H ATOMS ON GRAPHENIC-TYPE SURFACES: ADSORPTION, ABSTRACTION

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INTRACTIONS AND REACTIONS OF H (AND O) ATOMS ON GRAPHENIC SURFACES

H_2 (and OH) molecule formation on interstellar dust grains

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Interstellar medium (ISM)

gas (99%)

- H
- H_2

} ~ 75% – 90%

He ~ 25% – 10%

Interstellar medium (ISM)

gas (99%) → H, H_2 } ~ 75% – 90%

He ~ 25% – 10%

dust grains **(1%)**

Density < 1000 atoms per cm^3

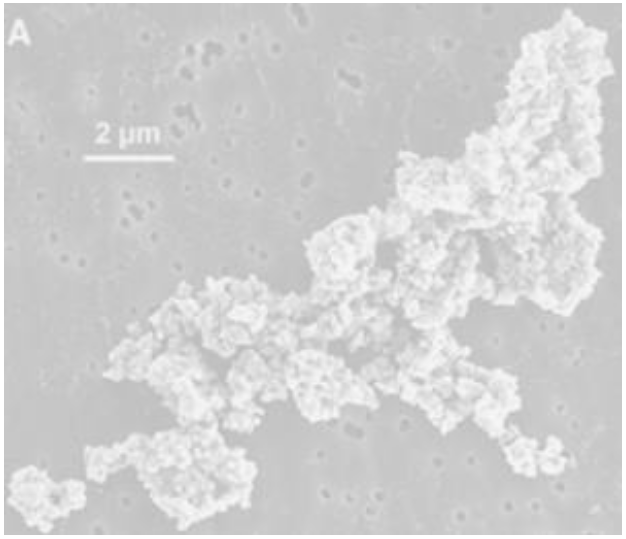
Temperature: 10K – 100 K

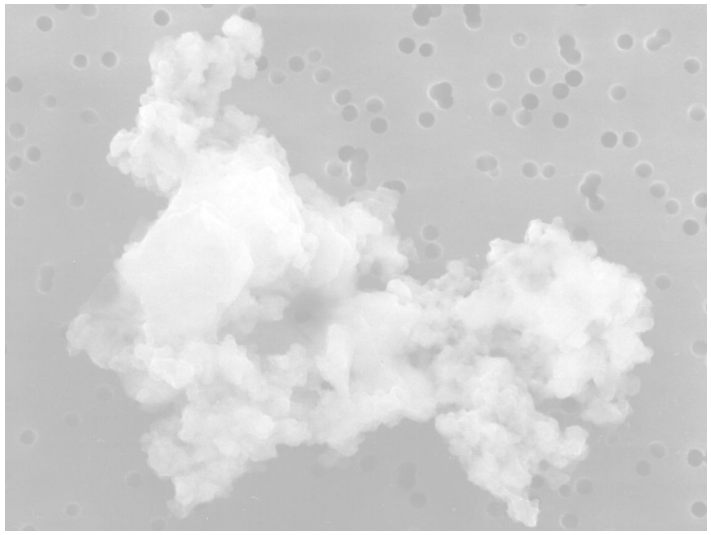
H_2 formation in the ISM

Heterogeneous catalysis

$H + H + grain \rightarrow H_2 + grain$

Interplanetary

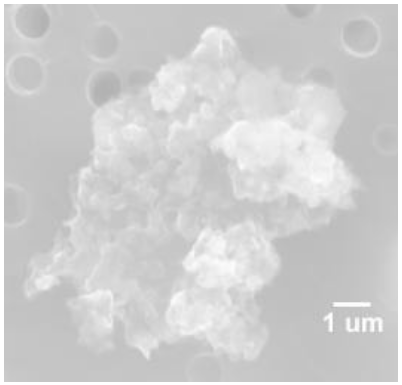




ISM

5 nm – 0.25 μm

Size distribution (~ r $^{-3.5}$)

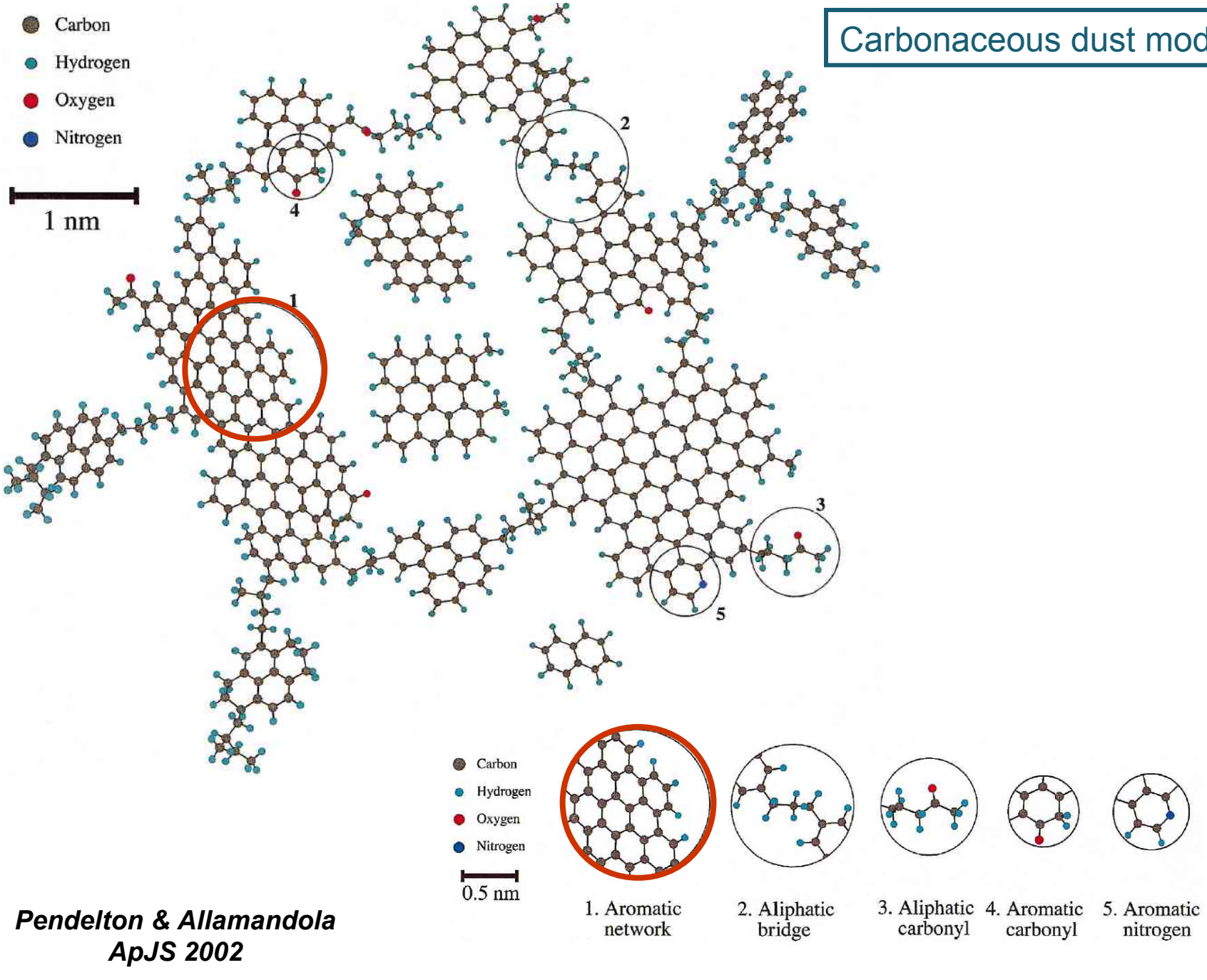


Silicates

Carbonaceous

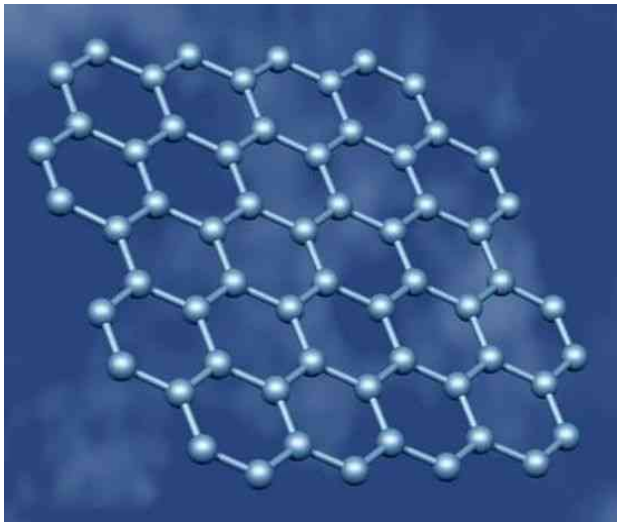
Weingartner & Draine ApJ 2001

Carbonaceous dust model

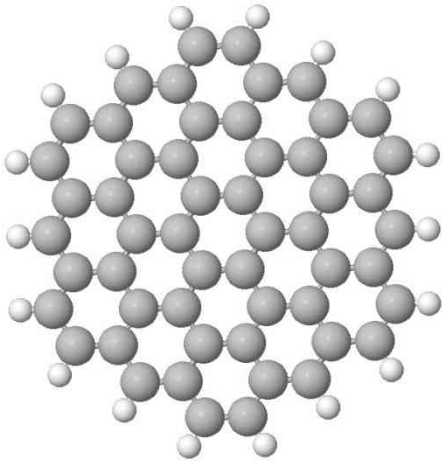


Pendelton & Allamandola
ApJS 2002

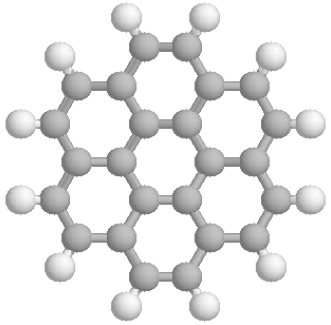
Graphitic/Graphenic surfaces



Graphene

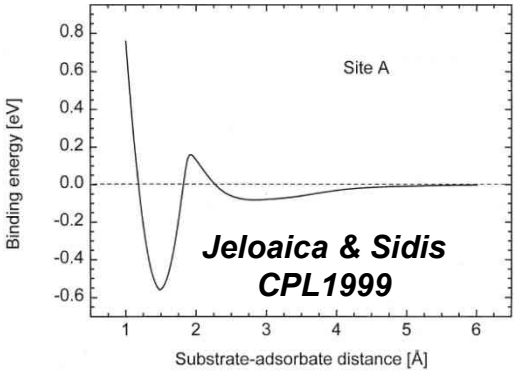


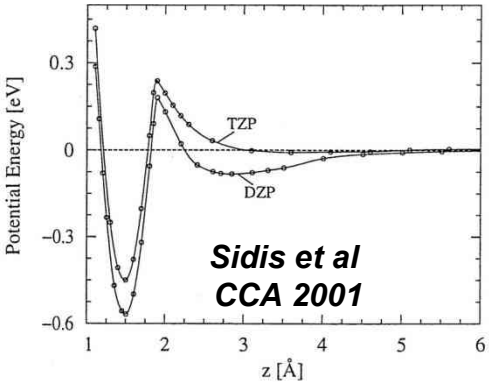
CircumCoronene
$C_{54}H_{18}$

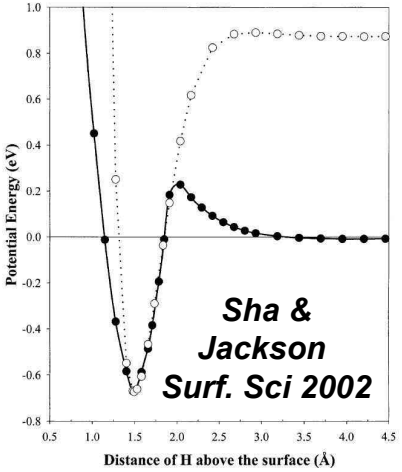


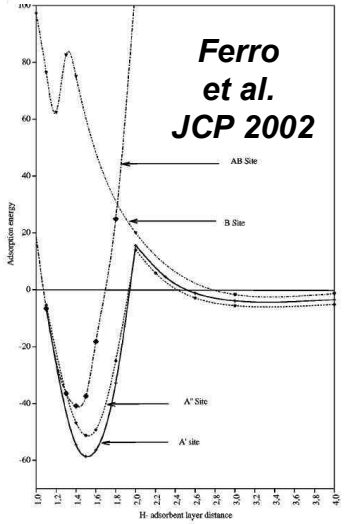
Coronene
$C_{24}H_{12}$

H adsorption on a graphenic surface

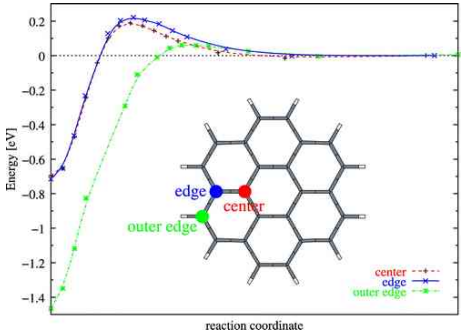


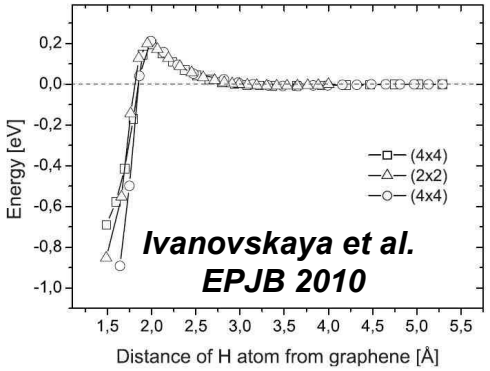


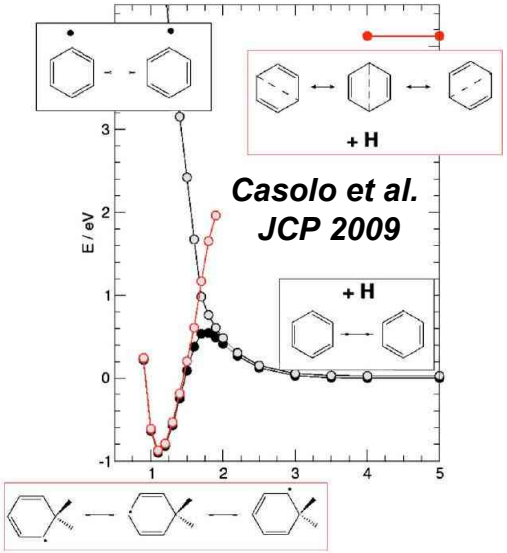




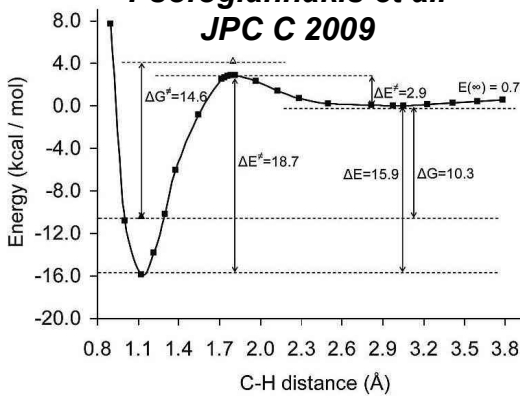
Rauls & Horneckaer ApJ 2008

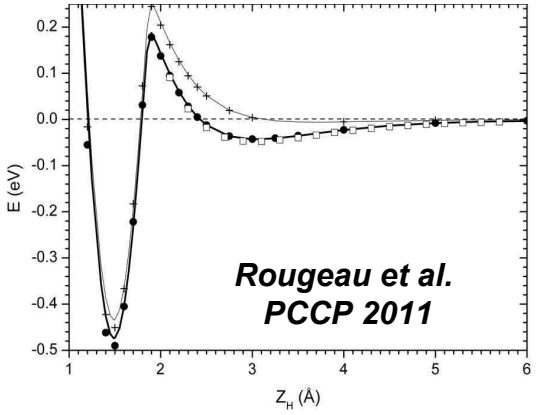


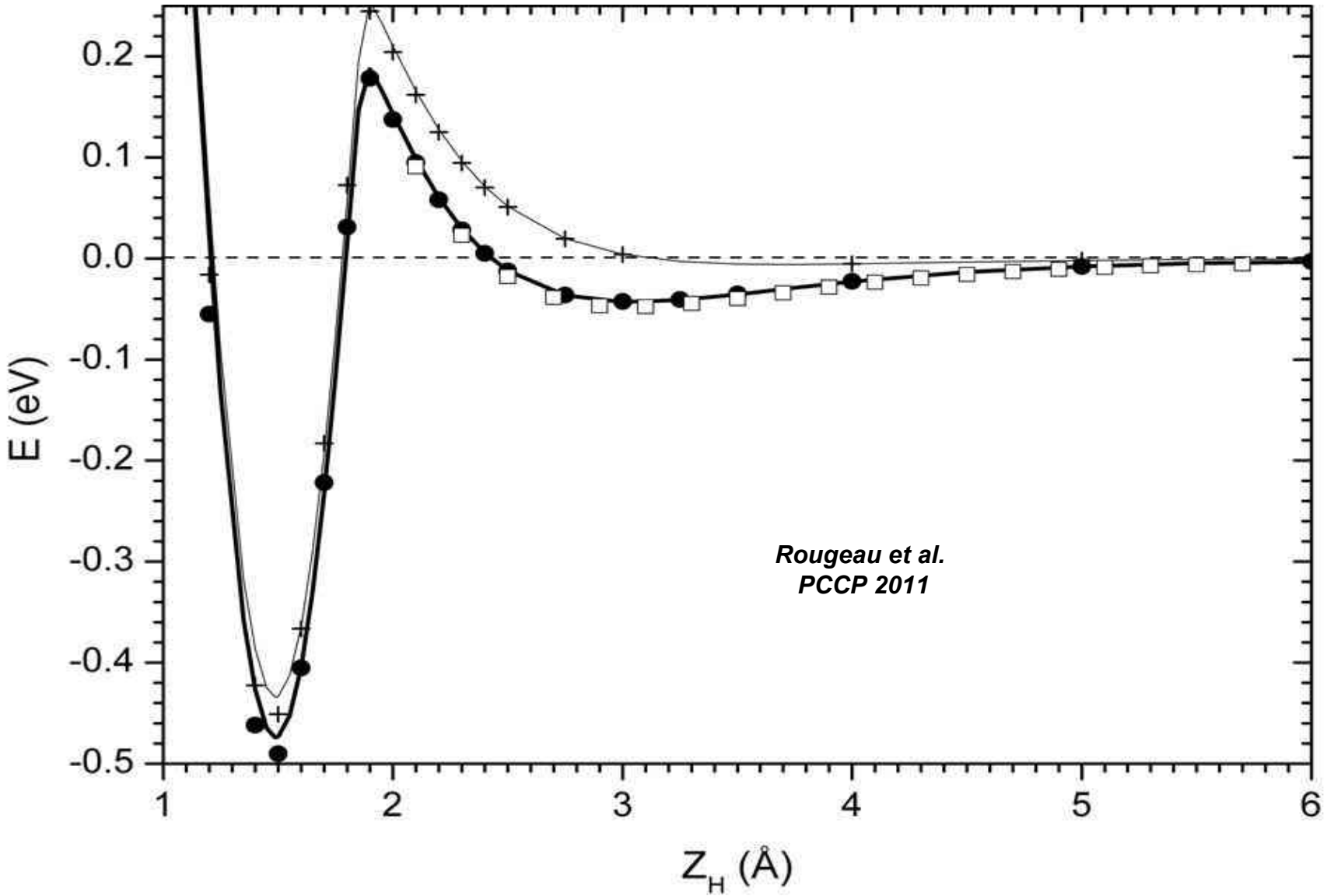


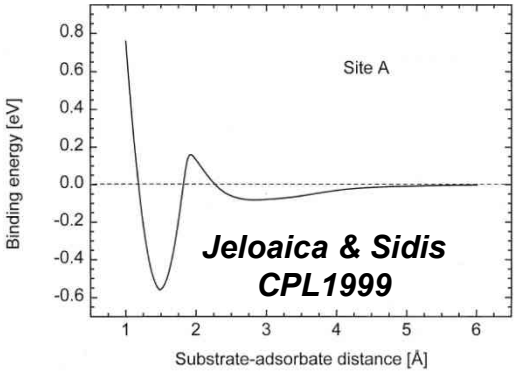


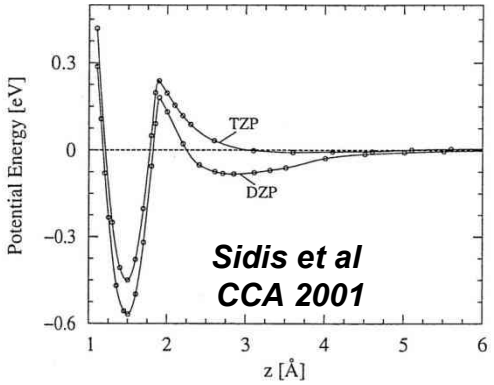
Psofogiannakis et al.
JPC C 2009

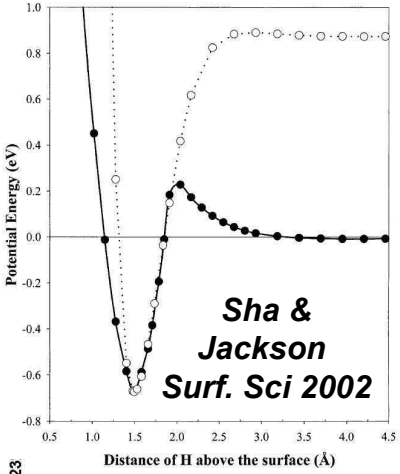


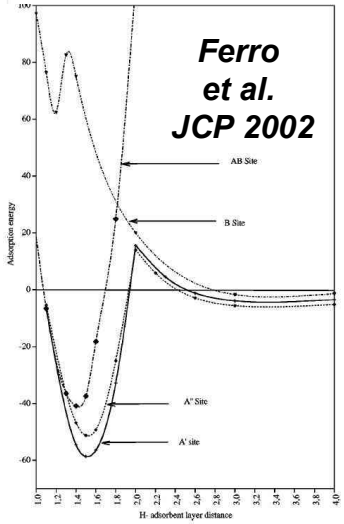



0.2
0.1
0.0
-0.1
-0.2
-0.3
-0.4
-0.5
E (eV)
1
2
3
4
5
6
Z_H (Å)
Rougeau et al.
PCCP 2011

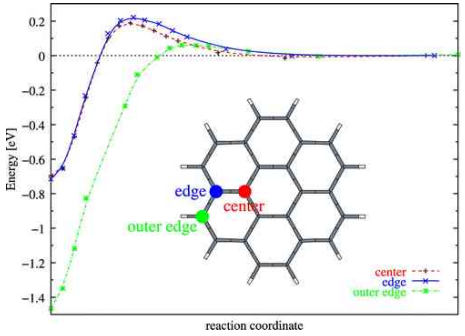


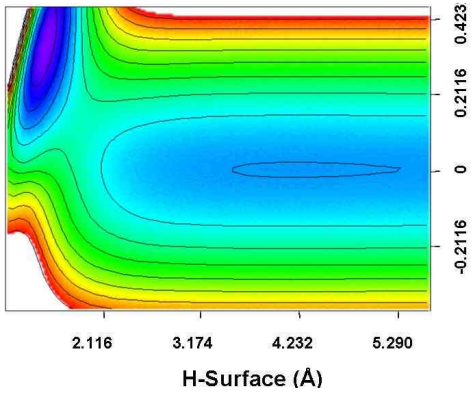


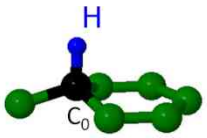


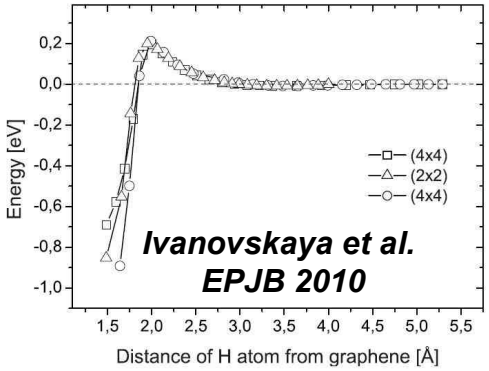


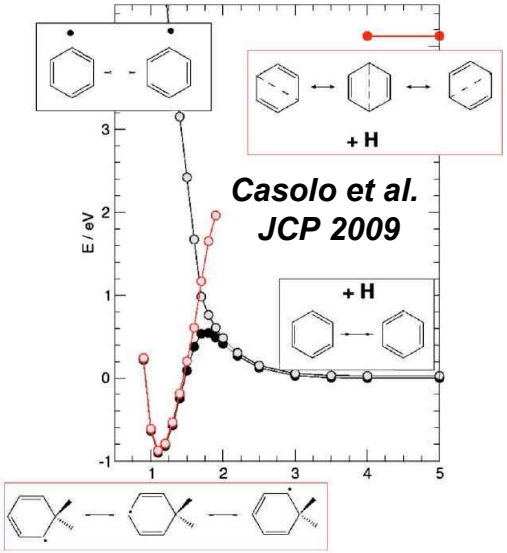
Rauls & Horneckaer ApJ 2008



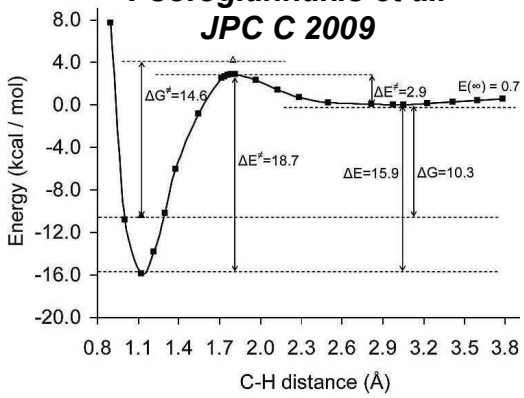


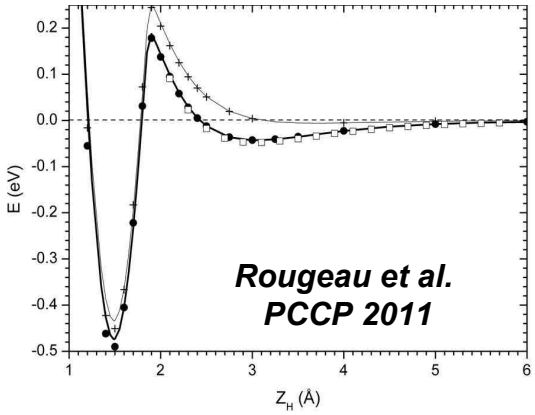




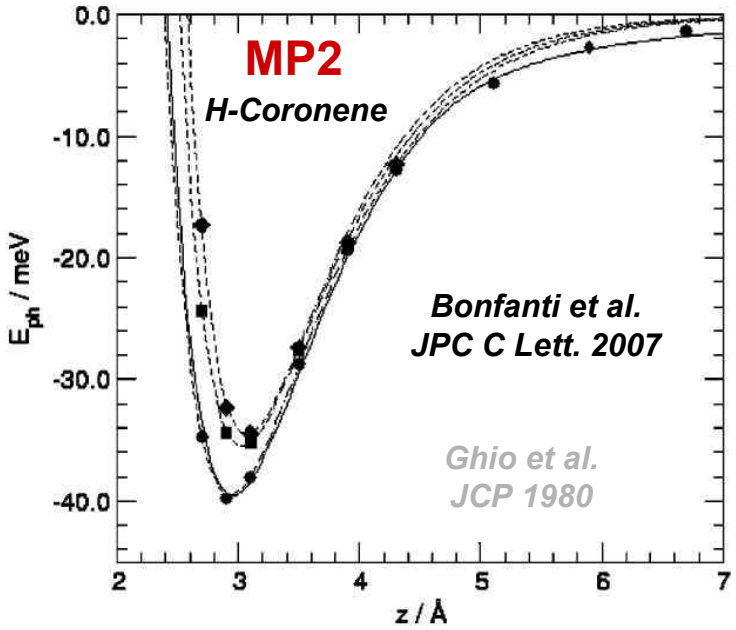


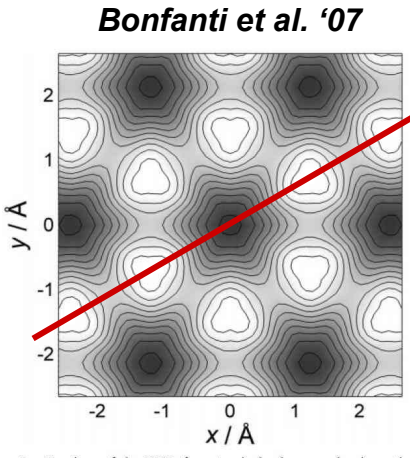
Psofogiannakis et al.
JPC C 2009

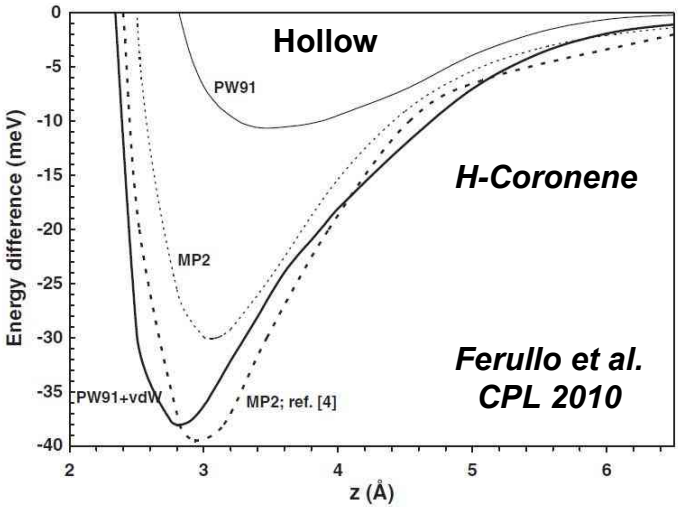


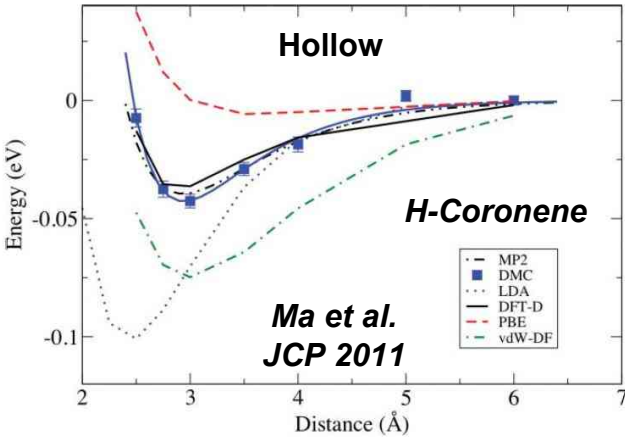


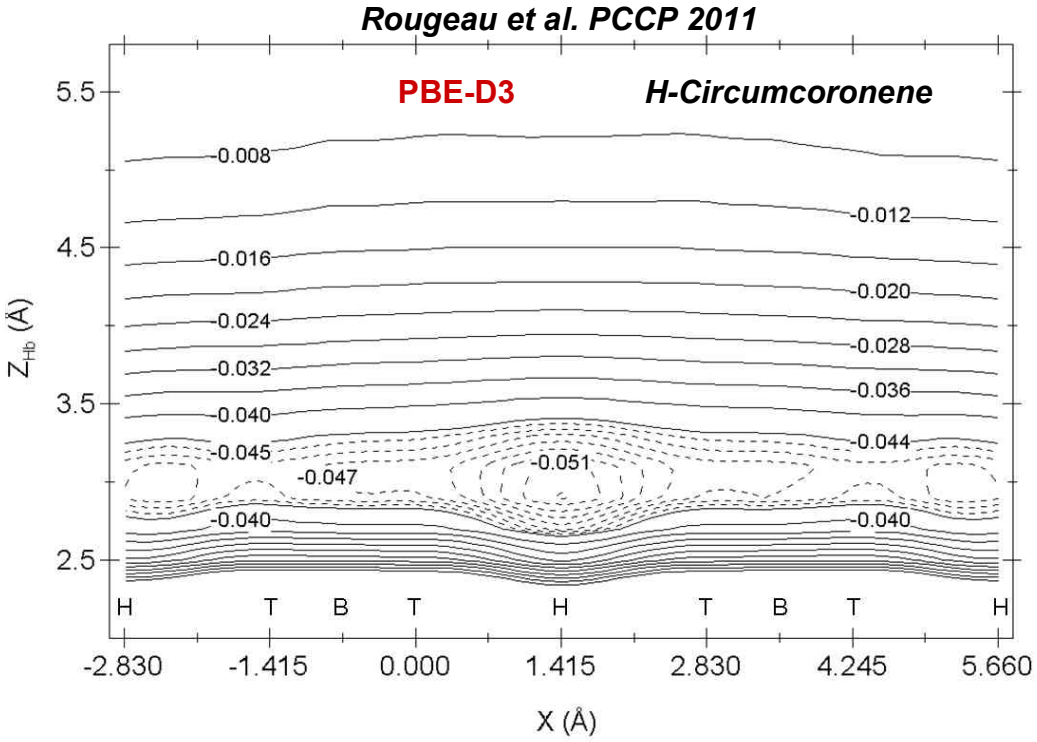
Physisorption

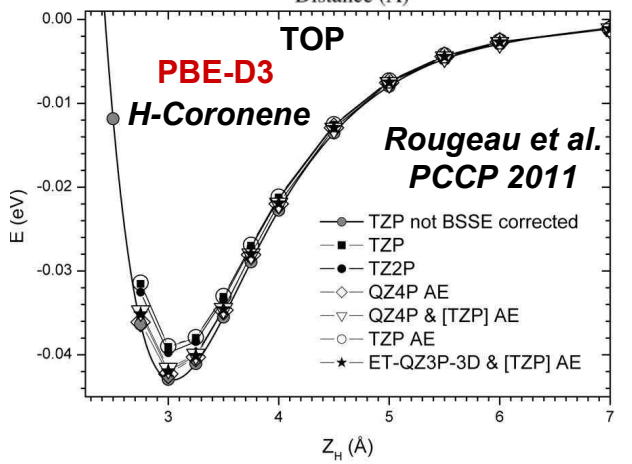




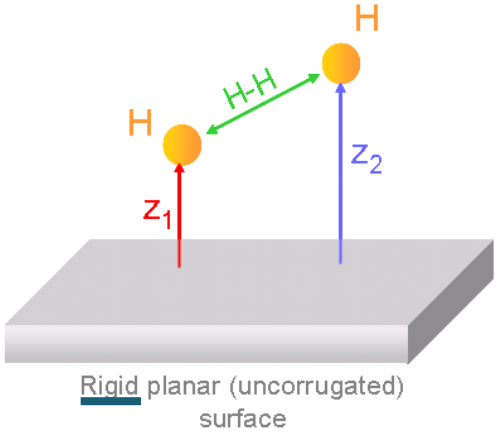








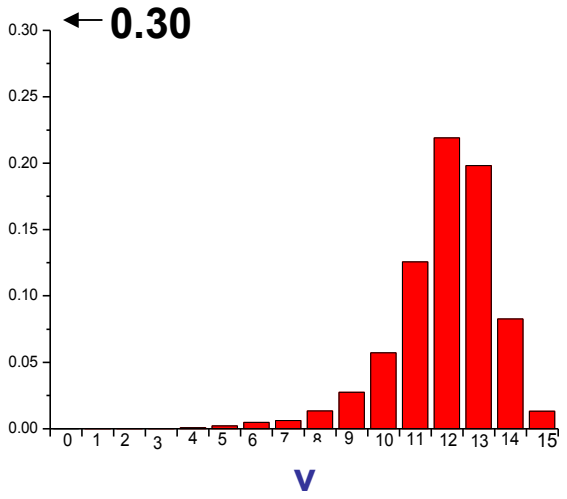
Langmuir-Hinshelwood mechanism



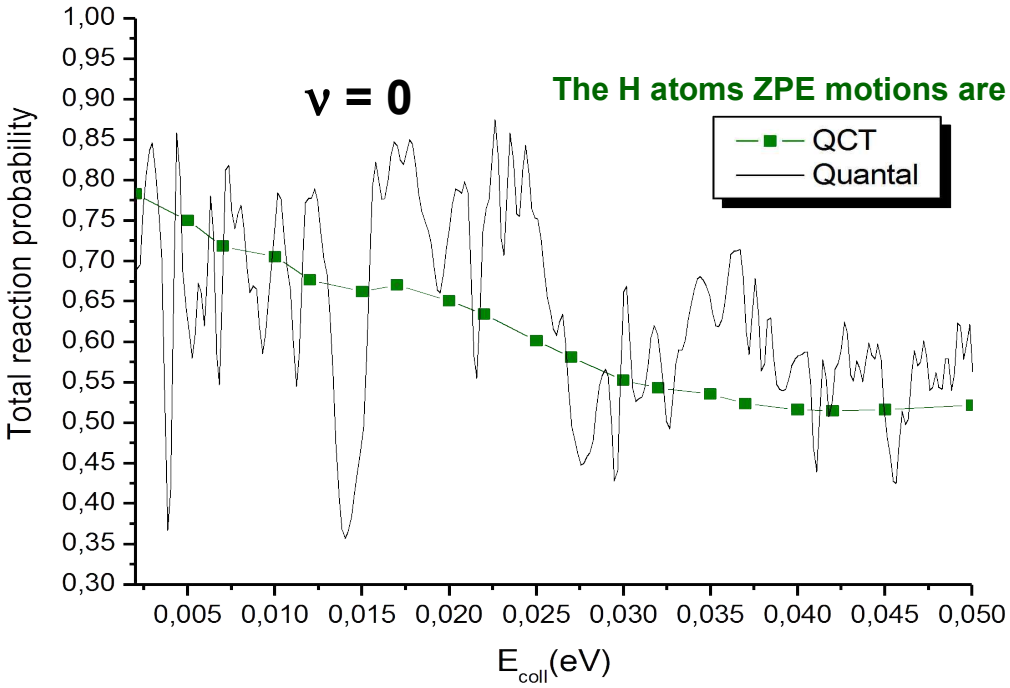
Morisset et al.
JCP 2004 - 2005

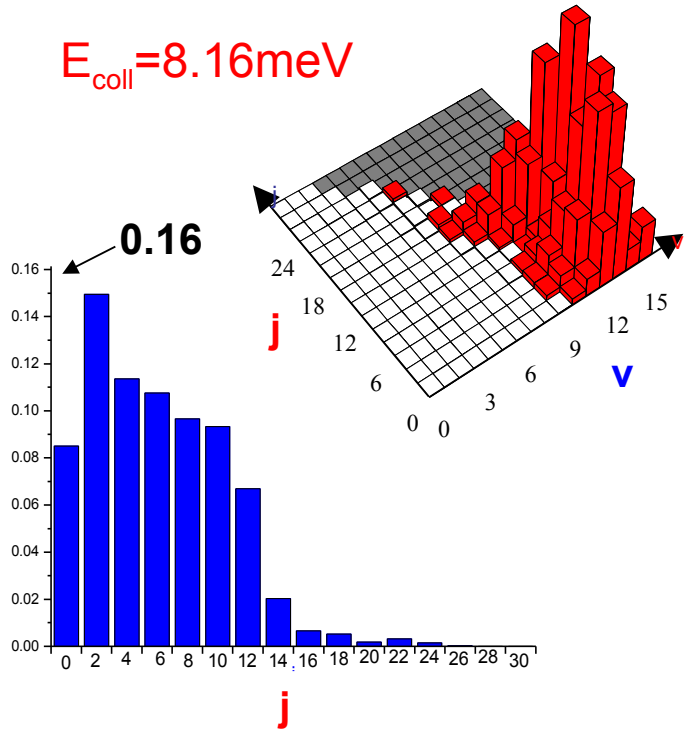
Pairwise additive potentials
4D Quantum
Wave Packet Propagation

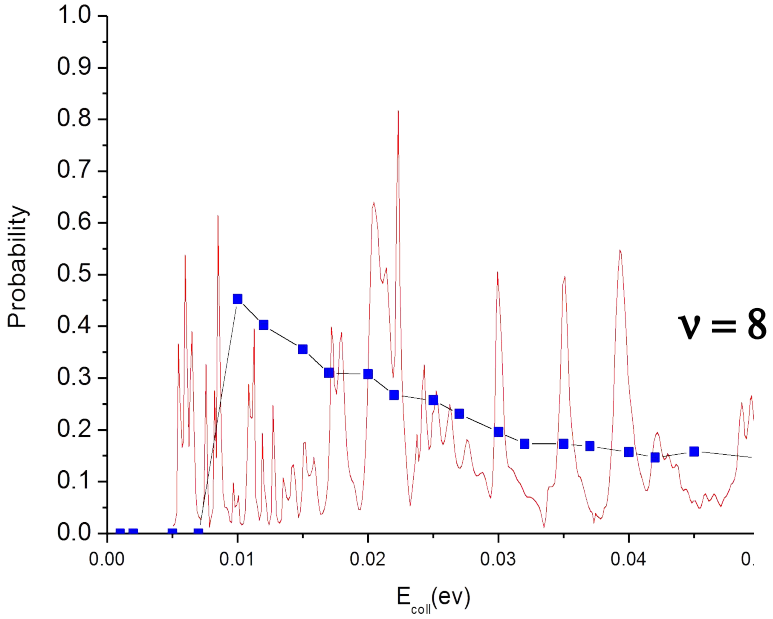
2 meV – 50 meV

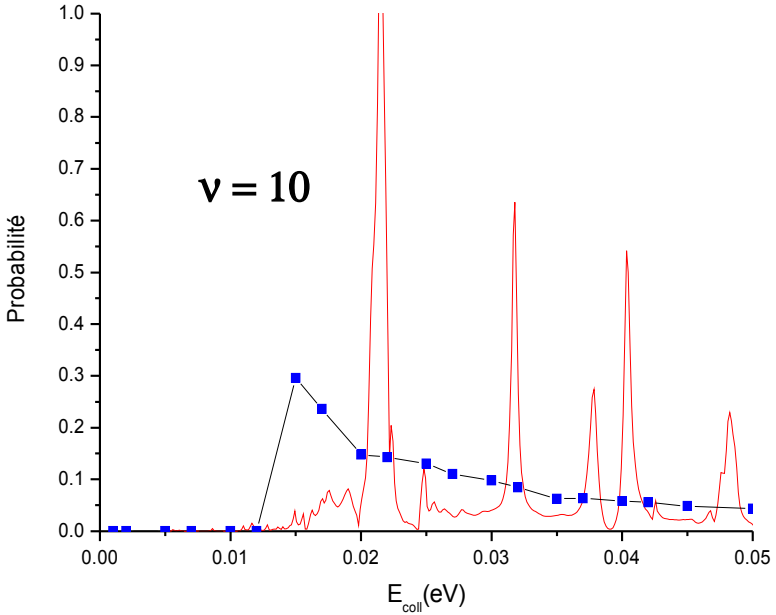


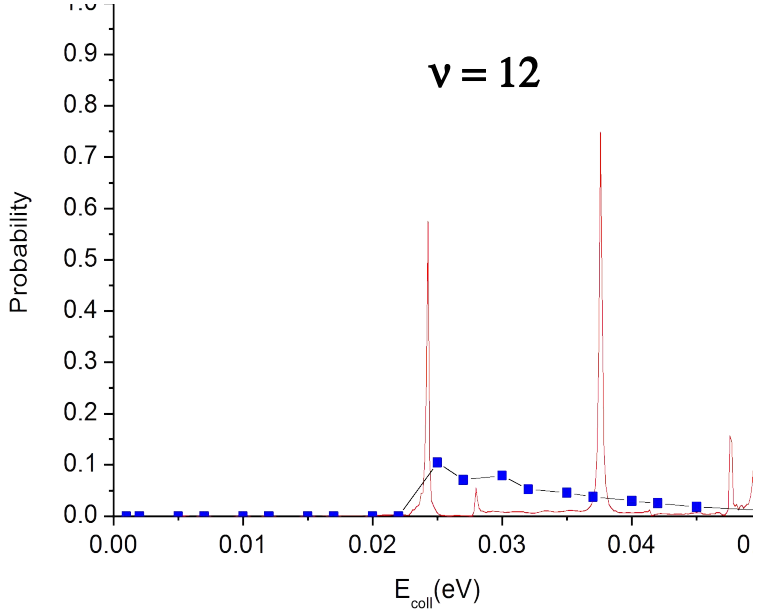
The reaction results from **momentum transfer** in the H-H collision and scattering near the surface

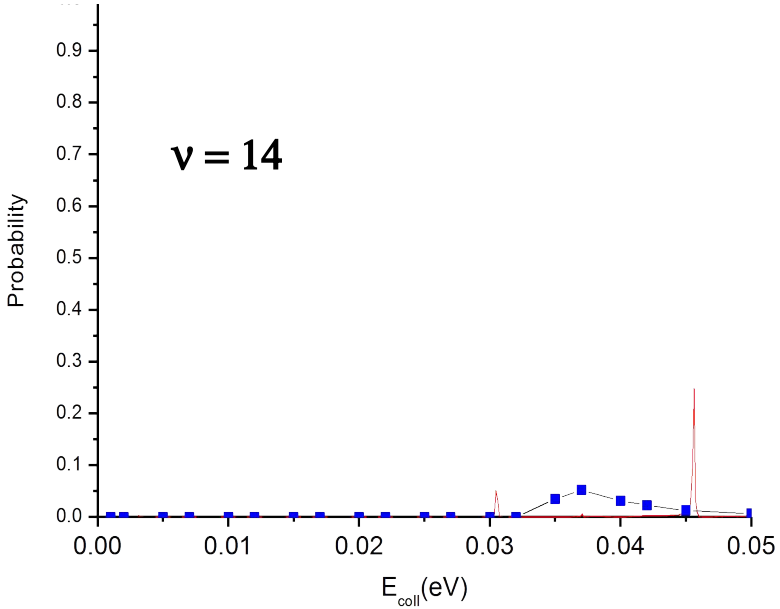





Probability
ν = 8
E_coll(ev)


Probabilité
ν = 10
E_coll(eV)


Probability
ν = 12
E_coll(eV)

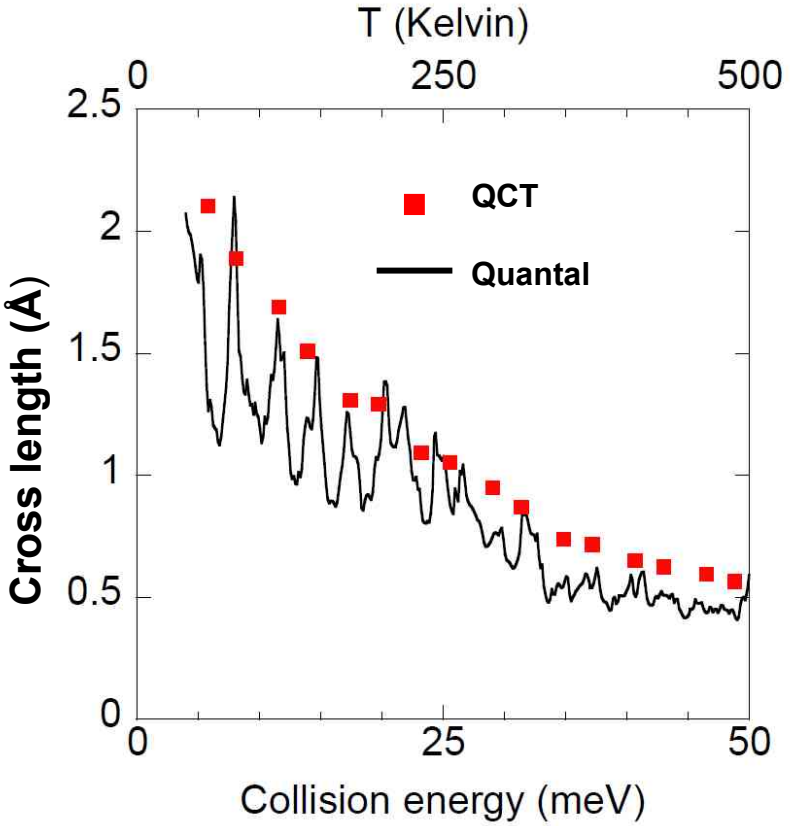

Probability
ν = 14
E_coll(eV)

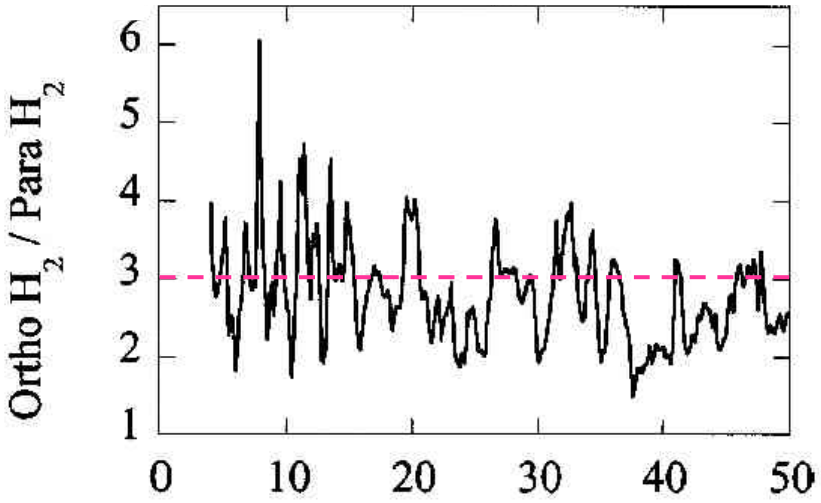
LH

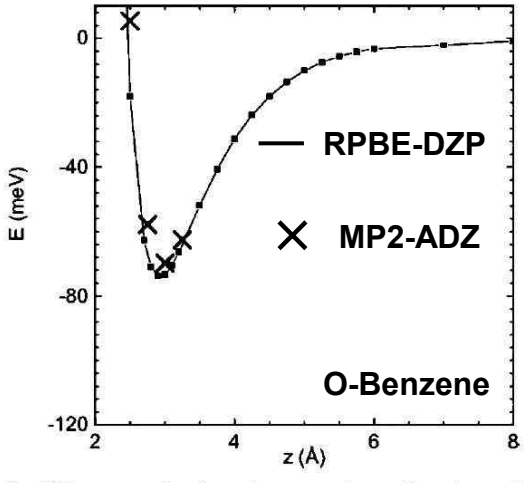
H + H → H-H(v,j)

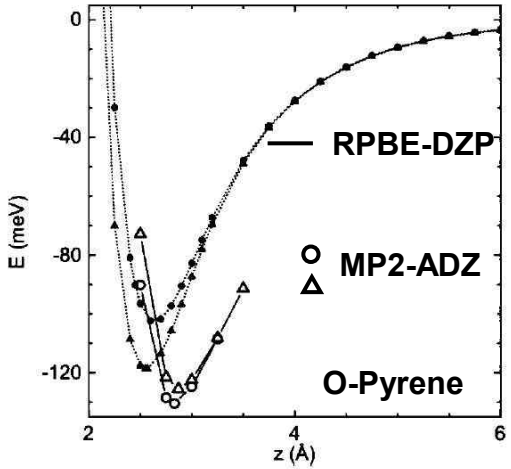
Gr

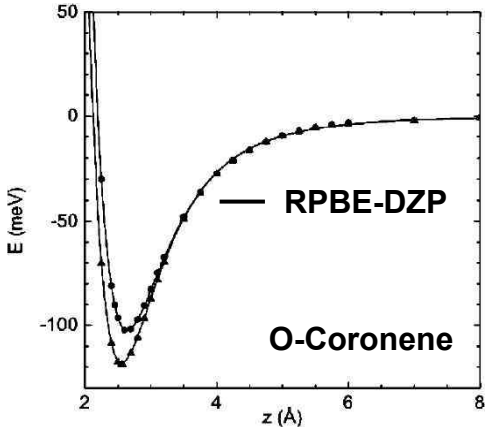
Morisset et al.
JCP 2004 - 2005

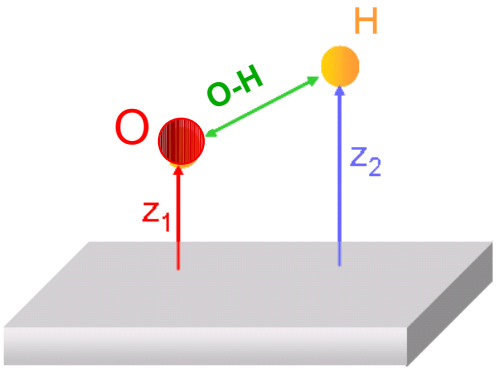












O + H (Gr) ⟶ **O-H(v,j)**

Bergeron et al. JPC A 2008

QCT

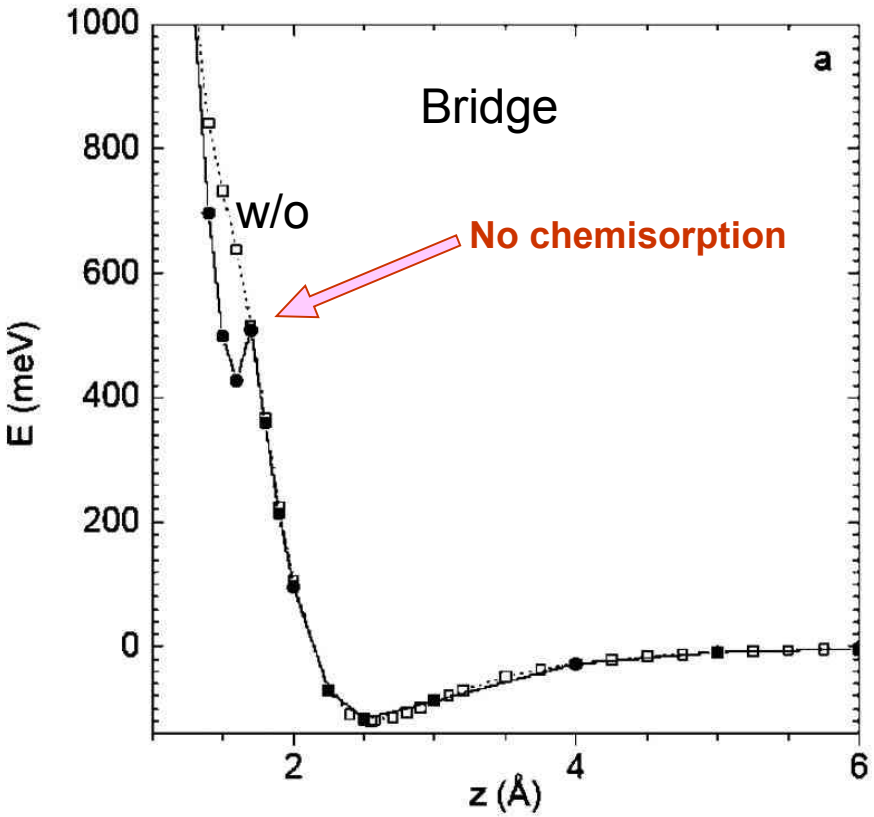
> 45 meV – 67 meV estimate
∝ Polarizabity scaling

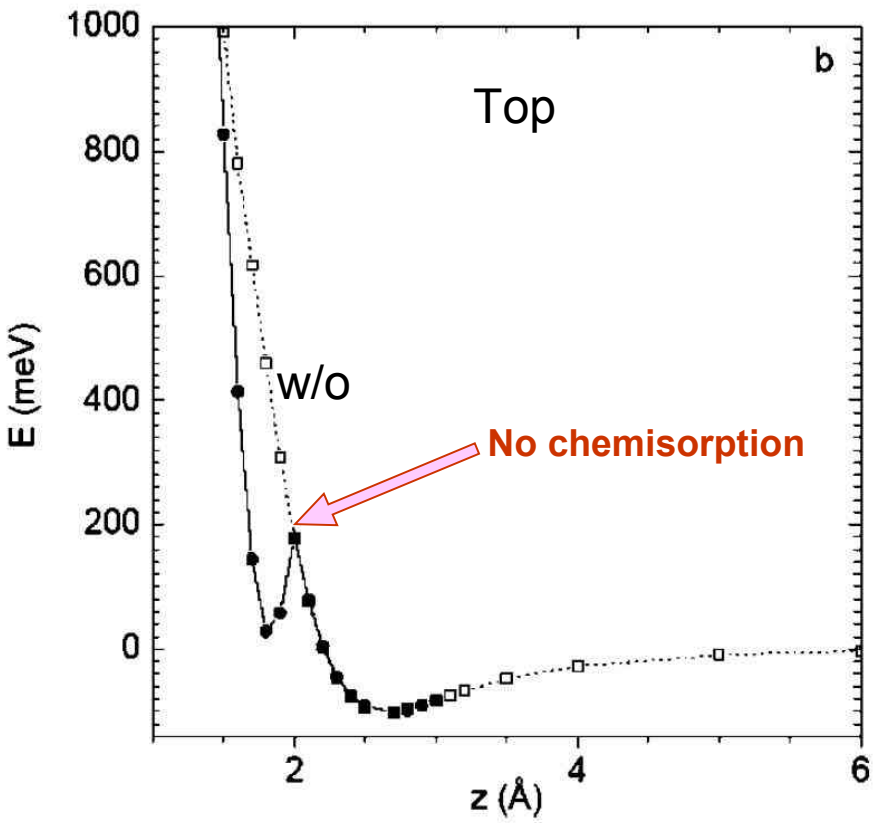
Some electron transfer (< 0.1)
substrate → atom

Goumans et al. MNRAS 2008
MPWB1K 6-311G*
71 meV
underestimated ?

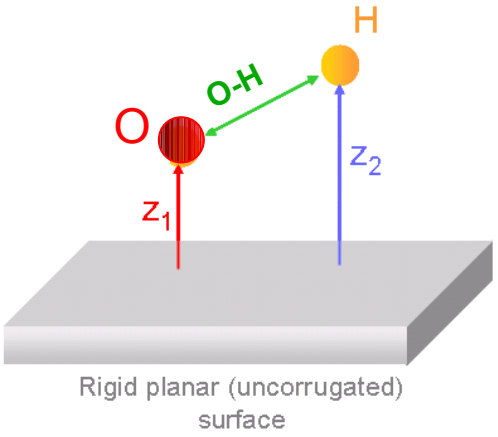
O(^{3}P) adsorption on GR (pyrene)

Bergeron et al. JPC A 2008
RPBE-DZP

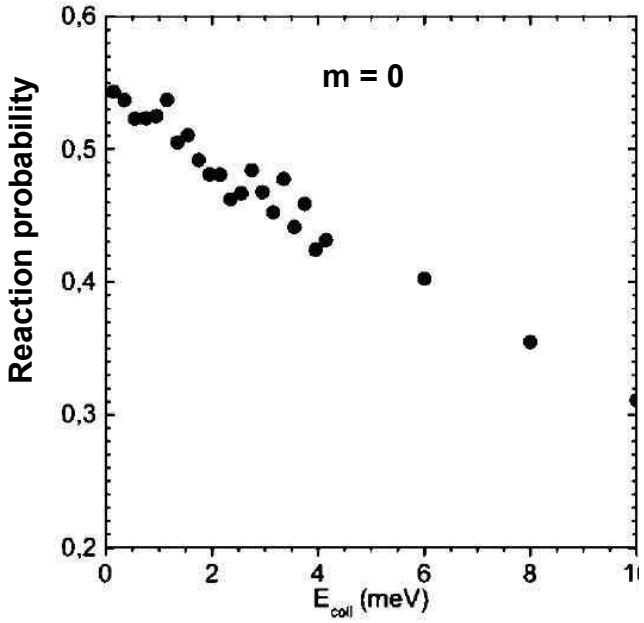


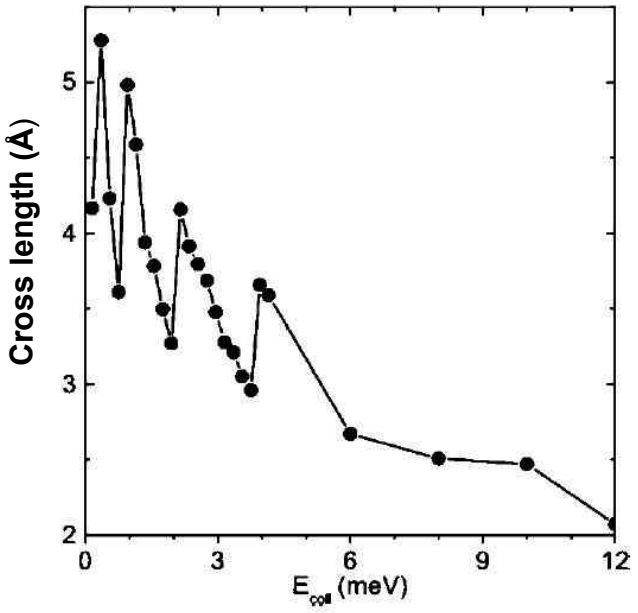


Also Goumans et al. MNRAS 2008



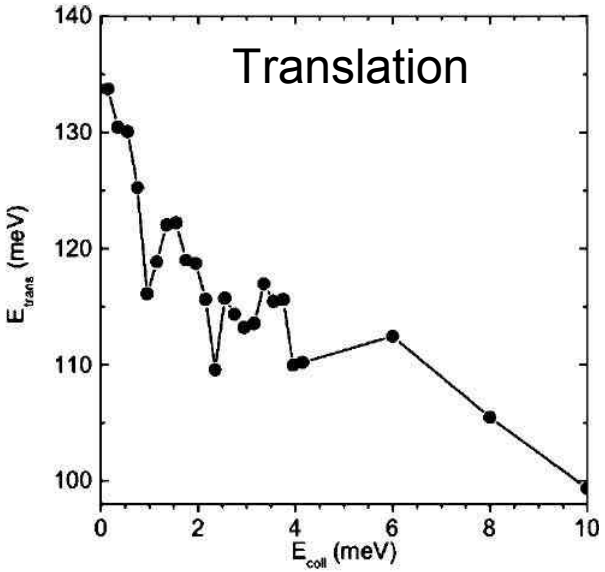
$$O + H \xrightarrow[Gr]{LH} O\text{-}H(v,j)$$

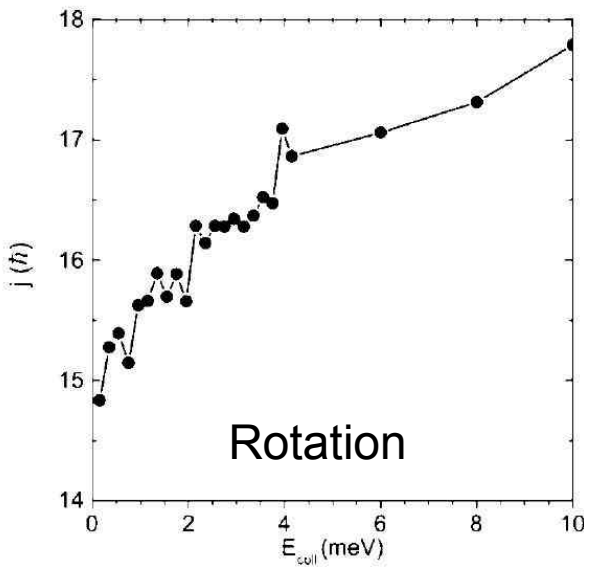


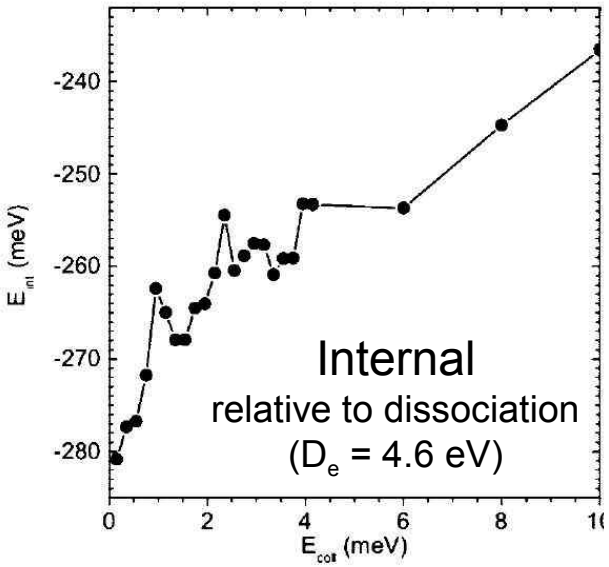


Bergeron et al. JPC A 2008

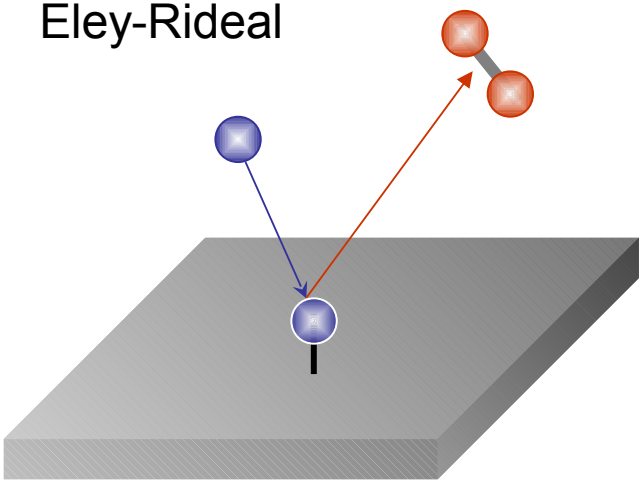
QCT



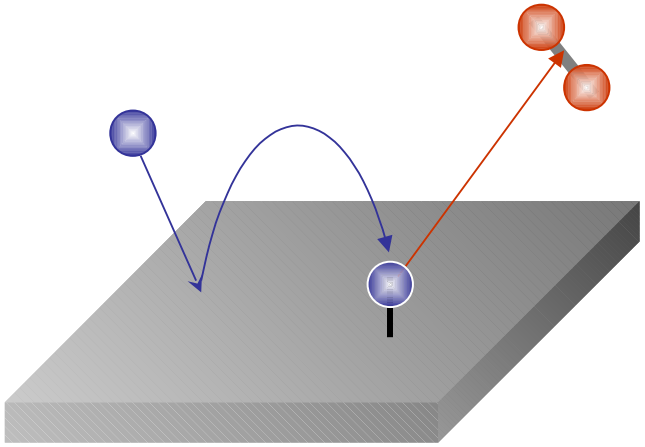




Eley-Rideal



Hot-atom
Harris-Kasemo



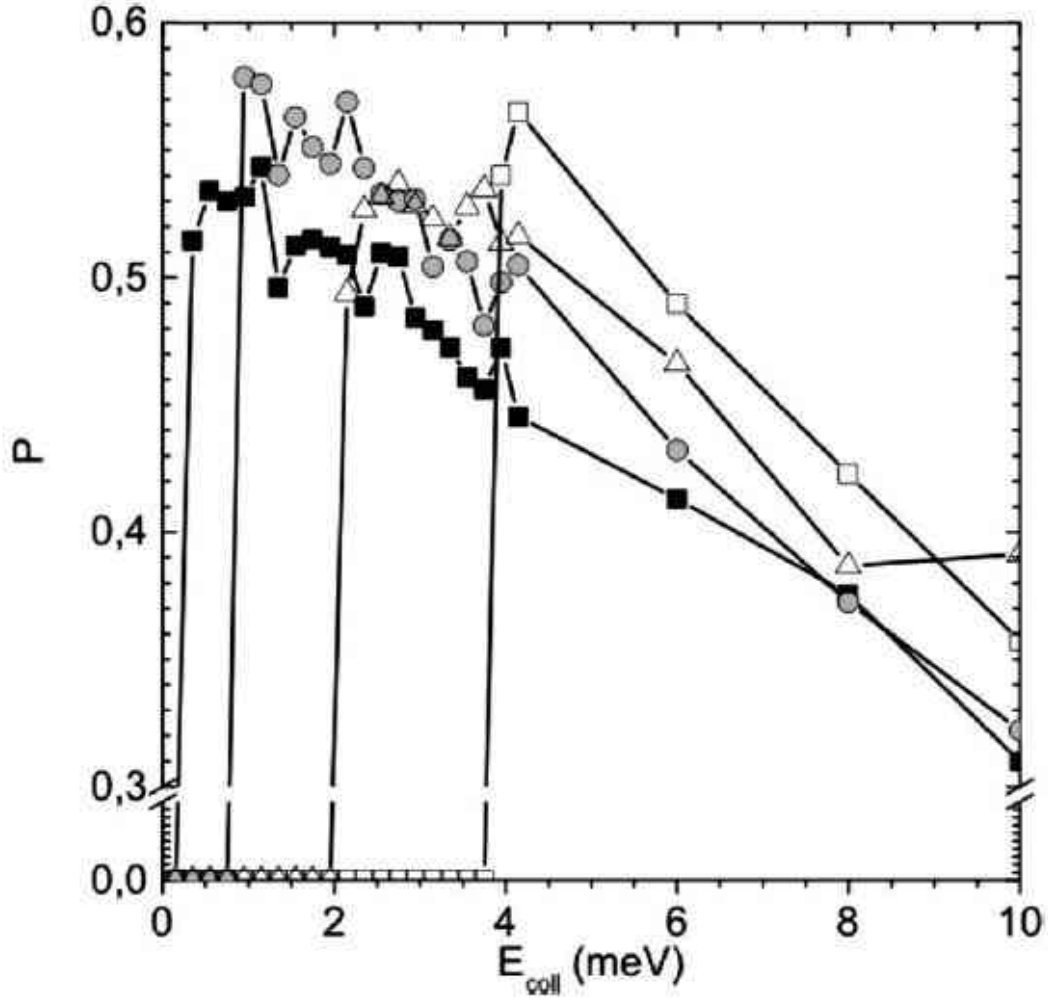
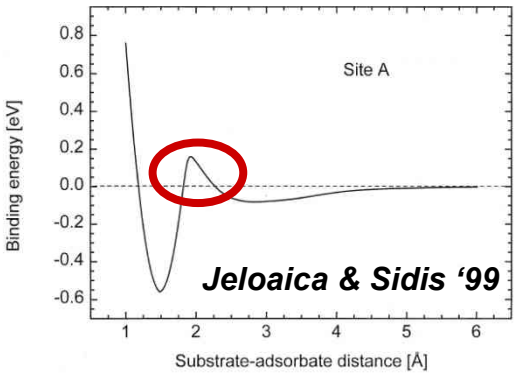
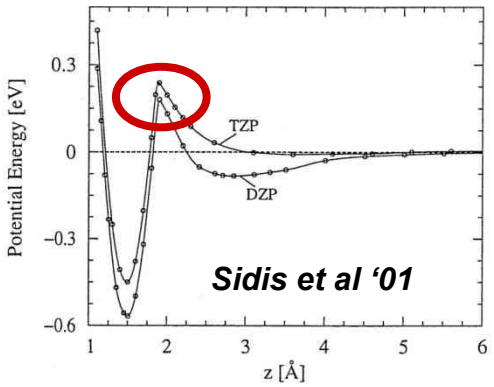
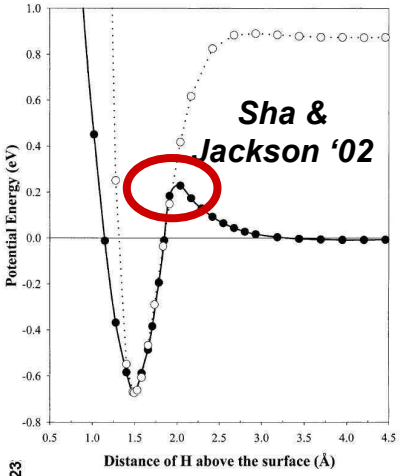
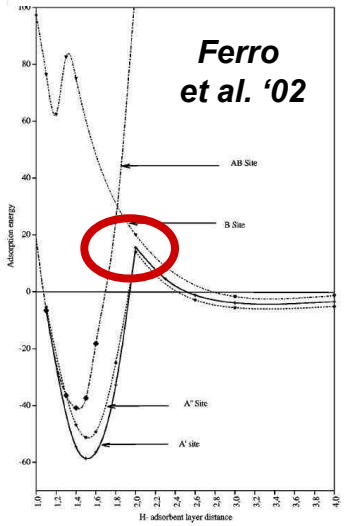


Figure 9. Probability of OH formation via the LH reaction as a function of the collision energy between the reacting O and H atoms on the surface for different values of $l_z = m\hbar$: $m = 1$ closed squares, $m = 2$ circles, $m = 3$ triangles, $m = 4$ open squares.

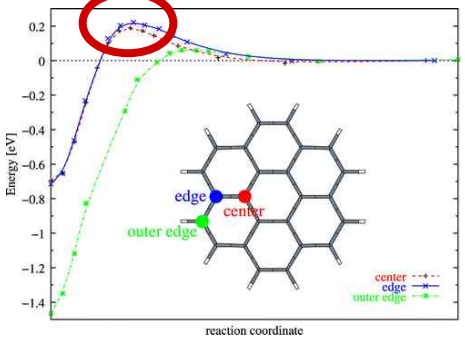


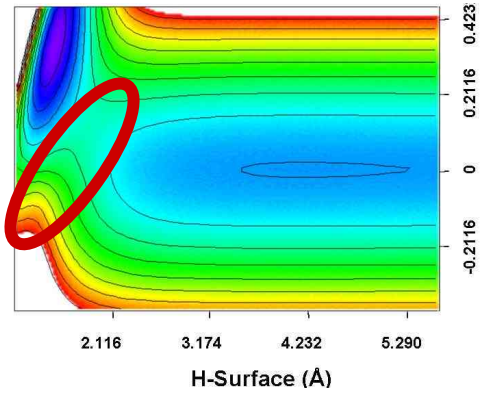


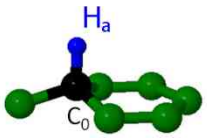


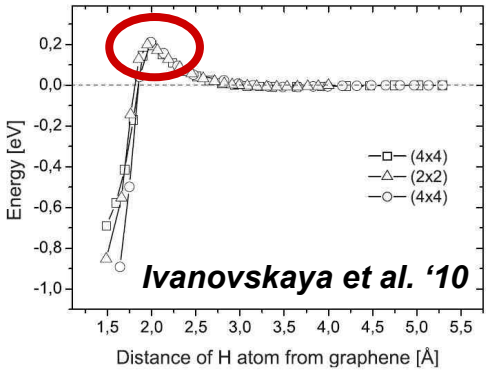


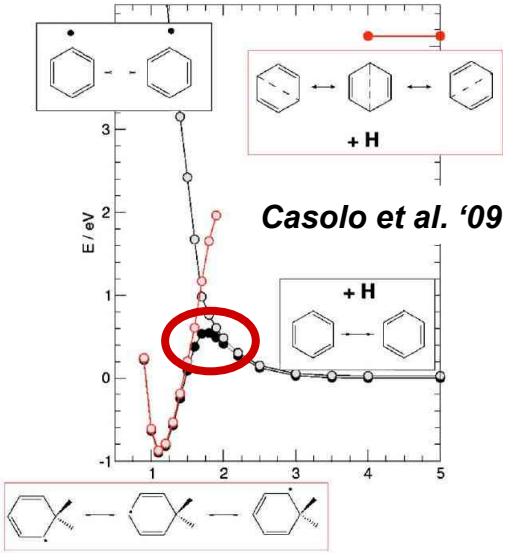
Rauls & Horneckaer '08



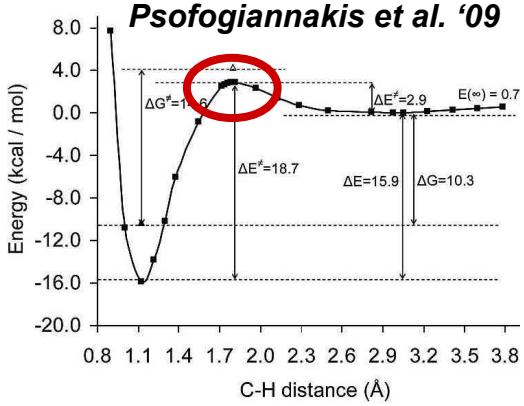


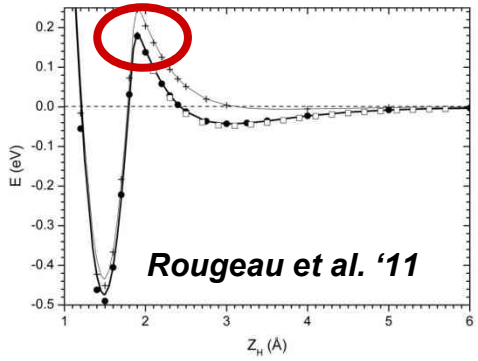






Psofogiannakis et al. '09

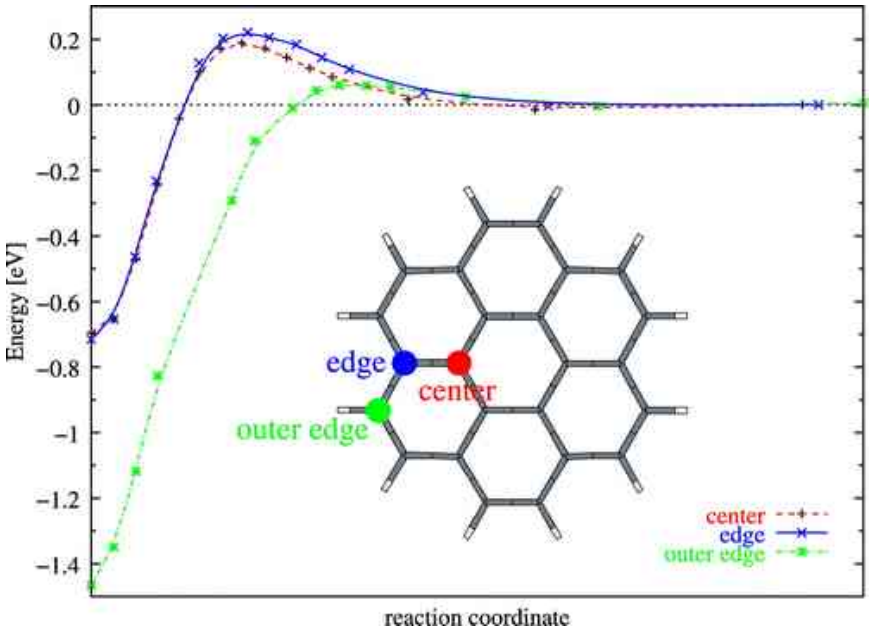




PAH edges

Rauls & Horneckaer ApJ 2008
DACAPO PW91

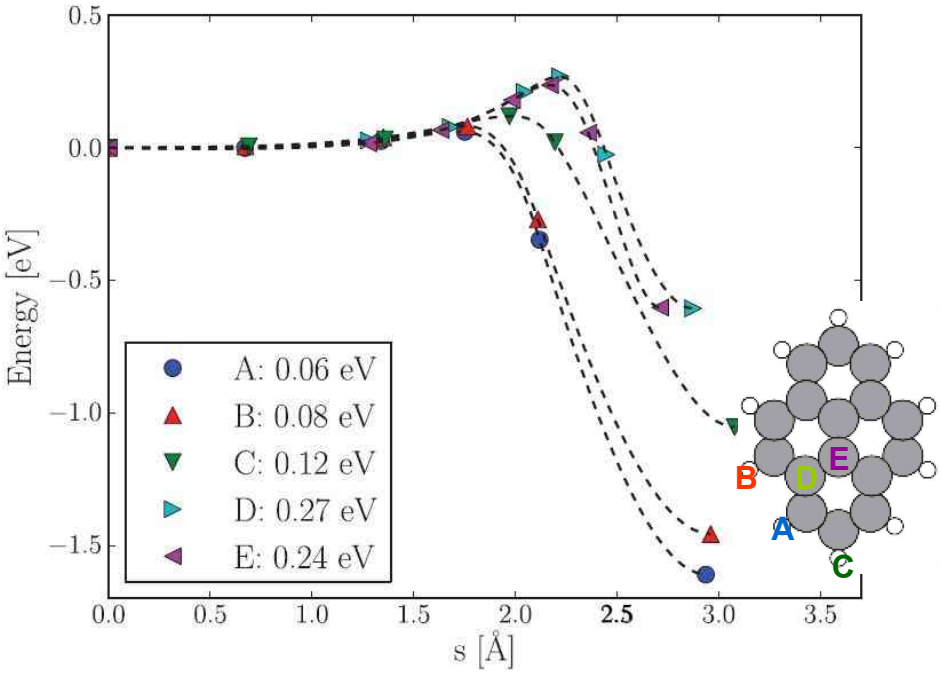
Coronene



Also Thrower et al. EAS Pub. Ser 2011

Rasmussen et al. JCP 2011
GPAW PBE

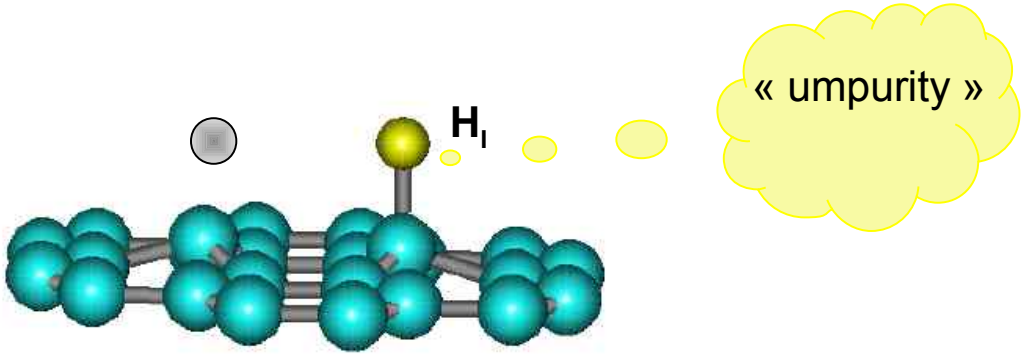
Pyrene



Also Goumans MNRAS 2011
MPWB1K
BUT …

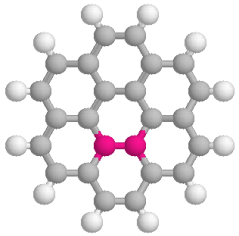
~~2000 K – 3000K~~
720 K – 1200 K

Double adsorption of H atoms on a graphitic surface

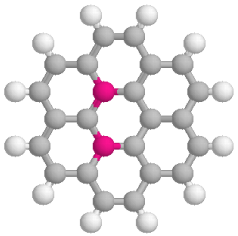


2 atoms H on the same aromatic ring

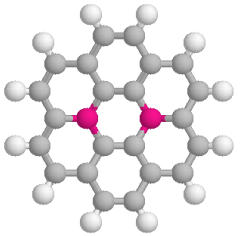
Hornekaer et al. *PRL 2006*
Rougeau et al. *CPL 2006*



ortho
(adjacent)

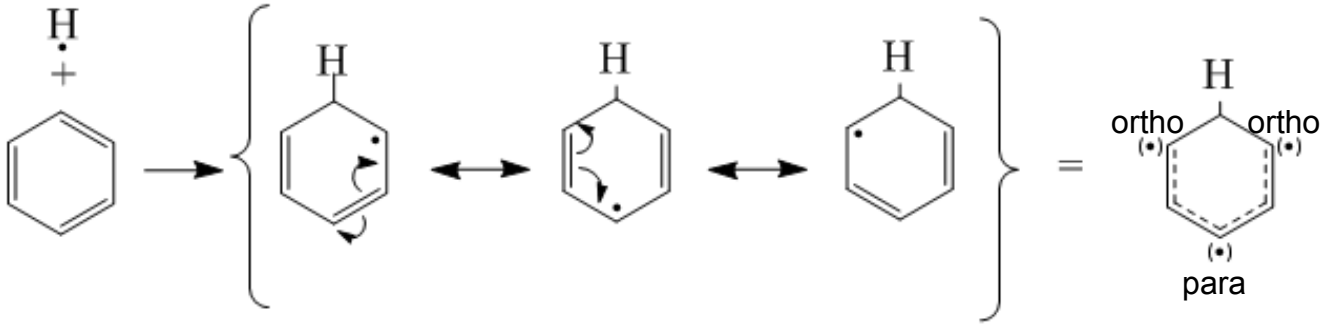


meta

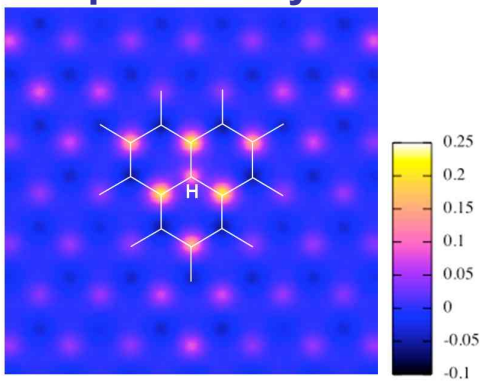


para
(opposite)

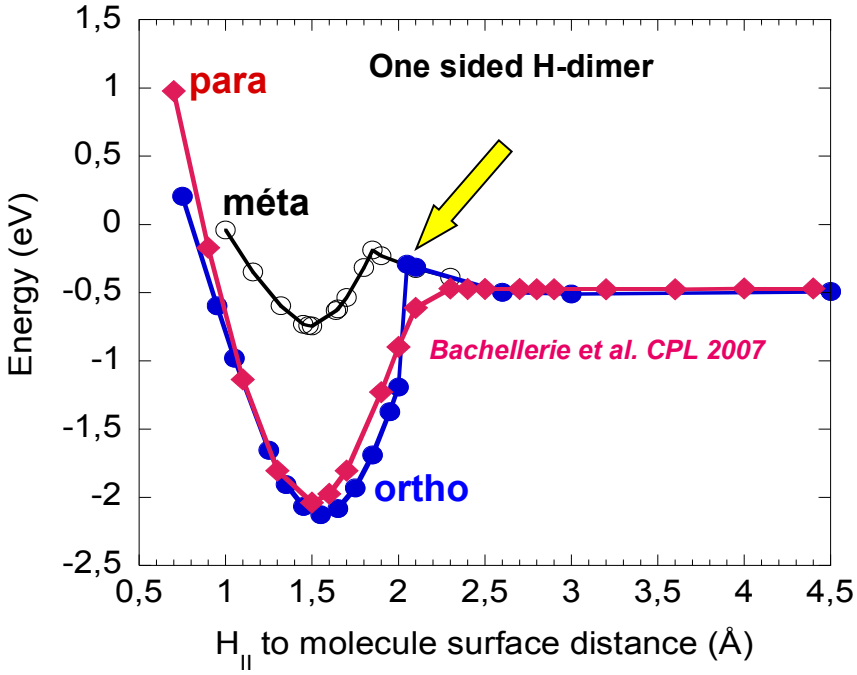
Ferro et al. PRB 2008

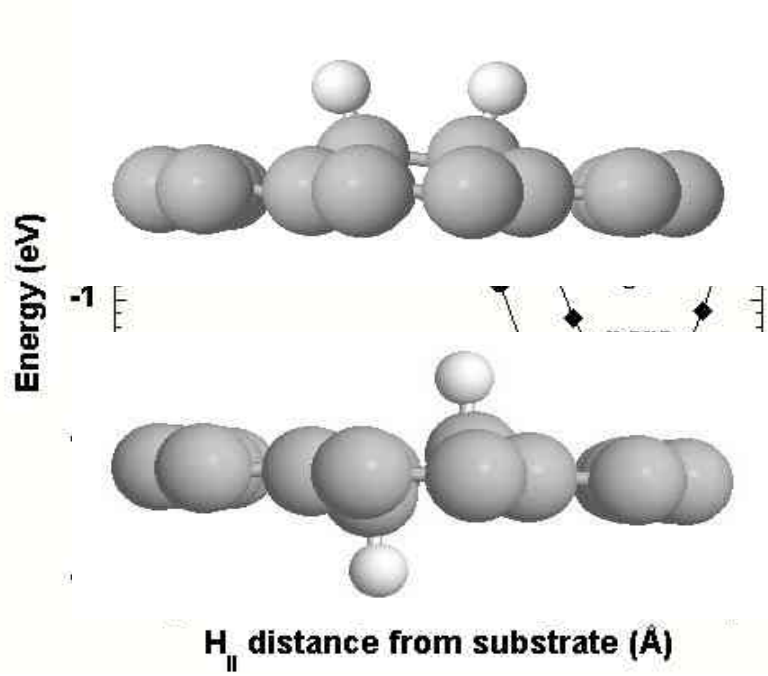


Spin density



Coronene $C_{24}H_{12}$



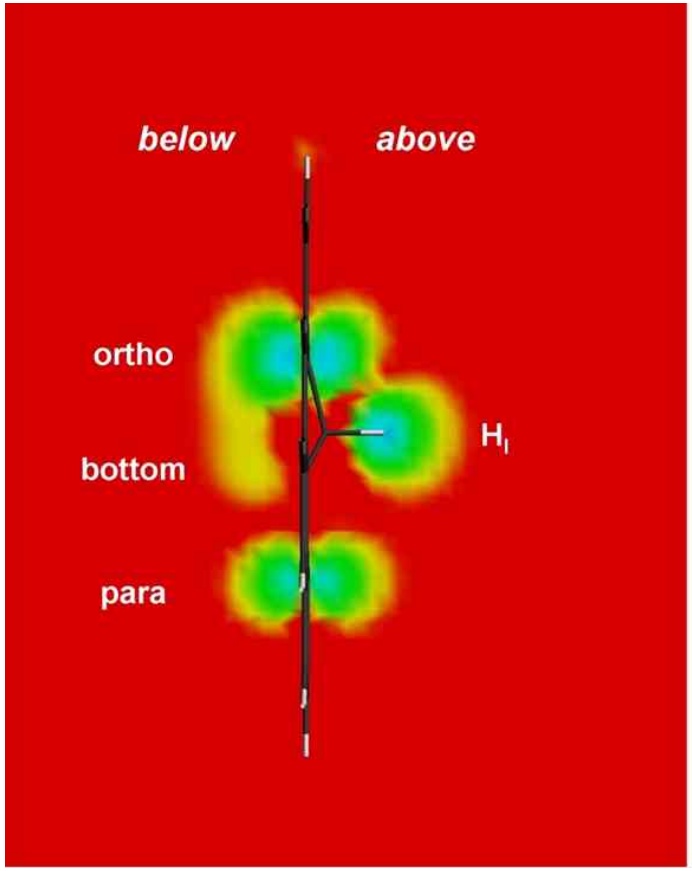


Rougeau et al. CPL 2006

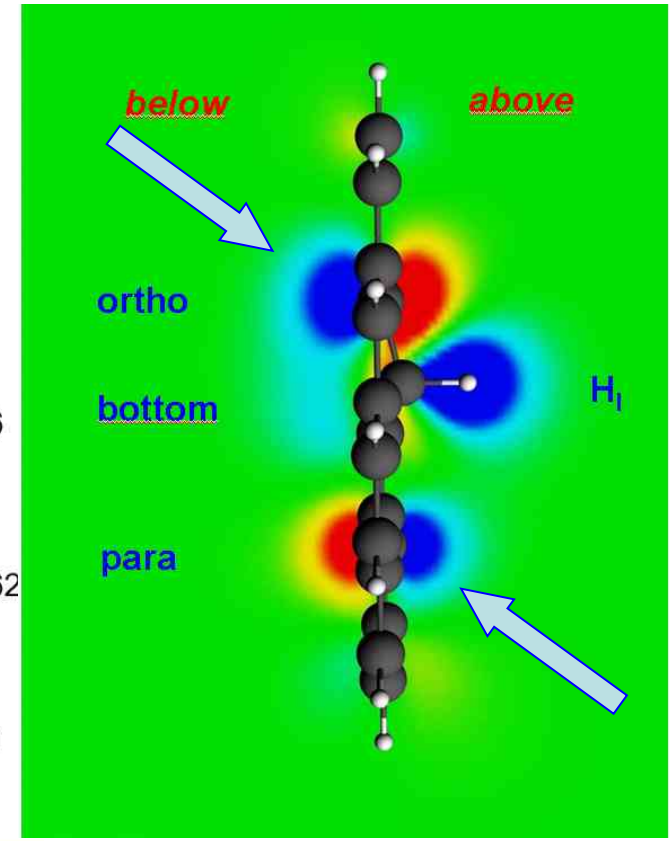
Teillet-Billy et al. IJQC 2010

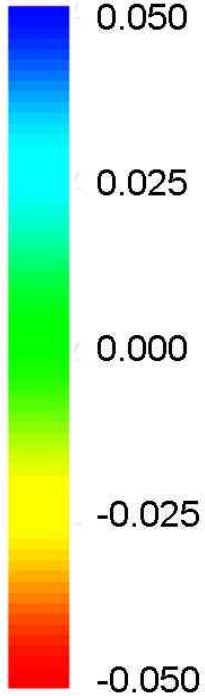
H-Circumpyrene $C_{42}H_{16}$

Spin density

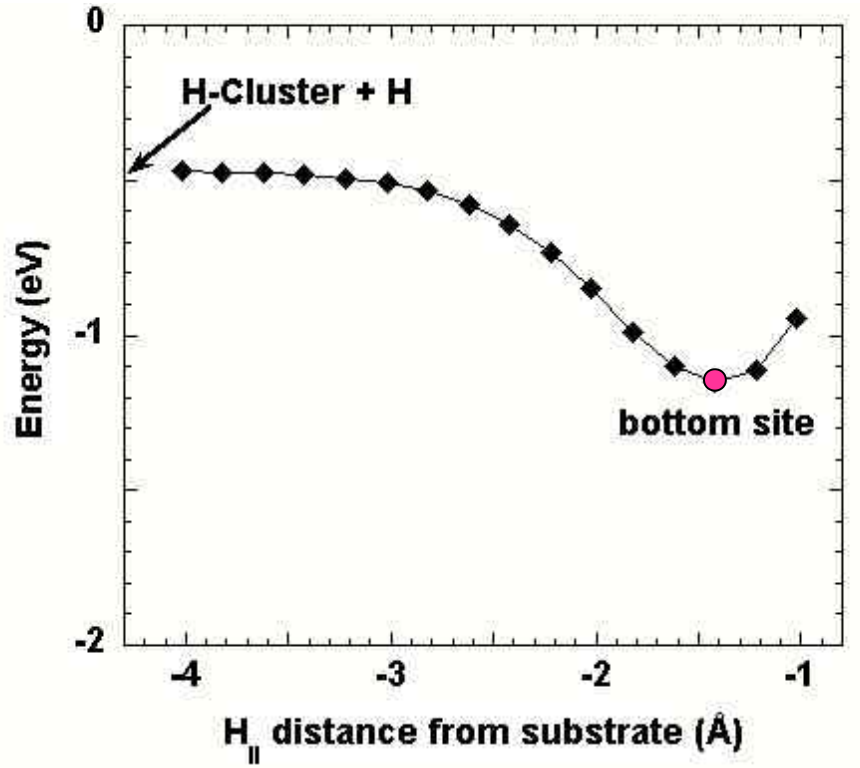


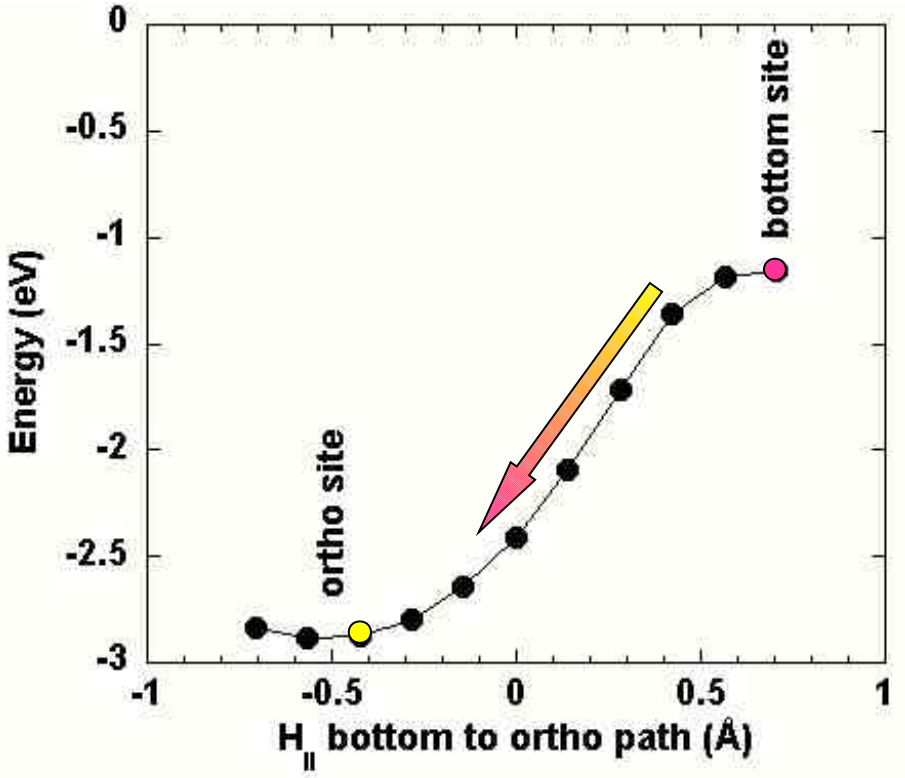
HOKSO





Teillet-Billy et al. IJQC 2010

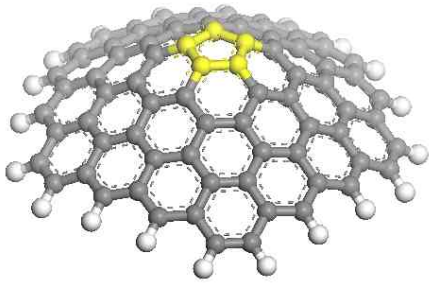




Teillet-Billy et al. IJQC '2010

Cluster with a pentagonal defect

Ivanovskaya et al. PRB 2010
AIMPRO
PBE

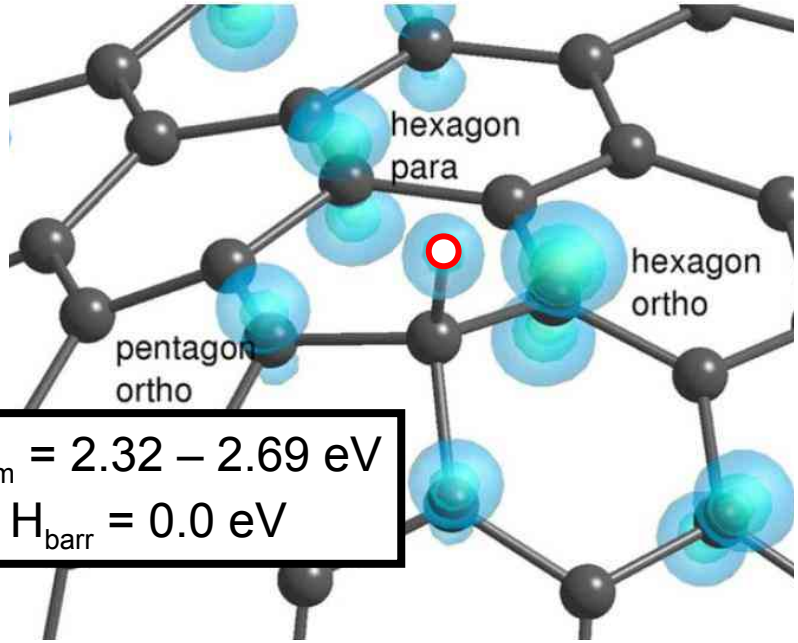


Local curvature of the graphenic flake

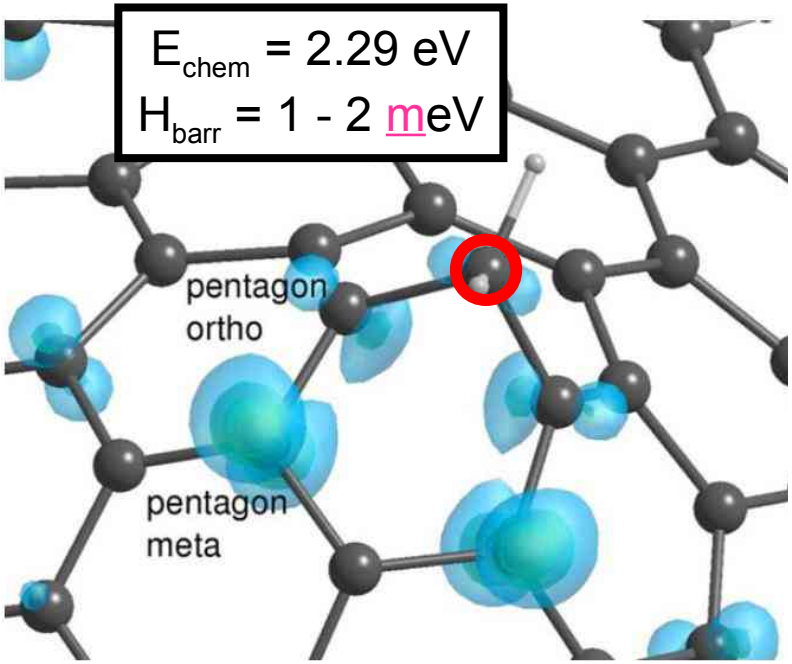
No barrier for Eley-Rideal Recombinative abstraction

HOKSO

E_{chem} = 1.89 eV
H_{barr} = 0.02 eV

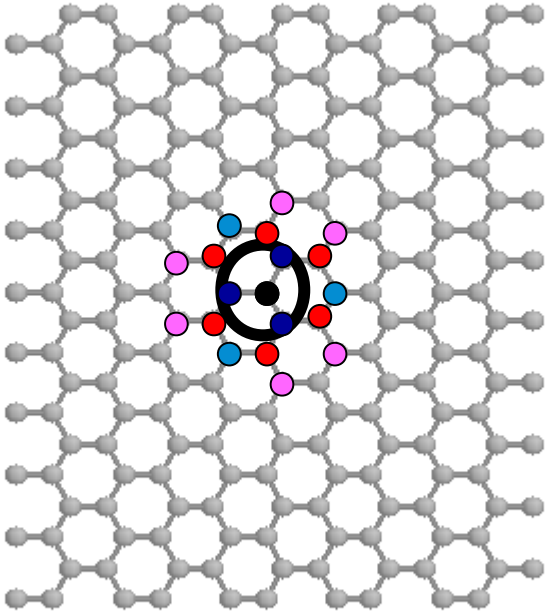


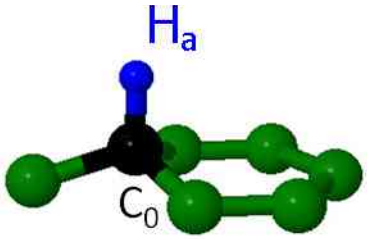
E_{chem} = 2.32 – 2.69 eV
H_{barr} = 0.0 eV



E_{chem} = 2.29 eV
H_{barr} = 1 - 2 meV

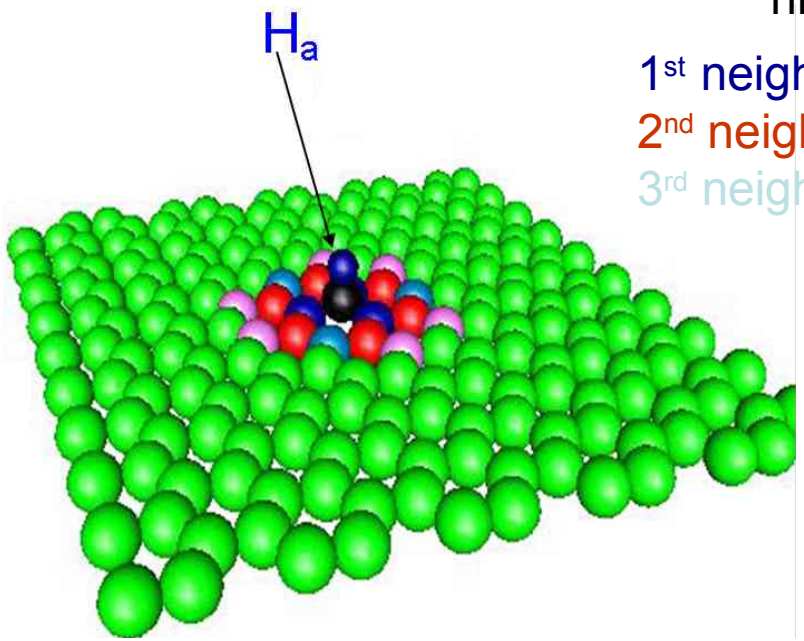
Graphenic surface





« ***puckering*** »
Tetrahedrization
$sp_2 \rightarrow sp_3$

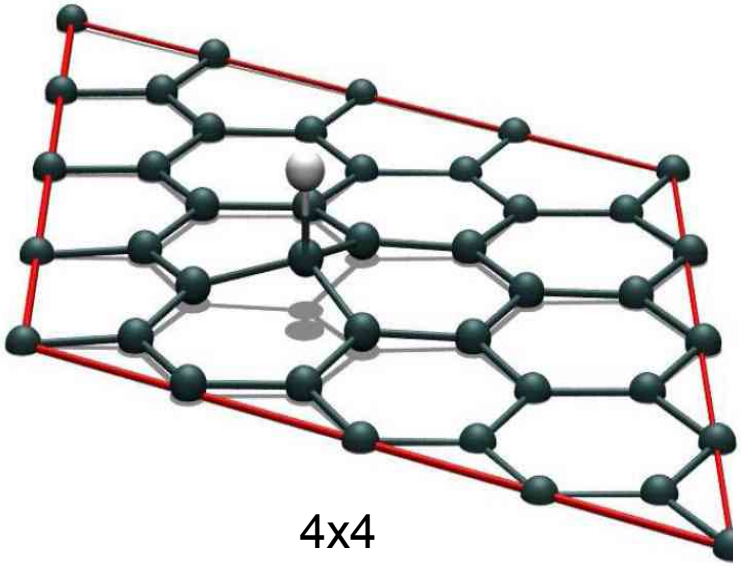
« ***extended puckering*** »
hillock



1st neighbors : 0.21 Å
2nd neighbors : 0.04 Å
3rd neighbors : 0.005 Å

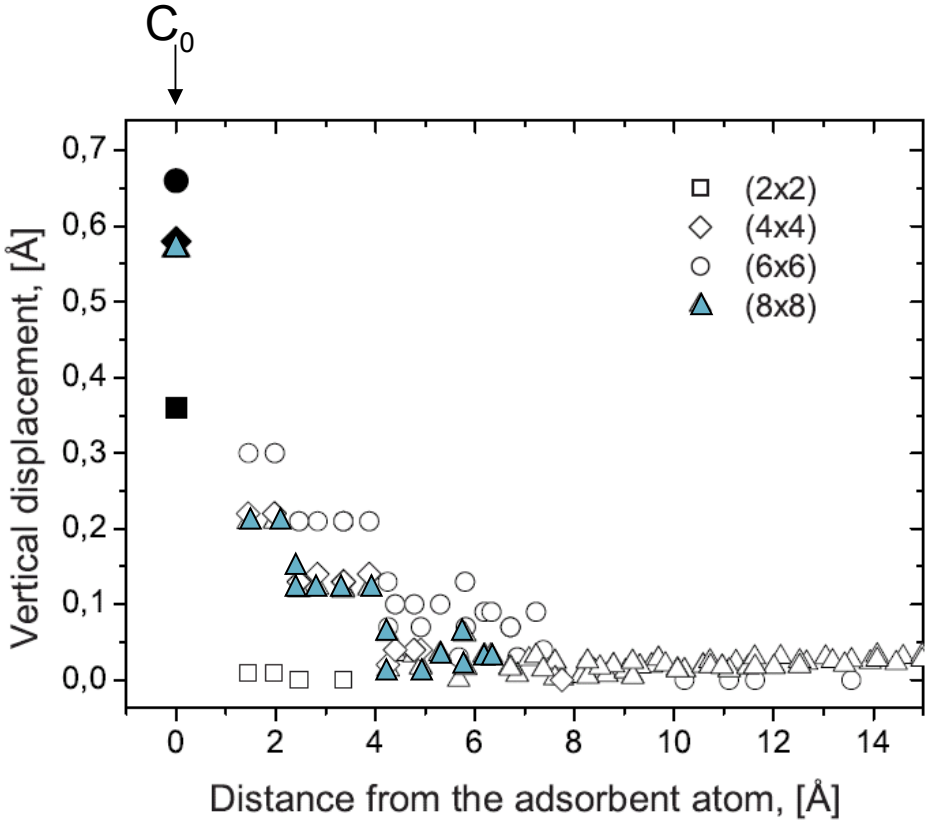
Bachellerie et al. PCCP 2009
(adaptation of Brenner potential force field)

Ferro et al. PRB 2008
DFT



4x4

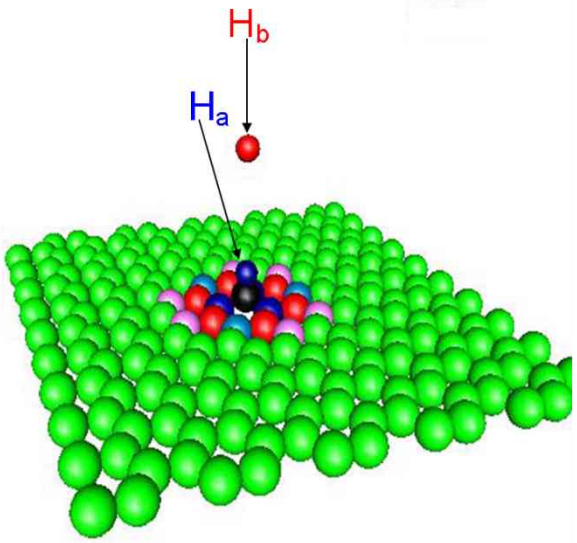
Periodic calculations
DFT-GGA (PBE)
AIMPRO
Gaussian orbital basis



Sticking

Ivanovskaya et al. EPJB (2010)

Movements of the nearest C neighbors of C_0 during a trajectory leading to ER recombination

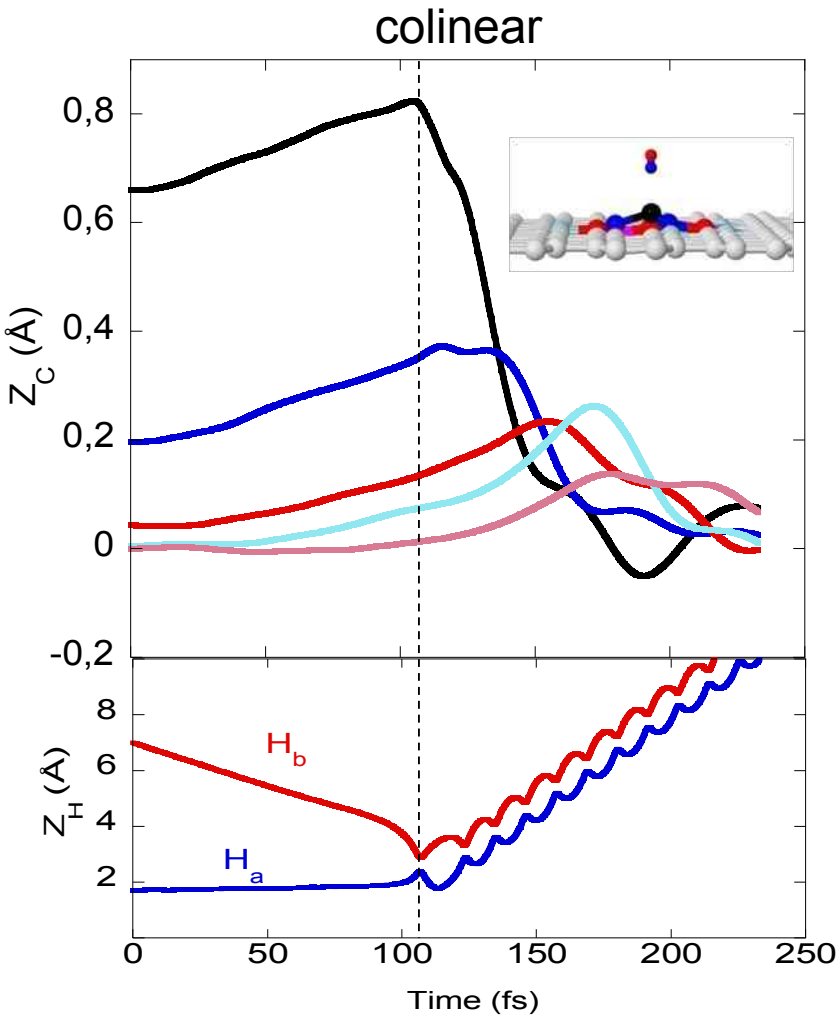


Hillock release abstraction

Imparts 0.75 – 1 eV
into the surface

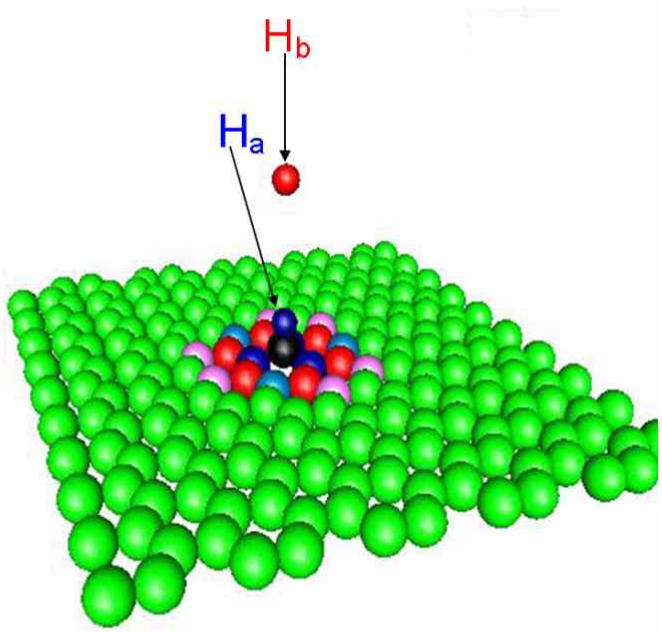
Reduces the internal energy of the nascent H_2 ($v = 8 \rightarrow v = 5$)

Bachellerie et al. PCCP 2009
Sizun et al. CPL 2010



Dynamics of ER recombinative abstraction

Quantum colinear 3D (H_a, H_b, C_0): ***Morisset et al. JPC A 2004***



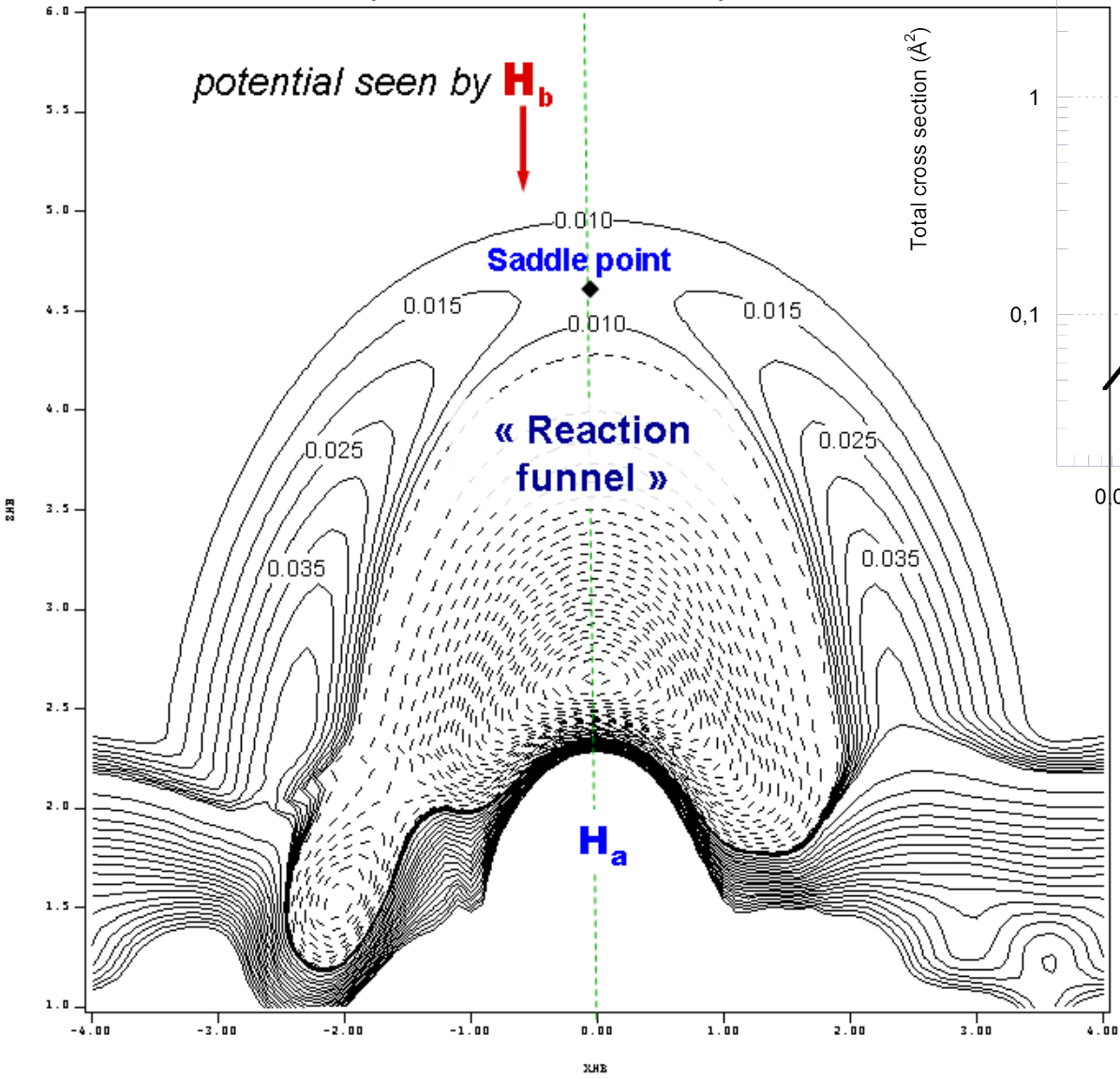
Bachellerie et al. PCCP 2009
Sizun et al. CPL 2010

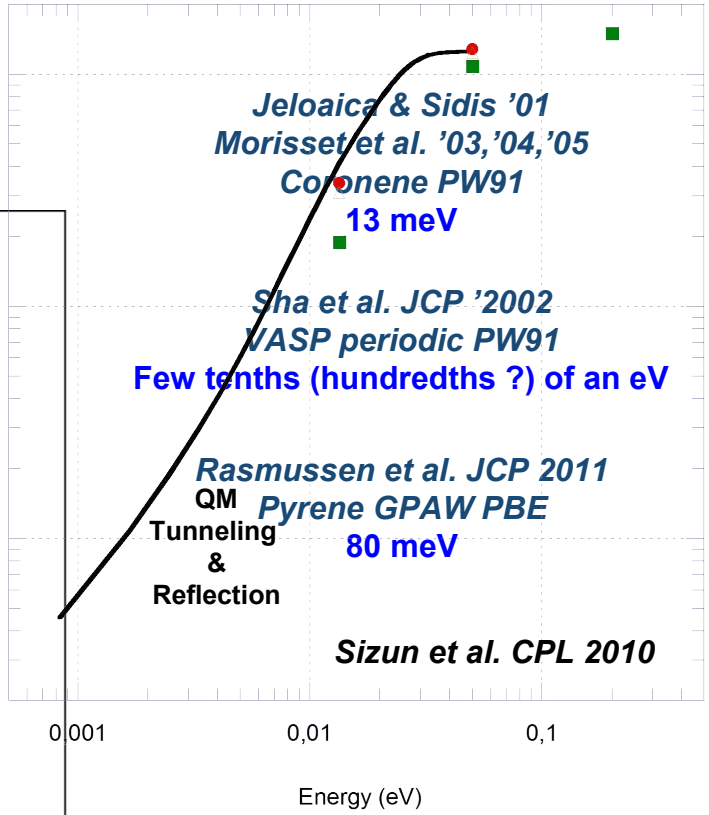
General: non colinear
with corrugated surface, and surface atom motions

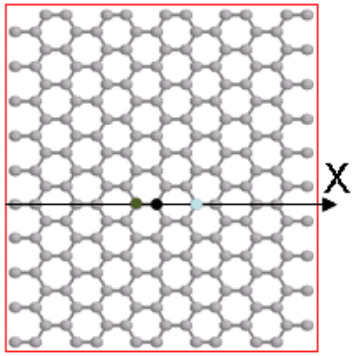
Classical molecular dynamics
QCT
Adaptation of the Brenner potential

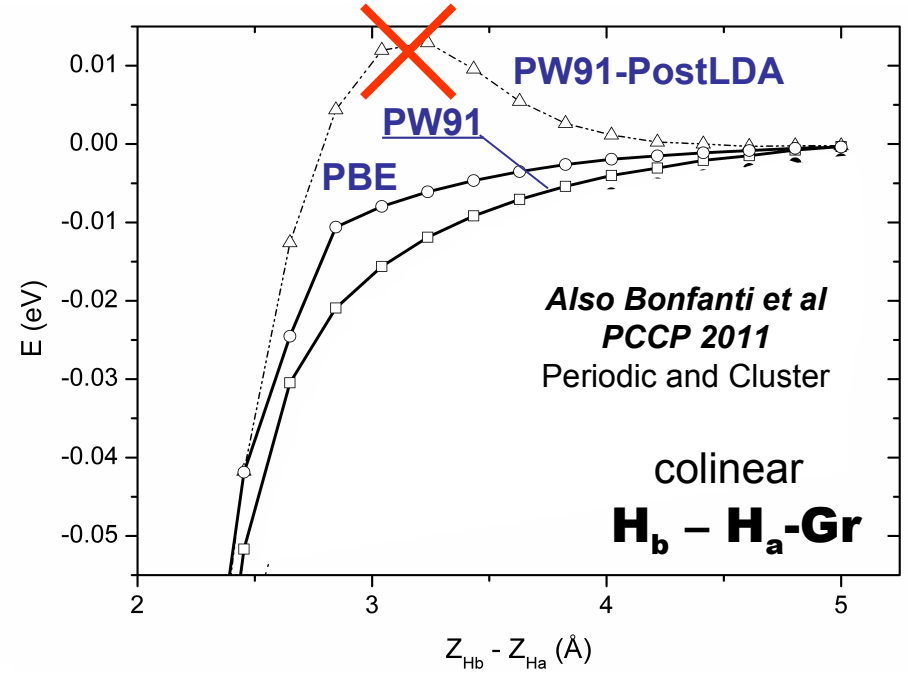
Bachellerie et al. PCCP 2009
Sizun et al. CPL 2010

Classical molecular dynamics
QCT
Adaptation of the Brenner potential



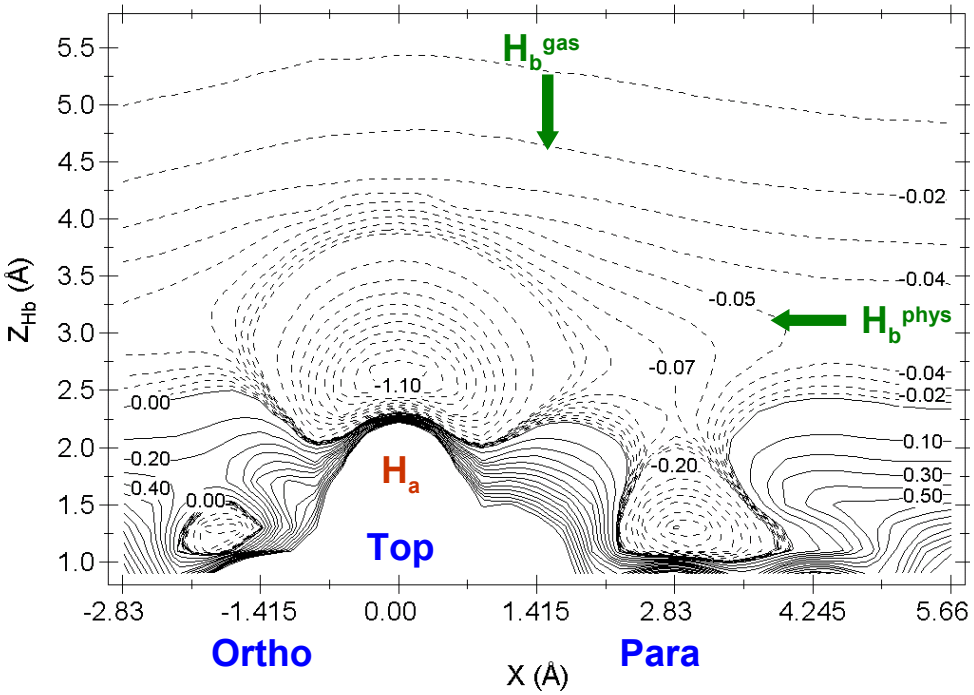






Rougeau et al. PCCP 2011

Aréou et al. JCP 2011



H_b - H_a-Circumcoronene

Extended puckering

PBE-D3

Dynamics calculations on the ER reaction that used a **barrierless H_b–H_a-GR** PES are brought to the fore

Sha et al. JCP 2002, Casolo et al. JPC A 2009

"adiabatic" and "diabatic" (fixed puckered) cases

Hillock relaxation during the reaction

Restricted puckering: Morisset et al JPC A 2004
Extended puckering: Bachellerie et al PCCP 2009, Sizun et al. CPL 2010

Surface corrugation
Zero point energy effects
Energy dissipation by exchange with surface phonons

Restricted puckering: Morisset et al JPC A 2004
Extended puckering: Bachellerie et al PCCP 2009, Sizun et al. CPL 2010

Classical Molecular Dynamics
with
Quantum railings

Realistic PES (force field)
on the fly