Simulation of Cluster Dynamics in High Kinetic Energy IMS (HiKE-IMS)

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Introduction

The reduced field strength and therefore the effective ion temperature impact significantly on the dynamics of clustering reactions in Ion Mobility Spectrometry (IMS) [1]. Increased reduced field strengths enhance the destruction rates of ion-molecule clusters. Using a High Kinetic Energy Ion Mobility Spectrometer (HiKE-IMS) allows a deeper insight into the chemical kinetics at elevated ion temperature. The reduced field strength in this drift tube instrument may exceed 120 Td. Numerical simulations of proton-bound water clusters under various conditions were performed. These results were directly compared to experimental results. Furthermore, simulations were performed to investigate the effects of diffusion and space charge in the drift tube of the HiKE-IMS. Additionally, the proton-bound watercluster/ acetone system was experimentally investigated and compared with numerical results. Kinetic simulations of this cluster system show that at elevated acetone background concentrations the mixing ratio of the acetone dimer is increasing with increasing reduced field strength.

Methods

Numerical Simulations:

Ion Transport Simulations:

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

Chemical Kinetic Simulations:

Customized version of "RS" Monte Carlo kinetics code [2]

IMS Experiments:

High Kinetic Energy Ion Mobility Spectrometer (HiKE-IMS) [3, 4]:
Background pressure: 20 - 25 mbar
Field Strength: 10 - 125 Td

Simulation approach

Protonbound watercluster system

$$[H + (H_2O)_n]^+ + H_2O + N_2 \rightleftharpoons [H + (H_2O)_{n+1}]^+ + N_2$$

The temperature dependence of the equilibrium constants and thus of the rate constants are approximated using the van't Hoff equation [5].

Ion Mobility

Ion mobility K is the proportionality factor of the drift velocity v_d and the electric field strength E [6]:

$$v_d = K \cdot E$$

At low field conditions the ion mobility can be considered as constant. However, the ion mobility is a function of the reduced field strength at high 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 Hard Sphere Gas Collision Model. To calculate space charge interactions, a Barnes-Hut method was implemented in the simulation code.

The HiKE-IMS [3, 4] consists of a reaction and a drift tube, which are separated by an ion shutter. The applied reduced field strength in the reaction region is 12 Td with a residence time of approximately 10 ms. The reduced field strength in the drift region was varied between 35 and 120 Td; the drift times are between 0.4 ms and 1.6 ms. To calculate the RIP drift time, kinetic simulations were performed in order to determine the cluster equilibrium state in the reaction region. Subsequent transport simulations were performed with the results of the equilibrium simulation.

Outlook

- Simulation of additional cluster systems, such as the acetonitrile/ water cluster system, which is already measured with the HiKE-IMS.
- Improvement of the assumed collision cross sections of acetone and acetone water clusters.
- Consideration of space charge effects with multiple species and chemical interactions.
- Addition of a Fast Multipole Methode (FMM) to decrease the computational time when calculating space charge effects.
- Fully parallelization for improved computational performance.

Proton bound Water Cluster System

The watercluster system was experimentally and numerically investigated in the HiKE-IMS. The mean cluster size is dependent on the reduced field strength, as shown in the figure on the right. Consequently, cluster transitions are observed when the reduced field strength is ramped in the drift region. The numerical results are verified with experimental data at different conditions. The simulations are in a very good agreement with the experimental results. Thus, the simulation framework can be used to model other cluster systems, such as the acetone/water cluster system. The results of the water cluster system are shown below.

Left:
Water cluster distribution at 49 °C and a dew point of -35.6 °C (220 ppmV H_2O). The mean cluster size decreases with increasing field strength as smaller cluster species become more abundant. Cluster 3 is dominating at 60 Td. With increasing field strength cluster 3 dissociates and a cluster transition occurs. The maximum concentration of Cluster 2 is at 85 Td. At very high reduced field strengths cluster 1 is dominant. Note that all abundance maxima are well separated from each other.

Water cluster RIP - Experimental and numerical results

Top:
Experimental (top panel) and numerical (bottom panel) RIP-drift times at different reduced field strengths and 25 °C background temperature. The water mixing ratio at a dew point of -35.6 °C was estimated as 220 ppmV. The numerical simulations are in a very good agreement with the experimental results. With increasing field strength a transition from cluster 3 to cluster 2 (roughly at 70 Td) and from cluster 2 to cluster 1 (from 85 Td - 105 Td) occurs. The broadened peak widths indicate cluster transitioning.

Top:
Experimental (top panel) and numerical (bottom panel) RIP-drift times at 49 °C background temperature and a dew point of -35.6 °C. Previous simulations show that the simulated peak width increases with decreasing water mixing ratios. The drift times at lower water mixing ratios decrease slightly. Further simulation results at different water mixing ratios and background temperatures are in a very good agreement with experimental data.

Right:
Kinetic simulation of the water cluster system. At high water mixing ratios such as present at a dew point of -35.6 °C (220 ppmV) the cluster equilibrium is achieved in less than 0.1 ms. However, the cluster relaxation at very low water mixing ratios (0.02 ppmV at -99 °C DP) is achieved only after 300 ms. Due to the residence time in the reaction tube of 10 ms, the cluster system is thus not in equilibrium at such low water mixing ratios. Simulating the drift time at different reduced field strengths results in only one discernable cluster transition since only cluster 1 and 2 are present at such low water mixing ratios.

Diffusion and Space Charge Effects

In order to consider only diffusion and space charge interaction, the simulations were performed without chemical reactions. and only one simulated species. The results show a strong dependence of the peak width (indicated here by the standard deviation of the axial positions of the simulated particles) on the residence time and thus the reduced field strength. So, the peaks are sharper at high field strengths, which is already observed in the RIP-drift time simulations and experiments. However, cluster transitions superimpose the effects of diffusion and are the main cause for broadened peak widths in chemical reactive systems. Further simulations show that with increasing mass the peak width becomes slightly narrower, but compared to the other effects this is not significant.

Left:
Standard deviation of the x-position of the simulated particles at different reduced field strengths. Space charge interactions cause broader peak widths due to the coulomb repulsion of ions. With increasing field strength the residence time decreases, resulting in lower standard deviations.

Top:
Histogramm of the x position over time and the associated standard deviations. The peaks broaden with increasing residence time. The dependence of the standard deviation on the drift time is root-shaped. Space charge interactions result in broadened peak widths due to Coulomb repulsion. The diffusive and space charge effects increase less with longer residence time due to the particle distances being greater

Conclusions

- The drift time simulation of the water cluster system is in a very good agreement with experimental results at various conditions.
- With increasing field strength cluster transition occurs.
- Residence time in the drift tube and chemical reactions are the main contributors to peak width.
- The lower the background water mixing ratio, the wider the peak widths of ions clustered with water.
- The acetone dimer is formed with increasing field when acetone is present at mixing ratios in the ppmV range.
- Drift time simulations of the acetone/water cluster systems are qualitatively in an agreement, the collision cross sections of the acetone species have to be refined with changes up-to 6 %.
- Cluster systems can be characterized with the aid of numerical simulations.

Acetone Water Cluster System

The acetone/water cluster system, which is sketched below, was simulated at 49 °C and 22 ppmV water mixing ratio. The formation of acetone-water clusters is dependent on the water mixing ratio, whereas the formation of the acetone dimer is independent. Equilibrium state simulations were peformed in order to characterize the chemical system at different reduced field strengths. The dimer concentration increases with increasing field strength. This is explained through the dissociation of acetone-water clusters at higher reduced field strengths, forming [H+Ac]+. If the background mixing ratio of acetone is sufficient, the dimer is formed due to its high stability. However, the kinetic energy gained from the electric field can lead to dimer dissociation, as shown in the figure at the bottom. The drift time simulations are qualitatively in an agreement. However, the collision cross sections of the acetone species have to be corrected (up-to 6 %). Further simulations show that the peak widths increase with lower water mixing ratios. Thus, the water mixing ratio in the simulation seems to be underestimated, resulting in broadened peak widths. The thermodynamic data of the acetone dimer are taken from [7].

Left:
Scheme of the acetone/water cluster reaction system

Right:
Experimental (upper panel) and numerical (lower panel) drift time spectra of the acetone/water cluster systems at different field strengths. The difference between the simulation and the experiment can probably be reduced with corrected water mixing ratios and collision cross sections of the acetone species. See poster ThP 297 for more experimental results.

Bottom:
Numerical drift times splitted into drift times of the water clusters (bottom panel) and of the acetone species (panel at the bottom right).

Left:
Cluster distribution (upper panel) and bar plot of the acetone species mixing ratios (lower panel) at different field strength.

water cluster RIP   acetone

Literature

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