Progress in VUV measurements of a spark discharge lamp used for capillary Atmospheric Pressure Photoionization (cAPPI)

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Introduction

At the ASMS 2011 we introduced a novel approach for Atmospheric Pressure Photoionization (APPI), employing a spark discharge lamp mounted windowless on a custom glass transfer capillary of a mass spectrometer.

Challenge:
Characterization of the VUV emission of different discharge gas compositions in particular below 100 nm at atmospheric pressure.

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)

APPI lamp

- Kr-RF, PhotoMate®, Syagen Technology, Inc., Tustin, CA, USA equipped with a PKR 106 lamp from Heraeus Noblelight GmbH, Hanau, Germany

VUV spectrometer

- ARC VM-502 VUV spectrometer (Acton Reasearch 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, RS232-ADC16/24, taskit GmbH, Berlin, Germany
- custom software (VB 2010 Express)

General cAPPI Setup

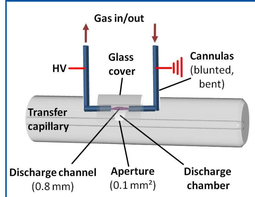

Figure 1: setup example

- no window material between lamp and ionization region
- 7 – 17 eV photon energy
- high photon flux on small illuminated area
- flexible and cost efficient ion source design
- flexible discharge gas selection (selective ionization)
- low discharge gas flow

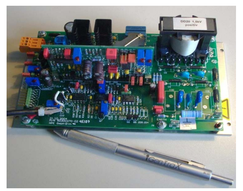

Figure 2: HV power supply

- 0 – 1500 Vdc
- 0 – 15 mA
- 0 – 1500 Hz
- discharge pulse length: 7 µs
- small-sized circuit board
- secure operation
- cost efficient (400 US $)
- input: 24 DC, 30 W

Experimental Setup for VUV Spectroscopy @ Atmospheric Pressure

- spark discharge and APPI lamps were directly positioned in front of the entrance slit (width 250 µm) with a continuous helium counter flow of 100 ml/min to prevent reactive species entering the chamber
- helium background pressure 950 mbar
- discharge gas was provided by a 2 l/min flow controller for helium and a 1 ml/min flow controller for the admixing gas species, respectively
- scintillator (Na-salicylate) coated lens between grating and photo multiplier tube converted the dispersed VUV radiation to visible light (420 nm)
- entire setup may be evacuated down to $2x10^{-4}$ mbar

Note on scintillator coatings
Homogeneous, reproducible and efficient fluorescent coatings were made with a simple piezo-nebulizer setup and a water solution of sodium-salicylate.

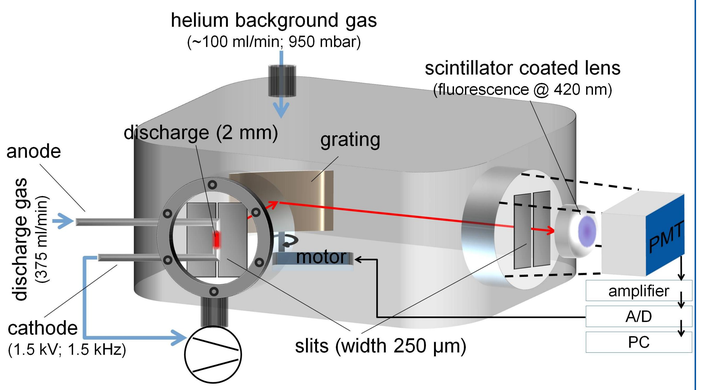

Figure 3: VUV spectrometric setup

Conclusions

- photo ionization ranging from 7 – 17 eV at atm. pressure
- flexible discharge gas selection for selective ionization
- minor hardware (power supply) and gas effort compared to other discharges operating at atm. pressure
- for applications where high brilliance is required

Future aspects:
- spark discharge setup in AP-GC-MS applications
- investigation on the competing photo induced processes of auto ionization and photo dissociation at atm. pressure
- Funding for a three year research proposal was granted recently by the German Research Foundation (DFG) regarding a fundamental spectroscopic and mass spectrometric investigation of the spark discharge lamp plasma characteristics (KE 1816/1-1).

VUV Spectra of different Discharge Gases vs. APPI lamp (Kr-RF)

spark discharge lamp (He gas flow of 375 ml/min; admixture of second gas species up to 1 ml/min)

APPI lamp (Kr-RF)

Results

- significant VUV emission below 100 nm with He and admixtures of Ar, Ne and O_2
- flexible discharge gas selection for selective ionization
- compounds with ionization energies > 10 eV are accessable
- the spark discharge lamp is the more efficient radiation source for small illuminated areas compared to the Kr-RF APPI lamp
- investigation of novel photo ionization characteristics at atmospheric pressure (e.g. auto ionization vs. photo dissociation)

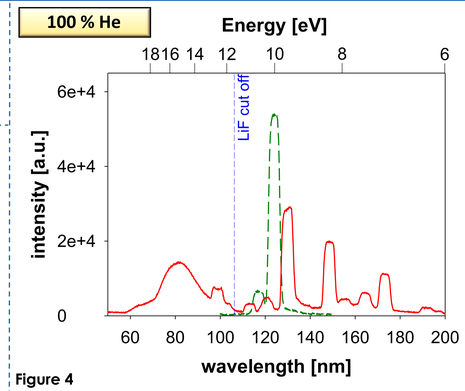

Figure 4

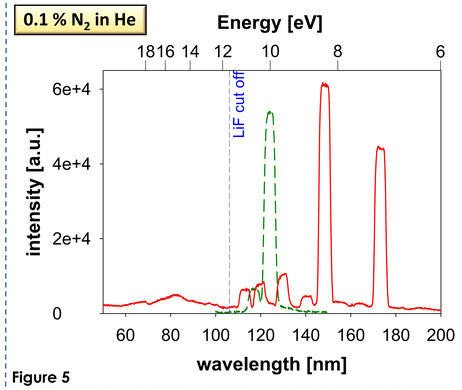

Figure 5

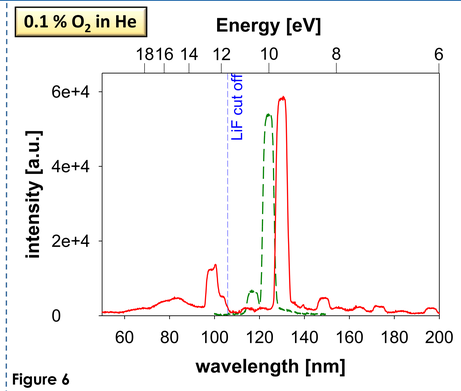

Figure 6

VUV emission of the spark discharge lamp relative to the integrated emission of the Kr-RF APPI lamp (area = slit width x 10 mm)

Figure (gas)	> 8 eV	> 10 eV	>12 eV	>16 eV
4 (He pure)	226 %	125 %	108 %	33 %
5 (N_2)	213 %	76 %	48 %	21 %
6 (O_2)	193 %	71 %	60 %	14 %
7 (Ne)	147 %	73 %	52 %	35 %
8 (Ar)	217 %	172 %	116 %	37 %

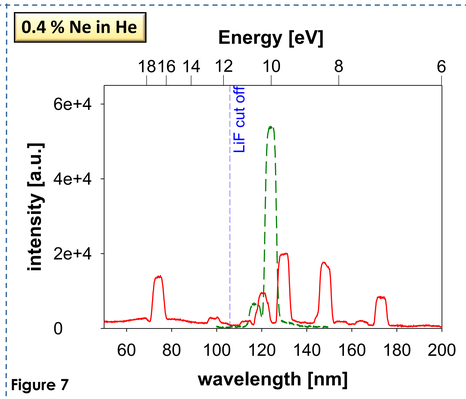

Figure 7

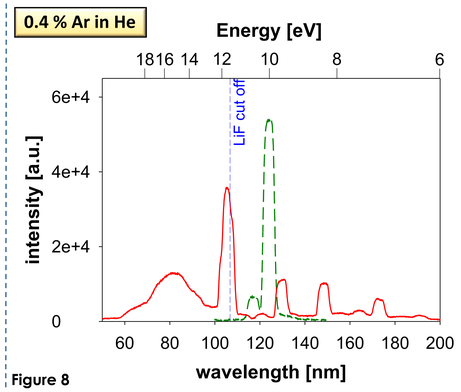

Figure 8

Literature

[1] Kersten, H.; Brockmann, K. J.; Benter, T.; O'Brien, R. Windowless Miniature Spark Discharge Light Sources 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, (July 2011)*

[2] Vaikkinen, A.; Haapala, M.; Kersten, H.; Benter, T.; Kostiainen, R.; Kauppila, T. J.: Comparison of Direct and Alternating Current Vacuum Ultraviolet Lamps in Atmospheric Pressure Photoionization. *Analytical Chemistry.* ***84, 1408-1415***

[3] Kumar, V.; Datta, A. K.: Vacuum ultraviolet scintillators: sodium salicylate and p-terphenyl. *Appl. Opt.* ***18, 1414-1417 (1979)***

Acknowledgement

Financial support of this work by the German Research Foundation (DFG) within project POXSA (BE 2124/4-1) is gratefully acknowledged.