessed electron transport coefficients for this molecule (and for C_2F_6 and C_3F_8) are given in Fig. 4. Both the electron collision cross sections and the electron transport and rate coefficients for CF_4 are

sufficiently well known that they can serve as bench marks for this type of data for polyatomic molecules. This may also be the case for SF_6, but, unfortunately, it cannot be said for the rest of the molecules under discussion. However, cross sections for a number of electron collision processes and electron transport coefficients have been recommended or suggested for most of the molecules we studied (see respective references in Table 1).

3.4. Value and use of assessed cross sections

State-of-the-art knowledge. The assessed cross sections and coefficients represent the most up-to-date data for individual electron collision processes and coefficients. Thus, they constitute the most reliable database for a fundamental understanding of electron–molecule collisions and their dependence on molecular and electronic structure, for bench mark computations,
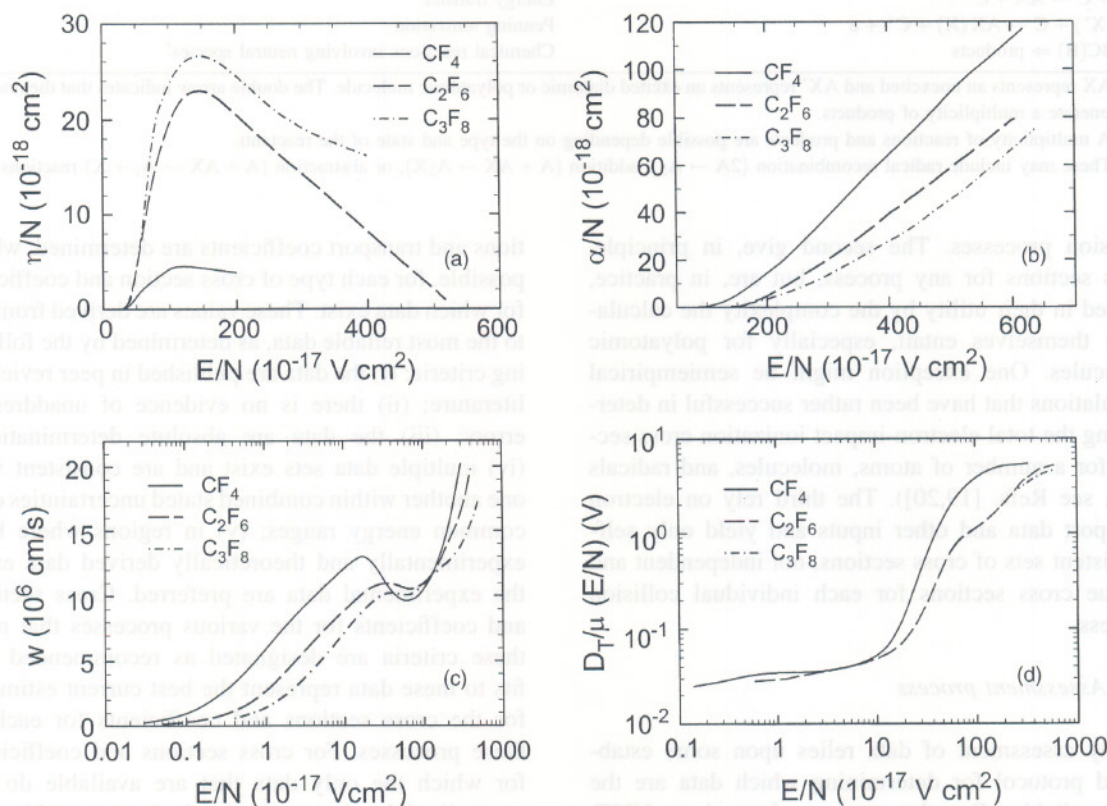

Fig. 4. Assessed electron transport and rate coefficients for CF_4, C_2F_6 and C_3F_8 (Refs. [10,11]).

for use in models, and for the deduction of cross section data for significant processes for which no data exist. Also, they filter out less reliable or erroneous data and identify further data needs. And while it is recognized that the acquisition of reliable data and the data themselves are dynamic processes that evolve with time, we believe that at any given time the best possible values should be discerned and should be used as such—not as variables—in calculations, codes, or models. Unless, that is, there is a scientific basis to question the data. There is no substitute for accurate reliable experimental data and there is no substitute for a sound assessment and verification of the data before they enter the system. In this way, erroneous data are prevented from triggering a chain reaction of erroneous computational results.

Fundamental understanding. The assessed cross sections for individual molecules quantify the significance of the various electron collision processes and their dependence on the structural and electronic properties of molecules. Their understanding is significant, and so is the meaning of the physical reality they represent and are a measure of. Such understanding is necessary for the proper use of the data.

The assessed cross sections for the 10 molecules under consideration in this paper enhance the understanding of electron–molecule interactions in a number of ways. For instance, significant understanding was developed concerning the NISs of these molecules and their effects on the various types of electron collision processes and their respective cross sections (see Refs. [18,21–28]), and the dominant energy loss mechanisms in various energy regions. For example, analysis showed that vibrational excitation is the dominant inelastic process below the threshold for electronic excitation for the CF_4 molecule. This vibrational excitation is dominated by excitation of the infrared active modes v_3 and v_4 via direct dipole scattering below the negative ion resonance region (6–8 eV) and by indirect scattering in the resonance region. Also, assessed cross sections often allow the establishment of trends in the various cross sections and coefficients (especially for a series of structurally similar molecules; see, for instance, Fig. 4) and their dependence on molecular parameters (e.g., the dependence of the magnitude of the electron scattering cross section on molecular polarizability for nonpolar molecules [18], or the electric dipole moment for polar

molecules [21], or the dependence of the magnitude of the dissociative electron attachment cross section on the position of the negative ion resonances [13]). These correlations have predictive value.

Guide for computations. Assessed cross sections can guide calculations especially for polyatomic molecules. For example, the establishment of the Ramsauer–Townsend minimum in the assessed momentum and total electron scattering cross sections of CF_4 (Refs. [10,11]) led to its theoretical calculation [29]. Furthermore, assessed and recommended cross sections for some molecules (e.g., CF_4, Refs. [10,11]) can serve as bench marks for both theory and experiment.

Use in models. The independently assessed cross sections are most significant inputs in models, such as those using Boltzmann and Monte Carlo codes. In this regard, it is emphasized that for all ten molecules under consideration here, the cross section for each electron–molecule collision is assessed independently. Each cross section is, therefore, unique. This is in sharp contrast with the *sets* of electron collision cross sections which are determined from computational models and are "validated" as sets indirectly through the ability of the computational code to reproduce the macroscopic rate coefficients of the molecule in question. In the present work, the rate and transport coefficients are similarly obtained by individual independent assessment of existing data under a set protocol (Section 3.2).

Deduction of unavailable data. The critically assessed cross sections for each molecule can oftentimes be used to deduce needed data, which are not otherwise available. Particularly significant examples are the deduced cross sections for vibrational excitation (Refs. [10,11,22,25,26]) and for dissociation into neutral fragments (Refs. [10,11,23,26]). As an example, we refer to the deduced cross section for indirect (resonance enhanced) vibrational excitation cross section of CF_4 below ~12. 5 eV shown earlier in Fig. 2 which was deduced (see Refs. [10,11]) from

$$\sigma_{\text{vib,indir,t}}(\varepsilon) = [\sigma_{\text{sc,t}}(\varepsilon) - \sigma_{\text{e,int}}(\varepsilon)] - [\sigma_{\text{vib,dir,t}}(\varepsilon) + \sigma_{\text{da,t}}(\varepsilon)] \quad (3)$$

where $\sigma_{\text{sc,t}}(\varepsilon)$, $\sigma_{\text{e,int}}(\varepsilon)$, $\sigma_{\text{vib,dir,t}}(\varepsilon)$, and $\sigma_{\text{da,t}}(\varepsilon)$ are respectively the assessed cross sections for total electron scattering, integral elastic, total direct vibrational
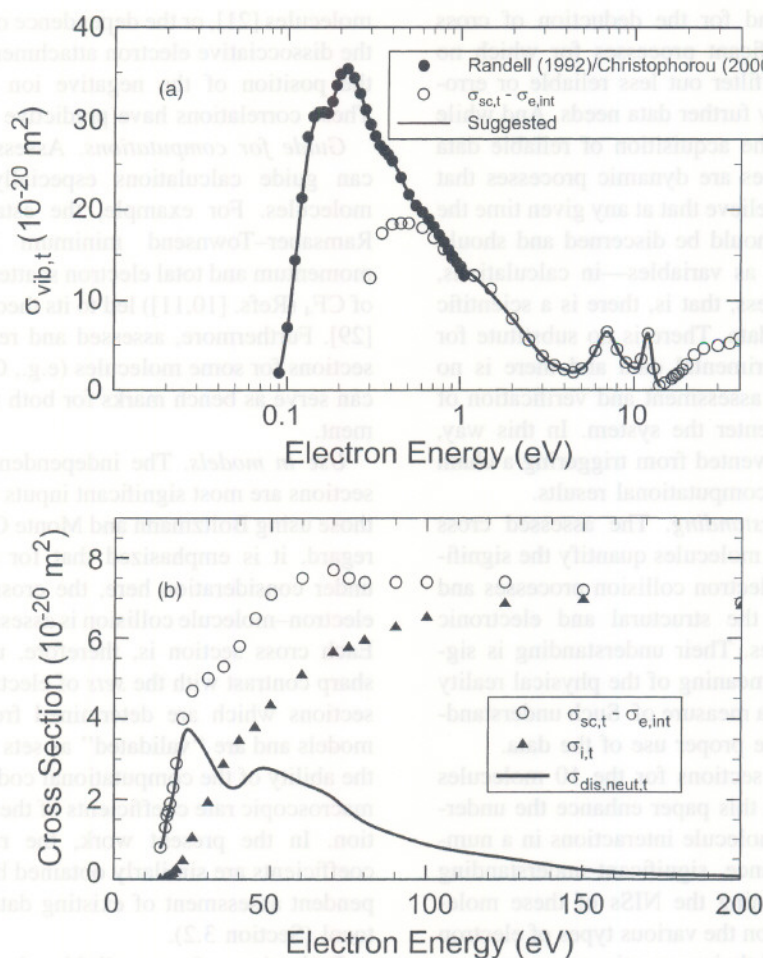
Fig. 5. (a) Deduced total vibrational excitation cross section, $\sigma_{vib,t}(\varepsilon)$ for SF_6: (●) normalized data [26] based on the relative measurements of Ref. [30]; (○) difference $\sigma_{sc,t}(\varepsilon) - \sigma_{e,int}(\varepsilon)$ of the assessed values of $\sigma_{sc,t}(\varepsilon)$ and $\sigma_{e,int}(\varepsilon)$. (b) Deduced cross section for total dissociation into neutral fragments, $\sigma_{dis,neut,t}(\varepsilon)$ for SF_6 from the recommended values of $\sigma_{sc,t}(\varepsilon)$, $\sigma_{e,int}(\varepsilon)$, and $\sigma_{i,t}(\varepsilon)$ for this molecule (see Ref. [26]).

excitation, and total dissociative electron attachment. As a further example, we show in Fig. 5 deduced cross sections for the total vibrational excitation cross section of SF_6, $\sigma_{vib,t}(\varepsilon)$, and for the total dissociation of SF_6 into neutral fragments, $\sigma_{dis,neut,t}(\varepsilon)$, deduced [26], respectively, from

$$\sigma_{vib,t}(\varepsilon) = \sigma_{sc,t}(\varepsilon) - \sigma_{e,int}(\varepsilon)$$
$$- \sigma_{a,t}(\varepsilon) \approx \sigma_{sc,t}(\varepsilon) - \sigma_{e,int}(\varepsilon) \qquad (4)$$

and

$$\sigma_{dis,neut,t}(\varepsilon) \approx \sigma_{sc,t}(\varepsilon) - \sigma_{e,int}(\varepsilon) - \sigma_{i,t}(\varepsilon) \qquad (5)$$

Expression (5) applies for energies above ~15 eV where $\sigma_{vib,t}(\varepsilon)$ is small (see Ref. [26]). While the uncertainties of these cross sections may be large, they represent a good estimate of magnitude when no direct data are available.

Identification of gaps in database. 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 uncertain or incorrect; (ii) data that are needed, but are not available. The state of our knowledge regarding electron collision data for the 10 gases

Table 4
The state of present knowledge on electron collision data for CF_4, C_2F_6, C_3F_8, CHF_3, CCl_2F_2, Cl_2, SF_6, CF_3I, c-C_4F_8, and BCl_3

Cross section/ coefficient	CF_4	C_2F_6	C_3F_8	CHF_3	CCl_2F_2	Cl_2	SF_6	CF_3I	c-C_4F_8	BCl_3
$\sigma_{sc,t}(\varepsilon)$	R[a]	S[b]	R	R	R	R	R		S	None
$\sigma_{m}(\varepsilon)$	R	S	S	None	C[c]	C	S	C	None	C
$\sigma_{e,diff}(\varepsilon)$	M[d]/C	M/C	M	M/C	M/C	None	M/C	M	M/C	C
$\sigma_{e,int}(\varepsilon)$	R	S	S	None	R	S	S	None	None	C
$\sigma_{vib,indir,t}(\varepsilon)$	R/D[e]	–[f]	–[f]	None	D	D	D	None	–[f]	None
$\sigma_{vib,dir,t}(\varepsilon)$	R	–[f]	–[f]	None	R	–[f]	D	None	–[f]	C
$\sigma_{i,t}(\varepsilon)$	R	R	R	S	R	R	R	S	S	S
$\sigma_{i,part}(\varepsilon)$	M	M	M	M	M	None	M	S	M	S
$\sigma_{ip}(\varepsilon)$	None	None	None	None	None	S	None	None	None	None
$\sigma_{i,mult}(\varepsilon)$	M	None	None	None	M	None	None	None	None	None
$\sigma_{dis,t}(\varepsilon)$	R	None	None	R	None	–[f]	None	None	None	C
$\sigma_{dis,neut,t}(\varepsilon)$	R	None	None	M	None	M/C	D	None	M[g]	None
$\sigma_{a,t}(\varepsilon)$	R	R	R	None	R	S	S	S	S	M
$\alpha/N\ (E/N)$	R	R	R	None	R	S	R	None	None	None
$\eta/N\ (E/N)$	R	R	R	None	R	S	R	None	None	None
$(\alpha-\eta)/N\ (E/N)$	R	R	R[h]	S	R	R	R	None	None	None
$k_{a,t}(\langle\varepsilon\rangle)$	R	R	R	None	R	S	R	None	R	M
$w\ (E/N)$	R	S	S	R	S	M	R	None	S	None
$D_T/\mu\ (E/N)$	S	R	S	None	S	M	S	None	S	None

[a] Recommended.
[b] Suggested.
[c] Calculated.
[d] Measured.
[e] Deduced.
[f] See corresponding reference (Table 1).
[g] Sum of the reported partial dissociation cross sections [28].
[h] Deduced from the recommended values of α/N (E/N) and the density-independent values of η/N (E/N) [18].

we have considered so far is summarized in Table 4. With the sole exception of CF_4 and possibly SF_6, the database for the other eight gases needs much improvement. In general, 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 and electronic excitation, partial ionization, multiple ionization, ion-pair formation, and dissociation into neutrals. Existing data for electron transport and electron attachment and ionization coefficients are reliably known for CF_4, C_2F_6, C_3F_8, SF_6 and to some degree also for CCl_2F_2. However, such knowledge is meager for Cl_2, CHF_3, CF_3I, c-C_4F_8, and BCl_3. 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.

4. Data needs

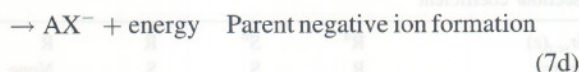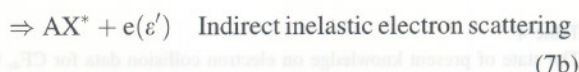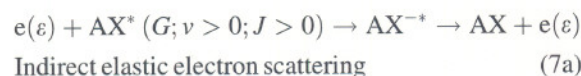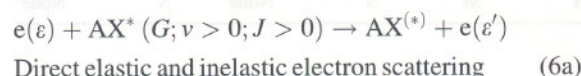### 4.1. Ground-state species

While the data needs for ground-state molecules vary from one molecule to another, there seems to be an universal need for certain types of data, foremost measurements of vibrational excitation cross sections, electronic excitation cross sections, differential scattering cross sections at small and large scattering angles, and cross sections for dissociation into neutral fragments. Cross sections for ion-pair formation and for multiple ionization are scarce.

4.2. Excited species

As stated in Section 1, the initial electron–molecule interactions depend not only on the electron energy

and the target, but also on the internal energy of the latter. In spite of the basic and applied significance of electron-excited molecule (atom) interactions, studies of the interactions of slow electrons with excited atoms and molecules as a function of their internal energy are meager. One of the reasons for this paucity of experimental data, especially for electronically excited targets, is the difficulty of producing sufficient numbers of excited atoms and molecules to study under experimentally controlled conditions. However, this is now being overcome with the availability of pulsed lasers which allow much higher number densities and selectivity of excited states (e.g., see Refs. [7,8,31,32]).

The interactions of low-energy electrons with excited molecules can be conveniently separated into two groups: (i) electron interactions with ro-vibrationally excited ("hot") molecules; (ii) electron interactions with electronically excited molecules. Electron interactions with ro-vibrationally excited molecules are symbolically expressed as

$$e(\varepsilon) + AX^* (G; v > 0; J > 0) \rightarrow AX^{(*)} + e(\varepsilon')$$

Direct elastic and inelastic electron scattering   (6a)

$$e(\varepsilon) + AX^* (G; v > 0; J > 0) \rightarrow AX^{-*} \rightarrow AX + e(\varepsilon)$$

Indirect elastic electron scattering   (7a)

$$\Rightarrow AX^* + e(\varepsilon') \quad \text{Indirect inelastic electron scattering}$$
(7b)

$$\Rightarrow A + X^- \quad \text{Dissociative electron attachment} \quad (7c)$$

$$\rightarrow AX^- + \text{energy} \quad \text{Parent negative ion formation}$$
(7d)

where the letters G, v, and J refer to species, respectively, in their ground electronic, v vibrational, and J rotational states.

There are very limited data on reactions (6a) and (7b) which have been discussed by Christophorou and Olthoff [8]. The effects of enhanced electron scattering from vibrationally excited molecules can significantly influence the behavior of free electrons in plasmas, for instance, their transport properties and energy distributions.

Of the reaction channels (7a)–(7d), channel (7c) has been most frequently studied (e.g., see Refs. [7,8,13]). Thus, it has been firmly established that the cross section for exothermic dissociative electron attachment processes generally increases with increasing total internal energy of the molecule. An example of this type of behavior is shown in Fig. 6 for the case of the CCl_2F_2 molecule [22,23]. Such profound increases in the dissociative electron attachment cross section are
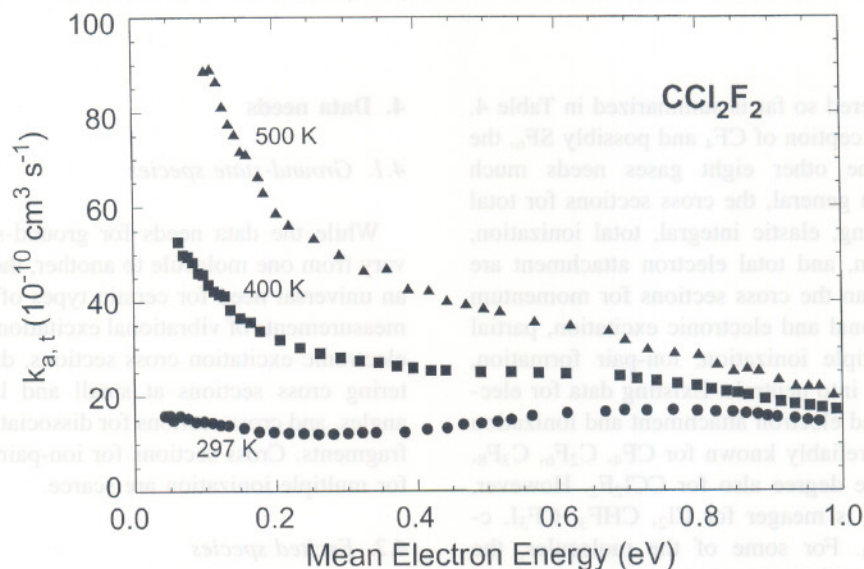

Fig. 6. Total dissociative electron attachment rate constants as a function of the mean electron energy, $k_{da,t}(\langle\varepsilon\rangle)$, for CCl_2F_2 measured in N_2 buffer gas at temperatures of 297, 400, and 500 K (Refs. [22,33]).
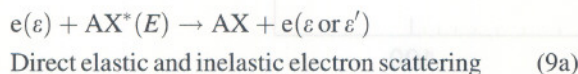
common for many halogenated molecules and indicate an efficient way to increase radical production by small increases in gas temperature. The effect of ro-vibrational excitation of molecules on dissociative electron attachment depends on the negative ion sate involved and the total internal energy of the molecule. The dissociative electron attachment cross section increases with increasing internal energy as long as the total internal energy of AX* is less than the energy required to reach the dissociating negative ion sate.

In contrast with channel (7c), increases in the ro-vibrational energy of molecules forming parent negative ions decrease the overall production of parent negative ions mainly because of enhanced autodetachment and thermally induced detachment from the stable parent anion AX⁻, viz.

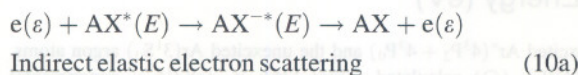$$AX^- + heat \rightarrow AX^{-*} \rightarrow AX + e \qquad (8)$$

The effectiveness of reaction (8) is a function of the electron affinity of the molecule [8,34]. Thus, the effect of ro-vibrational excitation of molecules on electron attachment depends on the mode (dissociative or nondissociative) of electron attachment and the negative ion sate involved (see further discussion in Refs. [7,8,34]).
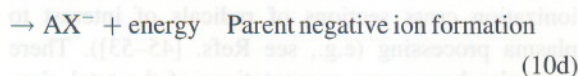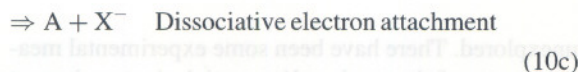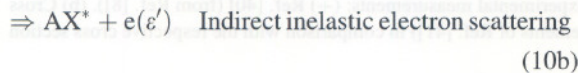
Little quantitative work has been done on electron scattering from and electron attachment to electronically excited molecules. The processes involved can be represented as

$$e(\varepsilon) + AX^*(E) \rightarrow AX + e(\varepsilon \text{ or } \varepsilon')$$

Direct elastic and inelastic electron scattering $\qquad$ (9a)

$$e(\varepsilon) + AX^*(E) \rightarrow AX^{-*}(E) \rightarrow AX + e(\varepsilon)$$

Indirect elastic electron scattering $\qquad$ (10a)

$$\Rightarrow AX^* + e(\varepsilon') \quad \text{Indirect inelastic electron scattering}$$

$$(10b)$$

$$\Rightarrow A + X^- \quad \text{Dissociative electron attachment}$$

$$(10c)$$

$$\rightarrow AX^- + energy \quad \text{Parent negative ion formation}$$

$$(10d)$$

There have been only limited measurements and calculations of the cross section for reaction (9a) (see Ref. [8]), which show that the cross section for excitation of a given electronic state is much higher if the upward

transition originates from an excited state. To illustrate the profound effects of electronic excitation on the electron scattering cross section we refer to the data in Fig. 7 on the cross sections for electron scattering and ionization from ground-state Ar and from metastable Ar*. It is seen from Fig. 7a that the total electron scattering cross section, $\sigma_{sc,t}^*(\varepsilon)$, for the excited argon atom Ar*($4^3P_2 + 4^3P_0$) (Refs. [32,35,36]) is very much larger than the total electron scattering, $\sigma_{sc,t}(\varepsilon)$, cross section [37–39], or the momentum transfer, $\sigma_m(\varepsilon)$, cross section [40] for the ground-state argon atom Ar(3^1S_0). This large enhancement and the disappearance of the Ramsauer–Townsend minimum in the excited state cross section is largely due to the much higher polarizability of the excited atom [the polarizability of Ar*(4^3P_2) is ~319.4 a_0^3] compared to that for the ground-state atom [the polarizability of Ar(3^1S_0) is ~11.07 a_0^3] (see Ref. [8]).

Similarly (Fig. 7b), the cross section for electron-impact ionization, $\sigma_i^*(\varepsilon)$, of metastable Ar* (Ref. [41]) far exceeds that, $\sigma_i(\varepsilon)$, of the ground-state atom Ar (Ref. [41]). The lower ionization thresholds and the higher cross sections of the excited states cause a shift of the ionization cross section to lower energies, which, in turn, affects the rate coefficients of the various discharge processes.

There have been a few studies of reaction (10c) (see Refs. [7,8]), and Fig. 8 shows one of the early examples. In Fig. 8 the cross section for dissociative electron attachment to singlet $O_2^*(a^1\Delta_g)$ (prepared in a microwave discharge [43,44]) is compared with that for the ground-state $O_2(^3\sum_g^-)$ molecule [2]. Dissociative electron attachment to singlet oxygen, $O_2^*(a^1\Delta_g)$, is seen to be about four times larger than that to ground-state oxygen, $O_2(^3\sum_g^-)$. Subsequent studies of dissociative electron attachment to a number of electronically excited molecules employing pulsed lasers in electron swarm type and in electron-beam type experiments have shown that the cross sections for electron attachment to electronically excited molecules can be many orders of magnitude larger in comparison to the ground-state molecules (see discussion and references in Ref. [8]). However, although these findings have been published for some time and the role of electronically excited species in gas discharge physics and plasma-based technologies is expected to be significant, no systematic study of electron attachment to electronically excited molecules has
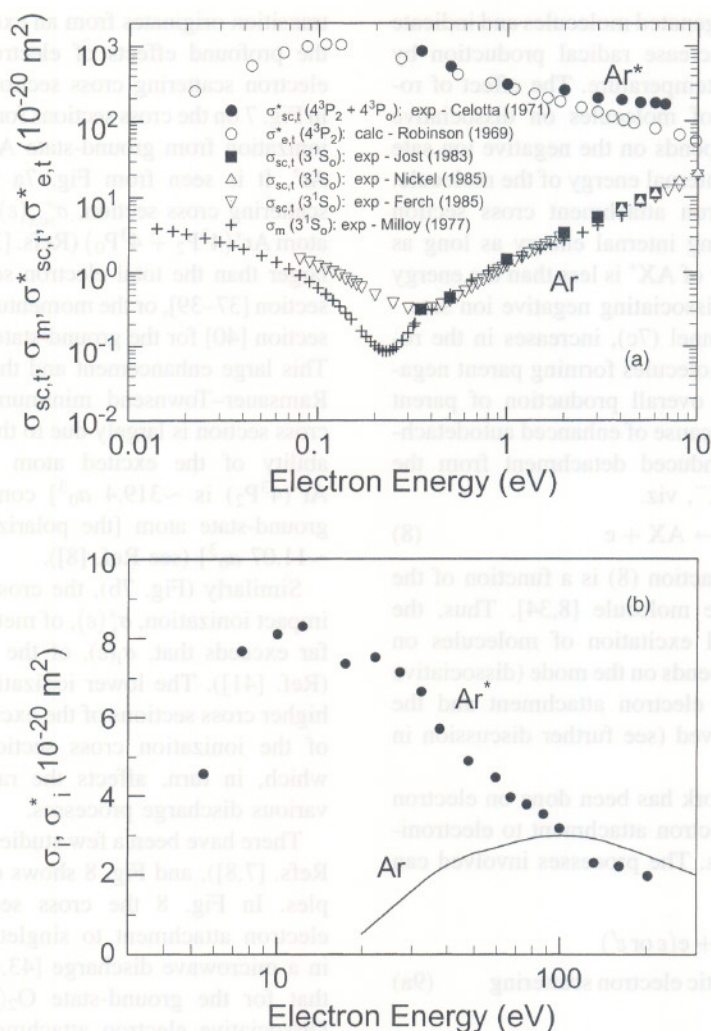
Fig. 7. (a) Comparison of the electron scattering cross section from the excited $Ar^*(4^3P_2 + 4^3P_0)$ and the unexcited $Ar(3^1S_0)$ argon atoms. $\sigma_{sc,t}^*(\varepsilon)(4^3P_2 + 4^3P_0)$: ($\bullet$) experimental measurements [32,35]; $\sigma_{e,t}^*(\varepsilon)(4^3P_2)$; ($\bigcirc$) calculated values [36]: $\sigma_{sc,t}(\varepsilon)(3^1S_0)$: experimental measurements: ($\blacksquare$) Ref. [37]; ($\triangle$) Ref. [38]; ($\triangledown$) Ref. [39]; $\sigma_m(\varepsilon)(3^1S_0)$: experimental measurements: (+) Ref. [40] (from Ref. [8]). (b) Cross section $\sigma_i^*(\varepsilon)$ for electron-impact ionization of metastable Ar^* (($\bullet$) measurements of Ref. [41]) in comparison with the respective cross section $\sigma_i(\varepsilon)$ for ground-state Ar ((—) measurements of Ref. [42]).

yet been undertaken and no reliable methods have as yet been devised to quantify the magnitude of the cross sections involved. There is a need for such knowledge.

4.3. Transient species (radicals)

With possibly the sole exception of electron-impact ionization of some radicals, the interactions of low-energy electrons with transient species are virtually unexplored. There have been some experimental measurements of the total and/or partial electron-impact ionization cross sections of radicals of interest to plasma processing (e.g., see Refs. [45–53]). There have also been some computations of the total electron-impact ionization cross sections [19,20]. Fig. 9 shows an example of the computed $\sigma_{i,t}(\varepsilon)$ for the SF_x $(x = 1-5)$ radicals [54]. To our knowledge, no measurements or computations of cross sections for the
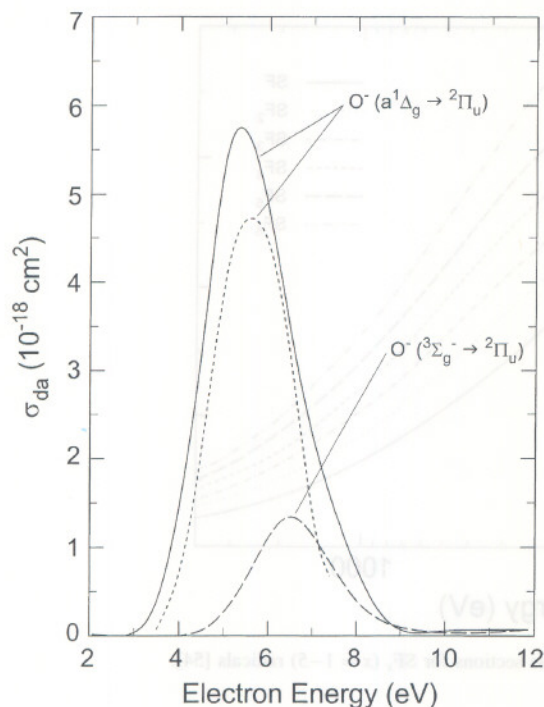
Fig. 8. Cross sections for the production of O^- by dissociative electron attachment to the ground-state $O_2(^3\sum_g^-)$ via the $O_2^{-*}(^2\Pi_u)$ resonance (– – –, Ref. [2]) and to the excited (singlet) $O_2^*(a^1\Delta_g)$ via the same negative ion resonance (—, Ref. [43]; - - -, Ref. [44]) (from Ref. [8]).

other basic electron scattering processes have been reported for transient species in plasma processing gases. Such knowledge is needed.

4.4. Reactions at surfaces and interfaces

Besides their dependence on the kinetic energy of the electron and the internal energy of the target molecule, the cross sections (and the energetics) of electron–molecule interaction processes are a function of the nature, density, and state of the medium in which they occur. While research on electron–molecule interaction processes at surfaces and interfaces is very limited, much insight can be gained from existing related knowledge that has been provided by similar studies in physics and chemistry on electron interactions and behavior in dense gaseous matter (e.g., Refs. [55–59]), liquids (e.g., Refs. [57–60]), layers of molecules deposited on cold surfaces (e.g., Refs. [59,61–63]), and clusters (e.g., see Refs. [59,64–66]).

For instance, such studies have shown that electron scattering, electron transport, NISs, electron attachment, ionization, recombination, and their energetics are among the physical quantities which are influenced, often profoundly, by the nature, density, and state of the medium. NISs while strongly influenced by the medium, occur in all states of matter. Their *formation* in the condense phase—as in gases—is localized in space and is dominated by short-range forces while their *decay* differs from that in the gas phase because it is affected by the medium due to polarization. Thus, a general effect of the medium on NISs is the lowering of the energy position of the NIS due to the polarization of the medium which surrounds the temporarily localized electron on the molecule and the resultant increase in the dissociative electron attachment cross section (see Fig. 10). Medium interactions may also affect the autodetachment lifetime of the transient anion, its decay channels (that is, indirect electron scattering processes), and may increase the number of NISs that contribute to indirect energy loss and dissociative electron attachment compared to the gas phase. Information on these and other aspects of the changes in electron–molecule interaction processes in going from the gaseous to the condense phase can be found in Ref. [59].

4.5. Electron energy losses

Along with the cross sections, computational models need the corresponding energy losses for the various processes, that is, the energy transferred to the gas per collision for each individual process. While often the energy threshold of the cross section for a given process is a measure of the electron energy— and, thus, the energy loss—required for that process (e.g., the energy thresholds of direct vibrational excitation or electronic excitations are roughly the difference between the excited and ground-state energy levels), the energy thresholds for dissociation processes are generally significantly larger than their thermodynamic values.

Moreover, since in plasma modeling both the size of the electron scattering cross section and the corresponding energy loss are significant, attention should be given to different energy losses connected with direct and indirect processes. For instance, the thresholds of indirect vibrational excitation of molecules are
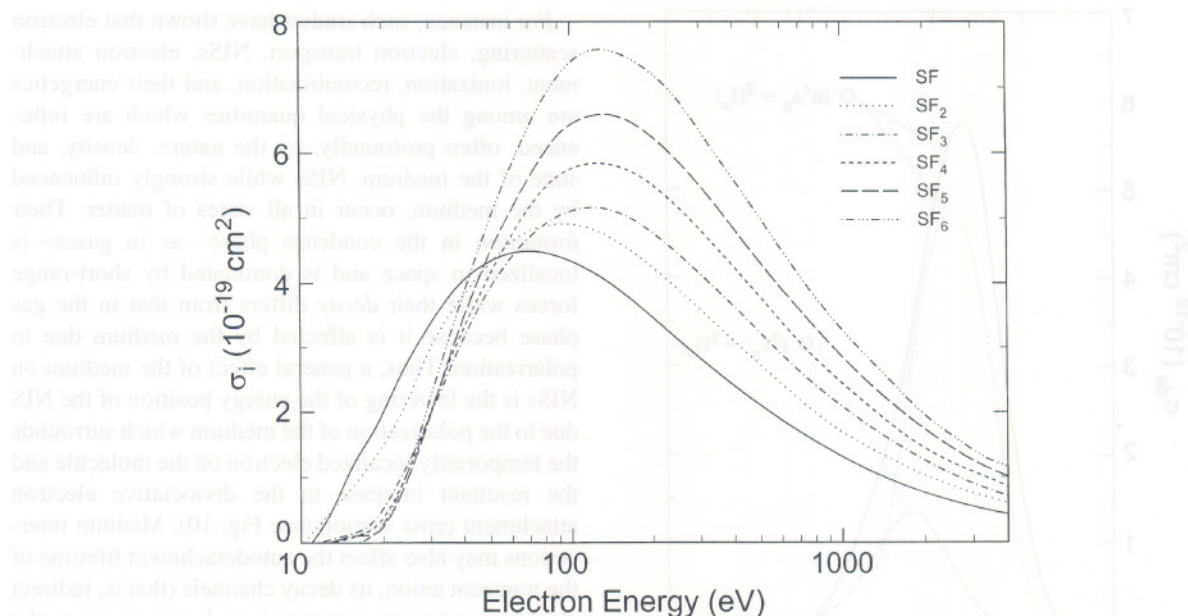
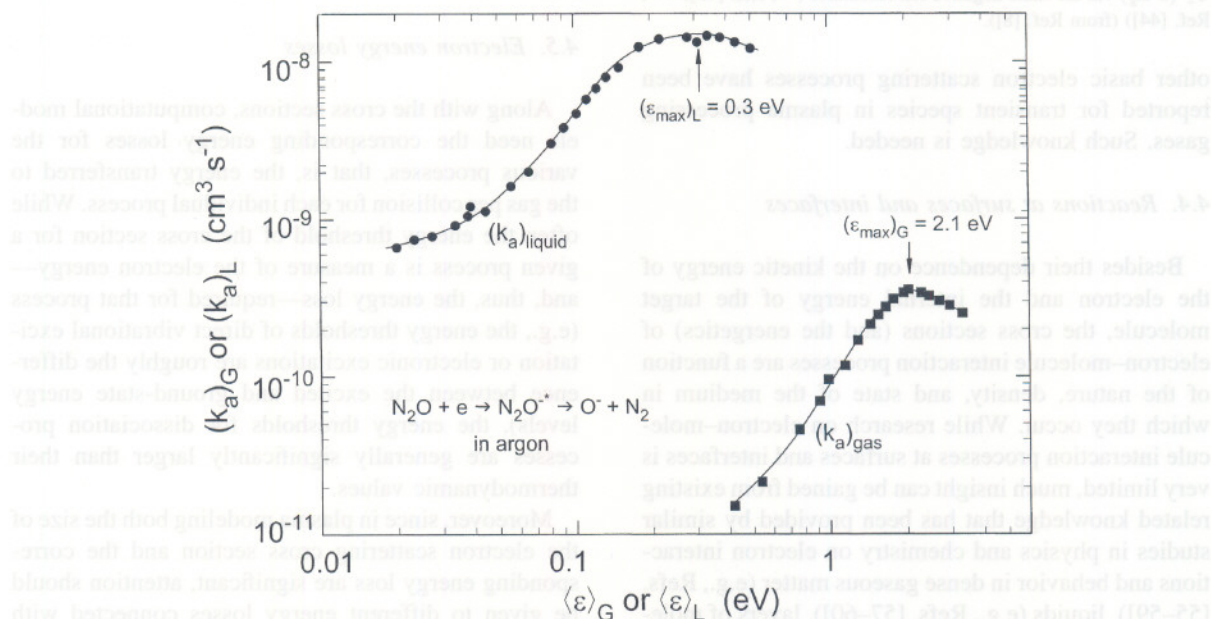Fig. 9. Calculated total electron-impact ionization cross sections for SF_x ($x = 1-5$) radicals [54].

Fig. 10. Rate constant for electron attachment to N_2O in gaseous ($(k_a)_G$) and liquid ($(k_a)_L$) argon plotted as a function of the respective, $\langle \varepsilon \rangle_G$ and $\langle \varepsilon \rangle_L$, mean electron energies [58].

determined by the positions of the negative ion resonances rather than by the vibrational thresholds themselves. The former can be much larger than the latter. Another aspect of the differences between direct and indirect processes is the proper consideration of the angular distribution of the scattered electrons in direct and indirect processes.

5. 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 provide a complete, yet concise, up-to-date review of data relevant to electron collision cross sections for these gases [21–28].

A much briefer summary of relevant data, containing primarily the recommended and suggested cross sections and coefficients for the plasma processing gases studied is also available on the World Wide Web at http://www.eeel.nist.gov/811/refdata. These data are updated as new measurements become available.

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