

ELECTRON COLLISION DATA FOR PLASMA CHEMISTRY MODELING

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I. Dedication

I dedicate this article to the late Professor Sir David R. Bates, F.R.S. (1916–1994), who was the founding editor of the *Advances in Atomic and Molecular Physics* series and my collaborator and mentor for the last dozen years of his life. David performed the original theoretical work on many of the atomic and

molecular processes that are directly involved in the plasma chemistries being discussed in this book. This list includes radiative recombination, dissociative recombination, collisional radiative recombination, bimolecular and termolecular ion-ion neutralization, and ion-molecule collisions. He was an early enthusiast for the use of digital computers in computing cross sections and rate coefficients for atomic and molecular collisions and in modeling such processes in ionized gases.

II. Introduction

The electron collision processes that occur in most laboratory plasmas are listed in Table 1.

The 300-K neutral gas pressures in plasma applications (excluding fusion plasmas) range from about 1 mtorr for the inductively coupled plasmas used in microelectronics processing applications to 1 to 10 torr for lighting applications to an atmosphere or more for excimer lasers or corona discharge processing of materials. The relative importance in a particular plasma of the various processes listed in Table 1 will depend upon the species of atoms or molecules present, the neutral gas density and temperature, the average electron energy, the distribution function, and the fractional ionization.

A major obstacle to accurate numerical modeling of plasma chemistry has been the lack of reliable electron collision cross-section data. Electron collisions drive the entire processing plasma chemistry and, hence, are among the most important and critical processes that we need to consider. In addition to cross sections for elastic scattering and momentum transfer, to which the electrical and thermal conductivities are directly related, it is necessary to consider all important

TABLE 1.
ELECTRON COLLISION PROCESSES IN PLASMAS

Collision type	Comments
Elastic/momentum transfer	Average energy loss equals approximately $2m/M$
Rotational excitation	Usually included in elastic because of small energy loss
Vibrational excitation	Cross sections often large; typically 0.1-0.25 eV energy loss
Electronic excitation/dissociation	Metastable excitation and dissociation are important to plasma chemistry
Ionization	May be dissociative
Attachment	Usually dissociative; negative ions are very important in plasma chemistry
Dissociative recombination	Often has a large rate coefficient and is an important electron loss process
Termolecular recombination	Collisional radiative recombination; important at high pressure
Termolecular attachment	May be important at high pressure

electron production and loss channels for ionization, attachment, and recombination, as well as inelastic electron energy-loss processes. Because the molecular gases most often used in plasma processing tend to be readily dissociated by electron collisions, densities of atomic and radical dissociation products are likely to be relatively large in high-density, low-pressure processing plasmas, and so electron collision cross sections for molecular and atomic targets are required.

For many of these processes, few measurements are available and the body of knowledge is very limited. Theoretical calculations have helped to fill some of the gaps in the database, but for some processes we must rely on estimates that come from either approximate models or analogies to other systems for which data are available.

III. Sources of Data and Interpretations

This section consists mostly of a discussion of how we are to interpret and reconcile the electron collision cross sections that we obtain from our three primary, but disparate, sources of such data and how these interpretations are related to the modeling and simulation for which we are assembling the basic collision data in the first place.

All our electron impact cross-section data arise from three sources:

1. Electron beam measurements (Christophorou, 1984), in which the textbook scattering experiment is performed whereby an electron beam is passed through a very low density gas and, we hope, either single scattering events are recorded as functions of scattering angle and incident electron energy or the excited or charged scattering products are observed.
2. *Ab initio* quantum theoretical calculations (Huo and Gianturco, 1995; Winstead and McKoy, 1999), in which Schrödinger's wave equation is solved in some approximation appropriate to the scattering problem and processes.
3. Electron swarm measurements (Huxley and Crompton, 1974), in which a burst of electrons is observed to drift along an electric field applied to a low-density gas and various transport coefficients, such as the drift velocity, transverse or longitudinal diffusion coefficients, attachment or ionization coefficients, and so on, are measured as functions of the applied electric field divided by the pressure or the gas number density (i.e., E/p or E/N); collision cross sections, which are related to the transport coefficients through Boltzmann's transport equation (Morgan, 1979; Morgan and Penetrante, 1990), can be extracted by a process of inversion.

Beam collision measurements represent the ideal for us in terms of potential quality of data, but they are the most scarce in terms of quantity. Many early beam measurements were of relative cross sections; nevertheless, they are useful when used in conjunction with calculations or swarm measurements. *Ab initio* calculations of electron impact cross sections for complex molecules, as discussed by Winstead and McKoy (1999), have become very sophisticated but require enormous computational resources for large molecules. The third technique has been in use for some three decades. There is a very large body of literature reporting on measurements and interpretations of electron transport or swarm coefficients in many of the same gases in which we are currently interested. This is an excellent technique, as I describe below, for estimating cross sections when no other data are available.

Whereas the beam and *ab initio* approaches directly yield cross sections from which we compute the transport coefficients that are used in modeling,

Cross sections \implies calculated transport coefficients

in the swarm approach, cross sections are themselves derived from measured transport coefficients (usually in carefully controlled experiments), as described by the sequence below:

Measured transport coefficients \implies cross sections

Cross sections \implies calculated transport coefficients

On the one hand, the cross sections that are derived from swarm data cannot be expected to possess the accuracy and detailed structure of good beam measurements or *ab initio* calculations, but, on the other hand, they naturally produce (if the procedure is carried out well) cross-section sets that accurately reproduce the macroscopic observables that are relevant to real plasmas. Such quantities are drift velocities or mobilities, which are directly connected with the power deposition in a discharge plasma, diffusion coefficients, and attachment and ionization coefficients, which are intimately related to the ionization balance of a plasma. These are the quantities that are used directly in most plasma models and that are measured in laboratory plasmas.

A. TRANSPORT COEFFICIENTS

The object of modeling plasma chemistry is to relate the external variables, such as discharge power or current, applied voltage, gas composition, pressure, temperature, discharge geometry, etc., which one can adjust in a laboratory device, to properties that are of interest, such as electron and ion densities, densities of excited or radical species, plasma radiation characteristics, etc. The electron impact processes in an ionized gas drive the plasma chemistry. In

modeling plasma chemistry, we use our knowledge of the microscopic physics of electron collisions with atoms and molecules to construct macroscopic transport coefficients, which are then used in rate equations and transport equations to predict discharge properties and species densities (Bukowski *et al.*, 1996).

The combined continuity and momentum and the energy fluid equations describing the transport of electron density and average energy in a plasma having gas density N_m , electron density N_e , and electron temperature T_e are

$$\frac{\partial N_e}{\partial t} = -\mathbf{V} \cdot \mathbf{\Gamma}_e + R_e \quad (1)$$

$$\frac{\partial}{\partial t} \left(\frac{3}{2} N_e k T_e \right) = -\mathbf{V} \cdot \mathbf{Q}_e - e \mathbf{E} \cdot \mathbf{\Gamma}_e + P_e + E_e \quad (2)$$

where \mathbf{E} is the electric field vector in the plasma and P_e is an external electron heating term, such as the period averaged inductive heating due to RF inductive coils external to the plasma (Jaeger *et al.*, 1995). Here $\mathbf{\Gamma}_e$ is the electron flux vector and \mathbf{Q}_e is the heat flux vector, which are given, respectively, by

$$\mathbf{\Gamma}_e = -D \nabla N_e - \frac{\sigma}{e} \mathbf{E} \quad (3)$$

and

$$\mathbf{Q}_e = \frac{5}{2} \mathbf{\Gamma}_e k T_e - \lambda_e \nabla (k T_e) \quad (4)$$

where σ^1 is the electrical conductivity, D is the diffusion coefficient, and $\lambda_e = \frac{5}{2} k N_e D$ is the thermal conductivity. R_e , the rate of gain or loss of electrons due to ionization, attachment, or recombination, is merely the product of the appropriate rate coefficient (defined below), the electron density, and a molecular density. E_e is the rate of energy gain or loss and is equal to the exo- or endothermicity of the reaction times the reaction rate. The definitions of the transport coefficients in terms of the microscopic electron collision cross sections follow.

The current density in a plasma is given by

$$\mathbf{j}_e = \sigma \mathbf{E} = e N_e \mu_e \mathbf{E} = -e N_e \mathbf{v}_d = -\frac{1}{3} e N_e \left(\frac{2e}{m} \right)^{1/2} \frac{\mathbf{E}}{N_n} \int_0^\infty \frac{df_0}{d\varepsilon} \frac{\varepsilon d\varepsilon}{\sigma_m(\varepsilon)} \quad (5)$$

¹ The Greek letter σ is used here to denote electrical conductivity. It is also used with the subscripts m , e , or i to denote momentum-transfer and elastic and inelastic electron collision cross sections, respectively. These are the standard notations.

where \mathbf{v}_d is the drift velocity and $f_0(\varepsilon)$ is the electron energy distribution function, which has units of $\text{eV}^{-3/2}$ and is normalized according to

$$\int_0^\infty f_0(\varepsilon)\varepsilon^{1/2} d\varepsilon = 1 \quad (6)$$

Since it is usually in the direction of the applied electric field, the drift velocity is usually denoted as the scalar v_d . $\sigma_m(\varepsilon)$ is known as the *momentum-transfer cross section* and is defined by

$$\sigma_m(\varepsilon) = 2\pi \int_0^\pi \frac{d\sigma_e(\varepsilon, \theta)}{d\theta} (1 - \cos \theta) \sin \theta d\theta \quad (7)$$

where $d\sigma_e(\varepsilon, \theta)/d\theta$ is the differential cross section for elastic scattering. The momentum-transfer cross section is also known in transport theory as the diffusion cross section. For a uniform differential cross section, i.e., $d\sigma_e(\varepsilon, \theta)/d\theta = \text{constant}$, the elastic and momentum-transfer cross sections are equal, i.e., $\sigma_m(\varepsilon) = \sigma_e(\varepsilon)$. When the differential cross section is strongly peaked in the forward direction, $\sigma_m(\varepsilon) < \sigma_e(\varepsilon)$, and when it is peaked in the backward direction, $\sigma_m(\varepsilon) > \sigma_e(\varepsilon)$.

Other transport coefficients are the transverse diffusion coefficient

$$D = \frac{1}{3N_n} \left(\frac{2e}{m} \right)^{1/2} \int_0^\infty f_0(\varepsilon) \frac{\varepsilon d\varepsilon}{\sigma_m(\varepsilon)} \quad (8)$$

and the rate coefficients for inelastic collisions

$$k_i = \left(\frac{2e}{m} \right)^{1/2} \int_0^\infty \sigma_i(\varepsilon) f_0(\varepsilon) \varepsilon d\varepsilon \quad (9)$$

Derived quantities often seen in the plasma literature are

1. The *characteristic energy* D/μ_e , where $\mu_e = v_d/E$ is the electron mobility, which has units of energy and is equal to the electron temperature T_e when the electrons have a Maxwell-Boltzmann distribution $f_0(\varepsilon) = (2/\sqrt{\pi}) \exp(-\varepsilon/kT_e)$; D/μ_e is a measure of how non-Maxwell-Boltzmann $f_0(\varepsilon)$ is.
2. The *ionization and attachment coefficients* $\alpha = k_{\text{ion}} N_n / v_d$ and $\eta = k_{\text{att}} N_n / v_d$, which have units of cm^{-1} and represent the increase or decrease in electron density per centimeter resulting from, respectively, ionization and attachment; these quantities are directly measurable in a drift tube.

B. OBTAINING CROSS SECTIONS FROM ELECTRON TRANSPORT DATA

The process of obtaining electron collision cross sections from electron swarm data involves inserting cross-section models in the collisional terms of Boltzmann's equation, calculating the distribution function and, hence, the swarm coefficients (Morgan, 1979; Morgan and Penetrante, 1990; Winkler, 1999), altering the model cross sections, and then iterating until an acceptable match between measured and computed coefficients is found. These techniques were developed by Phelps and various collaborators in the 1960s (see Phelps, 1968; Shkarofsky *et al.*, 1966; and Huxley and Crompton, 1974 for reviews of the methodology). One can also use numerical optimization techniques to manipulate the model cross sections (Taniguchi *et al.*, 1987; Morgan, 1991a; Morgan, 1991b; Morgan, 1993).

The so-called two-term expansion of Boltzmann's equation for transport of electrons in a dc electric field is typically used for swarm analysis. If one neglects the spatial and temporal dependence of the distribution function $f(\mathbf{r}, \mathbf{v}, t)$ in Boltzmann's equation and expresses $f = f(\mathbf{v})$ as the first two terms of a spherical harmonic expansion

$$f(\mathbf{v}) = f_0(v) + \frac{\mathbf{v}}{v} \cdot \mathbf{f}_1(v) \quad (10)$$

the following scalar equation for the energy distribution function $f_0(\varepsilon)$ (where $\varepsilon = mv^2/2$) in a gas having temperature T_g and density N_n and under the influence of a dc electric field E , is obtained:

$$\begin{aligned} & \frac{1}{3} \left(\frac{eE}{N_n} \right)^2 \frac{d}{d\varepsilon} \left(\frac{\varepsilon}{\sigma_m} \frac{df_0}{d\varepsilon} \right) + \frac{d}{d\varepsilon} \left\{ \left(\frac{2m\sigma_m}{M} \right) \varepsilon^2 \left[f_0(\varepsilon) + kT_g \frac{df_0}{d\varepsilon} \right] \right\} \\ & + \sum_i [(\varepsilon + \varepsilon_i) \sigma_i(\varepsilon + \varepsilon_i) f_0(\varepsilon + \varepsilon_i) - \varepsilon \sigma_i(\varepsilon) f_0(\varepsilon)] = 0 \end{aligned} \quad (11)$$

The transport equation for electrons is usually written in terms of electron energy because it is the energy loss ε_i that is quantized in inelastic collisions between electrons and atoms or molecules. Here it is assumed that the populations of the excited levels, labeled by i , are small enough that superelastic collisions and transitions among excited states are unimportant. If that is not the case, there is an additional sum over excited states having terms $[(\varepsilon - \varepsilon_i) \sigma_i(\varepsilon - \varepsilon_i) f_0(\varepsilon - \varepsilon_i) + \varepsilon \sigma_i(\varepsilon) f_0(\varepsilon)]$, which are multiplied by the fractional populations of the excited states. The electron collision cross sections involved are the momentum-transfer cross section $\sigma_m(\varepsilon)$ and the set of inelastic cross sections $\sigma_i(\varepsilon)$ for transitions from the ground state to the various excited states i . Note that the electric field and gas density enter only through the term containing E/N_n . This equation does a remarkably good job of describing the transport of electrons under the influence of an electric field in most gases. There

are, of course, more sophisticated treatments that go beyond the simple two-term spherical harmonic expansion. See the article by Winkler in this book for further details on Boltzmann's equation and its solution.

C. THE TRADITIONAL APPROACH IN GAS DISCHARGE MODELING

Most applications of swarm-derived cross sections in gas discharge modeling use what amounts to an effective momentum-transfer cross section. This is obtained by fitting calculated and measured electron swarm data and may include sizable inelastic contributions (Pitchford and Phelps, 1982). For this reason, the cross sections that are derived from swarm data may not agree with those that are separately measured in beam devices or computed using *ab initio* quantum techniques. The general wisdom is that this approach works well because the cross sections are derived by fitting exactly the same coefficients, i.e., drift, diffusion, ionization, attachment, etc., as are used in fluid models of discharge plasmas. This leads to a self-consistency that has worked well over the years.

D. THE ROLES OF BEAM DATA *AB INITIO* CROSS-SECTION CALCULATIONS, AND SWARM DATA

Modern high-vacuum beam measurement techniques and modern *ab initio* multichannel quantum calculations performed on supercomputers can provide very accurate cross sections for low-energy elastic and inelastic collisions. Often, however, when such data are assembled into a model for a molecule and transport calculations are performed, the agreement with measured transport, i.e., swarm, coefficients is poor. This leaves us somewhat dubious about the value of modeling a processing reactor using very detailed and correct cross sections if the model does not reproduce very accurately the plasma measurables in a well-defined, well-controlled swarm experiment. An easily conceivable example of this is one where we assemble a detailed model using what we consider to be accurate cross sections from disparate sources and find that the computed Townsend ionization coefficient α differs from that measured in a drift tube by an order of magnitude or more.

There are two reasons for such disagreements. First, the individual and independent errors (both in magnitude and in energy dependence) in the separate cross sections from different sources conspire to produce a possibly sizable overall error. Second, including all known cross sections does not necessarily mean including all possible collision processes. This is somewhat analogous to the missing matter problem in cosmology: All that we know may be only a fraction of what there is. This is where swarm analysis can make a very important contribution. By their nature, swarm-derived cross sections include all possible processes, either explicitly as individual cross sections or implicitly contained

within other cross sections. This is another reason why swarm-derived cross sections often differ from beam measurements and calculations.

The best procedure for dealing with the potential problem of a collection of cross sections producing erroneous plasma transport coefficients is to

1. Assemble the most complete models that we can, using data from the sources discussed above.
2. Perform swarm calculations for conditions appropriate to transport measurements when such data are available.
3. Systematically renormalize the cross sections in order to reproduce the measured transport coefficients.

E. VERIFICATION, VALIDATION, AND CONFIRMATION OF NUMERICAL PLASMA CHEMISTRY MODELS

Anyone who performs plasma chemistry modeling recognizes that cross sections and rate coefficients for an individual process are rarely used in isolation; rather, they are generally used as part of a model involving a number of other processes. An example of this can be seen in the schematic model for C_2F_6 plasma chemistry shown in Fig. 1. While not much is known about C_2F_6 plasma

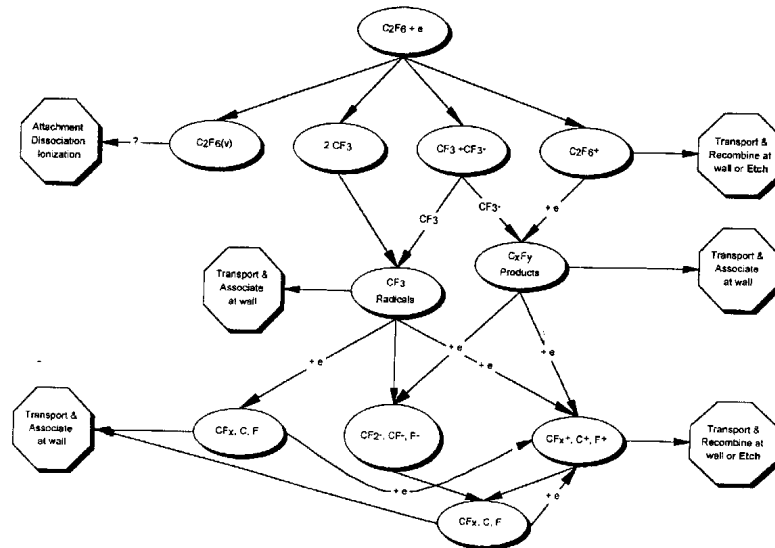


FIG. 1. Schematic diagram of a plasma chemistry model for C_2F_6 .

chemistry, this is a reasonable guess as to what the kinetic scheme might look like, although there are other possibilities as well. Key parts of the model are the cross-section sets for C_2F_6 and for the radicals that are formed when it is dissociated by electron impact.

The first step in constructing a plasma chemistry model in which one might have some confidence is to assemble a set of electron collision cross sections that can be shown to yield transport coefficients that are in agreement with swarm measurements. Such a cross-section set was assembled for C_2F_6 by Hayashi and Niwa (1987) and is shown in Fig. 2. The origin of the various cross sections is described by Hayashi and Niwa as follows:

1. Momentum transfer σ_m : The cross section was taken from those for CH_4 , C_2H_6 , and CF_4 and improved by analysis of swarm data.
2. Vibrational excitation σ_v : Born theoretical cross sections were used as the starting point and then were improved by swarm analysis.
3. Dissociation σ_{dn} : The measured total dissociation cross section σ_d of Winters and Inokuti (1982) was used, and σ_{dn} was determined from $\sigma_{dn} = \sigma_d - \sigma_i$.
4. Electronic excitation σ_e : The two electronic excitation cross sections were determined by analysis of swarm data.
5. Ionization σ_i : The cross section measured by Beran and Kevan (1969) was scaled by a factor of 0.79 based on swarm analysis.
6. Dissociative attachment σ_a : The cross section measured by Harland and Franklin (1974) was scaled by a factor of 2.21 and was made to coincide at 4 eV with the cross section derived by Hunter and Christophorou (1984).

This swarm analysis made use of the attachment and ionization coefficients and the drift velocity. Generally, however, the best swarm-derived cross sections are obtained when the transverse diffusion coefficient or the characteristic energy D/μ_e (equal to T_e for a Maxwell-Boltzmann distribution function) is used as well as the drift velocity. v_d and D sample different parts of the electron energy distribution function $f_0(\epsilon)$ and have different sensitivities to the momentum-transfer cross section $\sigma_m(\epsilon)$ in different energy ranges. Hence the most accurate cross sections are obtained when both of these transport quantities are available. Hayashi and Niwa made use of Hunter's D/μ_e data, but, unfortunately, the measurements were performed in a mixture of 90% CH_4 and 10% C_2F_6 . Since the cross sections for methane are not very accurate, the uncertainty in the cross sections derived from the characteristic energy measured in this mixture can be expected to be large.

Picasso said that "art is the lie that helps us see the truth." The same might be said of models and modeling. Oreskes *et al.* (1994) have discussed the concepts of verification, validation, and confirmation as they apply to numerical models of

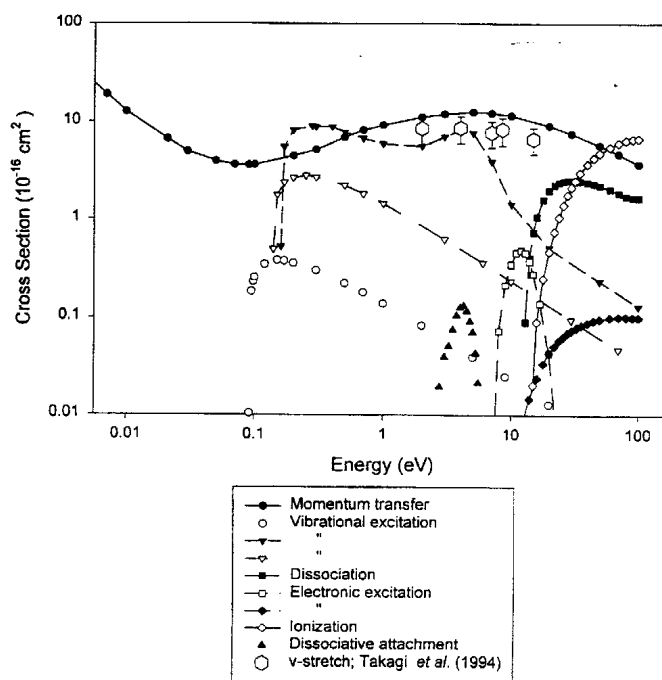


FIG. 2. Cross-section set for C_2F_6 assembled by Hayashi and Niwa (1987); the vibrational excitation cross sections measured by Takagi *et al.* (1994) are also shown.

physical phenomena. They point out that verification, a demonstration of truth, is not possible with numerical models. Confirmation, the framing of empirical observations as deductive consequences of a general theory, is not applicable to modeling. The authors regard a claim that a model has been verified because its results match observed data as being the logical fallacy of "confirming the consequent." The best that one can achieve is validation, or establishment of legitimacy, of models. That is, the model does not contain known flaws and is internally consistent, but it is not necessarily a representation of reality.

The C_2F_6 cross-section set shown in Fig. 2 provides very good agreement with measured swarm data. Despite this, there are more recent data of higher quality than those used to construct this cross-section set that, as shown below, differ substantially from these cross sections. Using these more recent data, one can construct (Morgan, 1998) a new C_2F_6 cross-section set that is different from that shown in Fig. 2 but that also agrees well with the swarm measurements. Hence, we must, in dealing with models and modeling, be aware of and live with the

uncertainty and lack of uniqueness of our models. This, however, should not hinder us in gaining valuable insights by constructing and using models.

IV. Discussion of Data for Specific Processes and Species

A. CROSS-SECTION SETS

Table 2 lists a number of atoms and molecules for which cross-section sets have been compiled or detailed cross-section reviews have been written. In Table 2, unless otherwise noted, the cross-section sets have been evaluated by comparison with electron transport data.

B. ELASTIC AND MOMENTUM-TRANSFER CROSS SECTIONS

Figure 3 shows the momentum-transfer cross section for C_2F_6 derived from swarm data by Hayashi and Niwa (1987) and the recent beam measurements by Takagi *et al.* (1994). Clearly the differences are substantial. Very recent unpublished calculations by Winstead and McKoy (1997) show much more structure than the measurements but agree quite well (see McKoy *et al.*, 1998 for a comparison of differential cross sections) with the Takagi *et al.* results, especially for the momentum-transfer cross section. These large differences in the momentum-transfer cross section imply, of course, that when constructing a cross-section set that will agree with the measured transport coefficients, one must modify other cross sections to bring things back into agreement.

An excellent example of the uncertainty that can be found in elastic or momentum-transfer cross sections is shown in the review of CF_4 cross sections by Christophorou *et al.* (1996). Elastic cross sections are difficult to measure using beam techniques below about 1 or 2 eV. At energies greater than 2 eV, most beam measurements in CF_4 are in good agreement, and theory also agrees well with these results. Below 2 eV, however, there are no absolute beam measurements, the theoretical results show no Ramsauer minimum, and the swarm-derived cross sections show a deep Ramsauer minimum but differ by nearly two orders of magnitude in the value of the cross section at the minimum. Recent *ab initio* calculations by Isaacs *et al.* (1998a) lend, for the first time, theoretical support for the Ramsauer minimum in CF_4 elastic scattering.

Generally, when one is constructing a cross-section set, one finds it necessary to make use of swarm results at low energies and measurements and theory at intermediate and high energies because the swarm-derived cross sections become more uncertain as inelastic channels open up.

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TABLE 2.
CROSS-SECTION SETS AVAILABLE FOR VARIOUS ATOMS AND MOLECULES

Species	Reference
N ₂	Phelps and Pitchford (1985); Hayashi (1987); Itikawa <i>et al.</i> (1986) ^a
O ₂	Phelps (1985); Itikawa <i>et al.</i> (1989) ^a
H ₂	Buckman and Phelps (1985); Tawara <i>et al.</i> (1990) ^a
CO	Land (1978)
CO ₂	Lowke <i>et al.</i> (1973); Hayashi (1990)
H ₂ O	Hayashi (1987); Yousfi and Benabdessadok (1996)
NO	Hayashi (1990)
N ₂ O	Hayashi and Niwa (1987)
SO ₂	Hayashi (1987)
NH ₃	Hayashi (1990); Yousfi and Benabdessadok (1996)
Hg	Rockwood (1973); Hayashi (1990)
O	Lafer and Gilmore (1990) ^{a,b} ; Itikawa and Ichimura (1990) ^{a,b}
F	Morgan (1998) ^b
Ar	Morgan and Tischenko (1997)
C ₂ H ₂	Hayashi (1990)
C ₂ H ₄	Hayashi (1990)
C ₂ H ₆	Hayashi (1987)
CH ₄	Morgan (1992b) ^d
SiH ₄	Morgan (1992b) ^d ; Perrin <i>et al.</i> (1996)
Si ₂ H ₆	Hayashi (1987)
Cl ₂	Morgan (1992a); Morgan <i>et al.</i> (1998)
F ₂	Morgan (1992a); Morgan (1998)
HCl	Morgan (1992a)
SF ₆	Phelps and Van Brunt (1988)
CF ₄	Morgan (1992b) ^d ; Bordage <i>et al.</i> (1996); Christophorou <i>et al.</i> (1996) ^a
C ₂ F ₆	Hayashi and Niwa (1987); Christophorou and Olthoff (1998a) ^a
CHF ₃	Christophorou <i>et al.</i> (1997a) ^a
CCl ₂ F ₂	Christophorou <i>et al.</i> (1997b) ^a
SiF ₄	Nagpal <i>et al.</i> (1995); Nagpal and Garscadden (1996) ^c ; Morgan (1998)
BCl ₃	Nagpal and Garscadden (1994) ^c ; Morgan (1998) ^c
HBr	Morgan (1998)
NF ₃	Morgan (1998)
BF ₃	Hayashi (1998)
C ₃ F ₈	Jeon and Nakamura (1998)

^a Comprehensive review without swarm analysis.

^b No swarm analysis because of lack of swarm data.

^c Partial results.

^d Review of previous work.

C. ELECTRON IMPACT IONIZATION AND DISSOCIATION

Dissociation, attachment, and ionization are among the most important inelastic electron collision processes that one needs to be able to treat in plasma chemistry modeling. The dissociation cross section is very difficult to measure directly but

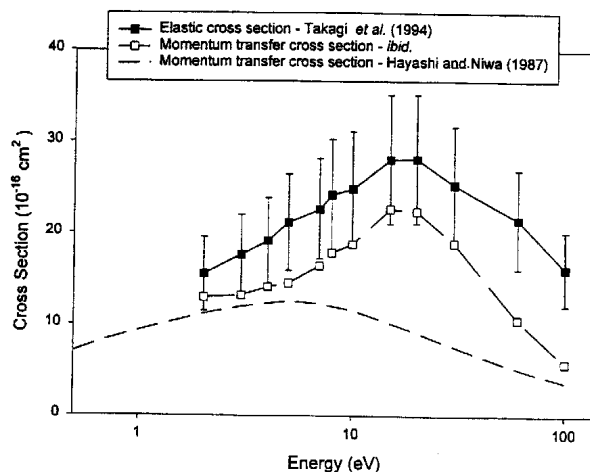


FIG. 3. C_2F_6 elastic and momentum-transfer cross sections.

can often be inferred from electron swarm data. The attachment rate, from which a cross section can be deduced, is easy to measure in a swarm apparatus. Ionization cross sections are relatively easy to measure using beam techniques. As discussed below, one can make use of beam-measured ionization cross sections and swarm-measured ionization coefficients in order to extract valuable information about the electronic excitation and dissociation cross sections.

1. Ionization

Perhaps the first comprehensive set of measurements, which is still widely used, of the ionization cross sections for a large number of gases,

H_2 , D_2 , He, Kr, CO, N_2O , CH_4 , H_2 , Ne, N_2 , Ar, CO_2 , Xe, SF_6 , C_2H_4

was performed by Rapp and Englander-Golden (1965). Beran and Kevan (1969) measured the ionization cross sections at 70 eV (and at 35 and 20 eV in some cases) of 62 gases. These were mostly organic and halogenated organic molecules. Since then, Freund and his collaborators (Freund, 1987; Wetzel *et al.*, 1987; Hayes *et al.*, 1987; Shul *et al.*, 1988; Hayes *et al.*, 1988; Shul *et al.*, 1989; Freund *et al.*, 1990a; Freund *et al.*, 1990b; Shul *et al.*, 1990) have performed ionization cross-section measurements on many gases, as have Becker and his collaborators (see Becker, 1999, and references contained therein; Becker, 1994; Becker and Tarnovsky, 1995). Unlike their predecessors, Freund's and Becker's groups have

measured ionization cross sections of radical fragments as well as the parent molecule.

The trend in recent years has been not only to provide total ionization cross-section data but to measure the partial cross sections for dissociative ionization. An example is shown in Fig. 4 for C_2F_6 . These are important data for modeling in that they show that the dominant ionization product is CF_3^+ .

Figure 4 also shows the ionization cross section, which is nearly indistinguishable from the measured total cross sections, computed by Nishimura *et al.* (1998) using the binary encounter Bethe (BEB) technique (Kim and Rudd, 1994; see also Winstead and McKoy, 1999). This technique, which is relatively straightforward, provides generally accurate total ionization cross sections. Kim and his collaborators (Kim and Rudd, 1994; Hwang *et al.*, 1996; Kim *et al.*, 1997a; Kim *et al.*, 1997b; Ali *et al.*, 1997; Nishimura *et al.*, 1998) have used this theory to compute the ionization cross sections for a large number of molecular species:

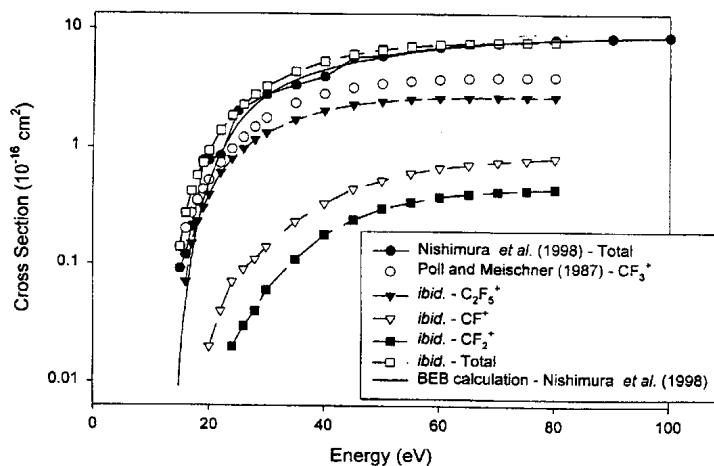
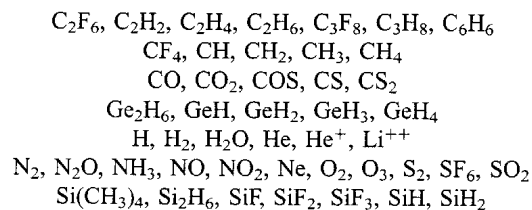


FIG. 4. Total and partial cross sections for ionization of C_2F_6 .

These cross sections are all presented on his Web site, which is mentioned at the end of this article. The BEB technique does well on ionization cross sections of some of these radicals that have been measured, leading us to expect that it may provide reasonable estimates of the total ionization cross sections of radical species for which we have no measurements.

a. Detachment: Ionization of Negative Ions. A process that can be important in electronegative plasmas of high fractional ionization is collisional detachment of negative ions. The detachment cross sections for H^- , C^- , O^- , and F^- were systematically measured by Peart *et al.* (1970, 1979a, 1979b, 1979c) in the 1970s. More recent measurements (Vejby-Christensen *et al.*, 1996) on O^- and D^- using an ion storage ring have investigated the near-threshold behavior and the possible existence of resonances, which were not found. Pindzola (1996) has performed distorted wave calculations on detachment of O^- and D^- and has gotten reasonable agreement with the storage ring measurements. He did find, however, that his results are very sensitive to the choice of polarization potential.

Fortunately, useful simplifications can be found. Robinson (1965) describes a modification of the classical impulse approximation using Slater's rules to estimate the average kinetic energy of the bound electron. Esaulov (1980) notes that a plot of $\sigma(\varepsilon)E_a^2$ versus ε/E_a , where E_a is the electron affinity of the neutral atom, provides an approximate universal curve for the detachment cross section.

2. Electronic Excitation and Dissociation

One of the most important features of using plasmas for processing is the copious quantity of radical fragments created by molecular dissociation. The ability to predict the densities of radical species in a plasma is one of the major goals of modeling. Because large molecules have a very great number of electronic excitation channels and many repulsive potential curves, once an electron excites an electronic transition, there are many paths available that lead to dissociation. For big molecules, one can expect that most electronic excitation will lead to dissociation. Measurement of the cross sections for electron impact dissociation of molecules into neutral ground-state fragments is, unfortunately, difficult. There have been relatively few such measurements published in all the electron collision literature. Although cross sections for dissociative excitation of molecules are relatively easy to measure, such processes often have much higher excitation thresholds and smaller cross sections than dissociation into ground-state fragments.

The difficulty of neutral dissociation cross-section measurements can be seen in the Christophorou *et al.* (1996) review of CF_4 , where the neutral dissociation cross-section measurements span an order of magnitude in peak value, have very

different energy dependences, and fall well below the cross section deduced from swarm data. Similarly, in their review of CHF_3 cross sections, Christophorou *et al.* (1997a) estimate a total neutral dissociation cross section by subtracting the measured total ionization cross section from the total dissociation cross section (i.e., including dissociative ionization) measured by Winters and Inokuti (1982) and find that it is much larger than and has a completely different energy dependence from the neutral dissociation measurements published by Goto *et al.* (1994) and by Sugai *et al.* (1995). Although such a subtraction potentially has quite large errors associated with it, the striking differences are not due to such errors.

Modern sophisticated electron-molecule collision theory, like that described by Winstead and McKoy in this volume, can be very useful in providing insight into the magnitude and energy dependence of dissociation cross sections. Such calculations have been performed, for example, for NF_3 by Rescigno (1995) and represent some of the best data that we have for that molecule. Similarly, McKoy *et al.* (1998) have computed a dissociation cross section for CHF_3 and have obtained a result that is much more like that deduced by Christophorou *et al.* (1997a) in the review mentioned above than like the cross sections measured by Goto *et al.* (1994) and by Sugai *et al.* (1995).

Perhaps the best means of obtaining a realistic value for a composite dissociation cross section is to make use of swarm data and ionization cross-section data. The procedure works as follows. One assembles a set of low-energy cross sections and adjusts it to agree with drift velocities, characteristic energies, and attachment coefficients, if the attachment cross section is large. Then one postulates an electronic excitation-dissociation cross section having the correct threshold and energy loss. One can either use a model cross section and adjust the magnitude or adjust the energy dependence and magnitude of the dissociation cross section in order to match the ionization coefficient. This is very effective if one has good ionization cross sections because the ionization coefficient

$$\eta \propto \frac{1}{v_d} \int \sigma_i(\varepsilon) f_0(\varepsilon) \varepsilon^{1/2} d\varepsilon$$

depends not only on the ionization cross section (presumably well known) but on the distribution function $f_0(\varepsilon)$, which is, via Boltzmann's equation, a function of the cross sections at energies less than ε . This is how Hayashi and Niwa (1987) arrived at the dissociation cross sections for C_2F_6 shown in Fig. 5.

The utility of such techniques can be seen in Fig. 6, where I have plotted various measured and swarm-derived cross sections for electron impact dissociation of molecular nitrogen. Winters (1966) and Cosby (1993) have measured the cross section for dissociation of N_2 in electron collisions. Winters measured the total dissociation cross sections [as we have seen previously in the Winters and Inokuti (1982) measurements of dissociation of C_2F_6] and subtracted the

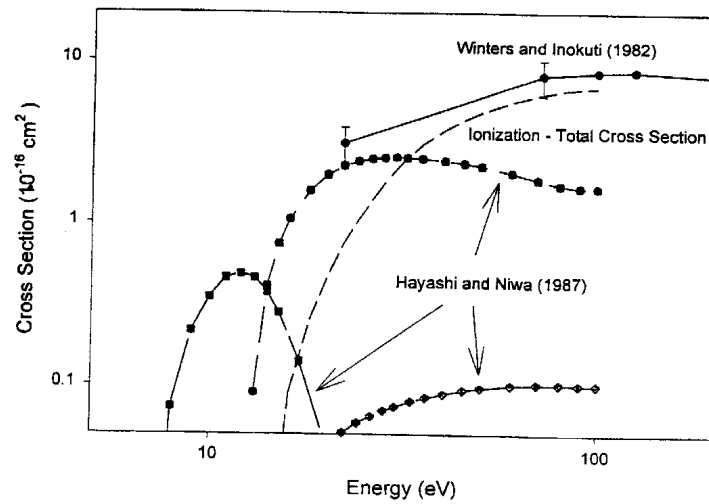


FIG. 5. Total dissociation cross section (Winters and Inokuti, 1982; Hayashi and Niwa, 1987), total ionization cross section, and swarm-derived dissociation cross sections for C_2F_6 .

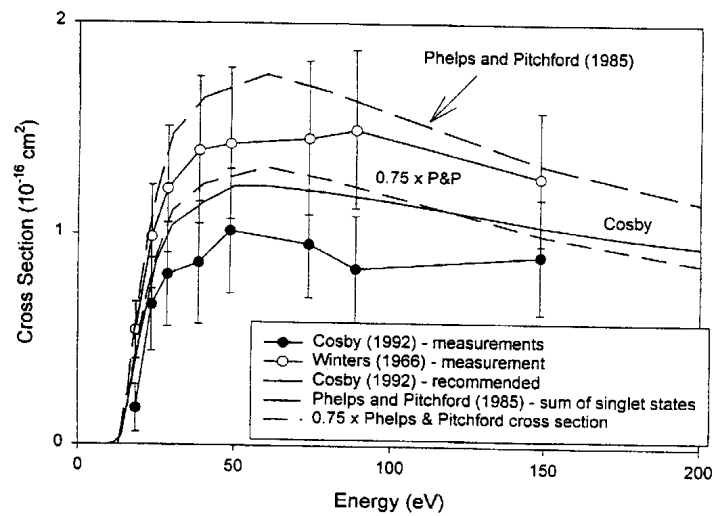


FIG. 6. Dissociation cross sections for N_2 .

measured total ionization cross section. Cosby used a crossed beam apparatus with microchannel plate detection to measure the dissociation cross section directly. Also shown in Fig. 6 along with Cosby's recommended dissociation cross section is the total cross section for the sum of the singlet excitations used by Phelps and Pitchford (1985) in their cross-section set. This last multiplied by a scale factor of 0.75 is also plotted in Fig. 6.

In addition to the CF_4 and C_2F_6 cross sections already mentioned, Winters and Inokuti (1982) measured total dissociation cross sections for CHF_3 and C_3F_8 . Similarly, in addition to N_2 , Cosby and Helm (1992) measured dissociation cross sections for O_2 , CO , CO_2 , Cl_2 , and NO_2 . Motlagh and Moore (1998) recently measured absolute total dissociation cross sections for the production of CF_3 , CH_3 , C_2F_5 , CH_2F , and CHF_2 radicals from CH_4 , CF_4 , CHF_3 , CH_2F_2 , CH_3F , C_2F_6 , and C_3F_8 for electron impact energies between 10 and 500 eV. When good measurements of dissociative ionization cross sections are available, total dissociation cross-section measurements, such as those of Motlagh and Moore, can be invaluable.

D. ATTACHMENT

Formation of negative ions is often very important in processing plasmas. It is very common in plasmas containing halogenated molecules. Common examples are Cl_2 , F_2 , NF_3 , BCl_3 , HCl , HBr , HF , and *cyclo*- C_4F_8 as well as oxygen-containing molecules such as O_2 itself, H_2O , SO_2 , and N_2O . A terrific amount of work in measuring the attachment rates and cross sections for a very large number of molecules was done at the Oak Ridge National Laboratory over a 25-year period beginning in the mid-1960s. This work through the early 1980s has been summarized in a book by Christophorou (1984). Smith and Spanel (1994) and Chutjian *et al.* (1996) have reviewed recent advances in attachment theory and experimental techniques.

1. Dissociative Attachment and Vibrational Excitation

A number of molecular species, such as NF_3 , HCl , HBr , HF , and N_2O , exhibit strong dependence of attachment rate on temperature. This comes about because the dissociative attachment cross section increases with increasing vibrational quantum number (see Christophorou *et al.*, 1994). This can be seen in the temperature dependence of the N_2O dissociative attachment cross section shown in Fig. 7a, and its effect on the attachment rate coefficient can be seen in Fig. 7b. The attachment cross section (Christophorou *et al.*, 1971), where the products are $\text{NO} + \text{O}^-$, is very temperature-dependent (Chantry, 1969), as shown in Fig. 7b, which means that it is very sensitive to the degree of vibrational excitation. In a plasma, one does not need an elevated gas temperature to populate the molecular

vibrational levels. In N_2O , for example, the lower vibrational levels have energies of 0.073, 0.159, and 0.276 eV with statistical weights of 2, 1, and 1, respectively. They would be expected to be populated at a fairly high vibrational temperature in a plasma as a result of electron collisions. At atmospheric gas pressures, the vibrational levels may be depopulated because of vibrational-to-translational energy transfer processes. At pressures on the order of torr, the vibrational temperature can be elevated as a result of anharmonic pumping. At the very low millitorr pressures found in inductively coupled processing plasmas, the vibrational temperatures may be expected to be on the order of the electron temperature. As we have seen, in some gases this can lead to very large dissociative attachment rates.

Christophorou and Stockdale (1968) published a diagram that is sometimes useful in assessing whether or not a given molecule might be expected to have a

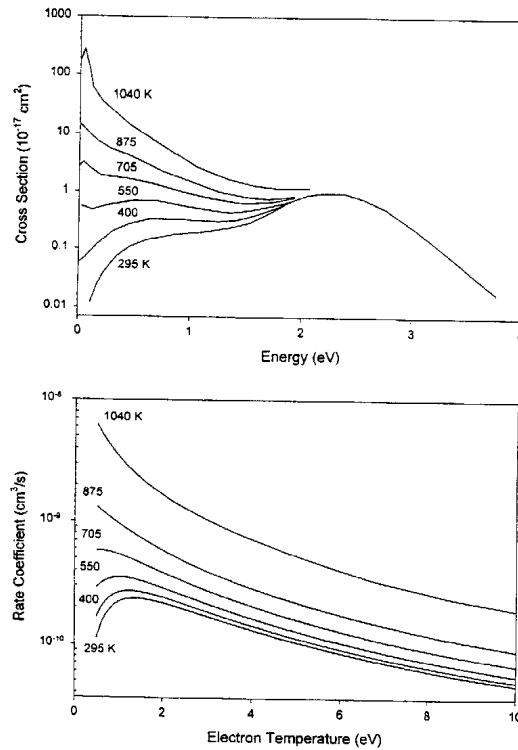


FIG. 7. (a) Temperature dependence of effective dissociative attachment cross section in N_2O ; (b) temperature dependence of dissociative attachment rate coefficient.

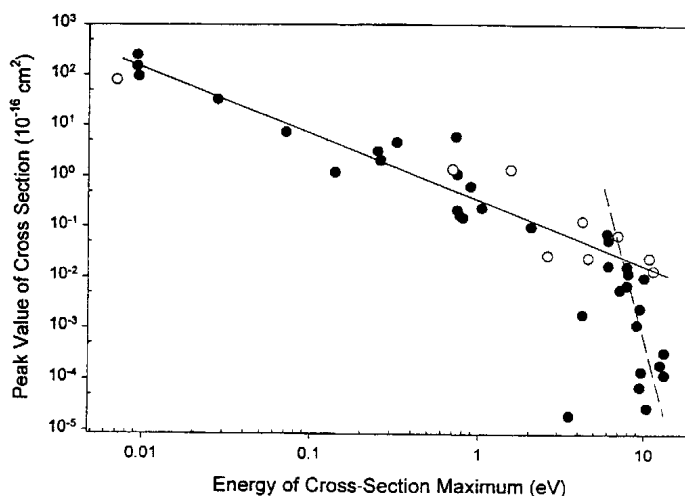


FIG. 8. Correlation between the peak values of dissociative attachment cross sections and energies of the cross-section maximum.

significant dissociative attachment cross section. Figure 8 plots the peak value of the dissociative attachment versus the energy of the cross-section maximum for a large number of molecules. The curve turns down above about 5 eV as a result of the competing channels of electronic excitation. Using thermochemical data and electron affinities, one can use this correlation diagram to very roughly estimate the possible significance of dissociative attachment in a particular molecule.

2. Transient Attachment and Long-Lived Negative Ions

Some molecules, such as BCl_3 and $c\text{-C}_4\text{F}_8$, are able to attach an electron and form a long-lived negative-ion complex (Christophorou, 1978). The interpretation of electron attachment data is made difficult in such gases because the measured attachment coefficient η/N becomes a function of pressure as well as of the size of the experimental apparatus. In the following I will describe attachment issues in BCl_3 .

There have been four quantitative measurements of the attachment cross section or the attachment rate coefficient in BCl_3 since 1959:

1. Buchel'nikova (1959) performed a direct measurement of the electron attachment cross section for energies between 0 and 1 eV using an electron beam apparatus.

2. Stockdale *et al.* (1972) performed a measurement of the attachment rate coefficient by thermal electrons in an N_2/BCl_3 mixture.
3. Petrovic *et al.* (1990) measured the rate coefficients for low-energy electron attachment to BCl_3 , as functions of E/N , electric field divided by gas number density, in an electric discharge in an N_2/BCl_3 mixture.
4. Tav *et al.* (1998) very recently measured the attachment rate of electrons in an N_2/BCl_3 mixture and derived an attachment cross section.

The Stockdale *et al.* rate coefficient measurements were performed at gas pressures in the range from 5 to 15 torr, and those of Petrovic *et al.* over the range 100 to 400 torr. The rate coefficient was observed to be independent of pressure in both measurements. The Tav *et al.* measurements were performed at 700 torr.

The possible plasma chemical processes involving BCl_3 in these measurements are

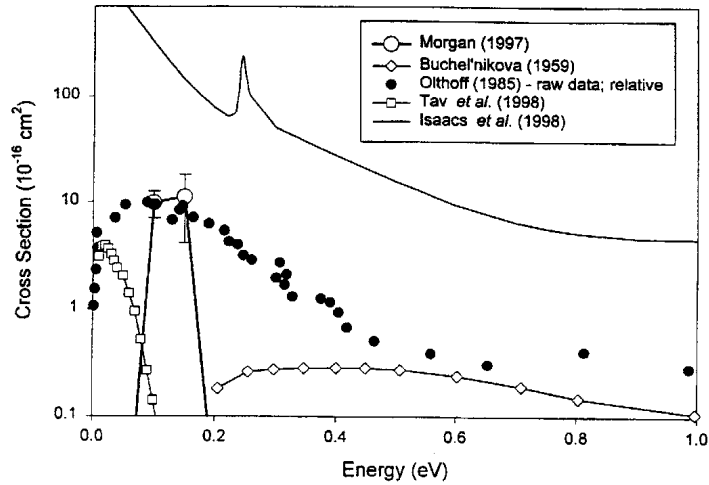
1. $e + BCl_3 \rightarrow BCl_3^*$
2. $BCl_3^* \rightarrow BCl_3 + e$
3. $BCl_3^* + N_2 \rightarrow BCl_3^- + N_2$
4. $e + BCl_3 \rightarrow BCl_2 + Cl^-$

Here BCl_3^* is the metastable negative ion state that eventually autodetaches or is stabilized by a collision with a molecule of the background gas. The electron affinity of BCl_3 is 0.33 eV, which is some 13 kT at 300 K. The energy threshold for the fourth dissociative attachment process is about 1 eV. The relative cross section for this process has recently been measured by Jiao *et al.* (1997). Looking at the correlation curve shown in Fig. 8, we would expect the dissociative attachment cross section to be relatively small. Tav *et al.* estimate the cross section to be smaller than about $5 \times 10^{-18} \text{ cm}^2$, which is the smallest cross section that can be detected with their apparatus.

Figure 9 shows the attachment cross section that I derived (Morgan, 1997) from Petrovic's data along with that derived by Tav *et al.* from their data, that measured by Buchel'nikova, and the raw data from a relative measurement by Olthoff (1985). Based on his experimental geometry, Olthoff estimated the autodetachment lifetime of BCl_3^* to be about 60 μs . Since Buchel'nikova performed her measurements nearly 40 years ago, before the advent of modern high-vacuum techniques, her measurements are suspect. Christophorou and Stockdale (1968) have noted that there are large discrepancies between her measured cross sections for a wide variety of molecules and more recent measurements. Figure 9 also shows the BCl_3 momentum-transfer cross section recently computed by Isaacs *et al.* (1998b), which shows a sharp temporary negative-ion resonance at 0.25 eV.

The attachment cross section for the formation of BCl_3^* has several consequences for plasma chemistry as well as for the interpretation of the other swarm

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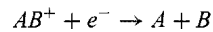
FIG. 9. BCl_3 attachment and momentum-transfer cross sections.

measurements and derived cross sections. With regard to the plasma chemistry of plasma processing discharges, the cross section and rate coefficient are large enough that, even without the formation of Cl^- and Cl_2^- , we can expect a reasonable negative ion density. The $60 \mu\text{s}$ autodetachment lifetime of BCl_3^* is long enough for it to be stabilized to BCl_3^- by collisions with neutral atoms and molecules even at a pressures of several millitorr. Because the attachment cross section is large, overlaps the BCl_3 vibrational excitation thresholds, and lies in the energy range of the Ramsauer minimum of Ar, it and the quite large momentum-transfer cross section may be expected to play a crucial role in the derivation of BCl_3 inelastic cross sections from drift velocities measured in Ar/ BCl_3 gas mixtures as has been done by Mosteller *et al.* (1993) and Nagpal and Garscadden (1994).

E. RECOMBINATION

1. Dissociative Recombination

In most molecular gases, dissociative recombination (Bates, 1950; Bardsley, 1968; Biondi, 1976; Biondi, 1982)



is the dominant volumetric electron loss process. The dissociative recombination cross section is a product of two factors:

$$\sigma_{dr}(\epsilon) = \sigma_c(\epsilon)S$$

where $\sigma_c \propto 1/\epsilon$ is the *capture* cross section and S is the *survival* factor, which is related to the curve-crossing probability. The rate coefficient at thermal energies, except in those rare cases for which there are no accessible crossings of the ionic and predissociating repulsive neutral curves, is typically in the range 10^{-7} to 10^{-6} cm^3/s with a dependence on electron temperature of $T_e^{-1/2}$.

The dissociative recombination rate coefficients have been measured for a number of molecular ions, although few of the ions are species that we expect to find in the processing discharges of interest here. Dissociative recombination is a curve-crossing process and, typically, has large rate coefficients, on the order of 10^{-8} to 4×10^{-7} cm^3/s (or even much greater for molecular clusters) at 300 K. The following table (Mitchell, 1990) lists the rate coefficients for species that might be of interest in plasma processing.

Species	k_r (cm^3/s)
$\text{H}_2^+(v=0)$	$1.6 \times 10^{-8}(300/T)^{0.43}$
$\text{N}_2^+(v=0)$	$3.6 \times 10^{-8}(300/T)^{0.42}$
O_2^+	$1.95 \times 10^{-7}(300/T)^{0.7}$
CO^+	$1.0 \times 10^{-7}(300/T)^{0.46}$
CO_2^+	3.8×10^{-7}
H_2O^+	$3.15 \times 10^{-7}(300/T)^{0.5}$
OH^+	$3.75 \times 10^{-8}(300/T)^{0.5}$
NO^+	$4.3 \times 10^{-7}(300/T)^{0.37}$
NH_3^+	$3.1 \times 10^{-7}(300/T)^{0.5}$
NH_2^+	$3.0 \times 10^{-7}(300/T)^{0.5}$
NH^+	$4.3 \times 10^{-8}(300/T)^{0.5}$
CH_4^+	$3.5 \times 10^{-7}(300/T)^{0.5}$
CH_3^+	$3.5 \times 10^{-7}(300/T)^{0.5}$
CH_2^+	$2.5 \times 10^{-7}(300/T)^{0.5}$
CH^+	$1.5 \times 10^{-7}(300/T)^{0.42}$
C_2H^+	$2.7 \times 10^{-7}(300/T)^{0.5}$
C_2H_2^+	$2.7 \times 10^{-7}(300/T)^{0.5}$
C_2H_3^+	$4.5 \times 10^{-7}(300/T)^{0.5}$
C_3H_3^+	1.0×10^{-7}
C_3H_5^+	3.5×10^{-7}
C_4H_3^+	6.2×10^{-7}
C_2H_5^+	7.4×10^{-7}

Such rate coefficients are usually measured in thermal systems, where the electron temperature is equal to the gas temperature. In modeling plasmas, one

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typically uses the electron "temperature" $T_e = 2(\epsilon)/3$, instead of the gas temperature T . Vibrational excitation can affect the overall rate coefficient and the temperature dependence. For example, when all vibrational levels are included, the dissociative recombination rate coefficients for H_2 and N_2 are $2.3 \times 10^{-7}(300/T)^{0.4}$ and $1.8 \times 10^{-7}(300/T)^{0.39}$, respectively, i.e., a number of times larger than the rate for the lowest ($v = 0$) vibrational level.

2. Collisional Radiative Recombination

At high gas pressures, the dominant volumetric electron loss process is often what is known as collisional radiative recombination. This is a multistep process whereby an electron is captured by an ion and collisionally stabilized into a Rydberg state by either a neutral or a charged third body. Further collisions on average drive electrons to lower levels, where, at some particular level called the bottleneck, radiative rates exceed collision rates and electrons drop down to a stable ground state. A number of authors, beginning with Bates, Kingston, and McWhirter (1962), have modeled this process in detail, using manifold levels, cross sections, and radiative rates.

For many practical purposes, the process can be simplified into a single formula for the net recombination rate as a function of gas density, electron density, and electron temperature (Flannery, 1996):

$$e^- + A^+ + e^- \rightarrow A + e^- : k = 2 \times 10^{-27} T_e^{-9/2} \text{ cm}^6/\text{s}$$

$$e^- + A^+ + M \rightarrow A + M : k = \frac{10^{-30}}{\mu} T_e^{-5/2} \text{ cm}^6/\text{s}$$

where μ is the reduced mass in amu of the molecular collision partners and T_e is the electron temperature in eV.

3. Recombination at High Gas Pressures: Inelastic Enhancement of Dissociative Recombination

It was found experimentally by Warman *et al.* (1979) and by Armstrong *et al.* (1982) that in some molecular gases at pressures ranging from 100 torr to several atmospheres, the dissociative recombination rate coefficient is enhanced by termolecular effects. This was simulated for electrons in H_2O , NH_3 , and CO_2 by Morgan and Bardsley (1983) and by Morgan (1984a, 1984b) using numerical Monte Carlo techniques. The effect comes about because of the large low-energy inelastic collision cross sections in these gases. H_2O and NH_3 are both strong dipoles having very large rotational excitation cross sections, and CO_2 has a large vibrational excitation cross section at 0.083 eV \simeq 3 kT. When an electron has a collision with one of these molecules while in the vicinity of a molecular ion, it

can lose a significant enough amount of energy to enhance its probability of recombining dissociatively with the molecular ion. This process has been called *collisional dissociative recombination* by Bates (1980, 1981). At present there is no simple general theory of the process.

V. Concluding Remarks: Journals, Databases, and the World Wide Web

A. ISSUES CONCERNING THE DISSEMINATION OF DATA

As can be seen from the bibliography, most data discussed in this article are available either in the standard physics and chemistry journals or in conference proceedings, which may be more difficult to obtain than are journals. A number of the works cited in this article are at present unpublished but sooner or later will appear in the literature. Comprehensive review papers are rare in this field, and there is no single data center or repository that covers the field. There once was such a data center at the Joint Institute for Laboratory Astrophysics (JILA) in Boulder, Colorado, but it closed in the mid-1990s after more than 25 years of operation. At the time of its closing, the JILA Data Center had a computerized database and library of papers on microfiche that comprised more than 22,000 entries. Operating such a data center is a formidable enterprise that, it appears, few organizations are willing to support. Fortunately there were a number of reports and bibliographies that were published by the JILA Data Center that are still very useful today, although they are becoming increasingly difficult to obtain as time goes on.

It appears that the World Wide Web is fast becoming a kind of global database that is readily accessible from anywhere in the world by anyone having an account on the Internet. In a panel discussion at a recent conference on atomic and molecular data, Smith *et al.* (1998) pointed out that the “classic database, a book with limited availability containing data critically evaluated by experts, is gradually becoming obsolete.” As a forum for dissemination of atomic and molecular data, this trend of posting data on the Web is not without controversy. There are frequent discussions—at conferences [see, for example, Mohr and Wiese (1998)] and in journals and trade magazines—of the use and possible misuse of the Web. Indeed, in a mixed state of optimism and pessimism, Heller (1996) entitled one such discussion “Chemistry on the Internet—the Road to Everywhere and Nowhere.”

The two major concerns about the Web as a universal database seem to be

1. The lack of standards and review and assessment by experts in the field
2. The often transient nature of Web sites, which makes true archiving and future referencing of data problematical

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Despite these valid concerns, the Web will continue to increase in importance as the medium of choice for both formal and informal dissemination, exchange, and even publication of data. People have always exchanged data informally and have always been aware that, even when using data from refereed publications, they must beware of bad data. Publication of data in a refereed journal is no guarantee that the data are of high quality or even correct. The stories are legion of papers that accumulate a large number of citations because they have significant errors or are wrong.

That Web sites posting data may be short-lived is, in many ways, no different from publishing data in proceedings or, for that matter, even books. Indeed, I have cited in this article a number of sources of data that, frankly, may be difficult for some readers to obtain.

B. USEFUL WEB SITES

There are a number of sponsored data centers in the world that deal, in varying degrees, with the kinds of atomic and molecular data that would be of interest to the users of this book. They all have found the Web to be the dissemination medium of choice. In addition, there are a number of informal sites that I list here as well. Despite the potential deficiencies referred to above, the Web has become the dominant medium for data dissemination and exchange by scientists worldwide, and this article cannot be complete without a listing of some of the important data sites on the Web. Even if the URLs (universal resource locators) of the sites change or disappear altogether, I have listed the institutions responsible for the sites. Just as people interested in the numerical solution of Boltzmann's equation have been able to locate me 20 years after JILA Report No. 19 (Morgan, 1979) appeared, despite the moving around that I have done in that time, the authors of these Web sites may be locatable for some time to come.

1. "Databases for Atomic and Plasma Physics," maintained by Yuri Ralchenko, Weizmann Institute of Science:

<http://plasma-gate.weizmann.ac.il/>

This is a list of hyperlinks to some three dozen atomic physics and plasma physics databases or data collections worldwide that reside on the Web.

2. The Oak Ridge National Laboratory (ORNL) Controlled Fusion Atomic Data Center:

<http://www-cfadc.phy.ornl.gov>

This database is primarily oriented toward multiply charged species (Schultz *et al.*, 1998).

3. NIFS Database, National Institute for Fusion Science, Toki, Japan:

<http://dbshino.nifs.ac.jp>

This database contains a large amount of atomic and molecular data in a number of different categories (Murakami *et al.*, 1998).

4. GAPHYOR Data Center, Université Paris-Sud, Orsay, France:

<http://gaphyor.lpgp.u-psud.fr>

This database has been under development for nearly two decades and contains about 500,000 entries on the properties and reactions of atoms, molecules, and neutral or ionized plasmas (Delcroix *et al.*, 1998).

5. The NIST Databases, National Institute of Standards and Technology, Gaithersburg, MD:

<http://physics.nist.gov/PhysRefData/contents.html>

NIST has numerous databases on its Web site (see Dragoset *et al.*, 1998), including the ionization cross sections of Y.-K. Kim and his collaborators (Kim *et al.*, 1998) referred to previously:

<http://physics.nist.gov/PhysRefData/Ionization/Xsection.html>

and, very recently, the complete tables of molecular constants of diatomic molecules. The NIST Web site

<http://www.eeel.nist.gov/811/refdata>

(Christophorou and Olthoff, 1998b) contains the numerical data from the critical reviews of electron impact cross sections for CF₄, CHF₃, CCl₂F₂, and C₂F₆ by Christophorou *et al.* (1996, 1997a, 1997b, 1998a), which have been mentioned in this article.

6. The Atomic and Molecular Data Information System (AMDIS) of the International Atomic Energy Agency in Vienna:

<http://www.iaea.org/programmes/amdis>

This is primarily for fusion plasma research, but it includes much related to plasma chemistry as well.

7. Finally, many tables of cross-section data discussed in this article can be found on the Kinema Research & Software Web site:

[http://www.kinema.com/kinema/.](http://www.kinema.com/kinema/)

VI. Acknowledgements

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