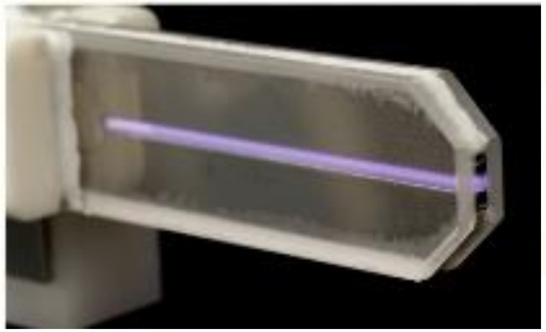


Mass Spectrometry for Atmospheric Pressure Plasmas

Jan Benedikt, Tristan Winzer, Tobias Hahn

Institut für Experimentelle und Angewandte Physik, Kiel University

Gert Willems, Simon Große-Kreul, Simon Schneider, Dirk Ellerweg

Research Department Plasmas with Complex Interactions, Ruhr University Bochum

Outline

Motivation

- The non-equilibrium atmospheric plasmas

Mass Spectrometry (MS)

Detection of reactive neutrals

- Molecular beam mass spectrometry (MBMS)
- Beam chopper with rotating skimmer
- Calibration issues in MBMS
- Threshold ionization MS (TIMS)

Detection of Ions

Analysis of Atmospheric Pressure Plasma jets

- Study of CO_2 conversion
- Time-resolved ion measurements in plasma needle

Conclusions

Motivation:

Non-equilibrium atmospheric pressure plasmas (APP)

Cold with T_{gas}<40°C, T_{el} > 20 000 K

Ozonizer, from 1857

6 t O_3/day Ozonia Ltd.

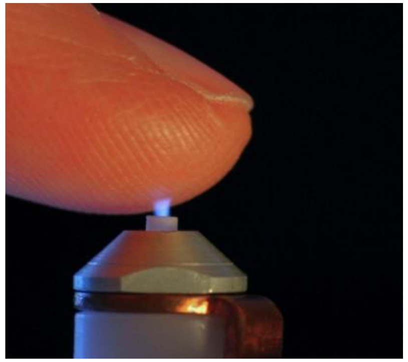
Established applications of APP:

- O_3 generation
- Surface activation: painting of plastics
- Excimer lamps in VUV und UV
- Air cleaning, particle precipitation

Drexel

Emerging applications of APP:

- Plasma medicine
- Plasmas with or in liquids
- Material synthesis:
  thin film deposition,
  nanoparticle generation



RUB

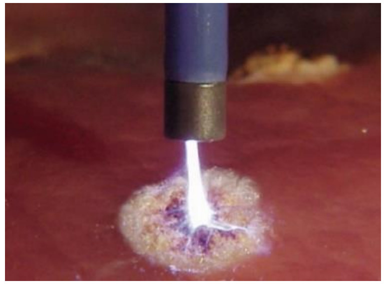
CINOGY

Motivation:

APP in contact with tissues and liquids

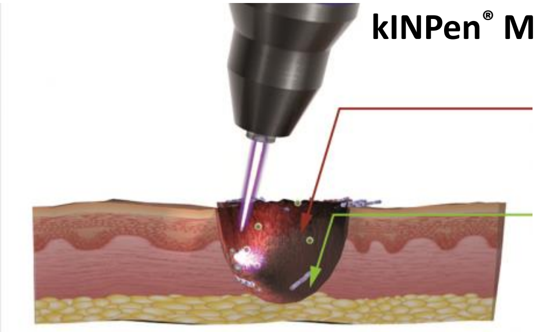
Plasma medicine, therapeutic plasma applications

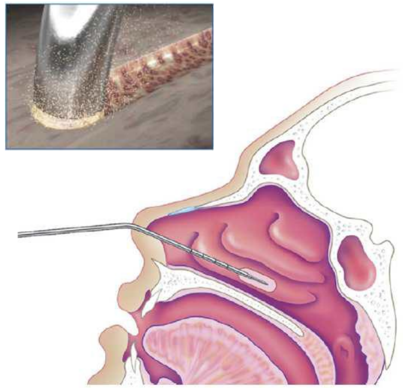
ERBE



CINOGY, PlasmaDerm® Quelle

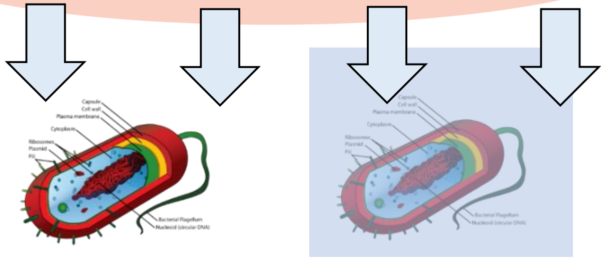
neoplas tools MEDICAL PLASMA





ArthroCare® Corporation

radicals ions + e$^-$ photons fields



free-standing or in aqueous solutions

Unique effect due to combination of several plasma components

Radical effects dominate

Outline

Motivation

- The non-equilibrium atmospheric plasmas

Mass Spectrometry (MS)

Detection of reactive neutrals

- Molecular beam mass spectrometry (MBMS)
- Beam chopper with rotating skimmer
- Calibration issues in MBMS
- Threshold ionization MS (TIMS)

Detection of Ions

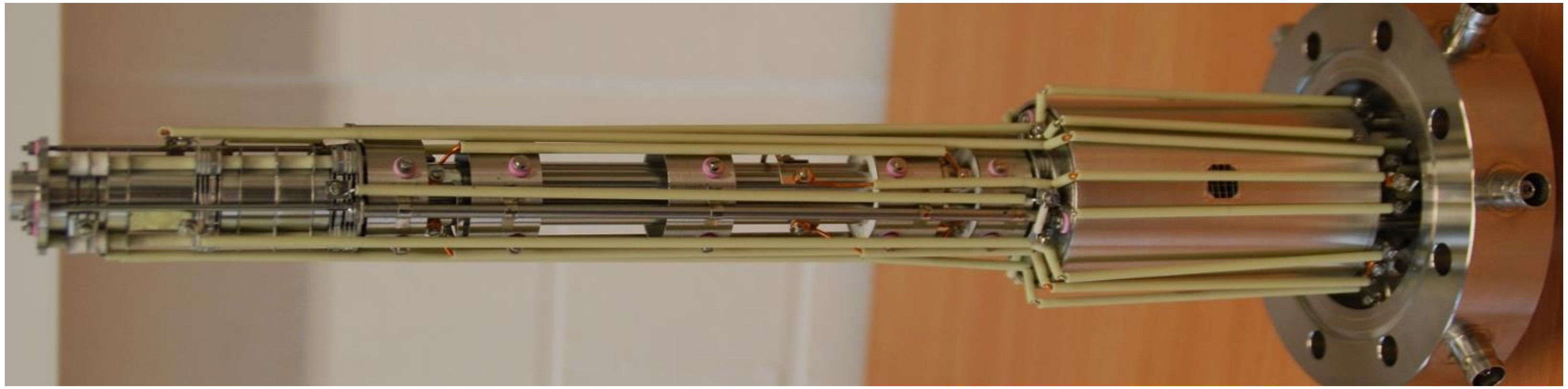
Analysis of Atmospheric Pressure Plasma jets

- Study of CO_2 conversion
- Time-resolved ion measurements in plasma needle

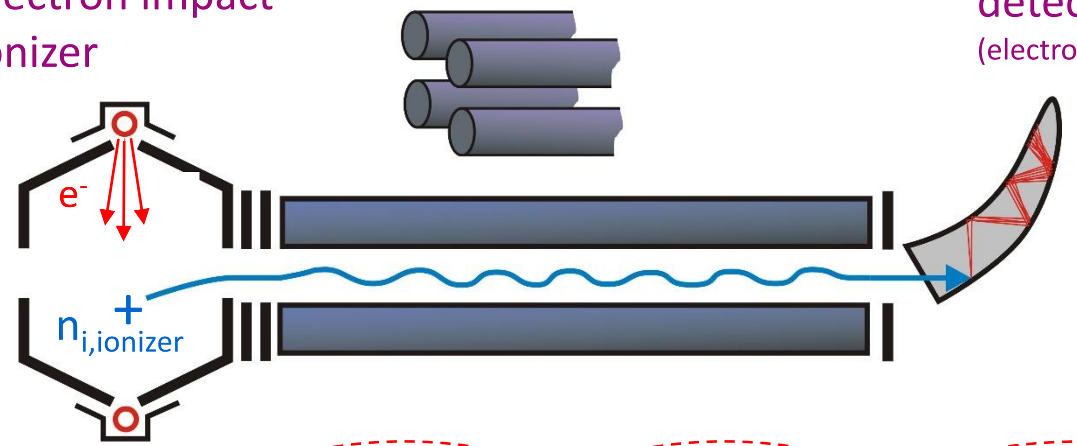
Conclusions

Why mass spectrometry?

- Versatile diagnostic technique measuring mass (and energy) resolved ions at a detector
- Can be used to measure neutral species as well as ions, typically in their ground state
- Not limited e.g. by existence of reachable optical transitions or quenching
- Measures densities at the wall - place of plasma treatment
- Can be absolutely calibrated (neutrals)



Neutral mass spectrometry: signal calibration



p <10^{-5} mbar

$$S_i = T(m_i)\cdot\theta(m_i)\cdot\beta\cdot L_{ionizer}\cdot I_e\cdot\sigma_i(E_{el})\cdot n_{i,ionizer}$$

mass filter And detector | ionizer | detected species

Signal calibration: measurement of species with known density

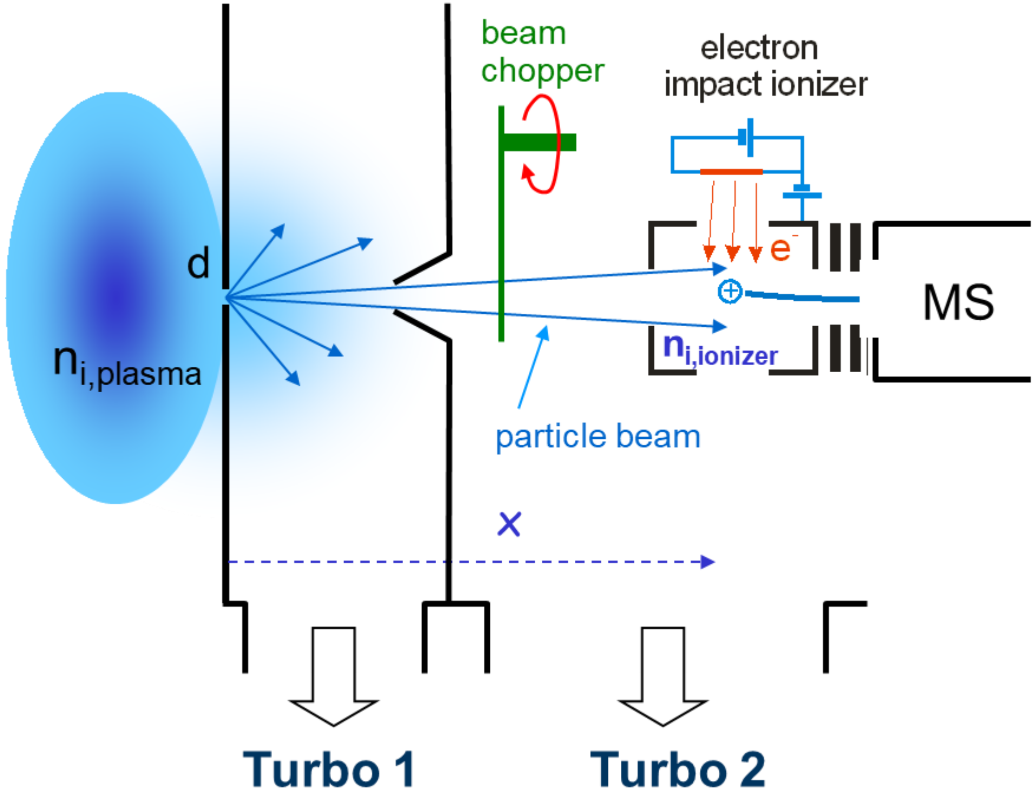
$$n_{i,ionizer} = F\left(m_i, m_{cal}\right)\cdot\frac{\sigma_{cal}(E_{el})}{\sigma_i(E_{el})}\cdot\frac{n_{cal,ionizer}}{S_{cal}}\cdot S_i$$

Measurement of the species from the plasma?

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

Plasma Diagnostics with mass spectrometry: Molecular Beam Mass Spectrometry (MBMS)

Multiple stage differential pumping



Aligned orifices →

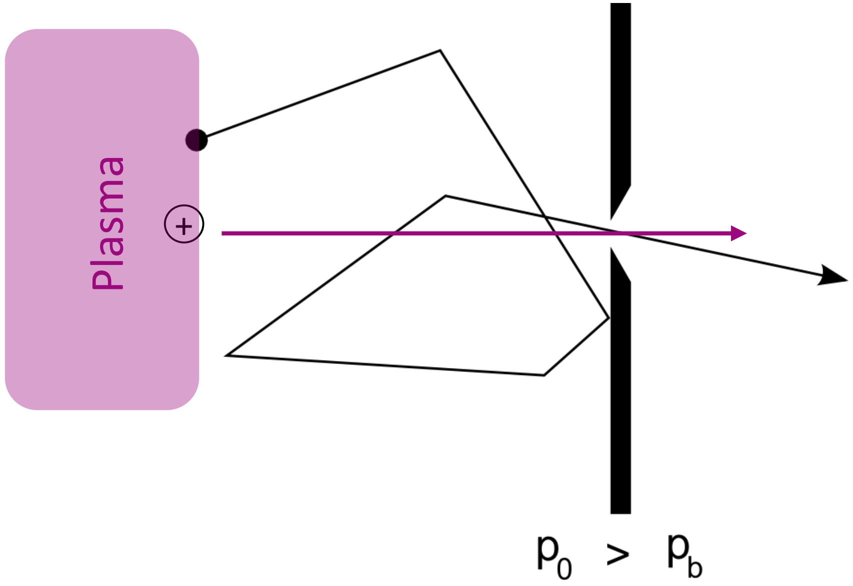
Molecular Beam (MB) formed

- Line-of-sight to ionizer
- Background pressure reduced
- Beam chopper for BG subtraction

Molecular Beam Sampling

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

$K_n > 1$ Free molecular flow without collisions



- sheath non-collisional or weakly collisional for ions → directed movement
- non-collisional sampling in orifice and molecular flow on MS side → no composition distortion

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

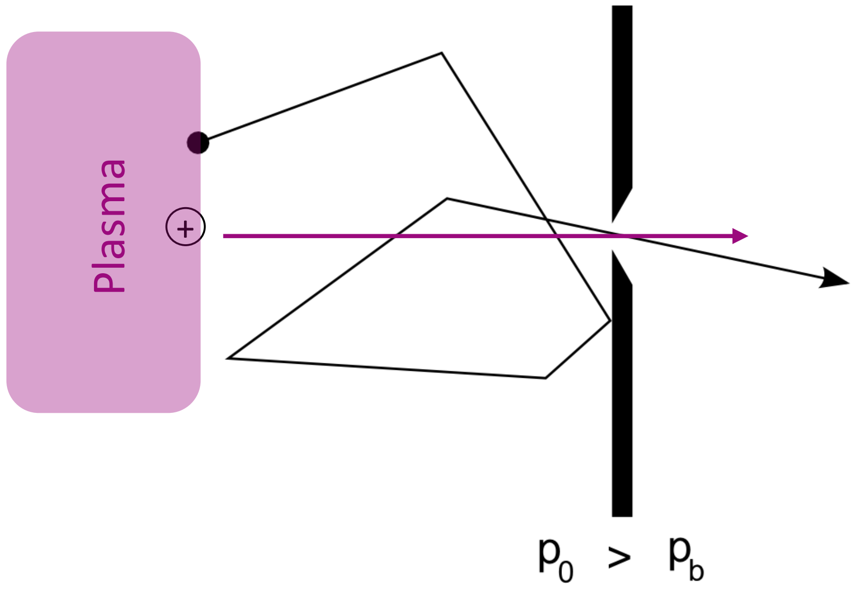
Große-Kreul *et al.*, Plasma Sources Sci. Technol. 24 (2015) 044008

Große-Kreul *et al.*, Eur. Phys. J. D 70 (2016) 103

Molecular Beam Sampling

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

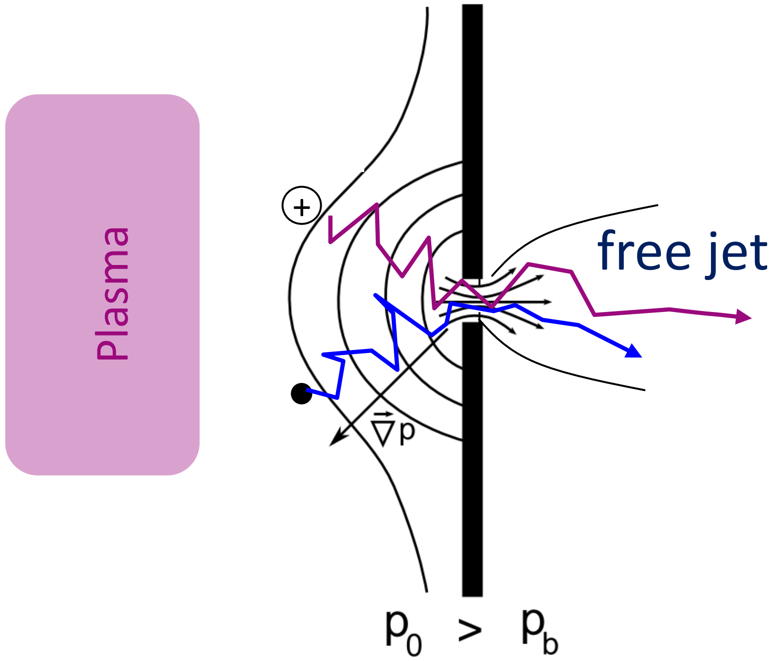
$K_n > 1$ Free molecular flow without collisions



- sheath non-collisional or weakly collisional for ions → directed movement
- non-collisional sampling in orifice and molecular flow on MS side → no composition distortion

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

$K_n << 1$ Collisional „continuum“ sampling



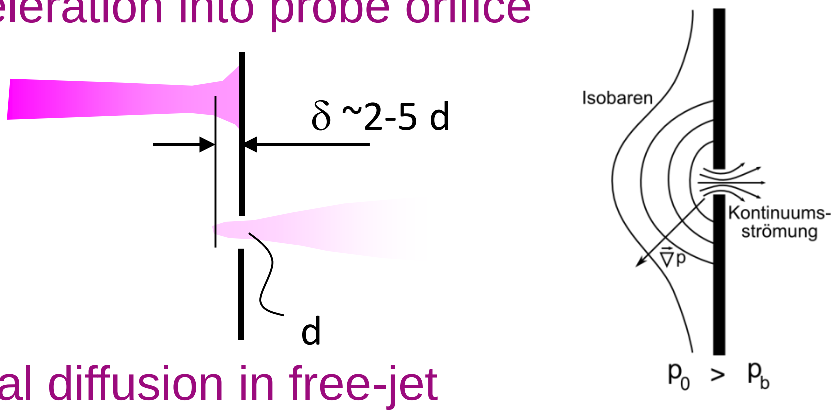
- sheath and sampling collisional → pressure gradient in front of the orifice
- supersonic expansion behind the orifice
  → free jet
  → composition distortion
  → seeded molecular beam

Große-Kreul *et al.*, Plasma Sources Sci. Technol. 24 (2015) 044008

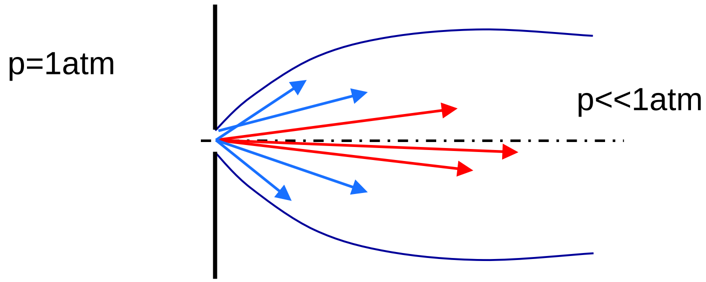
Große-Kreul *et al.*, Eur. Phys. J. D 70 (2016) 103

Molecular Beam Sampling composition distortion

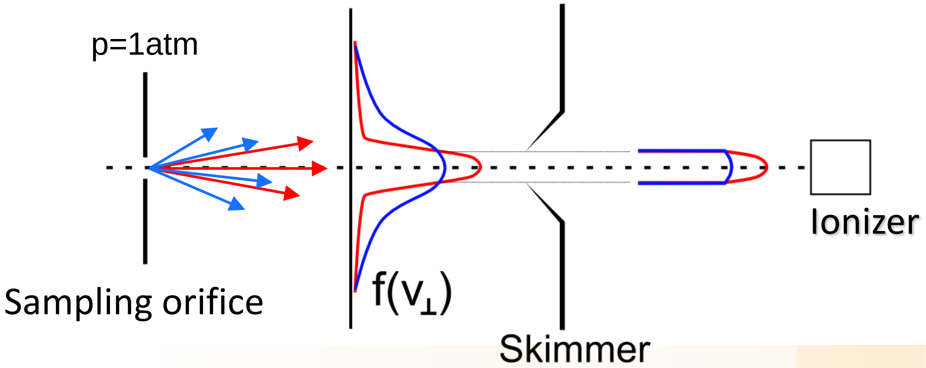
- Acceleration into probe orifice



- Radial diffusion in free-jet

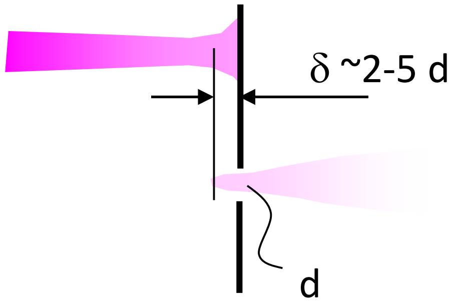


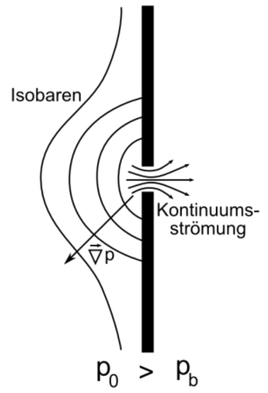
- Mach-number focusing



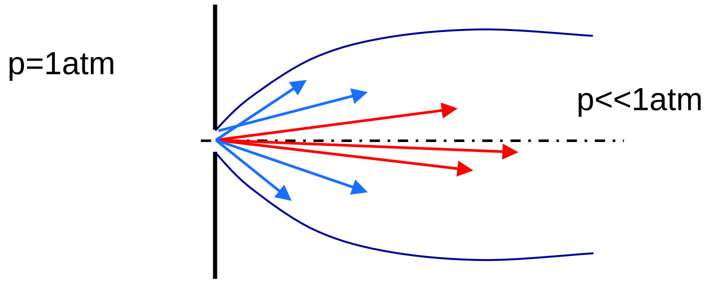
Molecular Beam Sampling composition distortion

- Acceleration into probe orifice

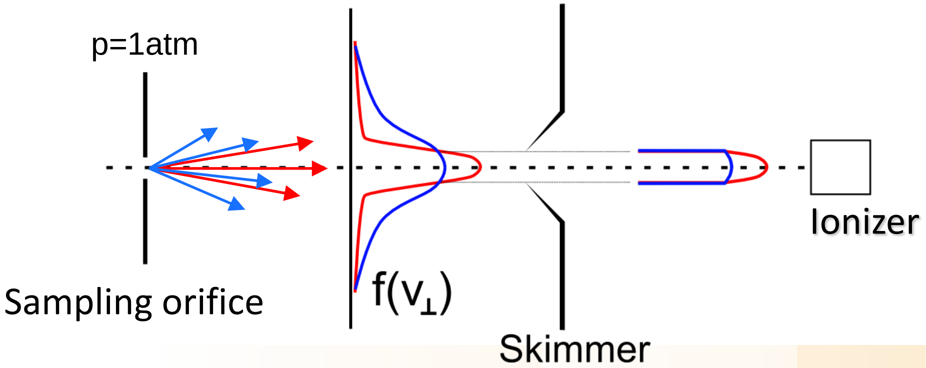




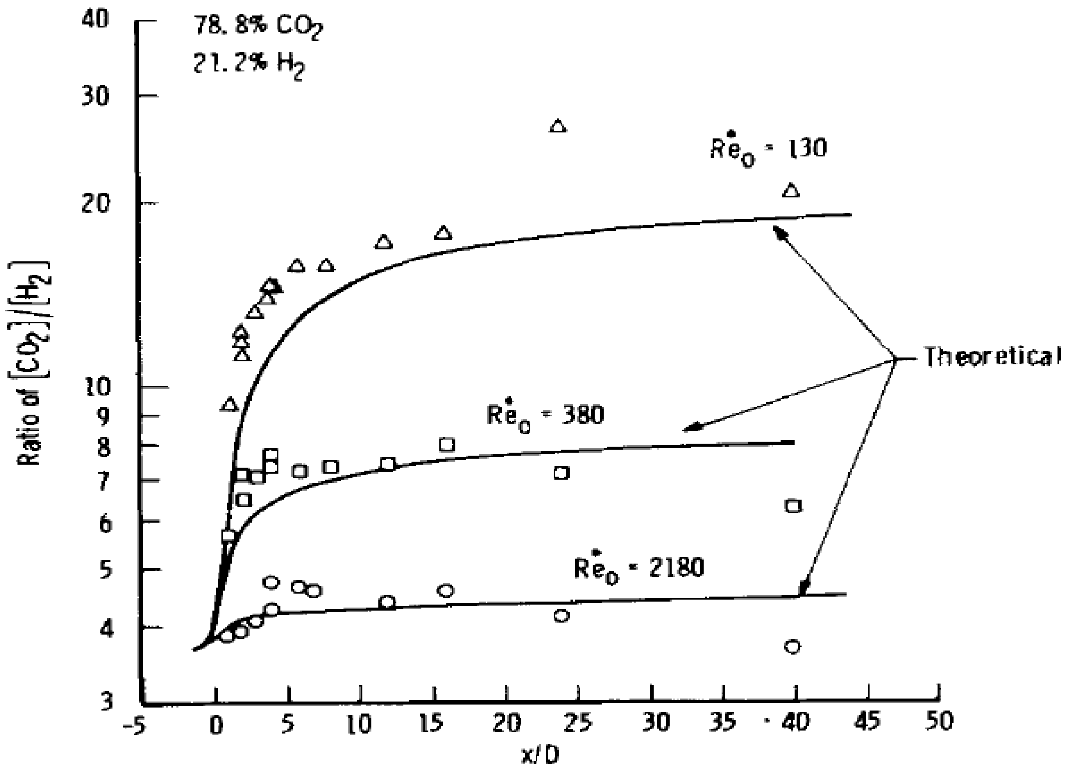
- Radial diffusion in free-jet



- Mach-number focusing

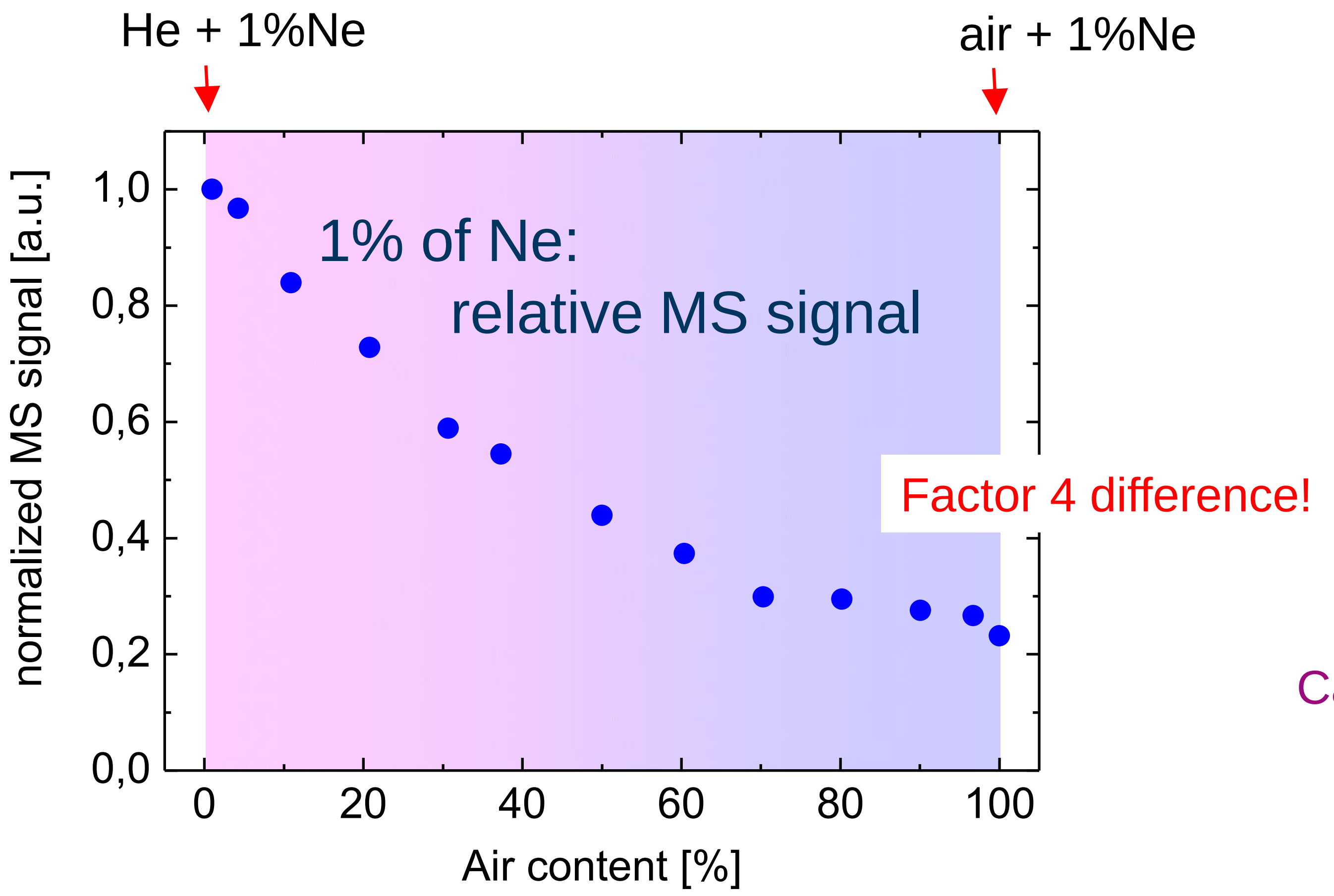


McCay T.D. et al., Phys. Fluids 26 (1983) 2115



MS calibration: effect of composition distortion

The change of the gas mixture has to be considered



Calibration gas should be measured under identical conditions as the species of interesst

Atomic O calibrated with Ne
O_3 calibrated with N_2O

D. Ellerweg *et al.*, New J. Physics **12** (2010) 013021
Corrigendum: G. Willems *et al.*, New J. Phys. 19 (2019) 059501

Molecular Beam Sampling: free jet to „vacuum“

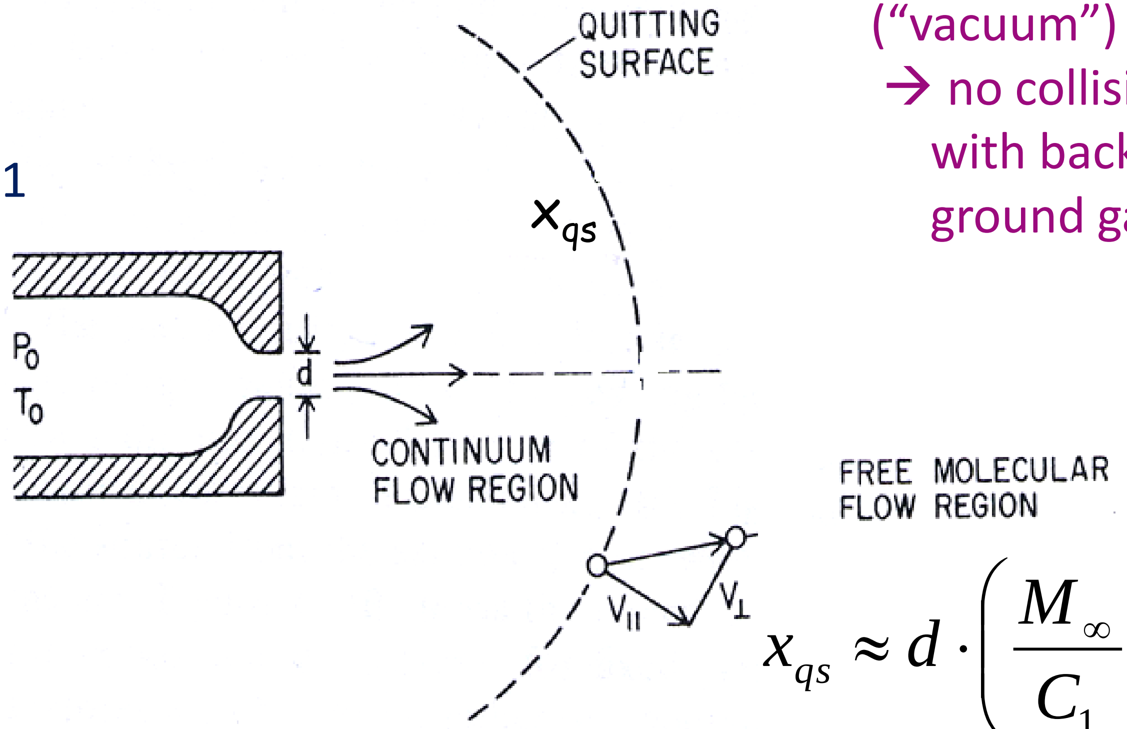
Supersonic „free jet“ expansion $(\lambda << d)$

$$\frac{P_o}{P_b} > \left(\frac{\gamma+1}{2}\right)^{\frac{\gamma}{\gamma-1}}$$

↓

Max 2.1

Low pressure (“vacuum”)
→ no collisions with back-ground gas

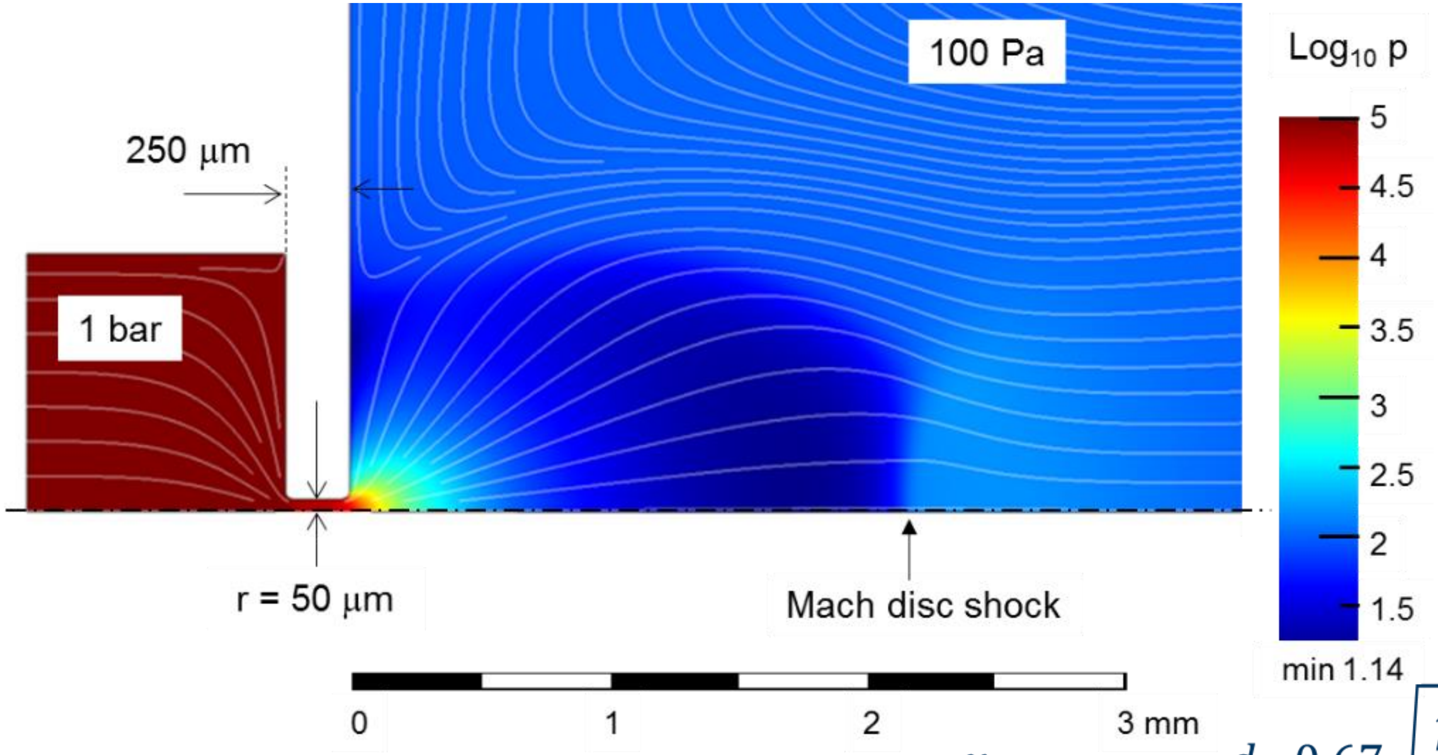


$$x_{qs} \approx d \cdot \left(\frac{M_\infty}{C_1}\right)^{1/(\gamma-1)}$$

Preferred case for the MB sampling from high pressure

Molecular Beam Sampling: free jet to background gas

Compressible Navier-Stokes equations for Ar



$$x_{Mach\ disk} = d \cdot 0.67 \sqrt{\frac{p_0}{p_{BG}}}$$

p_{BG} [Pa]	$x_{Mach\ disk}$ [mm]
100	2.1
10	6.7

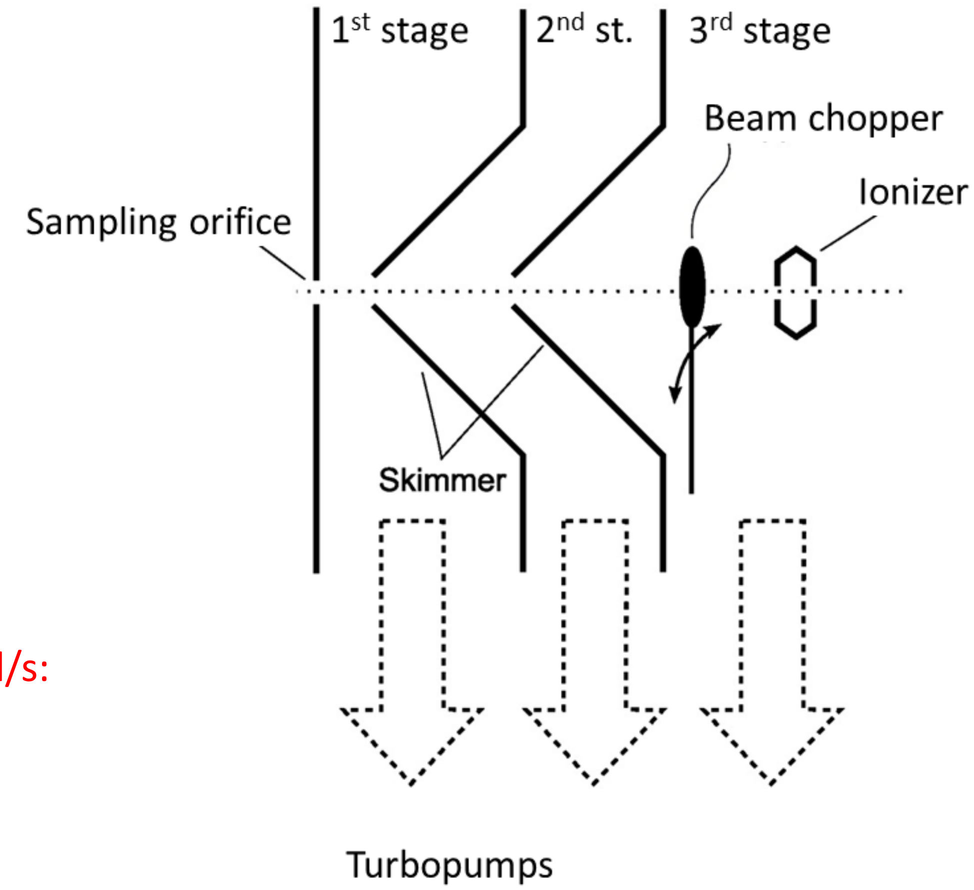
Typical MBMS system configuration

- Three pumping stages
- Beam-to-background ~1
- Chopper mounted in the 3rd stage

Used e.g. for analysis of
Combustion processes

But:
With 100 μm diameter sampling orifice
and effective pumping in 1st stage of 50 l/s:

$p_{BG,1st}$ ~ 10 Pa !



Outline

Motivation

- The non-equilibrium atmospheric plasmas

Mass Spectrometry (MS)

Detection of reactive neutrals

- Molecular beam mass spectrometry (MBMS)
- Beam chopper with rotating skimmer
- Calibration issues in MBMS
- Threshold ionization MS (TIMS)

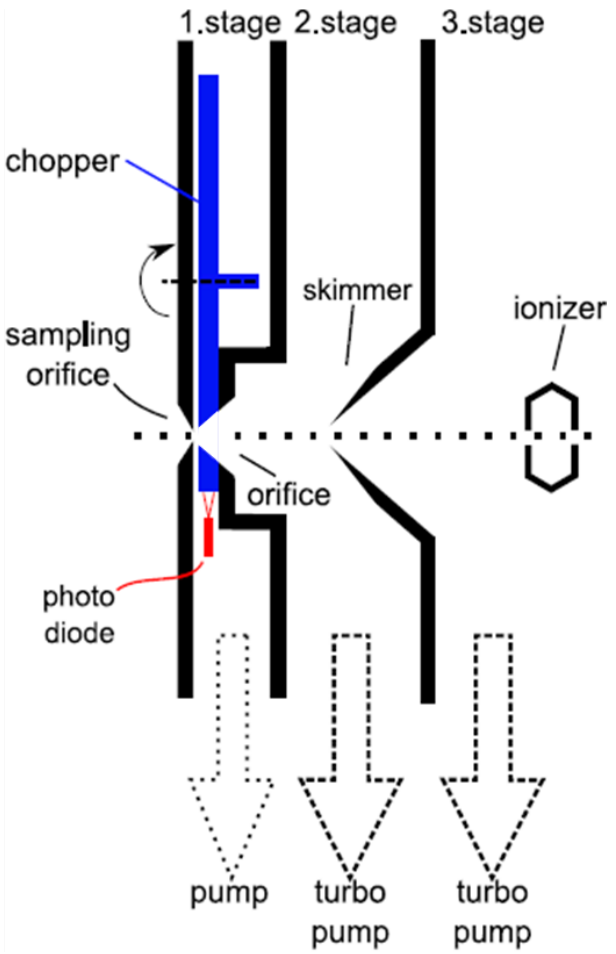
Detection of Ions

Analysis of Atmospheric Pressure Plasma jets

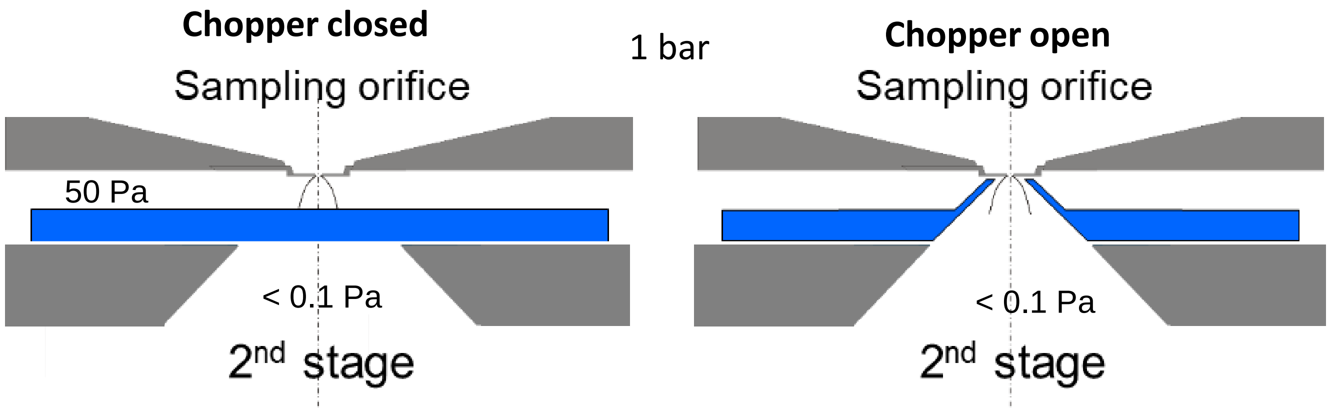
- Study of CO_2 conversion
- Time-resolved ion measurements in plasma needle

Conclusions

MBMS with special chopper design



Rotating chopper (14 Hz) with an imbedded skimmer

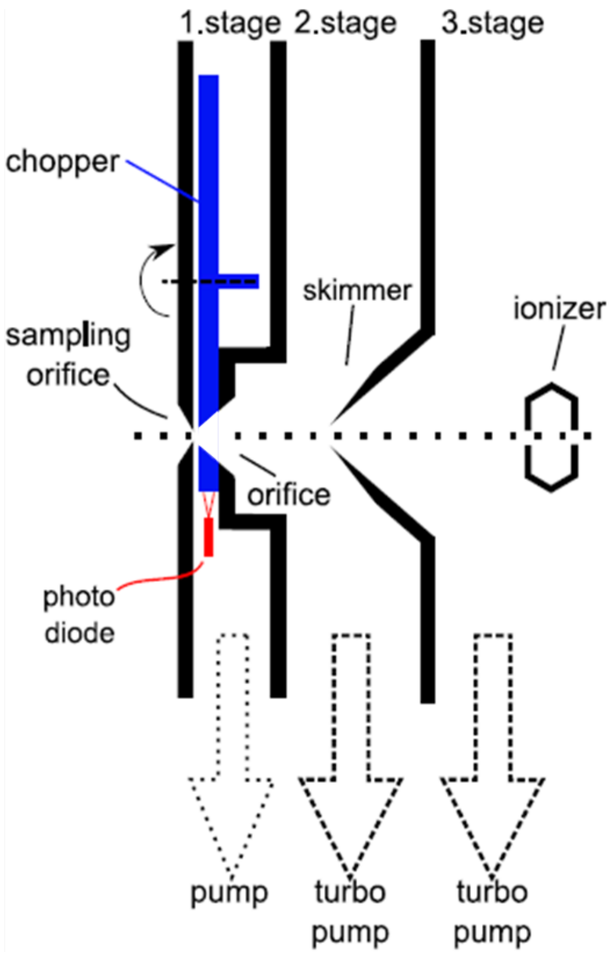


Chopper separates 1st and 2nd stage – it closes effectively the connection to the atmosphere → low pressures are achieved

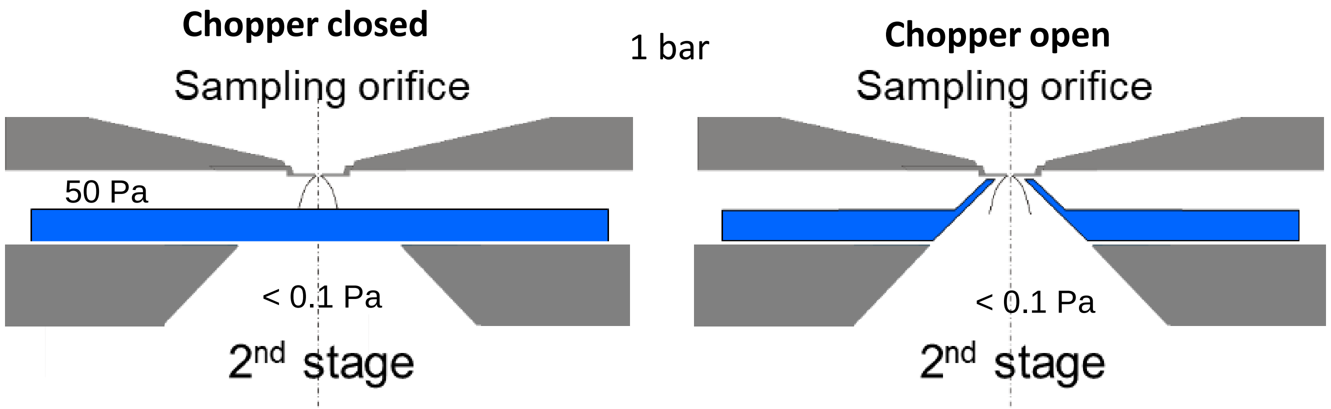
Allows formation of MB for a short time, which expands to a god vacuum region → very high beam-to-BG ratio can be achieved

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

MBMS with special chopper design

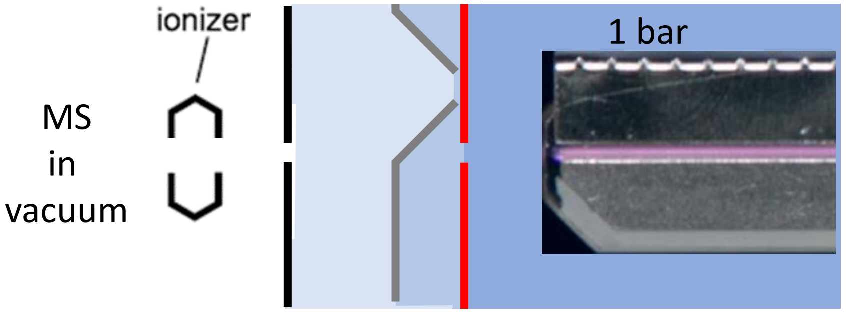


Rotating chopper (14 Hz) with an imbedded skimmer

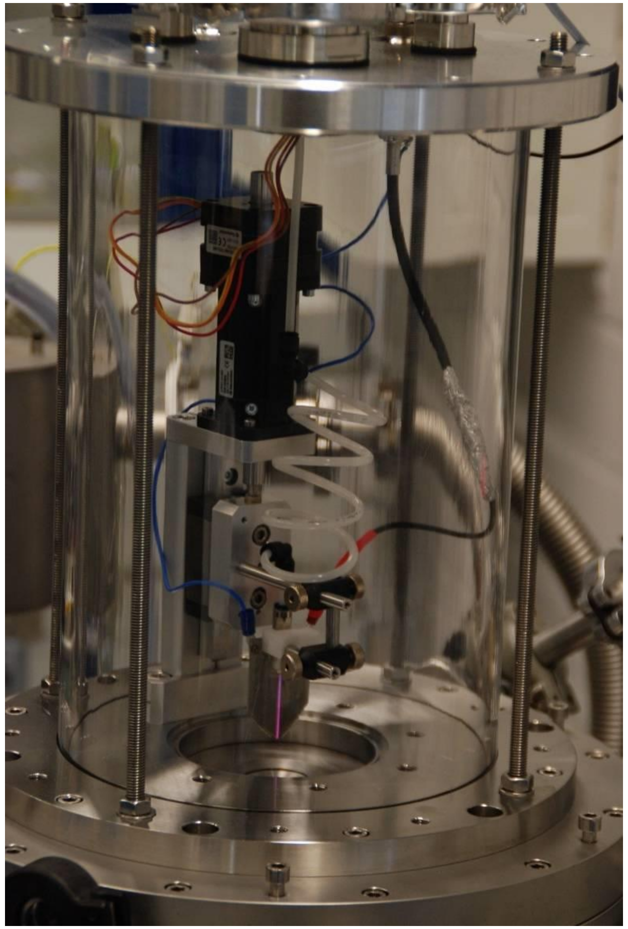


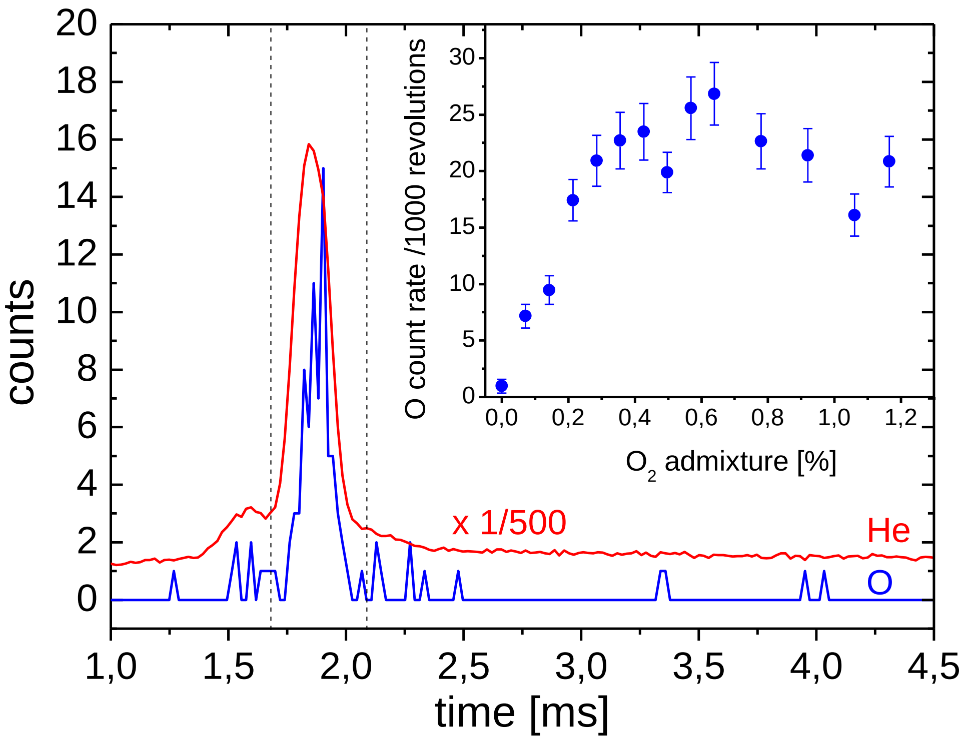
Chopper separates 1st and 2nd stage – it closes effectively the connection to the atmosphere → low pressures are achieved

Allows formation of MB for a short time, which expands to a god vacuum region → very high beam-to-BG ratio can be achieved

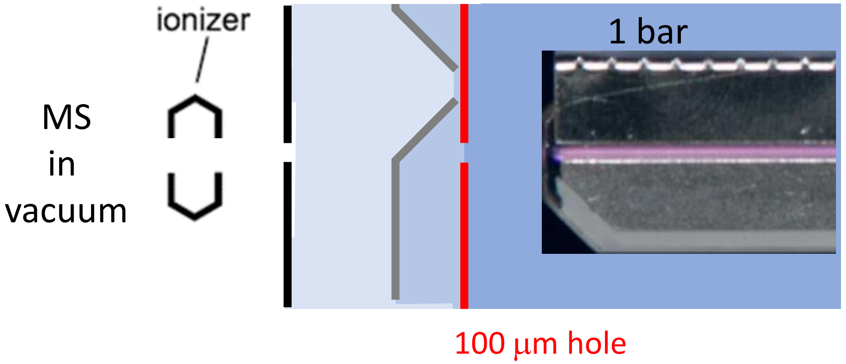


Atomic oxygen in He/O_2 microplasma jet





Benedikt *et al.*,
Rev. Sci. Instrum. 2009, 80, 055107



Outline

Motivation

- The non-equilibrium atmospheric plasmas

Mass Spectrometry (MS)

Detection of reactive neutrals

- Molecular beam mass spectrometry (MBMS)
- Beam chopper with rotating skimmer
- Calibration issues in MBMS
- Threshold ionization MS (TIMS)

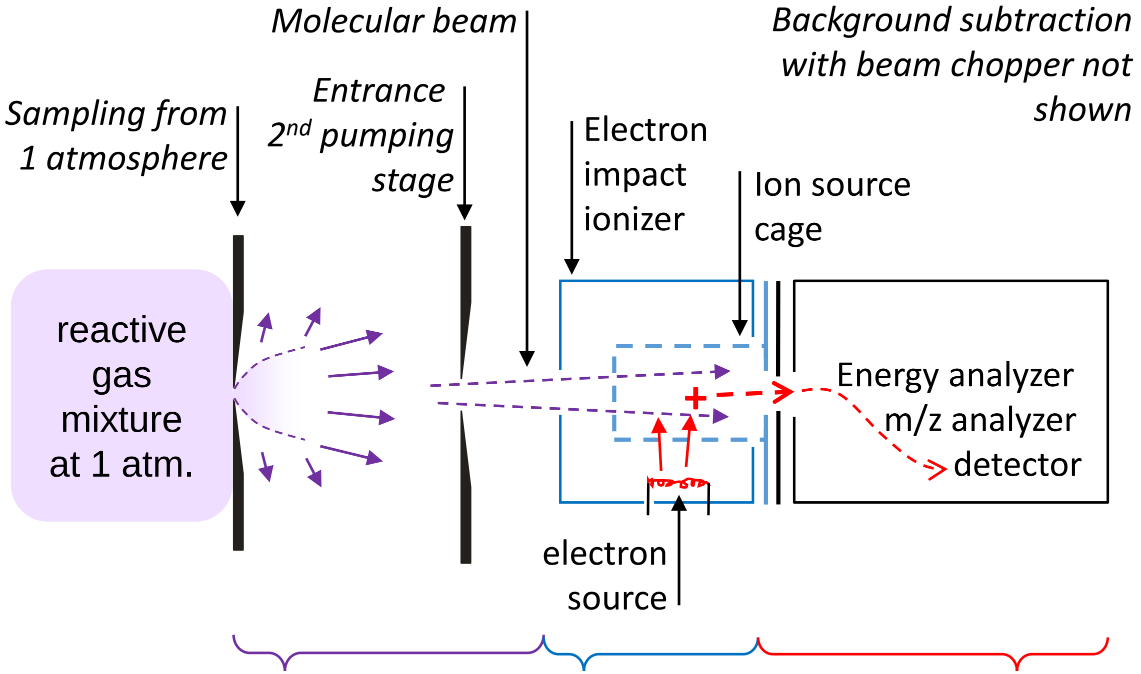
Detection of Ions

Analysis of Atmospheric Pressure Plasma jets

- Study of CO_2 conversion
- Time-resolved ion measurements in plasma needle

Conclusions

Important issues in signal calibration



Expansion with com-position distortions:
Acceleration into orifice
Radial diffusion
Mach-number focusing

Signal scaling with:
Electron emission current
Ionization cross section
Effective ionizer length
Ion extraction efficiency

Signal scaling with:
Mass-dependent ion transmission function

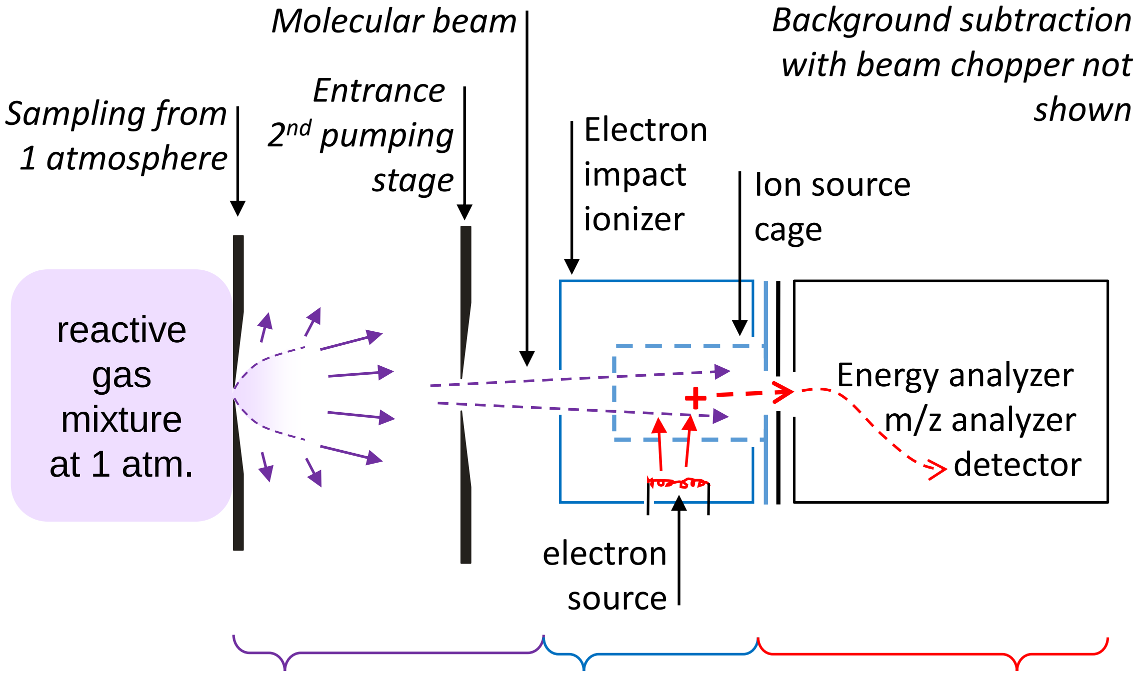
$$n_i^{mixture} \longrightarrow n_i^{ionizer}$$

$$\downarrow$$

$$\phi_i^{ionizer} \longrightarrow S_i^{detector}$$

G. Willems *et al.*, New J. Phys. 19 (2019) 059501

Important issues in signal calibration



Expansion with composition distortions:
Acceleration into orifice
Radial diffusion
Mach-number focusing

Signal scaling with:
Electron emission current
Ionization cross section
Effective ionizer length
Ion extraction efficiency

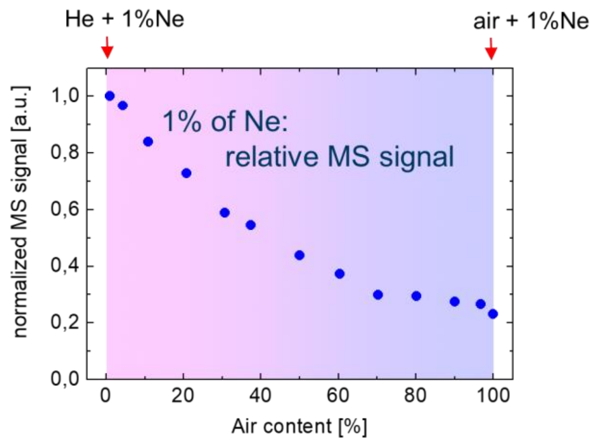
Signal scaling with:
Mass-dependent ion transmission function

$$n_i^{mixture} \longrightarrow n_i^{ionizer}$$

$$\downarrow$$

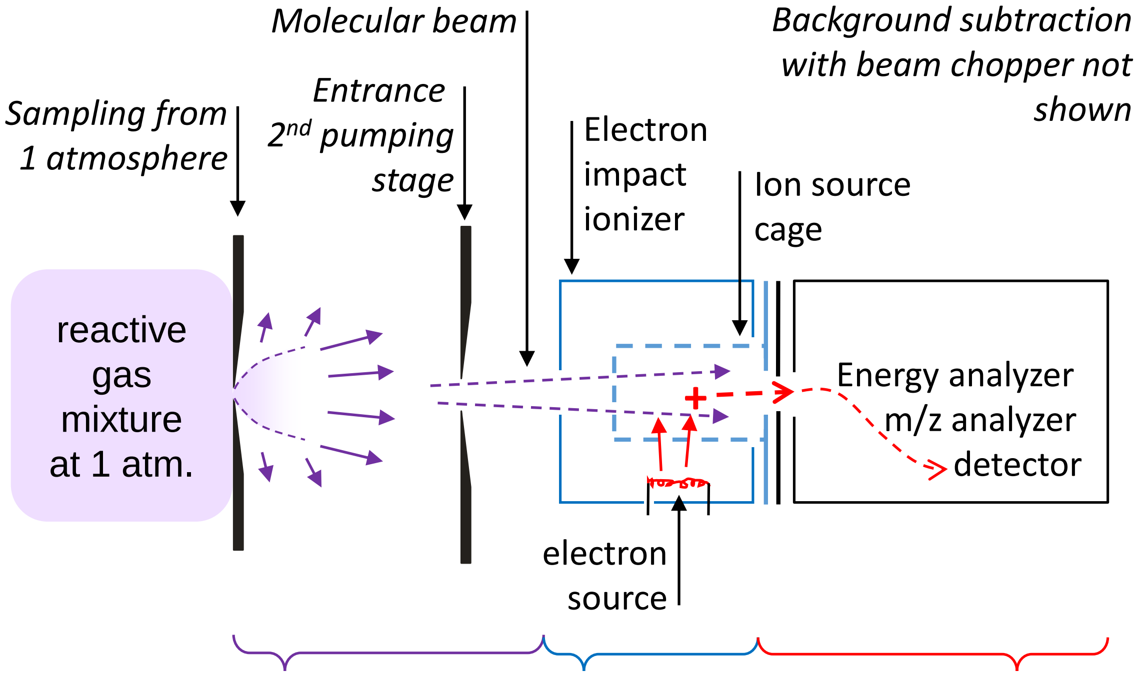
$$\phi_i^{ionizer} \longrightarrow S_i^{detector}$$

1) Composition distortion important



G. Willems *et al.*, New J. Phys. 19 (2019) 059501

Important issues in signal calibration



Expansion with composition distortions:
Acceleration into orifice
Radial diffusion
Mach-number focusing

Signal scaling with:
Electron emission current
Ionization cross section
Effective ionizer length
Ion extraction efficiency

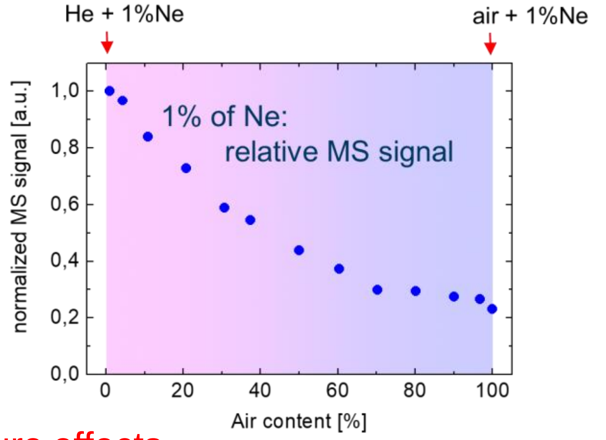
Signal scaling with:
Mass-dependent ion transmission function

$n_i^{mixture} \longrightarrow n_i^{ionizer}$

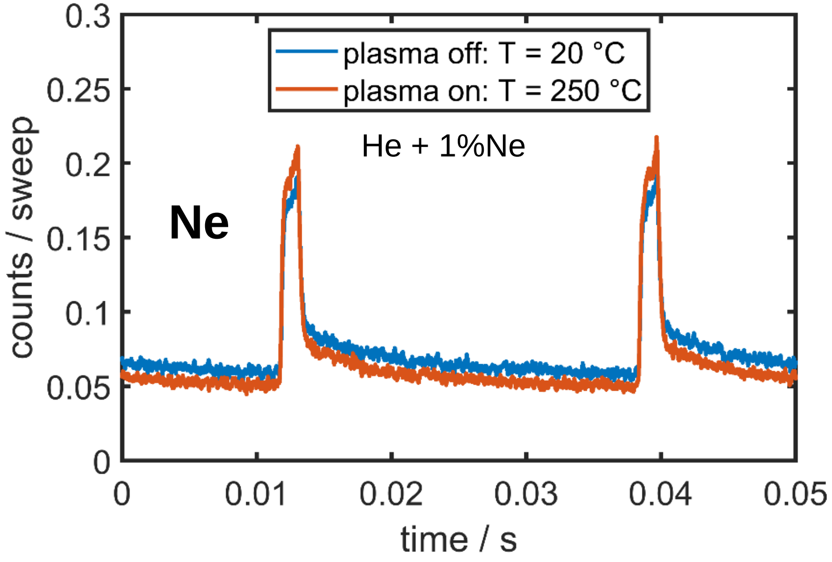
$\downarrow$

$\phi_i^{ionizer} \longrightarrow S_i^{detector}$

1) Composition distortion important

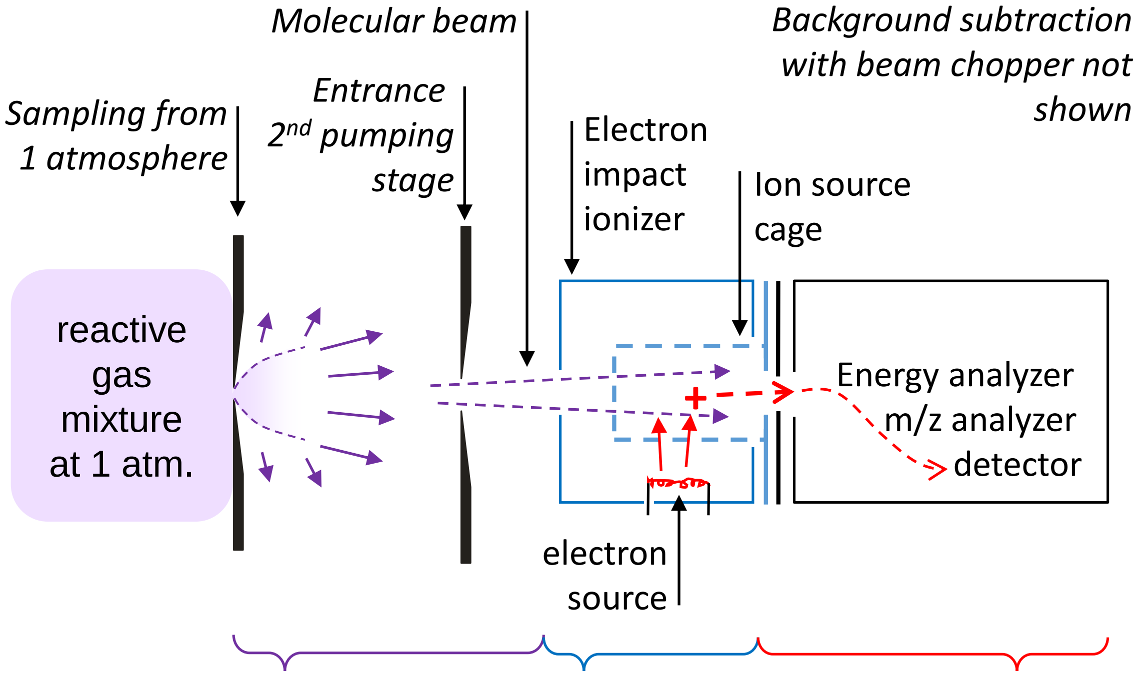


→ Including gas temperature effects



G. Willems *et al.*, New J. Phys. 19 (2019) 059501

Important issues in signal calibration



Expansion with composition distortions:
Acceleration into orifice
Radial diffusion
Mach-number focusing

Signal scaling with:
Electron emission current
Ionization cross section
Effective ionizer length
Ion extraction efficiency

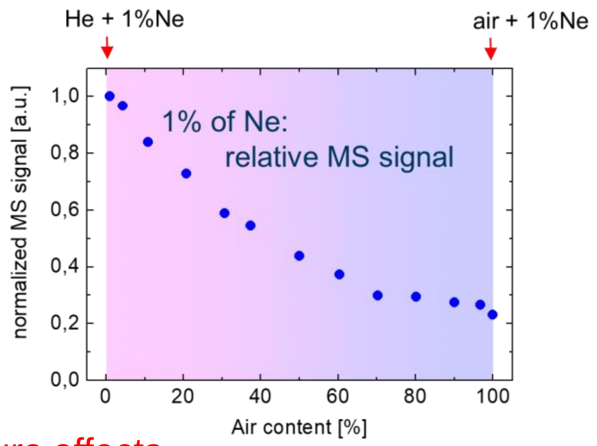
Signal scaling with:
Mass-dependent ion transmission function

$$n_i^{mixture} \longrightarrow n_i^{ionizer}$$

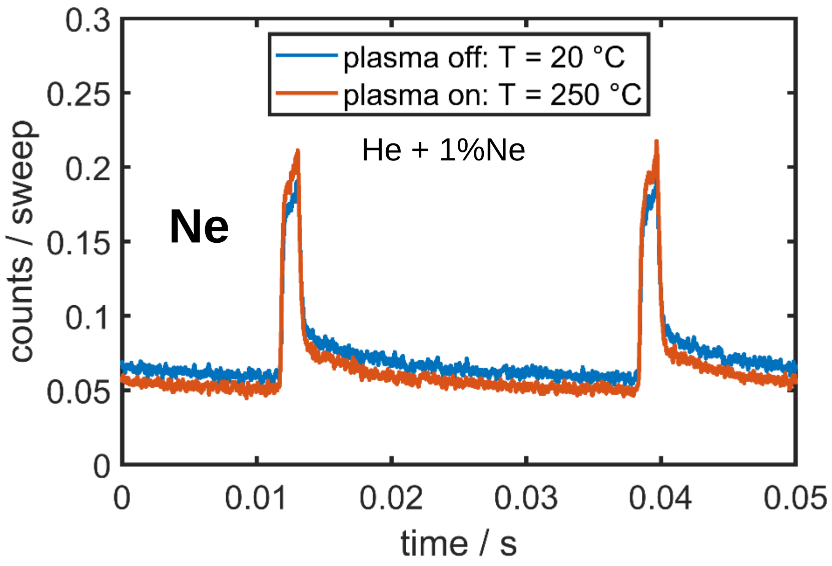
$$\phi_i^{ionizer} \longrightarrow S_i^{detector}$$

G. Willems *et al.*, New J. Phys. 19 (2019) 059501

1) Composition distortion important



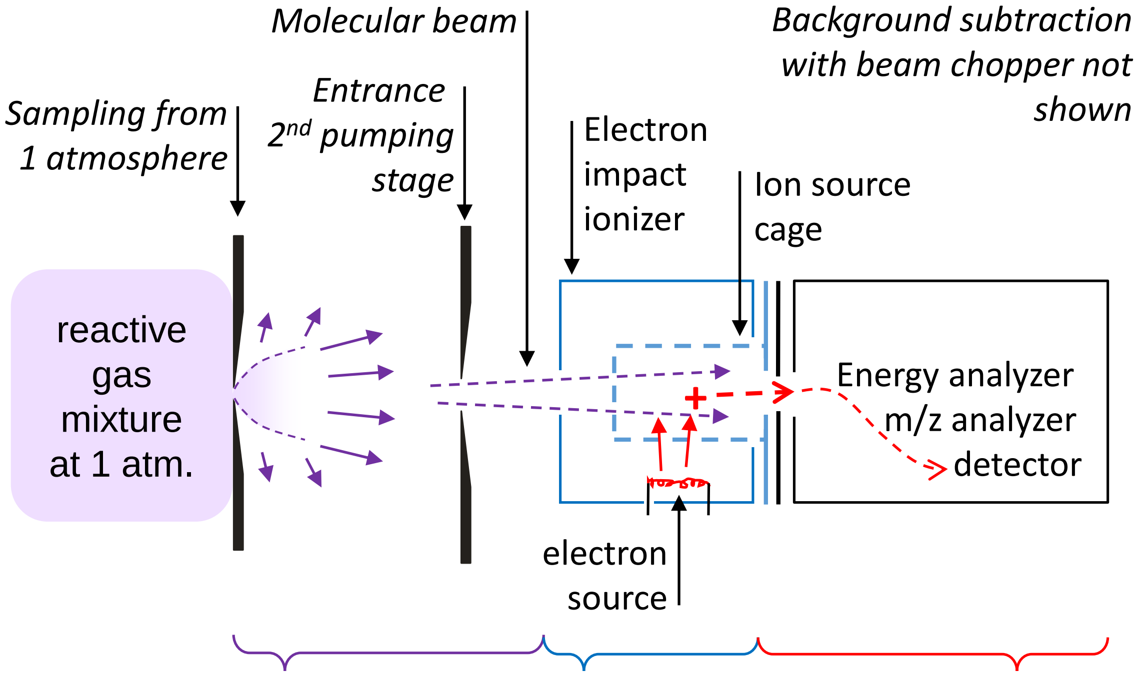
→ Including gas temperature effects



2) MS settings important

G. Willems *et al.*, New J. Phys. 19 (2019) 059501

Important issues in signal calibration



Expansion with composition distortions:
Acceleration into orifice
Radial diffusion
Mach-number focusing

Signal scaling with:
Electron emission current
Ionization cross section
Effective ionizer length
Ion extraction efficiency

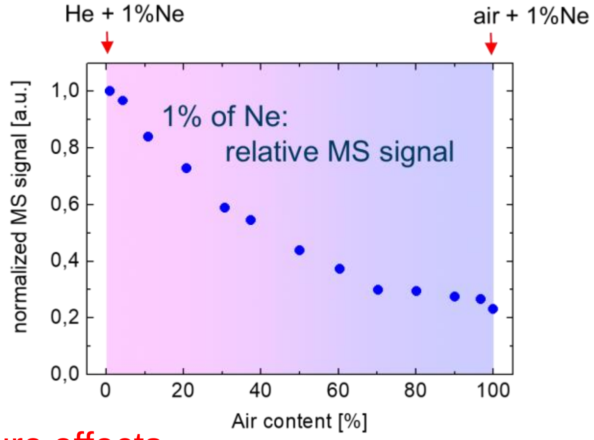
Signal scaling with:
Mass-dependent ion transmission function

$$n_i^{mixture} \longrightarrow n_i^{ionizer}$$

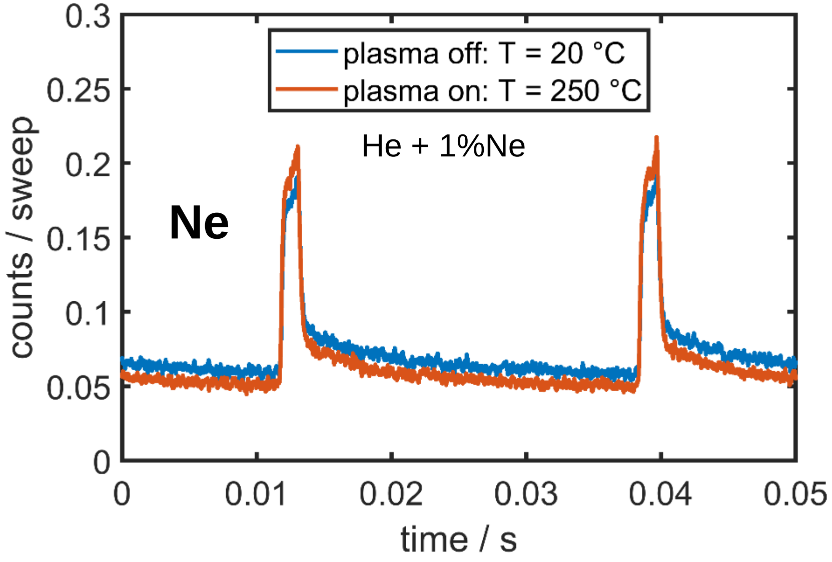
$$n_i^{ionizer} \downarrow \phi_i^{ionizer} \longrightarrow S_i^{detector}$$

G. Willems *et al.*, New J. Phys. 19 (2019) 059501

1) Composition distortion important



→ Including gas temperature effects



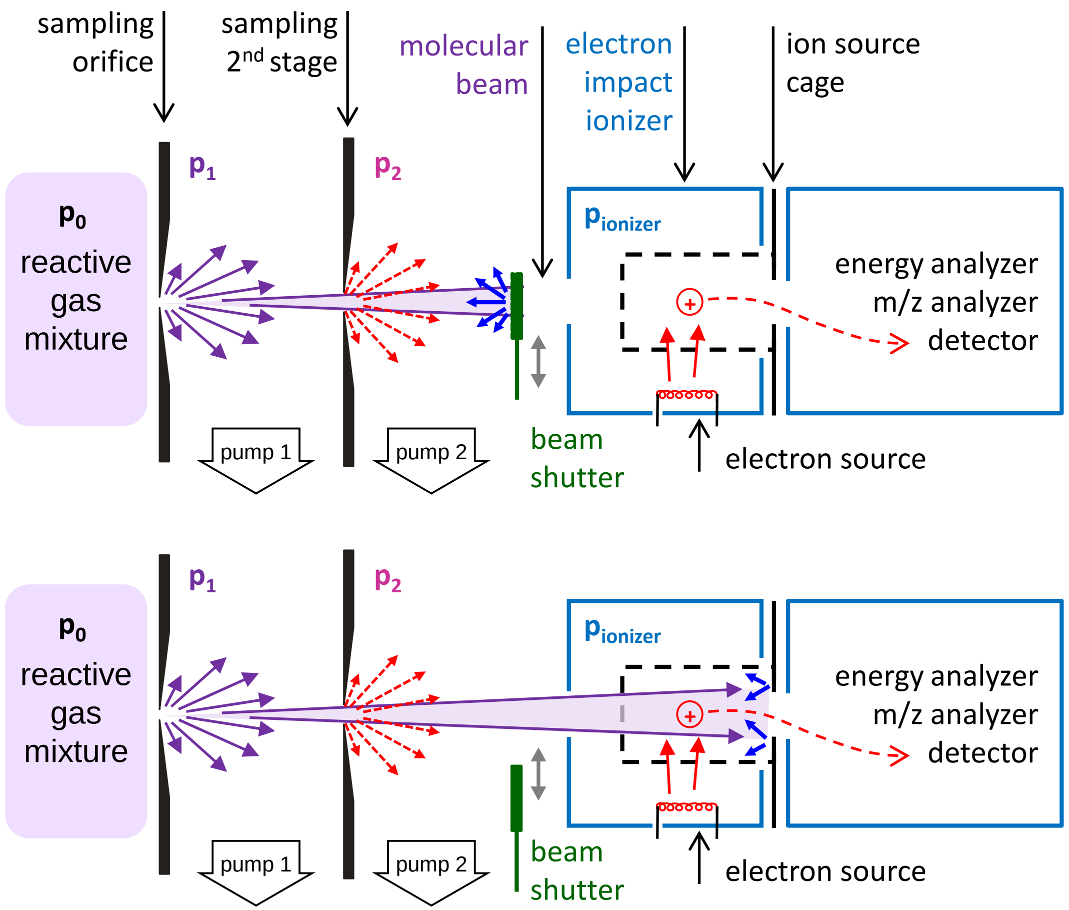
2) MS settings important

G. Willems *et al.*, New J. Phys. 19 (2019) 059501

3) Background subtraction important → next slide

Important issues in signal calibration

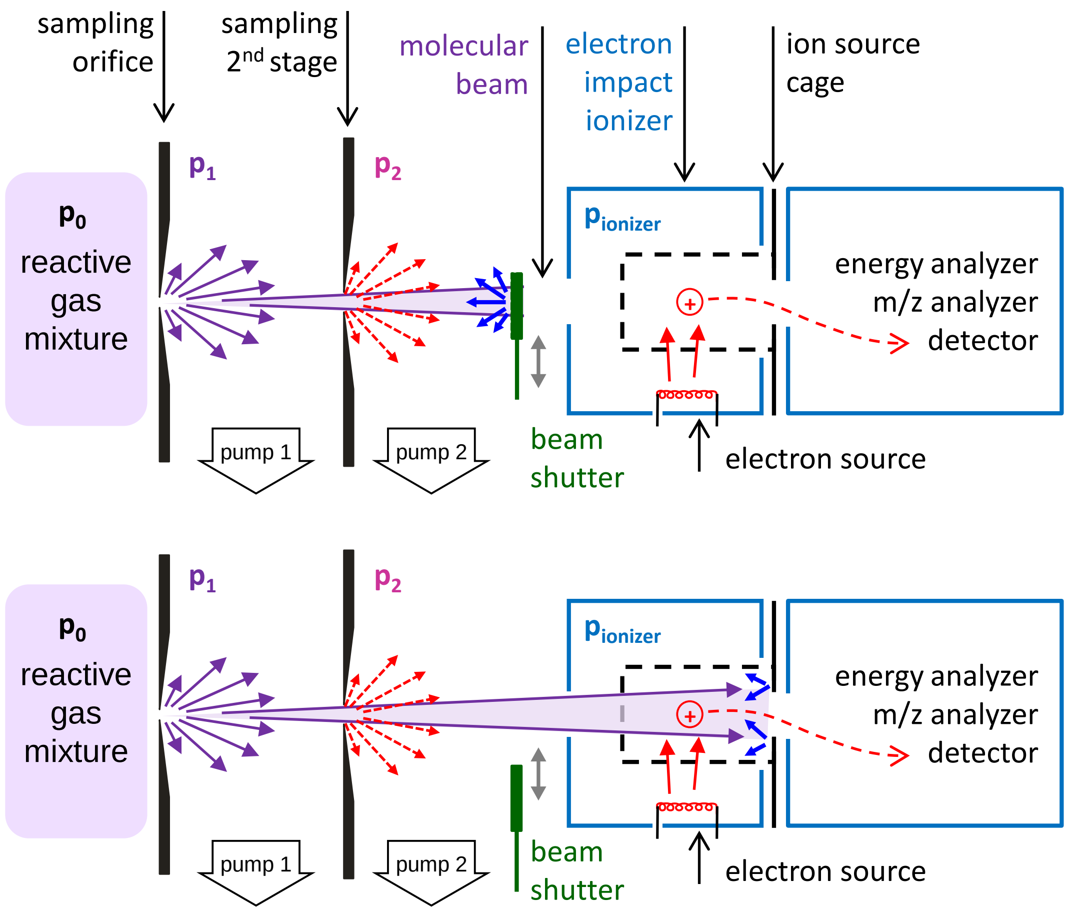
Background subtraction



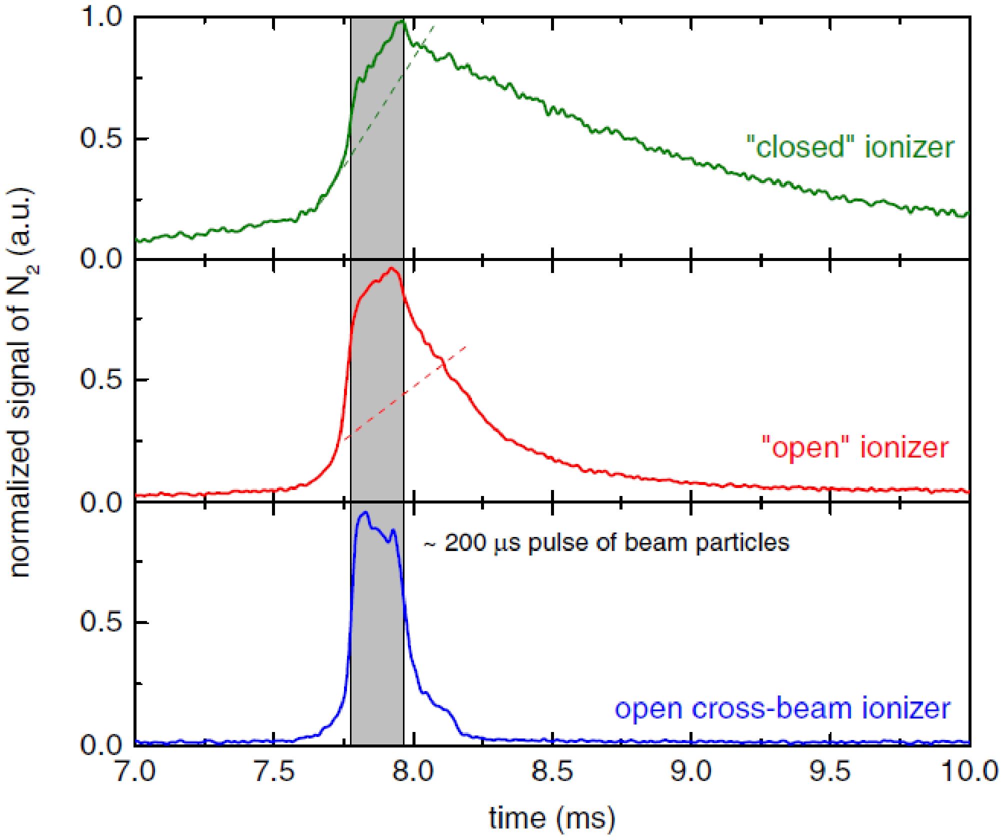
Benedikt *et al.*, (2021) 10.1088/1361-6595/abe4bf

Important issues in signal calibration

Background subtraction



Benedikt *et al.*, (2021) 10.1088/1361-6595/abe4bf



Große-Kreul *et al.*, Plasma Sources Sci. Technol. 24 (2015) 044008

Krähling *et al.*, Rev. Sci. Instrum. 83, 045114 (2012)

Outline

Motivation

- The non-equilibrium atmospheric plasmas

Mass Spectrometry (MS)

Detection of reactive neutrals

- Molecular beam mass spectrometry (MBMS)
- Beam chopper with rotating skimmer
- Calibration issues in MBMS
- Threshold ionization MS (TIMS)

Detection of Ions

Analysis of Atmospheric Pressure Plasma jets

- Study of CO_2 conversion
- Time-resolved ion measurements in plasma needle

Conclusions

Threshold Ionization Mass Spectrometry (TIMS)

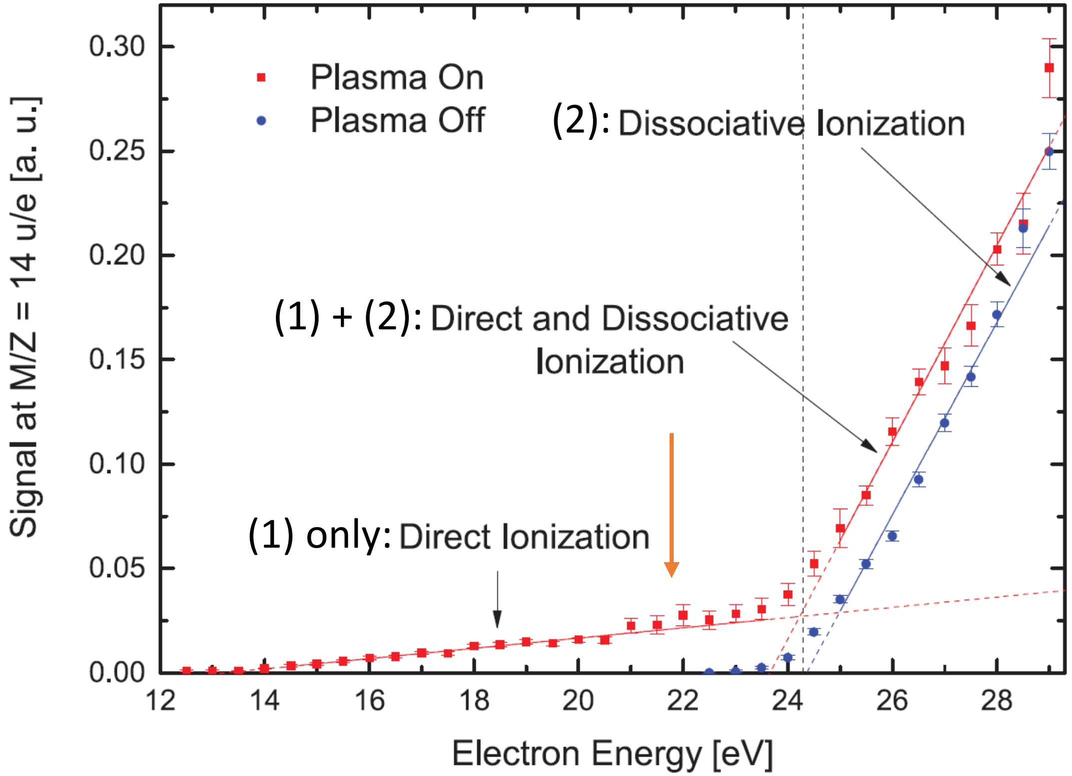
Measurement of N atoms at mass 14

(1) $\mathbf{N} + e \rightarrow \mathbf{N^+} + 2e$ $E_{el} > 14{,}5$ eV

(2) $\mathbf{N_2} + e \rightarrow \mathbf{N^+} + N + 2e$ $E_{el} > 24{,}3$ eV

Dissociation of N_2 has to be avoided.

Energy Scan at mass 14

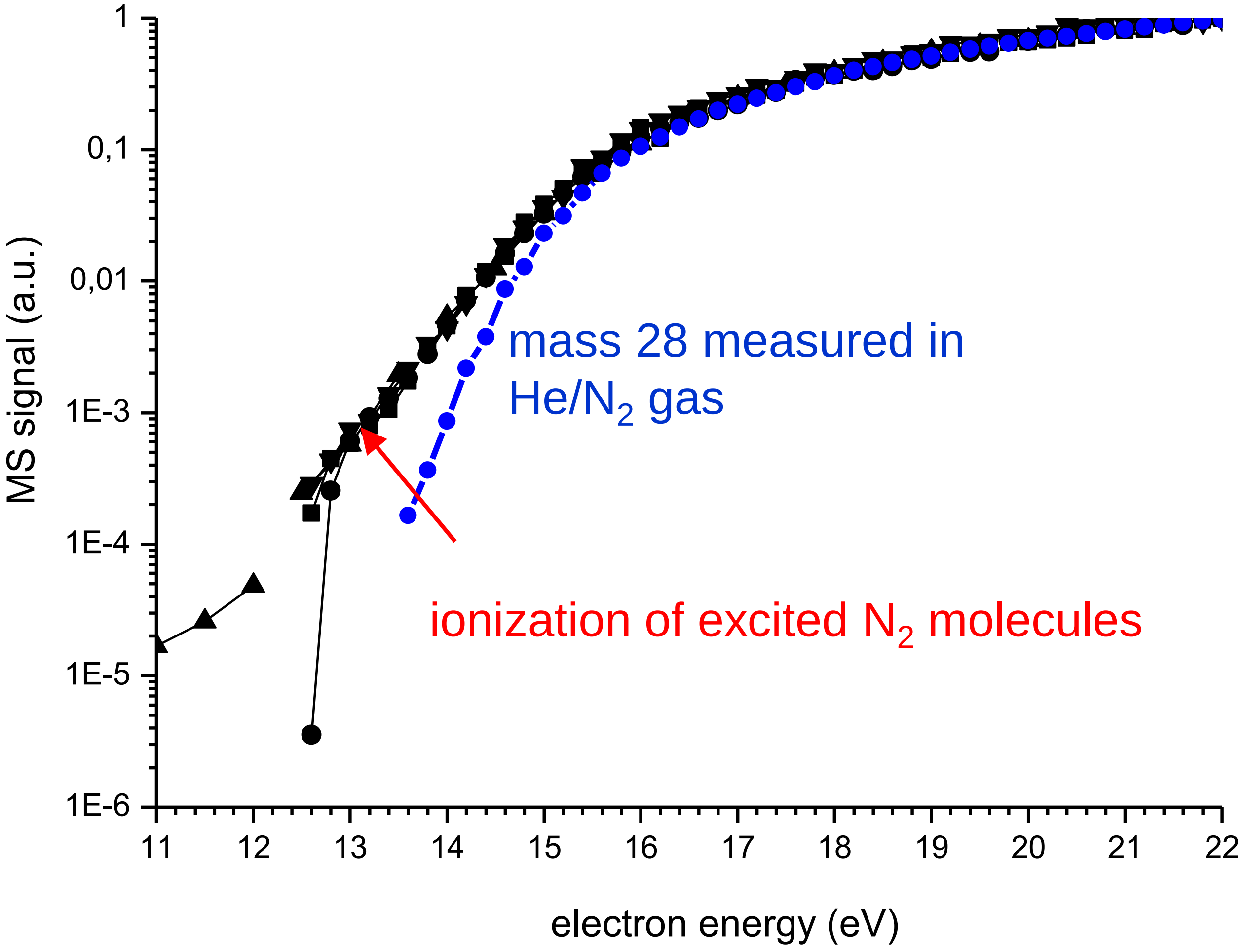


Measure N at electron energy in ionizer of 22 eV

Schneider *et al.*, J. Phys. D 47 (2014) 505203

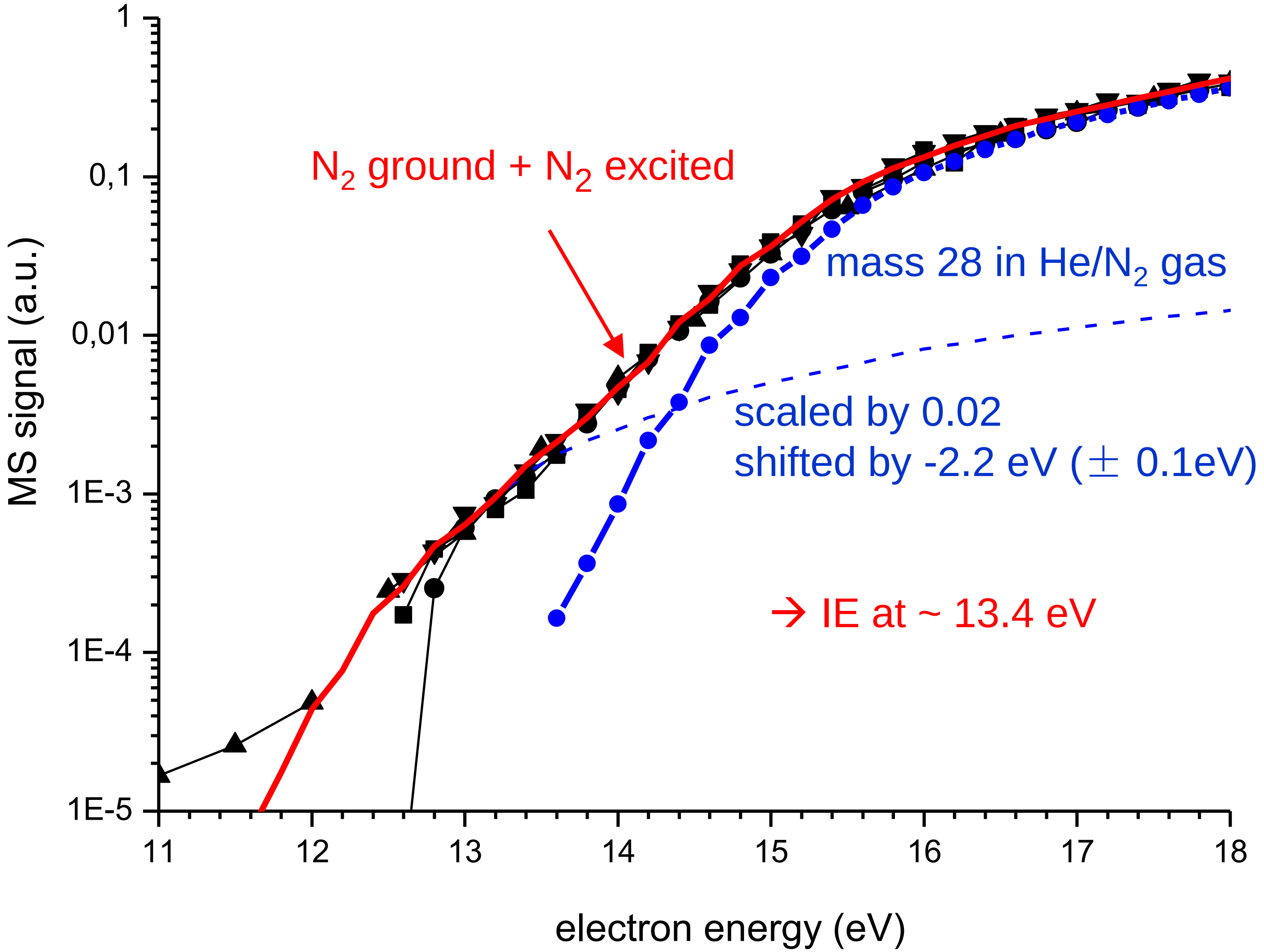
Plasma analysis: N_2 admixture – excited N_2

Mass 28 measured in He/N_2 plasma



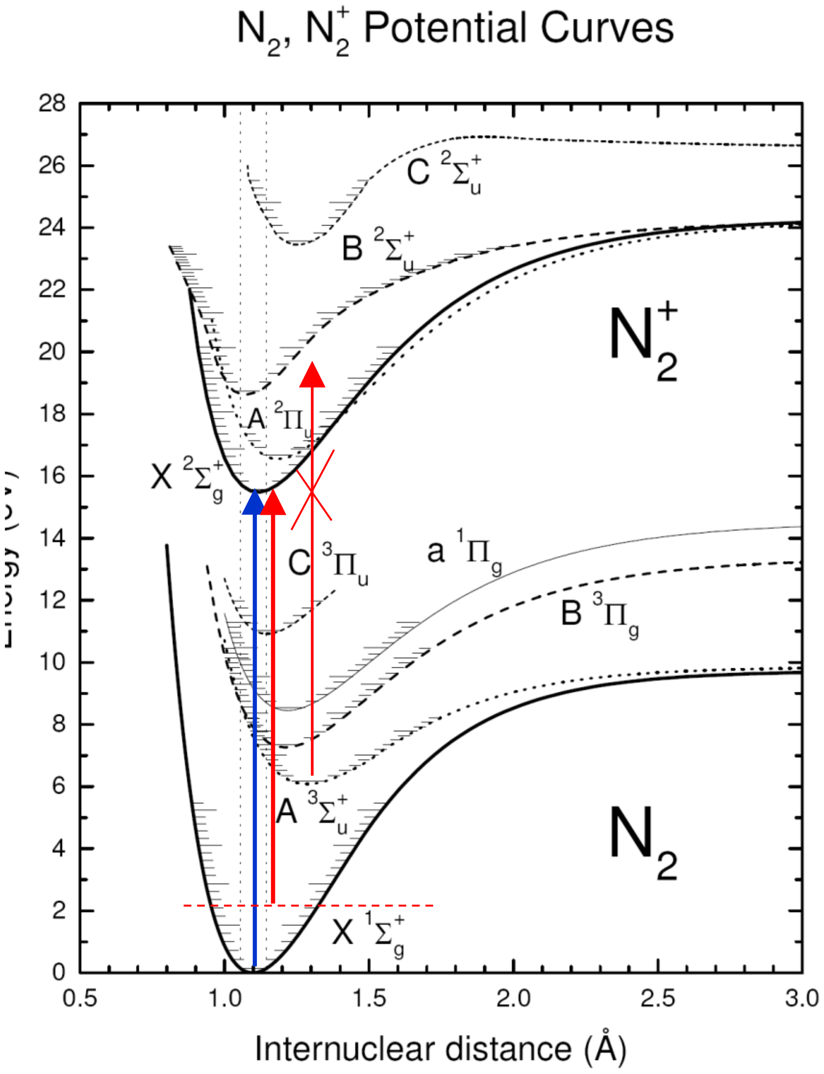
Große-Kreul *et al.*, Plasma Sources Sci. Technol. 24 (2015) 044008

Plasma analysis: N_2 admixture – excited N_2



Große-Kreul *et al.*, Plasma Sources Sci. Technol. 24 (2015) 044008

Plasma analysis: N_2 admixture – excited N_2



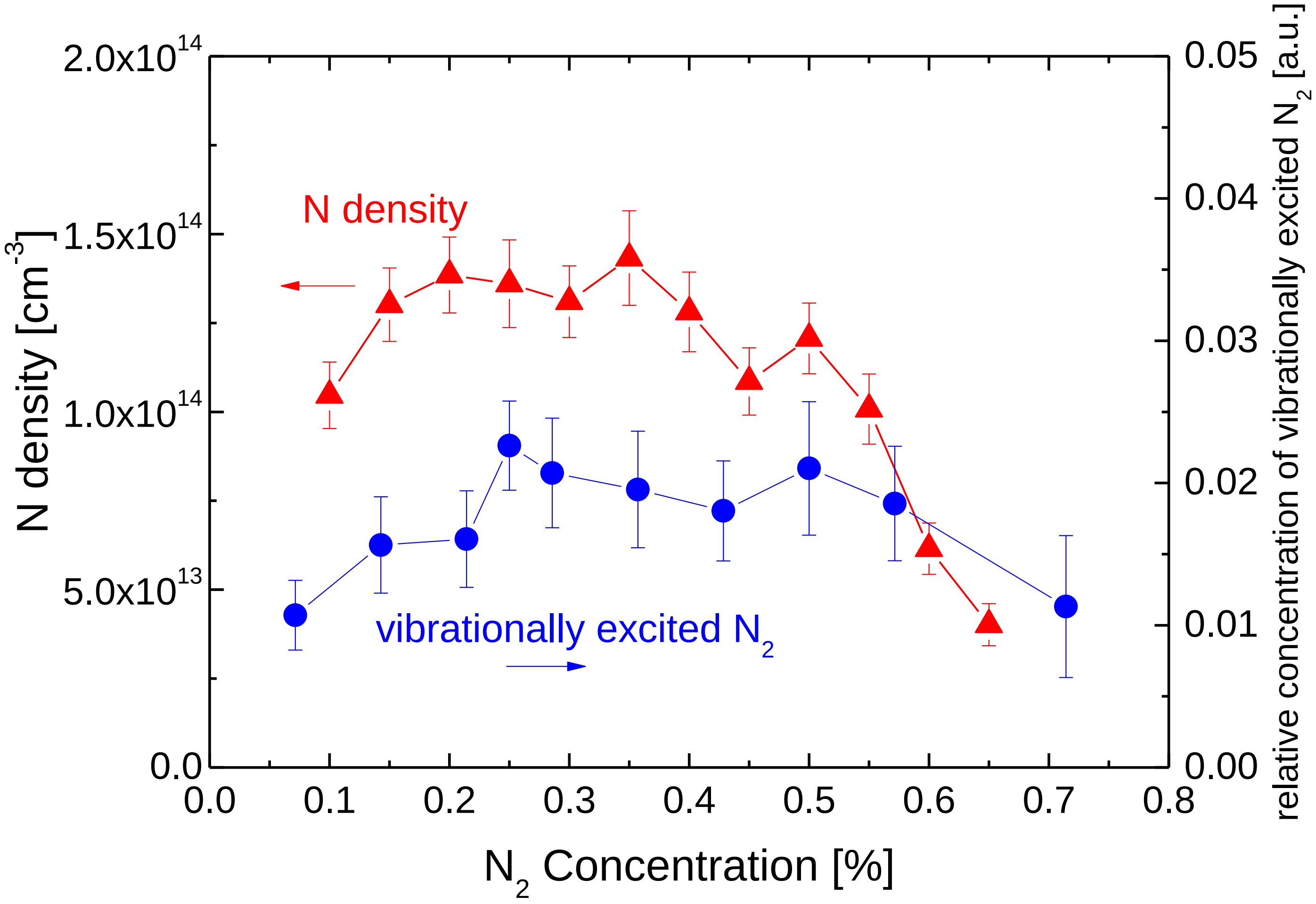
Große-Kreul *et al.*, Plasma Sources Sci. Technol. 24 (2015) 044008

Excitation probably from the 7th vibrational level…

Singlet delta oxygen measurements:

Jiang et al., Plasma Sources Sci. Technol. 29 (2020) 045023

Plasma analysis: N_2 admixture – excited N_2



Singlet delta oxygen measurements:

Jiang et al., Plasma Sources Sci. Technol. 29 (2020) 045023

Outline

Motivation

- The non-equilibrium atmospheric plasmas

Mass Spectrometry (MS)

Detection of reactive neutrals

- Molecular beam mass spectrometry (MBMS)
- Beam chopper with rotating skimmer
- Calibration issues in MBMS
- Threshold ionization MS (TIMS)

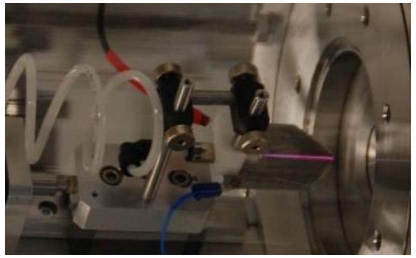
Detection of Ions

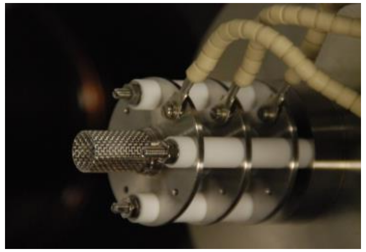
Analysis of Atmospheric Pressure Plasma jets

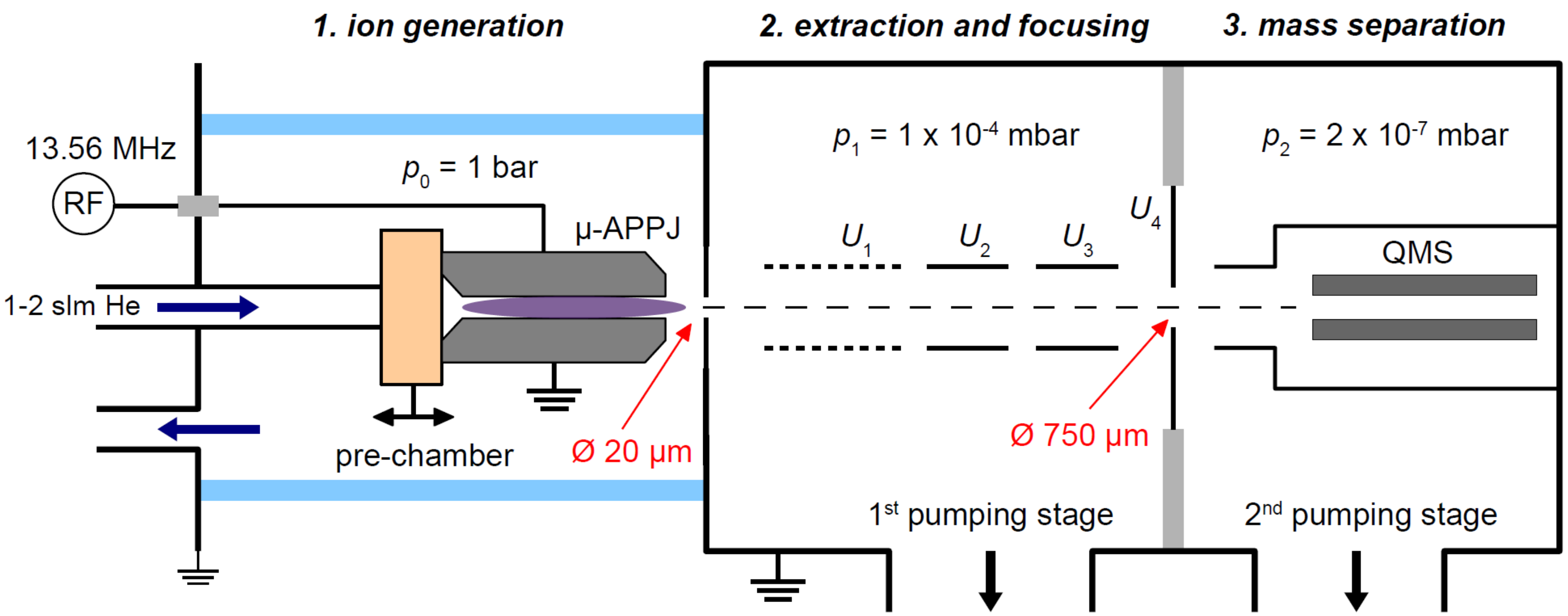
- Study of CO_2 conversion
- Time-resolved ion measurements in plasma needle

Conclusions

MS of ions: experimental setup: Schematic diagram

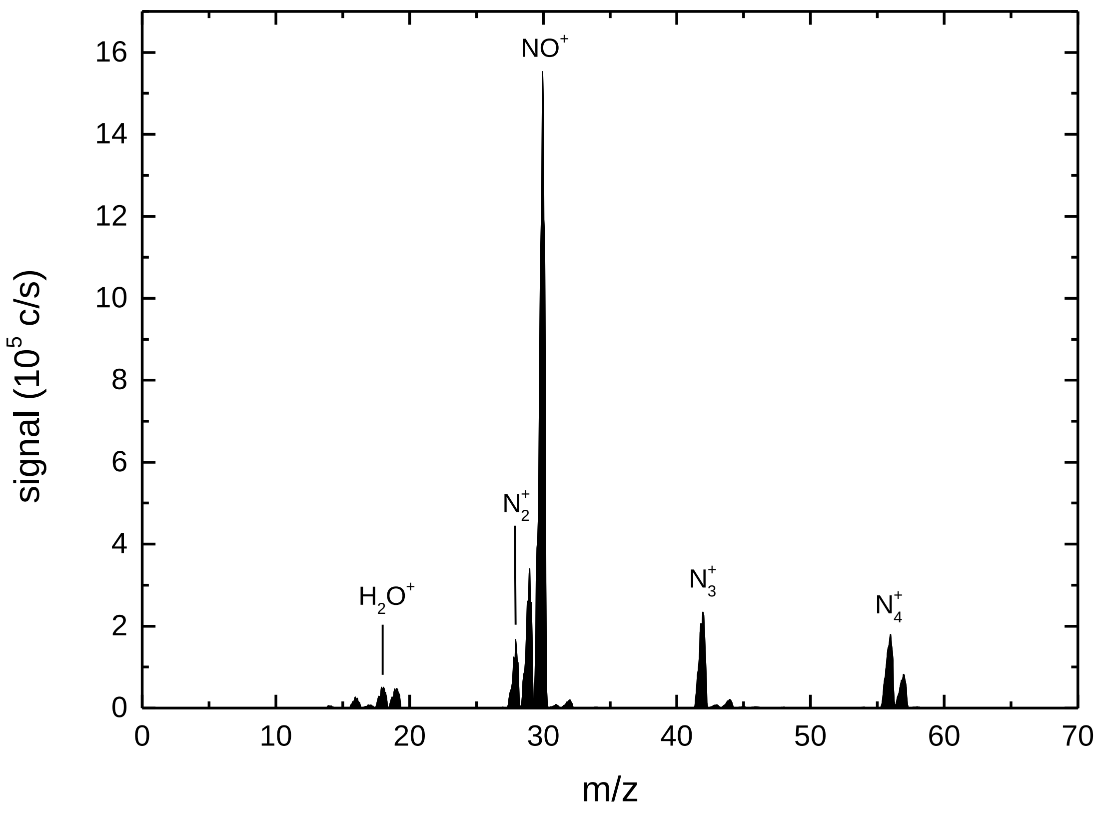






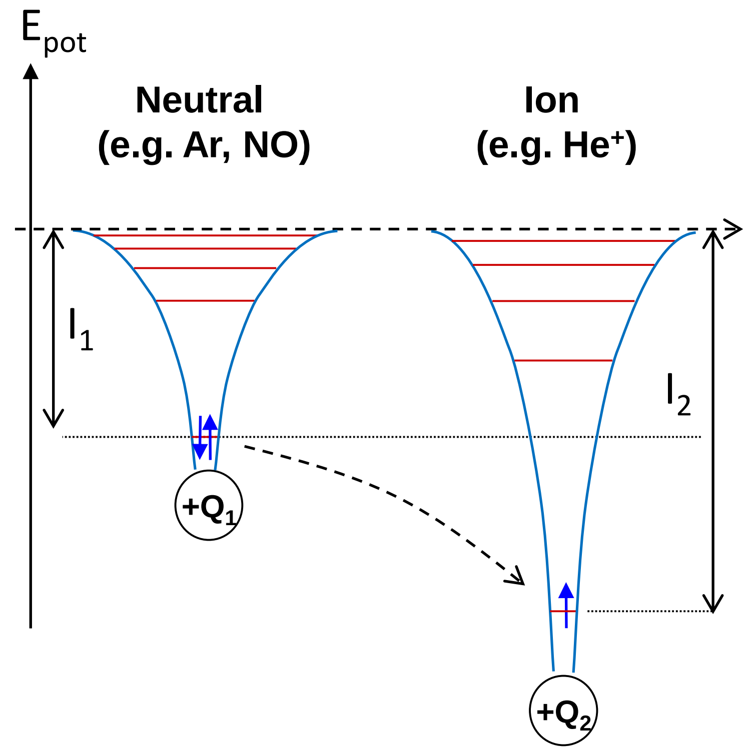
Results: Ion mass spectrum for He/N_2 plasma

1.4 slm He + 3.5 sccm N_2, distance 2 mm



mainly 2nd/3rd ion generation due to fast ion-neutral CT collisions

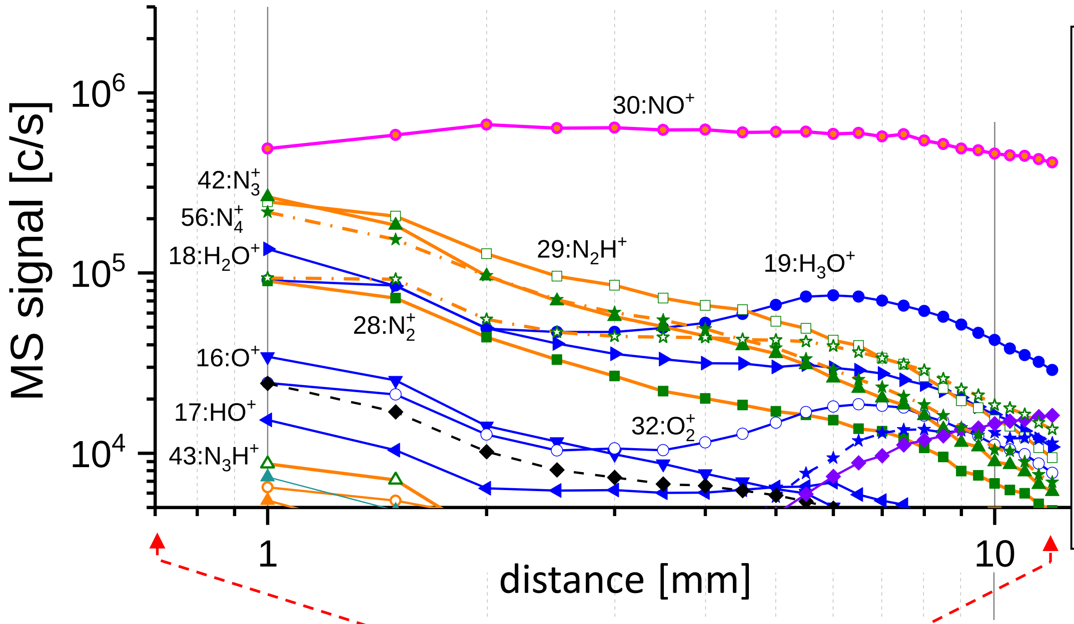
→ not primary ions from plasma

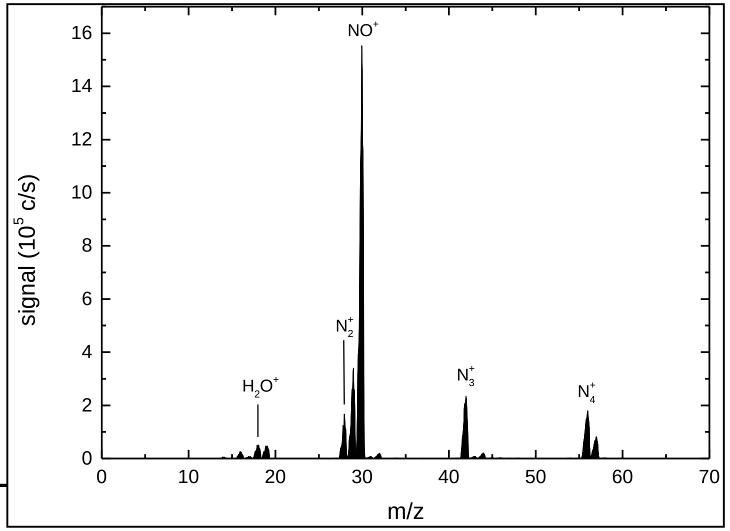


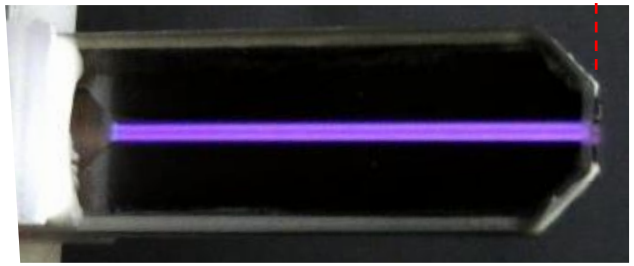
NO^+ dominates due to its low ionization energy of 9.26 eV

Results: Ion mass spectrum for He/N_2 plasma

1.4 slm He + 3.5 sccm N_2, distance variation

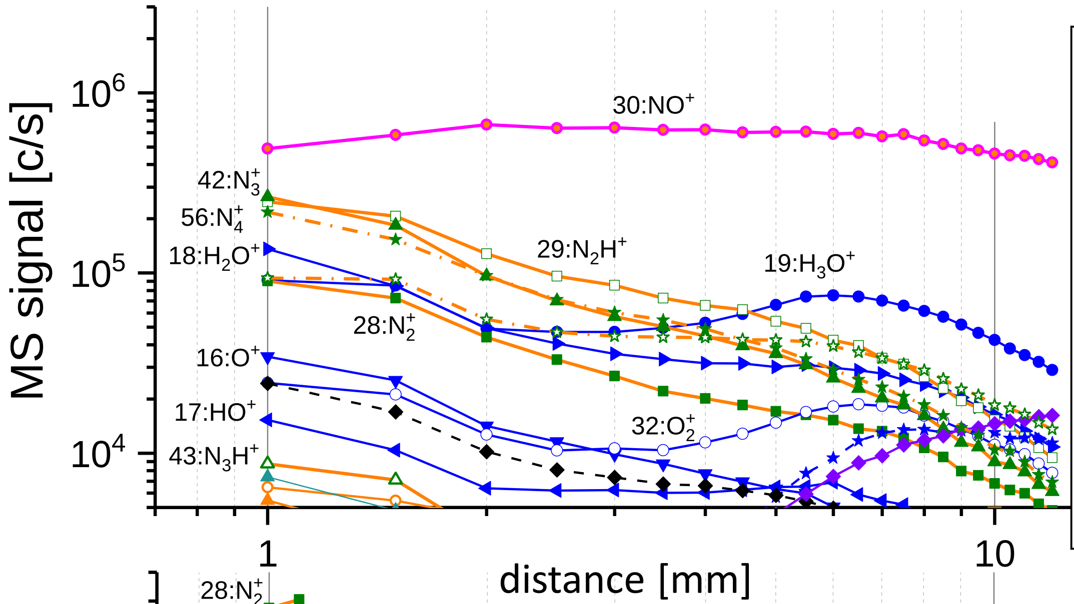


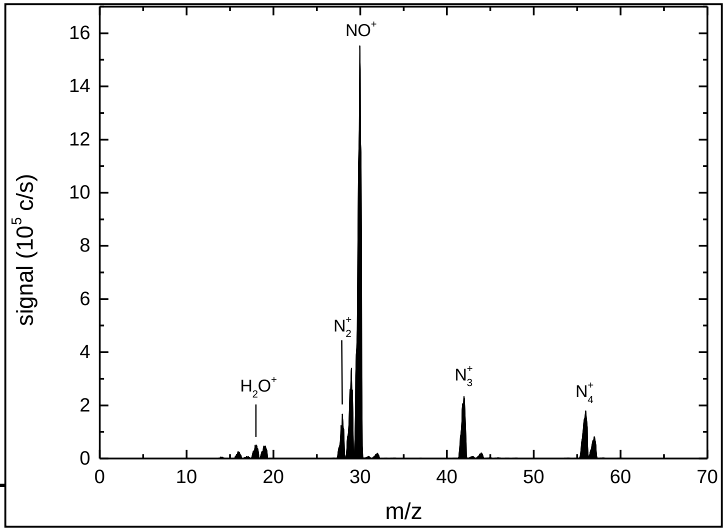


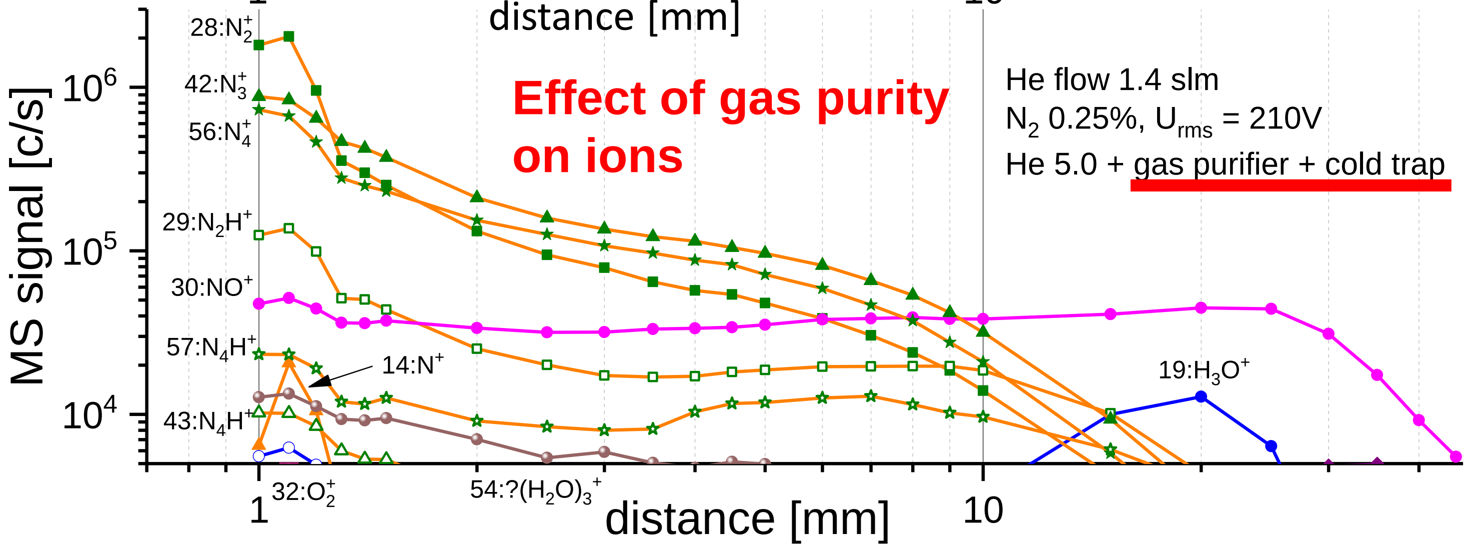


Results: Ion mass spectrum for He/N_2 plasma

1.4 slm He + 3.5 sccm N_2, distance variation





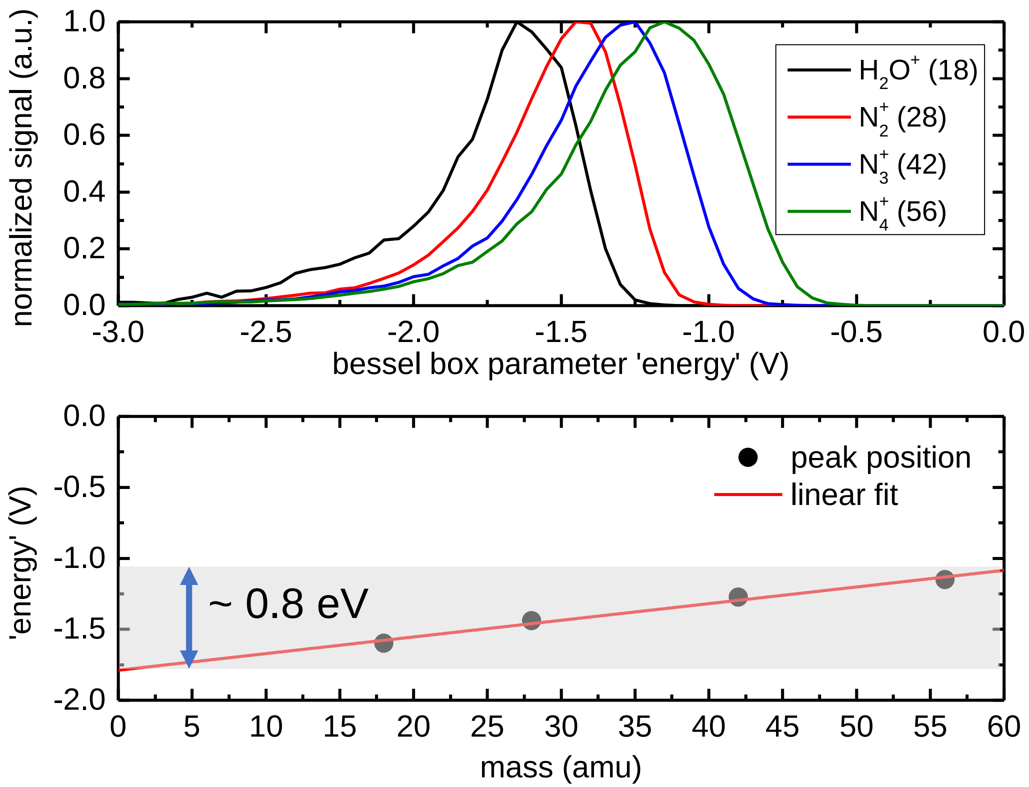


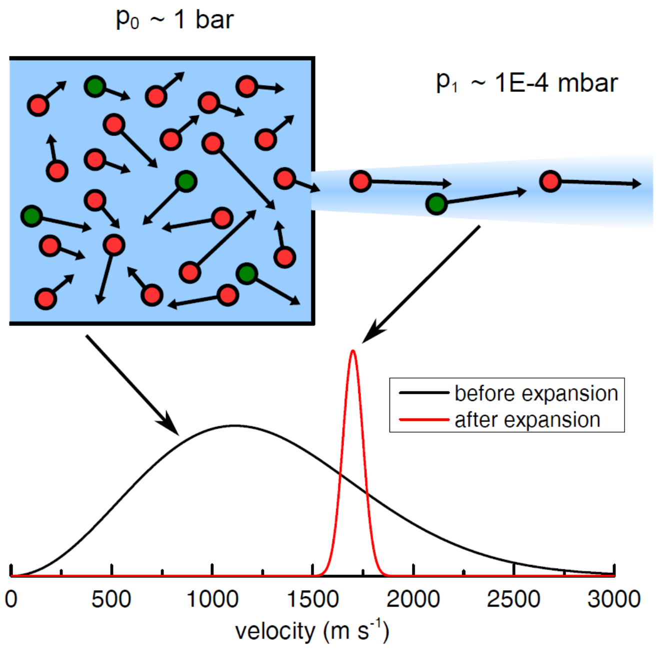
Effect of gas purity on ions

He flow 1.4 slm
N_2 0.25%, U_{rms} = 210V
He 5.0 + gas purifier + cold trap

MS of Ions: ion energy

Mass dependence of ion energy





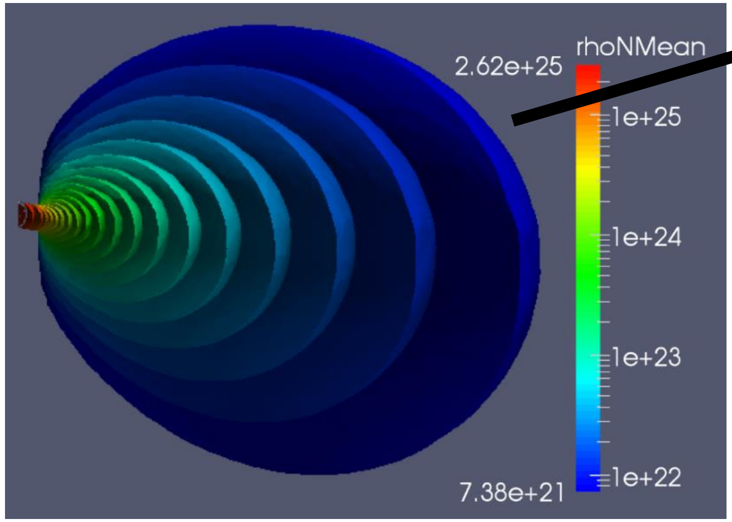
Velocity in the beam the same for all
→ mass-dependent terminal energy!

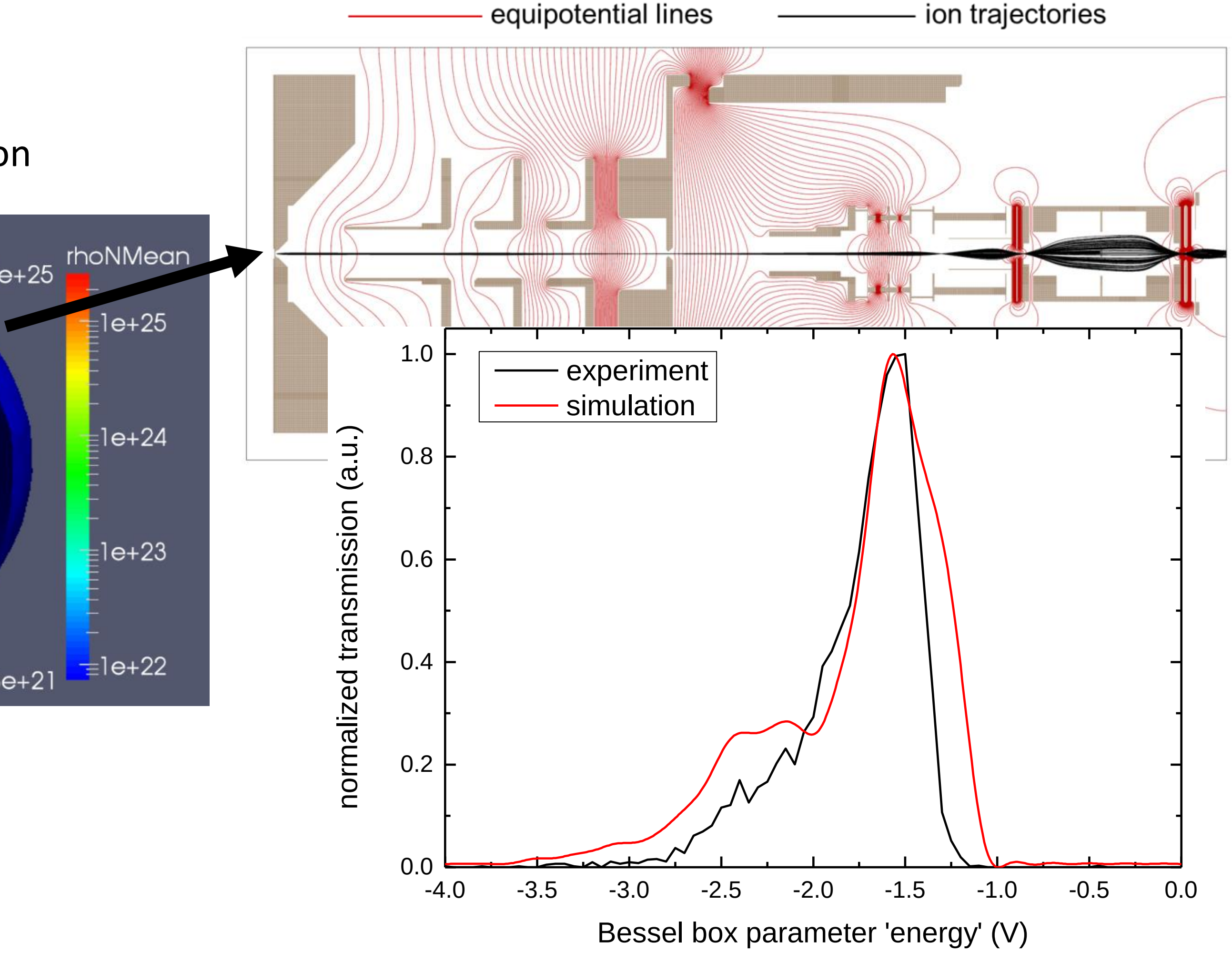
Important by relative measurements of different ions!

MS of ions: ion trajectory simulation

Ion trajectory calculation for ion energy and ion denisty determination

DSMC Foam simulation





Ion density in front of the sampling orifice can be reasonably estimated

Outline

Motivation

- The non-equilibrium atmospheric plasmas

Mass Spectrometry (MS)

Detection of reactive neutrals

- Molecular beam mass spectrometry (MBMS)
- Beam chopper with rotating skimmer
- Calibration issues in MBMS
- Threshold ionization MS (TIMS)

Detection of Ions

Analysis of Atmospheric Pressure Plasma jets

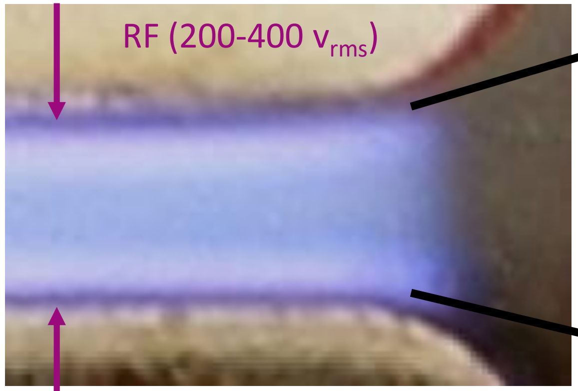
- Study of CO_2 conversion
- Time-resolved ion measurements in plasma needle

Conclusions

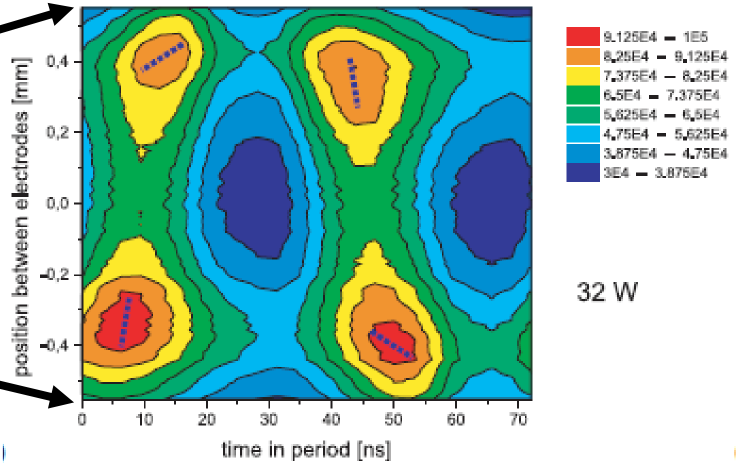
Microscale-APP Jet: μ–APPJ

Phase Resolved OES

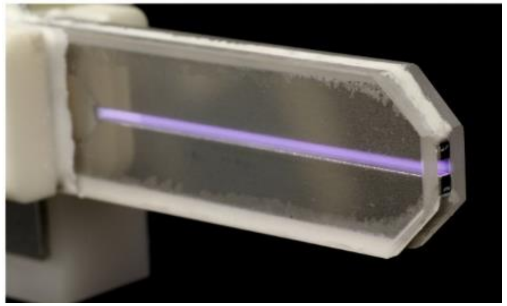
He (l/min)
+
Molecular gas (<1%)



0.2 – 2 mm (standard: 1mm)



alpha discharge, $n_e \sim 10^{11}$ cm^{-3}



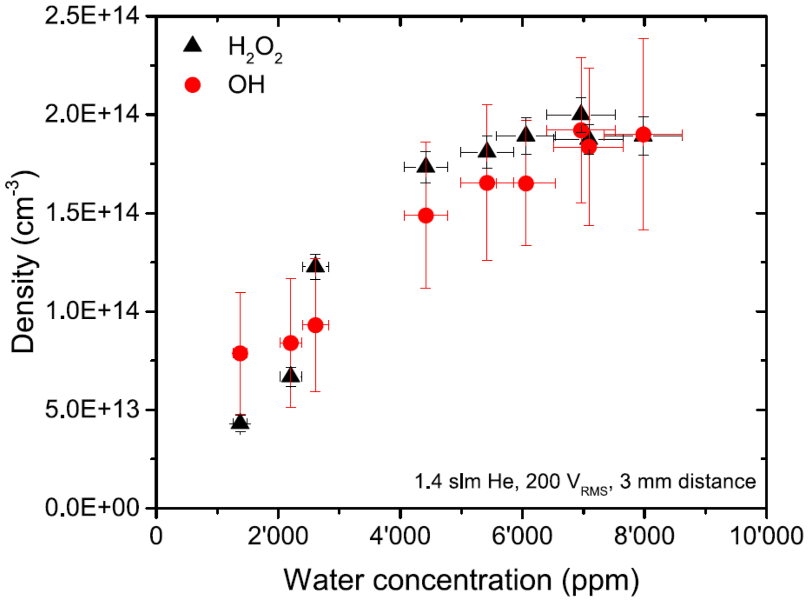
- **Effective source of radicals (O, OH, N, NO, O_3, …)**
- **Composition “tunable” by gas mixture**
- **Only effluent in contact with substrate**
- **Easy access for optical diagnostics**

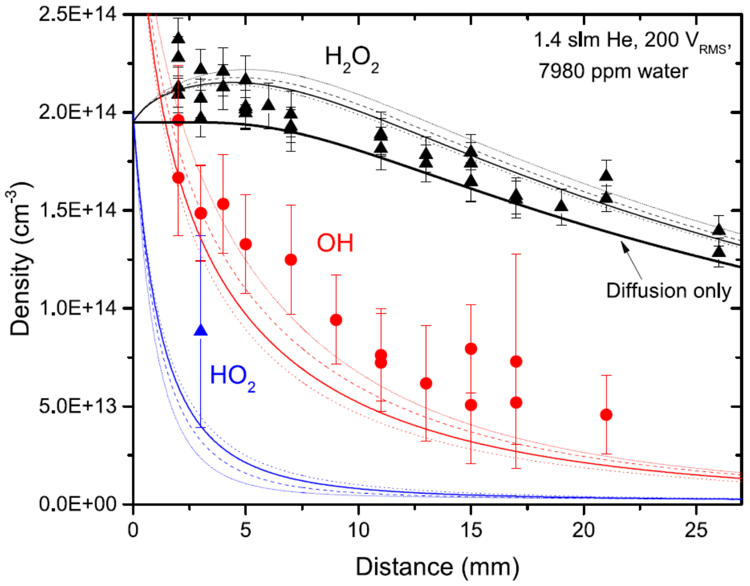
COST reference jet:

J. Golda et al., *Concepts and characteristics of the COST Reference Microplasma Jet*, J. Phys. D 49 (2016) 084003

MS results example: neutrals in He/H_2O plasma

Willems *et al.*, J. Phys. D: Appl. Phys. 50 (2017) 335204

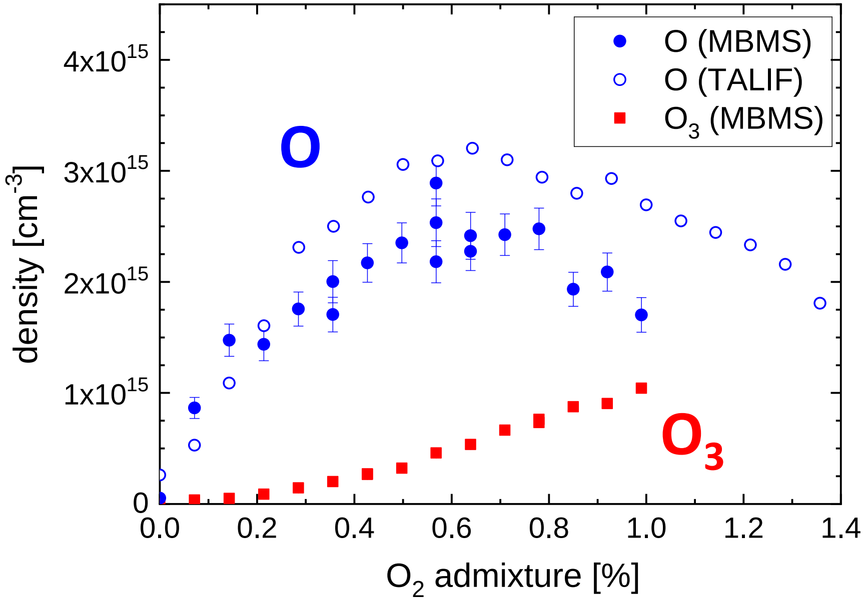


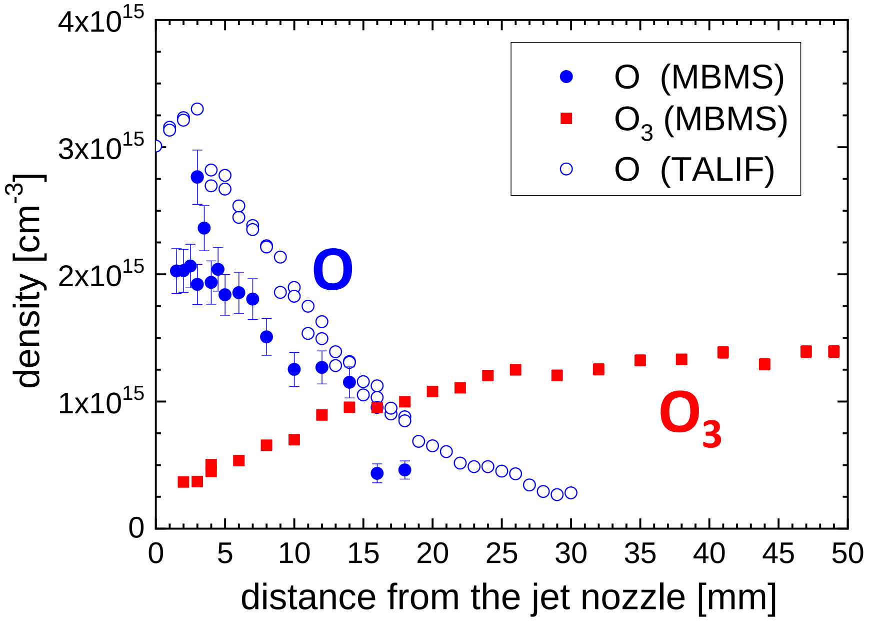


- Many reactive and stable species measurable
- Distance variation → recombination chemistry

He/H_2O	MS →	OH, H_2O_2, O_2H	Willems *et al.*, J. Phys. D: Appl. Phys. 50 (2017) 335204
He/0.3%N_2		N	Schneider *et al.*, J. Phys. D 47 (2014) 505203
He/0.6%O_2		O, O_3	Ellerweg *et al.*, New J. Physics **12** (2010) 013021 Corrigendum: G. Willems *et al.*, New J. Phys. 19 (2019) 059501
He/N_2/O_2		NO, N_2O, NO_2, N, O	Douat *et al.*, Plasma Sources Sci. Technol. 25 (2016) 025027

MS result example: neutrals in He/O_2 plasma



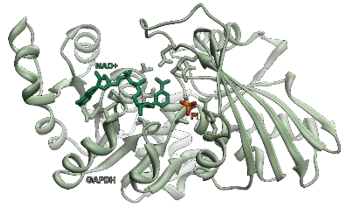


D. Ellerweg *et al.*, New J. Physics **12** (2010) 013021

Corrigendum: G. Willems *et al.*, New J. Phys. 19 (2019) 059501

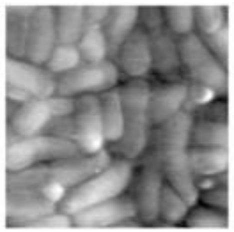
Used for treatment of:

biomolecules



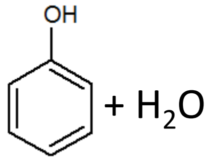
GAPDH

bacteria, spores



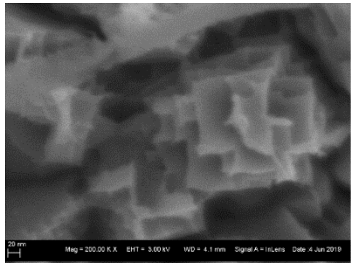
b. subtilis

liquids



Phenol oxidation

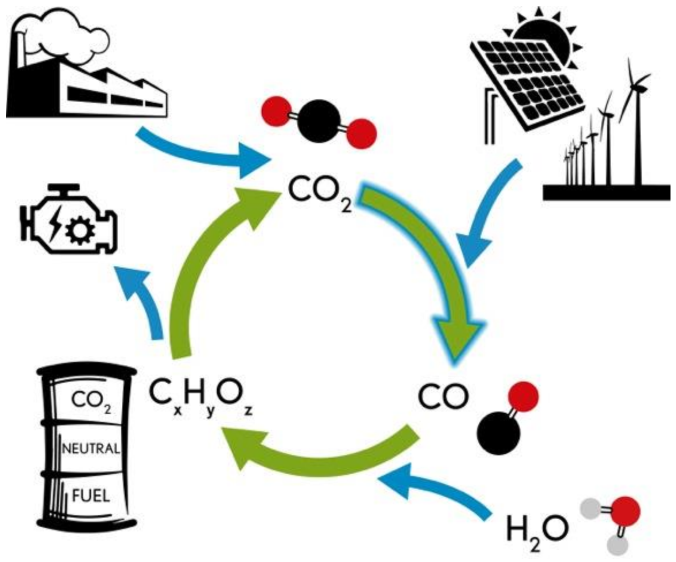
solids



Cu → CuO

MS result example: neutrals in He/CO_2 plasma

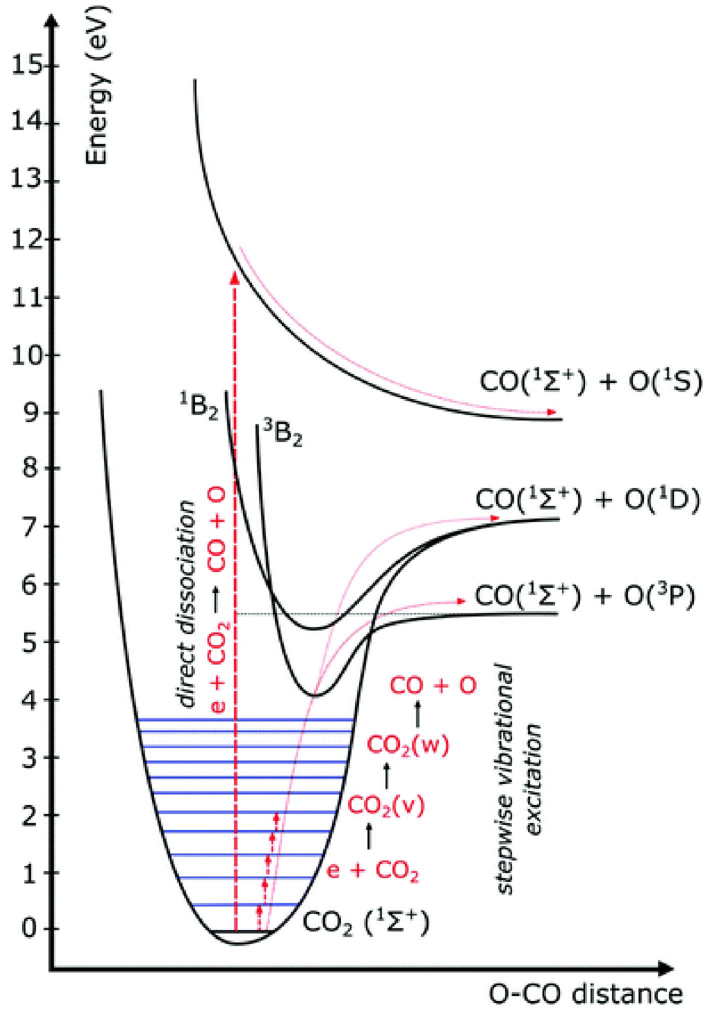
overall reaction: $2CO_2 \rightarrow 2CO + O_2$



A. Bogaerts *et al.*, Faraday Discuss. 183 (2015) 217

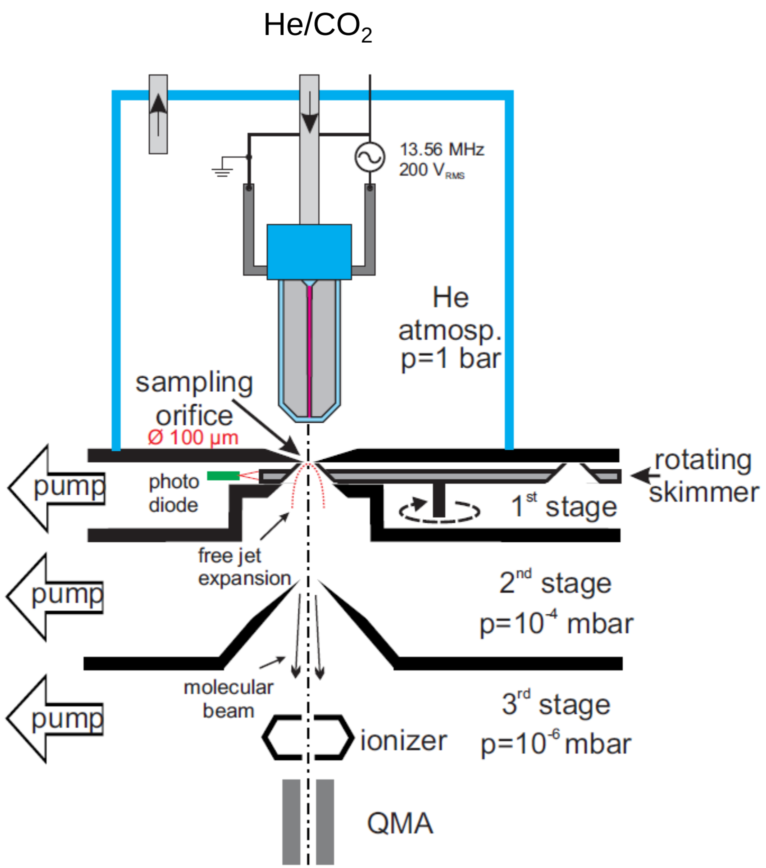
$CO_2 + e \rightarrow CO_2(v) \rightarrow \mathbf{CO} + O$

$CO_2(v) + O \rightarrow \mathbf{CO} + \mathbf{O_2}$

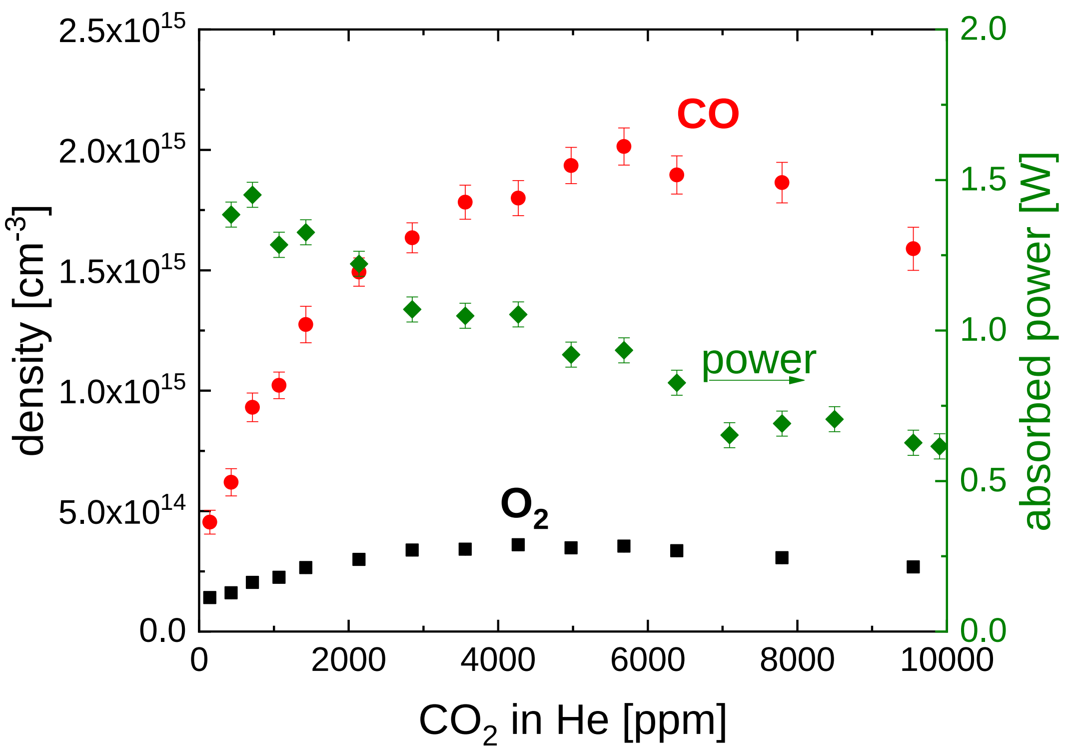


Plasma energetically more efficient than a thermal process (50% efficiency)

MS results: neutrals in He/CO_2 plasma



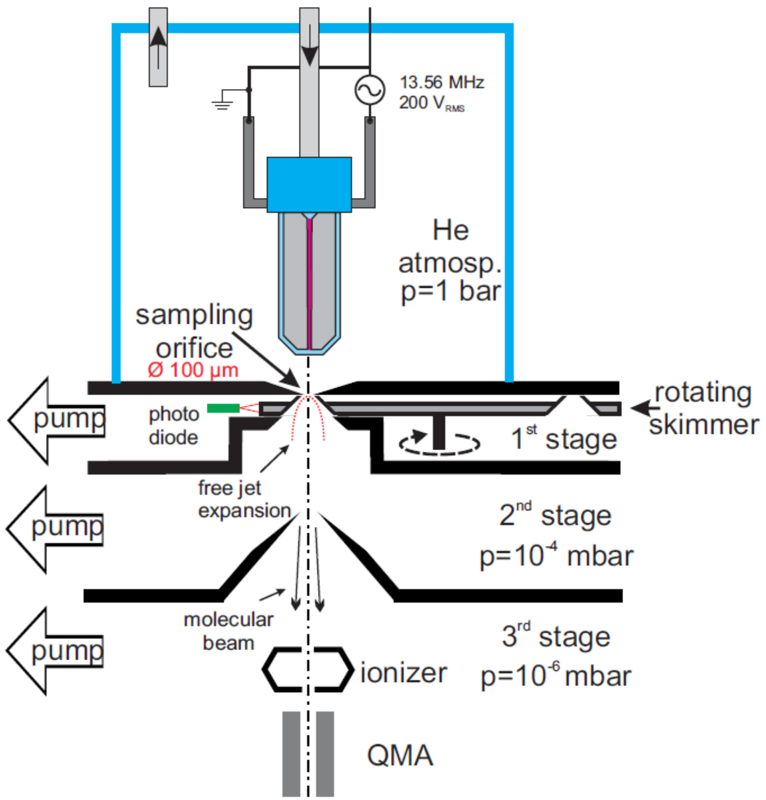
overall reaction: $2CO_2 \rightarrow 2CO + O_2$



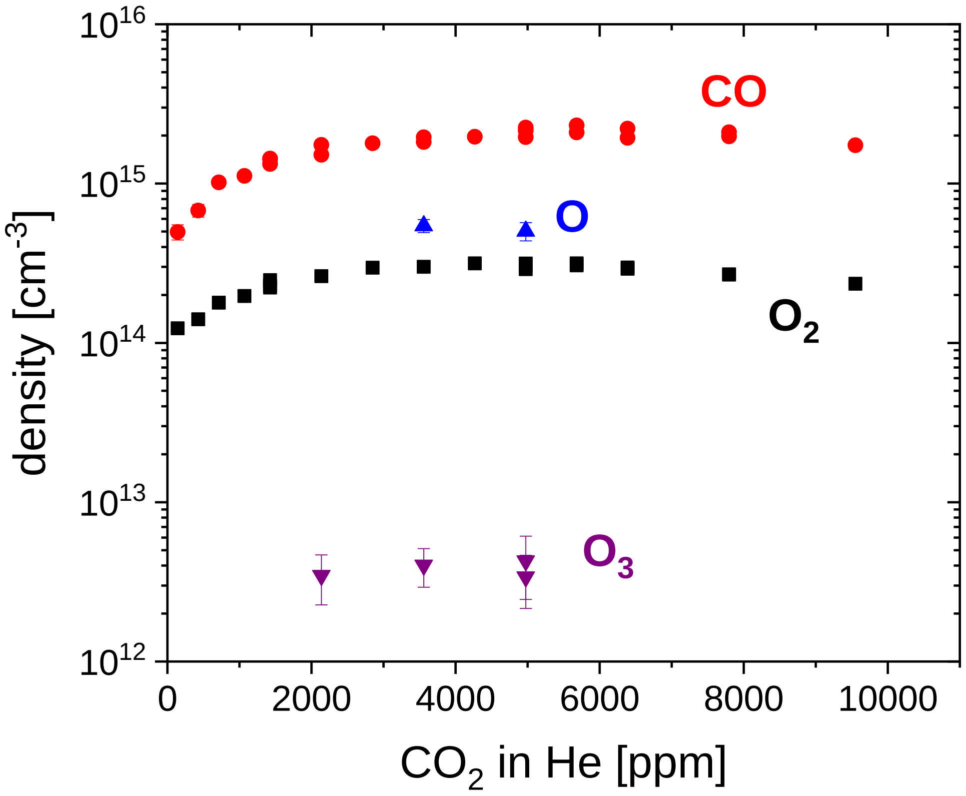
The CO/O_2 ratio much higher than two?!

Willems *et al.*, Plasma Phys. Control. Fusion 62 (2020) 034005

MS results: neutrals in He/CO_2 plasma



overall reaction: $2CO_2 \rightarrow 2CO + O_2$

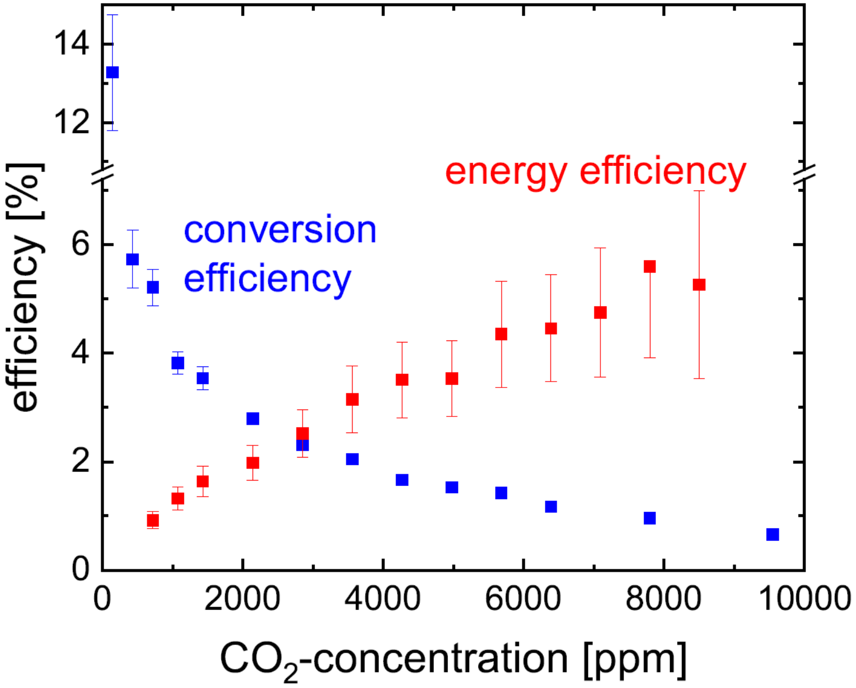


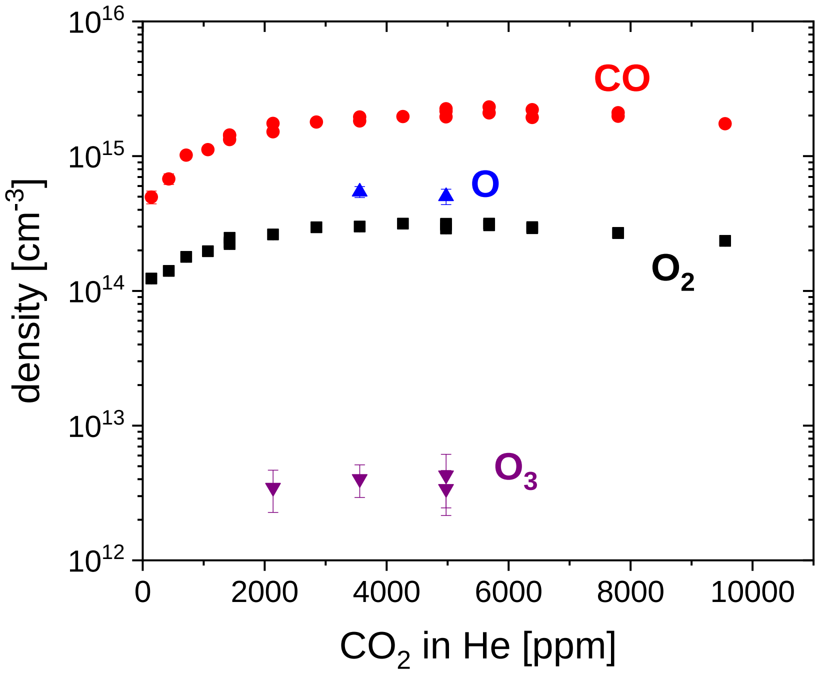
Additional Oxygen species: O atoms and O_3 $n_O > n_{O_2}$!

→ vibrational excitation ineffective in this type of plasma (below detection limit)

Willems *et al.*, Plasma Phys. Control. Fusion 62 (2020) 034005

μ-APPJ in He/CO_2 gas mixture





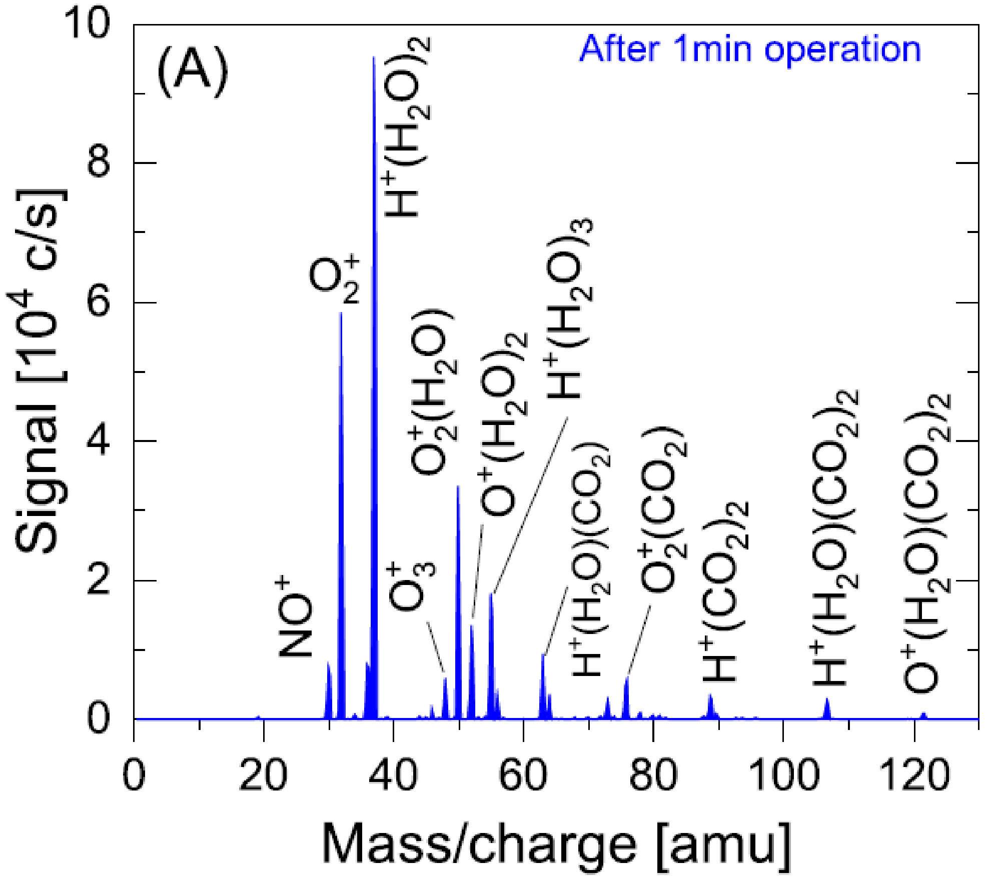
- Max energy efficiency ~ 14%
- Max conversion efficiency ~ 5 %

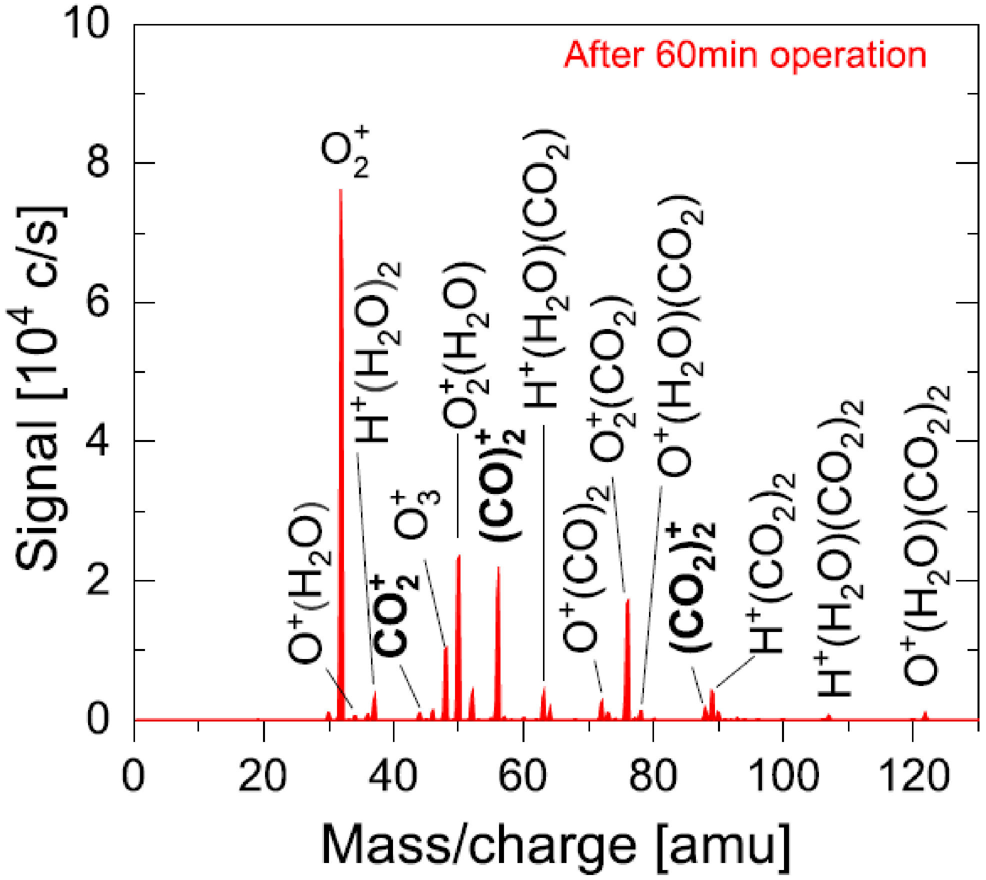
→ confirms low efficiency

Willems *et al.*, Plasma Phys. Control. Fusion 62 (2020) 034005

μ-APPJ in He/CO_2 gas mixture

Positive ions

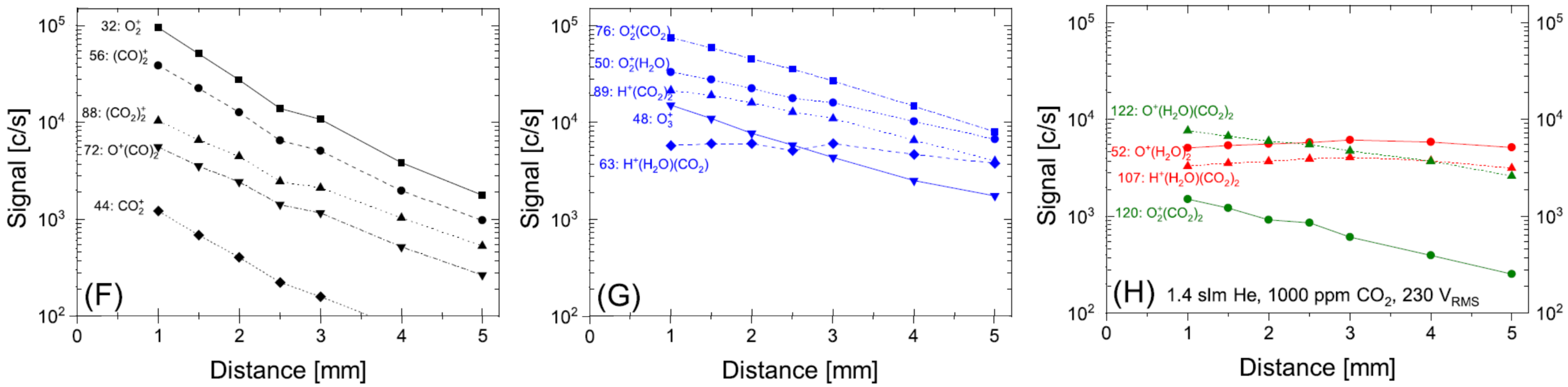




Willems *et al.*, Plasma Phys. Control. Fusion 62 (2020) 034005

μ-APPJ in He/CO_2 gas mixture

Positive ions

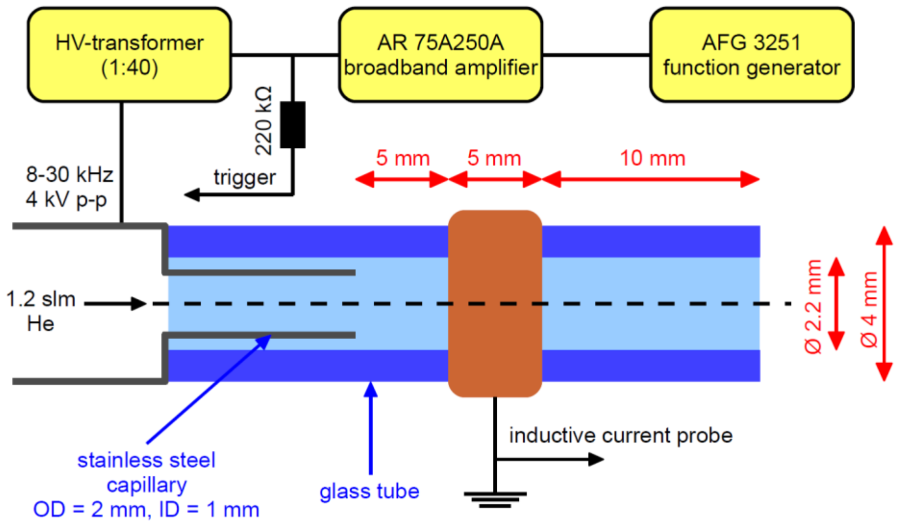


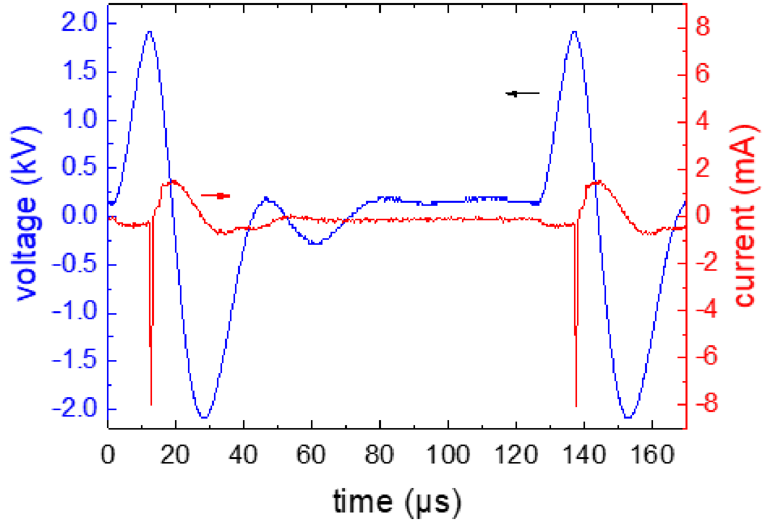
„primary“ ions and secondary ion clusters

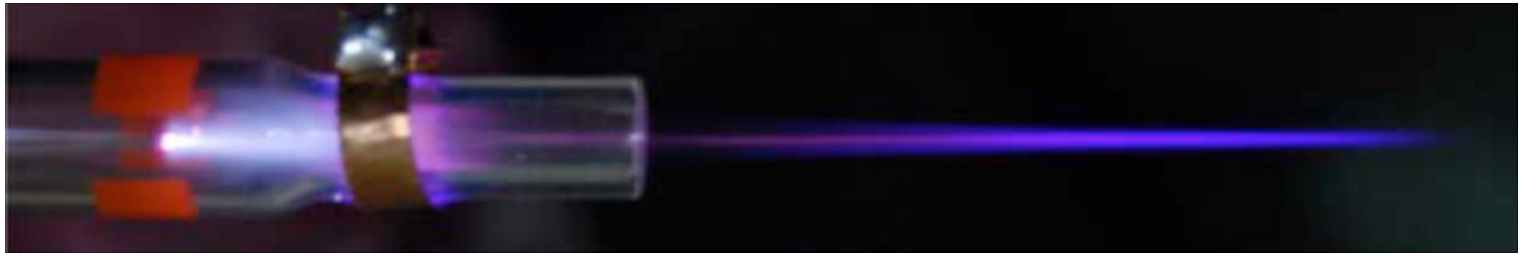
Willems *et al.*, Plasma Phys. Control. Fusion 62 (2020) 034005

Outline

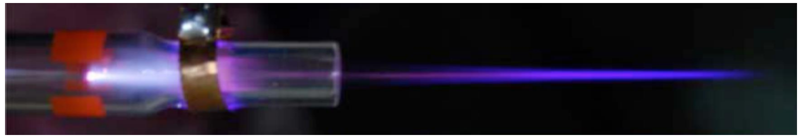
8 kHz plasma needle







Ion mass spectra in 8 kHz plasma needle



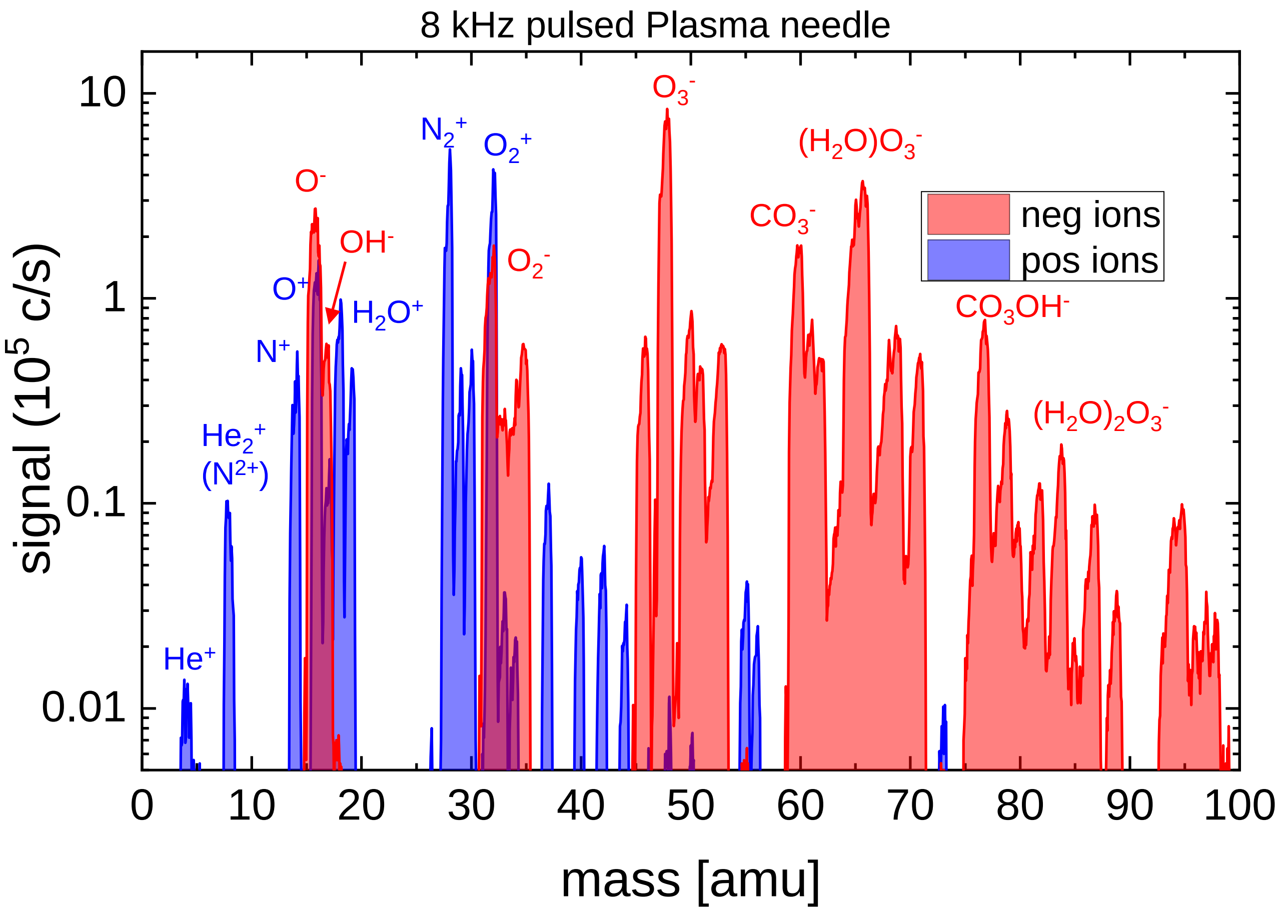
N_2^+ and O_2^+ dominant

He^+, $He_2^+(N^{2+})$, N^+, O^+ ions detected in the streamer head

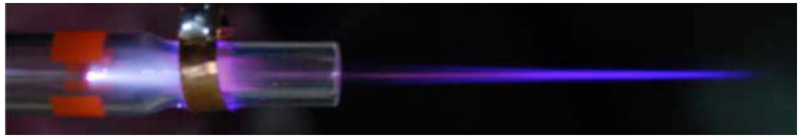
O^- the lightest negative ion

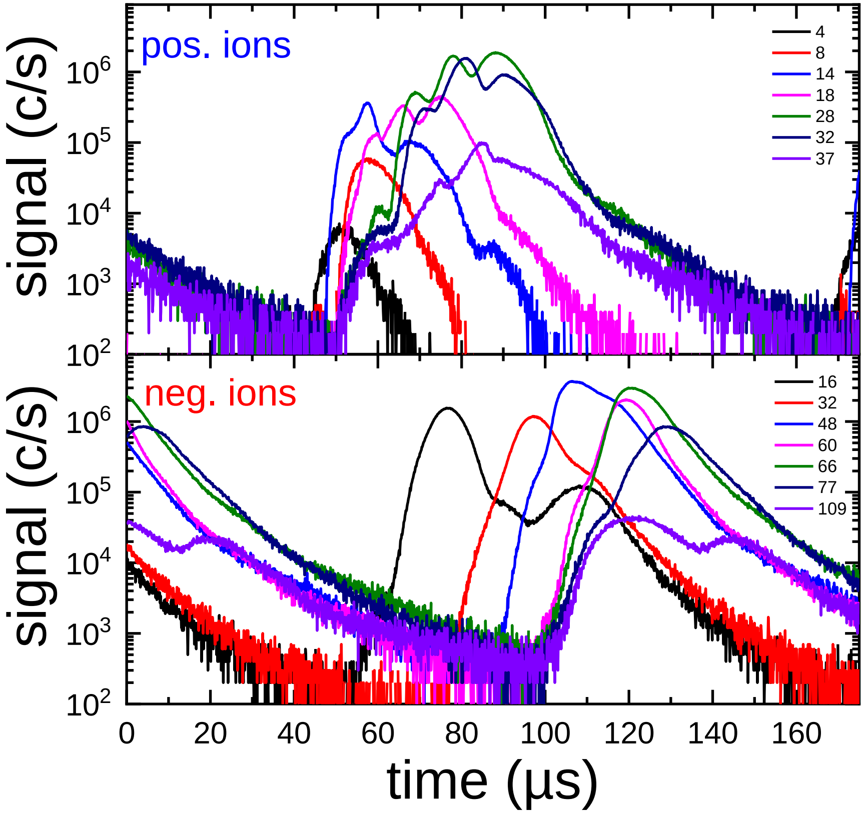
Mass 48 (O_3^-) dominant

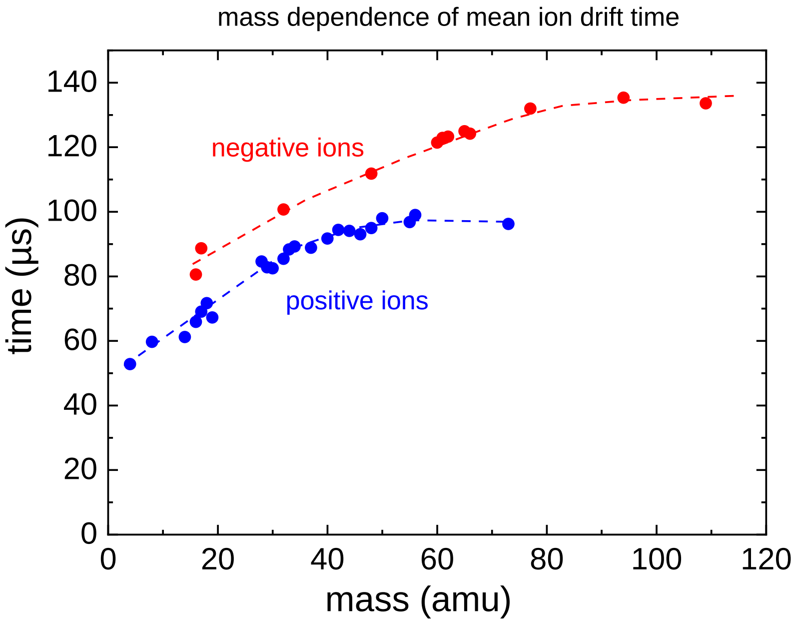
Many negative clusters present



Ion mass spectra in 8 kHz plasma needle

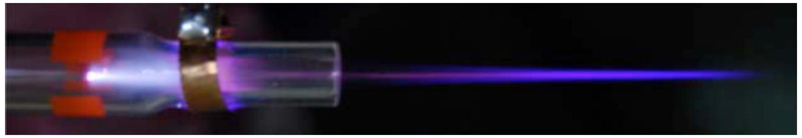




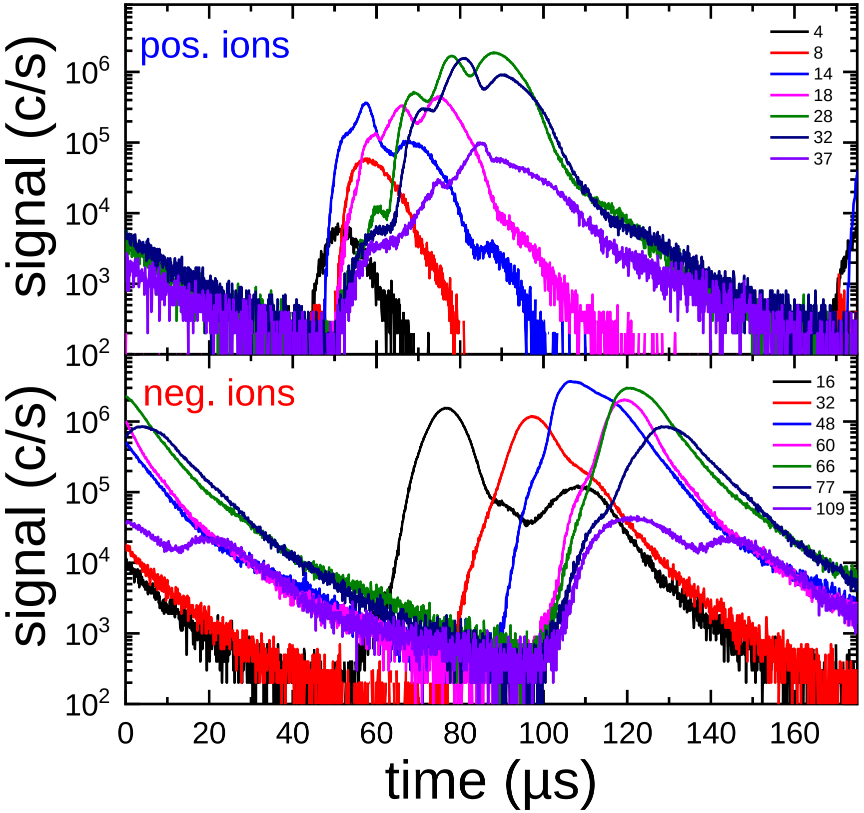


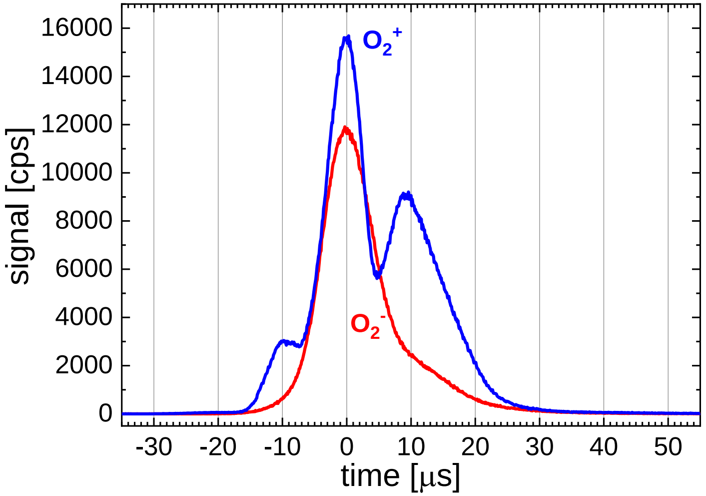
Mass dependent delay due to mass-dependent drift time in the mass spectrometer

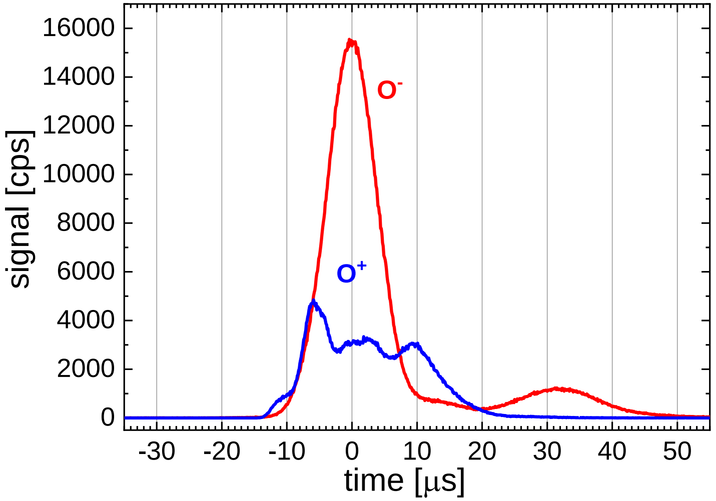
Ion mass spectra in 8 kHz plasma needle



- broader then the current pulse
- complex temporal behavior





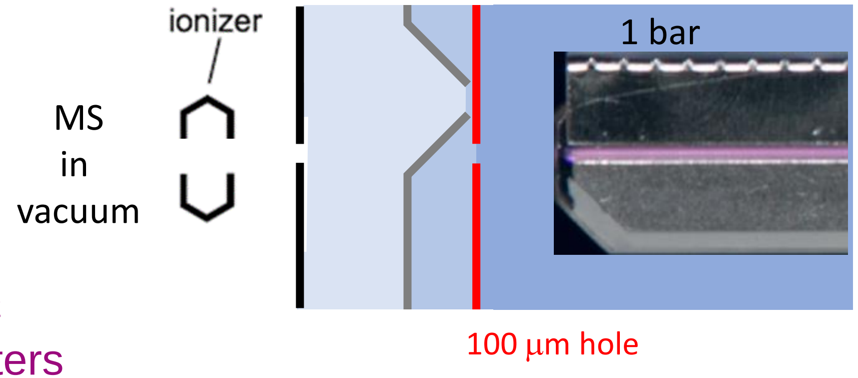


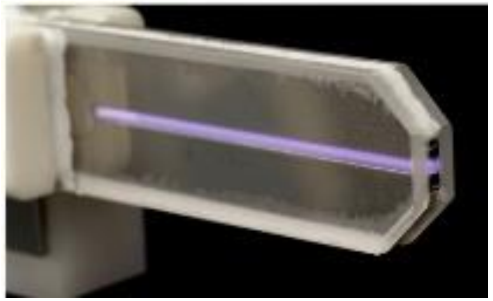
Validation of plasma chemistry models?

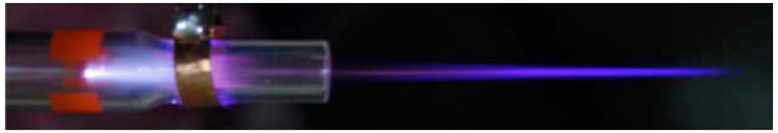
Conclusions

Mass Spectrometry at one atmosphere

- TI MBMS allows absolutely calibrated measurements of reactive and stable species densities:
  → N, O, OH, O_2H, NO_x
  → H_2O_2, O_3, O_2, N_2, CO_2, CO, HMDSO…
- Relative measurement of vibrationally excited species: $N_2(v)$, $^1O_2$
- Ion measurements: mainly ions resulting from CT reactions, clusters







MS analysis of Non-equilibrium APPs

- APPs are effective source of reactive species
- Study of plasma-chemical processes for solar fuels → CO_2 conversion
- Time-resolved ion measurements provide insights in plasma dynamics and ion chemistry

Acknowledgements: cost EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY www.cost.eu COST Action TD1208 Electrical discharges with liquids for future applications

DFG Deutsche Forschungsgemeinschaft

DFG PROJECT PACKAGES
Plasmadecon and **Placid**