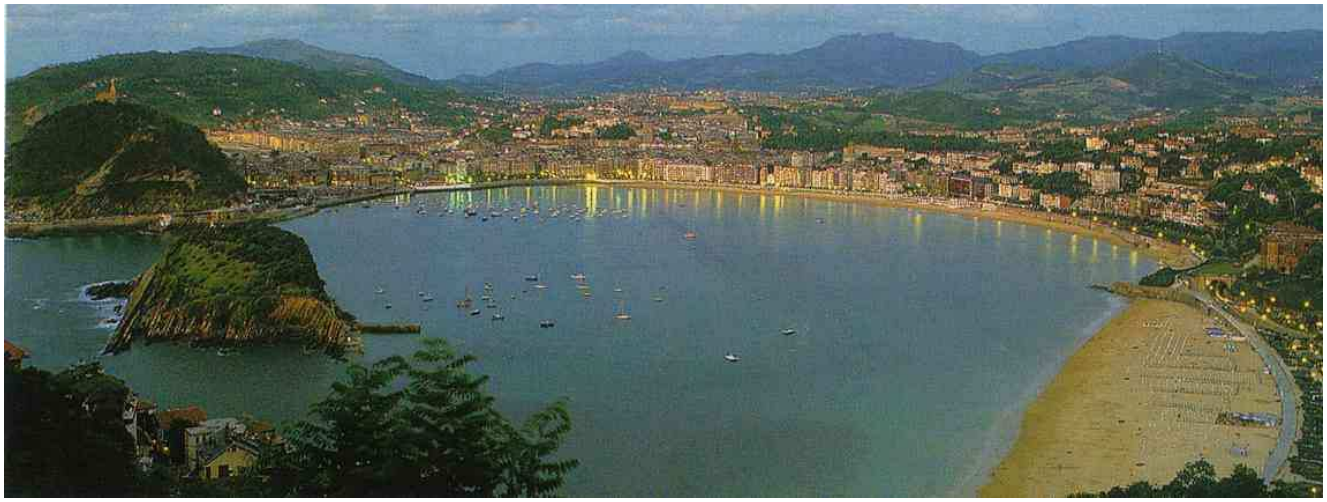

Why N_2 molecules with thermal energy abundantly dissociate on W(100) and not on W(110)

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'Predicting Catalysis: Ammonia Production from First Principles' Symposium
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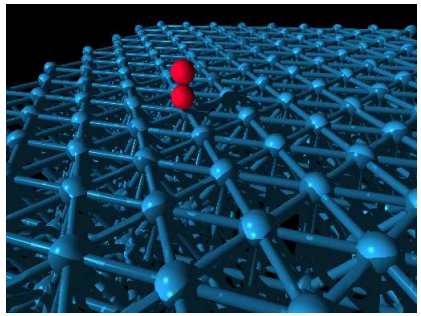


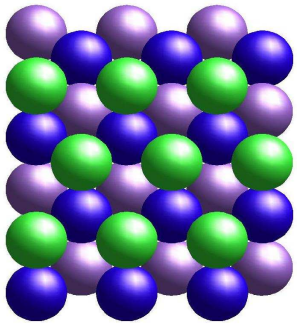
outline

- motivation: surface face and reactivity
- N_2/W(110):
  - potential energy surface from DFT
  - classical dynamics
- dissociation of N_2 on W(110) and W(100)
- conclusions

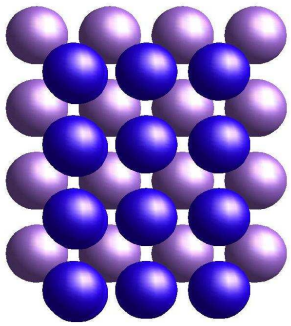
surface face and reactivity

$N_2 + 3H_2 \longrightarrow 2NH_3$

rates of ammonia synthesis over five iron single-crystal surfaces



Fe (111)



Fe (100)

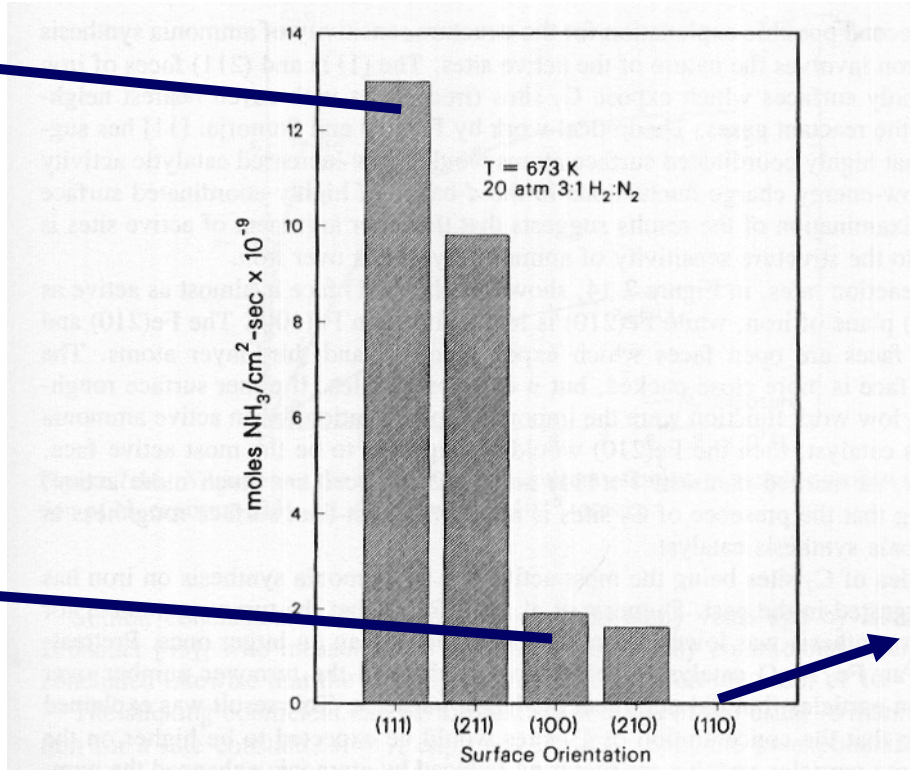
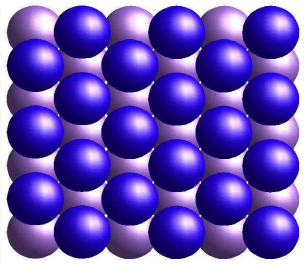
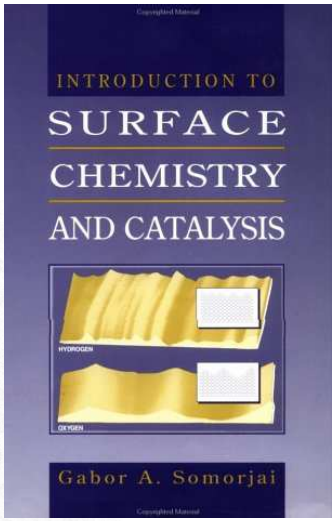


Figure 7.14. Rates of ammonia synthesis over five iron single-crystal surfaces with different orientations: (111), (211), (100), (210), and (110) [38].



Fe (110)



surface face and reactivity

- the rate-limiting step in ammonia formation is the dissociative adsorption of N_2 on the surface
- two possible reasons for the difference in reactivity over different faces:
  - surface roughness (work functions)
  - unique active sites at the surface

most reactive surfaces have C_7 sites (seven nearest neighbors)

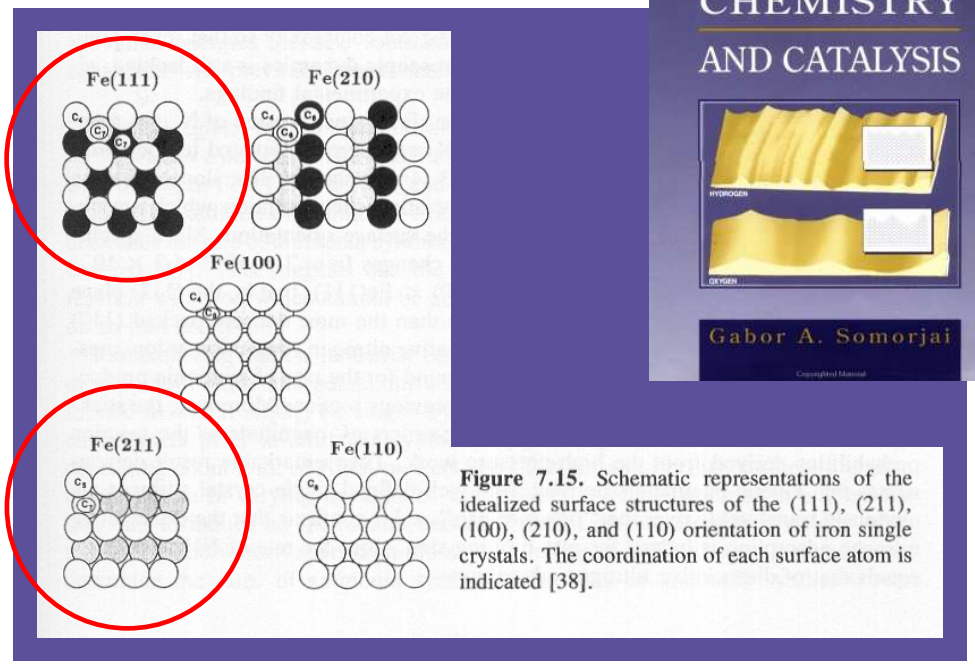
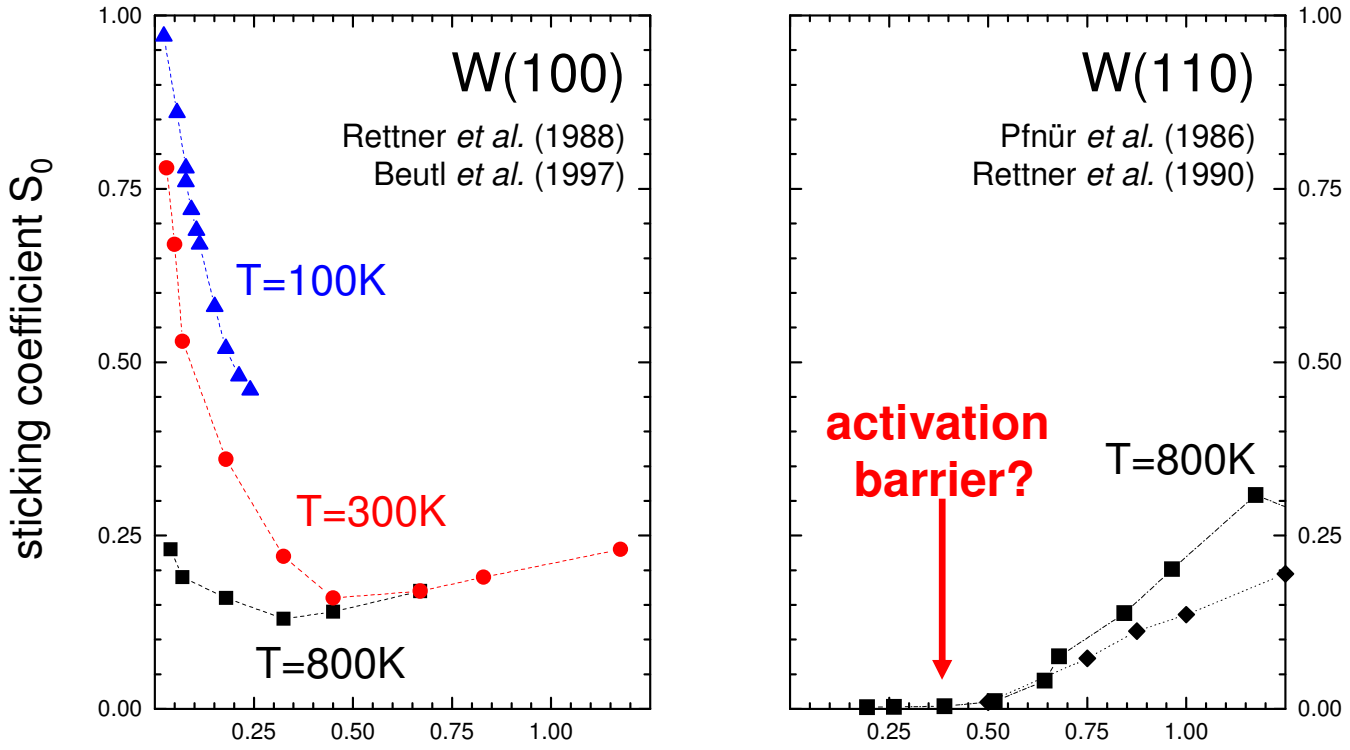


Figure 7.15. Schematic representations of the idealized surface structures of the (111), (211), (100), (210), and (110) orientation of iron single crystals. The coordination of each surface atom is indicated [38].

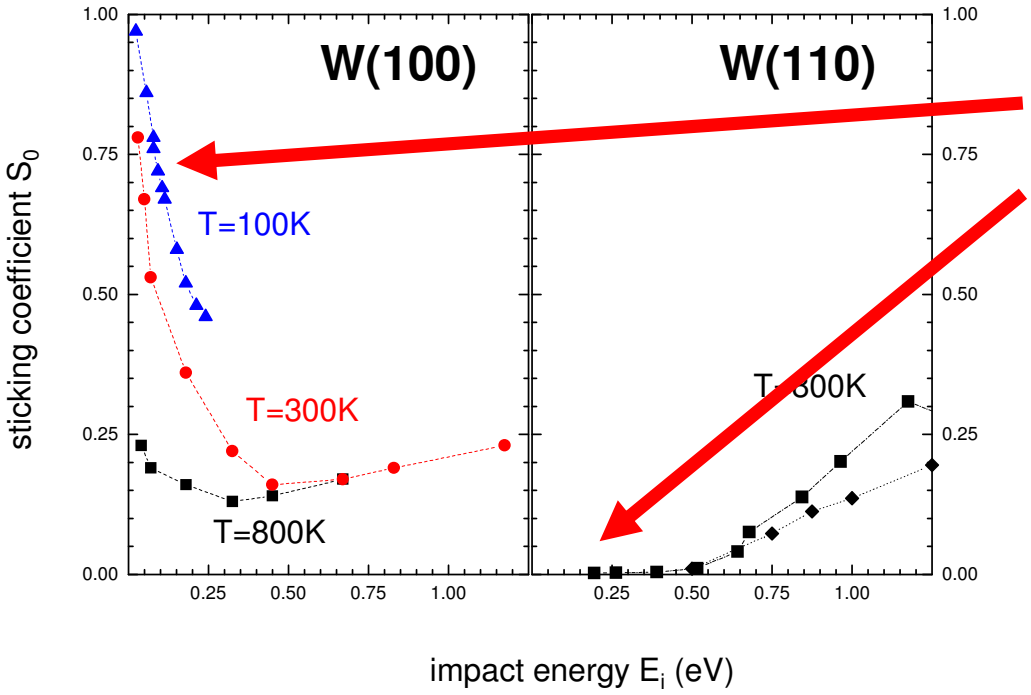
measurements of N_2 dissociation on W surfaces

normal incidence



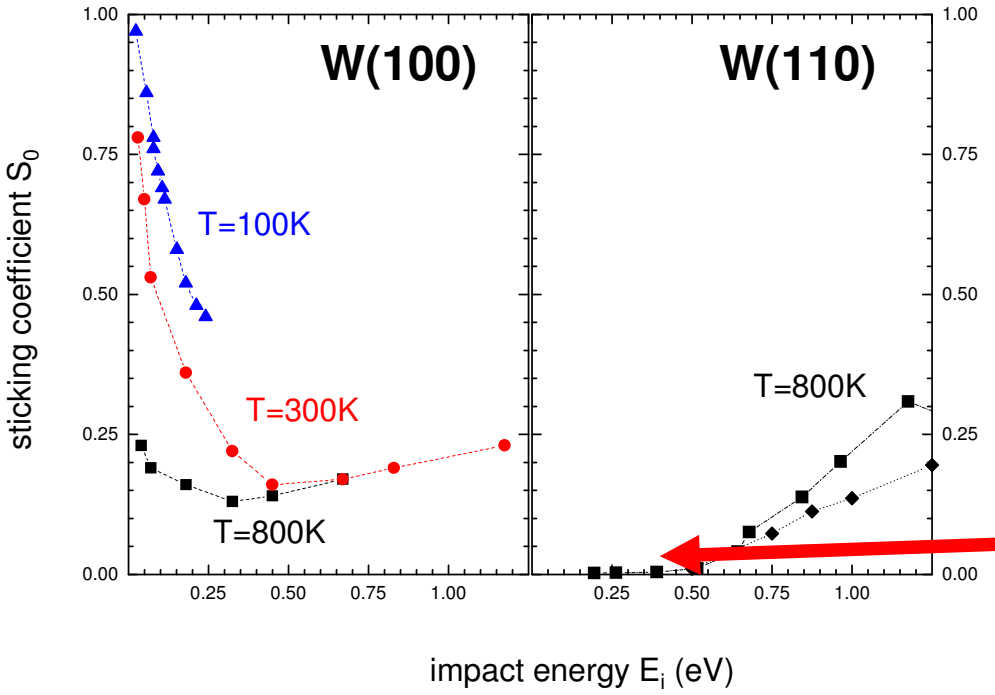
no threshold **threshold**

two questions to answer:



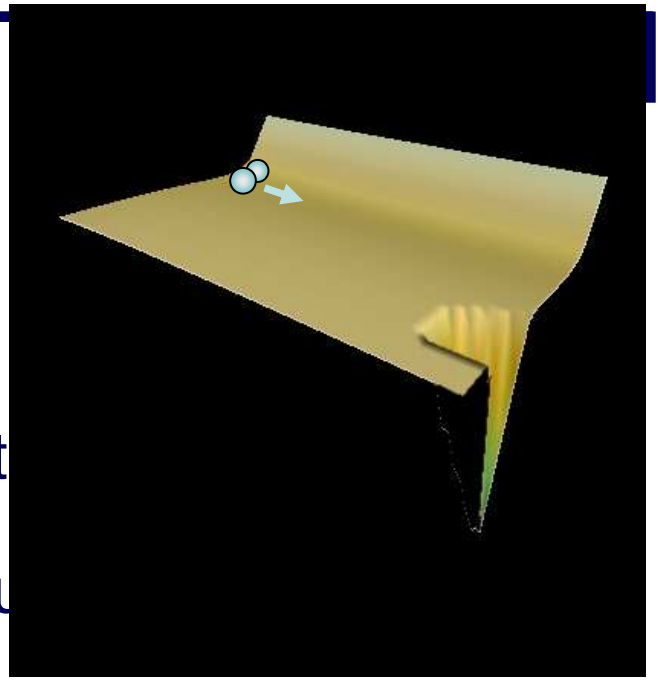
why the difference in the N_2 dissociation rate at low energies between the (100) and (110) faces of W?

two questions to answer:



why the difference in the N_2 dissociation rate at low energies between the (100) and (110) faces of W?

is there an activation barrier for the dissociation of N_2 on W(110)?

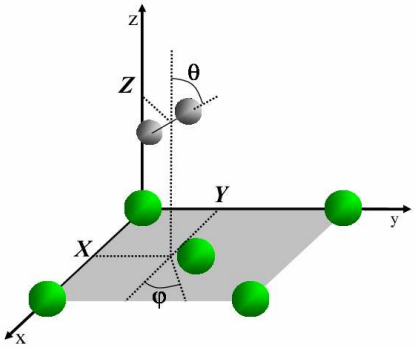


6D potential energy surface (PES) of N_2/W(110)

- DFT - GGA (PW91) calculation wit
- Plane-wave basis set and US pseu
- periodic supercell: 5-layer slab and 2x2 surface cell
- 30 configurations = 5610 ab-initio values
- interpolation through the corrugation reducing procedure

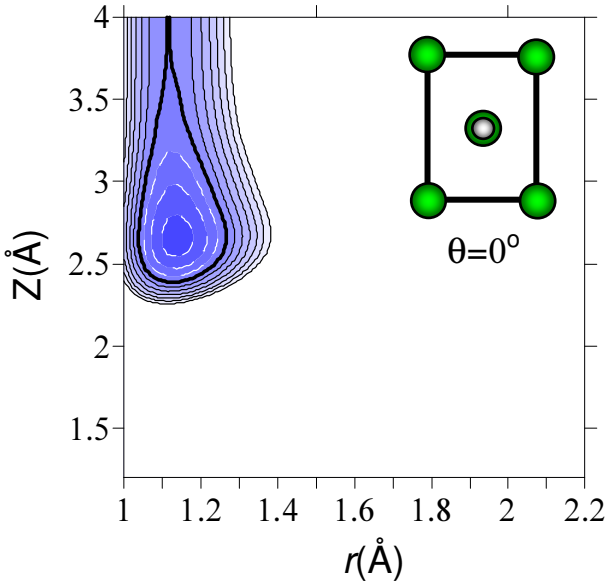
  [Busnengo *et al.*, JCP 112, 7641 (2000)]

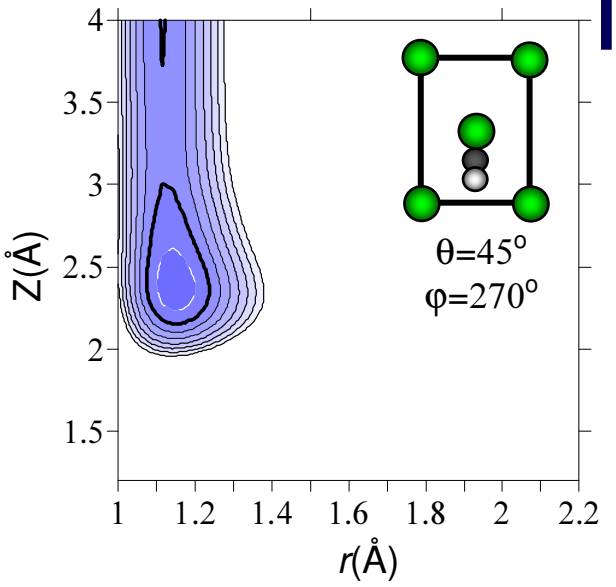
some elbow plots for the N_2/W(110) system

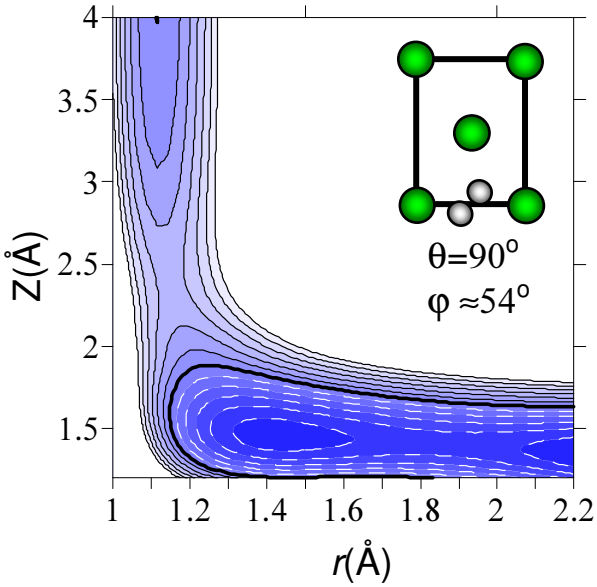


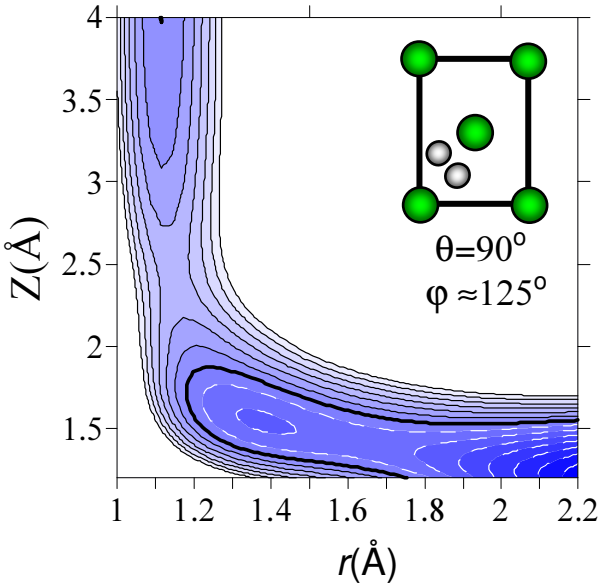
distance between contour lines = 0.2eV

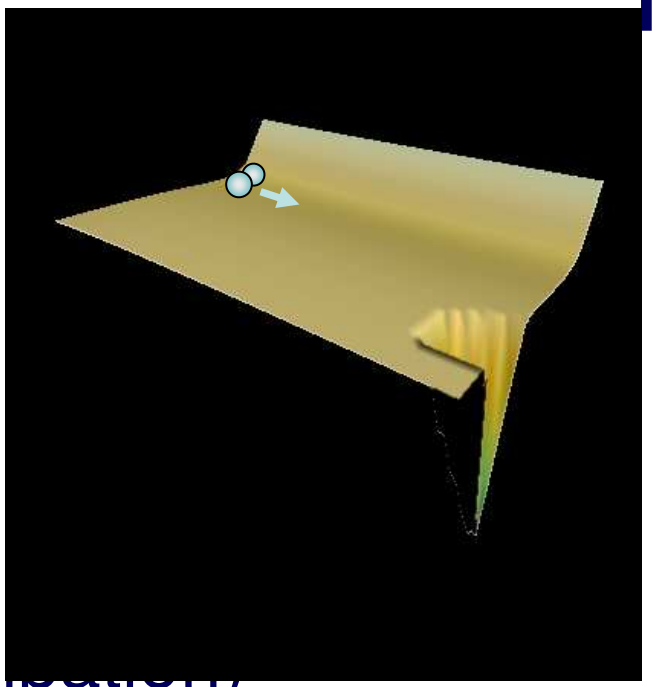
E<0
E=0
E>0







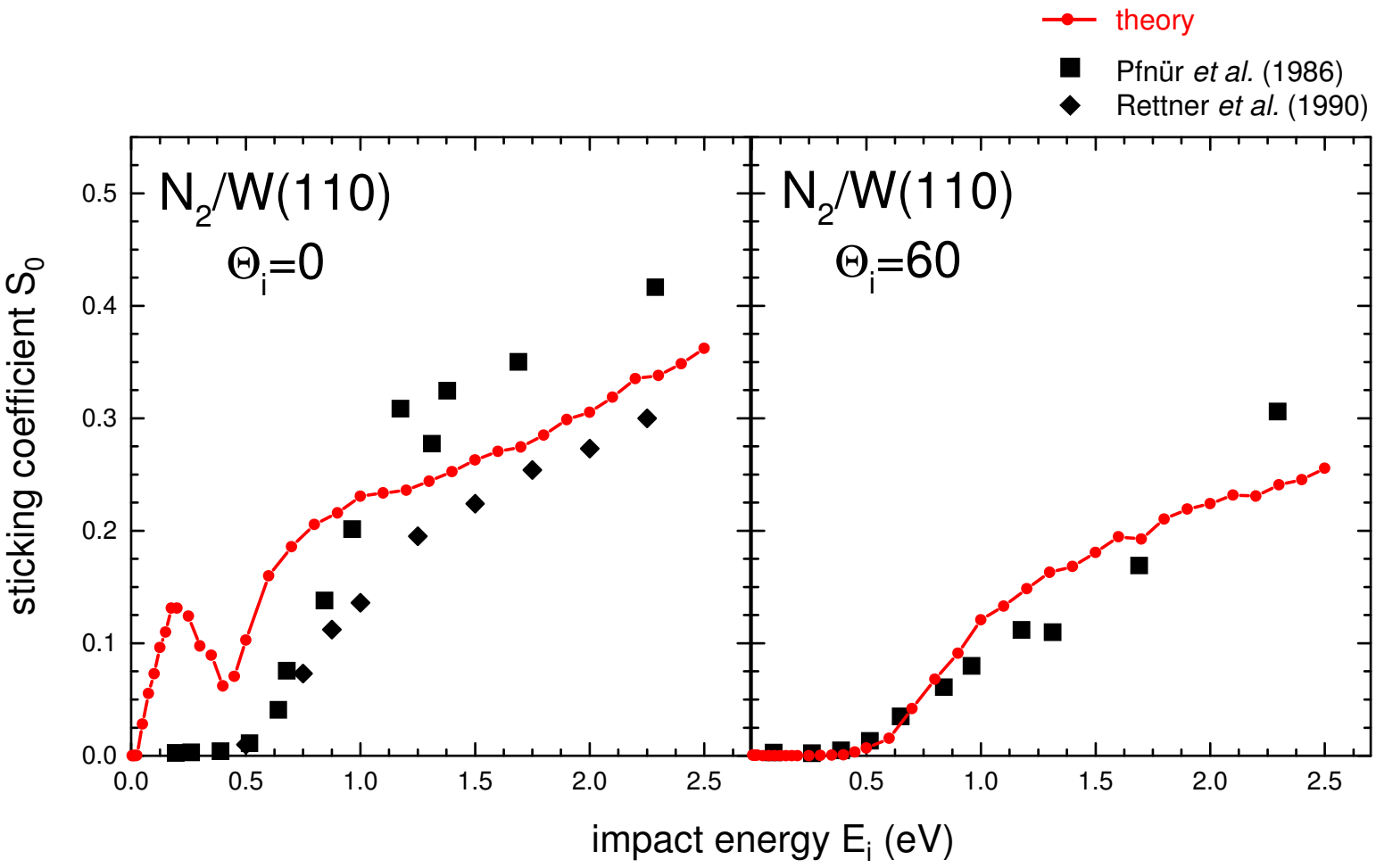




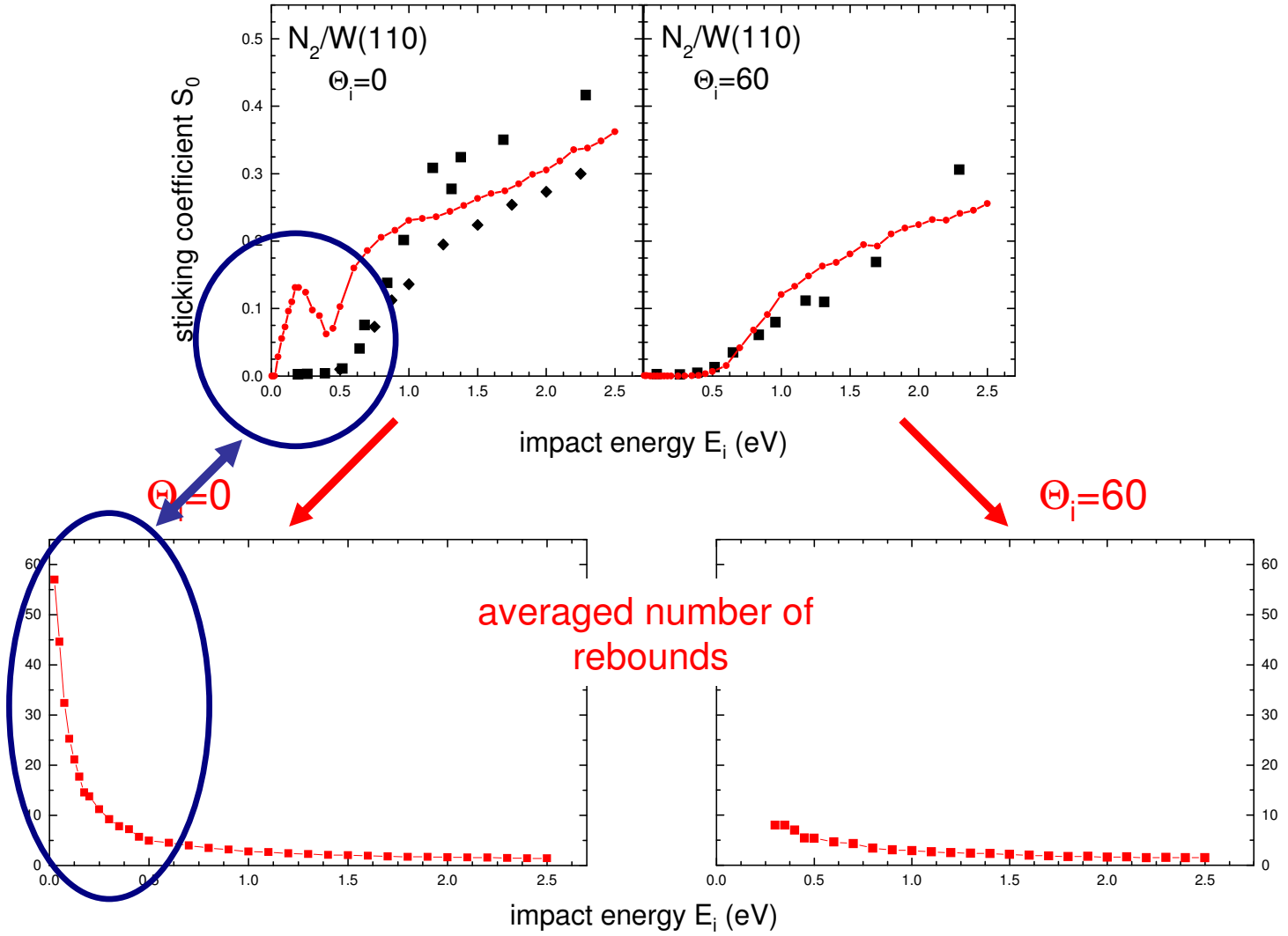
➡ classical dynamics

- classical trajectory method
- adiabatic description (no dissipation)
- 5000 trajectories per incident energy

classical dynamics in the 6D-PES

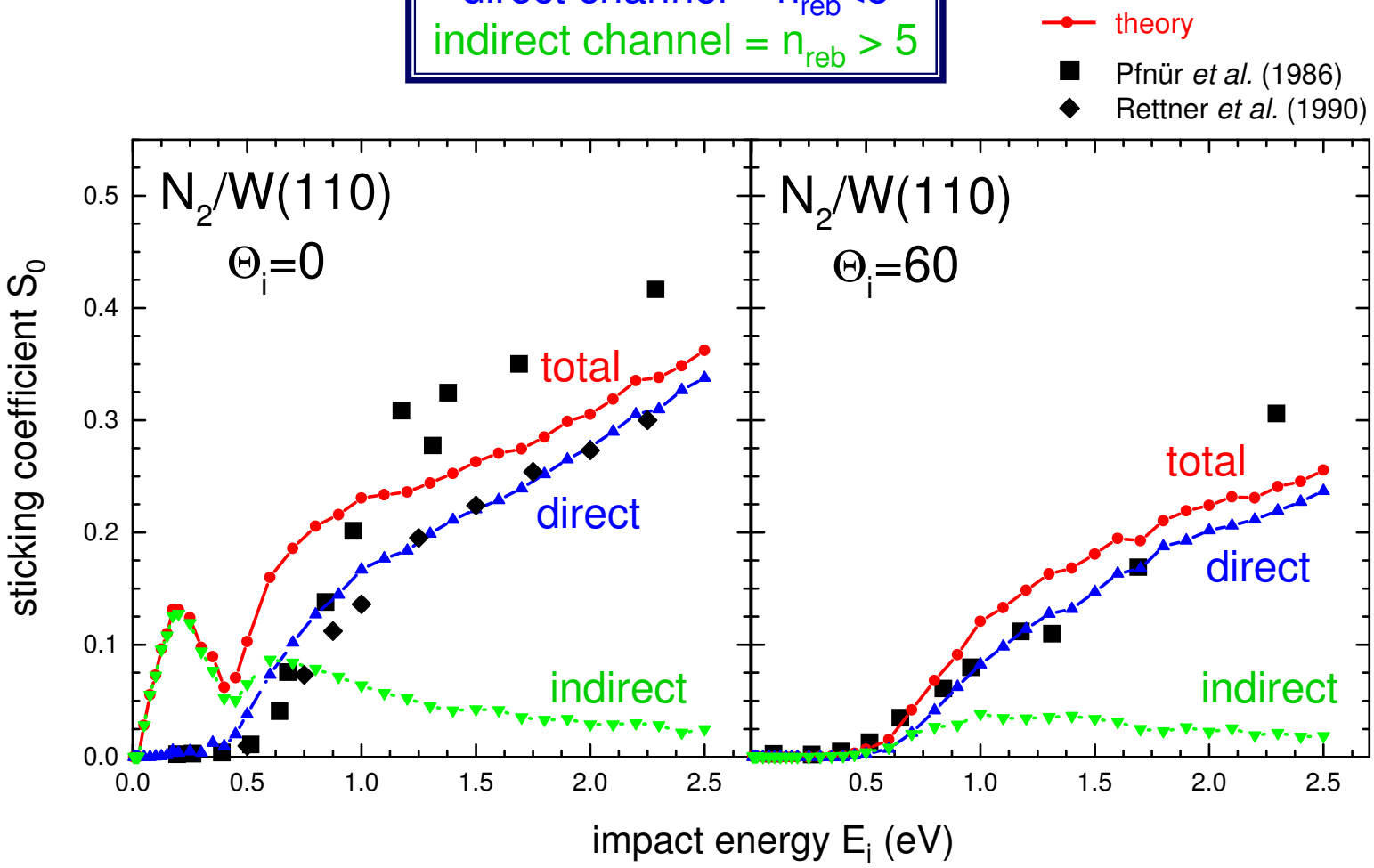


direct and indirect channels in the dissociation process

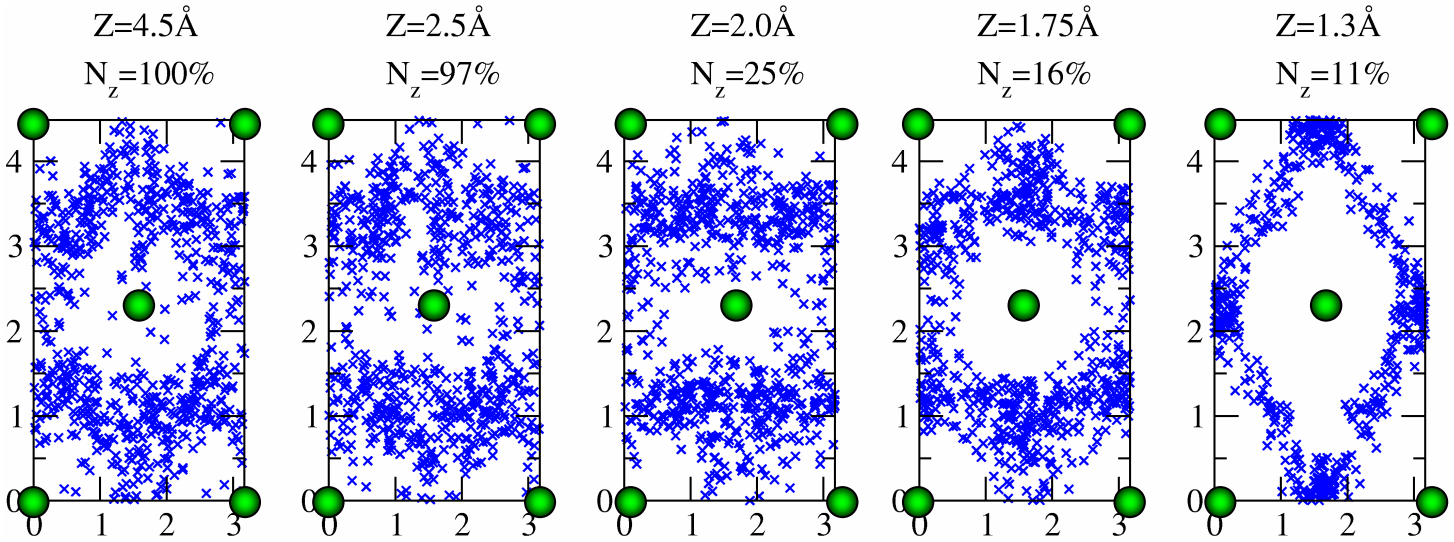


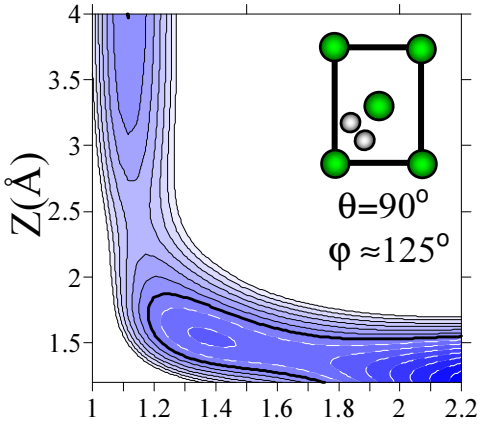
classical dynamics in the 6D-PES

direct channel = $n_{reb}<5$
indirect channel = $n_{reb} > 5$



two channels to reach dissociation: direct path

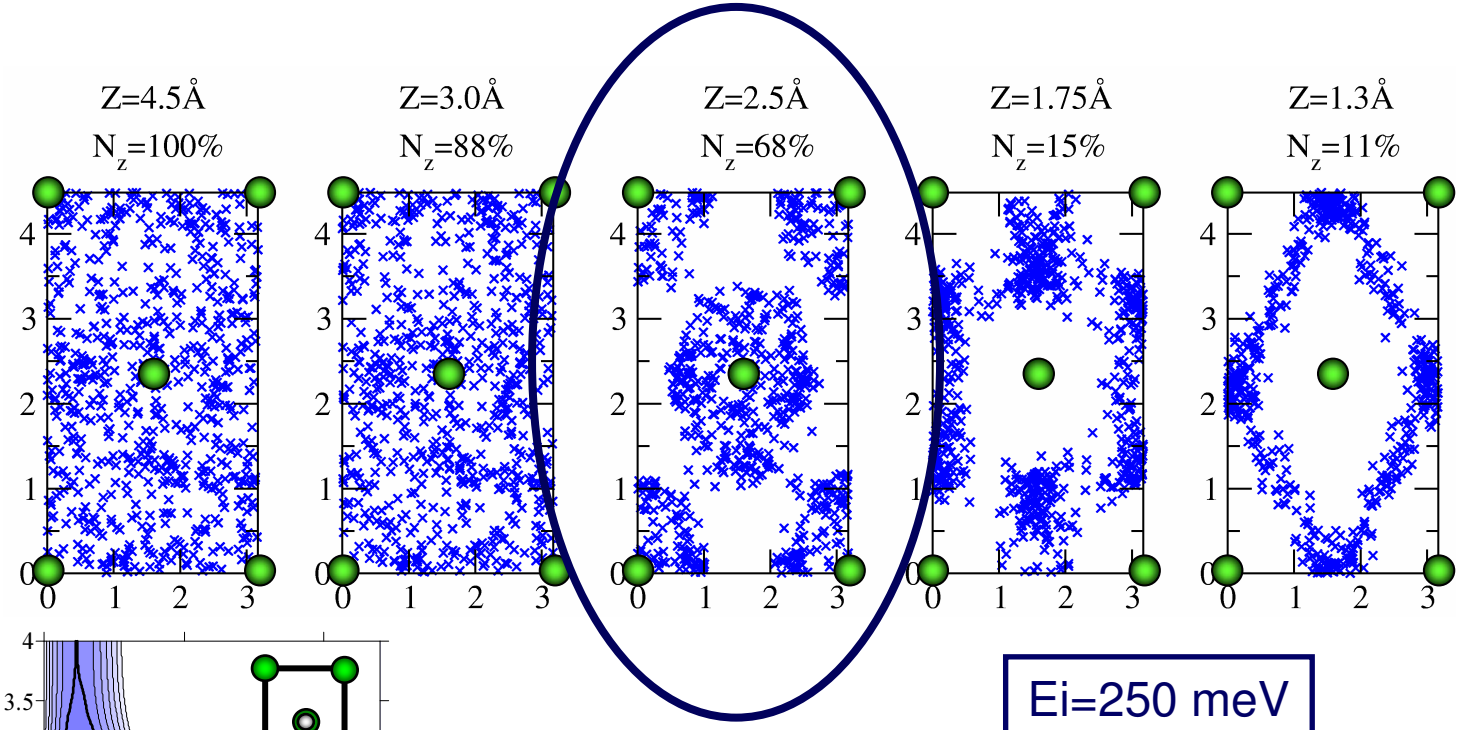


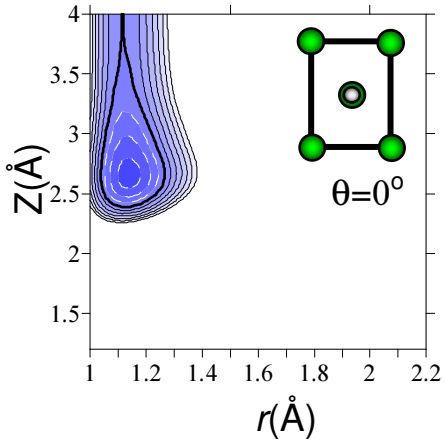


Ei=500 meV

direct dissociation
without much change
in the position of N_2
on the XY plane

two channels to reach dissociation: indirect path (trapping)

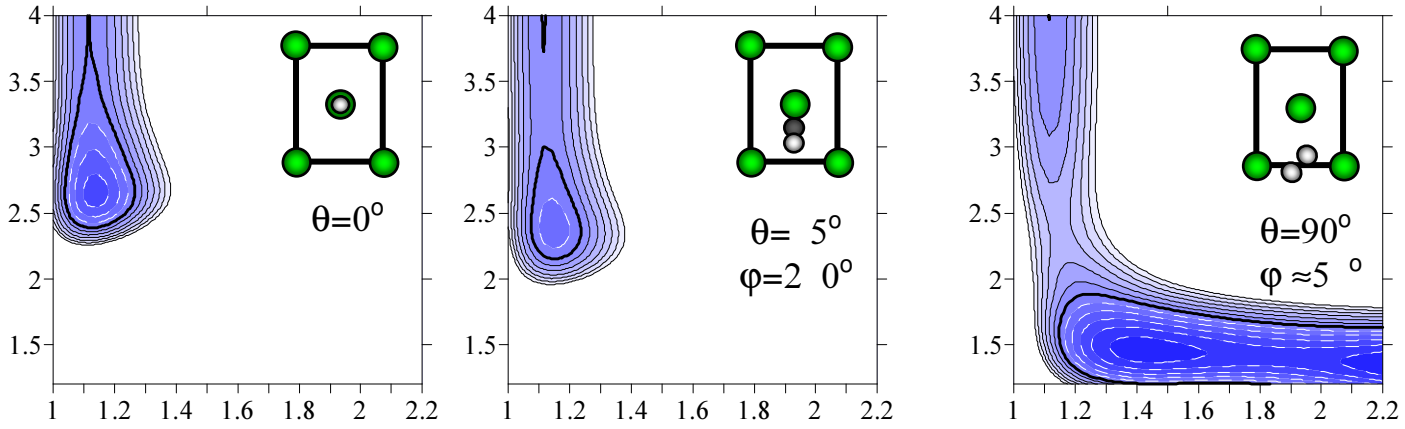




Ei=250 meV

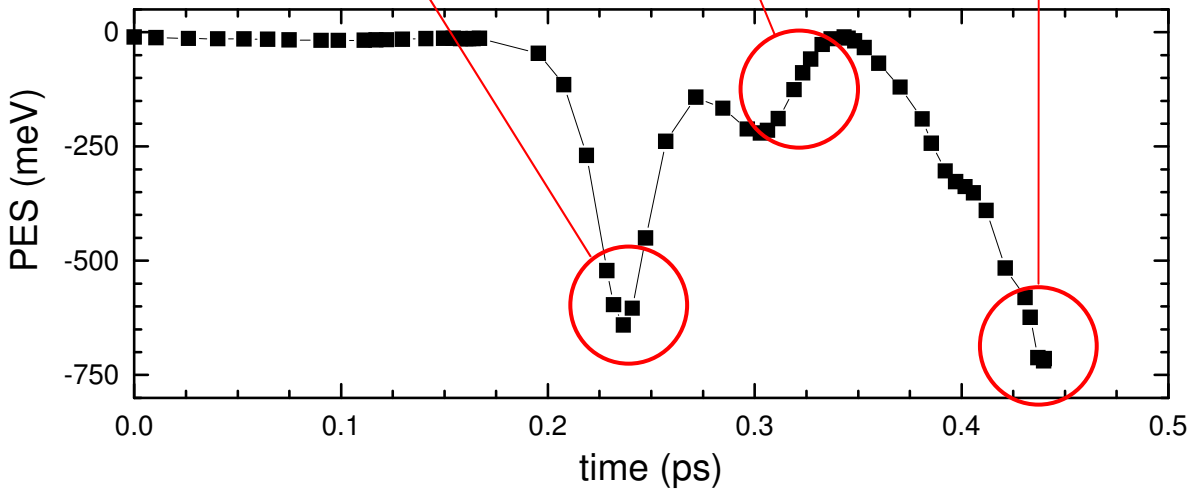
trapping in the well:
a few picoseconds bouncing
before dissociation

non-activated paths to dissociation



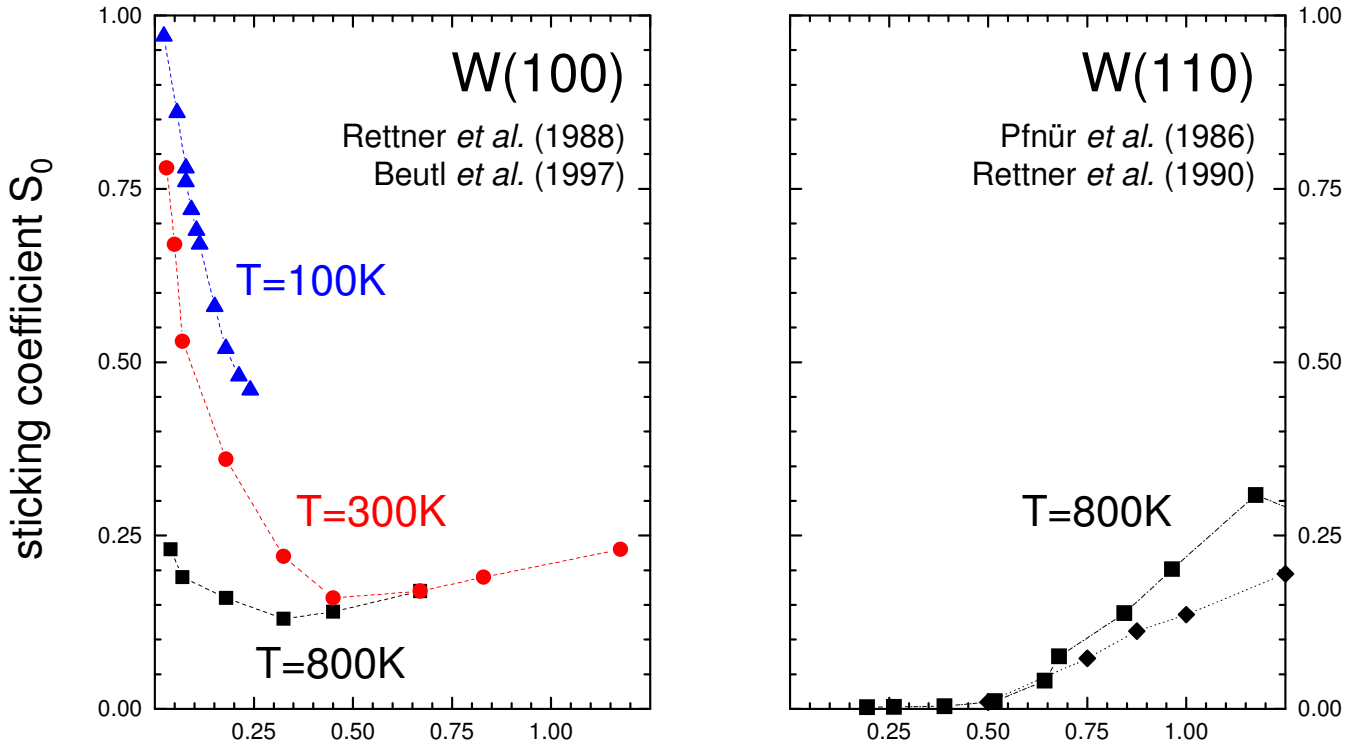
potential well

dissociation



measurements of N_2 dissociation on W surfaces

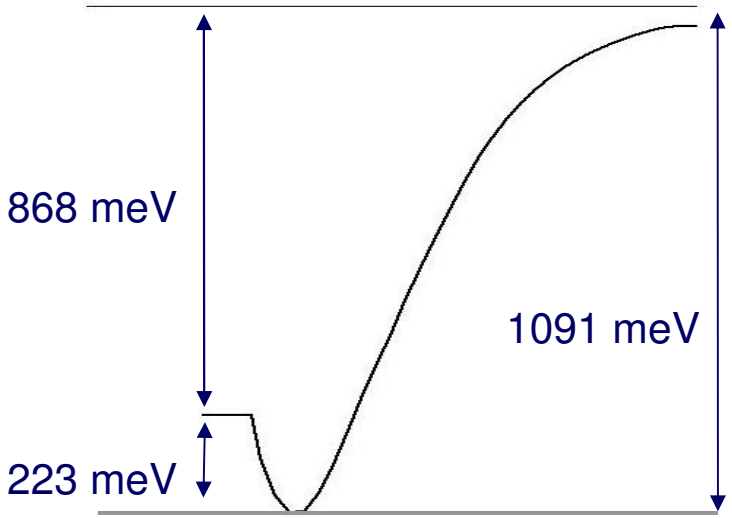
normal incidence



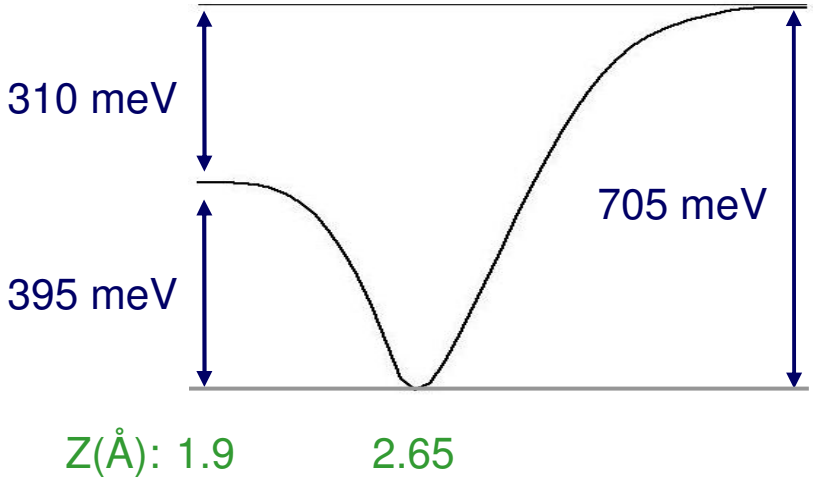
no threshold **threshold**

dynamic trapping in a well in both faces

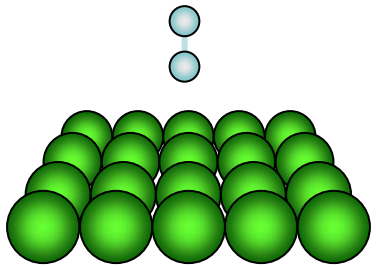
W(100)



W(110)

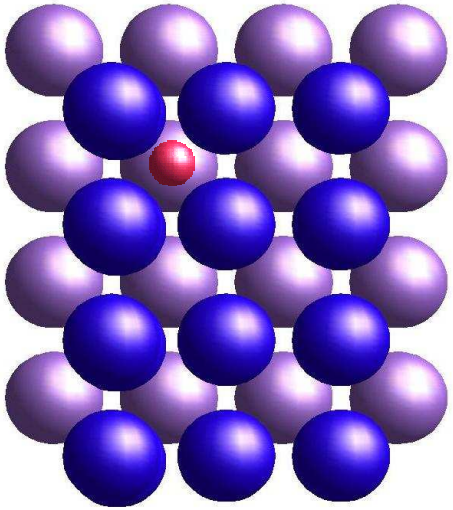


approach to surface:
vertical over a surface atom



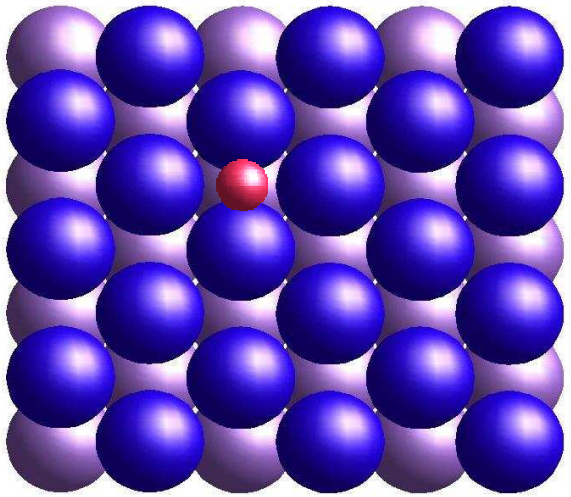
final state features: N adsorption on W

W(100)



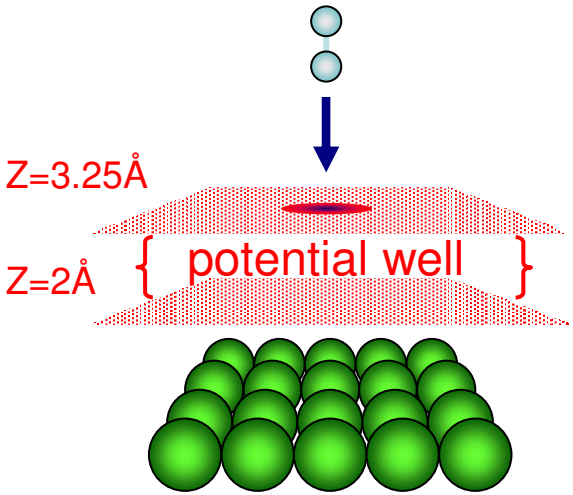
adsorption energy
DFT = 7.4 eV
Exp. = 6.6-7 eV
adsorption distance
DFT = 0.63 Å

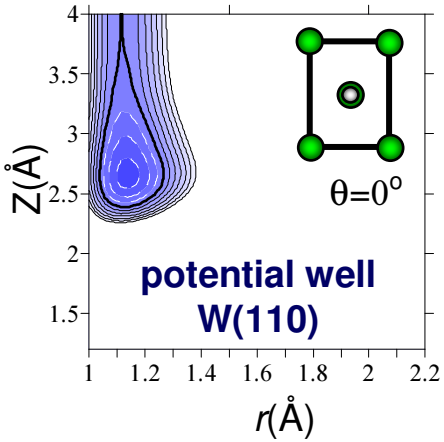
W(110)

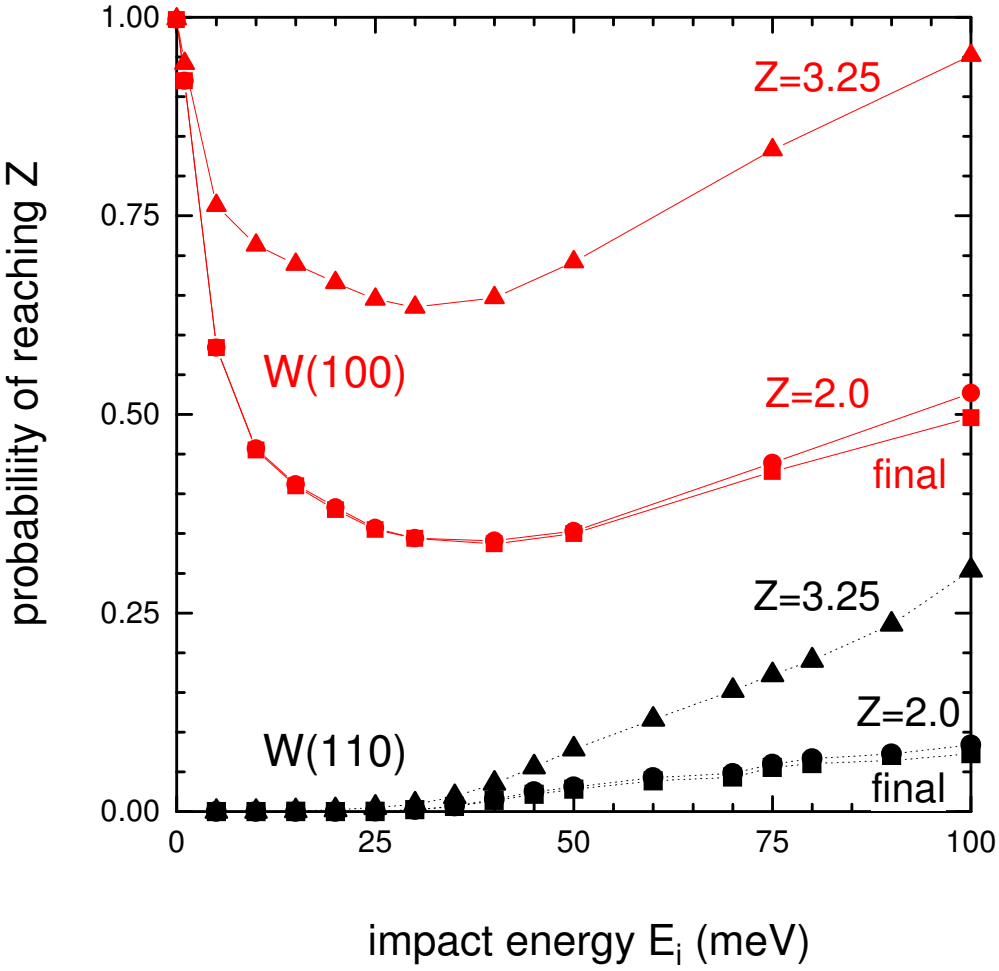


adsorption energy
DFT = 6.8 eV
Exp. = 6.6 eV
adsorption distance
DFT = 1.15 Å

for thermal energies, long distances matter







conclusions

dissociative adsorption of N_2 molecules at W(110) surfaces

is a non-activated process

nevertheless, classical dynamics show that

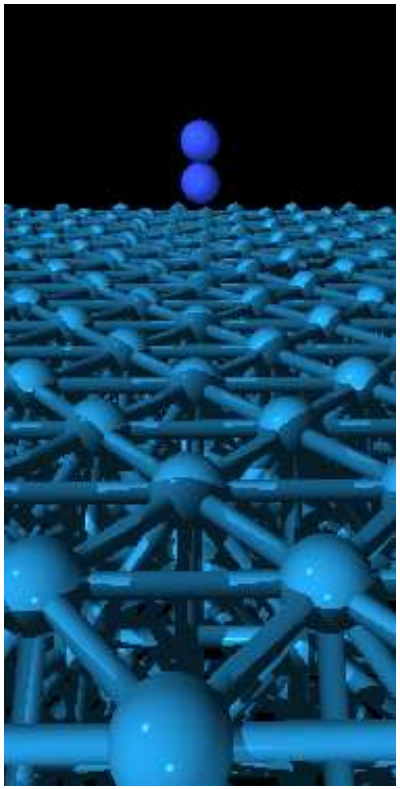
the sticking coefficient at thermal energies $S_0 \sim 10^{-3}$

is two orders of magnitude smaller than that of the W(100)

the big difference in the value of S_0 is already determined

at distances of Z = 3.25 Å from the surface and

arises from the behavior of the PES in the entrance channel



thank you for your attention

Leiden, 21th June 2006