



Physical & Theoretical  
Chemistry  
University of Wuppertal

# Numerical and Experimental Investigations of Proton-Bound Acetone/Water Clusters in Differential Ion Mobility Spectrometry

Duygu Erdogdu; Walter Wissdorf; Hendrik Kersten; Thorsten Benter

## Introduction

In Differential Ion Mobility Spectrometry (DMS), ions in an asymmetric electric field are separated by their differential ion mobility [1,2]. At increased electric field strengths (Separation Voltage, SV), the ion mobility is not constant. Different ion mobilities in the low and high field phase lead to a net ion drift towards one of the DMS electrodes. A DC voltage – the Compensation Voltage (CV) – is applied to guide the ions back to the main axis of the separation cell. With increasing electric field strength, the net ion drift becomes more pronounced. Polarization effects as well as the formation of ion molecule clusters lead to an increased ion mobility in the high field phase  $K(E)$  compared to the ion mobility in the low field phase  $K(0)$  [2]. However, with increasing electric field, the ions kinetic energy exceeds the thermal energy. At sufficiently high electric field strengths, this changes the collision statistics. Therefore,  $K(E)$  is lower than  $K(0)$ . This effect is known as the Hard Sphere effect [1,2]. The acetone/water cluster system is investigated experimentally and numerically. The proton-bound acetone monomer has negative CV values due to cluster formation [3] and polarization effects, whereas the proton-bound acetone dimer does not form any clusters with water and shows hard sphere behavior with increasing SV amplitude and background gas temperature, resulting in positive CV values.

## Methods

**Chemicals:** Acetone (HPLC grade, Sigma Aldrich, Germany)  
**Experiments:** SCIEX 6500 Triple Quad™™ SelexION® DMS - SCIEX Turbo V™™ APC  
**Simulation:** Ion Dynamics Simulation Framework (IDSImF) [5]

## Numerical Model

### Chemical Kinetics

Reaction Simulation in IDSImF [5]

Temperature dependence of the reaction rate coefficient [3,4]:

The forward rate coefficient is assumed to be collision controlled. Assuming  $\Delta H^\ddagger(T_{eff})$  is constant in the given temperature interval, the equilibrium constant at a higher temperature  $T_2$  can be calculated by the van't Hoff equation [8] with a given equilibrium constant at standard temperature [3, 4]:

$$K_{eq2} = \exp\left(-\frac{\Delta H^\ddagger(T_{eff})}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right) \cdot K_{eq1}$$

$\Delta H^\ddagger$ : Reaction enthalpy  
 $R$ : Ideal gas constant

$$k_{bwd} = \frac{k_{fwd}}{K_{eq2}}$$

Effective ion temperature:

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

$T$ : Background gas temperature  
 $M$ : Mass of background gas molecule  
 $K$ : Ion mobility

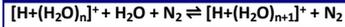
### CV calculation

Optimizing process, minimizing the ion drift velocity in the separation axis

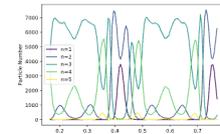
### Data Analysis

IDSImPy, Custom python programs

## Numerical Model

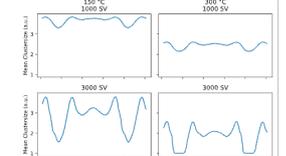


### Concentration-Time Profile



Above: Simulated concentration-time profile of the water cluster system  $[H+(H_2O)_n]^+$  at 3000 SV amplitude, 150 °C background gas temperature and 0.3 %V water mixing ratio. Due to the asymmetric electric field, the effective ion temperature is oscillating, which results in oscillating concentrations profiles. Cluster dissociation occurs during the high field phase, due to the increased effective ion temperature [3, 4]. Smaller cluster sizes are favored under these conditions ( $n=2, n=3$ ). At the low field phase, larger clusters are formed again ( $n=3, n=4$ ). The water cluster system is strongly influenced by, e.g., background gas temperature and water mixing ratio (as well as SV).

### Mean Cluster Size



Above: Simulated mean cluster size of the water cluster system at 3000 SV at 150 °C (left panels) and 300 °C (right panels). The water cluster system is heavily influenced by, e.g., the background gas temperature and the SV amplitude (as well as the water mixing ratio). The mean cluster size decreases with increasing background gas temperature and SV. Note that the mean cluster size at 3000 SV and 300 °C (lower right panel) is  $H_3O^+$  during the high field phase.

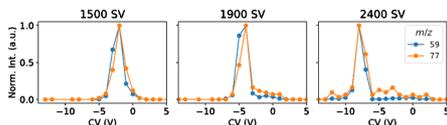
## Proton-Bound Acetone Monomer



Acn: CH<sub>3</sub>COCH<sub>3</sub>

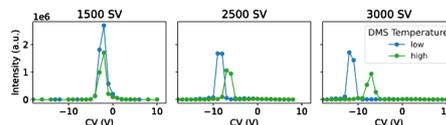
### Formation of Ion Molecule Clusters

Below: Experimental normalized ionograms of the proton-bound acetone monomer ( $m/z$  59) and the first proton-bound acetone/water cluster ( $m/z$  77). The formation of ion molecule clusters as well as polarization effects lead to a more negative CV values with increasing SV amplitude for both, the monomer signal, and the signal of the cluster.



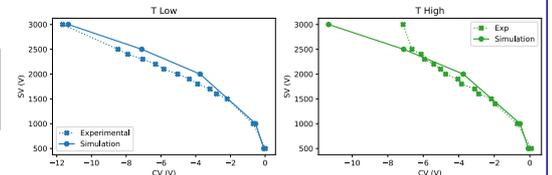
### Temperature Variation

Below: Experimental ionograms of the proton-bound acetone monomer at low (150 °C) and high (300 °C) DMS background temperature. The influence of the background temperature increases with increasing SV amplitude. The hard-sphere character of the collision increases, therefore, the CV is not as negative as at low background gas temperature.



### Dispersion Plots

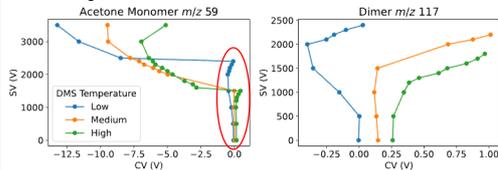
Below: Experimental and numerical dispersion plots of the acetone monomer/water cluster system. The simulation is performed with a constant ion mobility and a water mixing ratio of 1000 ppmV. However, the water mixing ratio in the experiment should be lower due to the use of boil-off nitrogen. Additional simulations with less water mixing, but with a field dependent ion mobility, are also in a good agreement with the experimental results. The field dependent ion mobility of the proton-bound acetone monomer is calculated by the model of Haack et al. [6]. For now, all ion species have the same field dependence of the ion mobility. In the near future, all species will have an individual field dependence of the ion mobility.



## Proton-Bound Acetone Dimer



A 1:1-mixture of acetone/water is experimentally investigated. With an increased acetone mixing ratio, the formation of the proton-bound acetone dimer is favored. The dissociation between the DMS cell and the mass spectrometer leads to the observed double peak structure of the monomer signal.

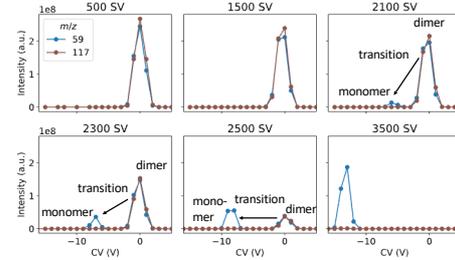


### Dispersion Plot

Above: Dispersion plot of  $m/z$  59 (monomer) and  $m/z$  117 (dimer). Until about 1500 – 2500 V SV (marked in red), the CV of the monomer is nearly 0 V. At higher SV amplitudes, the CV abruptly changes. This is in contrast to the dispersion plot shown before. This observation is due to acetone dimer formation, which partly dissociates in the MS transfer stage after the DMS cell, resulting in an  $m/z$  59 signal. This is supported by the ionograms on the right.

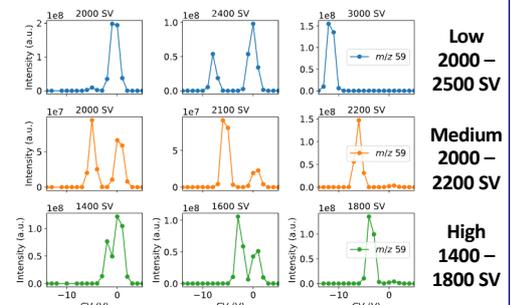
### Dimer/Monomer transition

Right: Ionograms at different SV amplitudes of monomer (blue) and dimer (orange) at low DMS temperature. The ionograms are nearly identical, until the dimer signal vanishes. Between 2100 and 2500 V SV, a chemical transition occurs, resulting in a double peak structure of the monomer signal. The  $m/z$  59 signal at 0 V CV originates from the dimer, which dissociates in the MS transfer stage. Meanwhile, the other maximum is the true monomer signal, which has a significantly lower CV.



### Temperature Dependence of the Dimer Transition

Right: Ionograms of  $m/z$  59 CV at different DMS temperatures during the chemical transition. With increasing DMS temperature, the transition occurs at earlier SV amplitudes due to the increase in mean collision energy. The dimer dissociates at comparatively lower SV amplitudes with increasing DMS temperature.



## Conclusion/Outlook

- Ion molecule chemistry heavily impacts the observed ionograms and dispersion plots
- The proton-bound acetone monomer has negative CV values due to formation of ion molecule clusters and polarization effects
- The proton-bound dimer shows hard-sphere behaviour. However, due to dissociation after the DMS transfer stage, it effects the signal of the proton-bound acetone monomer
- A new collision model is currently developed in IDSImF to calculate field dependent ion mobilities (see Poster 852)
- Additionally, a new variable-soft-sphere transport model is developed in IDSImF (see Poster 855)
- It is planned to model the acetone/water cluster system with the new models

## Conclusion/Outlook

- [1] Krylov, E. V.; Nazarov, E. G.; Miller, R. A.: *Differential mobility Spectrometry: Model of operation*. Int. J. Mass Spectrom. 266, 76–85, 2007.
- [2] Shvartsburg, A. A.: *Differential Ion Mobility Spectrometry: Nonlinear Ion Transport and Fundamentals of FAIMS*. CRC Press, Boca Raton, 2008.
- [3] Allers, M.; Kirk, A. T.; Eckermann, M.; Schäfer, C.; Erdogdu, D.; Wildorf, W.; Benter, T.; Zimmermann, S.: *Positive Reactant Ion Formation in High Kinetic Energy Ion Mobility Spectrometry (HIKE-IMS)*. J. Am. Soc. Mass Spectrom. 31, 6, 1291–1301, 2020.

- Erdogdu, D.; Wissdorf, W.; Allers, M.; Kirk, A. T.; Kersten, H.; Zimmermann, S.; Benter, T.: *Simulation of Cluster Dynamics of Proton-Bound Water Clusters in a High Kinetic Energy Ion-Mobility Spectrometer*. J. Am. Soc. Mass Spectrom. 32, 2436–2450, 2021.
- Institute for Pure and Applied Mass Spectrometry of the University of Wuppertal: *Ion Dynamics Simulation Framework – IDSImF 2020*. <https://github.com/IPAM/IDSImF>
- Haack, A.; Bissonnette, J. R.; Ierliano, C.; Hopkins, W. S.: *Improved First-Principles Model of Differential Mobility Using Higher Order Two-Temperature Theory*. J. Am. Soc. Mass Spectrom. 33, 535–547, 2022.

## Acknowledgement

Financial support by **Graduiertenförderung (Bergische Universität Wuppertal, Germany)** and by **AB Sciex (Concord, Canada)** is gratefully acknowledged. **Alexander Haack (University of Waterloo, Canada)** is gratefully acknowledged for providing the field dependent ion mobility data of the proton-bound acetone monomer.