

Introduction

- Recent research [1] has demonstrated that liquid charged droplets generated by Electrospray Ionization (ESI) penetrate deeply into the vacuum systems of commercial mass spectrometers (MS)
- The aspiration of droplets into the devices can have adverse effects on the performance (Fig. 1)
- The droplet fragmentation and generation of bare ions suspected to originate from those droplets takes in part place under medium or high vacuum conditions and potentially strong electric fields
- Since the dynamics of the droplets are largely unknown, classical molecular dynamics (MD) simulations are used to get an improved understanding of the complex droplet dynamics

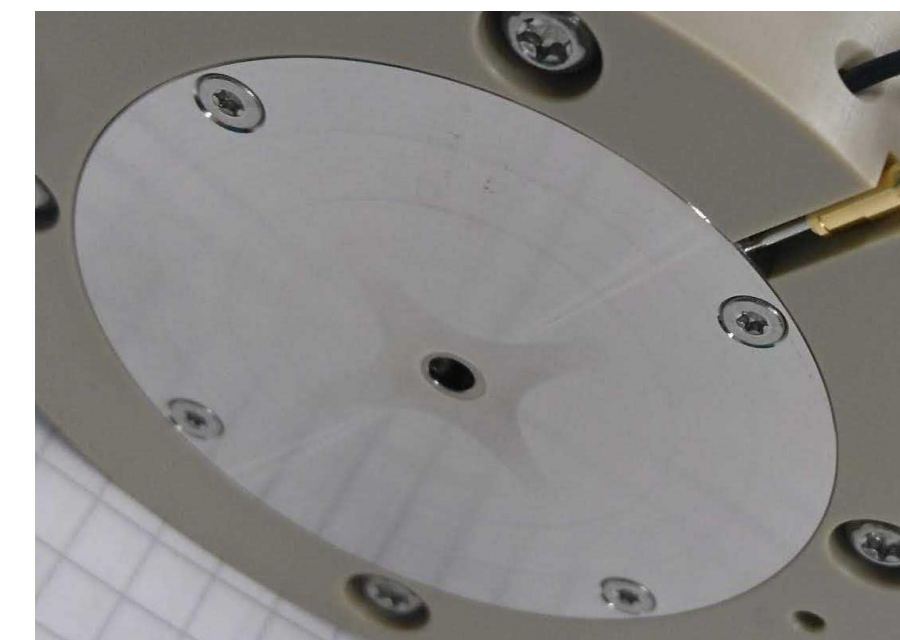


Fig. 1: Lens downstream a quadrupole with cross shaped aspiration of solvent

Methods

- Moltemplate is used for particle ensemble set-up
- Forcefield based MD simulations are performed with the open source code LAMMPS
- Simulated liquid nanodroplets of various composition and size are set up and heated with a numerical thermostat function
- The visualization and analysis of the resulting fragmentation patterns is carried out using Ovito in combination with custom Python programs

Droplet Heating

With higher temperatures the droplet evaporates small clusters of just a few molecules.

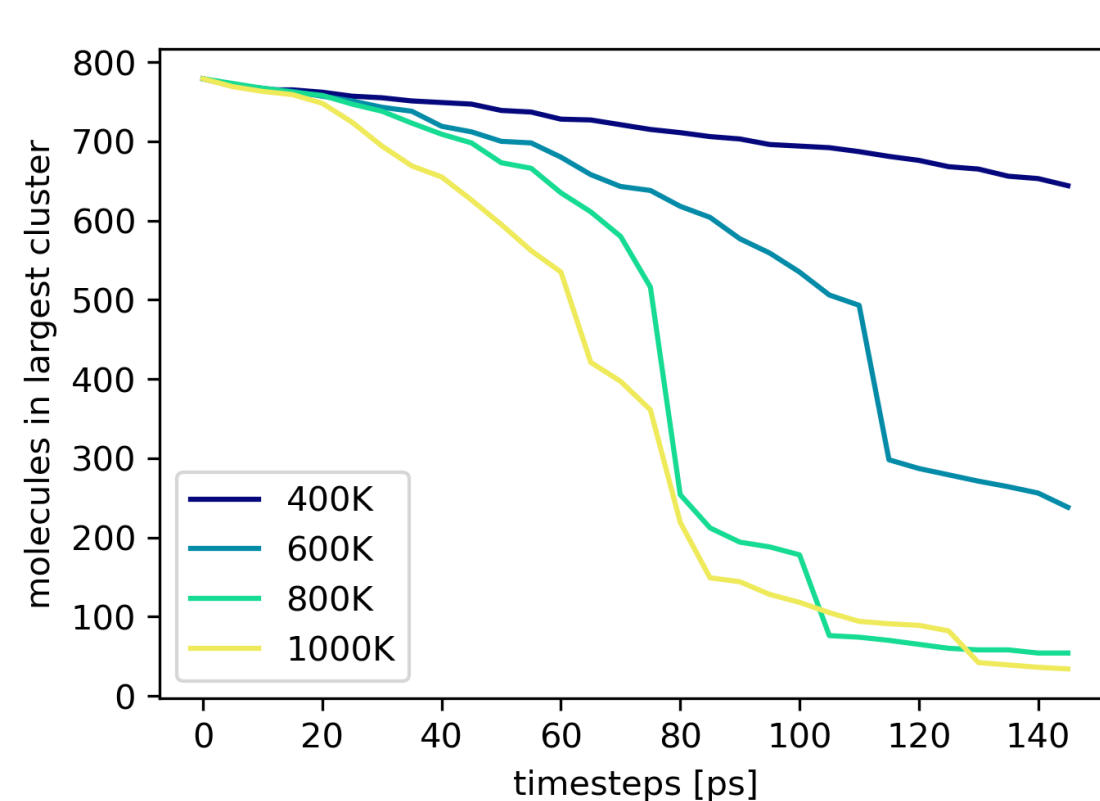


Fig. 2: Fragmentation of droplets in dependency of final temperature

Dependency on Charge

A higher number of charges destabilizes the droplet.

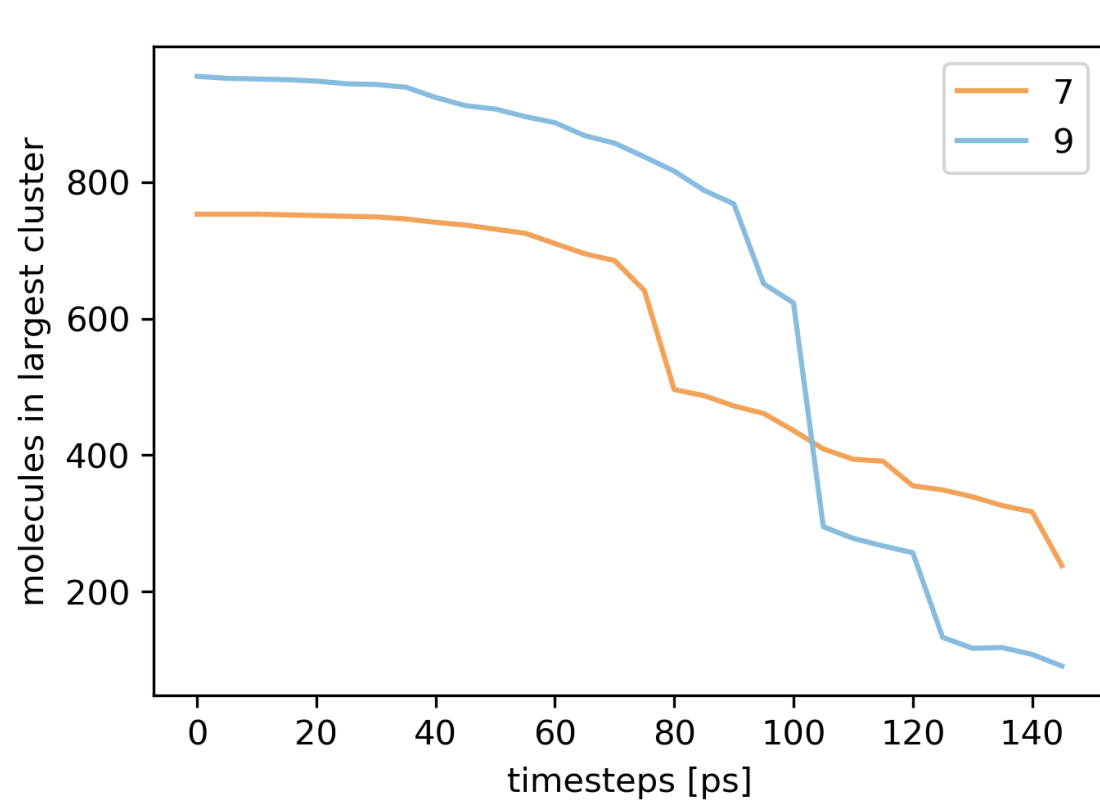


Fig. 3: Fragmentation of droplets of the same solvent and size but different number of charged analytes

Solvent and Analyte Dependency

The stability of the droplets depends heavily on the composition of the system as shown Fig. 4

- More polar solvents like water or alcohols can stabilize the droplets by arranging around the ions or secondary bonding forces like hydrogen bonding as presented in Fig. 4 a
- More surprising is the influence of analyte molecules on the stability of the droplet, as their concentration is much lower compared to the large number of solvent molecules. Fig. 4 b shows a simulation of droplets of the same initial conditions but different functional groups on the structurally and chemically similar analytes (Fig. 5). Droplets with NO₂-groups evaporate faster than droplets with a CH₃-group

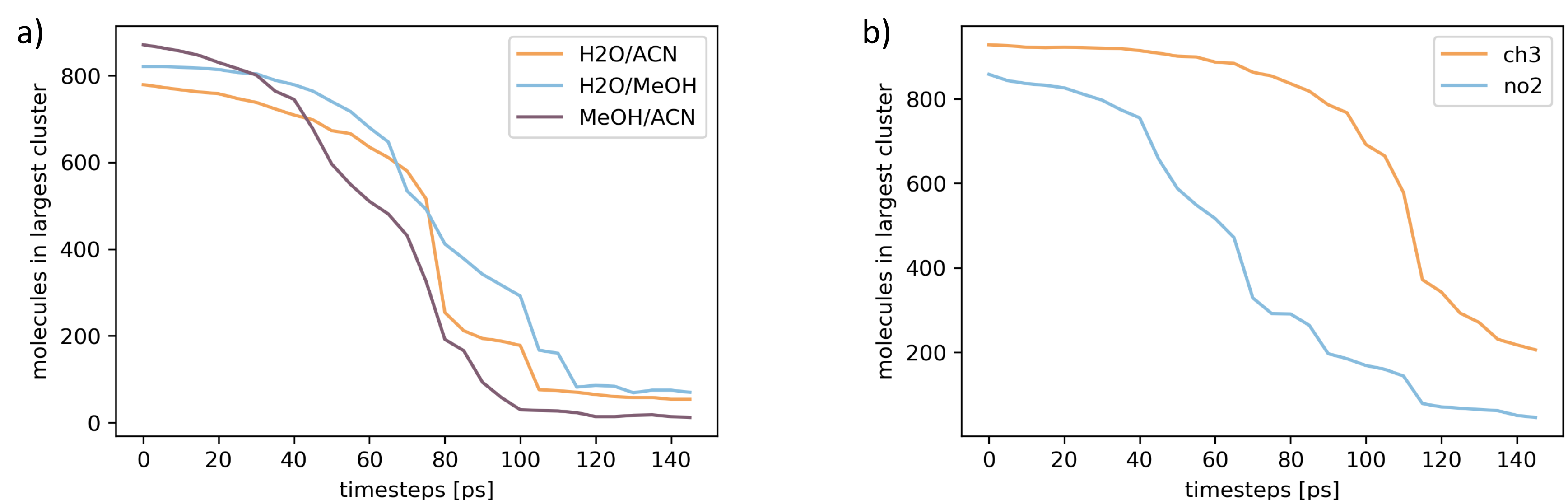


Fig. 4 Simulations of idealized solvent droplets a) with different solvents and b) different analytes in droplets of the same solvent and size

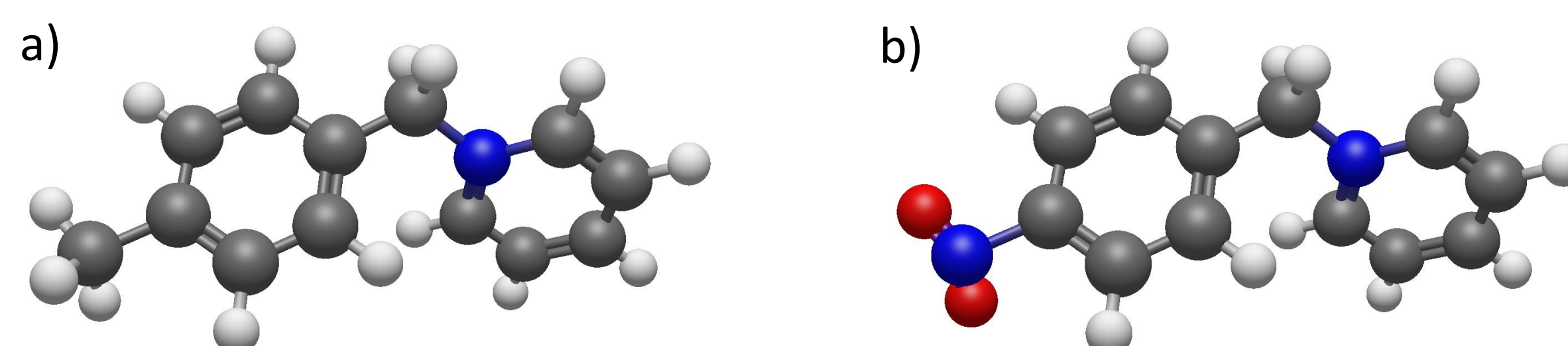


Fig. 5 Benzyl-Pyridinium thermometer-ions a) CH₃-group functionalized b) NO₂-group functionalized

Simulated Mass Spectra

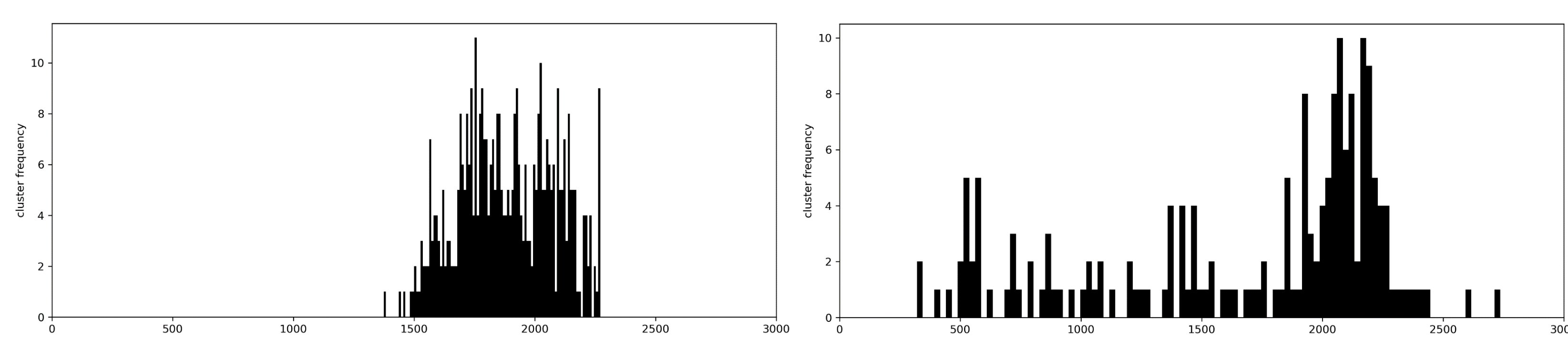


Fig. 6 Simulated mass spectra of droplets of acetonitrile and water with m/z = 2241 containing 3 ions (left) and 2253 with 8 ions (right)

- To derive simulated mass spectra, the same droplet is heated up several times with a different random seed until a sufficient statistical set of fragmentation events and thus resulting fragments can be obtained. Some examples for this process are shown in Fig. 6 and 7
- Fig. 6 shows different simulated mass spectra of similar m/z but different overall mass. Both show the shape of the experimentally observed characteristic double peak structure at least to some extent (also shown in Fig. 7)
- Fig. 7 especially shows the obtainable similarity between a real mass spectra and a simulated one. The simulated peak is broader, while the maximum is in the same m/z range. The discrepancies in the lower m/z-range between 500-1000 will be further examined in the future

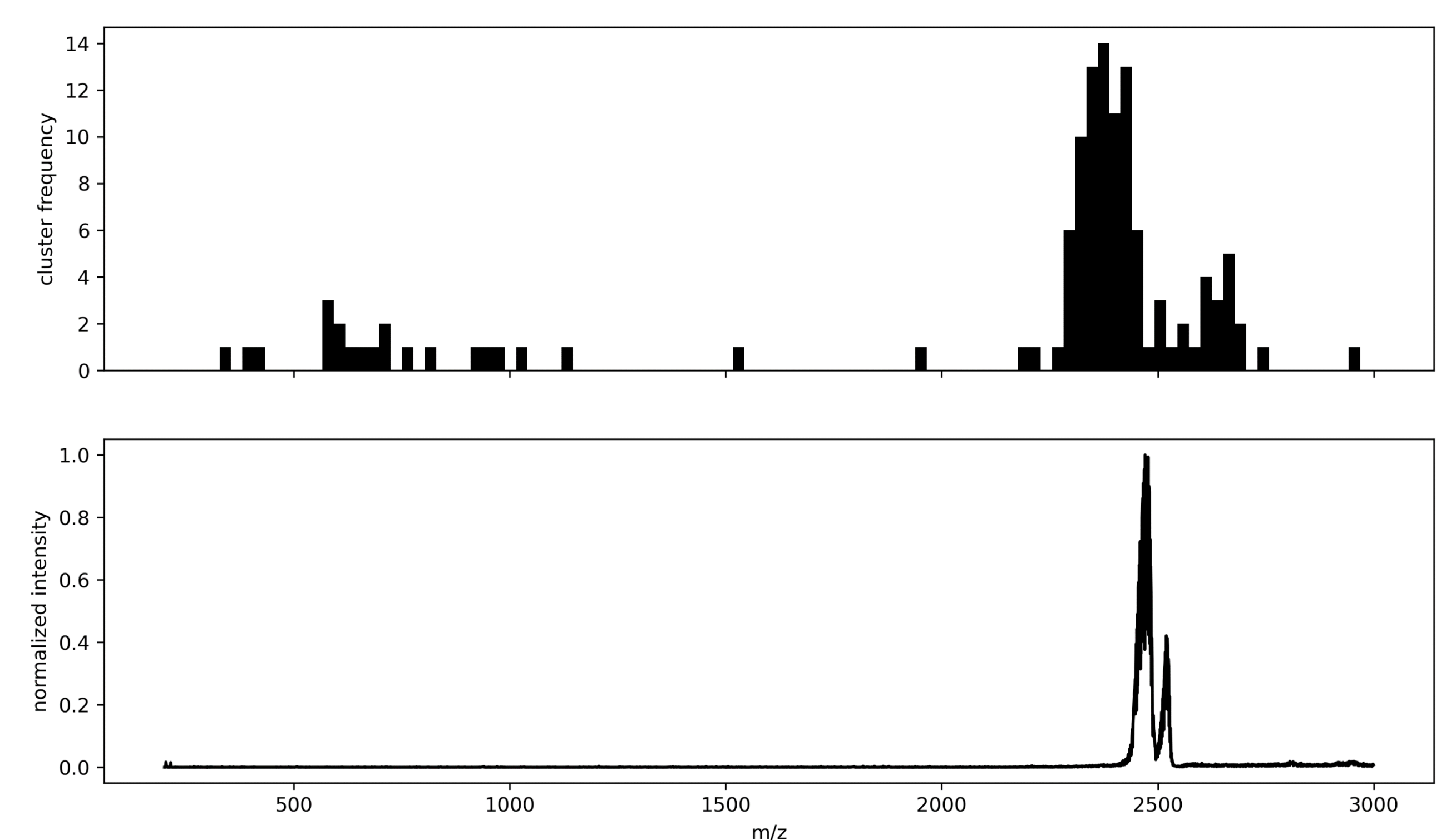


Fig. 7 Comparison of a simulated spectra derived from a droplet of acetonitrile and water with 7 ions and m/z = 3095 at a temperature of 400 (top) and a real mass spectrum from a Bruker amazon QUIT (bottom) [2]

Conclusion and Outlook

Simplified systems suffice to show preliminary qualitative estimations of the various chemical systems in droplets. However, modeling of larger and more complex droplets is also possible with LAMMPS and proves to be an interesting approach for comparison with experimental mass spectra of droplets. With this approach, systems of different size and composition can be simulated to better understand the process of droplet dynamics.

References

- [1] C. Markert, M. Thinius, L. Lehmann, C. Heintz, F. Stappert, W. Wissdorf, H. Kersten, T. Benter, B. B. Schneider, T. R. Covey, *Analytical and Bioanalytical Chemistry*, **2021**, *413*, 5587–5600
- [2] Clara Markert (2023). Investigation of Charged Droplets Aspiration in the Electrospray Ionization Process (Dissertation). Bergische Universität Wuppertal.