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A Critical Evaluation of
Low Energy Electron Impact Cross Sections
for Plasma Processing Modeling:
I. Cl₂, F₂, and HCl
II. CF₄, SiH₄, and CH₄

by

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INTRODUCTION

We have seen in the past decade the increasing use of discharge plasmas in the processing of microelectronic components. For example, silicon surfaces can be etched in a discharge containing a rare gas and fluorinated or chlorinated gases such as CF$_4$ or HCl. On the other hand, thin films of amorphous silicon can be deposited in a discharge containing silane, SiH$_4$. Examples of the gases of interest for such plasma processing are listed in Table 1. During the same period increasingly sophisticated techniques have been developed for modeling the plasma chemistry in such discharges. This includes extensive modeling of the chemical kinetics of these discharges and sophisticated treatment of the electron kinetics through solutions of the Boltzmann equation and Monte Carlo approaches to dealing with non-equilibrium electrons.

The ability to model the plasma chemistry of the discharges used in plasma processing is very dependent upon the availability of electron impact cross sections for the various atoms and molecules found in these devices. In the most simple models these data are convolved with a Maxwell–Boltzmann electron energy distribution $[f(\epsilon)=\frac{2}{\sqrt{\pi}} \frac{e^{-\epsilon/kT}}{(kT)^{3/2}}]$ to give an electron impact rate coefficient. Most modeling, however, is performed using a more realistic $f(\epsilon)$ obtained by solving the electron Boltzmann equation or by performing classical Monte Carlo trajectory simulations of the motion of electrons in the partially ionized gas. In the first instance, angle integrated electron impact cross sections are used for inelastic processes and the momentum transfer cross section, defined by $\sigma_m(\epsilon) = 2\pi \int \sigma_e(\epsilon, \theta)(1-\cos \theta) d(\cos \theta)$ due to the form of the Boltzmann collision integral, is used for elastic collisions. In a Monte Carlo simulation cross sections differential in scattering angle may be used, or, more frequently, an assumption concerning the angular dependence, along with the true elastic scattering cross section, $\sigma_e(\epsilon, \theta)$, rather than its cosine weighted integral.

In view of these needs for cross section information, a desire has been expressed by
Researchers in the field for a consistent set of data readily available to and in useful form for all. In the development of a "standard reactor" for doing plasma processing research, which is desirable for facilitating comparisons between experiments and theory, between different models, and between different experiments, it is of interest to have uniform sets of atomic and molecular data. In plasma cell calibration, for example, He and N\textsubscript{2} are used as standard reference gases; a set of standard reference cross sections for these species is of interest. Although the plasma chemistry of these gas mixtures is very complex, assembling a standard set of electron impact cross sections is an important beginning.

At present, those modeling plasma chemistry are using cross sectional data from all imaginable sources. Many of the data are gotten out of Kieffer's 1973 JILA report (No. 13) on cross sections for modeling of gas lasers and the reports that McDaniel and a number of coauthors produced for the Army in the late 1970's; others are gotten from publications and conference proceedings; some are obtained from private communications; and some are guessed at by analogy with better known cross sections of structurally similar molecules.

The goal of this work has been to perform a critical evaluation of some the low energy electron impact cross sections important in plasma processing applications and construct a data base on a floppy to contain the numerical information. The molecules studied are Cl\textsubscript{2}, F\textsubscript{2}, HCl, CF\textsubscript{4}, SiH\textsubscript{4}, CH\textsubscript{4}. The critical evaluation consisted primarily of examining how well electron transport, or swarm, coefficients computed using these cross sections agreed with measured swarm coefficients.

The critical review is divided into two sections:

I. Cl\textsubscript{2}, F\textsubscript{2}, HCl

II. CF\textsubscript{4}, SiH\textsubscript{4}, CH\textsubscript{4}
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I. Cl₂, F₂, HCl
A Critical Evaluation of
Low Energy Electron Impact Cross Sections
for Plasma Processing Modeling I: Cl₂, F₂, and HCl

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Abstract

The available information on low energy electron impact cross sections for Cl₂, F₂, and HCl is reviewed and critically evaluated. Of interest are the cross sections for momentum transfer; rotational, vibrational, and electronic excitation (with possible dissociation); and attachment and ionization. The bulk of the data available for these molecules are on dissociative attachment, as that is the property that is of greatest interest in applications and is relatively easy to measure. Recommended cross sections are identified where feasible. Much of the process of critical evaluation is performed by computing electron transport, or swarm, coefficients using the published cross sections and comparing with published measurements.

Key words: electron molecule collisions, cross sections, swarm analysis
I. INTRODUCTION

Cross sections for collisions of low energy electrons with \( \text{Cl}_2 \), \( \text{F}_2 \), and \( \text{HCl} \) are of interest in a several applications where these gases are used in discharges. Because they readily undergo dissociative attachment yielding a halogen negative ion, they are used in rare gas halide lasers\(^1,2\) in which the lasing species, such as the \( \text{ArF} \), \( \text{KrF} \), or \( \text{XeCl} \) excimers, are formed by ionic recombination of a rare gas positive ion and a halogen negative ion. The large cross sections for formation of \( \text{F}^- \) and \( \text{Cl}^- \) and the large rate coefficient for ionic recombination\(^3,4\) result in a very efficient kinetic channel for formation of the excimer species. These gases are also of interest in plasma etching of semiconductors. Here the molecules are dissociated in the discharge and the \( \text{F} \) and \( \text{Cl} \) atoms efficiently etch a silicon surface\(^5,6\).

In reviewing the published literature on low energy electron impact on these molecular species, I have found that few measurements and very little theory had been performed prior to the mid-1970's and that little work has been published since the mid-1980's. There was a ten year period of very vigorous experimental and theoretical research on \( \text{Cl}_2 \), \( \text{F}_2 \), and \( \text{HCl} \) that appears to coincide with the interest in and subsequent funding of research on rare gas halide excimer lasers in the United States.

Most of the discussion in this review is concerned with the construction of sets of cross sections, i.e. cross sections for momentum transfer; rotational, vibrational, and electronic excitation (with possible dissociation); and attachment and ionization, that may be useful in modeling the plasma chemistry of systems containing these molecules. Where measurements of cross sections are available they are discussed an analyzed and, in the absence of measurements, the available theoretical information is discussed. The object of this review is not to generally compare the capabilities and results of experiment versus
theory. The measurements comprise two classes having very different apparatus and technique. The two classes of measurements are the electron–beam method and electron–swarm techniques. Detailed discussions of these measurement techniques and discussion and comparison of results can be found in Refs. 7 and 8.

In evaluating cross sections I have relied heavily upon calculations of electron transport or swarm coefficients using the cross sections and how well they compare with measurements. As the ultimate use of electron impact cross sections in plasma chemistry modeling is the calculations of drift velocities, diffusion coefficients, and collision rate coefficients, this approach seems most appropriate. A short discussion of this procedure follows.

A. Swarm measurements and calculations

An electron swarm is a cloud of electrons in a neutral gas under conditions such that the dominant interactions are the collisions between the electrons and the gas atoms or molecules. Measurements on electron swarms are usually performed with the electron cloud drifting in an electric field. The quantities that can be measured comprise drift velocities; diffusion coefficients; rates of growth of electron density due to ionization; electron loss rates due to recombination or attachment; and, indirectly via measurement of radiation emitted from the gas, the rates of excitation of the various atomic or molecular energy levels. In some of the published measurements discussed below, the authors have utilized the afterglow of an electron–beam ionized discharge rather than the conventional electron swarm technique.

The most important application of electron swarm data is in deriving cross sections for low energy electron impact on atoms and molecules. The cross sections are fundamental quantities that depend only on the energy of the incident electron and the particular initial and final atomic or molecular states. The swarm parameters are derived quantities that depend on the local environment of the electron swarm. Variables in this
environment may be electric field; gas density and temperature; electron density and mean electron energy; and the number densities of rotationally, vibrationally, or electronically excited atoms or molecules. All of the swarm coefficients are integrals over the product of a cross section and the electron energy distribution function, \( f(\epsilon) \). These are generally very non-thermal or non-equilibrium systems. The distribution function \( f(\epsilon) \) is the function that maps the cross sections into the swarm coefficients. It is a solution of Boltzmann's transport equation, which describes non-equilibrium collisional systems. The relationship between the cross sections and the transport coefficients via the distribution function \( f_0(\epsilon) \) is highly nonlinear. It is a mapping

\[
\begin{align*}
\{ \sigma_m(\epsilon) \} & \quad \Rightarrow \quad \{ v_d(E/N) \} \\
\{ \sigma_i(\epsilon) \} & \quad \Rightarrow \quad \{ D/\mu(E/N) \} \\
\{ k_i(E/N) \} & \quad \Rightarrow \quad \{ k_i(E/N) \}
\end{align*}
\]

relating the momentum transfer and excitation cross sections to the drift velocity, characteristic energy, and excitation rate coefficients. The mapping rule is Boltzmann's equation. The general goal of swarm measurements and analysis is to find the reverse mapping given the transport data.

The process of obtaining cross sections from swarm data involves inserting cross section models in the collisional terms of Boltzmann's equation, calculating \( f(\epsilon) \) and, hence, the swarm coefficients, altering the model cross sections and, so, iterating until an acceptable match between measured and computed swarm coefficients is found. This is one method of estimating low energy collision cross sections for electrons on atoms and molecules and, also, of checking or normalizing cross sections gotten by other means. These techniques were developed by Phelps and various collaborators in the 1960's (see Refs. 9-12 for reviews of the methodology) but the field is not dormant; there has even been recent research directed toward automating the process of obtaining cross sections.
from transport data.\textsuperscript{13–15}

In computing the swarm coefficients as part of the analyses in this review I have used the so-called two-term expansion of Boltzmann's equation for transport of electrons in a uniform DC electric field.\textsuperscript{16,17} If one neglects the spatial and temporal dependence of the distribution function $f(r,v,t)$ of Boltzmann's equation and expresses $f=f(v)$ as the first two terms of a spherical harmonic expansion, that is

$$f(v) = f_0(v) + \frac{v}{v} f_1(v),$$

then the following scalar equation for $f_0(\epsilon)$ (where $\epsilon=mv^2/2$) is obtained (see Ref. 10 for details of the derivation):

\begin{equation}
\frac{1}{3}(eE/N)^2 \frac{d}{d\epsilon} \frac{d \epsilon}{\sigma_m} \frac{df_0}{d\epsilon} + \frac{d}{d\epsilon} \left( (2m\sigma_m/M) \epsilon^2 [f_0(\epsilon) + kT \frac{df_0}{d\epsilon}] \right) \\
+ \Sigma \left[ (\epsilon + \epsilon_i) \sigma_i(\epsilon + \epsilon_i) f_0(\epsilon + \epsilon_i) - \epsilon \sigma_i(\epsilon) f_0(\epsilon) \right] = 0. \tag{1}
\end{equation}

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. The electron impact cross sections involved are $\sigma_m(\epsilon)$, the momentum transfer cross section, and $\{\sigma_i(\epsilon)\}$, the set of cross sections for transitions from the ground state to the various excited states $\{i\}$. This equation does a remarkably good job of describing the transport of electrons under the influence of an electric field in most gases. This, or more sophisticated versions of it that go beyond the two-term expansion,\textsuperscript{18,19} is the equation that is repeatedly solved in the iterative process whereby one develops a set of cross sections given a collection of transport coefficients. There are molecules for which the two-term expansion solution of Boltzmann's equation is inaccurate\textsuperscript{18,19} but it is expected to be applicable to Cl$_2$, F$_2$, and HCl. There are also molecules for which there are unresolved
differences between cross sections obtained by beam methods and those obtained by swarm methods\textsuperscript{20,21} but, although that could be true of HCl, the precision of the measurements and theory is not sufficient for us to see such differences.

Some of the swarm calculations that I performed in the analysis of cross sections were on mixtures of gases. When measuring the attachment rate coefficient of a molecule one frequently performs the measurement with a small amount of the attacher in a diluent gas having, hopefully, known cross sections and transport coefficients. In these analyses I have examined experiments in which the attachment rate of Cl\textsubscript{2}, F\textsubscript{2}, or HCl was measured in He, Ar, or N\textsubscript{2} diluents. I have used the momentum transfer cross section for helium published by Crompton et al.\textsuperscript{22} The argon momentum transfer cross section is that of Haddad and O'Malley.\textsuperscript{23} I used a total excitation cross section for argon metastables from Schaper and Scheibner,\textsuperscript{24} although the values of E/N were generally small enough that this was unimportant. The cross sections for nitrogen are those developed by Phelps and Pitchford.\textsuperscript{25} These were determined by comparison with swarm data. Phelps and other coworkers have also similarly assembled cross sections for oxygen\textsuperscript{26} and for hydrogen.\textsuperscript{27} There have been recent compilations of beam data for nitrogen,\textsuperscript{28} as well as for oxygen\textsuperscript{29} and for hydrogen,\textsuperscript{30} but these have not critically evaluated the data nor have they suggested recommended cross sections. Ohmori, et al.\textsuperscript{31} have recently published a new determination of cross sections for nitrogen but these have not been compared with those of Ref. 25.

II. ELECTRON COLLISIONS WITH Cl\textsubscript{2}

The only published analysis attempting to provide a complete set of cross sections for electron impact on chlorine is that of Rogoff, et al.\textsuperscript{32} These authors developed a cross section set for use in their modeling of RF discharges in chlorine. As only the dissociative
attachment and ionization cross sections for Cl₂ have been measured directly, Rogoff, et al. postulated a complete set of cross sections and used the iterative procedure described above to develop a set that fit published transport coefficients, placing primary emphasis on the ionization coefficient. Their derived cross section set is shown in Fig. 1. Rogoff, et al. provide in their paper a description of the procedure that they used but do not present the comparisons between transport coefficients computed using their cross section set and measured coefficients. Consequently, I have performed such calculations and present them here as part of the critical evaluation of the cross sections.

A. Dissociative attachment: Cl₂ + e⁻ → Cl⁻ + Cl

There have been a number of published measurements of the rate coefficient for dissociative attachment of electrons to chlorine and two beam measurements of the attachment cross section. The beam measurements comprise the relative cross section measurement by Tam and Wong \(^{33}\) and the absolute measurement of Kurepa and Belic, \(^{34}\) who also measured the ionization cross section.. These agree well in shape. The Kurepa and Belic cross section was used in the set assembled by Rogoff, et al.\(^{32}\), shown in Fig. 1.

The rate coefficients for attachment were generally measured in gas mixtures with a very small amount of Cl₂ in a buffer gas. Bozin and Goodyear\(^ {35}\) have measured the attachment and ionization coefficients for electrons in pure Cl₂. They measured \(\eta\) and \(\alpha\), which are related to the attachment and ionization rate coefficients by a factor of \(v_d/N\). The rate coefficients for attachment and ionization in Cl₂ computed using the Rogoff, et al. cross section set and compared to the measurements of Bozin and Goodyear are shown in Fig. 2. We see reasonably good agreement between the measured and calculated attachment coefficients.

Measurements of attachment rate coefficients are frequently performed in mixtures, where the fraction of attaching gas is, in principle, small enough that the electron energy
distribution function and the transport coefficients are determined by the buffer gas and
the only role played by the attaching molecules is to cause a decay in time of the electron
density. Such measurements were performed for Cl$_2$ in Ar by Sze, et al. 36 and for Cl$_2$ in
al. measurements were performed in the afterglow of an electron beam ionized discharge.
The McCorkle, et al. measurements, on the other hand, were performed using a more
conventional configuration where a swarm of electrons produced by $\alpha$–particle ionization is
drifted between capacitor plates by an external uniform electric field.

The results of the swarm calculations are plotted for N$_2$/Cl$_2$ and Ar/Cl$_2$ along with
the published measurements in Figs. 3 and 4. Recall that these comparisons, subject to the
assumption that the cross sections for the buffer gas are accurate, should be a measure only
of the attachment cross section of the minor species in the mixture. We see from the
N$_2$/Cl$_2$ results that for E/N greater than a few Townsend there is good agreement between
the attachment rate coefficient computed using the Kurepa and Belic cross section for
chlorine and two of the three measurements. We see that the measurements of Sze, et al.
are quite high for E/N less than about 10 Td. We see similar behavior in their
measurements with an Ar buffer gas. This may be evidence that the Sze, et al.
measurements are suspect. We will find this evidence to be of value in assessing the
attachment cross sections for HCl later is this paper.

Although the computed rate coefficient in the N$_2$/Cl$_2$ mixture has approximately
the same shape as a function of E/N as the McCorkle, et al. measurements, it lies below
the measured values by nearly a constant factor over the whole range of E/N. Considering
the agreement with the pure Cl$_2$ measurements at high E/N as well as with the Ar/Cl$_2$
measurements at high E/N, it may be that some modification of the lowest energy portion
of the attachment cross section is all that is needed to improve agreement with most of the
measured data. One further piece of information is the near thermal flowing afterglow
measurements of the attachment rate coefficient by Sides, et al. 39 which yield a value of
3.7±1.7×10⁻⁹ cm³/s for the rate coefficient at a temperature of about 350 K.

B. Elastic and inelastic cross sections

Beyond having a very old measurement of drift velocity and characteristic energy in an He/Cl₂ mixture, several measurements of the ionization cross section, and one measurement of the ionization rate coefficient, we have no means of assessing the validity of the elastic and inelastic cross sections proposed by Rogoff, et al. The swarm measurements were performed by Bailey and Healey in 1935 in an 80% He and 20% Cl₂ mixture at rather large values of E/N corresponding to mean electron energies of 1.3 to 2.4 eV. Their results and the results computing by solving Boltzmann's equation are shown in Fig. 5. Bailey and Healey measured the drift velocity and a quantity called Townsend's energy factor, which is related to the characteristic energy as discussed in Refs. 11, 41, and 42. We see excellent agreement between the measured and computed drift velocities and fair agreement between the characteristic energies, indicating that the Rogoff, et al. estimates of the momentum transfer and low energy inelastic cross sections are reasonable.

The ionization cross section for chlorine has been measured by Center and Mandel, Kurepa and Belić, and Stevie and Vasile. We see in Fig. 6 substantial differences between these measurements, especially just above the ionization threshold. As mentioned above, Božin and Goodyear have measured the ionization coefficient in pure Cl₂. These results and the swarm calculations using the Rogoff, et al. cross section set are shown in Fig. 2. We see poor agreement at the lowest value of E/N, which samples the near threshold part of the ionization cross section. It is not clear, however, how much of the error in ionization rate is due to the ionization cross section and how much is due to uncertainties in the electronic excitation cross sections, for which there are no direct data.
III. Electron Collisions with $F_2$

Because fluorine has a very large attachment cross section, indeed it is finite at zero impact energy, it has been the negative ion donor of choice in rare gas fluoride lasers. Because of this there were a large number of papers published on the dissociative attachment of electrons to $F_2$, but there has been very little work on other electron collision processes involving fluorine. The only measurements of electron transport properties were drift velocity measurements performed by Nygaard, et al.\(^{45}\) in mixtures of 99% He and 1% $F_2$ but the error bars are so large that they are of little use for cross section estimation. Other than the ionization cross section, which has been measured, all other cross sections are computed theoretically. The only published attempt at assembling a complete cross section set is that of Hayashi and Nimura.\(^{46}\) These authors used a combination of beam measured and theoretical cross sections for dissociative attachment,\(^{47-49}\) the ionization cross section measured by Stevie and Vasile,\(^{44}\) and various published theoretical elastic, vibrational excitation, and electronic excitation cross sections. Their complete set of cross sections are shown in Fig. 7. Curiously, Hayashi and Nimura performed a large number of swarm calculations for fluorine for which there were no measurements available for comparison but did not perform calculations of the attachment rate coefficient for fluorine in binary mixtures with other gases even though published measurements were available. Due to the dearth of experimental information on processes other than attachment, this cross section is the only one that a serious evaluation can be made of. Fortunately, it is the attachment process in fluorine that is of the greatest interest.

A. Dissociative attachment: $F_2 + e^- \rightarrow F^- + F$

An early measurement of the fluorine dissociative attachment cross section by Mahadevan and Hoffland\(^{50}\) indicated a cross section that is finite and large at zero impact energy, is quite large $-180 \ \AA^2$—at its peak at an electron impact energy of 0.1 eV, and then falling off quite quickly to a plateau at about half an electron volt. This cross section,
however, was not consistent with the attachment rate coefficient measurements available at the time, those of Chen, et al.\textsuperscript{51} in an N\textsubscript{2}/F\textsubscript{2} mixture in an e–beam sustained discharge. The discrepancy was somewhat exacerbated by an error in the Chen, et al. paper when the rate coefficient was plotted versus what was claimed to be average energy and was, in fact, characteristic energy.\textsuperscript{52} The cross section was measured again by Chantry\textsuperscript{47,48} and is shown in Fig. 8. As we will see, this cross section is reasonably consistent with electron swarm measurements. Also shown in Fig. 8 are several theoretical calculations of the attachment cross section\textsuperscript{49,53,54}, which will be discussed below.

In Fig. 9 are shown values of the dissociative attachment rate coefficient measured by McCorkle, et al.\textsuperscript{55} in Ar and in N\textsubscript{2} and calculations using the cross section presented by Hayashi and Nimura\textsuperscript{46}, which uses the Hazi, et al.\textsuperscript{49} cross section below 0.1 eV, and that of Chantry.\textsuperscript{48} These rate coefficients are plotted versus E/N. We see that the calculations using Chantry's cross section is generally in much better agreement with the measurements than are those points computed using the Hayashi and Nimura cross section. The difference between the two lies in the presence or absence, respectively, of the large peak at very low energy. Of the three theoretical cross sections\textsuperscript{49,53,54} only Hall's\textsuperscript{53} exhibits an peak at zero energy, but that is nearly an order of magnitude smaller than Chantry's measured cross section. It would appear, however, that the evidence is in favor of the presence of the peak. A much more recent beam measurement by Chutjian and Alajajian\textsuperscript{56} at very low electron energy with very high energy resolution also shows the peak and is somewhat in agreement in magnitude with the Chantry's cross section measurement.

We see plotted in Fig. 10 various measurements\textsuperscript{39,51,55,57–59} of the attachment rate coefficient as well as calculations using Chantry's cross section as a function of mean electron energy. Clearly, since the mean energy cannot be measured, it is computed by solving Boltzmann's equation for f(ε), as described previously, for the experimental conditions. Because the energy distribution functions for electrons in He, Ar, and N\textsubscript{2} are
quite different, even when they have the same average energy, there will be some scatter in
the rate coefficients measured in different gases at approximated the same mean energy.
We see that the McCorkle, et al. measurements and the calculations fit the group
reasonable well. The major deviations are the Schneider and Brau\textsuperscript{57} measurements in both
Ar and N\textsubscript{2}, which were performed in the afterglow of an electron beam ionized discharge,
and the very low energy Sides, et al.\textsuperscript{39} thermal flowing afterglow measurements. We have
seen with Cl\textsubscript{2} and will see with HCl that the measurements of the Los Alamos group yield
rate coefficients much higher than all other measurements, which makes their measurement
technique suspect. The Sides, et al. data appear to favor an attachment cross section
having an energy dependence more like the theoretical cross sections but, as we have seen,
the evidence weighs heavily against this. It remains unclear why their measured rate
coefficients are so relatively small.

B. Elastic and inelastic collisions

Because there are no experimental data, no recommendations can be made about
most of the other cross sections for F\textsubscript{2}. The ionization cross section has been measured by
Center and Mandl\textsuperscript{43} and by Stevie and Vasile\textsuperscript{44} and the two measurements are in excellent
agreement.

A number of theoretical papers have been published on elastic and vibrationally and
electronically inelastic collisions between low energy electrons and F\textsubscript{2}. Elastic scattering
cross sections have been computed by Schneider and Hay\textsuperscript{60} and by Rescigno, et al.\textsuperscript{61} Both
calculations show a resonance at about 1.8 eV and are approximately in agreement. The
Schneider and Hay result was used by Hayashi and Nimura\textsuperscript{46} in their cross section set and
is plotted in Fig. 7. Hall\textsuperscript{53} and Bardsley and Wadehra\textsuperscript{54} have computed vibrational
excitation cross sections for F\textsubscript{2}. Hall's cross sections, which have been used by Hasashi and
Nimura in their collection, are nearly an order of magnitude larger than those computed by
Bardsley and Wadehra. Hall, Bardsley and Wadehra, and Hazi, et al.\textsuperscript{49} also predict
significant enhancement of the dissociative attachment cross section with increasing vibrational level. There is some evidence for this from the measurements of fluorine dissociative attachment rate coefficients at elevated temperature by Trainor and Jacob.\textsuperscript{59} Due to the paucity of experimental data on vibrational excitation and attachment to vibrationally excited fluorine we cannot assess the validity or accuracy of these calculations.

Electronic excitation of fluorine has been investigated by Rescigno, et al.\textsuperscript{62}, who computed Born cross sections for excitation of twelve state of \( \text{F}_2 \); Fliflet, et al.\textsuperscript{63}, who computed distorted wave cross sections (\( \text{F}_2 \) orbitals and \( \text{F}_2^- \) orbitals) for excitation of the lowest \( ^3\Pi_u \) state, which predissociates; and by Hazi\textsuperscript{64}, who performed impact parameter calculations of the excitation of \( \text{F}_2(\text{C}^1\Sigma_u^+) \) and the \( \text{F}_2(\text{H}^1\Pi_u) \) states. Hazi's calculations agree with the Born results of Rescigno, et al. at high energy but, presumably, yield a more realistic near threshold behavior. Hayashi and Nimura used in their cross section set the larger of the Fliflet, et al. cross sections (using \( \text{F}_2 \) orbitals; this is \( \sigma_e \) in Fig. 7) and Hazi cross sections (\( \sigma_e'' \) and \( \sigma_e''' \) in fig. 7). For the dissociative level \( \text{F}_2(\text{A}^1\Pi_u) \) they assumed a cross section (\( \sigma_e' \) in Fig. 7).

An important issue pertaining to fluorine is the cross section for dissociation of the molecule into two F atoms. The Fliflet, et al.\textsuperscript{63} result represents the only theoretical result available for dissociation. The experimental evidence of dissociation consists of the electron beam results of Wilson, et al.\textsuperscript{65}, which indicate an upper limit of about three fluorine atoms produced for each \( e^- + \text{F}_2 \) ionizing collision, and the electron beam sustained discharge measurements of Chen, et al.\textsuperscript{66}, which yield a sustainer enhancement factor for F atom production as a function of \( E/N \). These experiments were modeled by Morgan and Szoke\textsuperscript{67} and the cross sections for dissociation via excitation of \( \text{F}_2(\text{a}^3\Pi_u) \) and \( \text{F}_2(\text{A}^1\Pi_u) \) were determined; these are shown in Fig. 11. The \( ^3\Pi_u \) cross section lies close to the Fliflet, et al. result computed using \( \text{F}_2 \) orbitals. The \( ^1\Pi_u \) cross section is about half as large at the peak as that assumed by Hayashi and Nimura. As the Morgan and Szoke cross
sections are the only ones for electronic excitation based on measured data, they should be taken as the recommended ones for dissociation of fluorine by electron impact.

IV. Electron Collisions with HCl

There have been several complete cross section sets published for hydrogen chloride. Hayashi's cross section set appeared in a conference proceedings without a description of how it was obtained. That of Davies was derived on the basis of Davies' own comprehensive measurements of swarm coefficients in HCl and that published by Penetrante and Bardsley was a reanalysis of Davies' measurements and those of others using Davies' cross sections as a starting point. The Penetrante and Bardsley cross sections are plotted in Fig. 12. As we have seen for Cl₂ and F₂, the dissociative attachment cross section for HCl is of great interest and has been the subject of a number of experimental and theoretical studies. Vibrational excitation of HCl has also been studied to a large extent because of its unique features. These will be discussed below. Information on cross sections for other processes is generally either theoretical or from Davies' swarm analysis.

A. Dissociative attachment: Cl⁻ formation

1. HCl in the v=0 state

The most recent measurements involving the dissociative attachment of electrons to HCl in the ground vibrational state are the cross section measurements of Alan and Wong and of Orient and Srivastava and the swarm measurements of Kligler, et al.; Sze, et al.; Davies; and of Petrovic, et al. The measurements of Kligler, et al. and of Sze, et al. were performed in the afterglow of an electron beam excited discharge. The swarm measurements of Davies were performed in pure HCl while those of the others were performed variously in mixtures of Ar, N₂, or Ar/H₂ and HCl. Petrovic, et al. have
presented a detailed discussion and comparison of their results and those of the other authors listed above. While I have performed some swarm calculations in order to check some points, much of the following discussion is based on the results presented in their paper.

Figs. 13 and 14 summarize the hydrogen chloride dissociative attachment rate coefficients measurements in $N_2$ and in Ar buffer gases respectively. We see that the e–beam ionized discharge results of Kliger, et al. and of Sze, et al. lie somewhat above the more conventional swarm results of Christophorou, et al. and of Petrovic, et al. and possess substantial scatter. As we have seen previously, the Sze, et al. results may be suspect. The various dissociative attachment cross sections are shown in Fig.15. The rate coefficients for HCl in $N_2$ computed using the Penetrante and Bardsley and the Petrovic, et al. cross sections of Fig. 15 are plotted in Fig. 13. The major difference between the two cross sections is that the former rises more steeply from threshold to a higher value at the peak. The shapes and magnitudes of the two cross sections above the peak are very similar. For comparison are shown the Alan and Wong relative beam measurement, which has been normalized to the maximum value of the Petrovic, et al. cross section and the Orient and Srivastava beam measurement, which appears to have unrealistic low energy behavior and is substantially larger at the peak than the other cross sections. This latter property appears to be consistent with other cross sections reported by these authors. Their measurements of the $SO_2$ dissociative attachment cross section are substantially larger than other measurements. Similarly, Freund and Wetzel point out in a discussion of ionization cross sections measured by various laboratories that the "measurements of Orient and Srivastava tend to be the largest."

Because the Petrovic, et al. cross section was derived from swarm measurements made in dilute HCl and buffer gas mixtures, I believe it to be more accurate than the cross section derived from measurements on pure HCl. In performing swarm calculations on electrons in pure HCl one must take into account rotational and vibrational inelastic
collisions. This was done by Davies and by Penetrante and Bardsley, but there are uncertainties in these cross sections. In dealing with rotational excitation, Davies used the so-called continuous approximation to rotation (CAR)\textsuperscript{79} in his two-term Boltzmann calculations whereas Penetrante and Bardsley used the individual cross sections for j→j+1 computed by Padial, et al.\textsuperscript{80,81} (shown in Fig. 15) in their Monte Carlo calculation of the swarm coefficients. The CAR is a single level approximation based on the Born rotational cross sections of Takayanagi.\textsuperscript{82} We see from Fig. 16, which shows the total rotation cross section for HCl at 300 K, that these two approaches yield similar results but, on the other hand, they are both theoretical and we do not know what the true rotational cross sections are. Since the rotational cross section is taken as being known in the swarm unfolding process, the accuracy of the derived momentum transfer and attachment cross sections and, to some extent, the vibrational cross sections depend upon the how well know the rotational cross sections are. Because the attachment process creates a hole in the electron energy distribution in a region of energy space where the rotational and vibrational cross sections are large and where the elastic momentum transfer cross section is near a minimum (see Fig. 12), there is great sensitivity to the synergistic effects resulting from the convolution of all these cross sections.

Davies and Penetrante and Bardsley derived vibrational excitation cross sections from the HCl swarm data, which, as can be seen in Fig. 17, are similar in shape and magnitude to the beam measurements. The interest in vibrational excitation in HCl goes back to the measurements of the cross section by Rohr and Linder,\textsuperscript{83,84} which indicated a large resonance at threshold for excitation from v=0 to v=1 and v=2. This has prompted a flurry of theoretical work and further measurements, such as those of Knoth, et al.,\textsuperscript{85,86} of greater refinement. Discussion of the theoretical issues and results in vibrational excitation can be found in the reviews of Lane,\textsuperscript{87} Norcross,\textsuperscript{88} and Morrison.\textsuperscript{89} Recent theoretical results for electron impact vibrational excitation of HCl are presented by Domcke and Mundel\textsuperscript{90} and Morgan, Burke, and Gillian.\textsuperscript{91}
2. Vibrationally excited HCl.

Any discussion of the dissociative attachment of electrons to HCl would not complete without mention of Alan's and Wong's measurement\textsuperscript{71} of the phenomenal increase in the cross section for vibrationally excited HCl. Alan and Wong performed beam measurements of the relative dissociative attachment cross section of HCL at several temperatures from 300 K to 1200 K (see Fig. 19). The onset of the \( v=1 \) and \( v=2 \) processes is clear in their data. Their deduction is that the peak cross section for dissociative attachment to HCl(\( v=1 \)) is 38 times that for \( v=0 \) and for \( v=2 \) it is 880 times the \( v=0 \) value. Performing a deconvolution of their data and normalizing to the HCl(\( v=0 \)) cross section of Petrovic, et al. yields the cross sections shown in Fig. 20.\textsuperscript{92,93} Theoretical work on this has been performed by Bardsley and Wadehra\textsuperscript{54} who obtain cross sections very similar to those measured by Alan and Wong. Although it was immediately recognized\textsuperscript{94} that vibrationally enhanced dissociative attachment of HCl would lead to efficient formation of the upper laser level in XeCl excimer lasers and is still generally accepted as a key process in the XeCl kinetics (see Kannari, et al.\textsuperscript{95} and references contained therein), this has not been without controversy. This view has been disputed by the Hebrew Univeristy group (Kligler, et al.\textsuperscript{73} and Center, et al.\textsuperscript{96}) who claim, respectively, that their measurements of attachment rate as a function of electron beam current and that HCl fluorescence measurements under typical e—beam XeCl laser conditions are not consistent with the many—fold enhancement of the attachment rate that would be expected based on the Alan and Wong results.
V. CONCLUSIONS

The recommendations concerning what cross sections might be expected to be most reasonable to use are as follows:

(a) Cl₂: the only set of cross sections available is that of Rogoff, et al. This does not necessarily recommend it. As we have seen, however, this set of cross sections gives very reasonable results for the transport coefficients and, so, should be recommended.

(b) F₂: Hayashi and Nimura have assembled a set of cross sections that have not been tested against any experimental data because there are none other than attachment measurements and a beam measurement of the ionization cross section. The recommendation is to use the dissociative attachment cross section published by Chantry; the theoretical momentum transfer cross section, the modified theoretical dissociation cross sections (the a³Π_u and A¹Π_u states) from Ref. 67; the theoretical electronic excitation cross sections (the C¹Σ_u and H¹Π_u states); and the measured ionization cross section of Stevie and Vasile.

(c) HCl: the Davies cross sections as modified by Penetrante and Bardsley seem most reasonable. As we have seen (Fig. 17), the continuous approximation to rotation does quite well so that use of a large set of explicit rotational cross sections may not be necessary. The most controversial call concerns the cross section for dissociative attachment forming Cl⁻. I think that the cross section derived by Petrovic, et al. from swarm measurements in Ar and in N₂ should, for the reasons given in the text, be recommended.

A recommendation that can clearly be made, especially when one compares the quantity of experimental information on these molecules to, say that on methane, which is reviewed in the following paper, is that much more data are needed on aspects of electron collisions with these molecules beyond dissociative attachment.
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FIGURE CAPTIONS

1. Cl₂ cross sections derived by Rogoff, et al. [Ref. 32].

2. Comparison of measured (O,Δ) [Ref. 35] and computed (●,▲) attachment and ionization coefficients for electrons in Cl₂.

3. Comparison of measured (O, Ref. 36; □, Ref. 37) and computed (●) dissociative attachment rate coefficients in Ar/Cl₂ mixtures.

4. Comparison of measured (O, Ref. 36; □, Ref. 37; Δ, Ref. 38) and computed (●) dissociative attachment rate coefficients in N₂/Cl₂ mixtures.

5. Characteristic energies (triangles) and drift velocities (circles) for electron in Cl₂. The open symbols are the measurements of Ref. 40 and the filled symbols are calculations.

6. Measured cross sections for ionization of Cl₂ by electrons; Δ, Ref. 43; O, Ref. 34; and ●, Ref. 44.

7. F₂ cross sections published by Hayashi and Nimura [Ref. 46].

8. Cross sections for dissociative attachment of F₂ plotted over two ranges of energy; O, Refs. 47,48; □, Ref. 56; ●, Ref. 53; Δ, Ref. 49; and ▲, Ref. 54.

9. Dissociative attachment rate coefficient versus E/N for F₂ in Ar and in N₂ buffer gases; open symbols are for Ar/F₂ and filled symbols are for N₂/F₂. The circles are the measurements of McCorkle, et al. [Ref. 55]; the triangles are calculations using the Hayashi and Nimura [Ref. 46] cross sections as published; and the squares are calculations using the same cross sections except with Chantry's [Refs. 47,48] dissociative attachment cross section.

10. Dissociative attachment rate coefficient versus mean electron energy for F₂. The calculations using Chantry's [Refs. 47,48] cross sections are □, Ar/F₂ and ●, N₂/F₂. The measurements, performed in various buffer gases, are: O, (Ar) Ref. 55; ●, (N₂) Ref. 55; Δ, (Ar) Ref. 39; ▲, (N₂) Refs. 51,52; V (N₂) Ref. 57; • (Ar) Ref. 57; V (N₂) Ref. 59; and ◇ (He) Ref. 58.
11. Electron impact dissociation cross sections for $F_2$. Calculations by Fliflet, et al. [Ref. 63] for excitation of $F_2(a^3\Pi_u)$ with (●) and without (O) target polarization effects. Solid curves: cross sections for excitation of $F_2(a^3\Pi_u)$ (●) and $F_2(A^1\Pi_u)$ (■) derived from analysis of dissociation data of Refs. 65 and 66.

12. HCl cross sections derived by Penetrante and Bardsley [Ref. 70].

13. Rate coefficients for dissociative attachment of HCl in Ar. The measurements are: ●, Ref. 36 and ▲, Ref. 74. The points (□) are calculations using the cross section of Ref. 74.

14. Rate coefficients for dissociative attachment of HCl in $N_2$. The measurements are: O, Ref. 73; ●, Ref. 36; Δ, Ref. 75; ▲, Ref. 74. The points (○ and ■) are calculations using the cross section of Ref. 74 and of Ref. 70 respectively.

15. HCl dissociative attachment cross sections; ▲, Ref. 72; ●; Ref. 70; O, Ref. 74; and Δ, Ref. 71 normalized to the peak value of that of Ref. 74.

16. HCl rotational excitation cross sections computed by Padial, et al. [Refs. 80,81].

17. Effective HCl rotational excitation cross section for $T=300$ K. The curve of points (●) is the statistical mechanical average of the Padial, et al. cross sections [Refs. 80,81] and the curve (O) is the effective single level cross section used by Hake and Phelps [Ref. 79] in the continuous approximation to rotation.

18. The measured cross sections for vibrational excitation of HCl: (O,●), Refs. 83,84 and (Δ,▲,□), Refs. 85,86. The dashed line is the swarm derived cross section of Ref. 70.

19. Relative dissociative attachment cross section (Ref. 71) as a function of gas temperature: O, 300 K; ●, 880 K; Δ, 1000 K; ▲, 1180 K.

20. Dissociative attachment cross section for HCl in various vibrational states [Refs. 92,93] derived from the measurements of Alan and Wong [Ref. 71].
Cl$_2$ Cross Sections

Rogoff, Kramer, & Piejak (1986)

Figure 1
Cl₂ Attachment & Ionization

Figure 2
Figure 3

Cl₂ Dissociative Attachment

Rate Coefficient (cc/s)

E/N (Td)

Sze, et al. (1982)

calcs

Rokni, et al. (1979)

Ar/Cl₂
Cl$_2$ Swarm Coefficients

Characteristic Energy (eV)

Drift Velocity ($10^6$ cm/s)

E/N (Td)

Figure 5
Cl$_2$ Ionization Cross Sections

Stevie & Vasile (1981)

Kurepa & Belic (1978)

Center & Mandl (1972)

Cross Section ($\text{Å}^2$)

Energy (eV)

Figure 6
Figure 7

F$_2$ Cross Sections
Hayashi & Nimura (1983)

Cross Section (Å$^2$)

Energy (eV)
Figure 8
Figure 10
HCl Cross Sections
Penetrante & Bardsley (1983)

Figure 12
HCl Dissociative Attachment
Argon Buffer Gas

Rate Coefficient (10^{-10} \text{ cm}^{-3}\text{sec}^{-1})

$E/N$ (Td)

- Sze, et al. (1982)
- Petrovic, et al. (1988) (meas)
- Petrovic, et al. (1988) (calc)

Figure 13
HCl Dissociative Attachment

![Graph showing energy versus cross section for different studies.](image)

- Orient & Srivastava (1985)
- Penetrante & Bardsley (1983)
- Petrovic, et al. (1988)
- Alan & Wong (1981)

Cross Section ($\text{A}^2$)

Energy (eV)

Figure 15
HCl Rotational Cross Sections


\[ j = 0 \rightarrow 1 \text{ through } j = 9 \rightarrow 10 \]

Cross Section (Å²)

Energy (eV)

Figure 16
II. CF$_4$, SiH$_4$, CH$_4$
A Critical Evaluation of
Low Energy Electron Impact Cross Sections
for Plasma Processing Modeling II: CF$_4$, SiH$_4$, and CH$_4$

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Abstract

The available information on low energy electron impact cross sections for CF$_4$, SiH$_4$, and CH$_4$ is reviewed and critically evaluated. Of interest are the cross sections for momentum transfer; rotational, vibrational, and electronic excitation; dissociation; and attachment and ionization. Recommended cross sections are identified where feasible. Much of the process of critical evaluation is based on electron transport, or swarm, coefficients using the published cross sections and comparing with published measurements.

Key words: electron molecule collisions, cross sections, swarm analysis
I. INTRODUCTION

Cross sections for collisions of low energy electrons with CF$_4$, SiH$_4$, and CH$_4$ are of interest for plasma processing of semiconductors. The first is used in etching processes and the second two are used in deposition processes. In addition carbon tetrafluoride (or tetrafluoromethane) and methane have applications in discharge switches.

With the exception of methane, which, due to its unique properties and availability, has been the subject of investigation for many years, little research was performed on the electron impact cross sections for silane and tetrafluoromethane until relatively recently. All three have been the subjects of vigorous research for the past five years. In general we have the least information on CF$_4$ and the most on methane.

There are a number of similarities among these three molecules. They are all spherical tops having neither dipole nor quadrupole moment. Hence the rotational cross sections are expected to be very small. The cross section for the $\Delta J=0$ octopole transition in methane at low energies is only about $0.06 \text{Å}^2$, for example. These molecules also have small attachment cross sections (approximately $0.01-0.02 \text{Å}^2$ for CF$_4$ and SiH$_4$ and about $8x10^{-4} \text{Å}^2$ for CH$_4$) but large dissociation cross sections. They all have Ramsauer minima in their momentum transfer cross sections and large vibrational excitation cross sections in the energy range of the Ramsauer minimum. The four dominant vibrational modes are labeled $\nu_1$, symmetric stretch; $\nu_2$, symmetric bend; $\nu_3$, asymmetric stretch; and $\nu_4$, asymmetric bend. The energies of these states for all three molecules and their degeneracies are listed in Table I. The energies of the two stretching modes, $\nu_1$ and $\nu_3$, and of the two bending modes, $\nu_2$ and $\nu_4$, are each so close that experimentally there is insufficient energy resolution to distinguish them. Consequently two vibrational cross sections are reported for each molecule, $\sigma_v(1,3)$ for the stretching modes and $\sigma_v(2,4)$ for the bending modes. Hence, the former has a statistical weight of four and the latter a weight
of five.

Although the two-term spherical harmonic expansion approximation to the solution of Boltzmann's equation for electrons in gas is frequently used in the analysis of swarm data in these gases, it is of variable accuracy due to the size and location of the vibrational cross sections relative to the elastic cross section and due to the propensity of these molecules to forward scatter. Some of the authors whose work is discussed below have used Monte Carlo calculations in the swarm unfolding process. Most of these, however, have assumed isotropic scattering, as the data needs and the complexity of the simulation are increased greatly by any other assumption. Additionally, we do not have adequate energy and angle dependent data even for methane, the most well studied of these molecules. Kushner has performed anisotropic MC calculations in obtaining cross sections for methane$^8$ and for silane.$^9$ In his analyses the differential cross sections were characterized as:

$$\sigma(\theta) \propto [\cos(\theta/2)]^{x(\epsilon)}$$

The larger the energy dependent scattering parameter, $x(\epsilon)$, the more forward peaked the cross section. Note that this form lacks $180^0$ backscattering. The integrated cross sections obtained by Kushner are not radically different from those obtained by the other authors using two-term and isotropic Monte Carlo analyses. Haddad$^{10}$ presents an especially useful discussion of these issues. An exploration of swarm unfolding using the two-term approximation, isotropic MC, anisotropic MC, and some of the various multi-term methods operating on the same experimental data would be an interesting study.

As was the previous paper, this review is primarily concerned with the construction of sets of cross sections that may be useful in modeling the plasma chemistry of systems containing these molecules. The point here is not to compare theory and experiment, consequently most of the discussion concerns cross sections that have been derived from
experiments — usually a combination of beam and swarm measurements. I have not included graphs of measured and computed swarm data in this review because the authors of the swarm analyses cited herein have generally been very diligent about including detailed figures comparing their results with measurements and with other calculations.

II. ELECTRON COLLISIONS WITH CF$_4$

Hayashi$^{11}$ has published a cross section set for carbon tetrafluoride. Masek, et al.$^{12}$ and Stefanov, et al.$^{13}$ have attempted also to obtain momentum transfer and vibrational cross sections from published swarm data but their resulting cross sections are coarse and distinctly inferior to Hayashi's. Hayashi's complete set of cross sections is shown in Fig. 1.

In developing this set of cross sections Hayashi used the conventional two-term expansion approximation to the solution of Boltzmann's equation. The momentum transfer and vibrational cross sections were based on relative differential cross section measurements,$^{14}$ theoretical$^{15}$ and measured$^{16}$ total and momentum transfer cross sections, drift velocity measurements,$^{17,18}$ and characteristic energy measurements.$^{18,19}$ Note, however, that much more recent measurements by Hunter, et al.$^{20}$ have yielded drift velocities that are 10% to 15% smaller than those of Refs. 17 and 18. Kline$^{21}$ has performed isotropic Monte Carlo transport calculations for electrons in CF$_4$ and suggests that the vibrational excitation cross sections be multiplied by 0.7 to improve the fit to swarm data.

The ionization cross section used by Hayashi is that measured by Leiter, et al., which appeared in an unpublished proceedings,$^{22}$ multiplied by 1.1 in order to better fit the measured$^{18,19,23–26}$ ionization coefficient, $\alpha/N$. More recent measurements of $\alpha/N$ by Hunter, et al.$^{27}$ are in good excellent agreement with the older measurements used by Hayashi. In addition, more recent published$^{28}$ measurements of the ionization cross
section by the authors of Ref. 22 show a total cross section that is only a few percent larger than used by Hayashi and include partial cross sections for production of ionic fragments. The dominant ion is CF$_3^+$, the authors finding no evidence of stable CF$_4^+$ in their experiment. A more recent measurement by Chantry and Freidhoff$^{29}$ agrees with the results of Ref. 27, except for a need to shift the Stephan, et al. cross sections to higher energy by 0.55 eV. As a final note, however, an even more recent measurement by Ma and Bonham$^{30}$ yields an ionization cross section that has the same shape as that of Stephan, et al.$^{28}$ but is a factor of two larger!

The dissociation cross section has been measured by Winters, et al.$^{31,32}$ but probably includes a contribution from dissociative ionization. Hayashi has taken the neutral dissociation cross section to be $\sigma_{dn} = \sigma_d - \sigma_i$.

There have been several measurements$^{33-36}$ of the attachment cross section, which is small. Hayashi adjusted the measured cross section slightly to better fit the experimental attachment coefficient.$^{18,19,23-26}$

Since the publication of Hayashi's work, further information has appeared on carbon tetrafluoride. Curtis, et al.$^{37}$ have performed characteristic energy measurements and performed Monte Carlo swarm simulations to derive momentum transfer and vibrational excitation cross sections. Their momentum transfer cross sections as well as Hayashi's, the measured total cross section of Jones,$^{38}$ and the measured $\sigma_m$ of Sakae, et al.,$^{39}$ which starts at 75 eV, are shown in Fig. 2. The differences between the two swarm derived cross sections are substantial. The Curtis, et al. cross section has a dubious shape (as does the silane $\sigma_m$ derived by the same group). The high energy part of Hayashi's cross section is somewhat low in comparison with the recent measurements by Sakae, et al.

Figure 3 shows the vibrational cross sections derived by Hayashi$^{11}$ and by Curtiss, et al.$^{37}$ The Curtiss, et al. MC results have about the correct magnitude but an unrealistic energy dependence. Note that they have used the larger of $\nu_2$ and $\nu_4$ and of $\nu_1$ and $\nu_3$ as the excitation energy for the vibrational states. The dashed lines in Fig. 3 are cross
sections estimated using the Born approximation and measured absolute infra-red absorption intensities. These compare very well with Hayashi's swarm derived cross sections.

III. ELECTRON COLLISIONS WITH SiH₄

Garscadden, et al., Ohmori, et al., Hayashi, Mathieson, et al., Kushner, and Kurachi and Nakamura have all assembled sets of cross sections for low energy electrons on silane. All these authors primarily used analysis of swarm data to develop their cross sections. There are relatively few direct measurements of and theoretical calculations of electron impact cross sections on silane.

Fig. 4 shows a comparison of the momentum transfer cross sections deduced in four recent compilations. Fig. 5 shows a similar comparison for the two lowest energy vibrational cross sections. The differences are phenomenal. Until very recently there have been no beam data available for elastic scattering and vibrational excitation in silane. These cross sections were derived using drift velocity and characteristic energy data. Mathieson, et al.; Hayashi; and Ohmori, et al. used the 1968 drift velocity data of Pollock in their analyses. Mathieson, et al. used the recent Dₜ/μ measurements of Millican and Walker whereas Hayashi and Ohmori, et al. used the older data of Cottrell and Walker. Ohmori, et al. performed their swarm calculations using the two-term spherical harmonic solution to Boltzmann's equation for electrons in gas, as did Hayashi, with Monte Carlo calculations serving as a check, whereas Mathieson, et al. used MC calculations exclusively. The work of Kurachi and Nakamura is the most comprehensive. They measured transport coefficients in argon and determined a momentum transfer cross section for argon, then measured transport coefficients in Ar/SiH₄ mixtures, and finally derived a set for silane cross sections using their data on νₐ and Dₙ/μ in these
mixtures. They performed the swarm calculations using the two-term expansion assuming that, although the use of this approximation was dubious for pure silane, the accuracy may be acceptable for Ar/SiH₄ mixtures, which comprised 0.5% – 5% silane.

We see plotted in Fig. 4, in addition to the swarm derived cross sections, the momentum transfer cross measured by Tanaka, et al.⁴⁶ The closest swarm result to this is that published by Hayashi,¹¹ for which we have no details on its origin. The recent Schwinger multichannel calculation of Winstead and McCoy⁵⁵ is also in excellent agreement with the beam measurements for energies greater than about 7 eV. In Fig. 5 we see the relative cross section σᵥ(1,3), which has been normalized to the peak value of the Kurachi and Nakamura⁴³ cross section, plotted along with the swarm derived results. Clearly the Kurachi and Nakamura cross section is closest to the truth. That the peak lies closer to 2 eV, rather than the 7–8 eV shown by Ohmori, et al.⁴¹ and by Hayashi,¹¹ is also confirmed by the Tanaka, et al.⁴⁶ measurements.

The cross section set published by Kurachi and Nakamura is shown in Fig. 6. Unlike Ohmori, et al. who lumped electronic excitation and dissociation into a single cross section they have, following Hayashi, tabulated separate cross sections for each process. It is not clear, however, what the basis for this is. The sum of these cross sections is approximately equal to the dissociation cross section of Ohmori, et al., which was taken to be the measured cross section of Perrin, et al.⁴⁴ The ionization cross section is that measured by Chatham, et al.⁴⁴ Shimozuma and Tagashira⁶¹ report the first measurements of the ionization coefficient, α/N, for silane but, curiously, Kurachi and Nakamura⁴³ did not compute α/N using their cross sections.
IV. ELECTRON COLLISIONS WITH CH$_4$

Of the three molecules discussed in this review, methane is easily the most studied, especially its momentum transfer and total scattering cross sections, with numerous measurements, including some by Ramsauer himself, dating back to 1925 and numerous theoretical papers having been published. Complete sets of cross sections have been assembled and published by Hayashi,$^{11}$ Ohmori, et al.,$^{62}$ and Davies, et al.$^{63}$ The latter two, as will be discussed below, are very similar, differing in the treatment of dissociation and slightly in the high energy part of the momentum transfer cross section. Two very recent sets of cross sections, as yet unpublished, have been assembled by Nakamura$^{64,65}$ and by Peres, et al.$^{66,67}$ The latter were derived by swarm unfolding of electron drift velocity data for argon–methane mixtures. Further details of these last two studies are unavailable at this time.

Unlike the situation that we have seen with the other molecules discussed in this and in the previous review, there are a wealth of measured data on electron scattering cross sections in methane. There are numerous recent measurements of the total scattering cross section,$^{68-73}$ elastic cross section,$^{39,74-80}$ and vibrational cross sections.$^{76,78,81,82}$ See also the review by Trajmar, et al.$^{83}$

A. Momentum Transfer and Vibrational Excitation

Most of the swarm derived momentum transfer cross sections$^{10,11,41,56,64,66,84,85}$ in the vicinity of the Ramsauer minimum published within the past twenty two years are plotted in Fig. 7. The situation is not as hopeless as it looks; the most recently published cross sections, which are based on the most recent experimental information and analysis techniques, all lie relatively close to one another. That of Peres, et al.$^{66}$ has an unusual and, perhaps, suspicious shape near the minimum but, generally, agreement seems to have been achieved. Several$^{62,64,66}$ of the swarm derived cross sections up to an energy of 100
eV as well as the recent measurement by Sakae, et al.\textsuperscript{39} are plotted in Fig. 8.

The momentum transfer cross section obtained by Ohmori, et al.\textsuperscript{62} is based on the beam measurements of Sohn, et al.,\textsuperscript{76} Tanaka, et al.,\textsuperscript{75} and Vuskovic and Trajmar.\textsuperscript{77} They performed swarm calculations using the two term approximation for small values of E/N and Monte Carlo for larger E/N and were able to find a cross section that agreed with published swarm data and agreed, within the experimental error bars, with the beam measurements. Davies, et al., who also used the Monte Carlo technique in their analyses, used this momentum transfer cross section below 20 eV and increased it slightly, as shown in Fig. 8, for energies than this to achieve better agreement with their drift velocity measurements.

We see a greater disparity, however, among the vibrational excitation cross sections, which we see plotted in Fig. 9. Ohmori, et al. used the differential cross section measurements of Sohn, et al.\textsuperscript{76} and of Rohr\textsuperscript{74} for energies less than 3 eV and integrated them to obtain $\sigma_m$ having extrapolated to the 0 and 180\textdegree\ scattering angles. For energies in the range from 3 to 20 eV they used the published cross sections of Tanaka, et al.\textsuperscript{75} These cross sections were used as is by Davies, et al. Lacking the details of Nakamura's and Peres', et al. calculations, it is not clear why their vibrational excitation cross sections are so different from those of Ohmori, et al. at low energies. Haddad\textsuperscript{10} measured the drift velocity and characteristic energy and dervied momentum transfer and vibrational excitation cross sections using a multi-term solution to Boltzmann's equation. His $\sigma_m(\epsilon)$ is very similar to that given by Ohmori, et al. His derived vibrational cross sections, however, are very different. Their maximum value is only about 4 $\text{Å}^2$ and they decrease montonically above the maximum to about 2 eV and then are flat up to 10 eV, the maximum energy shown by Haddad. Haddad does point out, however, that the shape of the vibrational cross sections is somewhat arbitrary without more detailed beam measurements or theory.
B. Dissociation and Ionization

Total dissociation cross sections for methane have been measured by Winters\textsuperscript{85} and by Perrin, et al.\textsuperscript{44} Davies, et al. state that there are no known bound electronic states of methane; hence, all electronic excitation results in dissociation. Ohmori, et al. and Davies, et al. have subtracted the dissociative ionization cross section measured by Chatham, et al.\textsuperscript{45} from the total dissociation cross section of Winters to obtain the total neutral dissociation cross section. Davies, et al. have, somewhat arbitrarily, divided the dissociation cross section up into four partial cross sections of equal magnitude except the differences in threshold energy. This is shown in Fig. 10. They claim that the predicted values of the ionization coefficient for $E/N < 150$ Td are sensitive to the threshold behavior of the dissociation and ionization cross sections.

There have been several measurements\textsuperscript{45,86–89} of the total ionization cross section of methane over the past 25 years. Ohmori, et al. used the cross section published by Chatham, et al.\textsuperscript{45} without modification. Davies, et al. have used the Rapp and Englander–Golden\textsuperscript{86} cross section from threshold to 14.3 eV and that of Chatham, et al. above that energy. They then split this cross section into two representing $\text{CH}_4^+$ and $\text{CH}_3^+$ as products. These cross sections are equal above 70 eV. This is approximately in agreement with the measurements of Adamczyk, et al.\textsuperscript{87} of the partial ionization cross sections.

The complete cross section developed by Davies, et al.\textsuperscript{63} is displayed in Fig. 11.

V. CONCLUSIONS

The following recommendations can be made concerning electron impact cross sections:

(a) $\text{CF}_4$: Hayashi\textsuperscript{11} has assembled a reasonable set of cross sections for tetrafluoromethane. At this time it should be the recommended set although, as we have
seen above, Kline$^{21}$ has suggested a slight reduction in the vibrational cross sections and, as we have also seen, there appears to be some uncertainty in the ionization cross section.$^{28-30}$ Clearly much more experimental information is needed for carbon tetrafluoride.

(b) SiH$_4$: of the several sets of cross sections for silane that have been published the most recent and, perhaps, most thorough is that of Kurachi and Nakamura,$^{43}$ which should be the recommended set.

(c) CH$_4$: there is more experimental information on methane than on the other five molecules discussed in these two reviews combined. Of the sets of cross sections that have been published that of Davies, et al.$^{63}$ is to be recommended. It is very similar to that published by Ohmori, et al.$^{62}$ but is slightly more refined. The two most recent set of cross sections, those of Nakamura$^{64}$ and of Peres, et al.$^{66}$ were received too late to do more than graph them and make a few comments on them in this review. They need further study.
ACKNOWLEDGEMENTS

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REFERENCES


67. M.C. Bordage, personal communication.


Table I  Energies and degeneracies for vibrational states
of $\text{CF}_4$, $\text{SiH}_4$, and $\text{CH}_4$.

<table>
<thead>
<tr>
<th>Vibrational mode</th>
<th>$\text{CF}_4$ (eV)</th>
<th>$\text{SiH}_4$ (eV)</th>
<th>$\text{CH}_4$ (eV)</th>
<th>Degeneracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_1$</td>
<td>0.112</td>
<td>0.271</td>
<td>0.362</td>
<td>1</td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>0.0542</td>
<td>0.121</td>
<td>0.190</td>
<td>2</td>
</tr>
<tr>
<td>$\nu_3$</td>
<td>0.1568</td>
<td>0.271</td>
<td>0.374</td>
<td>3</td>
</tr>
<tr>
<td>$\nu_4$</td>
<td>0.078</td>
<td>0.113</td>
<td>0.162</td>
<td>3</td>
</tr>
</tbody>
</table>
FIGURE CAPTIONS

1. Cross sections for CF$_4$ derived by Hayashi [Ref. 11].

2. CF$_4$ cross sections: Momentum transfer cross sections from Hayashi [Ref. 11], (O); Curtis, et al. [Ref. 37], (□); and Sakae [Ref. 39], (◇). Total cross section was measured by Jones [Ref. 38].

3. CF$_4$ vibrational excitation cross sections: from Hayashi [Ref. 11], (O, ●) and from Curtis, et al. [Ref. 37], (□, ■, ▲, ▼).

4. SiH$_4$ momentum transfer cross section: from Hayashi [Ref. 11], (O); Ohmori, et al. [Ref. 41], (Δ); Mathieson, et al. [Ref. 42], (▲); Kurachi and Nakamura [Ref. 43], (●); and Tanaka, et al. [Ref. 46], (■).

5. SiH$_4$ vibrational excitation cross sections: from Hayashi [Ref. 11], (circles); Ohmori, et al. [Ref. 41], (squares); Mathieson, et al. [Ref. 42], (inverted triangles); Kurachi and Nakamura [Ref. 43], (triangles); and Tronc, et al. [Ref. 47], (dashed line). The open symbols denote $\sigma_v$(2,4) and the solid symbols $\sigma_v$(1,3).

6. Complete SiH$_4$ cross section set assembled by Kurachi and Nakamura [Ref. 43].

7. CH$_4$ momentum transfer cross section near the Ramsauer minimum: from Hayashi [Ref. 11], (▼); Pollock [Ref. 56], (▲); Ohmori, et al. [Ref. 62], (□); Nakamura [Refs. 64,65], (◇); Peres, et al. [Ref. 66], (▼); Ferch, et al. [Ref. 70], (■); Duncan and Walker [Ref. 84], (Δ); and Haddad [Ref. 85], (O).

8. CH$_4$ momentum cross section: from Ohmori, et al. [Ref. 62], (O); Nakamura [Refs. 64,65], (■); Peres, et al. [Ref. 66], (Δ); and Sakae [Ref. 39] (●).

9. CH$_4$ vibrational excitation cross sections: from Ohmori, et al. [Ref. 62], (circles); Nakamura [Refs. 64,65], (squares); and Peres, et al. [Ref. 66], (triangles). The open symbols denote $\sigma_v$(2,4) and the solid symbols $\sigma_v$(1,3).

10. CH$_4$ dissociation and ionization cross sections obtained by Davies, et al. [Ref. 63]. The partial dissociation cross sections are explained in the text.
11. Complete set of cross sections for CH$_4$ published by Davies, et al. [Ref. 63].
CF$_4$ Cross Sections

Hayashi (1987)

Figure 1
CF$_4$ Cross Sections

Cross Section (Å$^2$)

Energy (eV)

Figure 2
Figure 4: Momentum Transfer Cross Section

SiH₄ (meas.)

Tanaka, et al.

Hayashi (1987)

Kurachi & Nakamura (1989)

Ohmori, et al. (1986)

Mathieson, et al. (1987)

Cross Section (Å²)

Energy (eV)
SiH₄ Vibrational Excitation Cross Sections

Cross Section (Å²)

Energy (eV)

Figure 5
Figure 9

CH₄ Vibrational Excitation Cross Sections
CH$_4$ Dissociation & Ionization Cross Sections

Davies, Kline, & Bies (1989)

Figure 10
CH$_4$ Cross Sections

Davies, Kline, & Bies (1989)

Figure 11