量子化学理论及其在催化反应中的应用

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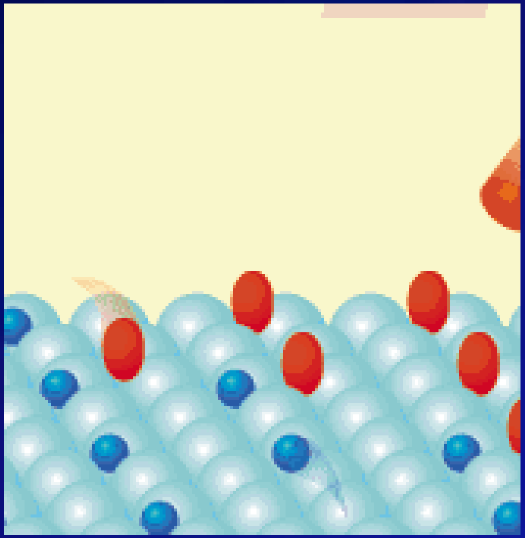
催化基础国家重点实验室

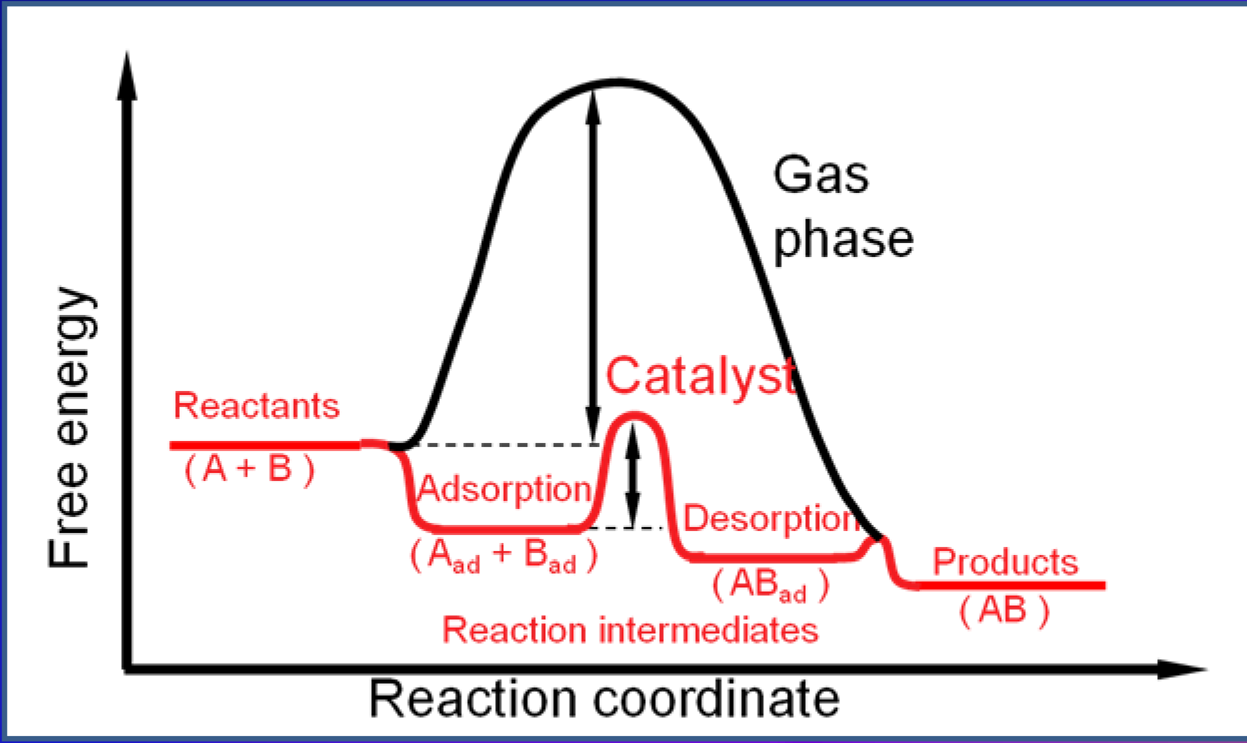
2007-7

Heterogeneous catalysis

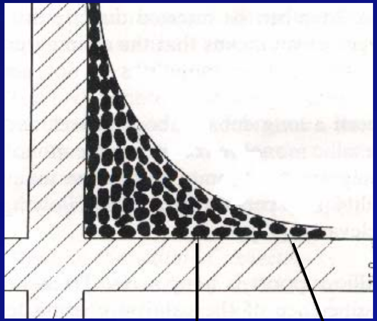


Worldwide turnover
~14 Trillion US$ (2000)

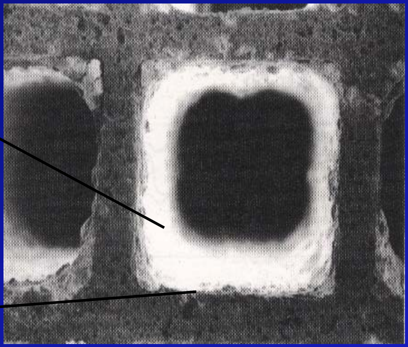
> 90% of all chemicals pass a catalyst
once during production



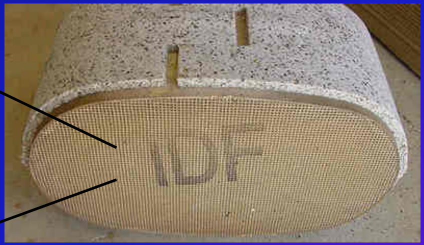
Catalysis: a playground on many levels



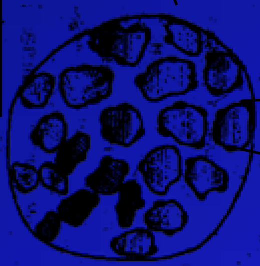
washcoat support



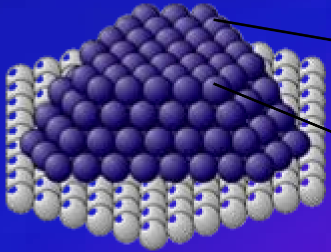
ceramic monolith cells
~500 μm



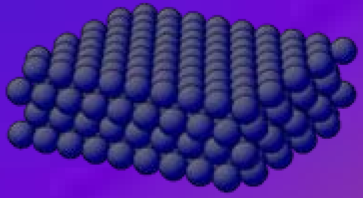
ceramic monolith



washcoat macropores
~1-10 μm

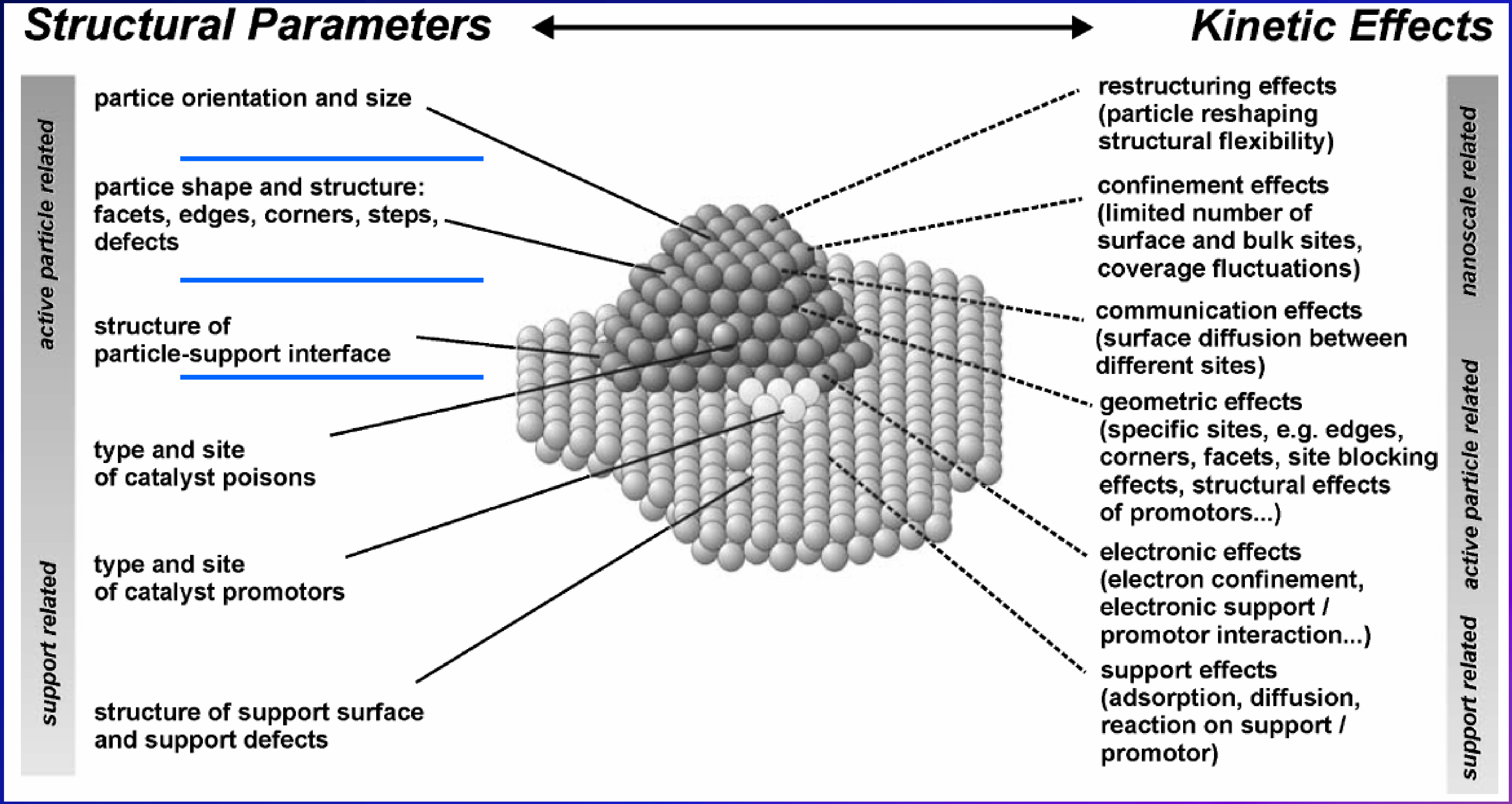


precious metal particles
~10-100 nm



single crystal surface

Supported Catalyst



Structural Parameters ⟷ **Kinetic Effects**

particle orientation and size

partice shape and structure: facets, edges, corners, steps, defects

structure of particle-support interface

type and site of catalyst poisons

type and site of catalyst promotors

structure of support surface and support defects

restructuring effects (particle reshaping structural flexibility)

confinement effects (limited number of surface and bulk sites, coverage fluctuations)

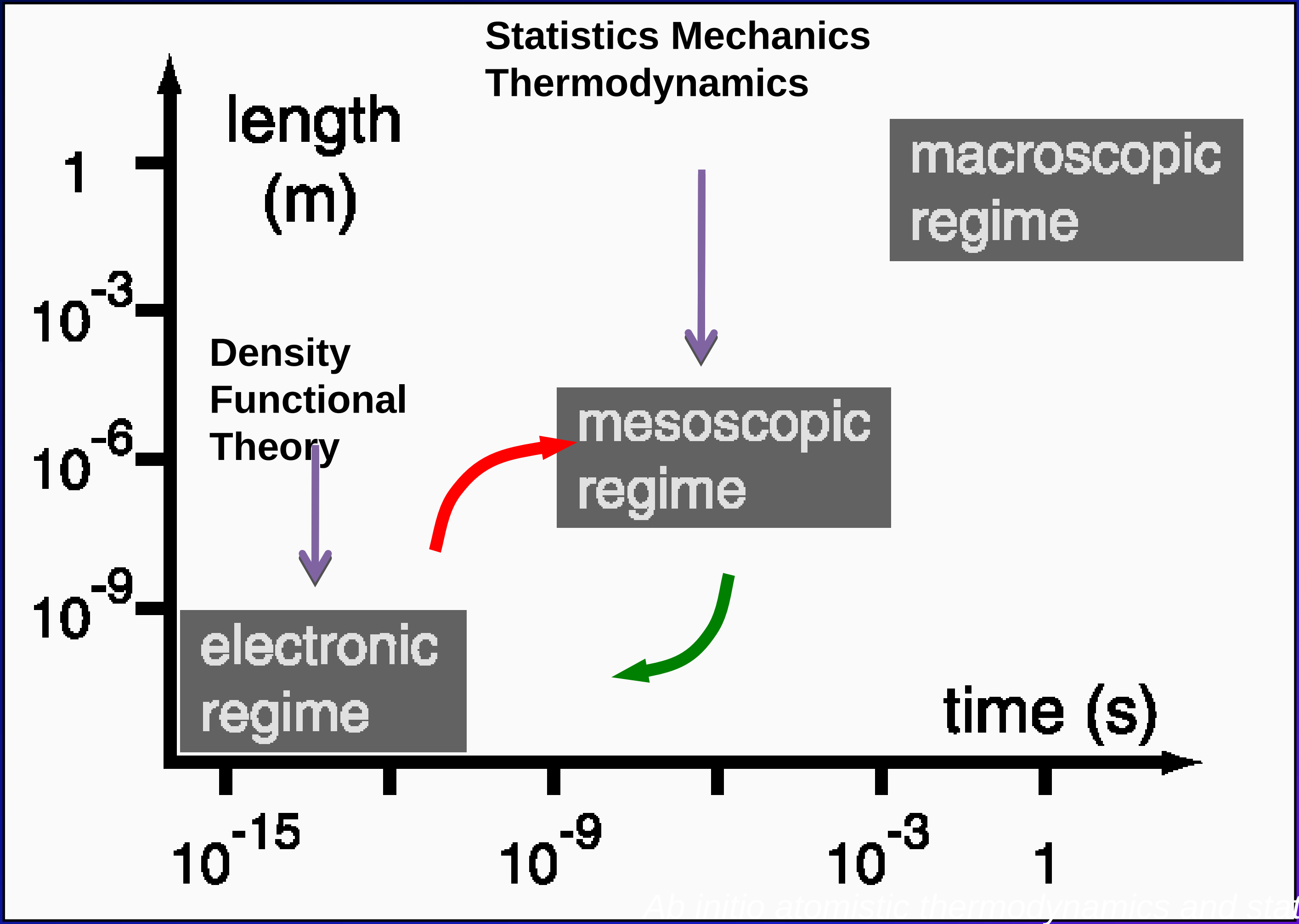
communication effects (surface diffusion between different sites)

geometric effects (specific sites, e.g. edges, corners, facets, site blocking effects, structural effects of promotors...)

electronic effects (electron confinement, electronic support / promotor interaction...)

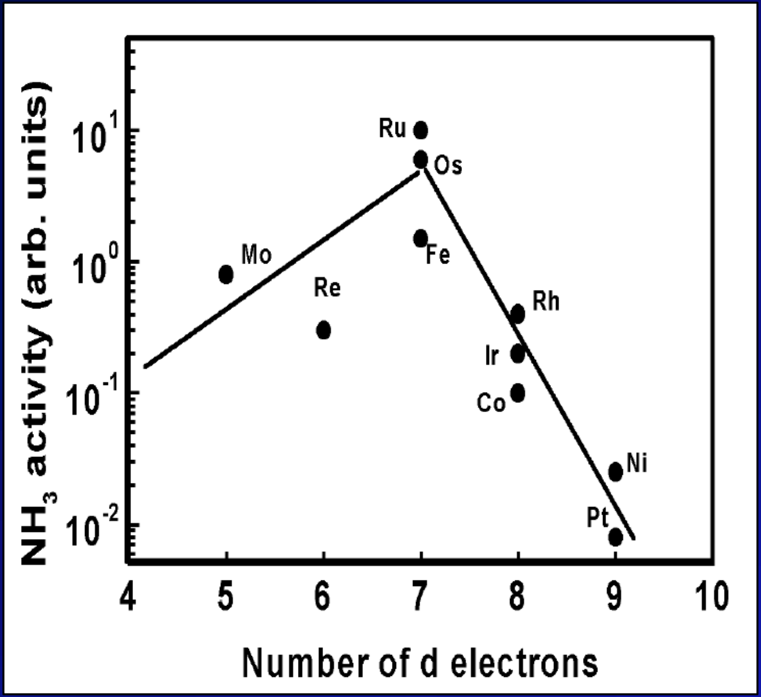
support effects (adsorption, diffusion, reaction on support / promotor)

Multiscale Process

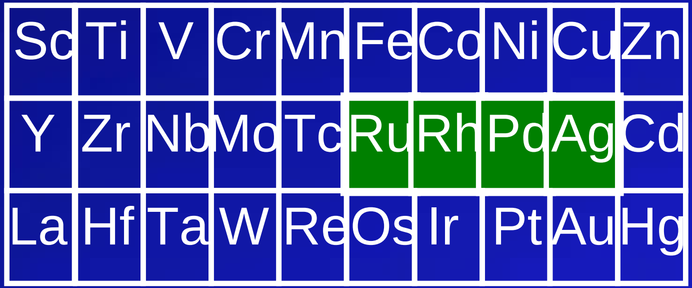


Ab initio atomistic thermodynamics and statistical mechanics of surface properties and functions
K. Reuter, C. Stampfl and M. Scheffler,
in: Handbook of Materials Modeling, Part A. Methods,
(Ed.) Sidney Yip, Springer (Berlin, 2005).
http://www.fhi-berlin.mpg.de/th/paper.html

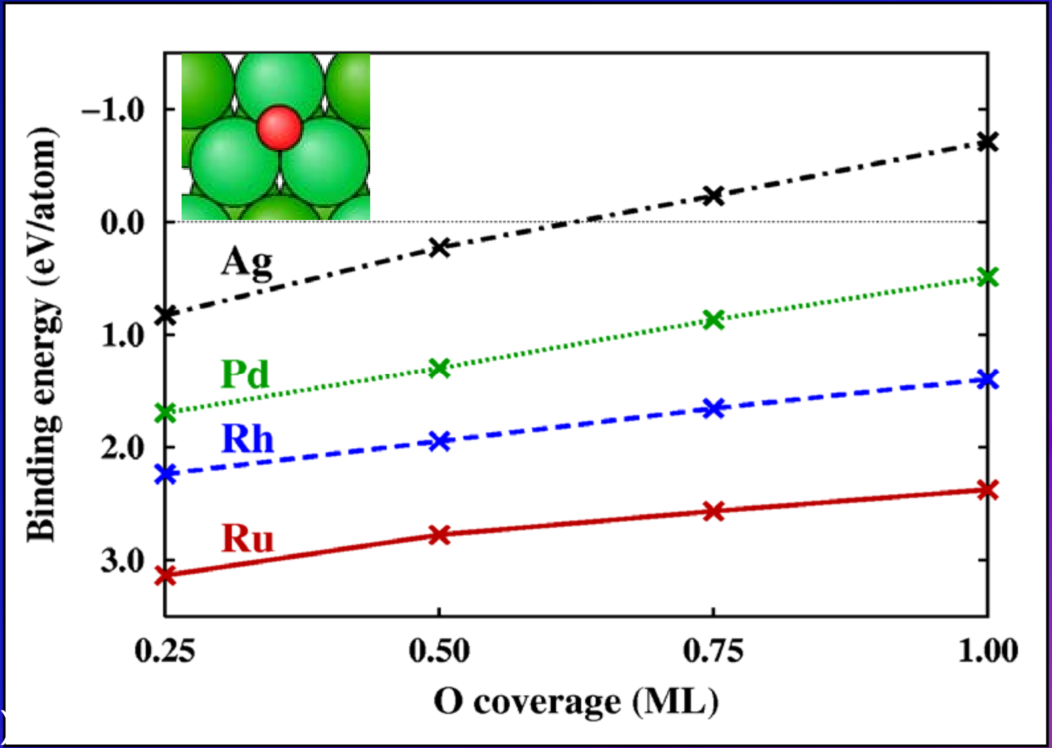
Sabatier principle



J.R. Jennings,
Ammonia Synthesis,
Plenum (1991)



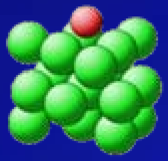
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg



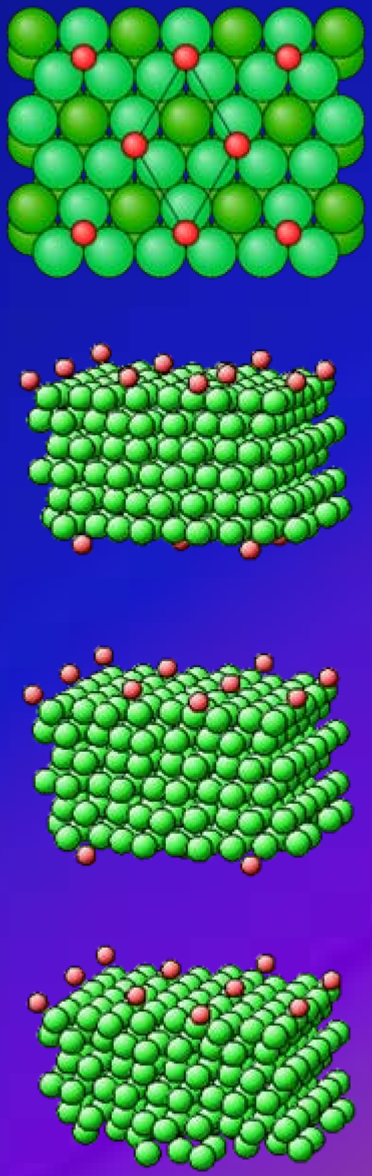
M. Todorova *et al.*,
Phys. Rev. Lett. 89, 096103 (2002)

Electronic structure theory calculations of surfaces

Tight-binding
Density-functional theory
Quantum chemical methods (> HF)
(Quantum Monte Carlo)



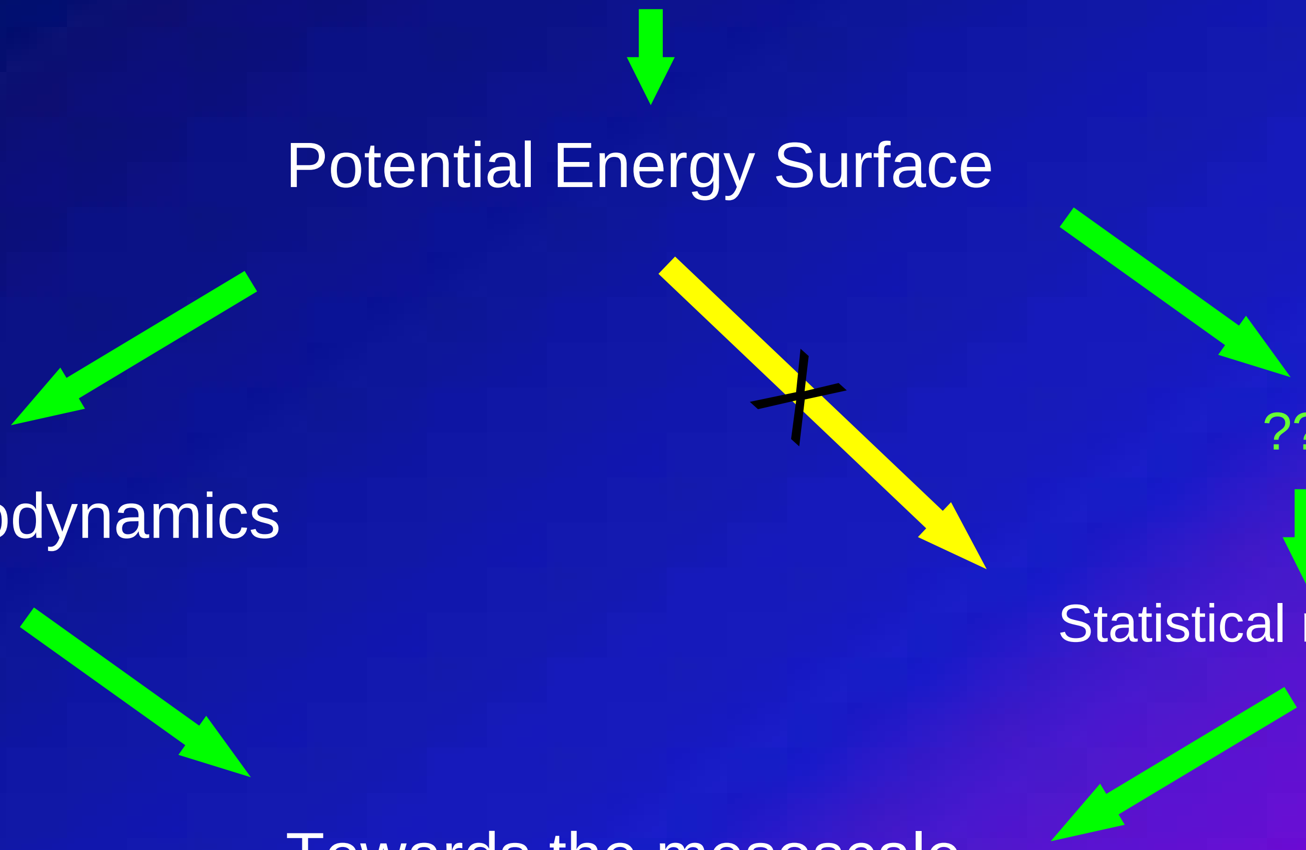
vs.



- Total energy
- Forces (relaxation, vibrations, MD…)
- Electronic structure (…)

But: manageable system sizes ~ 1000 electrons (DFT)

From micro to meso



Electronic Structure Theory
(DFT…)

Potential Energy Surface

Thermodynamics

???

Statistical mechanics

Towards the mesoscale
(real world…?)

Outline

I. Introduction

① Density functional theory
② Ab initio atomistic thermodynamics
③ Transition state theory

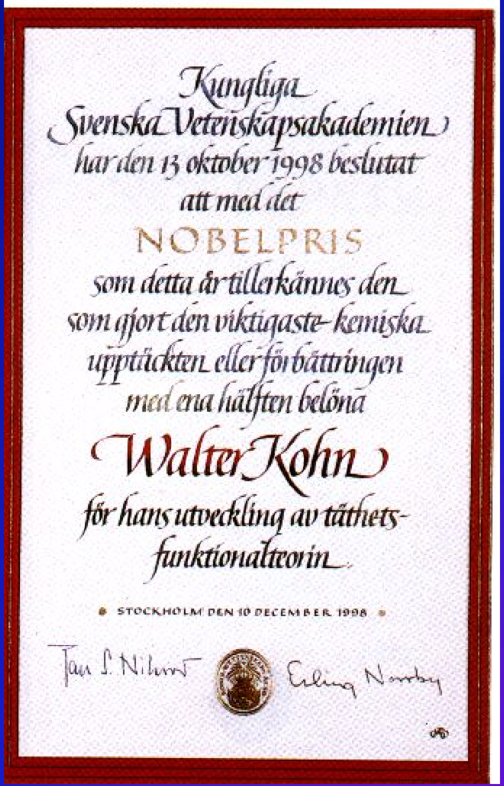
II. Examples

A. Interaction between molecules and metal surface
B. Manipulation of electron and reactivity: QSE
C. Oxidation of Pt(332) (DFT + XPS)
D. Reduction of nano-structural surface (DFT+STM)
E. Bridging pressures and materials gap
F. Ammonia Synthesis
G. Selectivity
H. Screening and rational catalysis design

Fast Guide to Density Functional Theory

Walter Kohn, Nobel Prize 1998

Walter Kohn



Kungliga
Svenska Vetenskapsakademien
har den 13 oktober 1998 beslutat
att med det
NOBELPRIS
som detta år tillerkännes den
som gjort den viktigaste kemiska
upptäckten eller förbättringen
med ena hälften belöna
Walter Kohn
för hans utveckling av täthets-
funktionalteorin.

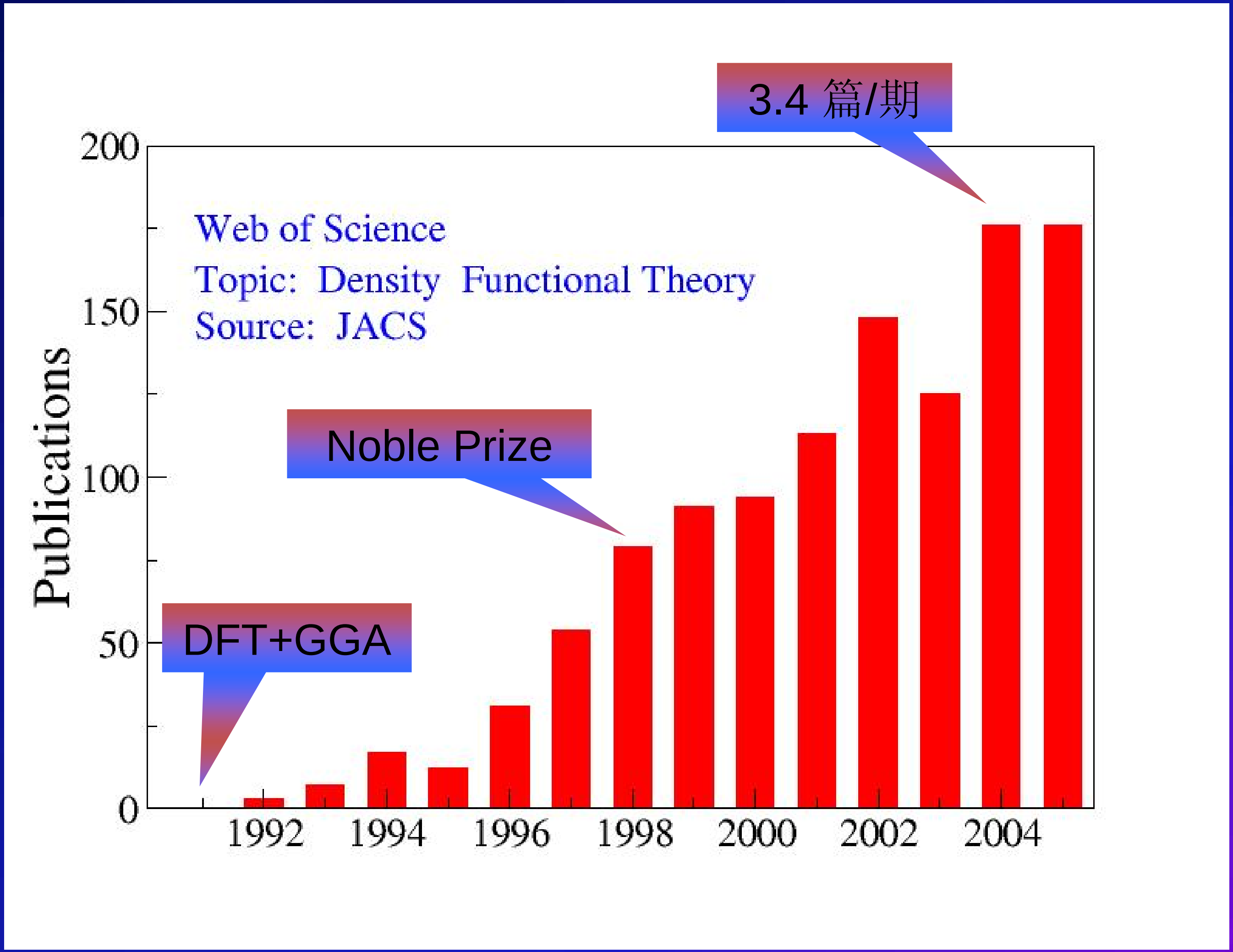
STOCKHOLM DEN 10 DECEMBER 1998

Jan S. Nilsson Erling Norrby

"Self-consistent Equations including Exchange and Correlation Effects"
W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965)

Literal quote from Kohn and Sham's paper:"… We do not expect an accurate description of chemical binding."

研究方法：密度泛函理论(DFT)



General 'condensed-matter' Hamiltonian

$$(\hat{T}^{e} + \hat{T}^{ion} + \hat{V}^{e-e} + \hat{V}^{e-ion} + \hat{V}^{ion-ion})\Psi = E\Psi$$

wavefunction $\Psi(\mathbf{r_1}, \cdots \mathbf{r_N}; \mathbf{R_I}, \cdots \mathbf{R_M})$

electronic coordinates $\mathbf{r_k}$, $k = 1, \cdots N$

ionic coordinates $\mathbf{R_I}$, $I = 1, \cdots M$

$$\hat{T}^{e} = \sum_{k=1}^{N} \frac{\mathbf{p}_k^2}{2m} \qquad \hat{T}^{ion} = \sum_{I=1}^{M} \frac{\mathbf{P}_I^2}{2M_I}$$

$$\hat{V}^{e-e} = \frac{1}{2}\frac{1}{4\pi\epsilon_0}\sum_{k\neq k'}^{N,N} \frac{e^2}{|\mathbf{r_k} - \mathbf{r_{k'}}|}$$

$$\hat{V}^{ion-ion} = \frac{1}{2}\frac{1}{4\pi\epsilon_0}\sum_{I\neq I'}^{M,M} \frac{Z_I Z_{I'}}{|\mathbf{R_I} - \mathbf{R_{I'}}|}$$

$$\hat{V}^{e-ion}(\mathbf{r_k}, \mathbf{R_I}) = \sum_{\mathbf{k=1}}^{\mathbf{N}} \sum_{\mathbf{I=1}}^{\mathbf{M}} \mathbf{v_I^{ion}}(|\mathbf{R_I} - \mathbf{r_k}|)$$

Born-Oppenheimer approximation

convenient, frequently made approximation (but not compulsary)

separation of variables → parametric dependence on set of coord. $\{\mathbf{R_I}\}$

$$\Psi(\mathbf{r_1}, \cdots \mathbf{r_N}; \mathbf{R_1}, \cdots \mathbf{R_M}) = \sum_{\nu} \Lambda_{\nu}(\{\mathbf{R_I}\})\Phi_{\nu,\{\mathbf{R_I}\}}(\mathbf{r_k})$$

electronic Schrödinger equation

$$H^e_{\{\mathbf{R_I}\}}\Phi_{\nu,\{\mathbf{R_I}\}}(\mathbf{r_k}) = E^e_{\nu,\{\mathbf{R_I}\}}\Phi_{\nu,\{\mathbf{R_I}\}}(\mathbf{r_k})$$

$$H^e = T^e + V^{e-e} + V^{e-ion}$$

frequently made approximations:

- neglect of non-adiabatic couplings (terms of order m/M_I)
- only one $\Lambda_\nu \neq 0$ (in a solid, this means neglect of electron-phonon couplings)

→ electronic and nuclear degrees of freedom decouple !

Limitations of Born-Oppenheimer

- doesn’t account for correlated dynamics of ionic and electronic coordinates
  Example:
  suprafluid He3, polaron-induced superconductivity

- breakdown of the restriction to a single ground-state Born-Oppenheimer surface
  Example:
  chemoluminescence

- breakdown of the adiabatic approximation
  Example:
  excitation of surface plasmons during scattering of an ion from a metal surface → time-dependent density functional theory

electronic many-particle Hamiltonian

$$\left[\sum_{k=1}^{N} \frac{\nabla_k^2}{2m} + v^{(0)}(\mathbf{r_k}) + \sum_{k \neq k'}^{N,N} \frac{1}{2} W(\mathbf{r_k}, \mathbf{r'_k})\right] \Phi(\mathbf{r_1}, \cdots \mathbf{r_N}) = E\Phi(\mathbf{r_1}, \cdots \mathbf{r_N})$$

$$W(\mathbf{r}, \mathbf{r}') = \frac{e^2}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|}$$

$$v^{(0)}(\mathbf{r}) = \sum_{I=1}^{M} v_I^{ion}(|\mathbf{R_I} - \mathbf{r}|)$$

still many (for a typical solid: 10^{23}) degrees of freedom

The many-particle problem can be solved only for small systems (atoms, molecules and clusters).

→ wavefunction-based methods

- Configuration-interaction, Coupled Cluster method
- Quantum Monte Carlo method

Density Functional Theory

Hohenberg-Kohn theorem:

For any given external potential $v^{(0)}$, the wavefunctions can be considered as functionals in the space of ground state densities, n:

$$E_{v^{(0)}}[n] = \langle \Phi[n] | \hat{T}^e + \frac{1}{2}\hat{W} + \hat{v}^{(0)} | \Phi[n] \rangle$$

The energy functional is stationary at the ground state energy, and the true ground state density n_0 coincides with n at the stationary point. Therefore a universal functional $\mathcal{F}$ exists with the property

$$E_{v^{(0)}}[n] = \mathcal{F}[n] + \int d\mathbf{r}\; v^{(0)}(\mathbf{r}) n(\mathbf{r})$$

Proof:

'$\Phi[n] \mapsto n$': trivial

'$n \mapsto \Phi[n]$': Note that $v_{ext} \rightarrow n \overset{\text{Raleigh−Ritz}}{\longmapsto} \Phi[n]$

Also: $v_{ext} \mapsto \Phi[n]$. Thus, $E_{v^{(0)}}[n]$ is uniquely defined.

Kohn-Sham theorem

idea: decompose $\mathcal{F}[n]$ into its major contributions

$$\mathcal{F}[n] = T_0[n] + \frac{1}{2}\int\int d\mathbf{r}\, d\mathbf{r}'\, n(\mathbf{r})W(\mathbf{r},\mathbf{r}')n(\mathbf{r}') + E_{XC}[n]$$

T_0:	kinetic energy of a system of non-interacting particles
$E_{XC}[n]$	exchange-correlation energy defined as 'the rest' → approximations
$V_{XC}[n](r) := \frac{\delta E_{XC}[n]}{\delta n(r)}$:	exchange-correlation potential

popular approximations for $E_{XC}[n]$:

- local-density approximation (LDA)
- generalized gradient approximations (GGAs)
- exact exchange formalism (EXX)

⋮

Kohn-Sham Hamiltonian

To find the stationary point, we do variations at fixed $N = \int d\mathbf{r}\, n(\mathbf{r})$, which leads to

$$\frac{\delta E_{v^{(0)}}}{\delta n(\mathbf{r})} = \mu \qquad \text{(Lagrange parameter)}$$

If we write the density as a sum over single-particle functions,

$$n(\mathbf{r}) = \sum_{\mathbf{j=1}}^{\mathbf{N}} \sum_{\mathbf{k} \in \mathbf{BZ}} |'_{\mathbf{j,k}}(\mathbf{r})|^{\mathbf{2}},$$

the variational principle $\delta E_{v^{(0)}}[\varphi^*]/\delta\varphi^*(\mathbf{r}) = \mathbf{0}$ leads to the Kohn-Sham equations

$$\left(-\frac{\nabla^2}{2m} + V_{\text{eff}}[n](\mathbf{r})\right) \varphi_{j,\mathbf{k}}(\mathbf{r}) = \epsilon_{j,\mathbf{k}} \varphi_{j,\mathbf{k}}(\mathbf{r})$$

with the effective potential

$$V_{\text{eff}}[n](\mathbf{r}) = v_{R_I}^{(0)}(\mathbf{r}) + \int d\mathbf{r}' \frac{e^2 n(\mathbf{r}')}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{XC}[n]}{\delta n}(\mathbf{r}).$$

How can we specify E_{XC} ?

At this point, we need to make approximations to get further.

Example: local density approximation (LDA)

$$
\begin{aligned}
E_{XC}[n(\mathbf{r})] &= \int d\mathbf{r}\, e_{XC}[n(\mathbf{r})]\, n(\mathbf{r}) \\
&\approx \int d\mathbf{r}\, [e_X^{hom}(n(\mathbf{r})) + e_C^{hom}(n(\mathbf{r}))]\, n(\mathbf{r}) \\
e_X^{hom}(n) &= -(81/64\pi)^{1/3} n^{1/3}(\mathbf{r}) \\
e_C^{hom}(n) &= \begin{cases} -0.1423(1 + 1.0529\sqrt{r_s} + 0.3334 r_s)^{-1} & \text{if} \quad r_s \geq 1, \\ \\ -0.0480 + 0.0311 \ln r_s - 0.0116 r_s + 0.002 \quad r_s \quad \ln r_s & \\ & \text{if} \quad r_s < 1. \end{cases}
\end{aligned}
$$

$r_s := (4\pi n(\mathbf{r})/3)^{-1/3}$ Wigner-Seitz radius

[see, e.g. J. Perdew & A. Zunger, Phys. Rev. B **23** 5048 (1981)]

The total energy (for static ions)

two equivalent definitions:

$$E_{tot}[n] = T_0[n] + \int d\mathbf{r}\, v^{(0)}_{\mathbf{R}_i}(\mathbf{r})n(\mathbf{r}) + \frac{1}{4\pi\epsilon_0}\int d\mathbf{r}\int d\mathbf{r}'\,\frac{e^2 n(\mathbf{r})n(\mathbf{r}')}{2|\mathbf{r}-\mathbf{r}'|} + E_{XC}[n] + V^{ion-ion}_{\mathbf{R}_I}$$

$$E_{tot}[n] = \sum_{j=1}^{N}\sum_{\mathbf{k}\in\mathrm{BZ}} \varepsilon_{j,\mathbf{k}} + \Delta E^{e-e}[n] + \Delta E_{XC}[n] + V^{ion-ion}_{\mathbf{R}_I}$$

$$\Delta E^{e-e}[n] = -\frac{1}{4\pi\epsilon_0}\int d\mathbf{r}\int d\mathbf{r}'\,\frac{e^2 n(\mathbf{r})n(\mathbf{r}')}{2|\mathbf{r}-\mathbf{r}'|} = -E^{e-e}[n]$$

$$\Delta E_{XC}[n] = E_{XC}[n] - \int d\mathbf{r}\, V_{XC}[n](\mathbf{r})\mathbf{n}(\mathbf{r})$$

E_{tot} is stationary with resp. to variations of n around n_0, but the individual terms are not !

Concepts when solving Schrödingers-equation in solids

Form of potential

(non-)selfconsistent
“Muffin-tin” MT
atomic sphere approximation (ASA)
Full potential : FP
pseudopotential (PP)

Relativistic treatment of the electrons

non relativistic
semi-relativistic
fully-relativistic

exchange and correlation potential

Hartree-Fock (+correlations)
Density functional theory (DFT)
  Local density approximation (**LDA**)
  Generalized gradient approximation (**GGA**)
  Beyond LDA: e.g. **LDA+U**

$$\left[-\frac{1}{2}\nabla^{2}+V(r)\right]\varphi_i^k=\varepsilon_i^k\varphi_i^k$$

Schrödinger - equation

Representation of solid

non periodic
(cluster)
periodic
(unit cell)

Treatment of spin

Non-spinpolarized
Spin polarized
(with certain magnetic order)

Basis functions

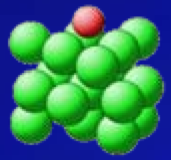
plane waves : PW
augmented plane waves : APW
atomic oribtals. e.g. Slater (STO), Gaussians (GTO), LMTO, numerical basis

Basic steps in an electronic structure calculation

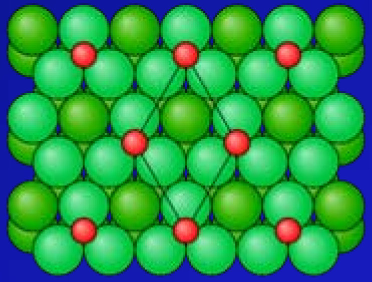
1. guess a starting charge density
   (e.g. superposition of atomic densities)
2. set up the Hamiltonian for this charge density (usually done in a small, preliminary basis set)
3. diagonalize this approximative Hamiltonian
4. use the eigenvalues and wavefunctions to set up a new charge density
5. try to improve the wavefunctions using the variational principle for E_{tot}, thereby simultaneously approaching self-consistency

$$n^{(i-1)} \longrightarrow V_{eff}^{(i-1)} \longrightarrow \varepsilon_{j,\mathbf{k}}^{(i-1)}, \varphi_{j,\mathbf{k}}^{(i-1)} \longrightarrow n^{(i)} \longrightarrow V_{eff}^{(i)} \longrightarrow \varepsilon_{j,\mathbf{k}'}^{(i)}, \varphi_{j,\mathbf{k}'}^{(i)} \cdots$$

Surface models: slabs vs. clusters

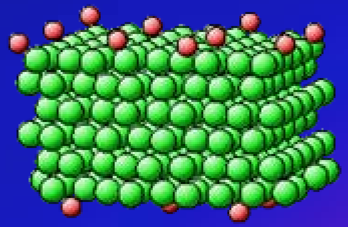


vs.



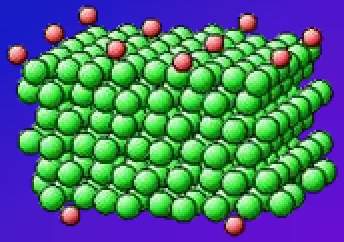
Cluster geometries:

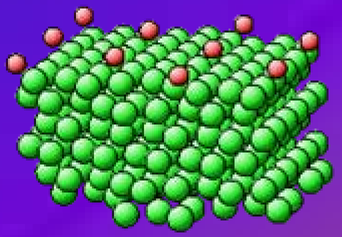
+ very cheap for small clusters (local basis sets)
+ ideal for local aspects (defects etc.)
– slow convergence with cluster size (embedding etc.)



Supercell geometries:

+ proper surface electronic structure (band structure)
+ good convergence with slab thickness (“semi-infinite”)
+ suitable for plane wave basis sets
– artificial lateral periodicity: “ordered arrays”
– inherently expensive (large systems)





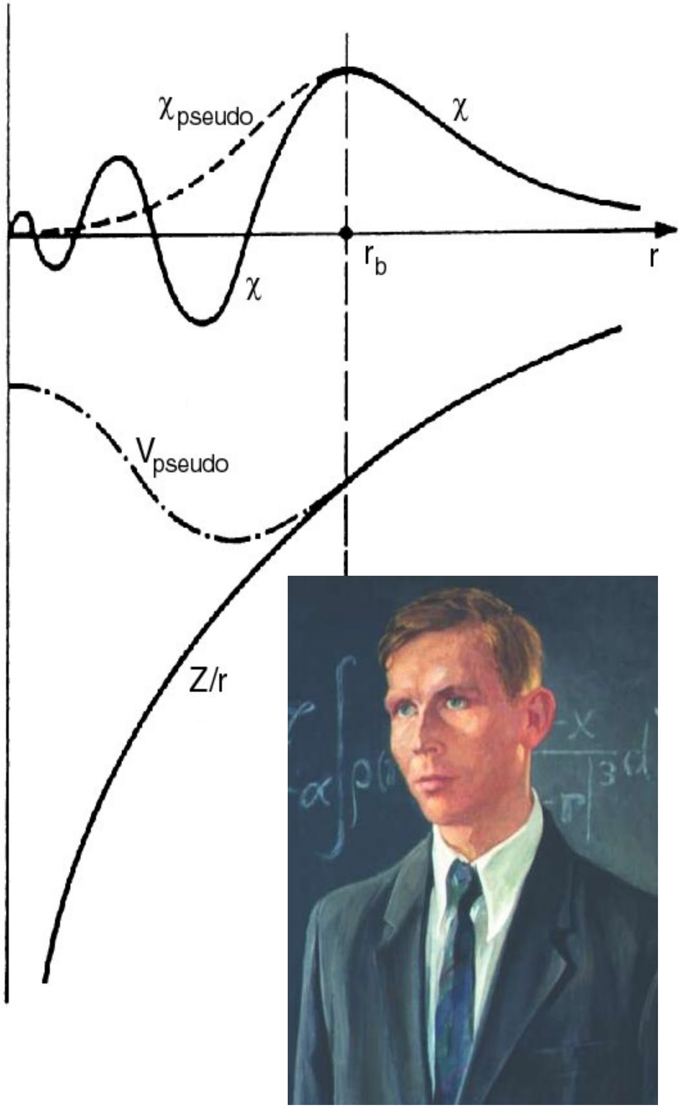
Basis Sets for Solids

- plane waves (pseudo potentials)
- space partitioning (augmentation) methods
  - **LMTO (linear muffin tin orbitals)**
    - ASA approx., linearized numerical radial function
    + Hankel- and Bessel function expansions
  - **ASW (augmented spherical wave)**
    - similar to LMTO
  - **FP-LMTO (full-potential LMTO)**
    - similar to LAPW, space partitioned with non-overlapping spheres
  - **KKR (Kohn, Koringa, Rostocker method)**
    - solution of multiple scattering problem, Greens function formalism
    - equivalent to APW
  - **(L)APW (linearized augmented plane waves)**
- LCAO methods
  - Gaussians, Slater, or numerical orbitals, often with PP option)

pseudopotential plane wave methods

- plane waves form a “complete” basis set, however, they “never” converge due to the rapid oscillations of the atomic wave functions χ close to the nuclei

- let´s get rid of all core electrons and these oscillations by replacing the strong ion–electron potential by a much weaker (and physically dubious) *pseudopotential*



How to compute observables

A) energy differences

between different structures, formation energy of defects, heat of adsorption, ...

B) derivatives of the thermodynamic potentials E_{tot}, F or G

For simplicity's sake, we consider a system with constant volume at $T = 0: \qquad F(T = 0, V) = E_{tot}(V)$

- pressure $p = -\frac{\partial E_{tot}(V)}{\partial V}$
- bulk modulus $B = V \frac{\partial^2 E_{tot}(V)}{\partial V^2}$
- forces $\vec{F}_I$ on atom I (in electronic ground state)

$$\vec{F}_I = -\frac{\partial E_{tot}}{\partial \vec{R}_I} = -\sum_j^N \langle \varphi_{j,\mathbf{k}} | \partial H / \partial \vec{R}_I | \varphi_{j,\mathbf{k}} \rangle$$

due to the Hellmann-Feynman theorem

How to compute observables

C) second derivatives

Examples:

1. force constant matrix

$$\frac{\partial E_{tot}}{\partial \vec{R}_i \partial \vec{R}_j}$$

→ calculation of phonon spectrum, vibrational entropy, …

2. particle number fluctuations

→ chemical softness and hardness

$$s(\mathbf{r}) = \left(\frac{\partial n(\mathbf{r})}{\partial \mu}\right)\Bigg|_{v,T} = \int \left(\frac{\delta^2 E_{tot}}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}\right)^{-1} d\mathbf{r}'$$

$$h(\mathbf{r}) = \frac{1}{2}\left(\frac{\partial \mu}{\partial n(\mathbf{r})}\right)\Bigg|_{v,T} = \int \frac{\delta^2 E_{tot}}{\delta n(\mathbf{r})\delta n(\mathbf{r}')} \frac{n(\mathbf{r}')}{2N} d\mathbf{r}'$$

Note: When calculating second derivatives, the response of the density to the perturbation must be taken into account.

→ Density Functional Perturbation Theory

What materials properties are accessible to calculation?

- structural properties
  Examples: structural phase transitions, surface reconstructions yes
- elastic properties
  Examples: bulk modulus, C_{11}, C_{12}, C_{44}, … yes
- chemical properties
  Examples: thermochemical stability of compounds, reactivity of surfaces yes
- transport properties
  Examples: conductance of nanowires, magneto-resistence
  developing field
- optical/spectroscopic properties
  Examples: photoemission spectra, cross sections for light absorption
  topic beyond Kohn-Sham theory → time-dependent DFT

$\vdots$

many other applications

Bridging scales:

Ab initio atomistic thermodynamics

General idea

Motivation:

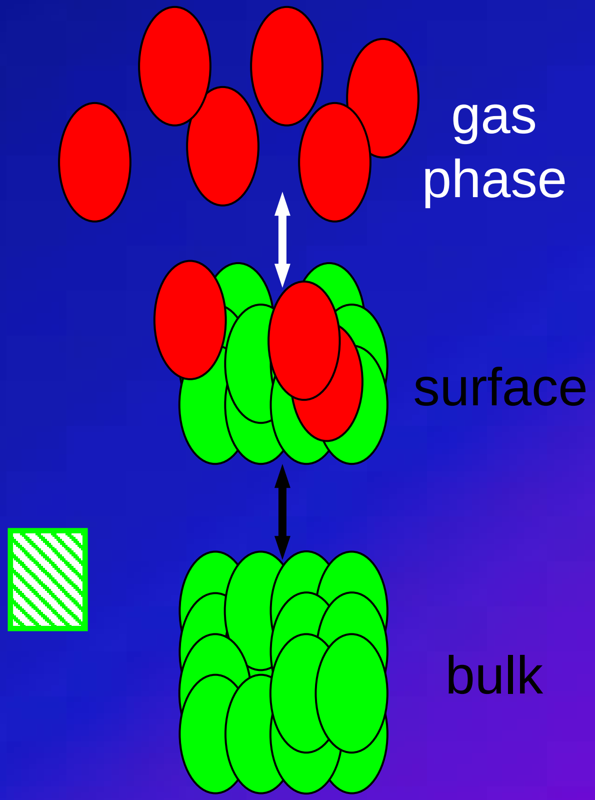
- extend length scale
- consider finite temperature effects

Approach:

- separate system into sub-systems (exploit idea of reservoirs!)
- calculate properties of sub-systems separately (cheaper…)
- connect by implying equilibrium between sub-systems

Drawback:

- no temporal information („system properties after infinite time“)
- equilibrium assumption



I. Connecting thermodynamics, statistical mechanics and density-functional theory

Statistical Mechanics,
D.A. McQuarrie, Harper Collins Publ. (1976)

Introduction to Modern Statistical Mechanics,
D. Chandler, Oxford Univ. Press (1987)

M. Scheffler in *Physics of Solid Surfaces 1987*,
J. Koukal (Ed.), Elsevier (1988)

Thermodynamics in a nutshell

Internal energy	(U)	$E^{tot}(S,V)$
Enthalpy	$H(S,p)$	$= E^{tot} + pV$
(Helmholtz) free energy	$F(T,V)$	$= E^{tot} - TS$
Gibbs free energy	$G(T,p)$	$= E^{tot} - TS + pV$

Potential functions

- Equilibrium state of system minimizes corresponding potential function

- In its set of variables the total derivative of each potential function is simple
  (derive from 1st law of ThD: $dE^{tot} = dQ + dW$, $dW = -pdV$, $dQ = TdS$)

$$dE = TdS - pdV$$
$$dH = TdS + Vdp$$
$$dF = -SdT - pdV$$
$$dG = -SdT + Vdp$$

⇒ These expressions open the gate to a whole set of general relations like:

$$S = -(\partial F/\partial T)_V\ ,\ p = -(\partial F/\partial V)_T$$

$$E^{tot} = -T^2 (\partial/\partial T)_V (F/T)$$ Gibbs-Helmholtz eq.

$$(\partial T/\partial V)_S = -(\partial p/\partial S)_V$$ etc. Maxwell relations

- Chemical potential $\mu = (\partial G/\partial n)_{T,p}$ is the cost to remove a particle from the system.
  Homogeneous system: $\mu = G/N$ $(= g)$
  i.e. Gibbs free energy per particle

Link to statistical mechanics

A many-particle system will flow through its huge phase space, fluctuating through all microscopic states consistent with the constraints imposed on the system. For an isolated system with fixed energy *E* and fixed size *V*,*N* (microcanonic ensemble) these microscopic states are all equally likely at thermodynamic equilibrium (i.e. equilibrium is the most random situation).

- Partition function $Z = Z(T,V) = \sum_i \exp(-E_i / k_B T)$ ⇒ Boltzmann-weighted sum over all possible system states

$\Rightarrow F = -k_B T \ln(Z)$

- If groups of degrees of freedom are decoupled from each other (i.e. if the energetic states of one group do not depend on the state within the other group), then

$$Z_{\text{total}} = \left(\sum_i \exp(-E_i^A / k_B T) \right) \left(\sum_i \exp(-E_i^B / k_B T) \right) = Z^A Z^B$$

$$\Rightarrow F_{\text{total}} = F^A + F^B$$

e.g. electronic ↔ nuclear (Born-Oppenheimer)
rotational ↔ vibrational

- *N* indistinguishable, independent particles: $Z_{\text{total}} = 1/N! \left(Z_{\text{one particle}} \right)^N$

Computation of free energies: ideal gas I

$$\boxed{Z = 1/N!\,\left(\cancel{Z_{\mathrm{nucl}}}\;Z_{\mathrm{el}}\;Z_{\mathrm{trans}}\;Z_{\mathrm{rot}}\;Z_{\mathrm{vib}}\right)^N}$$

$$\Rightarrow \quad \mu(T,p) = G\,/\,N = (F + pV)\,/\,N = (\,-\,k_BT\,\ln(\,Z\,) + pV\,)\,/\,N$$

i) Electr. free energy $\quad Z_{\mathrm{el}} = \sum_i \exp(-E_i^{\mathrm{el}}\,/\,k_BT)$

$\Rightarrow F_{\mathrm{el}} \approx E^{\mathrm{tot}} - k_BT\;\ln(\,I_{\mathrm{spin}}\,)$

Typical excitation energies eV >> k_BT, only (possibly degenerate) ground state contributes significantly

Required input: Internal energy E^{tot}

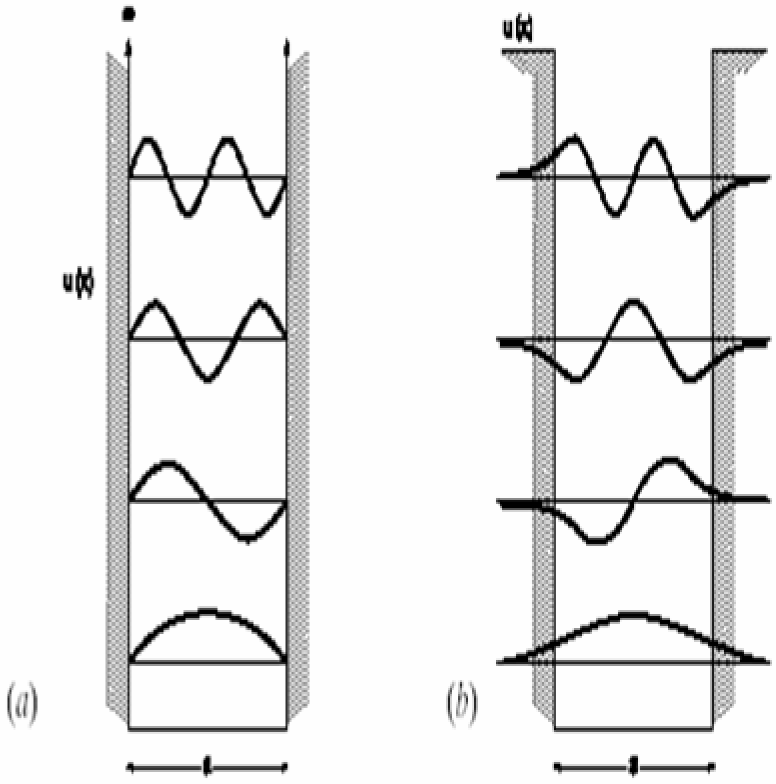
Ground state spin degeneracy I_{spin}

ii) Transl. free energy $\quad Z_{\mathrm{trans}} = \sum_{\underline{k}} \exp(-\hbar k^2\,/\,2mk_BT)$ $\quad$ Particle in a box of length $L = V^{1/3}$

$(L\rightarrow\infty) \quad \Rightarrow \quad Z_{\mathrm{trans}} \approx V\,(\,2\pi\, mk_BT\,/\,\hbar^2\,)^{3/2}$

Required input: Particle mass m

Particle in box



$$\lambda_n = 2L/n$$

$$E_n = n^2 \frac{h^2}{8mL^2}$$

$$\psi(z) \propto \sin\left(\frac{n\pi z}{L}\right).$$

Computation of free energies: ideal gas II

iii) Rotational free energy $Z_{\mathrm{rot}} = \sum_J (2J+1)\exp(-J(J+1)B_{\mathrm{o}} / k_B T)$ Rigid rotator

(Diatomic molecule) $\Rightarrow Z_{\mathrm{rot}} \approx - k_B T \ \ln(k_B T/\sigma B_{\mathrm{o}})$

$\sigma = 2$ (homonucl.),
$= 1$ (heteronucl.)
$B_{\mathrm{o}} \sim m d^2$ (d = bond length)

Required input: Rotational constant B_{o}
(exp: tabulated microwave data)

iv) Vibrational free energy $Z_{\mathrm{vib}} = \sum_{i=1}^{M} \sum_n \exp(-(n + \tfrac{1}{2})\hbar\omega_i / k_B T$ Harmonic oscillator

$$\Rightarrow \mu_{\mathrm{vib}}(T) = \sum_{i=1}^{M} \tfrac{1}{2}\, \hbar\omega_i + k_B T \ln(1 - \exp(-\hbar\omega_i/k_B T))$$

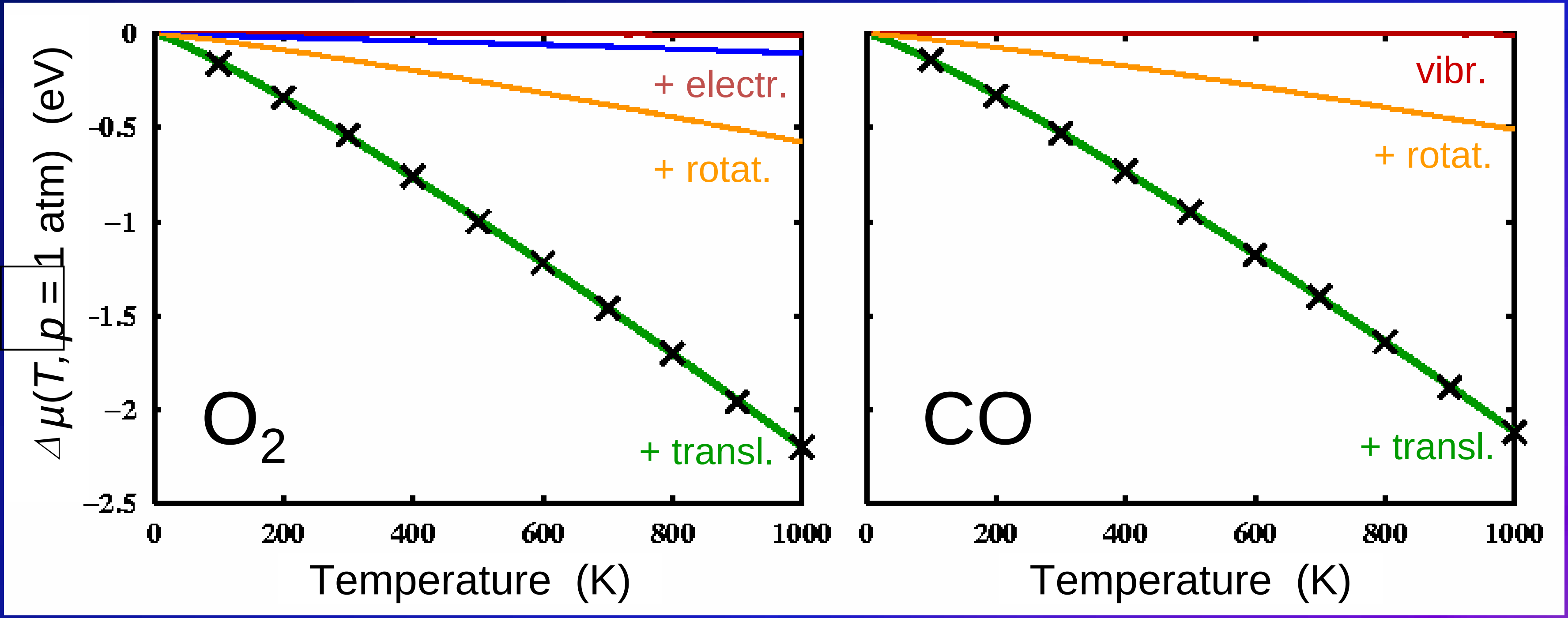
Required input: M fundamental vibr. modes ω_i

Calculate dynamic matrix $D_{ij} = (m_i m_j)^{-1/2} (\partial^2 E^{\mathrm{tot}}/\partial r_i \partial r_j)_{\underline{r}_{\mathrm{eq}}}$
Solve eigenvalue problem det(D – 1 ω_i^2)

Computation of free energies: ideal gas III

		O_2	CO
m	(amu)	32	28
ν_{stretch}	(meV)	196	269
B_o	(meV)	0.18	0.24
σ		2	1
I_{spin}		3	1

$$\boxed{\begin{aligned}\mu &= \mu(T,p)\\ &= E^{\text{tot}} + \Delta\mu(T,p)\end{aligned}}$$



Alternatively: $\Delta\mu(T, p) = \Delta\mu(T, p^o) + kT \ln(p/p^o)$

and $\Delta\mu(T, p^o = 1$ atm) tabulated in thermochem. tables (e.g. JANAF)

Computation of free energies: solids

$$\boxed{G(T,p) = E^{tot} + F^{trans} + F^{rot} + F^{vib} + F^{conf} + pV}$$

F^{trans}	Translational free energy	$\propto 1/M \to 0$
F^{rot}	Rotational free energy	
pV	$V = V(T,p)$ from equation of state, varies little	$\to 0$ for $p < 100$ atm
F^{conf}	Configurational free energy	→ Trouble maker…
E^{tot}	Internal energy	→ DFT
F^{vib}	Vibrational free energy	→ phonon band structure

E^{tot}, F^{vib} use differences

use simple models to approx. F^{vib} (Debye, Einstein)

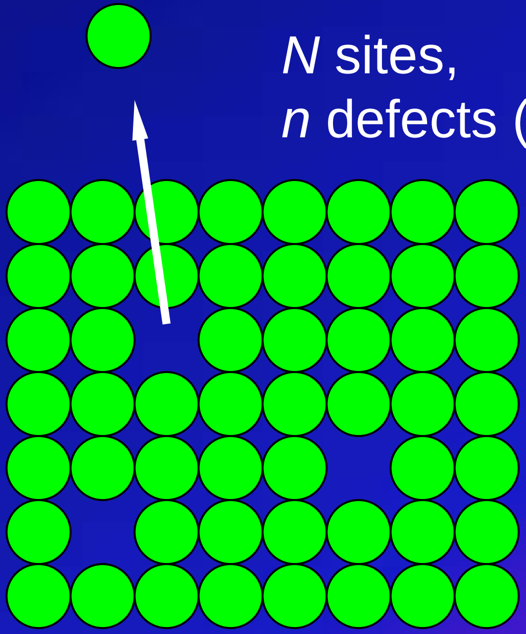
$\Rightarrow$ Solids (low T): $G(T,p) \sim E^{tot} + F^{conf}$

II. Starting simple:
Equilibrium concentration of point defects

Solid State Physics,
N.W. Ashcroft and N.D. Mermin, Holt-Saunders (1976)

Isolated point defects and bulk dissolution

On entropic grounds there will always be a finite concentration of defects at finite temperature, even though the creation of a defect costs energy ($E_D > 0$).



N sites,
n defects ($n \ll N$)

How large is it?

Internal energy: $E^{tot} = n\, E_D$

Config. entropy: $F^{conf} = k_B T \ln Z(n)$

$$\text{with} \quad Z = \frac{N\,(N-1)\ \ldots\ (N-n-1)}{1 \cdot 2 \cdot\ \ldots \cdot n} = \frac{N!}{(N-n)!\,n!}$$

Minimize free energy: $$(\partial G/\partial n)_{T,p} = \partial/\partial n_{T,p}\,(E^{tot} - F^{conf} + pV) = 0$$

Forget pV, use Stirling: $\ln N! \approx N(\ln N - 1)$ ⇒ $$\boxed{n/N = \exp(-E_D/k_B T)}$$

III. Slightly more involved:
Effect of a surrounding gas phase on the surface structure and composition

E. Kaxiras *et al*., Phys. Rev. B 35, 9625 (1987)

X.-G. Wang *et al*., Phys. Rev. Lett. 81, 1038 (1998)

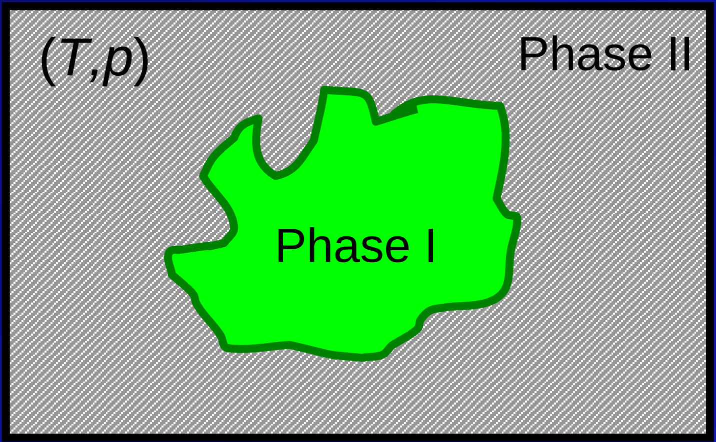
Surface thermodynamics

A surface can never be alone:
there are always
"two sides" to it !!!

solid – gas
solid – liquid
solid – solid ("interface")
…

Phase I / phase II alone (bulk):

$$G_{I} = N_{I}\,\mu_{I}$$
$$G_{II} = N_{II}\,\mu_{II}$$



Total system (with surface):

$$G_{I+II} = G_{I} + G_{II} + \Delta G_{surf}$$

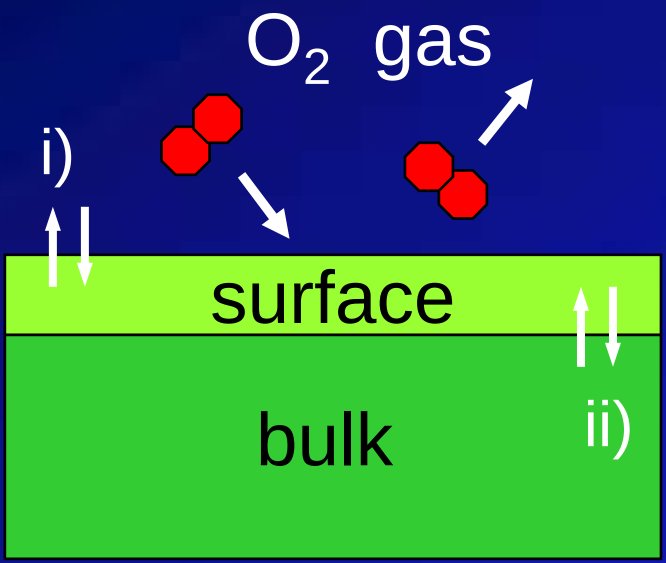
γA

$$\boxed{\gamma = 1/A \left(G_{I+II} - \sum_i N_i\,\mu_i \right)}$$

Surface tension
(free energy per area)

Example: Surface in contact with oxygen gas phase

$$\gamma_{\text{surf.}} = 1/A \left[\, G_{\text{surf.}}(N_{\mathrm{O}}, N_{\mathrm{M}}) - N_{\mathrm{O}}\, \mu_{\mathrm{O}} - N_{\mathrm{M}}\, \mu_{\mathrm{M}} \,\right]$$


O_2 gas

i)

surface

bulk

ii)

Use reservoirs:

i) μ_{O} from ideal gas

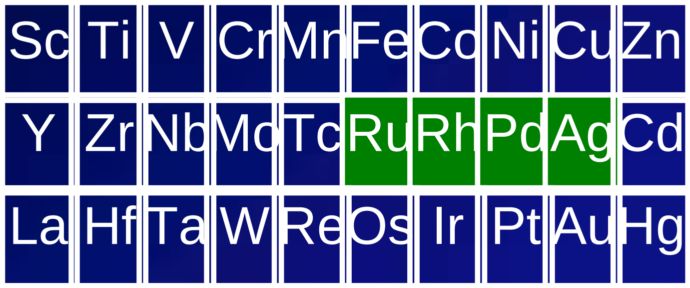
ii) $\mu_{\mathrm{M}} = g^{\text{bulk}}_{\mathrm{M}}$

Forget about F^{vib} and F^{conf} for the moment:

$$\boxed{\gamma(T,p) \approx \left(E^{(\text{slab})}_{\text{surf.}} - N_{\mathrm{M}}\, E^{\text{bulk}}_{\mathrm{M}} \right)/A \; - \; N_{\mathrm{O}}\, \mu_{\mathrm{O}}(T,p)\, /A}$$

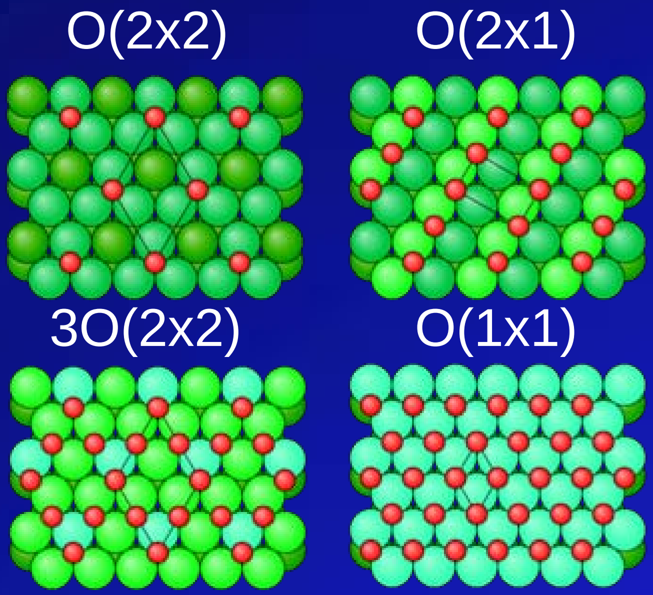
Surface Adsorption

Oxygen bond strength at basal TM surfaces



Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

Strong variation with element and coverage

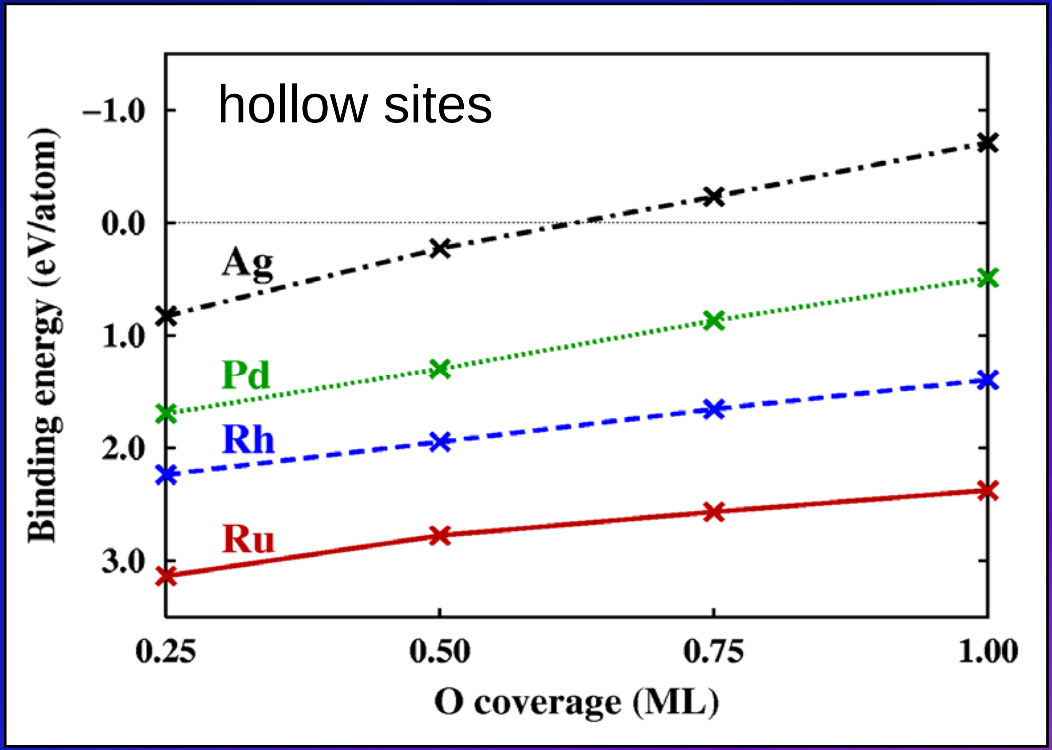


O(2x2)

O(2x1)

3O(2x2)

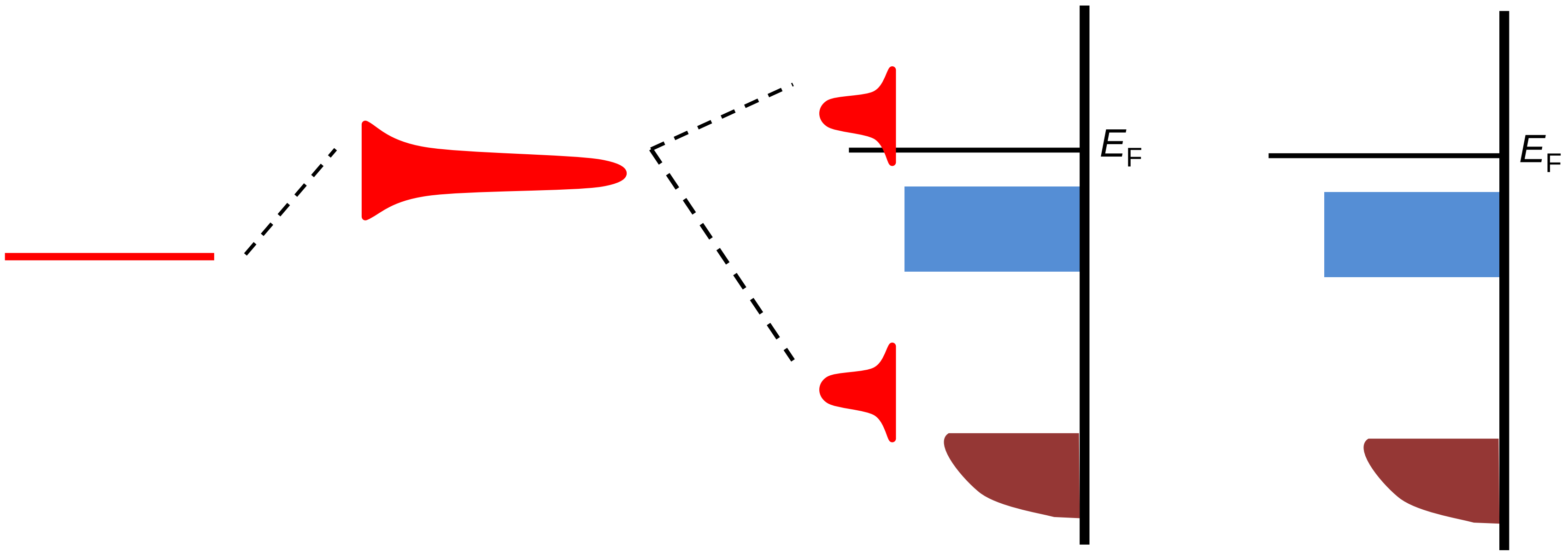
O(1x1)



M. Todorova *et al.*, Phys. Rev. Lett. 89, 096103 (2002)

Theory of adsorption : Newns-Anderson model

≈ a generalization of molecular orbital (MO) schemes to finite bands



free atom

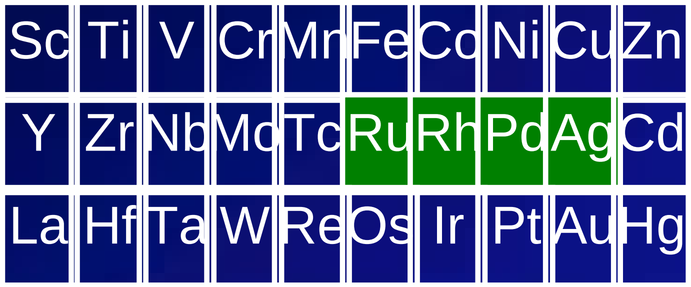
interaction with *s*-band:
renormalization and
broadening

interaction with *d*-band:
splitting in bonding and
anti-bonding peaks

clean surface

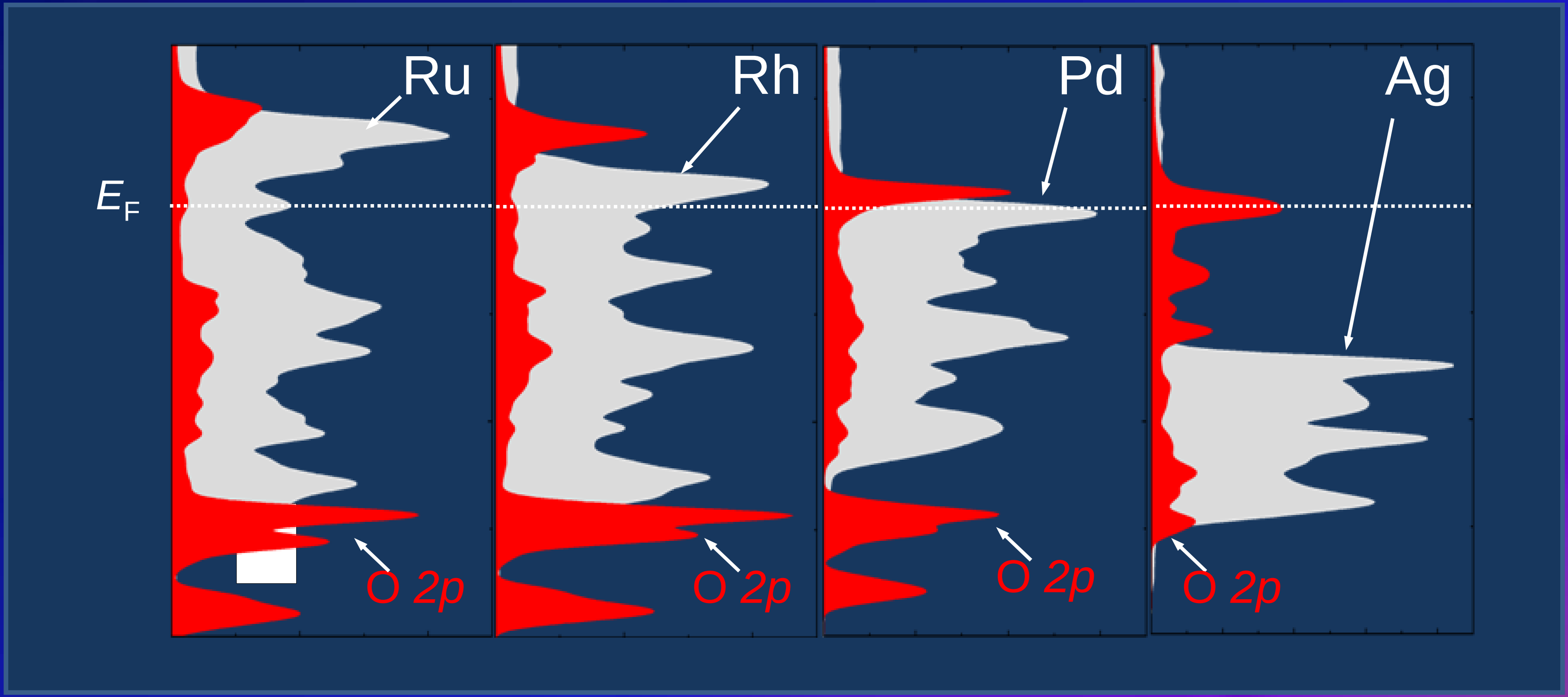
D.M. Newns, Phys. Rev. 178, 1123 (1969);
P.W. Anderson, Phys. Rev. 124, 41 (1961)

Theory of adsorption: Newns-Anderson model cont'd
And Hammer-Norskov Model

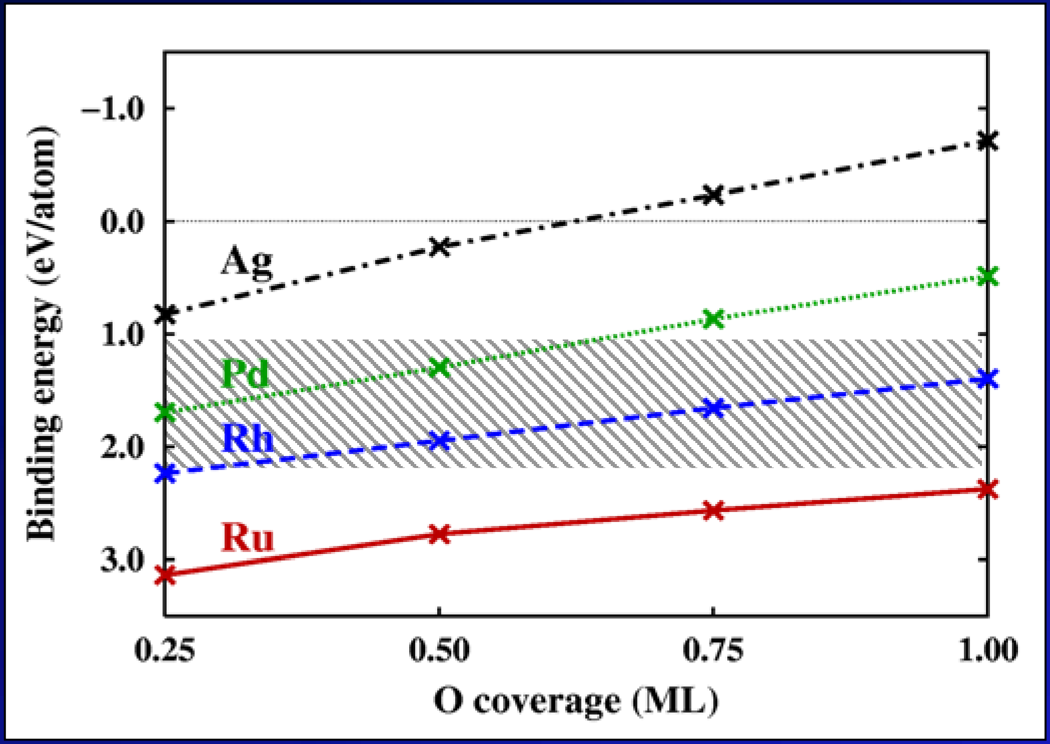


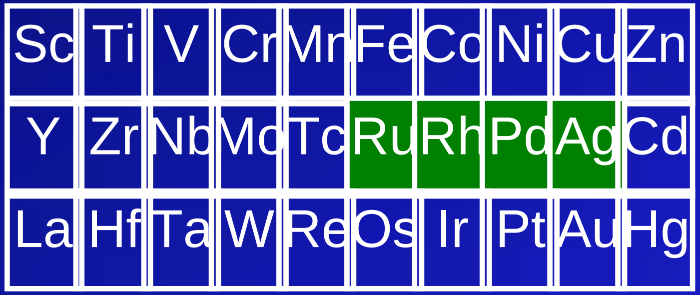
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

Filling of *d*-band occupies antibonding O-M states



Theory of adsorption: Newns-Anderson model cont’d





Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

Achievements:

- qualitative electronic structure at the surface
- correct trend in adsorption strength over TM series
- reactivity patterns → *d*-band center (Hammer/Nørskov)

Failures:

- no adsorbate induced reconstructions
- no site specificity (→ reactivity theory, HSAB, covalent/ionic)
- no lateral interactions

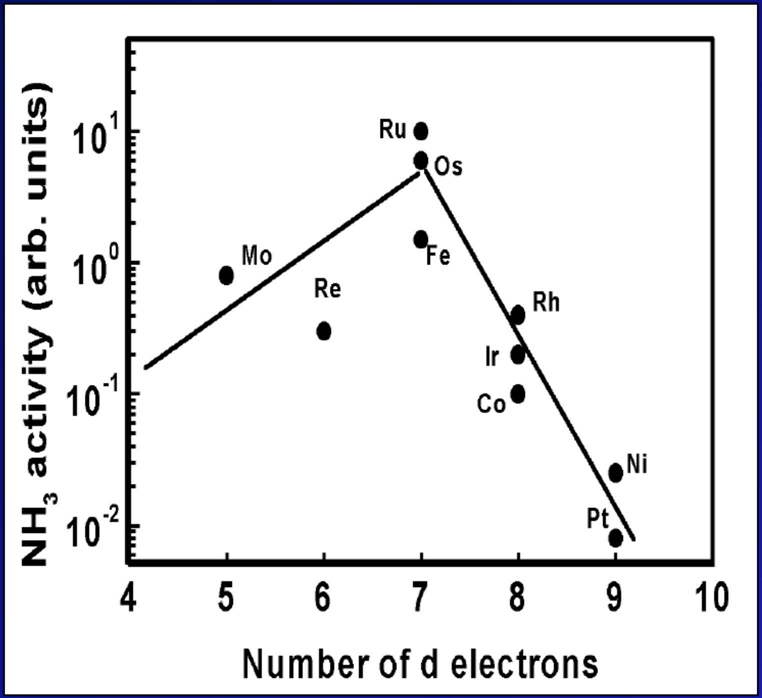
Importance of intermediate bond strength

Low bond strength: no incentive to form/ bind intermediates

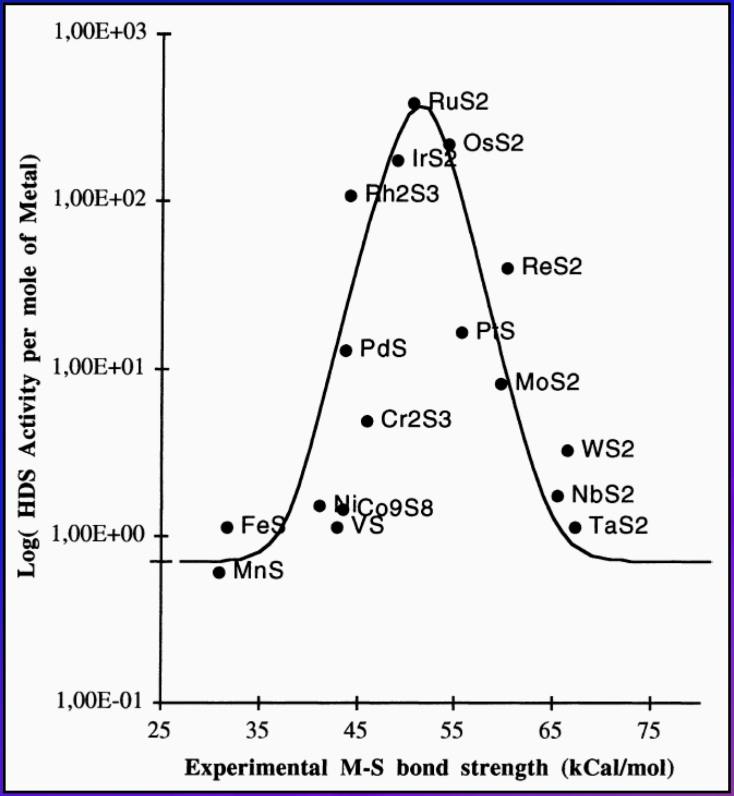
High bond strength: no incentive to form products

A good catalyst binds intermediates with medium bond strength

Sabatier principle (1913)



NH_3
J.R. Jennings,
Ammonia Synthesis,
Plenum (1991)

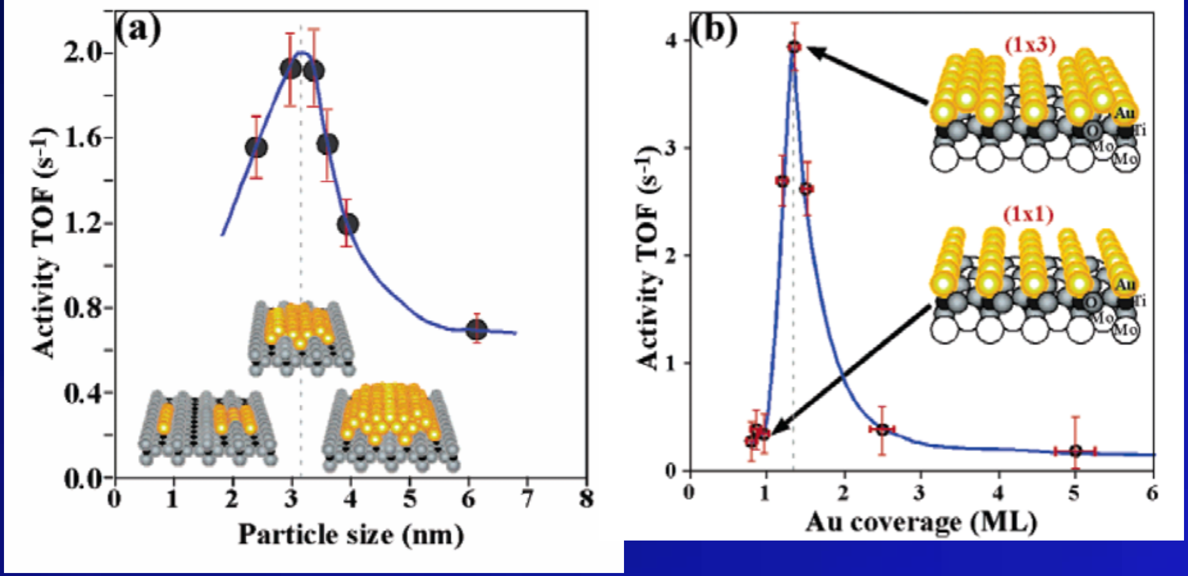


HDS
H. Toulhoat *et al*.,
Catal. Today 50,
629 (1999)

Two dimensional ultra-thin film

a playground for manipulation of electron and chemistry

Catalytically Active Gold: From Nano-particles to Ultrathin Films



Chen & Goodman
Acc. Chem. Res. (2006)

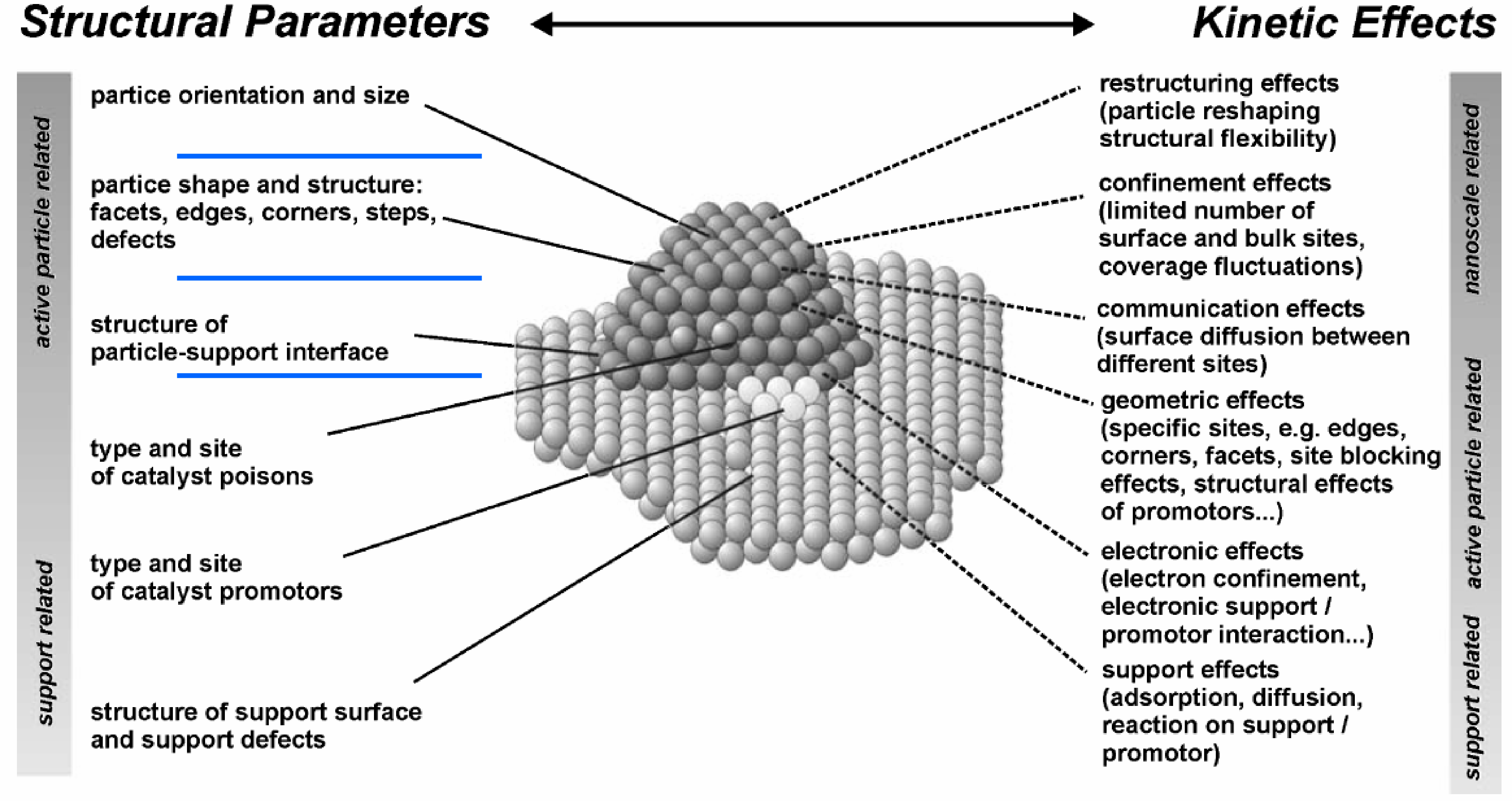
Origin:

1. Low-Coordination Sites small may not be always good
2. Electronic Effects
3. Quantum size effects

"Unfortunately the data in the literature and the discussion vary widely; therefore the nature of the active Au species or structure or site remains unclear."
-- W. Goodman

Lack of precise preparation and characterization in general

Supported Catalyst



Quantum Size Effects in Nanomaterials

Classical Mechanics

(m)

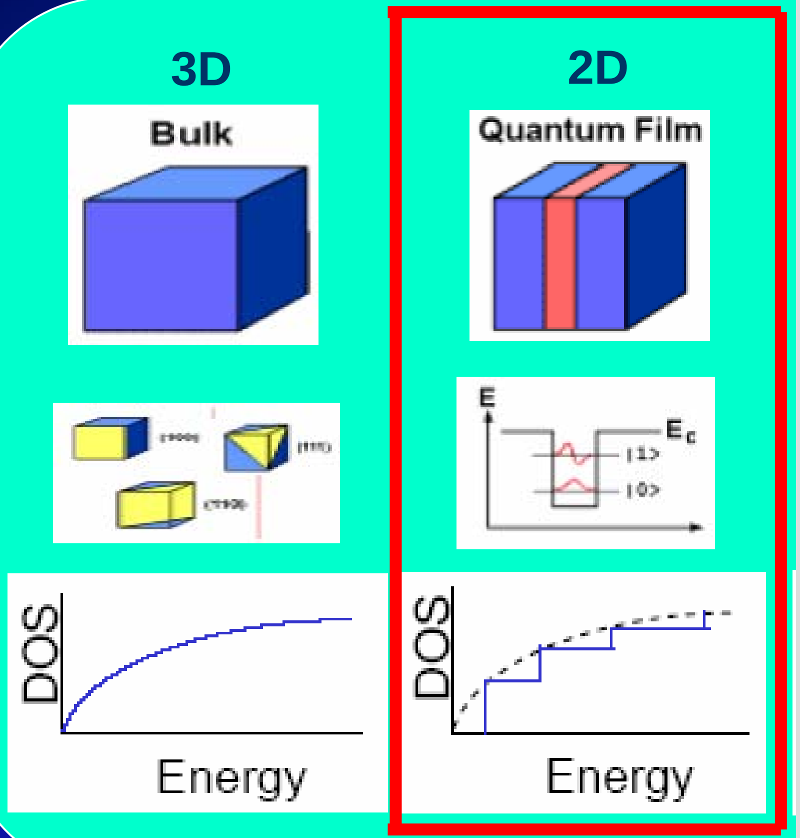
Fermi length

↔

critical size

Quantum Mechanics

(nm)

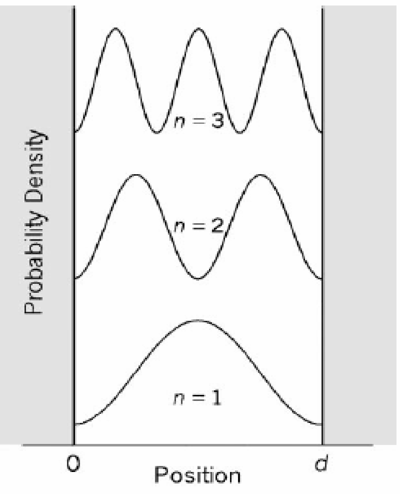


square potential well model

$$\lambda_n = 2L / n$$

$$E_n = n^2 \frac{h^2}{8mL^2}$$

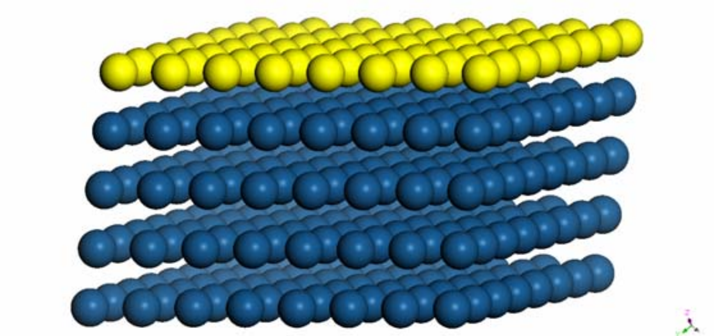
$$\psi(z) \propto \sin\left(\frac{n\pi z}{L}\right).$$

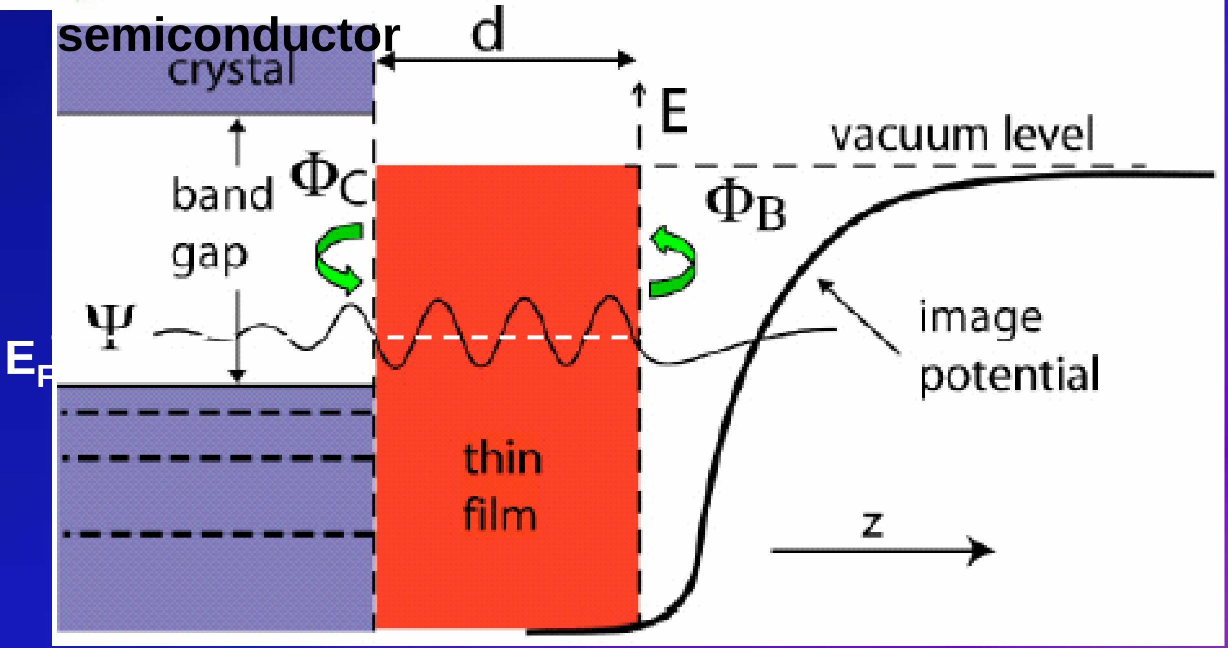


…quantized in the vertical direction

→ 量子阱态

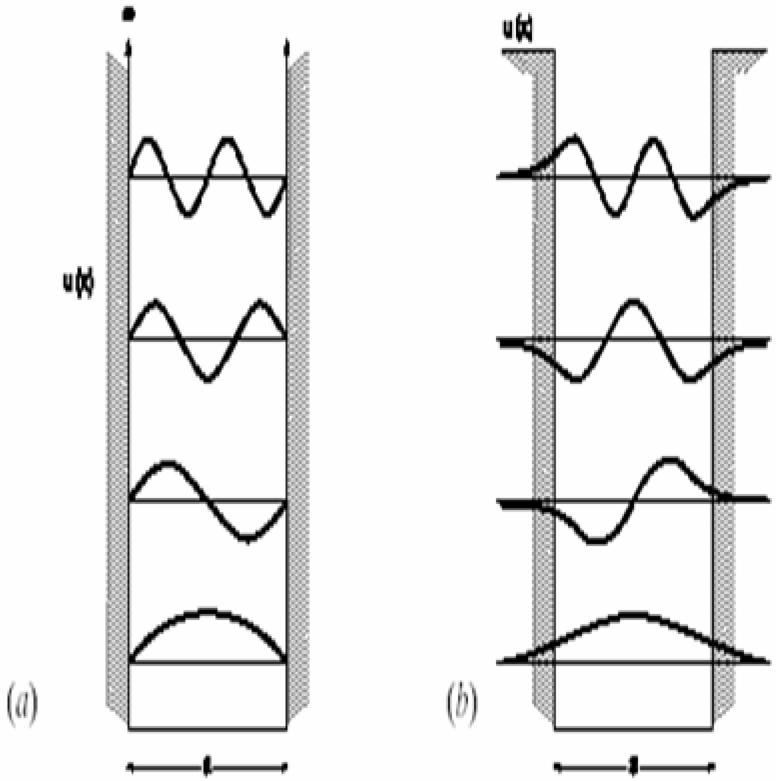
Electron Confinement in ultra thin film: Quantum Size Effect





P.M. Echenique, J.B. Pendry, **J. Phys. C: Solid State Phys.** 11 (1978) 2056.

Quantum Well States from Quantum Mechanics



$$\lambda_n = 2L/n$$

$$E_n = n^2 \frac{h^2}{8mL^2}$$

$$\psi(z) \propto \sin\left(\frac{n\pi z}{L}\right).$$

Bound states in infinite or finite potential wells

量子受限薄膜体系

量子阱态

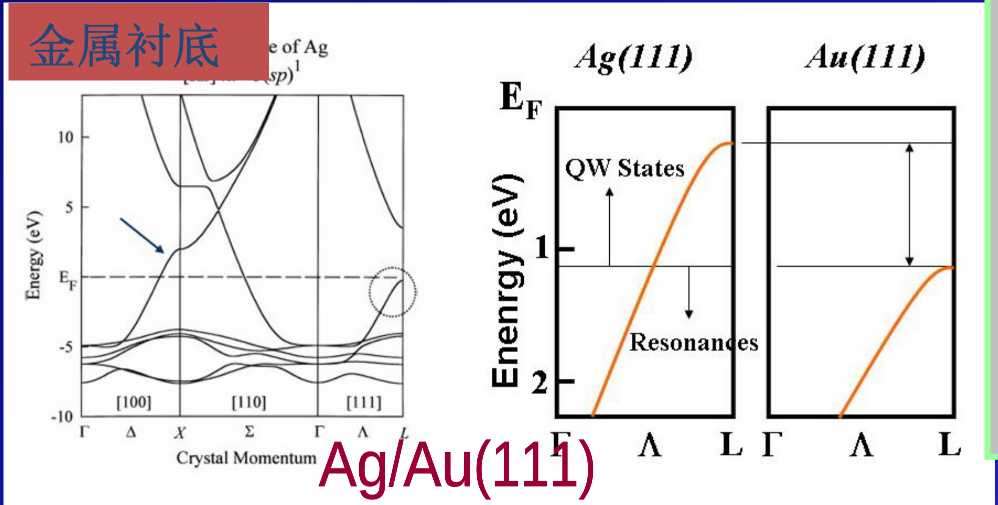
λ_F和ν_F与价电子数量和能带色散有关！

两个量子化电子态的能量差：

$$\Delta = \pi\hbar v_F / Nd$$

薄膜厚度从N到N＋1时的能谱移动：

$$\delta = 2d\Delta / \lambda_F$$



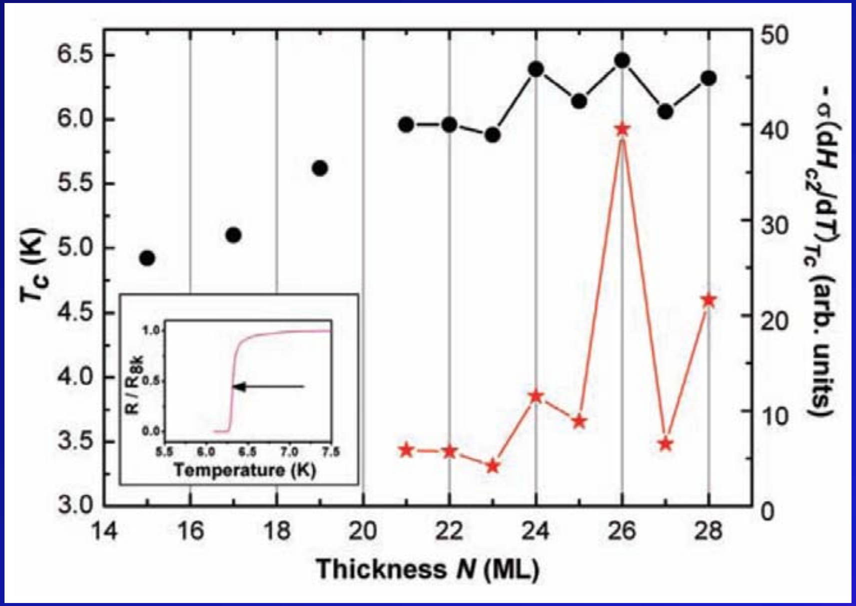
金属衬底

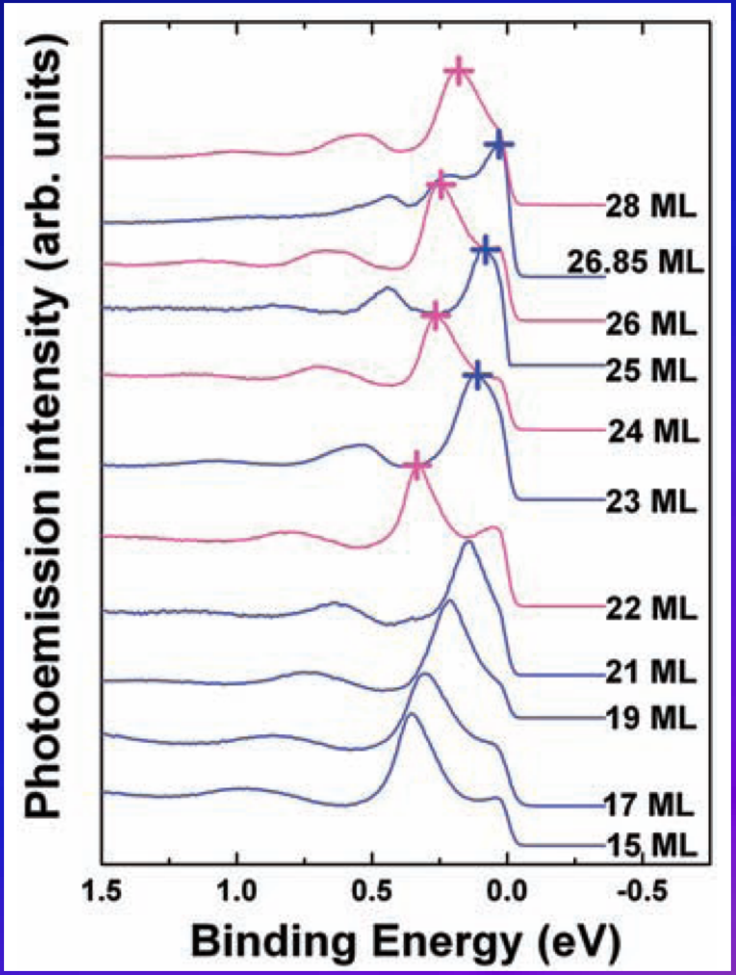
Ag/Au(111)

metal/metal	metal/semicondutor
Ag/Cu(111)	Pb/Si(111)
Pb/Cu(111)	Pb/Ge(111)
Ag/Ni(111)	Pb/Ge(100)
Ag/Fe(100)	Ag/Si(111)
	Al/Si(111)
	Ag/GaAs(110)

\# 通过改变薄膜的厚度来调控薄膜电子态及其催化性能

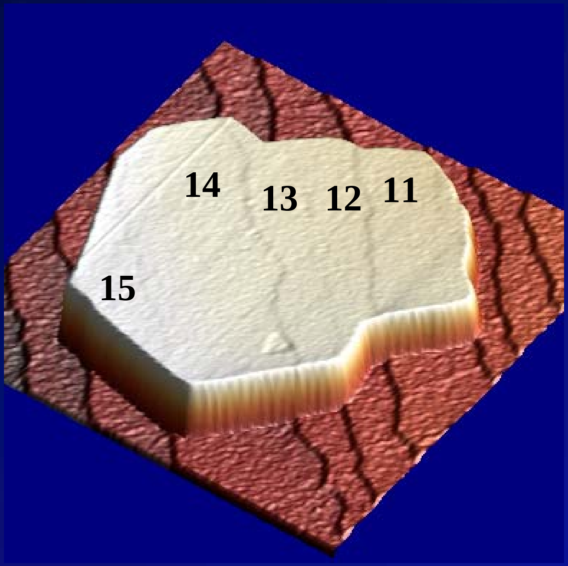
Superconductivity Modulated by Quantum Size Effect: Pb/Si(111)

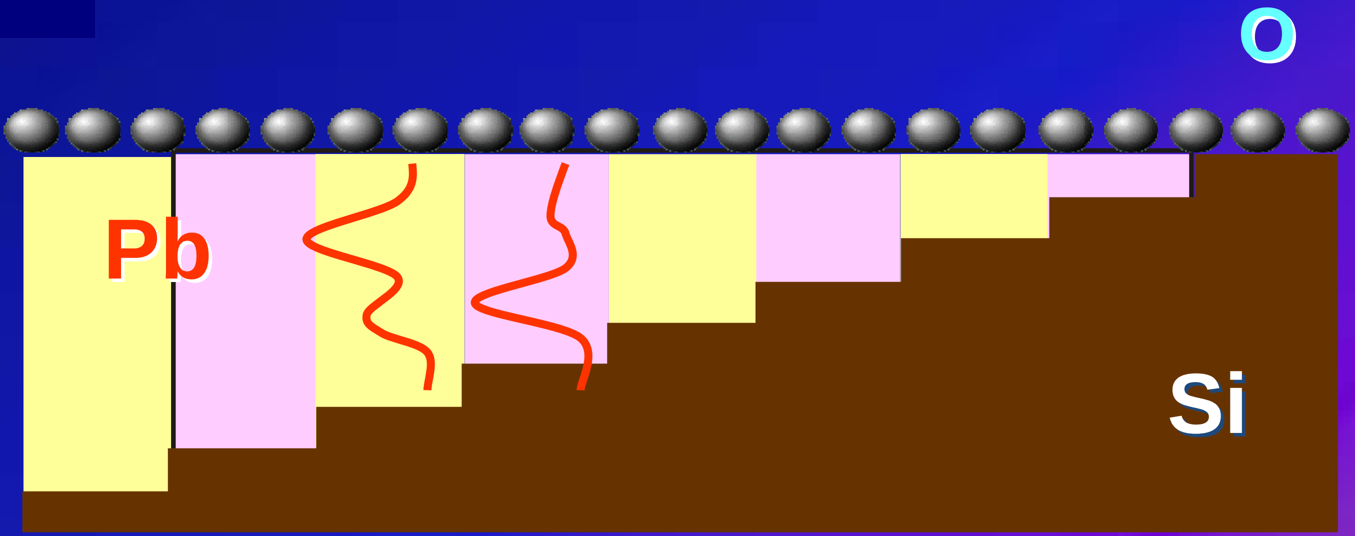




Q. K. Xue et. al Science 306, 1915(2004)

Tuning Chemical Reactivity by Quantum Well States

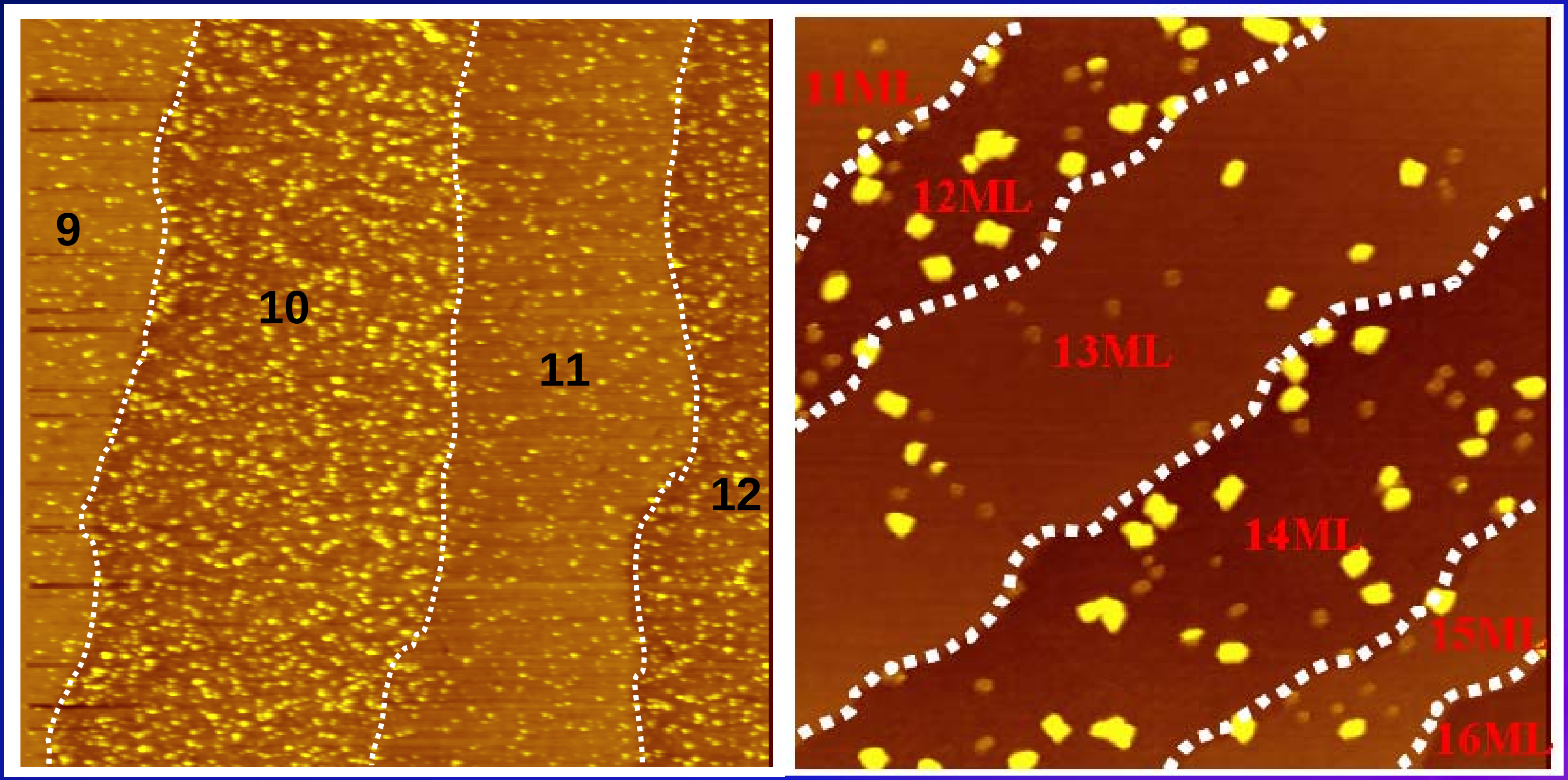




金属表面化学反应活性的量子振荡

- 铅岛样品具有相同的结构、组成，唯一变化的参量是薄膜厚度！
- 氧气在的Pb薄膜的表面吸附和氧化反应随着薄膜厚度的变化出现量子振荡现象

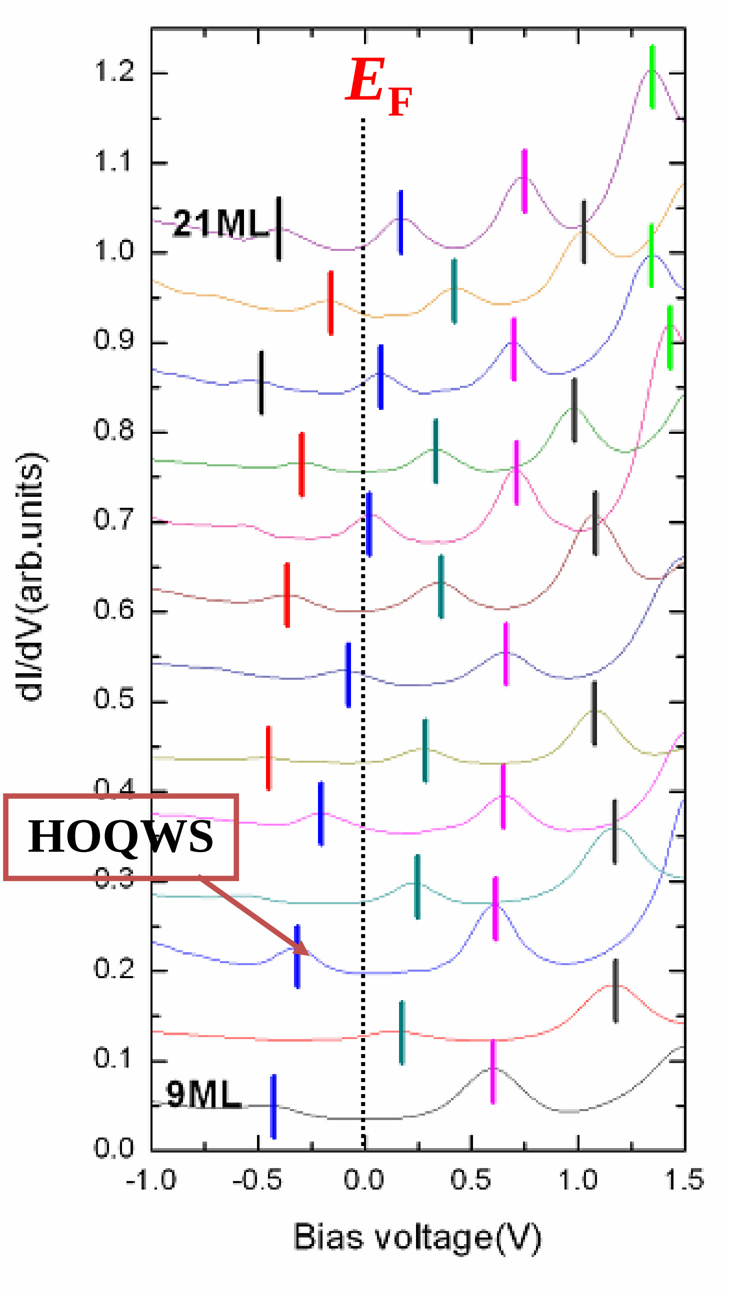
氧气吸附

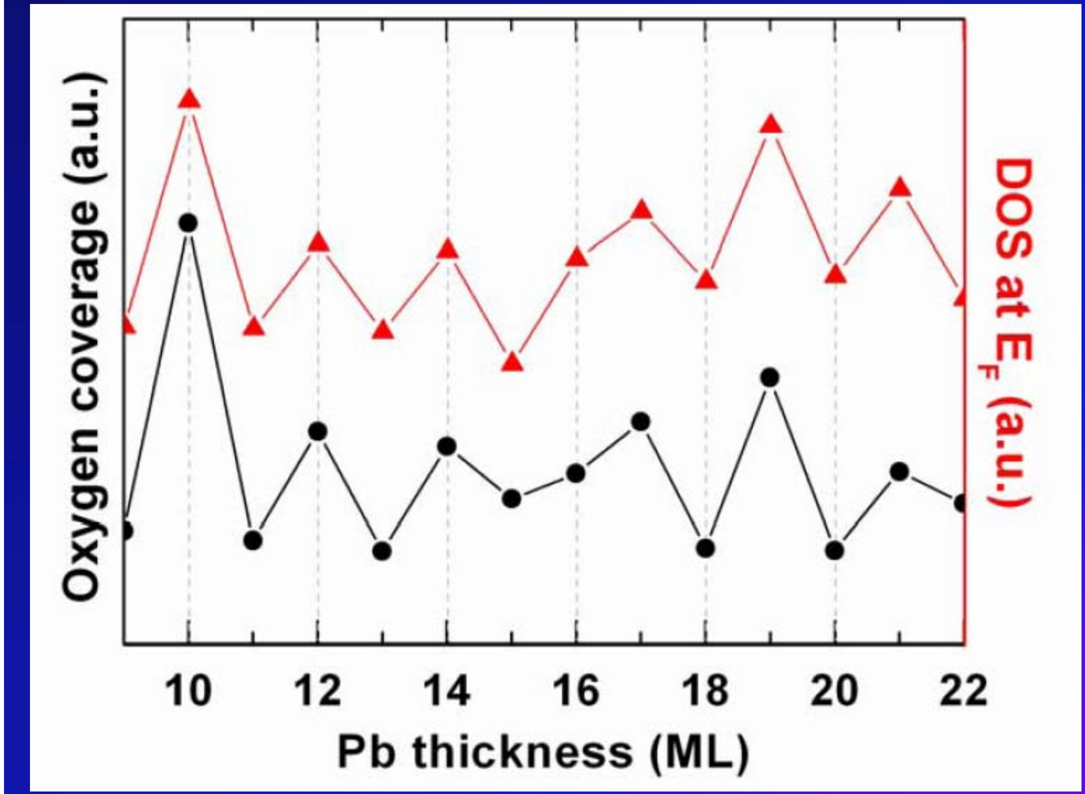


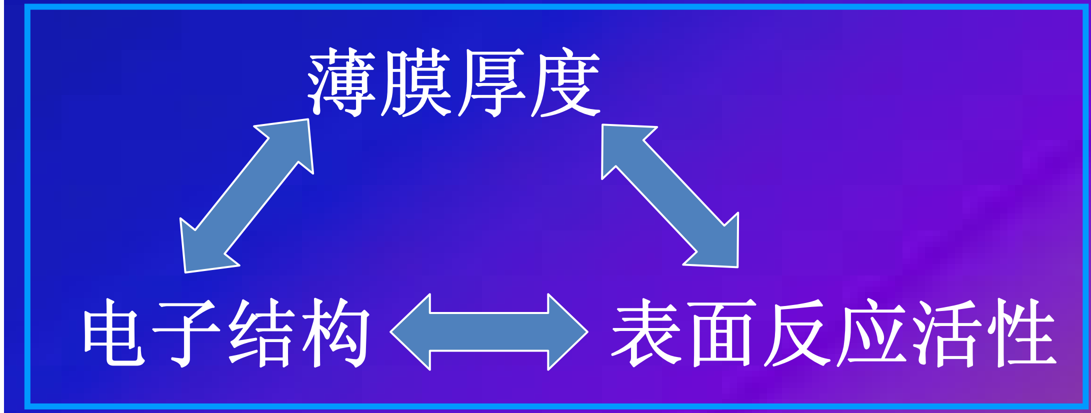
氧化反应

X. C. Ma, W. X. Li, Q. K. Xue et al, Proceeding of National Academy of Sciences (2007)

金属表面化学反应活性的量子振荡



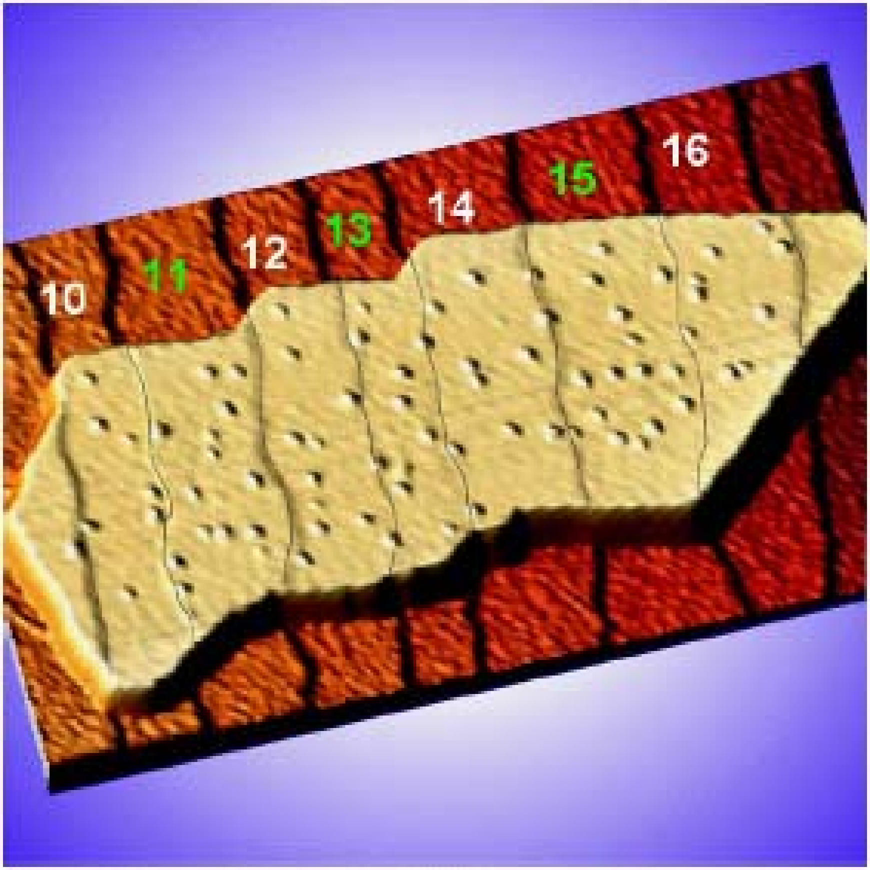




薄膜厚度

电子结构 ⟷ 表面反应活性

Effects of quantum well states: Fe adatom on Pb/Si



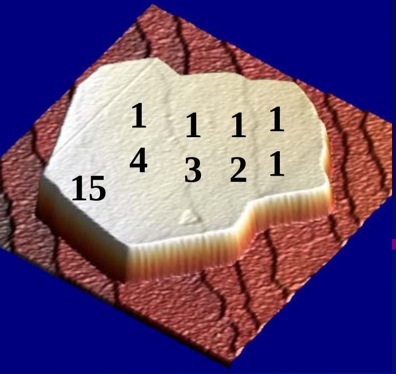
$n\ (\text{Fe islands})_{11,13,15}$

$>$

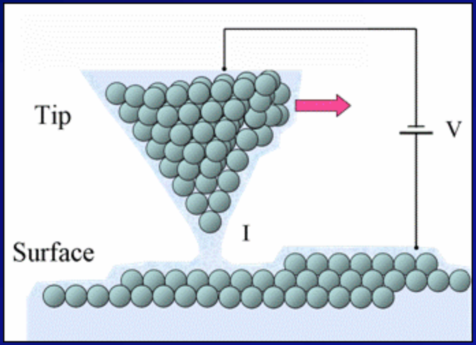
$n\ (\text{Fe islands})_{10,12,14,16}$

Density oscillation of Fe islands on QWS Pb films

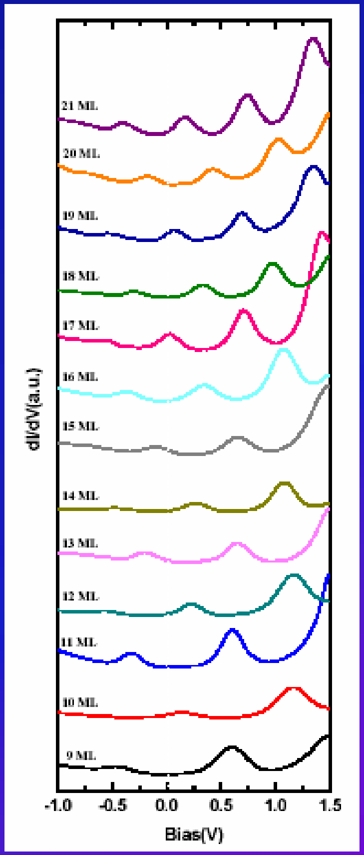
L.Y. Ma, J.F. Jia, Q.K. Xue, et al., **Phys. Rev. Lett.** 97 (2006) 266102.

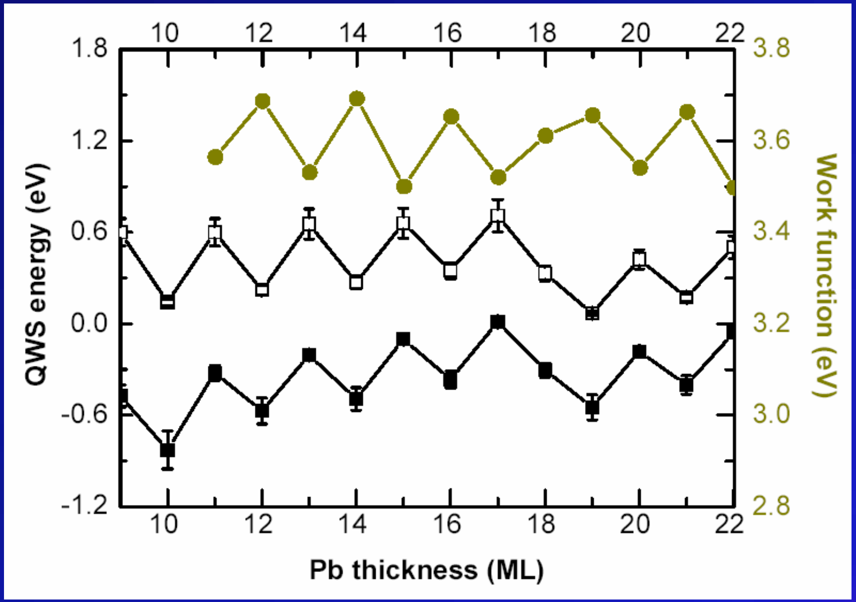


隧道扫描电镜(STM) 测量

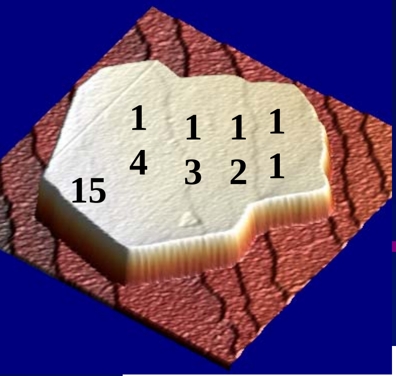


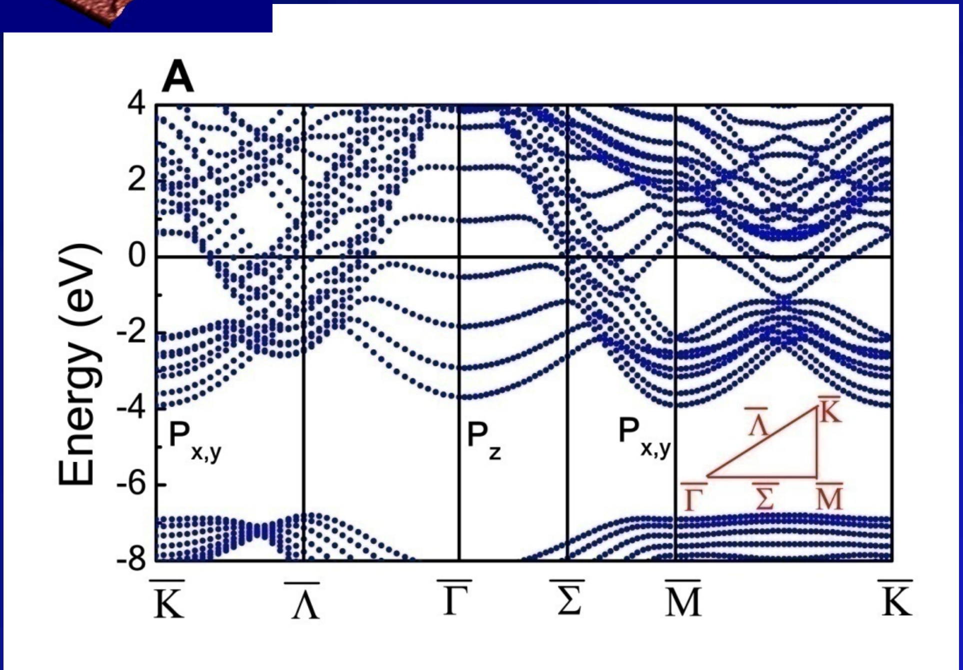
dI/dV





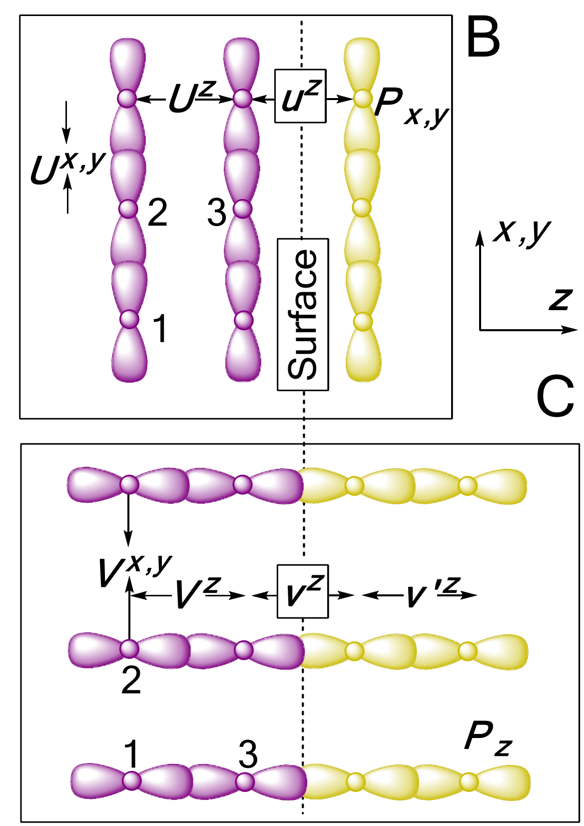
Pb(111）膜的UPS谱、及其随厚度的调制





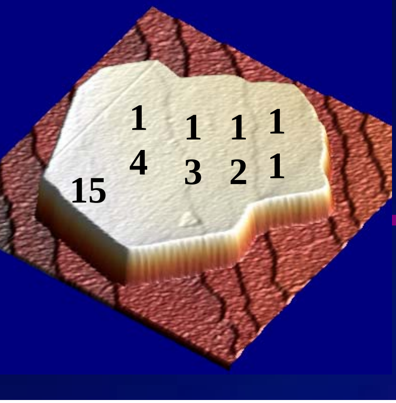
角分辨*UPS*谱

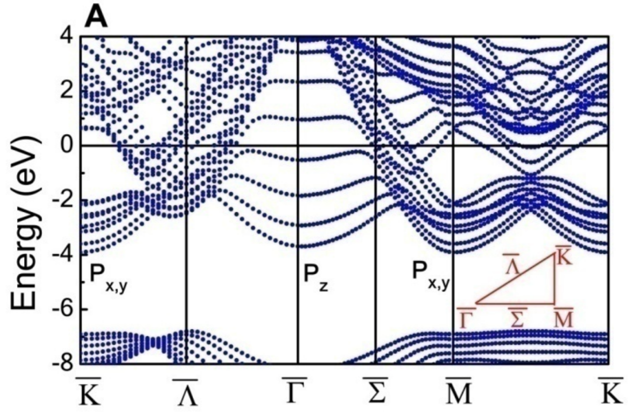
（$\bar{\Gamma}$：发向*UPS*）



Symmetry broken at surface affects Pz orbital
Gamma is dominated by Pz orbial

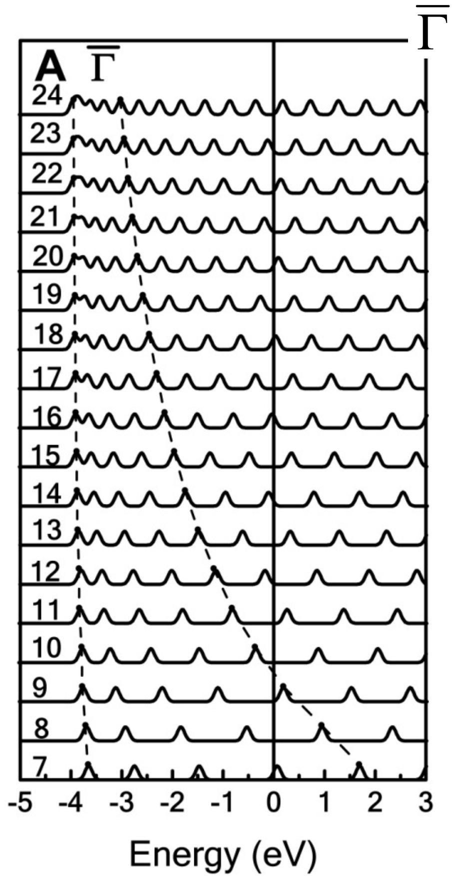
Pb(111）膜的UPS、及其随厚度的调制

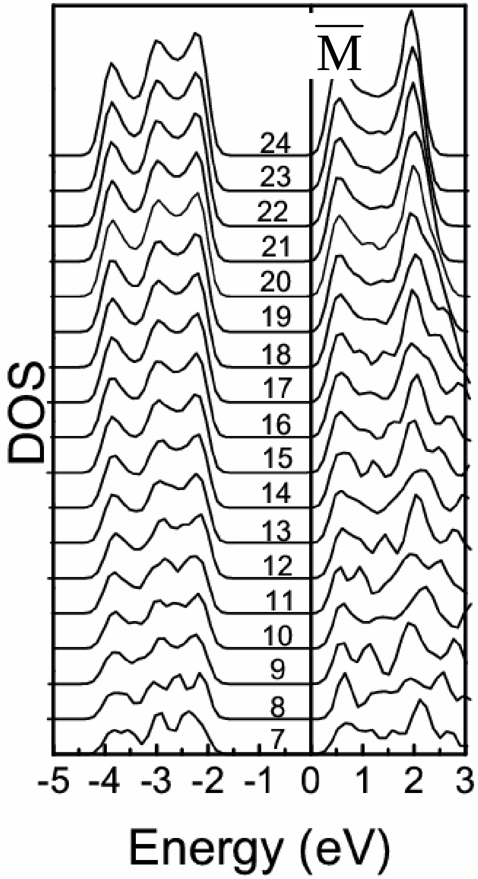




角分辨*UPS*谱

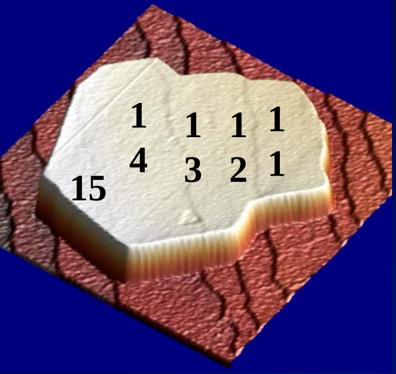
（$\bar{\Gamma}$：发向*UPS*）

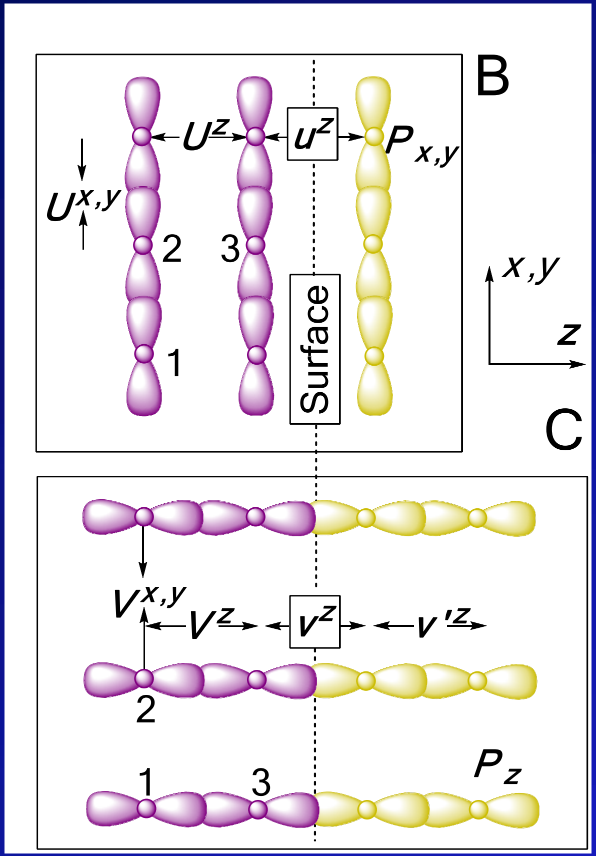


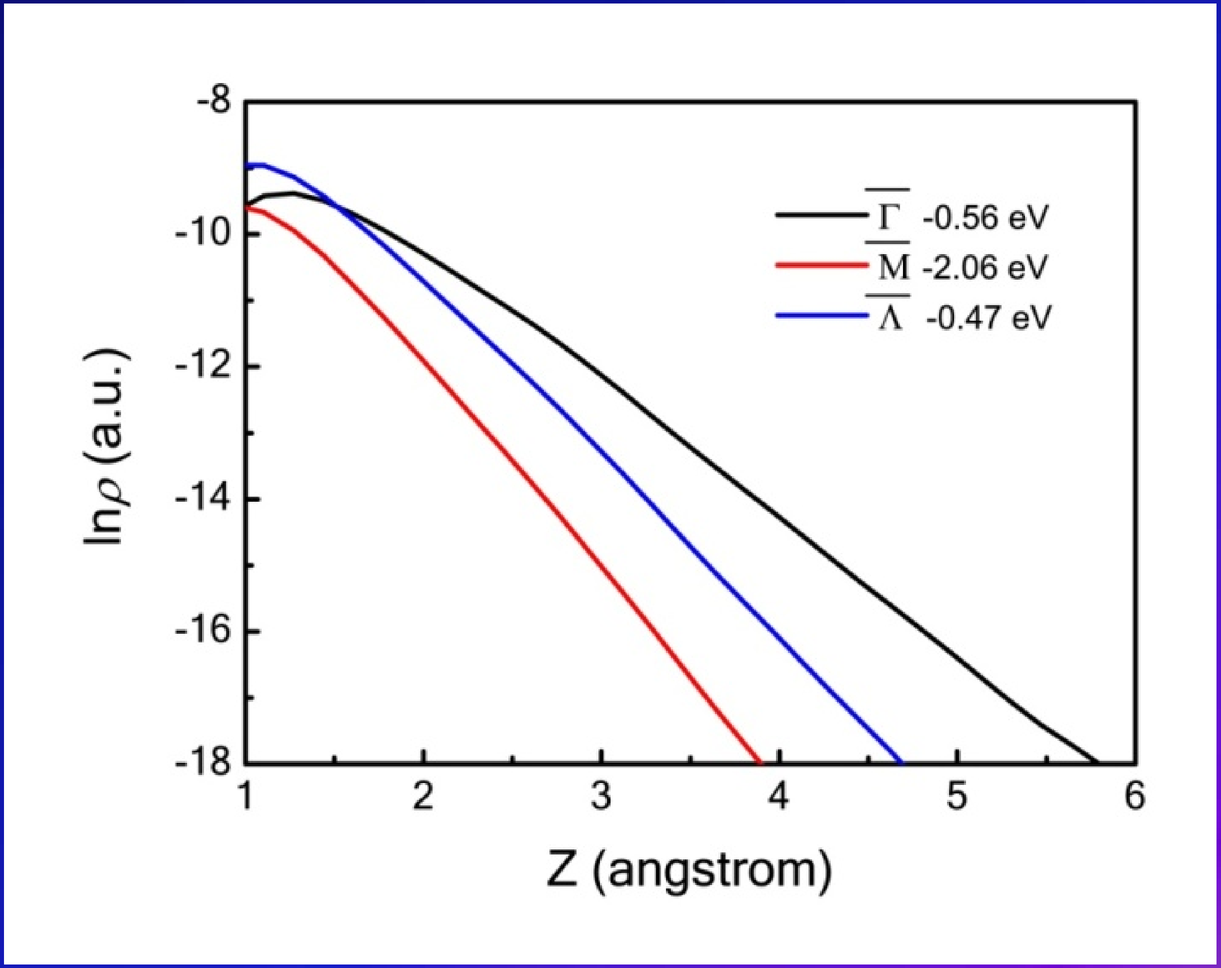


只有在发向**UPS**(布里渊区中心处)表现出量子尺寸调控效应 **(Pz orbital)**

表面电子密度的空间延展性/衰减长度



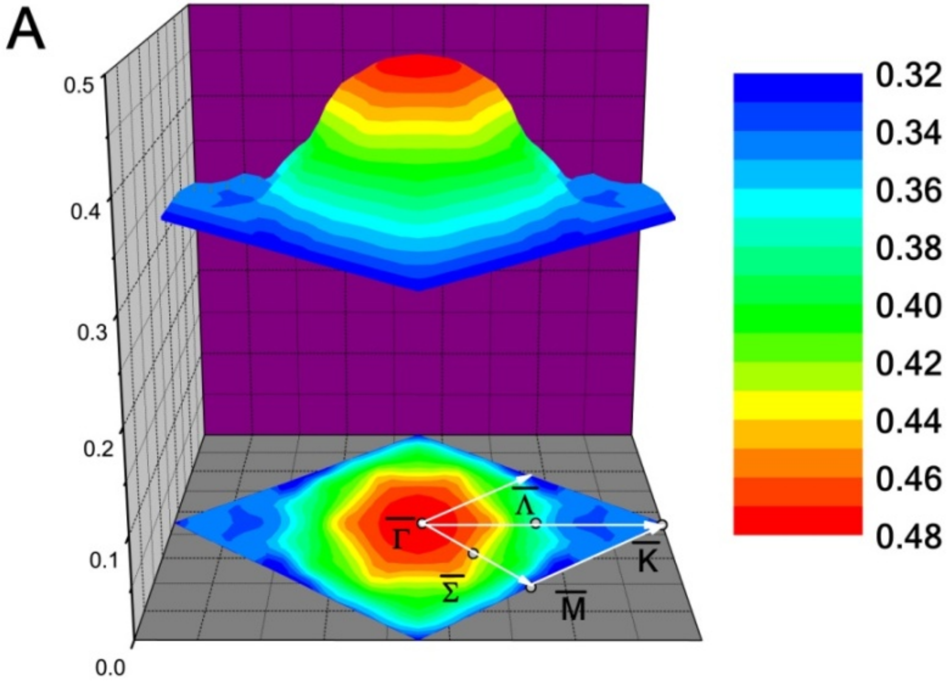


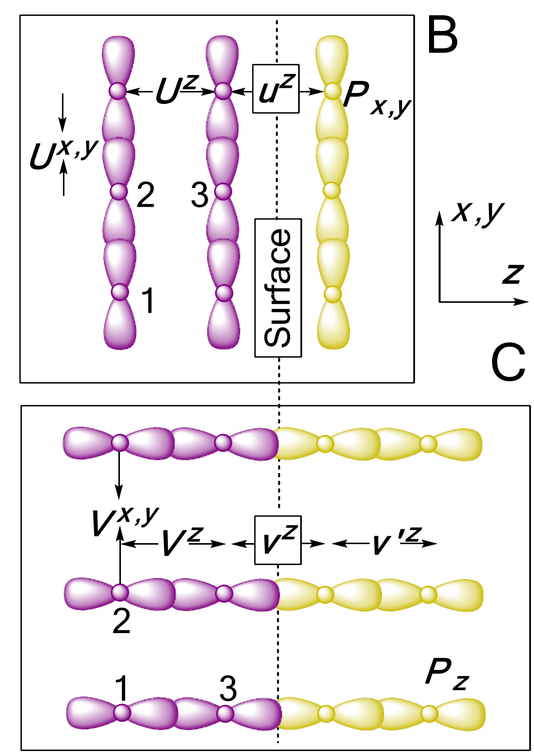


QSE对化学反应活性调制的起源

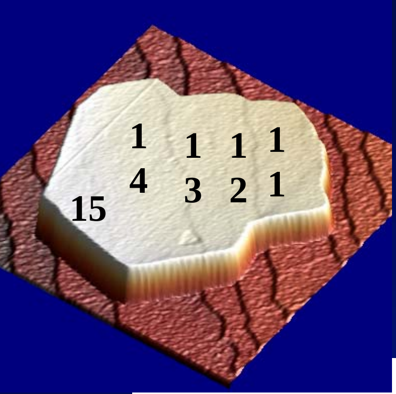
- 振荡的原因：费米能级处态密度以及电子波函数在真空衰减的快慢随膜的厚度调制而变化
- 二维薄膜原子轨道的对称性破缺决定了薄膜的量子尺寸效应及其表面活性

电子在动量空间的三维衰减图

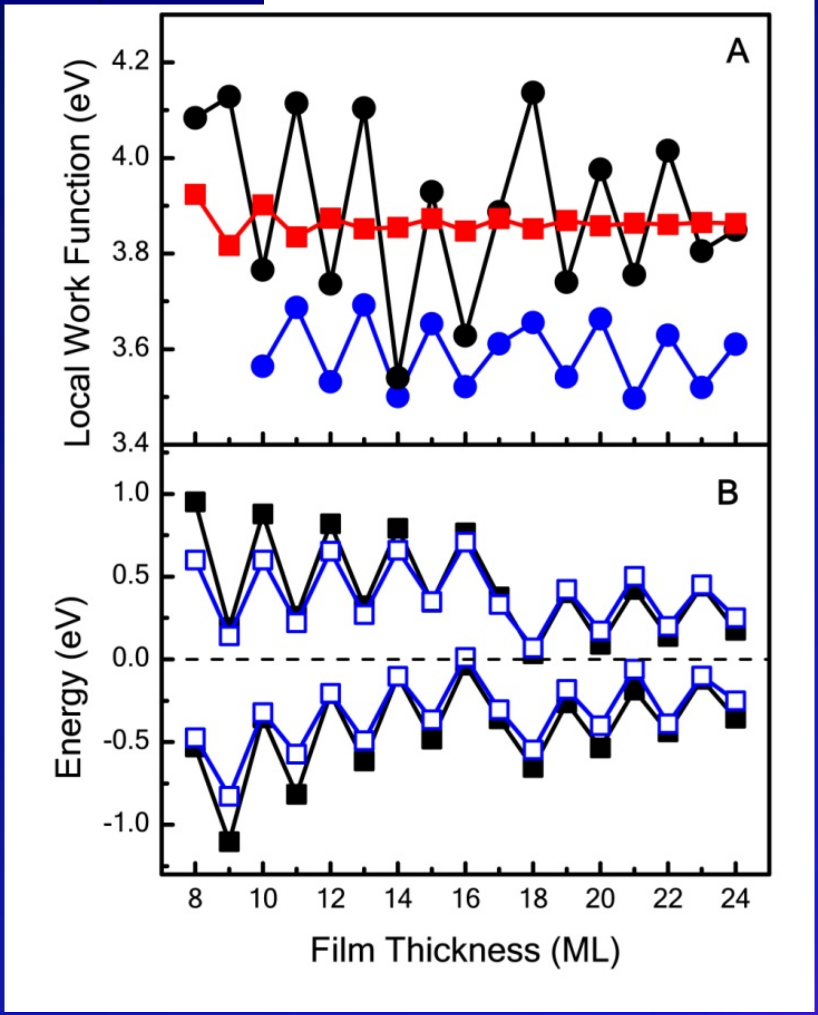


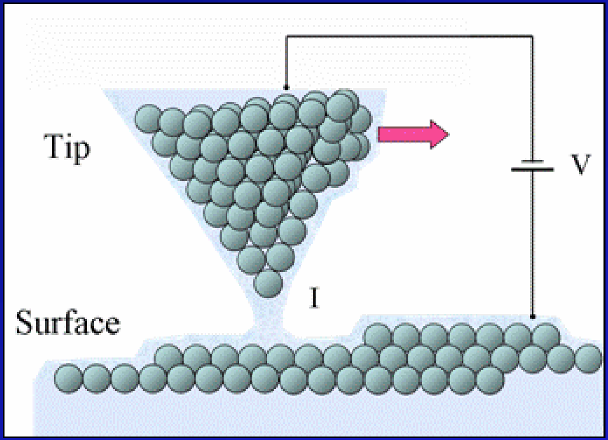


在动量空间Gamma点处电子衰减最慢，其相应的轨道对称性为P_Z轨道。



量子尺寸效应：
局域功函数 、 HOQWS & LUQWS (STM)





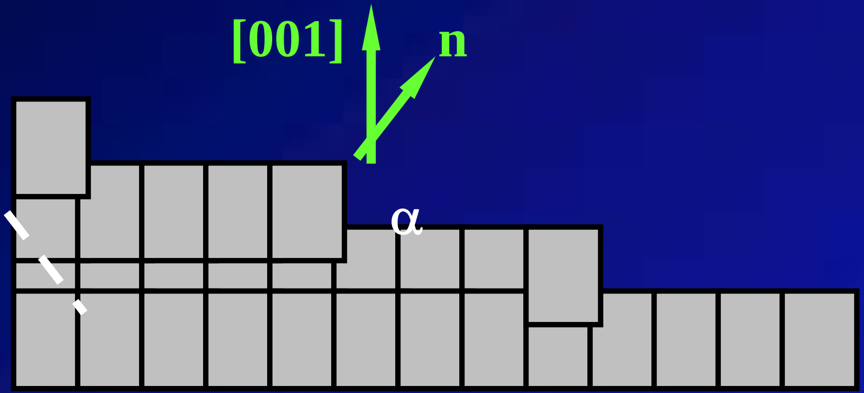
$$
\begin{aligned}
\phi_{LWF} &= 0.952\left[d\ln I/dz\right]^2 \\
&\approx 0.952\left[d\ln \rho/dz\right]^2
\end{aligned}
$$

黑色：理论
蓝色：实验

XPS + DFT

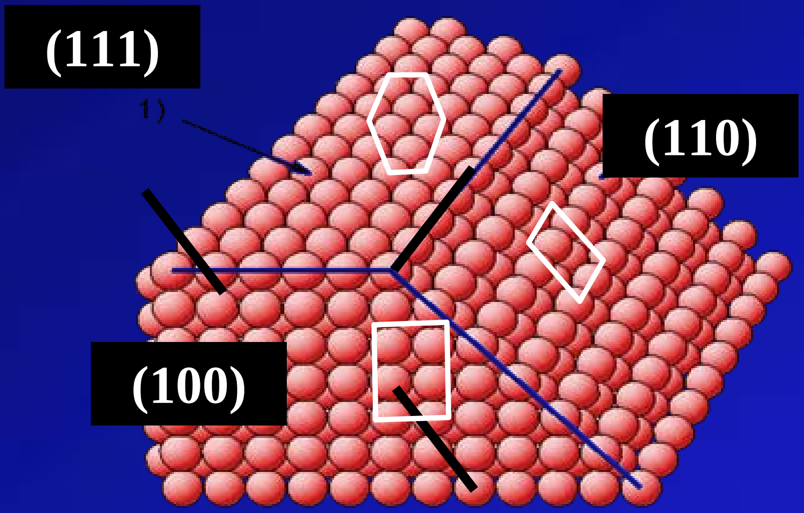
Oxidation of Pt(332) and CO Oxidation

Effect of Step Edge

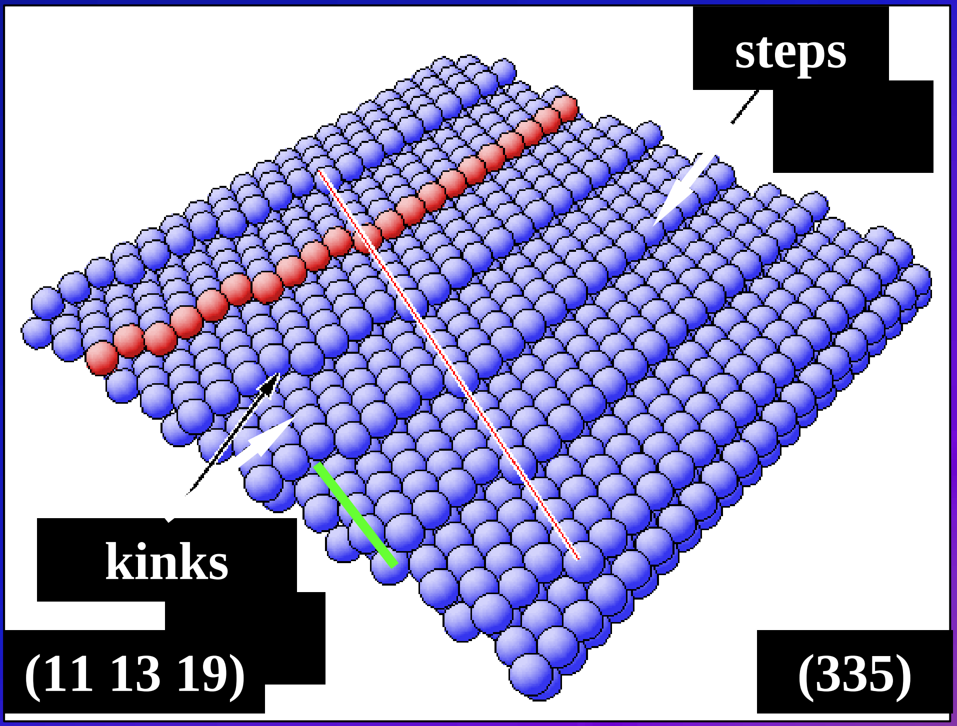


Cutting close-packed materials (fcc/hcp/bcc)

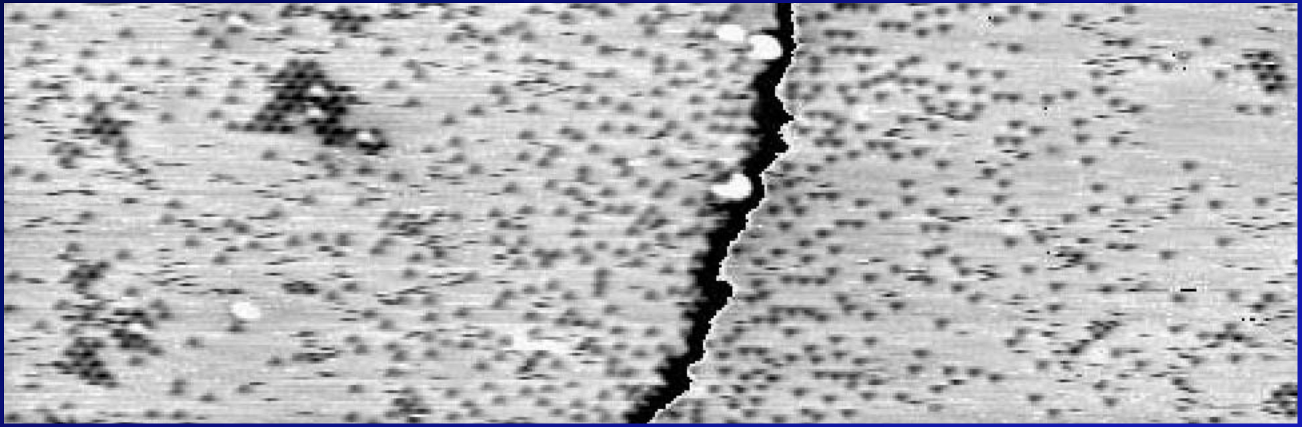
low-index surfaces



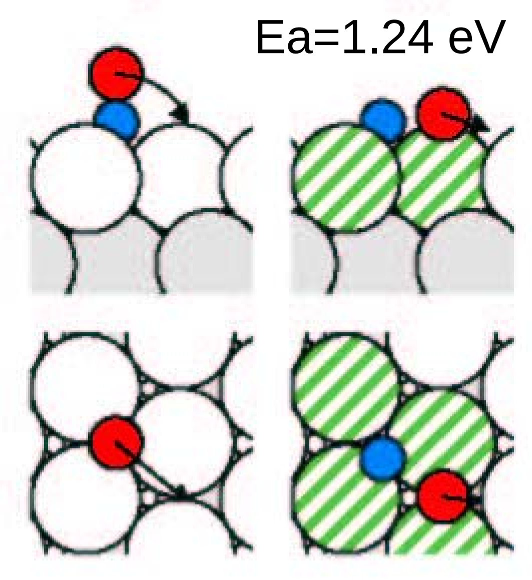
vicinal surfaces

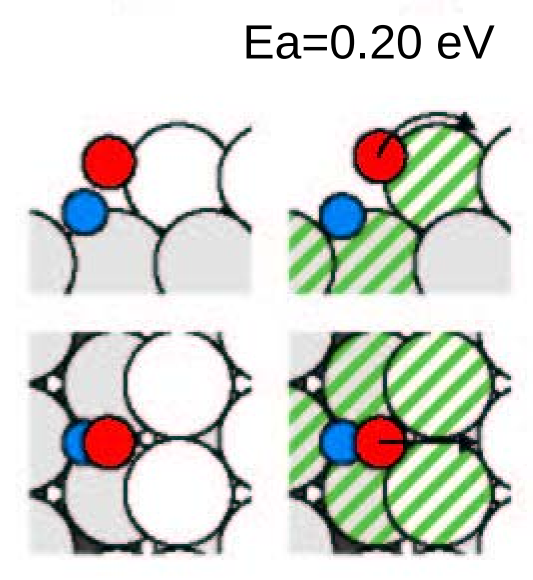


NO Dissociation at Ru Steps



T.Zambelli, J. Wintterlin, J. Trost, G. Ertl, Science **273**, 1688 (1996).

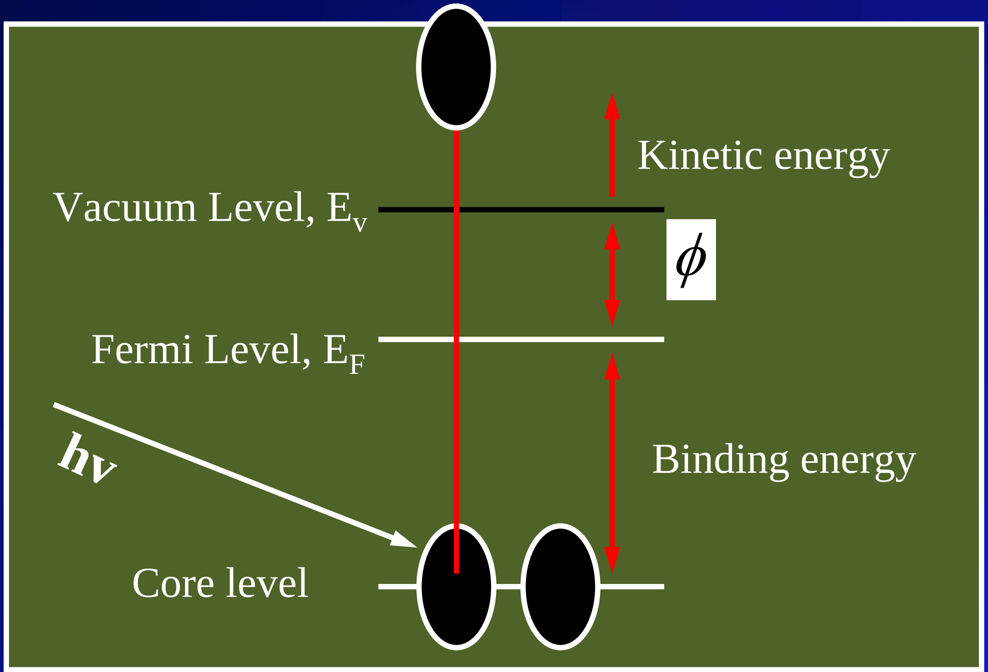




- High ε_d's at steps.
- More active metal atoms.

Hammer (1999).

X-ray Photoelectron Spectroscopy (XPS)



$$h\nu = E_{kin} + \phi + \varepsilon_c$$
$$\phi = \mathrm{E}_V - E_F$$

Core-electron Energy

$$\varepsilon_c = E(n-1) - E(n)$$

E(n) / E(n-1): total energy before / after core excited (frozen core approximation, valence electron relaxation included)

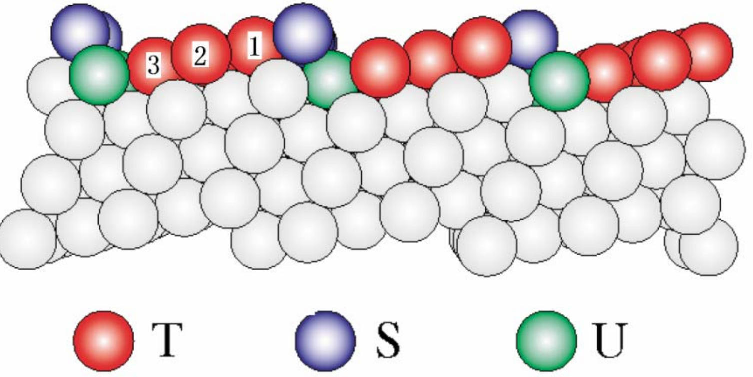
Surface Core Level Shift

$$\Delta_{SCLS} = \varepsilon_c^{surf} - \varepsilon_c^{bulk}$$

Final state effect included

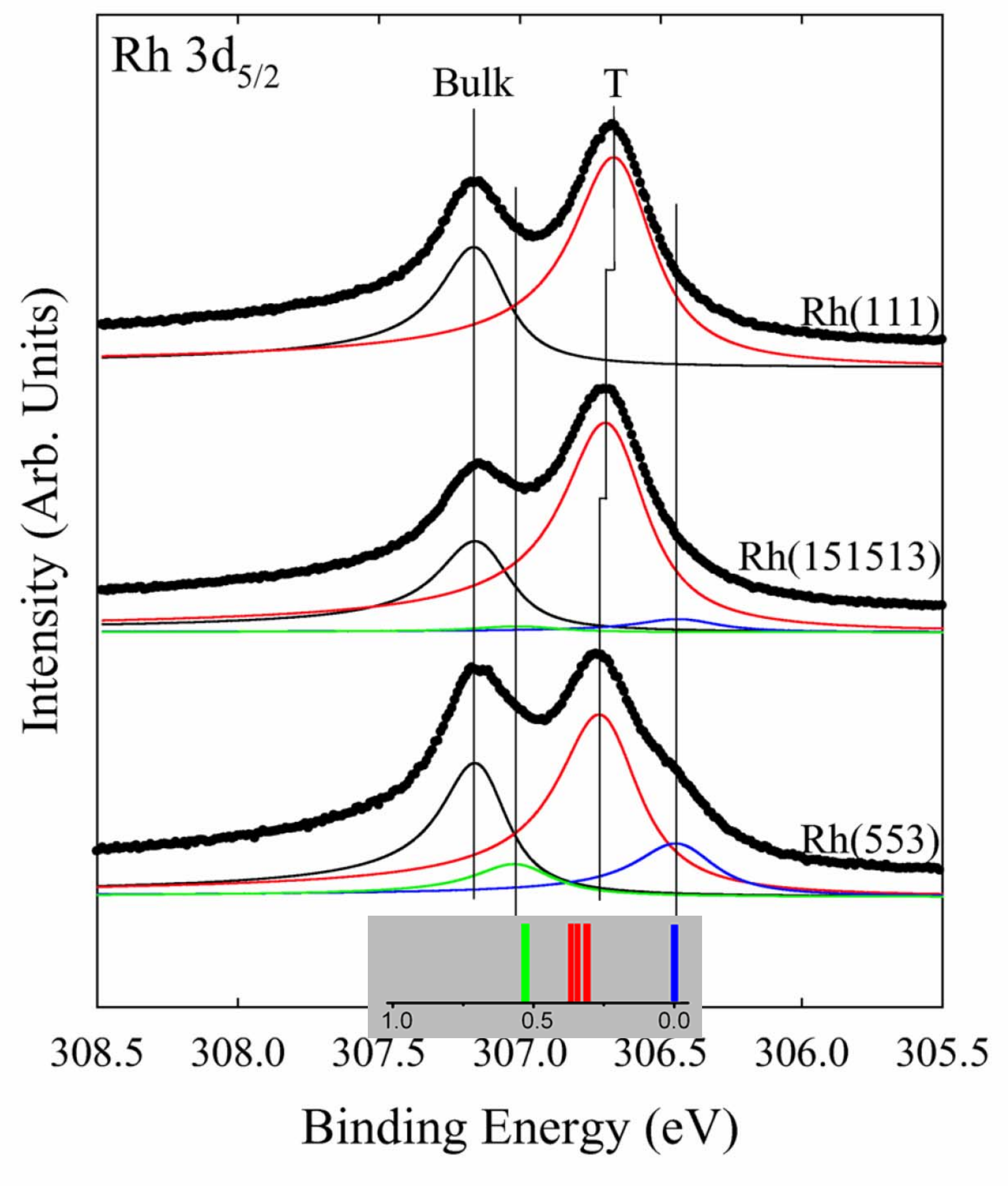
Element specific and geometric sensitive
Fingerprint as adsorption site and oxidation state

# Clean surfaces
Rh(553)



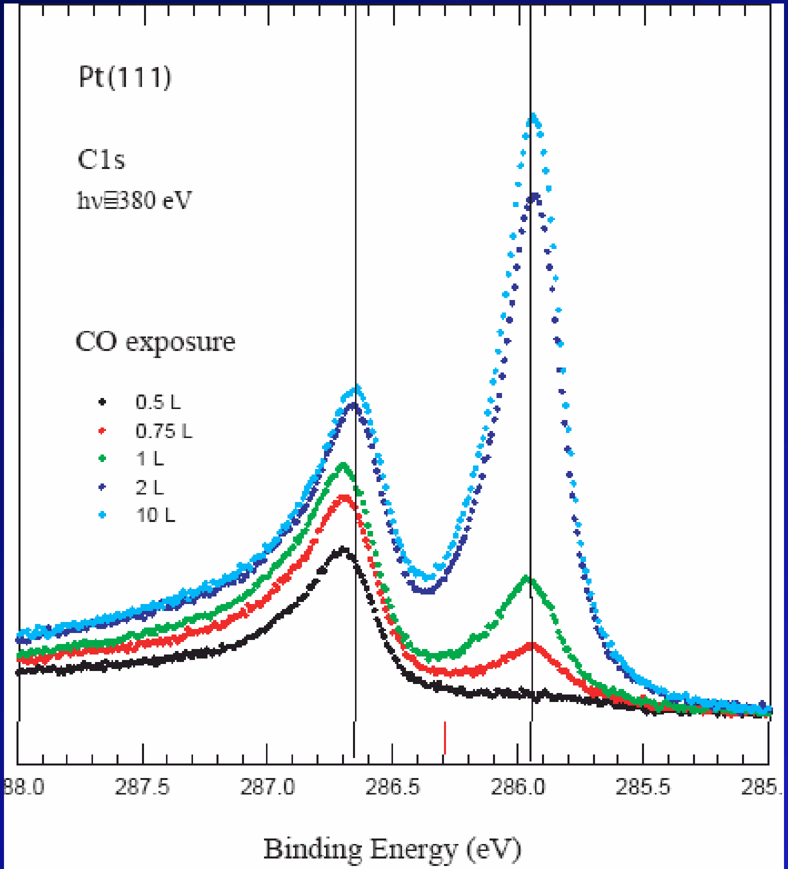
Rh 3d 5/2 from DFT

	SCLS (meV)
S	**0**
U	**530**
T-1	**310**
T-2	**350**
T-3	**370**

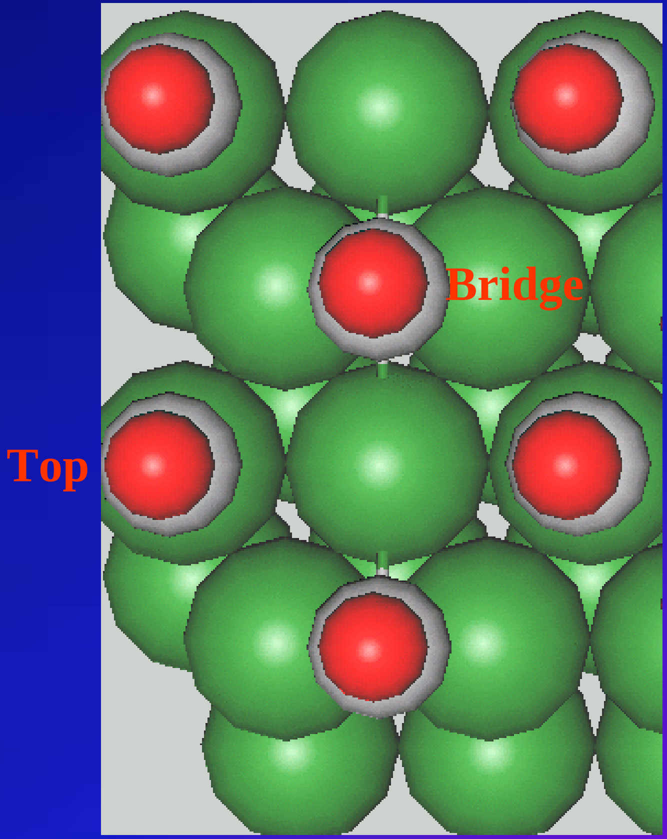


CO Adsorption on Pt(111)

Top Bridge

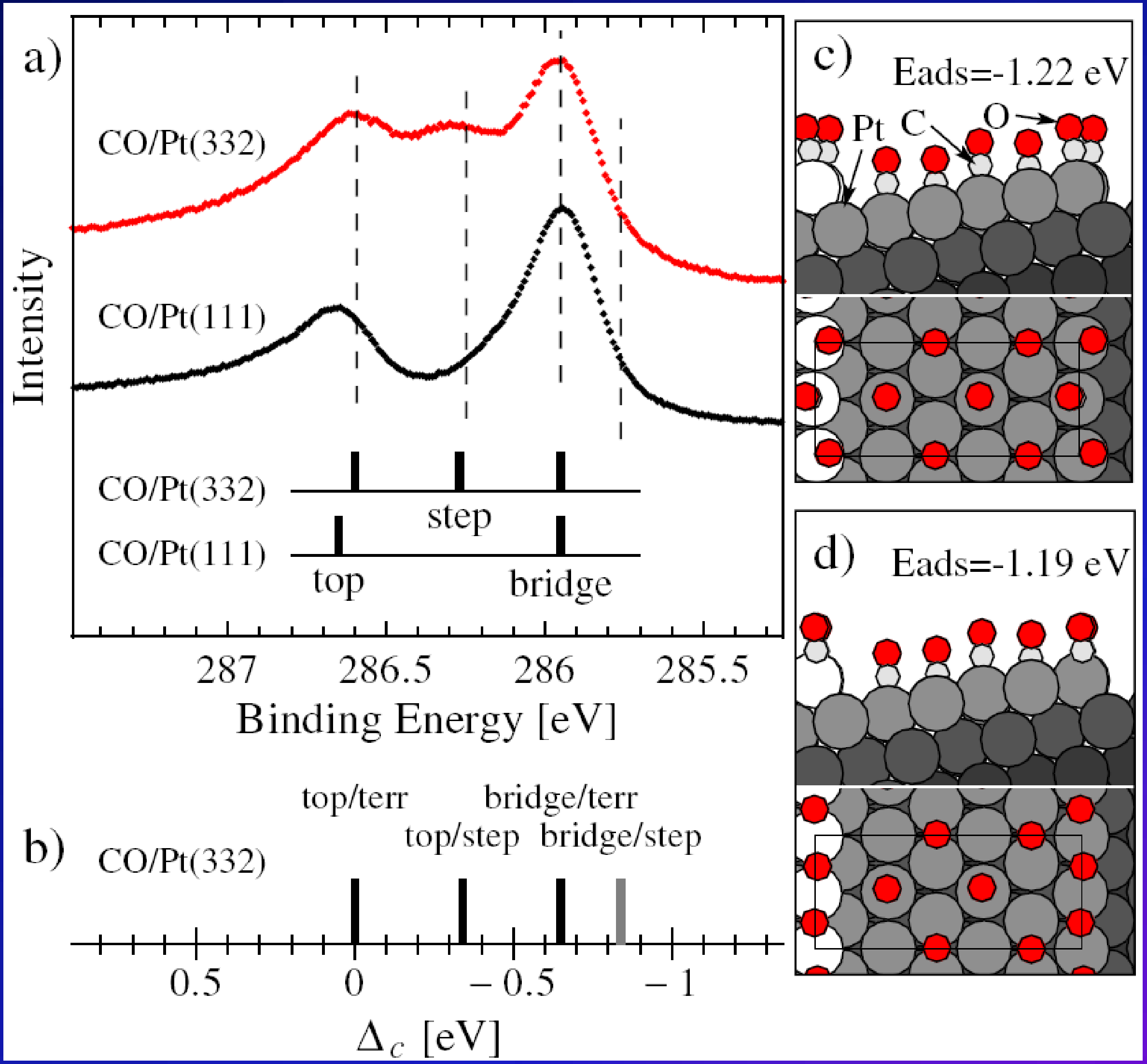


DFT Calculations



J.G. Wang, W. X. Li et al, Phys. Rev. Lett. 95, 256102 (2005)

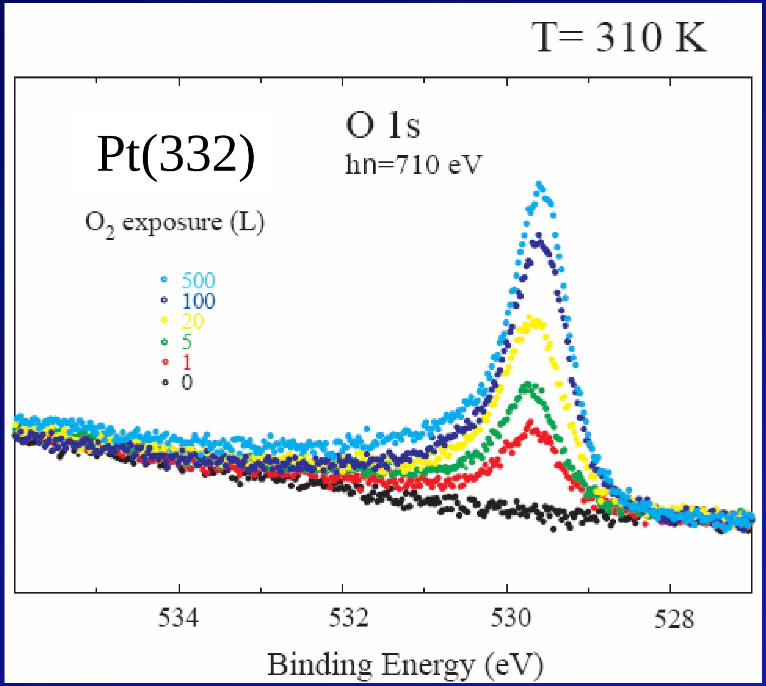
CO Adsorption on Pt(332)

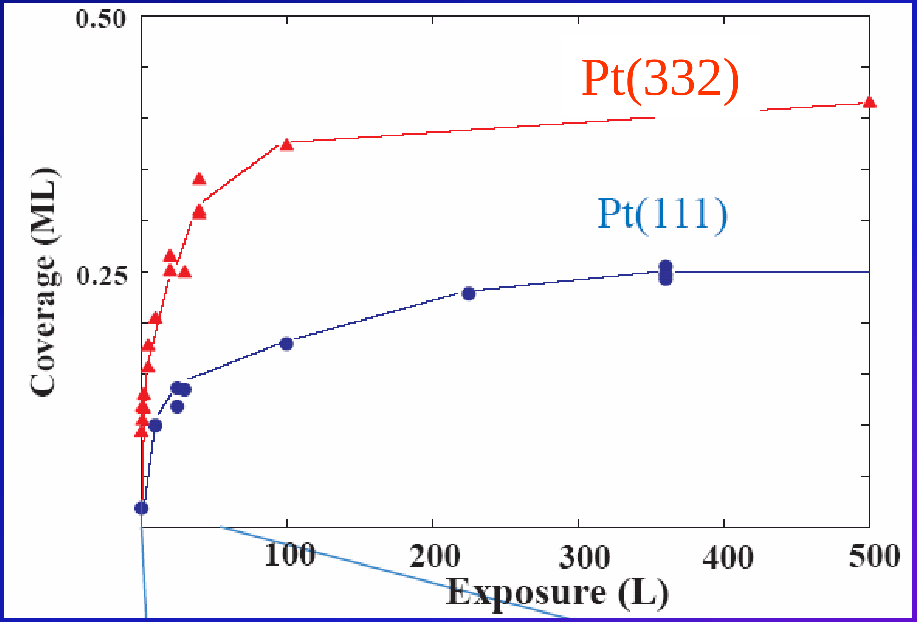


J.G. Wang, W. X. Li et al, Phys. Rev. Lett. 95, 256102 (2005)

O_2 Adsorption on Pt(332) and Pt(111)

Oxygen 1s binding energy



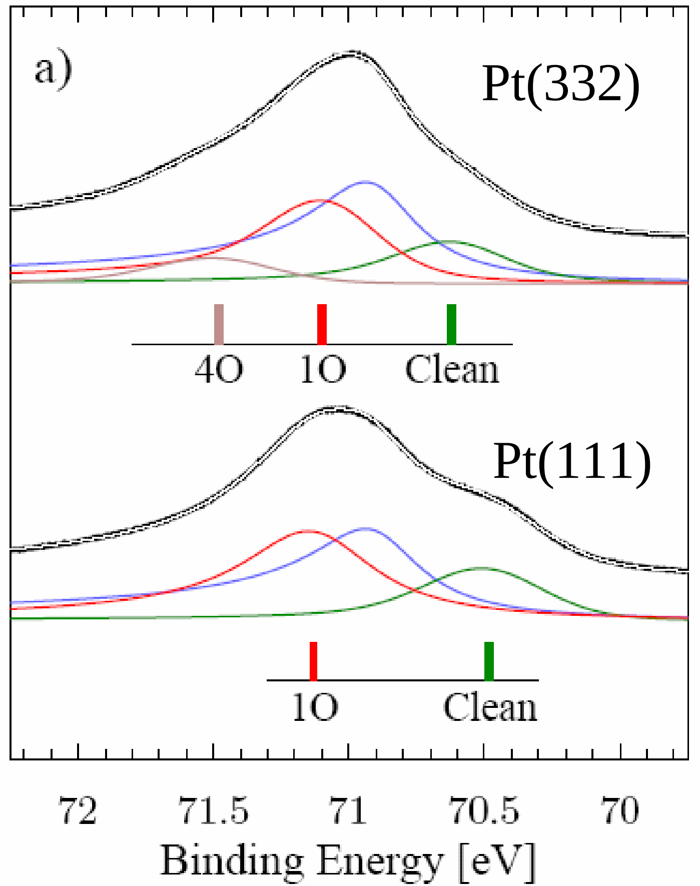


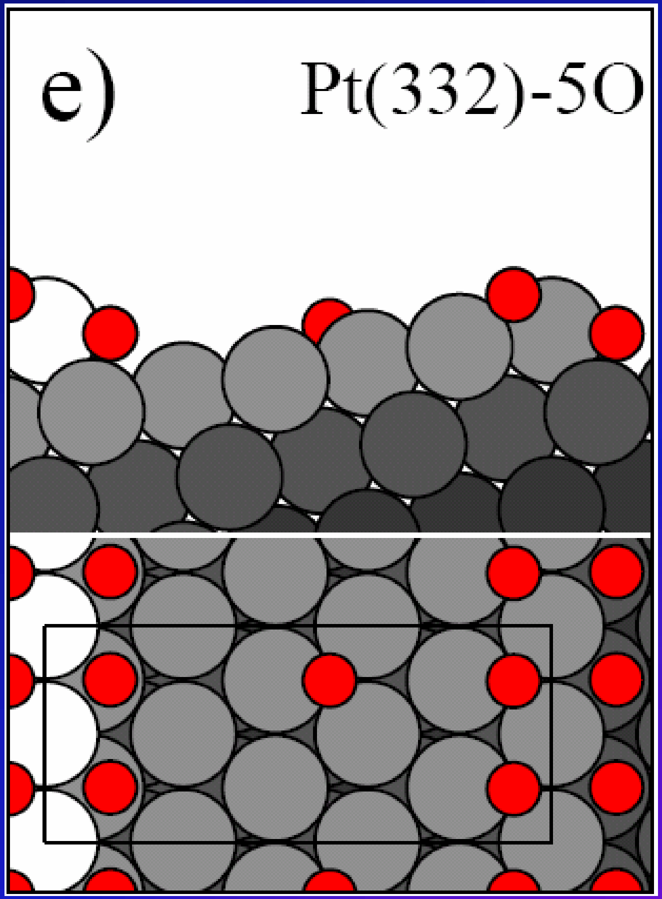
O1s binding energy:
529.75 eV for Pt(111)
529.55 eV for Pt(332)
Difference: 0.20 eV

Pt(111) saturated at 0.25 ML
Pt(332) saturated at 0.42 ML

J.G. Wang, W. X. Li et al, Phys. Rev. Lett. 95, 256102 (2005)

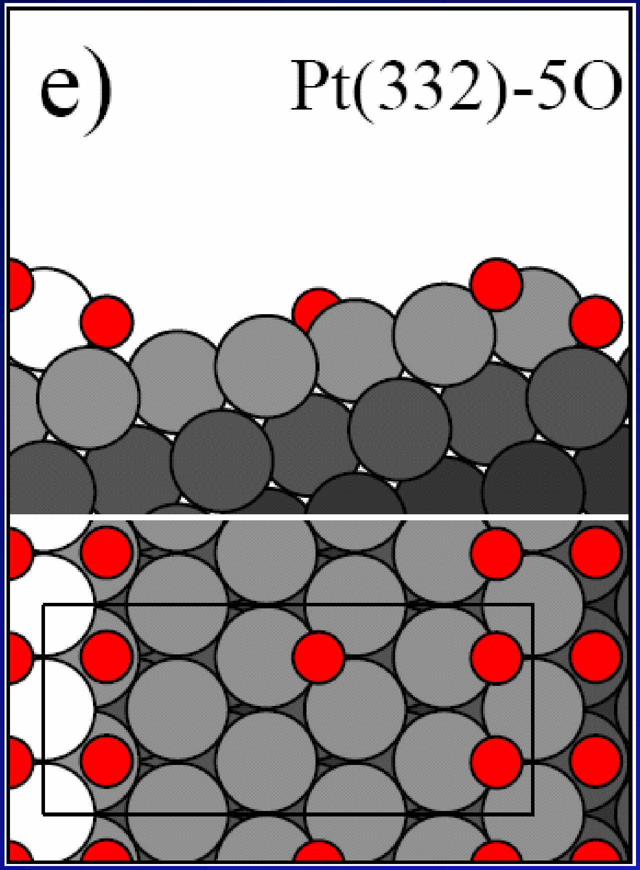
1D PtO_2 along Step Edge of Pt(332)



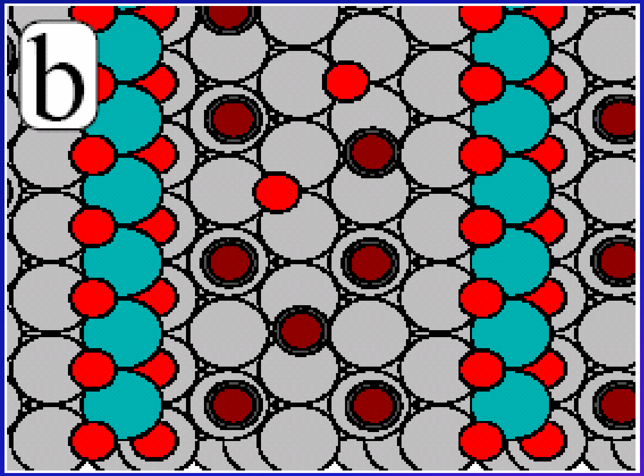


J.G. Wang, W. X. Li et al, Phys. Rev. Lett. 95, 256102 (2005)

CO Oxidation on O pre-covered Pt(332)

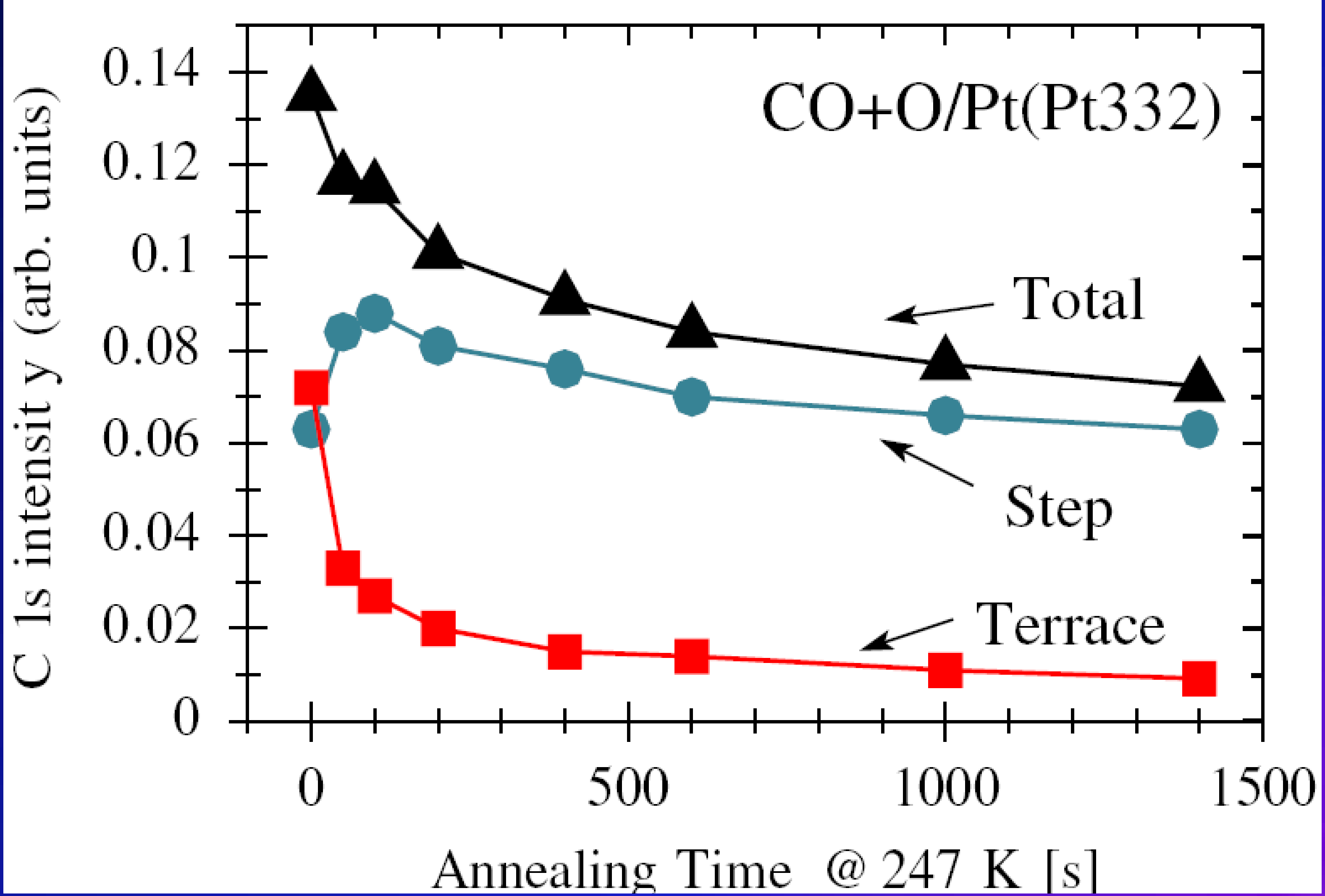


CO



reaction negligible at 220 K on Pt(332), instead of 270 K on Pt(111)

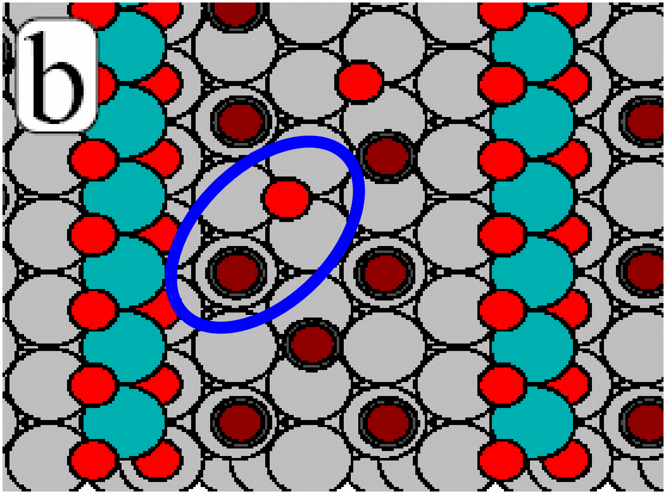
J.G. Wang, W. X. Li et al, Phys. Rev. Lett. 95, 256102 (2005)



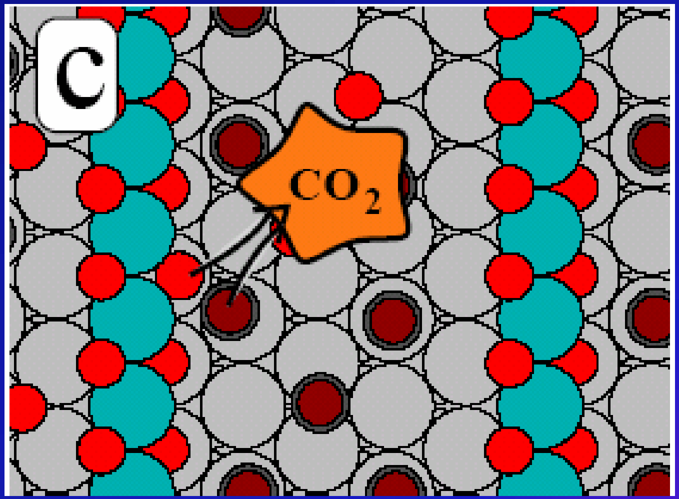
J.G. Wang, W. X. Li et al, Phys. Rev. Lett. 95, 256102 (2005)

CO Oxidation on Pt(332)

Initial State



TS



Reaction Barrier for CO oxidation:

0.60 eV for 1D PtO2 (E_b=0.77 eV for step oxygen)

0.71 eV for terrace oxygen (E_b =0.54 eV for terrace oxygen)

J.G. Wang, W. X. Li et al, Phys. Rev. Lett. 95, 256102 (2005)

DFT + Fast STM

Two step reaction on a nanostructured surface: (10×2)-O/Rh(110)

high local oxygen coverage

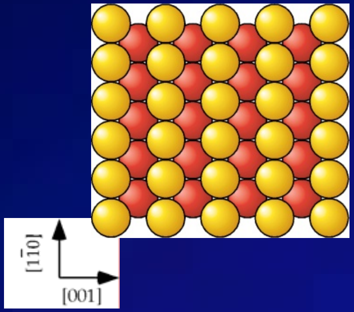
strained

nanostructured

C. Africh, F. Esch, W. X. Li, M. Corso, B. Hammer, R. Rosei, and G. Comelli1,
Phys. Rev. Lett. 93, 126104 (2004)

Formation of the (10×2) structure

(1×1)

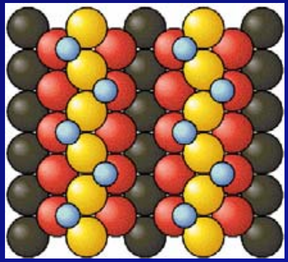


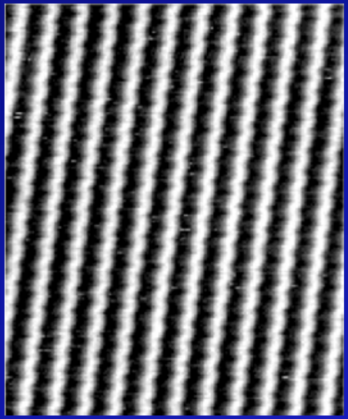
+0.5ML O

→

T>100° C

(2×2)p2mg





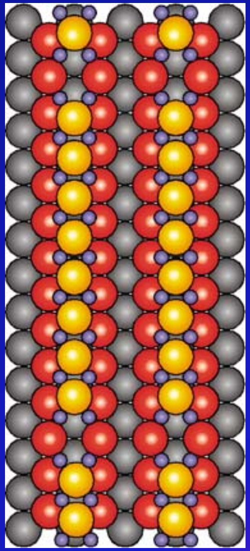
8×9 nm²

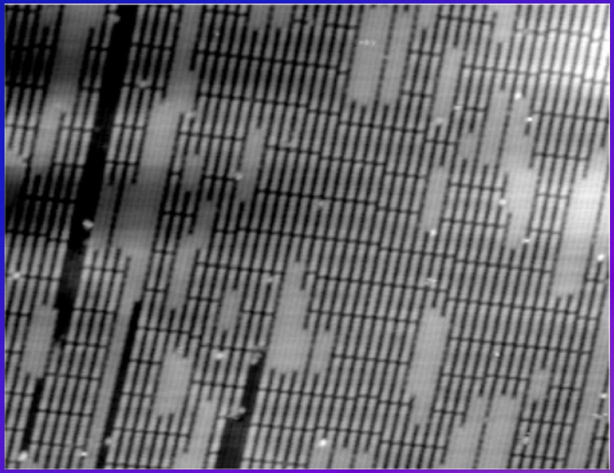
29L O_2 (200K)

→

annealed
to 530 K

(10×2)

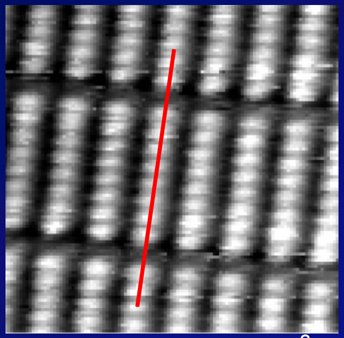




40×30 nm²

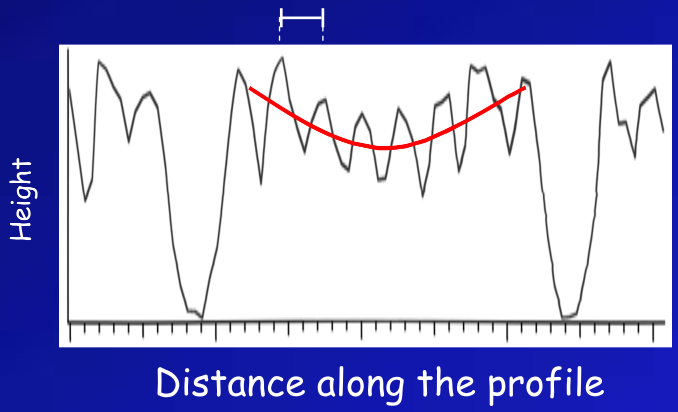
- (1×2) *missing row*
- O *threefold* in *zig-zag*

Characteristics of the (10×2) structure

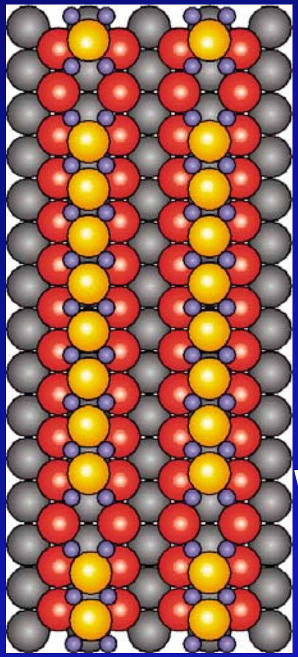


53×53 Å^2

3.0 Å instead of 2.7 Å



(10×2)



- *strained nanostructure*

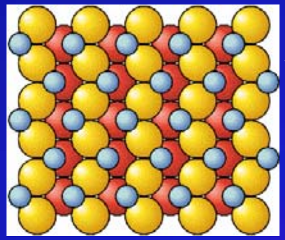
  increased Rh-Rh dist. (11%)

  2 Rh atoms out of 10 ejected

- reconstructed areas

  +

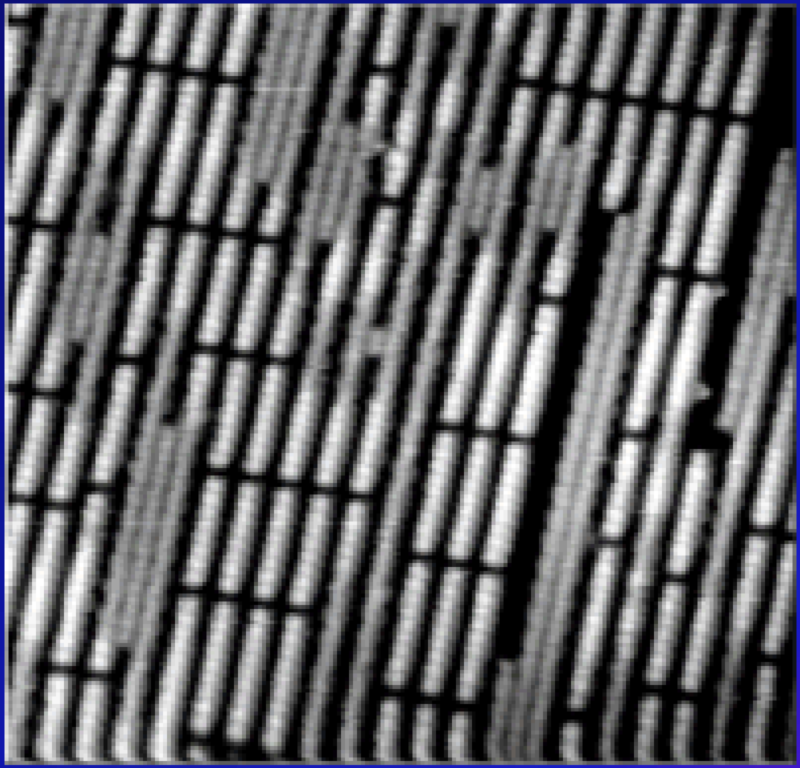
  unreconstructed areas covered by (2×1)p2mg-O



(2×1)p2mg

Two-Step Reaction

Room temperature, partial pressure of H_2: 10^{-8} mbar



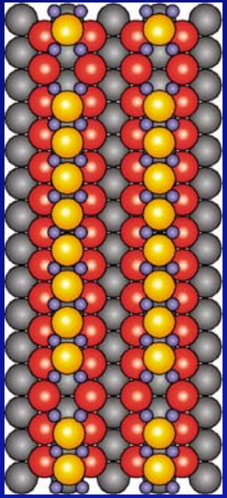
$40 \times 30 nm^2$

Acquisition time: 35 s per image

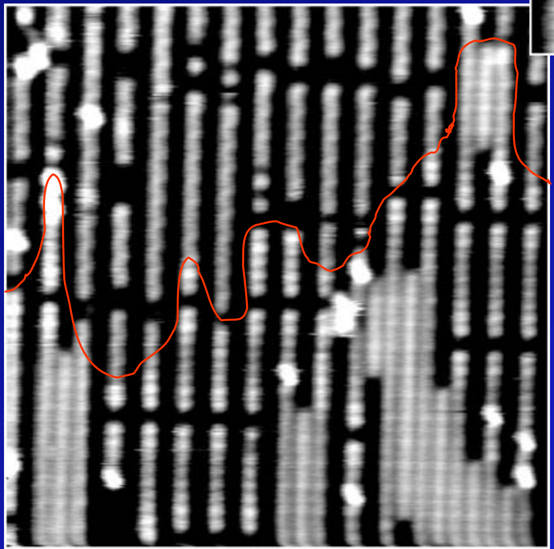
1st-step reaction

Initial surface: (10x2)

150 x 150 Å²



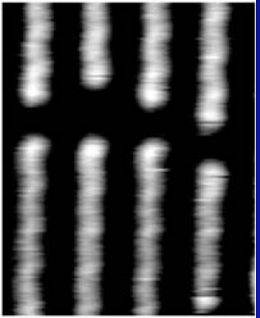
Distance between the segments increased: no more strain!



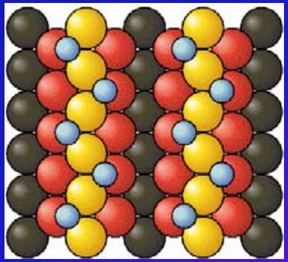
1^{st} oxygen removal:

- reaction front
- zig-zag oxygen left
- strain removal

40 x 50 Å²



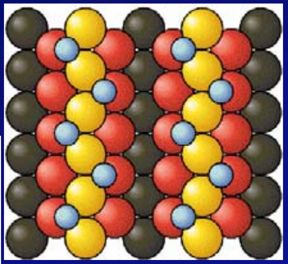
Zig-zaged appearance due to oxygen in threefold sites



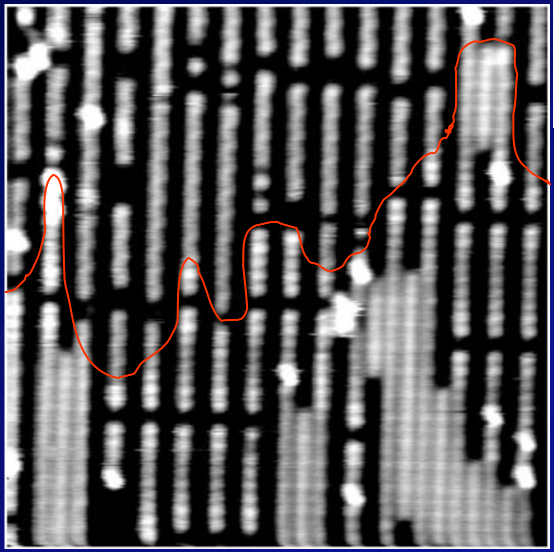
(2×2)p2mg segmented

2nd-step reaction

(2×2)p2mg
segmented

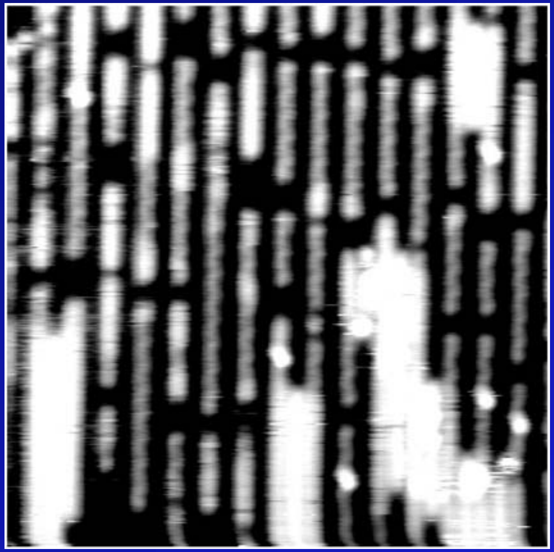


Brighter areas
where zig-zag
oxygen reacted
off



1^{st} oxygen removal:

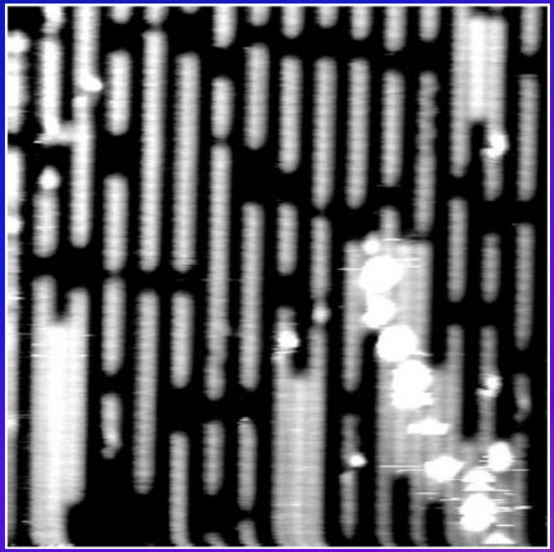
- reaction front
- zig-zag oxygen left
- strain removal



2^{nd} oxygen removal:

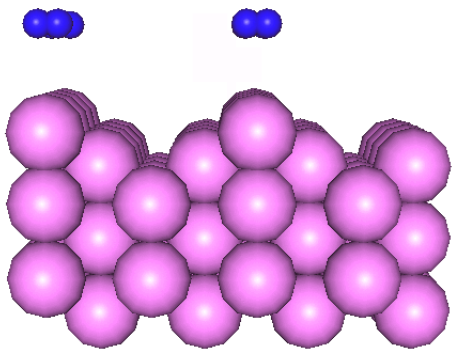
- homogeneous nucleation

150 x 150 Å²

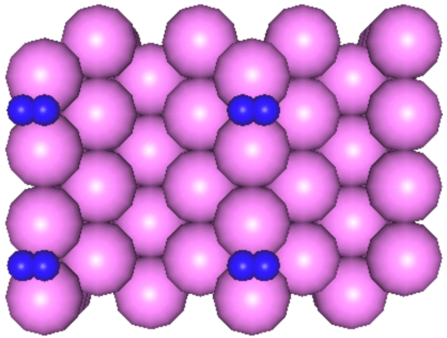


Final surface: clean,
segmented (1x2)

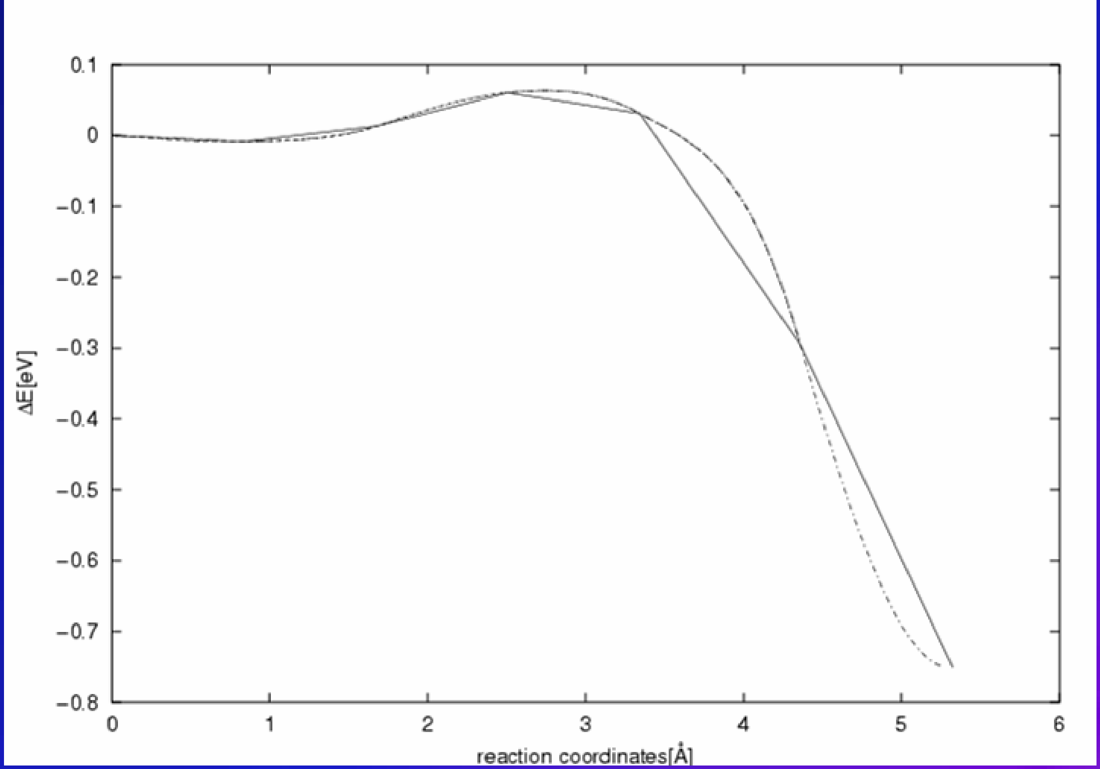
H_2 Dissociation on Rh(110)-(1x2)
Barrier: 0.09 eV



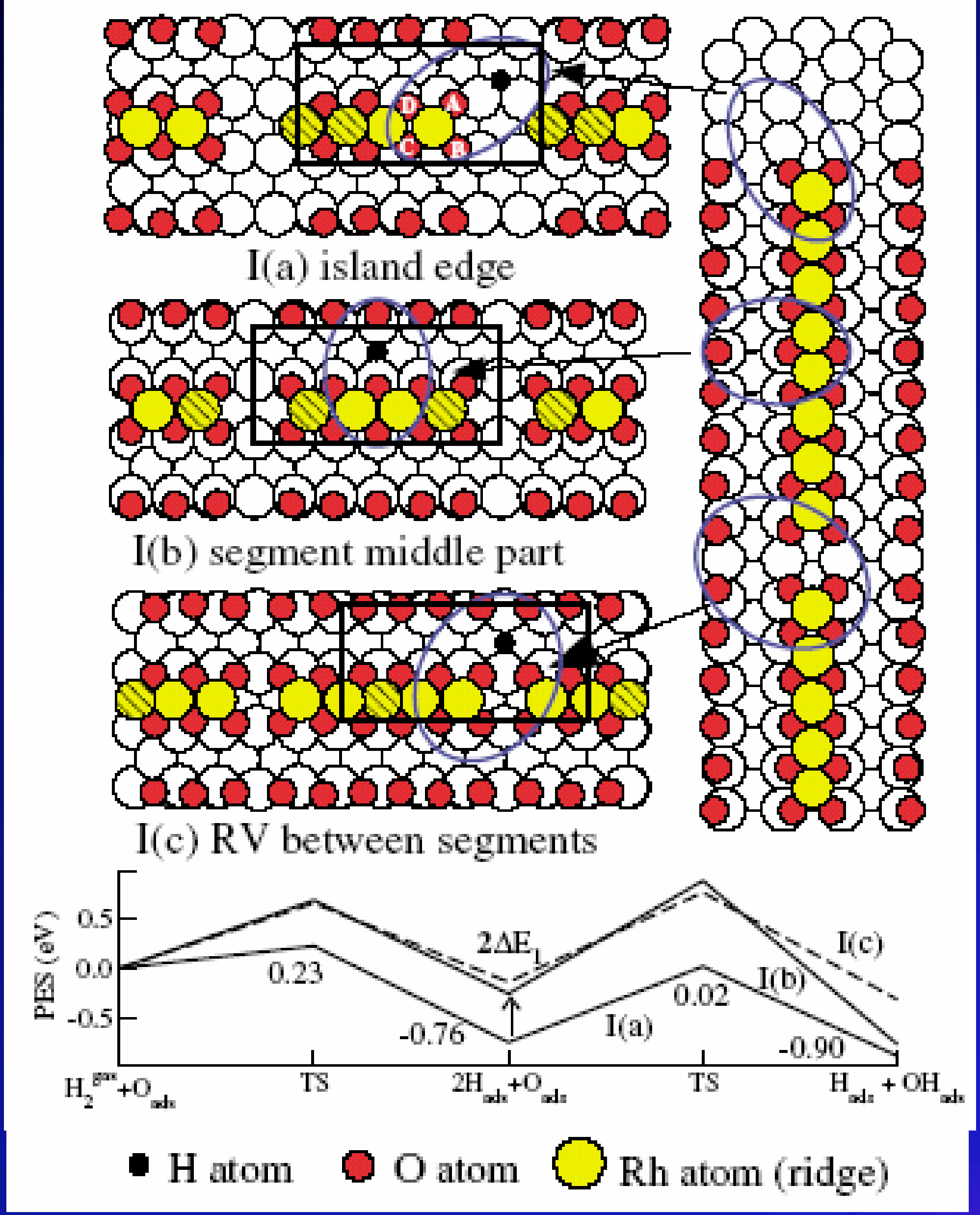
Side view



Top view

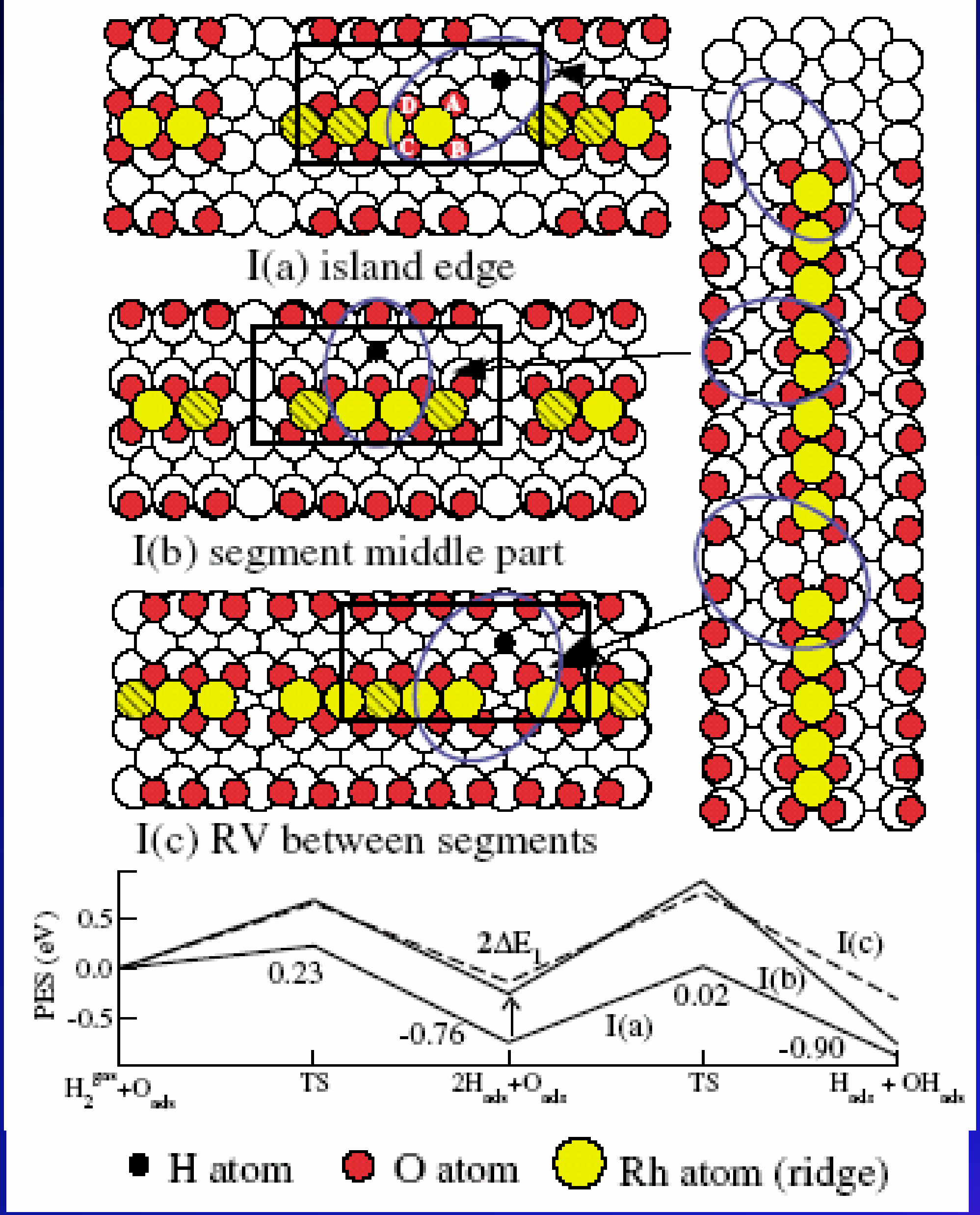


1st Step eaction



H_2 dissociation barrier:

- island edge: 0.23 eV
- middle part and RV between segments: larger than 0.67 eV



1st Step eaction

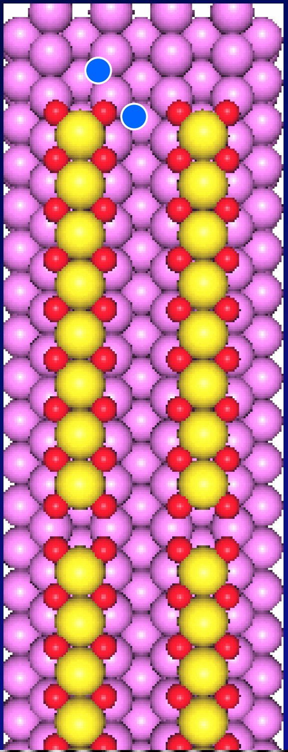
H_2 dissociation barrier:

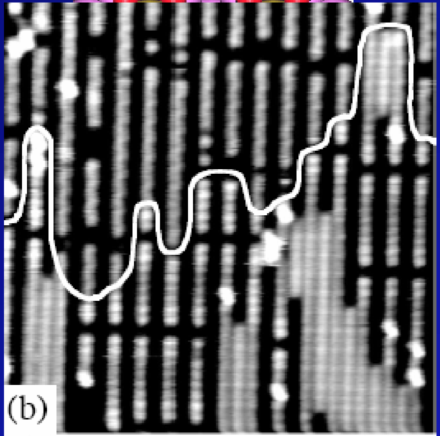
- island edge: 0.23 eV
- middle part and RV between segments: larger than 0.67 eV

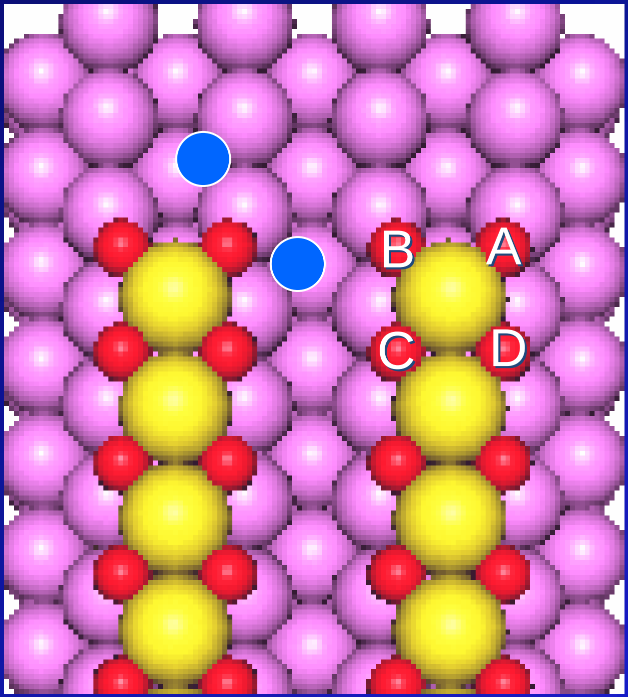
OH formation barrier:

- island edge: 0.78 eV
- middle part and RV between segments: 0.92 eV and 1.16 eV

Wavefront Formation





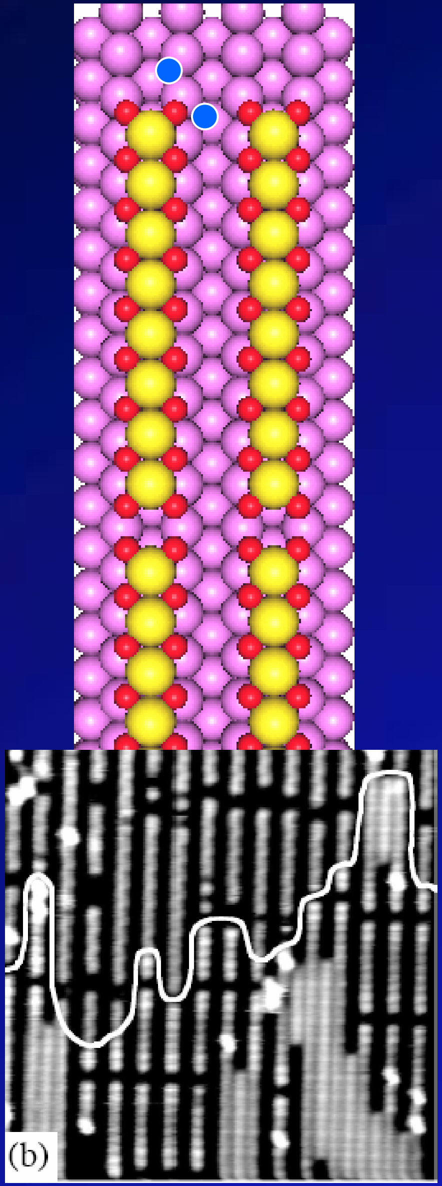


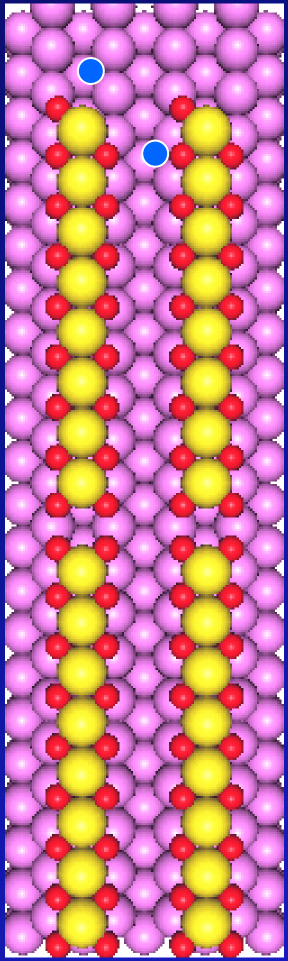
O’s Stability:

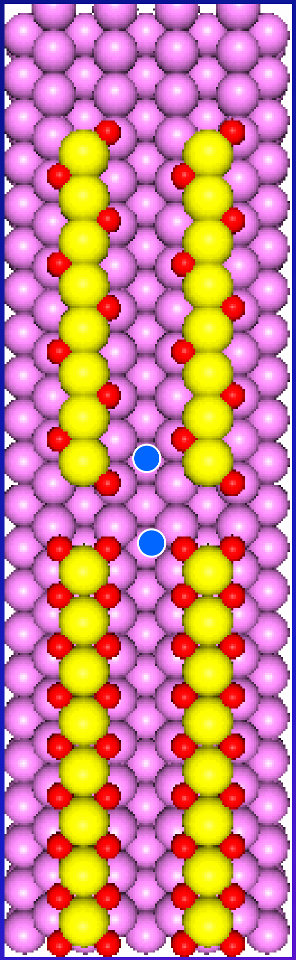
- Site A: 1.85 eV
- Site B: 1.85 eV
- Site C: 1.36 eV
- Site D: 1.98 eV

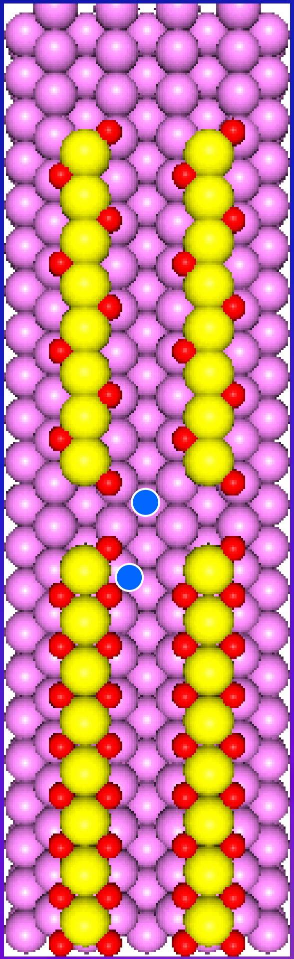
zig-zag structure preferred

Wavefront Formation

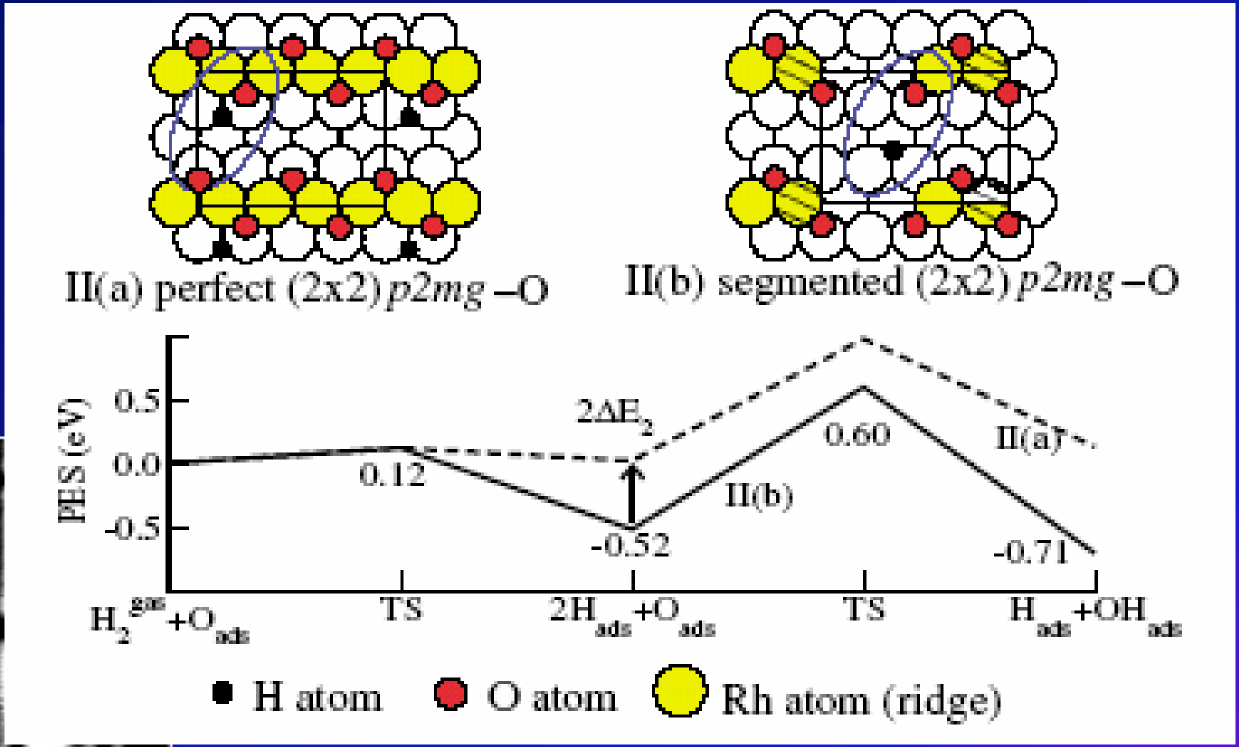








2nd Step Reaction



2nd oxygen removal:
- homogeneous nucleation

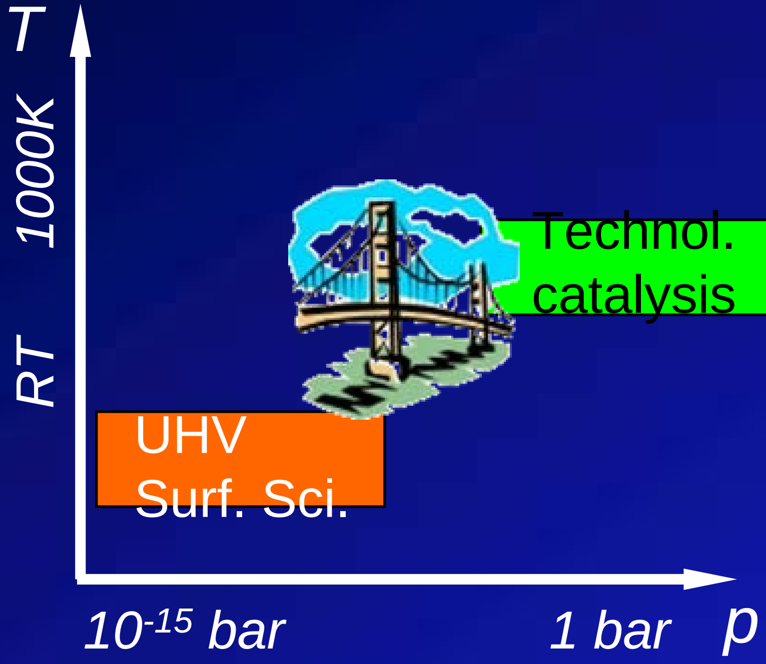
H2 dissociates barrier: 0.12 eV

H atom can only adsorb between the ridge

Bridge “pressure” and “materials” gap

First-principles, atomistic thermodynamics

Pressure / materials gap



T

1000K

RT

Technol. catalysis

UHV Surf. Sci.

10^{-15} bar

1 bar

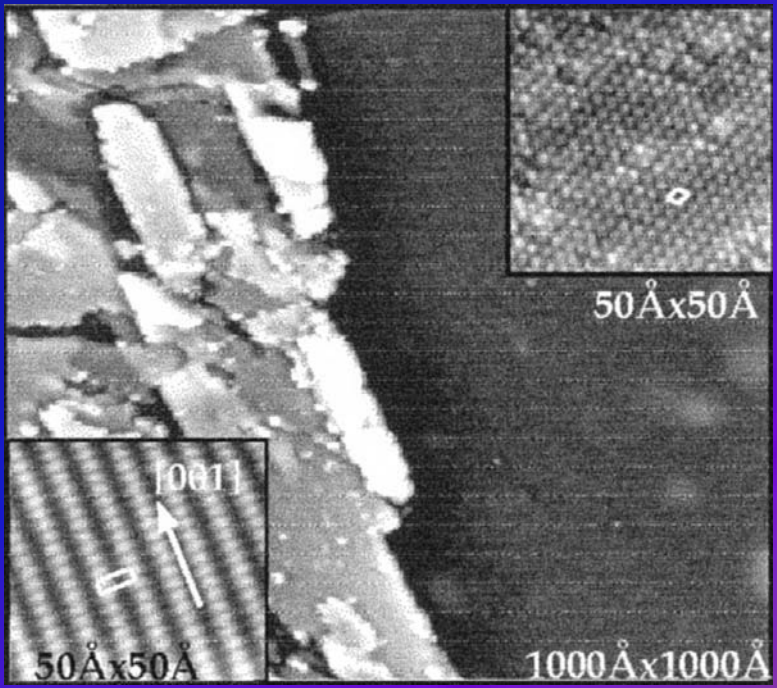
p

Low vs. high temperatures

Finite dosage vs. gas phase reservoir

Oxidation catalysis:

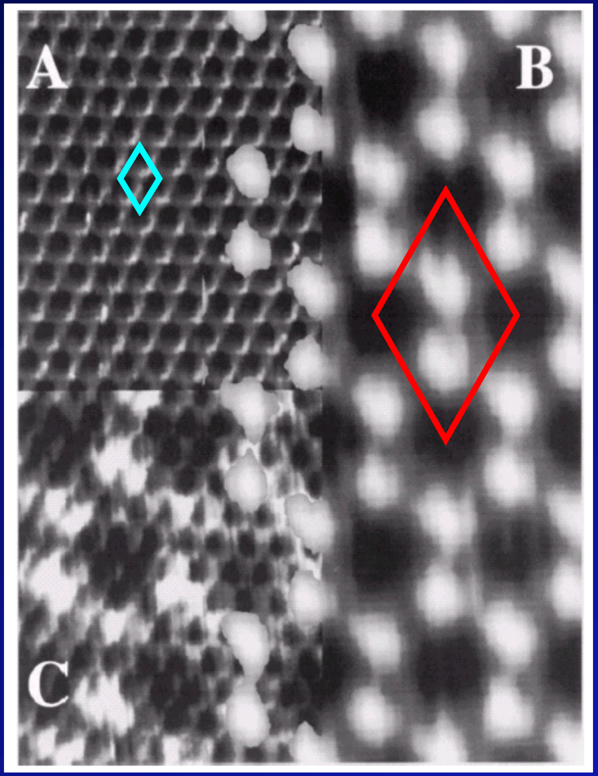
possible oxide formation at the catalyst surface

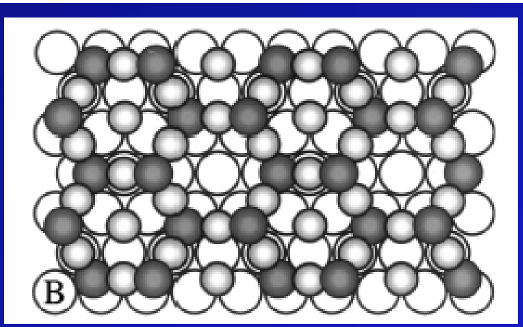


H. Over *et al.* , Science 287, 1474 (2000)

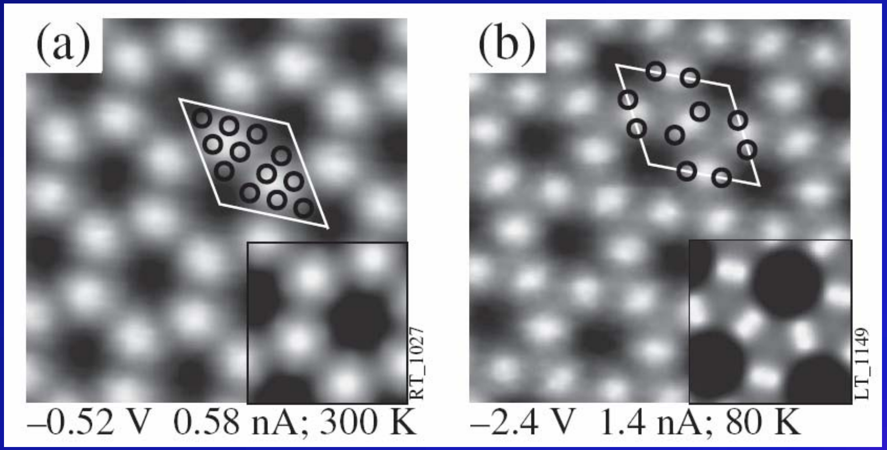
Ordered Structures: O/Ag(111)

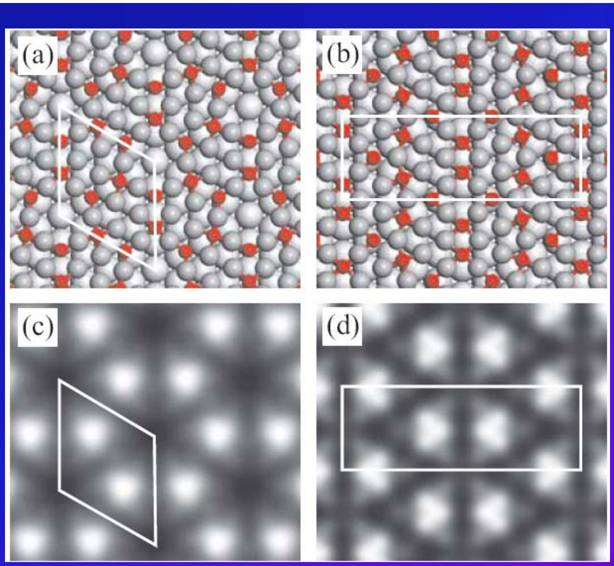
(4x4)-O *(Carlisle et al, PRL, 2000)*





Schmid et al, Phy. Rev. Lett. 96, 146102 (2006)

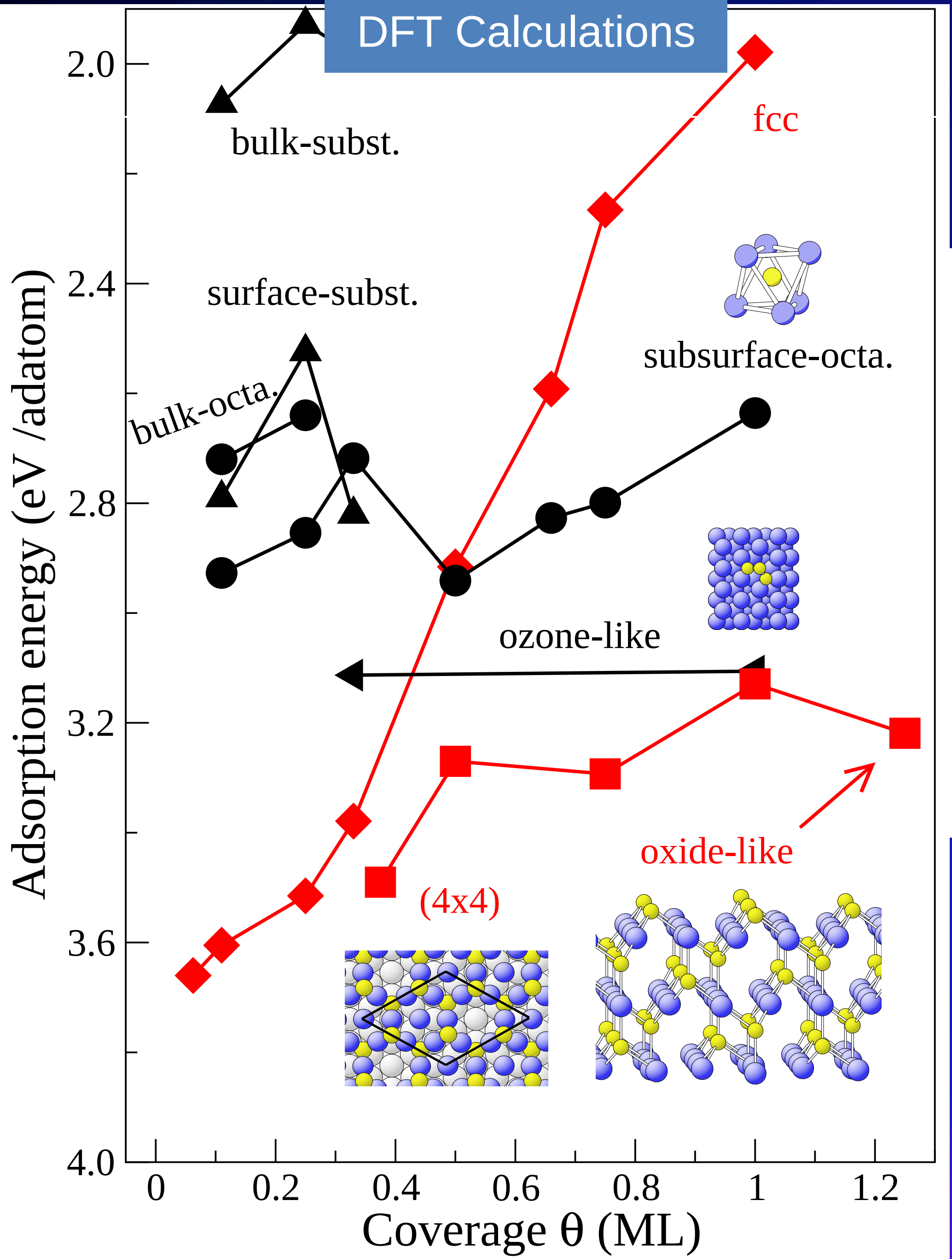




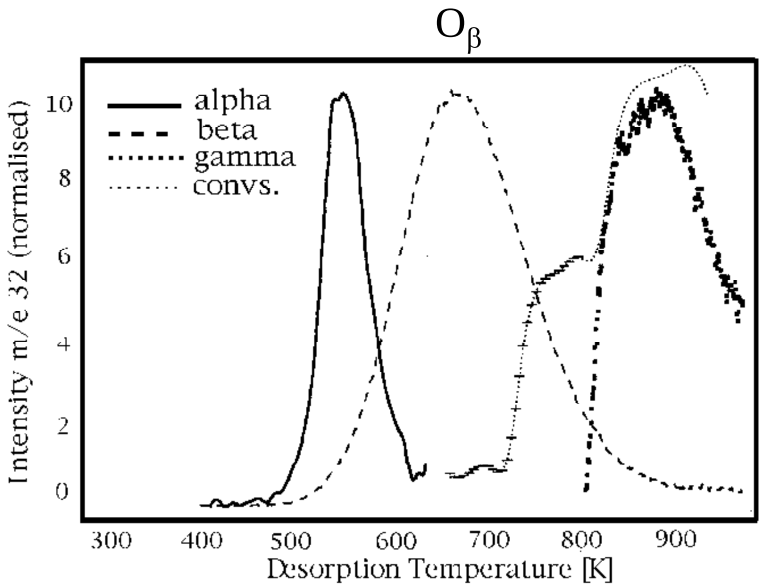
Schnadt et al, Phy. Rev. Lett. 96, 146101 (2006)

The Role of the O-Ag Interaction in the function of Silver as an Oxidation Catalyst

DFT Calculations



$C_2H_4 + \frac{1}{2}O_2 \rightarrow C_2H_4O$



Herein and Bao et al, Zeit. Phys.,1996

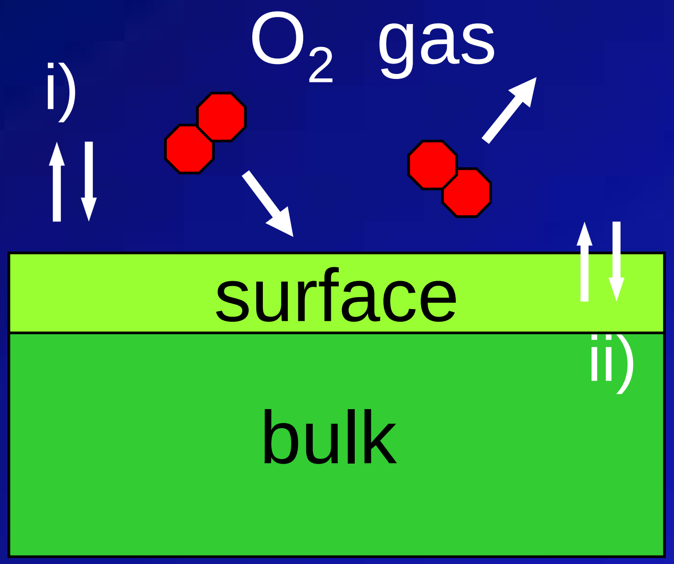
Active oxygen and Structure is missing

W. X.Li et al.,
Phys. Rev. B, 68, 165412 (2003),
Phys. Rev. B. 67, 045408 (2003),
Phys. Rev. B, 65, 075407 (2002)

From UHV to Real World (Theoretical Recipes)
Ab initio atomistic thermodynamics

Gibbs Formation Energy of Adsorption

$$G = 1/A \left[G_{\text{surf.}}(N_O, N_M) - N_O\,\mu_O - N_M\,\mu_M \right]$$



Use reservoirs:

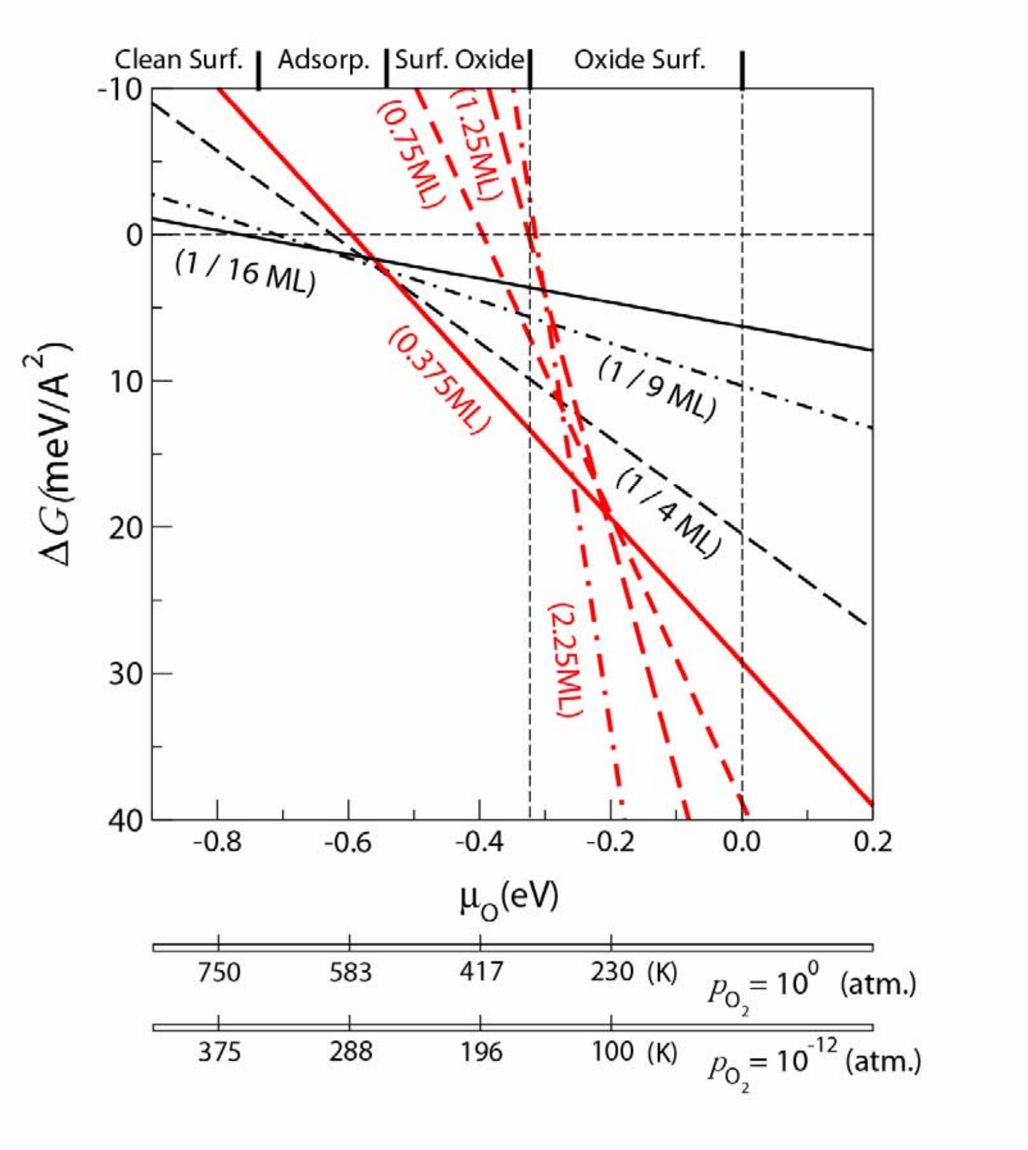
i) μ_O from ideal gas

ii) $\mu_M = g_M^{\text{bulk}}$

Forget about F^{vib} and F^{conf} for the moment:

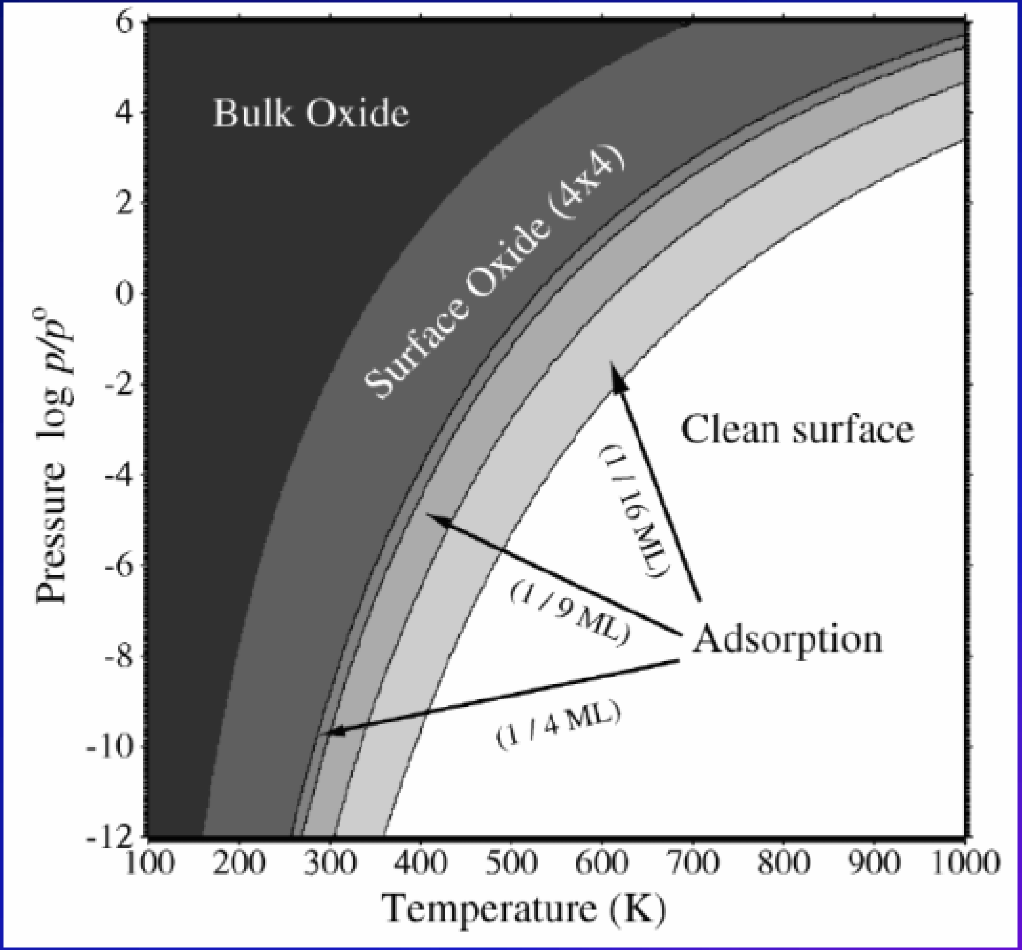
$$\boxed{\gamma(T,p) \approx \left(E^{(\text{slab})}_{\text{surf.}} - N_M\,E^{\text{bulk}}_M \right)/A - N_O\,\mu_O(T,p)\,/A}$$

Average Gibbs free energy of adsorption



W. X. Li et al. Phys. Rev. Lett. 90, 256102 (2003)

Pressure – Temperature Phase Diagram: O/Ag(111) bases on ab initio atomistic thermodynamics



W. X. Li et al. Phys. Rev. Lett. 90, 256102 (2003)

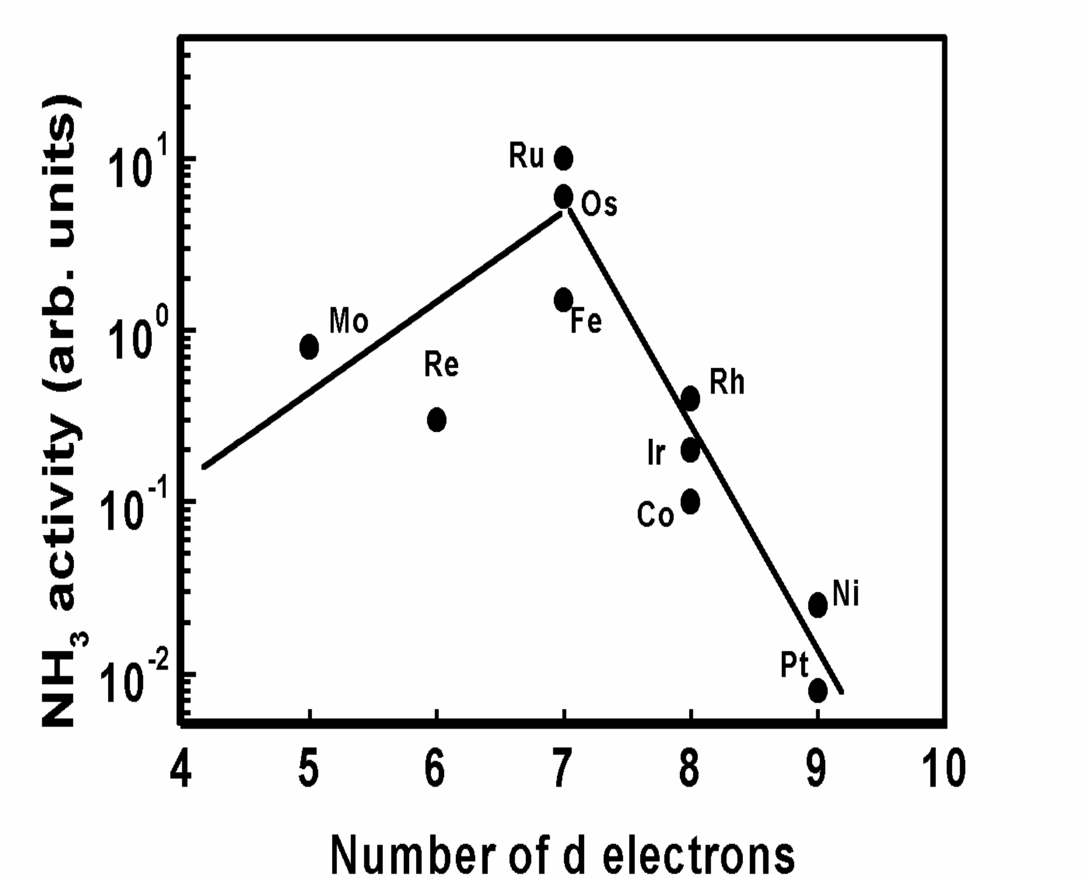
Can DFT do more than we expect ?

Ammonia Synthesis from First Principles Calculations

Honkala et al. Science **307**,555 (2005)

Catalytic ammonia synthesis

$N_2 + 3H_2 \rightarrow 2NH_3$



Ozaki and Aika, *Catalysis* **1** (Anderson and Boudart, Ed.)

Reaction mechanism

Reaction mechanism

Rate-limiting step

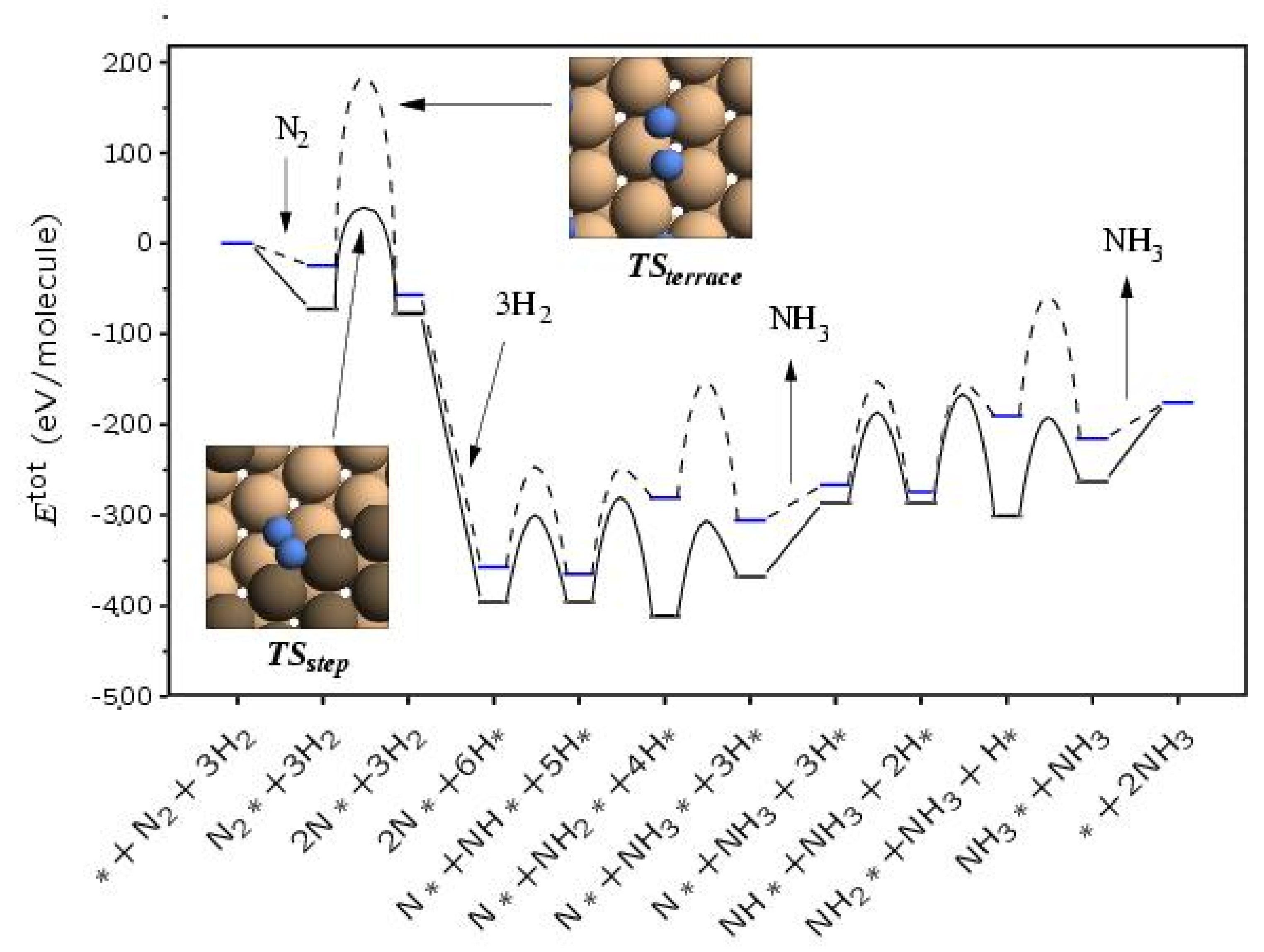
$$N_2 + 2* \rightarrow 2N*$$

At equilibrium

$$\left\{\begin{array}{l} N* + H* \leftrightarrow NH* + * \\ NH* + H \leftrightarrow NH_2* + * \\ NH_2* + H* \leftrightarrow NH_3* + * \\ NH_3* \leftrightarrow NH_3 + * \\ H_2 + 2* \leftrightarrow 2H* \end{array}\right.$$

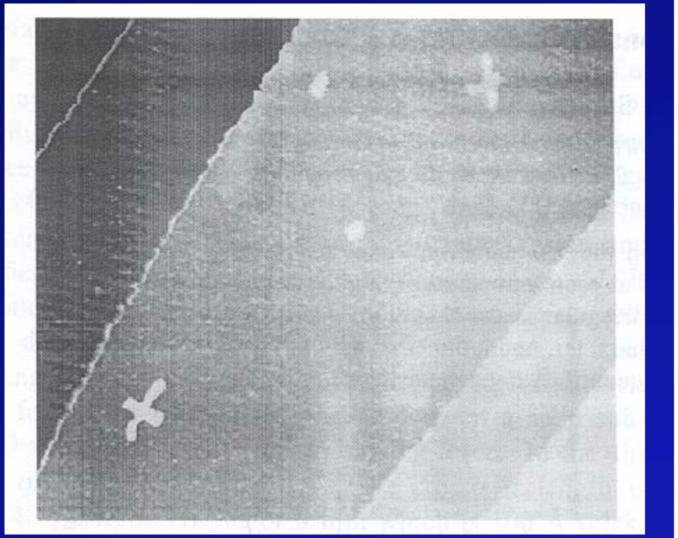
Ammonia synthesis over Ru

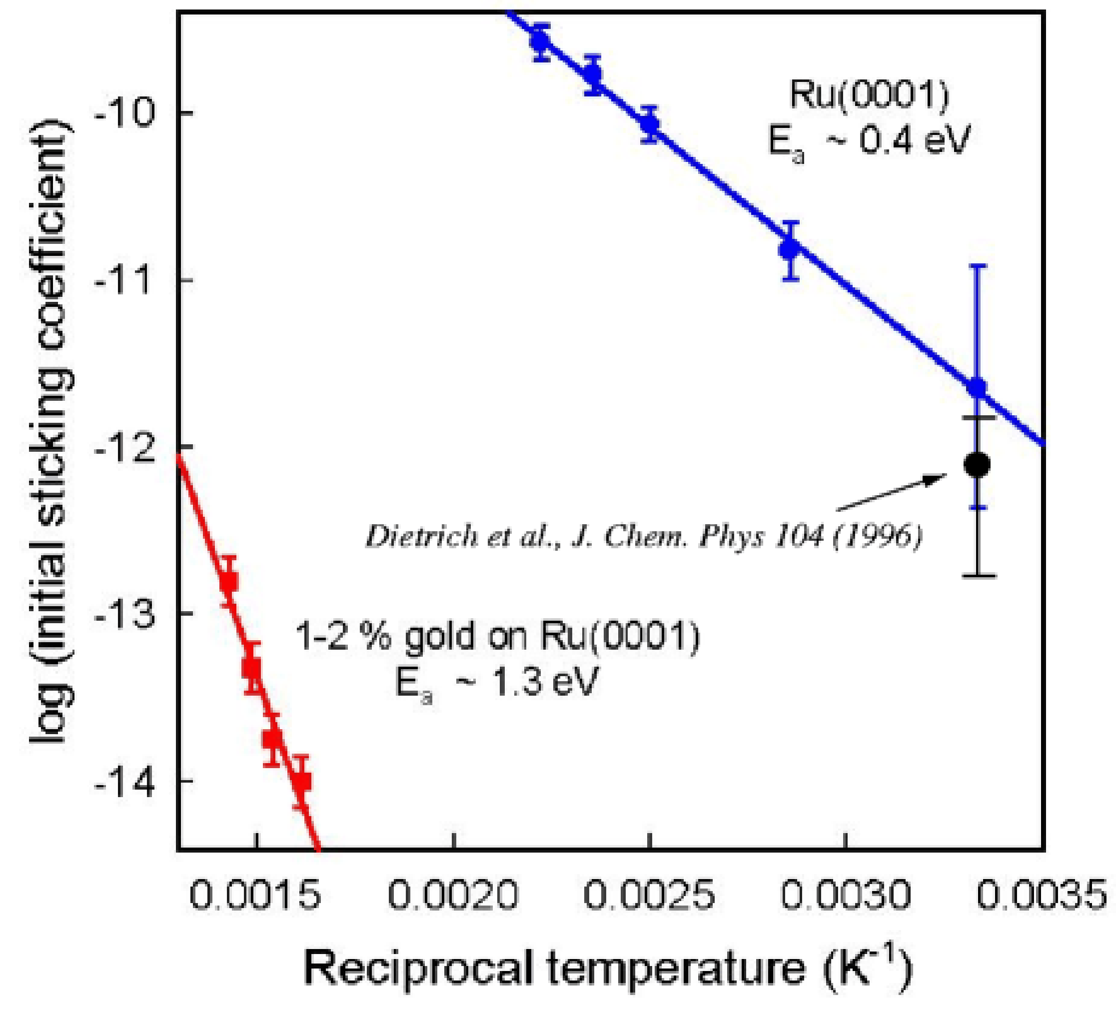
Logadottir, Nørskov, J. Catal. **220**, 273-279 (2003)



Steps do everything

Au decorates steps:
Hwang, Schroder, Gunther, Behm,
Phys. Rev. Lett. 67, 3279 (1991)





Dahl, Logadottir, Egeberg, Larsen, Chorkendorff, Törnqvist, Nørskov,
Phys.Rev.Lett. **83**, 1814 (1999)

Rates of elementary steps

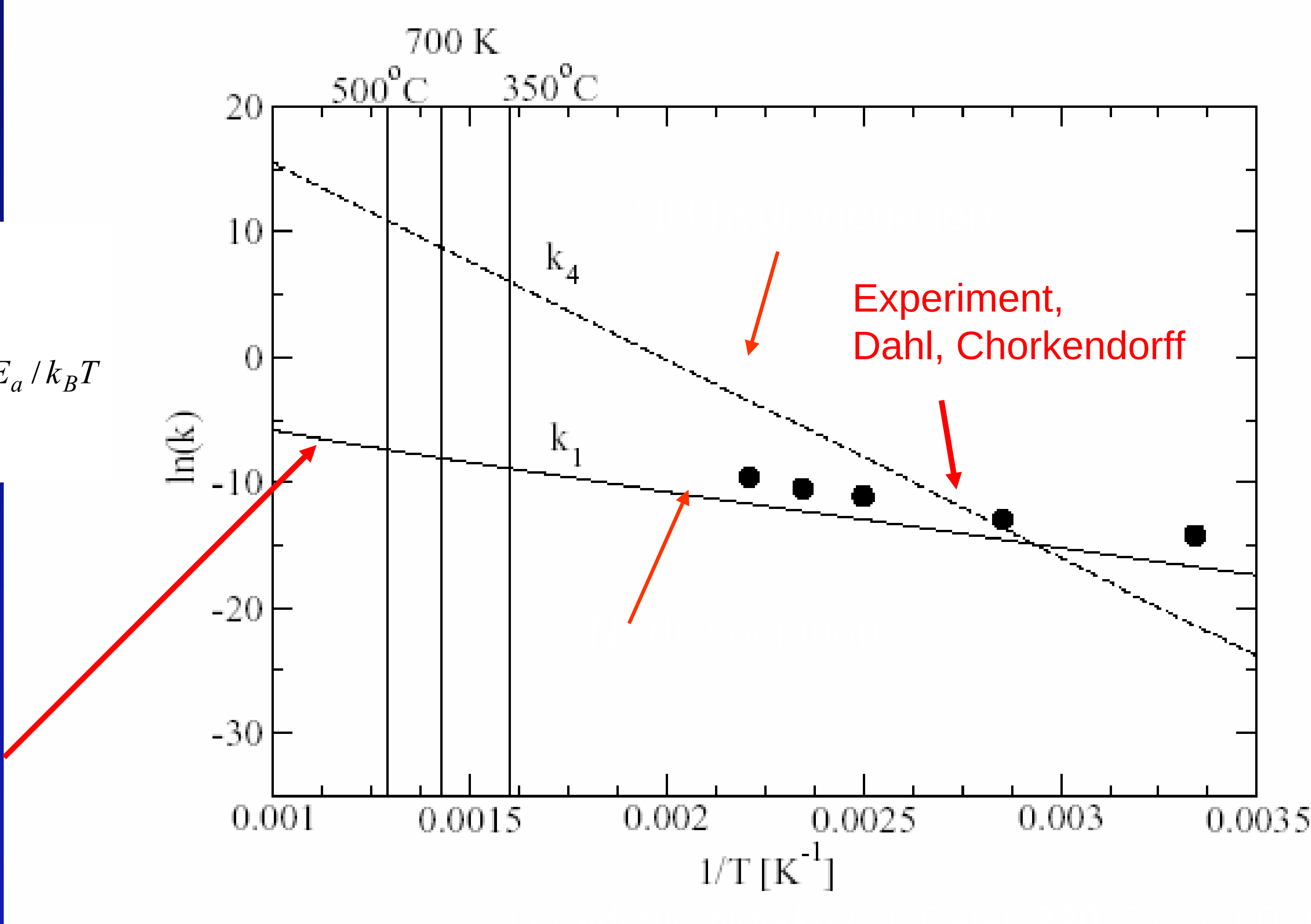
Harmonic transition state theory:

$$k = \nu\, e^{-E_a/k_BT}$$

$$= \frac{k_BT}{h}\frac{q_{TS}}{q_{initial}}\, e^{-E_a/k_BT}$$

Rate-limiting step

Emmett, Brunauer, JACS **55** 1738 (1933)

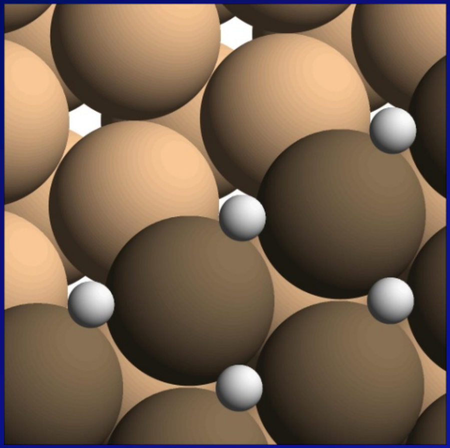


Experiment, Dahl, Chorkendorff

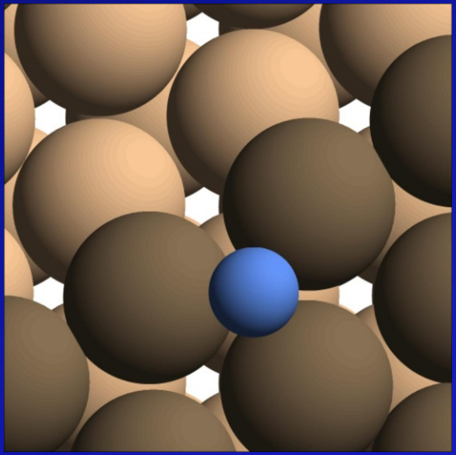
Logadottir, Nørskov, J. Catal. **220**, 273 (2003)

Adsorption geometries for different intermediates

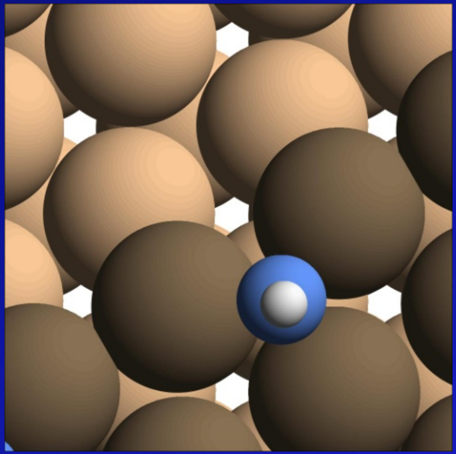
$\Delta E=-34.3$ kJ/mol



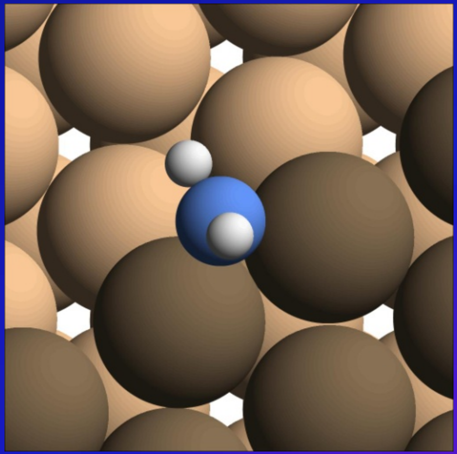
$\Delta E=-37.6$ kJ/mol



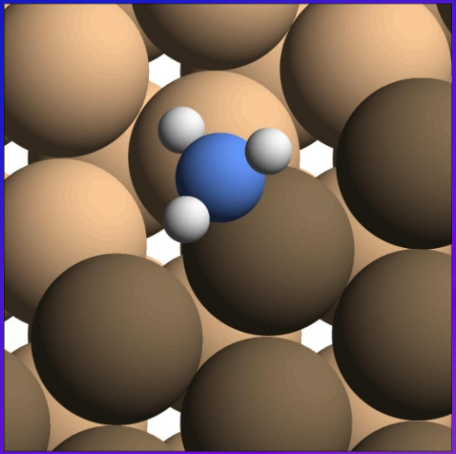
$\Delta E=-97.0$kJ/mol



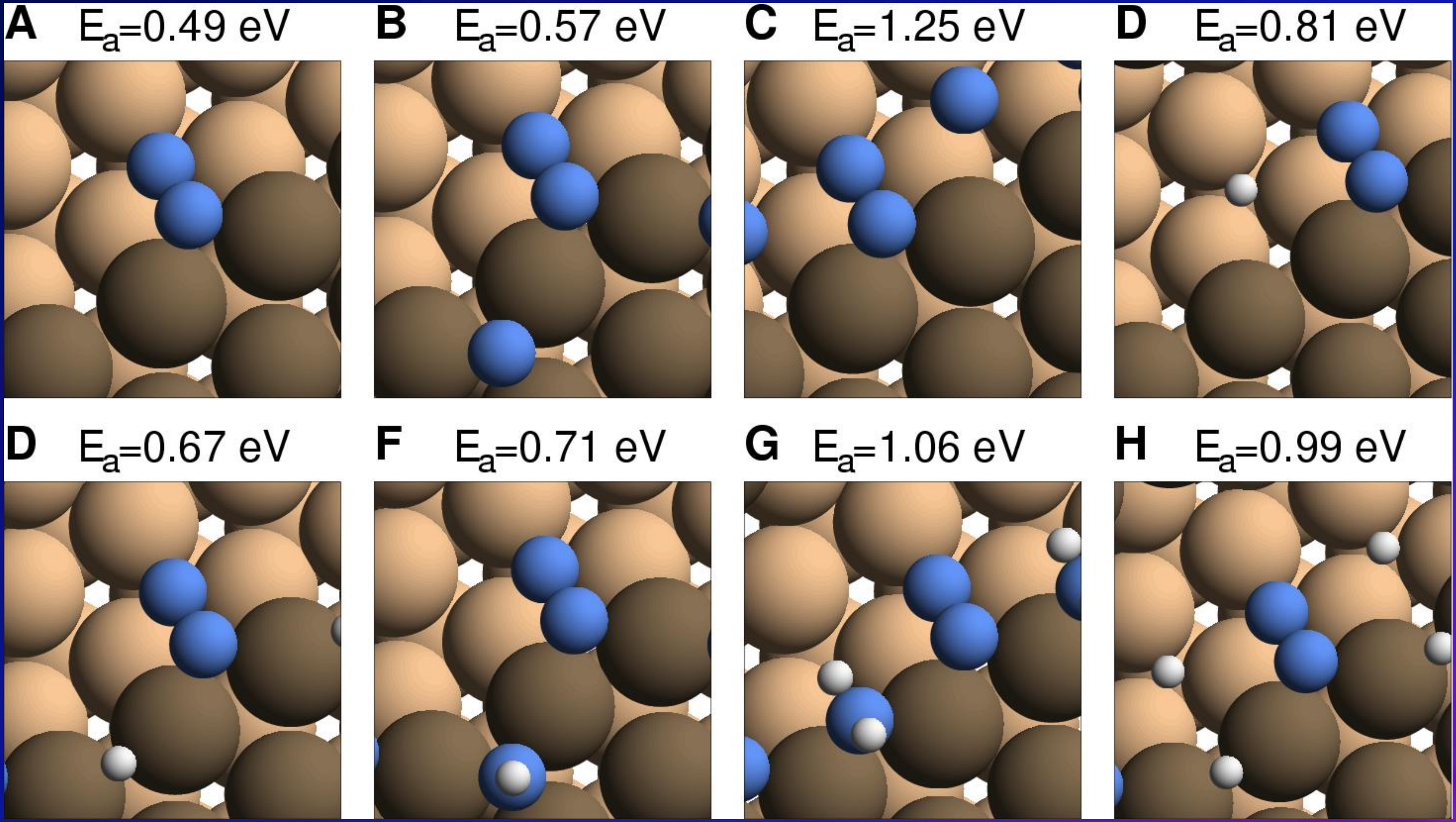
$\Delta E=-167.8$ kJ/mol



$\Delta E=-178.2$ kJ/mol



Different N_2 transition state geometries



Kinetic model

Reaction rate per site:

$$r_{tot}(T, p_{N_2}, p_{H_2}, p_{NH_3}) = (1-\gamma) r^f$$

$$r^f = \sum_i P_i k_i p_{N_2}$$

$$\gamma = \frac{p_{NH_3}^2}{K_g p_{N_2} p_{H_2}^3}$$

Harmonic transition state theory:

$$k_i = \nu \exp(-E_a / k_B T)$$

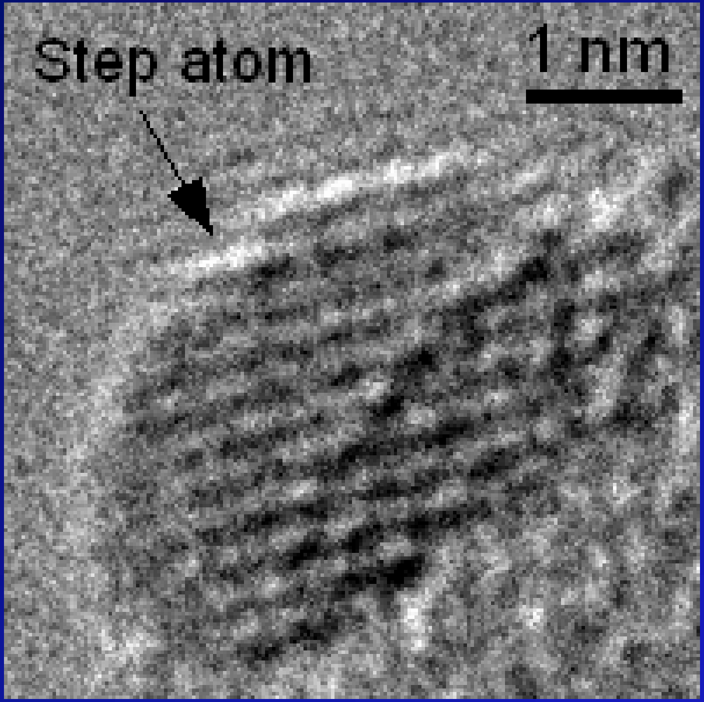
P_i is the probability to have a certain local environment

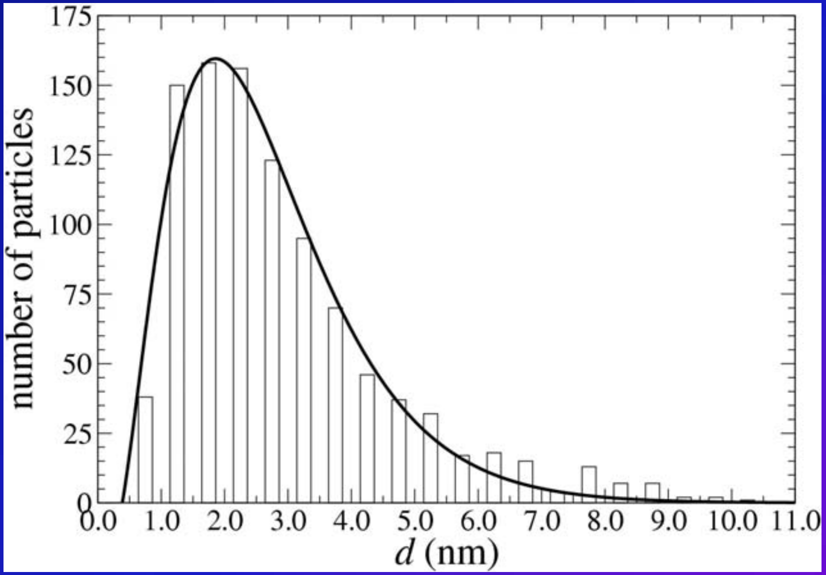
Total rate through the reactor:

$$r_{PFR}^{total} = \sum_{j=0}^{N} r(T, p'^{j}_{N_2}, p'^{j}_{H_2}, p'^{j}_{NH_3}) \times \frac{\rho m}{\mathrm{N}}$$

How to get the number of active sites

A real ammonia synthesis catalysts:
TEM figure of a Ru particle over spinel support

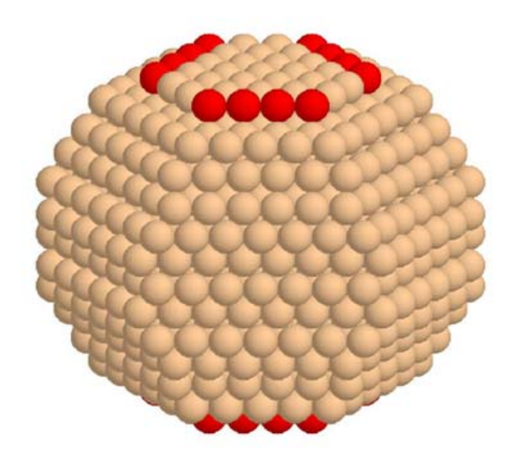




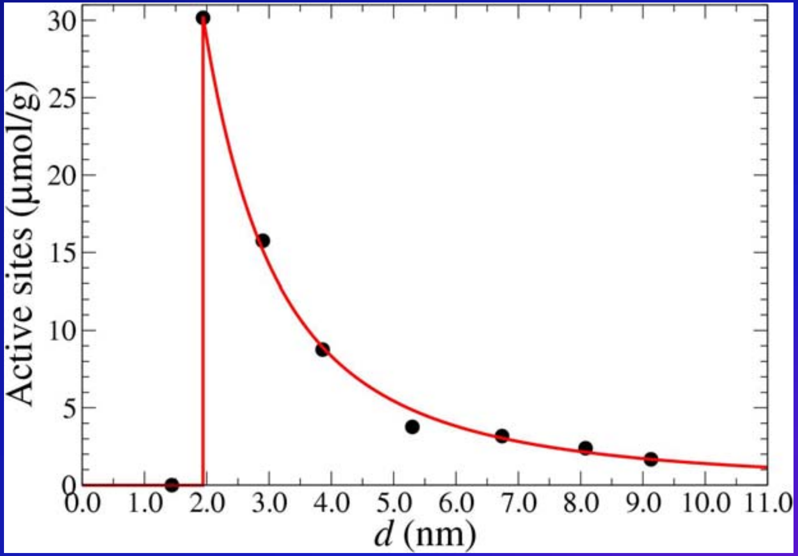
A. Carlsson, S. Dahl, Haldor Topsøe A/S

From size distibution to number of active sites: ρ

Wulff construction based on DFT:



A typical calculated Ru particle with an average diameter 2.9 nm.

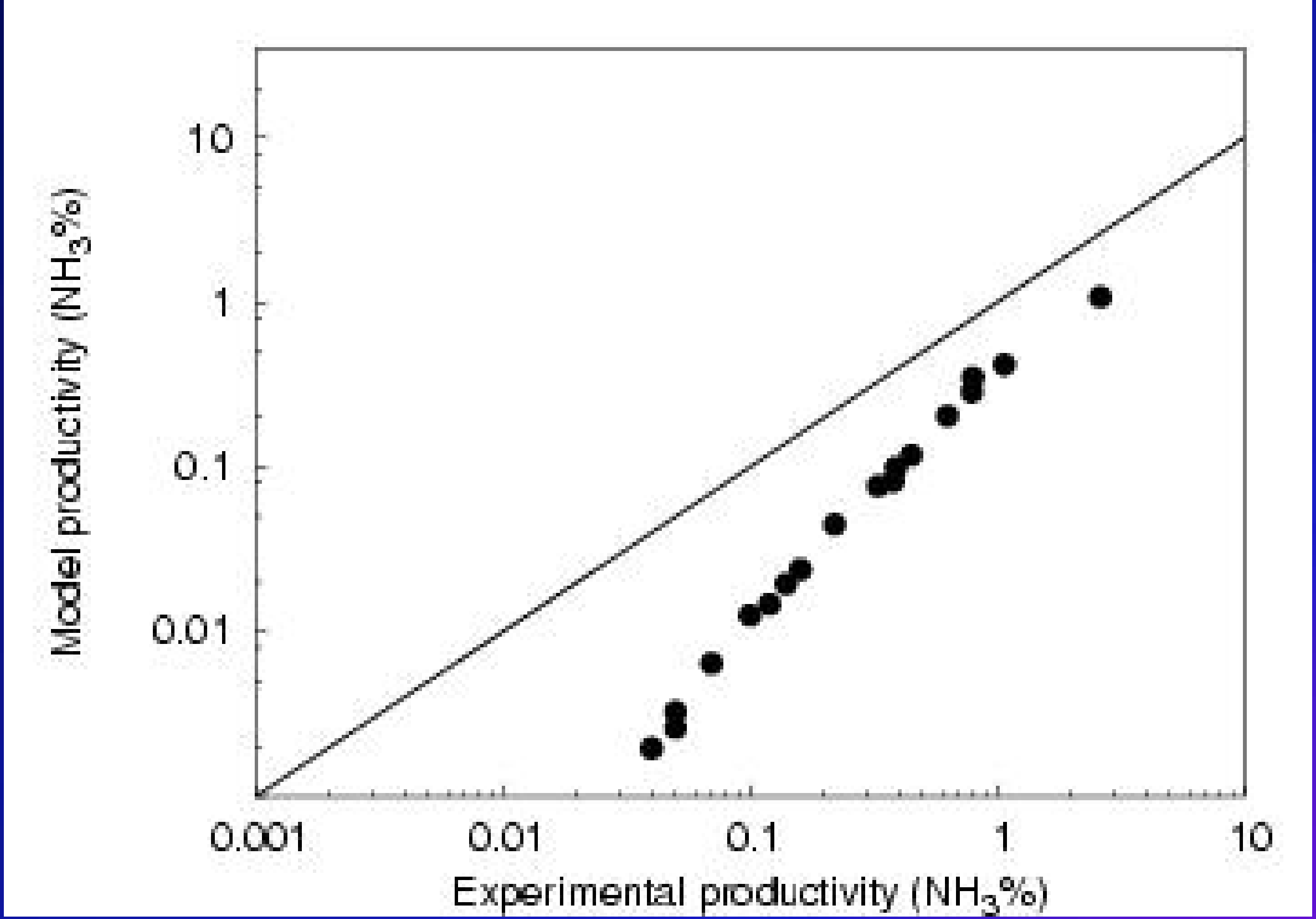


Honkala et al. Science **307**,555 (2005)

I. Remediakis

Ab initio prediction of the rate of the real catalyst

Experimental data: S Dahl & C. Christensen, Haldor Topsøe AS



Total pressure 100 bar, H_2:N_2=3:1

Honkala et al. Science **307**,555 (2005)

Summary

1. *ab initio* prediction for NH_3 productivity on the supported metal particle

2. The absolute error in DFT calculations is about 0.2-0.3 eV but the relative errors are in in order of 0.06 eV (~ k_BT at reaction conditions).

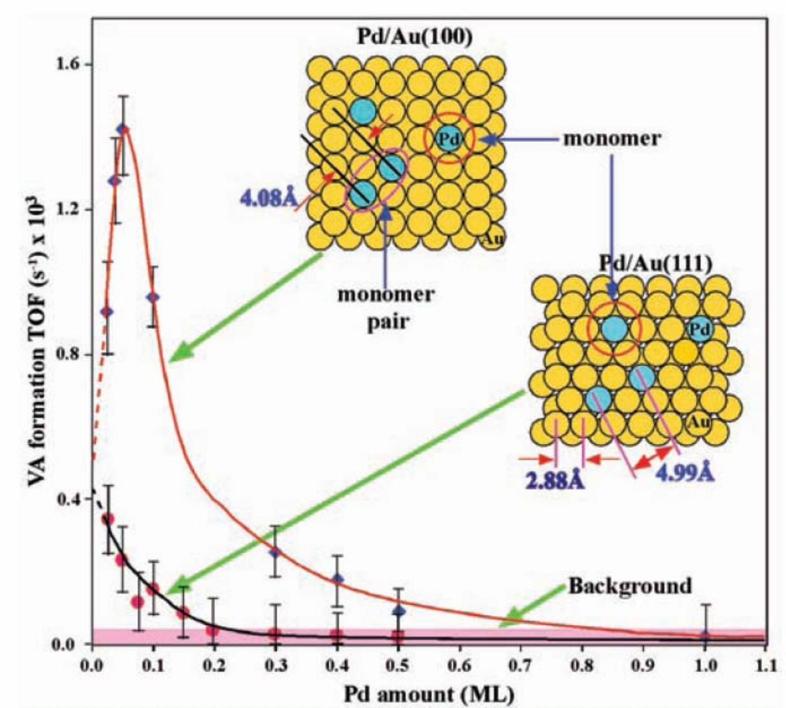
3. The build-in insensitivity to absolute errors together with the higher accuracy of the DFT methods for relative energies, offers hope that DFT calculations can give a good overall description of the catalytic activity of other reactions as well

Can DFT do more than we expect ?

Selectivity

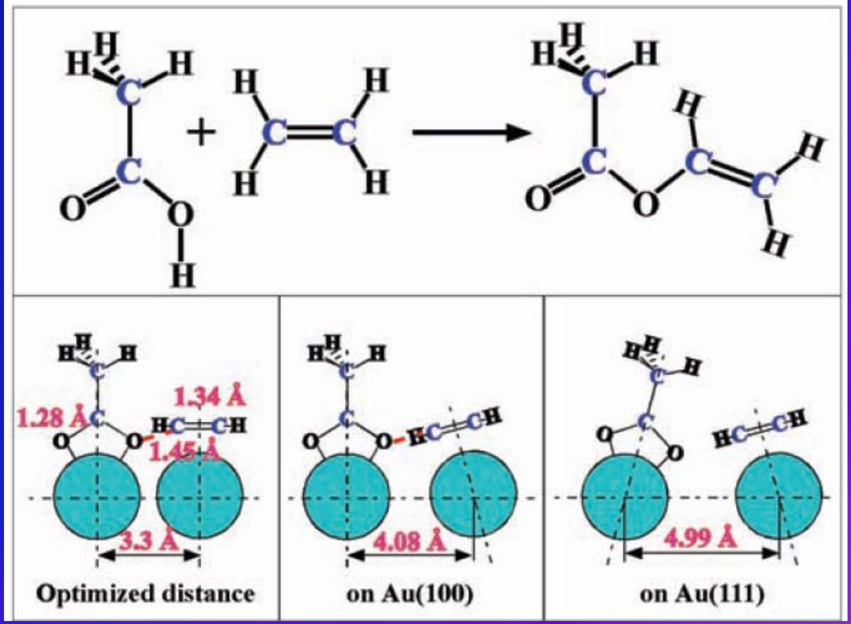
Greely &Norskov,
Nature Materials (2006)

Promotional Effect of Gold in Catalysis by Palladium-Gold



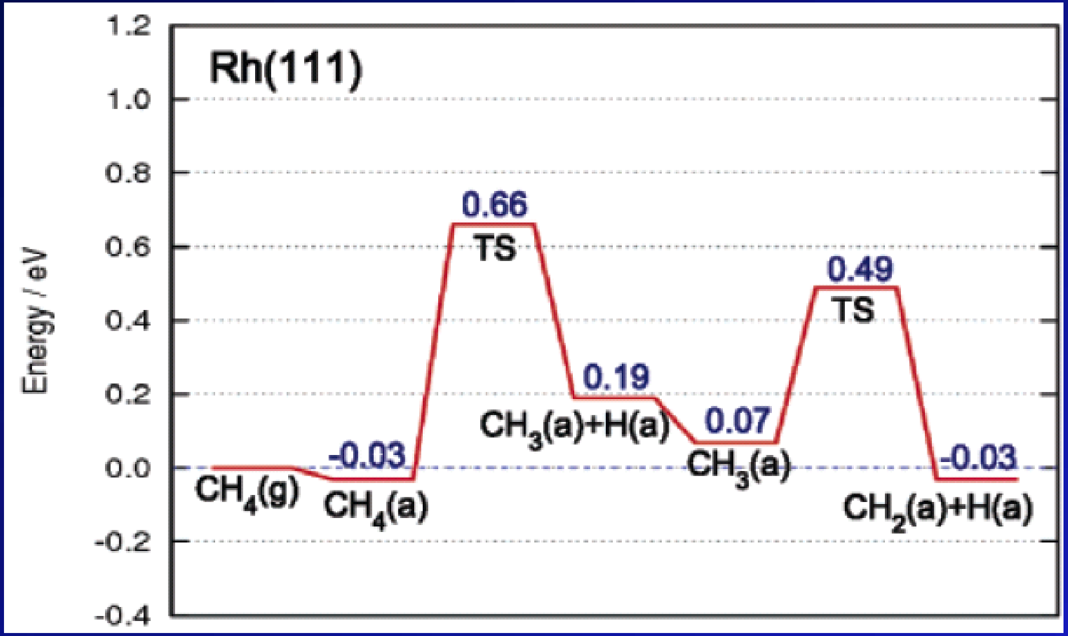
$CH_3COOH + CH_2CH_2 + 1/2\ O_2 \rightarrow CH_3COOCH{=}CH_2 + H_2O$

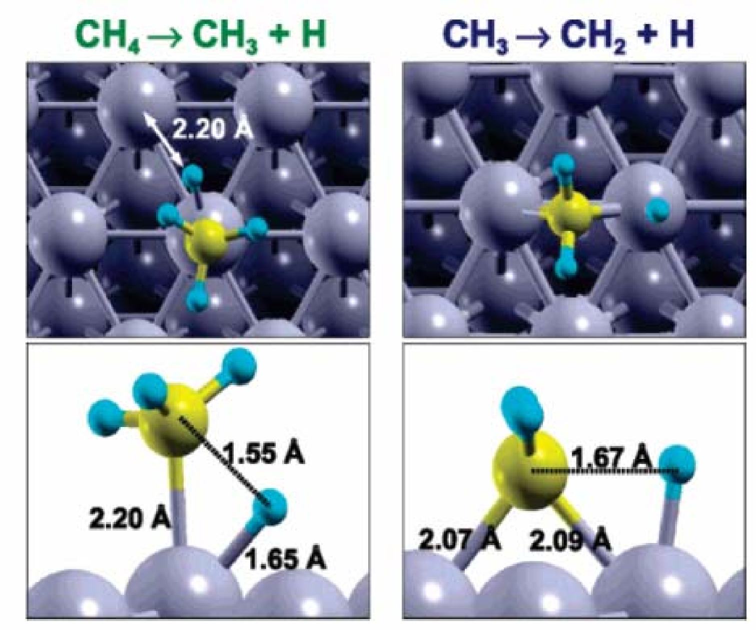
on Pd/Au alloy better selectivity for vinyl acetate than on Pd (Wayne Goodman, Science (2005))



Goodman believes that selectivity is increased because the unwanted reactions need more than two Pd atoms.

Methane Dehydrogenation on Rh@Cu(111)

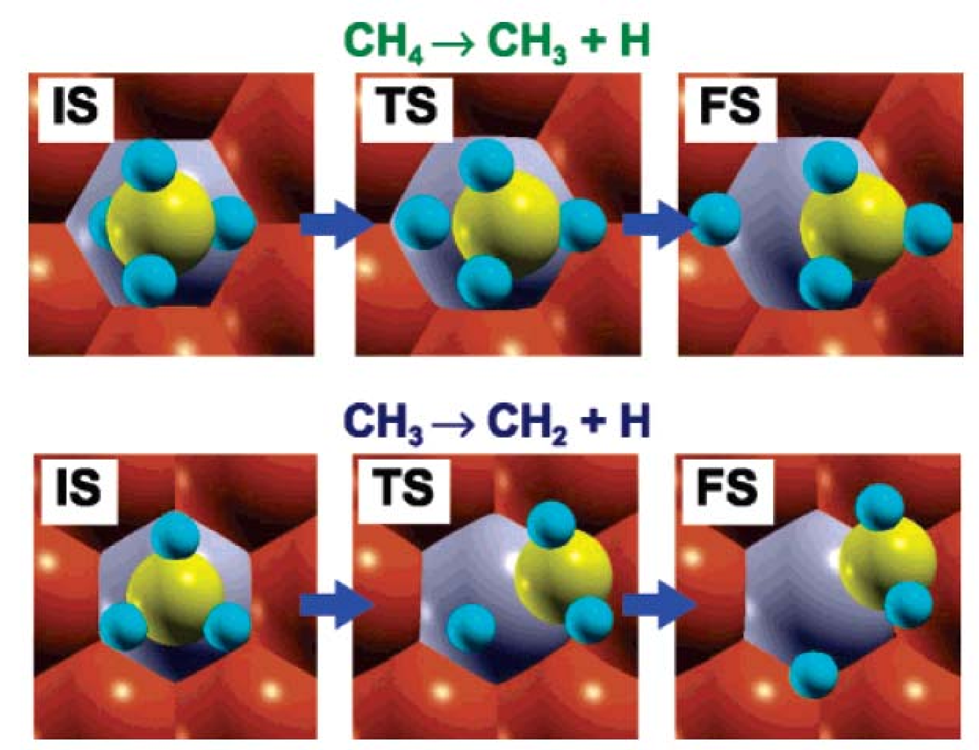


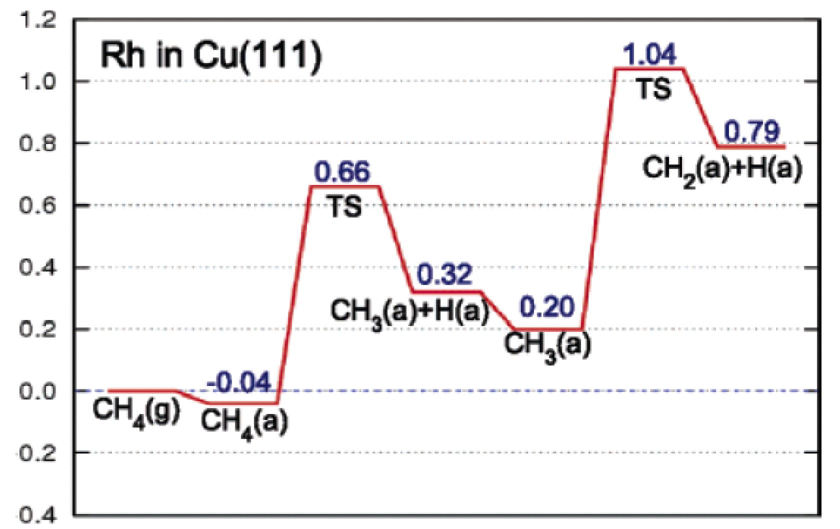


1. First C-H bond breaking is rate limiting step
2. CH3 → CH2 + H: require bridge site

A. Kokalj et al JACS (2006)

Methane Dehydrogenation on Rh@Cu(111)





1. Second dehydrogenation of methane is prevented
2. C-C coupling or formation of methanol may be preferential

A. Kokalj et al JACS (2006)

Controlling the catalytic bond-breaking selectivity of Ni surfaces by step blocking

C_2H_4 Activation and Selectivity

C - H bond breaking :

$$C_2H_4 = C_2H_3 + H$$

$$C_2H_3 = C_2H_2 + H$$

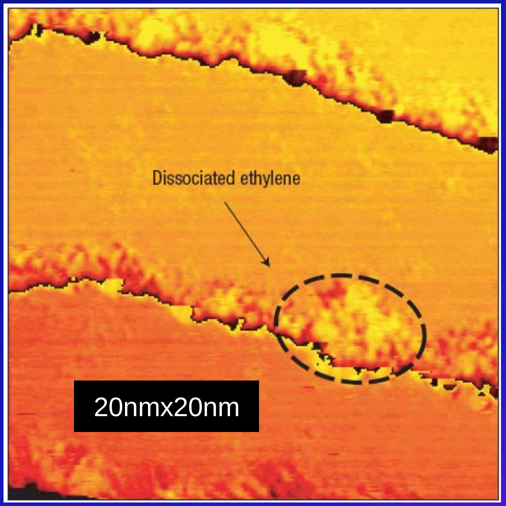
C - C coupling (Ni(211) and Ni(111))

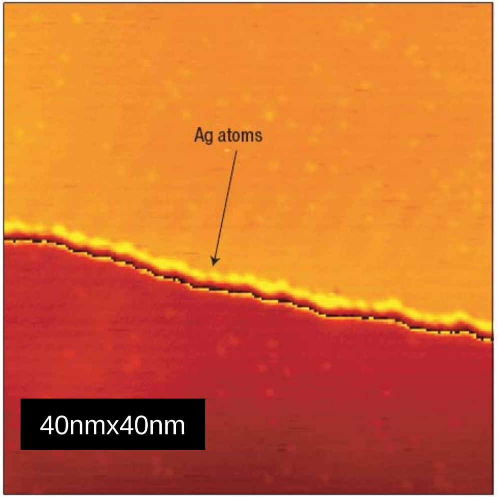
C - C bond breaking

$$C_2H_4 = 2CH_2$$

$$CH_2 = C + 2H$$

C coke (Ni(211))

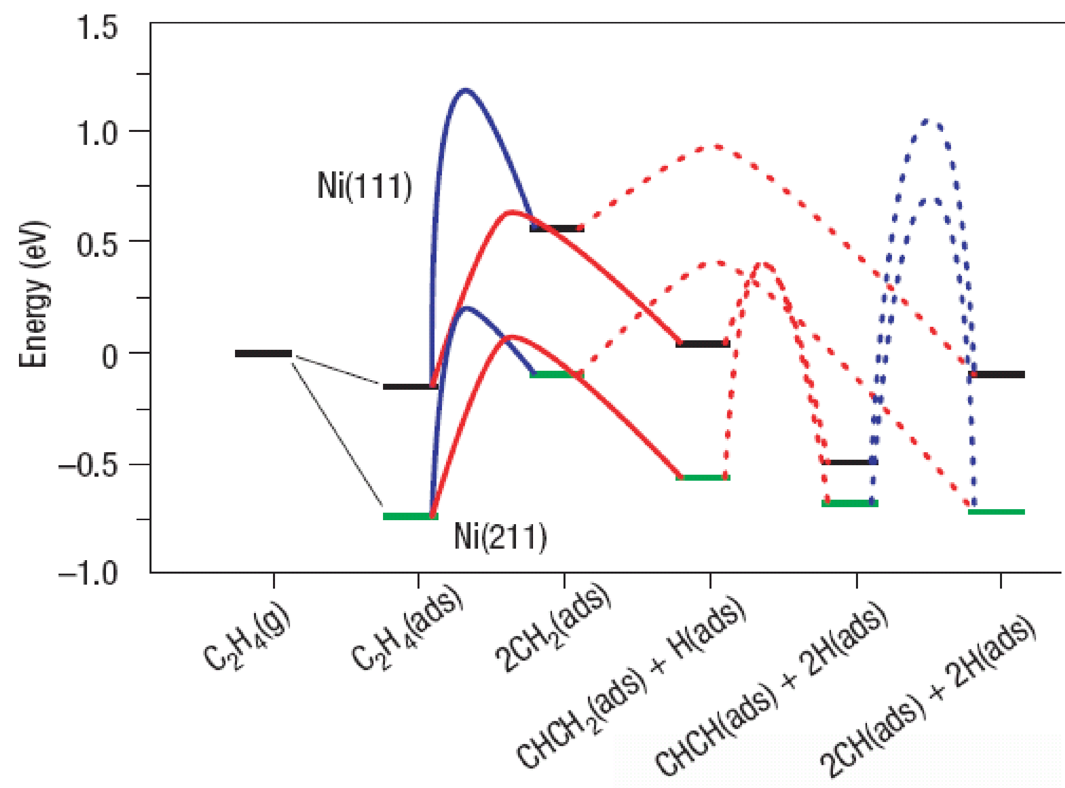


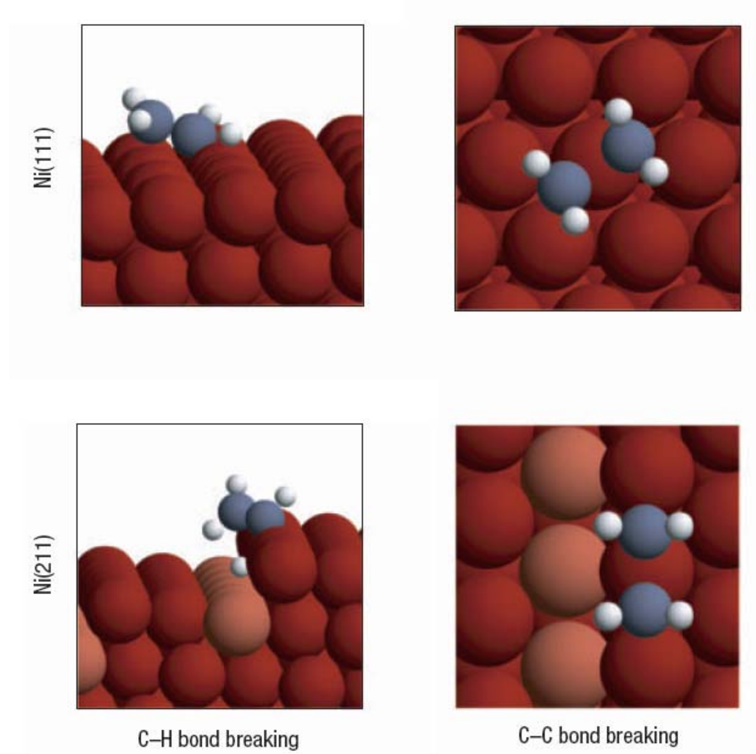


R. T. Vang, J. K. Norskov and
F. Besenbacher et al, Nature Materials (2005)

Blocking Ni step with Ag prevents carbon formation

Controlling the catalytic bond-breaking selectivity of Ni surfaces by step blocking





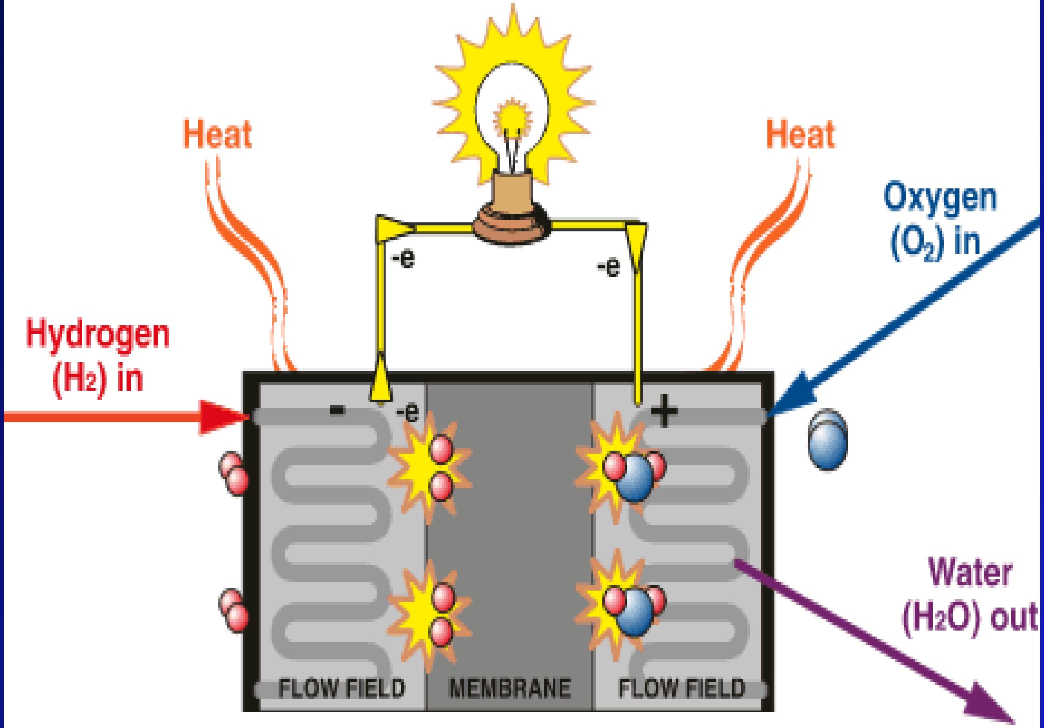
R. T. Vang, J. K. Norskov and
F. Besenbacher et al, Nature Materials (2005)

Can DFT do more than we expect ?

Computational high-throughput screening of electrocatalytic materials for hydrogen evolution

Greely &Norskov,
Nature Materials (2006)

Hydrogen driven Fuel Cell



Proton exchange membrane fuel cell

Anode:

$2H_2 \rightarrow 4H^+ + 4e^-$

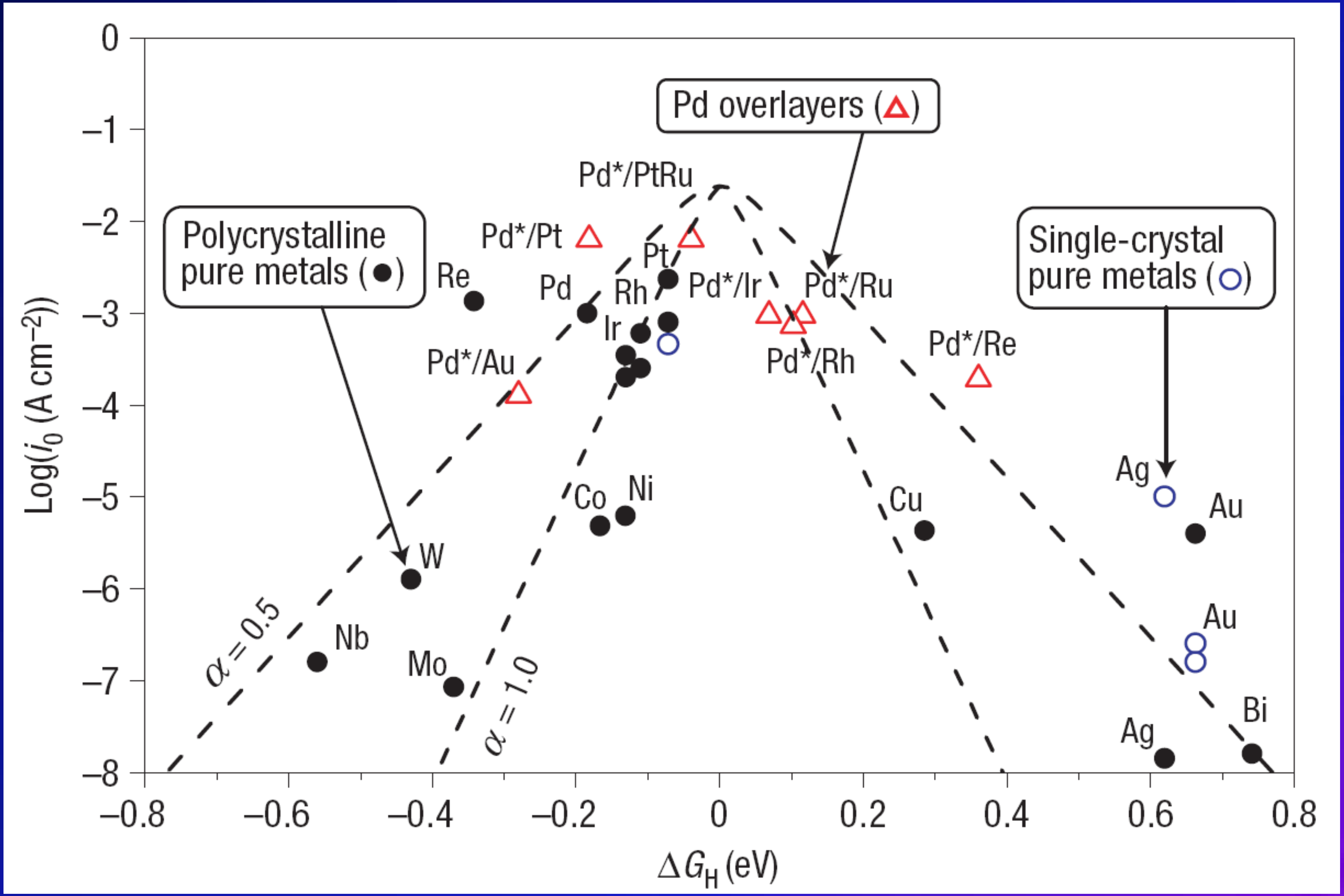
Cathode:

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

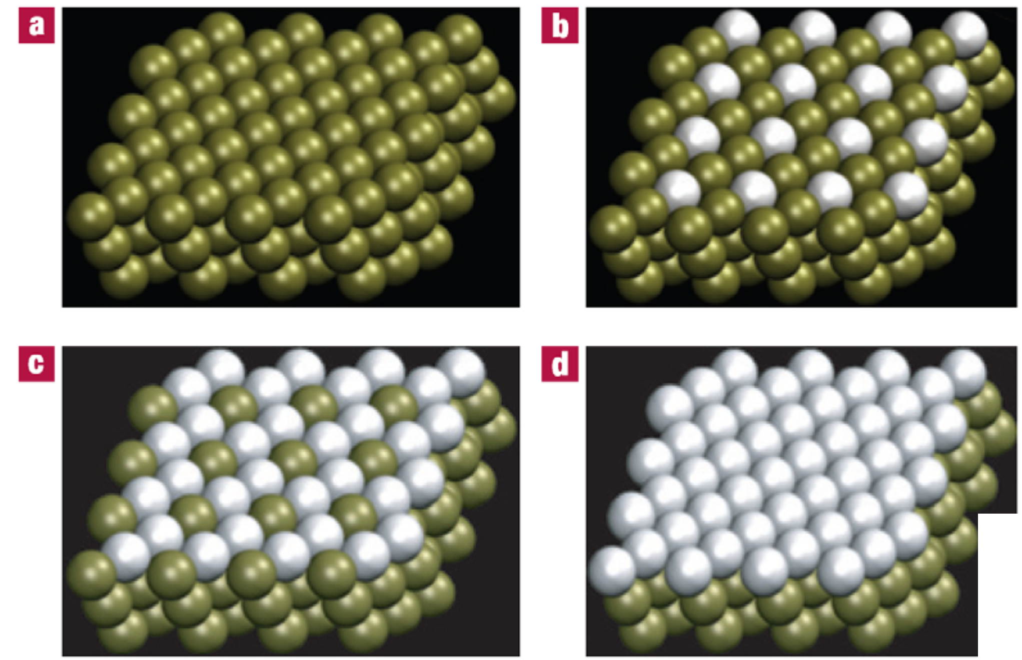
$2H_2 + O_2 \rightarrow 2H_2O$ + Heat

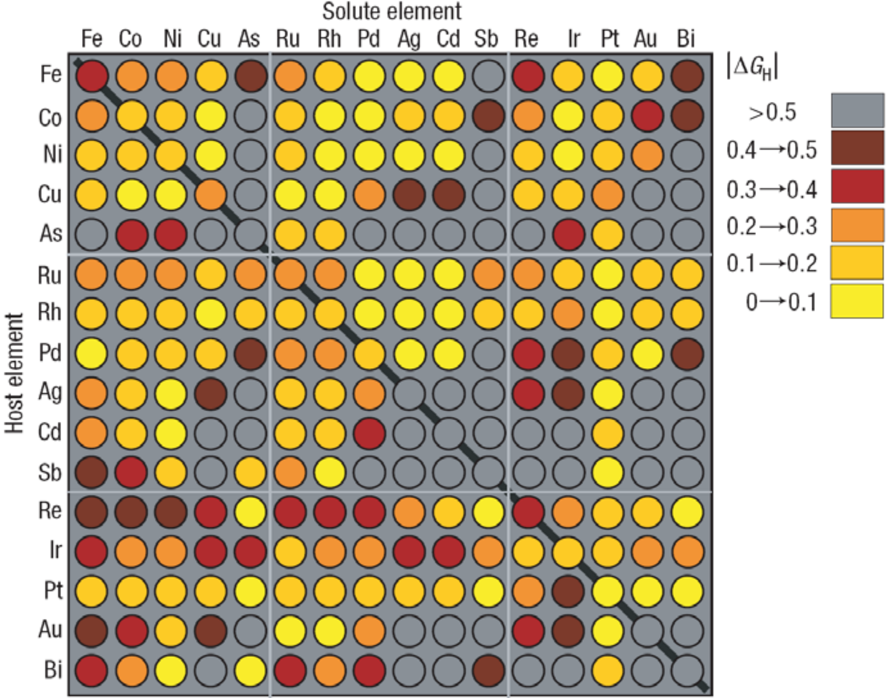
Chemical Energy $\xrightarrow{\text{Electrochemical reactions}}$ **Electricity**, **Heat**

Computational high-throughput screening of electrocatalytic materials for hydrogen evolution



Computational high-throughput screening of electrocatalytic materials for hydrogen evolution



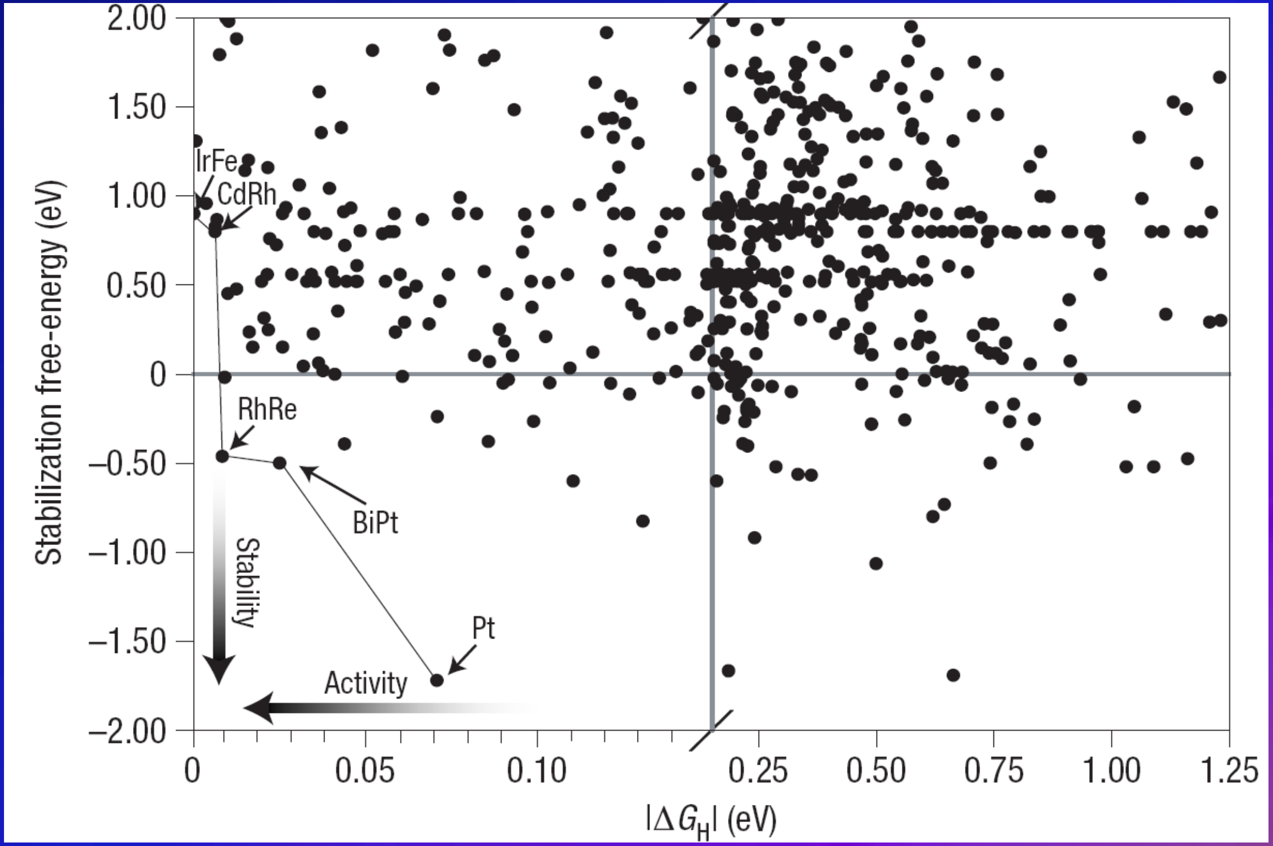


Computational high-throughput screening of electrocatalytic materials for hydrogen evolution

Environment Effects

Surface Segregation
Island Formation
Water splitting and oxygen
Metal dissolution

BiPt$_{\text{surface alloy}}$



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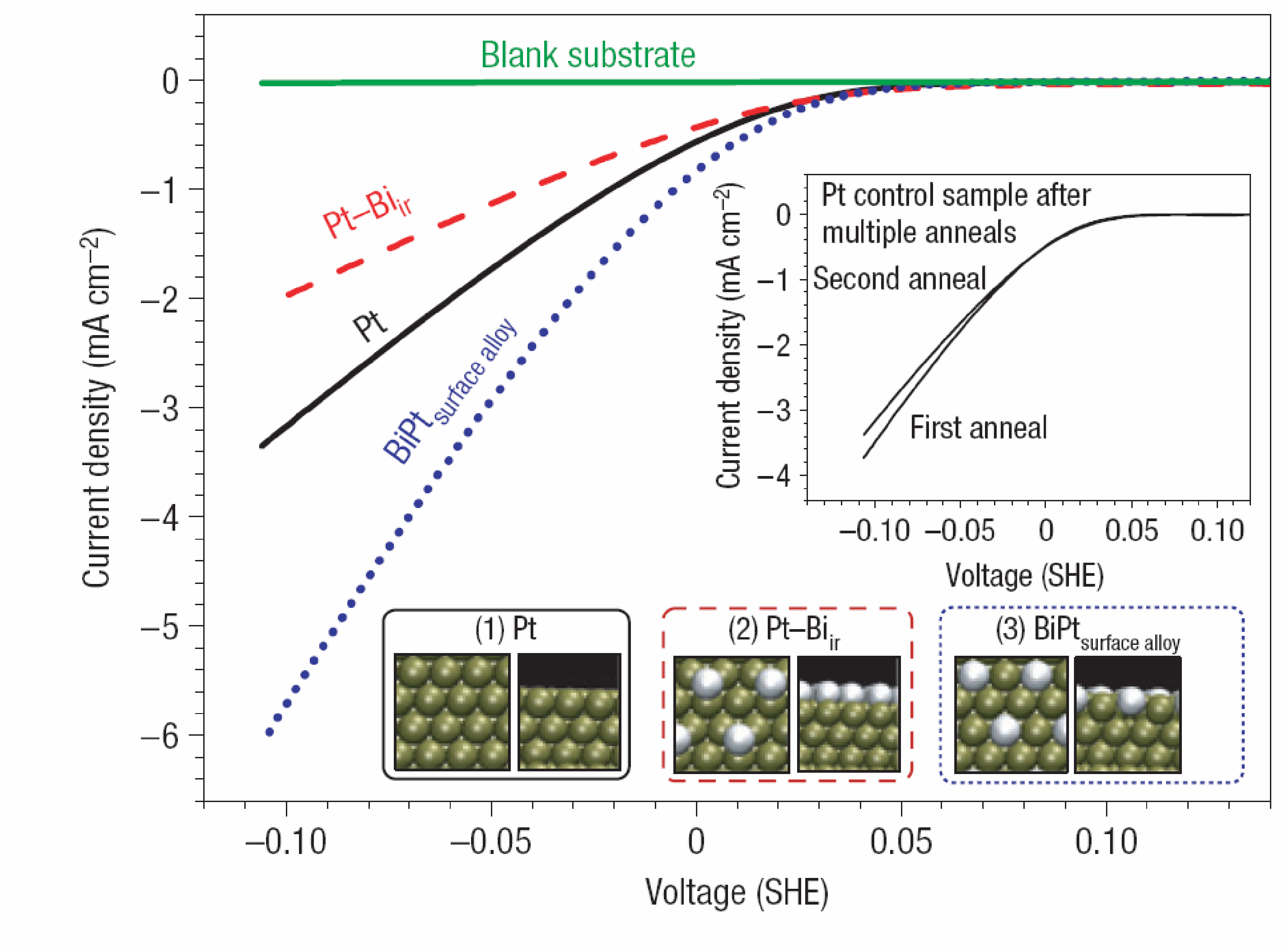

Thank you for your attention