

Electronic excitations in elementary reactive processes at metal surfaces



Contributors

Donostia - San Sebastián

Maite Alducin (CSIC)

Ricardo Díez Muiño (CSIC)

Itziar Goikoetxea (PhD, CSIC)

Iñaki Juaristi (UPV)

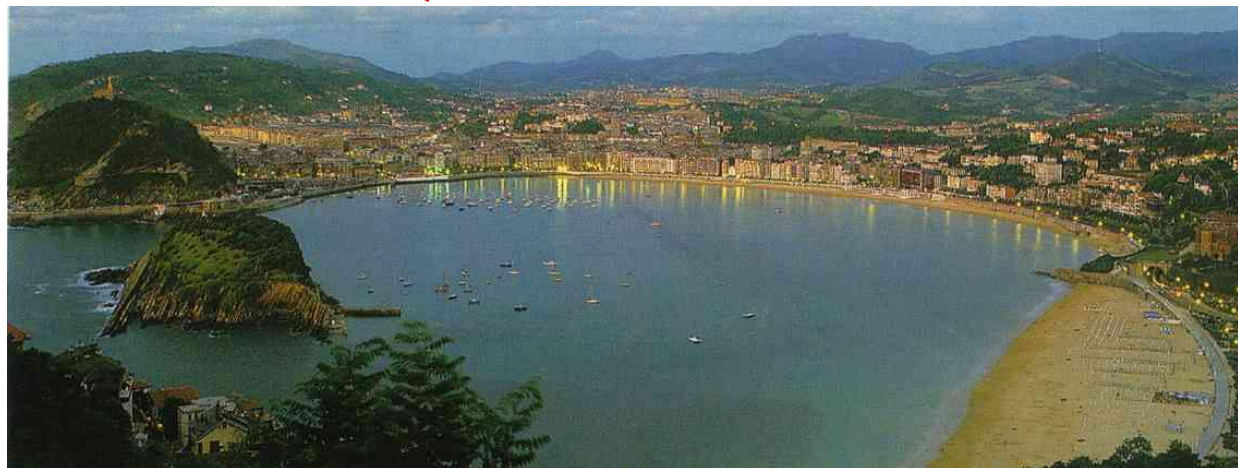
Geetha Kanuvakkarai (Post-doc, CSIC)

Ludovic Martin (Post-doc, DIPC)

Others

Fabio Busnengo (Rosario, Argentina)

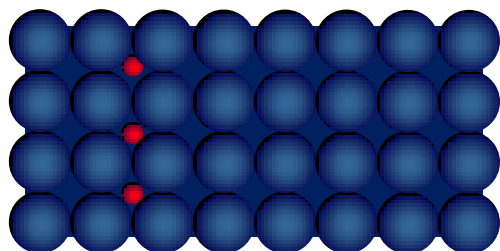
Antoine Salin (Bordeaux, France)



outline

- **brief introduction: adiabatic processes**
- **electronic excitations at the surface: friction**
- **electronic excitations at the molecule**

➔ gas/solid interfaces

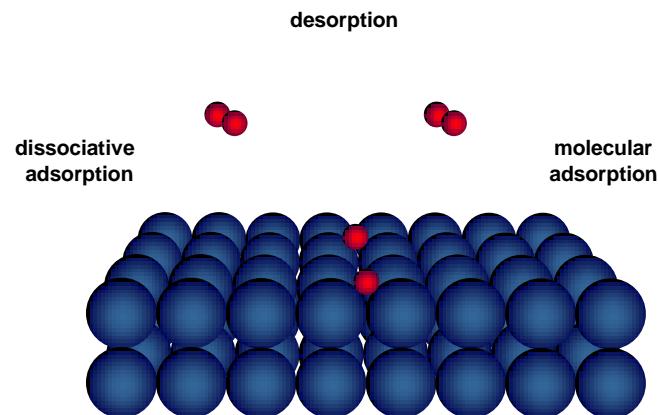


static properties (equilibrium)

- adsorption sites and energies
- chemical bonding
- induced reconstructions
- self-assembling

experimental techniques:

- LEED, STM, PE, etc.



dynamical properties

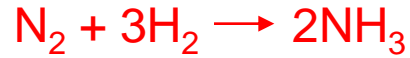
- reaction rates (adsorption, recombination, ...)
- diffusion
- induced desorption
- energy and charge exchange

experimental techniques:

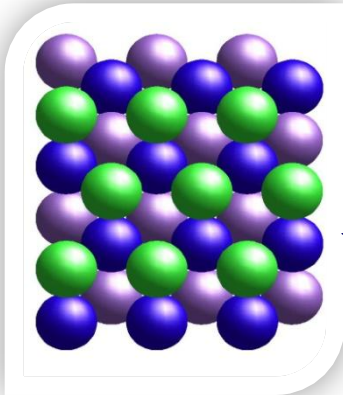
- molecular beams, TPD, etc.

an important goal is to understand how solid surfaces can be used to promote gas-phase chemical reactions

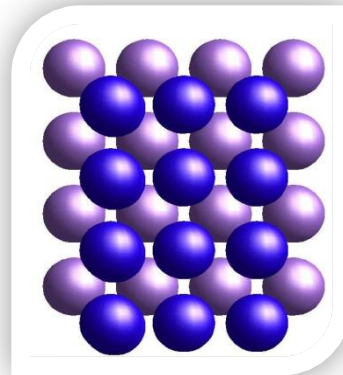
➔ surface face and reactivity



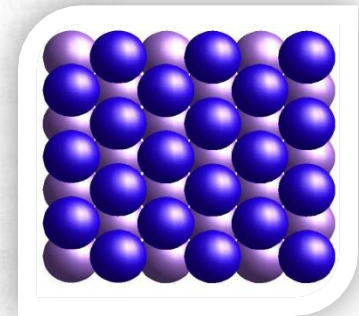
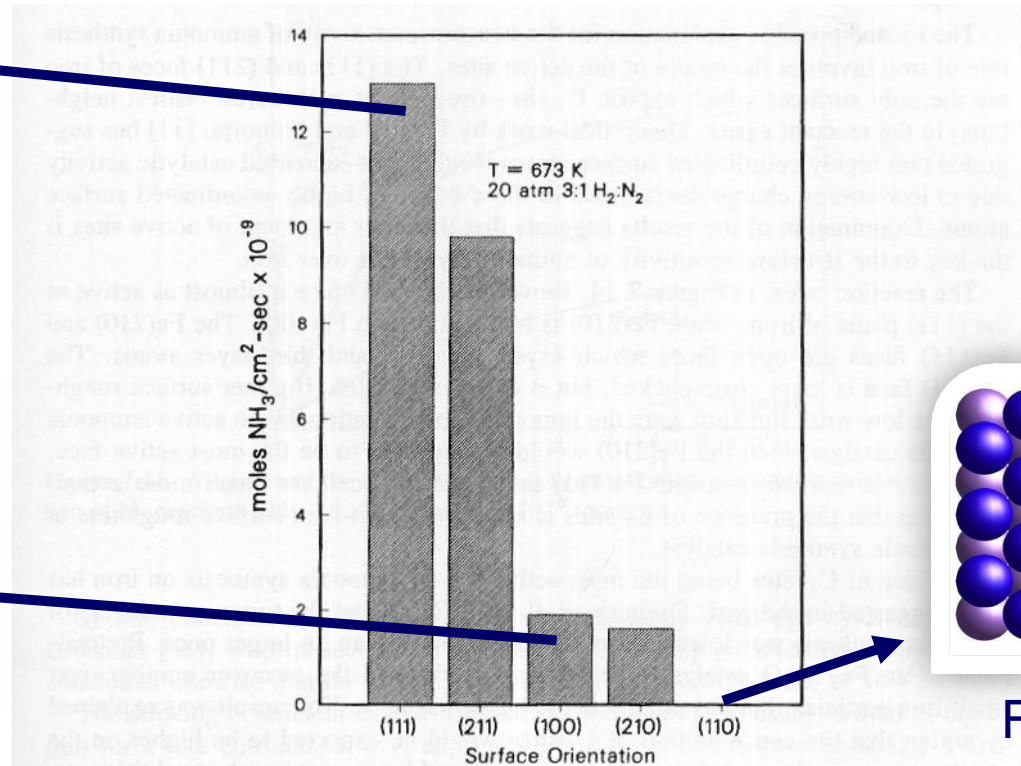
rates of ammonia synthesis over five iron single-crystal surfaces



Fe (111)



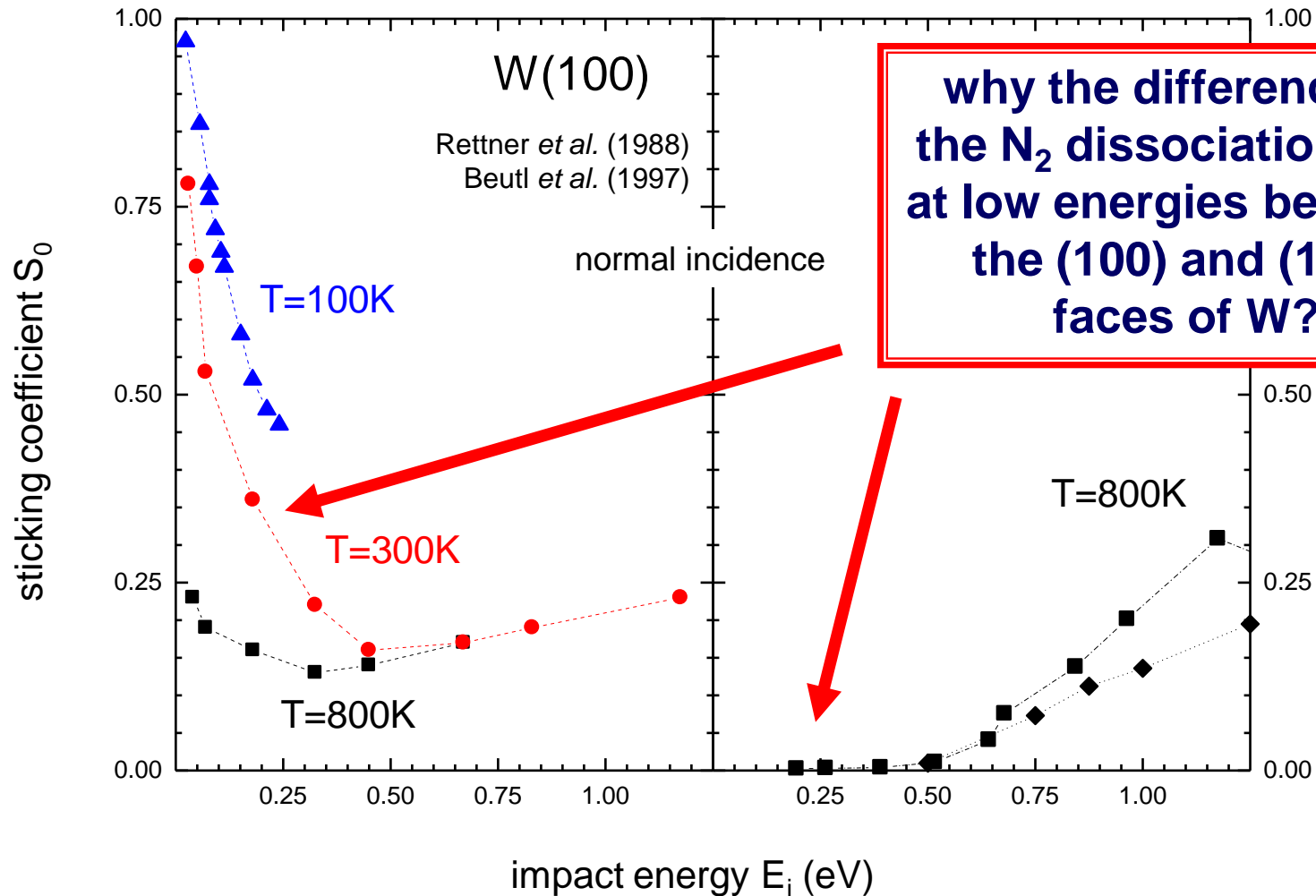
Fe (100)



Fe (110)

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

➔ dissociative adsorption of N₂ on W(100) and on W(110)



➔ dynamics of diatomic molecules on metal surfaces: theory

theoretical model: two steps

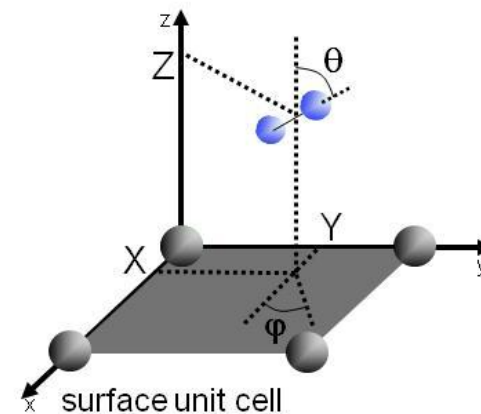
1.- calculation of the Potential Energy Surface (PES)

- adiabatic approximation
- frozen surface approximation \Rightarrow **6D PES**: $V(X, Y, Z, r, \theta, \varphi)$

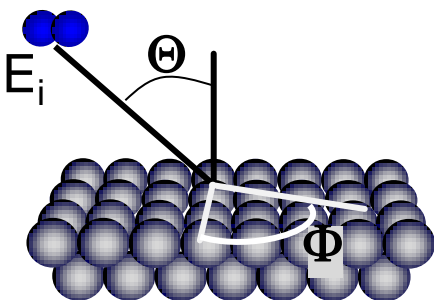
6D PES construction

- extended set of DFT energy values, $V(X, Y, Z, r, \theta, \varphi)$
- interpolation of the DFT data: corrugation reduction method

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

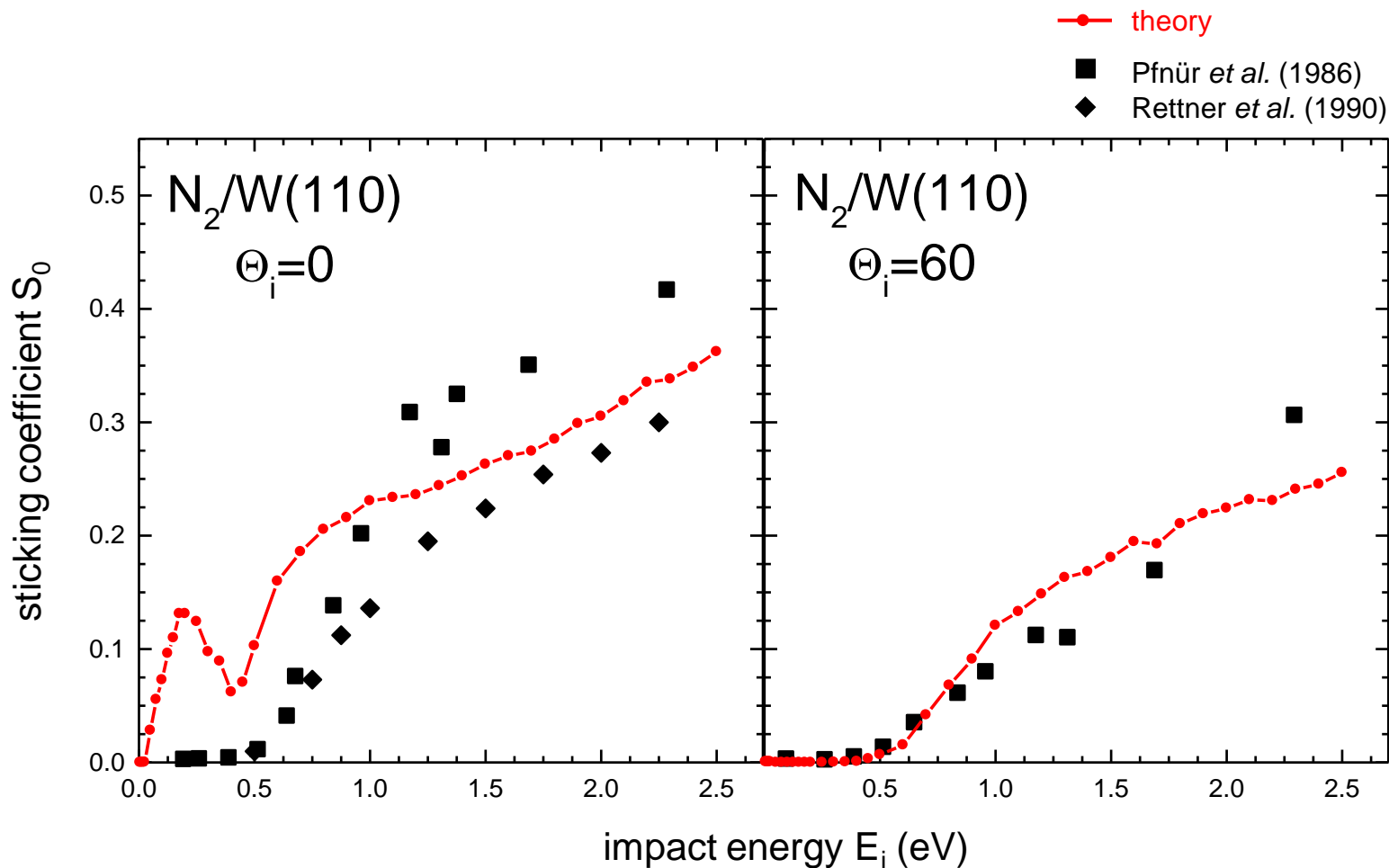


2.- classical trajectory calculations: Monte Carlo sampling

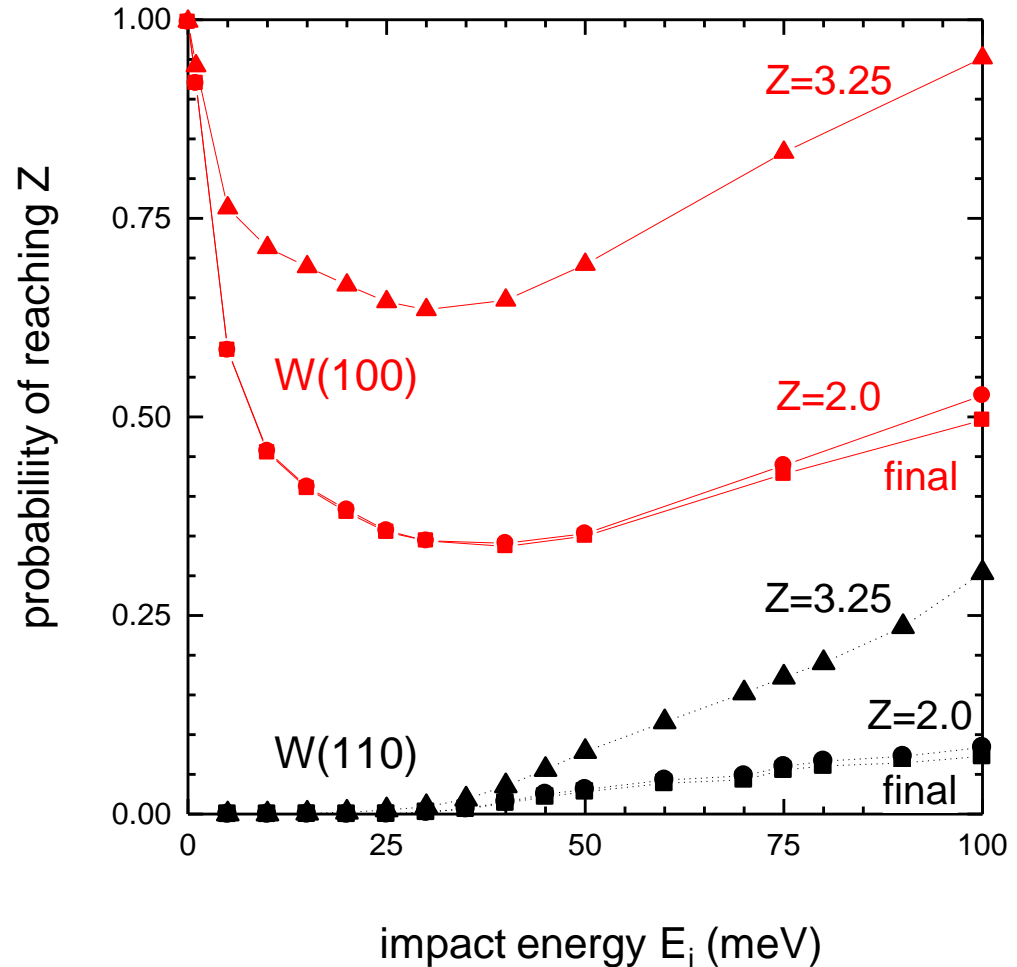
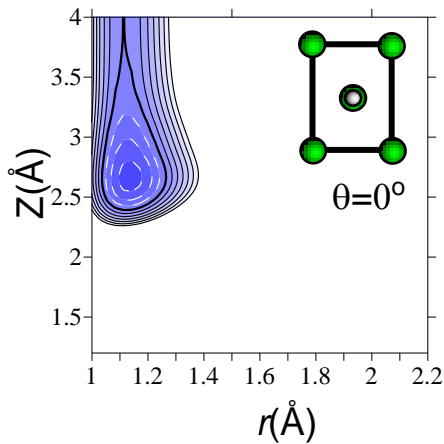
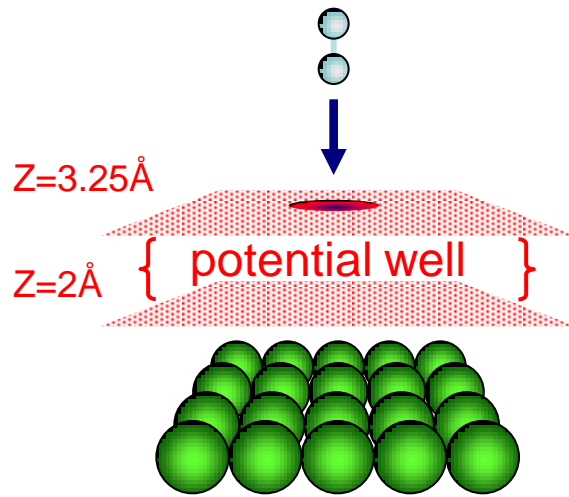


- incidence conditions are fixed: (E_i, Θ)
- sampling on the internal degrees of freedom: (X, Y, θ, φ) and on Φ (azimuthal angle of trajectory)

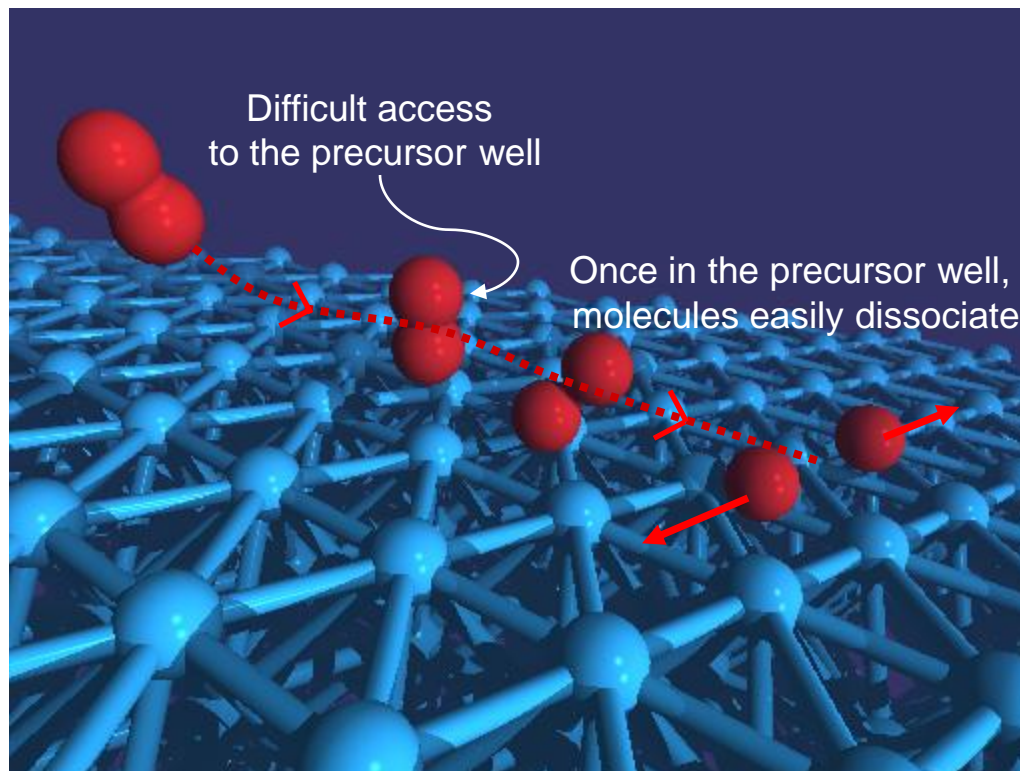
➔ dissociation of N₂ on W(110)



➔ why N_2 abundantly dissociate on W(100) and not on W(110)



➡ in summary, dynamics matters



outline

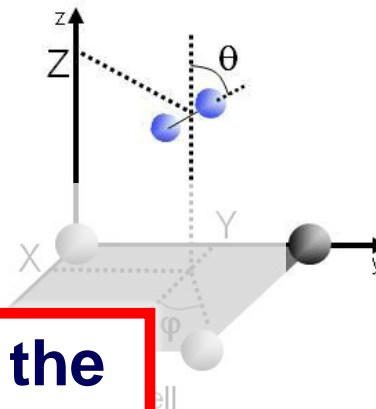
- brief introduction: adiabatic processes
- **electronic excitations at the surface: friction**
- electronic excitations at the molecule

➔ dynamics of diatomic molecules on metal surfaces

theoretical model: two steps

calculation of the Potential Energy Surface (PES)

- adiabatic approximation
- frozen surface approximation \Rightarrow 6D PES: $V(X, Y, Z, r, \theta, \varphi)$

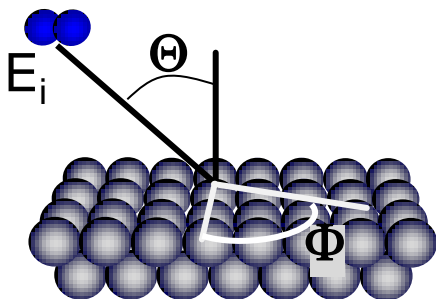


6D PES construction

- exten
- interp

We are assuming the validity of the Born-Oppenheimer approximation

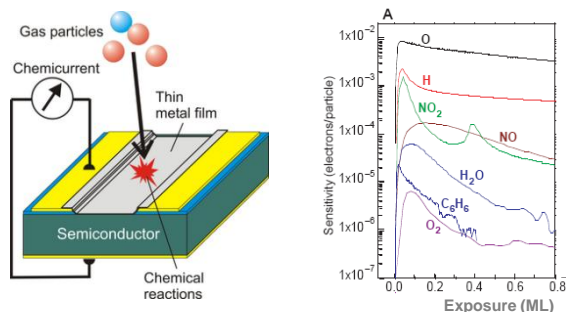
classical trajectory calculations: Monte Carlo sampling



- incidence conditions are fixed: (E_i, Θ)
- sampling on the internal degrees of freedom: (X, Y, θ, φ) and on Φ (azimuthal angle of trajectory)

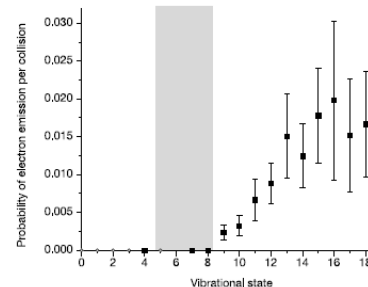
non-adiabatic effects: electron-hole pair excitations

chemicurrents



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

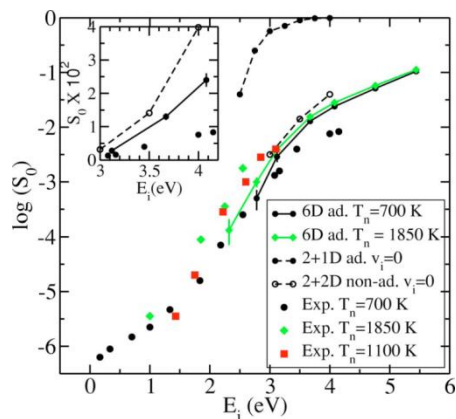
vibrational promotion of electron transfer



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

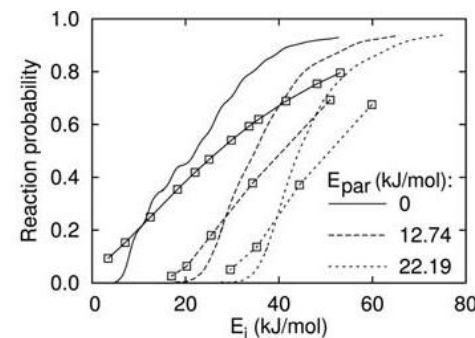
Huang *et al.*, Science **290**, 111 (2000)
 White *et al.*, Nature **433**, 503 (2005)

friction in N₂/Ru(0001)



Luntz *et al.*, JCP **123**, 074704 (2005)
 Díaz *et al.*, PRL **96**, 096102 (2006)

adiabatic approximation for H₂ on Pt(111)



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

description of electronic excitations by a friction coefficient

previously used for:

- damping of adsorbate vibrations: Persson and Helsing, PRL49, 662 (1982)
- dynamics of atomic adsorption Trail, Bird, *et al.*, JCP119, 4539 (2003)
- dissociation dynamics (low dimensions) Luntz *et al.*, JCP 123, 074704 (2005)

classical equations of motion

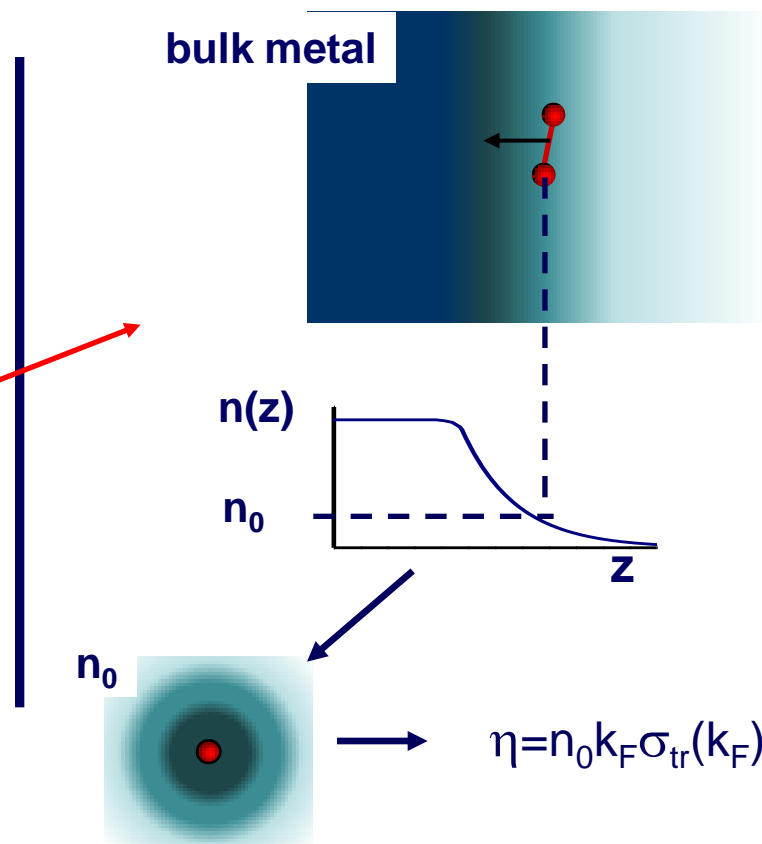
for each atom "i" in the molecule

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

adiabatic force:
6D DFT PES

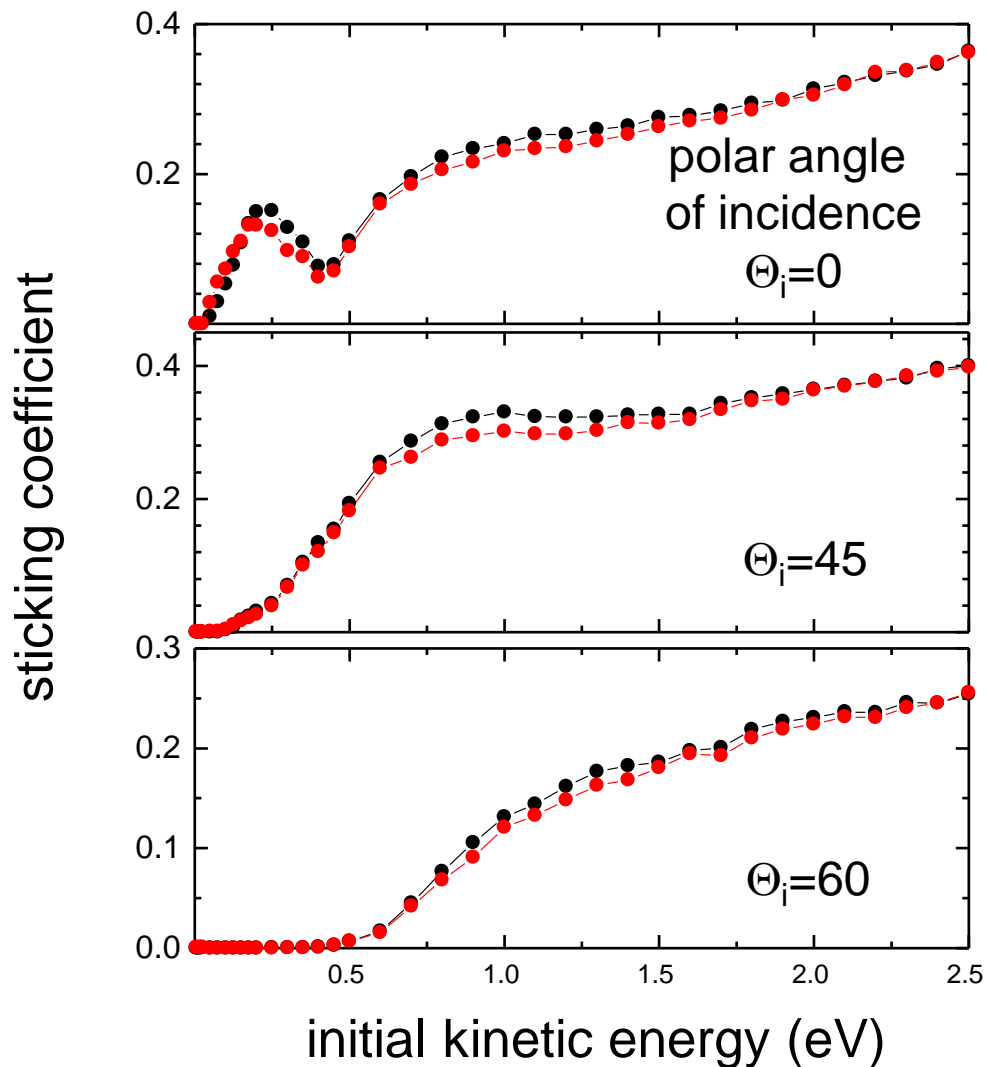
friction coefficient

friction coefficient: effective medium approximation

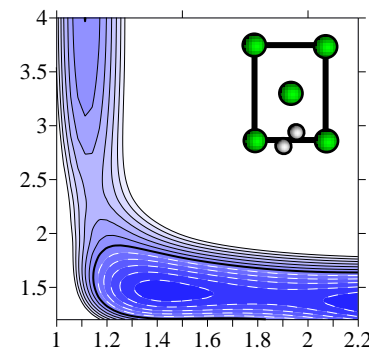


effective medium:
FEG with electronic density n_0

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

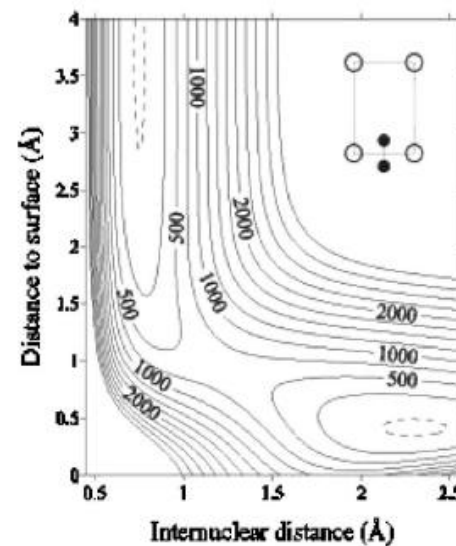
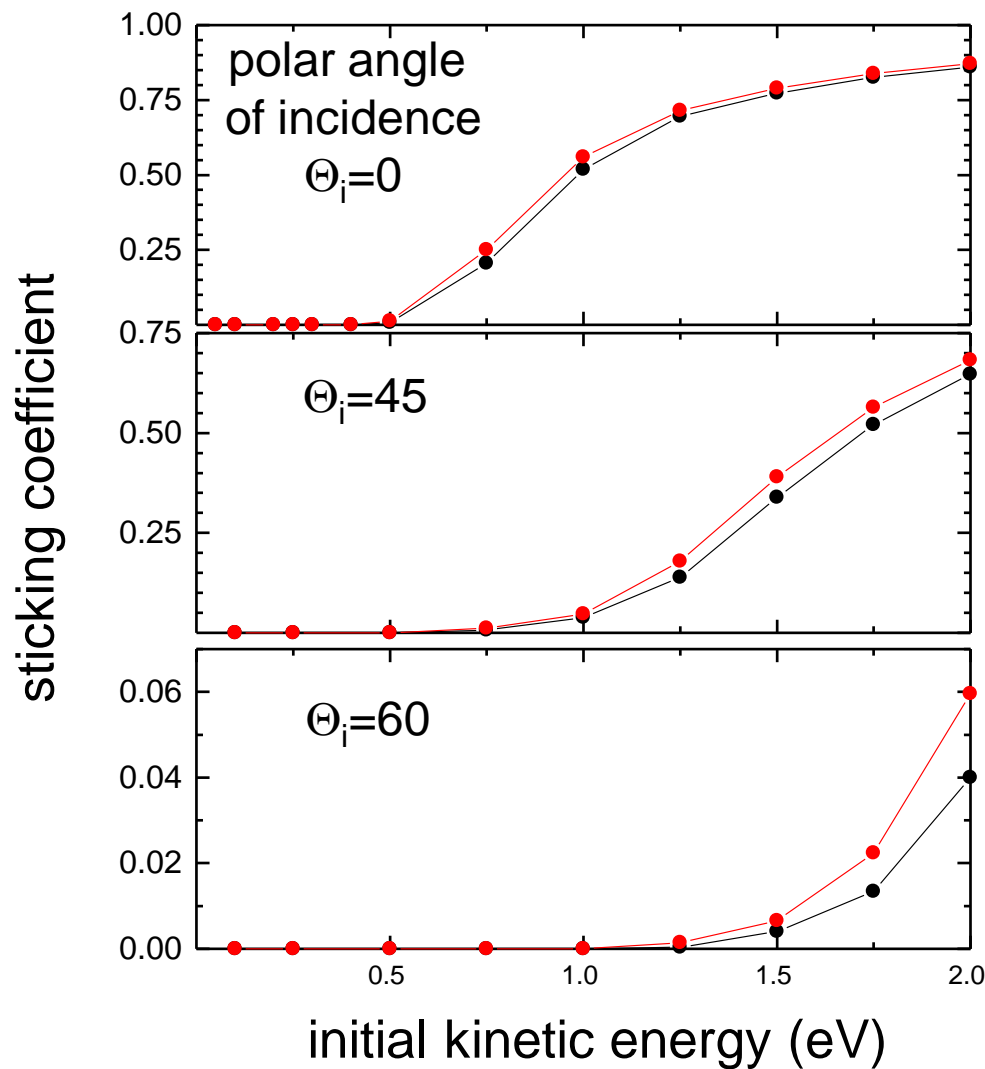


● non-adiabatic
 ● adiabatic



but for this system, dissociation is roughly decided at $Z=2.5\text{\AA}$ (low energies)

probability of dissociative adsorption: H₂ on Cu(110)



[Salin, JCP 124, 104704 (2006)]

● non-adiabatic

● adiabatic

➡ why the excitation of electron-hole pairs is not relevant

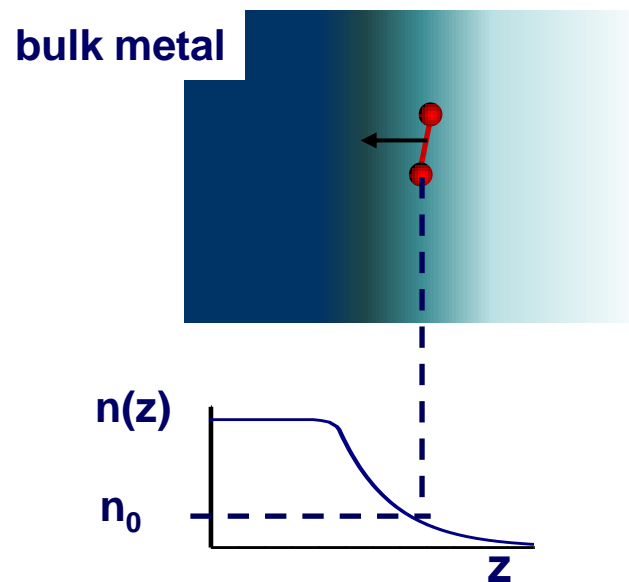
classical equations of motion

for each atom "i" in the molecule

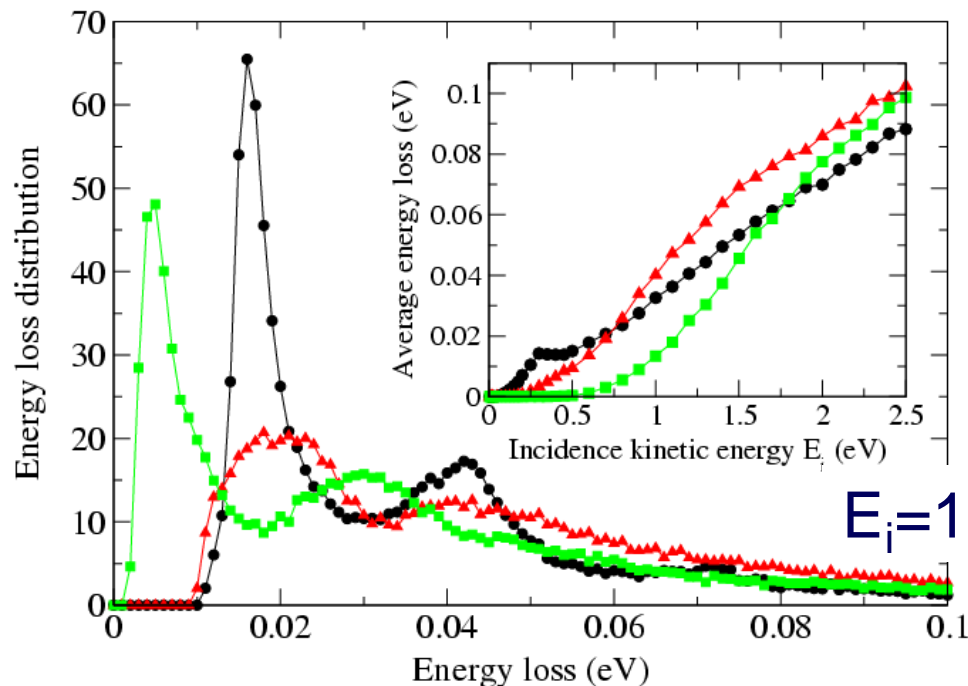
$$m_i(d^2r_i/dt^2) = -dV(r_i, r_j)/d(r_i) - \eta(r_i)(dr_i/dt)$$

friction coefficient

velocity



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



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

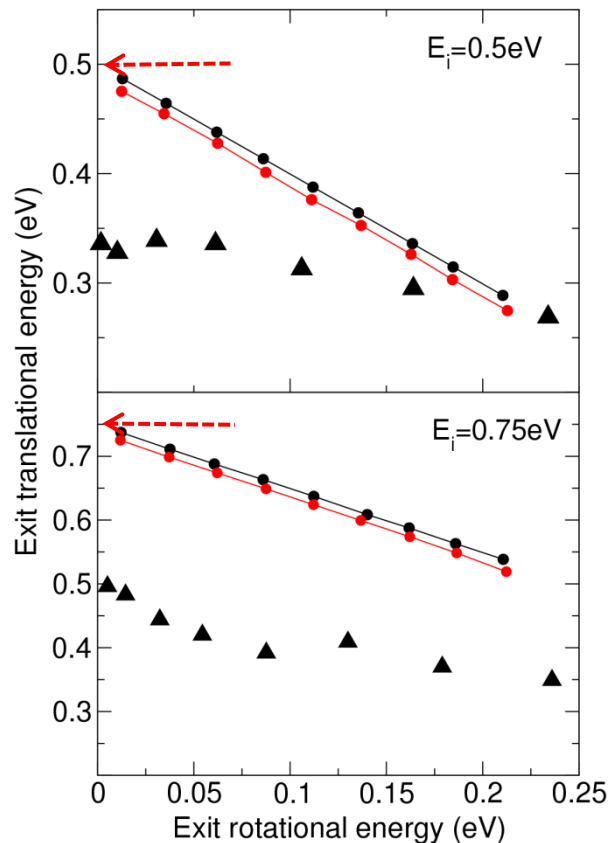
$E_i = 1.5 \text{ eV}$

energy losses in the reflected molecules due to electronic excitations are $< 100 \text{ meV}$

Energy loss of reflected molecules: N₂ on W(110)

Experimental conditions

- $T_s=1200\text{K}$
- $T_{\text{rot}} < 5\text{K}$ ($J=0$)
- Normal incidence and detection

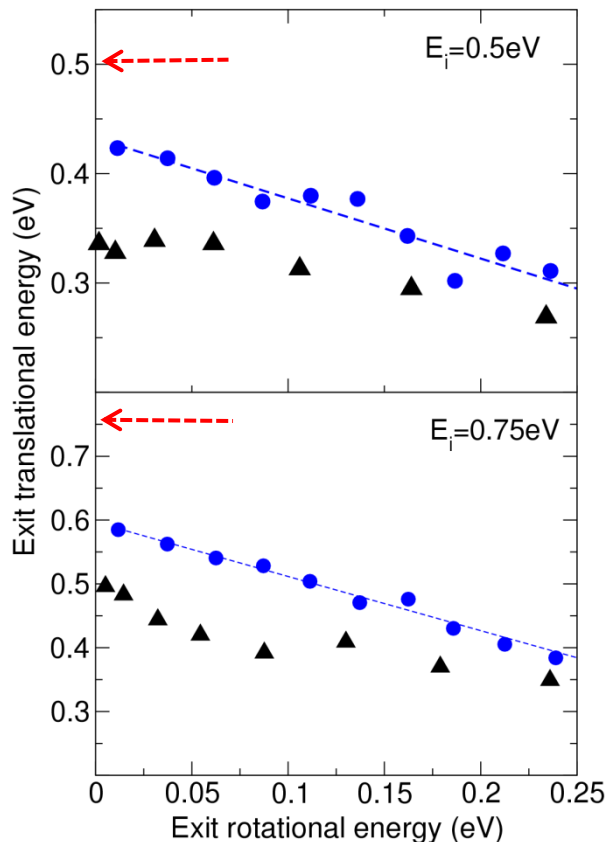


- ▲ Experimental data by Hanisco *et al.* J.Vac.Sci.Technol. A 11, 1907 (1993)
- adiabatic
- electronic friction

Energy loss of reflected molecules: N₂ on W(110)

Experimental conditions

- $T_s = 1200\text{K}$
- $T_{\text{rot}} < 5\text{K}$ ($J=0$)
- Normal incidence and detection



▲ Experimental data by Hanisco *et al.*
 J.Vac.Sci.Technol. A 11, 1907 (1993)

● adiabatic

● GLO: phonons

Phonon excitations are responsible for the energy transfer observed experimentally

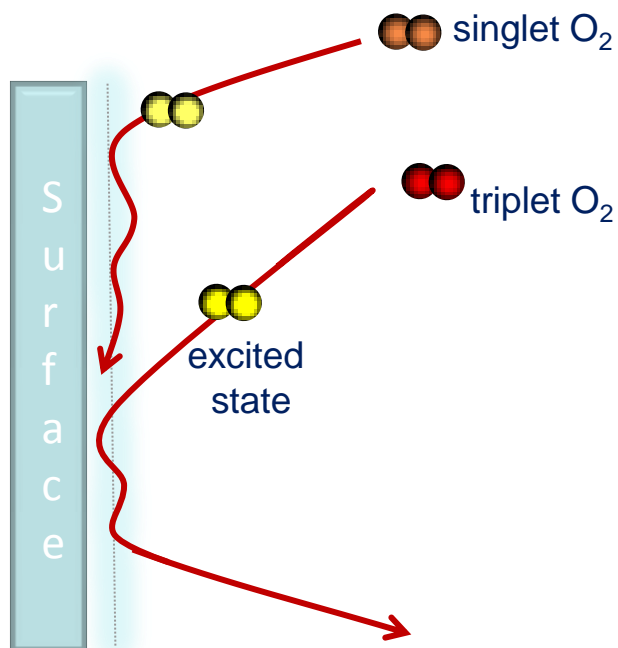
➔ conclusions

- A local description of the friction coefficient shows that electronic excitations play a minor role in the dissociation of N_2/W and H_2/Cu :
The Born-Oppenheimer approximation remains valid in these systems.
- Open questions still remain about the role of electron-hole pair excitations in other situations, in which non-adiabatic effects are due to the crossing of two or more potential energy curves, with possible transfer of charge included.

outline

- brief introduction: adiabatic processes
- electronic excitations at the surface: friction
- **electronic excitations at the molecule**

➡ O₂ on metal surfaces : can we enhance dissociation?

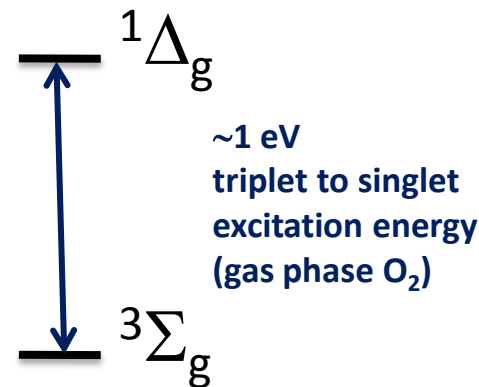


electronic excited states may play a role

non-adiabatic effects in the incoming O₂ molecule

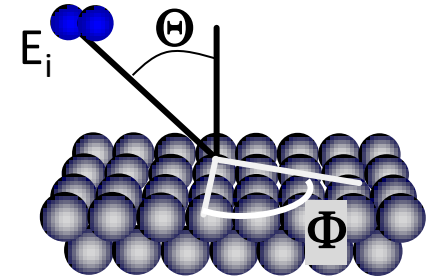
- Yourdshahyan *et al.*, PRB **65**, 075416 (2002)
- Behler *et al.*, PRL **94**, 036104 (2005)
- Carbogno *et al.* PRL **101**, 096104 (2008)

we prepare the incoming O₂ molecule in an excited state

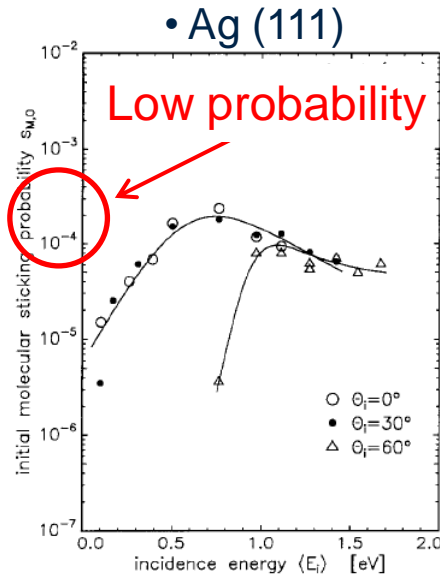


adsorption of O₂ on flat Ag surfaces

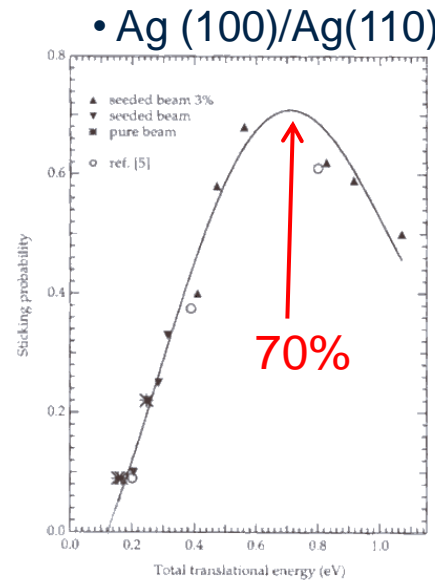
- Ts < 150K: O₂ adsorbs **only molecularly** (E_i < 1eV)



molecular beam experiments



A. Raukema *et al.*,
Surf. Sci. 347, 151
(1996).



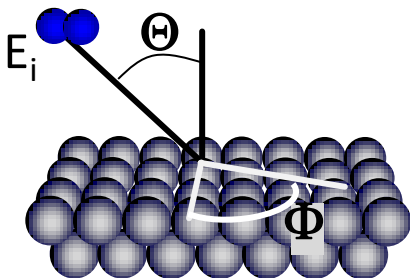
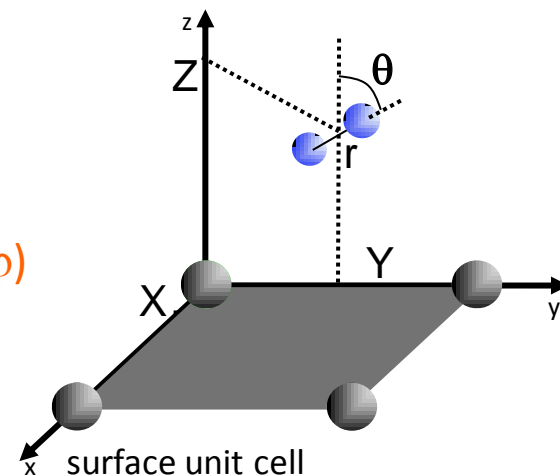
L. Vattuone *et al.*,
Surf. Sci. 408, L698
(1998).

➡ O₂/Ag(100) - theoretical calculations

calculation of the Potential Energy Surface (PES)

- Born-Oppenheimer approximation
- frozen surface approximation \Rightarrow 6D PES: $V(X, Y, Z, r, \theta, \varphi)$

classical trajectory calculations

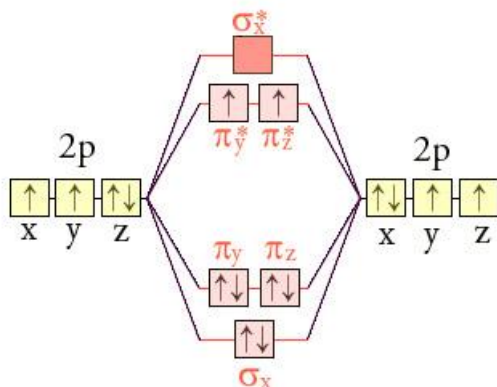


- incidence conditions are fixed:
(E_i, θ)
- Monte-Carlo sampling on the internal degrees of freedom:
(X, Y, θ, φ) and on Φ (parallel velocity)

➡ building the 6D PES

numerical procedure

- O₂ in vacuum **spin-triplet** ground state:



- about 2300 **spin-polarized DFT** values
- interpolation of the DFT data:

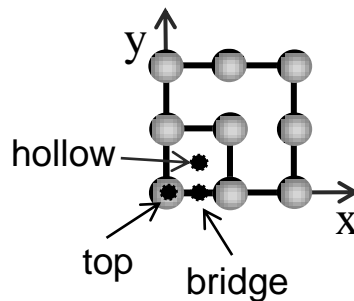
Corrugation reducing procedure

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

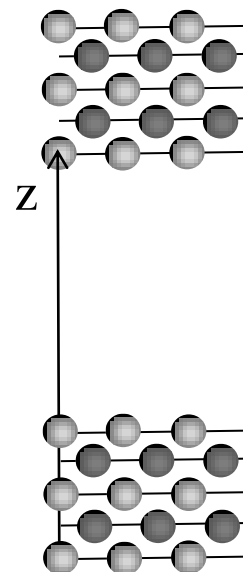
DFT energy data

- DFT - GGA (**PW91**) calculation with **VASP**
- plane-wave basis set and US pseudopotentials
- periodic supercell: (2 x 2) and 5-layer slab

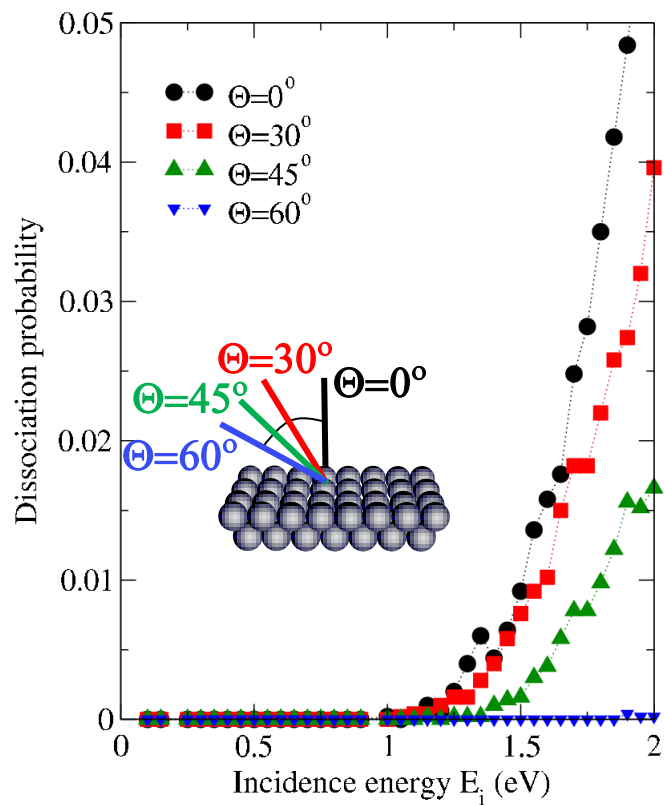
top view



front view



➡ dissociation probability of spin-triplet O₂/Ag(100)

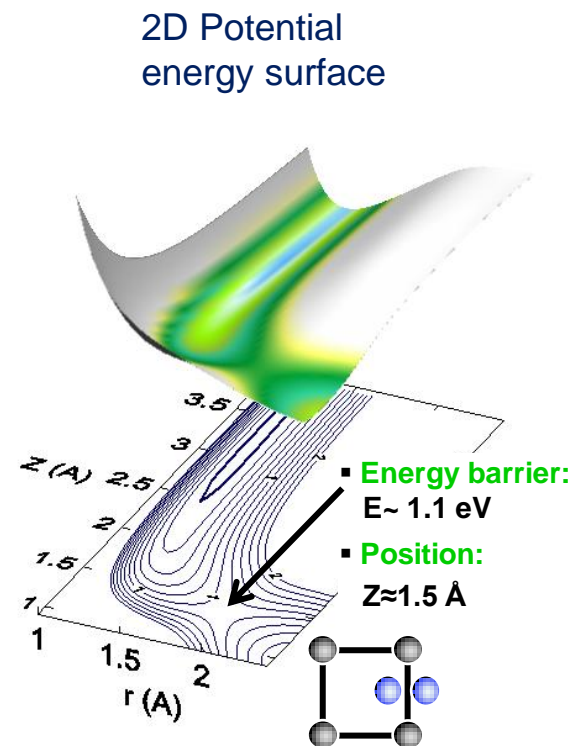


General features:

- Activation energy: ~ 1.1 eV
- Low dissociation probability

Reason:

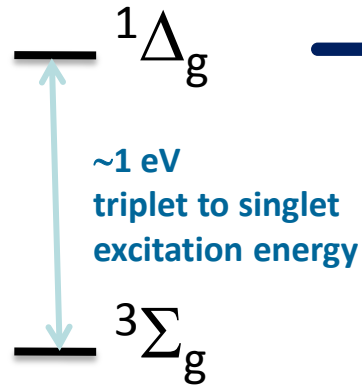
Only configurations around bridge lead to dissociation



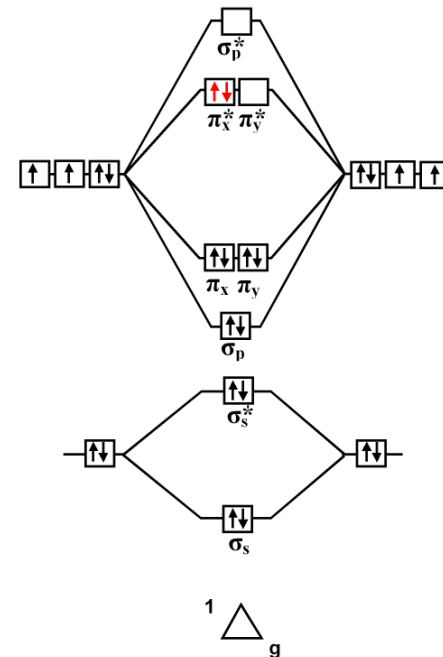
➡ the question

can we enhance O₂ dissociation on clean Ag(100) ?

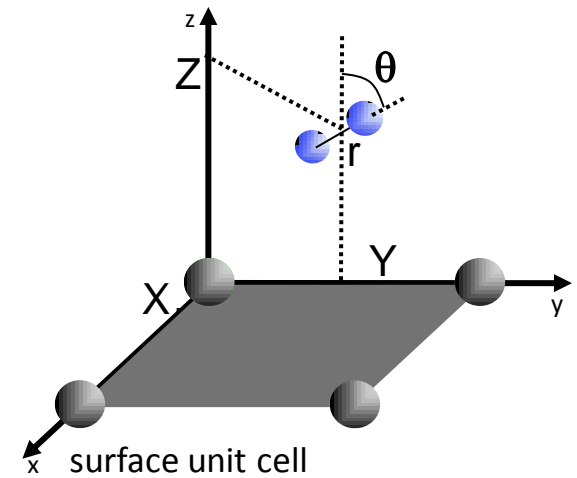
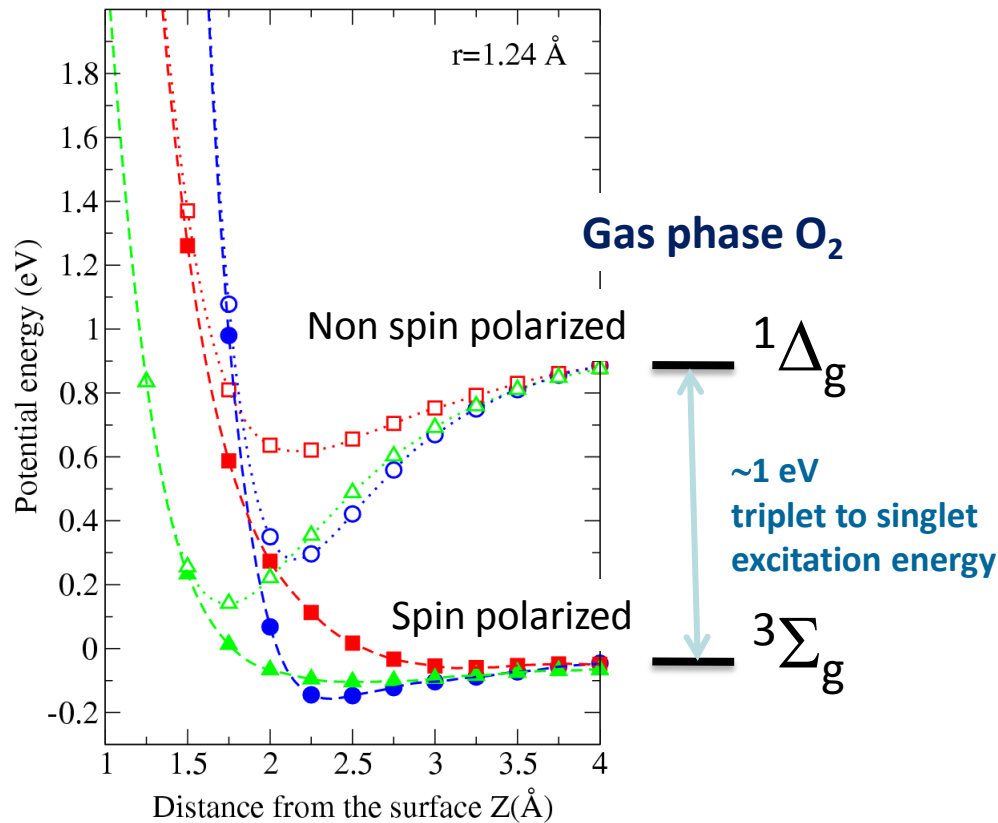
Gas phase O₂



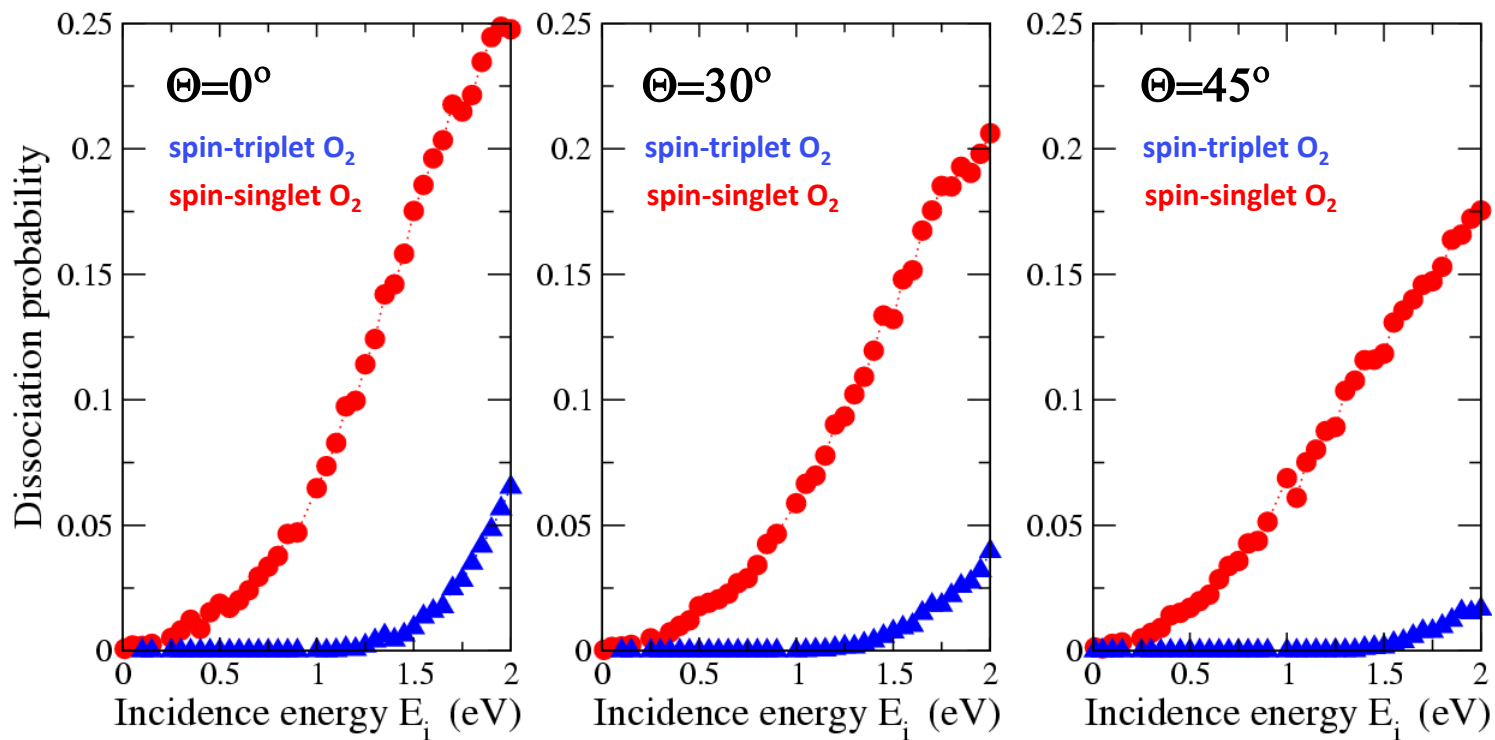
6D PES calculation: Non spin polarized DFT



➔ differences between SP and NSP PESs

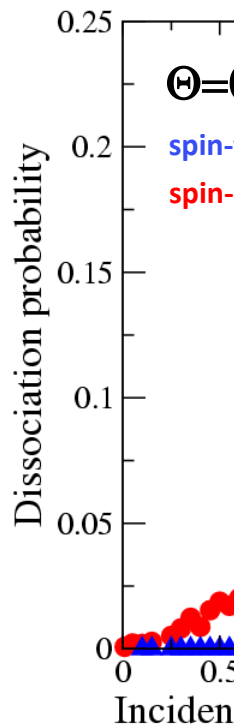


➔ dissociation is enhanced for singlet O₂



dissociation occurs for $E_i < 1$ eV
 dissociation can increase in one order of magnitude

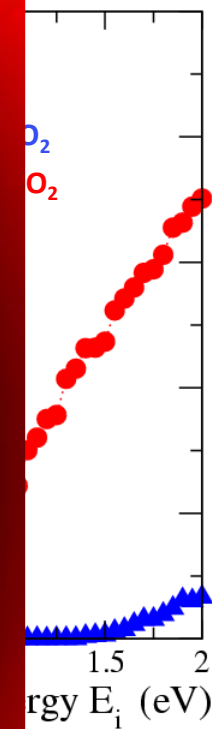
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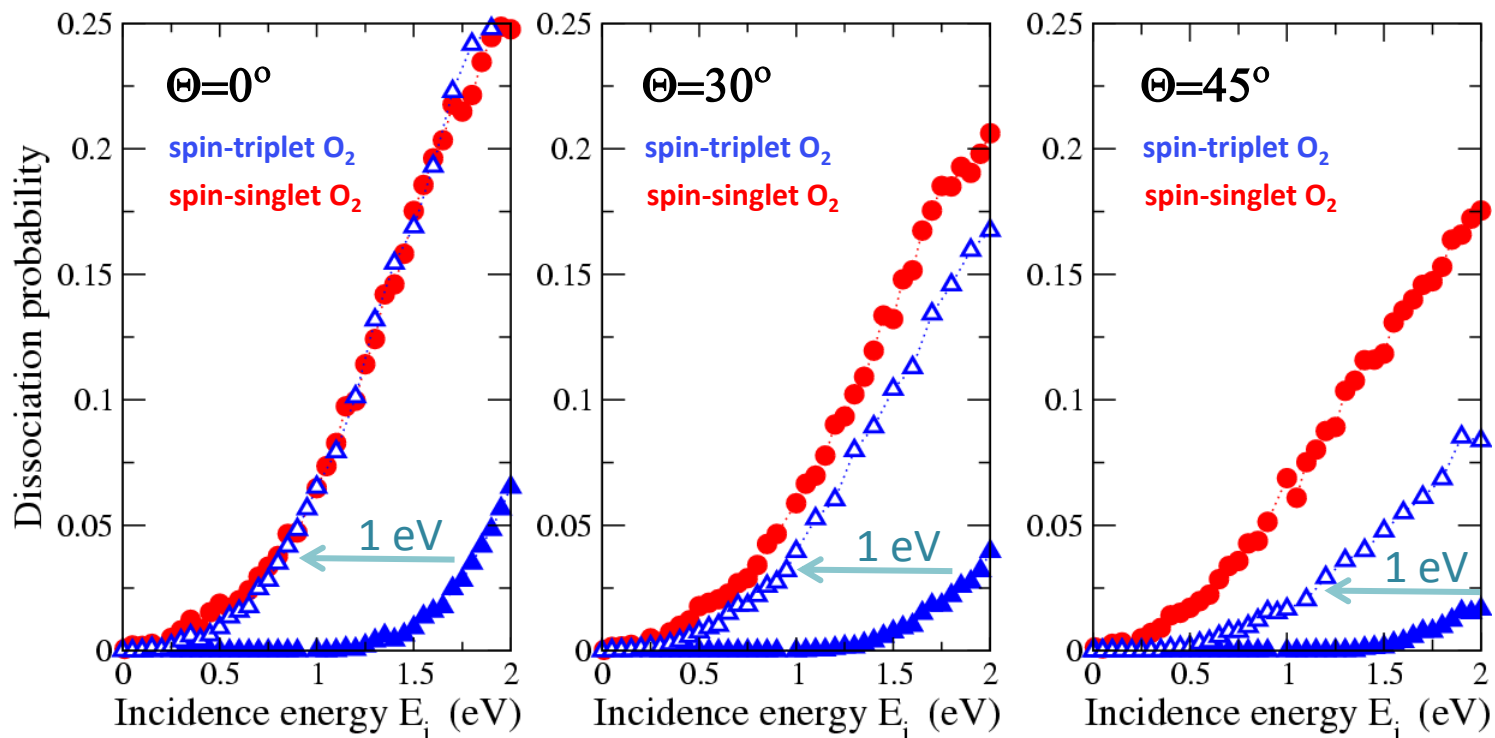
But there is a trick here!
The total energy is 1 eV larger for the singlet O₂

Gas phase O₂

Energy level diagram for Gas phase O₂. The upper level is labeled $1\Delta_g$ and the lower level is labeled $3\Sigma_g$. A vertical double-headed arrow between the levels is labeled $\sim 1\text{ eV}$ triplet to singlet excitation energy.



➡ dissociation is enhanced for singlet O₂

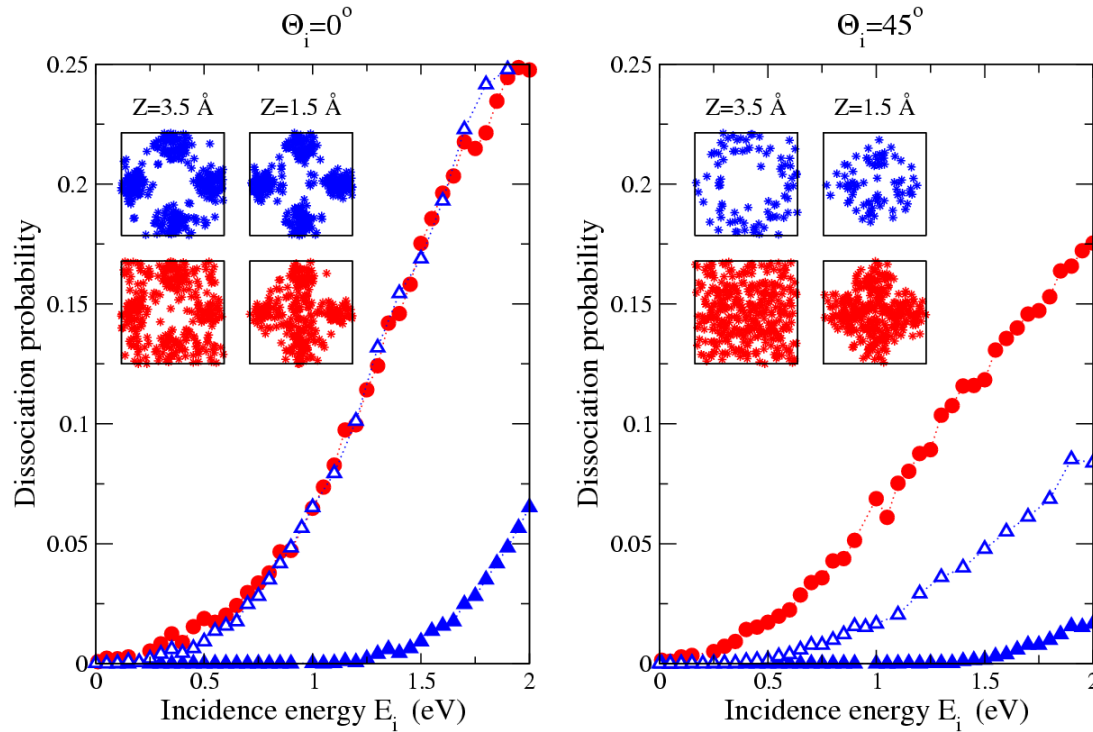


dissociation occurs for $E_i < 1$ eV

dissociation can increase in one order of magnitude

for $\Theta \neq 0^\circ$, singlet-O₂ is more efficient than triplet-O₂ with the same total energy

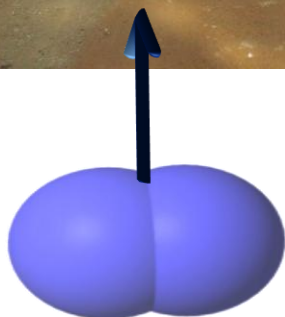
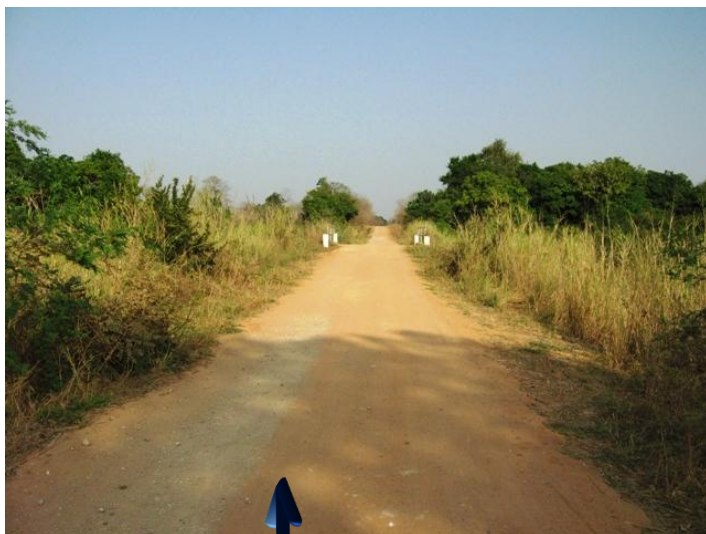
➡ why is that?



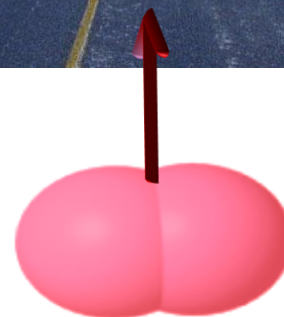
spin-triplet O₂
 spin-singlet O₂

available paths to dissociation are different
 (and more!)

➡ it is not the same road



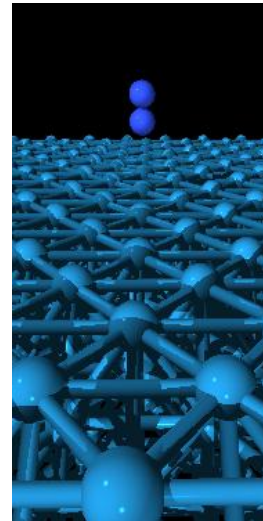
triplet O₂



singlet O₂
+ 1 eV

⇒ conclusions

- Dissociation increases in about one order of magnitude, if singlet- O_2 molecular beams are used.
- The enhancement of the dissociation rate is not only due to the extra energy that we are adding to the system. A different spin state in the incoming O_2 molecule opens new paths to dissociation.



thank you for your attention

