Investigations on the field dependence of cluster dynamics using High Kinetic Energy IMS (HiKE-IMS)

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Introduction

The dynamic clustering and declustering processes of ions with neutrals in the gas phase are very important in many modern methods used in chemical analytics. The electrical mobility K which governs ion separation in **I**on **M**obility **S**pectrometry (IMS) is dependent on the collision cross section which is generally influenced by clustering reactions[1] and therefore also by the addition of chemical modifiers to the gas phase.[2]

In addition to this technique, which is running at a red. field strength below 10 Td, clustering processes under high field conditions are of great relevance, too. Typical regions with high field conditions are the transfer stages of mass spectrometers and **D**ifferential **M**obility **S**pectrometry (DMS) systems. The ion separation with DMS is based on the different mobilities of ions in an oscillating electric field.[3] In previous results, the dynamic cluster system with neutrals, like added modifiers, was identified as one root cause of this effect in certain cases.[4] Thus, a deeper understanding of cluster stabilities and the resulting dynamics at high reduced field strength is essential for the understanding of these complex chemical systems.

By using a **H**igh **Ki**netic **E**nergy **IMS** (HiKE-IMS), similar high field conditions can be recreated with a less complex analytical method. Based on a classic drift tube IMS, a reduced field strength up to >120 Td can be realized by running the system at reduced pressure of 20–30 mbar (see *"Experimental"*).[5]

Experimental[5]

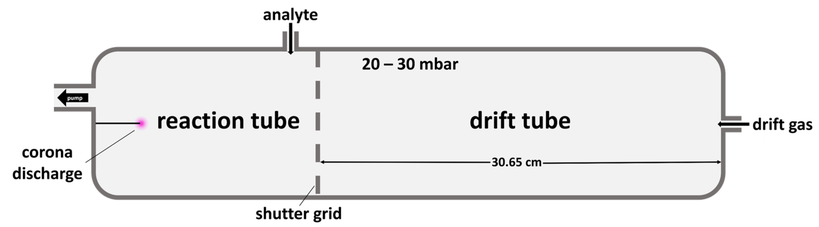

Figure 1: Schematic of the HiKE-IMS

Simulations:

- the chemical reaction system can be simulated by a particle based kinetic code (customized version of a Monte Carlo method)[6]

HiKE-IMS:

- basic setup close to a classic drift tube IMS
- pressure of 20-30 mbar in the reaction and the drift tube (30.65 cm)
- operated with pure nitrogen
- ionization by a corona discharge
- analytes are added in pure nitrogen to the reaction tube and the modifiable matrix drift gas to the drift tube
- heatable up to 45 °C

Water clusters

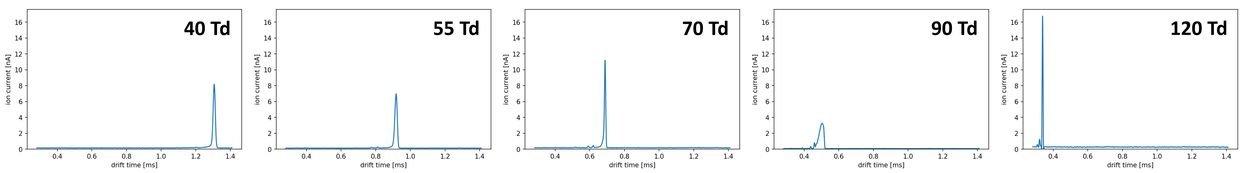

Figure 2: Experimental HiKE-IMS-spectra in dependence of representative reduced field strength (from left: 40 Td, 55 Td, 70 Td, 90 Td and 120 Td) and the main species in the postulated declustering process.

Without analytes present, a dominant signal of pure water clusters ("RIP") can be observed which shifts to lower drift times with increasing red. field strength (fig. 2). The cluster transitions are observed as temporary broadening of the peaks as the result of a combination of two cluster species. Note the pre-RIP-signals at lower drift times.

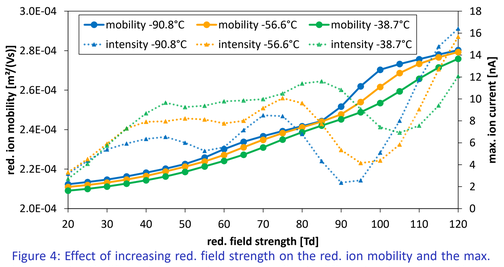

Figure 4: Effect of increasing red. field strength on the red. ion mobility and the max. ion current with different dew points, corresponding to different water mixing ratios.

The reduced ion mobility can be calculated from the drift time. Cluster transitions can be clearly observed in the ion mobilities and intensities. By increasing water mixing ratio, the red. ion mobility is decreasing (increasing average cluster size, fig. 4).

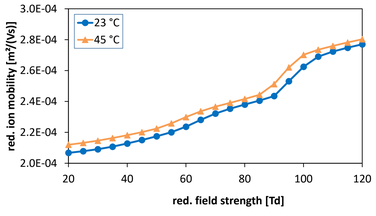

Figure 5: Effect of rising temperature in the drift tube on the red. ion mobility of water cluster system

Rising the temperature results in an increase of red. ion mobility (fig. 5). This can be explained by a lower average cluster size and a dynamic cluster system.

Mixed water-acetone clusters

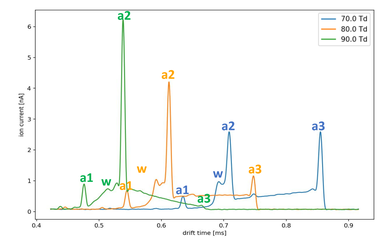

Figure 6: Cluster-transition processes at three representative reduced field strengths. The typical signals of the water-system (RIP) is marked with **w** and the analyte-specific signals with **aX**; (1.3 ppmV acetone in the reaction tube and 2.2 ppmV acetone in the drift gas)

Adding acetone results in three main analyte signals, which indicates multiple cluster species. The humidity dependence of a1 and a2 indicates mixed water-analyte clusters. The third signal seems to be the stable, non clustering acetone dimer (mobility known from previous results). The temperature effect confirms this notion: Note the decreasing cluster size by rising temperature.

Modifying the drift gas does not show any effect with the used concentrations.

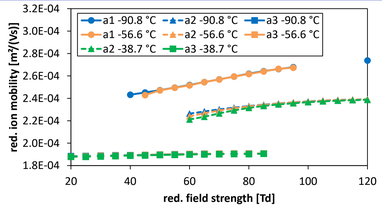

Figure 7: Humidity effect of water-acetone cluster system

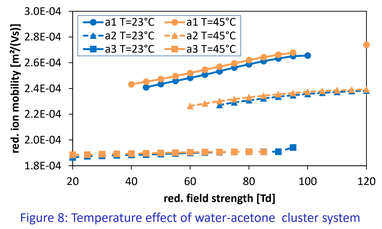

Figure 8: Temperature effect of water-acetone cluster system

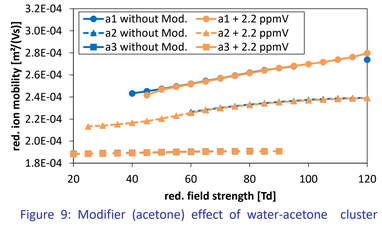

Figure 9: Modifier (acetone) effect of water-acetone cluster system

The qualitative results can be reproduced by simulations (fig. 10): Just small shifts of all peaks, probably due to slightly inaccurate collision cross sections can be recognized.

Note the cluster transition in both spectra at nearly the same red. field strength.

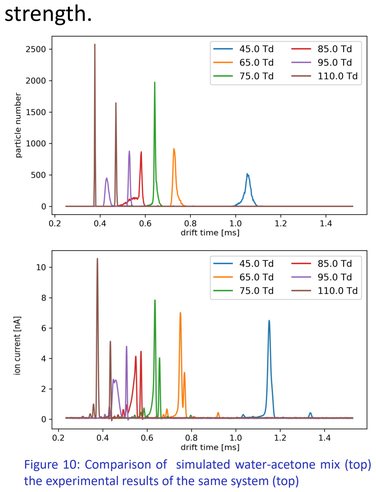

Figure 10: Comparison of simulated water-acetone mix (top) and the experimental results of the same system (top)

Conclusion

- Dynamic cluster systems at high red. field strength can be investigated with a "simple" analytical method.
- All cluster systems are dominated by water as neutral clustering agent, if there is not a high concentration of other neutral species.
- A qualitative rating of modifier effectiveness is possible.
- Cluster transitions can be detected. The transitions are generally influenced by humidity and temperature effects.
- Even one analyte can generate a group of new species and a very complex chemical system in result.
  - ➢ Only a well running HiKE-IMS-MS-coupling can help to understand all signals (first steps are done).
- Findings can be transferred to other comparable systems like DMS or ion optics.
- The basic cluster reactions are confirmed by suitable simulations.

Outlook

- The modifier effect will continue to be investigated with HiKE-IMS, IMS and DMS: A selected set of particularly small analytes with typical functional groups will be measured with and without modifier.
- An In-depth investigation of the detected signals with a HiKE-IMS-MS-coupling is currently being carried out (Leibniz University Hannover).
- Kinetic simulations to explain the observed pre-RIP-signals are planned, as well as a further optimization of the used collision cross sections.

Literature

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Acknowledgement

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