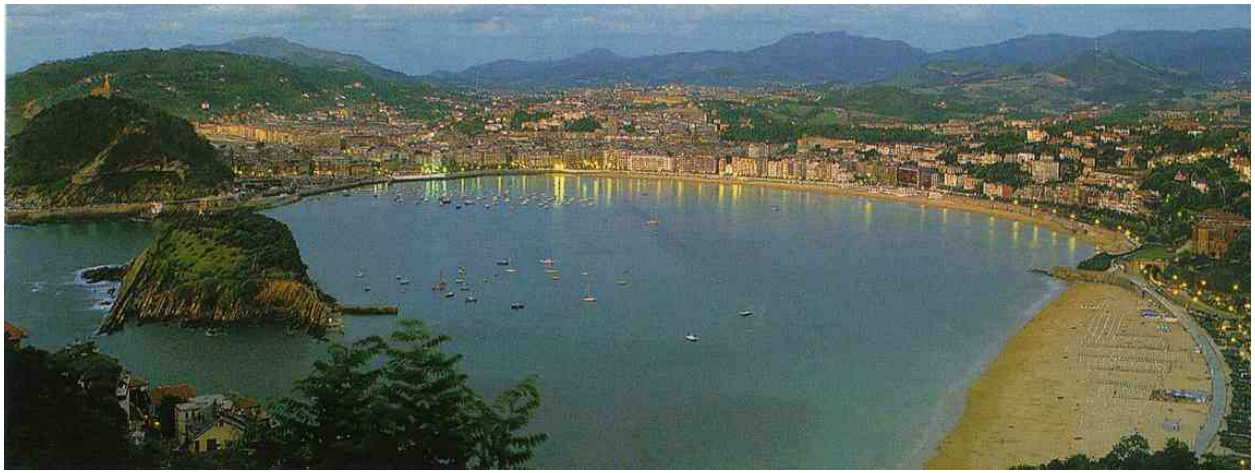

Non-adiabatic effects in the reactivity of molecules at metal surfaces

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

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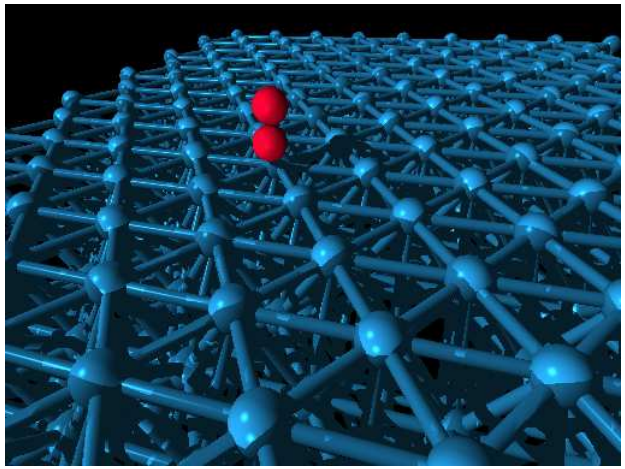


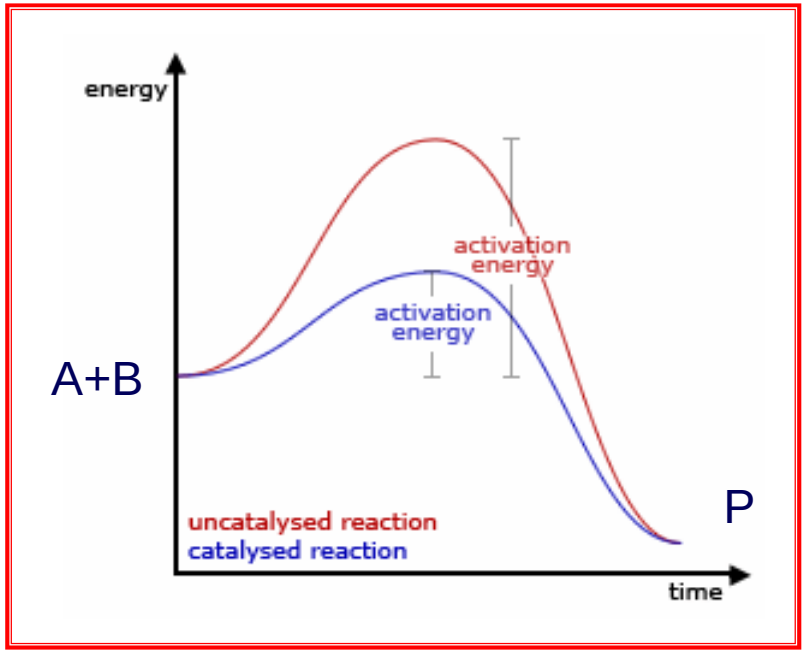
outline

- 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+B → P direct reaction
A+B+C → P+C catalyzed reaction

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

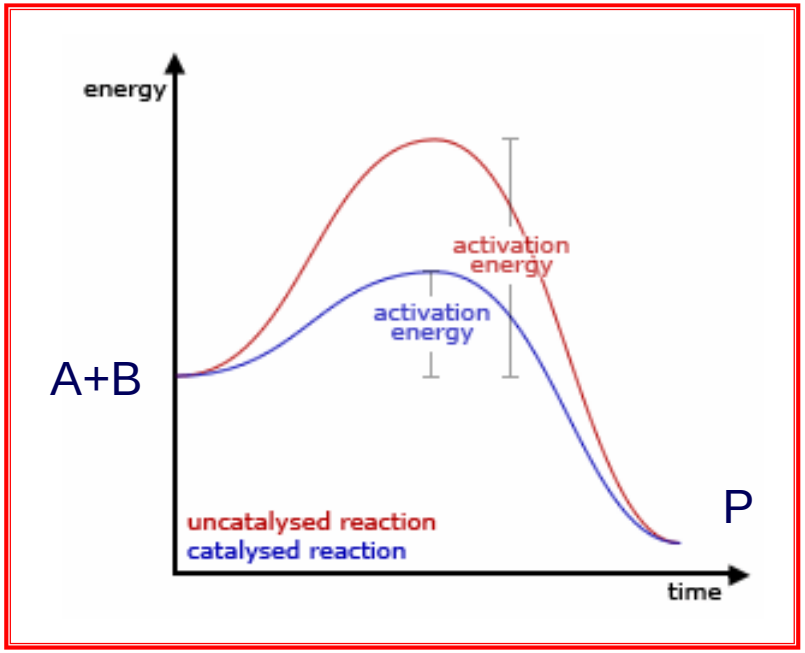
Heterogeneous catalysis*:*

The catalyst is in a different phase → solid surfaces.

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.



觸媒

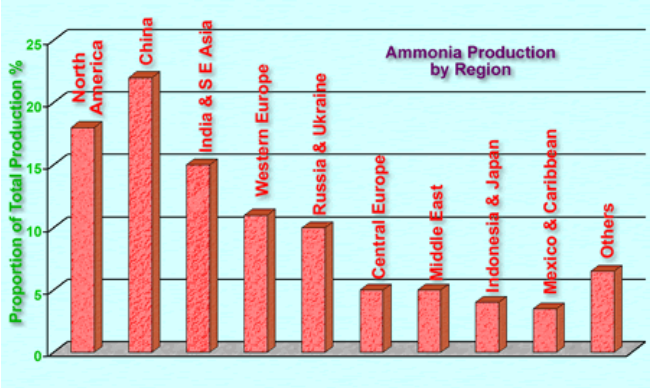
The chinese symbol
for catalyst
is the same as the one
for marriage broker
(matchmaker)

Heterogeneous catalysis*:*

The catalyst is in a different phase → solid surfaces.

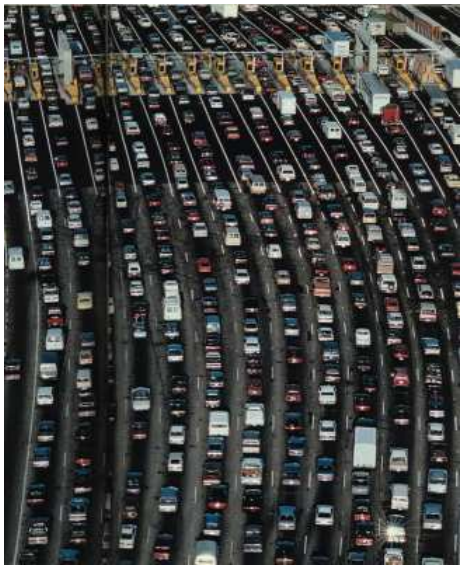
global context: chemical industry

ammonia synthesis:
$3H_2(g) + N_2(g) \leftrightarrow 2NH_3(g)$
(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 NO_2 are formed.

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

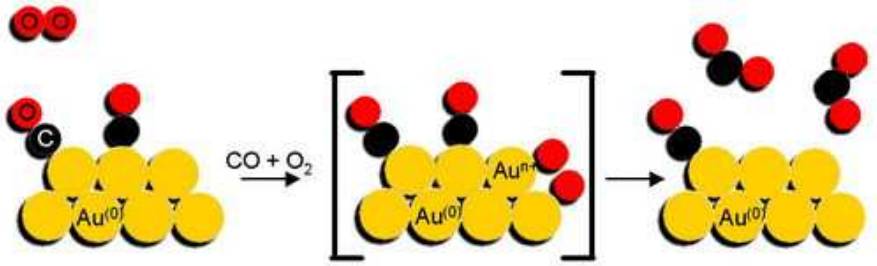
CO_2 and N_2 are desorbed from the surface and emitted as relatively harmless gases:

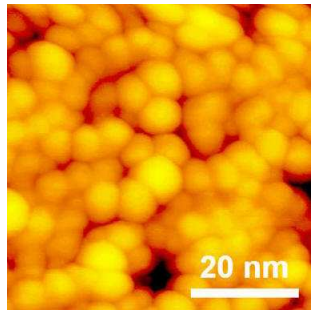
$$2CO + 2NO \quad 2CO_2 + N_2$$

catalysis and nanoscale

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

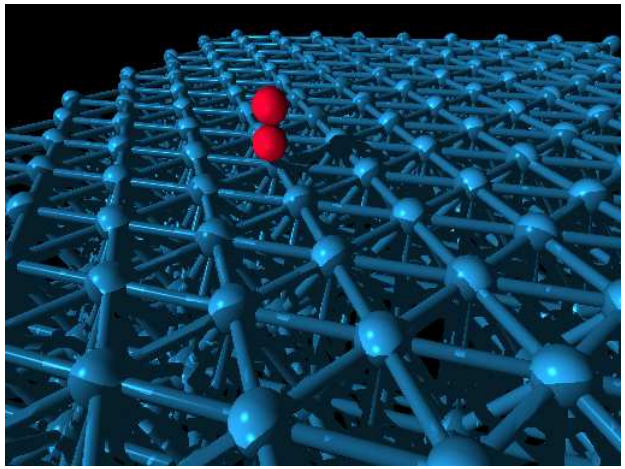
Au as a catalyst





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 CO_2 when it comes in the form of nanoparticles.



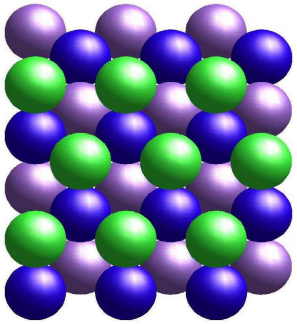
outline

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

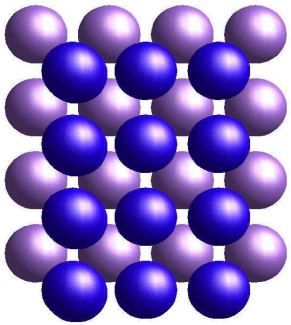
surface face and reactivity

$N_2 + 3H_2 \longrightarrow 2NH_3$

rates of ammonia synthesis over five iron single-crystal surfaces



Fe (111)



Fe (100)

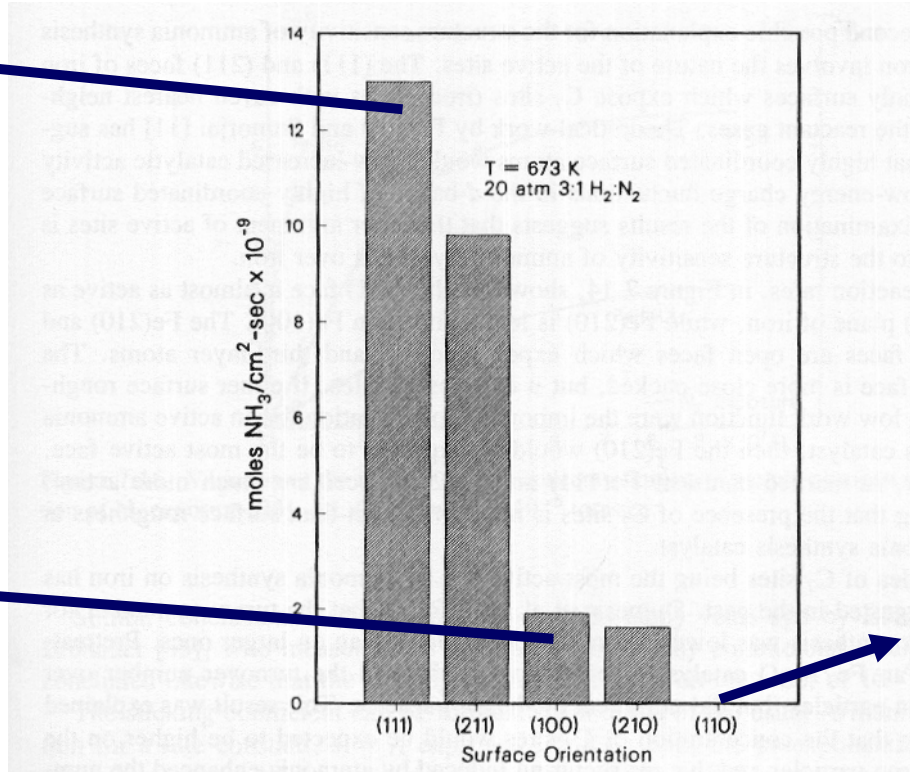
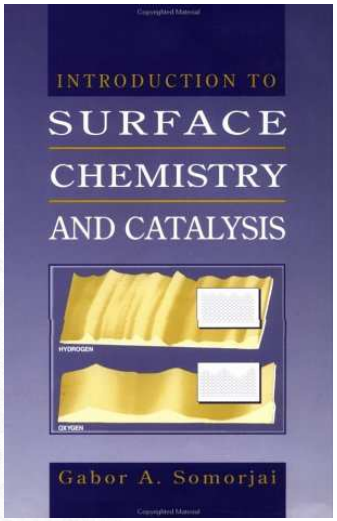
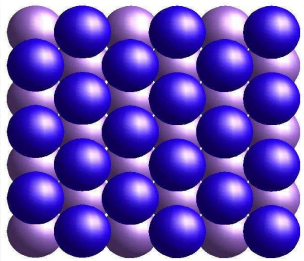


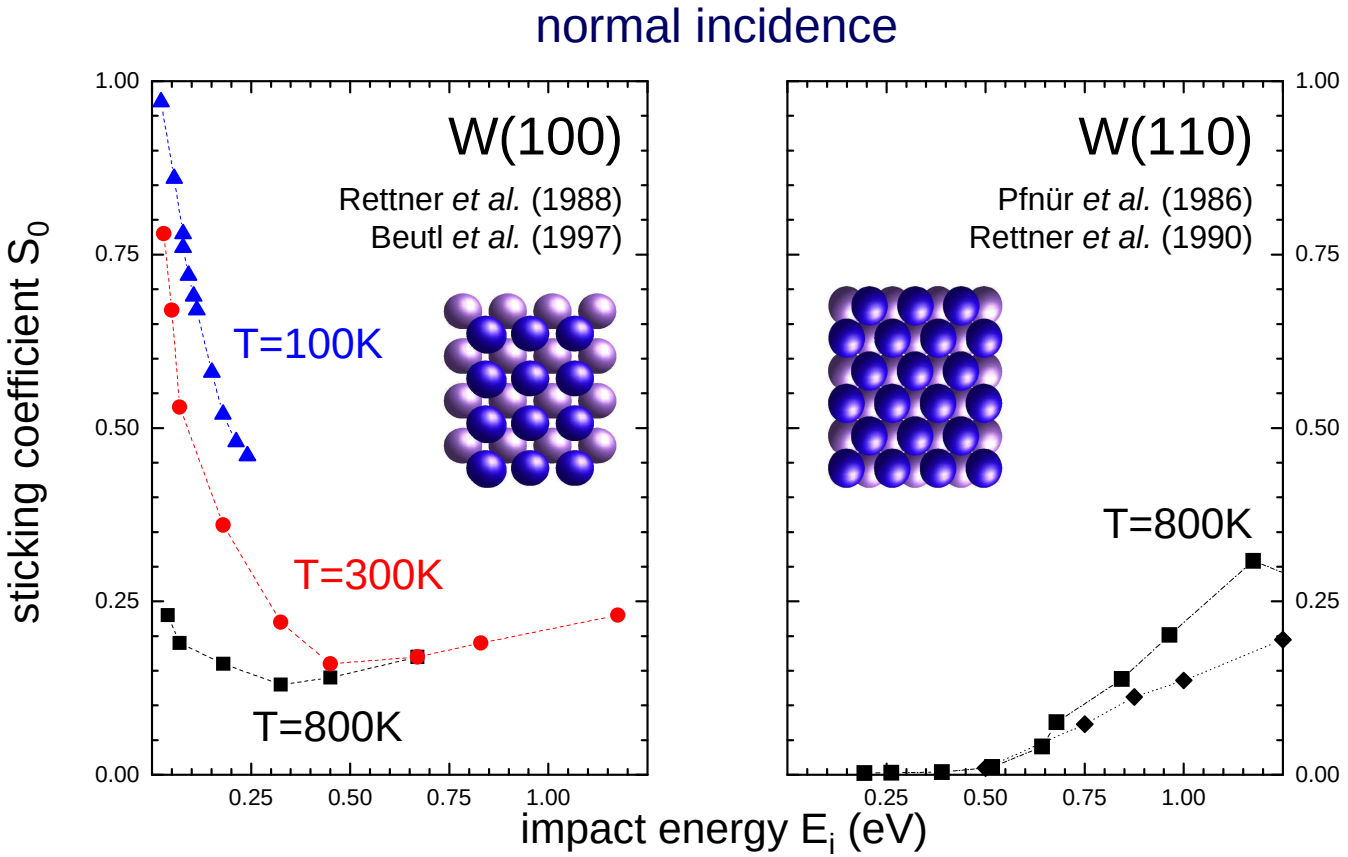
Figure 7.14. Rates of ammonia synthesis over five iron single-crystal surfaces with different orientations: (111), (211), (100), (210), and (110) [38].





Fe (110)

surface face and reactivity: measurements of N_2 dissociation on W surfaces



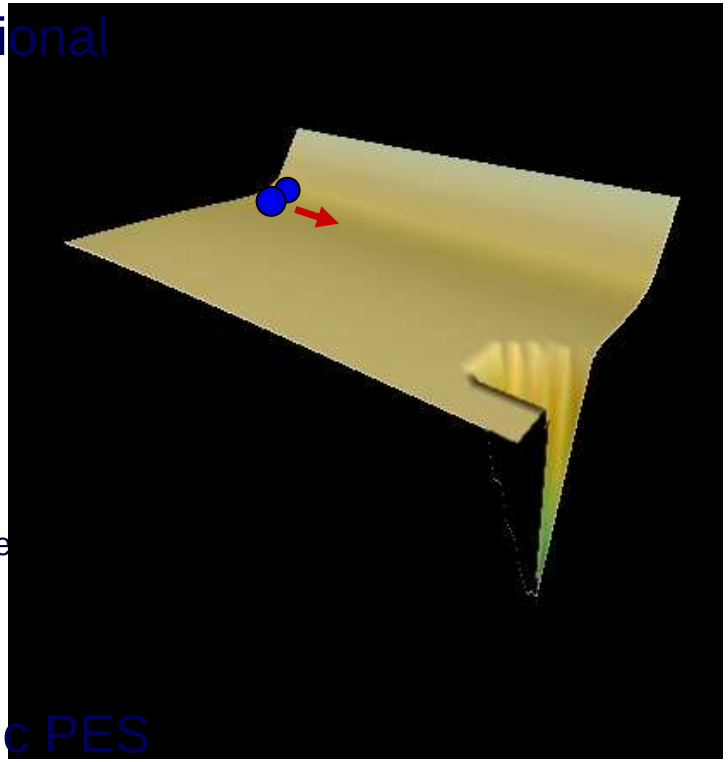
no threshold **threshold**

theoretical method

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

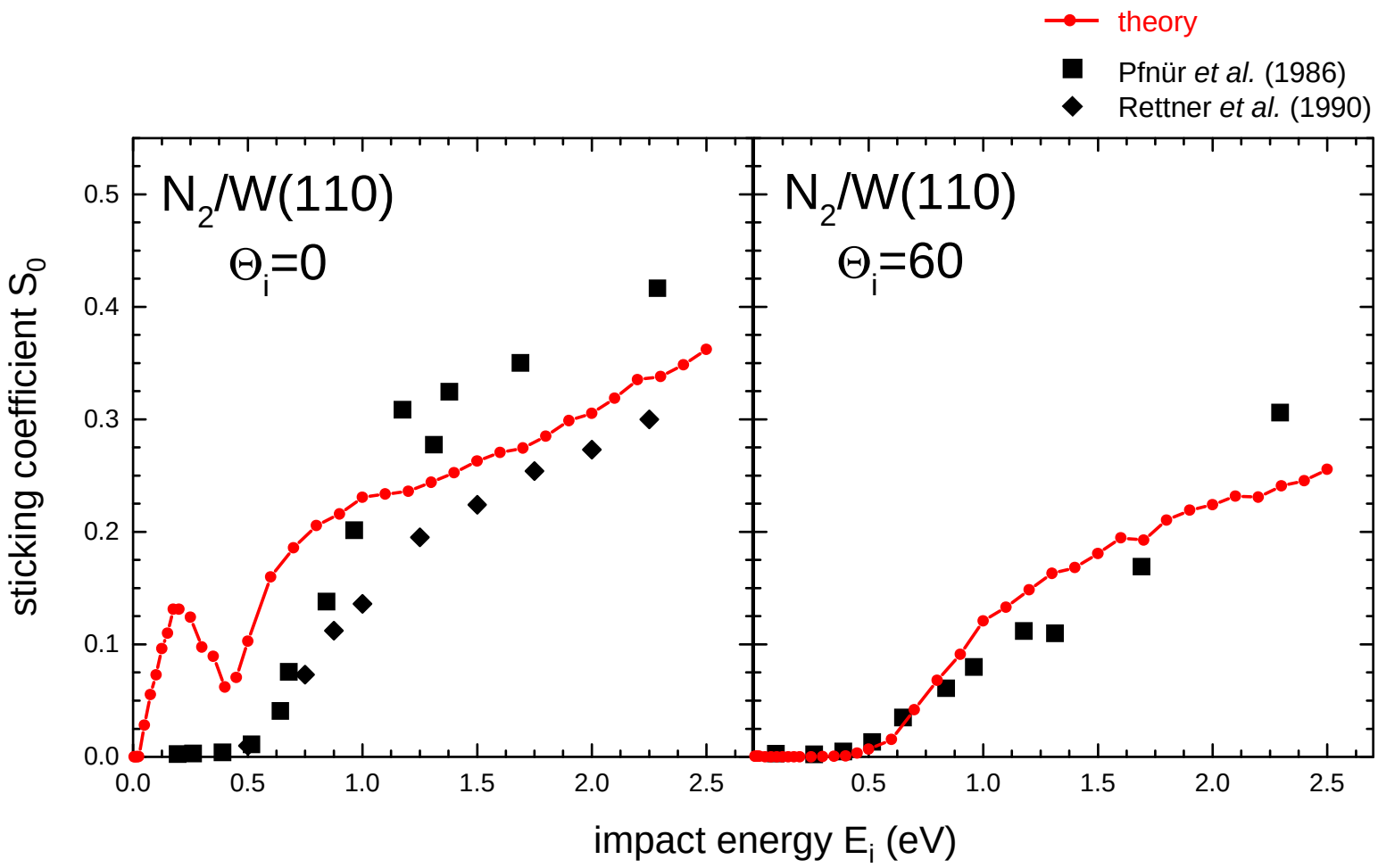
In our particular case:

- 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)]



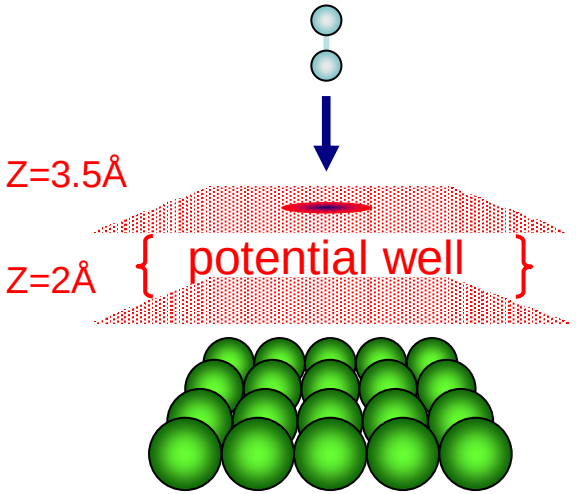
- classical dynamics in the adiabatic PES

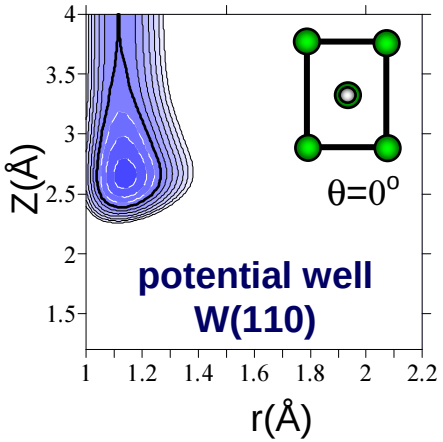
classical dynamics in the 6D-PES

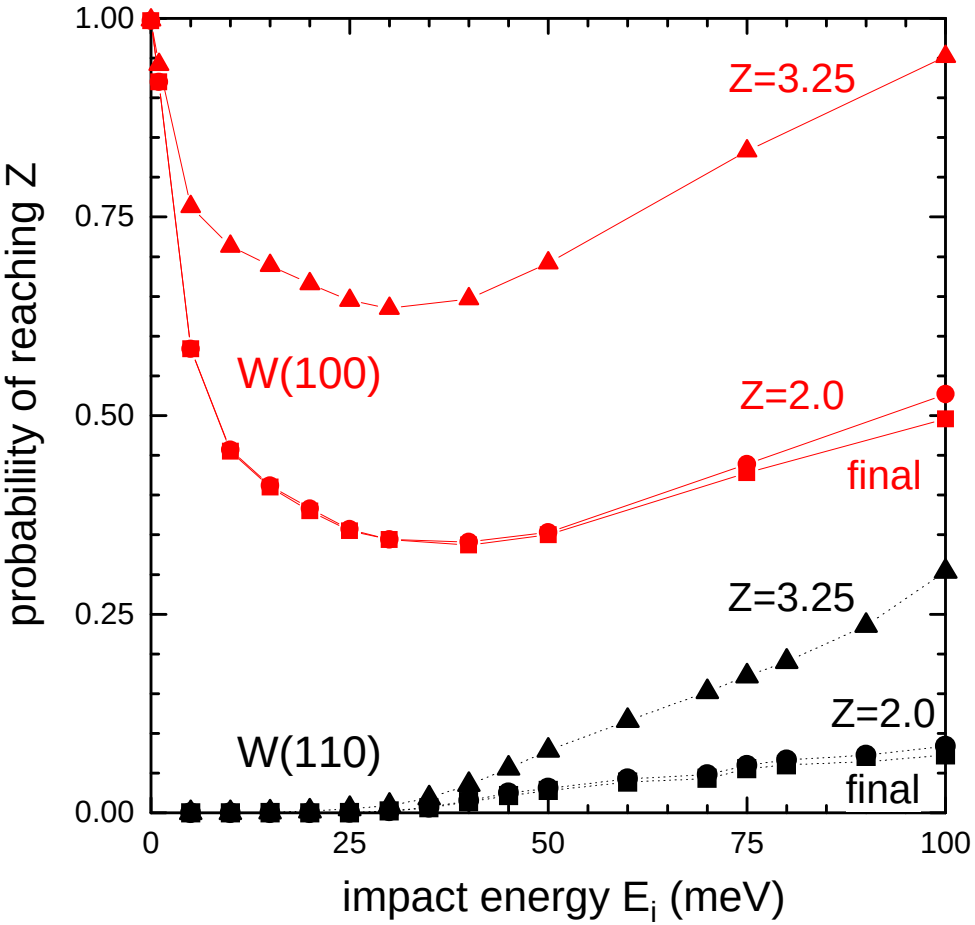


Alducin *et al.*, PRL **97**, 056102 (2006); JCP **125**, 144705 (2006)

➡ for thermal energies, long distances matter

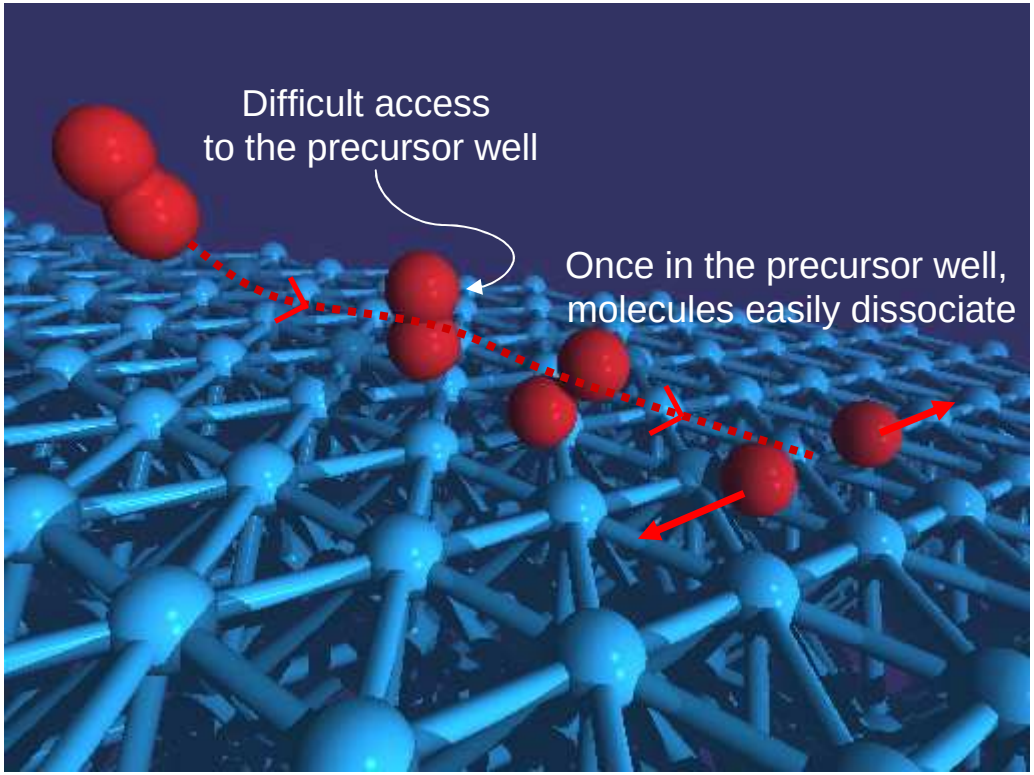


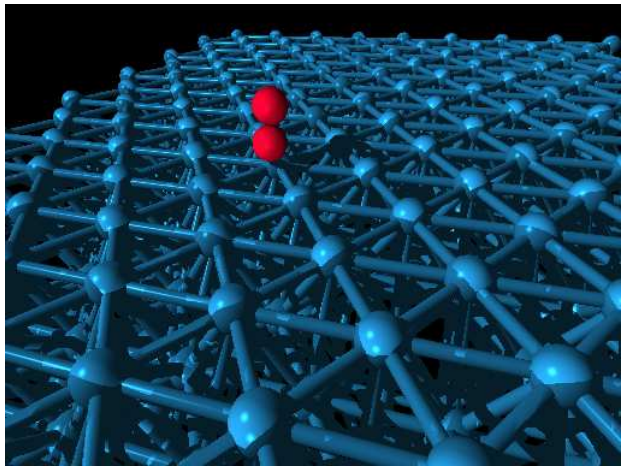




Alducin *et al.*, PRL **97**, 056102 (2006)

in summary, dynamics matters





outline

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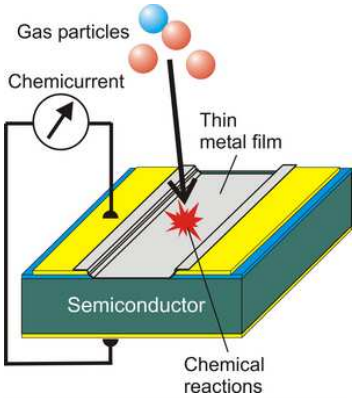
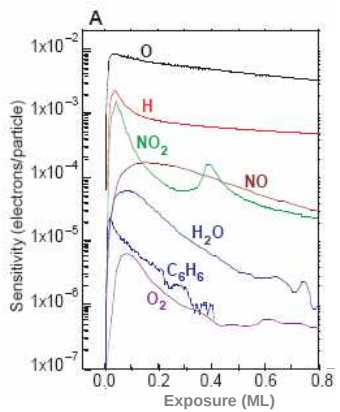
- non-adiabatic effects: electronic excitations
- conclusions

non-adiabatic effects: electron-hole pair excitations

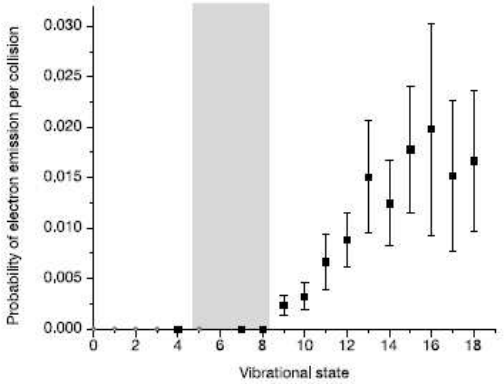
chemicurrents





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

vibrational promotion of electron transfer

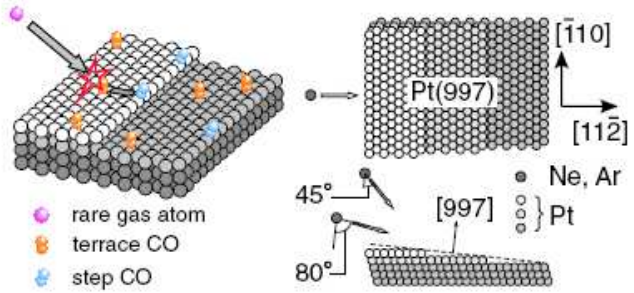


NO on Cs/Au(111)
electron emission as
a function of initial
vibrational state

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

non-adiabatic effects: electron-hole pair excitations

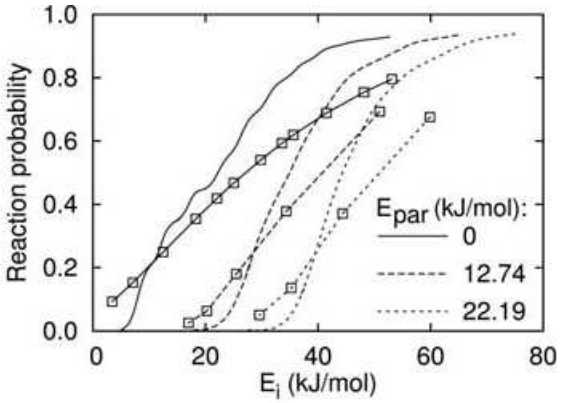
friction of a single chemisorbed CO molecule



CO on Pt(997)
migration to step edges

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

electron excitation during H_2 dissociation



H_2 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

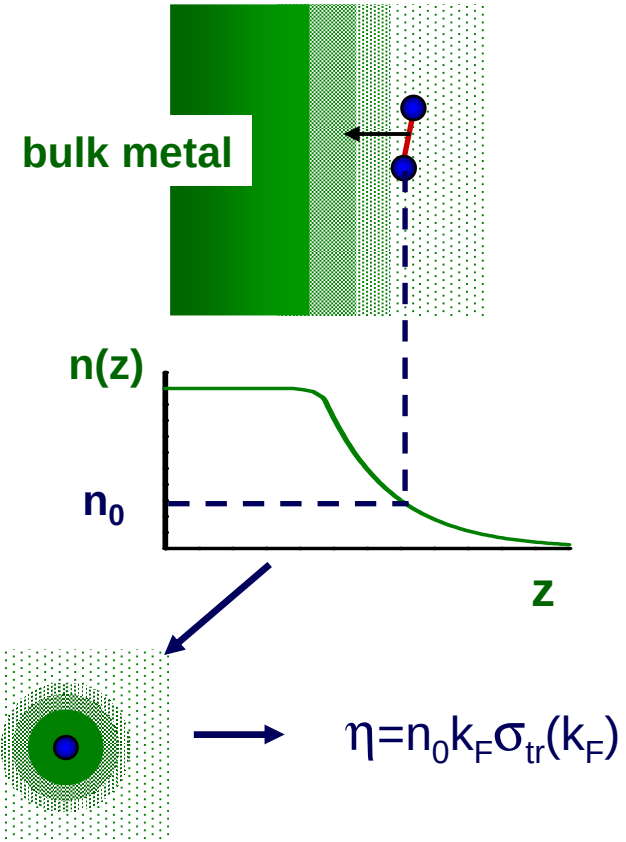
for each atom "*i*" in the molecule

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

adiabatic force: 6D DFT PES

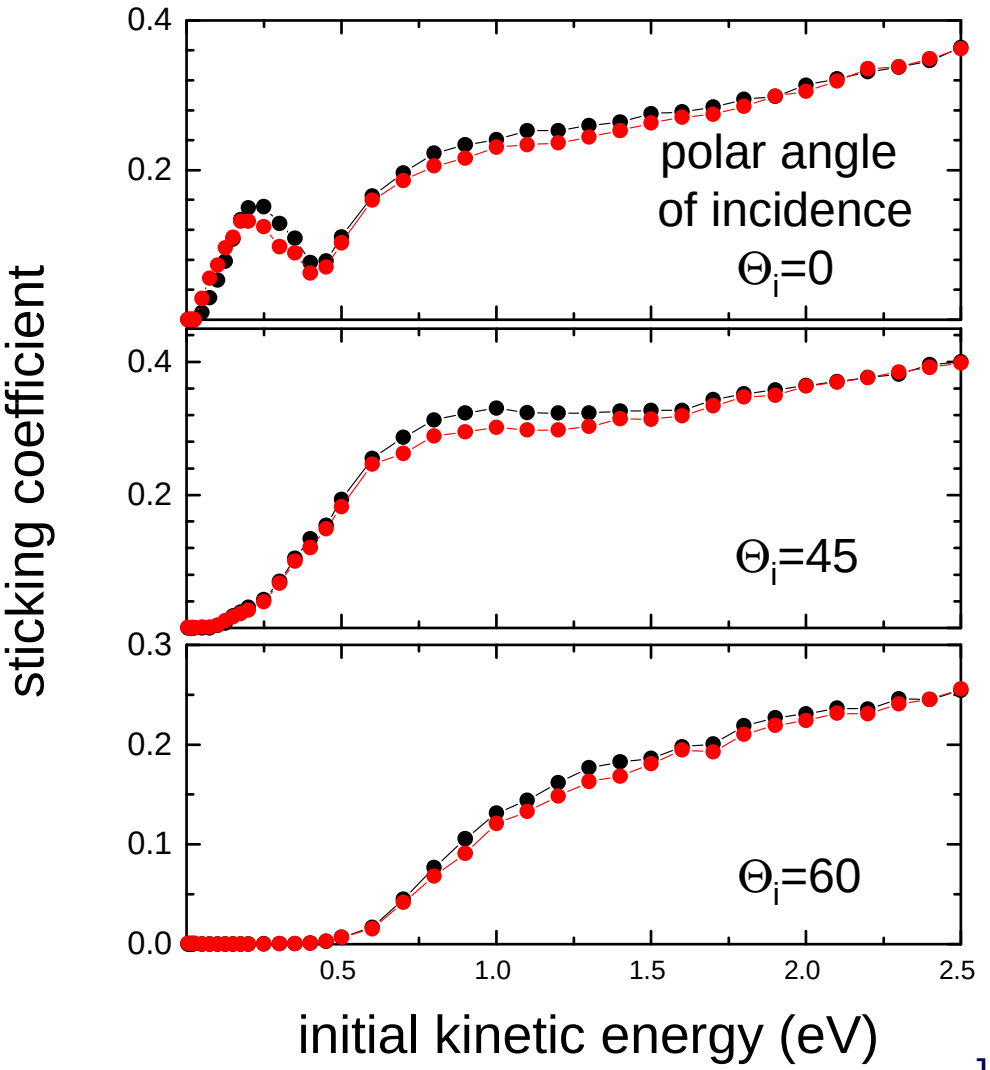
friction coefficient

friction coefficient: effective medium approximation



effective medium:
FEG with electronic density n_0

probability of dissociative adsorption: N_2 on W(110)



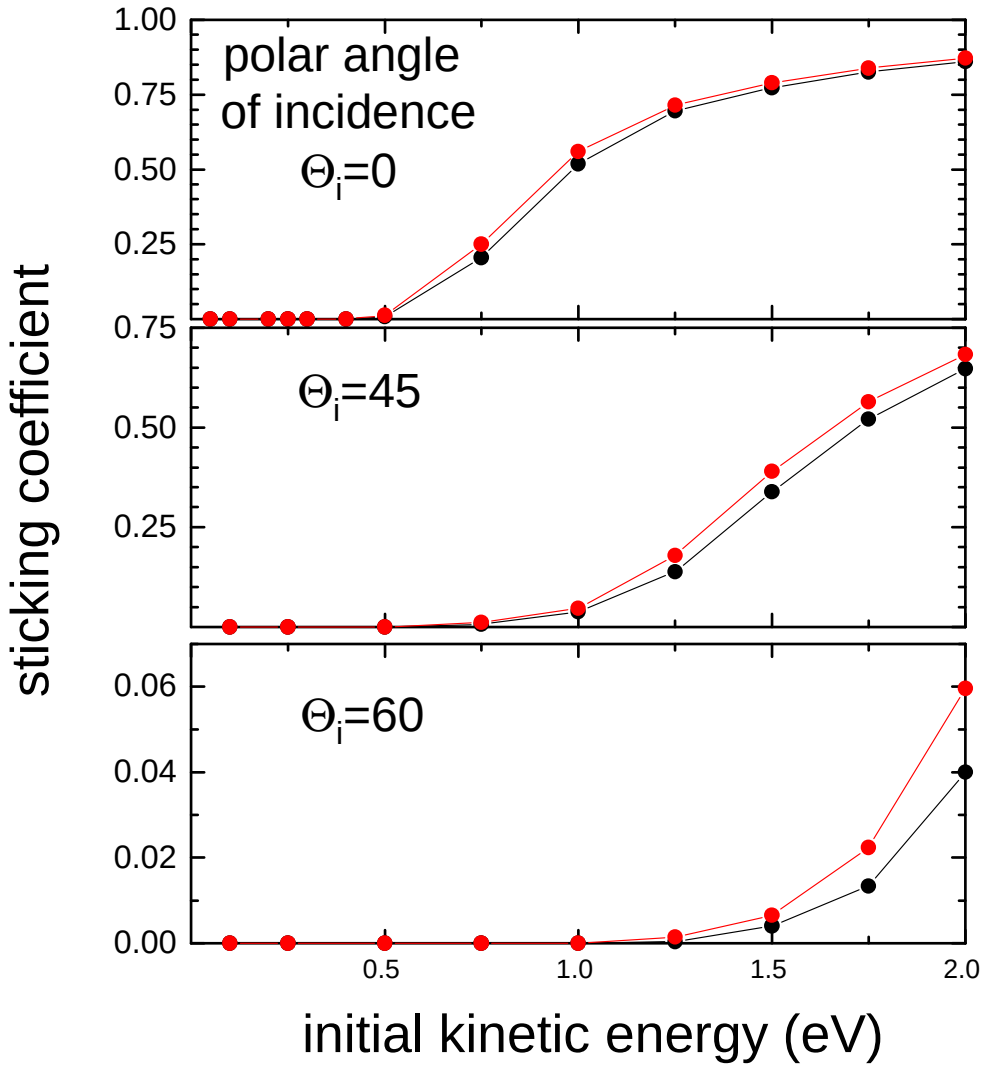
non-adiabatic

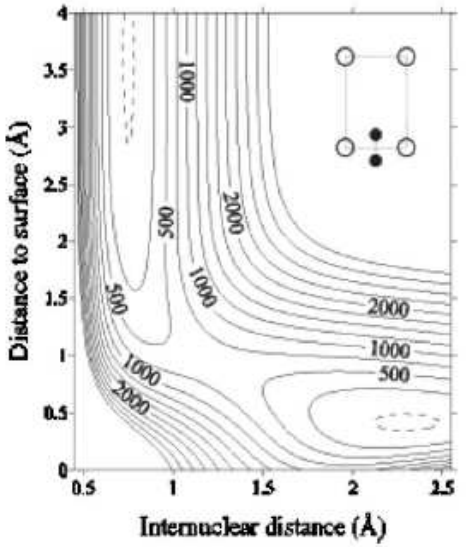
adiabatic

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

Juaristi *et al.*, PRL 2008 (in press)

probability of dissociative adsorption: H_2 on Cu(110)





[Salin, JCP **124**, 104704 (2006)]

non-adiabatic

adiabatic

Juaristi *et al.*, PRL 2008 (in press)

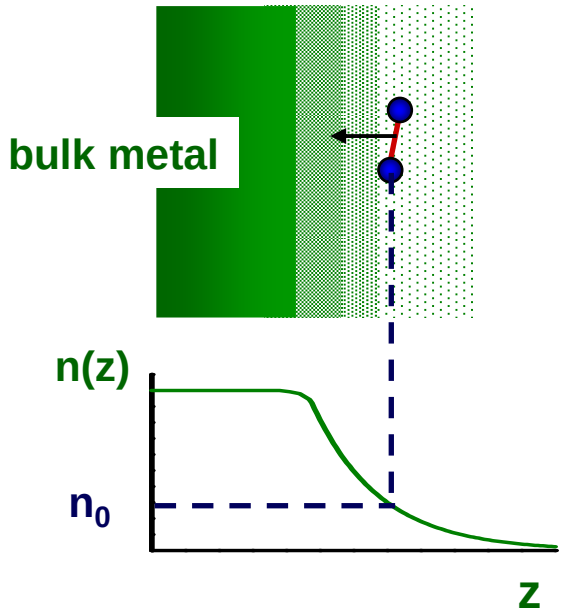
classical equations of motion

for each atom "*i*" in the molecule

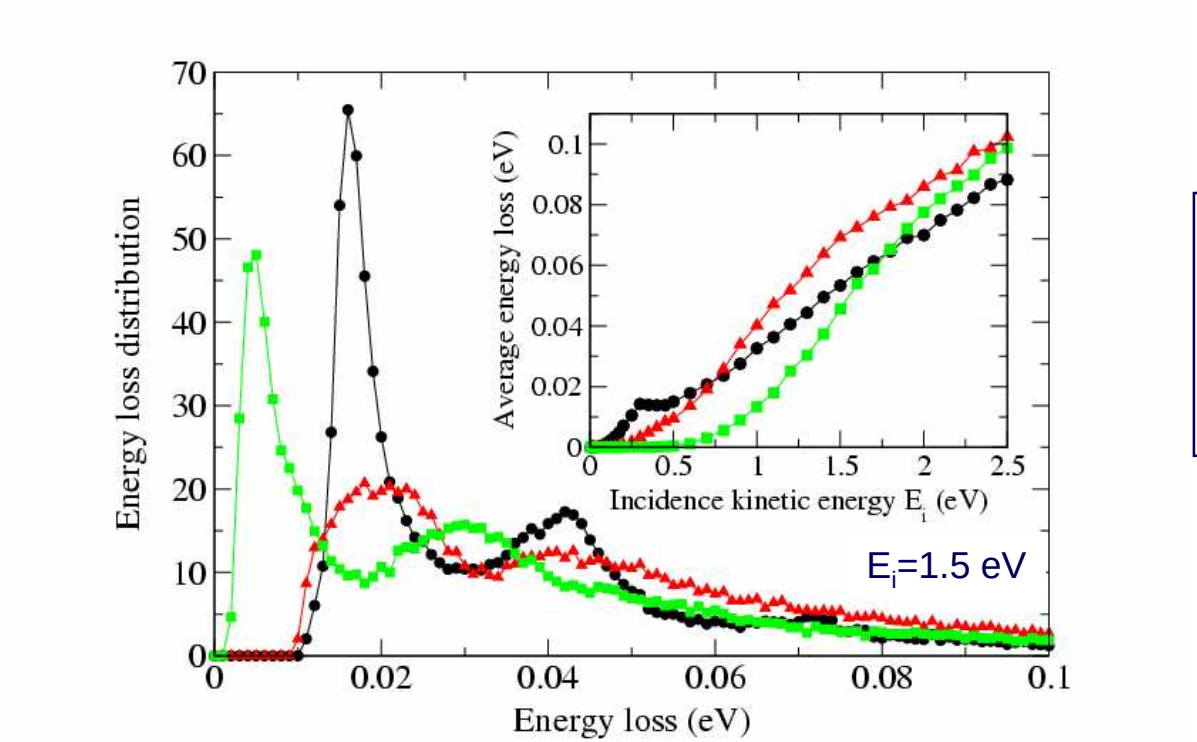
$$m_i(d^2r_i/dt^2) = -dV(r_i,r_j)/d(r_i) - \eta(r_i)(dr_i/dt)$$

friction coefficient

velocity



energy loss of reflected molecules: N_2 on W(110)



Θ_i=0
Θ_i=45
Θ_i=60

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

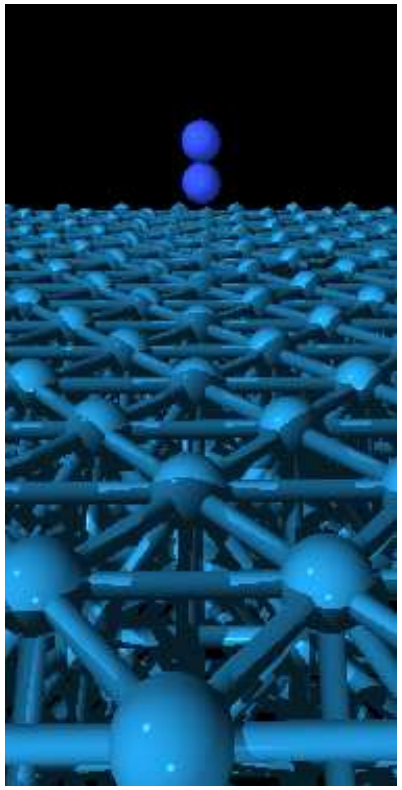
Juaristi *et al.*, PRL 2008 (in press)

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 Å) 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
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