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Institutionen för Fysik och astronomi

Electronic interactions of medium-energy ions:

Some recent results and their implications for high-resolution depth profiling

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Tandemaccelerator
Ion-Implanter + MEIS
Anders
Ångström

High resolution depth profiling: Ion energies: keV/amu

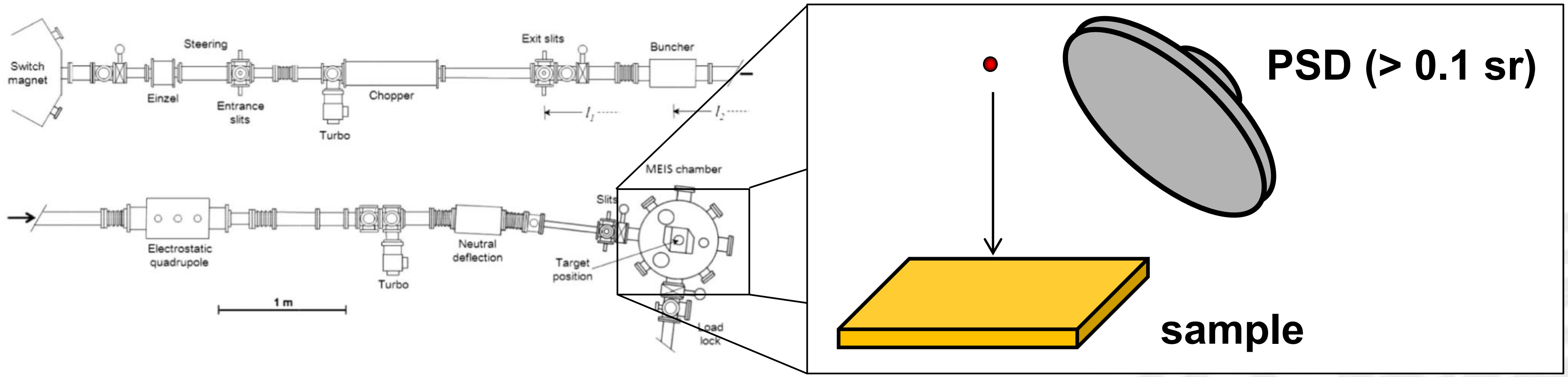
Possible complications:

- Contribution from nuclear energy loss along trajectories becomes relevant
- Low ion energy ↔ low energy transfer to electrons
- Excitation of valence and conduction electrons ↔ chemical effects
- Ion velocity comparable to electron velocity ↔ response of system
- Increased weight of surface (contaminations, deviations from bulk stoichiometry)

Outline

- Motivation: Stopping power research at keV energies
- Stopping power experiments by TOF-techniques
  - Heavy ions (Ne, I) in noble metals (Au, Ag, Pt)
  - Light ions in hafniumdioxide HfO_2
- Conclusions/Summary

The Uppsala TOF-MEIS: an ideal tool



M. Linnarsson et al., Rev. Sci. Instr. (2012)

- **Almost any ion, 20-350 kV acceleration voltage**
- **Microchannelplate detector + TOF: No problem with charge states**
- **Large solid angle: Extremely low dose!**

Heavy ions… Ne!

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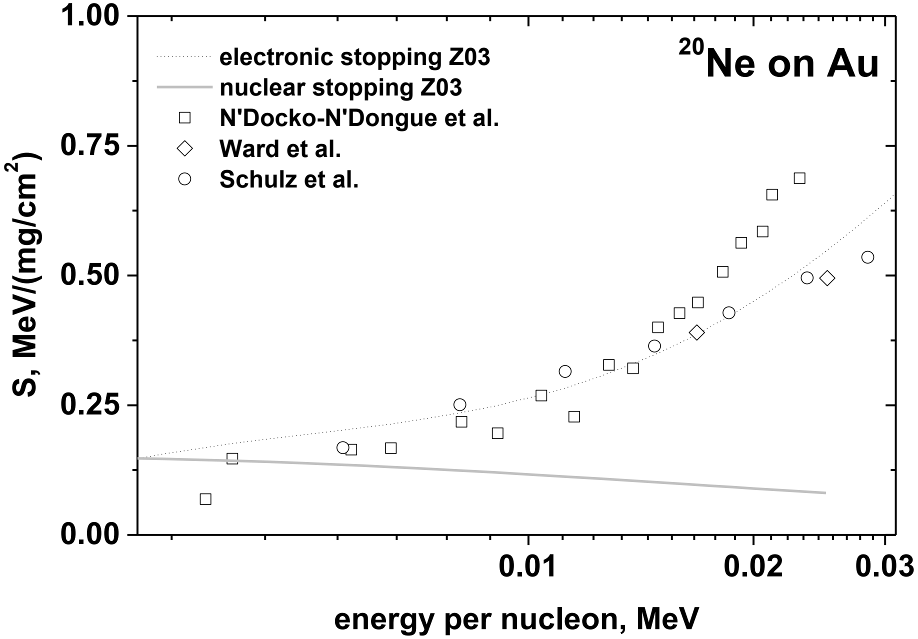
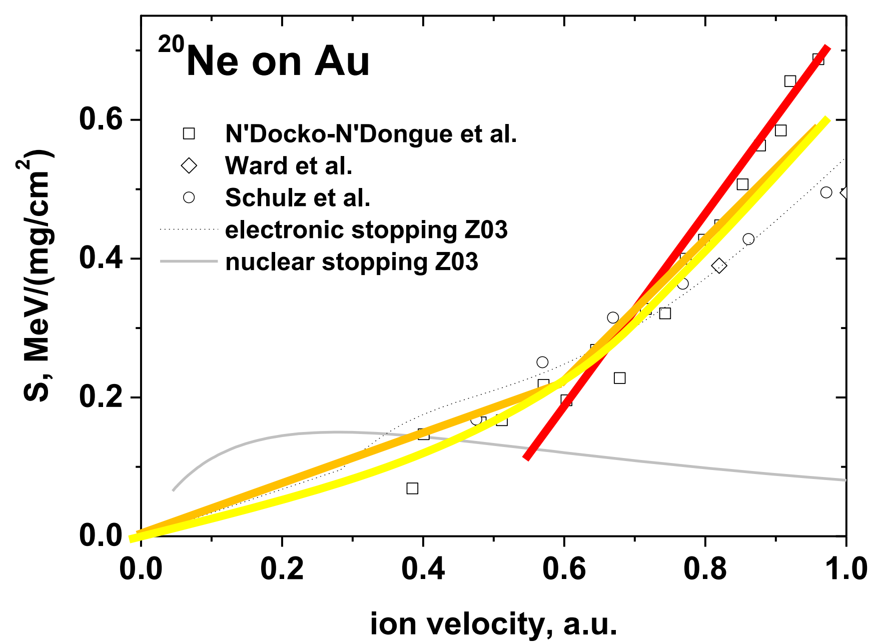
Heavy ions… Ne!

At low energies (< 1MeV):

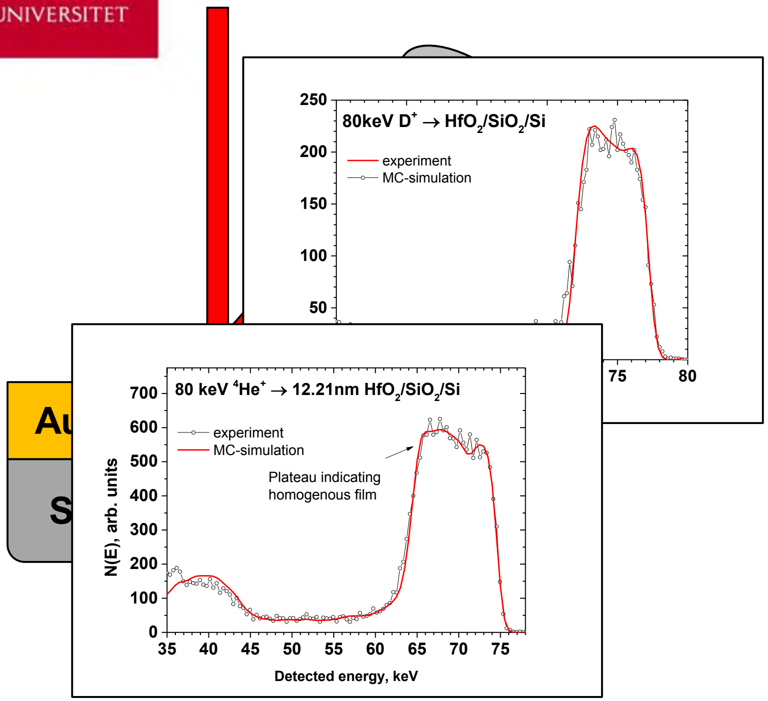


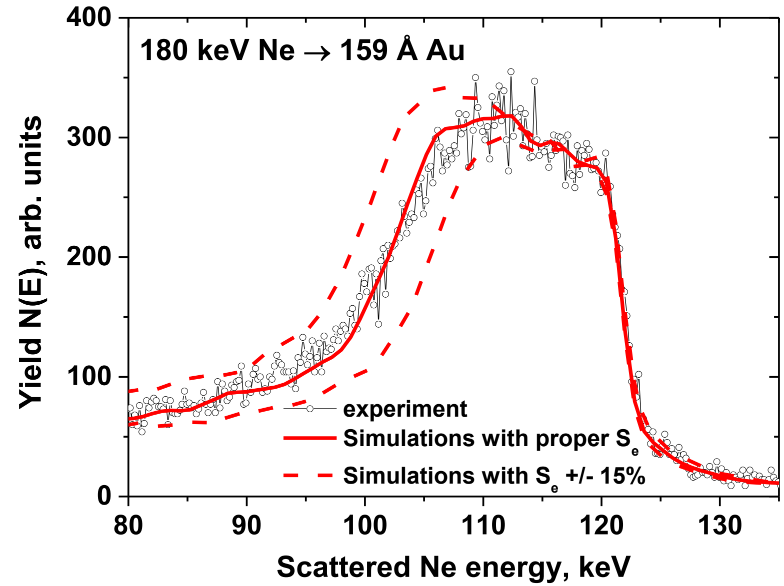


N'Docko-N
Ward et al
Schulz et
electronic
nuclear st

- Set of 3 transmission experiments from the literature
- Data shows a clear non-linear velocity dependence

Backscattering of Ne: dE/dx

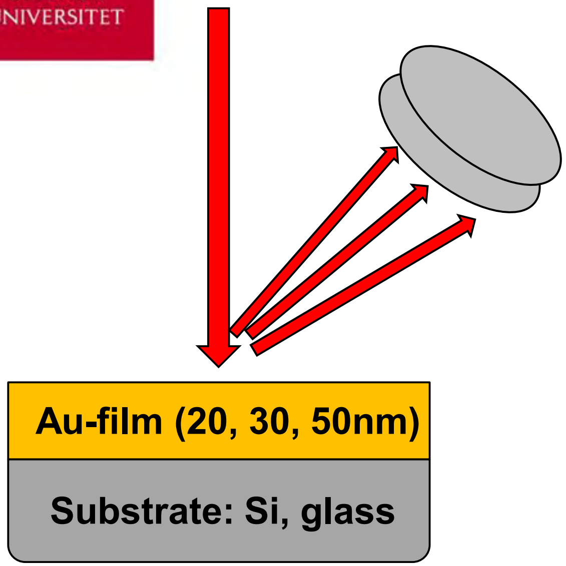


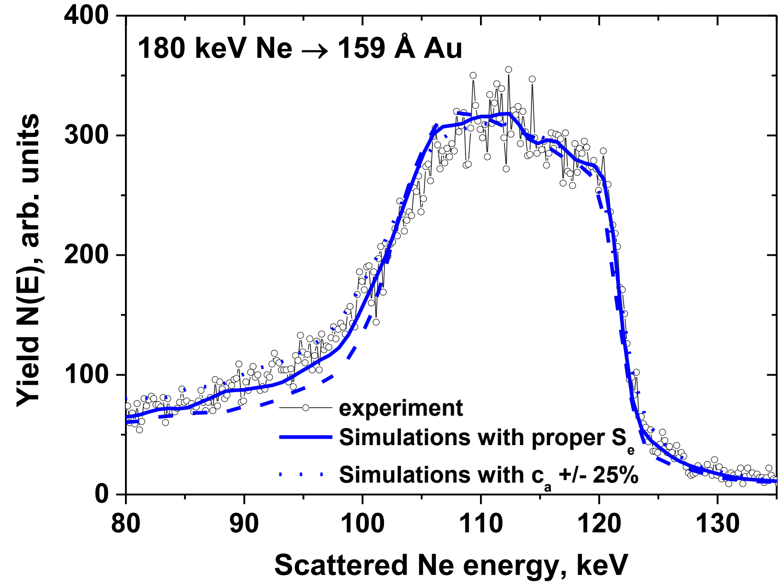


D. Primetzhofer, Nucl. Instr. Meth. B (2013)

- **Electronic stopping can be obtained with high precision**
- **Multiple scattering affects low-energy edge of spectrum**

Backscattering of Ne: dσ/dΩ

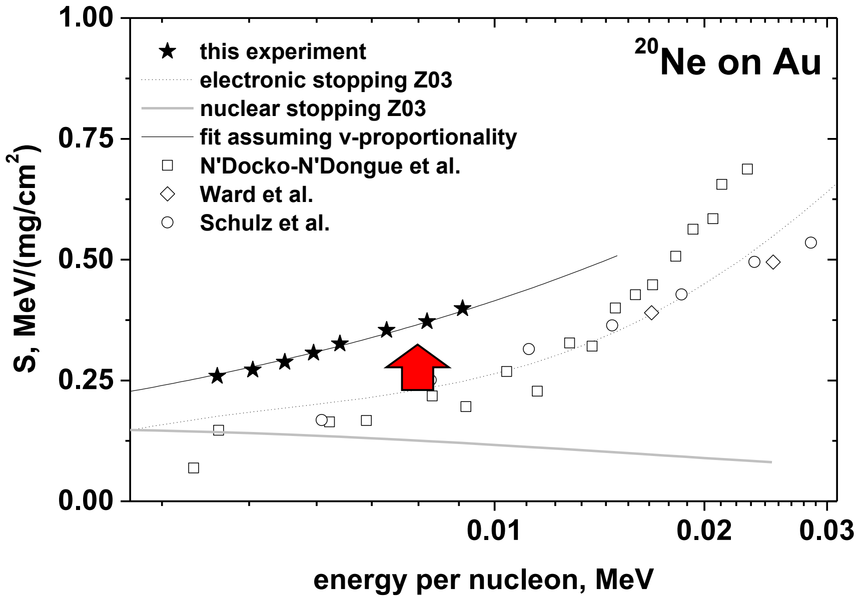


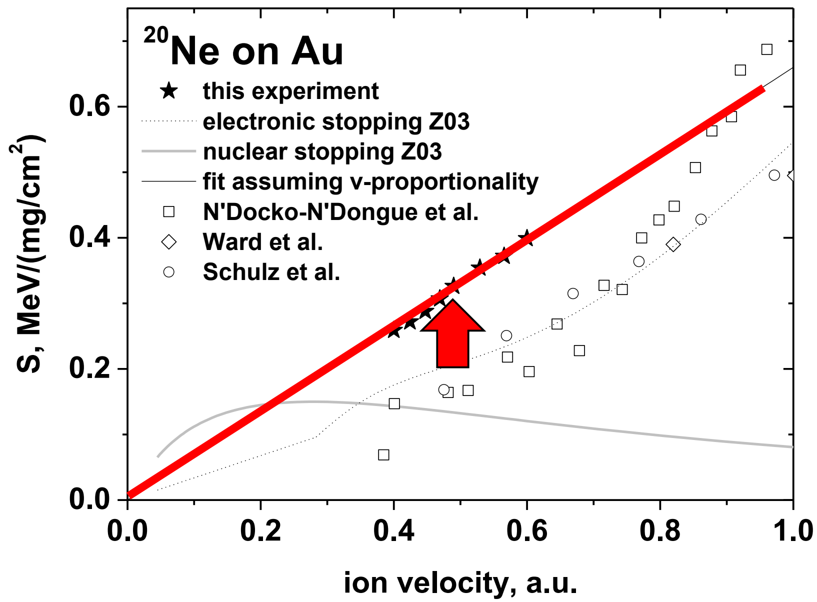


D. Primetzhofer, Nucl. Instr. Meth. B (2013)

- **Electronic stopping can be obtained with high precision**
- **Multiple scattering affects low-energy edge of spectrum**
- **Spectrum width unaffected by change in potential strength**

Experimental stopping powers for ^{20}Ne:

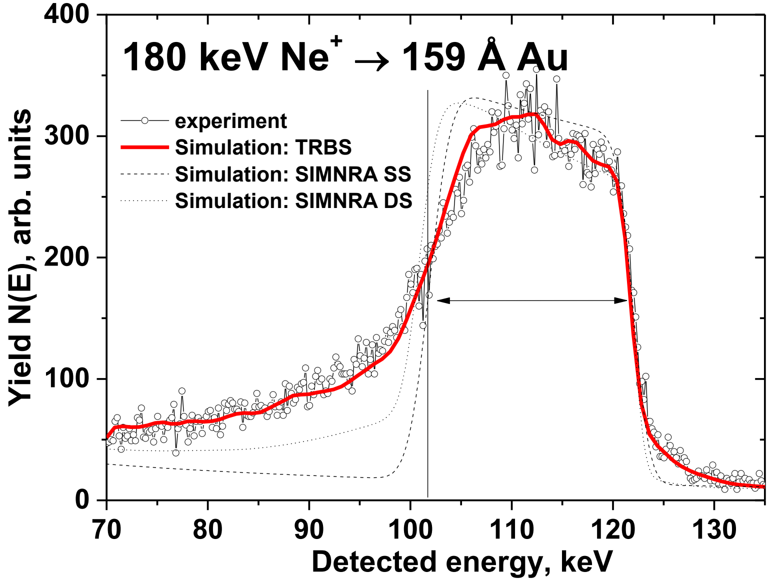




D. Primetzhofer, Nucl. Instr. Meth. B (2013)

- **Values deduced in backscattering are exceeding values in transmission**
- **Velocity proportionality of stopping cross sections**

Evaluation by different models:



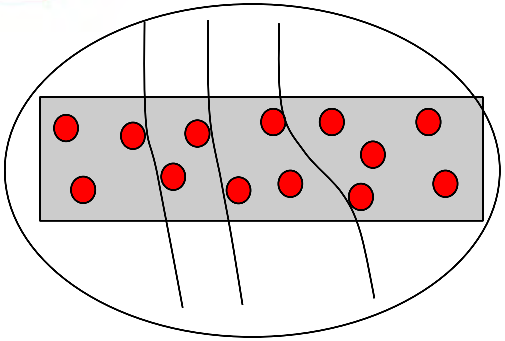
- Single scattering model by SIMNRA
- Dual scattering model by SIMNRA
- Hands-on evaluation (Warter's method)
- MC-simulation by TRBS

→ Almost equivalent results!

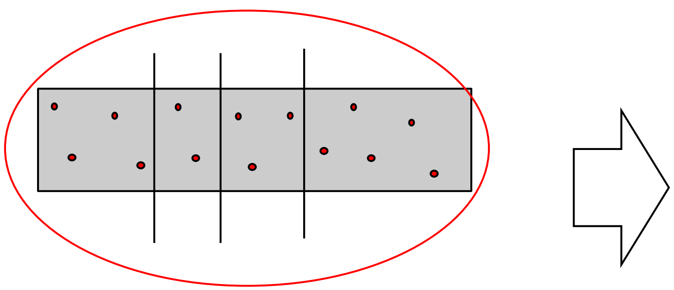
THUS:

- Nuclear stopping contribution to this experiment is apparently small!
- Contribution in transmission is expected to be even smaller!

Monte-Carlo: nuclear stopping?

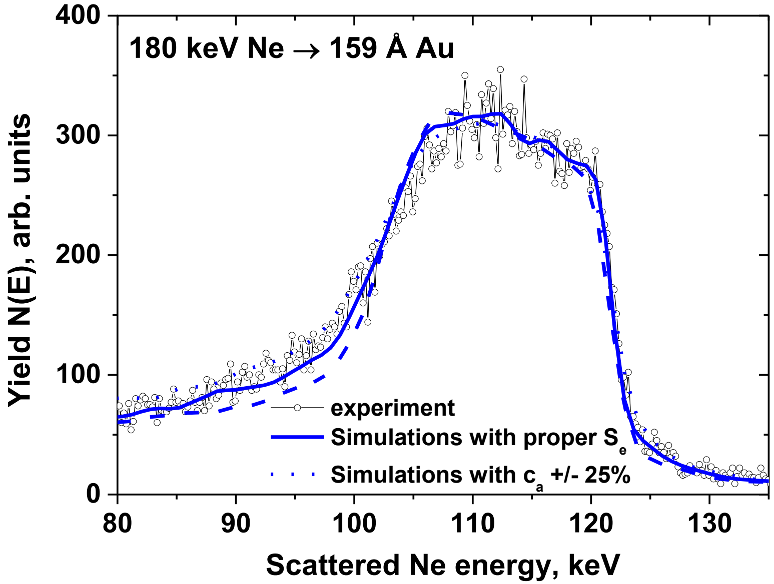


”Realistic” interaction potential +/- 25%



Reducing/turning off
the interaction potential

Electronic stopping exclusively…



D. Primetzhofer, Nucl. Instr. Meth. B (2013)

Monte-Carlo: nuclear stopping?

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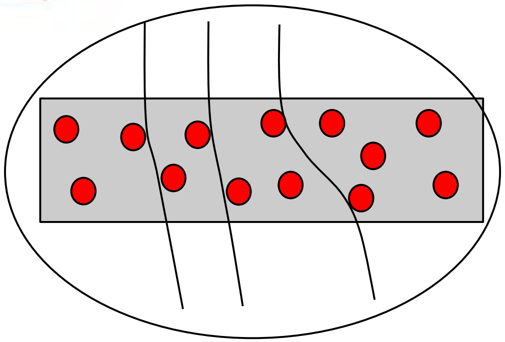
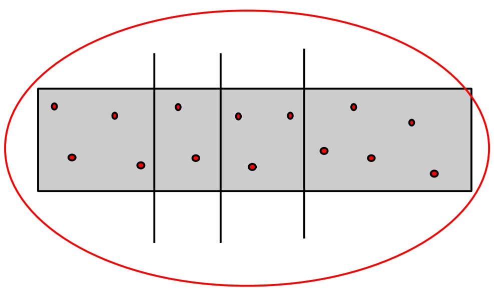
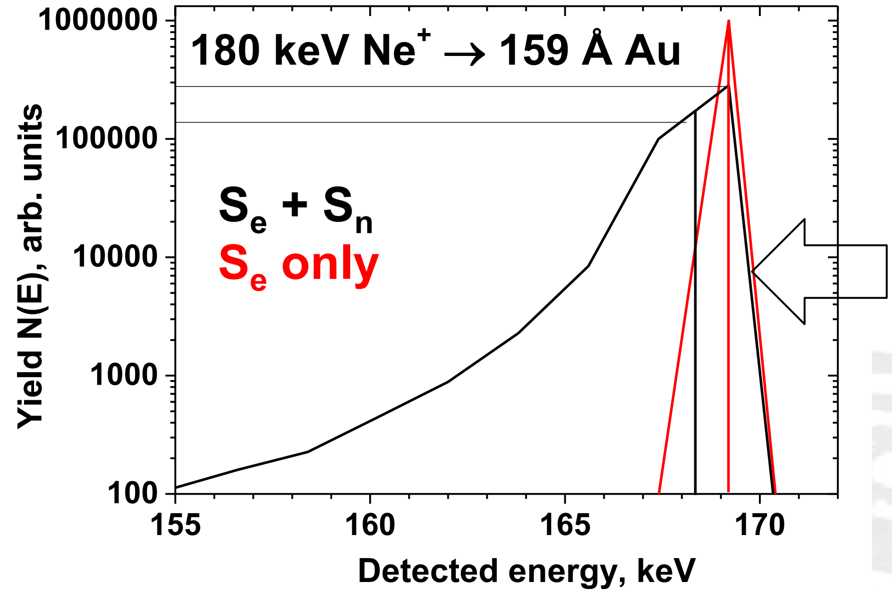
In transmission:



"Realistic" interaction potential +/- 25%



Reducing/turning off the interaction potential

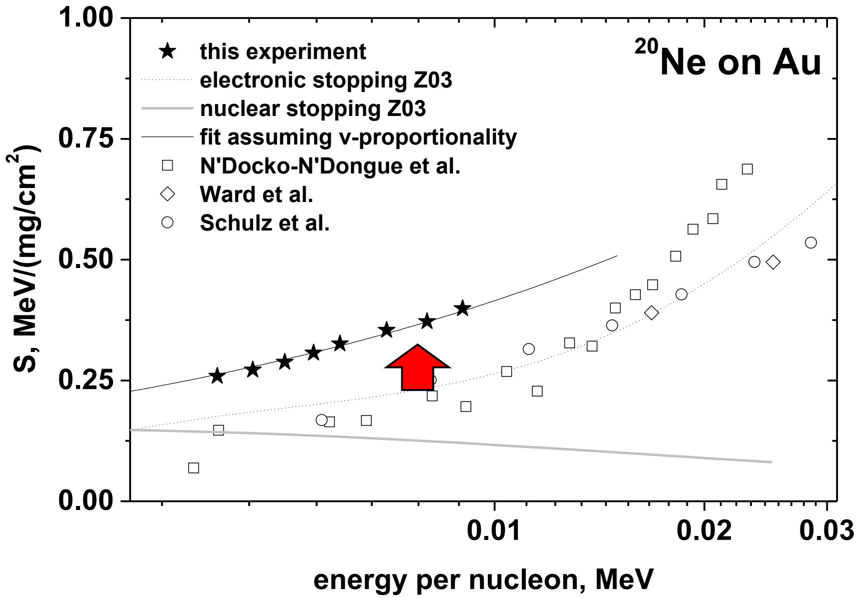


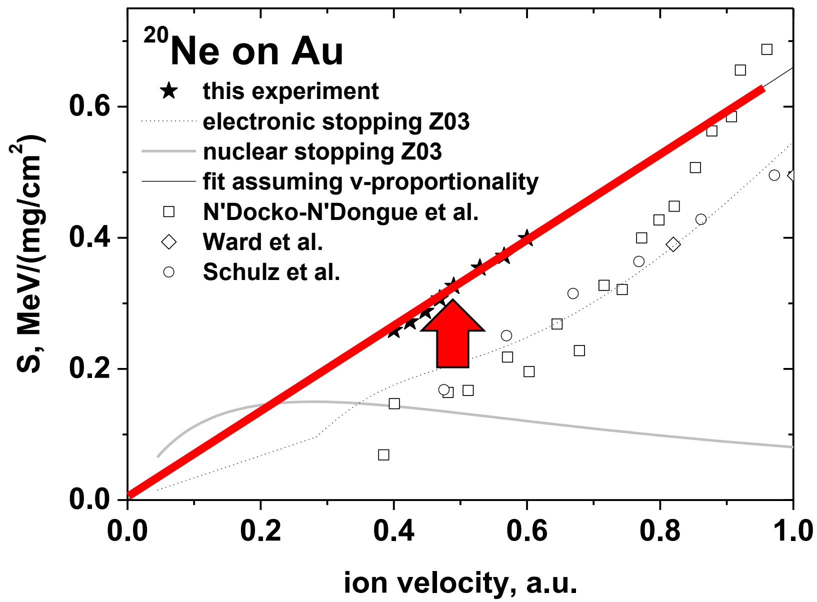
- **Electronic stopping shifts spectrum**
- **Broadening due to nuclear stopping**

BUT: only minor shift of median

$$S_{nucl} < S_{elec}/10$$

Experimental stopping powers for ^{20}Ne:

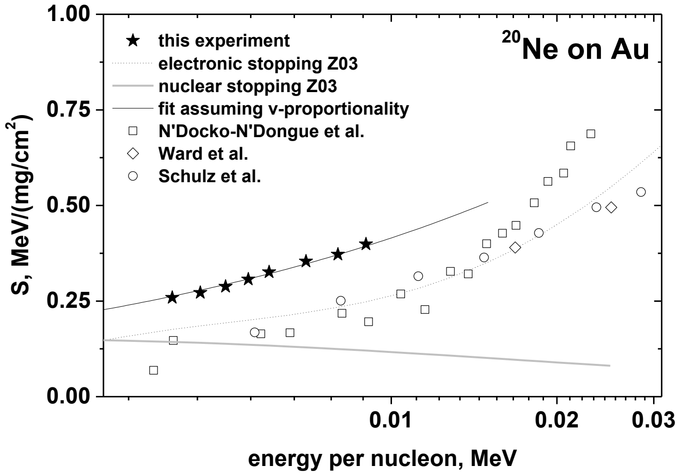




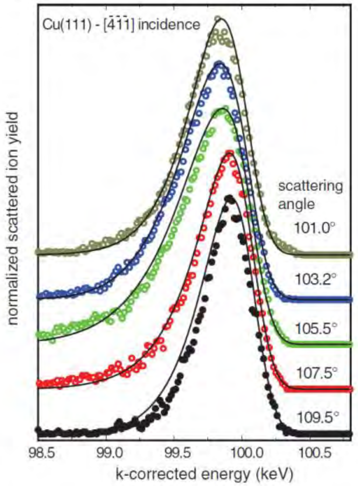
D. Primetzhofer, Nucl. Instr. Meth. B (2013)

- **Values deduced in backscattering are exceeding values in transmission**
- **Velocity proportionality of stopping cross sections**

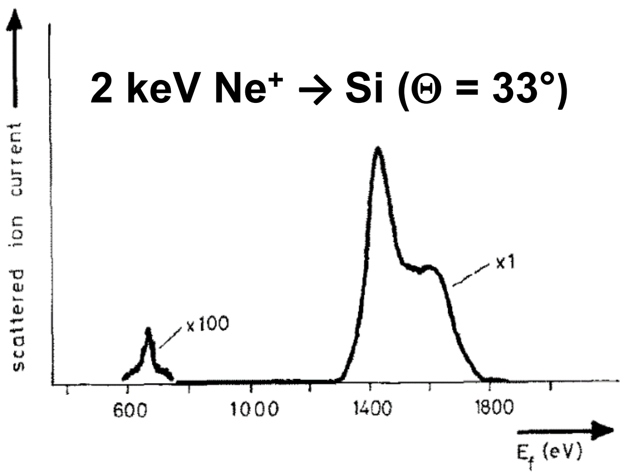
Experimental data - revisited:



D. Primetzhofer, Nucl. Instr. Meth. B (2013)



A. Hentz et al., PRL (2009)



H.H. Brongersma et al., Surf. Sci. (1973)

Enhanced electronic stopping:

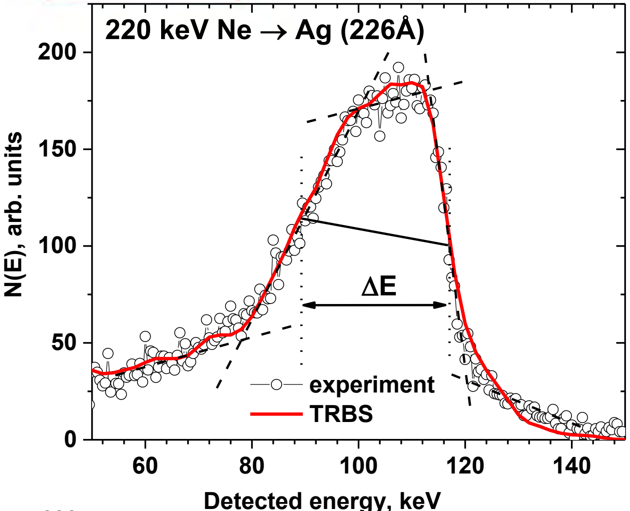
- Different impact parameters: backscattering vs. transmission
- Different charge state distribution: backscattering vs. transmission

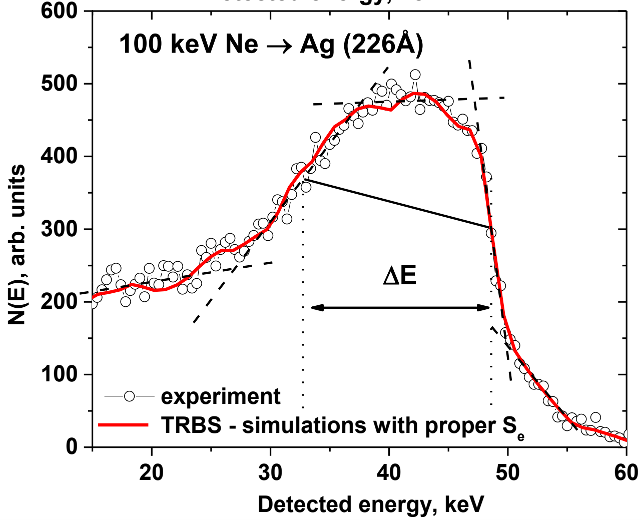
Other systems: Pt, Ag

- **Platinum results compare well with Au**
  similar electronic structure – similar kinematics

- **Silver: very different scattering kinematics**

Ne: Evaluating S_n for Ag in backscattering



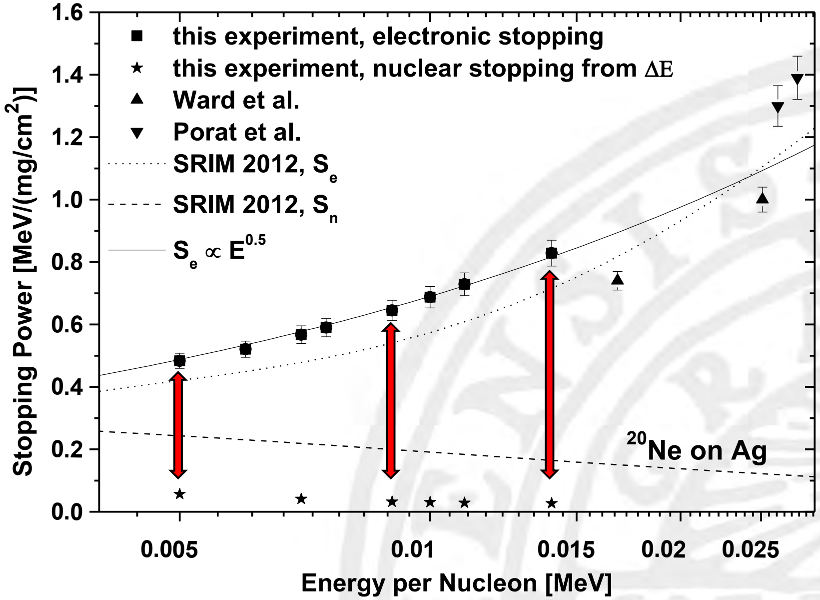


Assumption 1: MC works correct

$$\Delta E = \Delta E_{elec.(TRBS)} + \Delta E_{nuclear}$$

Assumption 2: S_n scales as in SRIM

$$\Delta E_{nuclear} = k \cdot x \cdot S_n^{in} + \frac{x}{\cos\theta} . (c . S_n^{in})$$



Naqvi et al. Nucl.Instr. Meth. B (2016)

S_n is only about 15% of S_e in this experiment

Comparing with transmission (MC)

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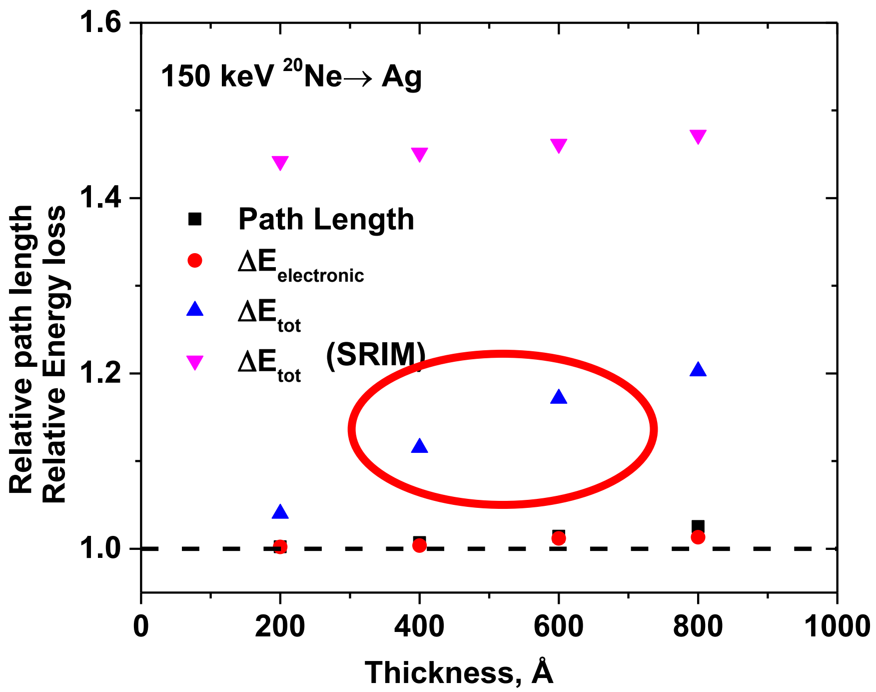
TRIM: Transmission - exit angle 0 – 2 deg.



Naqvi et al. Nucl.Instr. Meth. B (2016)

- **Path length grows only slightly relative to thickness x.**
- **Electronic energy loss grows in accordance with path length**
- **Total energy loss shows increasing nuclear contribution.**

Almost identical nuclear contribution of about 10-15% for relevant thickness

Comparing with transmission (MC)

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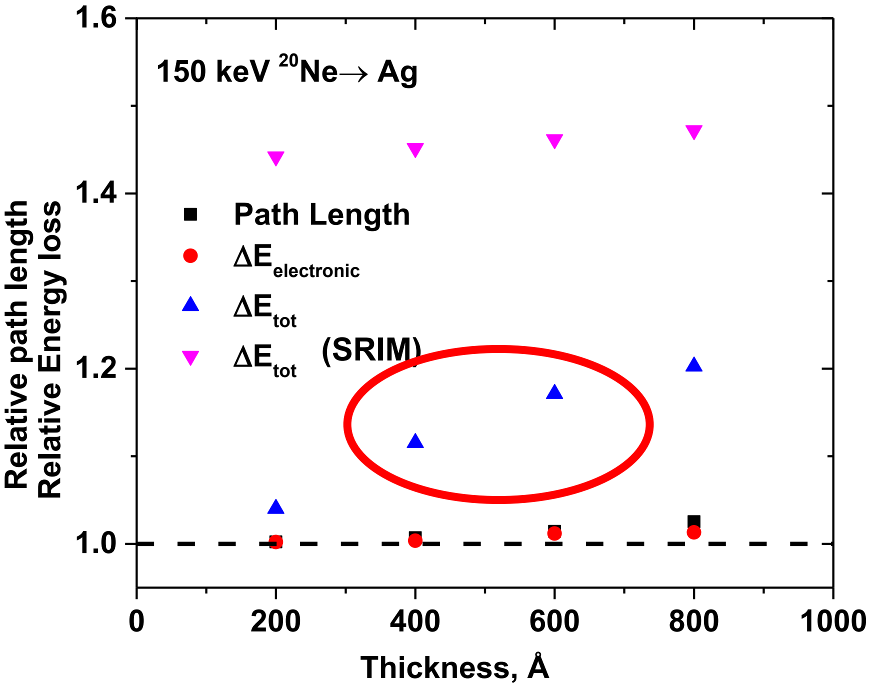
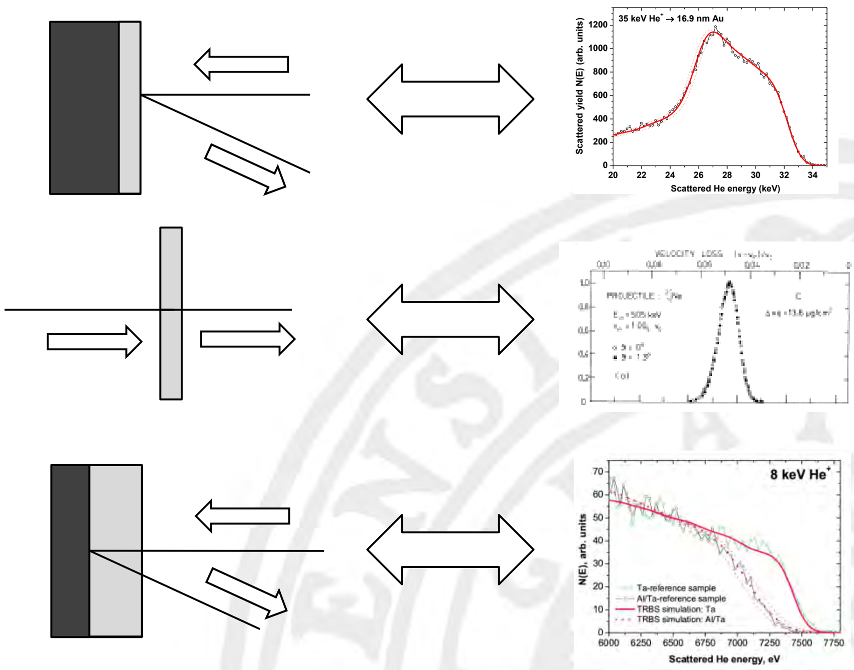
TRIM - Transmission



Naqvi et al. Nucl.Instr. Meth. B (2016)

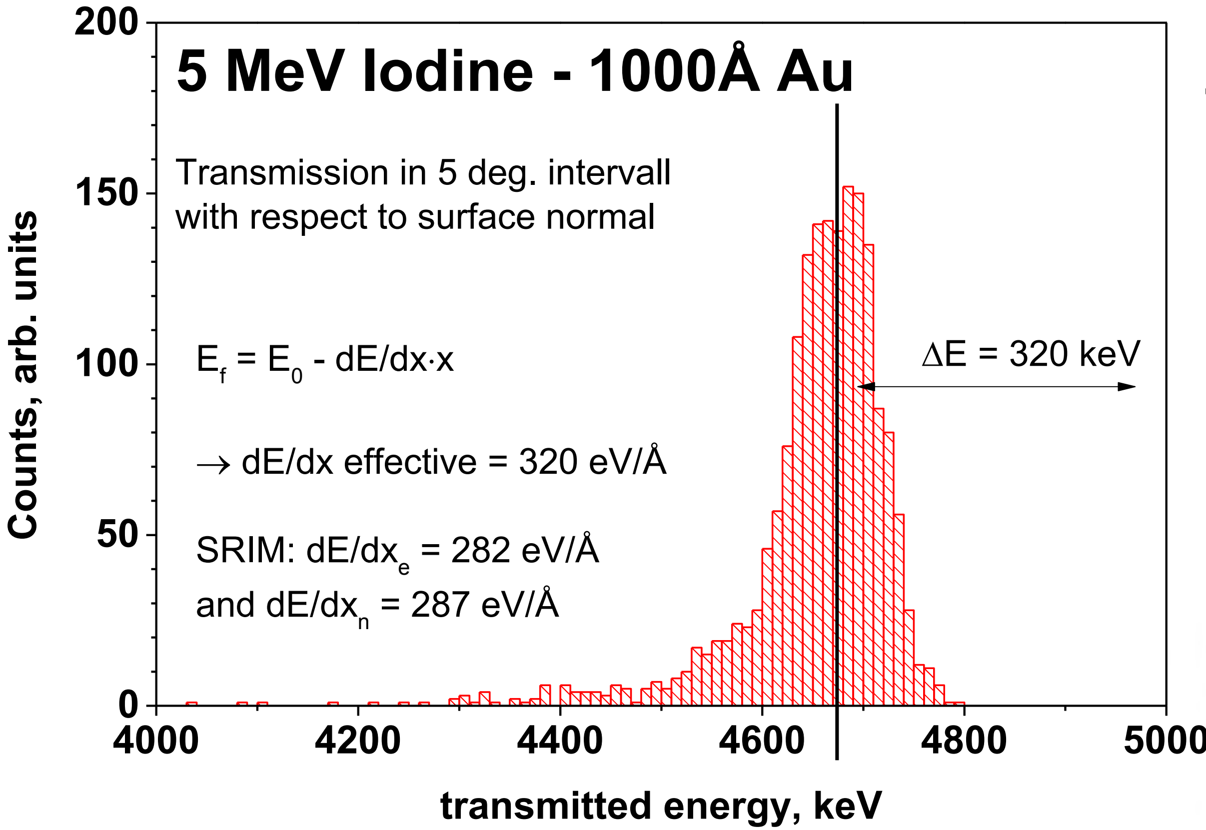
Any experiment is trajectory selective…



…when looking on characteristic spectral features!

Applicable for even heavier ions?

- MeV ions like Bromine, Iodine employed in ERD

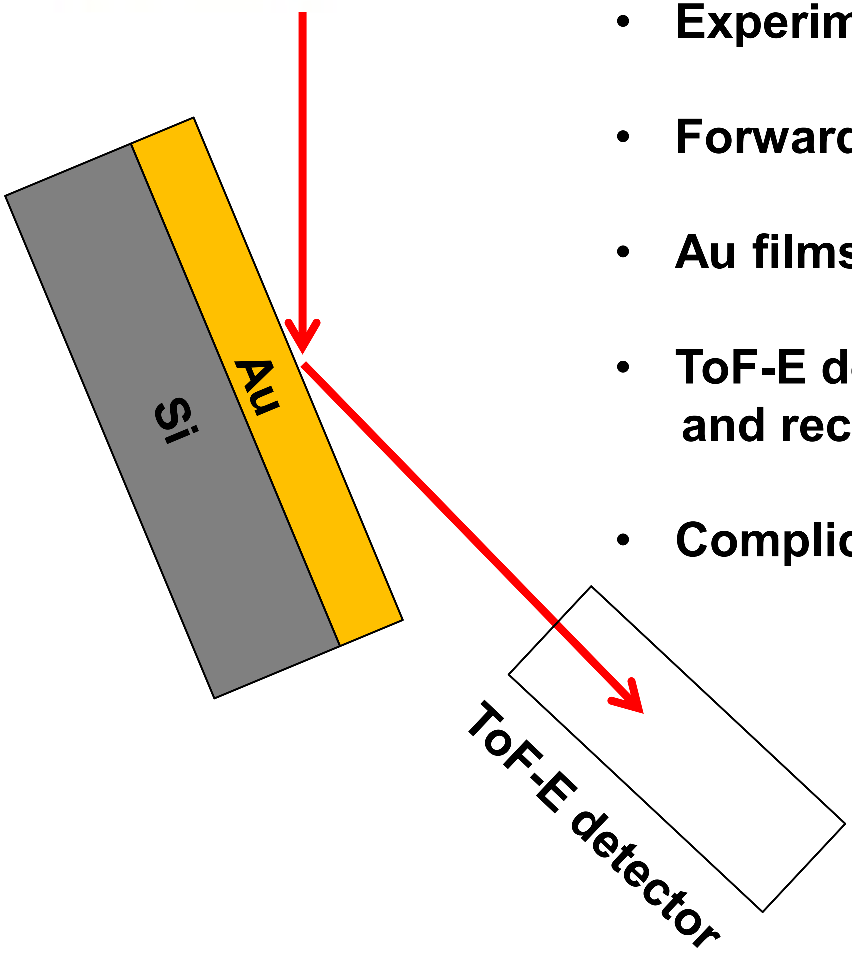


TRIM-simulations:

Only very minor contribution of dE/dx_n for films in transmission

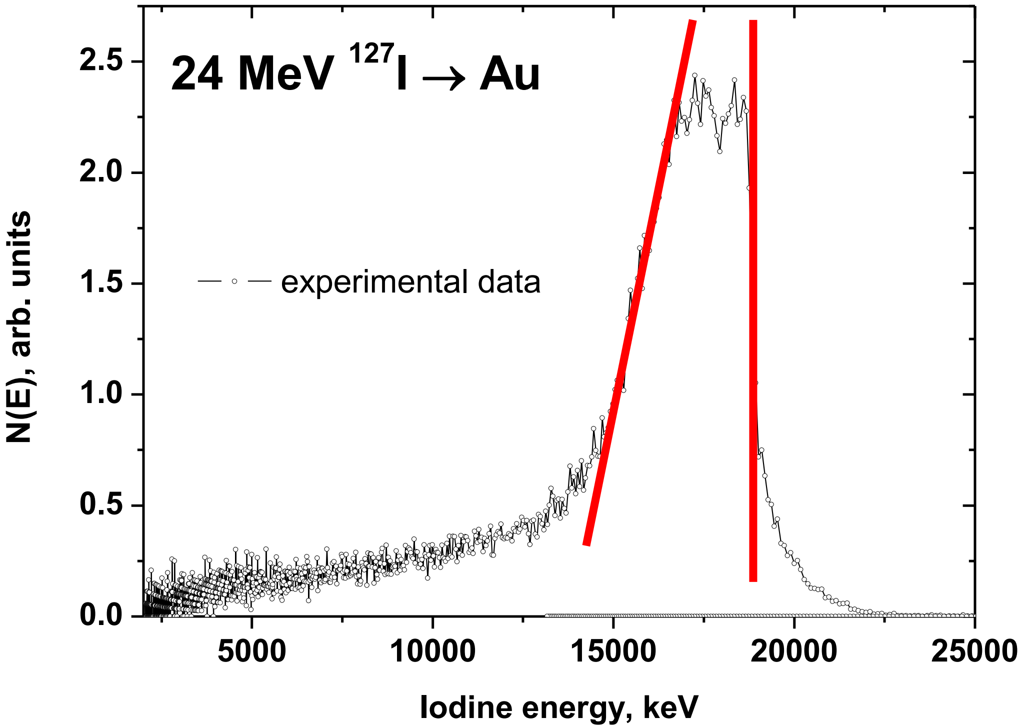
What do we see experimentally?

Forward scattering of Iodine



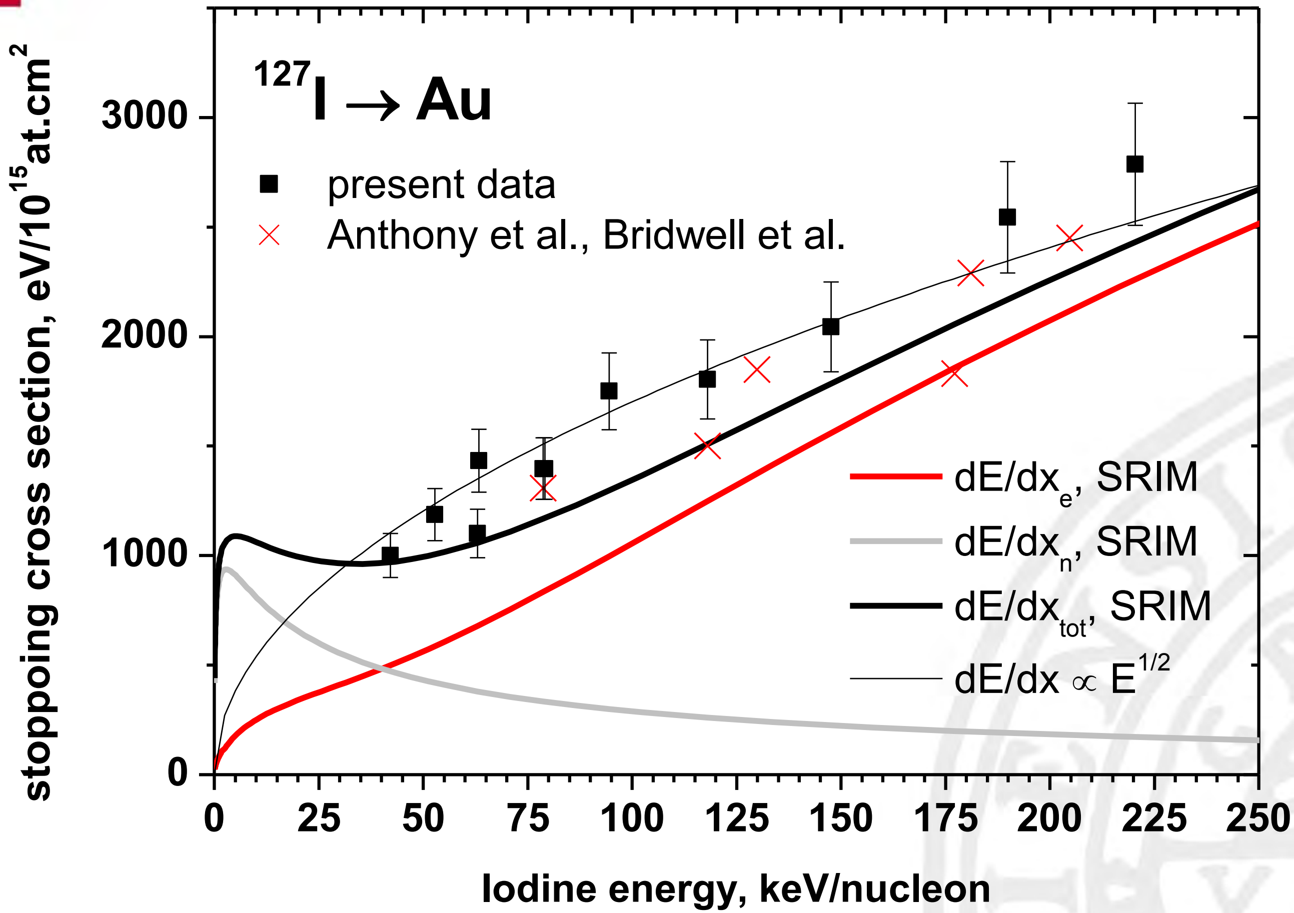
- Experiment performed with 5 MV NEC Tandem
- Forward scattering under 45 degrees
- Au films of up to 50 nm thickness
- ToF-E detector for discrimination of scattered and recoiling particles
- Complication: no 2π-symmetry (simulations)

Forward scattering of Iodine: spectra



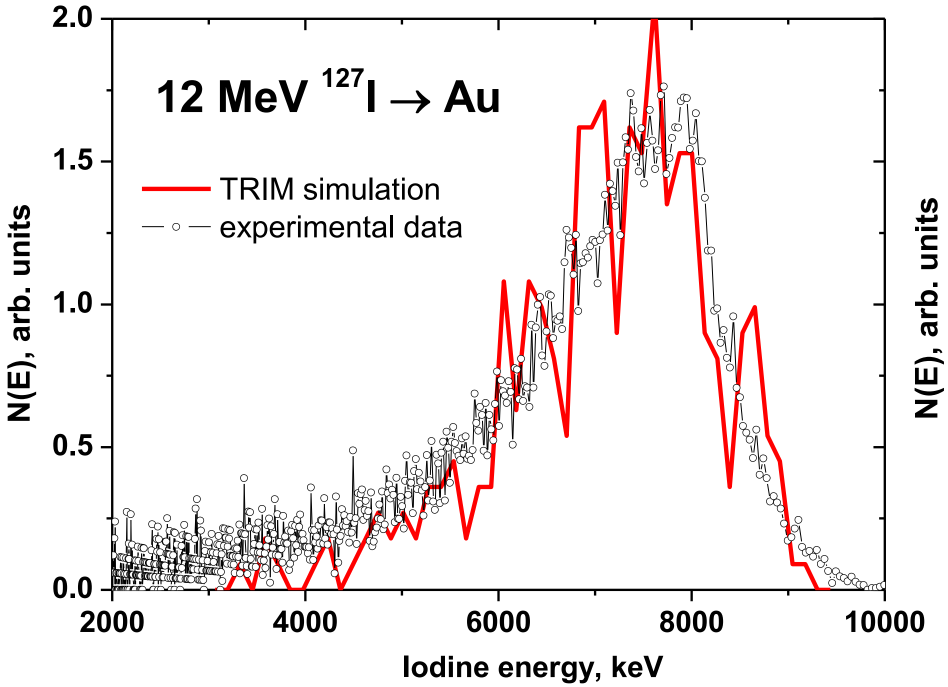
- Spectra resemble RBS-spectra for thin films
- Reasonable definition of ΔE
- Stopping power evaluation performed as for Ne

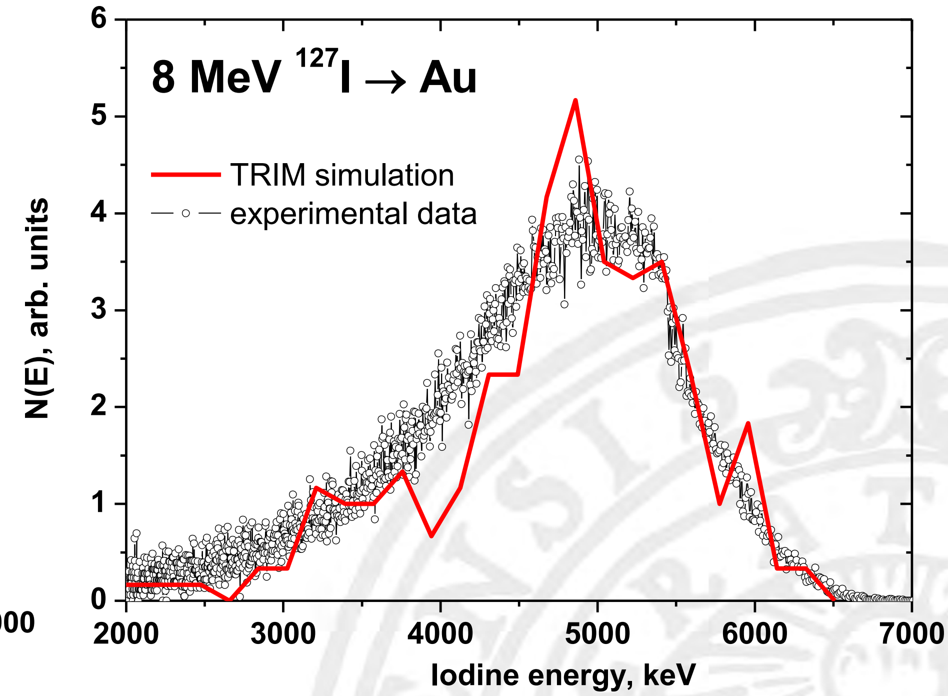
Total stopping power deduced for I in Au



- **High absolute total stopping power with reasonable v/E scaling**

Future steps: simulation by TRIM and evaluation of the relative contributions



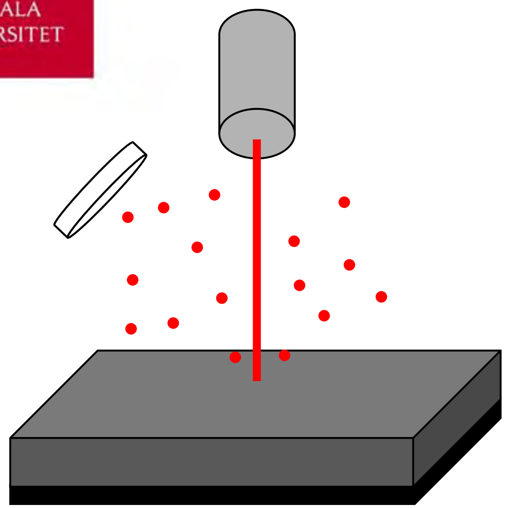


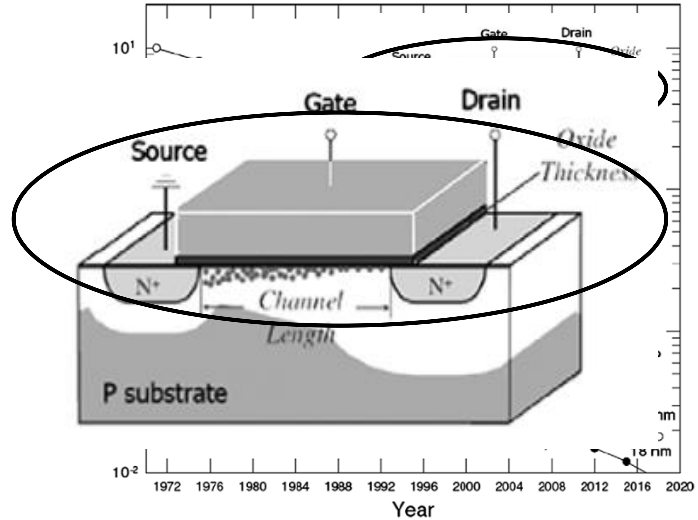
1. **Simulation by TRIM**
2. **Characterization of trajectories: separate dE/dx_e and dE/dx_n**

Energy loss of light ions: H and He

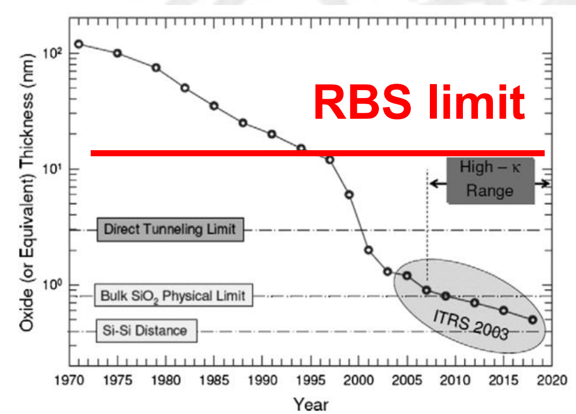
Energy loss of light ions: H and He in HfO_2

Why HfO_2 at keV energies?



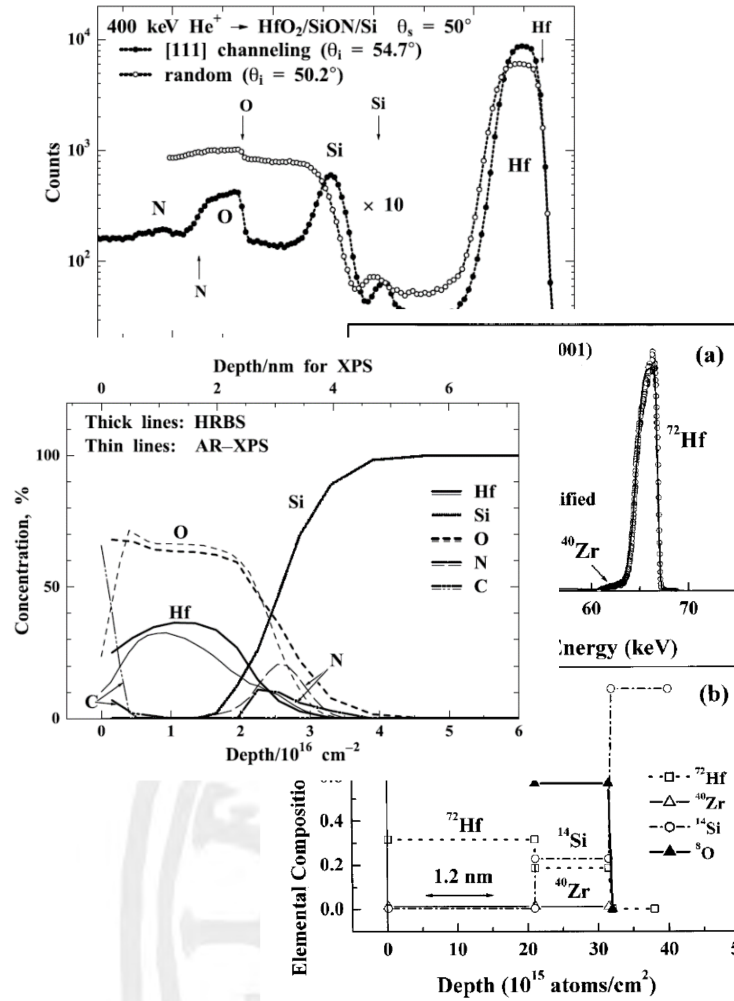


H. Wong, H. Iwei, Microelec. Eng. (2006)



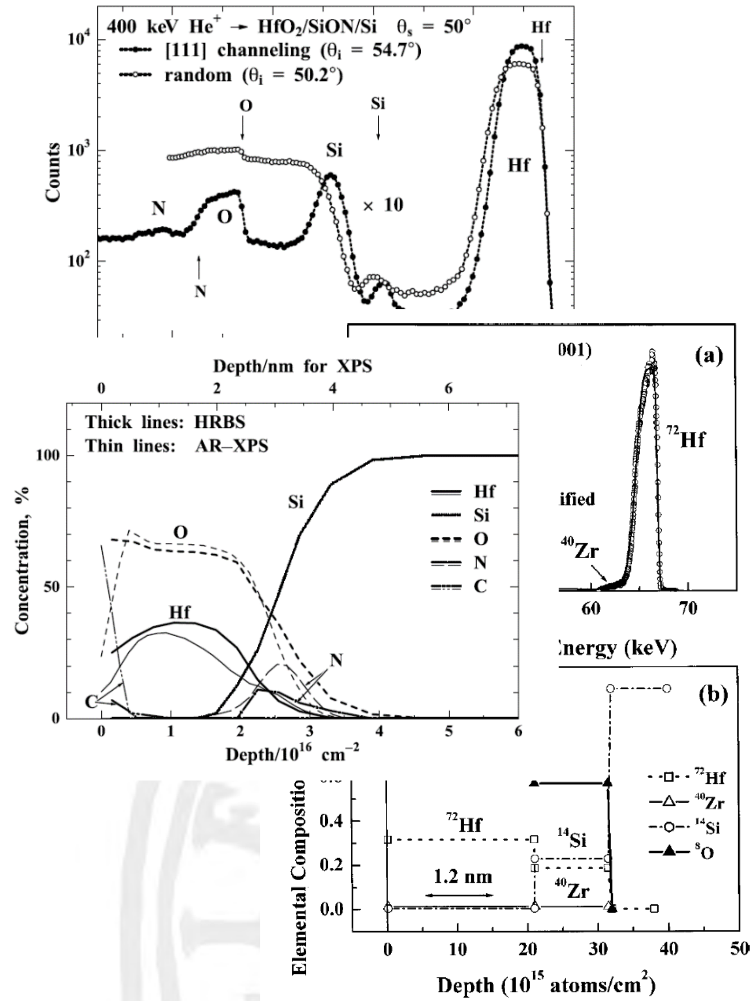
- **Ion scattering for depth profiling**
- **Thin films from e.g. electronics (gate-stacks)**
- **90's: Ongoing miniaturization: Film thickness below resolution limits for "conventional" RBS**
- **Last decade: high-k materials – good scatterers**
- **Higher ΔE/E: → development of MEIS**

Characterization of high-k dielectrics…



- **Investigations of stacks containing HfO_2 are common**

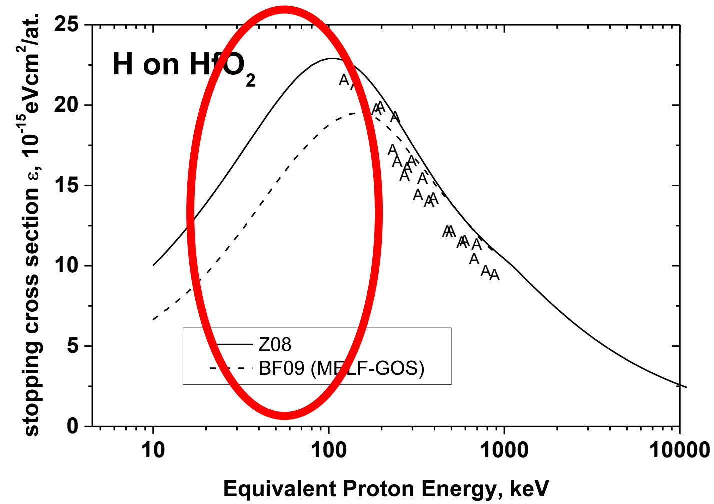
…a MEIS-success story…



- **Investigations of stacks containing HfO_2 are common**

…with open questions.

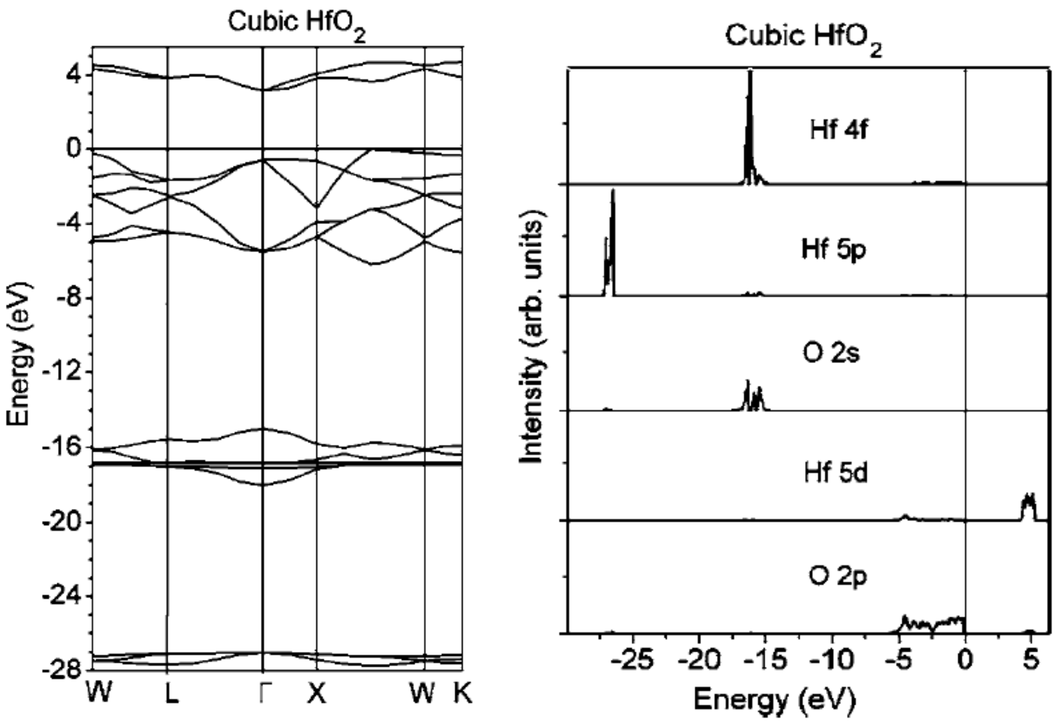
- **Investigations of stacks containing HfO_2 are common**



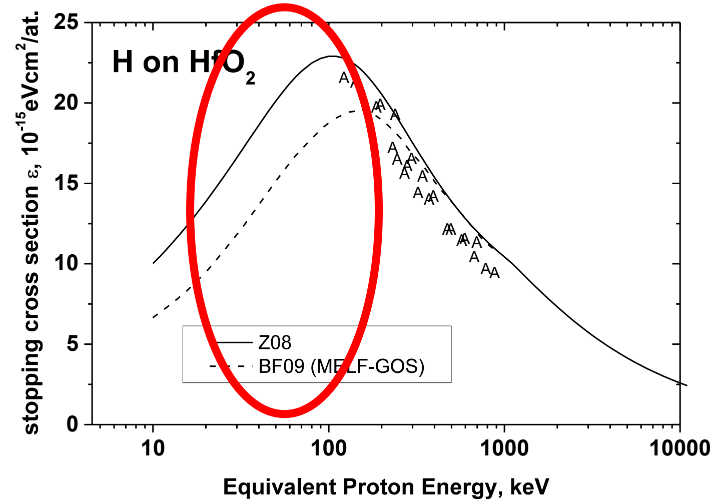
from H. Pauls stopping collection:
www-nds.iaea.org/stoppinggraphs/

- **Experimental stopping data is scarce**

…with open fundamental questions.



T.V. Perevalov et al., J. Appl. Phys. (2007)



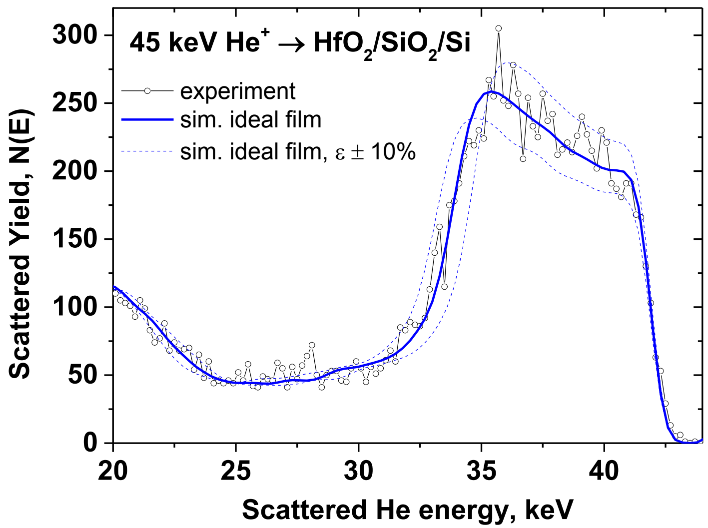
from H. Pauls stopping collection:
www-nds.iaea.org/stoppinggraphs/

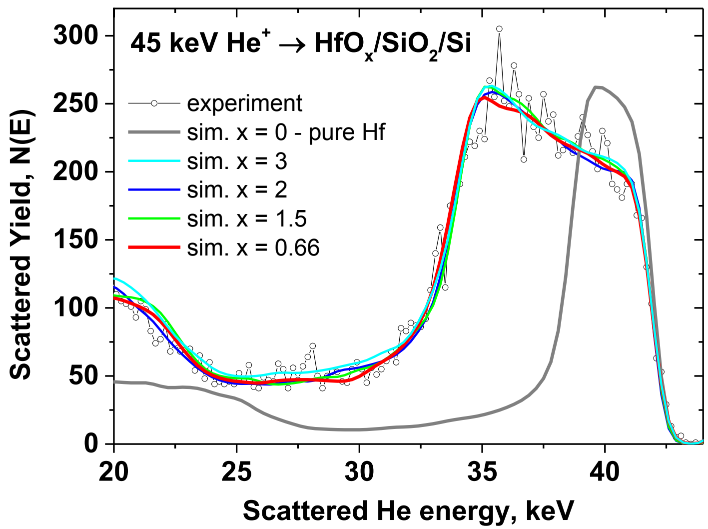
- **Experimental stopping data is scarce**
- **Insulator with ~ 5-6 eV gap**

Relevance for analysis of thin films

Potential complications:

- **Energy loss in the thin film ↔ Thickness calibration in MEIS**
- **Entanglement of compositional information and energy loss**





D. Primetzhofer et al., Nucl. Instr. Meth. B 332 (2014)

Analysis of electronic energy loss in HfO_2

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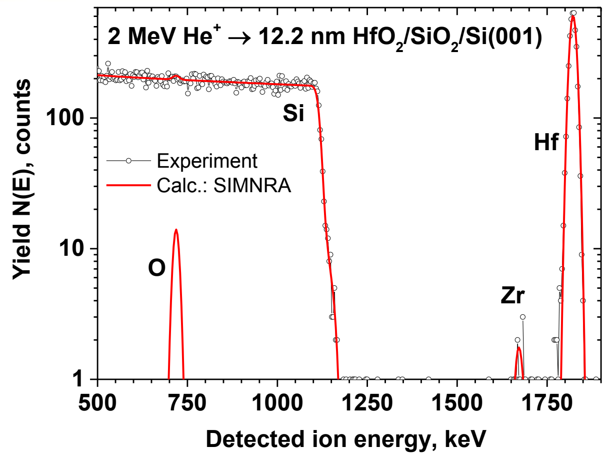
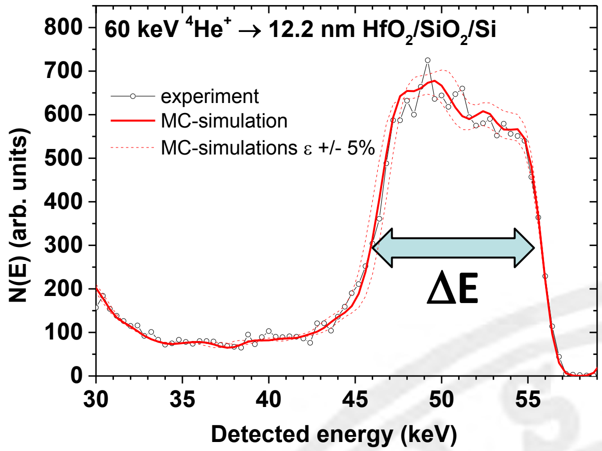
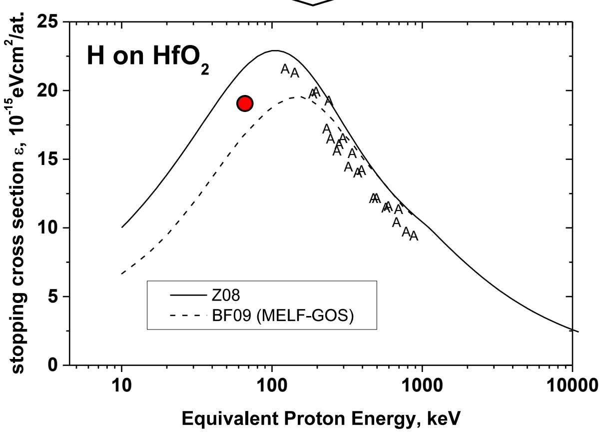
- Fit width of ToF-MEIS energy spectra





- Determine Hf content from RBS



Uncertainty from:

- **Statistics**
- **Thickness calibration**
- **Composition**

Analysis of electronic energy loss in HfO_2

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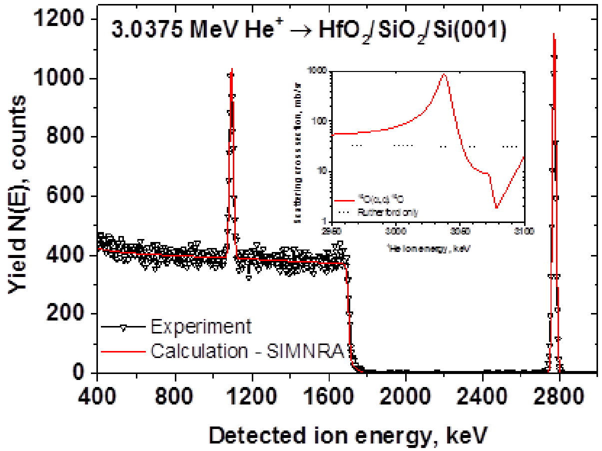
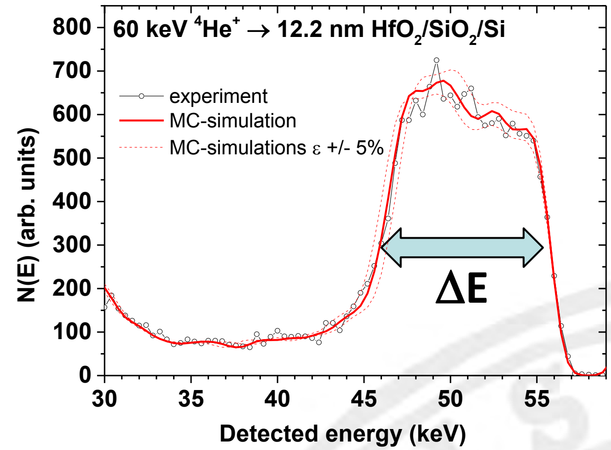
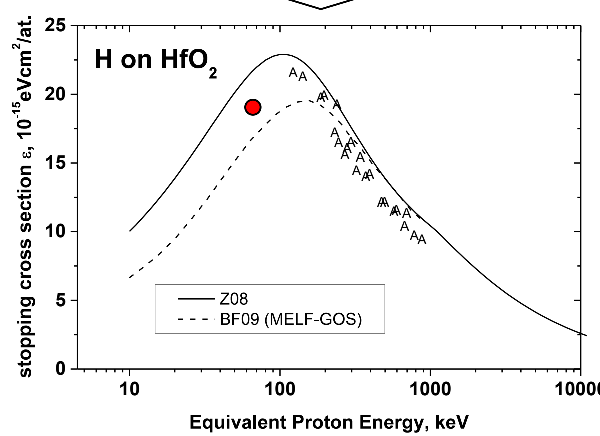
- Fit width of ToF-MEIS energy spectra



C.J. Zoller, Nucl. Instr. Meth. B 347 (2015)



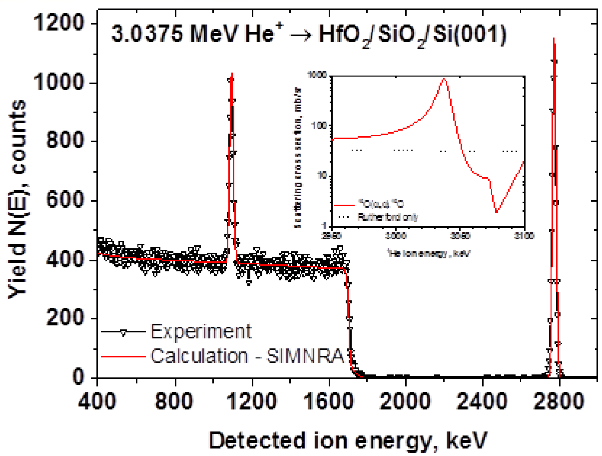


- Determine Hf content from RBS
  (check oxygen by e.g. EBS, channeling,…)

Uncertainty from:

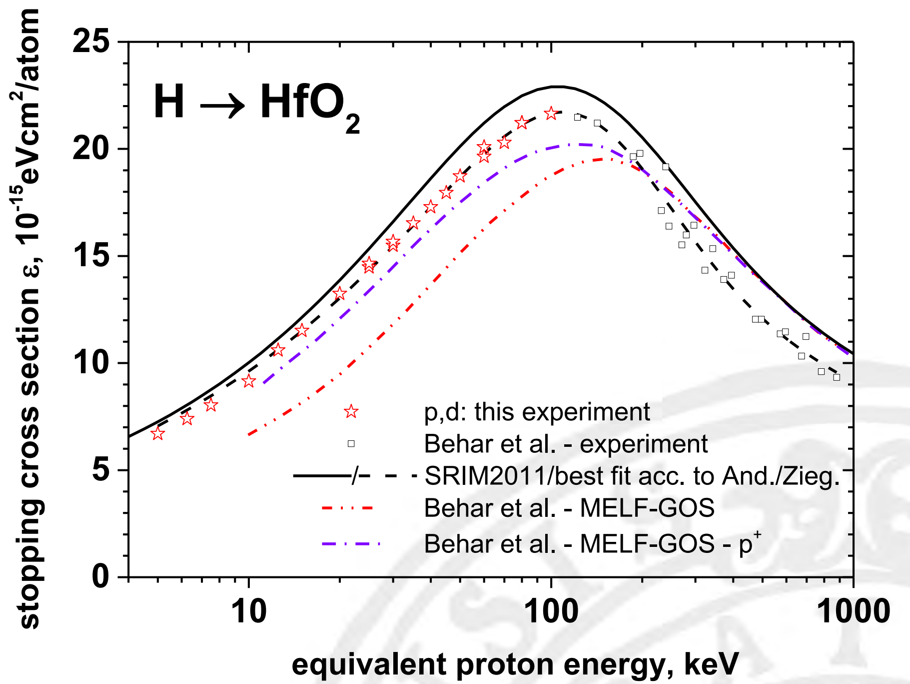
- **Statistics**
- **Thickness calibration**
- ~~**Composition**~~

Analysis of electronic energy loss in HfO_2



C.J. Zoller, Nucl. Instr. Meth. B 347 (2015)

- Determine Hf content from RBS



D. Primetzhofer, Nucl., Instr. Meth. B 320 (2014)

Uncertainty from:

- **Statistics**
- **Thickness calibration**
- ~~**Composition**~~

- **Very good agreement with data of Behar et al.**
  - **S ∝ $E^{1/2}$ down to 5keV/u.**

Analysis of electronic energy loss in HfO_2

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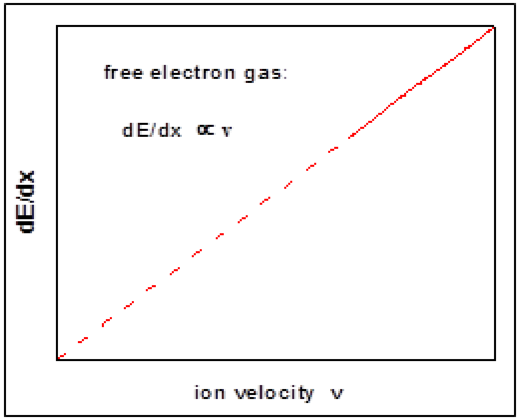
Theory:



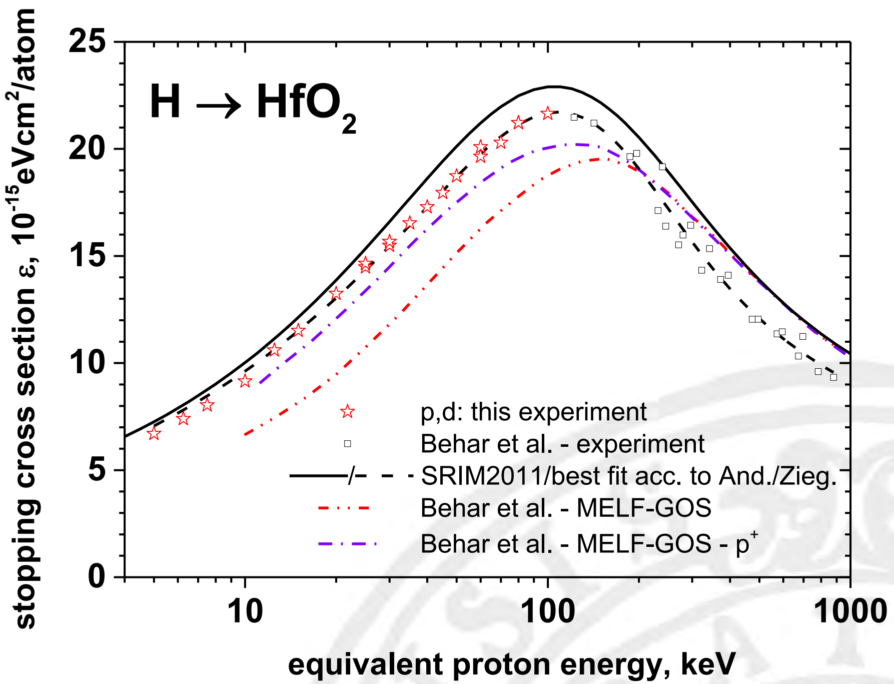
Fermi et al. Phys. Rev. (1947)

$dE/dx = Q(r_s,\ldots)\cdot v$

$\Delta E_{max} \leq 2\cdot m_e\cdot v\cdot v_F$

Maximum energy transfer
+ Excitation limits

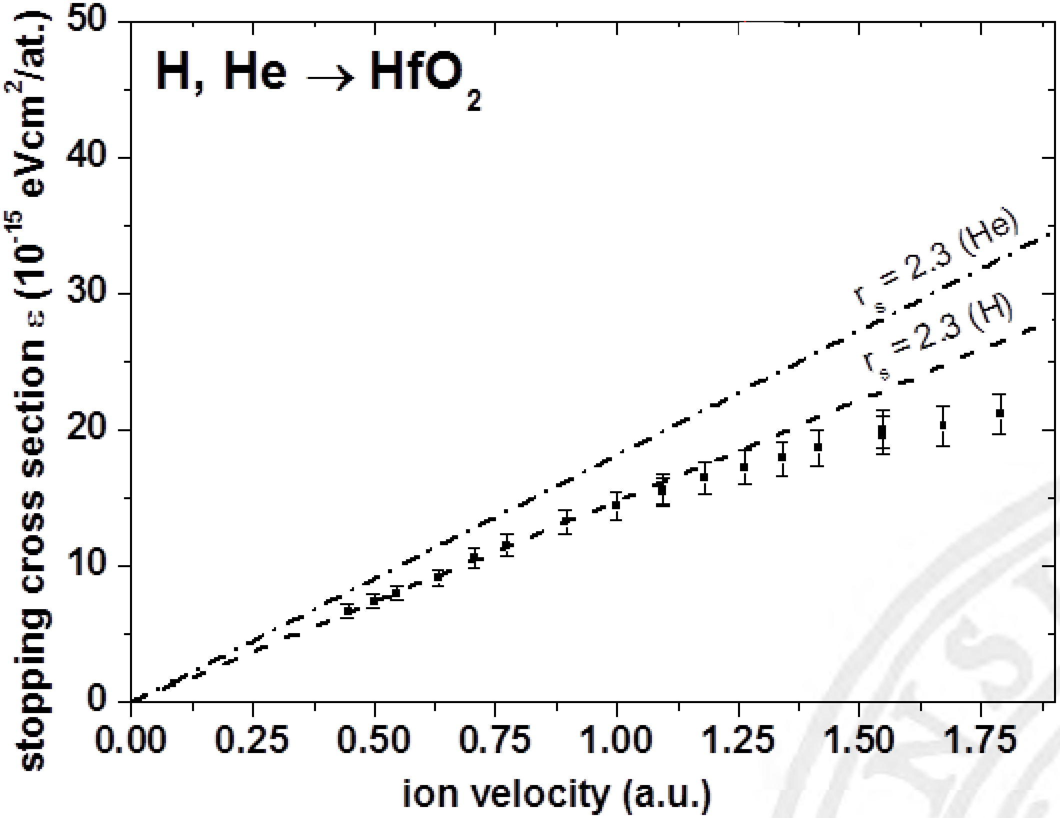
Effects on stopping



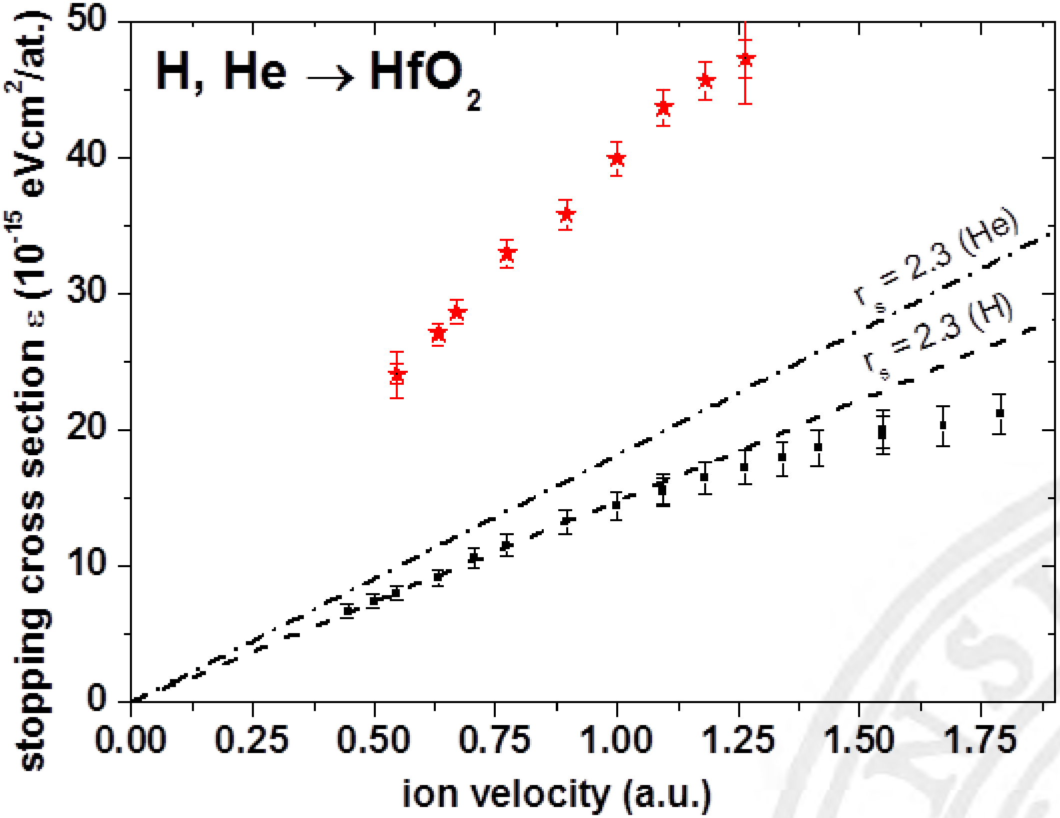
D. Primetzhofer, Nucl., Instr. Meth. B 320 (2014)

- **Very good agreement with data of Behar et al.**
- **$S \propto E^{1/2}$ down to 5keV/u.**

Electronic stopping in HfO_2: He

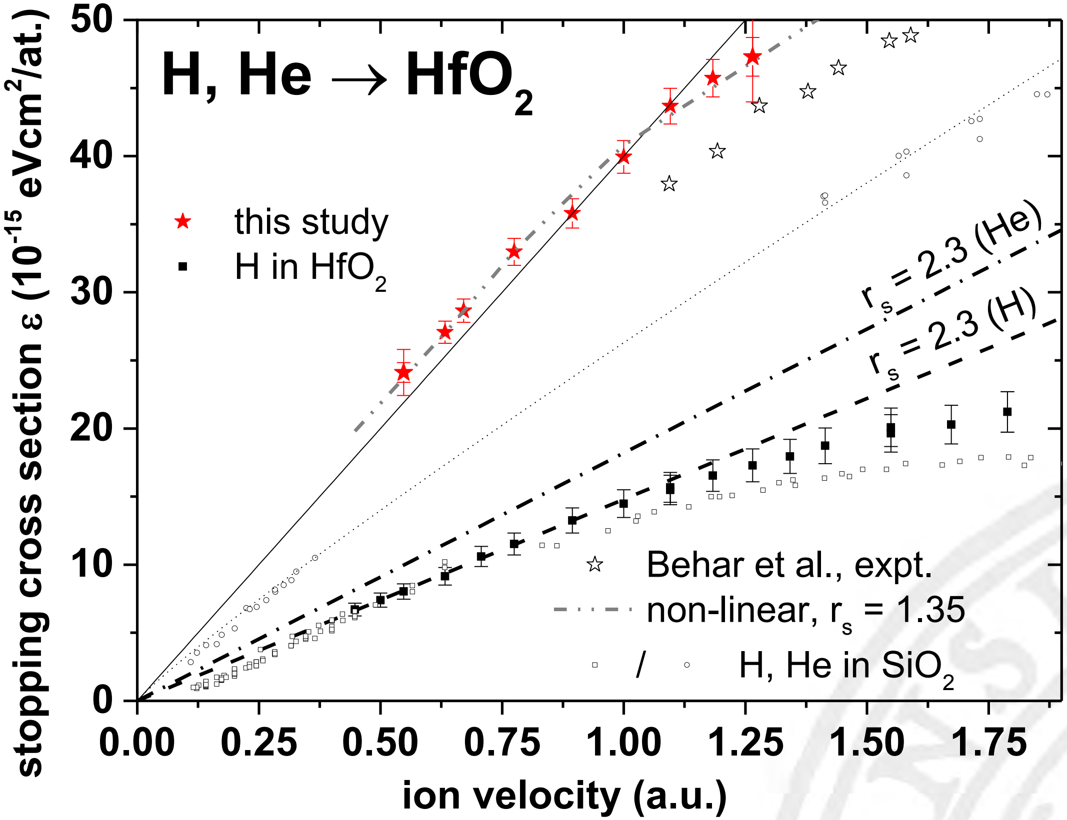


Electronic stopping in HfO_2: He



- **Totally different electron density in DFT-models necessary**

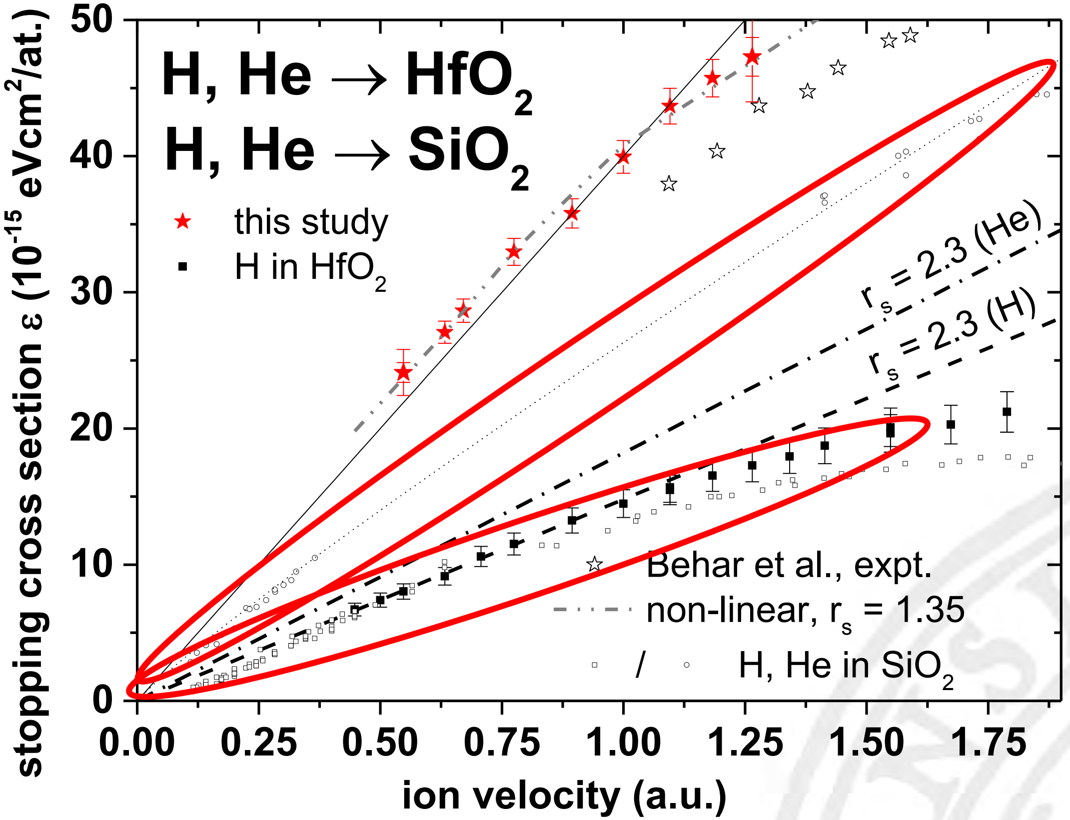
Electronic stopping in HfO_2: He



D. Primetzhofer, Phys. Rev A 89 (2014)

- **Totally different electron density in DFT-models necessary**
- **Energy loss shows a non-linear behaviour!**

Comparison: SiO_2 vs. HfO_2: He



D. Primetzhofer, Phys. Rev A 89 (2014)

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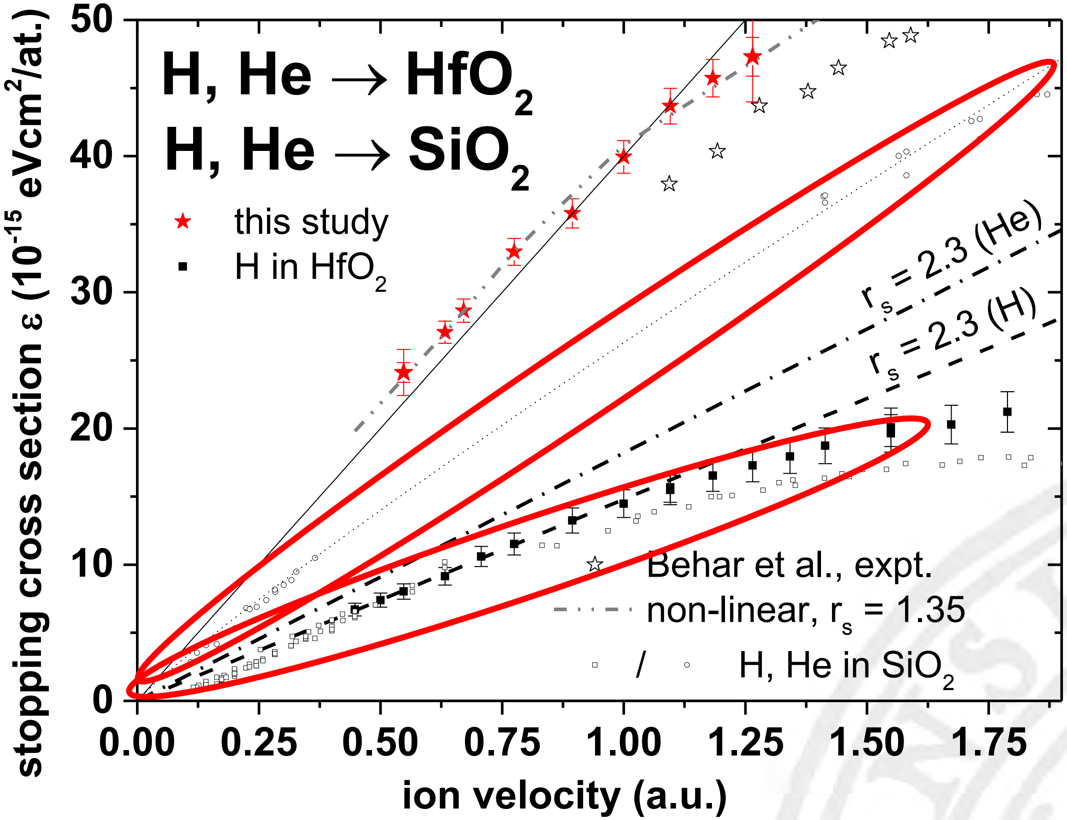

D. Primetzhofer, Phys. Rev A 89 (2014)

- **Protons show no large discrepancy – excitation of O-2p states!?**
- **He-stopping high in both materials**

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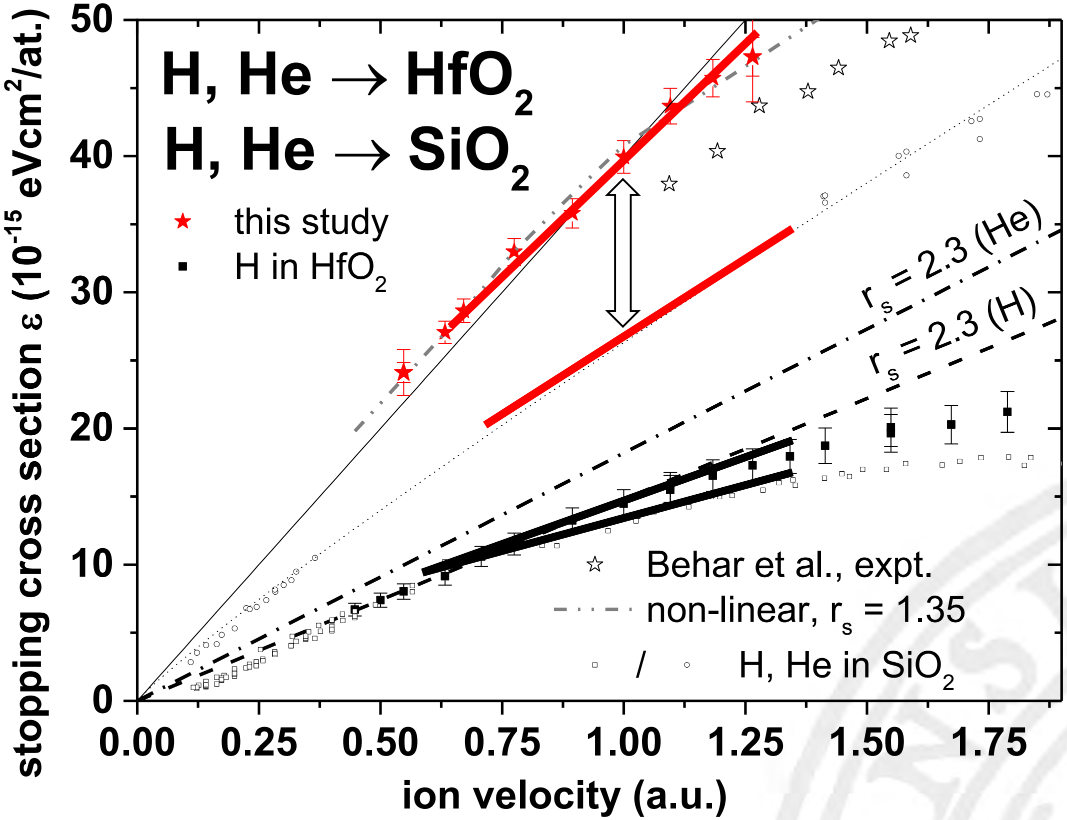
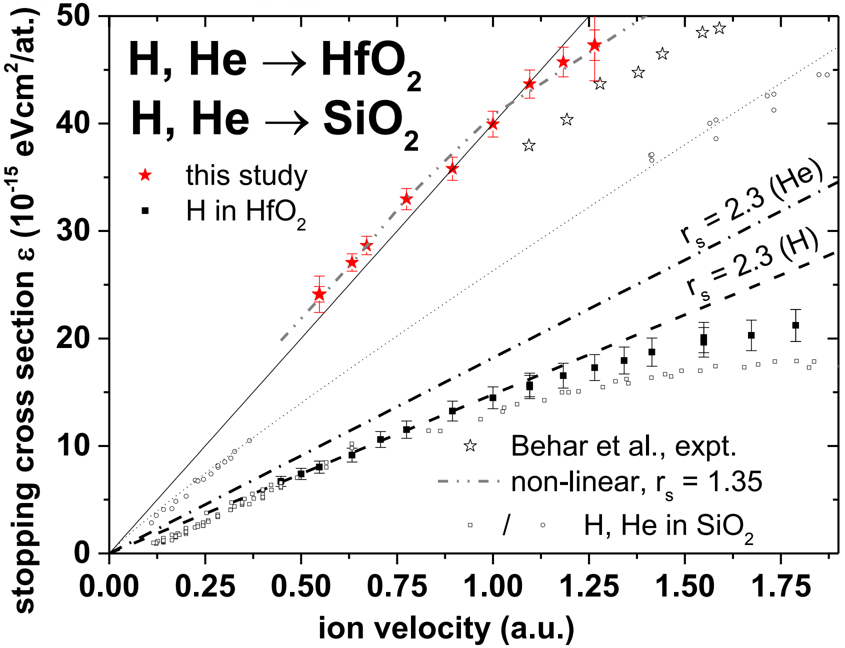
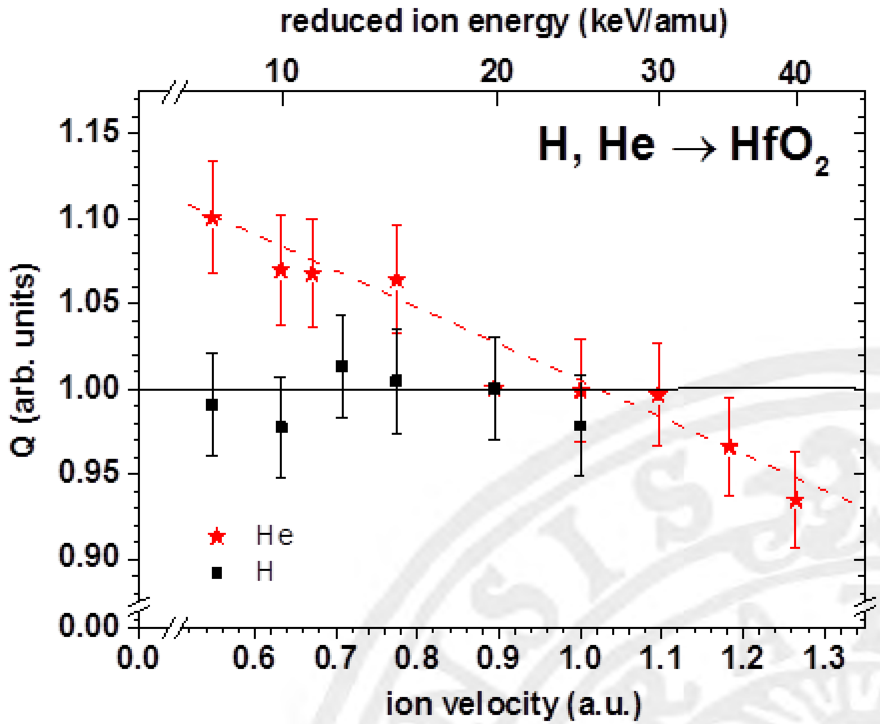


D. Primetzhofer, Phys. Rev A 89 (2014)

- **Protons show no large discrepancy – excitation of O-2p states!?**
- **He-stopping high in both materials but much higher in HfO_2**

Electronic stopping in HfO_2: He

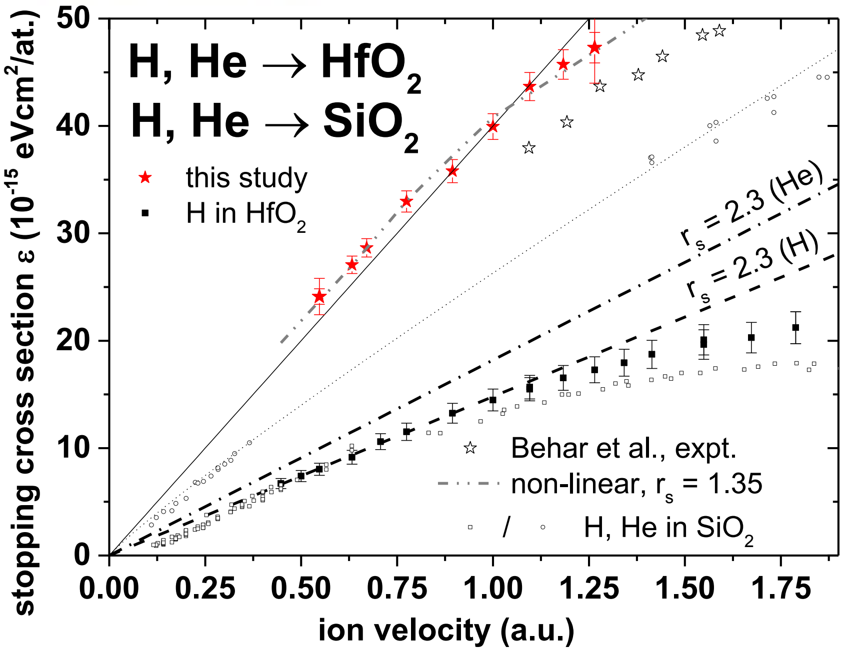


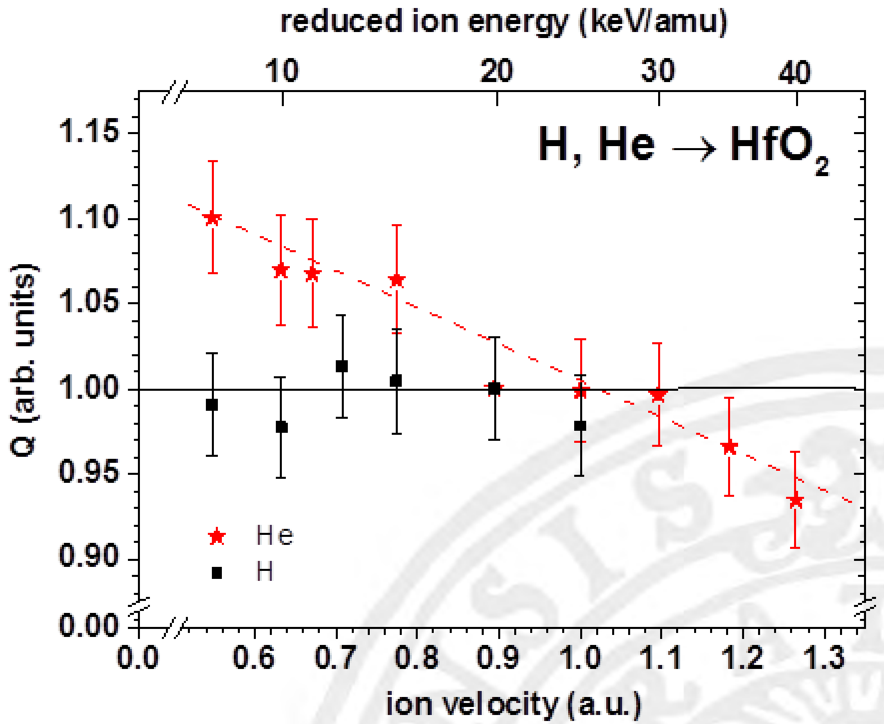


D. Primetzhofer, Phys. Rev A 89 (2014)

- **Protons: $dE/dx \propto E^{0.5}$ ↔ He: non-linear velocity dependence**
- **Different electron density in DFT-models necessary**
- **Very high energy loss compared to SiO_2 – different from protons**

Electronic stopping in HfO_2: He





D. Primetzhofer, Phys. Rev A 89 (2014)

- **Protons: $dE/dx \propto E^{0.5}$ ↔ He: non-linear velocity dependence**
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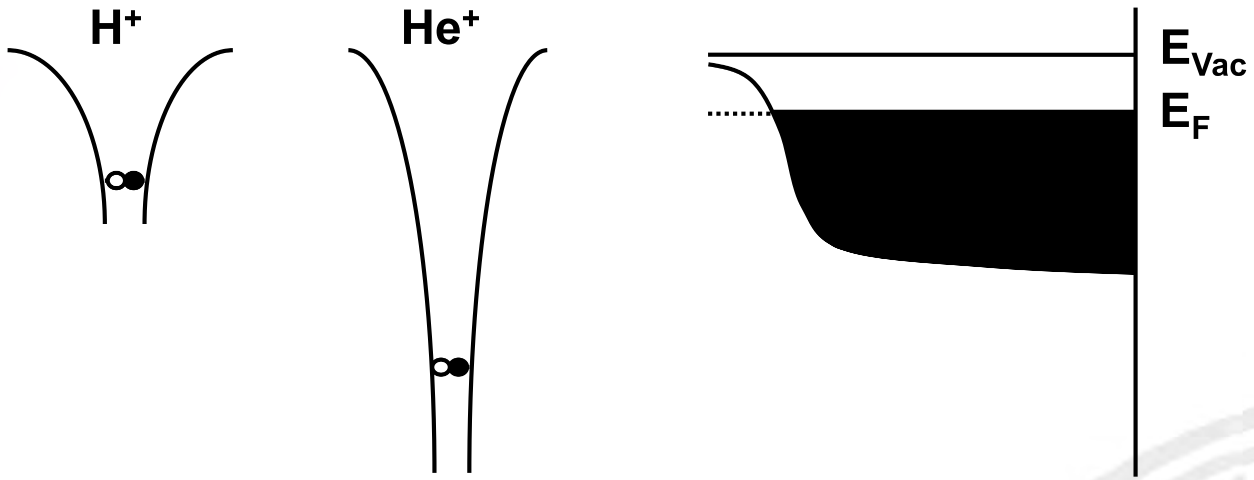
So why is He so much different?

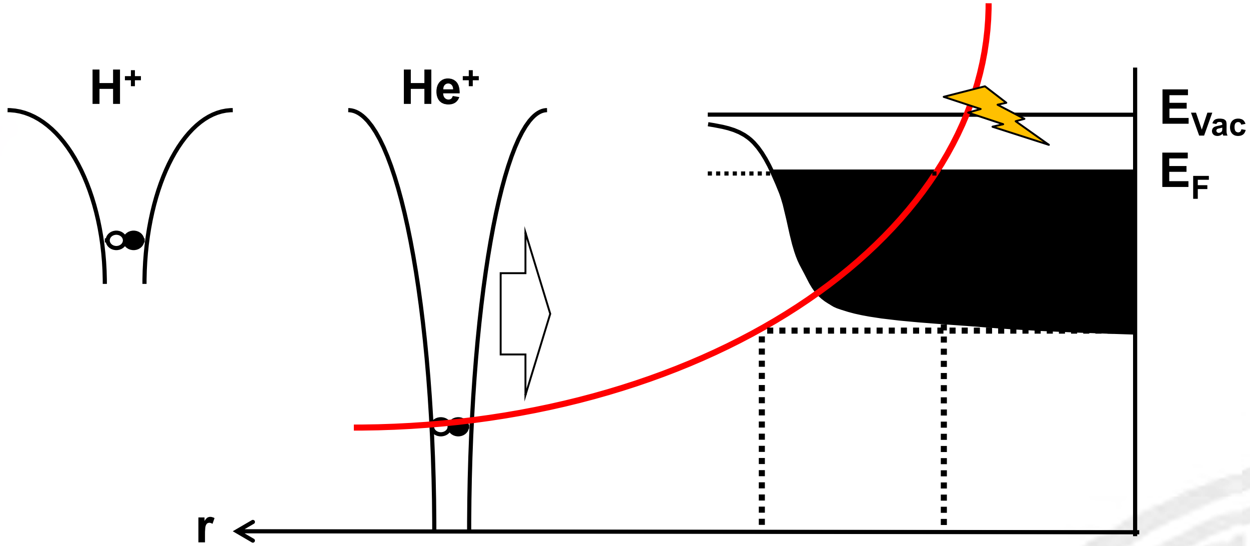


Difference in position of unoccupied atomic level:

H(1s) = 13.6 eV vs. He(1s) = 24.4 eV

H(1s) resonant with bands in solid ↔ He(1s) below lower band edge

So why is He so much different?



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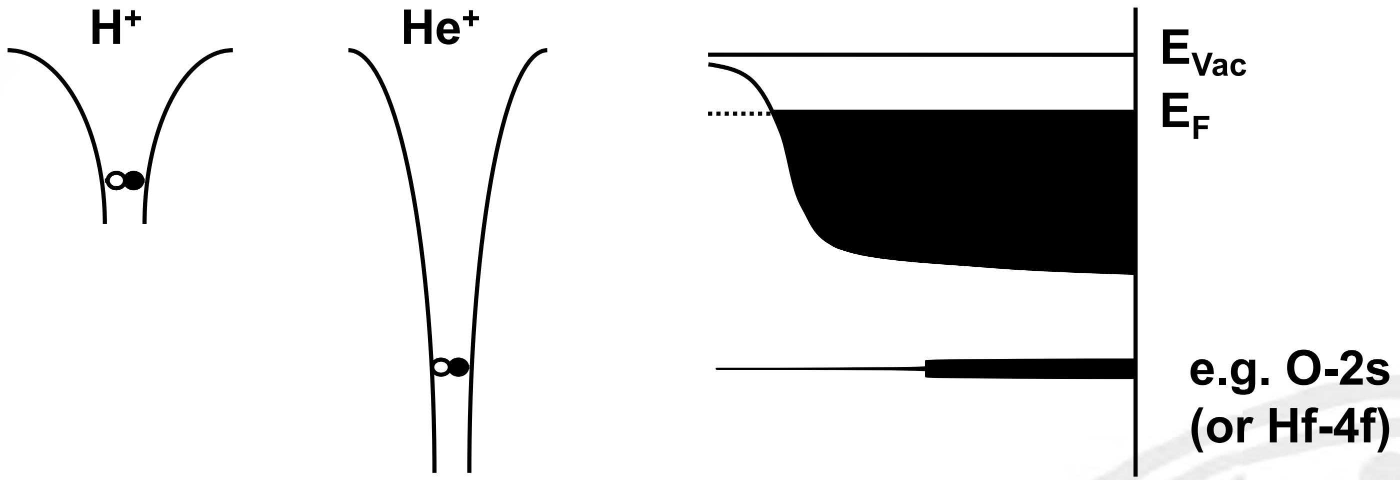
Levels are dynamic: E(r) with r = distance between nuclei

He: Critical distance for resonant neutralization and reionization

More possible differences:



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He: Quasi-resonant levels influence charge states

Reionization well known from LEIS

Table for reionization thresholds (see Section 6.3.3(b))

Element	He		
	Method 1	Method 2	Method 3
Ag	>2000 [113]	≤1500 [37]	
Al	300 [113]	≤500 [37]	400 [110]
Au		≤1000 [37]	
Ba	600 [114]		
C	200 [113]		
Mo	400 [113]	≤1000 [37]	900 [5]
Na	≤200 [113]		
Ni	>2000 [113]	≤1500 [37]	2300 [6]
O			700 [91]
Pb	>2000 [113]		
Pd		≤1000 [37]	1100 [115]

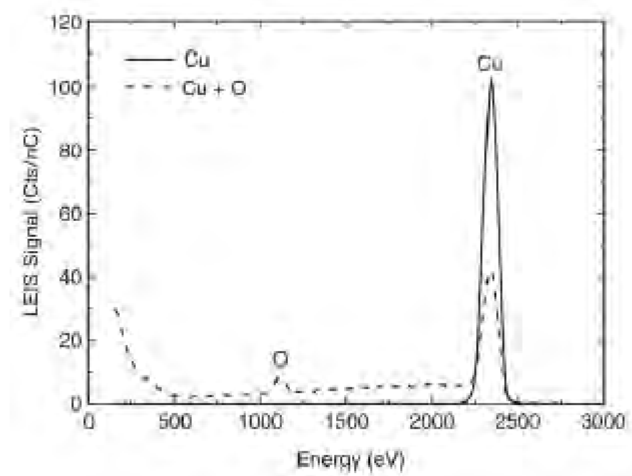
H.H. Brongersma et al., Surf. Sci. Rep. (2007)

Thresholds for reionization:

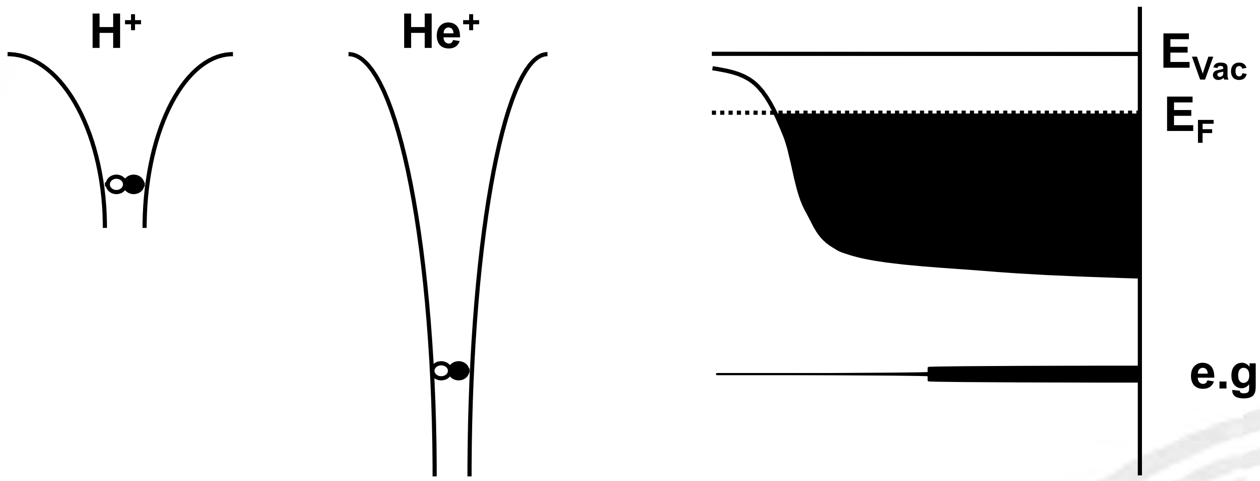
O: 700 eV

Determined from reionization tails

→ even lower in backscattering



More possible differences



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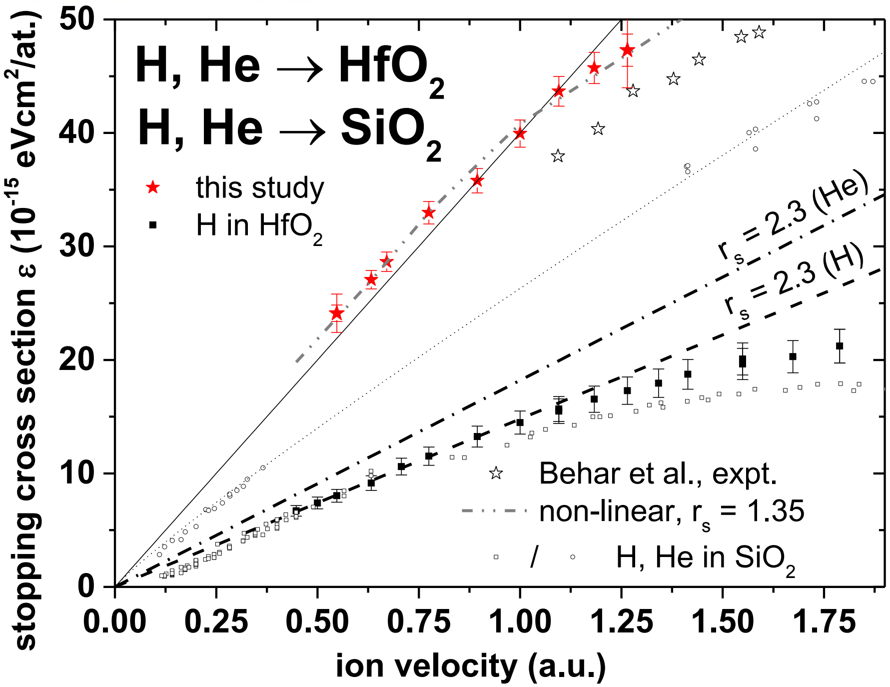
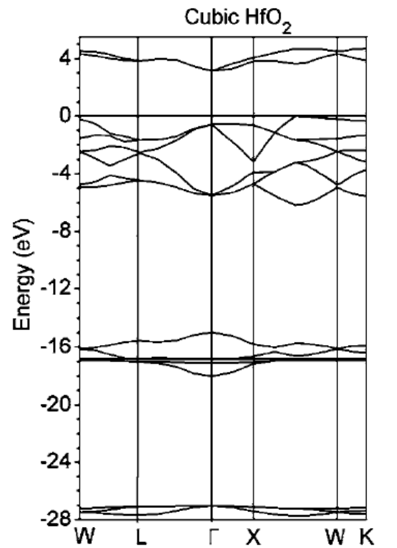
H(1s) resonant with bands in solid ↔ He(1s) below lower band edge

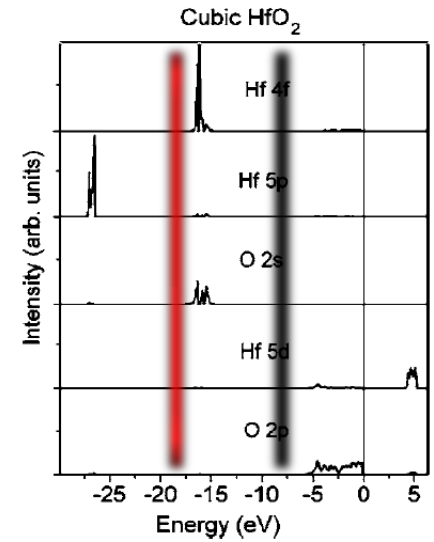
Levels are dynamic: E(r) with r = distance between nuclei

He: Quasi-resonant levels influence charge state & dissipate energy

Analysis of electronic energy loss in HfO_2







T.V. Perevalov et al., J. Appl. Phys. (2007)

- **Interaction of He-1s with O-2s in both HfO_2 and SiO_2**
- **In HfO_2 additional interaction with heavily populated 4f-states**

Conclusions (I):

- (ToF-) MEIS offers an ideal tool for high-resolution thin film profiling.
- Energy loss at medium energies (quantification!) can be complex!
- Trajectory dependent loss in atomic collisions can be relevant (He, Ne).

Conclusions (II):

- (ToF-) MEIS offers an ideal tool for high-resolution thin film profiling.
- Energy loss at medium energies (quantification!) can be complex!
- Trajectory dependent loss in atomic collisions can be relevant (He, Ne)..
- **Heavier Ions: Nuclear stopping in backscattering experiments found low compared to SRIM (random trajectories).**
- **Inherent trajectory selectivity of each experiment affects energy loss.**
- **Selective mechanisms in backscattering almost as effective as in transmission.**
- **Monte Carlo calculations should be performed for relevant geometry. (Use TRIM not SRIM)**