Kiel University
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Time-resolved ion mass spectrometry to investigate the ion chemistry of a dielectric barrier discharge

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Christian-Albrechts-Universität zu Kiel
Mathematisch-Naturwissenschaftliche Fakultät

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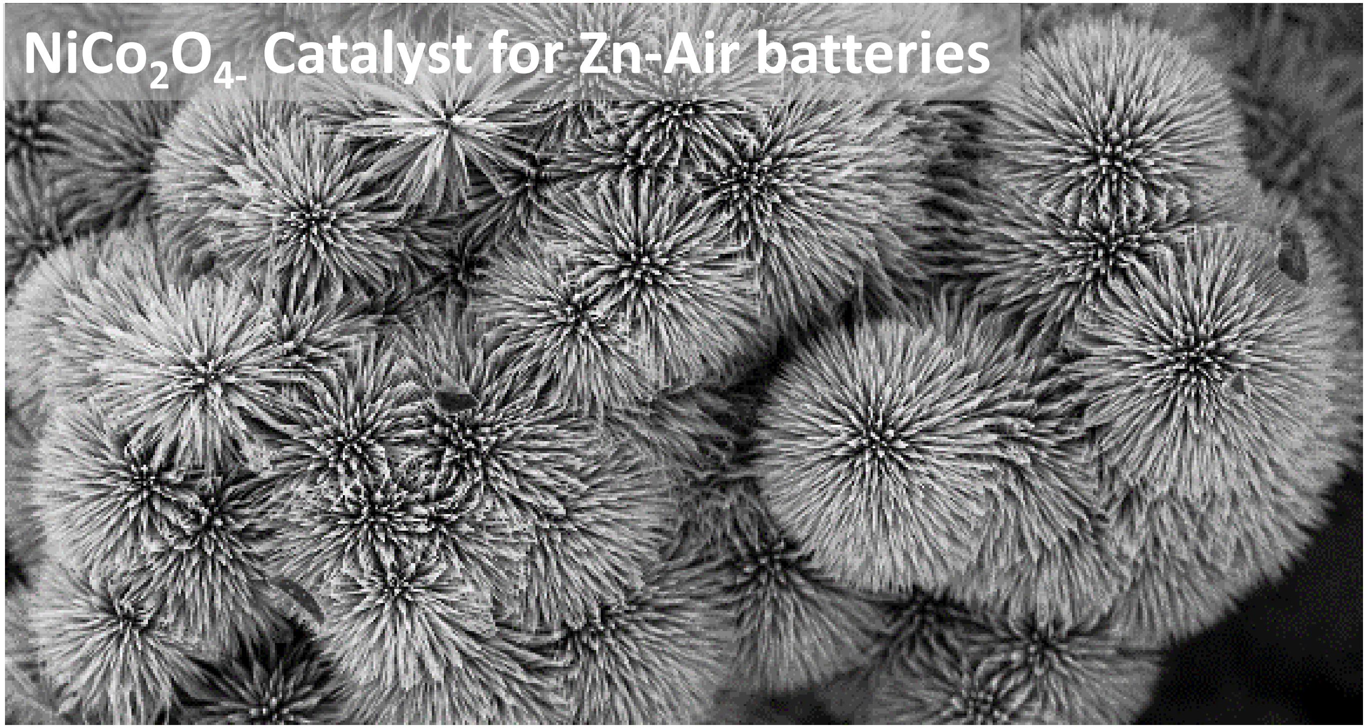
Experimental Plasma Physics Group

Experimental Plasma Physics Group

Research topics:

- Plasma treatment of materials



N_2-Plasma refinement of catalysts

H. Li *et al.*, 2023 *Int. J. Hydrog. Energy* **48** 26107-26118
H. Li *et al.*, 2024 *Small* 2310660

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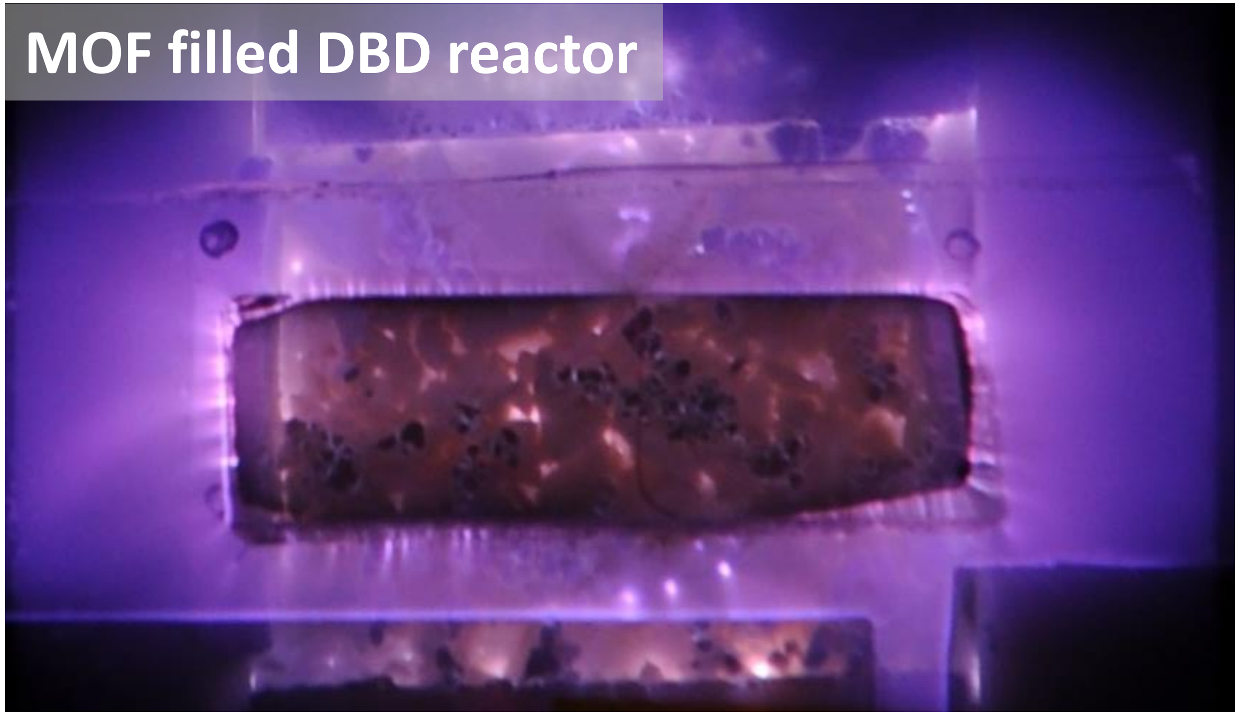
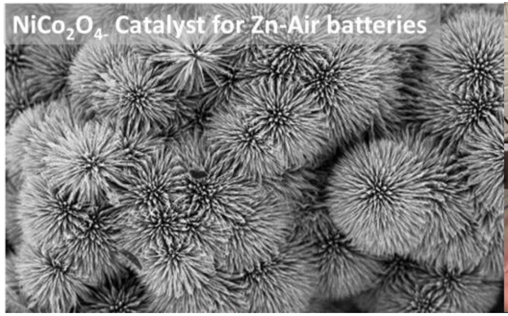
- Cold atmospheric pressure plasmas for catalysis





N_2-Plasma refinement of catalysts

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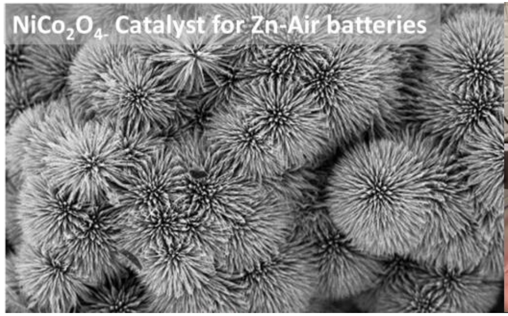
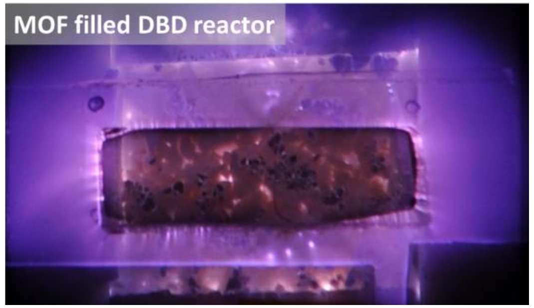
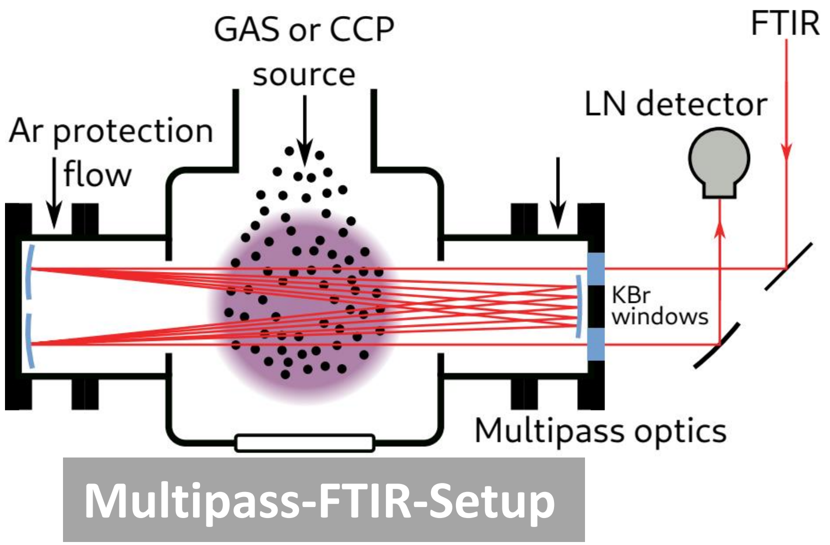
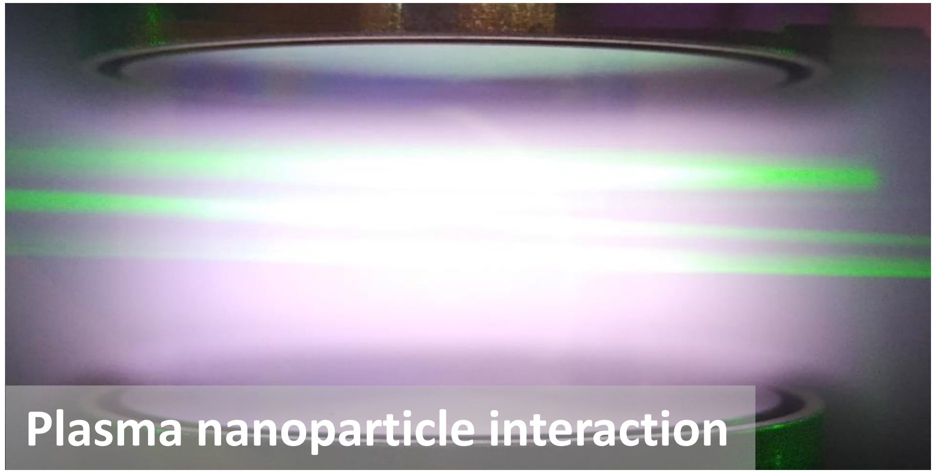


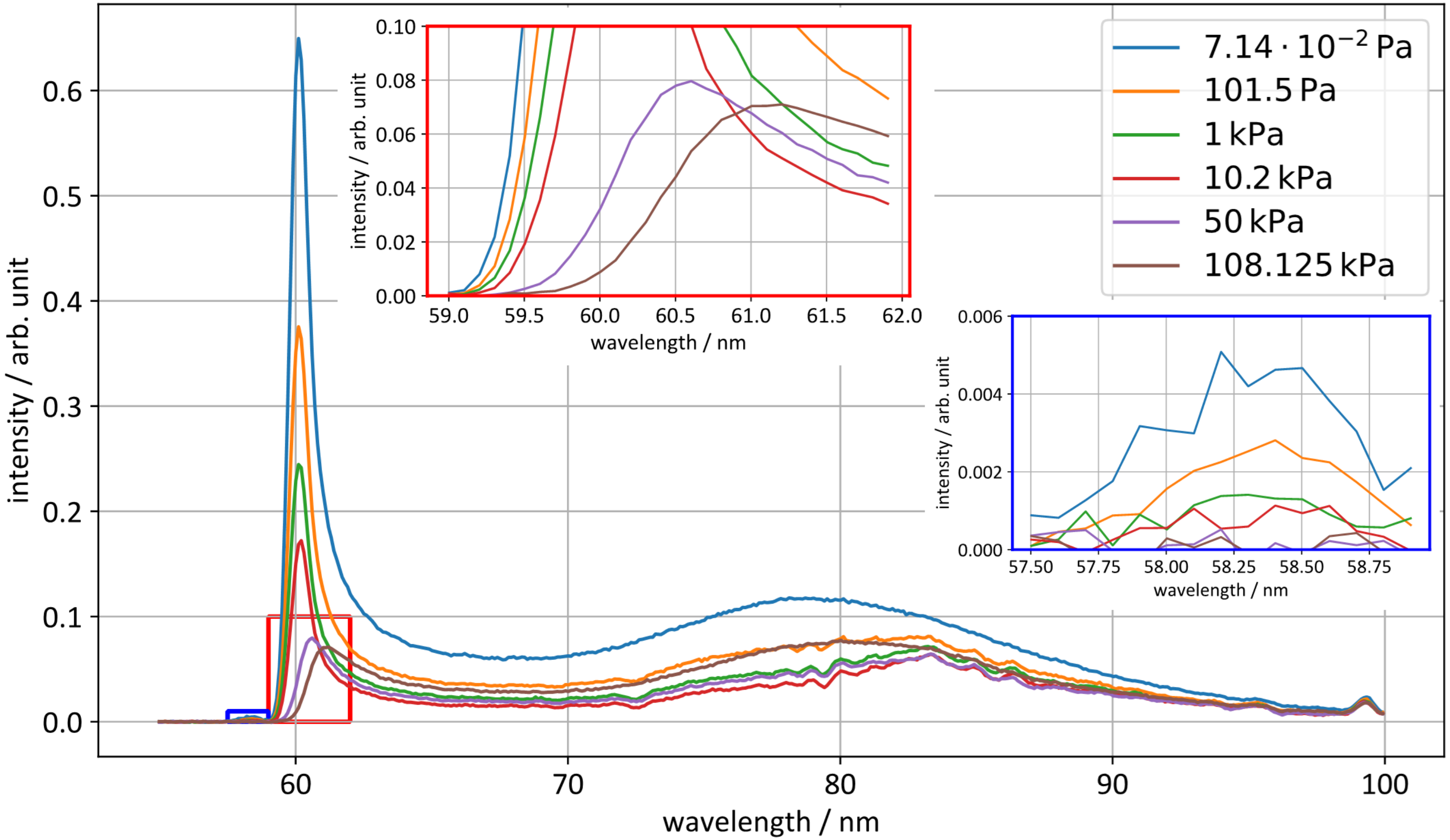




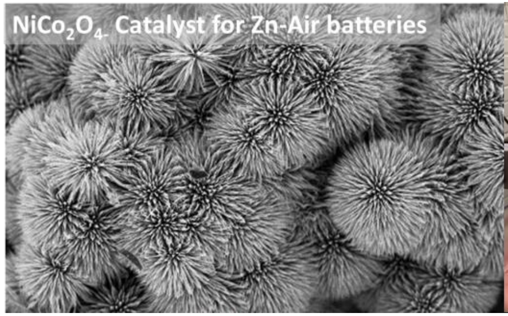


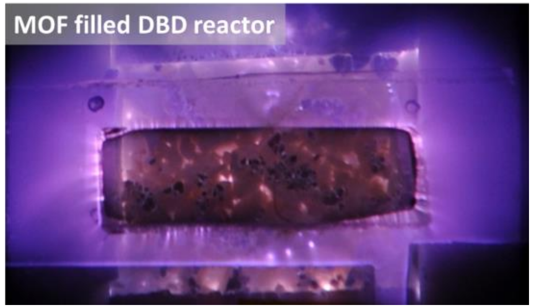
O. H. Asnaz *et al.*, 2023 *Nanoscale Adv.* **5** 1115-1123

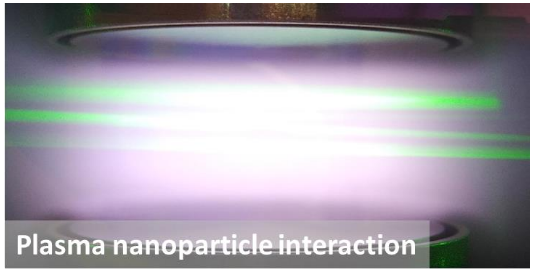
Experimental Plasma Physics Group



Vacuum UV spectroscopy and source development







Experimental Plasma Physics Group

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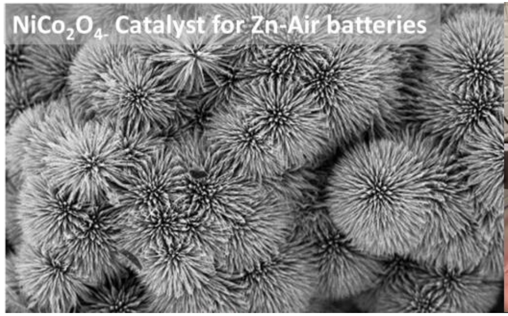
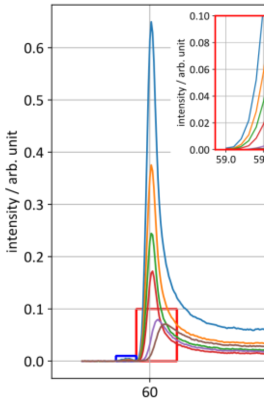
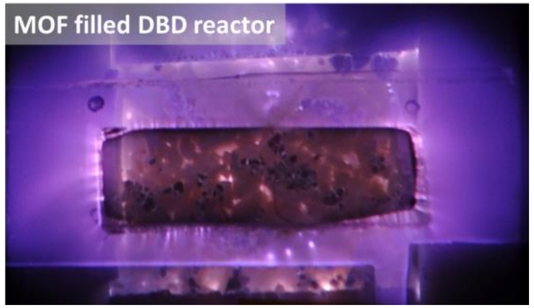
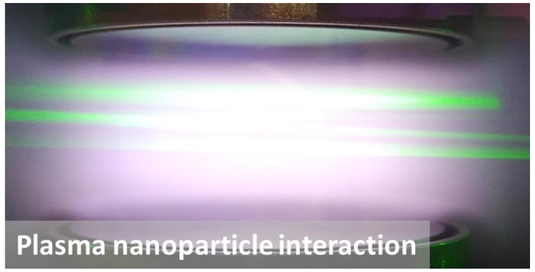
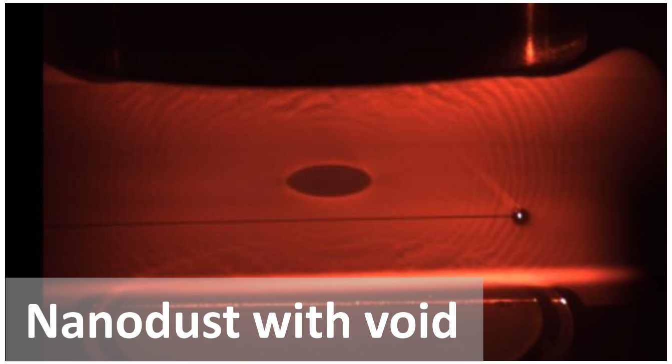
- Cold atmospheric pressure plasmas for catalysis
- In situ (core shell) nanoparticle diagnostics
- Vacuum UV spectroscopy and source development
- Foundations and applications of dusty plasmas







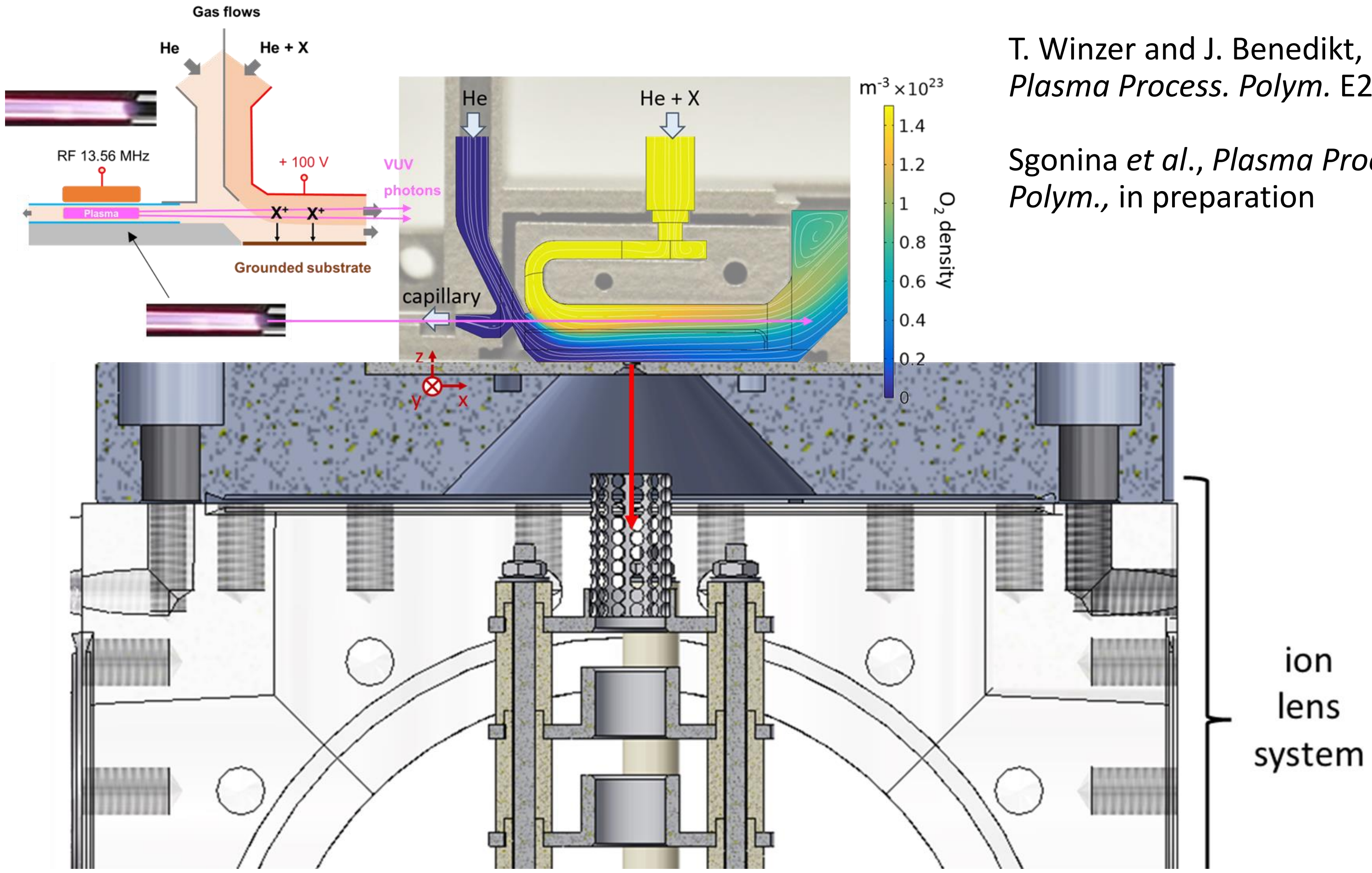




A. Schmitz *et al.*, 2023 *J. Phys. D: Appl. Phys.* **56** 445202

D. Block *et al.*, 2023 Phys. Plasmas **30** 043703

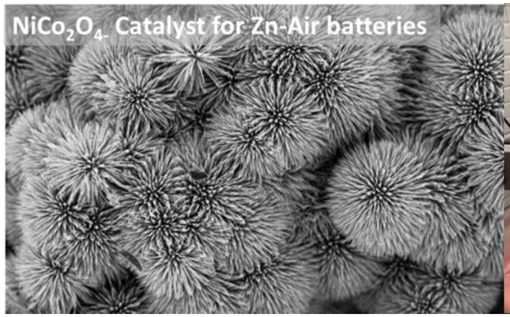
Experimental Plasma Physics Group

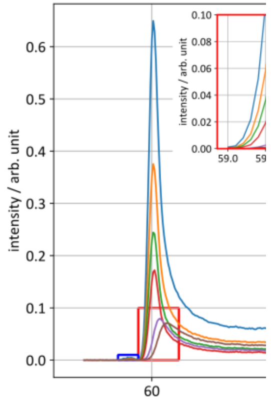


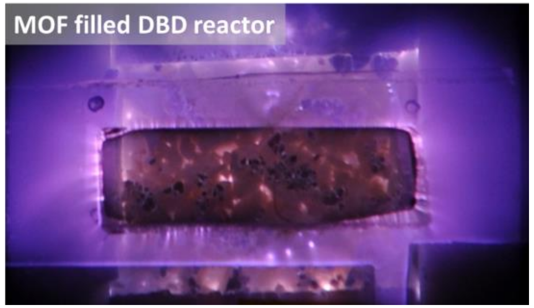
Mass spectrometry at plasma jets and ion sources

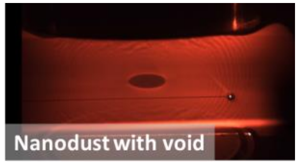
T. Winzer and J. Benedikt, 2024
Plasma Process. Polym. E2300226

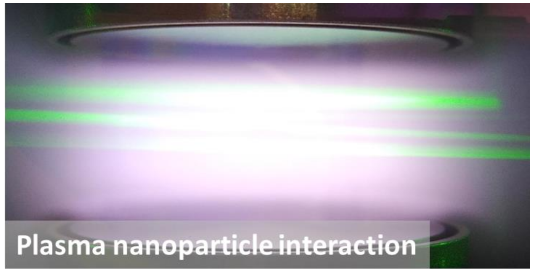
Sgonina *et al.*, *Plasma Process. Polym.*, in preparation











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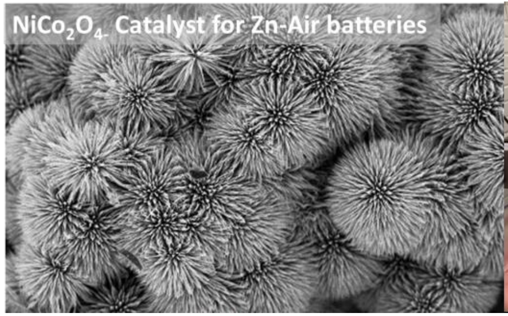
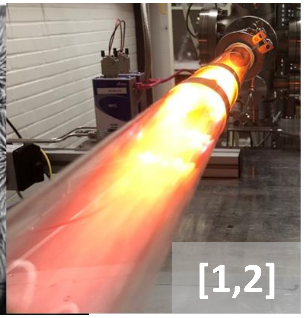
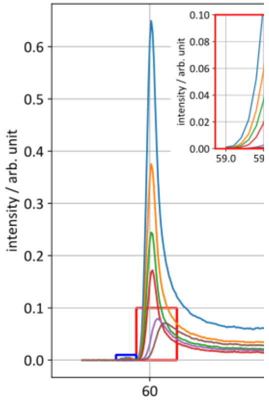
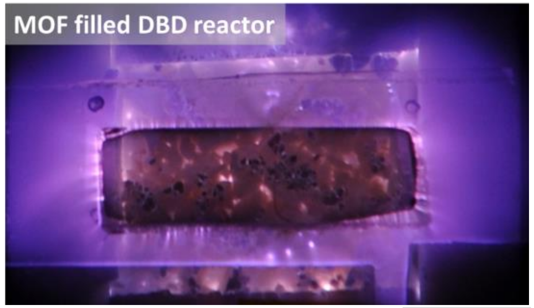
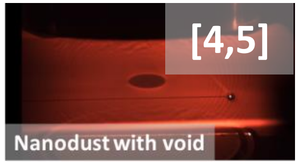
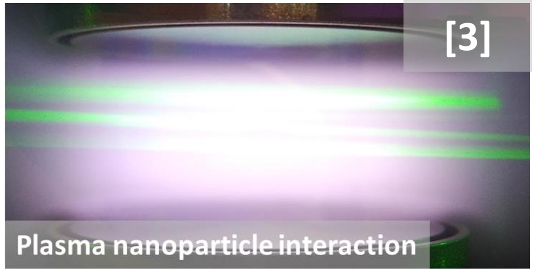


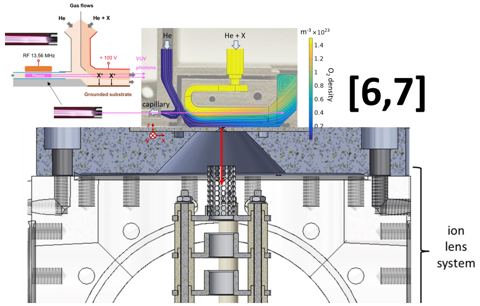












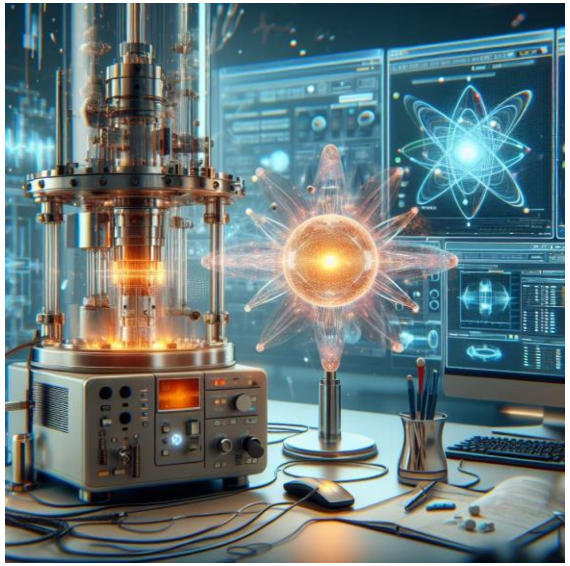
[6,7]

[1] H. Li *et al.*, 2023 *Int. J. Hydrog. Energy* **48** 26107-26118
[2] H. Li *et al.*, 2024 *Small* 2310660
[3] O. H. Asnaz *et al.*, 2023 *Nanoscale Adv.* **5** 1115-1123
[4] A. Schmitz *et al.*, 2023 *J. Phys. D: Appl. Phys.* **56** 445202
[5] D. Block *et al.*, 2023 Phys. Plasmas **30** 043703
[6] T. Winzer and J. Benedikt, 2024 *Plasma Process. Polym.* E2300226
[7] Sgonina *et al.*, *Plasma Process. Polym.,* in preparation

Motivation

- Ions play a crucial role in the plasma chemistry and plasma surface interaction[1,2]
- Low ion densities are balanced by their higher reactivity[3,4]

Ion-based plasma chemistry



Atmospheric pressure plasma jet creating ion-based plasma chemistry

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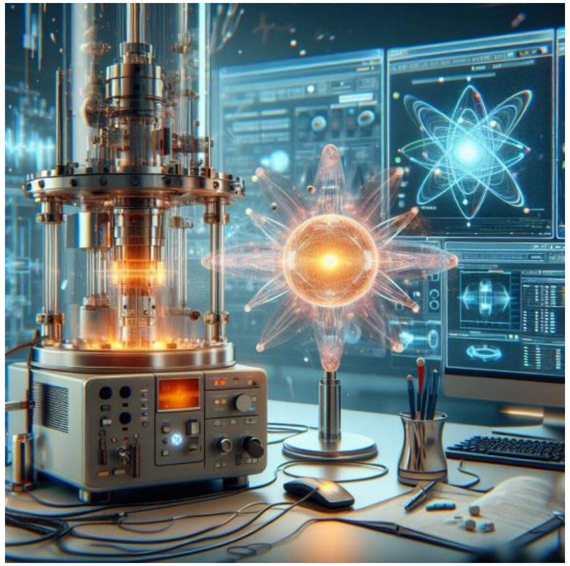
Copilot Designer, https://www.bing.com/images/create?FORM=GENILP

[1] P. Tosi *et al.*, 2009 *Plasma Sources Sci. Technol.* **18** 034005
[2] L. Hansen *et al.*, 2023 *Thin Solid Films* **765** 139633
[3] P. Tosi *et al.*, 1995 *J. Phys. Chem.* **99** 15538-43
[4] P. Mehta *et al.*, 2019 *ACS Energy Lett.* **4** 1115-33

Motivation

- Ions play a crucial role in the plasma chemistry and plasma surface interaction[1,2]
- Low ion densities are balanced by their higher reactivity[3,4]
- Mass spectrometry allows absolute ion density measurements after calibration[5,6]
- Time-resolved measurements help to understand the ion formation pathways

Ion-based plasma chemistry



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[4] P. Mehta *et al.*, 2019 *ACS Energy Lett.* **4** 1115-33
[5] G. Willems, J. Benedikt and A. von Keudell, 2017 *J. Phys. D: Appl. Phys.* **50** 335204
[6] J. Jiang and P. J. Bruggeman, 2021 *J. Phys. D: Appl. Phys.* **54** 15LT01

Ion formation

Time

Plasma phase | Plasma + early afterglow | Late afterglow

Based on: S. Große-Kreul *et al.* 2015 Plasma Sources Sci. Technol. **24** 044008

Ion formation

Time

Plasma phase | Plasma + early afterglow | Late afterglow

Initial phase | **Conversion phase** | **Clustering**

Based on: S. Große-Kreul *et al.* 2015 Plasma Sources Sci. Technol. **24** 044008

Ion formation

Time

Plasma phase | Plasma + early afterglow | Late afterglow

Initial phase

e.g.

- Electron impact ionization

$e^- + N_2 \rightarrow N_2^+ + 2e^-$

- Electron attachment

$e^- + O_2 \rightarrow O_2^-$

Conversion phase

e.g.

- Charge transfer

$O_2^- + O_3 \rightarrow O_3^- + O_2$

- Proton transfer

$H_2O^+ + H_2O \rightarrow H_3O^+ + OH$

Clustering

- Positive clustering

$NO^+ + H_2O \rightarrow NO^+(H_2O)$

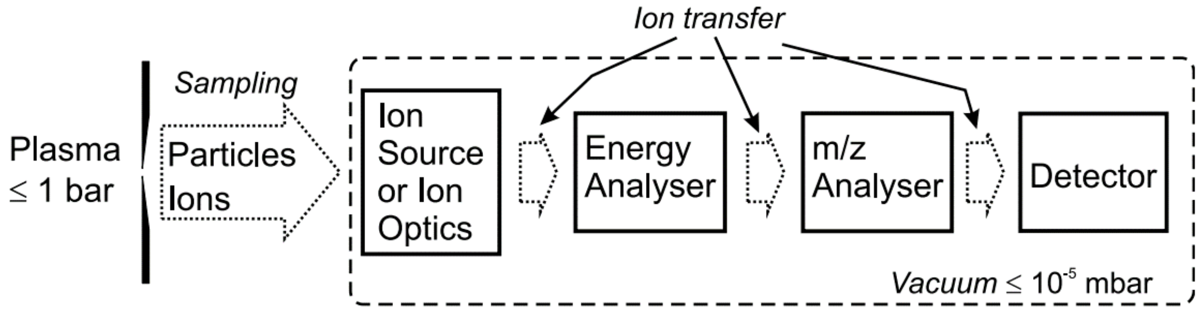
- Negative clustering

$NO_3^- + H_2O \rightarrow NO_3^-(H_2O)$

Based on: S. Große-Kreul *et al.* 2015 Plasma Sources Sci. Technol. **24** 044008

Mass spectrometry

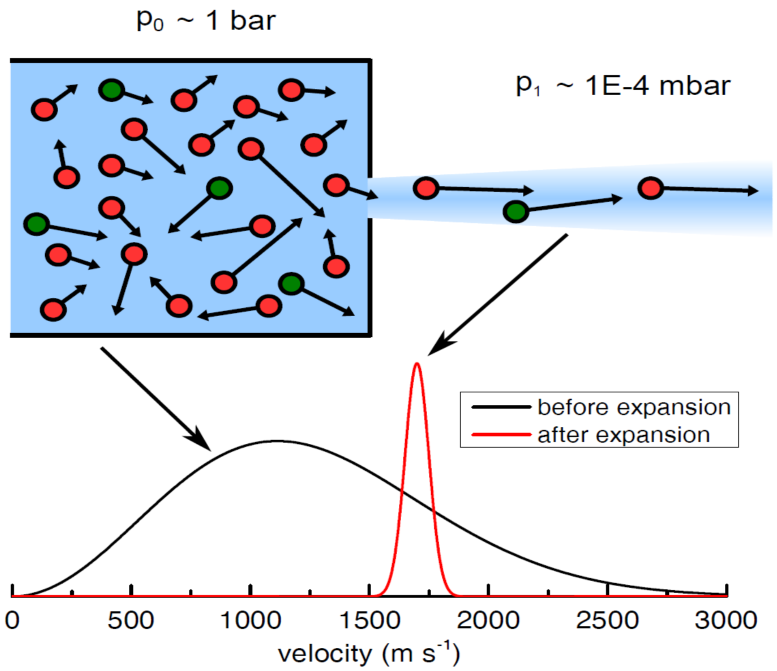
- Ion transfer through multiple elements



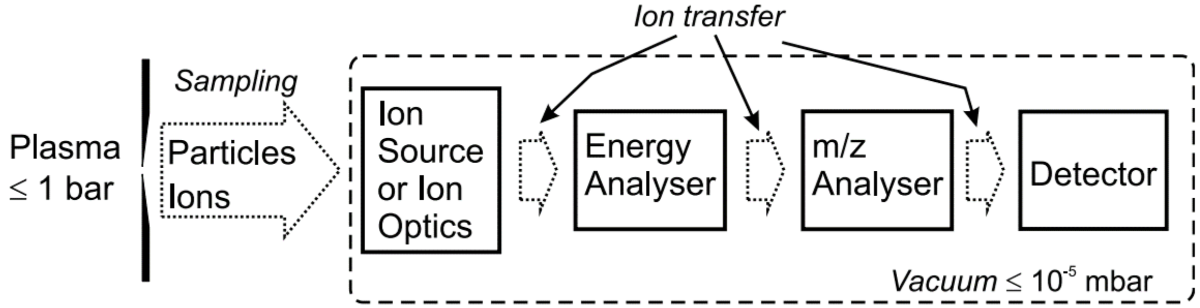
J. Benedikt *et al.* 2012 *J. Phys. D: Appl. Phys.* **45** 403001

Mass spectrometry

- Ion transfer through multiple elements
- Super sonic expansion due to pressure gradient
    - Velocity distribution functions changes
    - Kinetic energy mass dependent



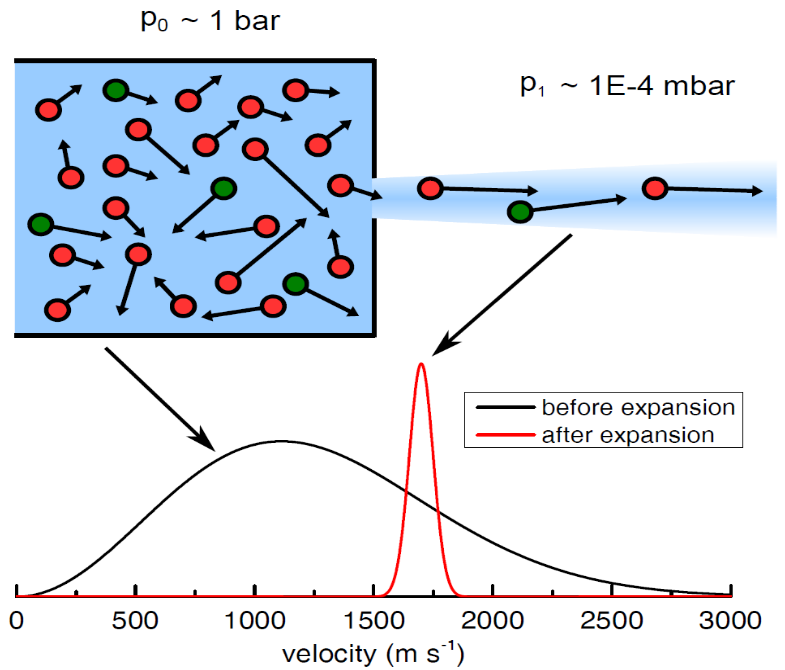
S. Große-Kreul, Mass spectrometry of ions from atmospheric pressure plasmas, PhD Thesis, Ruhr Universität Bochum, 2015



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

Mass spectrometry

- Ion transfer through multiple elements
- Super sonic expansion due to pressure gradient
  - Velocity distribution functions changes
  - Kinetic energy mass dependent
- Quitting surface marks transition to collision free environment



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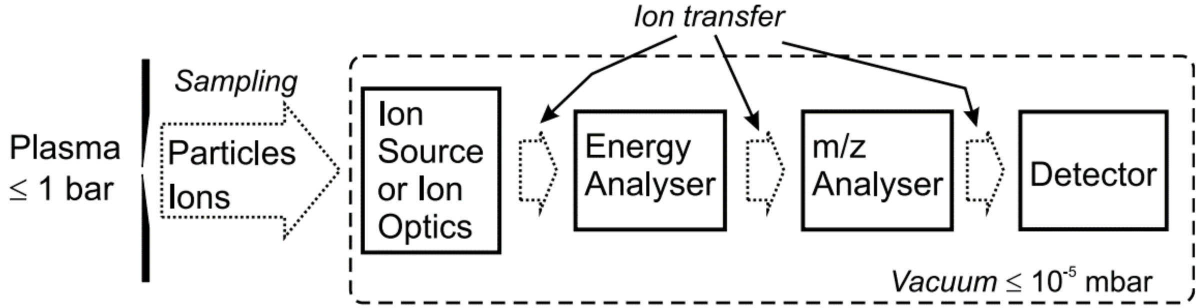

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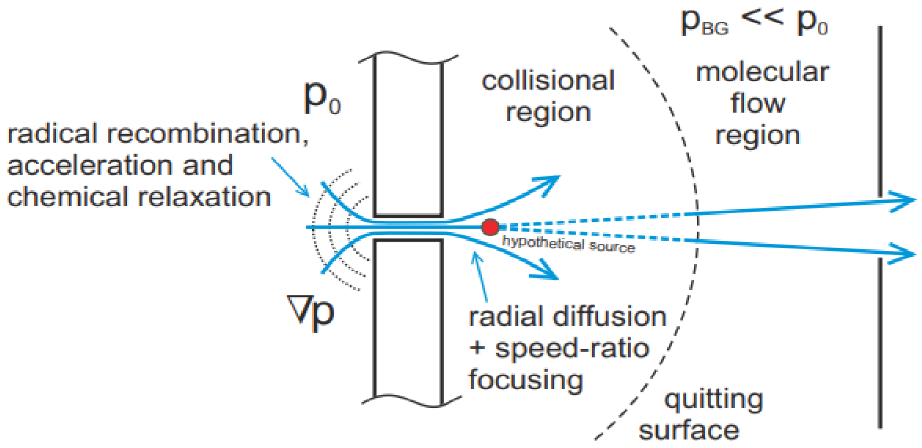
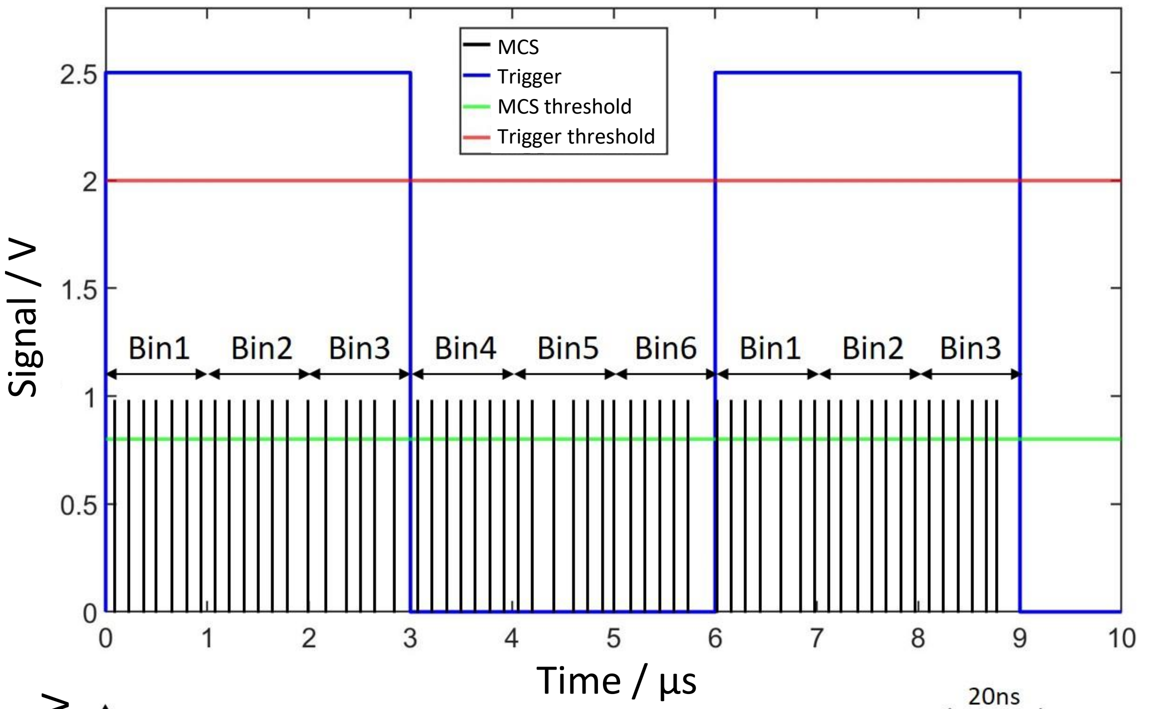
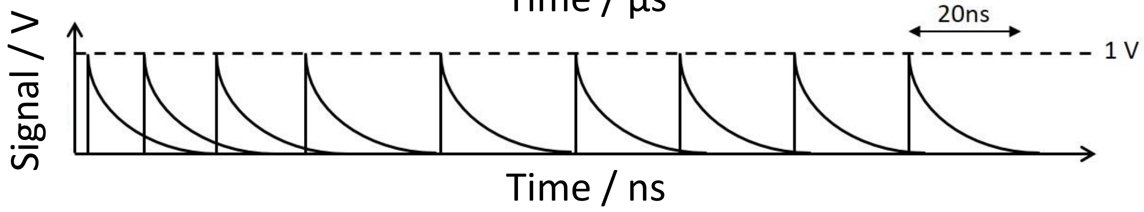


S. Große-Kreul *et al.* 2015 *Plasma Sources Sci. Technol.* **24** 044008

Multi Channel Scaler

- Allows measurements with time resolution up to 10 ns
- SEM pulses are sorted into time bins
- Up to 16384 bins with variable width (≥ 10 ns) can be measured per trigger
- Accumulation with multiple trigger events is possible up to 255 counts per bin

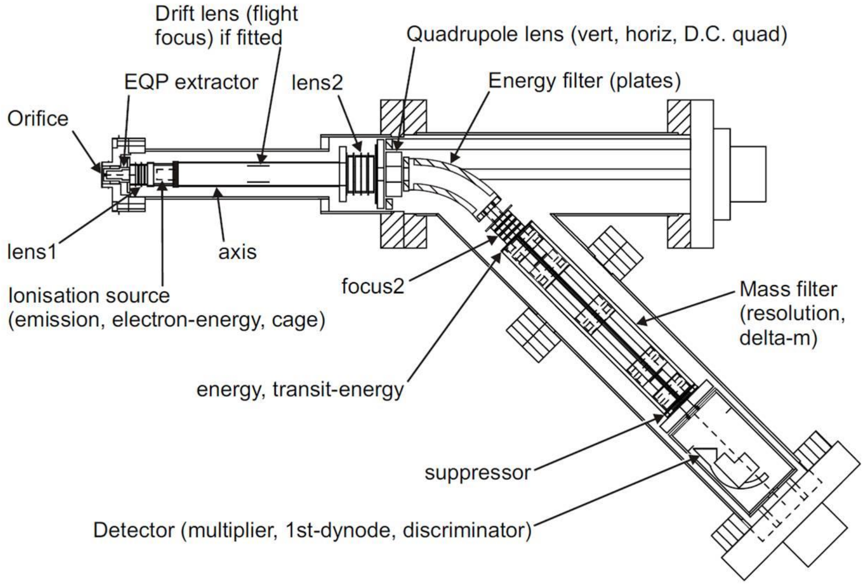




Acknowledgement:

SIMION flight time simulations

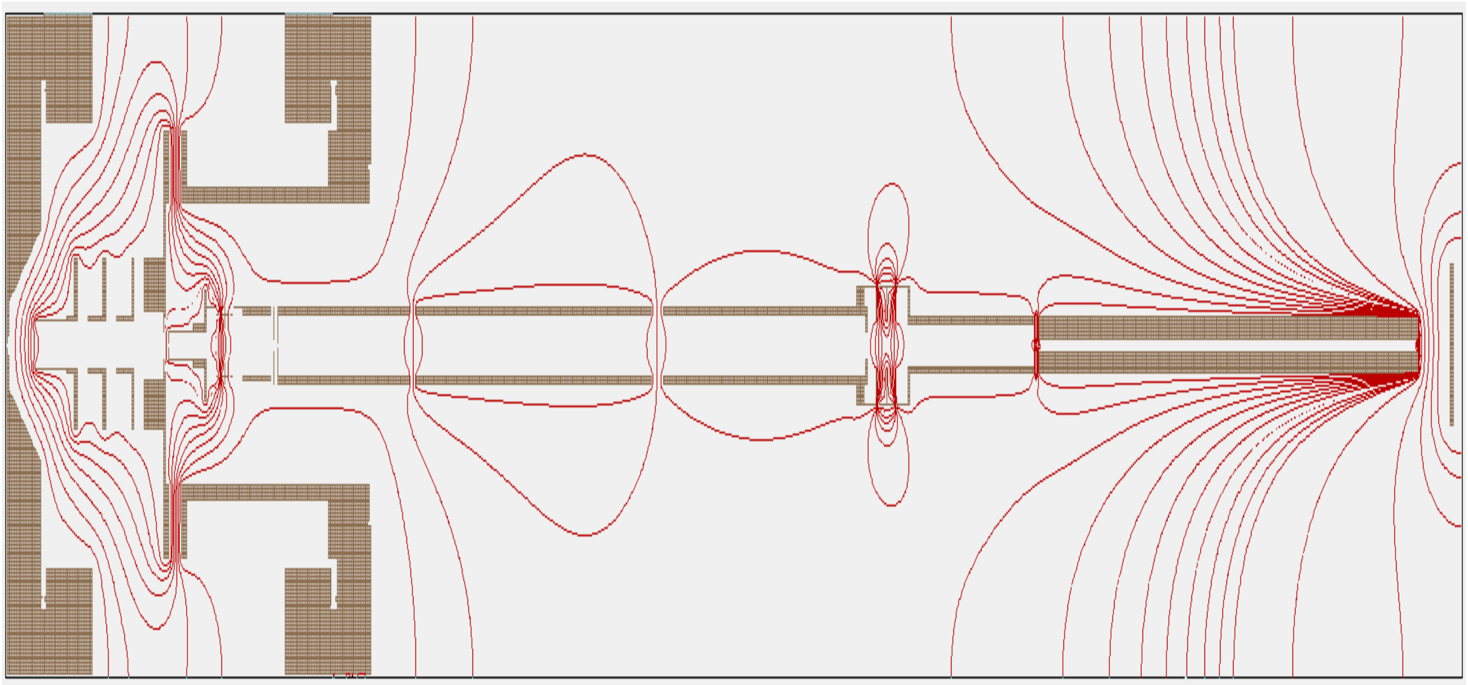
- Simulation of ion trajectories to correct the flight time

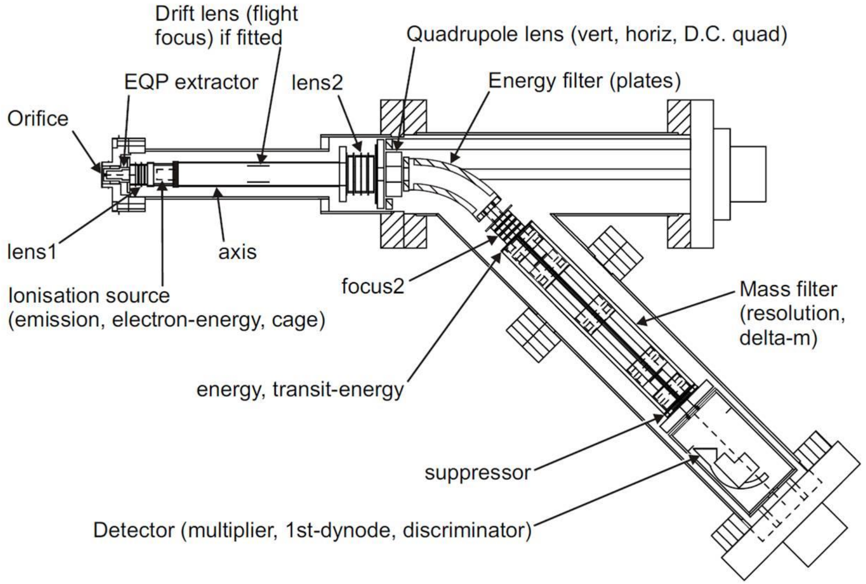


Hiden Analytical Limited *EQP Analyser User Manual* 2014

SIMION flight time simulations

- Simulation of ion trajectories to correct the flight time
- Input: lens and MS electrode voltages, ion entrance energies and quitting surface





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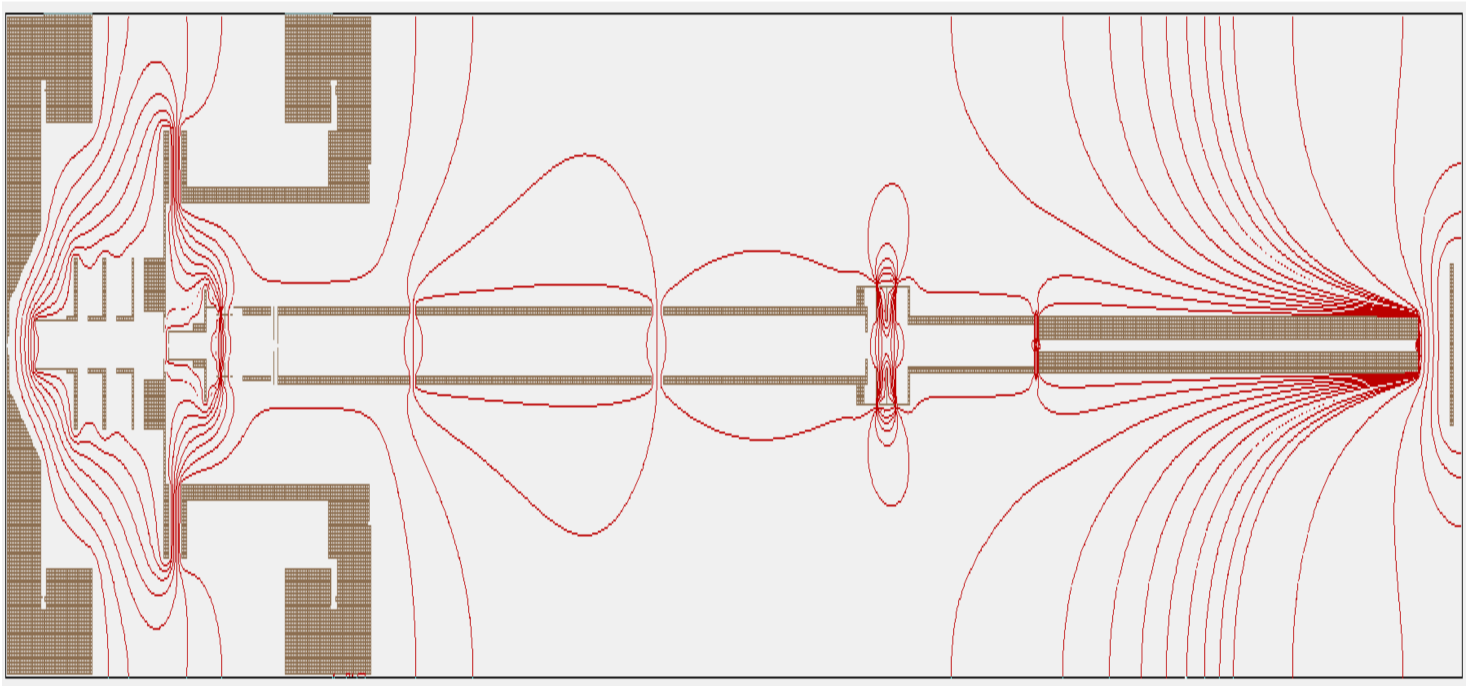
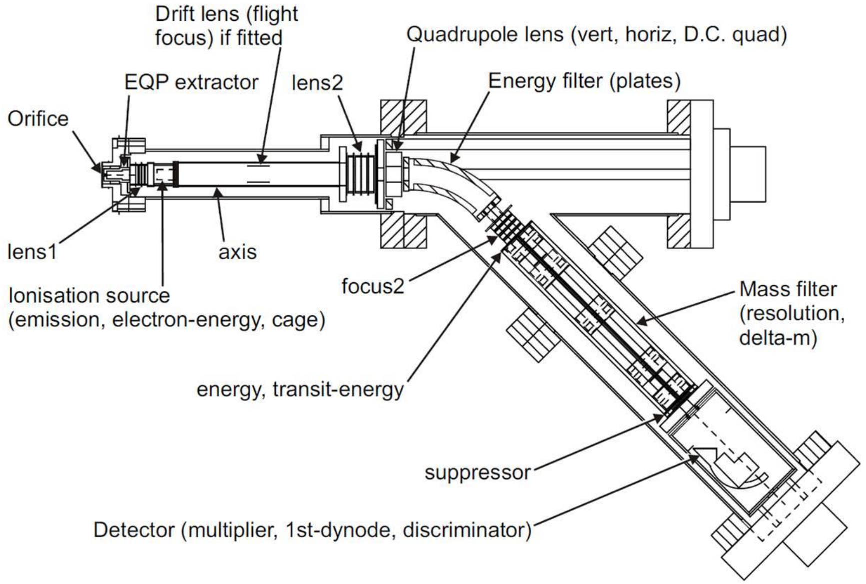


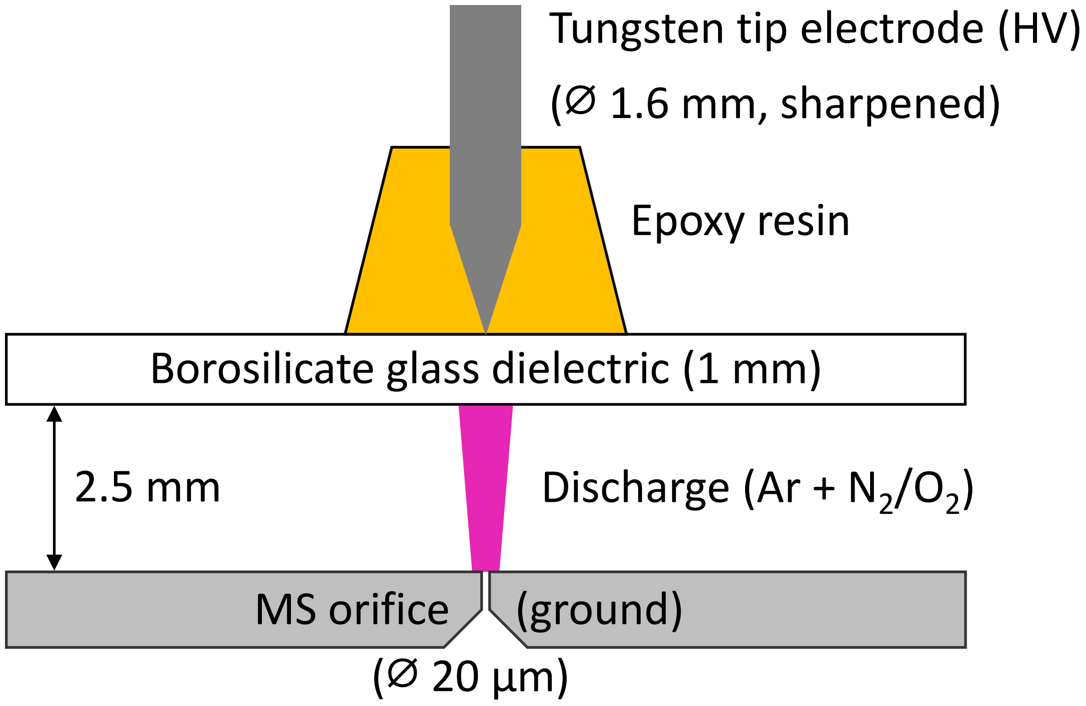


Hiden Analytical Limited *EQP Analyser User Manual* 2014

- Quitting surface can be estimated by comparison of experiment and simulation

Atmospheric pressure DBD

- Single-filament DBD
  - Discharge gap: 2.5 mm
  - Dielectric thickness: 1 mm



Adapted from
L. Bröcker, G. S. Perlick and C.-P. Klages 2020 *Plasma Process. Polym.* **17** e2000129

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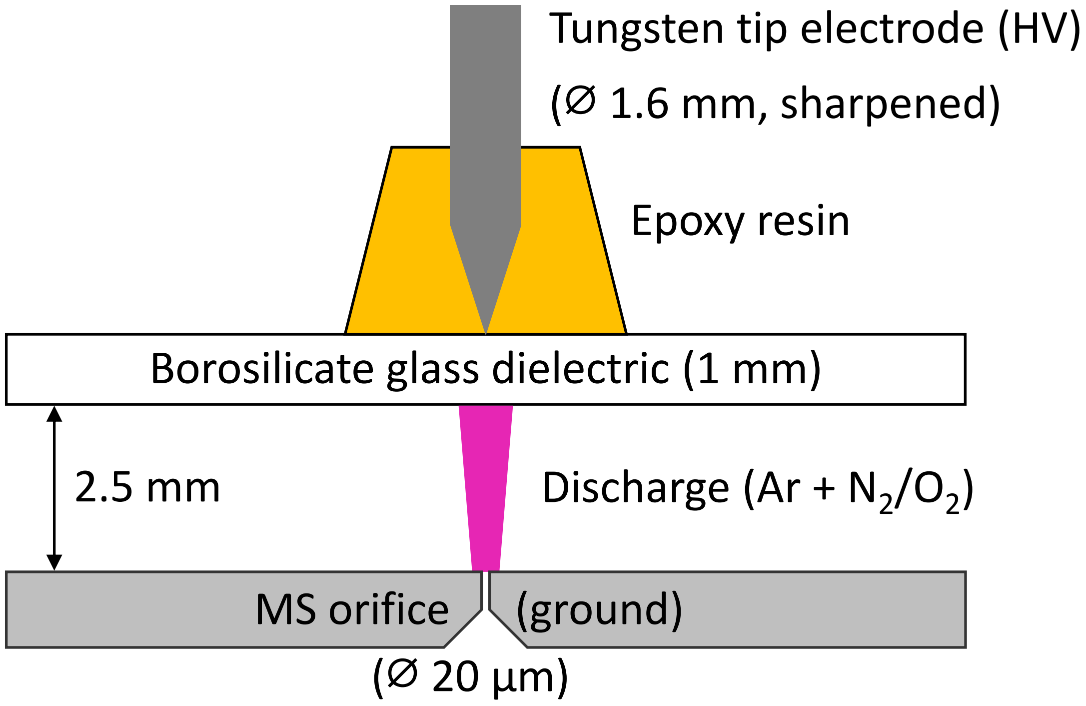
- HF or pulsed operation
  - Sine wave, up to 18 kV_{pp}, 20 kHz (PVM500/DDR10, amazing1)



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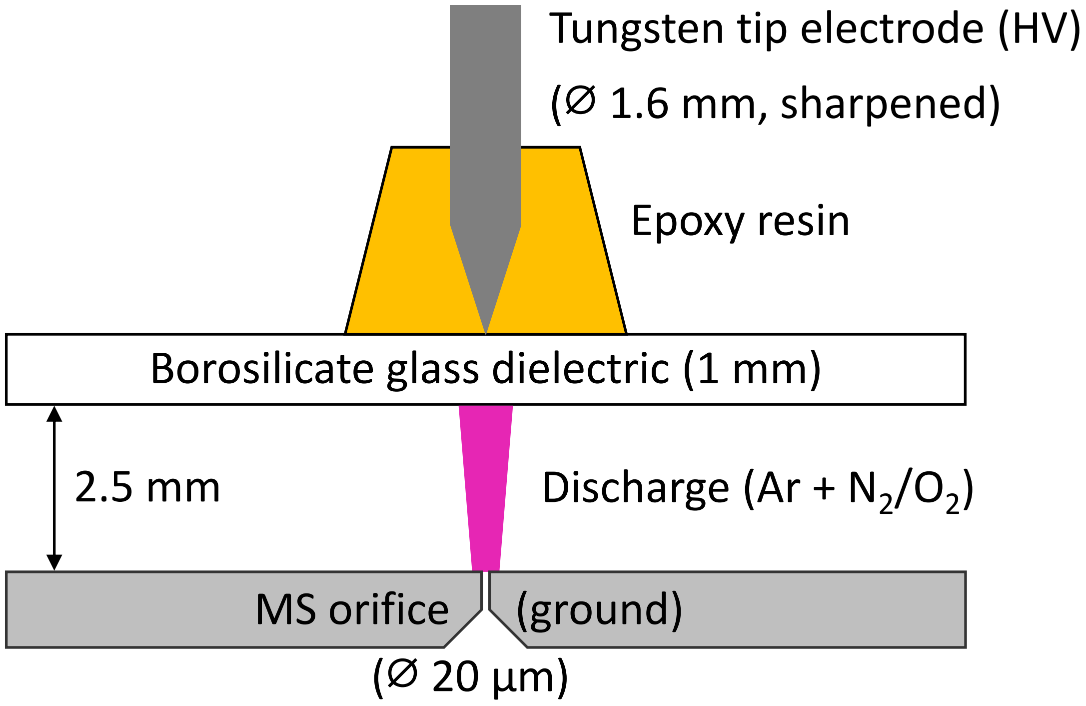
  - Positive 150 ns pulse, up to 20 kV, 100 kHz (Custom, based on HTS331-06, Behlke)



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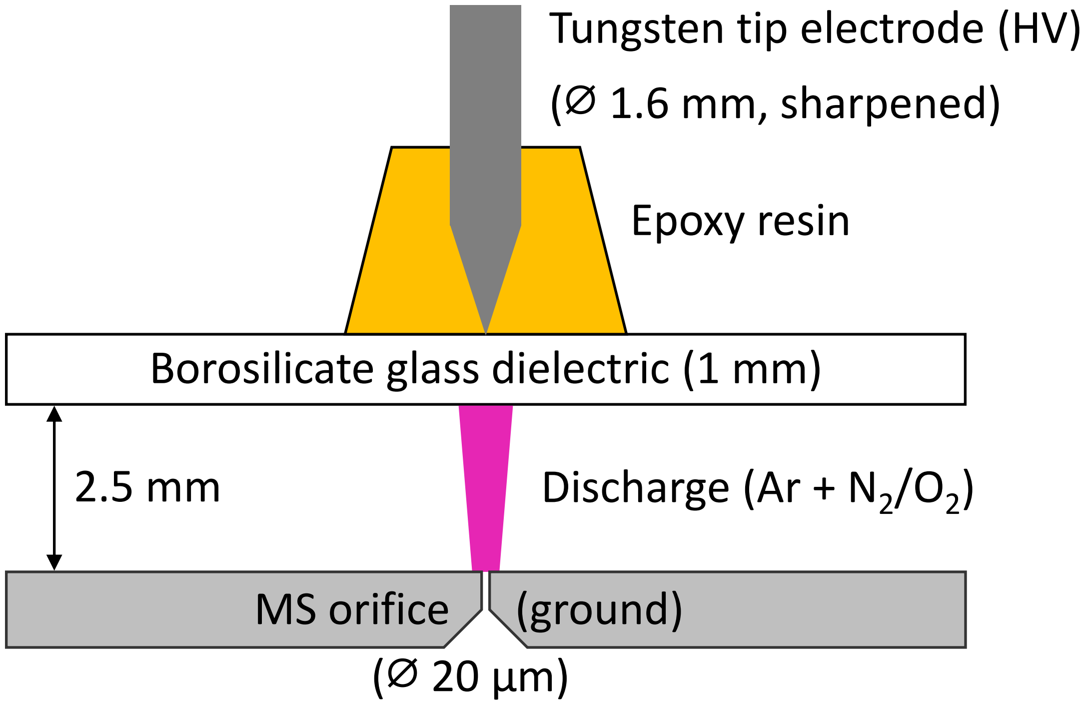
  - Positive 150 ns pulse, up to 20 kV, 100 kHz (Custom, based on HTS331-06, Behlke)
- 2 slm Ar + up to 0.8 % N_2/O_2 admixture



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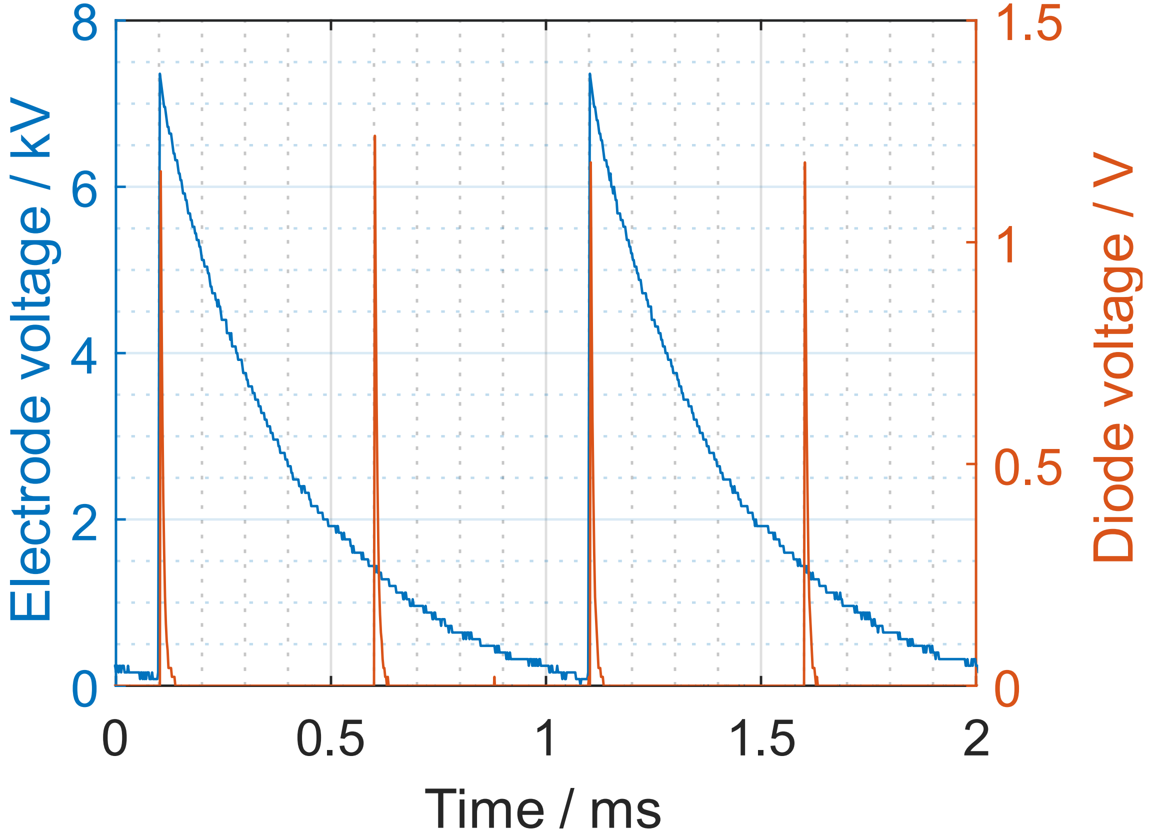
Flight time measurements utilizing the pulser

- Single short and separated pulses
  - Photodiode for ignition control
  - 7.4 kV, 1 kHz, 2 slm Ar
  - Pulse 100 µs delayed to MCS and oscilloscope trigger



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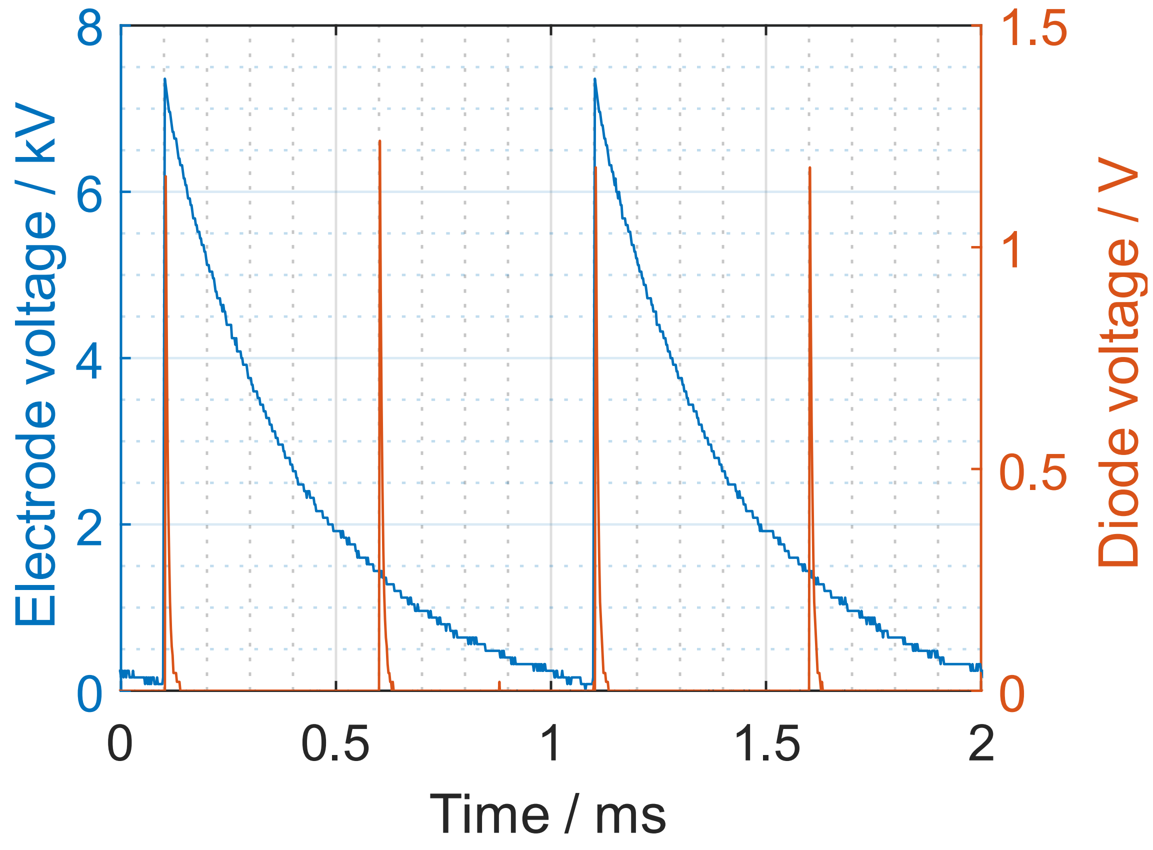
- Pulses prolonged due to capacitive load
- Two separated discharge events per pulse
  - Back discharge due to surface charges
  - Temporal separation large enough for flight time calibration



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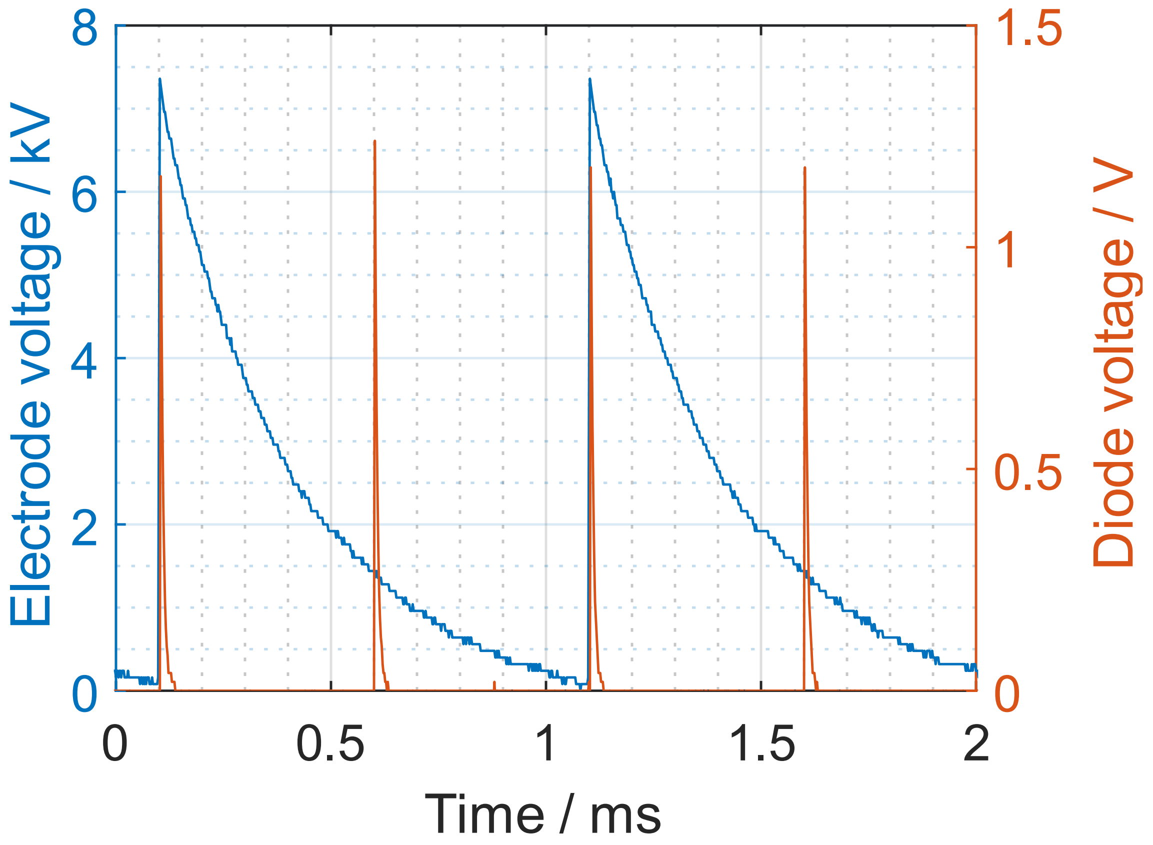
  - 7.4 kV, 1 kHz, 2 slm Ar
  - Pulse 100 µs delayed to MCS and oscilloscope trigger

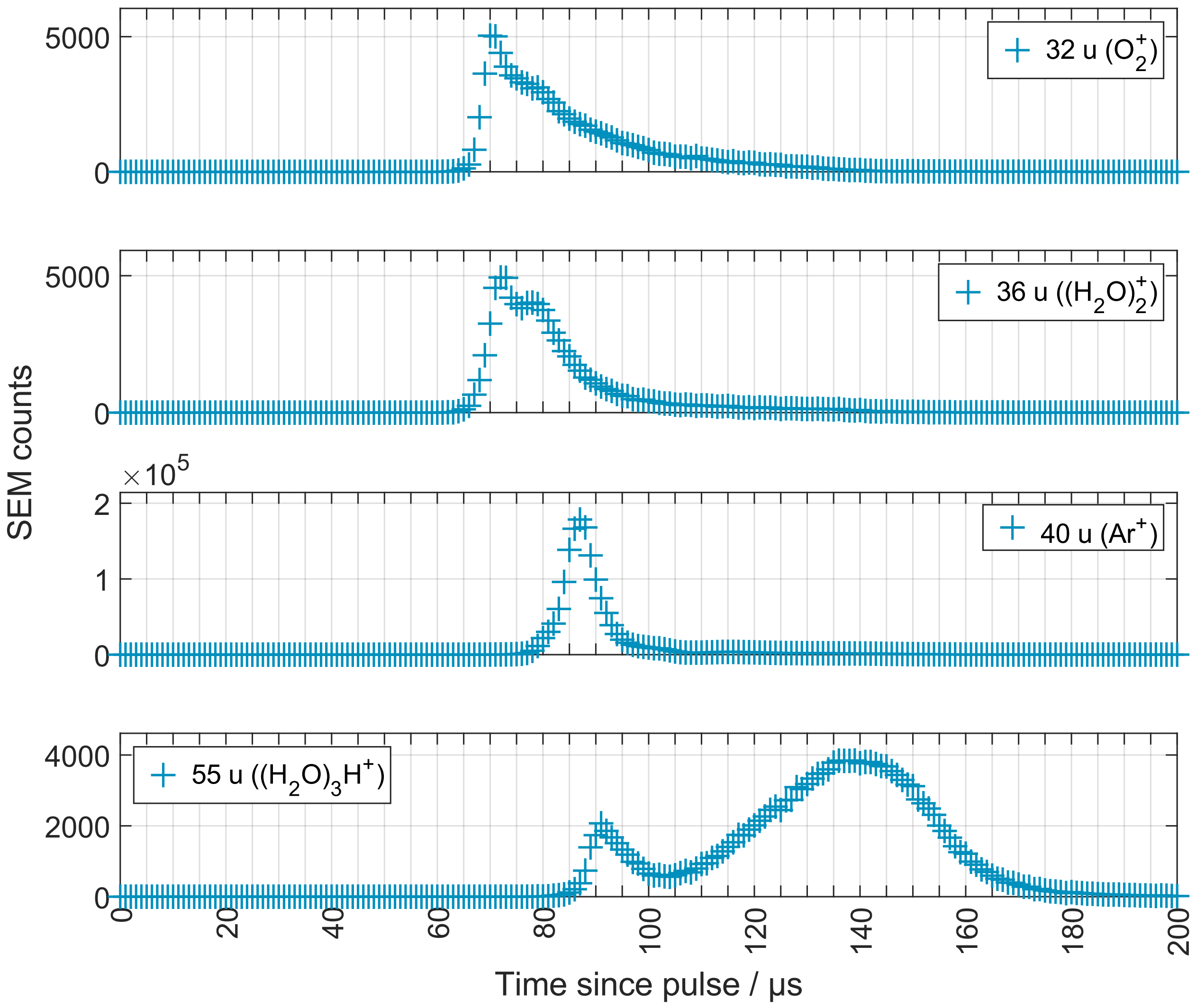
- Pulses prolonged due to capacitive load
- Two separated discharge events per pulse
  - Back discharge due to surface charges
  - Temporal separation large enough for flight time calibration



✓Pulser suited for flight time measurements

Flight time measurements utilizing the pulser

- Multi Channel Scaler (MCS)
  - 20 ns bin width
  - Binning of 50 bins to 1 µs bins



Flight time measurements utilizing the pulser

- Multi Channel Scaler (MCS)
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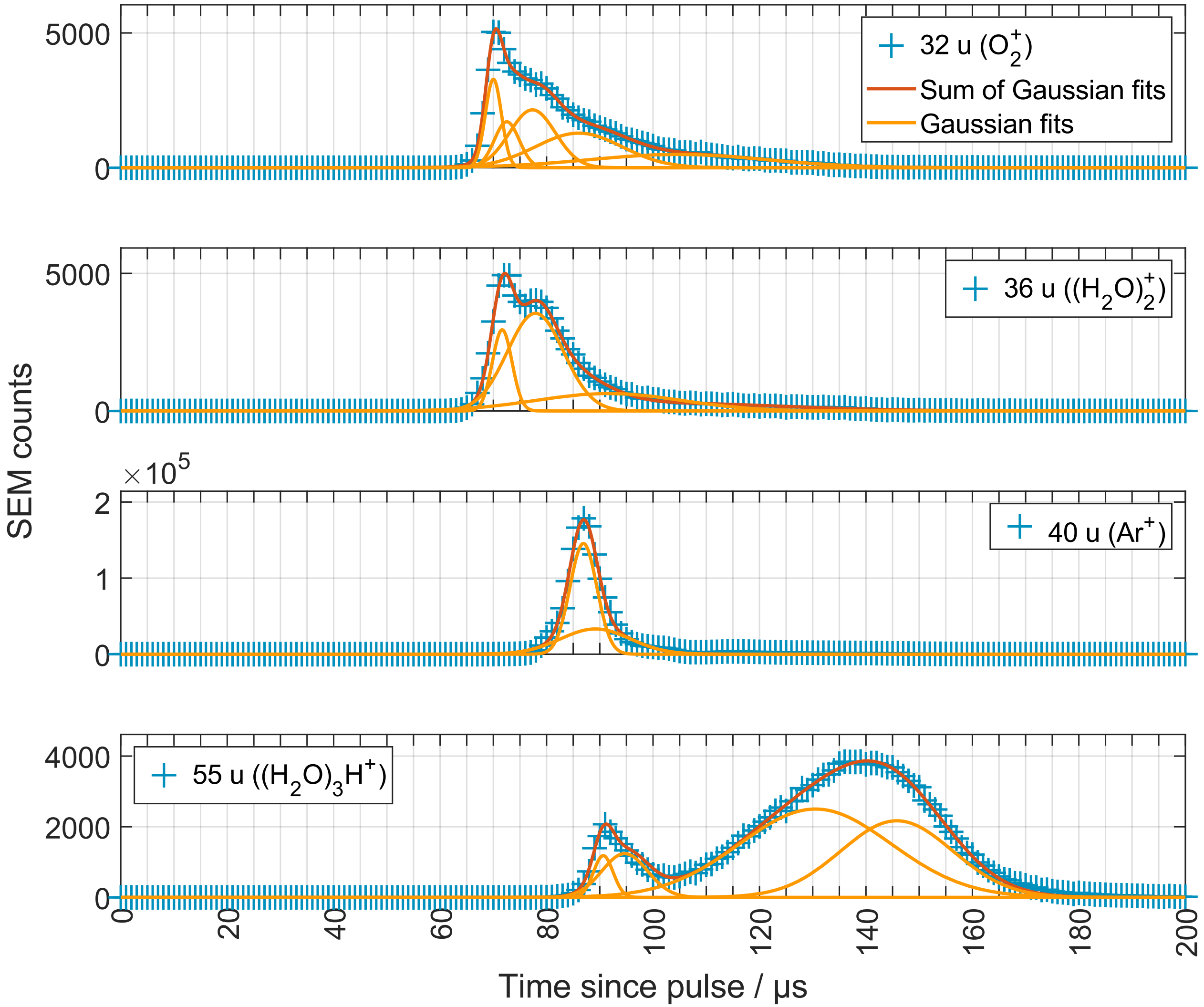
- Allow for a sum of Gaussians as multiple ion production points in time are possible

$$f(x) = \sum_{i=1}^{N} \frac{1}{\sqrt{2\pi\sigma_i}} e^{-\frac{1}{2}\left(\frac{x-\mu_i}{\sigma_i}\right)^2}$$



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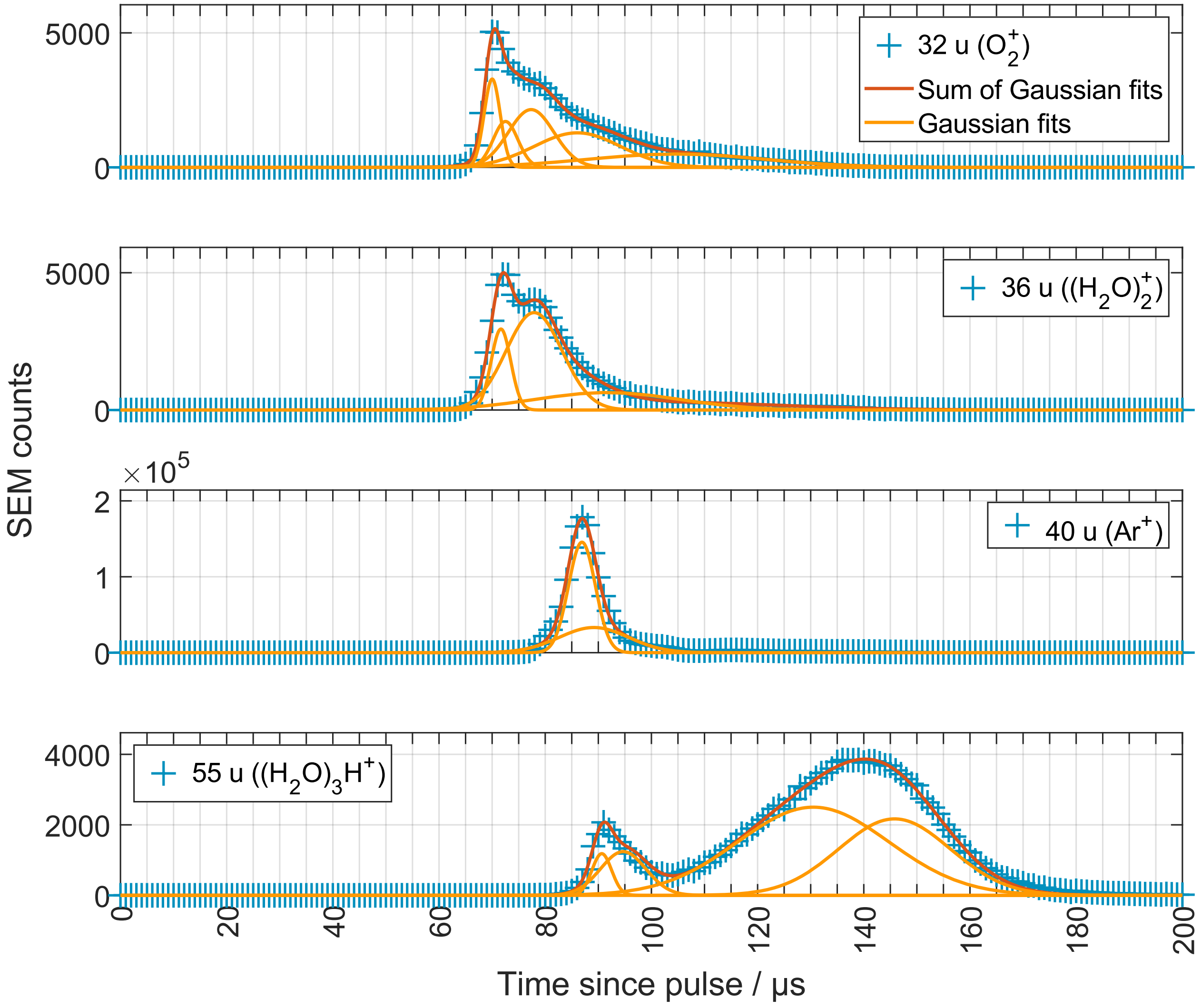
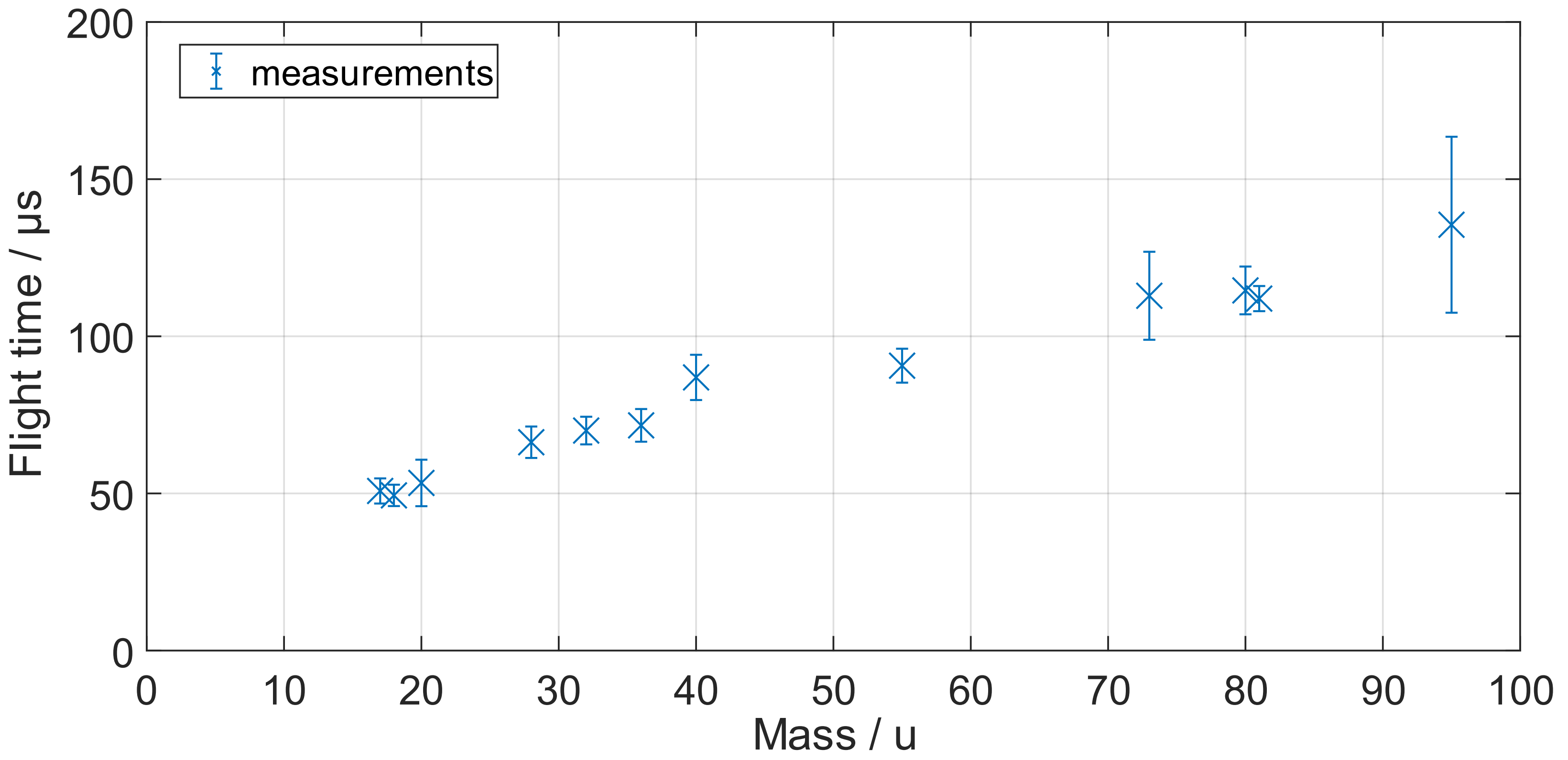
- Mean value of first Gaussian chosen as flight time



Flight time measurements utilizing the pulser

- Flight times should depend on kinetic energy

$$E_{kin} = \frac{1}{2}mv^2$$
$$t \propto \frac{1}{v} \propto \sqrt{m}$$



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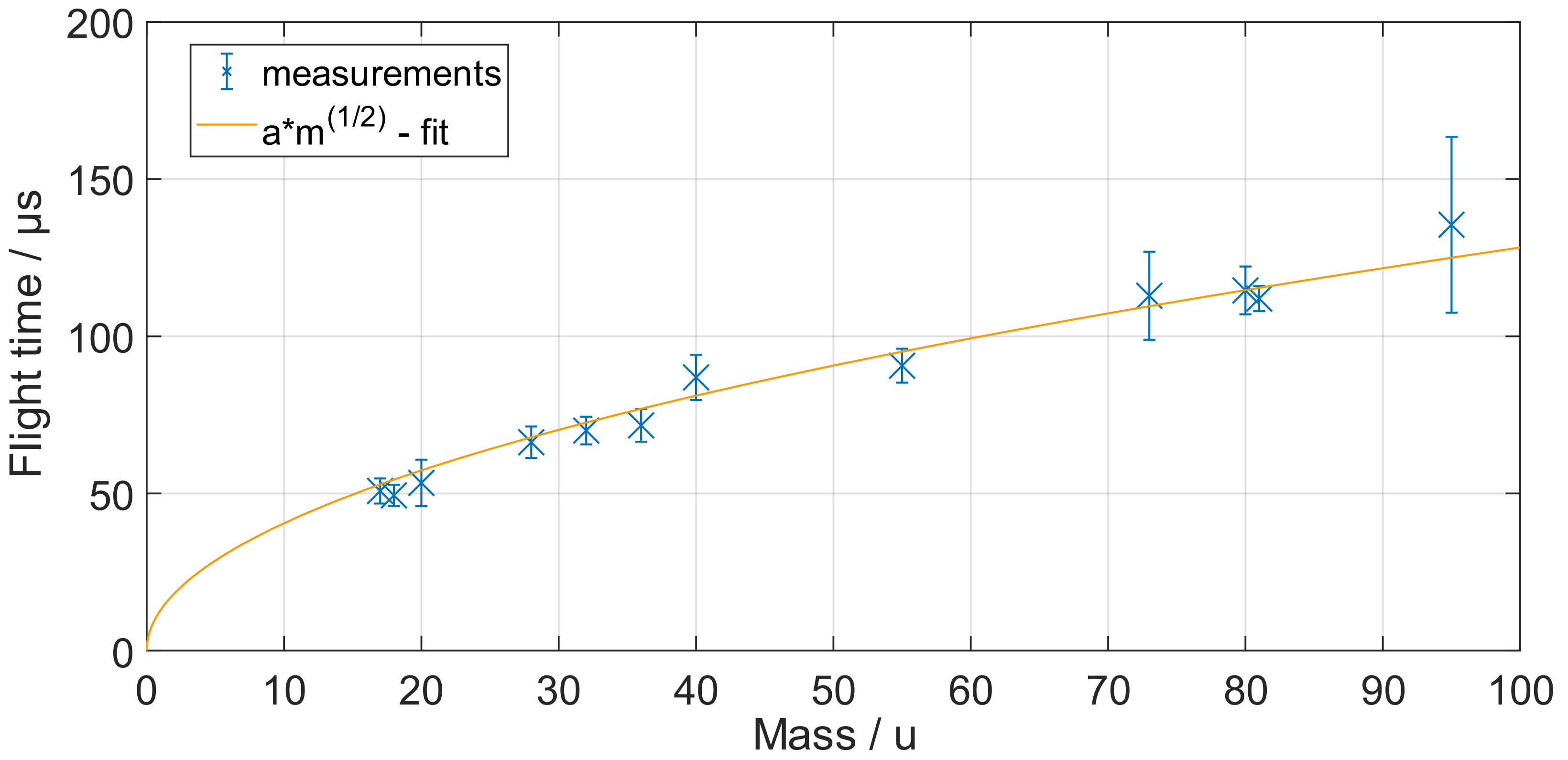
- Fit: $f(m) = a * \sqrt{m}$

$$a = (12.8 \pm 0.2)\frac{\mathrm{s}}{\sqrt{\mathrm{kg}}}$$



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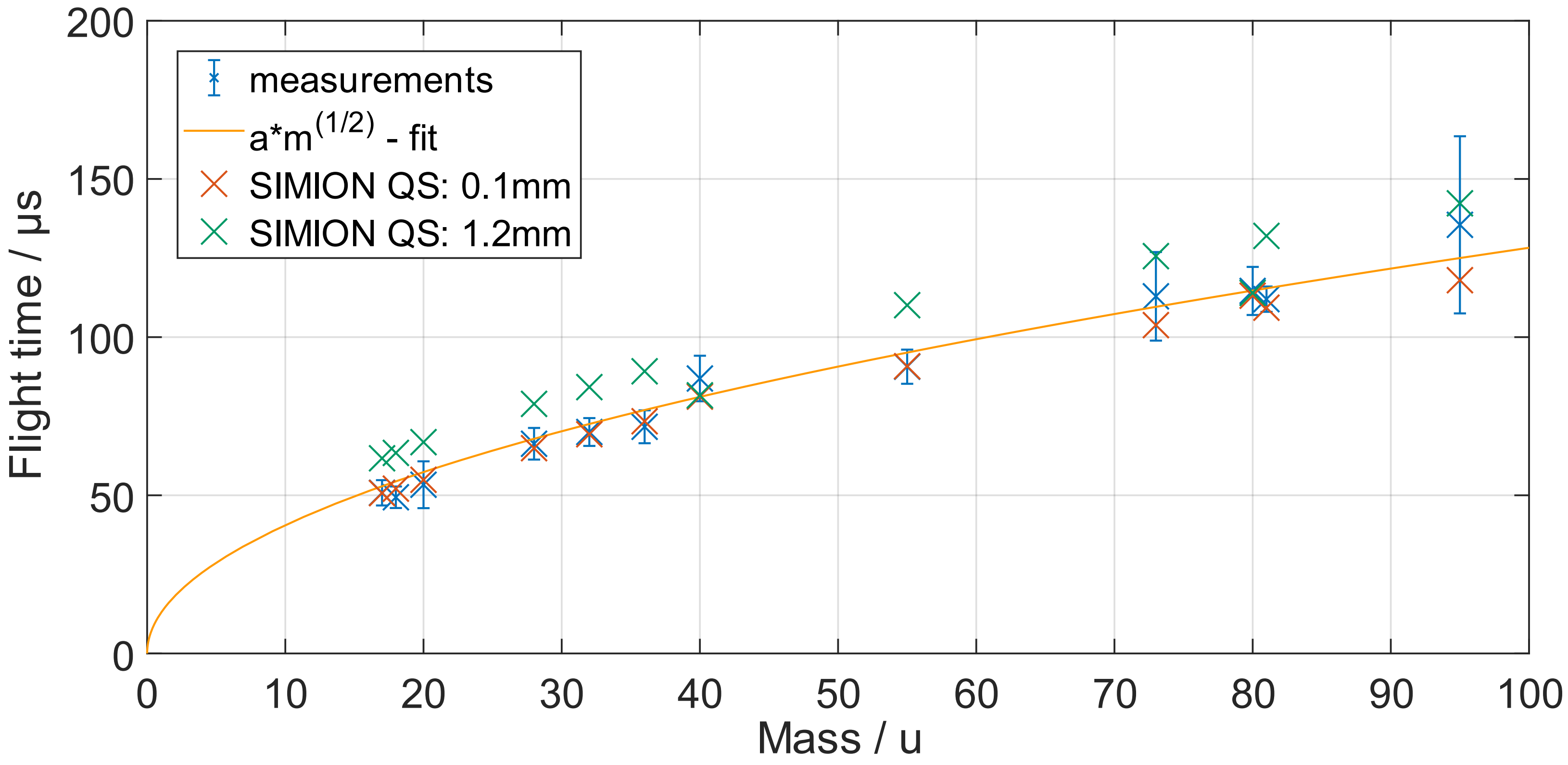

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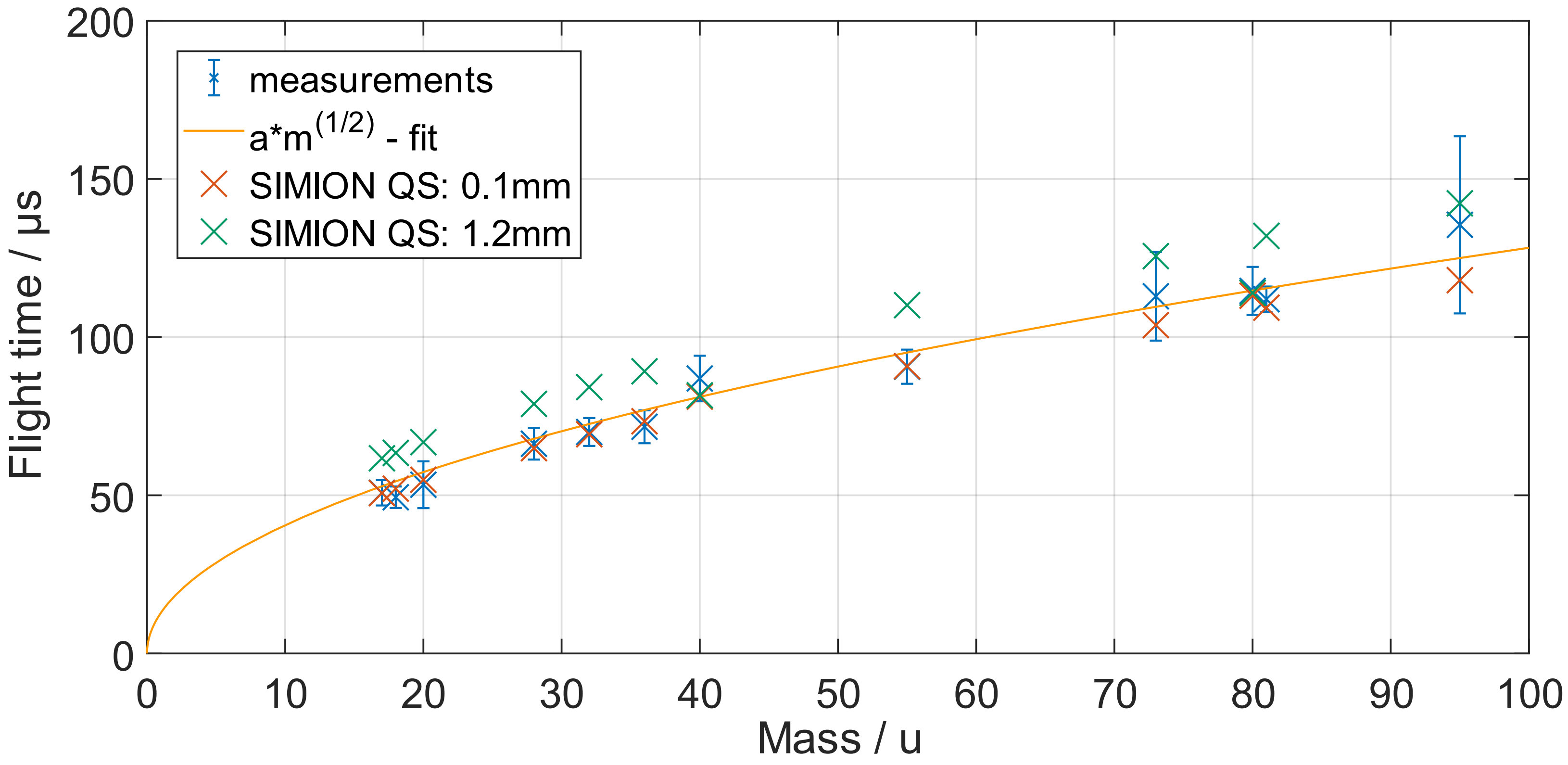
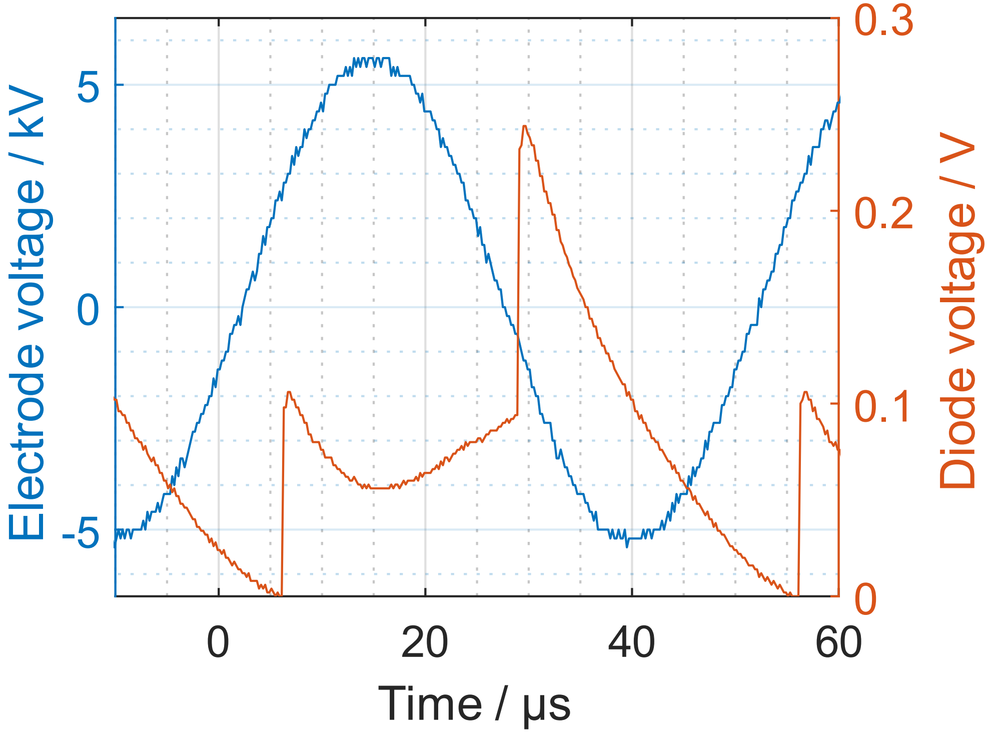


✓ Calibration for flight time correction

“Typical“ DBD plasma operation

- High frequency operation
  - 10.8 kV_{pp} - 14.8 kV_{pp}, admixture dependent
  - 20 kHz, sine wave
  - 2 slm Ar + 0.8 % (16 sccm) O_2/N_2



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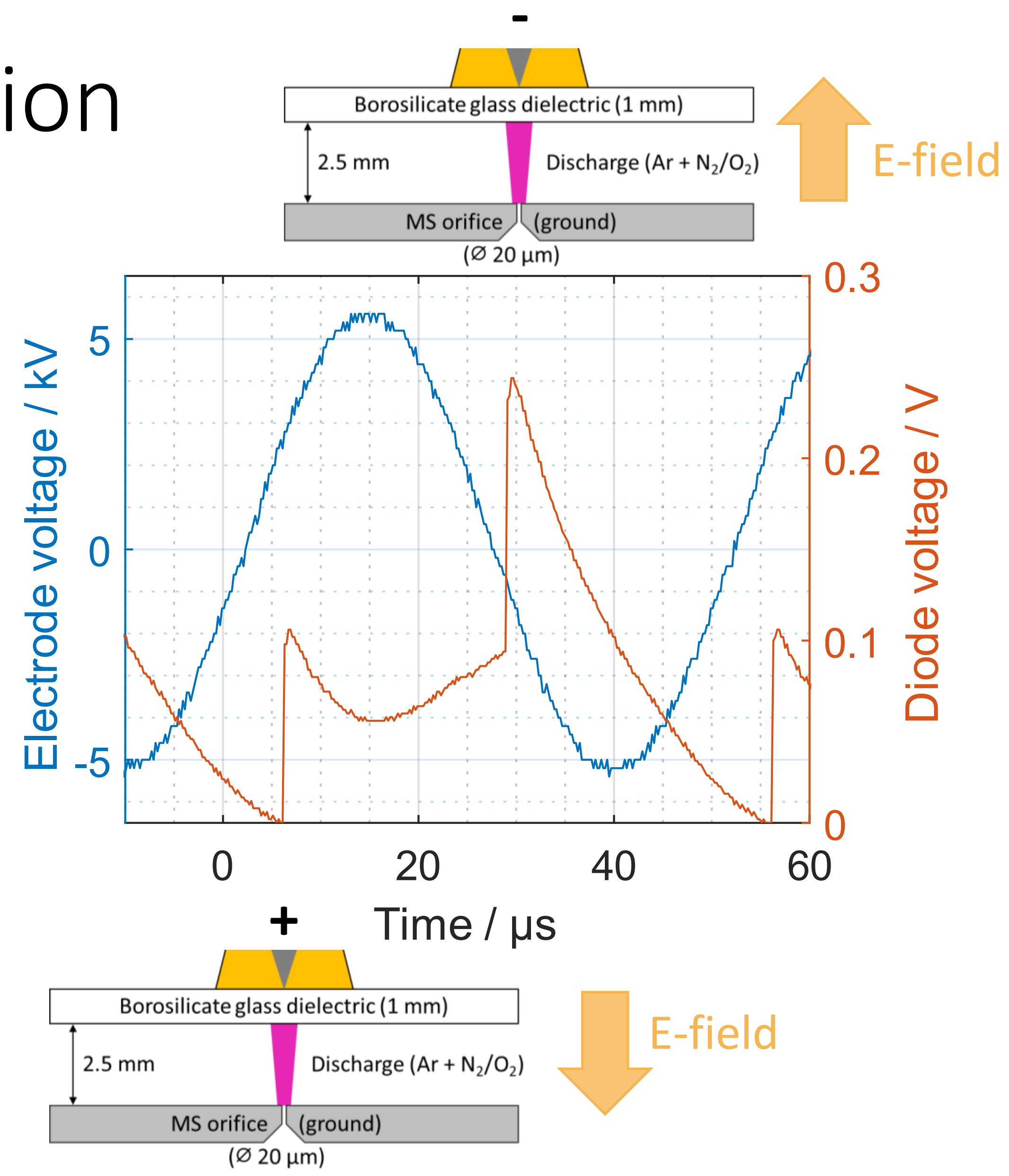
- Two ignitions per period
- Emission between pos. and neg. filament



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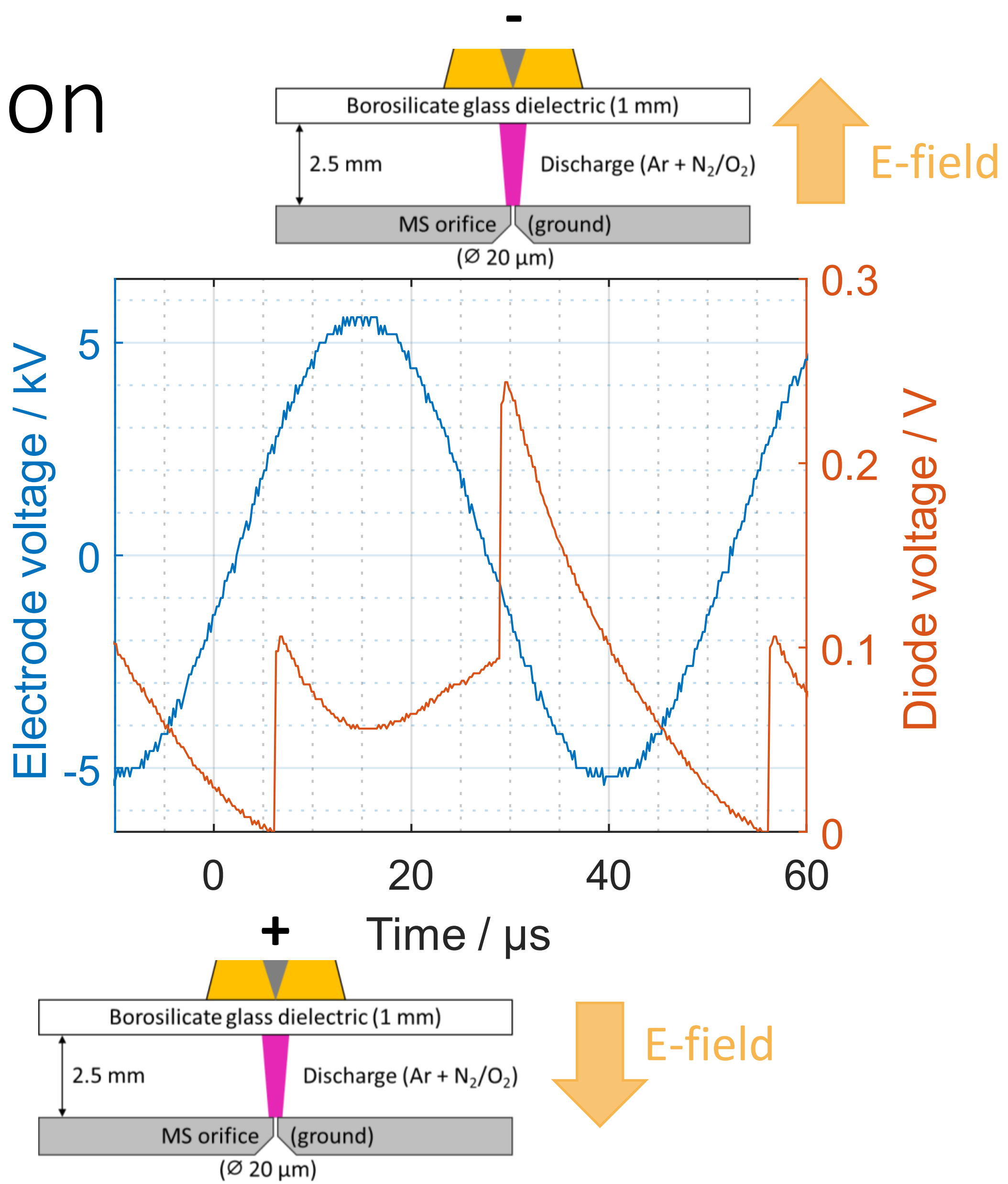
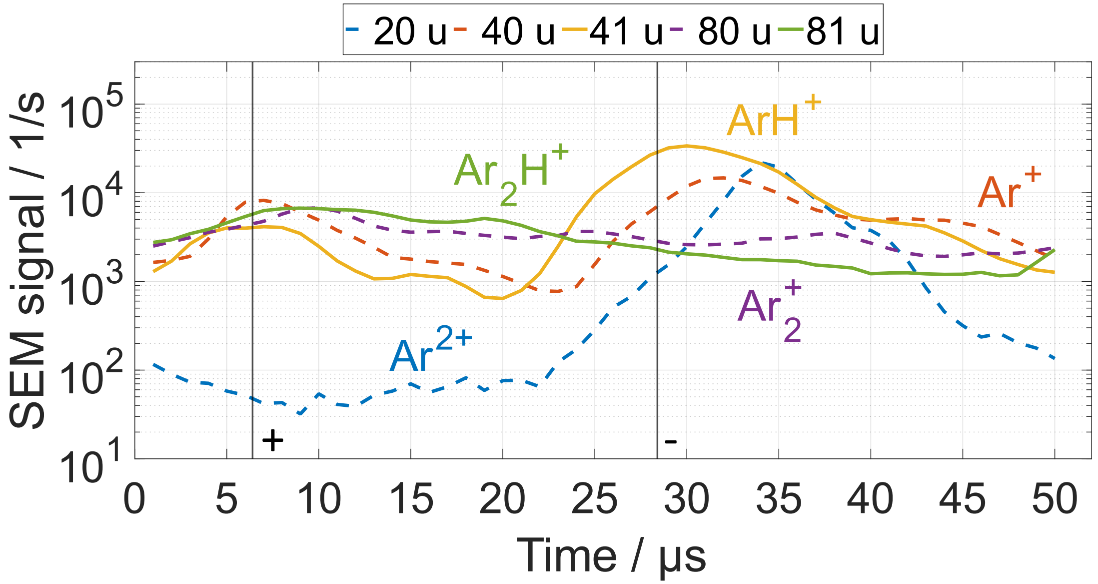
- Two ignitions per period
- Emission between pos. and neg. filament
- Emission stronger for neg. filament
  - May due to surface charges



Results $Ar_x(X)$ ions

- Ion signals are corrected by their corresponding flight time and smoothed
- Dashed lines indicate an artificial signal reduction by ion lens defocusing



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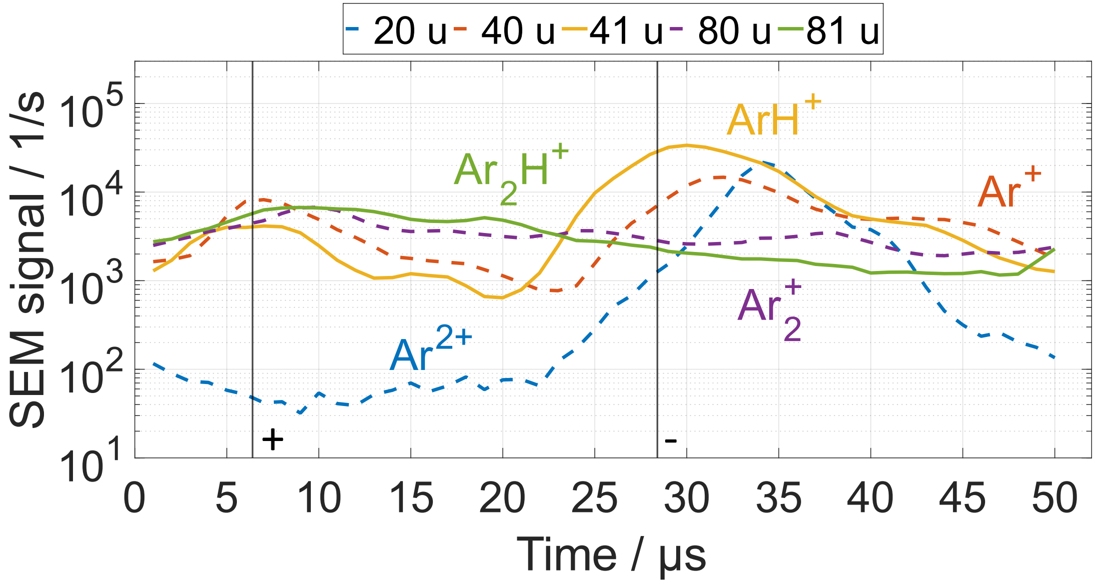
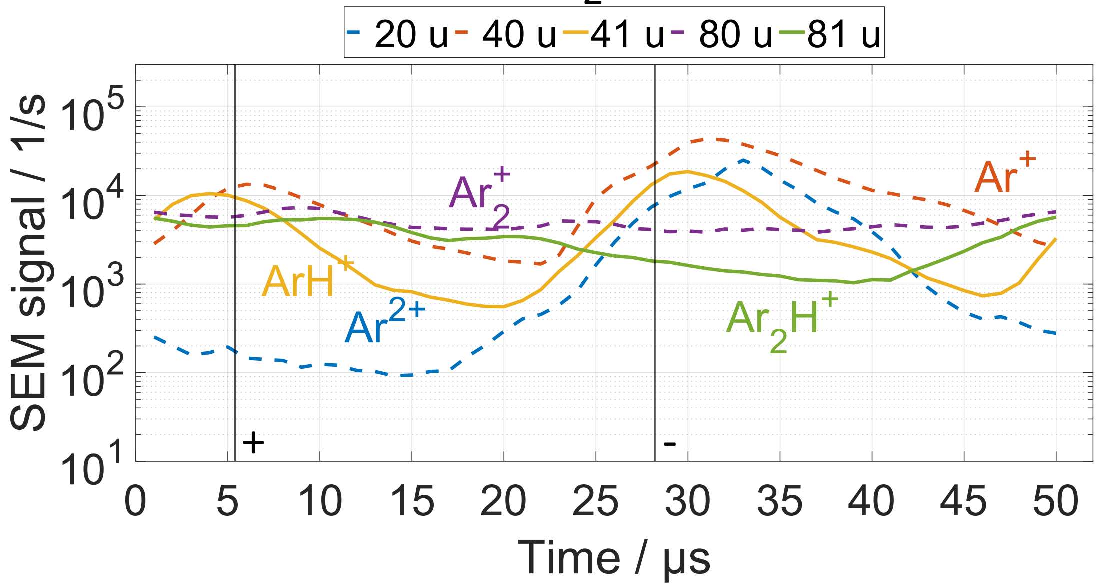
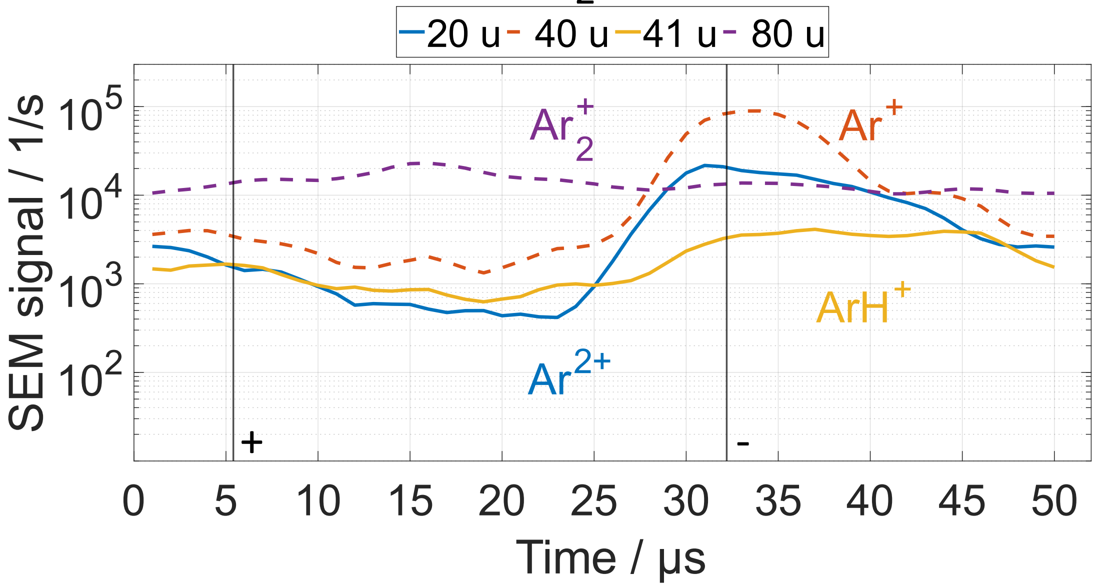


0.08 % N_2 admixture



0.08 % O_2 admixture



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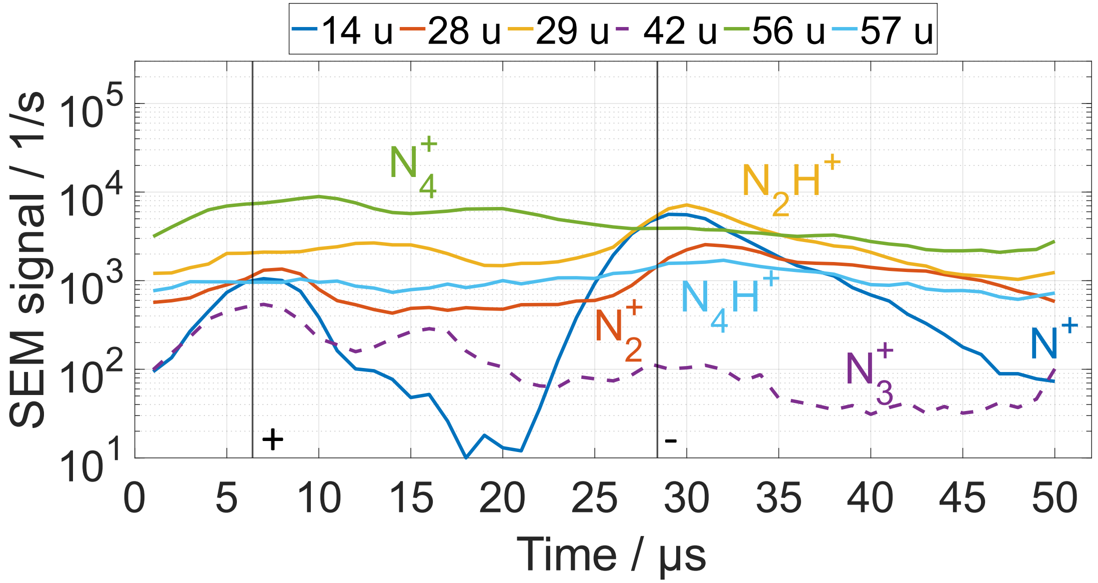

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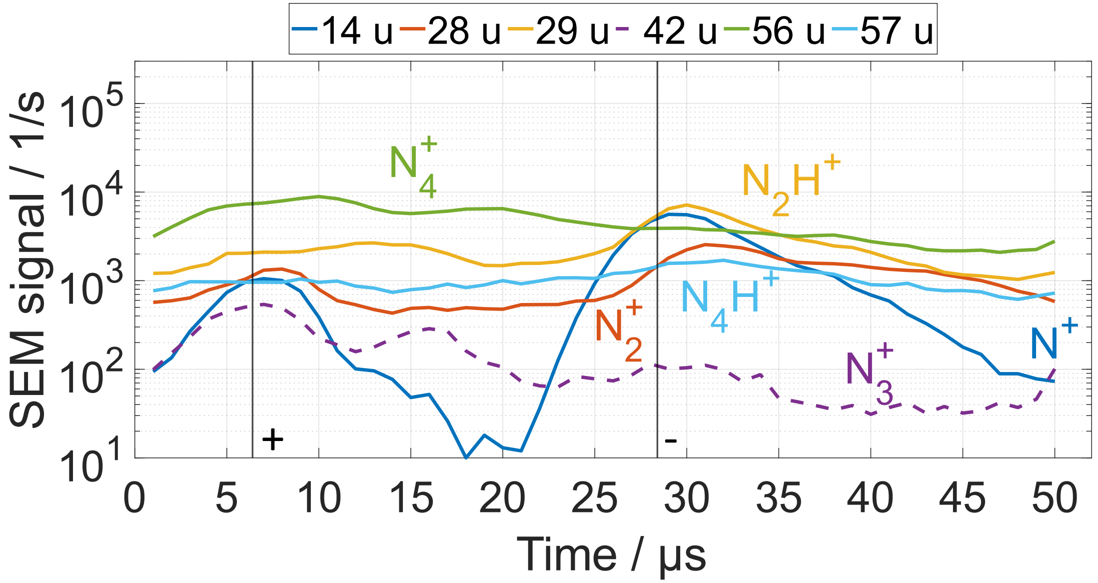

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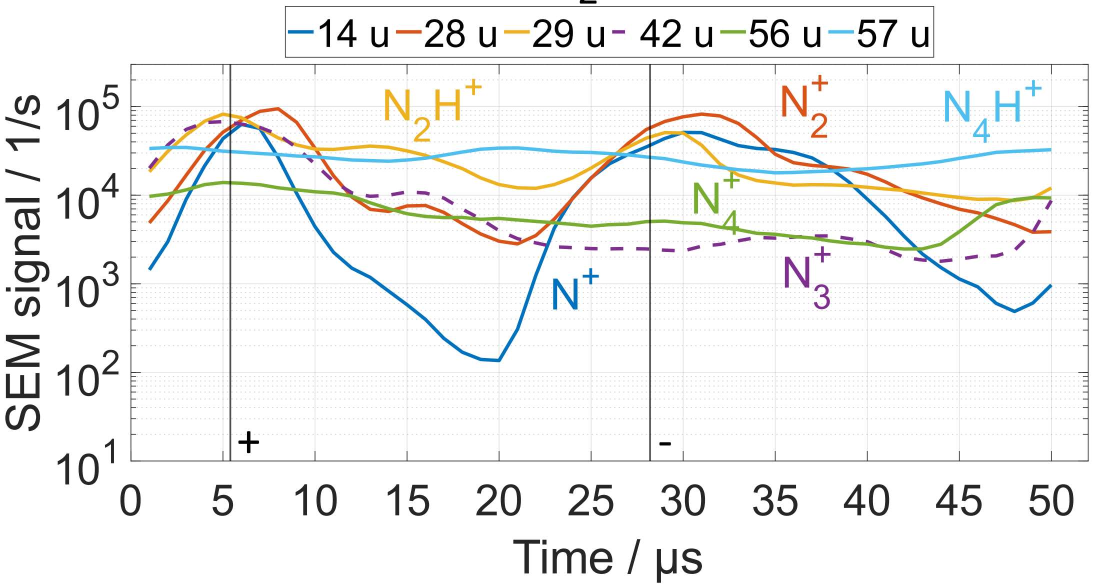

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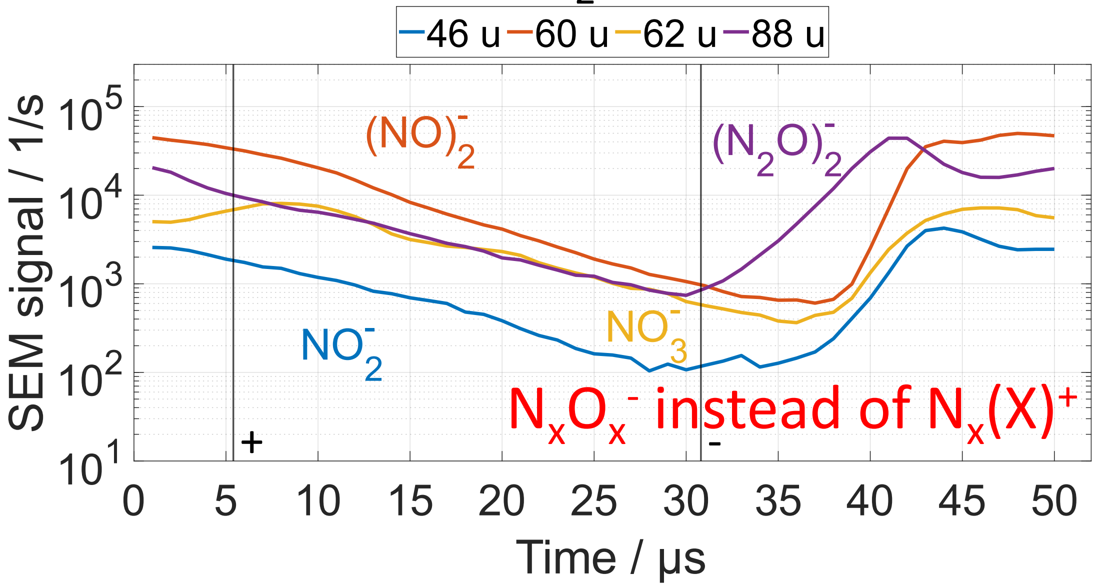

Results $(H_2O)_x(X)$ cluster

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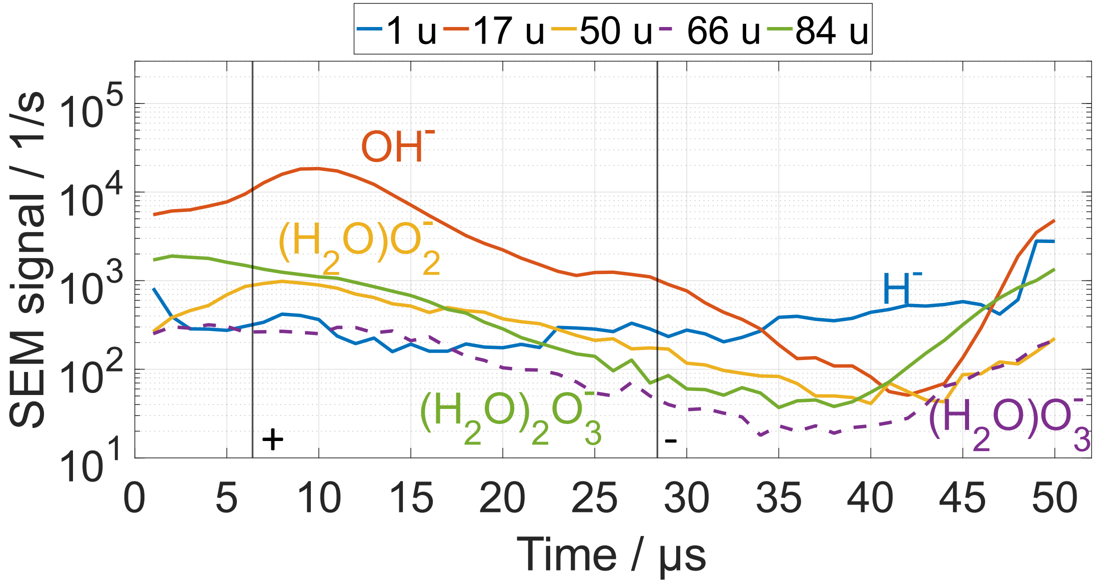

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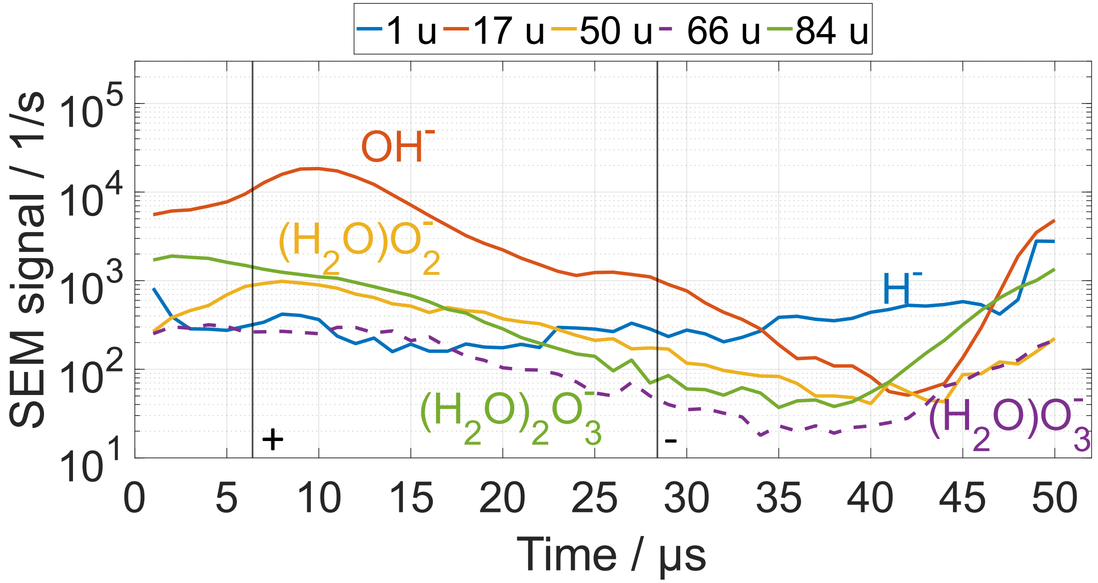

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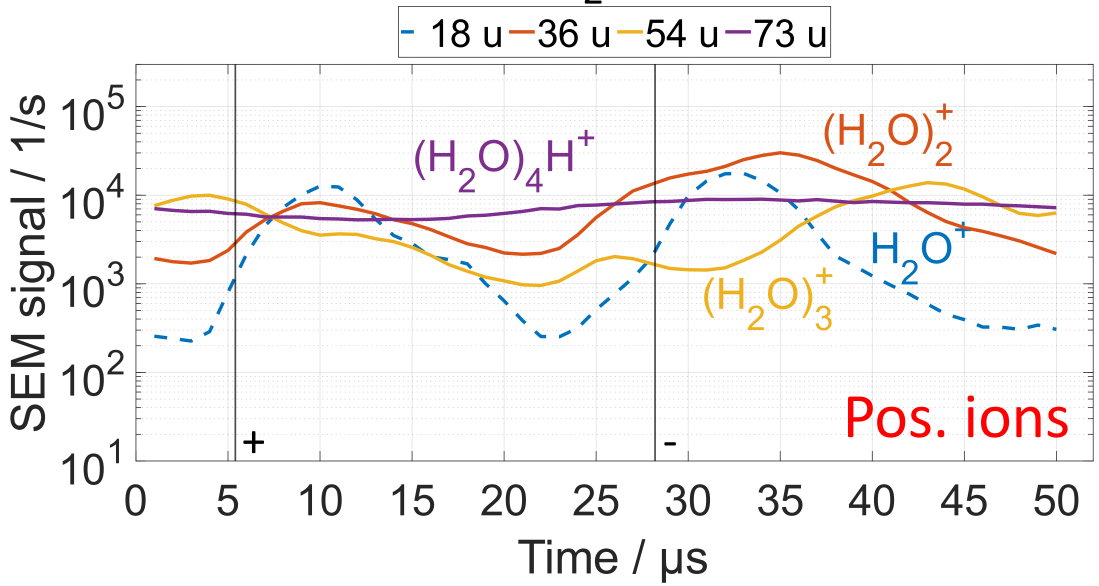

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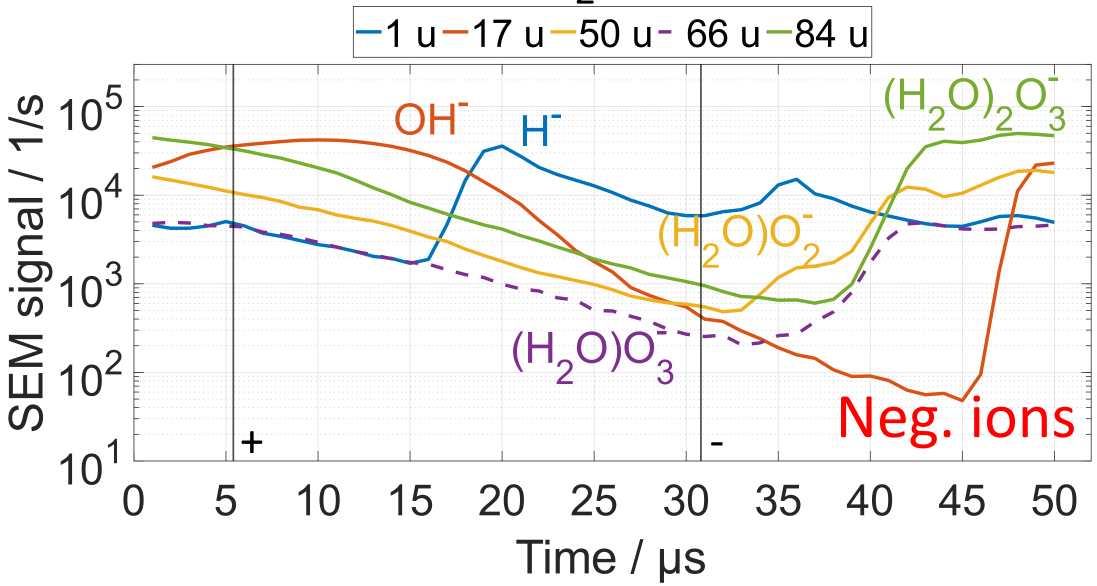
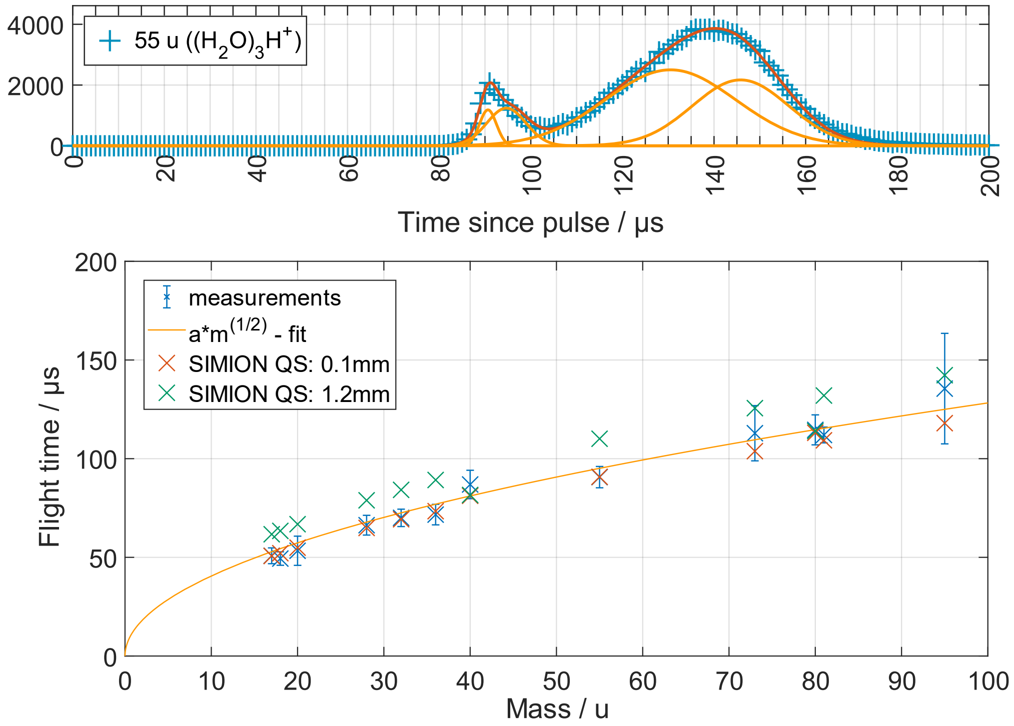


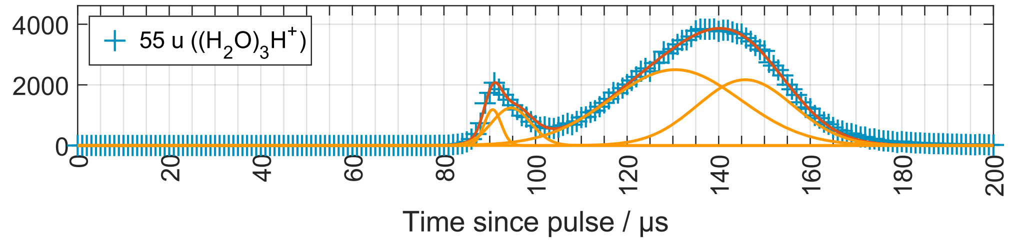
Conclusions & outlook

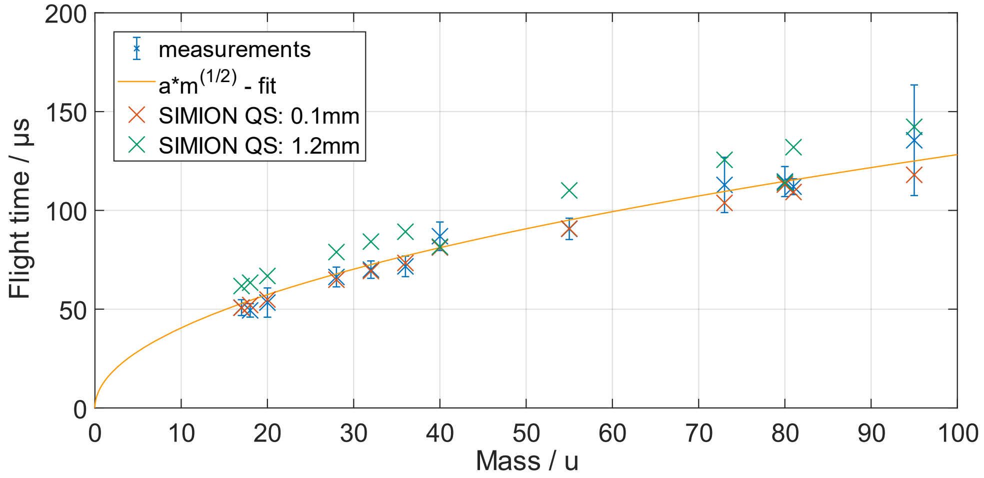
- Successful flight time calibration



Conclusions & outlook

- Successful flight time calibration
- Comparison with SIMION yields information about quitting surface





Conclusions & outlook

- Successful flight time calibration
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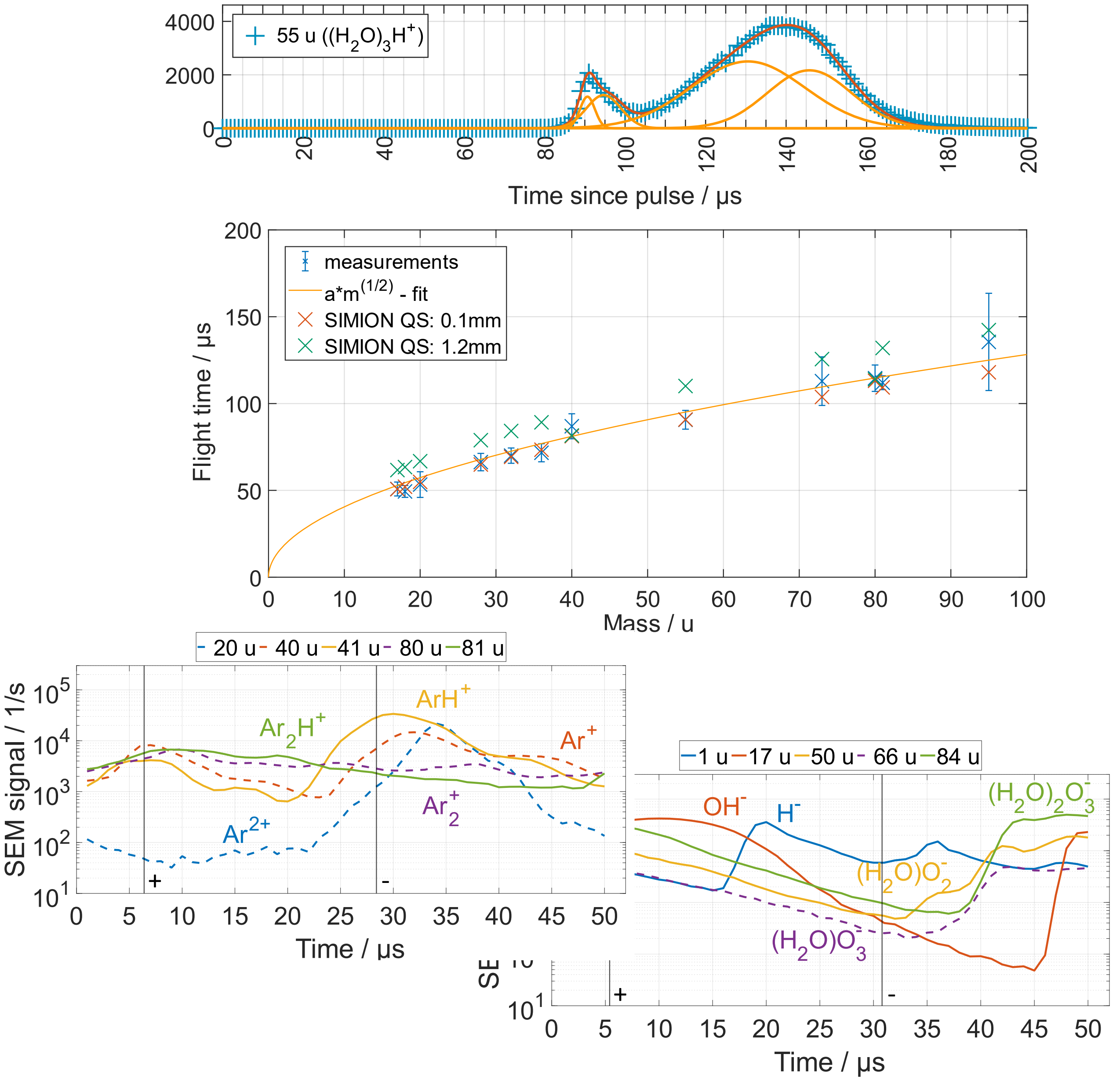
- Ion formation phases visible
- Time-resolved ion MS measurements possible utilizing a MCS



Conclusions & outlook

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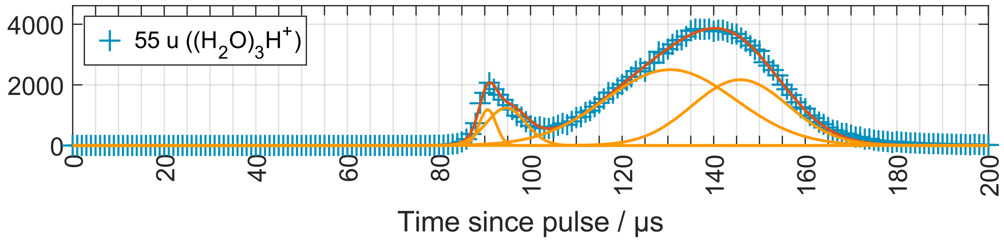
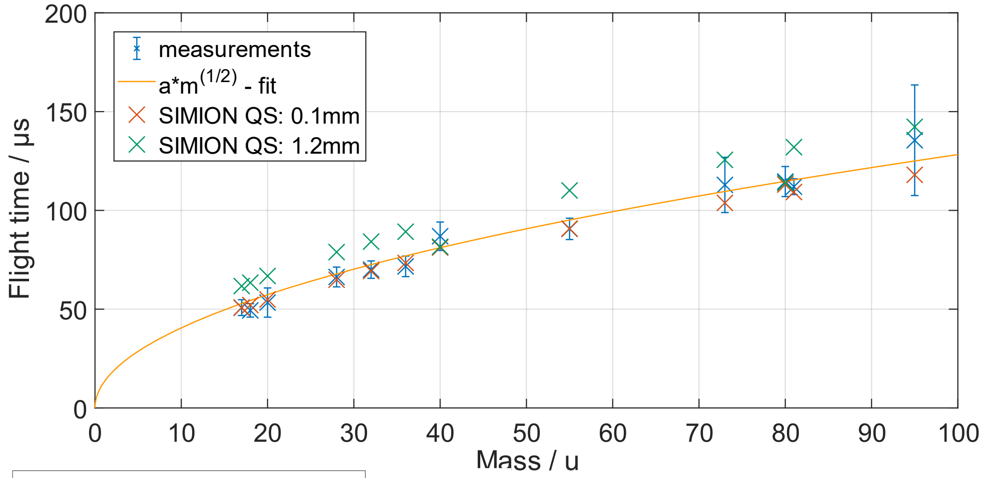
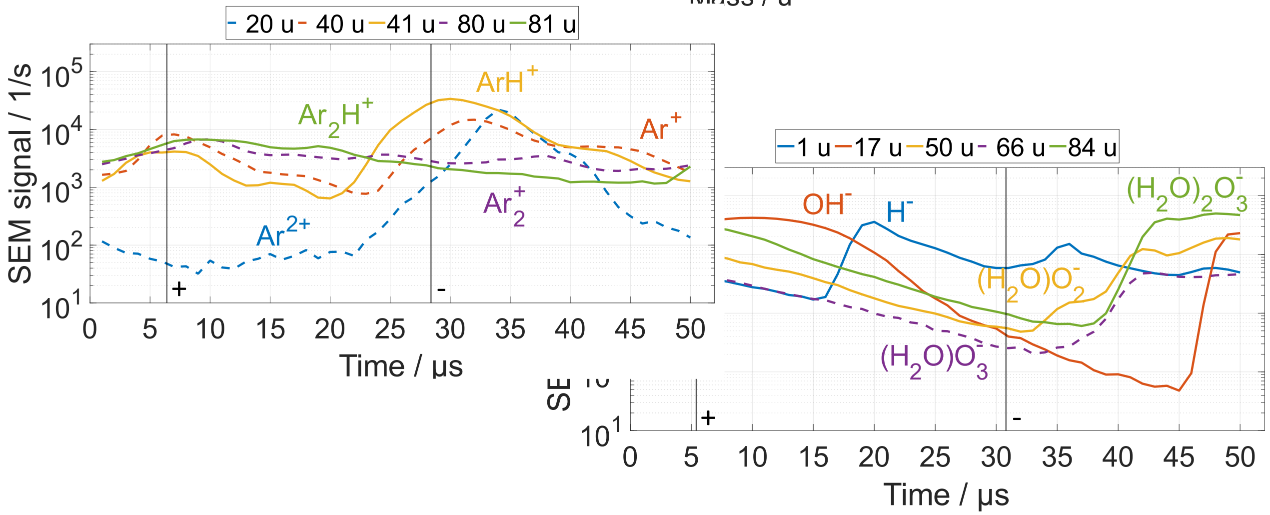
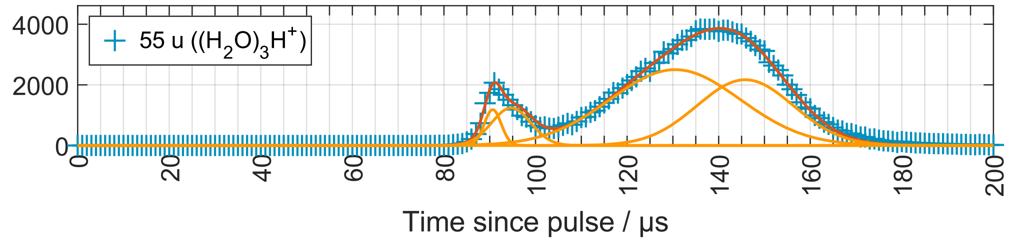
- Utilizing deposition precursors
- Applying diagnostic to other sources

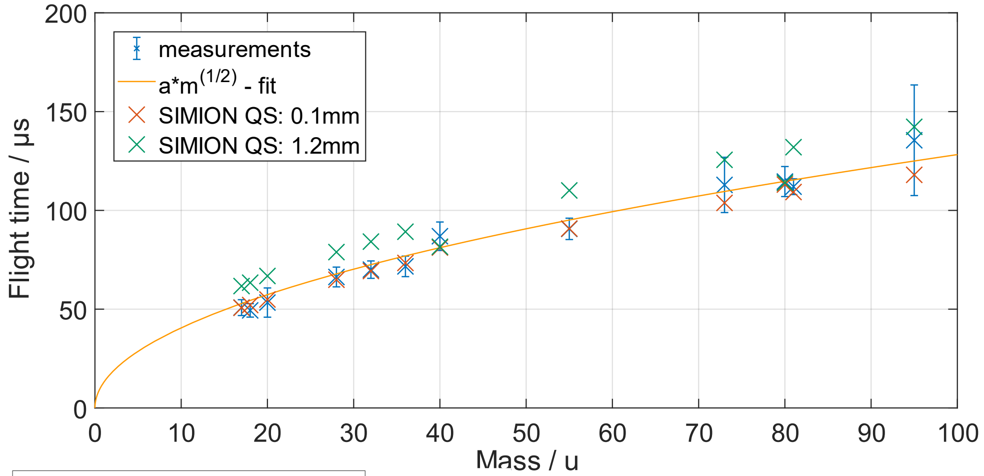






Conclusions & outlook





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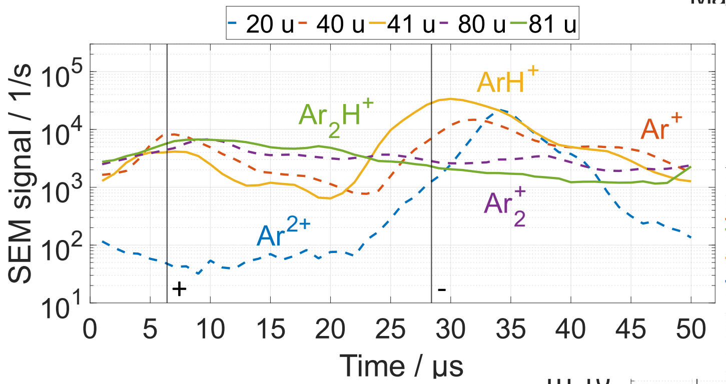

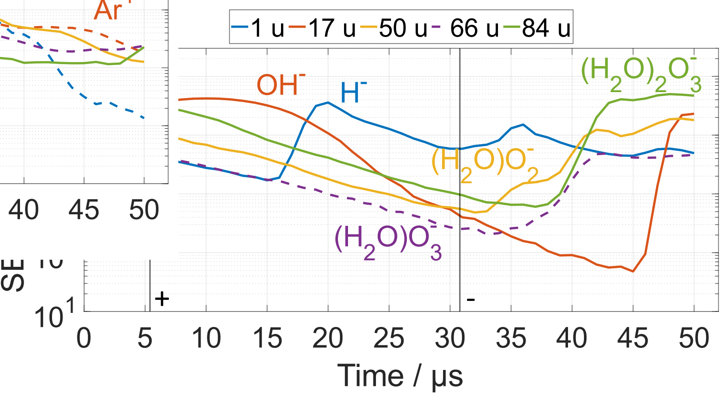

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Support of Tobias Hahn (Plasma Technology, Kiel University) with the MCS and financial support of KiNSIS is gratefully acknowledged.

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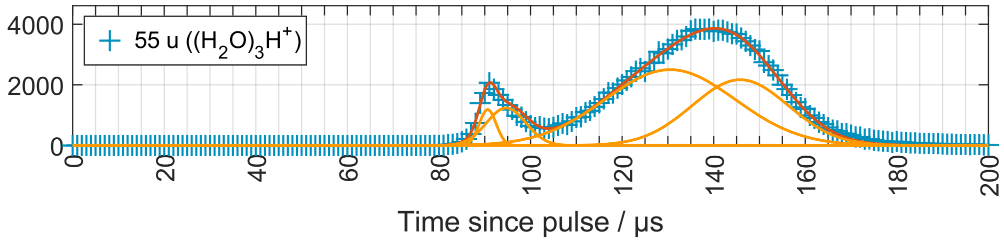

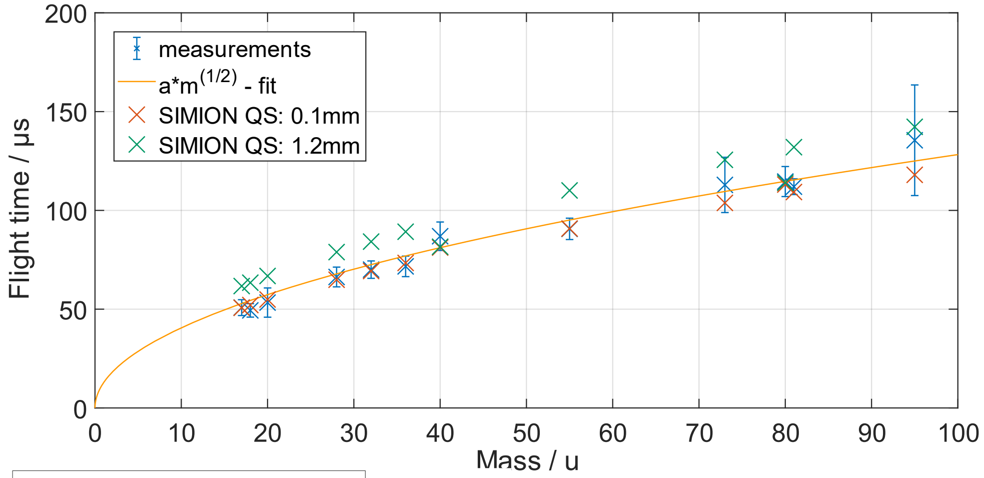

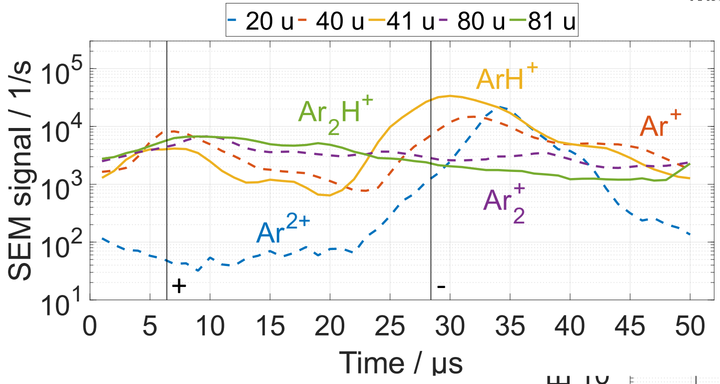

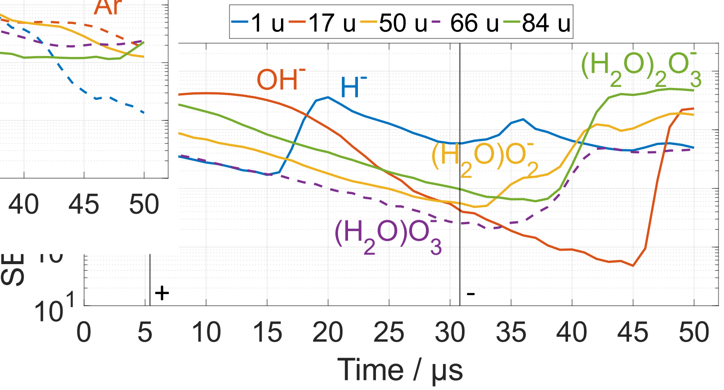

Thank you for your attention

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