



*The Abdus Salam*  
**International Centre for Theoretical Physics**



**2028-15**

**Joint ICTP/IAEA Workshop on Atomic and Molecular Data for  
Fusion**

**20 - 30 April 2009**

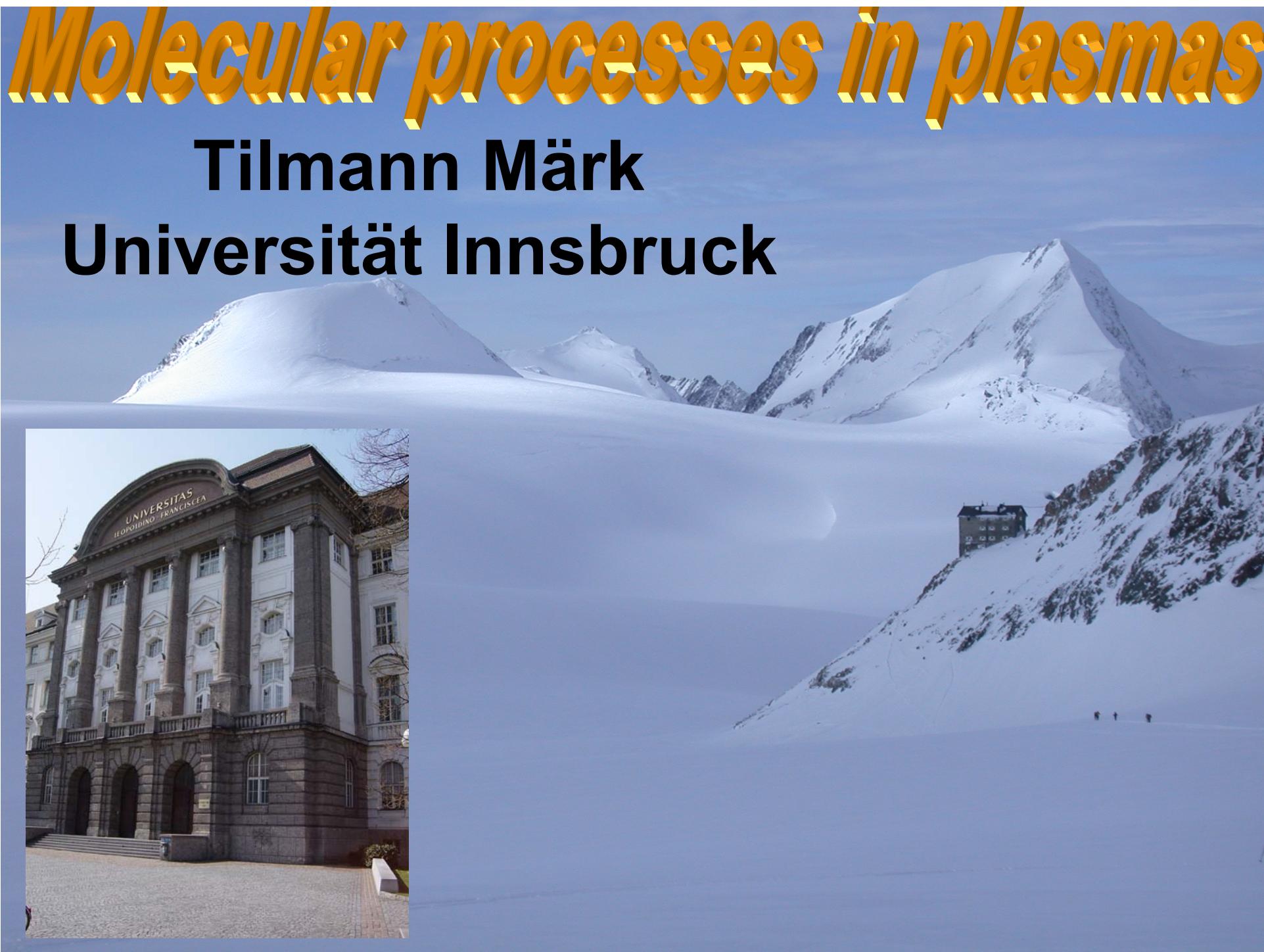
**Molecular Processes in Plasmas**

Tilman MAERK

*Universitat Innsbruck, Institut fuer Physik, 81 Technikerstrasse, A-6020  
Innsbruck  
Austria*

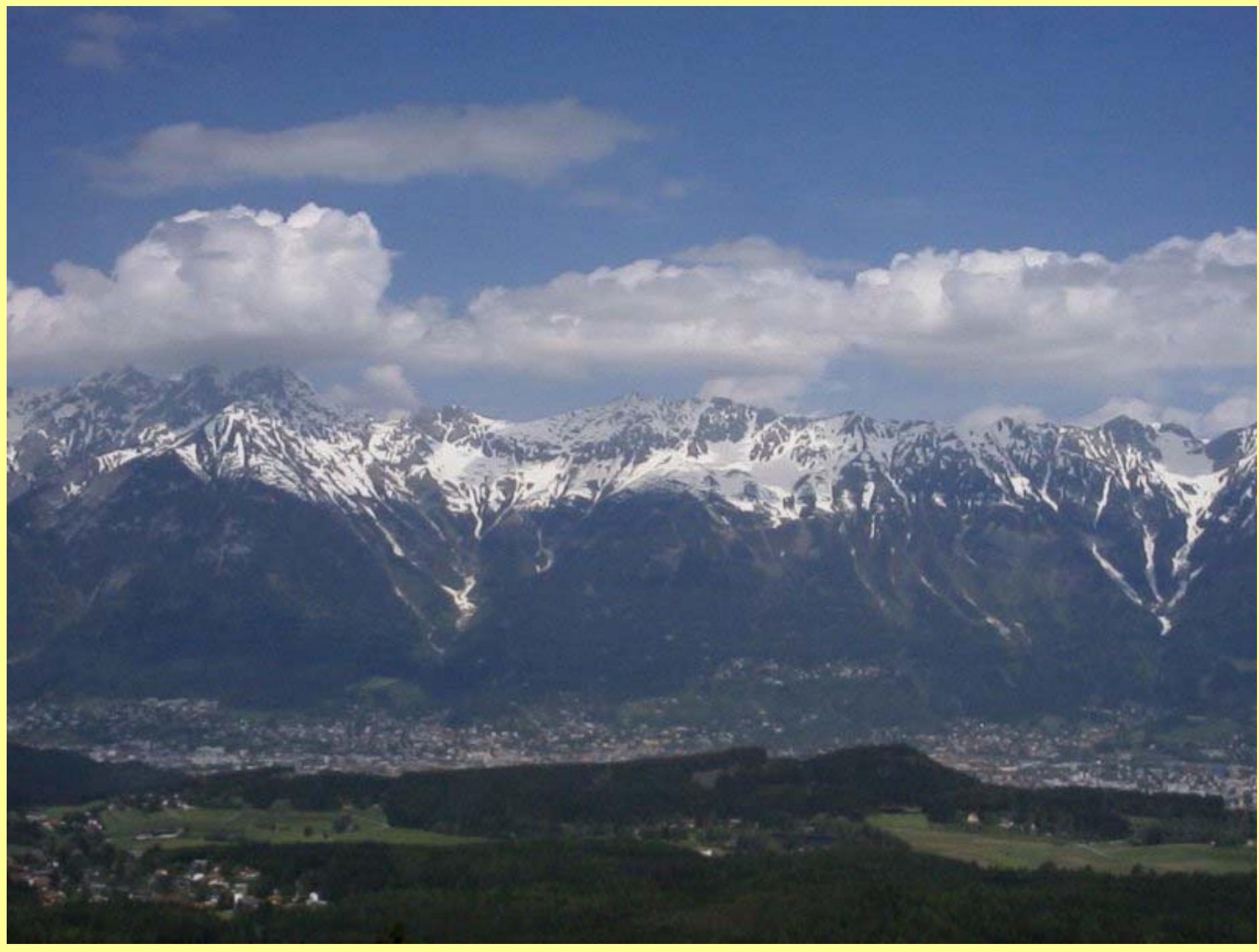
# *Molecular processes in plasmas*

Tilmann Märk  
Universität Innsbruck

















## Institut für Ionenphysik und Angewandte Physik

<http://info.uibk.ac.at/ionenphysik>

**Ion Physics / Plasma Physics**

**Clusterphysics, Biomolecules**

**Mass Spectrometry**

**Environmental Physics and Analysis**



Elahe Alizadeh  
PhD student  
6268 / Lab: 6257  
[Elahe.Alizadeh@uibk.ac.at](mailto:Elahe.Alizadeh@uibk.ac.at)

- E. Alizadeh, F. Ferreira da Silva, F. Zappa, A. Mauracher, M. Probst, S. Denifl, A. Bacher, T. D. Märk, P. Limao-Vieira, P. Scheier, Dissociative electron attachment to nitromethane. *Int. J. Mass. Spectrom.* 1-3/**271** (2008) 15-21 [PDF](#); [doi:10.1016/j.ijms.2007.11.004](https://doi.org/10.1016/j.ijms.2007.11.004); IF:2.337
- A. Mauracher, P. Sulzer, E. Alizadeh, S. Denifl, F. Ferreira da Silva, M. Probst, T. D. Märk, P. Limao-Vieira, P. Scheier, Electron attachment studies to musk ketone and high mass resolution anionic isobaric fragment detection. *Int. J. Mass. Spectrom.* 1-3/**277** (2008) 123-129 [PDF](#); [doi:10.1016/j.ijms.2008.06.006](https://doi.org/10.1016/j.ijms.2008.06.006); IF:2.411
- S. Ptasinska, E. Alizadeh, P. Sulzer, R. Abouaf, N. J. Mason, T. D. Märk, P. Scheier, Negative ion formation by low energy electron attachment to gas-phase 5-nitouracil. *Int. J. Mass. Spectrom.* 1-3/**277** (2008) 291-295 [PDF](#); [doi:10.1016/j.ijms.2008.06.008](https://doi.org/10.1016/j.ijms.2008.06.008); IF:2.411
- P. Sulzer, E. Alizadeh, A. Mauracher, T. D. Märk, P. Scheier, Detailed dissociative electron attachment studies on the amino acid proline. *Int. J. Mass. Spectrom.* 1-3/**277** (2008) 274-278 [PDF](#); [doi:10.1016/j.ijms.2008.06.001](https://doi.org/10.1016/j.ijms.2008.06.001); IF:2.411



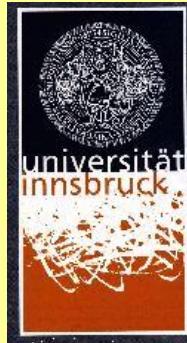
Masoomeh Mahmoodi-Darian  
PhD student  
6268 / Lab: 6251  
[Masoomeh.Mahmoodi@uibk.ac.at](mailto:Masoomeh.Mahmoodi@uibk.ac.at)



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## **Elementary processes considered:**

Inelastic electron interactions with  
atoms/molecules/nanoparticles  
(ionization and attachment)



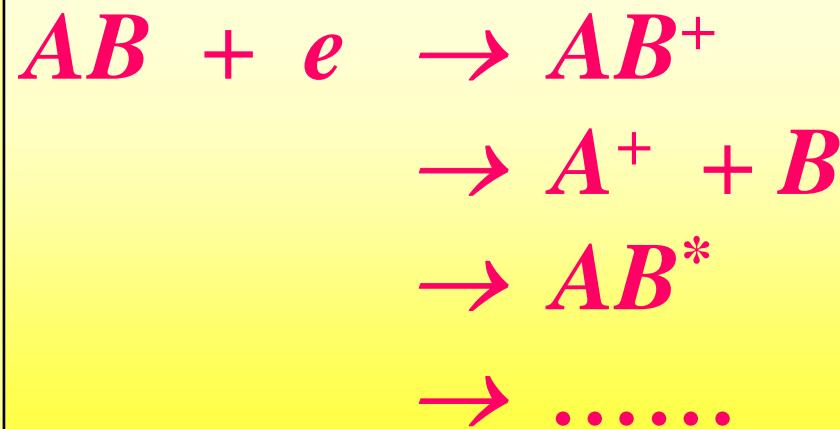
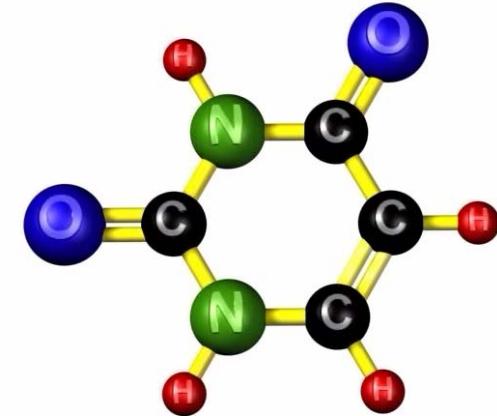
- 1. Intrinsic fundamental interest**
- 2. Provide data needed for plasma modelling  
and diagnosis and other applications**
- 3. Radiation damage**



EURATOM  
ÖAW

**Data acquisition (processes, properties)**  
**Data analysis and assessment**  
**Data compilation (ADAS, IAEA)**

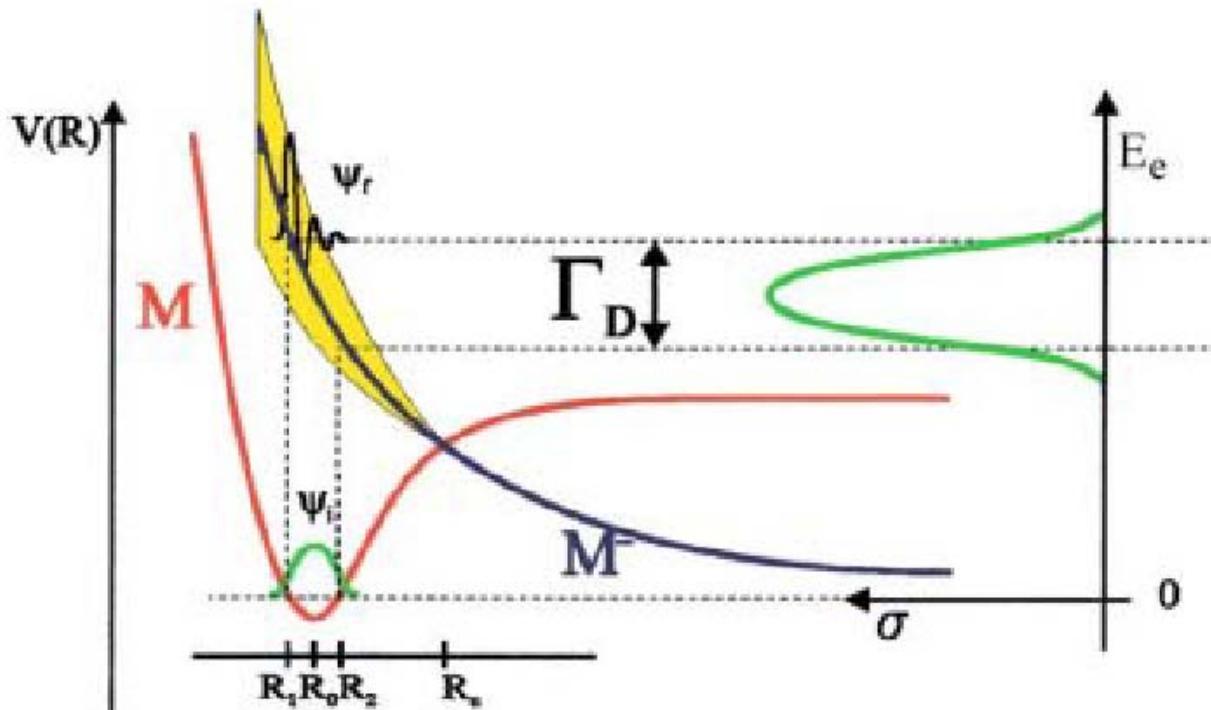
## Inelastic low-energy electron interaction with molecules



*ionization*  
*dissociative ionization*  
*excitation*

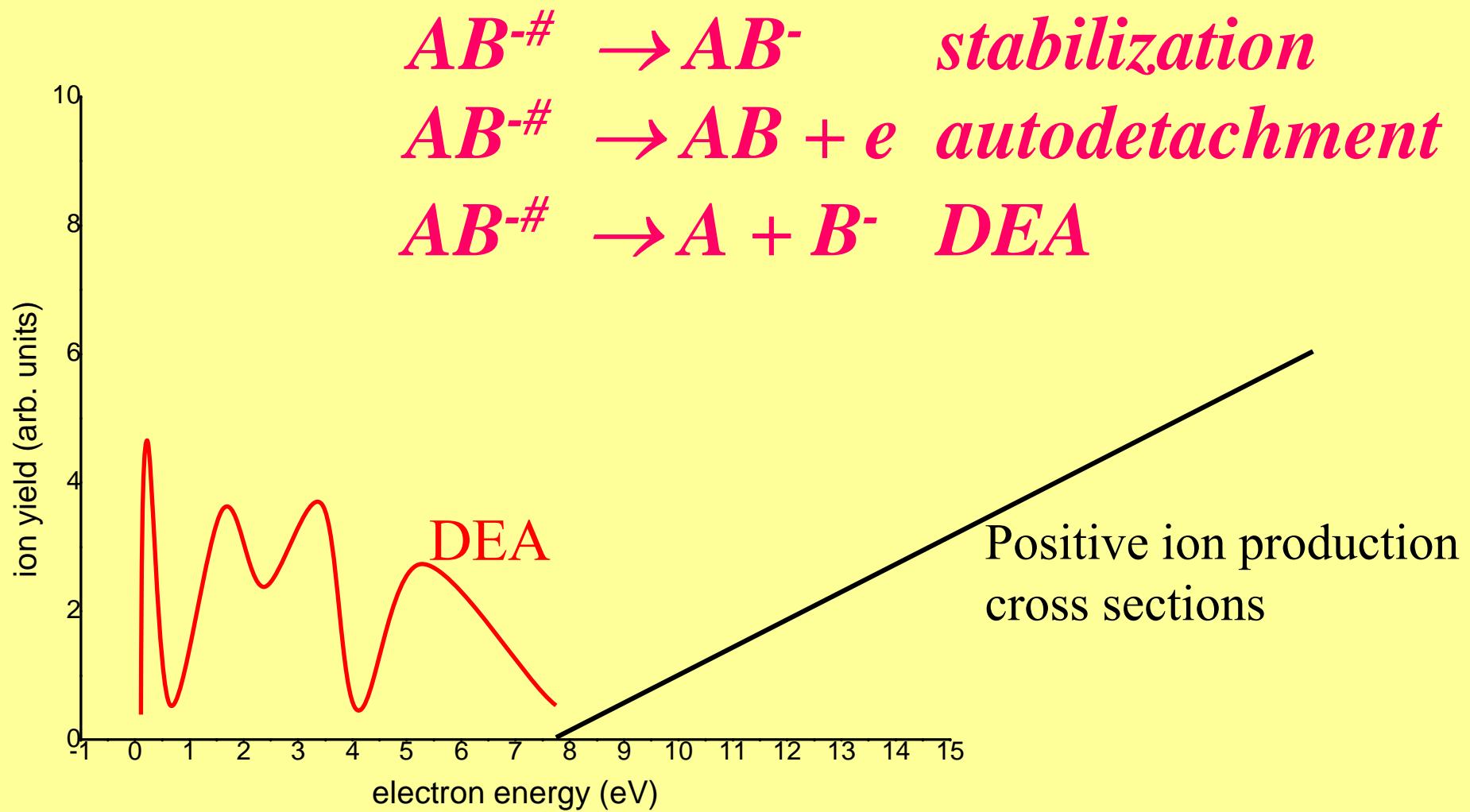


# Dissociative Electron Attachment



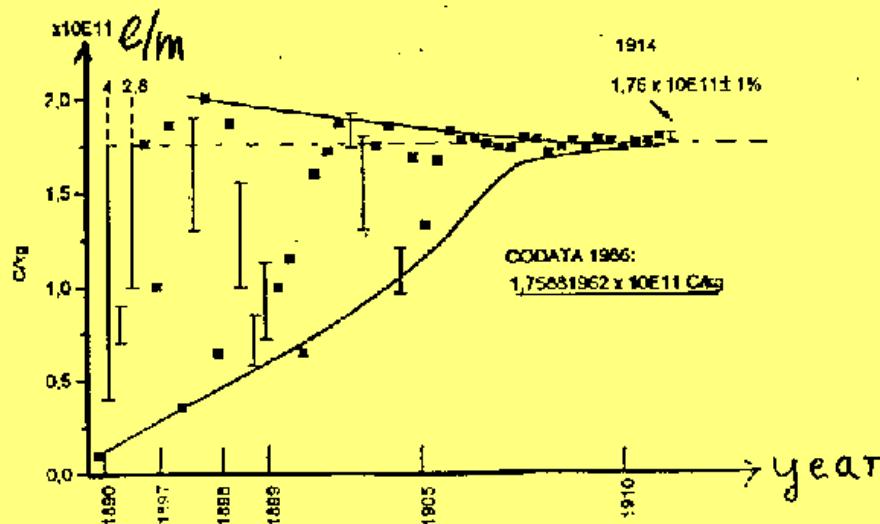
Dissociative electron attachment  $AB + e^- \Rightarrow AB^{-*} \Rightarrow A^- + B$  can be described via the formation of a temporary negative ion  $AB^{-*}$ . The electron in this molecular anion state  $AB^-$  (also called the resonant state) can autodetach with a finite lifetime (related to the width of the resonance), leaving behind a vibrationally excited neutral molecule. On the other hand, if the lifetime of the resonance is long enough, the anion  $AB^-$  can dissociate into  $A+B^-$ , leading to the process of dissociative electron attachment.

# Electron attachment to molecules



# *Motivation*

## 1. The discovery: the e/m determination



## 2. Other properties accurately known:

(*besides spin*)

### Elementary charge:

$$e = 1.602\ 177\ 33 \times 10^{-19} \text{ C}$$

### Mass:

$$m_p/m_e = 1836.152\ 470 \quad IJMSIP, 66 (1985) 327$$

### Magnetic moment: $\mu = g_e(e/2m)\mathbf{s}$

-2x(1+0.001 159 652 188) *Dehmelt et al., PRL, 59(1987)26*

-2x(1+0.001 159 652 140) *Kinoshita, Quant.Electr., 1990*

5. „Why investigate still properties of the electron?“

## Motivation:

1. Most important primary ionizing agent

(compare ionization cross sections for  $e^-$ ,  $h\nu$ ,  $p^+$ )

2. Simple and cheap to produce

3. Many applications :

- ♣ mass spectrometry
- ♦ plasma physics and chemistry
- ♥ atmospheric physics and chemistry
- ♠ radiation physics

## 1. Plasma: Electrons, Ions, Neutrals

## 2. Ion Production:

Electron impact

Ion impact

Photon impact

(Ion molecule reaction)

## 3. Neutral targets:

Atoms

Molecules

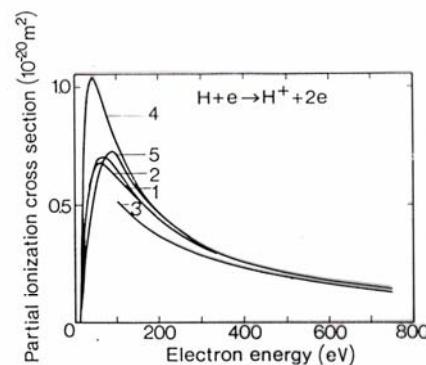
Radicals

Clusters

(Excited states)

## 4. Photons

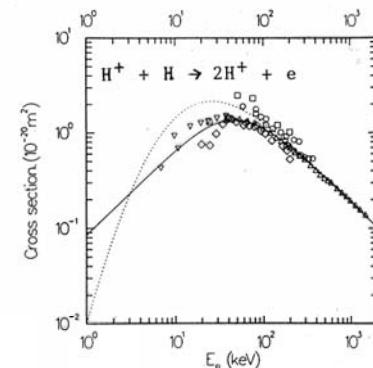
### Ion production:



Electron impact:

$$\sigma_{\max} \sim 1 \times 10^{-20} m^2$$

at 100 eV

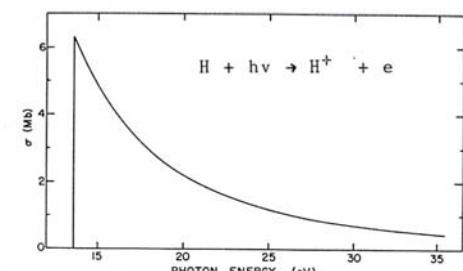


Proton impact:

$$\sigma_{\max} \sim 1 \times 10^{-20} m^2$$

at 100 keV

$$(m_p/m_e)$$



Photon impact:

$$\sigma_{\max} \sim 5 \times 10^{-22} m^2$$

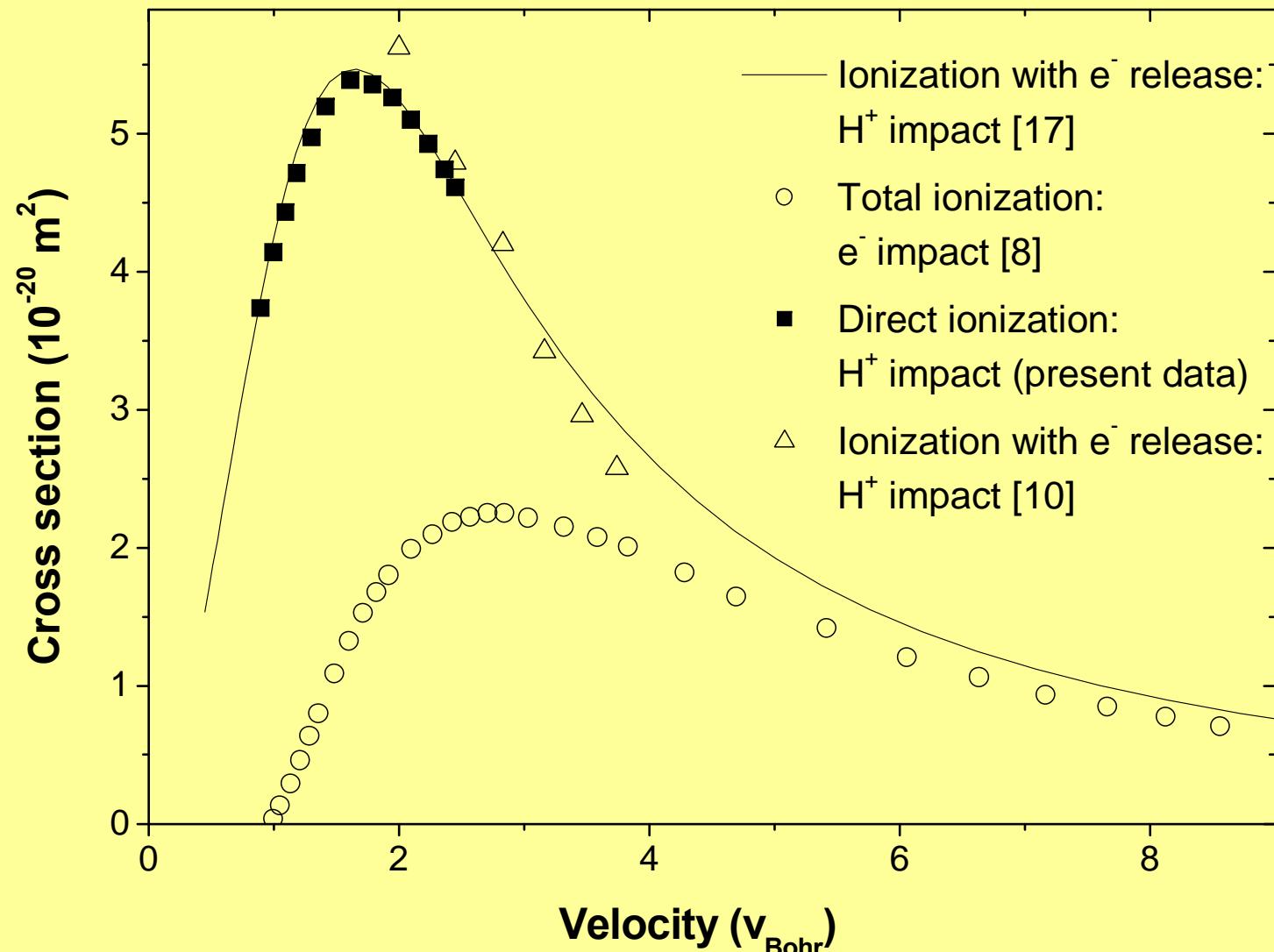
at  $\sim 10$  eV



*DI*



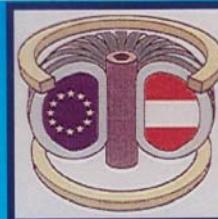
*EC*



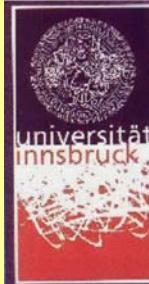
# Motivation



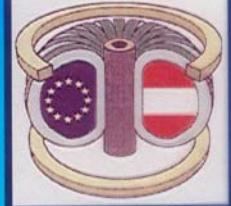
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- (1) Astrophysical plasmas
- stellar atmosphere
  - ionosphere
  - lightning
  - solar corona

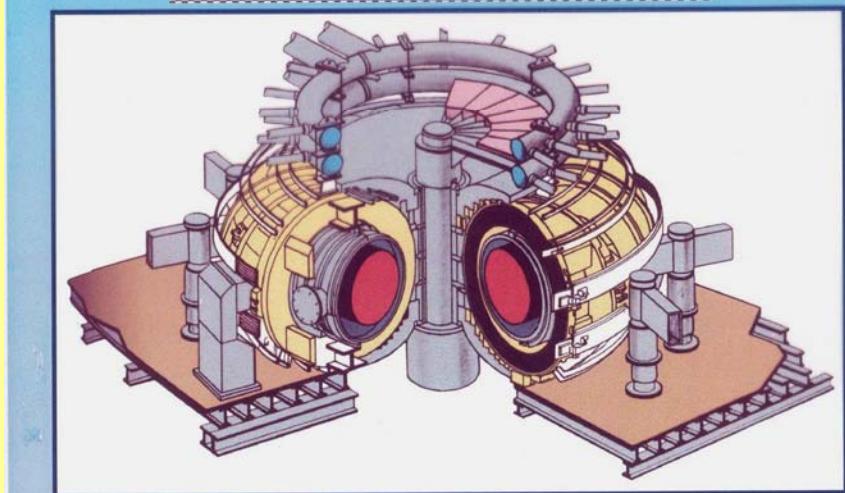


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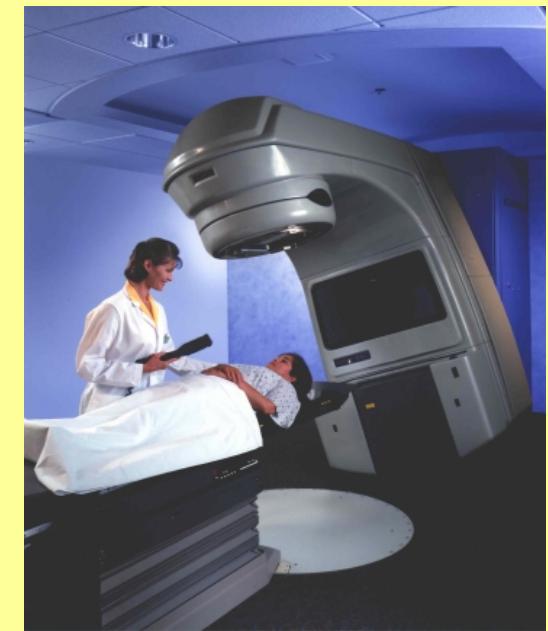
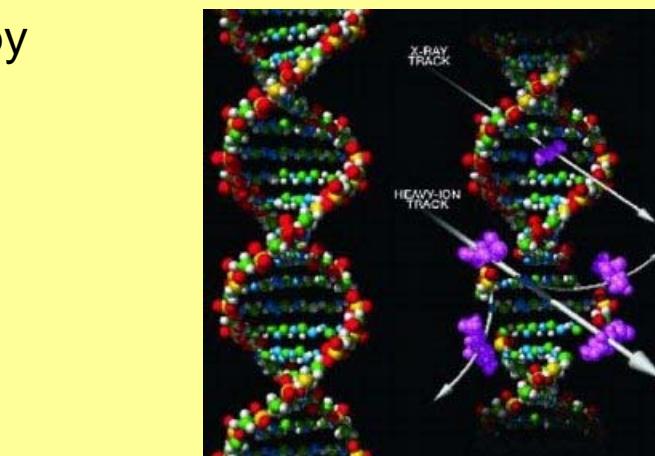
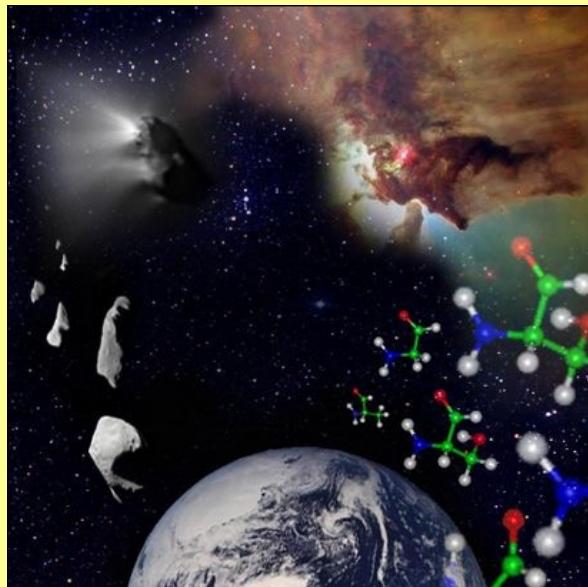
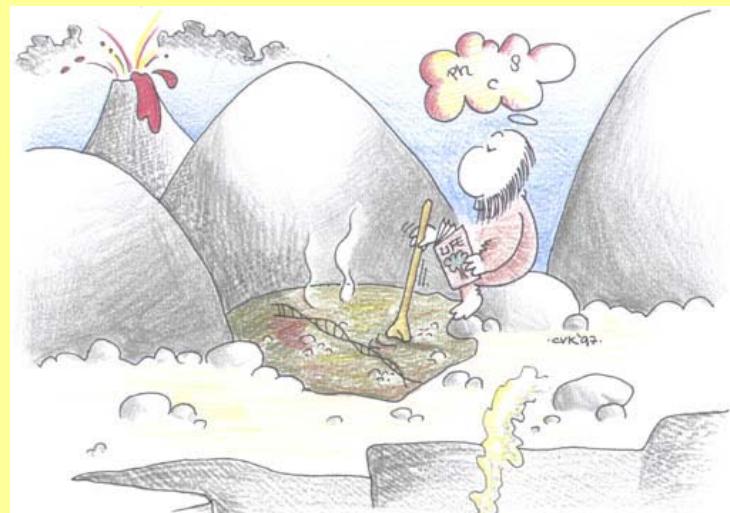
- (2) Industrial plasmas
- plasma deposition
  - plasma etching

- (3) Laboratory plasmas
- gas discharges
  - ion sources
  - gas lasers
  - fusion plasmas



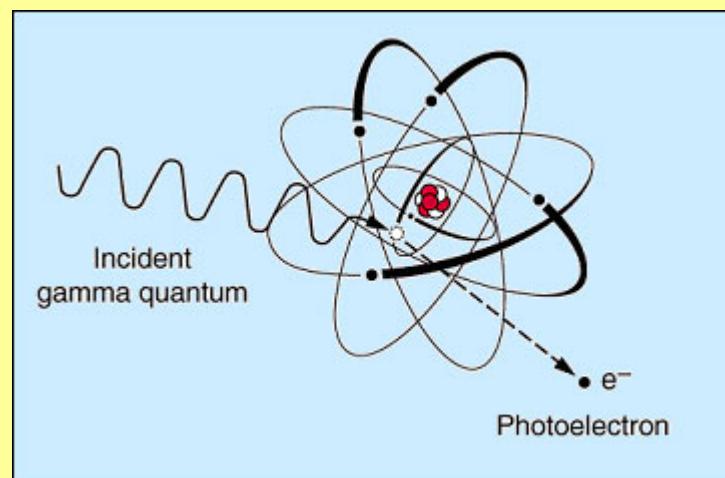
# Motivation

- Origin of life (photosynthesis)
- Life in space
- Radiation damage at a molecular level
- Improved radiation therapy



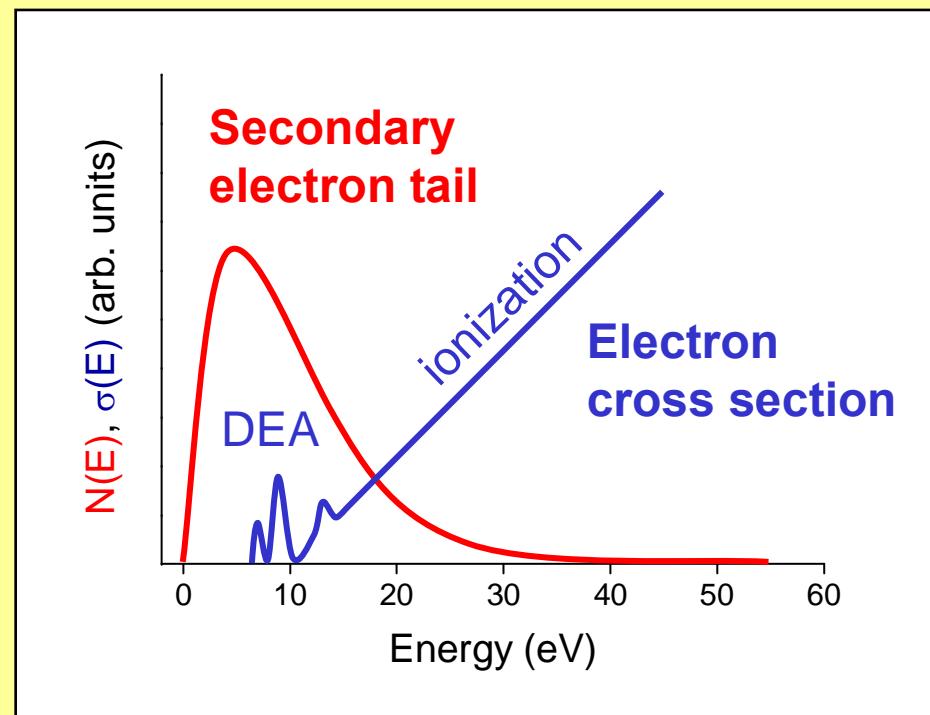
# *Why electrons ?*

- In space electrons are released via photon matter interactions (photo effect and photo ionization): **origin of life**



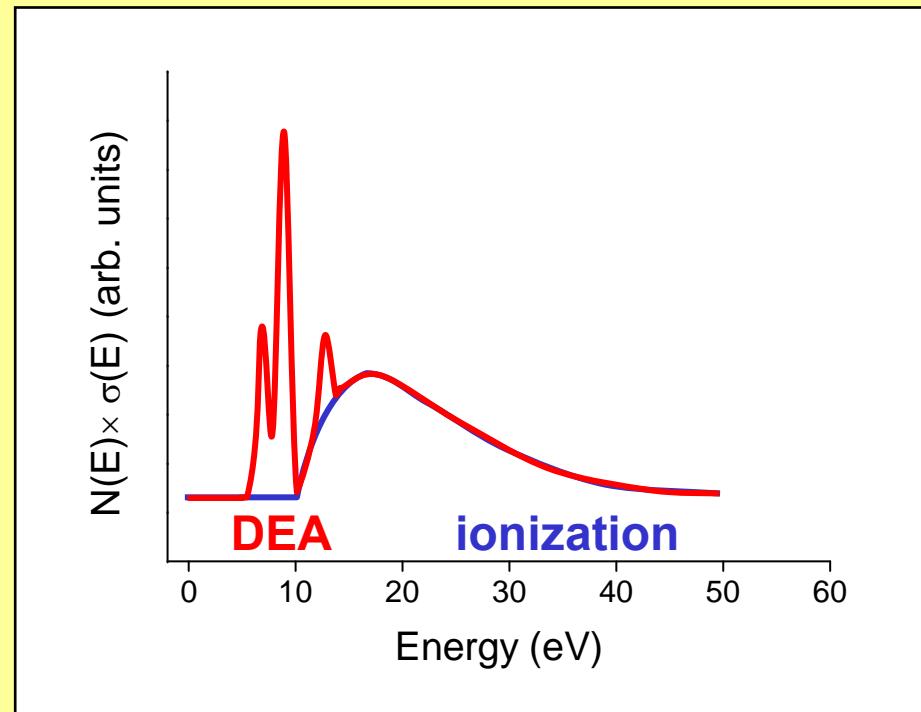
# Why electrons ?

- High-energy projectiles release in matter ~40000 electrons per MeV deposited energy with kinetic energies below 20eV: **radiation damage**



# Why electrons ?

- Low-energy electrons have high damage cross sections



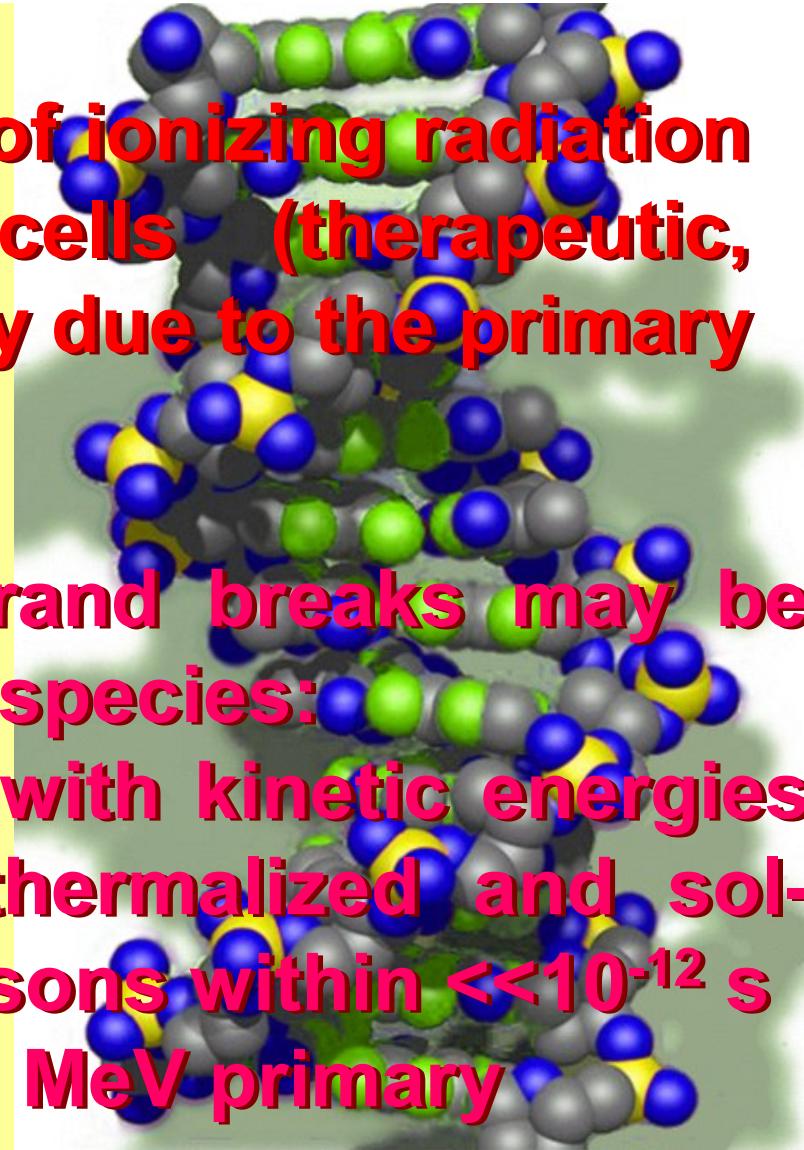
# DNA-strand breaks

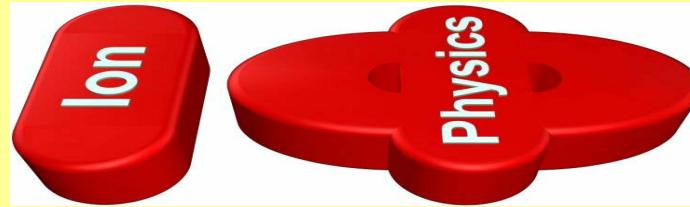


The genotoxic effects of ionizing radiation ( $\alpha, \beta, \gamma, X$ ) in living cells (therapeutic, diagnostic) are not only due to the primary impact.



Single and double strand breaks may be induced by secondary species:  
=secondary electrons with kinetic energies below about 20 eV thermalized and solvated by inelastic collisions within  $<<10^{-12}$  s  
= $4 \times 10^4$  electrons per 1 MeV primary





# Outline

## Part I: Fundamentals

- A. Ionization processes and Ions produced
- B. Ionization mechanisms

## Part II: Kinetics and energetics for the production of cations and anions

## Part III: Electron attachment



## Part I: Fundamentals

### A. Ionization processes and Ions produced

Direct Ionization – Indirect ionization

Stable ions – unstable (metastable) ions

Singly-charged ions

Multiply-charged ions

Parent ions – fragment ions

Cations - anions

# Electron-Particle Interaction

e + atom :

- ♠ *electronic excitation*

e + molecule :

- ♠ *electronic excitation*
- ♠ *vibrational excitation*
- ♠ *rotational excitation*
- ♠ *dissociation*

e + cluster :

- ♦ multiple collisions
- ♦ intra-cluster reactions

# Electron-Particle Interaction



Primary ionization event

Energy storage and disposal

Final reaction products

# Electron impact ionization processes

$A + e \rightarrow A + e$	elastic scattering
$A^* + e$	excitation
$A^{**} + e$	double excitation
$A^+ + 2e$	ionization
$A^{+*} + 2e$	excited ion
$A^{++} + 3e$	double ionization
$A^- + h\nu$	attachment

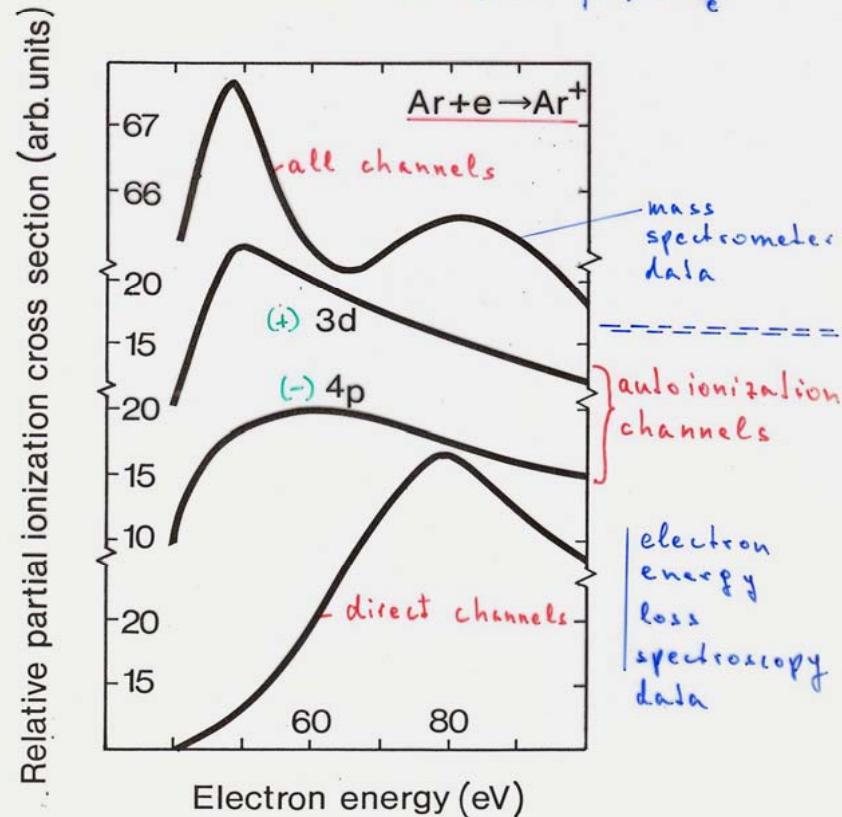
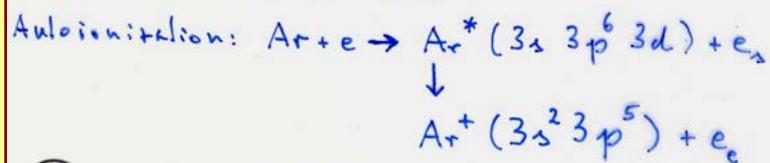
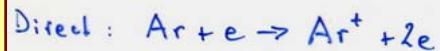
# Electron impact ionization processes

$AB + e \rightarrow AB + e$	elastic scattering	
$AB^* + e$	excitation	
$AB^{**} + e$	double excitation	$(AB^{**} \rightarrow AB^+ + e)$
$AB^+ + 2e$	ionization	
$AB^{+*} + 2e$	excited ion	$(AB^{+*} \rightarrow AB^{++} + e)$
$AB^{++} + 3e$	double ionization	
$AB^- + h\nu$	attachment	$(AB^- \rightarrow A^- + B)$

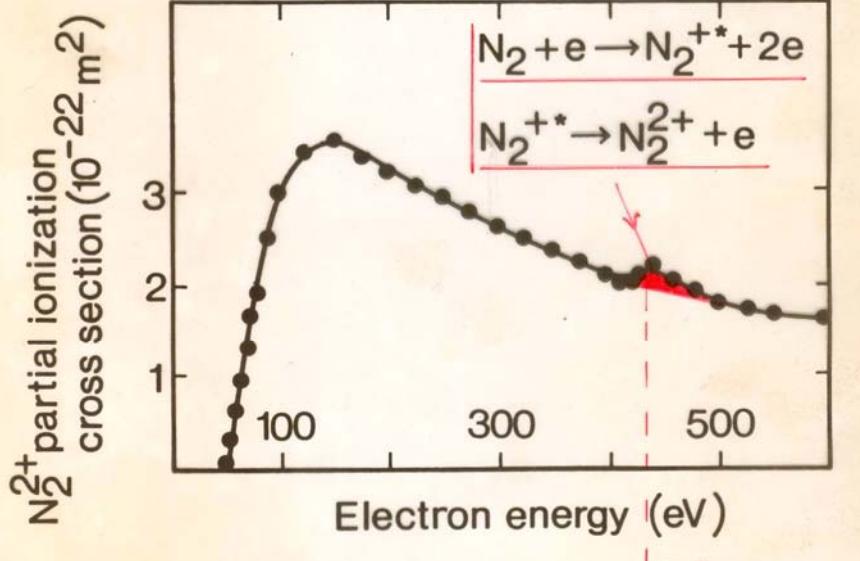
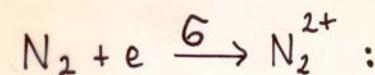
$AB + e \rightarrow AB(v,k) + e$	vibrational, rotational excitation
$A + B$	dissociation
$A^+ + B + 2e$	dissociative ionization
$A^+ + B^+ + 3e$	dissociative double ionization
$A^+ + B^{+-} + e$	ion pair formation
$A^{++} + B + 3e$	double dissociative ionization

# Direct and indirect ionization processes

Crone et al. 1972

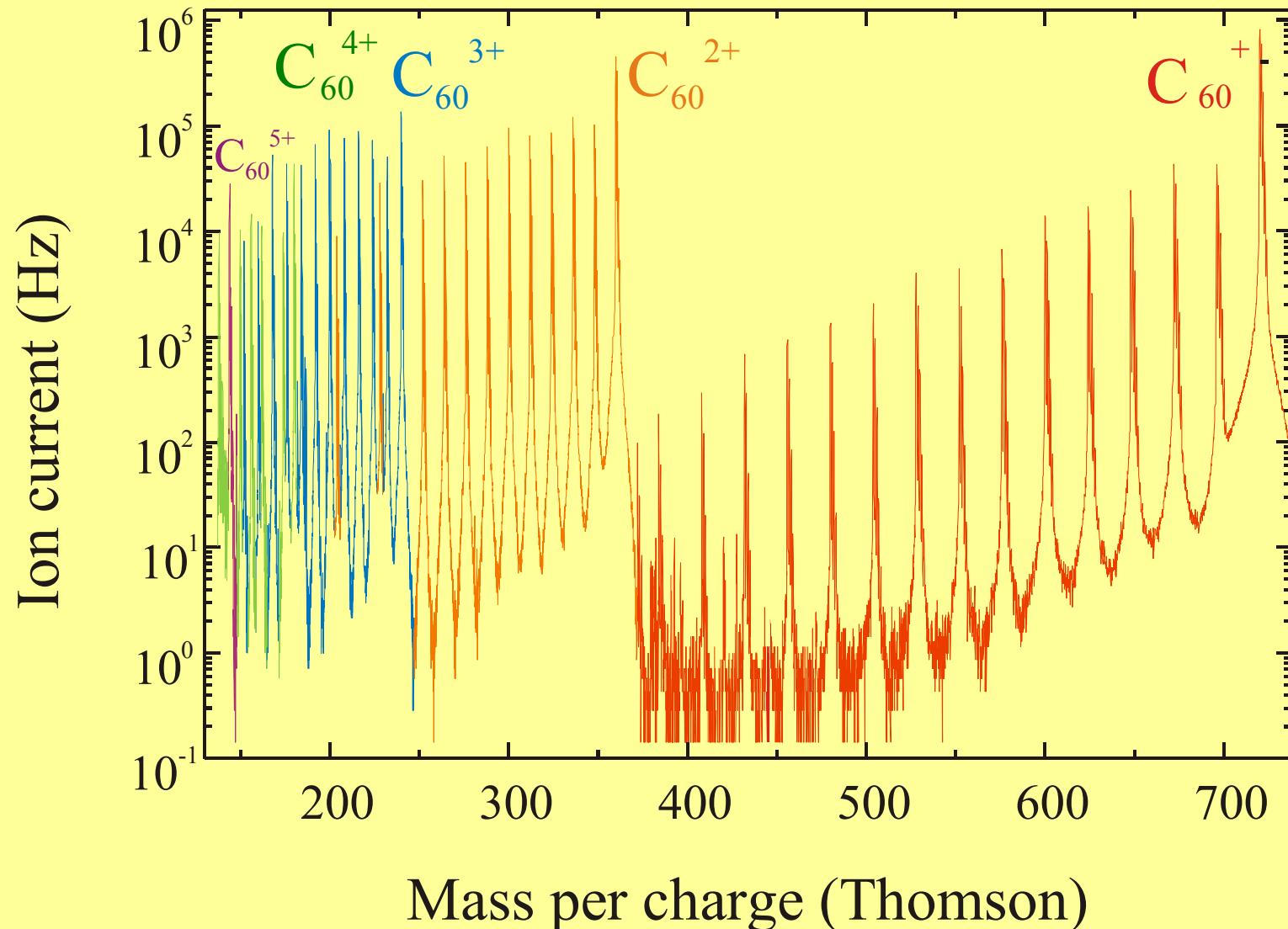
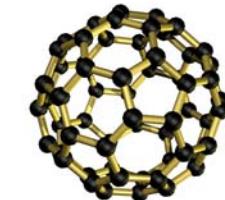


Adamczyk et al., 1972

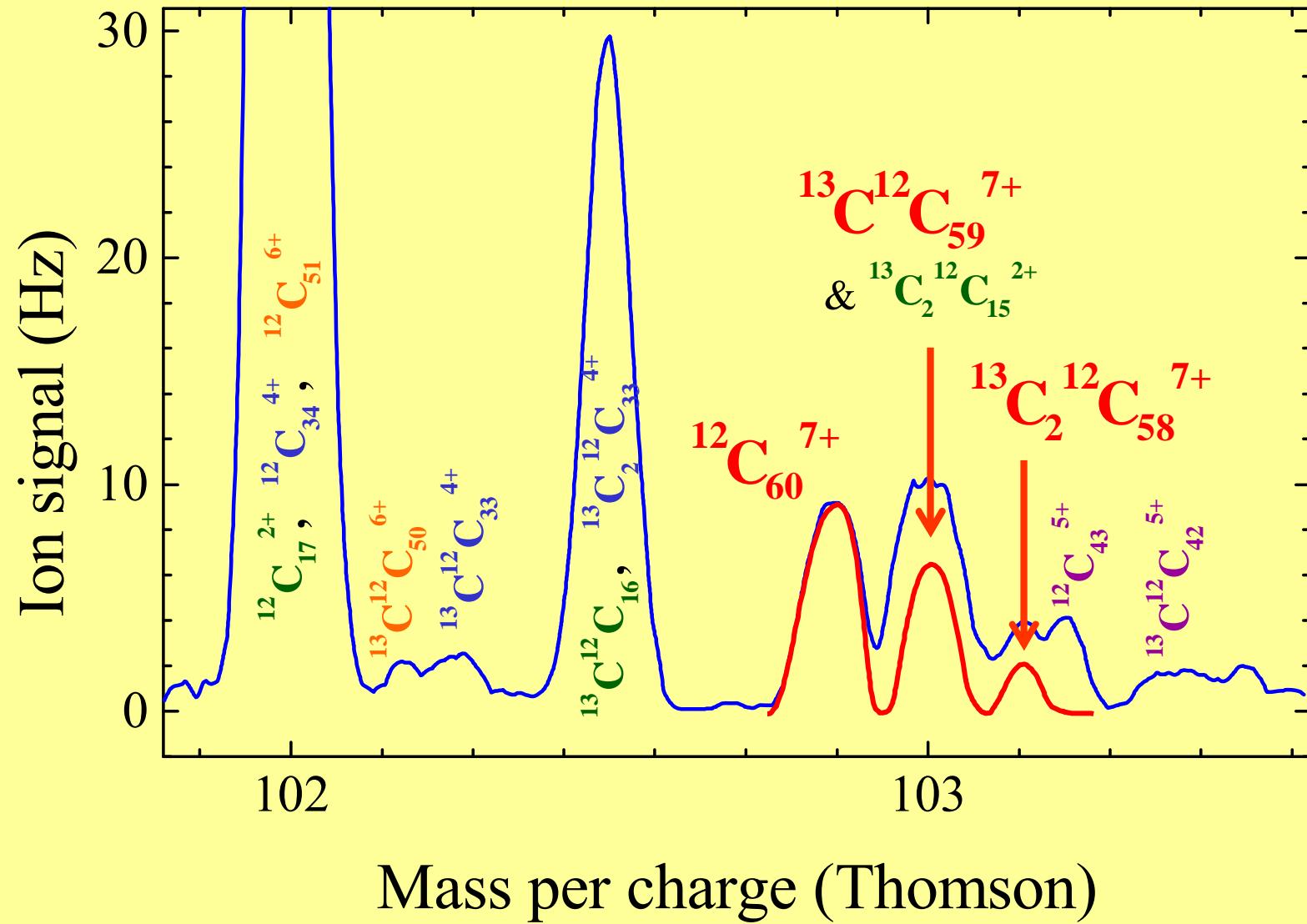


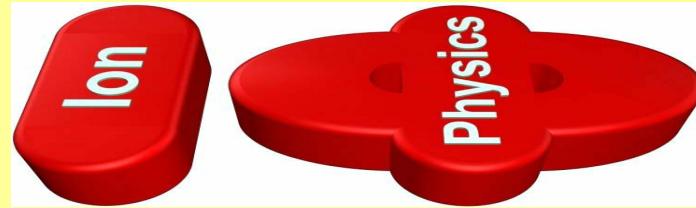
Calc. by Nesbet : 427 eV

$\text{C}_{60}^+ + \text{e} \rightarrow$  parent & fragment ions (200 eV)



$C_{60} + e \rightarrow$  multiply charged ions





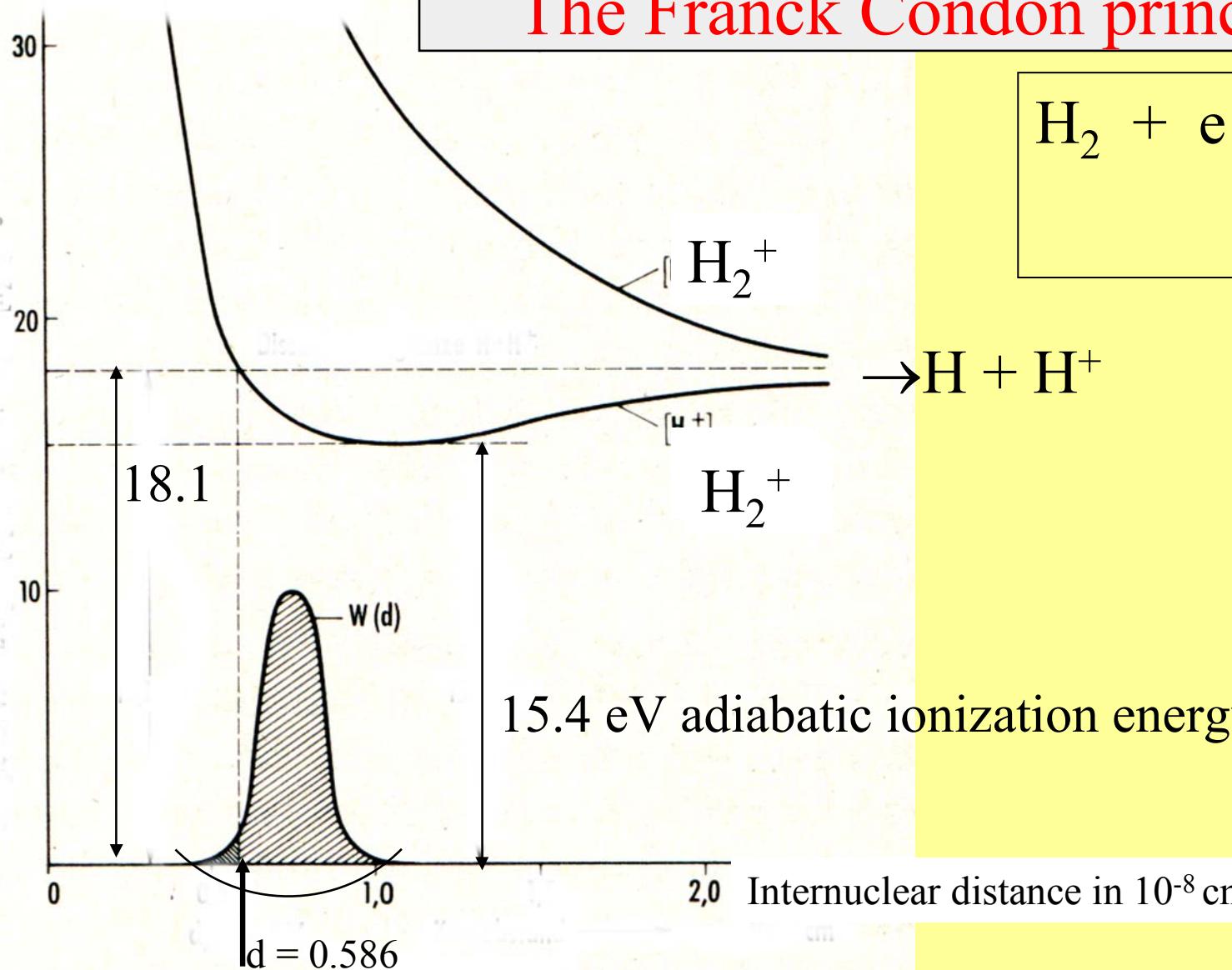
## Part I: Fundamentals

### B. Ionization mechanisms

1. Franck Condon principle
2. Unimolecular dissociation

$V(r)$  in eV

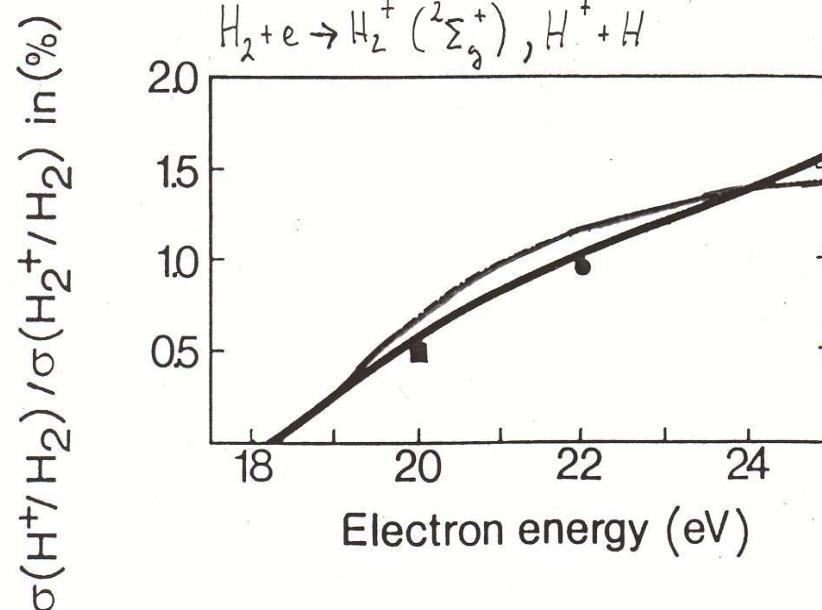
## Ionization mechanism I: The Franck Condon principle



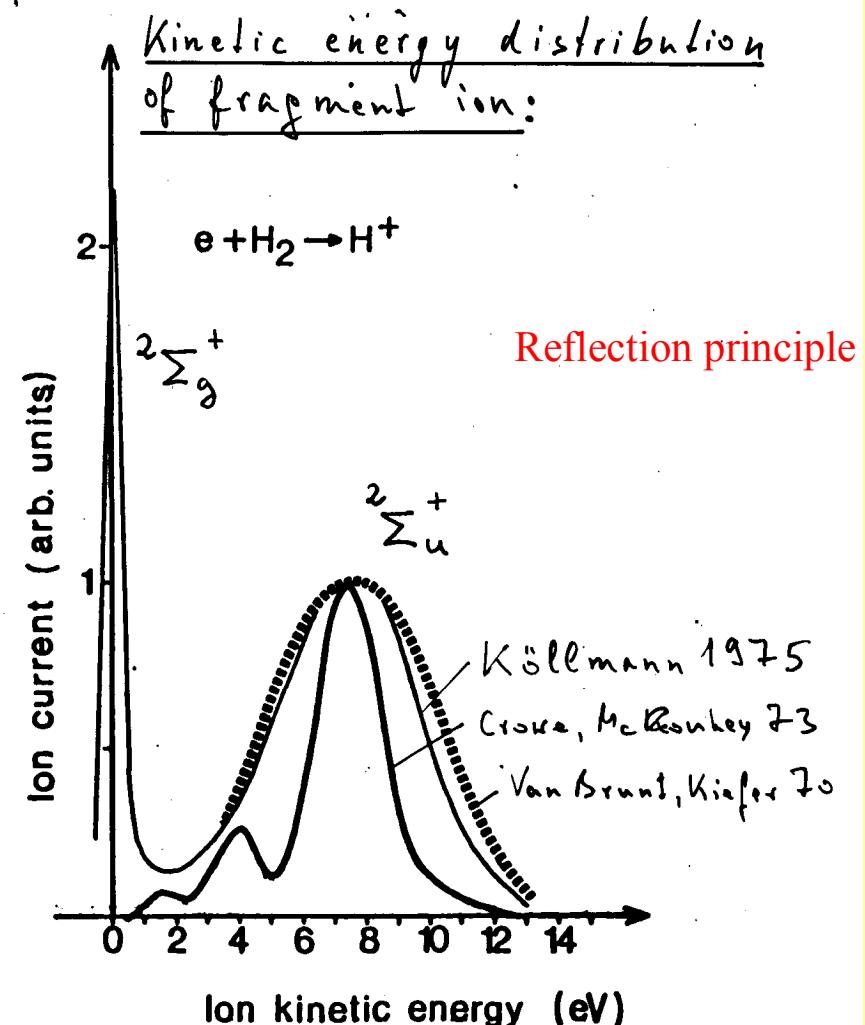
$$E = 100 \text{ eV}; v = 6 \times 10^8 \text{ cm/s}; t = s/v = 10^{-8}/6 \times 10^8 \sim 2 \times 10^{-17} \text{ s} \ll t_v \sim 10^{-14} \text{ s}$$

# Electron impact ionization: mechanism

## The Franck Condon principle

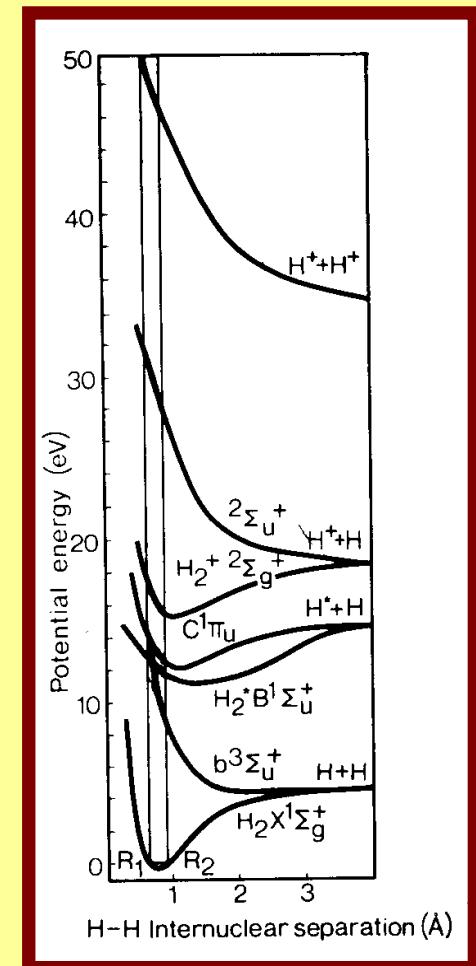
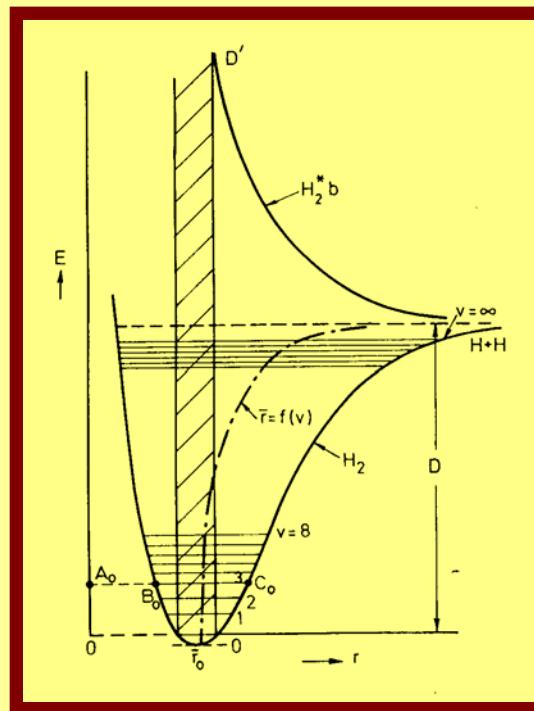
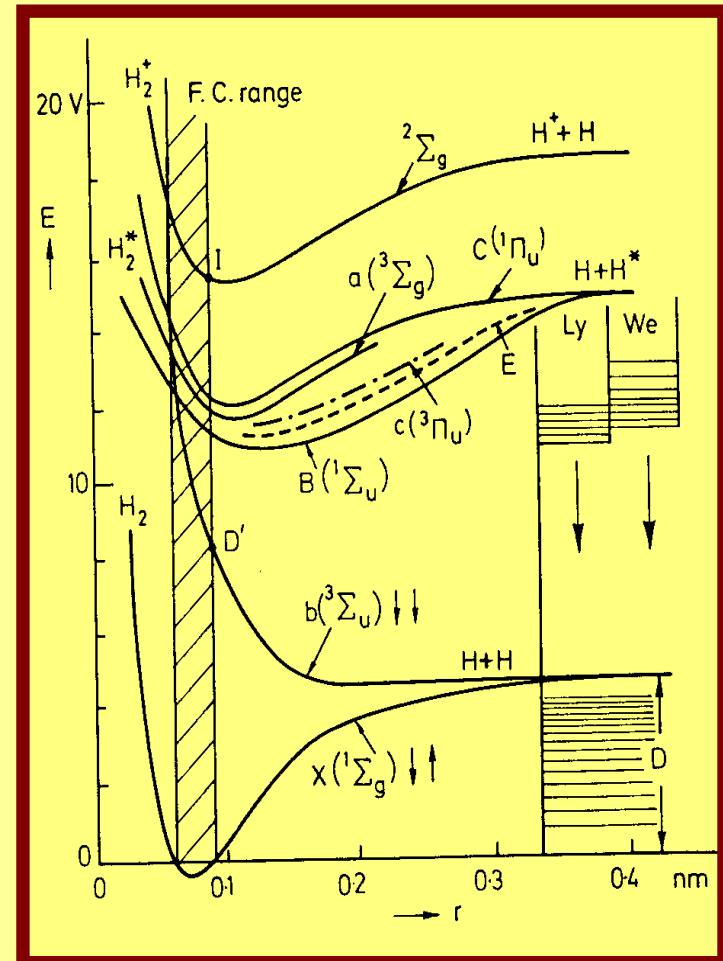


- Hipple (1937)
- Adamczyk et al. (1966)
- Crowe & McConkey (1973)
- Browning & Tigar (1971); theor.



# Electron impact ionization: mechanism

## The Franck Condon Range and different Cases



$$E=100 \text{ eV}; v=6 \times 10^8 \text{ cm/s}; t=s/v=10^{-8}/6 \times 10^8 \sim 2 \times 10^{-17} \text{ s} \ll t_v \sim 10^{-14} \text{ s}$$

# Electron impact ionization: mechanism

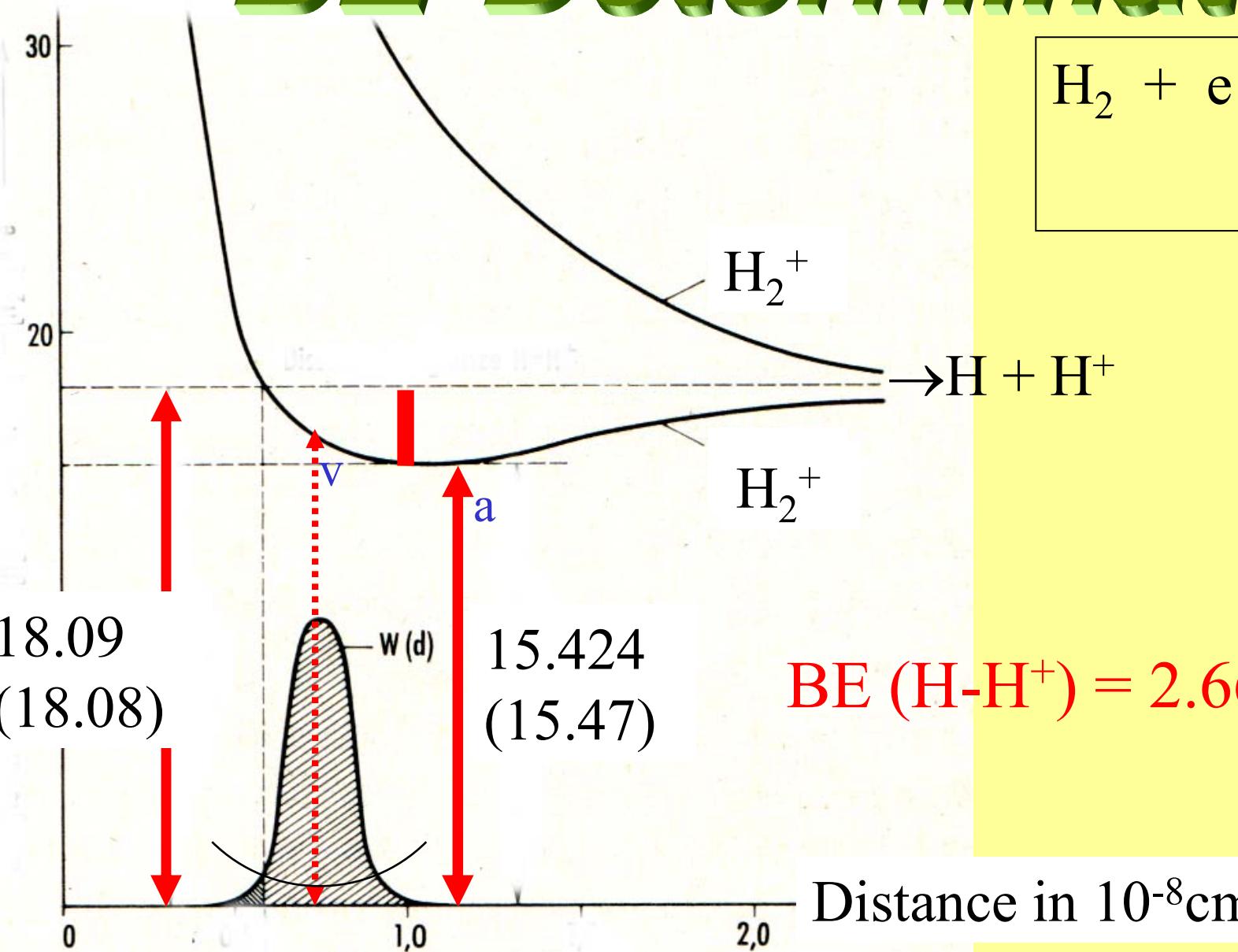
## The Franck Condon principle

Several cases are possible:

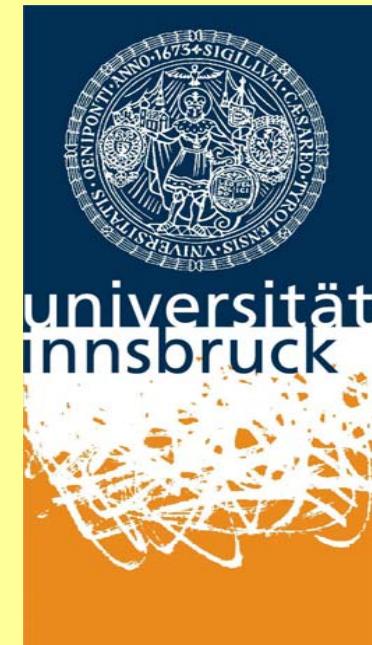
- (1) The final level accessible lies within the region of discrete vibrational states of the upper potential energy curve (e.g. transition  $H_2 (X^1\Sigma_g^+) \rightarrow H_2 (B^1\Sigma_u^+)$  in Fig. 1). The probability that the vibrational quantum number will change depends on the relative position of the potential energy curves.
- (2) The final level accessible lies not only within the region of discrete vibrational states but includes some part of the continuum (e.g. transition  $H_2 (X^1\Sigma_g^+) \rightarrow H_2^+ ({}^2\Sigma_g^+)$ ). Hence, some of the transitions will lead to dissociation.
- (3) The final level accessible lies within the continuum of a repulsive state and all transitions lead to dissociation (e.g. transition  $H_2 (X^1\Sigma_g^+) \rightarrow H_2^+ ({}^2\Sigma_u^+)$ ).

$V(r)$  in eV

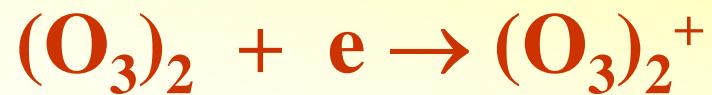
# BE-Determination



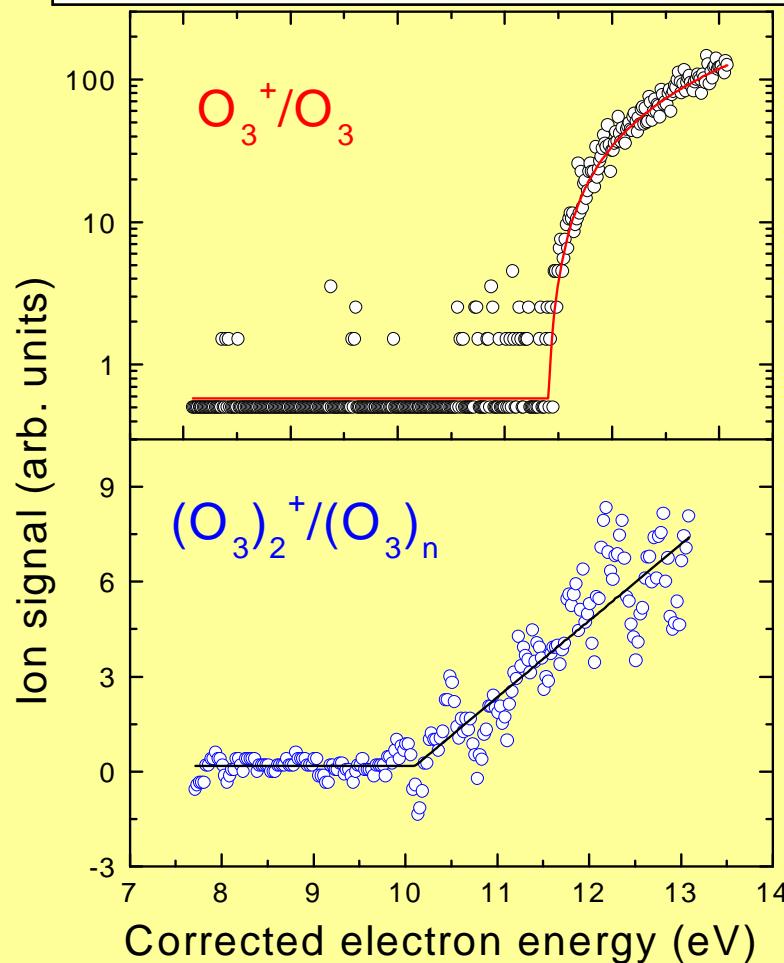
# AE and BE of molecules



# HEM data analysis:



Fit function:  $\sigma(E) = b + \sigma_0 \cdot (E - IE)^p$



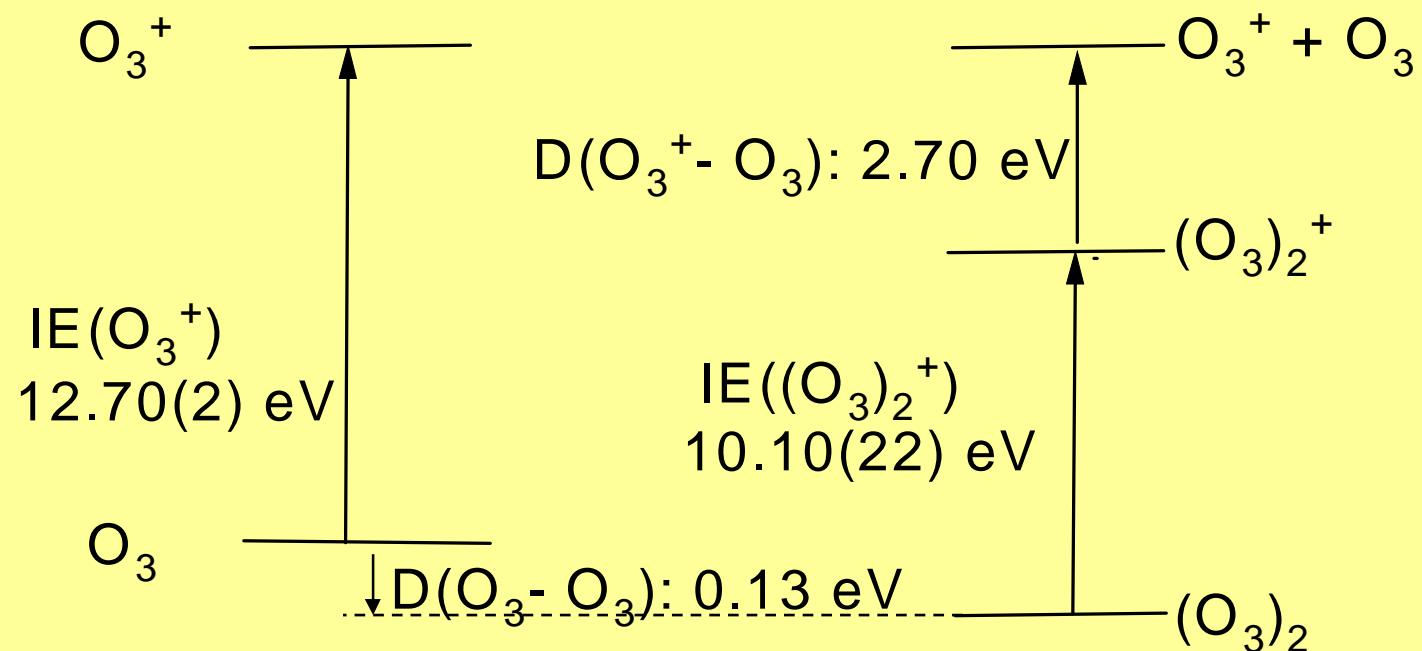
AE:  $12.70 \pm 0.02$  eV

AE:  $10.10 \pm 0.2$  eV

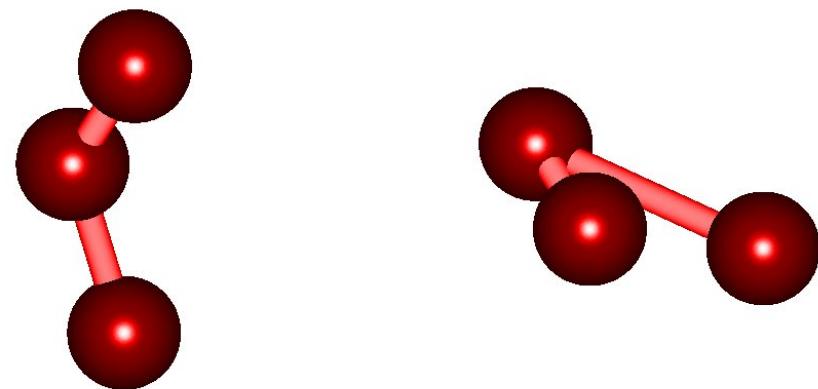
## HEM data analysis:



Binding energy of ozone dimer ion:

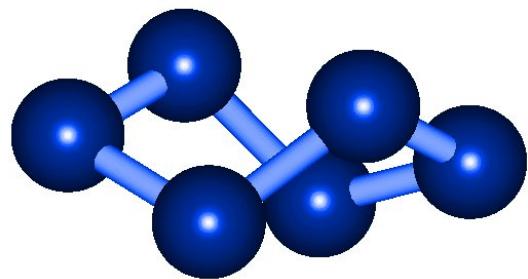


a)



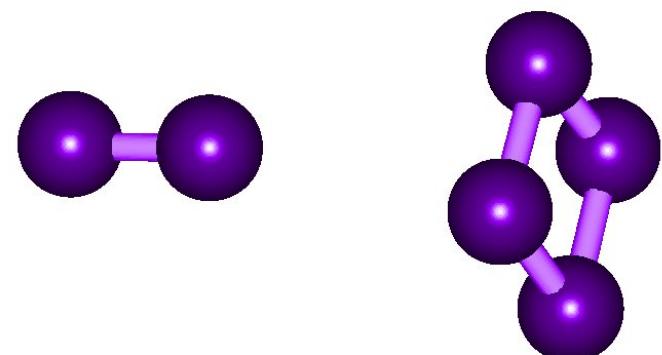
„dimer geometry“

b)



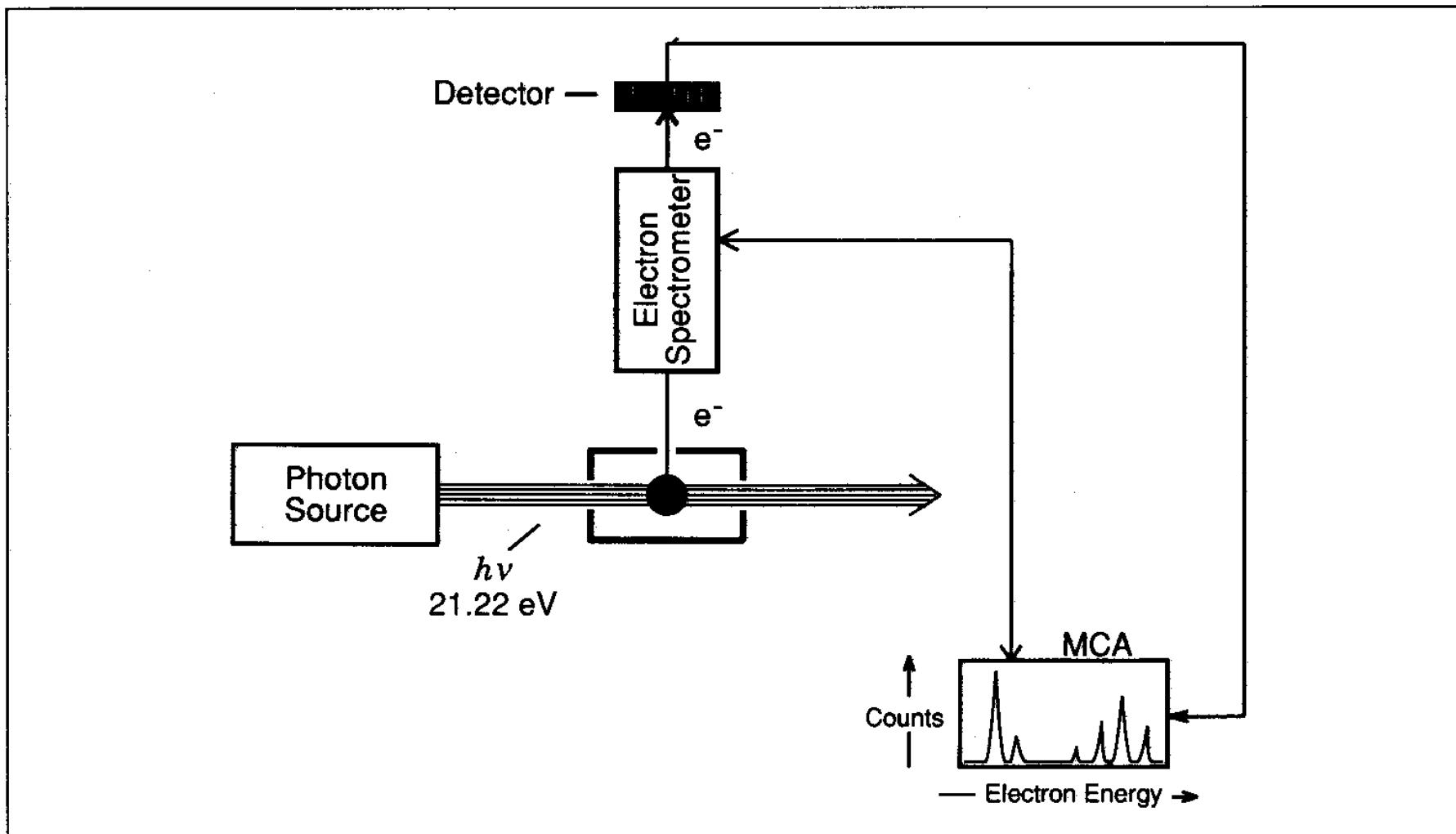
„twisted boat“

c)



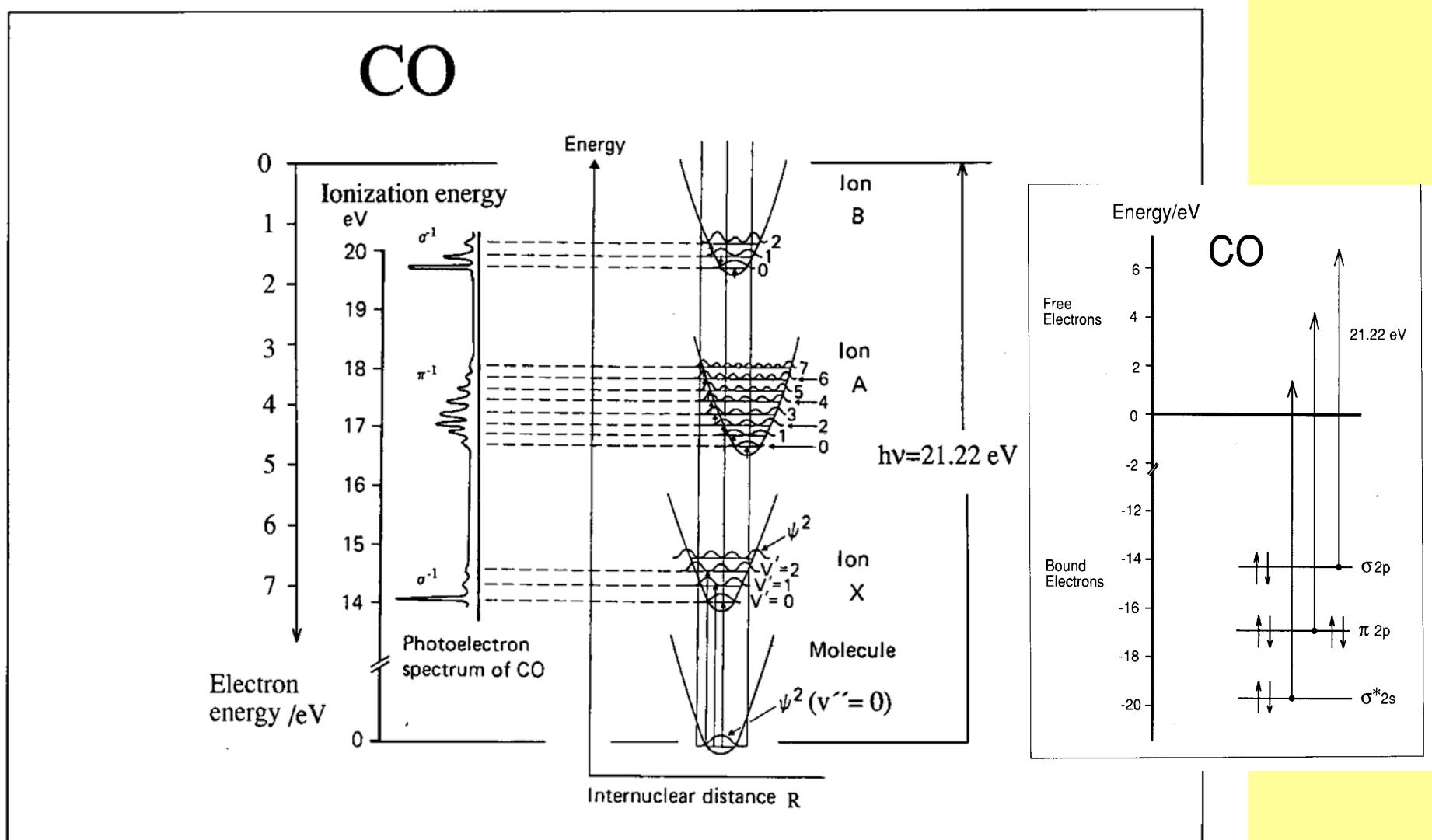
„ $\text{O}_2 - \text{O}_4^+$ “

# Photoelectron spectroscopy: Adiabatic & vertical IE



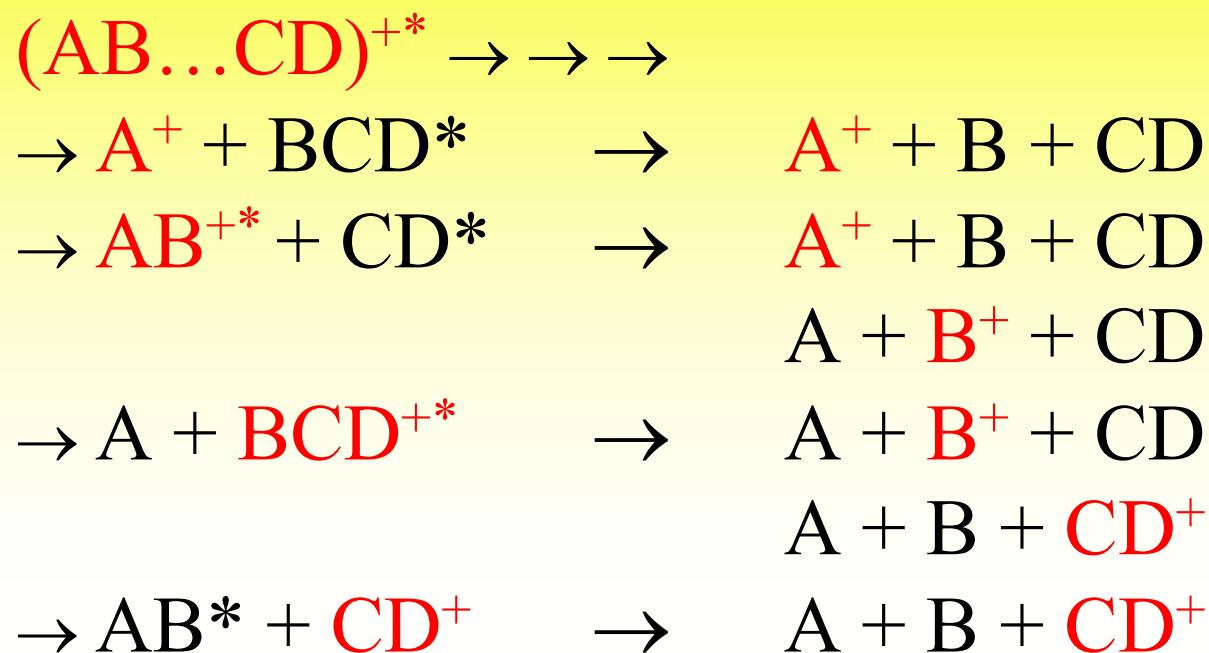
**Fig. 2.1.** Schematic of the experimental arrangement for photoelectron spectroscopy (PES). MCA: multichannel analyzer.

# Photoelectron spectroscopy: Adiabatic & vertical IE



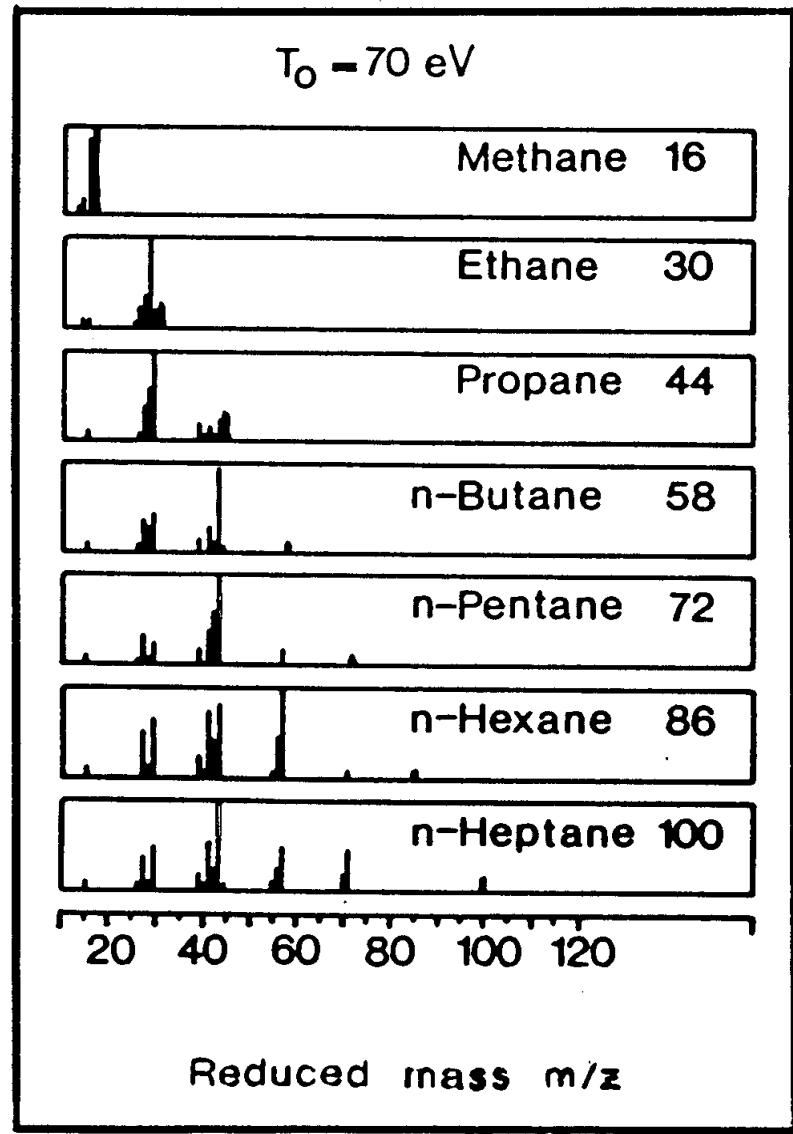
**Fig. 2.3.** PE spectrum of CO obtained by HeI radiation and potential energy curves for the neutral molecule and the three ionized states (adapted from [48]).

## Ionization mechanism II: Vibrational predissociation

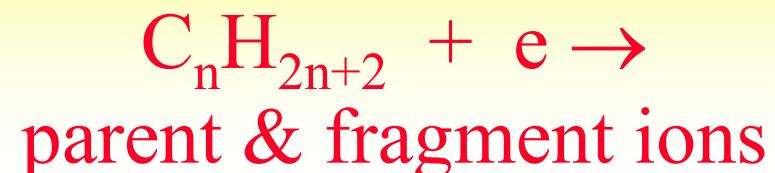


Decay paths for parent ion formed: If the the molecular ion is complex enough so that Lissajous motion on the potential energy hypersurface is sufficiently complicated, the existence of metastable ions can be rationalized in the framework of QET or RRKM.

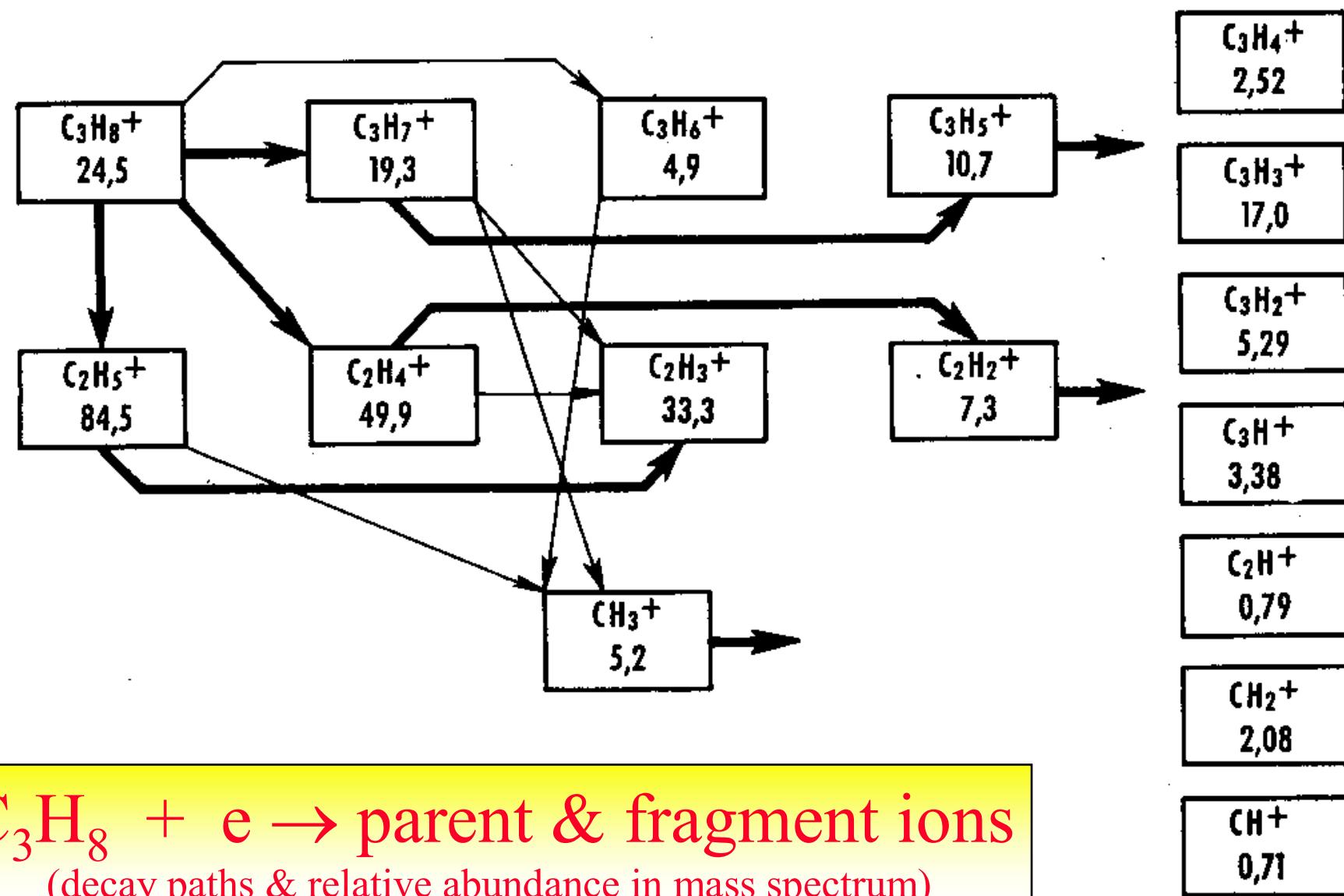
## Ionization mechanism II: Vibrational predissociation



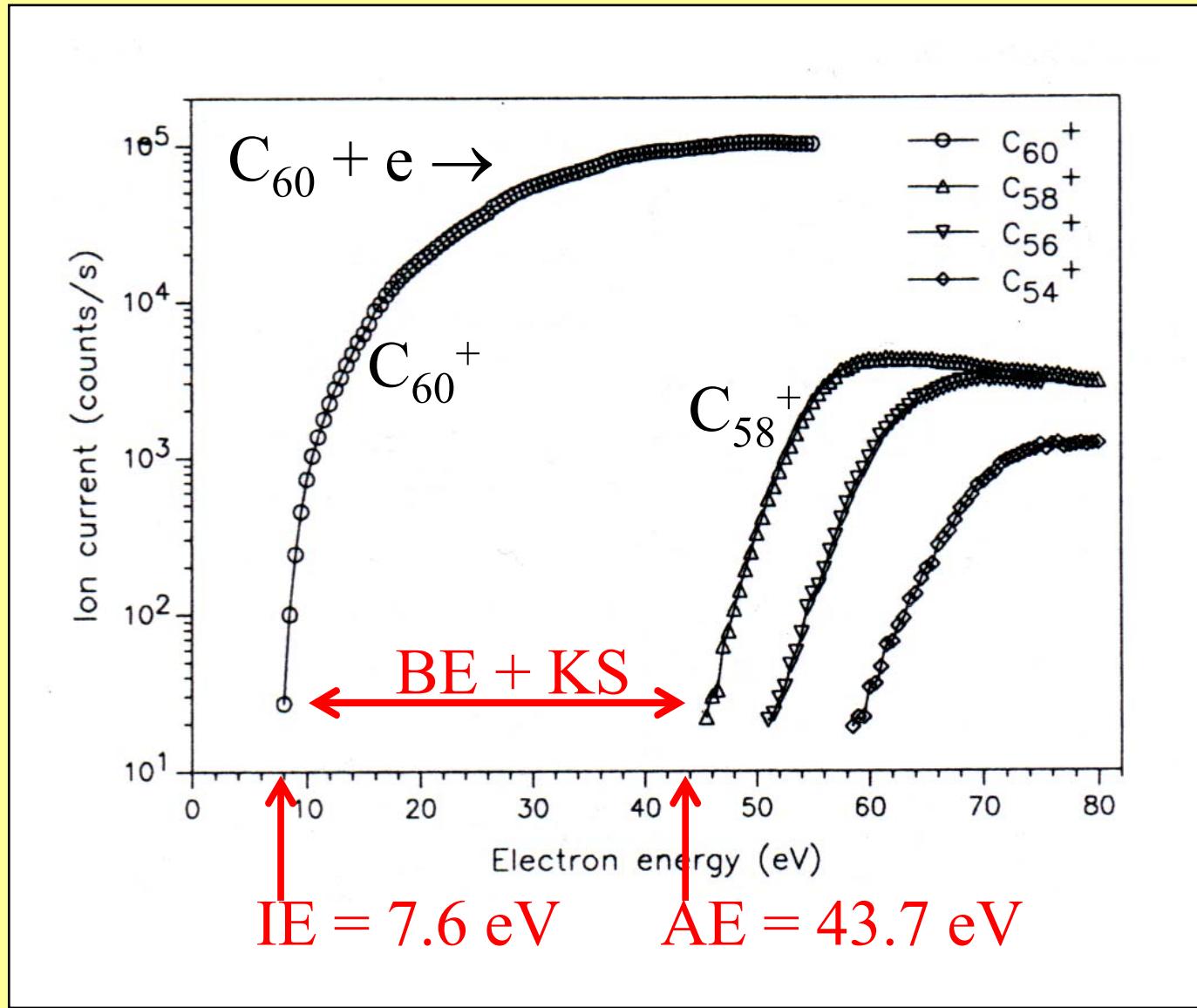
Ionization of alkenes:



## Ionization mechanism II: Vibrational predissociation



# High appearance energy



## Final result for the $C_{60}^+$ binding energy

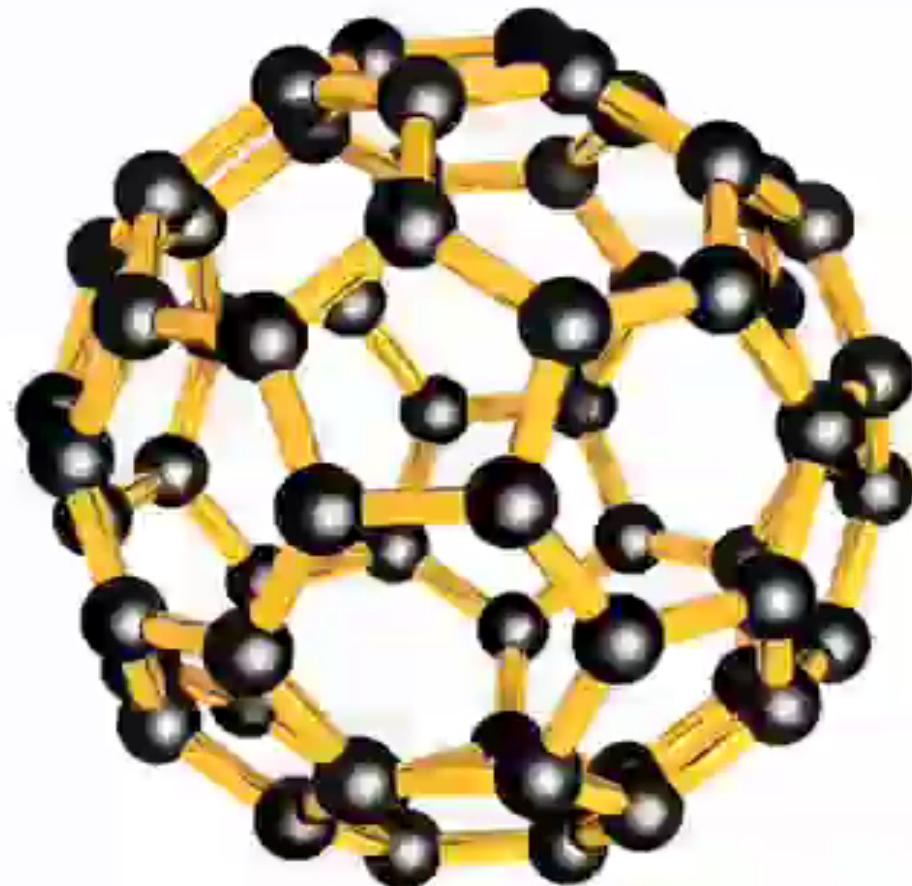
Experiment: 17 Measurements - which have been analysed by using the complete today's knowledge- yield a binding energy (mean value) of

$$10.0 \pm 0.2 \text{ eV}$$

Theory: A.D.Boese and G.E.Scuseria have carried out very accurate D(ensity)F(unctional)T(hory) calculations and obtain for the ionic  $C_{60}^+$  binding energy

$$10.2 \text{ eV}$$

Binding energy (10 eV) larger than ionization energy (7.6 eV) !!!



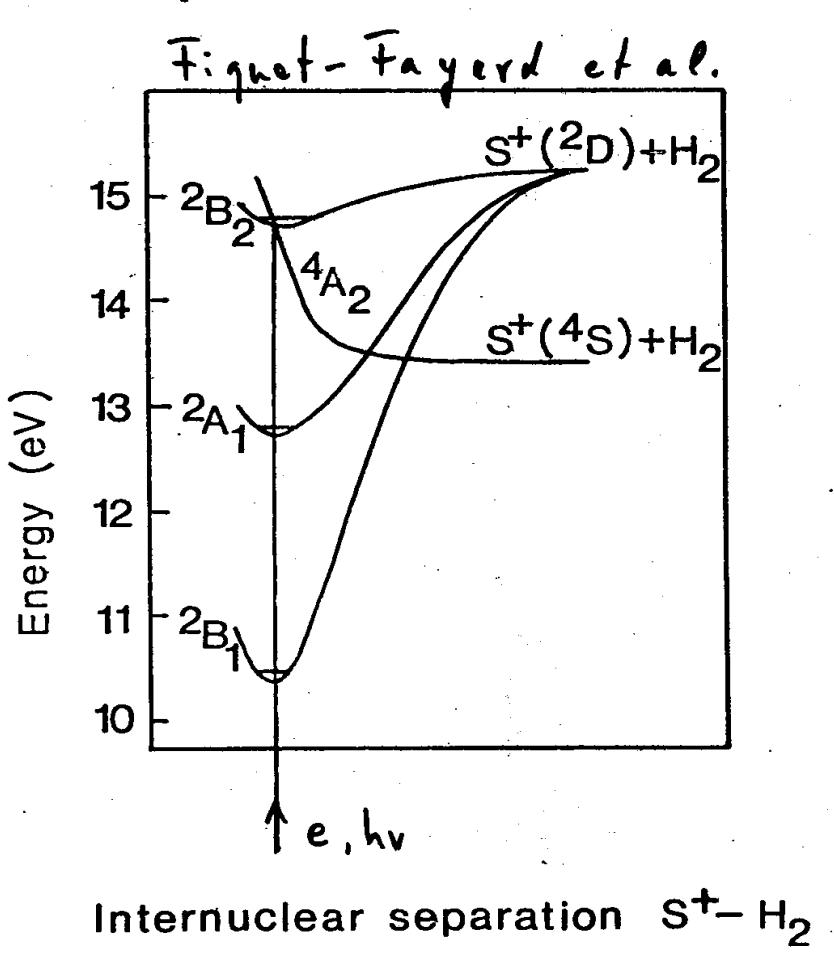
Infrared multiphoton excitation, dissociation and ionization of  $C_{60}$ , M.Hippler,  
M.Quack, R.Schwarz, G.Seyfang, S.Matt, T.D.Märk, Chem.Phys.Lett. 278(1997)111

## Unimolecular (metastable) dissociation

### 3 major mechanisms:

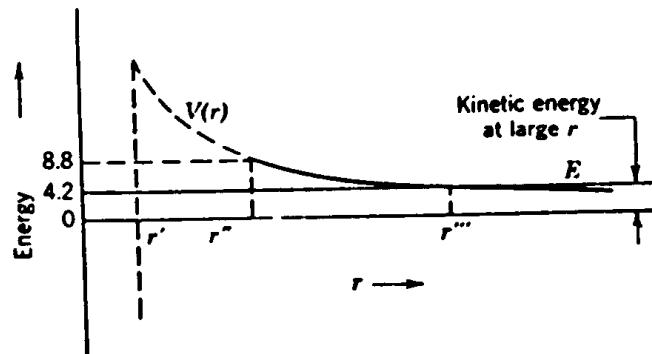
1. Vibrational (statistical) predissociation
2. Electronic predissociation
3. Tunneling through a (rotational) barrier

Electronic predissociation:  
 Transition forbidden by (i) some selection  
 rule or (ii) hindered by small overlap integral



RULES OR HINDERED BY A SMALL OVERLAP INTEGRAL.

3. (ROTATIONAL) TUNNELING THROUGH A BARRIER



$$T \approx \exp\left(-2 \int_{r'}^{r''} \sqrt{\frac{2m}{\hbar^2}} [V(r) - E] dr\right)$$

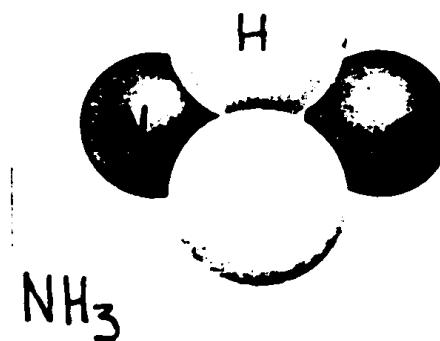
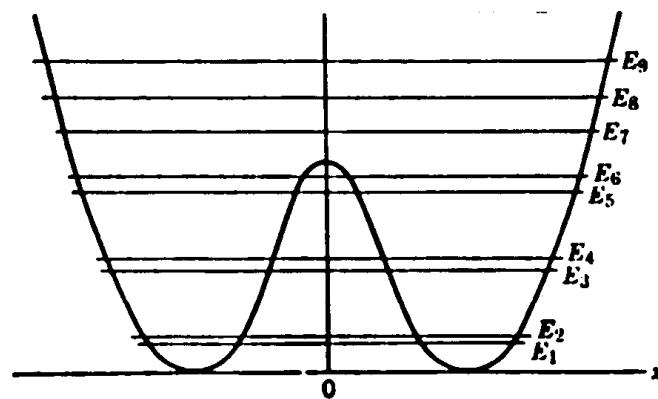


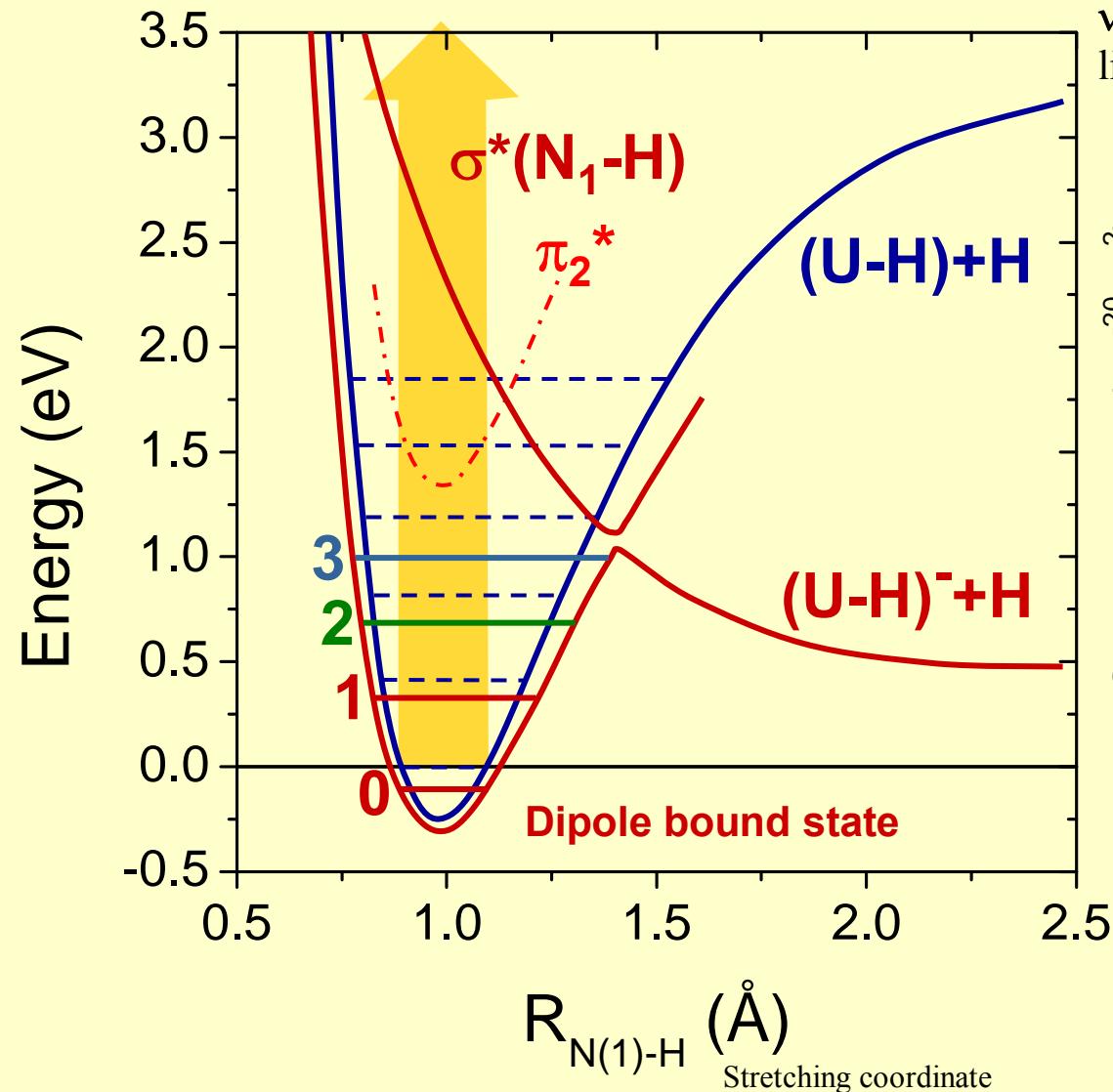
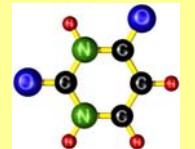
FIGURE 6-22

The potential energy of the N atom in the  $\text{NH}_3$  molecule, as a function of its distance from the plane containing the three H atoms, which lies at

Tunneling through a barrier

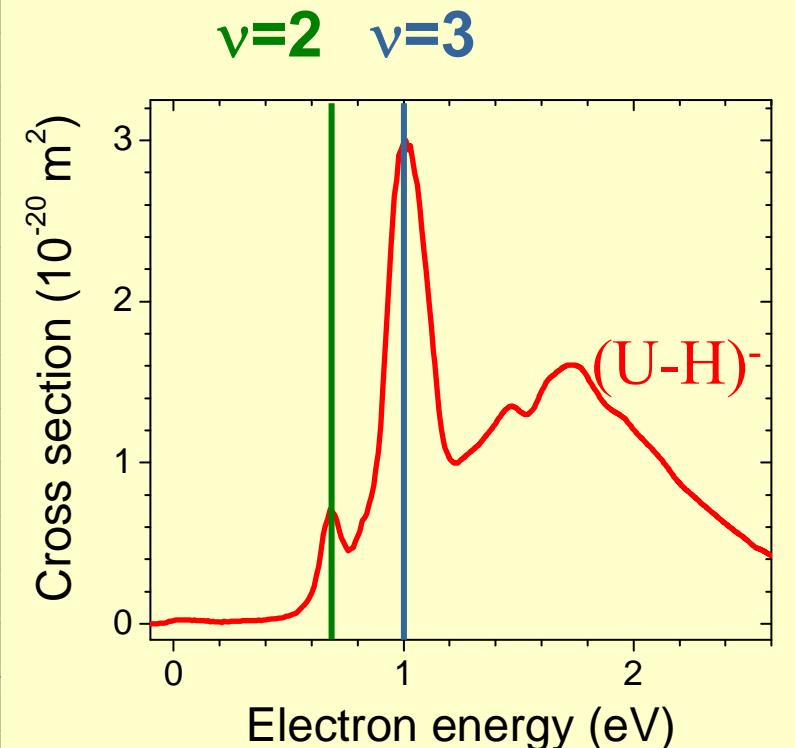
# Schematic potential energy curves for uracil

along the N<sub>1</sub>-H stretching coordinate. DBS: Kaufmann, Bowen, Schermann



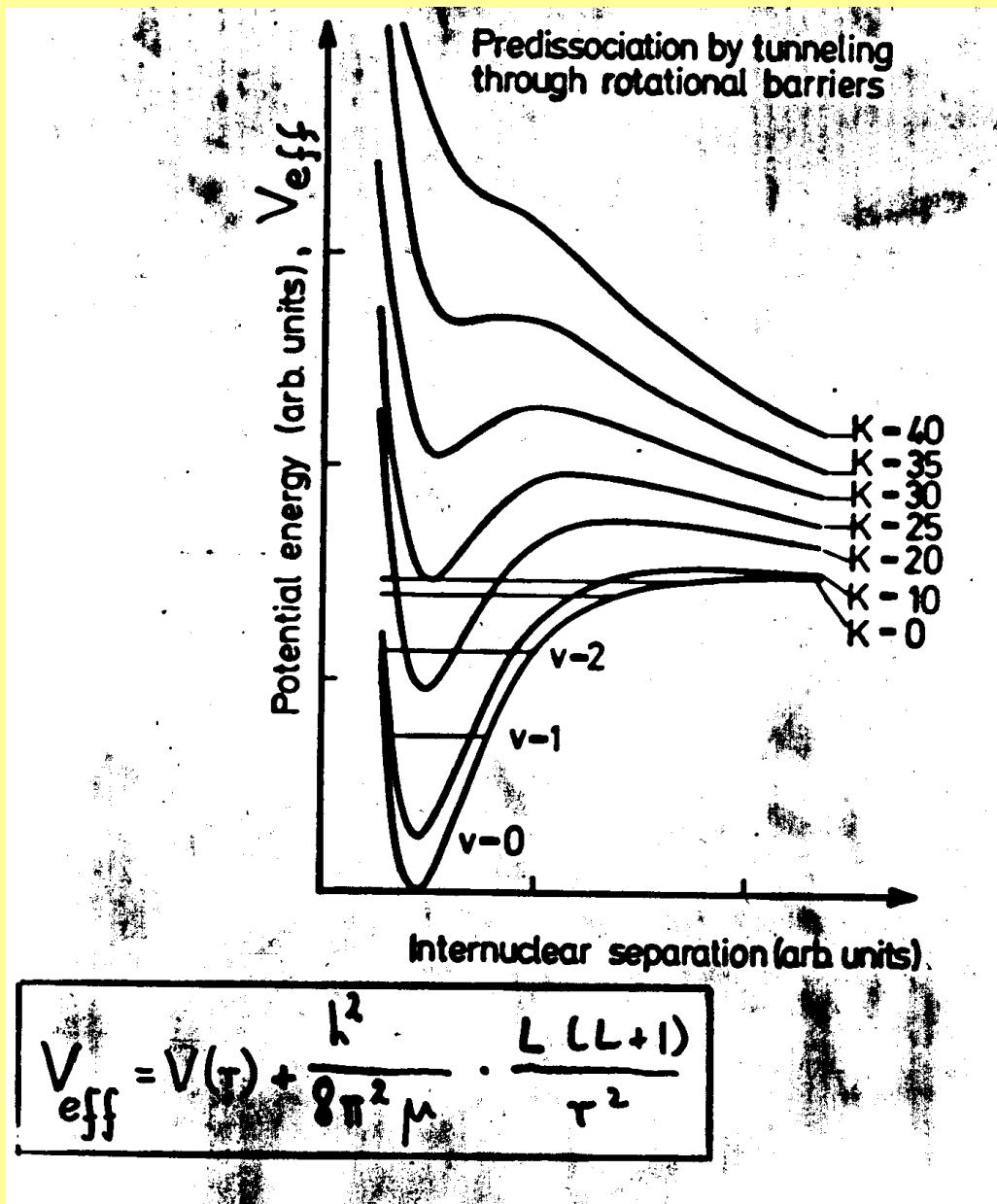
v3: N Feshbach Resonance: H atom tunneling will be rapid (broad width)

v2: NFR: barrier for tunneling large, lifetime longer and narrower width



Tunneling of H from N1 site, through potential barrier formed by avoided curve crossing of the dipole bound state and the antibonding  $\sigma^*(N1-H)$  anion state

# Tunneling through barrier



$V_{\text{eff}}$  effective potential energy  
combination of  $V$  plus  
rotational energy of diatomic

$V$  potential for  $L=0$

$J=K=L$   
rotational quantum number

# Electron impact ionization: mechanism

## Time evolution of the ionization process

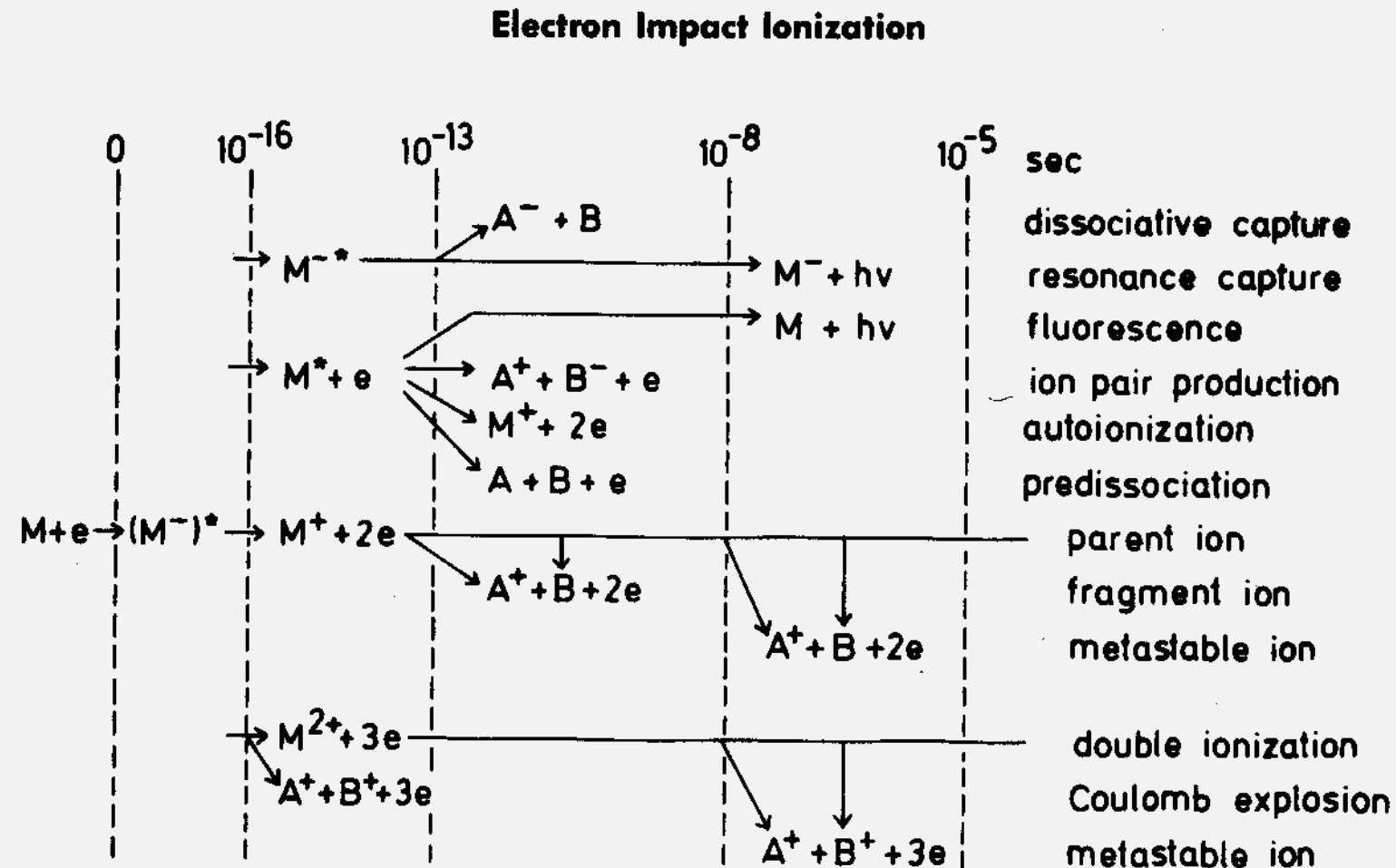
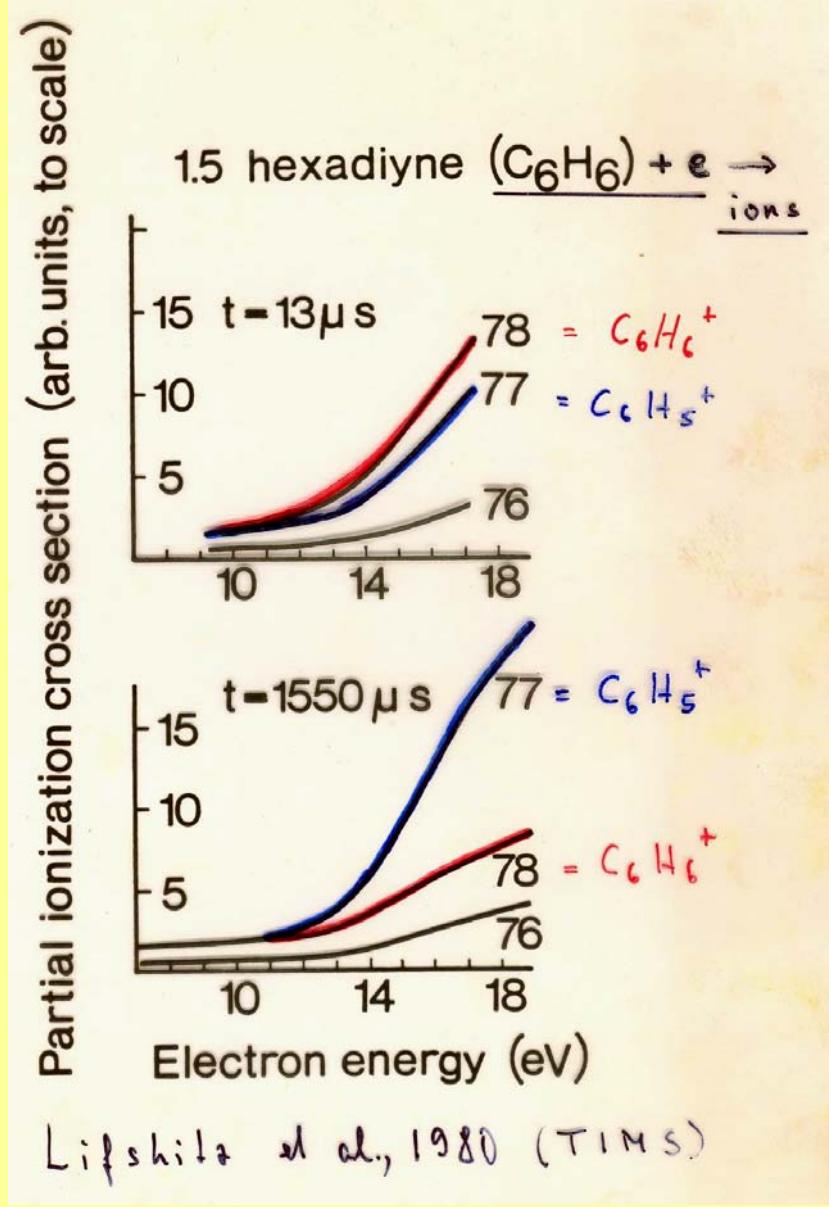


Figure 4. Schematic time chart of possible electron impact ionization processes.

# Electron impact ionization: mechanism



Time evolution of  
the ionization  
process