

# Numerical Simulation of Reacting Flows of Ions at Atmospheric Pressure - the Reactant Ion Peak in IMS

Walter Wissdorf<sup>1</sup>; Valerie Derpmann<sup>1</sup>; Sonja Klee<sup>1</sup>;  
Hendrik Kersten<sup>1</sup>; Thorsten Benter<sup>1</sup>; Wolfgang Vautz<sup>2</sup>

## Introduction

At atmospheric pressure (AP), ions experience a very high collision rate with bulk gas particles. In addition to the electrical force, the motion of ions under AP conditions is governed by viscous drag / viscous transport and molecular diffusion.

In the past years, the successful simulation of ion transport phenomena at AP conditions became possible through the development of powerful numerical models like the statistical diffusion simulation (SDS) extension for the commercial ion optics simulation software package SIMION [1][2].

In addition to pure transport, reactive ions can undergo complex chemical transformations at AP due to the high collision rate. Due to the resulting high number of possible reactive collisions, even reactions with relatively small rate constants may proceed efficiently.

In common atmospheric pressure ion sources, the total transformation of any set of reactive ions is almost inevitable due to the long residence times of ions in the ion source and the high concentrations of possible reaction partners.

Therefore, a comprehensive model of the dynamics of ions at AP conditions has to include a chemical reaction model in addition to a numerical description of the pure ion transport effects.

In efforts to achieve a step towards such a complete description of the dynamics at AP, we have developed a reaction simulation (RS) extension for a previously existing ion transport model (SIMION / SDS).

To validate and test this new model we performed simulations of the reactant ion peak (RIP), which is a common observation in Ion Mobility Spectrometry (IMS) and served as a demanding benchmark problem for the reaction simulation.

In this contribution we present a detailed discussion of the developed numerical model, the simulation results and a comparison of the numerical results with another chemical kinetics model and experimental data.

## Monte Carlo Reaction Simulation (RS)

The Reaction Simulation (RS) Module uses a Monte Carlo approach to simulate chemical reactions.

Instead of calculating an exact result with a deterministic algorithm, Monte Carlo methods use random sampling to describe a system statistically.

They often allow the numerical simulation of complex systems, which would be difficult with other methods.

### Current Implementation

The actual implementation of RS is capable of simulating reactions of ions with neutral reaction partners (no ion-ion reactions at present)

### Basic Simulation Loop

The reaction simulation module performs the following operations in every time step of the trajectory calculation of SIMION / SDS:

- For every ion, calculate the local reaction probability  $p$ :

$$p = \prod_i (c_i) \cdot k \cdot dt$$

$k$  = reaction rate constant,  
 $c_i$  = concentration of  $i$ -th reaction partner  
 $dt$  = time step length

- Generate a uniform distributed random value  $r$
- If  $p < r$  the reaction event is considered "successful":

- remove educts from simulation
- add products to simulation
- move on to next reaction

## Reactant Ion Peak (RIP)

### Ion Mobility Spectrometry (IMS)

Ion Mobility Spectrometry (IMS) separates ions by their electrical mobility at elevated gas pressure:

- Ions are gated into a drift tube with an linear electrical gradient
- Ions with low mobility have lower drift velocities and therefore longer drift times
- Drift time directly corresponds to the ion mobility

### RIP: Signal of Primary Ions

In IMS with chemical ionization (APCI) distinct ion signals occur, which do not correspond to analytes. They are called **Reactant Ion Peaks (RIP)**.

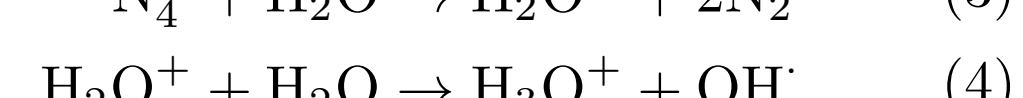
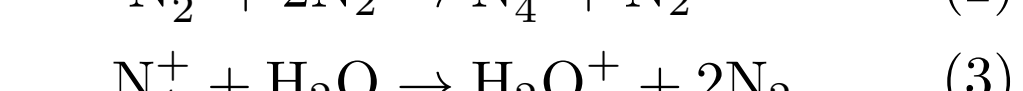
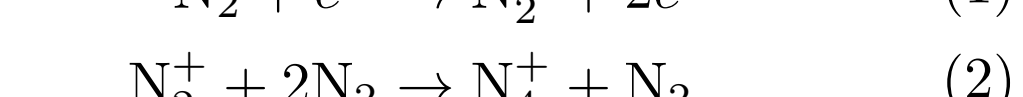
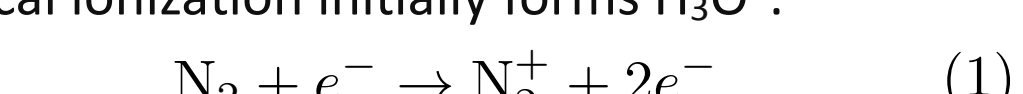
Those signals result from primary ions, generated in the chemical ionization process which transfer the charge to the analytes by chemical reactions.

One important RIP results from **proton bound water clusters**.

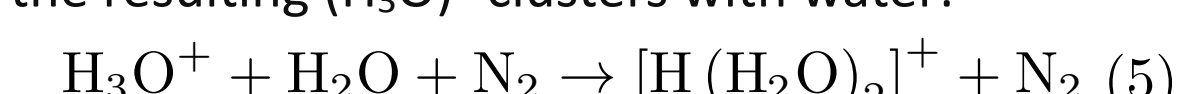
### Proton Bound Water Clusters<sup>4,5</sup>

#### [H(H<sub>2</sub>O)<sub>n</sub>]<sup>+</sup> from Chemical Ionization

Chemical ionization initially forms H<sub>3</sub>O<sup>+</sup>:

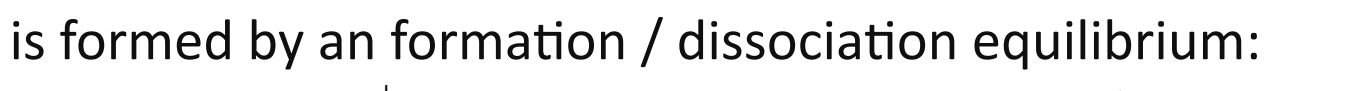


the resulting (H<sub>3</sub>O)<sup>+</sup> clusters with water:



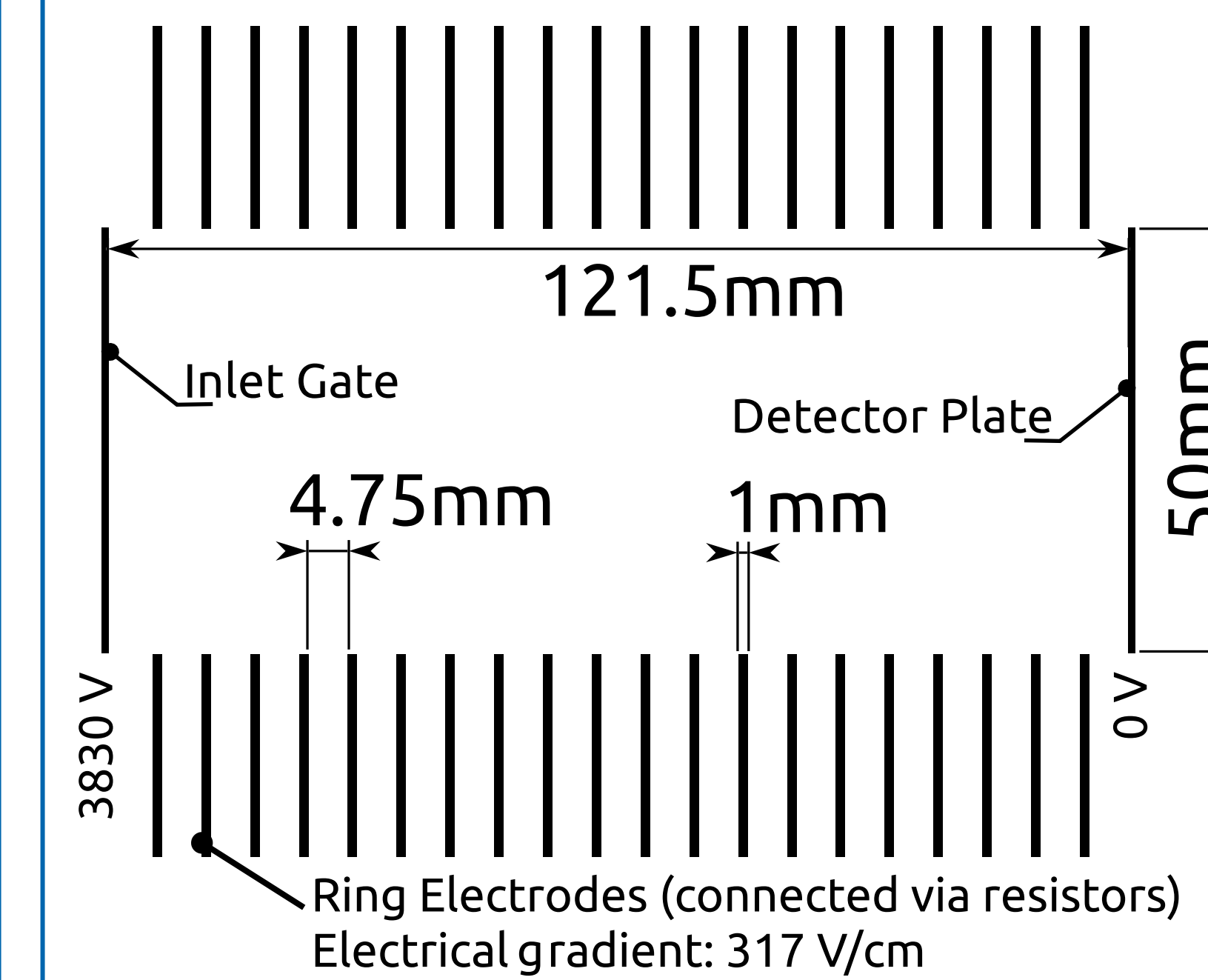
#### Fast Water Cluster Equilibrium

A distribution of proton bound water clusters [H(H<sub>2</sub>O)<sub>n</sub>]<sup>+</sup> is formed by an formation / dissociation equilibrium:



The relaxation time of this equilibrium is much faster than the drift time in IMS [3], therefore in the whole cluster distribution occurs as **one distinct signal** - the Reactant Ion Peak (RIP)

## Model Geometry

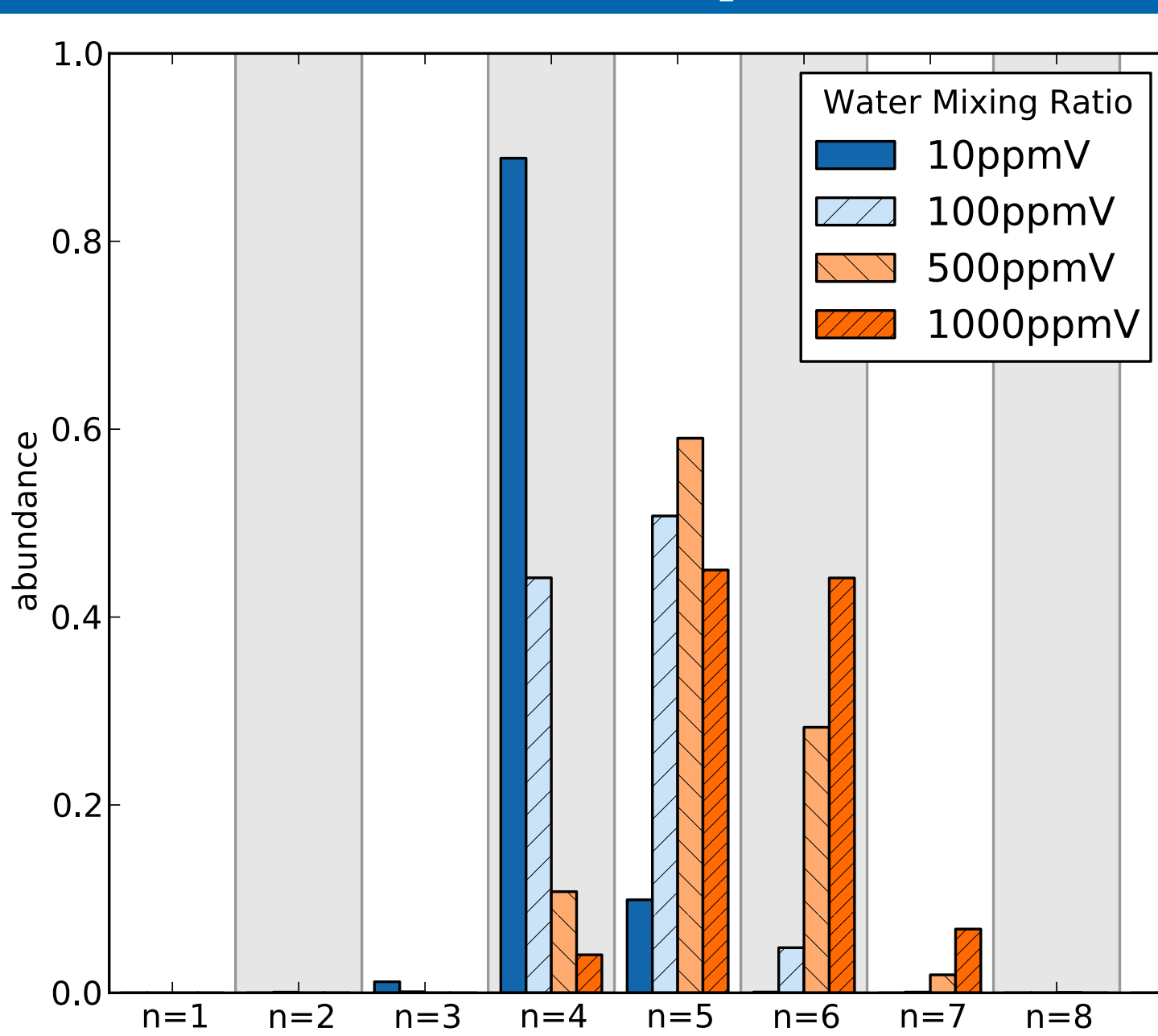


## Conclusions

- A new extension to SIMION / SDS for the simulation of chemical reactions (RS) of ions at atmospheric pressure was developed and validated
- The system of **proton bound water clusters [H(H<sub>2</sub>O)<sub>n</sub>]<sup>+</sup>** at "moist" atmospheric pressure conditions was successfully modeled with the RS extension
- The results from RS are in very good agreement to the results from a mathematically different numerical model (Chemked)
- The simulated peak shape of the reactant ion peak (RIP) is in good agreement with actual experimental data
- Considering the given uncertainties in the simulation input parameters (ion mobilities, reaction rates) the simulated RIP drift times are in very good agreement with the experimental results
- The RIP simulation is numerically very demanding (fast reactions, high water concentrations). Therefore the RS extension appears to be suitable for modeling of most reaction systems in terms of numerical costs
- If the thermochemical data are available, **most of the usually encountered reaction systems in API can be modeled** with RS, for example:
  - Clustering of analyte ions in Ion Mobility Analyzers
  - Cluster Systems relevant in Atmospheric Pressure Ionization (See also Session MP29, Poster 672 and our Talk in Session MOG)
  - Declustering processes in ion funnels and similar ion optical devices

## Results

### Cluster Species Distribution



The water cluster distribution depends on the water mixing ratio in the background gas:

- Primary cluster at 10 ppmV water is  $n=4$
- At 1000 ppmV the primary clusters are  $n=5$  and  $6$
- The water dependent mean cluster size results in a **water dependent mean ion mobility**
- Virtually **no small clusters** ( $n=1,2,3$ ) even at very low water mixing ratios

Figure 2) Simulated equilibrated distribution of proton bound water clusters [H(H<sub>2</sub>O)<sub>n</sub>]<sup>+</sup>

### Cluster Concentration Time Series

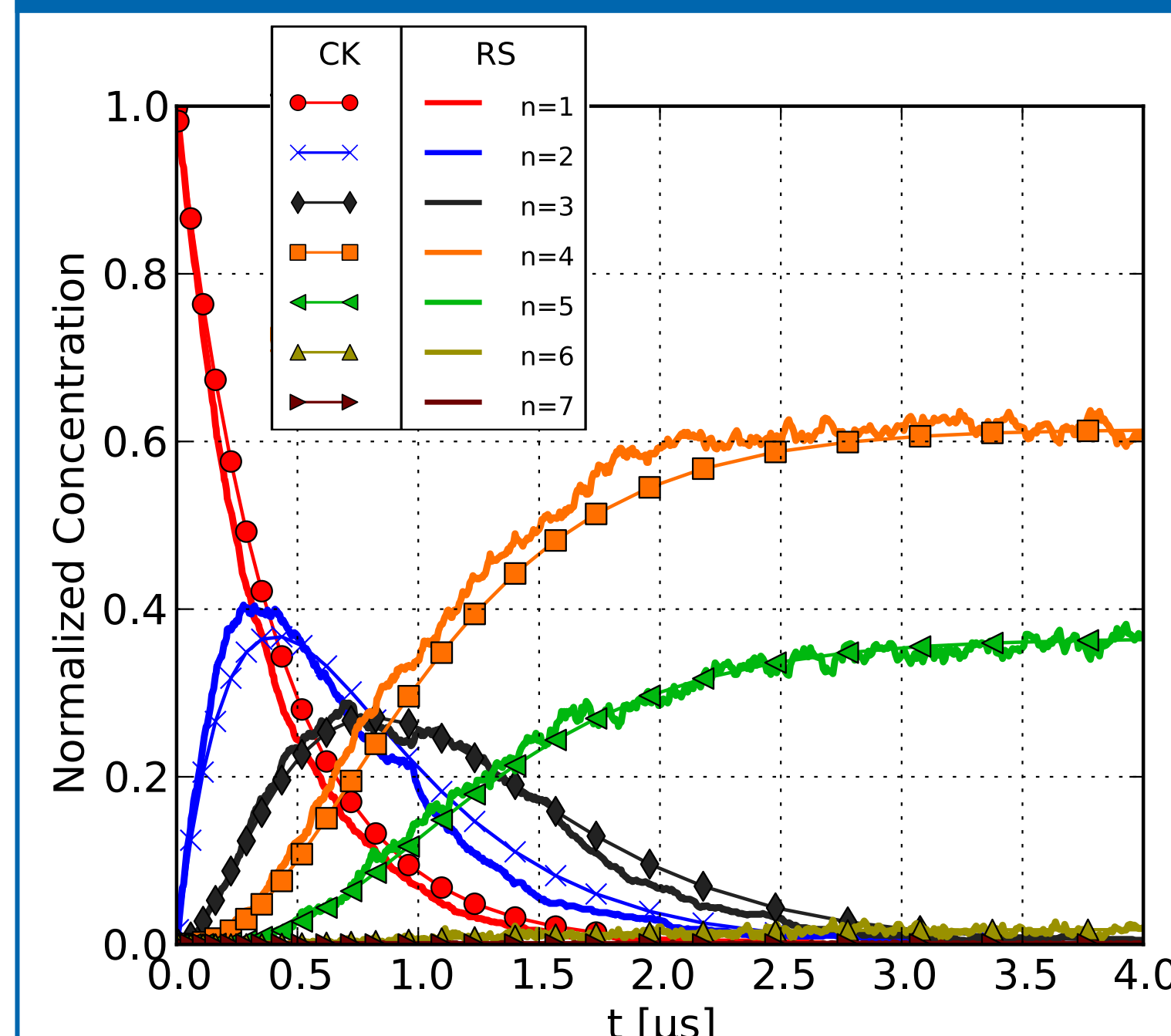


Figure 3) Simulated evolution of the water cluster distribution (water mixing ratio 50 ppmV) (CK = Chemked; RS = Reaction Simulation ext.)

- Very good agreement between Chemked and SIMION / RS
- Very **fast relaxation** of the proton bound water cluster system: The equilibrium is reached after at last **3 μs**.
- Short relaxation times correspond to very high reaction rates
- Individual clusters undergo dissociation and association reactions with high frequencies
- The whole cluster system is detected as only **one** ion mobility signal in IMS (see Fig. 4 on the right)

### RIP Peak

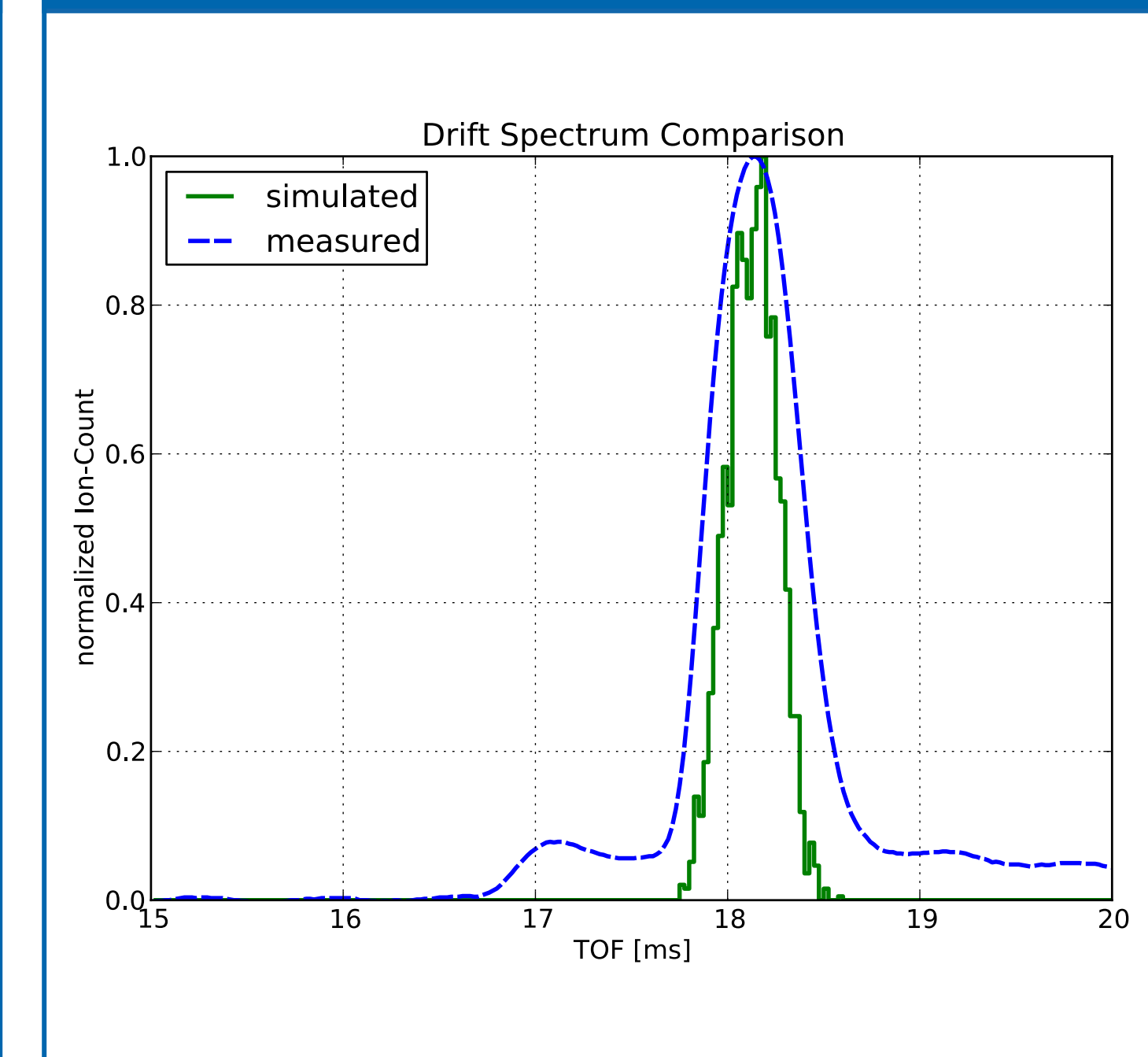


Figure 4) Simulated and measured RIP of the proton bound water clusters [H(H<sub>2</sub>O)<sub>n</sub>]<sup>+</sup>

- Good agreement** between experiment and simulation in terms of **basic peak shape**
- The axial diffusion of ions, which leads to peak broadening, is underestimated by the simulation with SIMION / SDS / RS.
- Space charge effects, which were not considered in the calculation could lead to an increased axial diffusion

## Methods

### Numerical Methods

#### Ion Trajectory Simulation:

SIMION charged particle simulator (v8.01) with Statistical Diffusion Simulation (SDS) Extension

#### Reaction Simulation:

- Custom developed chemical reaction simulation (RS) extension for SIMION / SDS
- Chemked reaction kinetics solver (Version 3.3)

#### Experimental Methods

##### Ion Mobility Spectrometer:

- Custom made IMS (ISAS, Dortmund, Germany)
- 12.1 cm drift distance, 317 V/m linear electrical gradient
- Faraday Plate detector
- Entrance shutter grid: Bradbury Nielsen grid, opened for 300 μs every 100 ms

##### Ion Source:

- Atmospheric Pressure Chemical Ionization (APCI), primary electrons are generated by a Tritium β radiation source (500 MBq)

##### Drift Gas Dilution:

- Nitrogen with 2000 ppmV water was provided by a calibration gas generator (HovaCAL 3834-VOC, IAS, Frankfurt, Germany)
- Lower water mixing ratios were generated from this gas by exponential dilution in a flushed glass bottle
- The water mixing ratios were checked with a moisture monitor (Panametrics, Series 35, Hoheim a.T., Germany)

### RIP Drift Time vs. Water Concentration

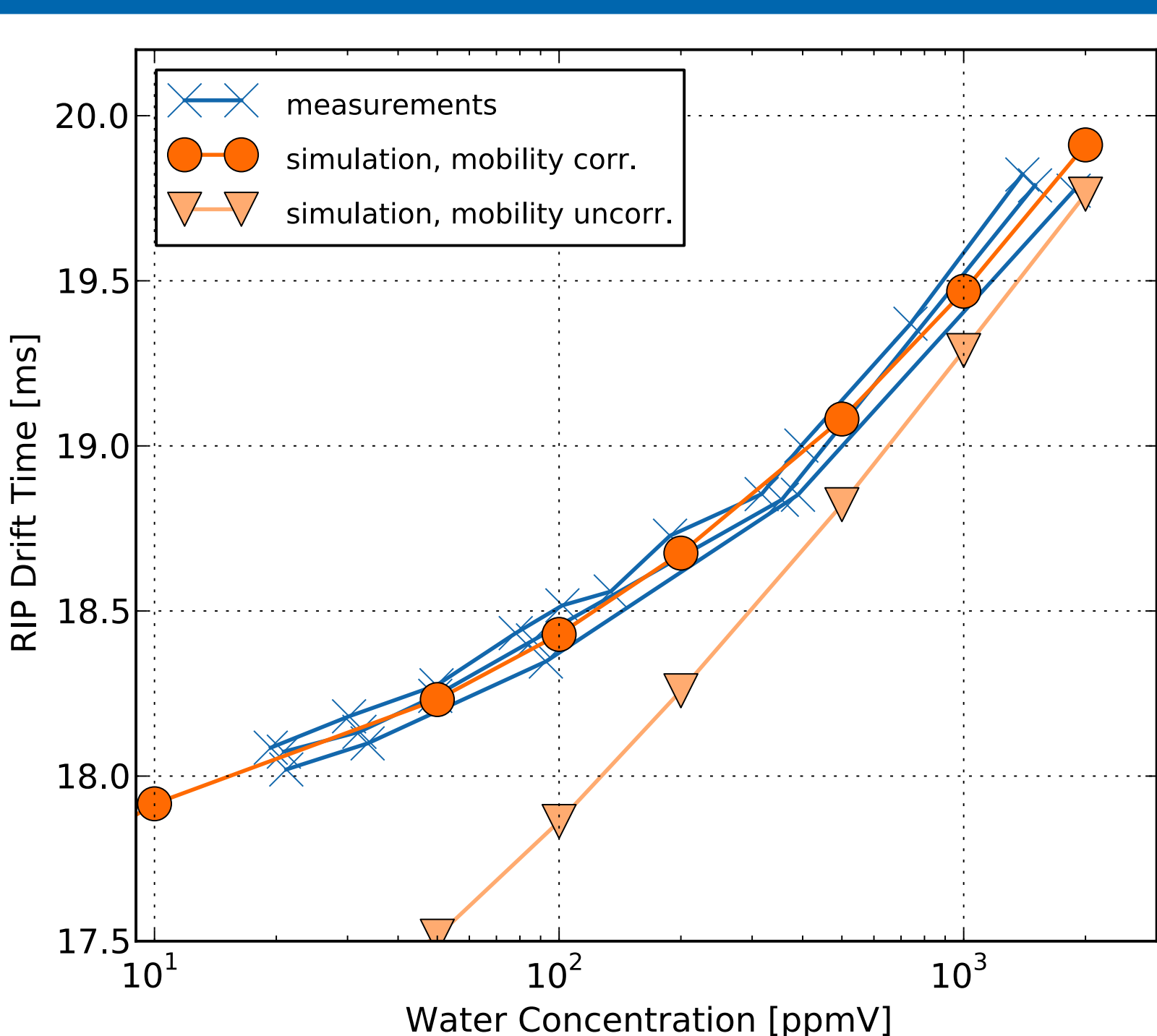


Figure 5) Dependence of experimentally recorded ion current on the deflection voltage

- RIP drift time is directly dependent on the water mixing ratio due to the mean cluster size which is water dependent (see Fig. 2)
- If the ion mobility ( $K_0$ ) of the individual cluster species is estimated from their mass [1], (ignoring ion geometry) the simulation diverges from the experimental data ("uncorr." in Figure 5).
- A slight correction of the **estimated** ion mobilities of distinct cluster species gives a very good agreement between simulation and experiment ("corr." in Figure 5)

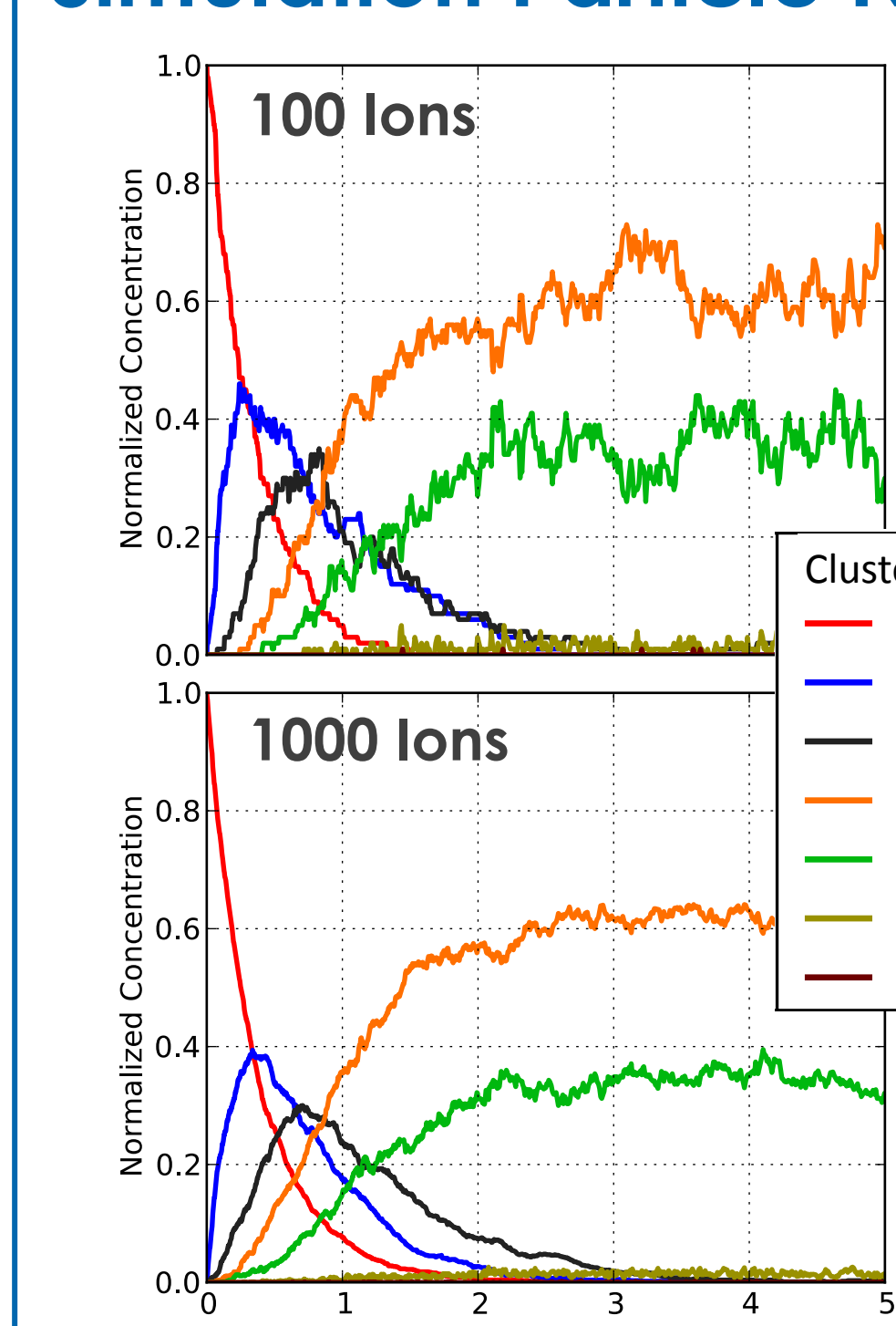
#### Ion Mobilities:

Cluster Size	$K_0$ (uncorrected)	$K_0$ (corrected)
$n=1$	3.57	3.57
$n=2$	2.76	2.76
$n=3$	2.35	2.35
$n=4$	2.09	<b>1.97 (-5.5%)</b>
$n=5$	1.90	<b>1.88 (-1.0%)</b>
$n=6$	1.77	1.77

reduced ion mobilities ( $K_0$ ) are given in  $10^{-4} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$

### Numerical Quality

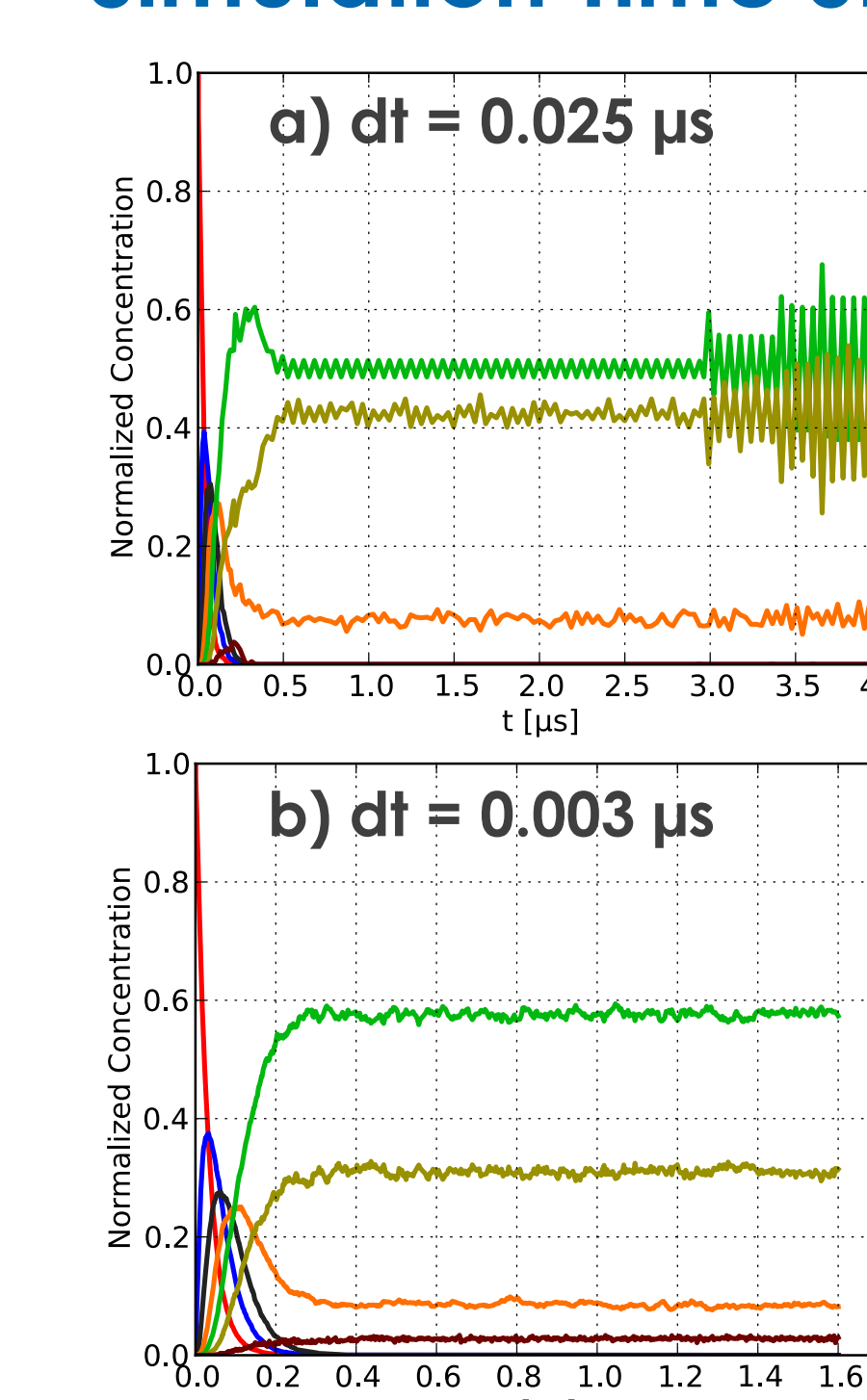
#### Simulation Particle Number



- The level of numerical noise decreases with increasing number of simulated particles
- Even with only 100 simulated ions, the rough temporal concentration development is observable
- 1000 simulated particles allow to model the RIP drift times with sufficient accuracy: The numerical noise is well below the uncertainties of the simulation input parameters

Figure 6) Effects of simulation particle number on RS simulations

#### Simulation Time Step Length



- If the time step becomes too long, the local reaction probability  $p$  can become  $> 1$
- If the number of such "invalid" reaction events gains significance, the simulation result becomes invalid
- A typical effect of this is the occurrence of severe oscillations (see a) after 3 μs)
- Inappropriate time step lengths lead also to wrong final concentration distributions (note the difference in a) and b) in the stable region)

Figure 7) Effects of simulation time step length (dt) on RS simulations (600 ppmV water mixing ratio)

## Literature

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