



# Chemical Modification and Cluster Dynamics in High Kinetic Energy IMS (HiKE-IMS)



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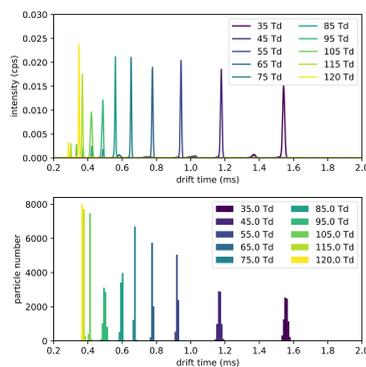
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## Introduction

Ion separation building on the electrical mobility  $K$  is a classical method in analytical chemistry. The traditional ion mobility spectrometry (IMS) uses the absolute mobility  $K$ , while more modern methods, e.g. differential ion mobility spectrometry (DMS) use the electric field dependence of the ion mobility, which is described by the  $\alpha$ -function.<sup>[1]</sup> Dynamic clustering/de-clustering processes and the change of the collision cross section are primary reasons for this effect.<sup>[2]</sup> Recently, the High-Kinetic-Energy-IMS (HiKE-IMS) was introduced<sup>[3]</sup> – a technique, which is operating at reduced electric field strengths comparable to DMS and other high-field separation methods.



The HiKE-IMS allows experiments at reduced electric field strengths ( $E/N$ ) also prevailing in DMS or in the ion optics of API-MS. Previously, we successfully modeled the drift time of proton bond water clusters in an HiKE-IMS inducing chemical transitions between clusters (see figure 1).<sup>[4]</sup> In this work the effect of *chemical modification* of the drift gas in an HiKE-IMS is studied. Chemical modification is the deliberate introduction of effective clustering agents to the drift gas, which significantly change the mobility of many analytes. This technique is frequently used in DMS<sup>[1]</sup> and IMS<sup>[5]</sup> to improve separation efficiency.

Figure 1: Comparison of experimentally generated water-RIP (top) and simulations (down) of the same system ( $T = 322.15$  K;  $DP = -35.6$  °C) in dependence of the reduced field strength

For Detailed simulation results see poster ThP 299: D. Erdogdu et al.; *Simulation of Cluster Dynamics in High Kinetic Energy IMS (HiKE-IMS)*

## Experimental<sup>[3]</sup>

### HiKE-IMS (Leibniz University Hannover):

- Method is based on a classic drift tube IMS
- Ion separation in the drift tube ( $L = 30.65$  cm), which is coupled to the reaction tube (separated by a shutter grid assembly)
- Analytes (Acetonitrile (ACN) and 1,3-Diaminopropane) are added in pure nitrogen to the reaction tube and are ionized with a corona discharge
- Nitrogen is used as modifiable matrix drift gas in the drift tube (pumped through the reaction tube)
- Operated at low pressure (20-30 mbar) and a temperature of max. 45 °C (min.: RT)

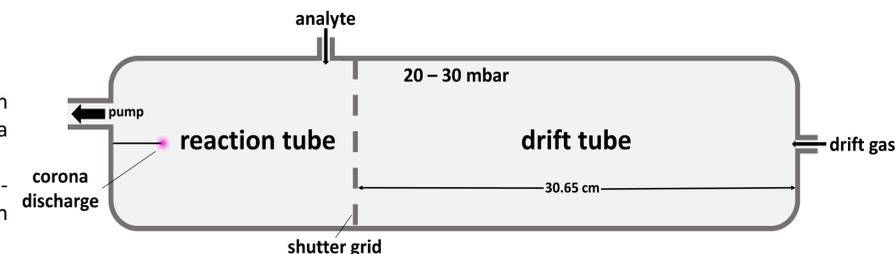


Figure 2: Schematic setup of the HiKE-IMS

- High reduced field strength ( $> 120$  Td) comparable to DMS or ion optics are possible
  - High resolution (even cluster transitions are observed)
- Ideal conditions to study cluster dynamics

## Drift gas modification with ACN

### ACN

With Acetonitrile (ACN) as analyte and modifier two main signals are observed as shown in figure 3. Note the tilted plateau between the signals, which indicates a chemical connection between both species (cluster "switch"), also seen in figure 4. The noticeable step between 60 and 70 Td indicates a change in the clustering state.

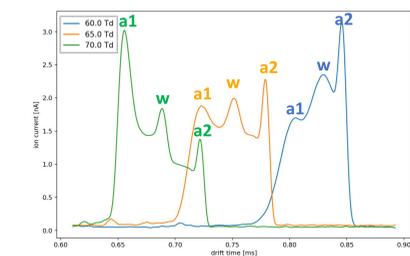


Figure 3: Observed cluster-transition processes of ACN (0.9 ppmV in the reaction tube and 1.6 ppmV in the drift gas) at three representative  $E/N$ . (Signals of the water-RIP marked with w and analyte-specific signals with ax)

Every analyte leads to typical signal patterns in the HiKE-IMS-spectra (see figure 3). The number of new signals depends on the analyte, the matrix/modifier and the  $E/N$  value. The drift times are converted to the reduced ion mobility  $K_0$  which represents a species selective physical parameter.

**Ion mobility  $K$ :**  $v_d = K \cdot E$

$v_d$ : drift velocity  
 $E$ : electric field strength

**Reduced ion mobility  $K_0$ :**

$$K_0 = K \cdot \frac{p \cdot T_0}{p_0 \cdot T}$$

$T_0$ : 273.15 K  
 $p_0$ : 101325 Pa

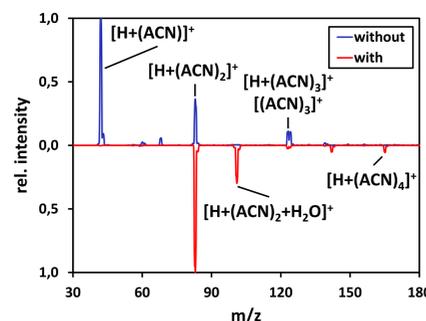


Figure 5: Mass spectra (APCI) of ACN without (top) and with (bottom) 1.5 % ACN as modifier in the curtain gas. Measured with a 6500™ TripleQuad (Sciex)

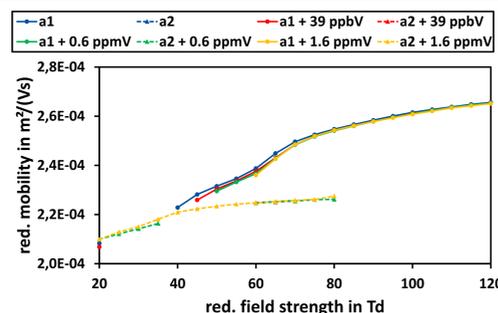


Figure 4: Red. mobility of the two main signals of ACN in dependence of the red. field strength with different modifier mixing ratios (ACN) in the drift gas

The exemplary mass spectra shown in figure 5 demonstrate the clustering behavior of ACN with itself and with water. This suggests that the plateaus in the IM-spectra shown in figure 3 as well as the steps in the graphs showing red. mobility data are caused by similar chemistry as the previously observed cluster chemistry of water.

Note the existence of mixed water-ACN-clusters.

### 1,3-Diaminopropane

Similar to ACN as analyte, 1,3-Diaminopropane generates (1,3-DAP) specific signal patterns (three main signals, see figure 6). All detected species have a different rising red. mobility with rising  $E/N$ , which suggests that pronounced clustering mechanisms are effective.

Note the missing change with modification of the drift gas. The ACN self-clustering chemistry is thus much more pronounced than any direct DAP-ACN interaction.

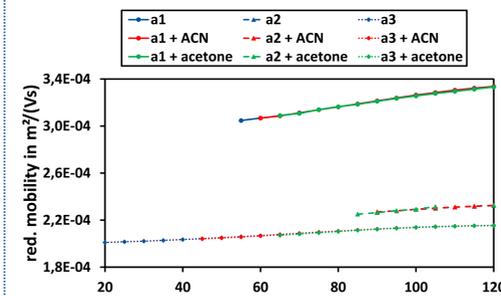


Figure 6: Red. mobility of the three main signals of 1,3-Diaminopropane in dependence of the red. field strength with different modifiers present in the drift gas: ACN: 1.6 ppmV; acetone: 2.2 ppmV.

## ACN: Temperature and water dependency

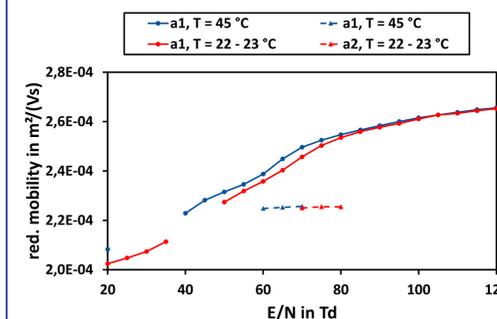


Figure 7: Red. mobility of the two main signals of ACN in dependence of the red. field strength with temperature

Increasing the water concentration in the drift gas results in a similar behavior as decreasing the temperature: The mean cluster size increases with rising dew point and as result the red. mobility is decreasing. Only species (e.g. a2), which do not cluster with water (i.e., exhibiting a slope close to zero) remain unchanged. Note that all clustering effects decrease at high red. field strengths.

Comparable observations were also made with acetone and methanol as analyte and modifier.

Even without additionally attached modifier most of the analyte specific signals exhibit rising red. mobility with rising  $E/N$ . Thus, another clustering species must be present. This is most probably residual water in the drift gas. Note the negative temperature dependency of the ACN-species (see figure 7), which supports this presumption. The residual water concentration seems to be much higher than any modifier concentration; thus the shifts of figure 6 are explainable by water-analyte clustering.

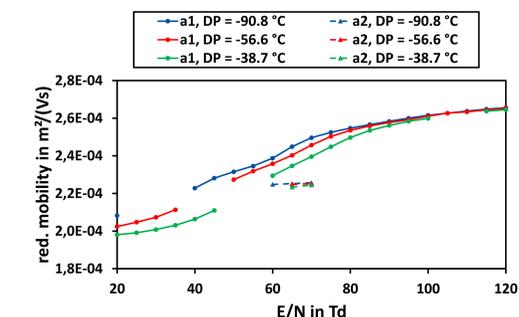


Figure 8: Red. mobility of the two main signals of ACN in dependence of  $E/N$  at different dew points (water concentrations) in the drift gas

## Conclusion

- Similarly to the water cluster system, the chemical dynamics of other small polar molecules are of great importance in IMS.
- Both, the modifier concentration present in the drift gas and the extent of analyte-modifier cluster chemistry is important for an enhanced separation efficiency.
- Since water is a strong clustering agent, a modifier has to be present in at least comparable concentrations to yield a noticeable modification effect.
- A qualitative classification of the modifier potential is possible.
- Cluster dynamics and stabilities in comparable setups (DMS or ion optical stages) can be investigated with present experimental and simulation approaches.
- Even one single analyte can exhibit complex chemical cluster dynamics. Such a system becomes rapidly extremely complex when additional active analyte species are present.
- A deeper analysis and assignment of all signals seems to be impossible without a suitable IMS-MS-coupling or comparable experimental setups.

## Outlook

- | Experimental  | Simulation  | Bringing together   |
|---|---|---|
| <ul style="list-style-type: none"><li>Setup of an HiKE-IMS-MS to mass selectively analyze the drift signals</li><li>Deeper investigations of modifying processes and the significant parameters</li></ul> | <ul style="list-style-type: none"><li>Simulation of an HiKE-MS coupling stage without changing the ion-temperature</li><li>Extension of the existing simulation code for more complex systems</li></ul> | <ul style="list-style-type: none"><li>Combination of simulations and experimental results</li><li>Integration of knowledge of other cluster based experiments (DMS or super charging)</li></ul> |

## Literature

- Schneider, B. B.; Nazarov, E. G.; Loundry, F.; Vuoros, P.; Covey, T. R.; *Differential mobility spectrometry/ mass spectrometry history, theory, design optimization, simulations, and applications*; Mass Spectrometry Reviews; 35; 687-737 (2015).
- Stappert, F.; Schneider, B. B.; Thinius, M.; Wissdorf, W.; Kersten, H.; Covey, T.; Hager, J.; Benter, T.; *Effects of chemical dynamics and clustering reactions of chemical modifiers with analyte ions in differential mobility spectrometry (DMS)*; 65th ASMS Conference on Mass Spectrometry and Allied Topics; Indianapolis; Indiana; USA; (2017).
- Langejuergen, J.; Allers, M.; Oermann, J.; Kirk, A.; Zimmermann, S.; *High Kinetic Energy Ion Mobility Spectrometry: Quantitative Analysis of Gas Mixtures with Ion Mobility Spectrometry*; Analytical Chemistry; 86;7023-7032 (2014).
- Erdogdu, D.; *Chemische Kinetik- und Ionentransportsimulationen des protonengebundenen Wasserclustersystems in der Ionenmobilitätsspektrometrie*; Masterthesis; university of wuppertal; 2018.
- Fernández-Maestre, R.; Wu, C.; Hill, H. H. Jr.; *Using a buffer gas modifier to change separation selectivity in ion mobility spectrometry*; International Journal of Mass Spectrometry; 298; 2-9 (2010)

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