Measuring ion and electron mobility in a Laser-HiKE-IMS based on a 1+1 REMPI scheme

BERGISCHE UNIVERSITÄT WUPPERTAL

Physical & Theoretical Chemistry
University of Wuppertal

David Pawlowski*[1], Adem Bulut[1], Christoph Schaefer[2], Jannik Wuttke[2], Stefan Zimmermann[2], Walter Wißdorf[1] and Thorsten Benter[1]

*david.pawlowski@uni-wuppertal.de

[1]*Department of Physical and Theoretical Chemistry, University of Wuppertal, Wuppertal, Germany*
[2]*Institute of Electrical Engineering and Measurement Technology (GEM), University of Hannover, Hannover, Germany*

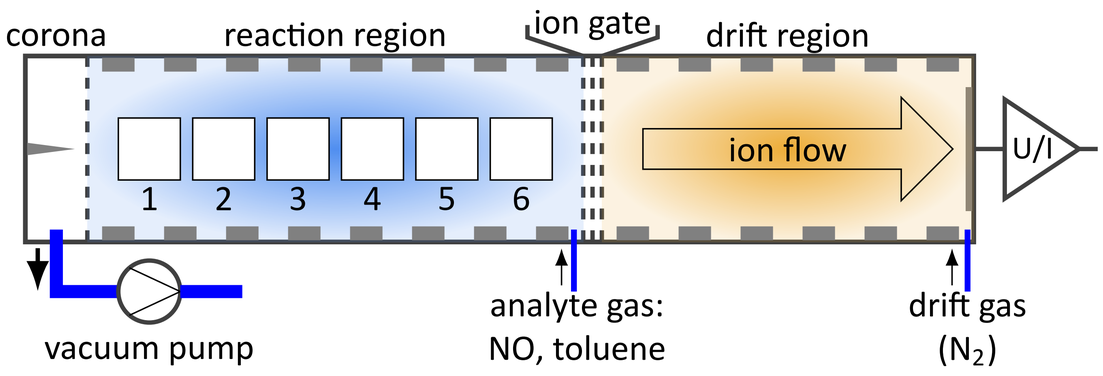
Introduction

The conditions in high kinetic energy ion mobility spectrometry (HiKE-IMS) instruments induce a complex and interesting ion chemistry. One approach to gain insight in such ion dynamics is to create extremely well defined starting conditions by photo ionization via 1+1 REMPI instead of regular corona discharge (APCI) ionization:

$$M + 2\,h\nu \longrightarrow M^{+\bullet} + e^{-} \qquad (1)$$

A HiKE instrument with laser photo ionization option is used to study ion dynamics in an IMS drift tube at high electric field in positive and negative mode.

Methods

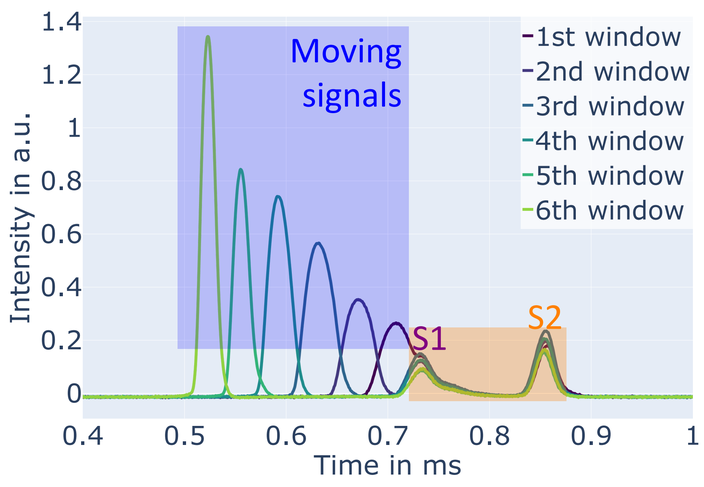


- Custom build by GEM, Uni. Hannover
- Operates at approx. 20 mbar
- Red. field: up to 80 Td (1 Td = $1 \cdot 10^{-21}$ V m^2)

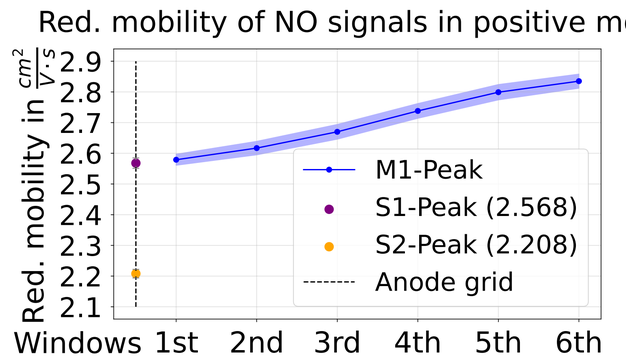
Figure 1: Scheme of the Laser-HiKE-IMS.

With 1+1 REMPI, analytes can selectively and instantaneously be ionized at one of the designated window positions (1 to 6). The measurements are triggered on the laser pulses and the ion gate is kept open for all measurements to enable the detection of spatially resolved drift time spectra.

Spatially resolved drift time spectra



- Three signals instead of one
- One group of moving signals (blue, M)
- Two stationary signals (orange, S)
- Stationary signals appear at +45 Td in RR



The reduced mobility K_0 is determined by

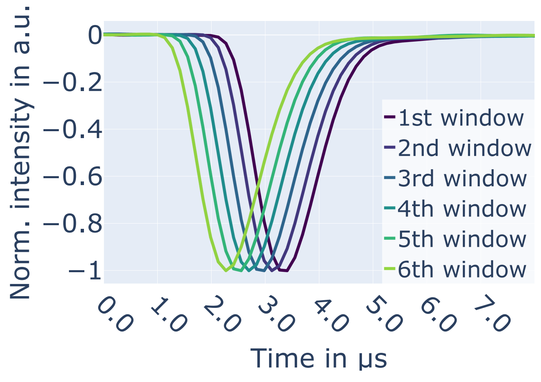
$$K_0 = \frac{l_d}{t_d \cdot N_0 \cdot \frac{E}{N}} \qquad (2)$$

- K_0 of M1-Peak = 2.579–2.835 $\frac{cm^2}{V\,s}$
- Drift in K_0-values of M1-Peak caused by field defect in RR (up to 10 %)
- Stationary signals identified as NO^+ (S1-Peak) and NO_2^+ (S2-Peak) [1]

Appearance of stationary signals is explained with a secondary heterogenic ionization at the anode grid of the experiment caused by the generated photoelectrons (e^-) of the fundamental ionization process at sufficient high electric fields.

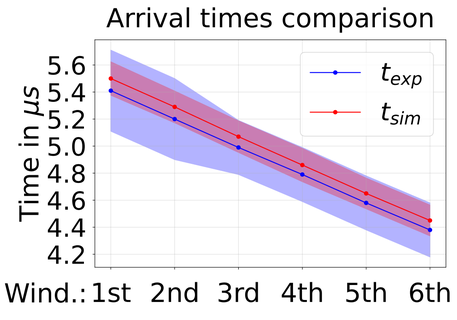
Photoelectrons

1. Measuring
Measurement of photoelectrons for different laser positions provides spatially resolved spectrum with drift times of electrons (t_{exp})



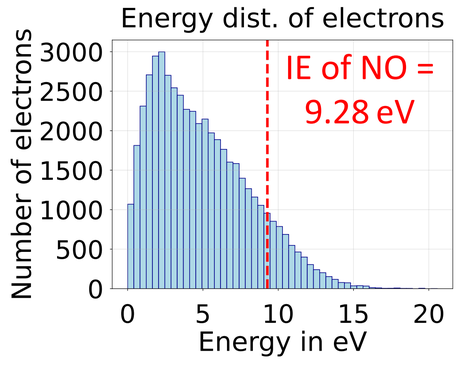
$t_{exp} = t_{measured} + t_{delay}$ (2 µs)

2. Building
Building a Monte-Carlo based simulation system of electrons in nitrogen with reactive collisions in IDSimF [2]



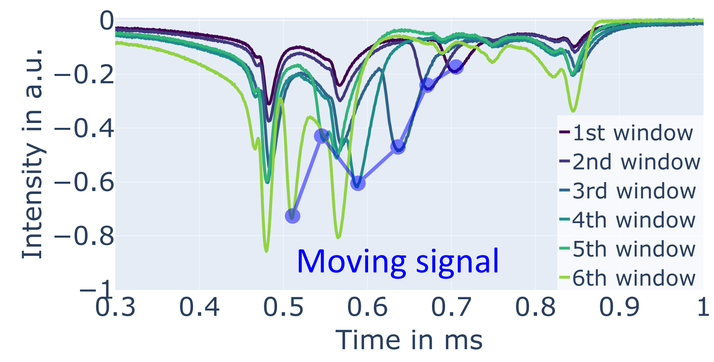
Comparing simulated drift times t_{sim} with experiment

3. Calculating
Calculating electron energy distributions at different red. fields to evaluate possible ionization by electrons



Mean electron energy not sufficient for ionization

Anionic signals



- Anions observable for measurements with toluene
- Also 1 moving signal, but up to 6 stationary signals
- Moving signals caused by electron attachment to O_2 in an analyte gas mixture

Conclusion

- Spatially resolved spectra with REMPI are possible
- Complex spectra due to complex chemistry even with very well defined starting conditions
- Photoelectrons cause secondary heterogenic ionization. Detailed mechanism currently unclear.

Acknowledgment

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References

[1] Maria Allers, Ansgar T. Kirk et al., J. Am. Soc. Mass Spectrom. 2020, 31, 2191–2201

[2] Michelle Rajkovic, Sanna Benter et al., J. Am. Soc. Mass Spectrom. 2024, 35 (7), 1451-1460

Conflicts of interest's disclosure

The authors declare no conflicts of interests with other parties.