Ludwig-
Maximilians-
Universität

Prospects for Ion Mobility Spectrometry at the heaviest elements

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in collaboration with SHIPTRAP / TASCA @ GSI

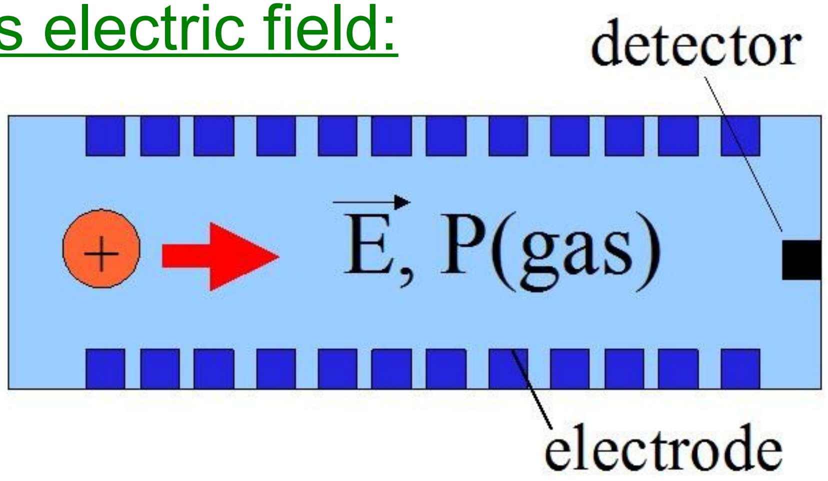
Overview:

1- Motivation & basics
2- The developed ion mobility spectrometer
3- Experimental results
4- Outlook

9th Workshop on Recoil Separator for Superheavy Element Chemistry, GSI, Darmstadt, November 18, 2010

1- Basics: (Ion drift motion & ion mobility)

Ion drift motion in gas & homogeneous electric field:



$$v_d = K(\mathrm{P},\mathrm{T}) \cdot \mathrm{E}$$

- $K_0(\mathrm{P_0},\mathrm{T_0})$ is a characteristic parameter for certain molecules/elements given in [cm²/Vs]

- Measurement conditions are given by the ratio:

$$E/n \ [\mathrm{Td}=10^{17}\ \mathrm{V\ cm^2}]$$

⇒

$$t_d = \mathrm{s}/(K \cdot \mathrm{E})$$

- characteristic time spectra
- very fast method (1/E)

v_d: Ion velocity
K: Ion mobility
s: Ion path
t_d: Drift time
K_0: Reduced ion mobility
E: Electric field strength
n: Number Density of Buffer Gas Atoms

1- Ion mobility spectrometry (IMS):

Application of IMS:

- Detection of molecules / biological materials:

explosives, drugs, hazardous chemicals, peptides, sugars, pesticides, bacteria, proteins, nucleotides, DNA, ...

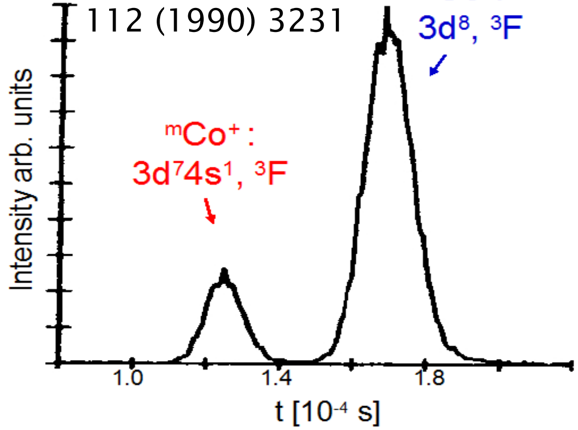
8th International Conference on IMS, 8.-13.Aug.1999

IMS in research:

- State selected ion chemistry ...
- Study of molecule-molecule interaction potentials

C. Iceman, et al., J. Am. Soc. Mass Spectrom. 18 (2007) 1196

P. Kemper, et al., J. Am. Chem. Soc. 112 (1990) 3231



M. Laatiaoui, PhD thesis, LMU (2010)

IMS @ heavy elements:

- Access to ion-atom interaction potentials of short-lived isotopes ($t_{1/2}$<1s)
- Study of molecular bond lengths
- Access to polarizabilities of heavy elements
- Study of reaction rate constants (via ATD or Ion-Rate analysis)
- Potential for studies of valence electron configuration of SHEs
- Potential for isobaric purification in stopping cells, ...

1- Basics: Ion Drift Motion

Ion drift motion in gas & homogeneous electric field:

For molecule ions (in N_2, air) => *K* almost sensitive to size / shape

For monoatomic ions (in He, Ar) => *K* sensitive to:

- mass, if ion mass << mass of gas atom
- size, if ion mass >> mass of gas atom
- both, for nearly equal masses

According to Viehland-Mason theory:

Mobility <=> Collision Cross Section <=> Ion-Neutral Interaction Potential V(r)

$$V(r) = (C_n/r^n) - (C_6/r^6) - (C_4/r^4)$$

Pauli repulsion

London dispersion &
high order contributions

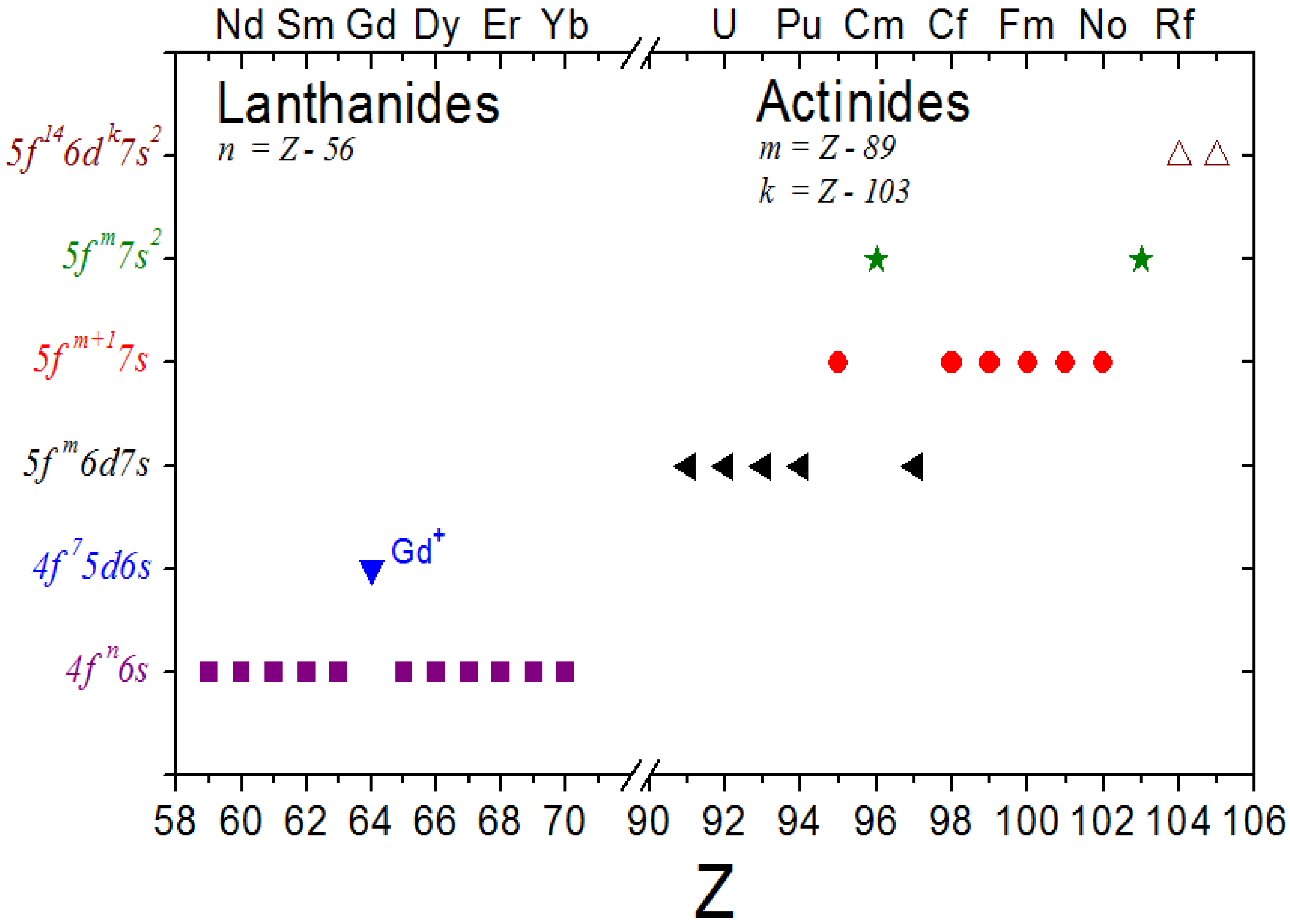
dipole attraction

C_i: Constants
r : Molecular distance
n : Fitting parameter

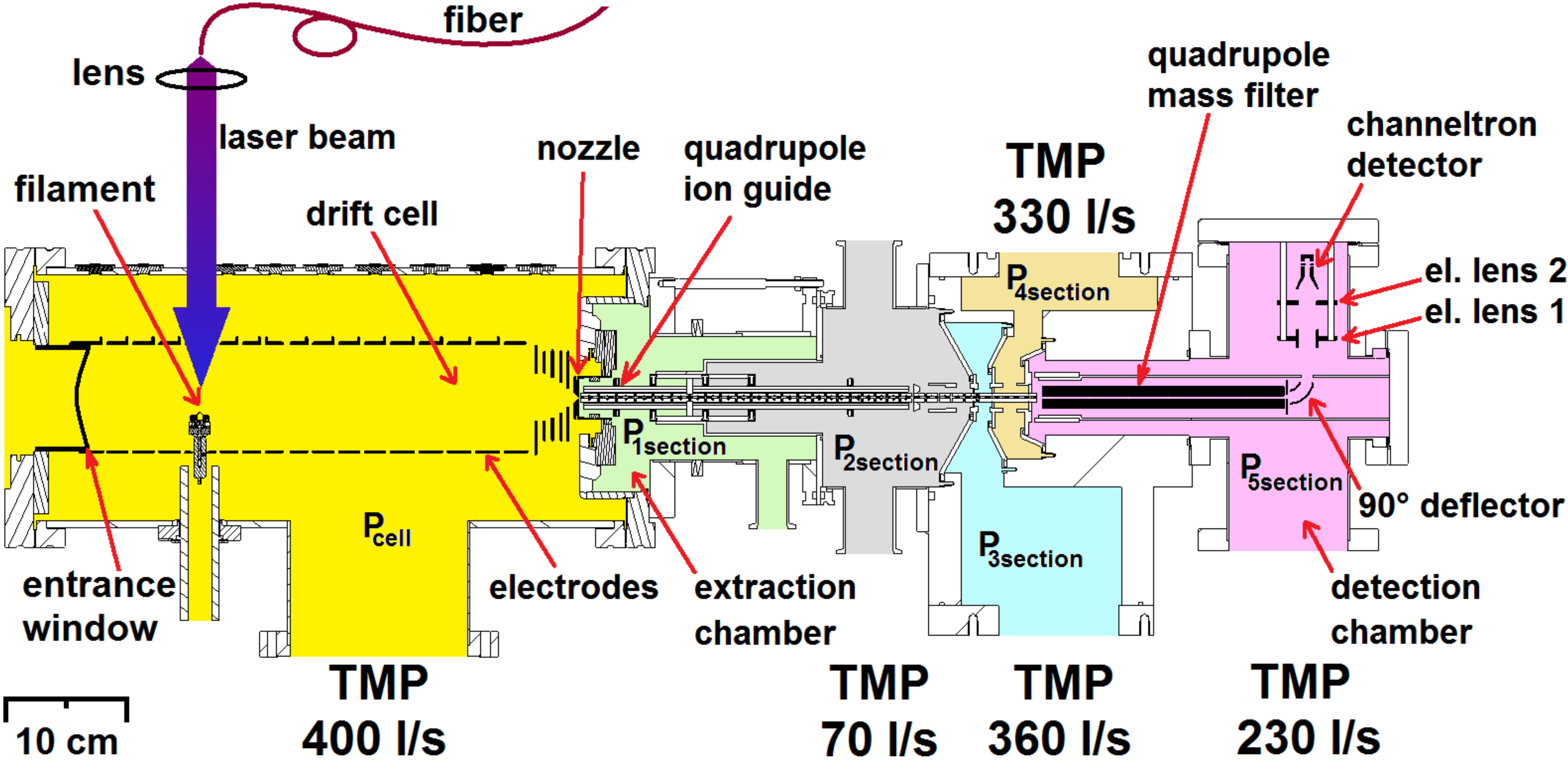
Potential for studying the impact of electron configuration on V(r) of the heaviest elements by IMS methods

1- Valence electron configuration of singly charged ions:

P. Indelicato, et al., EPJ D (2007)



2- The on line ion mobility spectrometer:



starting time: t_0

arrival time: t_a

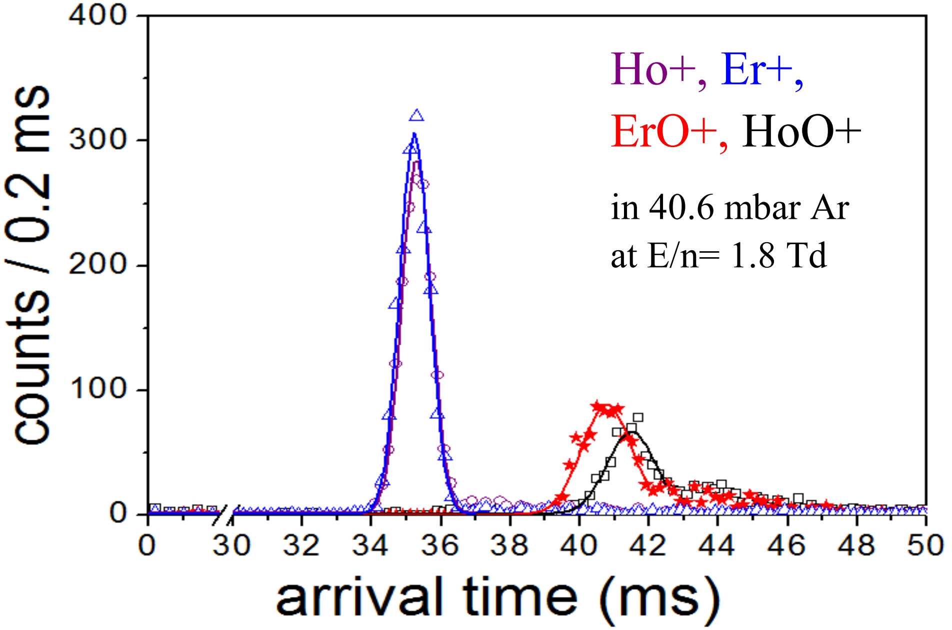
drift time: t_d >> transit time: t_t

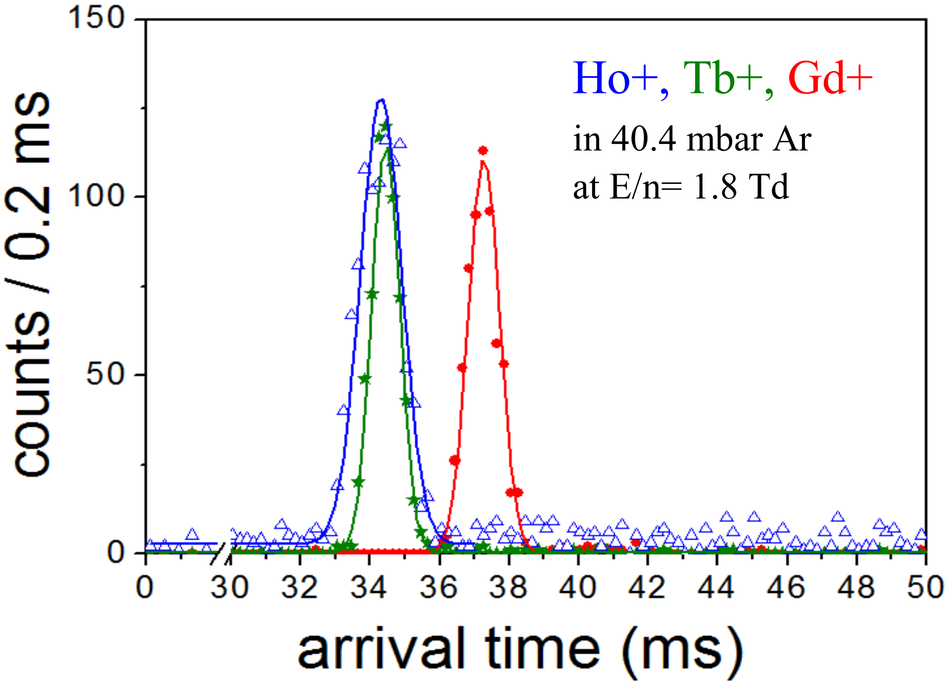
3- Experimental results (I):

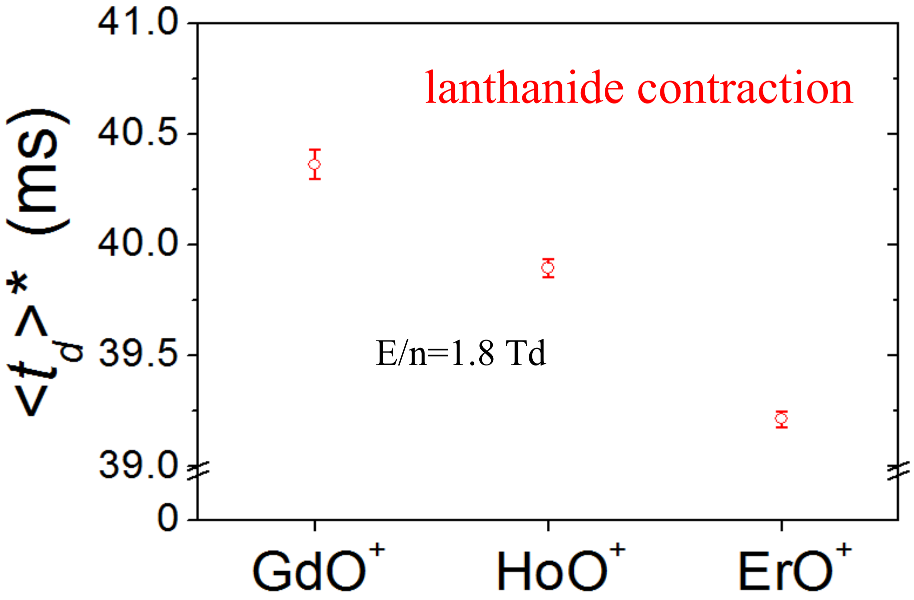
* Molecular ions are larger than monoatomic ions

=> they are detected later.

* Lanthanide oxides could be discriminated in time due to lanthanide contraction.





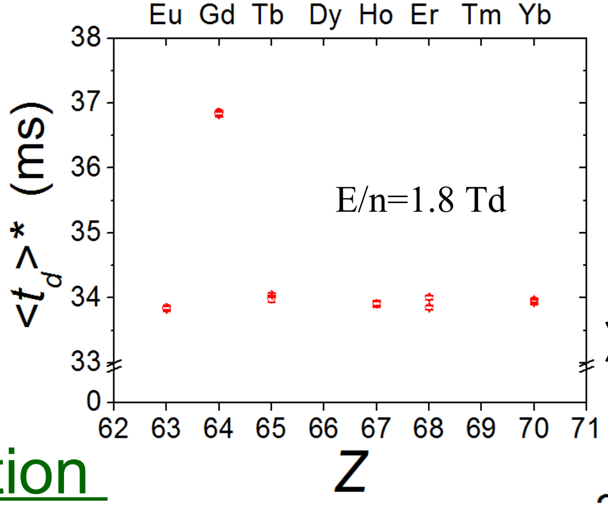


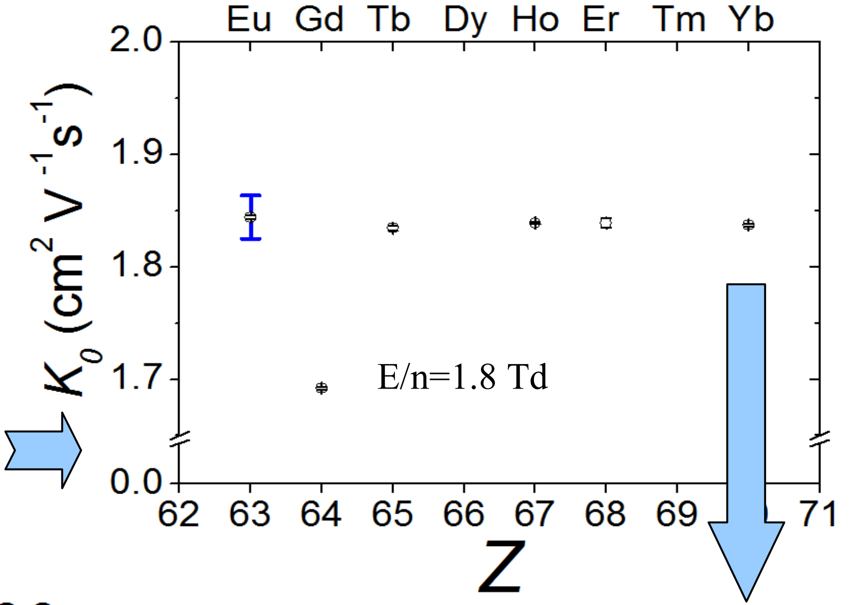
3- Experimental results (II):

Ion mobility of Lanthanides:

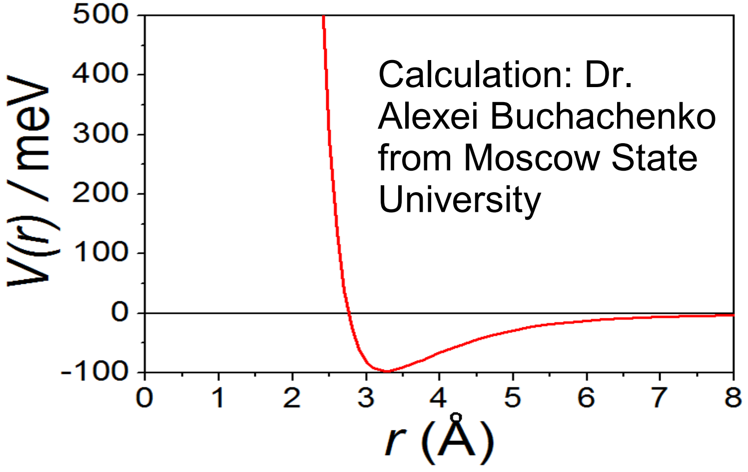
* All lanthanide ions exhibited nearly the same drift time except for gadolinium

=> Sensitivity to valence electron configuration

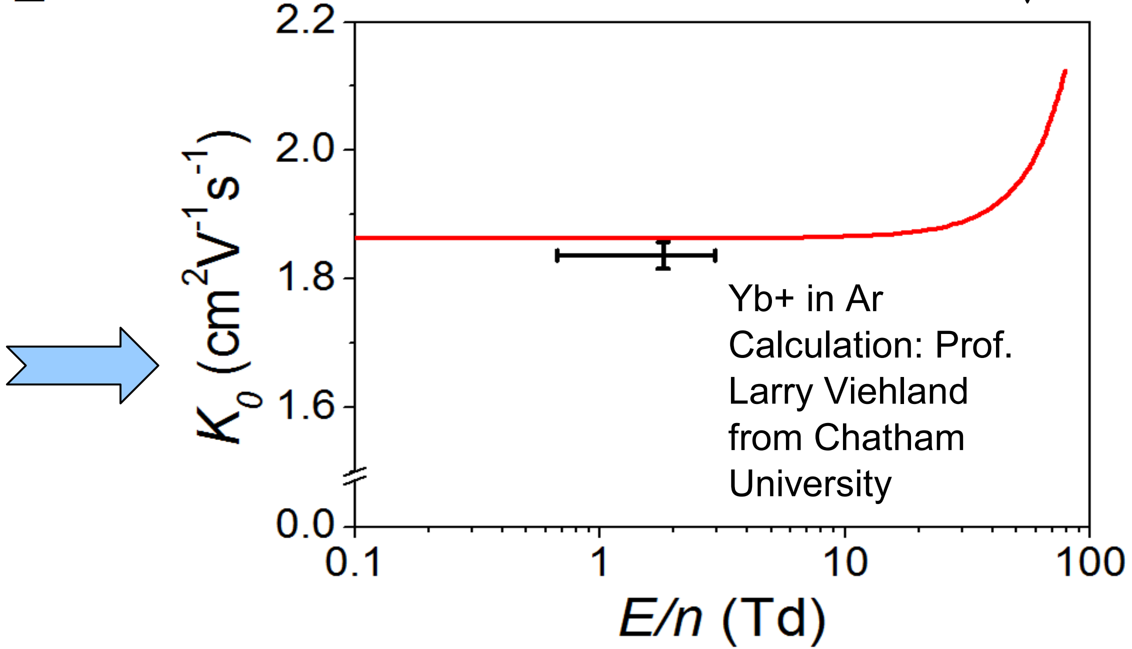




Relativistic calculation of V(r) for Yb-Ar system:



Calculation: Dr. Alexei Buchachenko from Moscow State University



Yb+ in Ar
Calculation: Prof. Larry Viehland from Chatham University

4- IMS, an isobaric purification method!

Isobaric purification by IMS methods:

* Gd among lanthanides

* Cm/Bk/Lr among actinides

Gas cell

thermalizing + cooling of fusion reaction products

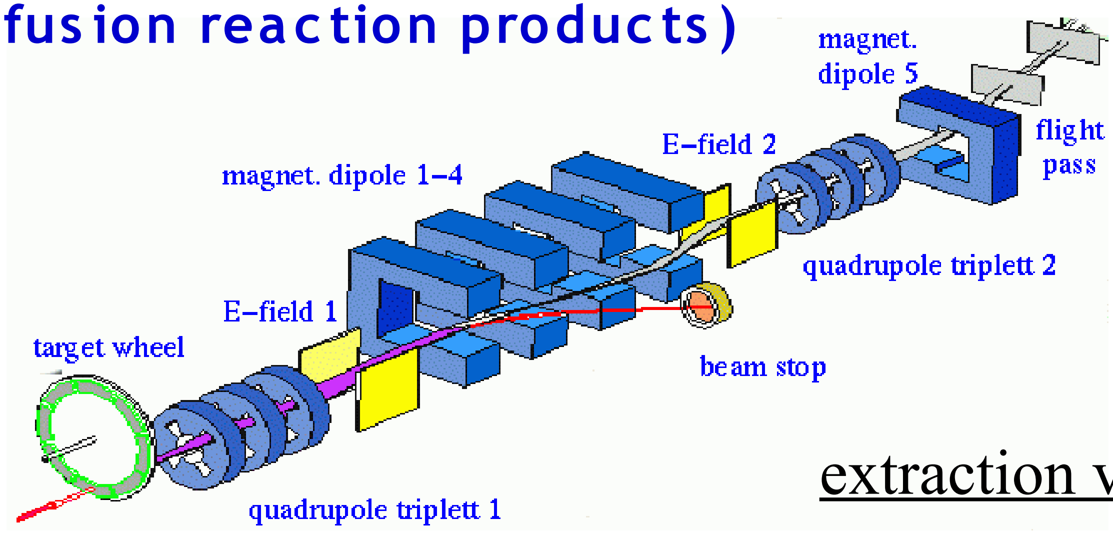
Z-selection

QMS

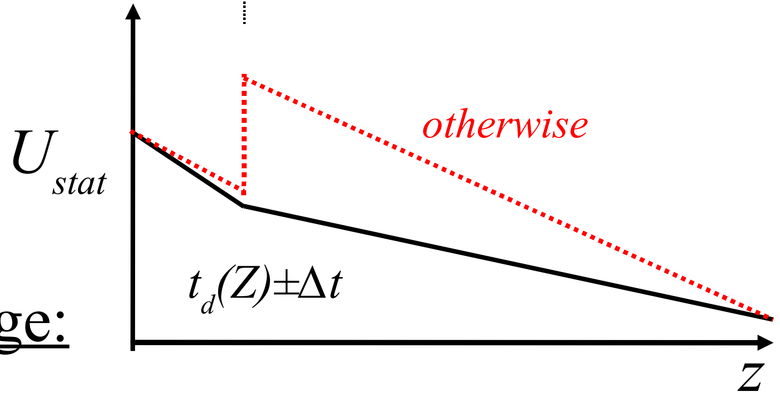
A-selection

isobaric suppression
+
high transmission

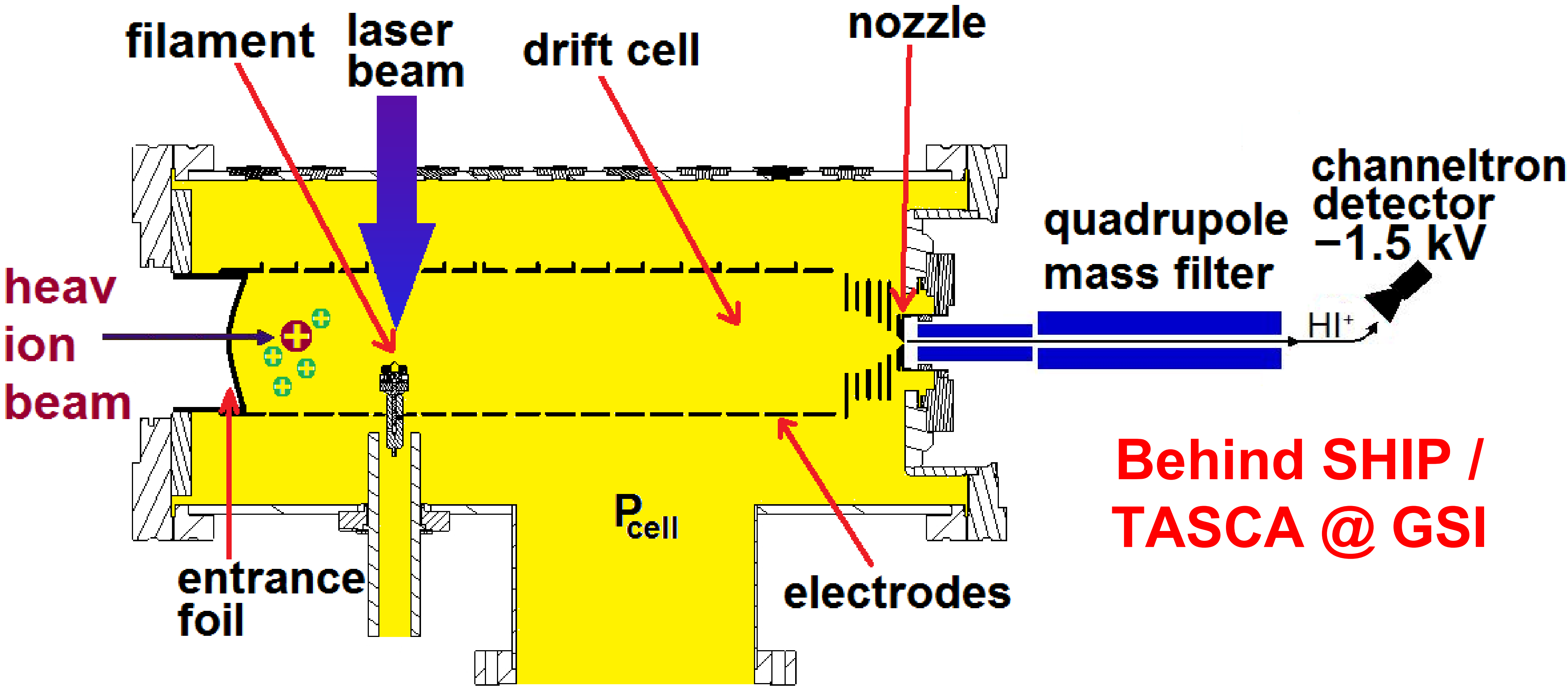
Velocity Filter SHIP (GSI)
(in-flight separation of fusion reaction products)



extraction voltage:



4- IMS @ actinides:

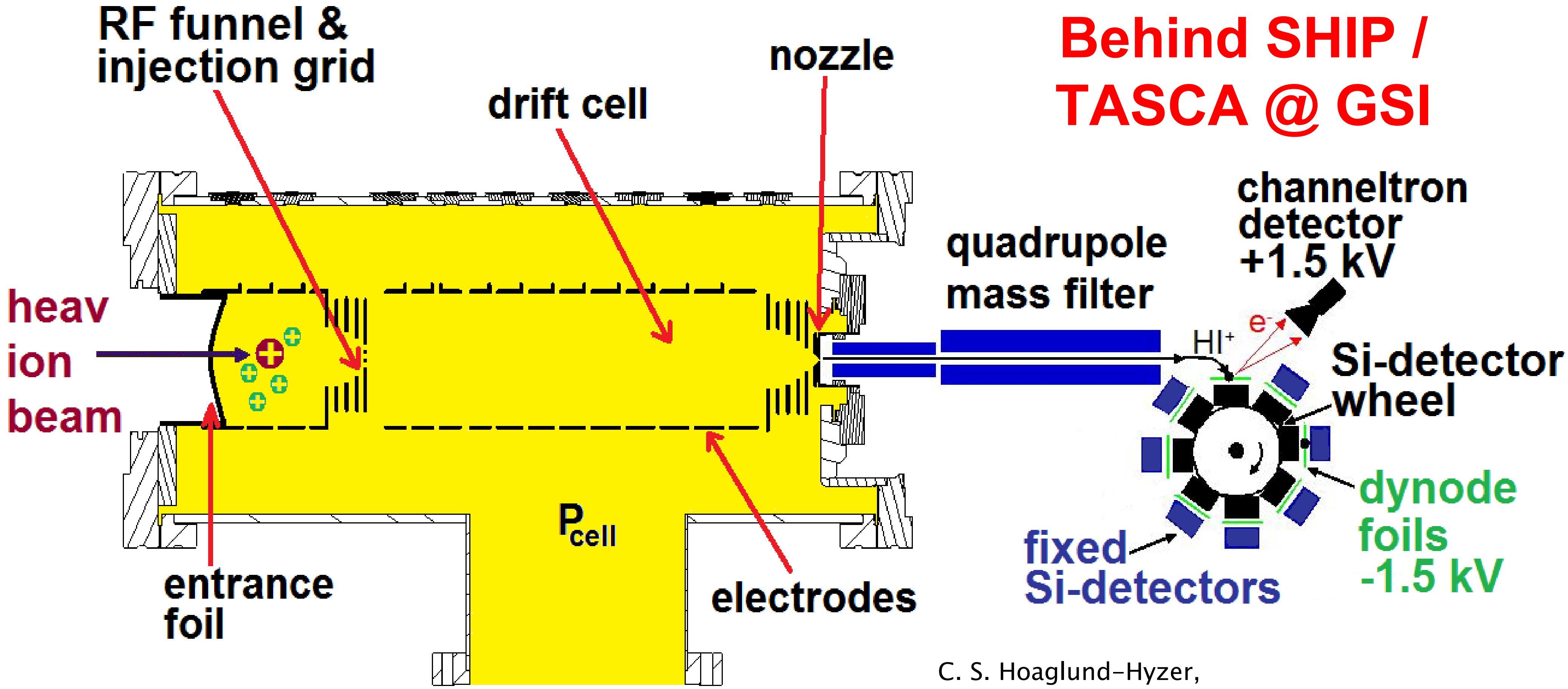


Behind SHIP / TASCA @ GSI

*** Suitable for abundant elements / elements of known atomic excitation schemes (up to fermium with Z=100)**

M. Sewtz et al., Spectrochimica Acta Part B 58 (2003) 1077–1082

4- IMS @ short-lived SHEs:



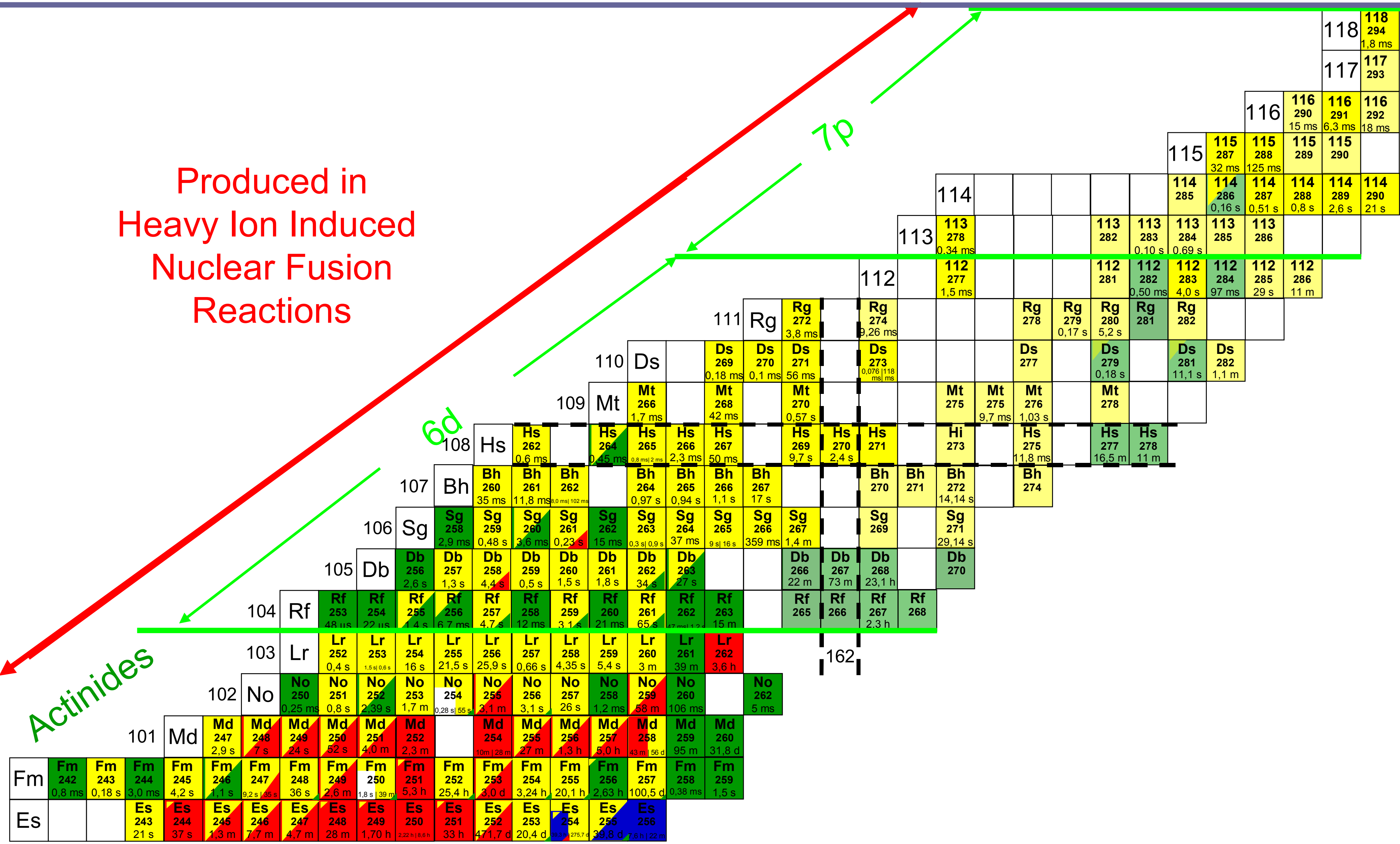
C. S. Hoaglund-Hyzer, et al., Anal. Chem., 2001, 73 (2), pp 177-184

and

B. H. Clowers, et al., Anal. Chem., 2008, 80 (3), pp 612-623

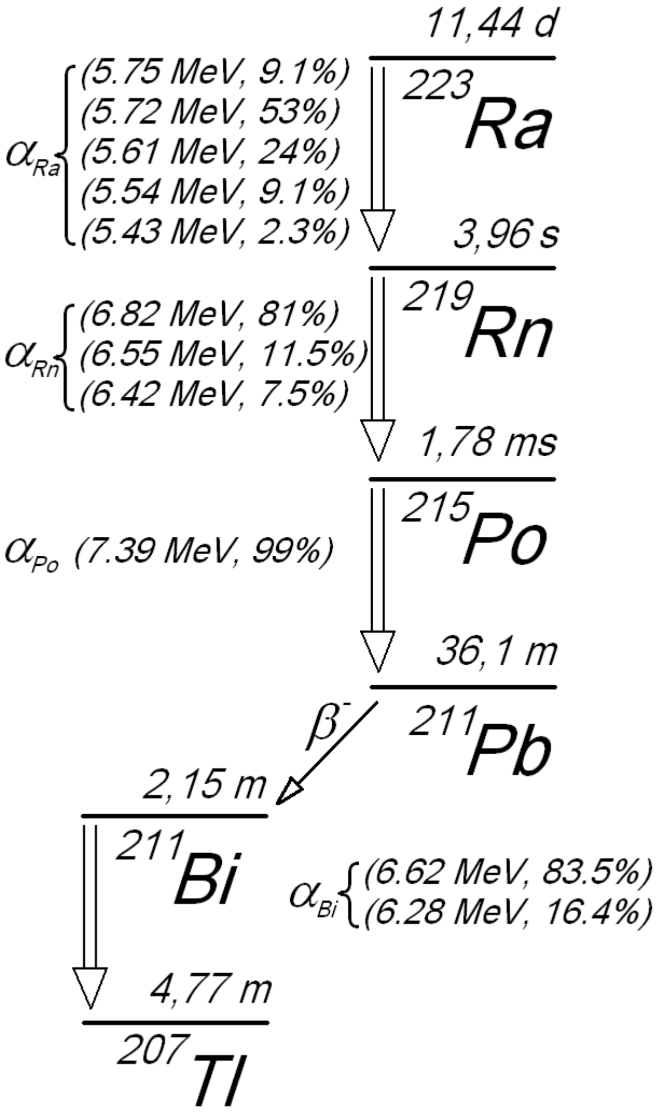
* **Ion trap & injection grids inside the gas cell to determine t_0 and z_0**

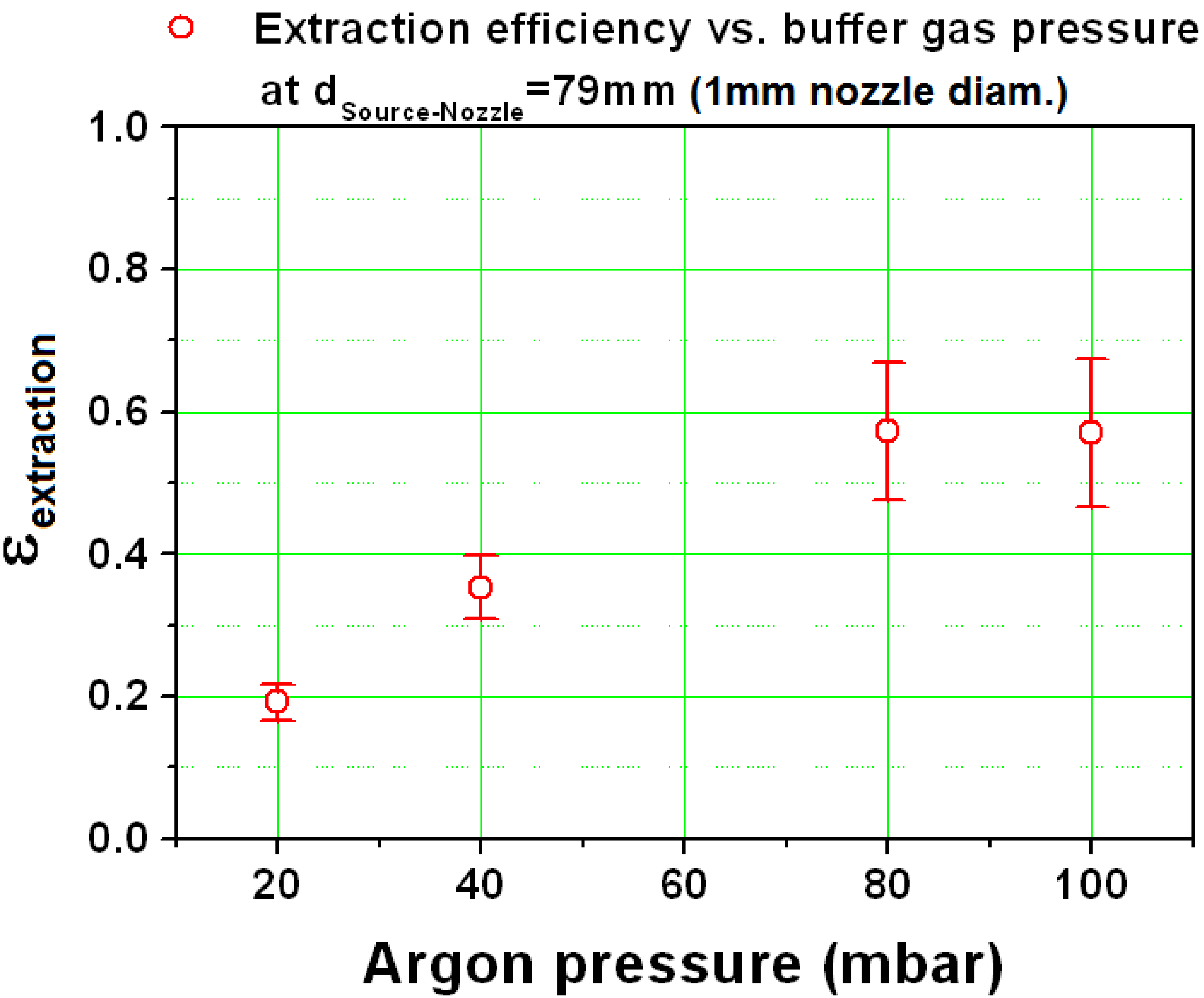
IMS studies at the super heavy elements:



Produced in
Heavy Ion Induced
Nuclear Fusion
Reactions

Extraction efficiency vs. gas pressure:





Viehland-Mason theory of ion mobility in gases:

$$K = \frac{3}{16}\frac{e}{N}\sqrt{\frac{2\pi}{\mu\, k_B T_{eff}}}\;\frac{1+\alpha}{\bar{\Omega}_{1,1}(T_{eff})}$$

In first order approximation:

$$\bar{\Omega}_{1,1}(T_{eff}) = \frac{1}{2(k_B T_{eff})^3}\int_0^\infty \bar{Q}^{(1)}(\varepsilon)\exp(-\varepsilon / k_B T_{eff})\varepsilon^2\, d\varepsilon$$

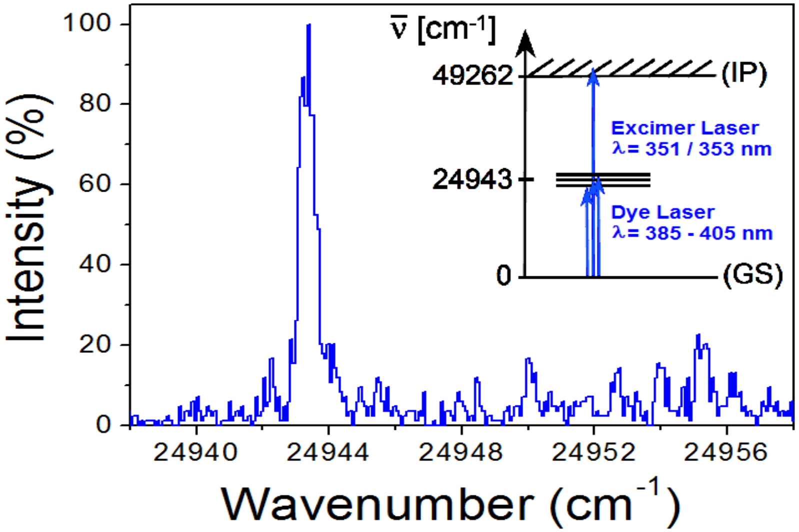
$$\bar{Q}^{(1)}(\varepsilon) = 2\pi \int_0^\infty (1 - \cos\,\theta) b\, db$$

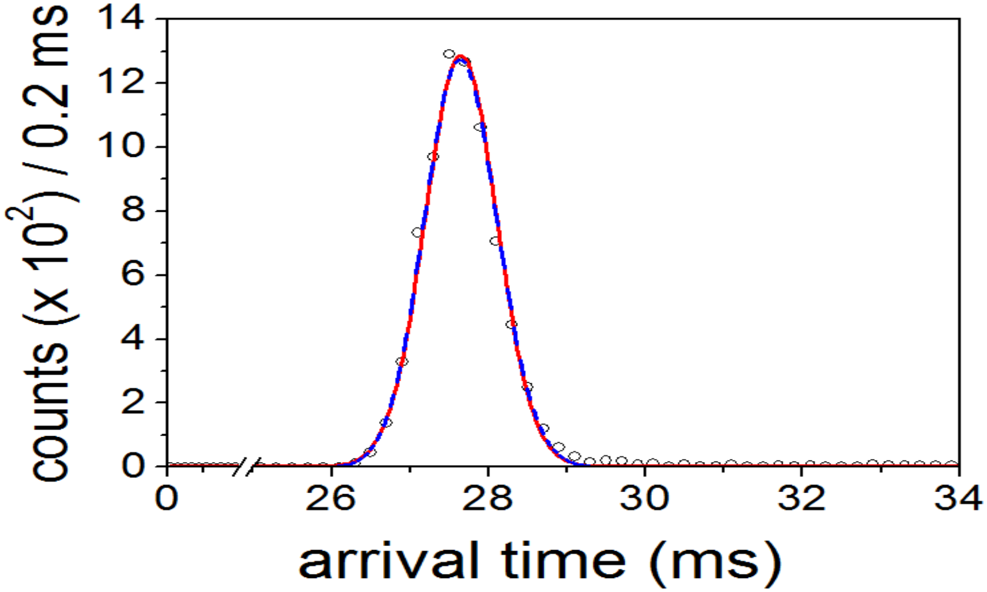
$$\theta = \pi - 2b \int_{r_a}^{\infty} \left[1 - \frac{b^2}{r^2} - \frac{V(r)}{E}\right]^{-1/2} \frac{dr}{r^2}$$

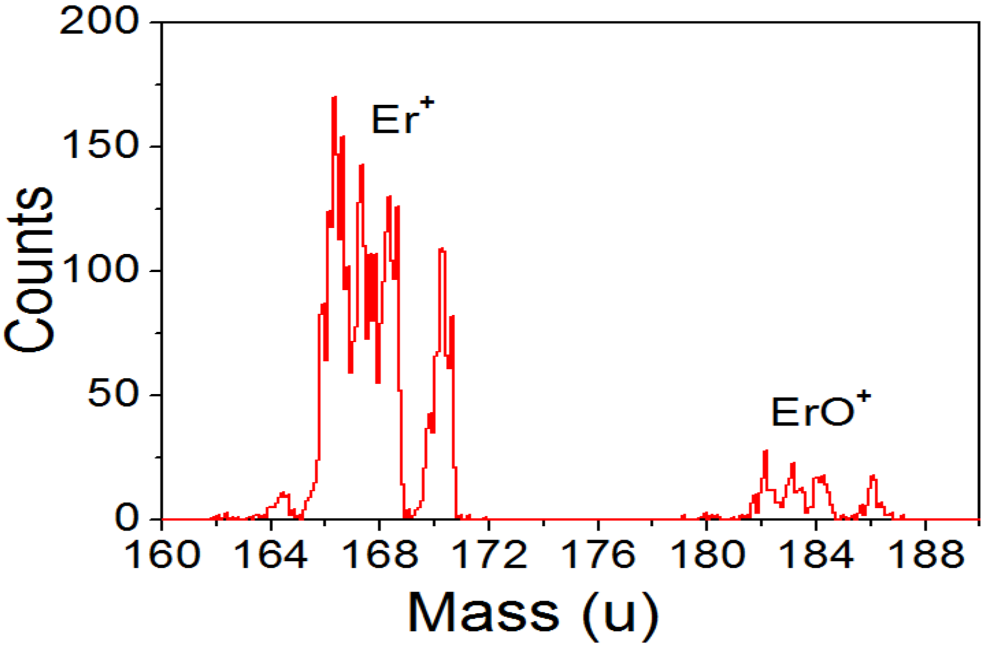
With: $1 - \frac{b^2}{r_a^2} - \frac{V(r_a)}{E} = 0$ and $E = \frac{1}{2}\mu v^2$

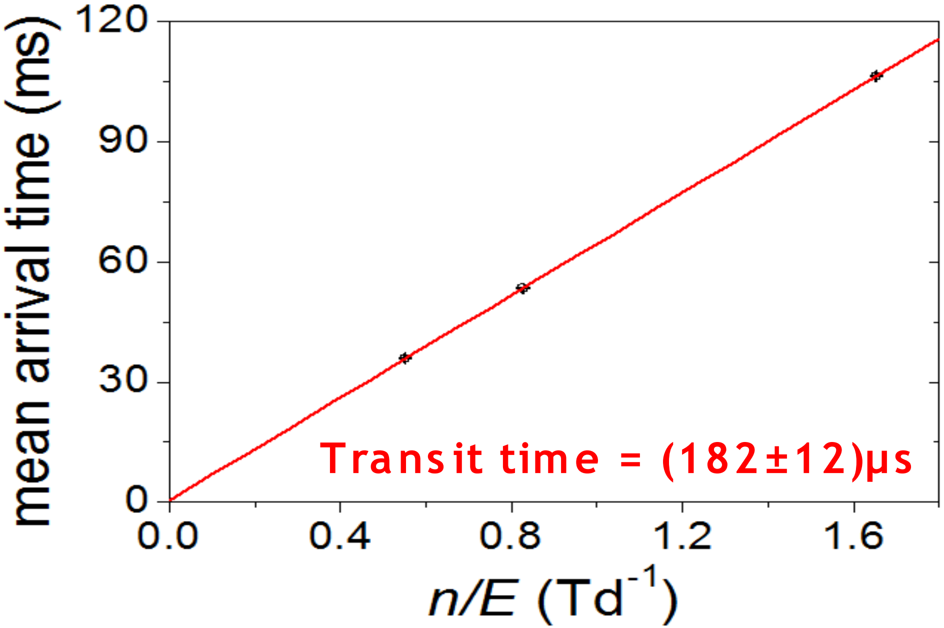
e: Charge
N: Number Density
of Buffer Gas Atoms
μ: Reduced Mass
k_B: Boltzmann Constant
T_{eff}: Effective Temperature
$\bar{\Omega}_{1,1}(T_{eff})$: Collision Cross Section
α: Higher Order Corrections
T: Gas Temperature
m: Ion mass
M: Mass of the buffer gas atom
α_p: Ar polarizability
$\bar{Q}^{(1)}(\varepsilon)$: *1st. Order approx transport cross section*
ε: rel. energy of ion-atom collision
v: mean collision velocity
b: Impact parameter
r_a: Distance of closest approach
V(r): Ion molecule potential energy
E: Initial relative kinetic energy

Spectra for Er filament:





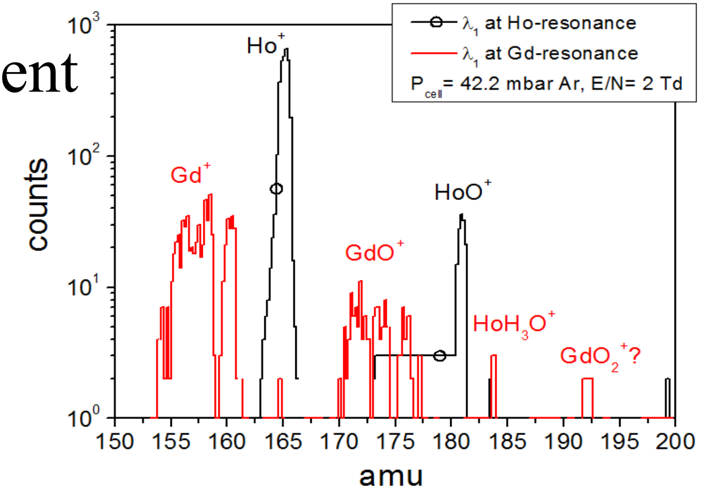




Transit time = (182±12)µs

Mass-time spectra when using multi-filaments:

Ho-Gd filament



Problems:

- impurities
  => chemical bonds (ion losses)
- nozzle gas jet
  => molecule cracking (different time spectra)
- different evaporation temperatures
  => thermal ionization (background) and charge transfer reactions (losses)