



# Chemical Kinetics and Ion Transport Simulations: Cluster Dynamics in Differential Ion Mobility Spectrometry



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## Introduction

Ions are separated in Differential Ion Mobility Spectrometry (DMS) by the field dependency of their mobility in an alternating electric field [1, 2]. The ion mobility in chemical reactive systems, e.g., proton-bound water clusters, is determined primarily by the formation and destruction of ion-bound clusters. Previous simulations showed a deviation of the temperature dependence between simulated and experimental dispersion plots [3]. Temperature measurements within a commercial DMS cell reveal that a temperature gradient along the DMS cell is present. Therefore, a non-isothermal and an advanced transport model were implemented in the existing simulation framework. Additionally, diffusive and particle-particle interactions are considered. Furthermore, the ion transmission at various conditions, e.g. isothermal and non-isothermal conditions and different gas flow velocity profiles, are presented.

## Methods

### Numerical simulations:

#### Ion transport simulations:

Verlet Ion Trajectory Integrator (C++), Gas Collision Model (Statistical Diffusion Simulation) and Space charge model (Barnes-Hut Tree)

#### Chemical Kinetic simulations:

Customized version of "RS" Monte Carlo kinetics code [4]

### DMS experiments:

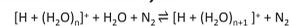
**DMS / MS system:** Sciex 6500 Triple Quad™ with Selexion® DMS

**Ion source:** Sciex Turbo V™ (APCI-mode)

**Data Processing:** Sciex Analyst® 1.6.2

## Simulation approach

### Proton bound water cluster system



The temperature dependence of the equilibrium constants and thus the temperature dependence of the rate constants are approximated using the van't Hoff equation [3].

### Differential Mobility

The differential ion mobility is the difference between the ion mobility at high field and low field conditions [1, 2]. An applied AC voltage (separation voltage, SV) with an asymmetric waveform causes ions to drift in a zig-zag shape towards the electrodes. The ion trajectories are dependent on the differential mobility. Usually, this results in a net drift towards one electrode. To redirect the ions

to the center axis of the detector, a DC voltage (compensation voltage, CV) is applied. The  $\alpha$ -function describes the dependency of the CV on the SV with the ion mobility at high field ( $K(H)$ ) and low field ( $K(L)$ ) conditions [1, 2]:

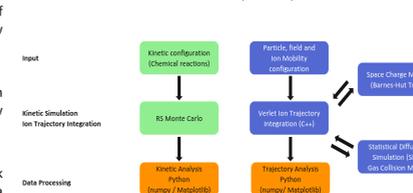
$$\alpha(E) = [K(H) - K(L)] / K(E)$$

At high field conditions, the ion temperature is high, which results in small clusters and therefore a high ion mobility and vice versa at low field conditions.

### Kinetic and Transport Simulations

Ion transport simulations were performed with the IDSim framework using a Verlet Integrator, which is implemented in C++ with a Statistical Diffusion Simulation (SDS) Gas Collision model. A Barnes-

Hut tree method is used to calculate particle-particle interactions.



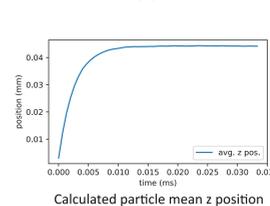
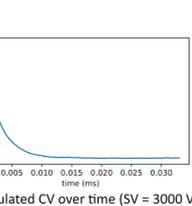
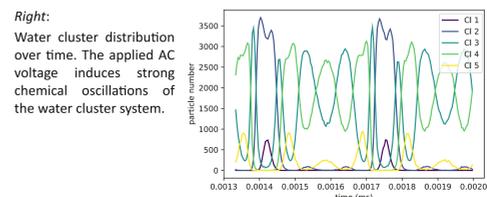
## Outlook

- Measurements of the proton-bound water cluster system at different water mixing ratios.
- Addition of different temperature gradient models, e.g., an exponential model.
- Addition of a Fast Multipole Method (FMM) to decrease computational time.
- Fully parallelization of the framework.

## Ion Transmission

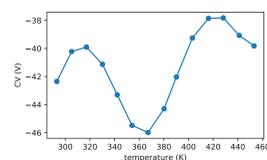
### Cluster distribution at alternating field strength

The alternating field strength has a strong impact on the equilibrium of the proton-bound water cluster system as shown in the figure on the right. Only cluster 1 and cluster 2 are present at high field conditions, resulting in an increased overall ion mobility as compared to low field conditions, where cluster 3 and cluster 4 are mainly present. The differential mobility of the water cluster system is thus affected by chemical oscillations. Due to the dependence of the ion temperature on the electric field strength, the cluster concentrations are modulated with the applied AC voltage, which is a superimposed sinusoidal oscillation.



### Automatic iteration for the optimal CV

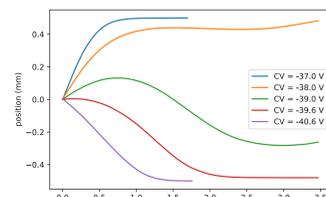
In order to calculate the optimal CV, the average drift perpendicular to the separation electrodes of the simulated particles is minimized by variation of the CV. The converging CV value as well as the average z position of the particles is shown on the right. In the figure below the optimal CV in dependence of the background temperature is shown. However, the slope is not monotone, resulting in a strong dependence of the optimal CV on the background temperature.



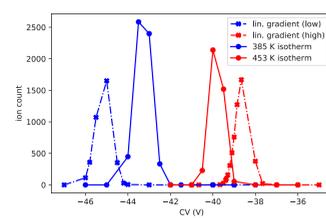
**Left:** Calculated optimal CV of the proton-bound water cluster system at 3000 V SV and different background temperatures.

### Temperature gradient in the DMS cell

Temperature measurements within the DMS cell showed that a temperature gradient is present as shown in the figure on the right (upper panel). Thus, a linear temperature gradient is added to the simulation. This has a strong impact on the ion trajectories within the DMS cell as shown in the figure below. The mean z position does not converge to a stable value due to the background temperature gradient. Thus, the iteratively calculated CV becomes unstable, too, as shown in the figure on the right (lower panel). In order to calculate the optimal CV, it is varied manually with respect to the ion transmission at the end of the DMS cell. The CV value of the maximal ion transmission is considered as an optimal CV.



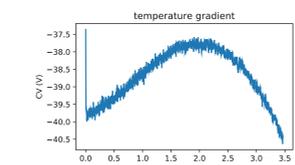
**Left:** Calculated particle mean z position over time at different CV values (SV = 3000 V). Note that the ion trajectories are S-shaped and do not converge due to the present temperature gradient within the DMS cell.



**Left:** Ion transmission vs. CV. The temperature in the isothermal simulations is also the initial temperature of the linear gradient. Note that when the isothermal temperature is the average temperature of the gradient, the optimal CV will be approximately the same (upper panel).



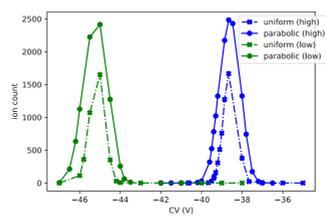
**Left:** Temperature measurements within the DMS cell at the temperature settings "low" and "high" reveal a temperature gradient.



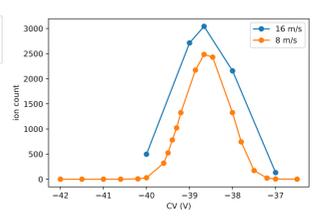
**Left:** CV value during the minimization process with a background temperature gradient present. Note that the CV does not converge, which means that the ion drift perpendicular to the DMS electrodes depends on the axial position. The CV value with the maximum overall ion transmission represents the experimentally observed value.

### Simulated Ion transmission spectra

The CV was varied to generate simulated ion transmission spectra. The comparison between isothermal and temperature gradient simulations as well as varied drift velocity profiles and gas flow velocities are shown below (3000 V SV).

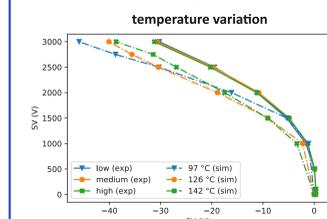


Ion transmission at uniform and parabolic velocity profiles (left panel). The maximum CV is the same, but with a parabolic profile the ion transmission is higher due to slightly shorter residence times. The same result is shown at different gas flow velocities (right panel).

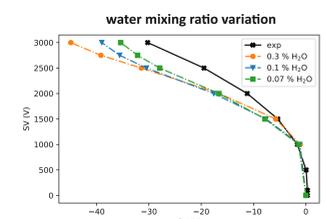


## Dispersion Plots

Previous simulations [3] of a DMS stage were in good qualitative agreement with experimental results but showed systematic differences regarding the temperature dependence of the SV/CV plots. In contrast to the experimental results, the simulations showed a temperature dependence. New simulations with the refined numerical model are presented below. However, even considering a temperature gradient the dispersion plots are temperature dependent. The isothermal and non-isothermal simulations do not differ significantly, when the isothermal simulation is performed with the mean background temperature of the linear gradient. The estimated water mixing ratio is 0.5 %.



Experimental and numerical SV/CV plots at different background gas temperatures. A water mixing ratio of 0.5 % is assumed in the simulation. The experimental results show no temperature dependence, in contrast to the numerical results.

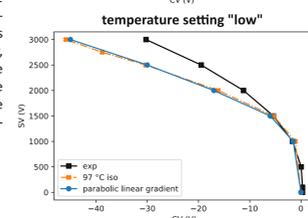
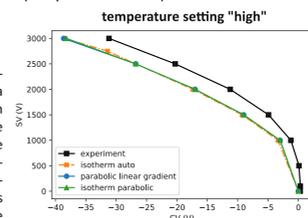


Numerical SV/CV plots at different water mixing ratios at 97 °C compared to the experimental measurement at the experimental temperature setting "low".

The simulation approaches the experimental result with decreasing water mixing ratio, but the shape of the dispersion plot differs (e.g. at 0.07 % H<sub>2</sub>O in the figure on the lower left). The experimental results cannot be fully described, even with the refined model. However, simulations of a HIKE-IMS at different background temperatures, which are based on essentially the same simulation framework, are in a very good agreement with experimental data (see poster ThP 299).

**Right:**

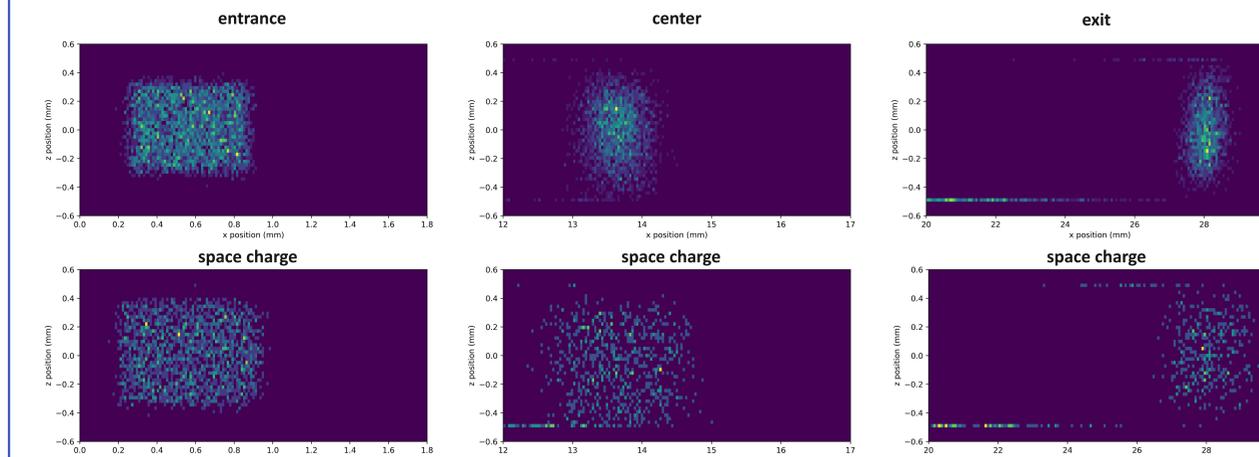
Numerical SV/CV plot at isothermal conditions and with a temperature gradient present in the simulations compared to the experimental results at the temperature setting "high" (upper panel) and "low" (lower panel). Surprisingly, the simulations are not sensitive to the temperature conditions (isothermal or linear gradient) or the gas velocity profile. Consequently, the temperature gradient in the DMS cell is most likely not the reason for the divergence between simulation and experiment.



## Diffusion and Space Charge Effects

Previous diffusion and space charge simulations show that the main ion loss is caused by the collisions of the particles with the electrodes. The modeled DMS cell is 30 mm long (x direction) and the gap between the two planar electrodes is 1 mm (z direction). The simulated particles are initialized as a cuboid with given edge lengths. Space charge leads to an additional spread of the ion cloud and therefore increased losses at the walls. In the figure below diffusion (upper panels) and space charge effects (lower panels) are shown at the entrance, center and exit of the DMS cell.

Due to the long computational time, the space charge factor (which is simply a weighting factor of the charge of an ion) was increased to decrease the number of simulated particles. Yet these results have to be considered with caution, because high space charge factors can alter the calculation result significantly. The simulations show that space charge effects cause the ions to spread wider, resulting in more collisions with the electrodes and thus lower ion transmissions. Further simulations showed that the ion loss increases with increasing residence time, giving the particles more time to diffuse.



## Literature

- [1] Krylov, E. V.; Nazarov, E. G.; Miller, R. A.: *Differential mobility spectrometry: Model of operation*. Int. J. Mass Spectrom. 266, 76–85 (2007).
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## Acknowledgement

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