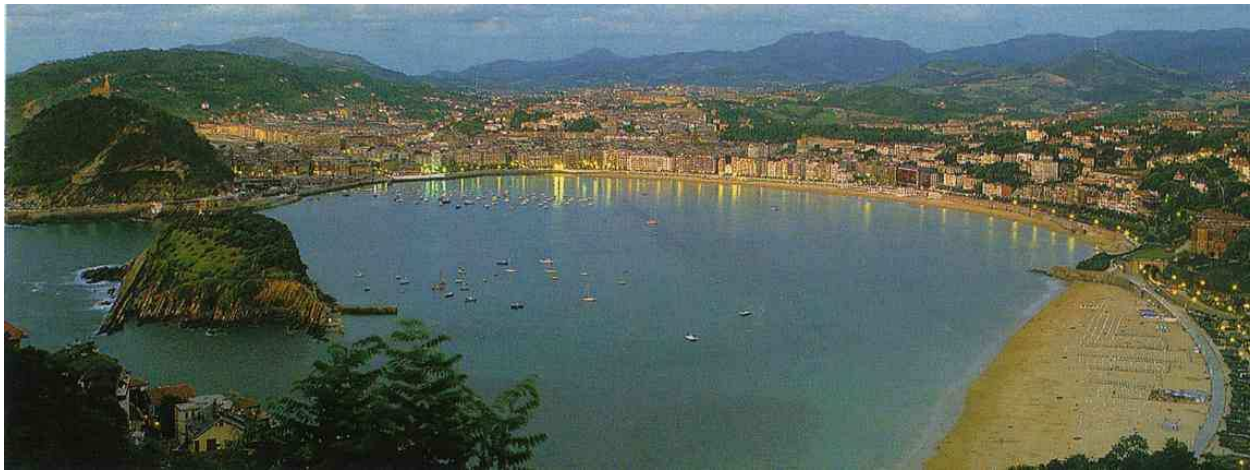

Accuracy of adiabatic DFT calculations in the description of molecular dissociation at metal surfaces

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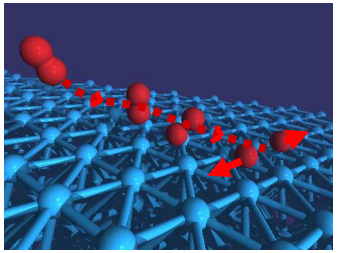
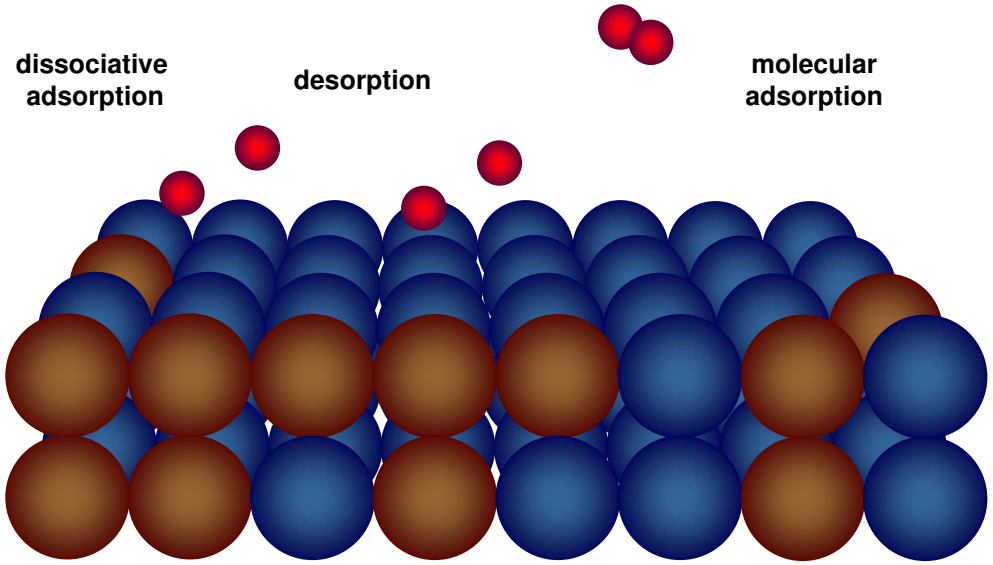
XII International Conference on Vibrations at Surfaces - VAS12
Erice (Italy), July 20-26, 2007

gas/surface dynamics



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



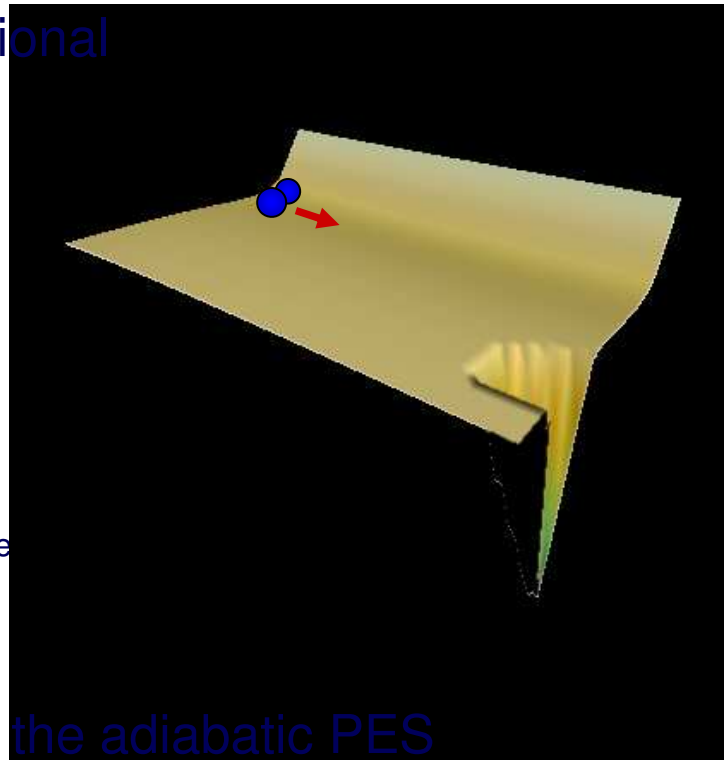
some elementary reactive processes at surfaces

theoretical method

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

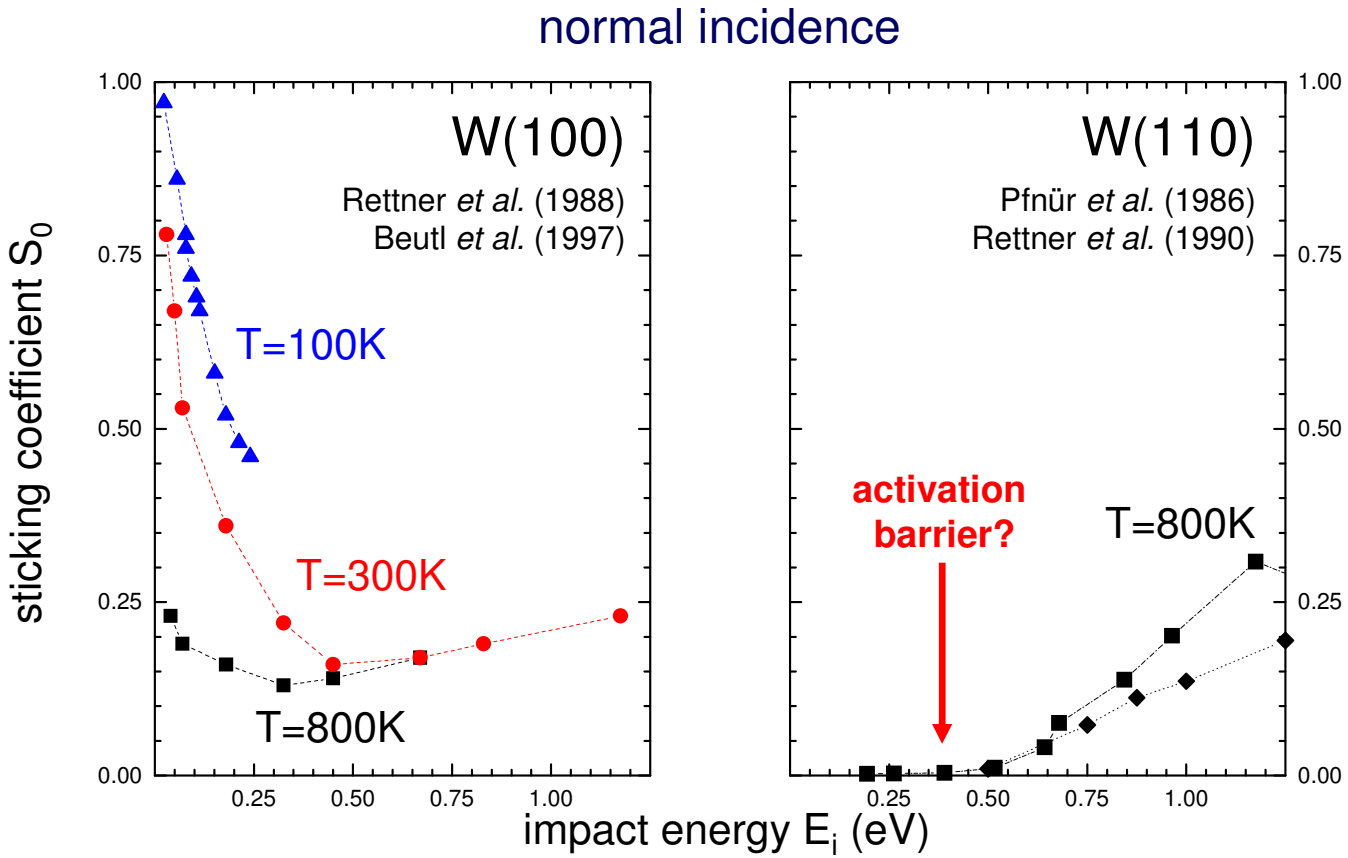
In our particular case:

- 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)]



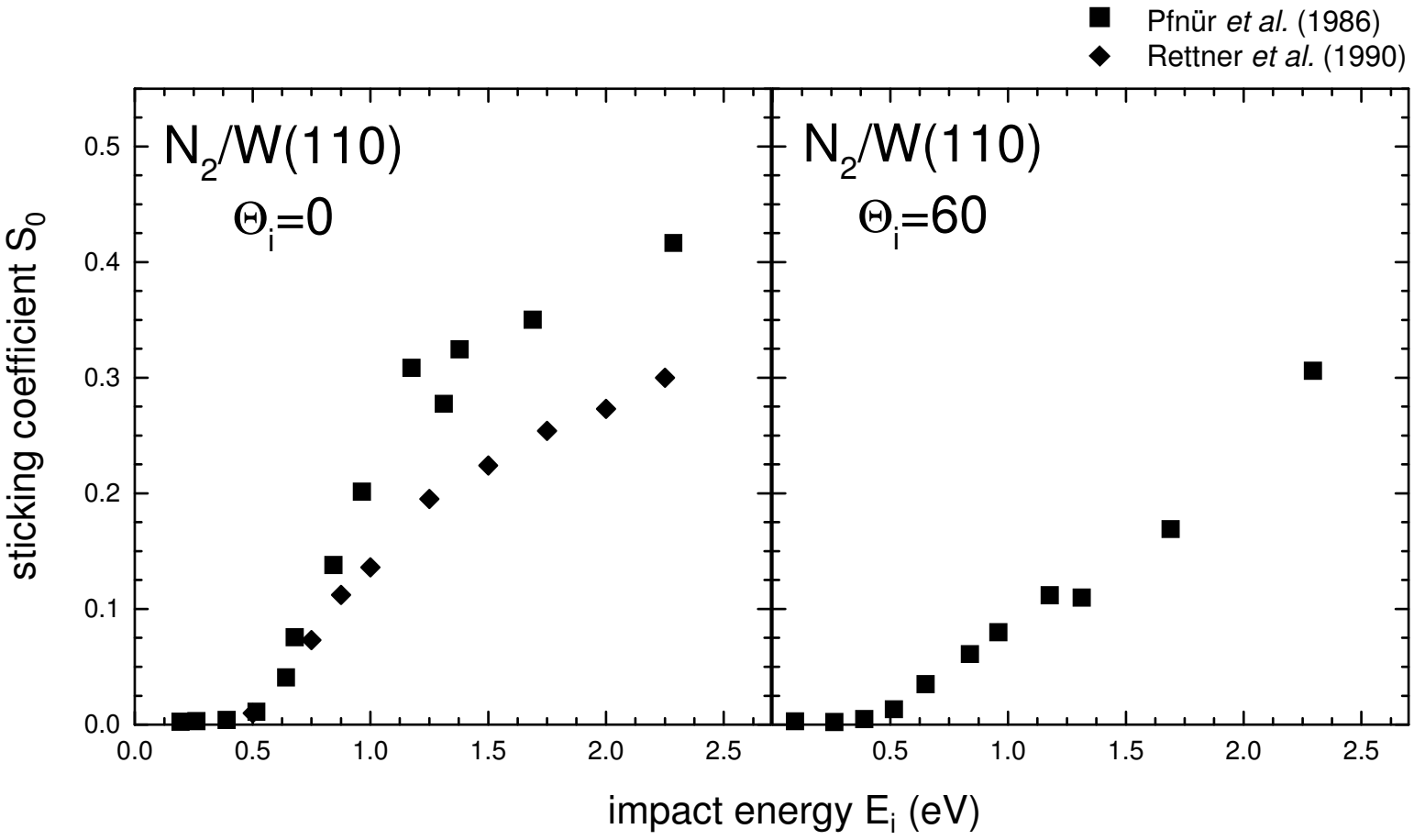
- classical or quantum dynamics in the adiabatic PES

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

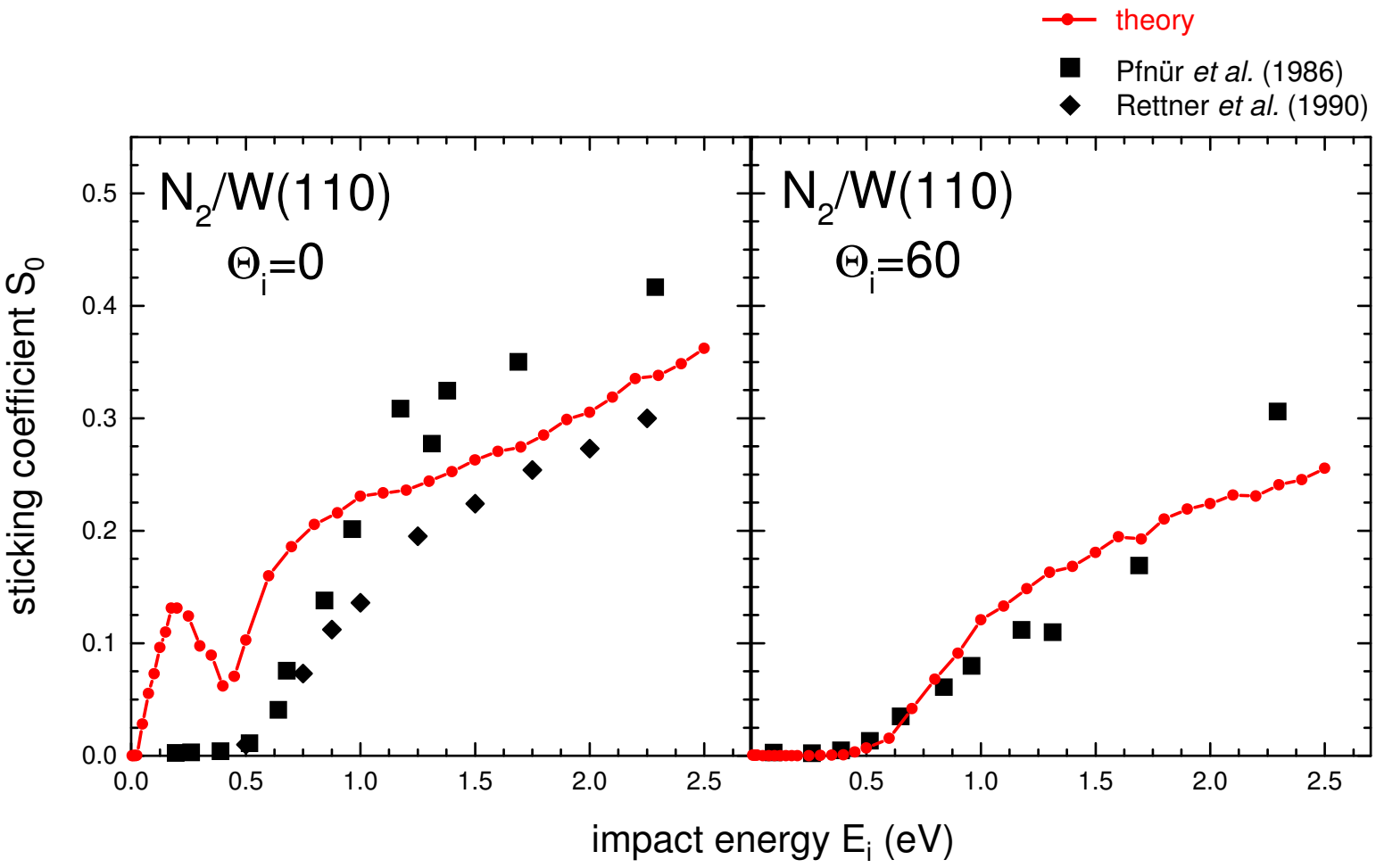


no threshold **threshold**

classical dynamics in the 6D-PES

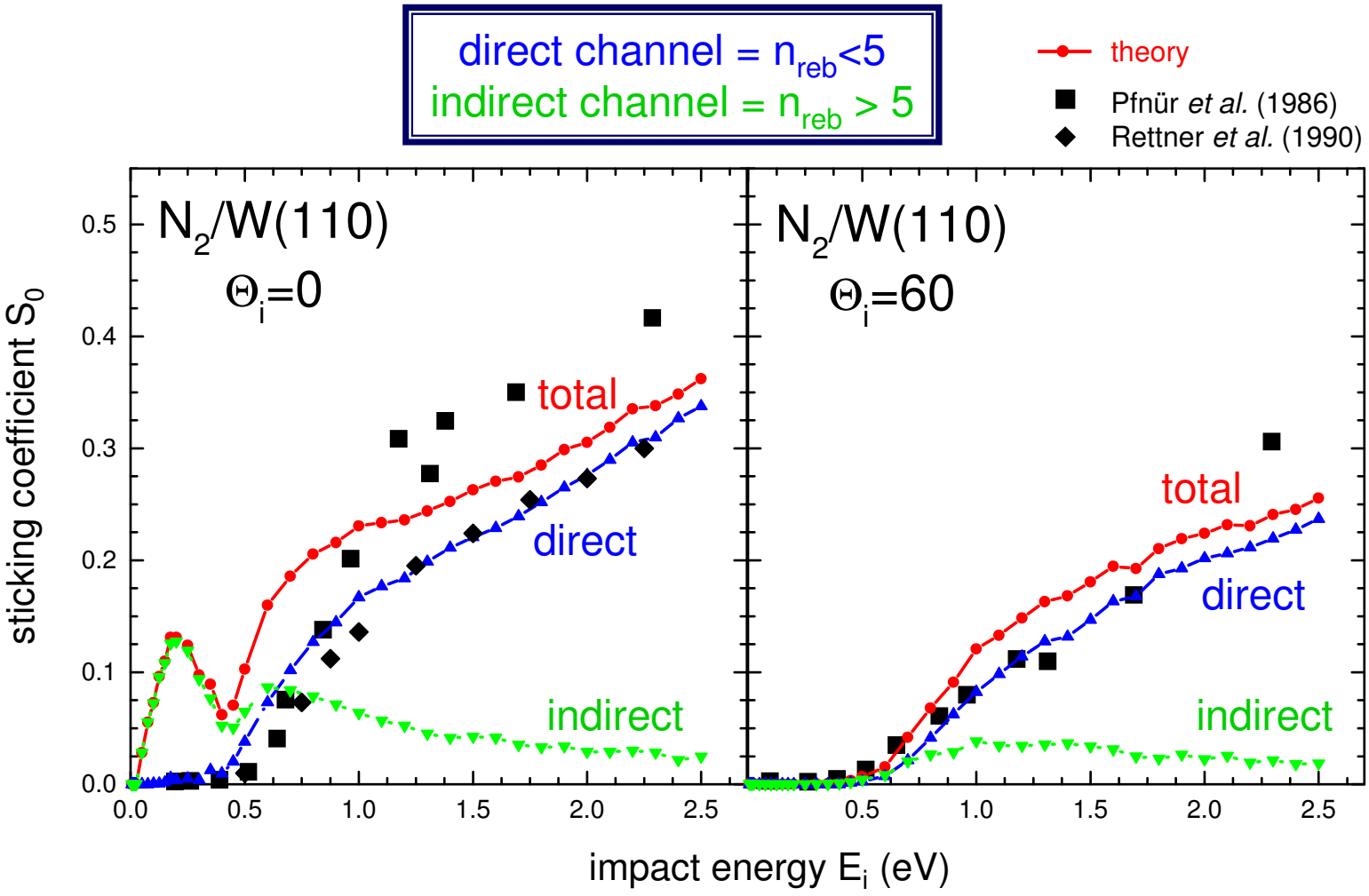


classical dynamics in the 6D-PES



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

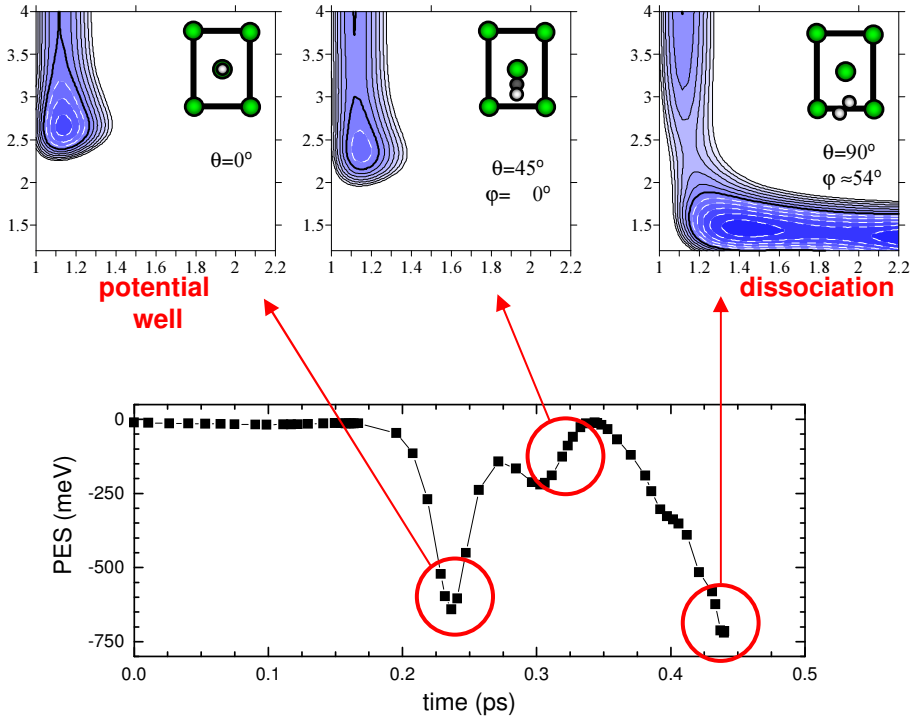
classical dynamics in the 6D-PES



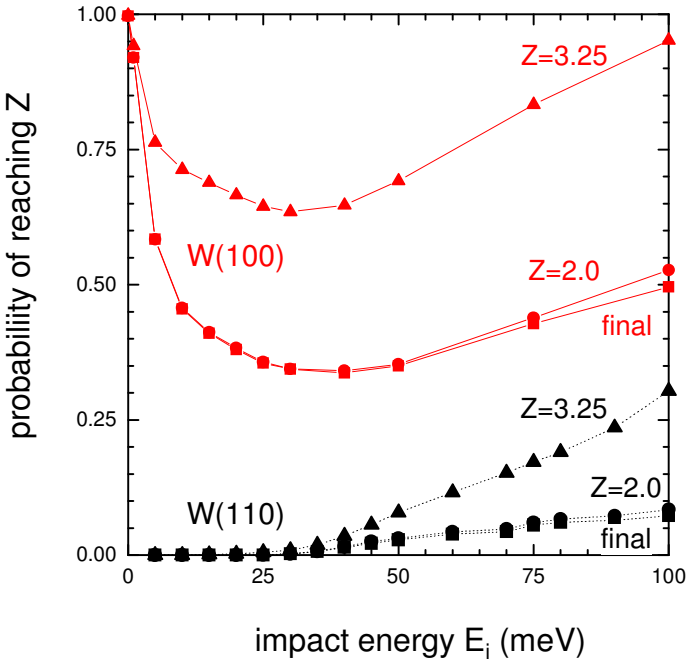
Alducin *et al.*, PRL **97**, 056102 (2006); JCP **125**, 144705 (2006)

dissociative adsorption of N_2 on W

non-activated paths to dissociation in W(110)



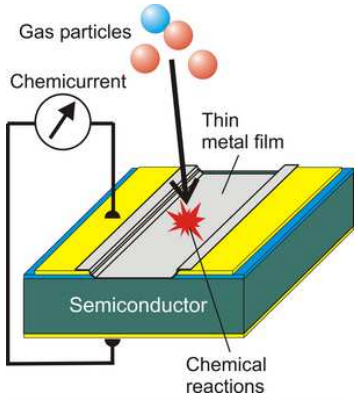
dynamics at long-distances matter

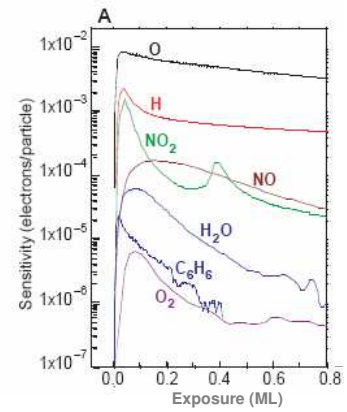


Alducin *et al.*, PRL **97**, 056102 (2006); JCP **125**, 144705 (2006)

non-adiabatic effects: electron-hole pair excitations

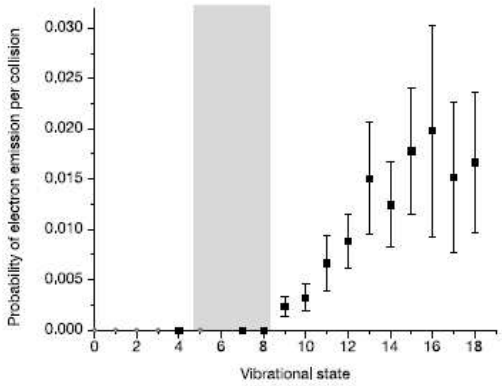
chemicurrents





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

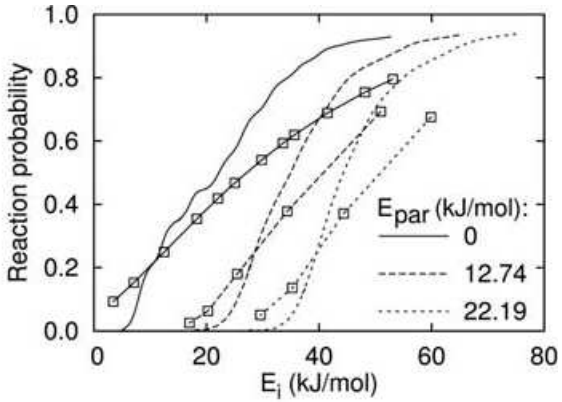
vibrational promotion of electron transfer



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)

electron excitation role during N_2 dissociation



N_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

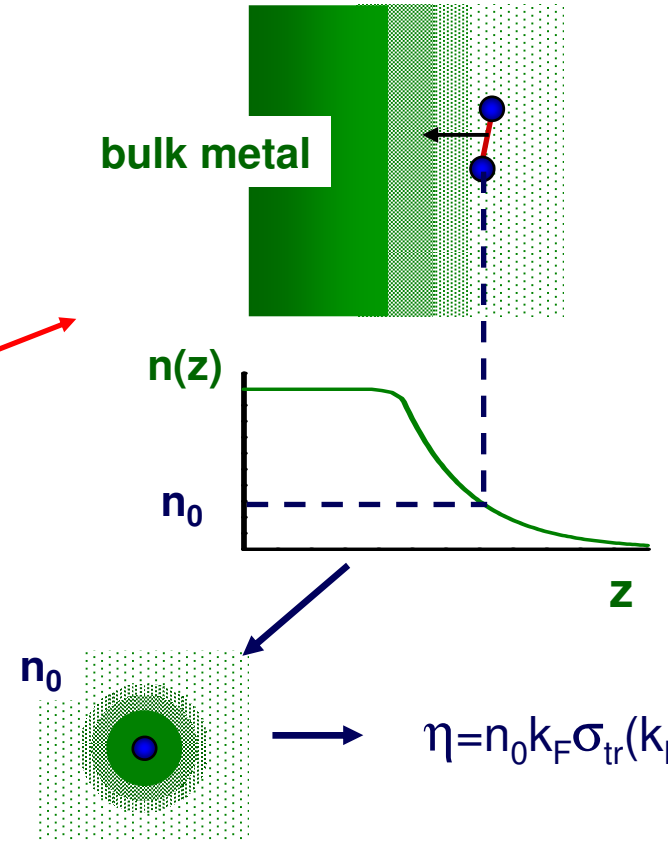
for each atom "*i*" in the molecule

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

adiabatic force: 6D DFT PES

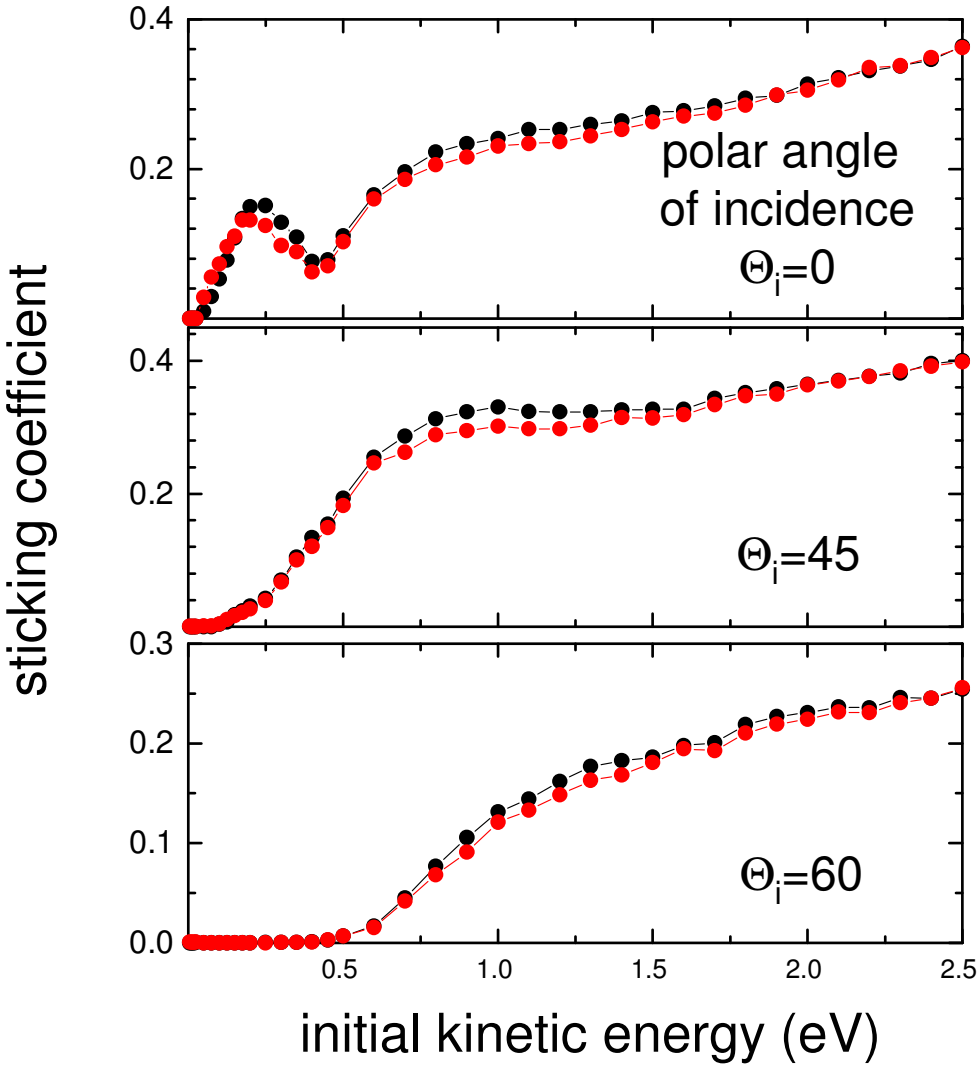
friction coefficient

friction coefficient: effective medium approximation



effective medium:
FEG with electronic density n_0

probability of dissociative adsorption: N_2 on W(110)

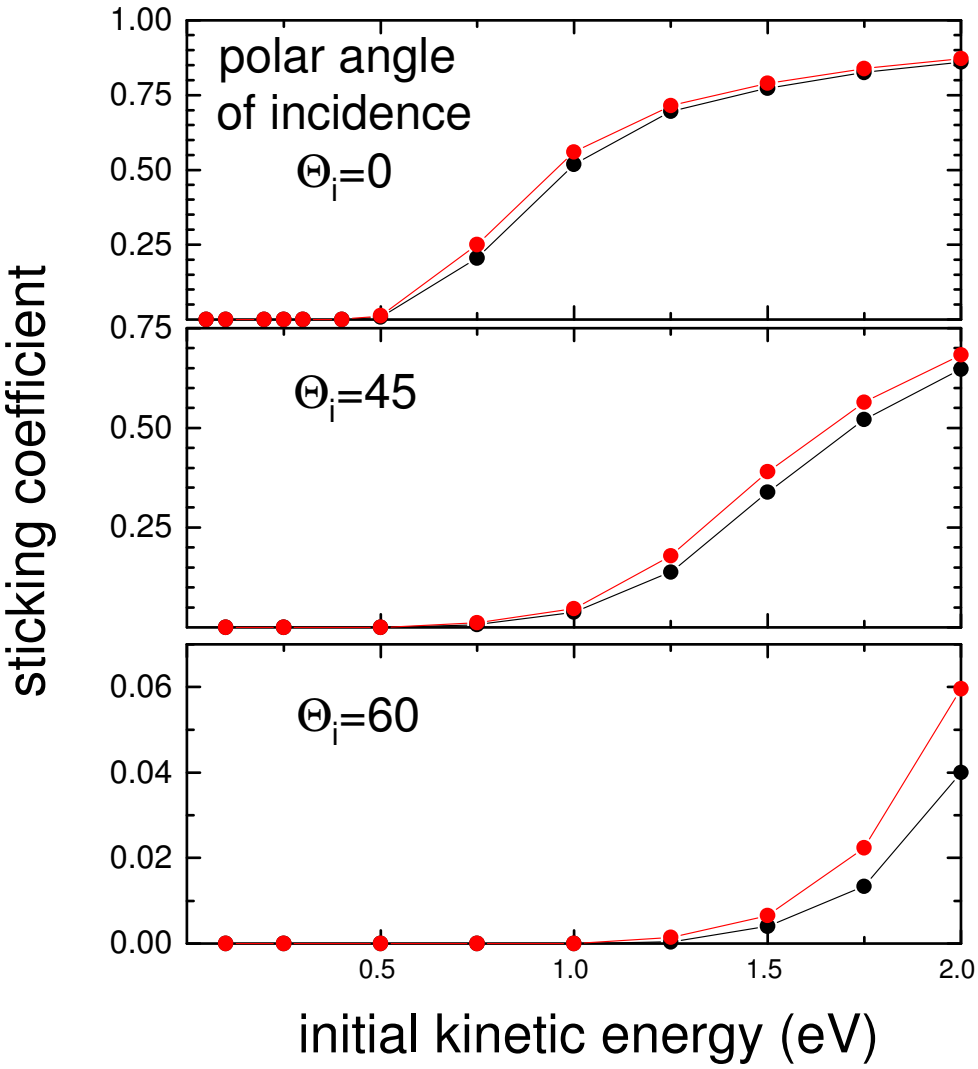


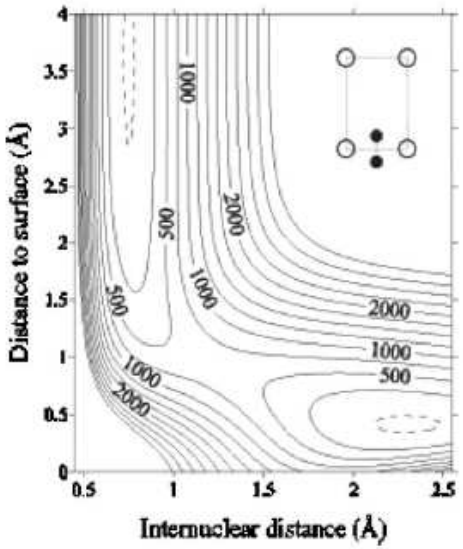
non-adiabatic

adiabatic

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

probability of dissociative adsorption: H_2 on Cu(110)





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

non-adiabatic

adiabatic

accuracy of adiabatic DFT calculations

Kohn-Sham equations solved self-consistently

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

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

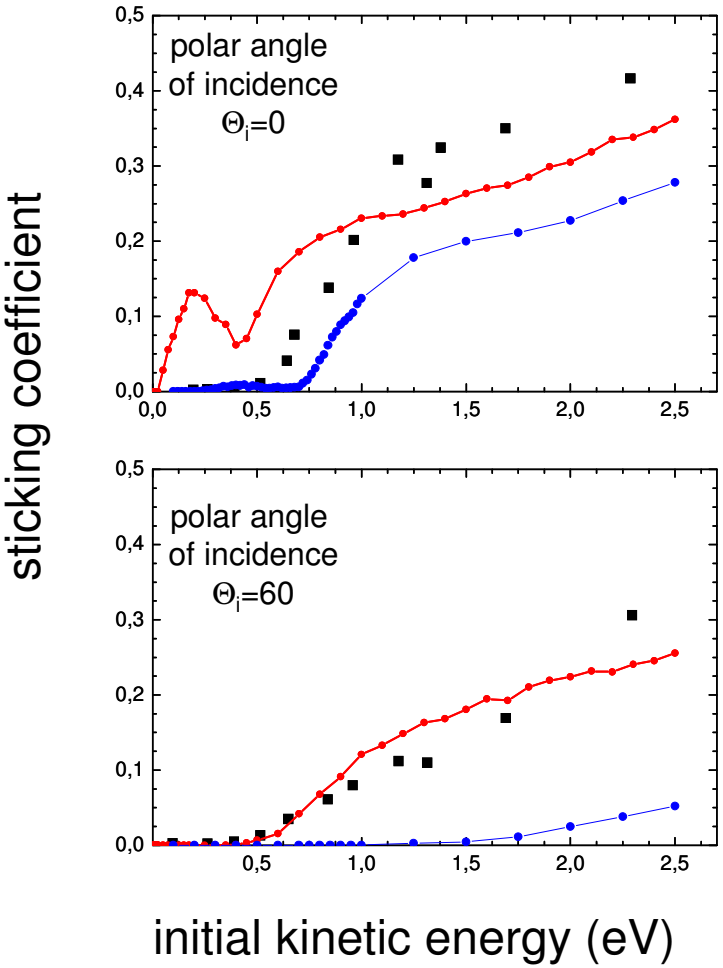
exchange-correlation term is not exact

	$E_{chem,\beta}$					E^{exp}_{chem}
	LDA	PW91	PBE	revPBE	RPBE	
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: N_2/W(110)



■ Pfnür *et al.*, JCP **85** 7452 (1986)

PW91

RPBE

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!

conclusions

classical dynamics based on DFT adiabatic calculations are able to describe the dynamics of dissociative adsorption

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

other uncertainties (choice of the exchange-correlation functional), intrinsic to the DFT-KS methodology, can lead to inaccuracies of the same order of magnitude

contributors to this work

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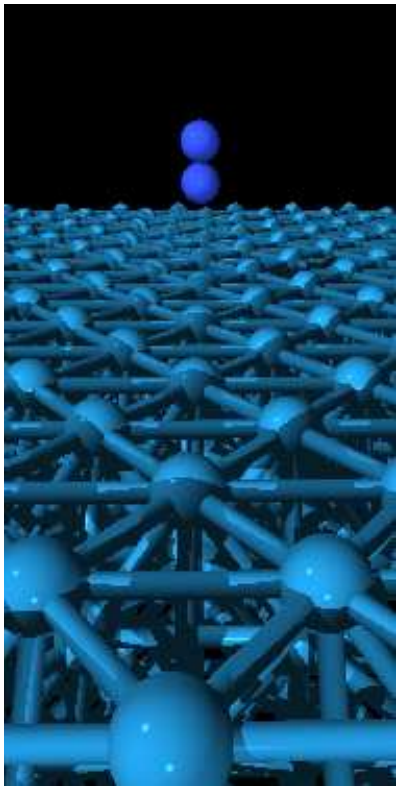
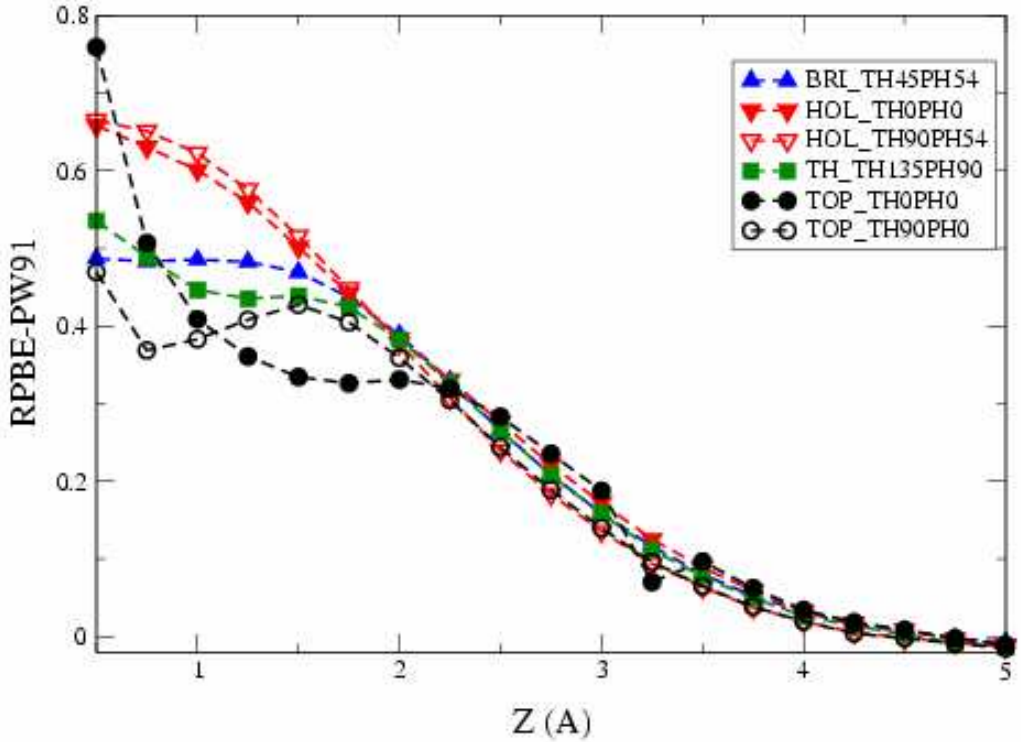


thank you for your attention

Erice, 23rd July 2007

N_2 on W(110): RPBE vs. PW91

E_{RPBE}-E_{PW91}
difference between total energy calculations using RPBE functional and PW91 XC-functionals, for several positions of the molecule



RPBE: Hammer *et al.*, PRB **59**, 7413 (1999)
PW91: Perdew *et al.*, PRB **46**, 6671 (1992)