Measurements of electronically excited noble gas species radiating in the far VUV

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Introduction

Main Question:

- A number of ambient ionization methods such as DART or FAPA are based on noble gas plasmas. It is assumed that in many ways the underlying mechanisms correspond to APCI, however, the basic reaction steps leading to the reactant ions are rather unknown.
- He^M are postulated to ionize the analyte molecules in ambient methods due to penning ionization.

Corresponding to long transfer distances to reach the analytes and the high collision rates at atmospheric pressure, is the use of He^M as direct reactant possible at all? What are the driving plasma mechanisms?

Approach:

- VUV-emission spectroscopy of Helium spark discharges with trace amounts of different noble gases.
- Time resolved measurements of the radiative decay of He_2*.

Methods

Spark discharge

power supply
- custom DD20_10 C-Lader, Hartlauer Präzisionselektronik GmbH, Grassau, Germany

electrode assembly
- blunted and bent cannulas (discharge region: 2 mm)
- anode: discharge gas supply
- cathode: actively pumped to balance the anode gas flow

discharge gas supply
- main gas flow of Helium (375 mL/min)
- admixture of N_2, O_2, Ne and Ar (< 1 mL/min)

VUV spectrometer
- ARC VM-502 VUV spectrometer (Acton Research Corporation, Acton, MA, USA) with a MgF_2 coated parabolic grating
- modified for operation with helium at atmospheric pressure (counter helium flow of 100 mL/min through the entrance slit)

detection/ signal processing system
- scintillator-coated lens with Na-salicylate (custom made via piezo-nebulizer)
- Photomultiplier tube, R955, Hamamatsu Photonics, K.K., Hamamatsu City, Japan
- custom made amplifier (factor 1000)
- A/D converter, R232-ADC16/24, taskit GmbH, Berlin, Germany
- custom software (VB 2010 Express)

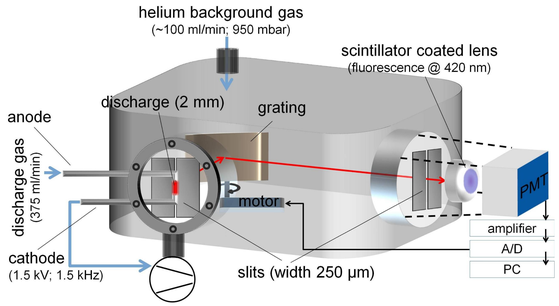
Oscilloscope

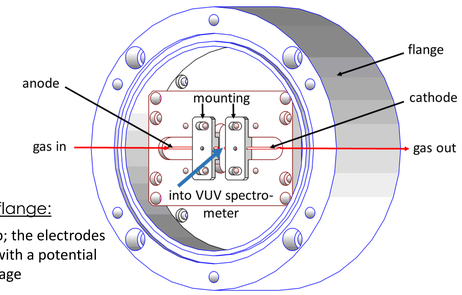
LeCroy LT344

VUV-Spectrometer for Time Resolved Measurements at Atmospheric Pressure

VUV-spectrometer:

- Helium background pressure 1030 mbar
- A scintillator, i.e., sodium salicylate coated glass window, between grating and photo multiplier tube converts the dispersed VUV radiation to visible light (420 nm)
- Spark discharge lamp is directly positioned in front of the entrance slit of the VUV spectrometer
- A continuous helium counterflow prevents that reactive species enter the chamber
- Discharge gas was provided by a 2 L/min flow controller for Helium and a 1 mL/min flow controller for the added noble gases
- Entire setup can be evacuated to $1 \cdot 10^{-5}$ mbar

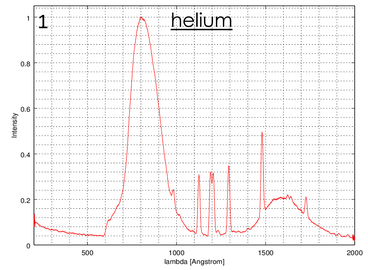


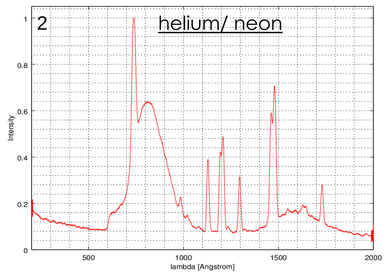


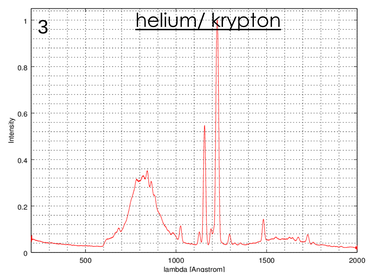
Close up of the spark discharge flange:

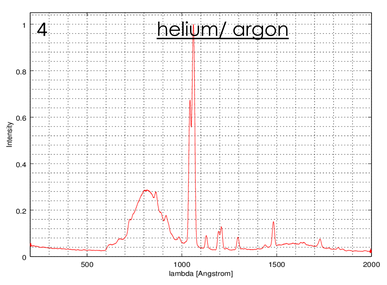
- Custom made spark discharge lamp; the electrodes are connected to the oscilloscope with a potential divider to monitor current and voltage
- Identical setup as the cAPPI ion source inside an inlet capillary

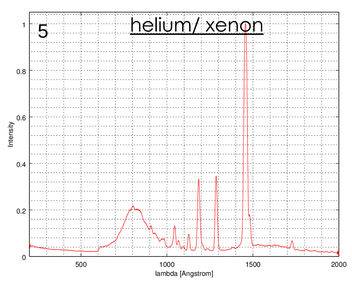
VUV Emission Spectra











1) The broad He_2* emission centered around 80 nm dominates the spectrum. The broad emission centered at 160 nm is the same emission in second order. The narrow lines are assigned to N_2 and O_2 impurities.

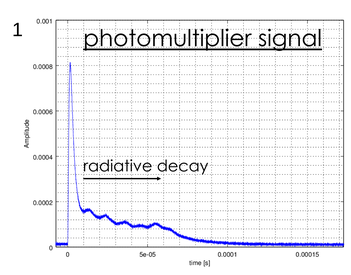
2) Addition of 0.4% neon slightly decreases the He_2* in favor of the neon emission centered at 73 nm. Impurity lines are not effected.

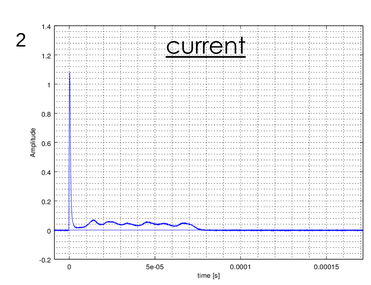
3) 0.4 % krypton added to the discharge decreases the helium excimer emission as well, in favor of the characteristic 116 and 124 nm emission.

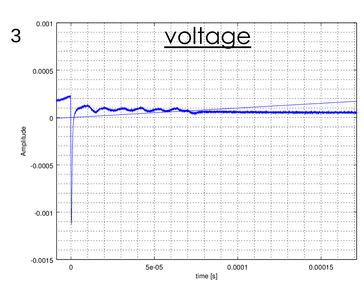
4) Addition of 0.4% argon decreases the excimer emission and the impurity emission in favor of the charakteristic 104 and 106 nm emission.

5) Xenon emits at 147 nm and a decrease in the helium excimer emission is observed. The impurity emission is not as much effected as in the case of krypton and argon.

Time Resolved Measurements





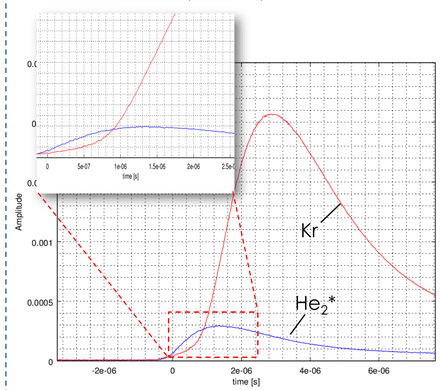


1) Time and wavelength resolved photomultiplier signal. The temporal profile follows the temporal current and voltage profile (2 and 3).

2) Temporally resolved current signal measured with a low resistor between anode and ground. The peak current is 1A, decreases within 10 µs and stays quite constant at 0.3 A for 50 µs.

3) The temporally resolved voltage signal is phase shifted by 90° compared to the current signal. The breakdown voltage is 1 kV which is in good agreement with the Paschen criteria.

temporally resolved He_2* (80nm) and Kr (124 nm) emission



Faster formation of the He_2* than electronical excitation of Kr. The slopes follow a characteristic pattern of a consequtive reaction, indicating fast quenching of the helium excimer by krypton.

Conclusions

- time resolved emission spectroscopy revealed a delay in the formation of the electronically excited trace species compared to the He_2*
- The quenching efficiency of helium dimers increases with the mass of the added rare gases in the buffer gas (0.4 % Ne, Ar, Kr or Xe in He)
- the emission line intensities of impurities, oxygen and nitrogen, decrease with increasing quenching efficiency
- based on time resolved VUV emission spectroscopy, this setup is capable of revealing fundamental mechanistic processes in plasma driven ion sources

Outlook

- kinetic measurements of the lifetimes of Helium dimers in dependence of different reactants
- use of the other rare gases as the main constituent with trace amounts of the remaining rare gases added
- observation of the Helium metastables with a custom designed mass spectrometer inlet

Literature

[1] Kersten, H.; Brockmann, K. J.; Benter, T.; O'Brien, R., Windowless Miniature Spark Discharge Light Source for efficient Generation of VUV Radiation below 100 nm for on-capillary APPI, *Proceedings of the 59th ASMS Conference on Mass Spectrometry and Allied Topics*; Denver, CO, USA, 2011

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