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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

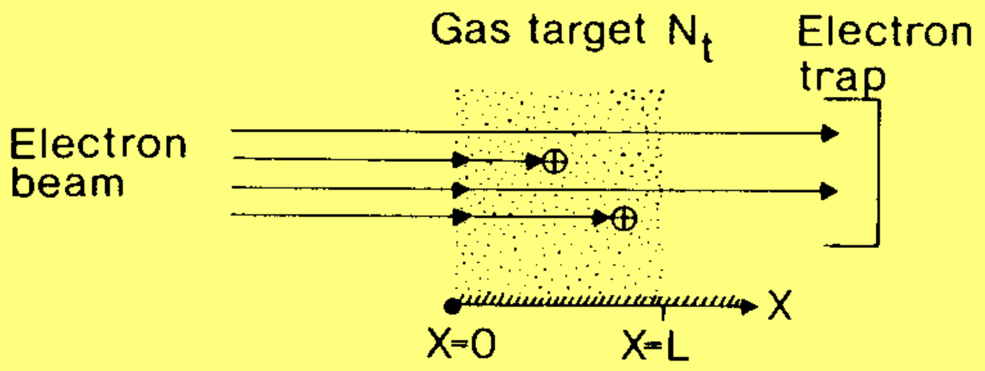
$$ABC + e \rightarrow [ABC^{+}]^{*} \rightarrow A^{+} + BC + KER$$

Properties to be determined:

$\sigma = \sigma(E)$, KER and AE (ions)

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 law and assuming single collision conditions: $N_t L \sigma_t << 1$

$$i_t = i_e N_t L \sigma_t$$

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

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

$$n(x)_e = n(0)_e \exp(-N_t q x). \tag{18}$$

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

$$n(L)_i = n(0)_e N_t q_c L, \tag{19}$$

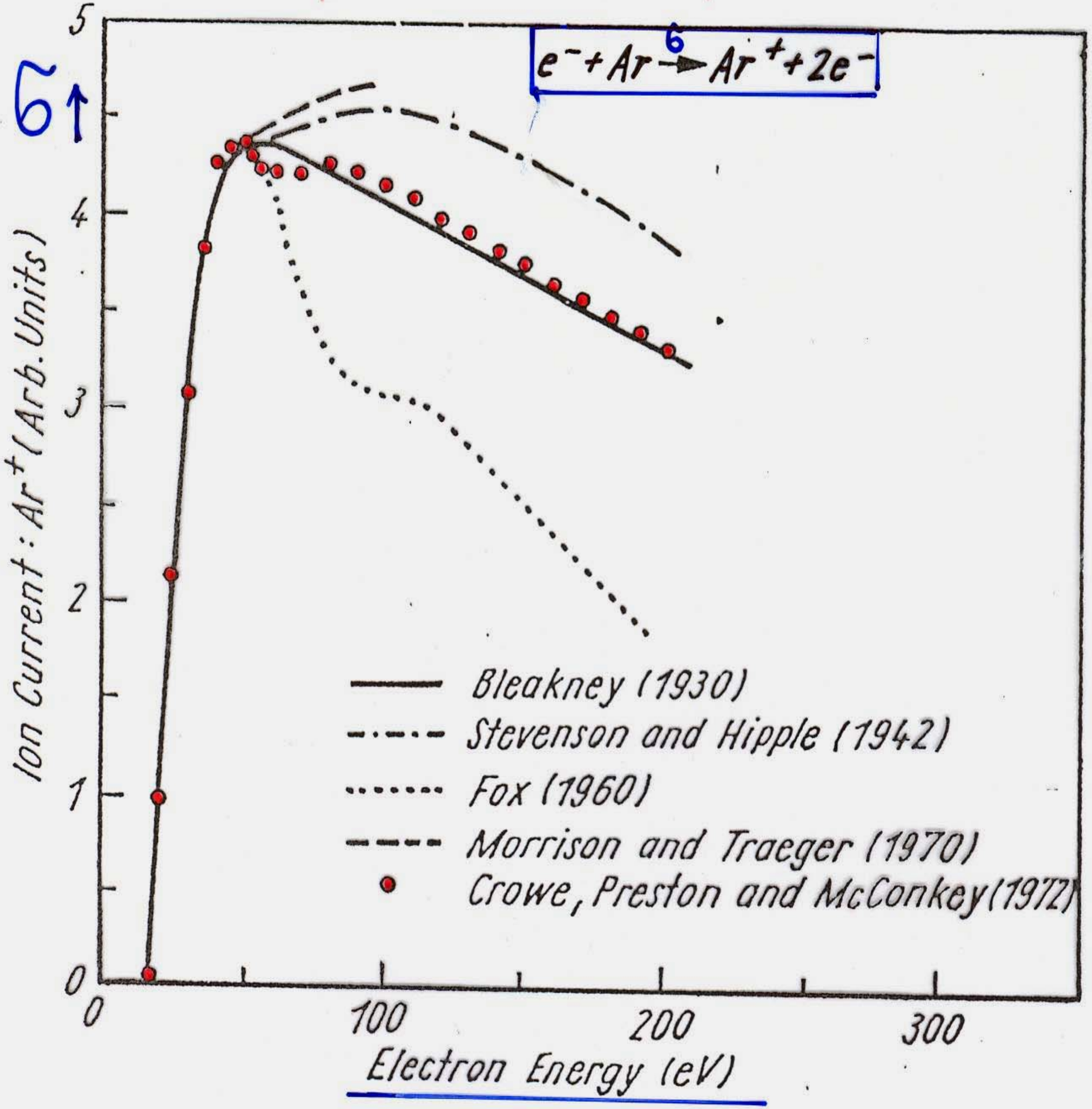
where q_c is the *counting ionization cross section* in square centimeters. The total positive-ion current i_t produced in this interaction volume is given by

$$i_t = n(0)_e e N_t q_t L, \tag{20}$$

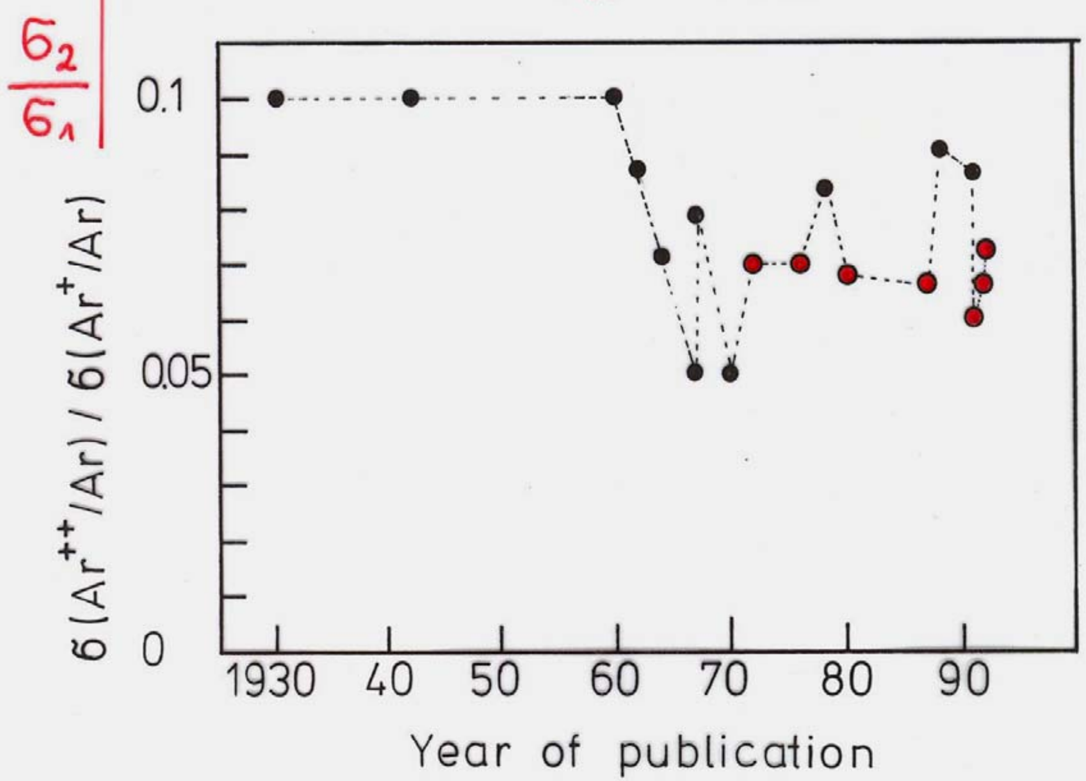
where q_t is the *total ionization cross section*. If the produced ions are analyzed with respect to their mass m and charge ze, the respective individual ion currents are given by

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

State of the art as of 1980!

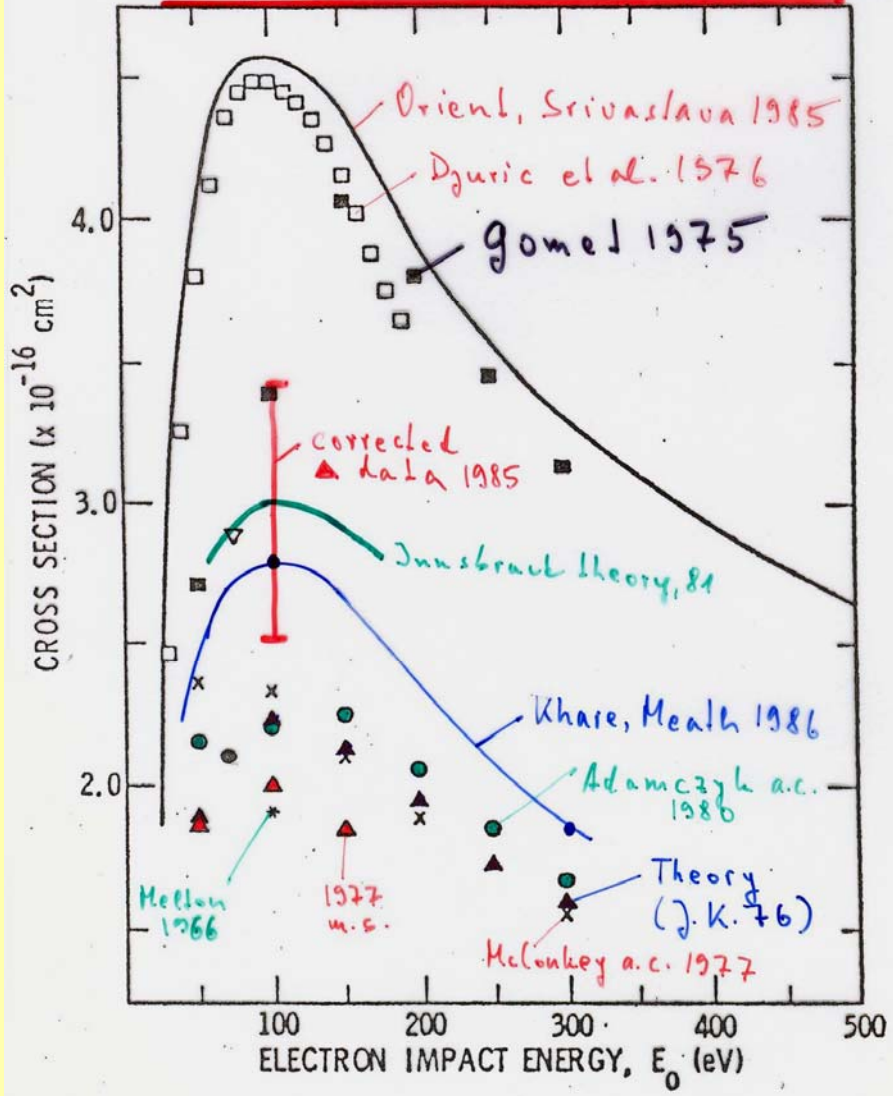


$$Ar + e \xrightarrow{\sigma_1} Ar^{+} + 2e$$
$$\xrightarrow{\sigma_2} Ar^{2+} + 3e$$



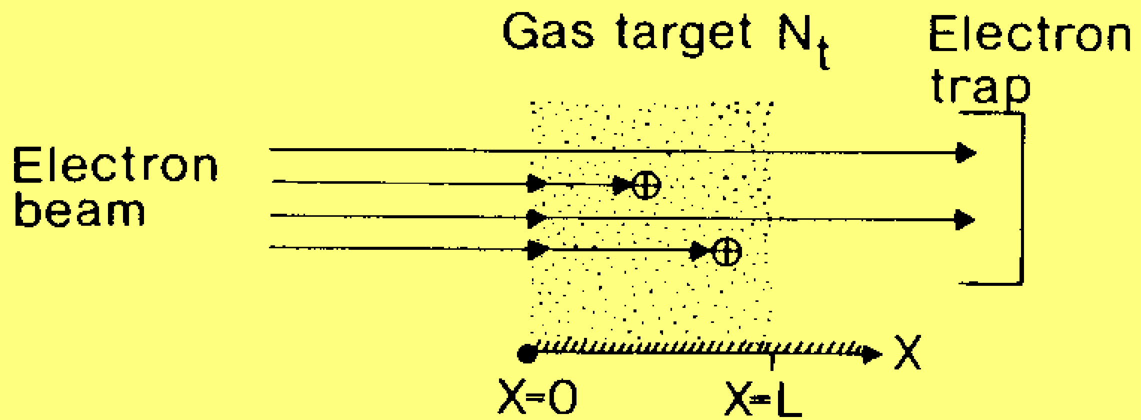
Theoretical results: 1972 0.15
1978 0.18
0.20

$NH_3 + e \rightarrow$ ions 1986:



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

Absolute calibration:

$$i_{ion} = i_e N_t L \sigma$$

N_t : Accurate number density determination: Methods

1. Absolute pressure measurement

2. Relative measurements:

- Summation method (σ_{total})
- Relative flow methods ($\sigma_X / \sigma_{Stand}$)
  - effusive flow method
  - constant gas porous plug method
- NEPO method (Negative/positive ion method)
  [Dünser et al., Phys.Rev.Letters, 74 (1995) 3364]

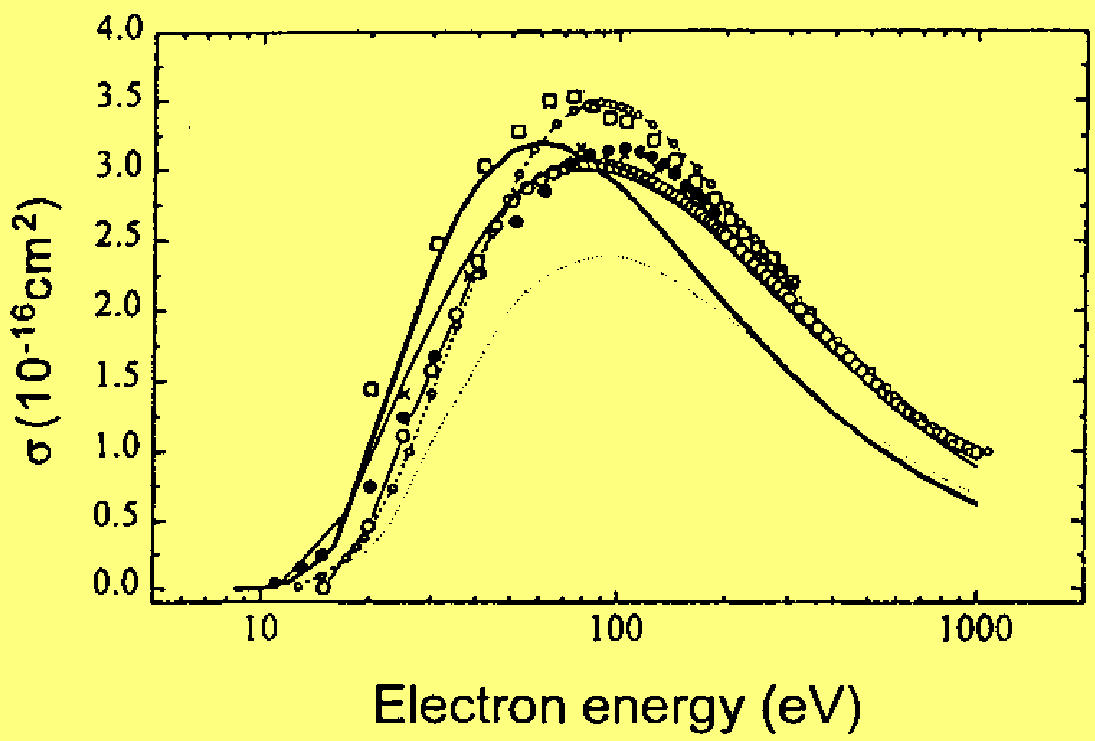
$$\sigma/(C_{60}^+)/\sigma/(C_{60}^-) = \boldsymbol{k}\ i(C_{60}^+)/i(C_{60}^-)$$

$$\sigma/(SF_4^+)/\sigma/(SF_4^-) = \boldsymbol{k}\ i(SF_4^+)/i(SF_4^-)$$

Electron impact ionization

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

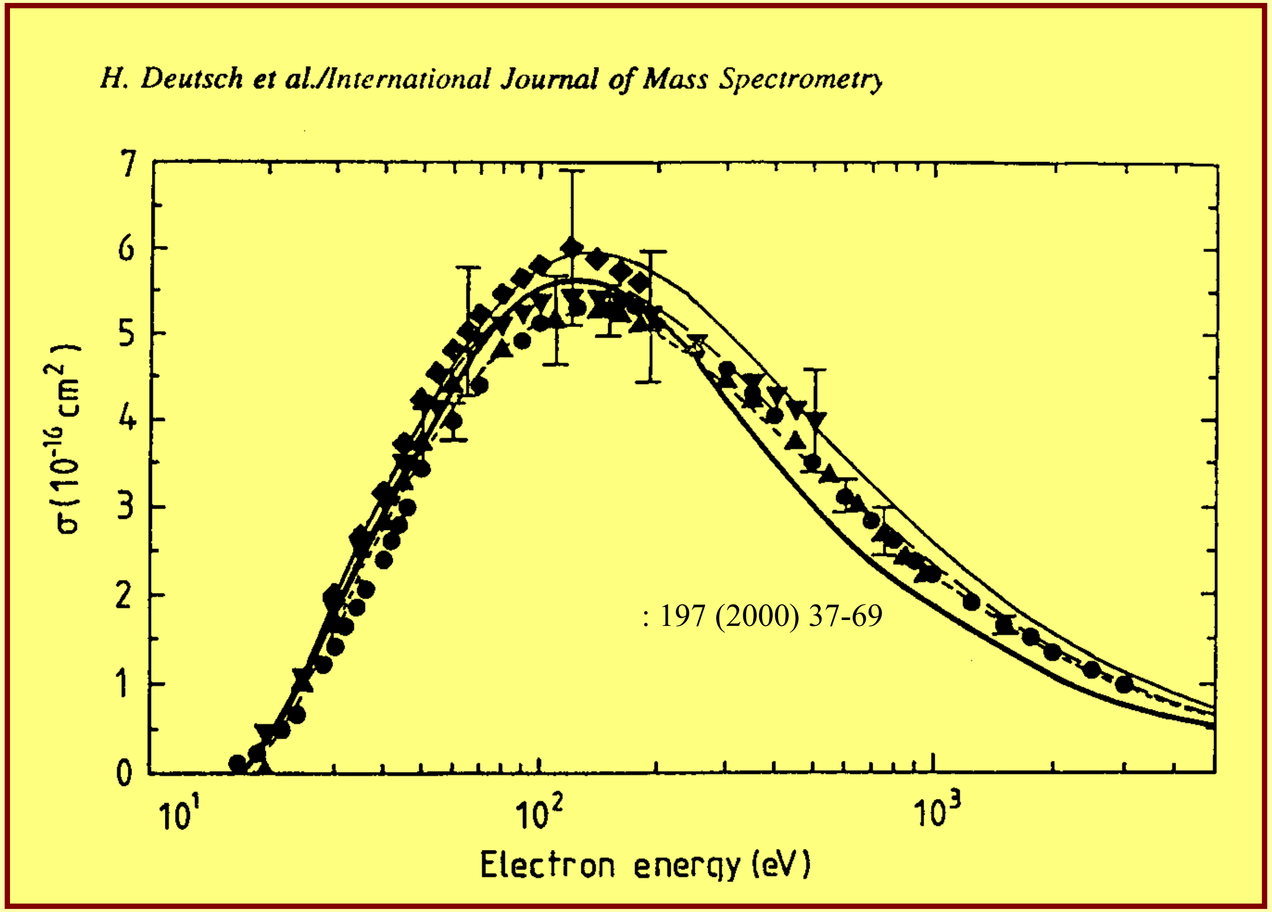
Thick line: Deutsch et al. 1999 (DM)

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

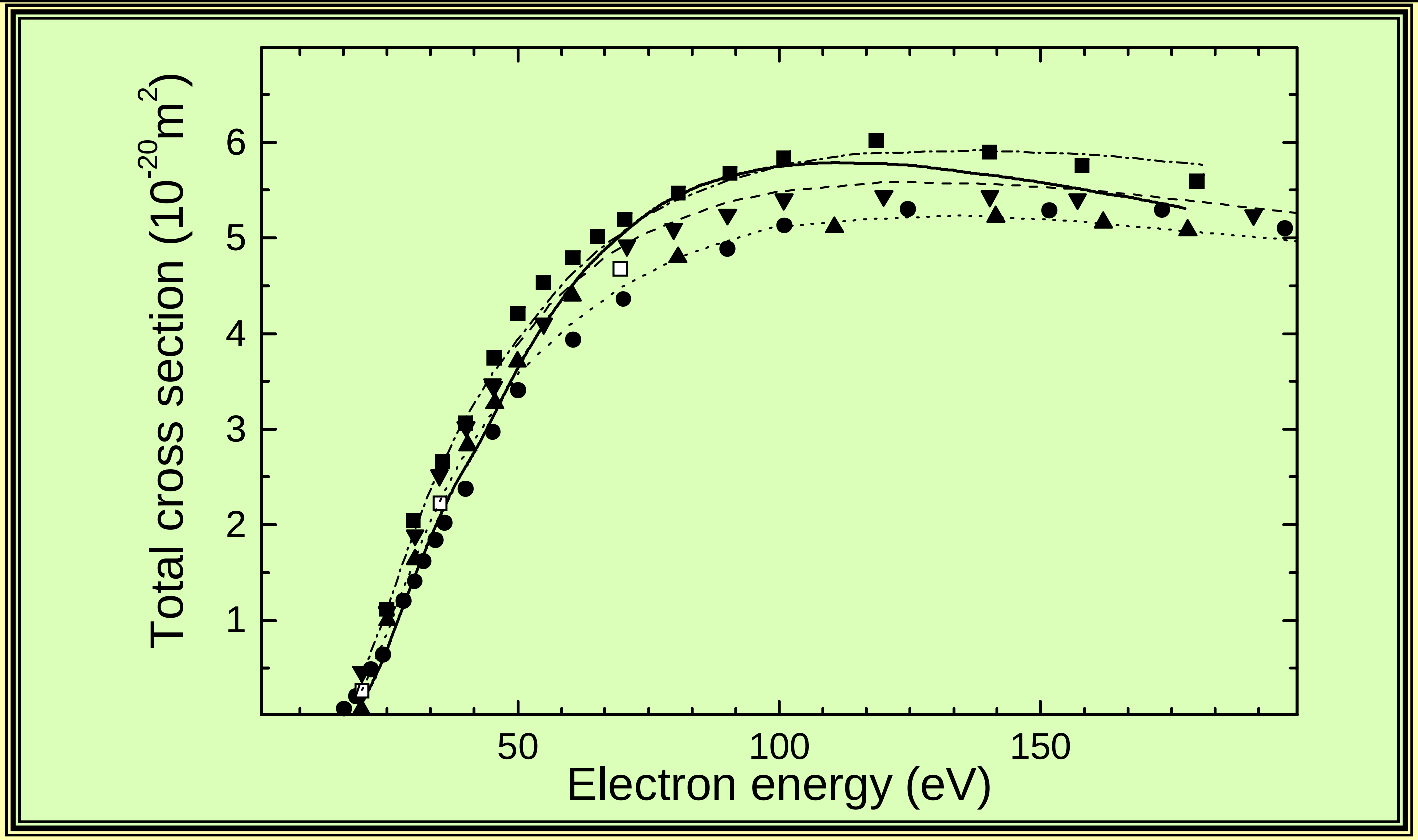


Full line: DM calculation 2000

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

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



Full line: DM calculation 1992

Interrupted lines: BEB calculations 1998

Open square: Beran 1969; full squares: Poll 1992; inverted triangles: Bruce 1993; full triangles: Rao 1997; filled circles: Nishimura 1998 universität innsbruck

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High resolution electron impact ionization of molecules

Ion Physics

Institut Ionenphysik

$$ABC + e \rightarrow ABC^+$$

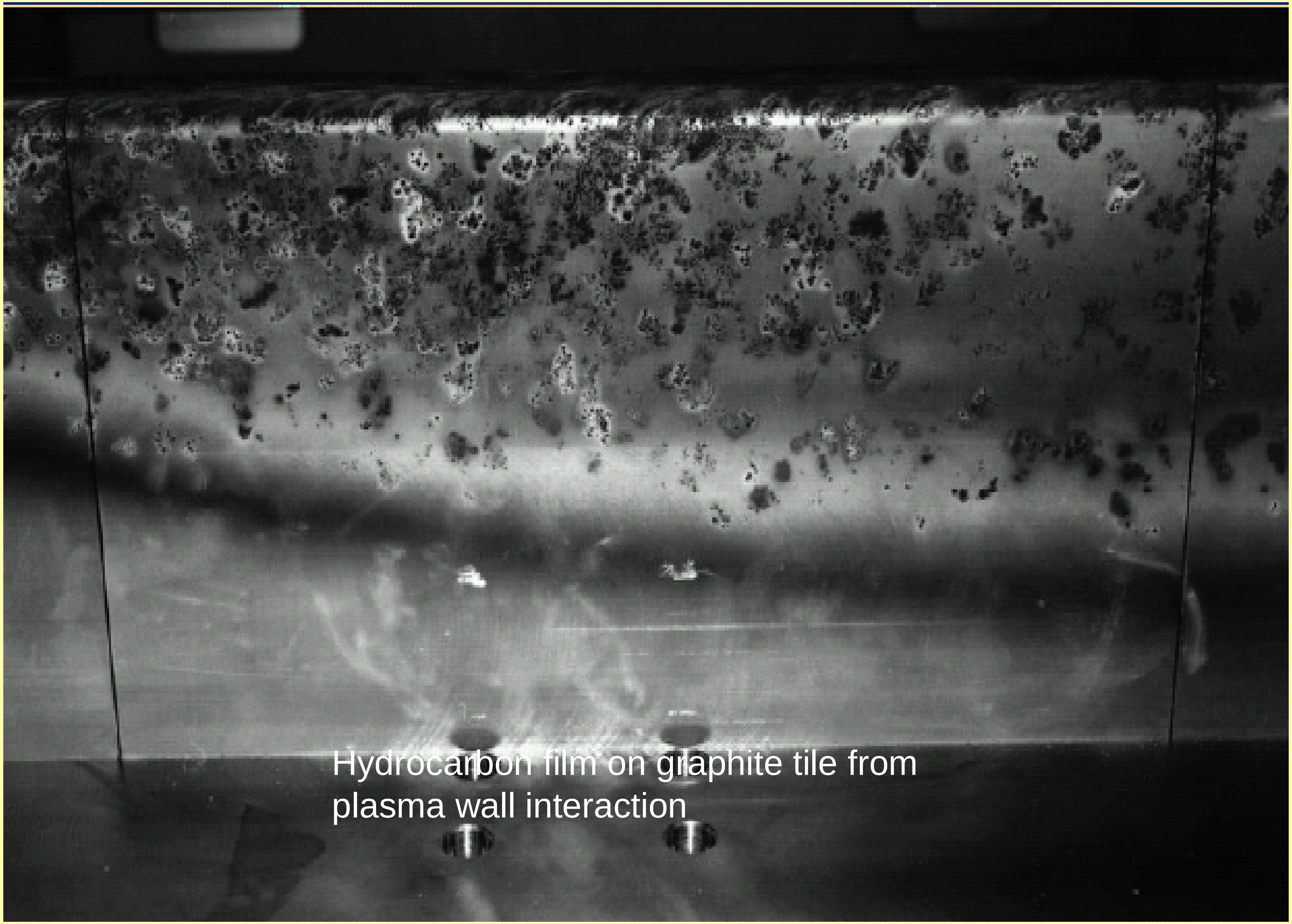
$$ABC + e \rightarrow A^+ + BC + KER$$

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

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

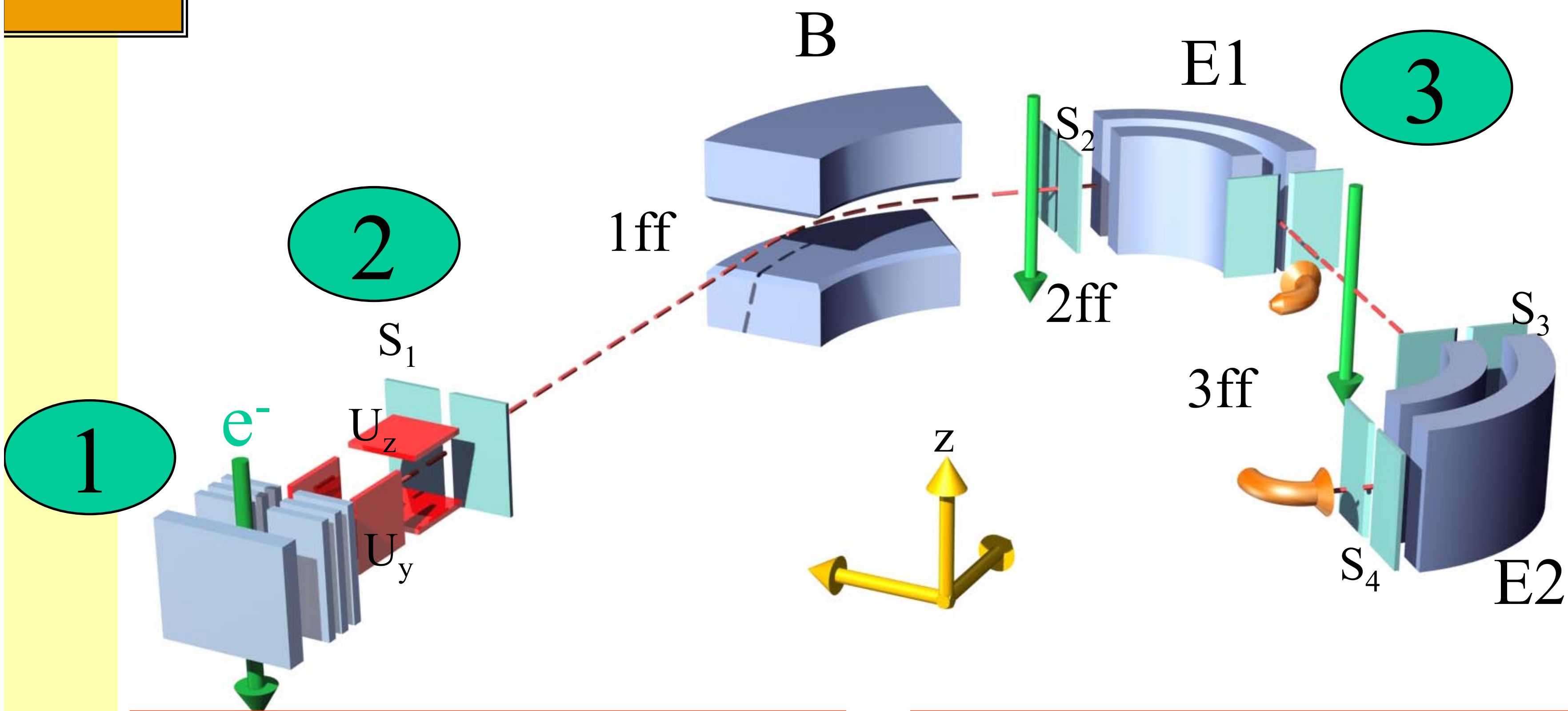
Motivation for hydrocarbons

- 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

Ionization cross sections from:

$$i_{ion} = i_e N_t L \sigma$$

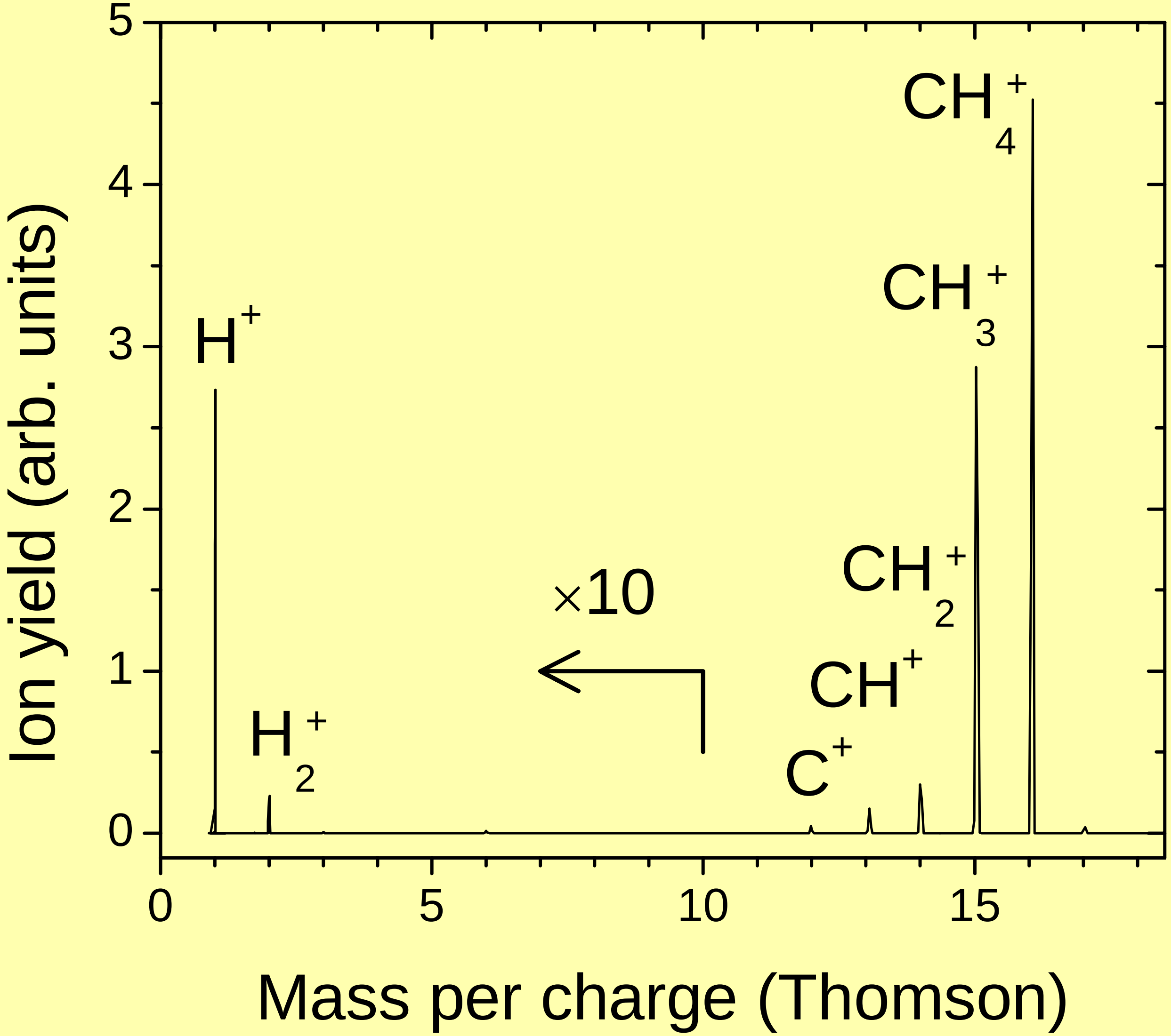


$AB + e \rightarrow AB^+$
$\rightarrow A + B^+ + KER$
$\rightarrow A^+ + B + KER$

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

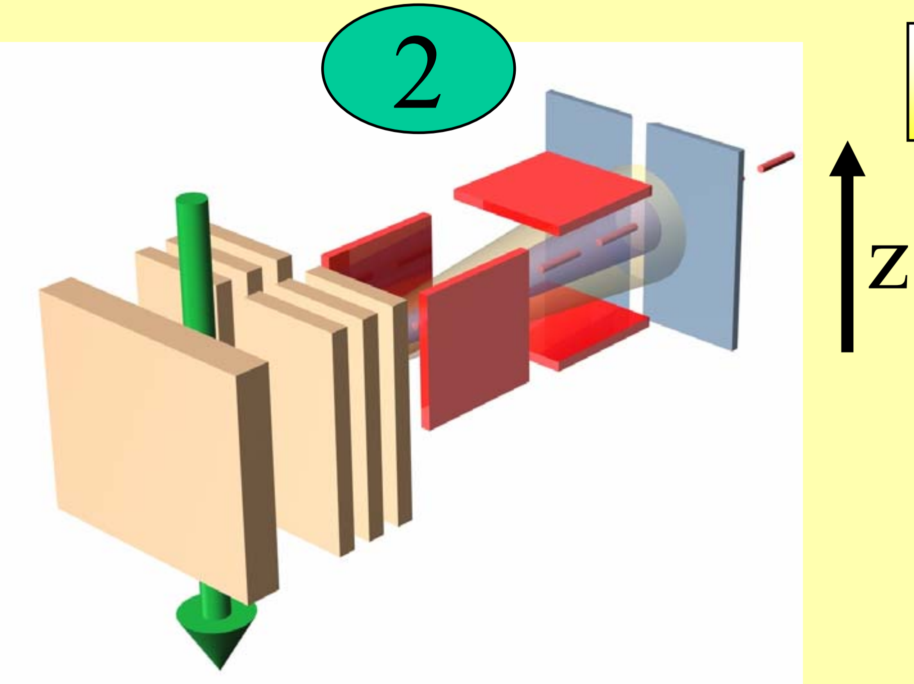
Electron ionization of molecular ions:
$CH_4 + e \rightarrow$ ions

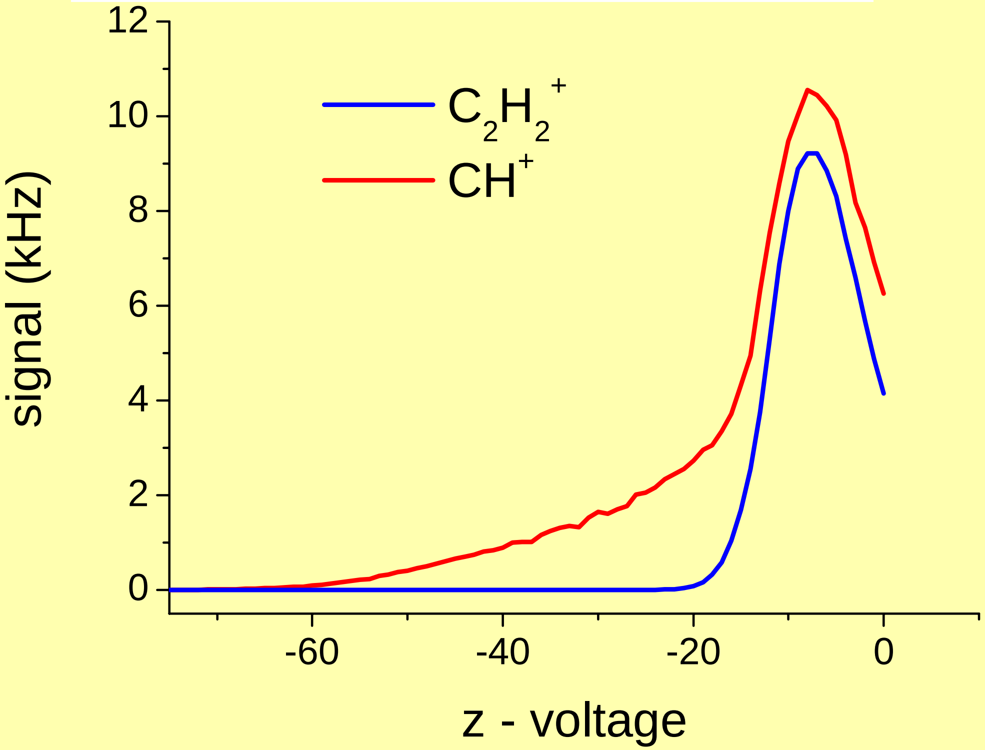
Mass spectrum



100 eV
10 μA
500K
$6x10^{-5}$ Pa

$$C_2\,H_2 + e \rightarrow C_2H_2^+ \text{, etc.}$$





Measurement z - profile

↓

Smoothing (with gauss) then differentiate → distribution function

↓

$$E_{kin} = c \times U_z^2$$

↓

c from parent ions

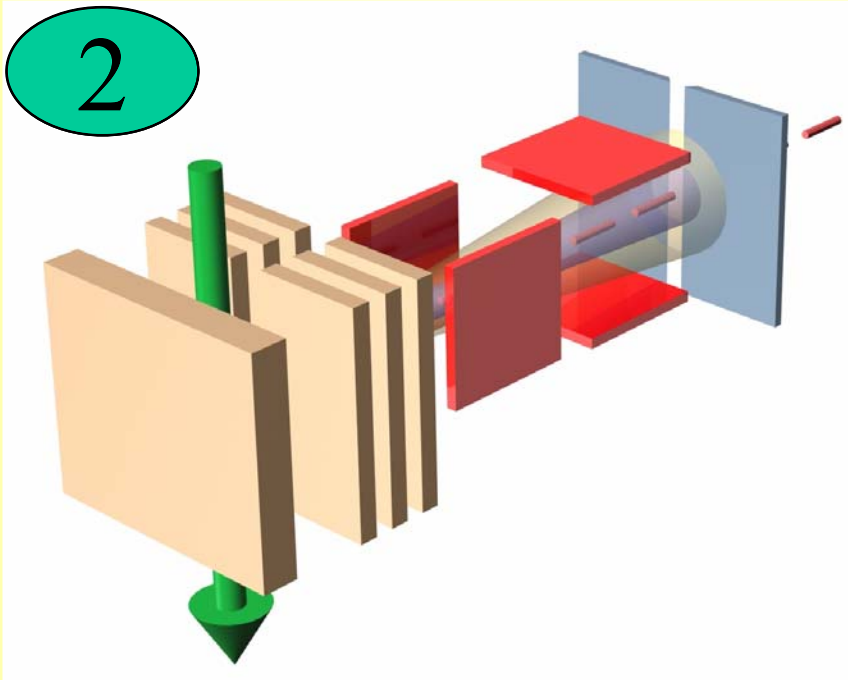
↓

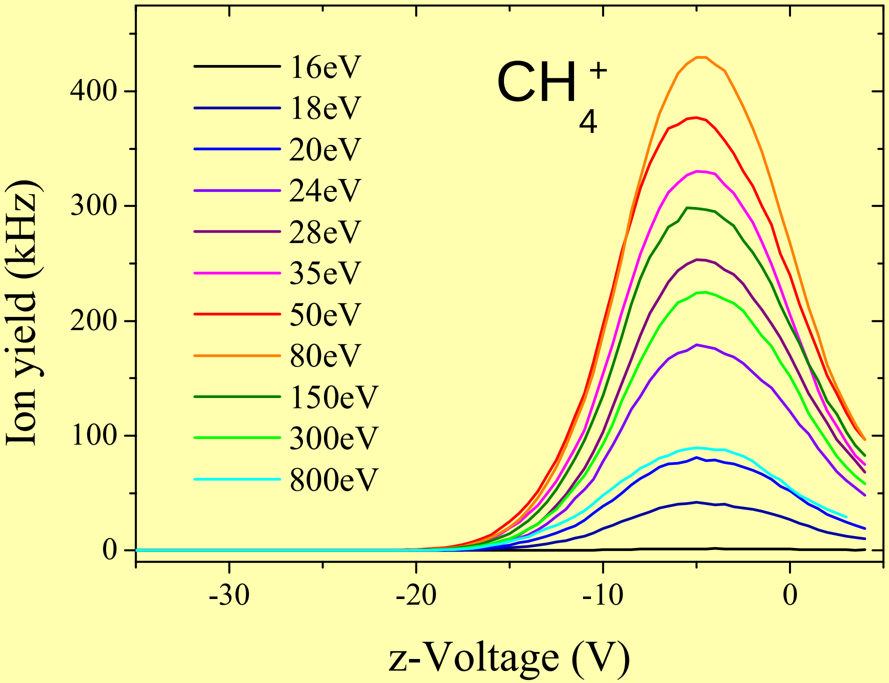
Include discrimination

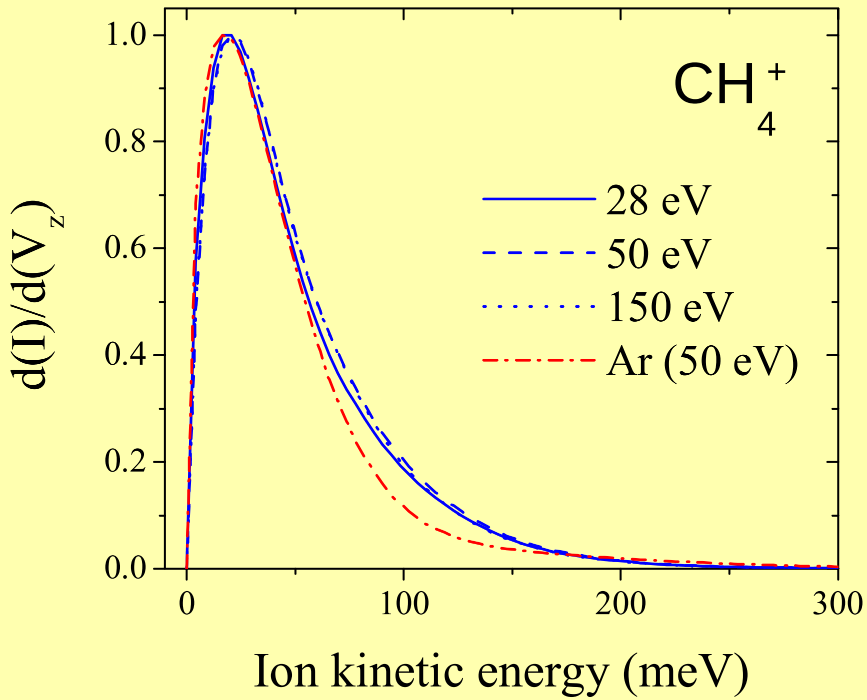
Electron ionization of molecules:

$CH_4 + e \rightarrow CH_4^+$

z-deflection curves and KERD

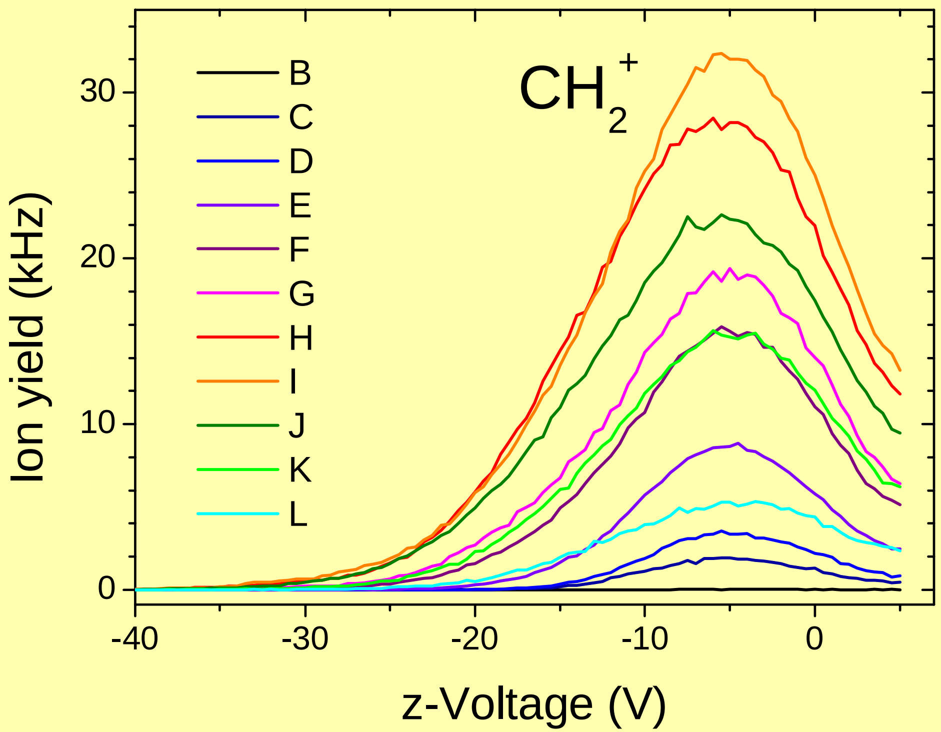


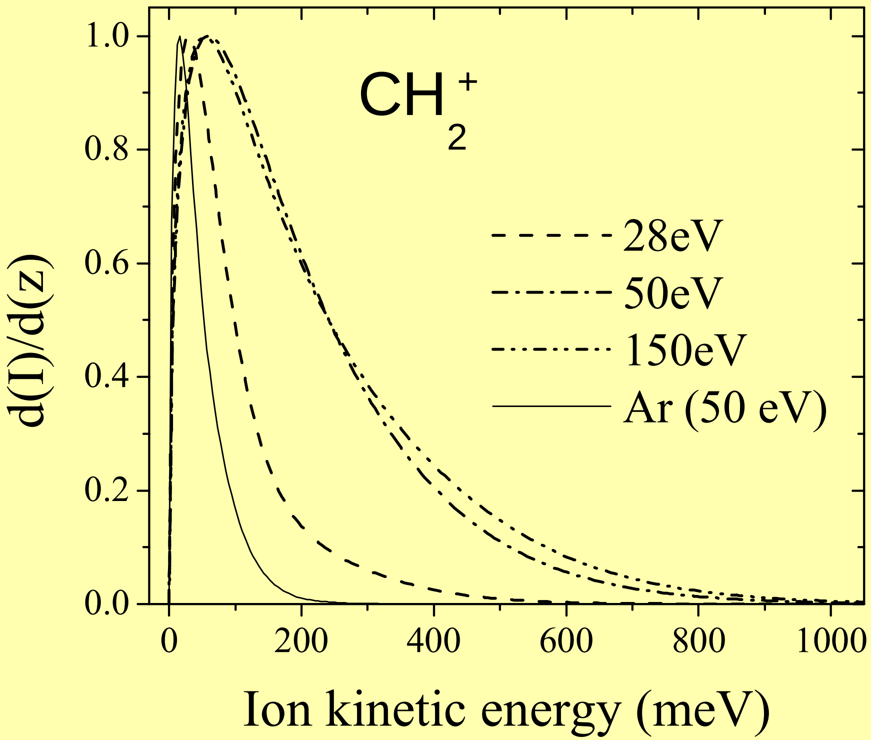




Dissociative ionization of molecules: $CH_4 + e \rightarrow CH_2^+$

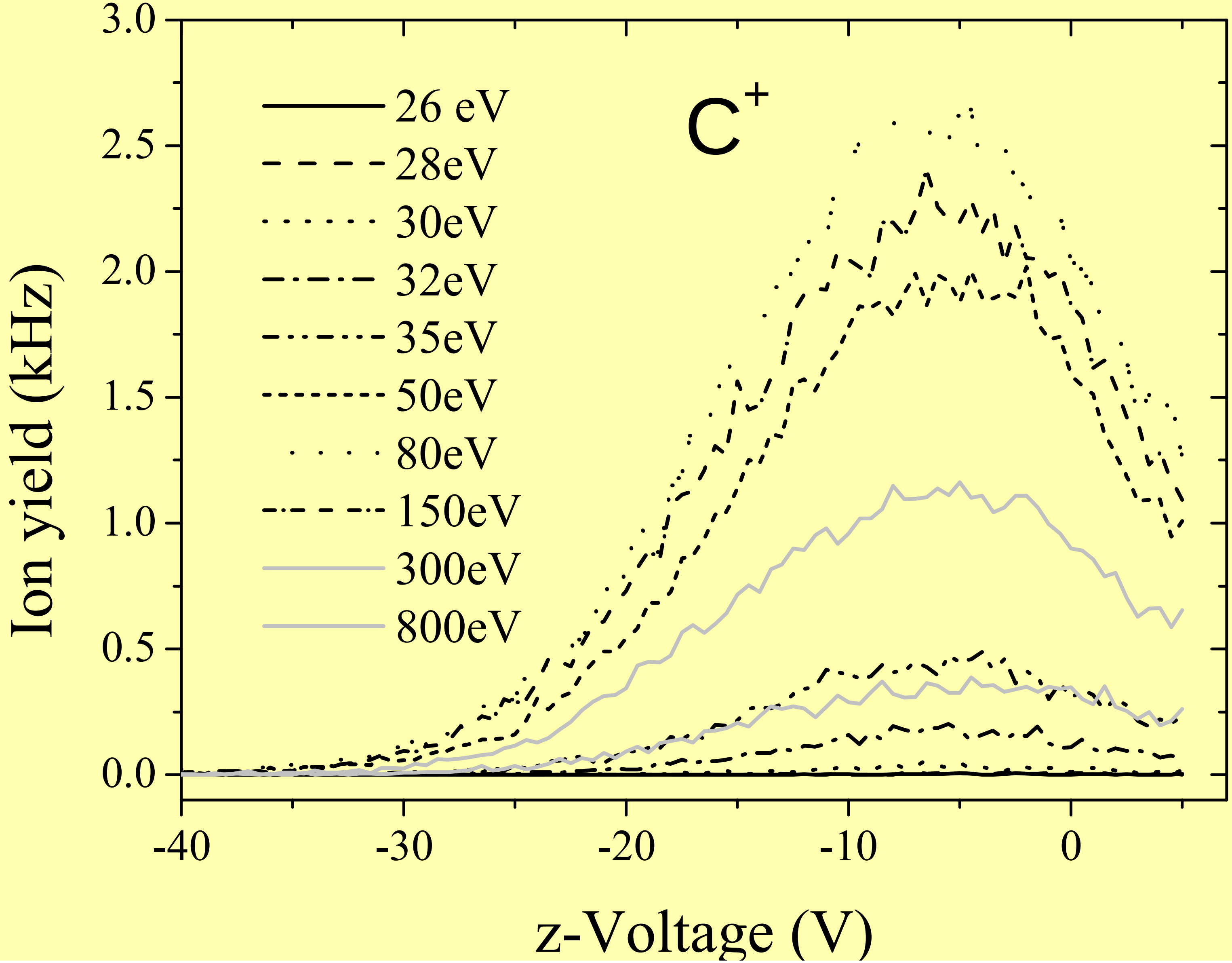
z- deflection curves and KERD





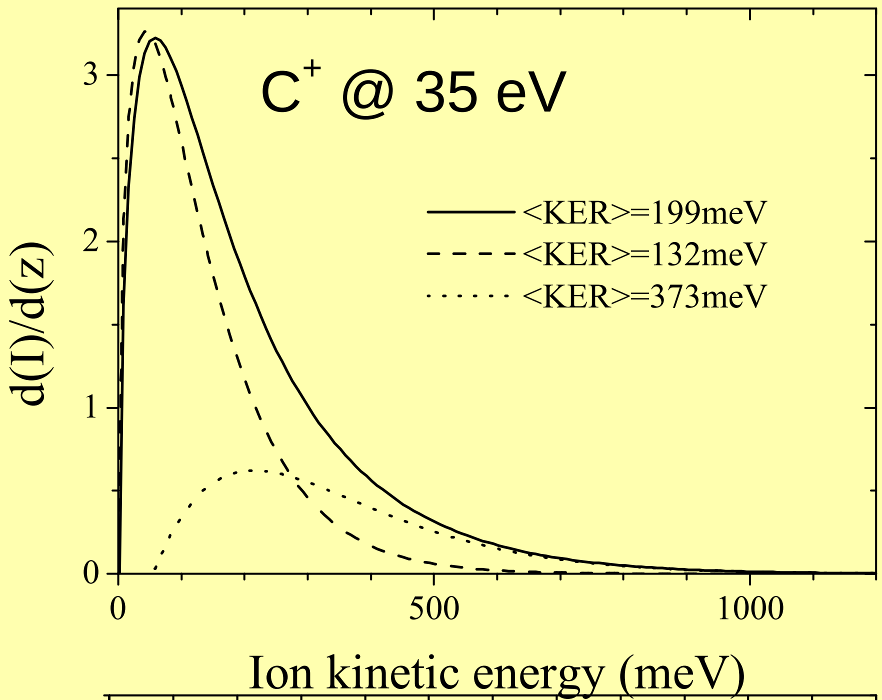
Electron ionization of molecular ions:
$CH_4 + e \rightarrow C^+$

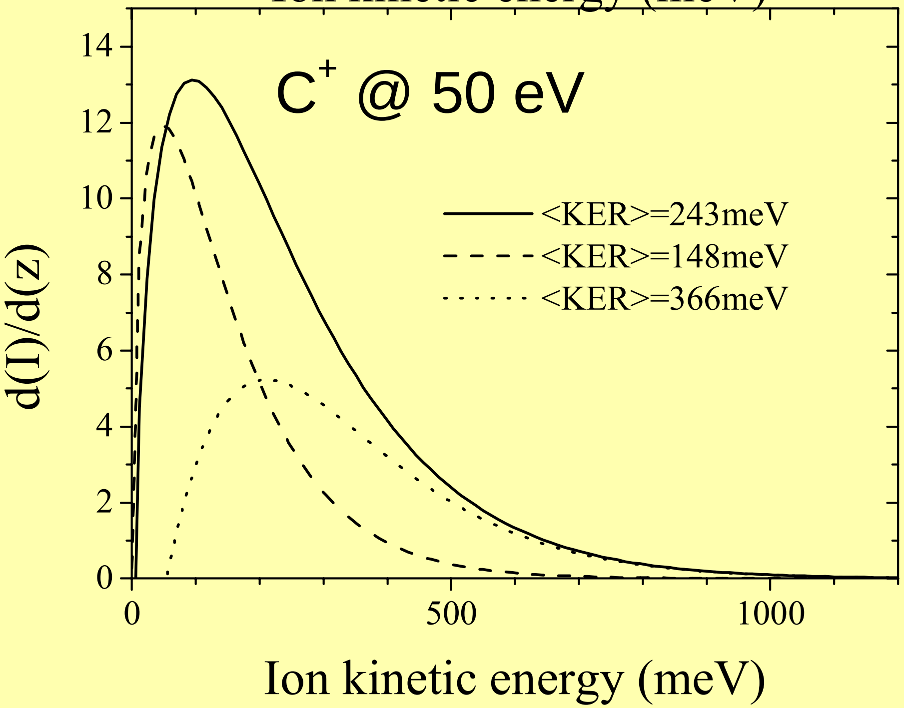
z-deflection curves

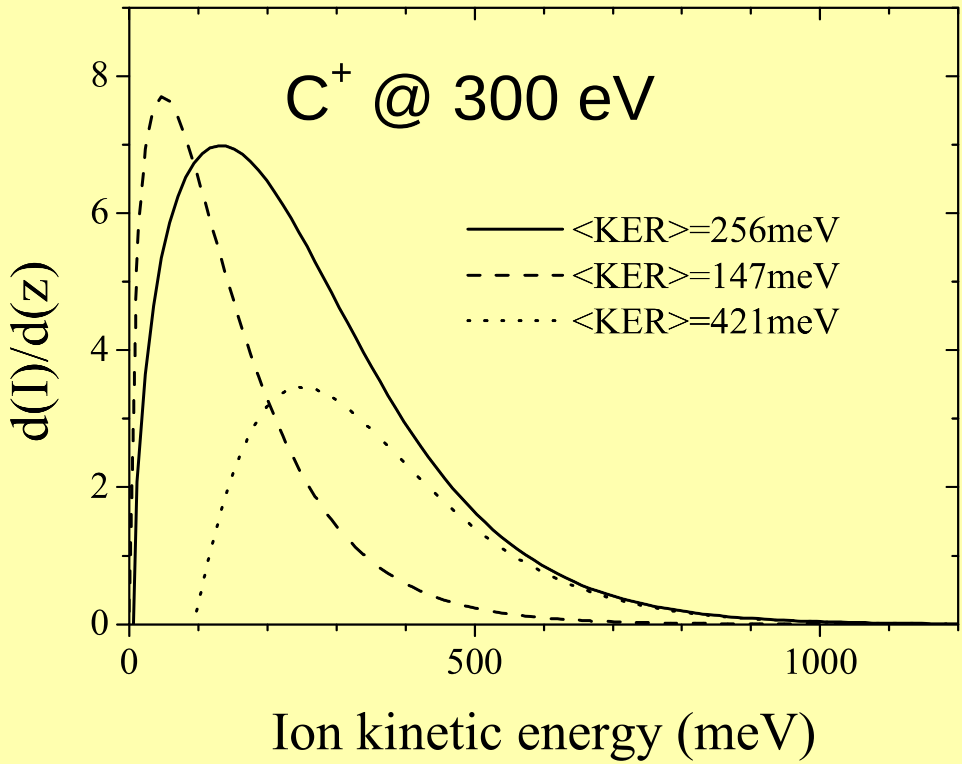


$CH_4 + e \rightarrow C^+$

KERD

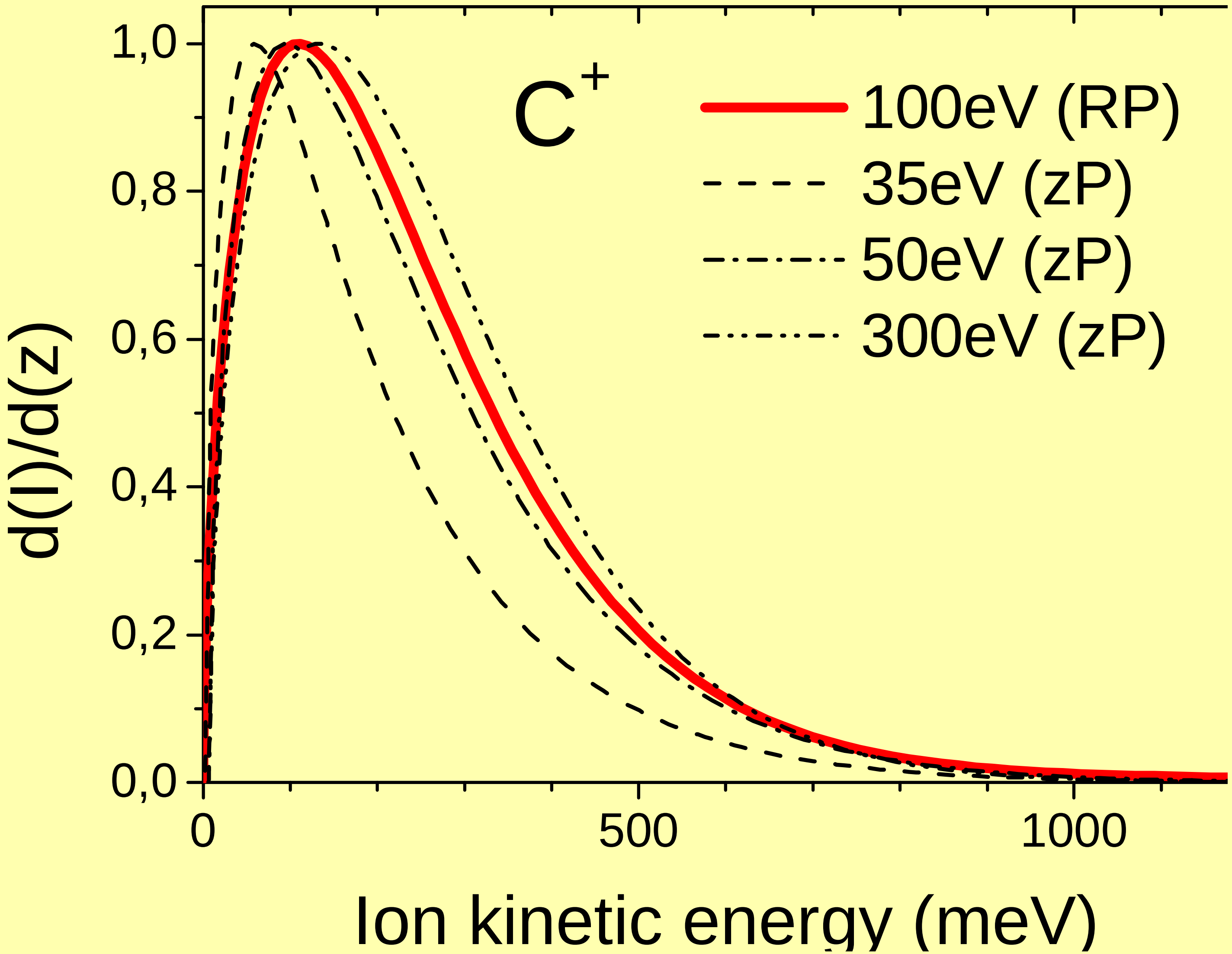






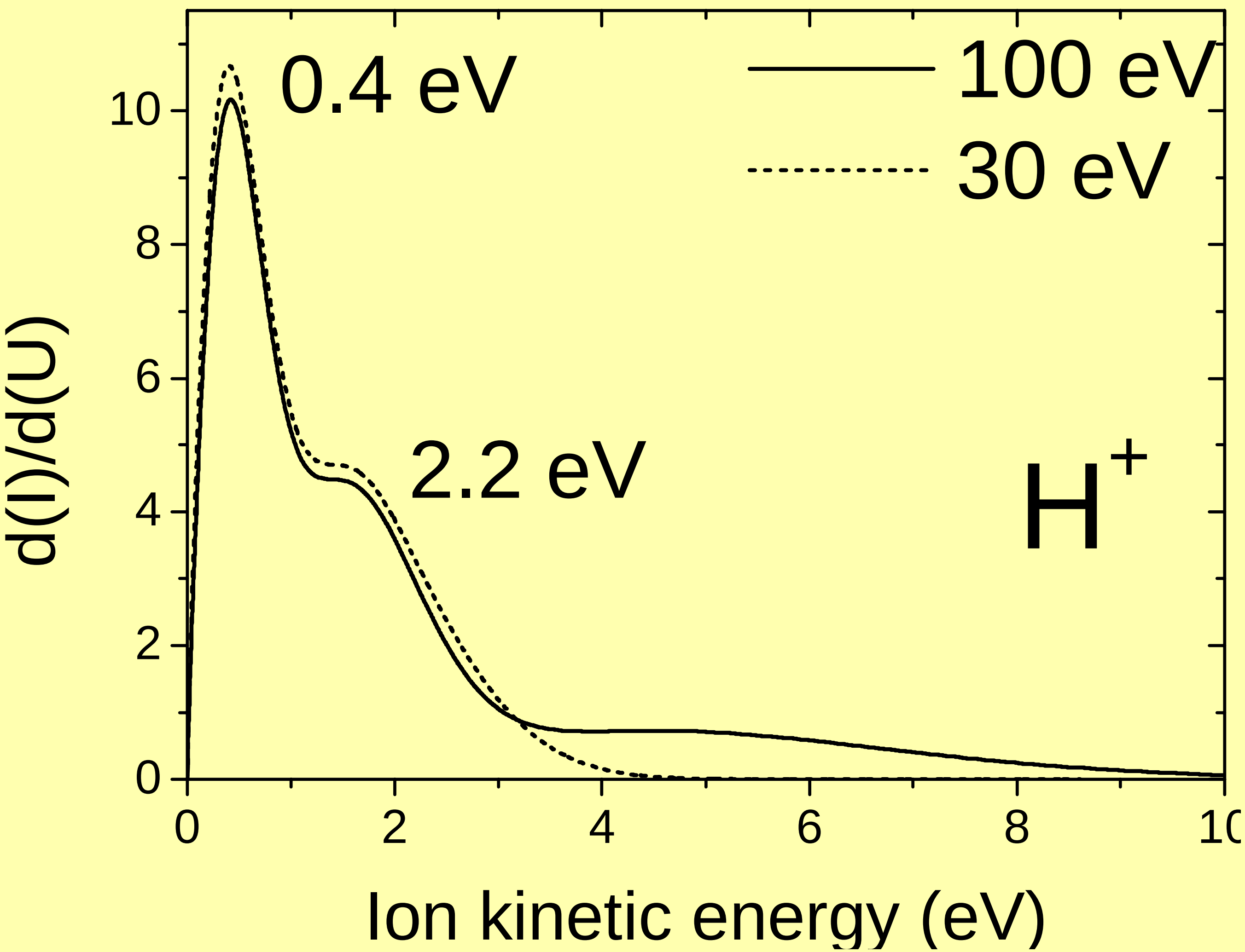
$CH_4 + e \rightarrow C^+$

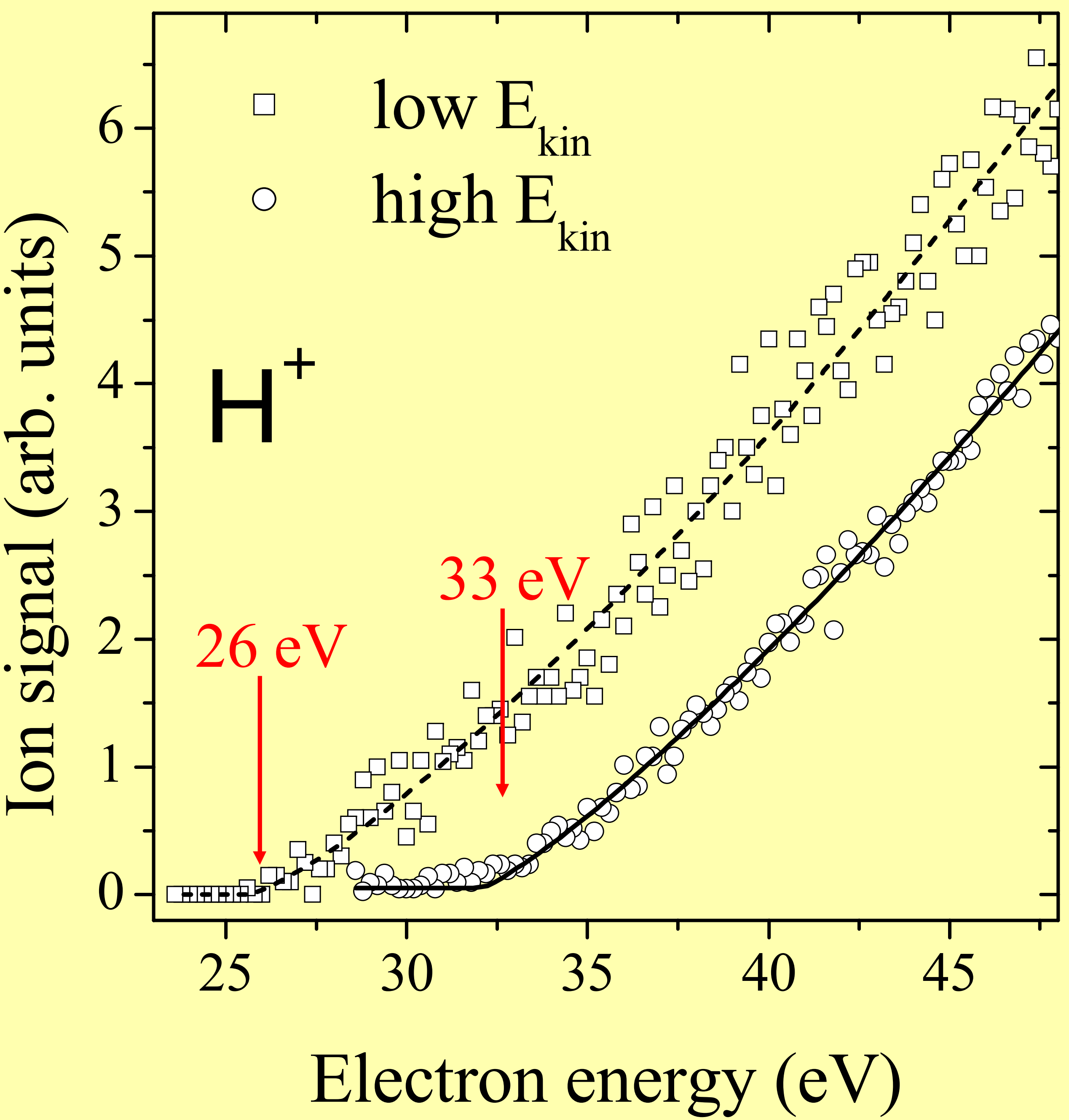
KERD



Electron ionization of molecules:
$CH_4 + e \rightarrow H^+$

KERD derived from retarding potential





Threshold behaviour of energy differential cross section:

$CH_4 + e \rightarrow H^+$

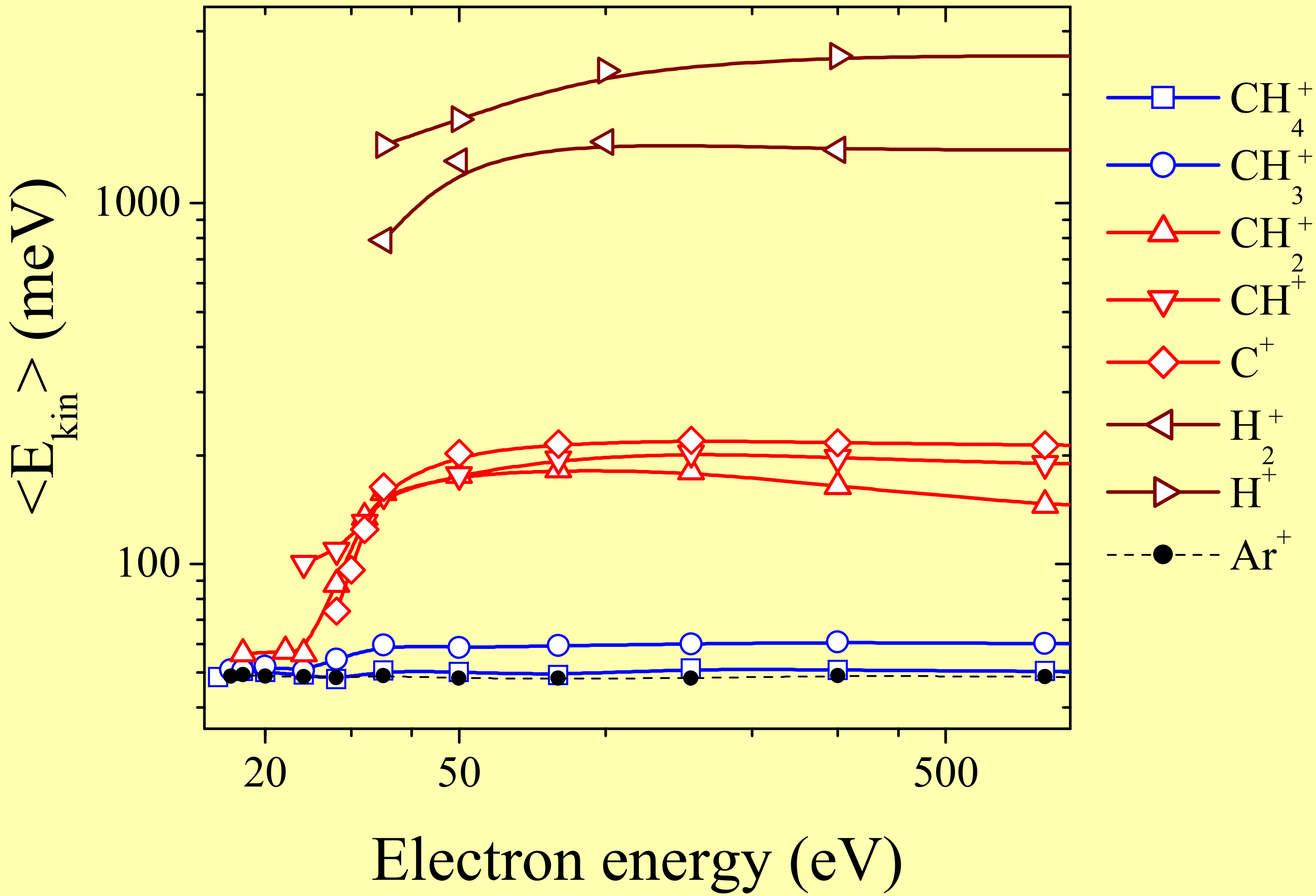
Latimer et al., JPB, B32(1999)2667: photoionization:

26.6eV: $(2a_1)^{-1}$ state

35eV: double ionization

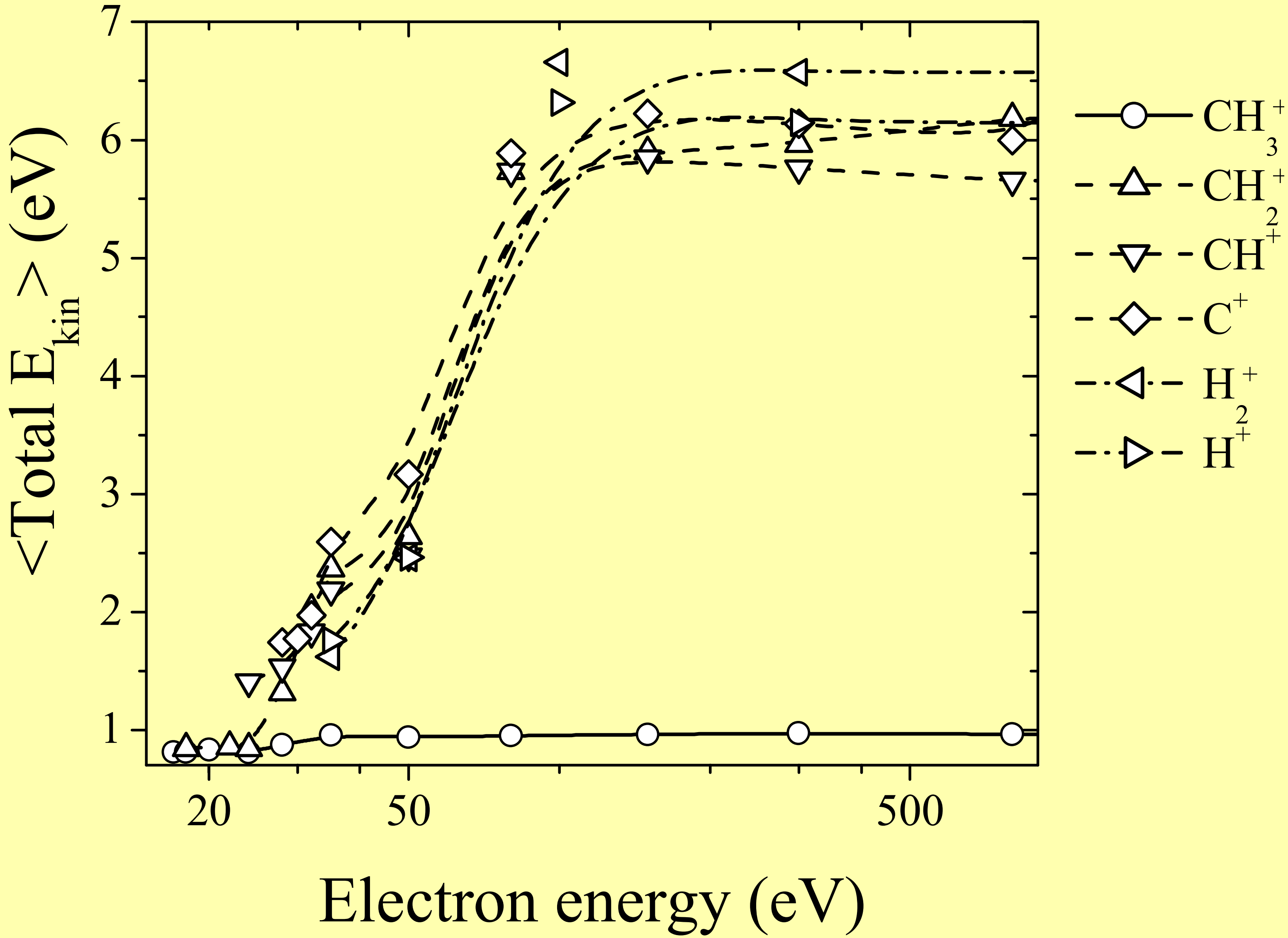
Electron ionization of molecular ions: $CH_4 + e \rightarrow$ ions

Average ion kinetic energy

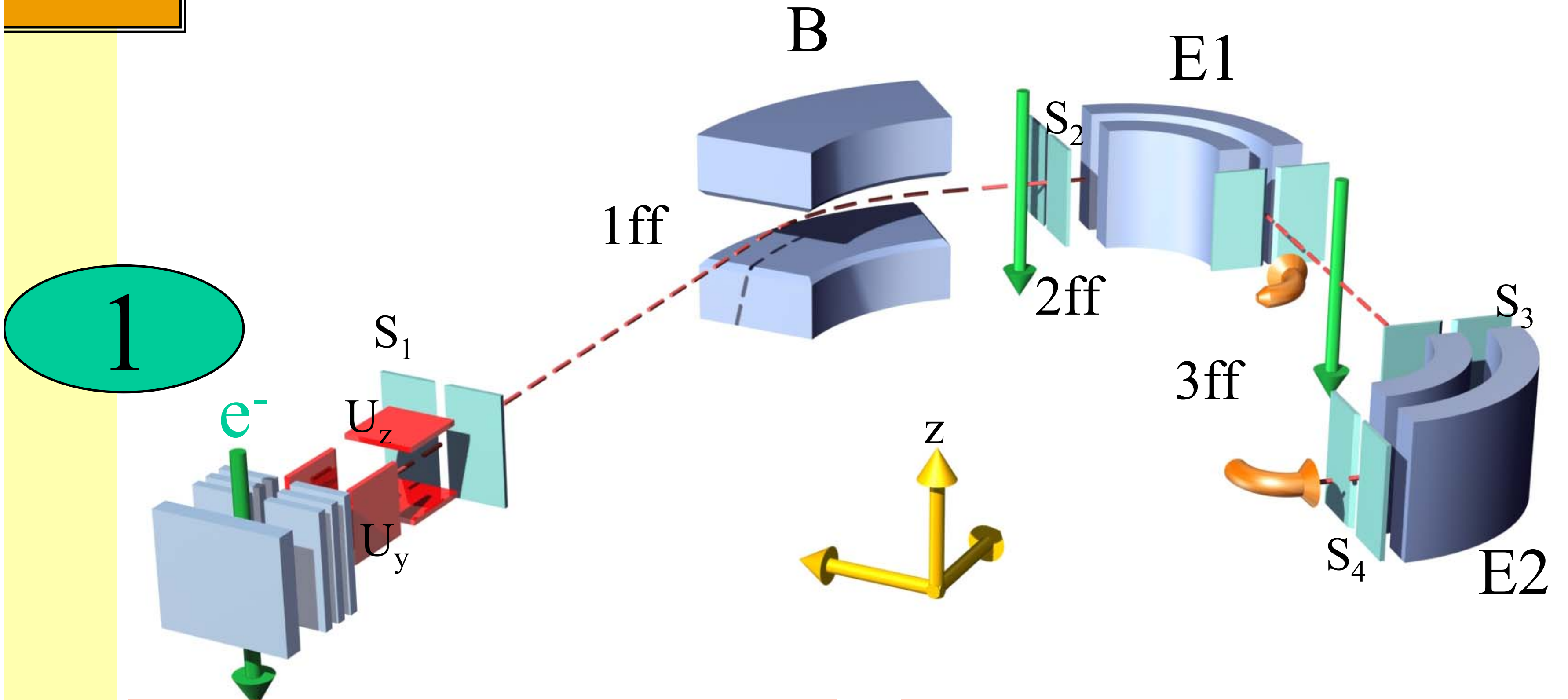


Electron ionization of molecular ions: $CH_4 + e \rightarrow$ ions

Total average kinetic energy released

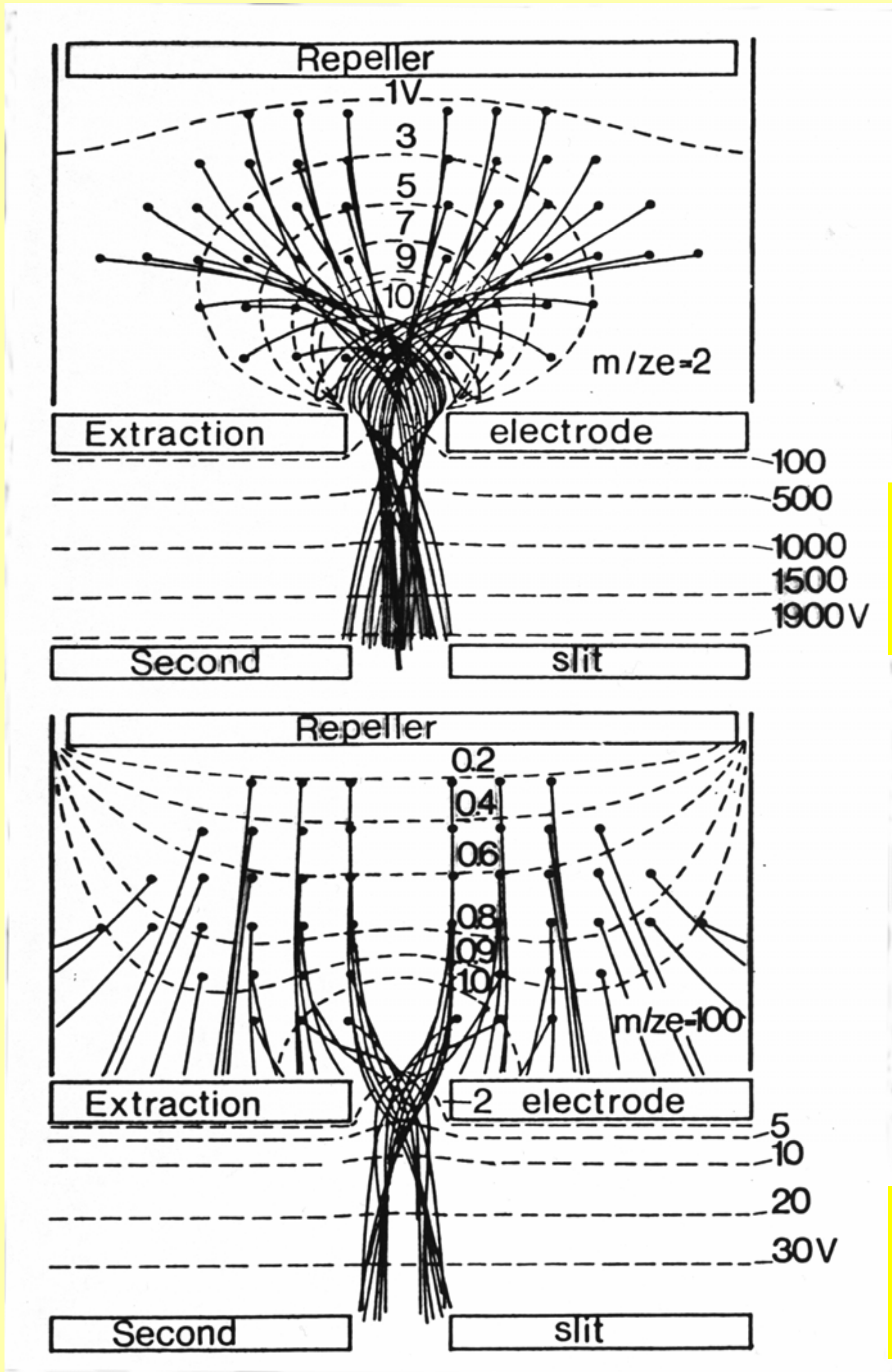


Ionization cross sections



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

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

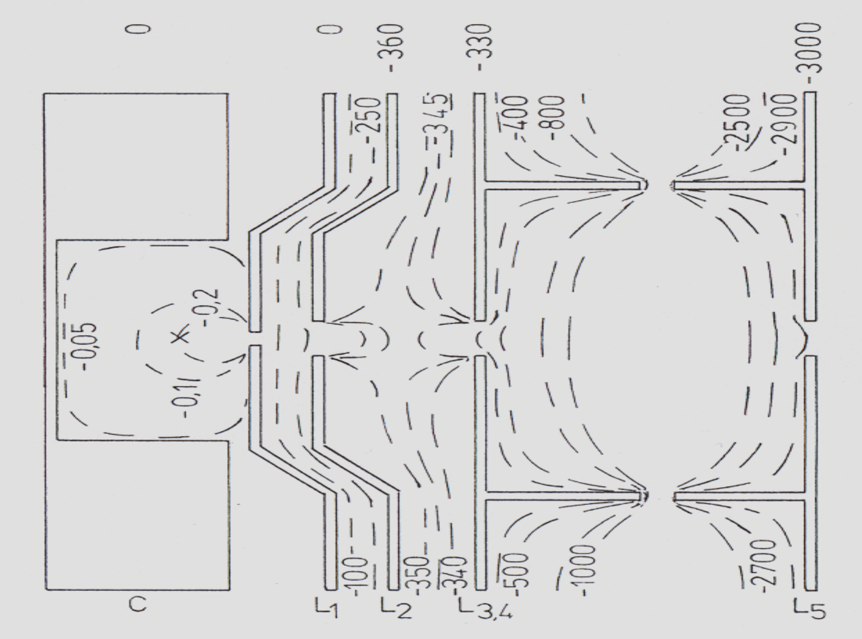


Calculated ion trajectories after Werner

Penetrating field extraction

Direct field extraction

Potential distribution and ion trajectories in ion source



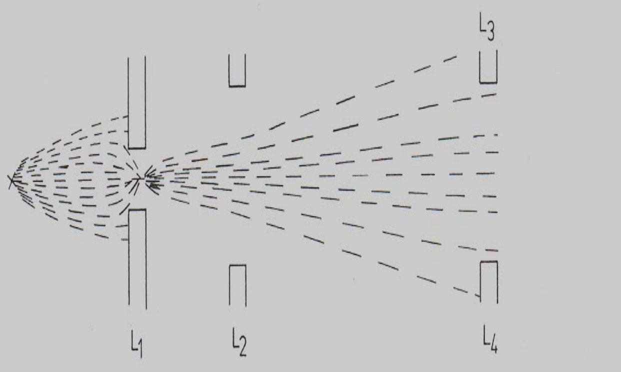
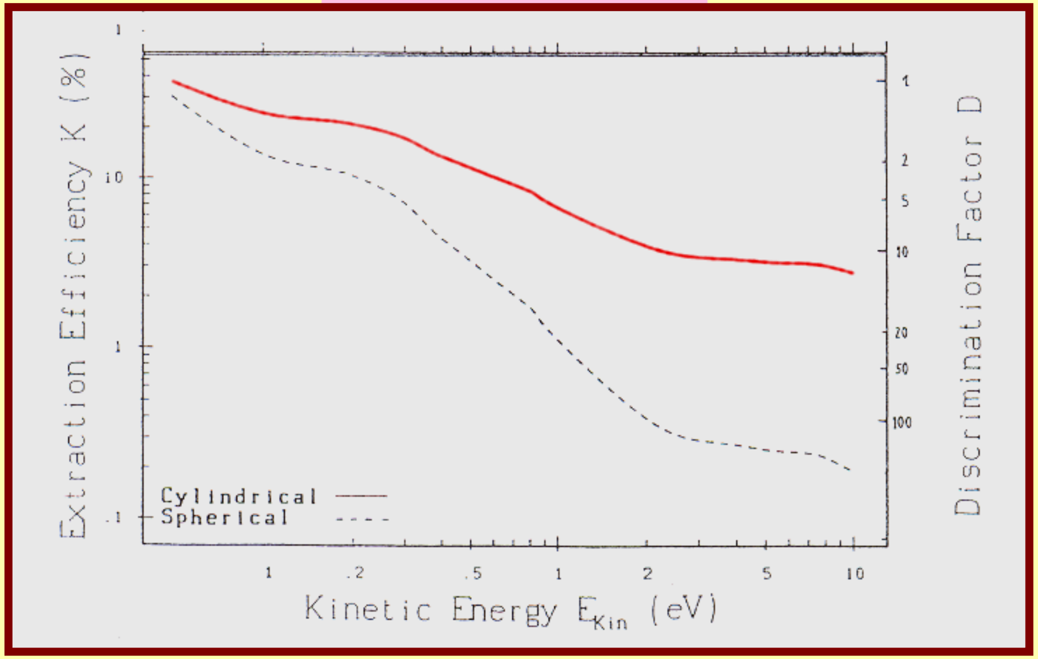
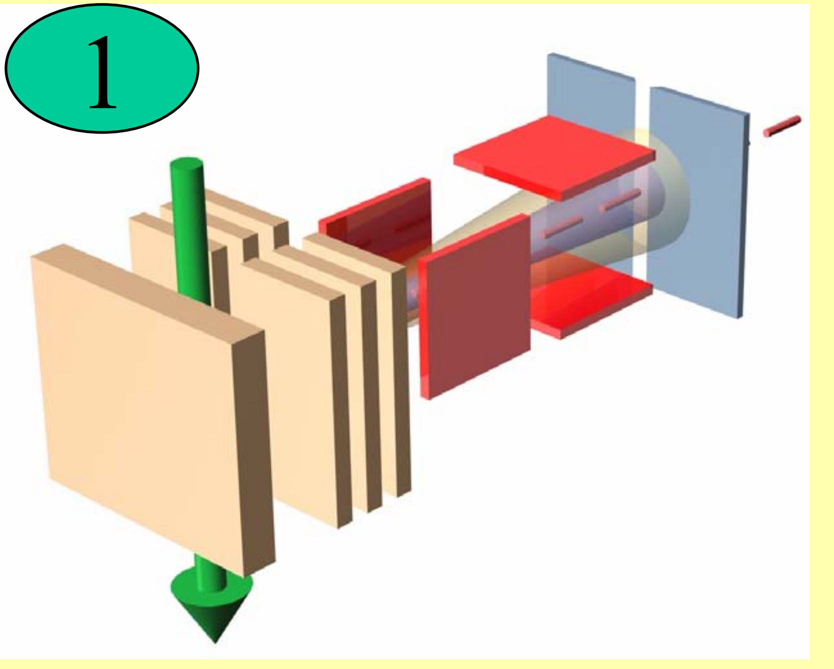


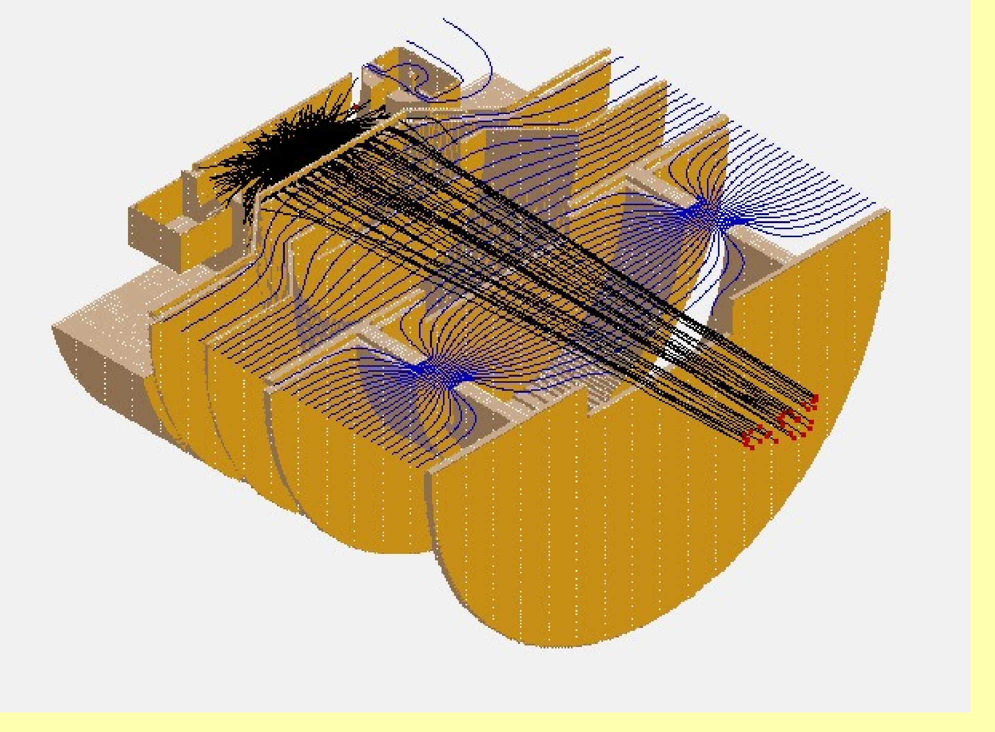
Fig. 3. Ion trajectories in the extraction region of the Nier-type ion source (Fig. 1) for ions with an initial energy of 1 eV. The figure shows the trajectories exemplarily with starting angles close to or smaller than the maximum starting angle ϑ_{max} (see text).

Discrimination function



Potential distribution and ion trajectories in ion source: discrimination



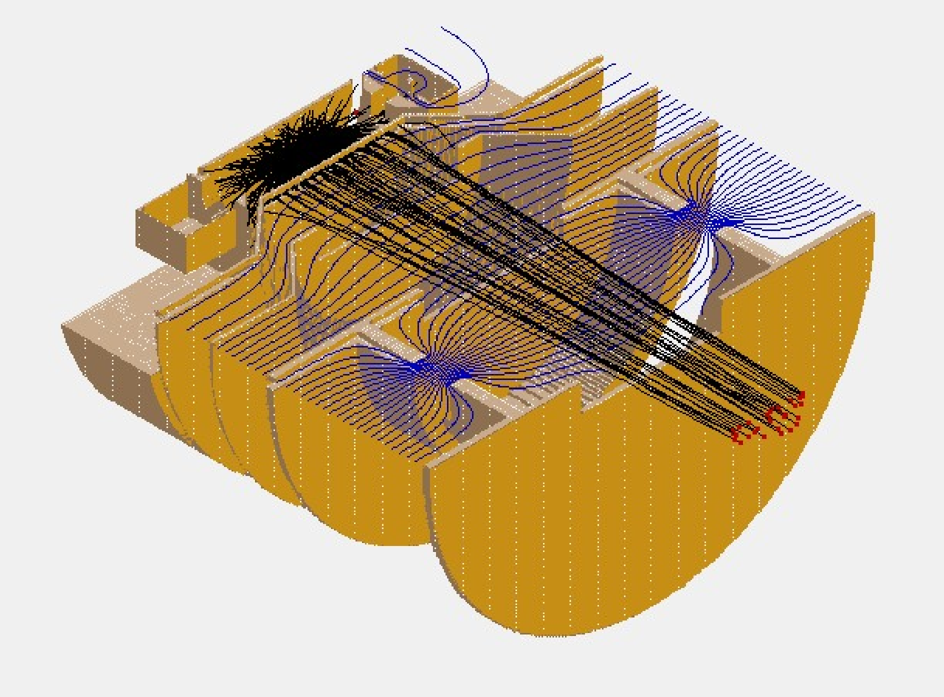


3D – Simulation with:

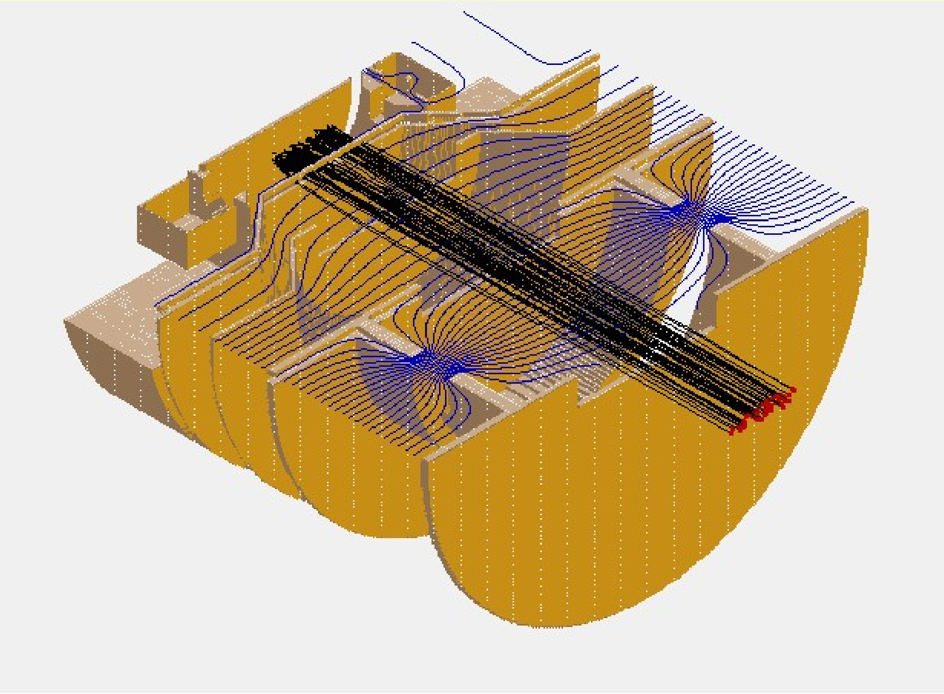
Simion

Pusher: 3000V
Ziehblenden: 3000V

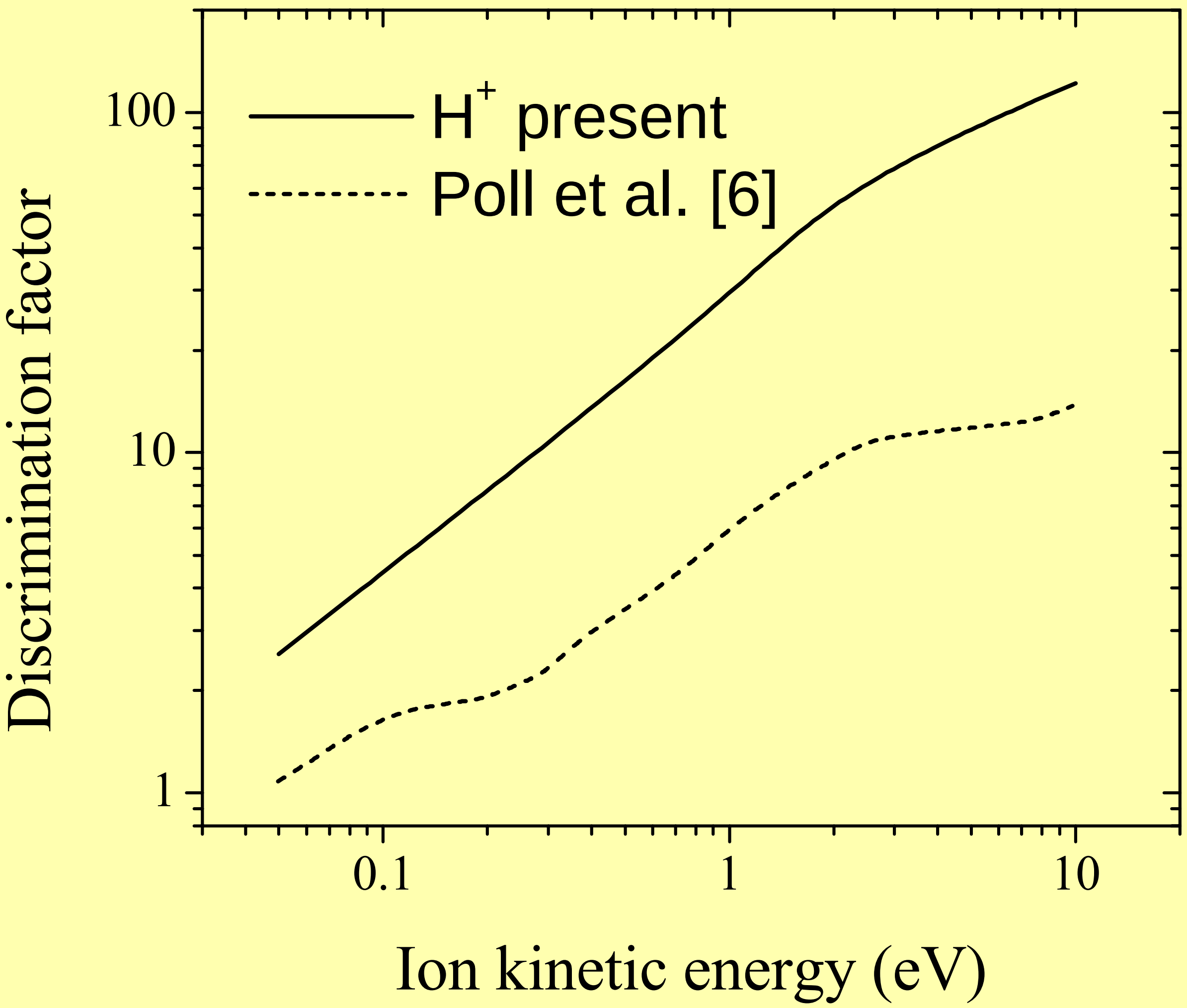
Pusher: 3000V
Ziehblenden: 3000V



Pusher: 3050V
Ziehblenden: 2950V



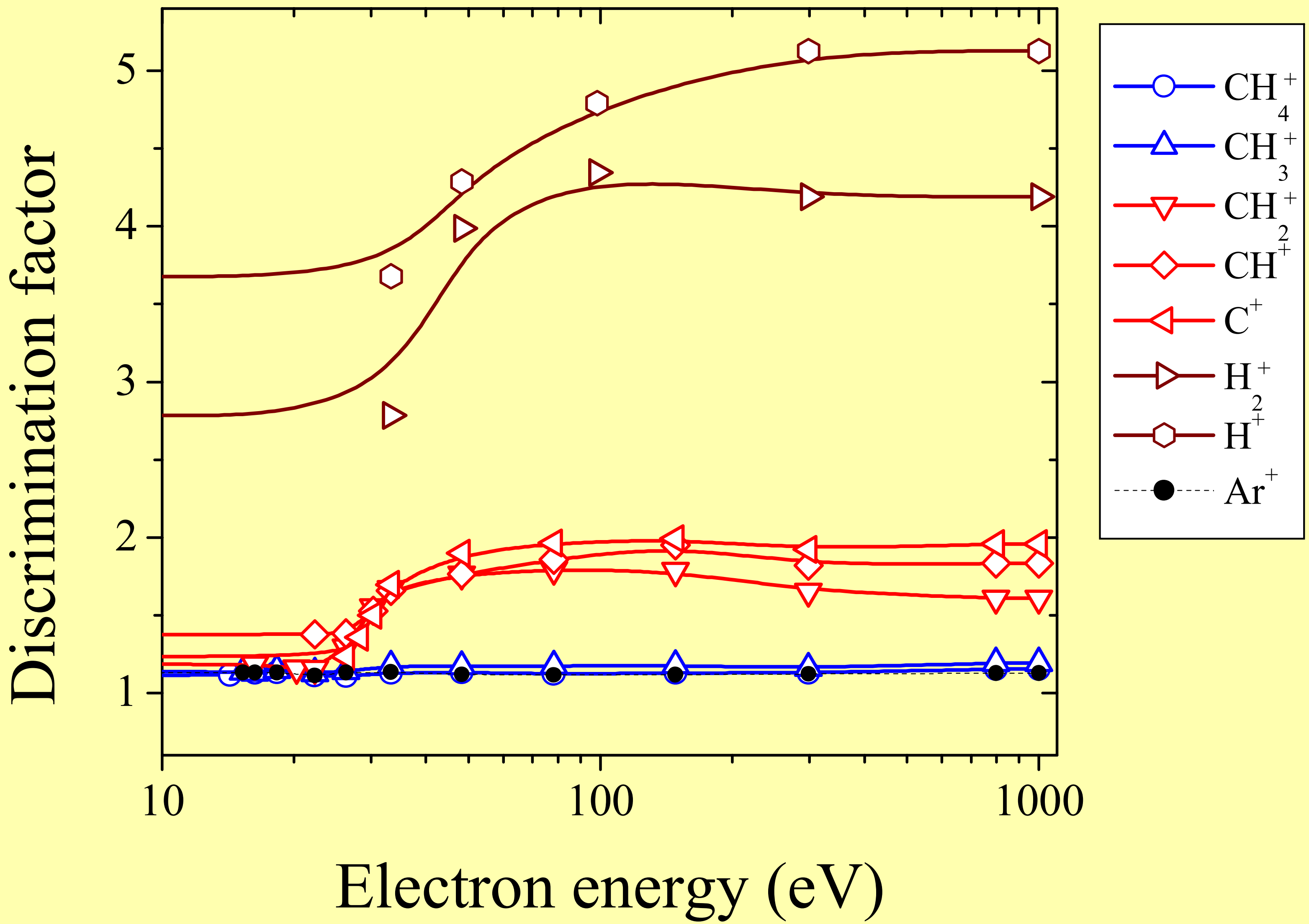
Discrimination



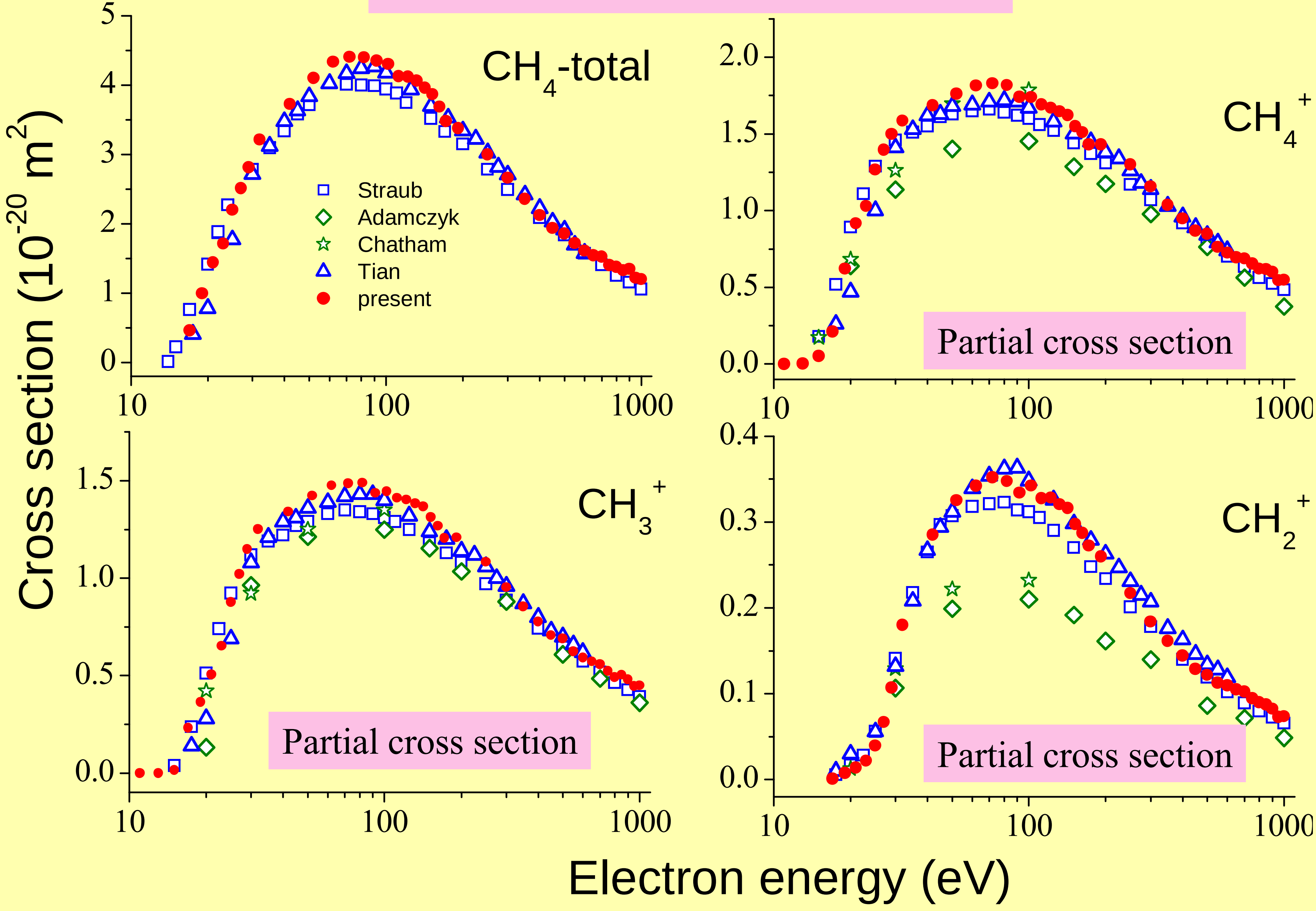
Discrimination function

Discrimination

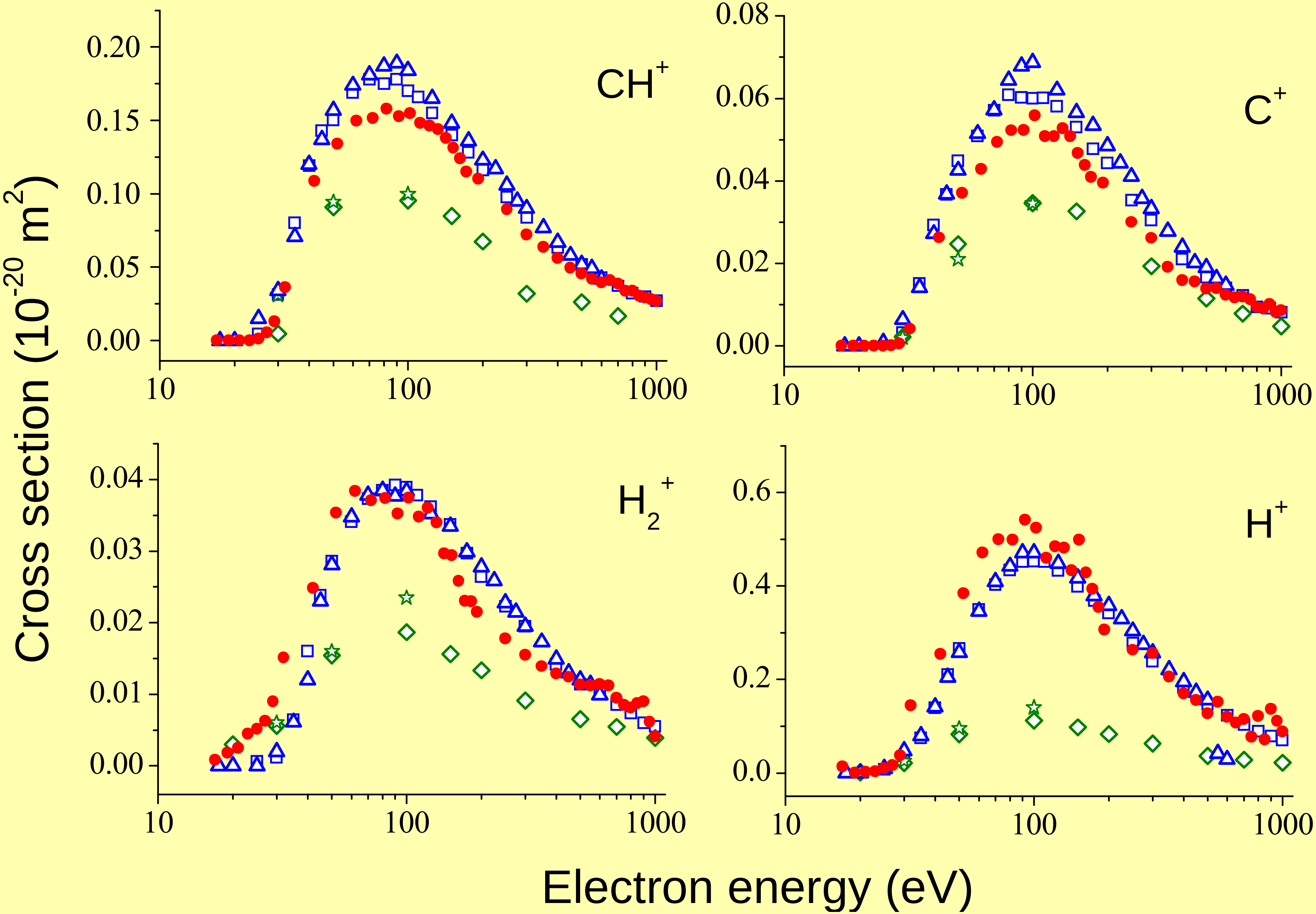
Integrated discrimination factor



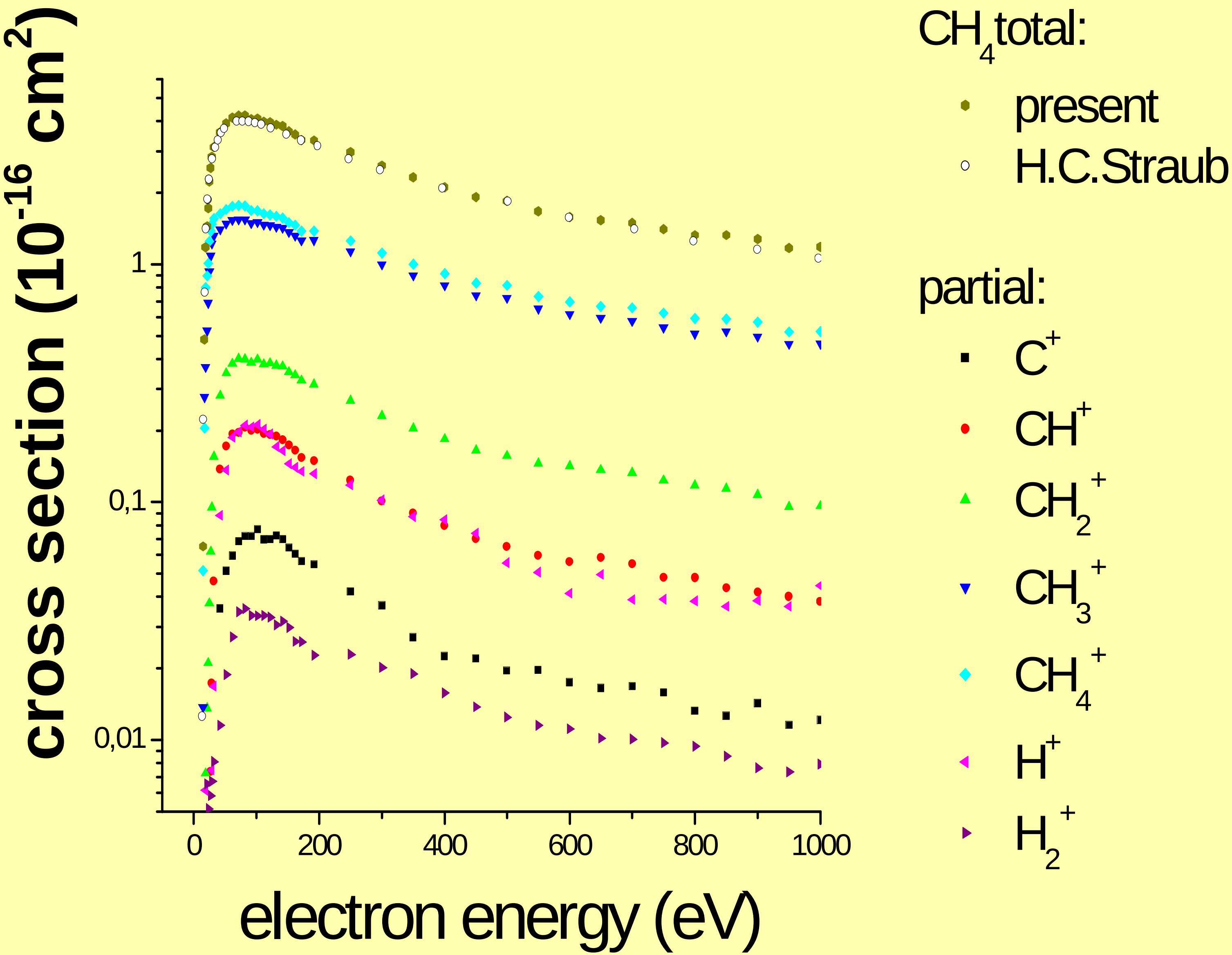
Partial and total cross section



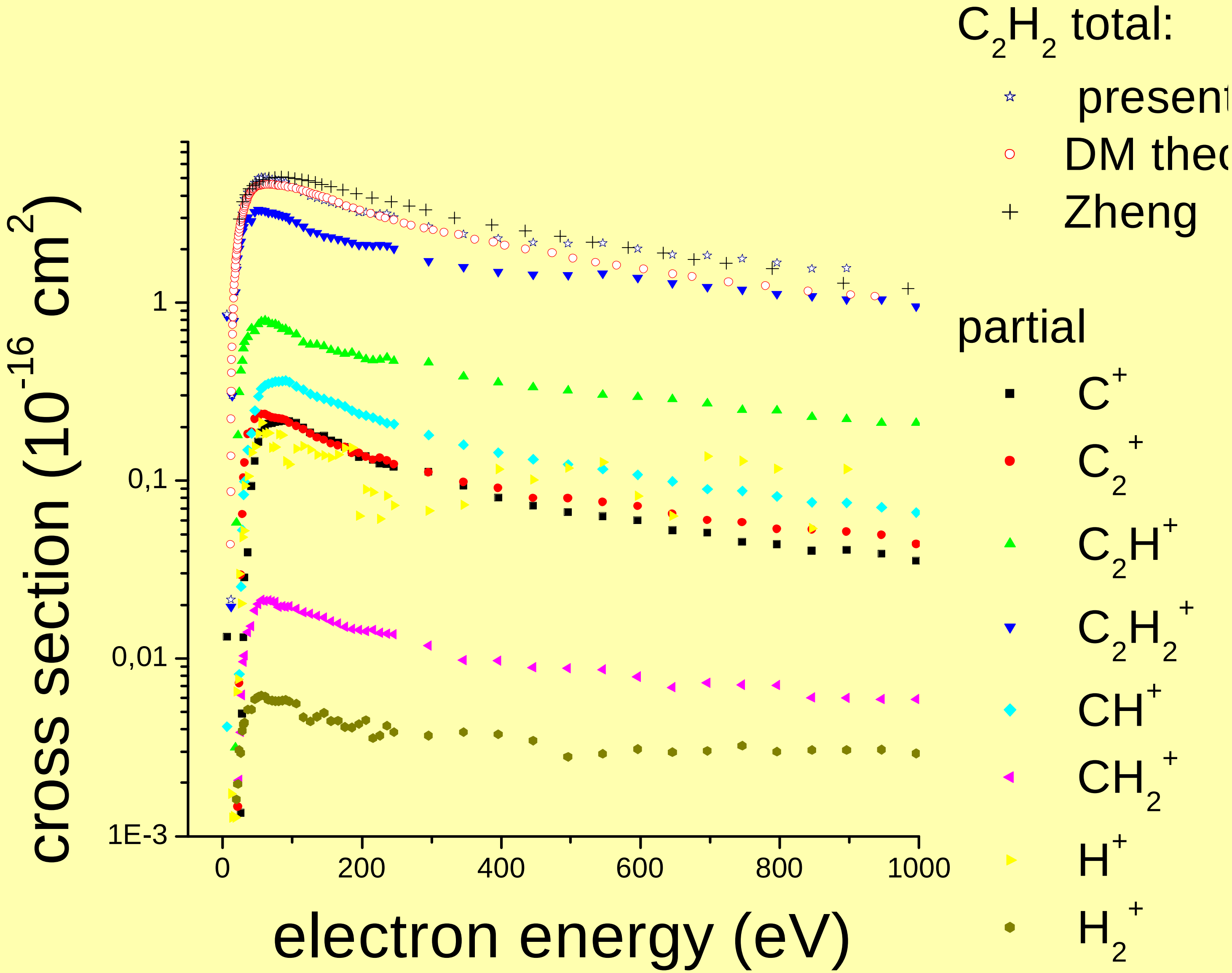
Partial cross sections:



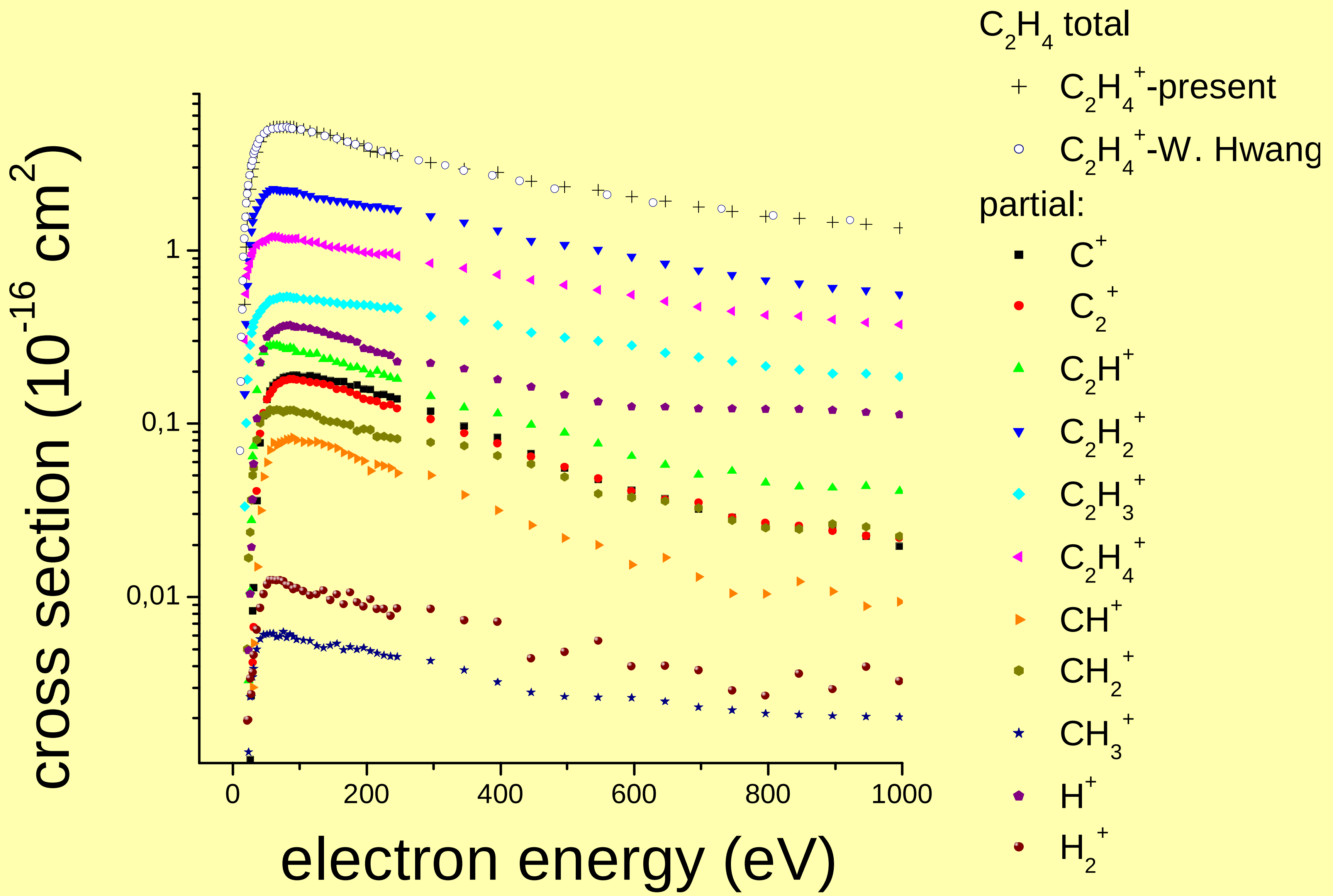
Cross sections CH_4



Cross sections C_2H_2



Cross sections C_2H_4



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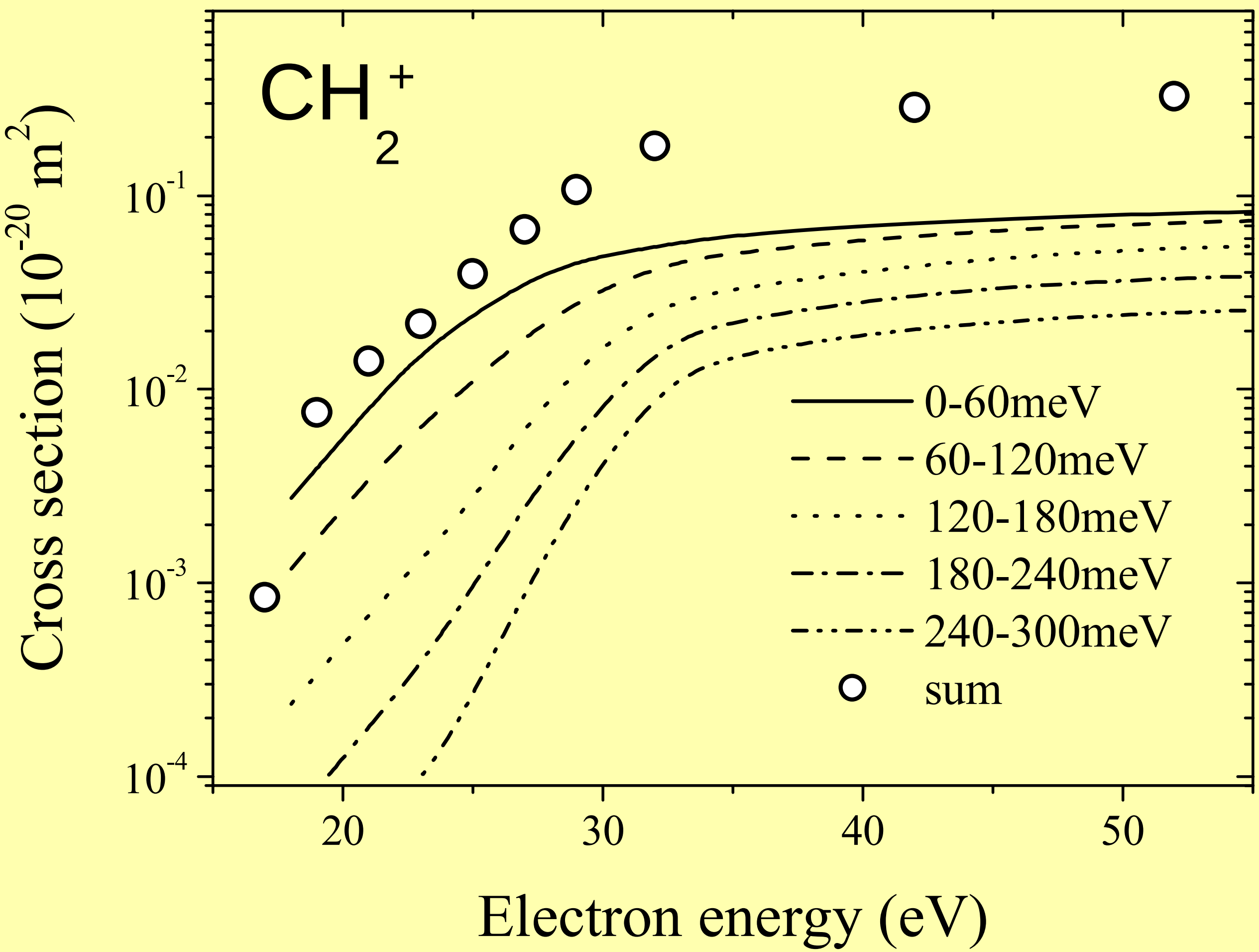
High resolution electron impact ionization of molecules

Institut Ionenphysik

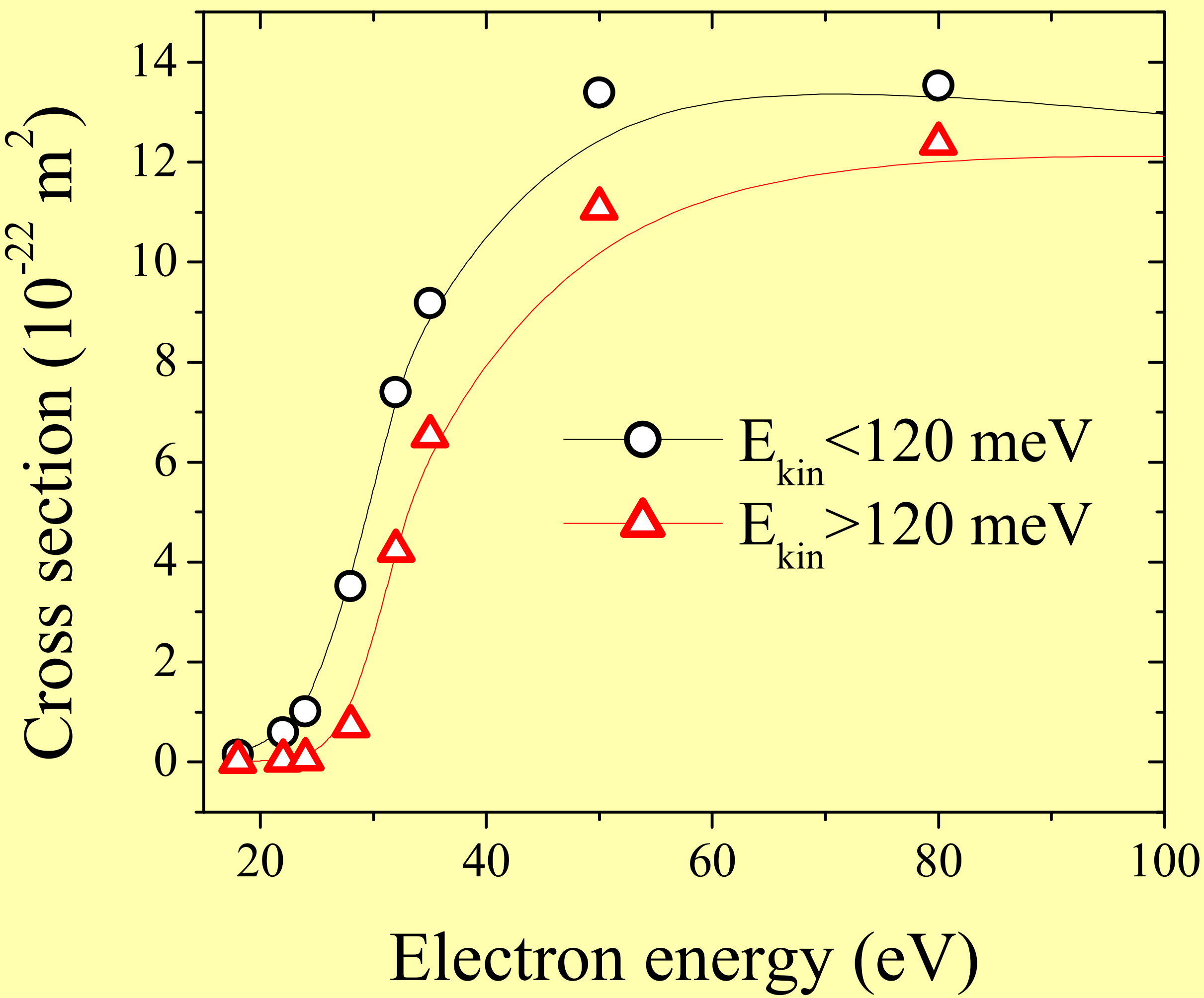
$$AB + e \rightarrow AB^{+}(AE)$$
$$AB + e \rightarrow A^{+}(AE) + B(KER)$$

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

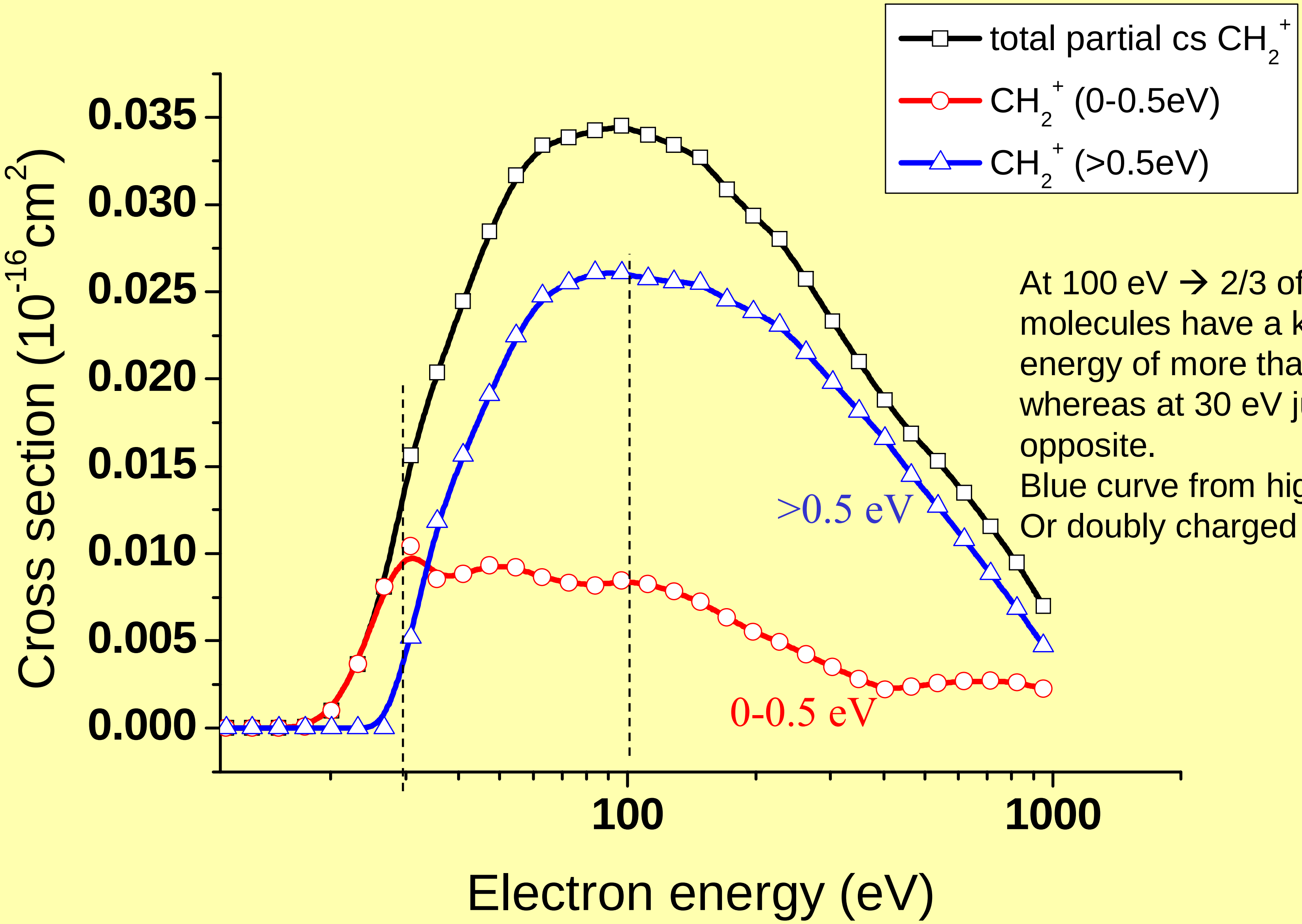
Energy differential partial cross sections: $CH_4 + e \rightarrow CH_2^+$



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



Example C_2H_2+e → CH_2^+

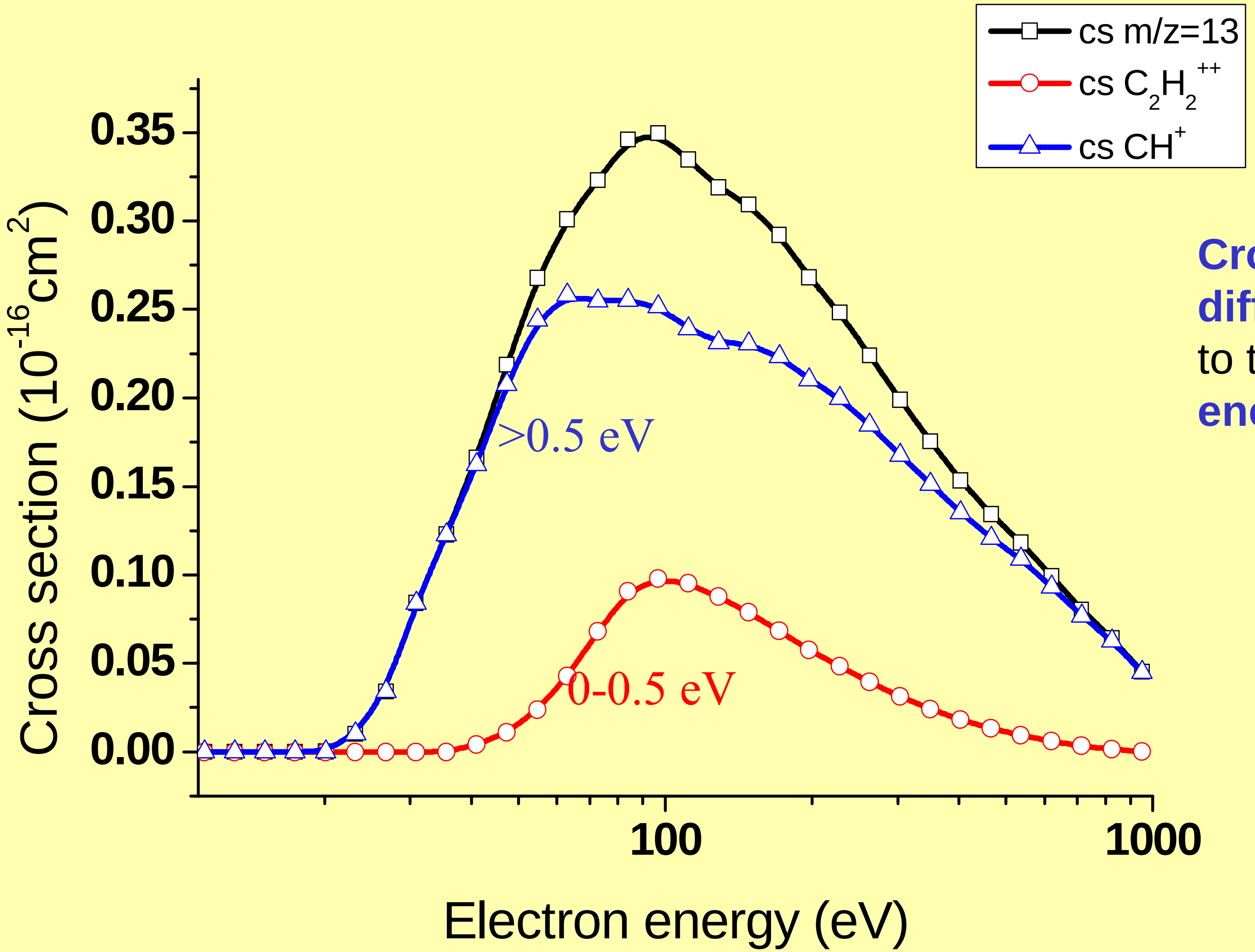


At 100 eV → 2/3 of the CH_2^+ molecules have a kinetic energy of more than 0.5eV, whereas at 30 eV just the opposite.

Blue curve from highly excited Or doubly charged parent ions

Example C_2H_2+e → CH^+

→ $C_2H_2^{++}$

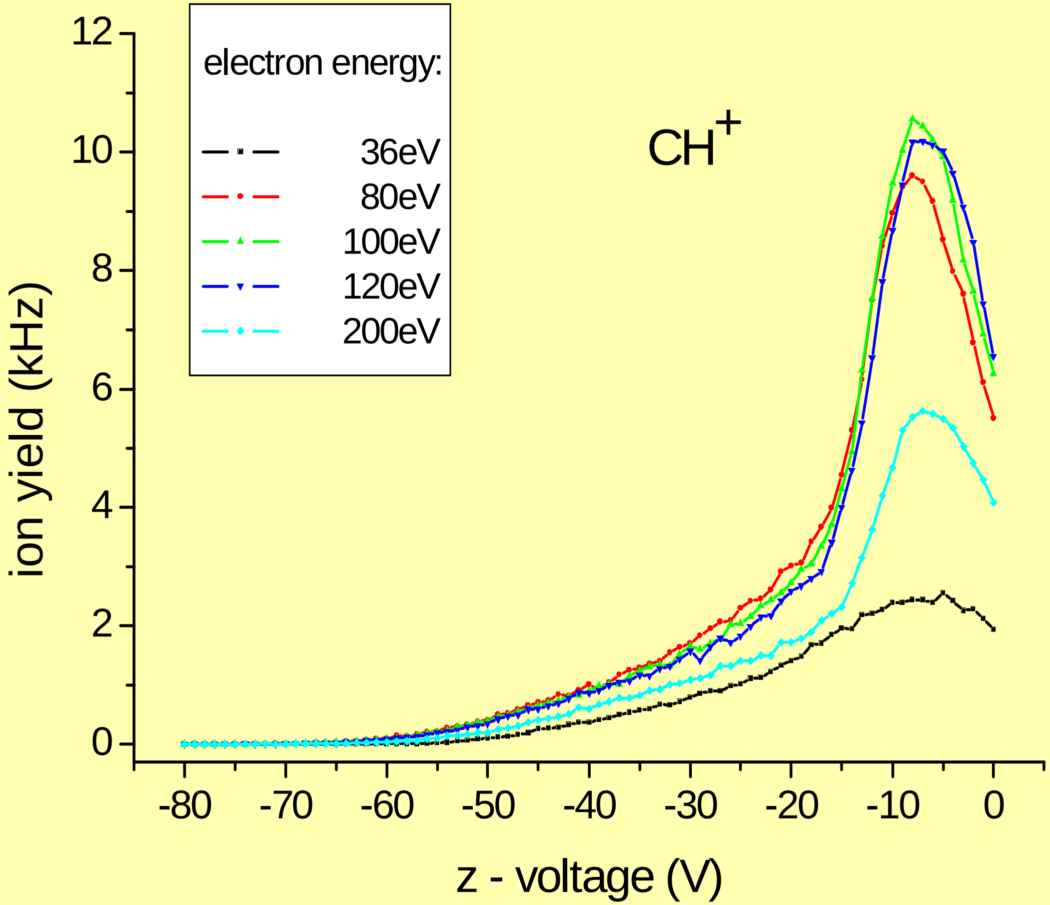


Cross section which is **differential** with respect to the **initial kinetic energy**

Isotopic labelling, AEs

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

Ion beam profile:

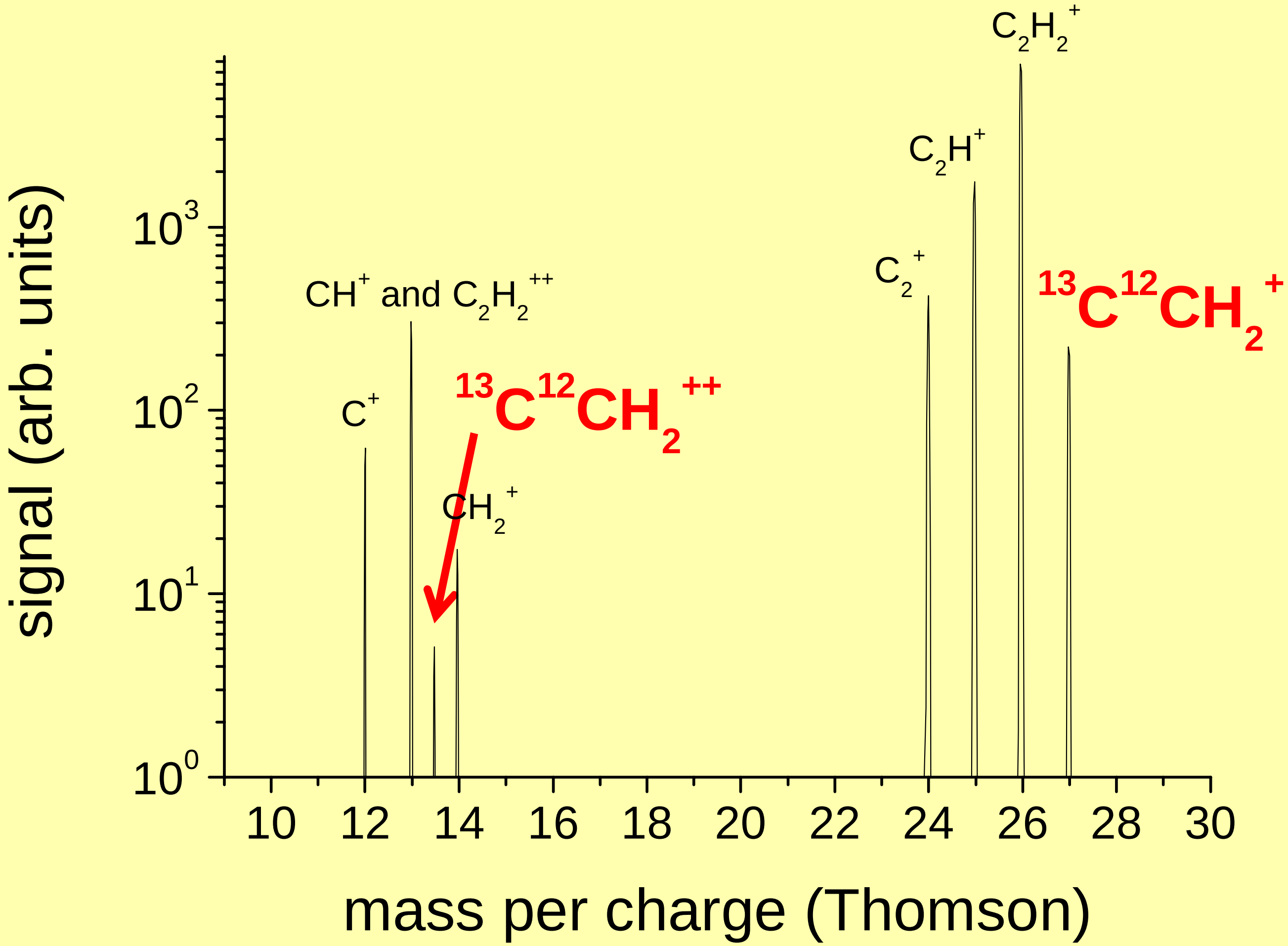


$C_2H_2 + e \rightarrow CH^+ + CH + 2e$

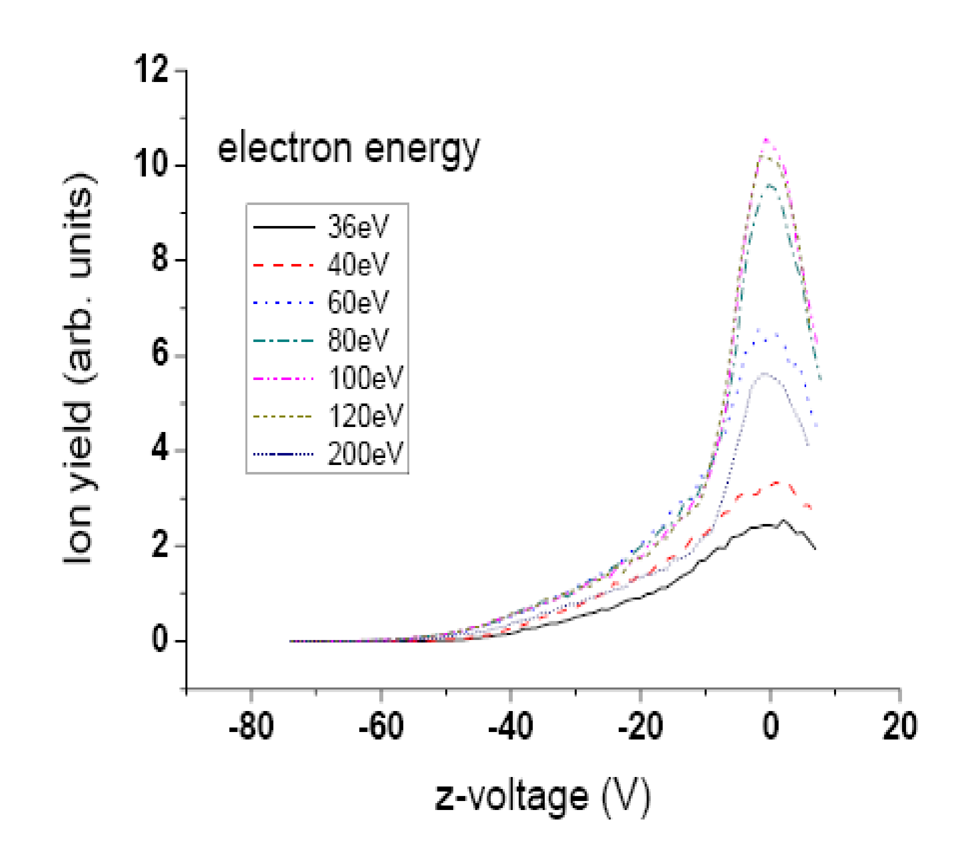
$C_2H_2 + e \rightarrow C_2H_2^{++} + 3e$

at same m/q ratio

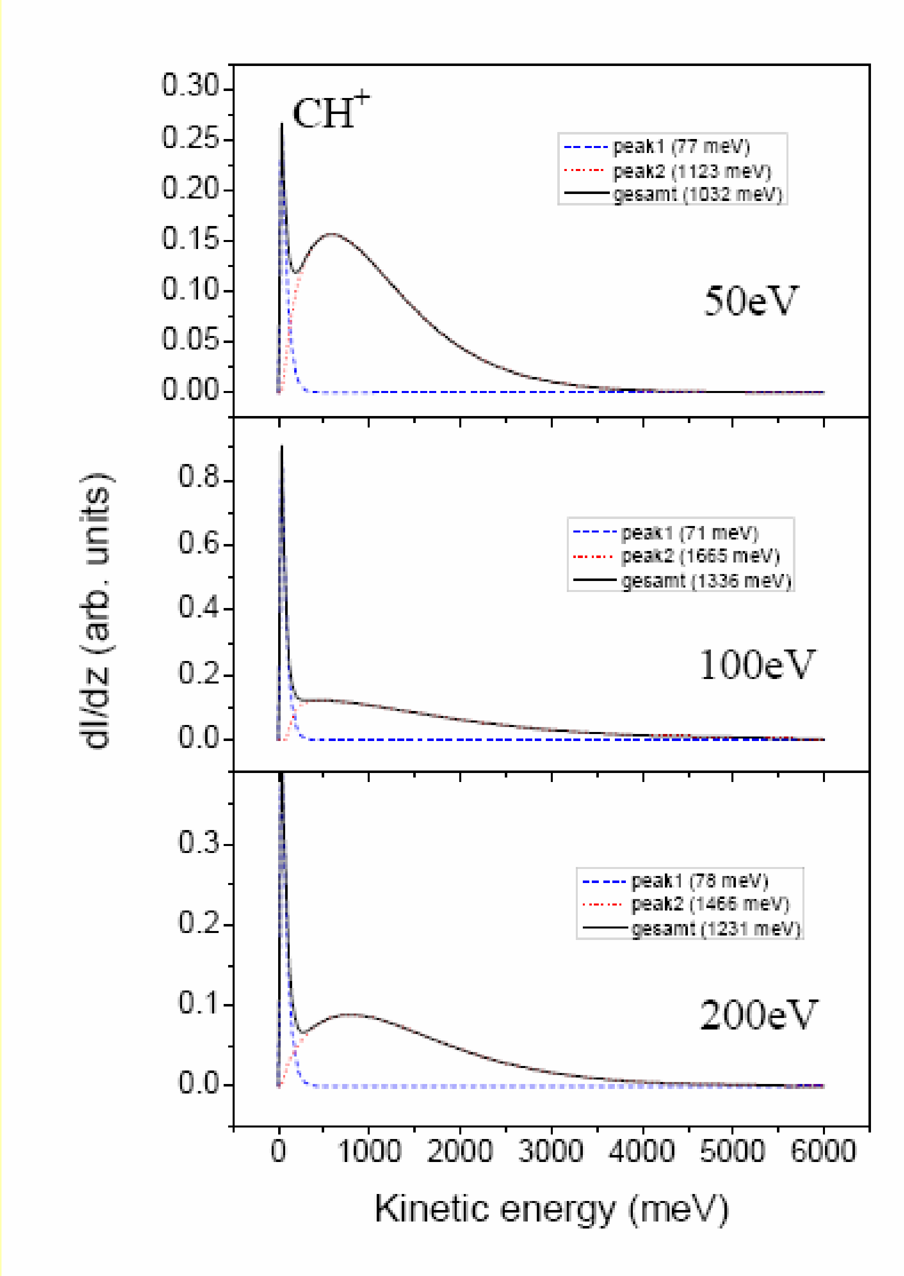
Mass spectrum of C_2H_2



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

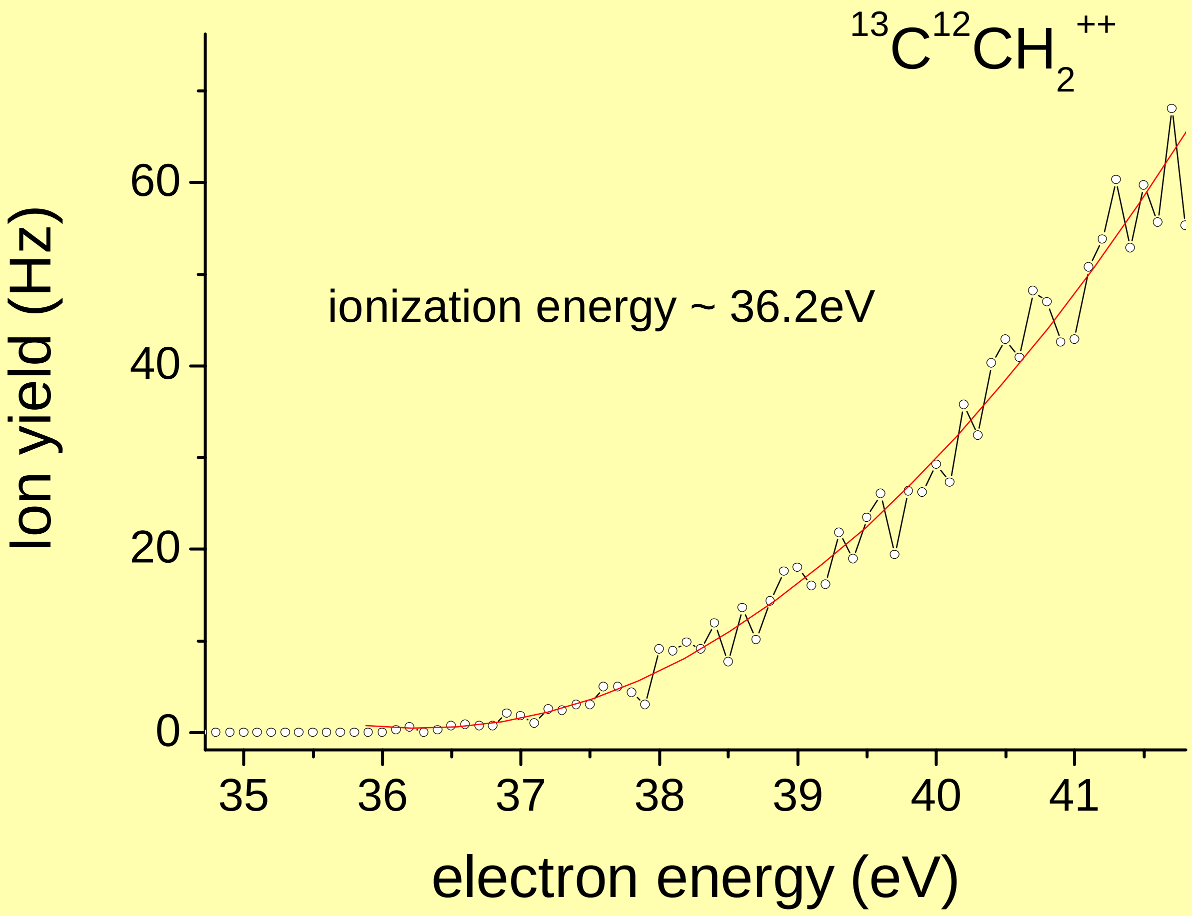


Ion yield (arb. units)
electron energy
36eV
40eV
60eV
80eV
100eV
120eV
200eV
z-voltage (V)



CH+
peak1 (77 meV)
peak2 (1123 meV)
gesamt (1032 meV)
50eV
peak1 (71 meV)
peak2 (1665 meV)
gesamt (1336 meV)
100eV
peak1 (78 meV)
peak2 (1466 meV)
gesamt (1231 meV)
200eV
dI/dz (arb. units)
Kinetic energy (meV)

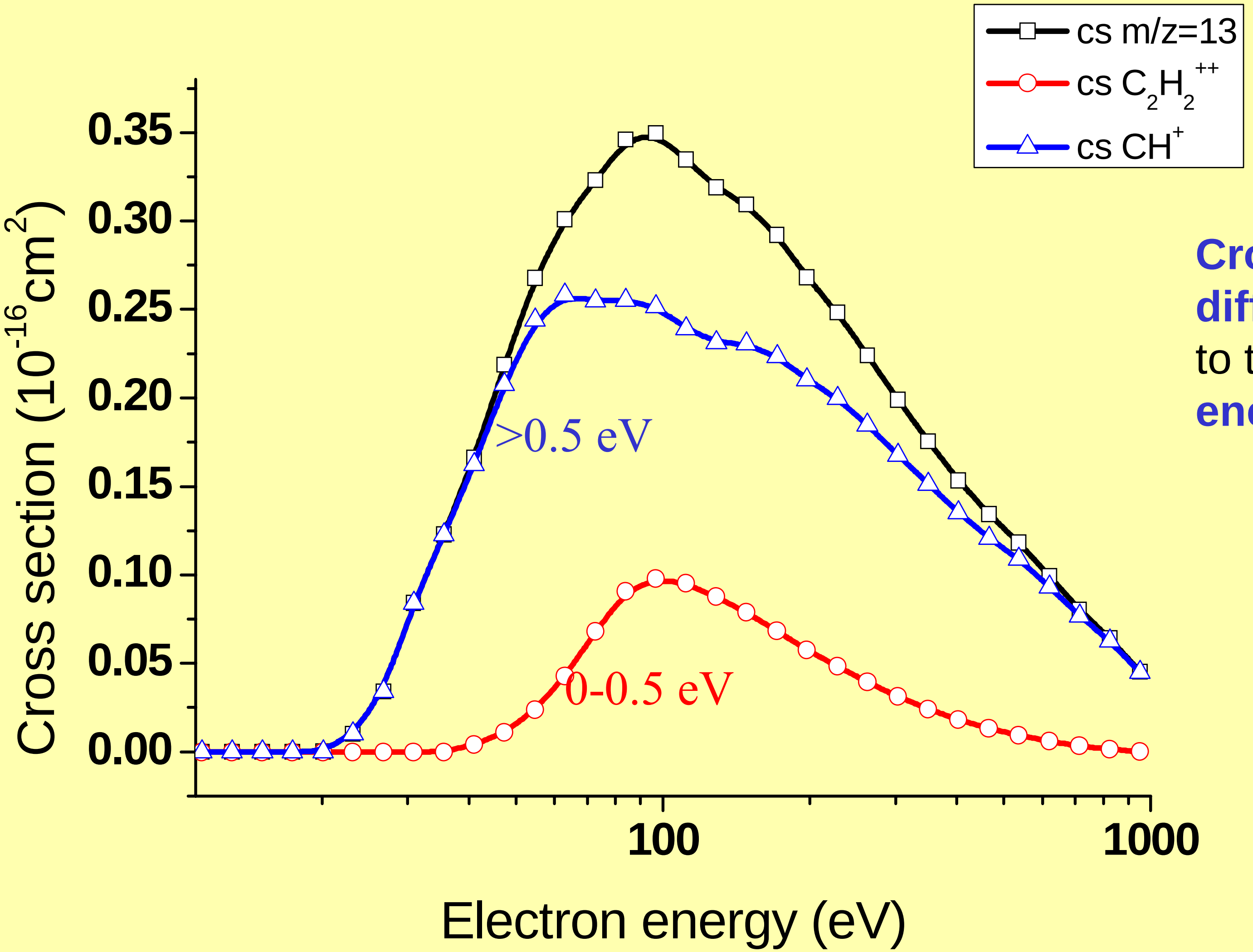
Ionization Energy of $C_2H_2^{++}$



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

Example C_2H_2+e → CH^+

→ $C_2H_2^{++}$

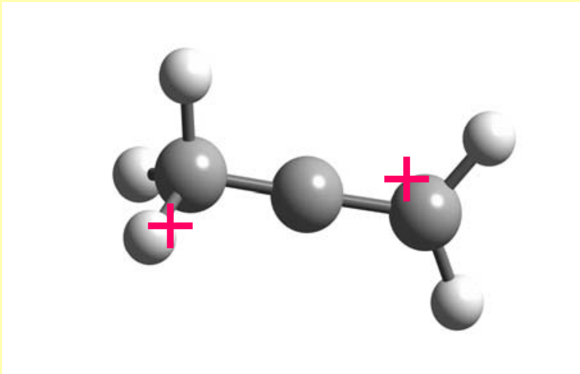


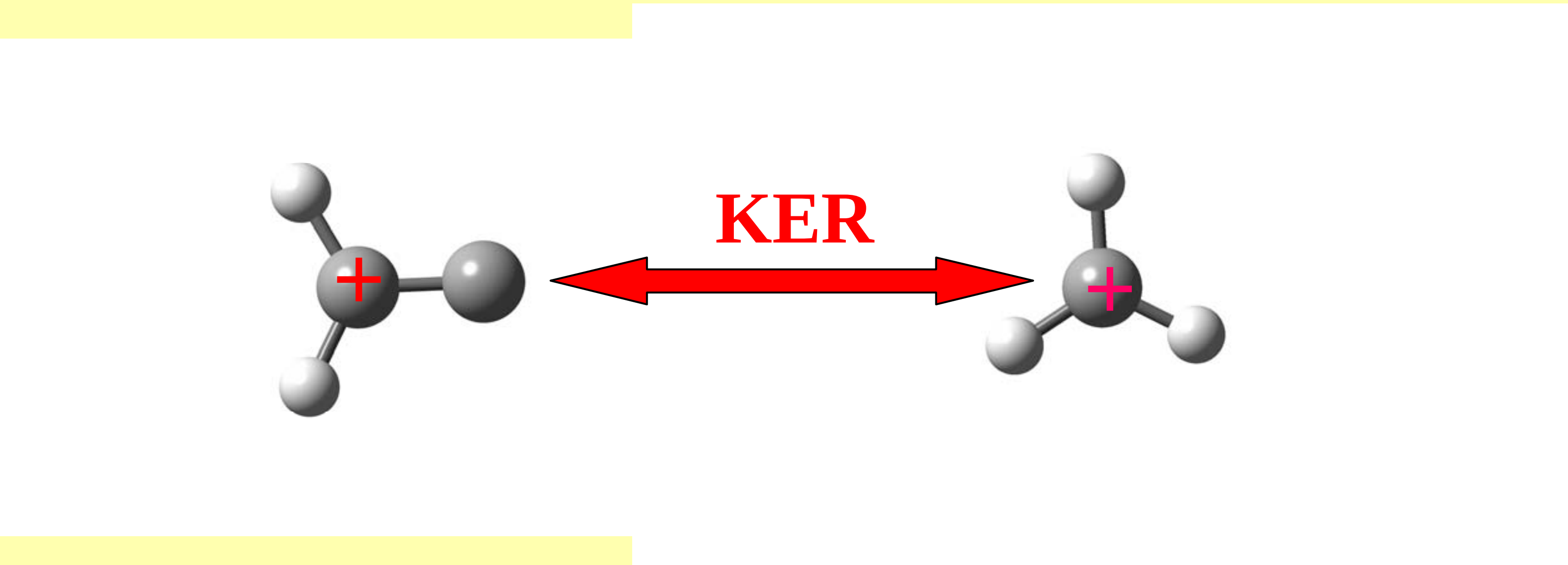
Cross section which is **differential** with respect to the **initial kinetic energy**

Isotopic labelling, AEs

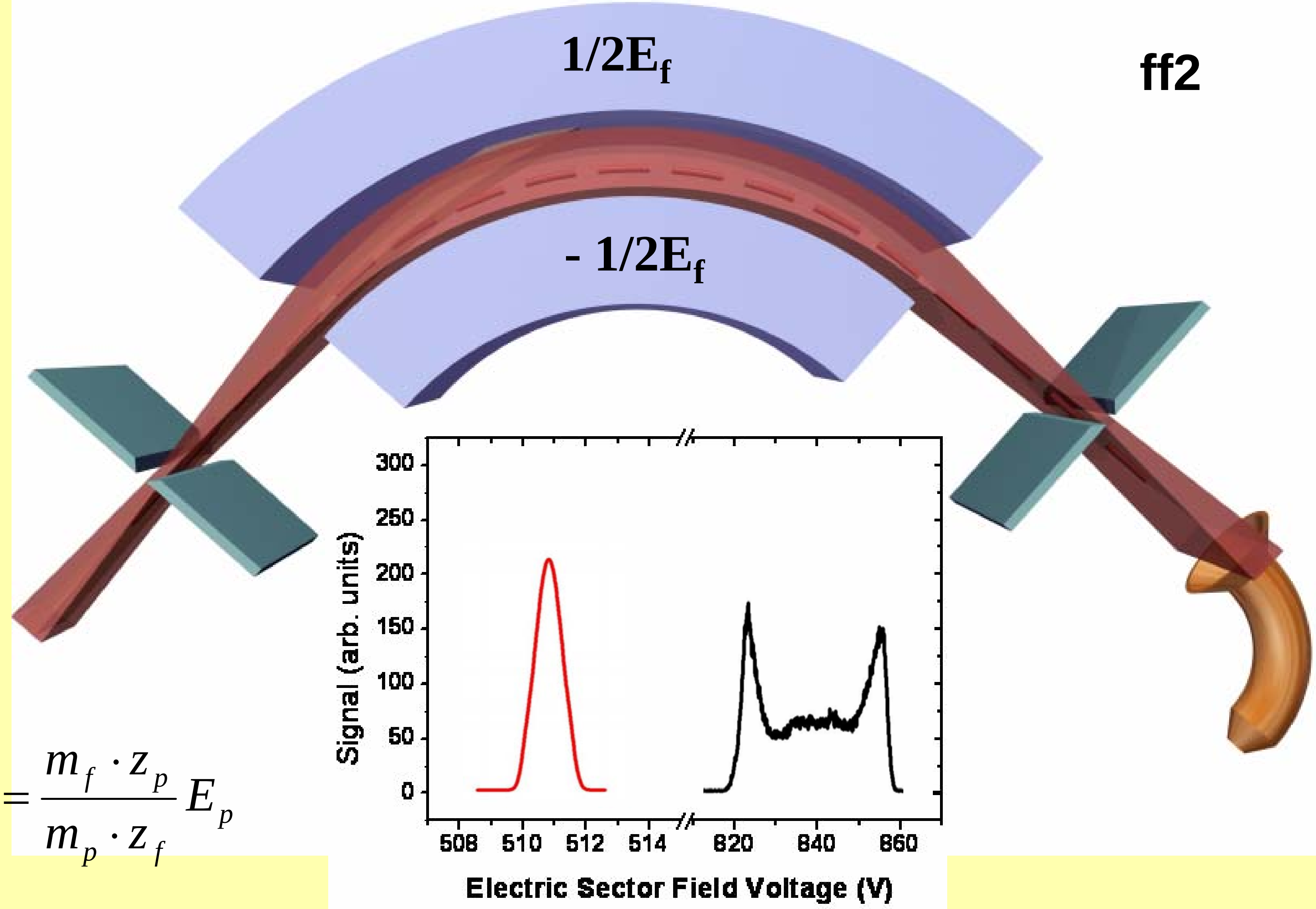
Decay of doubly charged ions: Coulomb explosion of $C_3H_5^{++}$

$$C_3H_8 + e \rightarrow (C_3H_5^{++})^* \rightarrow C_2H_2^+ + CH_3^+ + KER$$





MIKE scan technique

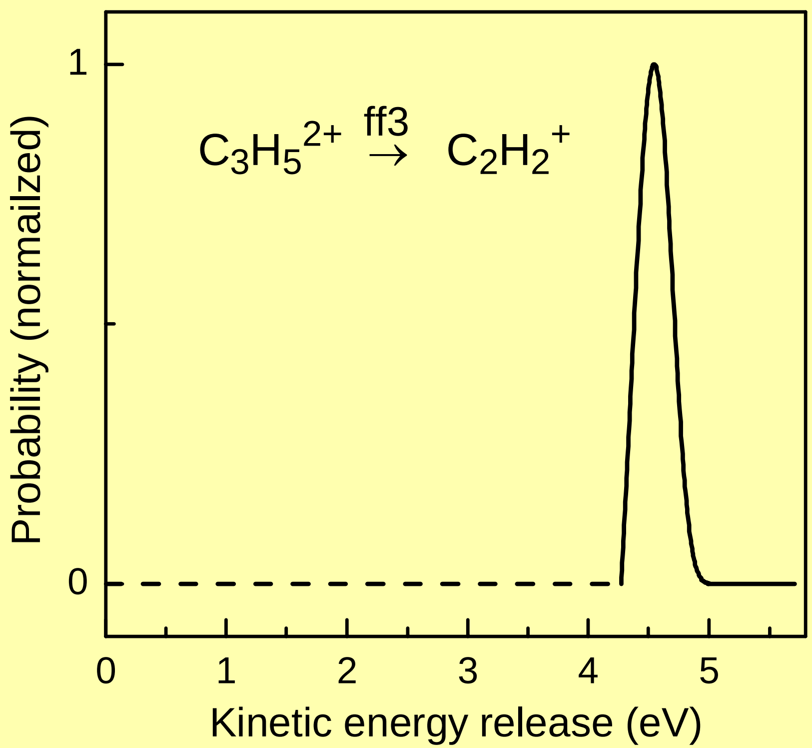


$$E_f = \frac{m_f \cdot z_p}{m_p \cdot z_f} E_p$$

Coulomb explosion of $C_3H_5^{++}$: Results

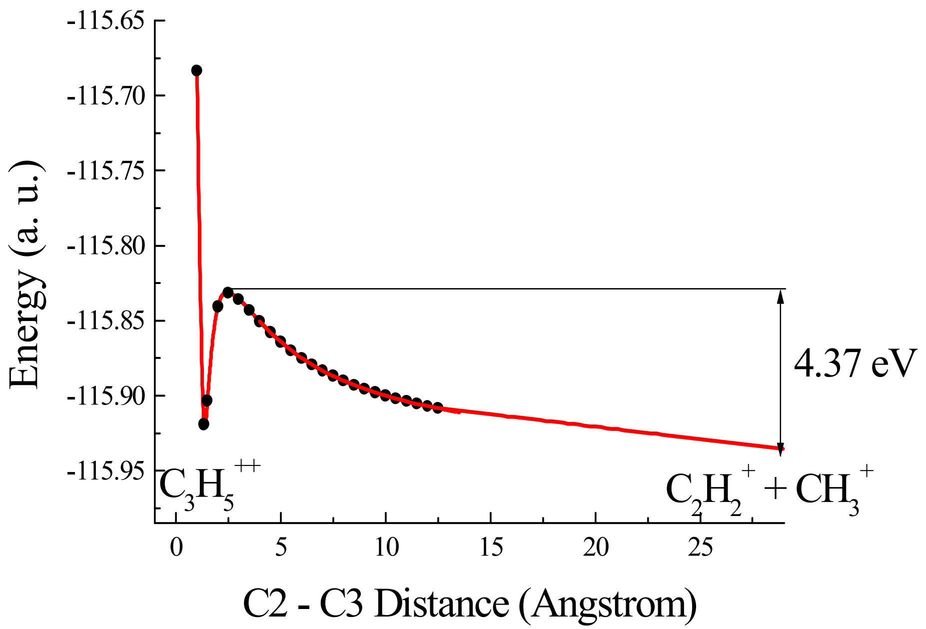
Experiment

4.58 ± 0.15 eV

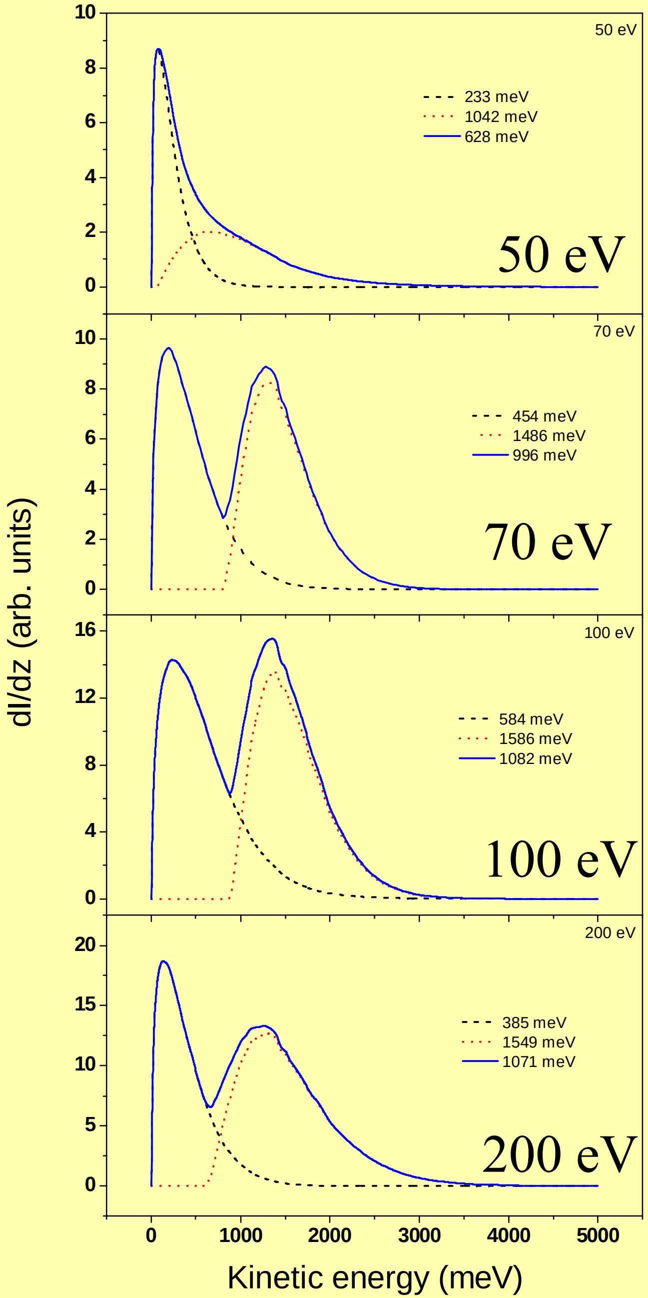


Calculation

[CCSD(T)/cc-pVTZ // MP2/aug-cc-pVTZ]



$C_3H_8 + e \rightarrow CH_3^+$



$$C_3H_8 + e \rightarrow (C_3H_5^{++})^* \rightarrow C_2H_2^+ + CH_3^+ + KER$$

Ion source

4.99 ± 0.5 eV

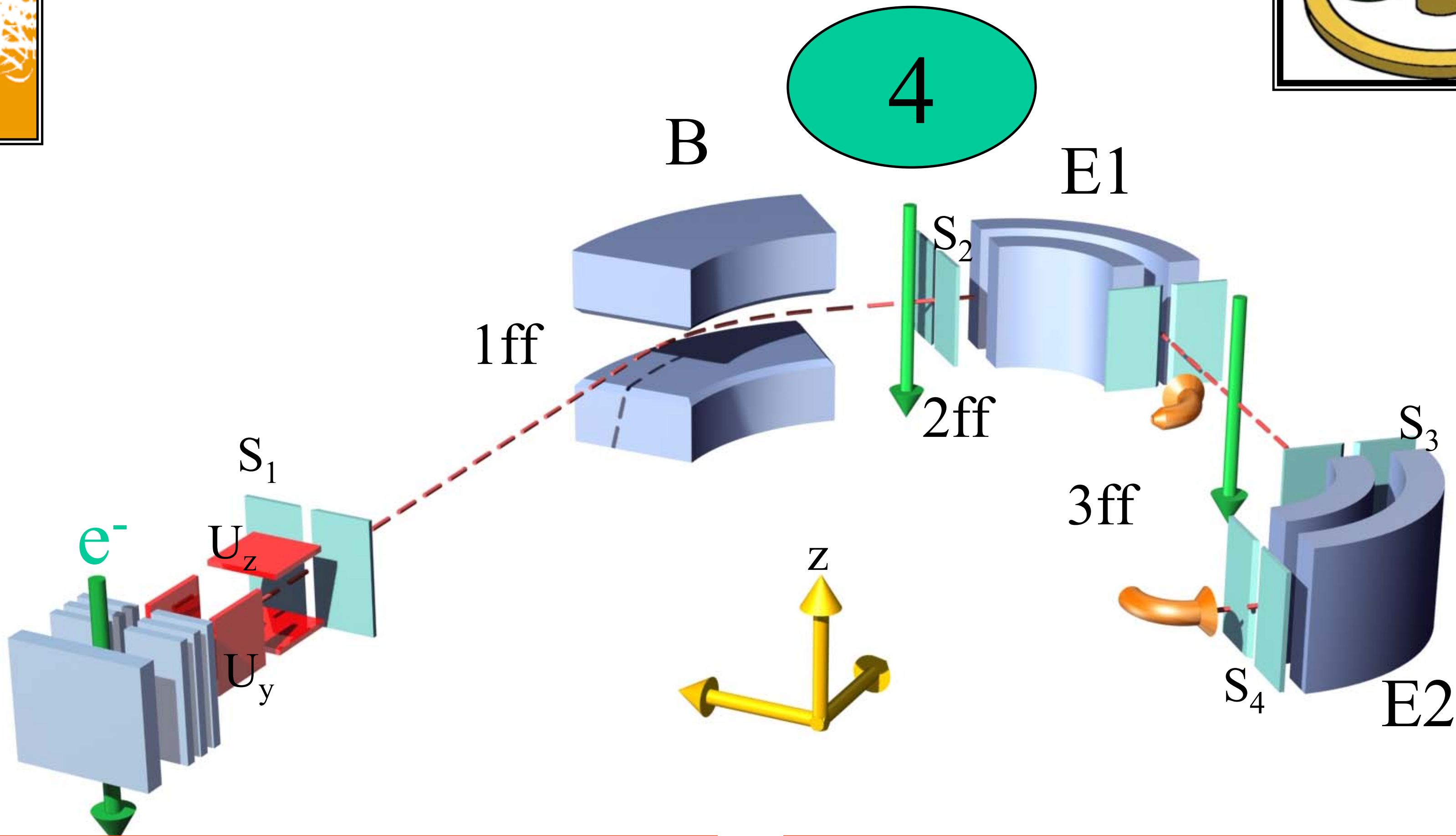
Various scans

4.58 ± 0.15 eV

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

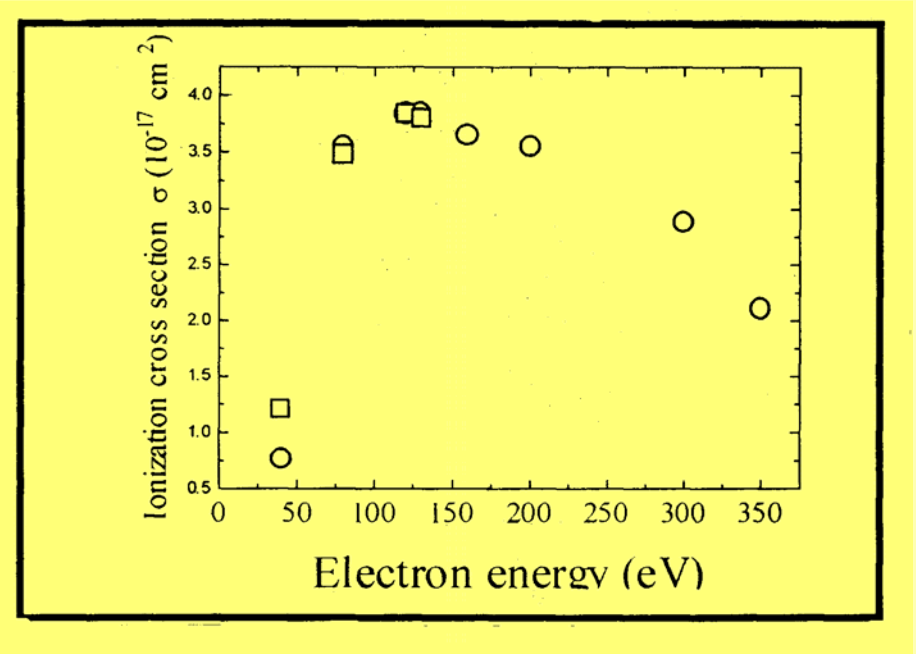


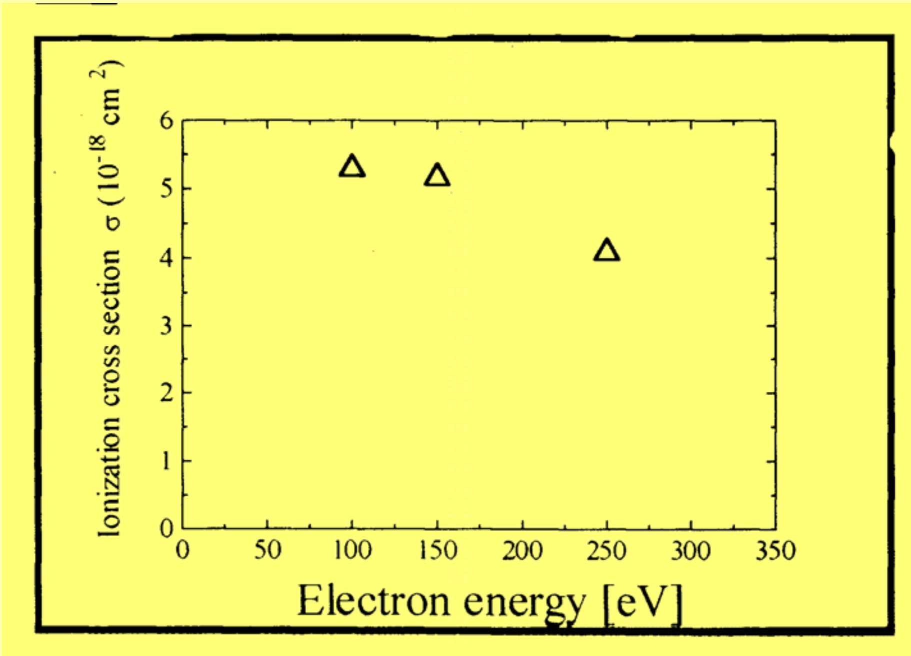
$AB + e \rightarrow AB^{+}$
$\rightarrow A + B^{+} + KER$
$\rightarrow A^{+} + B + KER$

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

Electron ionization of molecular ions:

$CO_2^+ + e \rightarrow CO_2^{2+}$, $CO_2^+ + e \rightarrow O^+$





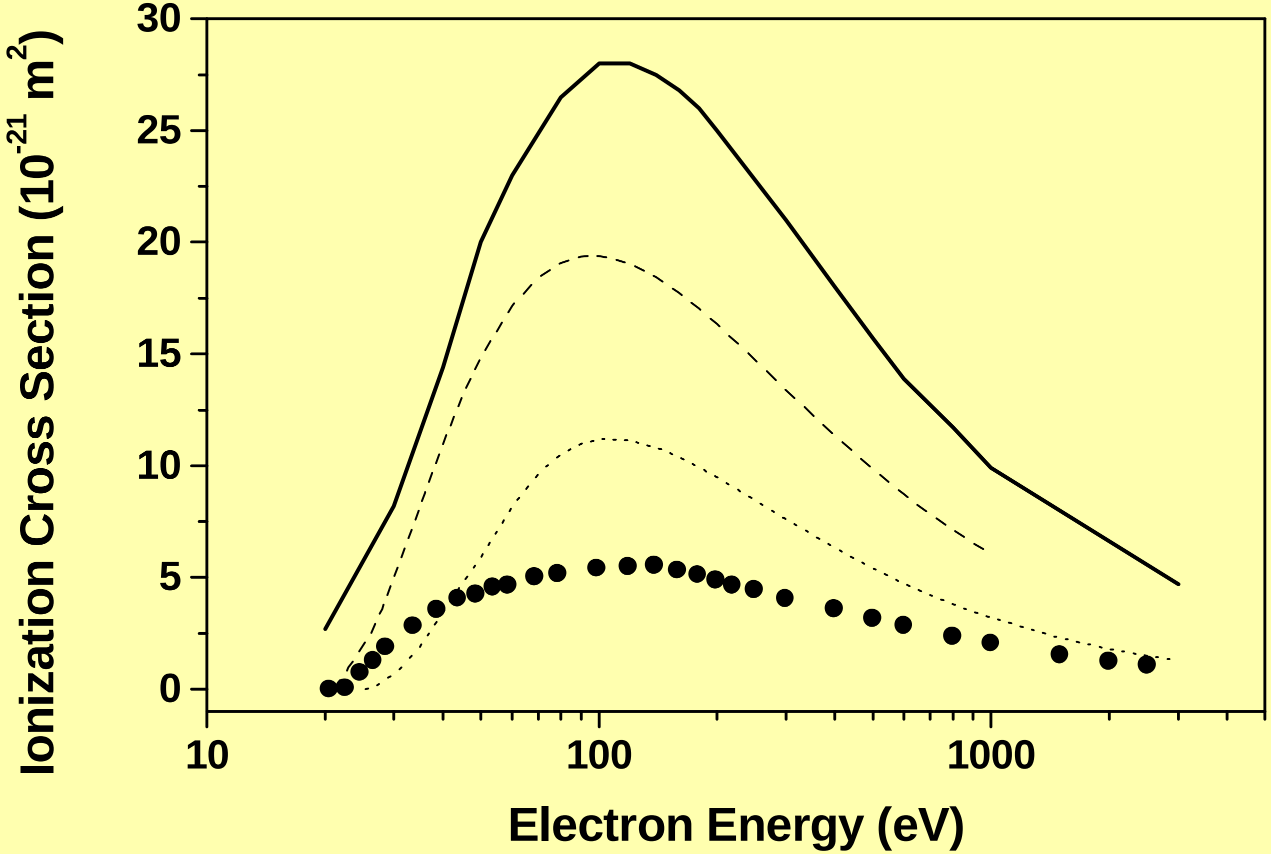
Open circles: CO_2^{2+} (Salzborn)

Open triangles: O^+ (present)

Open squares: CO_2^{2+} (present)

Electron ionization of molecular ions:

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



Previous results for the electron-impact ionization of C2H2+ 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

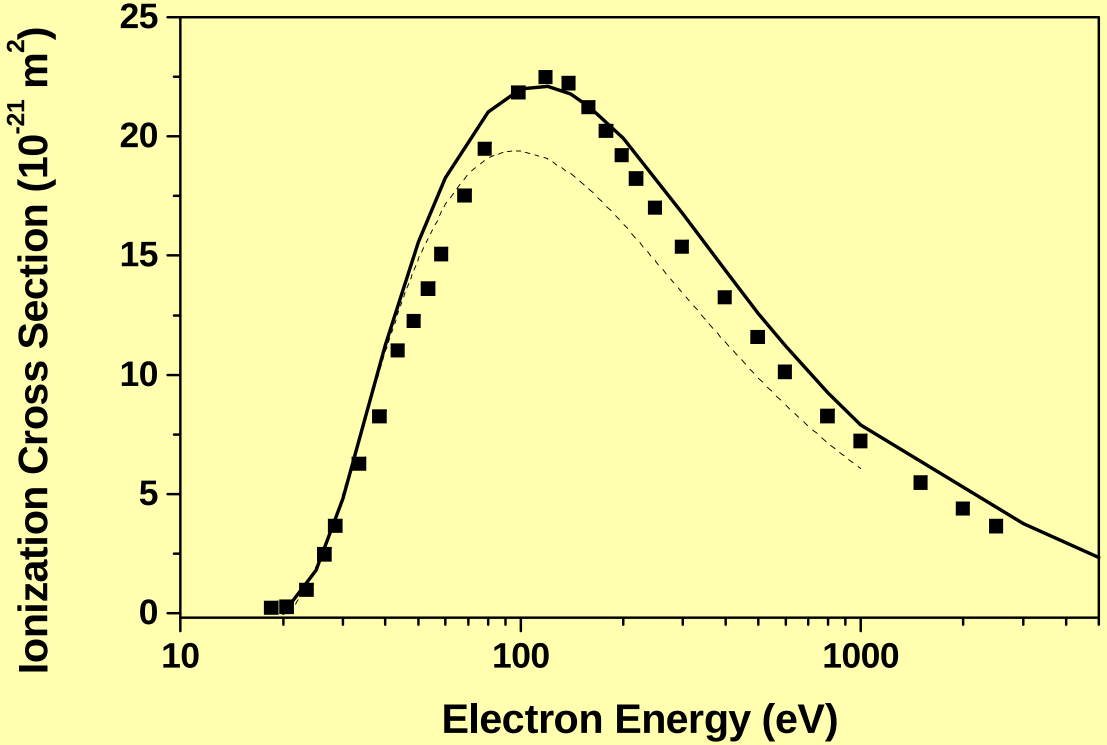
$C_2H_2^{+} + e \rightarrow C_2H_2^{++}$

$\downarrow \rightarrow$ 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].

Conclusion

Electron ionization of hydrocarbon molecules:

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

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

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

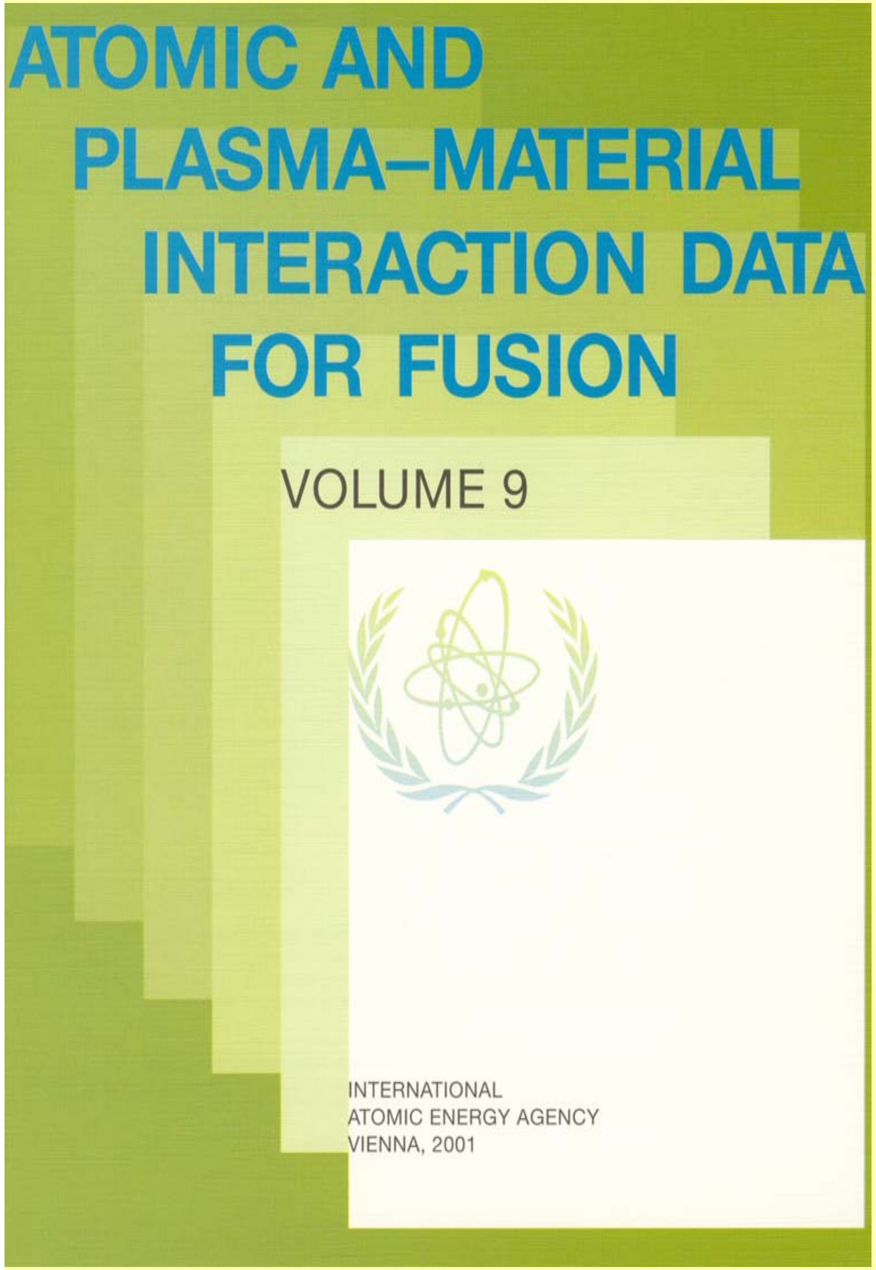
$$C_3H_6 + e \rightarrow \text{ions}$$

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

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

....

Total, partial, and differential cross sections;
Temperature effect on 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.

CONTENTS

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 well.

Electron Impact Ionization

Edited by
T. D. Märk and G. H. Dunn

Springer-Verlag Wien New York

TOPICS IN PHYSICAL CHEMISTRY

Edited by H. Baumgärtel, E. U. Franck, W. Grünbein

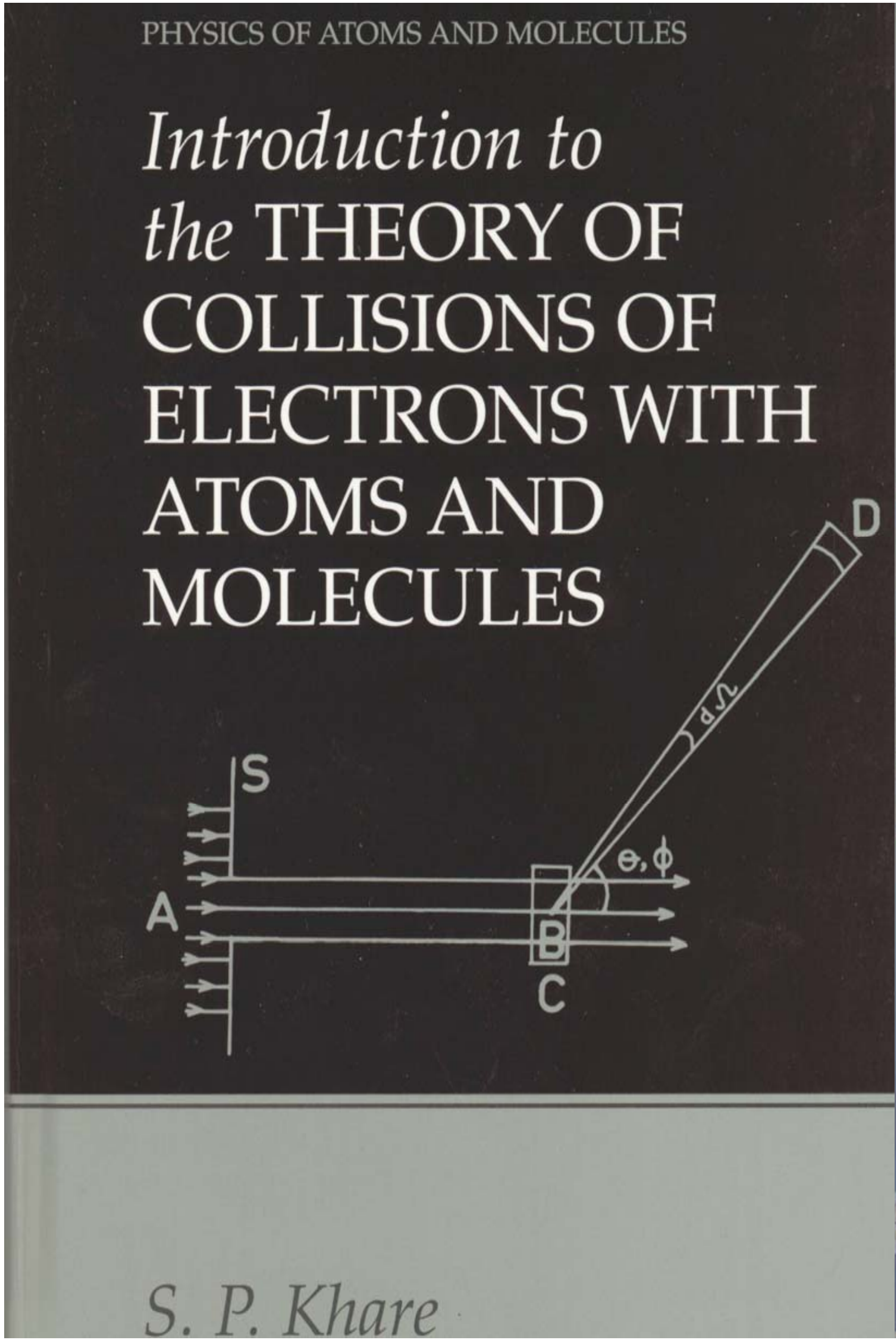
On behalf of Deutsche Bunsen-Gesellschaft
für Physikalische Chemie

Gaseous Molecular Ions

An Introduction to Elementary
Processes Induced by Ionization

E. Illenberger, J. Momigny

Steinkopff Verlag Darmstadt
Springer-Verlag New York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Introduction to the THEORY OF COLLISIONS OF ELECTRONS WITH ATOMS AND MOLECULES
D
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A
B
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θ, φ
dΩ
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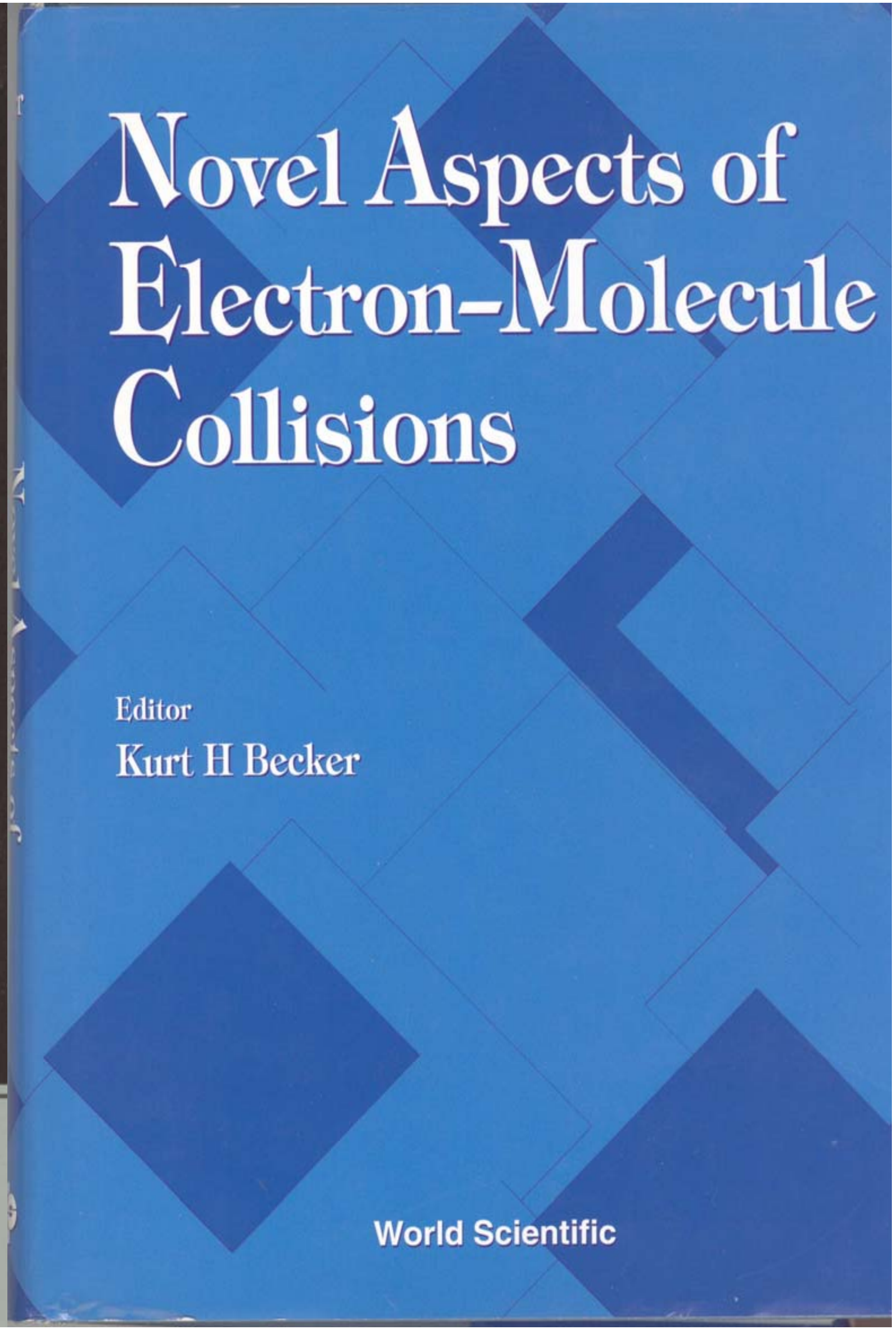

Novel Aspects of Electron–Molecule Collisions
Editor
Kurt H Becker
World Scientific

http://webbook.nist.gov/

Metastable Decay Reactions

Time dependent measurements of the KER of singly charged ions

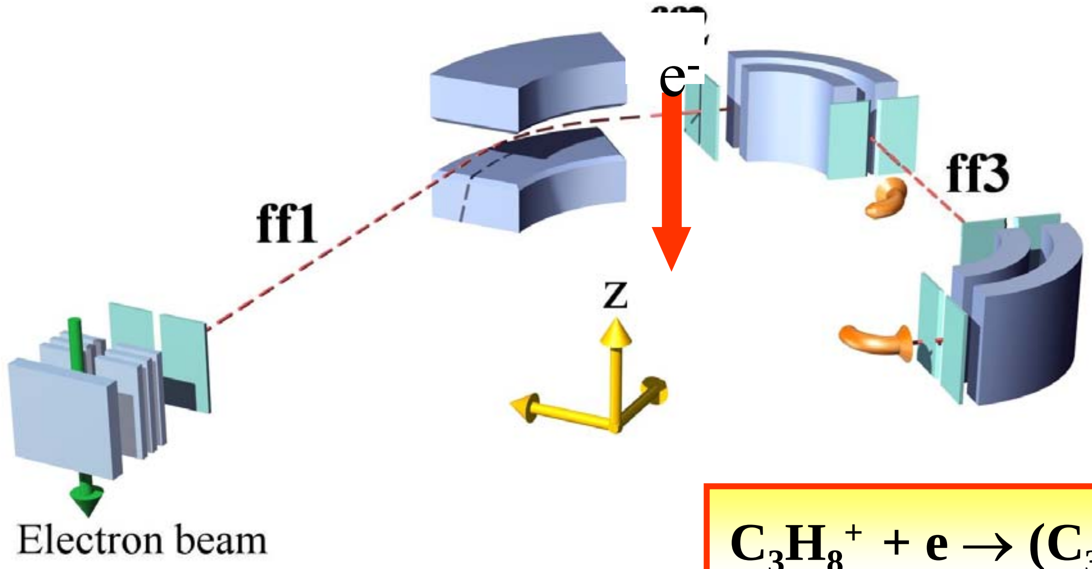
<u>Spontaneous decay reactions</u>: Excitation: Ion source

Decay in ff2: time delay 11-14 µs

Decay in ff3: time delay 17-25 µs

$$(C_3H_8^+)^* \rightarrow C_3H_7^+ + H + KER$$

Experimental set up



<u>Electron induced decay reactions</u>:

Excitation: ff2

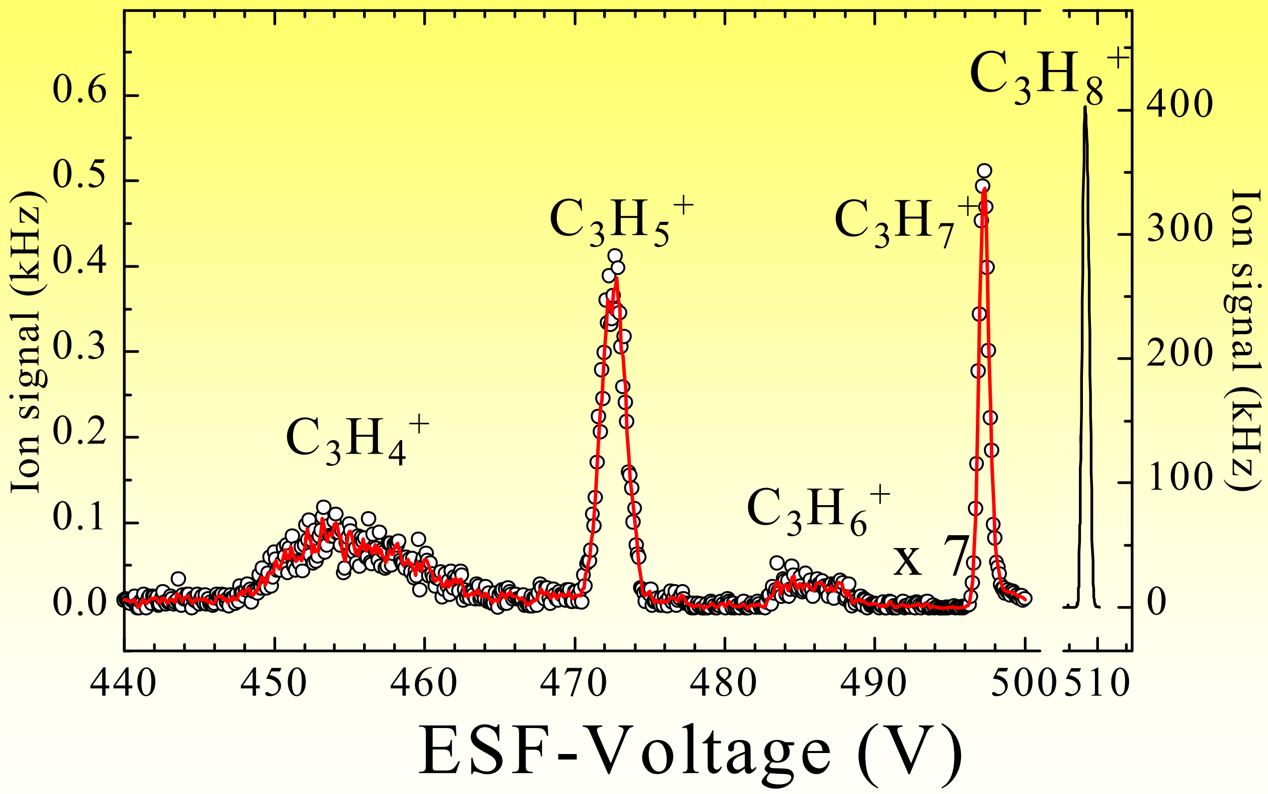
Decay: ff2

⬇

time delay of 0 - 0.75 µs

$$C_3H_8^+ + e \rightarrow (C_3H_8^+)^{**} + e \rightarrow C_3H_7^+ + H + KER$$

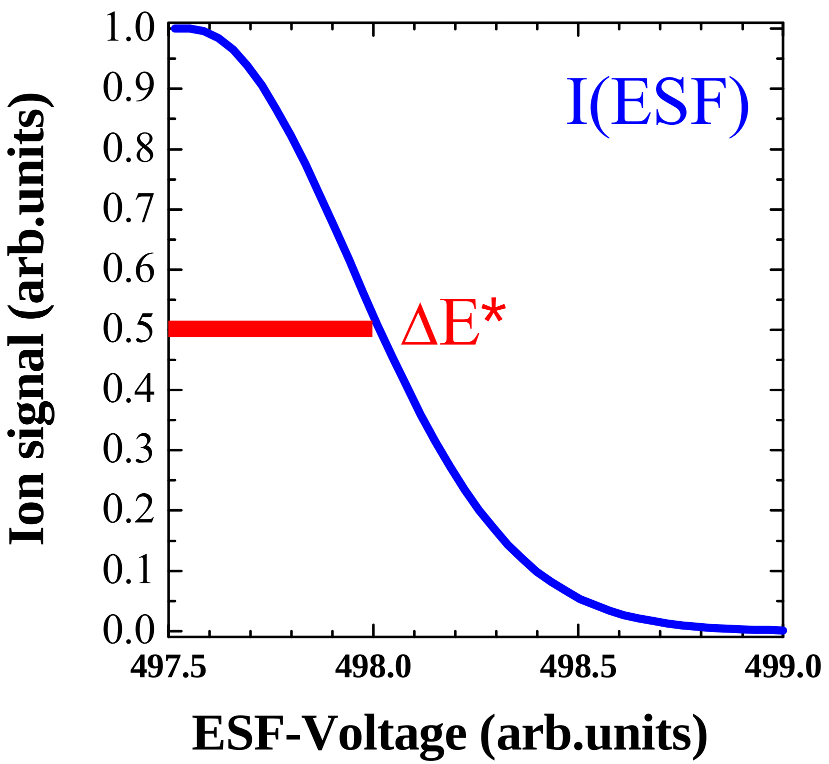
MIKE-Spectrum



Identification:

$$E^{*} = E^{0}\,\frac{q_1 m_2}{m_1 q_2}$$

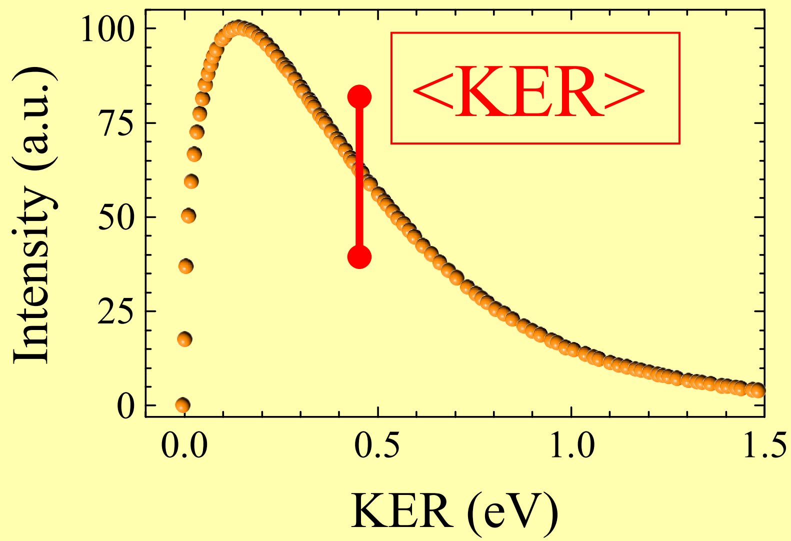
Determination of the kinetic energy release distribution - KERD



$$< KER >= 2.16 \frac{z_2^2 m_1^2 U_0}{16\, z_1 m_2 m_3} \left(\frac{\Delta E^*}{E^0} \right)^2$$

KER Distribution:

- 1st derivative to obtain the shape
- Lab system → CMS absolute numbers



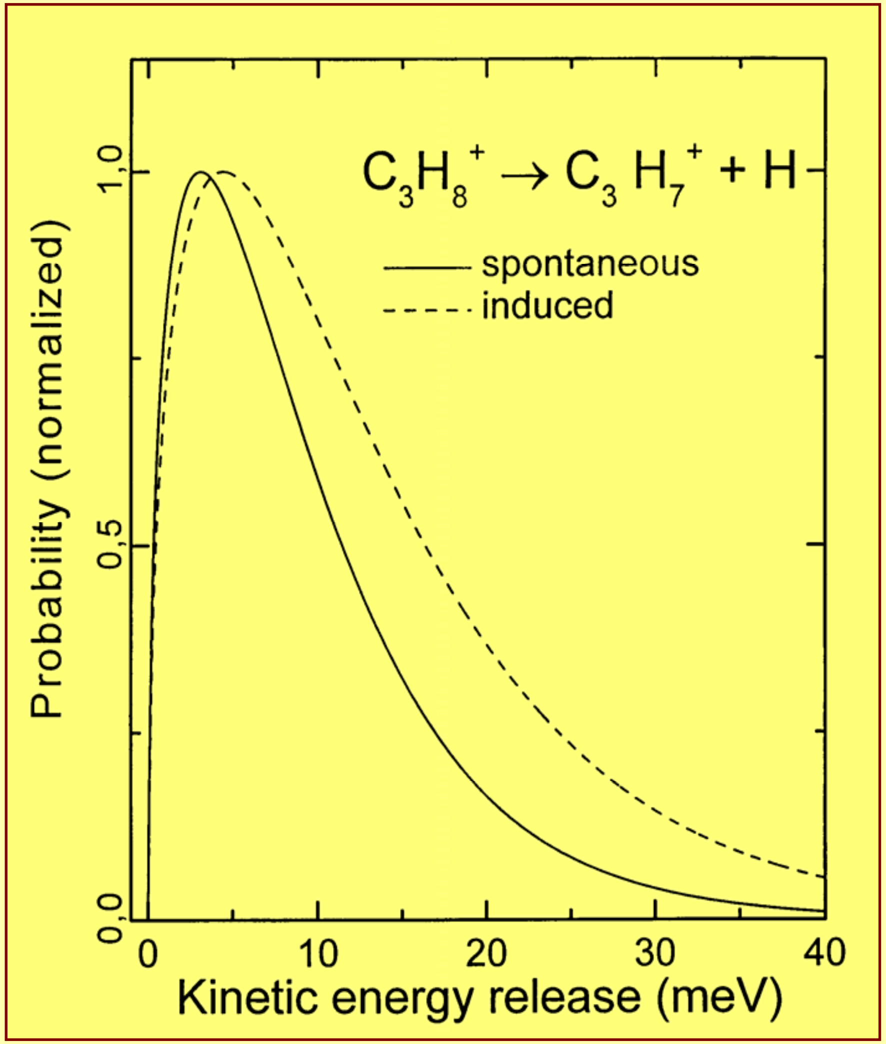
Time dependence of kinetic energy release for decay reaction

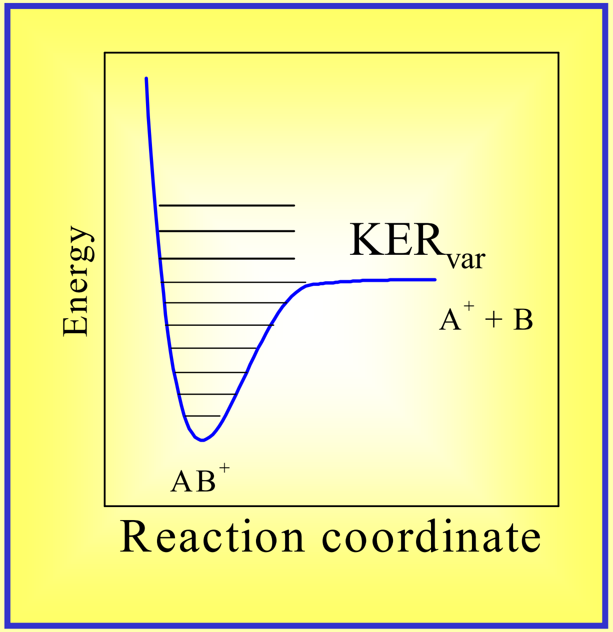
Electron-induced decay reaction:

0-1μs time regime

Spontaneous decay reactions:

11-14μs time regime





Finite heat bath theory

Experiment: <KER> measured in three different time windows

Theory: $$< KER >= 1.5 k_B T^{\#}$$ **$T^{\#}$ is the transition state temperature**

$$T^{\#} = T_b \frac{\gamma/(C-1)}{\exp(\gamma/(C-1))-1}$$

C....vibrational heat capacity, depends on T_b
calculated on the basis of the vibrational frequencies of the ion

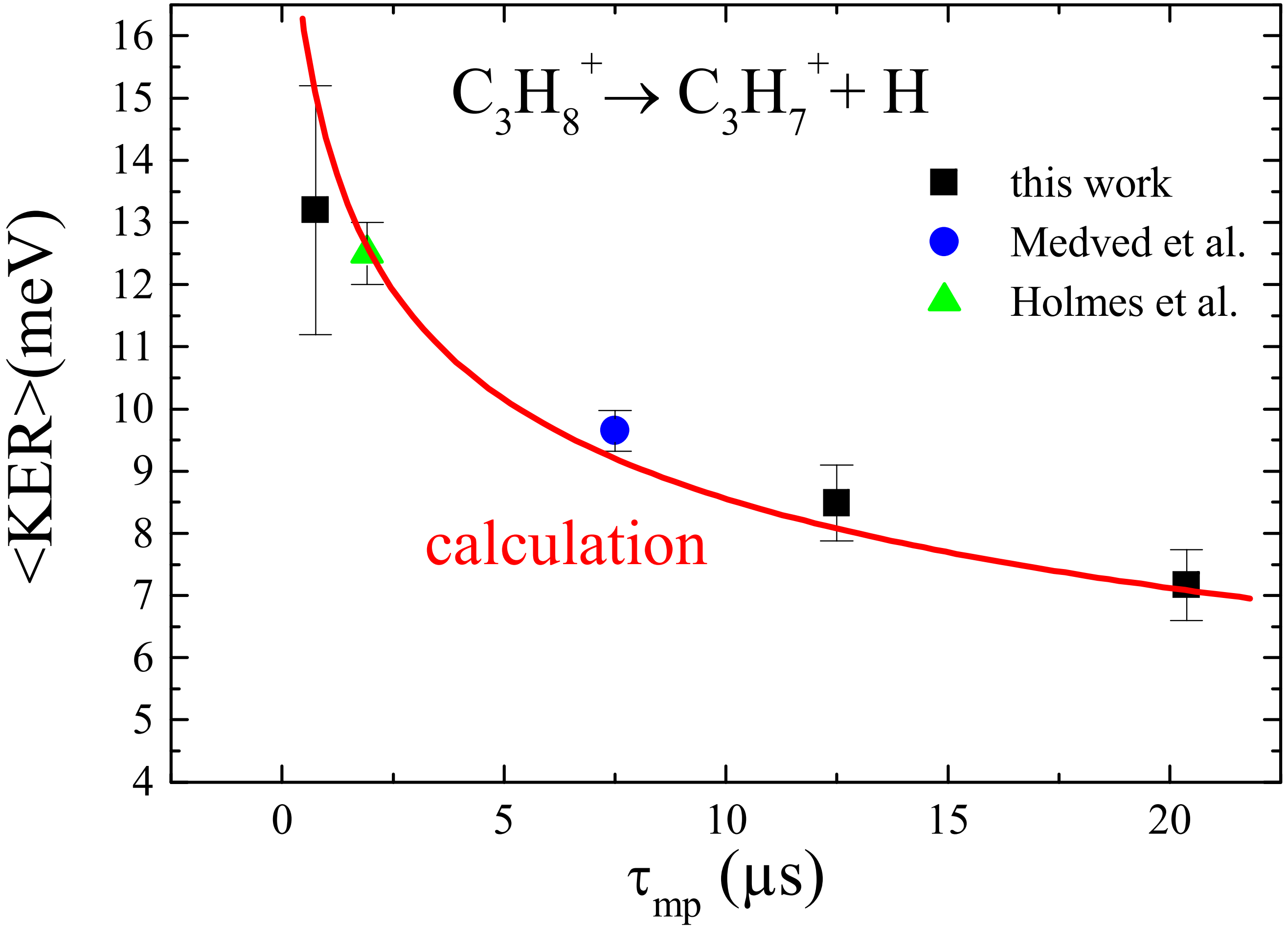
$$k(T_b) = k_{mp} \Rightarrow T_b(\tau_{mp})$$

$$\gamma = ln\left(\frac{A}{k_{mp}}\right) = \frac{E_a}{k_B T_b}$$

A.....$9.2 \times 10^{12} s^{-1}$ result of ab initio calculations
E_a....0.65 eV NIST: recommended value

$$[\gamma(\tau_{mp}), T_b(\tau_{mp})] \Rightarrow T^{\#}(\tau_{mp}) \Rightarrow <KER>(\tau_{mp})$$

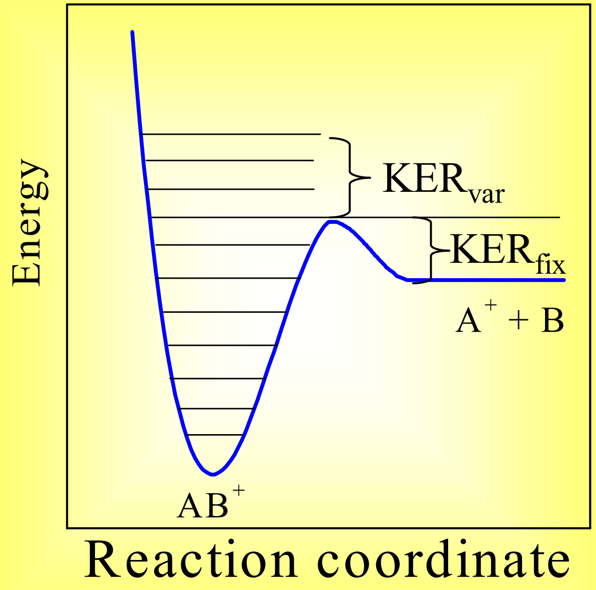
Time dependent measurements - results



A = 10^{13} s^{-1}

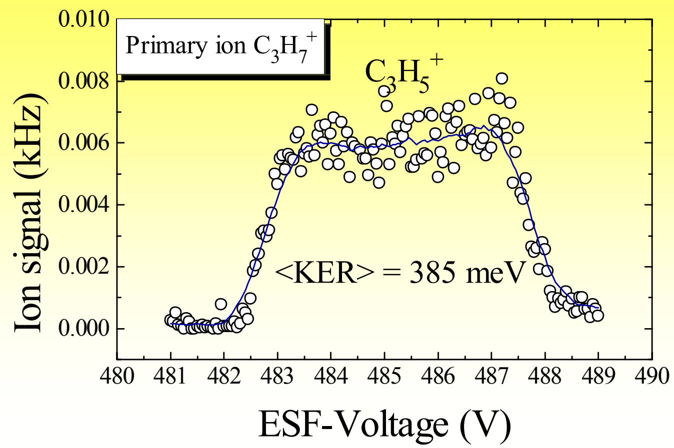
BE = 0.65 eV

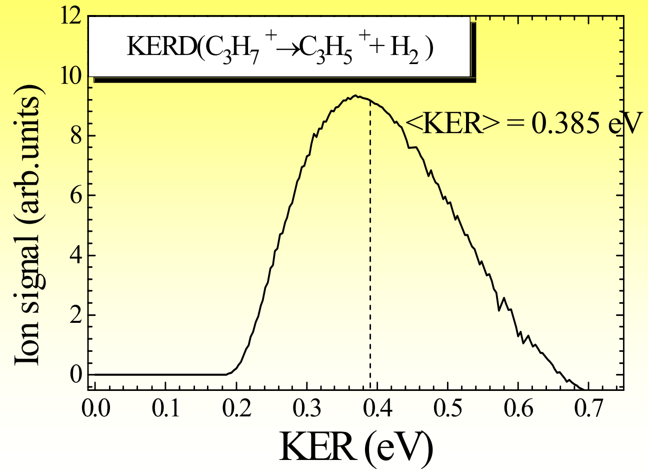
Kinetic energy release distributions (2)



$$E^* = E^0 \frac{q_1 m_2}{m_1 q_2} = 485.5$$

I(E*)=I(KER=0)





KER$_{meas}$ = KER$_{fix}$ + KER$_{var}$ ≥ KER$_{fix}$