

Characterization of an improved PTR3-TOF mass spectrometer for the detection of highly oxidized aerosol precursors

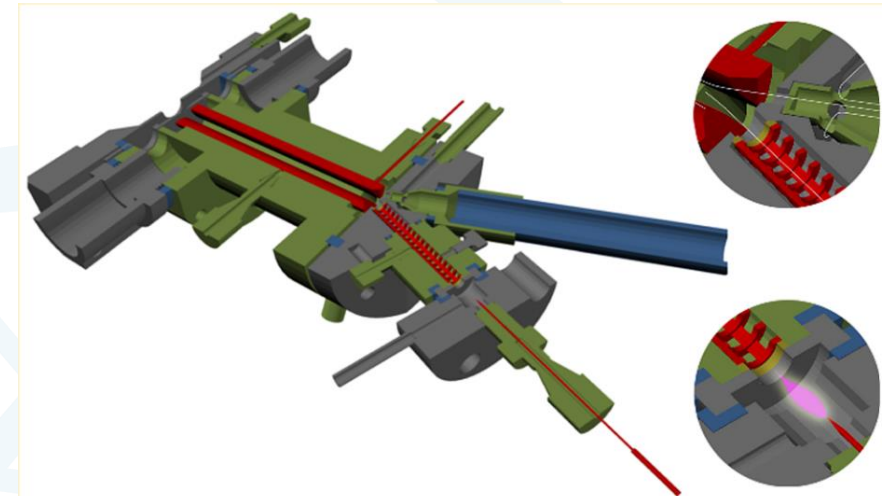
EGU 2020, SESSION AS3.1, CHAT SESSION TUE, 05 MAY, 08:30–10:15 | D3125

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Introduction I

PTR3-TOF

- ▶ **Proton-Transfer-Reaction Mass Spectrometry** is known for detecting volatile organic compounds (VOC) and their oxidation products in the gas phase and also from the particle phase (CHARON PTR-MS, see displays D3126 and D3127)
- ▶ The PTR3-TOF is a new type of Proton-Transfer-Reaction Time-Of-Flight (TOF) Mass Spectrometer developed by the University of Innsbruck, see [Breitenlechner](#) et al. (2017)
- ▶ Compared to traditional PTR-MS:
 - ▶ Elevated reaction pressure: 50 to 80 mbar
 - ▶ Increased reaction time: 3 ms instead of 100 μ s
 - ▶ Control of reaction kinetics via a reduced electric field strength (E/N) that is generated via a radio-frequency (RF) **Tripole** ion guide
 - ▶ Axial ion motion is flow dominated and decoupled from E/N
- ▶ With **mass resolution ($m/\Delta m$)** of 8000



First version of the PTR3 (Breitenlechner et al., 2017)

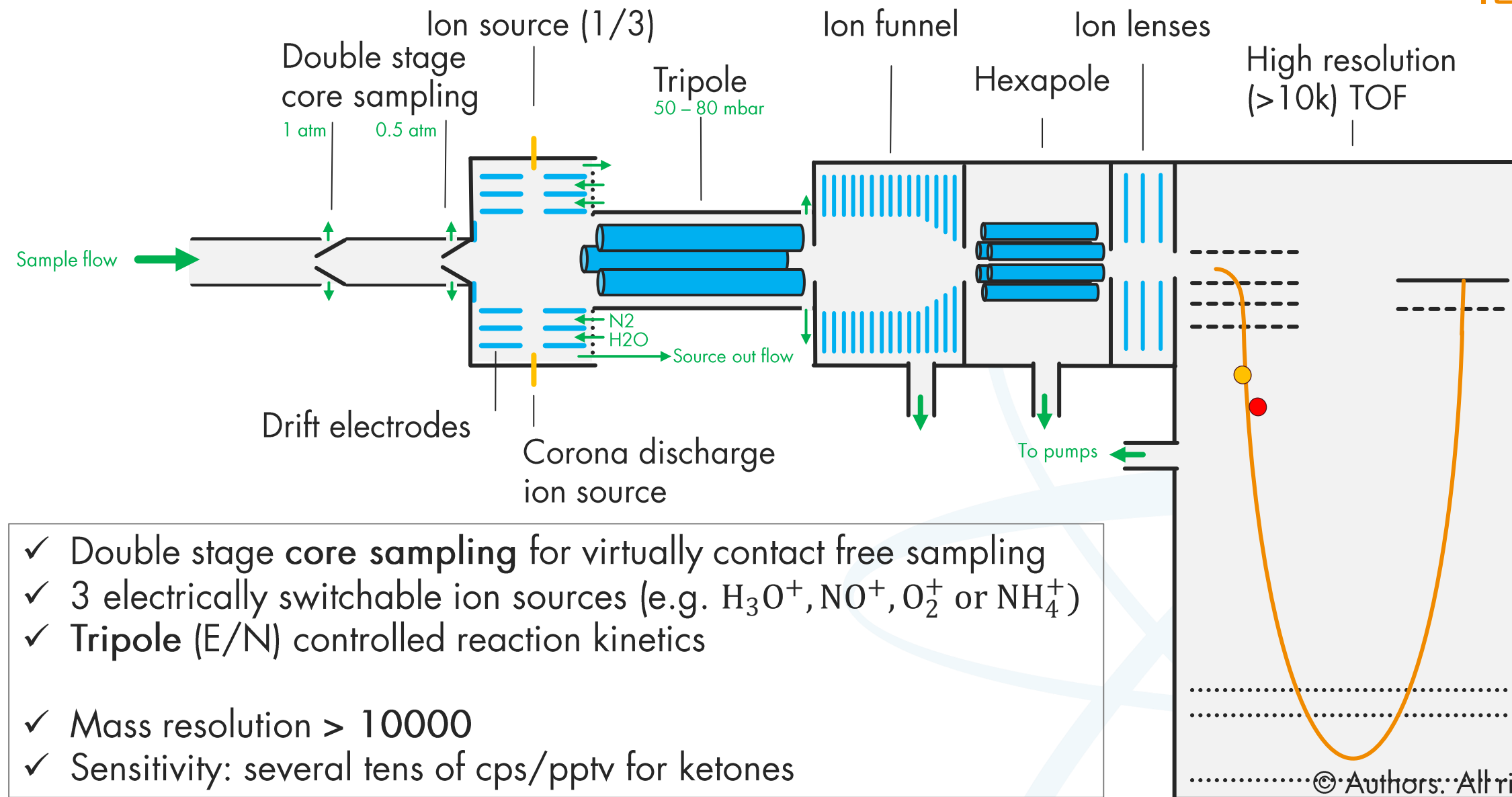
Introduction II



- ▶ The inlet is designed for virtually **wall loss free sampling** enabling the detection of **RO₂ radicals**, see [Hansel](#) et al. (2018)
- ▶ The inlet design is further well suited for the detection of organic compounds and their oxidation products in the range of volatile up to extremely low volatility (**VOC, SVOC, LVOC, ELVOC**), see Breitenlechner et al. (2017)
- ▶ We present a new PTR3-TOF mass spectrometer
 - ▶ The ion source is conceptually similar to the design by [Zaytsev](#) et al. (2019) with further modifications
 - ▶ Enhanced ion transfer via combination of ion funnel and hexapole ion guide
- ▶ We employ a high resolution time-of-flight mass spectrometer (ioniTOF 10k)
 - ▶ Mass resolution: > 10000 ($m/\Delta m$)
- ▶ Characterization of the new PTR3-TOF:
 - ▶ Mass resolution
 - ▶ Sensitivity
 - ▶ Reaction Kinetics in the Tripole

PTR3-TOF MS

Proton-Transfer-Reaction Time-Of-Flight Mass Spectrometer

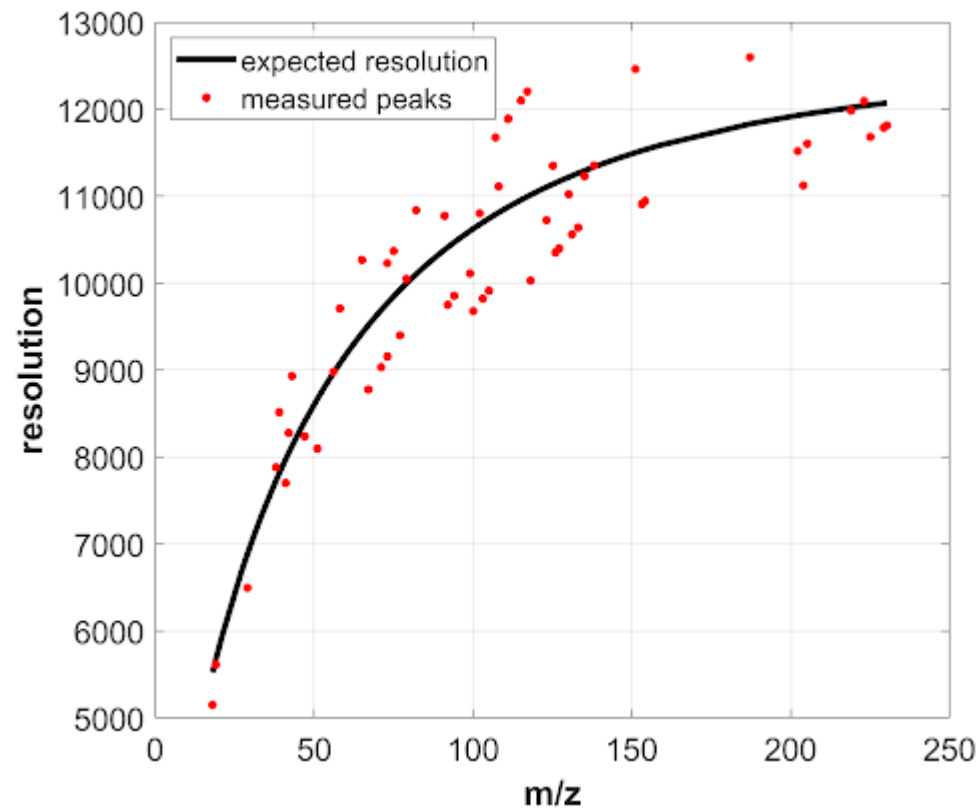


- ✓ Double stage core sampling for virtually contact free sampling
- ✓ 3 electrically switchable ion sources (e.g. H_3O^+ , NO^+ , O_2^+ or NH_4^+)
- ✓ Tripole (E/N) controlled reaction kinetics

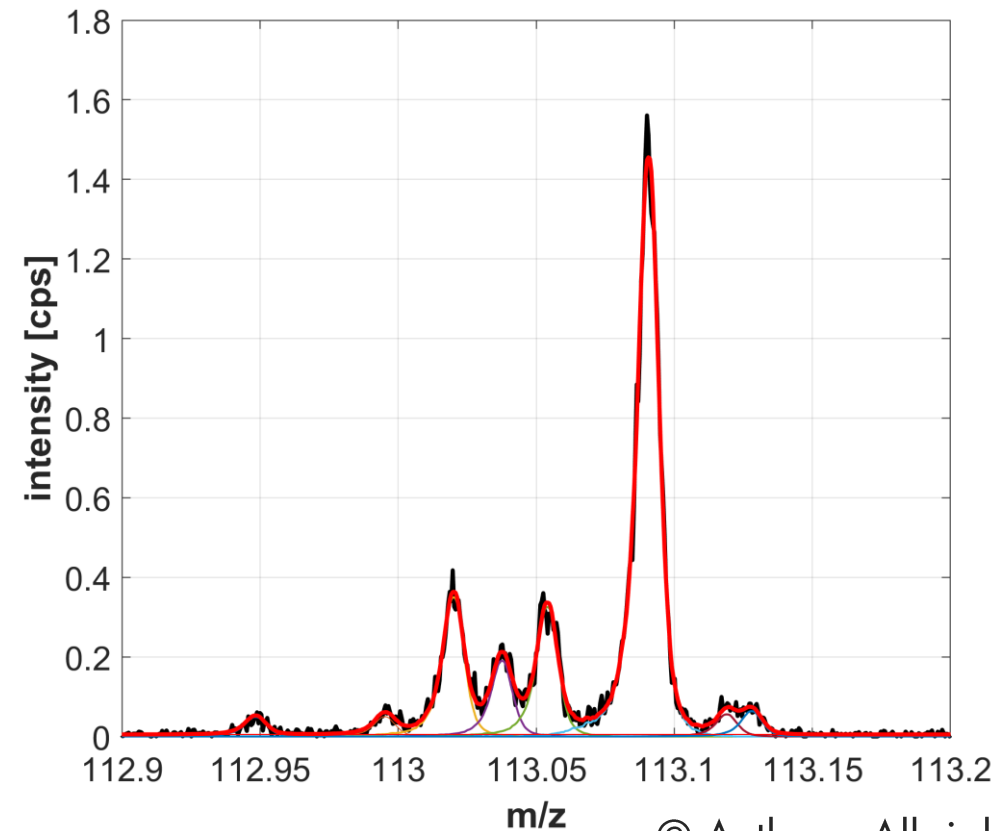
- ✓ Mass resolution > 10000
- ✓ Sensitivity: several tens of cps/ppbv for ketones

Mass resolution

- ▶ Mass resolution in FWHM of the ionITOF 10k

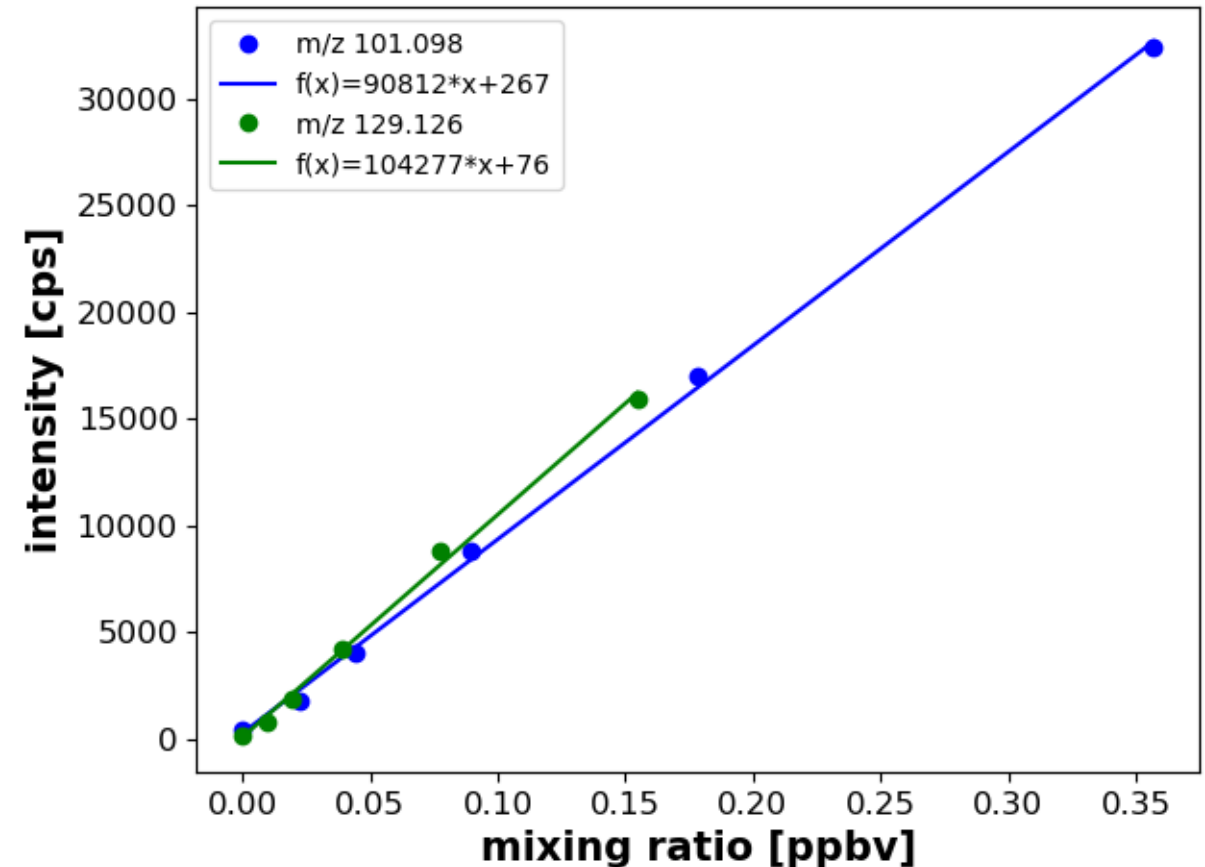


- ▶ Exemplary peak system showing 8 different peaks that are well separated with the instrument's resolving power of up to 12000 ($m/\Delta m$)



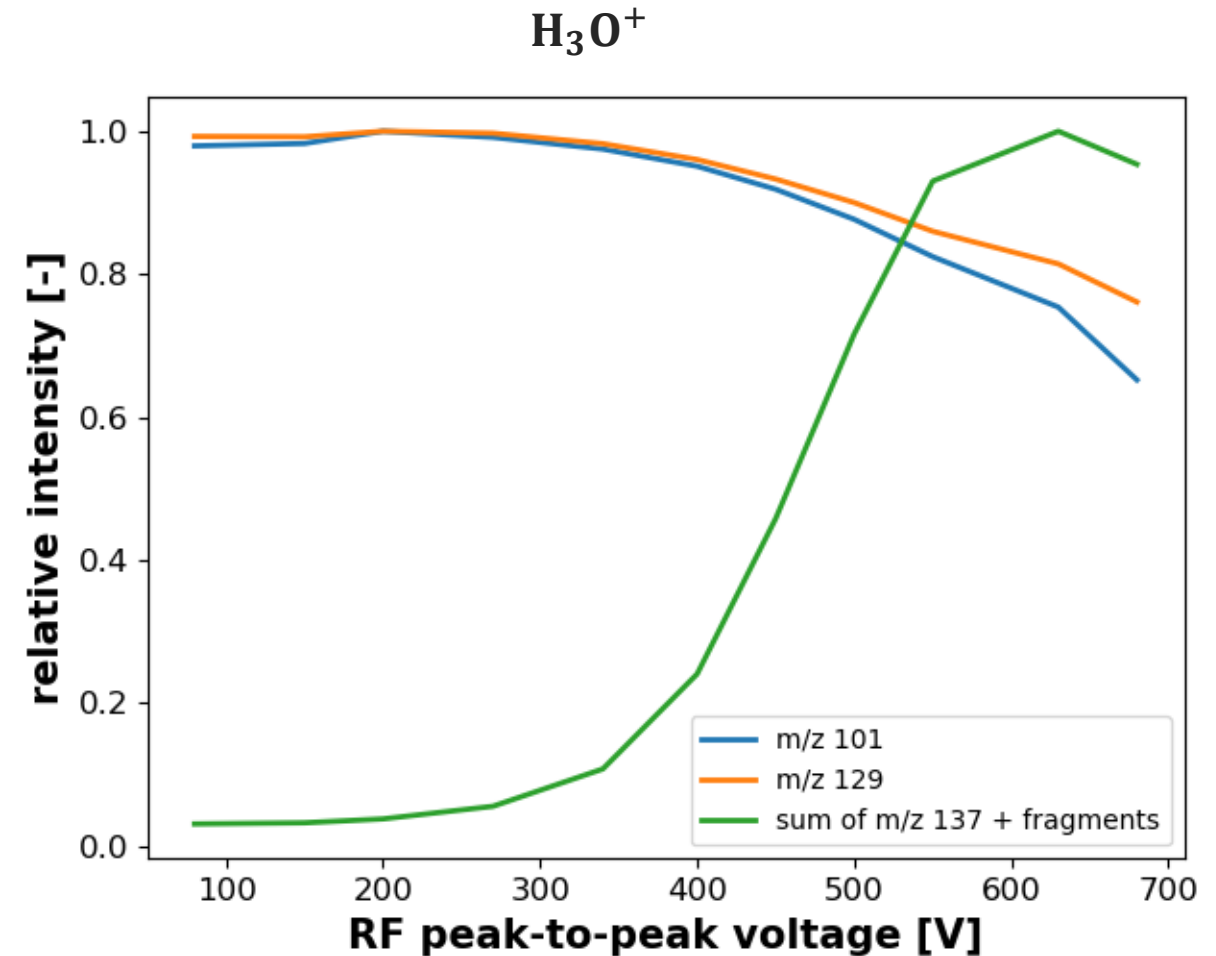
Sensitivity

- ▶ We have calibrated compounds of interest at sub-ppbv mixing ratios. The gas standard has an accuracy of 30 %. The signal intensity is given in counts per second.
- ▶ Here, we show results for hexanone (m/z 101) and octanone (m/z 129) for a mass resolution of 10000 ($m/\Delta m$).
- ▶ Experimental conditions are 26 °C and 30 % relative humidity
- ▶ We found sensitivities up to:
 - ▶ Hexanone 90,000 cps/ppbv
 - ▶ Octanone 104,000 cps/ppbv



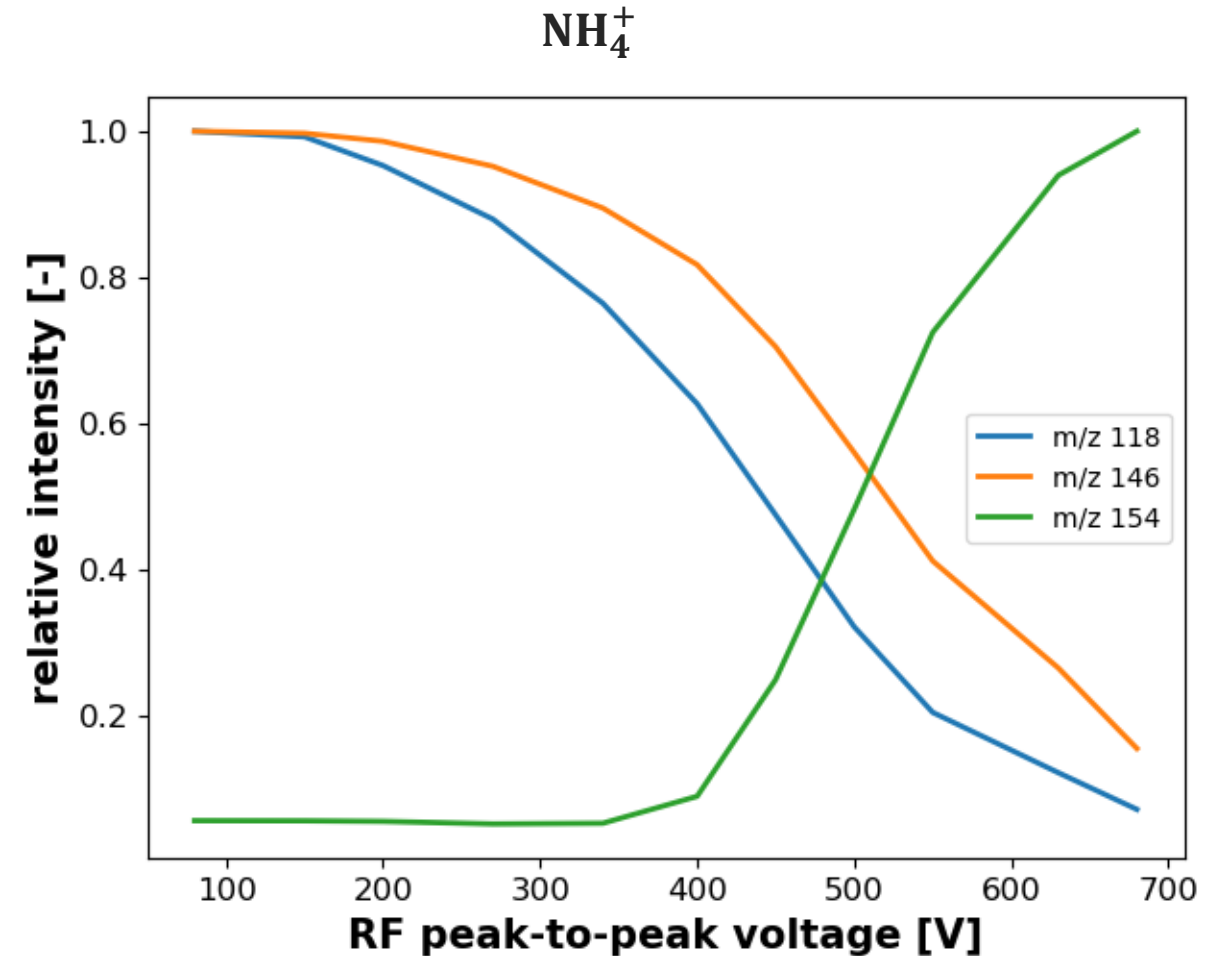
Tripole E/N scan

- ▶ Here, we run the PTR3-TOF in H_3O^+ mode at a pressure of 55 mbar in the reaction chamber
- ▶ The Tripole ion guide is operated at a radiofrequency of 7.5 MHz
- ▶ The relative intensity of hexanone (m/z 101) and octanone (m/z 129) with limonene (m/z 137, including the ionic fragment at m/z 81) varies with the amplitude of the electric field
- ▶ Ketones react with all hydrated hydronium ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_{n=0-3}$ while limonene is mainly charged with $\text{H}_3\text{O}^+(\text{H}_2\text{O})_{n=0-1}$
- ▶ The clustering of primary hydronium H_3O^+ and product ions with water molecules in the sample gas can be controlled by the radially directed electric field emitted from the Tripole



Tripole E/N scan

- ▶ Here, we scan the Tripole amplitude in NH_4^+ mode
- ▶ The experimental conditions are the same as those in H_3O^+ mode
- ▶ In NH_4^+ mode, analytes A are mainly detected as adducts in the form of $\text{NH}_4^+(\text{A})$
- ▶ We show the relative intensity of hexanone (m/z 118), octanone (m/z 146) and limonene (m/z 154) for an increasing RF amplitude
- ▶ Compared to the H_3O^+ mode, the sensitivities of ketones show a significant dependency on the E/N. Bond energies of NH_4^+ -ketones are lower and dissociate with higher E/N. Limonene has a proton affinity slightly lower than ammonia forming primarily adduct ions with NH_4^+ ([Canaval et al., 2019](#)).



Summary



- ▶ We developed a new PTR3-TOF instrument using a high resolution time-of-flight mass spectrometer.
 - ▶ Mass resolution: $> 10000 (m/\Delta m)$
- ▶ We characterized the instrument and determined **sensitivities of up to 100k cps/ppbv** for ketones, e.g. hexanone and octanone.
- ▶ We can **control the clustering of primary and product ions** in the reaction chamber via the E/N of the Tripole. This is demonstrated exemplarily for the H_3O^+ and NH_4^+ chemical ionization mode.
- ▶ Thank you very much for your interest!
- ▶ Please feel free to discuss with me during the chat at the **EGU 2020 Sharing Geoscience Online** or contact me via markus.leiminger@ionicon.com
 - ▶ **EGU session AS3.1, Chat session Tue, 05 May, 08:30–10:15 | D3125**