

# Kinetic energy distribution measurements for ion dynamics studies

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## Introduction

The kinetic energy distribution of ions in a mass spectrometer can be determined experimentally by applying a deceleration voltage in a collision-free region of the ion transfer stage. When this voltage is successively changed a portion of the ions, namely those who do not have a sufficient kinetic energy cannot pass the potential barrier and are removed from the detected ion ensemble.

Experimental evaluations of mass resolved kinetic energy distributions in Bruker ion trap mass spectrometers have shown systematic deviations from absolute ion current measurements with a faraday cup-electrometer setup. This was found to be a result of the superimposed kinetic energy dependent ion acceptance of the ion trap. Even though the absolute kinetic energy distribution cannot be evaluated without measuring absolute ion currents, relative changes of the distribution are very well detectable with this method. [1]

The KED analysis complements the Survival Yield method [2], which is used for determining internal energy distributions of ions. Both methods aim at analyzing the effects that instrumental parameters such as e.g. pressure, temperature and activation voltages have on ion formation and dynamics.

Preliminary results are presented, which suggest that kinetic energy distribution measurements can be a valuable tool for probing ESI droplet and ion release dynamics.

## Methods

### Mass Spectrometry:

amaZon Speed ETD, amaZon ETD and HCT plus Ion Traps with Apollo ESI source (Bruker Daltonics, Bremen, Germany)

### Simulations:

SIMION 8.1 (Scientific Instrument Services, Inc., Ringoes, NJ, www.simion.com) with hard sphere collision model (hs1)

### Data Processing and Visualization:

DataAnalysis 4.1 (Bruker Daltonics, Bremen, Germany), Python 3 with SciPy ecosystem

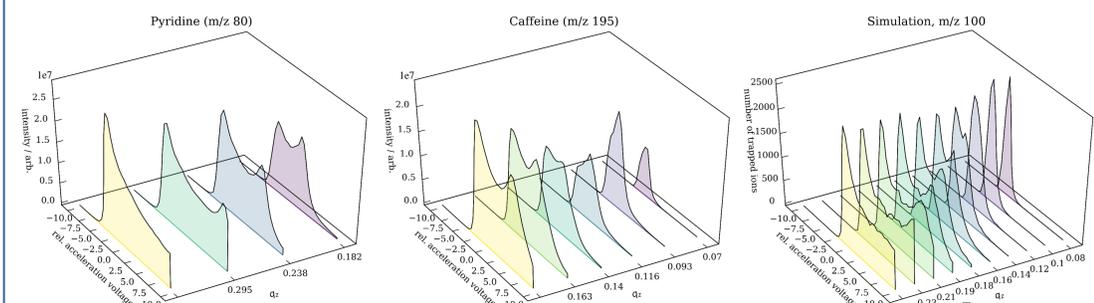
### Chemicals:

Benzylpyridinium salts were prepared by stirring the respective benzylpyridinium bromide derivate with an equimolar amount of pyridine in acetonitrile for 15-30 minutes at room temperature. After filtration the obtained white powder was washed with diethyl ether, dried and then stored at -26 °C until use.

HPLC grade acetonitrile and Millipore water were used for preparation of the analyte solutions. All analytes were diluted in water/acetonitrile (1/1) with 0.1% formic acid present.

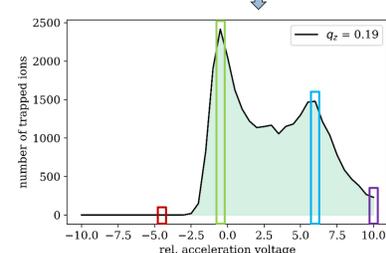
All chemicals were purchased from Sigma-Aldrich and used without further purification.

## Kinetic energy and QIT Ion Acceptance



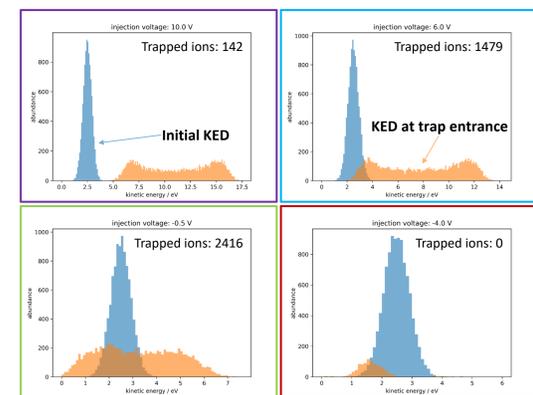
**Top:** Voltage scans at different  $q_z$  values (rf voltages) for the protonated molecules of caffeine (left) and pyridine (middle) recorded with the amaZon Speed ETD, and for ions with  $m/z$  100 from SIMION simulations (right)

- Rel. acceleration voltages < 0 V: the intensity depends on the number of ions reaching the ion trap and the kinetic energy dependent QIT ion acceptance
- With increasing  $q_z$  (increasing RF amplitude) the optimal operating point of the QIT is shifted to higher ion kinetic energies



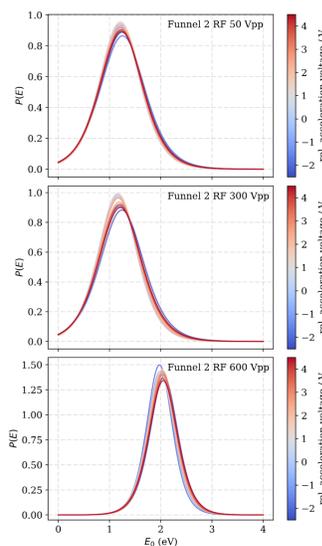
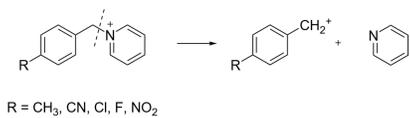
**Right:** KED (initial and at trap entrance) obtained from SIMION simulations for  $q_z = 0.19$

- KED is heavily modified by the fringe field at the trap entrance
- **No ions are stored:** ions are deflected from the trap a sufficient deceleration voltage is applied (e.g. -4.0 V)
- **Low trapping efficiency:** kinetic energy of ions is too high as observed for an injection voltage of 10.0 V
- **High trapping efficiency:** KED is in the optimal range and a minimum number of ions is deflected, as observed for injection voltages between -0.5 and 6.0 V



## KED and Survival Yield analysis

The fragmentation of *para*-substituted benzylpyridinium ions (**below**) are analyzed with the amaZon ETD instrument. The typical data processing sequence is shown **right**.

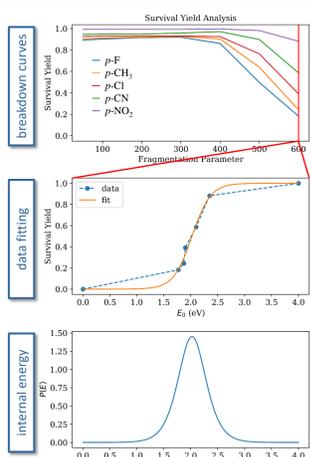


The Survival Yield (SY) for a precursor ion  $M$  with the corresponding fragment ion  $F$  is defined as:

$$SY = \frac{I(M)}{I(M) + I(F)}$$

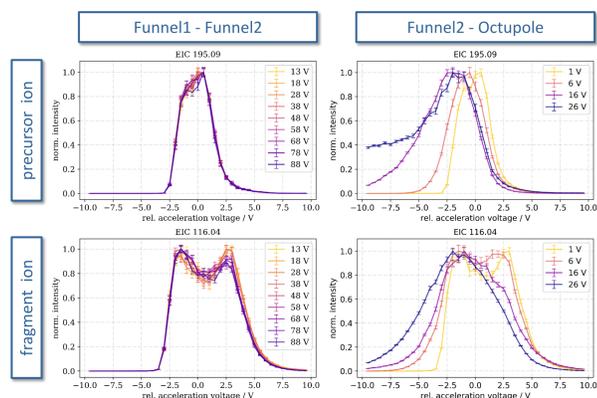
**Left:** Internal energy distributions obtained for different relative acceleration voltages at different Funnel2 RF amplitudes

- A shift towards higher mean internal energies are observed at RF amplitudes larger than 300 Vpp
- The internal energy distribution is independent of the acceleration voltage → no fragmentation inside the trap

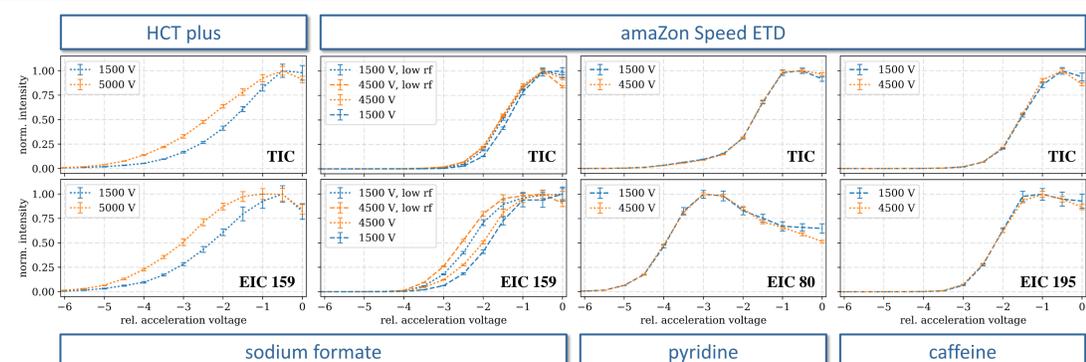


**Right:** acceleration voltage scans between the two funnels (left) and Funnel2 and the subsequent octupole (right)

- Gained kinetic energy is completely lost in the second funnel but only partly in the octupole



## KED shifts as a Diagnostic Tool



**Top:** Acceleration voltage scans for different samples with a skimmer (HCT plus) and a funnel instrument (amaZon Speed ETD)

- Changing the ESI voltage has a significant impact on the intensity progression observed with the HCT but not with the amaZon instrument (only partly observed for sodium formate)
- The funnel stage may lead to loss of upstream information
- Changes of the droplet evaporation and ion release dynamics are detectable with the skimmer inlet

## Conclusion

- Our current state of knowledge suggests that the KED analysis of ions arriving at the mass analyzer can reveal information that originates in upstream parts of the ion transfer stage or even the ion source, such as:
    - Droplet dynamics and ion release process in ESI
    - Collision numbers in different parts of the transfer stage
  - KED analysis is a complementary tool to the Survival Yield method:
    - No restrictions to specific analytes
    - No additional molecular information necessary (e.g. fragmentation energies)
  - Changing transfer voltages may heavily change the observed mass spectrum
- but:**
- instrument specific challenges (e.g. QIT, energy dependent performance) must be known and likely result in more sophisticated data analysis
  - Free configuration of all transfer potentials must be possible
  - so far observations still need interpretation and data processing may be incomplete

## Literature

[1] M. Thinius, N. Rutenbach, W. Wißdorf, H. Kersten, T. Benter, *Evaluation of kinetic energy distributions in API-MS ion transfer stages*, Proceedings of the 66th ASMS Conference on Mass Spectrometry and Allied Topics, San Diego, CA, USA, 2018

[2] V. Gabelica, E. De Pauw, *Internal energy and fragmentation of ions produced in electrospray sources*, Mass Spectrom. Rev. **24**, 566–587, 2005

## Acknowledgement

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