Adsorption at, Desorption from, and Chemical Activity of Metal Surfaces

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Outline

- *Fundamental concepts:* adparticles at surfaces

- *Adsorption of atoms and molecules at metal surfaces:* trends in dependence on site and substrate

- *Surface chemical reactions:* e.g. CO oxidation

- *Combined ab initio and statistical mechanical schemes to bridge micro and macroscopic scales:* **The way to go!**

Surface energy barrier

O/Ru(0001)
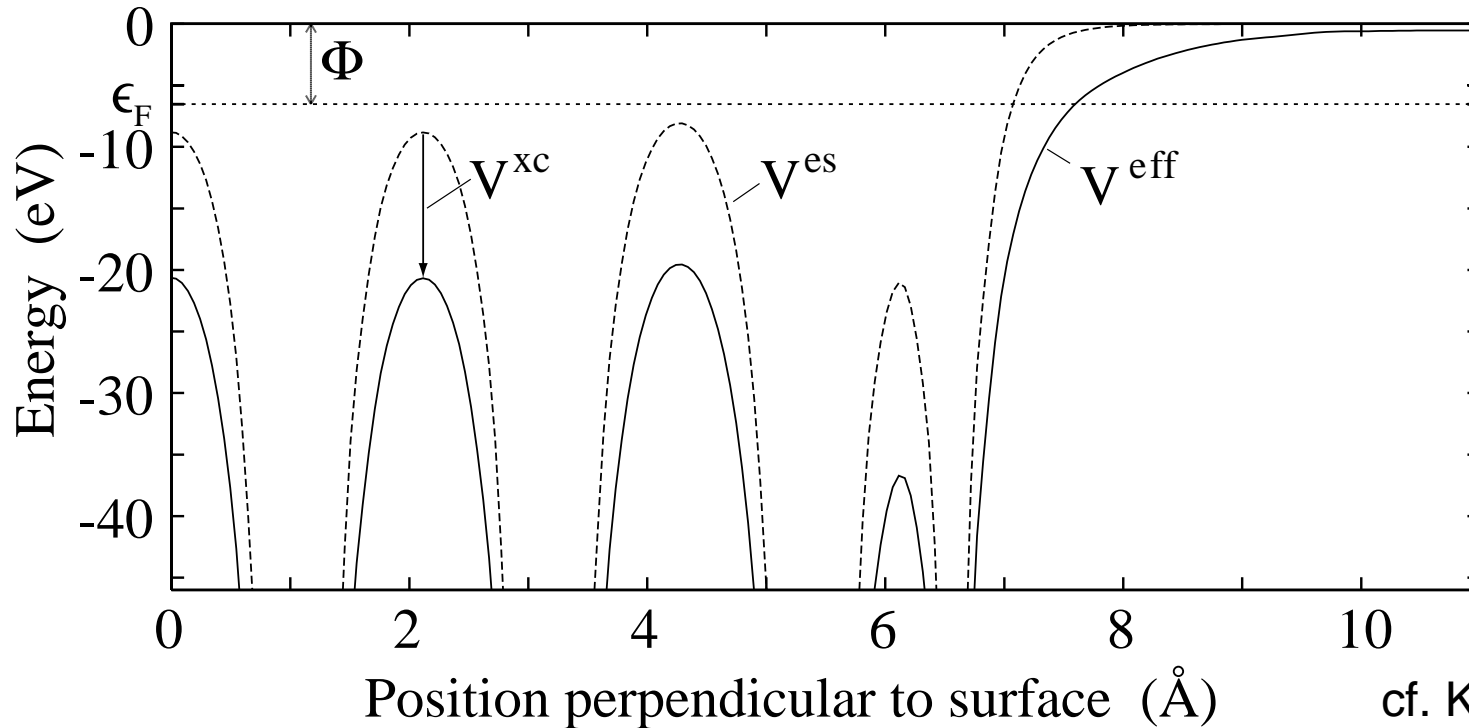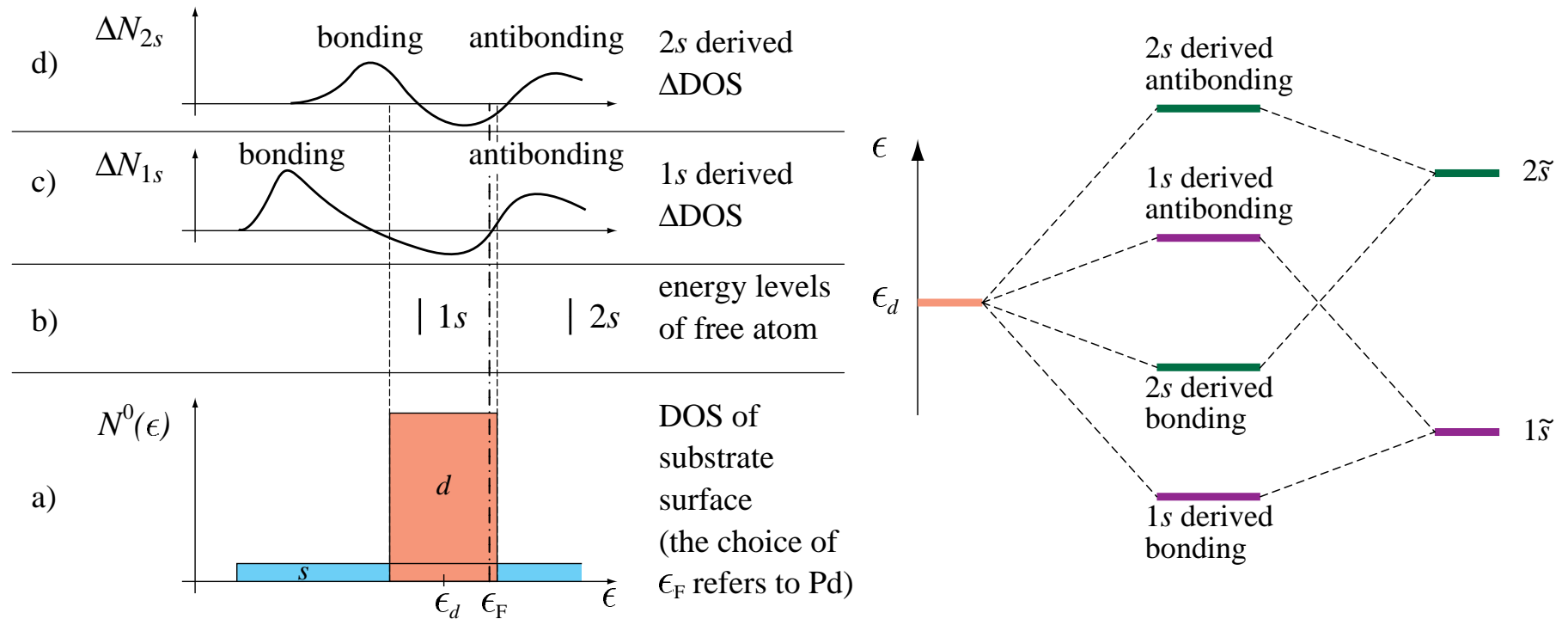

V^{eff} effective Kohn-Sham potential

V^{es} electrostatic potential

V^{ex} exchange-correlation potential

Classical image effect

$$V^{eff}(z) = \frac{-1}{4\pi\varepsilon_0} \frac{(e^-)^2}{4(z-z_0)}$$

(From Scheffler and Stampfl In: Handbook of Surface Science, Vol. 2: Electronic Structure, 2000)
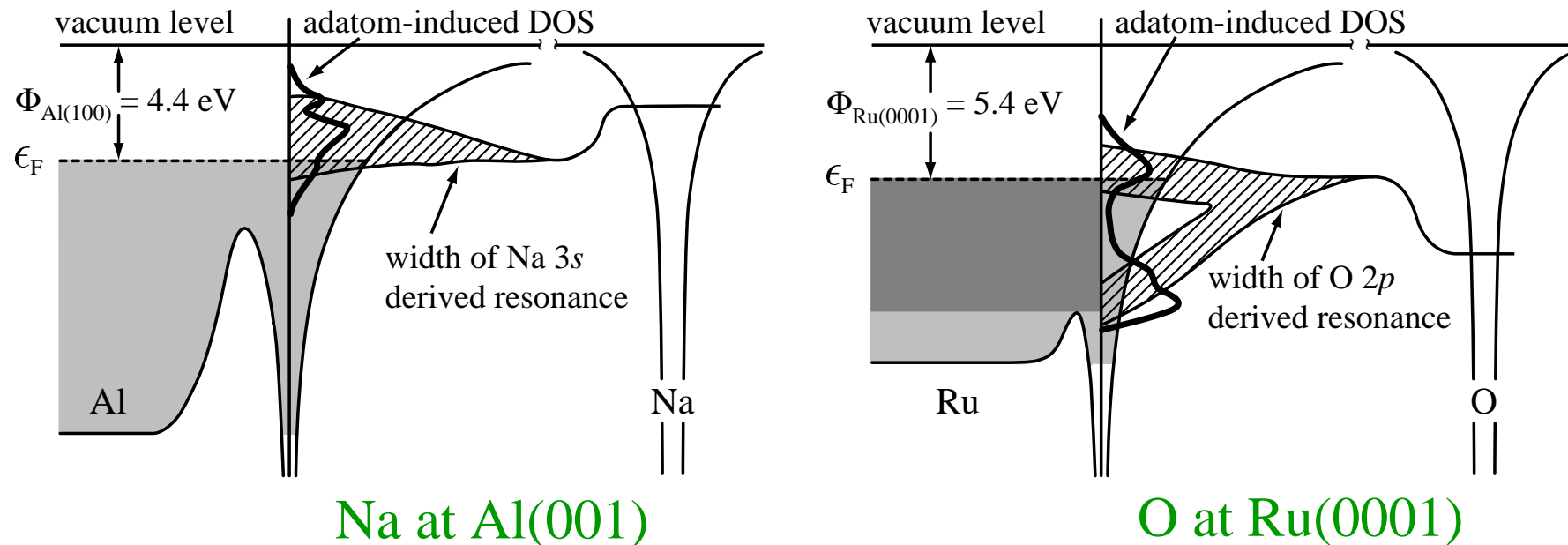
Adsorbate-substrate interaction

The example: H on Pd

(From Scheffler and Stampfl In: Handbook of Surface Science, Vol. 2: Electronic Structure, 2000)

Adsorbate-induced DOS versus distance

Na at Al(001)　　　　O at Ru(0001)

Distance dependence of the broadening and shift of the adsorbate energy level (Na 3s and O 2p)

For Na/Al partial charge transfer from adsorbate to substrate
For O/Ru partial charge transfer from substrate to adsorbate

(From Scheffler and Stampfl In: Handbook of Surface Science, Vol. 2: Electronic Structure, 2000)

DFT-LDA eigenvalues versus occupation

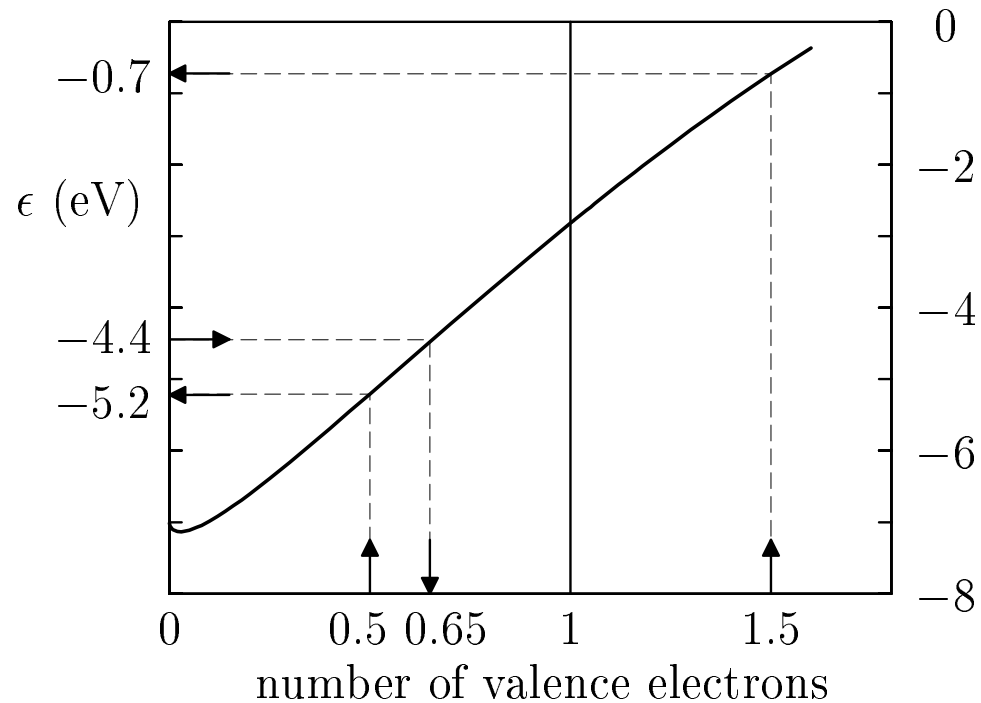**The Na 3s-state as a function of the number of valence electrons**

$f_{3s}=0$ is the Na$^+$ ion

$f_{3s}=1$ is the neutral atom

$f_{3s}=2$ is the Na$^-$ ion

For $f_{3s}=0.5$ the eigenvalue gives the ionization energy (5.2 eV; expt. 5.14 eV)

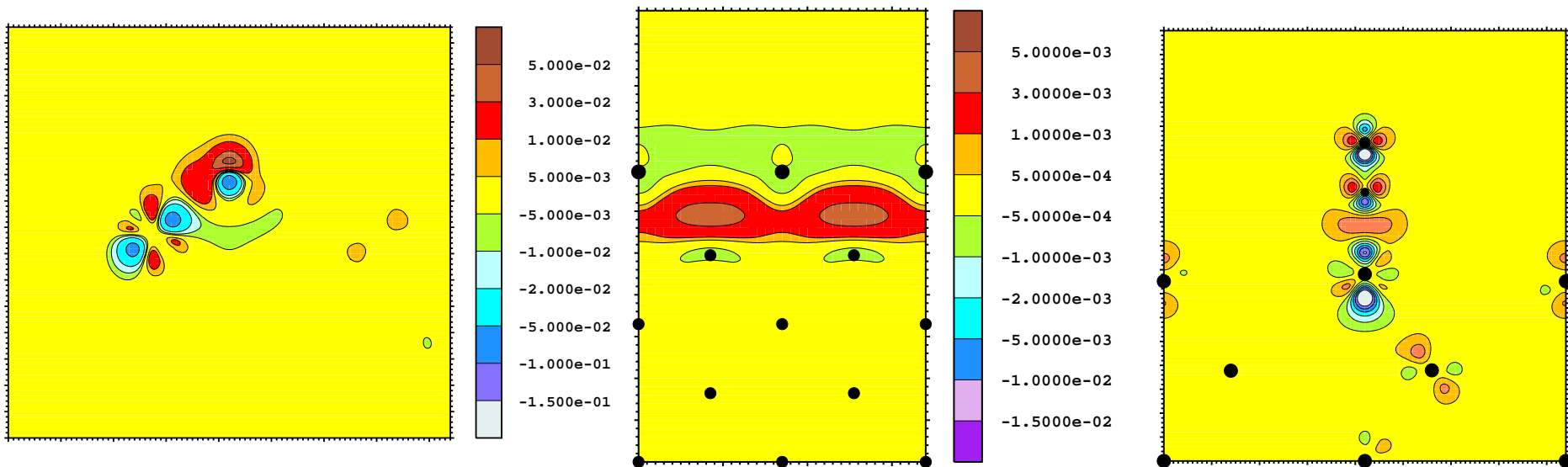For $f_{3s}=1.5$ the eigenvalue gives the electron affinity (0.7 eV; expt. 0.55 eV)

cf. M. Fuchs

$$I_k = E^{N-1} - E^N = \int_N^{N-1} dE^{N'}/dN' \, dN' = -\int_0^1 \varepsilon_k(f_k) \, df_k \approx -\varepsilon_k(f_k=0.5)$$

(From Scheffler and Stampfl In: Handbook of Surface Science, Vol. 2: Electronic Structure, 2000)

Bonding at surfaces: O, Na, CO

difference density: $n^\Delta(\mathbf{r}) = n(\mathbf{r}) - n^0(\mathbf{r}) - n^{\mathrm{ad}}(\mathbf{r})$

O/Ru(0001):
electronegative
adsorbate: charge
transfer to O

Na/Al(001):
electropositive
adsorbate: charge
transfer from Na

CO/Ru(0001):
donation/back-
donation
Blyholder model

(C. Stampfl et al. PRB (1998)) (MS & CS; Handbook (2000))

Binding energy at kink sites

The total energy of a system can be written as:

$$E = \Sigma_{I=1}^{N} E_I$$

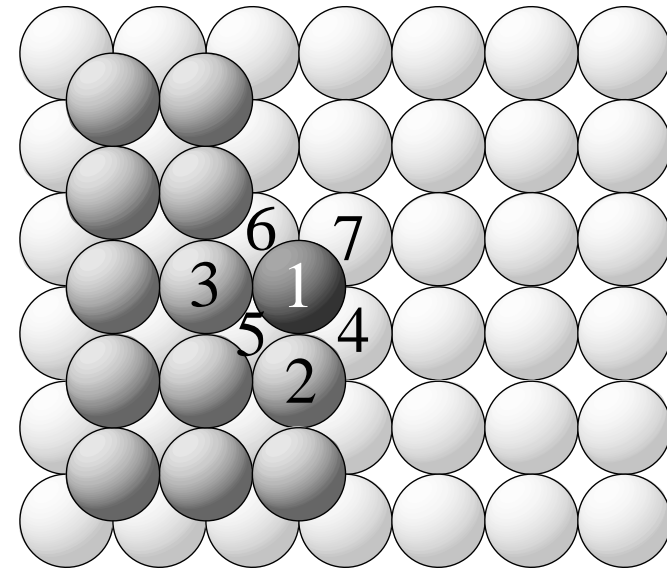E_I is the energy contribution due to atom I.

E_I can be expressed as a function of coordination of atom I fi ``*bond-cutting model*''
e.g. E_I C

For adsorption of an atom from the
gas phase at a kink site, the energy gain is:

$$E_{ad}^{kink} = -E^{after} + E^{before}$$

$$E_{ad}^{kink} = -(E_1(6) + E_2(7) + E_3(8) + E_4(10) + E_5(12) + E_6(11) + E_7(9))$$
$$+ E_1(0) + E_2(6) + E_3(7) + E_4(9) + E_5(11) + E_6(10) + E_7(8)$$
$$= -E_5(12) + E_1(0) \longrightarrow \textbf{The cohesive energy}$$

Why are processes at surface important?

- A surface is in contact with molecules from the gas or liquid phase $\longrightarrow$ bonds may break and new ones form and chemical reactions take place

- *Technological reasons:*

  Heterogeneous catalysis, e.g., reactivity, role of promoters and poisons

  Corrosion, e.g., protective coatings

  Electronic and magnetic devices, e.g., growth, stability

- *Fundamental reasons*

For understanding need to first study simple processes then more complicated - compare for different but similar systems

Trends in adsorption energies for different substrates

O adsorption on 4d transition metals

From left to right in the
Periodic Table, the weaker
the O-metal bond becomes.

This is due to lower lying
(and more occupied) d-bands
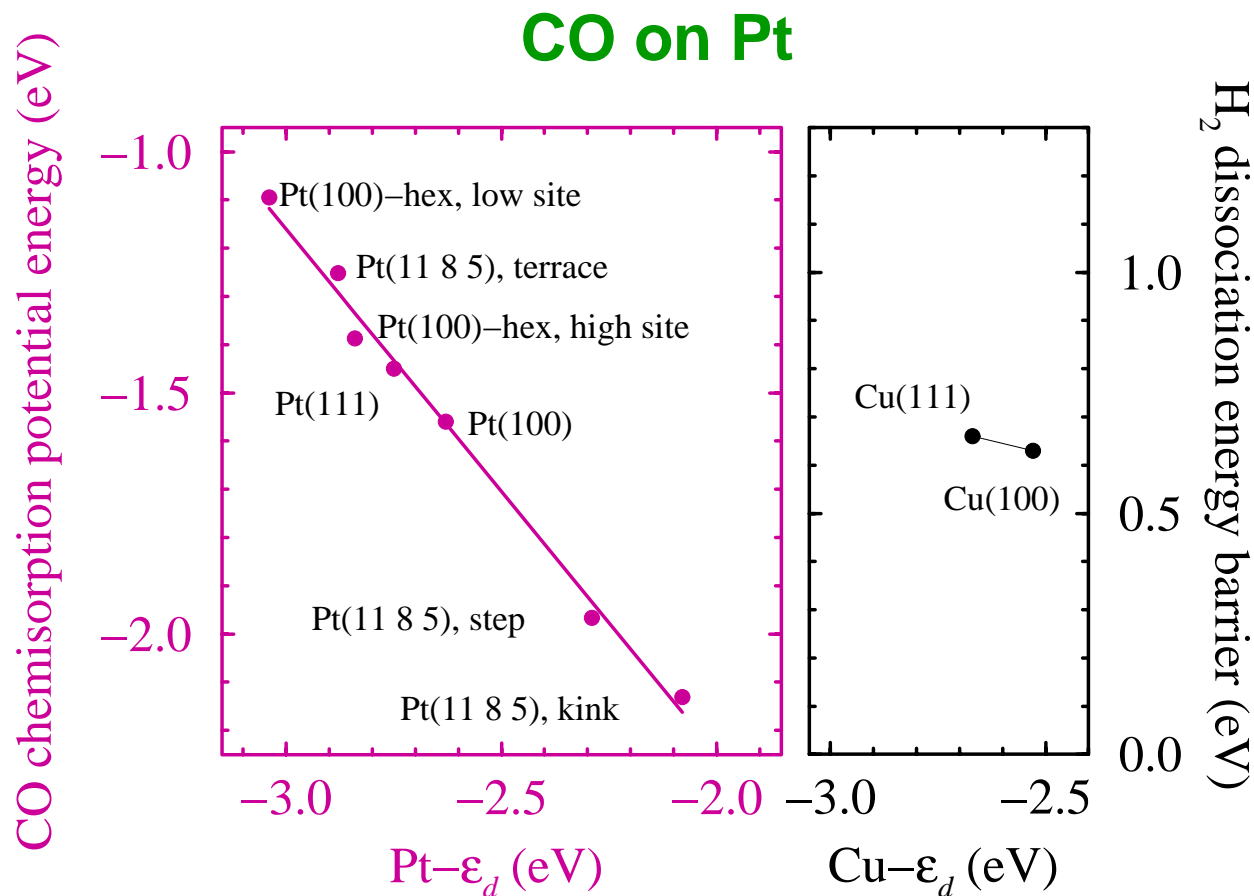which causes antibonding
O-metal states to become
occupied.
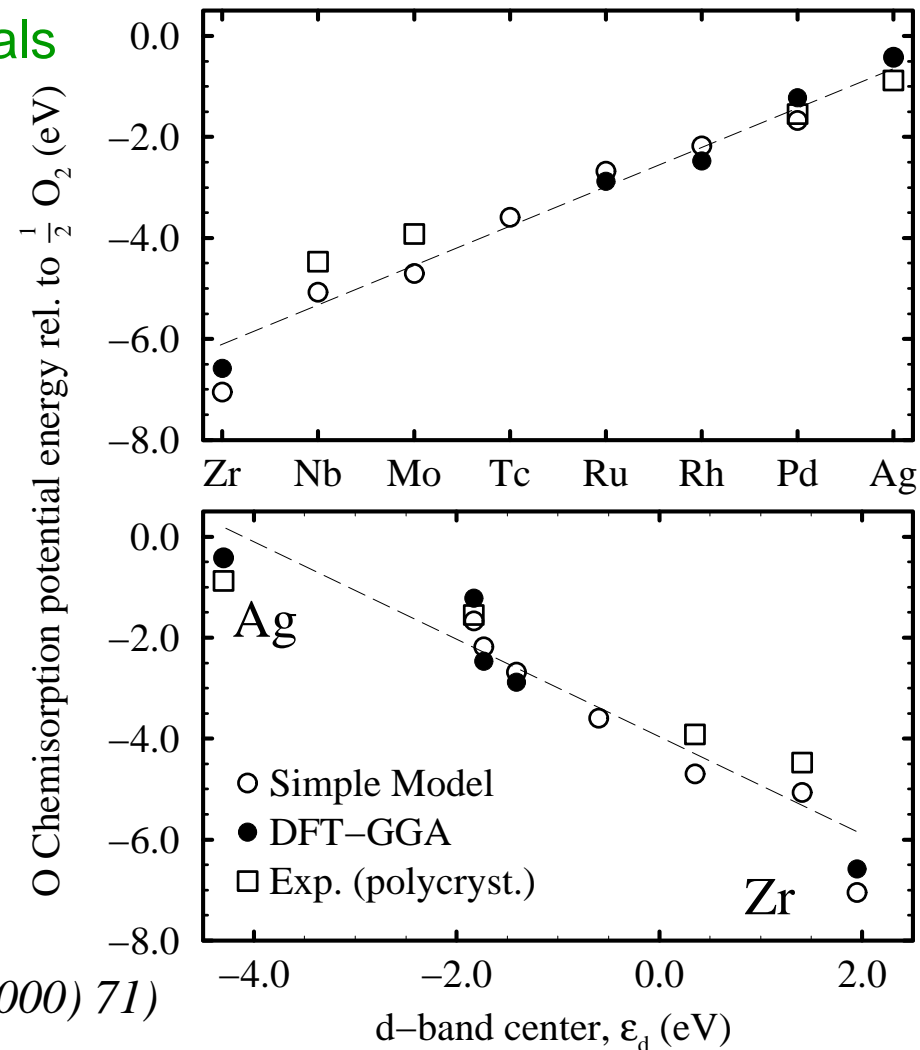
(Hammer and Norskov, Adv. Catal. 45 (2000) 71)

Trends in adsorption energy for differently coordinated sites

CO on Pt

Correlation of CO
adsorption energy
with *d*-band center for
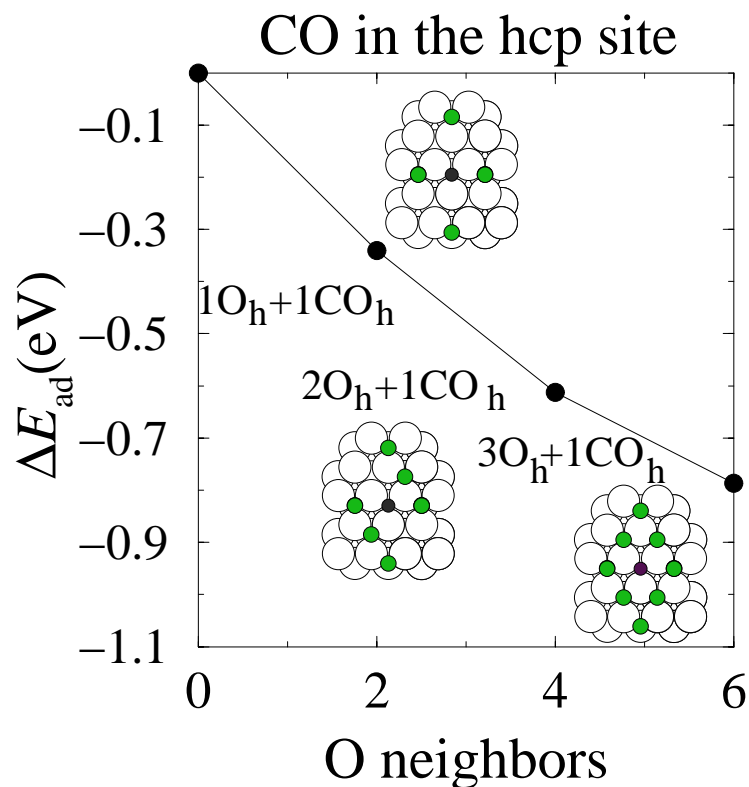adsorption in the top
site on Pt atoms with
different coordinations
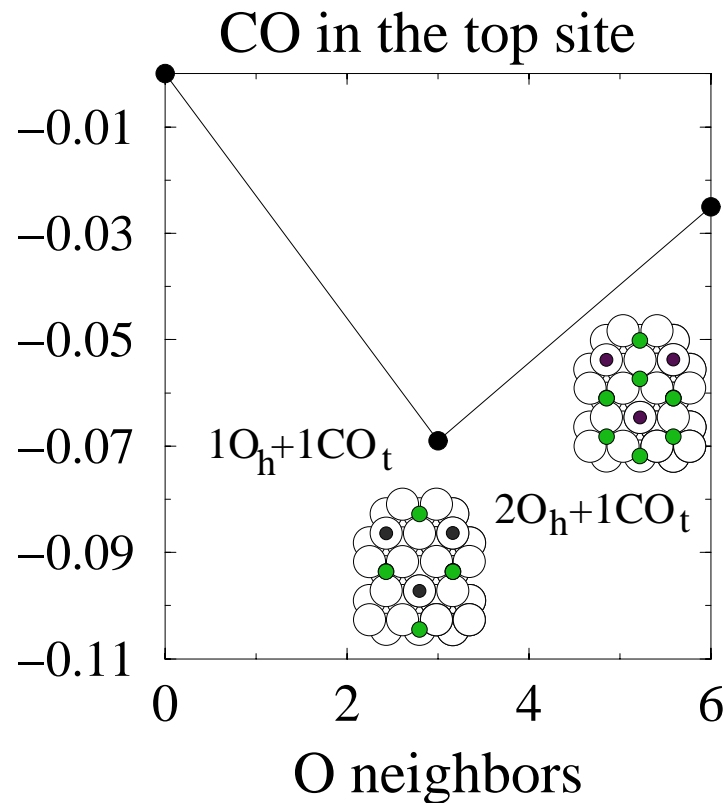
**Strongest binding
for highest d-band
center**

(Hammer and Norskov, Adv. Catal. 45 (2000) 71)

Coadsorption

CO+O on Ru(0001)

CO in the hcp site

ΔE_{ad} (eV)

$1O_h+1CO_h$

$2O_h+1CO_h$

$3O_h+1CO_h$

O neighbors

The CO adsorption energy decreases with increasing numbers of O atoms that bond to the same Ru atom

(Stampfl and Scheffler, to be published)

CO in the top site

$1O_h+1CO_t$

$2O_h+1CO_t$

O neighbors

Can remain practically unchanged or even exhibit a slight increase
→ due to O-induced lateral weakening of Ru-Ru bonds for non-O-bonded Ru atoms
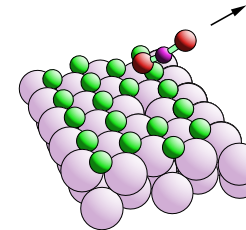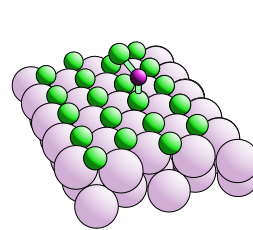
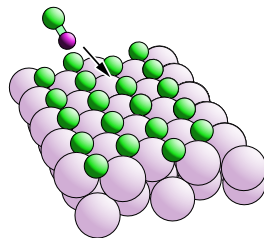# Coadsorption:barriers to adsorption
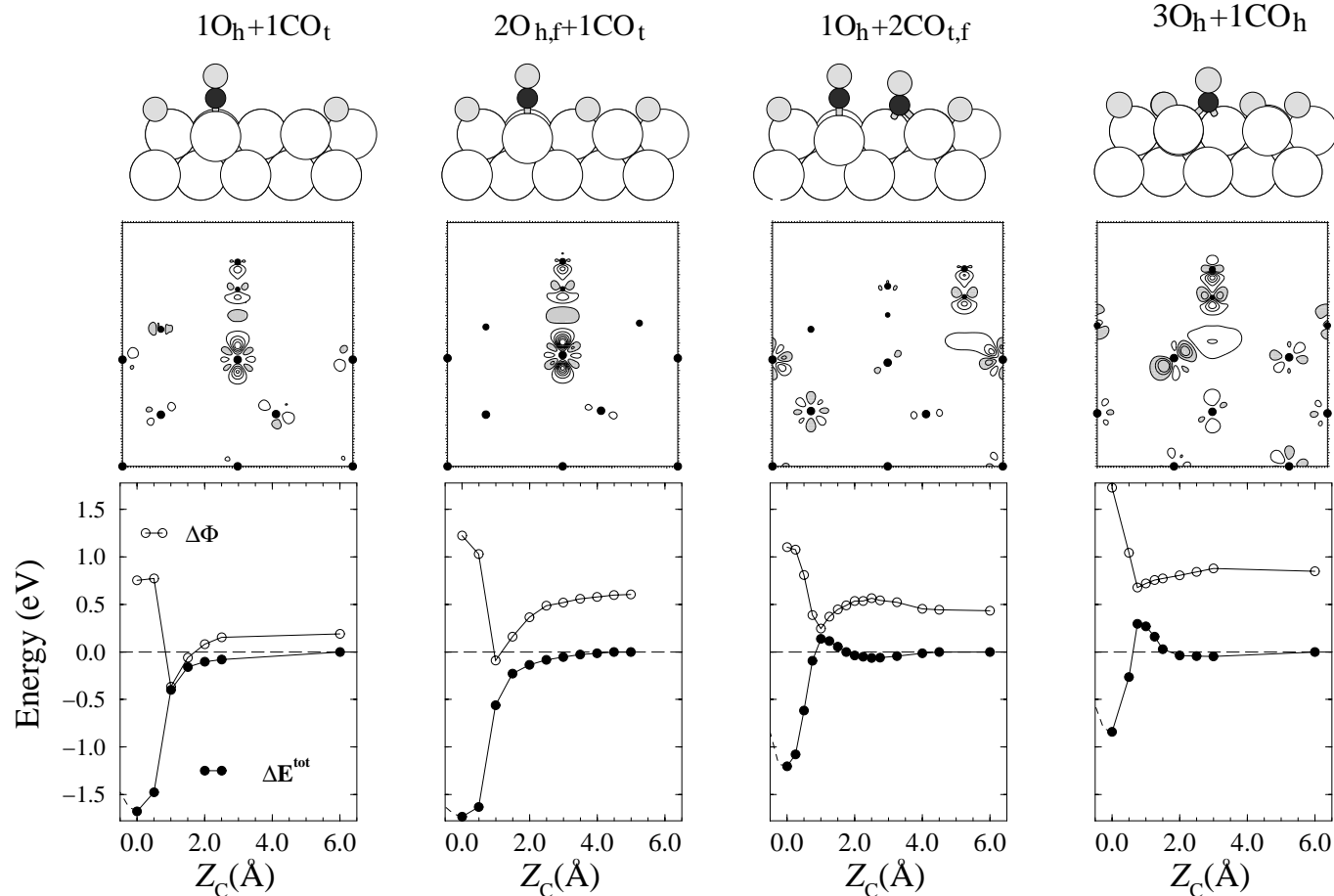
Pre-adsorbed O atoms can induce activation barriers to adsorption of CO (in the hcp site) well above the surface
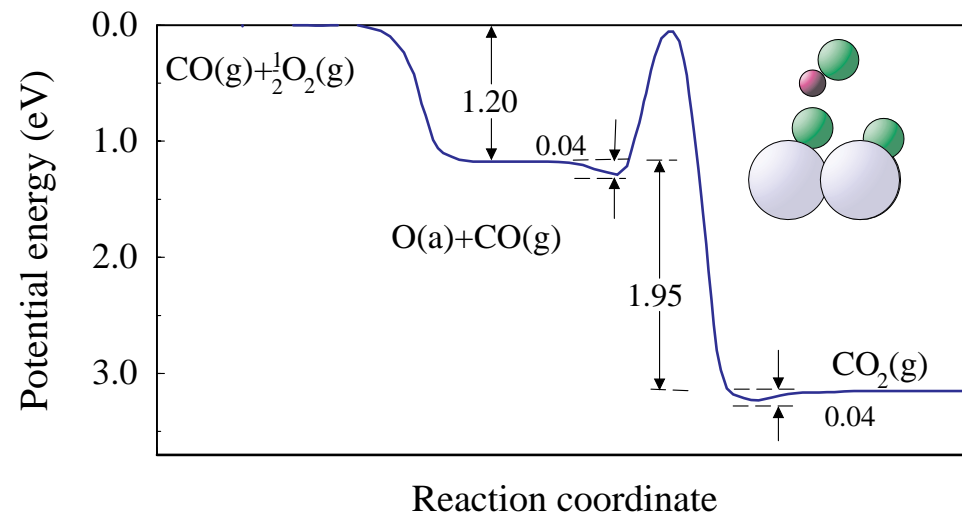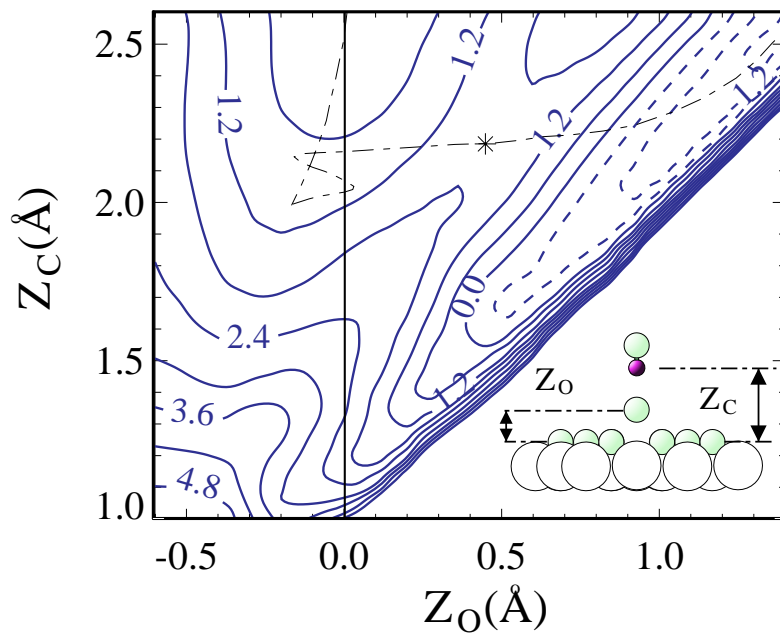
(Stampfl and Scheffler, to be published)

Surface chemical reactions:
CO oxidation - Eley-Rideal mechanism

CO incident from gas phase

CO_2 leaves surface with large energy gain

(Stampfl and Scheffler, PRL, 1997; Surf. Sci. (1999))

CO oxidation -
Langmuir-Hinshelwood mechanism

CO and O
both adsorb
on the surface
prior to reaction

Potential energy (eV) vs Reaction coordinate:

$CO(g) + \frac{1}{2}O_2(g)$

1.64

0.30

$O(a) + CO(g)$

0.85

$O(a) + CO(a)$

$CO_2(g)$

0.66

Reaction coordinate

(Stampfl and Scheffler, PRL, 1997; Surf. Sci. (1999))
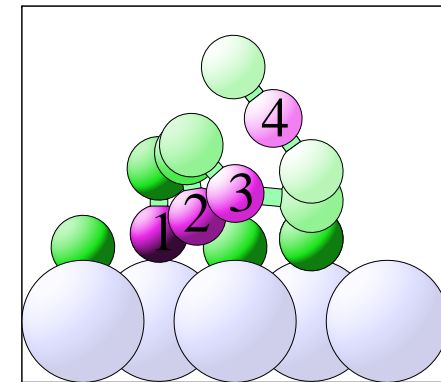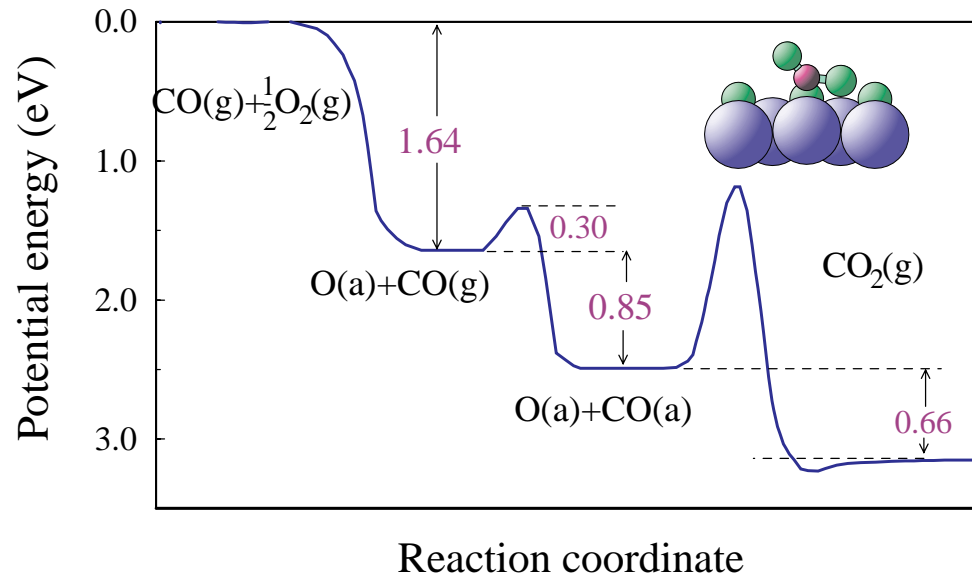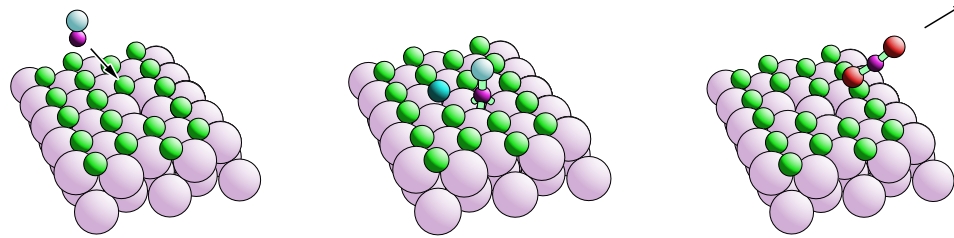
Atomic geometry
along minimum
energy pathway

Total electron density along reaction pathway for CO oxidation
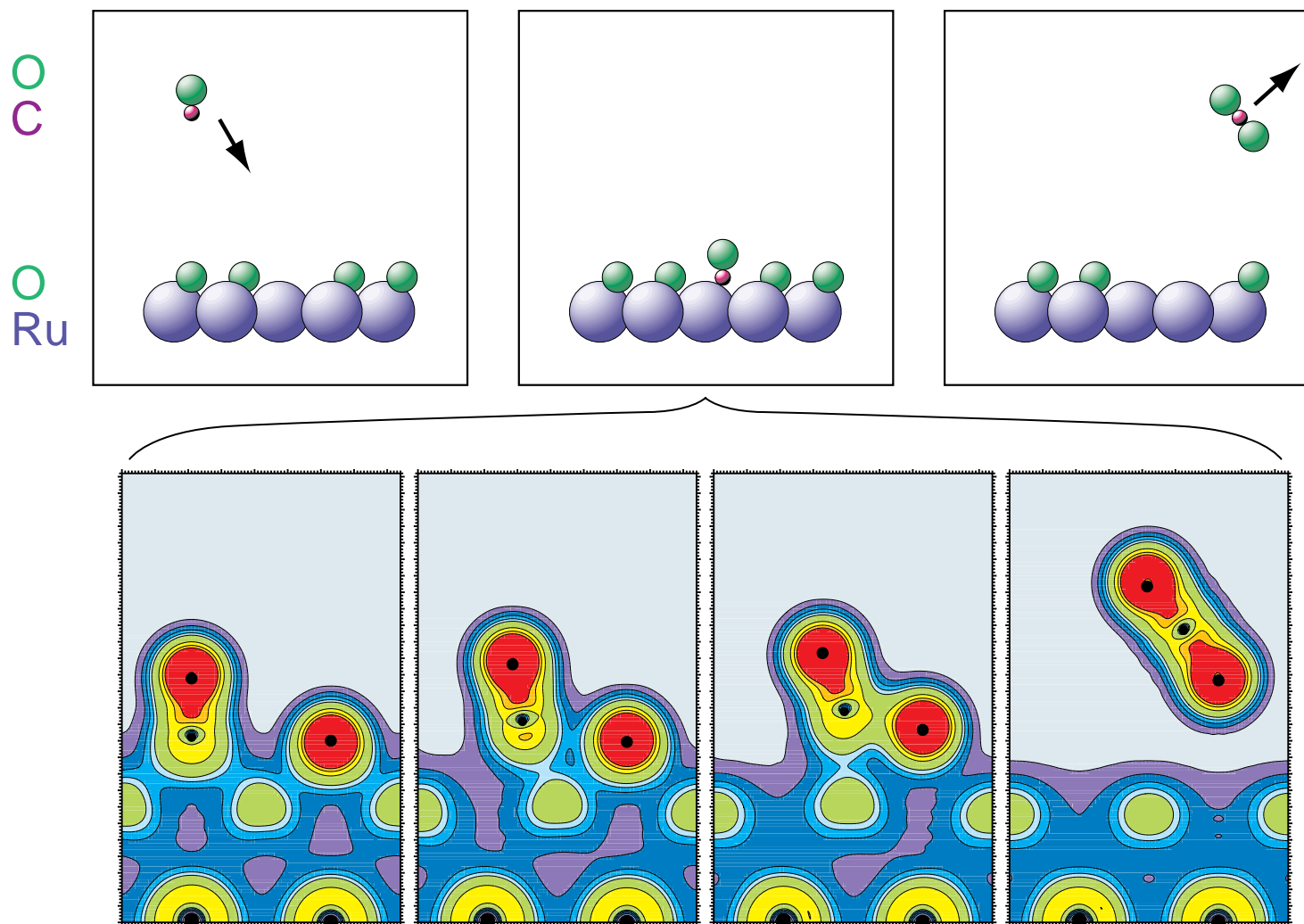
O
C

O
Ru

(From Scheffler and Stampfl In: Handbook of Surface Science, Vol. 2: Electronic Structure, 2000)

Difference electron density along reaction pathway
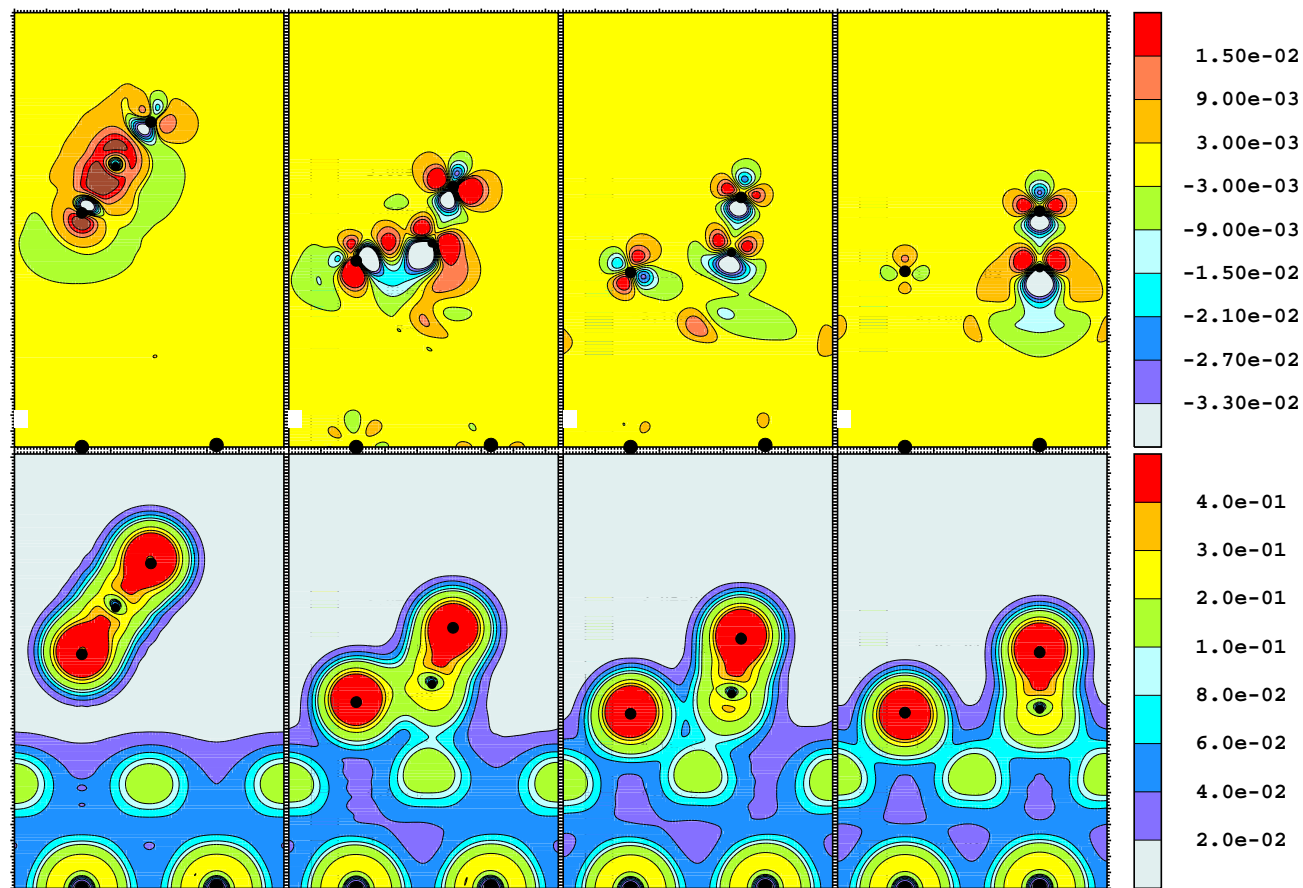
(Stampfl and Scheffler, Surf. Sci. (1999))

Activation energy barriers: Trends CO oxidation

Energy barrier increases from Pt to Rh to Ru

Correlates with total chemisorption energy of O and CO

Significant contribution to barrier due to weakening of O-metal bond
But also weakening of CO-metal bond important
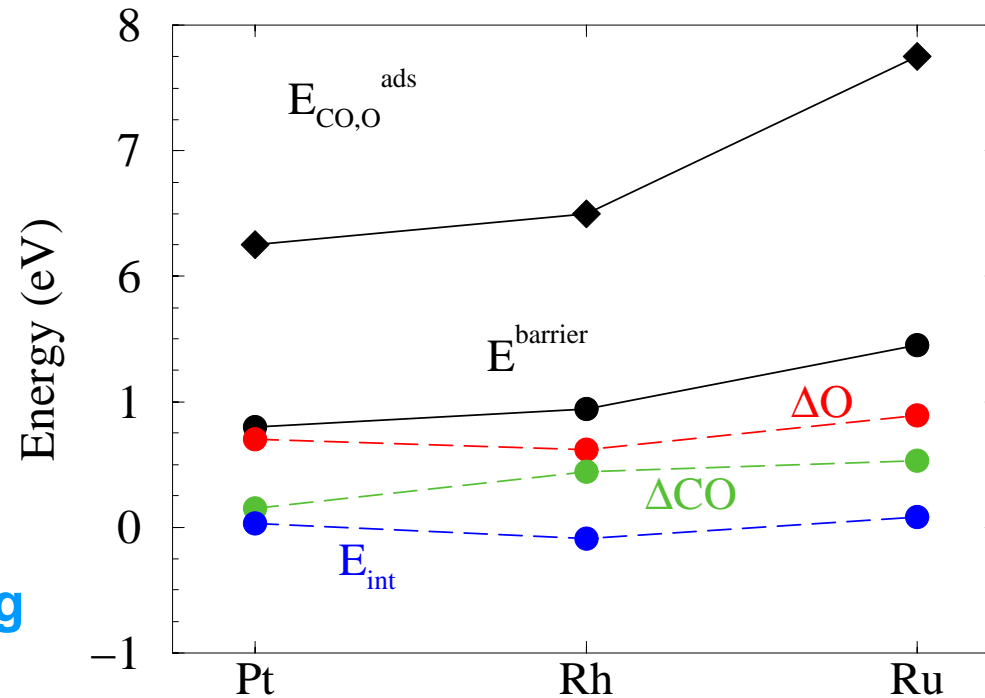
(Z.-P. Liu and P. Hu, J. Chem Phys. 2001)

Processes relevant to heterogeneous catalysis

- Adsorption (often dissociatively) on a solid surface from the gas phase.
- Diffusion on the surface, diffusion of adsorbates into the subsurface region and/or substrate atoms through a surface oxide layer.
- Interactions between adparticles and chemical reaction.
- Desorption of reaction products
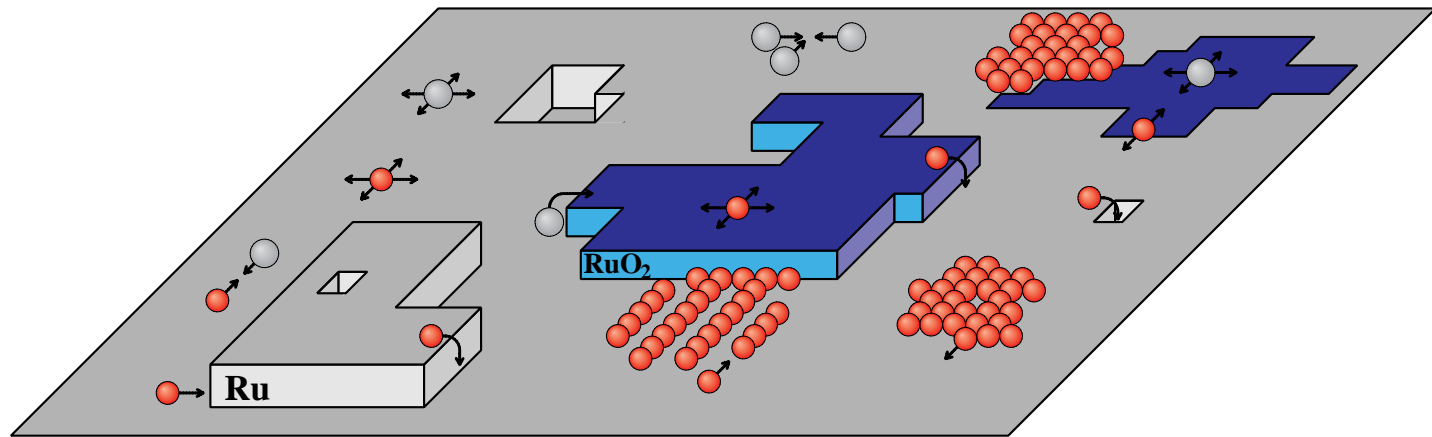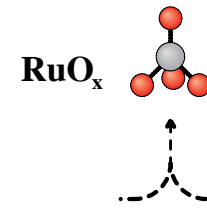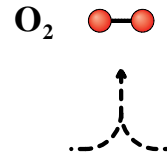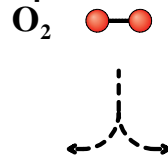
(C. Stampfl, M.V. Ganduglia-Pirovano, K. Reuter, and M. Scheffler, Surf. Sci. 500 (2001), in press.)

cf. K. Reuter

Combined ab initio and statistical mechanical approach

Processes at surfaces, and surfaces themselves, can be very different under standard UHV conditions compared to under more ``realistic conditions''  $\longrightarrow$  ``Pressure-gap''

Increasingly the importance and role of the atmospheric environment, *i.e.* species and gas pressure, as well as the temperature, in trying to understand various processes (e.g catalytic reactions), are being appreciated

For *detailed understanding* of the complex behavior of atoms and molecules at surfaces, require knowledge of both microscopic and macroscopic processes

$\longrightarrow$ predictive theoretical description that can link these different scales, and take temperature and pressure into account

Combining
Microscopic + Macroscopic Theories

Electronic Structure
DFT
Potential Energy Surface

Stable and metastable structures

Realistic description
Kinetics and
Thermodynamics

Interaction parameters
Vibrational frequencies

Partition function
Rate equations

Lattice-gas Hamiltonian

Lattice gas Hamiltonian

$$H = E_s \Sigma_i n_i + 1/2(V_{1n} \Sigma_{i,a} n_i n_{i+a} + V_{2n} \Sigma_{i,b} n_i n_{i+b}$$

$$+ V_{3n} \Sigma_{i,c} n_i n_{i+c} + V_{trio} \Sigma_{i,a,a'} n_i n_{i+a} n_{i+a'} + \ldots)$$

$\Theta=0.11: V_0$ $\Theta=0.22: V_{1n}$ $\Theta=0.25: V_{3n}$ $\Theta=0.33: V_{2n}$ $\Theta=0.5: V_{lt}$ $\Theta=0.66$

$(3 \times 3)\text{-O}$ $(3 \times 3)\text{-2O}$ $(2 \times 2)\text{-O}$ $(\sqrt{3} \times \sqrt{3})R30°$ $(2 \times 1)\text{-O}$ $(\sqrt{3} \times \sqrt{3})R30°$

$\Theta=0.75: V_{lt,tt}$ $\Theta=1.0$ $\Theta=0.22: V_{3n}^{h-f}$ $\Theta=0.5: V_{2n}^{h-f}$ $\Theta=1.25: V_{1n}^{h-f}$

$(2 \times 2)\text{-3O}$ $(1 \times 1)\text{-O}$ $(3 \times 3)\text{-2O}$ $(2 \times 2)\text{-2O}$ $(2 \times 2)\text{-5O}$
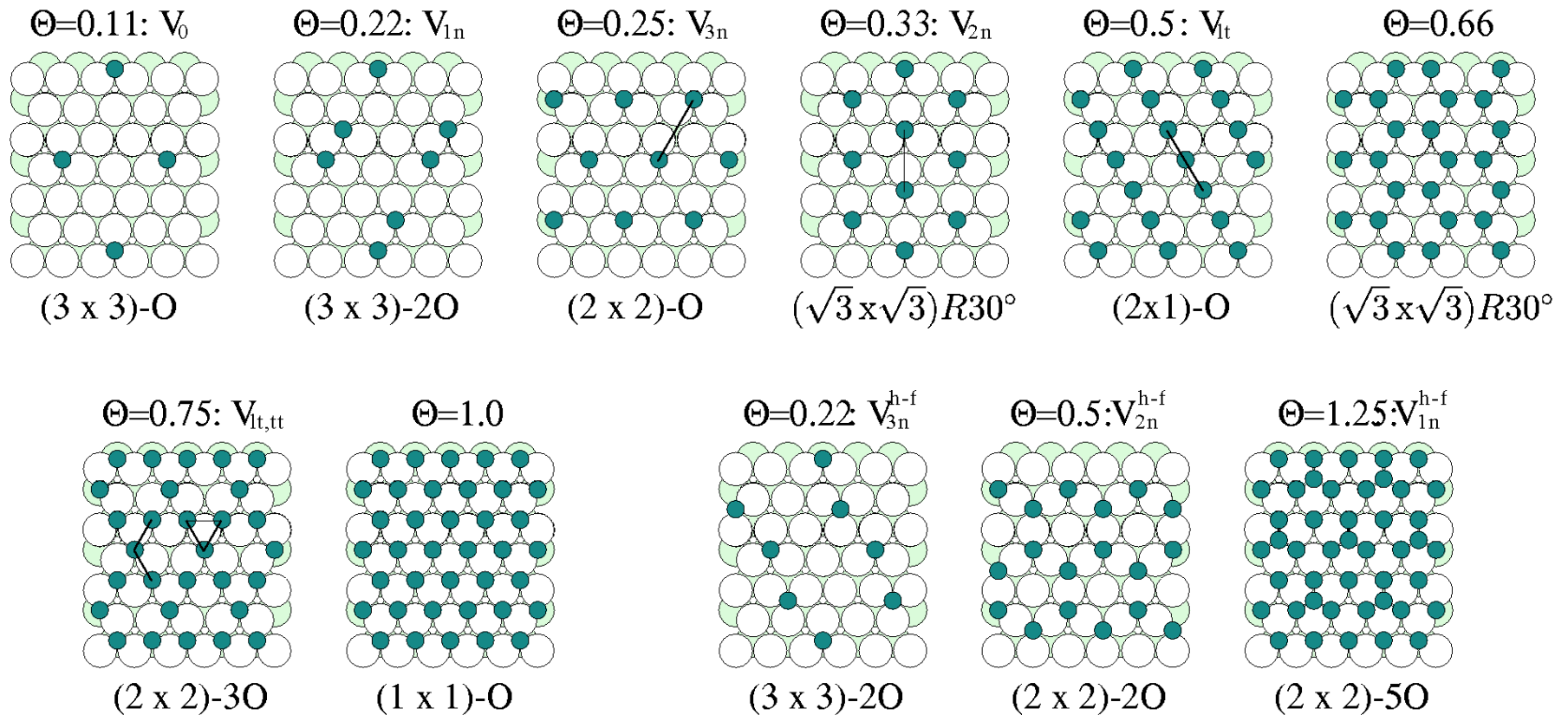
Pair and trio inter-atomic interactions
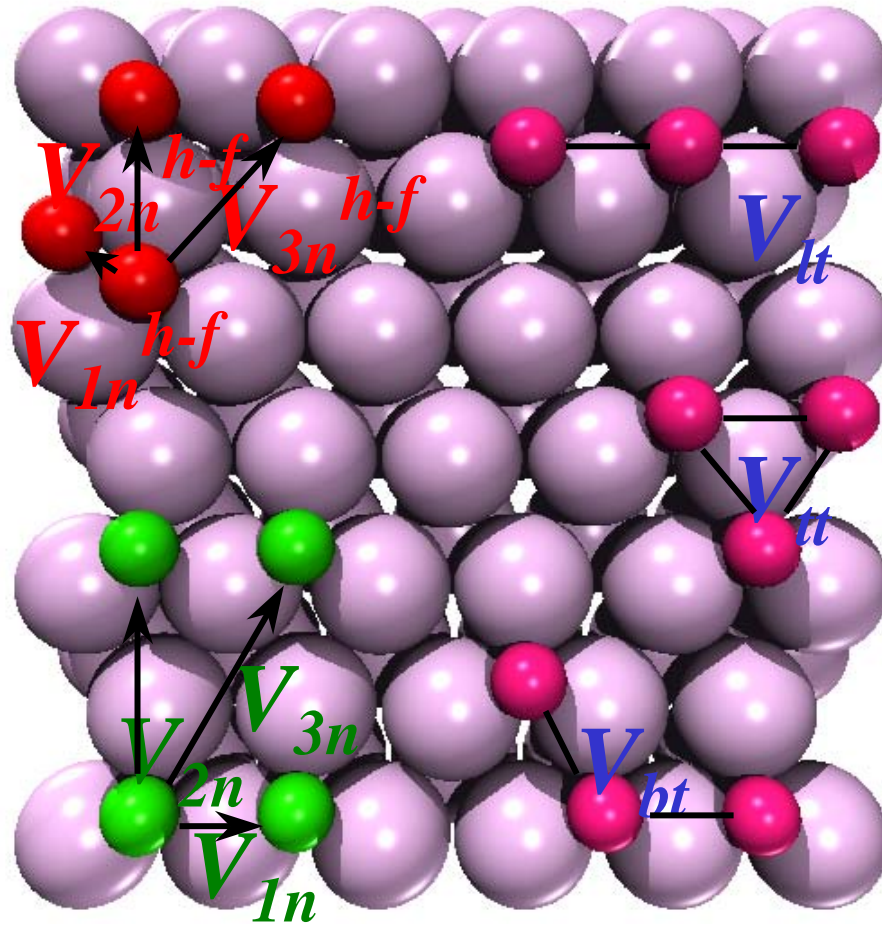
Schematic illustration of the types of two- and three-body interactions included in the lattice-gas Hamiltonian

Namely, first, second, and third two-body interactions for adsorbates in fcc and hcp site, as well as in combined fcc-hcp sites; three types of three-body (or trio) interactions
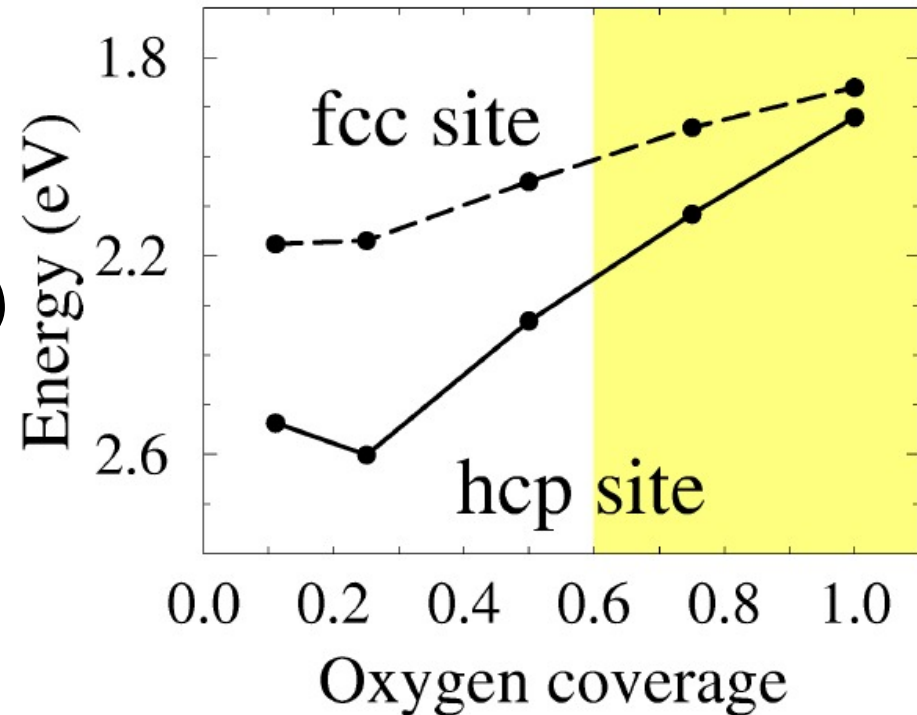
Adsorption energies of O on Ru(0001)

Kinetically hindered region

Stampfl et al.
PRL 77(1996) PRB 53 (1996)

Site	$E^{\theta=2/9}$	$E^{\theta=1/2}$	$E^{\theta=5/4}$
hcp-fcc	2.294	2.209	1.492

Site	$E^{\theta=1/9}$	$E^{\theta=2/9}$	$E^{\theta=1/4}$	$E^{\theta=1/3}$	$E^{\theta=1/2}$	$E^{\theta=2/3}$	$E^{\theta=3/4}$	$E^{\theta=1}$
hcp	2.503	2.417	2.577	2.370	2.307	2.150	2.091	1.895
fcc	2.152	2.107	2.145	2.105	2.025	2.015	1.942	1.865

Extracting Interaction Parameters

$$E^{\theta=2/9}=V_0+1/2(V_{1n}+V_{3n})$$
$$E^{\theta=1/4}=V_0+3V_{3n}$$
$$E^{\theta=1/3}=V_0+3V_{2n}$$
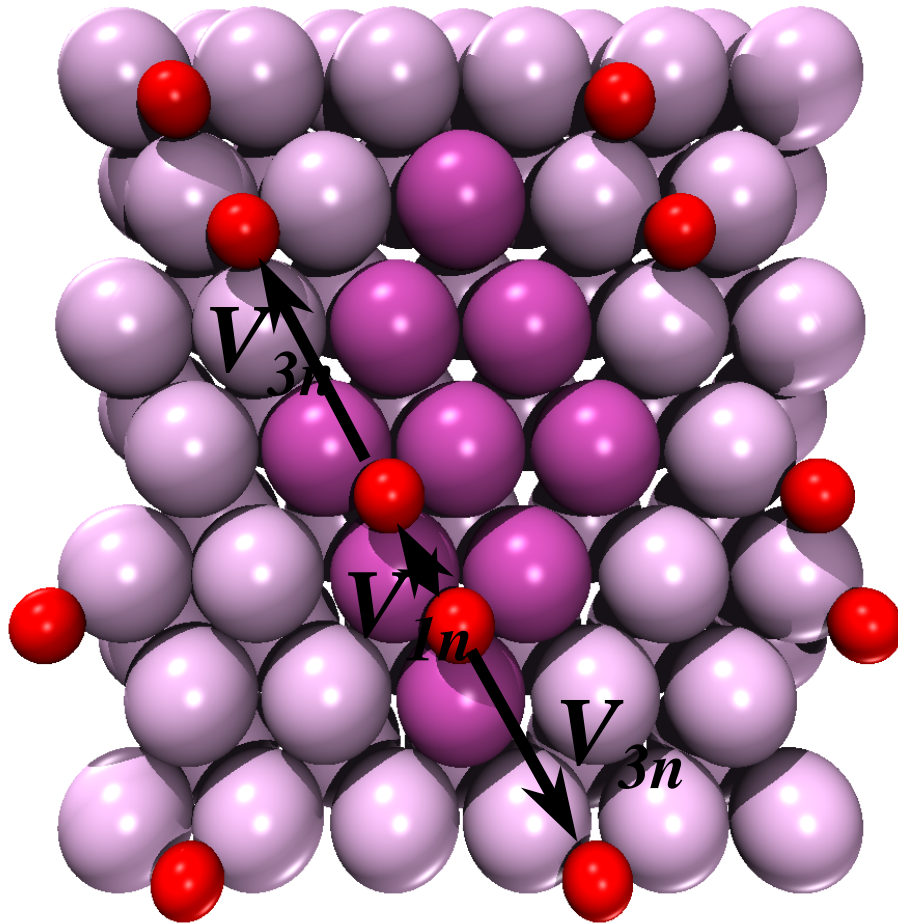$$E^{\theta=1/2}=V_0+V_{1n}+V_{2n}+3V_{3n}+V_{lt}$$
$$E^{\theta=2/3}=V_0+3/2V_{1n}+3V_{2n}+3/2V_{3n}+3V_{bt}$$
$$E^{\theta=3/4}=V_0+2V_{1n}+2V_{2n}+3V_{3n}+2V_{lt}+2V_{bt}+2/3V_{tt}$$
$$E^{\theta=1.0}=V_0+3(V_{1n}+V_{2n}+V_{3n})+3V_{lt}+6V_{bt}+2V_{tt}$$

Site	V_{1n}	V_{2n}	V_{3n}	V_{lt}	V_{bt}	V_{tt}
hcp	0.265	0.044	-0.025	-0.039	-0.046	0.058
fcc	0.158	0.016	0.002	-0.052	-0.044	0.076
hcp-fcc	0.586	0.101	0.033			

Extracting the interaction energies

Example:
Obtaining an expression involving the first and third two-body interactions at coverage 2/9.
The adsorption energy is written as:

$$E^{\theta=2/9}=V_0+1/2(V_{1n}+V_{3n})$$

There is one first neighbor interaction in the 3x3 unit cell, V_{1n}, and due to images in neighboring cells, there are interactions at third neighbor distances, V_{3n}

Rate equations: adsorption, desorption

$$d\theta/dt = R_{ad} - R_{des} \quad \textit{Kinetic equation}$$

Atomic adsorbate in contact with a gas of homonuclear molecules

Rate of adsorption:

$$R_{ad} = 2S_{dis}(\theta,T)P_m a\lambda_m/h$$

Rate of desorption:

$$R_{des} = 2S_{dis}(\theta,T)a\,k_B T Z_{vr}q_3^2/(h\lambda_m^2 q_3^2(1-q)^2)$$
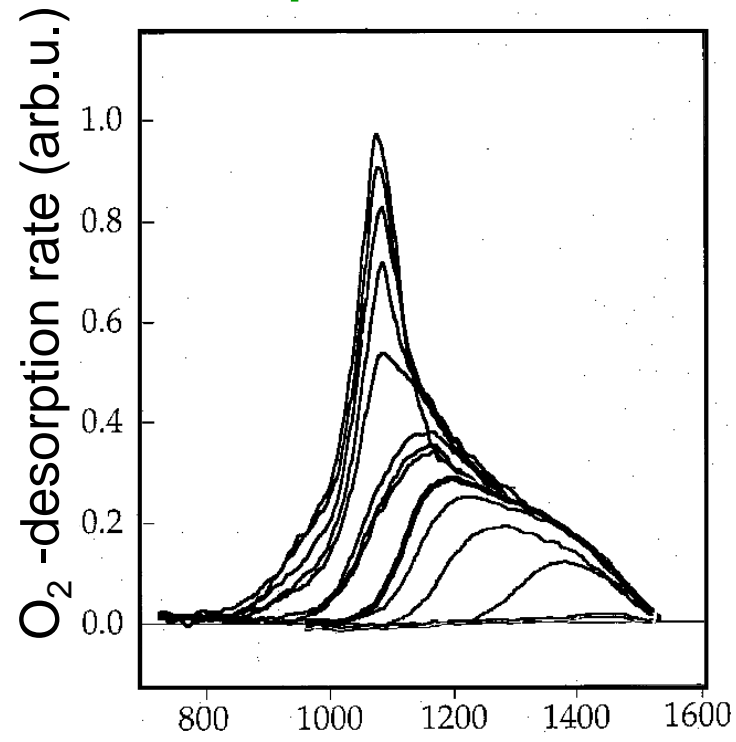$$*exp\{-(2V_0 - D_e^{(g)})/k_B T\}*exp\{2\mu^{(lat)}/k_B T\}$$

P_m is the molecular pressure, a area of unit cell, $\lambda_m = h/(2\pi m k_B T)^{1/2}$ the thermal wavelength of molecule, S_{dis} is the dissociative sticking coefficient, Z_{vr} partition function: vibrations and rotations of molecule, $D_e^{(g)}$ dissociation energy and $\mu^{(lat)}$ chemical potential

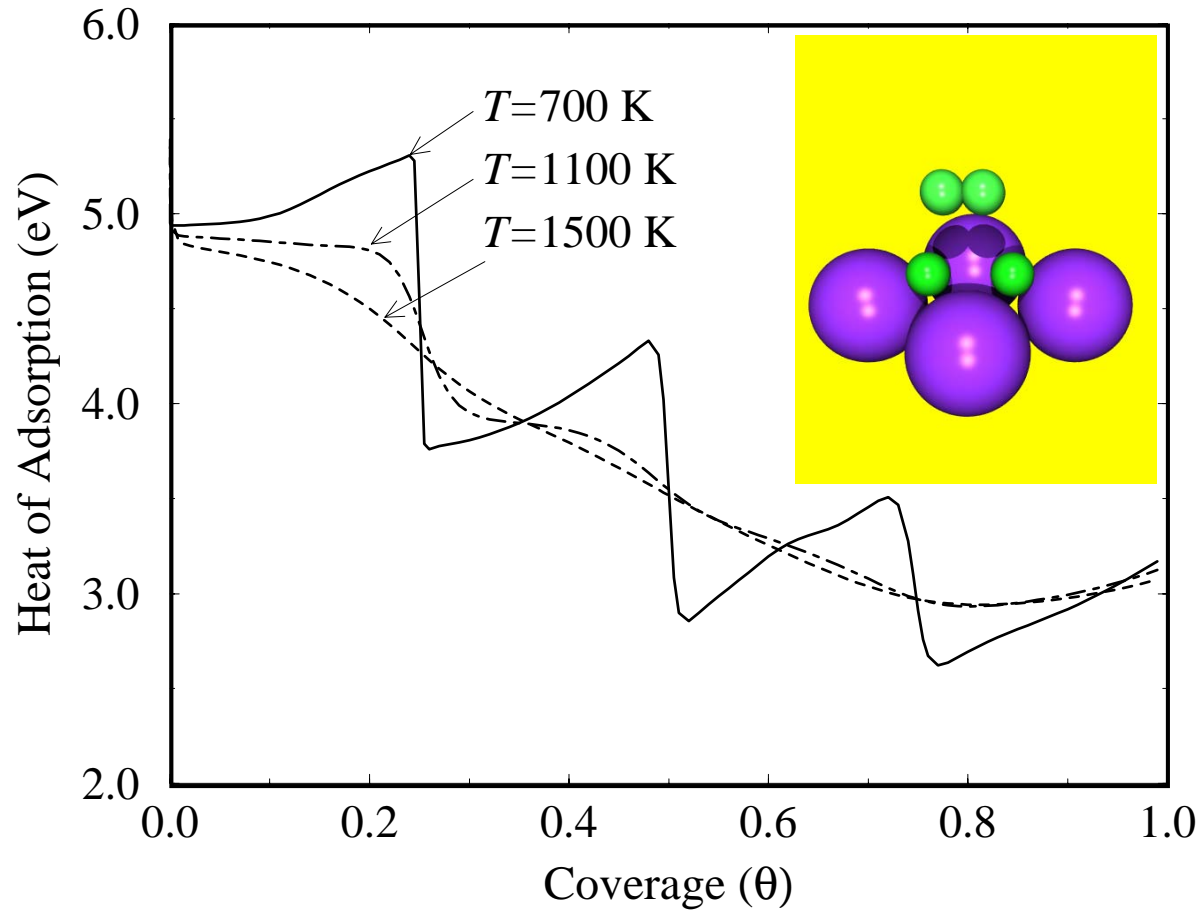# Temperature Programmed Desorption Spectra: O/Ru(0001)

Theory
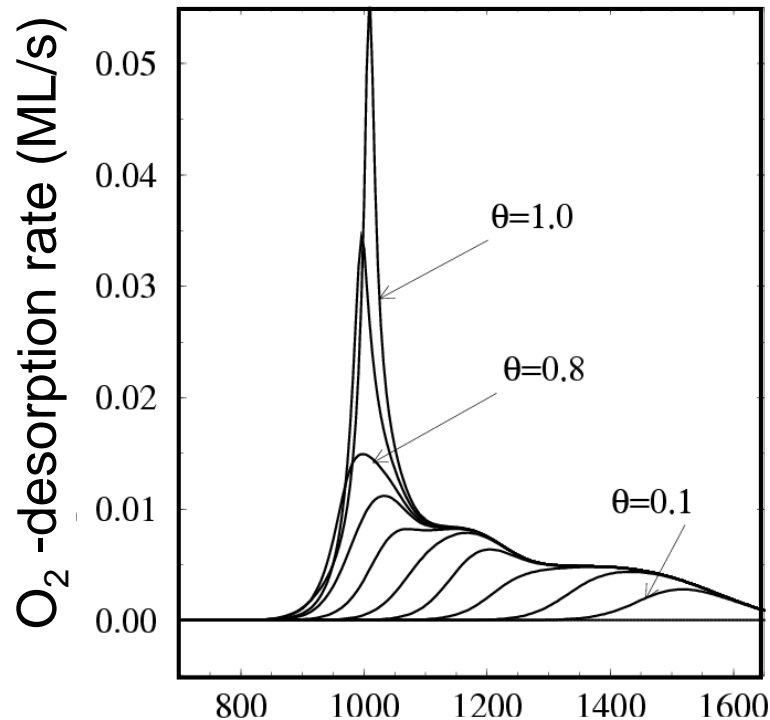
Experiment

Heating rate: 6 K/s

*Stampfl et al., PRL **83** (1999)*

Heat of Adsorption

$$E_{ad}=2E_{O\text{-metal}}+E_{O2\text{-gas}}$$

Peaks at low T predict stability of ordered structures at Θ=0.25,0.5,0.75,1.0 (2x2)-O, (2x1)-O, (2x2)-3O,(1x1)-O

Effect of T greater for higher O coverages with weaker adsorption energy

Y-axis: Heat of Adsorption (eV)

X-axis: Coverage (θ)

T=700 K
T=1100 K
T=1500 K

Summary

Hybrid approach, combining density-functional theory calculations with phenomenological methods, where various thermodynamic properties of adsorbates at surfaces were studied.

Describes evolution of surface structures as a function of temperature, pressure, and coverage. Can treat disordered and ordered, systems, as well as different species

Demonstrated through the example of oxygen at Ru(0001), reproducing experimental Temperature Programmed Desorption Spectra and heat of adsorption.

The methodology and concepts are general and can be applied to various problems