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United Nations Educational, Scientific and Cultural Organization

IAEA International Atomic Energy Agency

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Molecular Processes in Plasmas continued - Outline

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Austria

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Outline

Part I: Fundamentals
A. Ionization processes and Ions produced
B. Ionization mechanisms

Part II: Kinetics and energetics for the production of cations

Part III: Electron attachment

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Part II: Kinetics and energetics for the production of cations

$$ABC + e \rightarrow ions$$

$$ABC + e \rightarrow ABC^{+}$$

$$ABC + e \rightarrow A^{+} + BC + KER$$

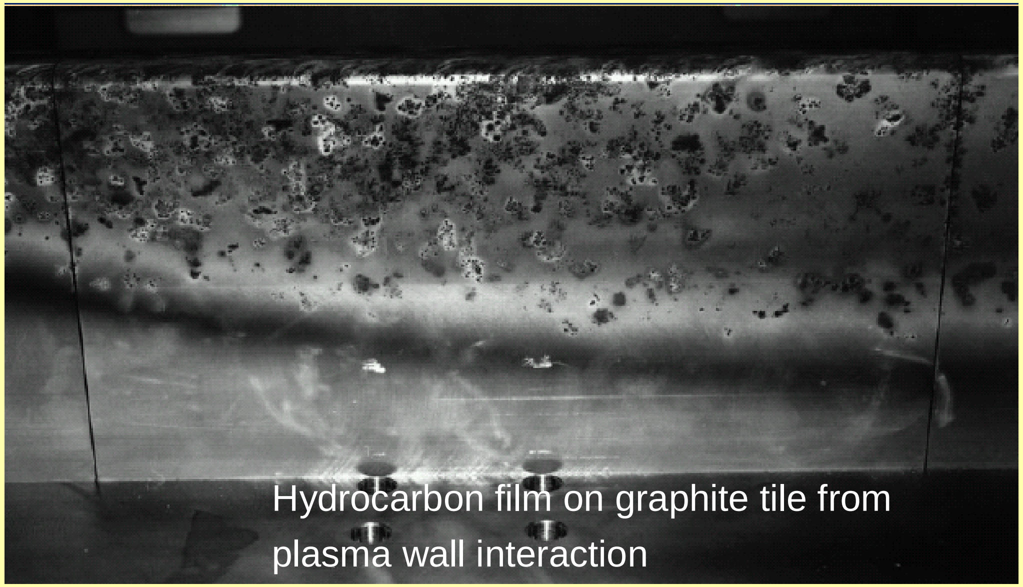
$$ABC^{+} + e \rightarrow ions$$

Properties to be determined:
$\sigma = \sigma(E)$, KER and AE (ions)

1. Kinetics: $\sigma = \sigma(E)$
2. Differential kinetics: KER
3. Energetics: AE

Motivation for hydrocarbons

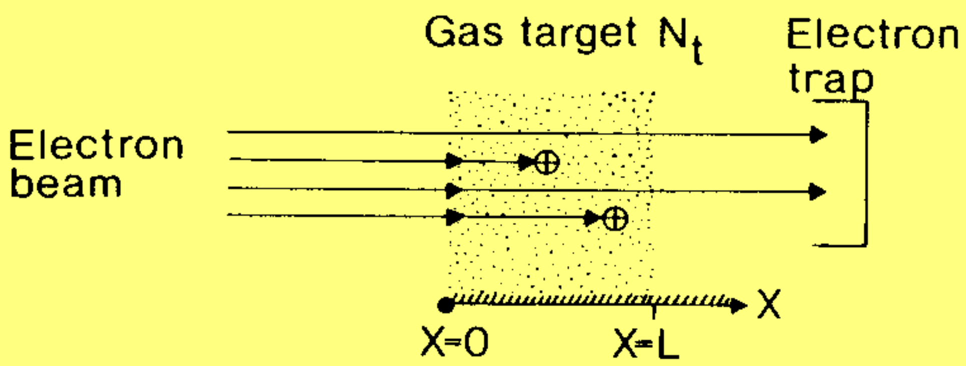
- Prototype of polyatomic molecules
- Formed in the edge region of fusion plasmas (wall plasma interaction)
- Cometary atmospheres, interstellar medium (synthesis of biomolecules?)
- Concentration of C_2H_2 in the atmosphere of earth is expected to nearly double by the year 2030 due to the increased use of automobiles
- Radiation chemistry



Hydrocarbon film on graphite tile from plasma wall interaction

Electron impact ionization

1. Principle of experimental set-up



$$dN \sim N_t N(x) dx$$

$$N(x) = N(0) \exp(-N_t x \sigma)$$

2. Principle of analysis

Using Beer's exponential absorption law and assuming single collision conditions: $N_t L\sigma_t \ll 1$

$$i_t = i_e N_t L \sigma_t$$

$$i_{ms} = i_e N_t L z \sigma_p$$

Electron impact ionization

Consider, as shown in Fig. 21, a parallel, homogeneous, and monoenergetic beam of electrons crossing a semiinfinite medium containing N_t target particles per cubic centimeter at rest. If $n(0)_e$ represents the initial intensity of the incident electrons per square centimeter per second, the density of the electron beam at depth x is given by the exponential absorption law

$$n(x)_e = n(0)_e \exp(-N_t q x). \quad (18)$$

If $N_t qx \ll 1$ (single-collision condition), the number of ions generated per second along the collision interaction path $x = L$ (over which the ions are collected and analyzed) is

$$n(L)_i = n(0)_e N_t q_c L, \quad (19)$$

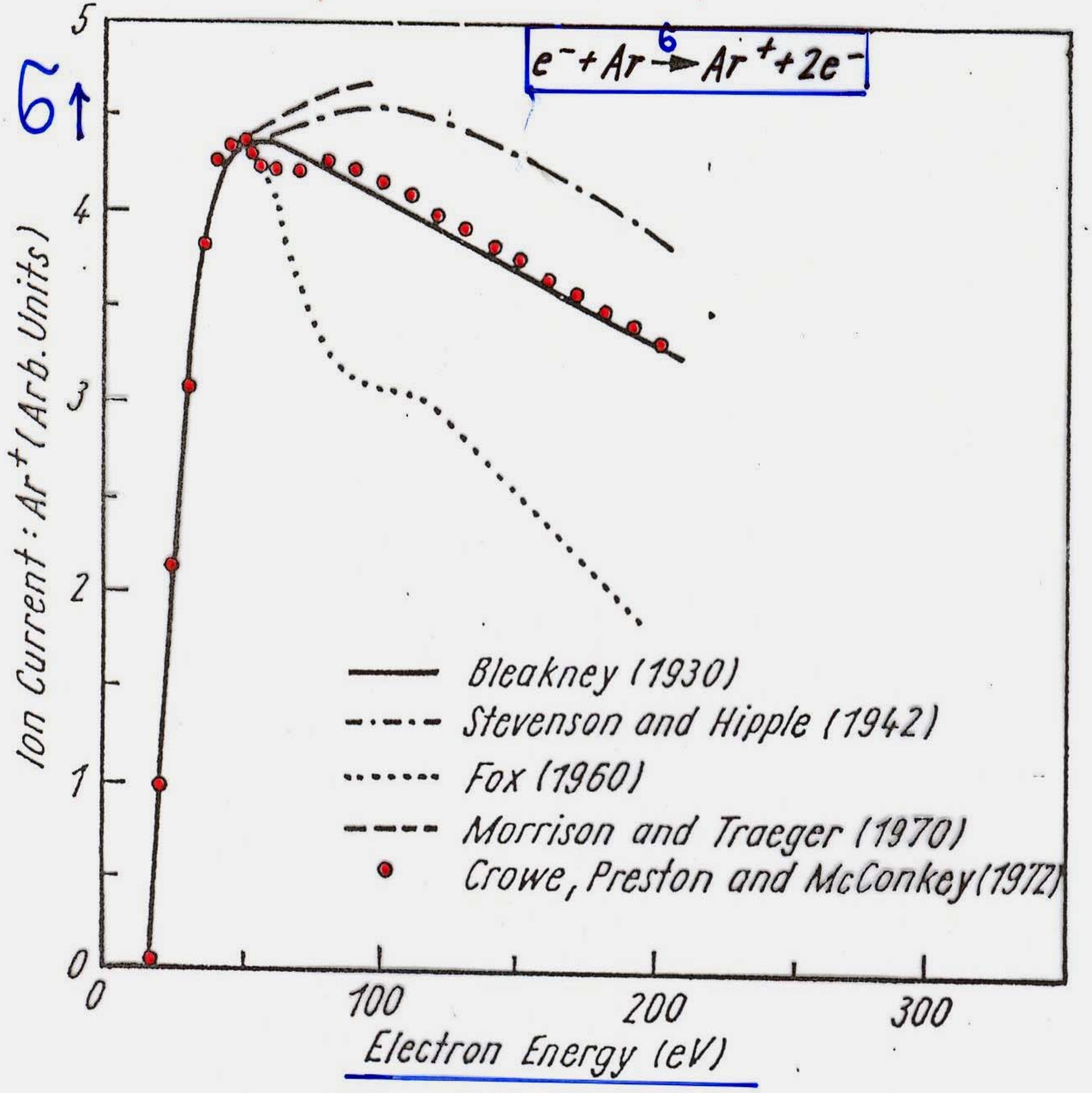
where q_c is the *counting ionization cross section* in square centimeters. The total positive-ion current i_t produced in this interaction volume is given by

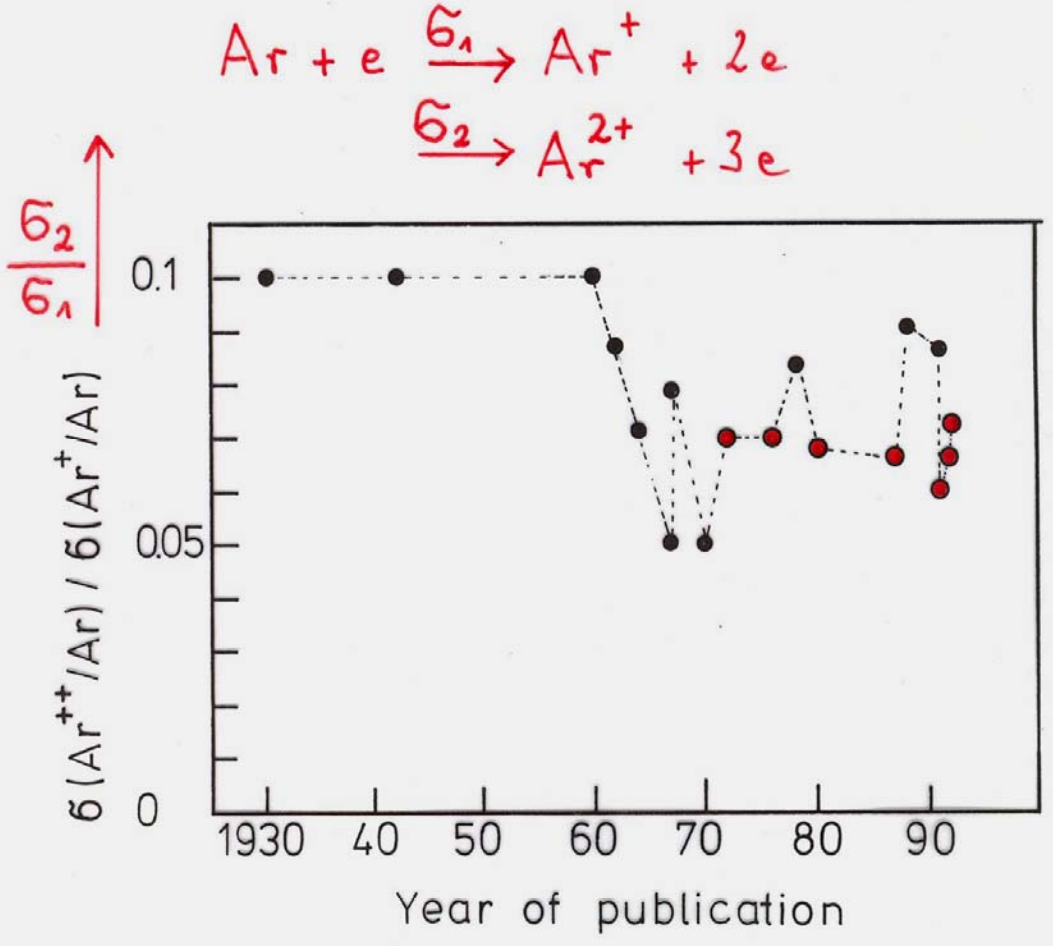
$$i_t = n(0)_e e N_t q_t L, \quad (20)$$

where q_t is the *total ionization cross section*. If the produced ions are analyzed with respect to their mass m and charge ze, the respective individual ion currents are given by

$$i_{\mathrm{ms}} = n(0)_e e N_t q_{zi} L, \quad (21)$$

State of the art as of 1980!

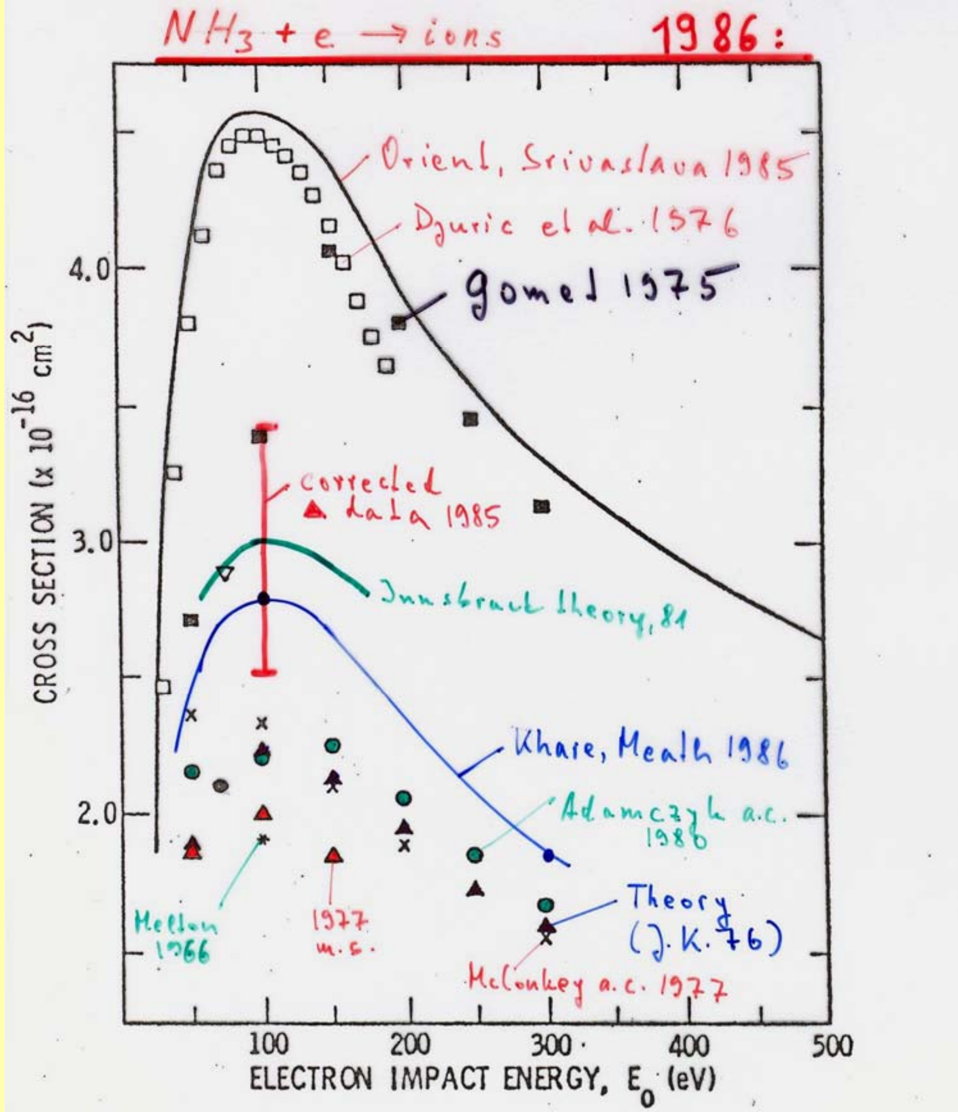




Theoretical results: 1972 0.15

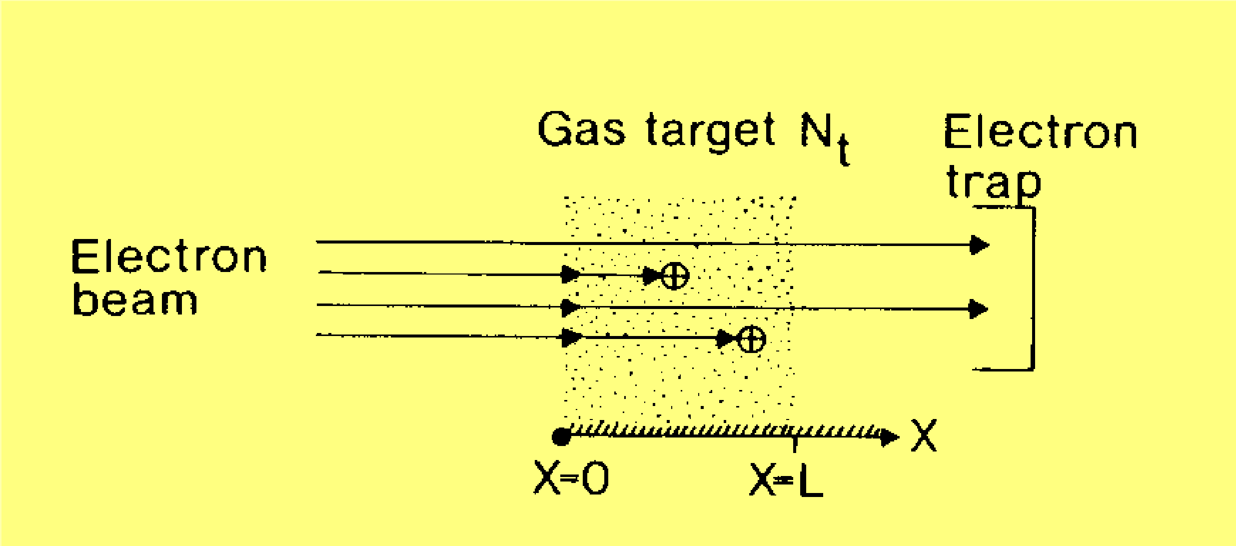
1978 0.18

0.20



Total ionization cross sections for NH_3. ● present measurements; □ Djuric-Preger et al.[3]; ▲ Märk et al.[4]; x Crowe and McConkey[5]; ▲ Jain and Khare[6]; ● Bederski et al.[7]; ● DeMaria et al.[8]; * Melton[9]; and ▽ Lampe et al.[10]; ▩ Gomet[12]; ——— Orient, Srivastava

Necessary conditions in order to obtain accurate ionization cross sections from: $i_{ion} = i_e N_t L \sigma$



i_{ion} : Collection of known fraction of ions

i_e : Total collection of electron current

N_t : Accurate number density determination

L : Path length known for electron orbits

Electron impact ionization. Determination of cross sections

1975 -1985 :

Some experimental progress

<u>Before 1985:</u> **Cross Sections for 31 Molecules**

1985 - 2005 :

Improved calibration techniques

pressure measurements

Improved experimental techniques

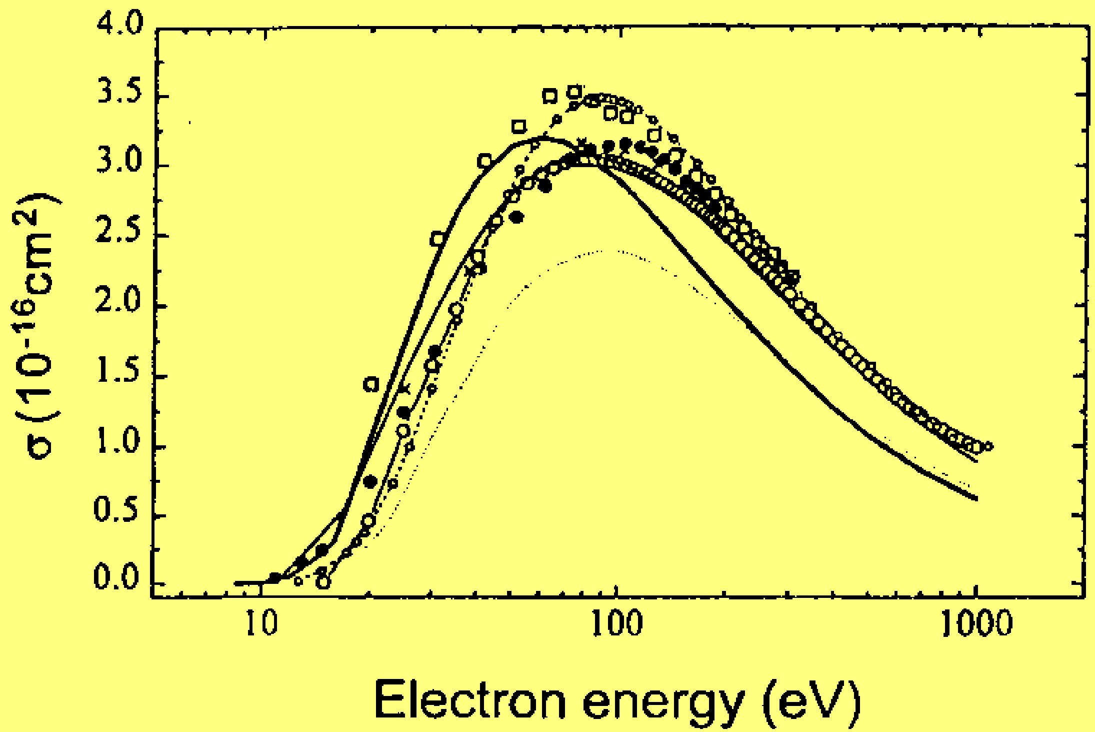
controlled extraction and transmission techniques

Improved theoretical methods

DM, BEB, BED, JK

Total ionization cross section for NH_3

Deutsch et al., Int.J.Mass Spectrom.,197 (2000)37-69



Open squares: Crowe et al. 1977

Filled circles:Djuric et al. 1985

Open circles Rao et al. 1992

Crosses: Bederski et al. 1980

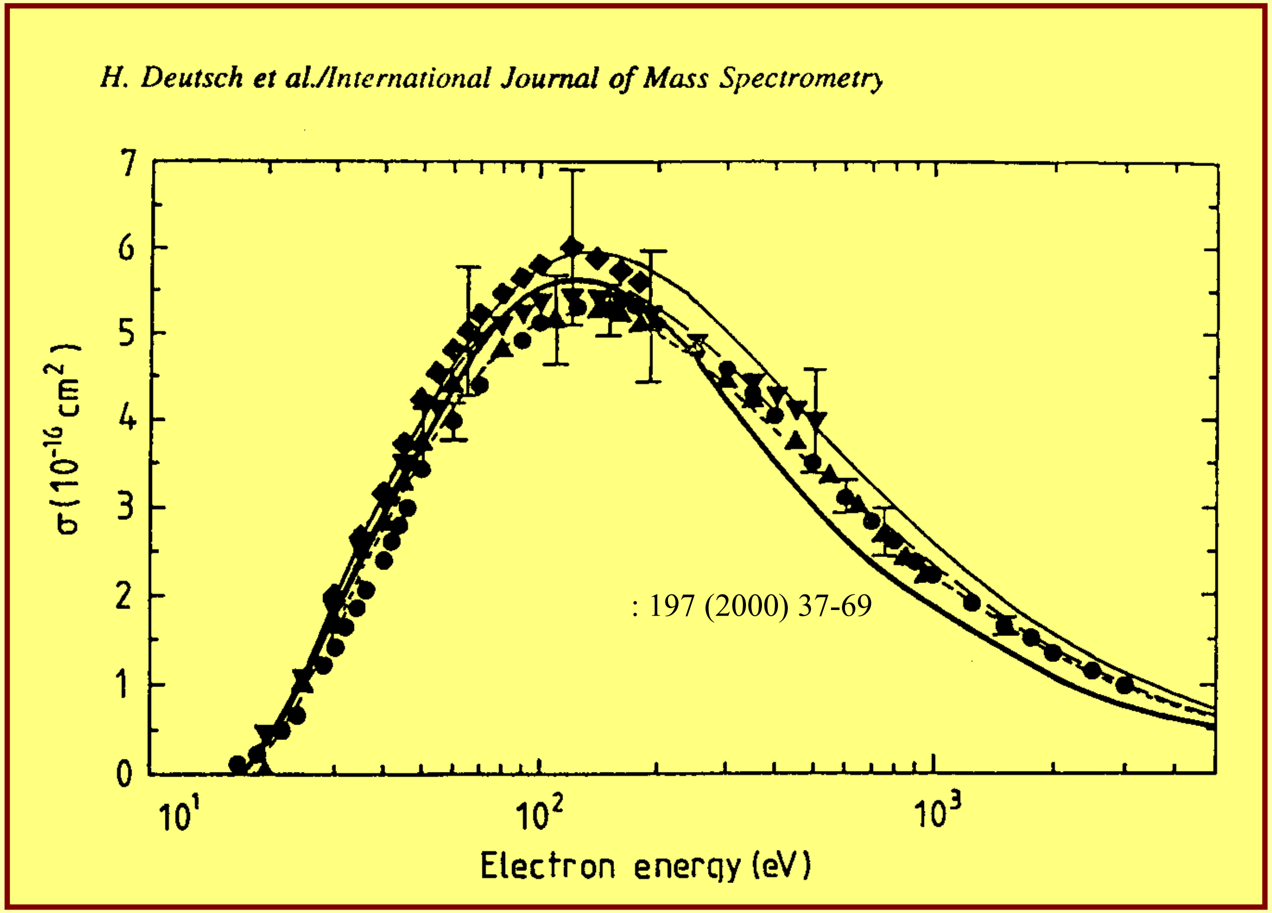
Thick line: Deutsch et al. 1999 (DM)

Thin line: Hwang et al. 1996 (BEB)

Dotted line: Jain et al. 1976

Dashed line: Saksena et al. 1997

Total electron ionization cross section: $CF_4 + e \rightarrow ions$



Full line: DM calculation 2000

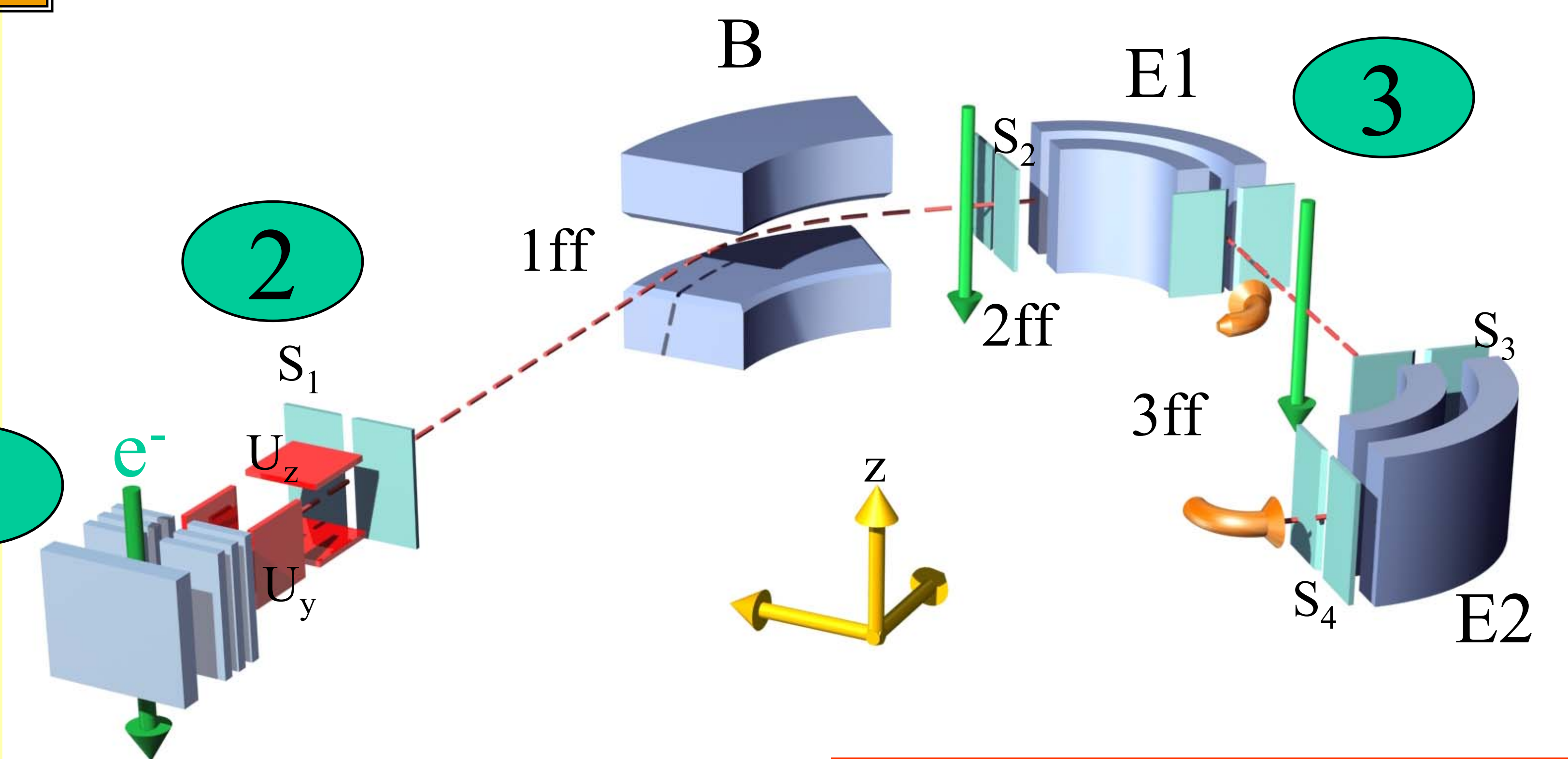
Interrupted lines: BEB calculations 1999

Filled circles: Nishimura et al.1999; filled diamonds: Poll et al.1992; filled triangles: Rao et al.1997; filled inverted triangles: Bruce et al.1993; filled square: Beran et al.1969

Partial ionization cross sections

Ionization cross sections from:

$$i_{ms} = i_e N_t L \sigma_{partial}$$

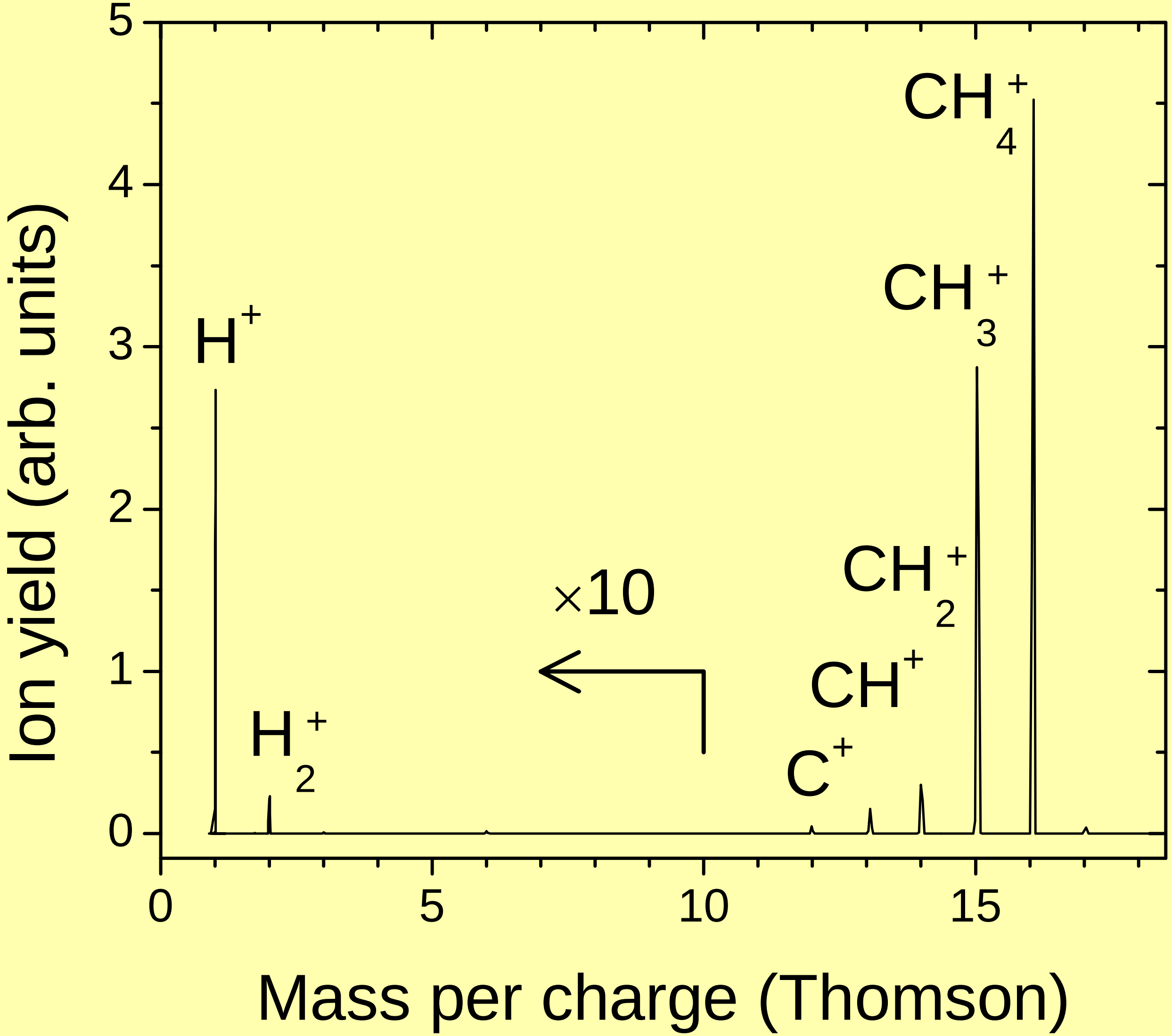


AB + e → AB^+
→ A + B^+ + KER
→ A^+ + B + KER

AB^+ + e → $(AB^{++})^*$
→ A^+ + B^+ + KER
→ A^+ + B + KER

Electron ionization of molecular ions:
$CH_4 + e \rightarrow ions$

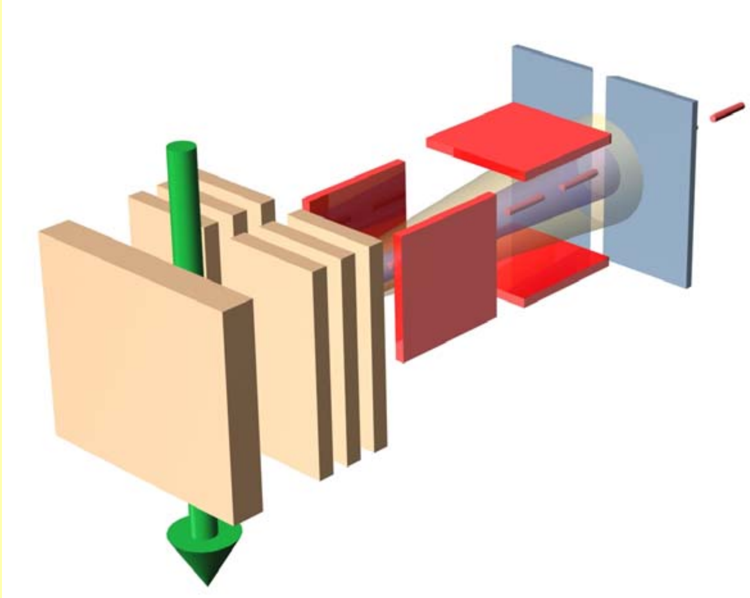
Mass spectrum

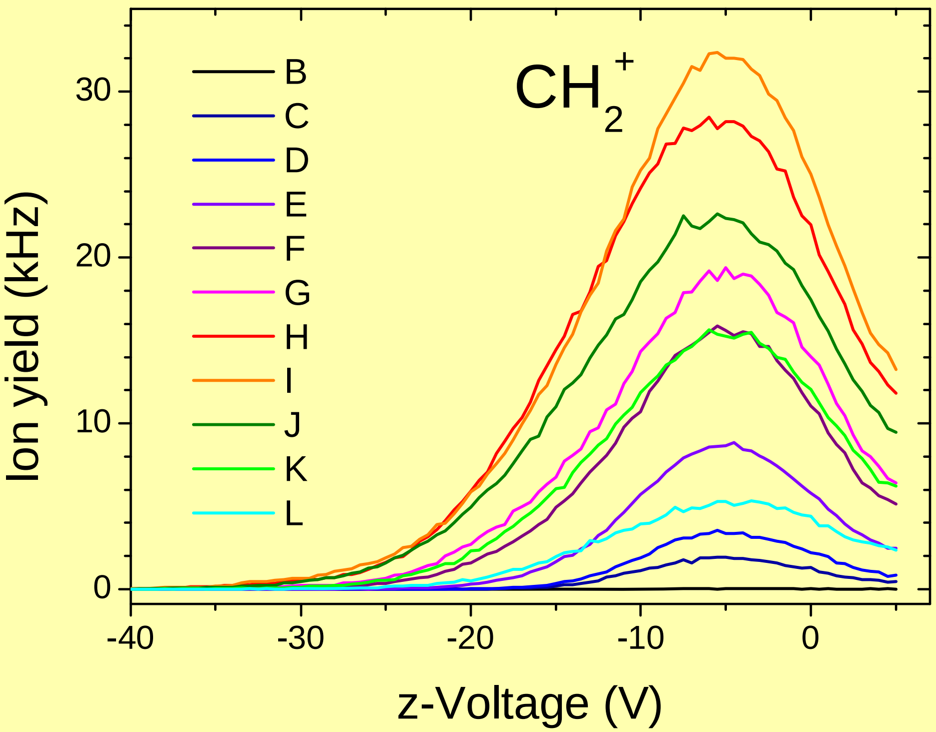


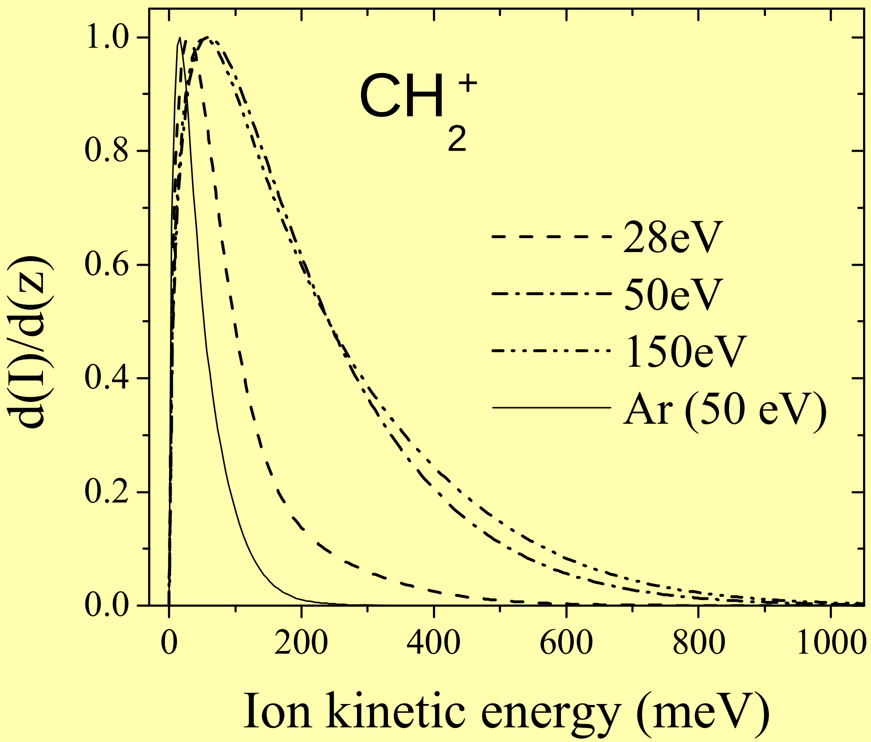
100 eV
10 μA
500K
$6x10^{-5}$ Pa

Dissociative ionization of molecules:
$CH_4 + e \rightarrow CH_2^+$

z- deflection curves and KERD

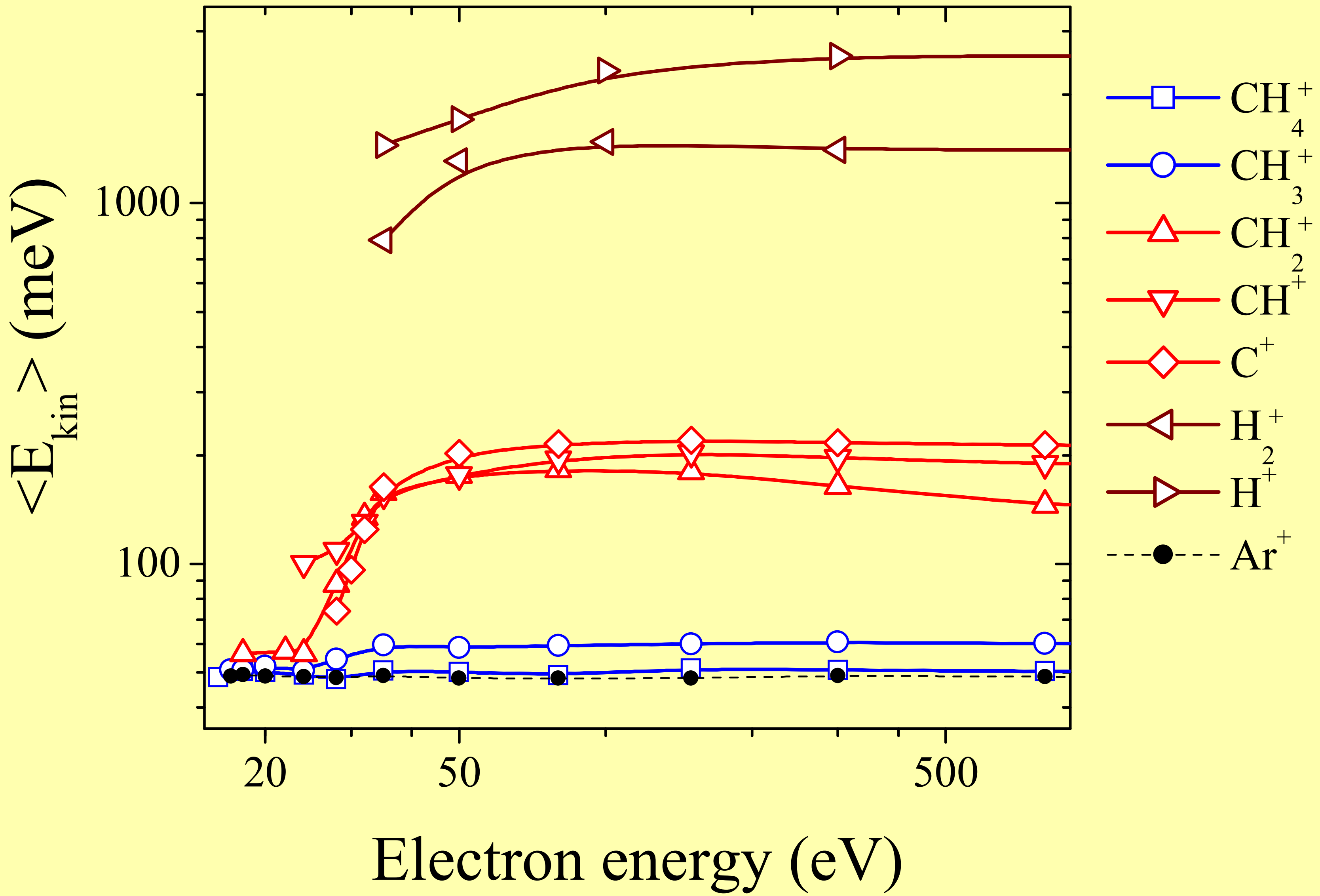






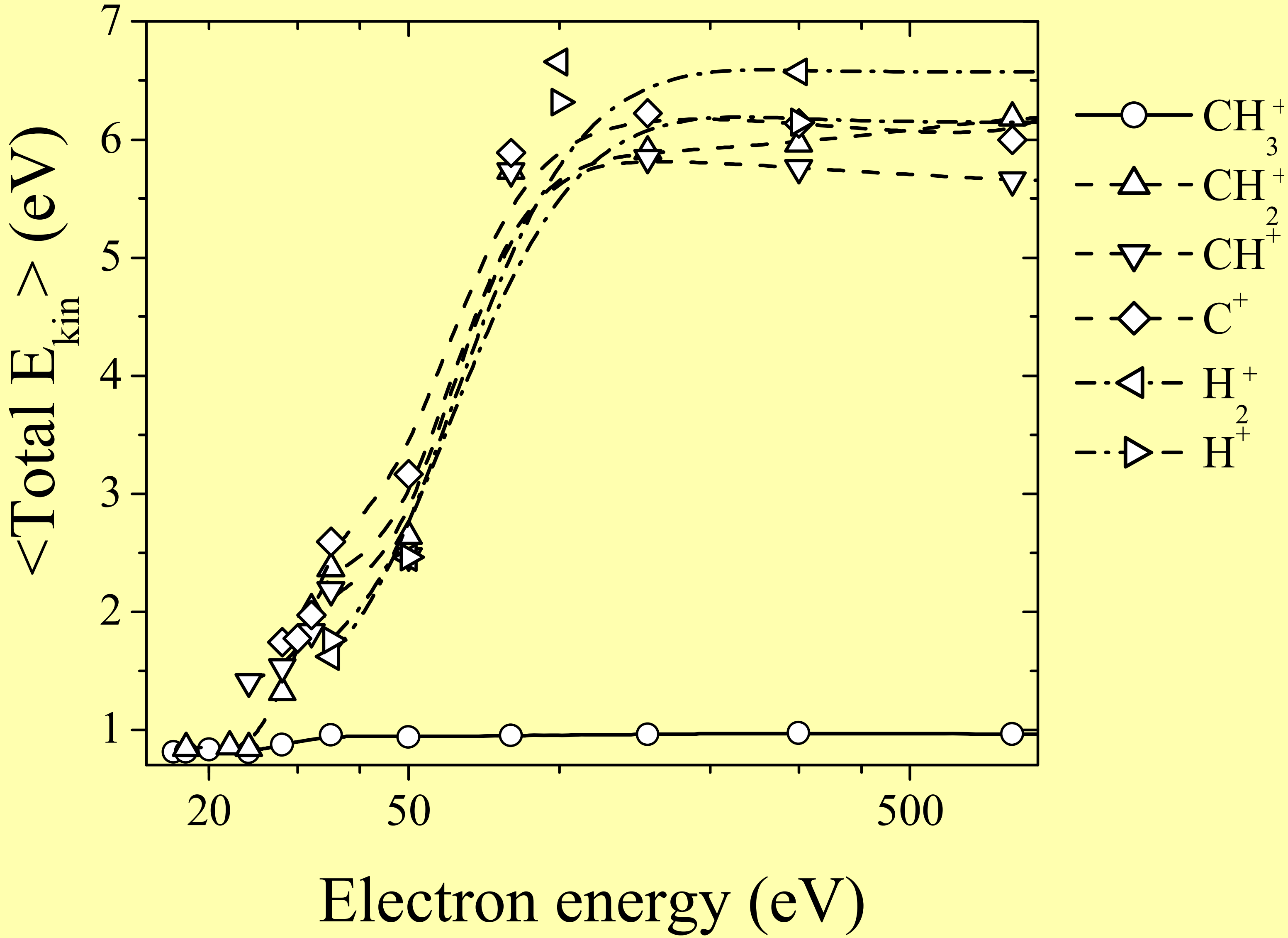
Electron ionization of molecular ions:
$CH_4 + e \rightarrow$ ions

Average ion kinetic energy

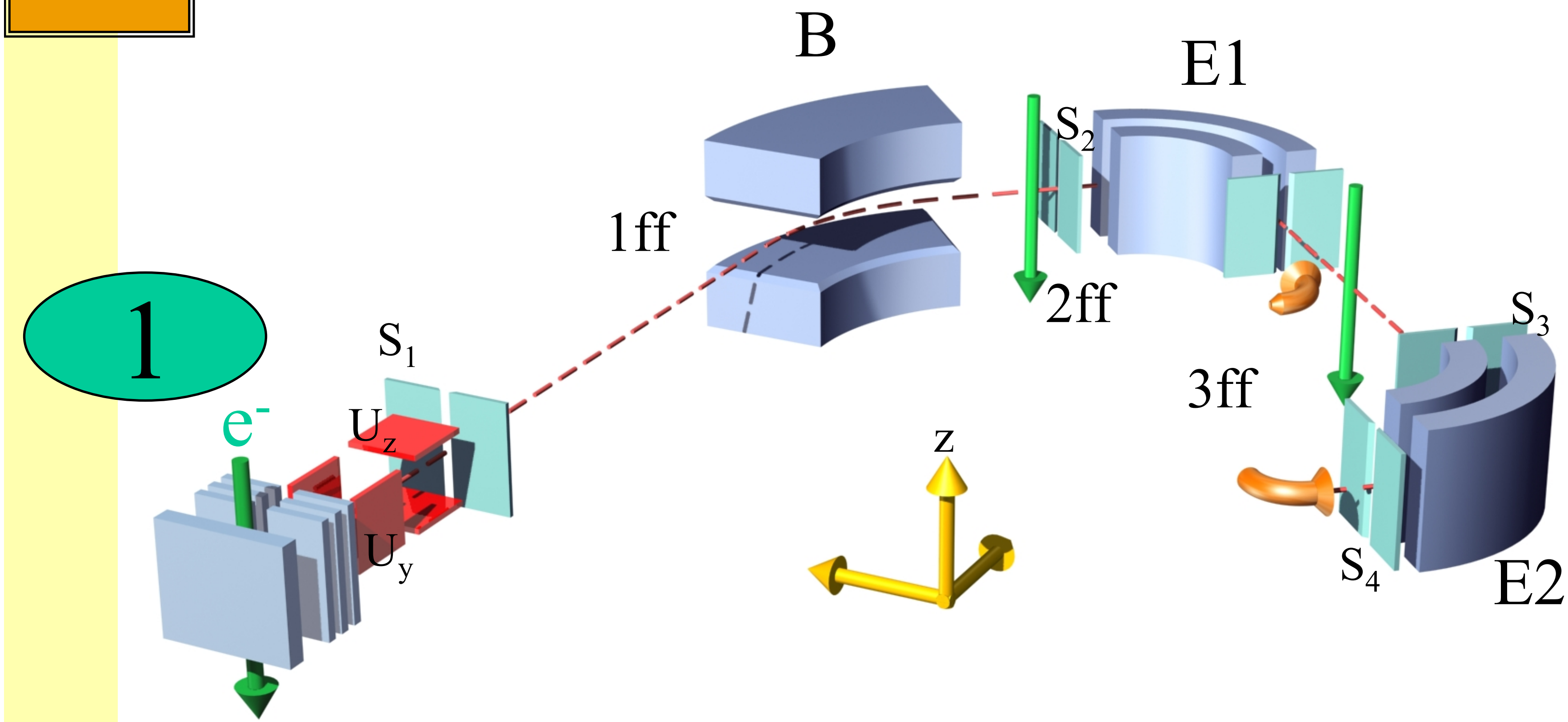


Electron ionization of molecular ions:
$CH_4 + e \rightarrow$ ions

Total average kinetic energy released



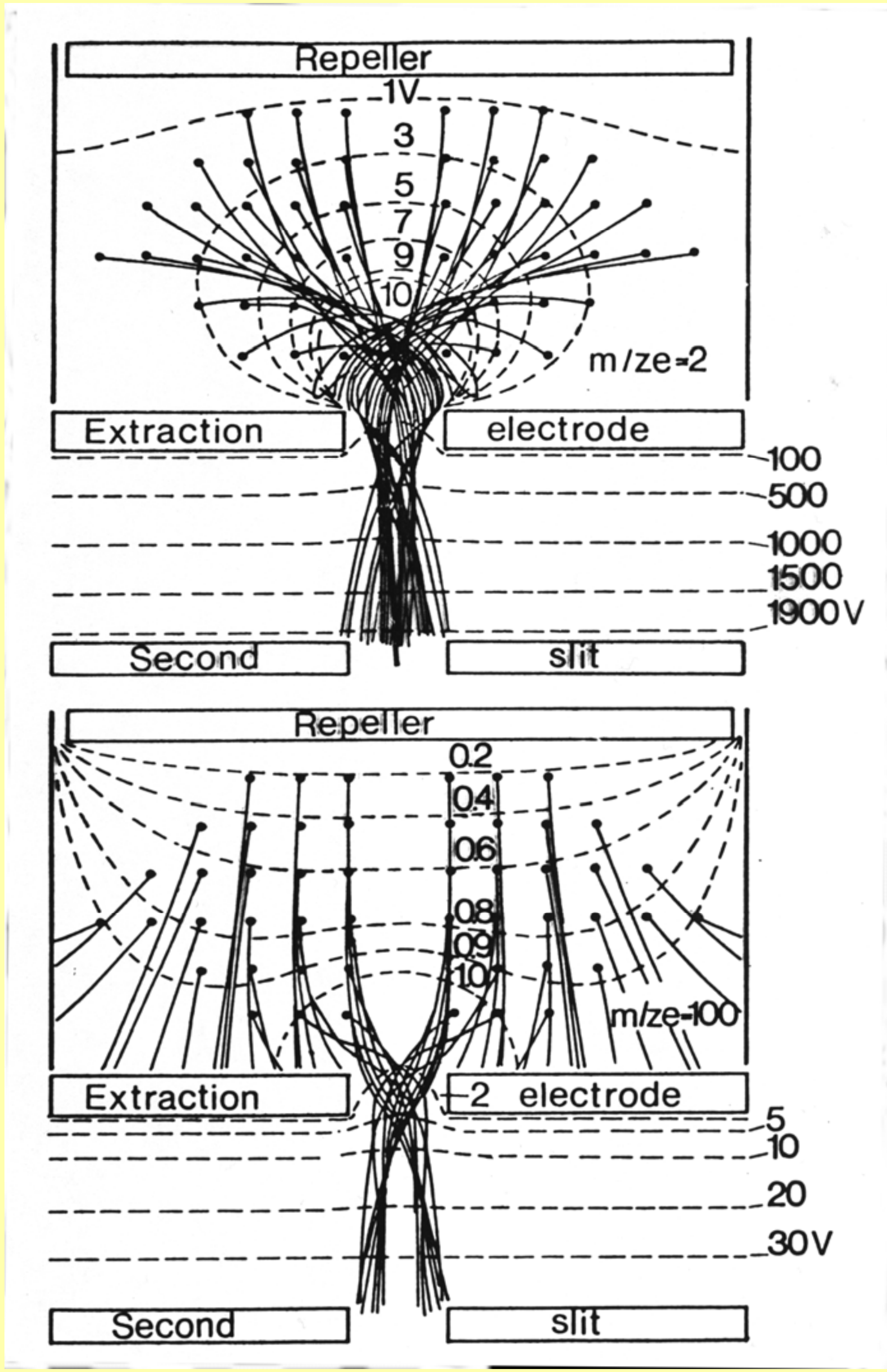
Ionization cross sections



$AB + e \rightarrow AB^{+}$
$\rightarrow A + B^{+} + KER$
$\rightarrow A^{+} + B + KER$

$AB^{+} + e \rightarrow (AB^{++})^{*}$
$\rightarrow A^{+} + B^{+} + KER$
$\rightarrow A^{+} + B + KER$

Calculated ion trajectories after Werner

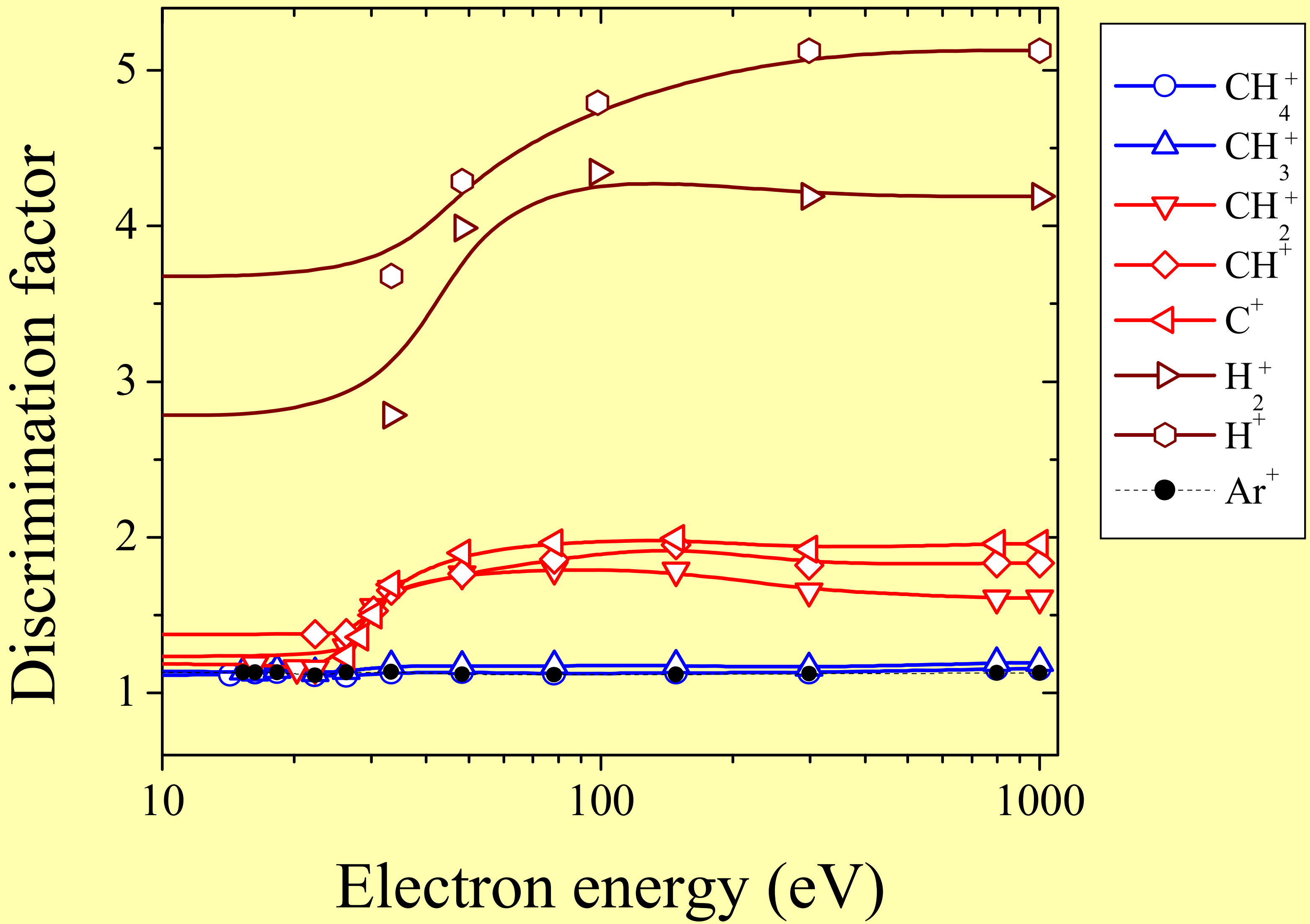


Penetrating field extraction

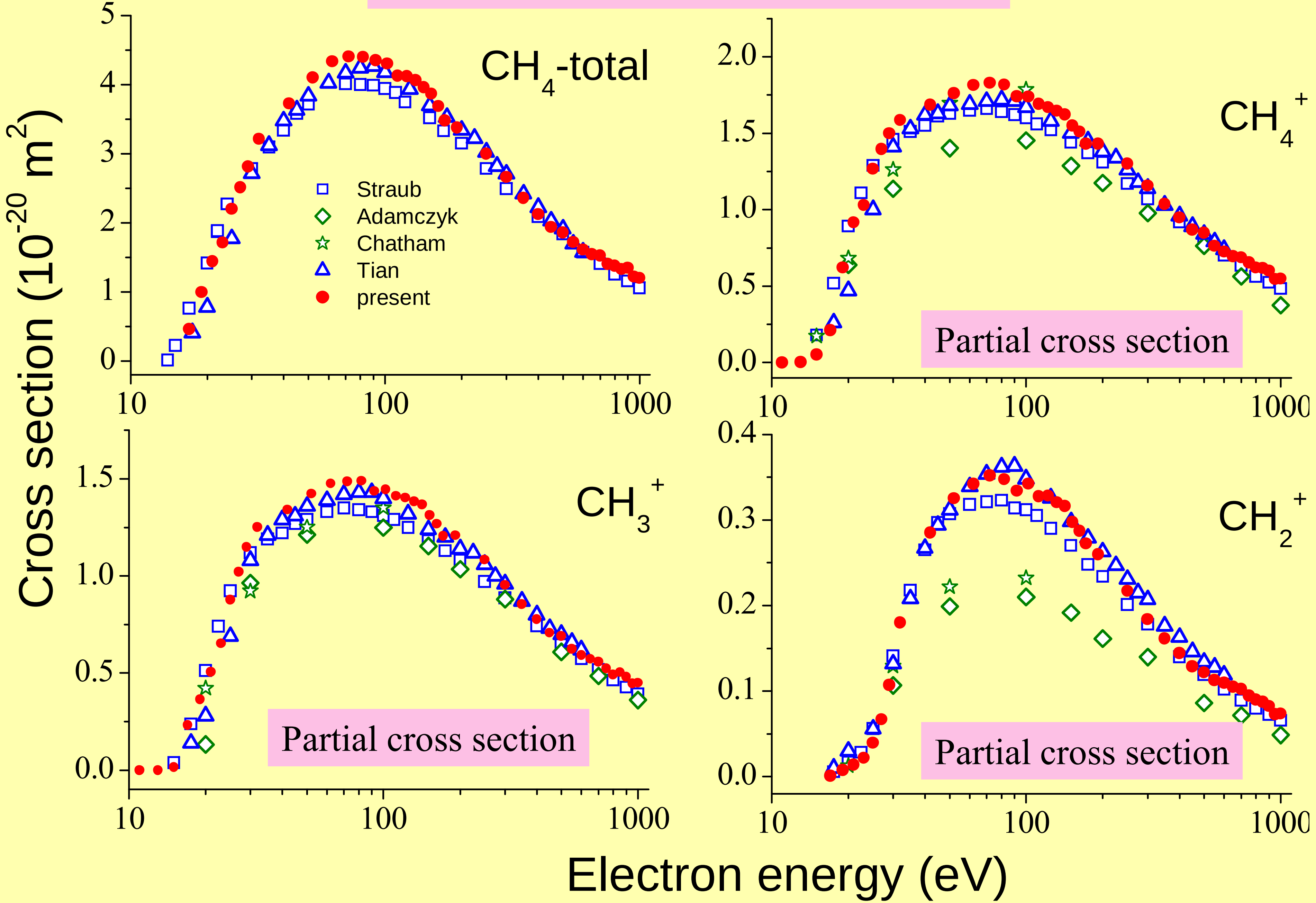
Direct field extraction

Discrimination

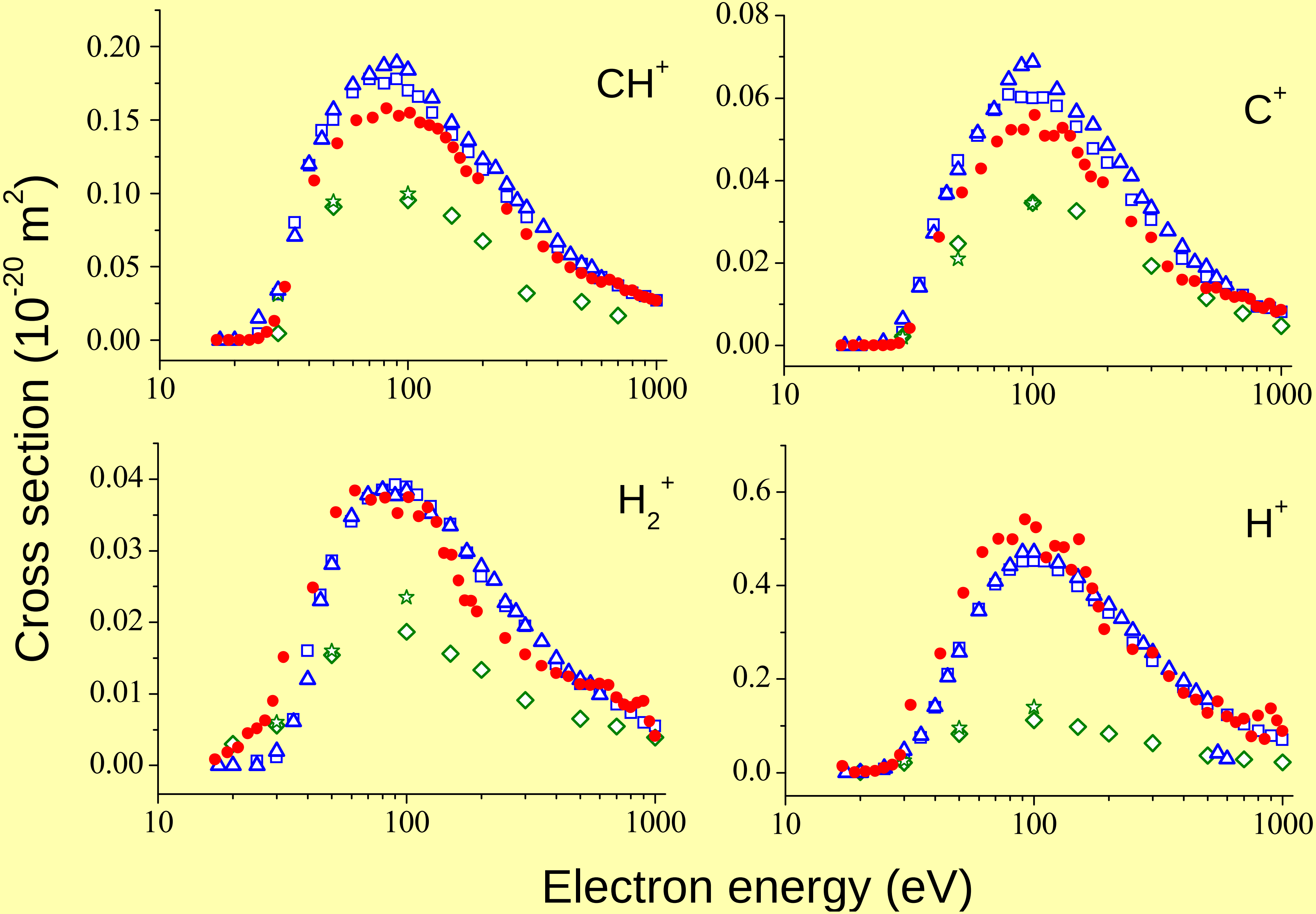
Integrated discrimination factor



Partial and total cross section



Partial cross sections:



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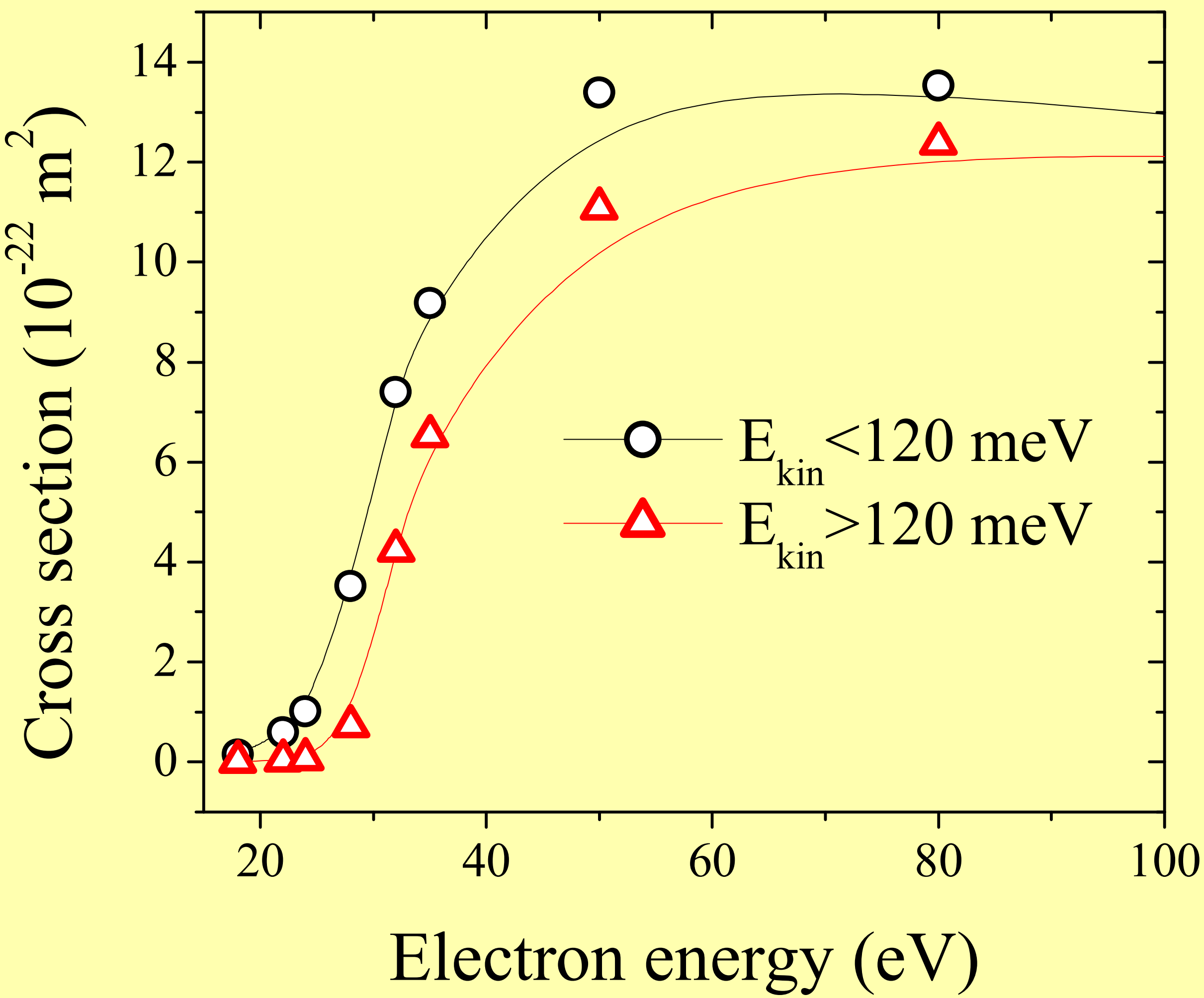
High resolution electron impact ionization of molecules

Institut Ionenphysik

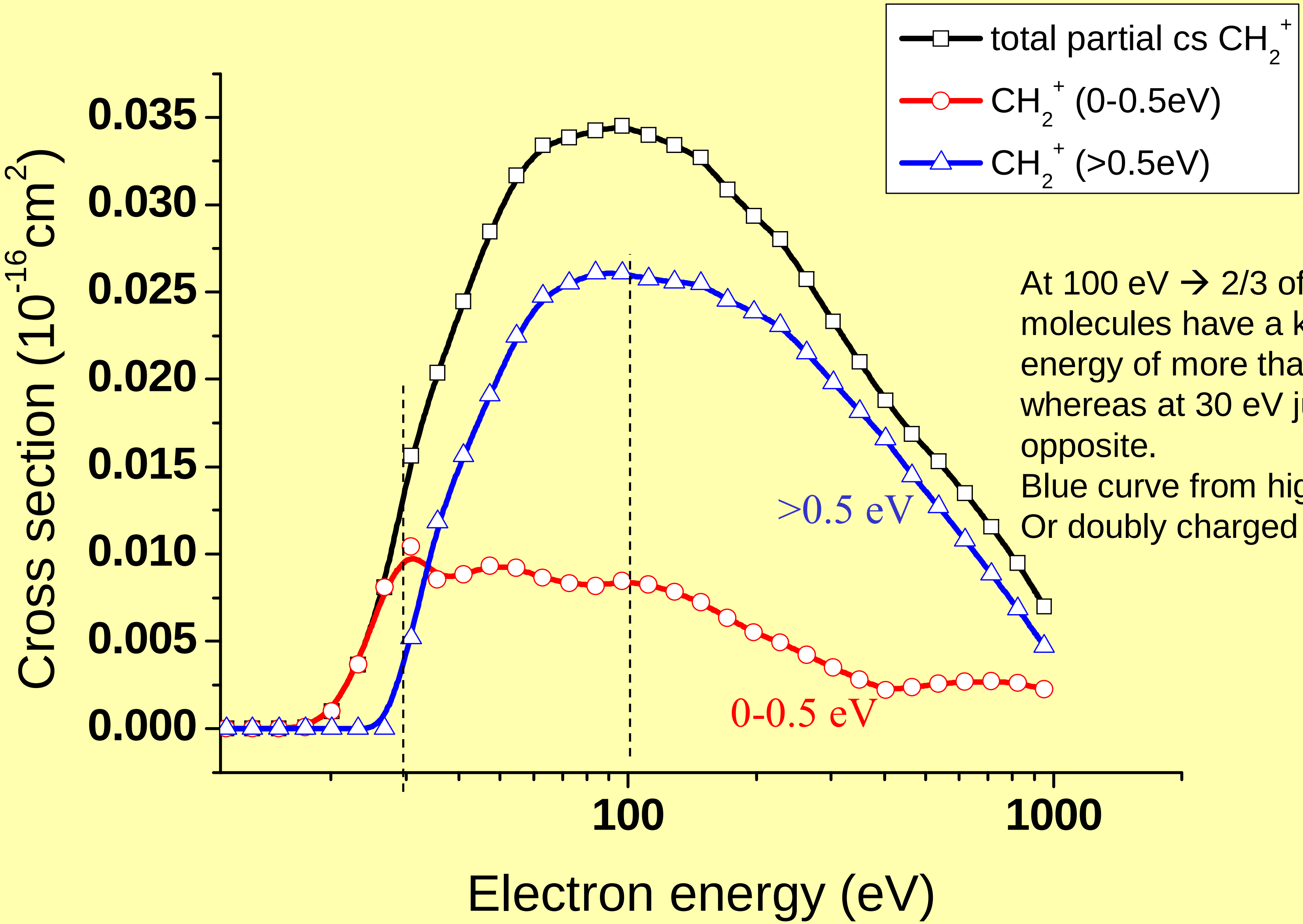
$$AB + e \rightarrow AB^{+}(AE)$$
$$AB + e \rightarrow A^{+}(AE) + B(KER)$$

1. Kinetics: $\sigma = \sigma(E)$
2. Differential kinetics: KER
3. Energetics: AE

Energy differential total cross sections:
$CH_4 + e \rightarrow CH_2^+$



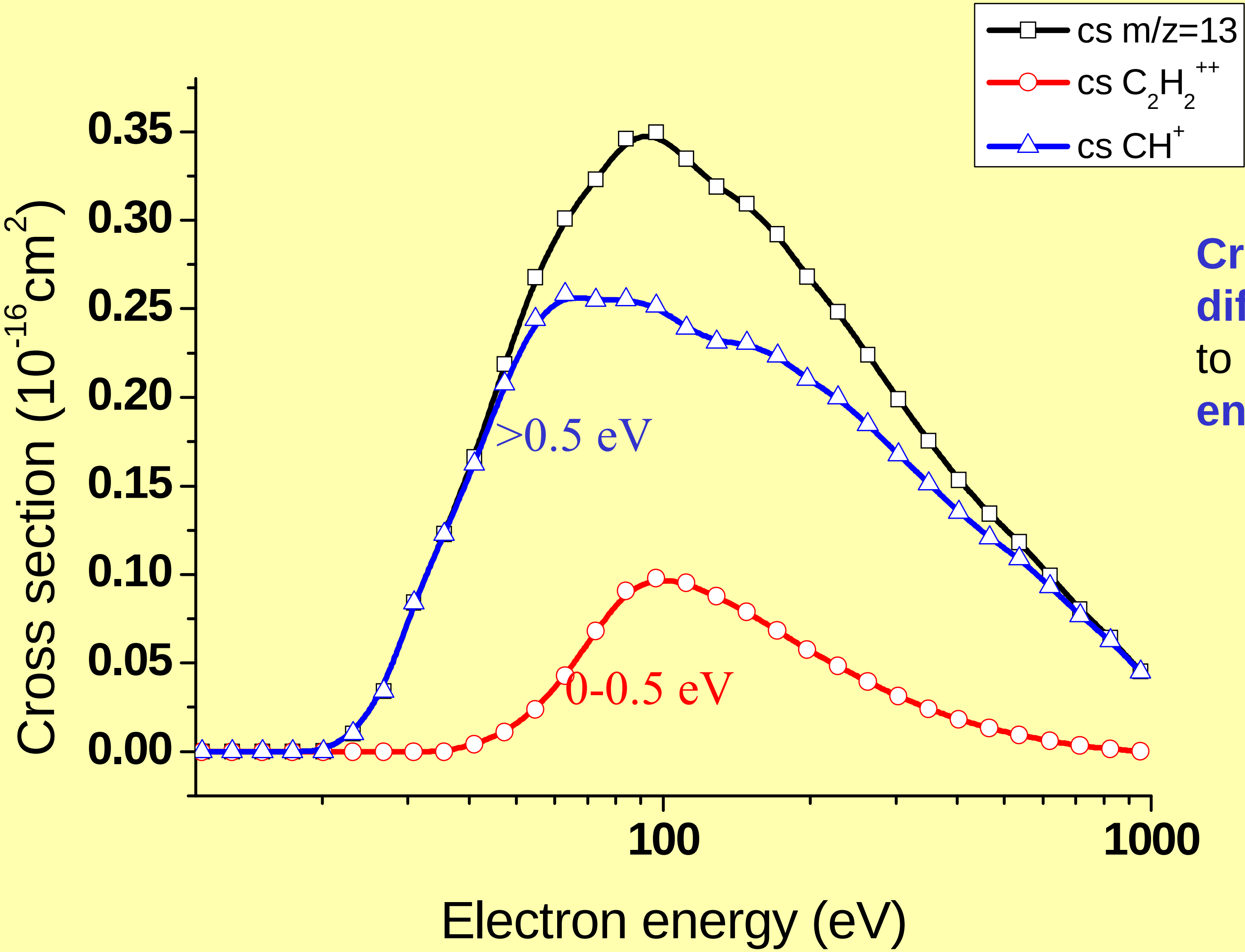
Example C_2H_2+e → CH_2^+



At 100 eV → 2/3 of the CH_2^+ molecules have a kinetic energy of more than 0.5eV, whereas at 30 eV just the opposite.
Blue curve from highly excited Or doubly charged parent ions

Example C_2H_2+e → CH^+

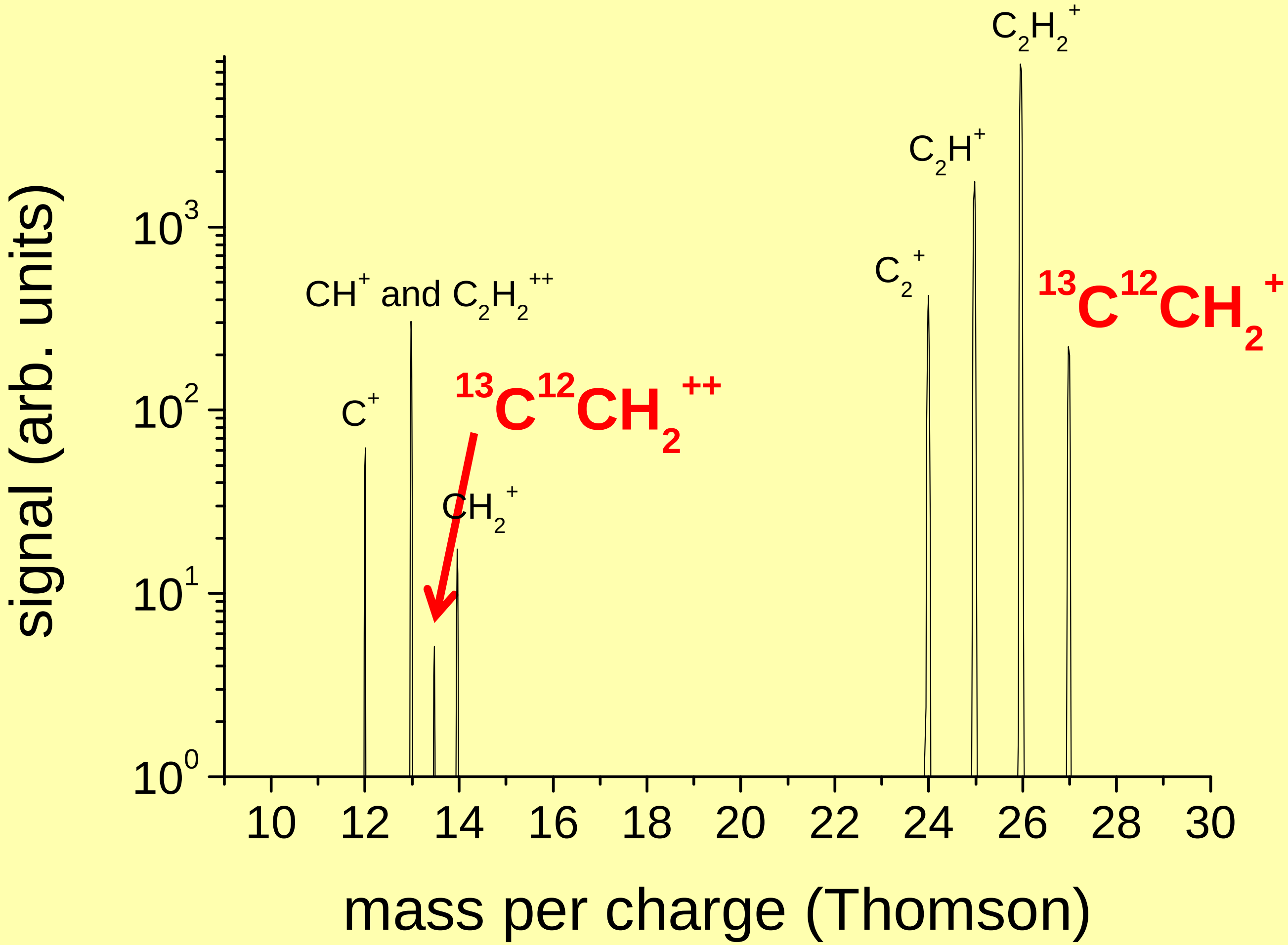
→ $C_2H_2^{++}$



Cross section which is **differential** with respect to the **initial kinetic energy**

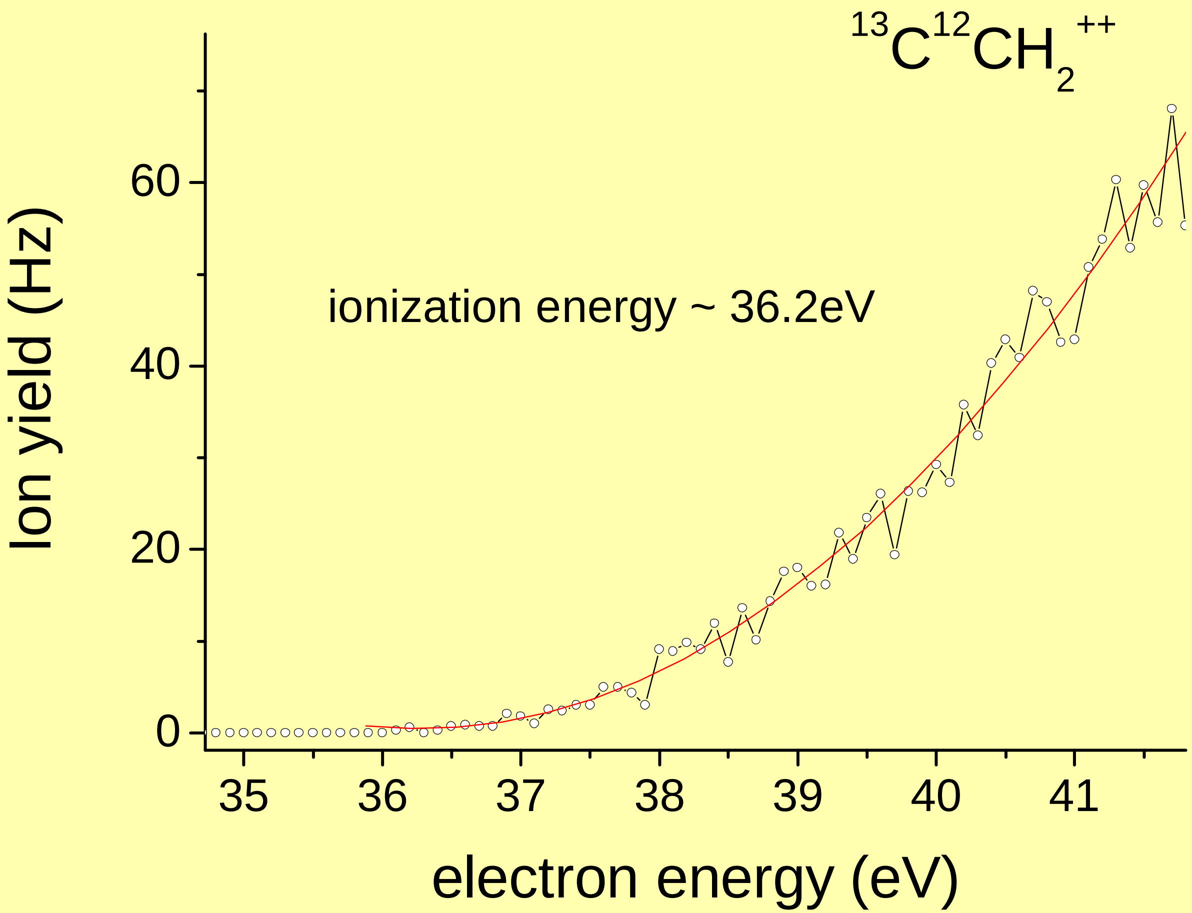
Isotopic labelling, AEs

Mass spectrum of C_2H_2



- An appreciable amount of m/q=13 is $C_2H_2^{++}$

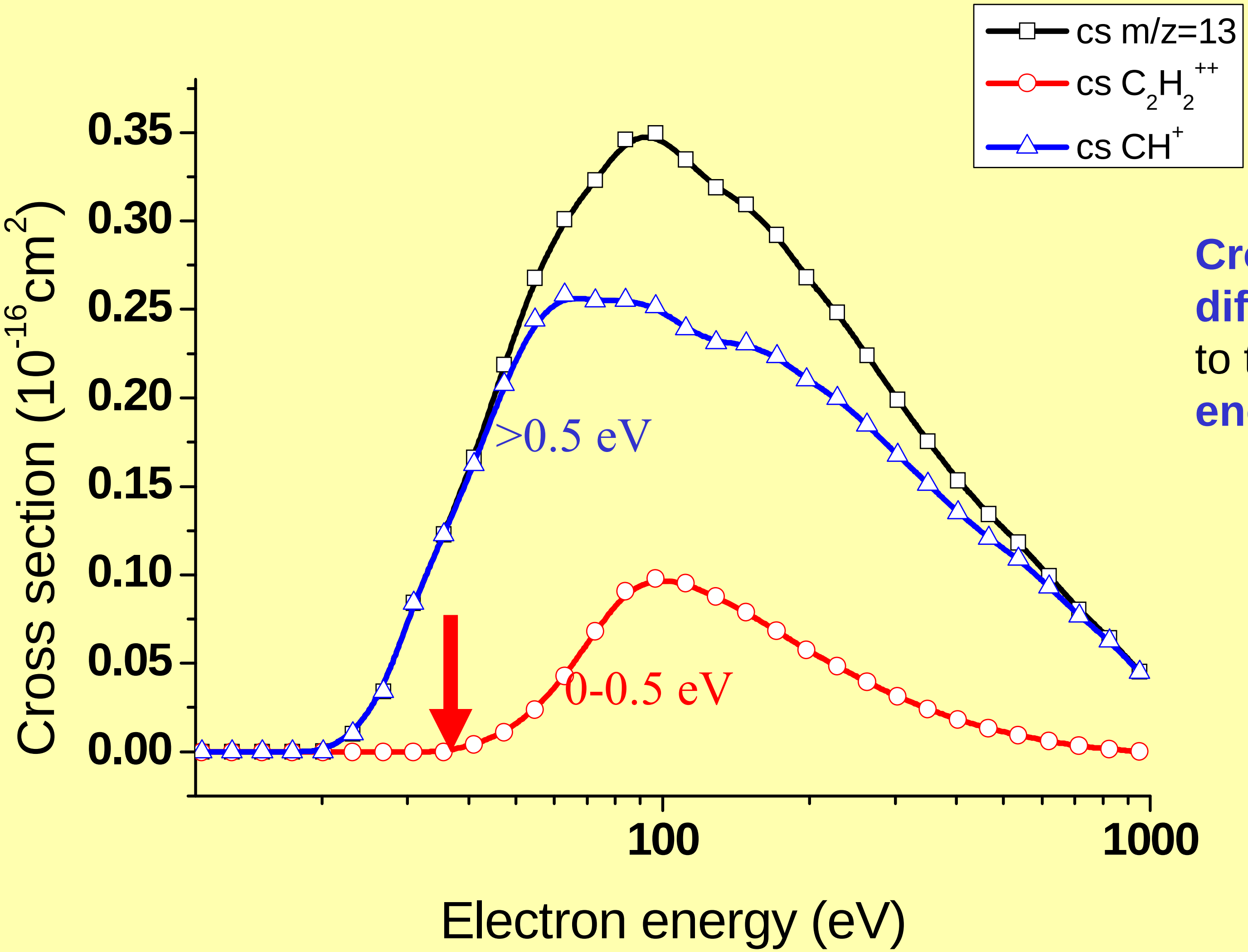
Ionization Energy of $C_2H_2^{++}$



One can deduce that the second (red) process comes only from the doubly charged acetylene

Example C_2H_2+e → CH^+

→ $C_2H_2^{++}$



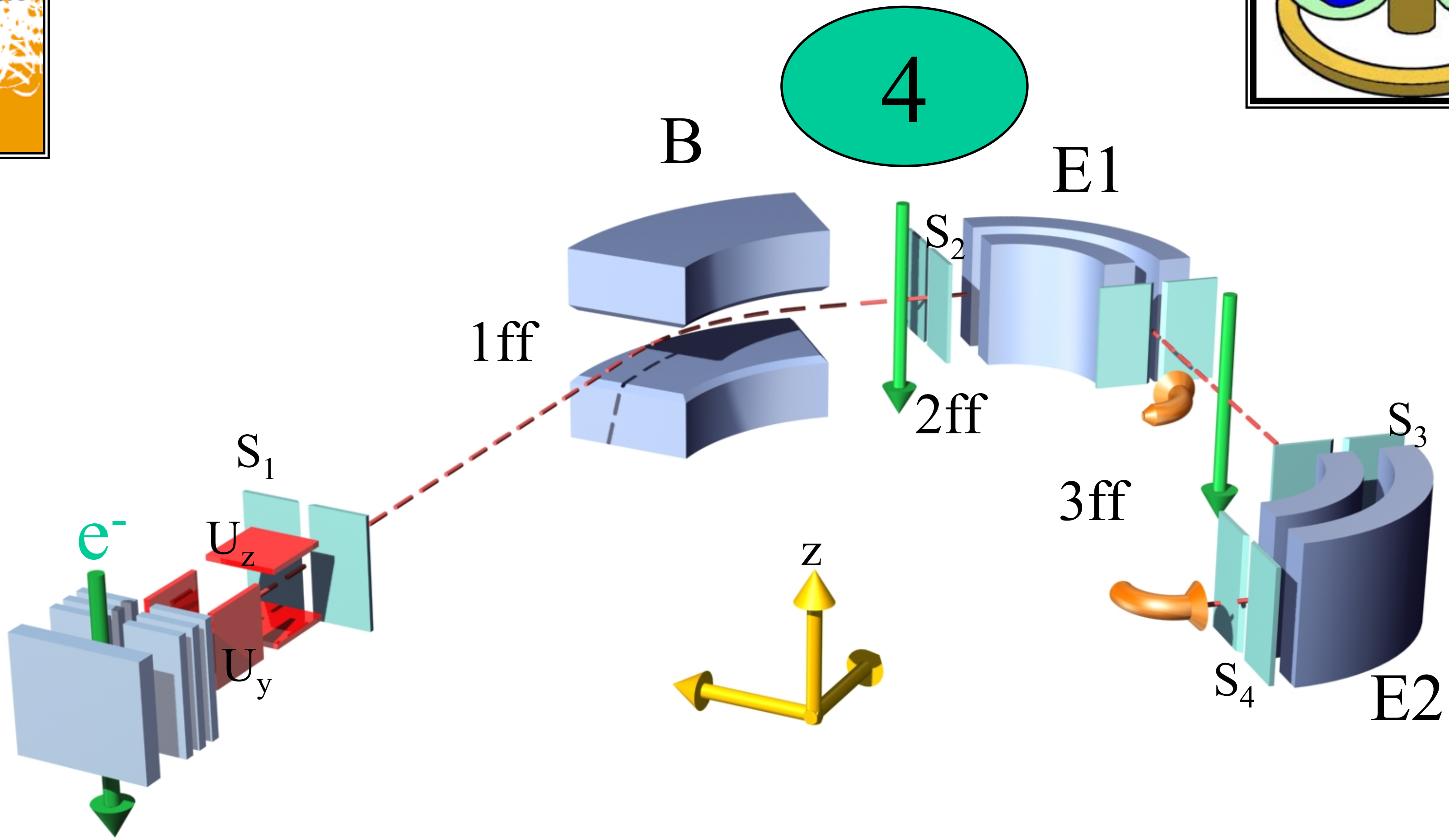
Cross section which is **differential** with respect to the **initial kinetic energy**

Isotopic labelling, AEs

Electron ionization of molecular ions: $C_2H_2^{\,+} + e \rightarrow$ ions

In collaboration with
Kurt Becker, New York,
Hans Deutsch, Greifswald and
Pierre Defrance, Louvain-la Neuve

Ionization cross sections

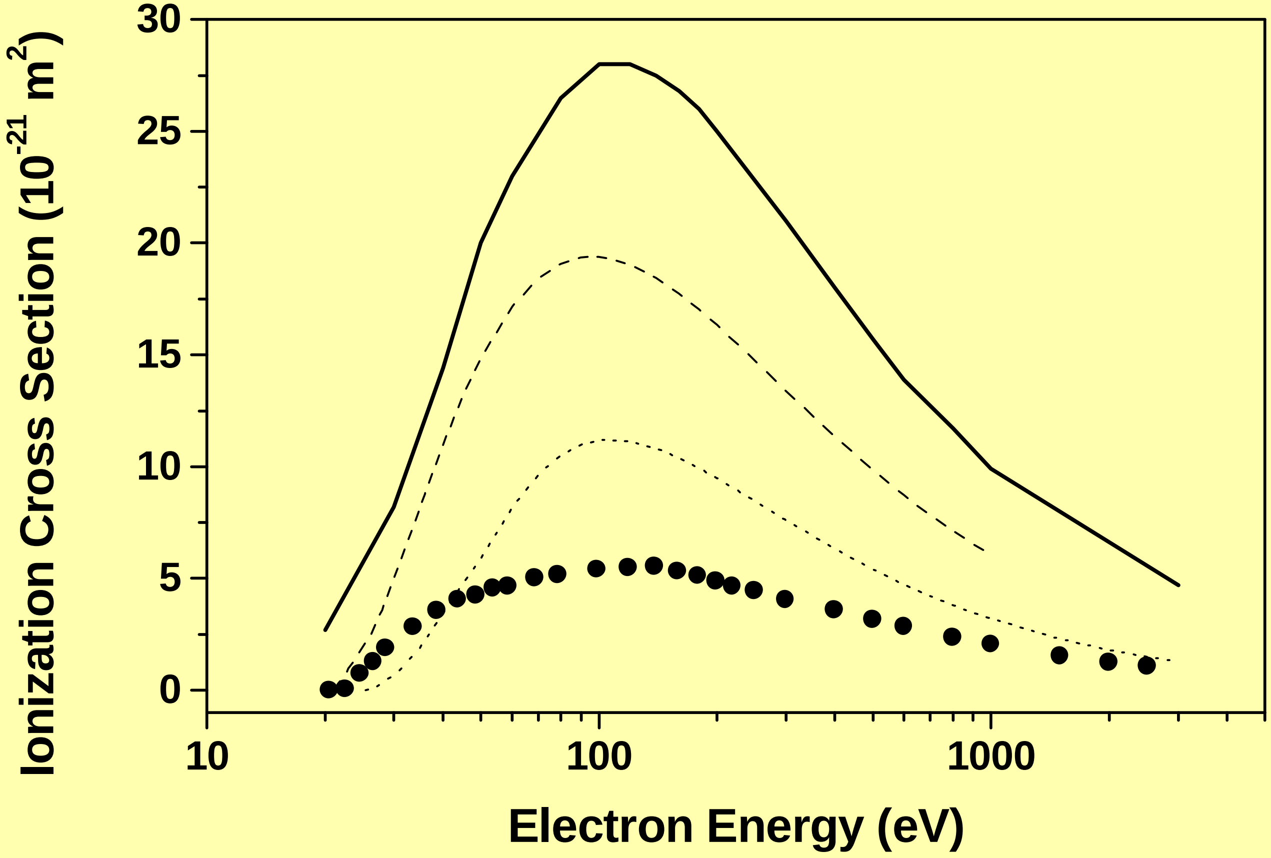


$$AB + e \rightarrow AB^{+}$$
$$\rightarrow A + B^{+} + KER$$
$$\rightarrow A^{+} + B + KER$$

$$AB^{+} + e \rightarrow (AB^{++})^{*}$$
$$\rightarrow A^{+} + B^{+} + KER$$
$$\rightarrow A^{+} + B + KER$$

Electron ionization of molecular ions:

$C_2H_2^+ + e \rightarrow$ ions



Previous results for the electron-impact ionization of $C_2H_2^+$ as a function of electron energy: Calculated absolute cross sections using our old formalism (thick solid line) [4,5] in comparison with the calculated cross sections of Kim et al. [3]) dashed line) and Janev and Reiter [7] (dotted line) and the measured cross section of Defrance and co-workers [8] (solid circles).

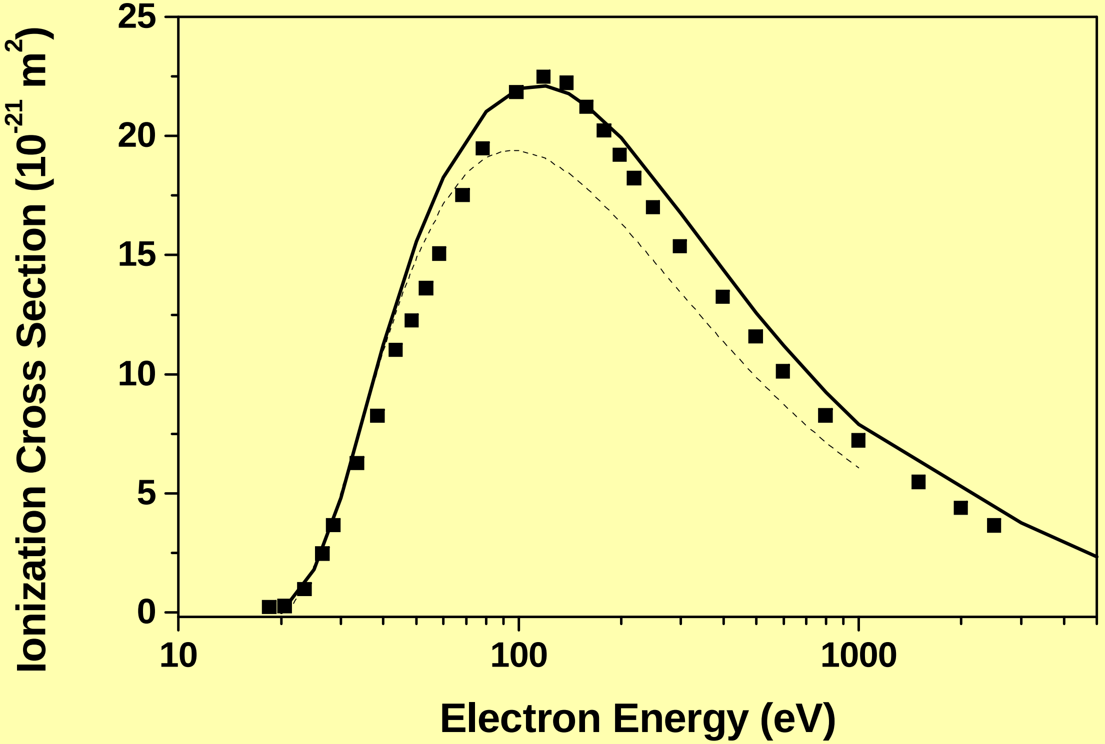
Electron ionization of molecular ions: $C_2H_2^+ + e \rightarrow$ ions

$C_2H_2^+ + e \rightarrow C_2H_2^{++}$

$\downarrow \rightarrow$ singly charged fragment ions via DI (eg. CH^+)

$C_2H_2^+ + e \rightarrow C_2H_2^{+*} \rightarrow$ singly charged ions via DE (eg. CH^+)

Electron ionization of molecular ions: $C_2H_2{}^+ + e \rightarrow$ ions



Calculated absolute cross section for the electron-impact ionization of C2H2+ as a function of electron energy using the present formalism (thick solid line) in comparison with the recently measured cross section of Defrance and co-workers [6] (solid squares) and the calculated cross section of Kim et al. [3].

Temperature effects on electron ionization of molecular ions

In collaboration with
Stefan Matejcik, Bratislava

1. Kinetics: $\sigma = \sigma(E)$
2. Differential kinetics: KER
3. Energetics: AE

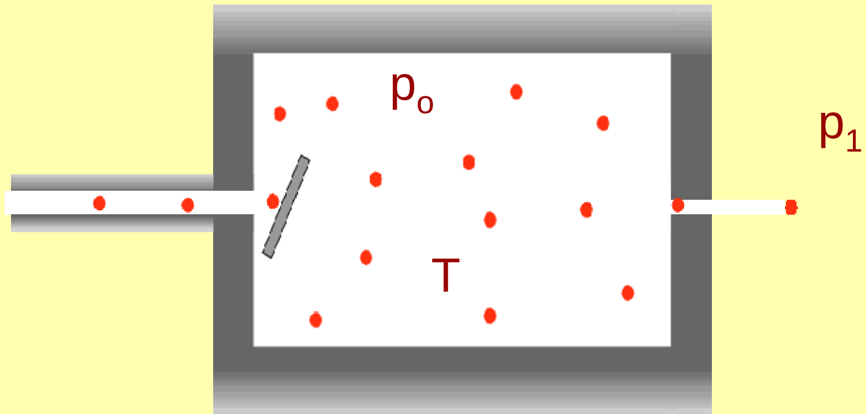
Effusive molecular beam source

- well defined temperature of the gas
- known gas density variation with T

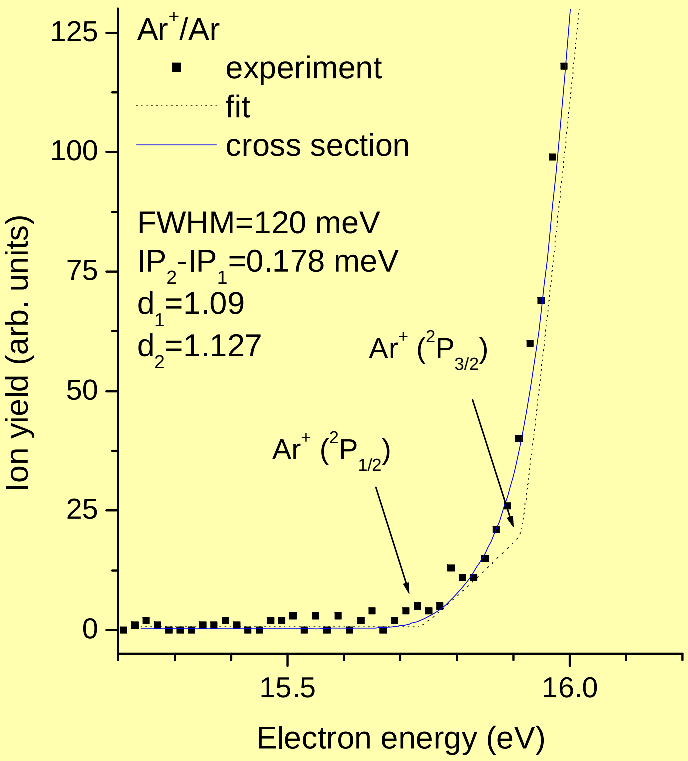
$p_o \sim 1$ pa
$p_1 = 10^{-6}$ pa
T=293-700 K

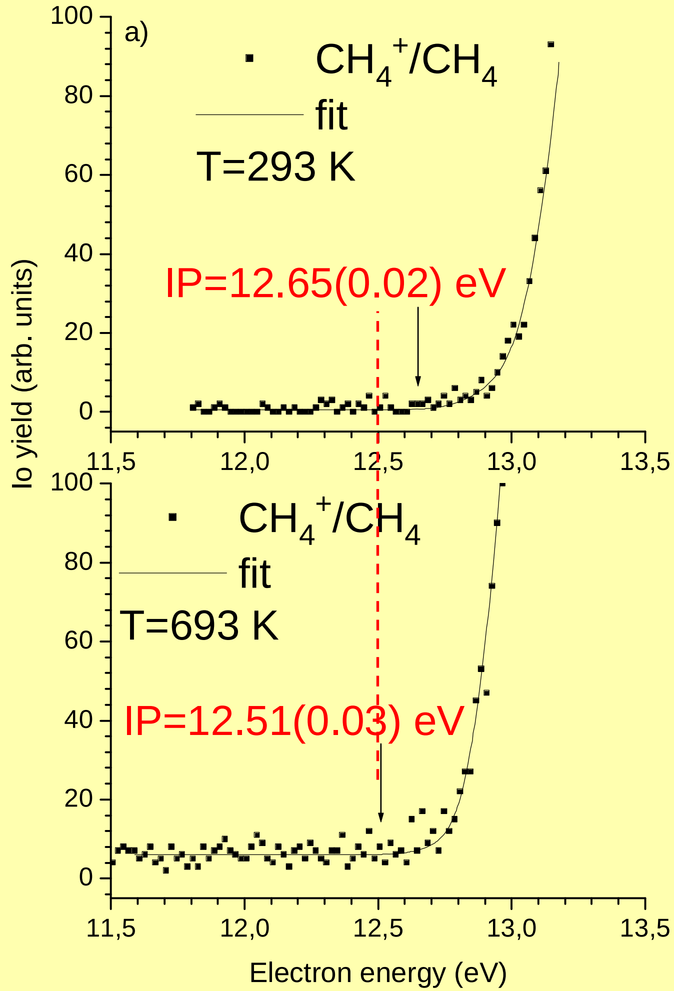
$\approx 10^4$ collisions

Channel :
d= 0.5mm
L= 5mm

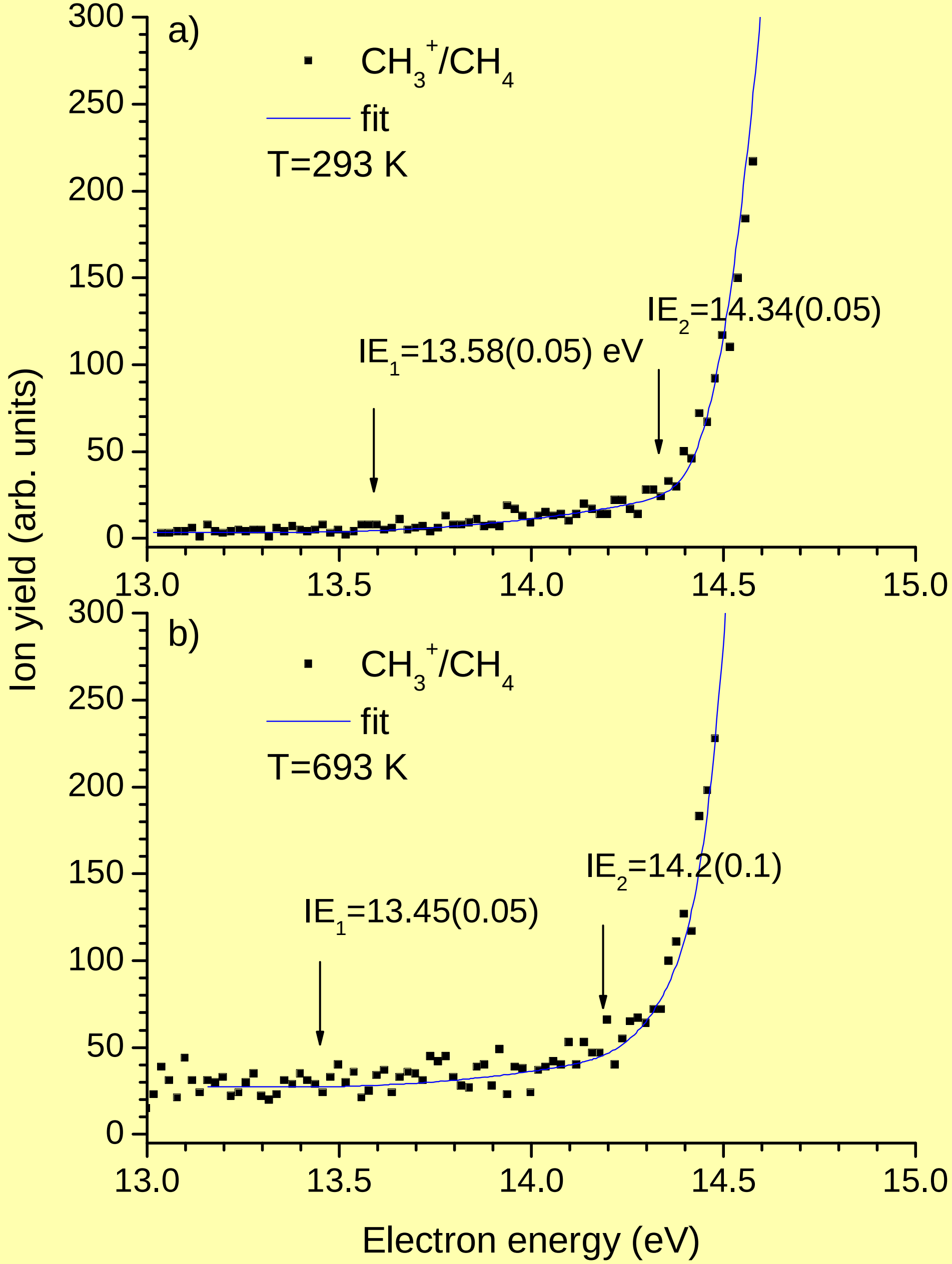


Temperature effects on appearance energy of molecular ions: $CH_4 + e \rightarrow$ ions





$\Delta IP_{spectr.} = 178$ meV



$e + CH_4 \rightarrow CH_3^+ + H^- + 2e$

Present value: 13.58±0.1 eV

EII: 13.25±0.08 eV (13.7±0.05)

PI: 13.50±0.05 eV

$e + CH_4 \rightarrow CH_3^+ + H + 2e$

Present value: 14.34±0.1 eV

EII: 14.01±0.08 eV (14.24, 14.3±0.2)

PI: 14.23±0.05 eV

Temperature effects on apperance energy of molecular ions: appearance energy

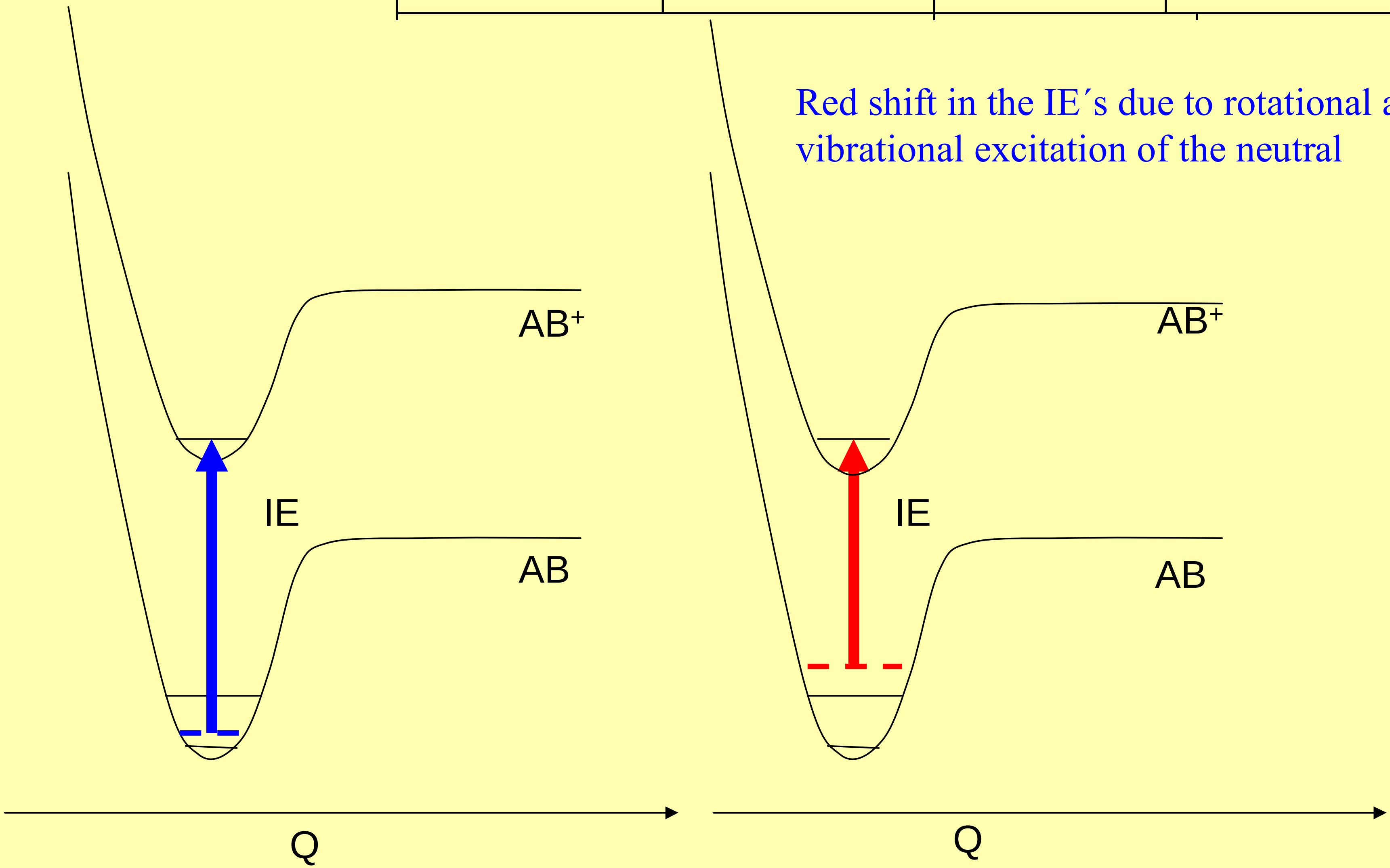
$CH_4 + e \rightarrow$ ions

CH_4^+/CH_4	T=293 K	T=693 K	
IP_1	12.65±0.04	12.51±0.04	140meV
CH_3^+/CH_4	T=293 K	T=693 K	
IP_2 (eV)	13.58±0.05	13.45±0.05	130meV

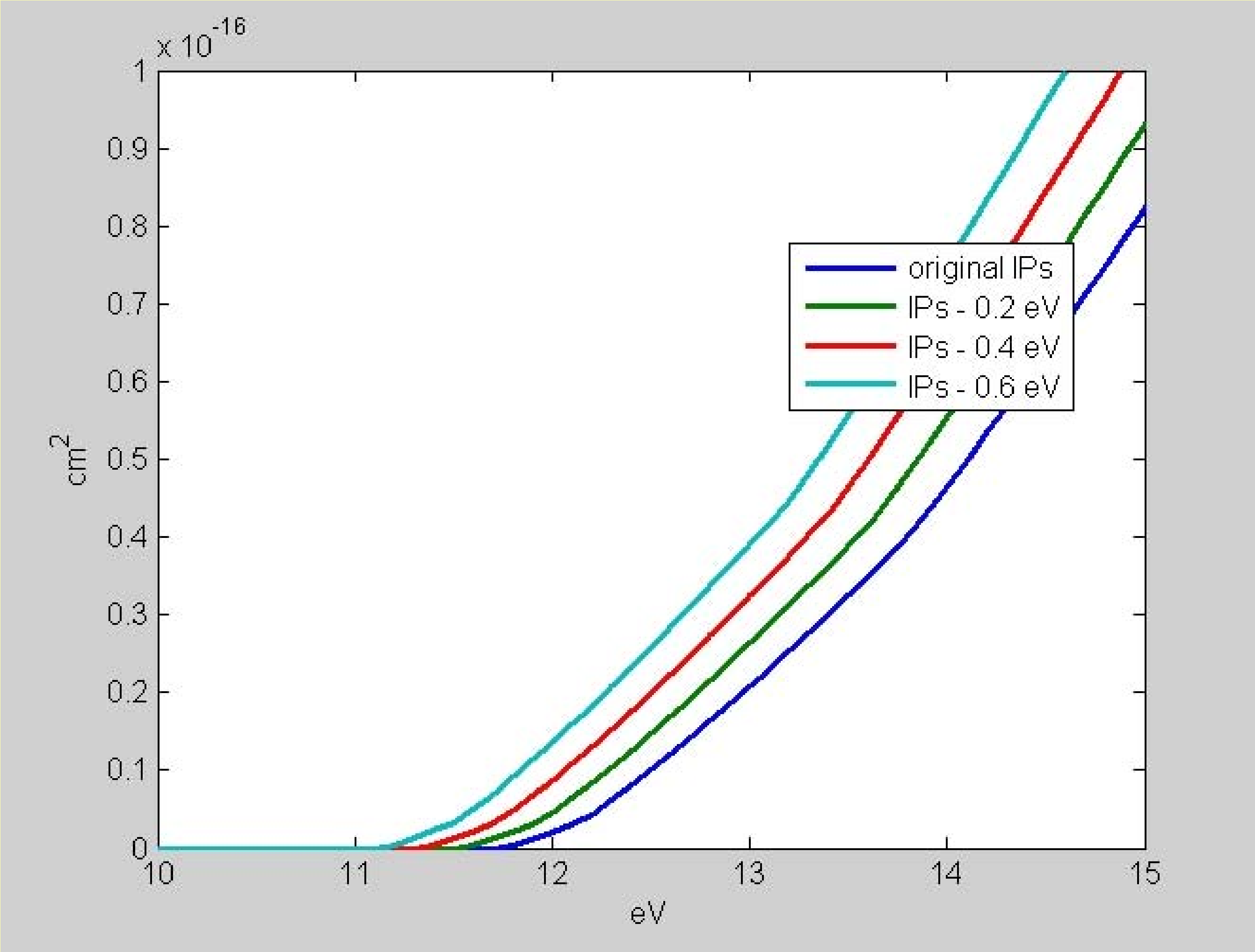
Internal energy of CH_4

E_i (eV)	E_v (eV)	E_r (eV)	T (K)
0.159	0.069	0.090	693
0.039	0.001	0.038	293

Red shift in the IE´s due to rotational and vibrational excitation of the neutral



Temperature effects on electron ionization cross sections of molecular ions (DM calculations):
$C_3H_8 + e \rightarrow$ ions



Conclusion

Electron ionization of hydrocarbon molecules:

$CH_4 + e \rightarrow \text{ions}$

$C_2H_2 + e \rightarrow \text{ions}$

$C_2H_4 + e \rightarrow \text{ions}$

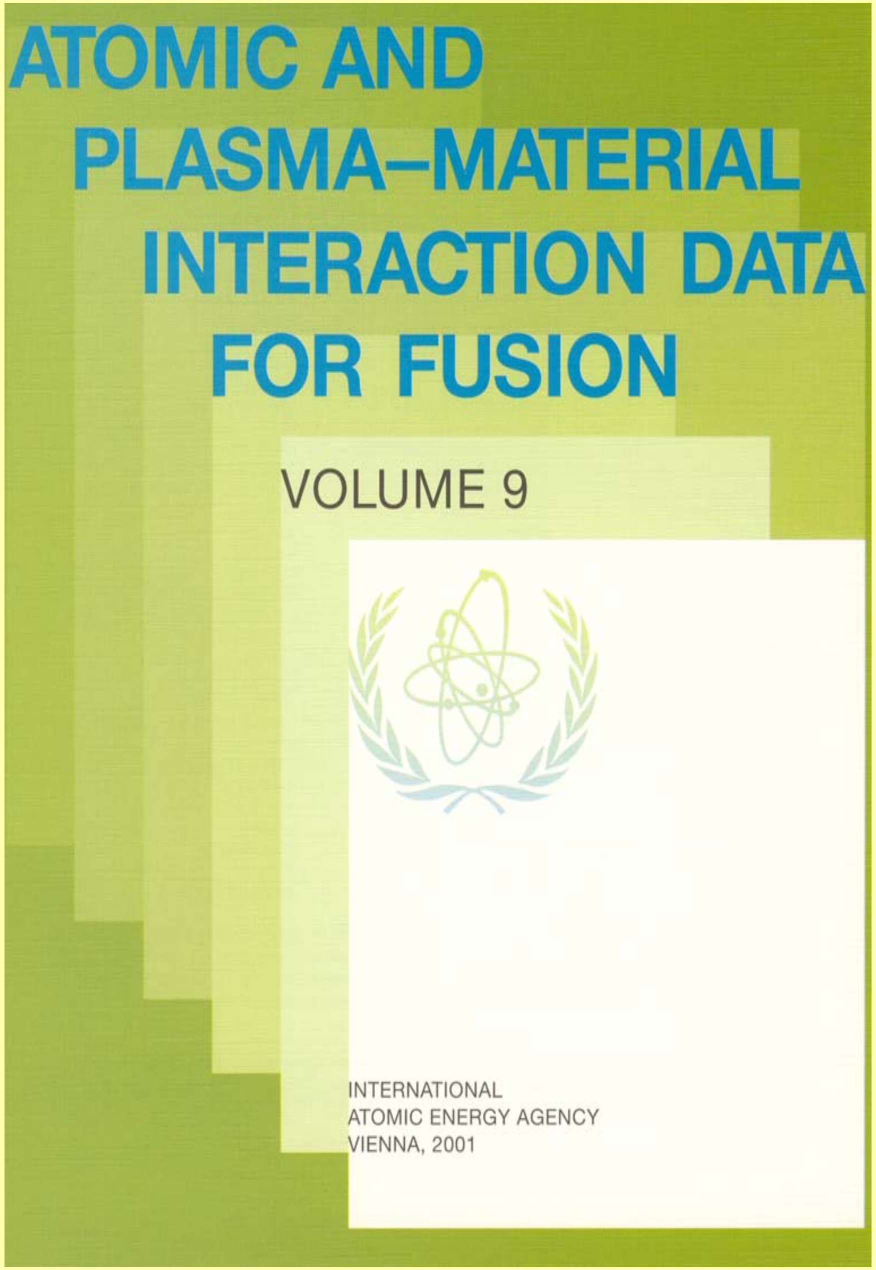
$C_3H_6 + e \rightarrow \text{ions}$

$C_2H_6 + e \rightarrow \text{ions}$

$C_3H_8 + e \rightarrow \text{ions}$

....

Total, partial, and differential cross sections



FOREWORD

The present volume of Atomic and Plasma-Material Interaction Data für Fusion is devoted to a critical review of the role of atomic, molecular and plasma-wall interaction processes in divertor plasmas of magnetic fusion devices.

This volume is intended to provide fusion reactor designers a detailed survey of existing, critically assessed data für the behaviour of plasma facing materials under particle impact.

Volume 9 ofAtomic and Plasma-Material Interaction Data für Fusion is the result of a three year Co-ordinated Research Project on Atomic and Plasma- Wall Interaction Data für Fusion Reactor Divertor Modeling, 1998-2000.

The International Atomic Energy Agency expresses its appreciation to the contributors to this volume für their dedicated effort and co-operation.

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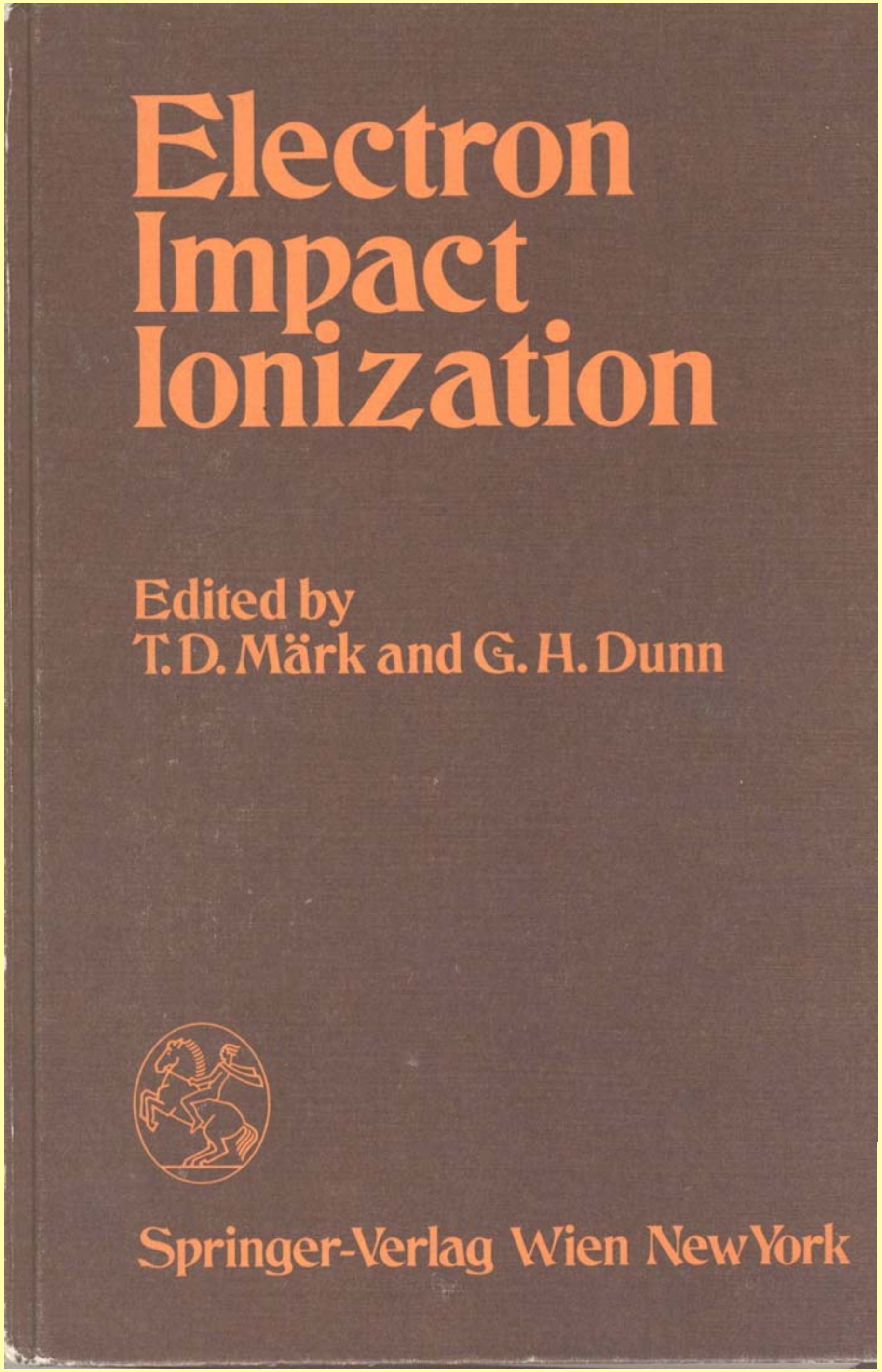
Abstract

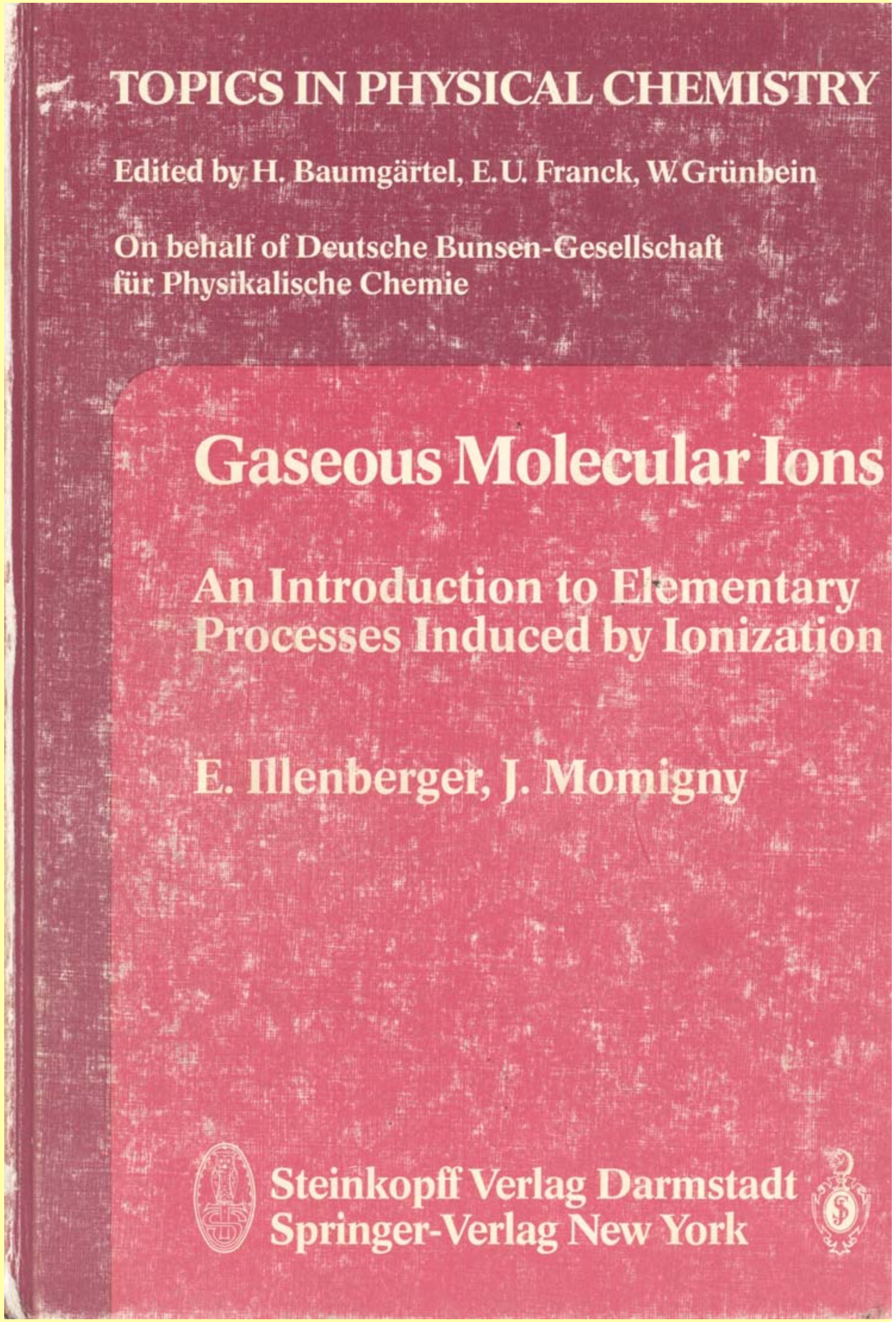
A critical assessment of available experimental and theoretical cross sections for electron-impact direct and dissociative ionization of hydrocarbon molecules, CzHy (x = 1 - 3, 1 :::; y :::; 2x + 2), has been carried out.

Recommended cross sections are suggested in the energy range from threshold to 10 keV for those reaction channels for which more than one set of data were found in the literatures. For the molecules for which no cross section information was found available, the cross sections for the dominant ionization channels were derived on the basis semi-empirical cross section relationships.

The recommended and derived cross sections are represented by analytic fit functions, the coefficients of which are provided. The rate coefficients for all the ionization channels have been calculated in the temperature range from 1 eV to 1 keV.

The cross sections and rate coefficients for all studied ionization channels are presented in graphical form as weIl.


Electron
Impact
Ionization
Edited by
T. D. Märk and G. H. Dunn
Springer-Verlag Wien New York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Processes Induced by Ionization
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Steinkopff Verlag Darmstadt
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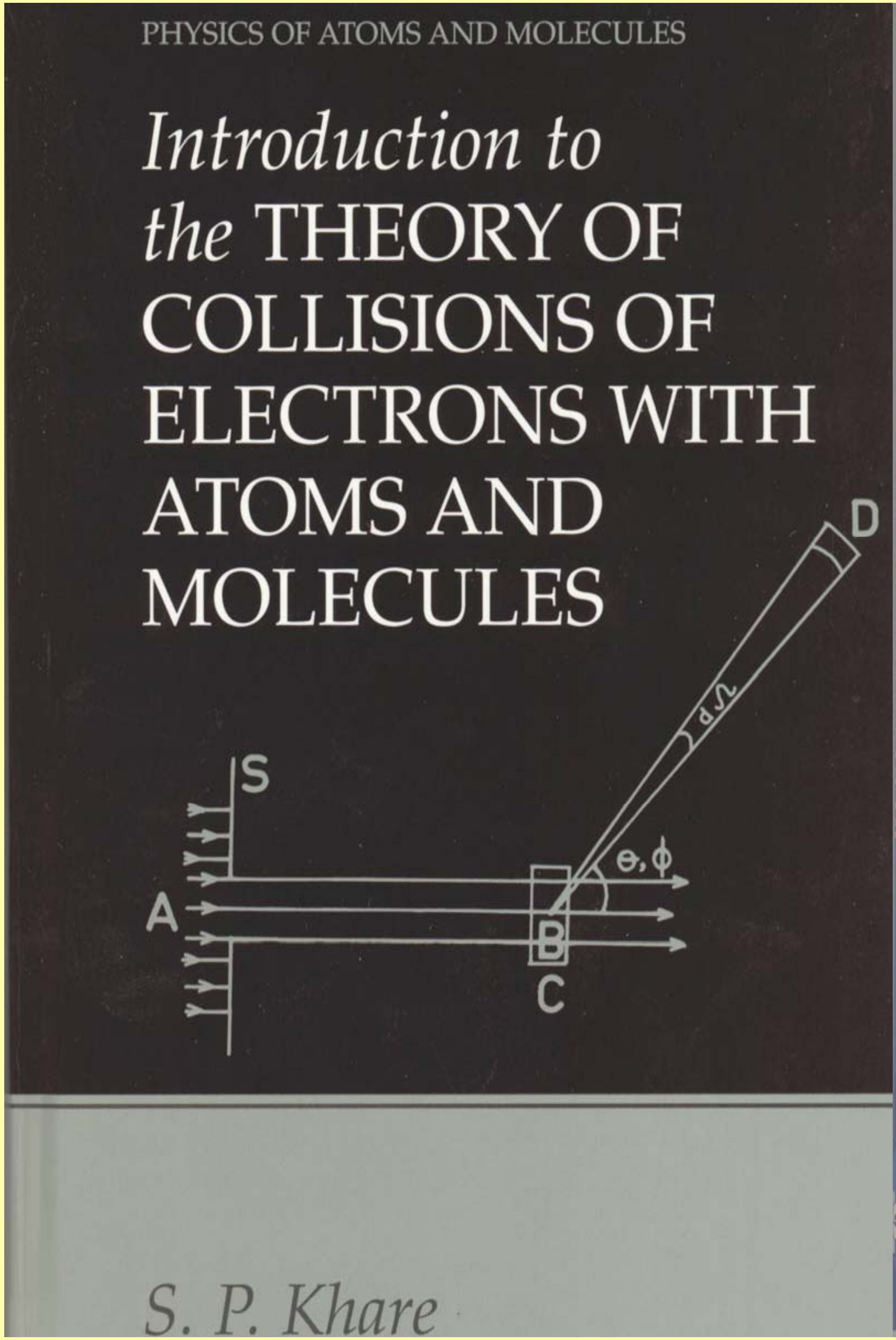
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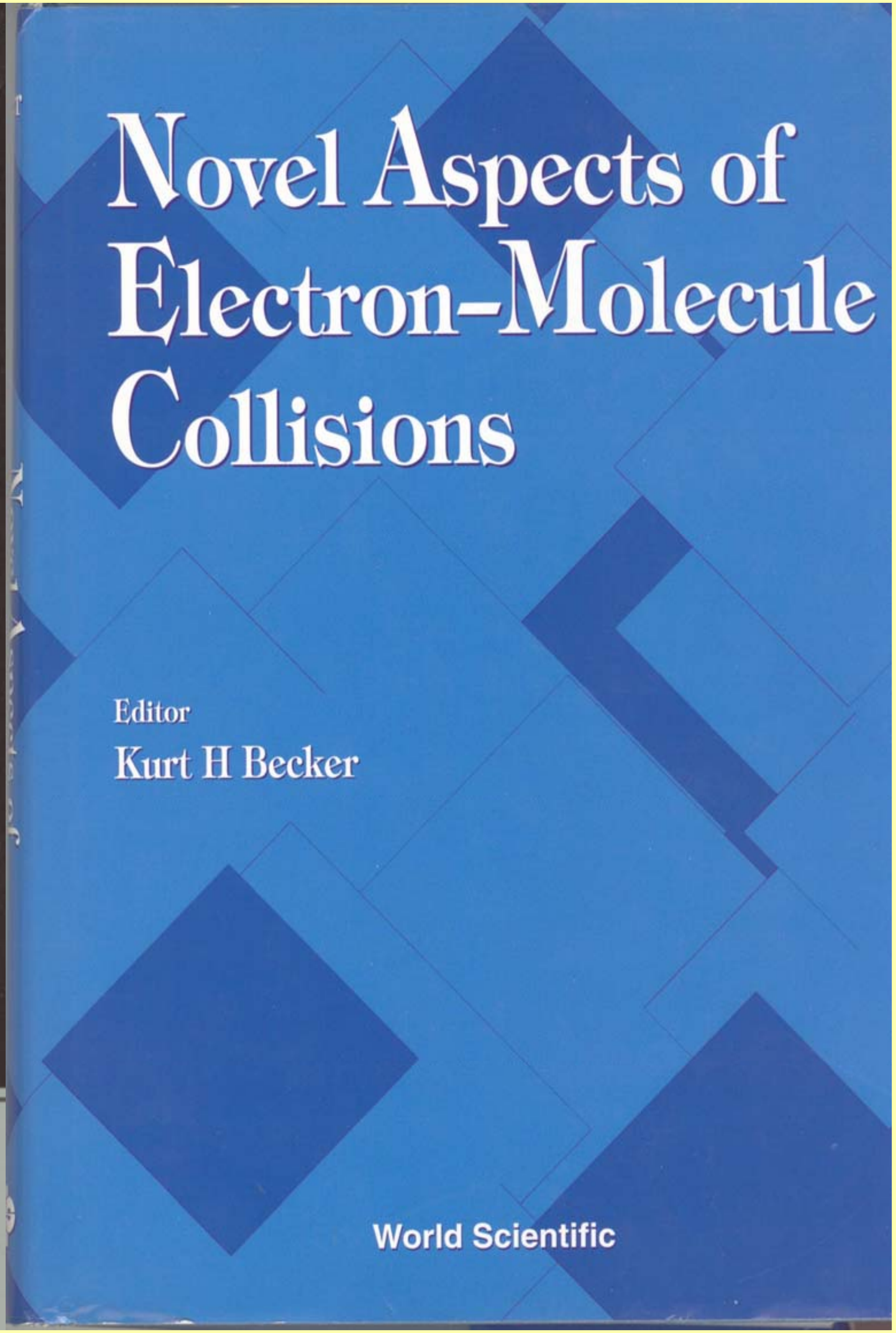
Introduction to the THEORY OF COLLISIONS OF ELECTRONS WITH ATOMS AND MOLECULES
D
dΩ
S
θ, ϕ
A
B
C
S. P. Khare


Novel Aspects of Electron–Molecule Collisions
Editor
Kurt H Becker
World Scientific

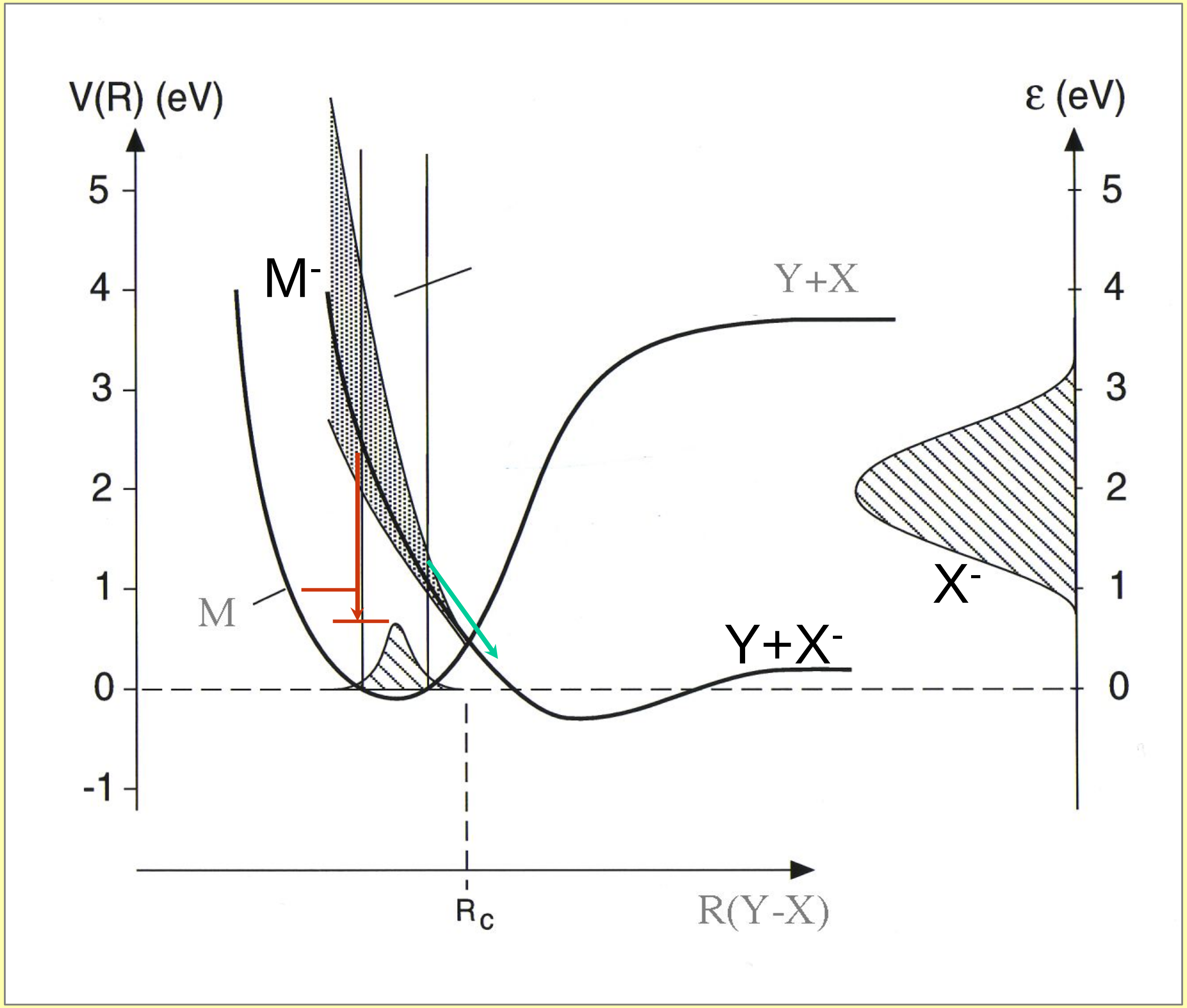
http://webbook.nist.gov/

Electron attachment of atoms/molecules

$$AB + e \rightarrow AB^- \ (AE)$$
$$AB + e \rightarrow A^- \ (AE) + B \ (KER)$$

Kinetics: $\sigma = \sigma\,(E)$
Energetics: AE

Dissociative Electron Attachment



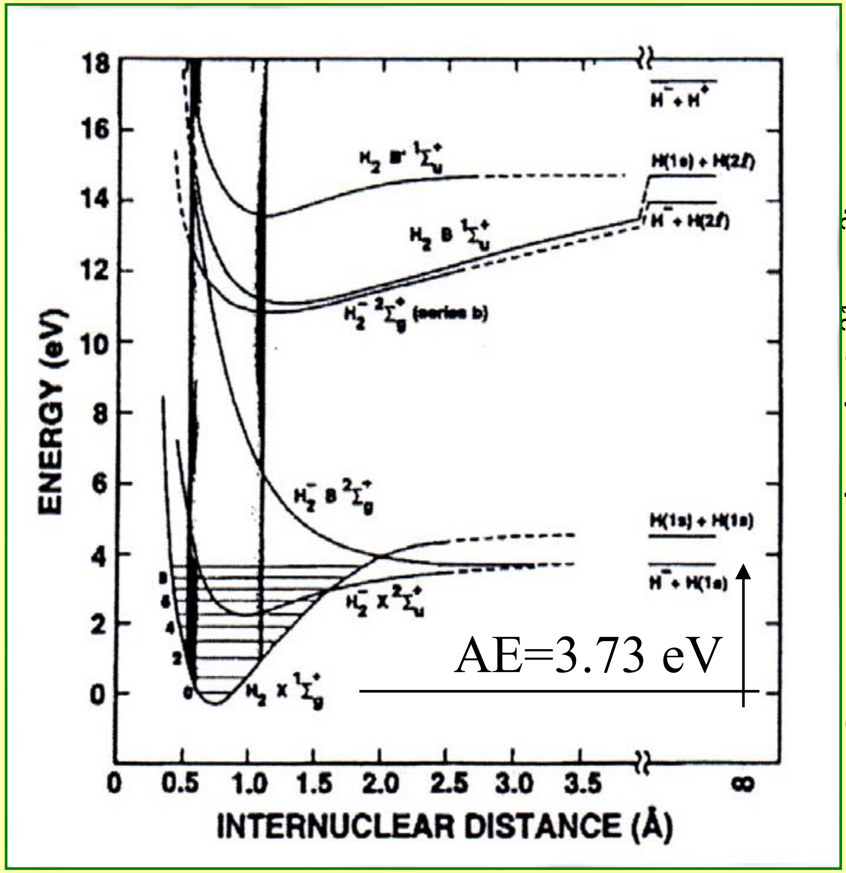
Dissociative electron attachment σ: H_2 (v=0) + e $\rightarrow$ H^-

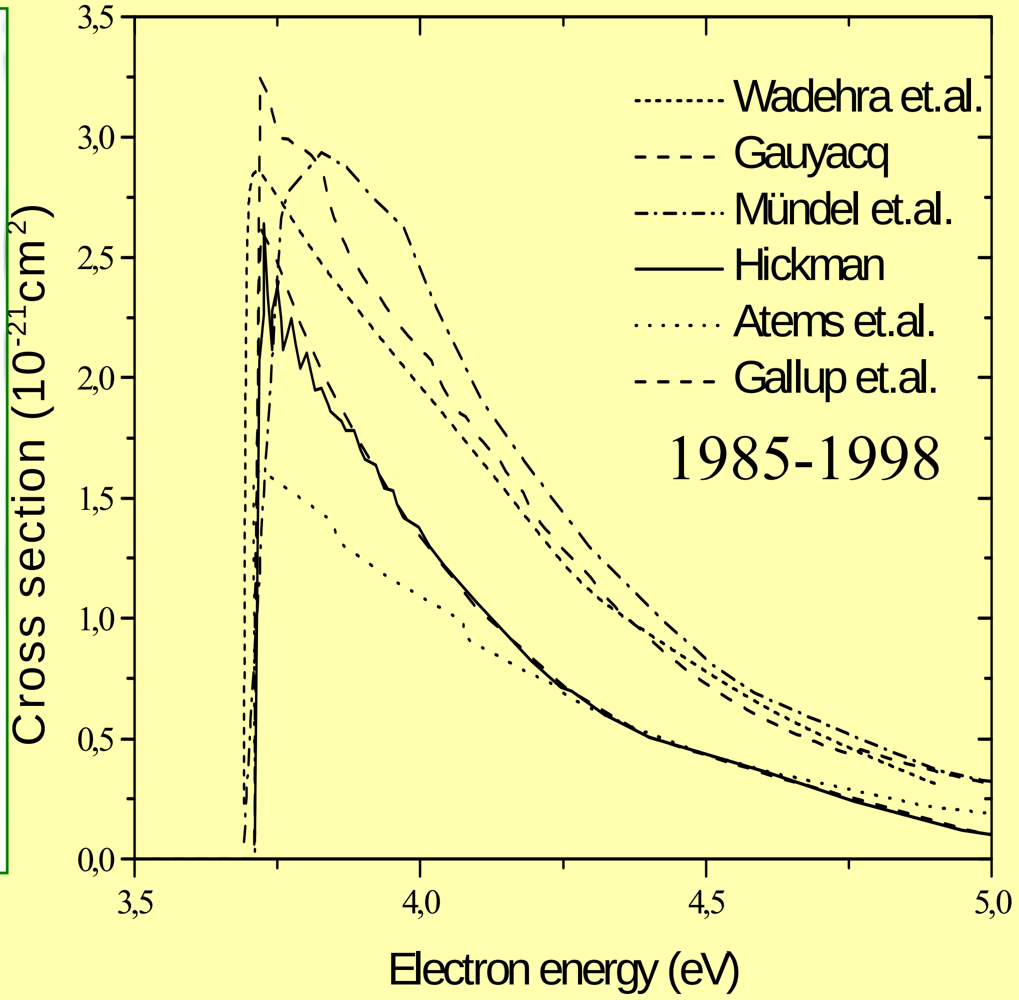
1. High current H^- ion sources are of potential interest in future fusion reactors for neutral beam production /heating.

2. These cross sections are also of importance in molecular hydrogen flux rate equations for plasma edge models (B2-EIRINE)

Electron Molecule Attachment

$$H_2(v=0,J=0) + e \rightarrow H_2^-\,(^2\Sigma_u^+) \rightarrow H^-(1s^2) + H(1s)$$

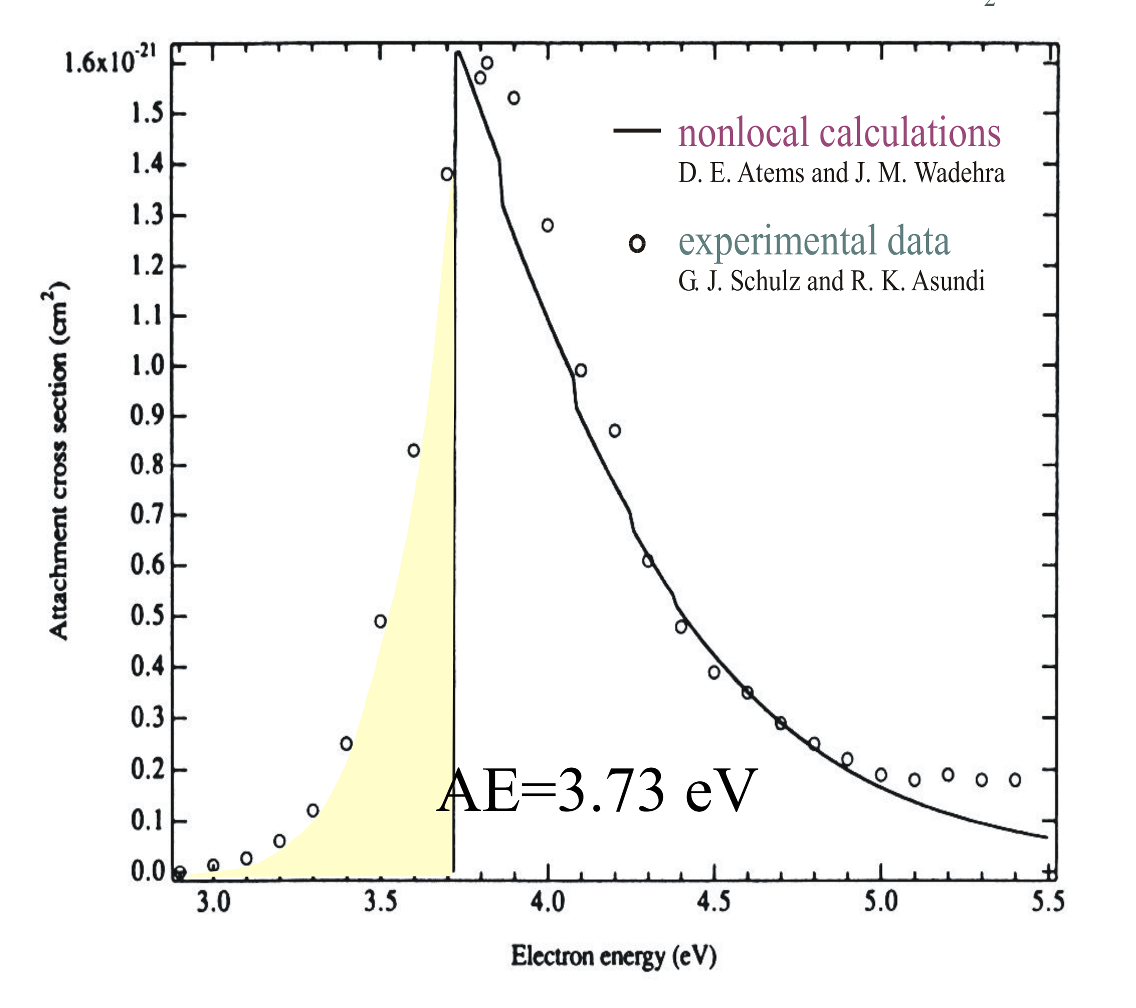




Electron Molecule Attachment

$H_2(v=0,J=0) + e \rightarrow H_2^-(^2\Sigma_u^+) \rightarrow H^-(1s^2) + H(1s)$

Cross section for H^- out of H_2.



Electron Molecule Attachment

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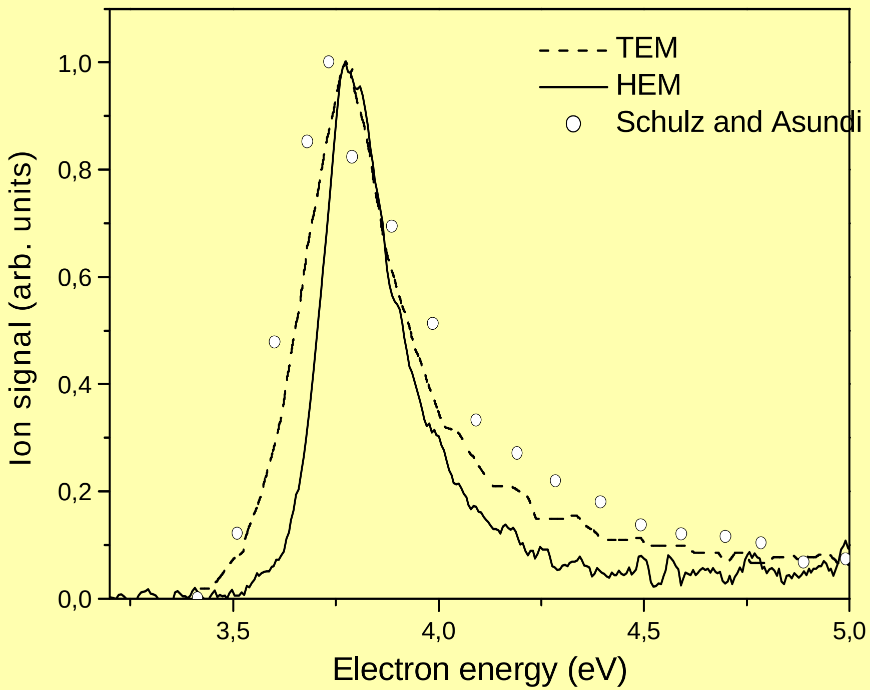

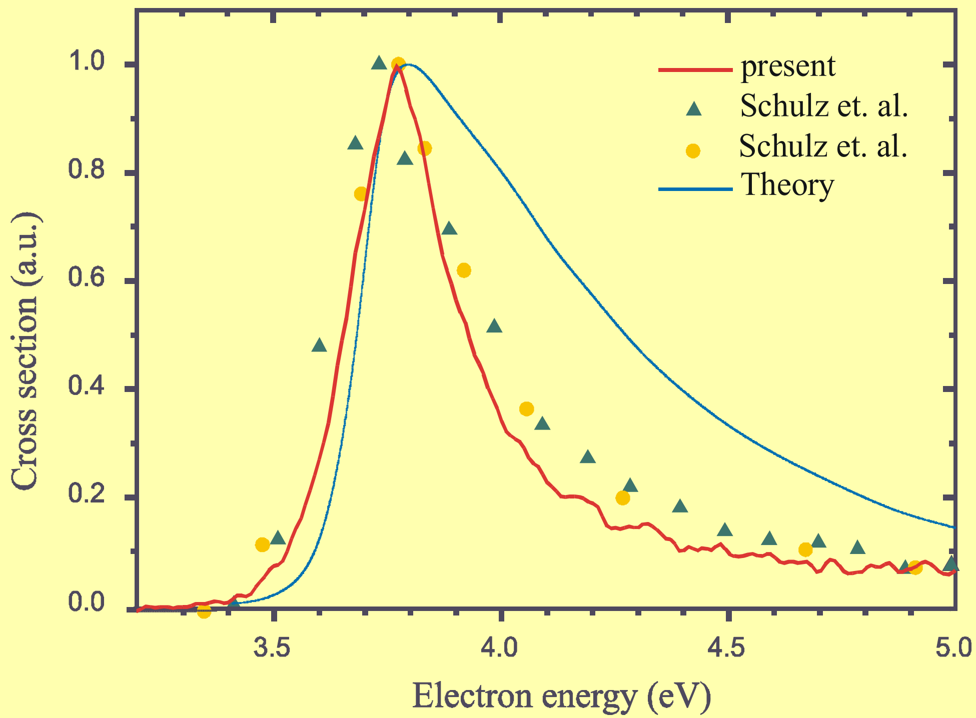

Electron Molecule Attachment

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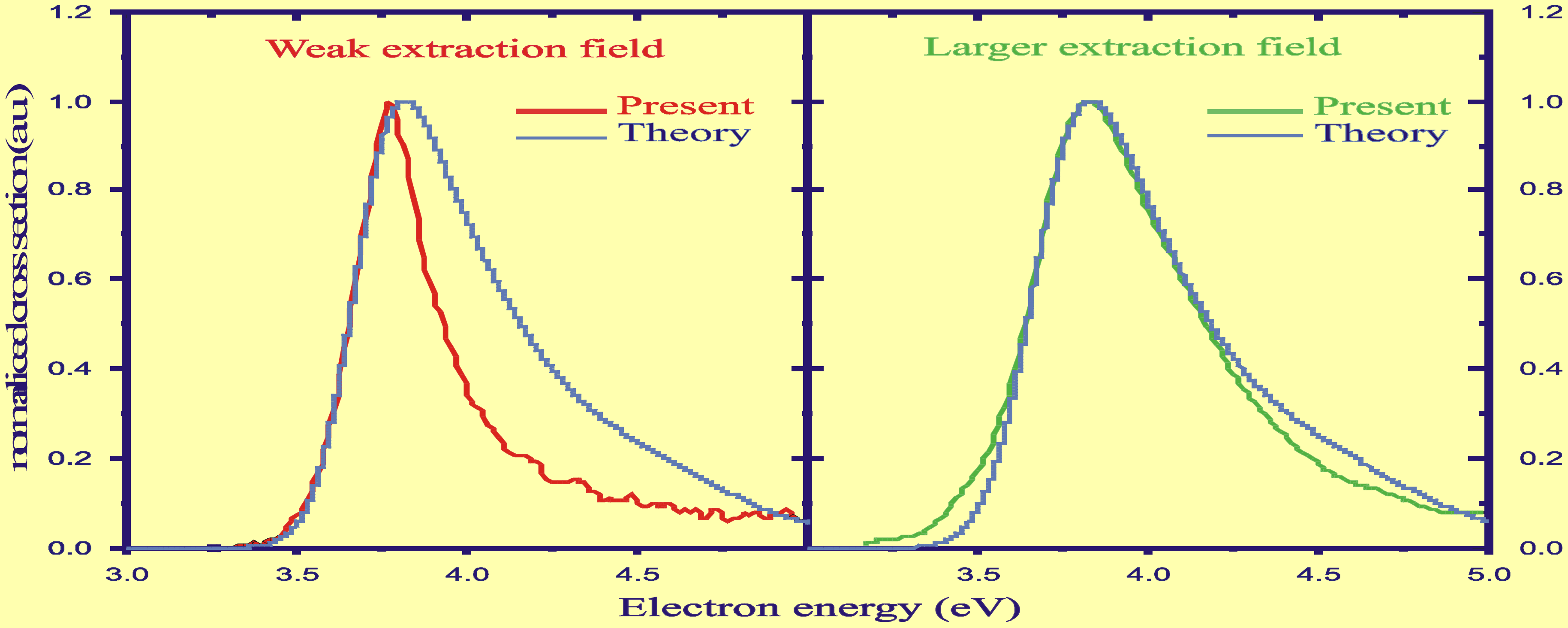
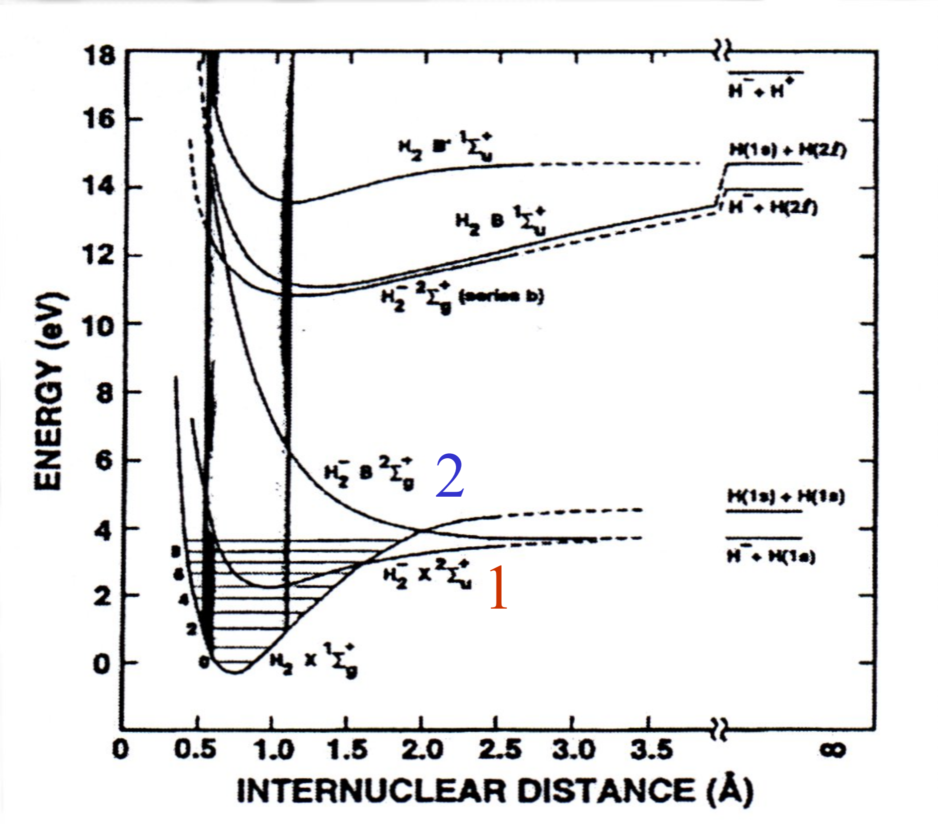


Theory: Hickmann 1991;Gauyaq 1985

Absolute calibration of the relative cross section

1: $H_2(v=0,J=0) + e \rightarrow H_2^- (^2\Sigma_u^+) \rightarrow H^-(1s^2) + H(1s)$

2: $H_2(v=0,J=0) + e \rightarrow H_2^- (^2\Sigma_g^+) \rightarrow H^-(1s^2) + H(2l)$



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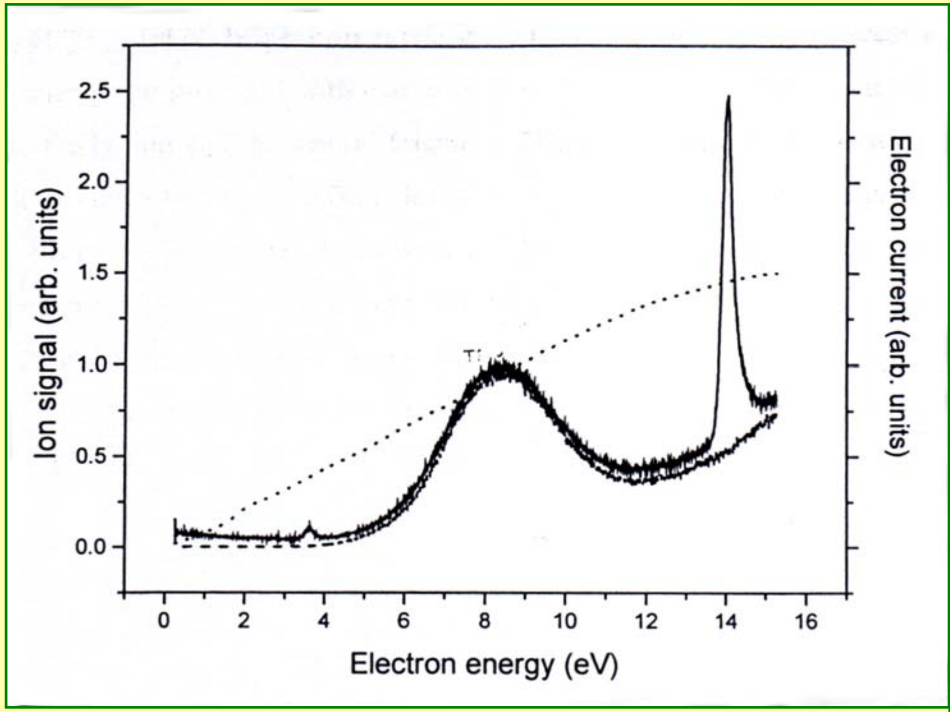
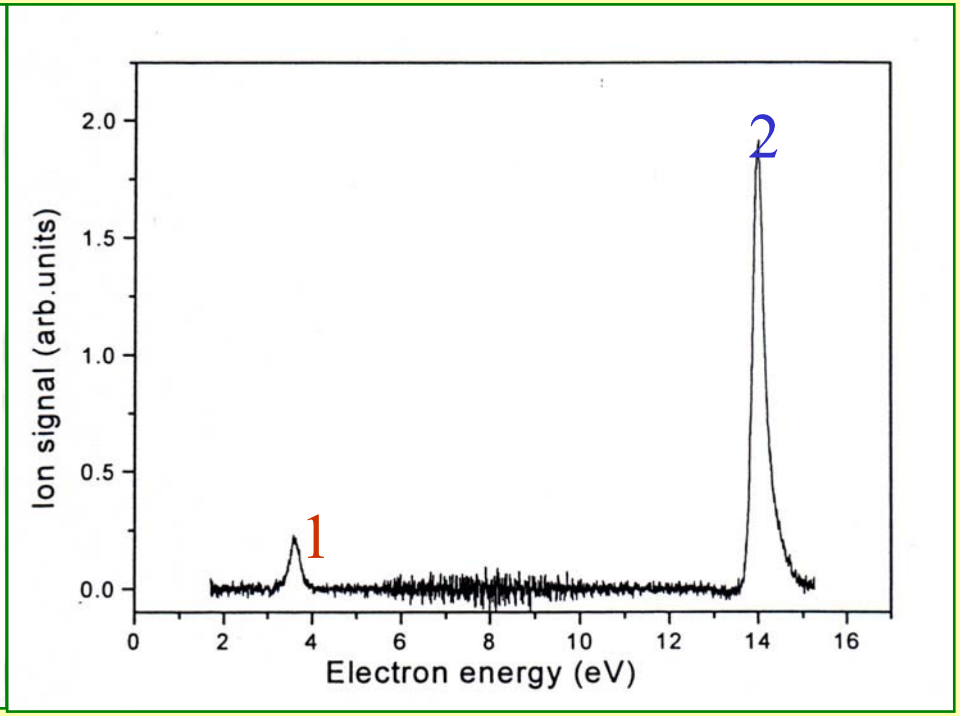


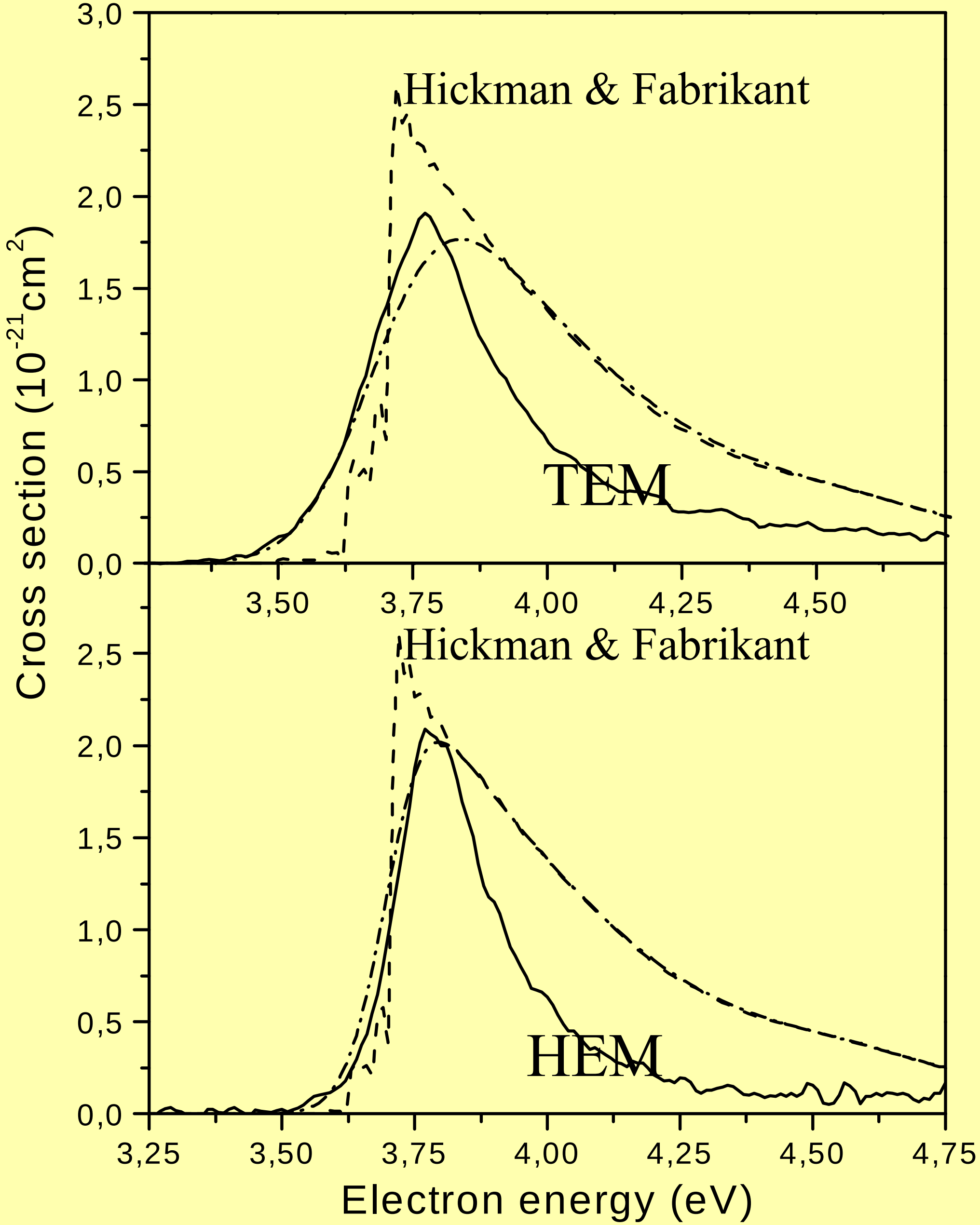


Measured peak ratio 1/2:	10%	HEM (100 meV)
	9%	TEM (200 meV)
	8%	Schulz (450 meV)

Calibration of relative cross sections using the measured peak ratio 1/2 and the measured absolute cross section for reaction 2:

Schulz 1965: 2.08×10^{-20} cm^2

Rapp 1965: 3.5×10^{-20} cm^2



Thus the peak σ:

instead of 1.6×10^{-21} cm^2

now 2.2×10^{-21} cm^2