Co-adsorption and adsorption on transition metal surfaces:

Cs+CO/Ru(0001)

OH/Pt(111)

water/Pt(111)

Ari P Seitsonen

Fritz-Haber-Institut der MPG, Berlin

INFM, Università La Sapienza, Roma

Laboratory of Physics, HUT

Rechenzentrum Garching der MPG, IPP

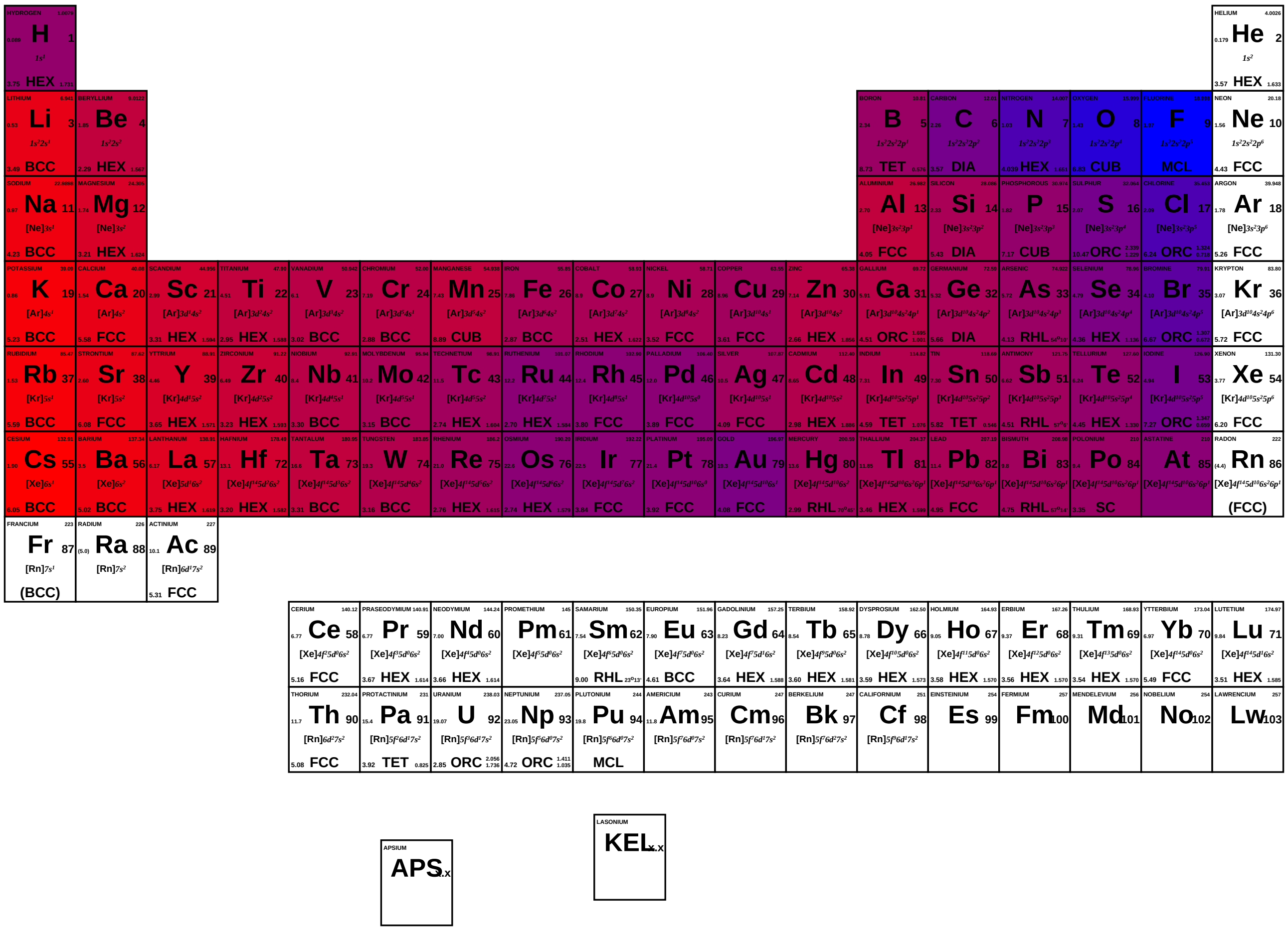
Herbert Over

Fritz-Haber-Institut der MPG, Berlin

Cs+CO/Ru: Model for catalytic system

[$CO + O \Rightarrow CO_2$]

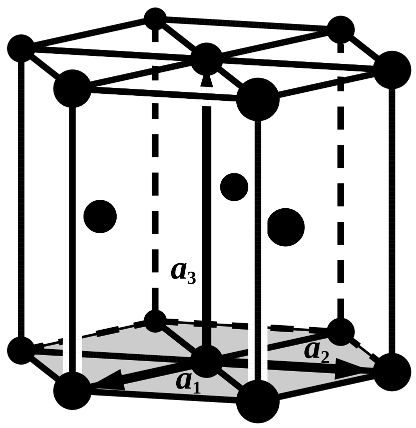
- Cs/Ru: "Ionicity", promoter action
- CO/Ru: Blyholder model
- (O+CO/Ru, O+CO/Cs/Ru; RuO_2 etc)

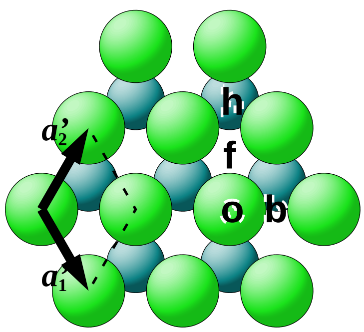


Technicalities

- Kohn-Sham/Car-Parrinello approach
- GGA exchange correlation (PBE)
- Slab geometry, five layers (three for some Cs/Ru)
- Ordered structures: (1×1) to $(2\sqrt{3} \times 2\sqrt{3})$
- Plane wave basis $E_{\mathrm{cut}} = 50$ Ry
- Pseudo potentials (TM); Cs^{9+}, V$_{\mathrm{H}} = -1/r$
- Surface dipole moment

hcp(0001):



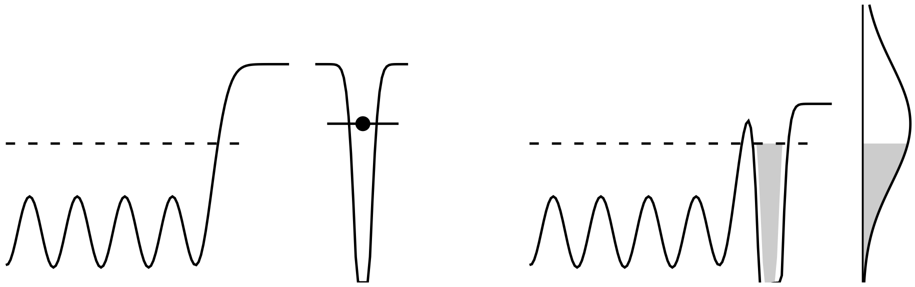


Faust

- Procedural f90
- $\Rightarrow$ KL AD 1994, features from `FHIxxCP`
- Parallellisation a'la Sami Pöykkö/Edinburgh
- Run-time control of calculational parameters
- WDA, LMA, MGGA, . . .
- Semi-local form of pseudo potentials

Cs/Ru(0001): Gurney model

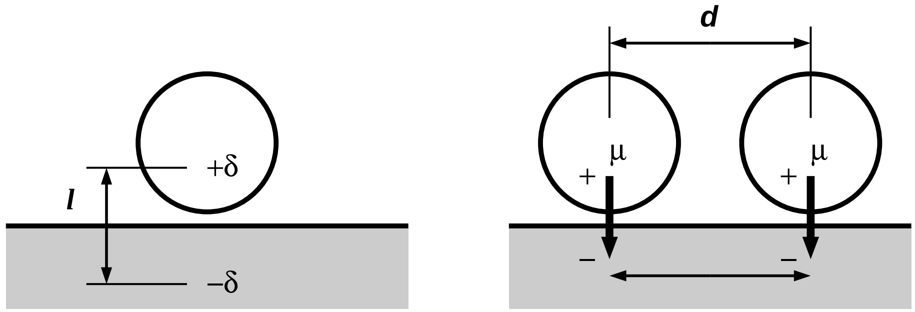
separated adsorbed



$\Longrightarrow$ Charge transfer from adsorbate to substrate

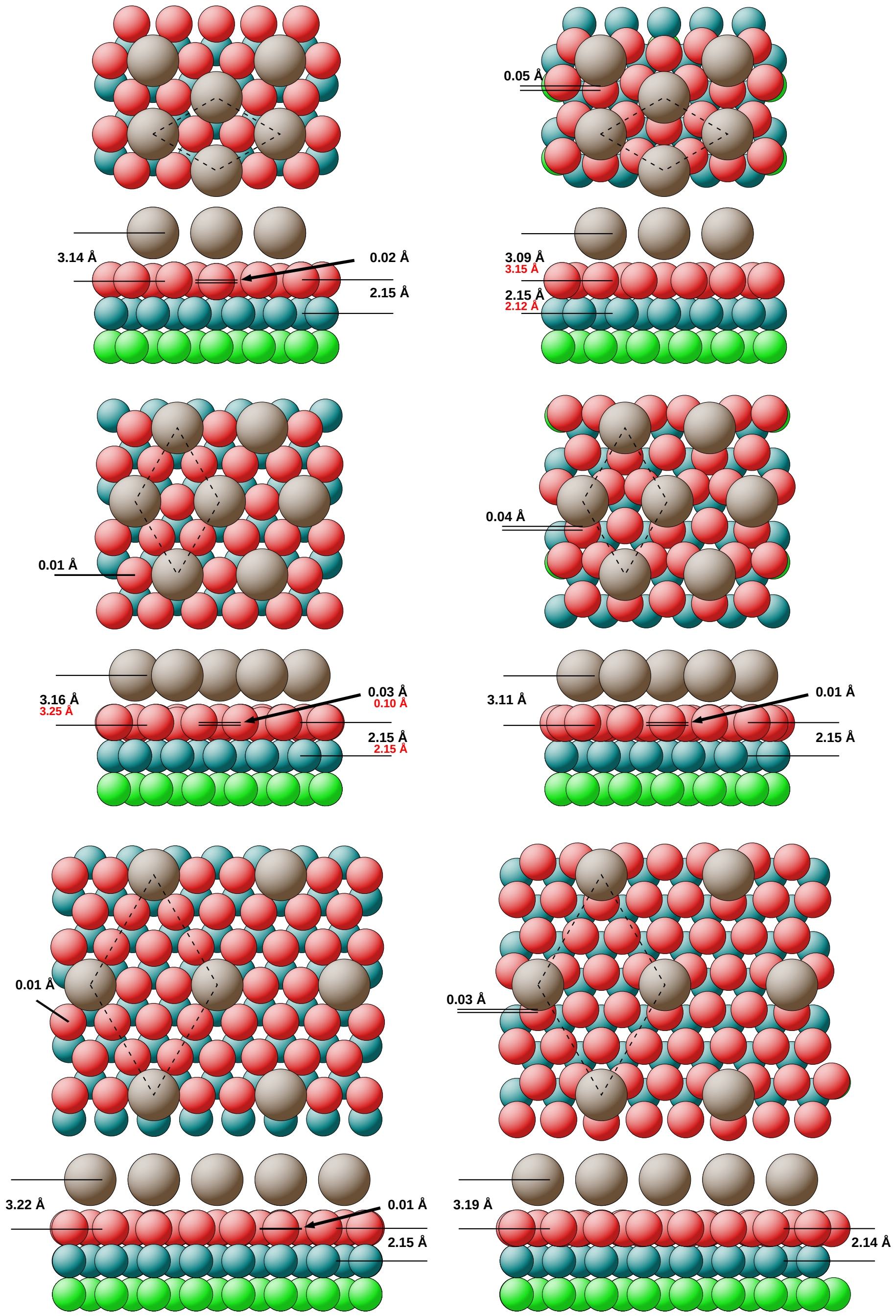
$\Rightarrow$ Formation of dipoles

Dipole-image Dipole-dipole



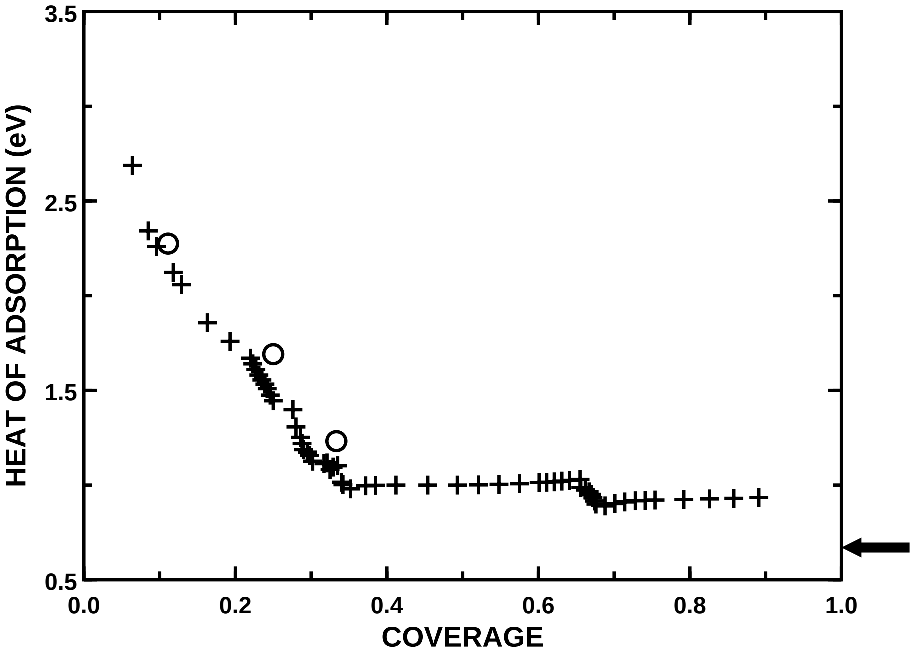
Attractive Repulsive

Cs/Ru(0001): Geometries

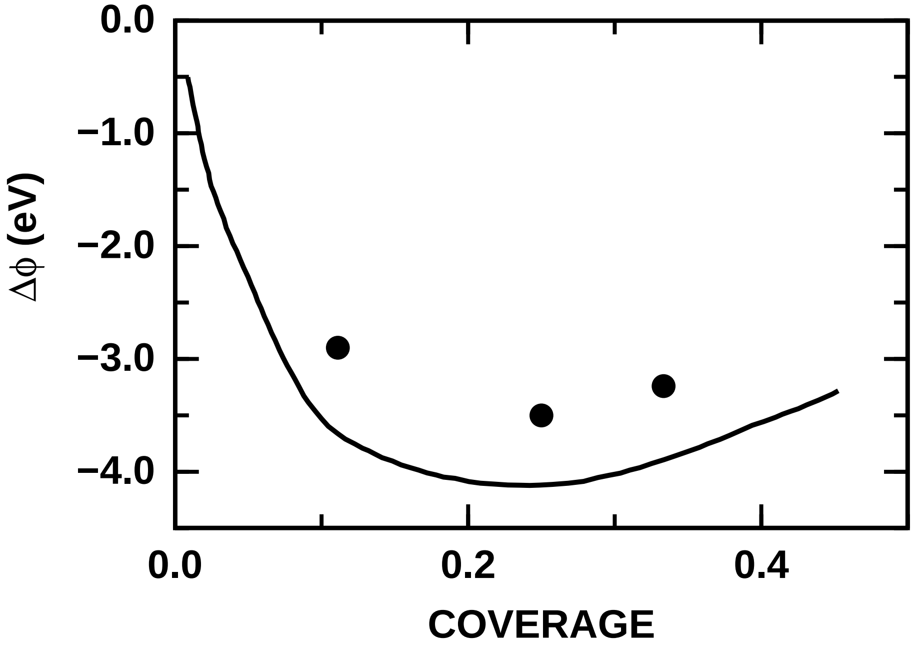


Cs/Ru(0001): Coverage dependence

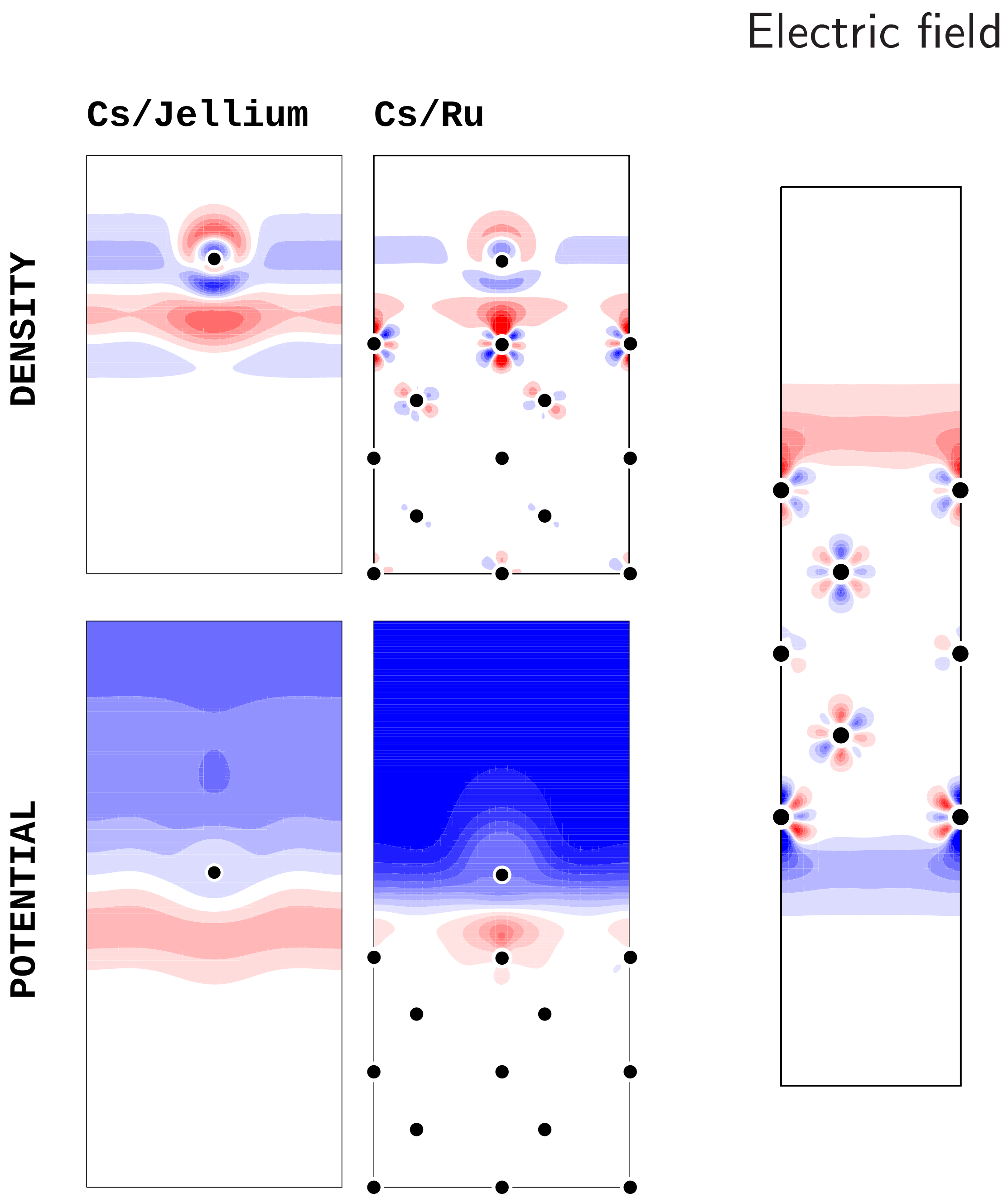
E_{bind} ($\circ$), H_{ads} ($+$) simulated by Payne *et al*



$\Delta\phi$ measured and calculated ($\circ$):



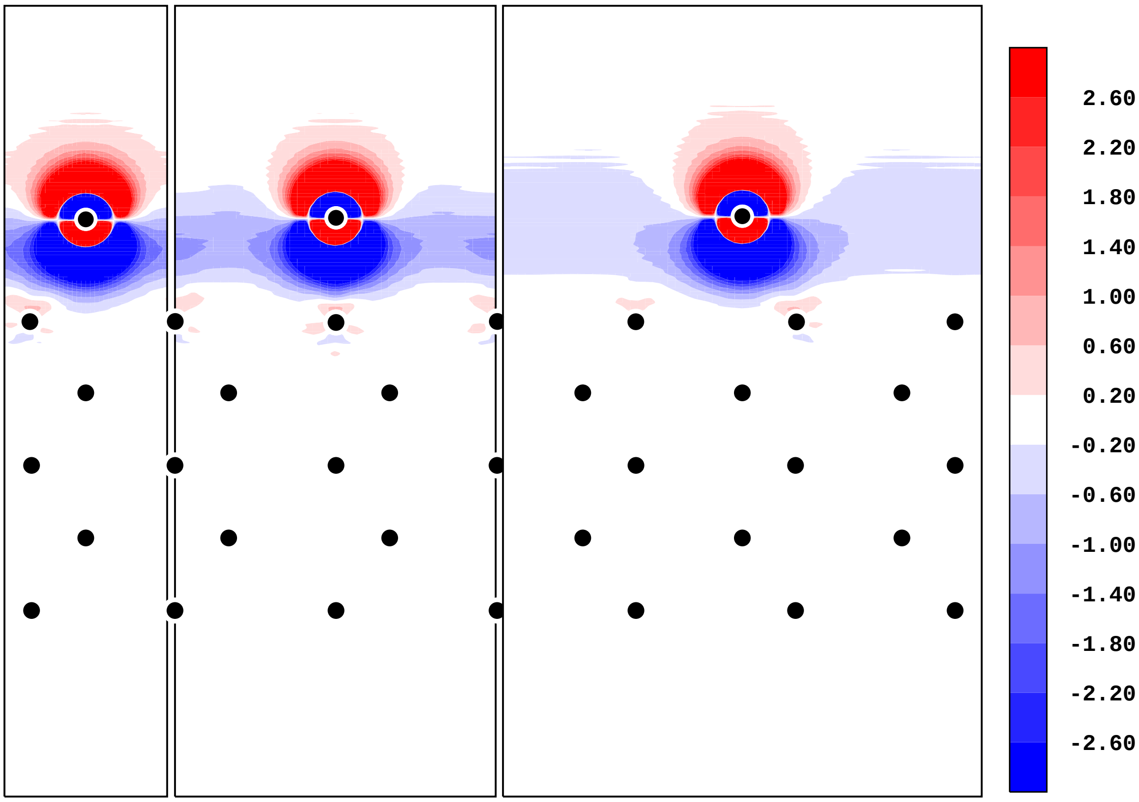
Cs/Ru(0001): Changes in n(r) and V(r)



Cs/Ru(0001): Induced electric field

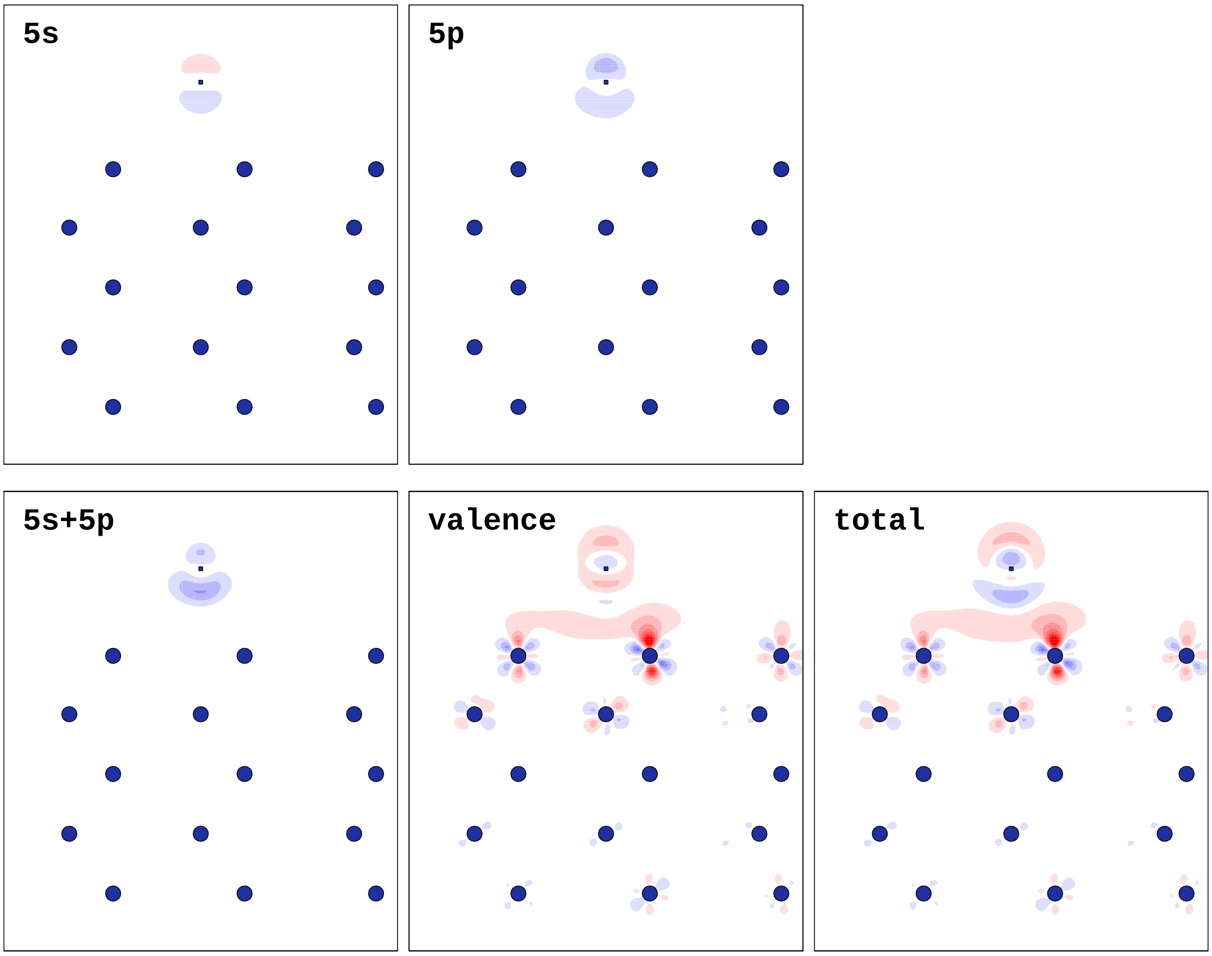
$$\mathbf{E} = -\nabla V_{\mathrm{el-stat}}$$

- In (2×2) structure the vertical field still ≈ 1.7 eV/Å



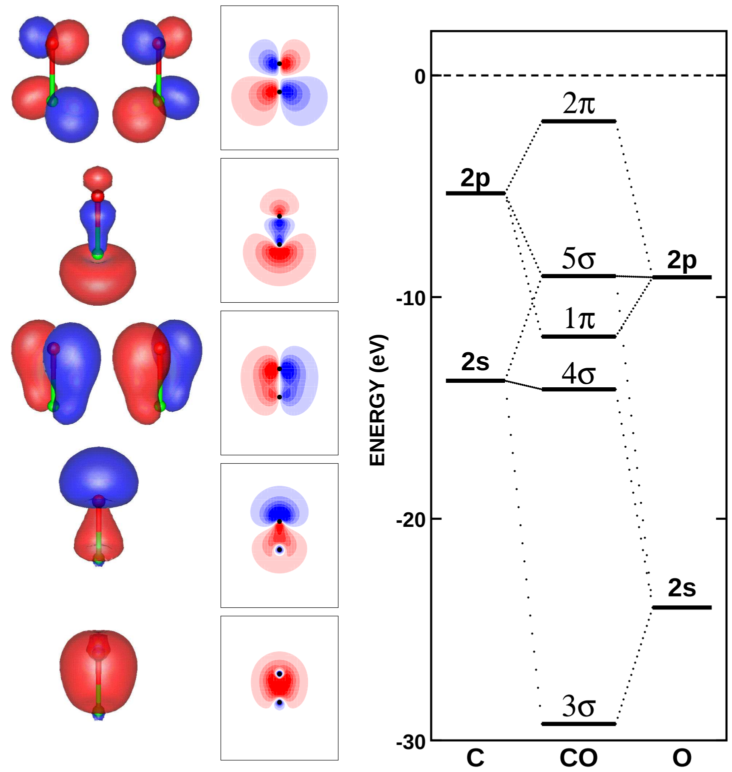
Cs/Ru(0001): Density difference

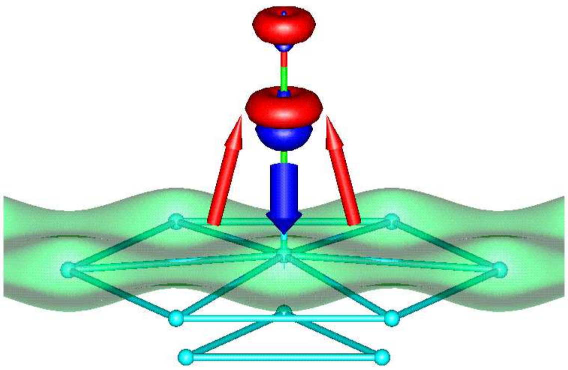
- Decomposed density difference: The semi-core orbitals dominate the effect

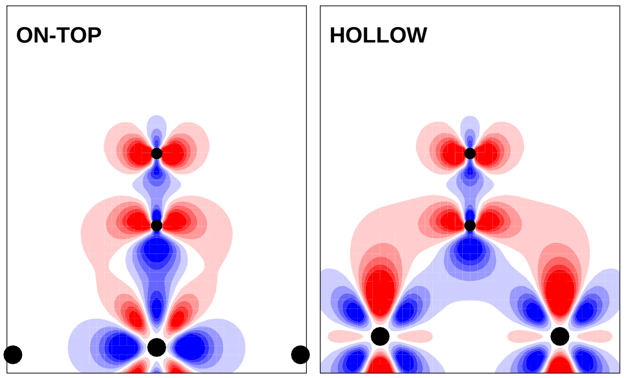


CO/Ru(0001): Blyholder model

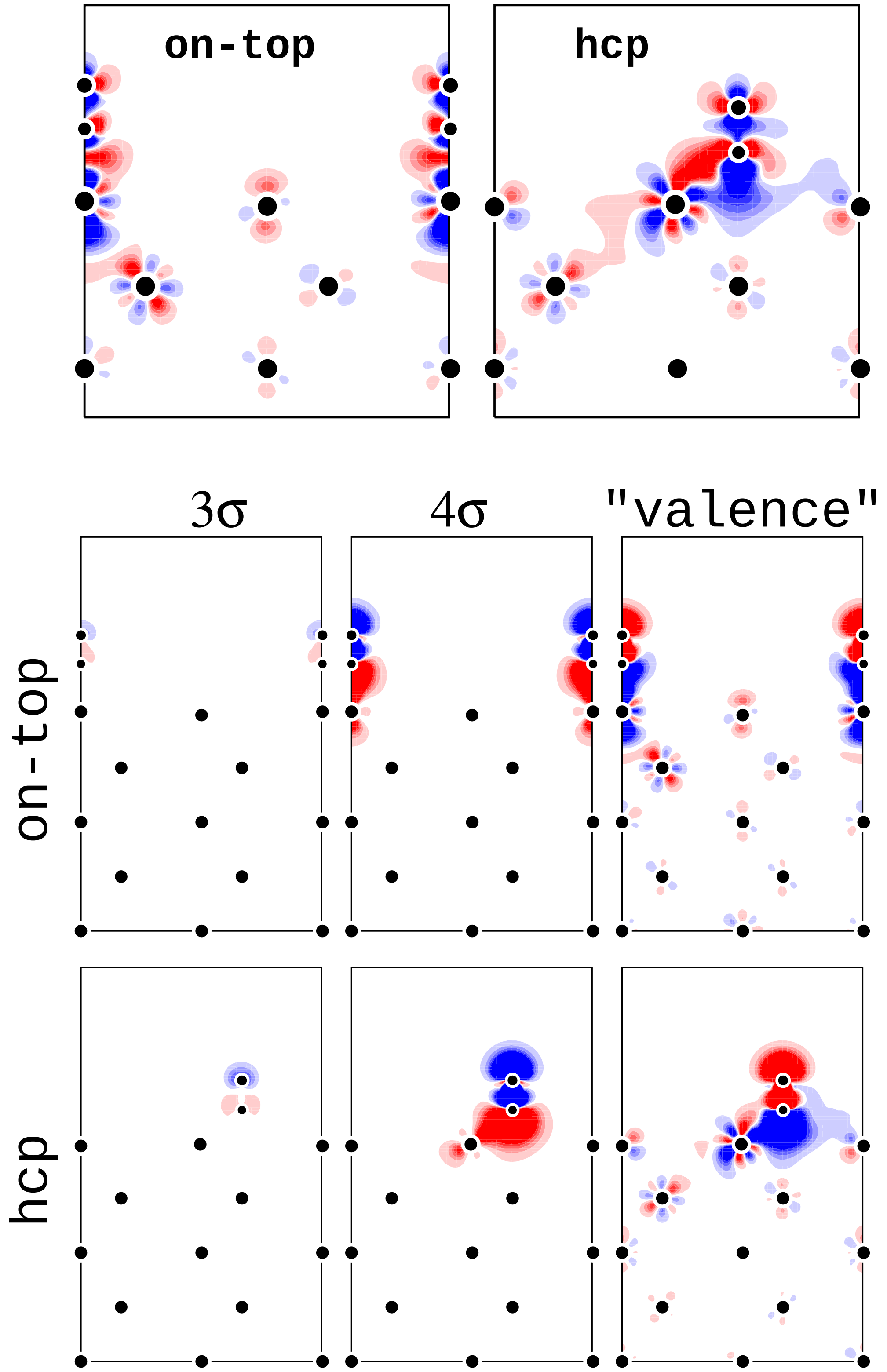
- Blyholder [1964]: HOMO (5σ) becomes somewhat emptied, LUMO ($2\pi^*$) occupied







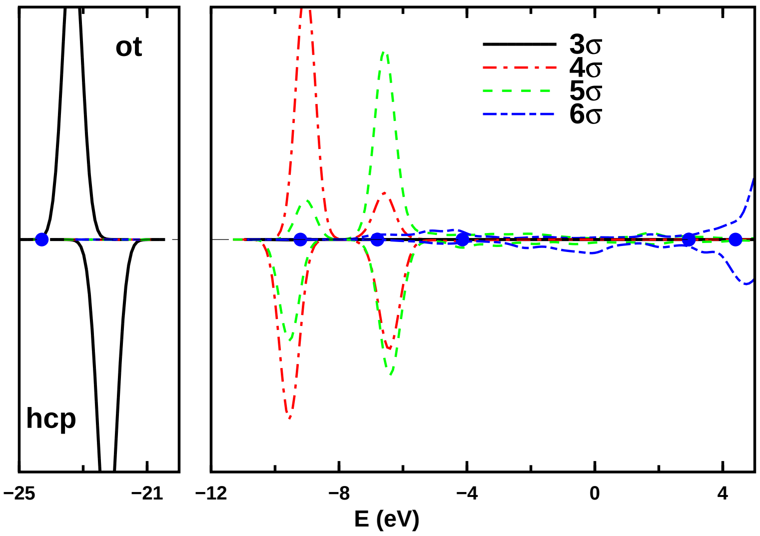
CO/Ru(0001): Density differences

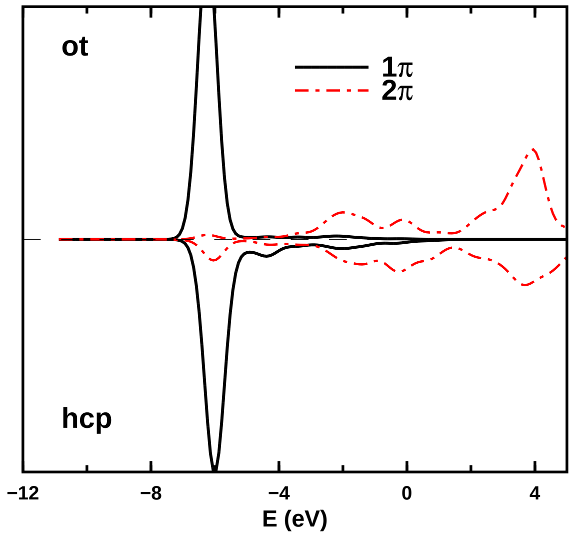


CO/Ru(0001): $4\sigma/5\sigma$ mixing

- PDOS at 4σ and 5σ exchange magnitude (Projection $\sum_i |\langle\psi_{\mathrm{CO,j}}|\psi_{\mathrm{CO/Ru,i}}\rangle)$

- $2\pi^*$ gains occupation



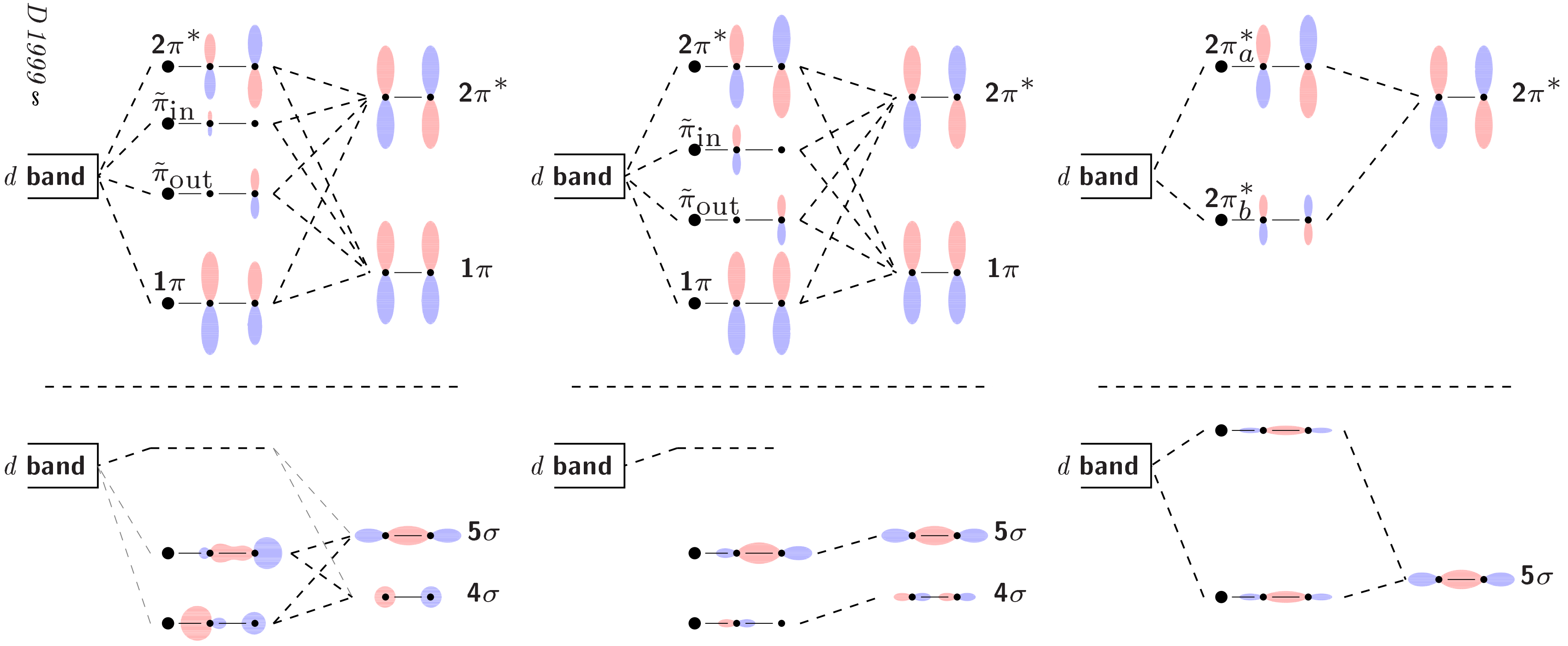


CO/Ru(0001): Orbital occupations

	Cs_{hcp}+CO_{ot}	CO_{ot}	CO_{ot}+O_{hcp}	Cs_{ot}+CO_{hcp}	CO_{hcp}
3σ	0.998	0.999	0.999	0.998	0.999
4σ	0.988	0.995	0.996	0.985	0.995
5σ	0.883	0.898	0.901	0.897	0.905
6σ	0.062	0.099	0.059	0.090	0.091
1π	0.969	0.984	0.984	0.961	0.977
$2\pi^*$	0.350	0.241	0.225	0.423	0.349
$4\sigma/5\sigma$ mix (%)	5	12	13	18	34
Charge at CO (e^-)	−1.14	−0.88	−0.75	−1.48	−1.28

- $4\sigma/5\sigma$ mixing = amount of 5σ character at $\varepsilon_{4\sigma}$

Revised Blyholder model



CO adsorption site

Experiments

	Co ot	Ni fcc	Cu ot
Ru ot	Rh ot	Pd fcc	
	Ir ot	Pt ot	

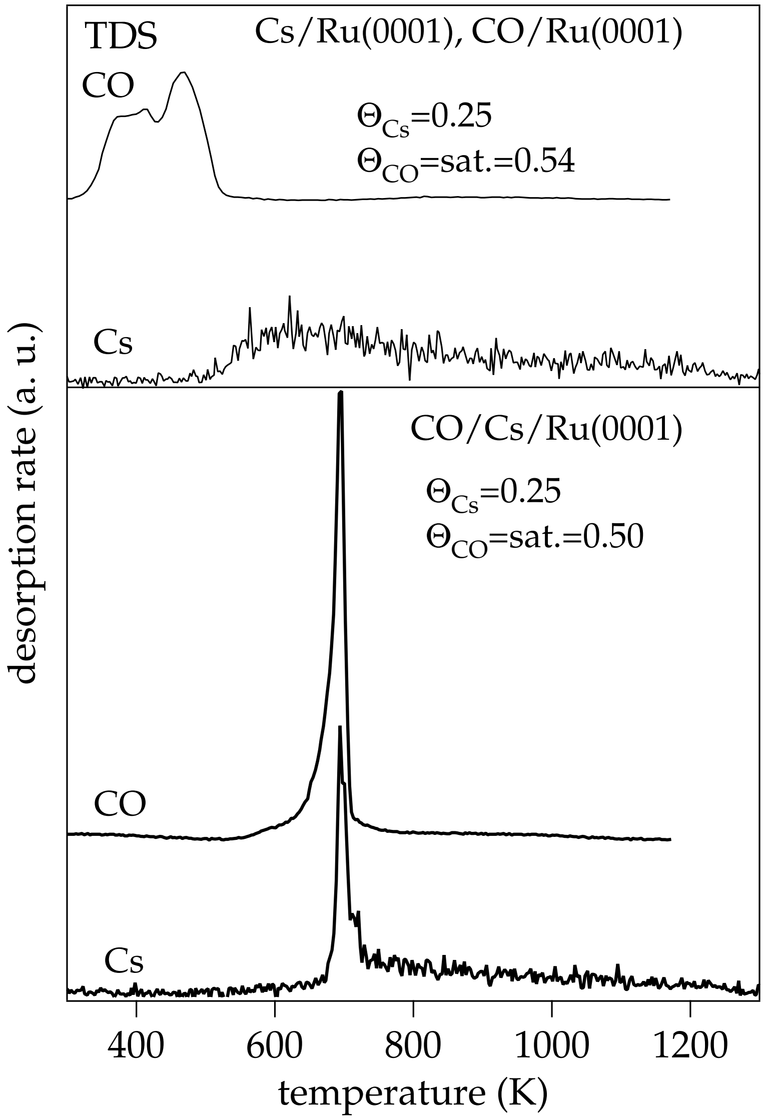
DFT-GGA

			Cu fcc
Ru ot	Rh ot	Pd fcc	
	Ir ot	Pt fcc	

Binding energy (**Experimental**)

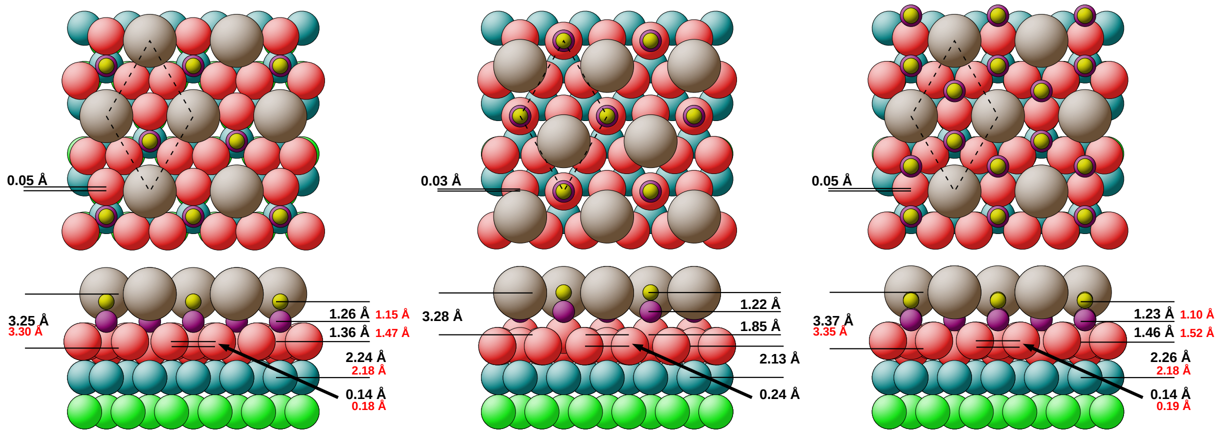
	on-top	fcc
Ru (0001)	−1.83	+0.22
	−1.66	
Rh (111)	−1.75	+0.04
	−1.79	
Pd (111)	+0.50	−1.87
		−1.47
Ir (111)	−1.99	+0.53
Pt (111)	+0.13	−1.62
	−1.50	

Cs+CO/Ru(0001): Energetics



	Cs/Ru	CO/Cs/Ru	2CO/Cs/Ru	CO/Ru
$E_{ads,CO}$ (eV)	—	2.68	2.06	1.83
$E_{ads,Cs}$ (eV)	1.94	2.79	—	—
E_{mix} (eV)	—	0.85	0.26	—
$\Delta\phi$ (eV)	−3.44	−3.32	−2.74	+0.81

Cs+CO/Ru(0001): Geometry



	$d_{\mathrm{C-O}}$ (Å)	$d_{\mathrm{C-Ru}}$ (Å)	$d_{\mathrm{A-Ru}}$ (Å)
$\mathrm{CO}^{\mathbf{E}}_{\mathrm{hcp}}$/Ru	1.21	2.16	—
$\mathrm{Cs}_{\mathrm{ot}}$/Ru	—	—	3.16
$\mathrm{CO}_{\mathrm{hcp}}/\mathrm{Cs}_{\mathrm{ot}}$/Ru	1.26	2.14	3.25
$2\mathrm{CO}_{\mathrm{hcp,fcc}}/\mathrm{Cs}_{\mathrm{ot}}$/Ru	1.23	2.17	3.37
$\mathrm{CO}_{\mathrm{hcp}}$	1.19	2.16	—
$\mathrm{CO}^{\mathbf{E}}_{\mathrm{ot}}$	1.18	1.90	—
$\mathrm{Cs}_{\mathrm{hcp}}$/Ru	—	—	3.52
$\mathrm{CO}_{\mathrm{ot}}/\mathrm{Cs}_{\mathrm{hcp}}$/Ru	1.22	1.85	3.67
$\mathrm{CO}_{\mathrm{ot}}$	1.16	1.92	—
$\mathrm{CO}_{\mathrm{gas}}$	1.13	—	—

Cs+CO/Ru(0001): Bond lengths

- C-O bond length increases, as expected; due to *i)* adsorption, *ii)* electric field and *iii)* change of adsorption site

1.13 Å (gas) $\Rightarrow$ 1.16 Å (ot) $\Rightarrow$ 1.18 Å (ot$^{\mathbf{E}}$)

$\Rightarrow$ 1.19 Å (hcp) $\Rightarrow$ 1.21 Å (hcp$^{\mathbf{E}}$) $\Rightarrow$ 1.26 Å (hcp+Cs)

- Expr. not seen on Ru(0001) but on Pt(111)

- Agrees with filling $2\pi^*$

∘ Cs-substrate *increases*:

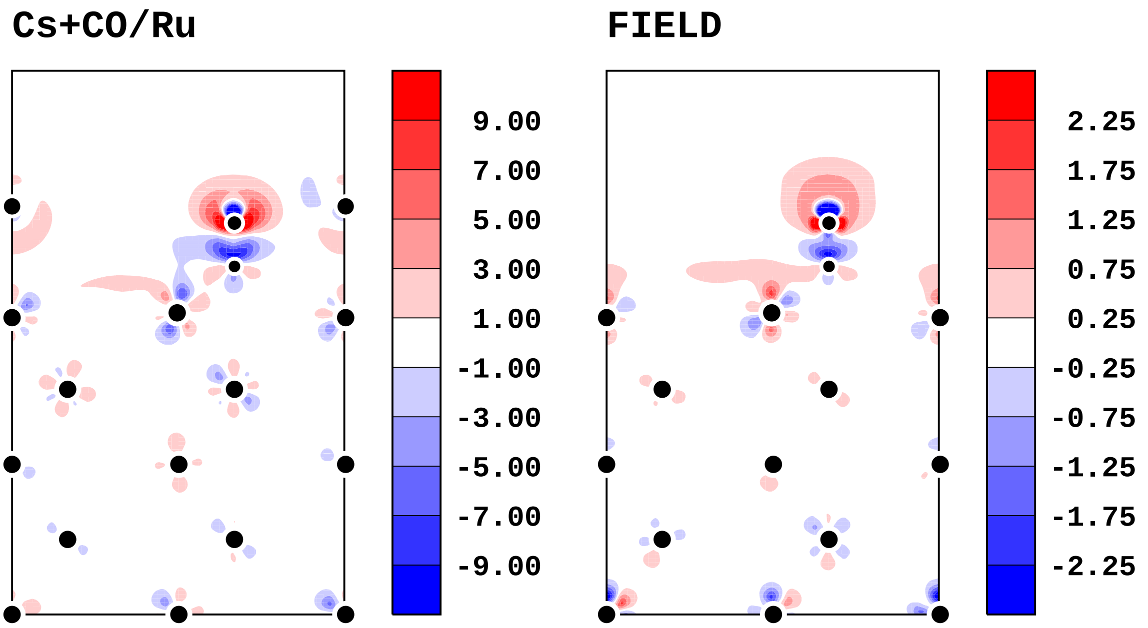
3.16 Å (ot) $\Rightarrow$ 3.25 Å (ot+CO) or

3.52 Å (hcp) $\Rightarrow$ 3.67 Å (hcp+CO)

Cs+CO/Ru(0001): Electric field

$$\Delta n_{\mathrm{WW}} = n(\mathrm{Cs+CO/Ru}) - n(\mathrm{Cs/Ru}) - n(\mathrm{CO/Ru}) + n(\mathrm{Ru})$$

$$\Delta E_{\mathrm{WW}} = E(\mathrm{Cs+CO/Ru}) - E(\mathrm{Cs/Ru}) - E(\mathrm{CO/Ru}) + E(\mathrm{Ru})$$



Binding energy of CO:

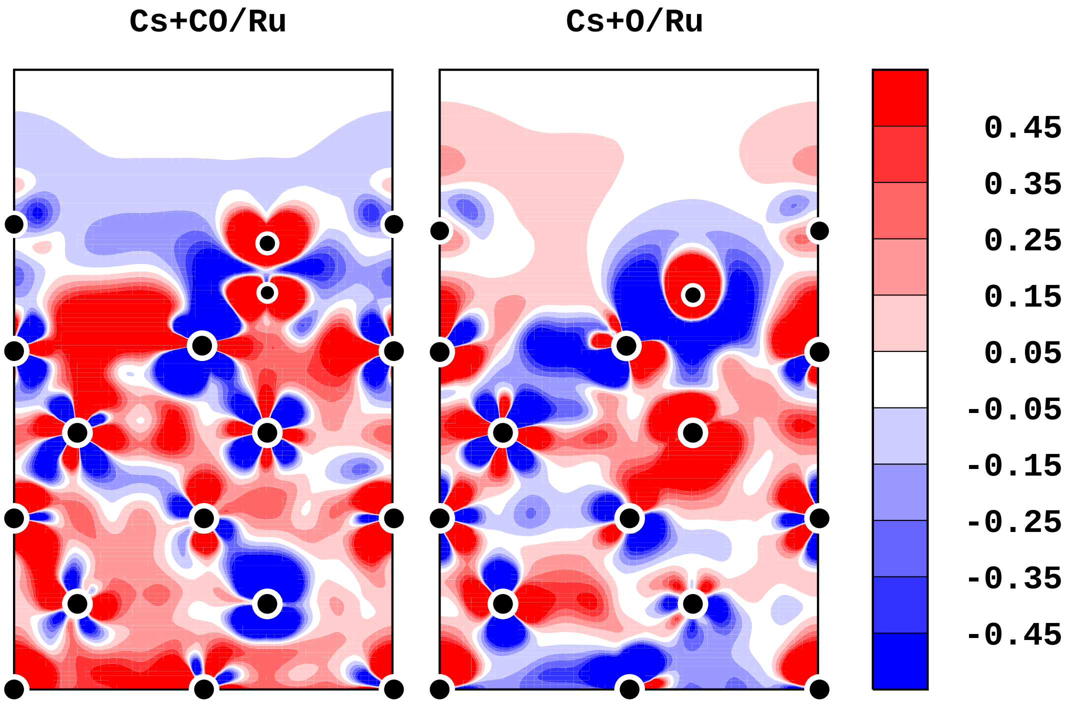
	on-top	hcp
Without field/Cs	1.80	1.76
$\mathrm{E_{Field}}$/Ru	1.84	1.85
Cs/Ru	2.23	2.68

Please note: The strength of field too small!

Cs+CO/Ru(0001): DFT vs. MDS

- He Meta-stable de-excitation spectroscopy: Measures (6s) electron density in the vicinity of Fermi energy

- Good agreement: Cs+CO/Ru decreases magnitude, Cs+O/Ru increases (Fichtner-Endruschat *et al*, 1998)



Cs+CO/Ru(0001): Conclusions

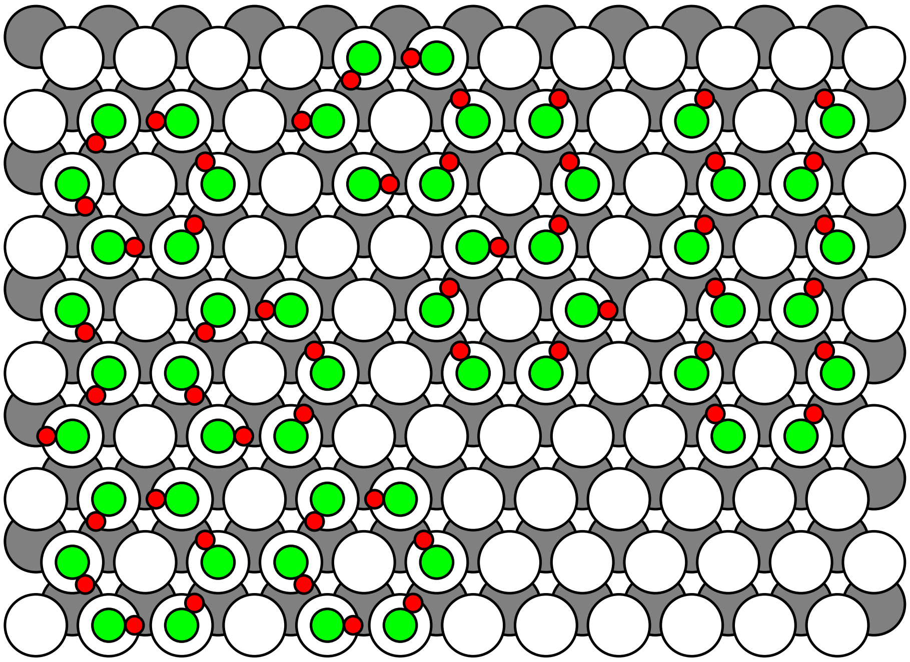
- Cesium: Adsorption induces a strong electric field
- Carbon monoxide: Blyholder model is qualitatively correct
- Small adjustments necessary ($4\sigma/5\sigma$)
- Cesium & carbon monoxide:
  - Strong attractive interaction
  - CO internally polarised due to the field, leads to increased occupation of $2\pi^*$
  - C-O bond length increases due to the combined effect of adsorption (site) and external field
- CO/Pt(111), CO/Cu(111): What goes wrong??

OH/Pt(111): On the way to fuel cells

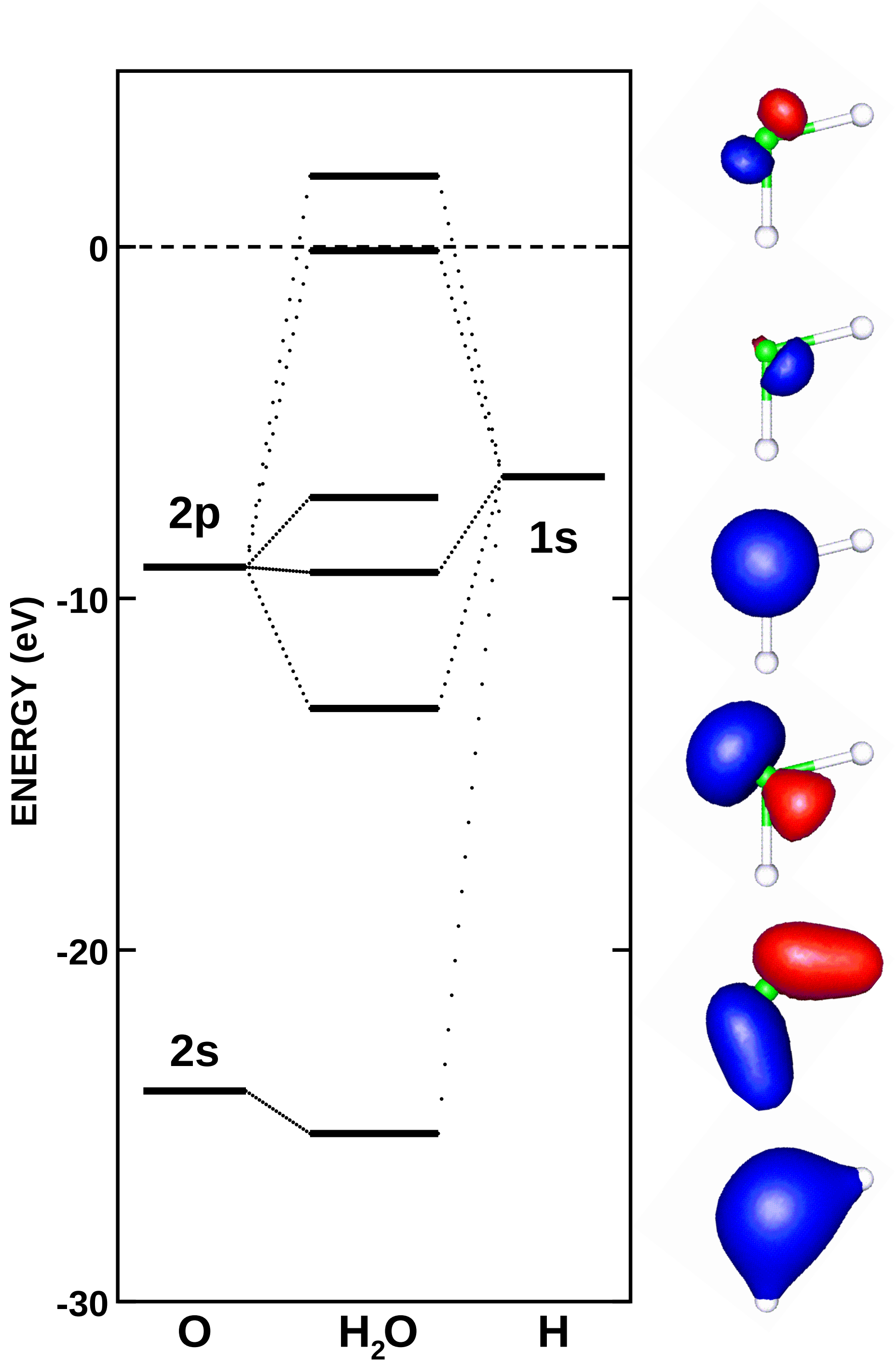
$[\ \mathsf{H_2} + \frac{1}{2}\mathsf{O_2} \Rightarrow \mathsf{H_2O} + \mathcal{E}\ ]$

- Efficient way to prepare OH/Pt:
  H_2O + O/Pt $\Rightarrow$ OH/Pt
  (Bedürftig, Wintterlin *et al*)

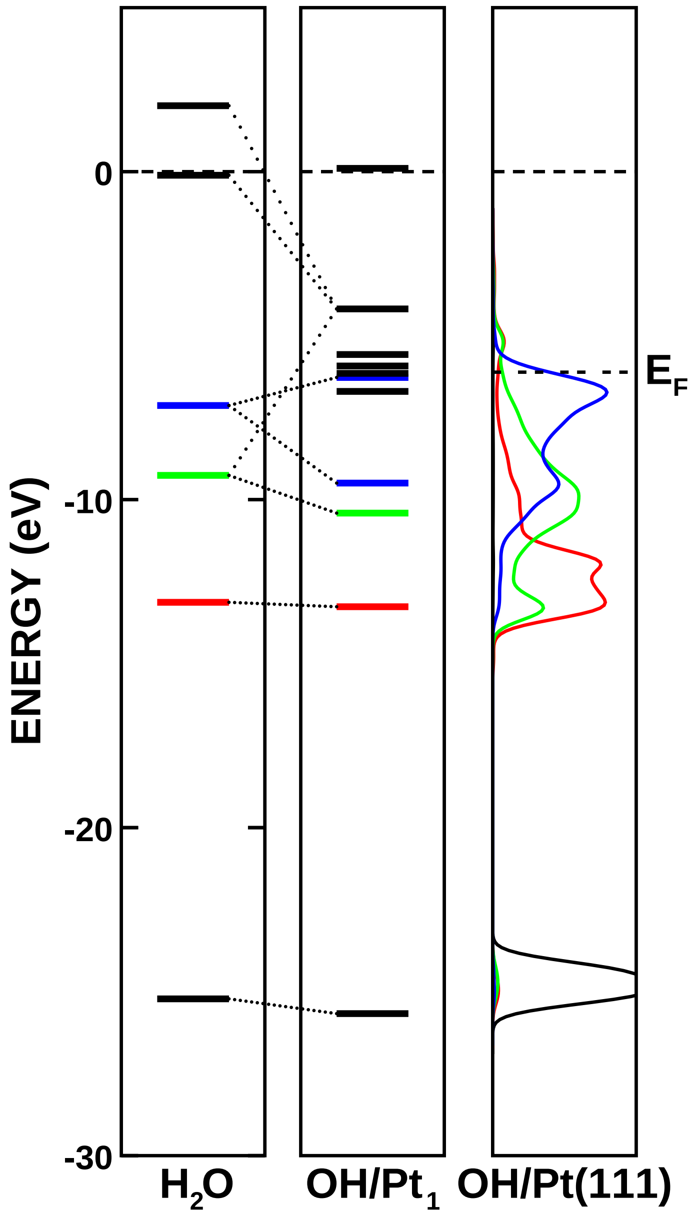
- $\Theta_{\mathrm{OH}} = 2/3$, honey-comb structure



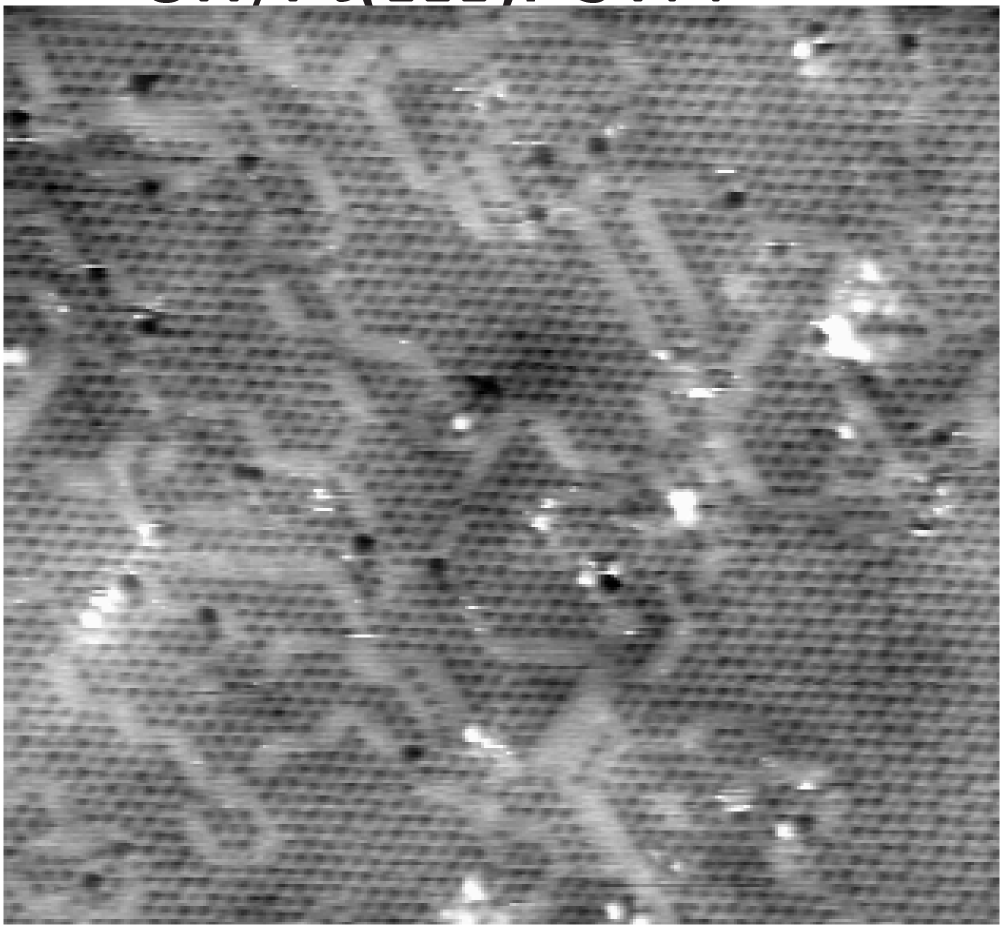
OH/Pt(111): Water molecule



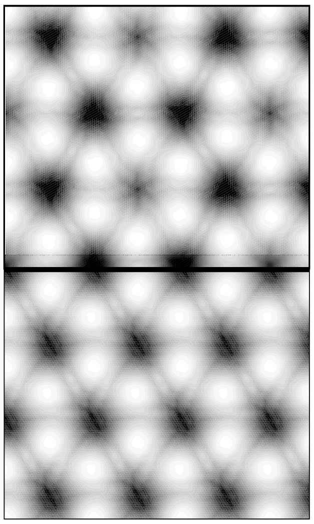
OH/Pt(111): Orbital diagram, LDOS



OH/Pt(111): STM



Simulated STM:

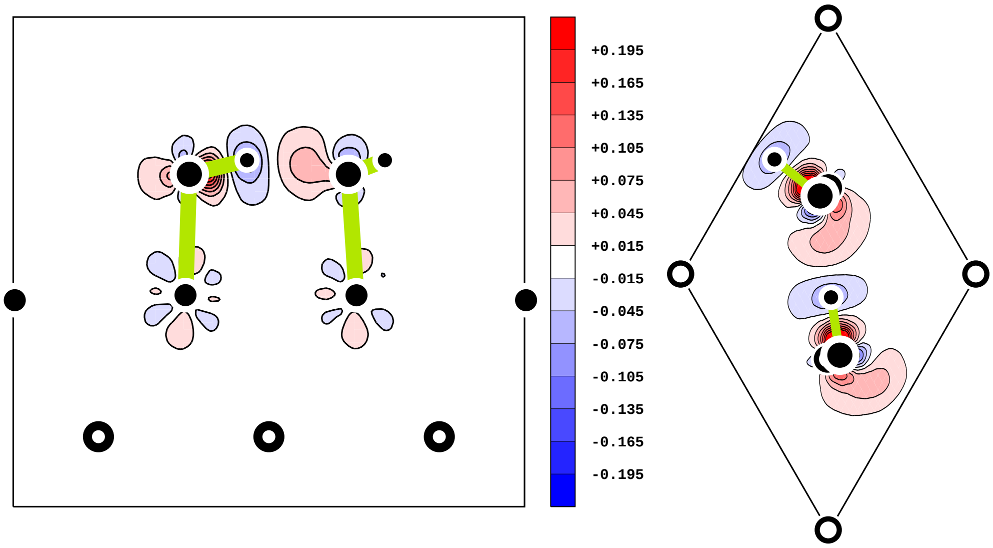


(3×3)

$(\sqrt{3} \times \sqrt{3})$**R30**$^\circ$

OH/Pt(111): Interaction

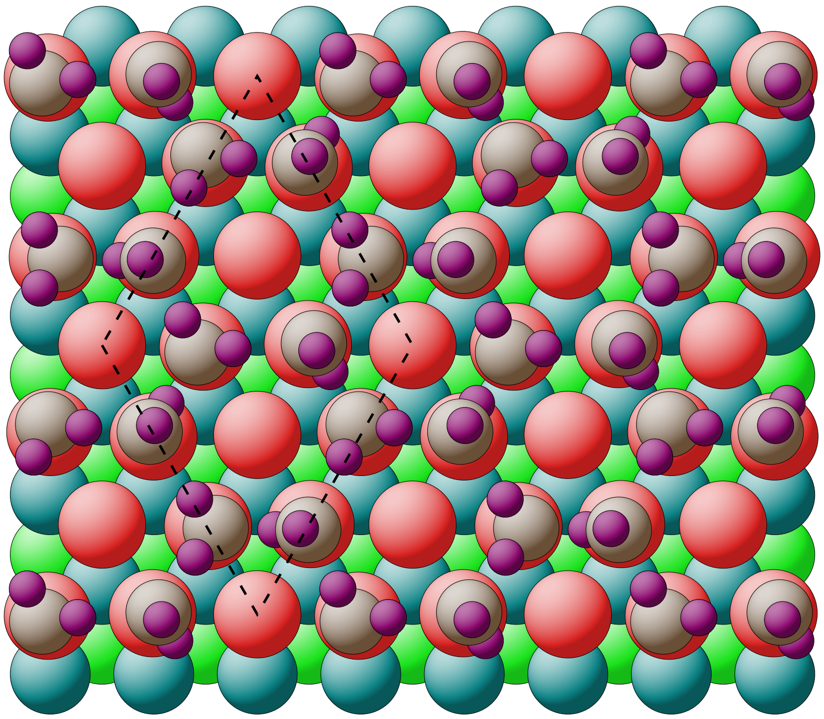
ww DENSITY

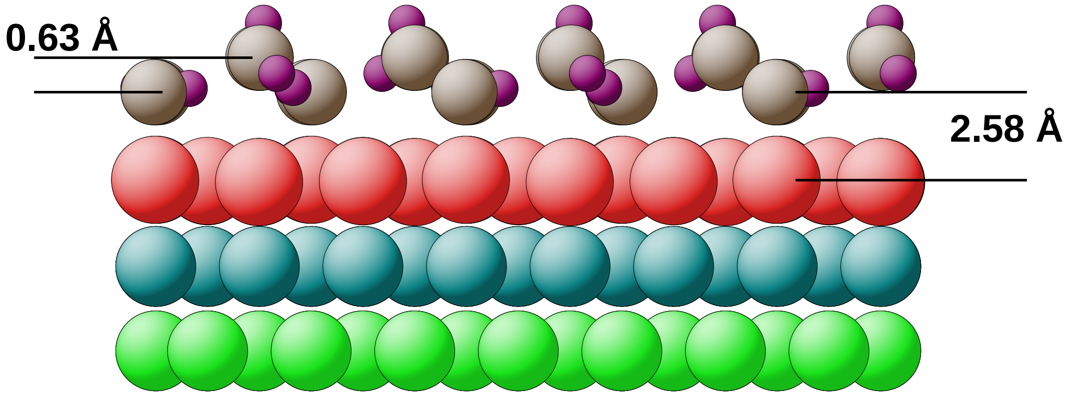


- $E_{ww} = 0.20$ eV/OH: typical strength for hydrogen-bond

H_2O/Pt(111): Geometrical model

- Generally accepted double-layer model:



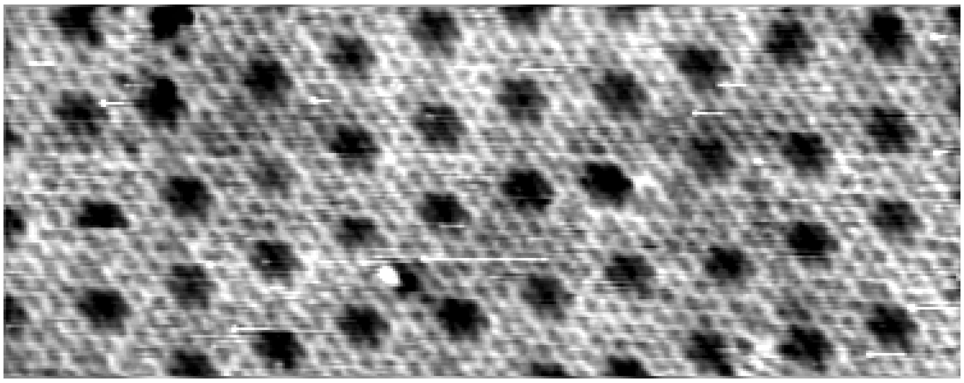


- Clustering of molecules seen recently in HR-EELS, HAS & DFT

H_2O: Geometry (O-O buckling)

- Over *et al*: Identical geometry to OH/Pt(111) (LEED: hydrogens not seen)

- STM (Morgenstern 1996, Völkening 1999): Incommensurate structures on Pt(111)

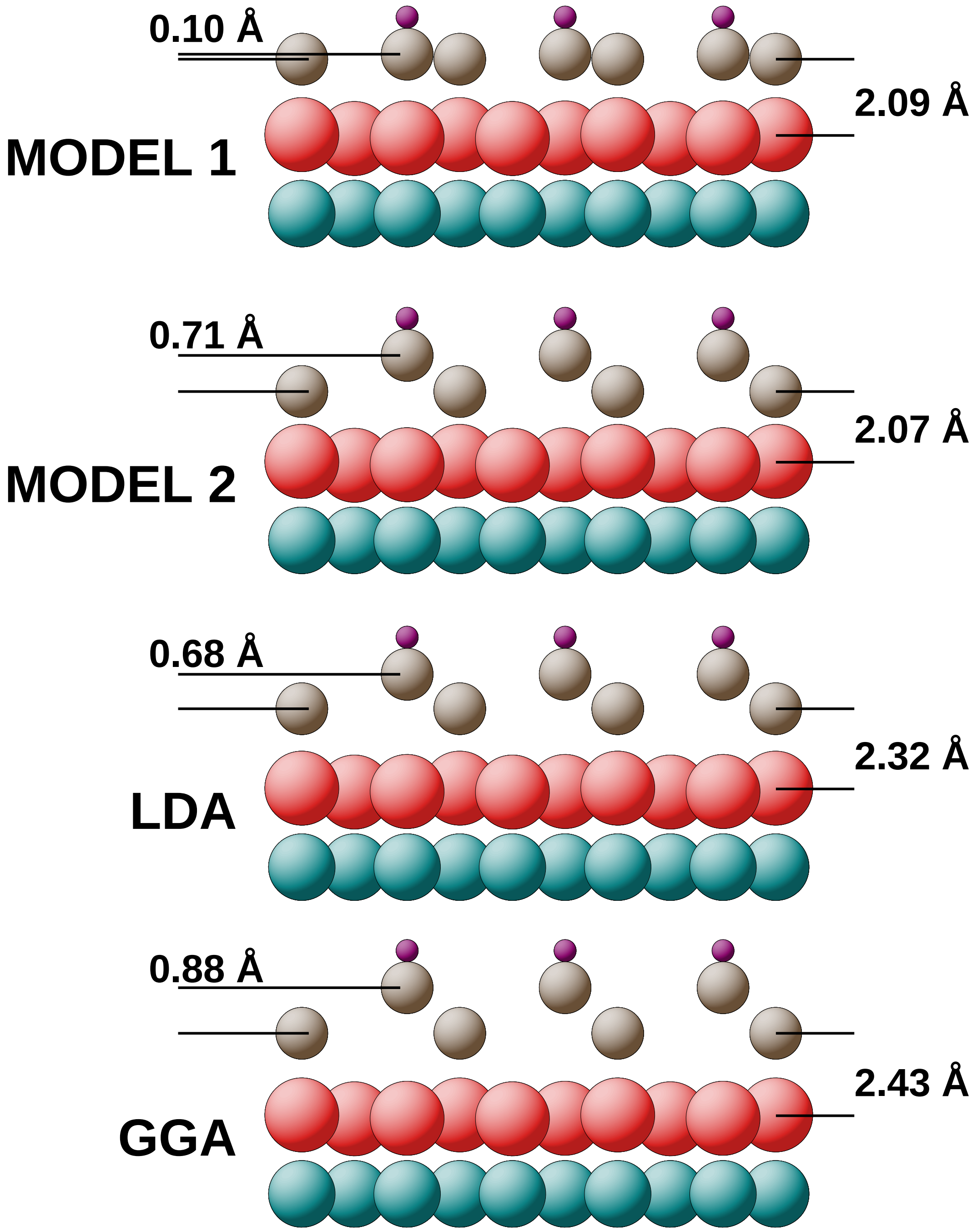


Experimentally:

	Ice	Ru(0001)	Pt(111)
Lateral distance	2.61 Å	2.71 Å	2.77 Å
Tension	0	3.6 %	6.1 %
O-O buckling	0.96 Å	0.08 Å / 0.71 Å	≈ 0

D_2O/Ru(0001): Geometry

- Held & Menzel (1994), LEED:
  two models, smaller buckling preferred



OH,H_2O/Pt(111): Conclusions

- Hydroxyl: Hydrogen-bond network of tilted molecules
- Substrate atoms act as replacement for hydrogen
- Water: Disagreement in geometry
  - LEED?
  - (LDA, GGA?)
- Solution: Vibrations? (HR-EELS)