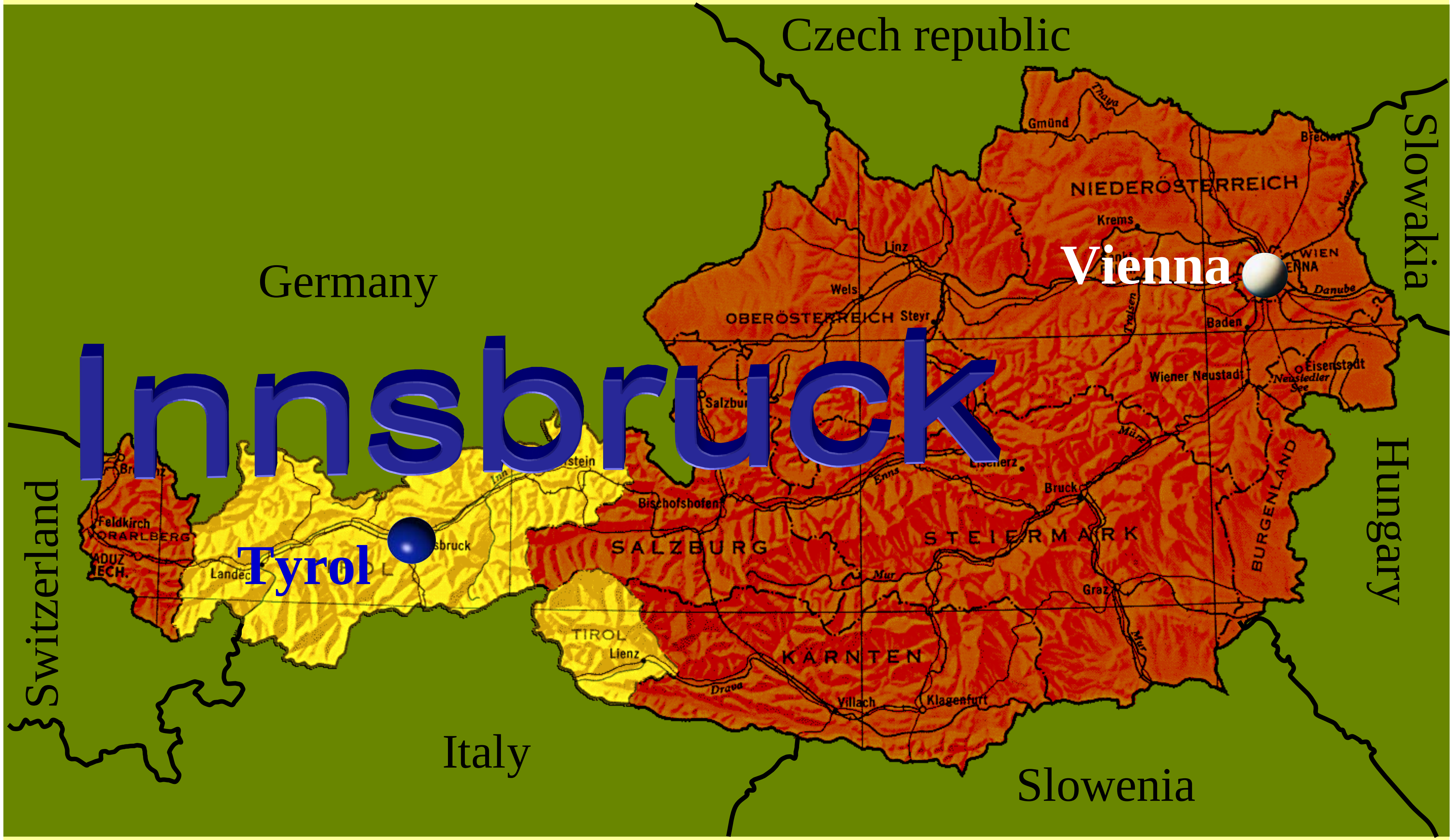
IAEA Training Workshop 2006

Tilmann Märk
Universität Innsbruck

Fundamental elementary processes in plasmas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Institut für Ionenphysik und Angewandte Physik

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

Ion Physics / Plasma Physics

Clusterphysics

Mass Spectrometry

Environmental Physics and Analysis

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Elementary processes considered:

1. Inelastic electron interactions with atoms/molecules/nanoparticles (ionization and attachment)
2. Ion/surface interaction

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

Data acquisition
Data analysis and assessment
Data compilation (ADAS, IAEA)

Motivation

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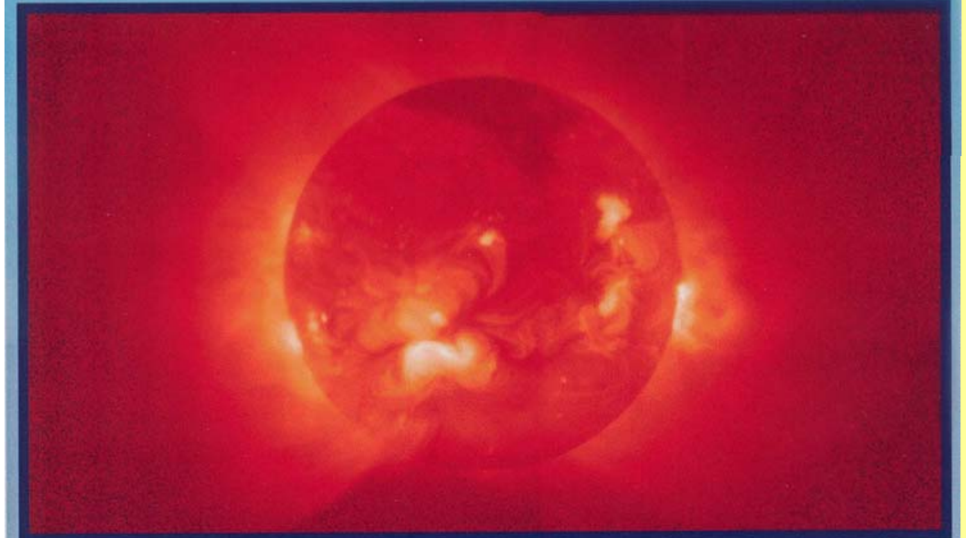
(1) Astrophysical plasmas
- stellar atmosphere
- ionosphere
- lightning
- solar corona



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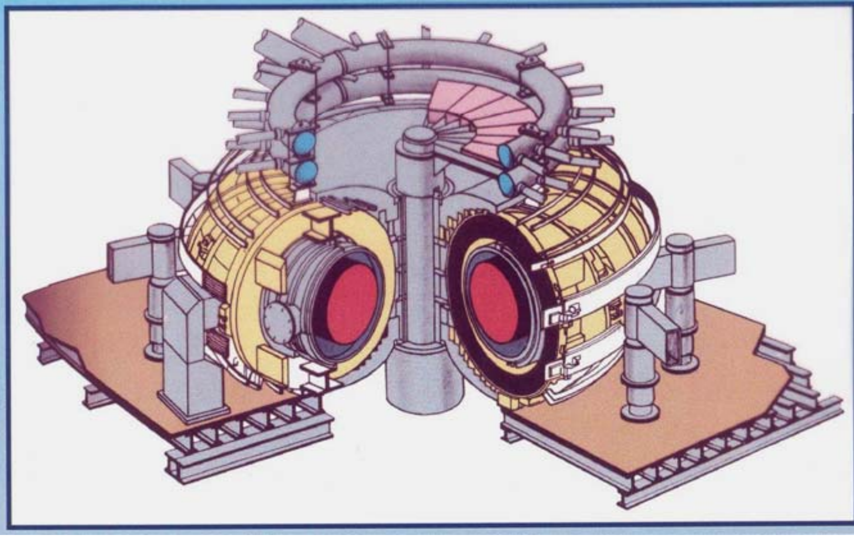
(2) Industrial plasmas
- plasma deposition
- plasma etching

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



1. Plasma: Electrons, Ions, Neutrals

2. Ion Production:

Electron impact

Ion impact

Photon impact

(Ion molecule reaction)

3. Neutral targets:

Atoms

Molecules

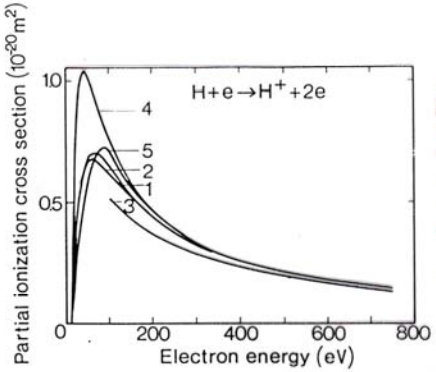
Radicals

Clusters

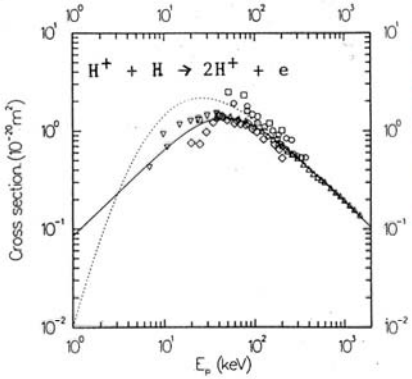
(Excited states)

4. Photons

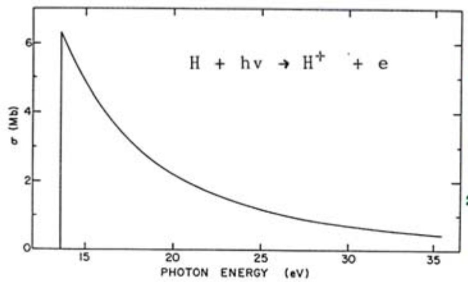
Ion production:



Electron impact: $\sigma_{max} \sim 1\times10^{-20}$ m^2 at 100 eV



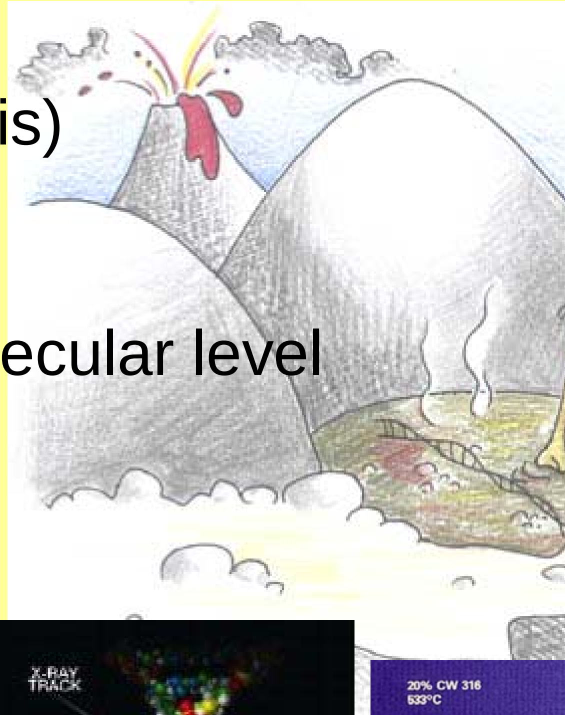
Proton impact: $\sigma_{max} \sim 1\times10^{-20}$ m^2 at 100 keV (m_p/m_e)

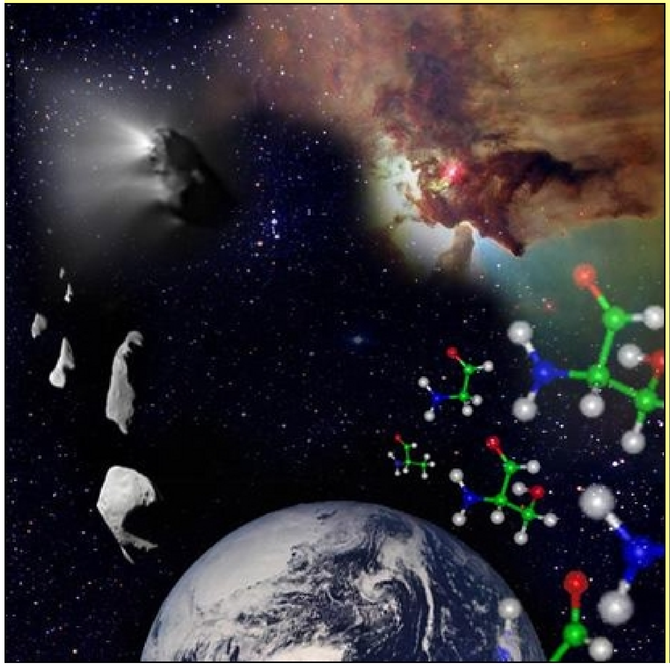


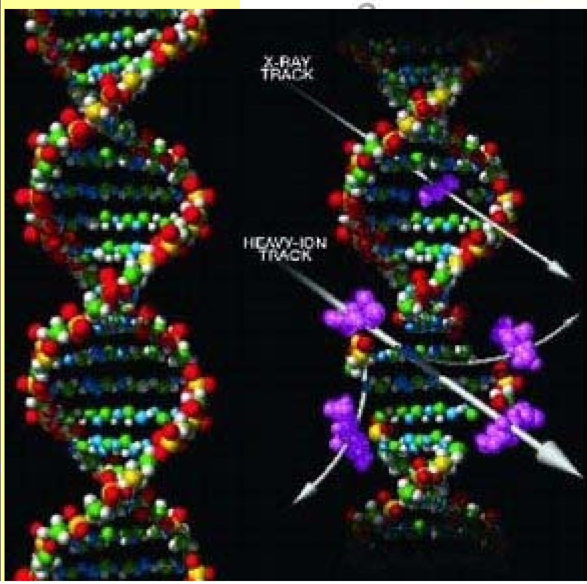
Photon impact: $\sigma_{max} \sim 5\times10^{-22}$ m^2 at ~13 eV

Motivation

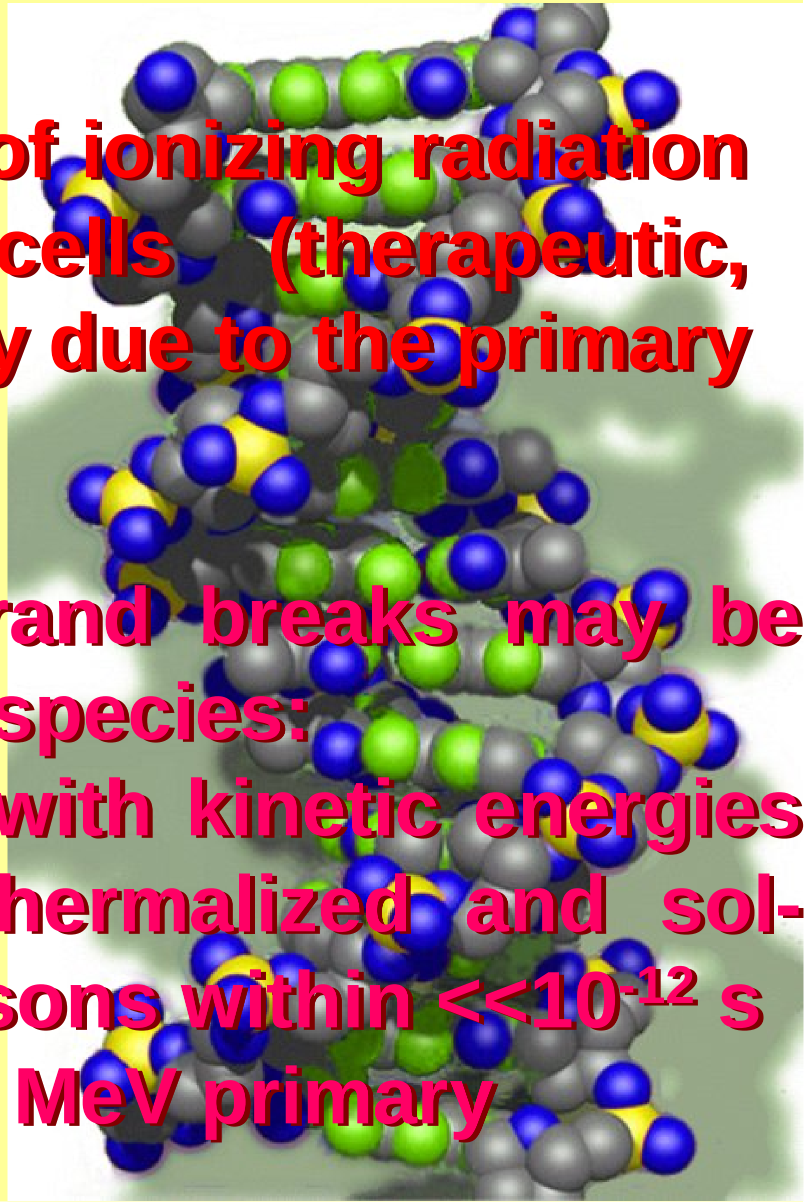
- Origin of life (photosynthesis)
- Life in space
- Radiation damage at a molecular level
- Improved radiation therapy







DNA-strand breaks



- **The genotoxic effects of ionizing radiation (α,β,γ,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 sol-vated by inelastic collisons within $<<10^{-12}$ s
  =$4x10^4$ electrons per 1 MeV primary

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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 and anions

Part III: Electron attachment

Part IV: Ion/surface interactions

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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

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

Primary ionization event

Energy storage and disposal

Final reaction products

Electron impact ionization processes

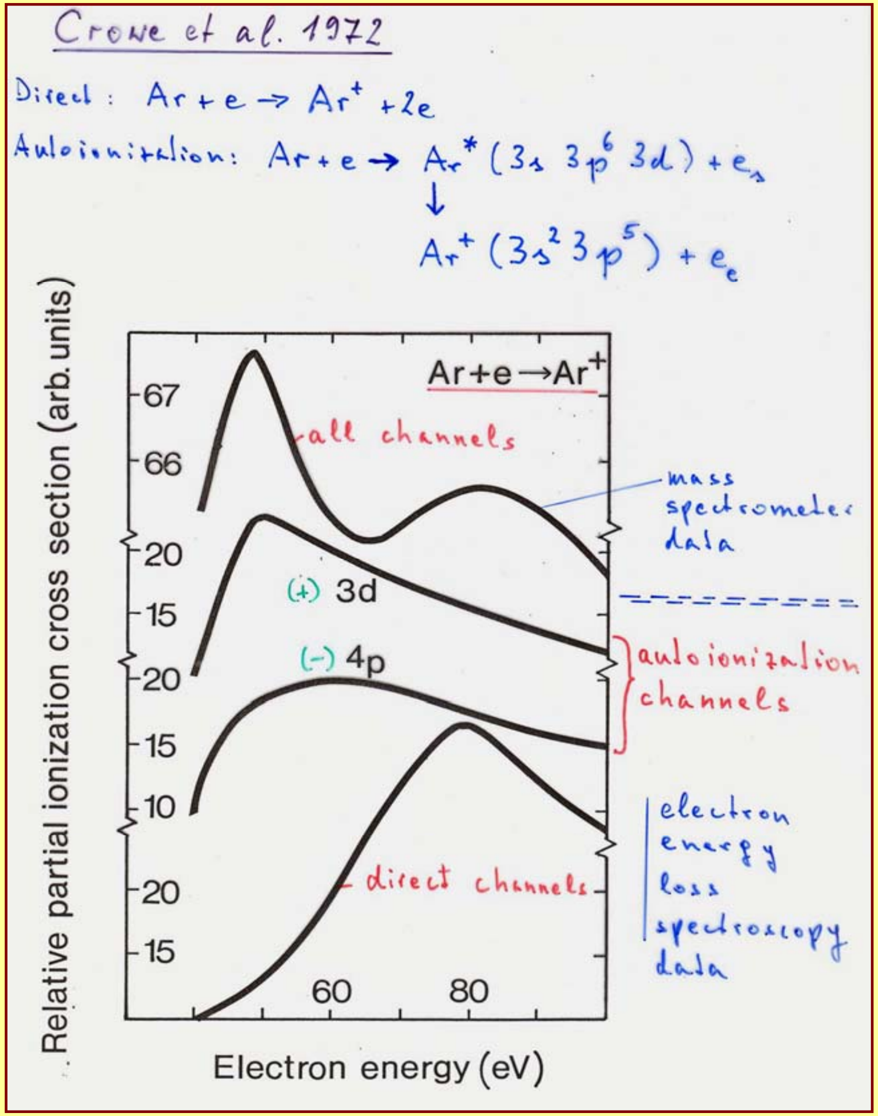
$A + e \rightarrow$	$A + e$	elastic scattering	
	$A^* + e$	excitation	
	$A^{**} + e$	double excitation	$(A^{**} \rightarrow A^+ + e)$
	$A^+ + 2e$	ionization	
	$A^{+*} + 2e$	excited ion	$(A^{+*} \rightarrow A^{++} + e)$
	$A^{++} + 3e$	double ionization	
	$A^- + hv$	attachment	

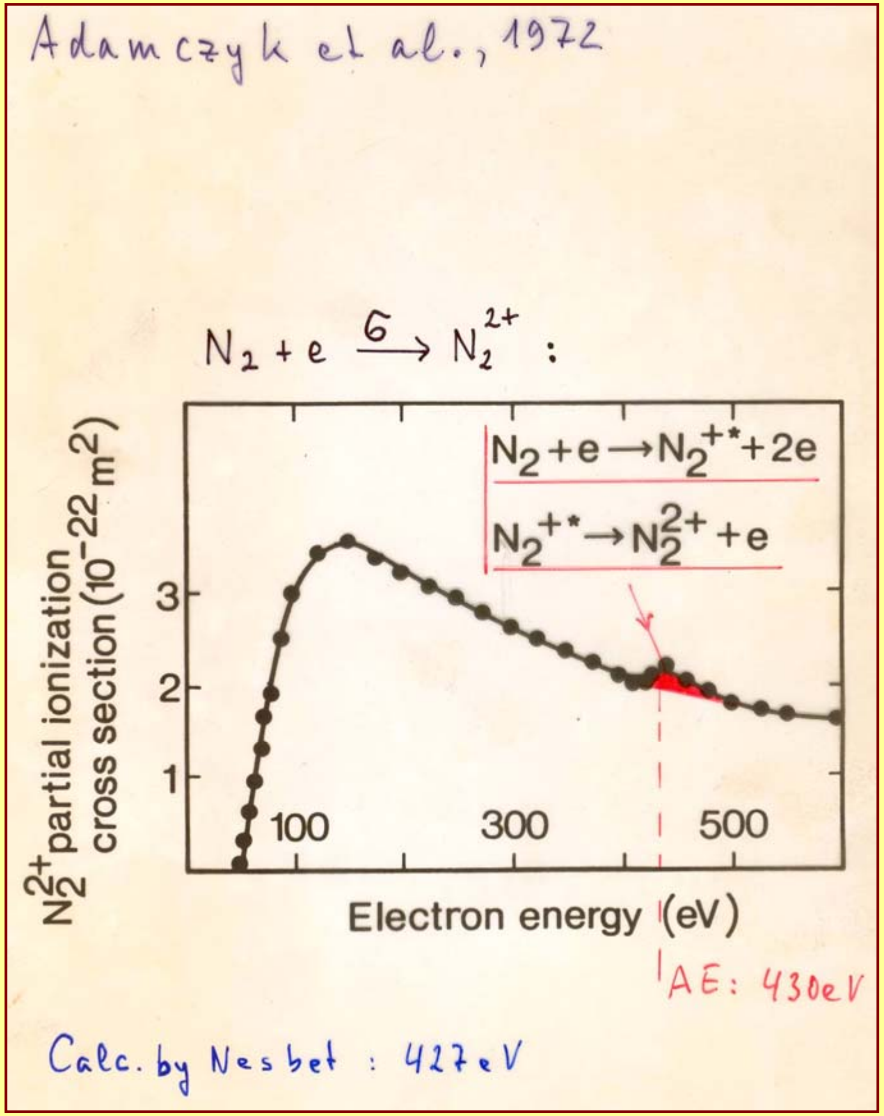
Electron impact ionization processes

$AB + e \rightarrow$	$AB + e$	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	
	$AB^- + hv$	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
	$AB^{++} + 3e$	double ionization

Direct and indirect ionization processes





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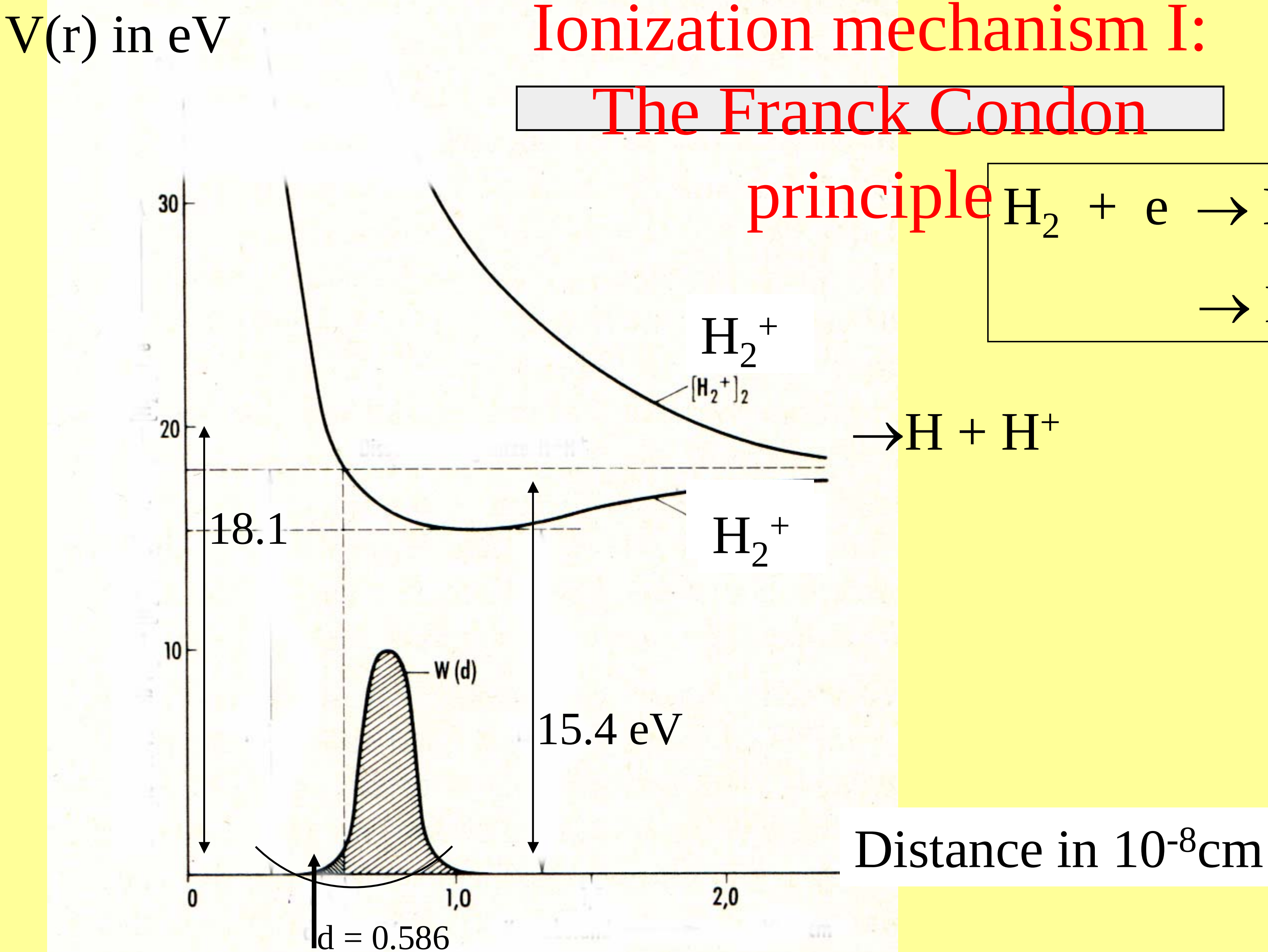
Part I: Fundamentals
B. Ionization mechanisms

Franck Condon principle
Unimolecular dissociation

Ionization mechanism I: The Franck Condon principle

$H_2 + e \rightarrow H_2^+$

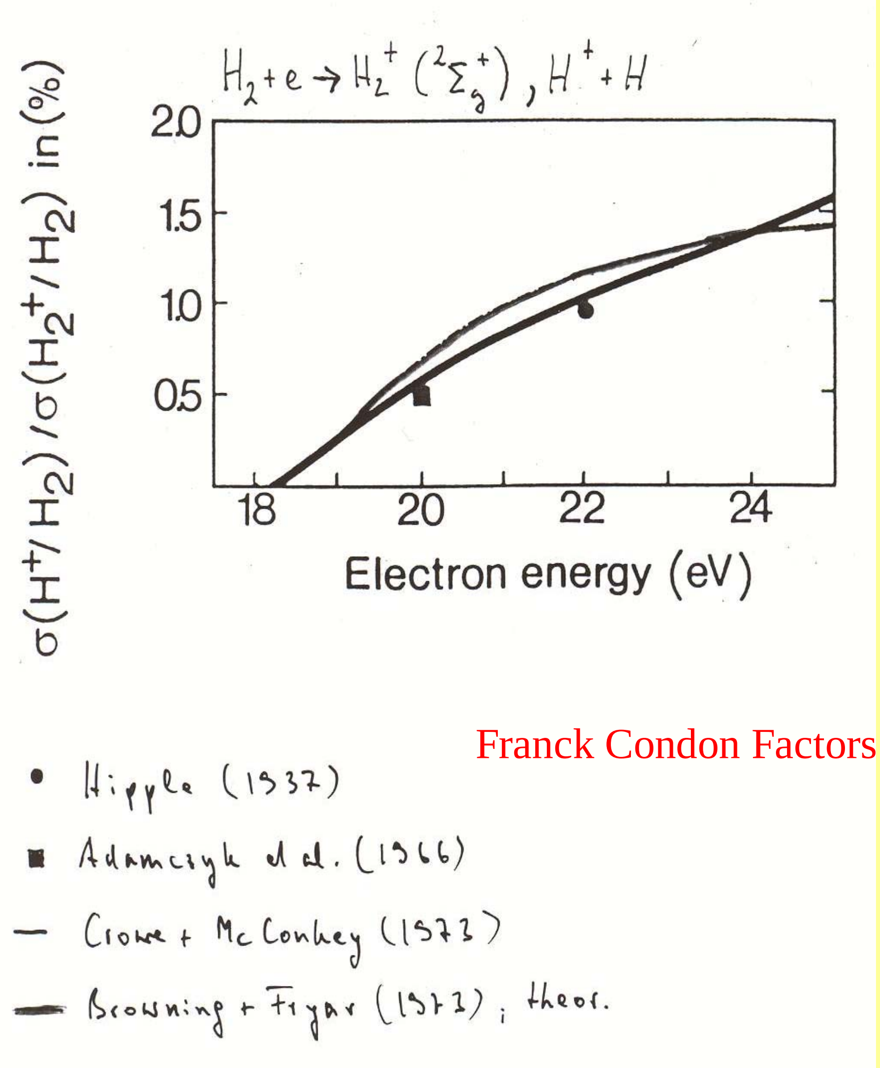
$\rightarrow H^+$



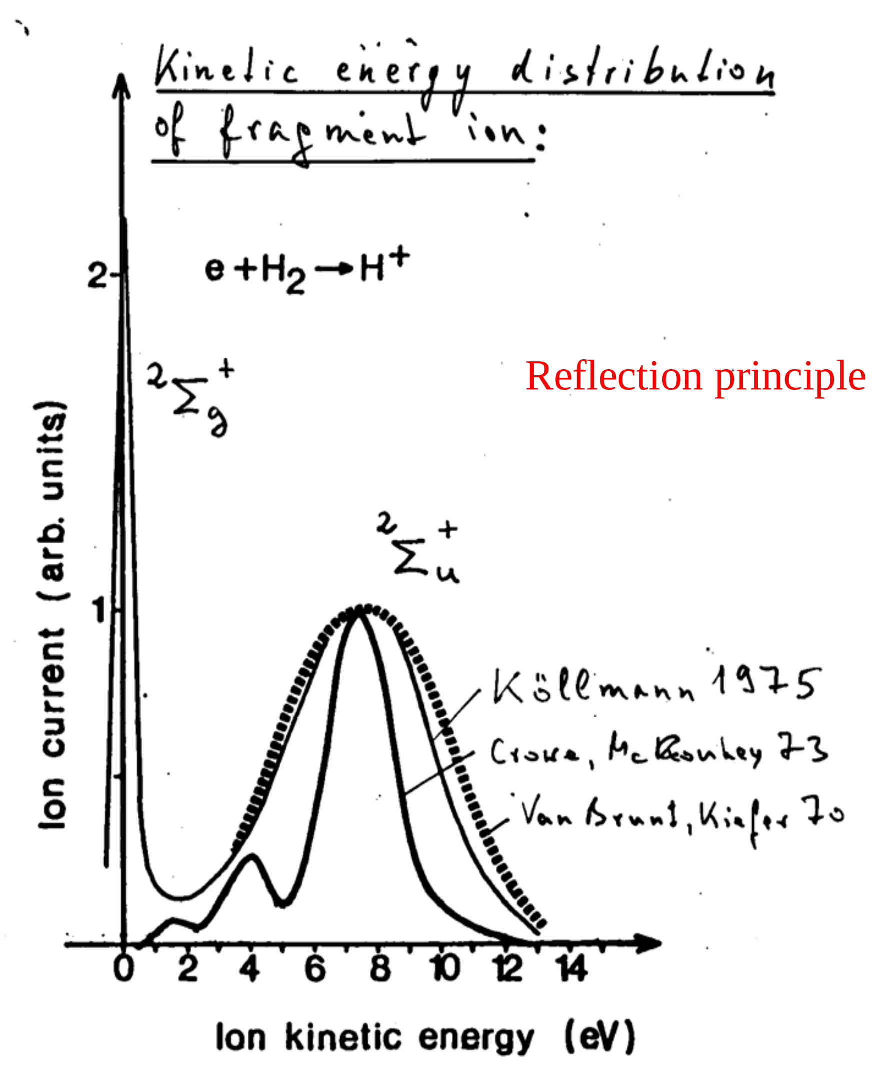
E=100 eV: $v=6x10^8$cm/s; $t=s/v=10^{-8}/6x10^8 \sim 2x10^{-17}$s « $t_v \sim 10^{-14}$s

Electron impact ionization: mechanism

The Franck Condon principle



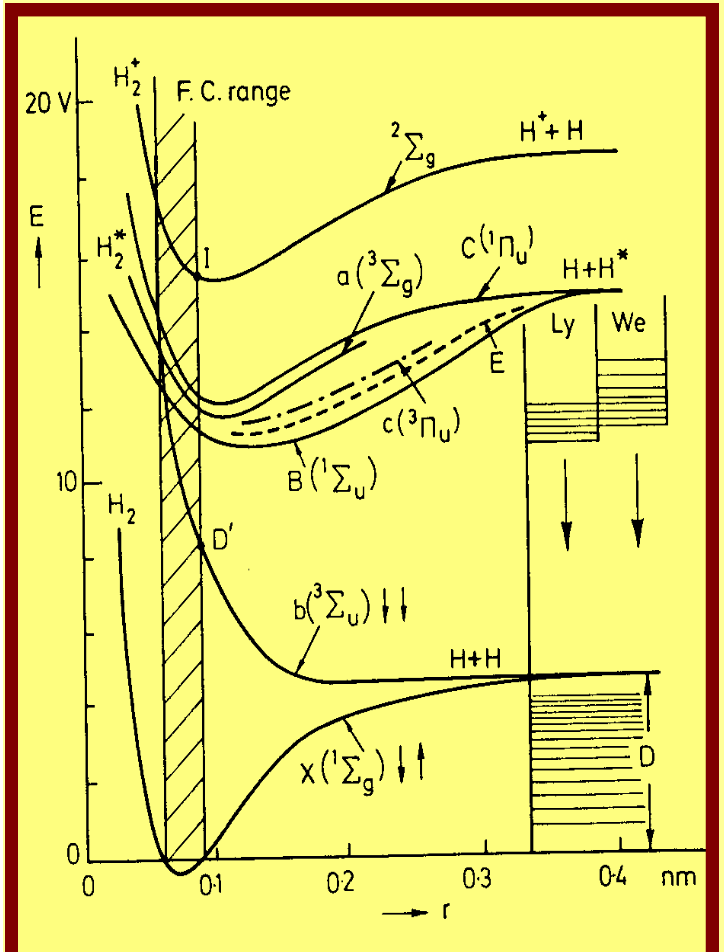
Franck Condon Factors

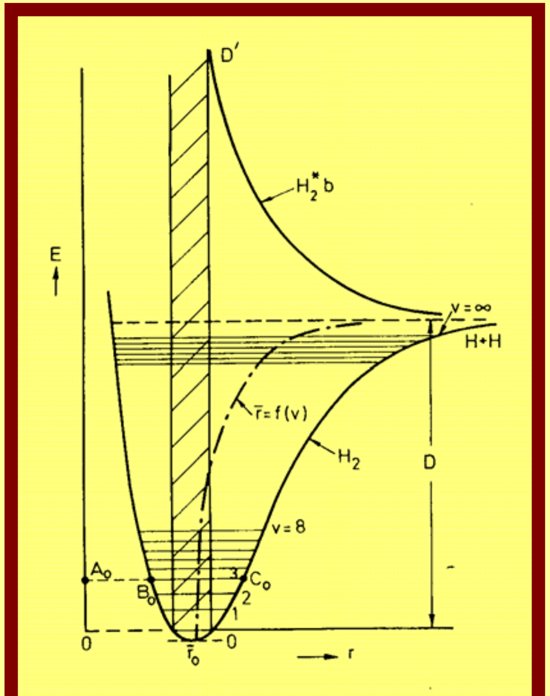


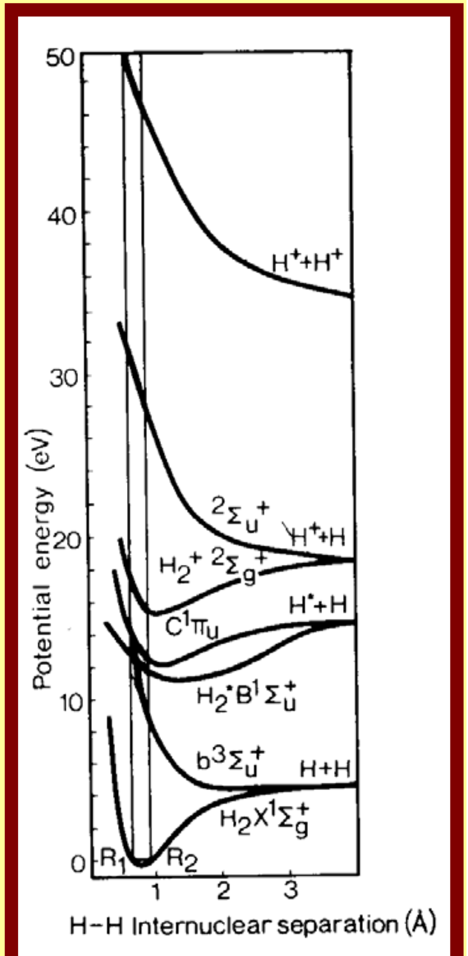
Reflection principle

Electron impact ionization: mechanism

The Franck Condon Range and Cases







E=100 eV: v=6x10^{8}cm/s; t=s/v=10^{-8}/6x10^{8} ~ 2x10^{-17}s « t_v~10^{-14}s

Electron impact ionization: mechanism

The Franck Condon principle

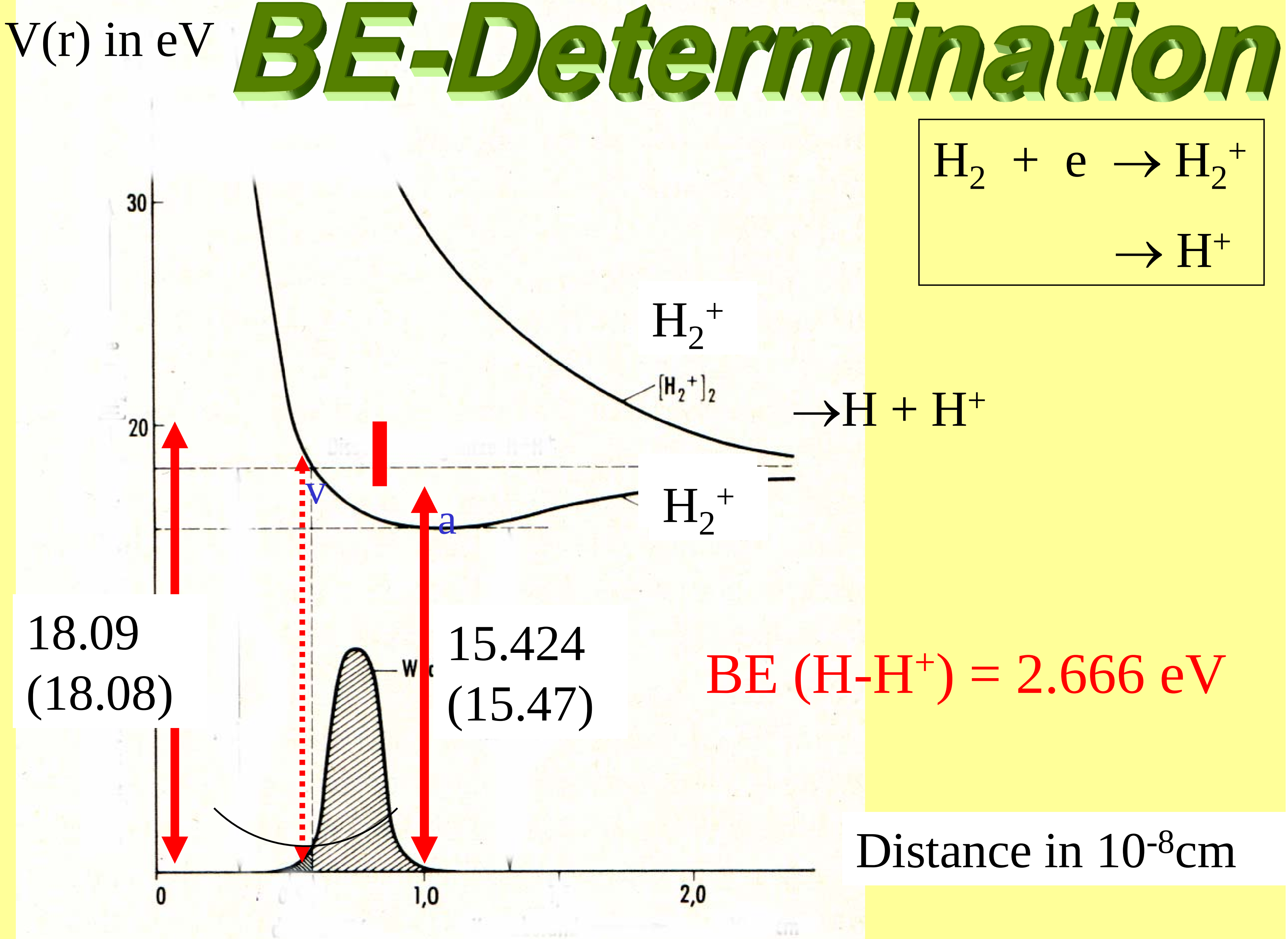
Several cases are possible:

(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 $(X^1\Sigma_g^+) \rightarrow H_2^+$ $(^2\Sigma_u^+)$).

BE-Determination



$H_2 + e \rightarrow H_2^+$

$\rightarrow H^+$

BE (H-H^+) = 2.666 eV

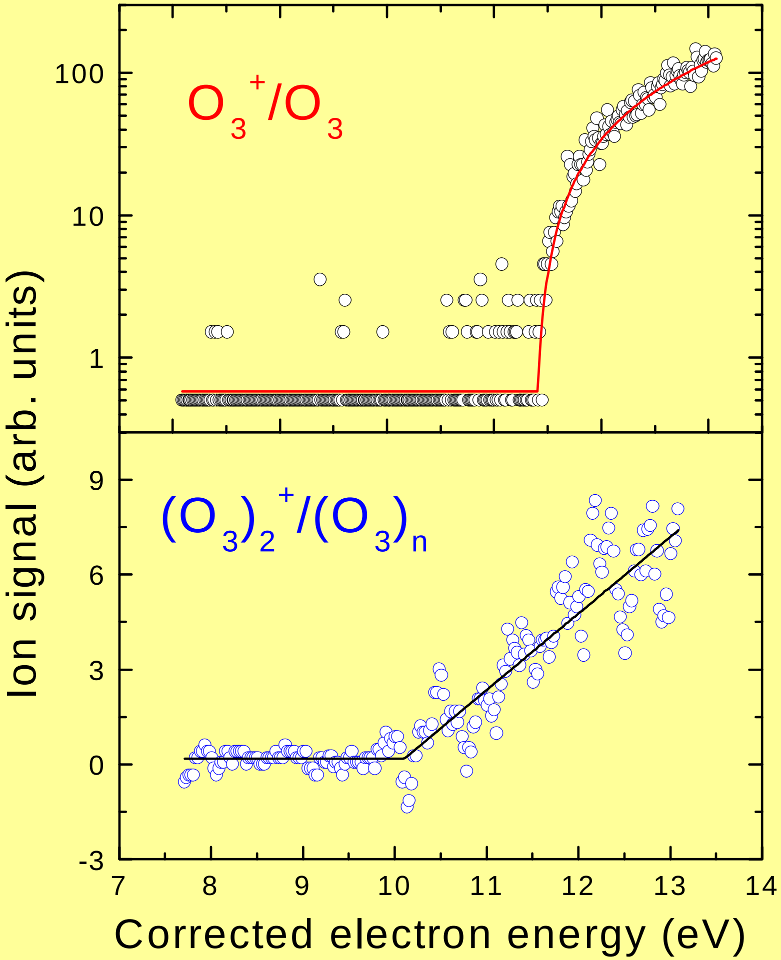
AE and BE of molecules

HEM data analysis:

$O_3 + e \rightarrow O_3^+$

$(O_3)_2 + e \rightarrow (O_3)_2^+$

Fit function: $\sigma(E) = b + \sigma_o \cdot (E\text{-}IE)^p$



AE: 12.70 ± 0.02 eV

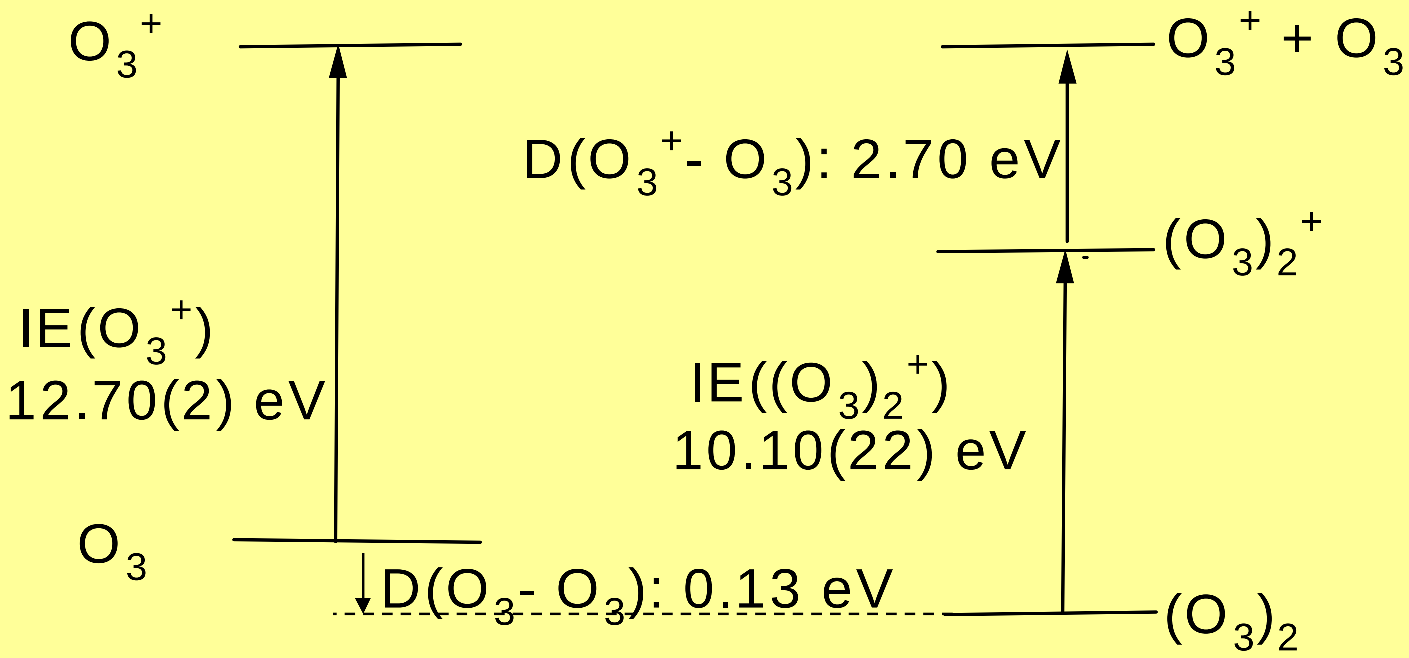
AE: 10.10 ± 0.2 eV

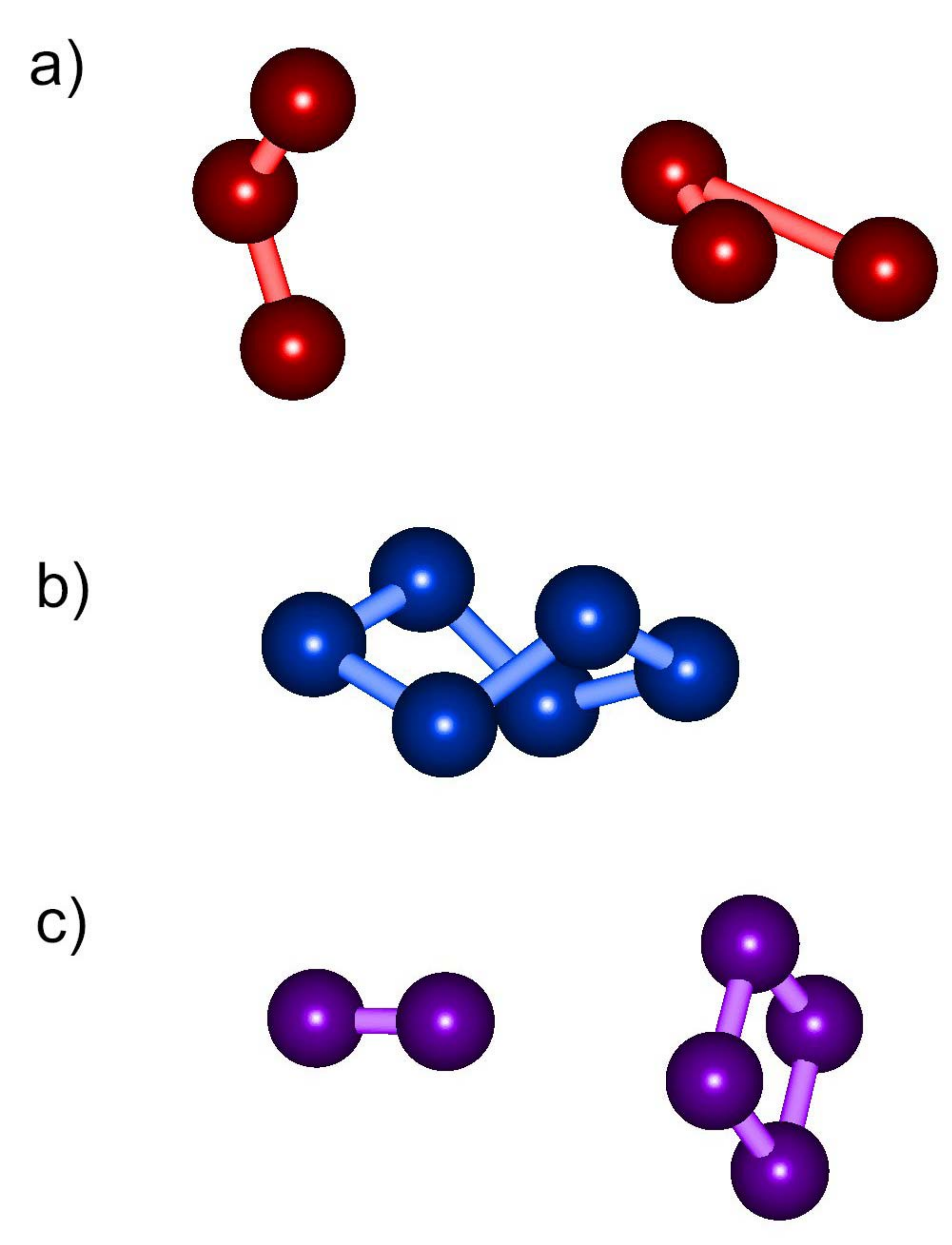
HEM data analysis:

$$O_3 + e \rightarrow O_3^+$$

$$(O_3)_2 + e \rightarrow (O_3)_2^+$$

Binding energy of ozone dimer ion:





„dimer geometry“

„twisted boat“

„$O_2 - O_4^+$ “

Photoelectron spectroscopy:Adiabatic & vertical IE

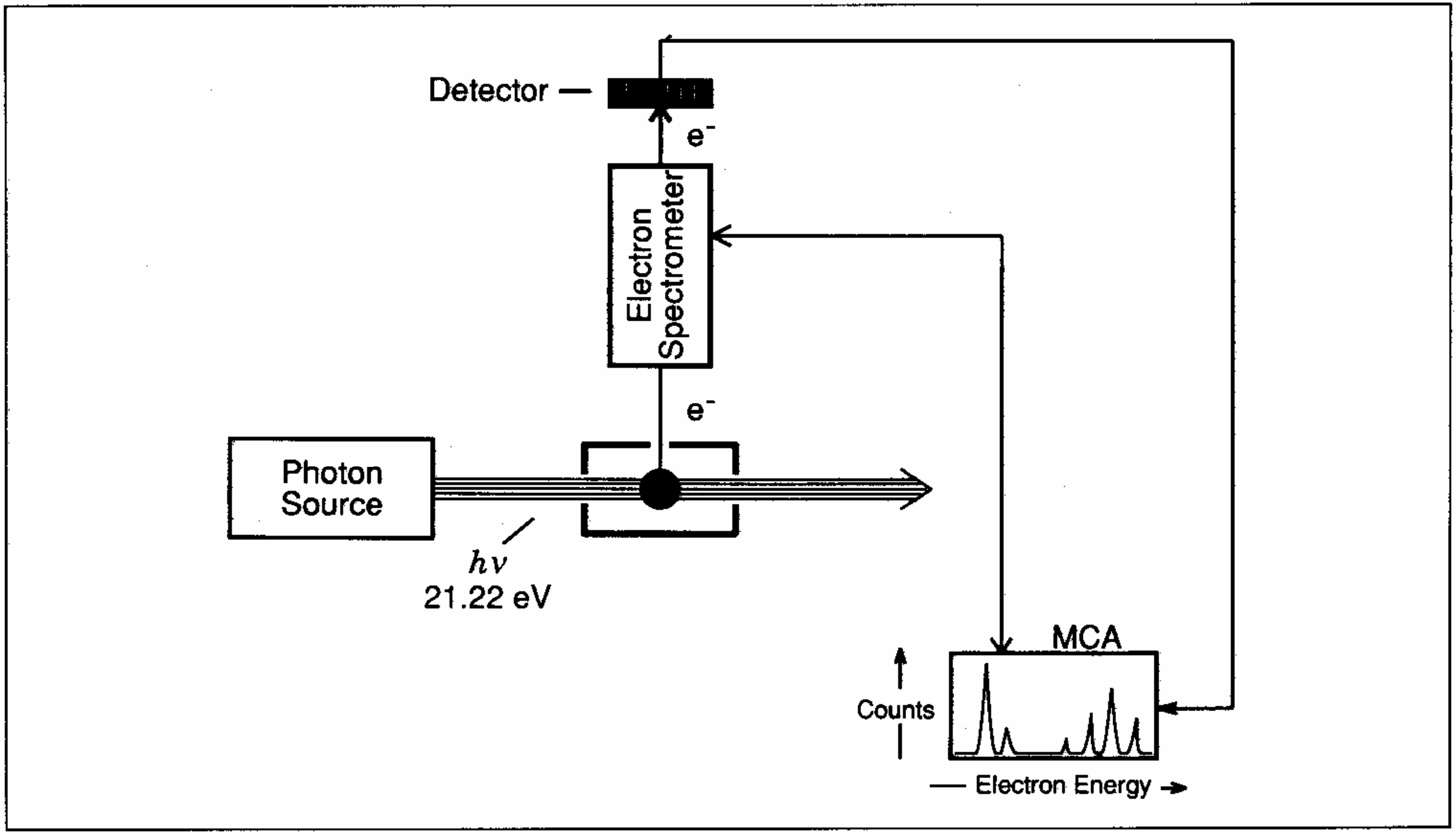
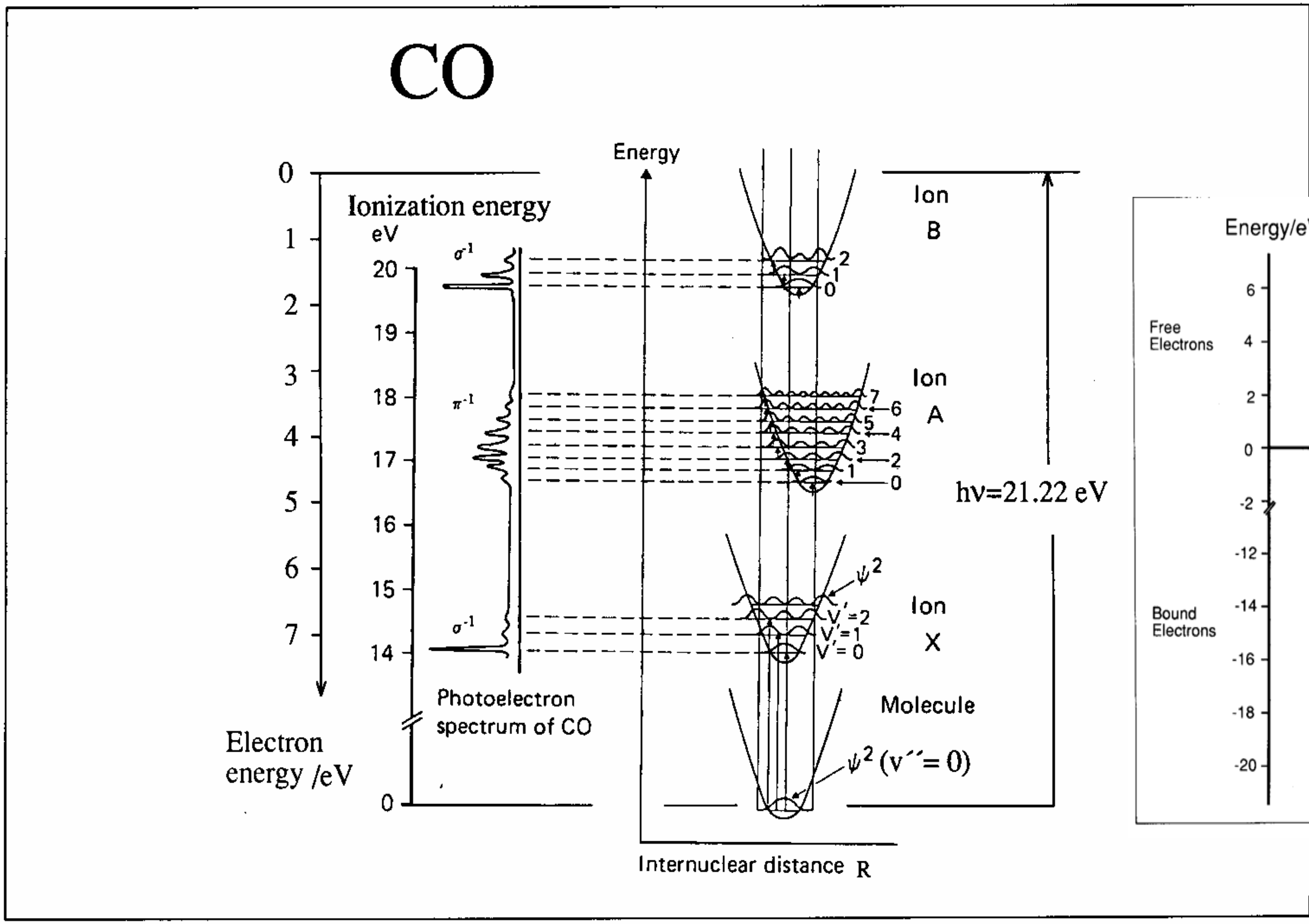


Fig. 2.1. Schematic of the experimental arrangement for photoelectron spectroscopy (PES). MCA: multichannel analyzer.

Photoelectron spectroscopy:Adiabatic & vertical IE



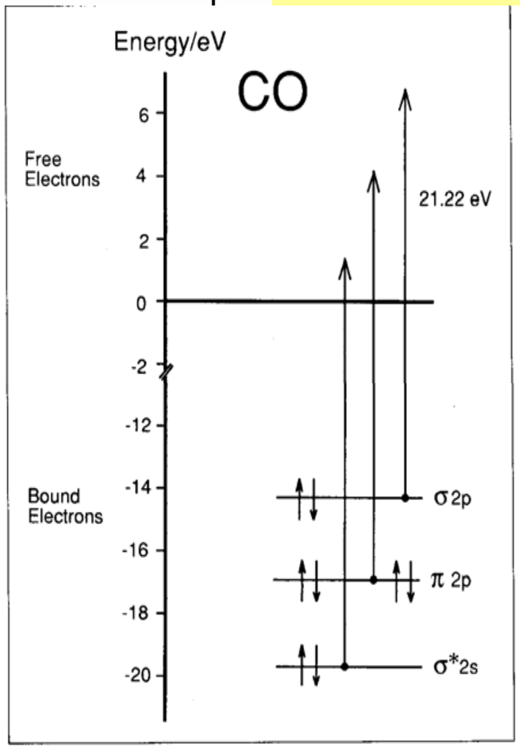


Fig. 2.3. PE spectrum of CO obtained by HeI radiation and potential energy curves for the neutral molecule and the three ionized states (adapted from [48]).

Ionization mechanism II: Vibrational predissociation

$ABC + e \rightarrow\rightarrow$ parent & fragment ions

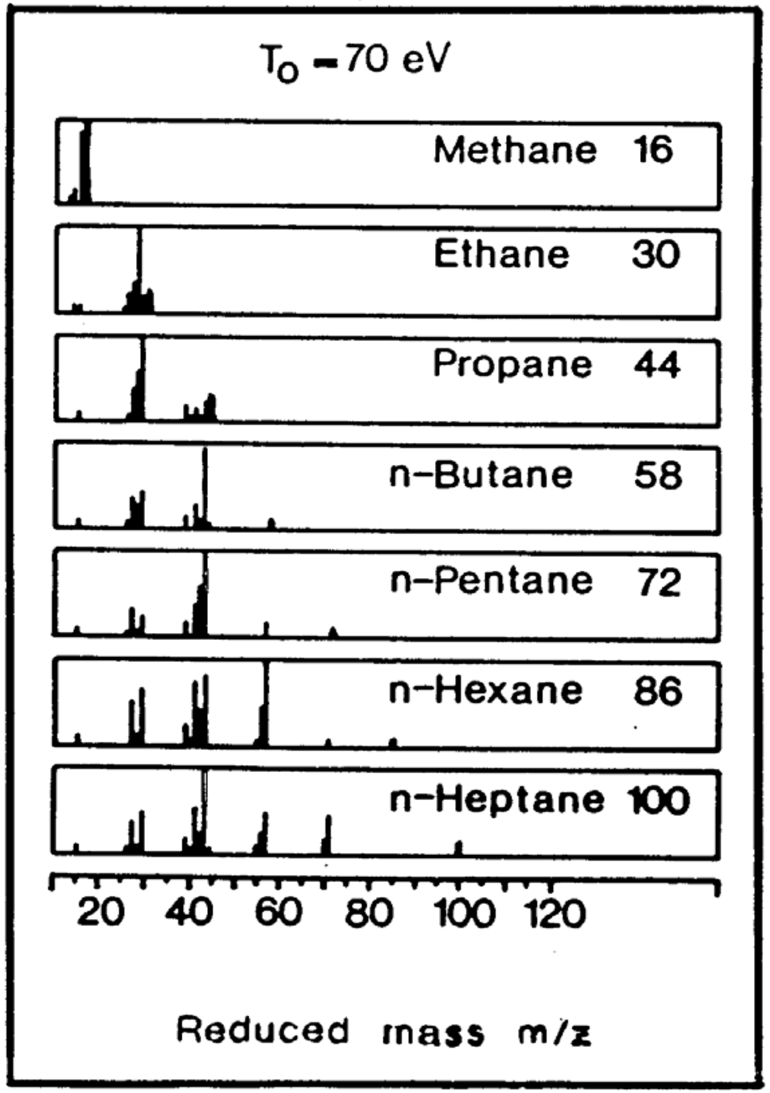
Decay paths for parent ion formed:

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

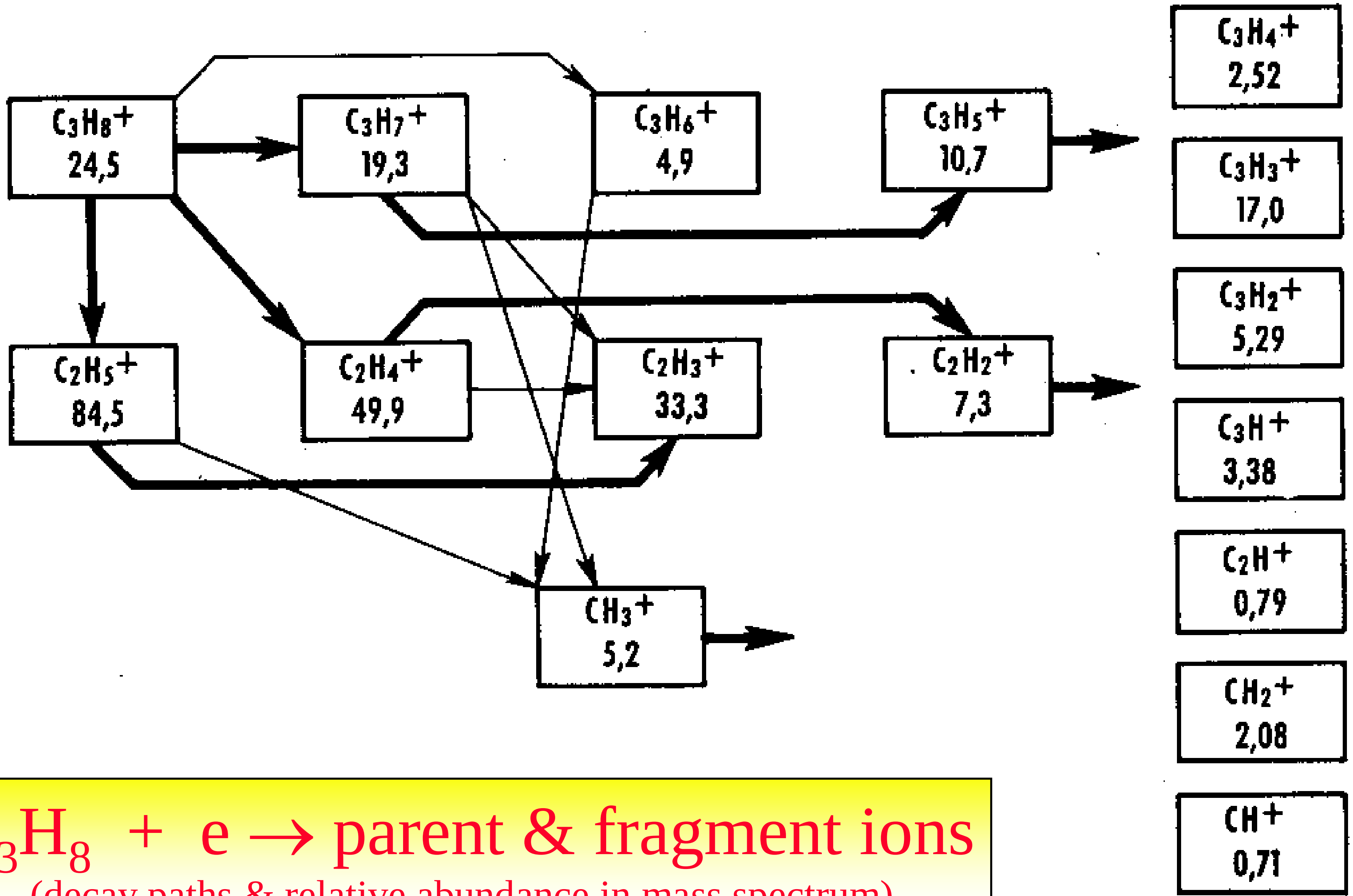
$\rightarrow A^{+} + BC \rightarrow$	$A^{+} + B + C$
$\rightarrow AB^{+} + C \rightarrow$	$A^{+} + B + C$
	$A + B^{+} + C$
$\rightarrow A + BC^{+} \rightarrow$	$A + B^{+} + C$
	$A + B + C^{+}$
$\rightarrow AB + C^{+} \rightarrow$	$A + B + C^{+}$

Ionization mechanism II: Vibrational predissociation

C_nH_{2n+2} + e → parent & fragment ions



Ionization mechanism II: Vibrational predissociation



C_3H_8 + e → parent & fragment ions

(decay paths & relative abundance in mass spectrum)

Unimolecular (metastable) dissociation

3 major mechanisms:

1. Vibrational (statistical) predissociation

2. Electronic predissociation
3. (Rotational) tunneling through a barrier

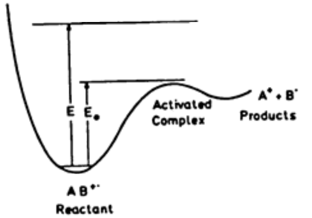
Vibrational (statistical) predissociation

METASTABLE (UNIMOLECULAR) DISSOCIATION OF IONS:

MECHANISMS:

1. VIBRATIONAL (STATISTICAL) PREDISSOCIATION

   (IF THE MOLECULAR ION IS COMPLEX ENOUGH SO THAT THE LISSAJOUS MOTIAN ON THE POTENTIAL ENERGY HYPERSURFACE IS SUFFICIENTLY COMPLICATED, THE EXISTENCE OF METASTABLE IONS CAN BE RATIONALIZED IN THE FRAMEWORK OF THE QUASI-EQUILIBRIUM THEORY.)

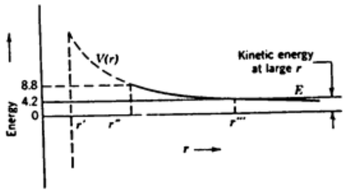


$$k(E) = \frac{\sigma}{h}\,\frac{W^{\neq}(E - E_0)}{\rho(E)}$$

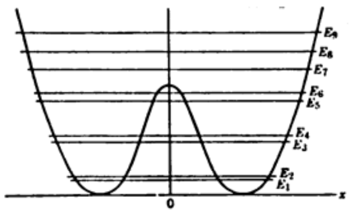
$$k_{min} = \frac{\sigma}{h\rho(E_0)}$$

2. ELECTRONIC PREDISSOCIATION, FORBIDDEN BY SOME SELECTION RULES OR HINDERED BY A SMALL OVERLAP INTEGRAL.

3. (ROTATIONAL) TUNNELING THROUGH A BARRIER



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



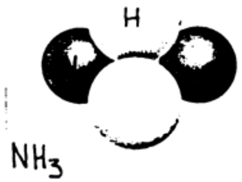
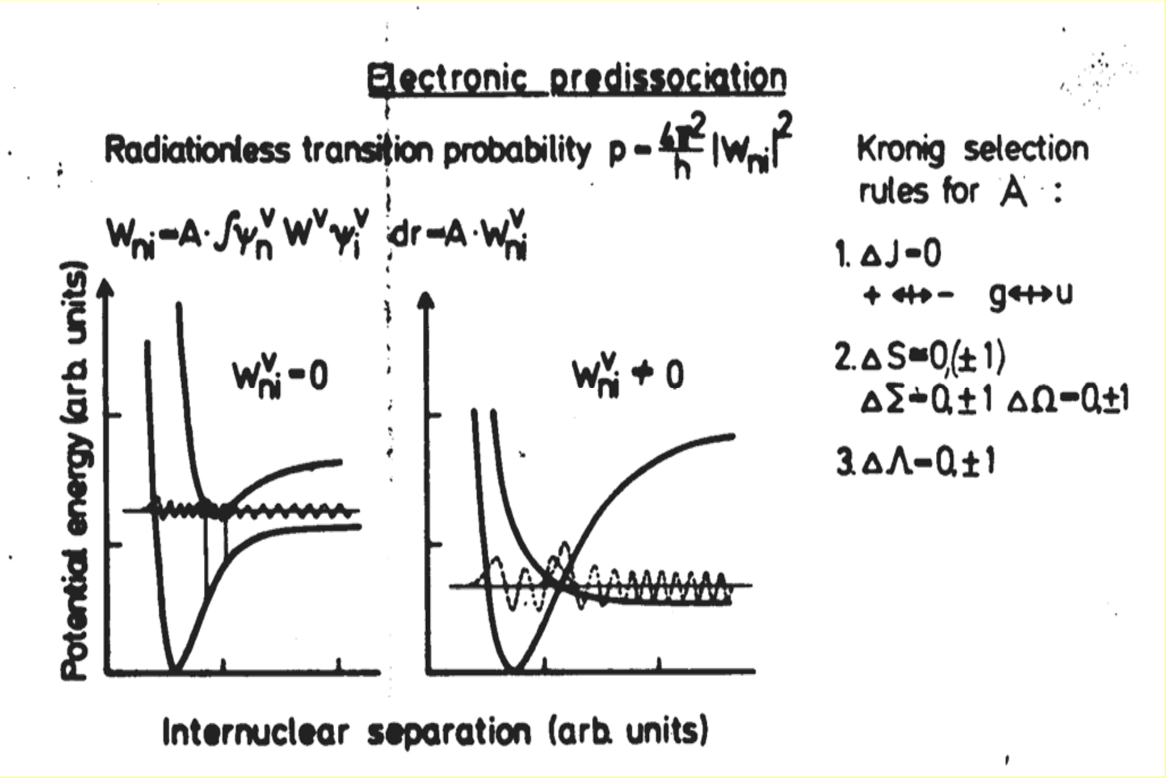
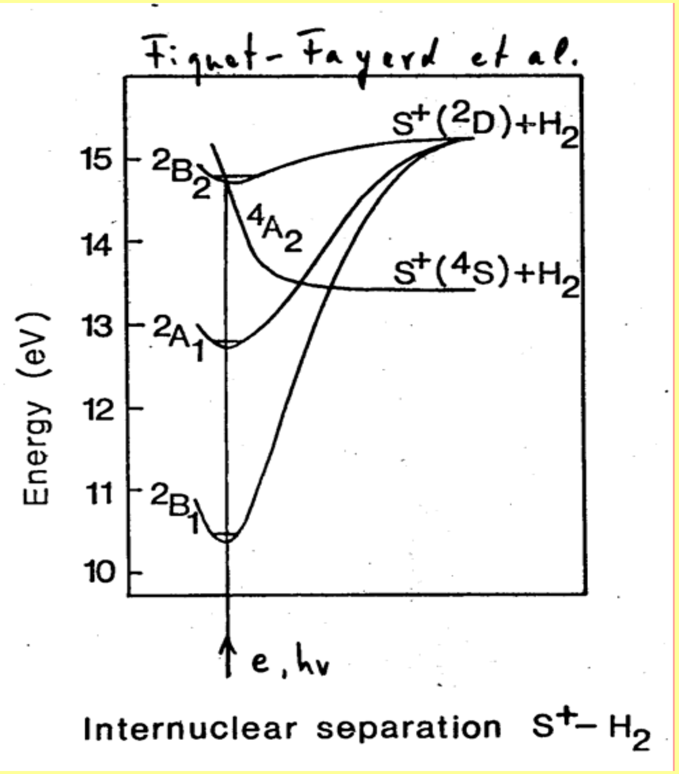


FIGURE 6-22

The potential energy of the N atom in the NH_3 molecule, as a function of its distance from the plane containing the three H atoms, which lies at

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





METASTABLE (UNIMOLECULAR) DISSOCIATION OF IONS:

MECHANISMS:

1. VIBRATIONAL (STATISTICAL) PREDISSOCIATION

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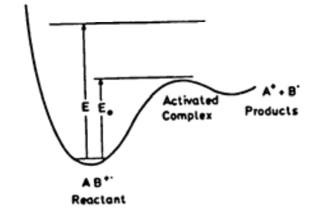
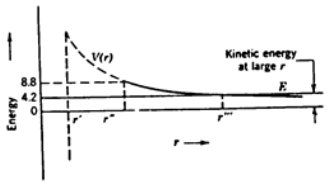


$$k(E) = \frac{\sigma}{h}\,\frac{W^{\neq}(E - E_o)}{\rho(E)}$$

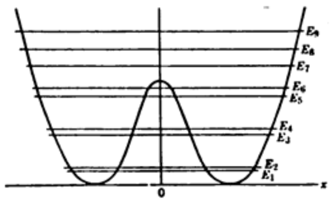
$$k_{min} = \frac{\sigma}{h\rho(E_o)}$$

2. ELECTRONIC PREDISSOCIATION, FORBIDDEN BY SOME SELECTION RULES OR HINDERED BY A SMALL OVERLAP INTEGRAL.

3. (ROTATIONAL) TUNNELING THROUGH A BARRIER



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



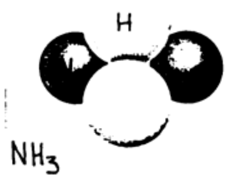
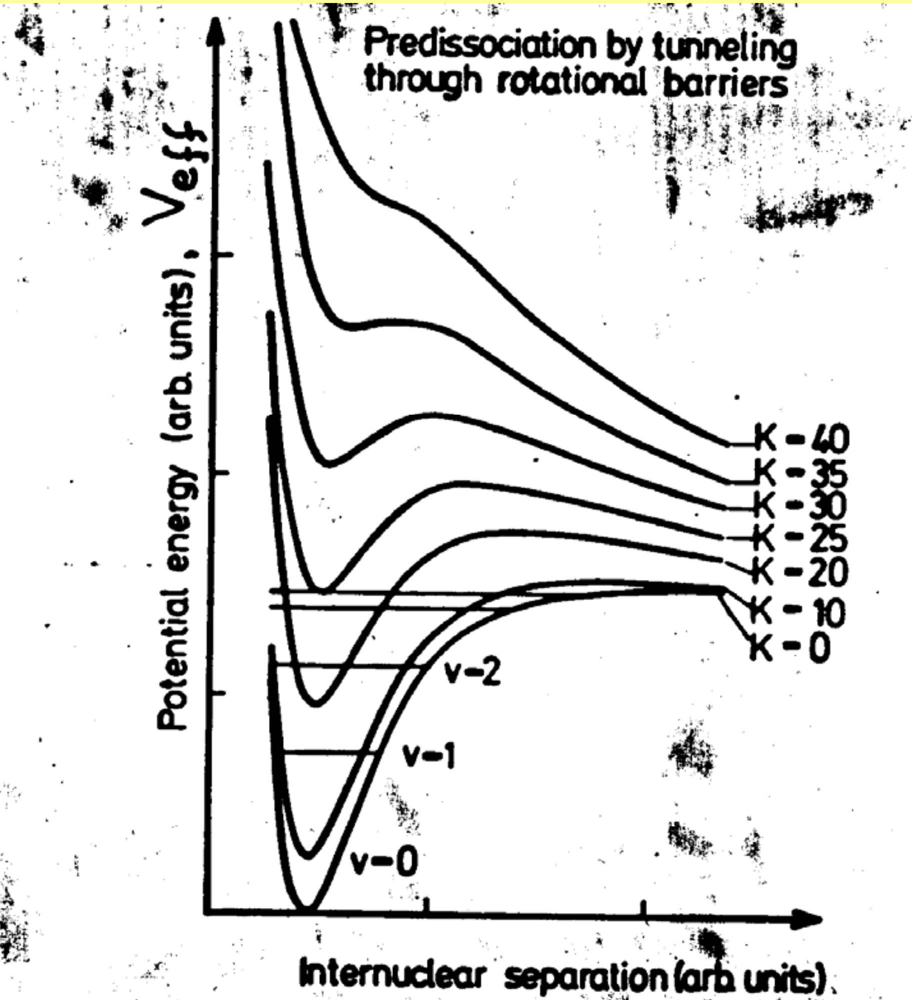


FIGURE 6-22
The potential energy of the N atom in the NH_3 molecule, as a function of its distance from the plane containing the three H atoms, which lies at

Tunneling through barrier

Tunneling through barrier



$$V_{eff} = V(r) + \frac{h^2}{8\pi^2\mu} \cdot \frac{L(L+1)}{r^2}$$

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

V potential for L=0

J =K rotational quantum numbe

Electron impact ionization: mechanism

Time evolution of the ionization process

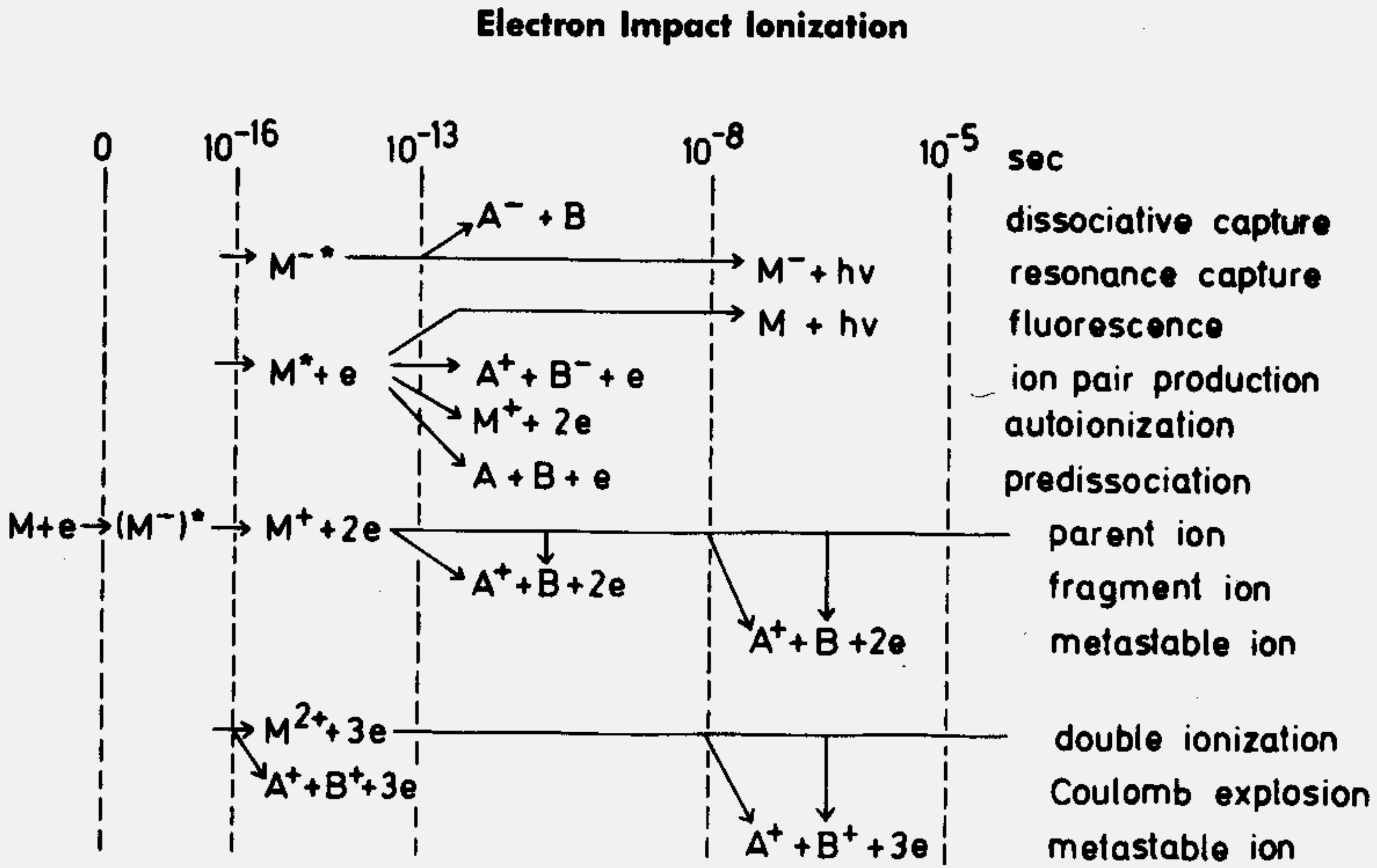
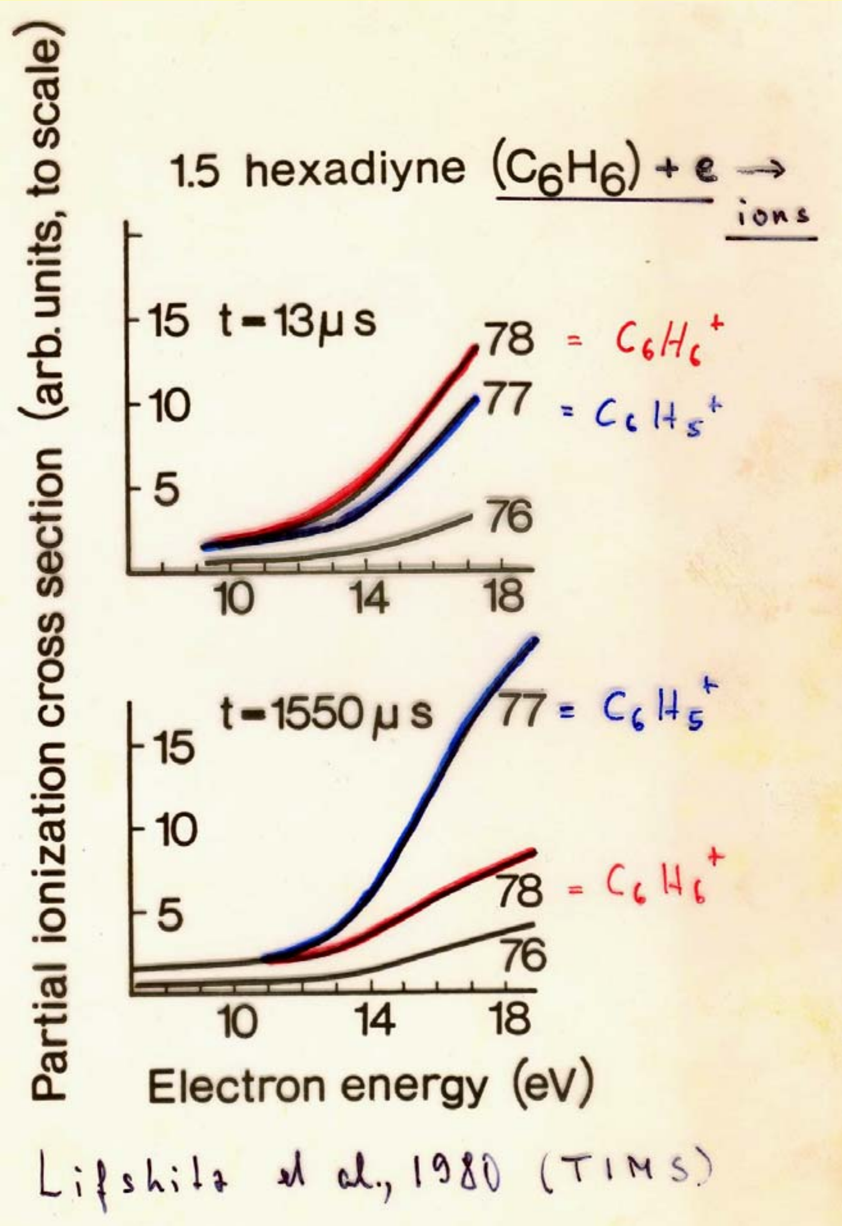


Figure 4. Schematic time chart of possible electron impact ionization processes.

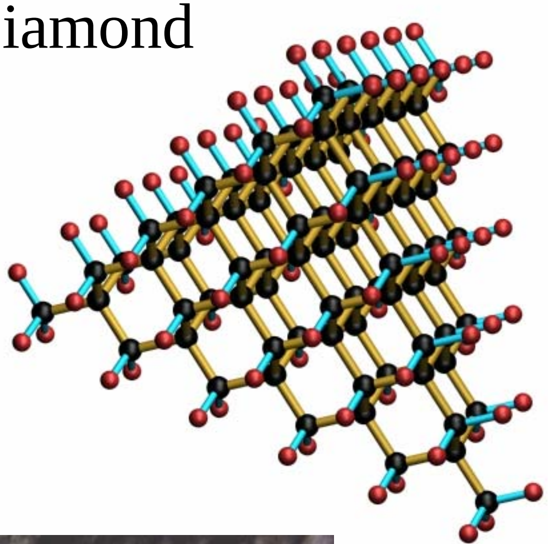
Electron impact ionization: mechanism



Time evolution of the ionization process

Example: Forms of carbon

Diamond



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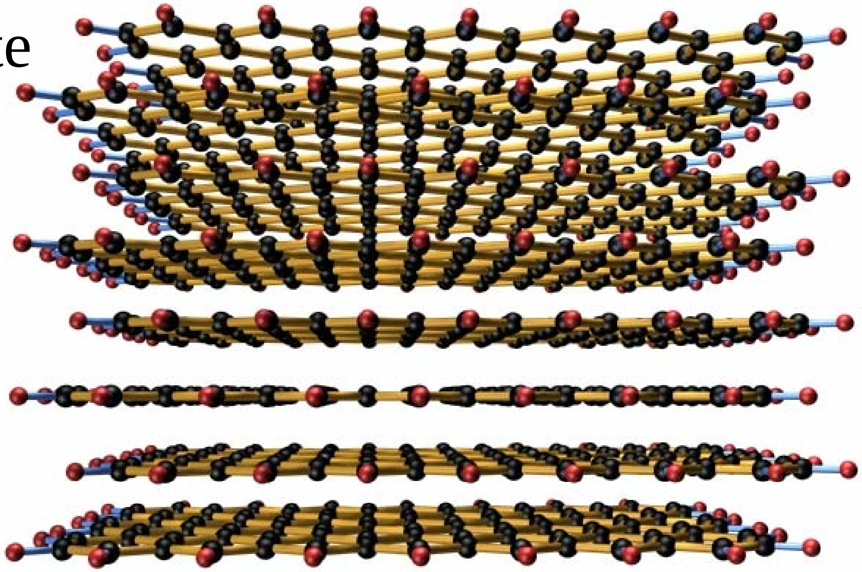
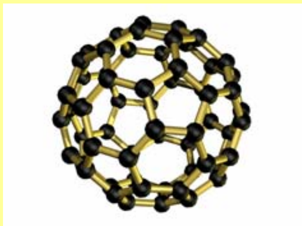
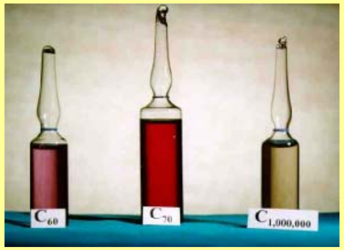


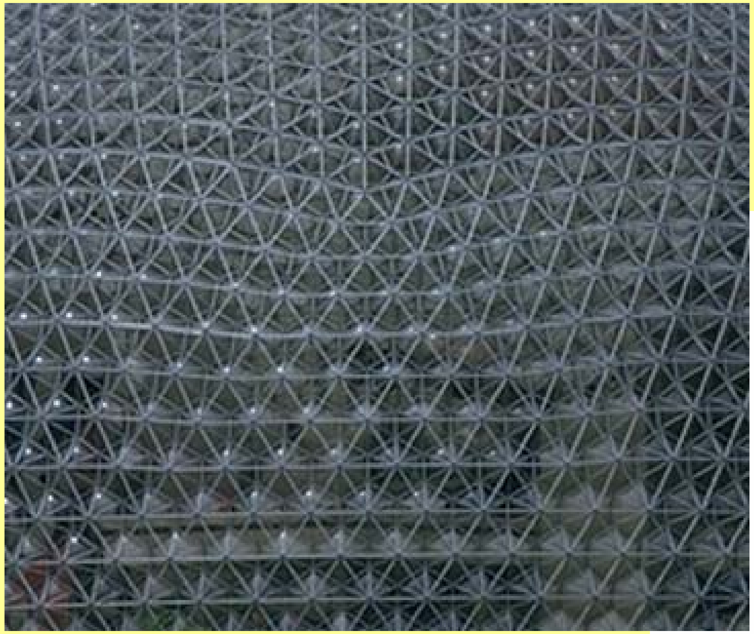
Buckminster Fullerene C_{60}

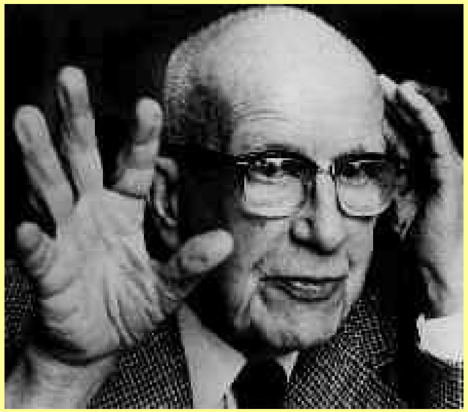


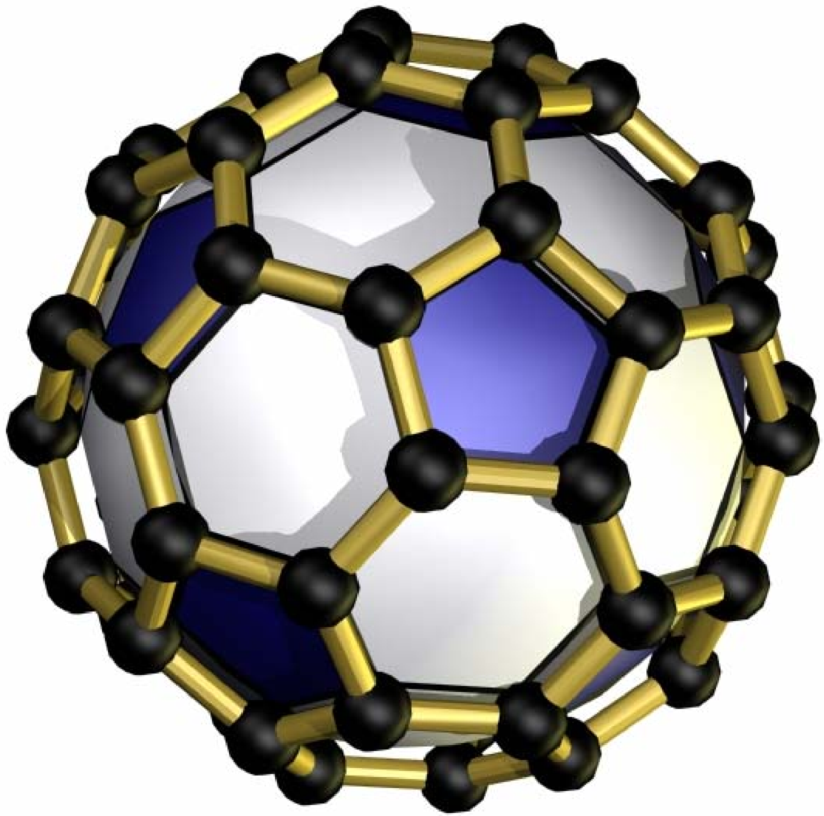


Strictly speaking only fullerenes are made exclusively from carbon.

Buckminster Fuller

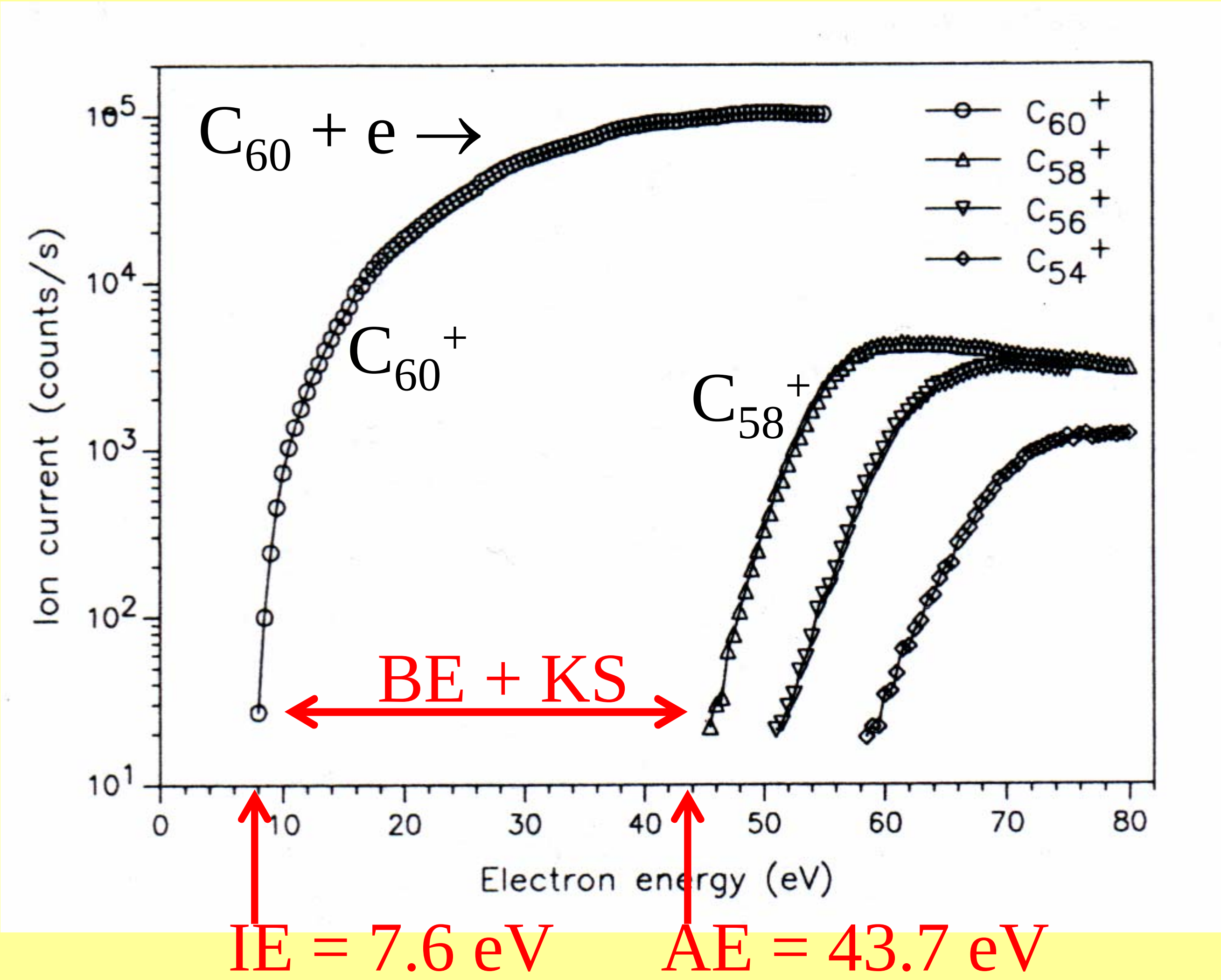


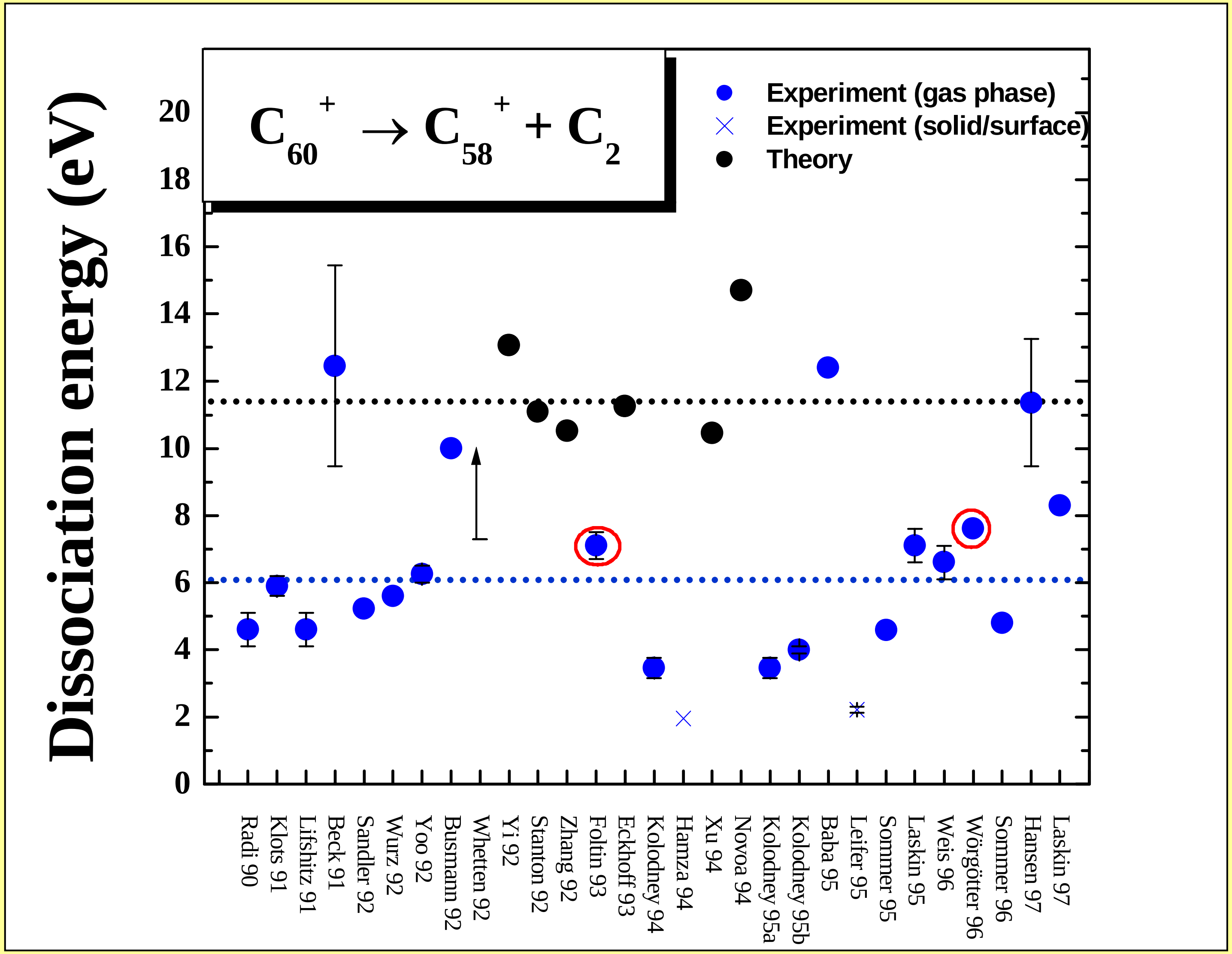




Truncated icosahedron

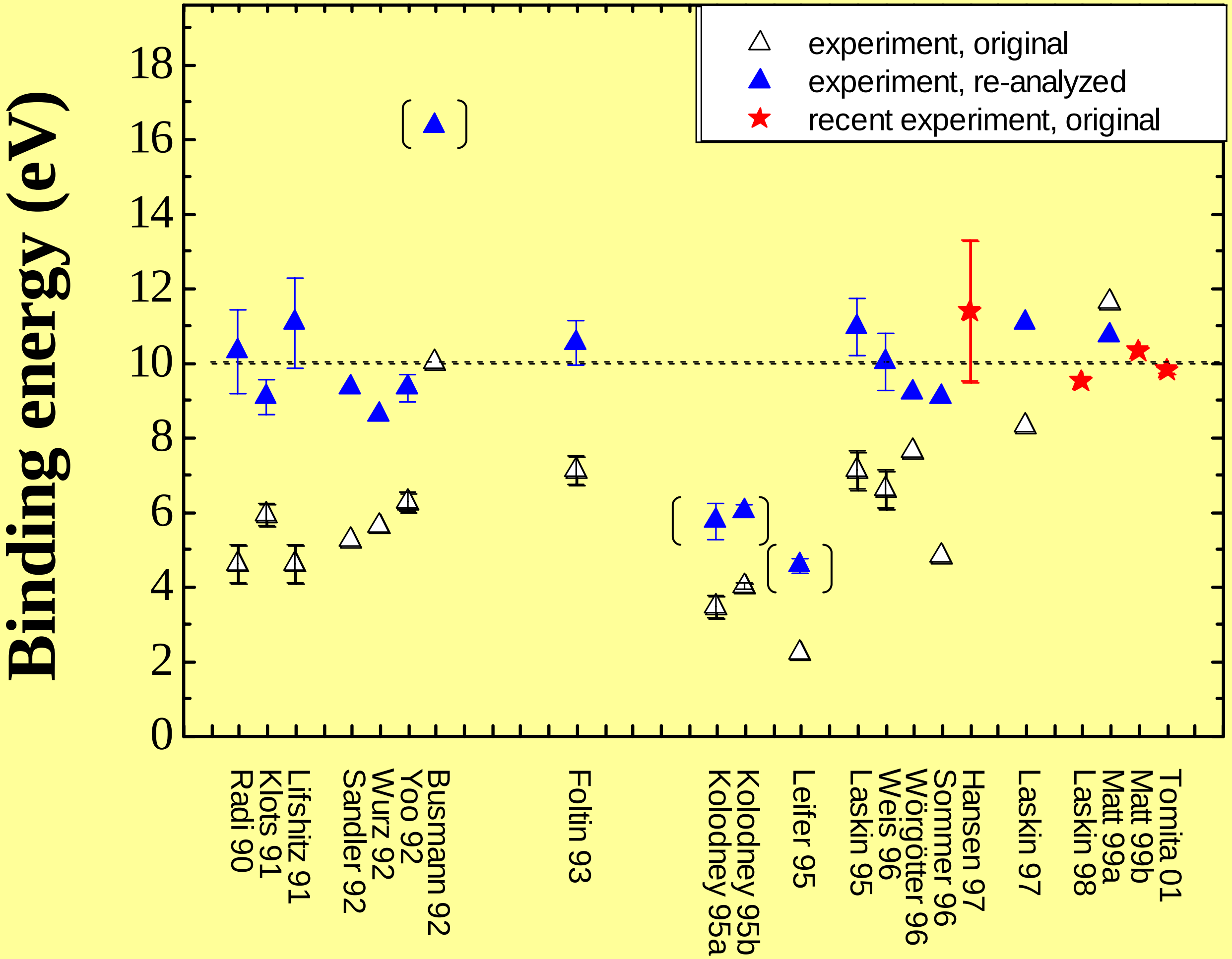
High appearance energy





Situation in 1997:

- about 30 published results on the C_{60} binding energy
- no agreement within experiment and no agreement between theory and experiment



Binding energy (eV)
0
2
4
6
8
10
12
14
16
18
experiment, original
experiment, re-analyzed
recent experiment, original
Radi 90
Klots 91
Lifshitz 91
Sandler 92
Wurz 92
Yoo 92
Busmann 92
Foltin 93
Kolodney 95a
Kolodney 95b
Leifer 95
Laskin 95
Weis 96
Wörgötter 96
Sommer 96
Hansen 97
Laskin 97
Laskin 98
Matt 99a
Matt 99b
Tomita 01

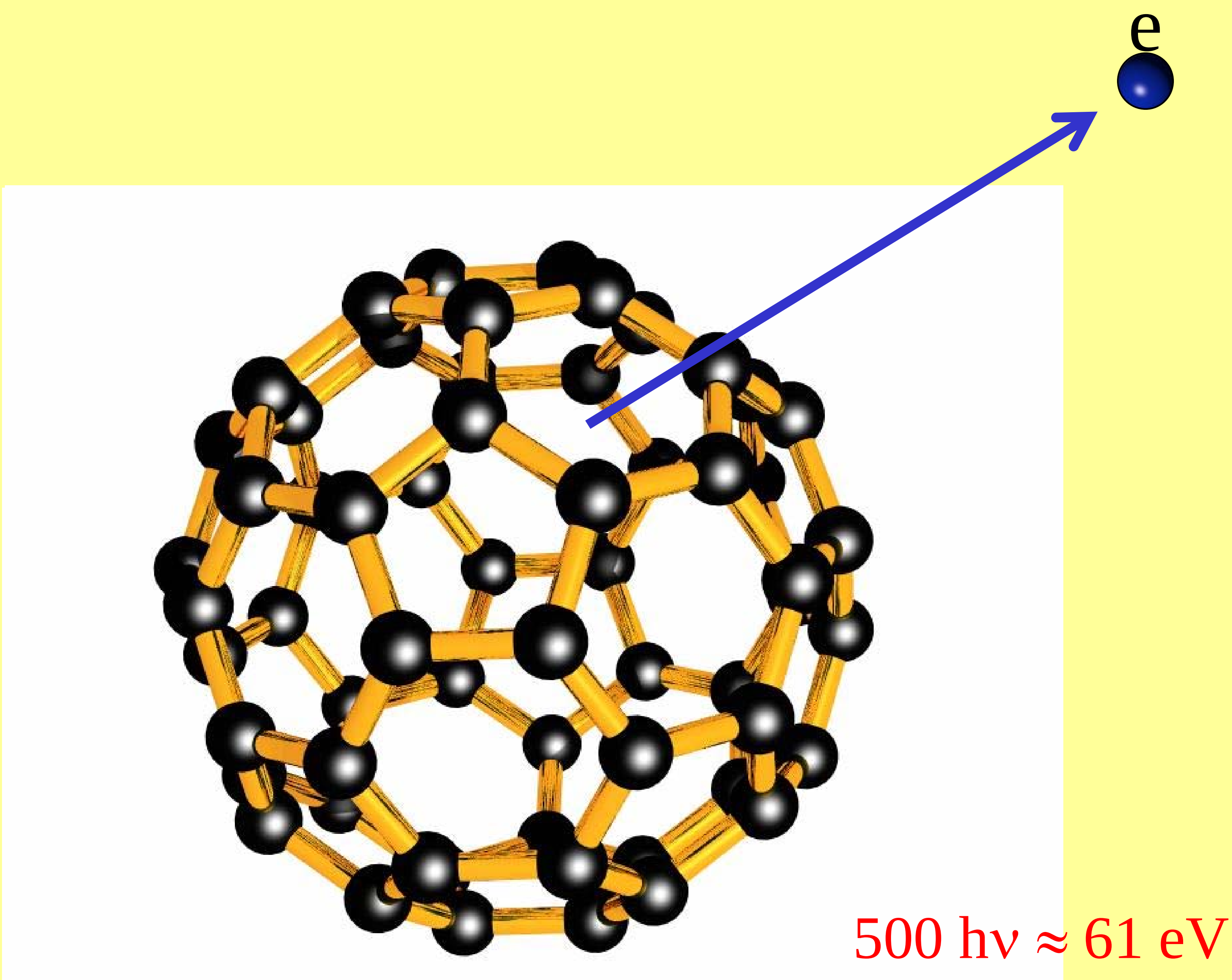
Final result for the C_{60}^{+} binding energy

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

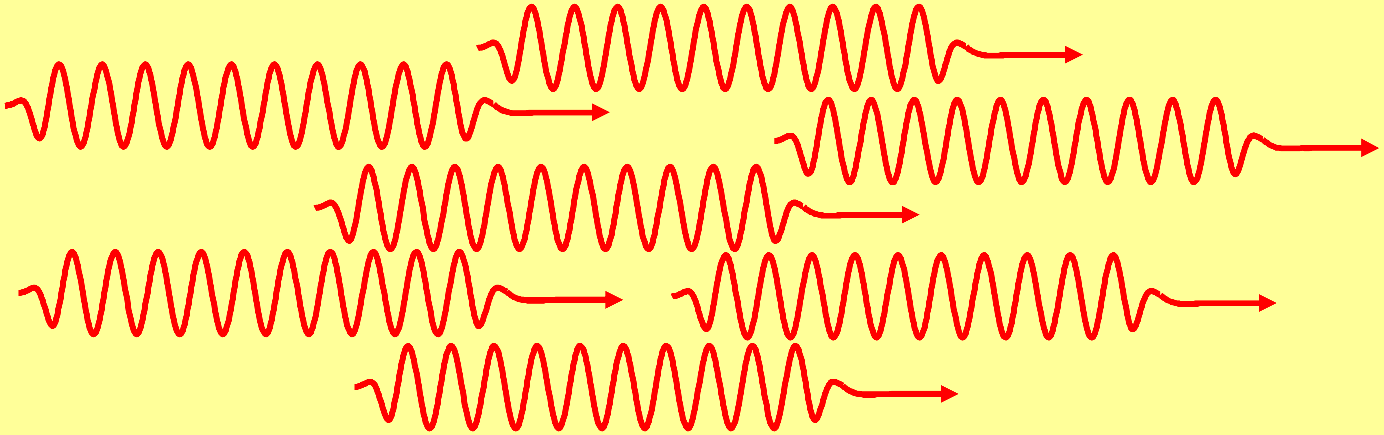
10.0 ± 0.2 eV

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

10.2 eV

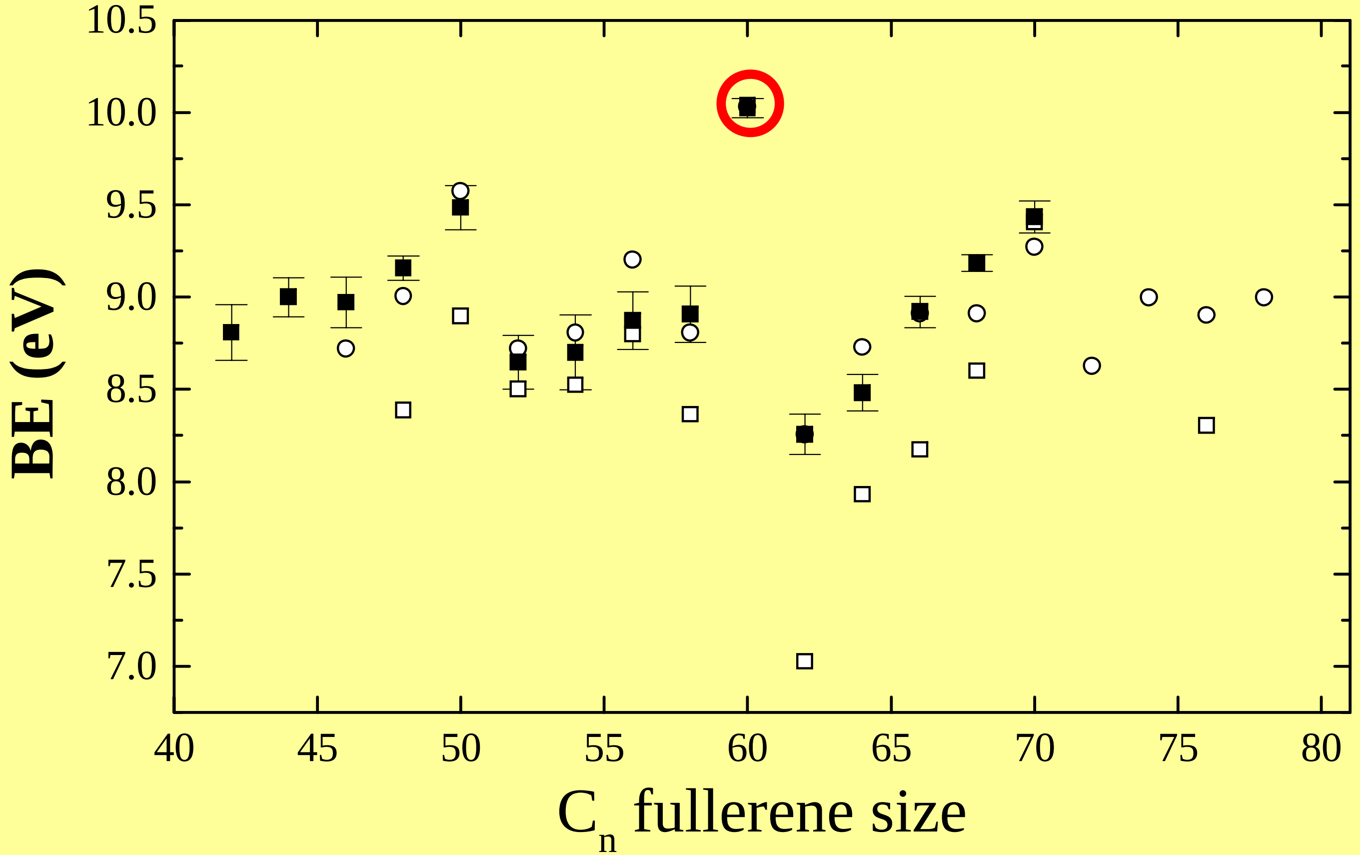


Infrared multiphoton excitation, dissociation and ionization of C_{60} , M.Hippler, M.Quack, R.Schwarz, G.Seyfang, S.Matt, T.D.Märk, Chem.Phys.Lett. 278(1997)111



Metastable decay of cluster ions:

Results: **Absolute** binding energies for fullerenes C_n^+ , $42 \leq n \leq 70$

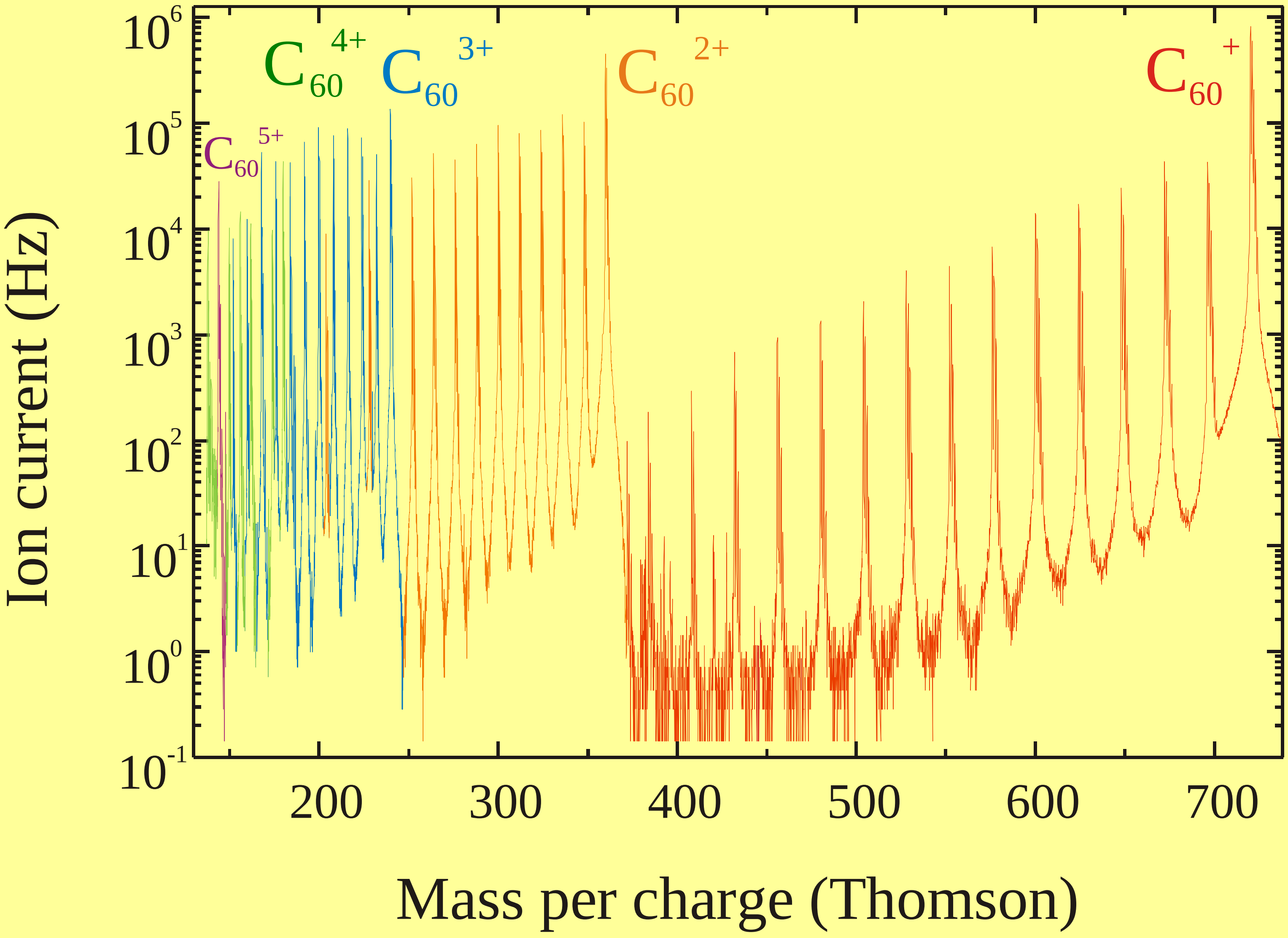


■ present measurements

□ S.Tomita, J.A. Andersen, C Gottrup, P.Hvelplund and U.V.Pedersen :'Dissociacion Energy for C_2 Ios from Fullerene Cations in a Storage Ring' Physical RevieW Letters, 13 Aug. 2001, Vol 87, nr. 7

○ P.E.Barran, S.Firth, A.J.Stace, H.W.Kroto, K.HAnsen,and E.E.B. Campbell, Int. J. Mass Spectrom. Ion Process. 167/168,127 (1997)

C_{60} + e → parent & fragment ions



C_{60} + e → multiply charged ions