universität innsbruck

EURATOM ÖAW

High resolution electron impact ionization of molecules

Ion Physics

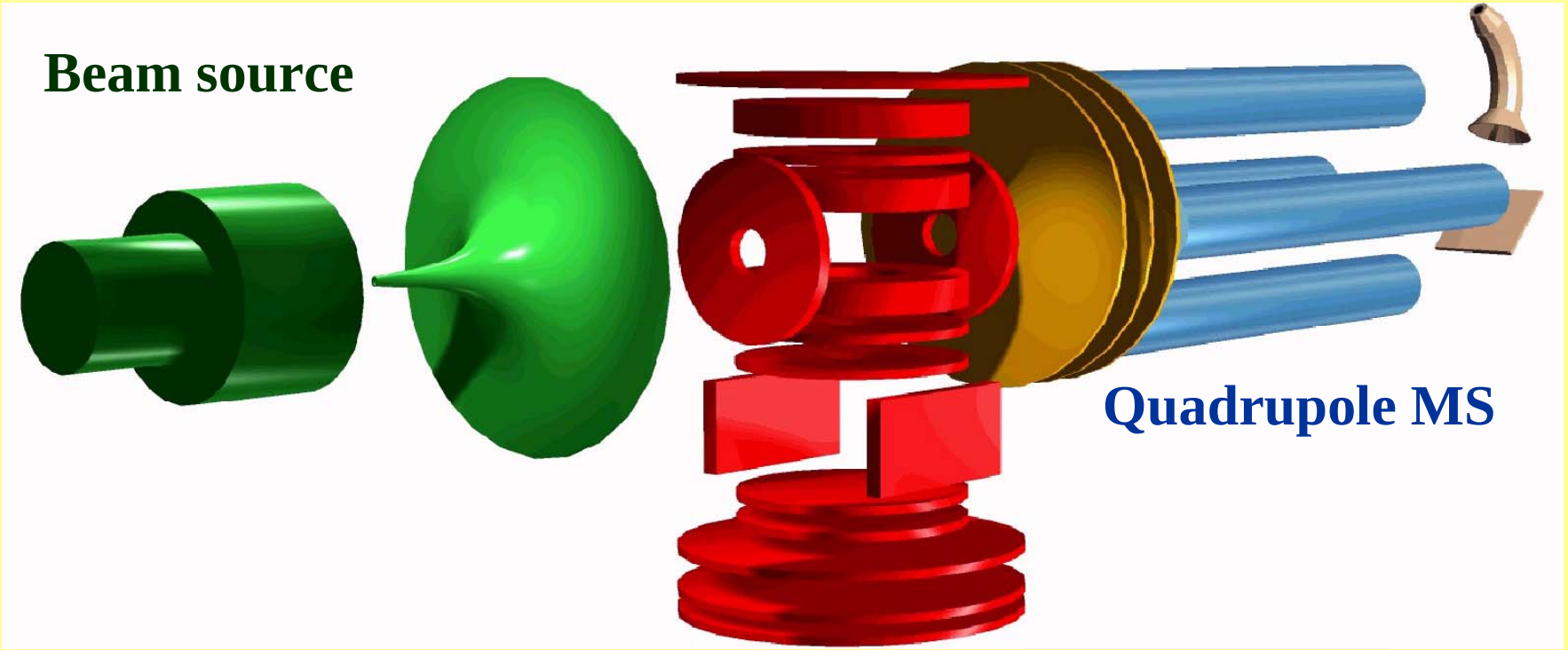
Institut Ionenphysik

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

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

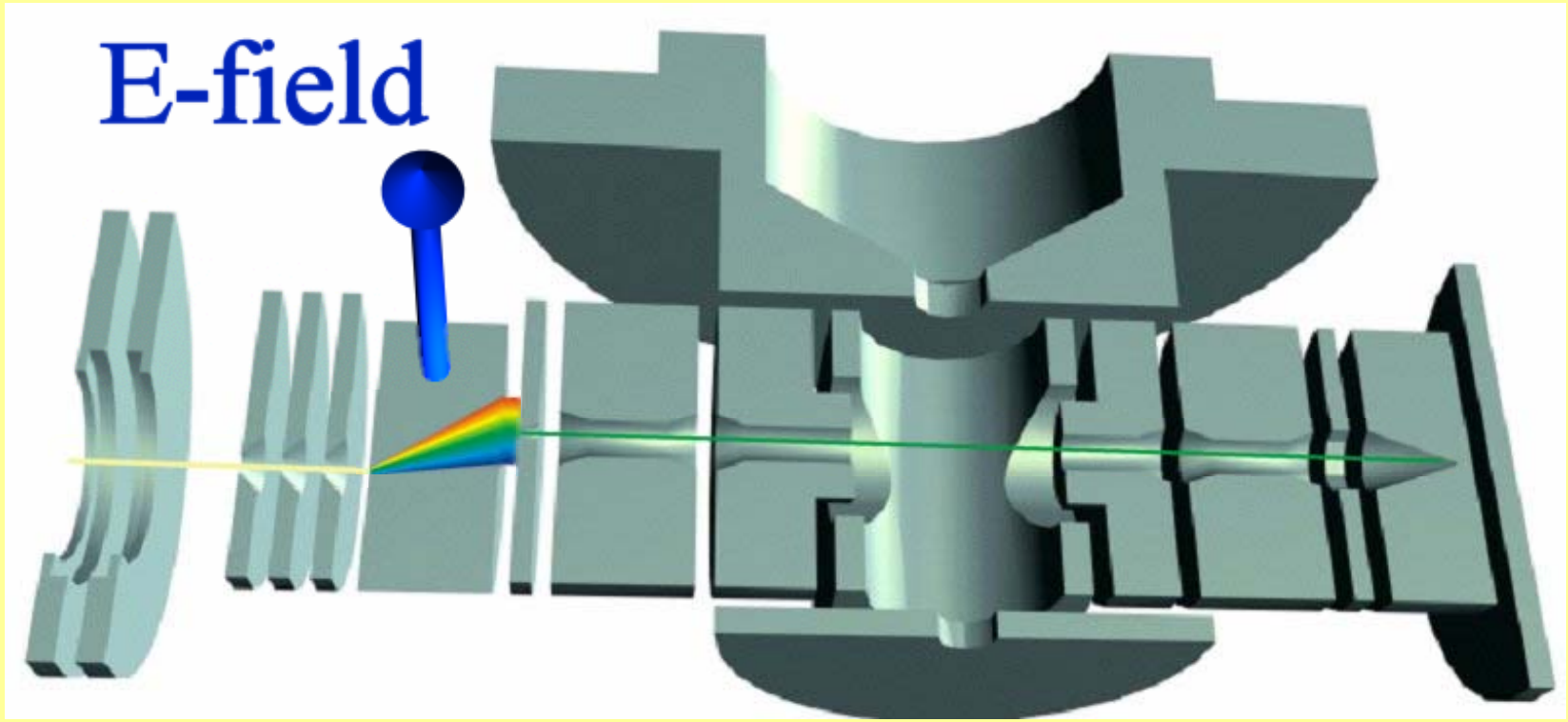
TEM-QM

Channeltron



Trochoidal monochromator

Trochoidal electron monochromator



Trochoidal electron monochromator

Ion source: trochoidal electron monochromator

Resolution: 40meV, 1nA; 100meV, 150nA

Energy range: 0eV to 100eV

Maximum ion current: 1pA

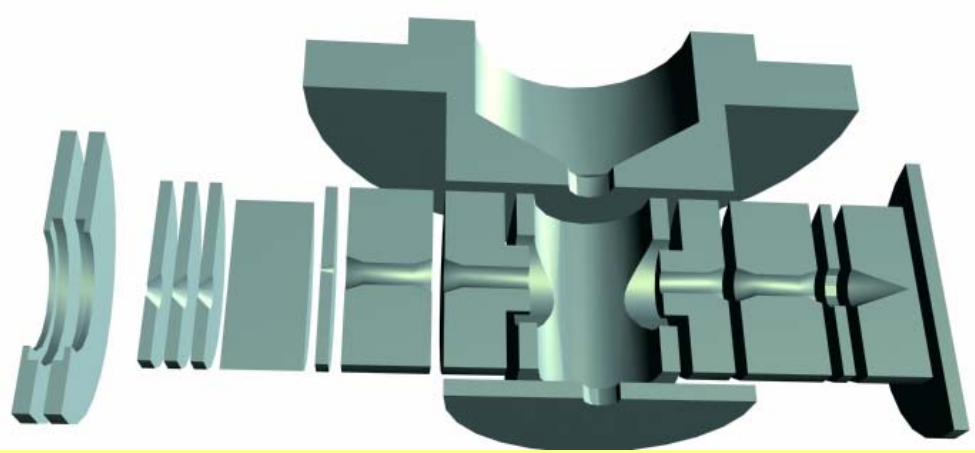
Purpose: electron attachment studies

Recent results:

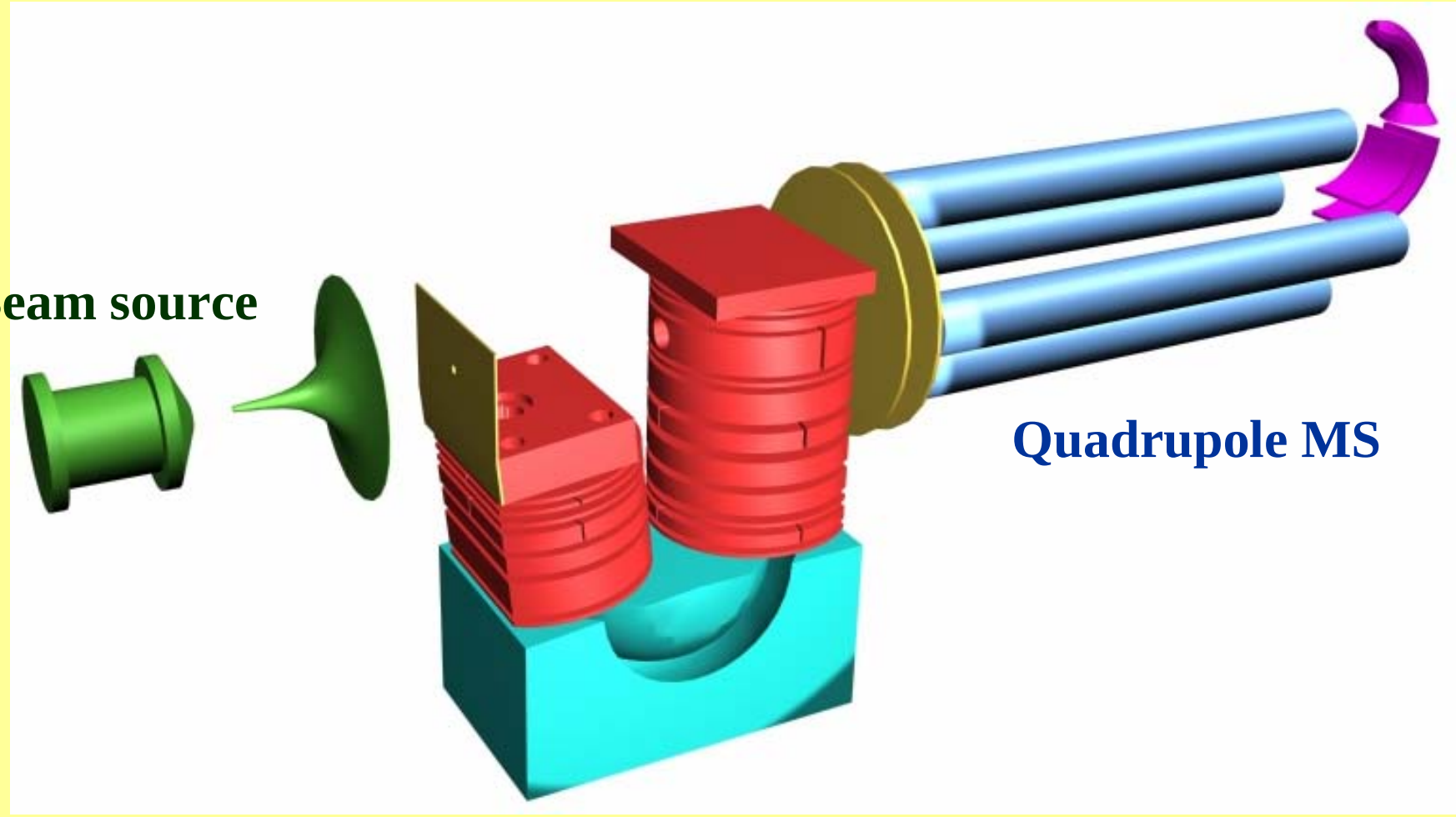
$(O_2)_n + e^- \rightarrow O_2^-$: vibrational structures

DEA to H_2, C_2Cl_4, OClO, ClOCl, Cl_2, SF_5CF_3 ,..

Biomolecules, explosives



HEM-QM


Channeltron
Beam source
Quadrupole MS
Hemispherical monochromator

HEM-QM

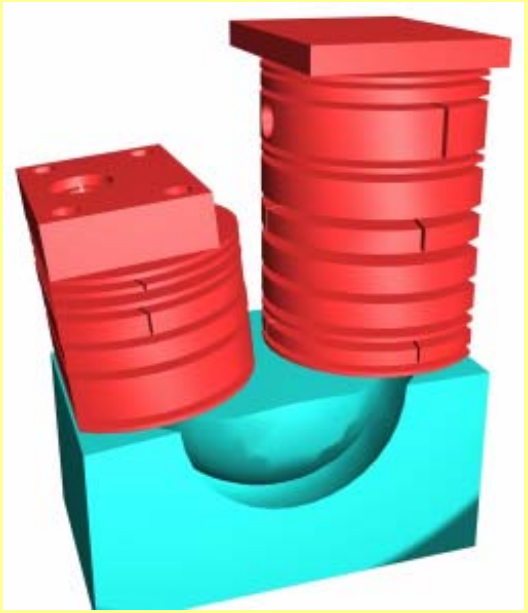
Ion source: hemispherical electron monochromator

Resolution: 40meV, 5nA; 120meV, 50nA

Energy range: 0eV to 600eV

Maximum ion current: 200nA

Purpose: electron attachment studies and
determination of appearance energies

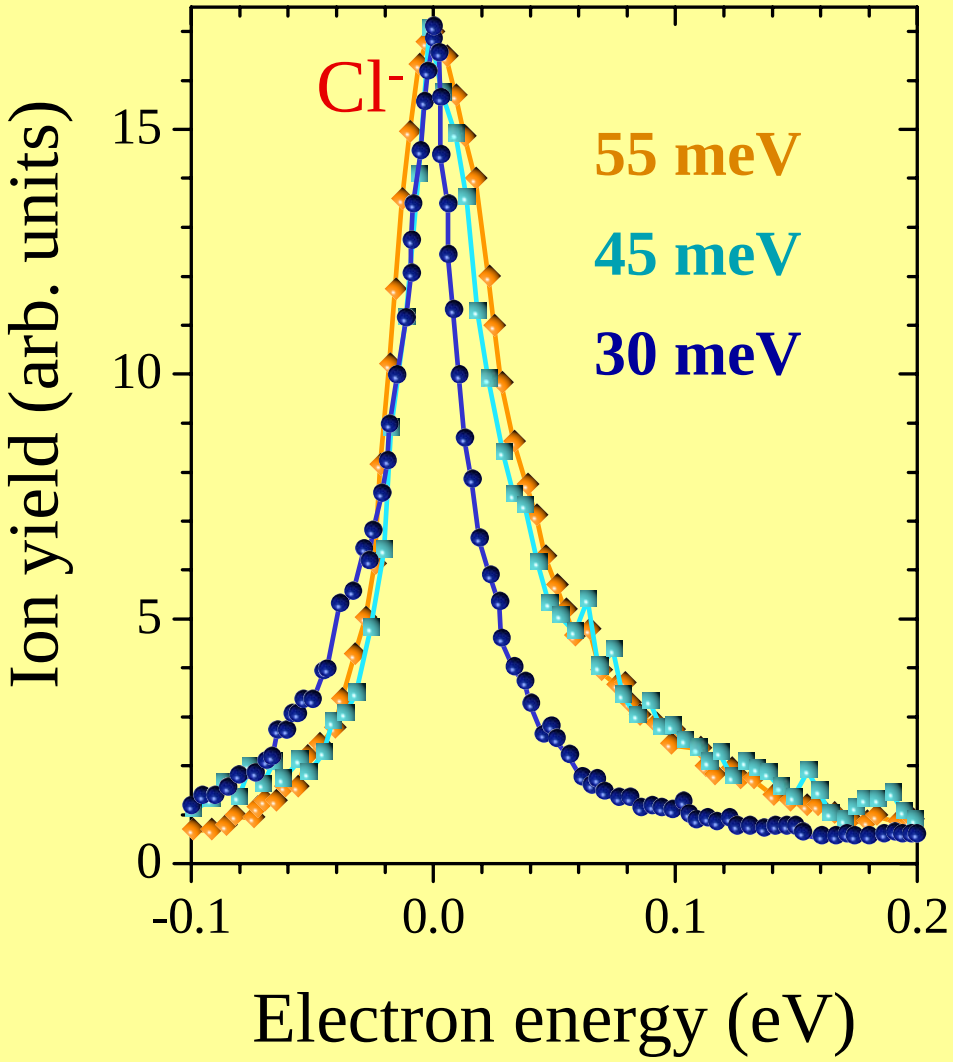


Recent results:

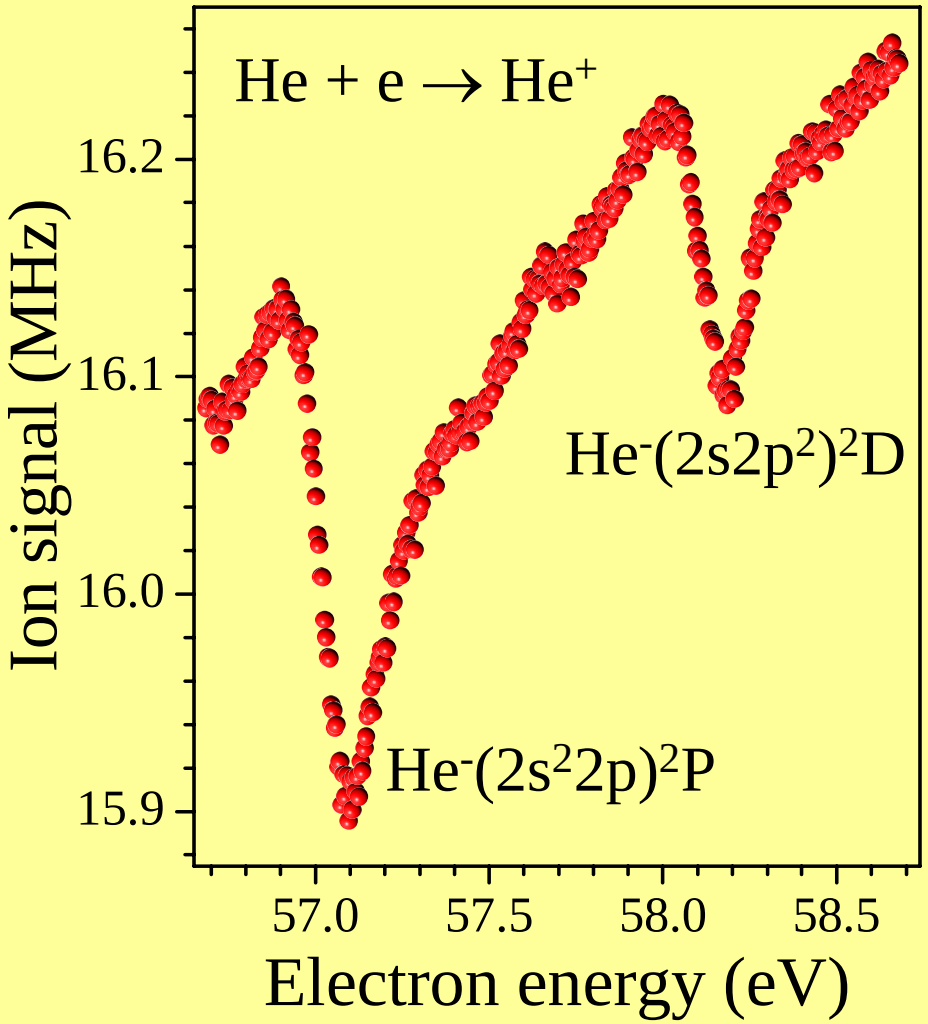
1. Appearance energies of various cluster series $X_n + e^- \rightarrow X_m^+$:
(X=Ne, Ar, Kr, Xe, H_2, D_2, N_2, N_2O)
2. Appearance energies of molecules
(H_2O, D_2O, C_6H_6, C_6D_6, OCl_2, SF_5CF_3,)
3. DEA to H_2, C_2Cl_4, OClO, ClOCl, Cl_2, SF_5CF_3 , uracil,...

Determination of the resolution

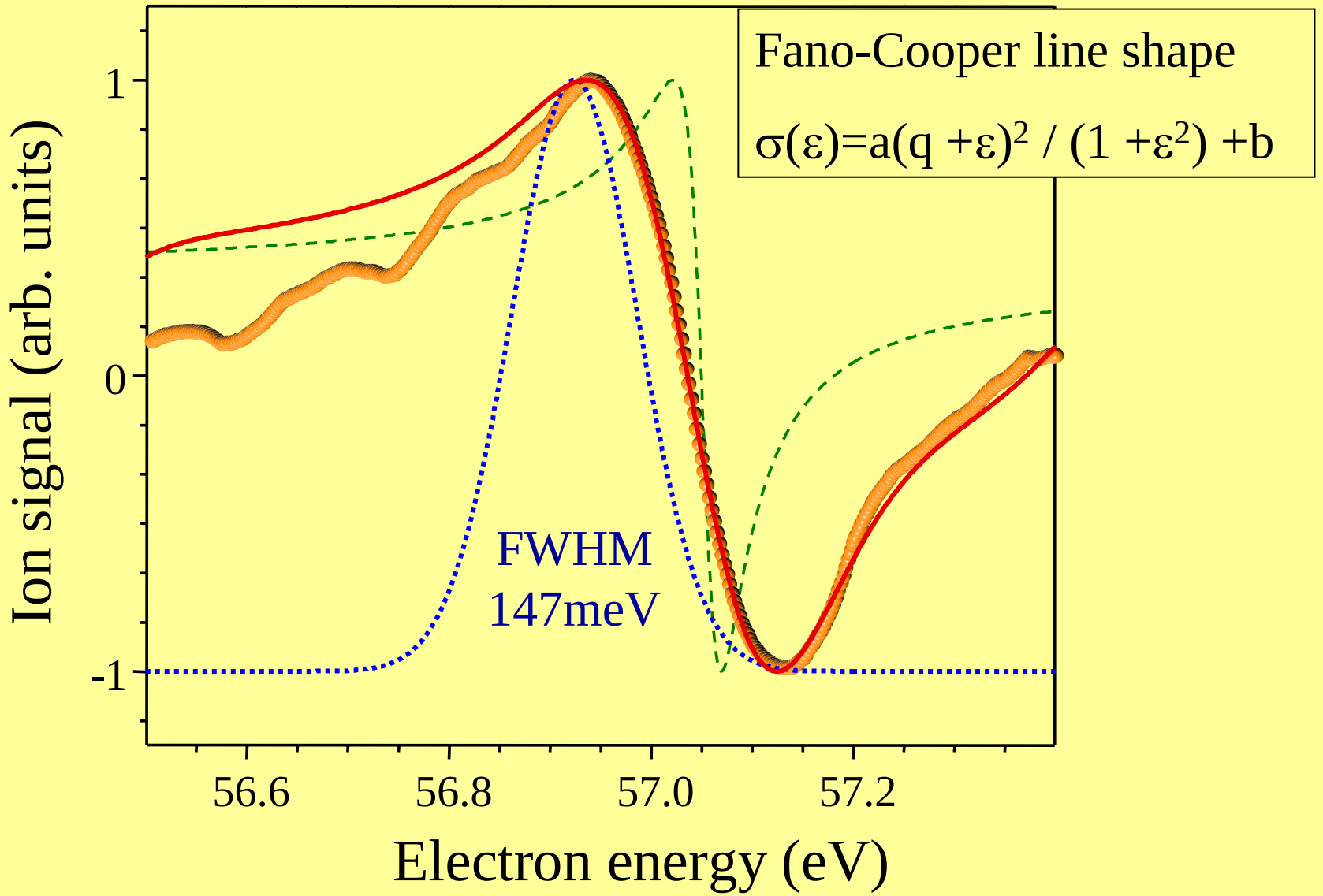
1: $CCl_4 + e \rightarrow Cl^-$



2: n = 2 intrashell He^- resonances



Determination of the resolution

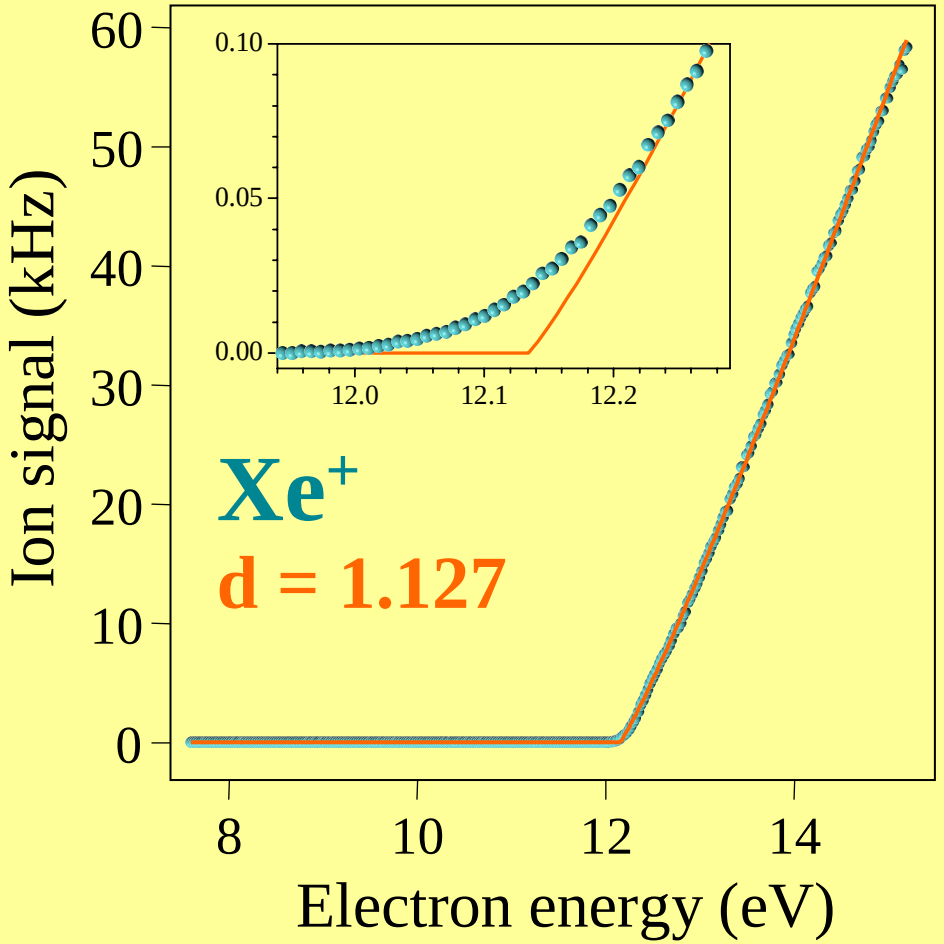


Threshold behavior

$$\sigma_{ion} \propto E^{d}$$

For Z = 1 $\Rightarrow$ d = 1.127

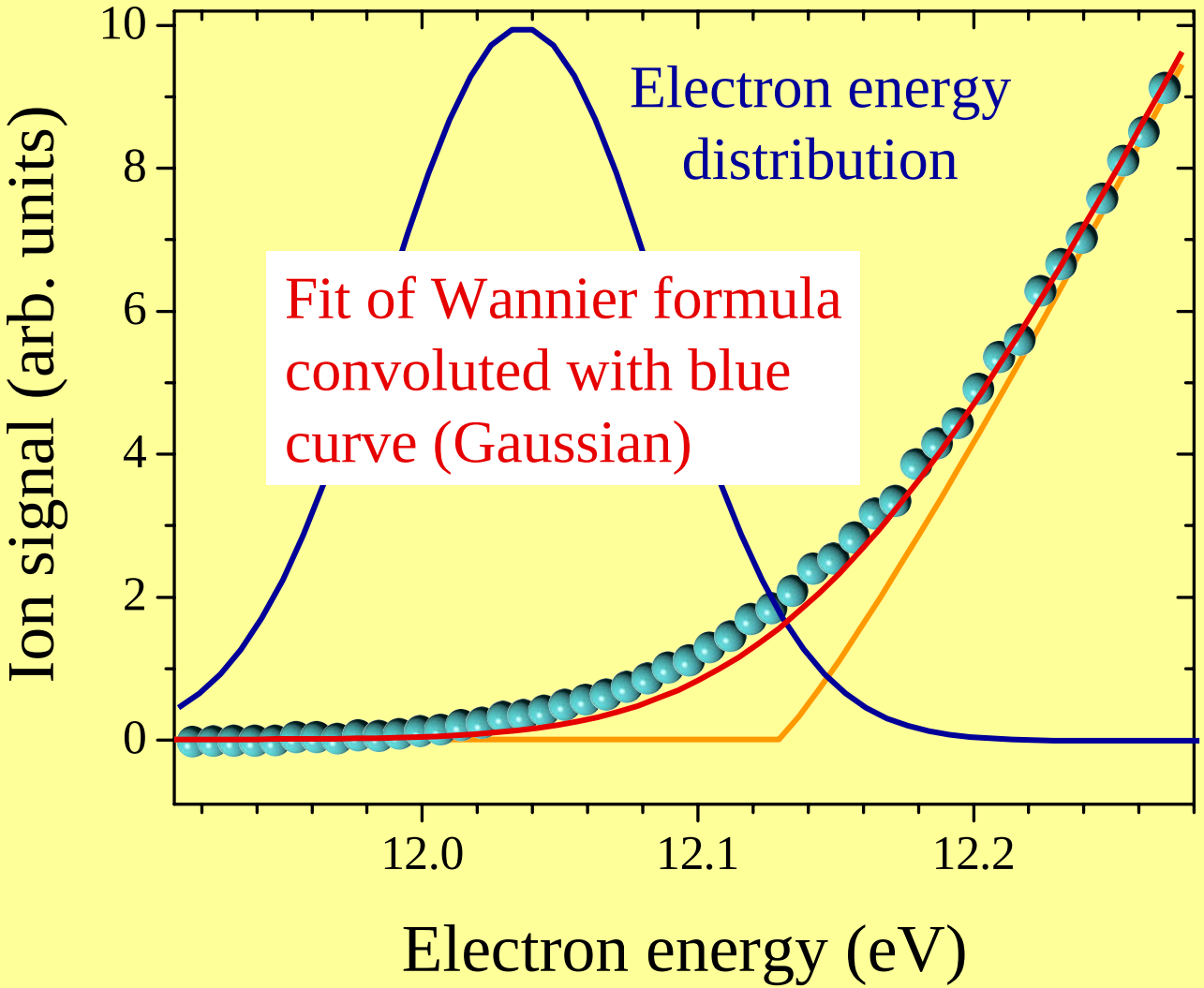
G. H. Wannier, *Phys. Rev.* **90** (1953) 817



$f(E) = b$ for $E < E_T$

$f(E) = b + c\,(E - E_T)^d$ for $E > E_T$

Threshold behavior



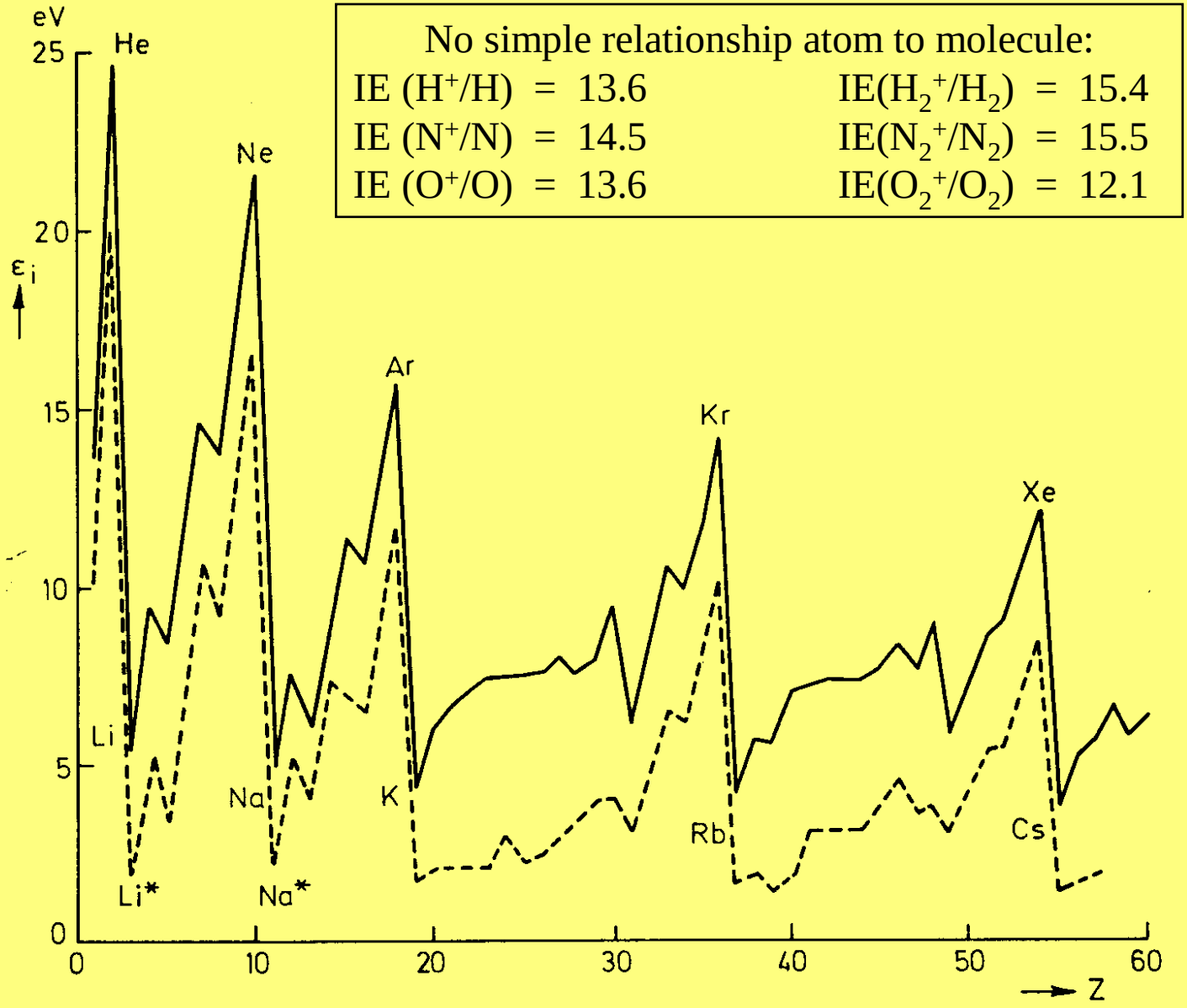
Test of applied method

Measured appearance energies for positive ions of some rare gases and molecules compared to standard values derived from photoionisation results (taken from NIST tables) using Xe to calibrate the energy scale.

Target	Present AE value (eV)	NIST value (eV)	Difference (meV)	d value
Xe	12.12987	12.12987	0	1.12
Ar	15.749±0.012	15.759±0.001	-10	1.30
Kr	13.990 ±0.015	13.999±0.001	-9	1.22
N_2	15.590±0.011	15.581±0.008	+9	1.18
O_2	12.073±0.021	12.0697±0.0002	+3	1.24
N_2O	12.865±0.009	12.889±0.004	-24	1.28

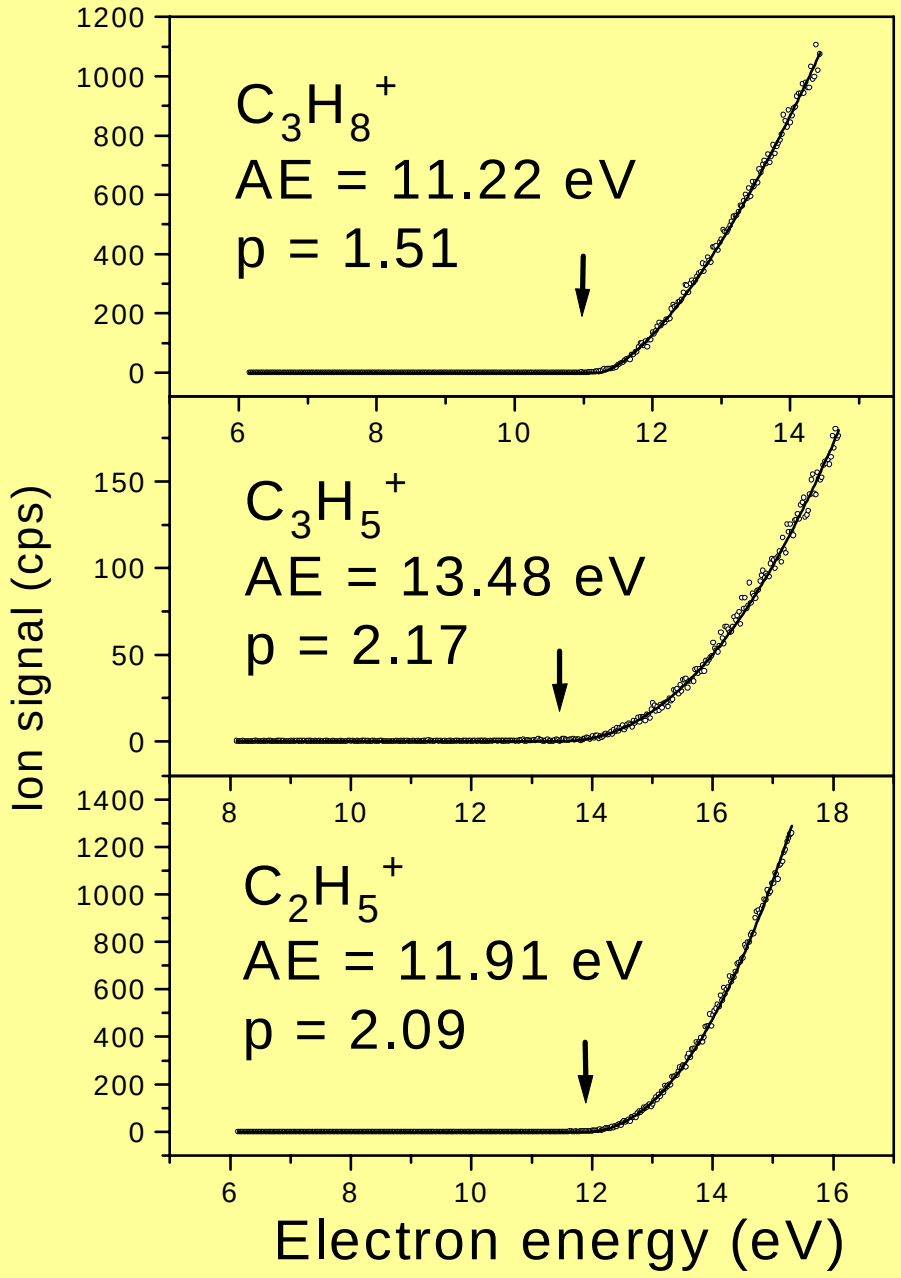
No simple relationship atom to molecule:

IE (H^+/H) = 13.6	IE(H_2^+/H_2) = 15.4
IE (N^+/N) = 14.5	IE(N_2^+/N_2) = 15.5
IE (O^+/O) = 13.6	IE(O_2^+/O_2) = 12.1



Ionization and lowest excitation energies of atoms as a function of Z.

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



HEM data analysis:

$C_3H_8 + e \rightarrow C_3H_8^+$

$C_3H_8 + e \rightarrow C_3H_5^+$

$C_3H_8 + e \rightarrow C_2H_5^+$

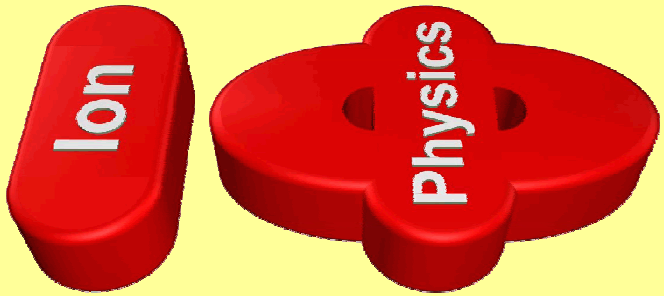
Ibk:	13.48 ± 0.05 eV
Bratislava:	13.48 ± 0.05 eV
photoionization:	13.50 ± 1.0 eV
electroionization:	14.76 ± 1.0 eV

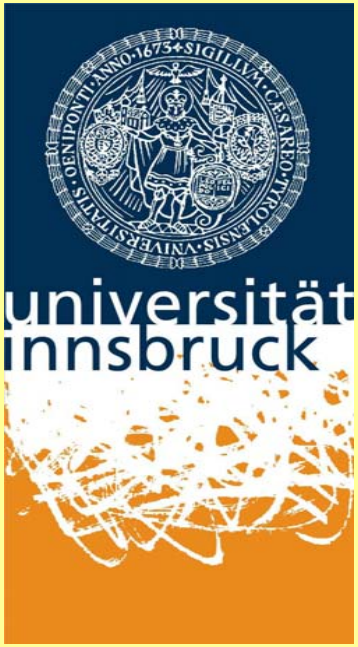
Ion Physics

Institut Ionenphysik

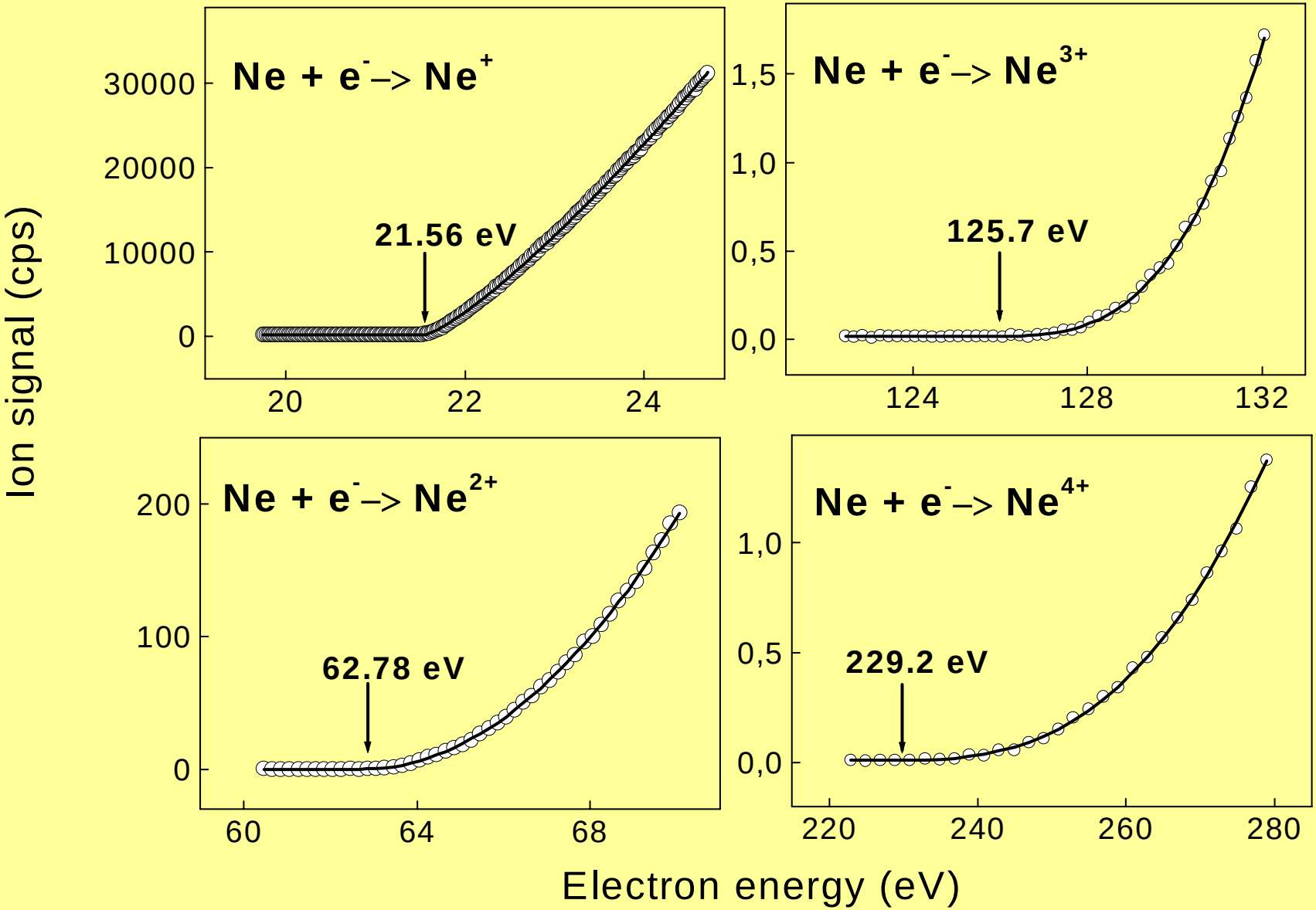
EURATOM ÖAW

AE and exponent of multiply charged rare gas atoms

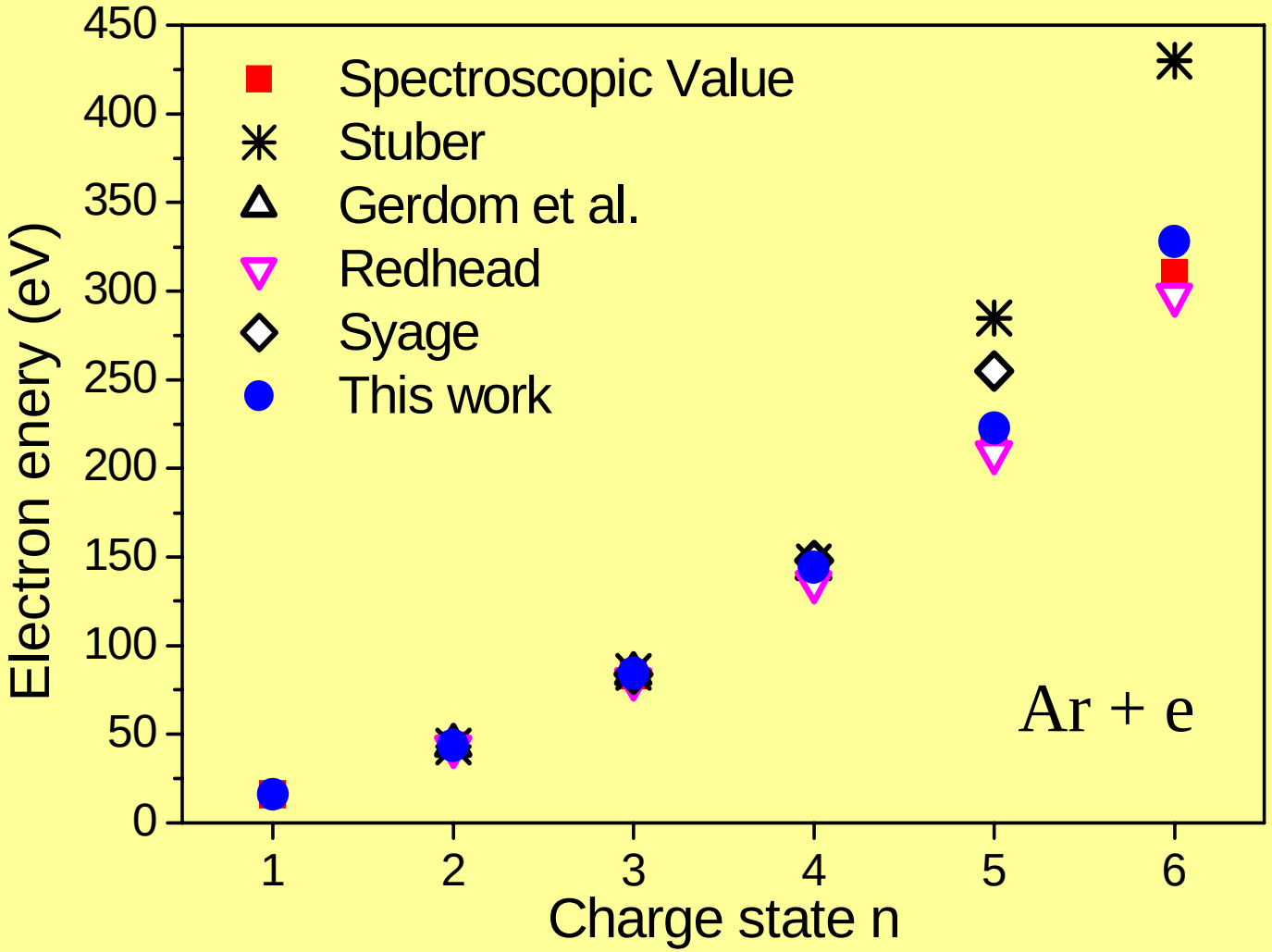




Ionization efficiency curves



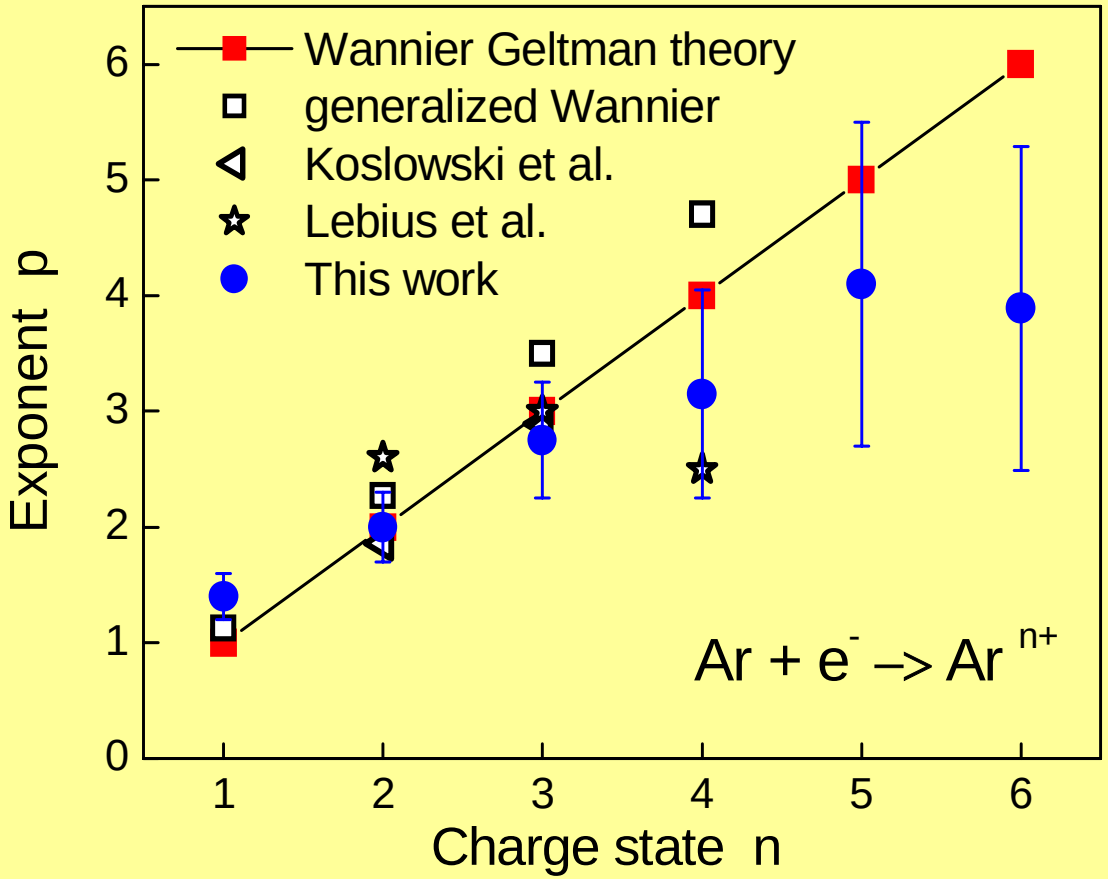
Appearance energy



Threshold behavior

$$\sigma_{ion} \propto E^{d}$$

Generalized Wannier:		Wannier Geltman:	
z:	d :	z:	d :
1	1.127	1	1
2	2.270	2	2
3	3.55	3	3
4	4.70	4	4



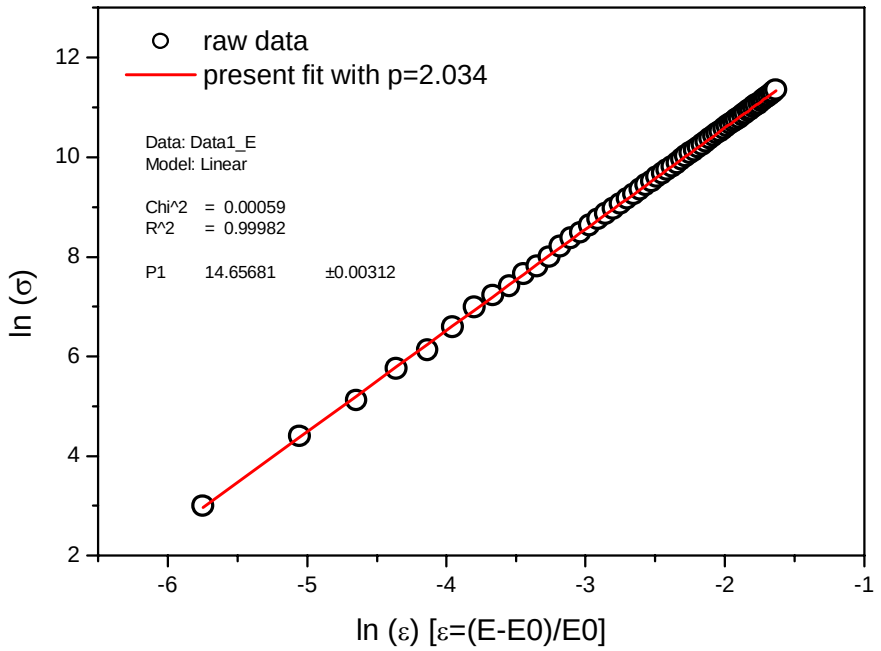
Threshold behavior

$\sigma_{ion} \propto E^{d}$

$He + e \rightarrow He^{2+} + 3e$

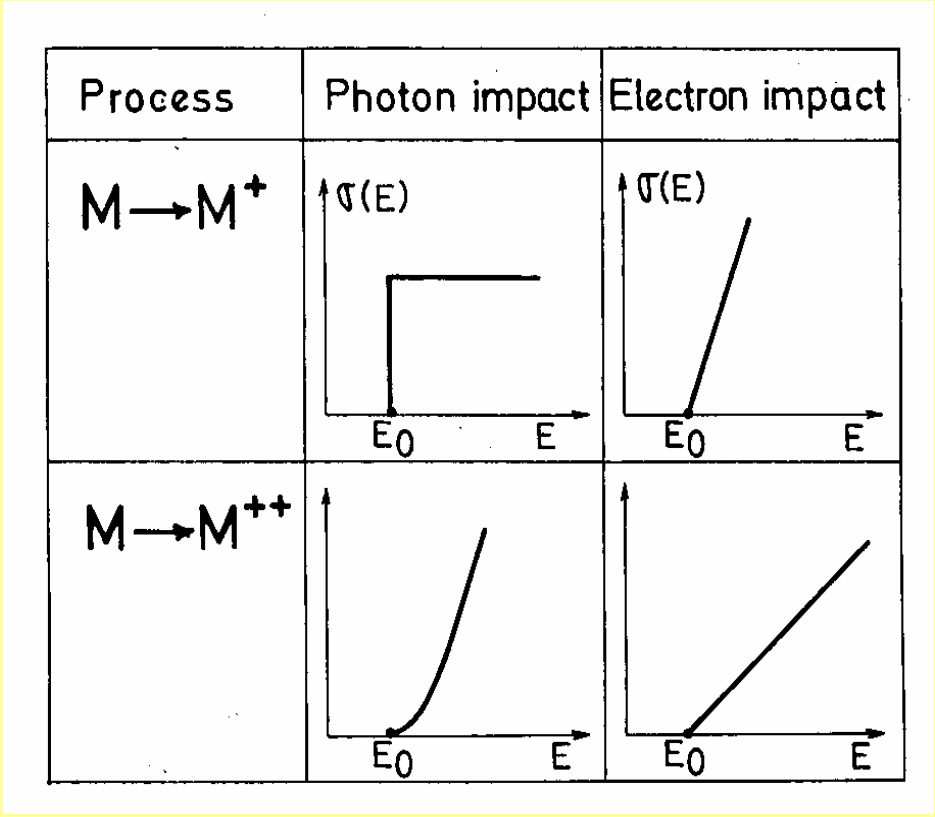
Generalized Wannier:

z:	d :
1	1.127
2	2.270
3	3.55
4	4.70



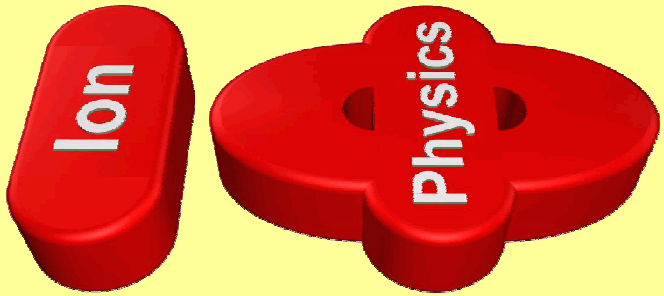
Threshold law: Wigner, Geltman

$$\sigma(E)_{ion} \propto (E-E_o)^{n-1}$$



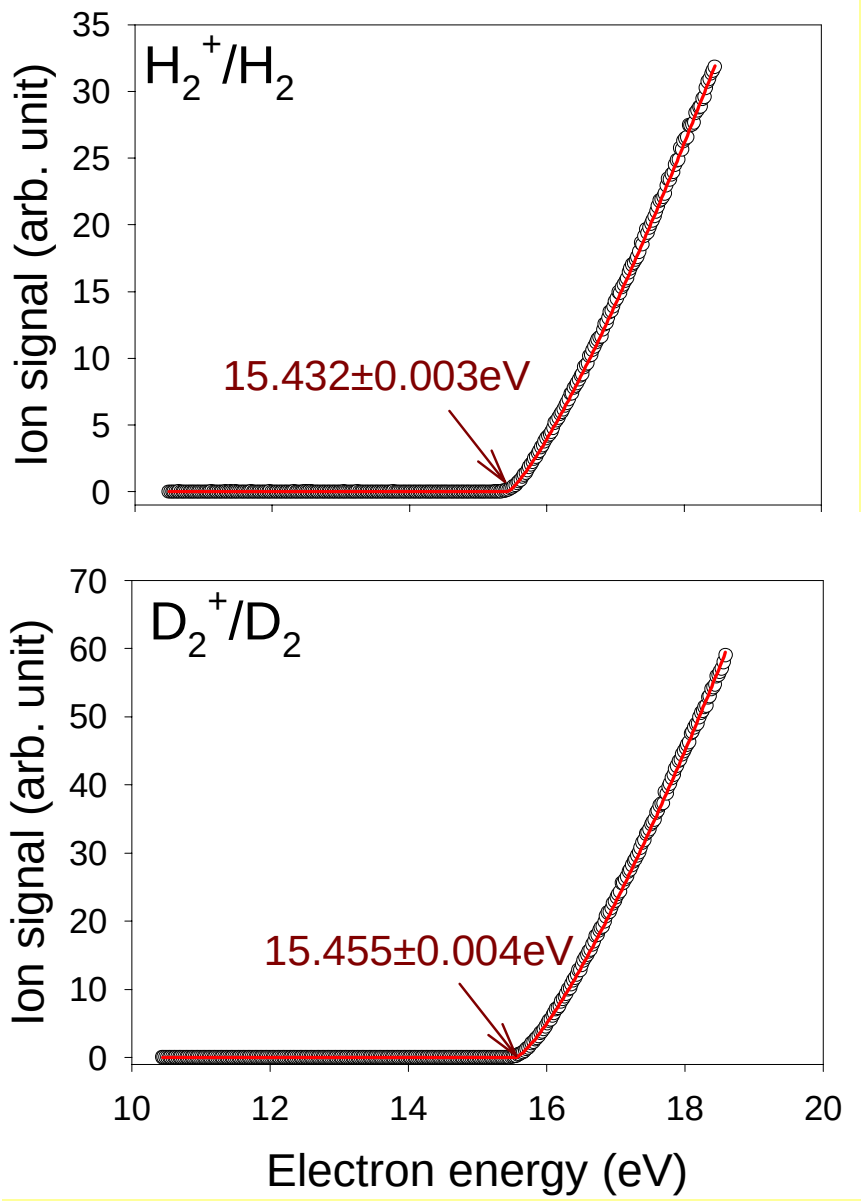
n number of emitted electrons

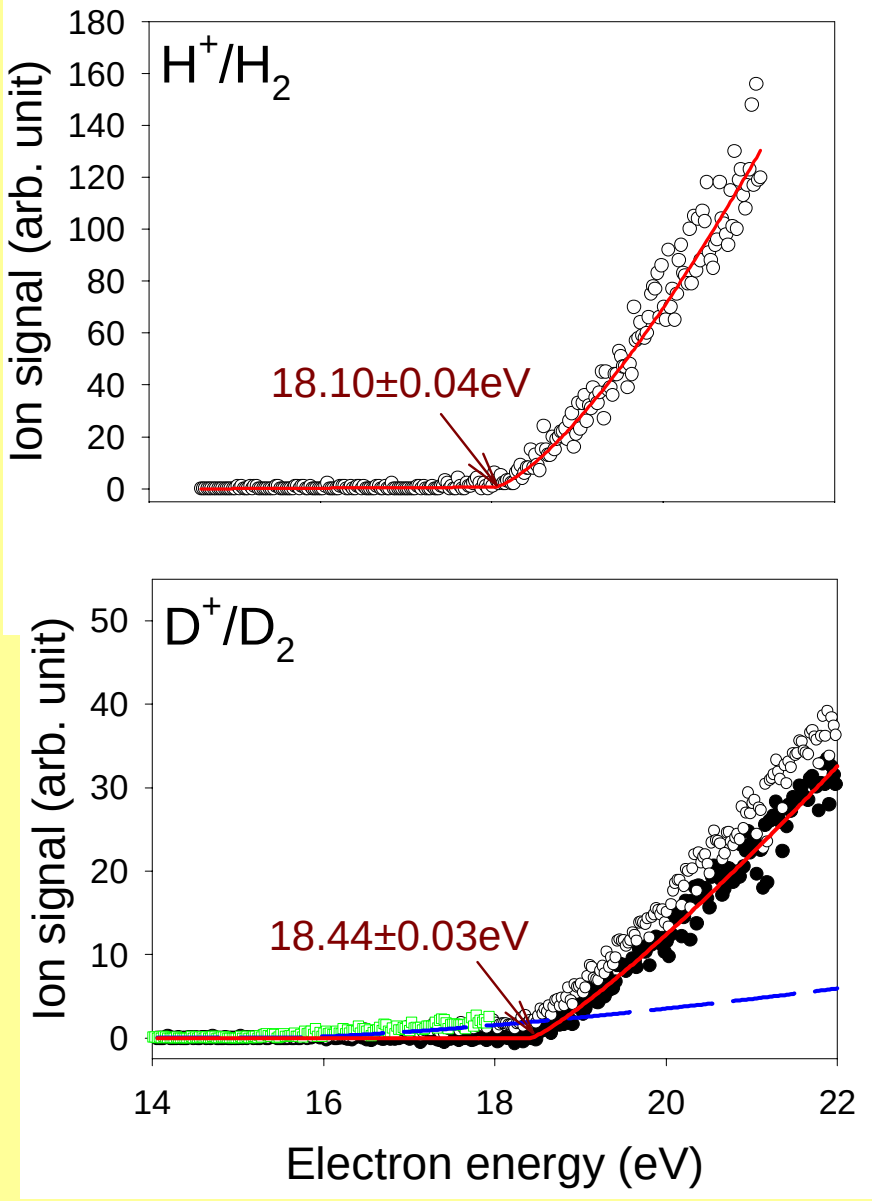
Isotope effects for AE‘s of molecules



universität innsbruck

Appearance energy for isotopes





Isotope effects for H_2/ D_2

	IE [2] (eV)	AE_m (eV)	AE_c (eV)	Δ_m (meV)	Δ_c (meV)
H_2^+/H_2 --- D_2^+/D_2	15.42593±0.00005 --- 15.46660±0.00010	15.428±0.025 --- 15.463±0.025	15.47 --- 15.52	35 (41)	49
H^+/H_2 --- D^+/D_2	18.078±0.003 --- (25.3±2)*	18.09±0.08 --- 18.41±0.2	18.08 --- 18.17	320	87

$IE(H^+/H) = 13.59844$ eV

$IE(D^+/D) = 13.603$ eV Δ : 5meV

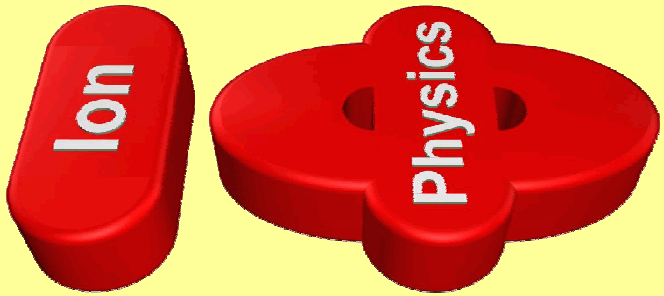
$EA(H) = 0.75419$ eV

$EA(D) = 0.754580$ eV Δ : 0.4 meV

Isotope effects for H_2O/ D_2O

	AE_m (eV)	AE_c [B3LYP] (eV)	AE_c [MP4] (eV)	Δ_m (meV)	Δ_c [B3LYP] (meV)	Δ_c [MP4] (meV)
H_2O^+/H_2O --- D_2O^+/D_2O	12.56±0.03 --- 12.60±0.03	12.29 --- 12.31	11.88 --- 11.86	40	21	22
OH^+/H_2O --- OD^+/D_2O	18.13±0.09 --- 18.24±0.14	17.66 --- 17.77	16.69 --- 16.83	110	117	148
H^+/H_2O --- D^+/D_2O	18.75±0.05 --- 18.94±0.05	18.33 --- 18.43	17.96 --- 18.08	190	106	125
O^+/H_2O --- O^+/D_2O	18.38±0.15 --- 18.52±0.15	18.41 --- 18.50	17.01 --- 17.12	140	88	106

Temperature dependence of appearance energy



universität innsbruck

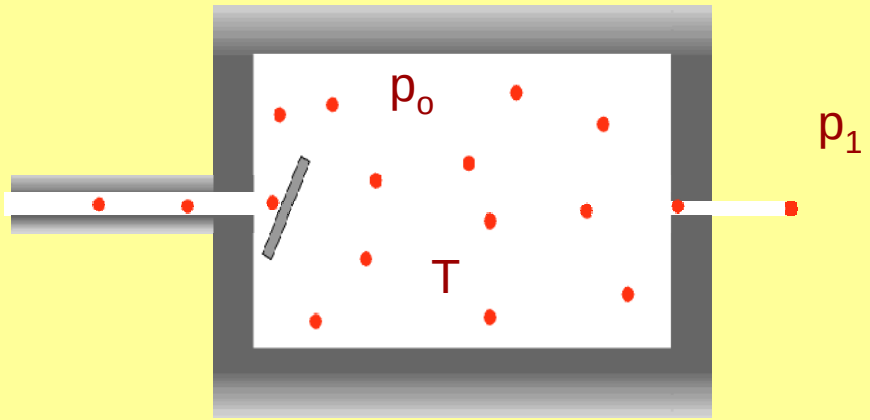
Effusive molecular beam source

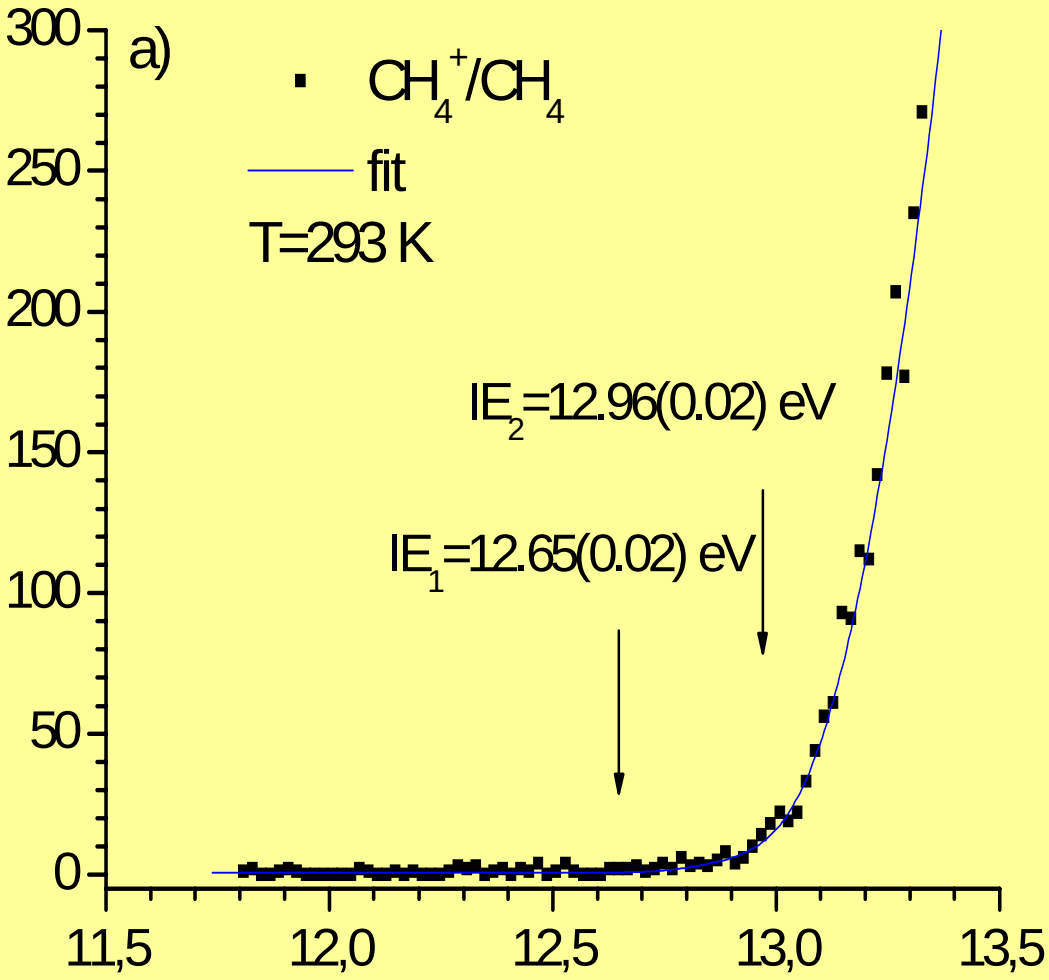
- well defined temperature of the gas
- known gas density variation with T

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

$\approx 10^4$ collisions

Channel :
d= 0.5mm
L= 5mm





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

Present value:12.65±0.04 eV

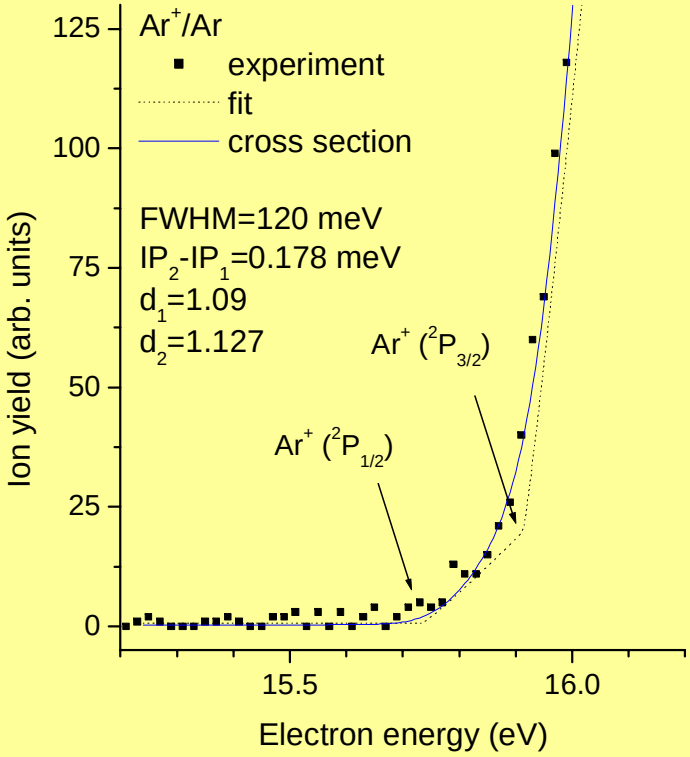
EII:12.63±0.02 eV

PI: 12.615±0.01 eV

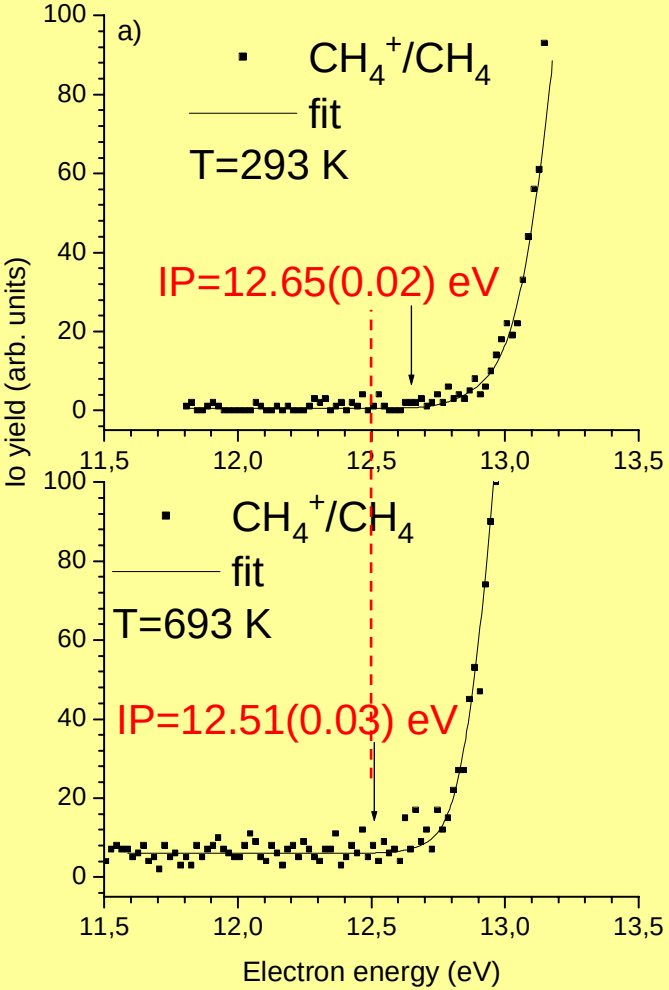
Additional structure at 12.96 eV

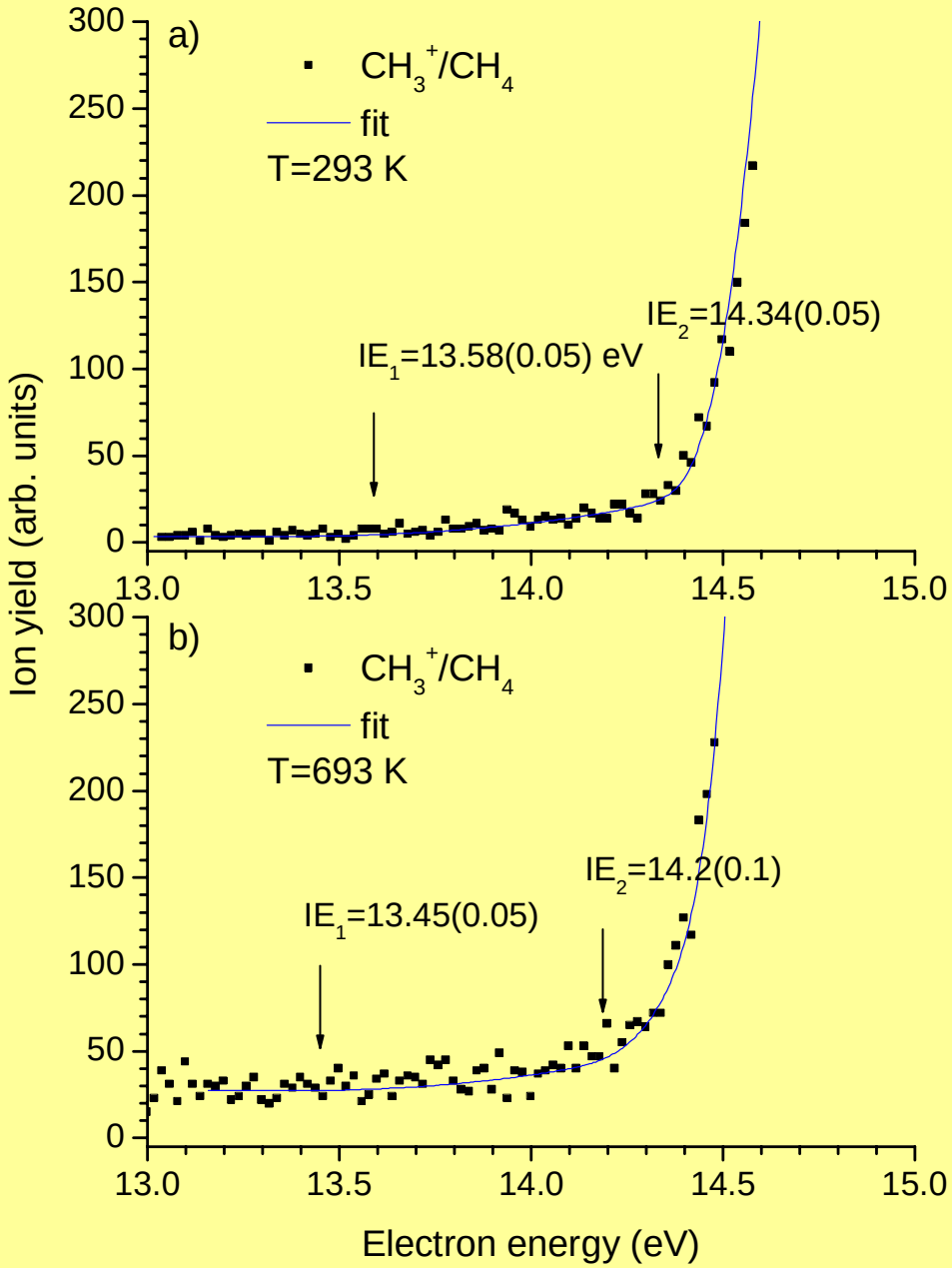
Temperature effects on electron ionization of molecular ions:

$CH_4 + e \rightarrow$ 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 electron ionization 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

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

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