

Elevation of the Baseline in Quadrupole Mass Spectrometers: Mechanism and Solution

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Introduction

- A pronounced baseline shift has been observed in single stage quadrupole devices
- This baseline shift reduces the limit of detection and dynamic range significantly
- Experiments and simulations were conducted to investigate the mechanism of the false positive signal and propose a solution.

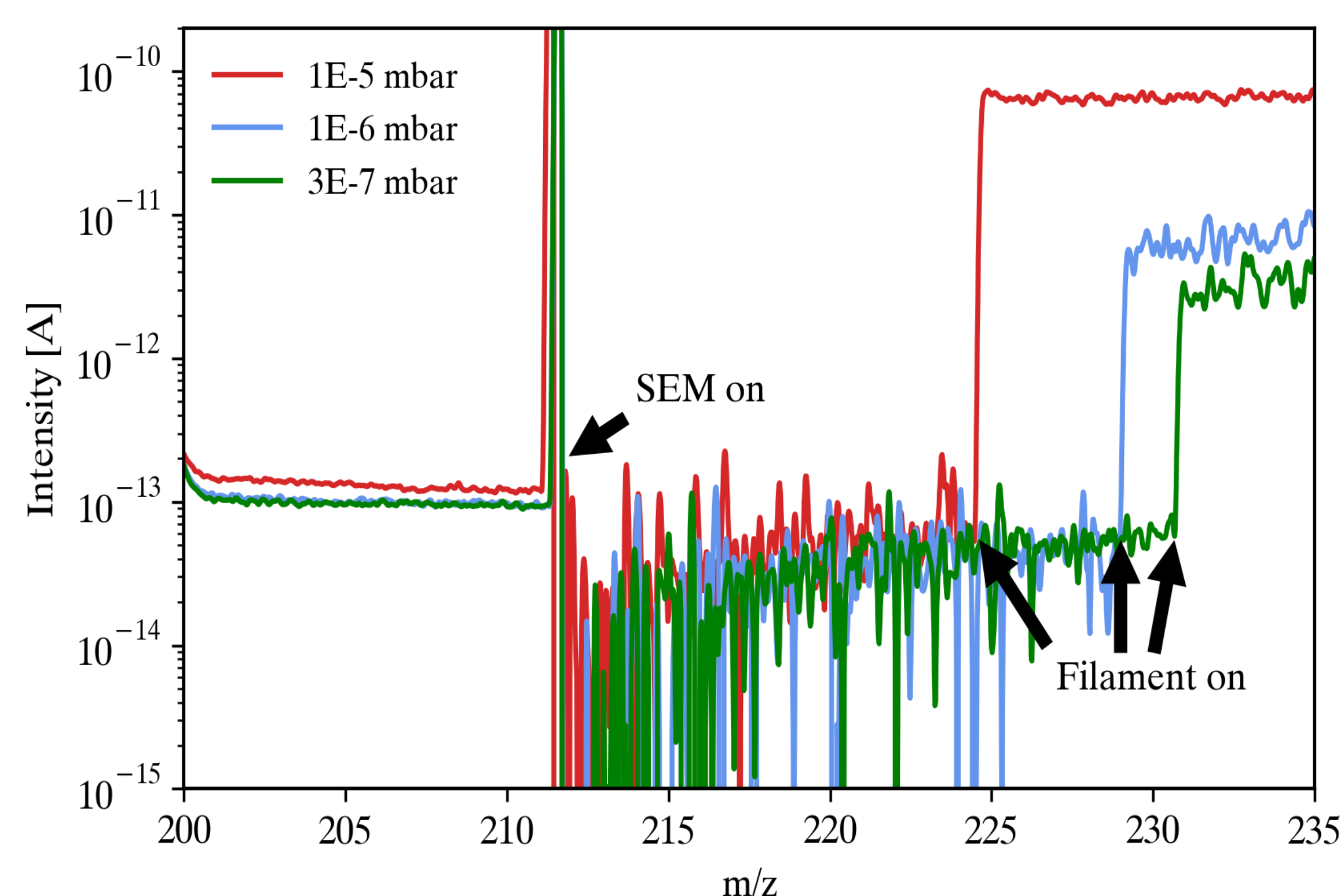
Methods

MS: QMG 422 (Inficon, Bad Ragaz, Switzerland) with 20 cm rod length and equipped with both Faraday cup and off-axis SEM detector

Ion Source: SPM source

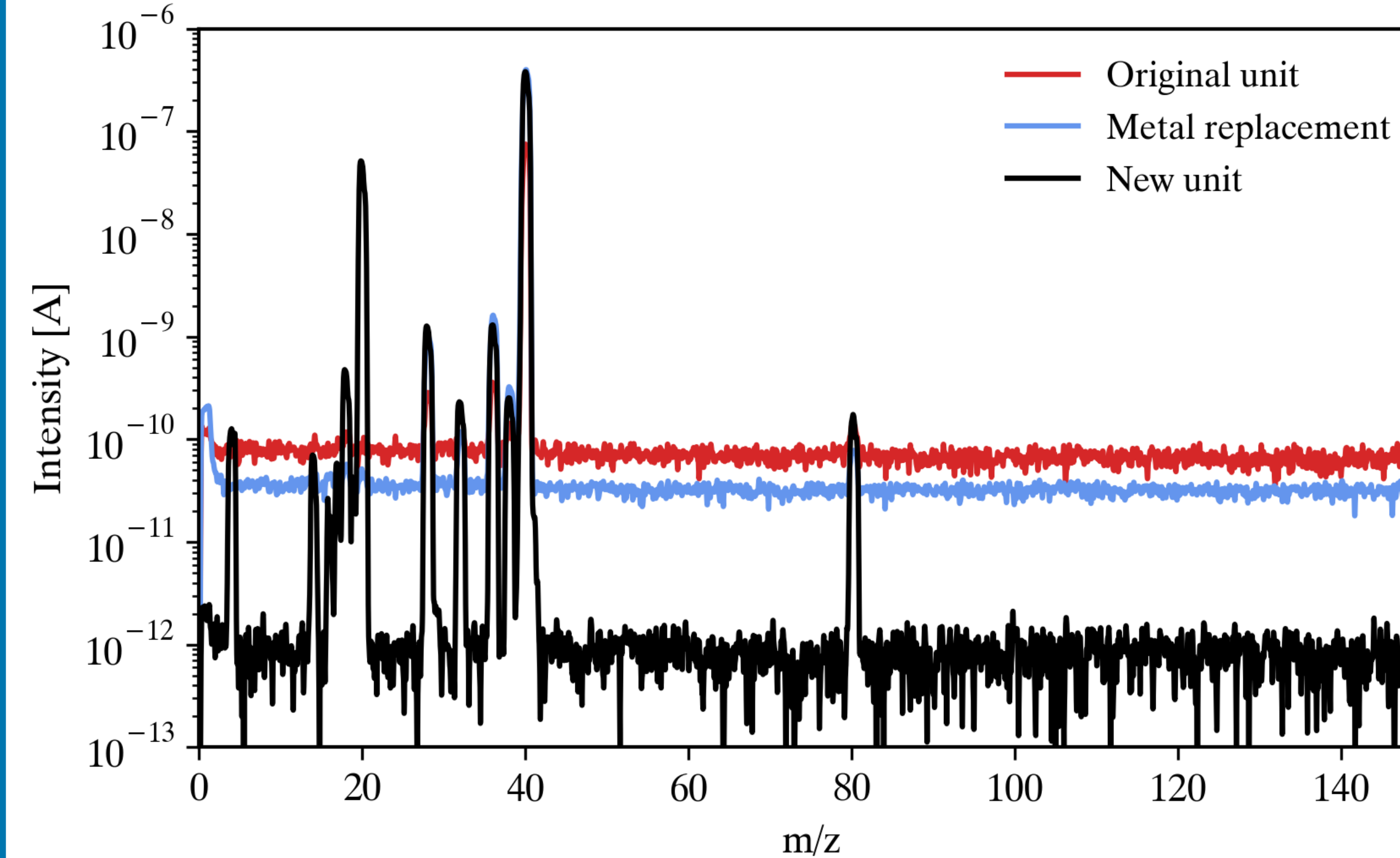
Chemicals: Argon 5.0 (Messer Industriegase GmbH, Bad Soden, Germany)

The baseline shift



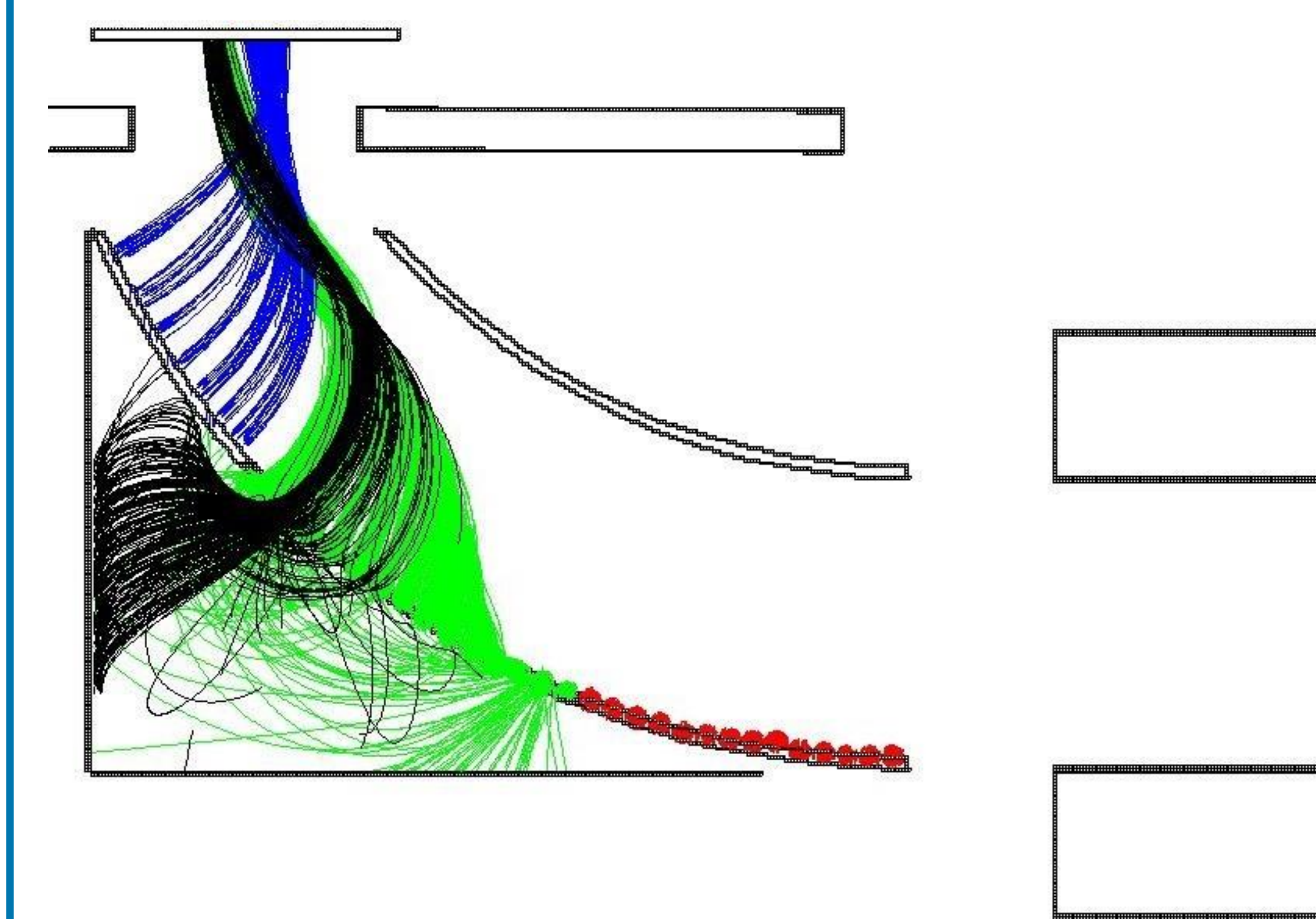
- The shift is mass-independent and is not affected by the progression of the mass scan of the quadrupole
- Potentials applied to the lens system of the ion source do not influence the level of the baseline at all
- Downstream of the quadrupole rod system the baseline is affected by electric fields

Comparison of different surfaces



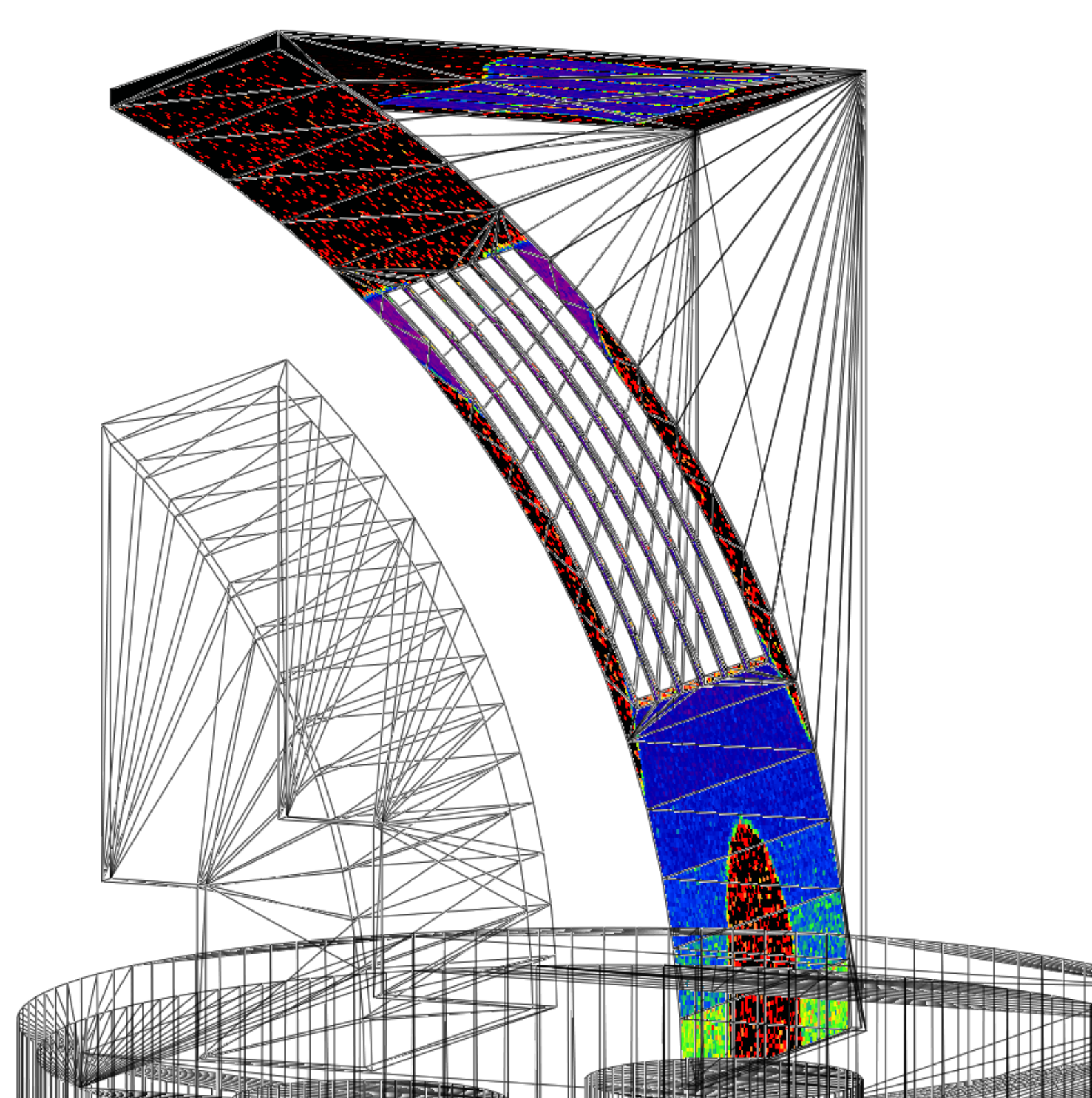
- Experiments with a) the original deflection unit, b) a metal replacement surface oriented perpendicularly to the ion beam and c) with the new unit were conducted
- A flat metal surface, replacing the original unit, decreases the elevation slightly (b)
- There is still a shift of one order of magnitude with the new unit installed (c)

Simulation^[5] of the deflection unit



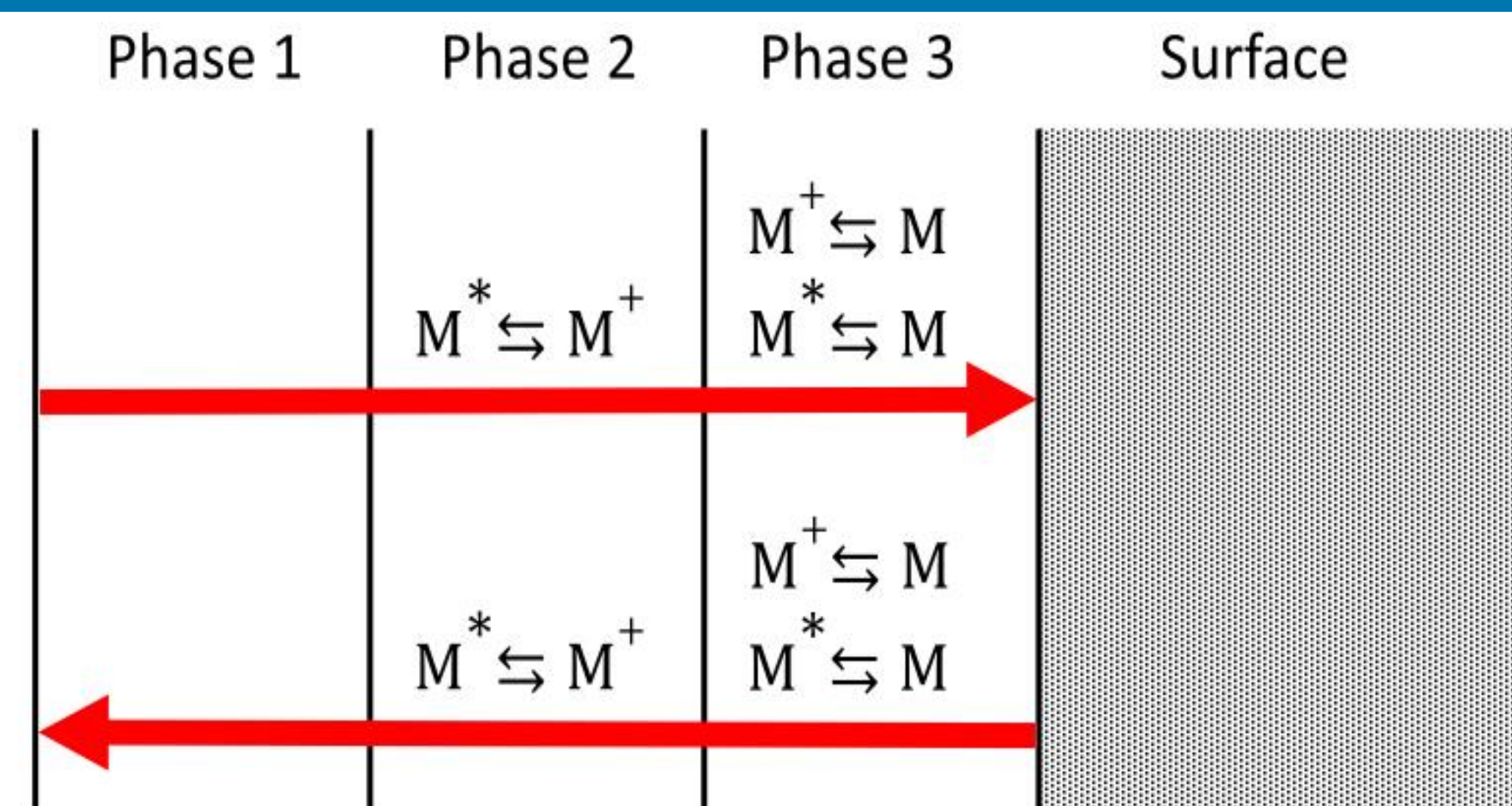
- Ions of $m/z2$ are generated at different positions of the original deflection unit
- Results are very similar to experiments with varying deflection potentials
 - Most cations reach the SEM at 0V deflection potential
 - Sharp decrease as either positive or negative potential is applied

The deflection unit



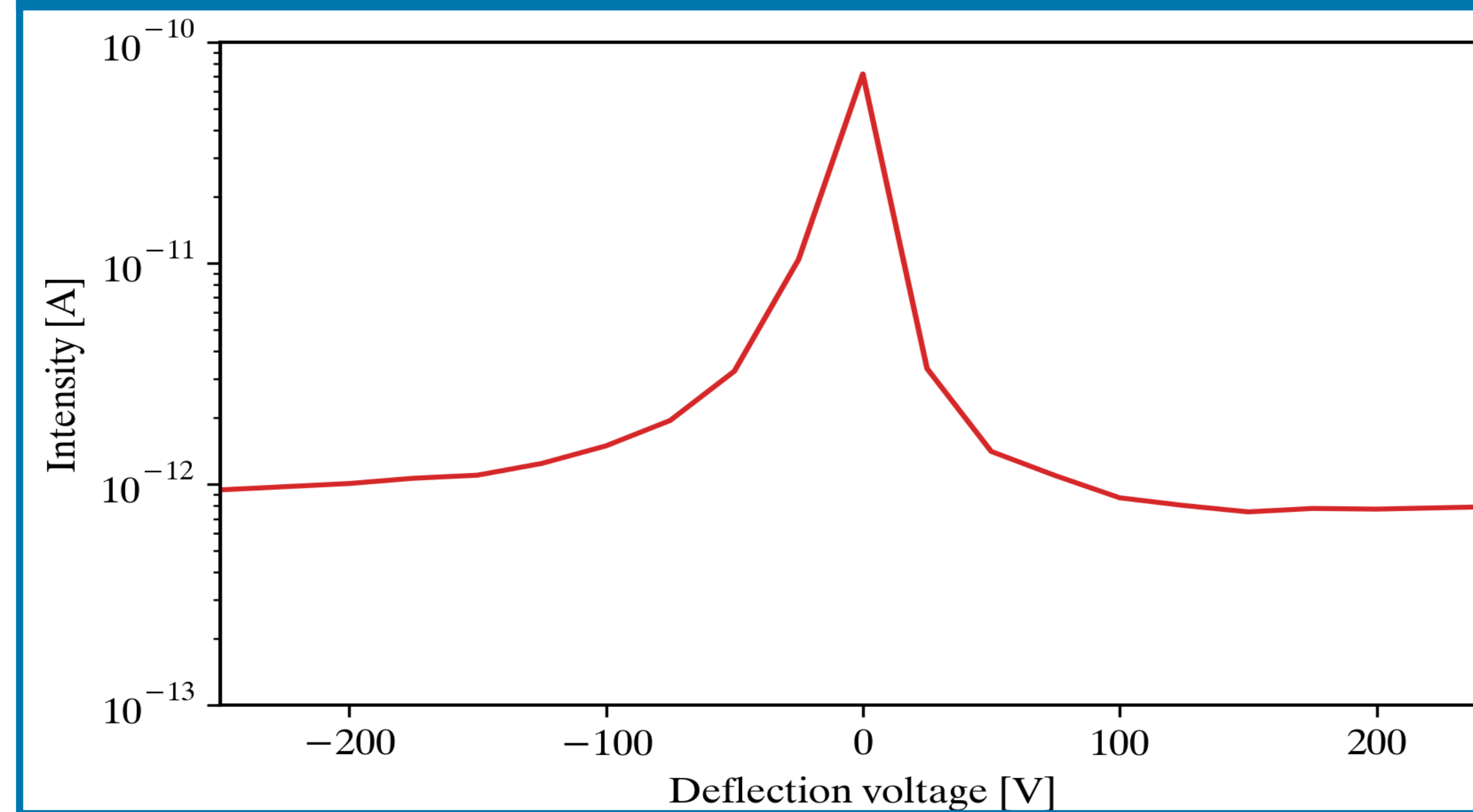
- MOLFLOW simulations^[4] of the deflection unit exhibit particle impact on the surfaces of this component.
- 0.1% of *neutral* particles leaving the ion source reach the deflection unit
- If metastable species undergo ionization on these surfaces, they might be collected by the SEM
- Especially in the lower area, close to the rod system

Resonant Ionization



- The effective ionization energy of an excited species is reduced due to electrostatic repulsion of electrons^[1]
- As a result the potential curves for the ion and the excited levels can overlap^[2]
- If a particle in a metastable state undergoes ionization when departing from the surface, it can not be neutralized on the surface^[3]

Deflection potential



- Same effect for both polarities
- Upstream of this part of the device no potentials lead to a variation of the baseline
- Ions that make out the baseline are generated in this part of the mass spectrometer

Acknowledgment

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Literature

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- H. D. Hagstrum. "Reflection of noble gas ions at solid surfaces"; doi: 10.1103/PhysRev.123.758.
- H. Winter. "What ions experience on their way into a metal surface"; doi: 10.1007/BF01426264
- R. Kersevan Ady "Recent developments of Monte-Carlo codes MolFlow+ and SynRad+M."; doi: 10.18429/JACoW-IPAC2019-TUPMP037
- D. A. Dahl. "Simion for the Personal Computer in Reflection"; doi: 10.1016/S1387-3806(00)00305-5

Conclusion

- A mechanism is proposed for the hitherto unexplained baseline shift in single-stage quadrupole mass spectrometers
- Experiments demonstrate the ionic nature of the elevation downstream of the rod system
- The mechanism involves resonant ionization of metastable species upon interaction with metal surfaces
- An alternative deflection unit was designed to eliminate the effect nearly quantitatively
- A minor shift is still visible, which is probably caused by photons or ionizing reactions in the gas-phase