

Non-adiabatic effects in the reactivity of molecules at metal surfaces

Ricardo Díez Muiño
Centro de Física de Materiales
Centro Mixto CSIC-UPV/EHU
San Sebastián



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➔ **contributors to this work**



Maite Alducin
CFM San Sebastián
Spain

Gisela Bocan
DIPC San Sebastián
Spain



J. Iñaki Juaristi
UPV San Sebastián
Spain

Fernando Mingo
CFM San Sebastián
Spain

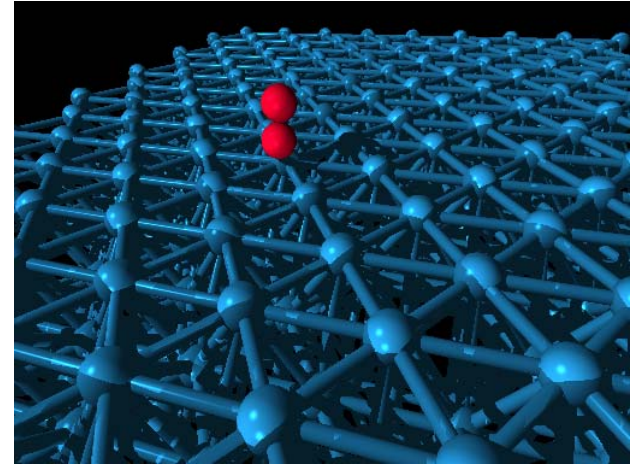


H. Fabio Busnengo
Universidad de Rosario
Argentina

Antoine Salin
Université de Bordeaux
France



 **outline**

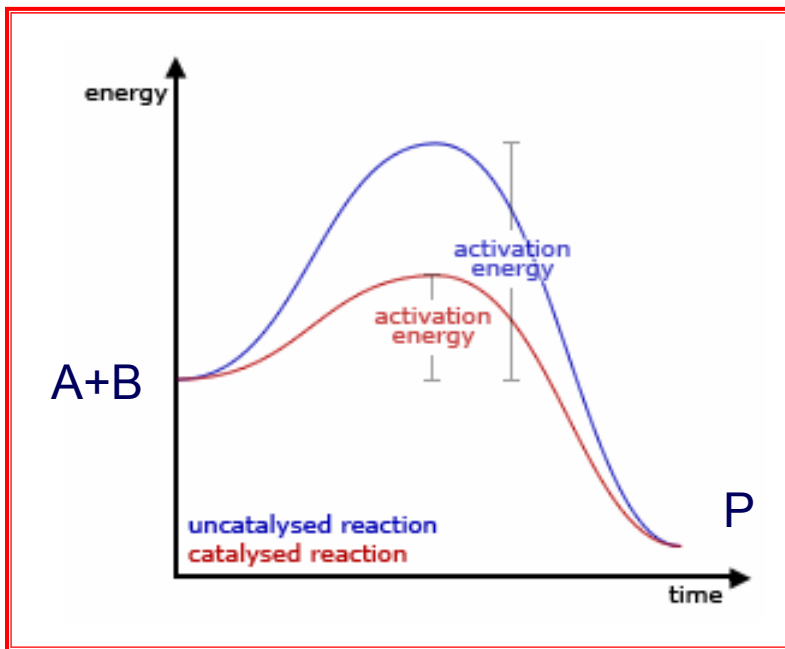


- introduction
- surface face and reactivity
- non-adiabatic effects: electronic excitations
- conclusions

➡ gas/solid interfaces and heterogeneous catalysis

What is catalysis?

The effect produced in facilitating a chemical reaction, by the presence of a substance, which itself undergoes no permanent change.

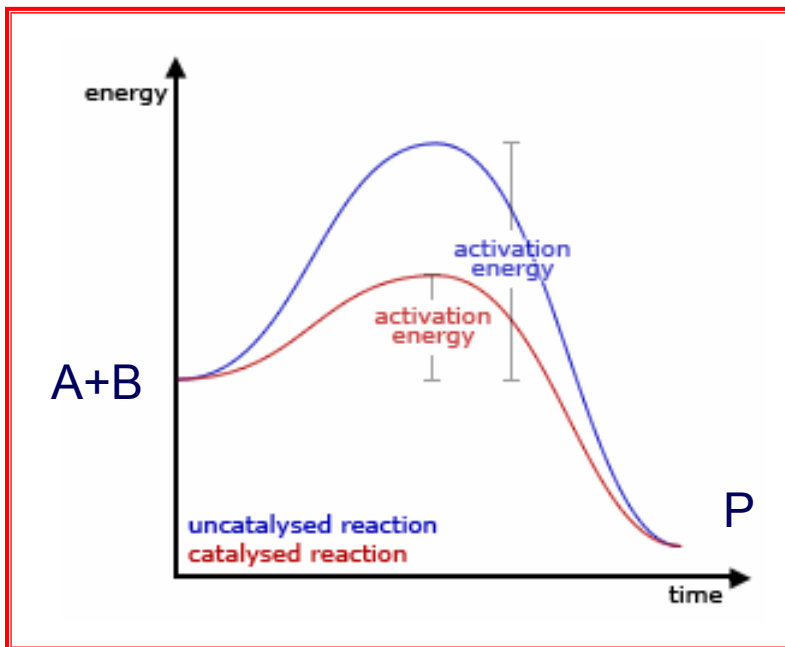


A and B are reactants
C is the catalyst
P is the reaction product

➡ gas/solid interfaces and heterogeneous catalysis

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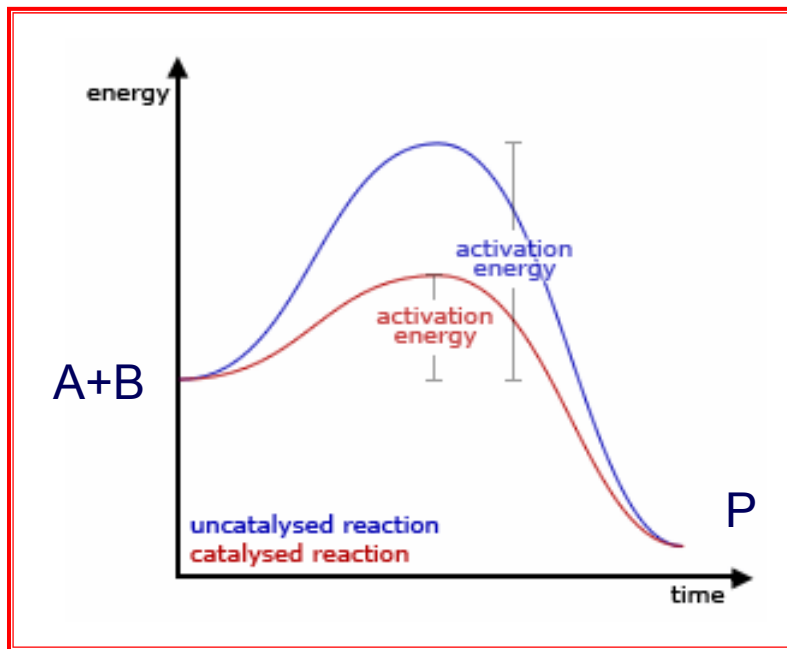
Heterogeneous catalysis:

The catalyst is in a different phase → solid surfaces.

➡ gas/solid interfaces and heterogeneous catalysis

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觸媒

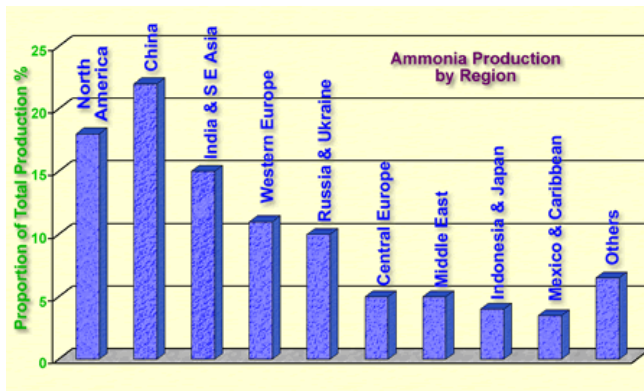
The chinese symbol
for catalyst
is the same as the one
for marriage broker
(matchmaker)

Heterogeneous catalysis:

The catalyst is in a different phase → solid surfaces.

➡ global context: chemical industry

ammonia synthesis:
 $3\text{H}_2(\text{g}) + \text{N}_2(\text{g}) \leftrightarrow 2\text{NH}_3(\text{g})$
(catalyzed by Fe surface)



world production:
130 million tons (year 2000),
~200US\$/ton



➡ global context: car industry



Catalysis in car industry:

In car engines, CO, NO, and NO₂ are formed.

Catalytic converters reduce such emissions by adsorbing CO and NO onto a catalytic surface, where the gases undergo a redox reaction.

CO₂ and N₂ are desorbed from the surface and emitted as relatively harmless gases:



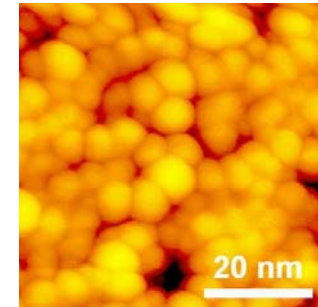
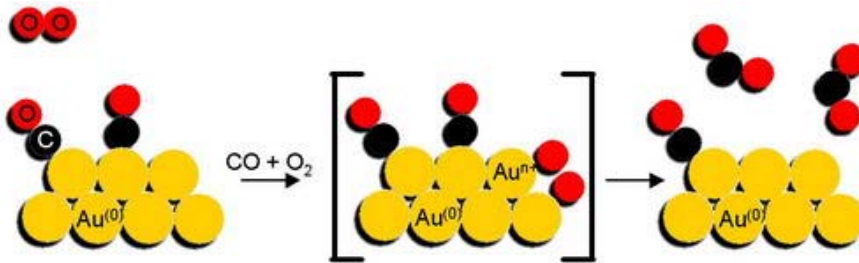
catalysis and nanoscale

- in the nanoscale, chemical properties can be changed
- tunability of electronic properties (optimization of reactivity)

➔ catalysis and nanoscale

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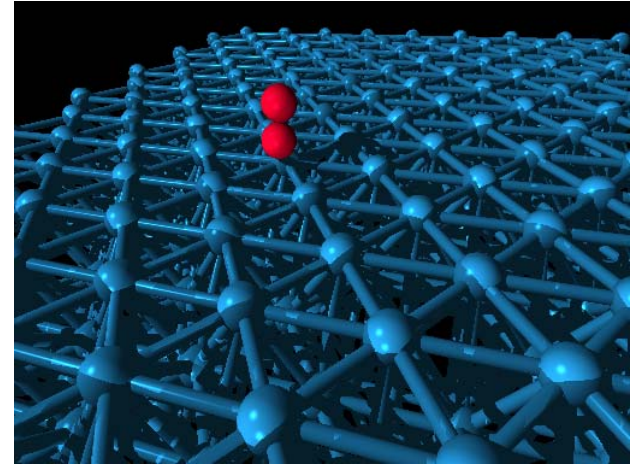
Au as a catalyst



In general, Au is a noble metal, the most inert bulk metal.

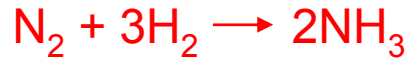
The chemical properties of Au dramatically change in the nanoscale. For instance, Au can act as a catalyst and transform CO into CO₂ when it comes in the form of nanoparticles.

➔ **outline**

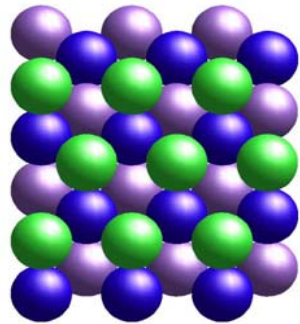


- introduction
- **surface face and reactivity**
- non-adiabatic effects: electronic excitations
- conclusions

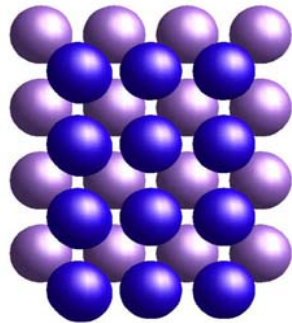
➔ surface face and reactivity



rates of ammonia synthesis
over five iron single-crystal surfaces



Fe (111)



Fe (100)

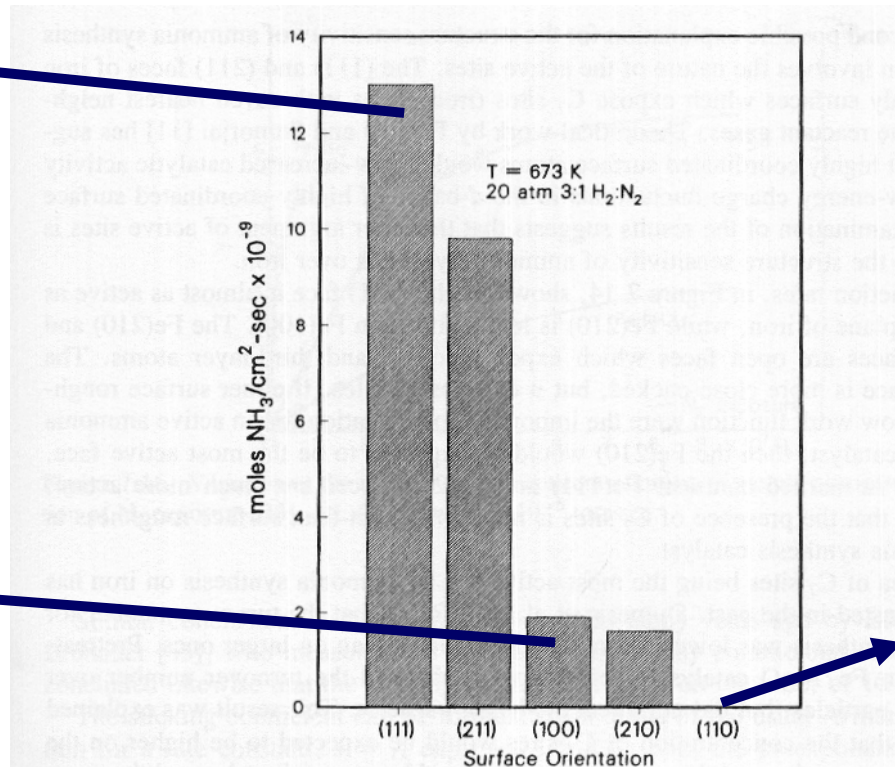
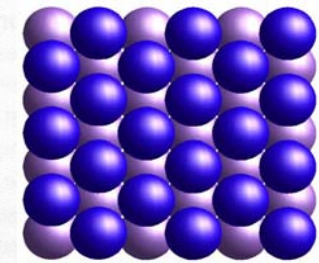
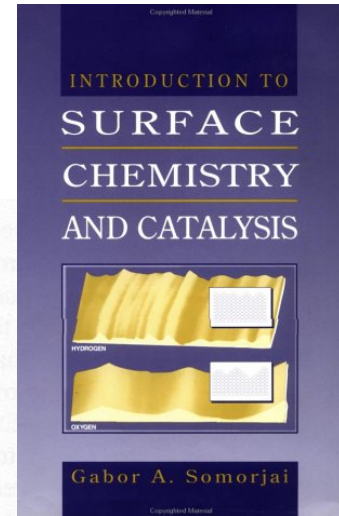


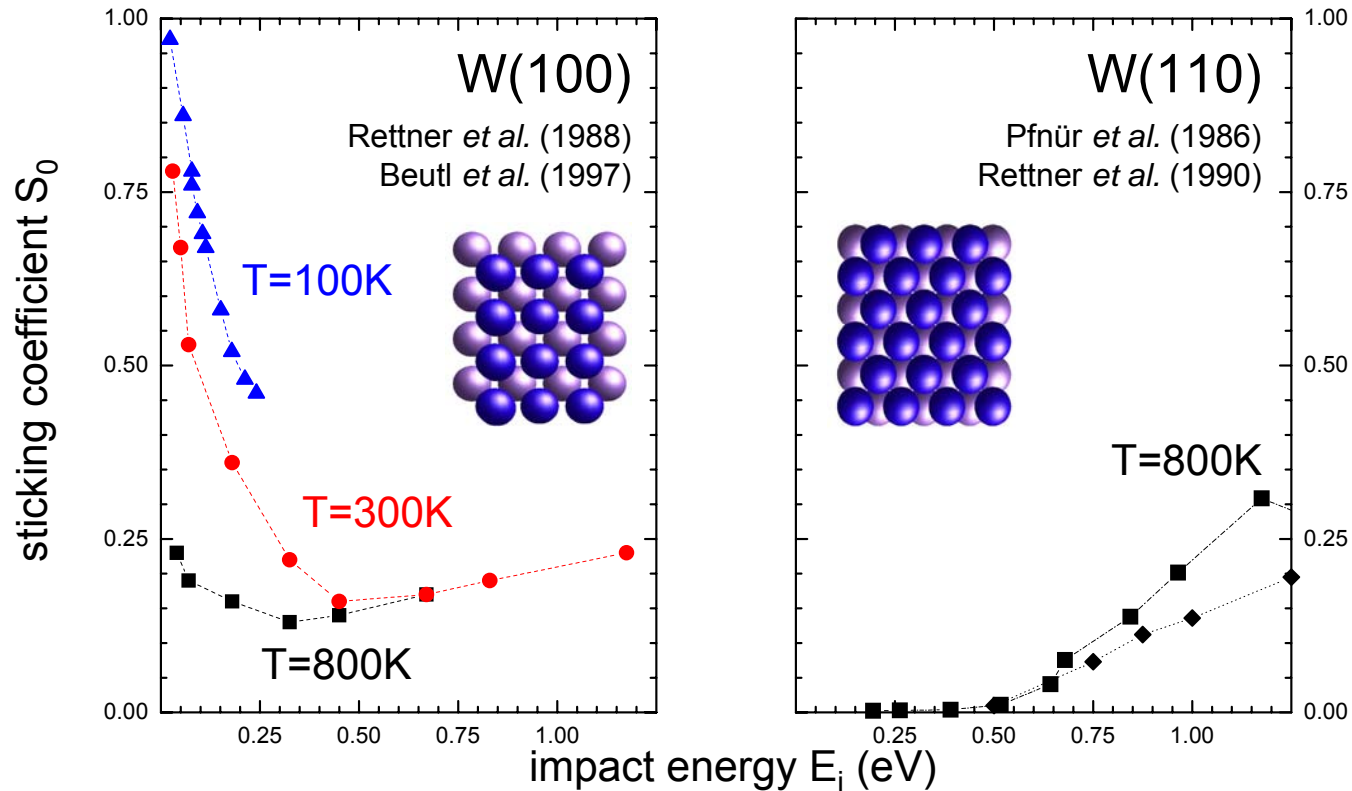
Figure 7.14. Rates of ammonia synthesis over five iron single-crystal surfaces with different orientations: (111), (211), (100), (210), and (110) [38].



Fe (110)

➔ **surface face and reactivity:
measurements of N₂ dissociation on W surfaces**

normal incidence



no threshold

threshold

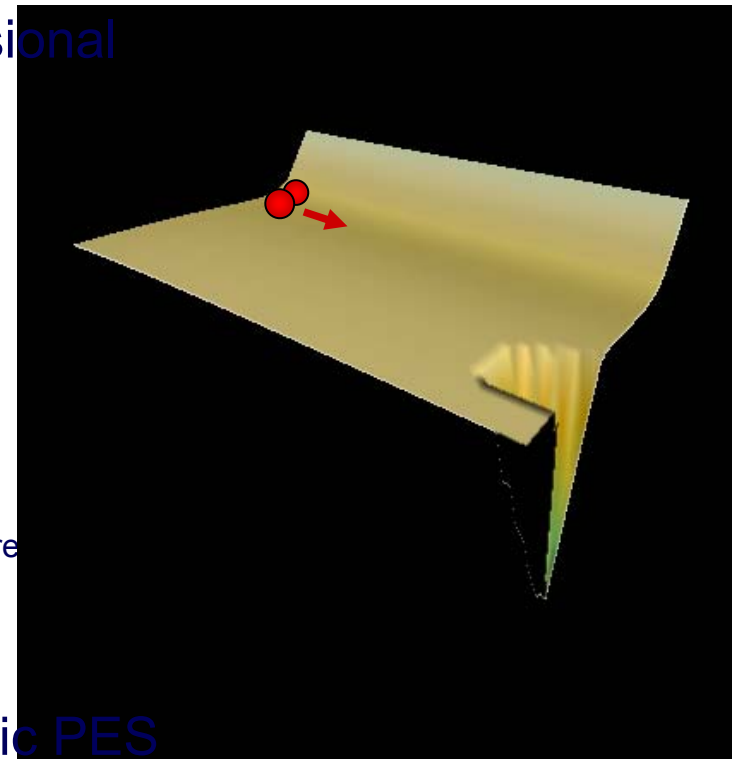
➡ theoretical method

- adiabatic calculation of the molecule / surface interaction through a multidimensional potential energy surface (PES)

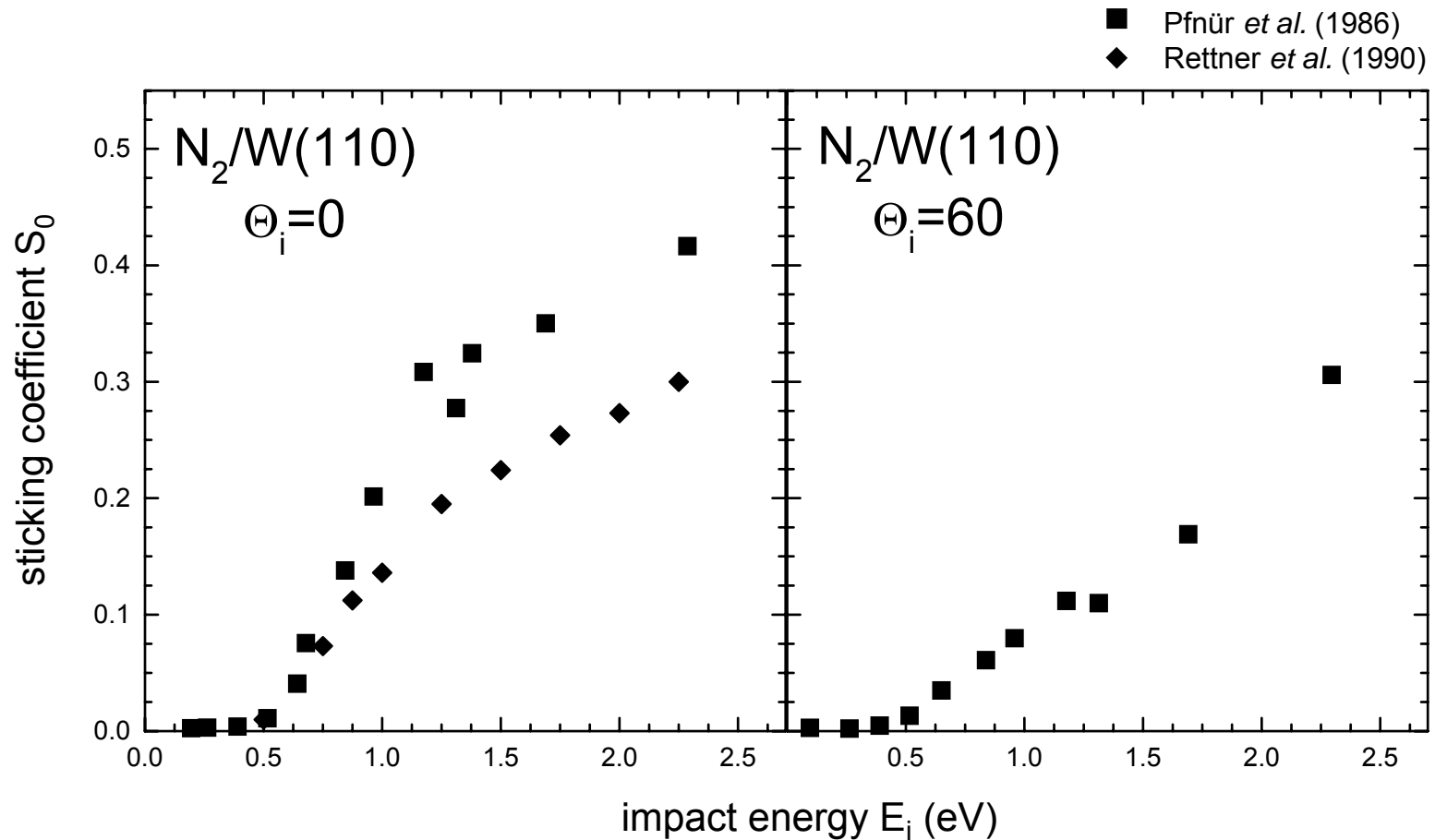
In our particular case:

- DFT - GGA (PW91) calculation with VASP
- Plane-wave basis set and US pseudopotentials
- 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)]

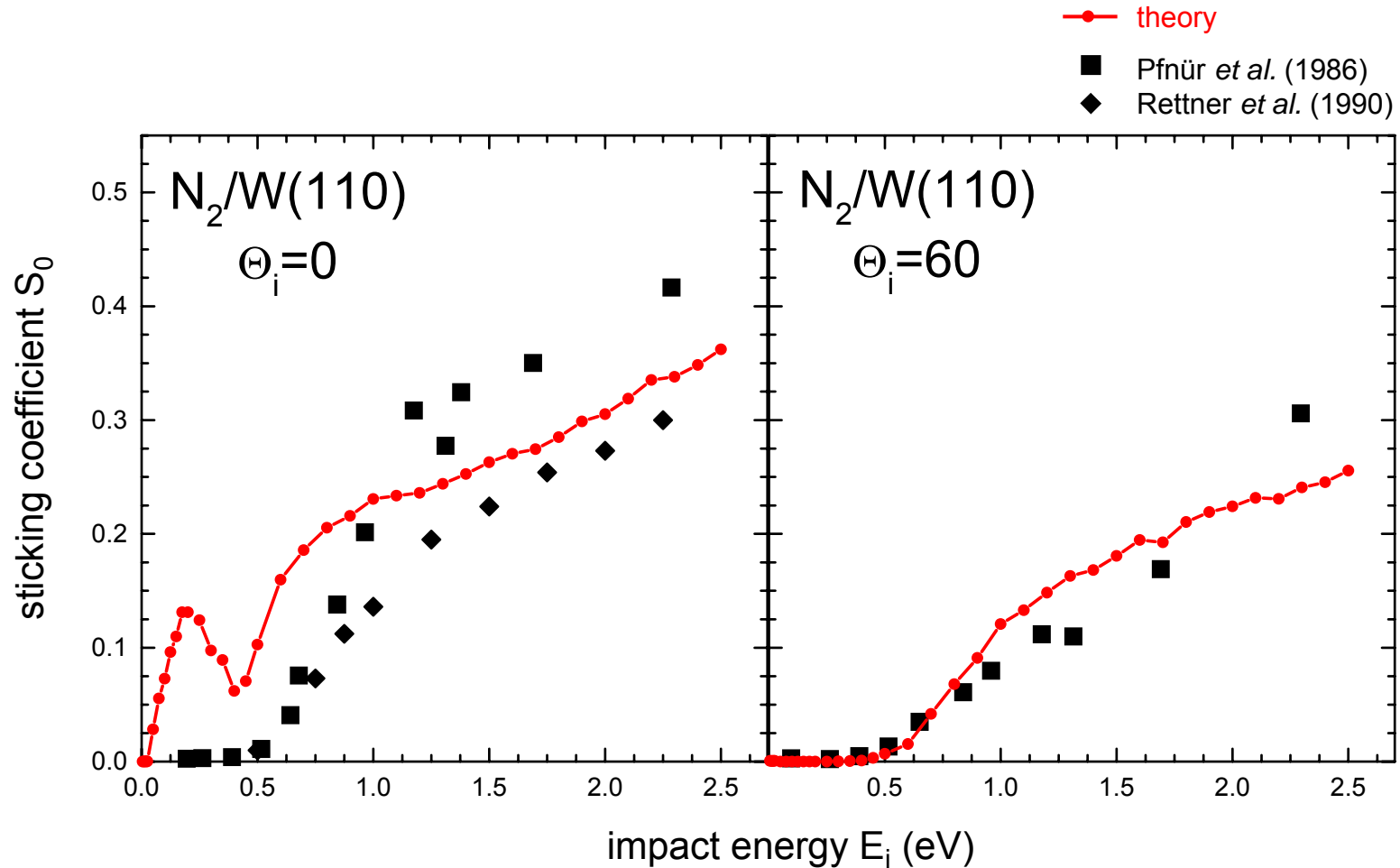
- classical dynamics in the adiabatic PES



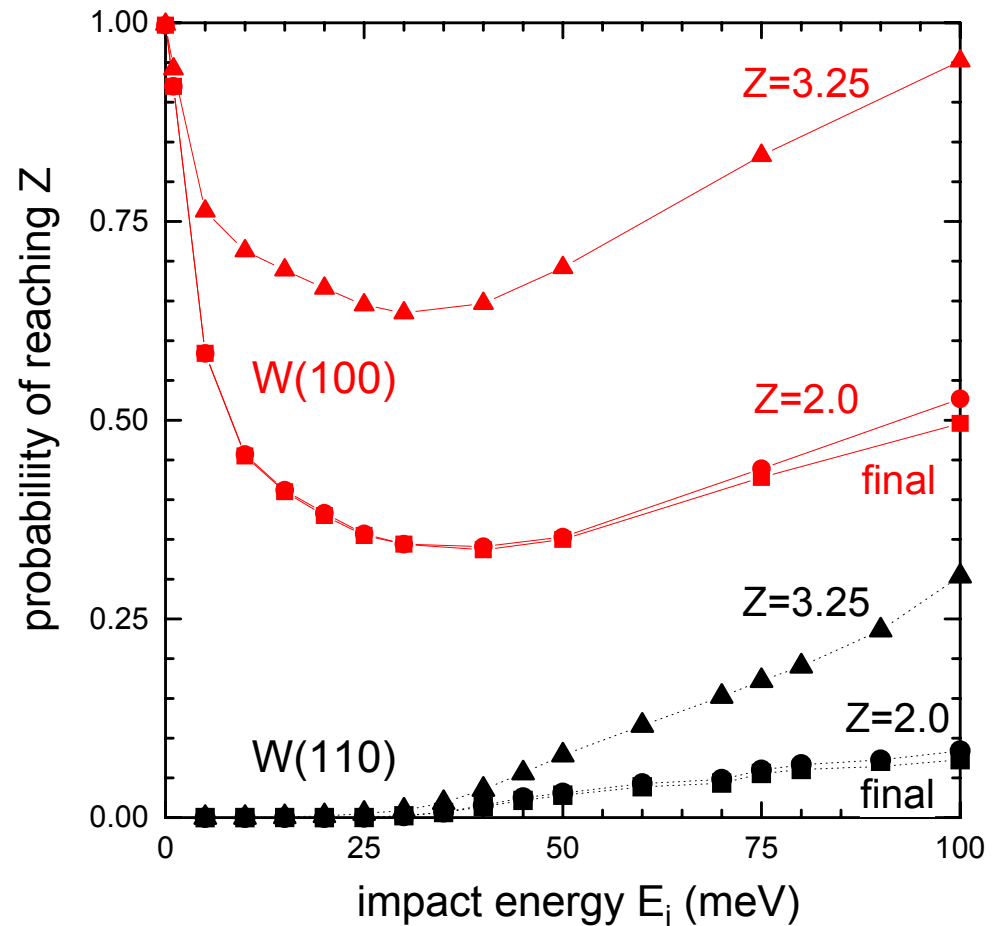
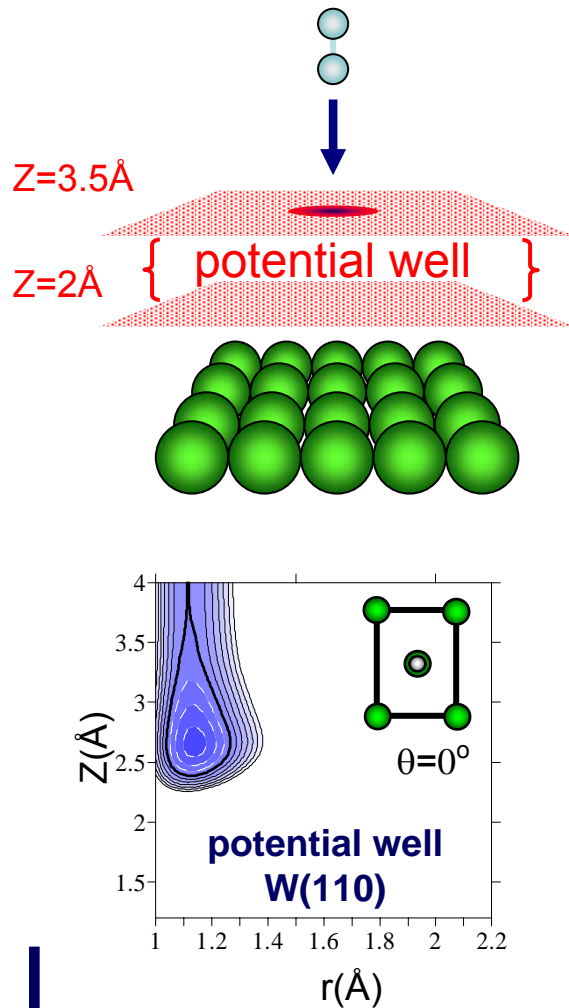
→ classical dynamics in the 6D-PES



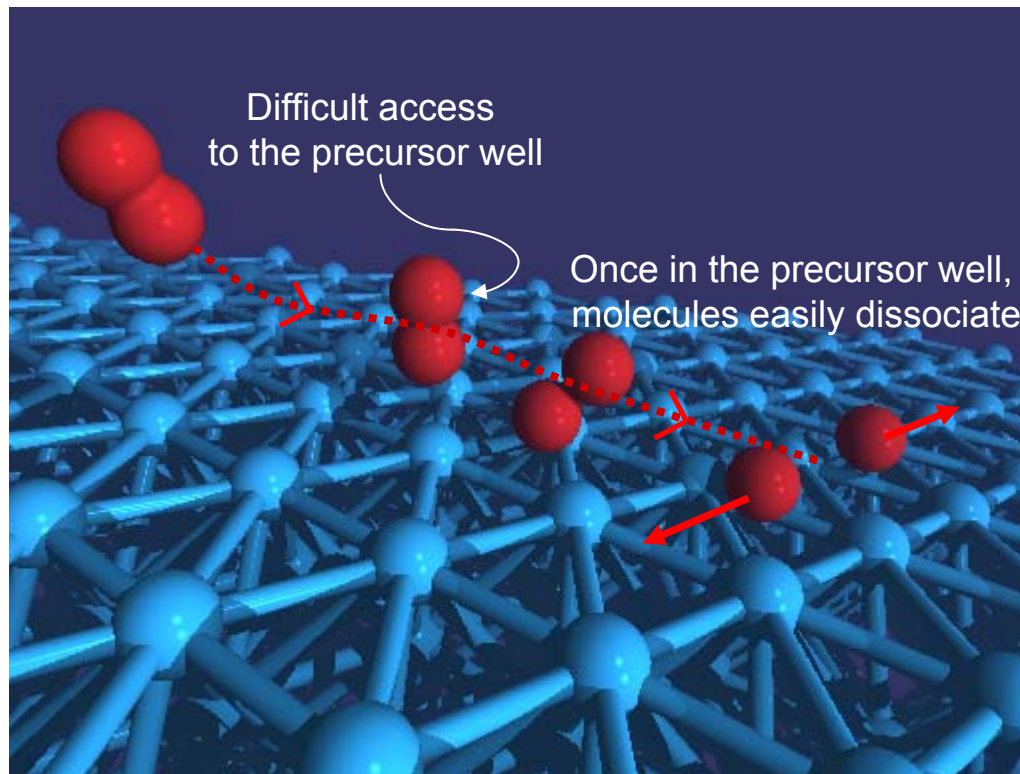
classical dynamics in the 6D-PES



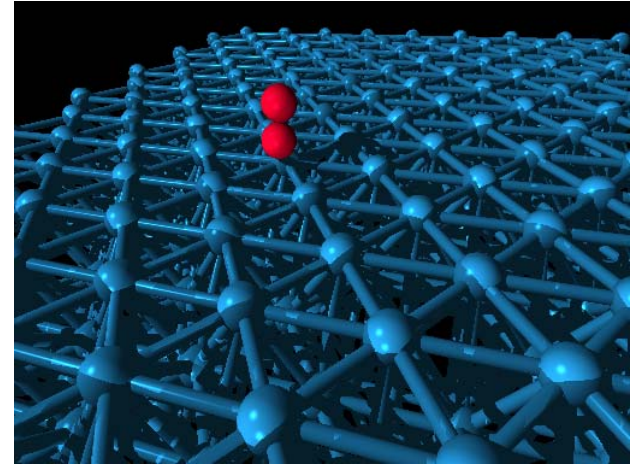
for thermal energies, long distances matter



➡ in summary, dynamics matters



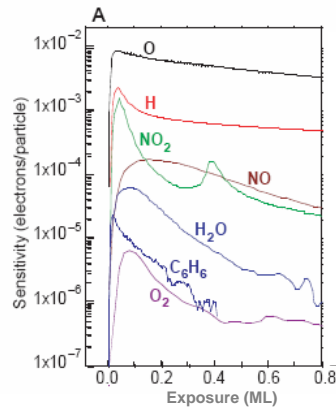
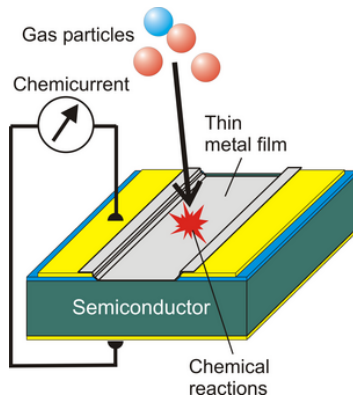
➔ outline



- introduction
- surface face and reactivity
- **non-adiabatic effects: electronic excitations**
- conclusions

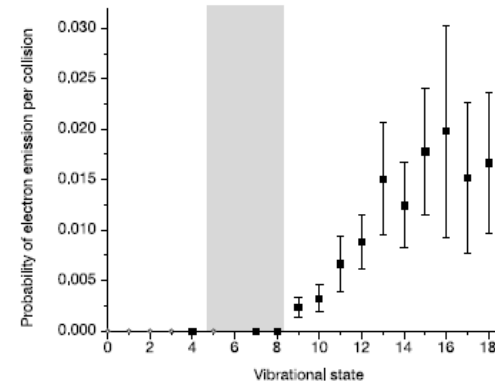
non-adiabatic effects: electron-hole pair excitations

chemicurrents



Gergen *et al.*, Science **294**, 2521 (2001).

vibrational promotion of electron transfer

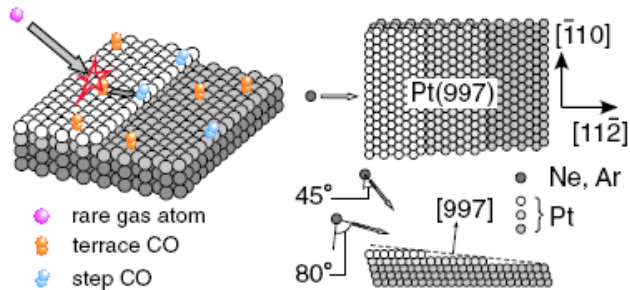


NO on Cs/Au(111)
electron emission as
a function of initial
vibrational state

Huang *et al.*, Science **290**, 111 (2000)
White *et al.*, Nature **433**, 503 (2005)

➔ non-adiabatic effects: electron-hole pair excitations

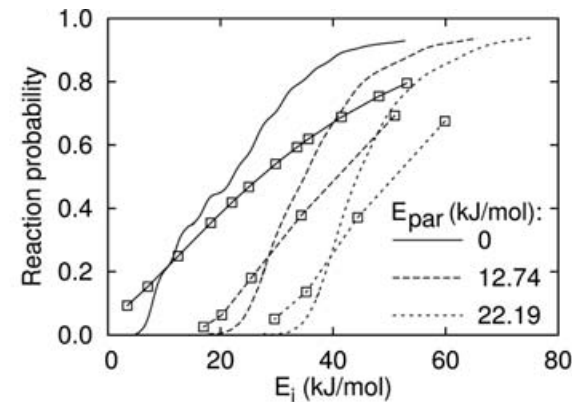
friction of a single chemisorbed CO molecule



CO on Pt(997)
migration to step edges

Takaoka *et al.*, PRL 100, 046104 (2008).

electron excitation during H₂ dissociation



H₂ on Pt(111)
sticking coefficient

Nieto *et al.*, Science 312, 86 (2006).

description of electronic excitations by a friction coefficient

previously used for:

- damping of adsorbate vibrations:
Persson and Hellsing, PRL49, 662 (1982)
- dynamics of atomic adsorption
Trail, Bird, *et al.*, JCP119, 4539 (2003)

classical equations of motion

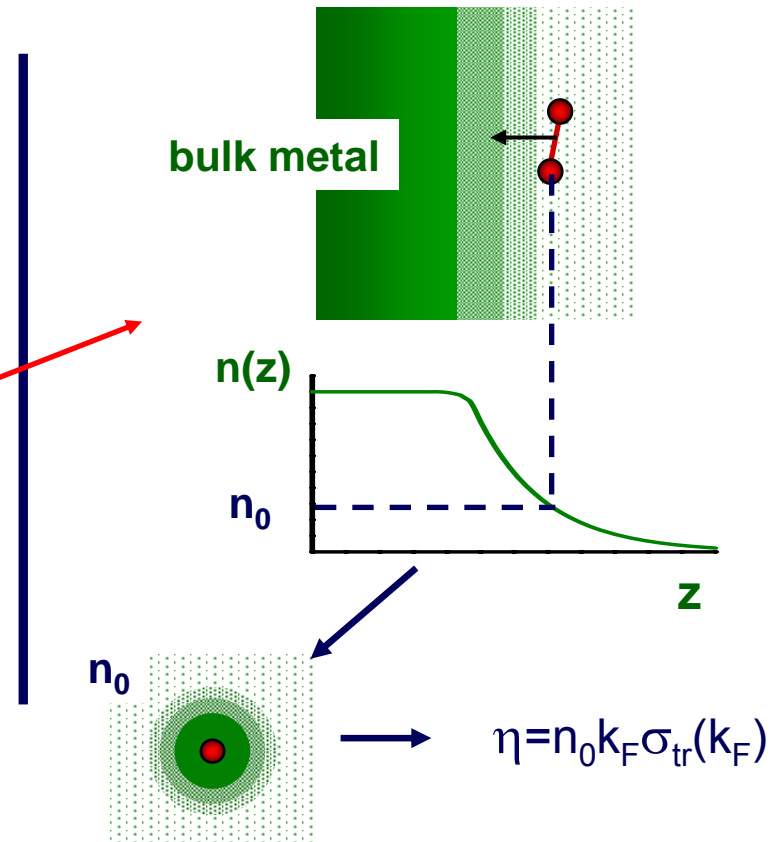
for each atom "i" in the molecule

$$m_i(d^2r_i/dt^2) = \underbrace{-dV(r_i, r_j)/d(r_i)}_{\text{adiabatic force: 6D DFT PES}} - \underbrace{\eta(r_i)}_{\text{friction coefficient}}(dr_i/dt)$$

adiabatic
force:
6D DFT PES

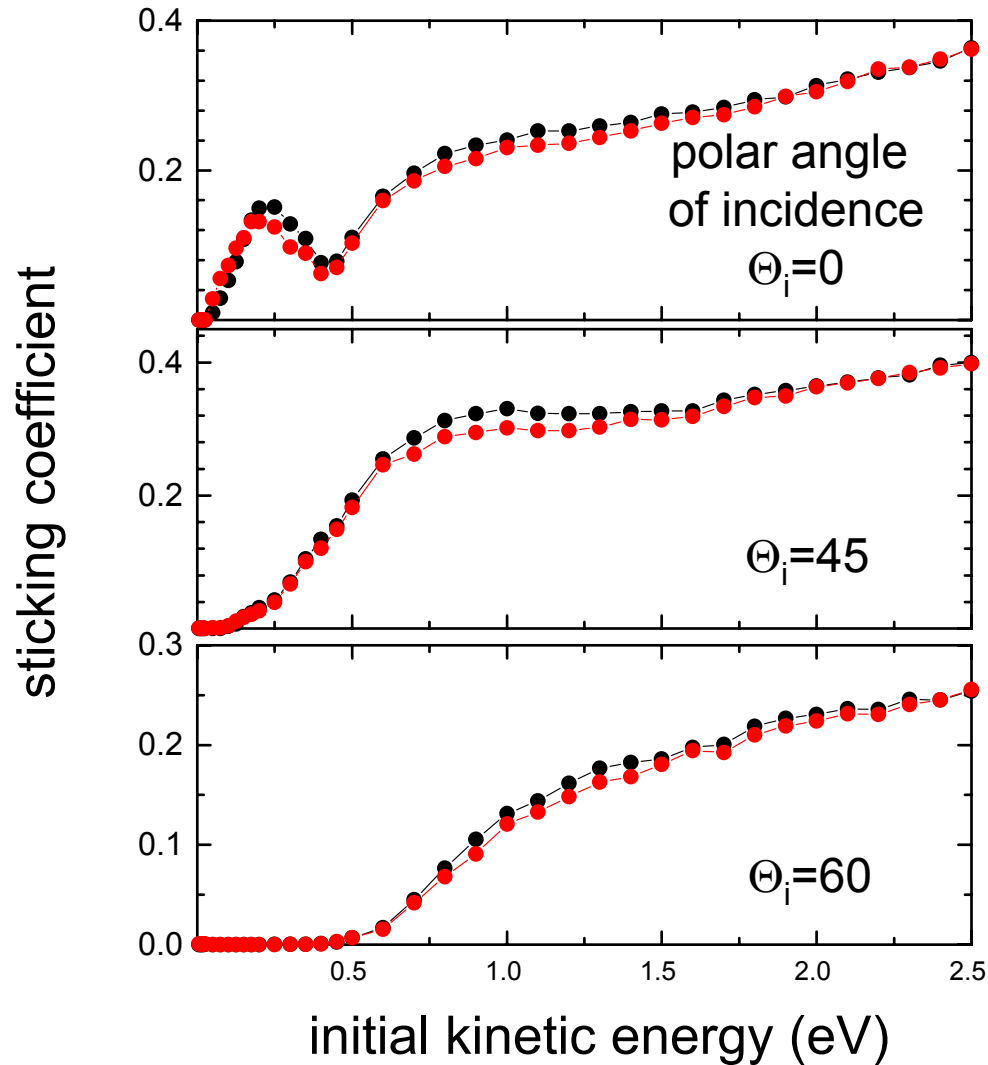
friction
coefficient

friction coefficient:
effective medium approximation



effective medium:
FEG with electronic density n_0

➔ probability of dissociative adsorption: N_2 on W(110)

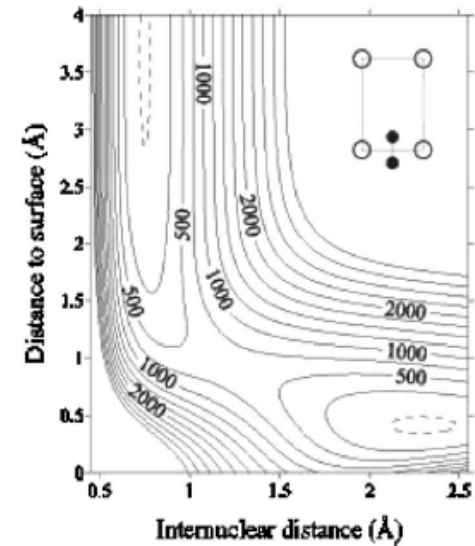
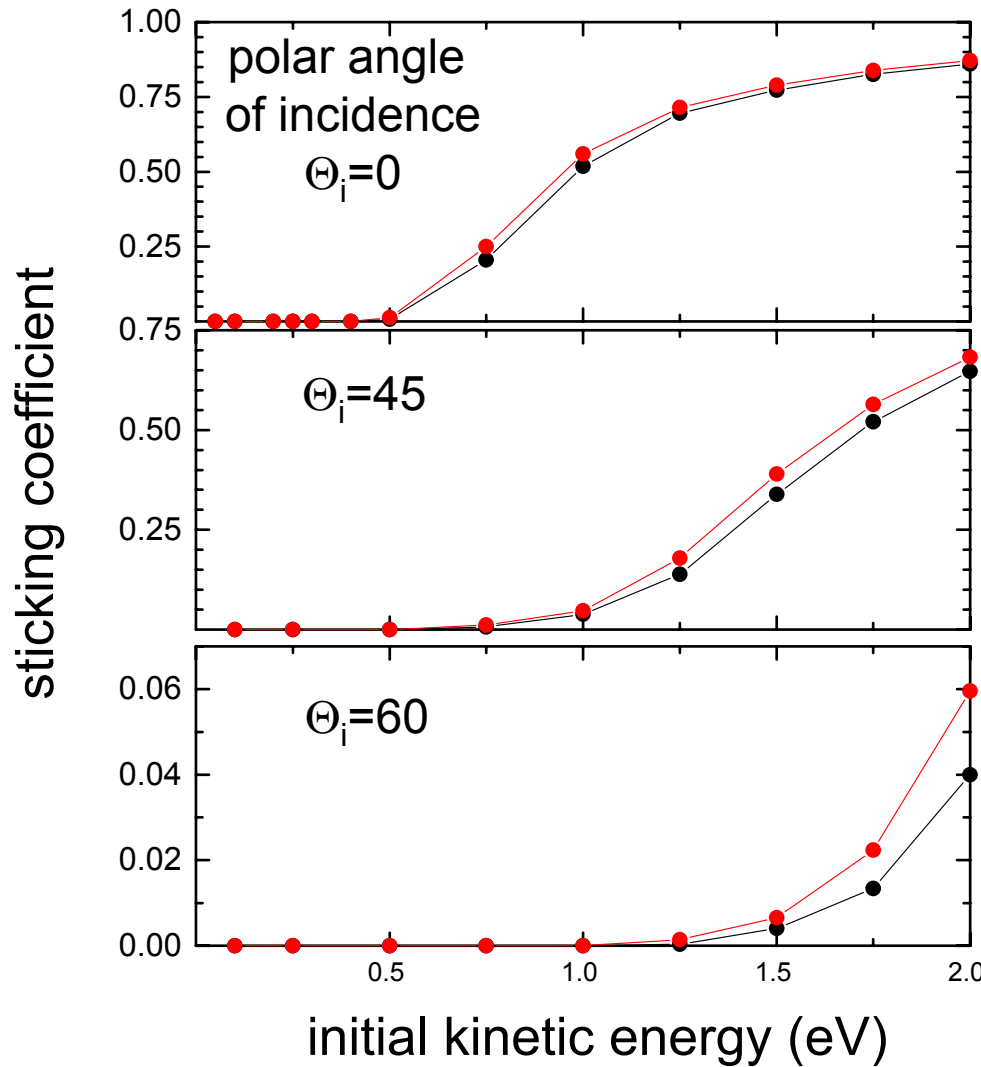


—●—
 non-adiabatic

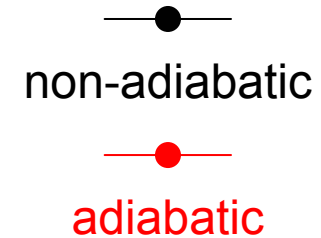
—●—
 adiabatic

but for this system,
 dissociation is
 roughly decided at
 $Z=2.5A$

probability of dissociative adsorption: H₂ on Cu(110)



[Salin, JCP 124, 104704 (2006)]



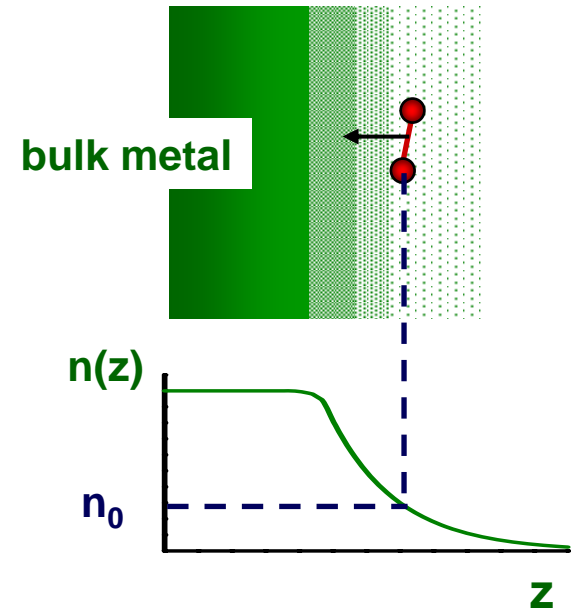
classical equations of motion

for each atom “ i ” in the molecule

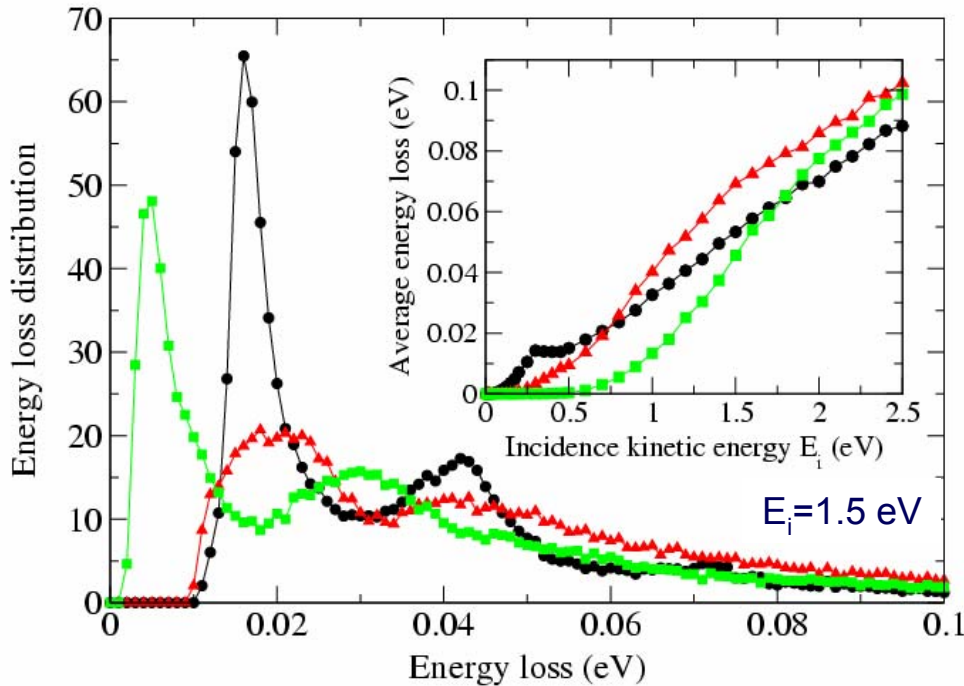
$$m_i(d^2r_i/dt^2) = -dV(r_i, r_j)/d(r_i) - \eta(r_i)(dr_i/dt)$$

friction coefficient

velocity

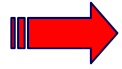


➔ energy loss of reflected molecules: N₂ on W(110)



$\Theta_i = 0$
 $\Theta_i = 45$
 $\Theta_i = 60$

energy losses in the reflected molecules
 due to electronic excitations are < 100 meV

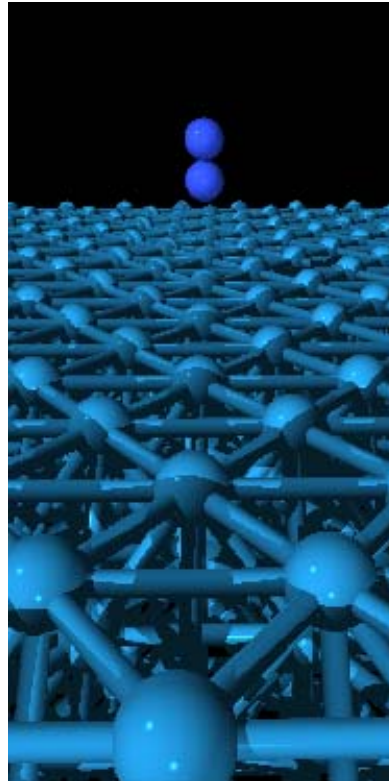


some conclusions

the reactivity of diatomic molecules on surfaces
can be very dependent on the particular surface face

in the particular case of N_2/W , we have shown
that the differences in reactivity arise from the
dynamics at long distances ($>3 \text{ \AA}$) from the surface

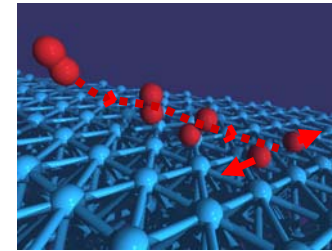
a local description of the friction coefficient shows that
electronic excitations play ***a minor role***
in the dissociation of diatomic molecules on metal surfaces



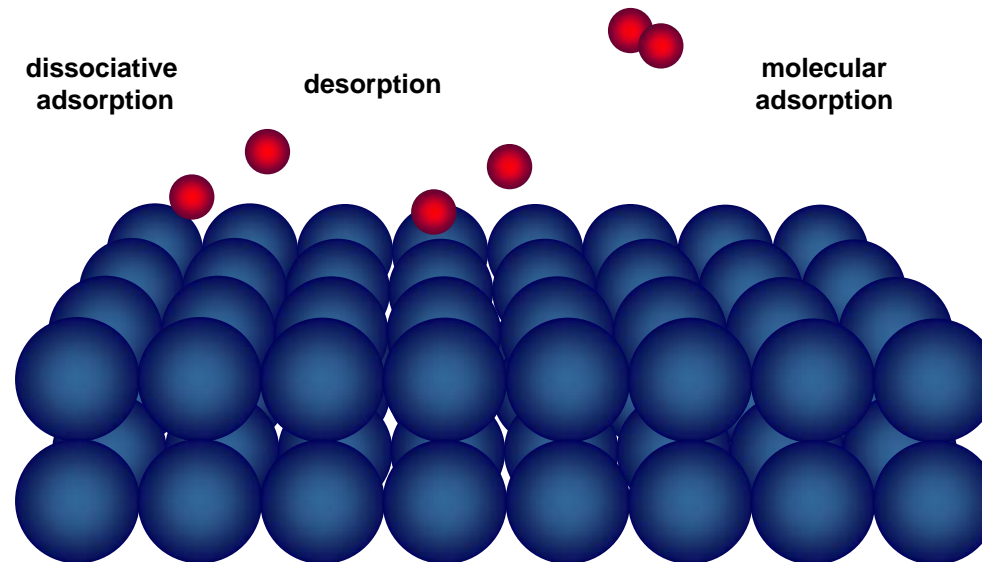
thank you for your attention

*1st nanoICT Symposium
Donostia – San Sebastian, February 26 2008*

➔ gas/surface dynamics





from the fundamental point of view, the goal is to understand how solid surfaces and nanostructures can be used to promote gas-phase chemical reactions



some elementary reactive processes
at surfaces

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 function)
 - unique active sites at the surface

➔ 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)

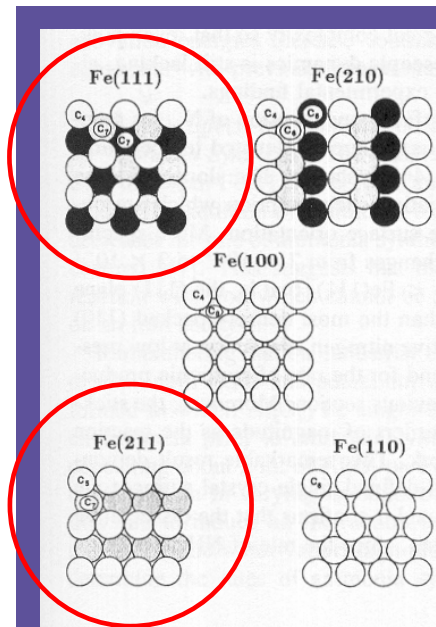
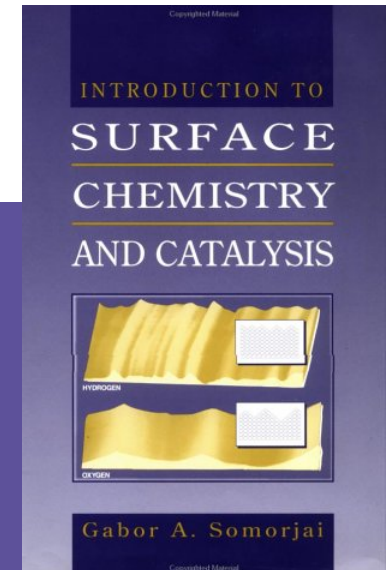
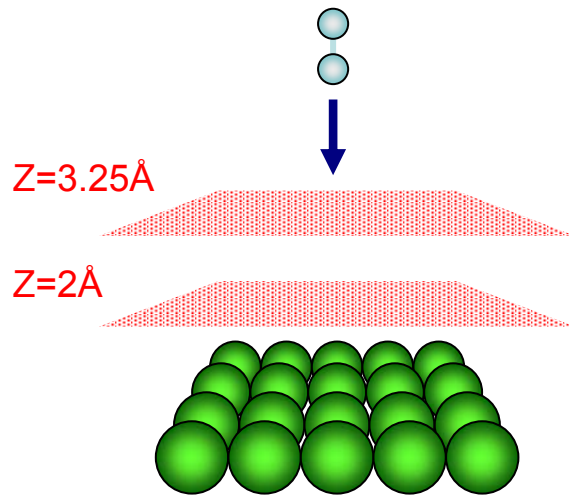


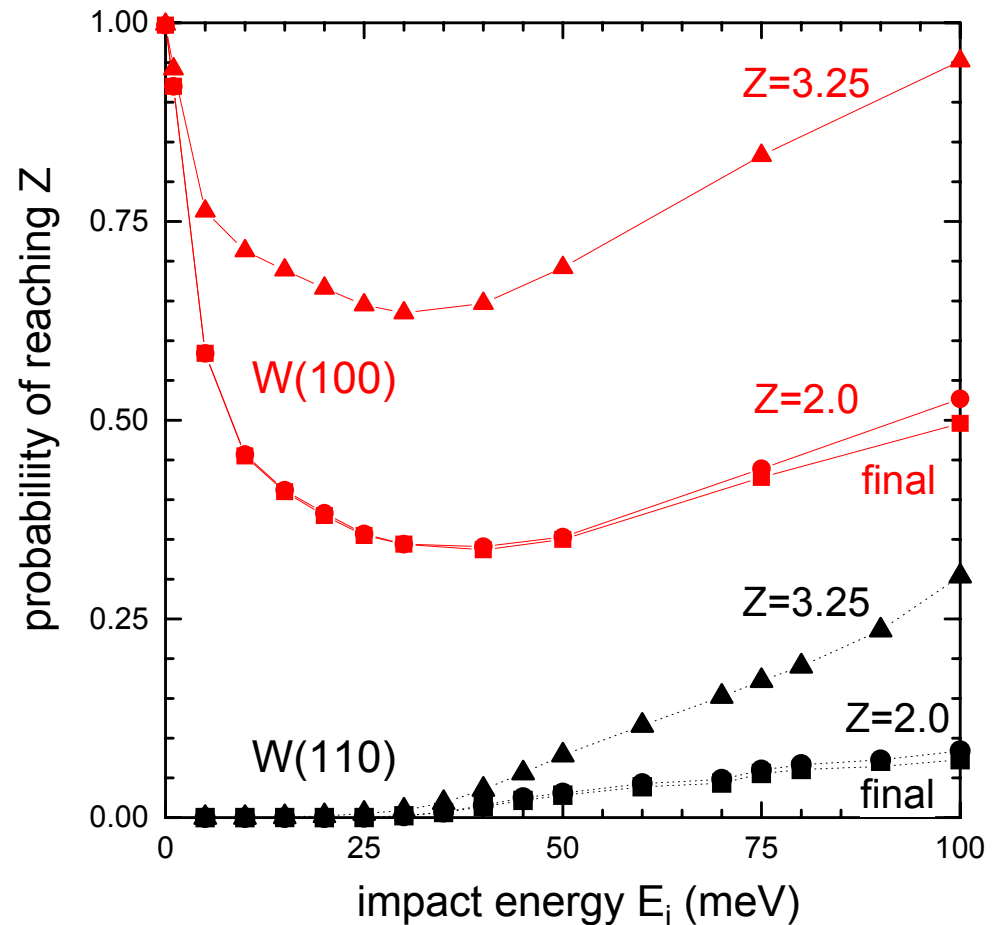
Figure 7.15. Schematic representations of the idealized surface structures of the (111), (211), (100), (210), and (110) orientation of iron single crystals. The coordination of each surface atom is indicated [38].



➡ for thermal energies, long distances matter

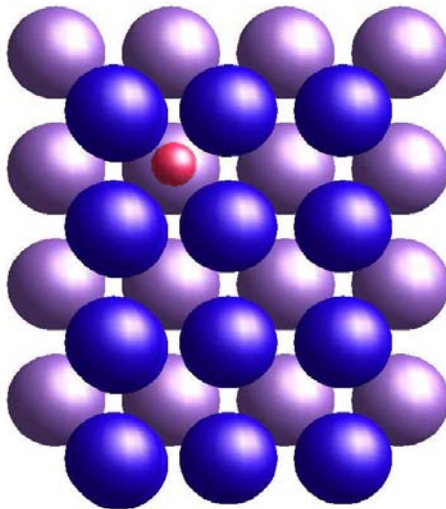


The amount of N_2 molecules that are able to reach $Z=3.25 \text{ \AA}$ is much smaller in the $W(110)$ face



➔ **final state features: N adsorption on W**

W(100)



adsorption energy

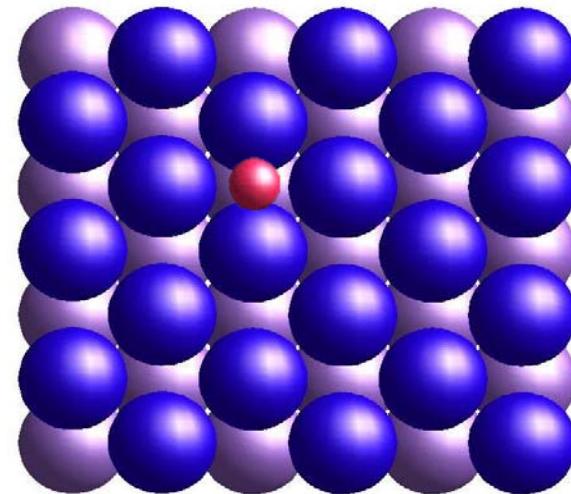
DFT = 7.4 eV

Exp. = 6.6-7 eV

adsorption distance

DFT = 0.63 Å

W(110)



adsorption energy

DFT = 6.8 eV

Exp. = 6.6 eV

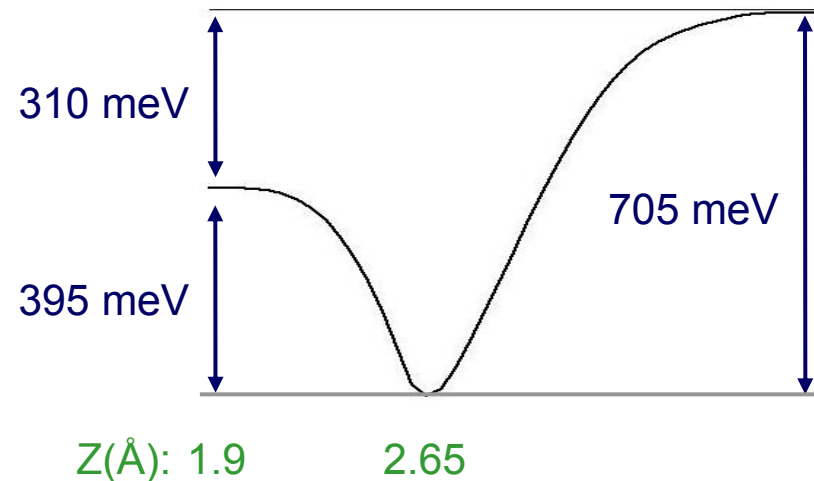
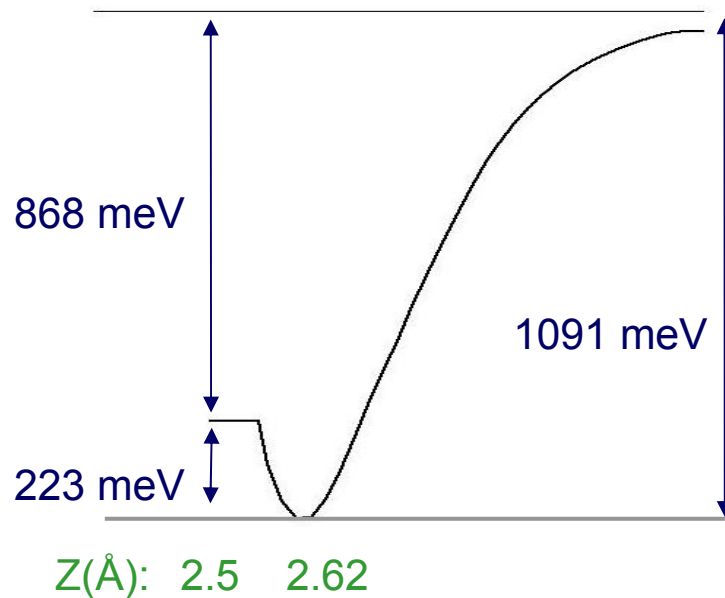
adsorption distance

DFT = 1.15 Å

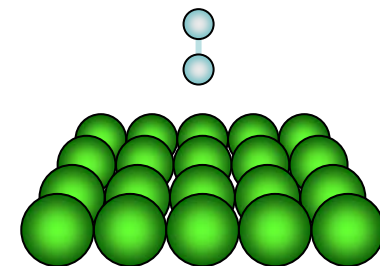
dynamic trapping in a well in both faces

W(100)

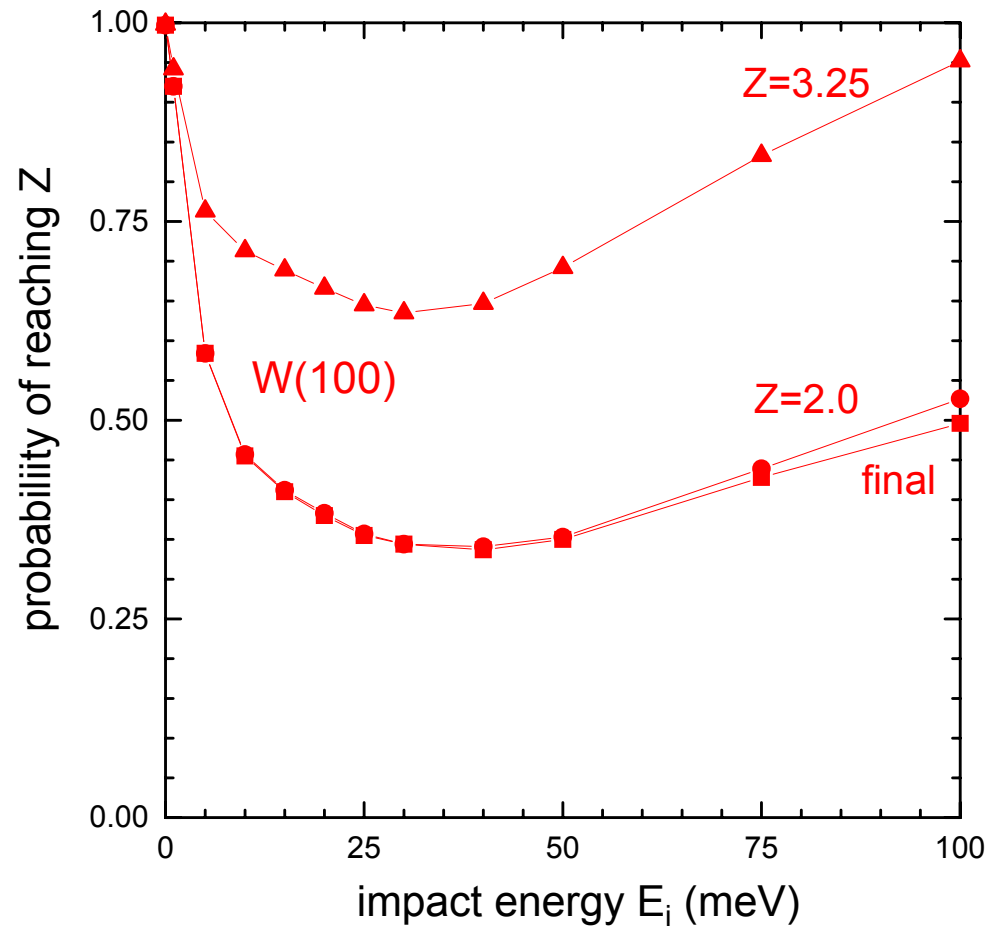
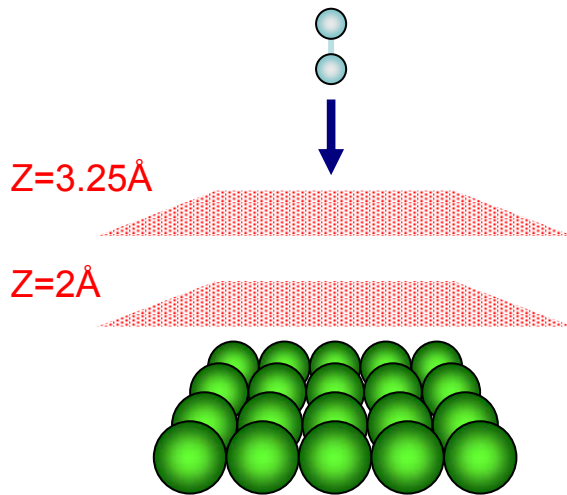
W(110)



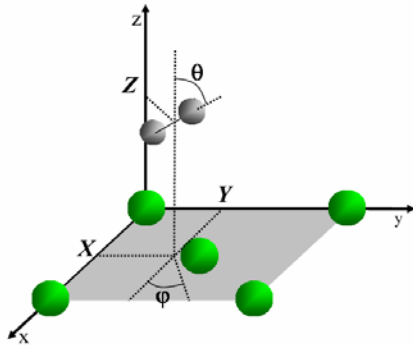
approach to surface:
vertical over a surface atom



➡ for thermal energies, long distances matter

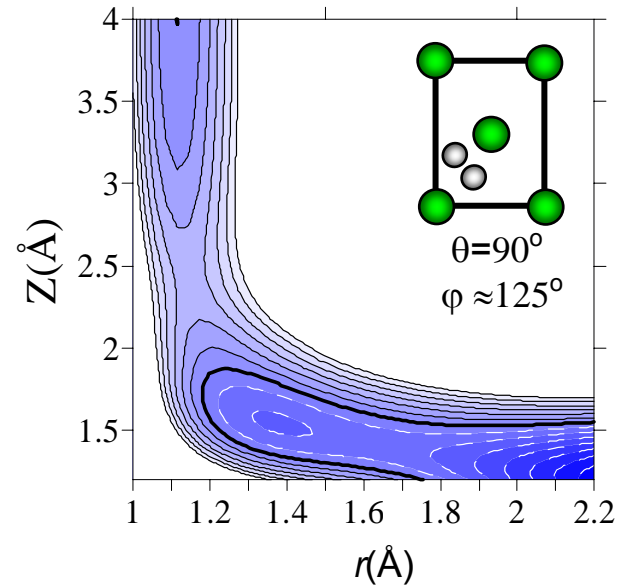
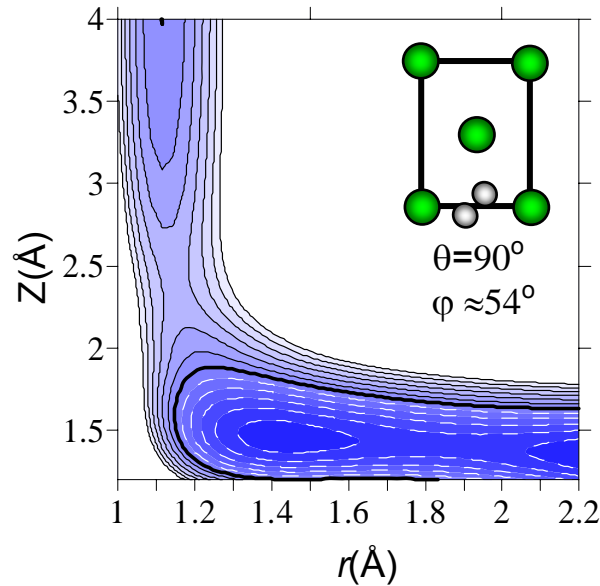
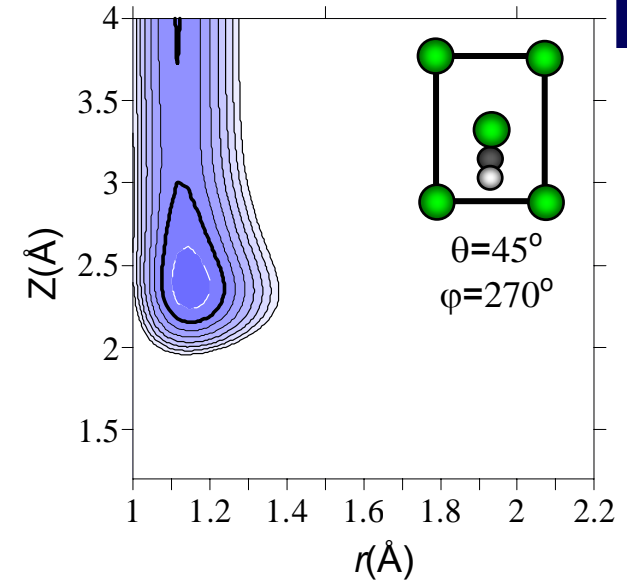
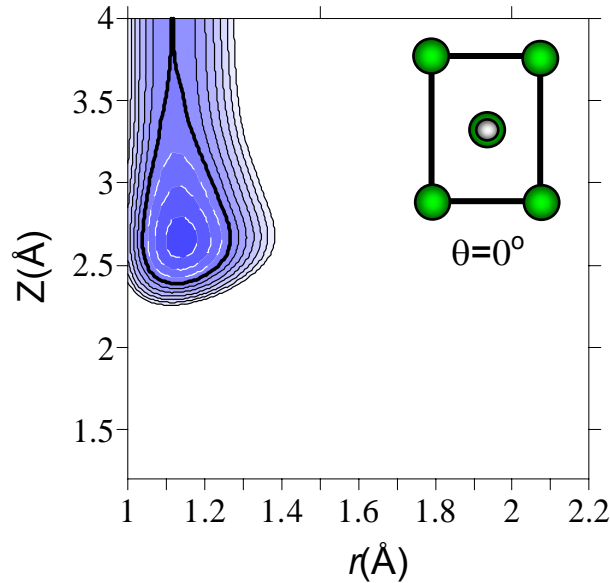


some
 elbow plots
 for the
 $N_2/W(110)$
 system



distance between
 contour lines = 0.2eV

--- E < 0
 — E = 0
 — E > 0



Today's key factors in the development of chemical processes are the concepts of "zero-waste" and "100 % selectivity".

In the field of catalysis, the chemistry at interphases, referred to as heterogeneous catalysis, is promising to achieve both goals.

MB Experiments in Catalysis

Beyond Single Crystal Kinetics

Some Kinetic Effects
on Catalyst Surfaces:

confinement effects
on small particles,
fluctuations

communication effects
between different sites
via surface diffusion

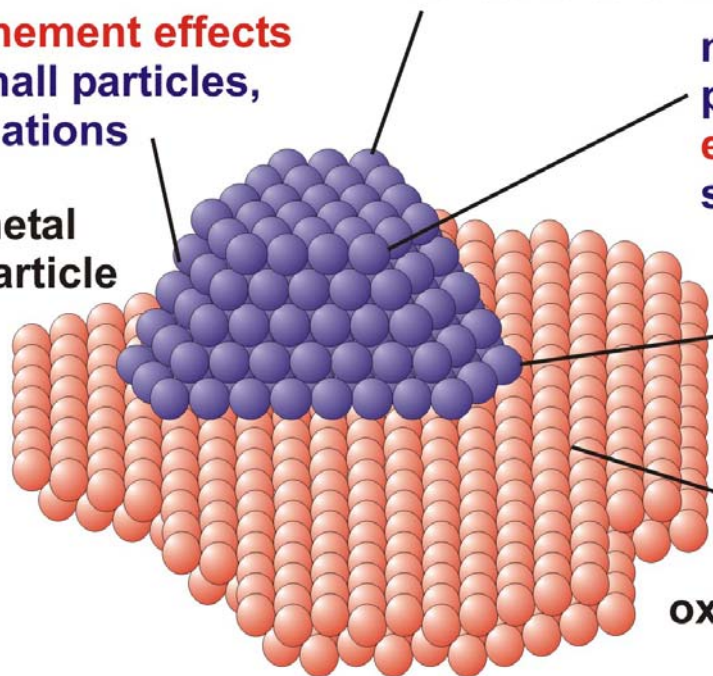
modified adsorption / reaction
properties due to **electronic**
effects (electron confinement,
support interaction)

metal
particle

new adsorption/reaction
sites due to **geometric effects**
(edges, corners, facets...)

trapping / adsorption /
diffusion on the **support**

oxide support



"supported metal catalyst"

➡ accuracy of adiabatic DFT calculations

Kohn-Sham equations solved self-consistently

$$\left\{ -\frac{1}{2}\nabla^2 + v_{\text{eff}}(\mathbf{r}) \right\} \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r})$$

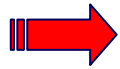
$$v_{\text{eff}}(\mathbf{r}) = v_{\text{jellium}}(\mathbf{r}) + v_{\text{Hartree}}(\mathbf{r}) - v_{\text{xc}}(\mathbf{r})$$

exchange-correlation
term
is not exact

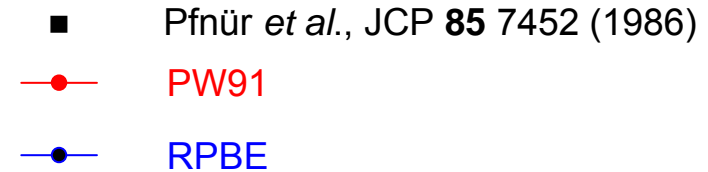
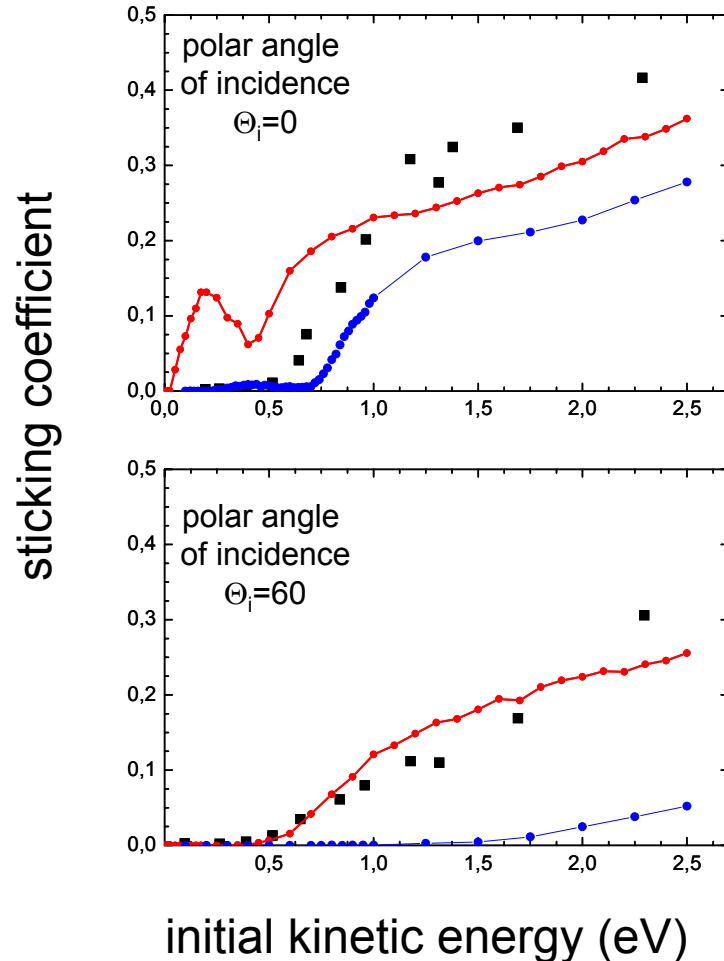
	LDA	$E_{chem,\beta}$			RPBE	E_{chem}^{exp}
		PW91	PBE	revPBE		
O(fcc)/Ni(111)	-6.68	-5.38	-5.27	-4.83	-4.77	-4.84 ^a
O(hol)/Ni(100)	-6.97	-5.66	-5.55	-5.10	-5.03	-5.41 ^a
O(hol)/Rh(100)	-6.64	-5.34	-5.23	-4.77	-4.71	-4.56 ^a
O(fcc)/Pd(111)	-5.34	-4.08	-3.98	-3.54	-3.49	
O(hol)/Pd(100)	-5.39	-4.14	-4.04	-3.59	-3.53	

RPBE functional
provides better
atomic chemisorption
energies

Hammer *et al.*, PRB **59**, 7413 (1999)



influence of the exchange correlation functional in the sticking coefficient: N₂/W(110)



the RPBE XC functional:

- fits better the experimental chemisorption energies
- describes better the interaction very near the metallic surface
- but better dynamics??

not in this case!

