ATOM UND OBERFLÄCHEN PHYSIK

Quantitative Low Energy Ion Scattering: achievements and challenges

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Layout

- Intro
- Low energy ion scattering

  → ESA : ions only

- Achievements:

  → surface composition analysis

  - Scattering potential
  - Charge exchange
  - information depth

- Challenges

  → subsurface information

  - stopping power ↔ reionization probability

  → TOF-LEIS

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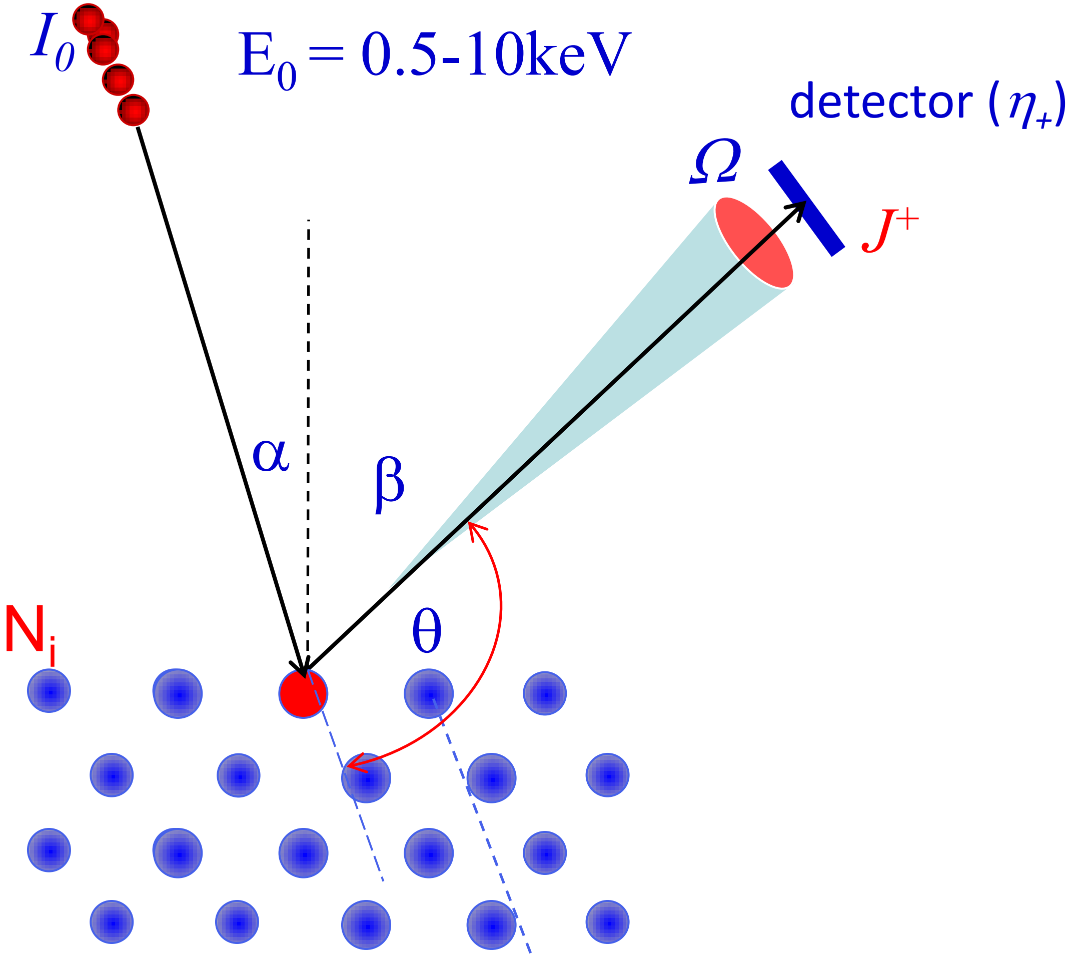
Low Energy Ion Scattering

projectiles: noble gas ions, large scattering angle (no grazing collisions)



$$J_i^+ = I_0 \cdot P_i^+ \cdot c_i N_s \cdot \frac{d\sigma_i}{d\Omega} \cdot \Omega \cdot \eta_+$$

Surface composition analysis

- J_i^+ ... detected ion current (ions/sec)
- I_0 ... primary ion current (ions/sec)
- c_i ... atomic surface concentration
- N_s ... atomic surface density (atoms/cm^2)
- P_i^+ ... ion fraction of atom i
- $d\sigma_i/d\Omega$ ...scattering cross section (atom i)
- Ω ... detector solid angle
- η_+ ... detector efficiency (incl. transmission)

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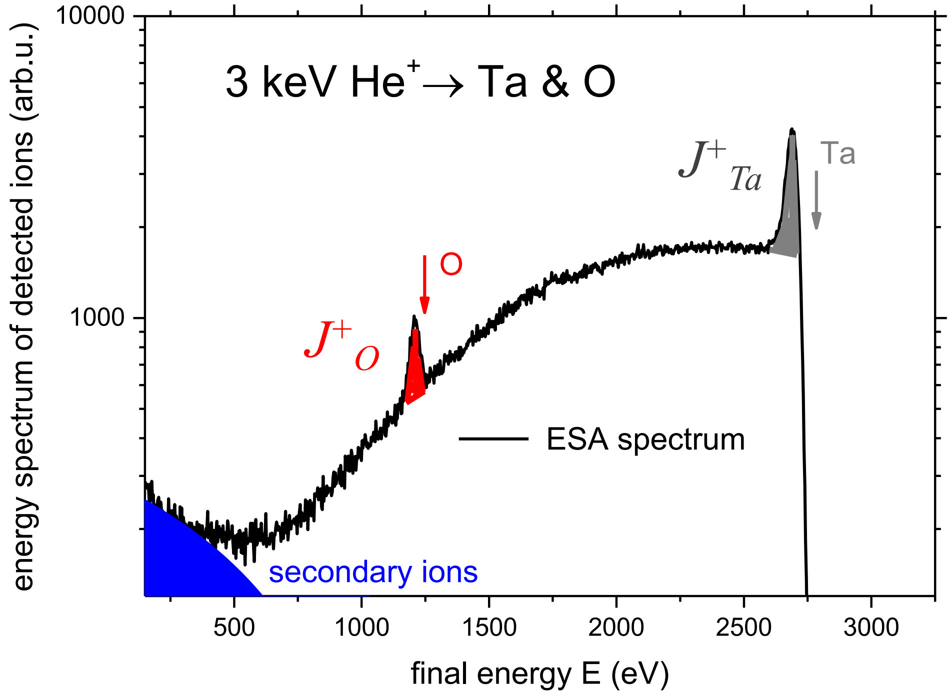
Low Energy Ion Scattering

ESA: only ions detected ↔ surface sensitivity



(B. Bruckner, 201 5)

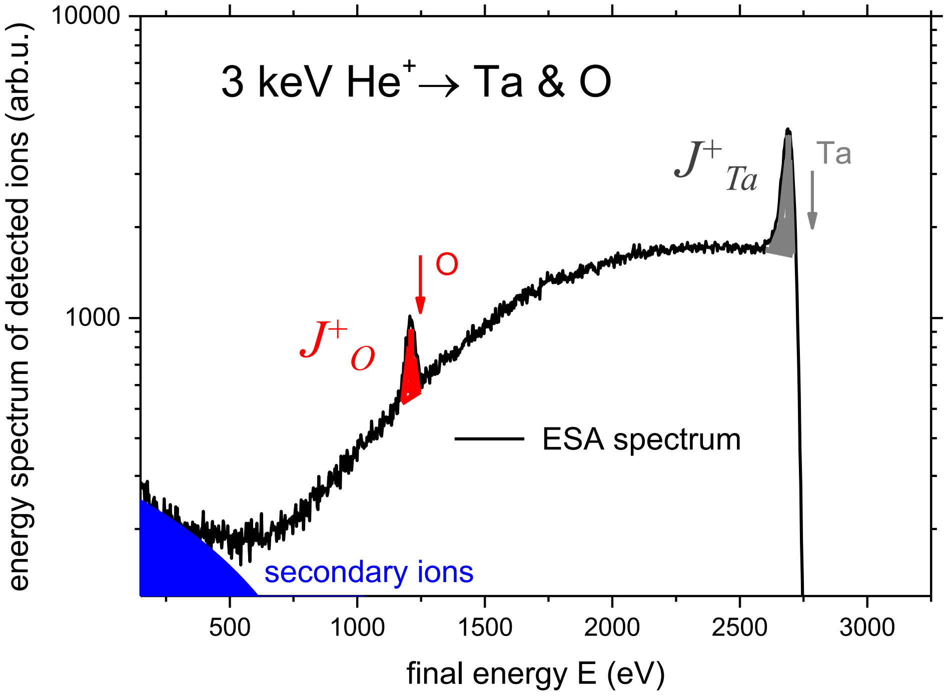
Sensitivity factor S_i^+

$$J_i^+ = I_0 \cdot P_i^+ \cdot c_i N_s \cdot \frac{d\sigma_i}{d\Omega} \cdot \Omega \cdot \eta_+$$

binary surface Ta & O: $c_{Ta} + c_O = 1$

Low Energy Ion Scattering

ESA: only ions detected ↔ surface sensitivity



(B. Bruckner, 201 5)

$$c_i = \frac{J_i^+}{I_0 N_0 \left(\frac{d\sigma}{d\Omega}\right)_i P_i^+ \, \eta^+} = C \, \frac{A_i^+}{P_i^+}$$

$\frac{J_i^+}{I_0 N_0 \left(\frac{d\sigma}{d\Omega}\right)_i} \equiv A_i^+$

Relative yield

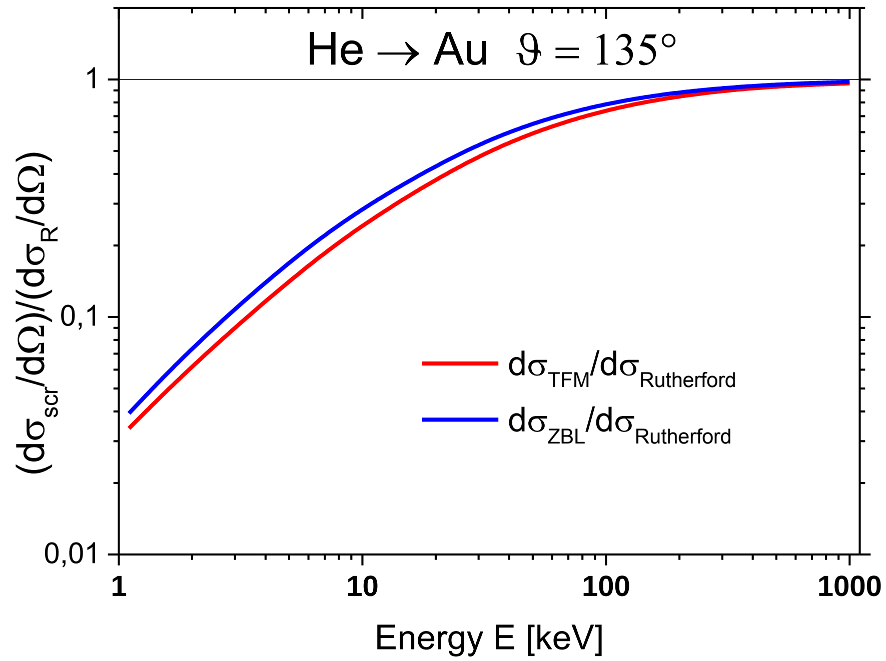
C ... expt. constant

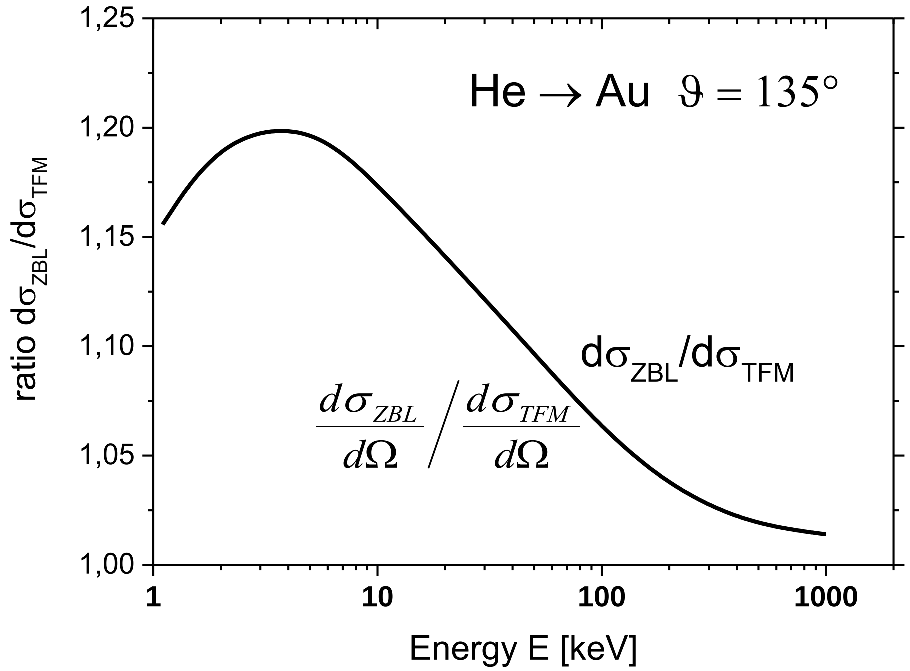
binary surface Ta & O: $c_{Ta} + c_O = 1$ ↔ $$\frac{A_{Ta}^+}{P_{Ta}^+} + \frac{A_O^+}{P_O^+} = \frac{1}{C}$$

Scattering cross section

Screened Coulomb potential: $V(r) = V_C(r) \cdot \Phi(r/a)$ $\Phi(r/a)$ ...screening function

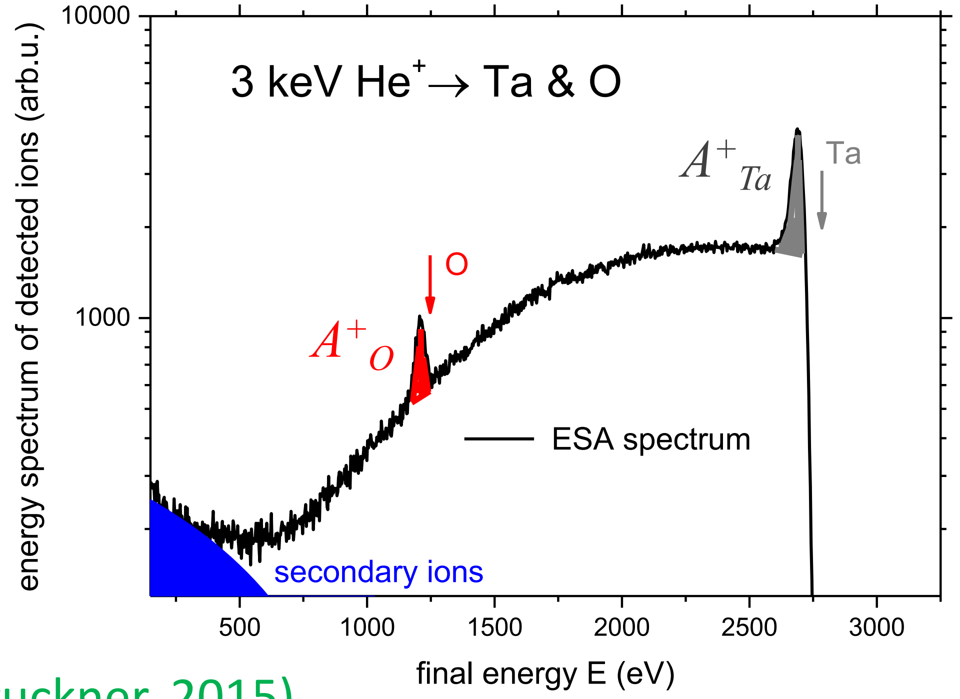
$d\sigma/d\Omega$ depends on $\Phi(r/a)$ model $\Phi(r/a) = \sum_{i=1}^{3} b_i \cdot \exp(-c_i \cdot r/a)$





Surface composition analysis

ESA: only ions detected ↔ surface sensitivity



(B. Bruckner, 2015)

$$c_i = \frac{J_i^+}{I_0 N_0 \left(\frac{d\sigma}{d\Omega}\right)_i P_i^+ \eta^+} = C\,\frac{A_i^+}{P_i^+}$$

$\equiv A_j^+$

constant?

→ charge exchange!

Charge exchange (He ions)

- **Auger neutralization (AN)**
  is possible at any ion energy E & at any surface atom

- **Resonant charge exchange** (reionization, res. neutralization)
  (reionization & resonant neutralization)
  E > threshold energy $E_{th} \leftrightarrow R_{min}(E_{th}, \vartheta) < R_{crit}$

- **Quasi resonant neutralization** (qRN)
  resonant levels at atom and ion
  ($\rightarrow$ quantum oscillations, difficult quantification)

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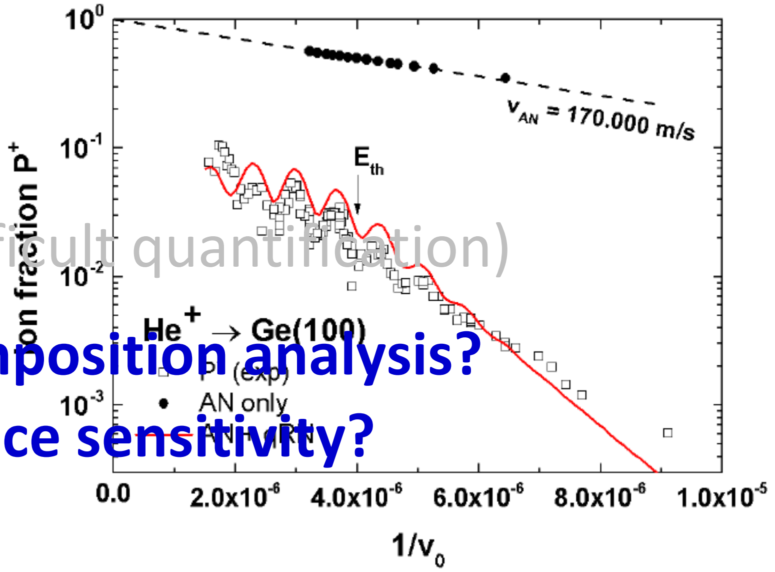

How to do quantitative composition analysis?

How to obtain surface sensitivity?

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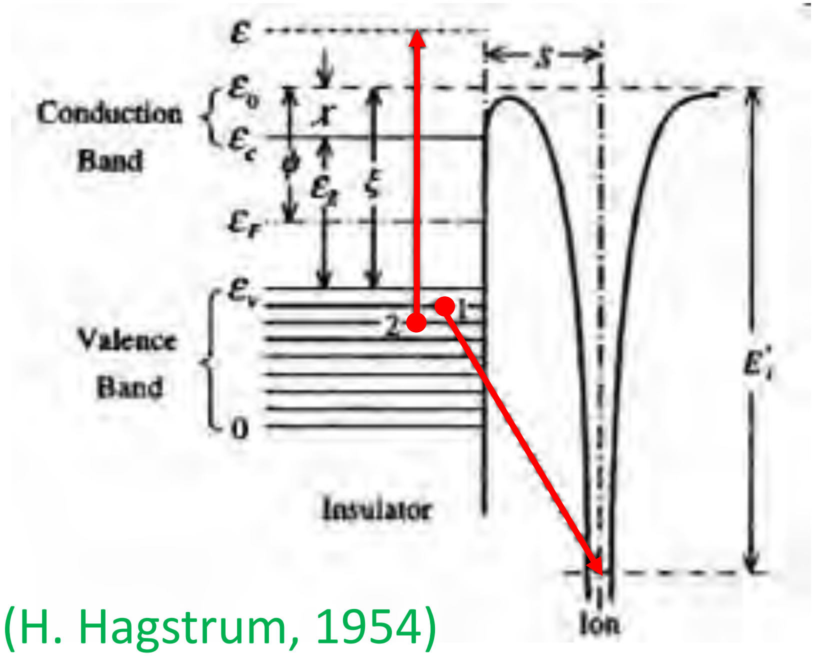
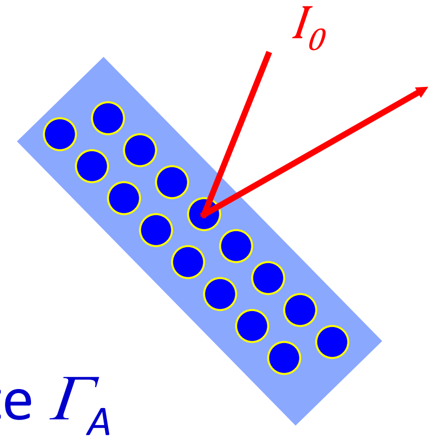
Auger Neutralization (AN)



(H. Hagstrum, 1954)



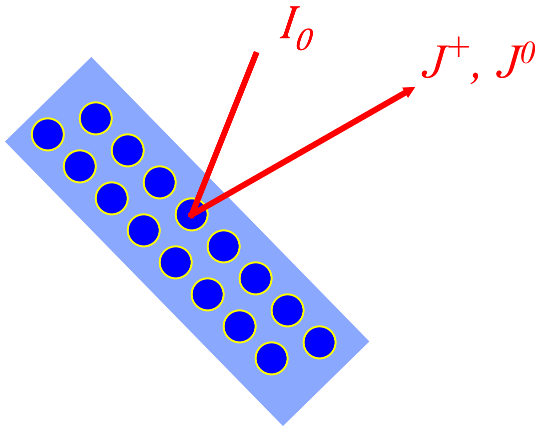
Auger transition rate Γ_A

Γ_A depends on electron density parameter r_s

$\rightarrow \Gamma_A(r_s(x,y,z))$ in front of a surface

Typically, $\langle\Gamma_A\rangle \approx 1 \ldots 2\cdot10^{15}$/s

Auger Neutralization (AN)



Rate equation (1D) for survival probability P^+

$$dP^+ = -P^+ \cdot \Gamma_A(z)dt = -P^+ \frac{\Gamma dz}{v_\perp}$$

→ survival probability $P^+ = \exp(-v_c/v_\perp)$ with $v_c = \int_0^\infty \Gamma_A(z)dz$

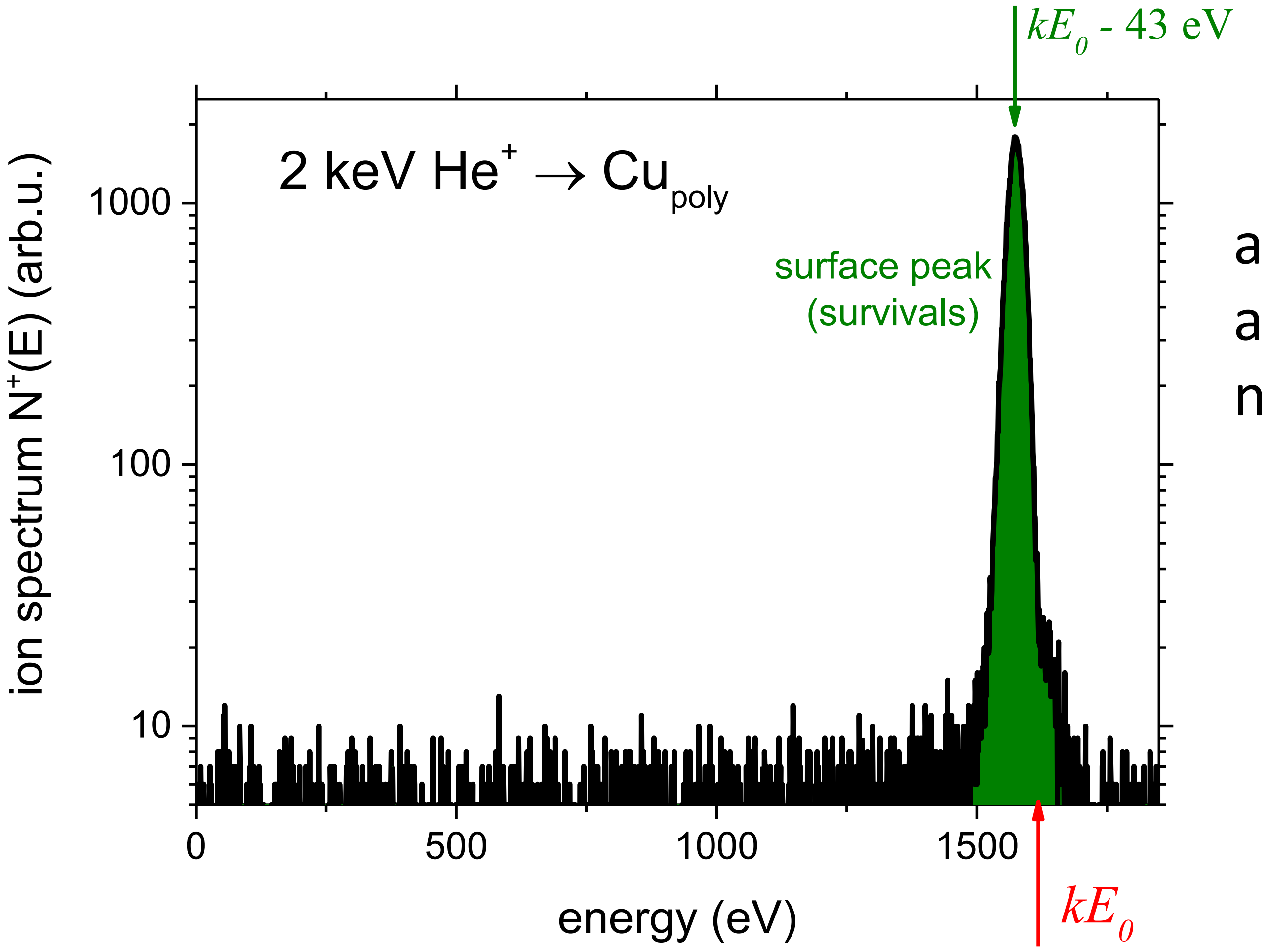
(He⁺ remains He⁺)

v_c … characteristic velocity ↔ AN efficiency

$v_c \approx 1 \ldots 2\cdot10^5$ m/s ≈ 0.1 a.u.

Typically, $\langle z\rangle \approx 1$Å … information depth due to AN

Energy spectrum of scattered ions in AN regime



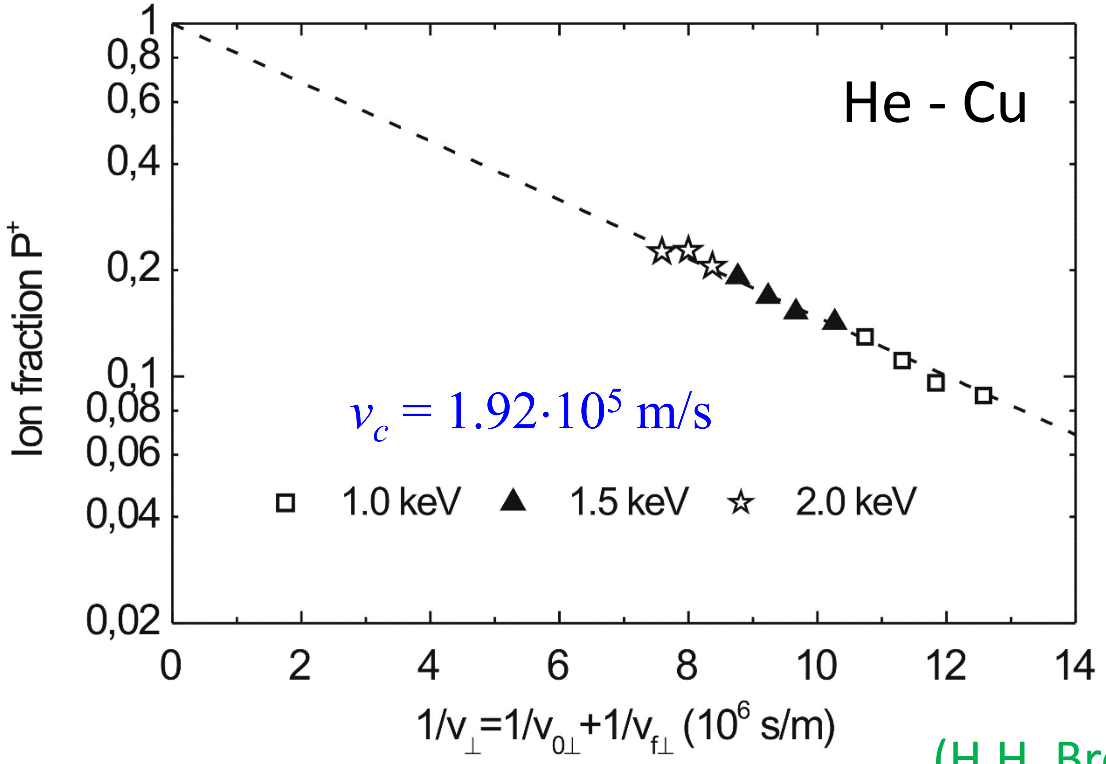
(collisional inelastic loss)

all detected ions are „survivals“ ↔ no charge exchange

$P^+(1/v_\perp)$ in the AN regime

He⁺ – Cu: for $E < 2.1$ keV, only AN is possible

ion signal: 1st atomic layer dominates



$v_c = 1.92 \cdot 10^5$ m/s

variation of geometry

variation of energy

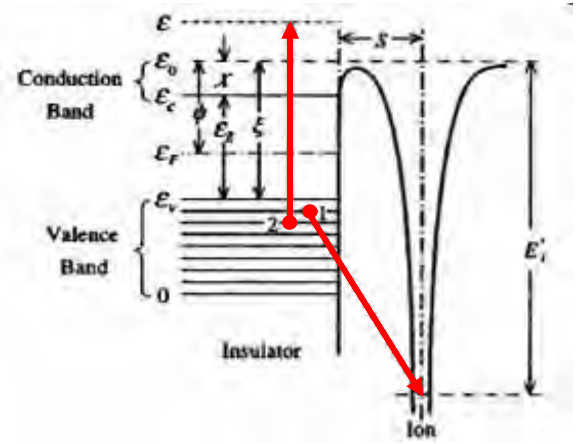
$\rightarrow \; P^+ = \exp(-v_c/v_\perp)$

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

Summary AN regime

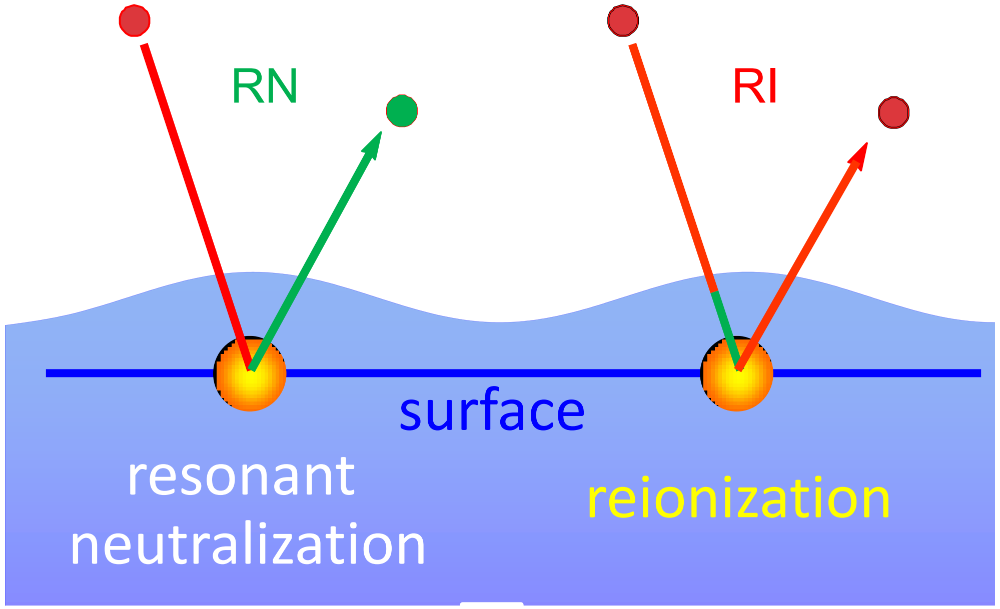
- **Information depth**
  high AN rate and long dwell time → information depth ≈ 1 ML

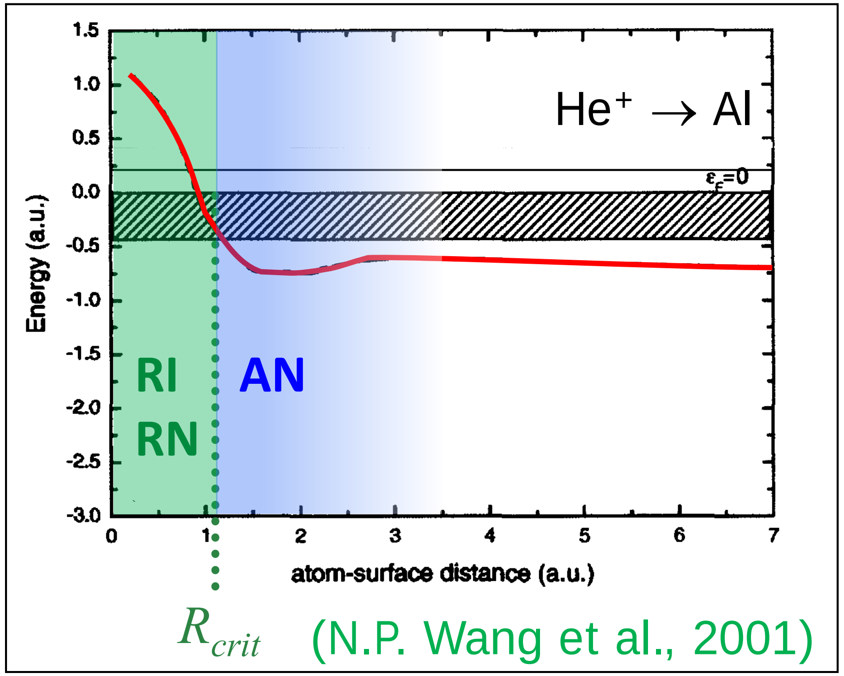
- **Quantitative composition analysis**
  AN depends on DOS → matrix effects to be expected
  → not first choice for composition analysis



Resonant charge exchange in a close collision

$R_{min} < R_{crit}$ → overlap of orbitals
→ electron promotion (atomic collision)
→ is active for $E > E_{th}$





$R_{min} < R_{crit} \leftrightarrow E > E_{th}$

Cu: $R_{crit} \approx 0.1$ Å ↔ $E_{th} \approx 2$ keV → AN dominant

Ta: $R_{crit} \approx 0.5$ Å ↔ $E_{th} \approx 0.4$ keV
Al: $R_{crit} \approx 0.5$ Å ↔ $E_{th} \approx 0.2$ keV } → RN, RI dominant

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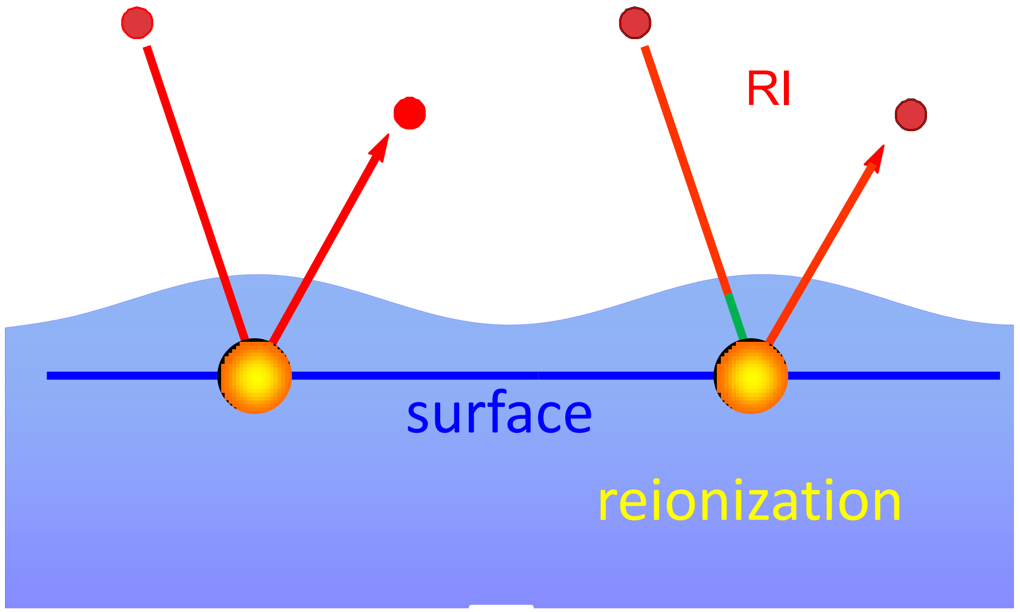
Resonant charge exchange in a close collision

$$P^{+} = P_{in}^{+} \cdot (1 - P_{RN}) \cdot P_{out}^{+} + (1 - P_{in}^{+}) \cdot P_{RI} \cdot P_{out}^{+}$$

Survivals (no AN, no RN) reionized projectiles (AN+RI)



Resonant charge exchange in a close collision

$$P^{+} = P_{in}^{+} \cdot (1 - P_{RN}) \cdot P_{out}^{+} + (1 - P_{in}^{+}) \cdot P_{RI} \cdot P_{out}^{+}$$

Survivals (no AN, no RN)   reionized projectiles (AN+RI)

AN: $P^{+} = \exp(-v_c/v_\perp)$ (survival probability)

RN: $P_{RN} = 1 - \exp(-v_{RN}/v)$ … neutralization probability due to rate Γ_{RN}

RI: $P_{RI} = \exp(-v_{RI}/v)$ … reionization probability due to rate Γ_{RI}

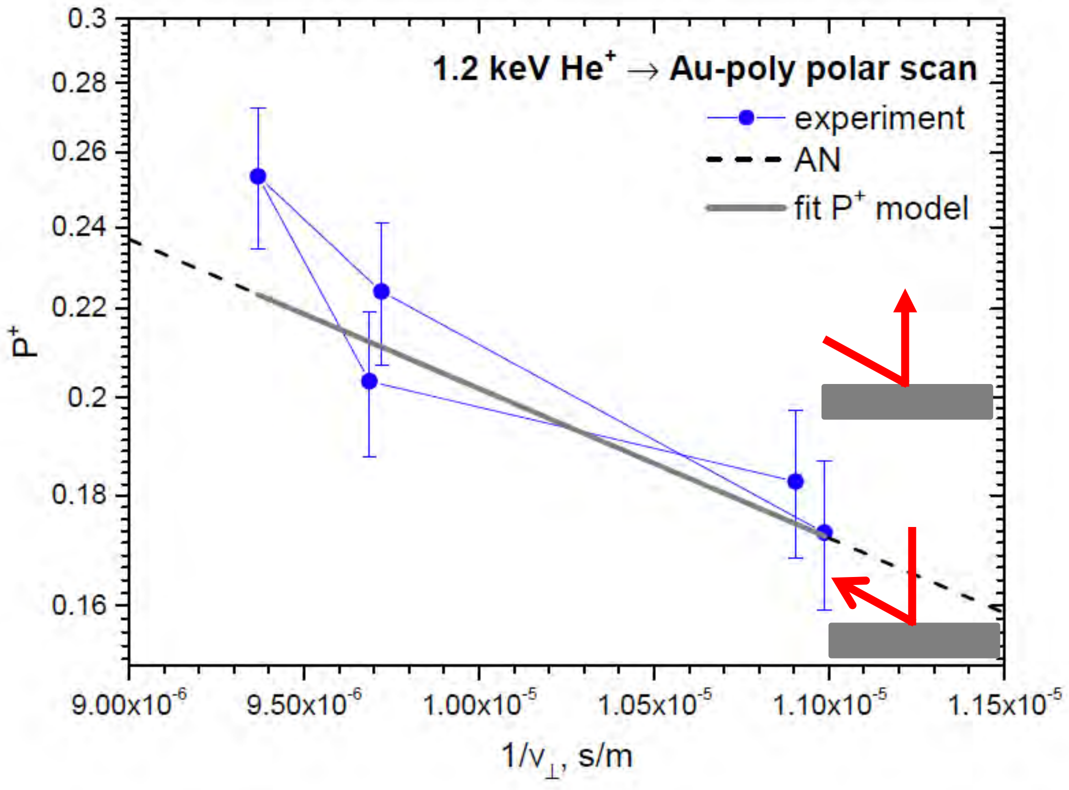
rates Γ_{RI}, Γ_{RN}: ???

RN, RI scale with velocity v

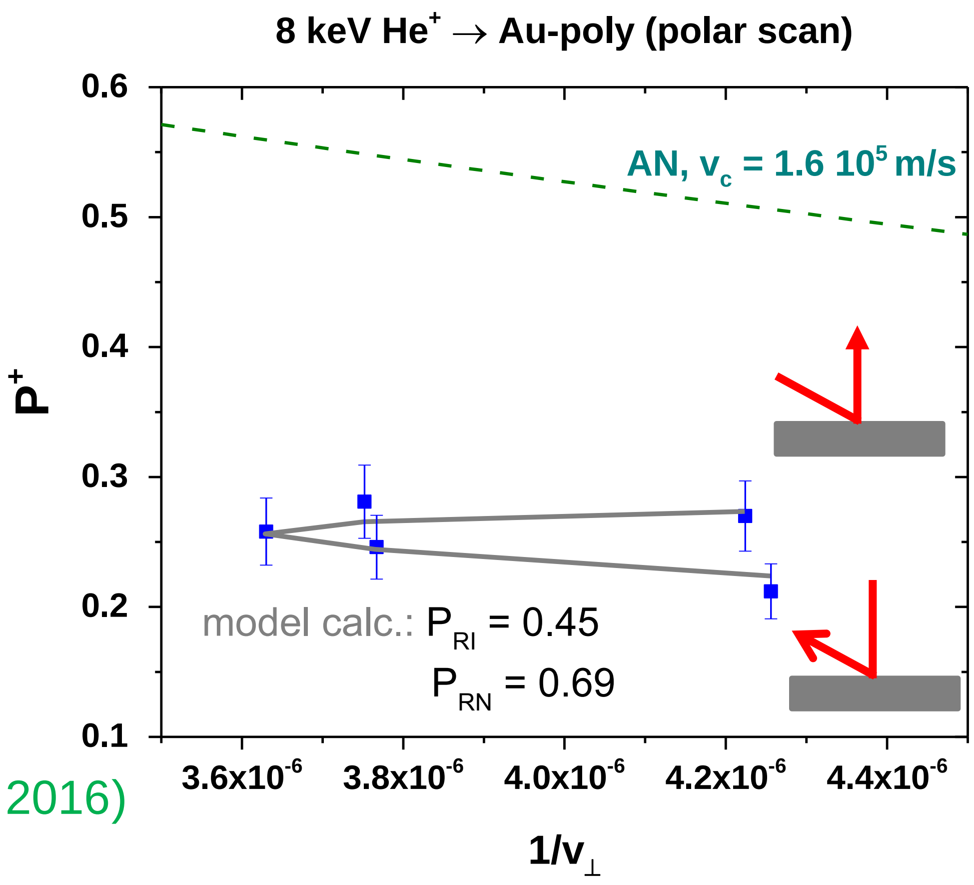
P^{+}: Variation of geometry

$E = E_{th}: P_{RI} = P_{RN} = 0$

$E > E_{th}: P_{RI} > 0, P_{RN} > 0$



(D. Roth, 2016)



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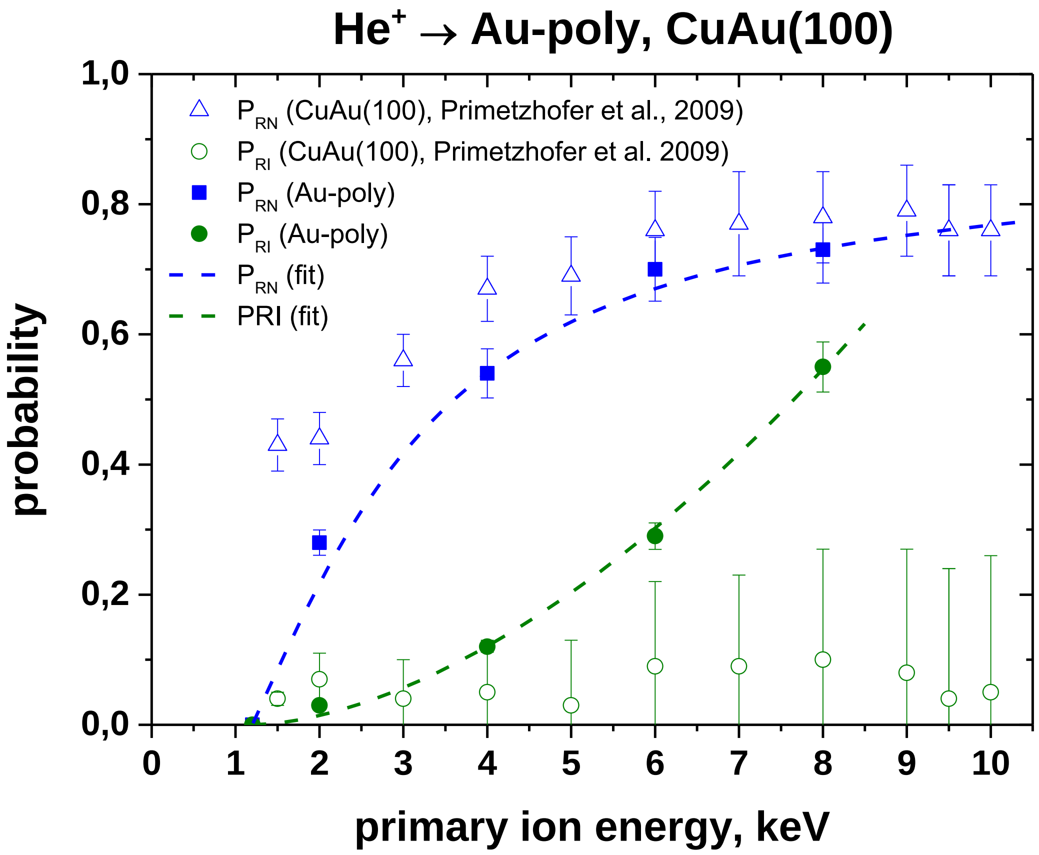
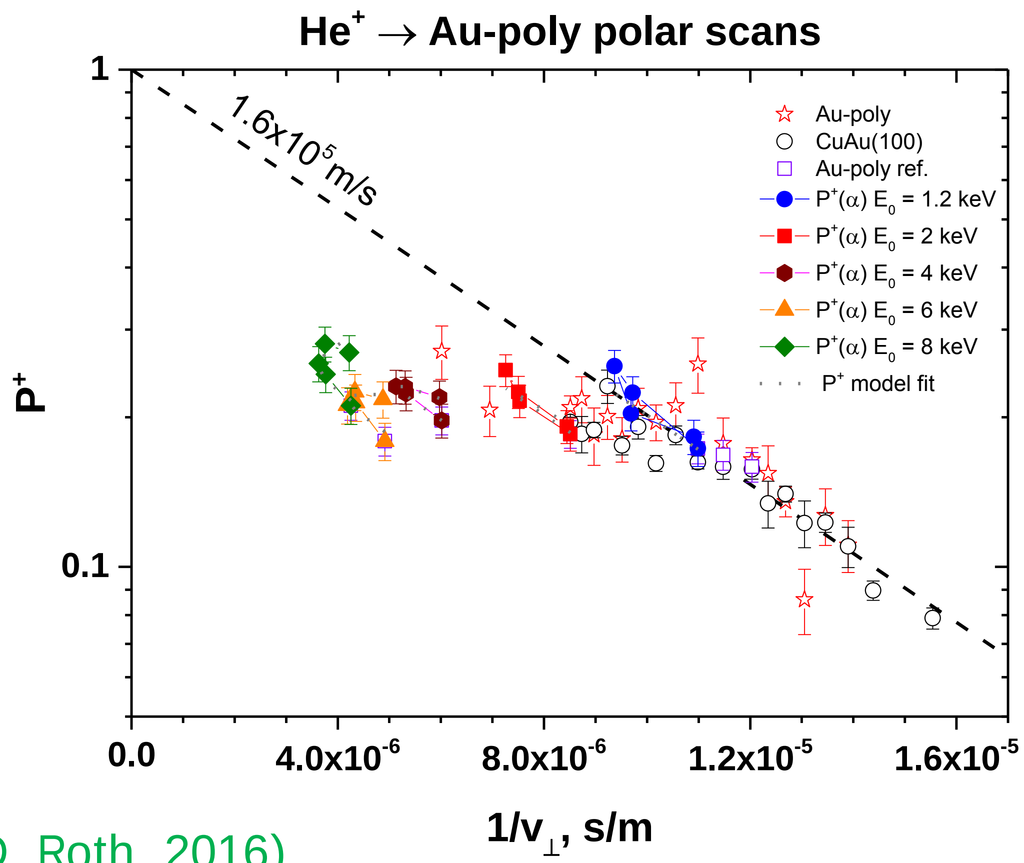
P^+: Variation of geometry



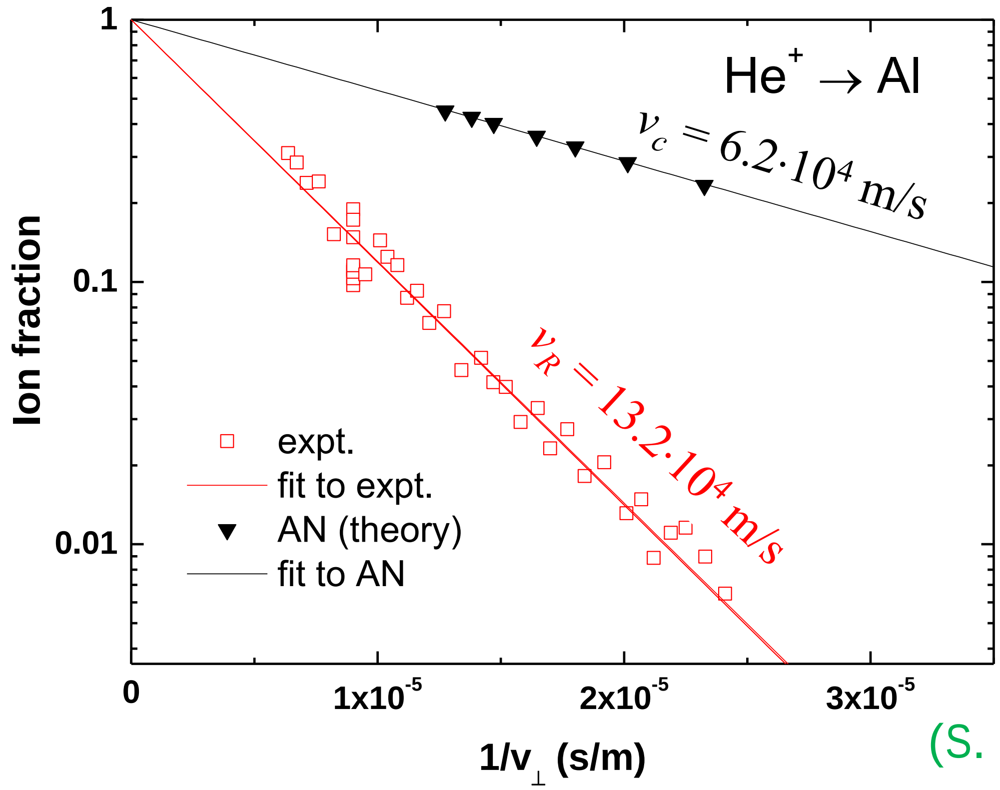


(D. Roth, 2016)

Reionization He^+ - Al_{poly}

- is active for $E > E_{th}$ (threshold energy)

consequences?



empirical fact:

variation of $E \rightarrow P^+ = e^{-v_R/v_\perp}$

$P^+_{expt} << P^+_{AN} \leftrightarrow RN$ dominant

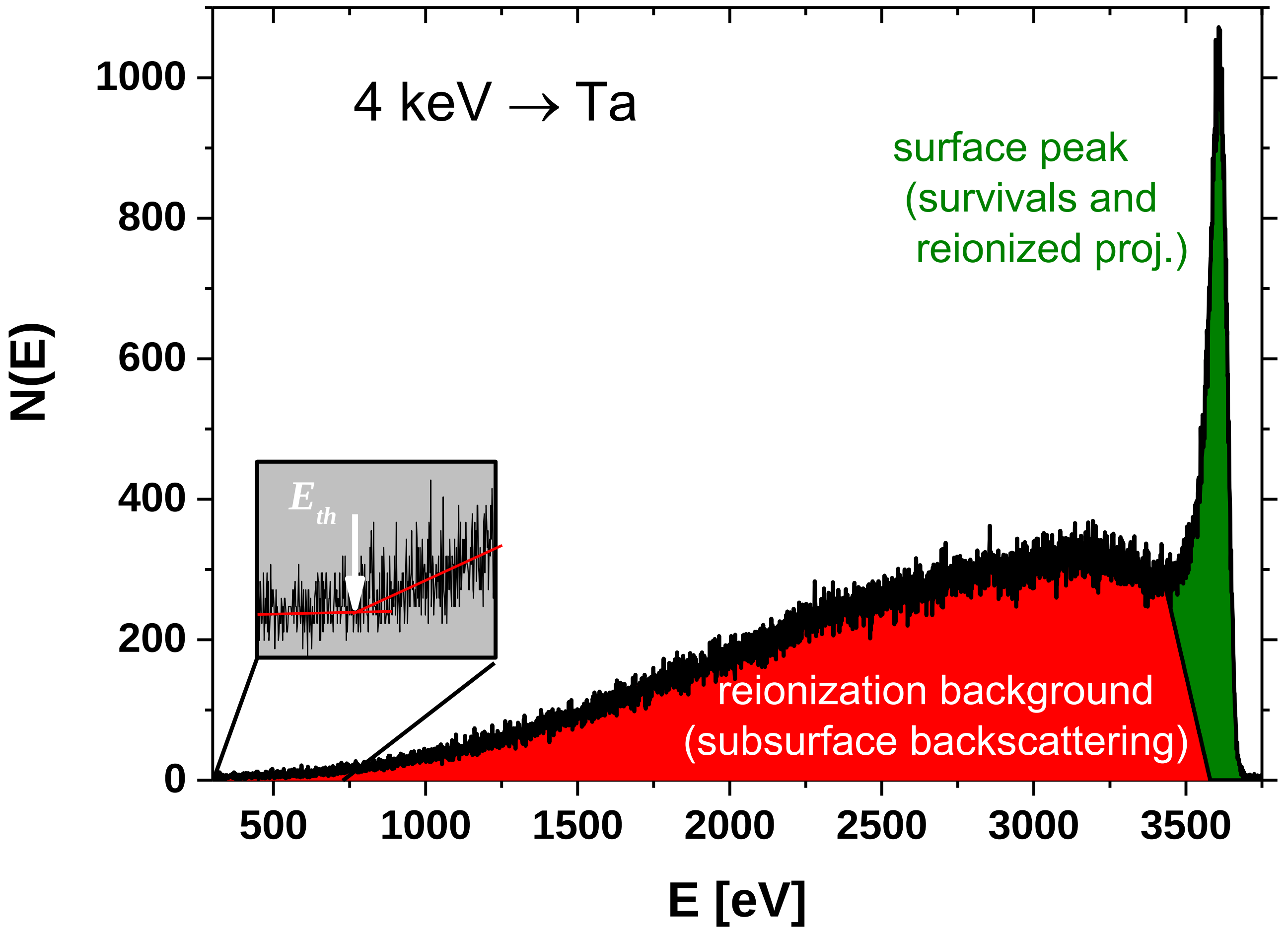
$v_R >> v_c$

Low ion signal

⟨charge state⟩ ≈ 0

(S. Rund et al., 2011)

4 keV $He^+ \rightarrow$ Ta: ion spectrum



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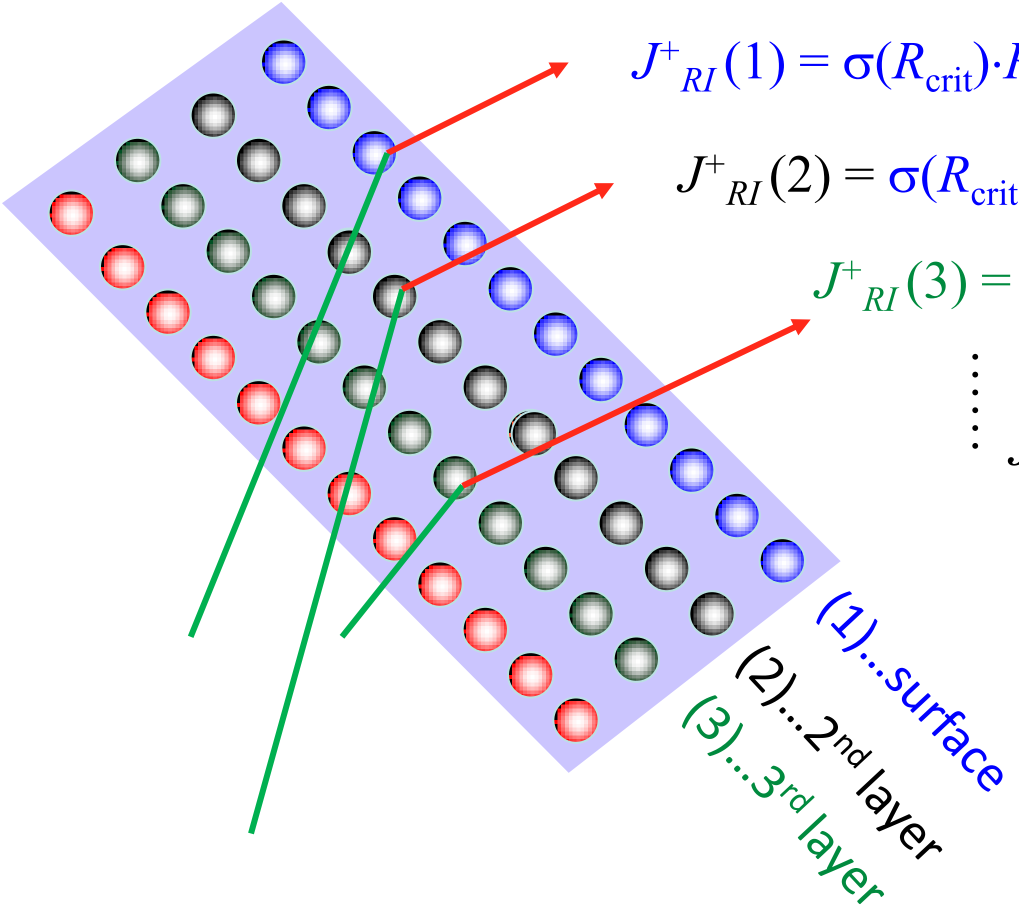
Information depth in reionization regime

penetration to deeper layers & reionization @ surface : → information depth is due to P^+_{out} (no AN on way out)



$$J^+_{RI}(1) = \sigma(R_{crit}) \cdot P_{RI} \cdot P^+_{out}$$

$$J^+_{RI}(2) = \sigma(R_{crit}) \cdot P_{RI} \cdot (P^+_{out})^3 = J^+_{RI}(1) \cdot {P^+_{out}}^2$$

$$J^+_{RI}(3) = \sigma(R_{crit}) \cdot P_{RI} \cdot (P^+_{out})^5 = J^+_{RI}(1) \cdot {P^+_{out}}^4$$

⋮

$$J^+_{RI} = J^+_{RI}(1) \cdot (1 + (P^+_{out})^2 + (P^+_{out})^4 + \ldots)$$

$$\rightarrow \quad J^+_{RI} = \frac{J^+_{RI}(1^{st}\,layer)}{1-(P^+_{out})^2} \approx J^+_{RI}(1^{st}\,layer)$$

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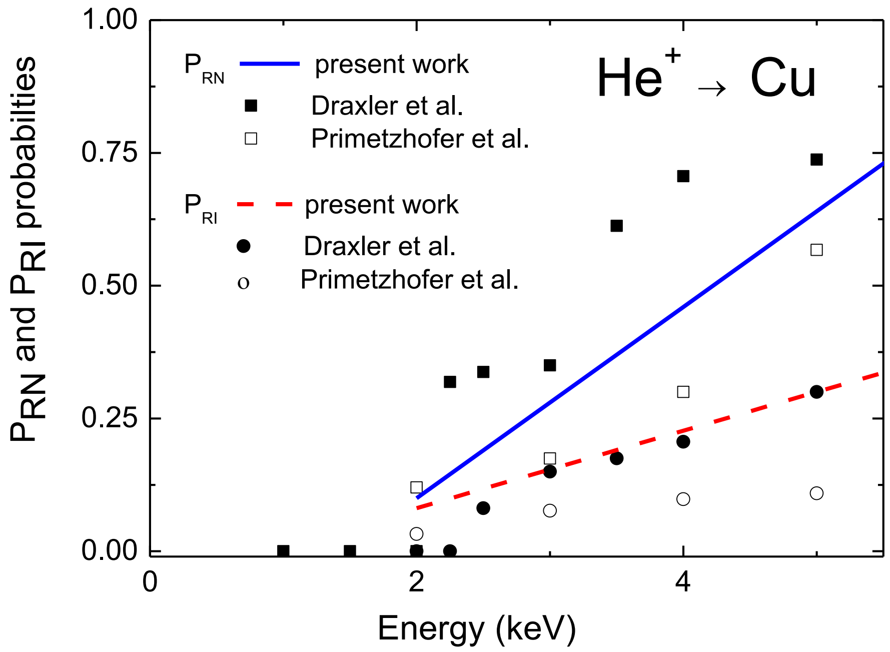
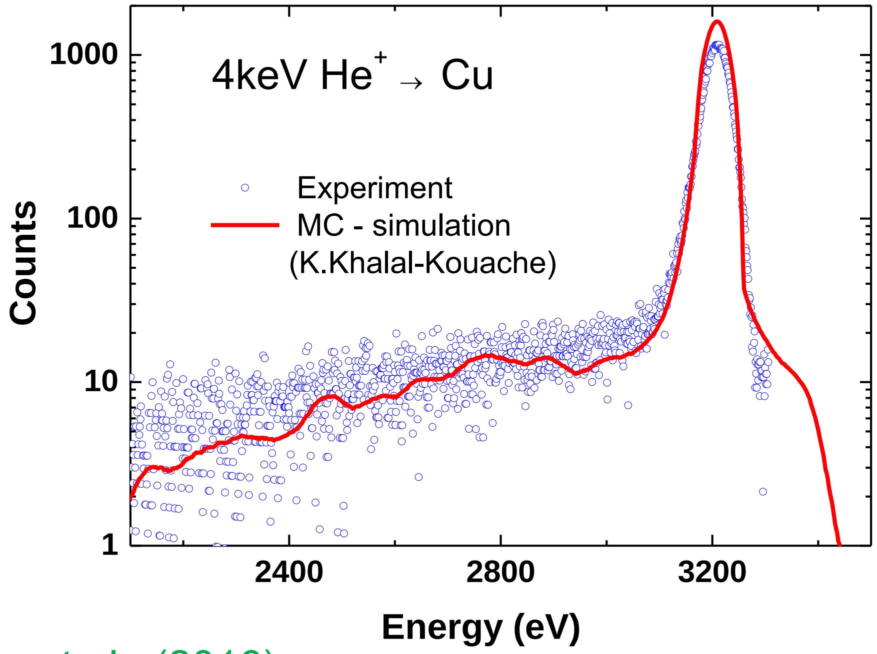
MC-simulations and charge exchange

modeling the reionzation background in TRIM
by introducing a minimum number of additional parameters

– 4 keV He → Cu:

Good agreement for $\Gamma_A = 1.635 \cdot 10^{15}$ /s





K. Khalal-Kouache et al., (2016)

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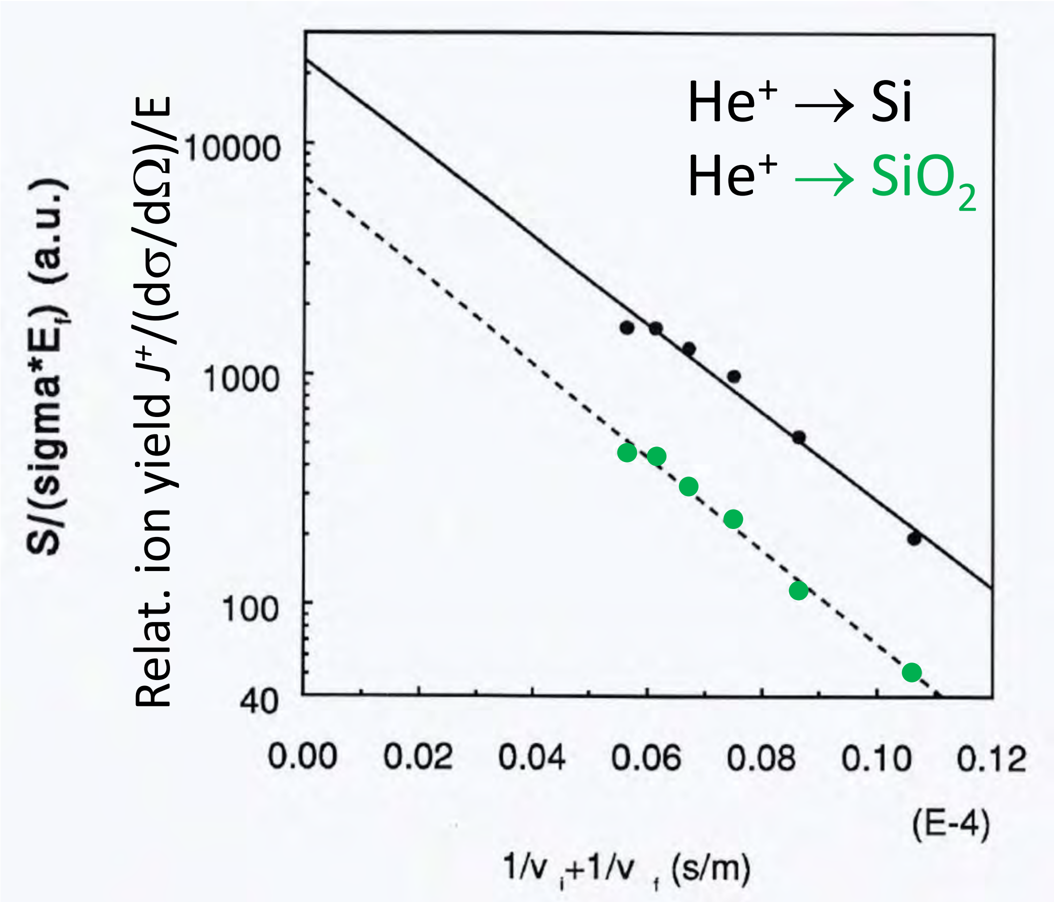
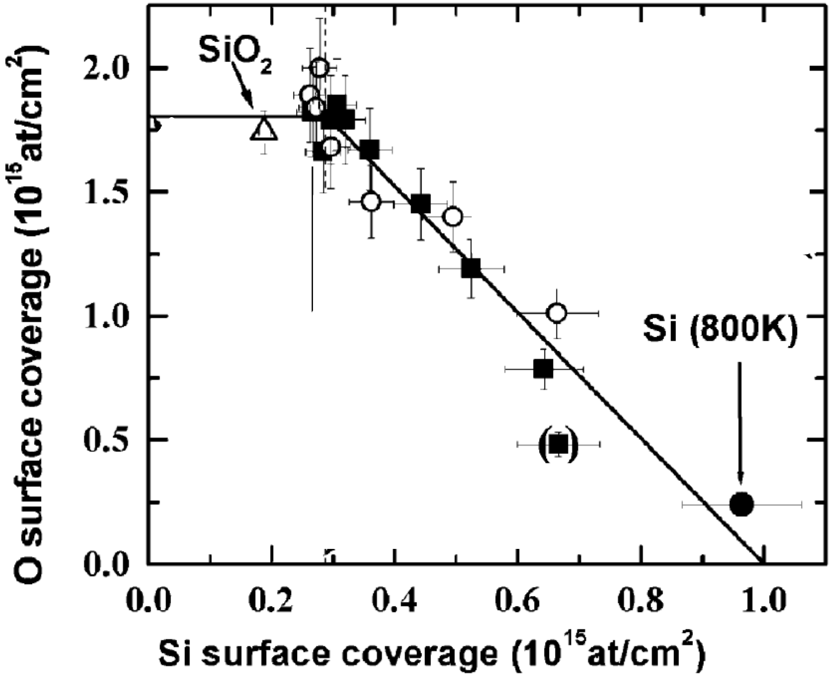
P^+ (He – Si) – influence of oxygen exposure



(Hidde Brongersma, 1992 (?))



(T. Jansens et al., 2003)

$$\frac{A_{Si}^{+}}{P_{Si}^{+}} + \frac{A_{O}^{+}}{P_{O}^{+}} = \frac{1}{C}$$

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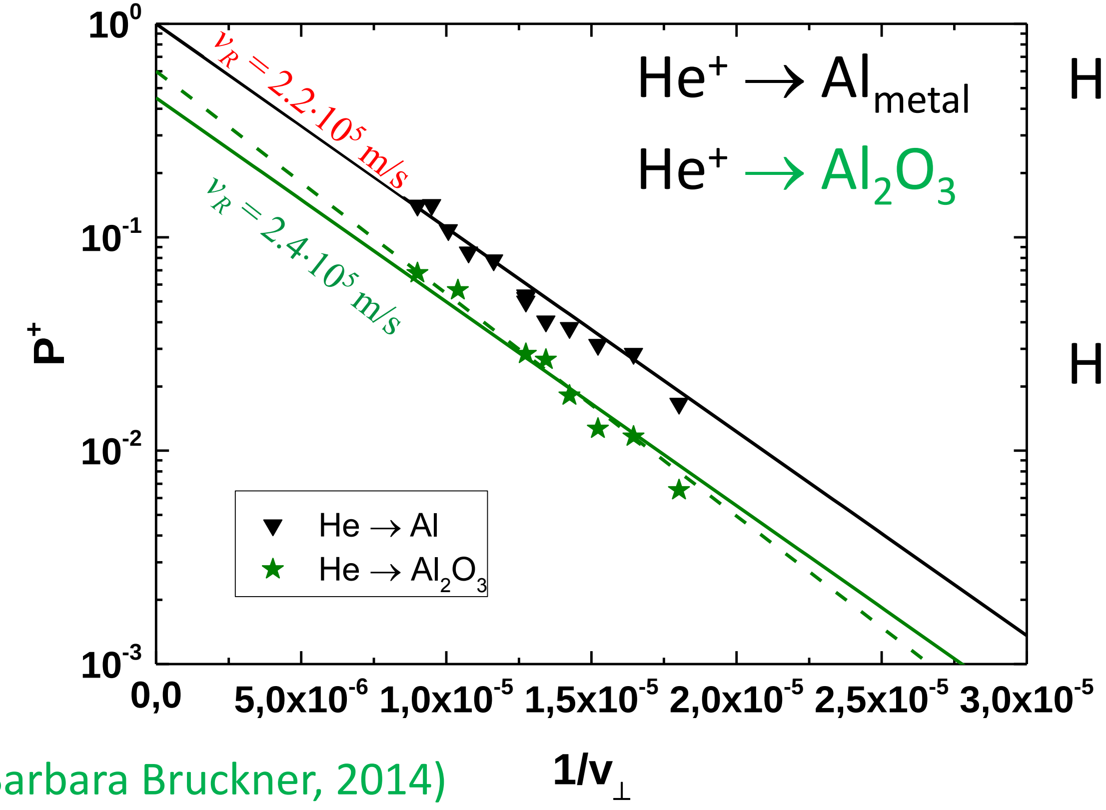
P^+ (He – Al) – influence of oxygen



(Barbara Bruckner, 2014)

$He^+ \rightarrow$ Al (metal):

$v_R = 2.2 \cdot 10^5$ m/s

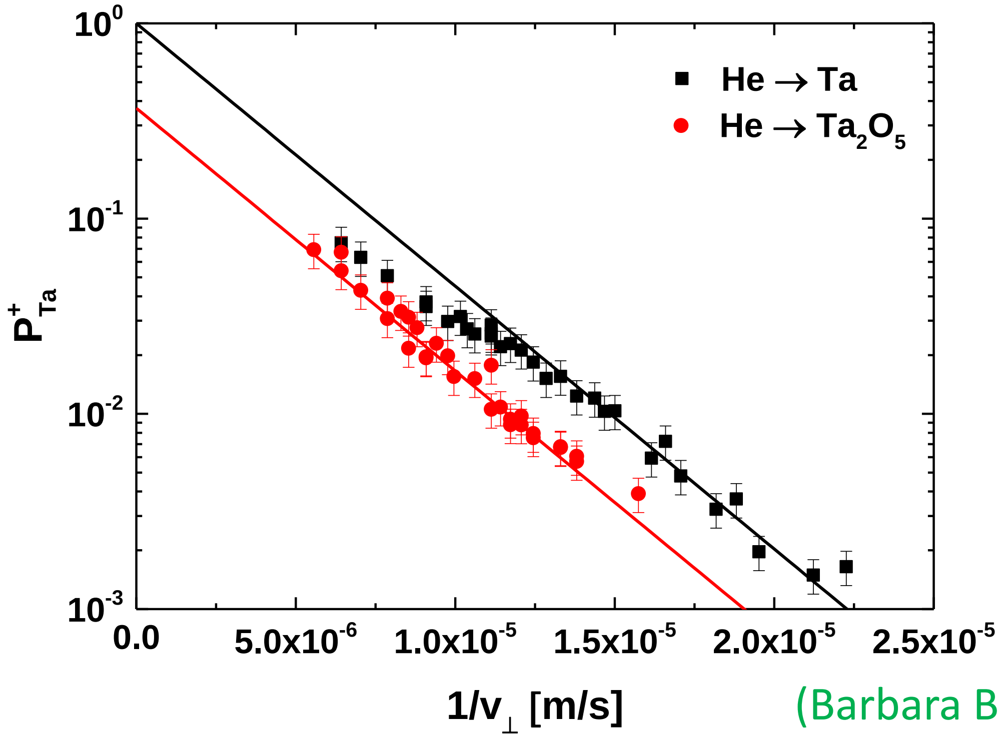
$v_R >> v_c$

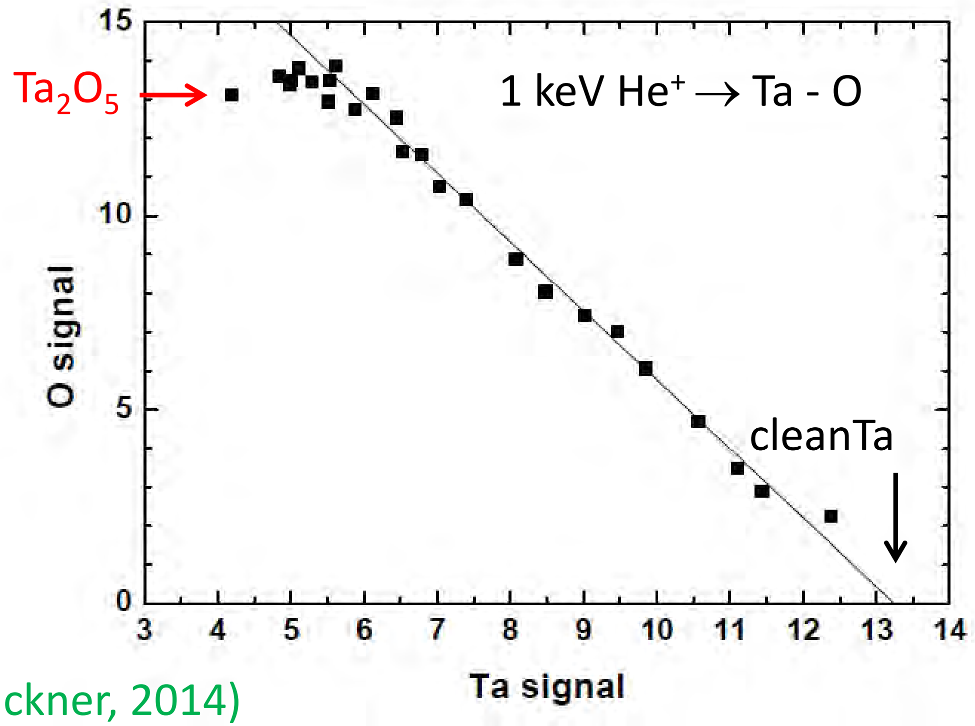
$He^+ \rightarrow$ Al in Al_2O_3:

$v_R = 2.4 \cdot 10^5$ m/s

$1/v_\perp \rightarrow 0$: $P^+ \rightarrow 0.45$

P^+ (He – Ta) – P^+ (He – Ta_2O_5)





(Barbara Bruckner, 2014)

Linear dependence signal - concentration!

Reionization regime is best suited for composition analysis

But: **physics of reionization is not yet understood**!

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Summary reionization regime

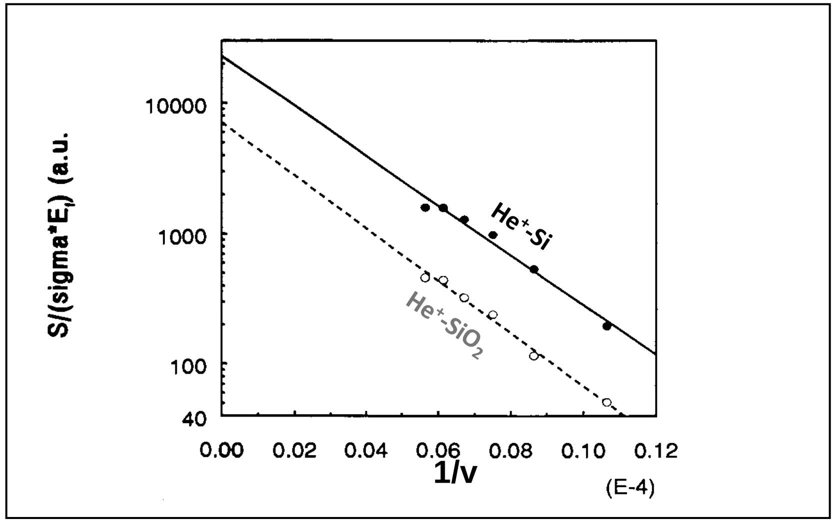
Information depth

polycrystals: surface peak $\rightarrow$ information depth $\approx$ 1 ML

quantitative surface composition analysis

probabilities P_{RN}, P_{RI}: depend only weakly on band structure

$\rightarrow$ „absence of matrix effects"!



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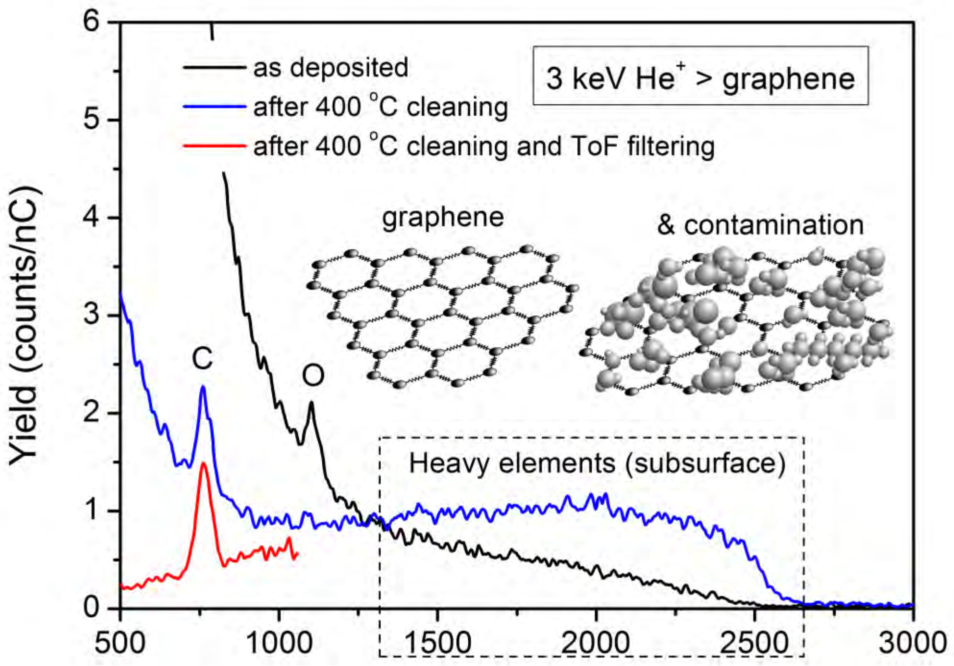
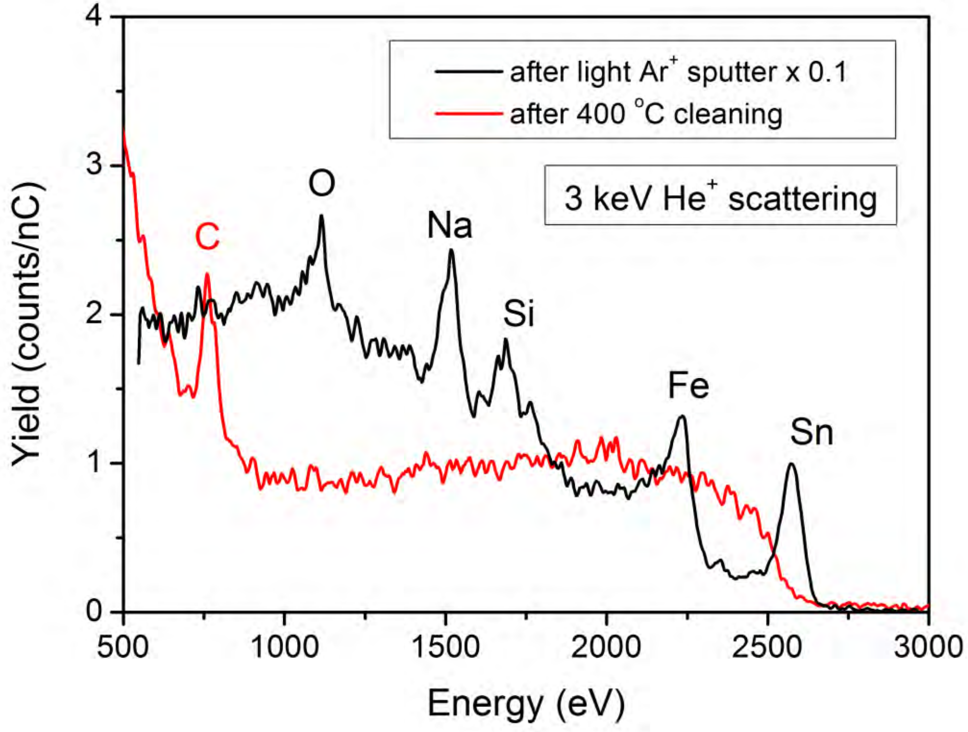
Characterization of graphene

3 keV $He^+ \rightarrow CH_x$ / graphene / metals? /Si

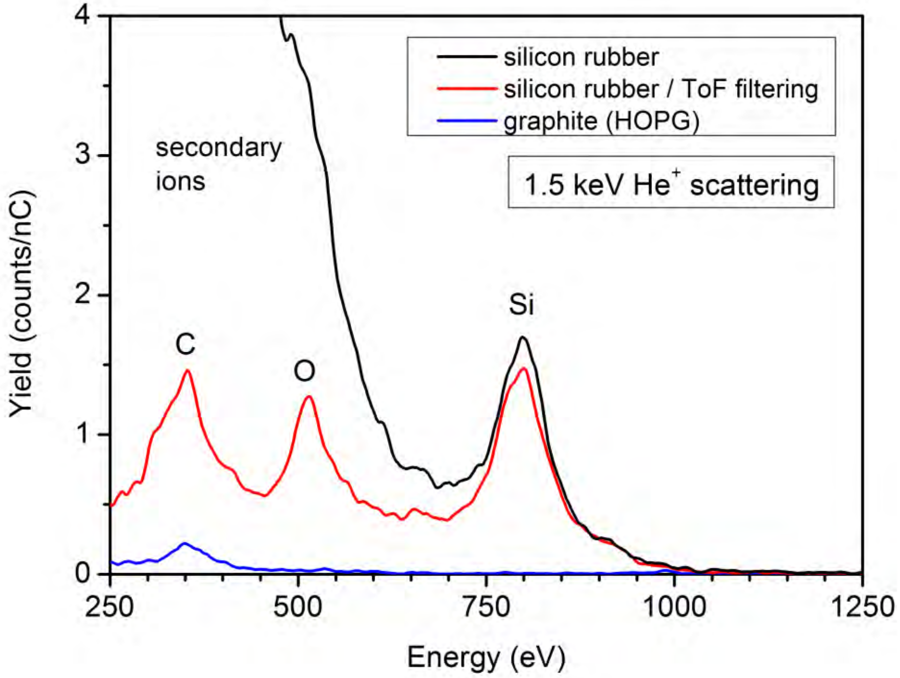


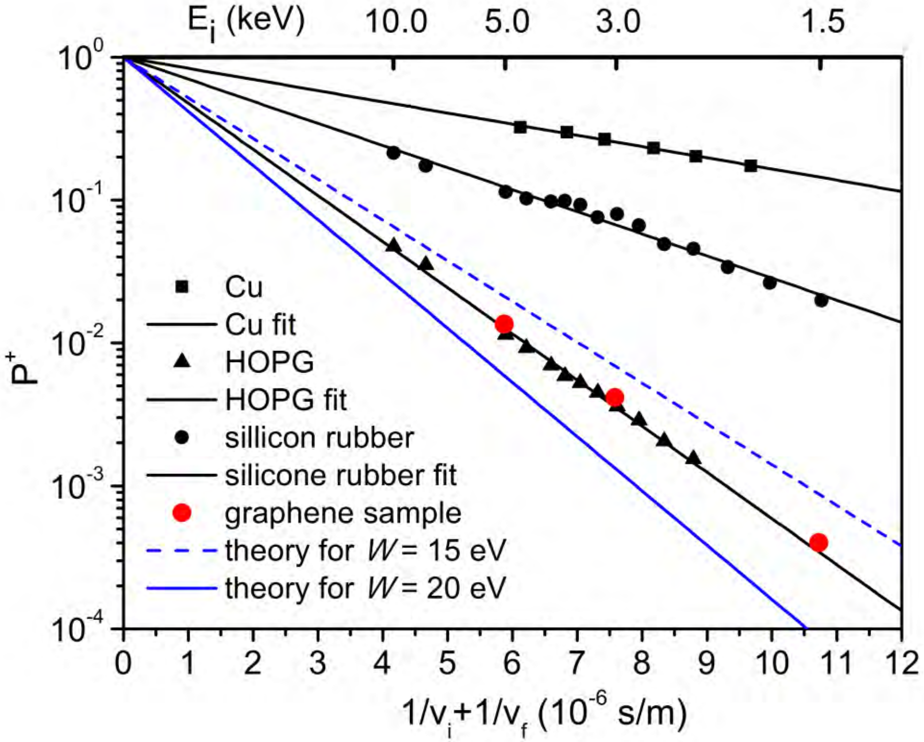


(Stan Prusa et al, Langmuir, 2015)

Characterization of graphene layers

3 keV $He^+ \rightarrow CH_x$ / graphene / metals? /Si





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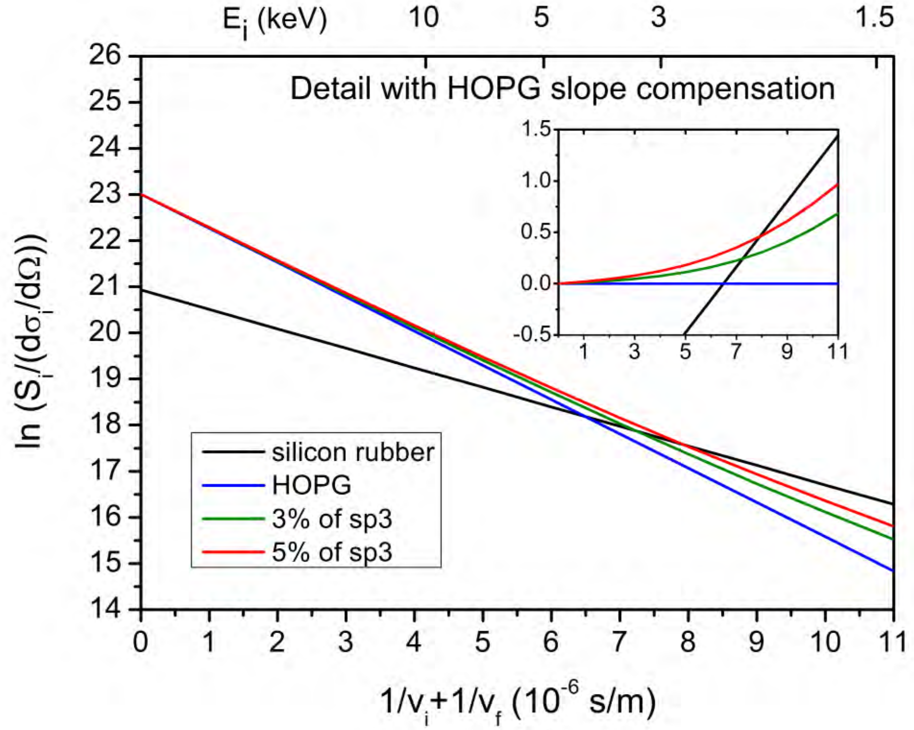

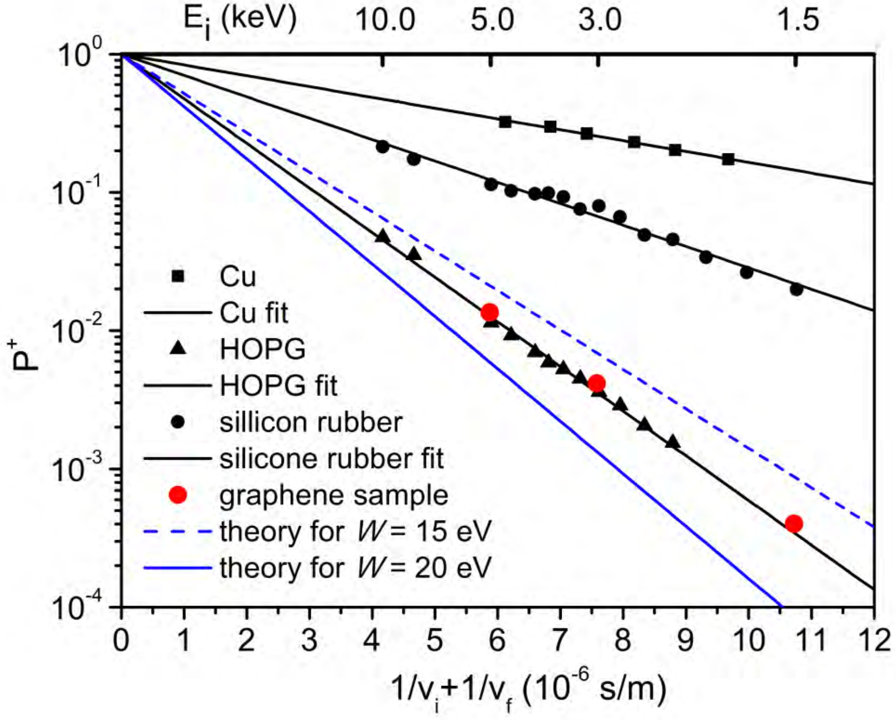

(Stan Prusa et al, Langmuir, 2015)

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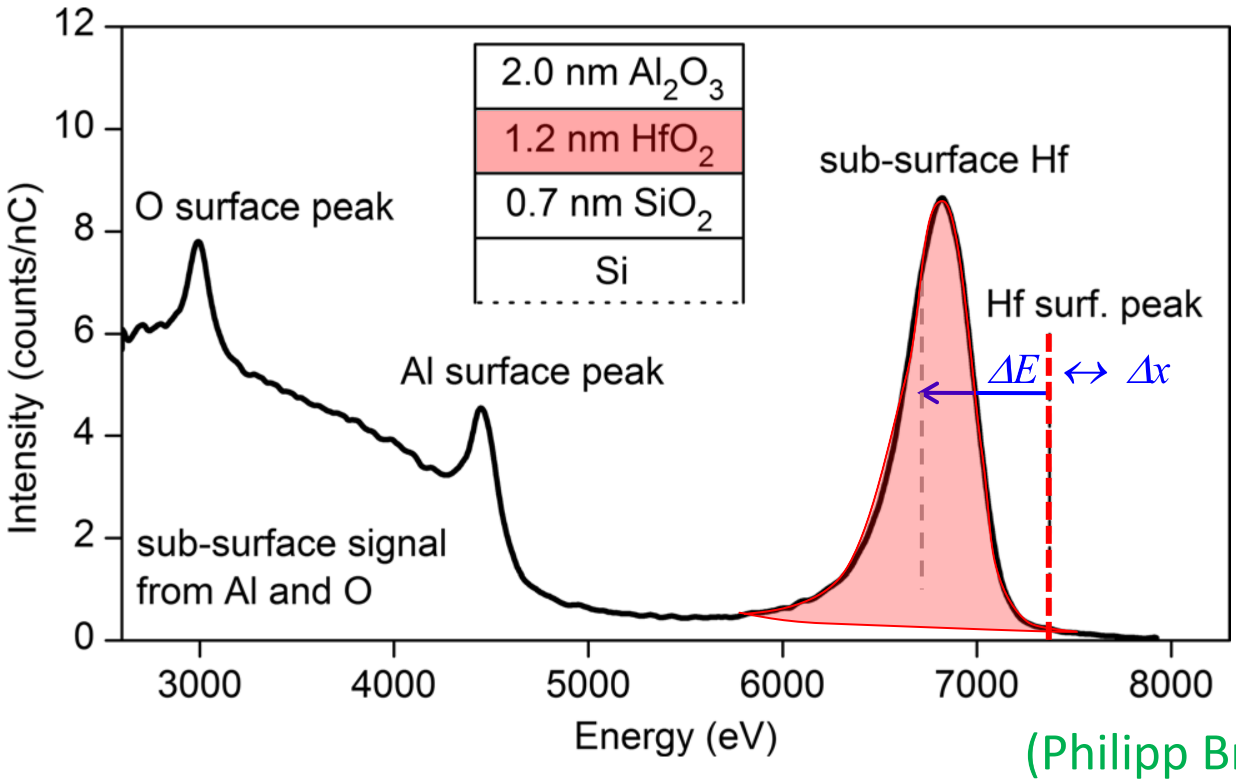
Challenges: subsurface information

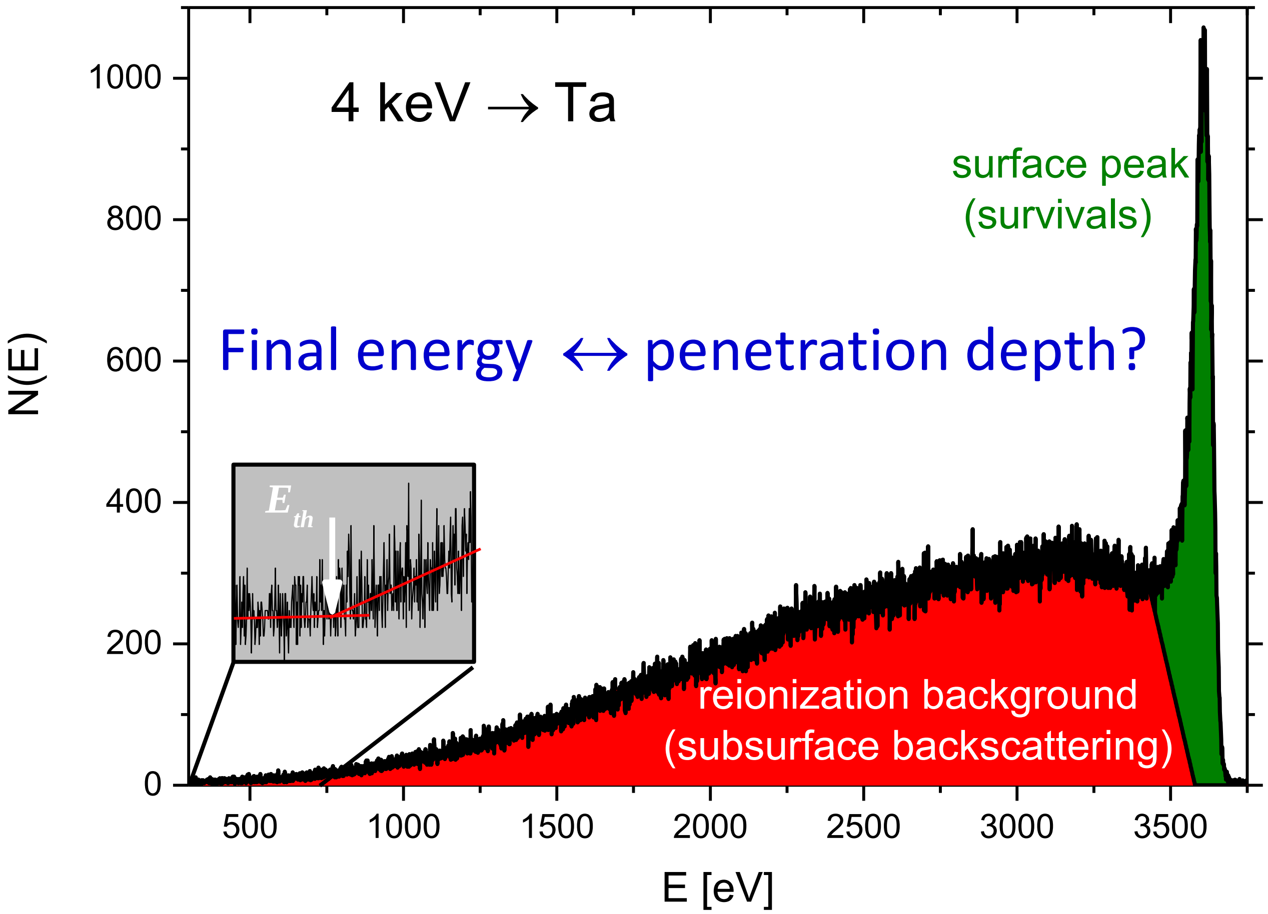
$He^+ \rightarrow$ subsurface Hf:



Required input:
- dE/dx in Al_2O_3
- multiple scattering
- reionization at surface

(Philipp Brüner, 2014)

Reionization → subsurface information



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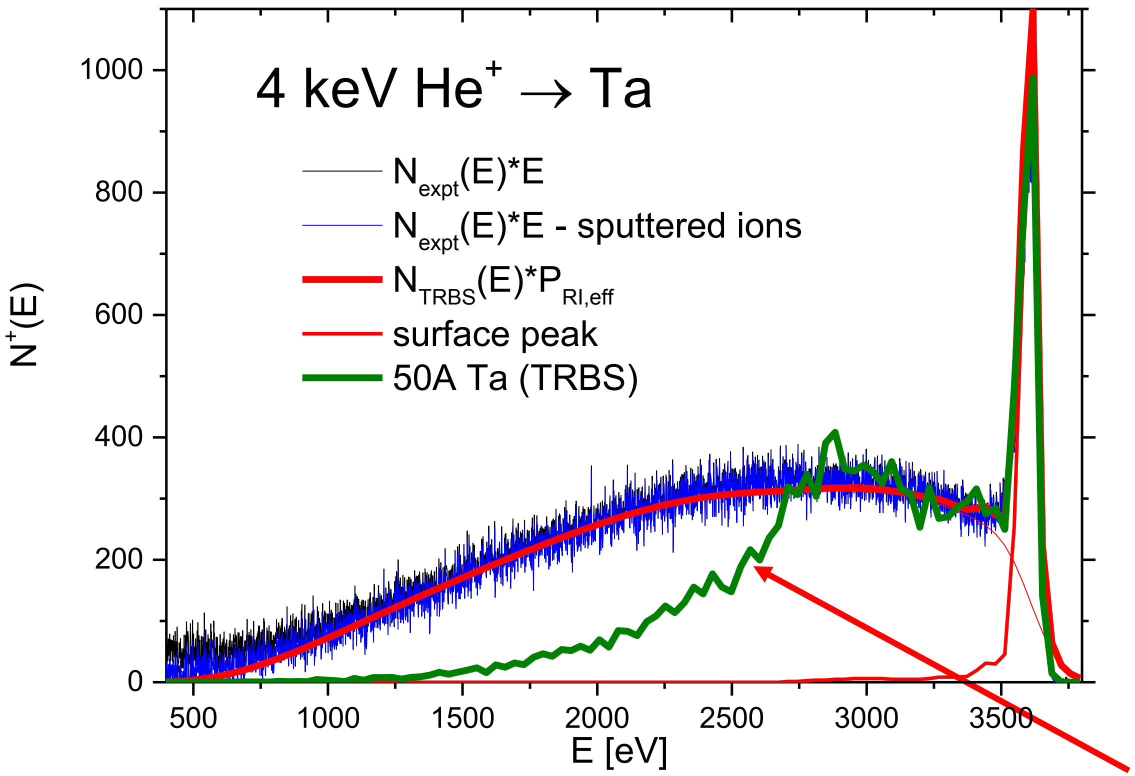
TRBS + charge exchange ↔ experiment



TRBS ↔ experiment:

$$N_{expt}(E) = N_{TRBS}(E) \cdot p_{RI,eff}$$

$$p_{RI,eff} = P_{RI} \cdot P^{+}_{out}$$

$p_{RI,eff}$ is a surface property

- Electronic stopping
- Multiple scattering
- Path length increase

Summary quantification

Reionization: best suited for composition analysis ☺

no matrix effects!

charge exchange still lacks basic understanding ☹

Auger regime: not recommended for composition analysis ☹

band structure (matrix effects) effects to be expected

quasi resonant neutralization: not recommended for composition analysis ☹

P^+ oscillation amplitudes of a factor $\sim$ 3,

P^+ depends on band structure

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Summary information depth

Reionization regime: ~ 1 ML for polycrystals (depending on E)
may be larger for single crystals (focusing collisions)

Auger regime: ~ 1 ML

quasi resonant neutralization: neutralizes much more effective than AN
information depth = 1 ML

☺

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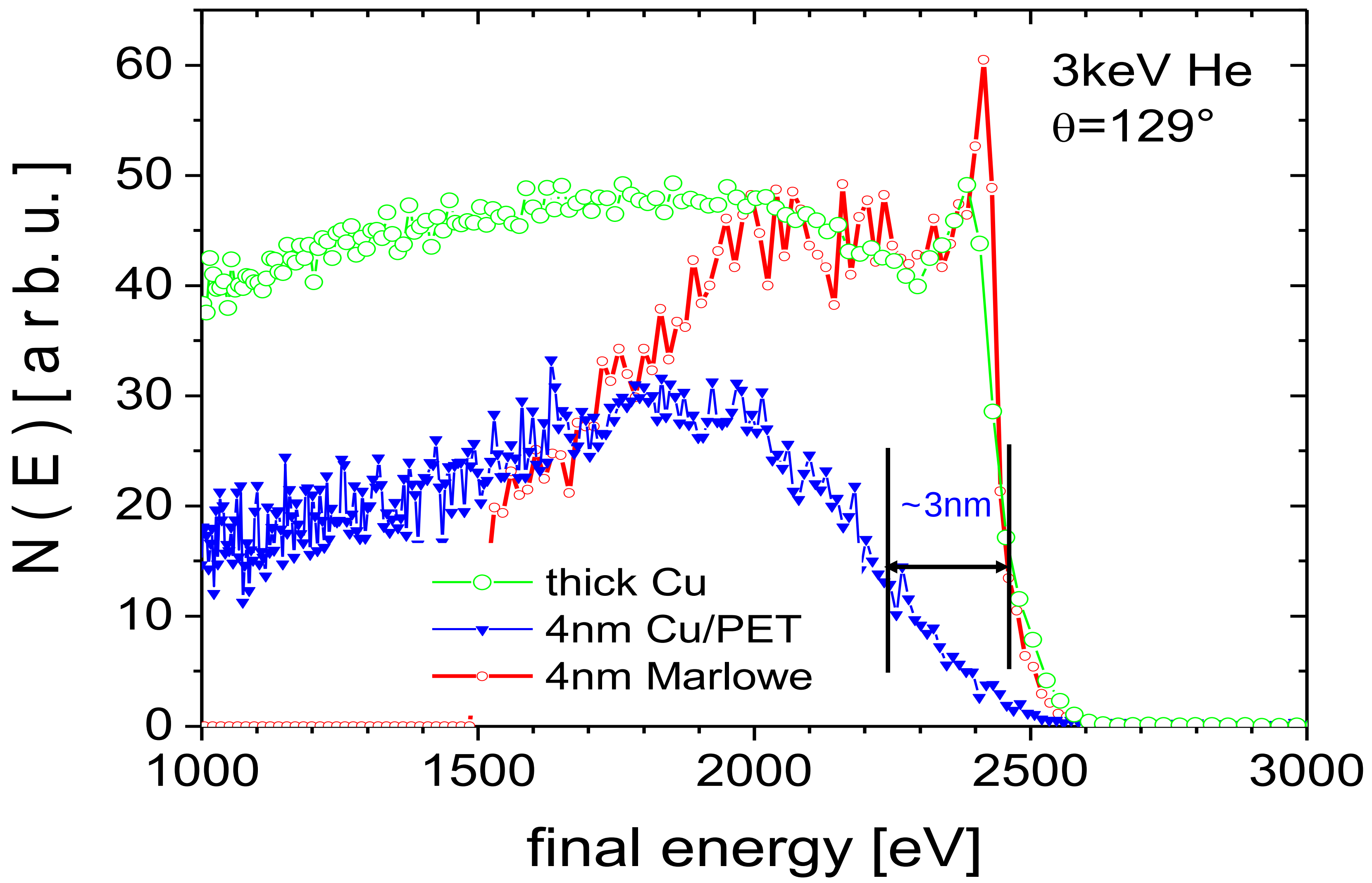
TOF-LEIS application: Cu/PET



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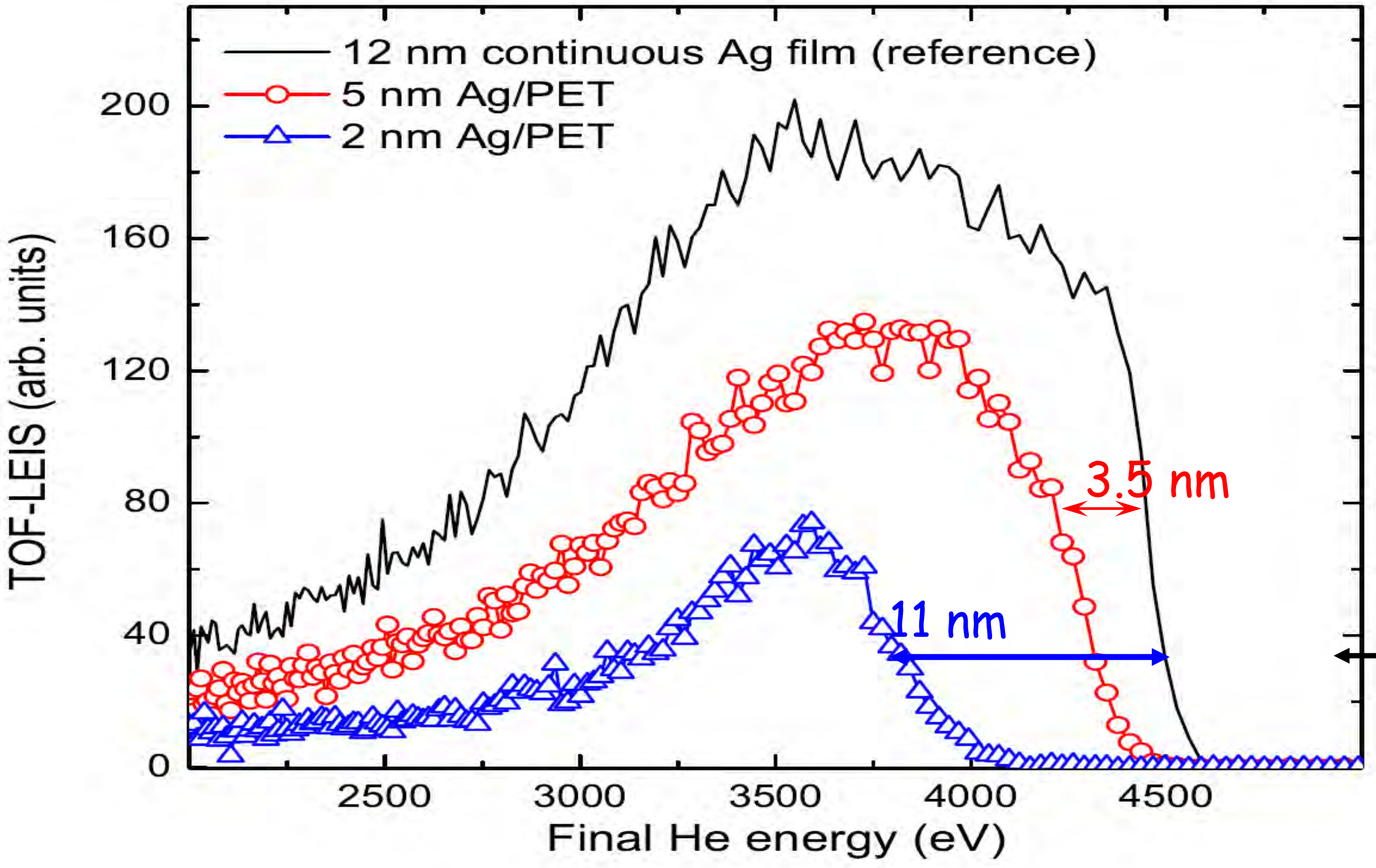
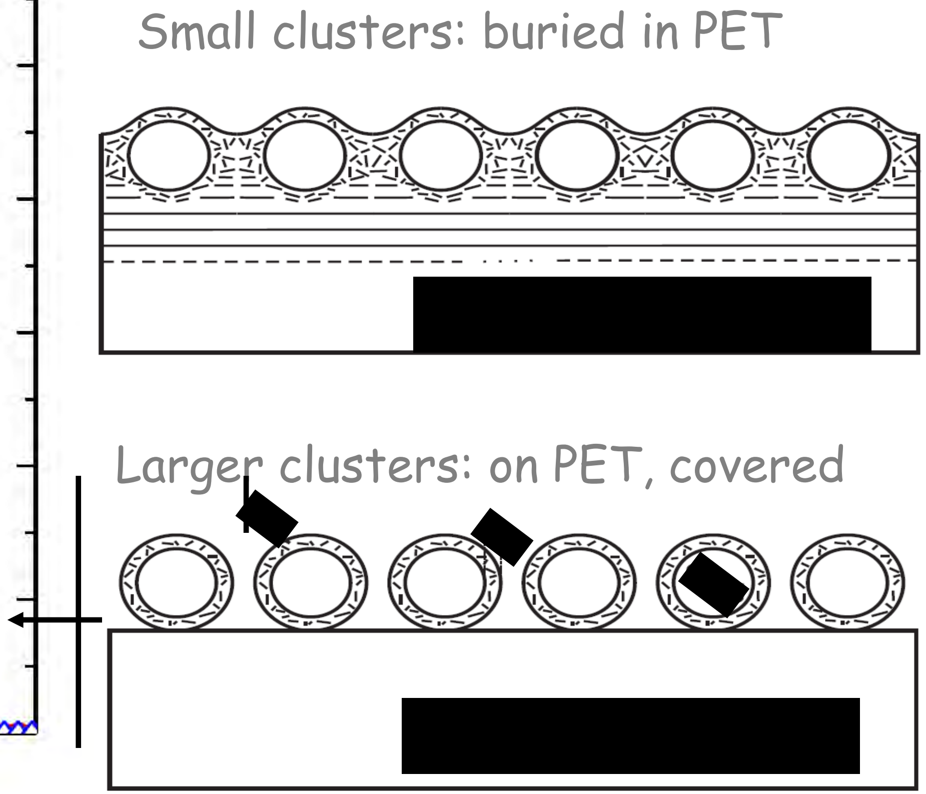
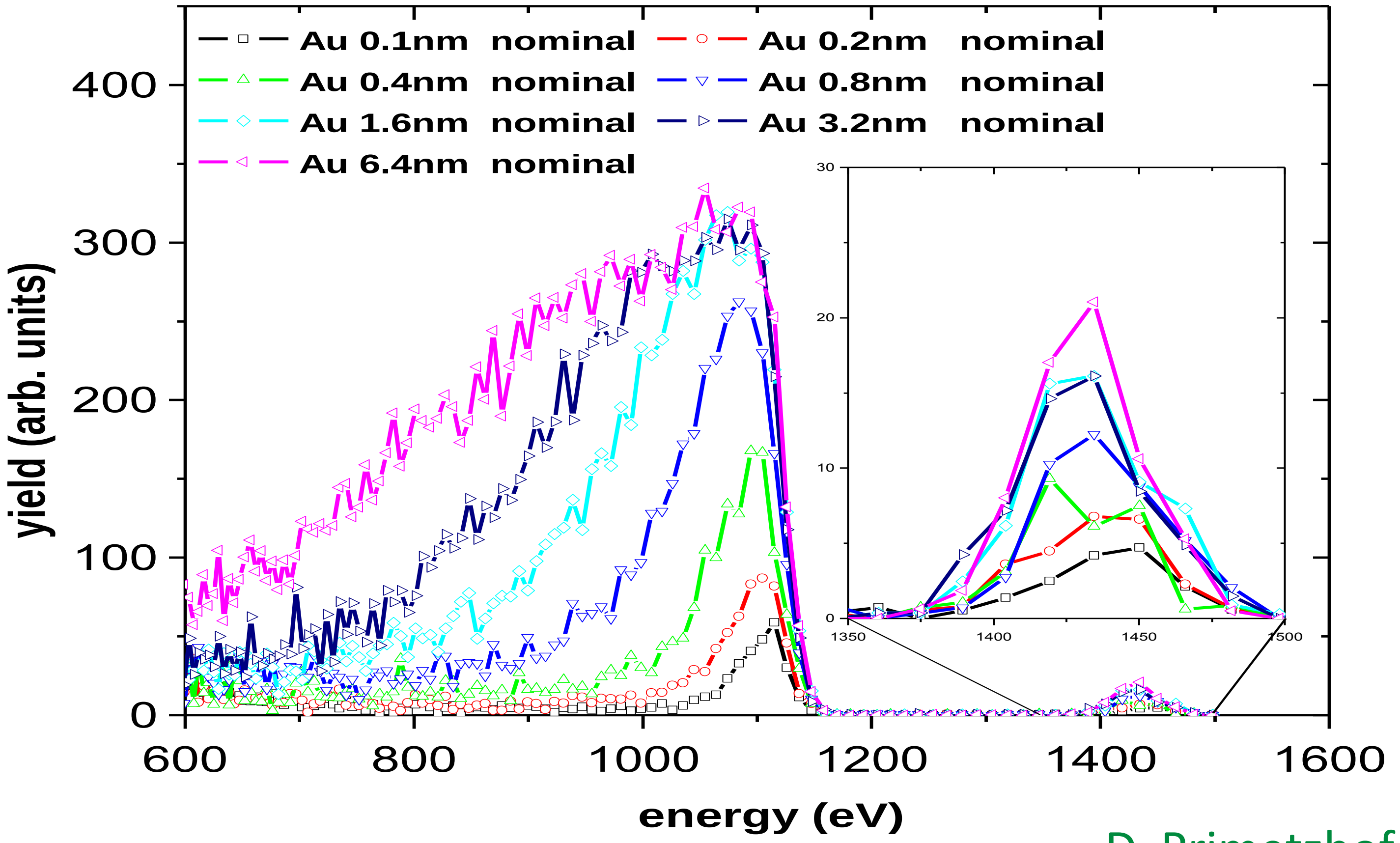
TOF-LEIS application: Ag clusters/PET





(J M Flores-Camacho, 2011)

TOF-LEIS: growth Au on B



D. Primetzhofer et al., APL (2008)

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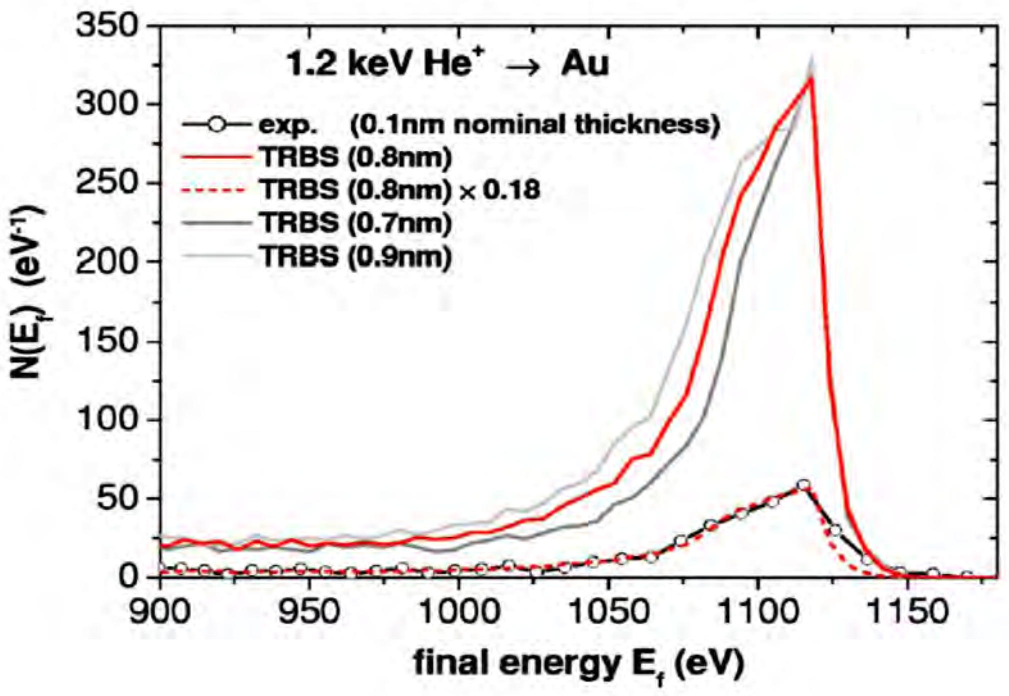
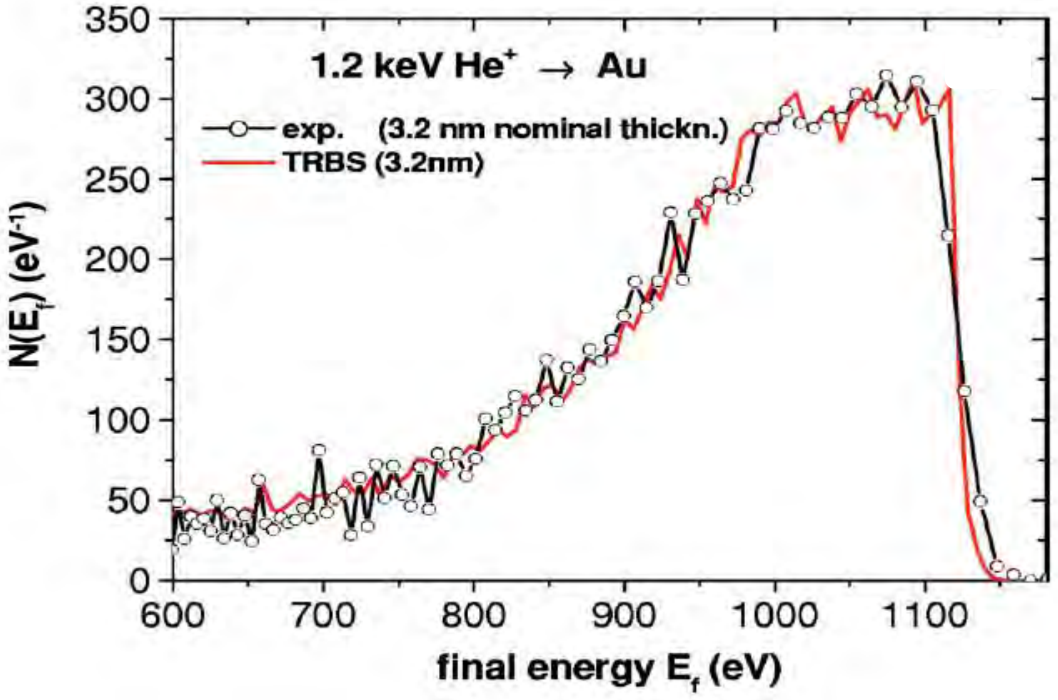
Growth of Au on B

TOF-LEIS: 1 - 10 keV $He^+ \rightarrow$ Au nanostructures on B

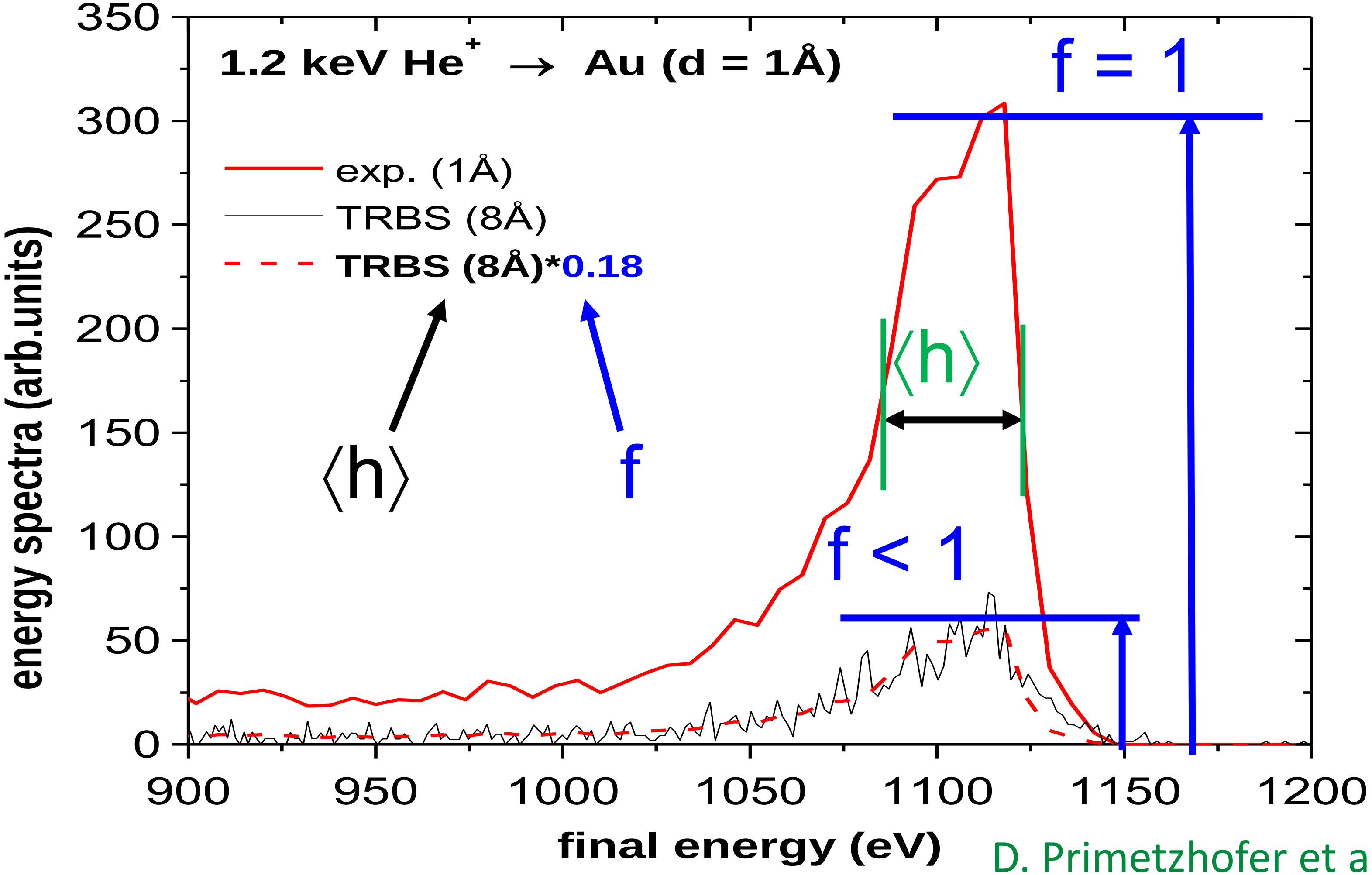
Information on coverage and height?





D. Primetzhofer et al., APL (2008)

TRBS-Simulations: 1 Å



D. Primetzhofer et al., APL (2008)

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ÖAW Österreichische Akademie der Wissenschaften

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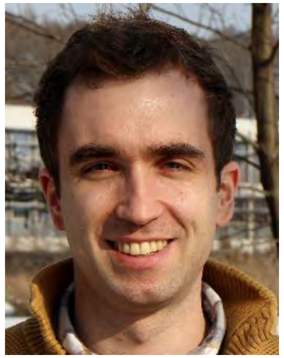
Dominik Göbl



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Edmund Taglauer

FWF Der Wissenschaftsfonds.

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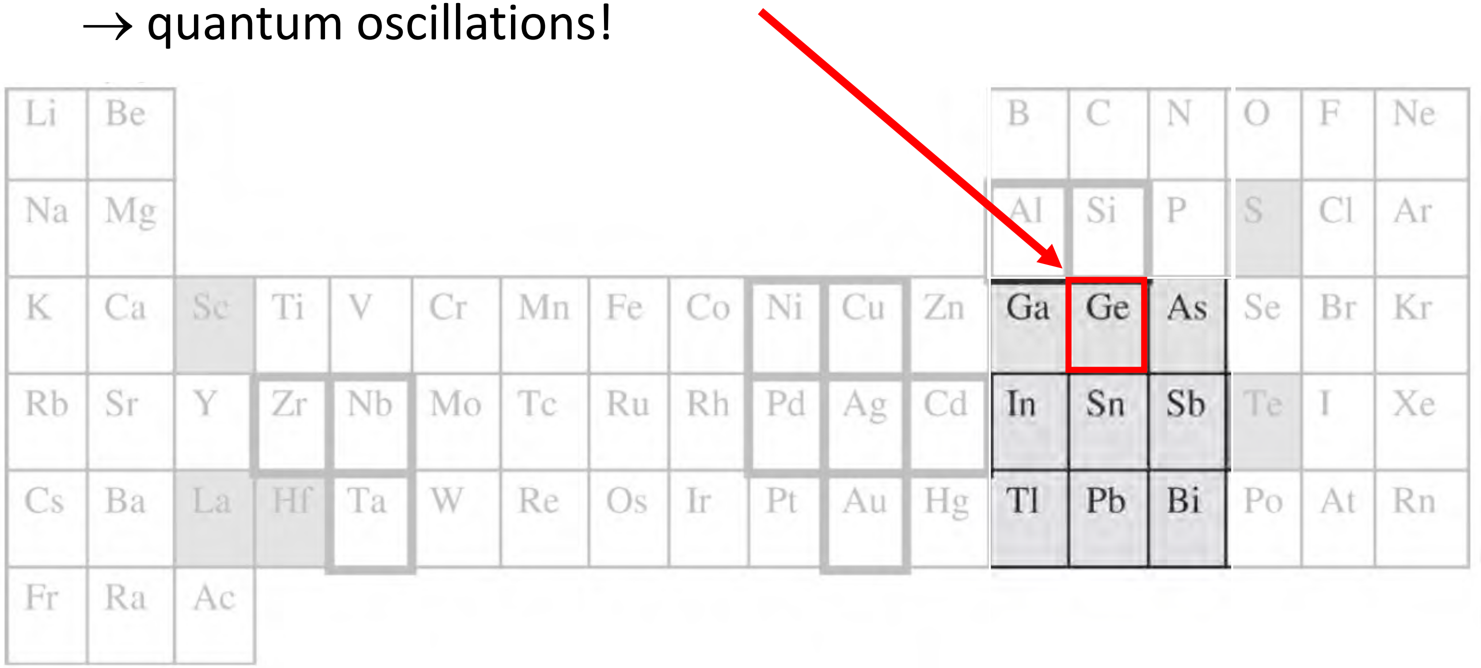
Thank you!

(c) Quasiresonant neutralization

- **d-electrons (e.g., of Ge)** are quasi resonant with He 1s level

  $\rightarrow$ quantum oscillations!



(Hidde Brongersma et al., Surf.Sci.Rep. 62(2007) 63)

Quantum oscillations

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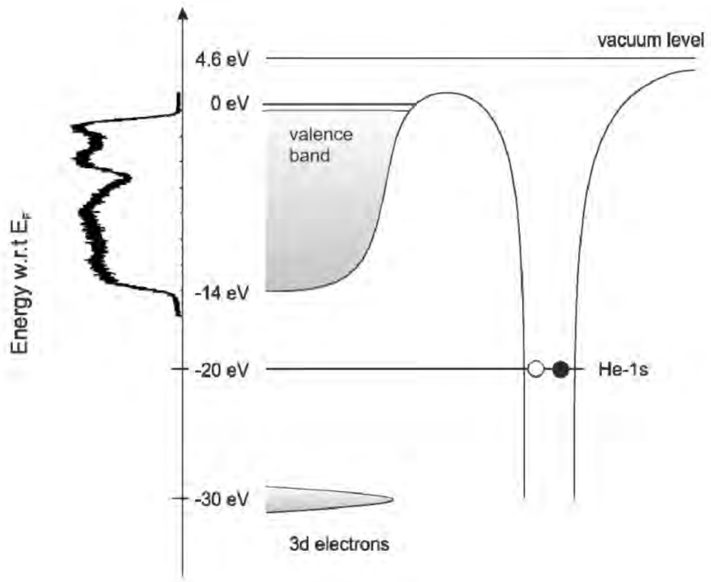
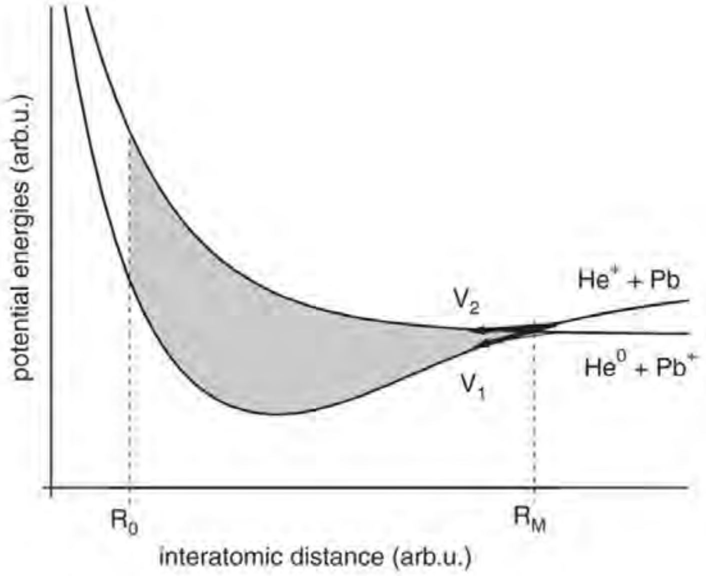




(Erickson et al. (1975))

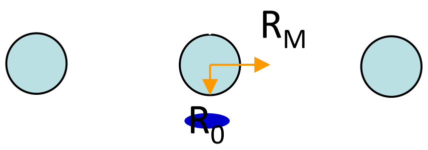
Quantum oscillations

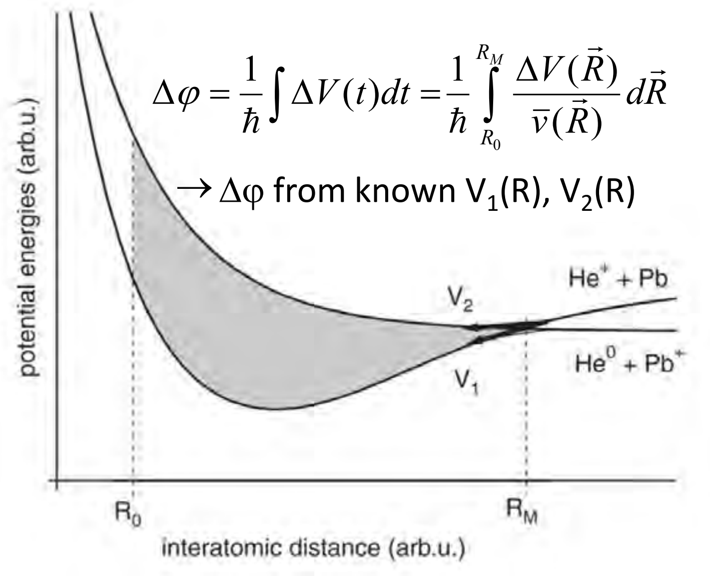
Way in: at mixing distance $\mathbf{R_M}$ the projectile „forgets“ its charge state

collision: phase difference $\Delta\varphi$ evolves between the two paths (V_1, V_2)

until projectile passes R_M again

qRN ≡ atomic collision: No dependence on α, β, no $1/v_\perp$ scaling!





$$\Delta\varphi = \frac{1}{\hbar}\int \Delta V(t)dt = \frac{1}{\hbar}\int_{R_0}^{R_M} \frac{\Delta V(\vec{R})}{\bar{v}(\vec{R})} d\vec{R}$$

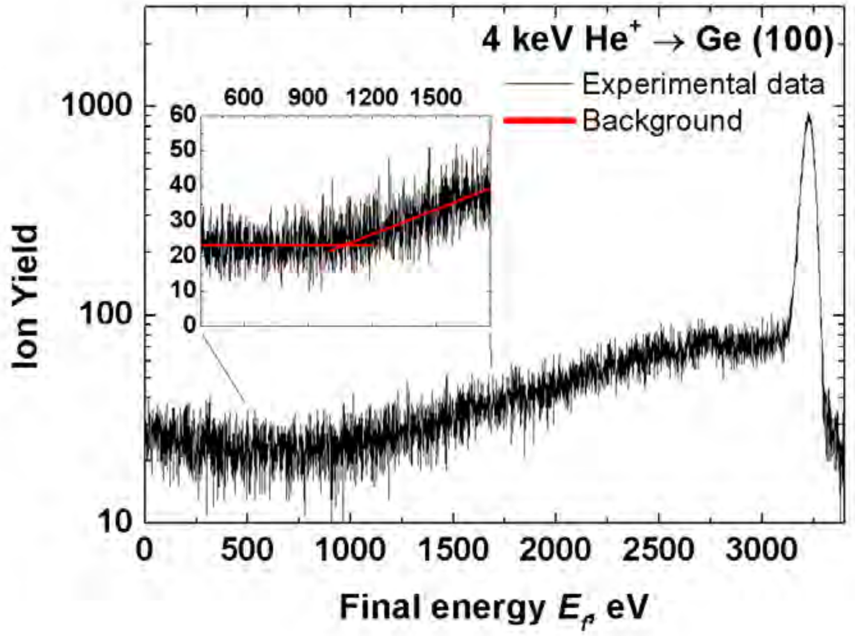
$\rightarrow \Delta\varphi$ from known $V_1(R)$, $V_2(R)$

$I_+ = a_+ + b\cdot\cos^2(\Delta\varphi/2)$, $I_0 = a_0 + b\cdot\sin^2(\Delta\varphi/2)$

$\rightarrow I_+$ oscillations are equidistant as $f(1/v)$

Interplay AN $\leftrightarrow$ qRN $\leftrightarrow$ RI

- **Threshold energy for reionization:** $E_f \approx 1200$ eV
  $\rightarrow$ for $E_f < 1200$ eV only Auger neutralization $\leftrightarrow$ quasi-resonant neutral.



Dominik Göbl et al., J. Phys.: Conden. Matt. (2013)

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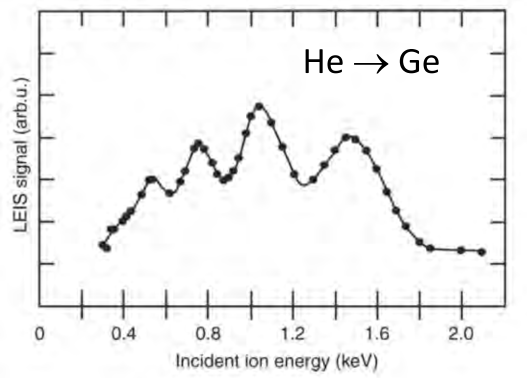
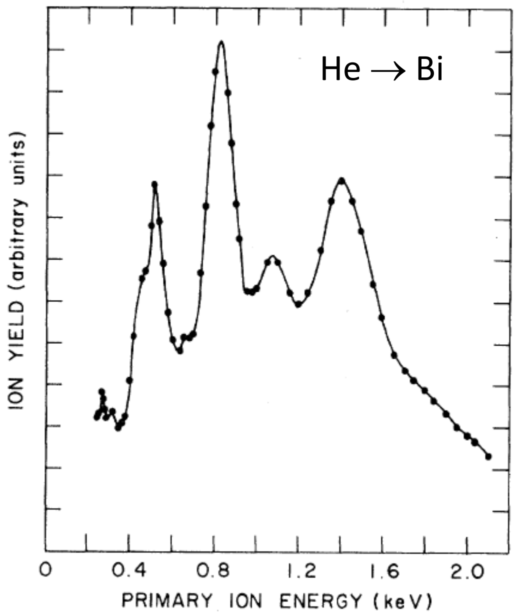
Quantum oscillations

- **d-electrons** are quasi resonant with He 1s level

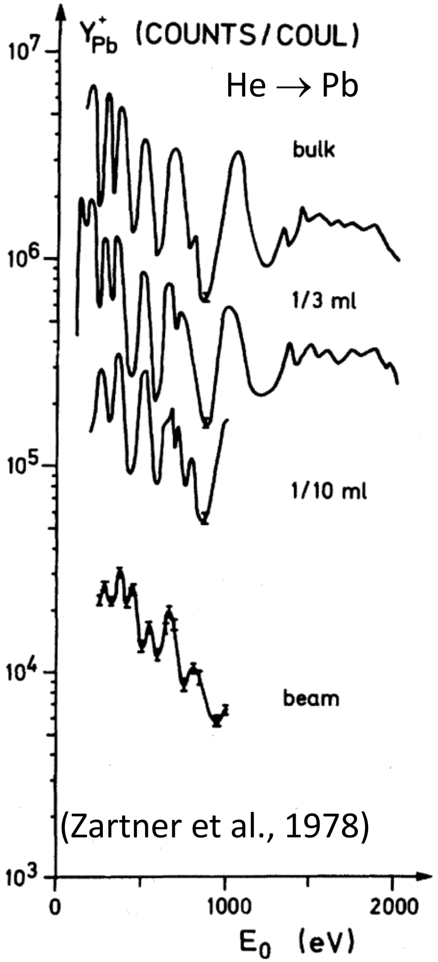
  $\rightarrow$ quantum oscillations!



(Erickson et al., 1975)

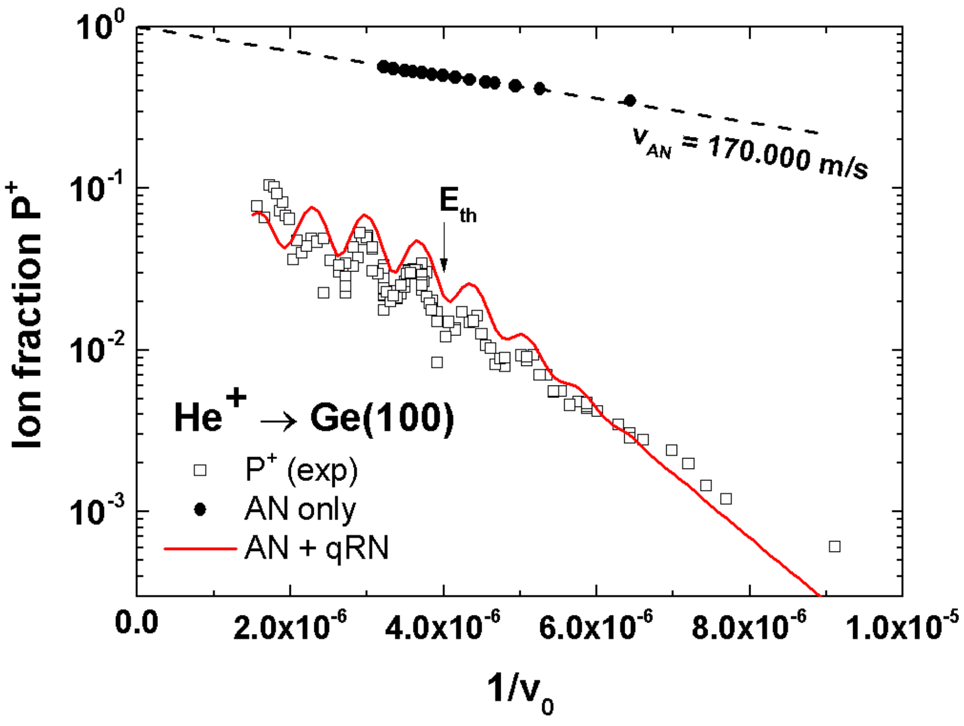


(Smith et al., 1974)



(Zartner et al., 1978)

Quantitative P^+ for $He^+ \rightarrow Ge$



(Goebl et al., 2013)

$P^+ << 1$: qRN is very effective

qRN works „one-way“: $He^+ \rightarrow He^0$

($He^0 \rightarrow He^+$ is not possible!)

No reionization up to 1.3 keV

$\rightarrow$ P^+ = qRN-surviving probability

$$P^+ = e^{-P_{qRN}} = e^{-v_{qRN}/v}$$

$P^+ \approx 10^{-2}$ @ 1 keV (v = 0.1 a.u.)

$\rightarrow$ $v_{qRN} \approx 10^6$ m/s $\approx 5 \cdot v_c$

$\rightarrow$ qRN dominates over AN

Information depth = 1 ML! (without reionization) ☺
Oscillation amplitude ≈ factor 2: quantification ☹

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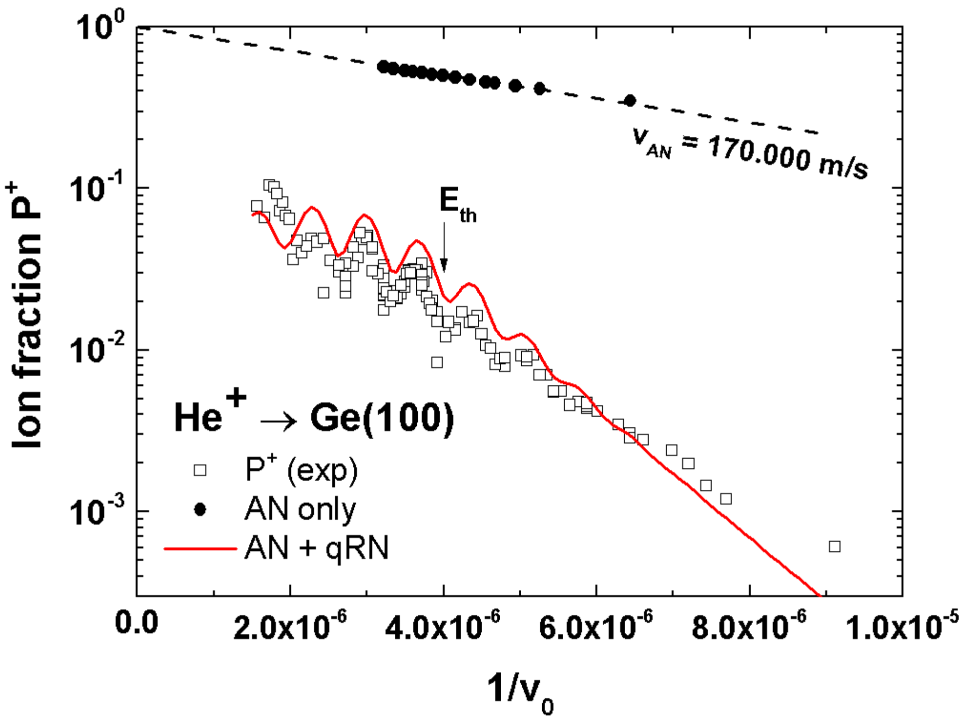
Quantitative P^+ for $He^+ \rightarrow Ge$



(Goebl et al., 2013)

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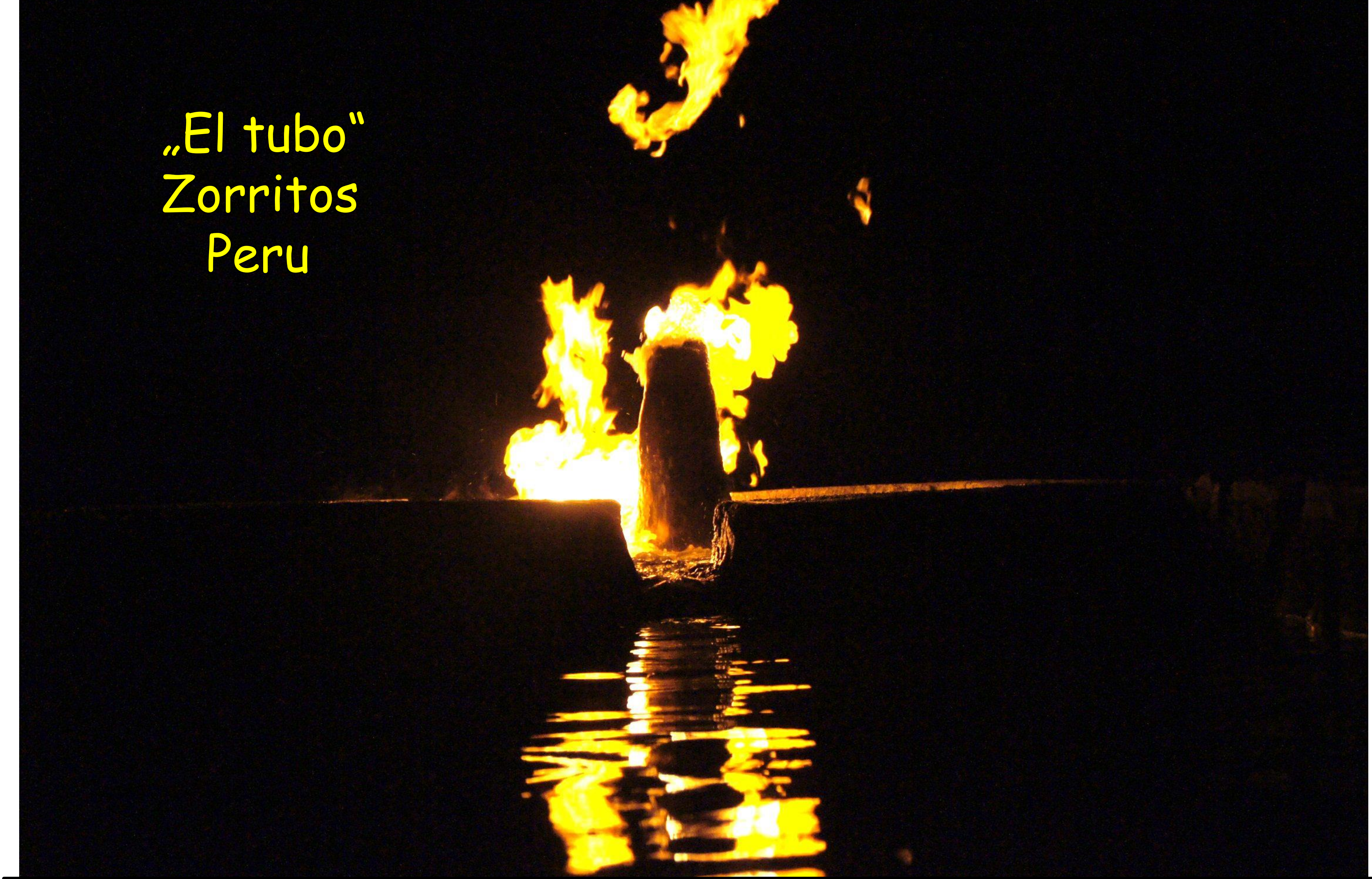

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TOF-LEIS Experiment: ACOLISSA