

## Introduction

This study focuses on detecting compounds generated by laser and/or RF-generated plasmas, which find applications in semiconductor manufacturing processes. Chemical and physical processes in such plasmas are of major interest for a deeper understanding of the dynamics of such systems. An accurate analysis and monitoring method with high temporal resolution is required to achieve this goal. For this purpose, two time-of-flight mass spectrometers (TOF-MS) were built in close collaboration with the manufacturer (TOFWerk, Thun, Switzerland).

Ultra-trace level detection (>100 ppbV at total pressures of 5 Pa and below) is mandatory. High resolution ( $m/\Delta m > 8000$ ) is required to distinguish between plasma constituents with the same nominal mass (e.g.  $m/z$  18:  $\text{NH}_4^+/\text{H}_2\text{O}^+$ )

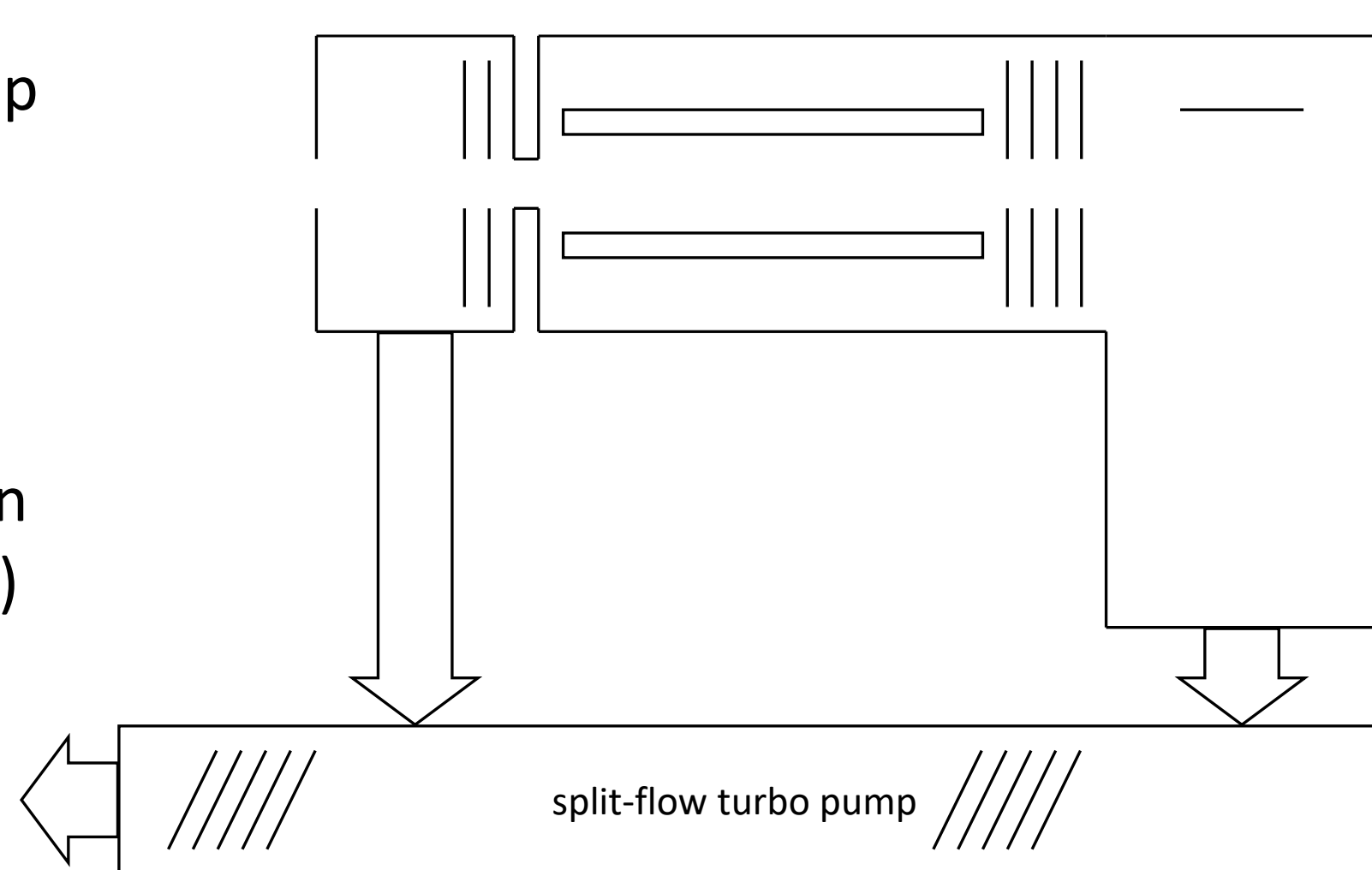
A mass analyzing system suitable for the aforementioned requirements is time-of-flight-MS. Due to the ability of recording entire mass spectra per ionization event, TOF-MS enables insight into complex ion-molecule reaction processes as they occur in plasmas.

Both TOF-MS used in this study feature orthogonal acceleration stages and allow for the event-synchronized recording of full mass spectra. The instruments can record up to 25000 spectra per second or can be synchronized with the plasma generating events, such as a laser pulse. They essentially represent two iterations for optimized ionization, ion guiding, and background signal reduction, while maintaining performance regarding sensitivity.

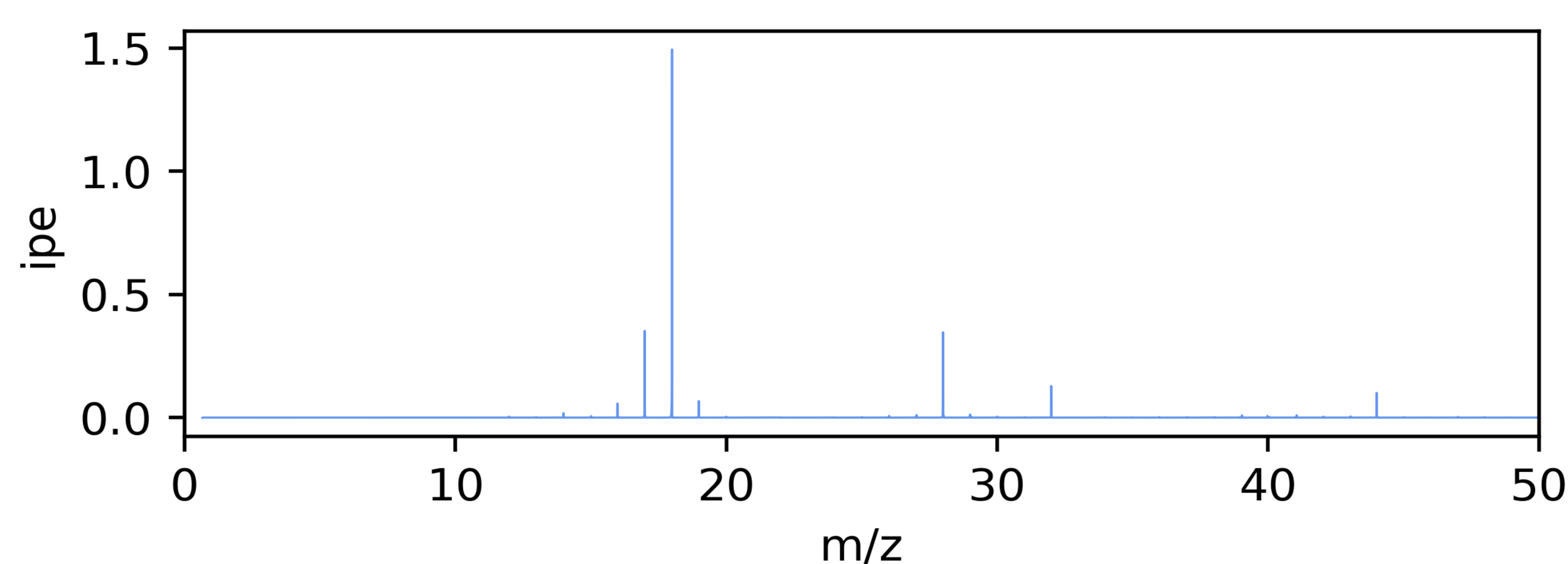
This work presents the characterization and comparison of these fundamental properties, representing a solid foundation for further applications in rather challenging environments.

## Instrument I

- Split-flow turbo molecular/scroll pump system
- Aluminum housing
- Custom ion source for EI and "ion fly-through"-mode
- Heated to max. 60 °C during operation due to sealing material (Viton O-rings)

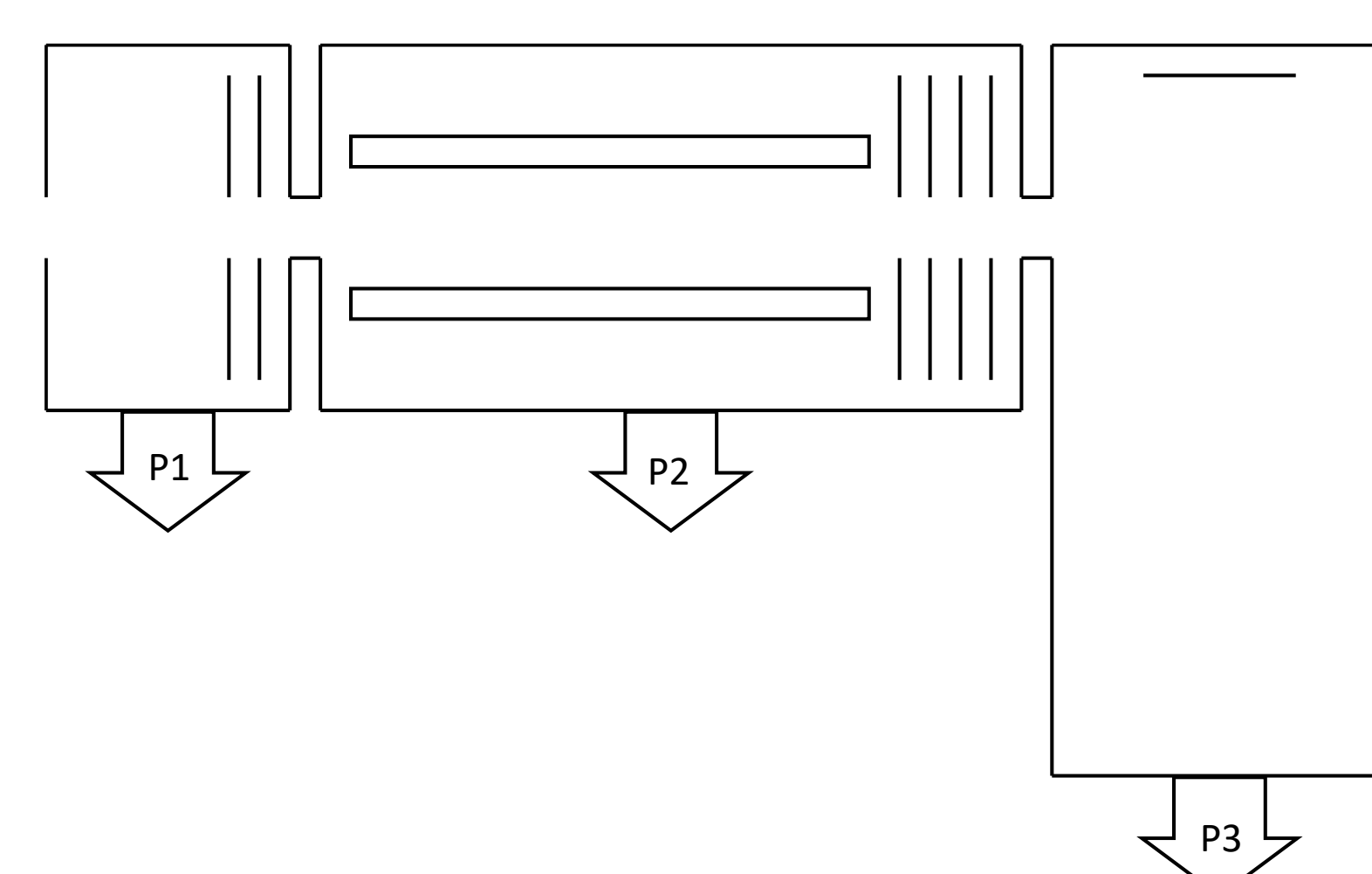


Background spectrum @  $p = 10^{-7}$  mbar, 40 V RF-amplitude

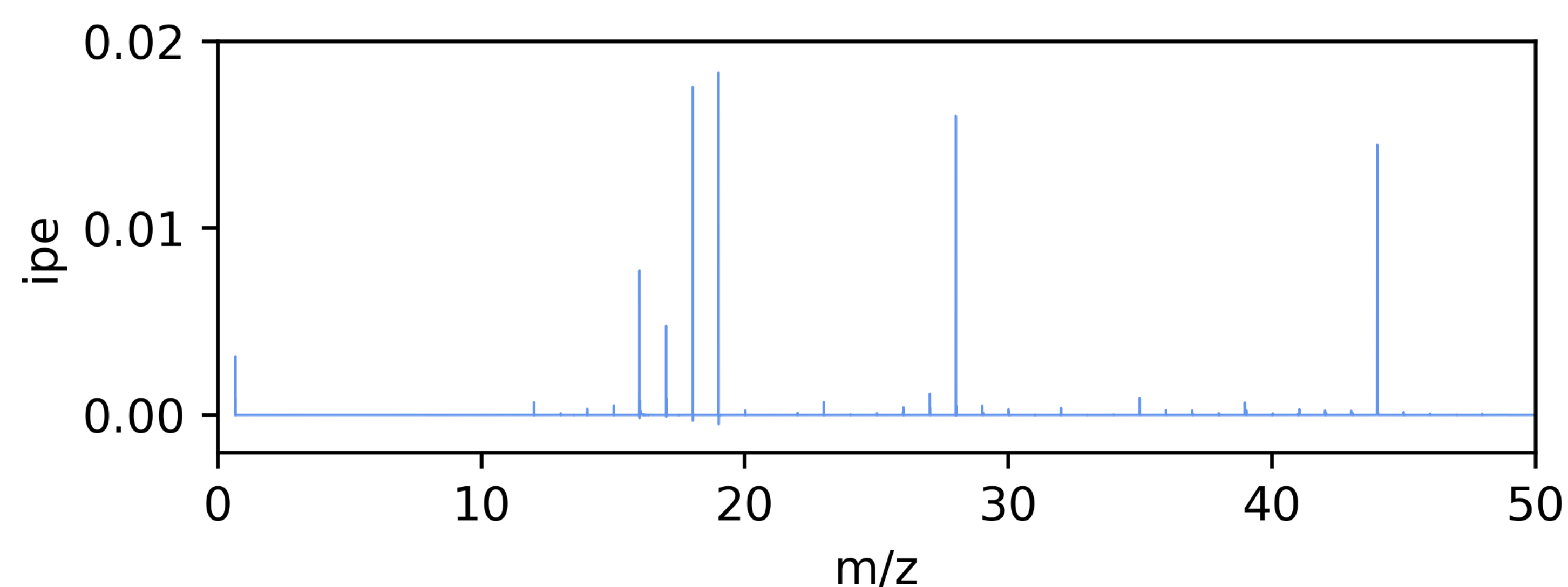


## Instrument II

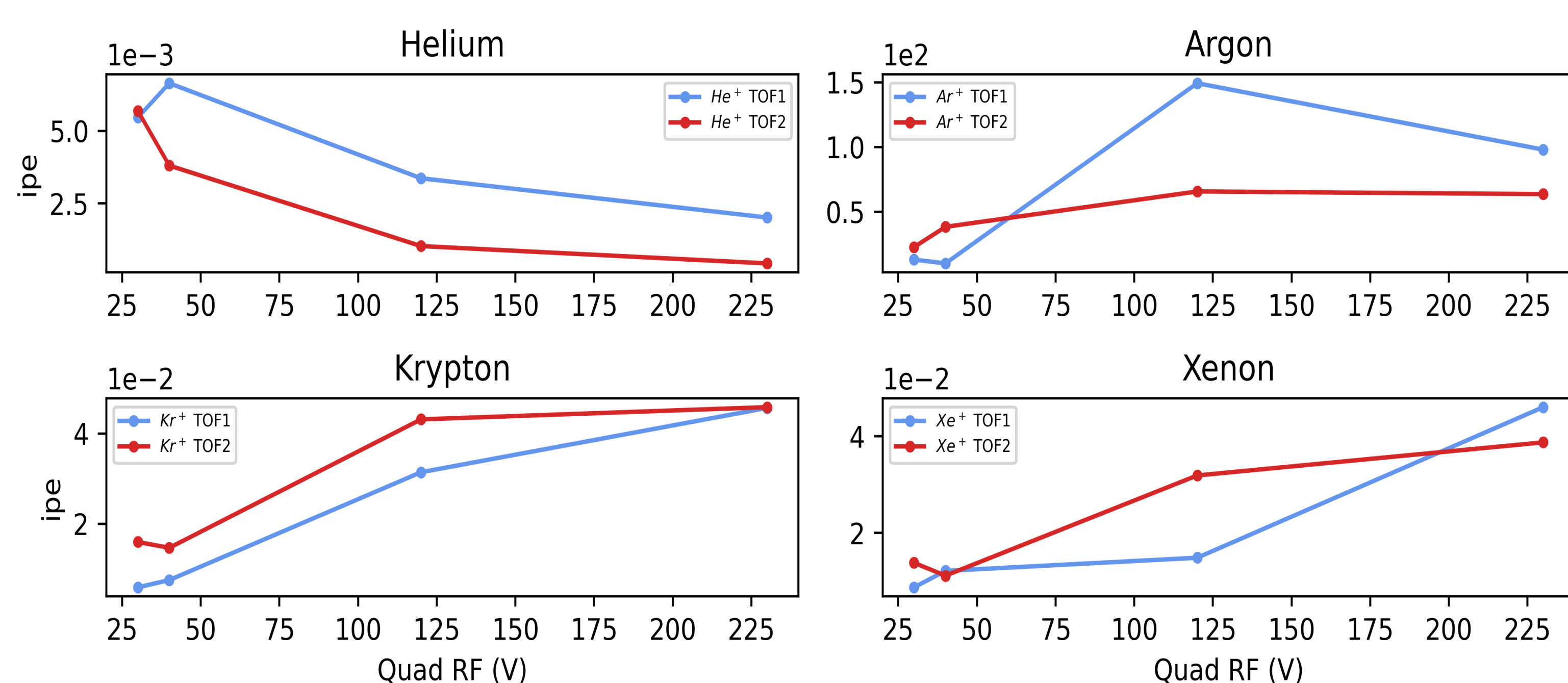
- Three dedicated pumping areas (analyzer, transfer region, ion source)
- Stainless steel ion source and transfer housing
- Custom ion source for EI/"ion fly-through"-mode
- Can be heated to 120 °C during operation
- Ion source entrance located close to the outer instrument frame



Background spectrum @  $p = 10^{-9}$  mbar, 40 V RF-amplitude

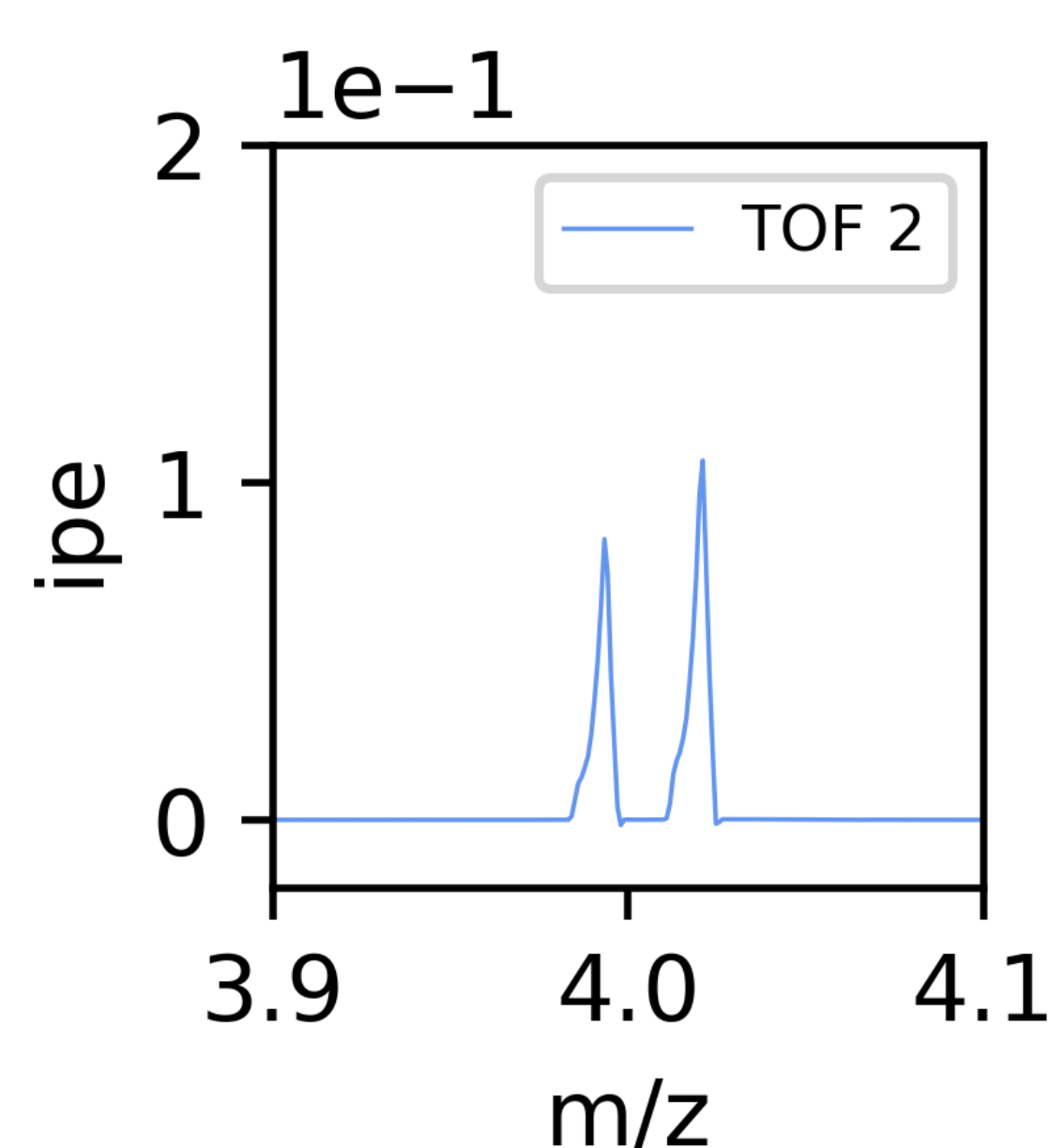


## Variation of the Transfer Quadrupole RF Amplitude



- Test gas: noble gas mixture (He, Ar, Kr, Xe; 10 ppm each in  $\text{H}_2$ )
- Characterization of transfer properties in both instruments
- According to general quadrupole theory, low masses are discriminated when applying higher RF-amplitudes, while high masses are discriminated at low RF-amplitudes. These trends are observed in both instruments.
- Despite the different transfer stage design, both MS systems exhibit similar mass discrimination behavior.
  - Deviations tend to have statistical reasons caused by the different geometry.
  - For RF-amplitudes spanning wide ranges, optimization of the lens potentials is mandatory
  - The determination of work functions for transfer properties for each instrument is now possible

## High resolution



- Separation of two peaks with nominal mass  $m/z$  4
- One peak represents 10 ppbV  $\text{He}^+$  from the noble gas mixture (exact mass = 4.002053 Da)
- The other signal arises from  $\text{DH}_2^+$  as  $\text{H}_2$  is used as matrix gas for the mixture (exact mass = 4.02943 Da)

## Conclusion

Comparative studies of the two TOF-MS systems demonstrate that measurements with high-resolution range are possible with both devices. Considering the background spectra without the addition of analyte gas, a pressure difference of two orders of magnitude (instrument I:  $10^{-7}$  mbar in the ionizer region; instrument II:  $10^{-9}$  mbar in the ionizer region) is observed.

It is apparent that the water signal in the spectrum of instrument II has decreased drastically. The lower partial pressure of water present in ion source allows the monitoring of water at ultra-trace levels, which was not possible with instrument I, as the residual background water exceeds the mixing ratio in relevant plasmas (approx.  $10^{-8}$  mbar). The recorded background  $\text{H}_2\text{O}$  signal in instrument II is about a factor of 2000 less than in instrument I, when normalized to the ionizer pressure in each instrument.

In future studies, the LODs for numerous plasma chemistry relevant compounds will be determined. Additionally, instrument II will be characterized in-depth with regard to the performance of additional externally coupled ion transfer stages for remote ion sampling, among many other figures of merit.

## Acknowledgment

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## References

- LTOF time-of-flight mass spectrometer; *Tofwerk AG, Thun, Switzerland*
- P. H. Dawson, *Quadrupole Mass Spectrometry and its applications*, Ed. 1, Elsevier (1976)
- Data from NIST Standard Reference Database 69: *NIST Chemistry WebBook*