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## Collision Data Involving Hydro-Carbon Molecules

H. Tawara, Y. Itikawa, H. Nishimura, H. Tanaka and Y. Nakamura

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NAGOYA, JAPAN

**Collision Data Involving Hydro-Carbon Molecules**

**H.Tawara, Y.Itikawa,<sup>a</sup> H.Nishimura,<sup>b</sup> H.Tanaka<sup>c</sup> and Y.Nakamura<sup>d</sup>**

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### Abstract

Hydro-carbon molecules are abundantly produced when graphites are used as internal wall materials of hydrogen plasmas and strongly influence properties of low temperature plasmas near the edges as well as those of high temperature plasmas at the center. In this report, following simple description of the production mechanisms of hydro-carbon molecules under the interactions between graphite and hydrogen plasma, the present status of collision data for hydro-carbon molecules by electron impact is discussed and the relevant data are summarized in a series of figures and tables. It should also be noted that, in addition to fusion plasmas, these hydrocarbon data compiled here are quite useful in other applications such as plasma chemistry and material processing.

[keywords : graphite, hydrocarbon, electron impact, collision data]

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## I INTRODUCTION

### -Graphite erosion and production of hydro-carbon molecules-

Graphites or carbon-coated materials are being tested and used as one of the most promising (coating) materials of the inner walls of fusion plasma apparatus in order to reduce radiation losses from high temperature plasmas because they are of low-z elements and readily available. However, they are found to be significantly eroded away through interactions with hydrogen plasmas. There are two major processes responsible to the erosion of graphite materials : (1) they are sputtered under impact of heavy particles such as hydrogens or impurities of carbons or oxygens or even more heavier particles which escape from the plasmas (physical sputtering). (2) they interact chemically with active hydrogens present near the edges of the plasmas, resulting in the production of some chemicals, mainly hydro-carbon molecules and are released from the surfaces (chemical sputtering).

#### (1) Physical sputtering<sup>1)</sup>

In Fig.1 are shown the measured sputtering yields<sup>2)</sup> of graphites at room temperatures under helium impact as a function of the impact energy (curve 1). With the threshold energy of about 20 eV, sputtering yields increase with increasing the impact energy and become maximum of 0.1 at around 500 - 1000 eV, finally decreasing at higher energies. This energy dependence is very typical in physical sputtering which is caused through collision cascades. Sputtering yields are found to increase under heavier ion impact and reach almost unity or even more (see Fig.2). In fact, self-sputtering due to carbon ion impact has relatively large sputtering yields. (This self-sputtering by carbon ions, particularly by multiply charged carbon ions, have been recently found to result in so-called "Graphite Catastrophe" where a large amount of graphites

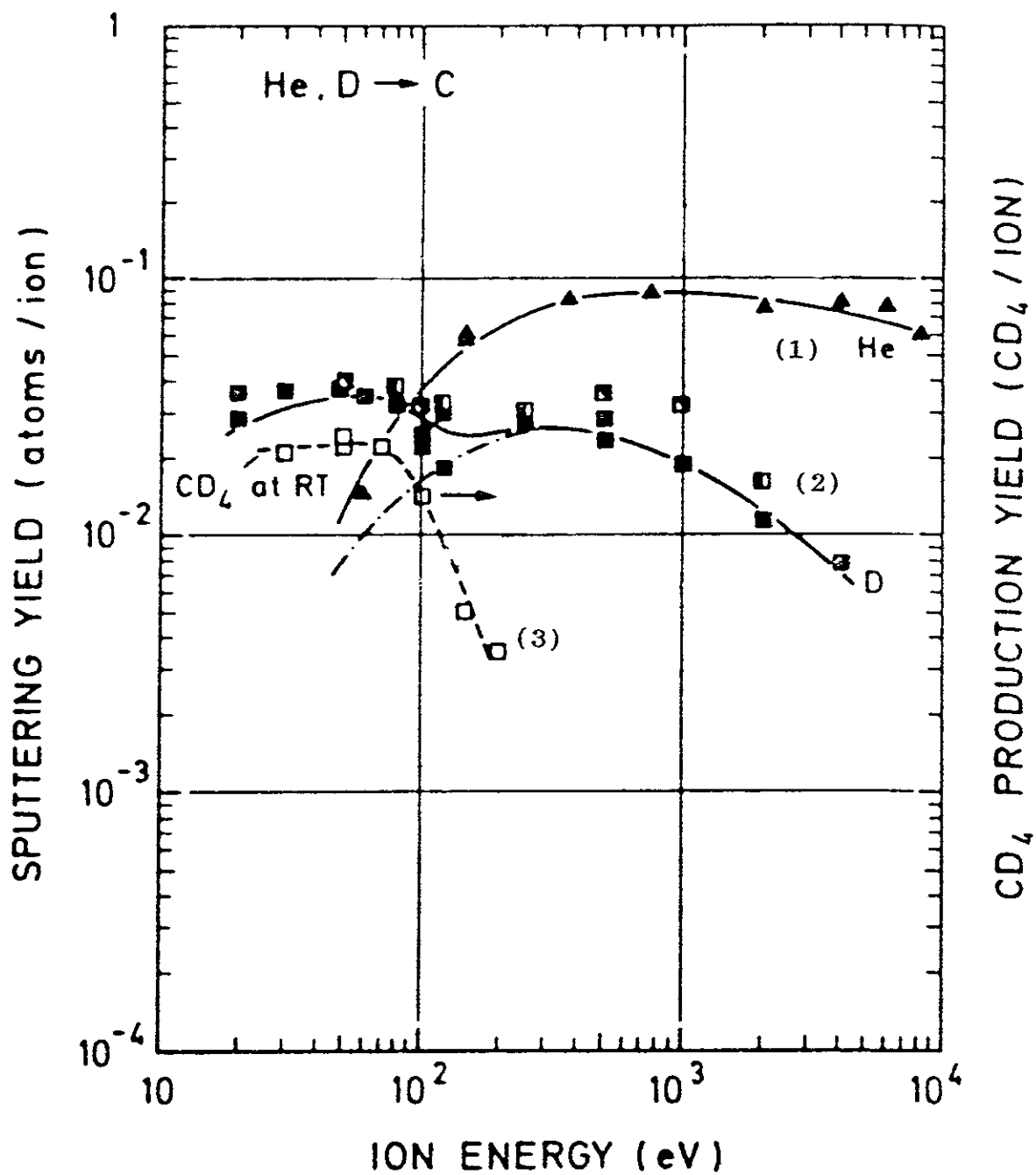


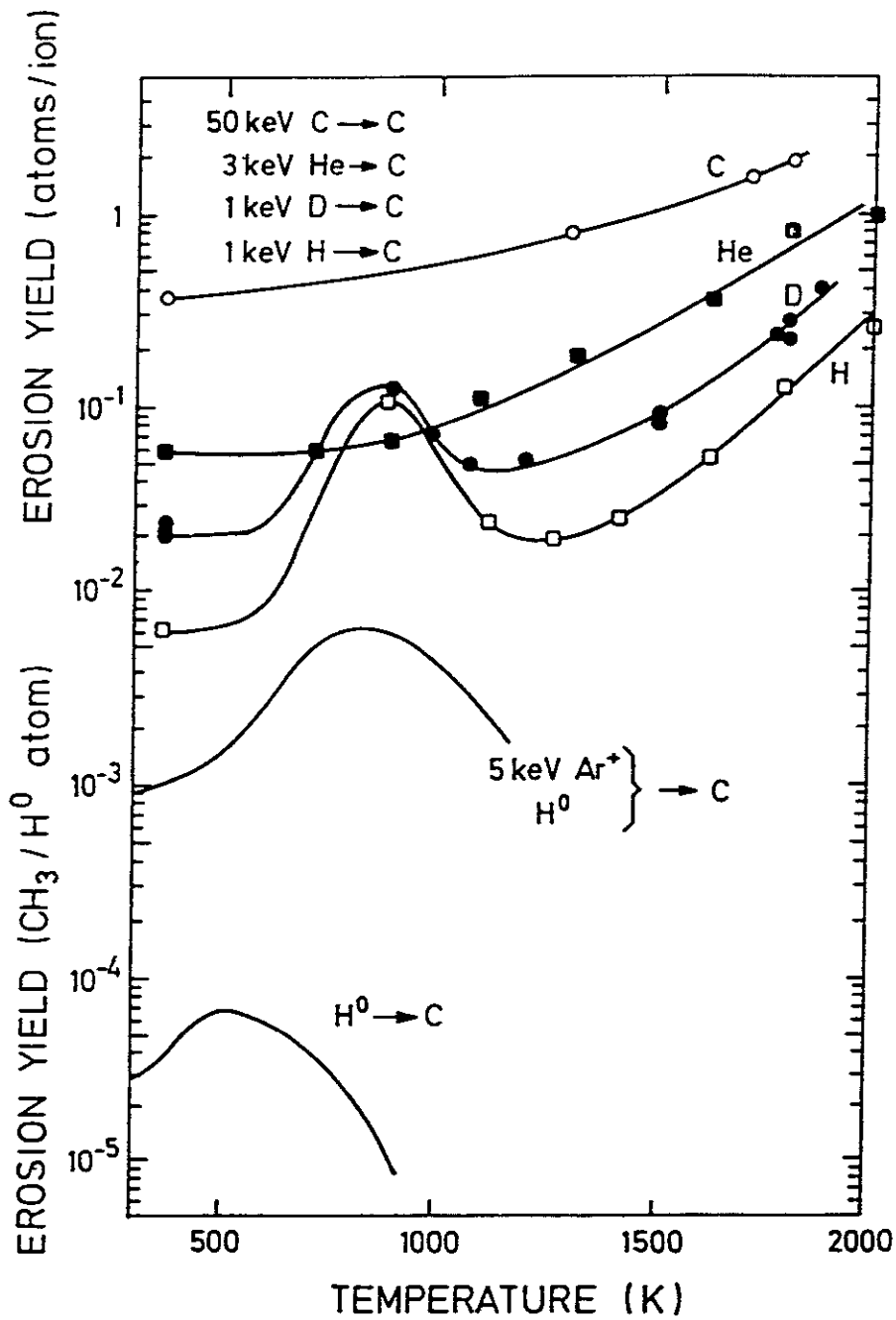
Fig.1 Sputtering yields of graphite at room temperatures under helium (curve 1) and deuteron (curve 2) ion impact as a function of the impact energy.<sup>2)</sup> Also the production rates of CD<sub>4</sub> molecules (curve 3) are shown.

are eroded into plasmas and strong plasma instabilities or even plasma disruptions are induced.) The general features of physical sputtering are understood reasonably well.

Sputtering yields under high energy hydrogen impact are similar to those under helium impact, though their absolute values are smaller, as expected from physical sputtering mechanism. However, sputtering yields at low energy hydrogen impact behave quite differently from those by helium. Indeed, with decreasing the impact energy, the yields stay nearly constant, instead of decreasing as expected from physical sputtering mechanism (curve 2 in Fig.1). This enhancement in sputtering yields at low energies is due to the erosion of graphites mostly in the form of  $\text{CH}_4$  gases, as seen in Fig.1 which indicates that  $\text{CH}_4$  production rates are nearly the same as total sputtering yields (curve 3). The production rates of  $\text{CH}_4$  gases show a sharp reduction at higher energies which indicates that they are produced deep inside the graphite. A large scattering of the observed sputtering yields might be due to the variations of structures or manufacturing processes of graphites used.

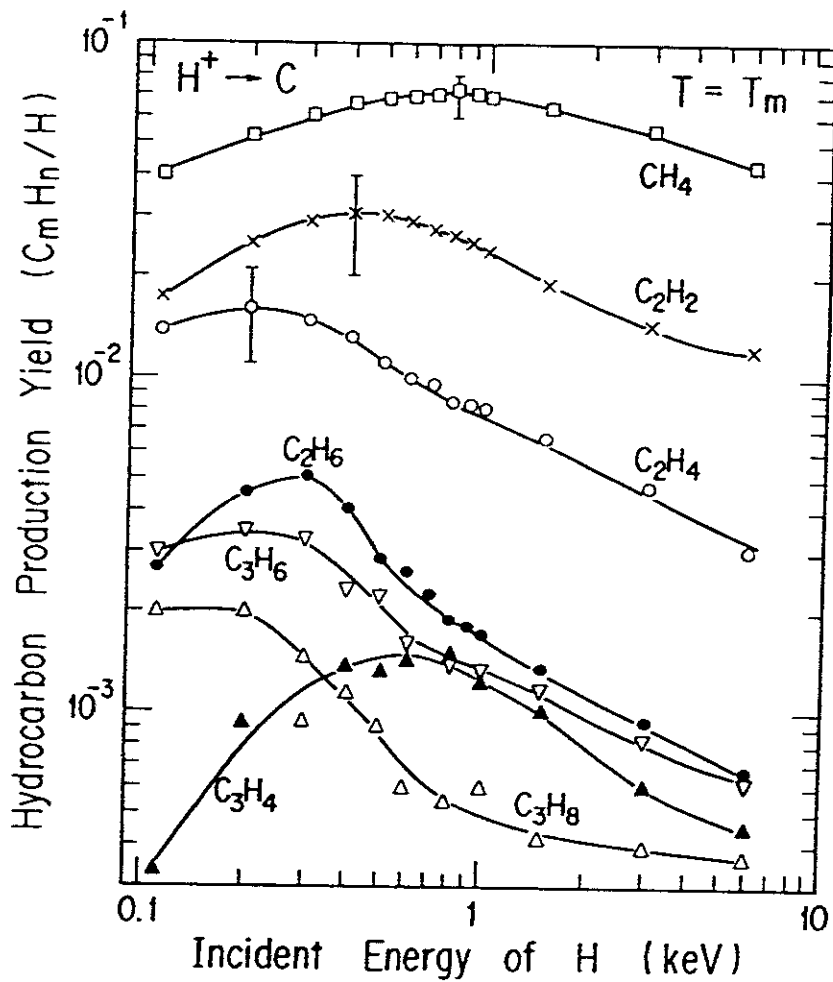
## (2) Chemical sputtering

Another interesting feature in graphite sputtering is strong temperature dependence. As shown in Fig.2,<sup>3)</sup> the sputtering yields of graphite under hydrogen impact increase drastically at the elevated temperatures of around 800 K and then decrease. This enhancement of sputtering yields is understood to be due to chemical reactions of carbon atoms with active hydrogen atoms, forming hydrocarbon molecules which are released from the surfaces and often called chemical sputtering. In fact, the chemical sputtering enhanced at the elevated temperatures is observed only under hydrogen impact, whereas self-sputtering yields under carbon ion impact do not change with the temperature. This suggests that the chemical interactions between hydrogen atom and carbon atom



**Fig.2** Sputtering yields for various particles as a function of the graphite temperature.<sup>3)</sup> The production rates of  $\text{CH}_3$  are also shown under thermal hydrogen impact. Note that under hydrogen impact significant enhancement of sputtering yields is seen at the elevated temperatures.

play a key role in the erosion of graphites under the presence of active atomic hydrogens. Even in thermal atomic hydrogen impact, graphites are eroded away whose erosion rates observed through the production of  $\text{CH}_3$  molecules are strongly dependent upon their temperature, as seen in the lower part of the figure. This also indicates the contribution of chemical processes involving both atomic hydrogens and carbon atoms to the erosion of graphite. **Figure 3** shows the production rates of various hydro-carbon molecules from graphite as a function of the energy of the incident hydrogen beams, measured at the temperatures of maximum yields<sup>4)</sup> (see Fig.2). As expected,  $\text{CH}_4$  molecules are the most prominent, followed by di-carbon molecules such as  $\text{C}_2\text{H}_2$ , with relatively small production of tri-carbon molecules such as  $\text{C}_3\text{H}_6$ . Under energetic hydrogen ion impact,  $\text{CH}_4$  molecules are believed to be produced through chemical reactions mostly near the end of the projected range of ions in graphite and, after passing through small holes or pores, arrive at and are released from the surfaces. Such chemical reactions forming hydro-carbon molecules in graphites could be greatly enhanced by the presence of defects whose densities are known to be maximum near the end of particle range. This is in sharp contrast to thermal hydrogen particle impact where  $\text{CH}_3$  molecules are the most prominent product, followed by  $\text{CH}_4$  molecules with the intensities weaker by one order of magnitude. These  $\text{CH}_3$  molecules are believed to originate from chemical reactions at or near the surfaces of graphite. These expectations are also supported by the observed fact that at high temperatures sputtering yields of thin carbon layers less than the range of the incident hydrogen particles are not much different from physical sputtering yields at room temperatures as most of the incident hydrogens having the reduced energies pass through carbon layer into substrate before forming hydro-carbon molecules, with no apparent enhancement due to chemical sputtering,<sup>5)</sup> meanwhile self-sputtering yields under carbon ion impact are found to be practically the same for both



**Fig.3** Production rates of various hydro-carbon molecules at maximum yield temperatures under hydrogen impact as a function of the impact energy.<sup>4)</sup>

thin carbon films and bulk graphites, even at the elevated temperatures.<sup>6)</sup> This chemical erosion is also found to be enhanced significantly if heavy, energetic particles are bombarded simultaneously with thermal hydrogens. As shown in the lower part of Fig.2, graphite erosion under simultaneous bombardment of thermal hydrogens and 5 keV Ar ions increases two orders of magnitude, compared with those under thermal hydrogen atoms only. This enhancement under simultaneous bombarding of different particles is understood to be due to so-called synergistic effect<sup>7)</sup> which is found to be quite complicated, depending upon various parameters such as the densities and energies of particles involved, the surface temperatures. In **Table 1** is shown a comparison of the production rates of hydro-carbon molecules under impact of 5 keV  $D_2^+$  ions only and of 5 keV  $D_2^+$  ions simultaneous with thermal hydrogen (deuterium) atoms. As mentioned already, under pure energetic particle impact,  $CH_4$  molecules are the most dominant, whereas  $CH_3$  molecules are found to be the most prominent under simultaneous impact.<sup>8)</sup> These facts again support that  $CH_4$  are produced mainly at the relatively deep layers inside graphite, whereas  $CH_3$  are produced near the surface.

In particular, the synergistic effects involving carbon ions/atoms bombarding graphite surfaces in the environments of high density hydrogen plasmas should be investigated. Up to now only qualitative, at best semi-quantitative,<sup>9)</sup> understanding of the synergistic effect has been obtained.

### (3) Radiation-enhanced sublimation

At extreme high temperatures (above 1200 K), the sputtering yields again start to increase with increasing the temperature and thus the third mechanism, called radiation-enhanced sublimation, plays a significant role in the erosion of graphites. Fraenkel pair are produced in graphite by radiations at such high temperatures where vacancies produced move easily. Interstitials, mobile



between graphite planes even at room temperatures, recombine with vacancies, diffusing to the grain boundaries and further to the surfaces. Thus, carbon atoms are finally released from the surfaces.

**Table 1**

Relative production rates of hydro-carbon molecules under pure energetic (5 keV) hydrogen particle impact and simultaneous energetic hydrogen + thermal hydrogen particle impact on graphite at the temperature of 800 K. The density of thermal hydrogens is 18 times that of  $D_2^+$  ions.<sup>8)</sup>

	$CD_4$	$CD_3$	$CD_2$
$D_2^+$	100	16	0
$D_2^+ + D$	13	100	6

Carbon atoms released from the graphite surfaces, in the form of either atoms or hydro-carbon molecules, come into contact with plasmas and they are excited, dissociated or ionized under various collision processes with electrons, atoms, molecules or ions in the plasmas. Then, they or collision products play a key role in determining characteristics and behavior of cold plasmas near the edge region as well as hot plasmas at the center and also in diagnosing them.

In order to provide important information for modelling and diagnosis of plasma, electron collision data involving hydro-carbon molecules seem requisite. Up to now, however, only a limited data for hydro-carbon molecules have been compiled for such purposes.<sup>10,11)</sup> In the present work, the present situations of data for hydro-carbon molecules under electron impact are surveyed and some relevant data are compiled.

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## II A short remark on theoretical aspects of electron-hydrocarbon molecule collisions

Recently Gianturco and Jain<sup>1)</sup> have reviewed theoretical aspects in electron + polyatomic molecule collisions and discussed validities of various theoretical models which have been proposed to reproduce the observed results. Most of theoretical calculations are addressed to methane, with a few contributions to acetylene. They provide total scattering cross sections as well as rotational excitation cross sections.

The calculations of total scattering cross sections are based upon one of the following approximations (only the references of the most elaborate calculations in each category are listed below) :

- a) one-center potential scattering model<sup>2-5)</sup>,
- b) multiple scattering model<sup>6-8)</sup>,
- c) Schwinger variational method<sup>9-10)</sup>,
- d) Kohn variational method<sup>11)</sup>.

On the other hand, the rotational excitation cross sections are calculated with one of the following methods :

- e) rotational close coupling method<sup>12-13)</sup>,
- f) rotational adiabatic approximation<sup>14-15)</sup>.

The theoretical results in the papers cited above are in reasonable agreement with experiment, if the interaction between the electron and the molecule (especially the target polarization and the electron exchange) is properly taken into account.

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### III Collision data for hydrocarbon molecules in electron impact

#### General comments

Differential cross sections (for elastic scattering, vibrational excitation, rotational excitation, electronic excitation, dissociation, (dissociative) ionization, attachment, momentum transfer collision process, etc.) are defined as the cross sections for electrons scattered into a particular angle with respect to the electron beam direction and are usually determined through a crossed-electron-molecule-beam method (see discussion below). Partial cross sections can be obtained by summing up over all the angles. Furthermore, summation of partial cross sections over all possible processes (excluding momentum transfer cross sections) gives total cross sections.

Various experimental techniques have been developed in order to determine the cross sections mentioned above. At relatively high energies (> a few eV), crossed-beam technique is the most reliable and can provide the detailed information on collision processes such as double differential cross sections. In this method, however, measurements at the extremely forward (<10°) and backward (>150°) angles are difficult to be performed and thus extrapolations to such angles are necessary under some assumptions to get partial cross sections, resulting in additional uncertainties. On the other hand, at energies less than 10 eV, swarm technique is most often used. In this method, the electron drift velocities, diffusion coefficients, ionization coefficients, etc. are determined experimentally and then the final collision cross sections are calculated through Boltzmann equations or Monte Carlo technique, incorporating the elastic scattering cross sections previously determined in

other methods such as the crossed-beam technique. Therefore, the final cross sections are strongly dependent upon these elastic scattering cross sections. Beam attenuation technique can provide total cross sections over a wide range of the electron energy which are used in determining the absolute cross sections in the crossed-beam technique but no detailed information could be obtained on each of the collision processes.

Thus, the cross sections obtained through these three techniques are interdependent upon each other and all the final collision cross sections should be determined to be consistent to those estimated among these methods. As seen later on, as a general trend in electron-molecule collisions, the elastic scattering cross sections are the largest over all the energy range and show the Ramsauer minimum around 0.4 eV. Nearby there various vibrational excitation processes begin to occur and the cross sections for these two processes become comparable. Broad structures around 7.5 eV are observed which are understood to be due to the shape resonance of short-lived ( $10^{-16}$  s), negative ion state with  $^2T_2$  symmetry. Then, the electron attachment, dissociation, electronic excitation and finally ionization processes occur.

### III-1 CH<sub>4</sub>

#### Elastic and inelastic electron scattering

##### 1) Total cross sections

One of the most common techniques for determining total cross sections is the measurement of attenuation of the incident electron beam passing through the known thickness of the target, as mentioned above. Some have been determined by summing up the measured differential cross sections obtained with the crossed beam technique. A number of the measurements have been reported so far. Some of old data taken in the 1920s show general agreement with recent measurements. Ramsauer minimum is clearly seen at around 0.4 eV where vibrational excitation begins to show up (see section III-1 5)). Those by Ferch et al. seem to be reasonably reliable at low energies over 0.085 - 12 eV. However, at higher energies still some discrepancies are observed. Data are shown in Fig.4 (curve 1). In Table 2 is shown some information on experimental work of total cross section measurements for CH<sub>4</sub>.

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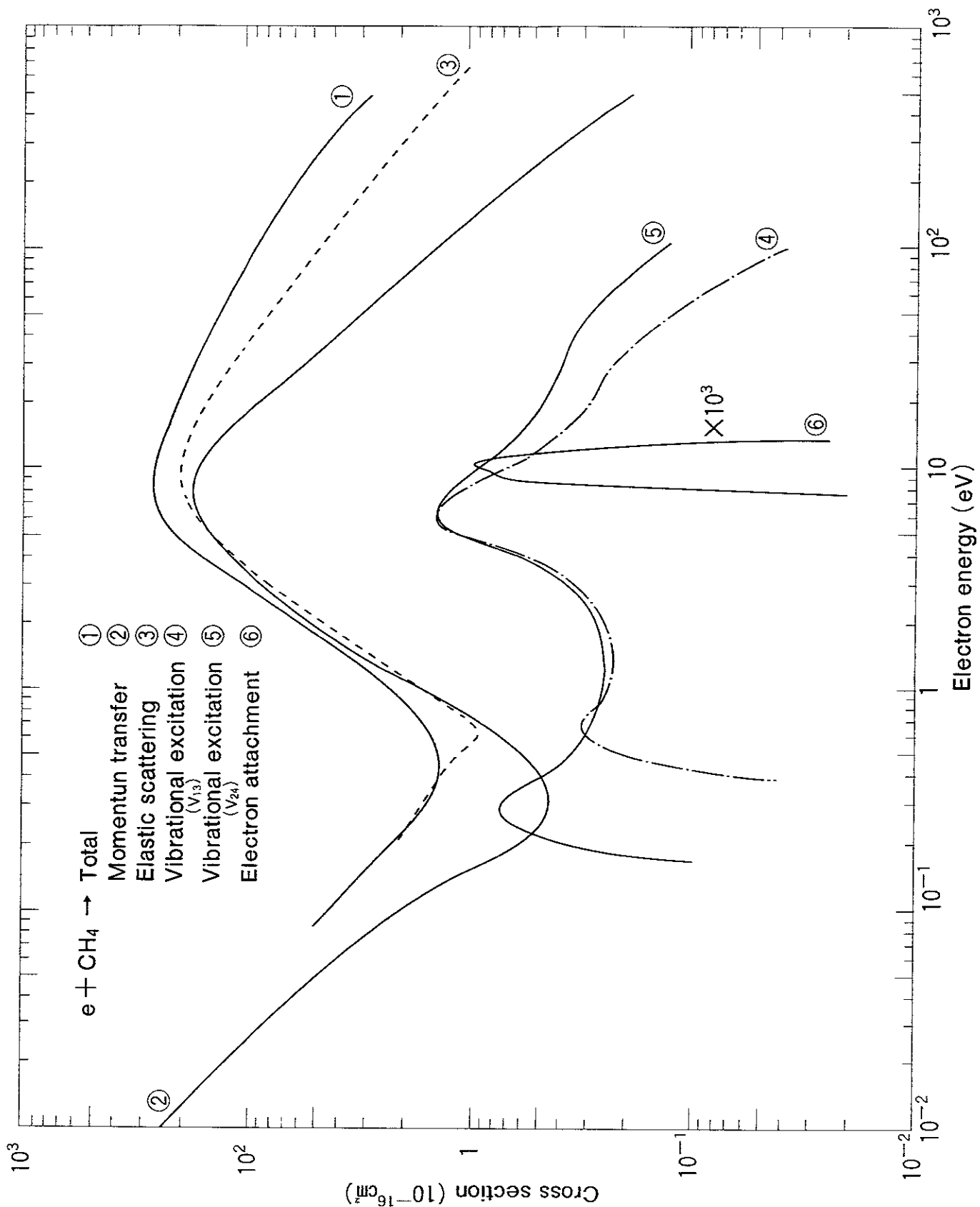
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**Table 2** Experiments on total cross sections of electrons for CH<sub>4</sub>

Author	(year)	Energy (eV)	Method	comments
Brode	(1925)	2-360	Ramsauer	A*)
Brüche	(1927)	1-38	Ramsauer	A
Ramsauer	(1930)	0.2-36	Ramsauer	A
Barbarito	(1979)	0.1-16	Transmission	A
Mathur	(1980)	5-19	Transmission	R
Floeder	(1985)	5-400	Transmission	A
Ferch	(1985)	0.085-12	Transmission	A
Jones	(1985)	1.3-50	Transmission	A
Sueoka	(1986)	1.0-400	Transmission	A
Nishimura	(1990)	5-500	Transmission	A

\*) A and R indicate absolute and relative values of the cross sections.





**Fig.4** Elastic and inelastic scattering cross sections  
 of electrons by  $\text{CH}_4$

## 2) Momentum transfer cross sections

Momentum transfer cross sections have been determined through two methods : swarm technique (for low energies) and crossed-beam technique (for high energies). In the former, the best values of the momentum transfer cross sections are estimated so as to reproduce the swarm parameters using Boltzmann equation or simulation. Data shown in **Fig.4** (curve 2) are taken from a recent analysis by Nakamura with some extrapolation of those by Sakae et al. and by Shyn and Cravens. In **Table 3** is given a list of experimental studies on momentum transfer processes for CH<sub>4</sub>.

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**Table 3** Experiments on momentum transfer cross sections  
of electrons for CH<sub>4</sub>

Author	(year)	Energy (eV)	Method	Comments
Cottrell	(1967)	<1	Swarm	to theory <sup>a</sup>
Pollock	(1968)	<1	Swarm	to theory
Duncan	(1972)	0.01-40	Swarm	to theory
Kline	(1982)	<1	Swarm	to theory
Tanaka	(1982)	3-20	Beam	to He <sup>b</sup>
Haddad	(1985)	0.01-10	Swarm	to theory
Ohmori	(1986)	0.05-500		simulation
Davies	(1989)	0.01-10000	Swarm	to theory
Sakae	(1989)	75-700	Beam	to He
Shyn	(1990)	3-50	Beam	to He
Nakamura	(1990)	0-100	Swarm	to theory

a) indicates the cross sections are normalized to theory.

b) indicates the cross sections are normalized to those for He.

### 3) Elastic scattering cross sections

Elastic scattering cross sections usually can not exclude the contribution of rotational (sometimes as well as vibrational) excitation because of the limited energy resolution of the detection system. Total (or integral) elastic scattering cross sections are obtained by summing up differential cross sections over the angles and shown in **Fig.4** (curve 3). In **Table 4** are shown experimental measurements of the cross sections for this process.

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- T.W.Shyn and T.E.Cravens, J. Phys. B 23, 293 (1990)

**Table 4** Experiments on elastic scattering of electron by CH<sub>4</sub>

Author	(year)	Energy(eV)/Angle(°)	Method	Comments
Arnot	(1931)	16-40 (10-120°)	Beam	R <sup>a)</sup>
Bullard	(1931)	4-30 (20-120°)	Beam	R
Mohr	(1932)	16-40 (10-40°)	Beam	R
Hughes	(1933)	10-800 (10-150°)	Beam	R
Rohr	(1980)	0.1-10 (20-120°)	Beam	to He <sup>b)</sup>
Tanaka	(1982)	3-20 (30-140°)	Beam	to He
Sohn	(1983)	0.1-1.8(30-120°)	Beam	to He
Vuskovic	(1983)	20-200 (8-130°)	Beam	to He
Curry	(1985)	7.5-200(30-140°)	Beam	to He
Sohn	(1986)	0.2-5 (15-138°)	Beam	to He
Sakae	(1989)	75-700 (5-135°)	Beam	to He
Shyn	(1990)	5-50 (12-156°)	Beam	to He

a) indicates relative measurements and b) represents that the cross sections are normalized to those for He.

#### 4) Rotational excitation cross sections

Differential rotational excitation cross sections for some limited processes have been measured over 0.5 - 10 eV by Müller et al. But no total cross sections have been given. In **Table 5** are shown experimental measurements of rotational excitation of CH<sub>4</sub>.

**Table 5** Experiments on rotational excitation  
of CH<sub>4</sub> by electrons

Author	(1983)	Energy(eV)/Angle(°)	Method	Comments
Müller	(1985)	0.5-10 (20-140°)	Beam	to He( $\Delta J=0,3,4$ )

#### Reference

R.Müller, K.Jung, K.H.Kochem, W.Sohn and H.Ehrhardt, J. Phys. B 18, 3971 (1985)

### 5) Vibrational excitation cross sections

CH<sub>4</sub> molecules are known to have nine vibrational modes in their ground state, among which only four ( $v_1 = 363$  meV,  $v_2 = 190$  meV,  $v_3 = 374$  meV,  $v_4 = 162$  meV) are separated in energy. However, the separation between two levels  $v_1$  and  $v_3$  and also  $v_2$  and  $v_4$  states are too small and they can not be resolved because of the limited energy resolution in spectrometer.

The cross sections for vibrational excitation have been determined from the threshold (162 meV) to 20 eV using crossed beam method or from threshold to 100 eV using swarm technique. Data evaluated by Nakamura, based upon swarm data, are shown in Fig. 4 (curves 4 for those of  $v_{13}$ , summed over  $v_1$  and  $v_3$ , and curve 5 for  $v_{24}$ , summed over  $v_2$  and  $v_4$ ). Maximum cross sections at around 7.5 eV are understood to be due to the enhancement by a broad T<sub>2</sub> symmetry resonance. Table 6 shows a list of experiments on vibrational excitation processes for CH<sub>4</sub>.

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Y.Nakamura, J. Phys. D (to be published (1990))

**Table 6** Experiments on vibrational excitation of CH<sub>4</sub> by electrons

Author	(year)	Energy(eV)/Angle(°)	Method	Comments
Pollock	(1968)	0-5	Swarm	v <sub>1</sub> +v <sub>3</sub> , v <sub>2</sub> +v <sub>4</sub>
Duncan	(1972)	0.01-40	Swarm	v <sub>1</sub> +v <sub>3</sub> , v <sub>2</sub> +v <sub>4</sub>
Rohr	(1980)	0.1-4 (20-120°)	Beam	v <sub>1</sub> +v <sub>3</sub> , v <sub>2</sub> +v <sub>4</sub>
Tanaka	(1982)	3-20 (30-140°)	Beam	v <sub>1</sub> +v <sub>3</sub> , v <sub>2</sub> +v <sub>4</sub>
Sohn	(1983)	0-1 (35-105°)	Beam	v <sub>1</sub> +v <sub>3</sub> , v <sub>2</sub> +v <sub>4</sub>
Müller	(1985)	0.5.7.5(30-140°)	Beam	v <sub>2</sub> , v <sub>4</sub>
Curry	(1985)	7.5-15 (30-140°)	Beam	v <sub>1</sub> +v <sub>3</sub> , v <sub>2</sub> +v <sub>4</sub>
Haddad	(1985)	0.15-10	Swarm	v <sub>1</sub> +v <sub>3</sub> , v <sub>2</sub> +v <sub>4</sub>
Ohmori	(1986)	0.2-200	Simulation	
Davies	(1989)	0.16-200	Swarm	v <sub>1</sub> +v <sub>3</sub> , v <sub>2</sub> +v <sub>4</sub>
Nakamura	(1990)	0.01-100	Swarm	v <sub>1</sub> +v <sub>3</sub> , v <sub>2</sub> +v <sub>4</sub>



## 6) Electronic excitation cross sections

Most experiments are concerned with spectroscopic investigations. Only a few reliable measurements have been reported for the cross sections of electronic excitation. In **Table 7** are shown experiments on electronic excitation of CH<sub>4</sub>.

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M.A.Dillon, R.G.Wang and D.Spence, J. Chem. Phys. 80, 5581 (1984)

**Table 7** Experiments on electronic excitation of CH<sub>4</sub> by electrons

Author	(year)	Energy(eV)/Angle(°)	Method	Comments
Ehrhardt	(1965)	70 (0-145)	Beam	
Lassetre	(1968)	50-180 (0-6°)	Beam	R (ΔE=8-14 eV)
Harshbarger	(1973)	400,500(0-5°)	Beam	to He(ΔE=8.55-10.95 eV)
Johnson	(1979)	30-250 (0-90°)	Beam	R (ΔE=5.5-18 eV)
Vuskovic	(1983)	20-200 (8-130°)	Beam	to He(ΔE=7.5-15 eV)
Dillon	(1984)	200 (0-15°)	Beam	R (ΔE=1-22.3 eV)

### 7) Electron attachment cross sections

The dissociative attachment cross sections resulting in the production of negative ions (mainly  $\text{H}^-$  and  $\text{CH}_2^-$ ) have been measured only by Sharp and Dowell and show a sharp resonance-like behavior as seen in **Fig.4** (curve 6). It is interesting to note that strong isotope effect is observed in dissociative attachment : practically no  $\text{CD}_2^-$  ions but only  $\text{D}^-$  for  $\text{CD}_4$ , though total negative ion production cross sections are roughly the same as those for  $\text{CH}_4$ .

### Reference

T.E.Sharp and J.T.Dowell, J. Chem. Phys. 46, 1530 (1967)

### Total (effective) ionization cross sections

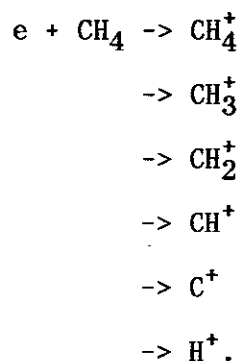
Total ionization cross sections are usually determined through measurements of all secondary (molecular as well as atomic) ions including weak multiply charged ions produced by electron impact.

This type of the measurements has been reported by a number of authors and the agreement among the observed results are generally good, as shown in Fig.5. The absolute measurements by Rapp and Englander-Golden (threshold - 1000 eV) are 5-30 % larger than those of Schram et al. (0.6 - 12 keV) in the overlapped energy range, both of which are often used as standards. Other measurements (for example, Adamczyk et al., Chatham et al. and Orient and Srivastava) are often normalized to one of these absolute values.

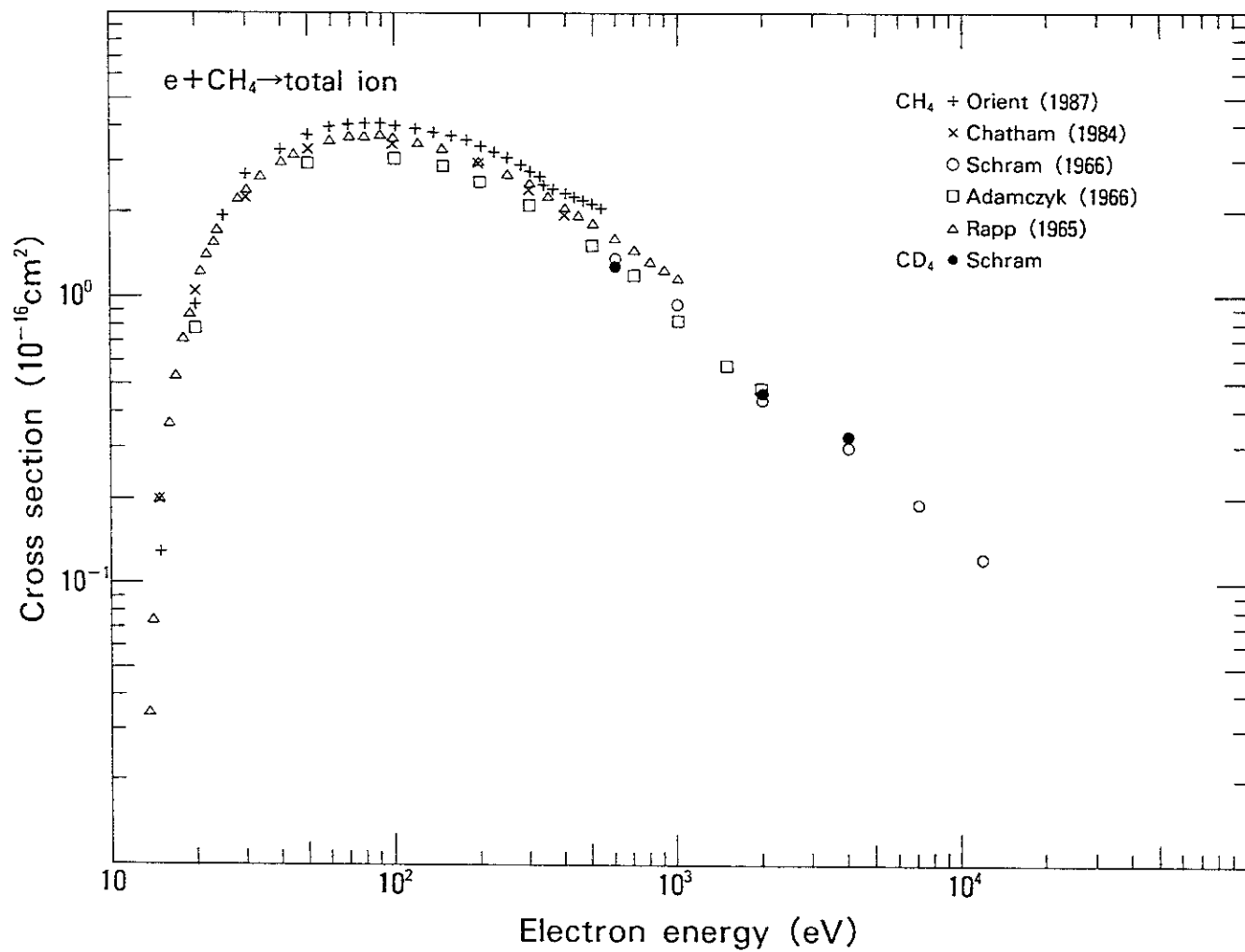
Rapp et al. also determined the cross sections for the production of charged particles with the kinetic energy above 0.25 eV and found that more than 90 % of the charged products have thermal energies, though the ratios are found to be varied with the impact energy.

It should be noted that the cross sections for CD<sub>4</sub> are practically the same as those for CH<sub>4</sub>, suggesting that the isotope effect is of a minor importance in ionization processes, as confirmed experimentally by Schram et al.

### Partial (dissociative) ionization cross sections



The appearance potentials for the production of these ions as well as CH<sub>2</sub><sup>2+</sup> ions



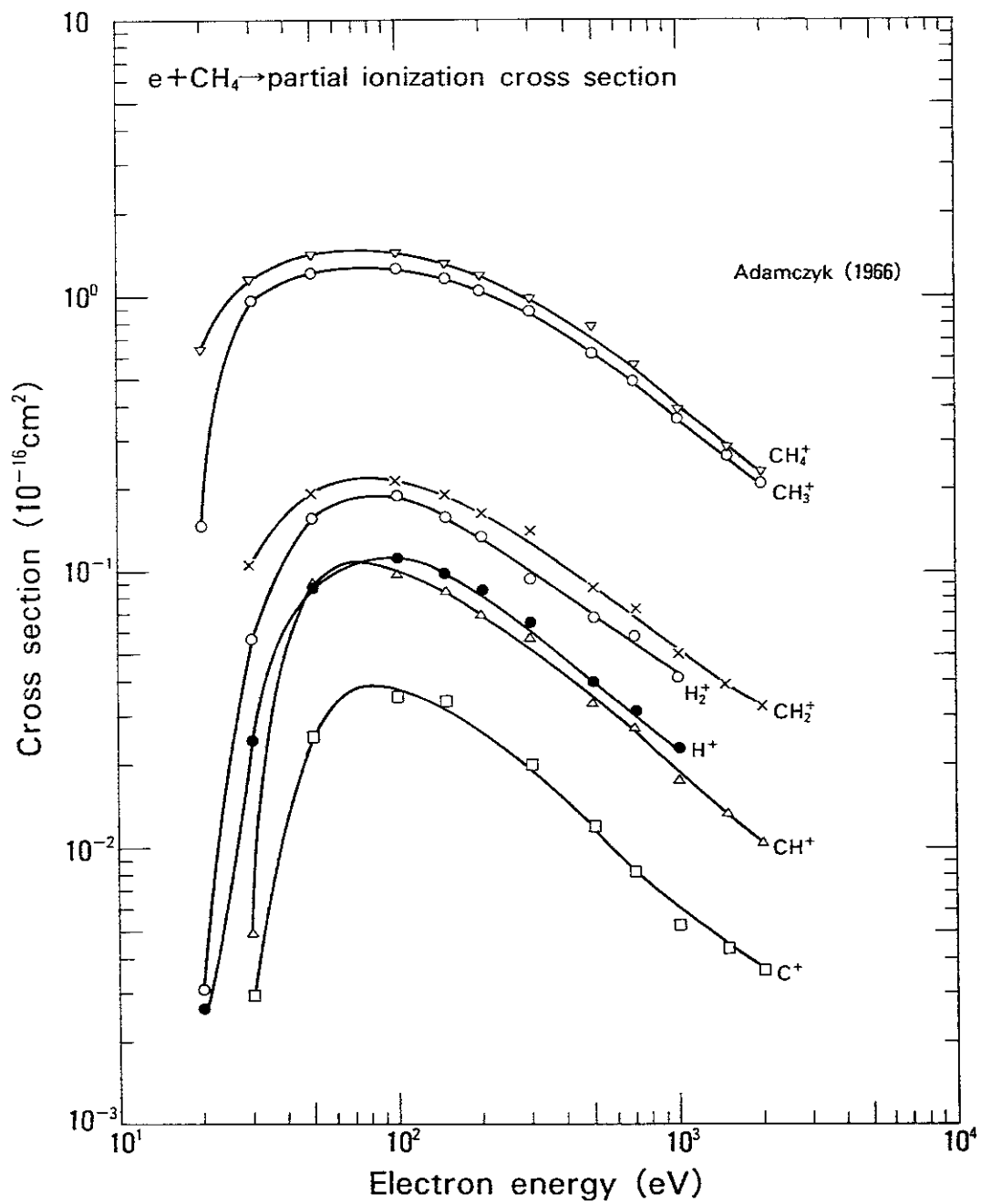
**Fig. 5** Total ionization cross sections of CH<sub>4</sub> by electrons as a function of electron energy

through pure ionization and various dissociative ionization processes have been investigated by Plessis et al.(see **Table 8** ).

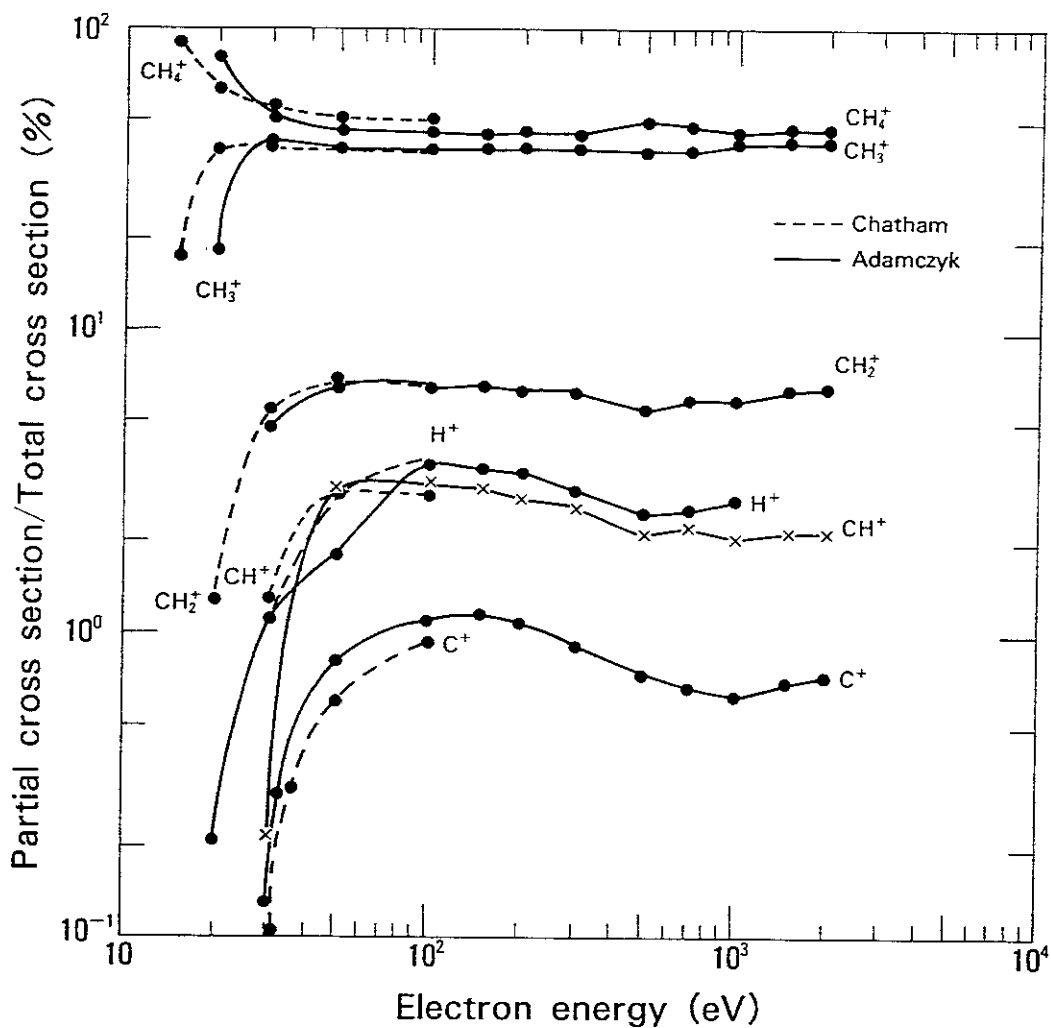
**Table 8** Appearance potentials for various ions from CH<sub>4</sub>  
by electron impact (Plessis et al.)

ion	appearance potential(eV)
CH <sub>4</sub> <sup>+</sup>	12.63
CH <sub>3</sub> <sup>+</sup> + H <sup>-</sup>	13.25
CH <sub>3</sub> <sup>+</sup> + H	14.01
CH <sub>2</sub> <sup>+</sup> + H <sub>2</sub>	15.06
CH <sup>+</sup> + H <sup>-</sup> + H <sub>2</sub>	19.11
CH <sup>+</sup> + H + H <sub>2</sub>	19.87
C <sup>+</sup> + 2H <sub>2</sub>	19.56
CH <sub>2</sub> <sup>2+</sup> + H <sub>2</sub>	<40.0

Adamczyk et al. have determined partial cross sections over a wide range of the energy, as shown in **Fig. 6**. Chatham et al. and Orient and Srivastava have also measured those in relatively limited energy region. As compared in **Fig. 7**, these partial cross sections are in agreement with each other at high energies, but significant disagreement is observed at low energies due to unexplained reasons, which have to be investigated. H<sub>2</sub><sup>+</sup> ions observed by Adamczyk et al. and Chatham et al. seem not to be due to primary collisions but due to double collisions (as they increase quadratically with the pressure) and therefore are



**Fig. 6** Partial ionization cross sections of CH<sub>4</sub>  
by electron impact as a function of electron energy



**Fig. 7** Comparison of the measured partial ionization cross sections of  $\text{CH}_4$  by different authors

Note that a significant discrepancy exists at low energies.

not listed here.

It has to be noted that partial ionization cross sections of molecules are strongly dependent upon their internal energy. In **Table 9** is shown a comparison of the measured relative partial ionization cross sections (so-called cracking patterns) of the ground state neutral  $\text{CH}_4$  gas molecules and those prepared through (resonant charge) neutralization of  $\text{CH}_4^+$  ions, which may have the internal energy different from  $\text{CH}_4$  gas molecules.

**Table 9** Cracking patterns in dissociative ionization of  $\text{CH}_4$   
by 100 eV electron impact (Baiocchi et al.)

	$\text{CH}_4^+$	$\text{CH}_3^+$	$\text{CH}_2^+$
gas $\text{CH}_4$	100	85	15
neutralized $\text{CH}_4$	100	400	15

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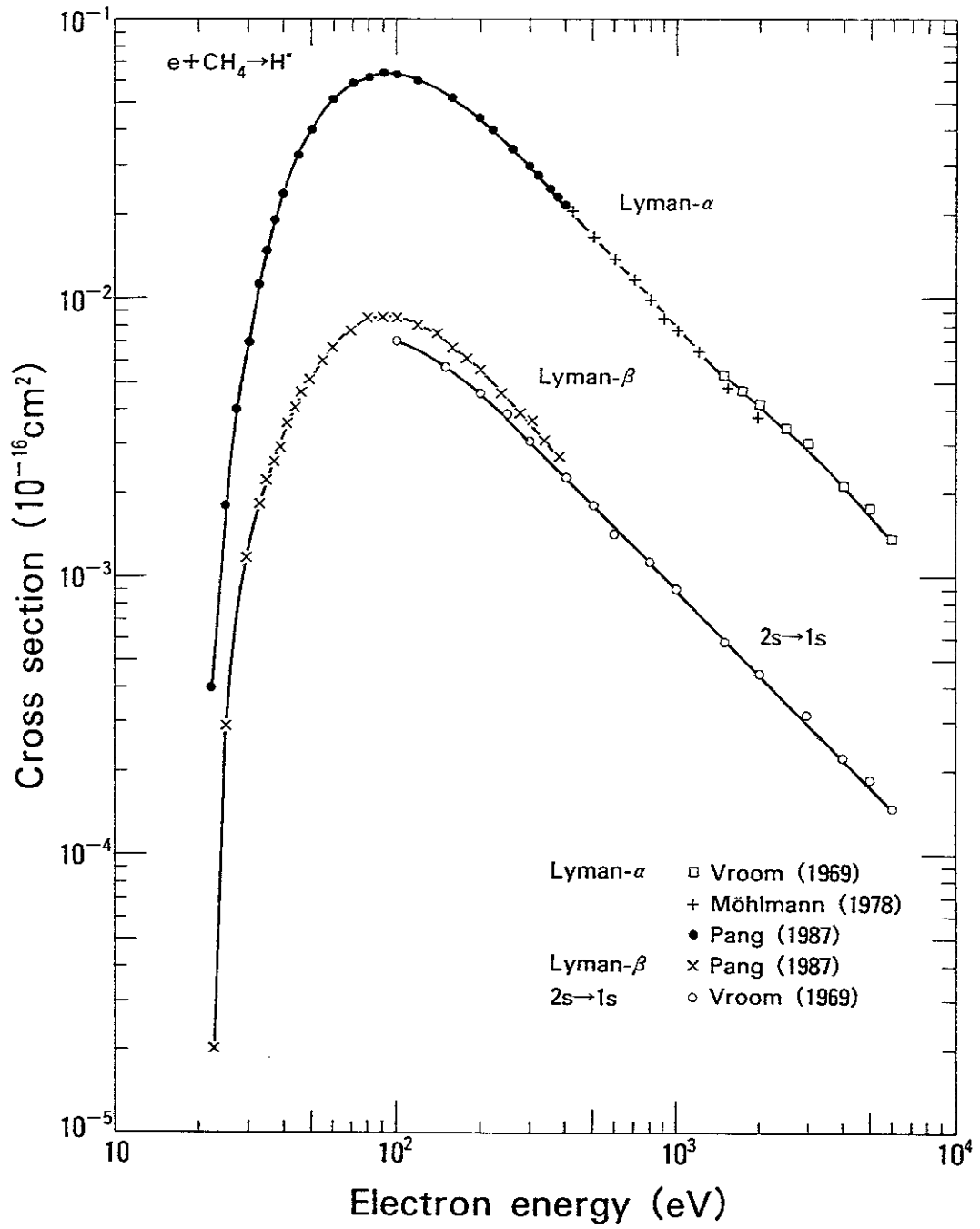
### Photon emission cross sections

Photons are emitted by ions, atoms or molecules in excited states formed through direct excitation, dissociation or dissociative ionization. The observation of the photons provides important information of production mechanisms of these particles.

### Lyman lines and 2s->1s transition from hydrogen atoms

Systematic measurements of the emission cross sections for these lines have been made by Vroom and de Heer (Lyman- $\alpha$  and 2s-1s transition : 50 - 6000 eV), Sroka (Lyman- $\alpha$ , - $\beta$ , - $\gamma$  and - $\delta$  : threshold - 440 eV), Morgan and Mentall (Lyman- $\alpha$  : threshold - 240 eV), M $\ddot{u}$ hlmann et al. (Lyman- $\alpha$  : 20 - 2000 eV), Orient and Srivastava (Lyman- $\alpha$  : threshold - 100 eV) and, most recently, Pang et al. (Lyman- $\alpha$  and - $\beta$  : 20 - 400 eV). However, absolute values of these cross sections (and sometimes even their energy dependence curves) are often scattered because of the normalization or calibration procedures of photon detection systems used. In fact, the cross sections for Lyman- $\alpha$  line by Sroka are a factor of four smaller than those by Vroom and de Heer, whereas that for Lyman- $\beta$  line at 100 eV by McLaughlin and Zipf seems to be too large by a factor of two, compared with that by Pang et al. who normalized their data to the newest cross sections for Lyman- $\alpha$  emission from H<sub>2</sub> molecules. **Figure 8** shows the recent results for Lyman- $\alpha$  and - $\beta$  line emissions by Pang et al. and those of Vroom and de Heer and of M $\ddot{u}$ hlmann et al. both of which are normalized to that of Pang et al. at 400 eV. Also are shown the renormalized cross sections for 2s->2p transition by Vroom and de Heer.

Concerning the isotope effect on Lyman- $\alpha$  emission, Vroom and de Heer also found that those for CH<sub>4</sub> are about 20 % larger than those for CD<sub>4</sub>, indicating a slight isotope effect in dissociation processes.



**Fig. 8** Emission cross sections of Lyman lines and 2s->1s transitions of hydrogen atoms in  $e + \text{CH}_4$  collisions

### Balmer lines of hydrogen atoms

Vroom and de Heer have determined the cross sections for Balmer- $\alpha$ , - $\beta$ , - $\gamma$  and - $\delta$  over 50 - 6000 eV. Also those for Balmer- $\beta$  have been measured by Aarts et al. (20 - 5000 eV) and those for Balmer- $\beta$ , - $\gamma$  and - $\delta$  by Koppe et al. (400 - 6000 eV). The agreement among these measurements seems to be reasonable. The cross section of Balmer- $\beta$  line emission by McLaughlin and Zipf at 100 eV is by a factor of 4 too large, compared with that by Vroom and de Heer. The results of Vroom and de Heer are shown in Fig. 9 (Those for Balmer- $\beta$  lines of Aarts et al. are about 10 % larger than those shown here).

It should also be noted that the isotope effect for Balmer lines results in the cross sections smaller (about 20 %) in  $CD_4$  than in  $CH_4$ , as observed by Vroom and de Heer.

### Emission from carbon atoms (C I)

The cross sections for emission of carbon atoms (C I : 165.72 nm  $2p3s \ ^3P \rightarrow 2p^2 \ ^3P^0$ , 193.09 nm  $2p3s \ ^1D \rightarrow 2p^2 \ ^1P^0$ , possibly with a small contribution of C II) have recently been determined by Pang et al. over 20 - 400 eV. Some structures in both emission cross sections are seen near thresholds due to different production channels, as seen in Fig. 10. Previous measurements by Sroka (C I : 165.72 nm and 156.1 nm  $2s2p \ ^3D \rightarrow 2p^2 \ ^3P$ ) and Morgan and Mentall (C I : 156.1, 165.72 and 193.09 nm) are found to be in disagreement with the recent results by Pang et al. by 20 - 50 %. Relative cross sections have also been reported for some of emissions of carbon atoms by Donohue et al. Most of these measurements could observe only weak lines from carbon ions and thus no cross sections for emission of lines from carbon ions,  $C^+$ , have been reported so far, except for that for C II 133.5 nm ( $2s2p^2 \ ^2D \rightarrow 2s^22p \ ^2P^0$ ) line by Morgan and Mentall ( $2.3 \cdot 10^{-20} \text{ cm}^2$  at 100 eV).

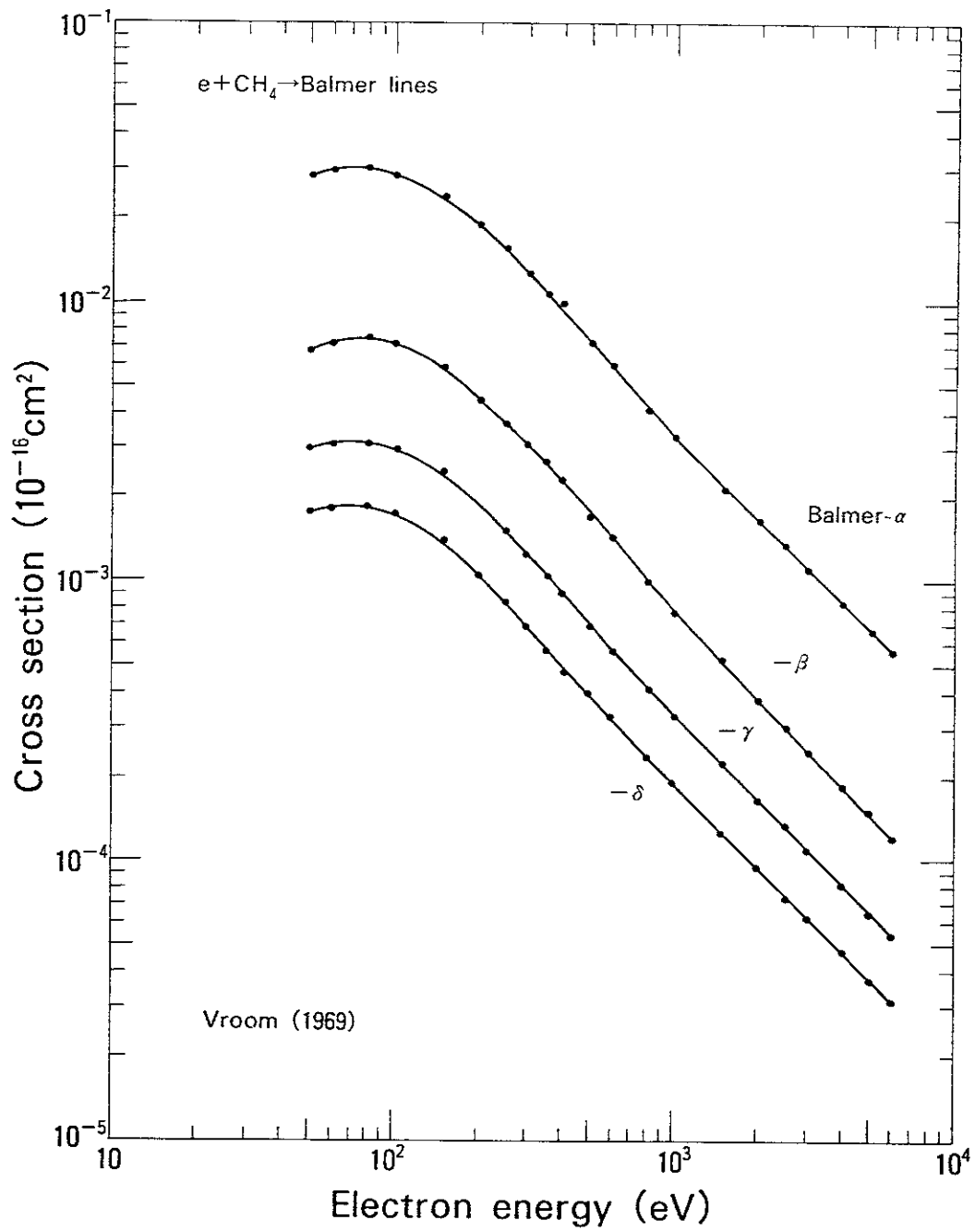
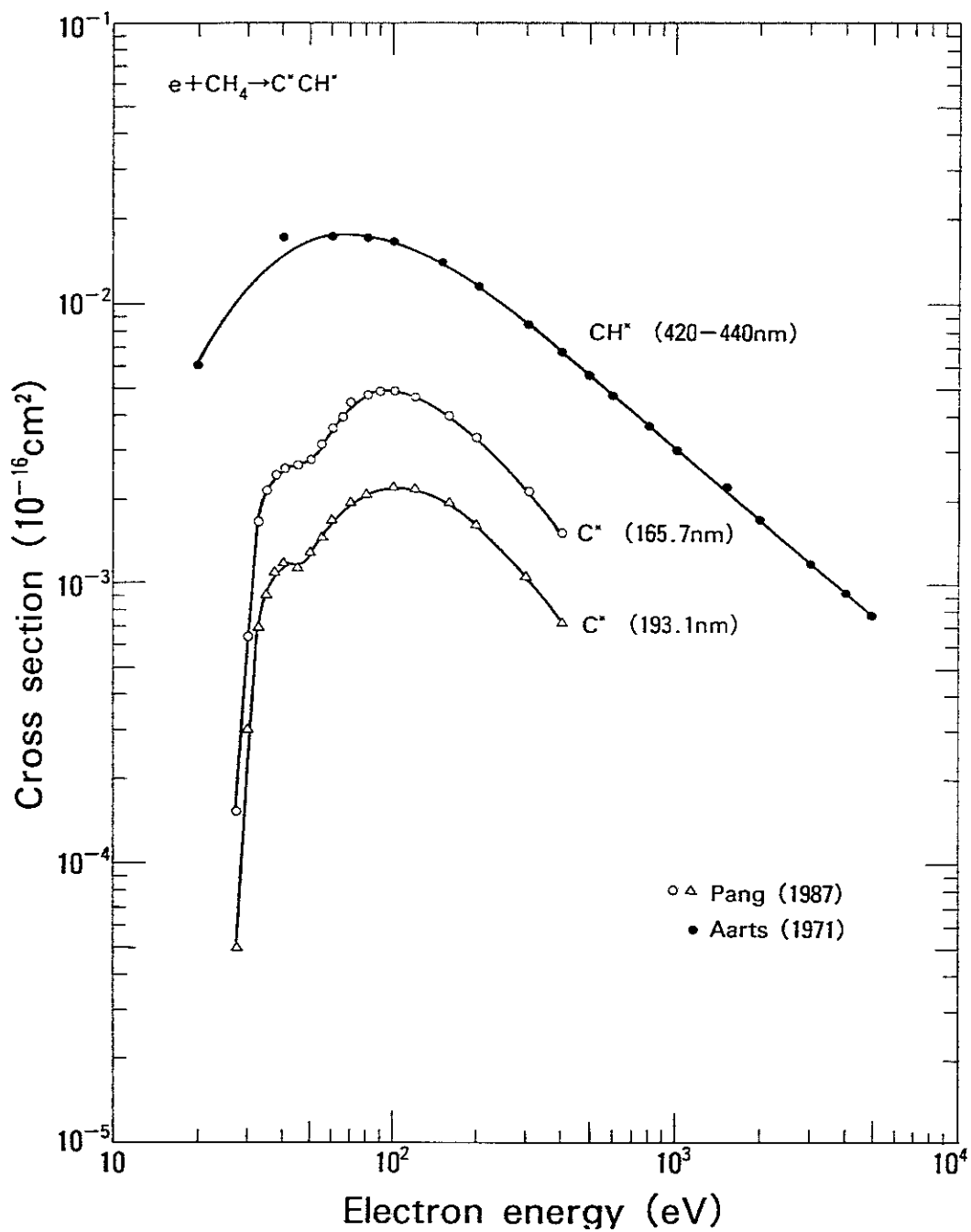


Fig. 9 Cross sections for emission of Balmer lines of hydrogen atoms in  $e + \text{CH}_4$  collisions as a function of electron energy



**Fig. 10** Cross sections for emission of carbon atom lines and CH molecular band in  $e + \text{CH}_4$  collisions

Emissions of molecular band (A  $^2\Delta$  - X  $^2\Pi$ ) from CH\*

The emission cross sections for this band (420.0 - 440.0 nm) have been determined by Aarts et al. over 20 - 5000 eV, as shown in **Fig. 10**. Also Koppe et al. measured these cross sections over 400 - 6000 eV which are in reasonable (<10 %) agreement with the result by Aarts et al.

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### Total dissociation cross section

Total dissociation cross sections have been determined over the energy range of 10 - 500 eV by Winters through measurements of the pressure variation when molecules are dissociated, as shown in Fig. 11. His results, which include the contribution of all inelastic excitation and ionization, indicate that at relatively high impact energies (above 50 eV), dissociation probabilities into ionic and neutral fragments are roughly equal, whereas at low energies the fragments are mostly uncharged, ground state molecules. In fact, the observed dissociation cross sections at 20 eV are a factor of three larger than the ionization cross sections and both become roughly equal at 100 eV. Data obtained by Perrin et al. with a different technique seem to be in agreement with those of Winters over the energy range up to 110 eV.

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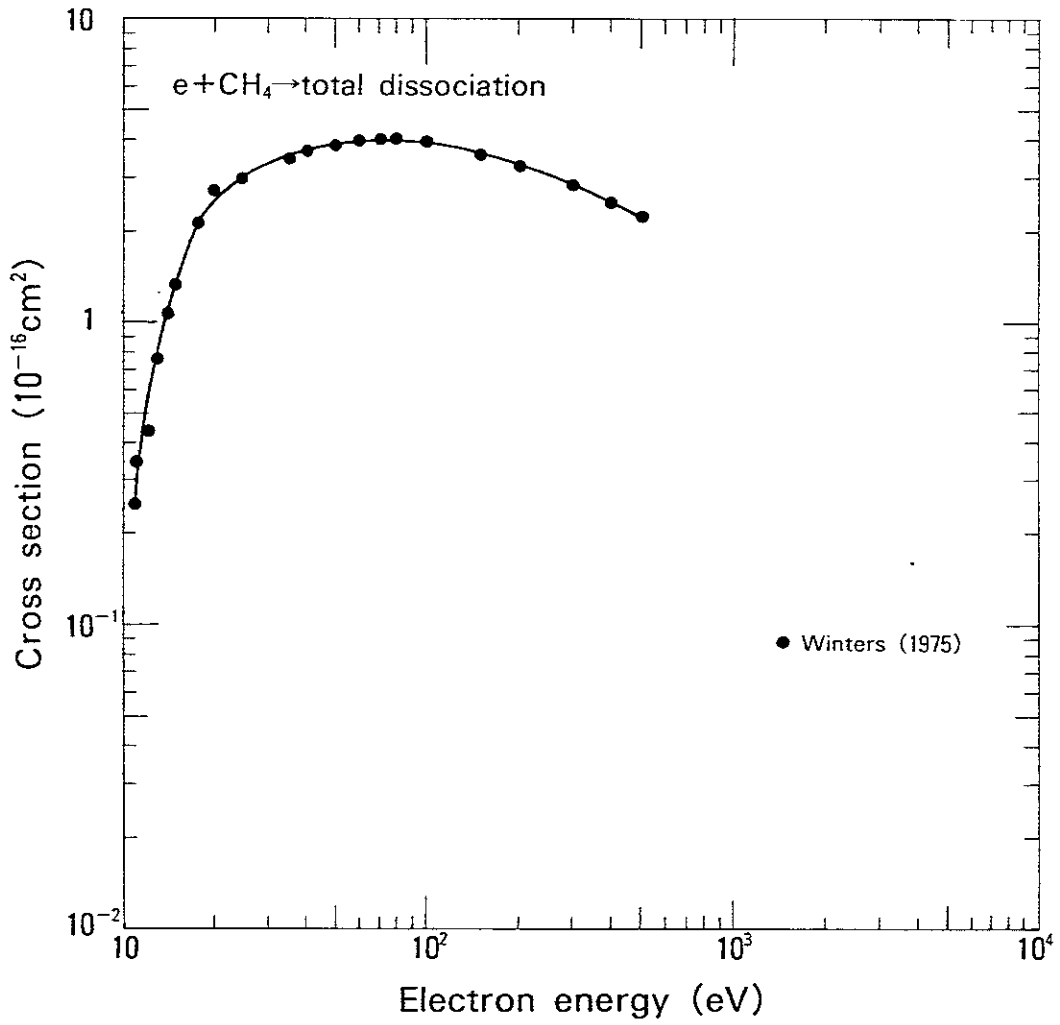


Fig. 11 Total dissociation cross sections for CH<sub>4</sub> by electrons



### Neutral products from dissociation

Only very limited information is available on neutral product spectra from dissociation of  $\text{CH}_4$  as it is difficult to detect them. These products formed in the first collision chamber have to be ionized in the separate, second collision chamber through electron (or photon) impact and then detected. Data by Flesch et al., as shown in **Table 10**, indicate that the majority of neutral products are found to consist of  $\text{CH}_3$  molecules as well as the parent molecules which arrive at the second chamber through elastic as well as inelastic scattering by electrons. The observed threshold energy for ionization of the product  $\text{CH}_3$  molecules suggests that they are in vibrationally excited states.

### Reference

G.D.Flesch, R.E.Utecht and H.J.Svec, Int. J. Mass Spectr. Ion Proc. 58, 151 (1984)

**Table 10** Neutral products from  $\text{CH}_4$  by 20 eV electron impact.

(Flesch et al.)

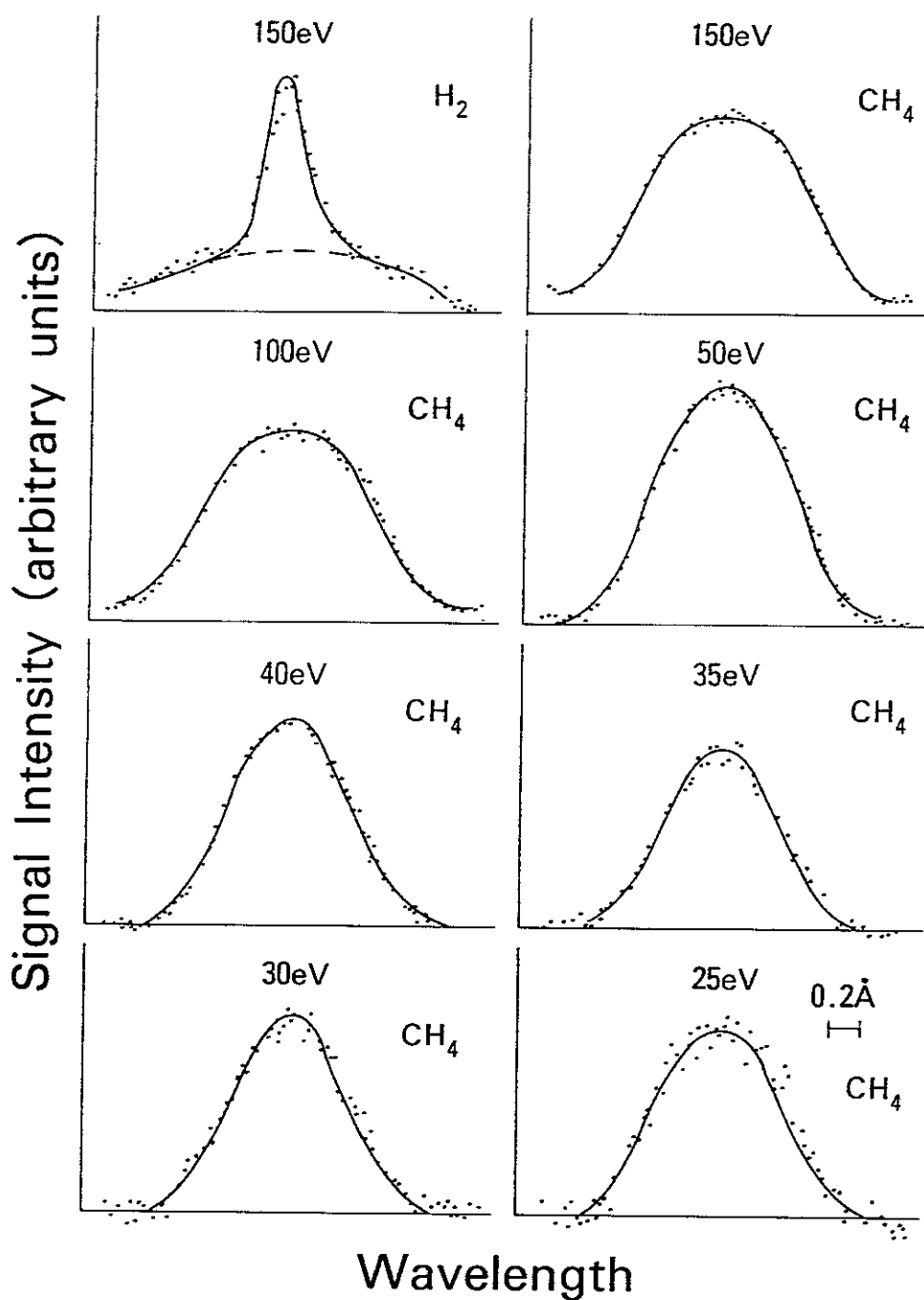
mass	2	15	16
fraction(%)	20	50	30

### Energy distributions of neutral hydrogen atoms

If they are in excited states, they may emit photons and can be detected optically. In particular, atomic hydrogens have been studied in some detail. The observation of broadening in Balmer or Lyman lines emitted from atomic hydrogens provides information of their energy distributions. For example, the observed results of Ito et al. on Balmer- $\alpha$  line from H( $n=3$ ), resulting from dissociation of CH<sub>4</sub> in electron impact, shows broad peaks with no particular structure, compared with that from H<sub>2</sub>, as shown in Fig. 12 but the peaks become broader with increasing the electron impact energy and indicates that a number of different dissociation channels contribute to this emission. Their results show the average energy of atomic hydrogens from CH<sub>4</sub> increase from 2.0 eV to 3.8 eV when the electron impact energy increases from 25 to 300 eV. Similar results have been reported on broadening of Balmer- $\beta$  line from H( $n=4$ ) dissociated from CH<sub>4</sub> by Ogawa et al.

Further measurements, based upon time-of-flight technique by Finn et al., of the energy distributions of atomic hydrogens in high Rydberg states ( $E > 5$  eV) indicate that their energy ranges from 1.7 to 3.5 eV at 25 eV electron impact, as shown in Fig. 13, and, with increasing the impact energy, new peaks corresponding to higher energy show up. At 100 eV electron impact, the most intense peak of atomic hydrogens is observed at 4 eV, meanwhile their energy extends up to 14 eV. However, no absolute cross sections have been measured for the production of these energetic atomic hydrogens.

Similar TOF work has been reported by Schiavone et al. Both measurements on the energy distributions are in general agreement with each other. Yet the detailed spectra are found to be largely different probably because of uncertain detection efficiencies.



**Fig. 12** Doppler-broadened Balmer- $\alpha$  lines from H( $n=3$ ) in  $e + \text{CH}_4$  collisions under different electron energy.  
 Note similar spectrum from H<sub>2</sub> at the top on the left side.

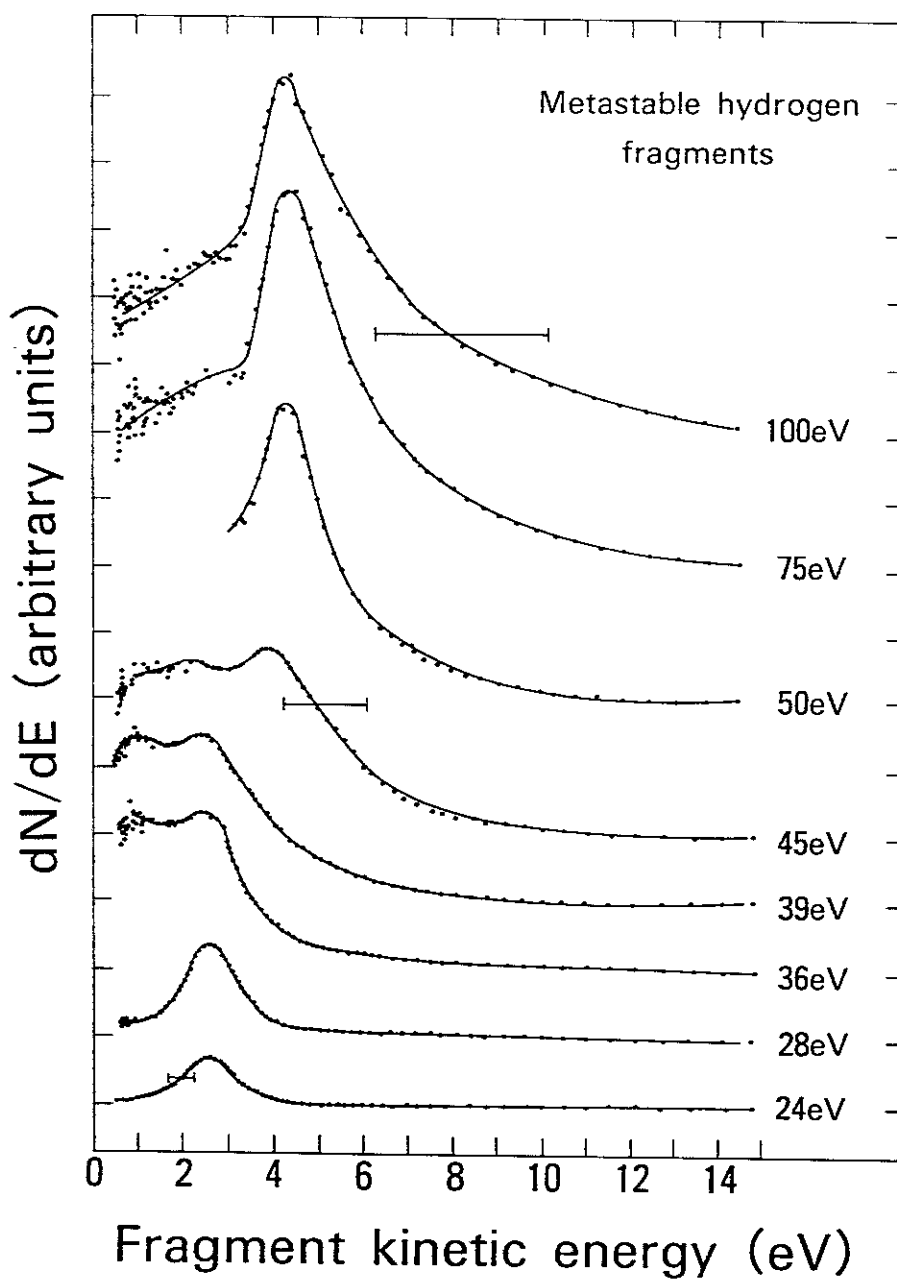


Fig. 13 Energy distributions of metastable atomic hydrogens produced in  $e + \text{CH}_4$  collisions under different electron energy impact

### Energy distributions of carbon atoms

Measurements of the energy distributions of neutral carbon products are very few. Results observed by Finn et al. and Schiavone et al. suggest that neutral (possibly metastable) carbon atoms in high Rydberg states have their energy ranging from 1 to 2 eV at 28 - 48 eV electron impact. Those for the ground and low excited states have not been reported yet.

### References

- K.Ito, N.Oda, Y.Hatano and T.Tsuboi, Chem. Phys. 21, 203 (1977)  
T.Ogawa, J.Kurawaki and M.Higo, Chem. Phys. 61, 181 (1981)  
T.Ogawa, H.Tomura, K.Nakashima and H.Kawazumi, Chem. Phys. 113, 65 (1987)  
T.G.Finn, B.L.Carnahan, W.C.Wells and E.C.Zipf, J. Chem. Phys. 63, 1596 (1975)  
J.A.Schiavone, D.E.Donohue and R.S.Freund, J. Chem. Phys. 67, 759 (1977)

### Energy distribution of hydrogen ions

The energy distributions of protons formed through dissociative ionization of CH<sub>4</sub> have been measured by Locht et al. who have found peaks at 0.0, 0.5, 0.9, 2.35 and 3.97 eV under 25 - 50 eV electron impact (note that most of previous measurements often failed to observe the peak at 0.0 eV, for example, Appell and Kubach). At all impact energies studied, the peak at thermal energy ( $\approx 0.0$  eV) with the threshold energies of 21.3 and 22.2 eV is the most intense, whereas the peak at 2.35 eV comes up at around 22 eV electron impact. With increasing the electron impact energy, other peaks show up. In particular, the peak at 0.9 eV superposed on a number of peaks becomes intense and overcome the peak at 2.35 eV. A series of different channels leading to the production of protons are listed by Locht et al., as shown in **Table 11**.

### References

- R.Locht, J.L.Olivier and J.Momigny, Chem. Phys. 43, 425 (1979)  
R.Locht and J.Momigny, Chem. Phys. 49, 173 (1980)  
J.Appell and C.Kubach, Chem. Phys. Letters 11, 486 (1971)

**Table 11** Appearance potential energies leading to proton production  
from CH<sub>4</sub> by electron impact (Locht et al.)

Dissociation product	Energy (eV)
from e + CH <sub>4</sub>	
H <sup>+</sup> + CH <sub>3</sub> ( $\tilde{B}^2A_1'$ ) + 2e	23.78
( $\tilde{C}^2E''$ )	26.30
( $\tilde{D}^2A_1'$ )	26.33
H <sup>+</sup> + H + CH <sub>2</sub> ( $\tilde{X}^3B_1$ ) + 2e	22.95
( $^1B_1$ )	24.75
( $^1A_1$ )	27.35
H <sup>+</sup> + H <sub>2</sub> + CH(X <sup>2P</sup> ) + 2e	22.85
(A <sup>2D</sup> )	25.70
(B <sup>2S<sup>-</sup></sup> )	26.08
(C <sup>2S<sup>+</sup></sup> )	26.79
H <sup>+</sup> + 2H + CH(X <sup>2P</sup> ) + 2e	27.32
(A <sup>2D</sup> )	30.17
(B <sup>2S<sup>-</sup></sup> )	30.55
(C <sup>2S<sup>+</sup></sup> )	31.26
H <sup>+</sup> + H <sub>2</sub> + H + C( <sup>3P</sup> ) + 2e	26.28
( <sup>1D</sup> )	27.54
( <sup>1S</sup> )	28.96
H <sup>+</sup> + 3H + C( <sup>3P</sup> ) + 2e	30.75
( <sup>1D</sup> )	32.01
( <sup>1S</sup> )	33.43
H <sup>+</sup> + CH <sub>3</sub> <sup>+</sup> ( $\tilde{X}^1A_1'$ ) + 3e	27.89
( <sup>3E''</sup> )	32.81
( <sup>1E''</sup> )	34.15
H <sup>+</sup> + H + CH <sub>2</sub> <sup>+</sup> ( $\tilde{X}^2A_1$ ) + 3e	33.35
H <sup>+</sup> + H <sup>+</sup> + CH <sub>2</sub> ( $\tilde{X}^3B_1$ ) + 3e	36.55
H <sup>+</sup> + H <sub>2</sub> + CH <sup>+</sup> (X <sup>1S<sup>+</sup></sup> ) + 3e	33.49
(A <sup>1S</sup> )	36.41
( <sup>1D</sup> )	37.03

### Dissociative recombination of CH<sub>4</sub><sup>+</sup> ions

Recently total cross sections for dissociative recombination of CH<sub>4</sub><sup>+</sup> ions in collisions with slow electrons have been determined with a merged-beam technique over 0.03 to 0.8 eV by Mul et al. who carefully controlled (but not specified) the internal excitation states of the parent CH<sub>4</sub><sup>+</sup> ions by mixing different gases with CH<sub>4</sub> in the ion source. It should be noted that these cross sections depend strongly upon the excitation energy of the parent molecular ions (see more discussions in the following section of CH<sup>+</sup> ions). In fact, as shown in Fig. 14, the observed cross sections decrease roughly as E<sup>-1</sup> up to 0.1 eV and then at higher energies fall off more rapidly. This quick fall-off above 0.1 eV can be understood to be due to the presence of ions in vibrationally excited states.

### References

P.M.Mul, J.B.A.Mitchell, V.S.D'Angelo, P.Defrance, J.Wm.McGowan and H.R.Froelich, J. Phys. B 14, 1353 (1981)



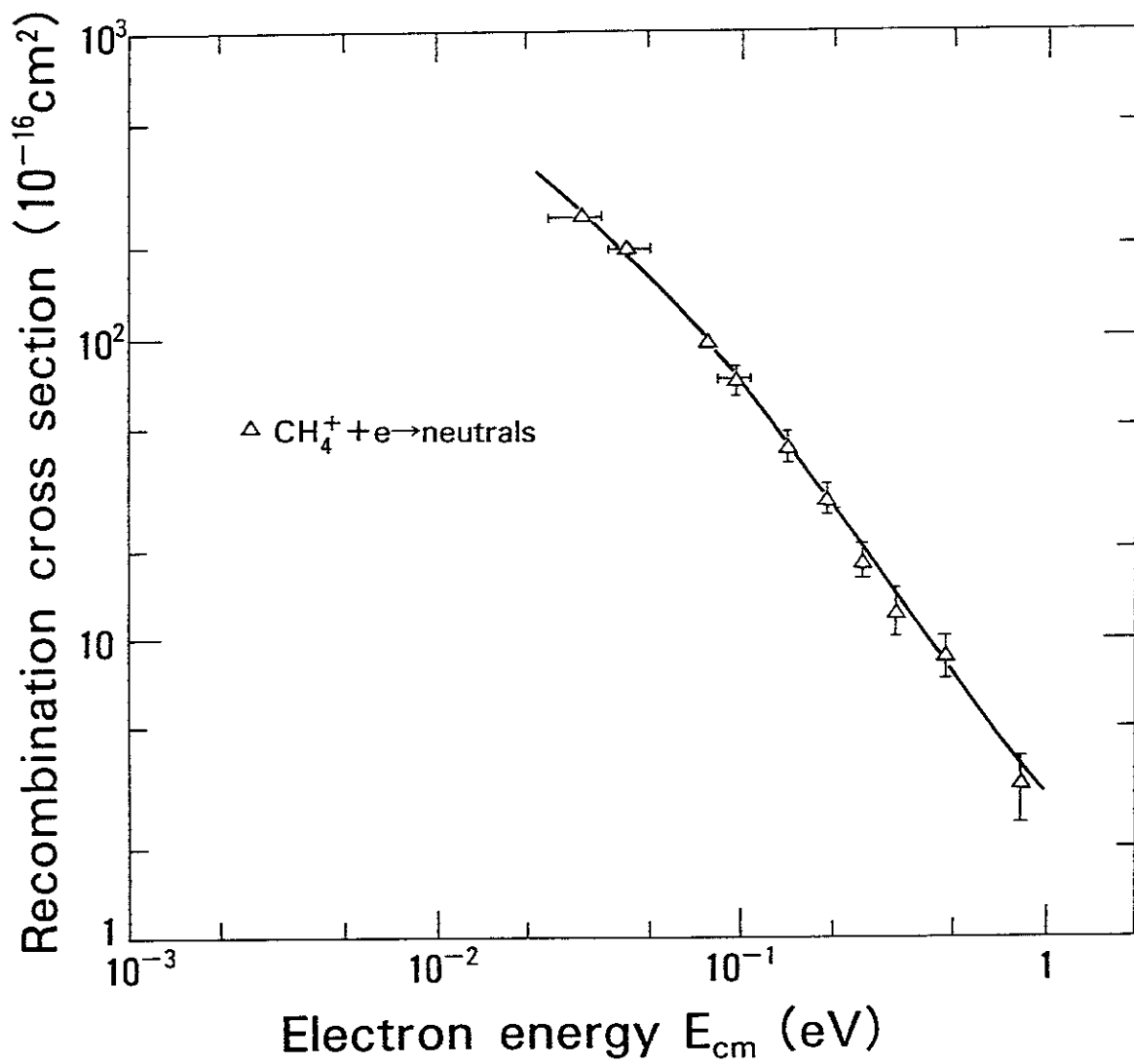


Fig. 14 Total cross sections for dissociative recombination of  $\text{CH}_4^+$  ions with electrons

Dissociative or pure ionization of CH<sub>4</sub><sup>+</sup> ions

Up to now no systematic measurement of dissociative or pure ionization of CH<sub>4</sub><sup>+</sup> ions by electrons has been reported except for a single preliminary result by Gregory and Tawara who found that the ionization as well as dissociation cross sections are strongly dependent upon the internal excitation energy of the parent CH<sub>4</sub><sup>+</sup> ions.

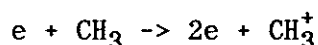
Reference

D.C.Gregory and H.Tawara, Abstract of XVI-th ICPEAC (New York, 1989) p.352

### III-2 CH<sub>3</sub>

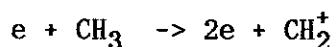
Until now no cross sections have been reported on total scattering, momentum transfer, elastic scattering, excitation and other processes except for those ionization and recombination processes below.

#### Pure ionization cross sections



Cross sections for ionization of CD<sub>3</sub> (instead of CH<sub>3</sub>) free radicals have been measured using two different crossed-beam techniques. To get CD<sub>3</sub> beam, fast CD<sub>3</sub><sup>+</sup> ions in the first technique used by Baiocchi et al. were produced from CD<sub>4</sub> molecules by electron impact and then neutralized. The neutralized CD<sub>3</sub> beam crosses an electron beam with the controlled impact energy over threshold to 200 eV (Baiocchi et al.). The measured cross sections, shown in Fig. 15, are relatively flat over 50 eV and the maximum values are  $1.6 \cdot 10^{-16} \text{ cm}^2$  at 50 - 100 eV. The second technique is based upon photodissociation of CH<sub>3</sub>OH by ArF excimer laser at 193 nm and the cross sections are determined over 8 to 14 eV (Wang et al.). Two measurements seem to be in general agreement with each other in the overlapped energy region.

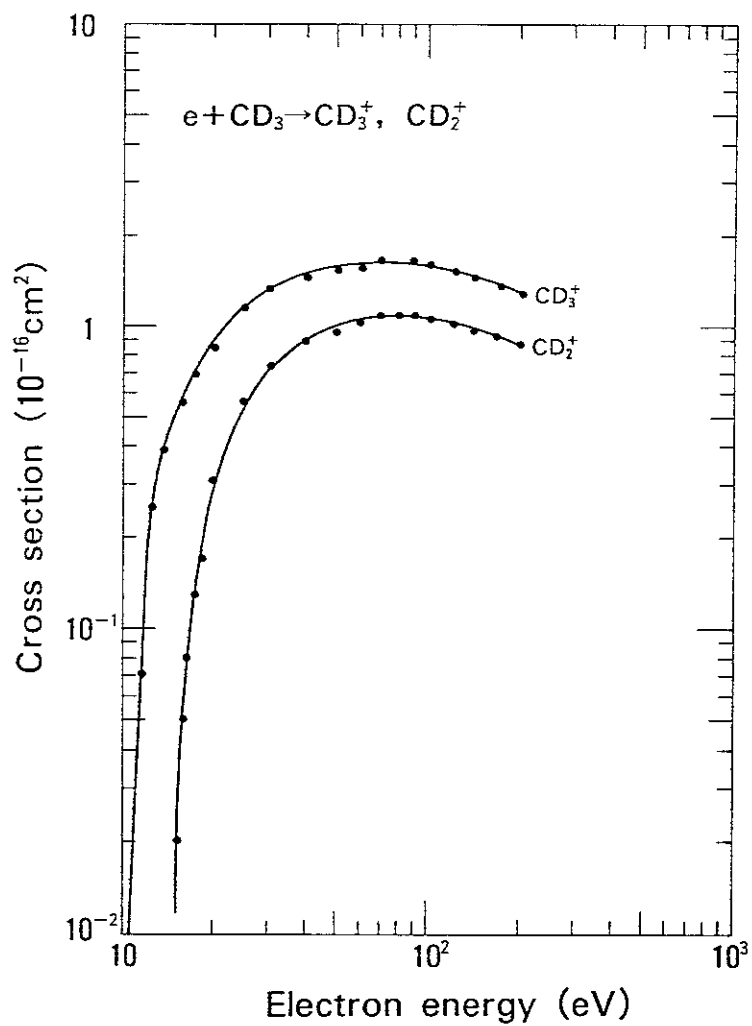
#### Dissociative ionization cross sections



The same technique as above by Baiocchi et al. is used to determine the cross sections for CD<sub>3</sub> which are shown in Fig. 15. and are found to be about 2/3 those for pure ionization mentioned above.

#### References

- F.A.Baiocchi, R.C.Wentzel and R.S.Freund, Phys. Rev. Letters 53, 771 (1984)  
D.P.Wang, L.C.Lee and S.K.Srivastava, Chem. Phys. Letters 152, 513 (1988)



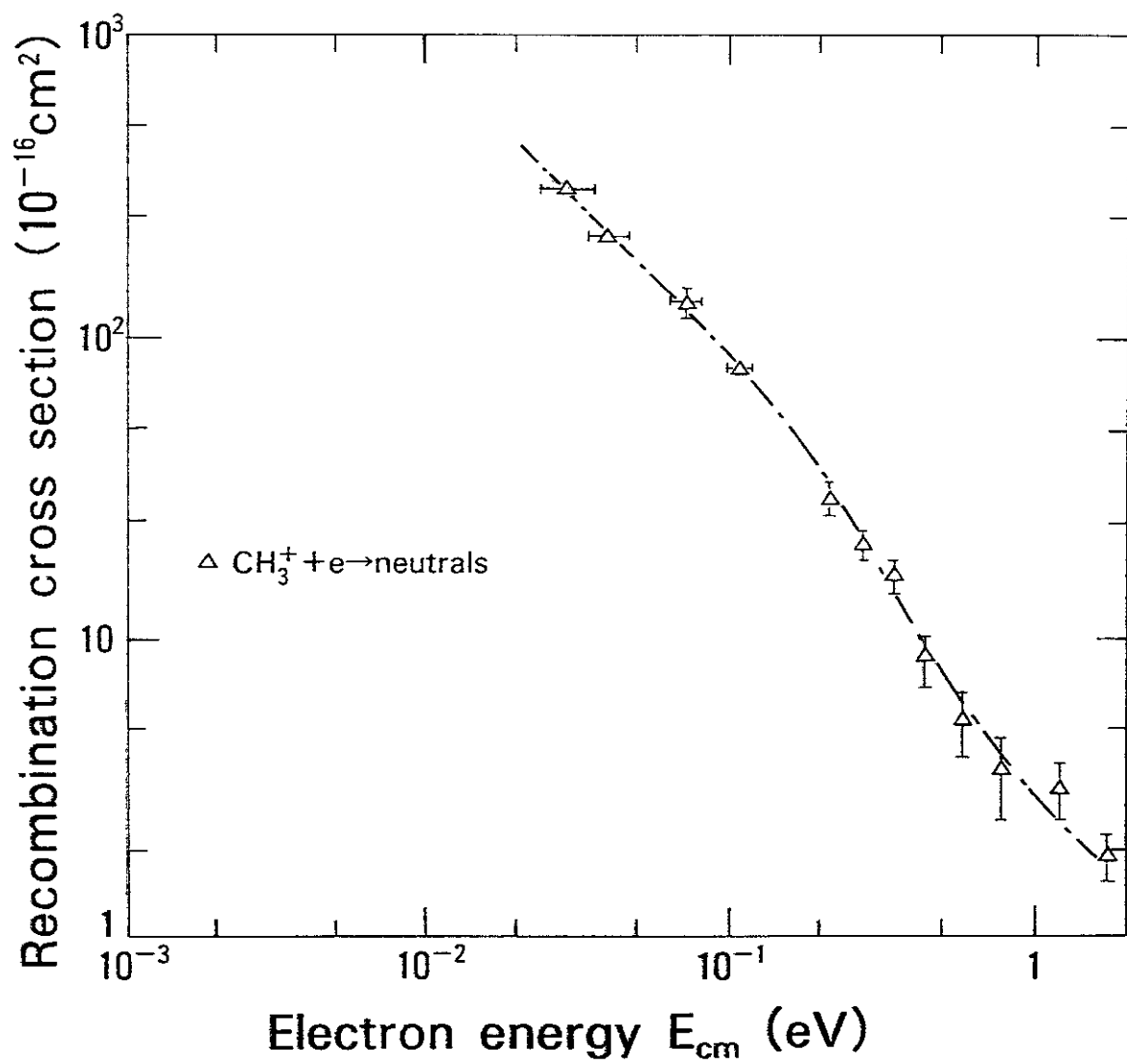
**Fig. 15** Pure ionization and dissociative ionization cross sections of  $\text{CH}_3$  by electron impact as a function of electron energy

### Dissociative recombination

The dissociative recombination cross sections of  $\text{CH}_3^+$  ions with slow electrons have been determined over 0.03 to 2 eV by Mul et al. In contrast to those for  $\text{CH}_4^+$  ions, the cross sections are found to be not much dependent upon how the parent  $\text{CH}_3^+$  ions are prepared either in pure  $\text{CH}_4$  or in mixtures with other gases. Yet their results shown in Fig. 16 suggest some contribution of ions in (vibrationally) excited states, as manifested in rapid fall-off at higher energies. It is also noted that the cross sections for  $\text{CH}_3^+$  ions are almost the same as those for  $\text{CH}_4^+$  ions, except for those at higher energies.

### Reference

P.M.Mul, J.B.A.Mitchell, V.S.D'Angelo, P.DeFrance, J.Wm.McGowan and H.R.Froelich, J. Phys. B 14, 1353 (1981)

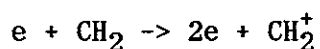


**Fig. 16 Total cross sections for dissociative recombination of  $\text{CH}_3^+$  with slow electrons**

### III-3 CH<sub>2</sub>

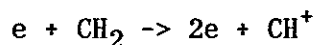
Similar to CH<sub>3</sub> molecules, no cross sections have been reported on total scattering, momentum transfer, elastic scattering, excitation and other processes except for those ionization and recombination processes below.

#### Pure ionization cross sections



The neutral CD<sub>2</sub> beam is produced through neutralization of CD<sub>2</sub><sup>+</sup> ions as above (Baiocchi et al.). The cross sections are shown in Fig. 17 and found to be the same order of magnitude as those for CD<sub>3</sub>.

#### Dissociative ionization cross sections



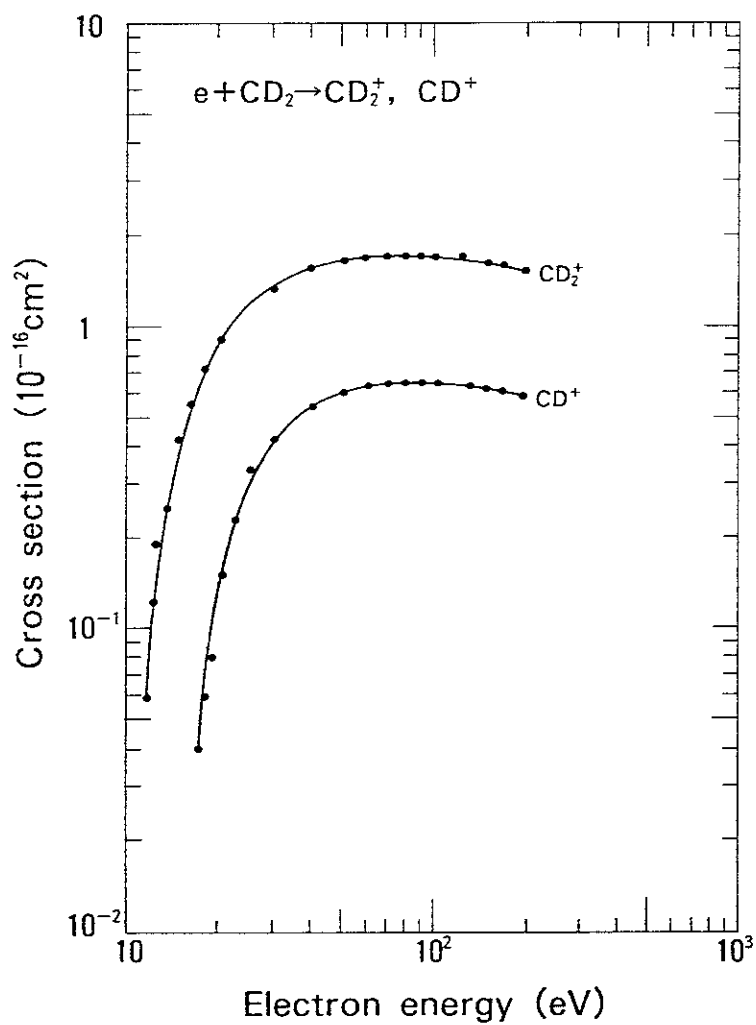
The observed dissociative ionization cross sections of CD into CD<sup>+</sup>, as shown in Fig. 17, are relatively flat over the energy range 50 to 200 eV and only 1/3 pure ionization cross sections mentioned above.

It should be bore in mind that the cross sections should be strongly dependent upon the internal energy state of the parent free radicals (see Table for CH<sub>4</sub>). Yet no detailed investigation has been made on the dependence on the internal energy state up to now.

No cross sections have been reported for other radicals resulting in ionization and dissociative ionization.

#### Reference

F.A.Baiocchi, R.C.Wentzel and R.S.Freund, Phys. Rev. Letters 53, 771 (1984)



**Fig. 17** Pure ionization and dissociative ionization cross sections of  $\text{CH}_2$  by electron impact as a function of electron energy

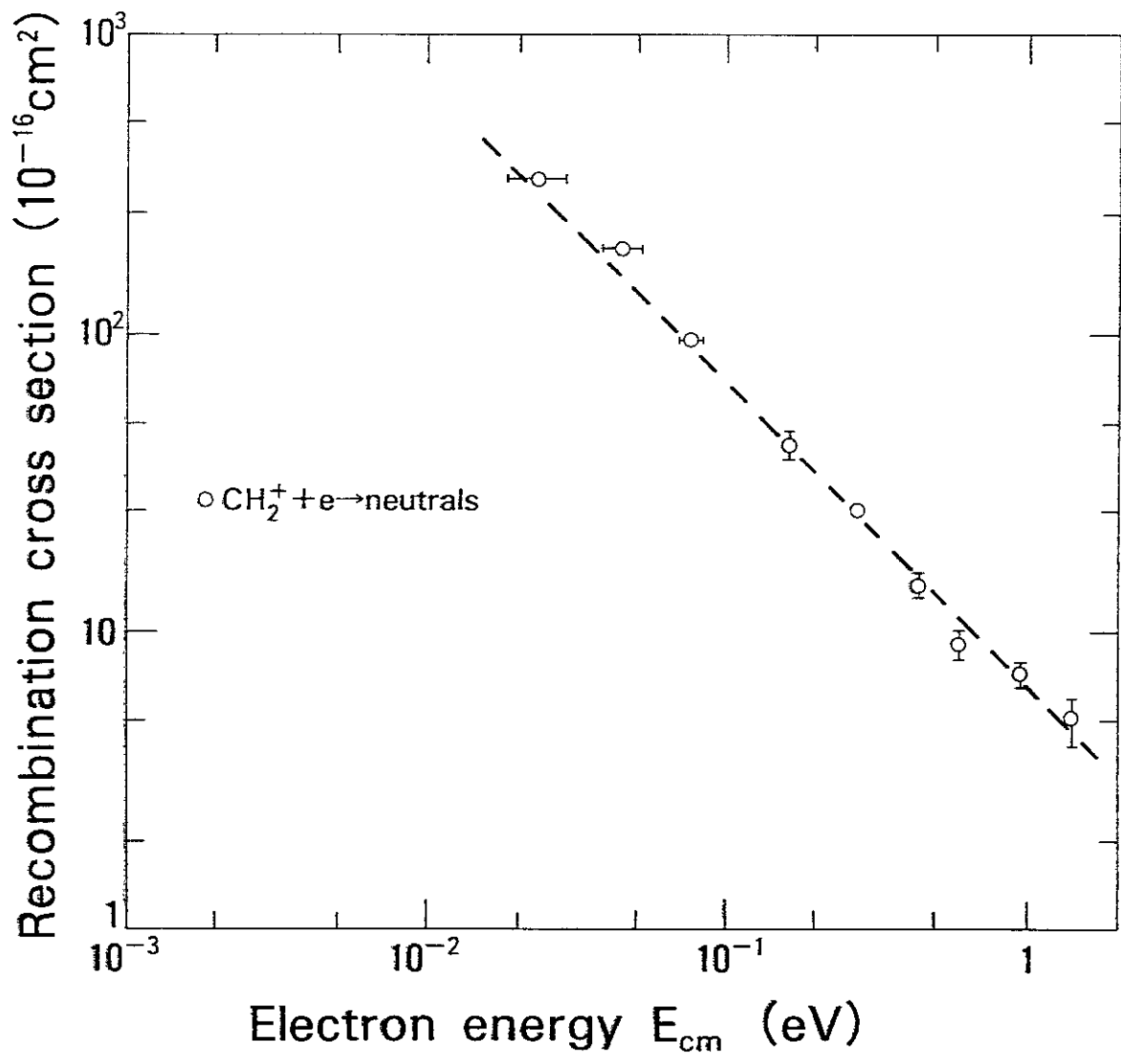


### Dissociative recombination

Total dissociative recombination cross sections for  $\text{CH}_2^+$  ions measured by Mul et al. using a merged beam technique show no significant dependence on the mixture of the quenching gases in the ion source, as seen in Fig. 18. This suggests that the parent  $\text{CH}_2^+$  ions produced are mostly in the ground state.

### Reference

P.M.Mul, J.B.A.Mitchell, V.S.D'Angelo, P.DeFrance, J.Wm.McGowan and  
H.R.Froelich, J. Phys. B 14, 1353 (1981)

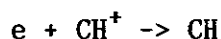


**Fig. 18** Total cross sections for dissociative recombination of CH<sub>2</sub><sup>+</sup> with slow electrons

### III-4 CH

Until now, no cross sections have been reported on total scattering, momentum transfer, elastic scattering, excitation and other processes except for those of recombination processes with electrons, though this is one of the most simple hydrocarbon molecules.

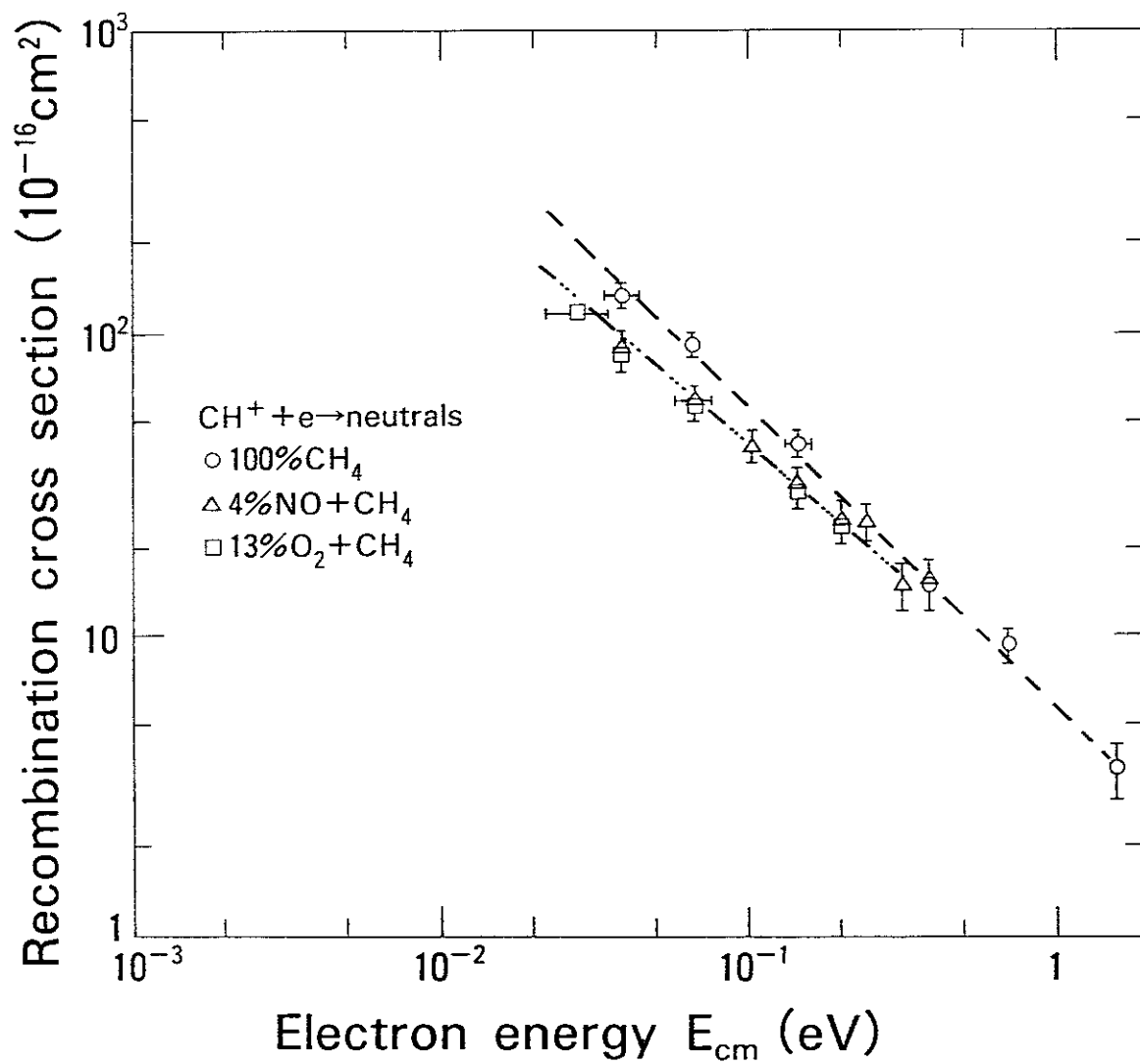
#### Recombination



Total dissociative recombination cross sections for  $CH^+$  ions with slow electrons have been determined by Mul et al. using a merged beam technique. They controlled the electronic state of the parent ions through mixture of various quenching gases with  $CH_4$  gas in the ion source. Their results, as shown in Fig. 19, suggest significant effects of the excitation energy of the parent molecular ions on recombination processes.

#### Reference

P.M.Mul, J.B.A.Mitchell, V.S.D'Angelo, P.Defrance, J.Wm.McGowan and H.R.Froelich, J. Phys. B 14, 1353 (1981)



**Fig. 19** Total cross sections for dissociative recombination of  $\text{CH}^+$  with slow electrons

### III-5 C<sub>2</sub>H<sub>6</sub>

#### Elastic and inelastic scattering

Total cross sections, recently remeasured by Floeder et al. and also by Sueoka and Mori over 1 - 400 eV, are in good agreement with each other within their uncertainties and found to also be in good agreement with the previous data by Brüche except for those at the lowest energies (see **Fig. 20**). **Table 12** shows experiments on total scattering cross section measurements for C<sub>2</sub>H<sub>6</sub>.

#### References

E.Brüche, Ann. Phys. (Leipzig) 4, 387 (1930)

K.Floeder, D.Fromme, W.Raith, A.Schwab and G.Sinapius, J. Phys. B 18, 3347 (1985)

D.Sueoka and S.Mori, J. Phys. B 19, 4035 (1986)

**Table 12** Experiments on total cross sections of electrons for C<sub>2</sub>H<sub>6</sub>

Author	(year)	Energy (eV)	Method	Comments
Brüche	(1930)	1-38	Ramsauer	A*)
Floeder	(1985)	5-400	Transmission	A
Sueoka	(1986)	1-400	Transmission	A

\*) A represents absolute measurements.

Momentum transfer cross sections below 1 eV are obtained through swarm technique. Those by McCorkle et al. seem to be uncertain above 0.2 eV because they measured the cross sections only in the limited energy range. On the other hand, Tanaka et al. determined the cross sections based upon beam technique over a wide range of the electron energy. Those based upon swarm data are found to be not in agreement with each other and also in disagreement with those obtained through beam technique by Tanaka et al. In **Table 13** is given a list of experiments on measurements of momentum transfer cross sections. At present it is difficult to give the recommended values for C<sub>2</sub>H<sub>6</sub>. More experiments are necessary to get reliable cross sections data for momentum transfer for C<sub>2</sub>H<sub>6</sub>.

#### References

- T.L.Cottrell, W.J.Pollock and I.C.Walker, Trans. Faraday Soc. 64, 2260 (1968)
- C.R.Bowman and D.E.Gordon, J. Chem. Phys. 46, 1878 (1967)
- C.W.Duncan and I.C.Walker, J. Chem. Soc. Faraday Trans. II 70, 577 (1974)
- D.L.McCorkle, L.G.Christophorou, D.V.Maxey and J.G.Carter, J. Phys. B 11, 3067 (1978)
- N.Gee and G.R.Freeman, Phys. Rev. A 22, 301 (1980)

**Table 13** Experiments on momentum transfer cross sections in C<sub>2</sub>H<sub>6</sub>

Author	(year)	Energy (eV)	Method	Comments
Cottrell	(1968)	0.05-3	Swarm	to theory <sup>a)</sup>
Bowman	(1967)	0.01-0.063	Swarm	to theory
Duncan	(1974)	0.01-1.0	Swarm	to theory
McCorkle	(1978)	0.01-0.23	Swarm	to theory
Gee	(1980)	0.005-0.3	Swarm	to theory
Tanaka	(1988)	2-100	Beam	to He <sup>b)</sup>

a) indicates the normalization to theory.

b) indicates the normalization to He data.

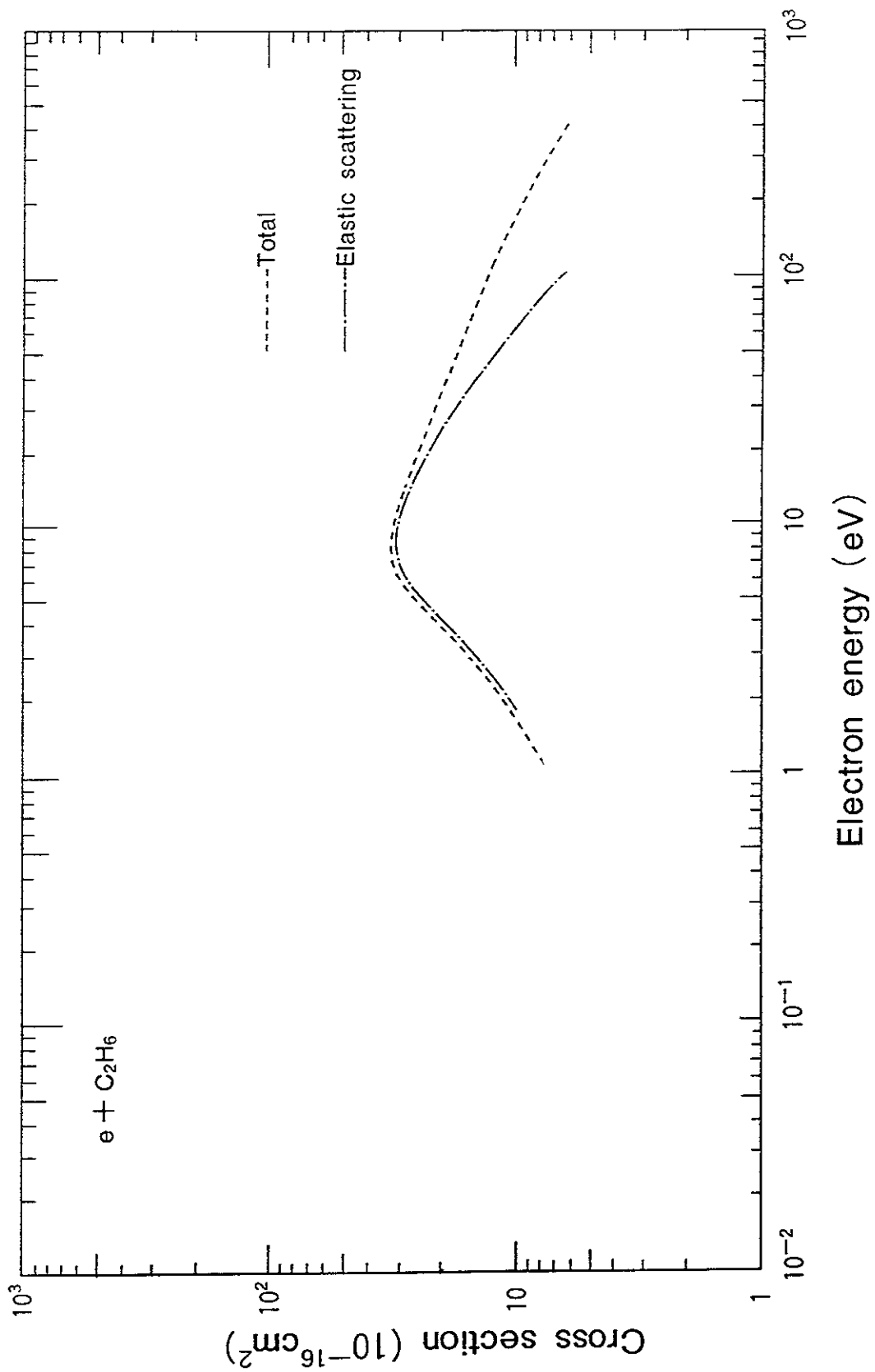


Fig. 20 Total cross sections and elastic scattering cross sections of electrons from C<sub>2</sub>H<sub>6</sub>



Differential elastic scattering cross sections, recently measured by Tanaka et al., have found to be in generally good agreement with those by Curry et al. but are a factor of two smaller than those by Fink et al. at the overlapped energy of 100 eV. Integrated elastic scattering cross sections are given only by Tanaka et al., as seen in Fig. 20. In Table 14 are shown experiments on elastic scattering cross section measurements.

#### References

- M.Fink, K.Jost and D.Hermann, J. Chem. Phys. 63, 1985 (1975)  
 P.J.Curry, W.R.Newell and A.C.H.Smith, J. Phys. B 18, 2303 (1985)  
 H.Tanaka, L.Boetzen, D.Matsunaga and T.Kudo, J. Phys. B 21, 1255 (1988)

**Table 14** Experiments on elastic scattering of electrons from  $C_2H_6$

Author	(year)	Energy(eV)/Angle(°)	Method	Comments
Fink	(1975)	100-1000(3-130°)	Beam	to He <sup>a)</sup>
Curry	(1985)	7.5-20 (32-142°)	Beam	to He
Tanaka	(1988)	2-100 (15-130°)	Beam	to He

a) indicates the normalization to He data.

Some differential cross sections for vibrational excitation have been obtained by Curry et al. using beam technique. Total cross sections, obtained through Boltzmann equation analysis, are given by Duncan and Walker only over a limited energy range. **Table 15** gives a list of experimental work on vibrational excitation of  $C_2H_6$ .

References

C.W.Duncan and I.C.Walker, J. Chem. Soc. Faraday Trans. II 70, 577 (1974)  
P.J.Curry, W.R.Newell and A.C.H.Smith, J. Phys. B 18, 2303 (1985)

**Table 15** Experiments on vibrational excitation of  $C_2H_6$  by electrons

Author	(year)	Energy(eV)/Angle(°)	Method	Comments
Duncan	(1967)	0.1-1.0	Swarm	total
Curry	(1985)	7.5-21 (32-140°)	Beam	to He ( $v_b, v_s$ )

Electronic excitation processes have been investigated in detail in order to obtain spectroscopic data but no cross section is available. **Table 16** gives a list of experiments on electronic excitation of C<sub>2</sub>H<sub>6</sub>.

#### References

- E.N.Lassetre, A.Skerbele and M.A.Dillon, J. Chem. Phys. 49, 2382 (1968)  
 K.E.Johnson, K.Kim, D.B.Johnson and S.Lipsky, J. Chem. Phys. 70, 2189 (1979)  
 K.E.Johnson, D.B.Johnson and S.Lipsky, J. Chem. Phys. 70, 3844 (1979)  
 M.A.Dillon, H.Tanaka and D.Spence, J. Chem. Phys. 87, 1499 (1987)

**Table 16** Experiments on electronic excitation of C<sub>2</sub>H<sub>6</sub> by electrons

Author	(year)	Energy(eV)/Angle(°)	Method	Comments
Lassetre	(1968)	50,180 (0-9°)	Beam	R (ΔE=7-13 eV)
Johnson	(1979)	30-250 (0-90°)	Beam	R (ΔE=6.5-15 eV)
Dillon	(1987)	200 (3-9°)	Beam	R (ΔE=6-26 eV)

### Ionization cross sections

Total ionization cross sections have been determined by Schram et al. over the energy range of 600 - 12000 eV and by Chatham et al. over 15 - 400 eV. Both measurements seem to be in fairly good agreement with each other if the extrapolation is made (see **Fig. 21**). Partial ionization cross sections have been determined only by Chatham et al. over the energy range of 15 - 300 eV and are shown in **Fig. 22**. The most intense ionization is due to  $C_2H_4^+$ , followed by the parent ions  $C_2H_6^+$ .

The appearance potentials for the production of these ions above as well as  $C_2H_5^{2+}$  and  $C_2H_3^{2+}$  ions have been investigated by Plessis and Marmet, as shown in **Table 17**.

### References

- B.L.Schram, M.J.van der Wiel, F.J.de Heer and H.R.Moustafa, J. Chem. Phys. 44, 49 (1966)
- H.Chatham, D.Hils, R.Robertson and A.Gallagher, J. Chem. Phys. 81, 1770 (1984)
- P.Plessis and P.Marmet, Can. J. Chem. 65, 1424 (1987)

**Table 17** Appearance potential energies for various dissociative ionization processes of  $C_2H_6$  by electron impact (Plessis and Marmet)

Products	Energy(eV)
$C_2H_6^+$	11.56
$C_2H_5^+ + H^-$	12.00
$C_2H_5^+ + H$	12.45
$C_2H_4^+ + H_2$	11.81
$C_2H_3^+ + H_2 + H^-$	13.76
$C_2H_3^+ + H_2 + H$	14.50
$C_2H_2^+ + 2H_2$	14.51
$C_2H^+ + 2H_2 + H$	22.4
$C_2^+ + 3H_2$	22.9
$CH_4^+ + CH_2$	16.63
$CH_3^+ + CH_3^-$	13.56
$CH_3^+ + CH_3$	13.65
$CH_2^+ + CH_4$	14.69
$CH^+ + CH_3 + H_2$	20.10
$C^+ + CH_4 + H_2$	20.3
$C_2H_5^{2+} + ^-$	31.60
$C_2H_5^{2+} + H$	32.3
$C_2H_3^{2+}$	35.5

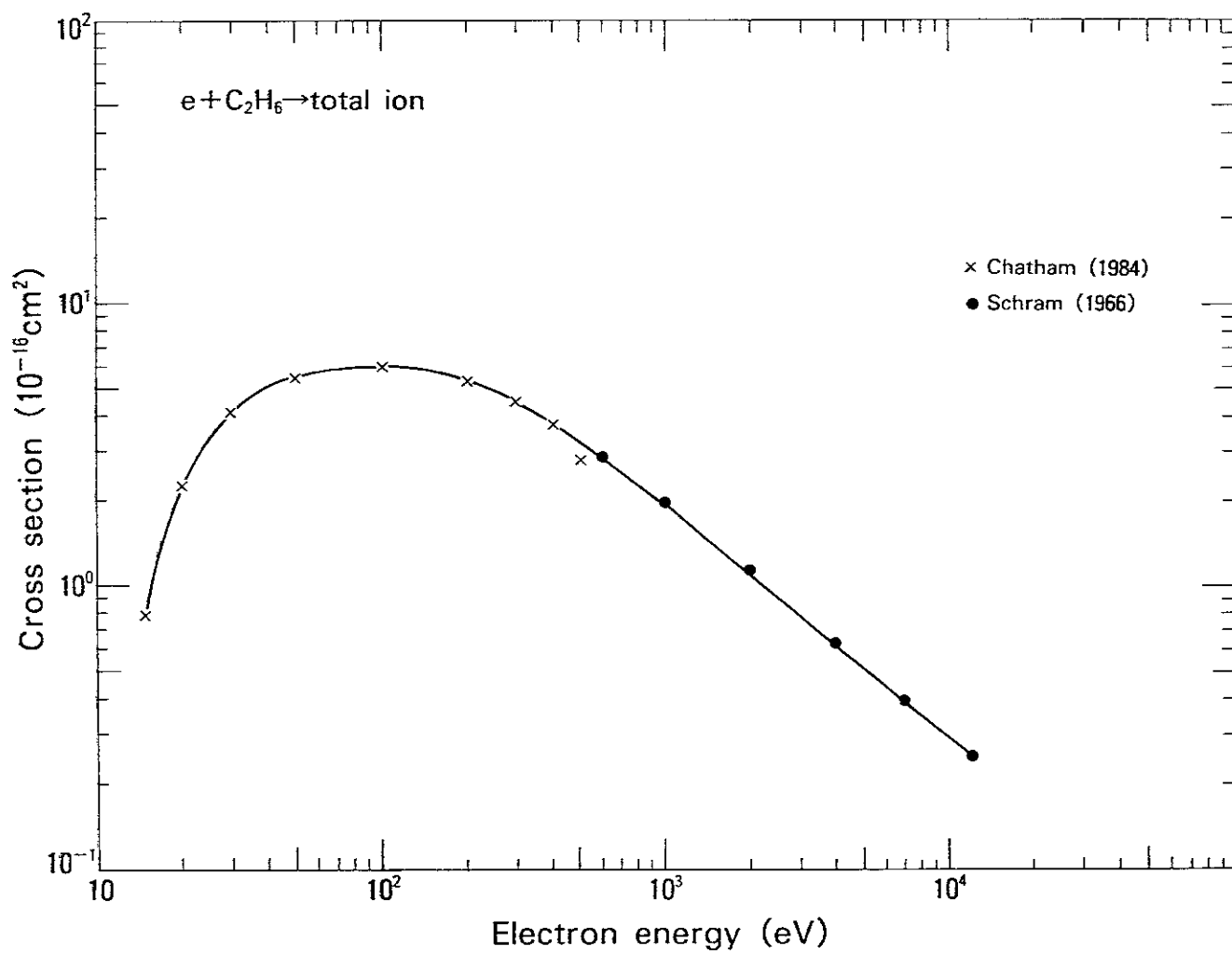
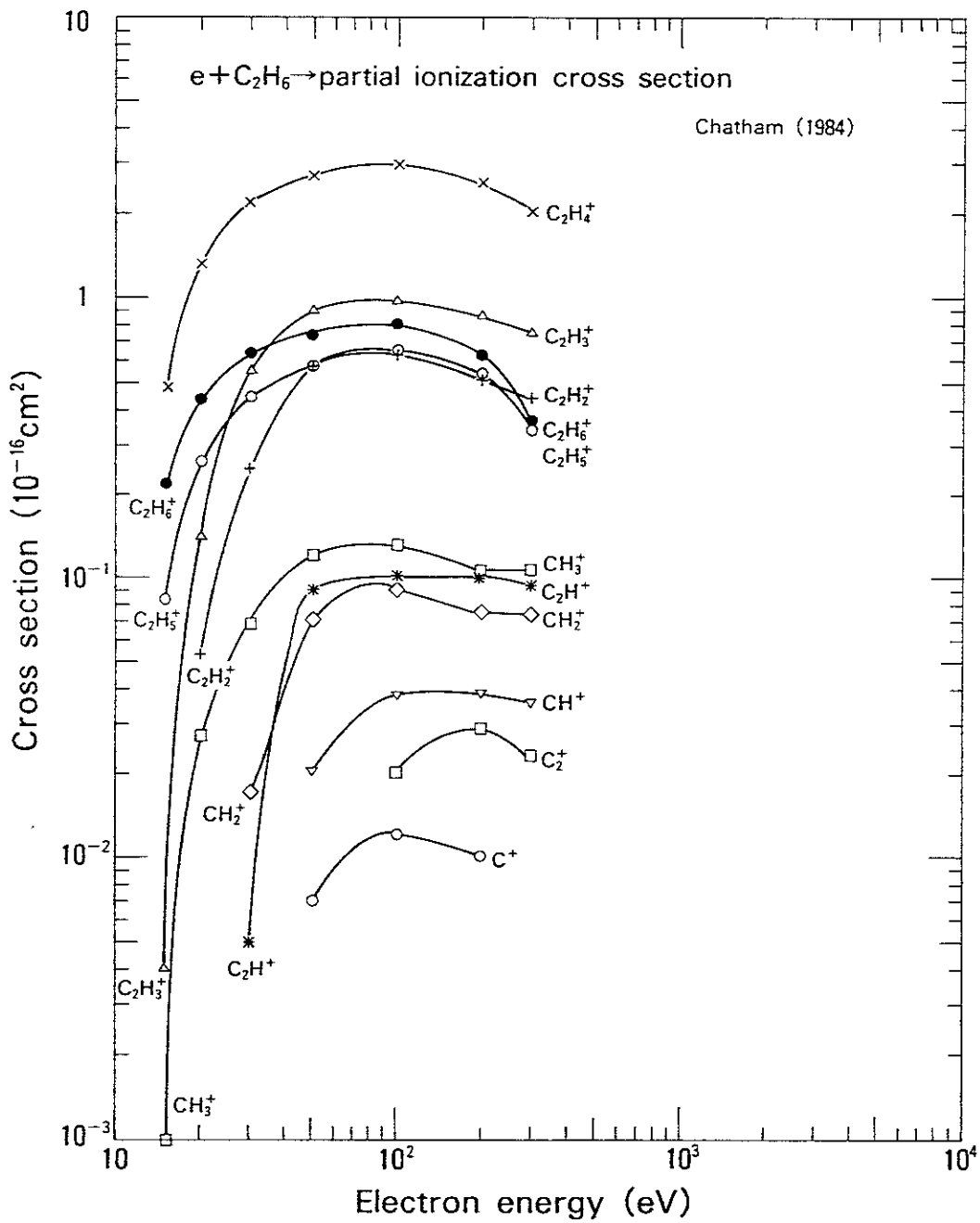


Fig. 21 Total ionization cross sections of  $C_2H_6$  by electron impact as a function of electron energy



**Fig. 22** Partial ionization cross sections of  $C_2H_6$  by electron impact as a function of electron energy

### Photon emission cross sections

Only a single measurement of the cross sections for emission of Lyman- $\alpha$ , 2s- $\rightarrow$ 1s transition and Balmer- $\alpha$ , - $\beta$ , - $\gamma$  and - $\delta$  lines has been reported by Vroom and de Heer over the energy range 0.5 - 6 keV. Their results are shown in Fig. 23. However, these Lyman- $\alpha$  data are renormalized to the most recent value of Lyman- $\alpha$  emission from CH<sub>4</sub> under electron impact by Pang et al. (see the previous section of CH<sub>4</sub>).

### References

D.A.Vroom and F.J. de Heer, J. Chem. Phys. 50, 573 (1969)  
K.D.Pang, J.M.Ajello, B.Franklin and D.E.Shemansky, J. Chem. Phys. 86, 2750 (1987). Some extra data tables at a single electron energy of 200 eV can be found in a separate document.



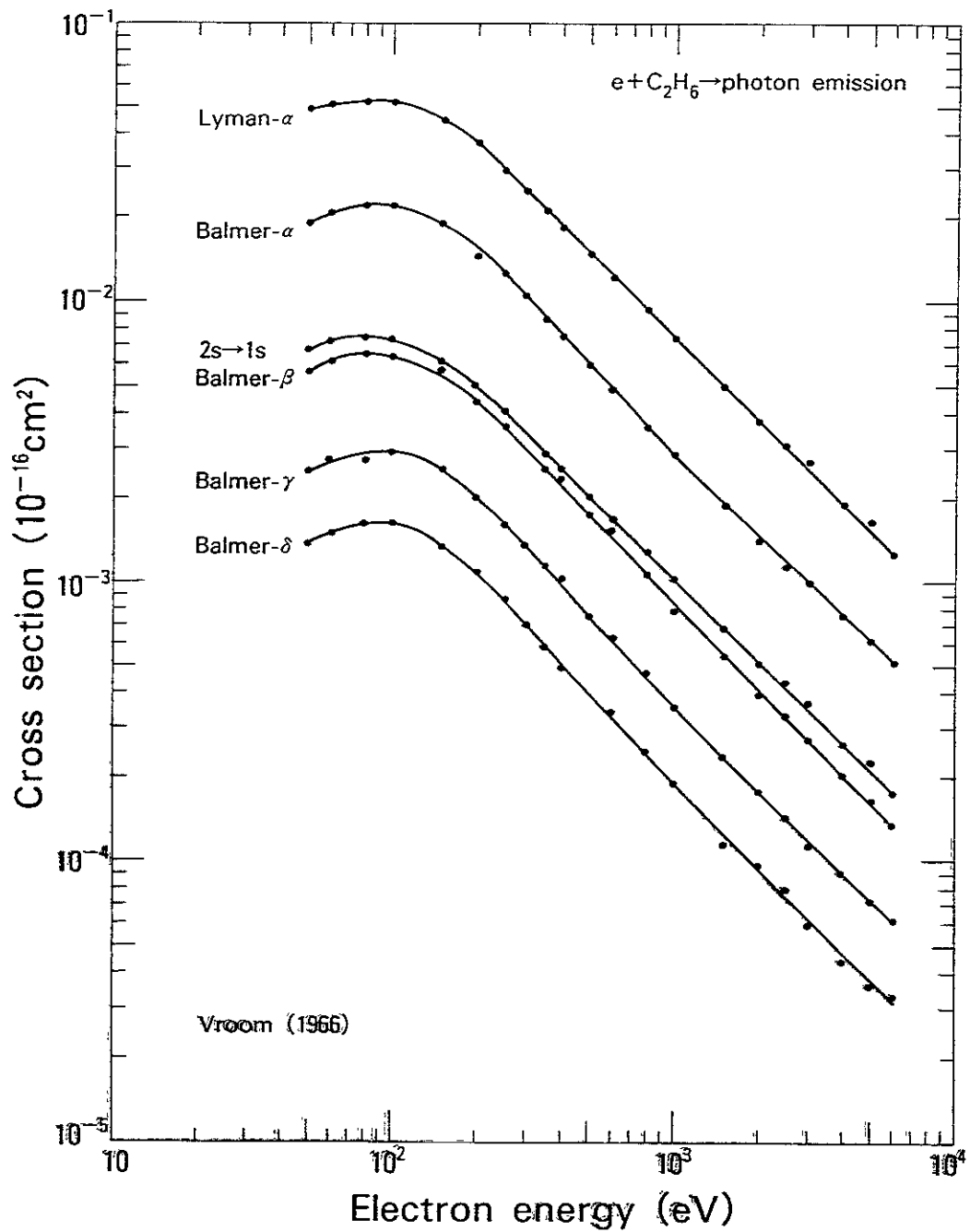


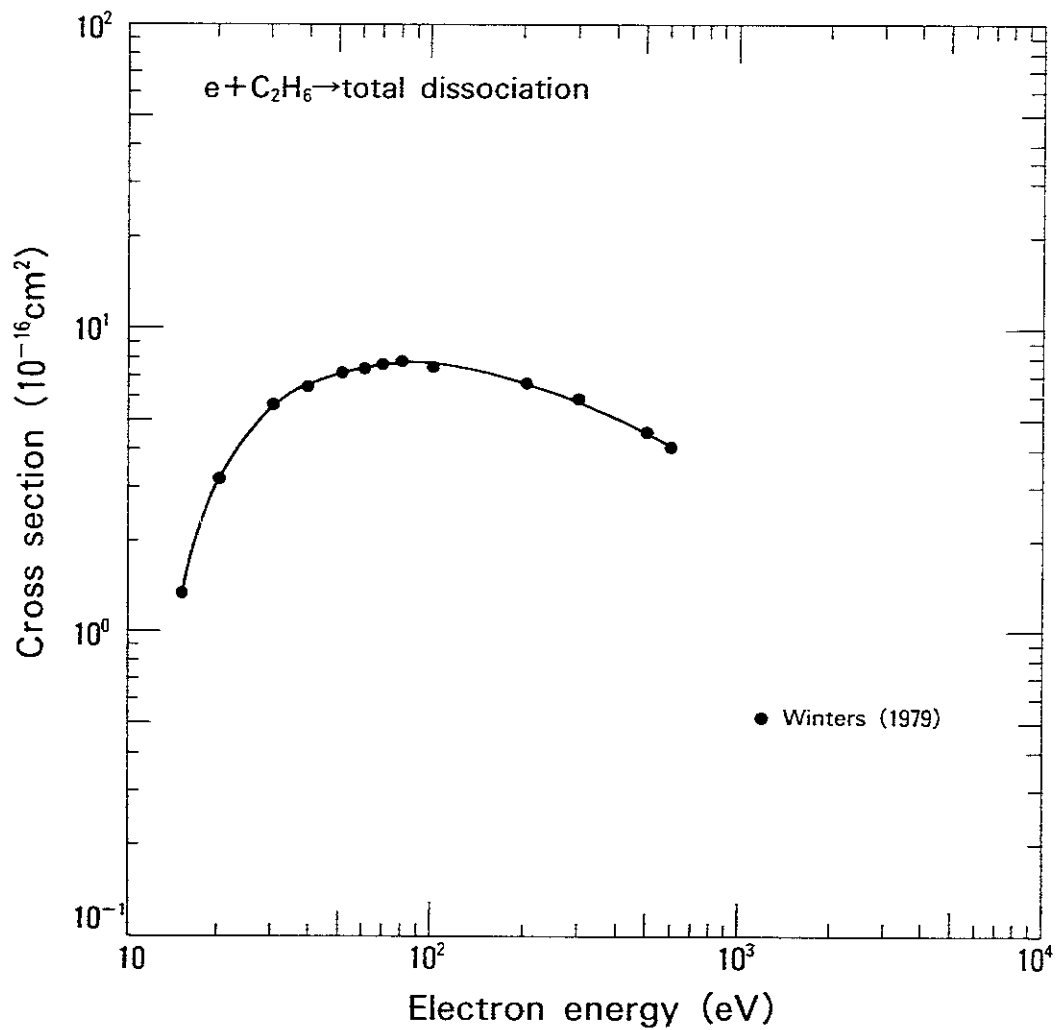
Fig. 23 Emission cross sections for various lines from C<sub>2</sub>H<sub>6</sub> by electron impact as a function of electron energy

### Dissociation cross sections

A technique, similar to that used for  $\text{CH}_4$  dissociation, was used to determine total dissociation cross sections by Winters, as shown in Fig. 24. Also he found that those for  $\text{C}_2\text{H}_6$  are consistently larger (by 8 % on average over the energy 50 - 600 eV) than those for  $\text{C}_2\text{D}_6$ . This isotope effect in dissociation process is understood from the fact that the time required for dissociation depends upon the velocity of particles involved, in contrast to ionization which is nearly independent of their velocity.

### Reference

H.F.Winters, Chem. Phys. 36, 353 (1979)



**Fig. 24** Total dissociation cross sections for  $C_2H_6$  by electrons as a function of electron energy

### Neutral products

A technique similar to that in CH<sub>4</sub> is used to determine the neutral product spectra from C<sub>2</sub>H<sub>6</sub> in 20 eV electron impact by Flesch et al., as shown in **Table 18**. Their observed results of ionization energies for these products suggest that H<sub>2</sub> and CH<sub>3</sub> are in some vibrationally excited states, whereas other products are in the ground states. Also the observed appearance potential energies for these neutrals show that the neutral products are due to dissociative ionization processes.

No information is available on the energy distributions of these neutral and also charged products.

### Reference

G.D.Flesch, R.E.Utecht and H.J.Svec, Int. J. Mass Spectr. Ion Proc. 58, 151 (1984)

**Table 18** Neutral products from C<sub>2</sub>H<sub>6</sub> by 20 eV electrons (Flesch et al.)

mass	2	15	26	27	28	29	30
fraction(%)	3	1	1	1	48	3	43

### III-6 C<sub>2</sub>H<sub>4</sub>

#### Elastic and inelastic scattering

Total cross sections have been measured by Floeder et al. and Sueoka and Mori over a wide range of the collision energy and are in agreement with each other in the overlapped energy range. Two peaks at around 2 and 8 eV are due to the shape resonances. The observed peak by Sueoka and Mori at the lower energy is slightly broader, compared with those by Brüche because of the energy resolution in the former work is poor. The final cross sections are shown in Fig. 25 (curve 1). Table 19 shows a list of experiments on total scattering cross sections.

#### References

- E.Brüche, *Ann. Phys. (Leipzig)* 2, 909 (1929)  
C.R.Bowman and W.D.Miller, *J. Chem. Phys.* 42, 681 (1965)  
P.D.Burrow and K.D.Jordan, *Chem. Phys. Letters* 36, 479 (1975)  
K.Floeder, D.Fromme, W.Raith, A.Schwab and G.Sinapius, *J. Phys. B* 18, 3347 (1985)  
D.Sueoka and S.Mori, *J. Phys. B* 19, 4035 (1986)

**Table 19** Experiments on total cross sections of electrons for C<sub>2</sub>H<sub>4</sub>

Author	(year)	Energy (eV)	Method	Comments
Brüche	(1927/9)	1-38	Ramsauer	A
Bowman	(1965)	1-12	Transmission	R
Burrow	(1975)	1-15	Transmission	R
Floeder	(1985)	5-400	Transmission	A
Sueoka	(1986)	1-400	Transmission	A

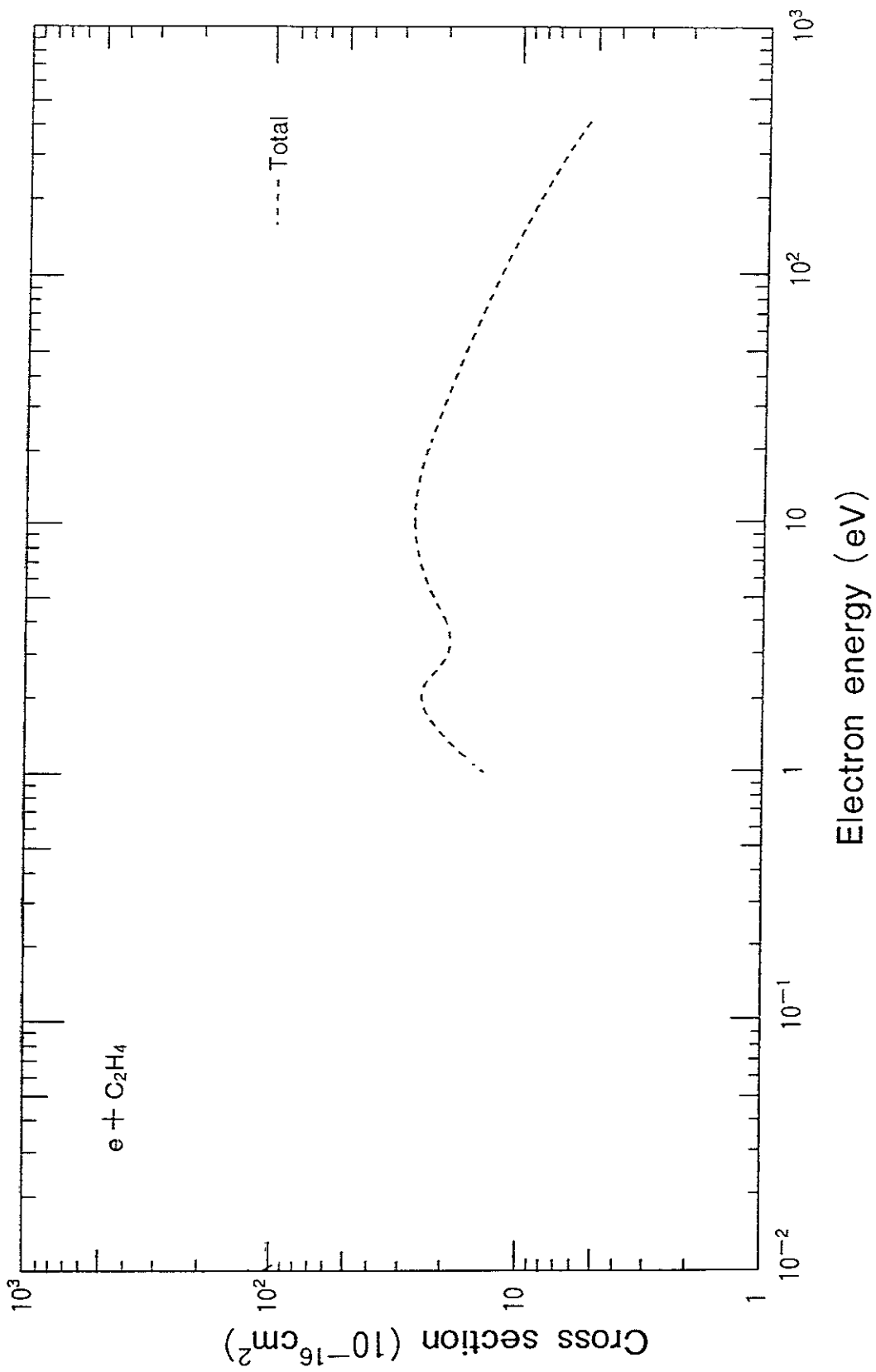


Fig. 25 Total cross sections of electrons for  $C_2H_4$

Cross sections for momentum transfer, based upon swarm technique, have been measured only below 1 eV. Yet no data are given here because they are quite scattered. **Table 20** gives a list of experiments on momentum transfer cross section measurements.

References

C.R.Bowman and D.E.Gordon, J. Chem. Phys. 46, 1878 (1967)  
 T.L.Cotttrell, W.J.Pollock and I.C.Walker, Trans. Faraday Soc. 64, 2260 (1968)  
 C.W.Duncan and I.C.Walker, J. Chem. Soc. Faraday Trans. II 68, 1514 (1972)  
 D.F.Dance and I.C.Walker, Proc. Roy. Soc. A334, 259 (1973)

**Table 20** Experiments on momentum transfer of electrons for C<sub>2</sub>H<sub>4</sub>

Author	(year)	Energy (eV)	Method	Comments
Bowman	(1967)	0.01-0.063	Swarm	to theory
Cotttrell	(1968)	0.05-1.6	Swarm	to theory
Duncan	(1972)	<1	Swarm	to theory
Dance	(1973)	<1	Swarm	to theory

Differential elastic scattering cross sections have been determined by Fink et al. over 100 - 1000 eV. But no total cross sections are given yet. In **Table 21** is listed experimental work on elastic scattering from C<sub>2</sub>H<sub>4</sub> molecules.

#### References

A.L.Hughes and J.H.McMillen, Phys. Rev. 44, 876 (1933)

M.Fink, K.Jost and D.Hermann, J. Chem. Phys. 63, 1985 (1975)

**Table 21** Experiments on elastic scattering of electrons from C<sub>2</sub>H<sub>4</sub>

Author	(year)	Energy(eV)/Angle(°)	Method	Comments
Hughes	(1933)	10-225 (10-140°)	Beam	R
Fink	(1975)	10-100 (3-140°)	Beam	to theory

The observed differential cross sections for vibrational excitation to  $v_n$  (n = 1, 2, 3, 7) show two strong peaks at 1.8 and 7.5 eV due to the shape resonance of <sup>2</sup>B<sub>2g</sub> and <sup>2</sup>A<sub>g</sub> states, as discussed by Walker et al. who also investigated the isotope effect between C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>D<sub>4</sub>. **Table 22** shows a list of experiments on vibrational excitation of C<sub>2</sub>H<sub>4</sub>.

#### Reference

I.C.Walker, A.Stamatovic and S.F.Wong, J. Chem. Phys. 69, 5532 (1978)

**Table 22** Experiments on vibrational excitation of C<sub>2</sub>H<sub>4</sub> by electrons

Author	(year)	Energy(eV)/Angle(°)	Method	Comments
Walker	(1978)	1-11 (25-110°)	Beam	to He



Most of measurements for electronic excitation, listed in **Table 23**, are concerned with spectroscopic data and no cross section is available at present.

#### References

- J.A.Simpson and S.R.Mielezarek, J. Chem. Phys. 39, 1606 (1963)  
 J.Geiger and K.Wittmack, Z. Naturforsch. 208, 628 (1965)  
 K.J.Ross and E.M.Lassettre, J. Chem. Phys. 44, 4633 (1966)  
 J.P.Doering and A.J.Williams, J. Chem. Phys. 47, 4180 (1967)  
 S.Trajmar, J.K.Rice and A.Kuppermann, Adv. Chem. Phys. 18, 15 (1970)  
 E.H.van Veen, Chem. Phys. Letters 41, 540 (1976)  
 D.G.Wilden and J.Comer, J. Phys. B 12, L371 (1979)  
 D.G.Wilden and J.Comer, J. Phys. B 13, 627 (1980) ; 13, 1009 (1980)

**Table 23** Experiments on electronic excitation of  $C_2H_4$  by electrons

Author	(year)	Energy(eV)/Angle(°)	Method	Comments
Simpson	(1963)	50 (<1°)	Beam	R ( E=0-13 eV)
Geiger	(1965)	33000 (0°)	Beam	R
Ross	(1966)	150 (0°)	Beam	R ( E=7-10.6 eV)
Doering	(1967)	11, 27 (90°)	Beam	R ( E=0-11 eV)
Lassettre	(1968)	40, 50 (0°, 7°)	Beam	R ( E=6.5-16 eV)
Trajmar	(1970)	40 (40°)	Beam	R ( E=2-13.5 eV)
van Veen	(1976)	threshold	Transmission	R ( E=1-12 eV)
Wilden	(1979)	2-100 (2-60°)	Beam	R ( E=3-6 eV, $E_T=5$ eV)
Wilden	(1980)	5-100 (0.5-60°)	Beam	R ( E=6.5-9 eV, $E_T=5$ eV)

### Ionization cross sections

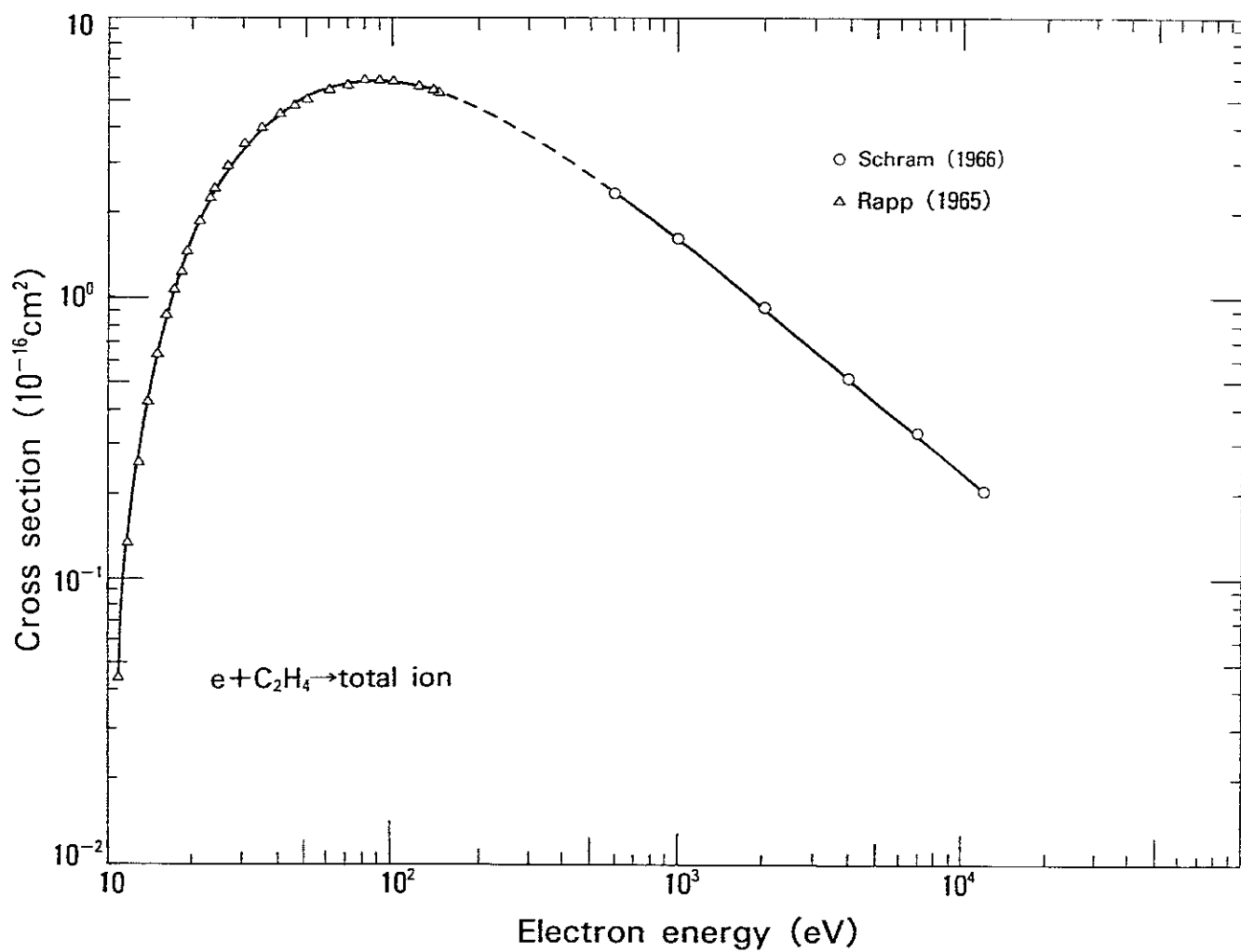
Total ionization cross sections measured by Rapp and Englander-Golden and Schram et al. are shown in **Fig. 26**. Though the measured energy region is not overlapped, the extrapolation seems to be in good agreement with each other. No partial cross sections are available, except for relative measurements at 75 and 3500 eV by Melton, as shown in **Table 24**. Practically no difference can be seen in relative partial ionization cross sections at both impact energies.

### References

- D.Rapp and P.Englander-Golden, J. Chem. Phys. 43, 1464 (1965)  
B.L.Schram, M.J.van der Wiel, F.J.de Heer and H.R.Moustafa, J. Chem. Phys. 44, 49 (1966)  
C.Melton, J. Chem. Phys. 37, 562 (1962)

**Table 24** Relative partial ionization cross sections of  $C_2H_4$   
by 75 and 3500 eV electron impact (Melton)

Energy(eV)	75	3500
$C^+$	0.94	0.74
$CH^+$	1.7	1.3
$C_2H_3^{2+}$	0.19	0.09
$CH_2^+$	3.8	3.6
$CH_3^+$	0.40	0.36
$C_2^+$	3.1	1.8
$C_2H^+$	9.6	5.8
$C_2H_2^+$	52	51
$C_2H_3^+$	62	60
$C_2H_4^+$	100	100



**Fig. 26** Ionization cross sections of  $C_2H_4$  by electron impact as a function of electron energy

## Photon emission cross sections

### Lyman and Balmer lines from hydrogen atoms

The emission cross sections for these atomic lines from atomic hydrogens have been measured by Vroom and de Heer (Lyman- $\alpha$ , 2s- $\rightarrow$ 1s transition, Balmer- $\alpha$ , - $\beta$ , - $\gamma$  and - $\delta$  : 50 - 6000 eV) and Aarts et al. (Balmer- $\beta$  : 20 - 5000 eV). The cross sections by Aarts et al. are about 20 % larger than those of Vroom and de Heer. The results of Vroom and de Heer are shown in **Fig. 27**.

### Molecular band from CH<sup>\*</sup>, C<sub>2</sub><sup>\*</sup> and CH<sup>++</sup>

The emission cross sections for the CH<sup>\*</sup>(A  $^2\Delta$  - X  $^2\Pi$ ) band have been determined by Aarts et al. over 20 - 5000 eV, as shown also in **Fig. 27**. Relative cross sections for both bands as well as those for CH<sup>++</sup>(B  $^1\Delta$  - A  $^2\Pi$ ) band at relatively low energies have been also reported by Donohue et al.

## References

- D.A.Vroom and F.J. de Heer, J. Chem. Phys. 50, 573 (1969)  
J.F.M.Aarts, C.I.M.Beenakker and F.J.de Heer, Physica 53, 32 (1971)  
D.E.Donohue, J.A.Schiavone and R.S.Freund, J. Chem. Phys. 67, 769 (1977)

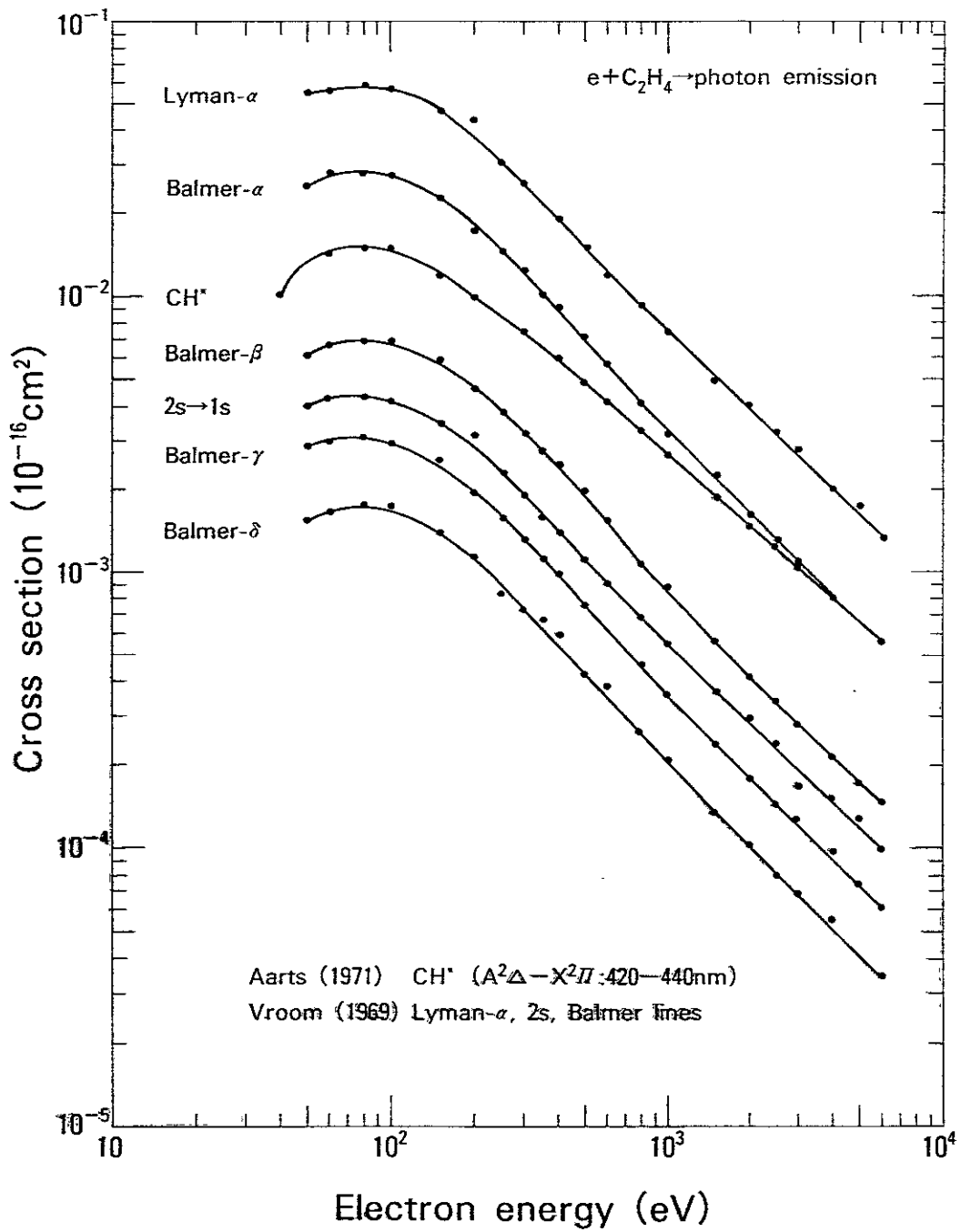


Fig. 27 Emission cross sections for various lines from C<sub>2</sub>H<sub>4</sub> by electron impact as a function of electron energy

### III-7 C<sub>2</sub>H<sub>2</sub>

#### Elastic and inelastic electron scattering

Only relatively old data by Brüche are available for total cross sections and are shown in Fig. 28 (curve 1). Table 25 shows a list of experiments of total scattering cross section measurements.

#### References

- E.Brüche, Ann. Phys. (Leipzig) 2, 909 (1929)  
C.R.Bowman and W.D.Miller, J. Chem. Phys. 42, 681 (1965)  
D.F.Dance and I.C.Walker, Proc. Roy. Soc. A334, 259 (1973)  
E.H.van Veen, Chem. Phys. Letters 41, 540 (1976)

**Table 25** Experiments on total cross sections of electrons by C<sub>2</sub>H<sub>2</sub>

Author	(year)	Energy (eV)	Method	Comments
Brüche	(1929/30)	1-38	Ramsauer	A
Bowman	(1965)	1-12	Transmission	R
Dance	(1973)	1-12	Transmission	R
van Veen	(1976)	1-12	Transmission	R

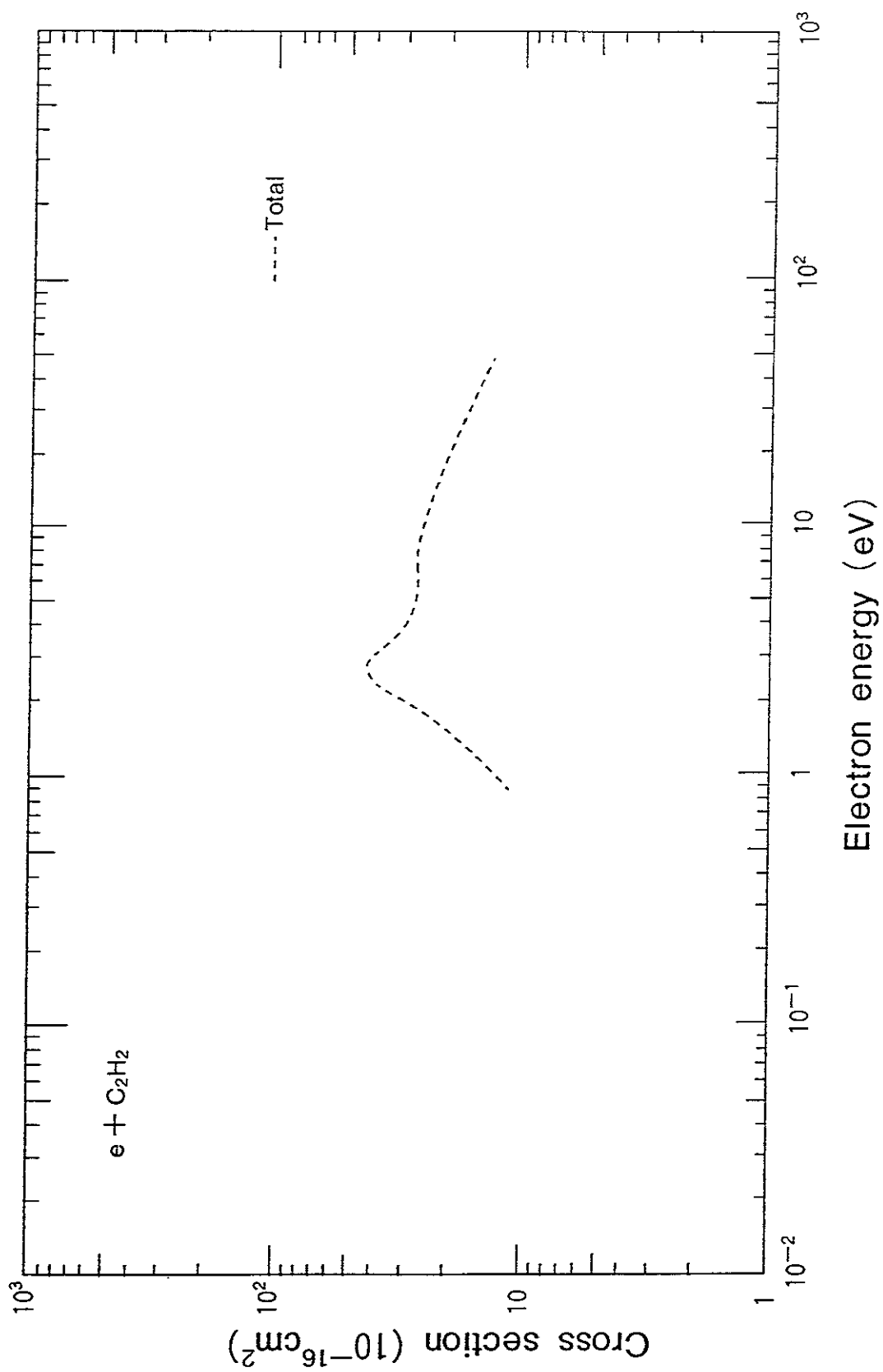


Fig. 28 Total cross sections of electrons from  $C_2H_2$

Also momentum transfer cross sections are limited both in quality as well as in quantity. Indeed the cross sections by Cottrell et al. is larger by a factor of three smaller than those by Bowman and Gordon. It is difficult to evaluate these data at present. **Table 26** shows a list of experiments for momentum transfer cross section measurements.

#### References

C.R.Bowman and D.E.Gordon, J. Chem. Phys. 46, 1878 (1967)

T.L.Cottrell, W.J.Pollock and I.C.Walker, Trans. Faraday Soc. 64, 2260 (1968)

**Table 26** Experiments on momentum transfer of electrons for  $C_2H_2$

Author	(year)	Energy (eV)	Method	Comments
Bowman	(1967)	0.01-0.063	Swarm	to theory
Cottrell	(1968)	0.05	Swarm	to theory



Differential elastic scattering cross sections have been measured only by Fink et al. at high energies (100 - 1000 eV) and by Kochem et al. at low energies (below 3.5 eV). However, no total cross sections have been given. **Table 27** show a list of experiments on elastic scattering.

#### References

- A.L.Hughes and J.H.McMillen, Phys. Rev. 44, 876 (1933)
- M.Fink, K.Jost and D.Hermann, J. Chem. Phys. 63, 1985 (1975)
- M.Tronc and L.Malegat, Lecture Notes on Chemistry 35 : Wavefunctions and Mechanisms from Electron Scattering Processes (eds. F.A.Gianturco and G.Stefani, Berlin, 1984) p.24
- K.H.Kochem, W.Sohn, K.Jung, H.Erhardt and E.S.Chang, J. Phys. B 18, 1253 (1985)

**Table 27** Experiments on elastic scattering of electrons from C<sub>2</sub>H<sub>2</sub>

Author	(year)	Energy(eV)/Angle(°)	Method	Comments
Hughes	(1933)	10-25 (10-150°)	Beam	R
Fink	(1975)	100-1000(3-140°)	Beam	to theory
Tronc	(1984)	2.6, 6.2, 21 (20-120°)	Beam	R
Kochem	(1985)	0-3.6 (5-108°)	Beam	to He

Differential cross sections for vibrational excitation for  $v_n$  ( $n = 1, 2, 3, 5$ ) have been measured in detail below 3.5 eV by Kochem et al. No total cross sections for vibrational excitation of  $C_2H_2$  have been reported yet. **Table 28** shows a list of experiments on vibrational excitation.

#### References

- M.Tronc and L.Malegat, Lecture Notes on Chemistry 35 : Wavefunctions and Mechanisms from Electron Scattering Processes (eds. F.A.Gianturco and G.Stefani, Berlin, 1984) p.24
- K.H.Kochem, W.Sohn, K.Jung, H.Erhardt and E.S.Chang, J. Phys. B 18, 1253 (1985)

**Table 28** Experiments on vibrational excitation of  $C_2H_2$  by electrons

Author	(year)	Energy(eV)/Angle(°)	Method	Comments
Tronc	(1984)	2.8-21	Beam	R ( $v_1, v_2, v_4+v_5, v_2+v_4$ )
Kochem	(1985)	0-3.6 (5-108°)	Beam	to He ( $v_1, v_2, v_3, v_5$ )

On the other hand, no data are available for electronic excitation except for some relative measurements. **Table 29** gives a list of experiments on electronic excitation of  $C_2H_2$  molecules.

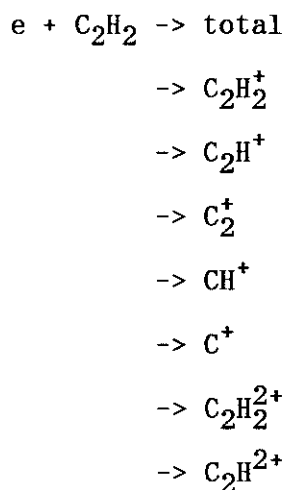
#### References

- E.N.Lassetre, A.Skerbele and M.A.Dillon, J. Chem. Phys. 49, 2382 (1968)  
 S.Trajmar, J.K.Rice and A.Kuppermann, Adv. Chem. Phys. 18, 15 (1970)  
 E.H.van Veen, Chem. Phys. Letters 41, 540 (1976)  
 D.G.Wilden, P.J.Hicks and J.Comer, J. Phys. B 10, L403 (1977)  
 D.G.Wilden, J.Comer and S.Taylor, J. Phys. B 13, 2849 (1980)  
 A.C.de A. e Souza and G.G.B.de Souza, Phys. Rev. A 38, 4488 (1988)

**Table 29** Experiments on electronic excitation of  $C_2H_2$  b electrons

Author	(year)	Energy(eV)/Angle(°)	Method	Comments
Lassetre	(1968)	50 (0-10°)	Beam	R ( $\Delta E=5-15$ eV)
Trajmar	(1970)	25-40 (10-50°)	Beam	R ( $\Delta E=4-12$ eV)
van Veen	(1976)	0-12	Transmission	R (threshold electron)
Wilden	(1977)	2-100 (2-60°)	Beam	R ( $\Delta E=3-6$ eV, $E_T=5$ eV)
Wilden	(1977)	5-100 (0.5-60°)	Beam	R ( $\Delta E=7-11$ eV, $E_T=5,100$ eV)
e Souza	(1988)	1000 (1-7°)	Beam	R ( $\Delta E=0-50$ eV)

### Total and partial ionization

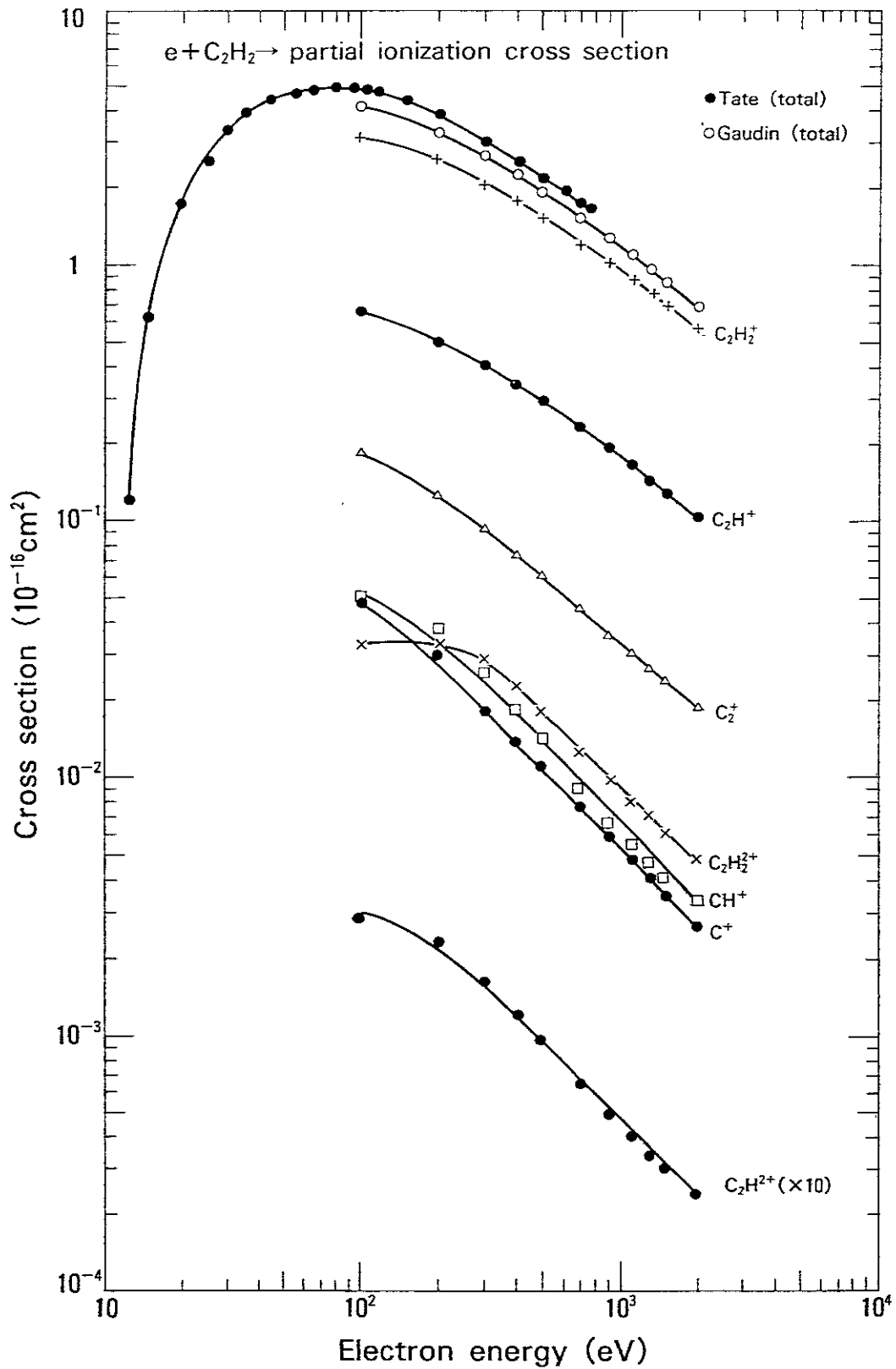


Total ionization cross sections have been determined by Tate and Smith and also by Gaudin and Hagemann covering from the threshold to 2000 eV, as shown in **Fig. 29** which indicates that the former data are slightly larger (by 20 % at 100 eV) than the latter but tend to converge at higher energies.

Partial cross sections have been determined by Gaudin and Hagemann, as shown also in **Fig. 29**. Melton also measured relative partial cross sections at 75 and 3500 eV which seem to be in reasonable agreement with data by Gaudin and Hagemann.

### References

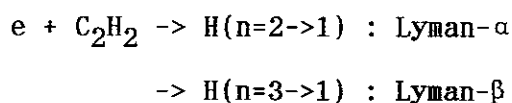
- J.T.Tate and P.T.Smith, Phys. Rev. 39, 270 (1932)  
A.Gaudin and R.Hagemann, J. Chim. Phys. 64, 917 (1967) ; 64, 1209 (1967)  
C.Melton, J. Chem. Phys. 37, 562 (1962)



**Fig. 29** Ionization cross sections of  $C_2H_2$  by electron impact as a function of electron energy

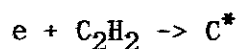
### Photon emission cross sections

#### Lyman lines and Balmer- $\beta$ line from hydrogen atoms



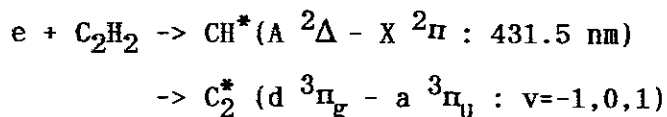
The most recent results for Lyman lines have been reported by Pang et al. over 20 - 400 eV. On the other hand, measurements of Balmer- $\beta$  line have been reported by Sushanin and Kishko over the energy range 10 - 150 eV. These results are shown in Fig. 30.

#### Line emission from carbon atoms



Carbon atom line at 165.7 nm has been studied by Pang et al. over 20 - 400 eV. Their emission cross sections are shown in Fig. 31. A slight structure near the threshold can be seen, similar to that in CH<sub>4</sub> (see Fig. 10 for CH<sub>4</sub>).

#### Molecular band emission from CH\* and C<sub>2</sub>\* radicals

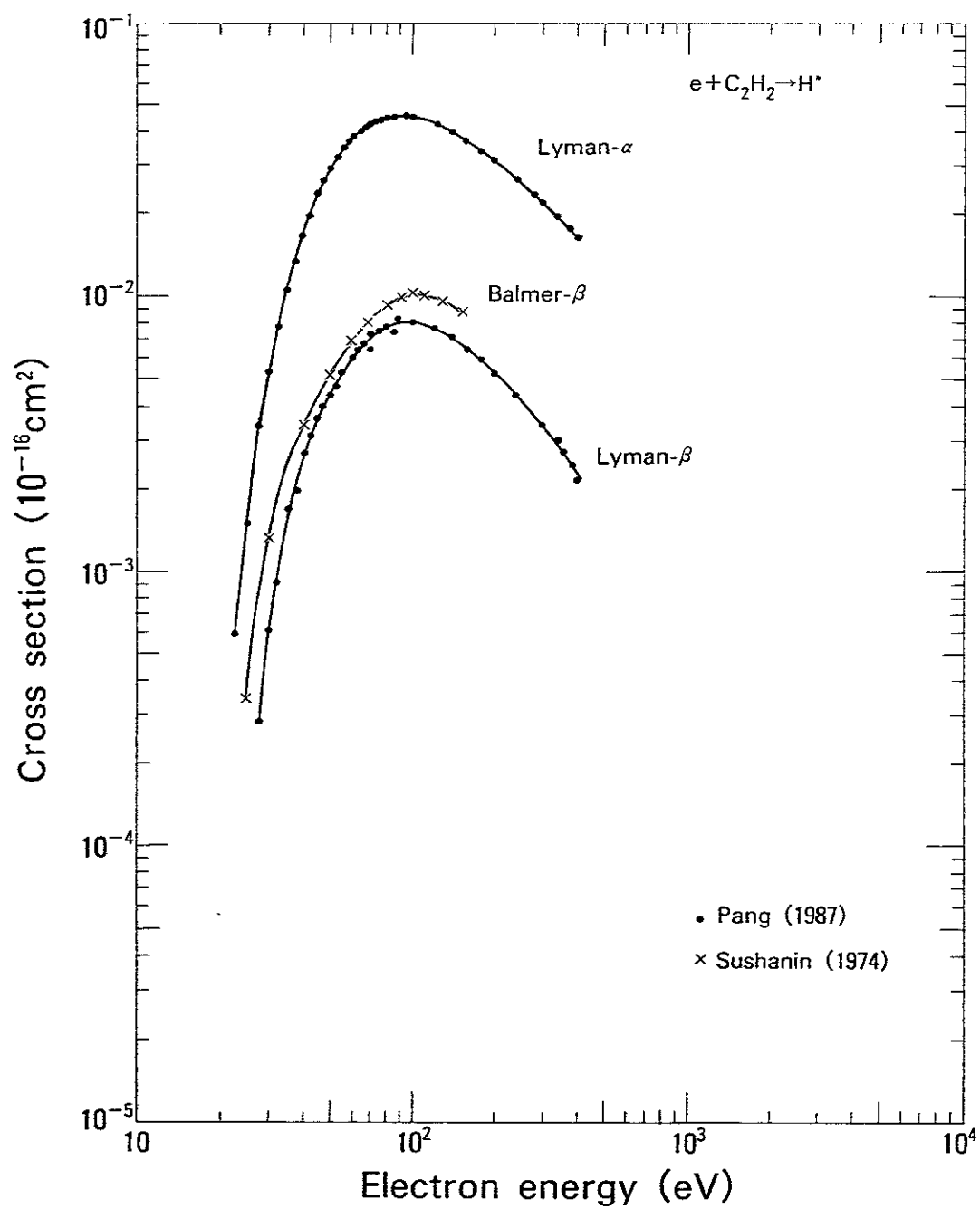


Only a single measurement has been reported by Sushanin and Kishko for the emission cross sections for transition A <sup>2</sup> $\Delta$  - X <sup>2</sup> $\Pi$  at 431.5 nm of CH\* radicals and the Swan bands (d <sup>3</sup> $\Pi_g$  - a <sup>3</sup> $\Pi_u$  transition) for v = -1, 0 and 1 of C<sub>2</sub>\* radicals over 10 - 150 eV, as shown also in Fig. 31.

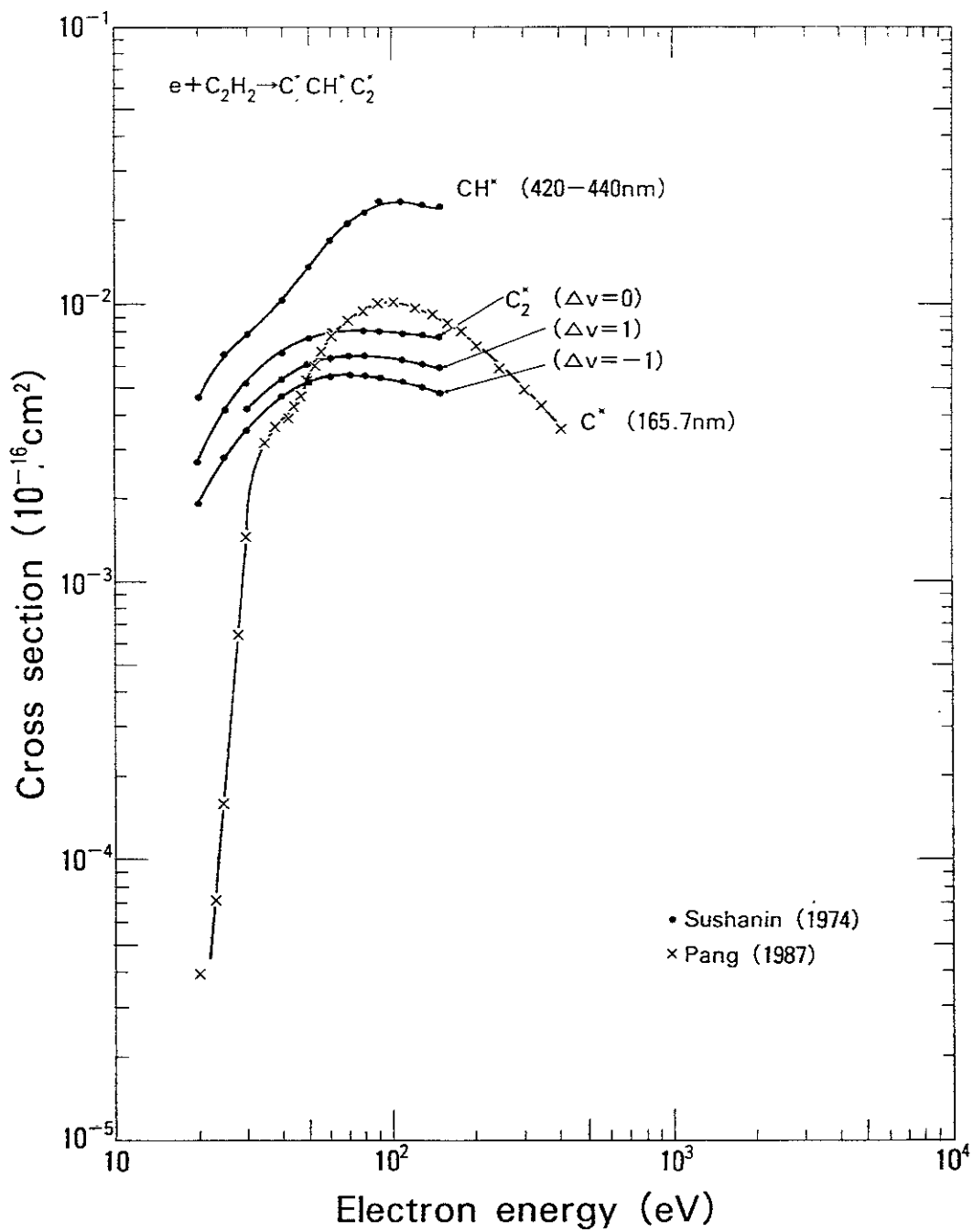
### References

K.D.Pang, J.M.Ajello, B.Franklin and D.E.Shemansky, J. Chem. Phys. 86, 2750 (1987). Some extra data tables at a single electron energy of 200 eV can be found in a separate document.

I.V.Sushanin and S.M.Kishko, Sov. Astron. 18, 265 (1974)



**Fig. 30** Emission cross sections of various lines of atomic hydrogens formed from  $C_2H_2$  by electron impact as a function of electron energy



**Fig.31** Emission cross sections of carbon atoms and molecular bands in  $e + C_2H_2$  collisions



### III-8 C<sub>3</sub>H<sub>8</sub>

#### Elastic and inelastic scattering

Total cross sections have recently been redetermined by Floeder et al. over the energy range 5 - 400 eV and found to be in agreement with the previous data by Brüche in the overlapped energy range, as shown in Fig. 32. Table 30 shows a list of experiments on total cross sections for C<sub>3</sub>H<sub>8</sub>.

#### References

E.Brüche, Ann. Phys. (Leipzig) 4, 387 (1930)

K.Floeder, D.Fromme, W.Raith, A.Schwab and G.Sinapius, J. Phys. B 18, 3347 (1985)

**Table 30** Experiments on total cross sections of electrons by C<sub>3</sub>H<sub>8</sub>

Author	(year)	Energy (eV)	Method	Comments
Brüche	(1930)	1-38	Ramsauer	A*)
Floeder	(1985)	5-400	Transmission	A

\*) A indicates absolute measurements.

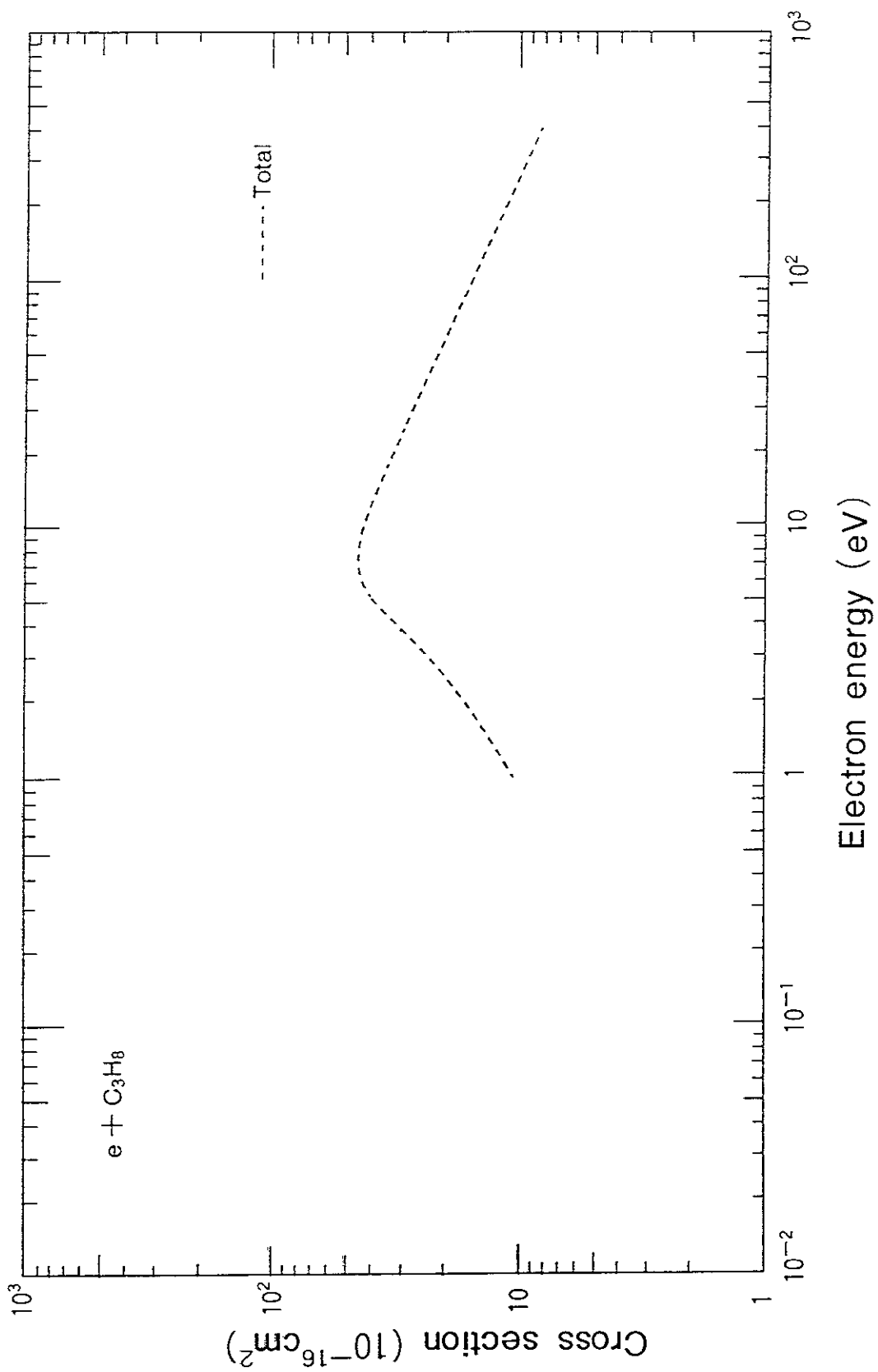


Fig. 32 Total cross sections of electrons for  $C_3H_8$

Cross sections for momentum transfer, estimated based upon swarm experiments, are found to be in significant disagreement with each other. Therefore, no data are given here. **Table 31** shows a list of experiments on momentum transfer cross section work.

#### References

T.L.Cottrell and I.C.Walker, Trans. Faraday Soc. 64, 2260 (1968)

C.W.Duncan and I.C.Walker, J. Chem. Soc. Faraday Trans. II 70, 577 (1974)

D.L.McCorkle, L.G.Christophorou, D.V.Maxey and J.G.Carter, J. Phys. B 11, 3067 (1978)

**Table 31** Experiments on momentum transfer in  $C_3H_8$

Author	(year)	Energy (eV)	Method	Comments
Cottrell	(1968)	0.05-3.0	Swarm	to theory
Duncan	(1974)	0.01-1.0	Swarm	to theory
McCorkle	(1978)	0.02-0.3	Swarm	to theory

Preliminary differential elastic scattering cross sections have been reported by Matsunaga et al. (1981) over 2 - 100 eV but the final results remain to be published. **Table 32** gives a list of elastic scattering experiments for C<sub>3</sub>H<sub>8</sub>.

Reference

D.Matsunaga, M.Kubo and H.Tanaka, XII ICPEAC (1981) p.358

**Table 32** Experiments on elastic scattering by C<sub>3</sub>H<sub>8</sub>

Author	(year)	Energy(eV)/Angle(°)	Method	Comments
Matsunaga	(1981)	3-20 (30-140°)	Beam	to He

Relative cross sections for electronic excitation were investigated only at 50 eV, as listed in **Table 33**.

Reference

E.N.Lassetre, A.Skerbele and M.A.Dillon, J. Chem. Phys. 49, 2382 (1968)

**Table 33** Experiments of electronic excitation of C<sub>3</sub>H<sub>8</sub> by electrons

Author	(year)	Energy (eV)	Method	Comments
Lassetre	(1968)	50 (0°)	Beam	R (ΔE=7-14 eV)

### Ionization cross sections

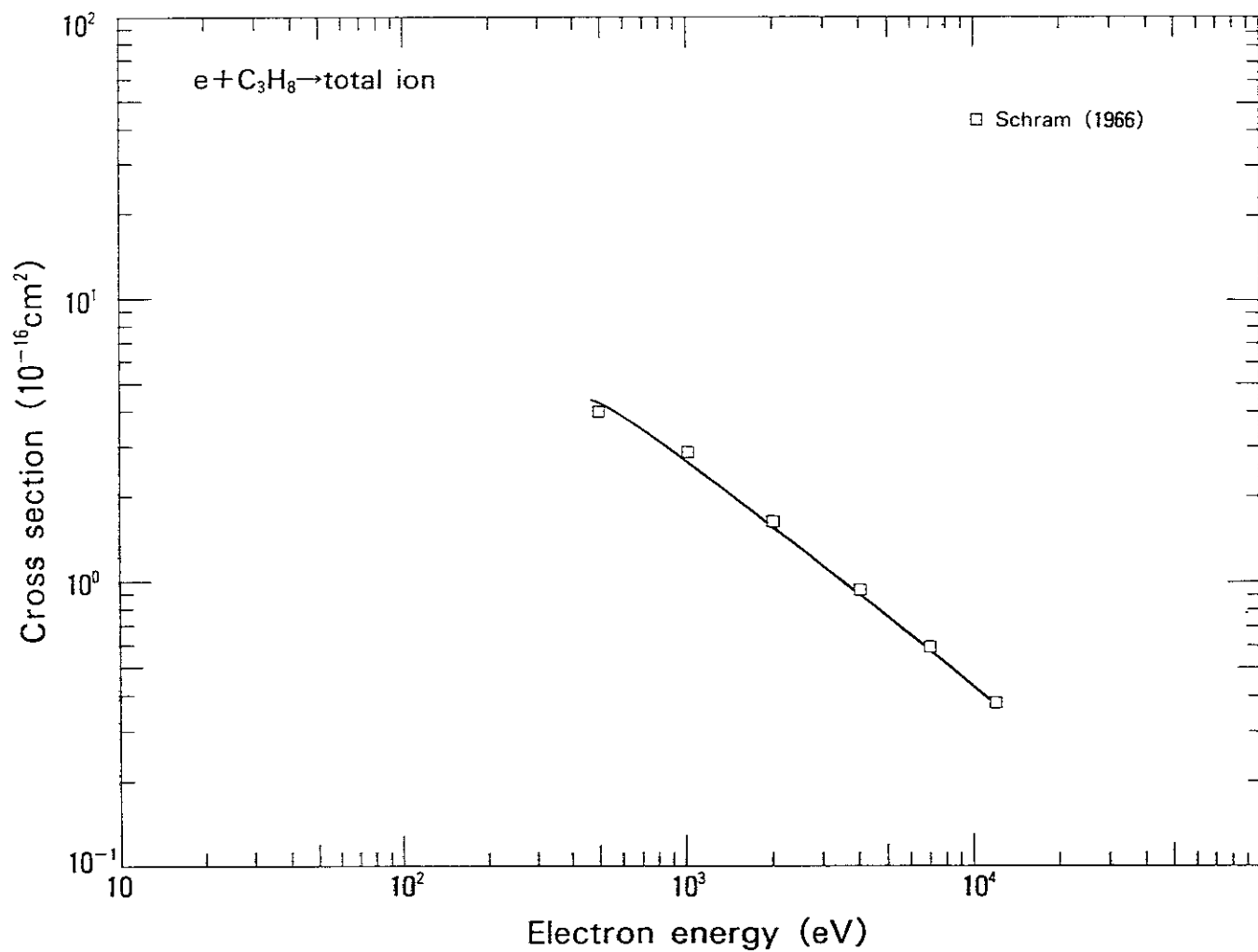
Total ionization cross sections have been determined over 600 - 3500 eV by Schram et al., as shown in **Fig. 33**. However, no partial cross sections have been reported yet. A single observation of neutral products has been reported by Flesch et al. at 20 eV electron impact and their results are shown in **Table 34**. It is interesting to note that the most intense product is C<sub>2</sub>H<sub>4</sub>, which is a form of the missing of CH<sub>4</sub> from the parent C<sub>3</sub>H<sub>8</sub>.

### References

- B.L.Schram, M.J.van der Wiel, F.J.de Heer and H.R.Moustafa, J. Chem. Phys. 44, 49 (1966)
- G.D.Flesch, R.E.Utecht and H.J.Svec, Int. J. Mass Spectr. Ion Proc. 58, 151 (1984)

**Table 34** Neutral products from C<sub>3</sub>H<sub>8</sub> by 20 eV electrons  
(Flesch et al.)

mass	2	15	26	27	28	29	30	41	42	43	44
fraction(%)	1	4	1	1	39	17	1	1	3	13	20



**Fig. 33** Total ionization cross sections of  $C_3H_8$  by electron impact as a function of electron energy

### III-9 C<sub>3</sub>H<sub>6</sub>

#### Elastic and inelastic scattering

Total cross sections for cyclopropane and propene have been determined only by Floeder et al. (5 - 400 eV) and practically no difference between two isomers is observed. Data shown in **Fig. 34** correspond to cyclopropane. **Table 35** shows a list of experimental work on total cross section measurements.

#### References

C.R.Bowman and W.D.Miller, J. Chem. Phys. 42, 681 (1965)

K.Floeder, D.Fromme, W.Raith, A.Schwab and G.Sinapius, J. Phys. B 18, 3347.  
(1985)

**Table 35** Experiments on total cross sections of electrons by C<sub>3</sub>H<sub>6</sub>

Author	(year)	Energy (eV)	Method	Comments
Bowman	(1965)	1-10	Transmission	R (only for propene)
Floeder	(1985)	5-400	Transmission	A (for both)

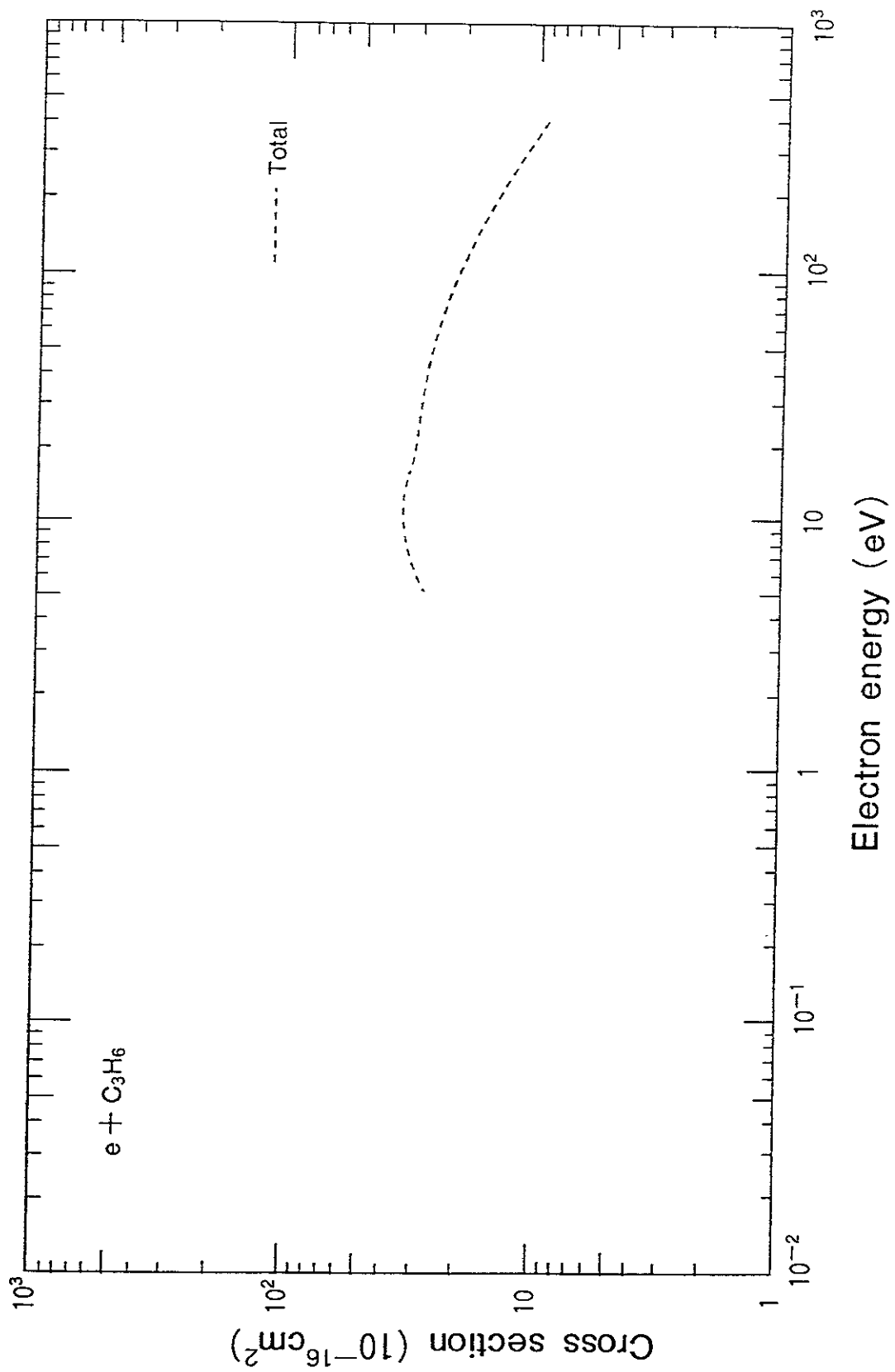


Fig. 34 Total cross sections of electrons for  $C_3H_6$



Momentum transfer cross sections have been determined below 1 eV for both propene and cyclopropane with swarm technique and the discrepancies are prominent at lower energies. The reported behavior seems to be quite different between two isomers. It is hard to evaluate these data at present. **Table 36** shows a list of experimental work on momentum transfer measurements for C<sub>3</sub>H<sub>6</sub>.

#### References

C.R.Bowman and D.E.Gordon, J. Chem. Phys. 46, 1878 (1967)

C.W.Duncan and I.C.Walker, J. Chem. Soc. Faraday Trans. II 70, 577 (1974)

**Table 36** Experiments on momentum transfer of electrons for C<sub>3</sub>H<sub>6</sub>

Author	(year)	Energy (eV)	Method	Comments
Bowman	(1967)	0.01-0.063	Swarm	to theory (only for propene)
Duncan	(1974)	0.01-1	Swarm	to theory (for both)

No vibrational excitation cross sections have been reported yet.

Some investigations of electronic excitation for propene have been reported by Johnson et al. over 20 - 150 eV, as listed in **Table 37** but no cross section is available.

#### References

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K.E.Johnson, D.B.Johnson and S.Lipsky, J. Chem. Phys. 70, 3844 (1979)

**Table 37** Experiments on vibrational excitation of C<sub>3</sub>H<sub>6</sub> by electrons

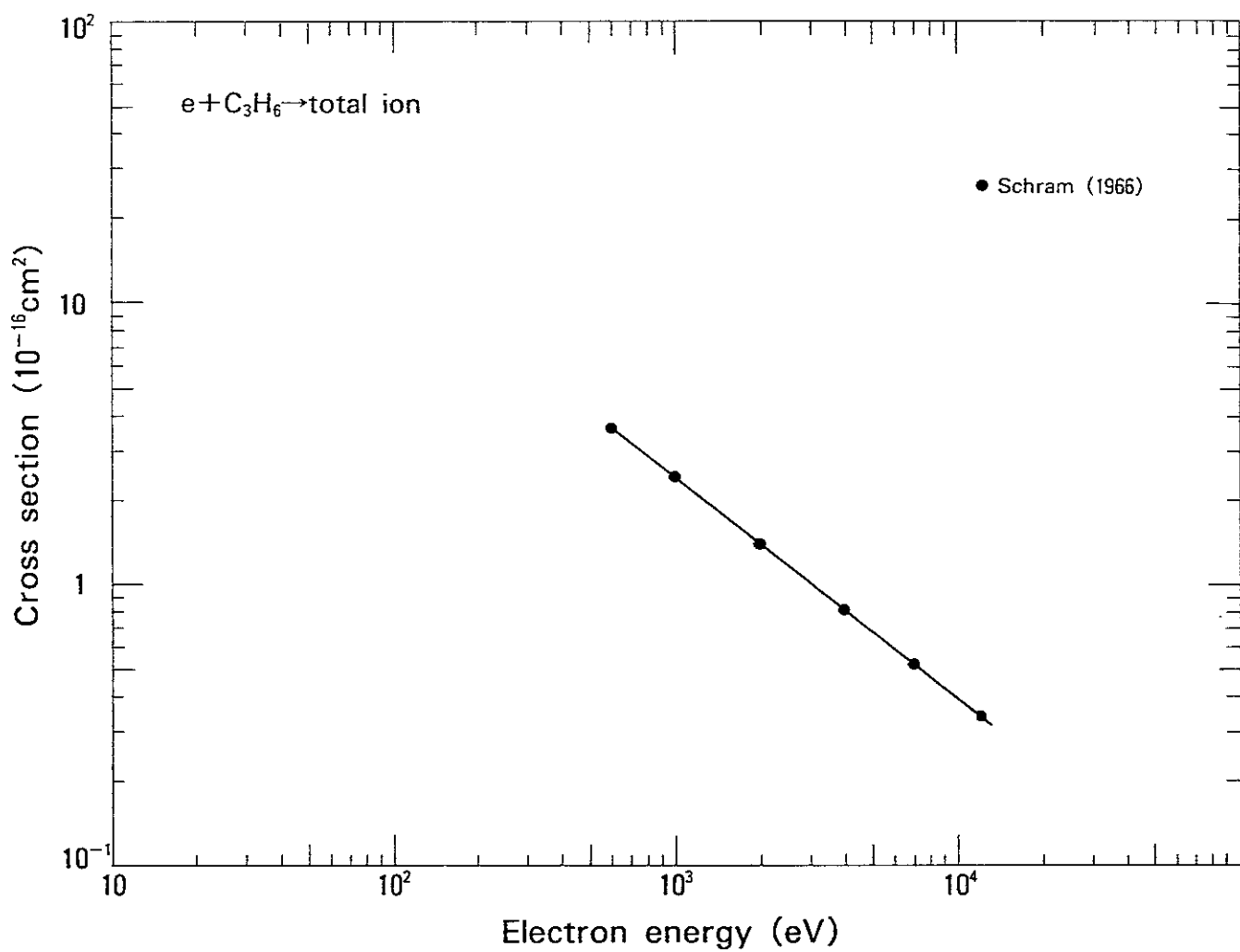
Author	(year)	Energy(eV)/Angle(°)	Method	Comments
Johnson	(1979)	20-150 (0-90°)	Beam	R ( $\Delta E=2.5-15$ eV, only for propene)

### Ionization cross sections

Total ionization cross sections have been determined for cyclopropane and propene ( $C_3H_6$ ) over 600 -12000 eV by Schram et al. and are shown in Fig. 35. Those for cyclopropane are about 10 % larger than those for propene. However, no partial cross section has been reported up to now.

### Reference

B.L.Schram, M.J.van der Wiel, F.J.de Heer and H.R.Moustafa, J. Chem. Phys. 44, 49 (1966)



**Fig. 35** Total ionization cross sections of  $C_3H_6$  by electron impact as a function of electron energy

#### IV Empirical estimation of the ionization cross sections of hydro-carbon molecules

A large body of data for the ionization of atoms as well as atomic ions including multiply charged ions by electron impact have been measured and compiled. Some convenient empirical formulas have been proposed and are found to be quite useful to estimate the ionization cross sections as long as the direct ionization processes are dominant. Similarly the ionization cross sections for molecules and molecular ions should also be able to be estimated based upon the empirical formulas similar to those used for atomic species. Most recently, Deutsch and Schmidt have compared several empirical formulas with experimental data presently available and found that, among many empirical, semi-empirical, classical and semi-classical formulas for ionization, the following (empirical) formulas by Gryzinski and Lotz can reproduce best the observed total single ionization cross sections for some hydro-carbon molecules, as seen in Fig. 36.

Gryzinski formula :

$$\sigma = \sum \sigma_i$$

$$\sigma_i = 6.51 \times 10^{-14} \left( \frac{n_i}{E_i^2 U} \right) \left( \frac{U-1}{U+1} \right)^{3/2} \left\{ 1 + \frac{2}{3} \left( 1 - \frac{U}{2} \right) \ln [2.7 + (U-1)^{1/2}] \right\} \quad (cm^2)$$

where  $\sigma$  : total ionization cross section

$\sigma_i$  : partial ionization cross sections for the i-th shell

$n_i$  : number of electrons in the i-th shell

$E_i$  : binding energy of electrons in the i-th shell (eV)

$U = E/E_i$

$E$  : electron impact energy (eV)

To apply this formula, we need to have information on the binding energy of electrons,  $E_i$ , and the number of electrons,  $n_i$ , in the  $i$ -th (sub-)shell. If all these data are not known, we can apply the following Lotz formula with three adjustable parameters, (a, b, c), to reproduce the observed data best.

Lotz formula :

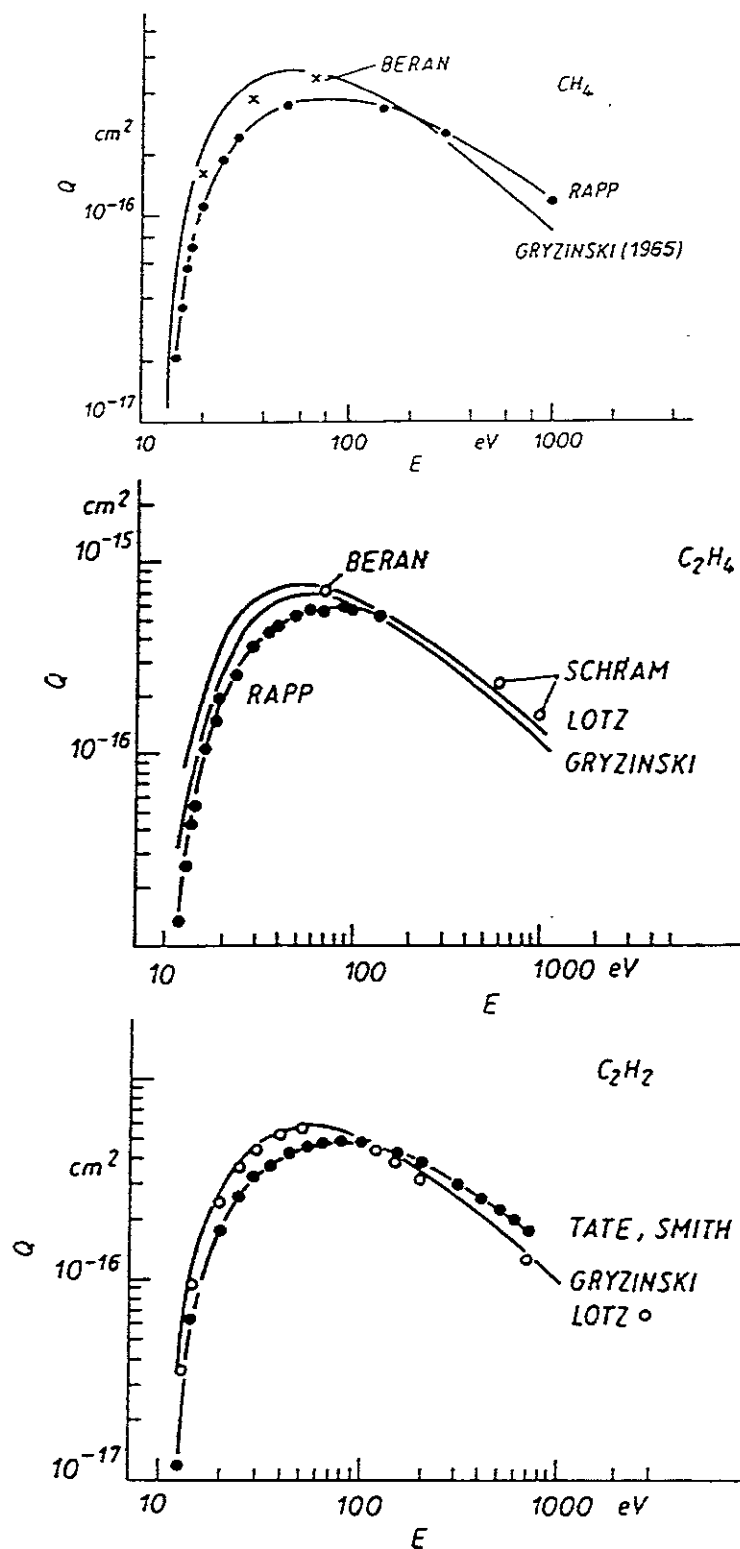
$$\sigma_i = a \left( \frac{n_i}{E_i^2 U} \right) \ln U \{1 - b \exp[-c(U-1)]\}$$

a,b,c : adjustable parameters.

On the other hand, as partial (dissociative) ionization cross sections of molecules have the complicated origins, compared with those of atomic species, no simple empirical or scaling formula has been found to be successful up to now, though some proposals have been made by Tan and Wu and more recently by Khare et al.

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**Fig. 36** Comparison among analytic formulas and experimental data for electron impact ionization of  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_2$  (Deutsch and Schmidt)

## V Concluding remarks

In the present work we have summarized the present situation on cross section data (electron scattering, momentum transfer, vibrational/rotational/electronic excitation, dissociation, ionization and light emission) of hydrocarbon molecules and their ions in colliding with electrons.

A considerable amount of collision data are available only for CH<sub>4</sub>, as seen above. For other hydrocarbons, among various electron scattering and excitation data, only total cross sections seem to be reasonably reliable above 1 eV.

Total ionization cross sections are also in good shape for most of hydrocarbons but partial (dissociative) ionization cross sections are still limited in quantity and, furthermore, scattered in quality.

One of the most important and urgently necessary data both in basic collision studies and applications is concerned with information on neutral products from hydrocarbons : production rates, energy distributions and angular distributions and possibly internal (energy) states.

Indeed, it is well known that collision data of molecules and molecular ions are strongly dependent upon their internal states (for example, as described in Table 1 for dissociative ionization of CH<sub>4</sub>, see p. 8) and cross section data may differ orders of magnitude depending upon whether molecule species are in the ground state or in the excited states. Such situations should be the same for most of molecule collision processes.

Therefore, it becomes quite important to measure collision cross sections after specifying the internal states of target molecules. In various fields of applications of molecule collisions, a large fraction of molecules or molecular ions produced in collisions with plasma particles may be more likely in the excited states than in the ground state. These so-called radicals could play an important role in many cases. However, as seen in sections III-2,3,4, collision data involving radicals such as CH<sub>m</sub> (m = 3 - 1) are very scarce even though



their internal states are not specified or data do not exist at all for radicals with the specified internal states.

Thus, when some data are planned to be used, it is prerequisite to know the experimental conditions where and how they had been obtained. This is particularly important when these data are used in plasma modelling. For example, collision products from molecules or molecular ions and possibly their energy distributions might be different according to their internal states and thus the resulting densities and density distributions of species might also be different, depending upon their internal states.

Another important factor, which is not treated in the present report, is the effects of solid surfaces on collisions of molecules. Collisions of molecules with solid surfaces often result in not only inelastic scattering but also dissociation or breaking-up in products which might be significantly different from those in electron collisions and also be dependent upon their internal states but those with the specified internal states have not been investigated to any degree up to now.

Of course, collisions among atoms, molecules and their ions are another key factor in order to understand the overall features in plasma and other application systems quantitatively. These could be one of our next topics to investigate.

Finally it should be mentioned that, as described in Introduction, the production mechanisms of hydrocarbon molecules from graphite in intense hydrogen plasma environments have been understood only qualitatively and the quantitative understanding of hydrocarbons which strongly influence the main plasma characteristics is still far from complete.

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