

A short introduction to physics and chemistry at crystalline surfaces

Željko Šljivančanin

Vinča Institute of Nuclear Sciences Belgrade, Serbia

outline

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

1. *catalysis*

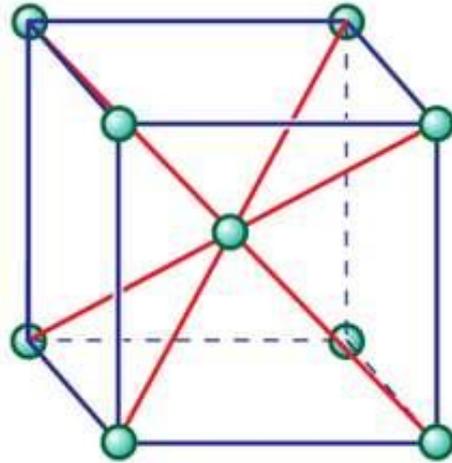
2. *nanostuctures at graphene*

- *DFT and experiments in surface science*

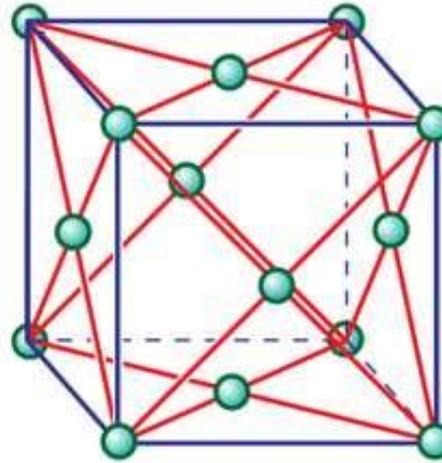
Common crystal structures

Common metallic crystal structures

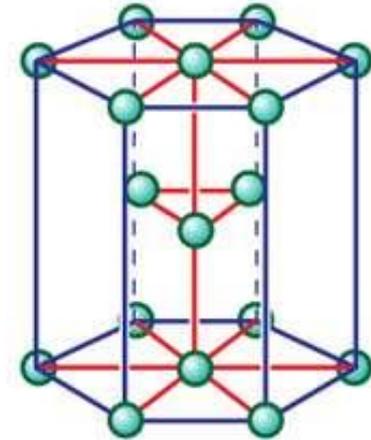
bulk



body-centred cubic (bcc)



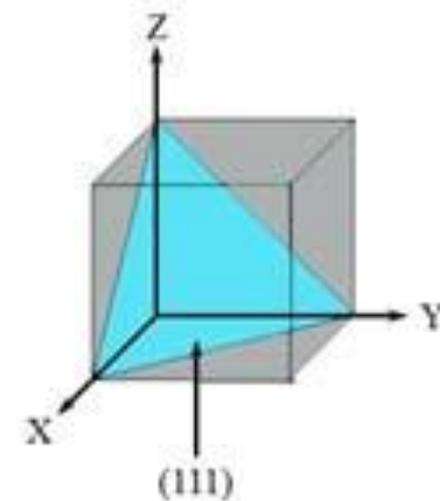
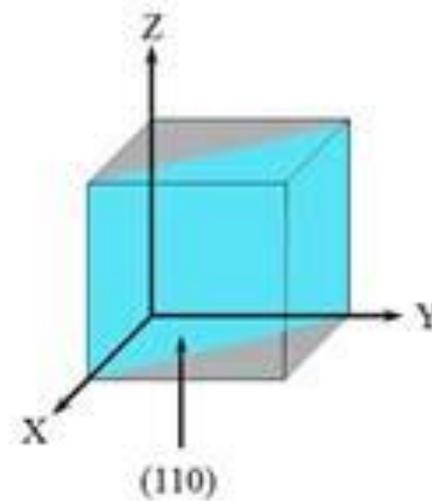
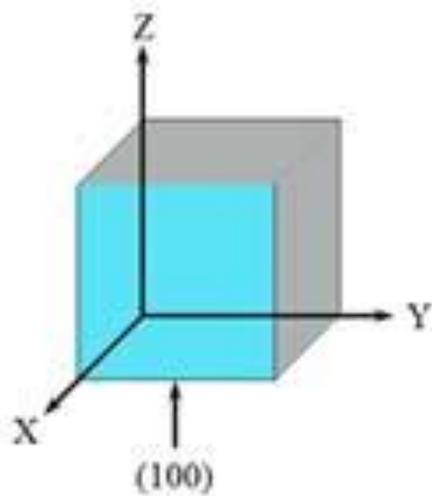
face-centred cubic (fcc)



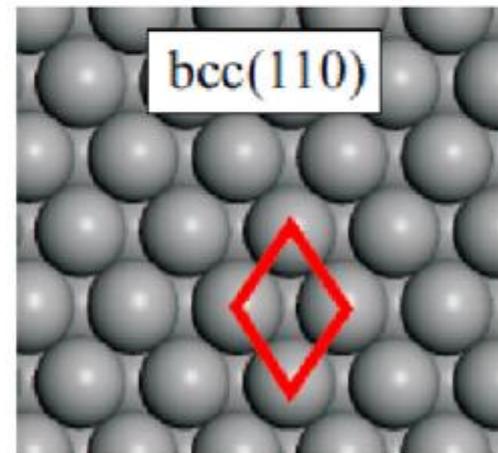
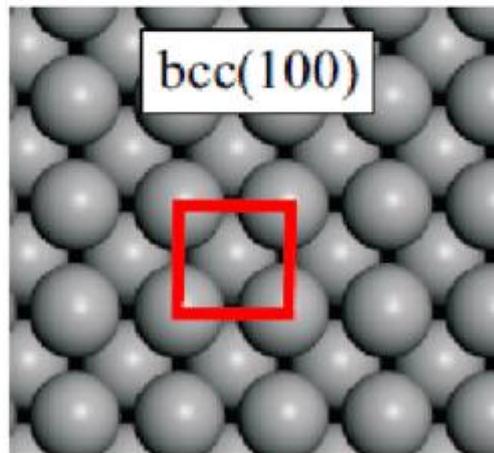
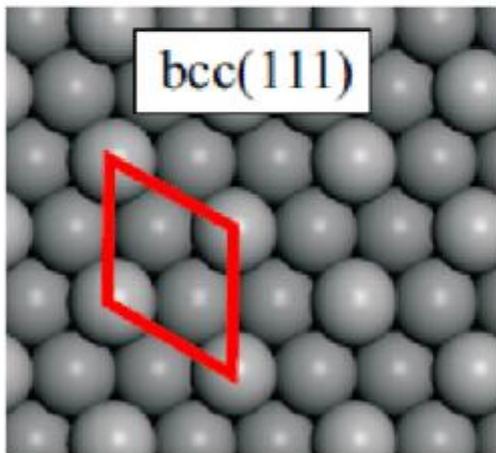
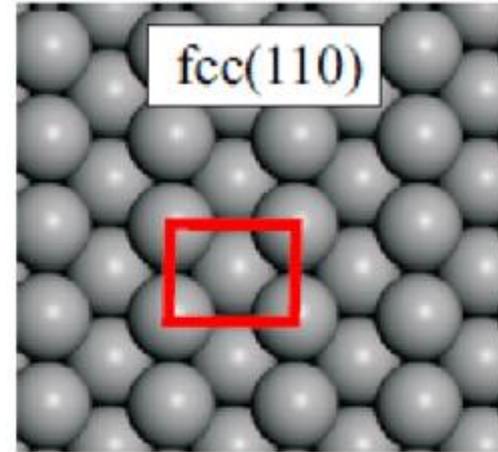
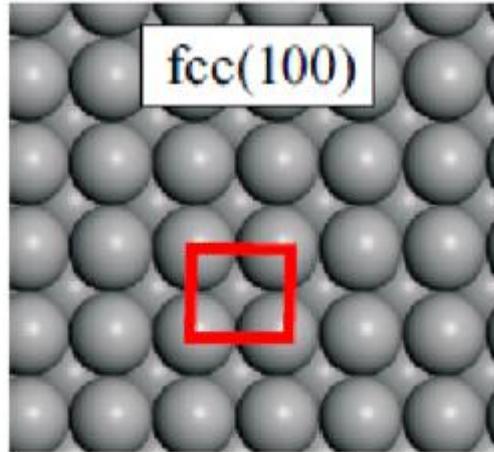
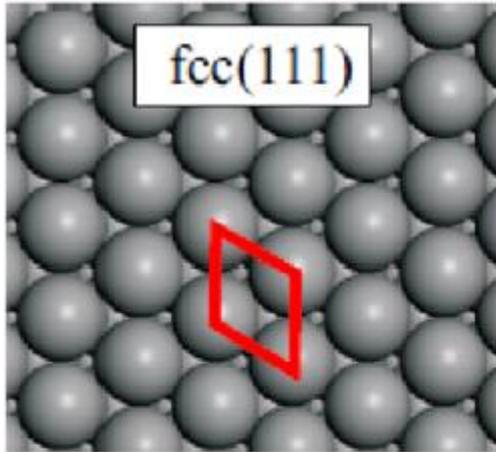
hexagonal close-packed (hcp)

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surfaces

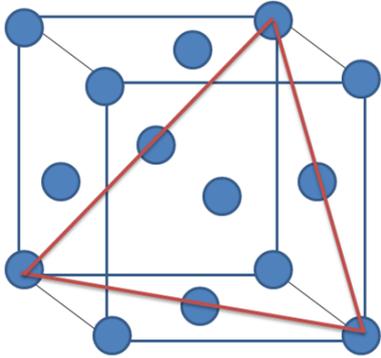


Common metal surfaces

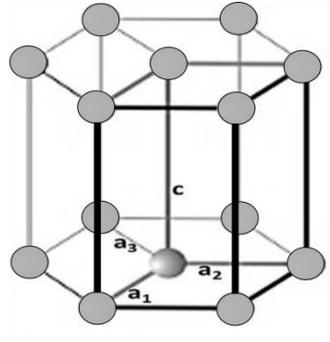


Common metal surfaces

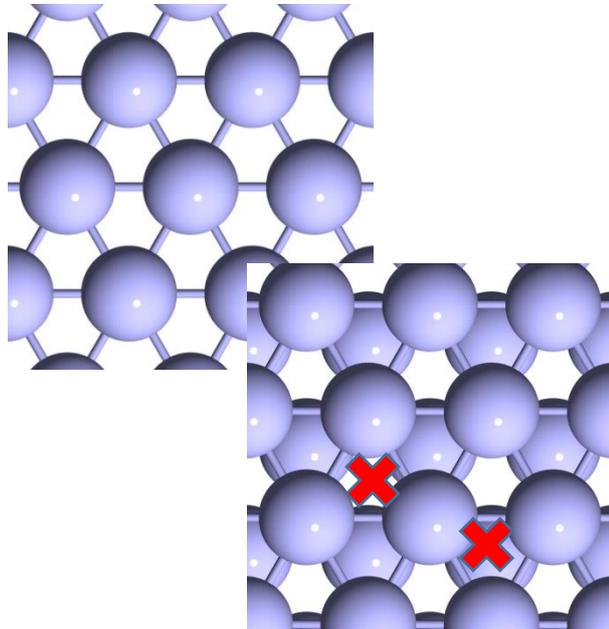
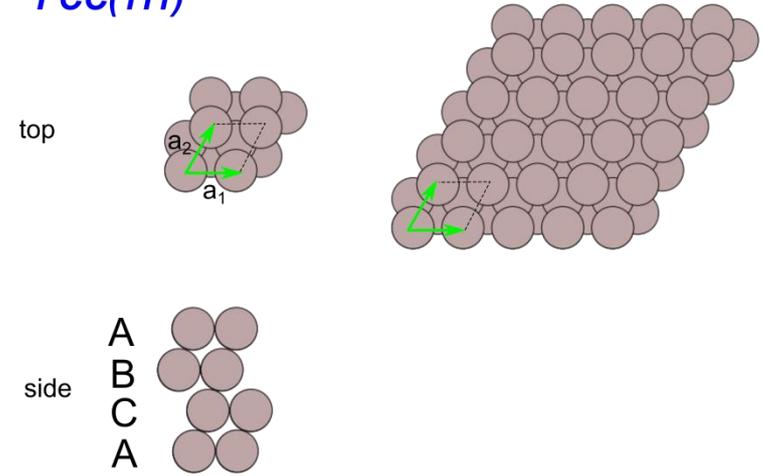
fcc(111)



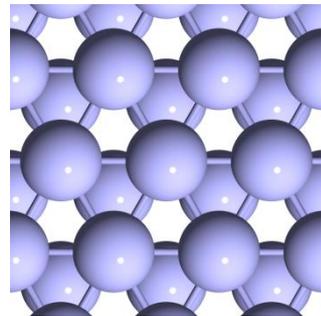
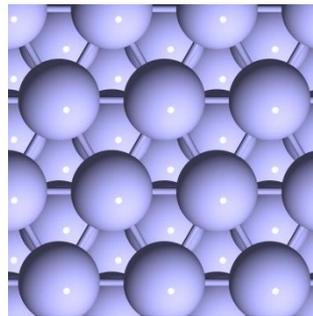
hcp(0001)



FCC(111)

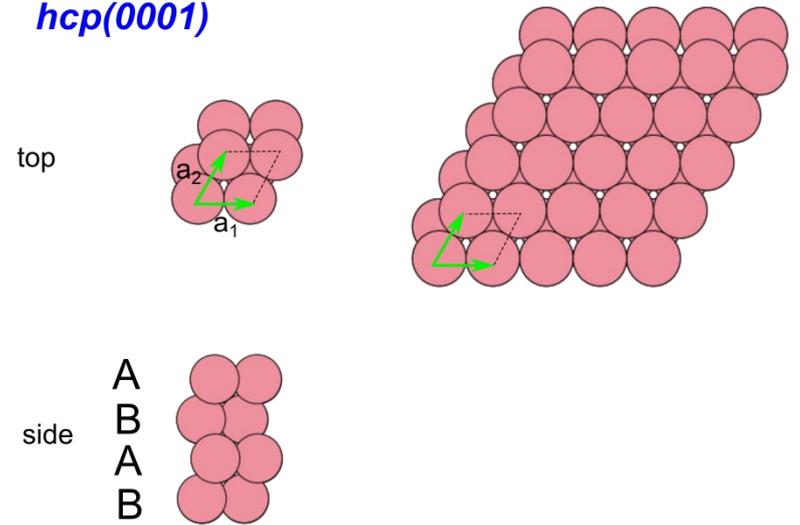


fcc



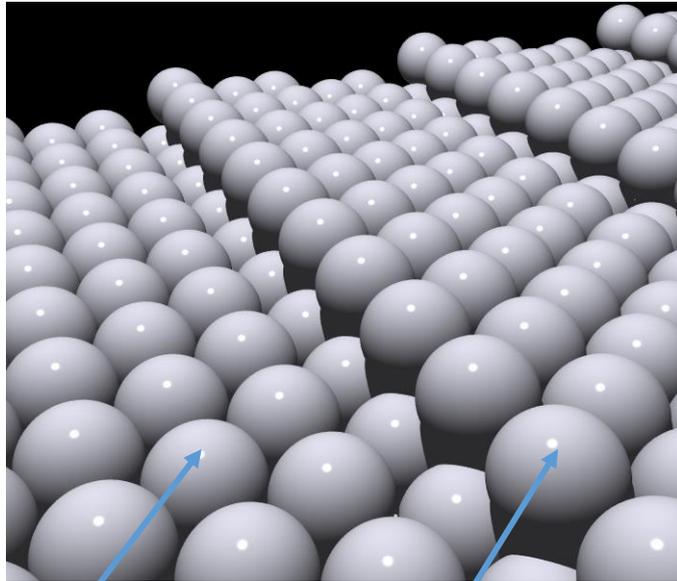
hcp

hcp(0001)



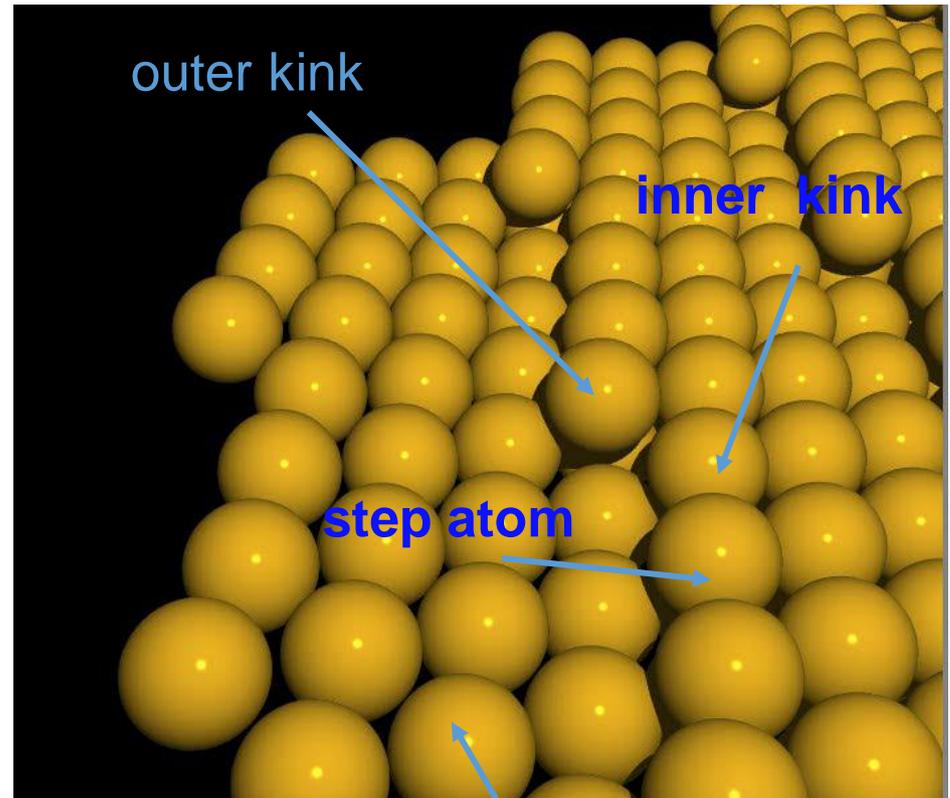
Defects at metal surfaces

stepped surface



terrace atom

step atom

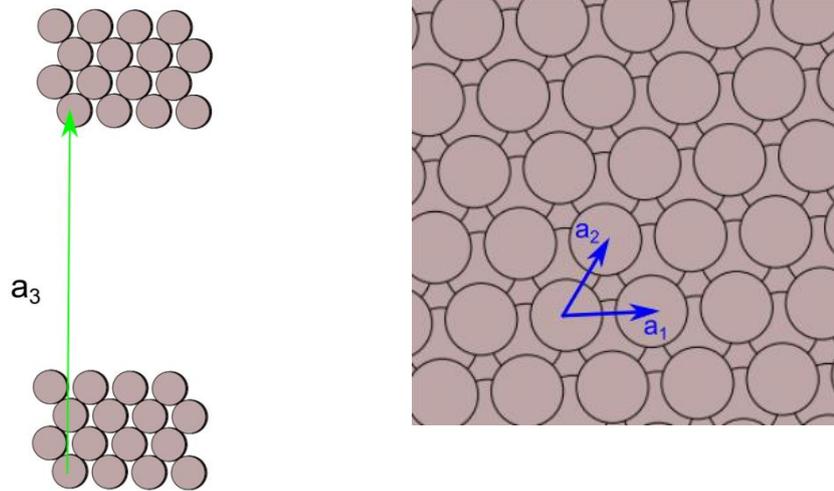


terrace atom

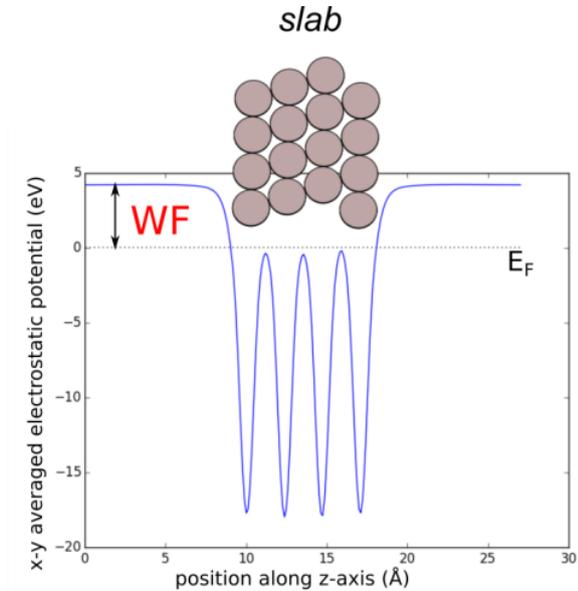
Atoms with reduced coordination number

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

Slab model of surfaces

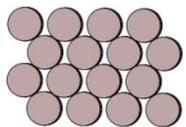


work function

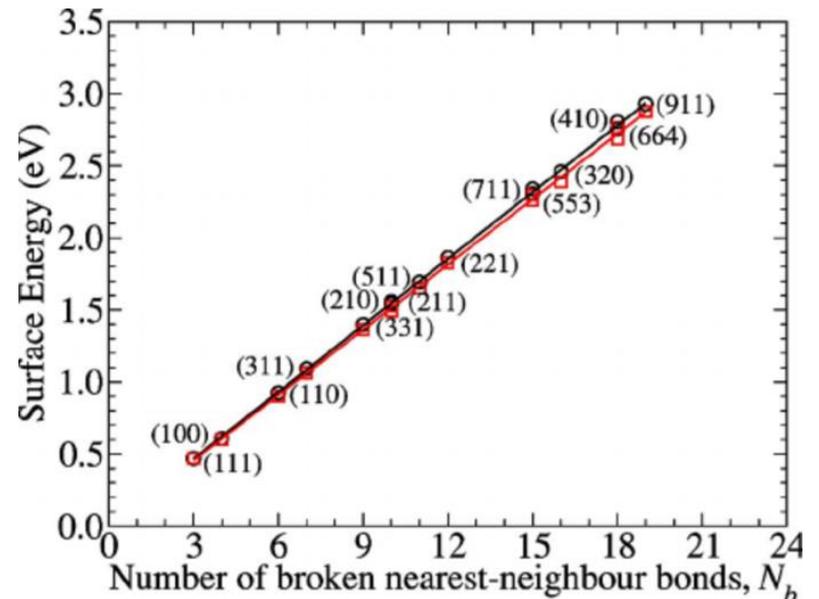


surface energy

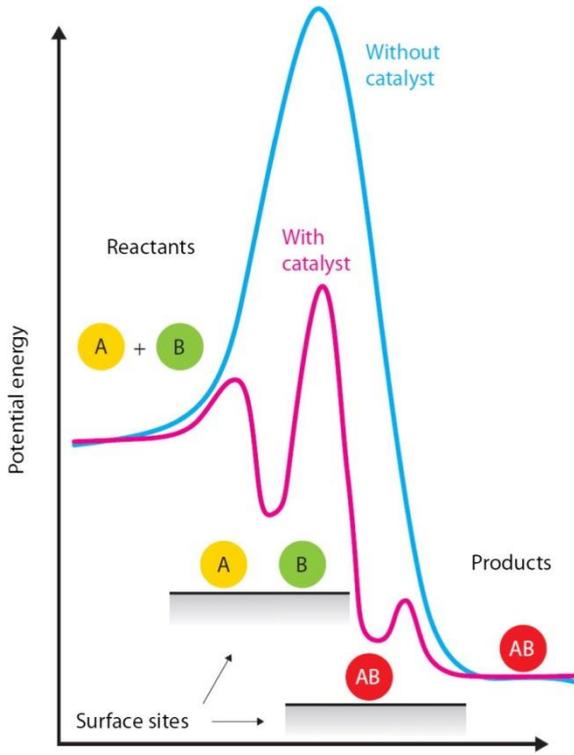
$$\gamma = \frac{E(\text{slab}, N) - N \cdot E(\text{bulk})}{2A}$$



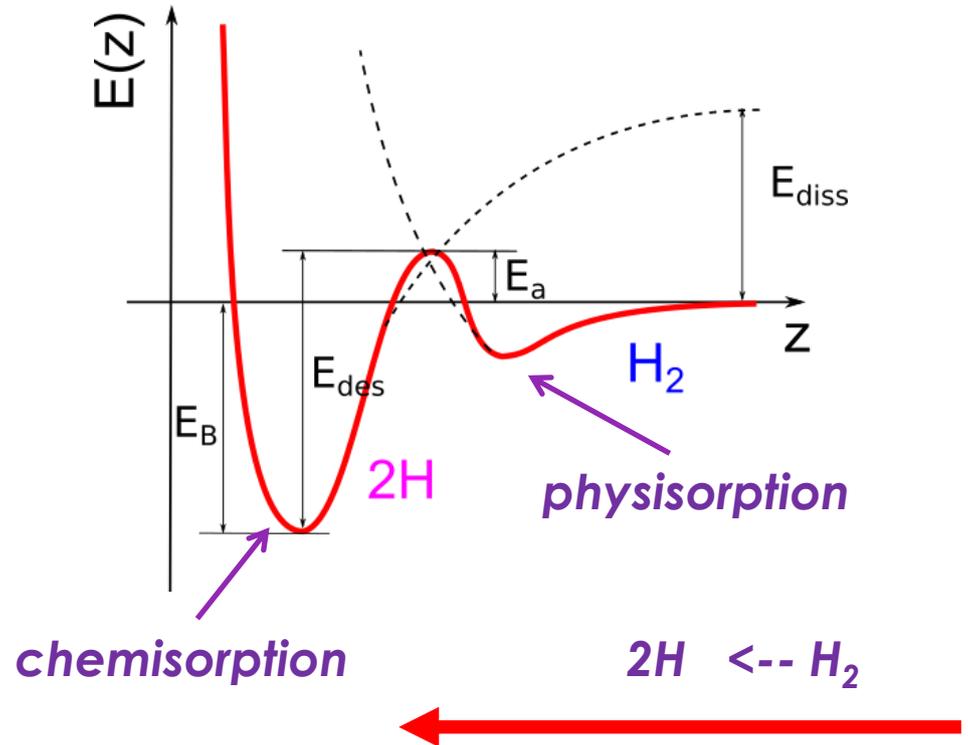
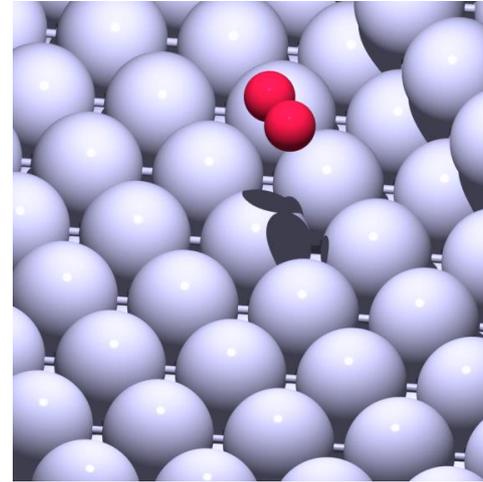
clear correlation between surface energy and the number of broken NN bonds



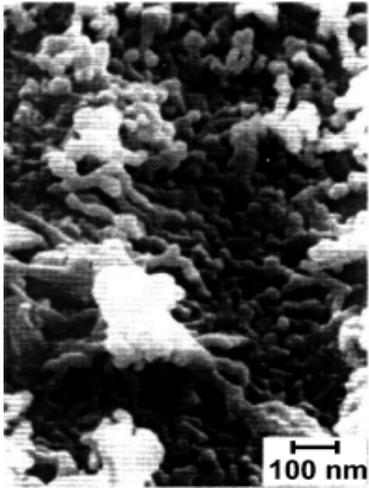
Catalysis



dissociative chemisorption



Catalysts



Technical conditions: $T \approx 400^\circ\text{C}$, $p \approx 300$ bar
promoted iron catalyst

BASF S6-10 catalyst [at. %]

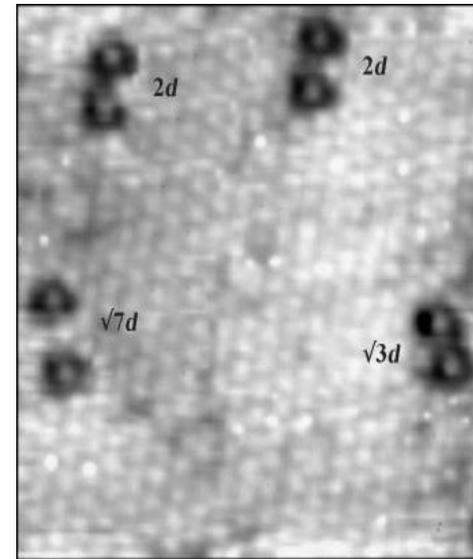
	Fe	K	Al	Ca	O
Bulk composition	40.5	0.35	2.0	1.7	53.2
Surface –					
unreduced	8.6	36.2	10.7	4.7	40.0
reduced	11.0	27.0	17.0	4.0	41.0
cat. active spot	30.1	29.0	6.7	1.0	33.2

Ammonia synthesis – industrial catalyst

very complicated structure

➤ *make a simple model*

O at Ru(0001)



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

Gerhard Ertl, Nobel prize in Chemistry 2007

“for his studies of chemical processes on solid surfaces”.

Catalysts: transition and noble metals

Periodic Table of the Elements

1 H 1.008																	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	12 Mg 24.305											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.066	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.88	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.69	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.906	46 Pd 106.42	47 Ag 107.868	48 Cd 112.411	49 In 114.82	50 Sn 118.710	51 Sb 121.757	52 Te 127.60	53 I 126.905	54 Xe 131.29
55 Cs 132.905	56 Ba 137.327	57 La 174.967	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.207	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.967	80 Hg 200.59	81 Tl 204.383	82 Pb 207.2	83 Bi 208.980	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.025	103 Lr (260)	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (264)	108 Hs (265)	109 Mt (266)	110 (267)	111 (272)							

metals

Pt, Pd, Rh, Fe, Ni, ...

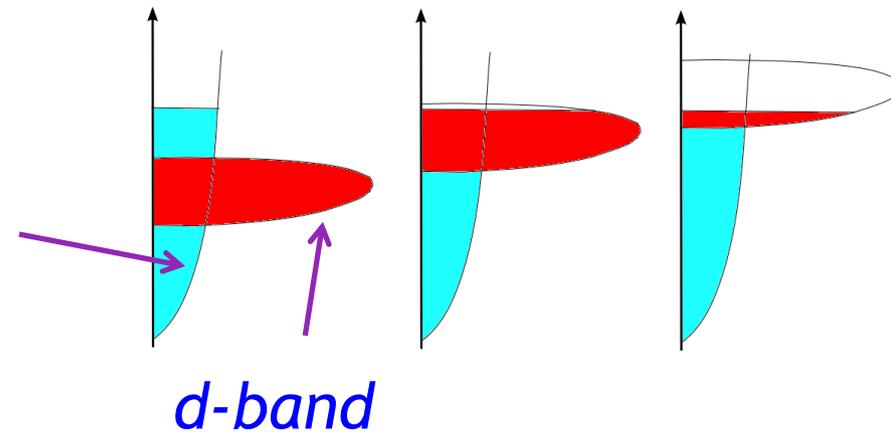
correlation between reactivity and electronic properties

s-band

Au

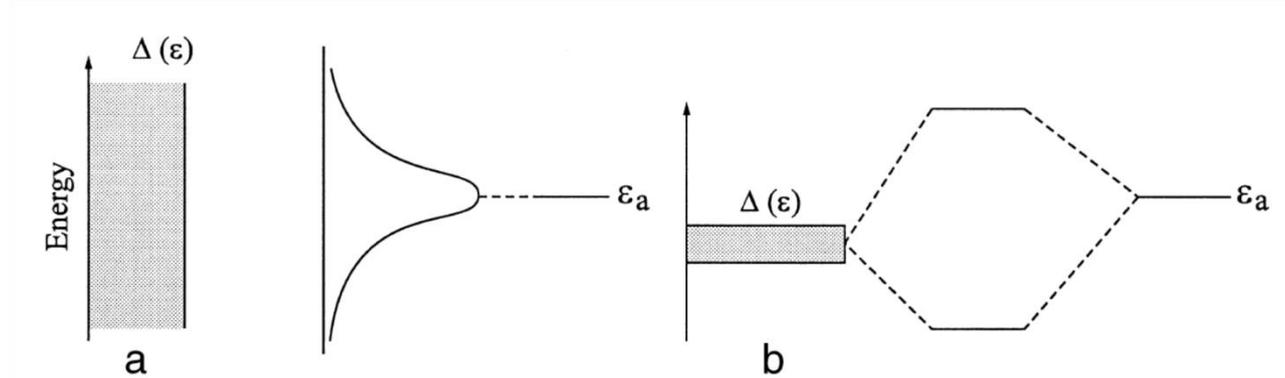
Co

Ti



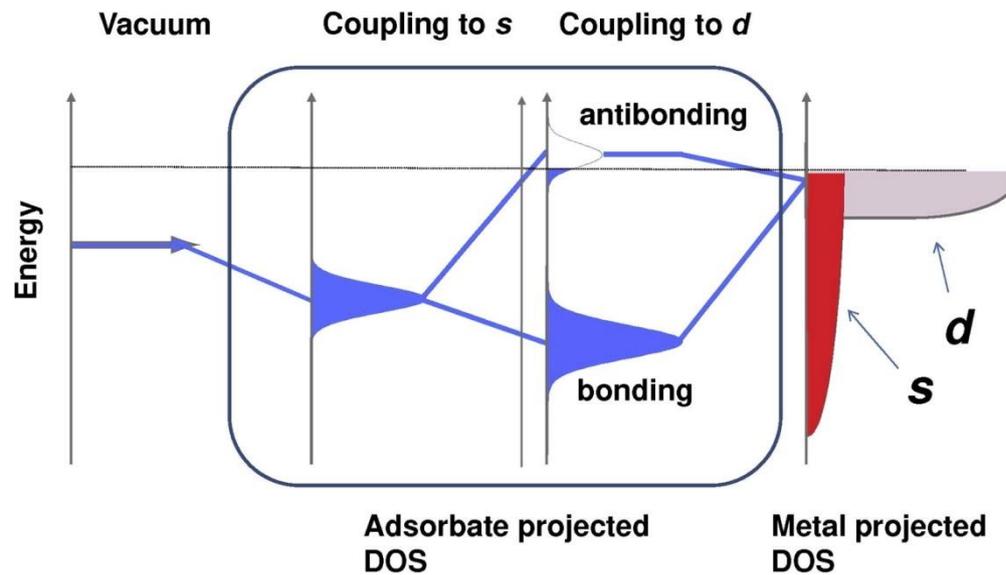
Theory of chemisorption

adatoms on transition-metal surfaces



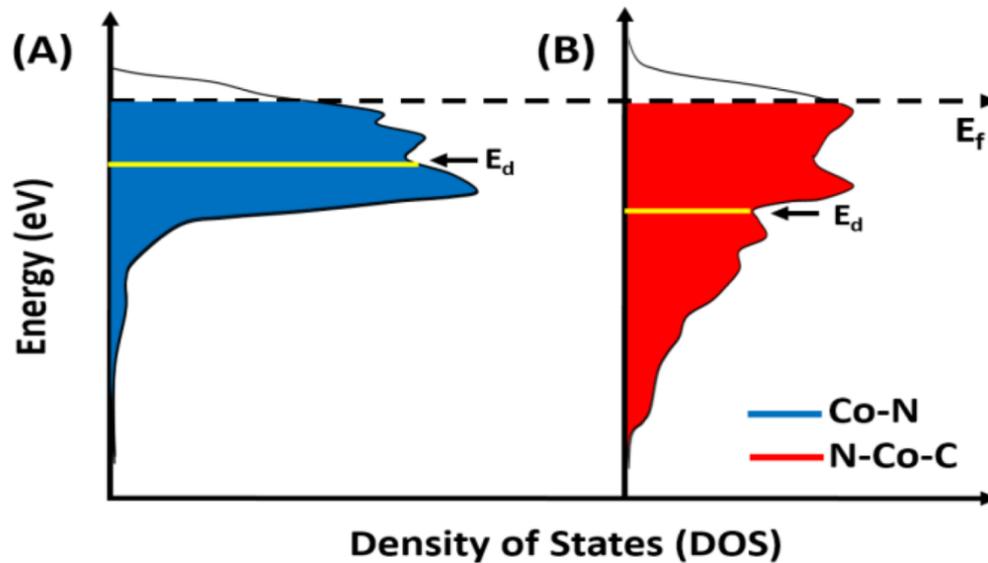
News-Anderson model

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



d-band model

Hammer-Norskov (d-band) model

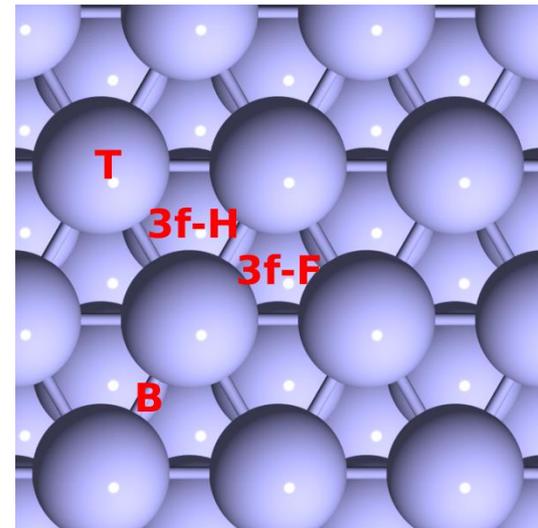


use it only for similar adsorption geometries!

d-band center

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

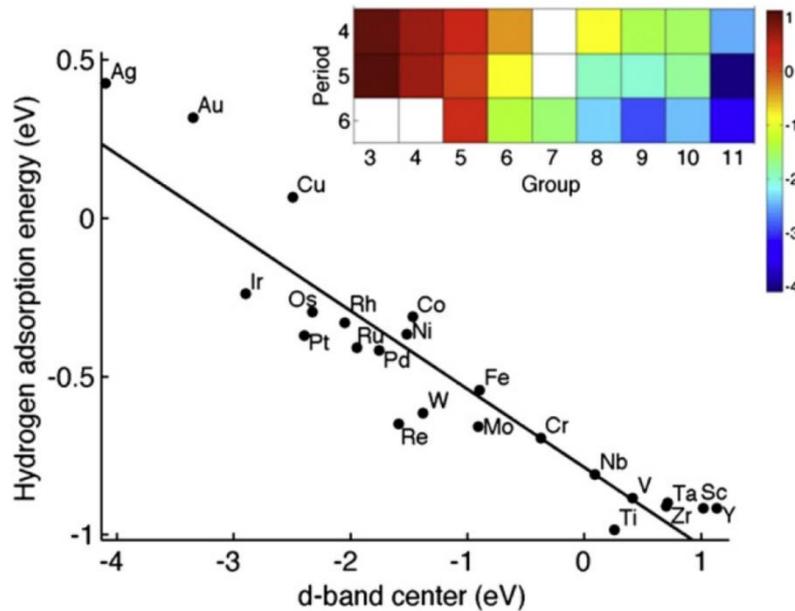
Understanding trends in reactivity based on a single parameter



d-band model

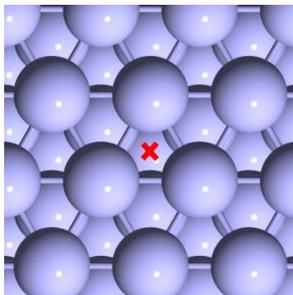
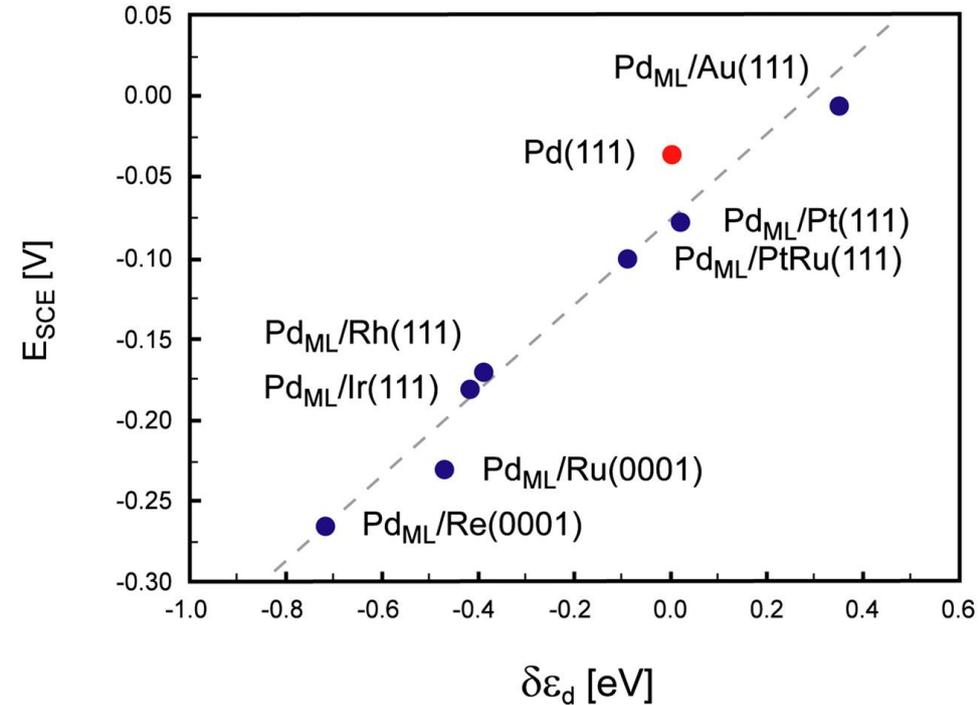
reactivity of different metals

H at metal surfaces

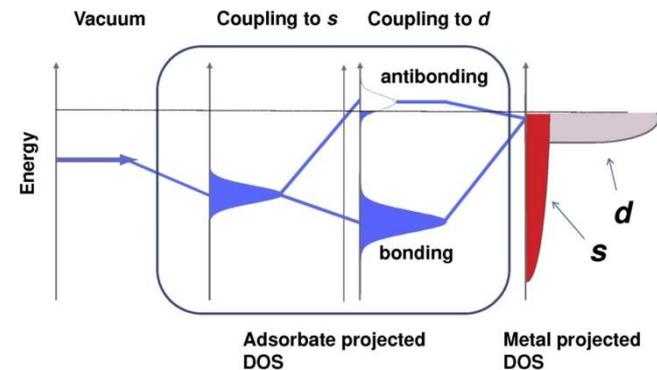


The "same" metal

oxygen adatom on Pd monolayers



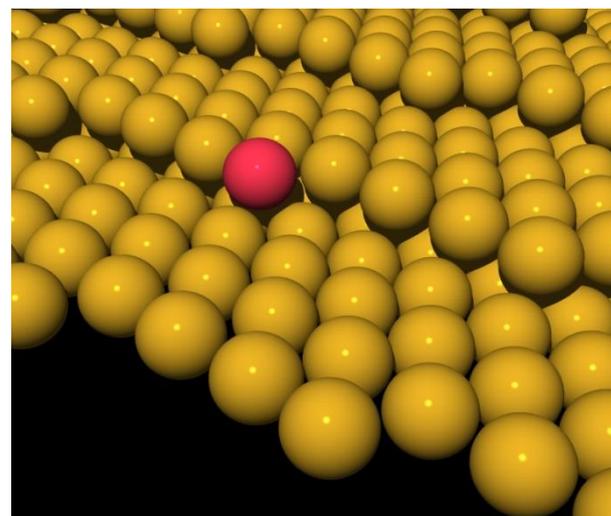
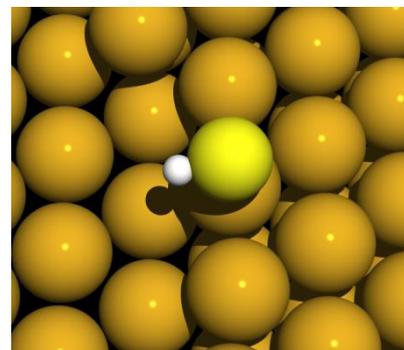
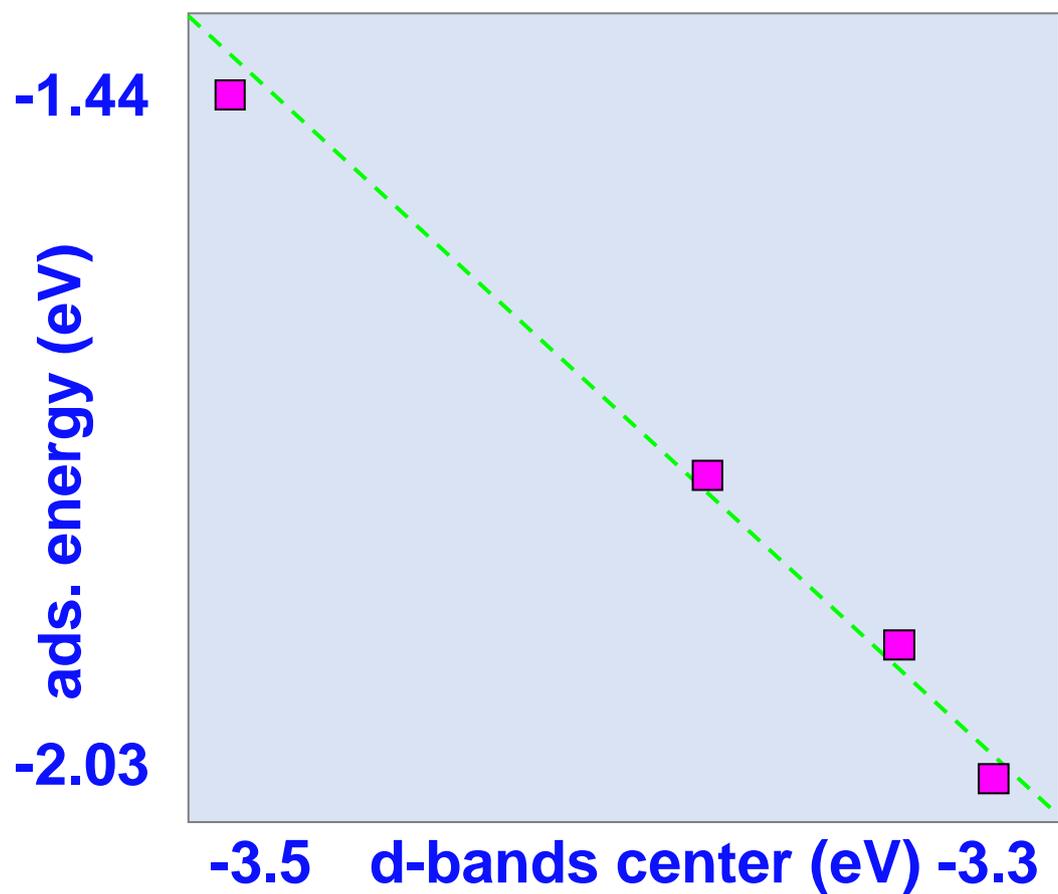
similar adsorption geometries!



d-band model

SH@Au(17 11 9) “on-top” geometry

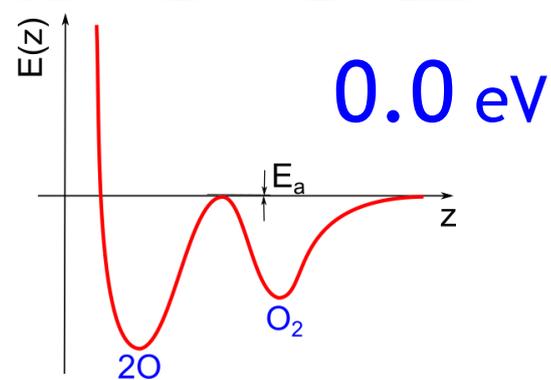
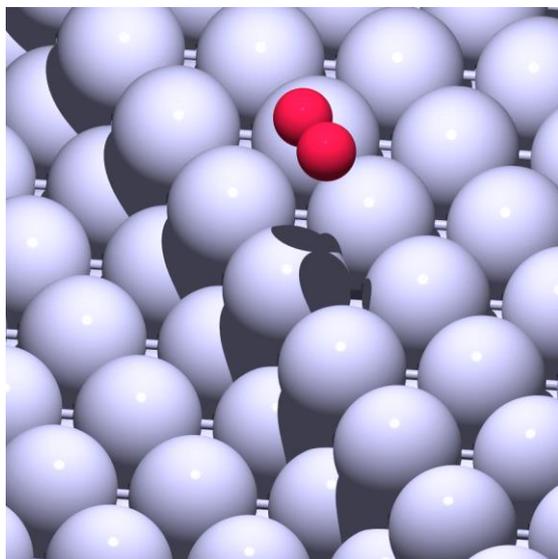
structural defects – trends in reactivity



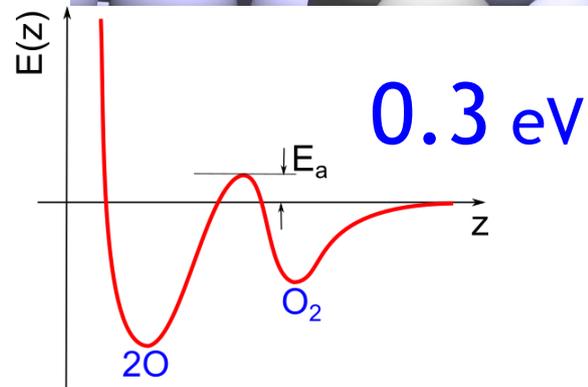
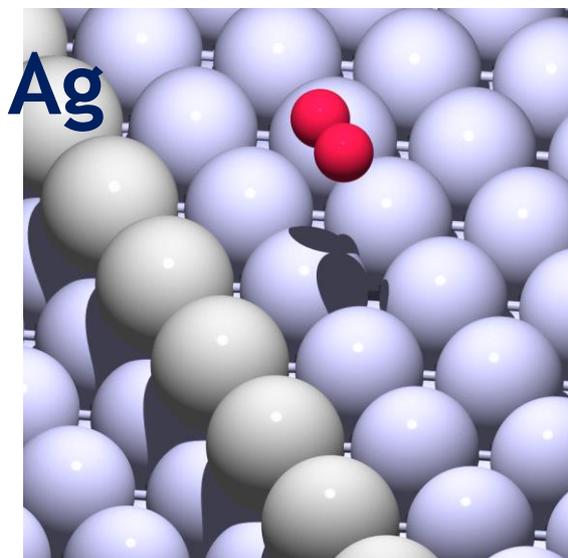
Defects at metal surfaces

DFT: O₂ dissociation on stepped Pt(111)

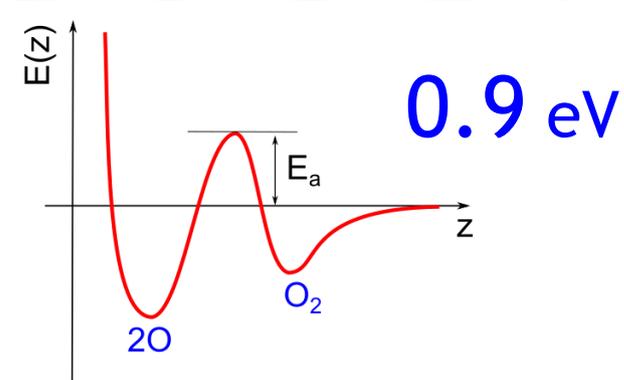
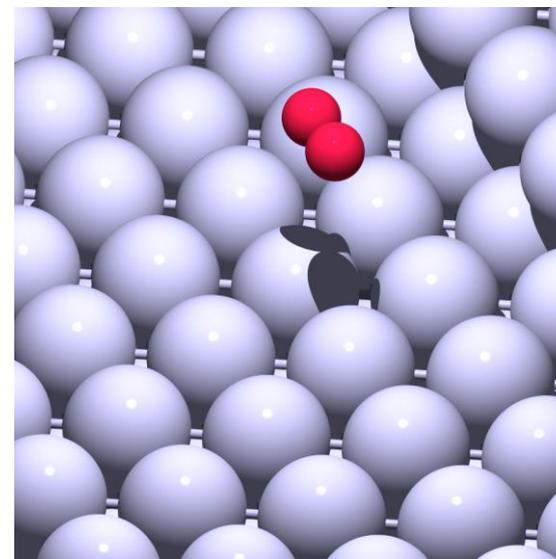
steps



Ag-covered steps



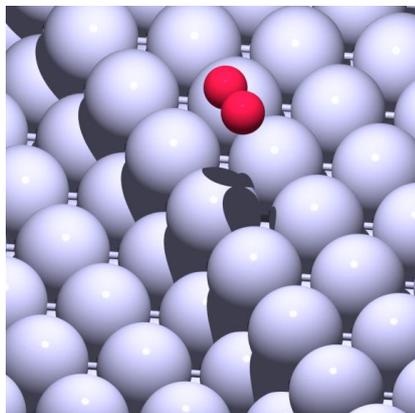
terraces



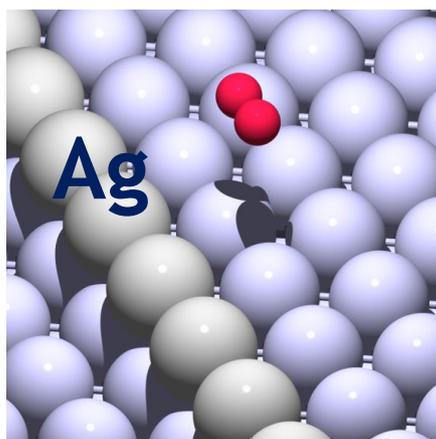
$$n = n_0 e^{-E_a/kT}$$

Atoms at steps billion times more reactive than terrace sites

Defects at metal surfaces



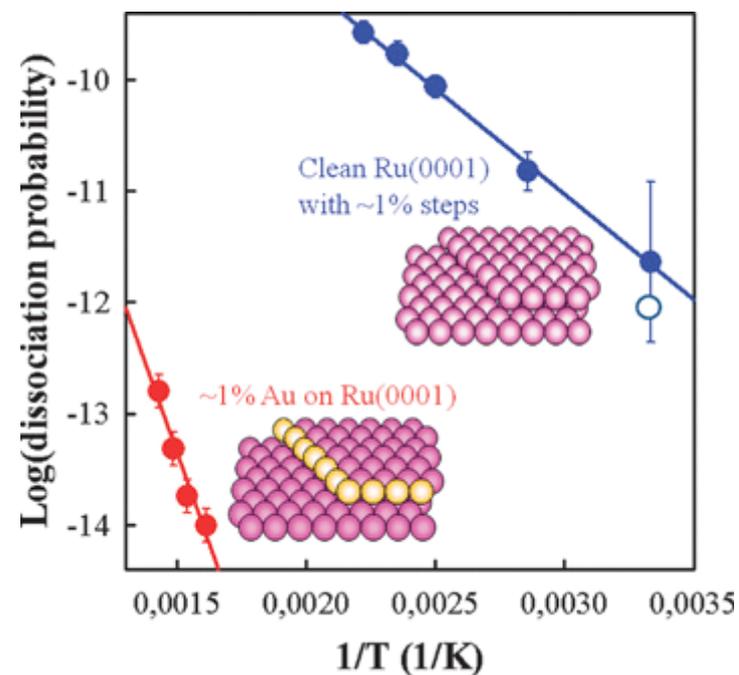
O₂ dissociation on Pt



Atoms at steps billion times more reactive than terrace sites

lead poisoning of catalysts

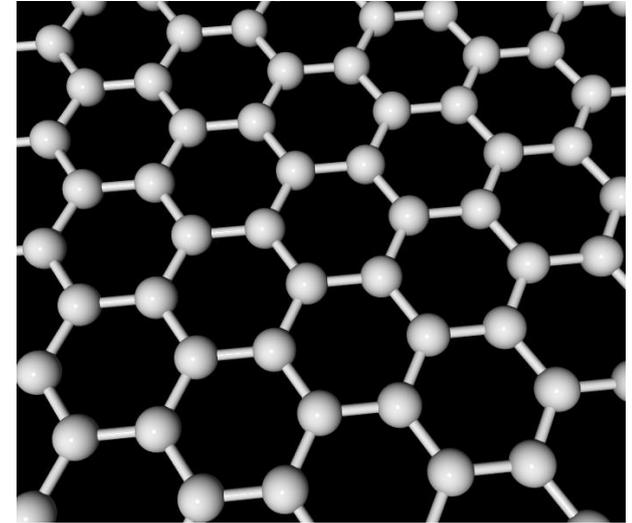
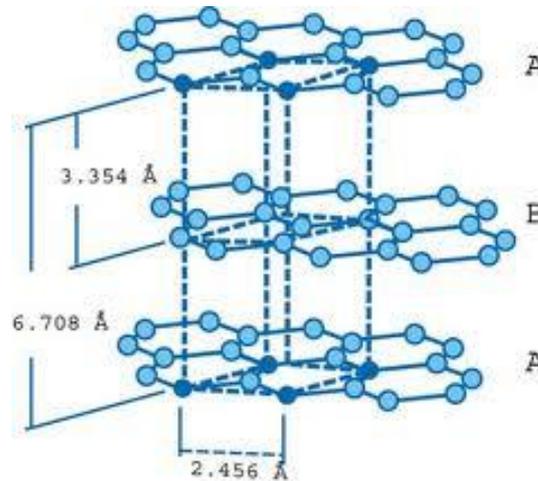
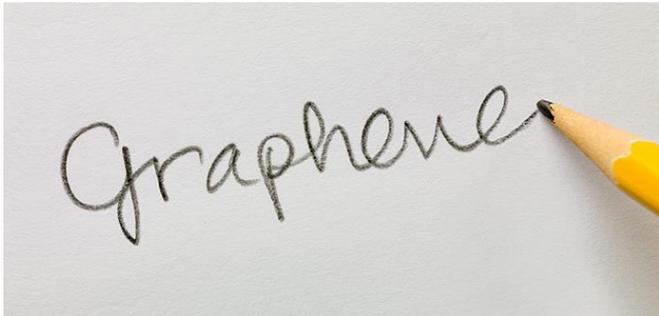
N₂ dissociation on Ru



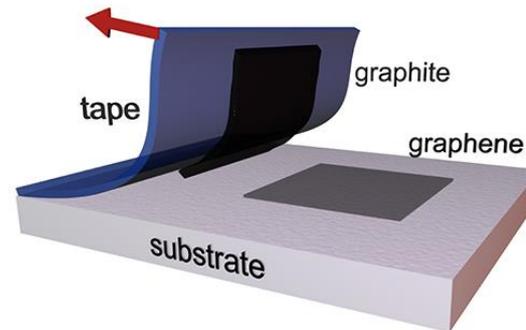
PRL **83**, 1814 (1999).

Special sites (defects) control reactivity

Graphite and graphene



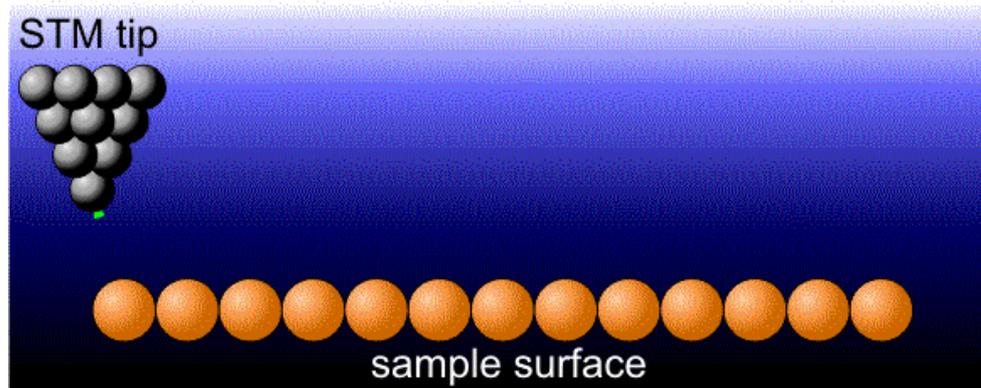
*thickness of graphite left by a pencil writing on paper is ~20 nm
50 to 60 graphene layers*



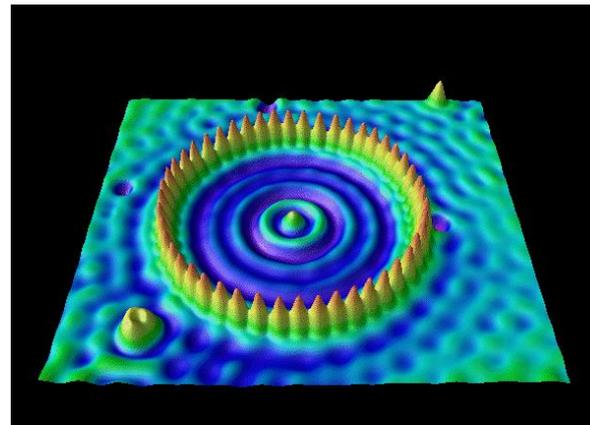
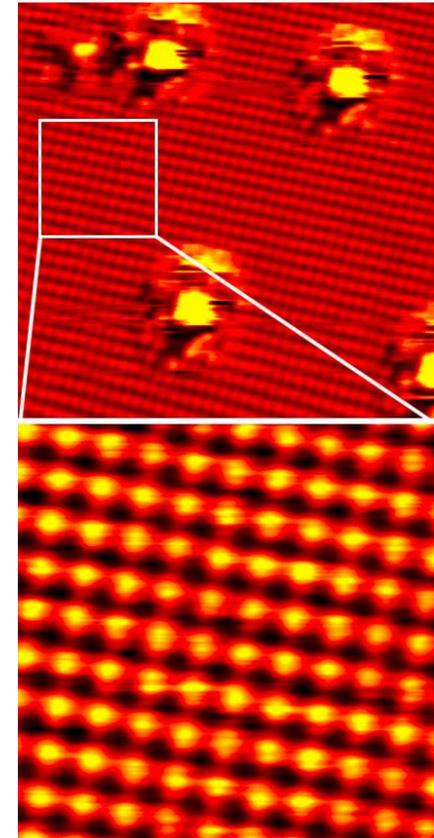
K. Novoselov and A. Geim, Nobel prize in Physics 2010

“for groundbreaking experiments regarding the two-dimensional material graphene.”

Scanning tunneling microscopy (STM)



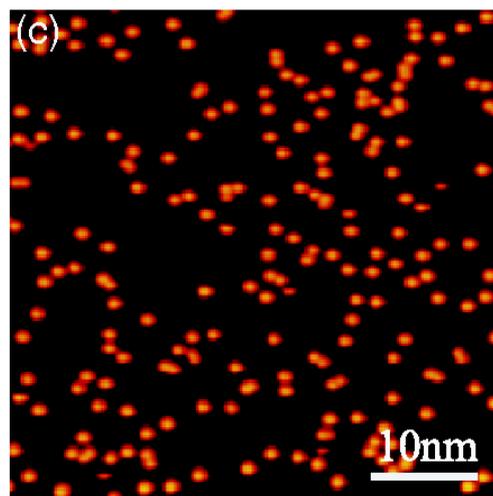
Ag(100)



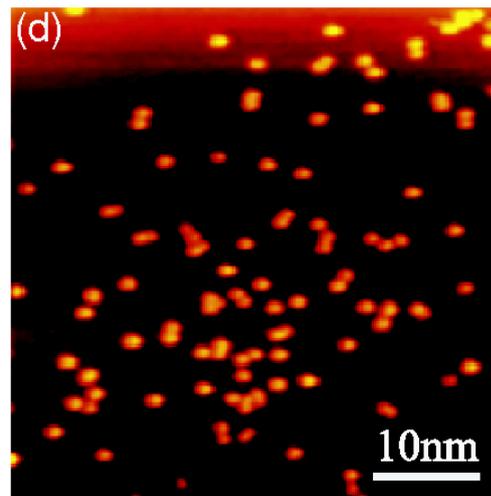
Fe atoms on Cu

2.5 nm x 2.5 nm на 160 K

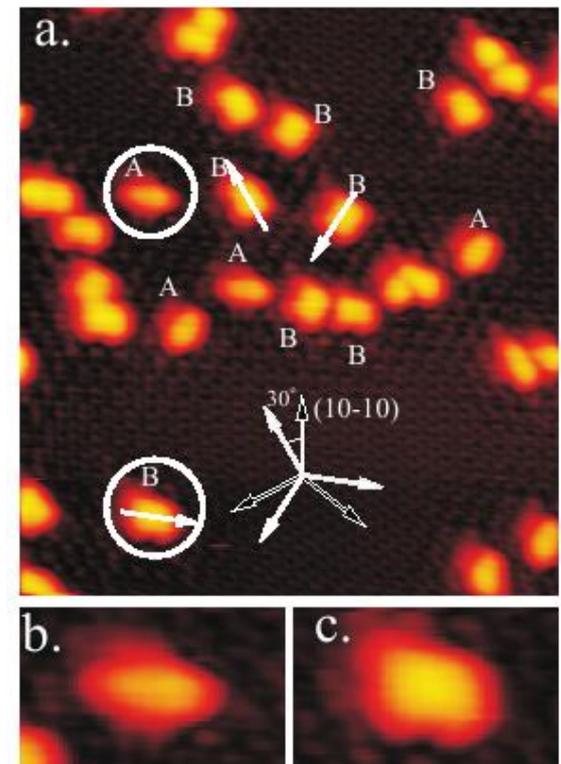
Hydrogen atoms on graphite



Anneal
to RT
→



STM images



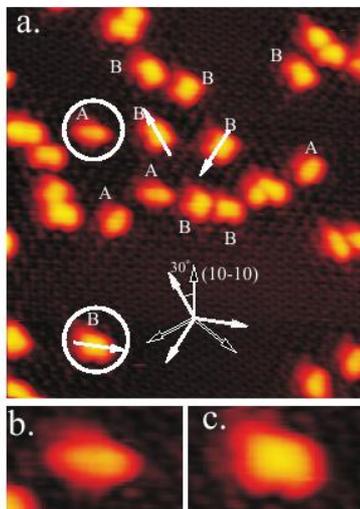
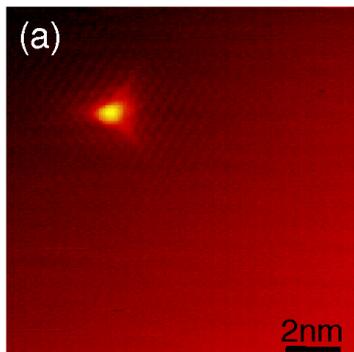
PRL 96, 156104 (2006)

two types of hydrogen structures

Atomic hydrogen on graphene (DFT)

STM results

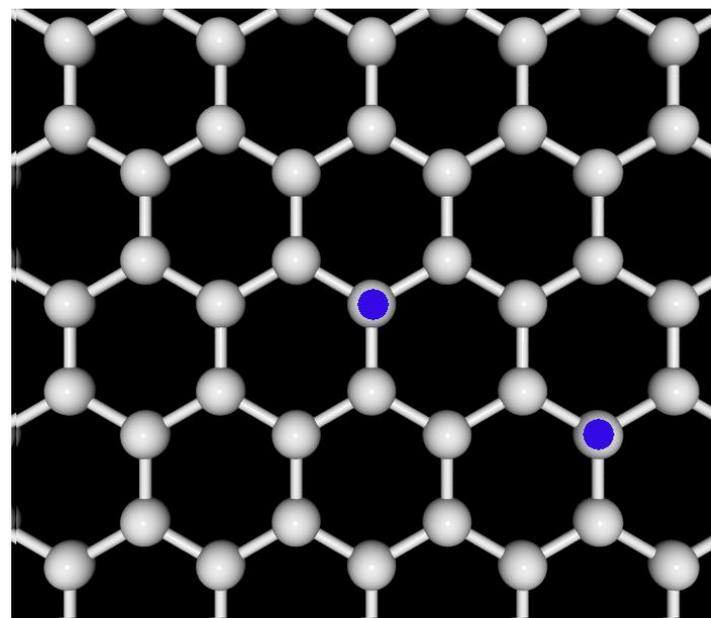
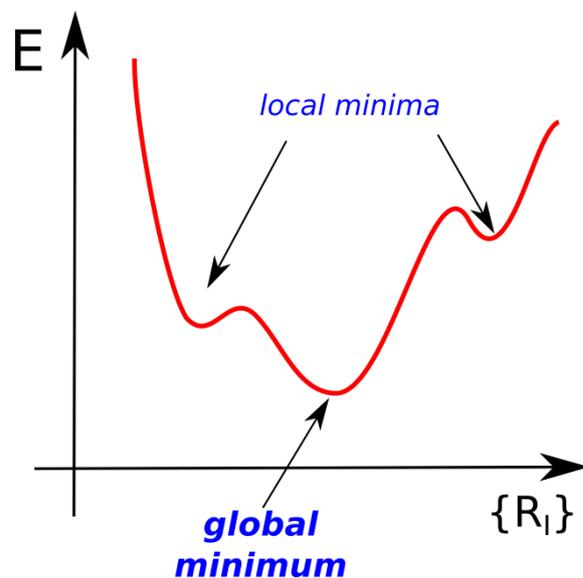
H adatom



unknown structures

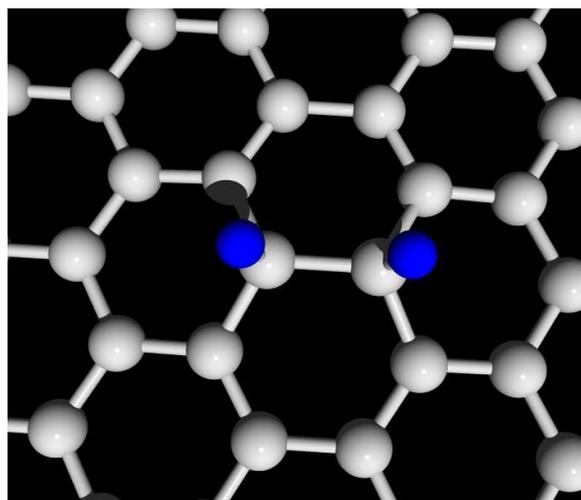
DFT used to search for favorable configuration of H adatoms

Let's start with TWO H atoms



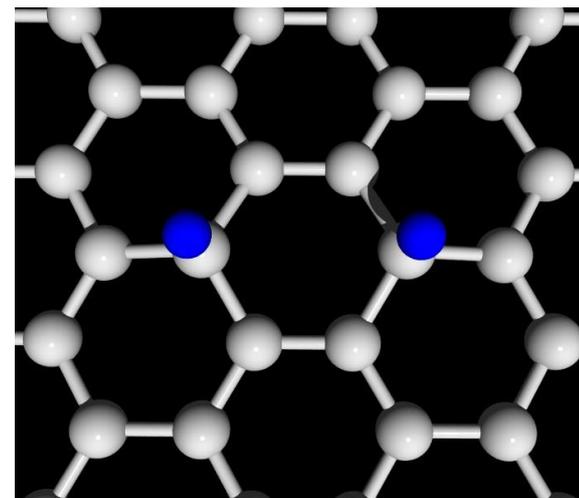
Atomic hydrogen on graphene (DFT)

H dimers

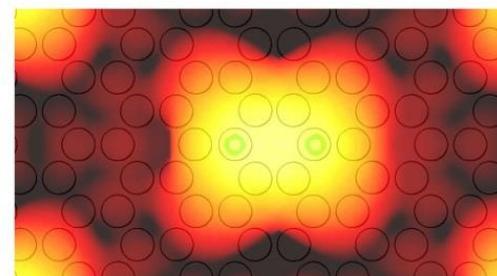
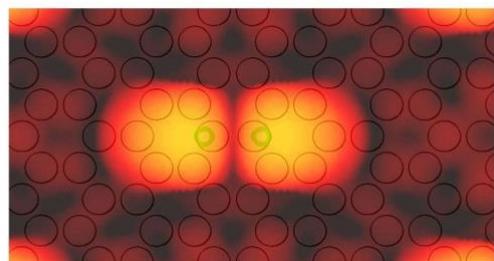


ortho dimer

$$E_B = 2.7 \text{ eV}$$



para dimer



DFT

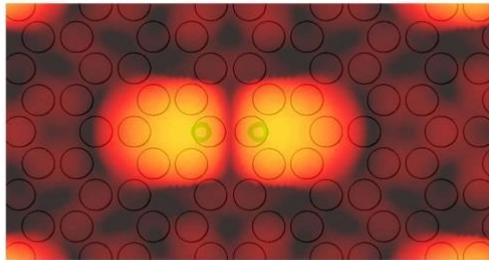


experiment

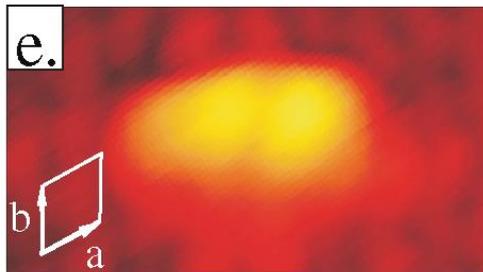
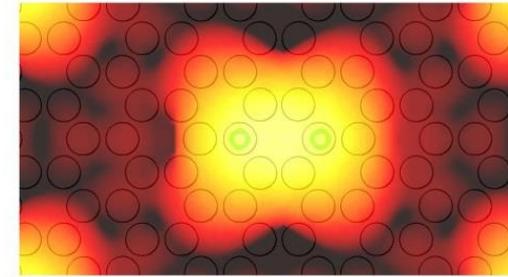
DFT can be use to simulate STM images and compare them with those obtained from STM imaging

Atomic hydrogen on graphene (DFT)

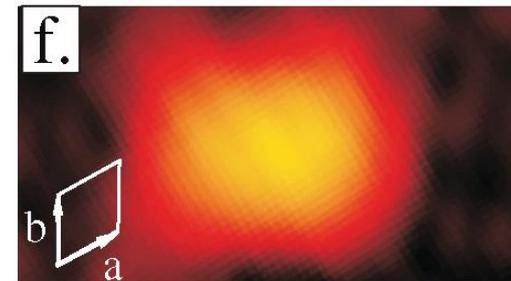
DFT can be used to simulate STM images



DFT



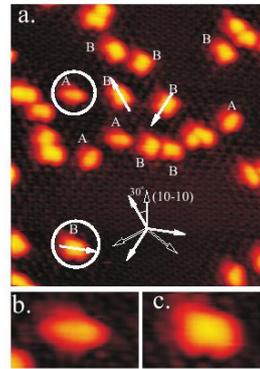
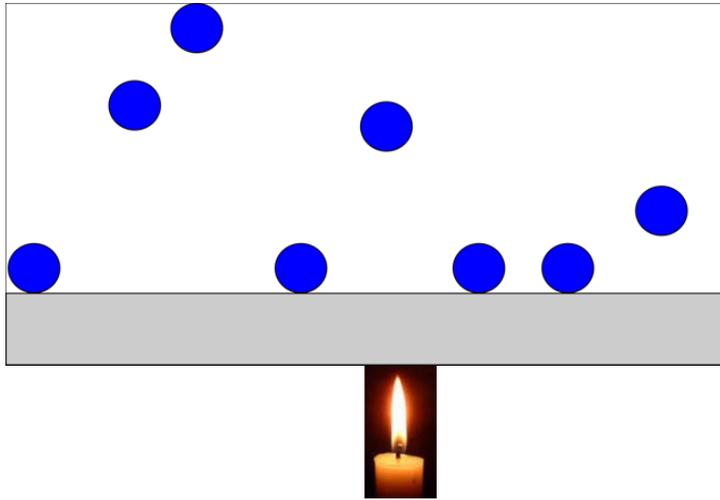
experiment



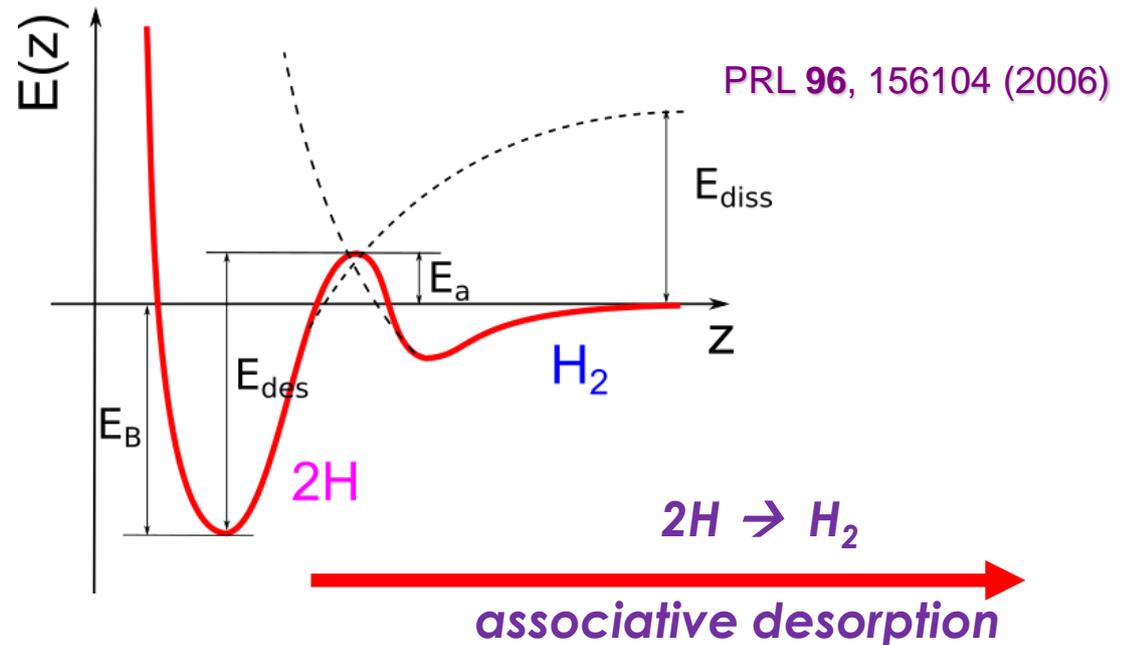
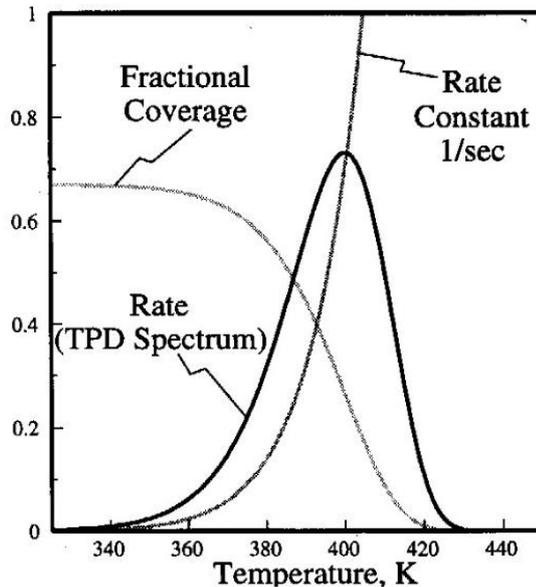
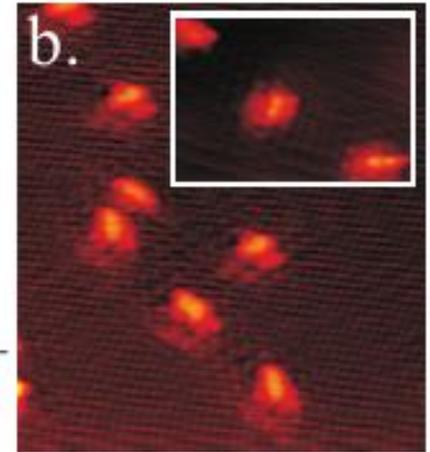
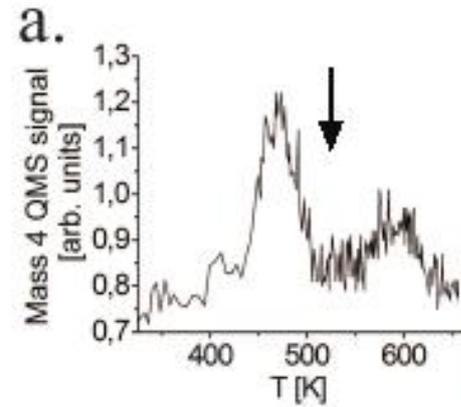
**Tersoff-Hamann scheme - local density of states
 $n(r, E)$**

Hydrogen atoms on graphite

Temperature programmed desorption (TPD)



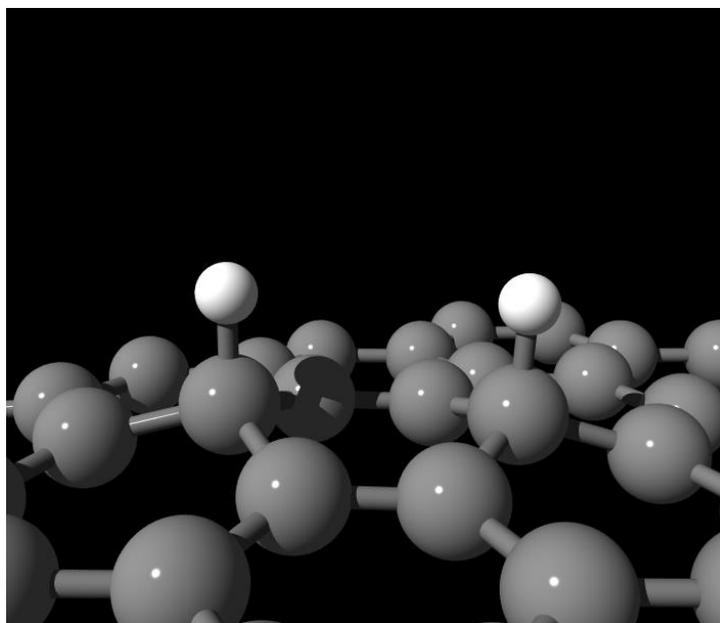
different desorption barriers



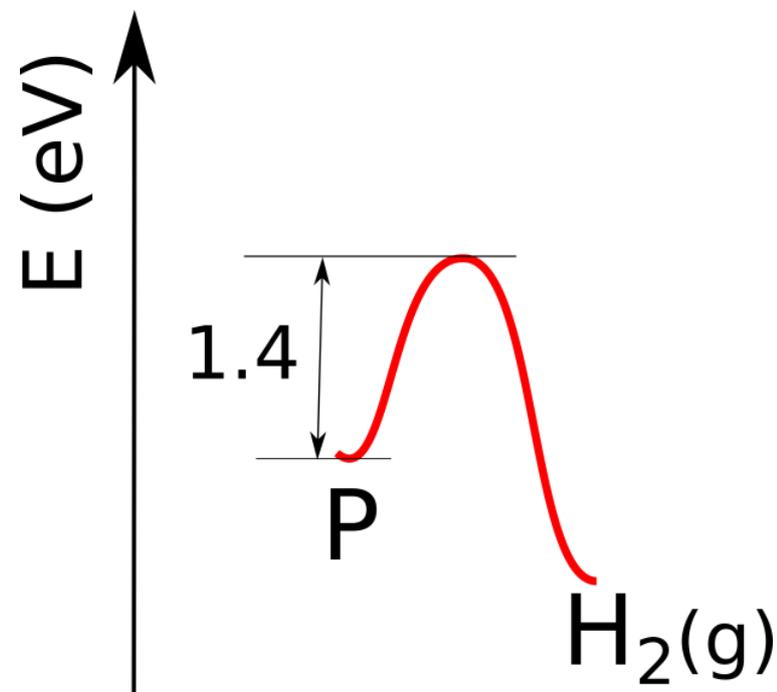
Atomic hydrogen on graphene (DFT)

associative desorption

para dimer



NEB used to calculate barriers

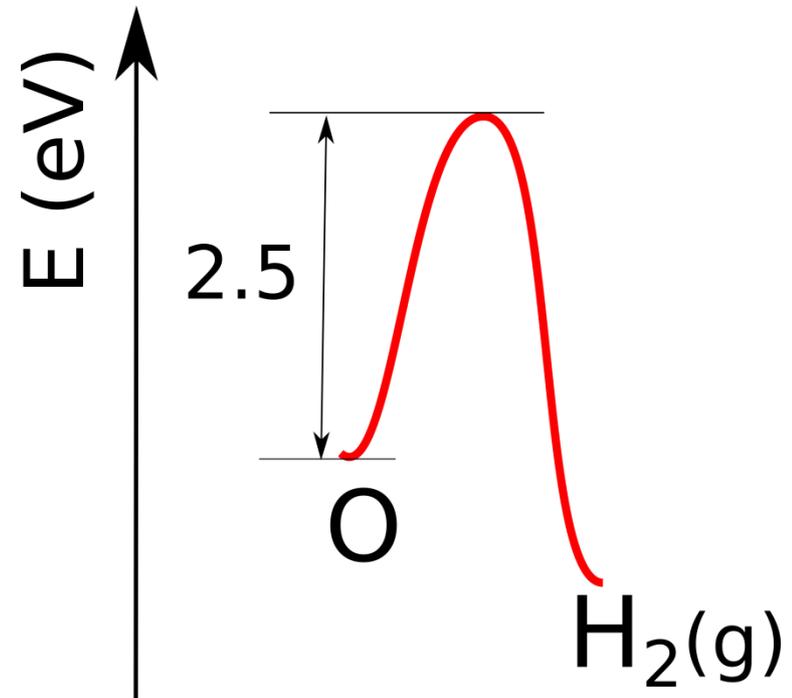
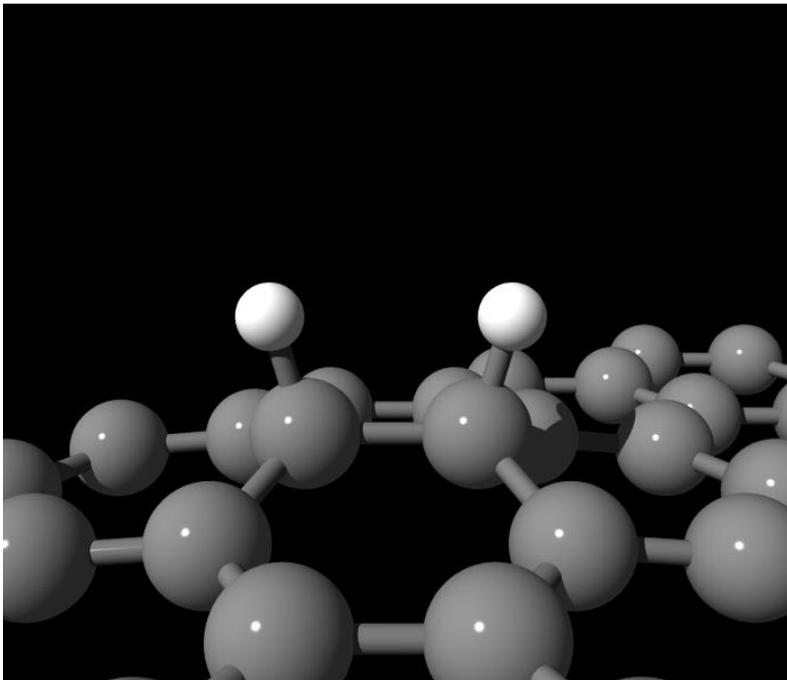


direct process: $O \rightarrow H_2$ occurs at 470K

Atomic hydrogen on graphene (DFT)

associative desorption

ortho dimer

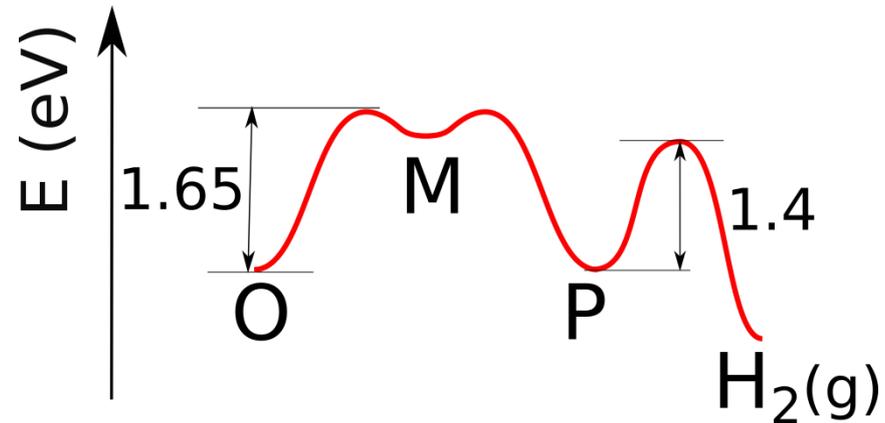
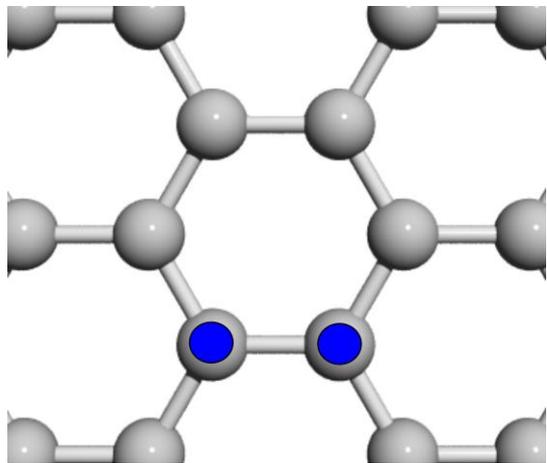


direct process: $O \rightarrow H_2$ does not occur

Atomic hydrogen on graphene (DFT)

associative desorption

ortho dimer

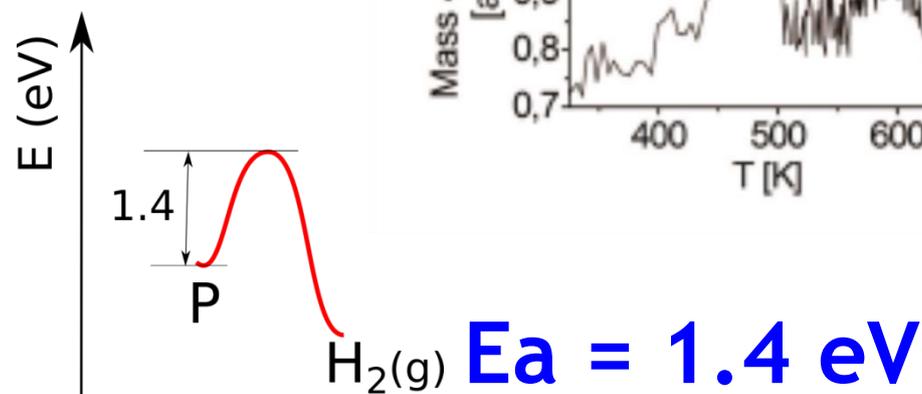
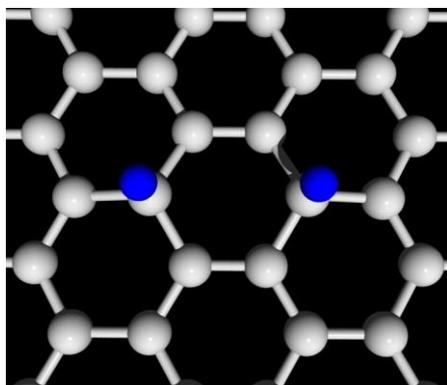


process: $O \rightarrow M \rightarrow P \rightarrow H_2$ occurs at 600K

Atomic hydrogen on graphene (DFT)

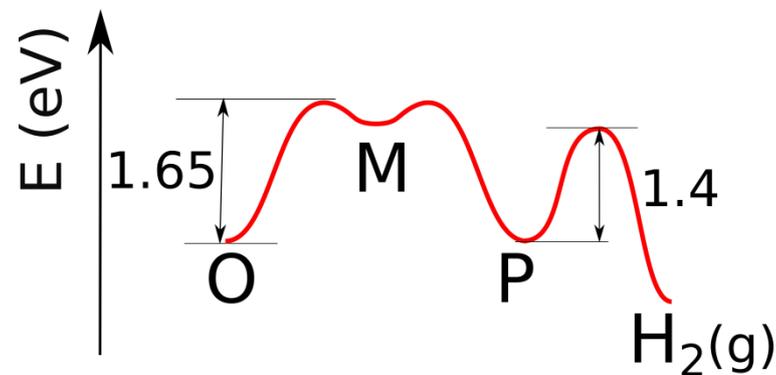
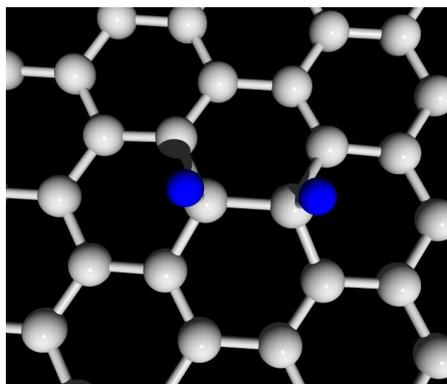
DFT and TPD

para dimer



$E_a = 1.4 \text{ eV}$

ortho dimer



$E_a = 1.65 \text{ eV}$

DFT in surface science

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

