Quantum Effects and Statistics in Chemical Reactions at Surfaces

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New methods:

- *ab initio* molecular dynamics
- *ab initio* quantum dynamics

New results: for example

- Catalytic oxidation of CO
- Dissociative adsorption of H_2
  - a) at Pd (100)
  - b) poisoning by adsorbed sulfur

Density Functional Theory

The energy of the ground state of a many-electron system : $E_0(\{\mathbf{R}_I\}) = \mathrm{Min}_\Psi \langle\Psi|H^e|\Psi\rangle$

Hohenberg and Kohn (1964): The functional

$$n(\mathbf{r}) = n[\Psi] = \langle\Psi|\sum_i \delta(\mathbf{r}-\mathbf{r}_i)|\Psi\rangle \quad (1)$$

can be inverted, *i.e.*,

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N) = \Psi[n(\mathbf{r})]$$

which implies:

$$E_0(\{\mathbf{R}_I\}) = \mathrm{Min}_{n(\mathbf{r})}\, E_{\{\mathbf{R}_I\}}[n]$$

$$E_{\{\mathbf{R}_I\}}[n] = T_s[n] + \int d^3r \; v^{\text{nuc}}_{\{\mathbf{R}_I\}}(\mathbf{r})n(\mathbf{r})$$

$$+\frac{1}{2}\int\int d^3r d^3r' \; \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E^{\text{xc}}[n]$$

with **local-density approximation**
or **generalized gradient approximation**

Accuracy of geometries is better than 0.1 Å. Accuracy of calculated energies (relative) is better than 0.1 eV [for special cases better than 0.01 eV].

Density functional theory

Methods

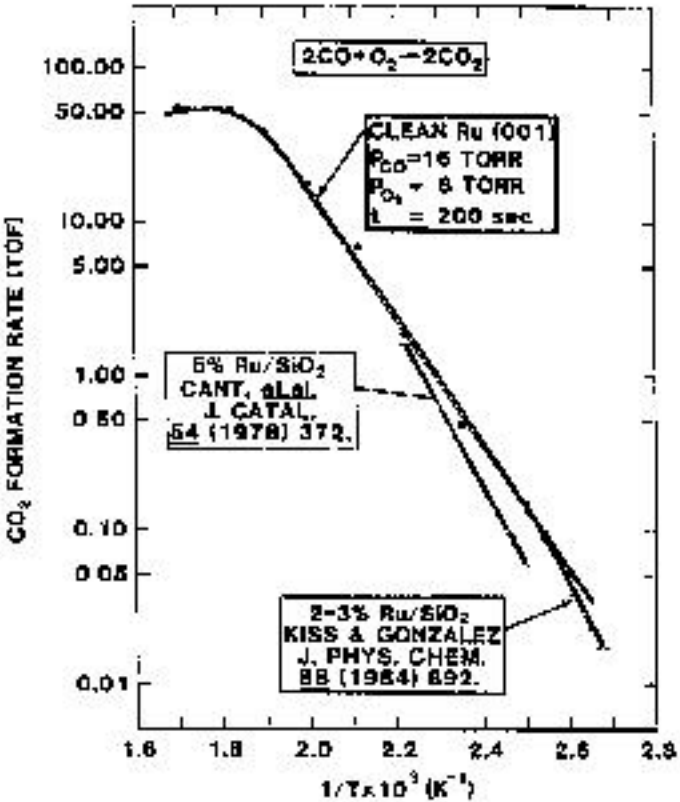
- *ab initio* pseudopotential -- *M. Bockstedte et al., Comp. Phys. Commun.* **XX** *(1998) http://www.fhi-berlin.mpg.de/th/th.html*
- full-potential linear augmented plane wave -- *P. Blaha et al., Comp. Phys. Commun.* **59** *(1990); M. Petersen et al.,Comp. Phys. Commun.* **XX** *(1998)*

unbiased, systematically improvable basis set

accurate forces; electronic self-consistency and optimization of the geometry

$$CO + \frac{1}{2}O_2 \longrightarrow CO_2$$

CO_2 formation at Ru supported catalysts and Ru single crystals

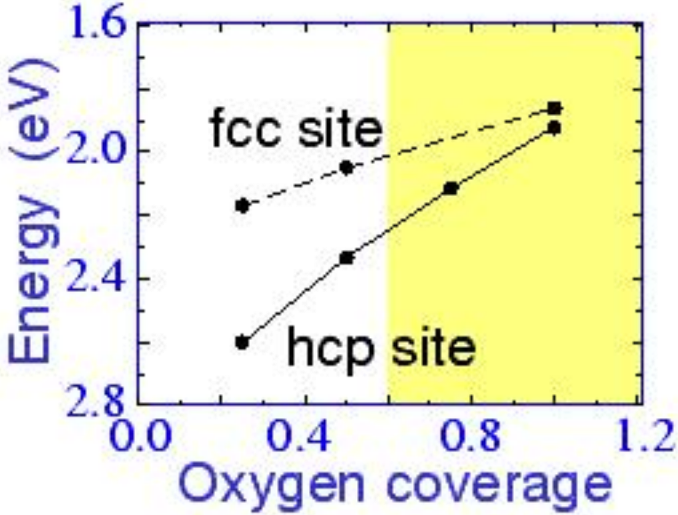


At UHV conditions Ru is least active for CO oxidation. At high-pressure conditions it is best.

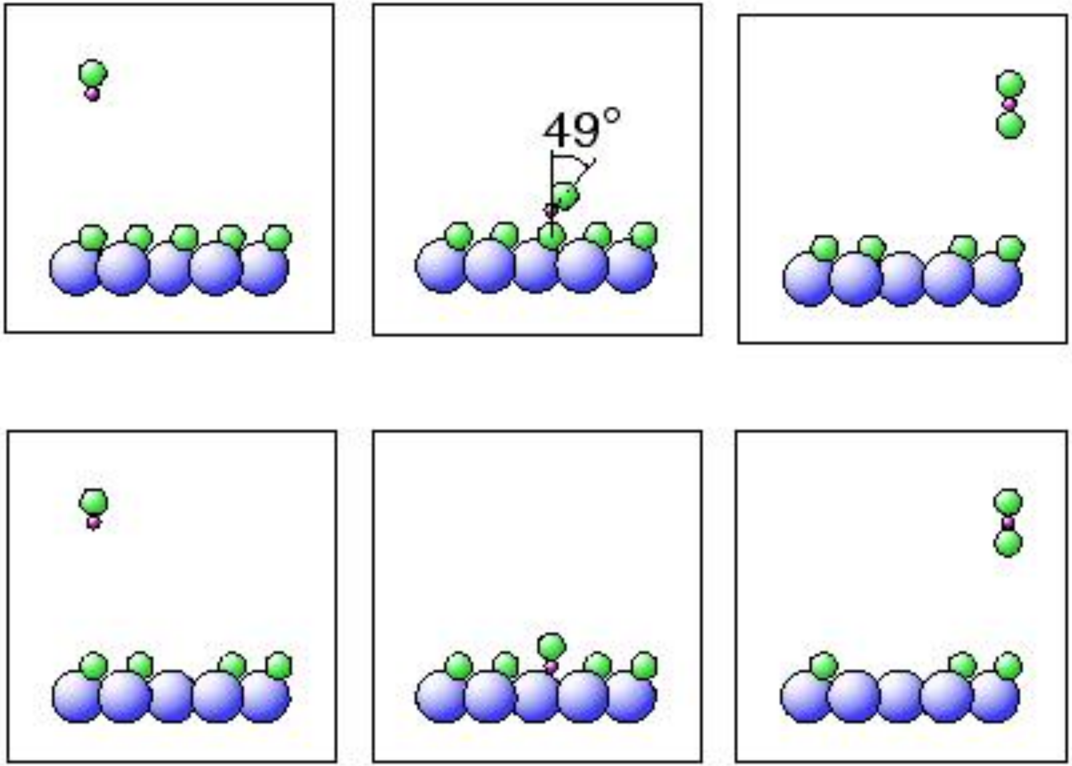
Catalytic Oxidation of CO

Example: the high efficiency of Ru

Energy of
O/Ru(0001) with
respect to O_2 gas
C. Stampfl, M.S.,
PRB **53** *(1996).*



kinetically hindered region == oxygen phase with atypically weak O - metal bond.
C. Stampfl et al., PRL **77** *(1997)*

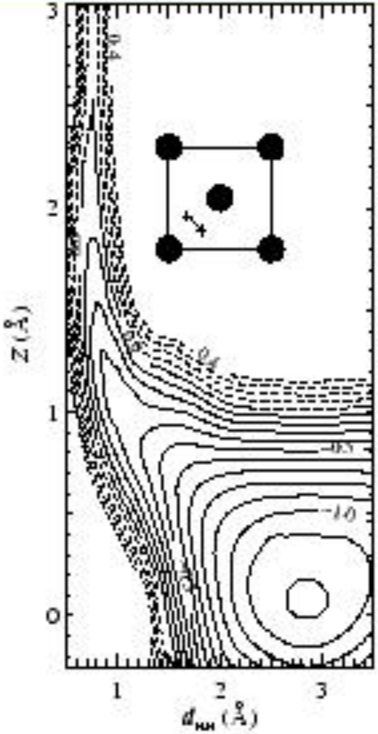

49°

Trends of the Chemical Activity

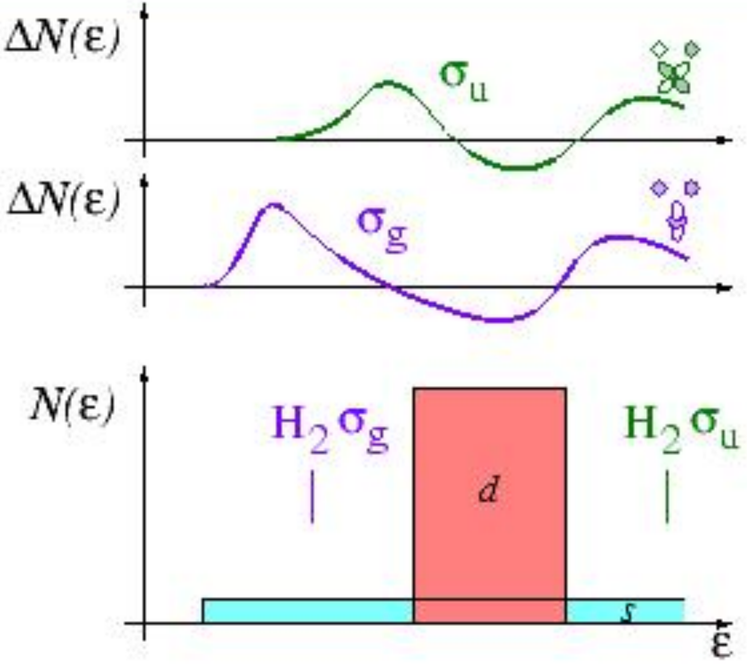
- e.g. for H_2 / Pd(100):
  no energy barrier

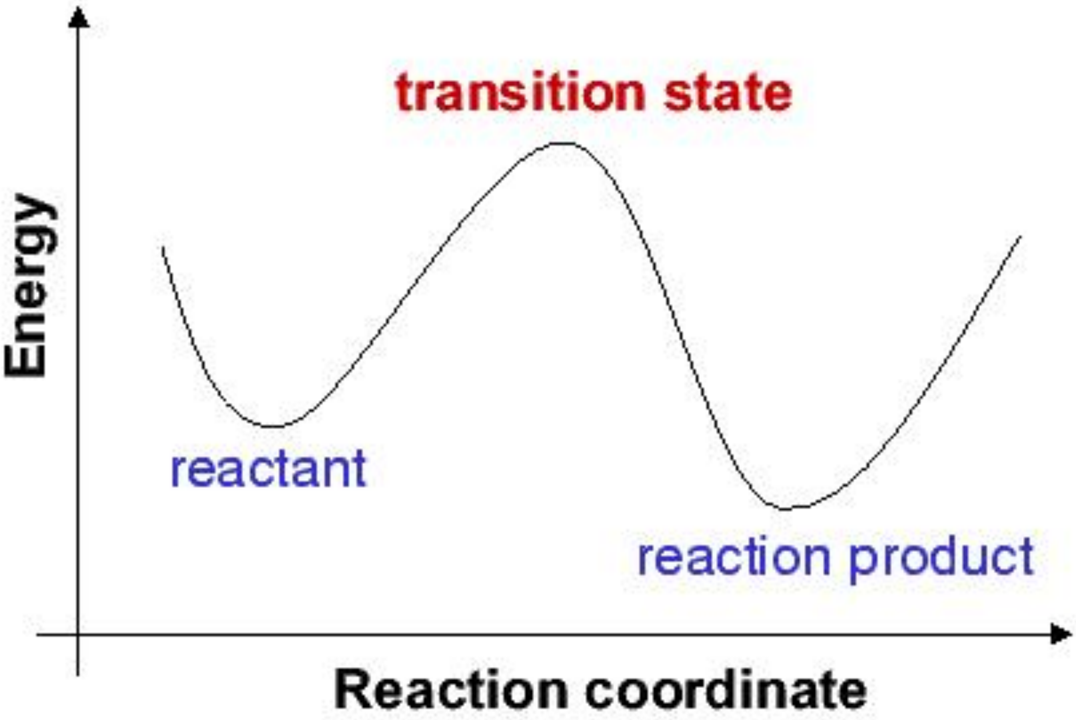
  S.Wilke, M.S.,
  Surf. Sci. (1995)

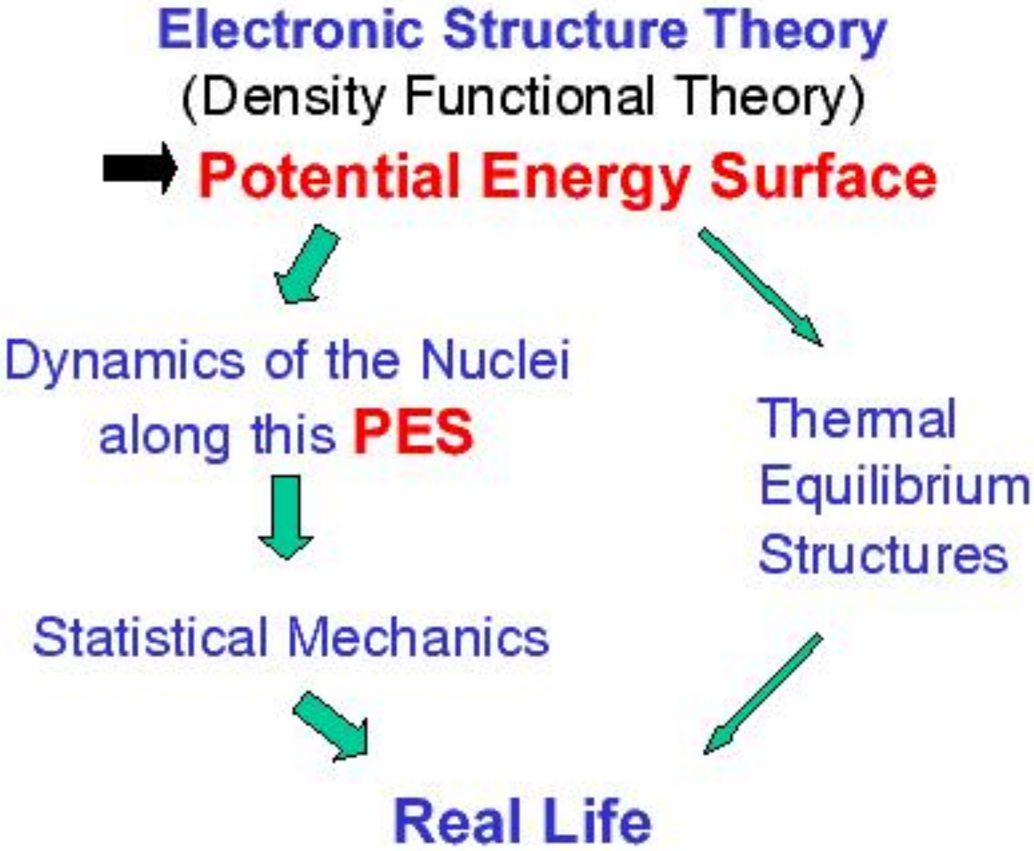
- e.g. for Cu(111):
  energy barrier = 0.5 eV
  at $Z = 1.3$ Å, $d = 1.08$ Å,
  i.e. in the "exit channel"



The Nature of the Interaction at the Transition State




transition state
Energy
reactant
reaction product
Reaction coordinate



Electronic Structure Theory

(Density Functional Theory)

➡ **Potential Energy Surface**

Dynamics of the Nuclei
along this **PES**

Statistical Mechanics

Thermal
Equilibrium
Structures

Real Life

1) Calculate the potential energy of the interaction of H_2 and the surface on a grid using DFT-GGA → PES, dimension > 6

2) Find a representation of this PES

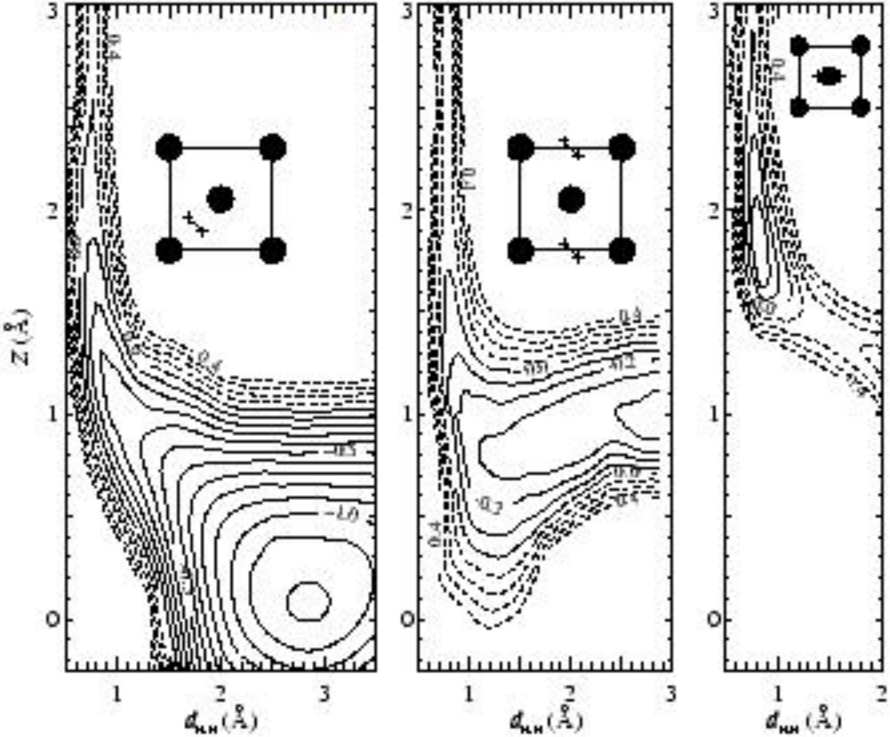
3a) Solve Newton equations of motion of the nuclei moving on such a PES (*ab initio* molecular dynamics)

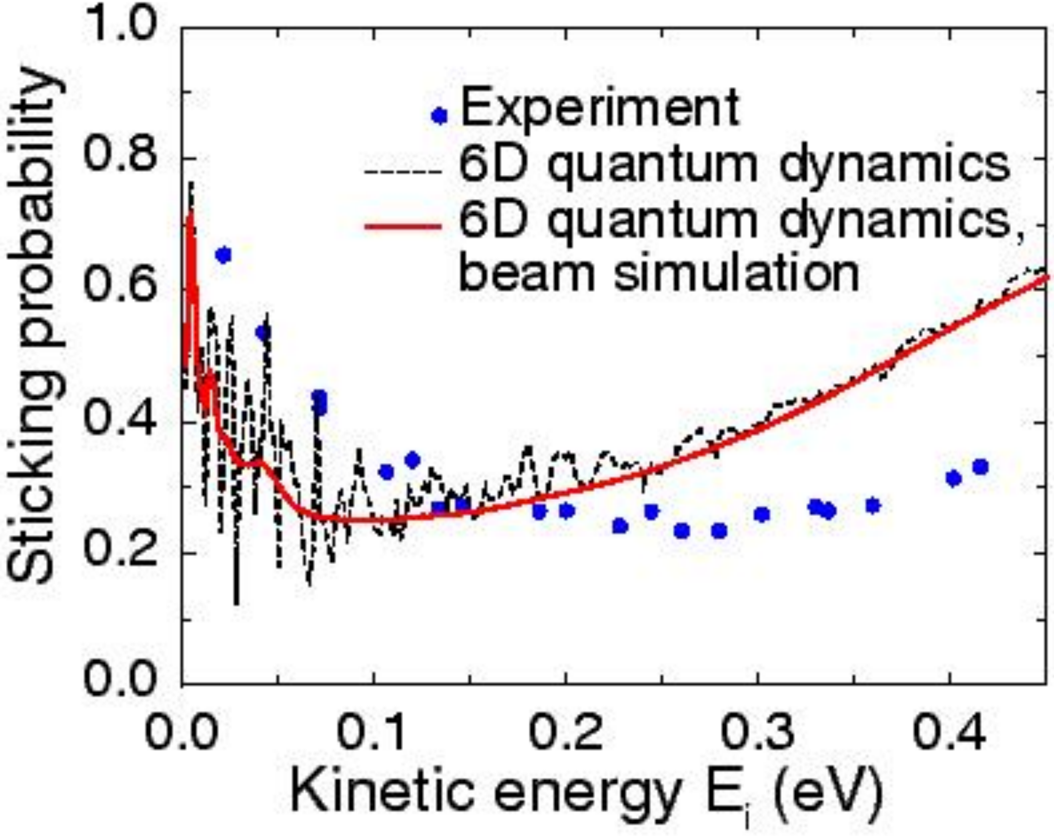
3b) Solve Schrödinger equ. of the nuclei with this PES (*ab initio* quantum dynamics)

$$\left\{ \sum_I \frac{-\hbar^2}{2M_I} \nabla^2_{\mathbf{R}_I} + V(Z,d;X,Y,\theta,\phi) \right\} \chi = E\ \chi$$

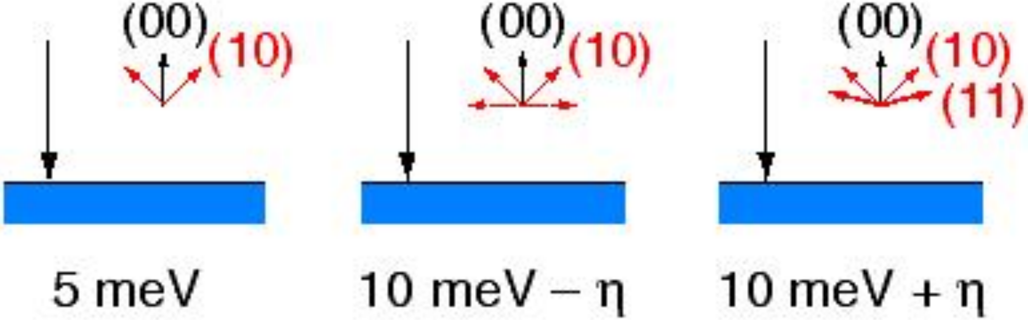
A. Gross, S. Wilke, M.S., PRL ***75****, (1995); PRB* ***57****, Jan. 1998*

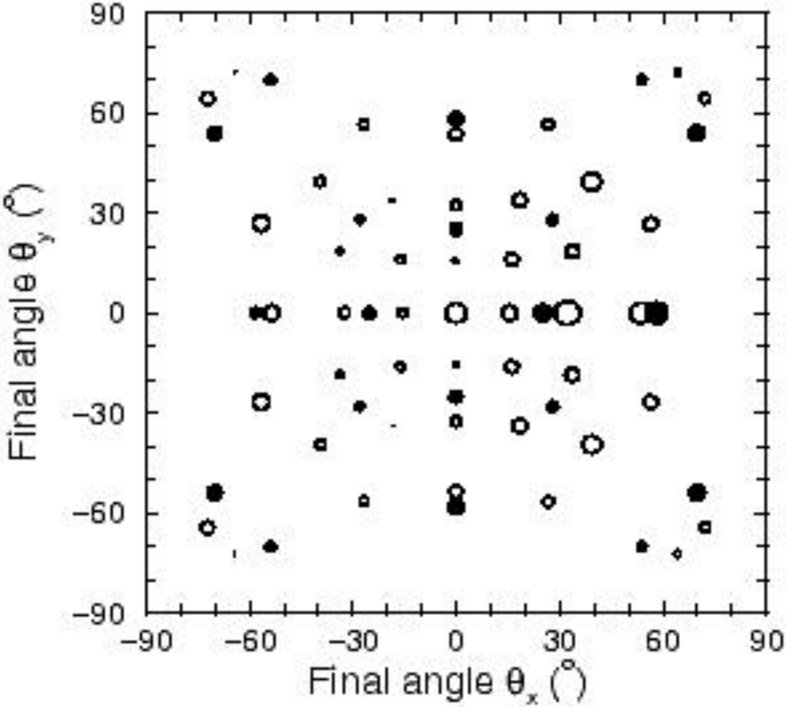
Ab initio potential-energy surface (PES) of H_2 at Pd(100)




Experiment
6D quantum dynamics
6D quantum dynamics, beam simulation
Sticking probability
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.1
0.2
0.3
0.4
Kinetic energy E_i (eV)

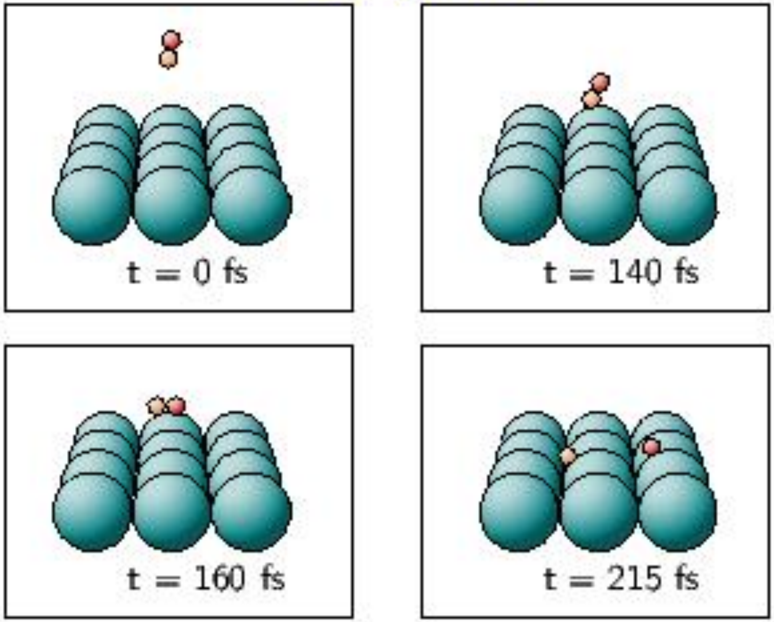
Oscillations reflect the thresholds
e.g., exit conditions of reflected beams



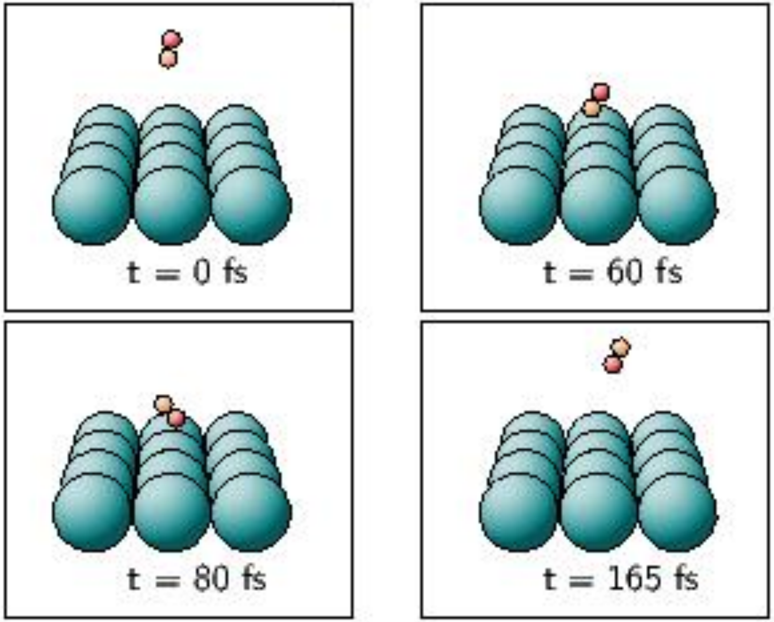

90
60
30
0
−30
−60
−90
−90
−60
−30
0
30
60
90
Final angle θ_y (°)
Final angle θ_x (°)

Molecular Dynamics Snapshots of $H_2 \rightarrow Pd(100)$

Steering effect: aligning the incoming molecule (at low energies; here: $E_i = 0.01$ eV)



$E_i = 0.12$ eV

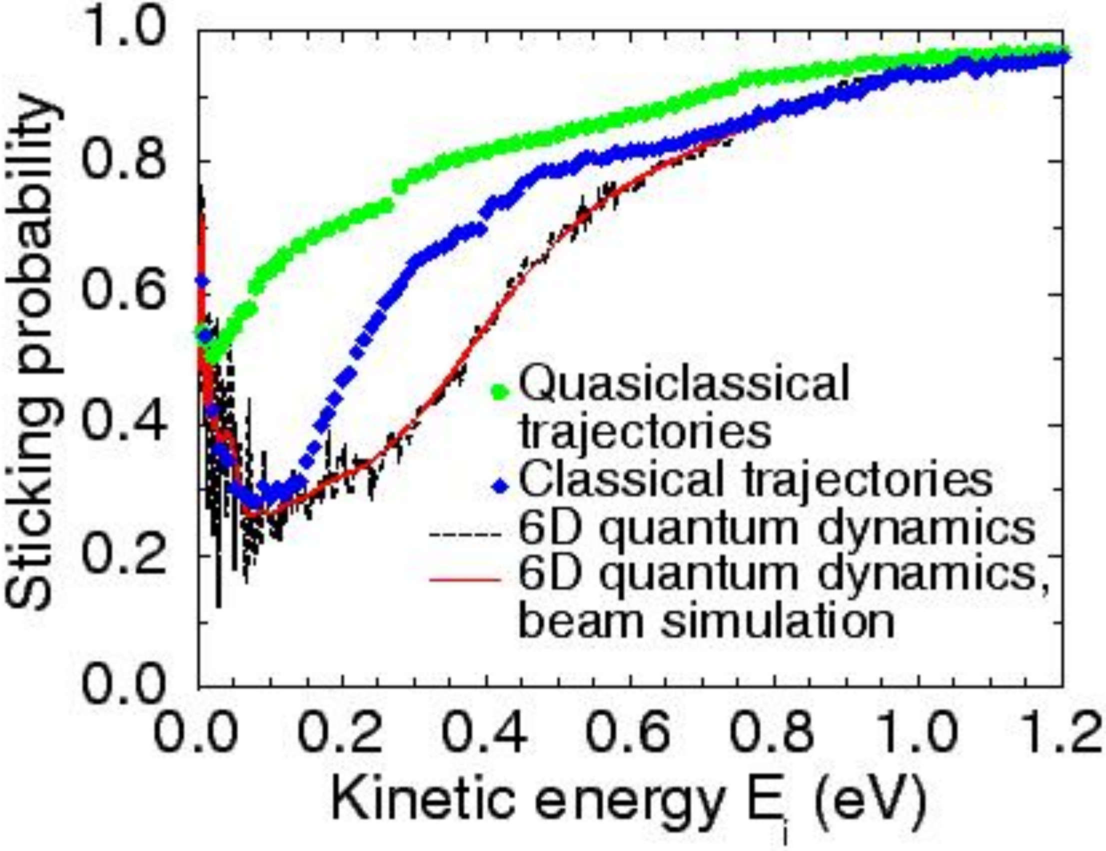


Comparison of quantum dynamics

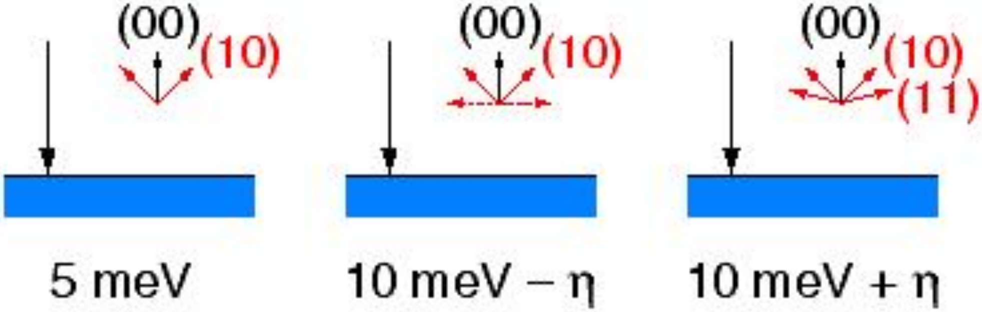
and

molecular dynamics

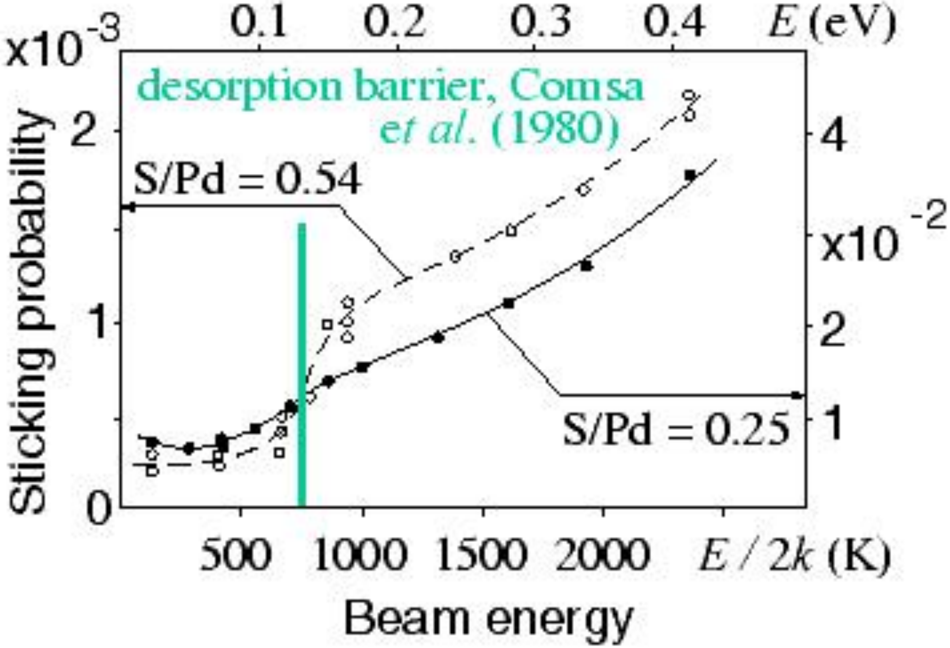
using the same *ab initio* PES


Sticking probability
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.2
0.4
0.6
0.8
1.0
1.2
Kinetic energy E_i (eV)
Quasiclassical trajectories
Classical trajectories
6D quantum dynamics
6D quantum dynamics, beam simulation

Oscillations reflect the thresholds
e.g., exit conditions of reflected beams

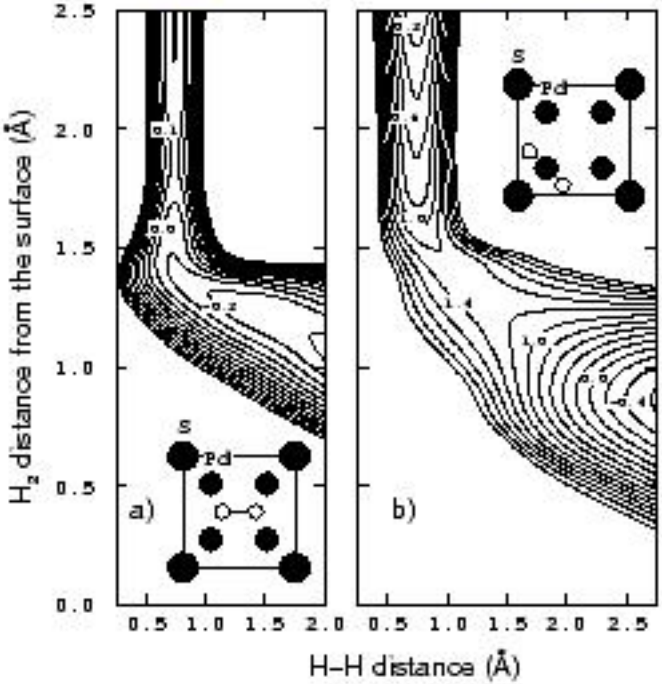


Adsorbed sulfur poisons the H_2 dissociation at Pd (100)



Rendulic *et al.* (1989)

$H_2 \rightarrow S - Pd (100)$ $?_S = 0.25$



adsorption
of H is only
weakly
affected
by sulfur

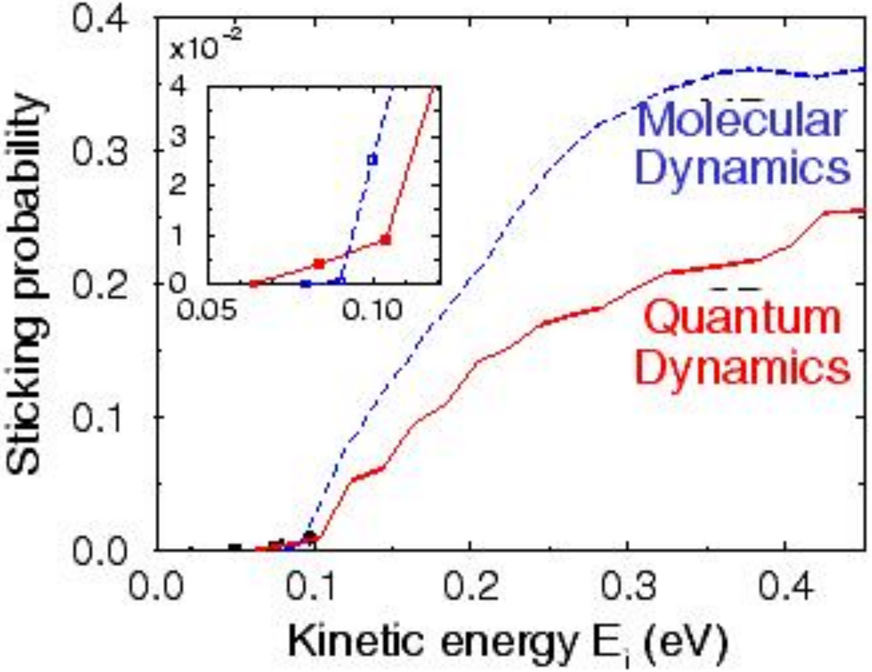
S. Wilke and M. Scheffler, PRL **76** (1996)
C.M. Wei, A. Gross, and M. Scheffler, submitted

"Established" concepts

Energy barriers in the entrance channel are effective, because the H-H bond is not yet weakened when the molecule meets the barrier.

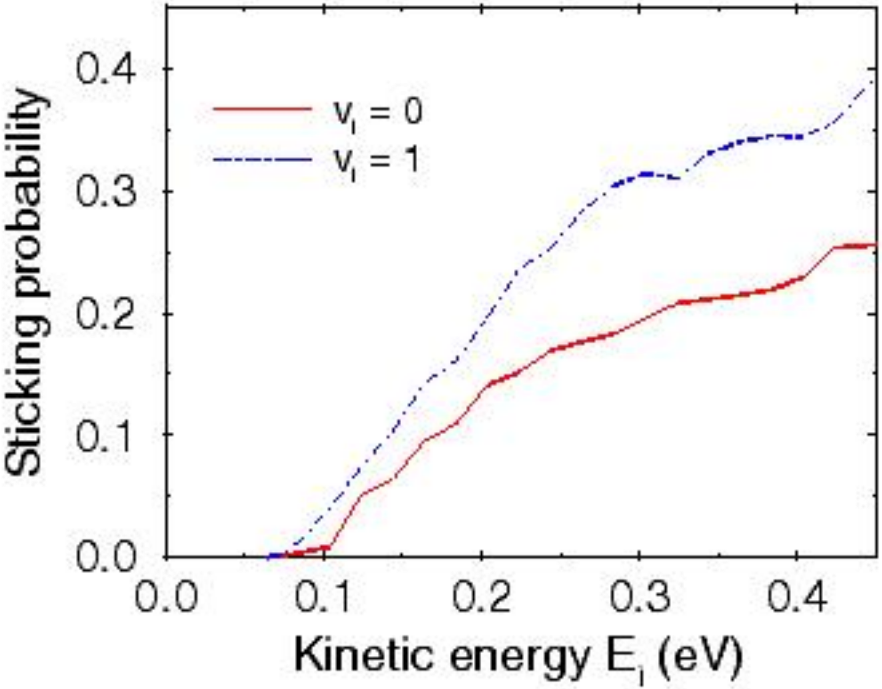
Vibrational excitation of the impinging molecules does not help the dissociation very much; desorbing molecules are vibrationally cool.

H_2 → S - Pd (100) $?_S = 0.25$



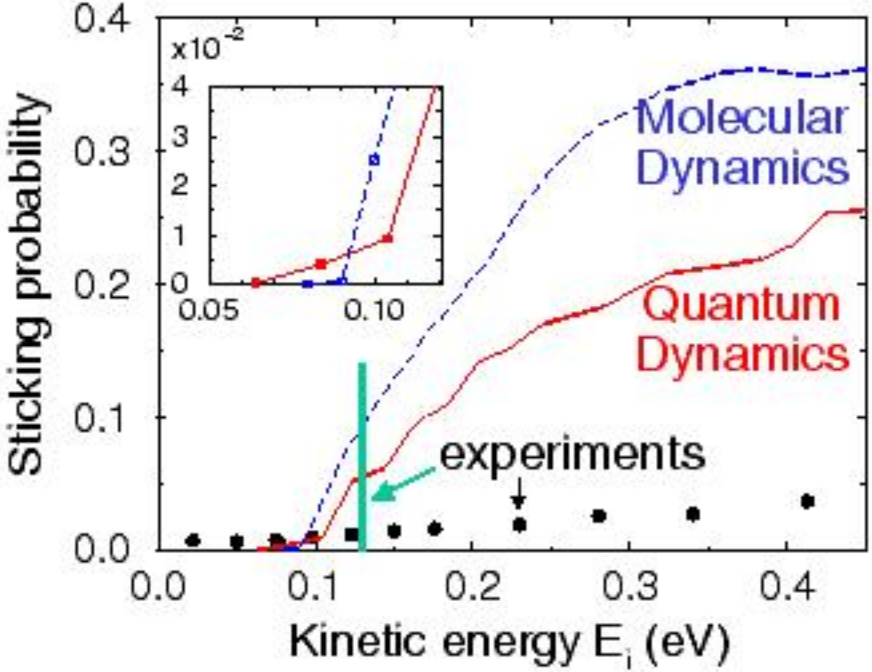
A. Gross, C.-M. Wei, and M. Scheffler, Phys. Rev. B (1998)

$H_2 \rightarrow$ S - Pd (100)



A. Gross, C.-M. Wei, and M. Scheffler (1998)

H_2 → S - Pd (100) $?_S = 0.25$



A. Gross, C.-M. Wei, and M. Scheffler (1998)

Summary:

- **Efficient and accurate DFT methods for big systems**
  http://www.fhi-berlin.mpg.de/th/th.htm
- ***ab initio* molecular dynamics with more than 100,000 trajectories**
- ***ab initio* quantum dynamics**

we speculate that subsurface adsorbates play a bigger role than hitherto anticipated.

Fotos of

Axel, Cathy, Steffen, Ching-Ming