

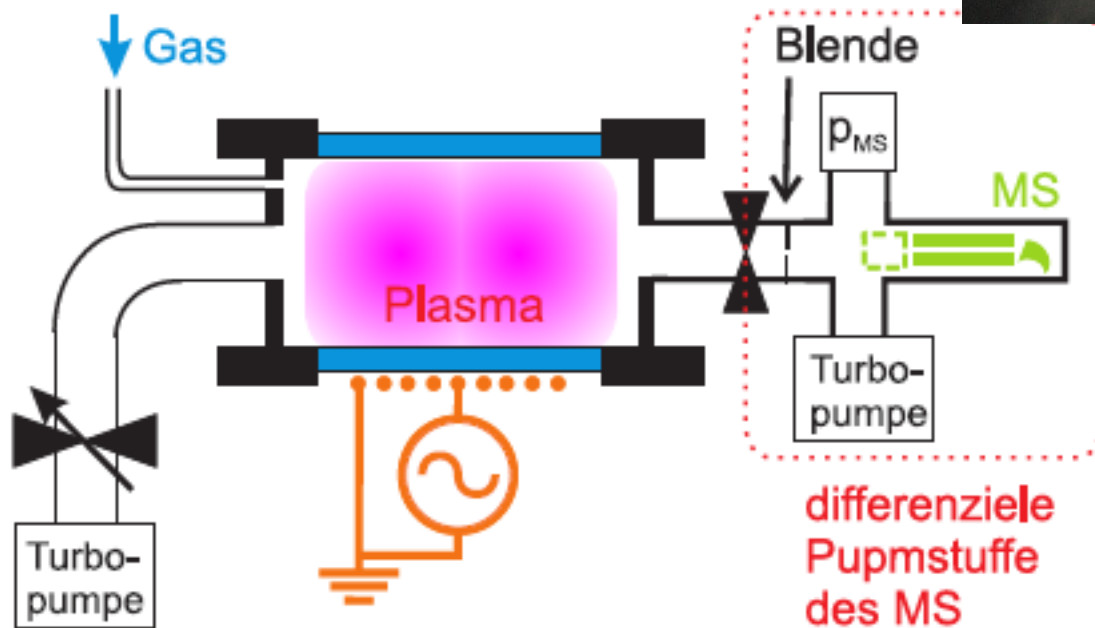
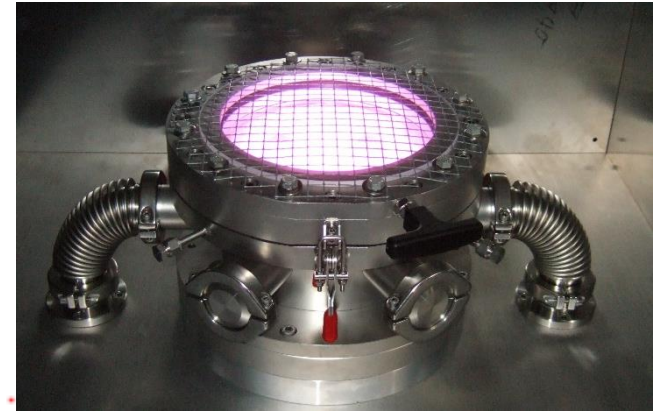
# Kvadrupólová hmotnostní spektrometrie reaktivního plazmatu

**Jan Benedikt**  
Ruhr-University Bochum

Thanks to: **Simon Schneider**  
**Simon Große-Kreul**  
**Dirk Ellerweg**  
**Simon Hübner**  
**Achim von Keudell**

# Motivation: analysis of the plasma

Example of CCP or ICP plasmas  
Stable species x highly reactive species x ions



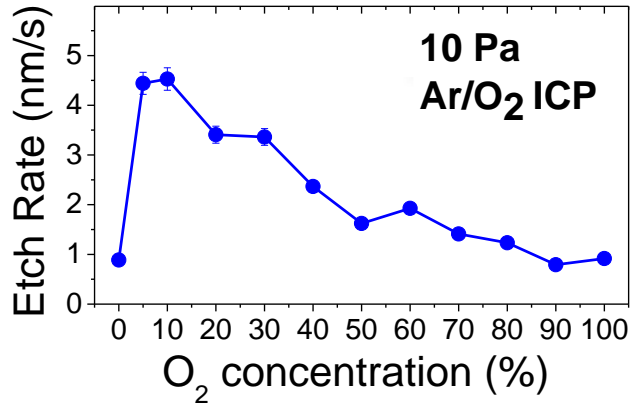
Measurement of  
stable products

Abbildung 3.1: Skizze des Versuchsaufbaus. (entnommen aus [10])

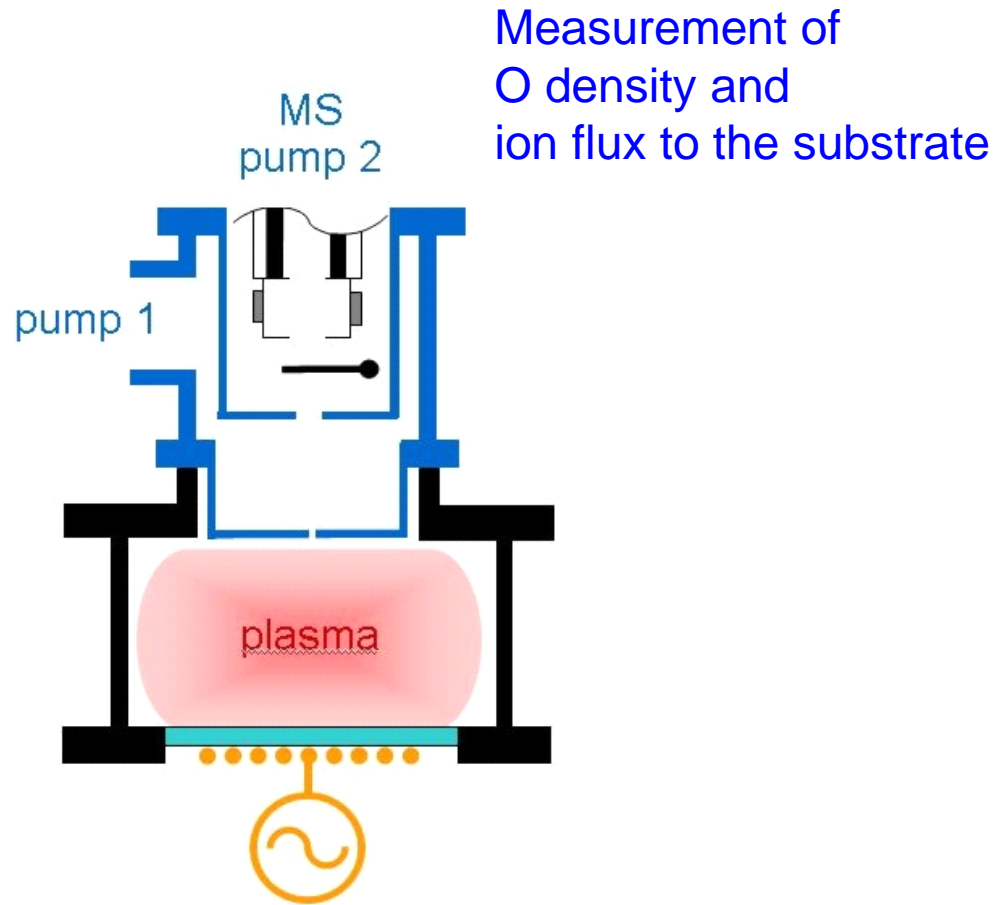
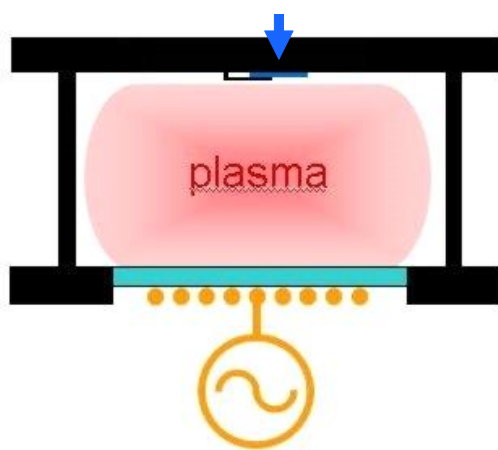
# Motivation: analysis of the plasma

Example of CCP or ICP plasmas

Stable species x highly reactive species x ions



a-C:H coated wafer



# Motivation: analysis of the HiPIMS plasmas

Example of HiPIMS discharges

- highly transient plasma
- mainly reactive short-lived species



Even stable species (such as Ar or O<sub>2</sub>) have a spatial density profile

Ionization zones (“spokes”)

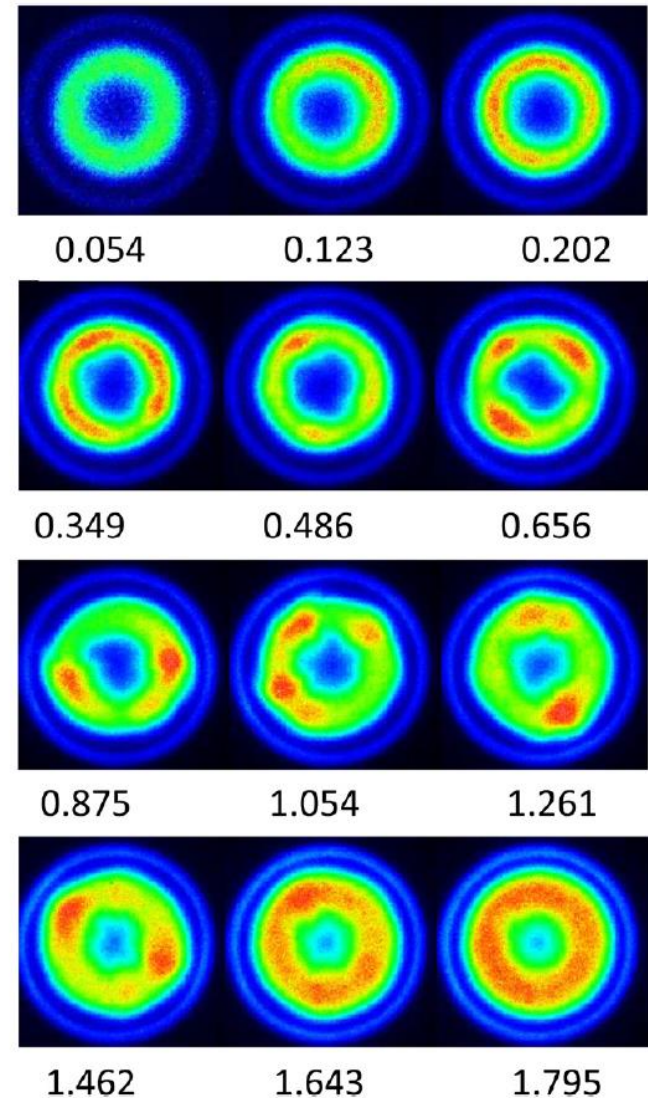
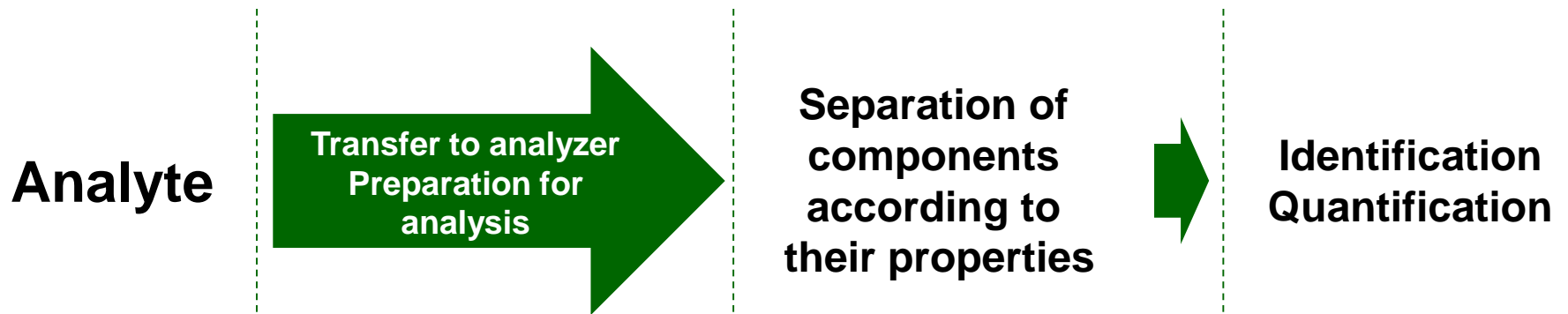
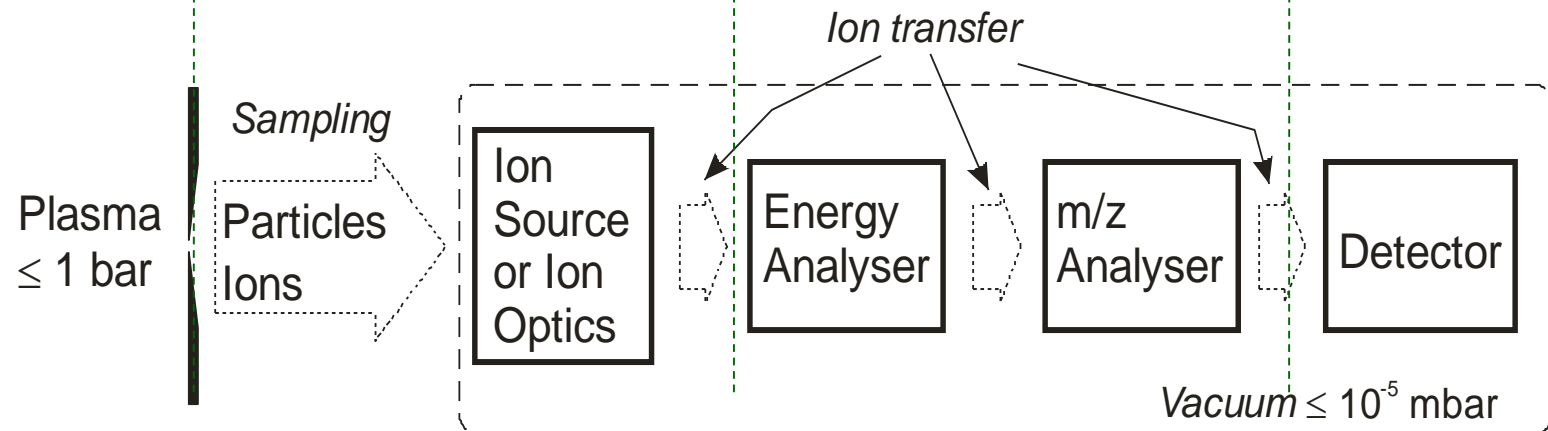


Figure 2. ICCD images of a chromium target at different power densities in kW cm<sup>-2</sup> as indicated. The images are taken at 180 μs of 200 μs pulses and Ar at 0.26 Pa.

# Motivation: Analysis of unknown analyte

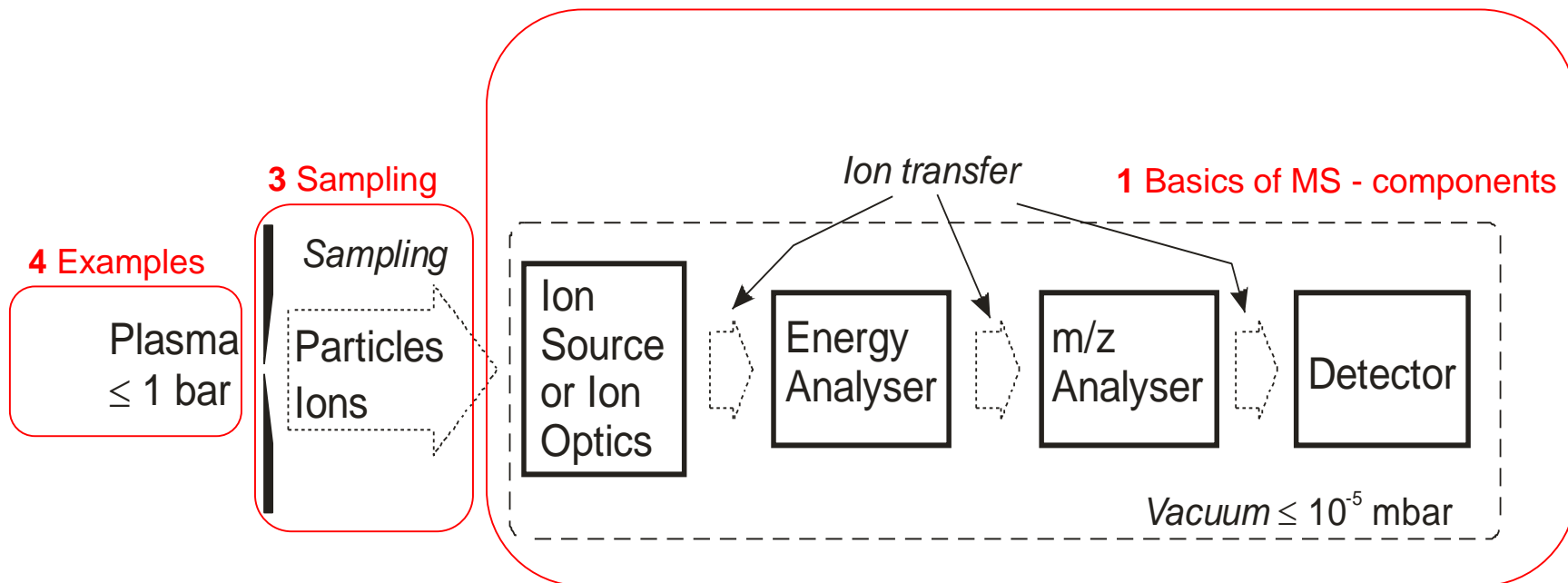


## Mass spectrometry in general

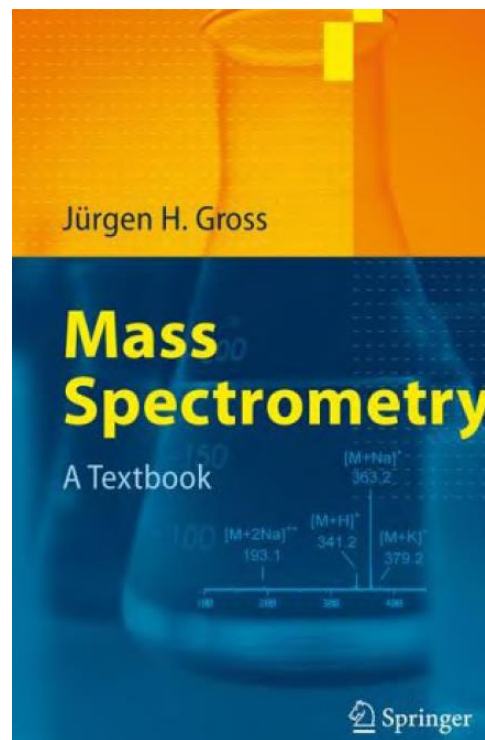


# Outline

## 2 Species identification and quantification



# Literature



J. Phys. D: Appl. Phys. **45** (2012) 403001 (23pp)

## TOPICAL REVIEW

# Quadrupole mass spectrometry of reactive plasmas

J Benedikt, A Hecimovic, D Ellerweg and A von Keudell

Plasma Sources Sci. Technol. **24** (2015) 044008 (15pp)

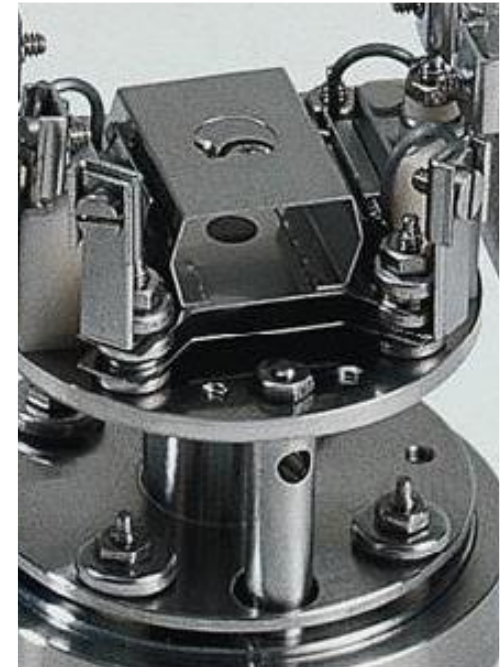
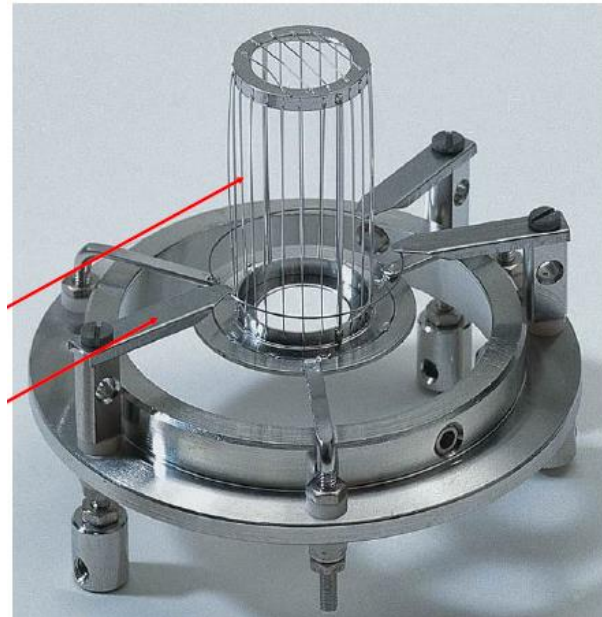
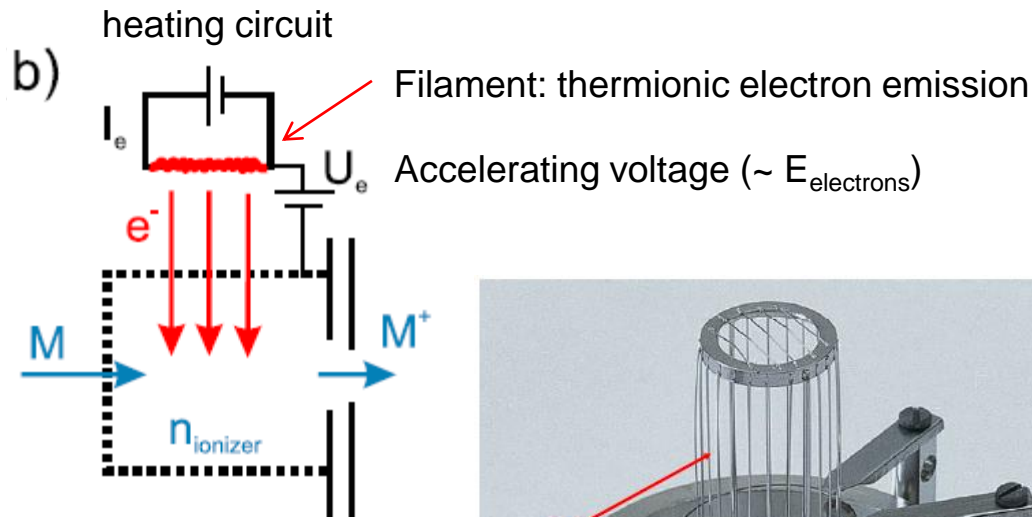
[doi:10.1088/0963-0252/24/4/044008](https://doi.org/10.1088/0963-0252/24/4/044008)

# Mass spectrometry of atmospheric pressure plasmas

S Große-Kreul<sup>1</sup>, S Hübner<sup>1</sup>, S. Schneider<sup>1</sup>, D Ellerweg<sup>1</sup>, A von Keudell<sup>1</sup>,  
S Matejčík<sup>2</sup> and J Benedikt<sup>1</sup>

# MS components: electron impact ionizer

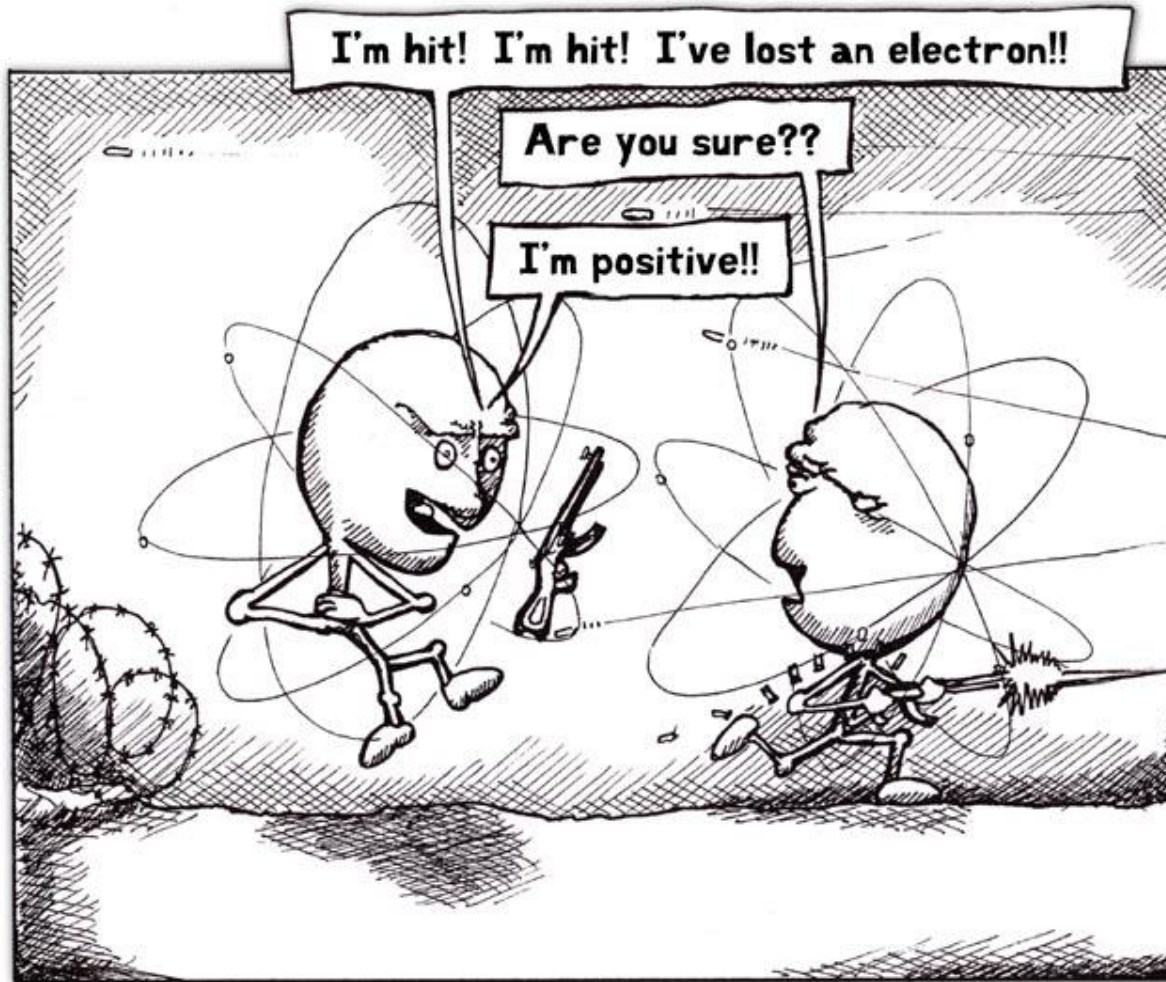
Electron source: heated filament



**INFICON**  
distributed by  
**PFEIFFER** VACUUM



# MS components: electron impact ionizer

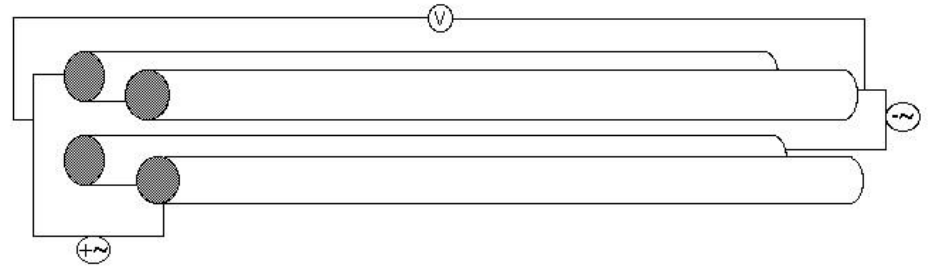
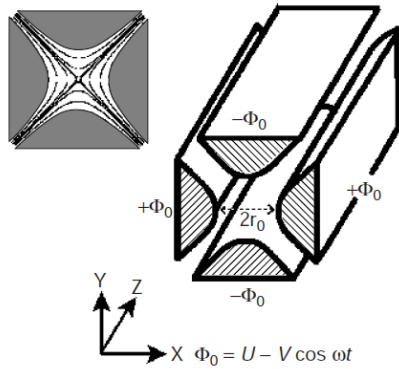


Another casualty in the War of the Atoms

# MS components: Quadrupole Mass Filter

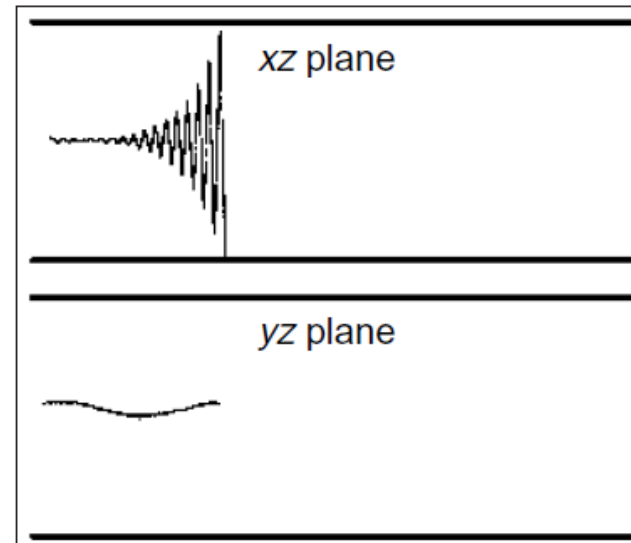
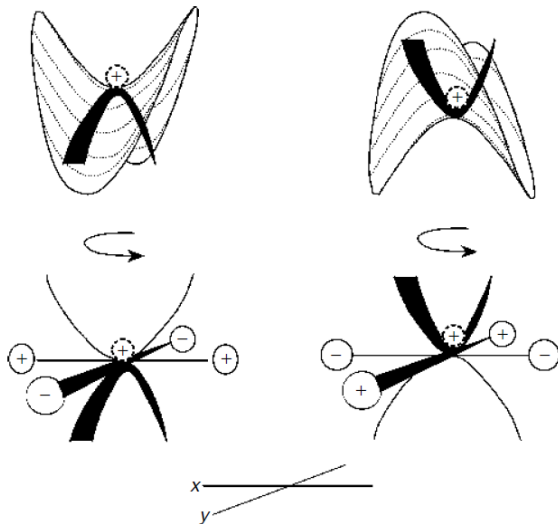
Combined RF and DC electric fields for mass analysis

Quadrupole Mass Filter

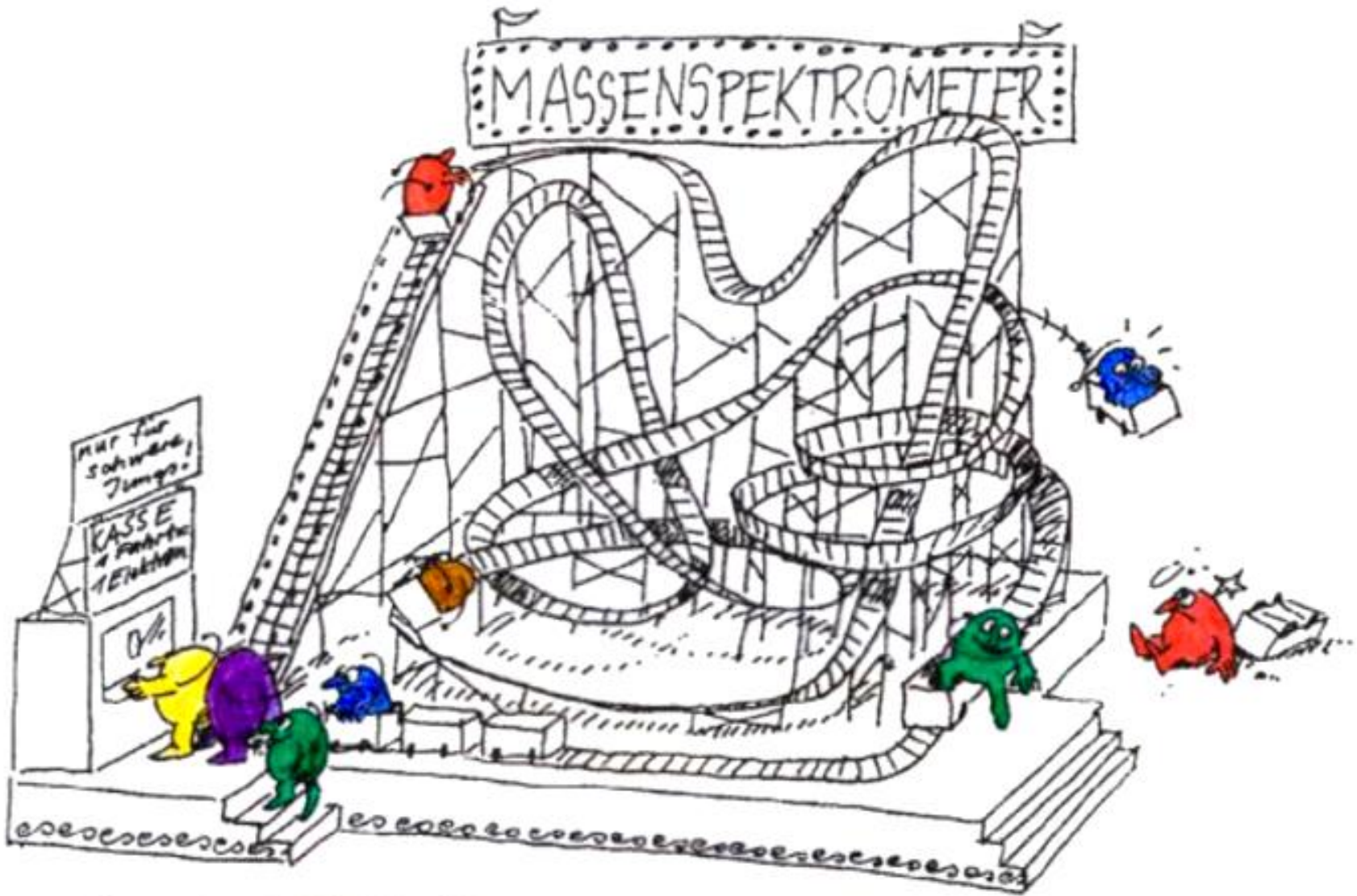


**Figure 2.5**  
Quadrupole with hyperbolic rods and applied potentials. The equipotential lines are represented above, on the left.

Ion trajectories



Stable along y, unstable along x

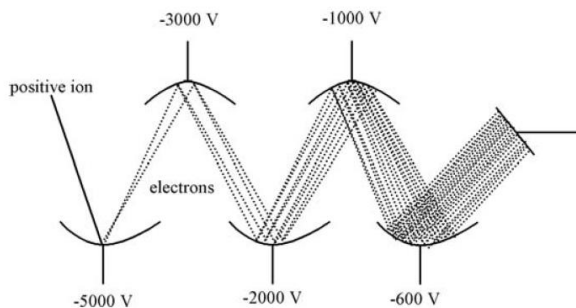
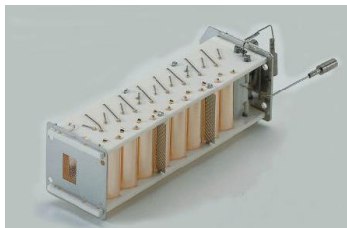


FALSCHER SELBSTEINSCHÄTZUNG HAT SCHON MANCHES ATOMI  
AUS DER BAHN GEWORFEN.

# MS components: Detectors

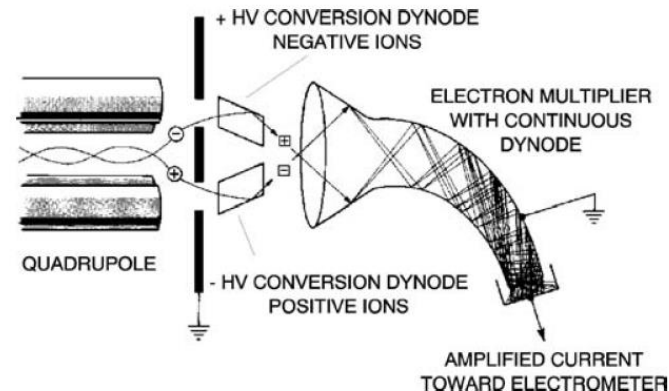
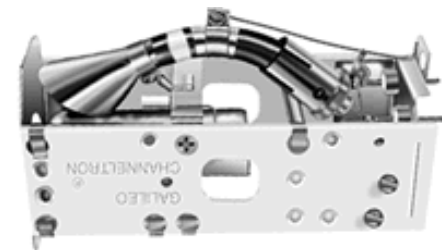
## Secondary electron multipliers (SEM)

With discrete dynodes



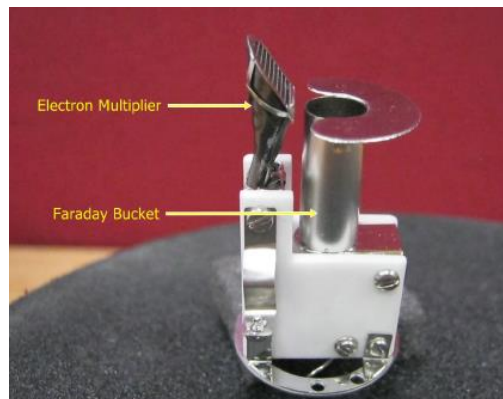
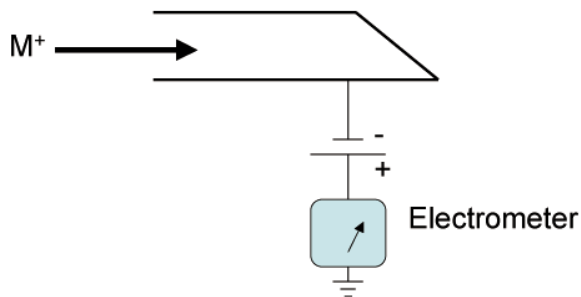
**Figure 3.2**  
Schematic diagram of electron multiplier. The first dynode is a conversion dynode to convert ions into electrons.

## Channeltron



**Figure 3.3**  
Continuous dynode electron multiplier, also known as the channeltron. ○, incident ions; □, secondary particles. Reproduced (modified) from Finnigan MAT documentation, with permission.

## Faraday cup



# MS components: Detectors

A typical operating curve for the detector is shown in Figure 3.1.

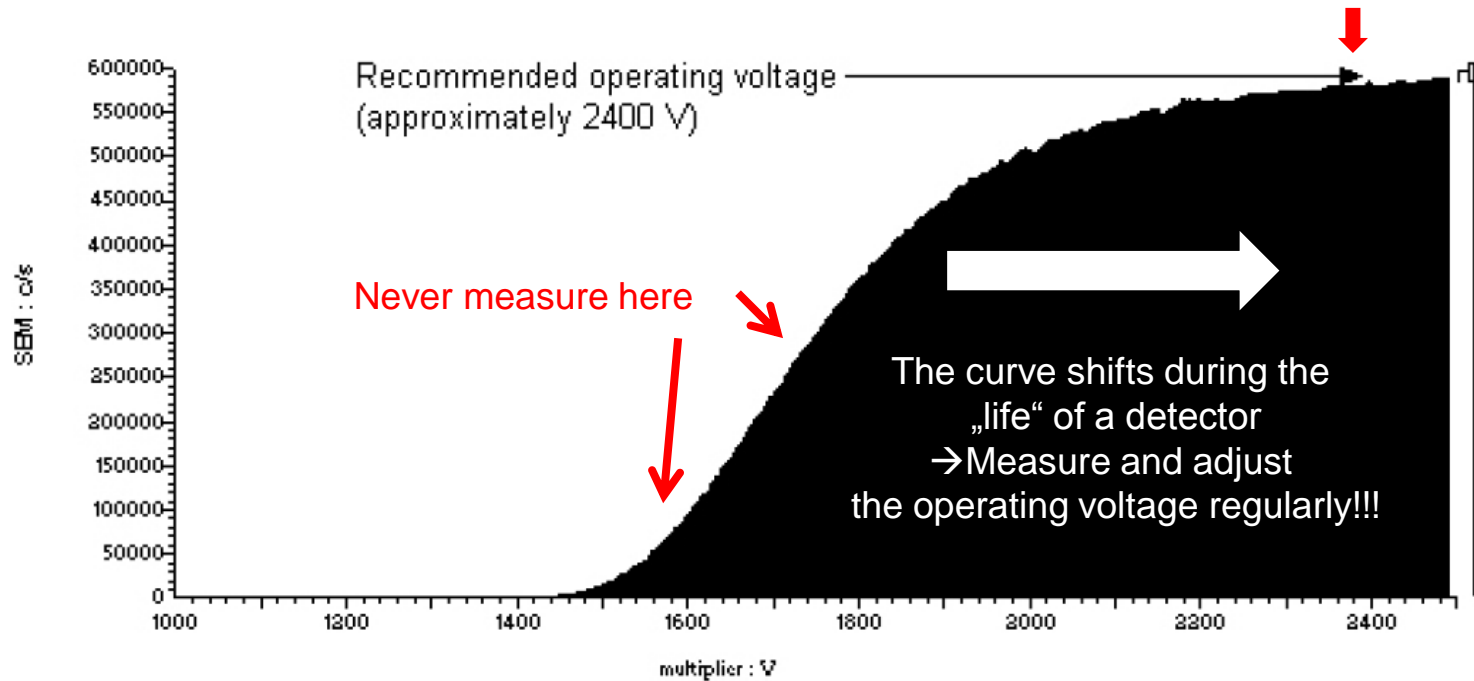


Figure 3.1 Typical detector operating curve

Detector is a „consumable“ – has a limited lifetime depending on overall number of counts measured!!!

Typical lifetime ~ 1-5 years

# MS components: Detectors

## Remark: The Use of Channeltron® Detectors

The Channeltron® Electron Multiplier has a history of dependability in mass spectrometer applications. The following instructions and precautions are presented here in order that the user can achieve the maximum useful lifetime of a Channeltron detector.

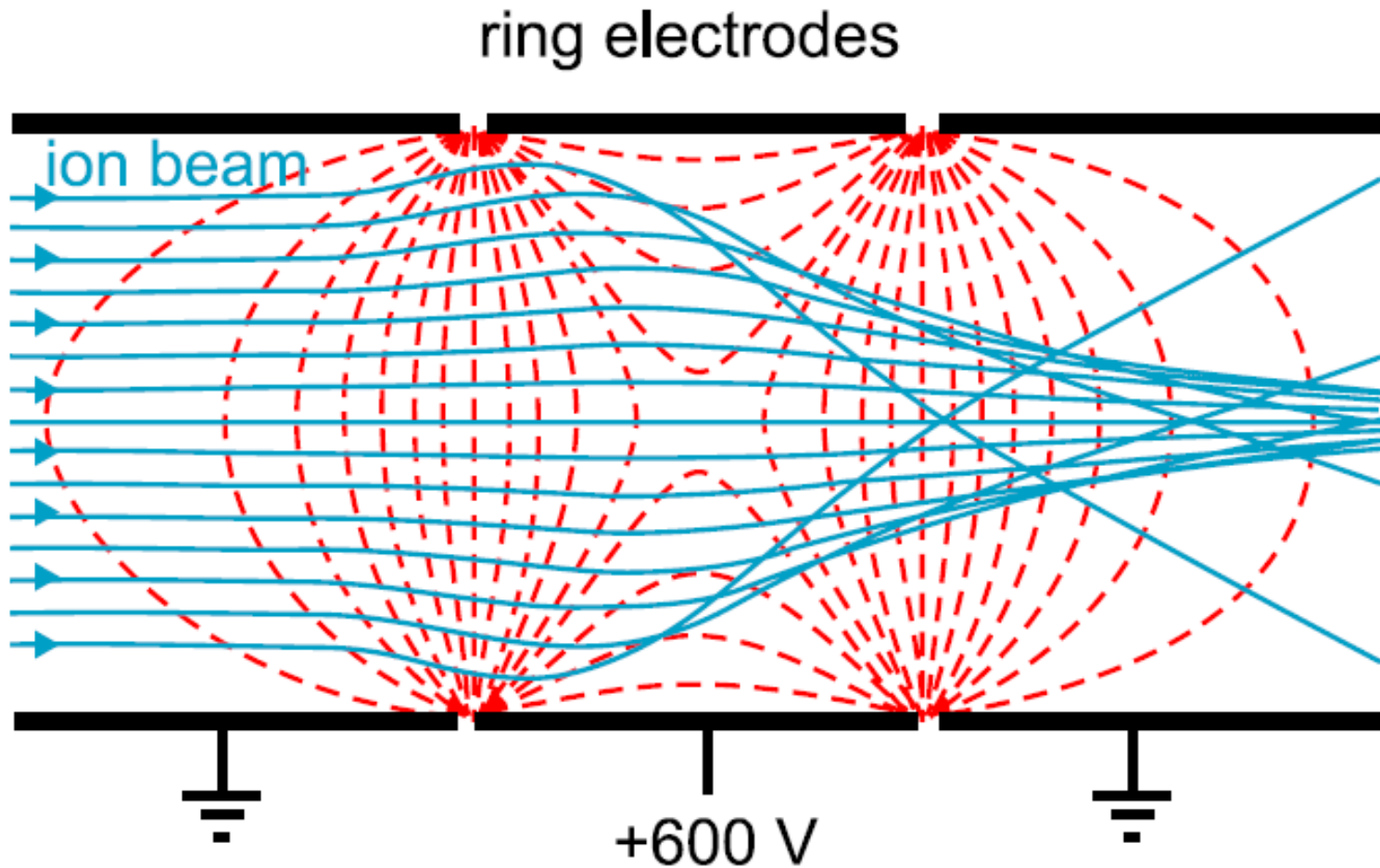
1. Mounting work should be done in clean vacuum fashion, i.e., the detector should be handled with talc free finger cots or lint free gloves. Care should be taken to avoid dust, lint, or other particulate matter. Nothing should touch the active areas of the detector.
2. Channeltrons are normally operated at pressures of  $10^{-5}$  or lower. Higher pressure operation is observed to increase the background current and can result in shortened life. **Do not apply high voltage at pressures greater than  $10^{-4}$  torr as arcing can occur and permanent destruction of the Channeltron surface is possible.**
3. Channeltrons are customarily operated at 1500 to 3000 volts. The maximum rated voltage difference between input and output leads is 3000 volts. Care should be taken to operate at a voltage which gives sufficient gain to achieve acceptable results. **Higher gains will shorten Channeltron lifetimes in inverse proportion, i.e. 2x the gain results in 1/2 the potential lifetime.**
4. During the first few days of operation of a new detector, it is recommended that high output currents be avoided (i.e. inputs above  $10^{-9}$  amps while operating at gains in excess of  $10^7$ ). Taking this initial burn-in precaution can prevent premature failure.
5. Backstreaming from oil diffusion pumps or roughing pumps should not be permitted. It is recommended that cold traps and molecular sieve traps be operated and maintained to manufacturers specifications.

**Warranty** - All multipliers come with a **one year prorated warranty starting at the date of shipment**. Multipliers with insufficient gain or excessive noise should be returned to S.I.S. for evaluation and testing. If the multiplier proves to be defective due to manufacturing defects it will be replaced at no charge during the first three months of use and prorated thereafter based on a one year life and a gain of  $1 \times 10^5$  at 3 KV. Multipliers which test properly or which were damaged due to operator fault or carelessness will not be replaced, and user will be billed --- for testing.

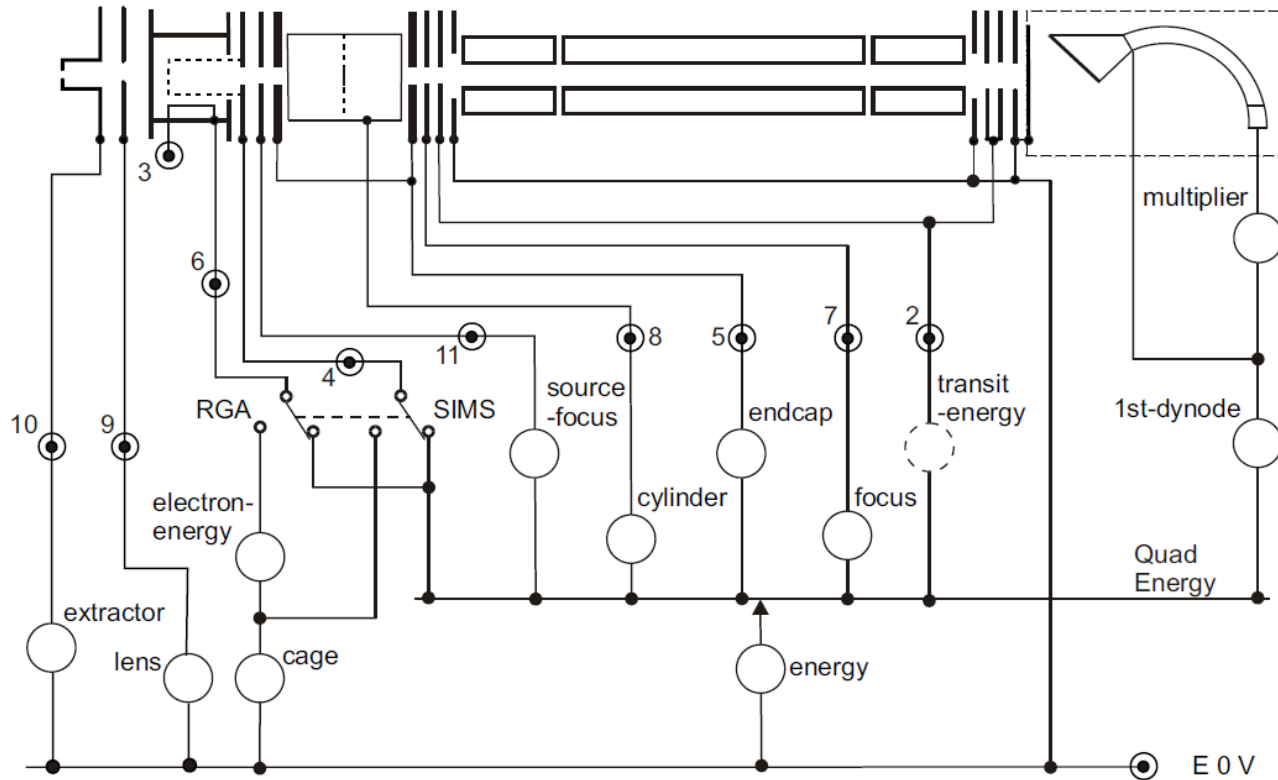
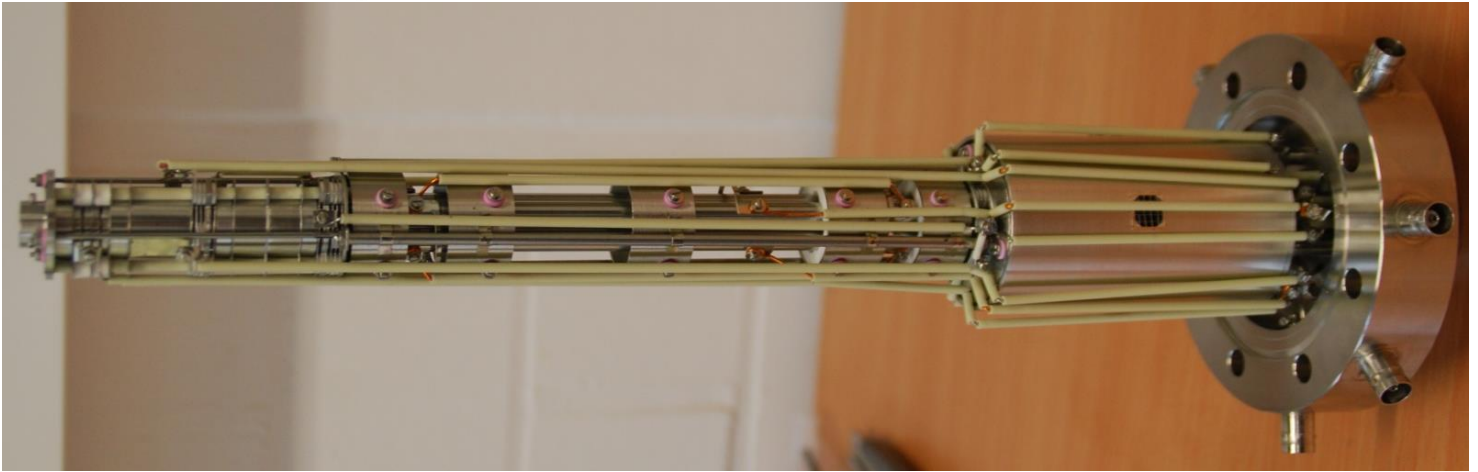
Channeltron® is a registered trademark of Burle Electro Optics Corp.

# MS components: single ion lens

Used to guide and focus the ions in the MS

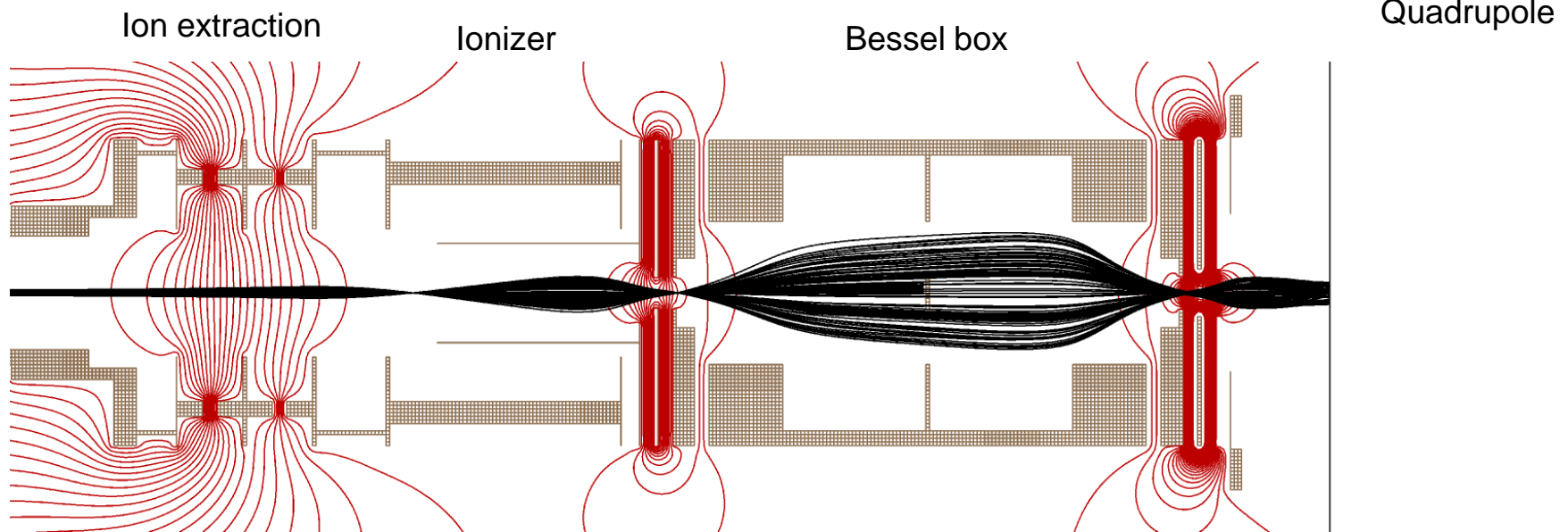
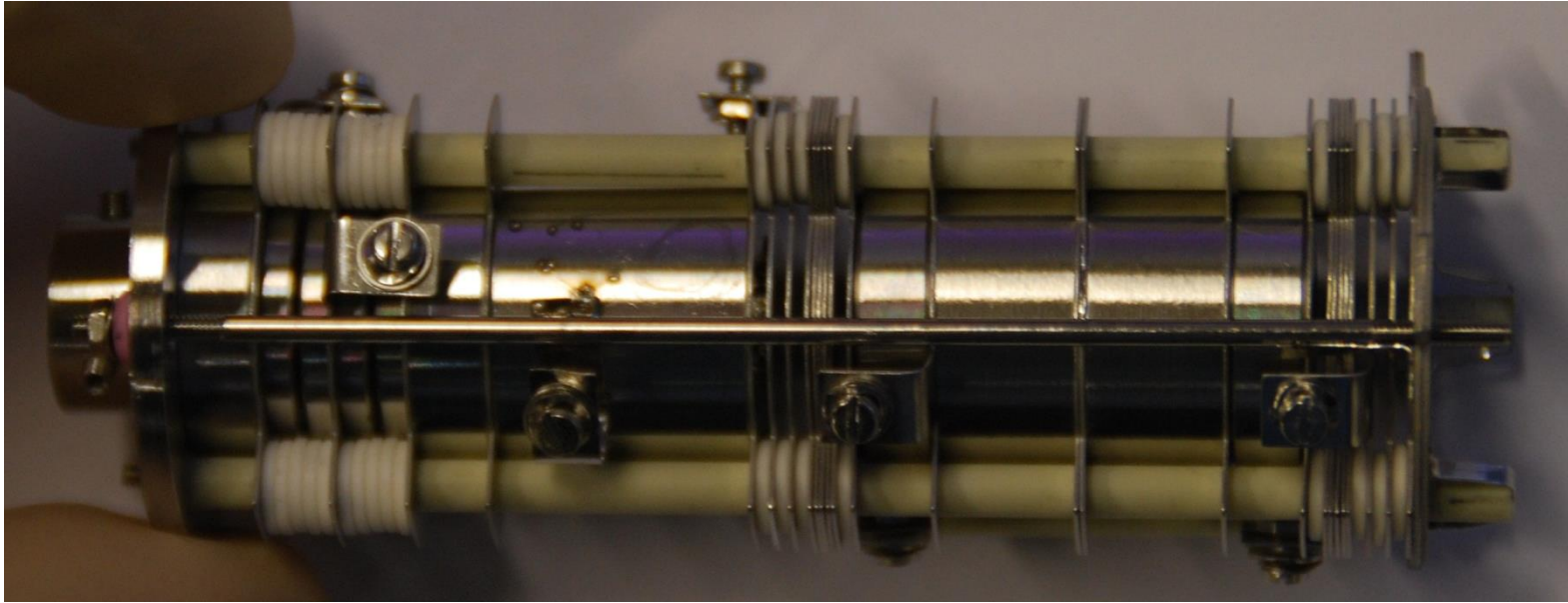


# All components together: for example HIDDEN PSM





# MS components: combination of ion lenses



Simulation: Simion 8.1 SW

# MS components: energy filters

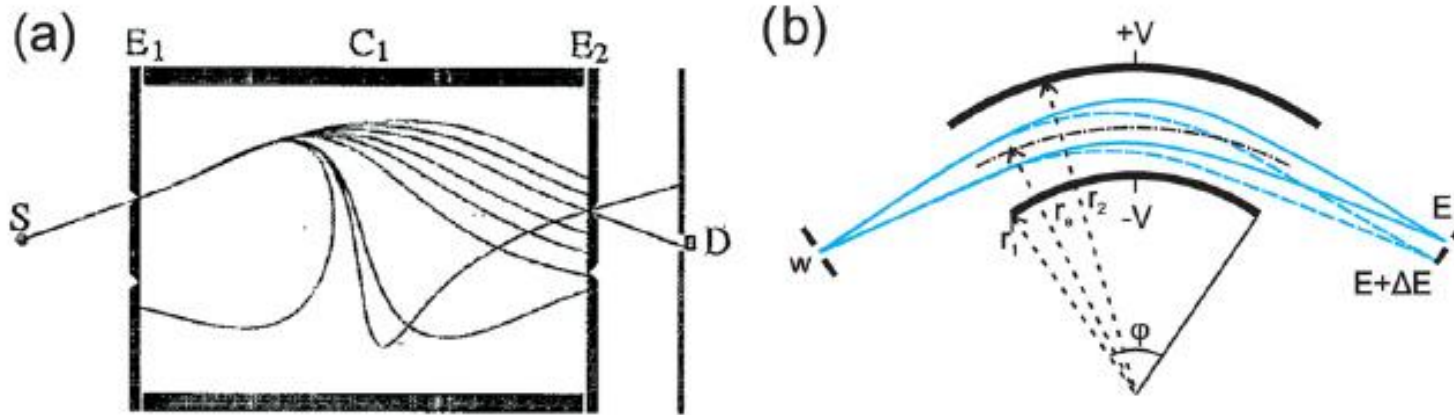
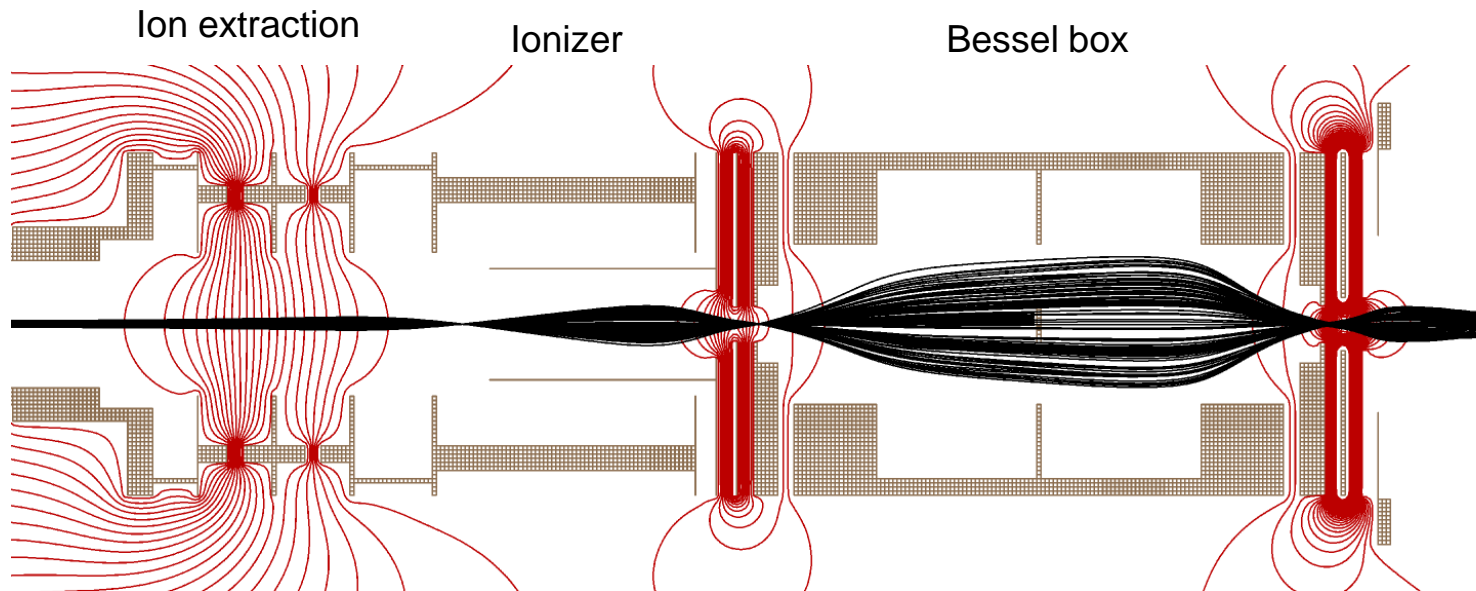


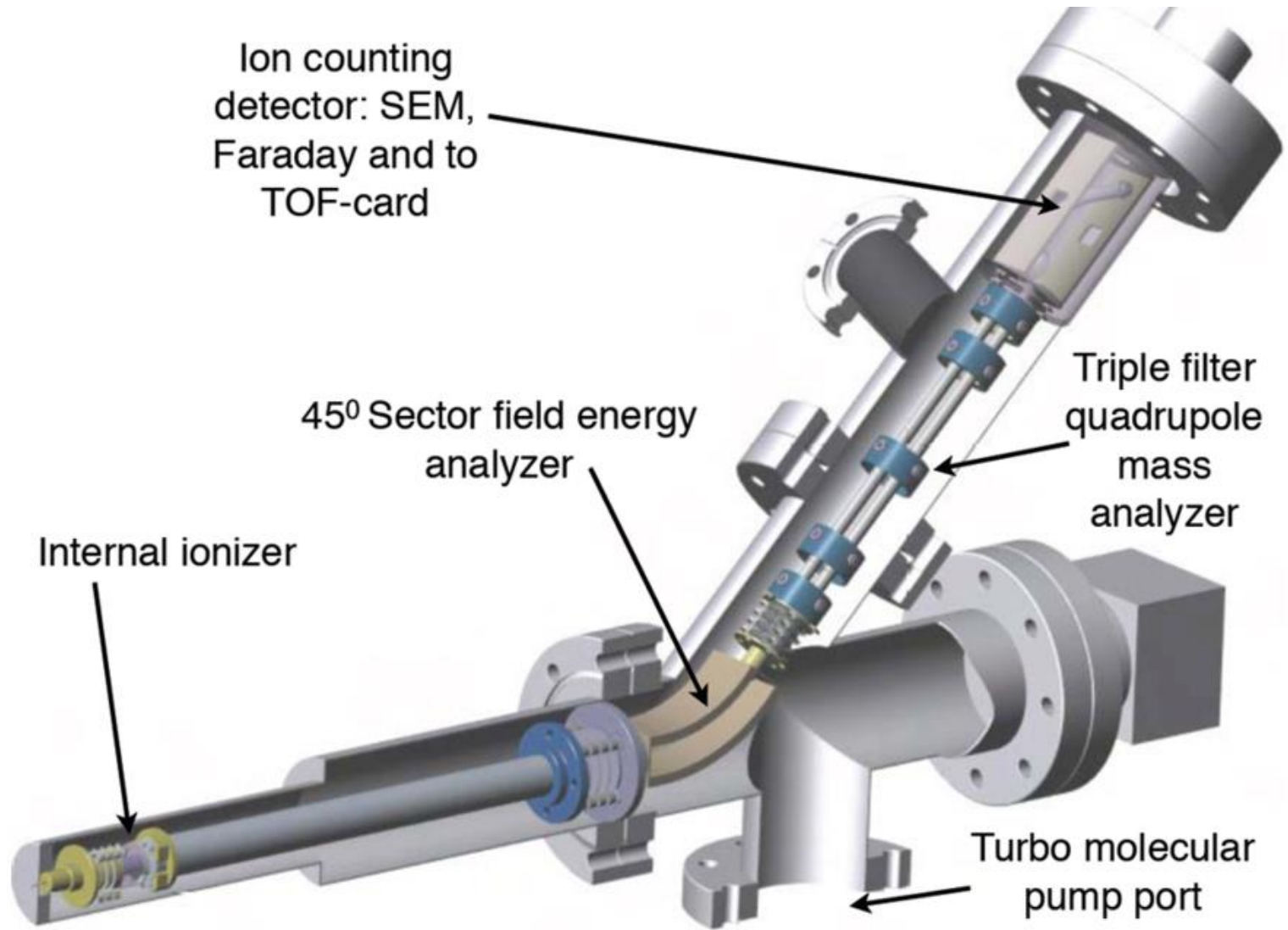
Figure 5. Ion trajectories within (a) the Bessel box (reprinted with permission from [28], copyright 1995, American Institute of Physics) and (b) schematic representation of electrostatic energy analyser (ESA).

Benedikt *et al.*, J. Phys. D: Appl. Phys. **45** (2012) 403001



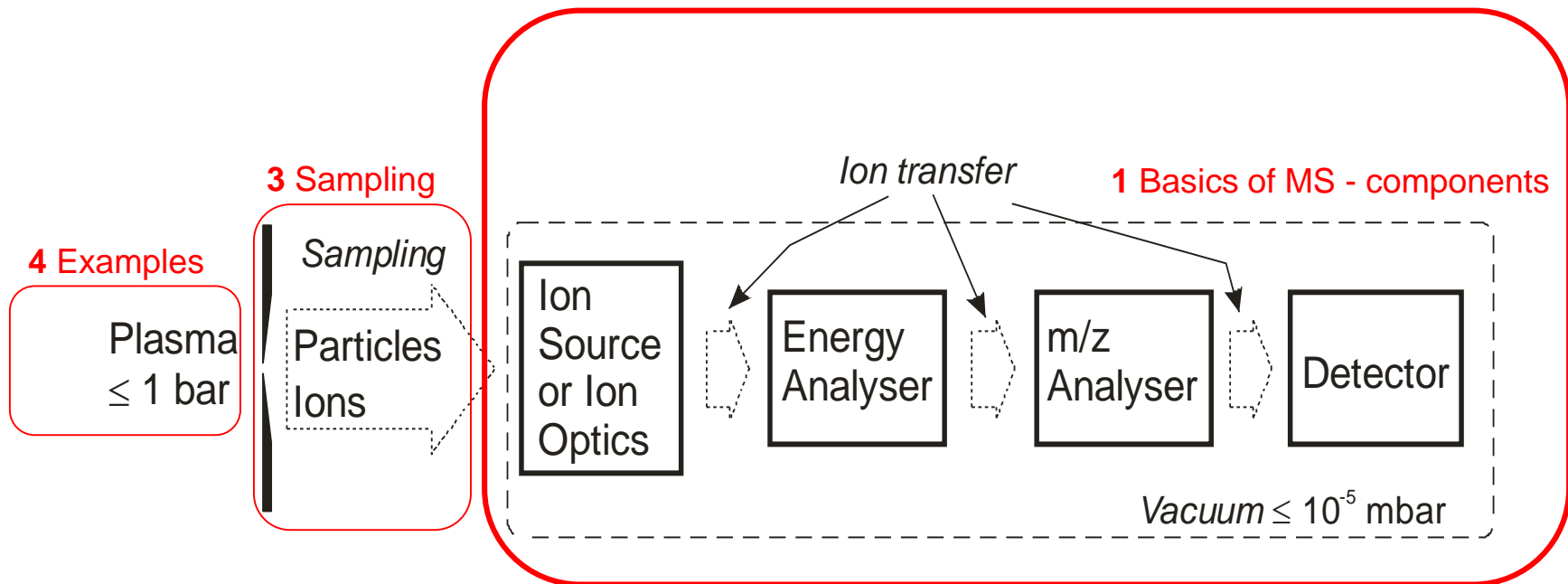
Simulation: Simion 8.1 SW

# All components together: for example HIDDEN EQP

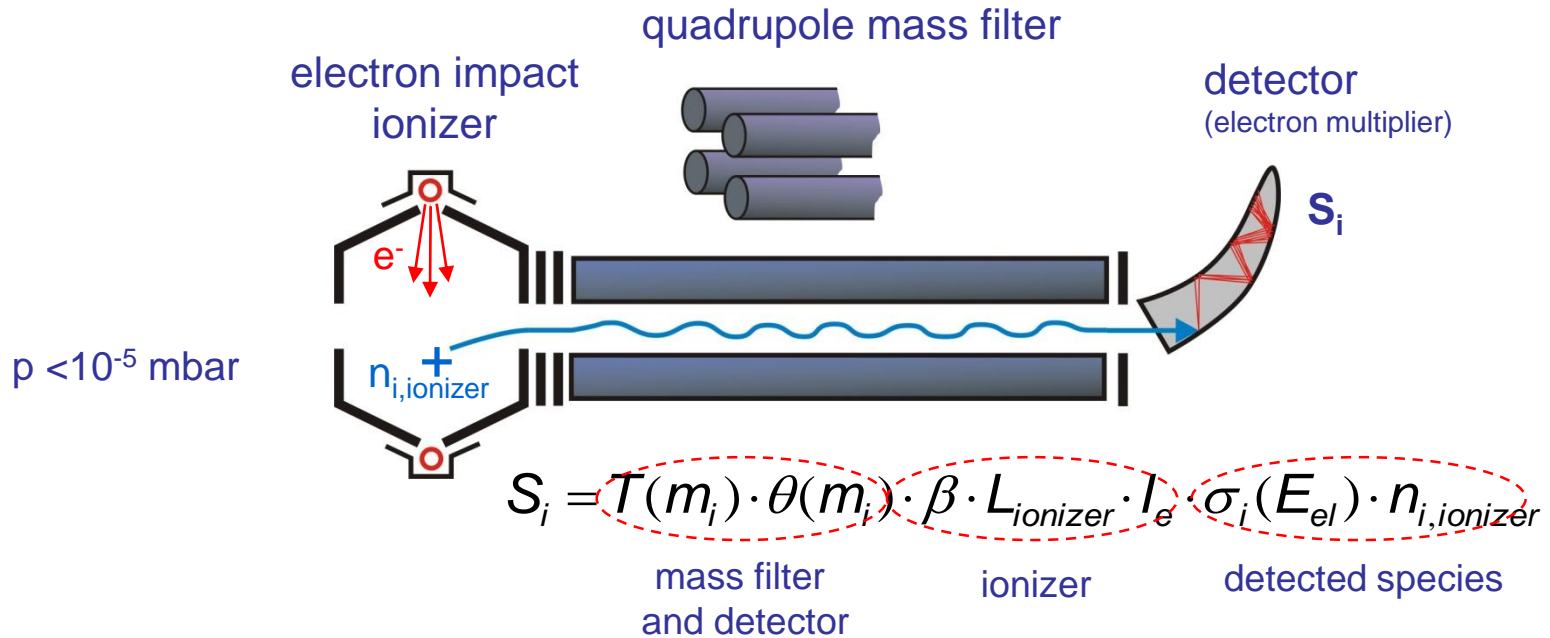


# Outline

## 2 Species identification and quantification



# Mass spectrometry Quantification of neutral species



Signal calibration: measurement of species with known density

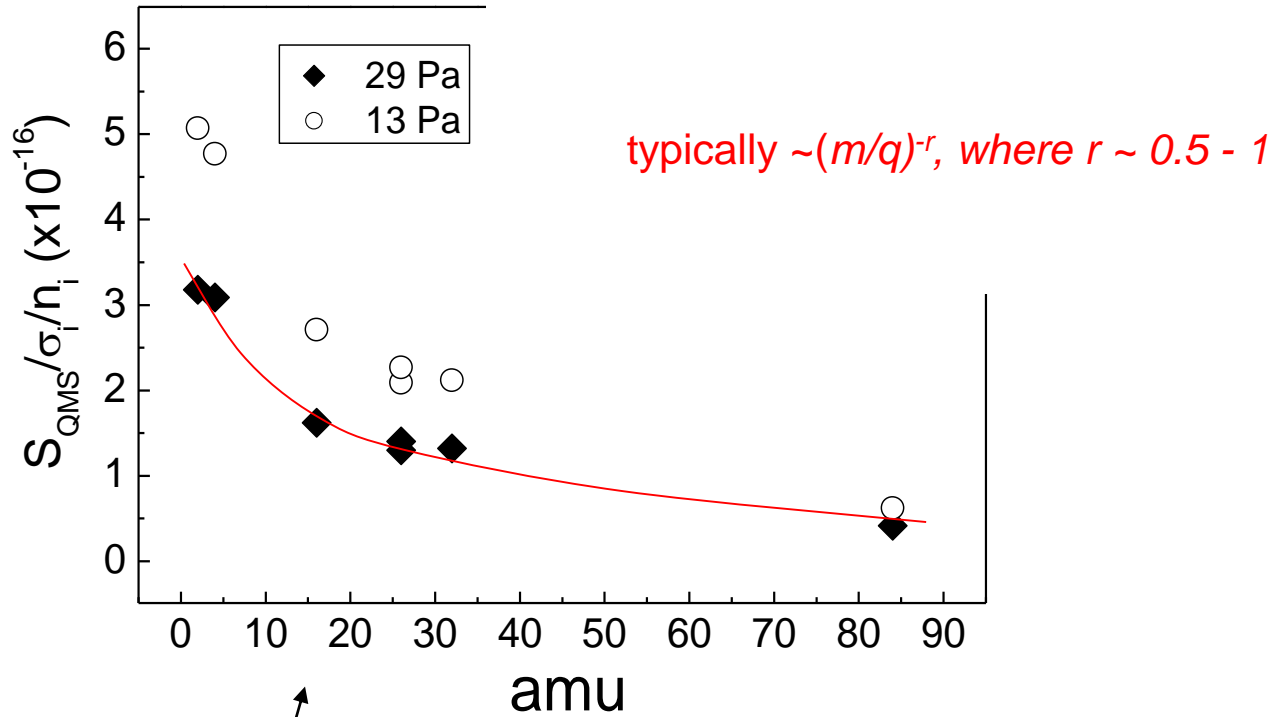
$$S_{cal} = T(m_{cal}) \cdot \theta(m_{cal}) \cdot \beta \cdot L_{ionizer} \cdot I_e \cdot \sigma_{cal}(E_{el}) \cdot n_{cal,ionizer}$$



$$n_{i,ionizer} = F(m_i, m_{cal}) \cdot \frac{\sigma_{cal}(E_{el})}{\sigma_i(E_{el})} \cdot \frac{n_{cal,ionizer}}{S_{cal}} \cdot S_i$$

# Mass dependent MS transmission function

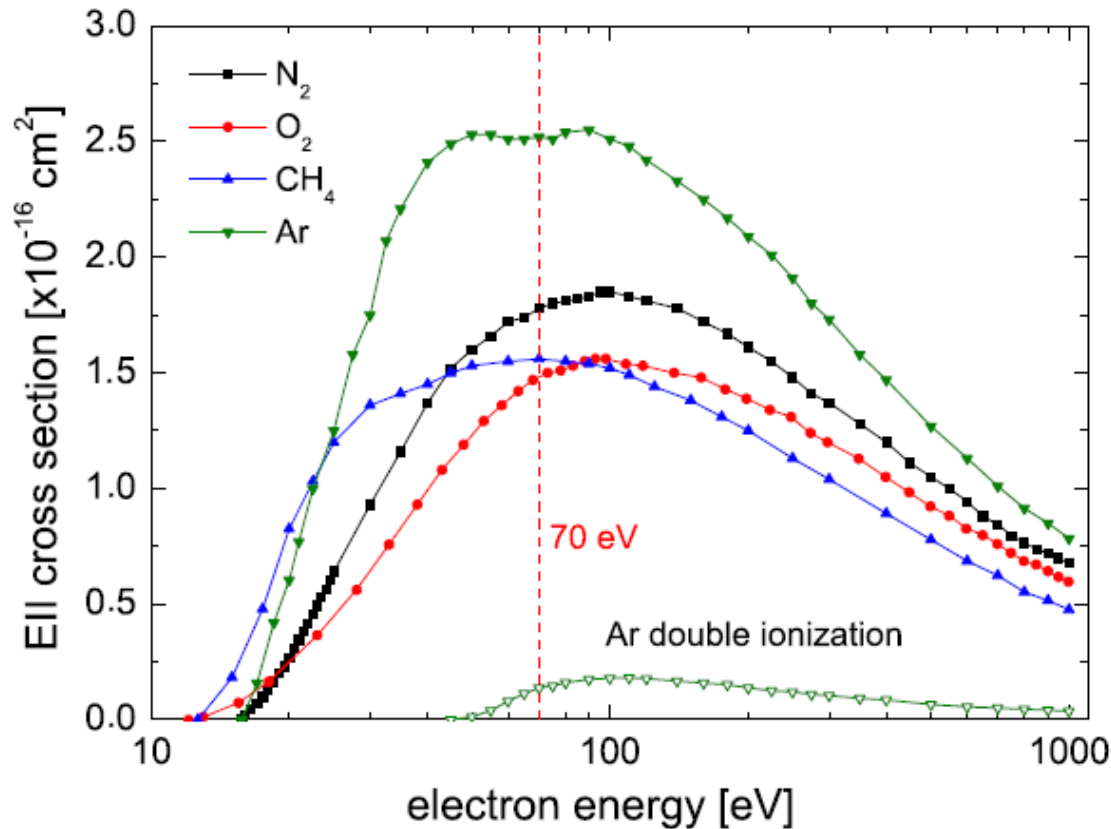
The mass-to-charge ( $m/q$ ) dependent MS response can be calibrated by stable gases of known densities:



$$n_{i,ionizer} = F(m_i, m_{cal}) \cdot \frac{\sigma_{cal}(E_{el})}{\sigma_i(E_{el})} \cdot \frac{n_{cal,ionizer}}{S_{cal}} \cdot S_i$$

# Electron Impact Ionization Cross Section

Known for most of the stable gases



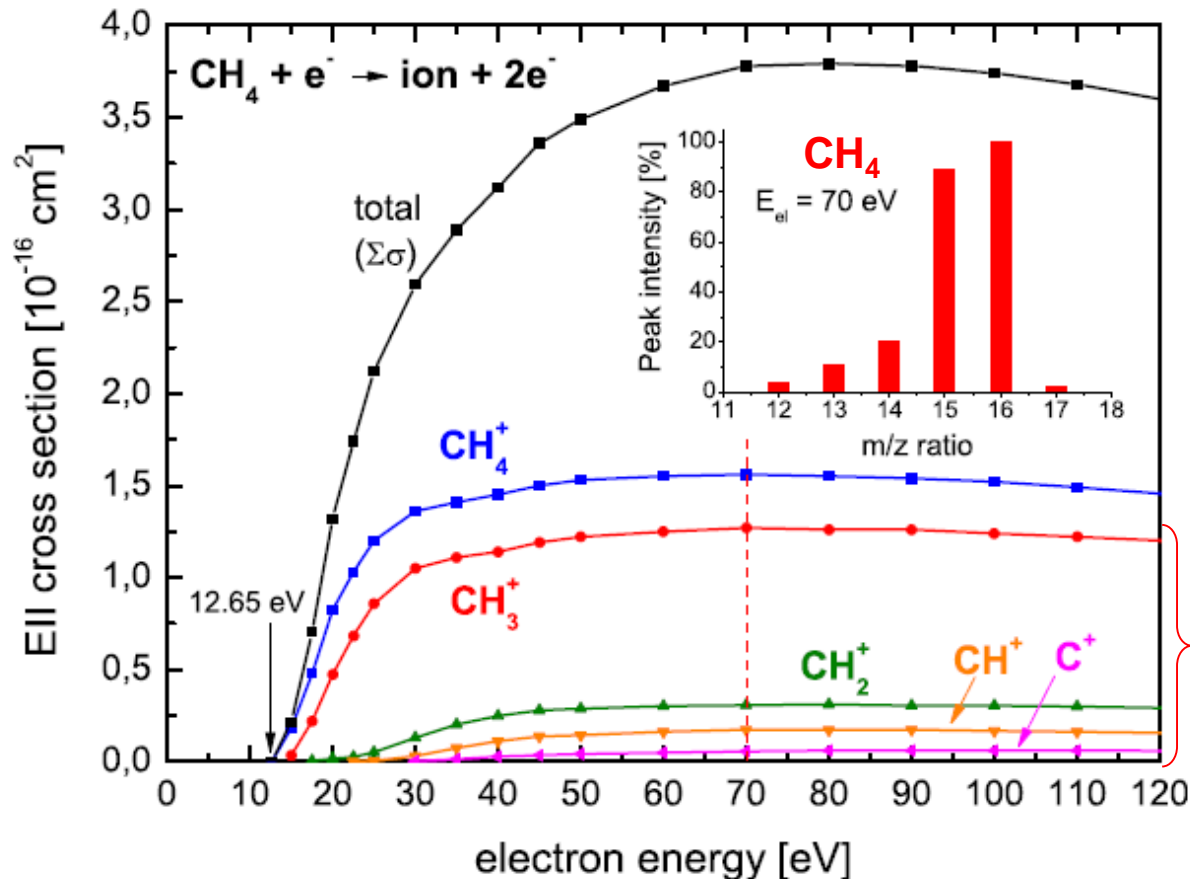
Typical shape

Highest sensitivity at electron energy around 70 eV

**Figure 2.** Electron impact ionization cross-section for different gases as a function of the electron energy. Data taken from [6, 7].

# Electron Impact Ionization Cross Section

However: at high  $E_{el}$  also dissociation or multiple ionization possible



ions appear at many masses

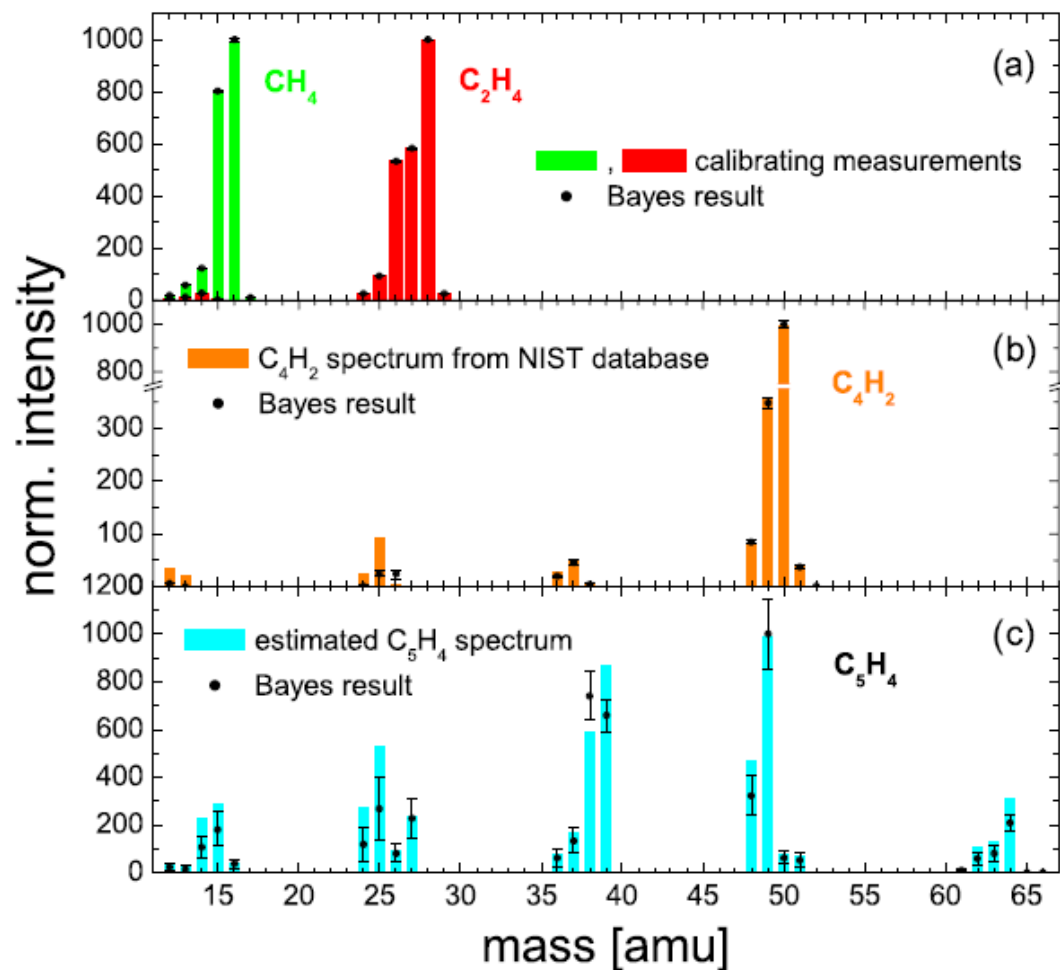
fragment ions

**Figure 3.** The direct and dissociative EII cross-sections for  $\text{CH}_4$  molecule [6] and its CP at  $E_{el} = 70 \text{ eV}$  [9].



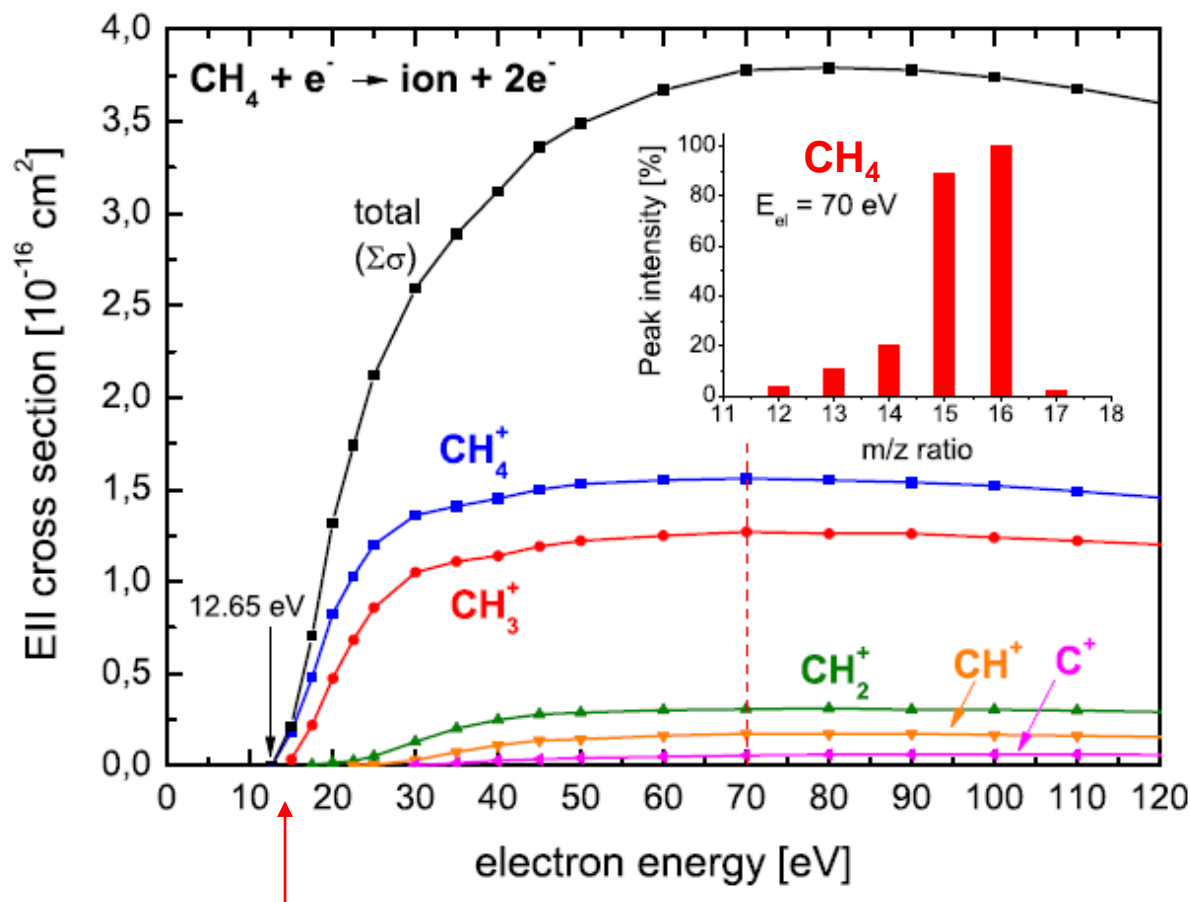
# Electron Impact Ionization Cross Section

However: at high  $E_{el}$  also dissociation or multiple ionization possible



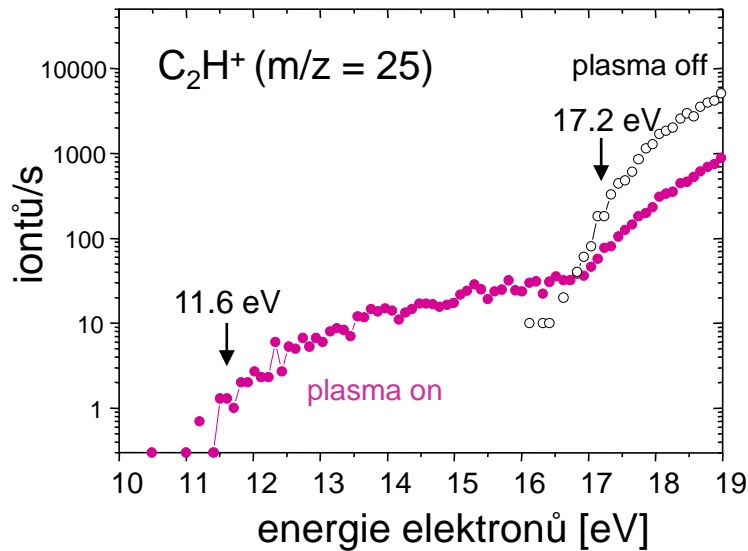
# Threshold Ionisation Mass Spectrometry (TIMS)

Possible solution for identification of overlapping mass spectra



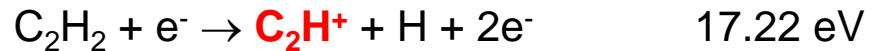
measure here, close to the ionization threshold  
→ formation of fragment ions limited or avoided

# TIMS measurements: C<sub>2</sub>H radical

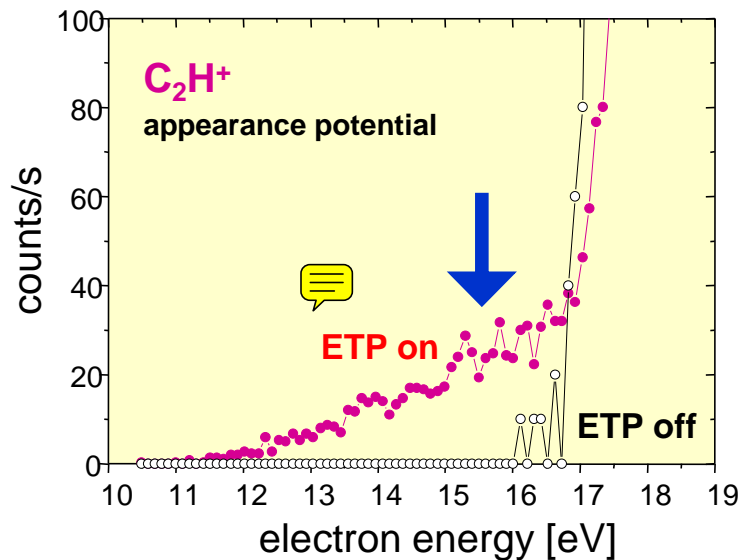


C<sub>2</sub>H<sup>+</sup>: ion can originate from two sources:

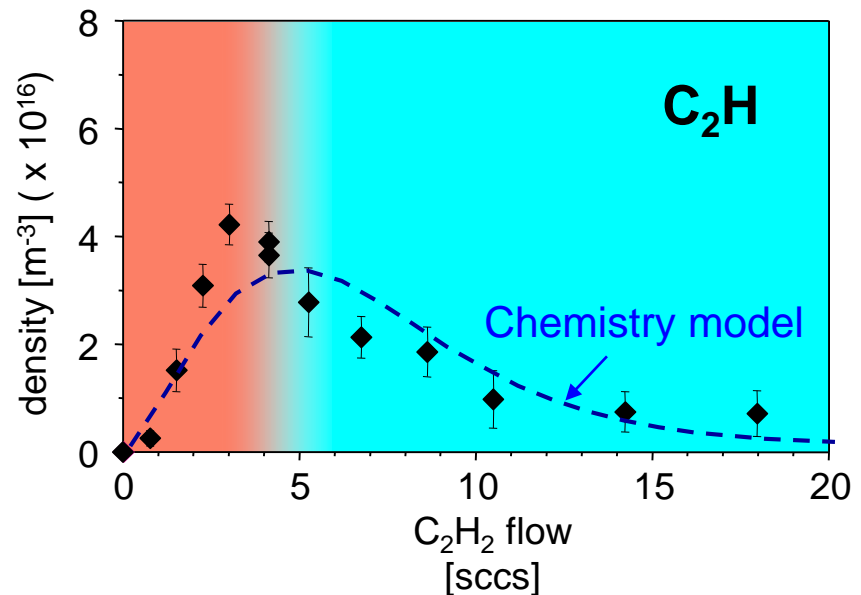
**Dissociative ionization** of C<sub>2</sub>H<sub>2</sub>:



**Direct ionization** of C<sub>2</sub>H:



15.5 eV electron energy used



# TIMS measurements: other hydrocarbons radicals

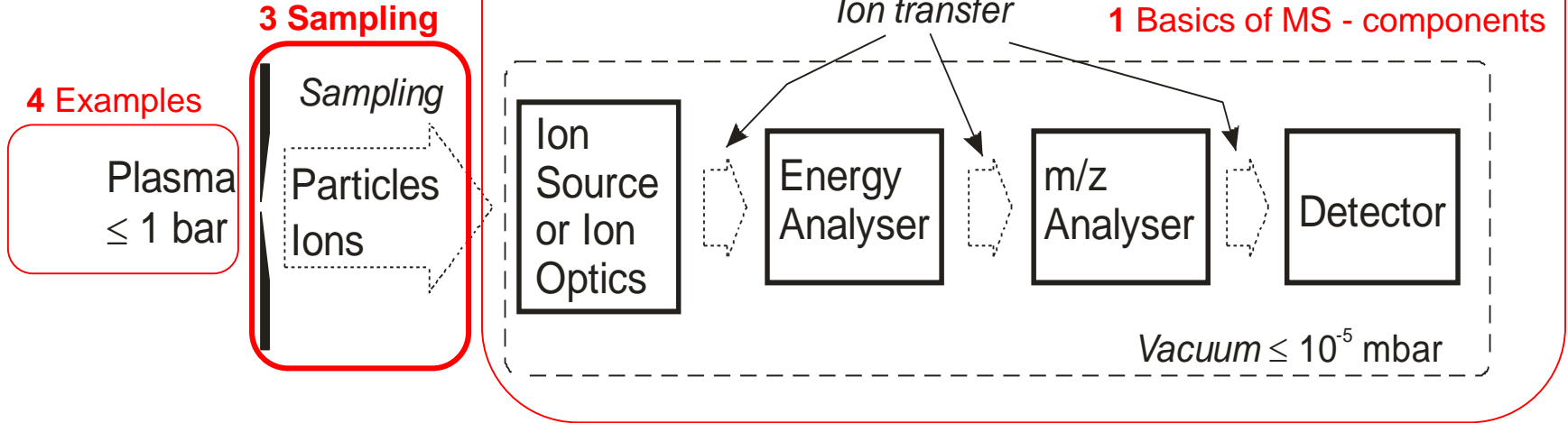
TABLE I. Radicals and molecules identified by means of TIMS in an Ar/C<sub>2</sub>H<sub>2</sub> ETP, their measured and reported IP, the electron energy used for they measurement and the EII cross section taken from the literature or estimated based on the arguments given in the text. The experimental error of IP is  $\pm 0.2$  eV if not indicated otherwise. The literature source for IP values is Ref. 30 and references therein.

Species (amu)	Measured IP [eV]	Literature IP [eV]	$E_{\text{electron}}$ (eV)	$\sigma_1(E) \times 10^{-16}$ (cm <sup>2</sup> )
C (12)	11.3	11.26	19	0.96/0.84 <sup>a</sup>
CH (13)	10.5	10.64	19	0.72/0.90 <sup>a</sup>
CH <sub>2</sub> (14)	10.5	10.35	14	0.31/0.43 <sup>a</sup>
CH <sub>3</sub> (15)	9.9	9.84	13	0.26/0.37 <sup>a</sup>
CH <sub>4</sub> (16)	12.6	12.61	17	0.60/0.51 <sup>a</sup>
C <sub>2</sub> (24)	11.5	11.41	18	0.73 <sup>a</sup>
C <sub>2</sub> H (25)	11.7	11.61	15.5	0.45 <sup>a</sup>
C <sub>2</sub> H <sub>2</sub> (26)	11.4	11.40	14	0.31
C <sub>3</sub> (36)	12.1	11–13 <sup>b</sup>	14	0.23 <sup>a</sup>
C <sub>3</sub> H (37)	9.7	9.8	15	0.59 <sup>a</sup>
C <sub>3</sub> H <sub>2</sub> (38)	9.2	8.7/9.15/10.43 <sup>c</sup>	12	0.33 <sup>a</sup>
C <sub>3</sub> H <sub>4</sub> (40)	10.3	10.37	13	0.31 <sup>a</sup>
C <sub>4</sub> (48)	11.9 $\pm$ 0.5	12.6	18	0.61 <sup>a</sup>
C <sub>4</sub> H (49)	11.7 $\pm$ 0.5	Not known	15	0.39 <sup>a</sup>
C <sub>4</sub> H <sub>2</sub> (50)	10.2	10.17	50	4.8 <sup>d</sup>
C <sub>5</sub> (60)	11.4 $\pm$ 0.5	12.3	17	0.63 <sup>a</sup>
C <sub>5</sub> H (61)	9.8	Not known	18	0.89 <sup>a</sup>
C <sub>5</sub> H <sub>4</sub> (64)	10.0	8.67/9.5/10.1 <sup>c</sup>	13	0.35 <sup>a</sup>
C <sub>5</sub> H <sub>6</sub> (66)	10 $\pm$ 1	8.0–9.3	13	0.35 <sup>a</sup>
C <sub>6</sub> H <sub>2</sub> (74)	Not measured	9.50	50	7.1 <sup>d</sup>
C <sub>6</sub> H <sub>6</sub> (78)	Not measured	8.1–9.9 <sup>c</sup>	50	Not estimated

ETP - expanding thermal plasma

# Outline

## 2 Species identification and quantification



**How to connect measured ionizer density with density in the plasma?**

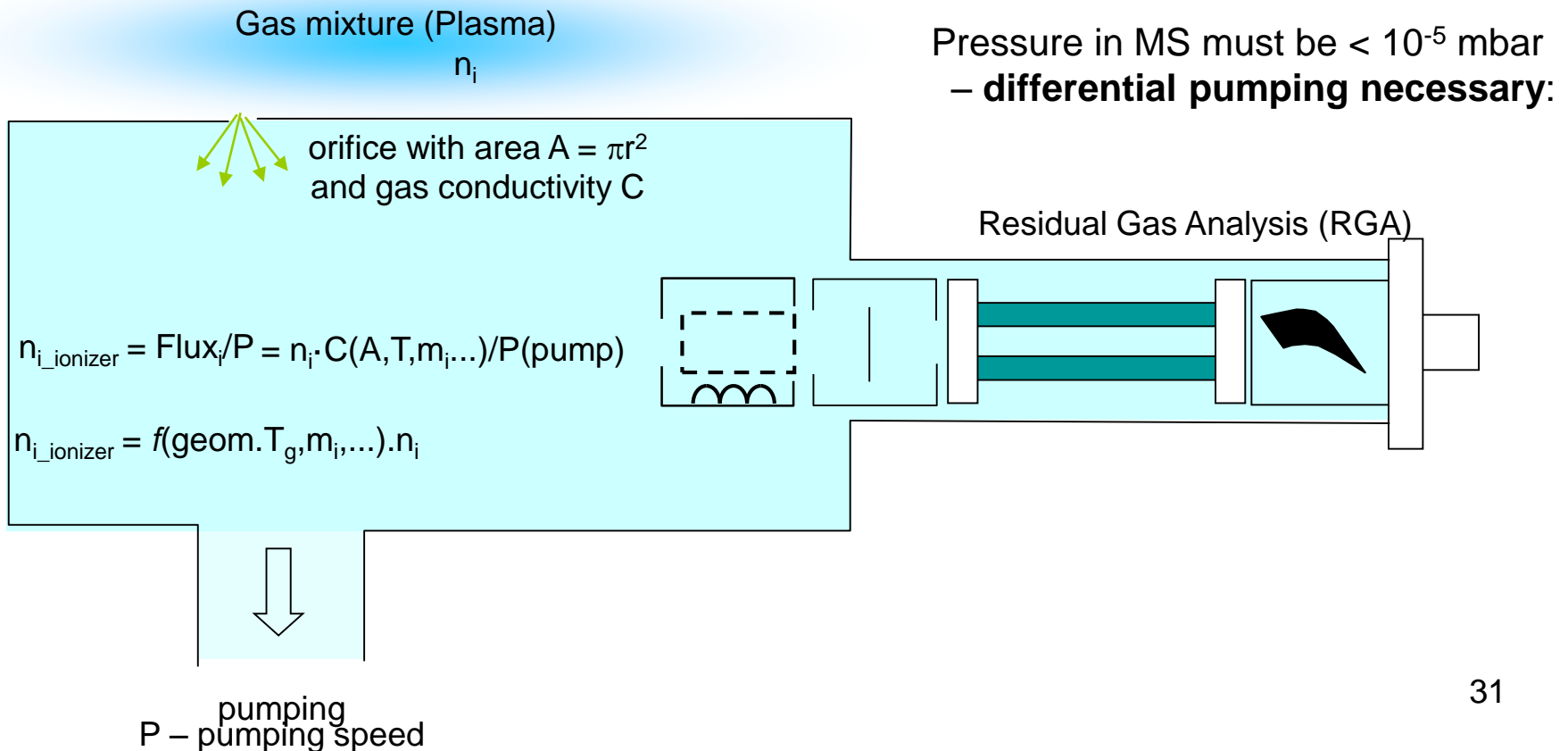
**What is the use of differential pumping...?**

**How to sample ions?**

# Measurement of stable species

$$n_{i,ionizer} = F(m_i, m_{cal}) \cdot \frac{\sigma_{cal}(E_{el})}{\sigma_i(E_{el})} \cdot \frac{n_{cal,ionizer}}{S_{cal}} \cdot S_i$$

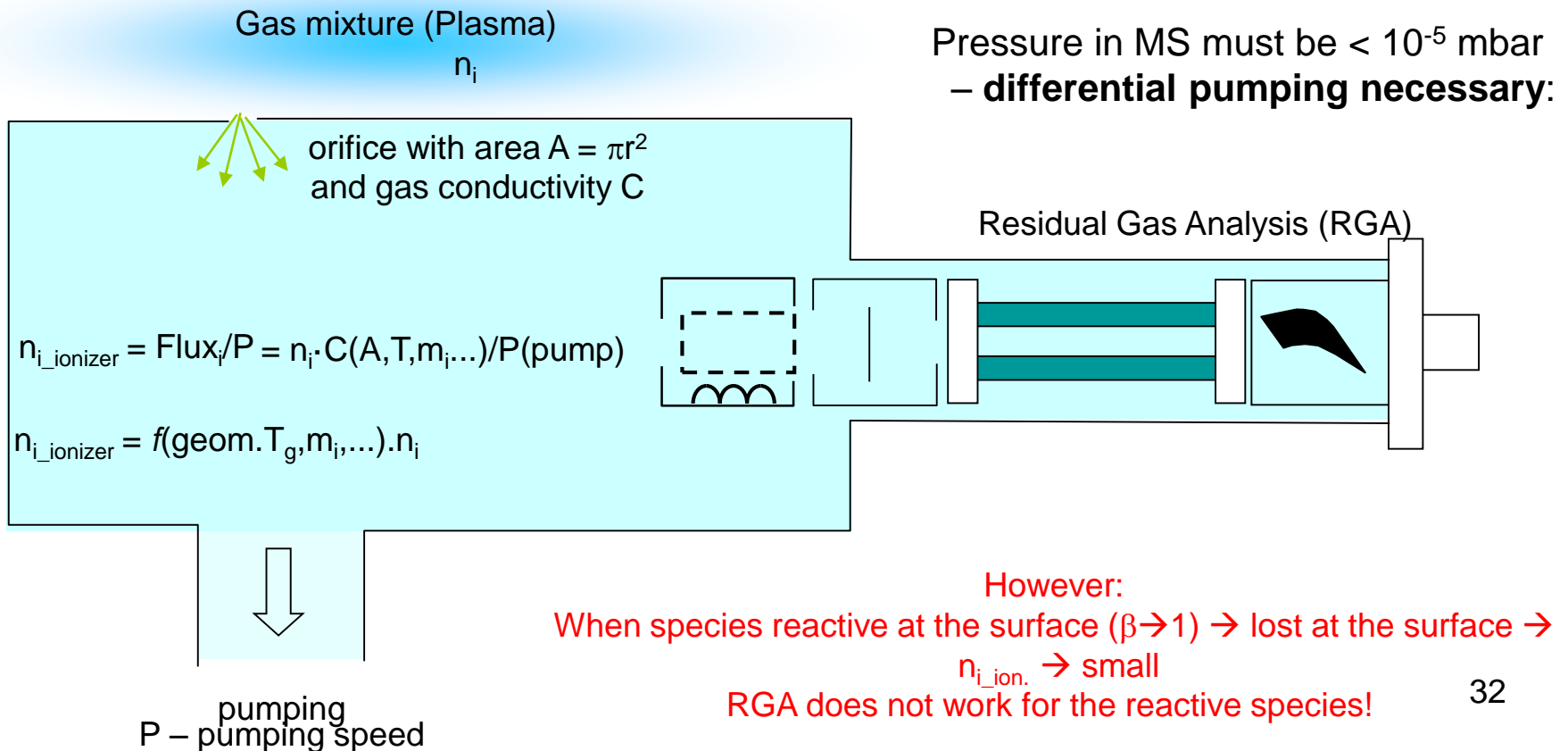
How to connect it with density at the sampling orifice? → differential pumping



# Measurement of stable species

$$n_{i,ionizer} = F(m_i, m_{cal}) \cdot \frac{\sigma_{cal}(E_{el})}{\sigma_i(E_{el})} \cdot \frac{n_{cal,ionizer}}{S_{cal}} \cdot S_i$$

How to connect it with density at the sampling orifice? → differential pumping



# Measurement of reactive neutrals: Molecular Beam Sampling

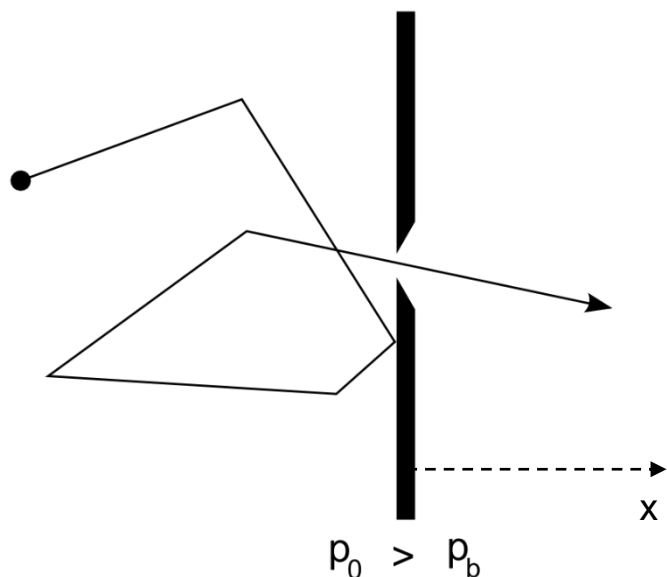
$$n_{i,ionizer} = F(m_i, m_{cal}) \cdot \frac{\sigma_{cal}(E_{el})}{\sigma_i(E_{el})} \cdot \frac{n_{cal,ionizer}}{S_{cal}} \cdot S_i$$

How to connect it with density at the sampling orifice? → molecular beam sampling

Formation of molecular beam depends on Knudsen number  $Kn = \frac{\lambda}{d}$

$Kn > 1$

Free molecular flow without collisions



Density in the beam easy to determine:

$$n_{Beam}(x) = \frac{1}{4} \left( \frac{d}{x} \right)^2 n_0$$

Orifice aspect ratio important  
- sharp edge needed!

$x$  (position of the ionizer) should be as small as possible!



# Measurement of reactive neutrals: Molecular Beam Sampling

Multiple differential pumping stages + formation of molecular beam

→ Reactive species measurement possible

**Ionizer density:**

$$n_{i\_ionizer} = n_{i\_ionizer\_BG} + n_{i\_ionizer\_Beam}$$

(1) measured without chopper blocking the beam

**Background density:**

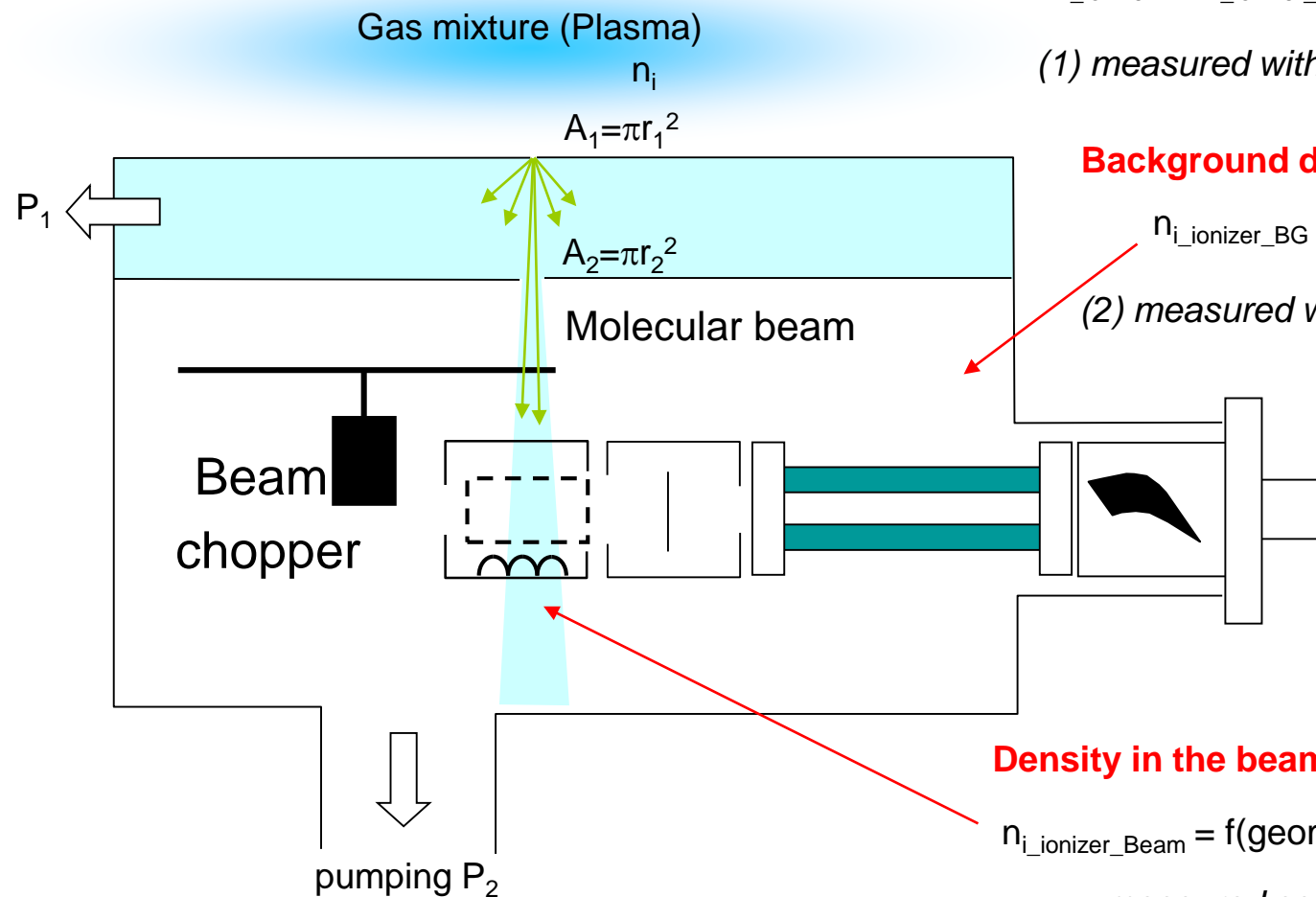
$$n_{i\_ionizer\_BG} = n_i \cdot C_1 \cdot C_2 / P_1 P_2$$

(2) measured with chopper blocking the beam

**Density in the beam:**

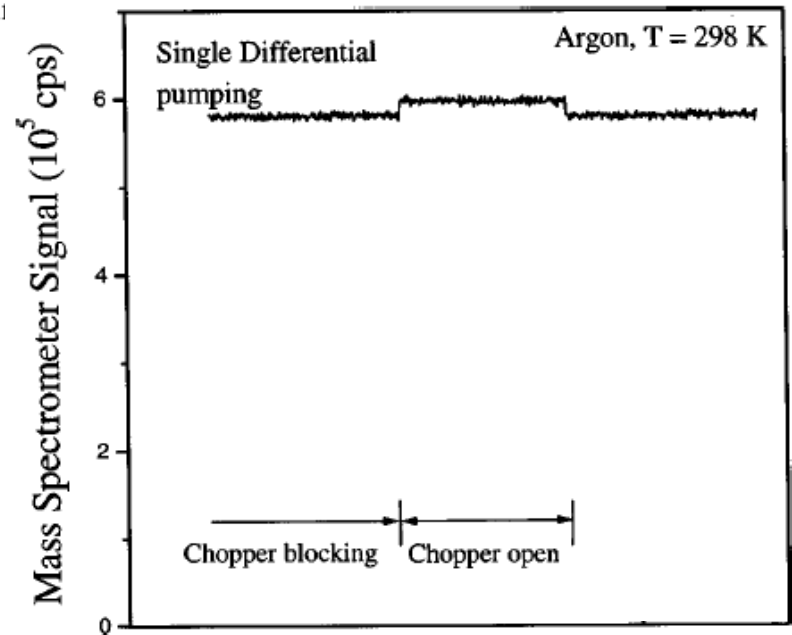
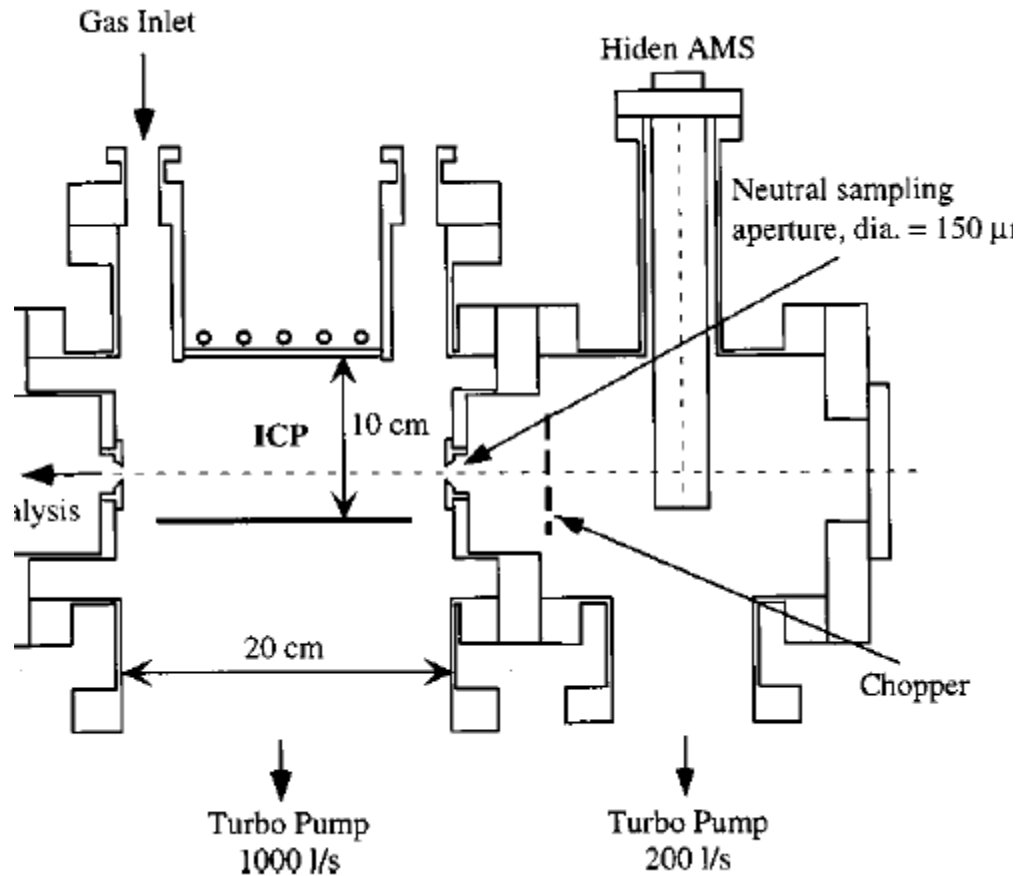
$$n_{i\_ionizer\_Beam} = f(\text{geom.}, T_g, m_i, m_{cg}, \dots) \cdot n_i$$

measured as difference (1) – (2) 34



# Example: CF<sub>x</sub> species measurement

Single stage differential pumping

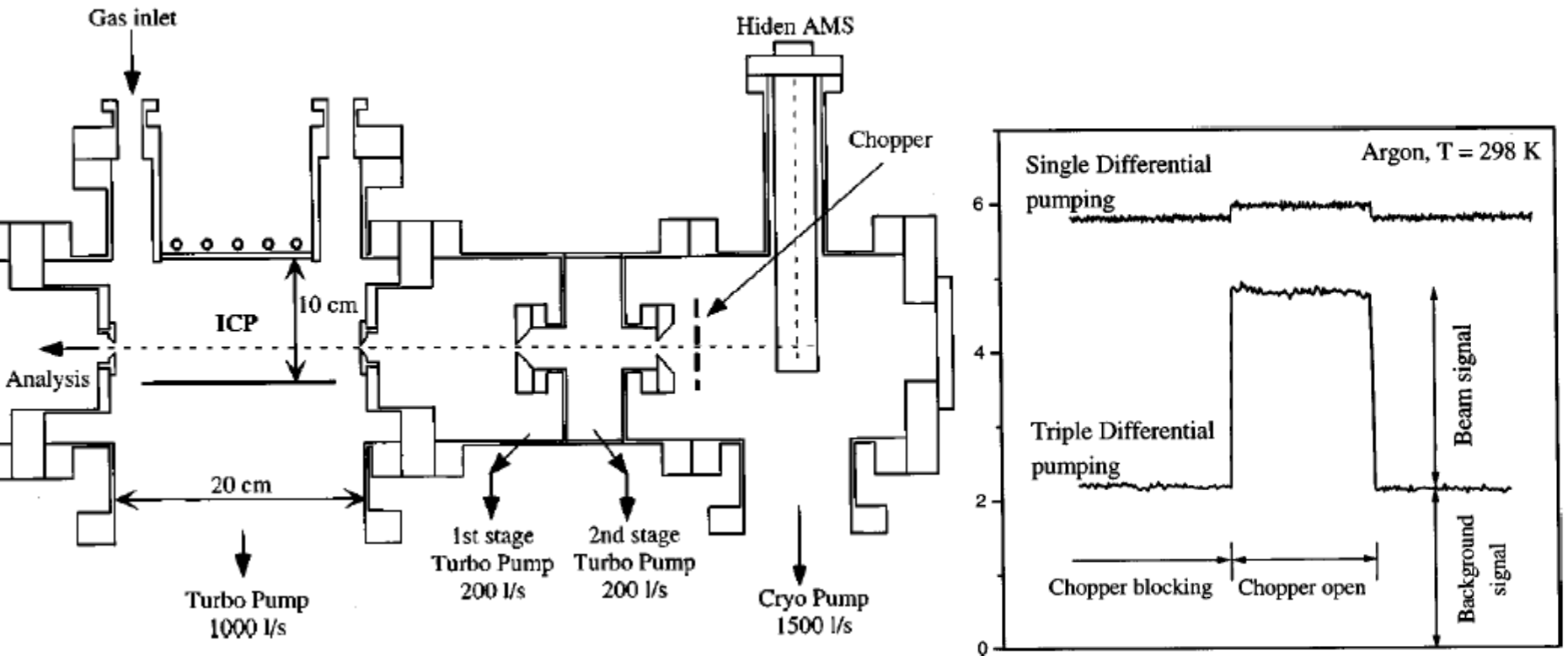


$$n_{i\_ionizer\_BG} = n_i \cdot C(A, T) / P$$

$$n_{i\_ionizer\_Beam} = 1/4 \cdot n_i \cdot (r/x)^2$$

# Example: CF<sub>x</sub> species measurement

Tripple stage differential pumping

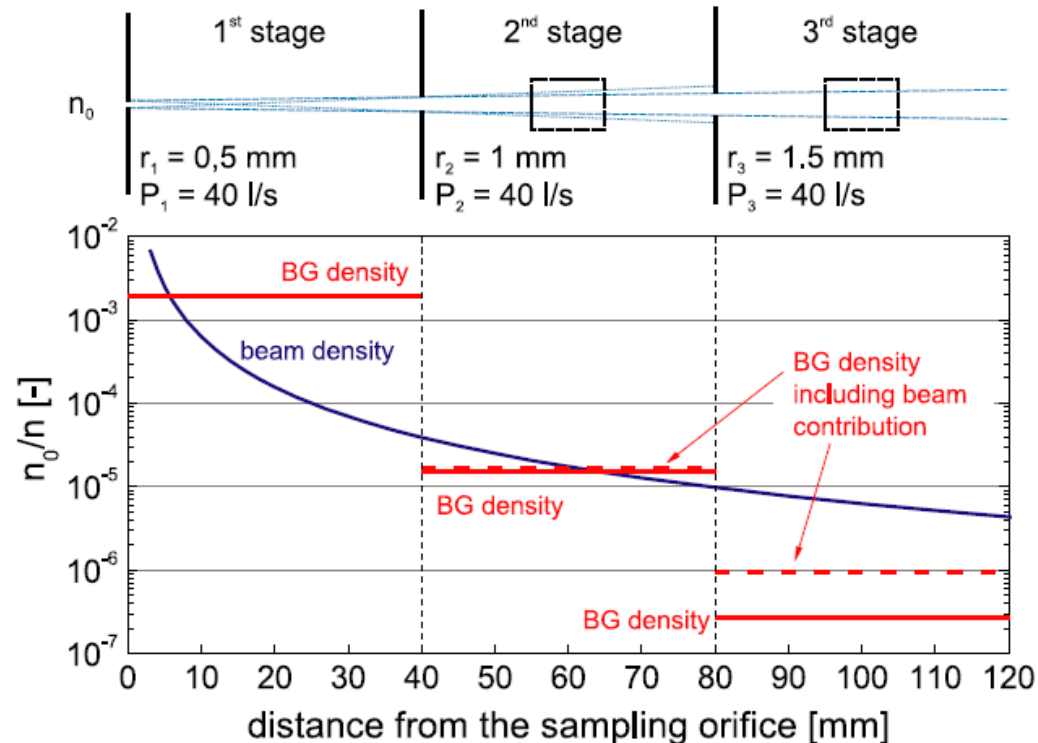


$$n_{i\_ionizer\_BG} = n_i \cdot C_1 \cdot C_2 \cdot C_3 / (P_1 P_2 P_3)$$

$$n_{i\_ionizer\_Beam} = 1/4 \cdot n_i \cdot (r/x)^2$$

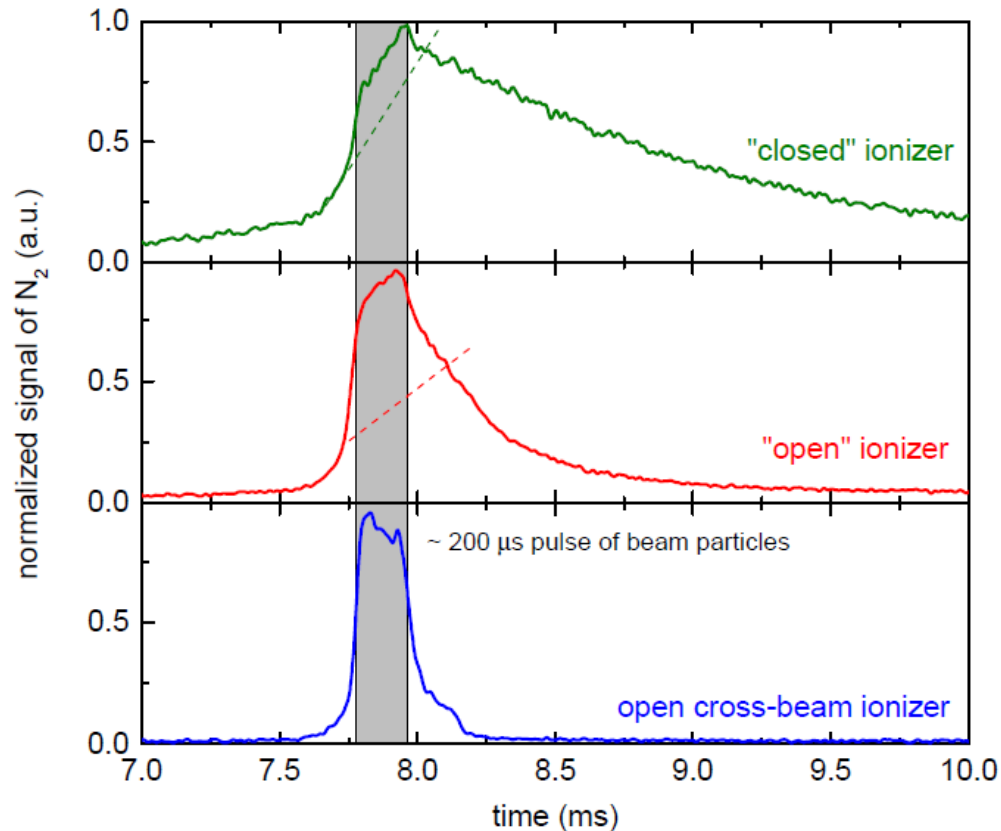
# Comparison beam x background densities

J. Phys. D: Appl. Phys. 45 (2012) 403001



**Figure 11.** Model calculation of beam and BG densities in the differentially pumped stages of the sampling system. The BG density is calculated for two cases: (i) solid red line: the beam particles are not taken into account as a source of BG density and (ii) dashed red line: the beam particle are added as a source of BG particles.

# Molecular beam sampling – ionizer issue



Measurement of the pulsed molecular beam have shown that the “closed” ionizer can be filled with “beam particles”

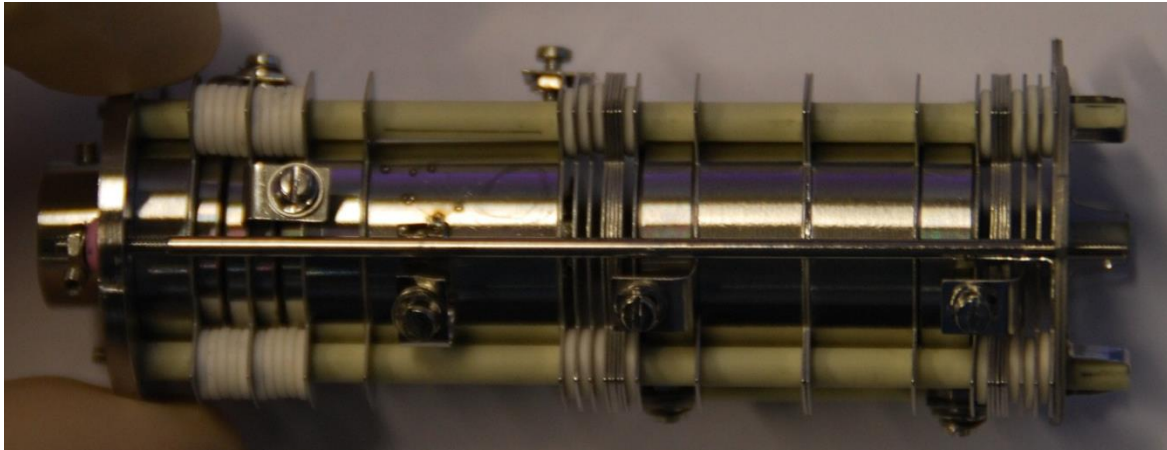
→ problem in the calibration!

**Figure 6.** Time resolved normalized MS signals at mass 28 (nitrogen molecules) of a pulsed MB with pulse length of 200  $\mu$ s as measured with an “open” and “closed” ionizer, after [32]. Additionally, the signal obtained with modified ionizer, where 40 % of the surface area of the closed ionizer has been replaced by a mesh. The beam is generated with the chopper shown in Fig. 4.

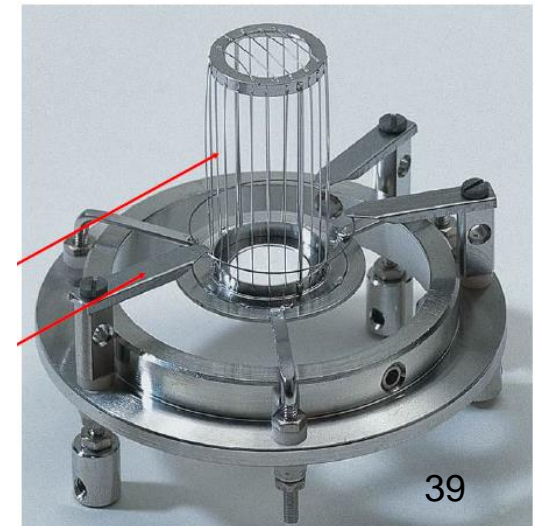
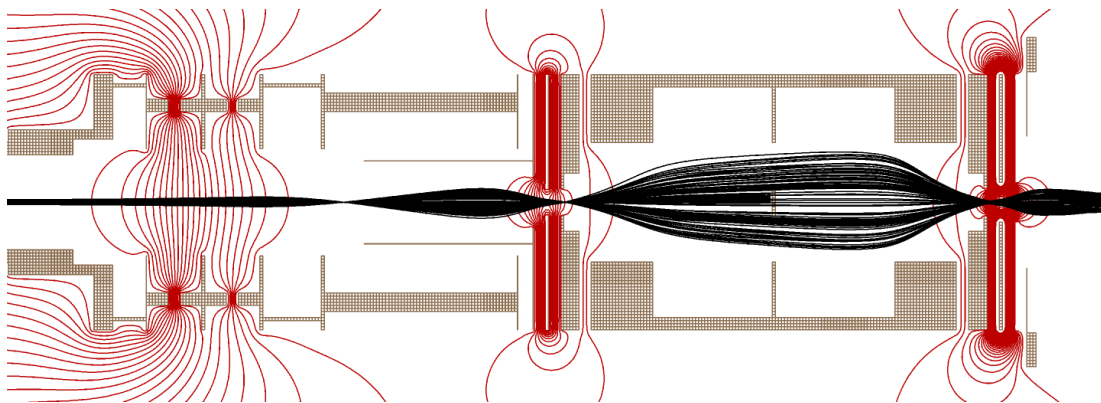
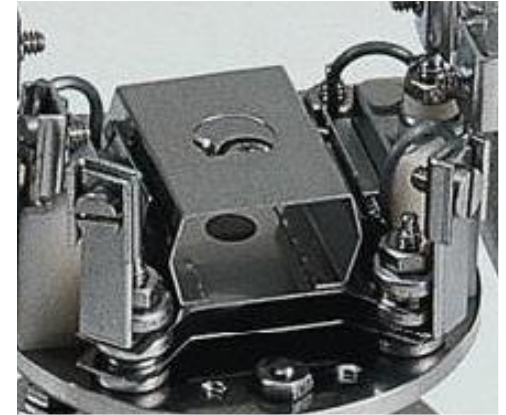
S. Große-Kreul et al.,  
accepted in J. Phys. D

# Issue of a closed and open ionizer

closed ionizer

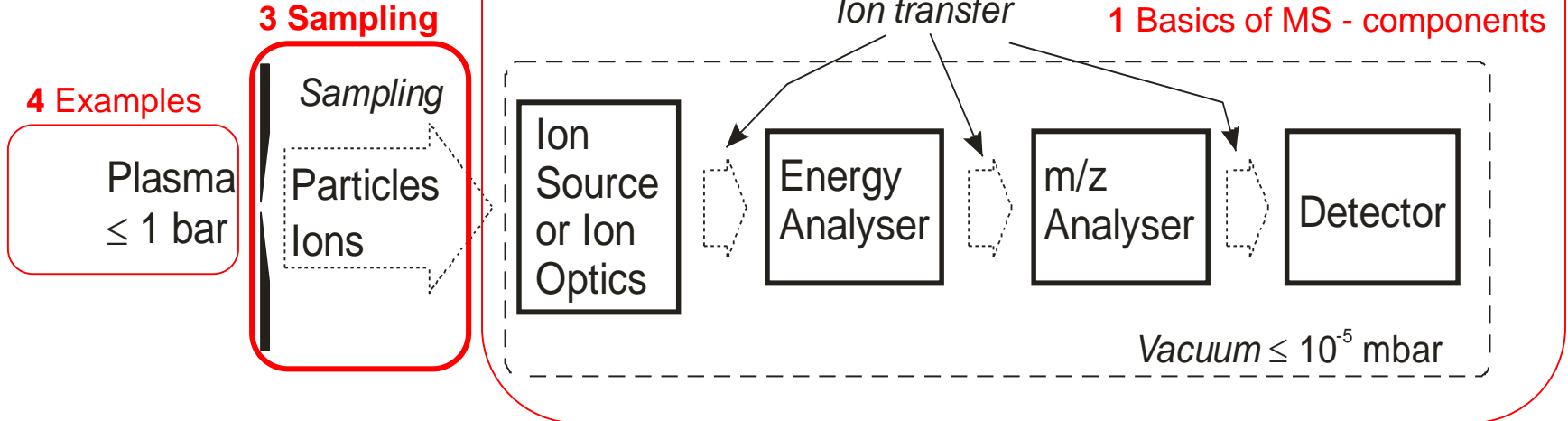


open ionizer



# Outline

## 2 Species identification and quantification

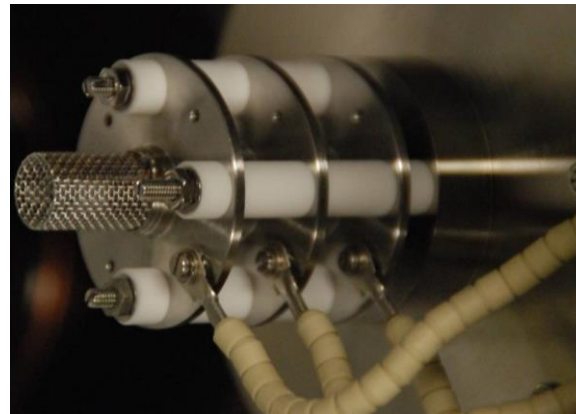
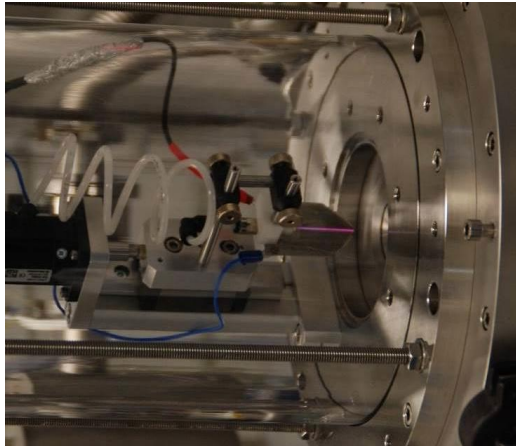


How to connect measured ionizer density with density in the plasma?

What is the use of differential pumping...?

How to sample ions?

# Mass spectrometry of ions



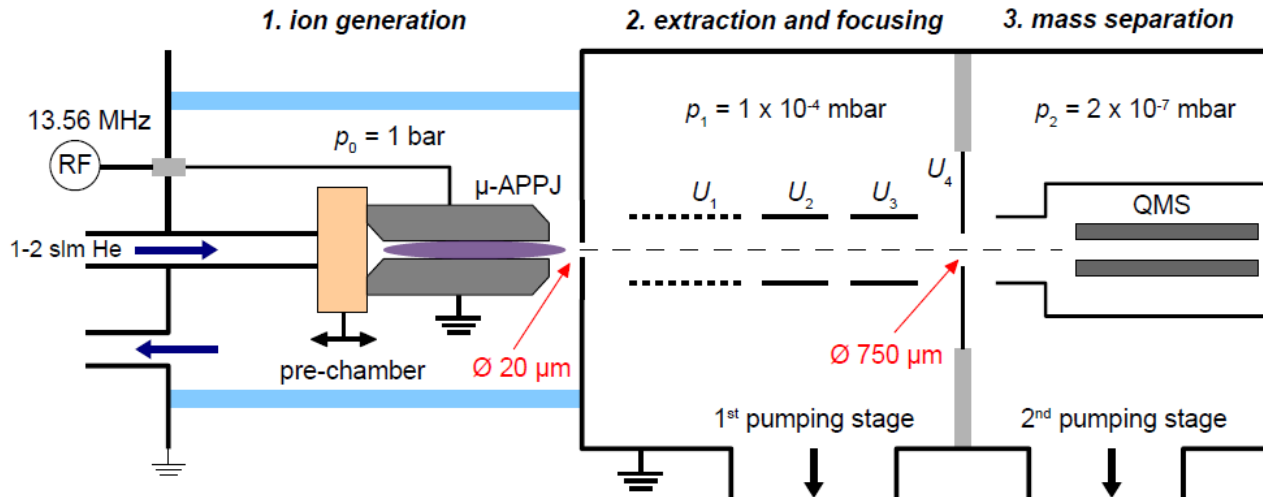
Ions manipulated and focused into MS with ion optics

No ionization and no background correction are needed

More diff. pumping stages needed only for measurement of atm. plasmas

But only relative fluxes are measured, not densities!

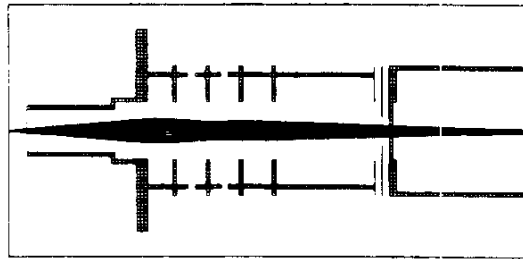
The ion lenses have to be properly tuned and calibrated



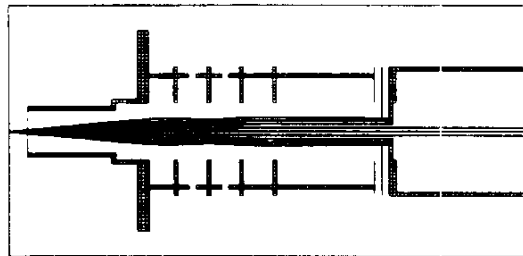


# Tuning of ion lenses – depends on ion energy

avoiding chromatic (energy) aberration



(a)



(b)

Fig. 2. Calculated ion trajectories in the case where lens 1 suffers from chromatic aberration ( $V_{\text{Ext}} = -5$  V,  $V_{\text{L1}} = -100$  V) at different ion energies: (a) 10 eV, (b) 20 eV. The voltage  $V_{\text{L2}}$  amounts  $-200$  V. The angle between subsequent ion trajectories is  $1.5^\circ$ .

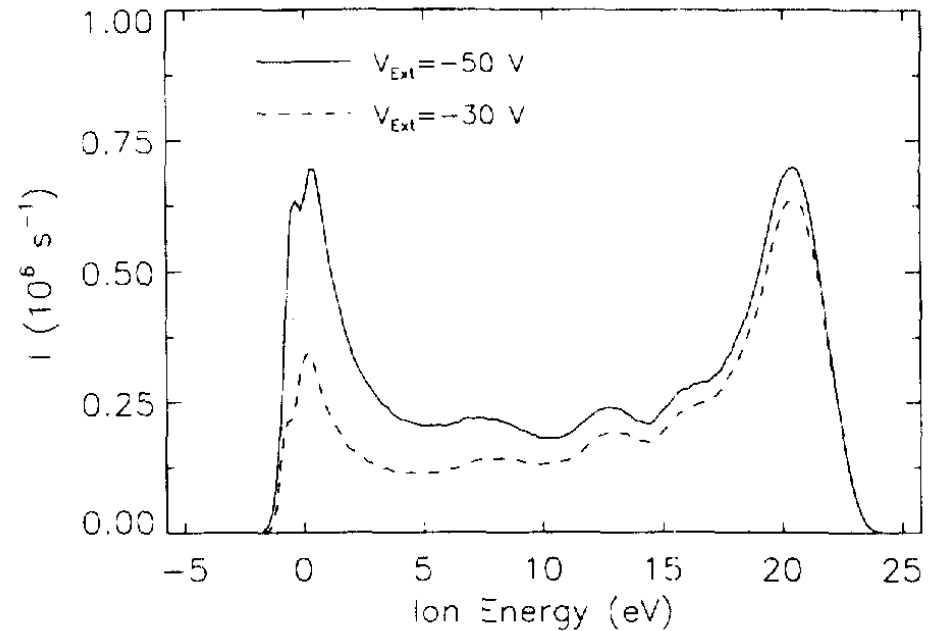
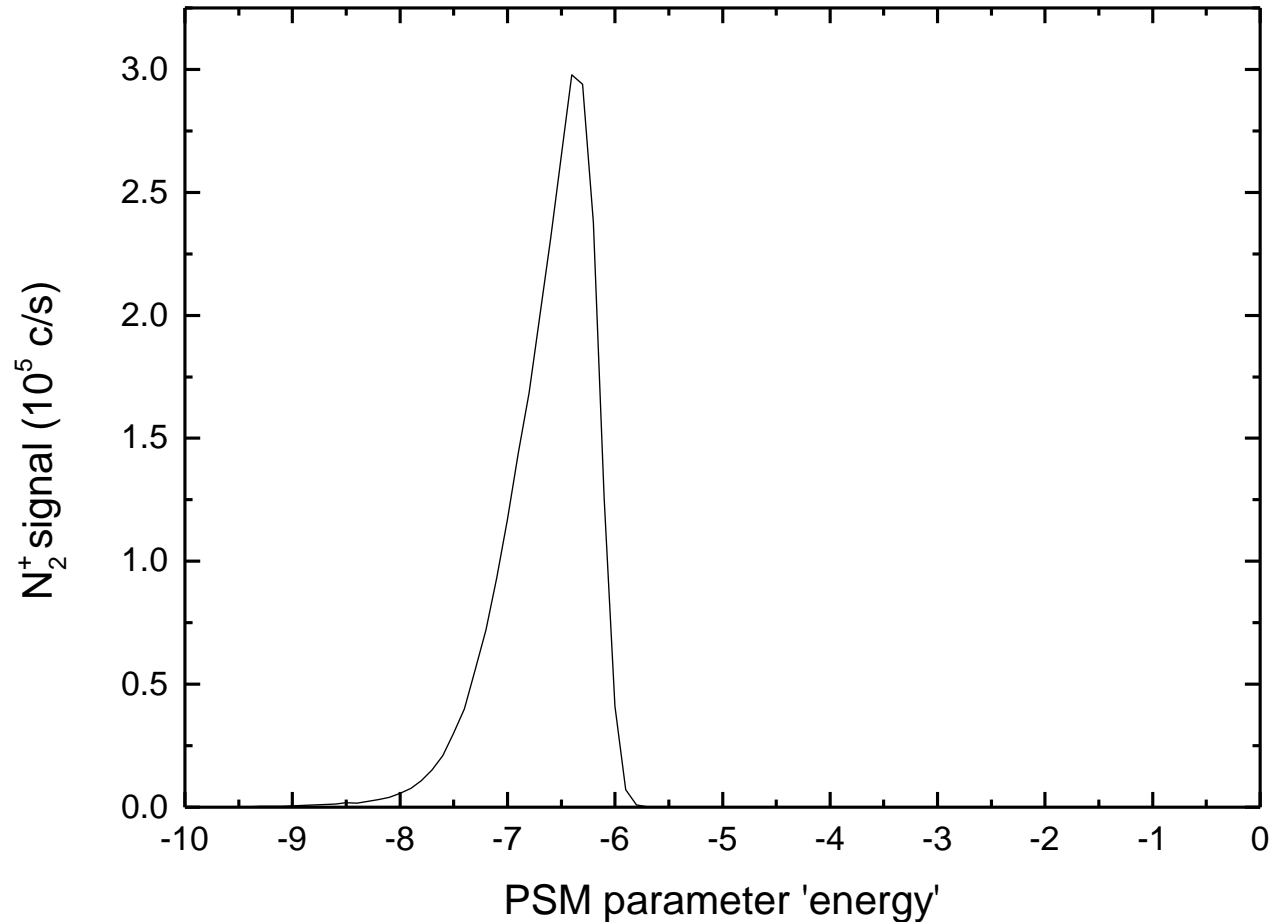


Fig. 6. Ion-energy distributions of  $\text{Ar}^+$  in argon, measured with two different  $V_{\text{Ext}} - V_{\text{L1}}$  combinations: solid line,  $V_{\text{Ext}} = -50$  V; dashed line,  $V_{\text{Ext}} = -30$  V. The power input into the reactor is 30 W at a gas pressure of 5 Pa. Along the  $x$ -axis  $V_{\text{Ext}}$  is plotted.

# Calibration of the ion optics - energy scale

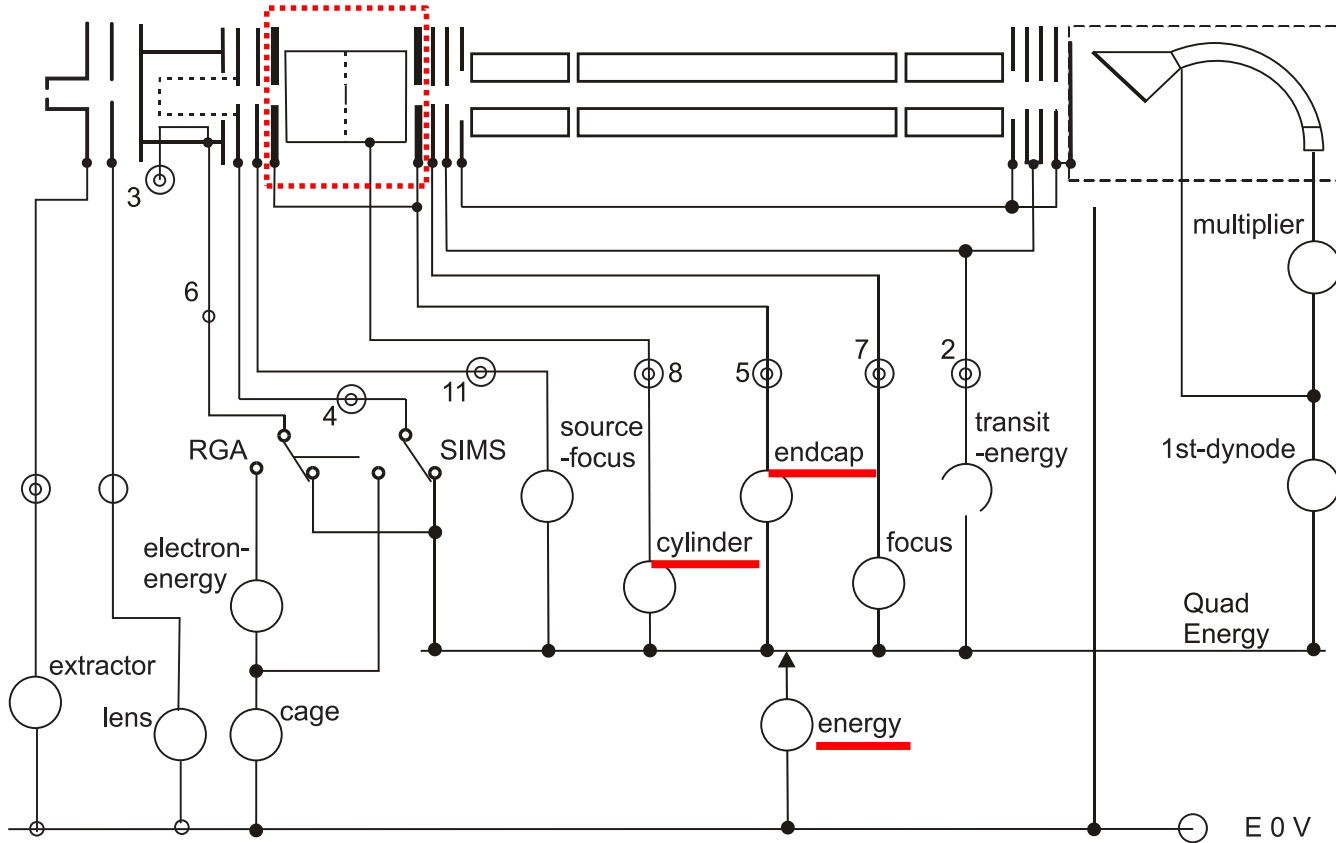
He/N<sub>2</sub> atmospheric plasma



Negative → does not make really sense...

# Experimental setup

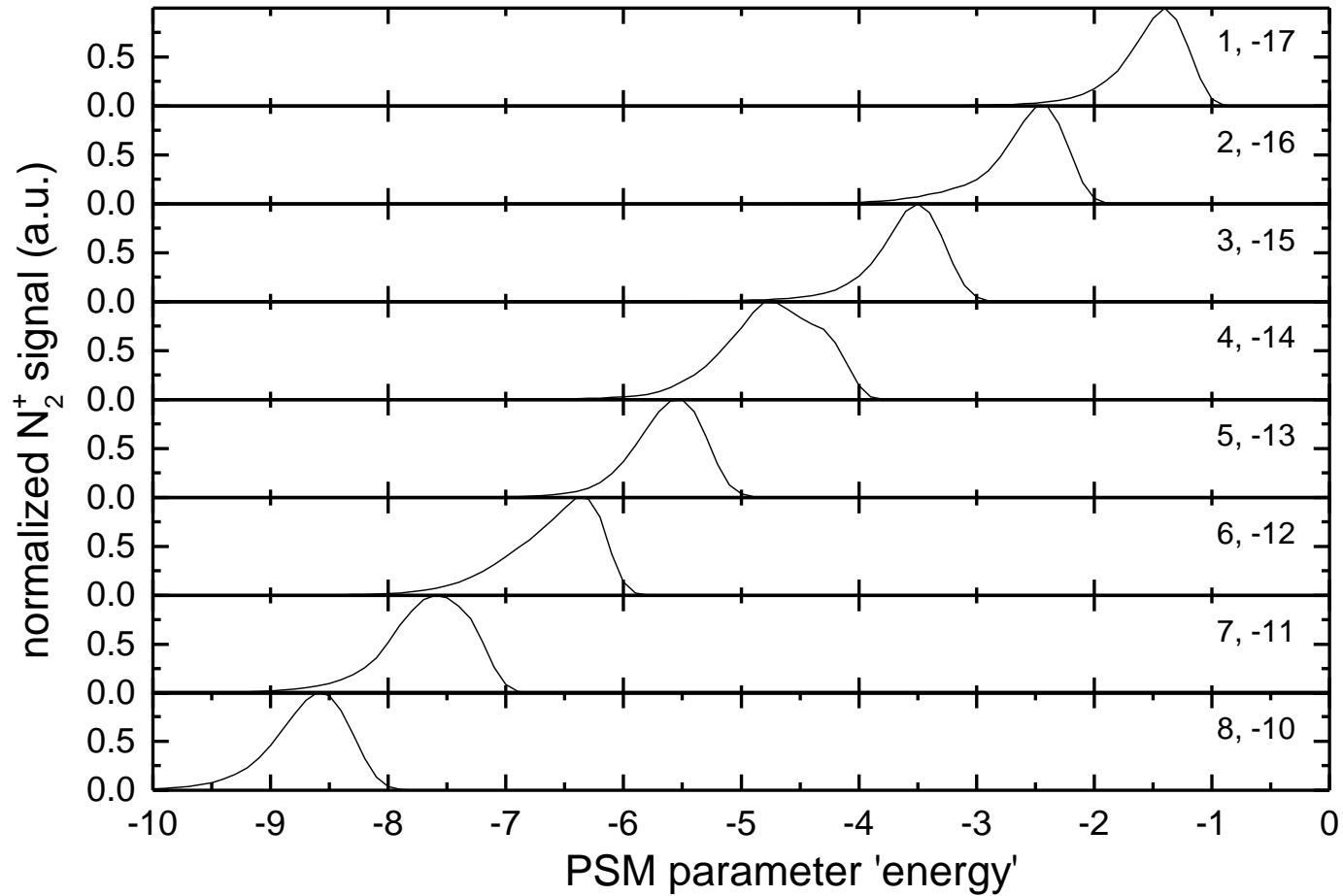
PSM mass spectrometer from HIDEN Analytical



Energy filter: „Bessel Box“ with parameters: *cylinder*, *endcap*, *energy*

# Results

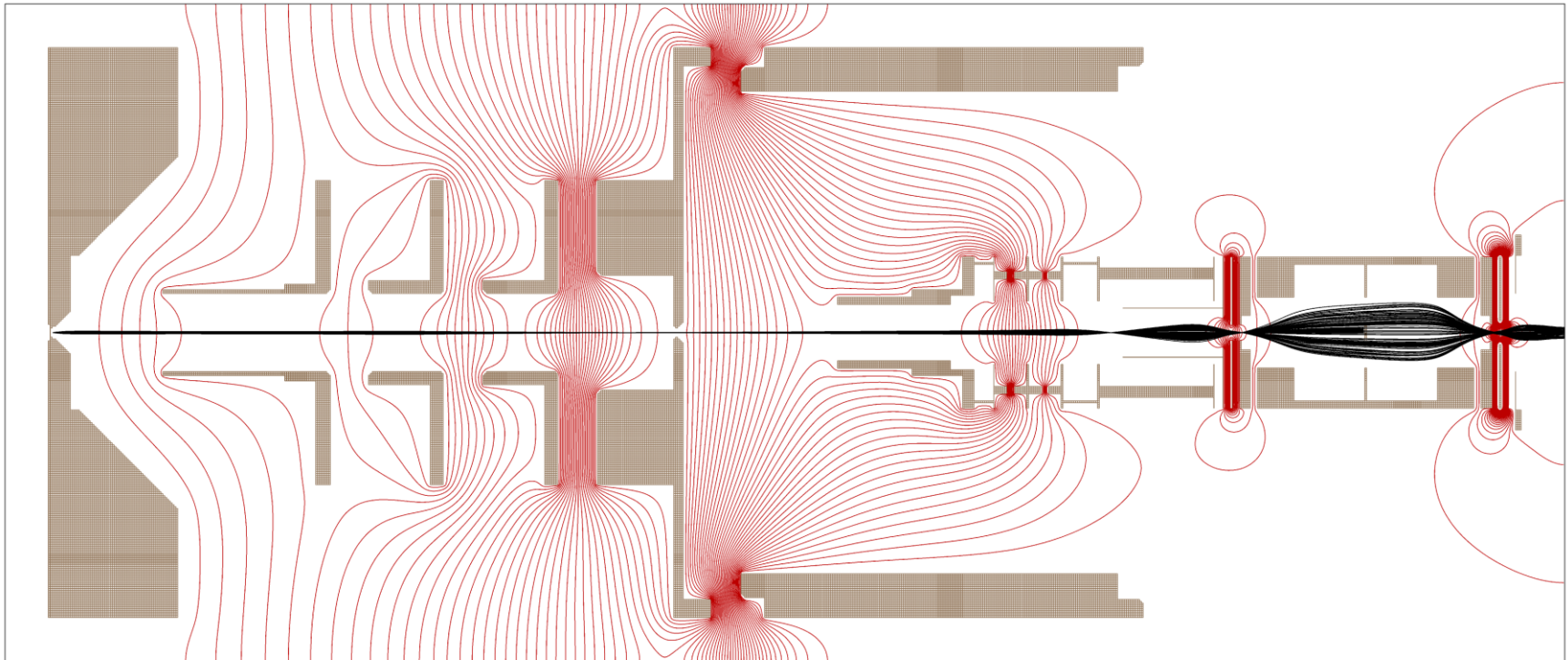
Variation of the Bessel-box parameters: *cylinder*, *endcap*, *energy*



What is the real ion energy?

# Simulation of ion optics in the sampling system

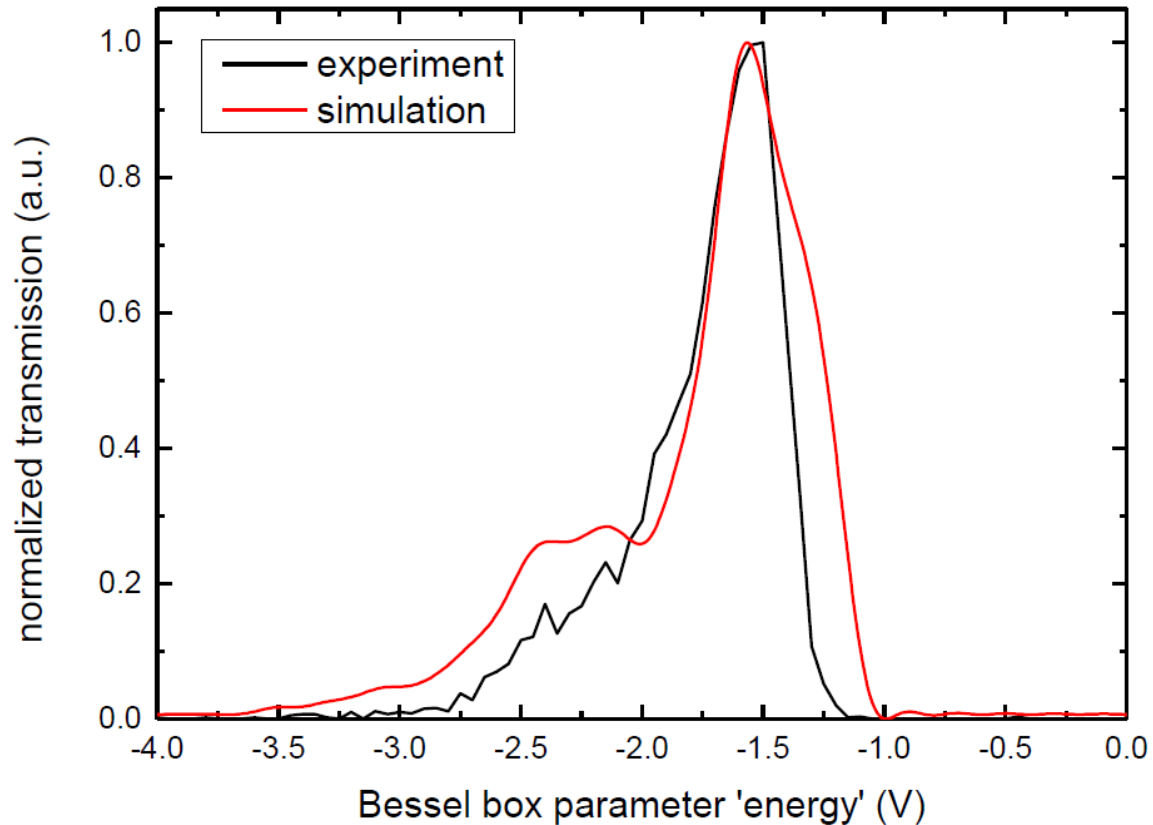
SIMION simulations



Real ion energy to maximize the transmission efficiency with all tuned MS parameters:  $E_{\text{ions}} = +0.8 \text{ eV}$

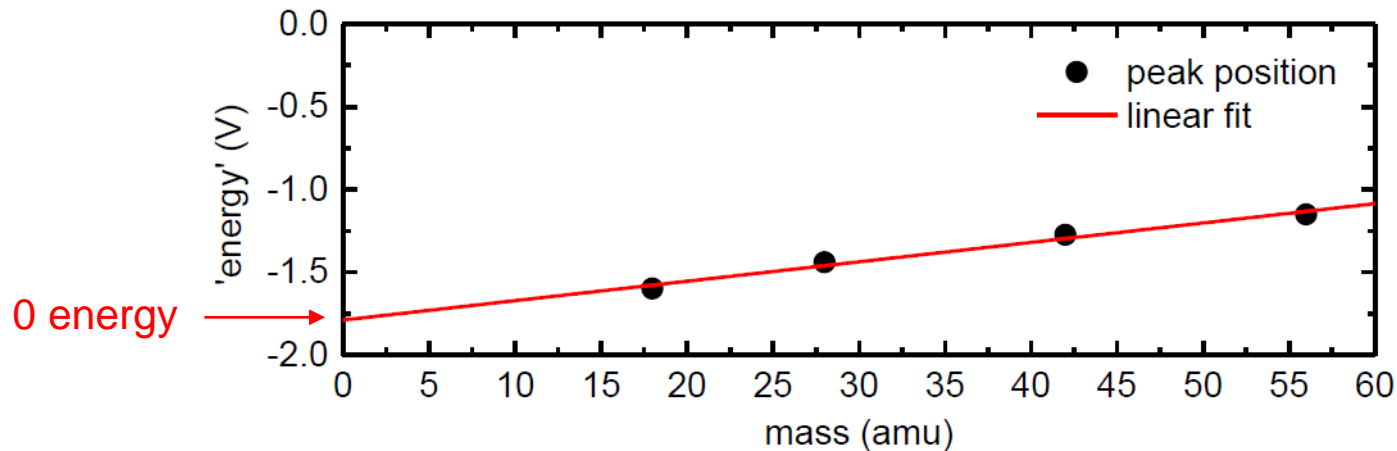
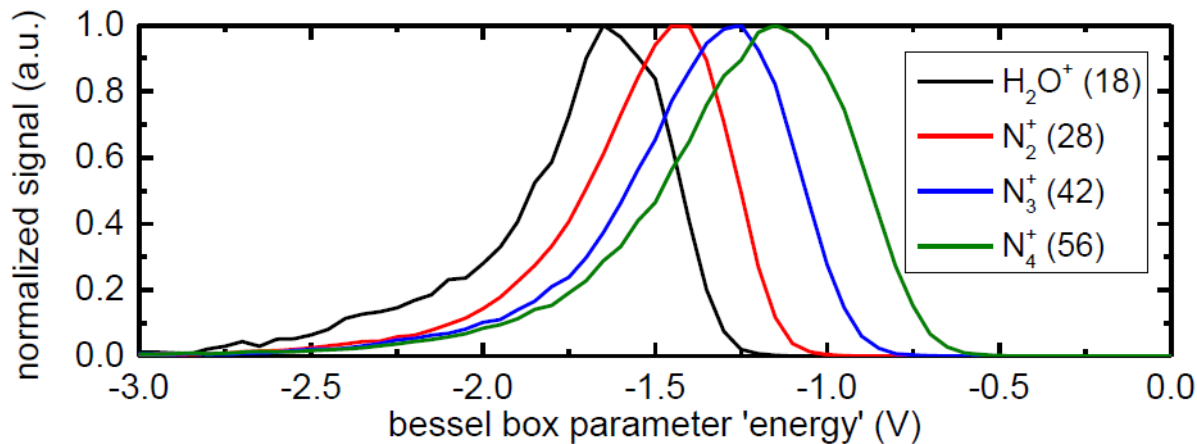
# Simulation of ion optics x measurement

## SIMION simulations



Real ion energy to maximize the transmission efficiency with all tuned MS parameters:  $E_{\text{ions}} = +0.8 \text{ eV}$

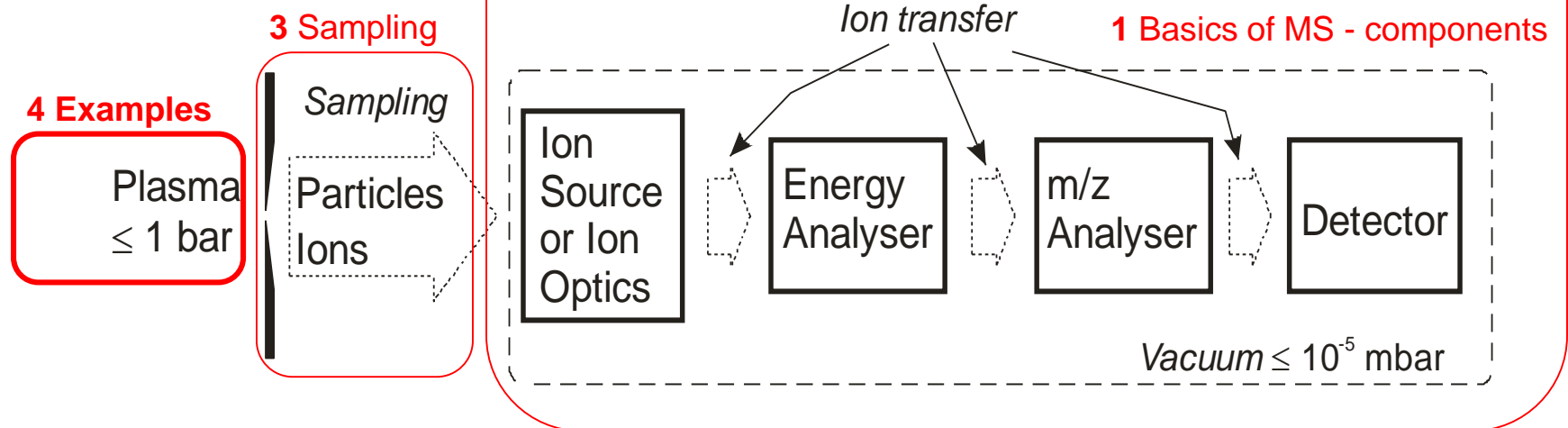
# Ion measurement from atmospheric plasmas



Seeded He beam – all ions reach the same velocity in the expansion – energy scales linearly with their mass!

# Outline

## 2 Species identification and quantification





# Example: analysis of an etch process of a-C:H

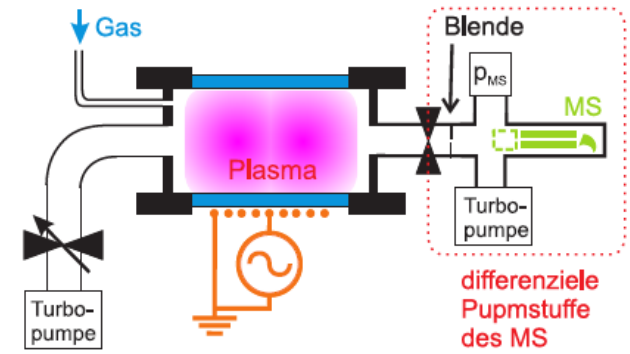
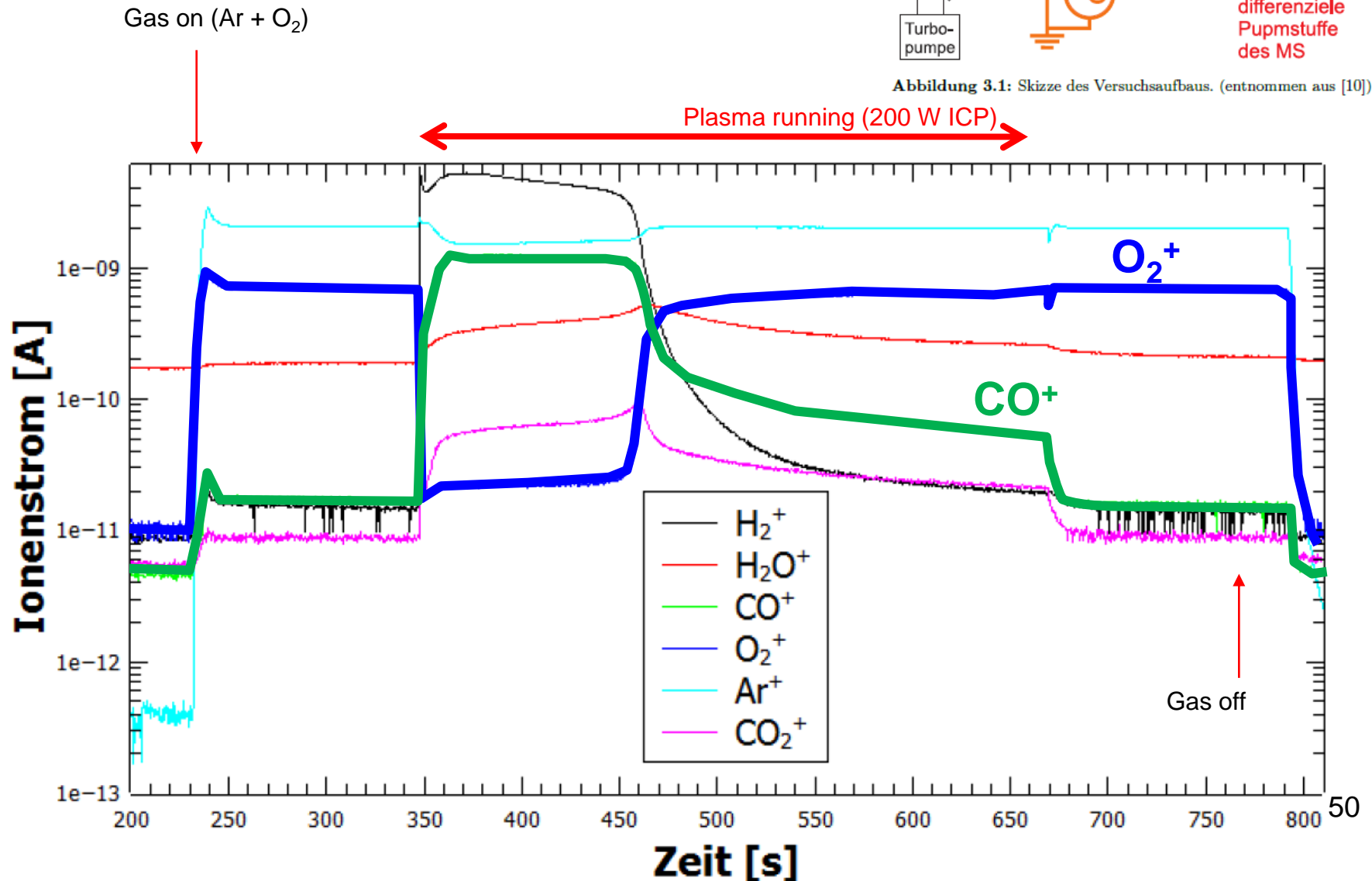
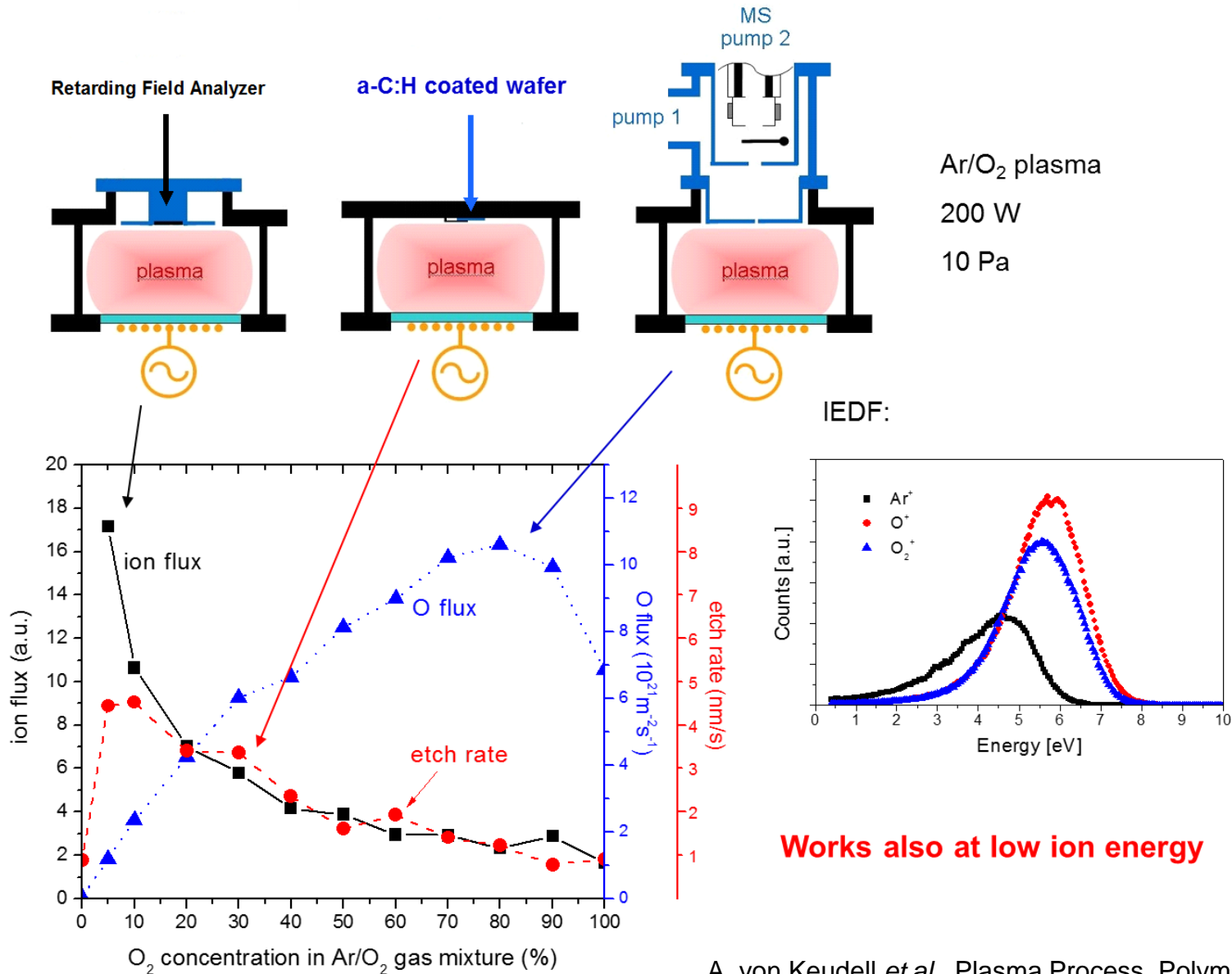


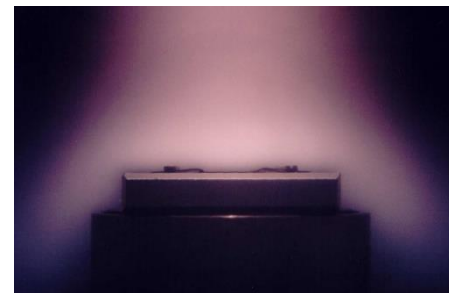
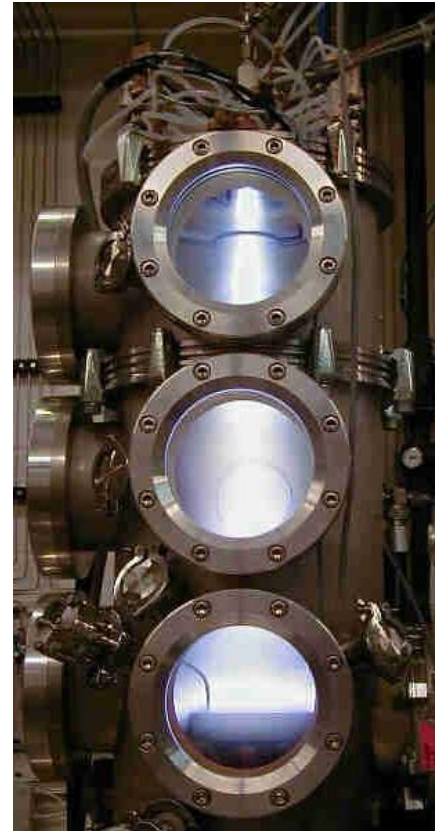
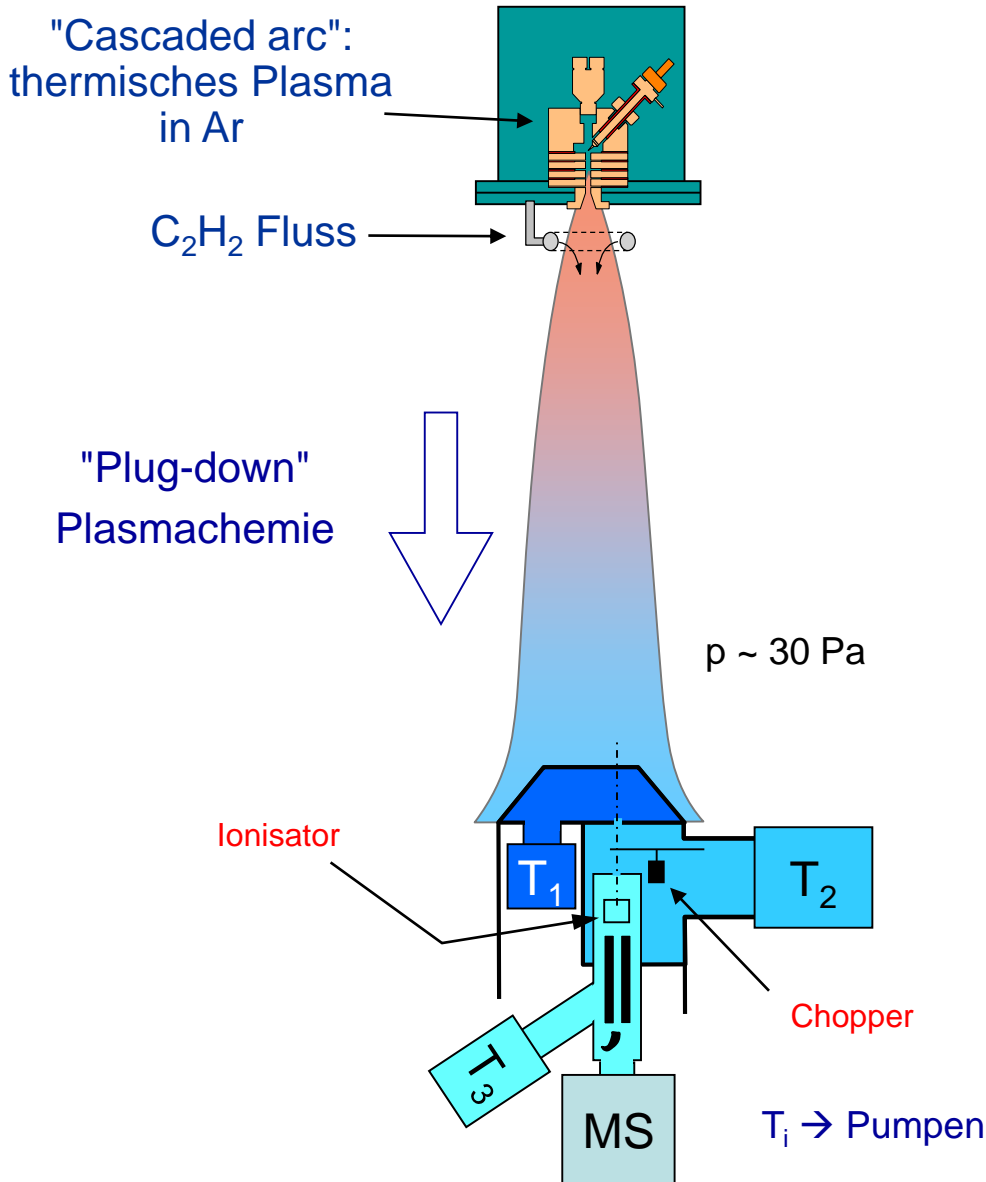
Abbildung 3.1: Skizze des Versuchsaufbaus. (entnommen aus [10])



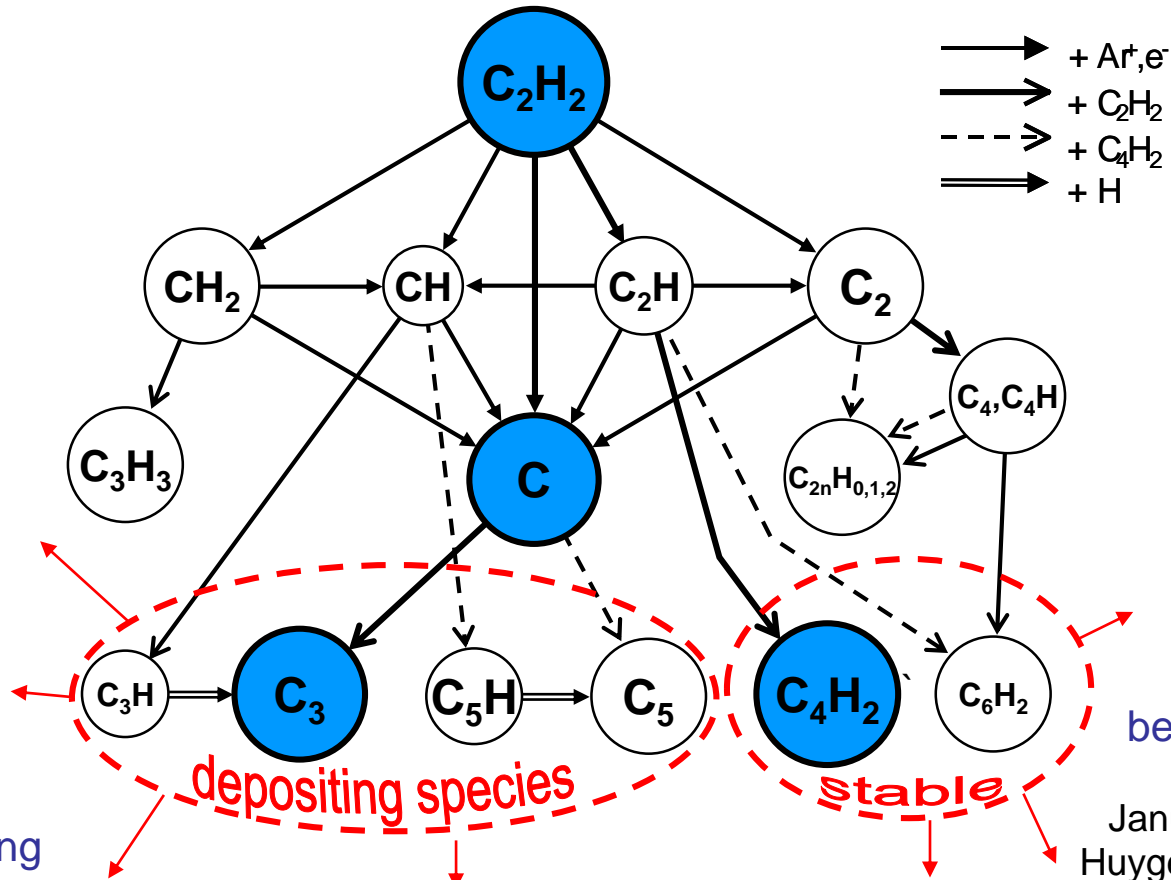
# Example: a-C:H etching mechanism in Ar/O<sub>2</sub> ICP



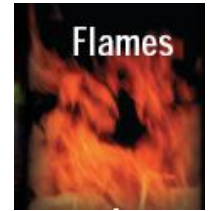
# Example: MS of radicals in C<sub>2</sub>H<sub>2</sub> plasma



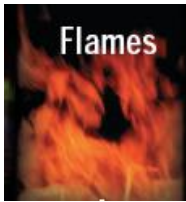
# Example: reaction path in Ar/C<sub>2</sub>H<sub>2</sub> plasma TU/e



im interstellaren Raum



Flames



Flames

bei der Verbrennung

bei der Verbrennung

Januar 2005:  
Huygens Sonde!



Neu:

bei der Abscheidung  
von a-C:H Schichten



in Fusionsreaktoren



auf dem Saturn-Mond Titan



53

# Example: Ion energy distribution functions in rf-plasma

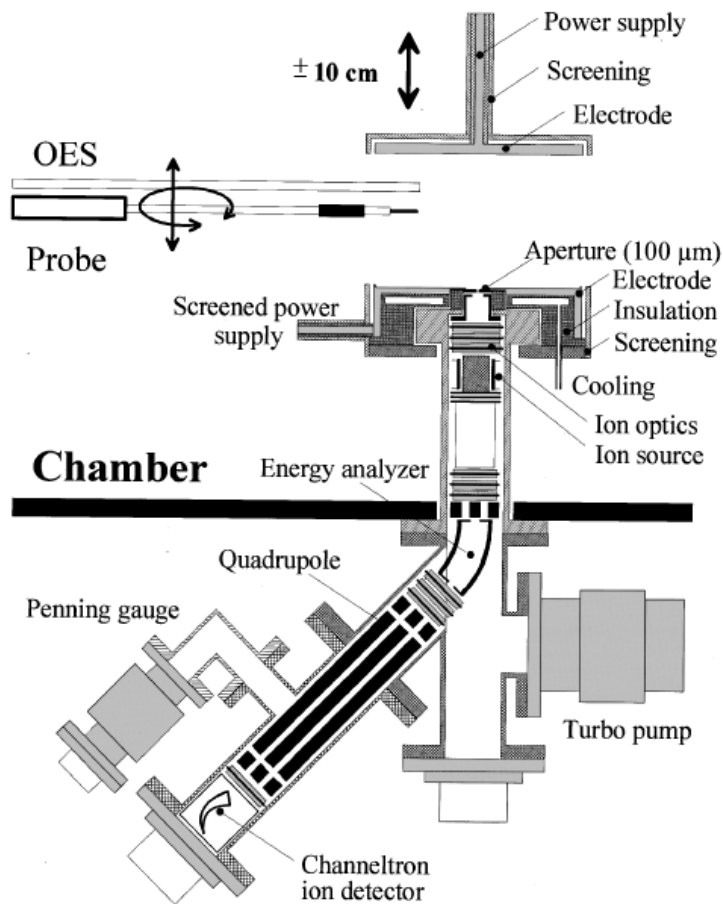
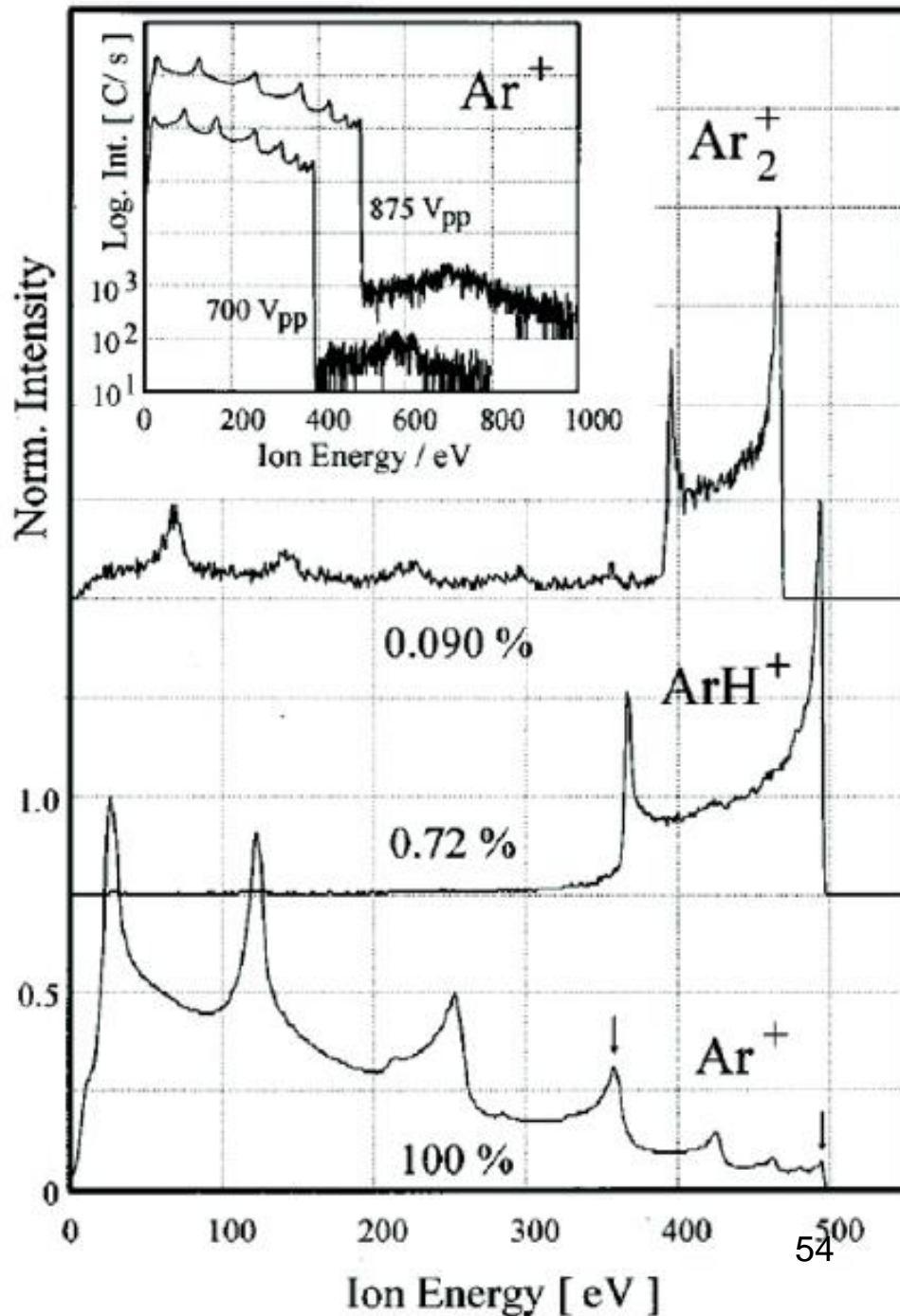
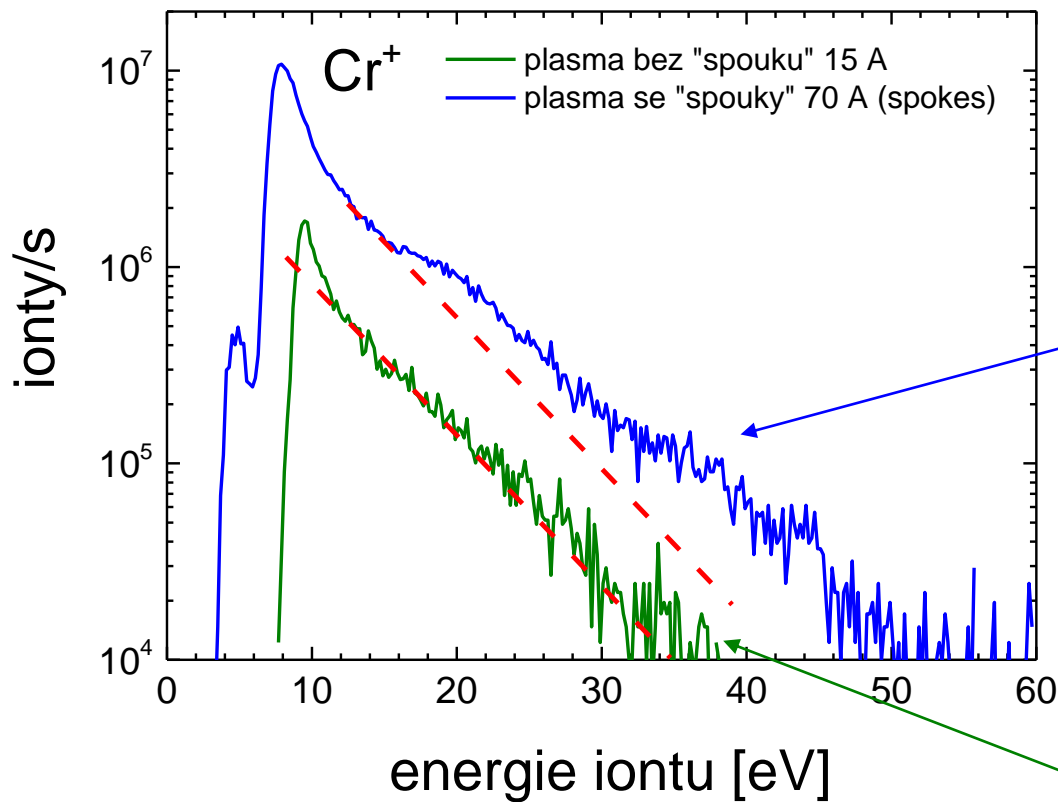


FIG. 1. Schematic diagram of the discharge arrangement.

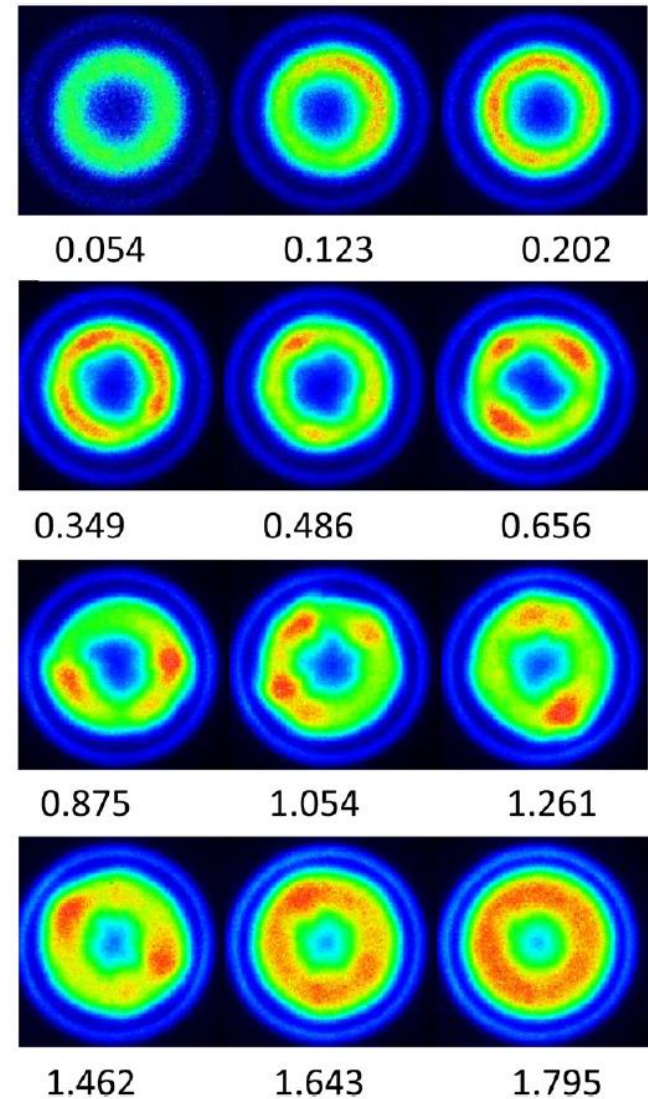
[92] Zeuner M, Neumann H and Meichsner J  
1997 J. Appl. Phys. 81 2985



# Example: Ion energy distribution functions in HiPIMS plasmas



Ionization zones ("spokes")



**Figure 2.** ICCD images of a chromium target at different power densities in  $\text{kW cm}^{-2}$  as indicated. The images are taken at  $180 \mu\text{s}$  of  $200 \mu\text{s}$  pulses and Ar at 0.26 Pa.

# Conclusions

MS is a powerful diagnostic for plasma analysis:

- Detects the relative fluxes of positive and negative ions including the information about their energies
- Provides absolute densities of neutral stable and reactive species
- Careful design of MS diagnostic setup important (is not trivial)
- Can be successfully applied to analysis of atmospheric pressure plasmas