Time-Resolved Characterization and Analysis of Pulsed Ion Sources by Synchronized oaTOF-MS

BERGISCHE UNIVERSITÄT WUPPERTAL

Physical & Theoretical Chemistry
Institute for Pure and
Applied Mass Spectrometry
University of Wuppertal

Franziska Schuler*, Joshua Rieger, Maja Hammelrath, Sanna Benter, Hendrik Kersten, Thorsten Benter
*schuler@uni-wuppertal.de

Introduction

Some ion sources or ion generation processes in general are operating discontinuously, i.e. pulsed, due to their mode of operation.
The application of pulsed ion sources in combination with orthogonally accelerating time-of-flight mass spectrometers (oaTOF-MS) generally render the performance of such systems unfavorably, when the ion source is not synchronized with the oa-stage.
Spectra are then recorded at high repetition rates (kHz range) by the MS even though no ions were ejected by the ion source. As the mass spectra of the individual extractions are rapidly accumulated into a mass spectrum transferred for further data treatment, as is the case for oaTOFs, mostly empty spectra (noise) are added up.
→ Reduction in sensitivity, increase in background noise

If i) high mass resolution, and ii) sampling of individual full mass spectra in the kHz regime are required, oaTOFs are the mass analyzers of choice.
Synchronization of the ion source with the oa-stage enables time-resolved characterization of the ion source and ion-molecule gas-phase reactions. Thus, in a pulsed plasma ionization source, the ionization region, plasma dynamics, and possible ionization mechanisms can be deduced.
In this work, broad bandwidth resonance enhanced multiphoton ionization (REMPI) of nitrogen monoxide (NO) was performed [1] to characterize this synchronization method for further application in pulsed plasma dynamics studies.

Experimental Set-Up and Methods

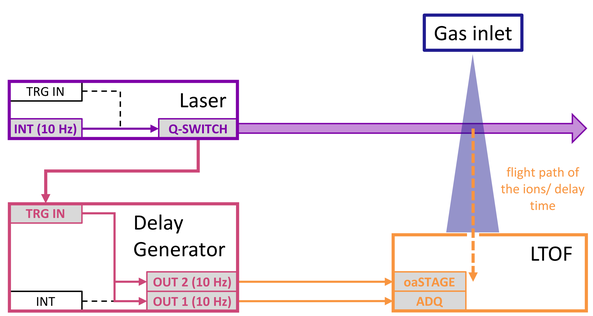

Fig. 1: Schematic overview of the experimental set-up for the synchronization of a pulsed ion source with an oaTOF-MS

Gas Supply

- 400 ppm NO in N_2 (Messer Industriegase GmbH, Bad Soden, Germany) are continuously fed into a vacuum chamber via a gas chromatography (GC) capillary.

Ionization

- A Nd:YAG pumped optical parametric oscillator (OPO) laser system (NT342 Series, EKSPLA, Vilnius, Lithuania) resonantly ionizes NO at 226.2 nm via (1+1) REMPI ([A(v=0) ← X(v=0)], pulse duration: 5 ns, repetition rate: 10 Hz). An electrode has been placed in close vicinity to the ionization region, to which voltages can be applied.

Ion Detection

- For ion detection, the vacuum chamber is coupled to a high resolution oaTOF-MS (LTOF, Tofwerk AG, Thun, Switzerland).

Synchronization

- The LTOF is synchronized with the laser system using the ''trigger out'' signal of the Nd:YAG laser's Pockels cell driving unit. The time interval between the laser pulse and the push pulse of the oa-stage of the LTOF as well as the data acquisition system is adjusted with a delay generator (81150A, Keysight Technologies, Santa Rosa, USA).

Experimental and Simulation Results

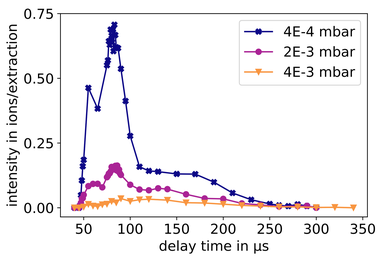

Fig. 2: Detected ions as a function of the delay time at different pressures

- Maximum detected ions per extraction at a delay time of 70 µs
- For a flight distance of 22 cm, a delay time of 70 µs corresponds to an ion velocity of about 3000 m/s and thus a kinetic energy of 1.5 eV.
- Kinetic energy for the fastest ions: about 3.5 eV
- When the background pressure in the chamber is increased, fewer ions are detected, and the average velocity of the ions becomes smaller, as expected.

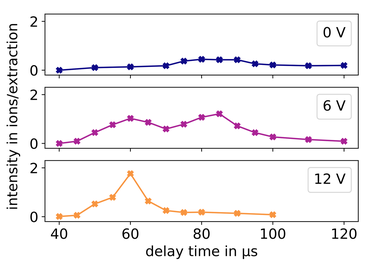

Fig. 3: Effect of ion acceleration on the arrival times

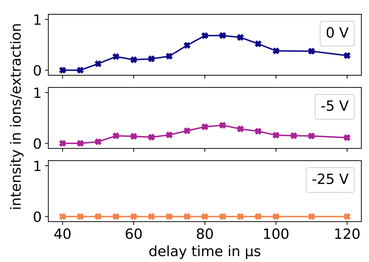

Fig. 4: Effect of ion deceleration on the arrival times

Ion Acceleration:

- Applying a positive potential to the electrode

Ion Deceleration:

- Applying a negative potential to the electrode

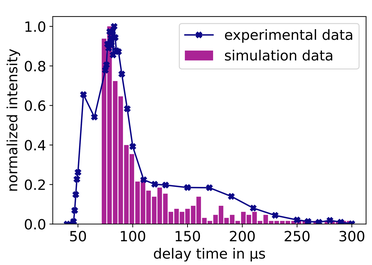

Fig. 5: Comparison of experimental results with IDSimF simulations

- The simulations were performed using the in-house developed Ion Dynamics Simulation Framework (IDSimF) [2].
  It is an open source software written in C++ that contains various models and functions for the simulation of ion trajectories.
- Ion density: 4E14 ions/m^3
- Acceleration of the ions is caused by space charge forces.
- Very good agreement between experimental and simulation results is observed.

New Experimental Set-Up

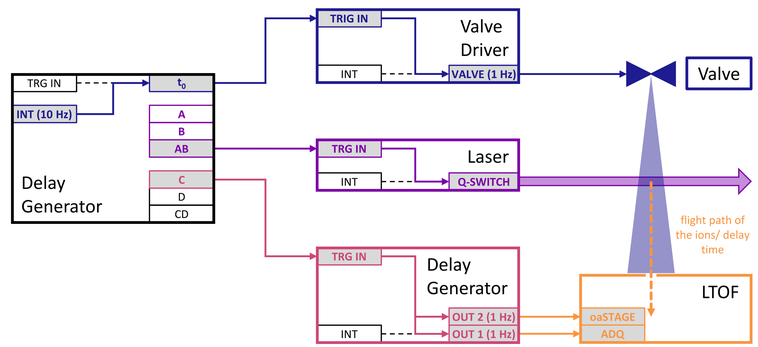

Fig. 6: Schematic overview of the new experimental set-up including a pulsed valve for pulsed gas injection

Gas Supply

- A pulsed valve (ALD3, Swagelok, Solon, USA) controlled by a valve driver (Iota One, Parker Hannifin Corporation, New Jersey, USA) is used for pulsed gas injection (repetition rate: 1 Hz). The capillary is replaced by a new stainless steel inlet system (orifice: 200 µm), which can also function as an electrode.

Ionization

- The OPO laser system resonantly ionizes NO at 226.2 nm (repetition rate: 10 Hz).

Ion Detection

- The ions are detected by the LTOF (repetition rate: 1 Hz).

Synchronization

- An additional delay generator (9650A, Signal Recovery, Berwyn, USA) is used as a master trigger source (repetition rate: 10 Hz). The valve is triggered at time t_0. The laser is triggered with delay A. The energy scan is performed with delay C. The LTOF is synchronized with a second delay generator.

Conclusion and Outlook

Conclusions:

- Successful synchronization of a low repetition-rate pulsed ion source and an oaTOF-MS
- Simulations with IDSimF are in very good agreement to the experimental results
- Realization of a new experimental set-up with a pulsed gas inlet

Outlook:

- Performing energy scans with a pulsed gas inlet using the new set-up
- Application of this synchronization method for pulsed plasma ion sources
- Time-resolved characterization of different pulsed plasma ion sources

References

[1] R. M. Garnica, M. F. Appel, L. Eagan, J. R. McKeachie, T. Benter, *Anal. Chem.* **2000**, *72*, 5639–5646.

[2] IDSimF, ion dynamics simulation framework, https://idsimf.readthedocs.io/en/latest/.

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