Spark discharge VUV lamps for Atmospheric Pressure Ionization – Mass spectrometric investigations of the plasma chemistry

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Introduction

At the *ASMS conference 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 an API mass spectrometer. In *2012* a thorough investigation on the generated VUV emission of different discharge gases was presented [1, 2]

Challenge in 2013:
Characterization of generated meta-stables at atmospheric pressure.

Methods

spark discharge

power supply
- custom DD20_10 C-Lader, Hartlauer Präzisionselektronik GmbH, Grassau, Germany (small-sized circuit board; 1500 Vdc, 15 mA; 1.5 kHz)

spark assembly
- anode: MS sampler with 0.2 mm orifice
  cathode: stainless steel capillary
- o-ring sealed ceramic and metal housing, directly attached to the orifice of the MS
- evacuable down to 10^{-2} mbar
- optical access to the spark region via fiber optical assembly

discharge gas supply
- helium and argon (100 - 500 ml/min)
- rare gas purifier (< 10 ppbV)
  (Valco Instruments Co. Inc.)

mass spectrometer

Quadrupole mass spectrometer HPR-60 (Hiden Analytical Ltd, Warrington, UK)
- direct sampling from atmospheric pressure plasmas (with up to 100% He)
- EI source with adjustable electron-energy (0.4 - 150 eV)
- operation in ± RGA and ± ion SIMS mode
- data acquisition with 0.1 µs resolution
- raw count accumulation
- adjustable scan dwell time

UV/VIS spectrometer

- high resolution fiber optic spectrometer AvaSpec-3848 (Avantes BV, Eerbeek, The Netherlands); range: 200 - 900 nm

Principle of Measurement [3]

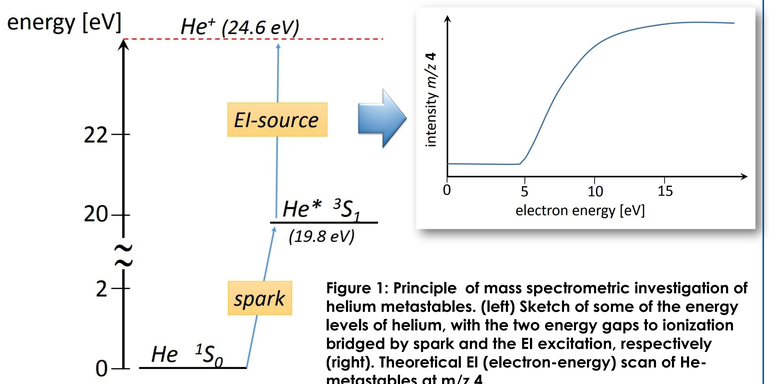


Figure 1: Principle of mass spectrometric investigation of helium metastables. (left) Sketch of some of the energy levels of helium, with the two energy gaps to ionization bridged by spark and the EI excitation, respectively (right). Theoretical EI (electron-energy) scan of He-metastables at m/z 4.

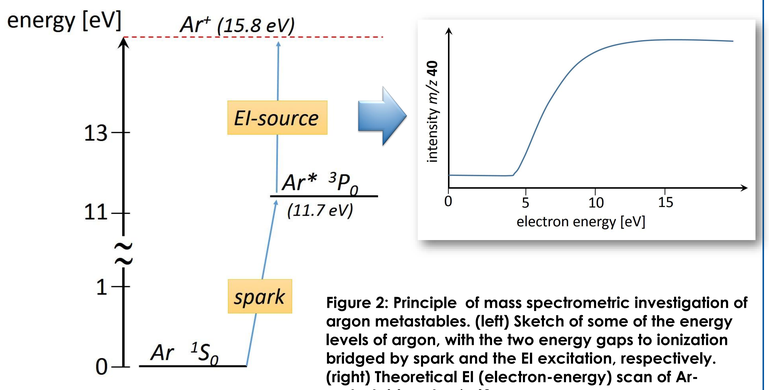
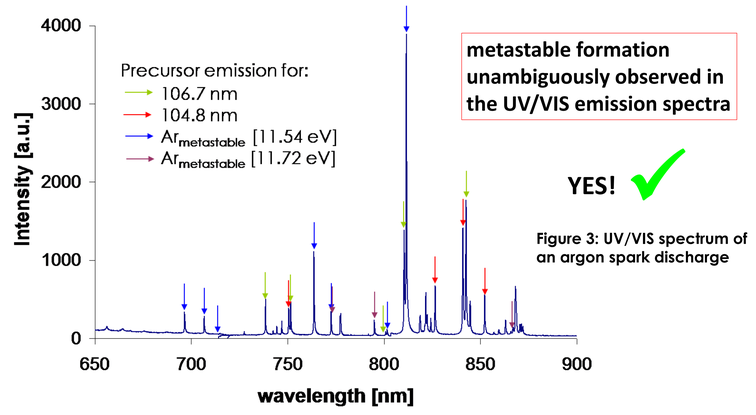


Figure 2: Principle of mass spectrometric investigation of argon metastables. (left) Sketch of some of the energy levels of argon, with the two energy gaps to ionization bridged by spark and the EI excitation, respectively. (right) Theoretical EI (electron-energy) scan of Ar-metastables at m/z 40.

Spectroscopic Evidence of Metastable Formation



metastable formation unambiguously observed in the UV/VIS emission spectra

YES!

Figure 3: UV/VIS spectrum of an argon spark discharge

Experimental Setup for Investigation of Metastable Formation

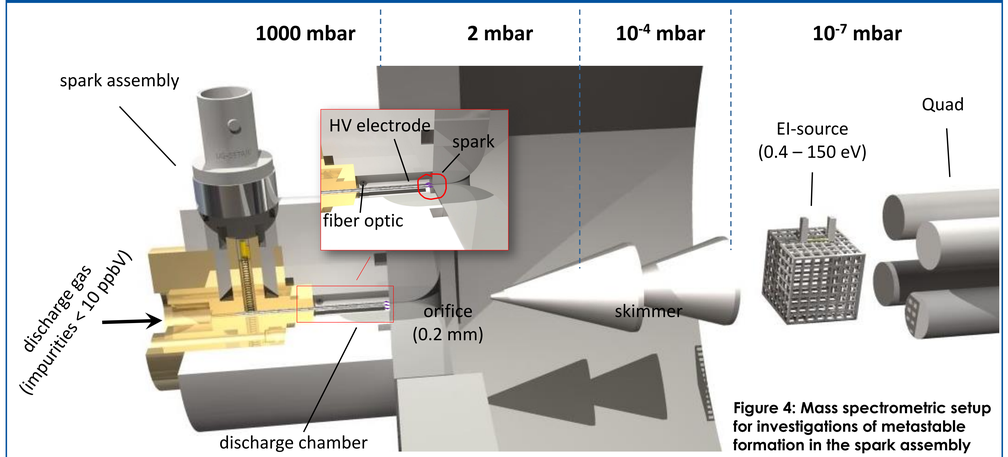


Figure 4: Mass spectrometric setup for investigations of metastable formation in the spark assembly

Mass Spectrometric Evidence of Metastable Formation?

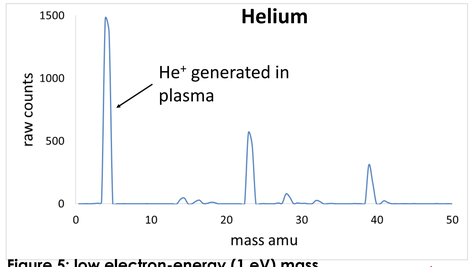


Figure 5: low electron-energy (1 eV) mass scan of an helium discharge

NO!

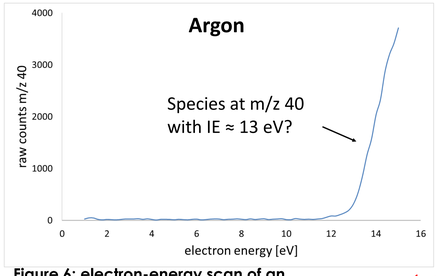


Figure 6: electron-energy scan of an argon discharge

NO!

- Several experimental variations (e.g., pressure, spark-gap distance, extended raw-count accumulation, etc.) – however, to date metastables from the spark discharge were not observed with the present mass spectrometric setup

Where do the metastables go?

-What should be taken care of for future experiments?

Dimer formation at elevated pressure
- *No dimers observed in the MS.*
- *Radiative decay of dimers?*

Reaction with impurities?
- *Spark source needs to be evacuable down to 10^{-6} mbar.*
- *…*

Loss to the wall?
- *Implement spark source in 1st differential pumping stage*

Conclusions

To date:
- metastable formation is unambig-uously observed in UV/VIS spectra
- mass spectrometric investigation via low energy electron scans is well known [3]
- to date no metastables could be observed with our mass spectrometric setup

Future experimets:
- cleaner matrix (spark assembly evacuable to 10^{-6} mbar)
- spark position closer to the 1. differential pumping stage
- minimize noise on mass trace – higher accumulation times
- chemical tracer for metastable formation

Future applications:
- spark discharge setup in AP-GC-MS applications

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] Kersten, H.; Dlugosch, M.; Kroll, K.; Brockmann, K. J.; Benter, T.; O'Brien, R. Progress in VUV measurements of a spark discharge lamp used for capillary Atmospheric Pressure Photoionization (cAPPI) *Proceedings of the 60th ASMS Conference on Mass Spectrometry and Allied Topics; Vancouver, BC, Canada, (**June 2012**)*

[3] Long, D. R.; Geballe, R.: Electron-Impact Ionization of He(2s ^{3}S). Physical Review A. 1, 260-265 (**1970**).

[4] Kramida, A., Ralchenko, Yu., Reader, J., and NIST ASD Team (2012). *NIST Atomic Spectra Database* (ver. 5.0), [Online]. Available: http://physics.nist.gov/asd [**2013, May 30**]. National Institute of Standards and Technology, Gaithersburg, MD

Acknowledgement

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