Chemical Reaction and Transport Simulations of Positive Reactant Ions in High Kinetic Energy Ion Mobility Spectrometry (HiKE-IMS)

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Introduction

In Ion Mobility Spectrometry (IMS), ions are separated based on their mobility. Usually, the analyte is ionized by electrospray ionization, corona discharge or beta radiation of a radio-active source [1]. In contrast to common IMS, the High Kinetic Energy IMS (HiKE-IMS) is operated at lowered pressures (14-20 mbar) and high reduced field strengths up to 120 Td [2]. The reaction rates are lower due to the pressure and short residence times. Thus, chemically active systems are not in equilibrium as they are in conventional atmospheric pressure drift tube IMS. The reactant ions produced by corona discharge in the HiKE-IMS reaction region determine the ion ensemble that is introduced into the mobility analyzer. The chemical reactions are strongly dependent on the present reduced electric field strength [3]. Furthermore, the amount of generated reactant ions (e.g. O_2^+) depends on the background gas composition. The transition of several cluster species of small molecules is visible in HiKE-IMS.

Numerical simulations were performed in order to investigate the chemical dynamics in HiKE-IMS:
- Resonant charge transfer of O_2^+ in air alters the drift time of the observed species.
- O_2^+ can form clusters, e.g. $O_2^+(H_2O)$, and thus form proton-bound water clusters.
- The experimentally observed cluster transition of the proton-bound water cluster system is investigated with numerical simulations. Additionally, the number of reaction events was calculated.

Methods

HiKE-IMS experiments: 12 – 120 Td, 15 – 20 mbar background gas pressure [3]

Ion Dynamics Simulation Framework (IDSimF): Hard-sphere collision model, Verlet-integration method, Monte Carlo kinetics code [4]

Ab initio calculations: Gaussian 16
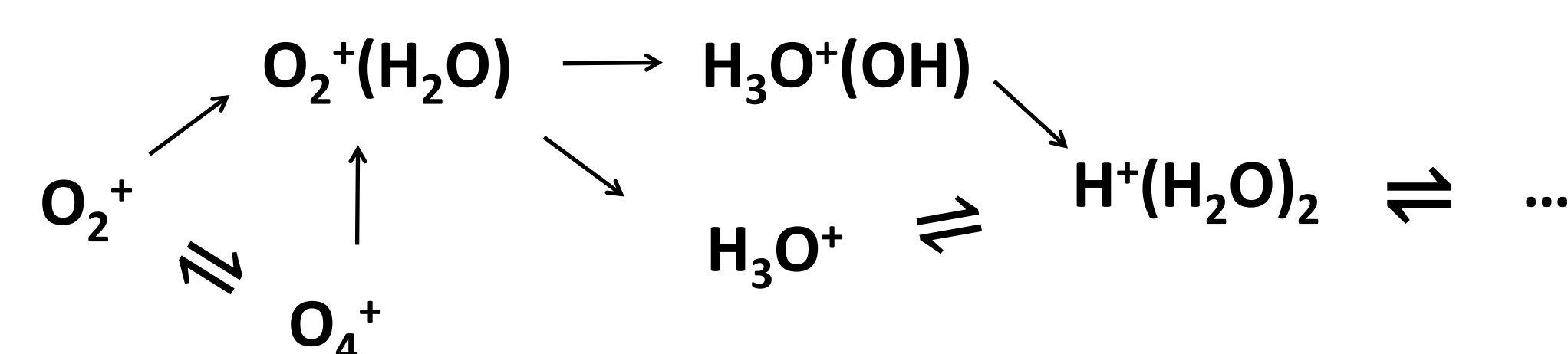
Data Analysis: Python

Oxygen Cluster System
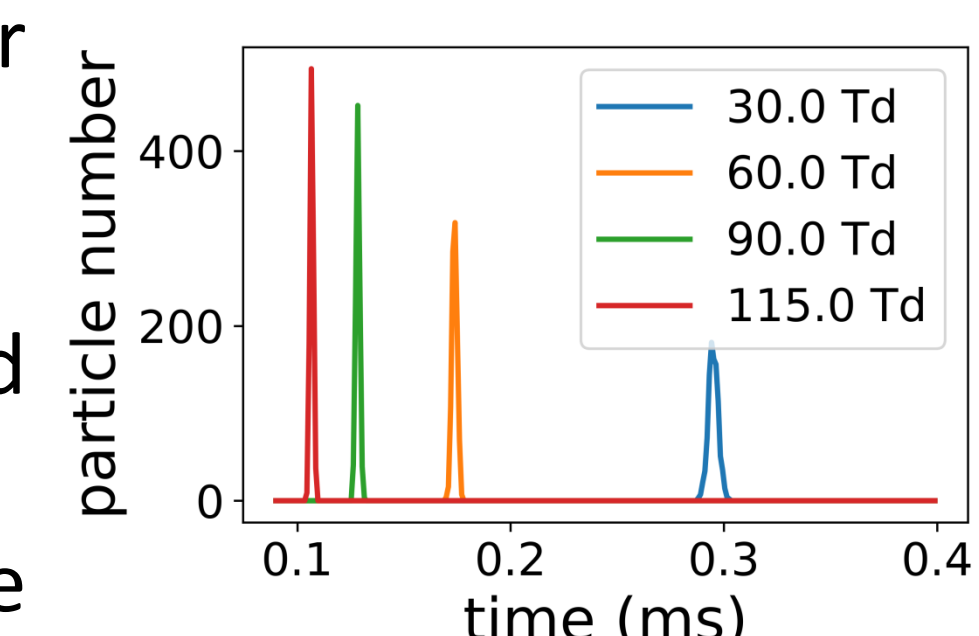
Resonant charge transfer
- Significantly higher drift time of O_2^+ measured in air compared to nitrogen [3]
- $O_2^+ + O_{2(therm)} \rightarrow O_2 + O_{2(therm)}^+$
- Initially thermal neutral molecule has to be accelerated again
- Drift time of the observed O_2^+ in air is therefore significantly higher
- *Right*: Drift time simulation of O_2^+ at different reduced field strengths in the reaction region

No resonant charge transfer

Resonant charge transfer

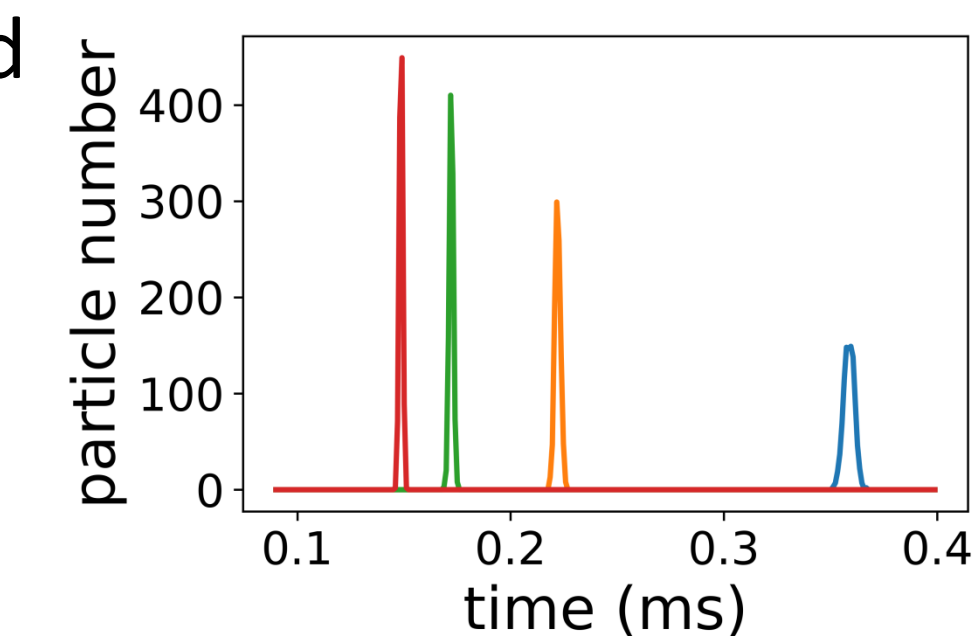### Cluster formation of $O_2^+(H_2O)$ and O_4^+
The schematic overview shows possible reaction pathways of O_2^+ in the reaction region of the HiKE-IMS. Kinetic simulations without considering the increased effective ion temperature in the drift field show that the formation of $O_2^+(H_2O)$ is around four times faster in air than in nitrogen, due to the higher oxygen mixing ratio.


Left: Schematic reaction mechanism of O_2^+ forming proton-bound water clusters [5]

Chemical kinetics
- Variation of the reduced field strength in the reaction region
- Depending on the applied reduced electric field strength, the reaction system is eventually not in equilibrium, which is shown in the time-concentration profiles on the right
- This is due to shorter residence times (in the range of ms) and the reaction rates being 100 times slower compared to atmospheric pressure IMS
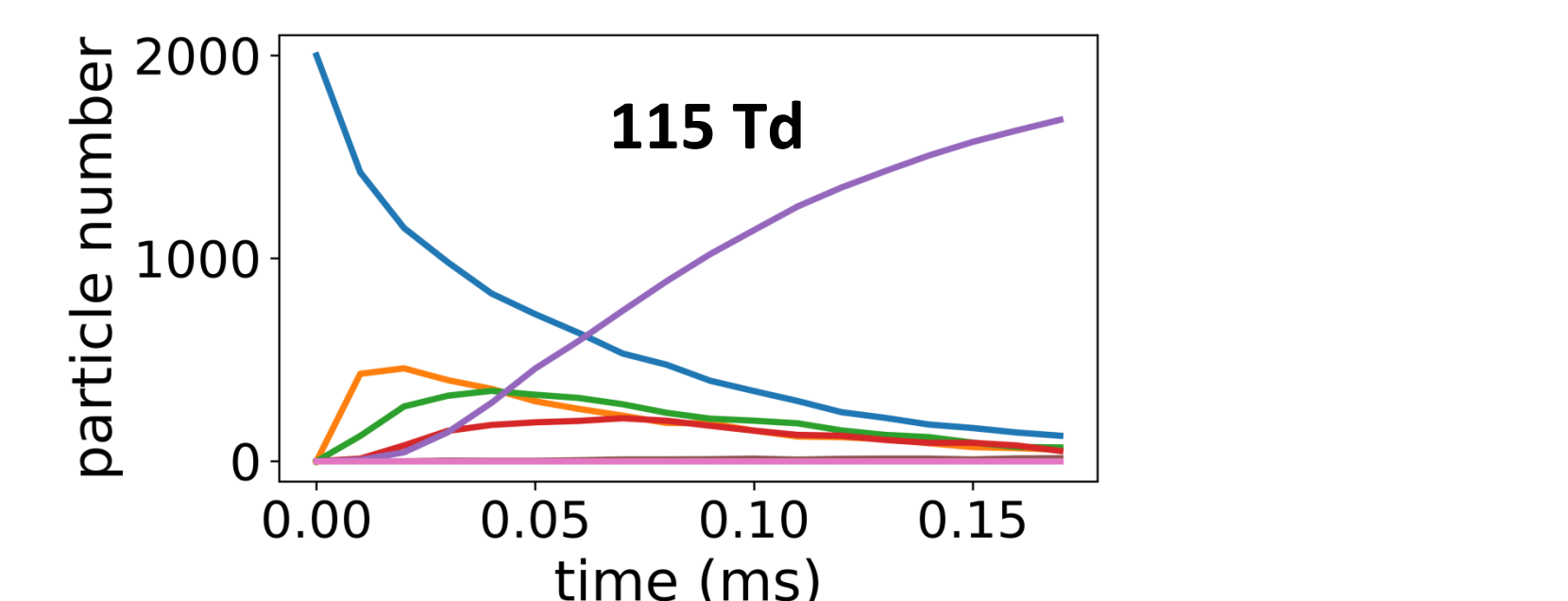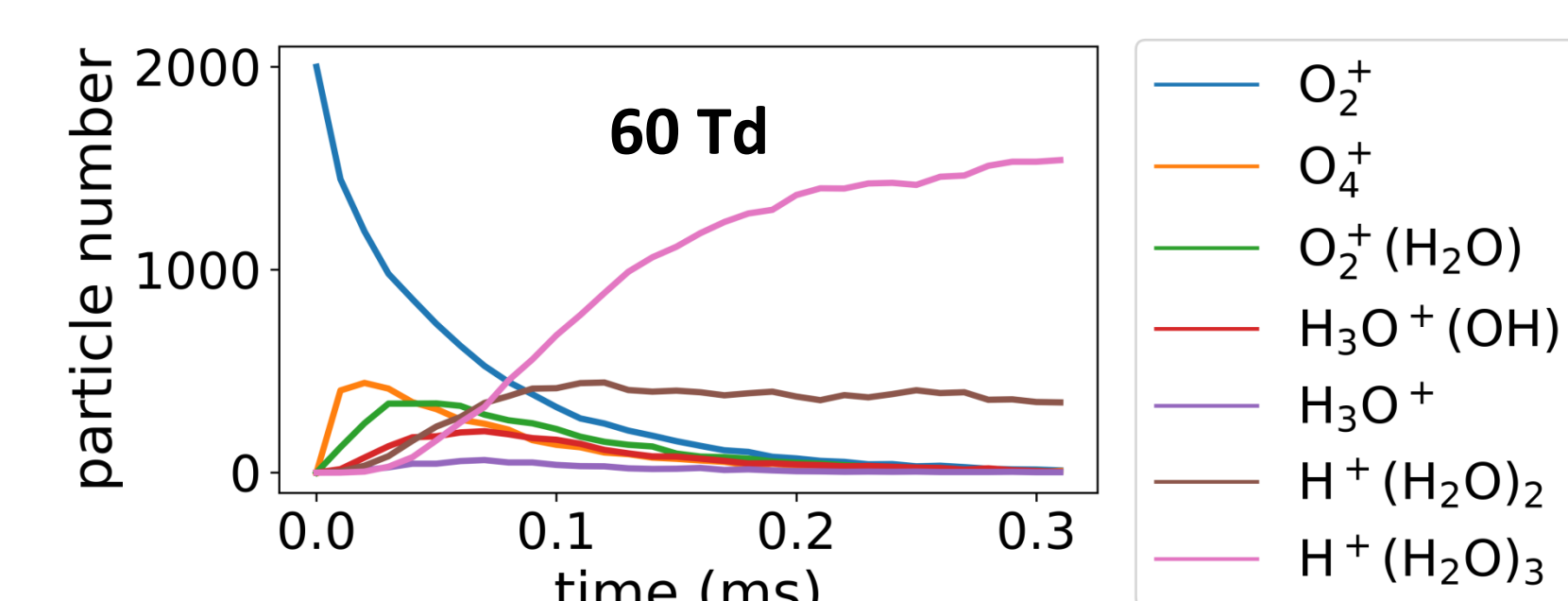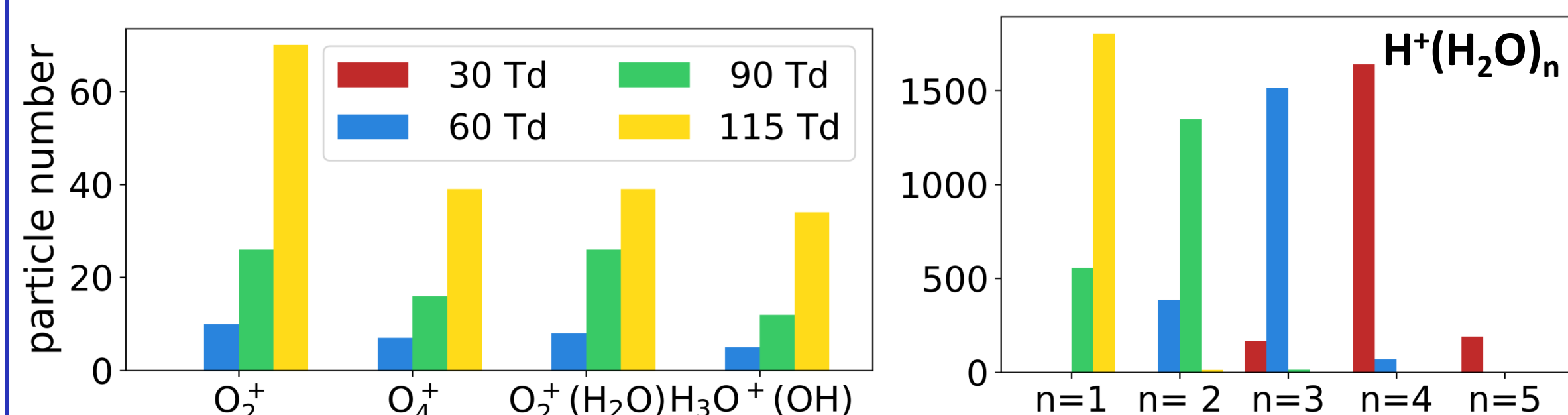
Left: Species distribution at the end of the reaction region at different reduced field strengths. The cluster size decreases with increasing field strength and oxygen species are more abundantly present.
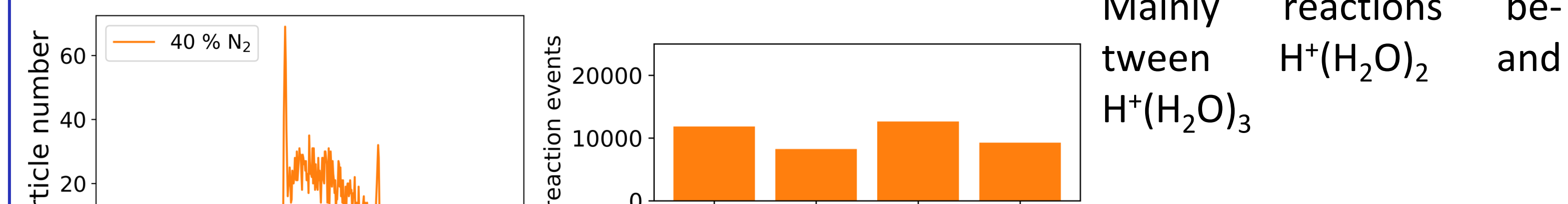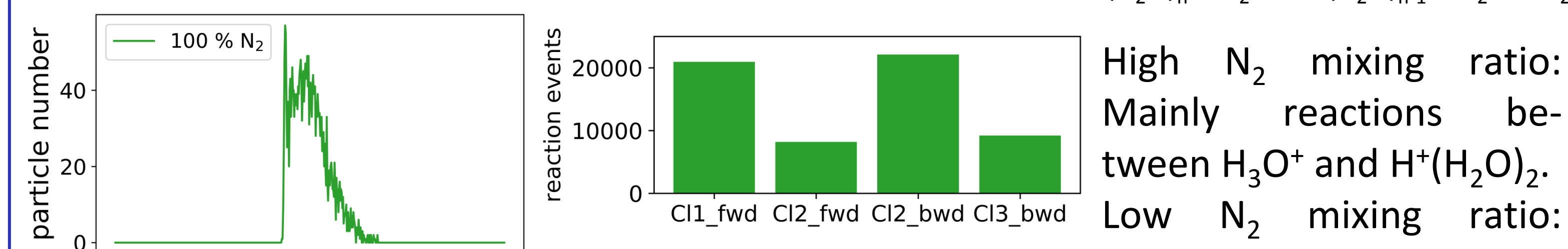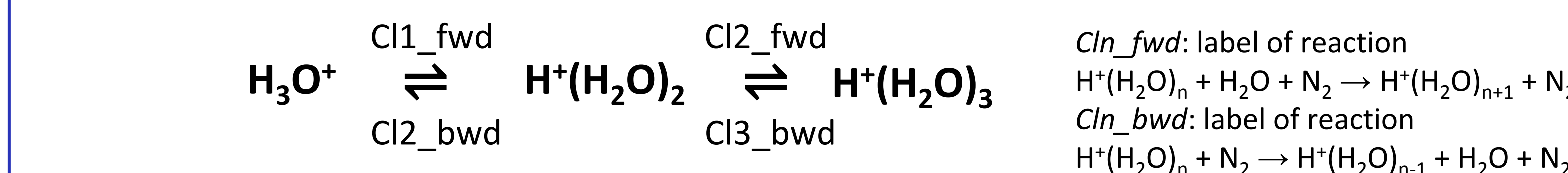
Water Cluster System

- When measuring chemical cluster systems in HiKE-IMS, e.g. proton-bound water clusters, the peaks are distorted at defined reduced field strengths
- *Right*: Experimental drift spectra of the proton-bound water cluster system in a HiKE-IMS at 20 °C background temperature and 20 mbar pressure
- Reduced electric field strength in the reaction region is 12 Td (equilibrium is assumed to be reached)
- Distorted peak at 89 Td is investigated with numerical simulations performed with IDSimF

Reaction system
$$H^+(H_2O)_n + H_2O + N_2 \rightleftharpoons H^+(H_2O)_{n+1} + N_2$$
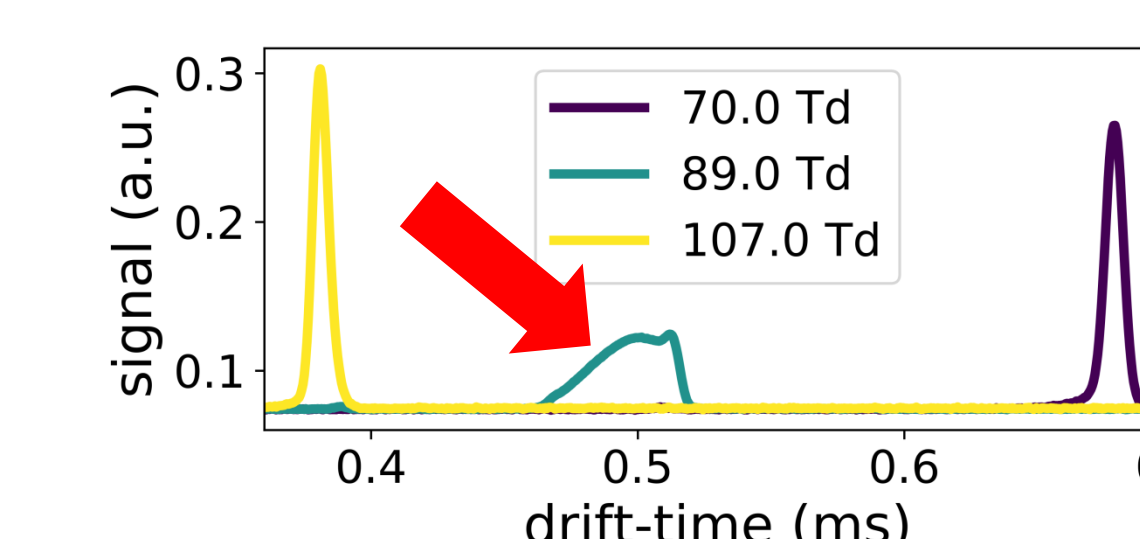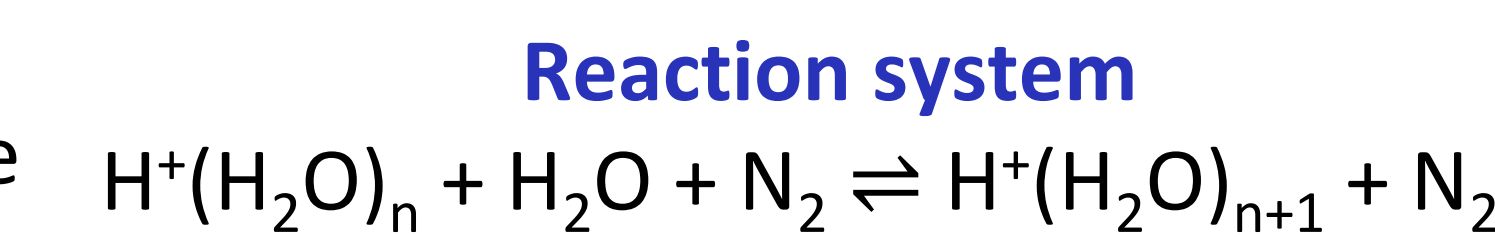
Partially "freezing" the reactions in the simulations

- Slowly decreasing the probability of chemical reactions by decreasing the simulated nitrogen mixing ratio from 100 % to 10 % (100 % is the normal case)
- Peak distortion as observed in the experimental results are reproduced in the simulations (lower left panels)
- Peaks begin separating with decreasing background gas mixing ratio
- Two individual peaks can be observed at 10 % and 40 % N_2 mixing ratio (partial separation); the peaks are distorted
- Number of reaction events is calculated in the simulations (lower right panels)

$$H_3O^+ \underset{Cl2\_bwd}{\overset{Cl1\_fwd}{\rightleftharpoons}} H^+(H_2O)_2 \underset{Cl3\_bwd}{\overset{Cl2\_fwd}{\rightleftharpoons}} H^+(H_2O)_3$$

Cln_fwd: label of reaction
$H^+(H_2O)_n + H_2O + N_2 \rightarrow H^+(H_2O)_{n+1} + N_2$
Cln_bwd: label of reaction
$H^+(H_2O)_n + N_2 \rightarrow H^+(H_2O)_{n-1} + H_2O + N_2$

High N_2 mixing ratio: Mainly reactions between H_3O^+ and $H^+(H_2O)_2$. Low N_2 mixing ratio: Mainly reactions between $H^+(H_2O)_2$ and $H^+(H_2O)_3$

At 89 Td, both H_3O^+ and $H^+(H_2O)_2$ are present, thus high turnover rates distort the peak. At e.g. 107 Td, only H_3O^+ is present, and the peaks are far less distorted

Conclusion/Outlook

Conclusion
- The drift time of O_2^+ in air is significantly altered due to resonant charge transfer as compared to nitrogen as background gas.
- At high reduced field strengths in the reaction region, the reactions of positive reactant ions impact the ion distribution.
- The reaction system is not in equilibrium at high reduced field strengths.
  - Therefore, positive reactant ions enter the drift region and react here with the analyte (distorting drift times).
- Population of reactant ions depends on the reduced field strength in the reaction region and on the background gas.
- Peak distortion of proton-bound water clusters occurring at defined reduced field strengths are due to high turnover rates between two cluster species.

Outlook
- Development of a model to estimate and track internal energies of the chemical species.
- Improving the numerical model to simulate a larger quantity of particles.

Literature

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