

Proton Transfer Mass Spectrometry (PT-MS) with H_3^+ as reagent ions

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Introduction

Challenge:

- Establish a universally applicable protonation source with no significant electrical field gradients present in the ionization region
- Adaptation of such ion source to a commercially available mass spectrometer (MS)
- Possibility to switch cleanly between charge transfer (CT) and proton transfer (PT) ionization mode

Implementation:

- Application of H_3^+ as the main primary charge carrier → one of the strongest known gas phase acids
- The Helium metastable enriched effluent of a DC-micro plasma source (PS) is mixed with a low-volume Hydrogen gas flow
- In a multi-stage process H_3^+ is formed, with primary ionization of H_2 and subsequent reactions with neutral Hydrogen [1]
- Spatial separation of the primary proton carrier generation and analyte ionization region

Methods

Detection

Mass spectrometer [2]

- The PT stage is directly coupled to a TOFWerk CTOF mass analyzer equipped with a custom ion transfer stage
- Narrow mass range filtering of reagent and carrier gas ions or other dominating ionic species allows the efficient enhancement of the dynamic range of the TOF mass analyzer

Ionization

Protonation stage

- As protonation stage ("ion source") the first intermediate pressure chamber between skimmer and sampler is used
- The analyte gas stream is sampled through an orifice with less than 1 mm diameter
- Orthogonal arrangement of analyte delivery, plasma source, and skimmer

Plasma source

- Micro plasma operated with Helium 5.0 (Messer Industriegase GmbH, Germany)
- Hydrogen is supplied through a custom 3-way chamber ("T-piece"), with H_2 mixing ratios ranging from 15 ppmV up-to 15 %V in the plasma effluent
- Expansion of the reagent gas mixture into the first pressure stage ("ionization region") held at approximately 2 mbar
- All gas flows are controlled by mass flow controllers (MKS Instruments Deutschland GmbH, Germany)

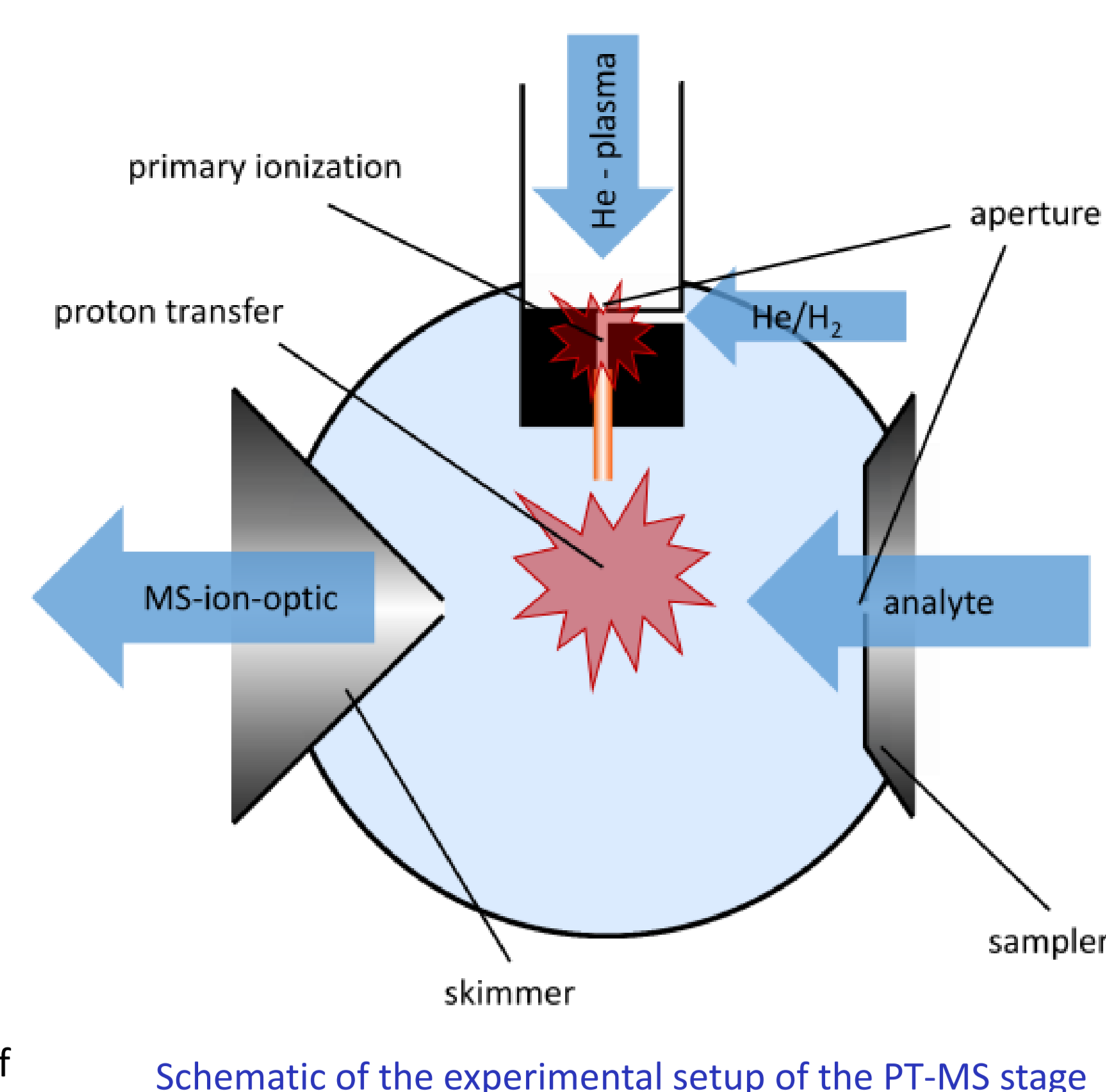
Experimental Setup

PT-MS stage:

- First pumping stage of a TOFWerk CTOF with custom designed ion transfer optics [2]
- Orthogonal arrangement of the plasma source with respect to the skimmer
- Windows allow visual inspection of the reaction region
- Bath gas pressure of approximately 2 mbar depending on flow rates

Plasma source:

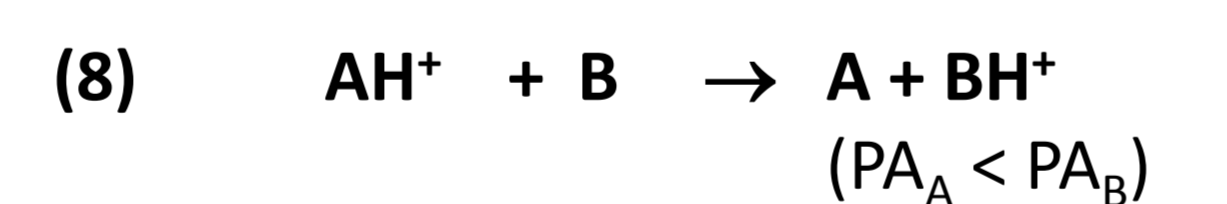
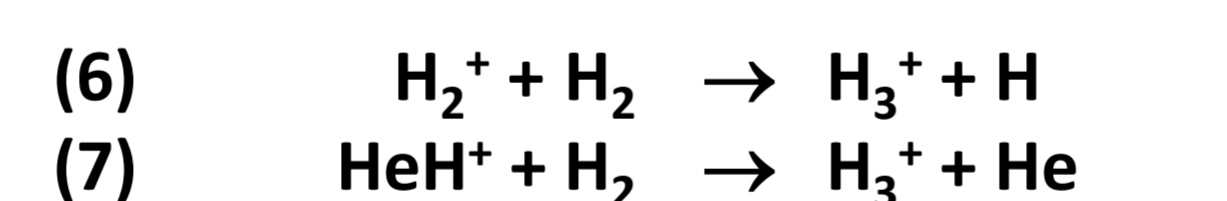
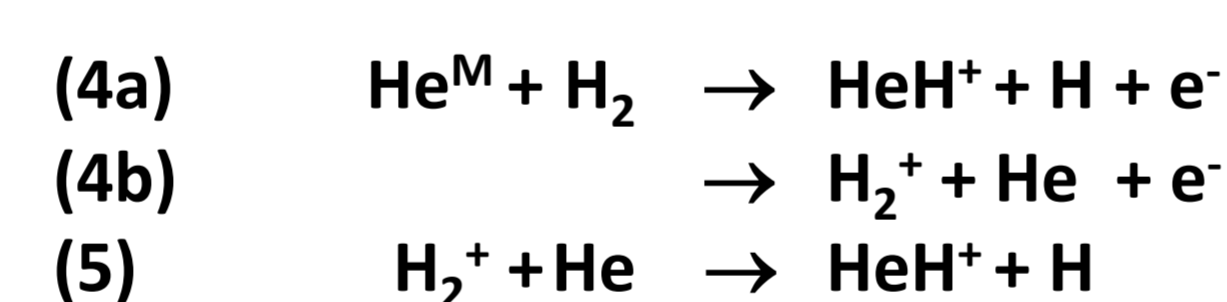
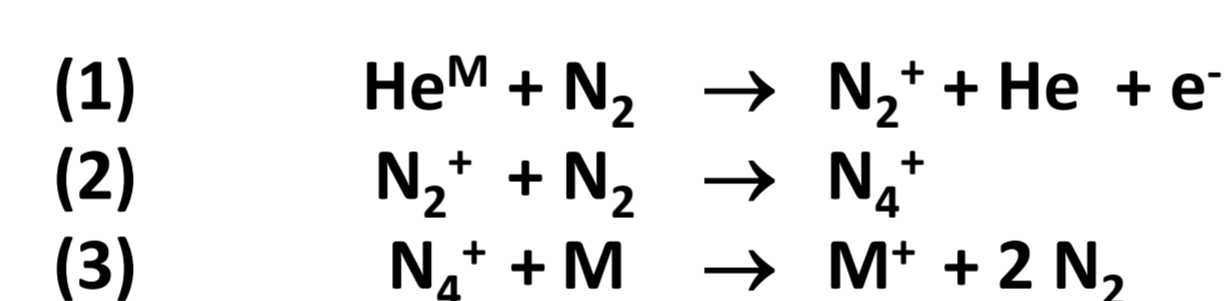
- DC- Plasma operating with Helium at reduced pressure
- Helium metastable enriched effluent is expanded in a gas flow of either pure Helium or a He/H_2 mixture
- "T-piece" arrangement allows the spatial separation of reagent ion preparation and analyte ionization region
- For an enhanced separation of these two zones a piece of an uncoated quartz GC-capillary was tested



Schematic of the experimental setup of the PT-MS stage

Primary Proton Carrier

- The formation of the primary charge carriers is driven in the reaction cascades 1-2 (CT) and 4-7 (PT)
- The plasma produces metastable Helium atoms (He^M) which are expanded into a Helium gas flow containing approximately 750 ppmV H_2
- Since plasma-generated cations cannot not leave the primary PS region, reagent ions are restricted to HeH^+ , H_2^+ and H_3^+
- The proton is then transferred collisionally controlled (in the ionization chamber held at about 2 mbar) via reaction 8 according to the proton affinities listed in Table 1
- As long as the measurement is taking place in N_2 as bath gas, the main reagent species is restricted to N_2H^+
- Therefore, with N_2 as bath gas it is possible to observe XeH^+ ($PA_{N_2} < PA_{Xe}$) but not KrH^+ ($PA_{N_2} > PA_{Kr}$)
- In the absence of N_2 and He as carrier gas KrH^+ is observed as well (see Figure 1)



Reaction system for CT mode (1 - 3) and PT-MS mode (3-8)

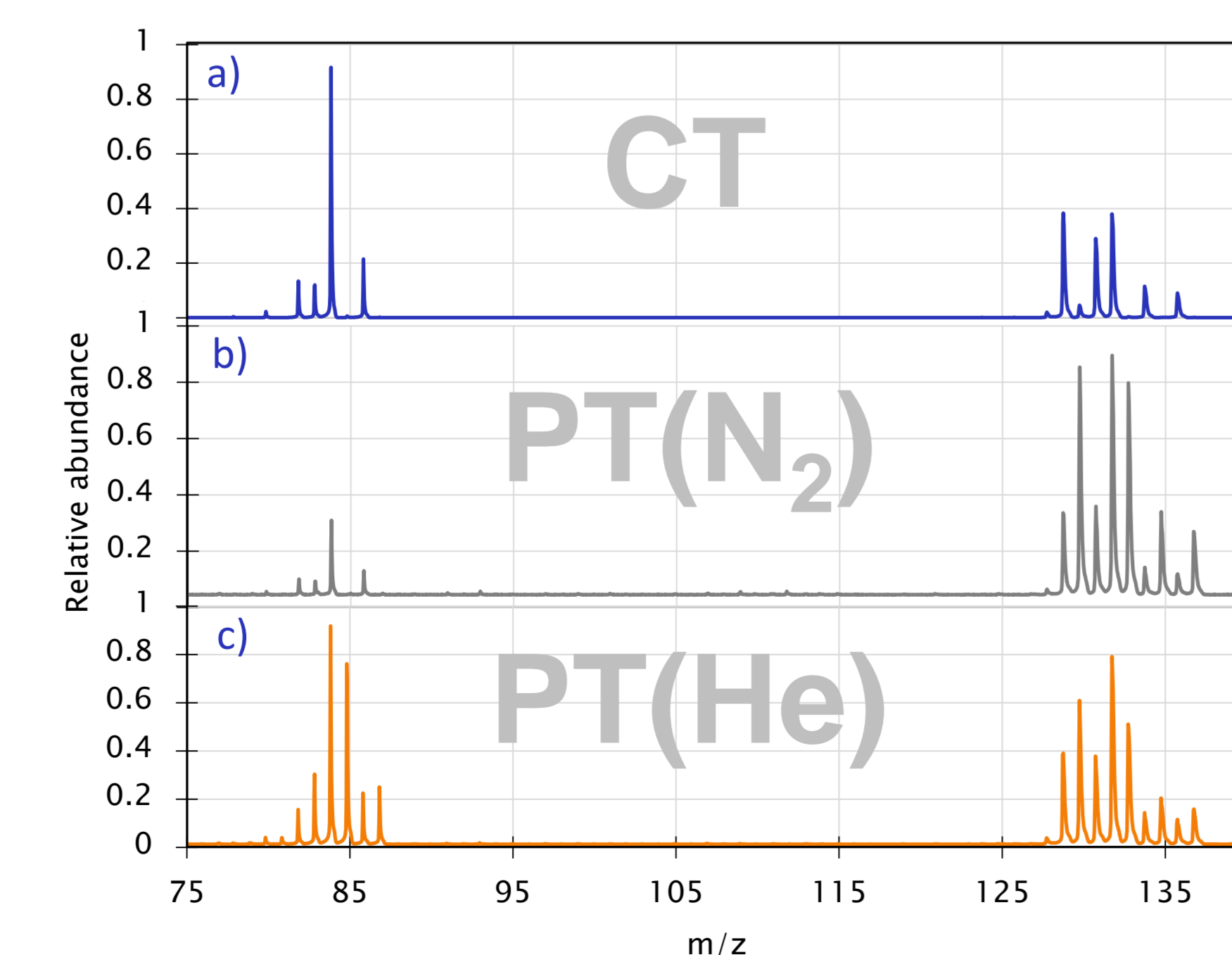


Figure 1: PT-MS mass spectra of Kr and Xe (10 ppmV each); a) charge transfer; b) proton transfer, N_2 as carrier gas; c) proton transfer, He as carrier gas

Analyte	Proton affinity [kJ/mol]
Helium	177.8
Neon	198.8
Argon	369.2
Oxygen	421.0
Hydrogen	422.3
Krypton	424.6
Nitrogen	493.8
Xenon	499.6
Water	691.0
Toluene	784.0

Table 1: Proton affinities of relevant matrix gases as well as Toluene as analyte for PT-MS [3]

Proton Transfer vs. Charge Transfer

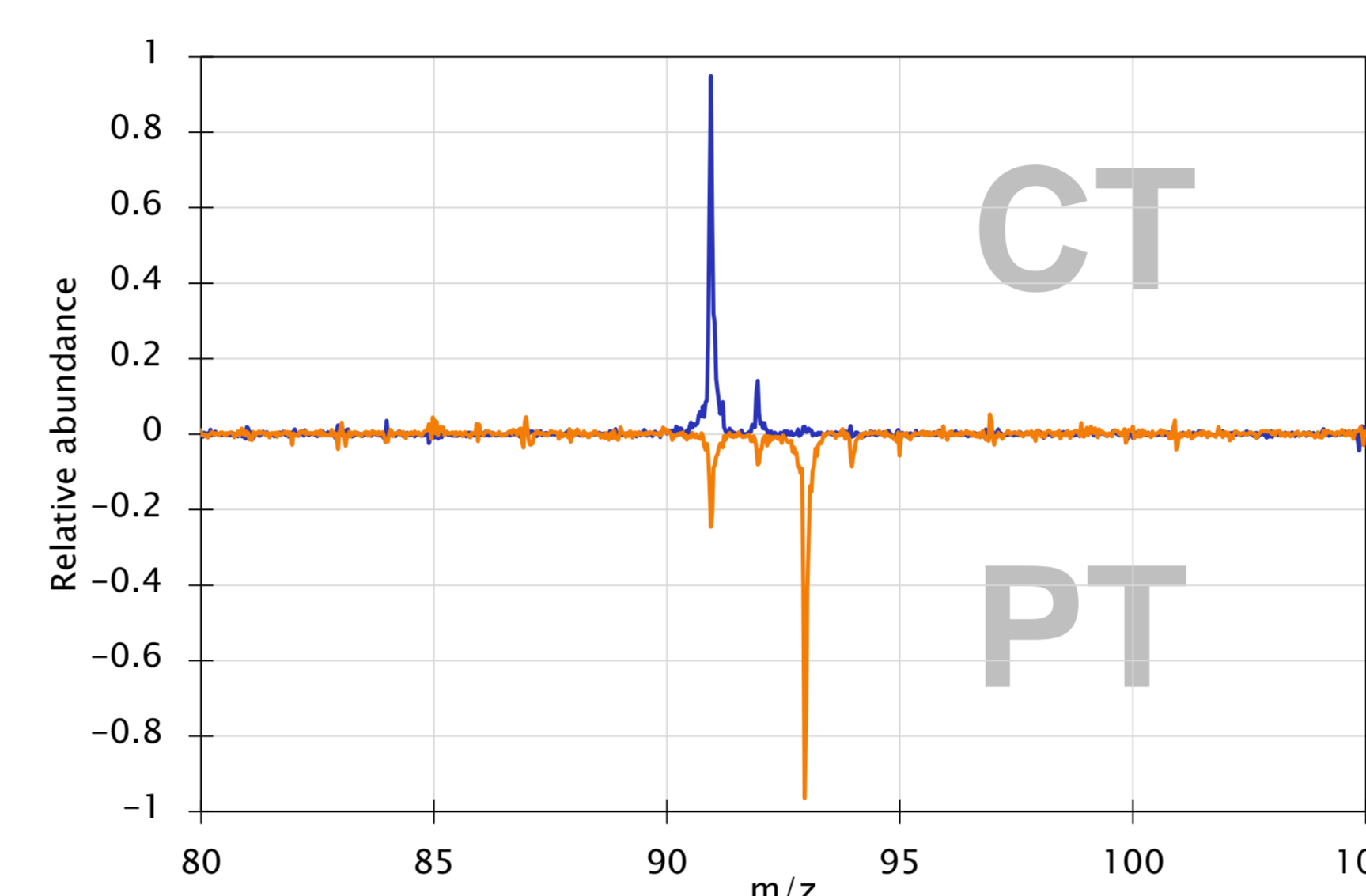


Figure 2: Mass spectra of Toluene in CT (top) and PT (bottom) mode; bath gas N_2 ; 1 ppbV Toluene; 1 sec. acquisition time

- Switching between charge transfer and proton transfer mode simply by adding Hydrogen to the Helium gas flow
- The appearing analyte species is switching from M^+ and/or fragments to mainly $[M+H]^+$
- Clearly the protonating mode leads to less fragmentation (see also Figure 4)
- Depending on the detailed setup the analytical performance of the system is comparable in both modes
- By using the GC-capillary the degree of protonation ($[M-H]^+/[M+H]^+$) is higher while the signal intensity decreases

Figure 3: Intensities of different Toluene ion signals depending on the Hydrogen mixing ratio; m/z 77 and 105 on secondary axis; 10 ppmV Toluene, setup without GC-capillary

- By changing the mixing ratio of H_2 the degree of protonation is adjustable
- As demonstrated for Toluene (see Figure 3) with increasing H_2 mixing ratio
 - The abundance of the fragment ion m/z 91 decreases
 - The product ion intensity (m/z 105) of the ion molecular reaction of m/z 91 and neutral Toluene decreases
 - The intensity of $[M+H]^+$ (m/z 93) and the reaction product ion m/z 77 increases
- By further increasing H_2 mixing ratio the intensities of all signals decrease

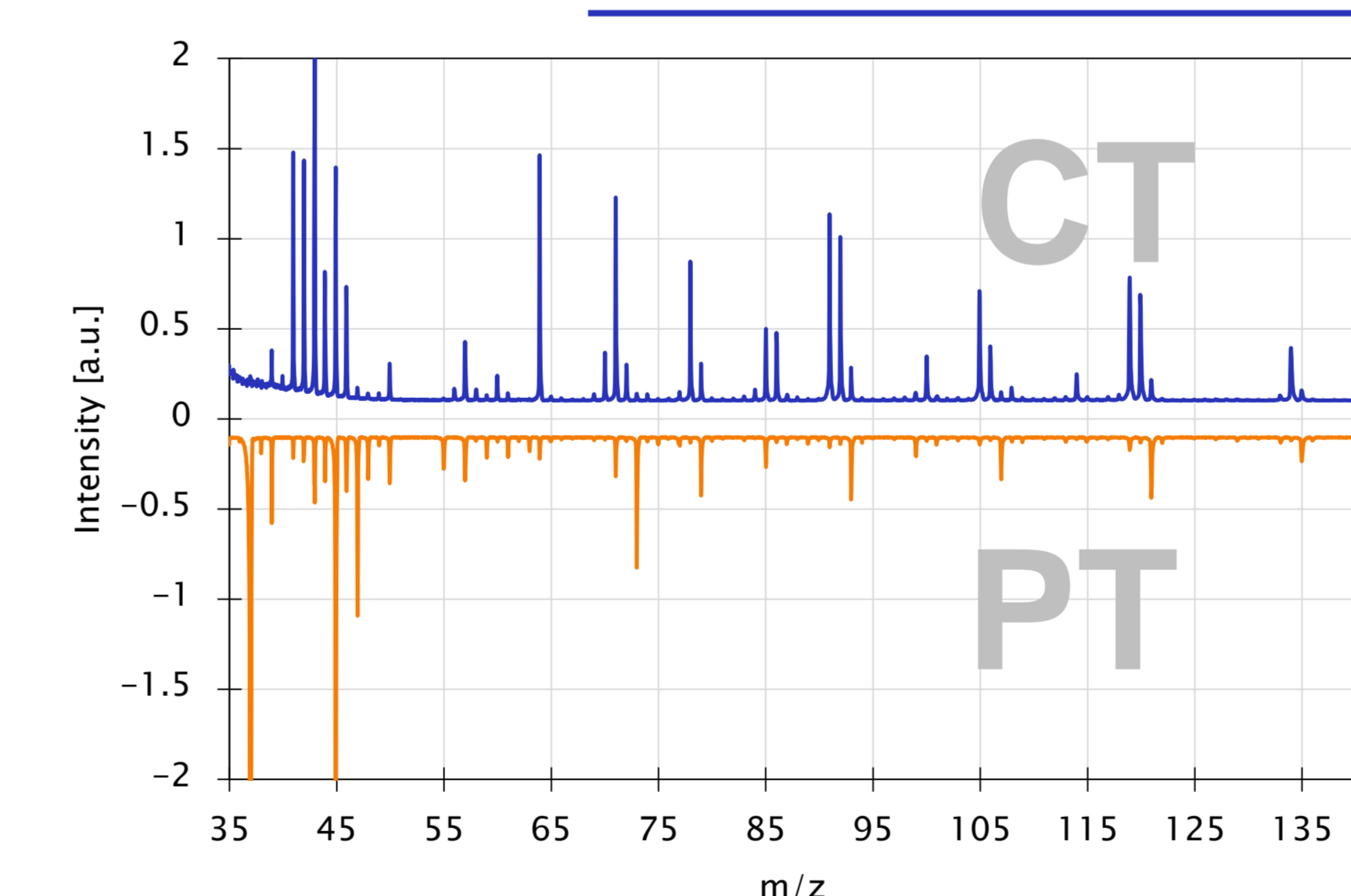
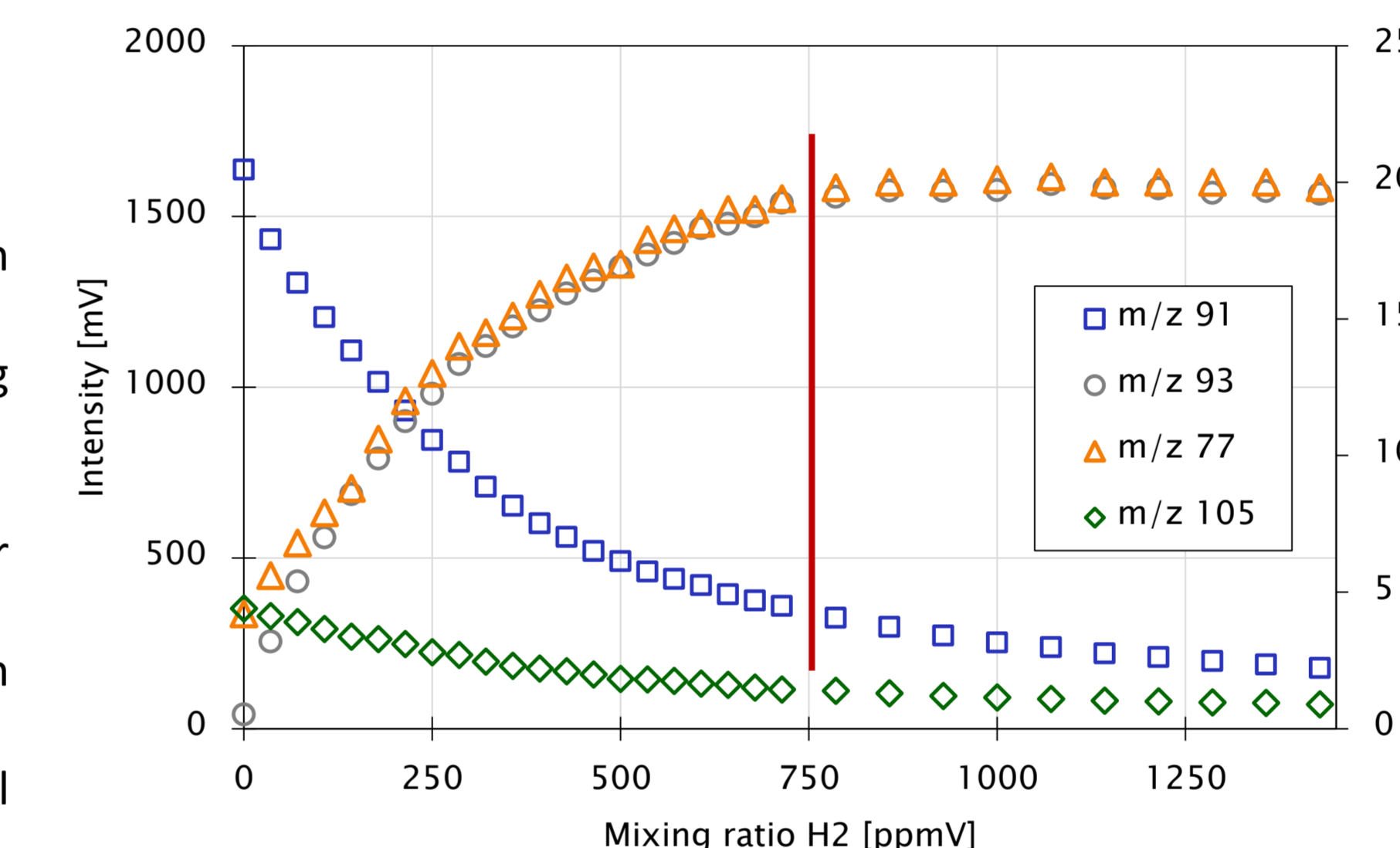


Figure 4: Mass spectra of a mixture of volatile organic compounds (VOCs) in synthetic air; top: ionized via charge transfer; bottom: with 750 ppmV H_2 present; VOCs are present at ppbV mixing ratios

- In CT mode most of the VOCs show two or more ionic species around the radical cation (e.g. M^+ , $[M-H]^+$, ...)
- In PT mode the spectrum is far less congested
- Most species appear as $[M+H]^+$
- In both modes all compounds present in the mixture are identified

Proton Capacity

- For analytical applications it is necessary to ensure a large proton capacity which allows to quantify
 - multiple compounds at the same time
 - trace compounds in the presence of large excess amounts of other analytes
- To determine the proton capacity the extent of protonation of Xenon is measured while increasing the mixing ratio of Toluene
 - 10 ppmV Xenon/Krypton in N_2
 - 10 ppbV to 400 ppmV Toluene
- Over the entire range the ratios Xe/XeH^+ and $[M-H]^+/[M+H]^+$ of Toluene are virtually constant
- Above 400 ppmV Toluene it appears as if the Xenon signal decreases slightly
- The $[M+H]^+$ signal of Toluene exhibits a linear response over the full range spanning 5 orders of magnitude

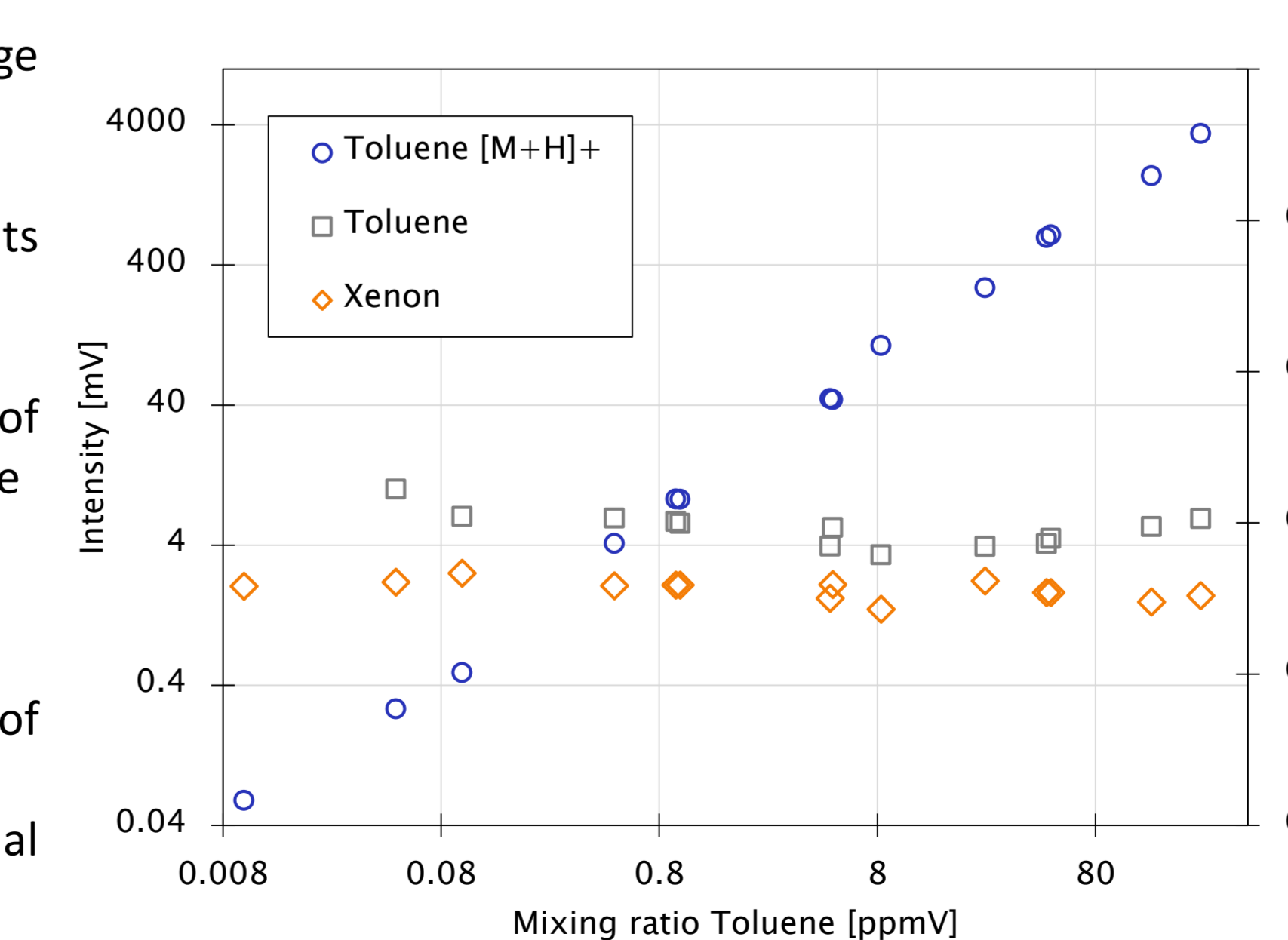


Figure 6: CT/PT ratio of Xenon at increasing mixing ratios of Toluene

Conclusions

Instrumentation:

- New powerful ionization source fully compatible for operation with a ToFwerk CTOF for PT-MS measurements
- "T-piece" geometry allows the separation of primary plasma, reagent ion formation and analyte ionization region, respectively
- Implementation of a GC-capillary leads to better protonation degrees but decreased sensitivity
- The protonation capacity of the source allows to fully protonate more than 400 ppmV analyte without observing competitive reactions

Mechanism:

- With Kr/Xe in He as analytes it is unequivocally demonstrated that the primary proton carrier must be either H_3^+ , HeH^+ , or H_2^+
 - It is speculated that HeH^+ and H_2^+ are short-lived intermediates and do not leave the "T-piece" chamber
- Ionization in PT mode leads to less fragmentation as compared to CT mode

Outlook:

- To minimize the Helium consumption, N_2 as bath gas is currently investigated (formation of N_2H^+ as highly acidic reagent ions)
- Further improvements of the geometry with focus on replacing the GC-capillary
- Investigations on the proton capacity at analyte mixing ratios exceeding 400 ppmV
- Measurements of atmospheric degradation reactions in the gas phase
- Investigations at strongly elevated water mixing ratios since water clusters represent a sink of protons

Literature

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