

# Field driven chemical effects in API: Numerical modeling of the ion temperature at atmospheric and intermediate pressure with SIMION-RS

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## Introduction

It is well established that the additional kinetic energy ions gain from an electric field can be modeled in terms of an elevated "ion temperature" [1,2]. At the relatively high reduced field strengths ions are subject to in modern mass spectrometric devices, particularly with medium pressure transfer stages e.g. ion funnels, the effective ion temperature can readily become drastically higher than thermal.

Numerical models which consider the chemical dynamics of ions under such conditions have thus to take into account the electrically driven temperature effects.

The reaction simulation (RS) algorithm [3, 4] in combination with SIMION is an ideal basis for such a model, which provides the foundation for the simulation of analytical methods inherently utilizing the elevated effective ion temperature (e.g. PTR, CID, FAIMS/DMS).

## Ion Temperature Model

The additional collision energy gained by ions from the electric field can be modeled in terms of a **two temperature model** with an increased effective ion reaction temperature  $T_{\text{eff}}$  [1]:

$$T_{\text{eff}} = T + \frac{M_R v^2 \frac{m+M_B}{m+M_R}}{3k_B}$$

$k_B$  = Boltzmann constant  
 $v$  = ion velocity  
 $M_R$  = mass reaction partner  
 $m$  = ion mass

If the particle masses are assumed as equal this simplifies to [5,2]:

$$T_{\text{eff}} = T + \frac{Mv^2}{3k_B}$$

which can also be expressed in terms of the ion mobility  $K$  and the electric field  $E$ :

$$T_{\text{eff}} = T + \frac{M(KE)^2}{3k_B}$$

## Chemical Reaction Systems

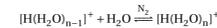
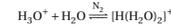
At atmospheric pressure ionization (API) conditions, a relatively high level of background water in the ppmV range is almost unavoidable. Therefore, the formation of **ion bound clusters** is commonly in API and AP methods such as ion mobility spectrometry (IMS) or differential ion mobility spectrometry (DMS / FAIMS). The cluster systems often exist in **very fast temperature dependent chemical equilibria** and thus allow the investigation of the validity of numerical ion temperature models.

### $H_3O^+$ from chemical ionization

As commonly known, chemical ionization (e.g. induced by corona discharge or  $\beta$  radiation) produces  $H_3O^+$  via  $N_2^+$  charge transfer to  $H_2O$  and subsequent self protonation.

### Proton bound water clusters (RIP)

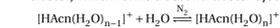
$H_3O^+$  clusters with neutral water:



The relaxation time of the resulting cluster equilibrium is very short. The corresponding signal is often called "Reactant Ion Peak" (RIP).

### Acetone-water clusters

Neutral acetone (Acn) can associate to the water cluster, which forms a second cluster system:



### Modeling of temperature dependence of reaction rates:

The cluster building (forward) reaction is considered as collision controlled [6], thus its rate  $k_f$  can be calculated from the collision frequency:

$$k_f = \sigma \sqrt{\frac{16RT}{\pi \mu}} \quad \sigma = \text{collision cross section} \quad \mu = \text{reduced mass}$$

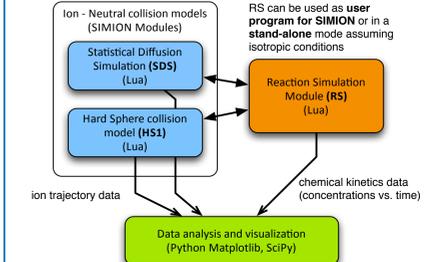
The backward reaction rate is calculated from the equilibrium constant  $K$ , which is given by the Gibbs enthalpy  $G^0$  of the clustering reaction:

$$G^0 = -RT \ln(K)$$

The temperature dependence of the equilibrium constant is estimated e.g. by the van't Hoff equation:

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{-\Delta H^0}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

## Methods



- Trajectory simulations with SIMION 8.2 + SDS / HS1
- RS module with integrated ion temperature model
- New implemented connection between RS and HS1

## Conclusions

### Results:

#### Verification of the reaction system at AP:

- Qualitative agreement between experimental and simulated IMS drift times for the RIP and acetone-water cluster systems
- Basic verification of the temperature dependent set of reaction rates

#### Verification of the reaction system at medium pressure:

- Good agreement of simulation and experiment for collision cell declustering at high reduced field
- Absence of clusters with  $n=5,6$  in experiment probably due to experimental conditions (injection of relatively hot ions into the collision cell)

#### New connection between hard sphere model and RS:

- The well established HS1 hard sphere collision model was coupled with RS
- Applicability of resulting model at medium pressure is demonstrated by declustering in ion funnel

#### Qualitative simulation of chemical kinetics in FAIMS:

- The basic chemical kinetics in a FAIMS / DMS device was qualitatively modeled for the RIP and the acetone-water clusters

### Outlook:

#### Investigation of model / experiment divergences:

- The temporal merging of the RIP and acetone signal in IMS is not well reproduced by the simulations, possibly this is due to chemical interactions of the two cluster systems at elevated temperature
- The current simulations tend to overestimate the compensation voltage for FAIMS (see [8] for experimental data)

#### More detailed estimation of temperature dependent reaction rates:

- A more sophisticated estimation of the temperature dependence of the reaction rates, in particular for high effective temperatures, will significantly improve the overall model accuracy

#### Alternative reaction models for very high reduced fields:

- More detailed reaction models for low pressure / high field conditions, e.g., incorporating three temperature models or explicit pooling of internal molecular energy

## SDS-RS: Temperature dependent drift in IMS

### higher temperatures = smaller clusters

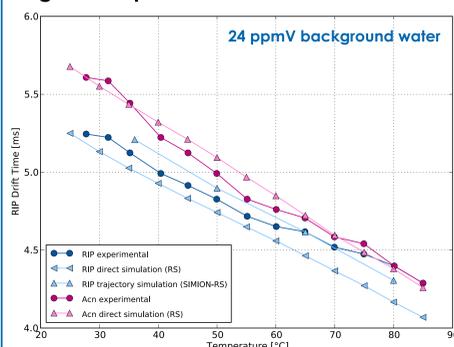


Figure 1) Experimental and simulated drift times for the water cluster RIP and the acetone-water clusters

The temperature dependent drift times in a low field ion mobility spectrometer (IMS) at atmospheric pressure were modeled to validate temperature dependent sets of reaction rates.

The experimental drift times decline due to the decreasing mean cluster size at elevated gas temperature (fig.2).

Due to nearly isotropic conditions in the drift tube, the simplified direct model (direct RS simulation) was applicable.

Trajectory simulation (SIMION-RS) and direct RS simulation reproduce the drift time decline, but the models exhibit significant discrepancies for the temporal behavior of the RIP with respect to both, arrival time and the non-linear response of the experimental RIP with the temperature.

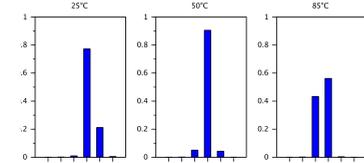


Figure 2) Decreasing water cluster sizes at 24 ppmV background water mixing ratio

The decomposition of proton bound water clusters in a collision cell at reduced pressure was modeled with RS in stand-alone mode under the assumption of isotropic conditions

#### Simulation parameter:

- background pressure approximately 1 mbar
- 1% water in the background gas
- isotropic conditions (assumption of an ideally stirred reactor)
- 1000 simulated particles
- analysis of the static equilibrated cluster distribution in dependence of the reduced field strength
- variation of the background pressure in the calculation of the local ion mobility ( $K$ ) for the calculation of  $T_{\text{eff}}$

## RS: Collision Cell Declustering

### Reduced field dependence and comparison with experiment:

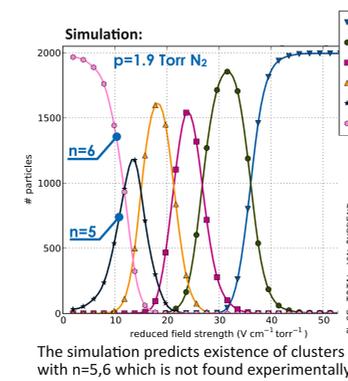
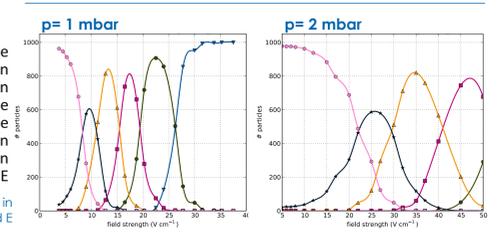


Figure 3) Simulated and experimental cluster concentrations in dependence on reduced field strength

### Absolute field dependence:

In terms of the absolute electric field, the effective ion temperature is strongly dependent on the background pressure in the collision cell. At medium pressure conditions, very high ion temperatures are readily achievable.

Figure 4) Ion temperature in dependence of electrical field E



The pressure dependence of the ion temperature results in a severe pressure sensitivity of the cluster decomposition reactions as function of the electrical field E

Figure 5) Cluster in dependence on field E

## HS1-RS: Declustering in ion funnel

The RS model was coupled to the HS1 hard sphere collision model to provide a trajectory model for reacting ions which is applicable for medium and low pressure conditions in addition to SIMION-SDS-RS.

As a proof of concept, the decomposition of proton bound water clusters in a medium pressure ion funnel was modeled with HS1-RS.

#### Simulation parameter:

- Calculation of the effective ion temperature directly from ion velocity
- SIMION example ion funnel model
- 40 V DC offset along the funnel
- 500 kHz RF frequency
- 10 ppmV water
- due to relatively long simulation times, reduced number of ions (50-200 ions per run)

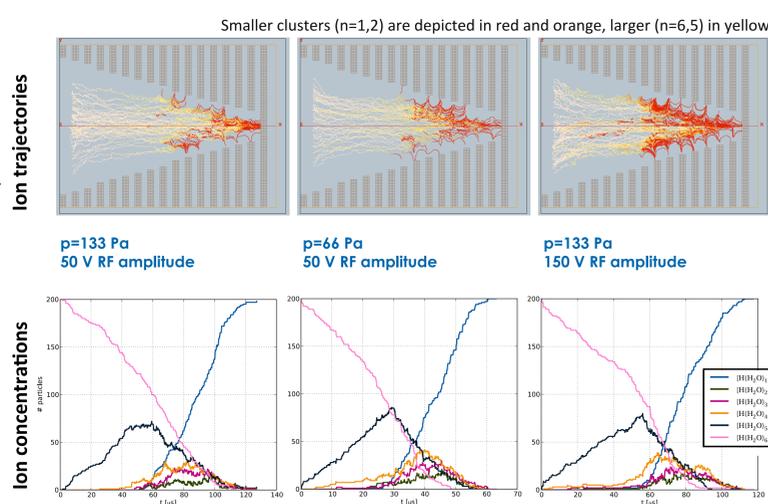


Figure 4) Cluster trajectories and concentrations in the ion funnel in dependence on the background pressure and the RF amplitude

The simulation clearly shows the decomposition of the water clusters in proximity to the funnel electrodes where the electric field becomes high.

At the modelled water concentration, the RF potential is able to produce bare  $H_3O^+$ .

## High fields at AP: Chemical effects in FAIMS / DMS (RS)

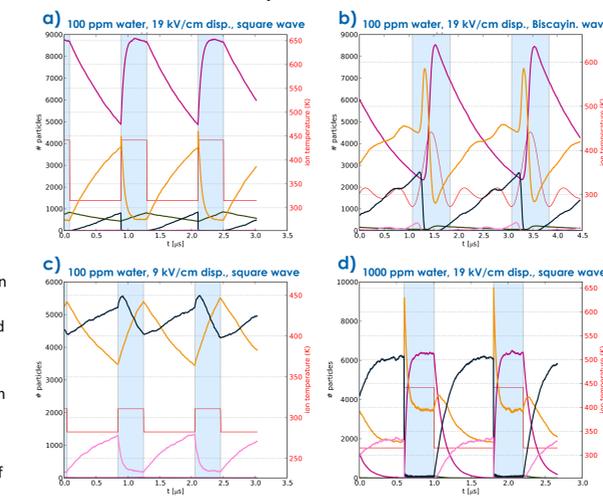
One possible mechanism which leads to a field dependence of the ion mobility  $K$  at high field strengths is the effect of the elevated ion temperature on chemical equilibria.

The RS model was used to simulate the chemical kinetics of the proton bound water cluster system (RIP) in Field Asymmetric Ion Mobility Spectrometry (FAIMS) or Differential Ion Mobility Spectrometry (DMS).

In those methods, ions oscillate rapidly between low and high field conditions in an asymmetric RF high voltage dispersion potential. The difference between high and low field mobility is compensated by a DC potential (compensation voltage - CV). By adjusting the CV a differential mobility scan can be performed.

In the presented RS simulations only chemical high field effects (modification of the water cluster equilibrium by the ion temperature) were considered while physical high field effects were not taken into account.

### Oscillation of the reaction system:



At atmospheric pressure, the chemical system is able to follow the field / ion temperature oscillation. The field strength (cf. a and c), water background (cf. a and d) and RF wave form (cf. a and b) strongly impact on the cluster response.

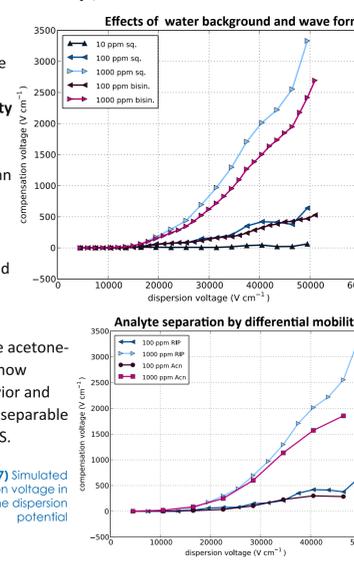
### Resulting differential mobility / CV:

From the mean cluster sizes in high (marked blue in fig. 8) and low field phases, the mean mobility in the phases and therefore a theoretical compensation voltage can be calculated.

The increase of the differential mobility with the dispersion voltage and water mixing ratio is clearly observable.

The RIP and the acetone-water cluster show different behavior and should thus be separable by FAIMS / DMS.

right: Figure 7) Simulated compensation voltage in dependence on the dispersion potential



Analyte separation by differential mobility. The plot shows compensation voltage (V cm^-1) vs. dispersion voltage (V cm^-1) for different conditions: 100 ppm RIP, 100 ppm AP, 100 ppm Acn, 1000 ppm RIP, 1000 ppm Acn. The plot shows that compensation voltage increases with dispersion voltage and is higher for higher water concentrations.

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