# Ion-solvent interactions in nanoESI-MS: Comparison of different ion transfer settings and analyzer systems

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Introduction

Motivation
- no comprehensive model exists for the *electrospray ionization* mechanism
- experimental observations are not sufficiently explained by current models

solvation → spraying → evaporation → transfer
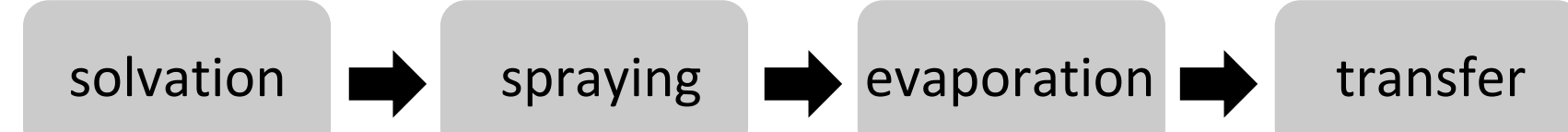
Approach
- ion-solvent interactions are present in every step of the ESI- ion transfer process
- rationalize the present results in a charge depletion/ charge conservation model
- forming stable ion-solvent-clusters seems to be crucial to prevent charge depletion via proton transfer reactions [1]
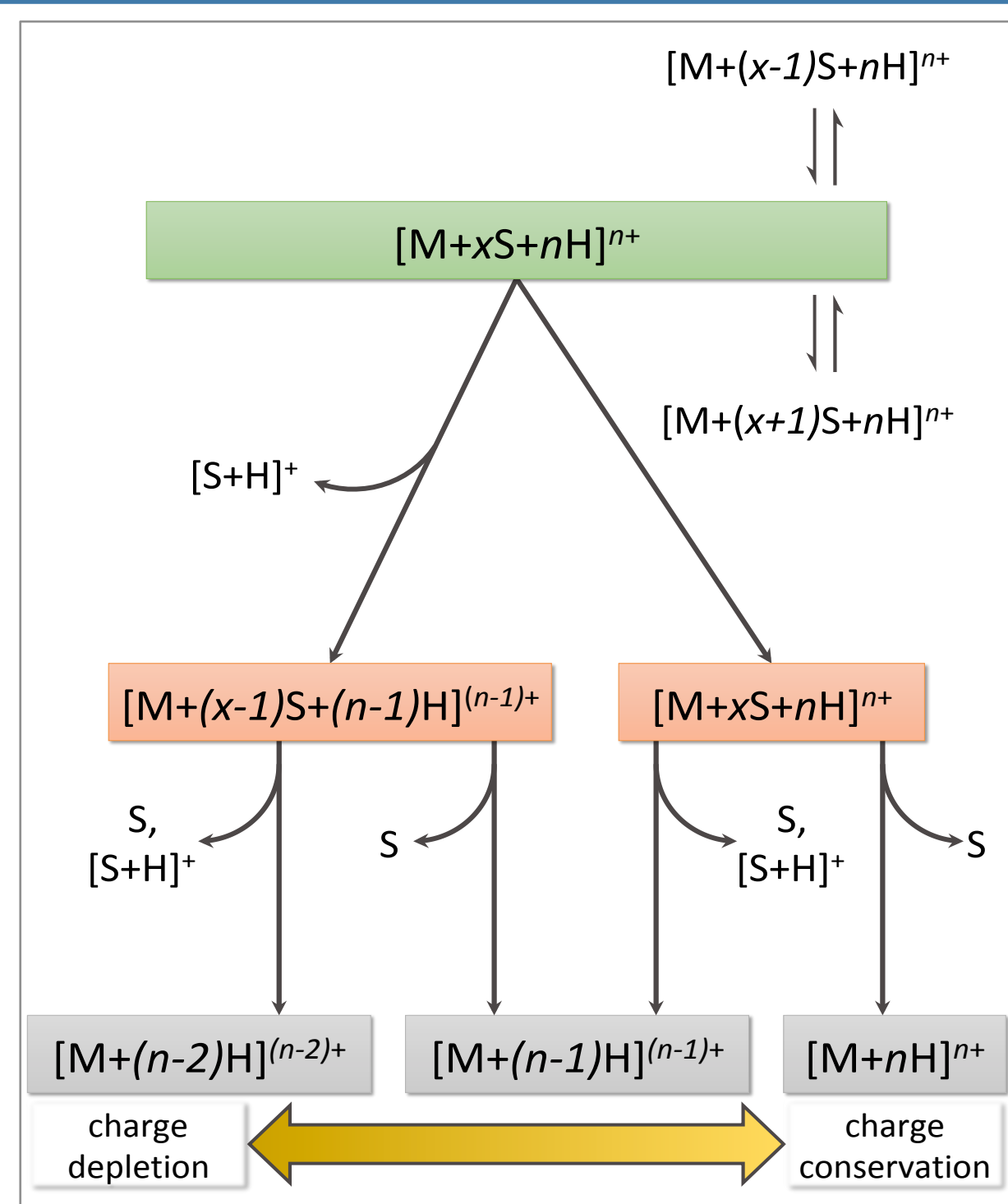
Experimental implementation
- exposing electrospray droplets to solvent vapor: charge depletion vs. charge conservation
- comparing different transfer and analyzer systems
- varying ion activation conditions

Challenge
- transfer and analyzer system determines the observation of ion-solvent-clusters
- minor changes in gas and/or solution phase composition strongly affect the observed ion distribution
- limited quantitative reproducibility
- inconsistent results in the literature
- elucidating underlying molecular mechanisms

Methods

MS: micrOTOF, esquire3000 HCT, esquire 6000 (all Bruker Daltonics, Bremen, Germany)

Ion Source: custom nano Electrospray Ion (nESI) Source [2]

Gas Supply: Nitrogen 5.0 (Messer Industriegase GmbH, Germany). All gas flows are controlled by mass flow controllers (MKS Instruments, Germany)

Chemicals: chemicals were purchased from Sigma Aldrich, Germany, and used without further purification, analyte: 1,9-diaminononane, modifiers: methanol (MeOH) and acetonitrile (ACN)
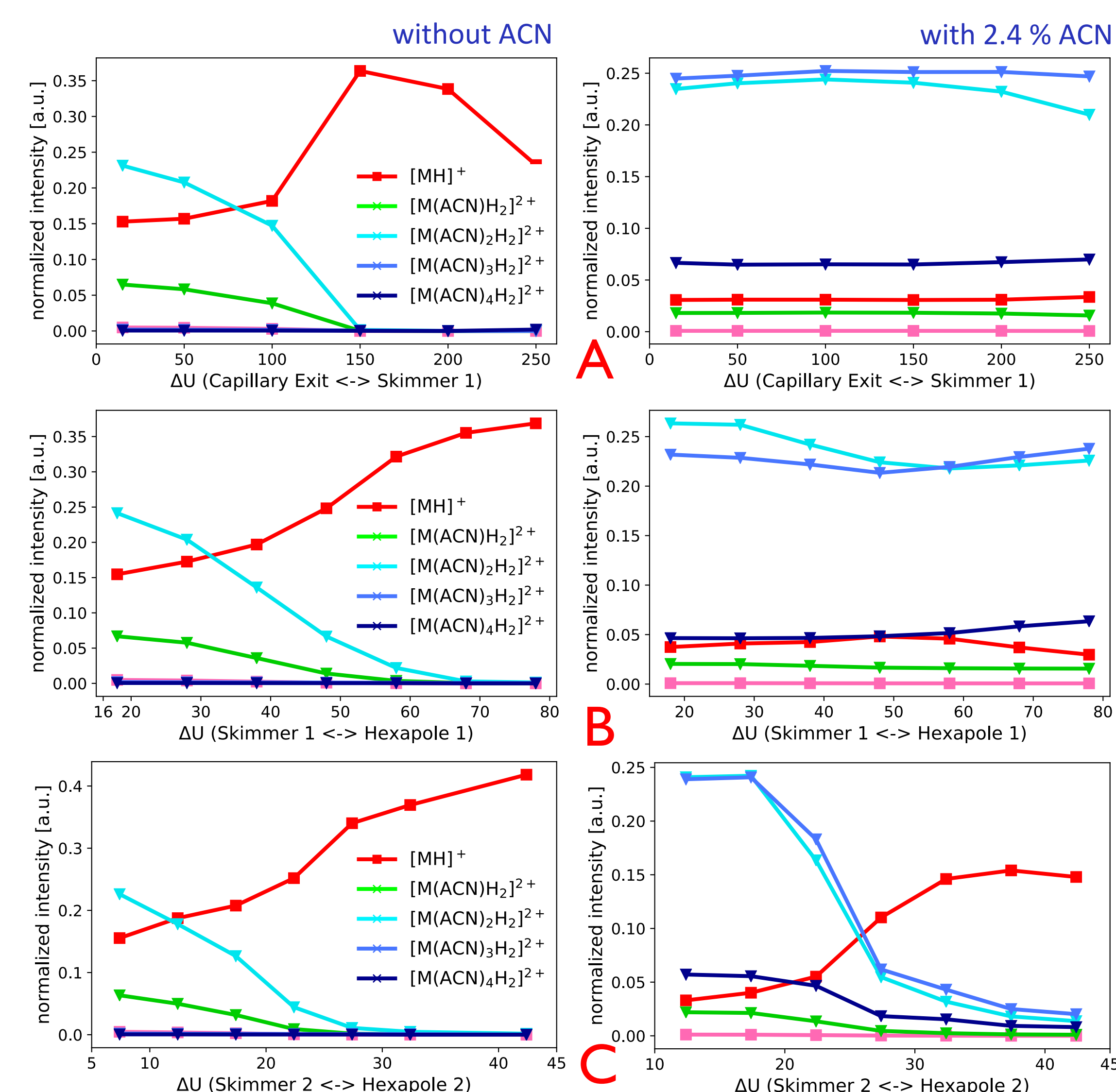
Trap vs. TOF: Impact of Transfer Stage Settings (with and without ACN addition)
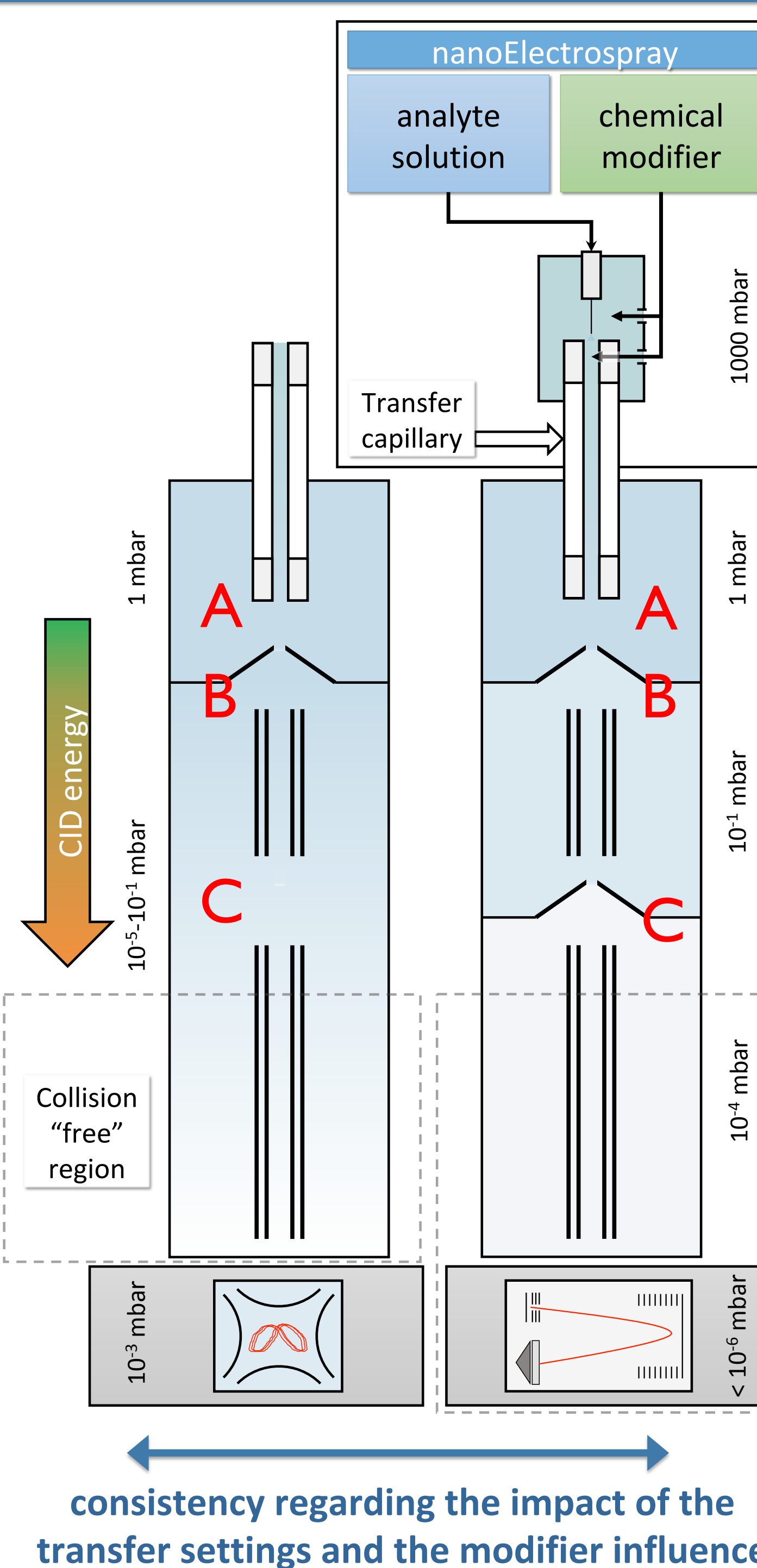
Trap: Bruker Esquire 3000

without ACN / with 4.8 % ACN
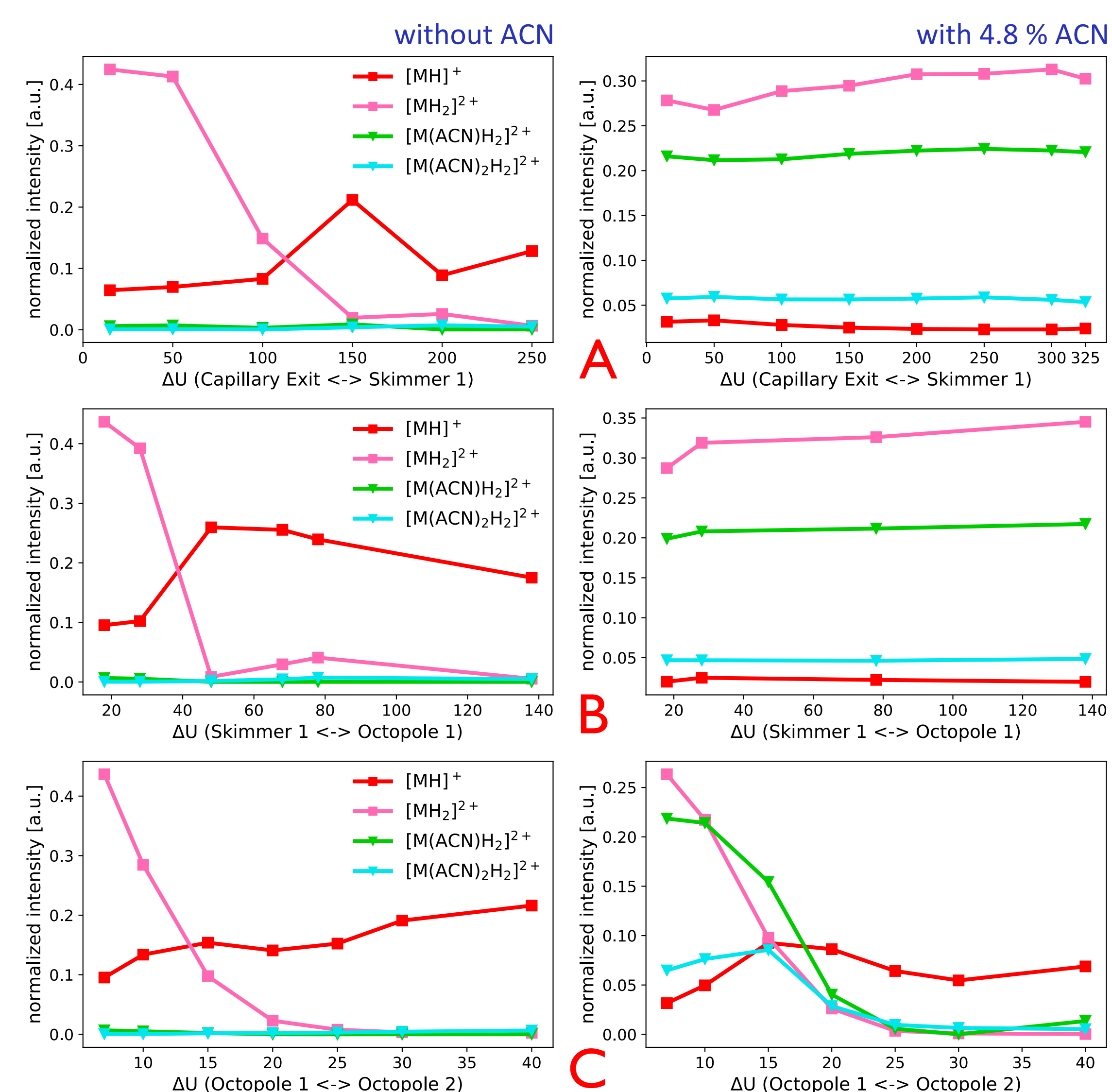
- signal depletion of the doubly protonated species
- normalized signal of the singly protonated diaminononan is roughly stable

- doubly protonated analyte-ACN-cluster up to n=2
- ion distribution is influenced by the transfer stage settings only in the last stage

consistency regarding the impact of the transfer settings and the modifier influence

TOF: Bruker microTOF

without ACN / with 2.4 % ACN

- "rougher" transfer settings result in declustering/fragmentation
- cluster signals even without ACN gas phase additon (cf. trap)

- higher cluster with ACN addition
- clusters are stable in the first two stages
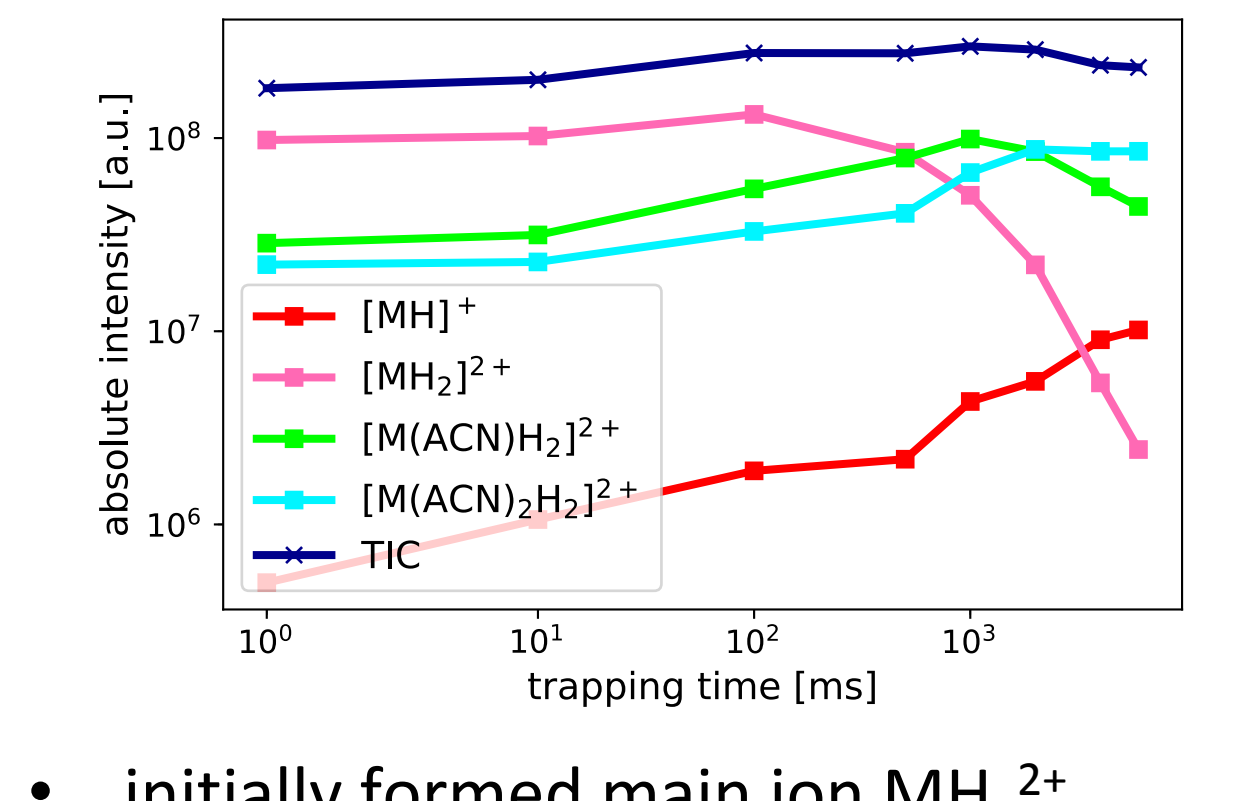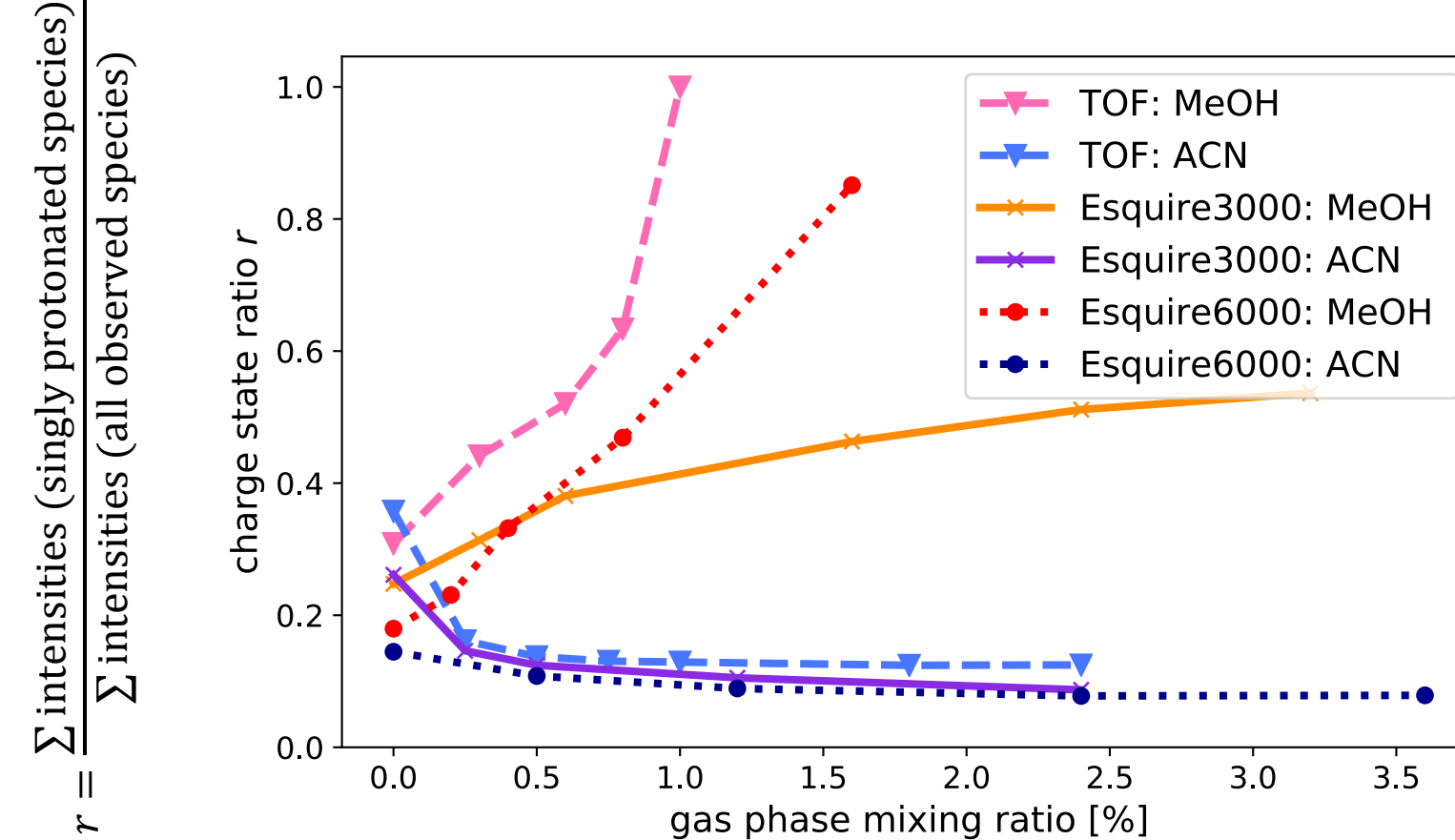- simultanous signal depletion for cluster ions in the last stage

Trap Drive

- the *trap drive* determines the RF voltage amplitude and thus field strength in the trap
- the absolute signal intensity decreases with elevated trap drive
- signal of doubly protonated molecules are much stronger reduced than the signals of singly protonated species
- increasing loss of NH_3 is observed
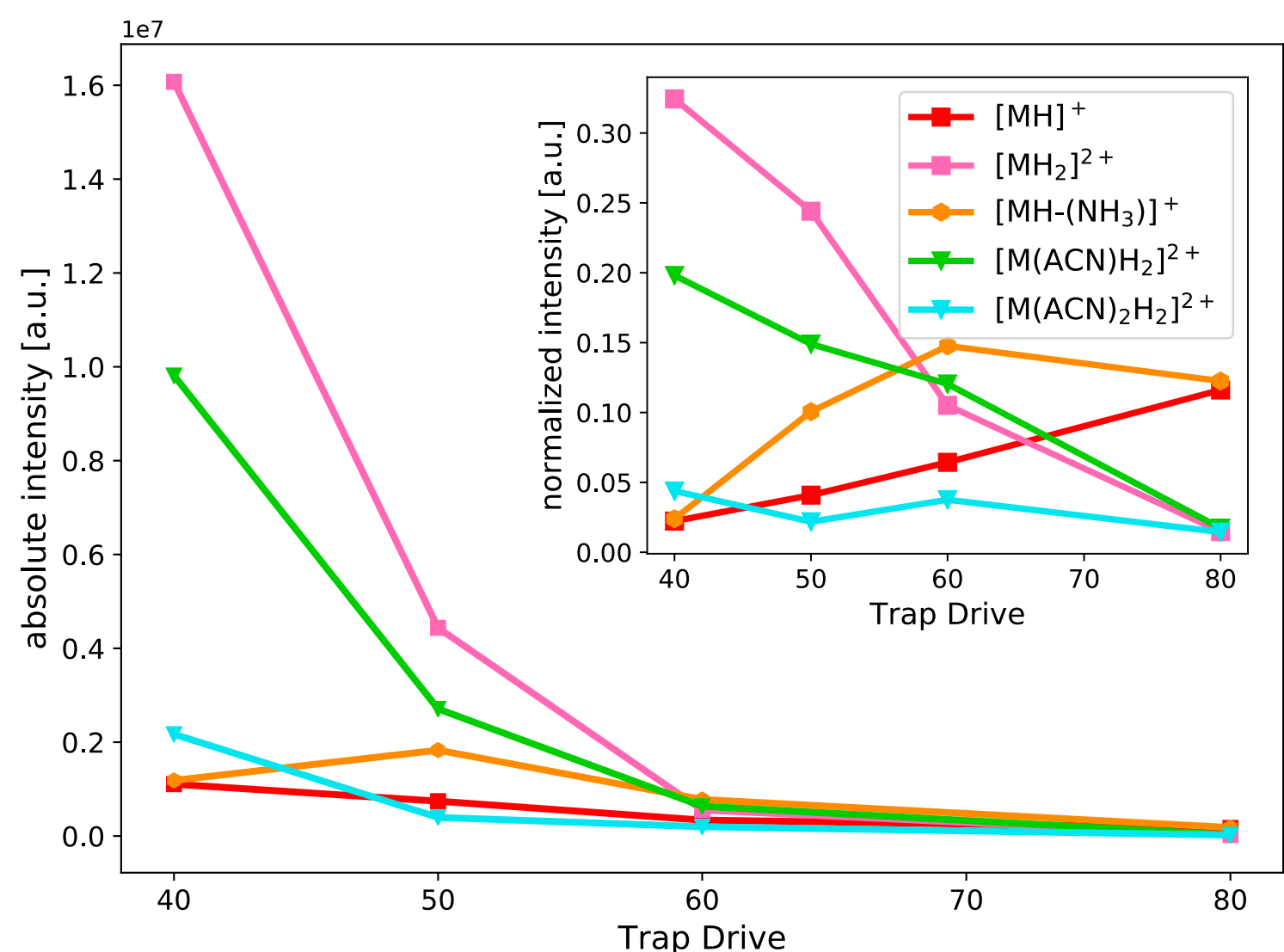
Trapping Time

- initially formed main ion MH_2^{2+} appears to be unstable/reactive
- intensity of MH^+ rises
- clustered doubly protonated species are stable; increase in intensity, particularly for cluster n=2
- no ion loss observed, but rather a gradual increase of the TIC
- charge depletion and charge conservation by protonated or neutral solvent molecules occur in the ion trap within the dwell time

Charge State Ratio

- diaminononane has two protonation sites
- ratio between singly and doubly protonated species is influenced by the modifier addition
- ACN: charge conservation
- MeOH: charge depletion
- with all used instruments qualitatively similar effects are observed
- TOF and Esquire 3000 HCT show solvent cluster signals
- with the Esquire 6000 no cluster species are observed

Summary/Outlook

Summary

- ion-solvent interactions affect the observed ion population and charge state distribution
- addition of ACN results in a charge conservation
- addition of MeOH resulst in a charge depletion
  -> observed with all instruments used
- ion population and charge state distribution are also dependent on
  - ion excitation
  - trapping time
  - analyzer system
  - helium pressure inside the trap
- traps show very different ion populations
  -> HCT vs. "normal" trap
- transfer systems of TOF and trap are similar but not identical

Outlook

- which parameters determine whether or not ion-solvent-clusters are observed in the recorded mass spectra
- elucidate the inconsistent results regarding the present work and published data

Literature

[1] C. Polaczek, A. Haack, M. Thinius, W. Wissdorf, H. Kersten, T. Benter, Ion-solvent interactions in nanoESI-MS: Characterization of charge depletion and charge conservation (supercharging) processes, *Proceedings of the 65th ASMS Conference on Mass Spectrometry and Allied Topics*, San Diego, CA, USA (2018)

[2] M. Thinius, M. Langner, H. Kersten, T. Benter, Impact of chemical USA (2016) modifiers on the cluster chemistry during electrospray ionization, *Proceedings of the 63th ASMS Conference on Mass Spectrometry and Allied Topics*, San Antonio, TX,

Acknowledgement