FORMATION OF MOLECULES AT THE GAS-SURFACE INTERFACE : EXPERIMENTAL AND THEORETICAL ADVANCES

Sabine Morisset, Nathalie Rougeau, François Aguillon, Hervé Bergeron, Dominique Teillet-Billy

Institut des Sciences Moléculaires d'Orsay(ISMO)

Interstellar Medium

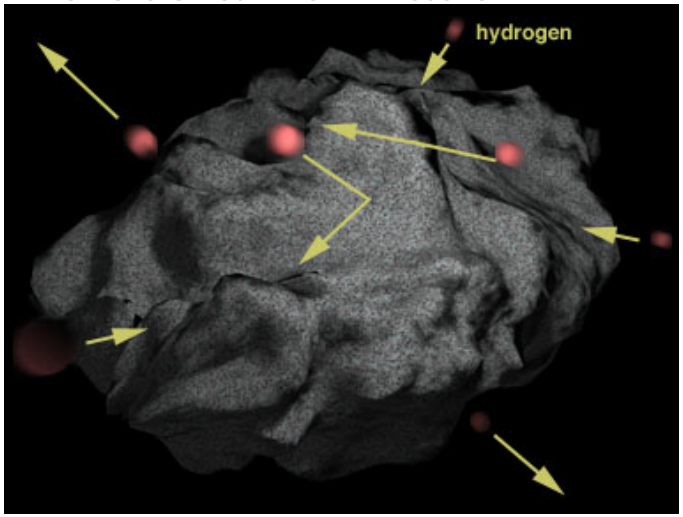
- atoms and molecules in gas phase
- interstellar dust grains
  - 1% of mass of ISM
- ISM regions
  - PDR
  - diffuse clouds
  - dense clouds

Interstellar Medium

Cloud type	Diffuse	Dense
Gas density (cm^{-3})	$10^2 - 10^4$	$10^4 - 10^6$
T_{gas} (K)	$50 - 100$	10
T_{dust} (K)	20	10
Gas	atoms + H_2, CH, CH^+, OH, NH, CO, ...	H_2, CO + lot of molecules
Dust	amorphous silicate, carbonaceous	ice mantle covered (CO_2, CO, CH_3OH, CH_4, NH_3, $HCOOH$)

Interstellar Medium

dust grain = catalyst for molecular formation



$$O + H \xrightarrow{dust\ grain} OH$$

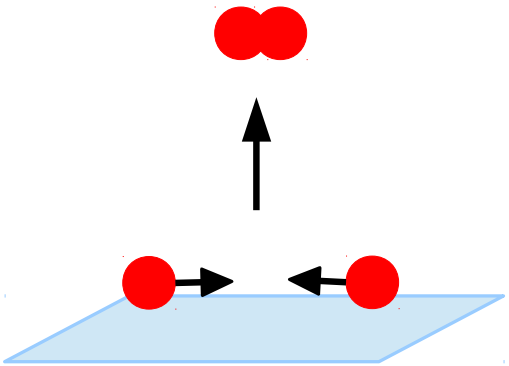
$$OH + H \xrightarrow{dust\ grain} H_2O$$

$$H + H \xrightarrow{dust\ grain} H_2$$

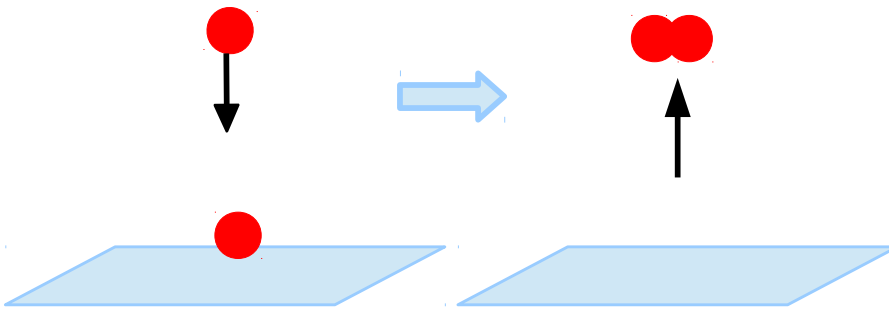
dust grain => carbonaceous materials surface => PAH and graphene

Mechanisms

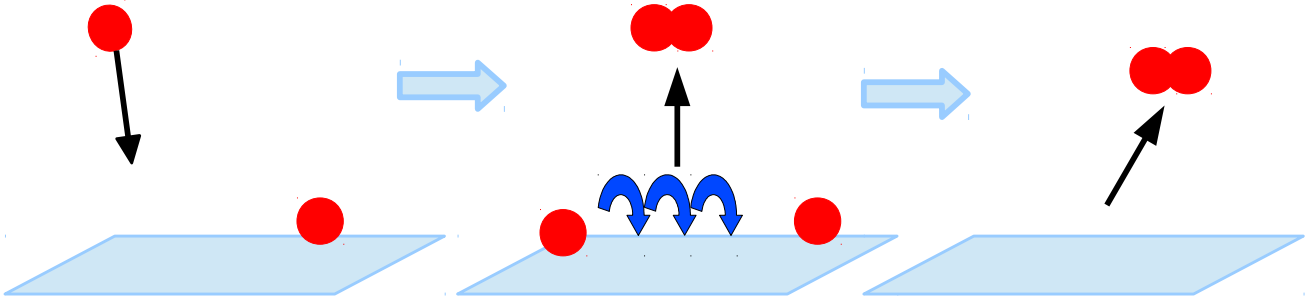
Langmuir Hinshelwood



Eley Rideal



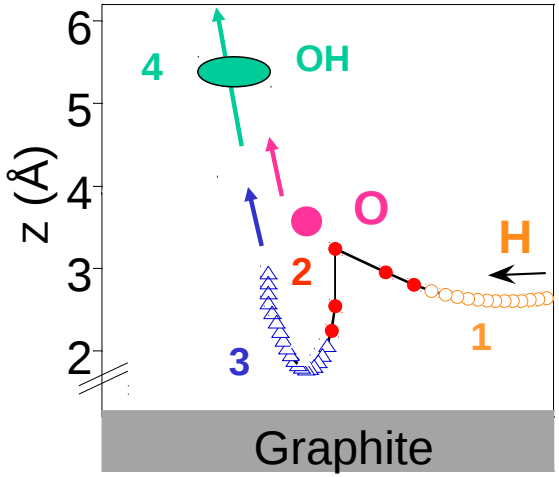
Hot atoms = Harris-Kasemo



OH formation through LH mechanism [1]

- RPBE-DZP ; MP2 calculations
- $O(^3P)$
- physisorbed H & O
- rigid surface
- QCT calculations
  - Large cross section
  - high rovibrational excitation of OH
  - indirect formation mechanism
- potential calculations :
  - good description of physisorption
  - chemisorption not described
  - barriers calculations

Indirect mechanism of OH formation



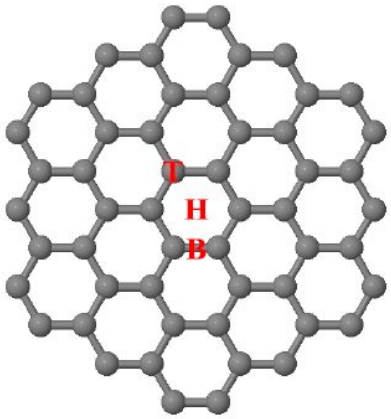
Phase 1 : Approche de atome O par H
Phase 2 : impact de H sur O
Phase 3 : rebond(s) de H sur la surface
Phase 4 : OH désorbe

1. Bergeron H. et al. J. Phys. chem. A 112 11921 (2008)

O(^3P)-graphite

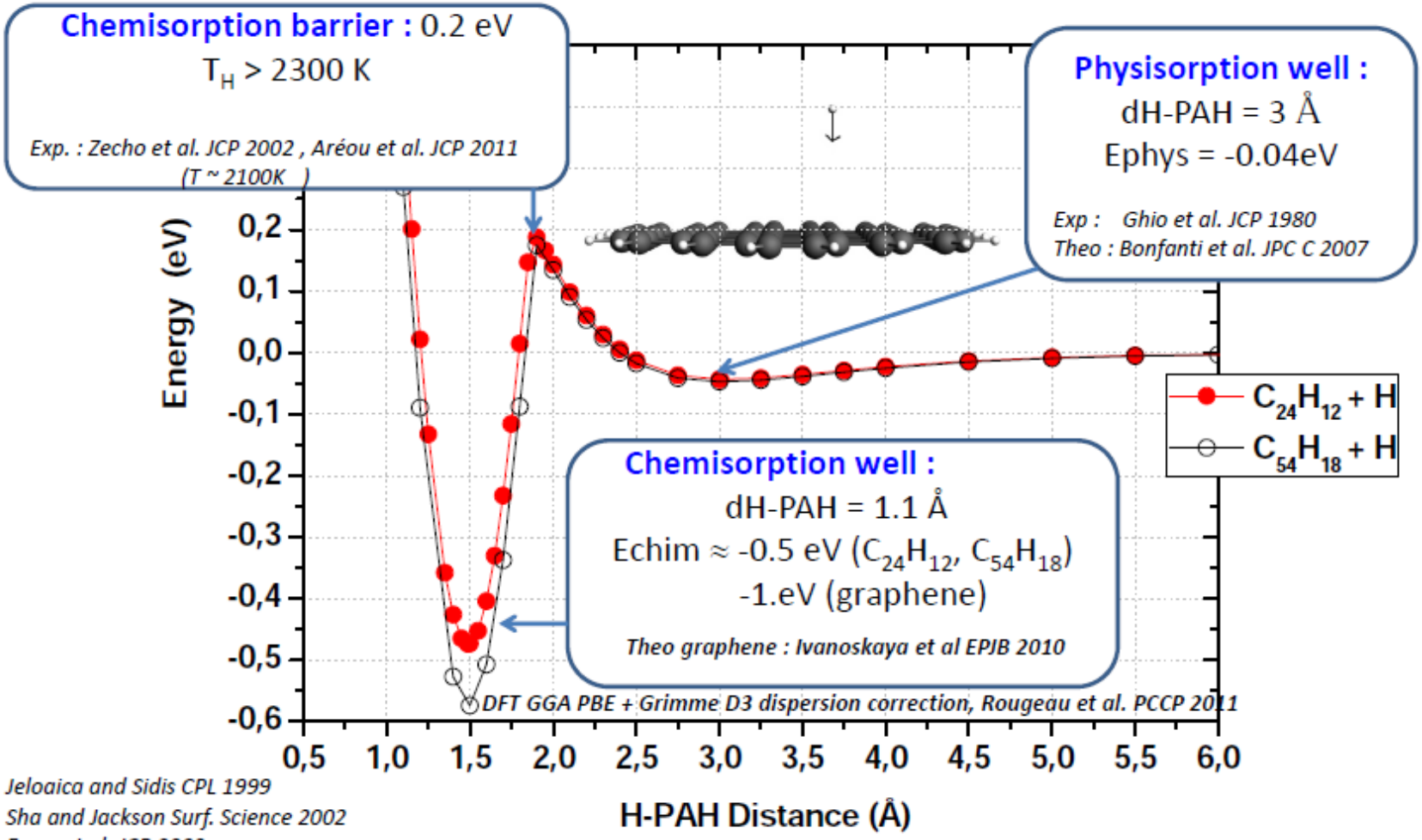
see poster for more details

- coronene, circumcoronene, graphene
- adsorption on top, bridge and hollow sites
- hollow site :
  - physisorption well :
    - large distance
    - independant of the system size
- top and bridge sites :
  - physisorption well same as hollow site
  - chemisorption well :
    - short distance
    - dependant on the system size
- E(top) > E (bridge)



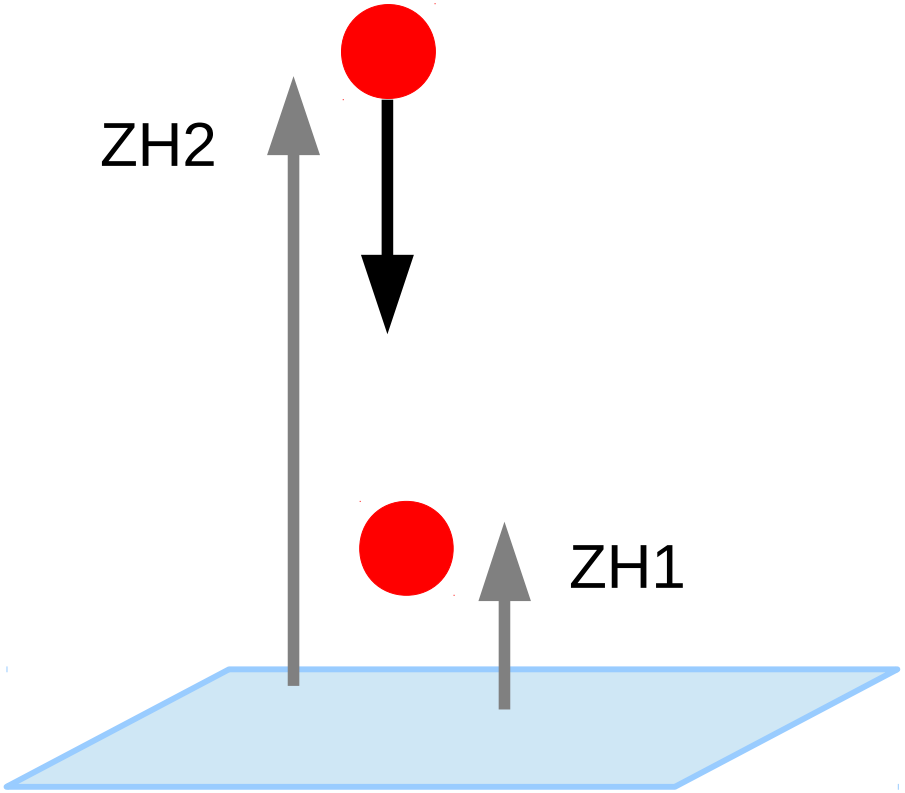
H_2 Formation

Interaction H - graphite-like surface



Jeloaica and Sidis CPL 1999
Sha and Jackson Surf. Science 2002
Ferro et al. JCP 2002
Rauls and Horneckaer ApJ 2008
Casolo et al. JCP 2009 JCP 2009
Psofogiannakis et al JPC C 2009

H_2 Formation through ER mechanism



H_2 Formation through ER mechanism

Dynamics calculations : rigid surface [2, 3, 4]

	Sudden		Adiabatic	
	Morisset et al.	Bonfanti et al.	Morisset et al.	Bonfanti et al.
$P_{H_2}(0.2eV)$	0.4	0.5	0.95	0.8
$P_{H_2}(0.1eV)$	0.2	0.04	0.9	0.7
$P_{H_2}(10meV)$	0.1	0.05	0.8	0.68

- 2D[2,3] = Z_{H1} and Z_{H2}
- sudden and adiabatic approximations[2,3]
- 2 potentials : graphene[2] and coronene[2,3]
- 3D[4] = Z_{H1},Z_{H2} and Z_C
- dynamics = quantum and classical

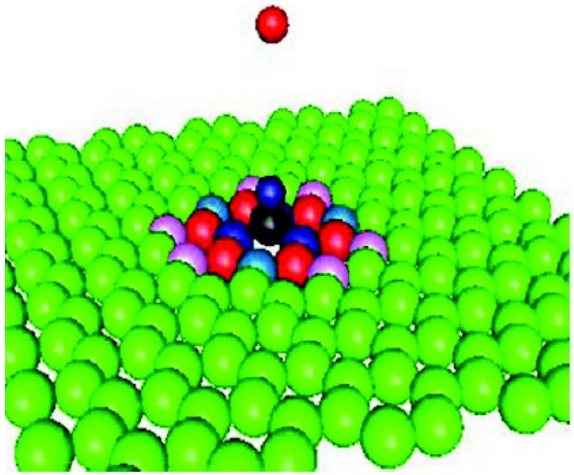
- resonances
- results depend on the surface
- high vibrational excitation of H_2
- surface relaxation is important[4]

2. Morisset S. et al. Phys. Chem. Chem. Phys 5 506 (2003)
3. Bonfanti M. Phys. Chem. Chem. Phys. 13 16680 (2011)
4. Morisset S. et al. J. Chem. Phys. A 108 8571 (2004)

H_2 Formation through ER mechanism

Dynamics calculations : relaxed surface [5]

Modified Brenner potential molecular dynamics calculations
Non collinear geometries



- $E_{col} = 0.015eV (=> 170K)$
- Cross section $= 1.9 \text{Å}^2$

$< E_{int}(H_2) > (\text{eV})$	2.7	68%
$< v >$	5	
$< j >$	2	
$< E_{trans}(H_2) > (\text{eV})$	0.49	12%
$< E_{surface} > (\text{eV})$	0.77	20%

- relaxation substrate :
  - v decrease
  - Probabilities increase

5. Bachellerie et al. PCCP 11 2715 (2009)

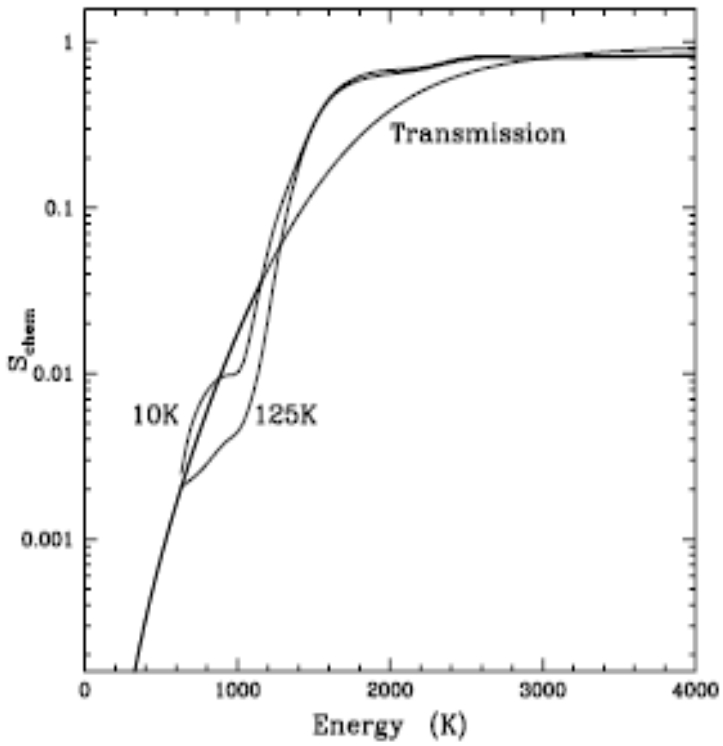
H_2 Formation through ER mechanism

Conclusions & Questions

- Conclusions
  - relaxation of the surface is important
  - large probabilities of reaction
  - results depend on the type of surface
- Questions
  - Chemisorption barrier 0.2eV
    - How can the H atom chemisorb on the surface ?
  - model of the surface
    - defects

Sticking of H atom in chemisorption [6, 7]

sticking => surface temperature => phonon in dynamics calculations[(6)] => one phonon exchange model



- mixte classical-quantum dynamics
- Energy exchange :
  - acoustic bands
  - low sticking in ISM temperature

6. Morisset S. et al. J. Chem. Phys 133 044508 (2010) ; Cazaux S. et al. A&A 535 A27 (2011)

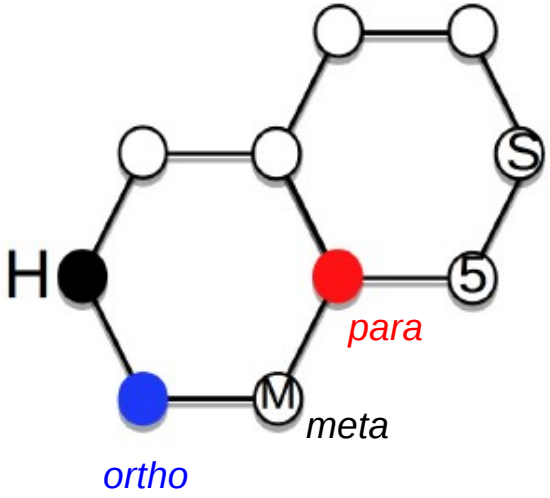
Sticking of H atom in chemisorption

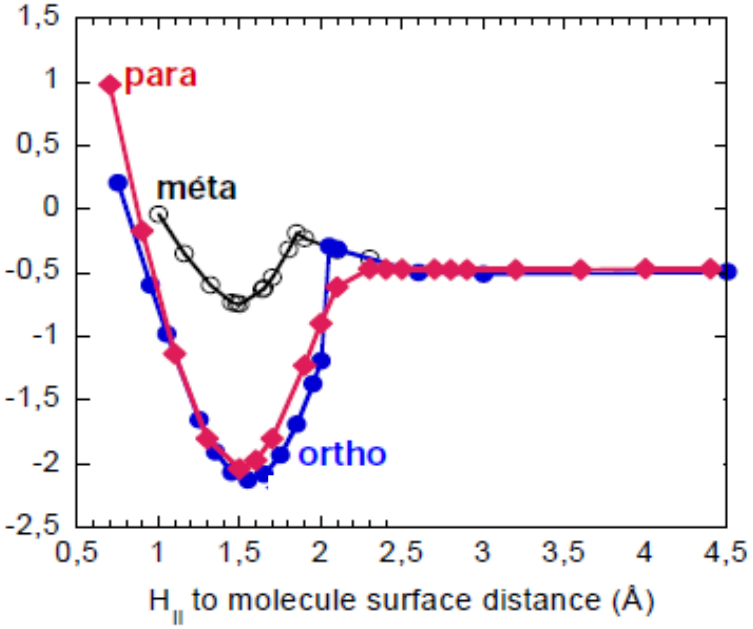
Sticking conclusion & perspectives

- low sticking probabilities
- ER mechanism not favorable
- Role of defects on the chemisorption ?

Defects

double adsorption [8]





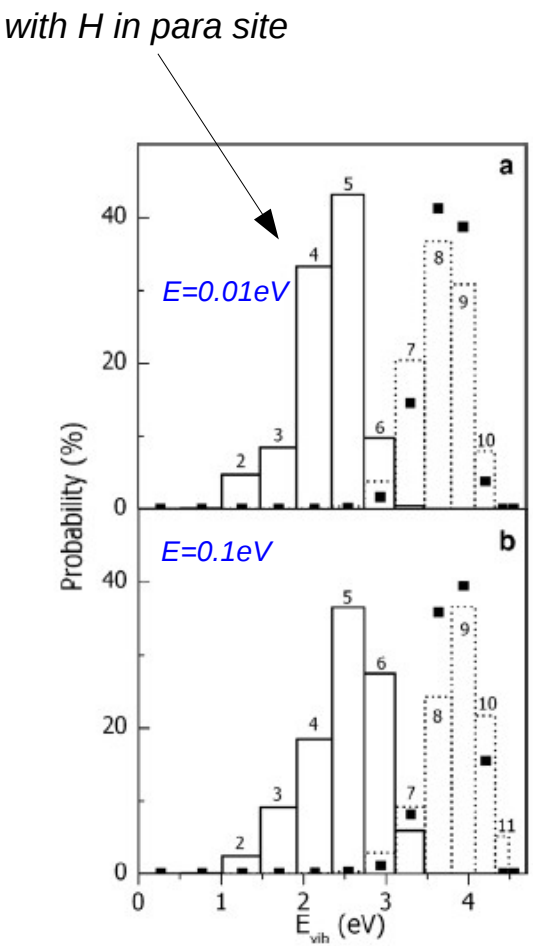
- para site : no adsorption barrier
- strong stabilization for para and ortho sites

8. Rougeau N. et al. CPL 431 135 (2006)

Defect and H_2 Formation

formation through ER mechanism with a defect [9]

one H adsorbed in para site



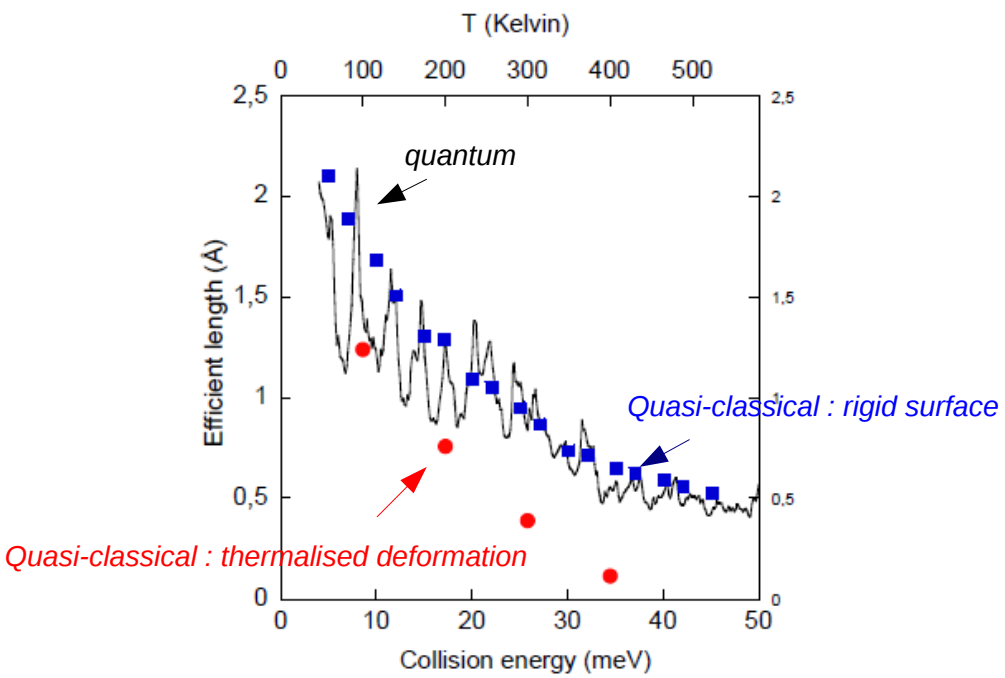
- adsorption without barrier in para site
- QCT dynamics
- lower H_2 vibrationnal state
- good agreement with observations

9. Bachellerie D. et al. Chem. Phys. Lett. 448 223 (2007)

Conclusion ER mechanism

- Electronic structure calculations
- Dynamics calculations (quantum, classical, QCT etc ...)
- Rigid surface => high v excitation of H_2
- motion of the surface => low v excitation of H_2
- large probability of formation
- chemisorption barrier = $2300K$
  - H can stick with low probablity
- around a defect
  - adsorption in para site is barrierless
  - H_2 formation favorable in para site

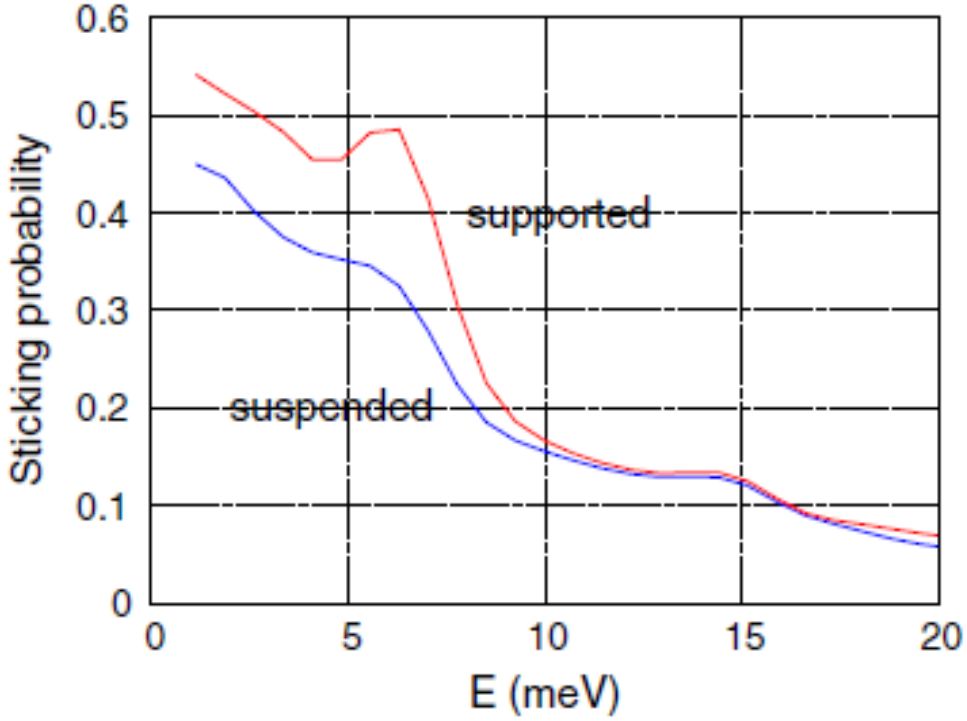
H_2 Formation through LH mechanism [10, 11]



- quantum calculations => rigid substrate
- two H atoms physisorb on the surface
- quantum calculations => high vibrational excitation
- effect of the motion of the substrate

10. Morisset S. et al. J. Chem. Phys 121 6493 (2004), 122 194702 (2005)
11. Bachellerie D. et al. J.Phys. Chem A 113 108 (2009)

Sticking of H atom in physisorption [12]



- semi-empirical model -> lattice dynamics
- $T_{surf} = 10K$
- Close Coupling Wave Packet

12. Lepetit B. et al. Phys. Rev. Lett. 107 236102 (2011)

Conclusion

- OH formation
  - rigid surface : indirect mechanism
  - potential calculations need more precision
- H_2 formation
  - ER, LH mechanisms
  - complexity of dust grain model
    - defect
    - role of surface relaxation
  - complexity of dynamics methods : degrees of freedom
- Astrophysical models
  - code rate equations [13, 14]
  - KMC [15]
  - these codes need
    - adsorption, desorption energy
    - barrier
    - probabilities of reaction (or cross section)

13. Le Bourlot et al. A&A 541 A76 (2012)
14. Cazaux et al. A&A 604 222 (2004)
15. Cazaux et al. A&A 535 A27 (2011)