A short introduction to physics and chemistry at crystalline surfaces

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outline

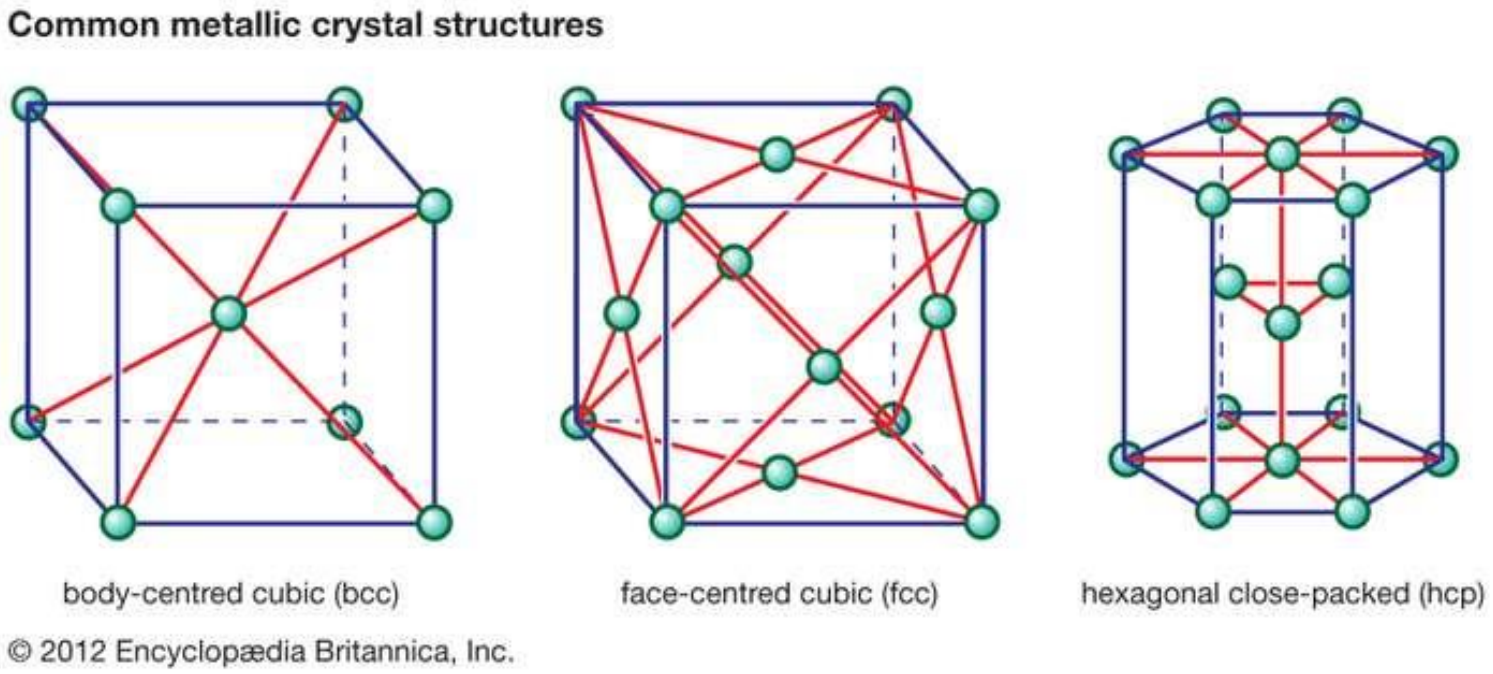
- *surfaces: metals, semiconductors, oxides, 2D materials*

1. *catalysis*
2. *nanostructures at graphene*

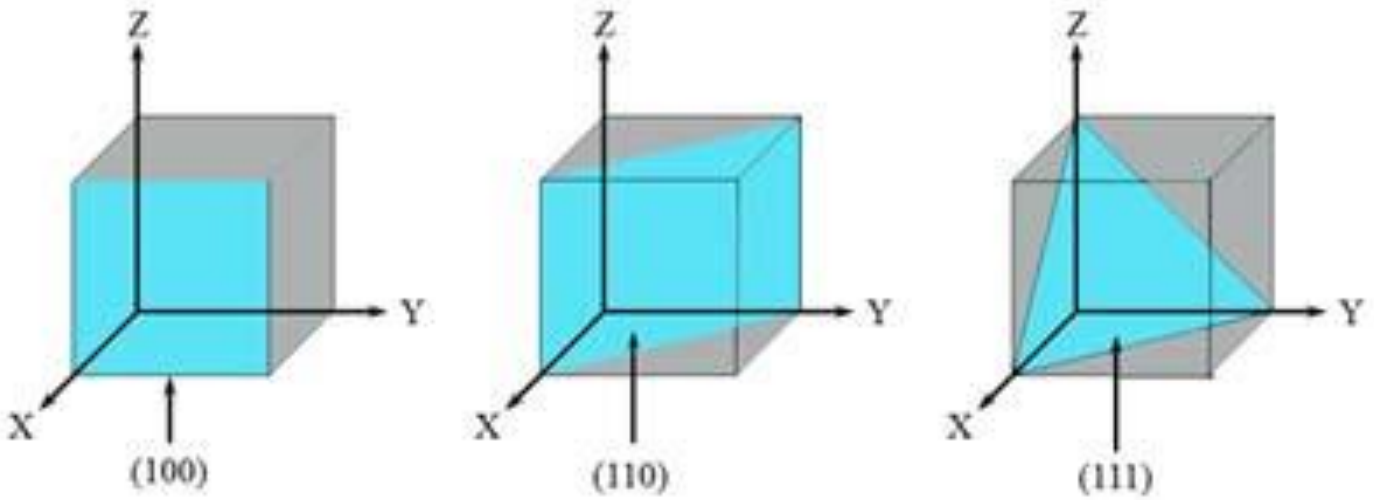
- *DFT and experiments in surface science*

Common crystal structures

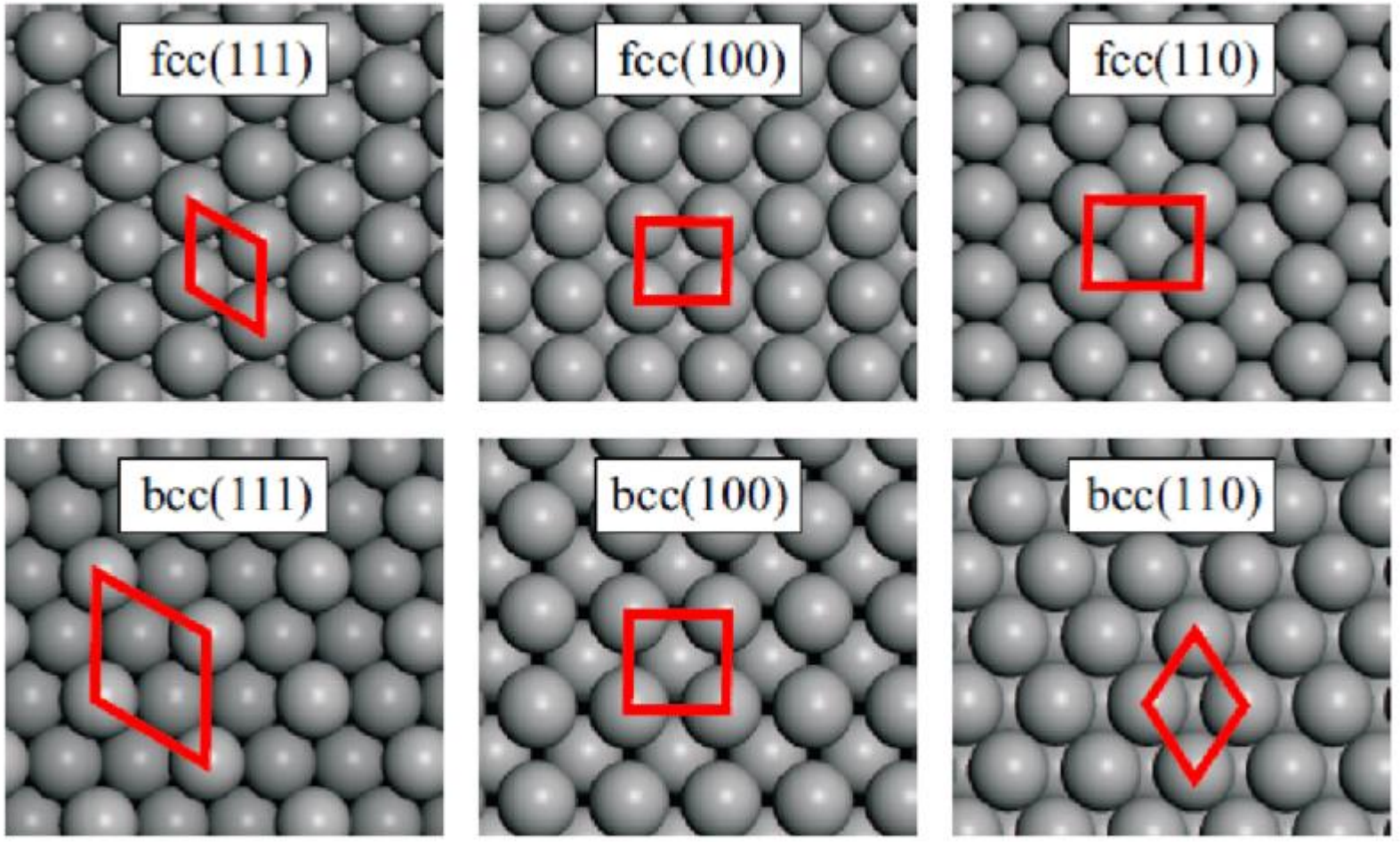
bulk



surfaces

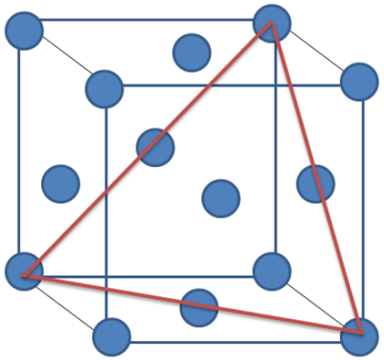


Common metal surfaces

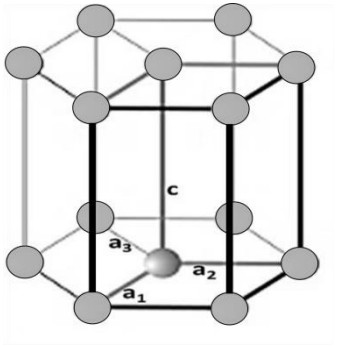


Common metal surfaces

fcc(111)

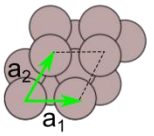


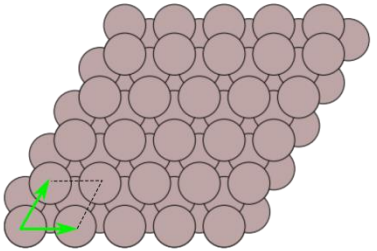
hcp(0001)



FCC(111)

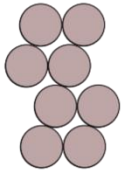
top

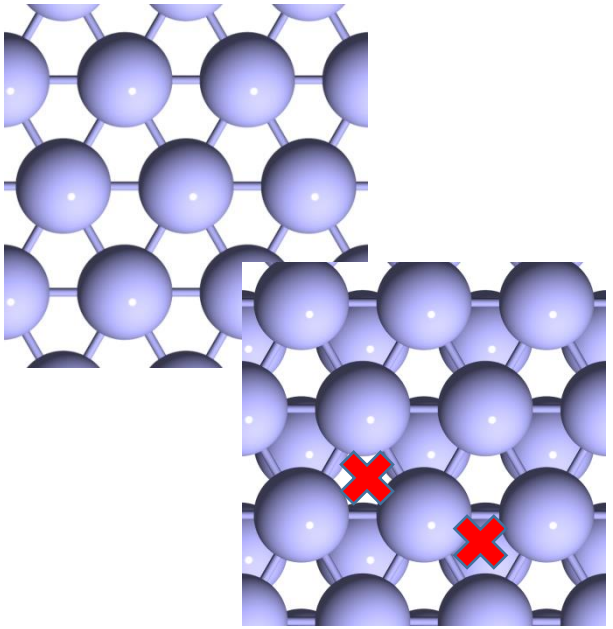




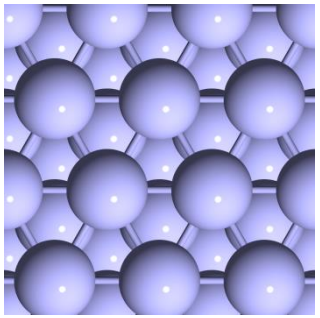
side

A
B
C
A



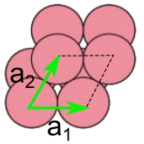


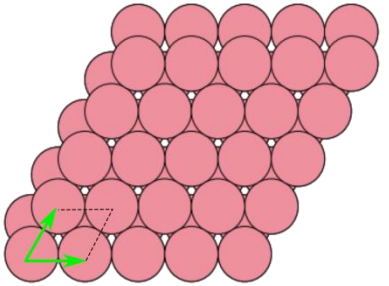
fcc



hcp(0001)

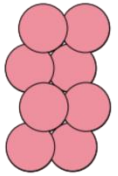
top

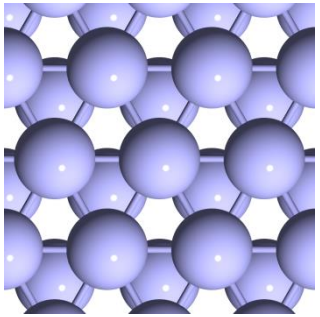




side

A
B
A
B

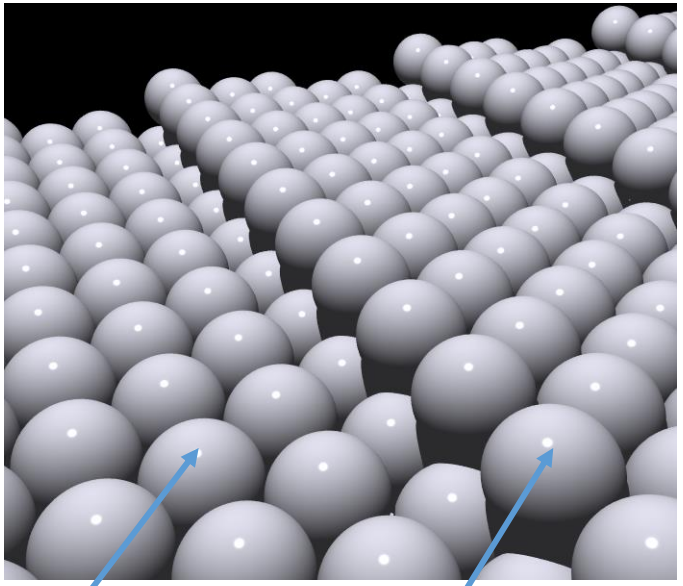




hcp

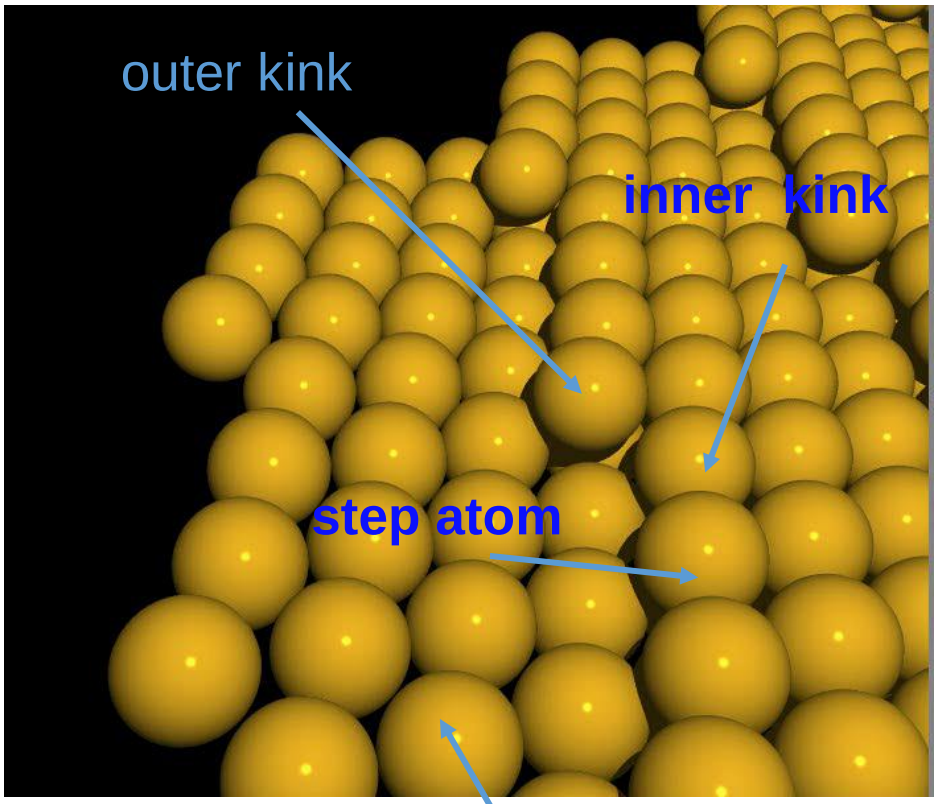
Defects at metal surfaces

stepped surface



terrace atom

step atom

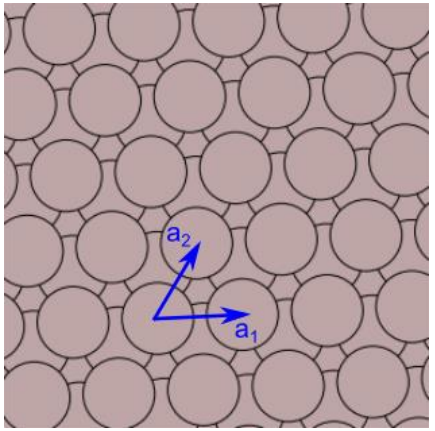


terrace atom

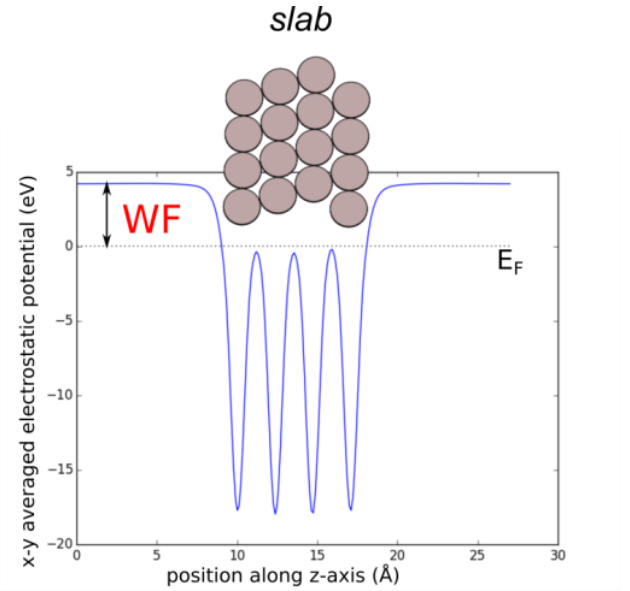
Atoms with reduced coordination number

Atomic Simulation Environment (ASE): https://wiki.fysik.dtu.dk/ase

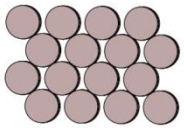
Slab model of surfaces



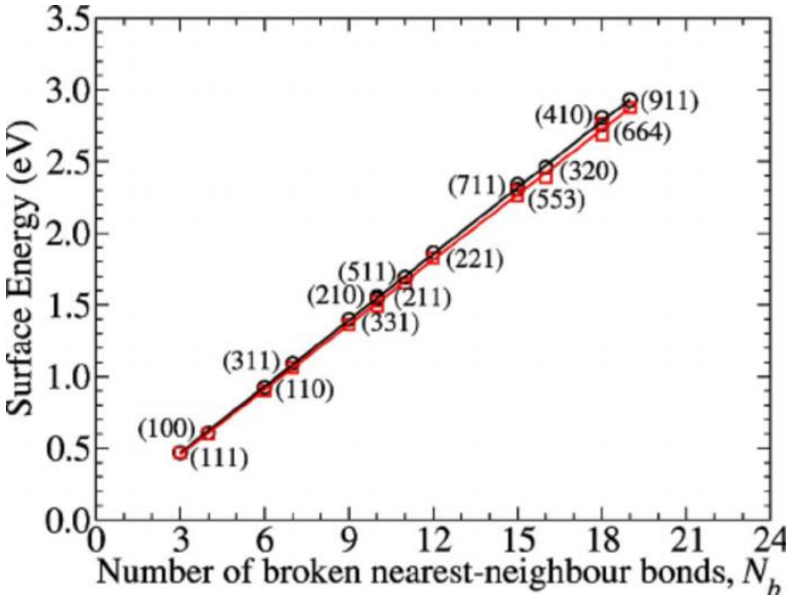
work function



surface energy

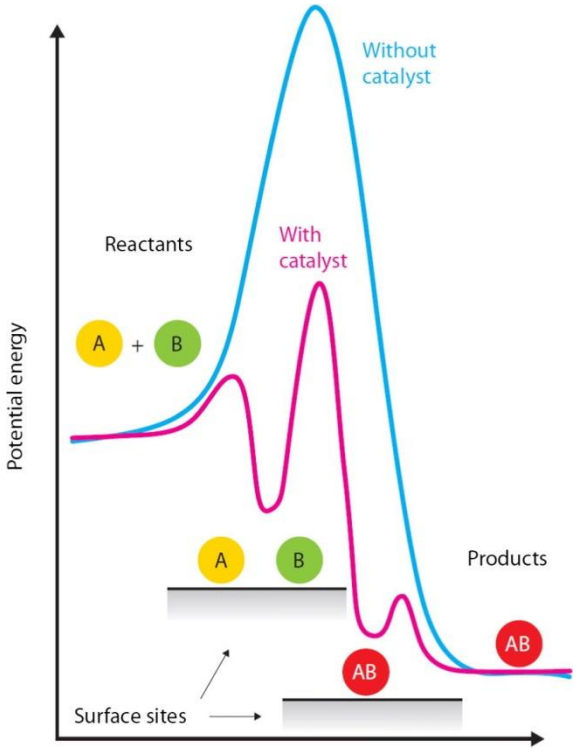


$$\gamma = \frac{\mathrm{E(slab, N)} - \mathrm{N} \cdot \mathrm{E(bulk)}}{2\mathrm{A}}$$

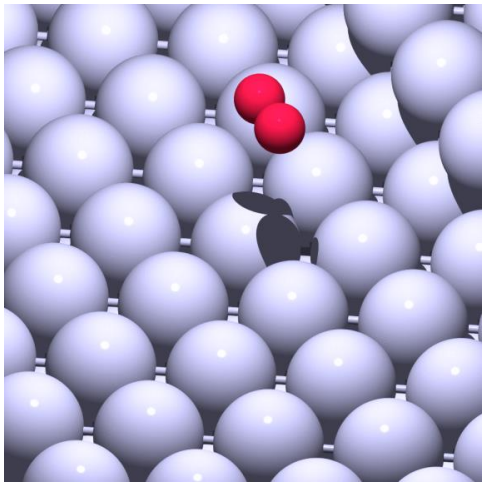


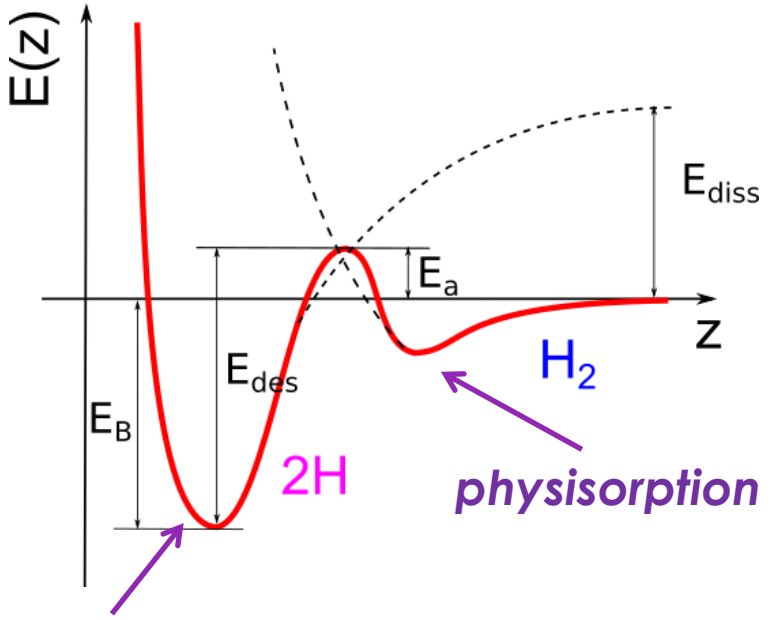
clear correlation between surface energy and the number of broken NN bonds

Catalysis



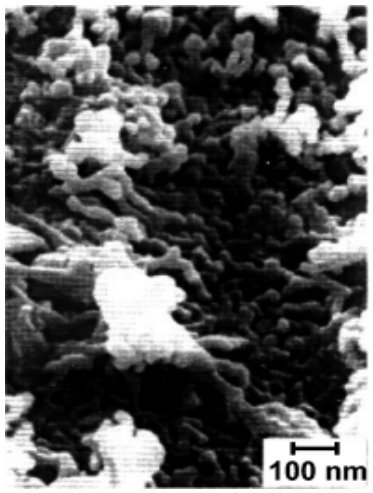
dissociative chemisorption





2H <-- H_2

Catalysts

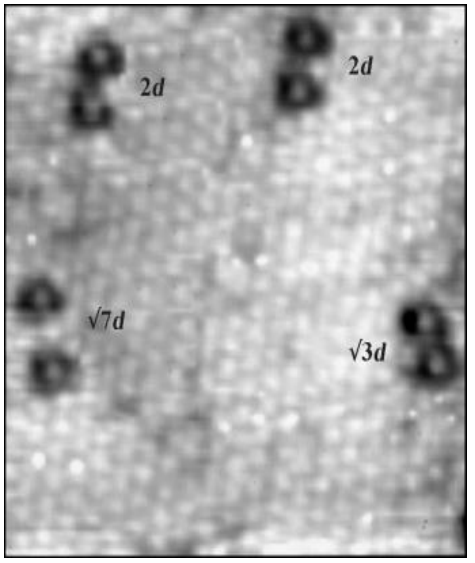


Technical conditions: $T \approx 400°C$, $p \approx 300$ bar
promoted iron catalyst

BASF S6-10 catalyst [at. %]

	Fe	K	Al	Ca	O
Bulk composition	40.5	0.35	2.0	1.7	53.2
Surface –					
unreduced	8.6	36.2	10.7	4.7	40.0
reduced	11.0	27.0	17.0	4.0	41.0
cat. active spot	30.1	29.0	6.7	1.0	33.2

O at Ru(0001)



G. Ertl, Angew. Chem. Int. Ed. 47, 3524 (2008).

Ammonia synthesis – industrial catalyst

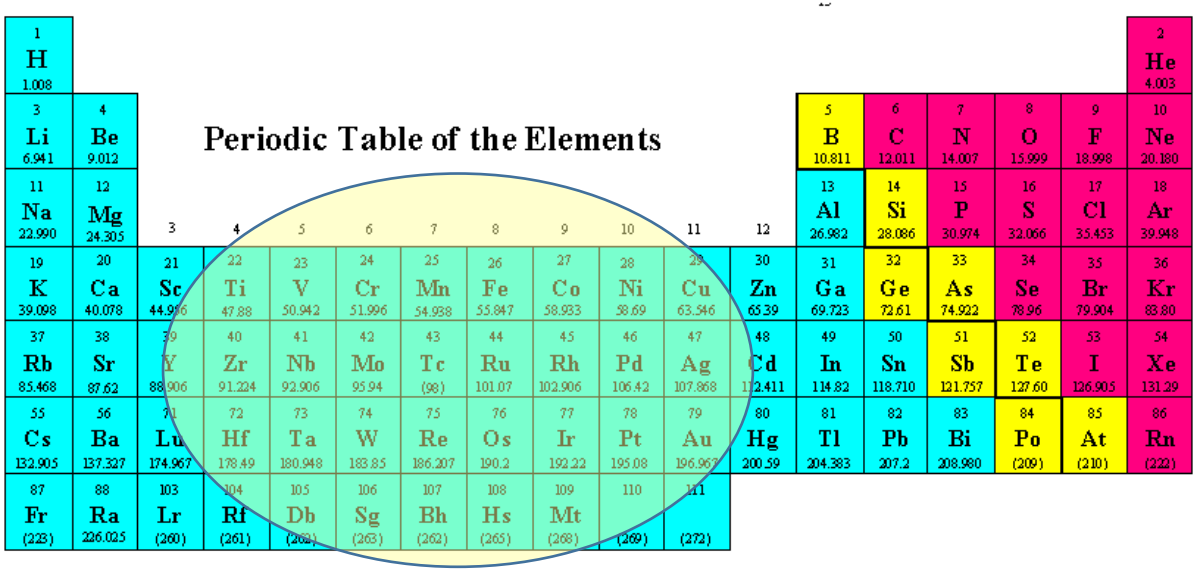
very complicated structure

➢ *make a simple model*

Gerhard Ertl, Nobel prize in Chemistry 2007

"for his studies of chemical processes on solid surfaces".

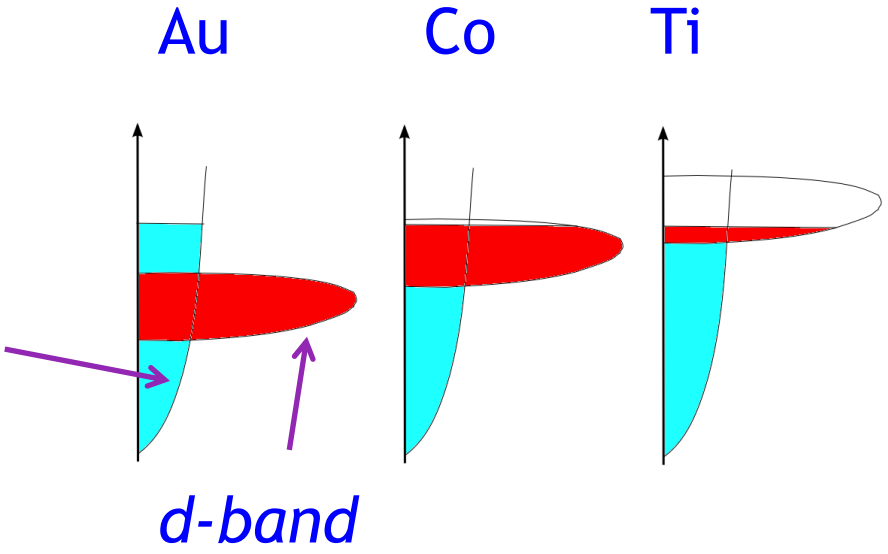
Catalysts: transition and noble metals



metals

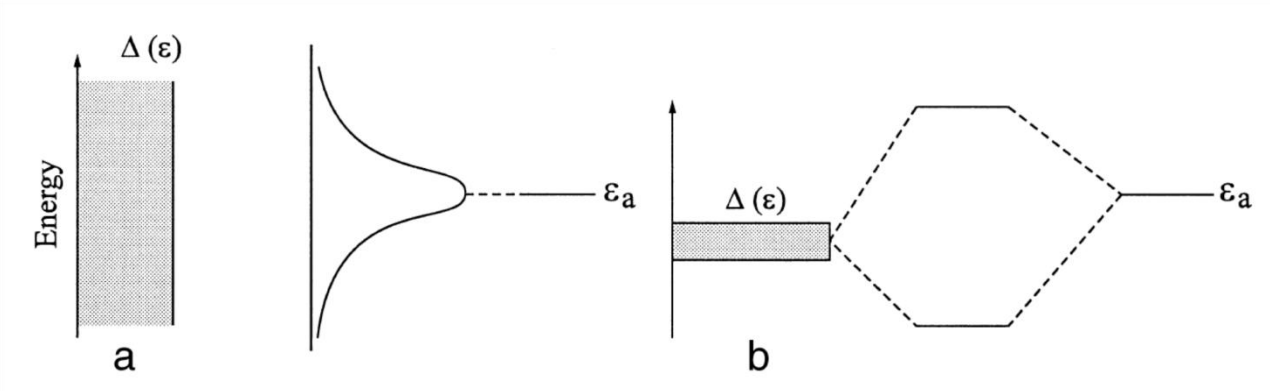
Pt, Pd, Rh, Fe, Ni, …

correlation between reactivity and electronic properties



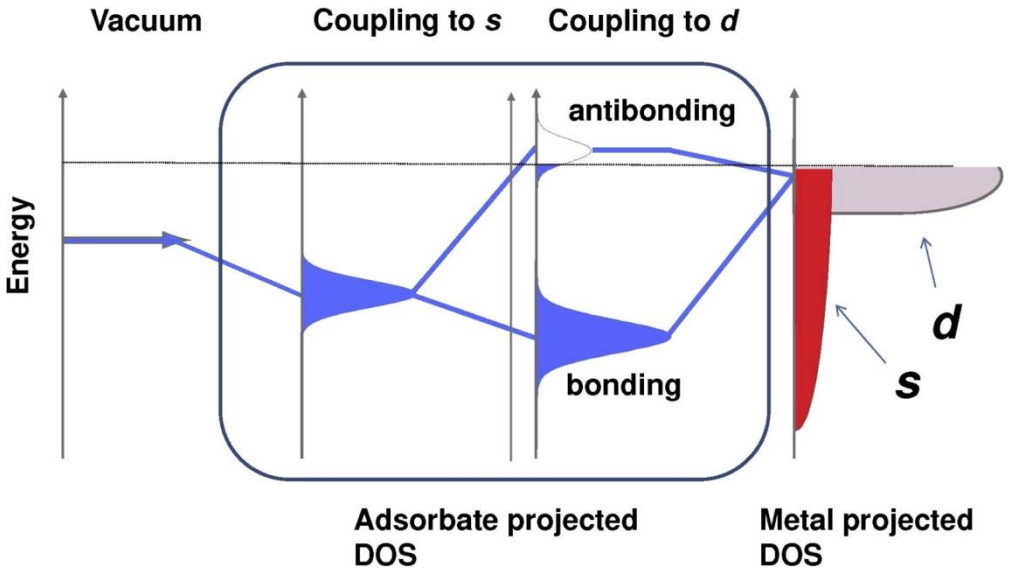
Theory of chemisorption

adatoms on transition-metal surfaces



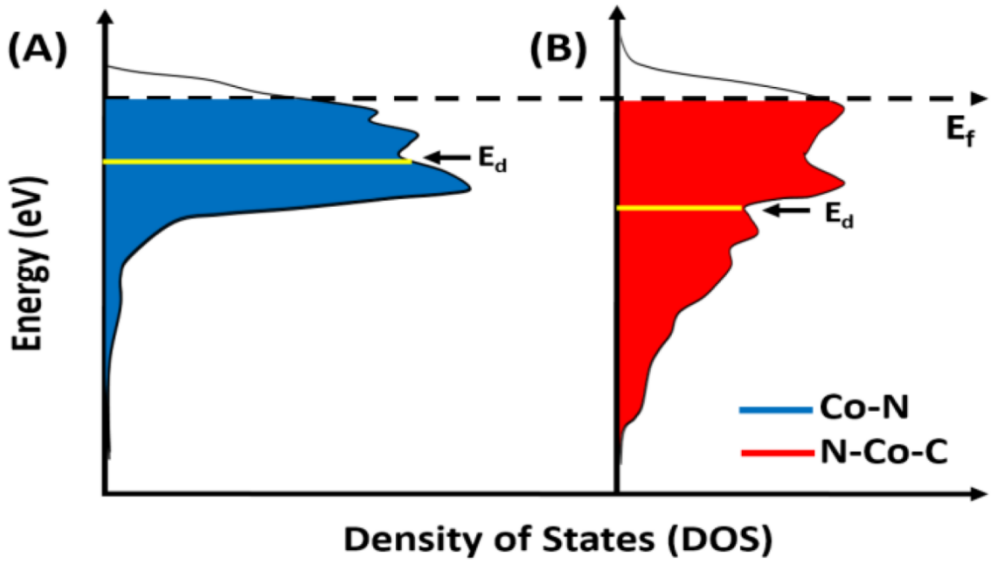
Newns-Anderson model

Phys. Rev. **178**, 1123 (1969).



d-band model

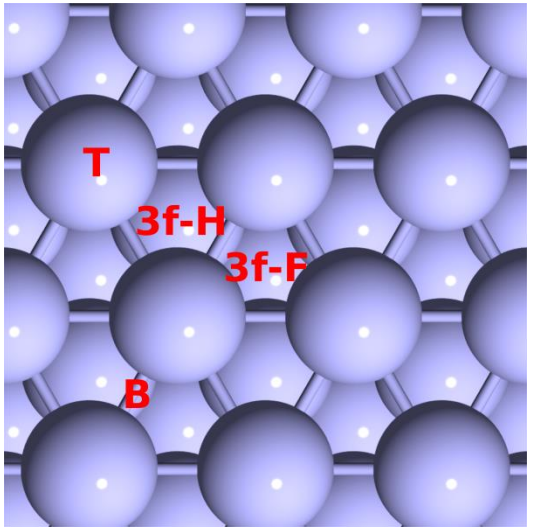
Hammer-Norskov (d-band) model



use it only for similar adsorption geometries!

d-band center

$$\epsilon_d = \frac{\int \mathrm{DOS(E)EdE}}{\int \mathrm{DOS(E)dE}}$$

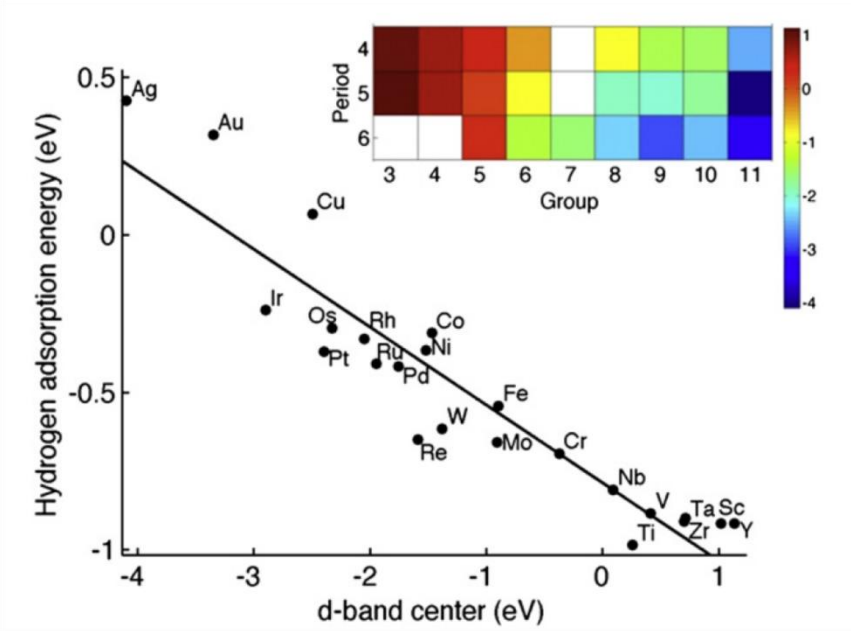


Understanding trends in reactivity based on a single parameter

d-band model

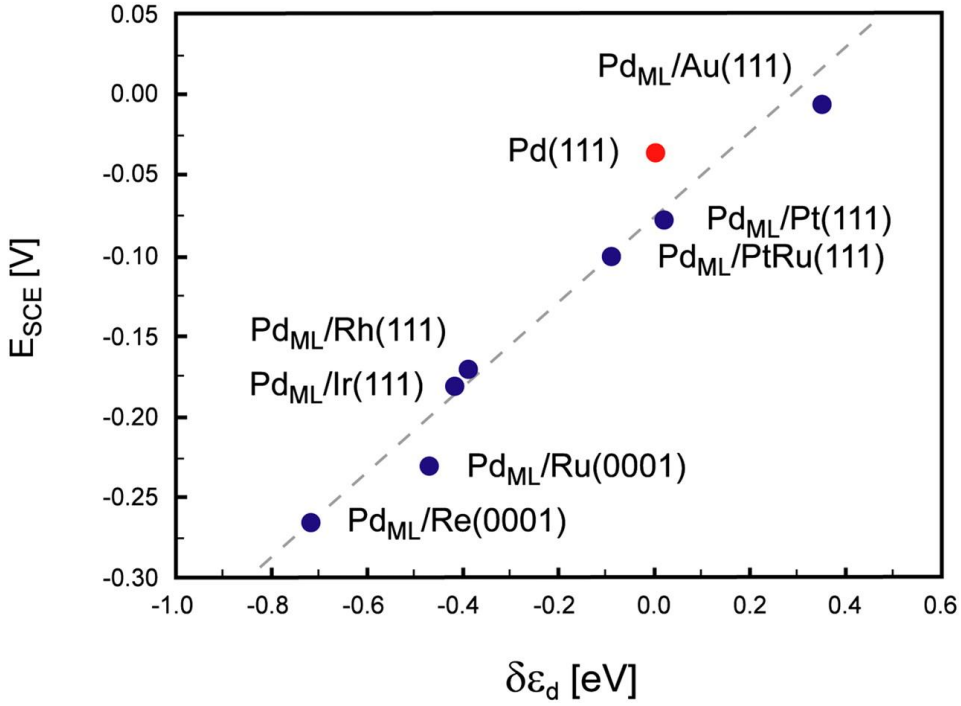
reactivity of different metals

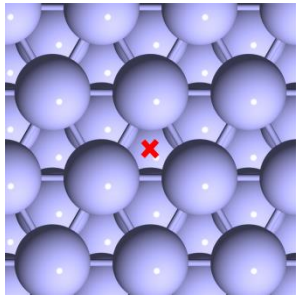
H at metal surfaces



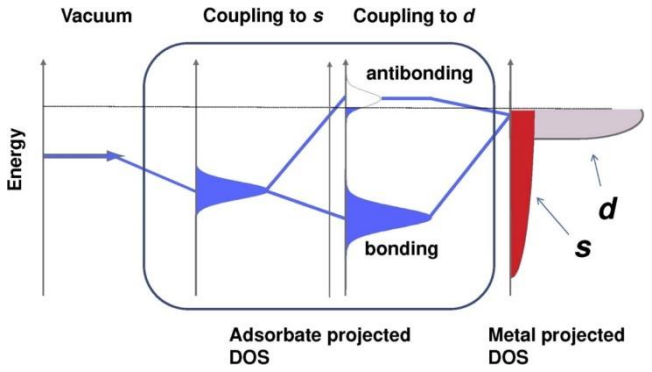
The "same" metal

oxygen adatom on Pd monolayers



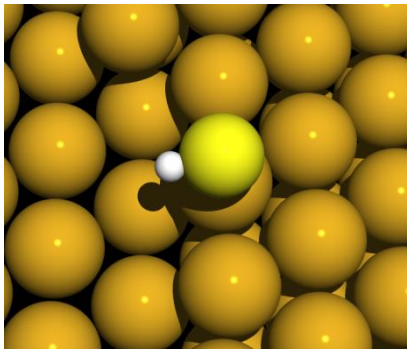


similar adsorption geometries!

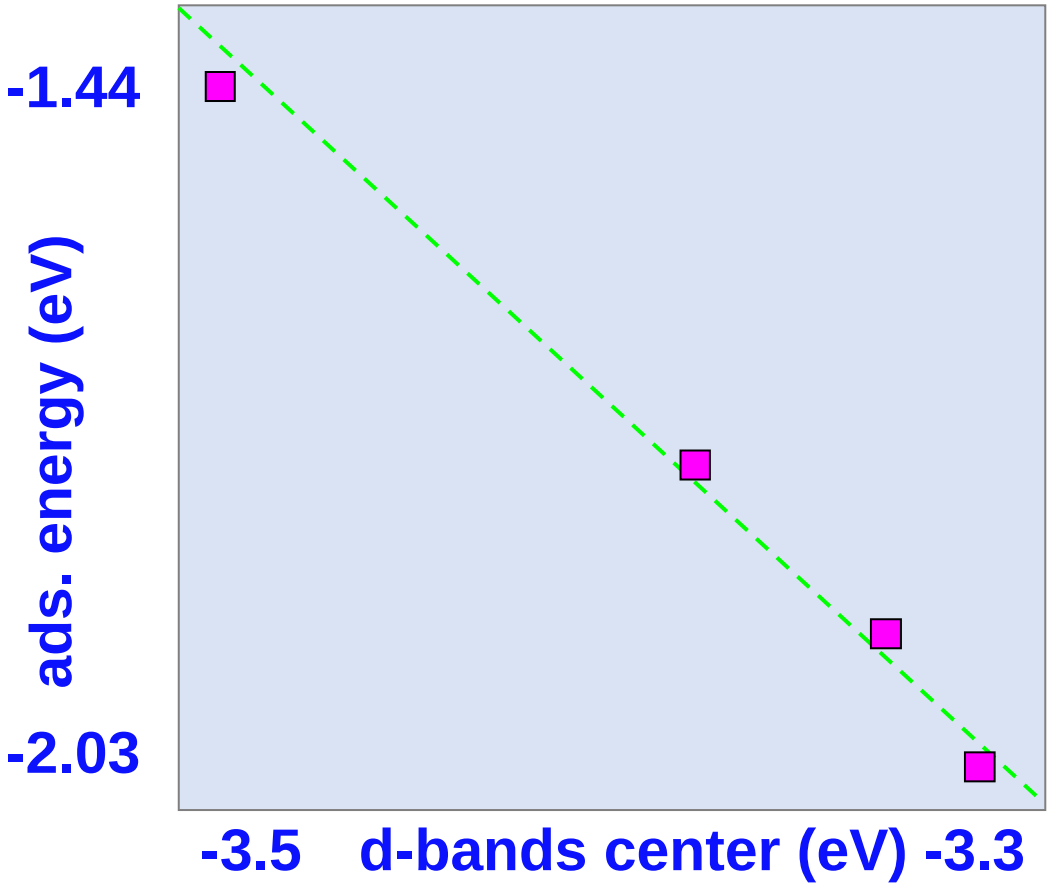


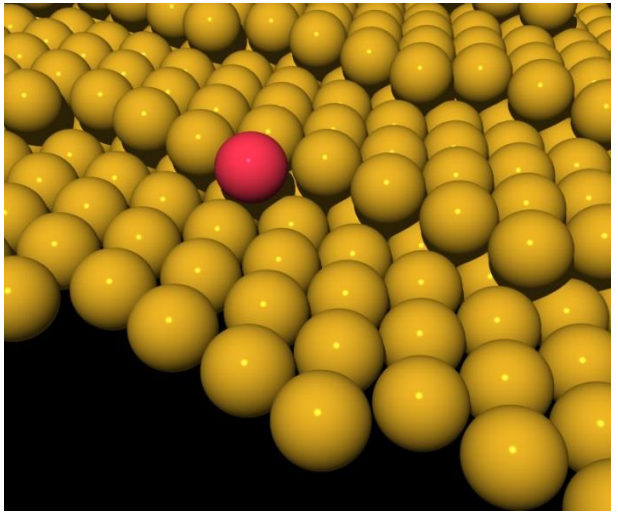
d-band model

SH@Au(17 11 9) "on-top" geometry



structural defects – trends in reactivity



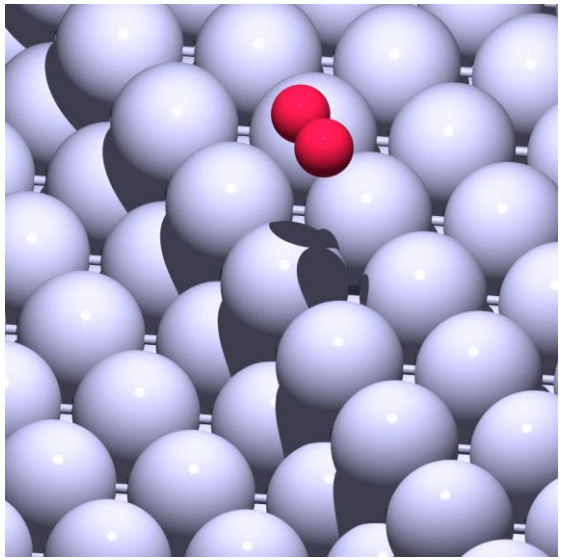


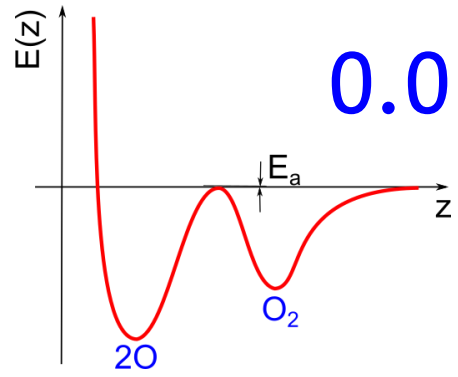
JACS **124**, 14789 (2002).

Defects at metal surfaces

DFT: O2 dissociation on stepped Pt(111)

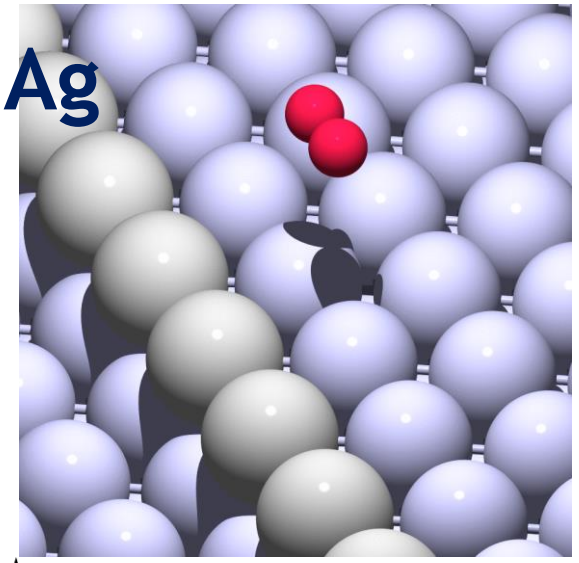
steps

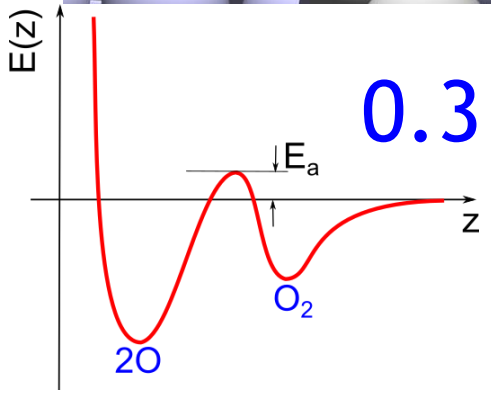




0.0 eV

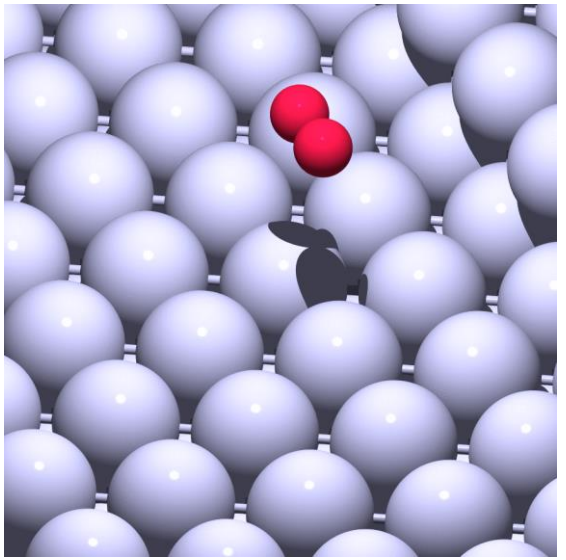
Ag-covered steps

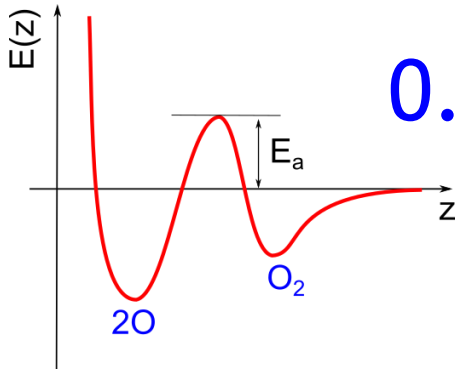




0.3 eV

terraces



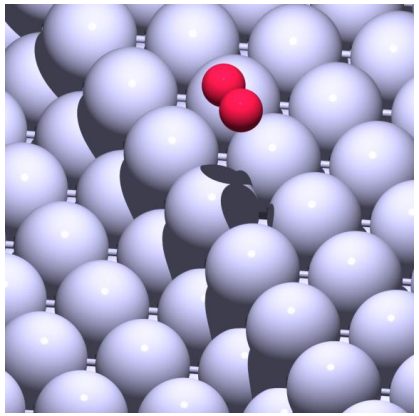


0.9 eV

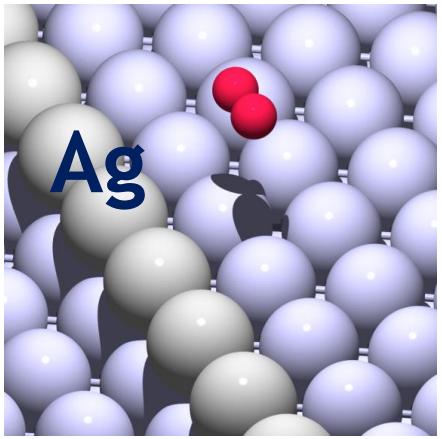
$$n = n_0 e^{-E_a/kT}$$

Atoms at steps billion times more reactive than terrace sites

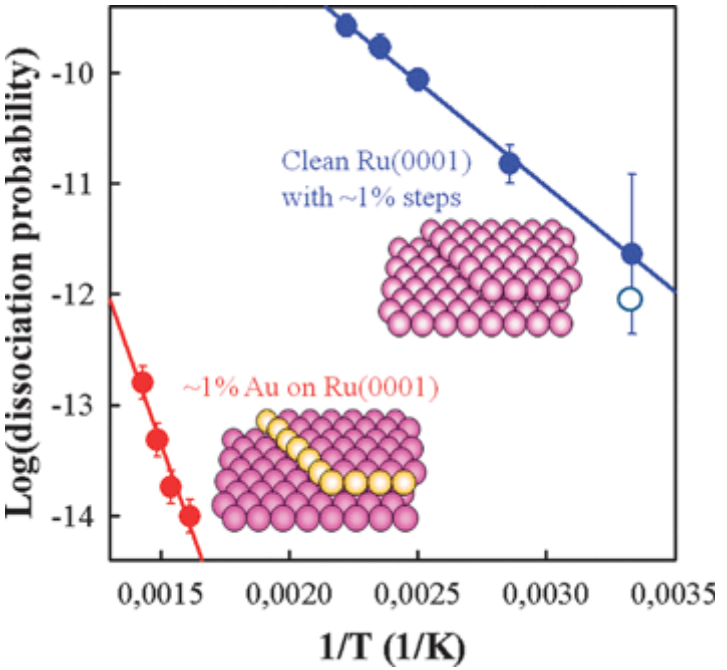
Defects at metal surfaces



O_2 dissociation on Pt



N_2 dissociation on Ru



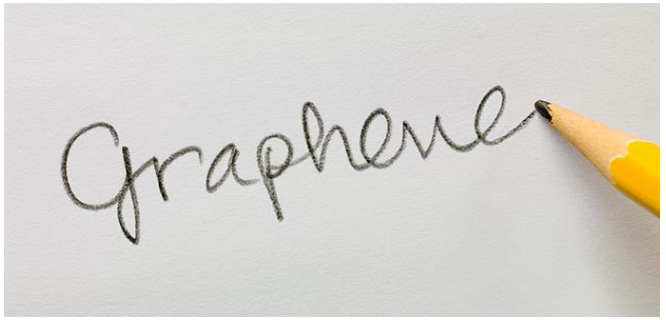
PRL **83**, 1814 (1999).

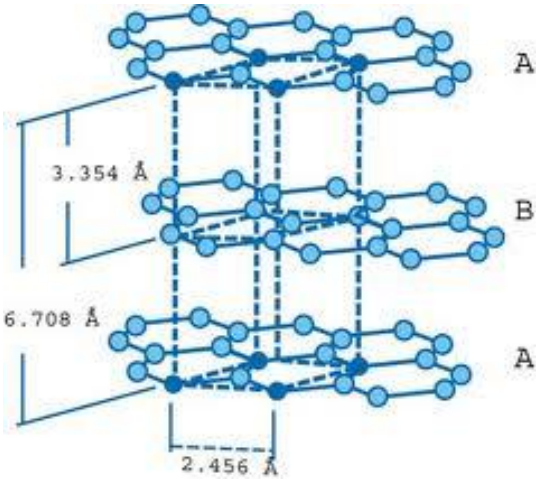
Atoms at steps billion times more reactive than terrace sites

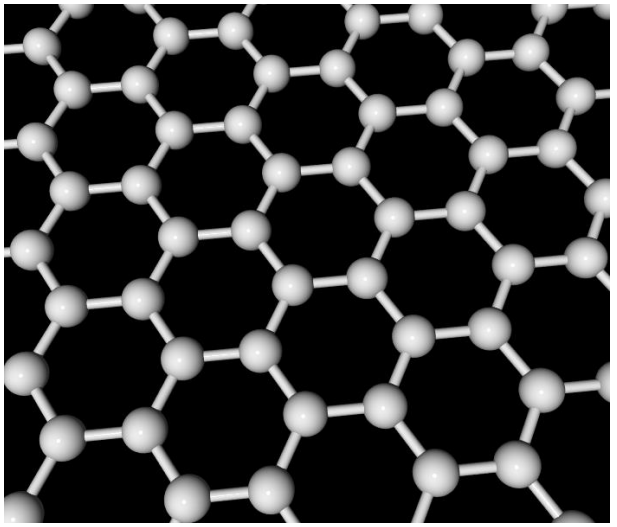
lead poisoning of catalysts

Special sites (defects) control reactivity

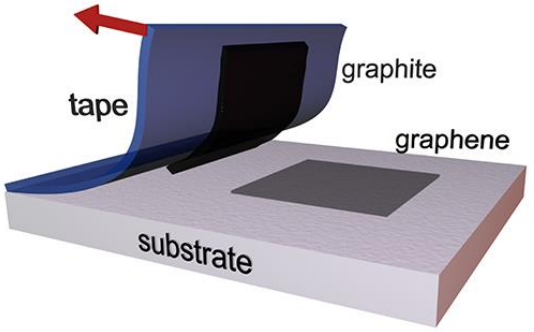
Graphite and graphene







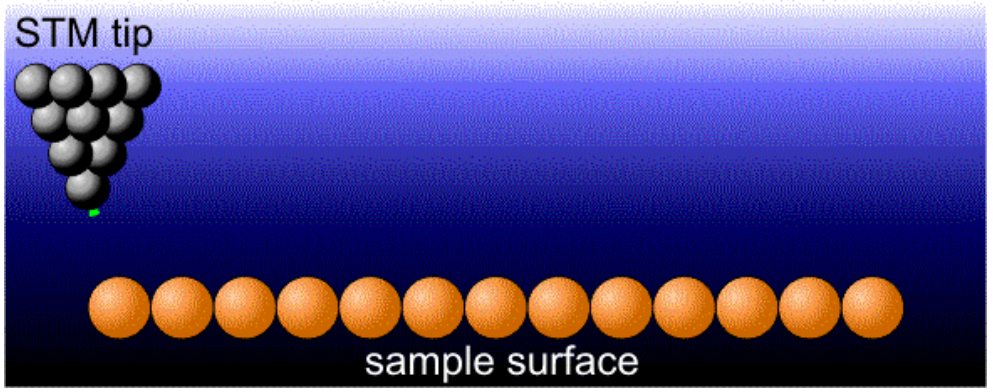
thickness of graphite left by a pencil writing on paper is ~20 nm
50 to 60 graphene layers



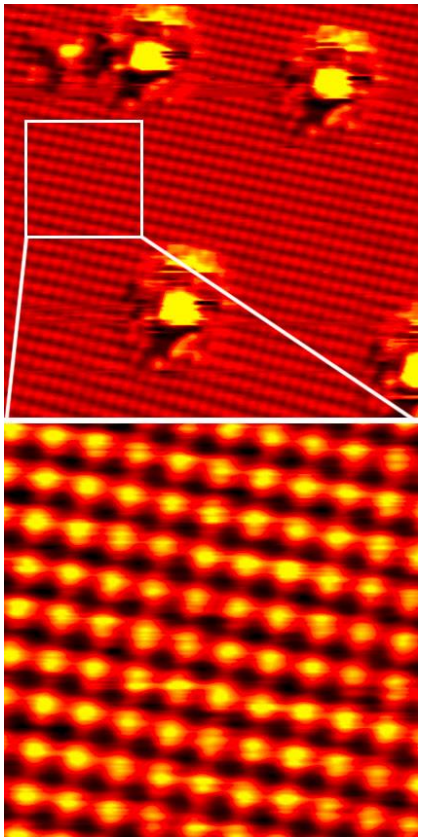
K. Novoselov and A. Geim, Nobel prize in Physics 2010

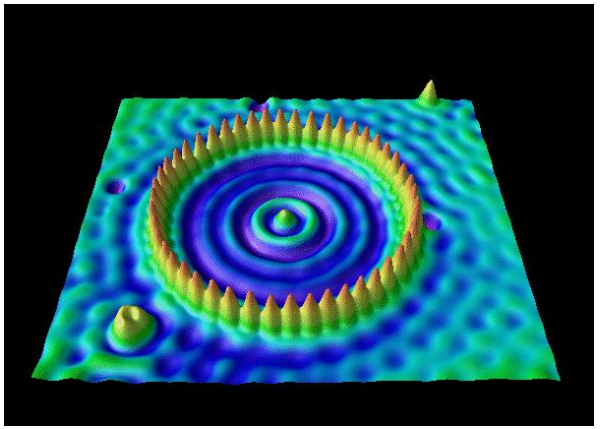
"for groundbreaking experiments regarding the two-dimensional material graphene."

Scanning tunneling microscopy (STM)



Ag(100)

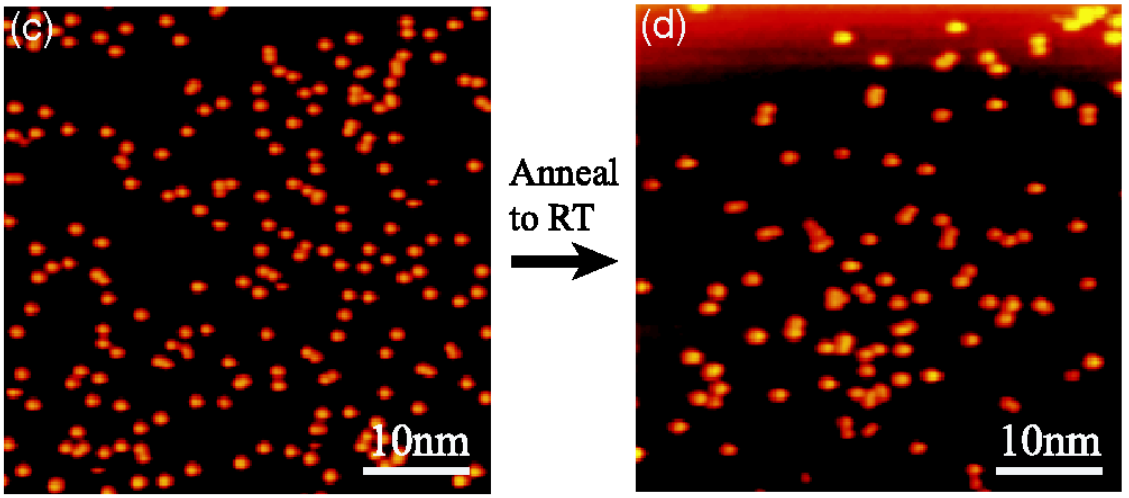




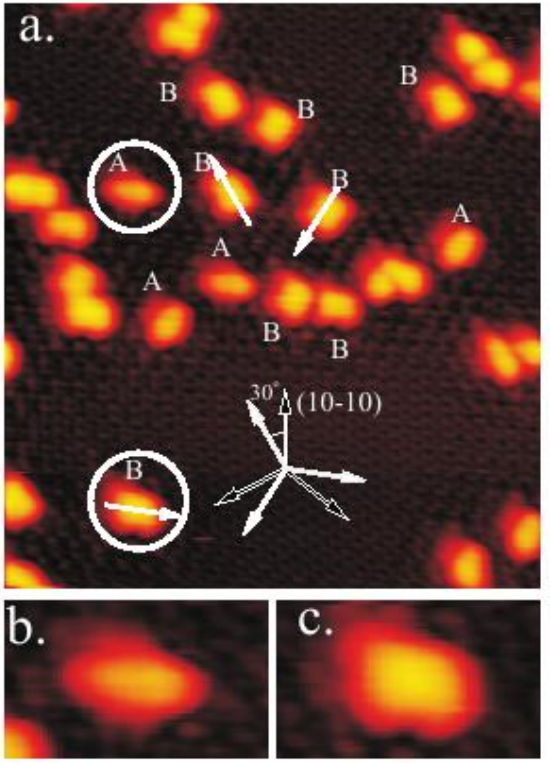
Fe atoms on Cu

2.5 nm x 2.5 nm на 160 K

Hydrogen atoms on graphite



STM images



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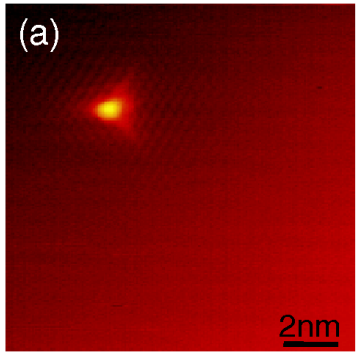
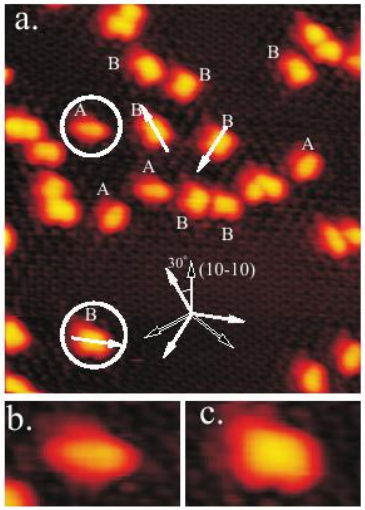
two types of hydrogen structures

Atomic hydrogen on graphene (DFT)

STM results

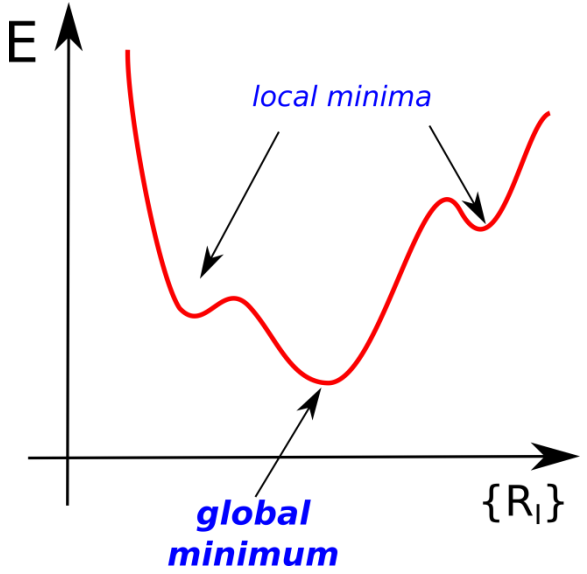
H adatom



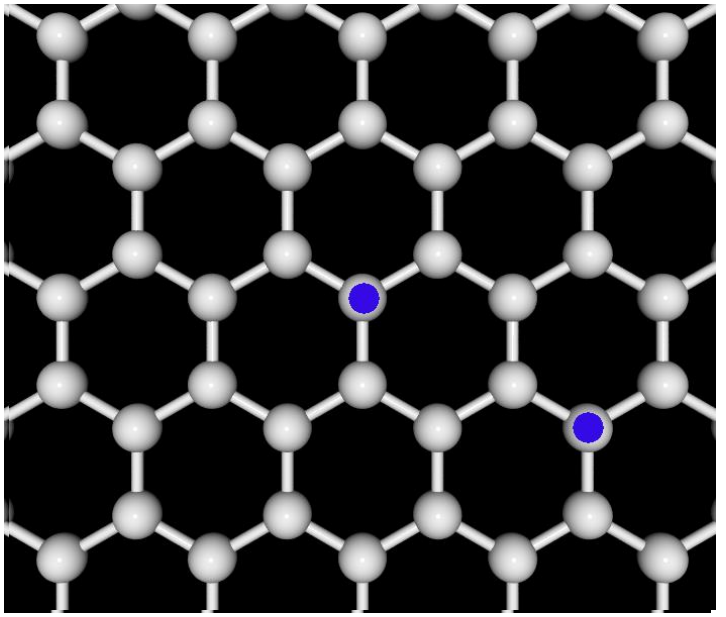


unknown structures

***DFT** used to search for favorable configuration of H adatoms*

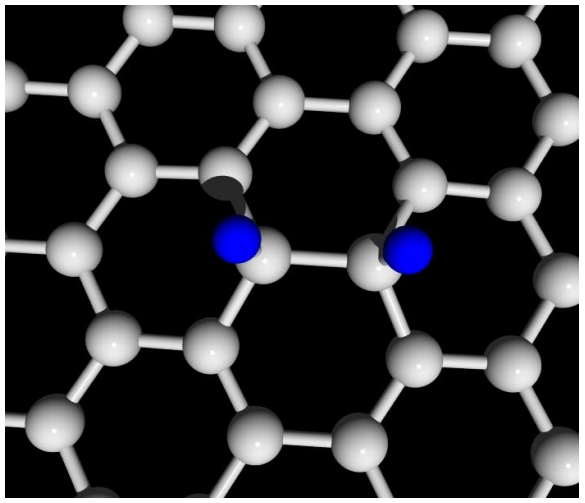


Let's start wit TWO H atoms



Atomic hydrogen on graphene (DFT)

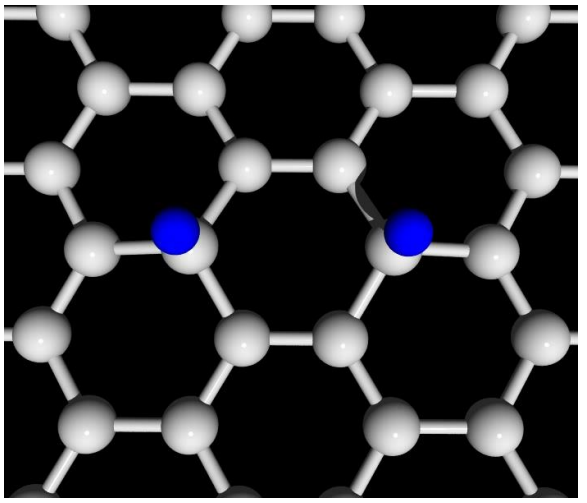
H dimers

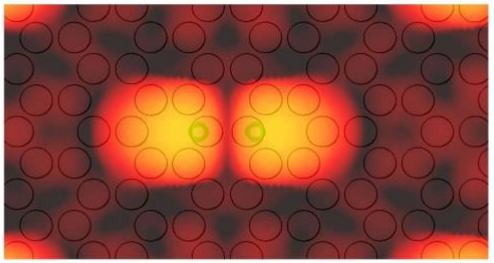


ortho dimer

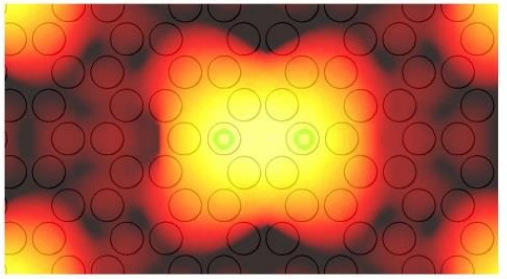
E_B = 2.7 eV

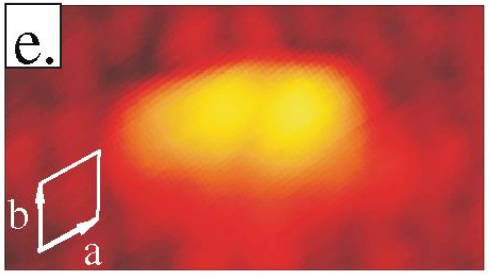
para dimer



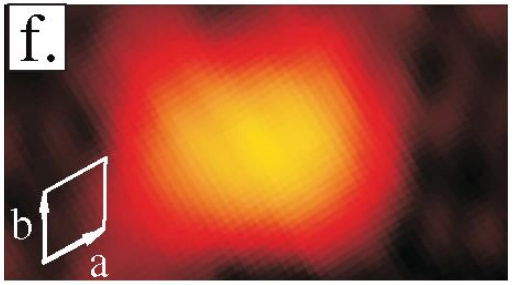


DFT





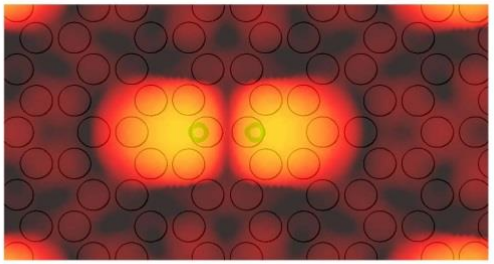
experiment



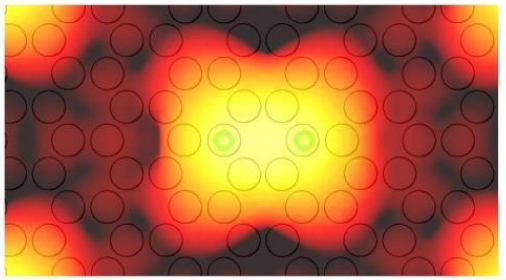
DFT can be use to simulate STM images and compare them with those obtained from STM imaging

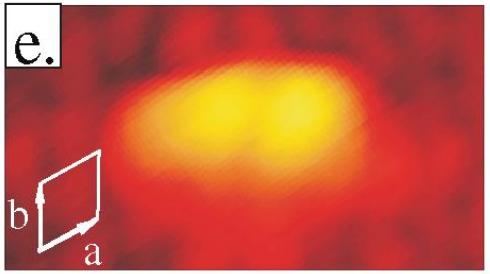
Atomic hydrogen on graphene (DFT)

DFT can be used to simulate STM images

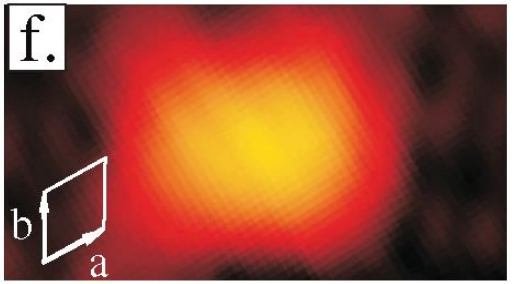


DFT





experiment

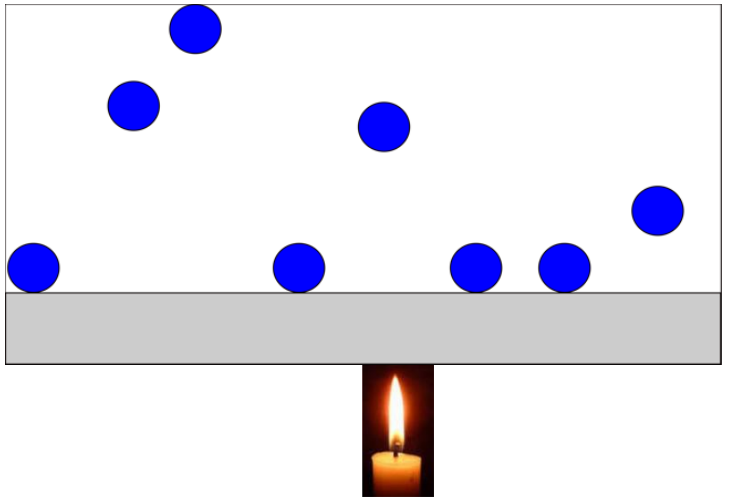


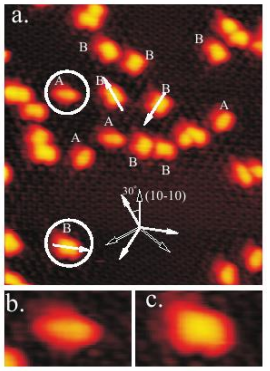
Tersoff-Hamann scheme - local density of states
n (r,E)

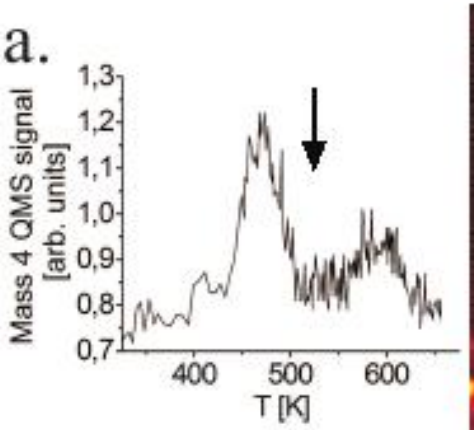
Hydrogen atoms on graphite

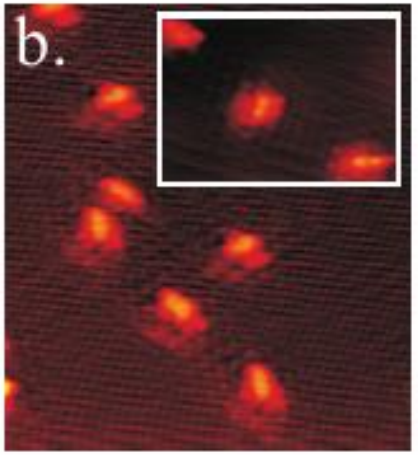
Temperature programmed desorption (TPD)

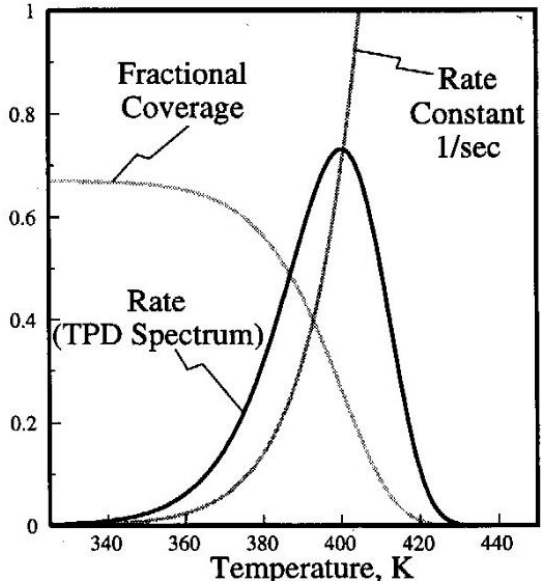
different desorption barriers

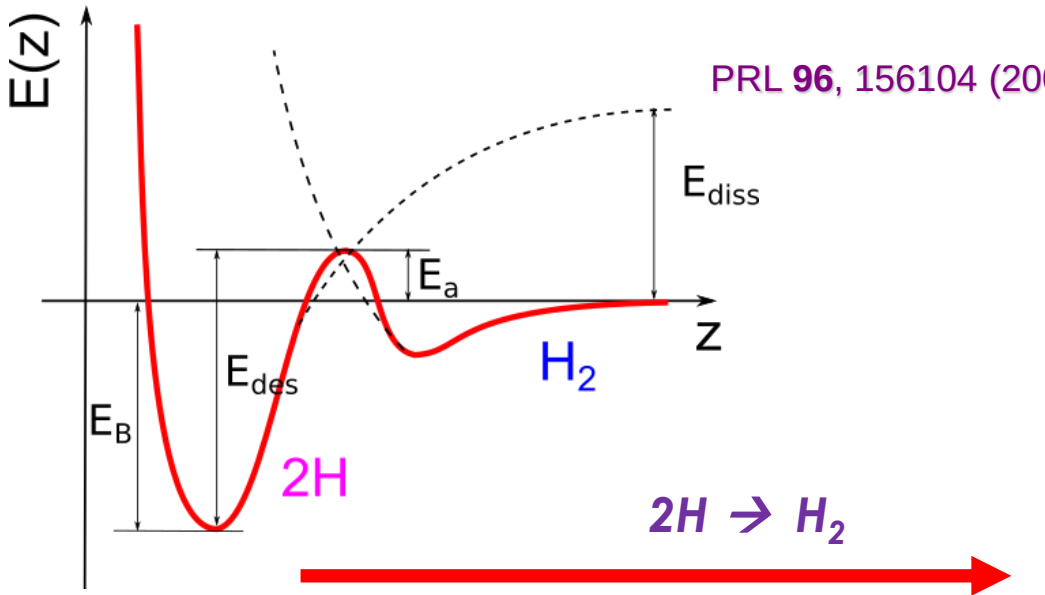












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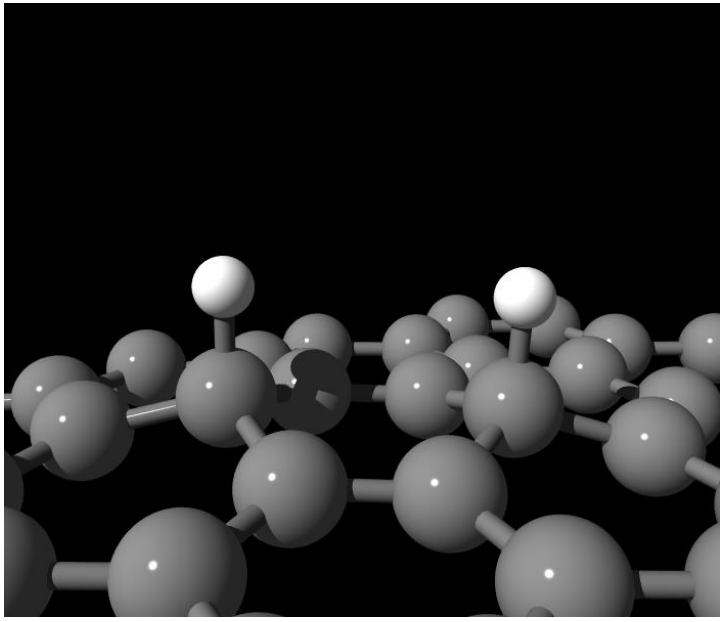
2H → H_2

associative desorption

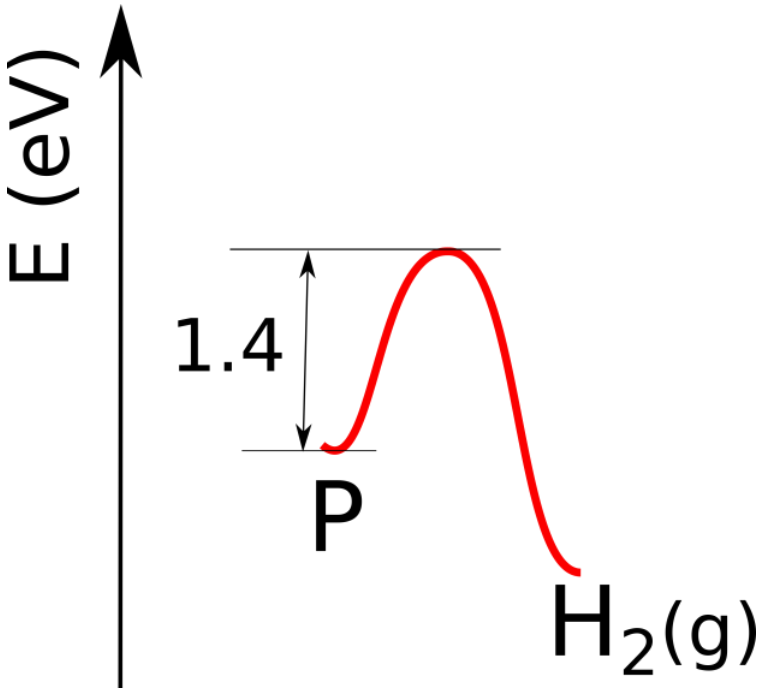
Atomic hydrogen on graphene (DFT)

associative desorption

para dimer



NEB used to calculate barriers

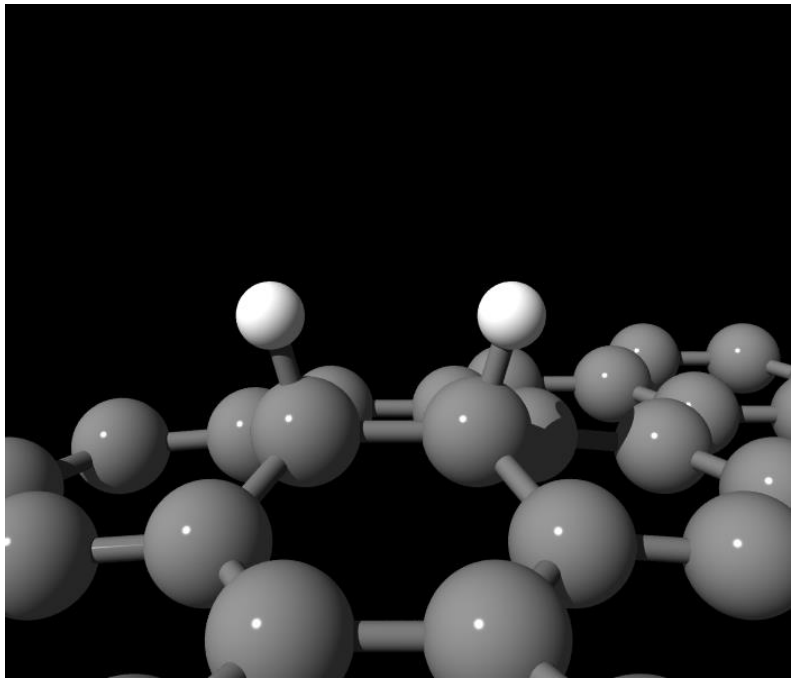


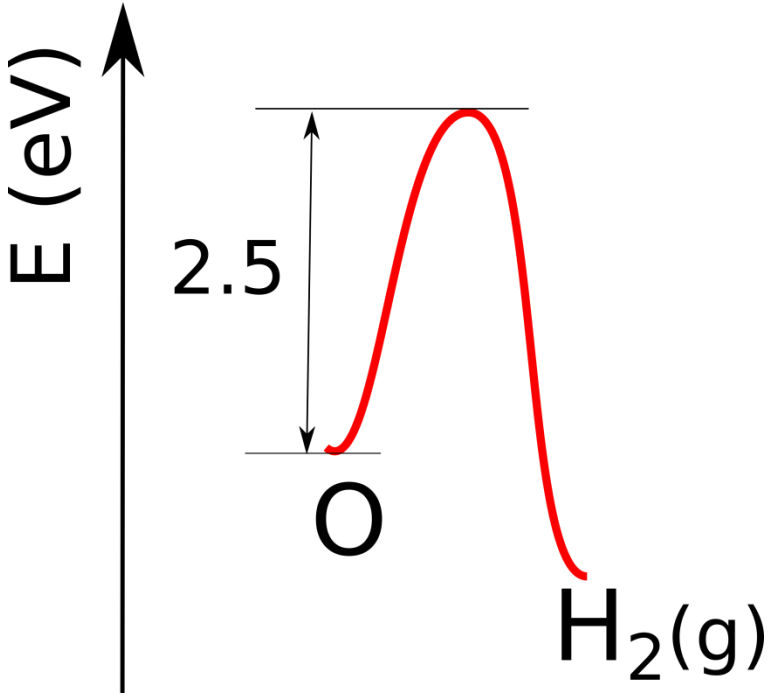
direct process: O → H_2 occurs at 470K

Atomic hydrogen on graphene (DFT)

associative desorption

ortho dimer



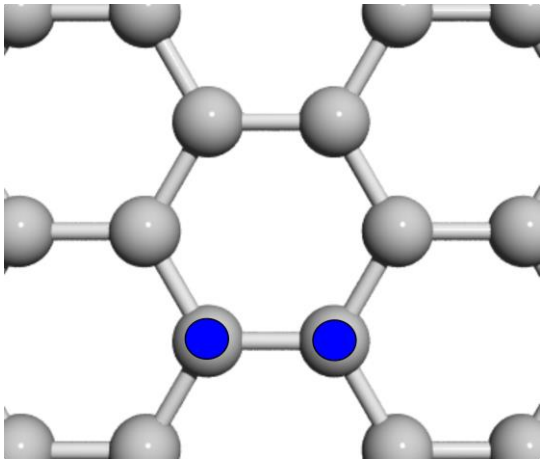


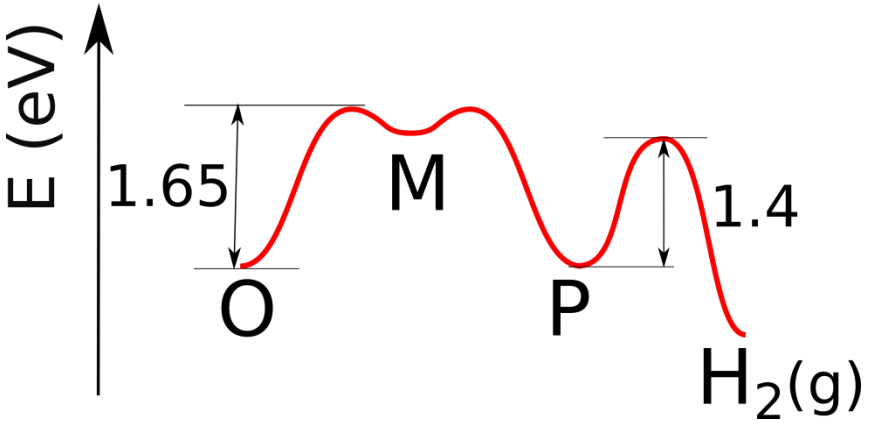
direct process: O → H_2 does not occur

Atomic hydrogen on graphene (DFT)

associative desorption

ortho dimer

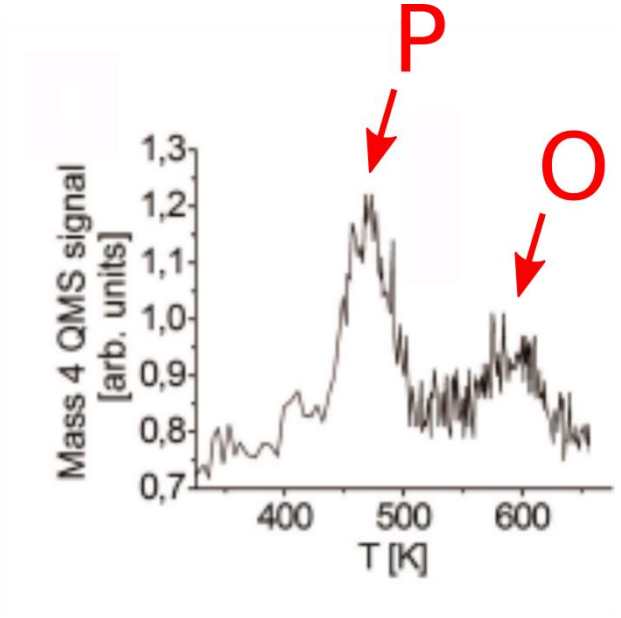




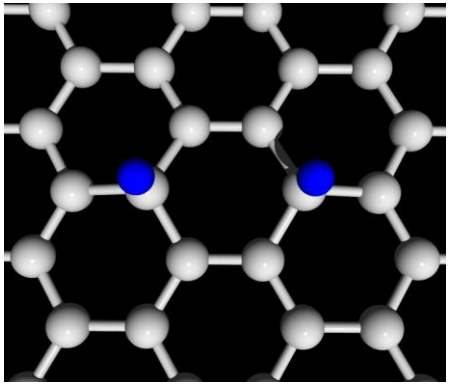
process: O → M → P → H_2 occurs at 600K

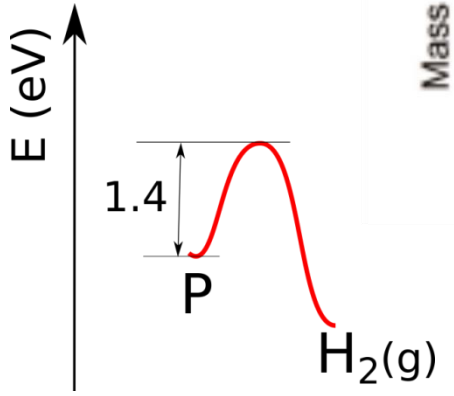
Atomic hydrogen on graphene (DFT)

DFT and TPD



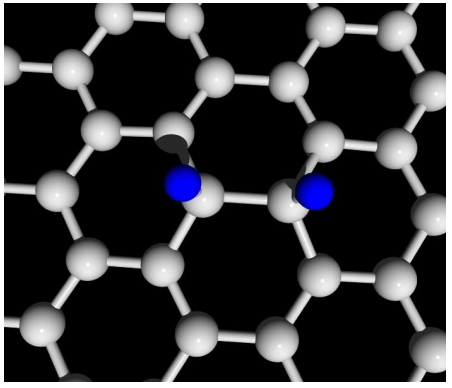
para dimer

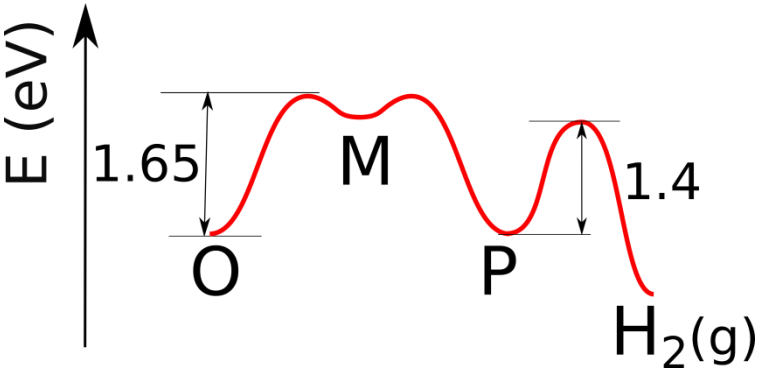




Ea = 1.4 eV

ortho dimer





Ea = 1.65 eV

DFT in surface science

- *structural properties of surface*
- *adsorption geometries, nanostructures*
- *chemical reactions*
- *DFT and STM, TPD, …*