

VUV Photoionization within Transfer Capillaries of Atmospheric Pressure Ionization Sources

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Introduction

• MS Application:

In situ product study of the OH radical initiated gas phase degradation of atmospherically relevant compounds.

• Problem:

Ion transformation processes occurring between ionization and detection.

→ Significant loss of important mass spectrometric information.

• Approach:

VUV photoionization within the transfer capillary which separates the atmospheric pressure region and the first differential pumping stage.

→ Effective reduction of the time between ionization and detection at still appreciable neutral analyte density.

Methods

MS Bruker esquire6000 quadrupole ion trap. The transfer capillary and the home-built laminar flow (LF) ion source were prepared with orifices for VUV radiation entry.

Radiation source homebuilt argon spark discharge lamps

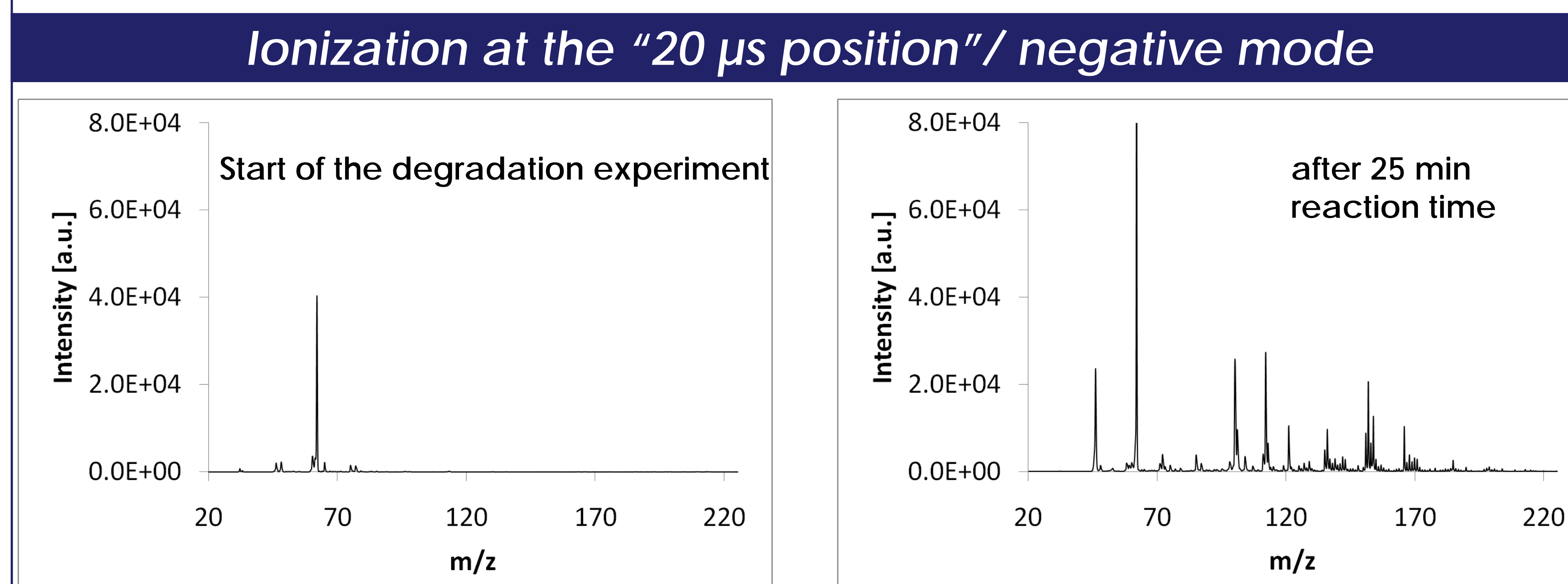
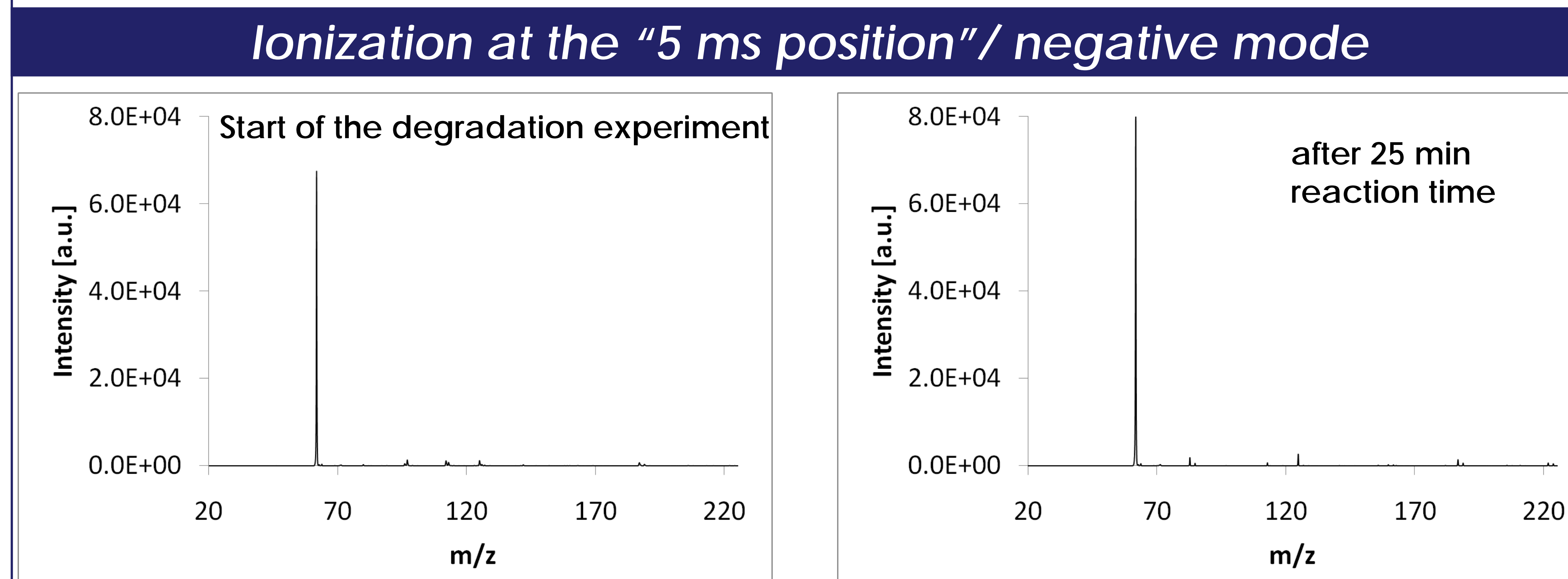
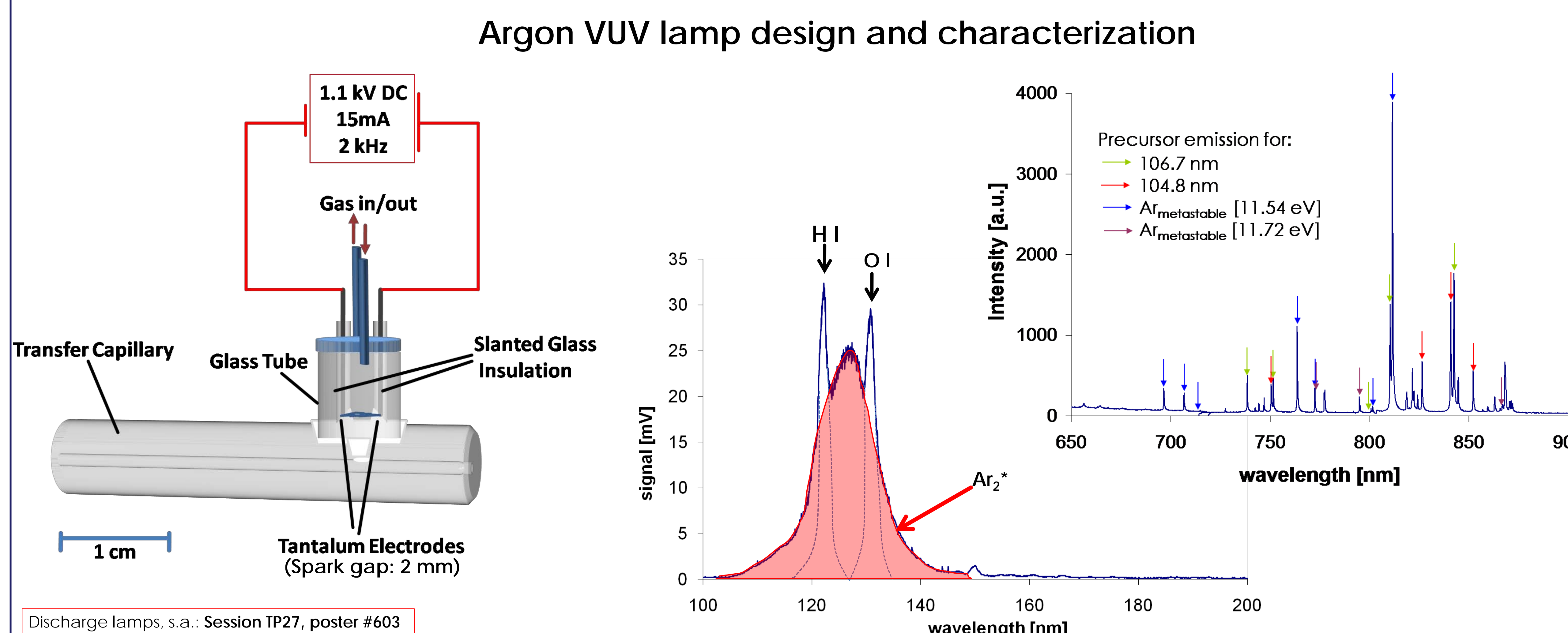
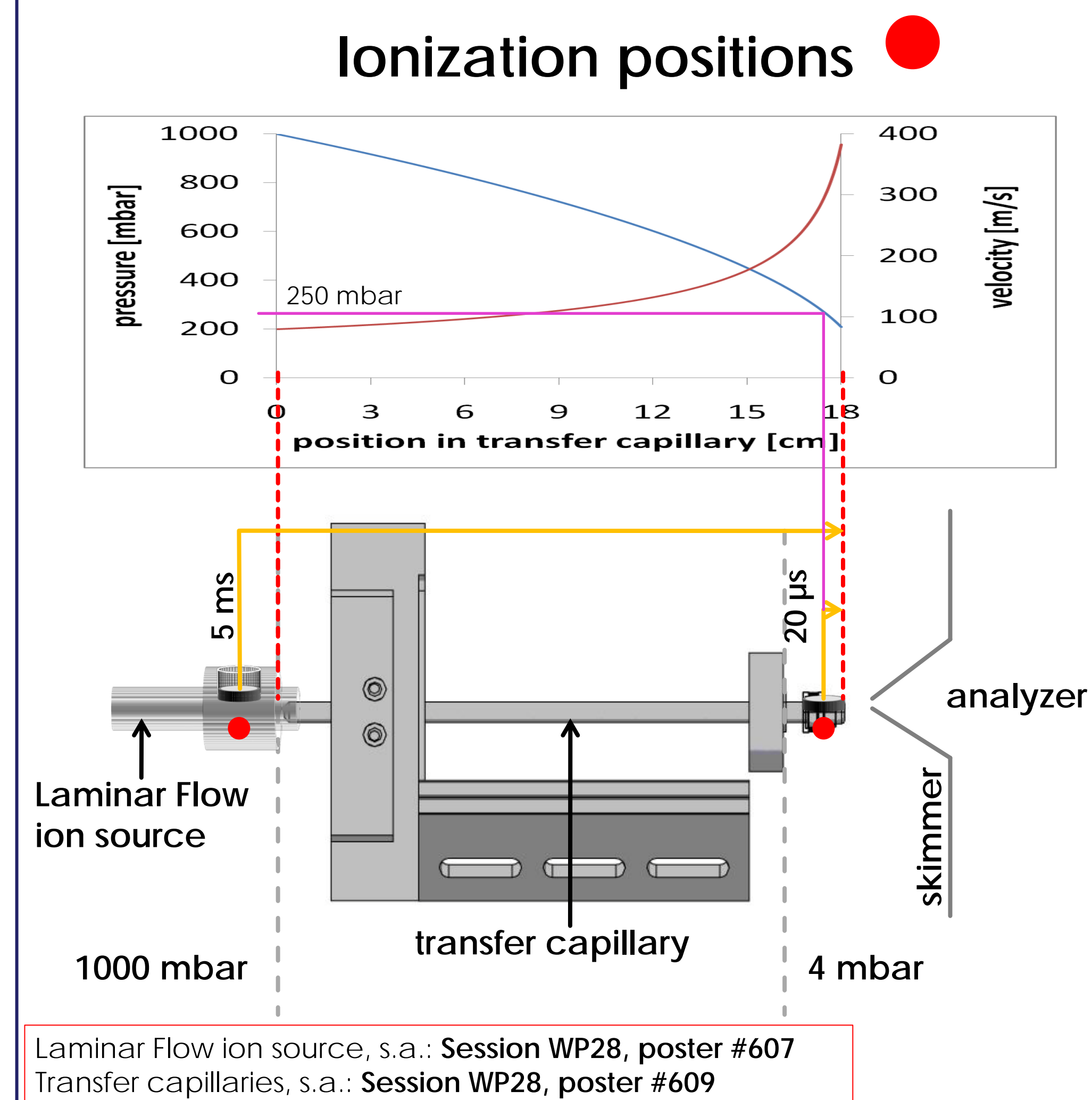
Power supply homebuilt with an HV power supply of an OPTex excimer laser (HPE CC400)

Spectroscopy UV/Vis spectrometer (AvaSpec-3648)
VUV spectrometer (ARC VM-502)

Gas phase samples Large volume photoreactor (1080 l) for gas phase degradation studies of atmospherically relevant compounds with OH and Cl radicals

Chemicals p-xylene, MeONO, NO

Experimental & Results



$\frac{dG}{d\epsilon} = 0$

Thermodynamically controlled ion distribution.
→ **Loss of MS information.**

$k(T) = A \cdot e^{-\frac{E_A}{RT}}$

Kinetically controlled ion distribution.
→ **Preservation of MS information.**

Conclusions

• Combination of a spark discharge lamp (*Lightning Source*) mounted windowless on a transfer capillary:

→ High photon flux on a small, precisely selectable illuminated area.

→ Discharge in an Argon flow (300 ml/min @ 200-1000 mbar). No perturbation of the analyte flow.

→ Broad Ar₂* excimer emission (127±13) nm.

→ Impact of Ar meta-stables?

• Effective reduction of ion transformation processes.

• Ionization occurs at still appreciable neutral analyte density, as compared to conventional high-vacuum ionization.

• Monitoring of degradation product studies is enhanced.

→ Preservation of MS information due to kinetically controlled ion distribution, demonstrated here for the negative ionization mode.

Literature

- (1) Kersten, H.; Funcke, V.; Lorenz, M.; Brockmann, K.; Benter, T.; O'Brien, R., Evidence of Neutral Radical Induced Analyte Ion Transformations in APPI and Near-VUV APLI. *Journal of the American Society for Mass Spectrometry* **2009**, *20*, (10), 1868-1880
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Acknowledgement

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