

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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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. Most of the cross sections reviewed have been determined by swarm techniques whereby cross sections are adjusted based on a comparison of predicted and measured electron transport, or swarm, coefficients.

KEY WORDS: Electron-molecule collisions; cross sections; swarm analysis; plasma processing.

1. 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.⁽¹⁻³⁾ 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.⁽³⁻⁶⁾

With the exception of methane, which due to its unique properties and availability, has been the subject of investigation for many years, little research has been 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.

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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 $\Delta J=0$ octupole transition in methane at low energies is only about 0.06 \AA^2 , for example.⁽⁷⁾ These molecules also have small attachment cross sections (approximately $0.01\text{--}0.02 \text{ \AA}^2$ for CF_4 and SiH_4 , and about $8 \times 10^{-4} \text{ \AA}^2$ 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 ν_1 , symmetric stretch; ν_2 , symmetric bend; ν_3 , asymmetric stretch; and ν_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, ν_1 and ν_3 , and of the two bending modes, ν_2 and ν_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 $\sigma_b(2, 4)$ for the bending modes. Hence, the former has a statistical weight of 4 and the latter a weight of 5.

A significant property of these molecules, which is important in the determination of electronic excitation cross sections, is that they have a large manifold of electronic states that predissociate when excited by electron impact. Electron energy loss spectra for methane have been measured by Vuskovic and Trajmar⁽⁸⁾ and Dillon *et al.*⁽⁹⁾ and show featureless spectra, indicating that the energy loss is nearly continuous and that specific excitation processes cannot be easily picked out. It is not clear then what is the best means of dealing with electronic excitation and dissociation of these molecules. As we will see, some authors use one cross section to represent the total excitation of these states while others use multiple cross sections at different, somewhat arbitrary, energies to approximately represent the continuous energy loss of these excitation processes.

Table I. Energies and Degeneracies for Vibrational States of CF_4 , SiH_4 , and CH_4

Vibrational mode	Energy (eV)			Degeneracy
	CF_4	SiH_4	CH_4	
ν_1	0.112	0.271	0.362	1
ν_2	0.0542	0.121	0.190	2
ν_3	0.1568	0.271	0.374	3
ν_4	0.078	0.113	0.162	3

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⁽¹⁰⁾ and for silane.⁽¹¹⁾ In his analyses the differential cross sections were characterized as

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

The larger the energy-dependent scattering parameter $\chi(\epsilon)$, the more forward peaked the cross section. Note that this form lacks 180° 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⁽¹²⁾ presents an especially useful discussion of these issues.

The use of two-term expansion solutions to Boltzmann's equation in the determination of cross sections for these molecules is somewhat controversial. On the one hand, it is clear that use of this expansion without the so-called multi-term corrections yields swarm coefficients that are in error, the degree of error depending on the coefficient and E/N . On the other hand, some take the perspective that the derived cross section is tantamount to a fitting parameter as it is used in discharge modeling. Taking this perspective obtaining a cross section using the two-term approximation and then using it again in plasma modeling with a two-term solution of Boltzmann's equation, which is computationally much quicker than other solutions, may be a reasonable thing to do. The same operational arguments apply to the use of isotropic versus anisotropic scattering, for instance. Some of the swarm-determined cross sections have come from mixture data. In that case it is often felt that these issues are minimized as long as the buffer gas being used, usually one of the rare gases, is suitable for the two-term approximation.

As is the preceding paper on electron impact cross sections for Cl_2 , F_2 , and HCl , 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. Theoretical calculations of electron impact cross sections for these molecules are very difficult and computationally intensive. Such calculations have been performed primarily for elastic scattering and vibrational excitation and have, generally, not yielded accurate cross sections for impact energies below several electron volts.

2. ELECTRON COLLISIONS WITH CF₄

Hayashi⁽¹³⁾ has published a cross section set for carbon tetrafluoride. Masek *et al.*⁽¹⁴⁾ and Stefanov *et al.*⁽¹⁵⁾ 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,⁽¹⁶⁾ theoretical⁽¹⁷⁾ and measured⁽¹⁸⁾ total and momentum transfer cross sections, drift velocity measurements,^(19,20) and characteristic energy measurements.^(20,21) Note, however,

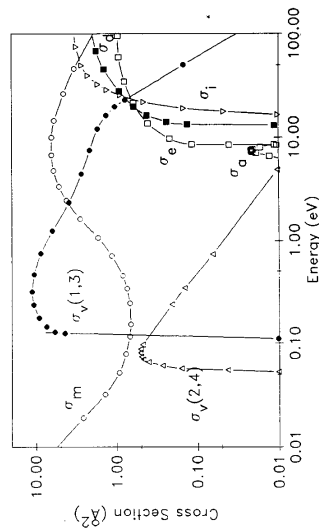


Fig. 1. Cross sections for CF₄ derived by Hayashi.⁽¹³⁾

that much more recent measurements by Hunter *et al.*⁽²²⁾ have yielded drift velocities that are 10–15% smaller than those of Refs. 19 and 20. Kline⁽²³⁾ has performed anisotropic Monte Carlo transport calculations for electrons in CF₄ and suggests that the vibrational excitation cross sections be multiplied by 0.7 to improve the fit to swarm data.

A possible issue that was not discussed by Hayashi is the effect of vibrational excitation on the determination of the cross sections.⁽²⁵⁾ We see in Table I that the energies of the ν_2 and ν_4 states are small enough relative to the mean thermal energy at 300 K that 17% of the CF₄ will be in the ν_2 state and 10% in the ν_4 . Superelastic collisions between electrons and vibrationally excited CF₄ should, consequently, be of significance. The effects of superelastic collisions on the derived cross sections appears to not have been explored.

The ionization cross section used by Hayashi is that measured by Leiter *et al.*, which appeared in an unpublished proceedings,⁽²⁵⁾ multiplied by 1.1 in order to better fit the measured^(20,21,26–29) ionization coefficient, α/N . More recent measurements of α/N by Hunter *et al.*⁽³⁰⁾ are in excellent agreement with the older measurements used by Hayashi. In addition, more recent measurements published by Stephan *et al.*⁽³¹⁾ (the authors of Ref. 25) of the ionization cross section 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 CF₃⁺, the authors finding no evidence of stable CF₂⁺ in their experiment. A more recent measurement by Chantray and Freidhoff⁽³²⁾ agrees with the results of Hunter *et al.* and shows a need to shift the Stephan *et al.* cross sections to higher energy by 0.55 eV.

Even more recent measurements by Ma, Bruce, and Bonham,^(33,34) however, yield an ionization cross section that has the same shape as that of Stephan *et al.*⁽³¹⁾ but is a factor of 2 larger. The authors note,^(33,35) however, that their cross sections are now in agreement with revised estimates by Stephan *et al.* Reconciliation of these new data with the ionization coefficient measurements will require adjustment of the other CF₄ inelastic cross sections. Ma *et al.* find that for impact energies greater than 30 eV dissociative ionization represents 80% of the total dissociation cross section. Issues of dissociative ionization and neutral dissociation are reviewed by Bonham and Bruce in a recent paper.⁽³⁶⁾

The dissociation cross section has been measured by Winters *et al.*^(37,38) 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^(39–42) of the attachment cross section, which is small. Hayashi adjusted the measured cross section slightly to better fit the experimental attachment coefficient.^(20,21,26–29)

Since the publication of Hayashi's work, further information has appeared on carbon tetrafluoride. Curtis *et al.*⁽⁴³⁾ 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⁽⁴⁴⁾ and the measured σ_m of Sakae *et al.*⁽⁴⁵⁾ which starts at 75 eV, are shown in Fig. 2. The Curtis *et al.* cross section is significantly different from that determined by Hayashi. 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⁽¹³⁾ and by Curtis *et al.*⁽⁴³⁾ The Curtis *et al.* MC results have about the same magnitude as Hayashi's but a very different energy dependence. Note that they have used the larger of ν_2 and ν_4 and of ν_1 and ν_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 infrared absorption intensities. These compare very well with Hayashi's swarm-derived cross sections.

As a final note on CF_4 , Boesten *et al.*⁽⁴⁶⁾ have very recently performed crossed beam measurements of low-energy differential cross sections over the energy range from 1 eV to 100 eV. Their integrated total cross section is fractionally smaller than that measured by Jones, and the momentum transfer cross section that they have determined is somewhat larger than that of Hayashi shown in Fig. 3.

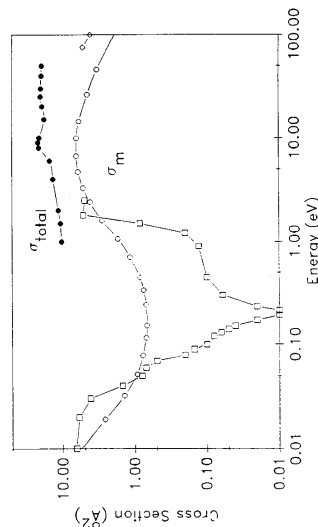


Fig. 2. CF_4 cross sections: momentum transfer cross sections from Hayashi,⁽¹³⁾ Curtis *et al.*,⁽⁴³⁾ and Sakae,⁽⁴⁵⁾ Total cross section was measured by Jones.⁽⁴⁴⁾

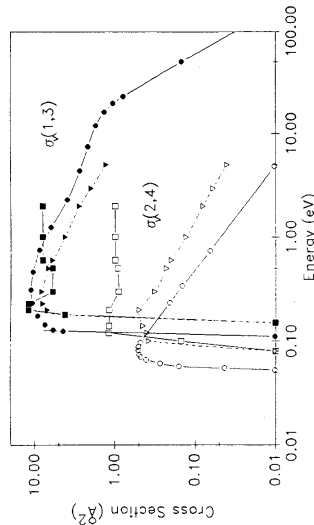


Fig. 3. CF_4 vibrational excitation cross sections: from Hayashi,⁽¹³⁾ (○, ●) and Curtis *et al.*⁽⁴³⁾ (□, ■, ▽, ▴).

3. ELECTRON COLLISIONS WITH SiH_4

Garscadden *et al.*⁽⁴⁷⁾ Ohmori *et al.*,⁽⁴⁸⁾ Hayashi,⁽¹³⁾ Mathieson *et al.*,⁽⁴⁹⁾ Kushner,⁽¹¹⁾ and Kurachi and Nakamura⁽⁵⁰⁾ 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⁽⁵¹⁻⁵⁴⁾ and theoretical calculations⁽⁵⁵⁻⁶³⁾ of electron impact cross sections on silane.

Figure 4 shows a comparison of the momentum transfer cross sections deduced in four recent compilations. Figure 5 shows a similar comparison for the two lowest-energy vibrational cross sections. The differences are substantial. Until very recently^(53,54) there had 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⁽⁶⁴⁾ in their analyses. Mathieson *et al.* used the recent D_T/μ measurements of Millikan and Walker,⁽⁶⁵⁾ whereas Hayashi and Ohmori *et al.* used the older data of Cottrell and Walker.⁽⁶⁶⁾ 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,⁽⁶⁷⁾ then measured transport coefficients in Ar/SiH_4 mixtures,⁽⁶⁸⁾ and finally derived a set for

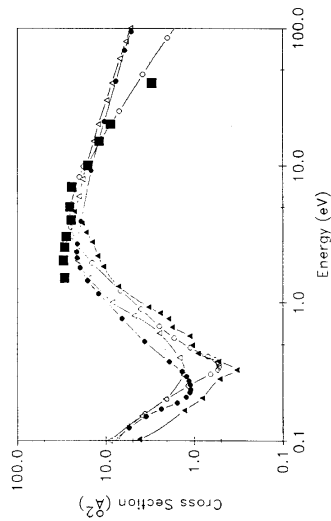


Fig. 4. SiH_4 momentum transfer cross section: from Hayashi⁽¹³⁾ (○), Ohmori *et al.*⁽⁴⁸⁾ (△), Mathieson *et al.*⁽⁴⁹⁾ (▲), Kurachi and Nakamura⁽⁵⁰⁾ (●), and Tanaka *et al.*⁽⁵¹⁾ (■).

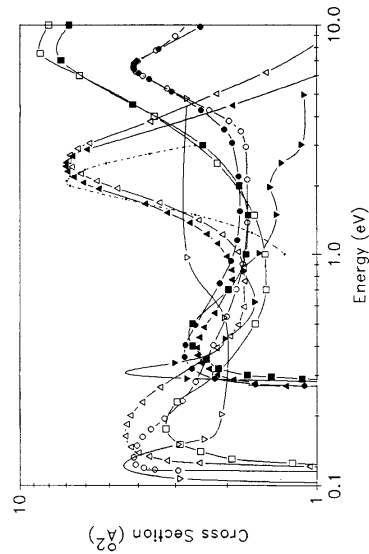


Fig. 5. SiH_4 vibrational excitation cross sections: from Hayashi⁽¹³⁾ (circles), Ohmori *et al.*⁽⁴⁸⁾ (squares), Mathieson *et al.*⁽⁴⁹⁾ (inverted triangles), Kurachi and Nakamura⁽⁵⁰⁾ (triangles), and Tronc *et al.*⁽⁵⁴⁾ (dashed line). The open symbols denote $\sigma_v(2,4)$ and the solid symbols $\sigma_v(1,3)$.

silane cross sections using their data on v_d and D_L/μ in these mixtures.⁽⁵⁰⁾ 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/ SiH_4 mixtures, which comprised 0.5–5% silane. This work has been refined further by these authors in a very recent publication.⁽⁶⁹⁾

We see plotted in Fig. 4, in addition to the swarm-derived cross sections, the momentum transfer cross measured by Tanaka *et al.*⁽⁵¹⁾ The closest swarm result to this is that published by Hayashi,⁽¹³⁾ for which we have no details on its origin. The recent Schwinger multichannel calculation of Winstead and McKoy⁽⁶²⁾ 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 $\sigma_v(1,3)$, which has been normalized to the peak value of the Kurachi and Nakamura⁽⁵⁰⁾ 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.*⁽⁴⁸⁾ and by Hayashi,⁽¹³⁾ is also confirmed by the Tanaka *et al.*⁽⁵¹⁾ 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 several values of energy loss. 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.*⁽⁵¹⁾ The

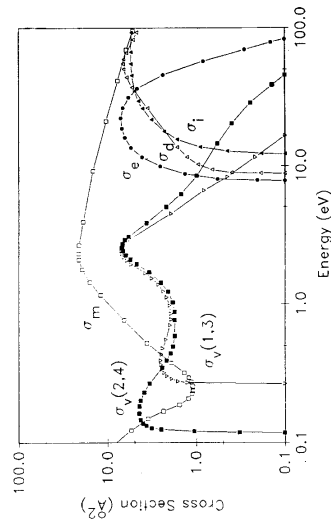


Fig. 6. Complete SiH_4 cross section set assembled by Kurachi and Nakamura.⁽⁵⁰⁾

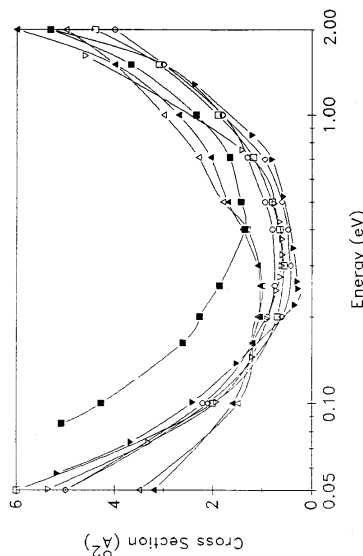


Fig. 7. CH₄ momentum transfer cross section near the Ramsauer minimum; from Hayashi⁽¹³⁾ (▽), Pollock⁽⁶⁷⁾ (▲); Ohmori *et al.*⁽⁷¹⁾ (□), Nakamura^(73,74) (●), Peres *et al.*⁽⁷⁵⁾ (▼), Ferch *et al.*⁽⁷⁶⁾ (■), Duncan and Walker⁽⁸²⁾ (△), and Haddad⁽⁸²⁾ (○).

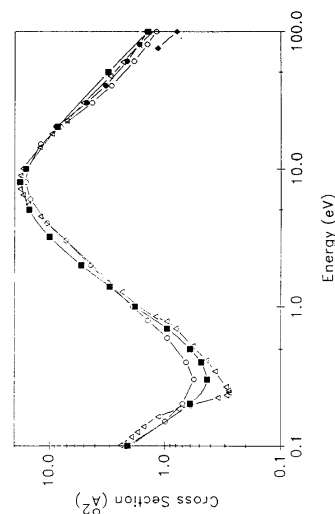


Fig. 8. CH₄ momentum cross section; from Ohmori *et al.*⁽⁷¹⁾ (○), Nakamura^(73,74) (■), Peres *et al.*⁽⁷⁵⁾ (△), and Sakae⁽⁴⁵⁾ (◆).

ionization cross section is that measured by Chatham *et al.*⁽⁵²⁾ Shimozuma and Tagashira⁽⁷⁰⁾ report the first measurements of the ionization coefficient, α/N , for silane but, curiously, Kurachi and Nakamura⁽⁵⁰⁾ did not compute α/N using their cross section set.

4. ELECTRON COLLISIONS WITH CH₄

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,⁽¹³⁾ Ohmori *et al.*,⁽⁷¹⁾ and Davies *et al.*⁽⁷²⁾ 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^(73,74) and by Peres *et al.*^(75,76) 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 is a wealth of measured data on electron scattering cross sections in methane. There are numerous recent measurements of the total scattering cross section,⁽⁷⁷⁻⁸²⁾ elastic cross section,^(45,83-88) and vibrational cross sections.^(85,86,89,90) See also the review by Trajmar *et al.*⁽⁹¹⁾

4.1. Momentum Transfer and Vibrational Excitation

Most of the swarm-derived momentum transfer cross sections^(12,13,48,64,73,75,92,93) in the vicinity of the Ramsauer minimum published within the past 22 years are plotted in Fig. 7. The situation is not as hopeless as it may look; 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.*⁽⁷⁵⁾ has the smallest minimum at somewhat lower energy than the others but, generally, agreement seems to have been achieved. Several^(71,73,75) of the swarm-derived cross sections up to an energy of 100 eV as well as the recent measurement by Sakae *et al.*⁽⁴⁵⁾ are plotted in Fig. 8.

The momentum transfer cross section obtained by Ohmori *et al.*⁽⁷¹⁾ is based on the beam measurements of Sohn *et al.*⁽⁶⁵⁾ Tanaka *et al.*⁽⁶⁴⁾ and Vuskovic and Trajmar.⁽⁸⁾ They performed swarm calculations using the

two-term approximation for small values of E/N and Monte Carlo calculations for larger E/N and were able to find a cross section that agreed with published swarm data and that agreed, within the experimental error bars, with the beam measurements. Davies *et al.*, who also used Monte Carlo simulations in their analyses, used this momentum transfer cross section below 20 eV and increased it slightly, as shown in Fig. 8, for energies greater 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.*⁽⁸⁵⁾ and of Rohr⁽⁸³⁾ for energies less than 3 eV and integrated them to obtain σ_{vib} , having extrapolated to the 0 and 180° scattering angles. For energies in the range from 3 to 20 eV they used the published cross sections of Tanaka *et al.*⁽⁸⁶⁾ 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⁽¹²⁾ measured the drift velocity and characteristic energy and derived 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 Å² and they decrease monotonically 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,

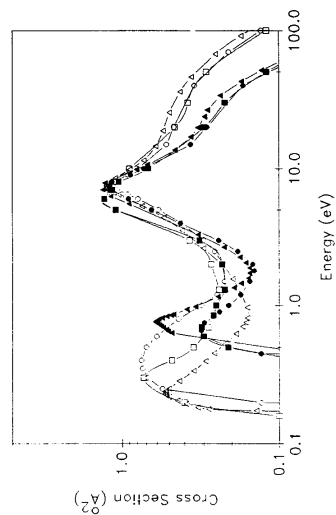


Fig. 9. CH₄ vibrational excitation cross sections: from Ohmori *et al.*⁽⁷¹⁾ (circles), Nakamura^(72,76) (squares), and Peres *et al.*⁽⁷⁹⁾ (triangles). The open symbols denote $\sigma_v(2,4)$ and the solid symbols $\sigma_v(1,3)$.

however, that the shape of the vibrational cross sections is somewhat arbitrary without more detailed beam measurements or theory.

4.2. Dissociation and Ionization

Total dissociation cross sections for methane have been measured by Winters⁽⁹³⁾ and by Perrin *et al.*⁽⁵¹⁾ 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.*⁽⁵²⁾ from the total dissociation cross section of Winters to obtain the total neutral dissociation cross section. Davies *et al.* have divided the dissociation cross section into four partial cross sections of equal magnitude except for differences in threshold energy in order to better emulate the continuous energy loss. 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^(52,94-97) 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.*⁽⁵²⁾ without modification. Davies *et al.* have used the Rapp and Englander-Golden⁽⁹⁴⁾ 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 CH₃⁺ and CH₂⁺ as products. These cross sections are equal above 70 eV. This is approximately in agreement

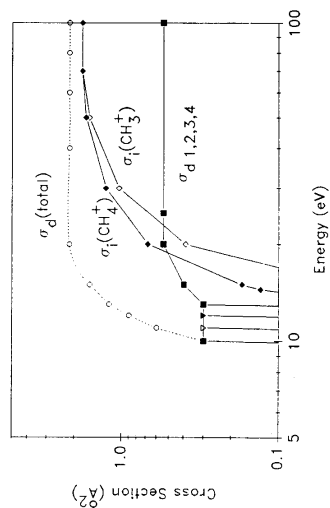


Fig. 10. CH₄ dissociation and ionization cross sections obtained by Davies *et al.*⁽⁷²⁾ The partial dissociation cross sections are explained in the text.

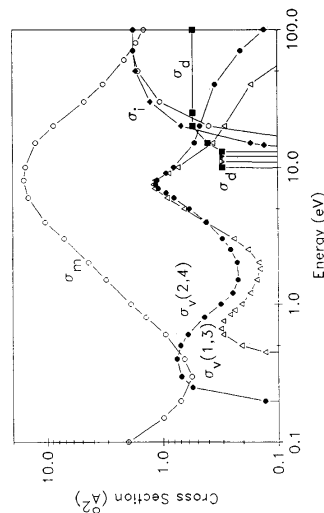


Fig. 11. Complete set of cross sections for CH_4 published by Davies *et al.*⁽⁷²⁾

with the measurements of Adameczyk *et al.*⁽⁹⁵⁾ of the partial ionization cross sections.

The complete cross section developed by Davies *et al.*⁽⁷²⁾ is displayed in Fig. 11.

5. CONCLUSIONS

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

(a) CF_4 : Hayashi⁽¹³⁾ 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, (i) Kline⁽²³⁾ has suggested a slight reduction in the vibrational cross sections, (ii) there appears to be some uncertainty in the momentum transfer cross section, and (iii) recent beam measurements of the ionization cross section⁽³³⁻³⁶⁾ indicate a need for adjustment of the inelastic cross sections. Clearly much more experimental information and much more analysis are 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,^(30,69) which should be the recommended set. Wang *et al.*⁽⁹⁸⁾ have recently determined low-energy cross sections in silane based on an analysis of swarm data using a multi-term solution to Boltzmann's equation, but it is too recent to have been included in this study.

(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.*⁽⁷²⁾ is to be recommended. It is very similar to that published by Ohmori *et al.*⁽⁷¹⁾ but is slightly more refined. We received the most recent set of cross sections, those of Nakamura,⁽⁷³⁾ Peres *et al.*,⁽⁷⁵⁾ and Schmidt,⁽⁶⁹⁾ who considered anisotropic effects in his analysis, too late to do more than graph them and comment on them in this review. They need further study. Finally, Mann and Linder⁽¹⁰⁰⁾ have very recently performed crossed beam measurements of elastic scattering from CH_4 in the 0.3–20 eV energy range and vibrational excitation in the 0.5–12 eV range. These measurements need to be included in future evaluations also.

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