Simulation of collisional interactions of background gas mixtures with trapped ions

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Introduction

Ion traps are among the most common mass analyzers in commercial mass spectrometric instruments. Buffer gas with low molecular weight is often used in such instruments to collisionally cool analyte ions during the trapping process. In contrast, collisions with heavier background gas particles can lead to unwanted collisional excitation and even ejection of ions from the trap. In commercial setups with in-trap ionization, e.g., the Zeiss iTrap system, the presence of complex gas mixtures in the trap is inevitable.

Experimental observations of cooling and heating effects are described in the literature [1], but to the best of our knowledge there is no systematic investigation of the collisional effects of *gas mixtures* present in ion traps. In this contribution we present numerical simulations to systematically investigate these effects.

In general, the mass ratio m_{gas}/m_{ion} determines the direction of energy transfer during the collision. The energy transfer occurs usually from the lighter to the lighter particle. Therefore, three basic situations can be readily distinguished [2]:

- $m_{gas} << m_{ion}$, this leads to collisional cooling, which is essentially a damping of the ion motion. With each collision a fraction of the ion kinetic energy is transferred to the background gas
- $m_{gas} = m_{ion}$, no change of the ion kinetic energy is observed
- $m_{gas} >> m_{ion}$, results in collisional heating. The kinetic energy of the ions and thus the oscillation radius increases, which eventually leads to ion loss.

Collisional cooling is usually favorable in a QIT, which is why Helium is used as a buffer gas in conventional scanning ion traps [3]. In a trap utilizing in-trap ionization, the composition of the sample and the pressure during the ionization process affects the extent of collisional cooling and heating.

Methods

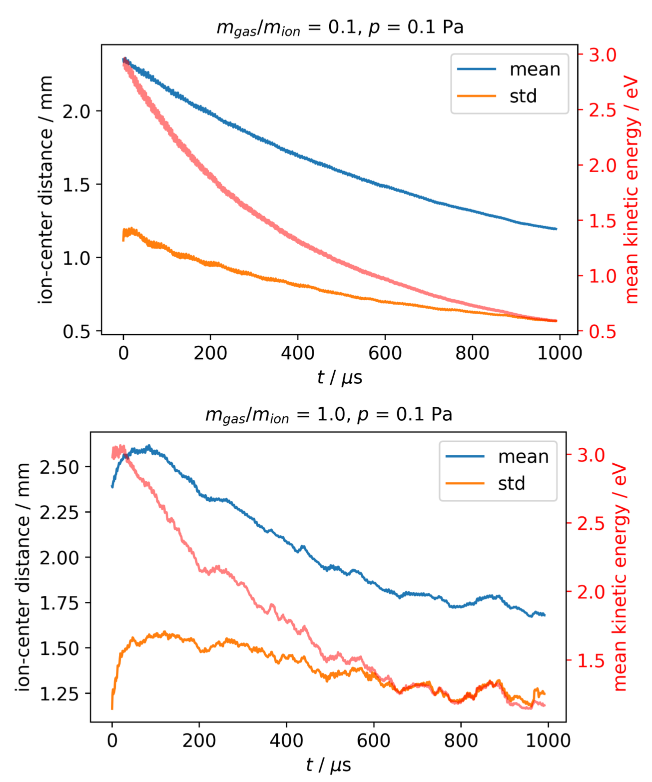
Simulations:

- SIMION® 8.1 (Scientific Instrument Services, Inc., Ringoes, NJ, www.simion.com) with hard sphere collision model (hs1)
- 3d ion trap model with temporally resolved RF field
- Ar^+ ions (40 Th) in: He (4 Th), Ne (20 Th), N_2 (28 Th), Ar (40 Th), Kr (84 Th), and mixtures of Ar and He

Data Analysis:

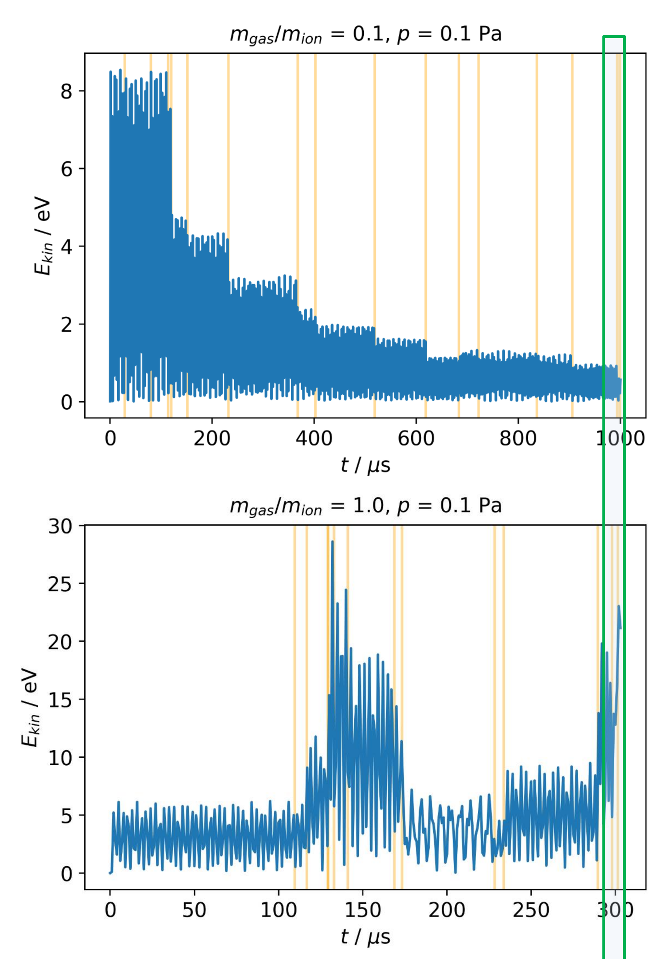
- Python 3 with numpy, pylab, scipy libraries

Collisional Cooling vs. Heating and Ion Loss



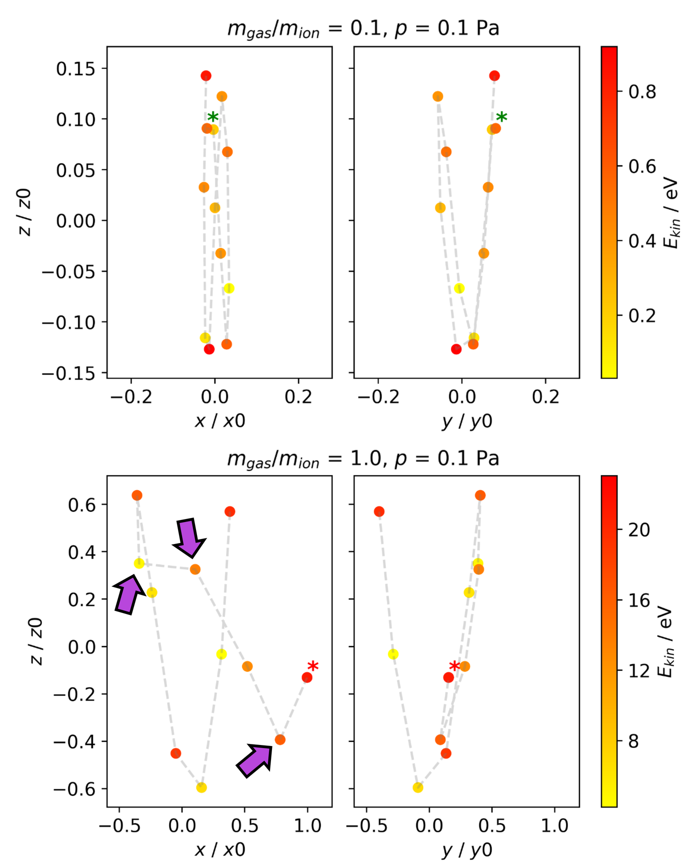
Left: Ion-center distance and mean kinetic energy over time.

- Typical collisional cooling situations ($m_{gas} << m_{ion}$,e.g., Ar^+ in He) lead to exponential damping of the ion motion, the size of the ion cloud and the average kinetic energy decreases accordingly (*top*)
- This is also observed when the background gas and ions have the same mass (*bottom*)
- The process becomes less efficient with increasing mass ratio m_{gas}/m_{ion}



Right: Kinetic energy evolution over time of single ions, the red lines indicate collisions.

- Collision induced excitation and damping of the ion motion becomes clearly discernible as sudden changes of the kinetic energy
- For higher mass ratios collisions are more likely to lead to an increase of the ion kinetic energy
- Ion loss is preceded by a significant kinetic energy gain



Left: 2d projections of the last 12 µs of single ion trajectories with color coded kinetic energy, the asterisks mark the end of the trajectories (green: end of the simulation, red: ion splat).

- Collisions leading to ion loss are characterized by strong deflection of the ion from its original trajectory (marked by purple arrows)
- This leads to dephasing of the ions and, thus, energy uptake from the RF field

Collisional cooling:

- Energy transfer from ions to the background gas
- Occurs in most collisions because ion kinetic energy is usually larger than background gas kinetic energy

Collisional heating:

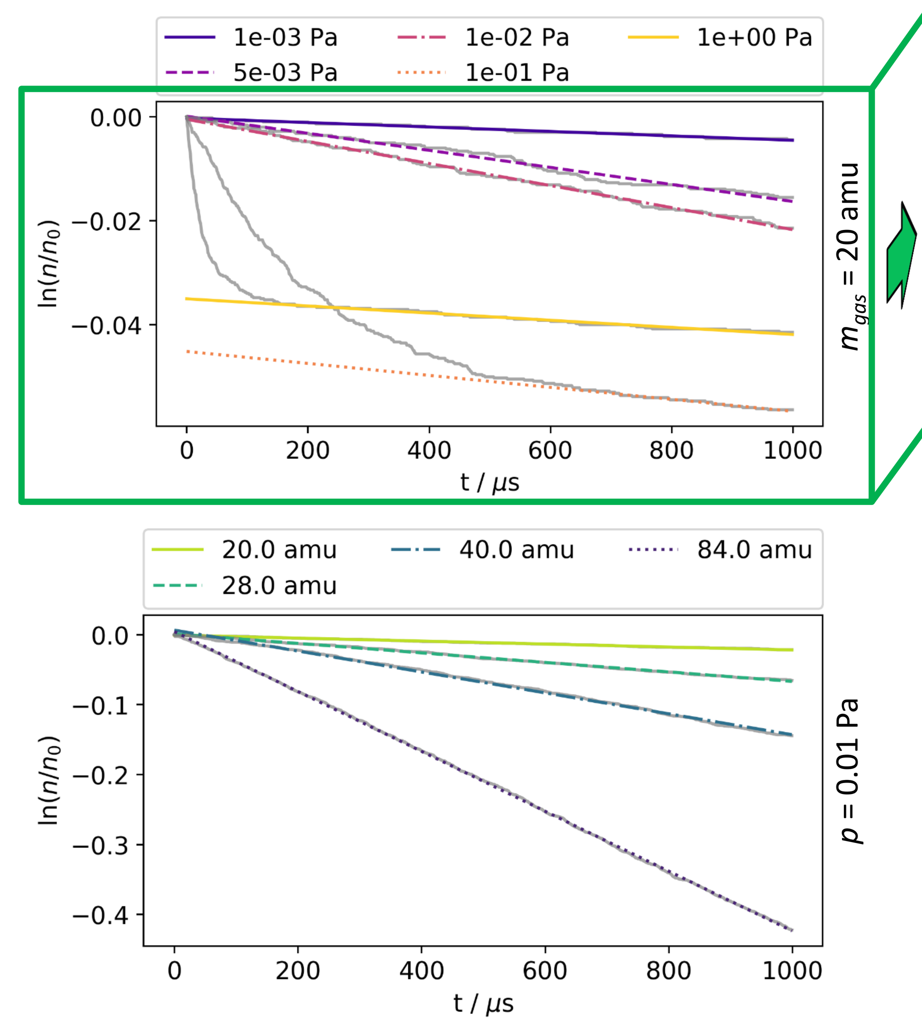
- Induced by ion scattering leading to dephasing of the ion motion from the RF field

→ Energy uptake from the RF field after the collision

Collision induced ion loss:

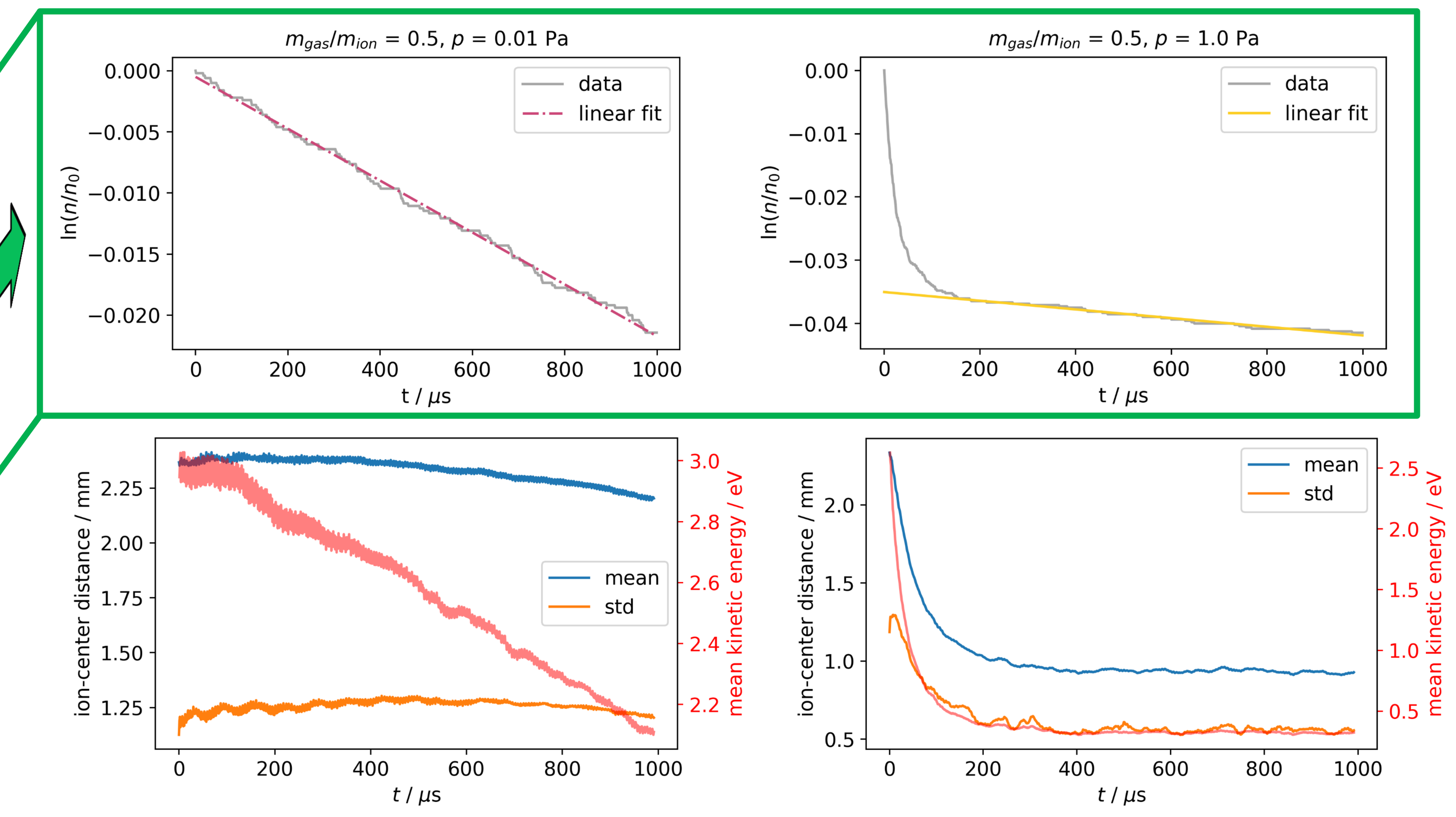
- Result of collisional heating
- Caused by discrete collision events with strong ion scattering
- Scattering near electrodes may more likely result in ion loss

Rate Constants and Lifetimes



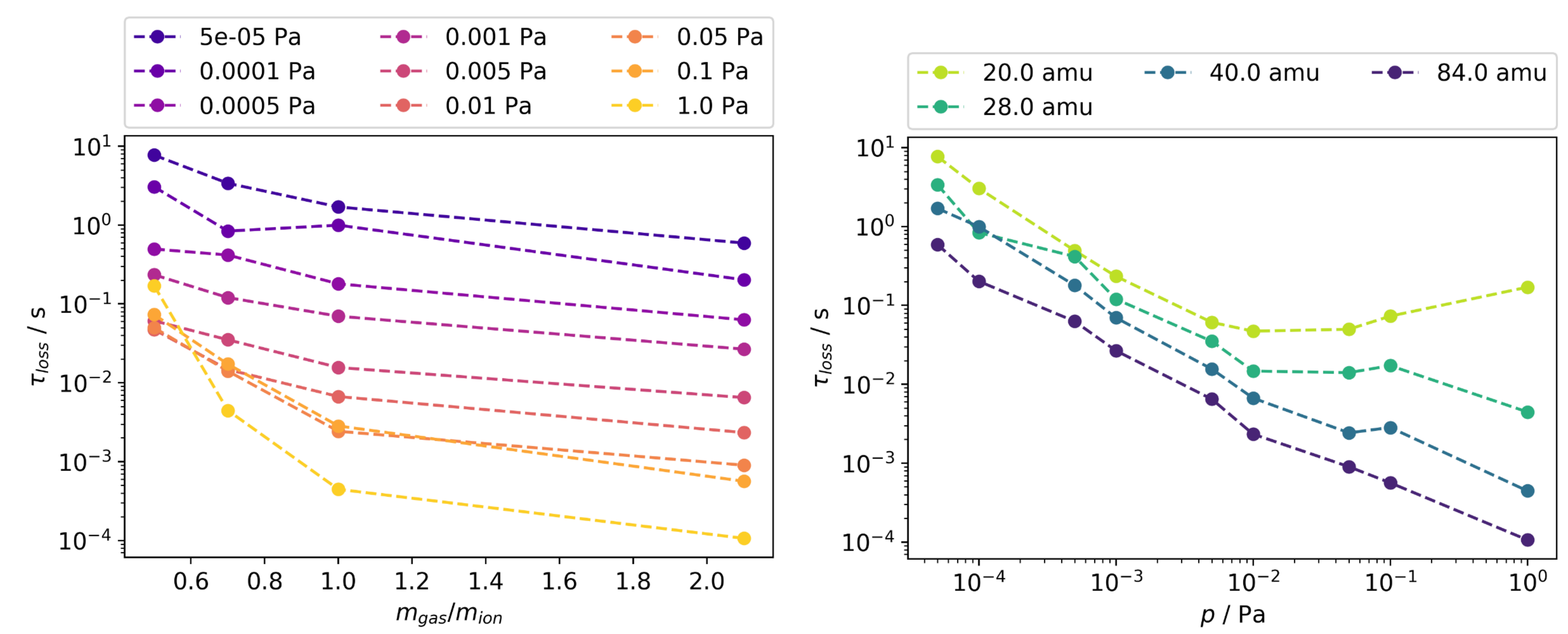
Top: Kinetic analysis for m_{gas} = 20 amu (*top*) and p = 0.01 Pa (*bottom*), data are shown in grey, linear fits are color coded

- The collision induced ion loss is a first order process at constant pressures (constant ion loss rate over time)
- At 10^{-2} Pa and below loss rates are variable with time
- Loss rates are higher for heavier background gases



Left: Investigation of variable loss rates, kinetic analysis (top) and mean ion cloud size and kinetic energy (bottom) for m_{gass} = 20 amu

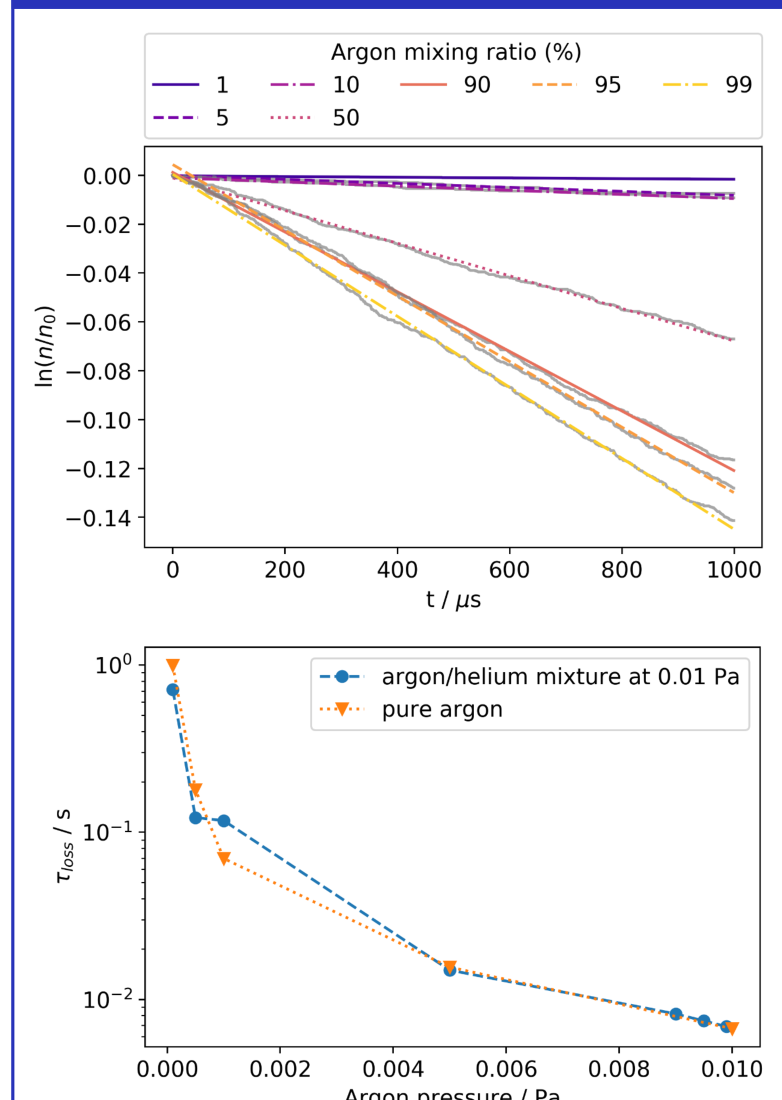
- For background pressures of 10^{-2} Pa and below the expected constant loss rates are obtained
- Above 10^{-2} Pa time dependent rates are derived from the same approach
  - → Significant collisional cooling leads to a reduction of the ion motion and thus collision rate
- Taking into account only the data after this initial phase constant loss rates are observed again



Left: lifetimes τ_{loss} ($1/k_{loss}$) for the *collision induced* ion loss in dependence of the mass ratio (*left*) and background pressure (*right*)

- Linear pressure dependency at and below 10^{-2} Pa
- The non-linear behavior at higher pressures is due to re-damping of ions after strong scattering, this effect is more pronounced at…
  - high pressures
  - light background gases

Gas Mixtures



The impact of a heavier background gas being added to ions in a light gas matrix on the lifetime of those ions inside the ion trap is evaluated.

Left: Kinetic analysis for ions in helium/argon mixtures at different argon mixing ratios, the total pressure is kept at 0.01 Pa, data is shown in grey, linear fits are colored (*top*); ion loss lifetimes τ_{loss} in dependence of the argon mixing ratio compared to lifetimes determined at the same pressure for pure argon (*bottom*)

- A higher argon mixing ratio leads to more collisions which result in strong ion scattering, the ion loss rate rises accordingly
- But: Lifetimes do not differ from the lifetimes determined for pure argon

→ At sufficiently low total pressures collisional cooling and collision induced ion loss are independent processes

Summary / Conclusion

The ion loss by collisions with the background gas is a first order process induced by strong deflection of ion trajectories.

- Even if the ion mass exceeds the neutral gas mass by a factor of two, collisions may lead to ion loss
- Ion lifetimes scale linearly with the background pressure, if the mean ion cloud size does not change significantly
- Collisional cooling leads to a decrease of the ion loss rate, this can be forced by adding a light gas in excess

→ Ion traps operated without Helium as a buffer gas should be held at a preferably low pressure

→ For in-trap ionization a low ionization pressure is favorable to diminish ion loss

→ Light matrix gases favor efficient ion trapping at elevated pressures, but the results shown here suggest that this effect is negligible below 0.1 Pa

Literature

[1] Church, D.: Collision measurements and excited-level lifetime measurements on ions stored in Paul, Penning and Kingdon ion traps. Phys. Rep. 228, 253–358 (1993)

[2] Major, F.G., Dehmelt, H.G.: Exchange-Collision Technique for the rf Spectroscopy of Stored Ions. Phys. Rev. 170, 91–107 (1968)

[3] Brodbelt, J.S.: Effects of collisional cooling on detection. in R. E. March and J. F. J. Todd (Eds.), Practical Aspects of Ion Trap Mass Spectrometry, Vol. 1, CRC Press, Boca Raton, FL, Chapter 5 (1995)

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