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Dynamics of H_2 dissociative adsorption on metallic surfaces

GDR ARCHES - Nouan le Fuzelier
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The gas/surface group in Bordeaux

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Outlines

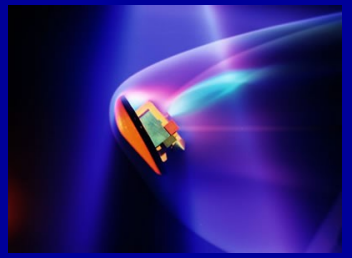
- Introduction – Why studying gas-surface reactions ?
- Models, approximations and simulation tools
- Example : H_2 + Pd(111) and the dynamic trapping mechanism
- Conclusion and prospects

Introduction

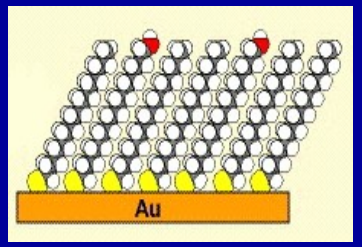
- Heterogeneous catalysis (industrial processes, reduction pollutants, storage of chemical compounds …)

- Chemistry in the atmospheric and interstellar media

- Heating of space shuttles during atmospheric re-entries : « Catalycity »



- Surface functionalization, preparation of self-assembled monolayers (SAM)



… and many other fields of application

Introduction

The reactivity is influenced by many parameters :

- electronic and geometric structure of the surface
- surface defects (adatoms, steps, reconstructions)
- nature of the surface (metal, semi-conductor, alloy)
- pre-adsorbed molecules or atoms (promotors or poisons)
- ro-vibrational state of the impinging molecules
- incidence angle (molecular beam)
- diffusion of the products on the surface etc …

The problem is quite complex !!!

Introduction

- **Experiments :**

  - Molecular beams + vacuum technology (UHV)

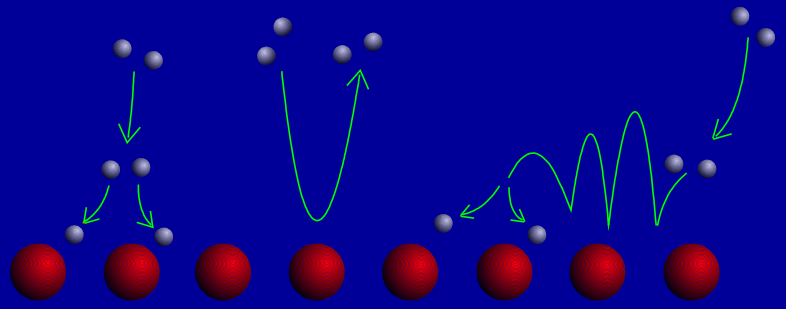
  - Probing the surface at the molecular level (HREELS, AES, LEED, STM, AFM)

- Theory :

  - Electronic structure calculations (DFT for periodic systems)

  - Determination of the PES by interpolation techniques

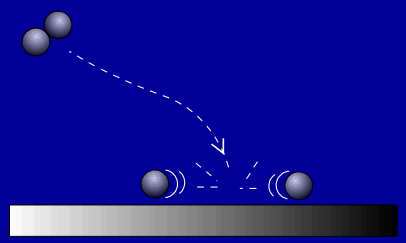
  - Simulation of the dynamics : classical or quantum approaches



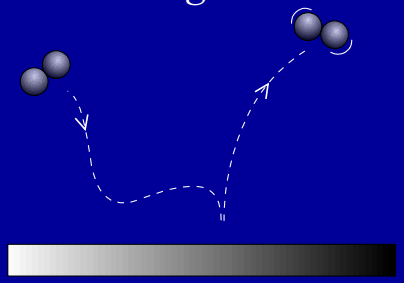
Models and approximations

- **Some types of mechanisms**

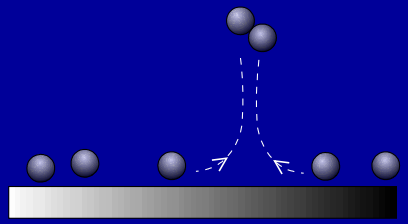
Dissociative adsorption



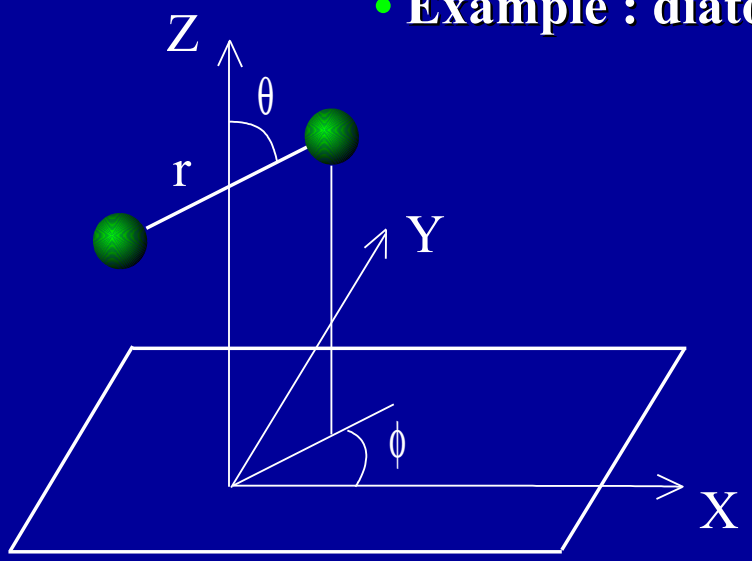
(in)elastic scattering



Associative desorption



- **Example : diatomic molecule / surface**



6D model (rigid surface)

Multi-dimensional dynamics

Models and approximations

- **Approximations :**
  - Born-Oppenheimer
  - Rigid surface (infinite, periodic, no defects, fixed atoms)
  - No energy loss by electronic excitation
  - Reduced models / classical approximation

- **More elaborated treatments :**
  - Surface atoms : thermic bath, generalised Langevin oscillators
  - Defects : surface with steps, clusters
  - Electronic effects : electron-hole pairs, friction terms
  - High-dimensional Quantum Dynamics : MCTDH ?

Example : H_2 + Pd(111)

Example : dissociative adsorption of H_2 on Pd(111)

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(ISM Bordeaux, France)

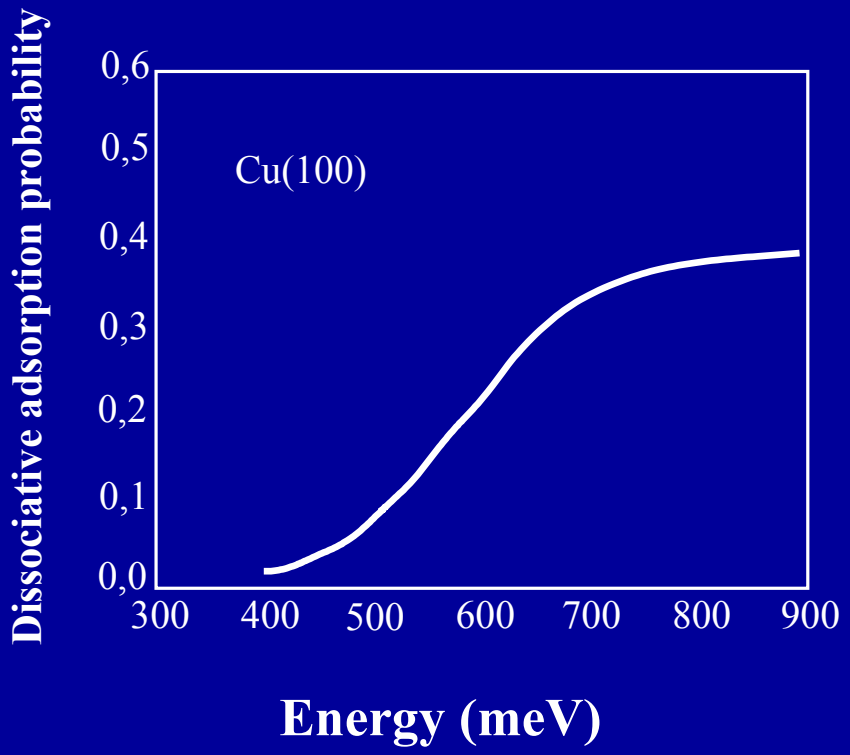
H.F. Busnengo
(Instituto de Fisica Rosario, Argentina)

W. Dong
(ENS Lyon, France)

Example : dissociative adsorption of H_2 on Pd(111)

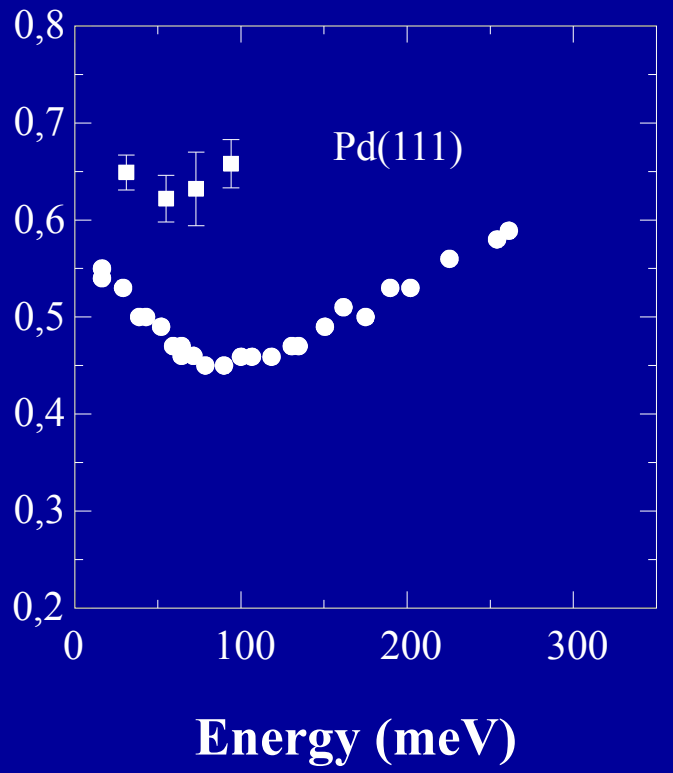
Activated system

= potential barriers



Non-activated system

= no barriers

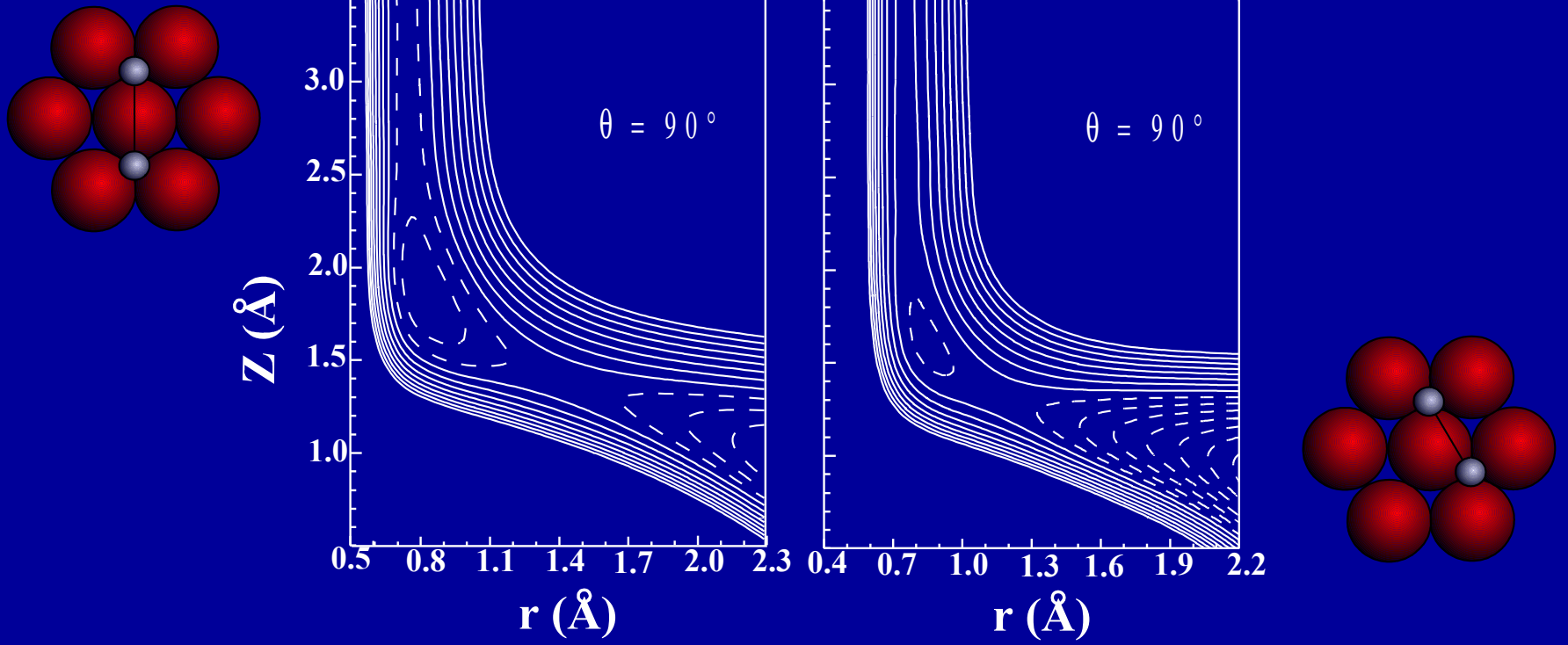


Example : dissociative adsorption of H_2 on Pd(111)

PES = cubic splines interpolation + corrugation reducing procedure

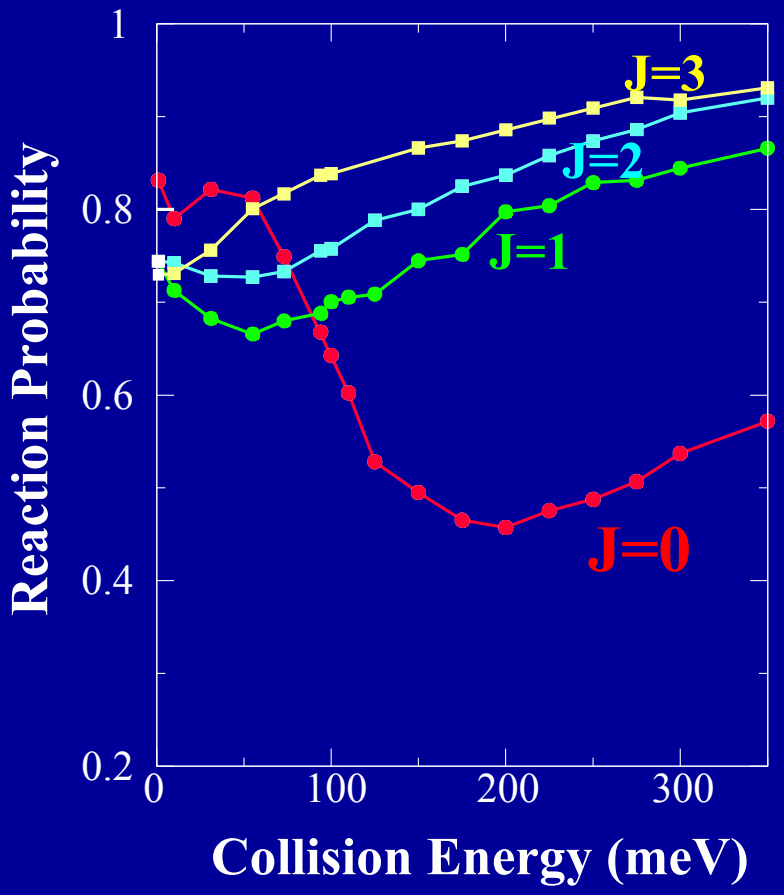
(H.F. Busnengo, A. Salin, J. Chem. Phys. 112, 7641(2000))

→ several non-activated reaction paths



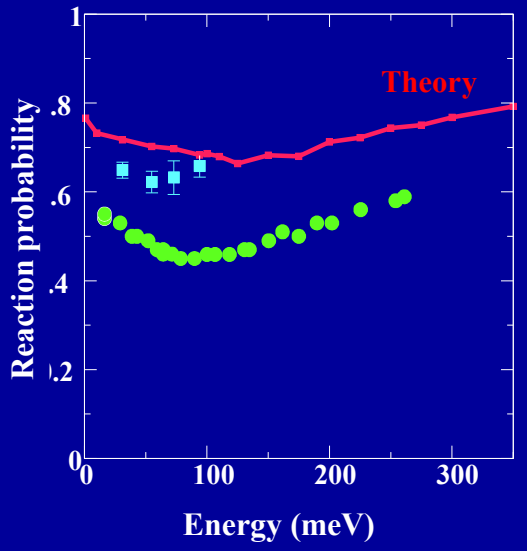
Example : dissociative adsorption of H_2 on Pd(111)

- Results of the simulation (v = 0)



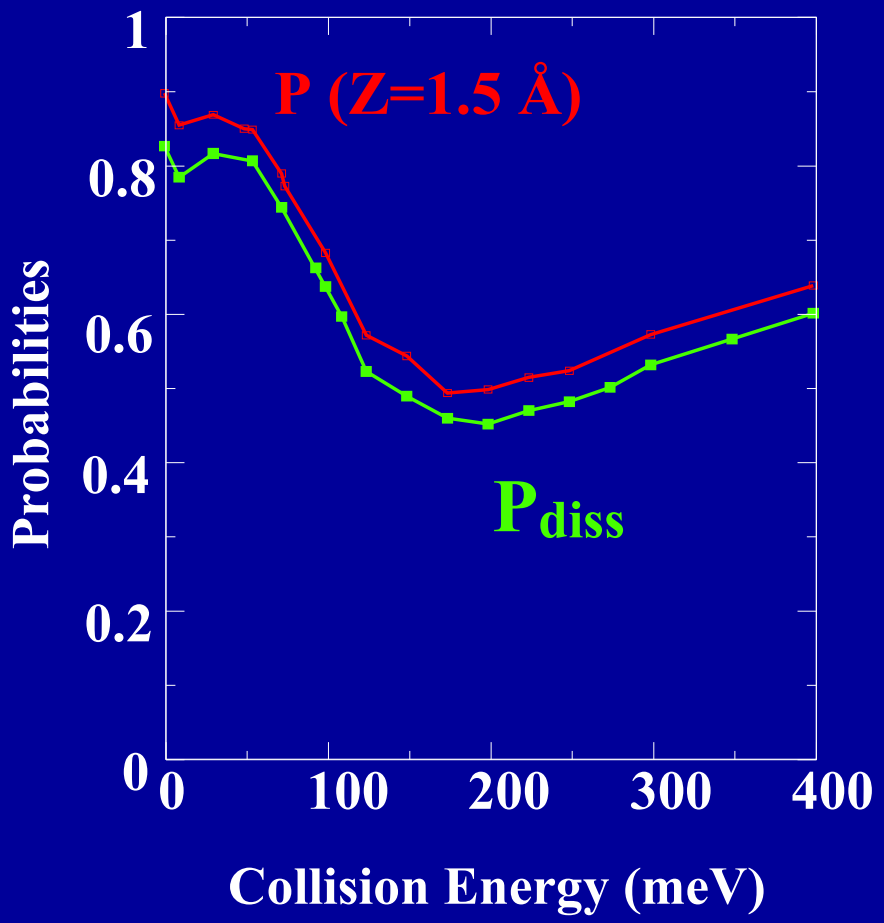
Comparison with experiments

n-Hydrogen: 0.25 (J=0) + 0.75 (J=1)



Example : dissociative adsorption of H_2 on Pd(111)

- **Analysis : P(Z), probability to reach the distance Z**



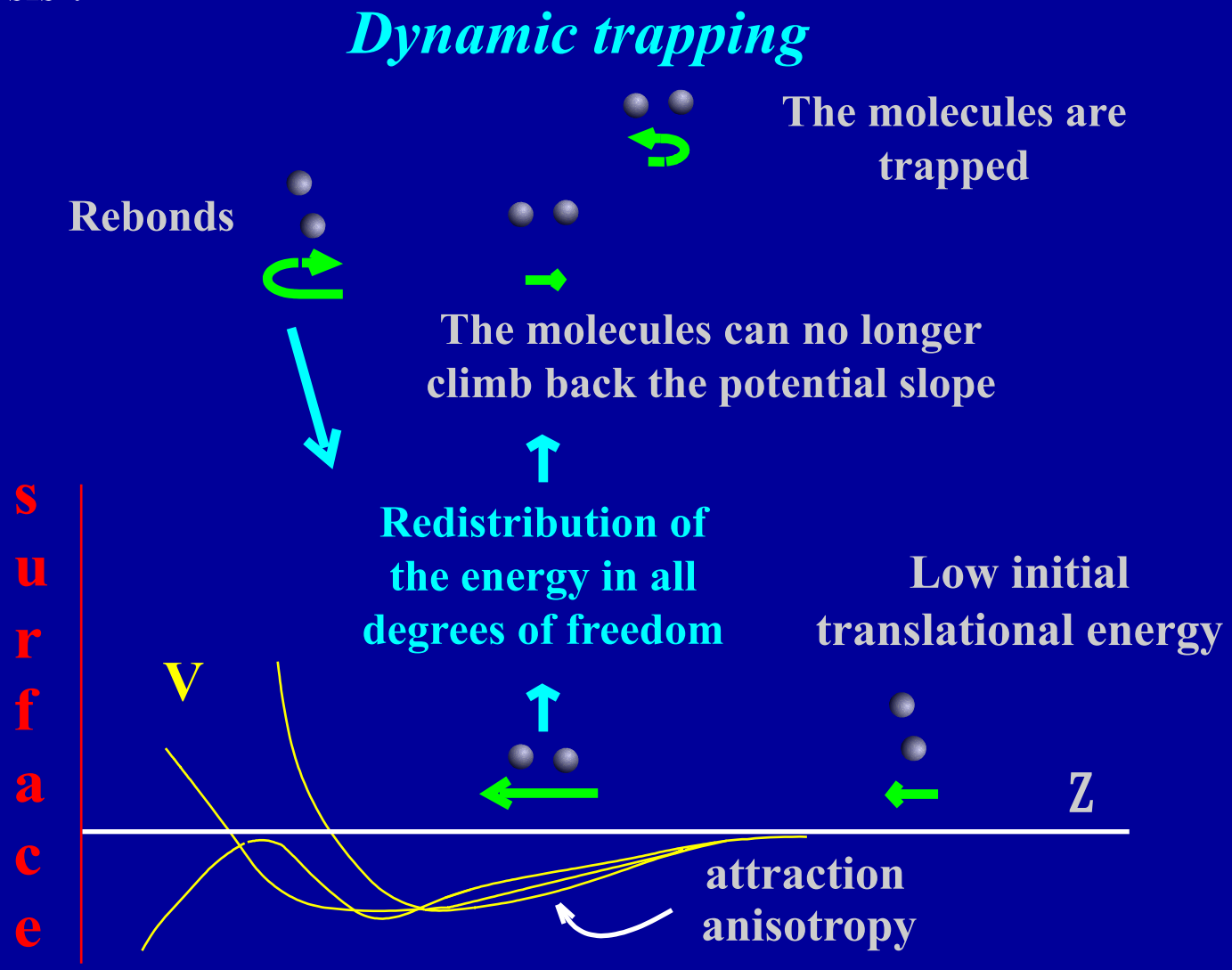
- Critical distance $Z=Z_0=1.5$ Å

- Dynamics takes place in the region $Z < Z_0$

- Study of $P(Z_0)=P_0$

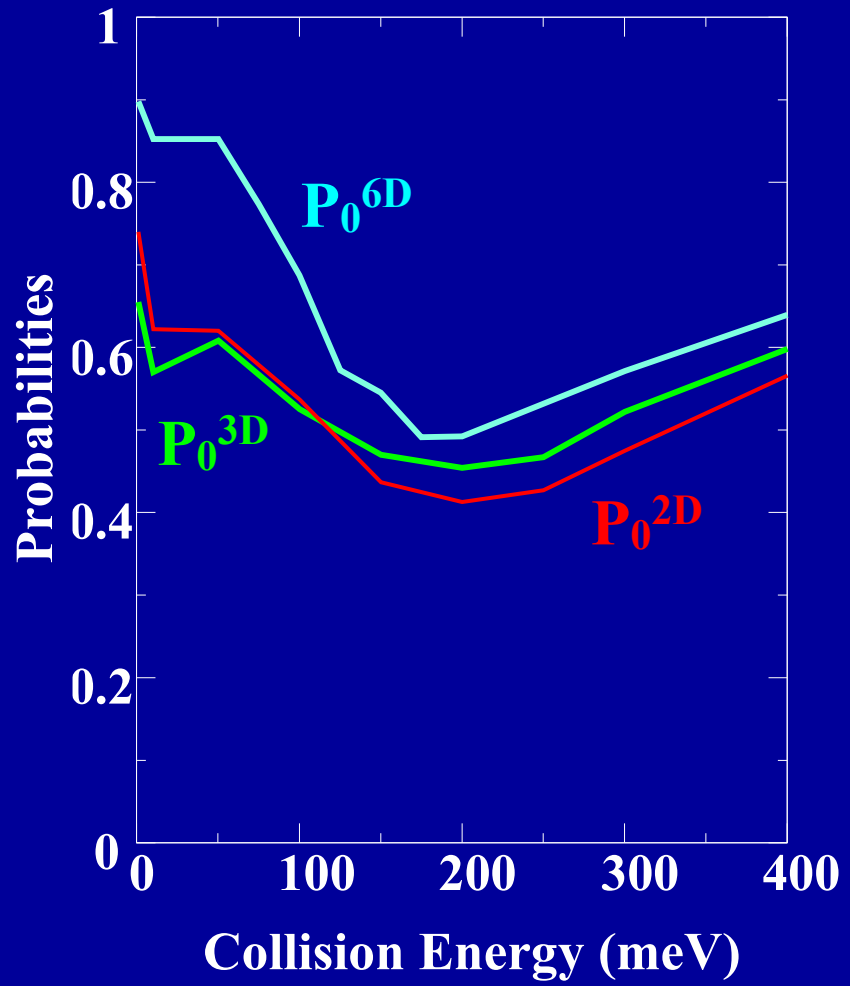
Example : dissociative adsorption of H_2 on Pd(111)

- **Analysis :**



Example : dissociative adsorption of H_2 on Pd(111)

- **Analysis : reduction of the dimensionality**



- Reduction 6D → 3D (r, θ, Z)

- Reduction 3D (r, θ, Z) → 2D (θ, Z)

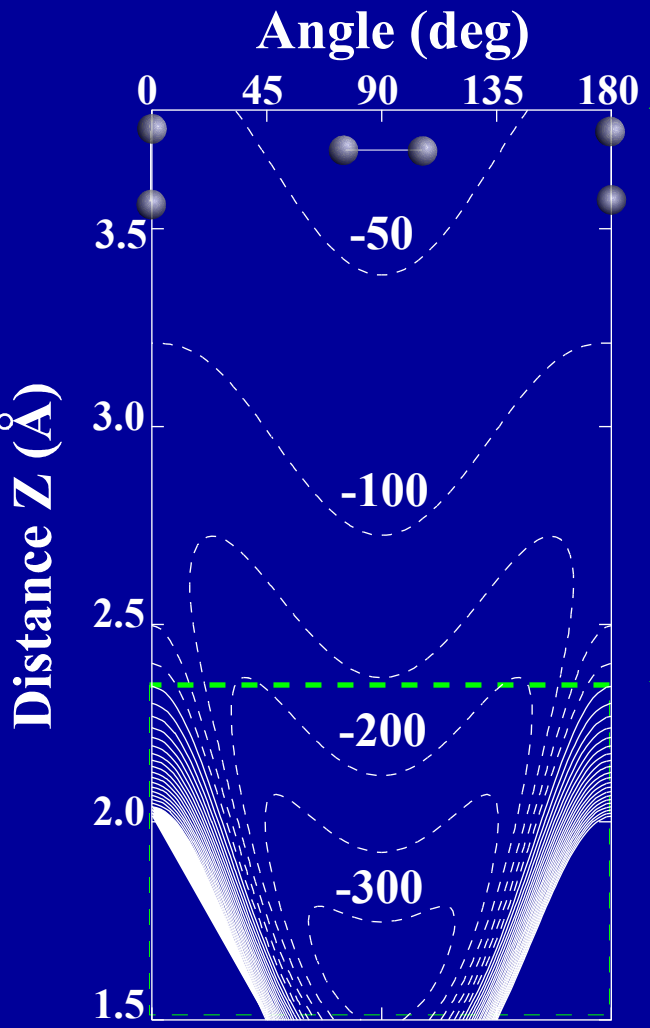
+ adiabaticity of the vibrational motion

- Role of the various degrees of freedom

in the region $Z > Z_0$

Example : dissociative adsorption of H_2 on Pd(111)

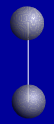
- Analysis : reduction of the dimensionality



Attractive part of the potential

Perpendicular orientation most favorable

θ = 0 or 180°



Rotational hindering channel

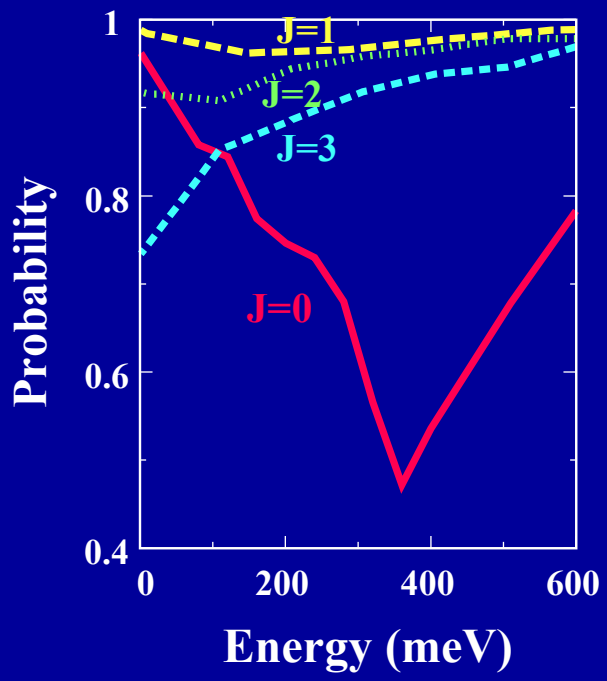
Parallel orientation most favorable

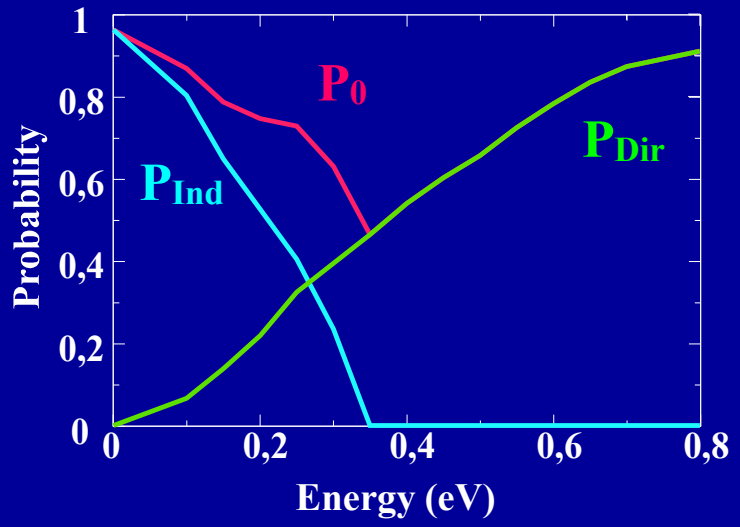
θ = 90°

Example : dissociative adsorption of H_2 on Pd(111)

- **Analysis : reduction of the dimensionality**

  - Classical trajectories : P_0 (Z_0=1.5 Å) for differents values of initial J





Decomposition of P_0 in two components :

direct mechanism + indirect mechanism (trapping)

Example : dissociative adsorption of H_2 on Pd(111)

- **Analysis : conclusions**

- Key role of the molecular orientation during the approach towards the surface (region $Z > Z_0$) : 2D mechanism

- The dynamics are sensitive to the representation of the potentiel in the asymptotic region

- A detailed study of the dynamics (accurate representation of the 6D PES) is required

- The dynamic trapping is a general mechanism which may be involved in other problems : rotational excitation H_2 ($J=1 \rightarrow 3$), non-normal energy scaling, angular distribution …

Conclusion and prospects

• Study of gas-surface reactions at the molecular level (molecular beams + dynamics simulations) → development of the theoretical approaches

• Multi-dimensionality of the problems → PES determination is one of the key issues

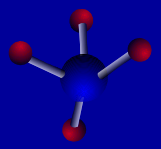
GDR

Wei Dong (ENS Lyon)

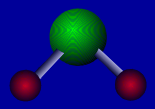
Reactive force fields
for benchmark systems
like H_2+Pt , H_2+Pd , H_2+Cu

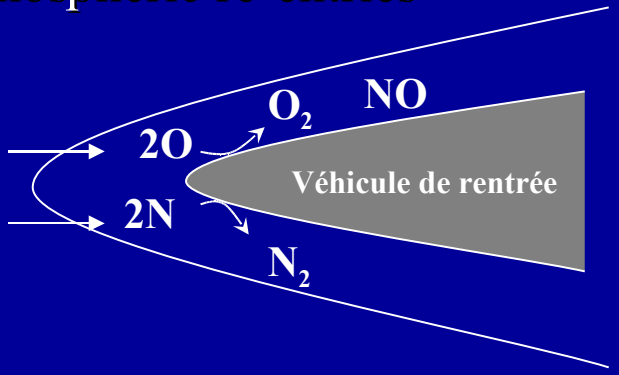
• Work in progress : polyatomic systems, atmospheric re-entries

CH_4 + Ni

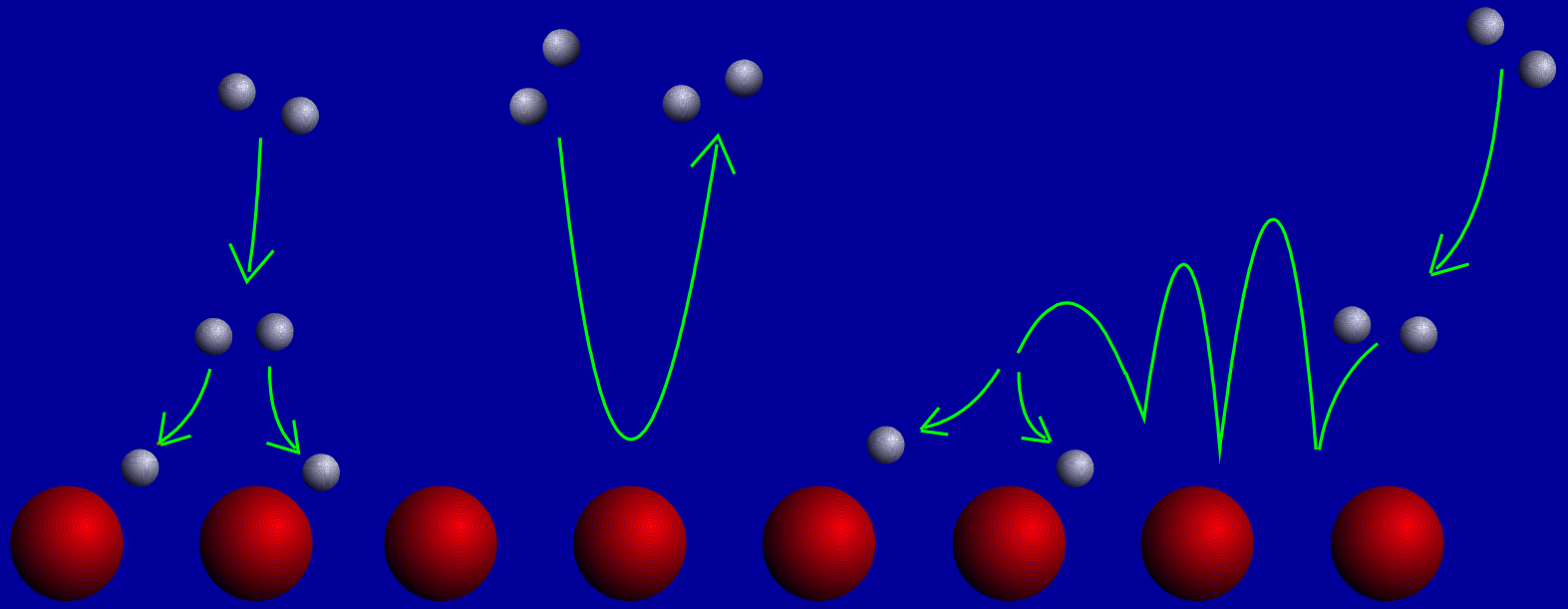


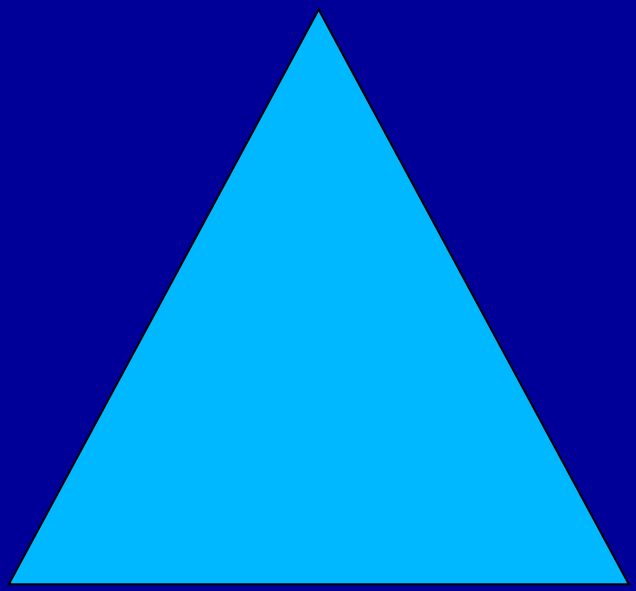
SH_2 + Au





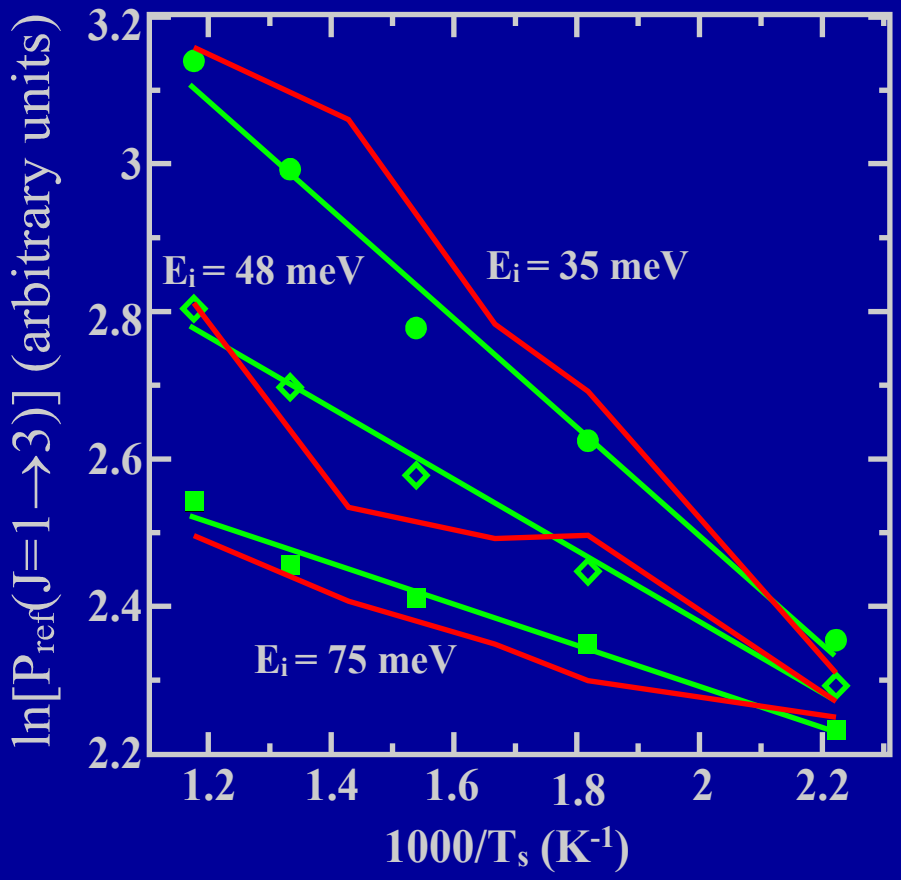
Thanks for your attention !!!





Dynamic trapping / interpretation of experimental data

- Surface temperature and rotational excitation H_2 ($v = 0$, $J = 1 \rightarrow 3$)



3D surface oscillator model

=

energy exchange between molecule and surface phonons

$\Delta E(J=1 \rightarrow 3) \sim 75$ meV

Experiments *(J. Chem. Phys. 111 (1999) 9791)*

Theory *(Phys. Rev. Lett. 87 (2001) 127601)*