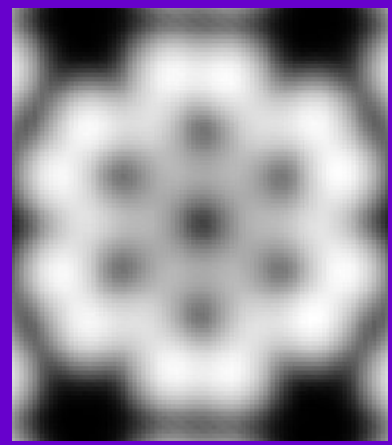
STM simulations as a strucutral tool

Jorge Iribas Cerdá
ICMM-CSIC (Spain)



Outline

- STM theoretical concepts
- Applications

Surface Studies by Scanning Tunneling Microscopy

G. Binning, H. Rohrer, Ch. Gerber, and E. Weibel
IBM Zurich Research Laboratory, 8803 Rüschlikon-ZH, Switzerland
(Received 30 April 1982)

Surface microscopy using vacuum tunneling is demonstrated for the first time. Topographic pictures of surfaces on an *atomic scale* have been obtained. Examples of resolved monoatomic steps and surface reconstructions are shown for (110) surfaces of $CaIrSn_4$ and Au.

PACS numbers: 68.20.+t, 73.40.Gk

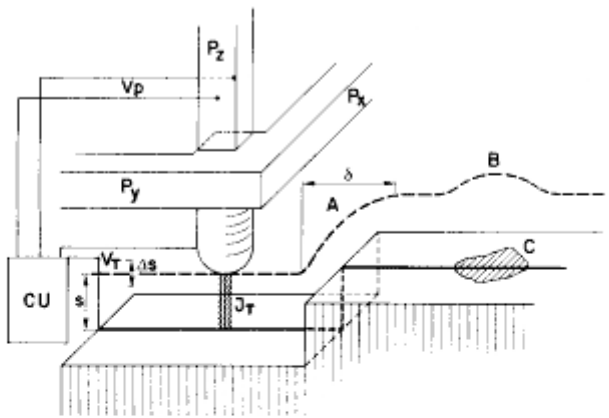


FIG. 1. Principle of operation of the scanning tunneling microscope. (Schematic: distances and sizes are not to scale.) The piezodrives P_x and P_y scan the metal tip M over the surface. The control unit (CU) applies the appropriate voltage V_p to the piezodrive P_z for constant tunnel current J_T at constant tunnel voltage V_T. For constant work function, the voltages applied to the piezodrives P_x, P_y, and P_z yield the topography of the surface directly, whereas modulation of the tunnel distance s by Δs gives a measure of the work function as explained in the text. The broken line indicates the z displacement in a y scan at (A) a surface step and (B) a contamination spot, C, with lower work function.

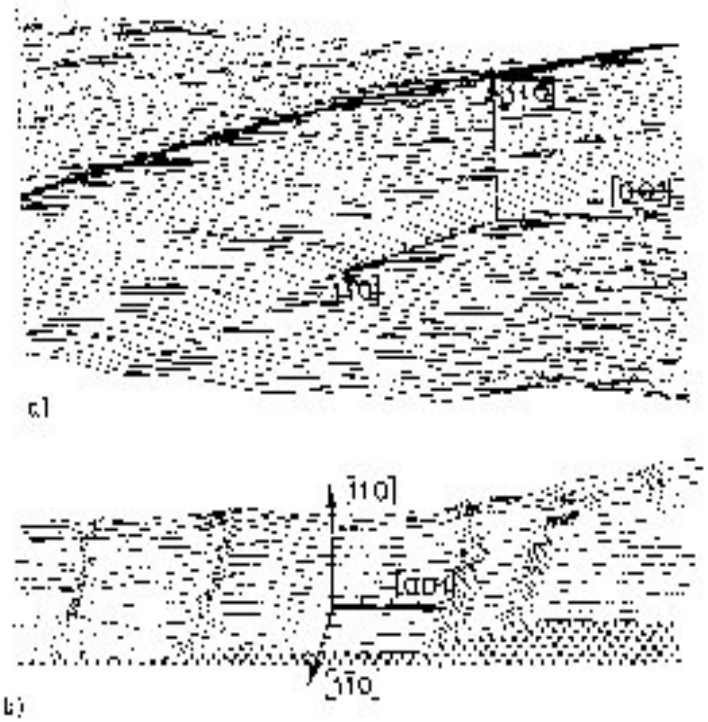
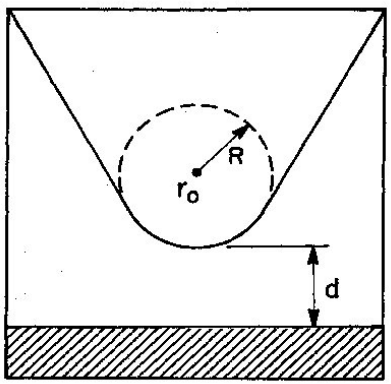


FIG. 3. Two examples of scanning tunneling micrographs of a Au (110) surface, taken at (a) room temperature, and (b) 300°C after annealing for 20 h at the

PHYSICAL REVIEW B VOLUME 31, NUMBER 2 15 JANUARY 1985

Theory of the scanning tunneling microscope

J. Tersoff* and D. R. Hamann
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
(Received 25 June 1984)



- Elastic Scattering
- Weak tip-sample interaction:
  - Potential drop localized at vaccuum region
  - First-order approximation for current (Bardeem approximation)
- s-wave model for the tip

STM does NOT image atoms,
but maps charge density at the tip position & E_f

GOODS

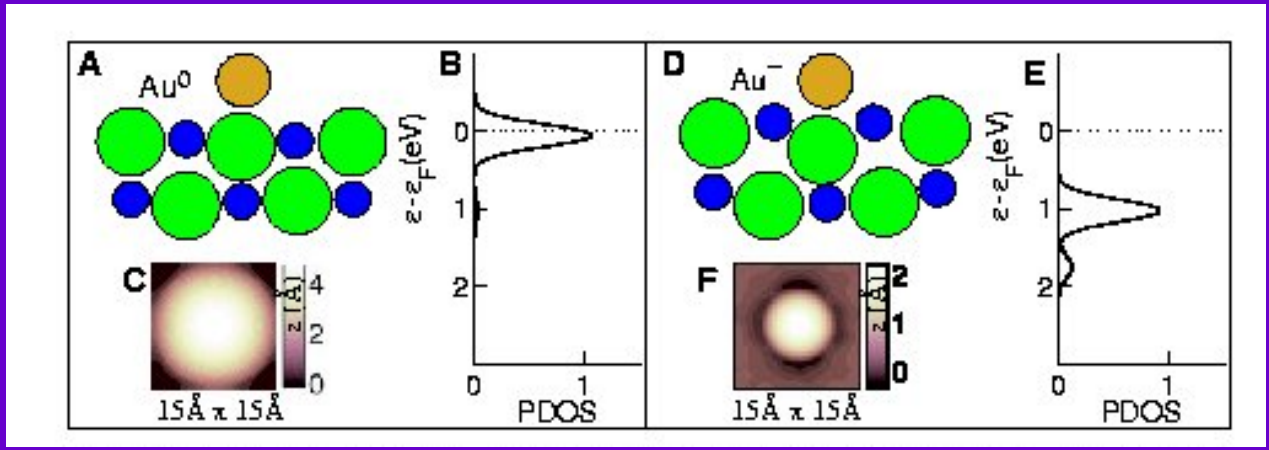
- Works fine for many systems
- Allows DFT formalisms
- Reproduces bias dependence in semiconductors

BADS

- No tip features
- Not fully reliable
- Wrong predictions ... (atomic resolution?)

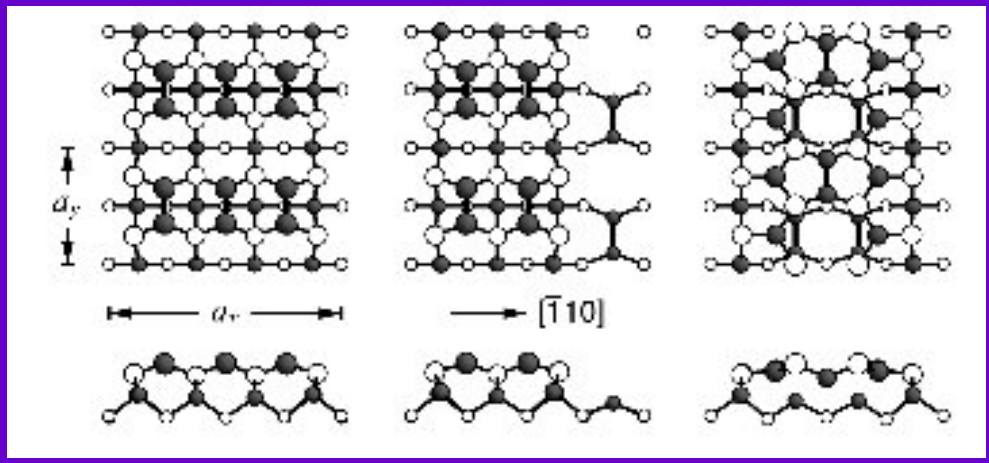
Tersoff-Hamann theory
Application to single Ag

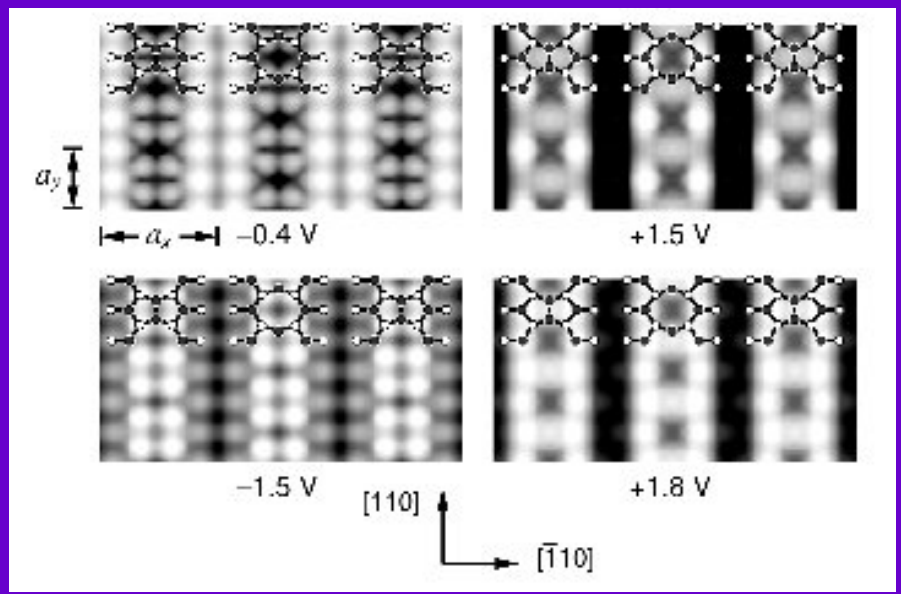
J. Repp et al, Science (04)



Tersoff-Hamann theory
Application to GaAs(100)-c(8x2)

S.-H. Lee et al, PRL (00)





STM Simulations: *green*

www.icmm.csic.es/jcerda

- Geometry
- Elastic Scattering
- k-sampling
- Tunneling regime
- EHT approximation

Structural Sensitivity

Very Variable !!!

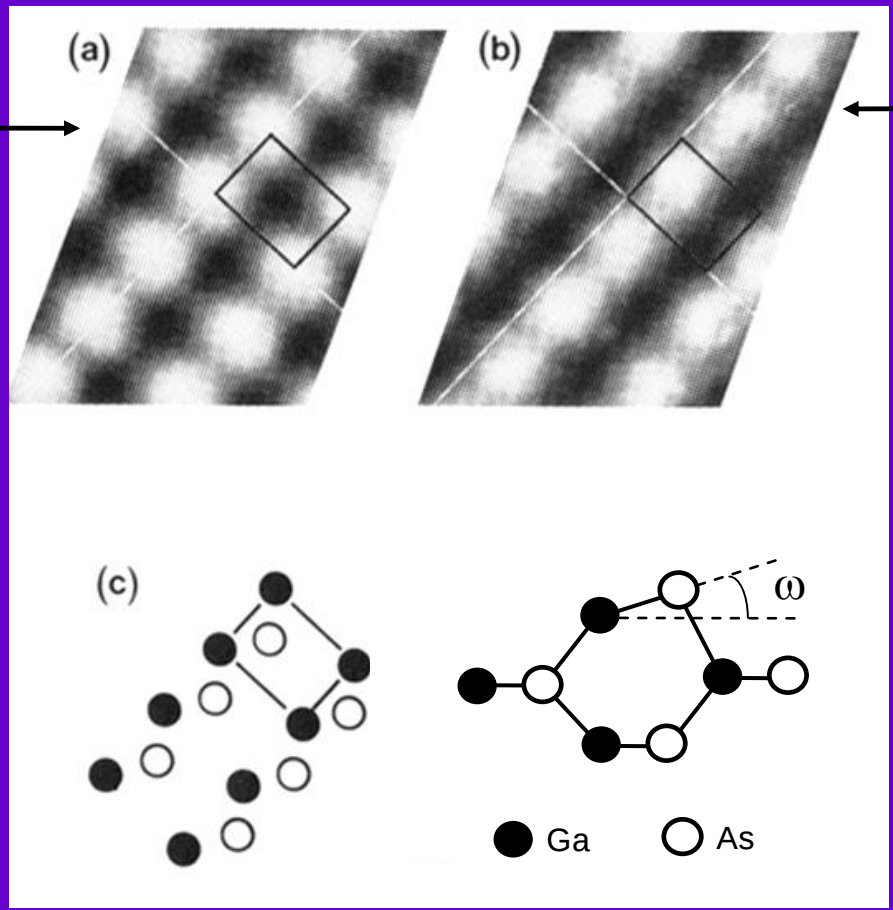
- Experiment vs. Theory comparison:
  - Image aspect
  - Corrugations

- Theoretical variables to play with:
  - Surface structure (DFT)
  - Tip: nature, structure, orientation, etc.

GaAs(110) Surface

R.M. Feensrta et al, PRL (87)

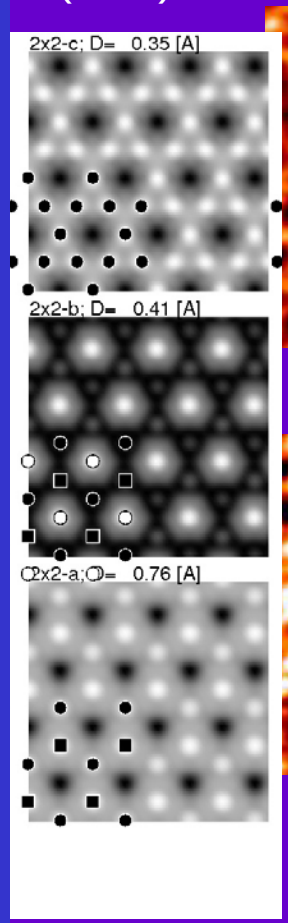
Empty states
Ga atoms

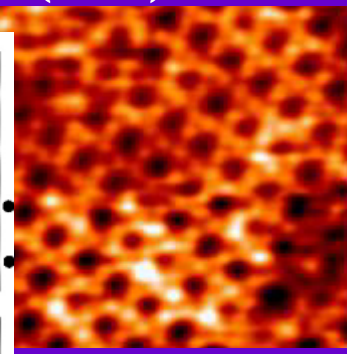


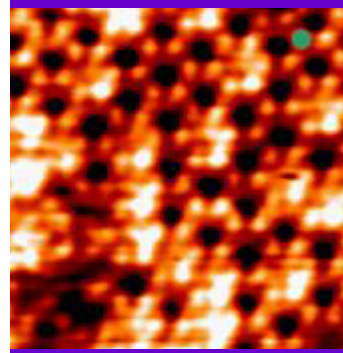
Filled states
As atoms

Rh(111)+nNO
(Tip matters)

W(111)+NO (2x2)+3NO

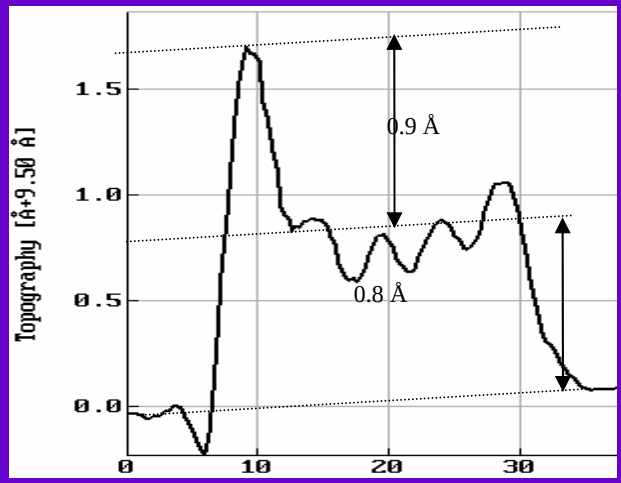


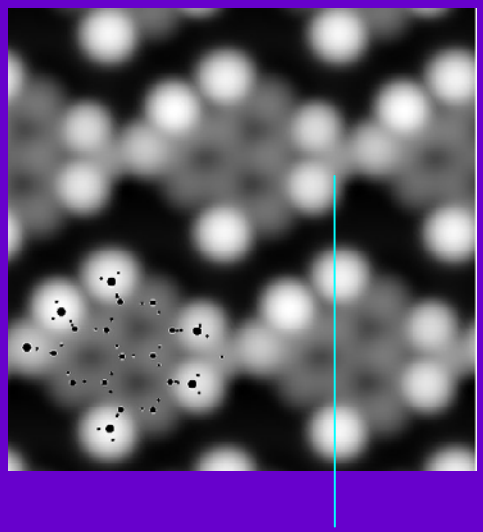


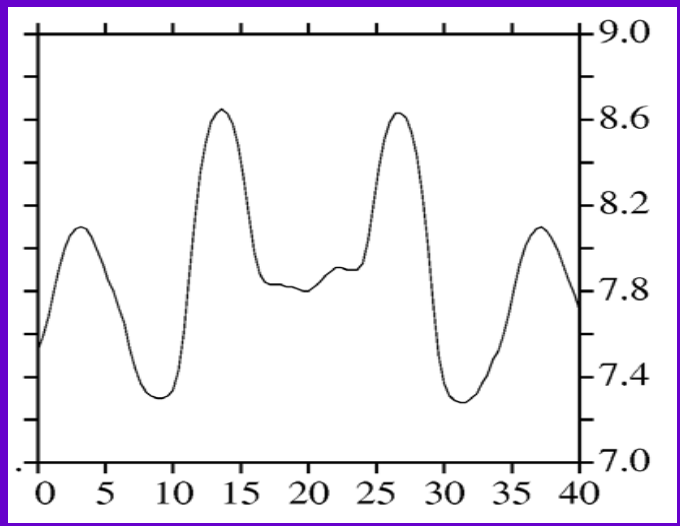


(2x2)+2NO

Pd(111)+H2O: Low T Water clusters (Corrugation matters)



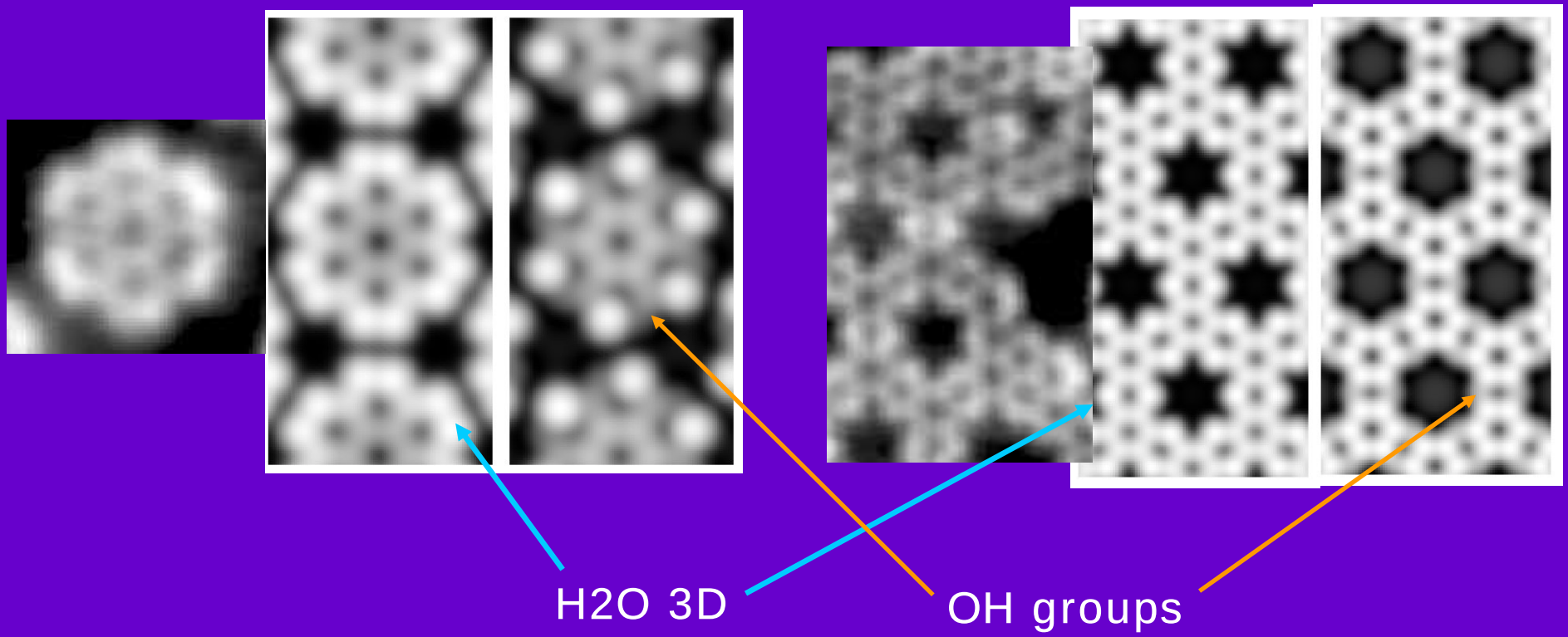




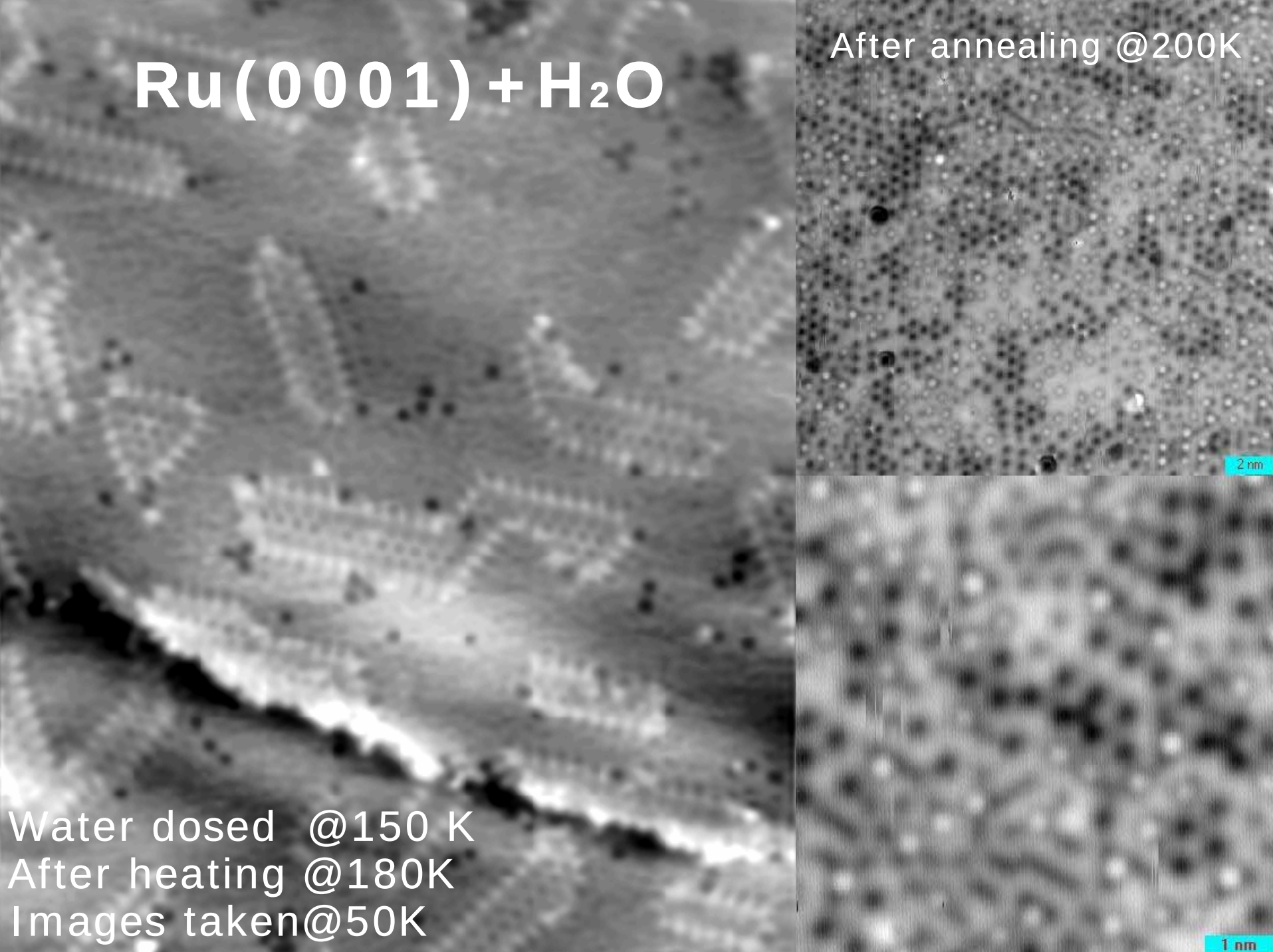
$Pd(111)+H_2O$
(Water 2D quasiperiodic structures)

Rosettes

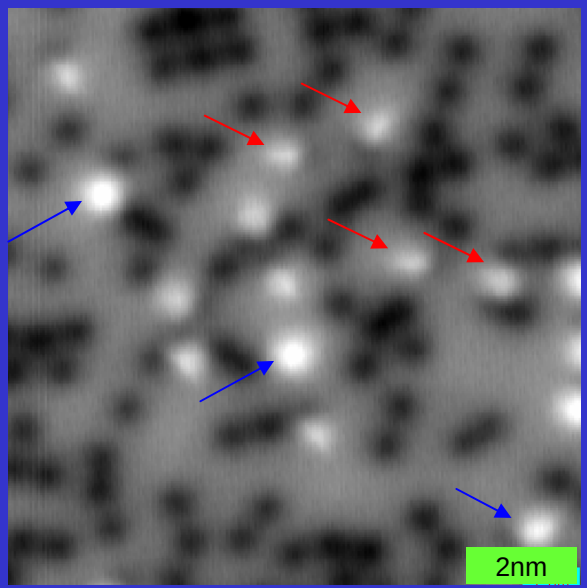
Lace

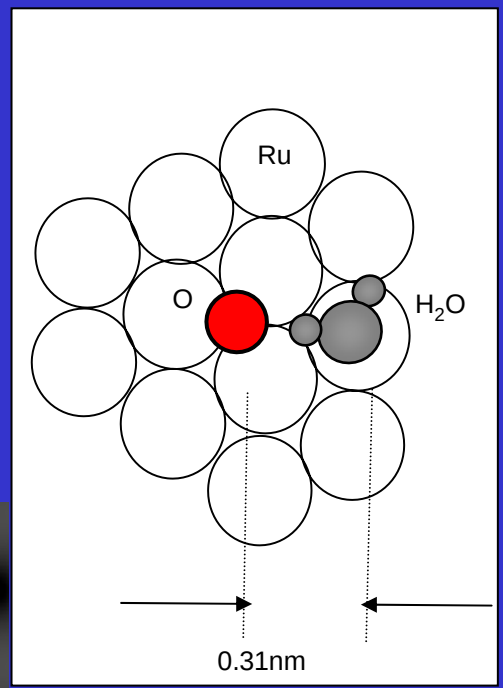


J. Cerdá et al, PRL (04)

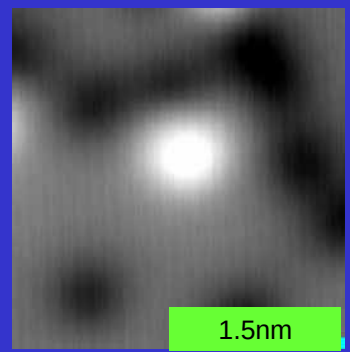

Ru(0001)+H2O
After annealing @200K
2 nm
Water dosed @150 K
After heating @180K
Images taken@50K
1 nm

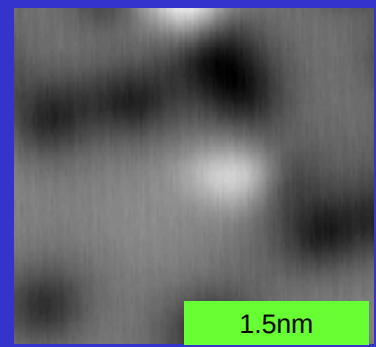
Species before Water Desorption (surface oxygen precovered)

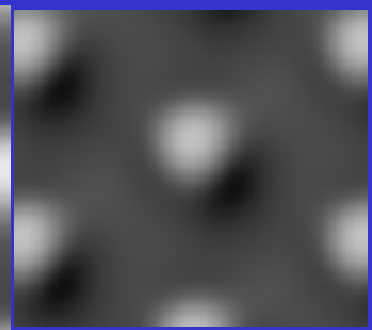




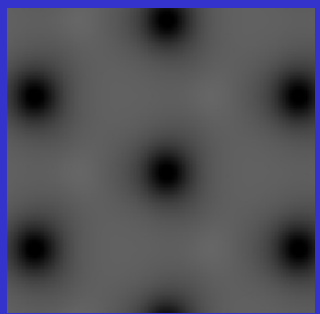
Experiment



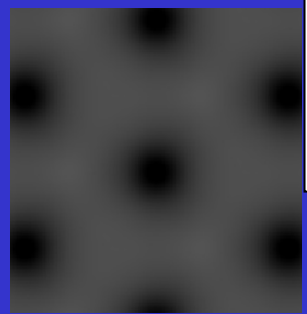




Theory

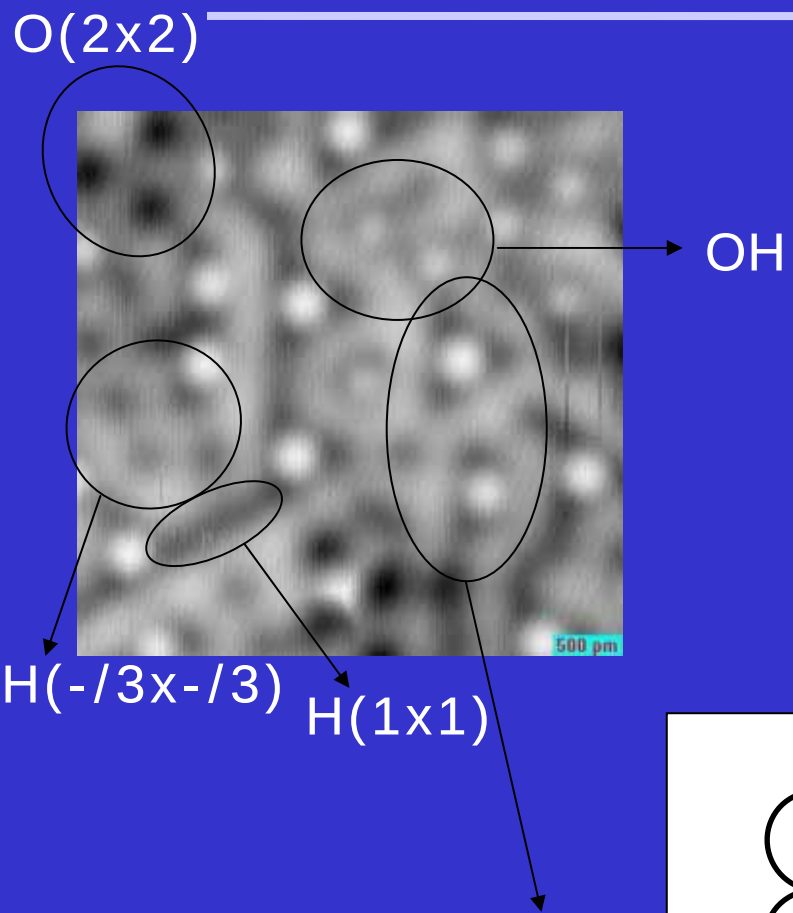


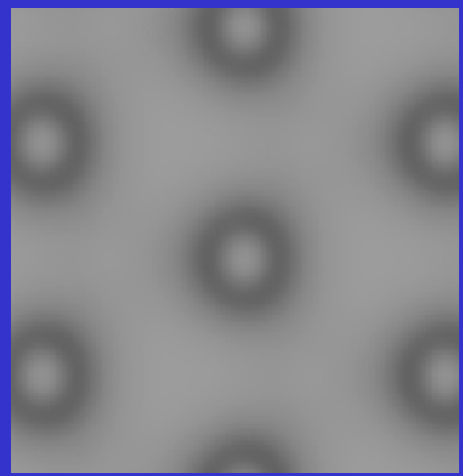
W(110) tip
C=0.43 A



W(111) tip
C=0.29

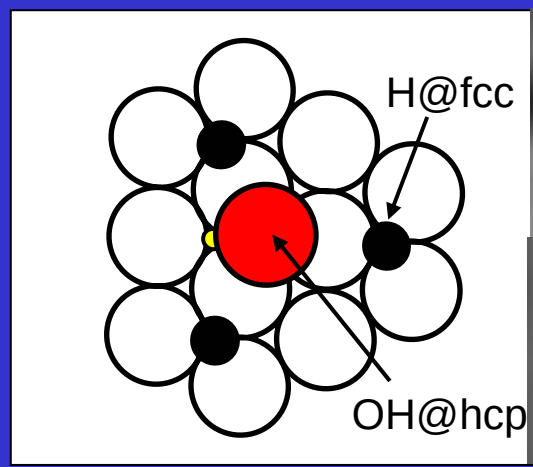
Species after Water Desorption (surface oxygen precovered)

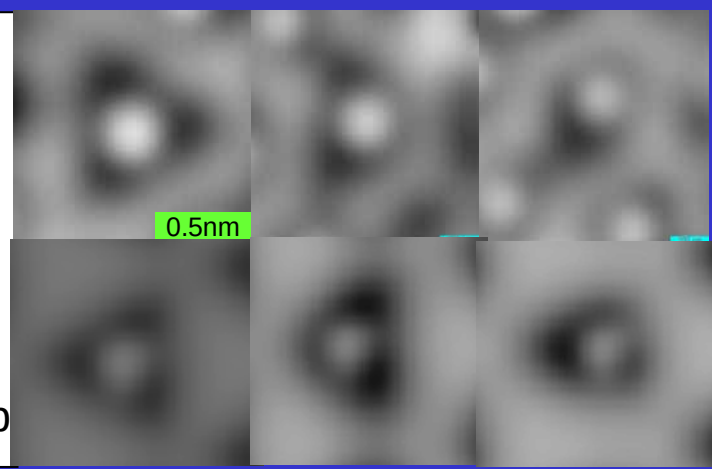




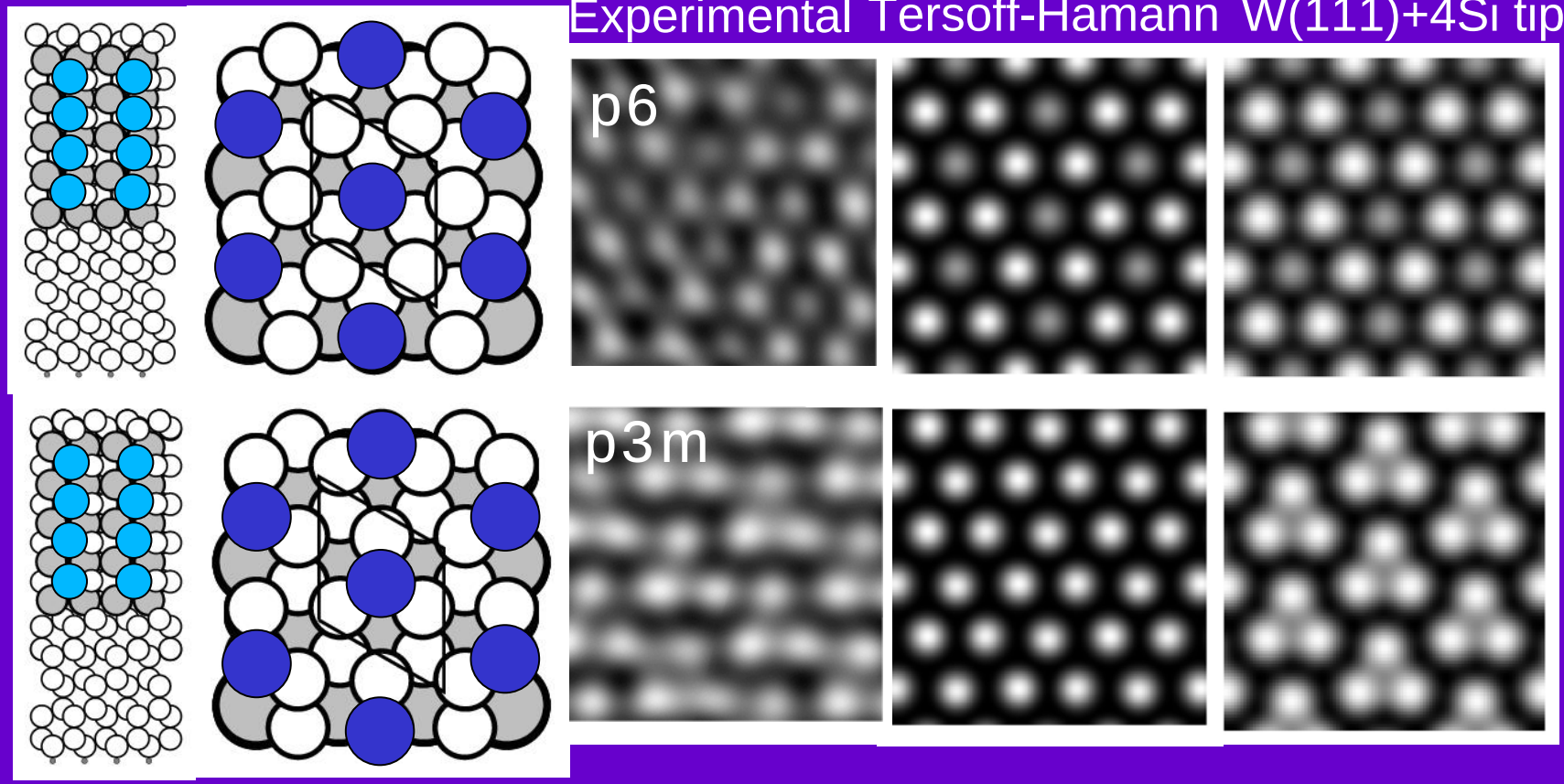
W(110) tip
C=0.21 A

W(111) tip
C=0.14



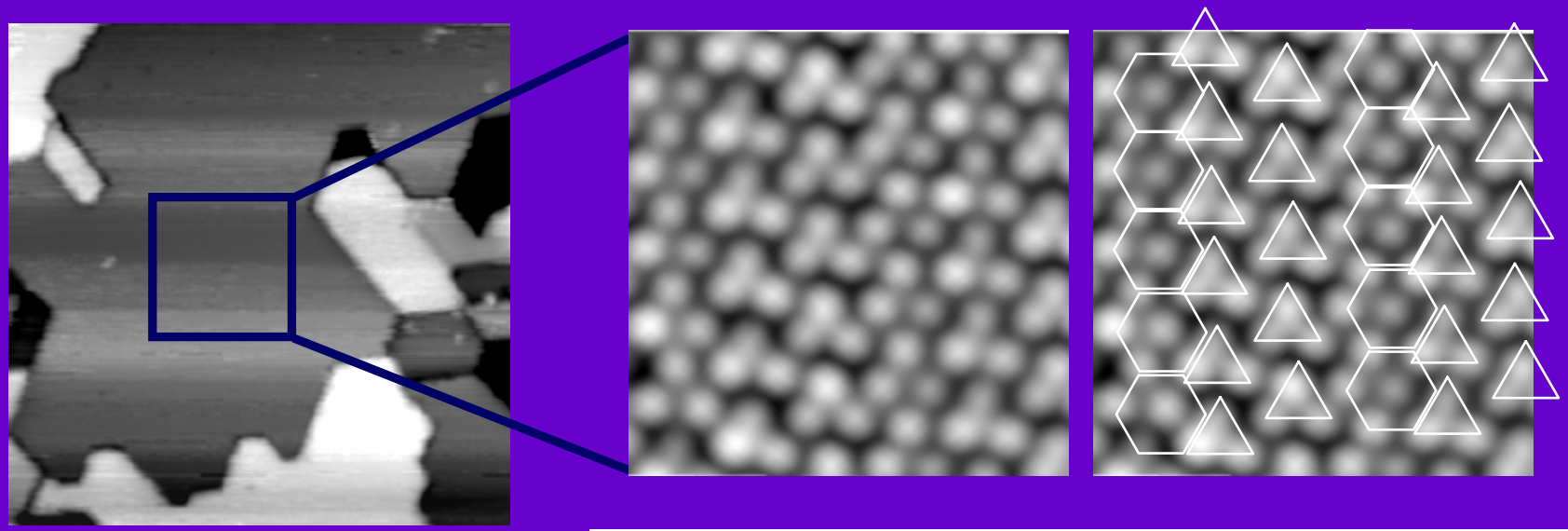


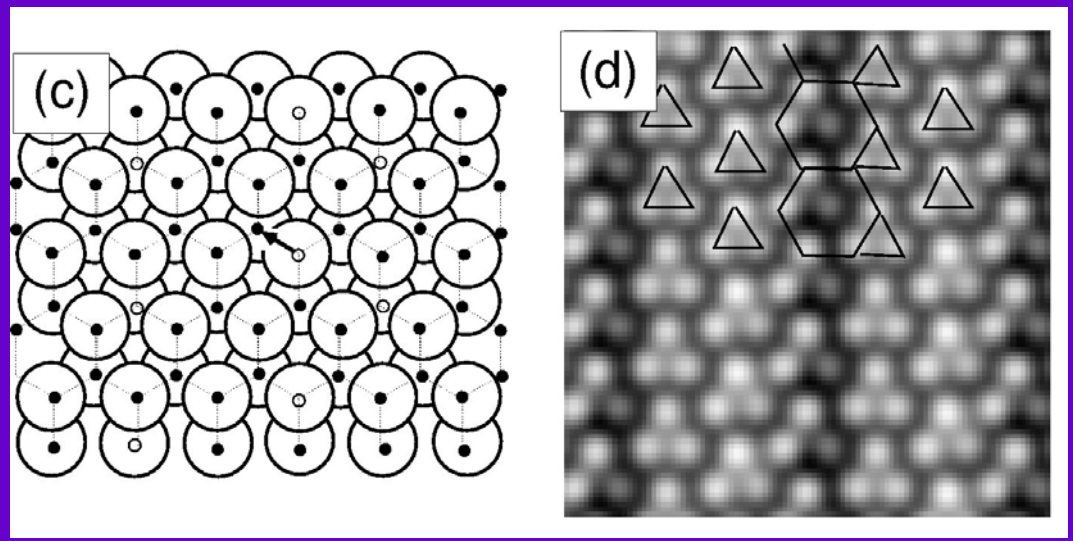
Si(111)-(-/3x-/3)R30+Y3Si5+2Si
STM depth sensitivity



Vacancies at 3rd layer (almost 5 A deep) dictate image aspect despite system is metallic!!

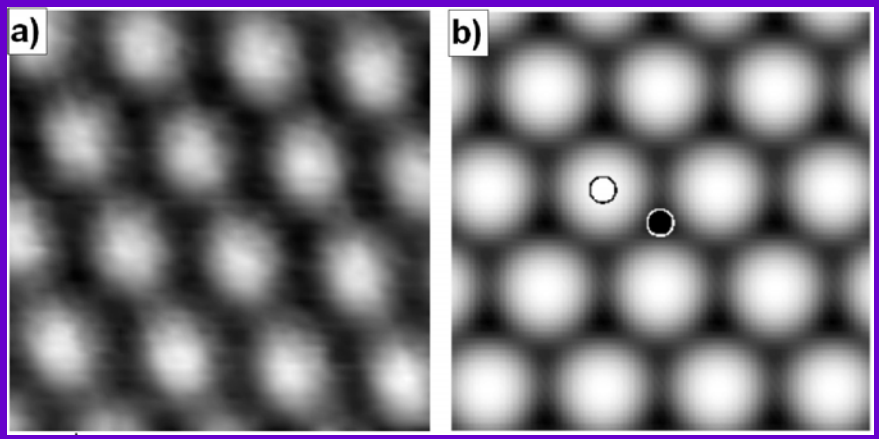
Si(111)-(-/3x-/3)R30+Y_3Si_5
Imaging Buried domain walls

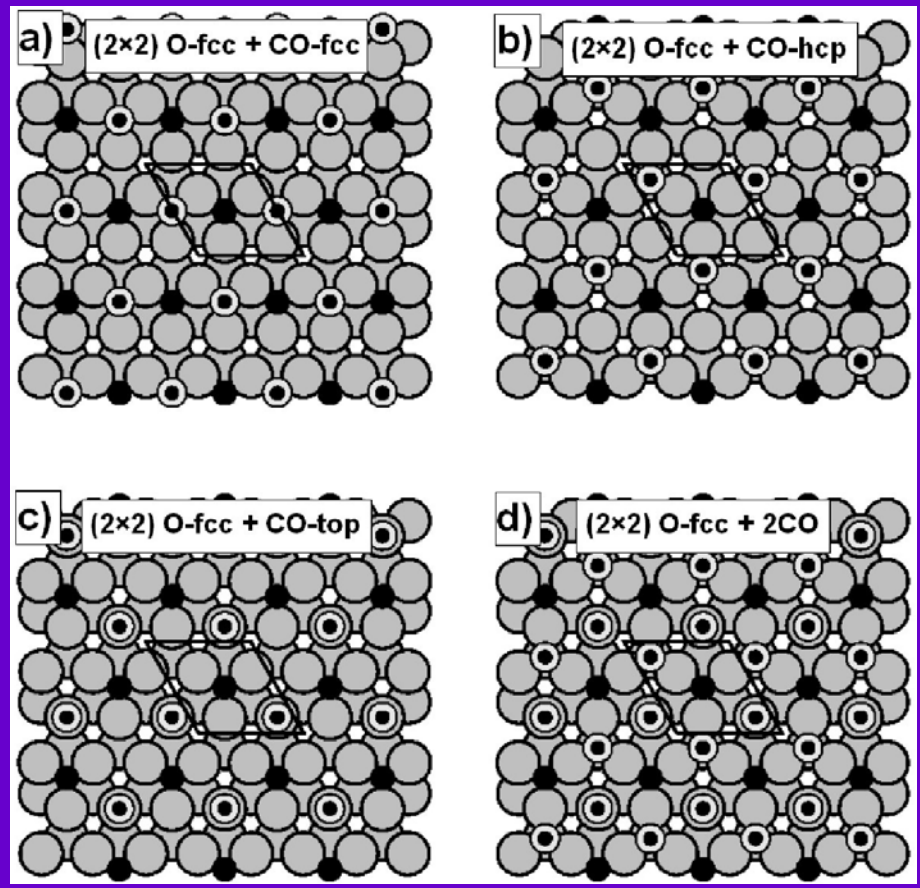




Pd(111)-p(2x2)+CO+O

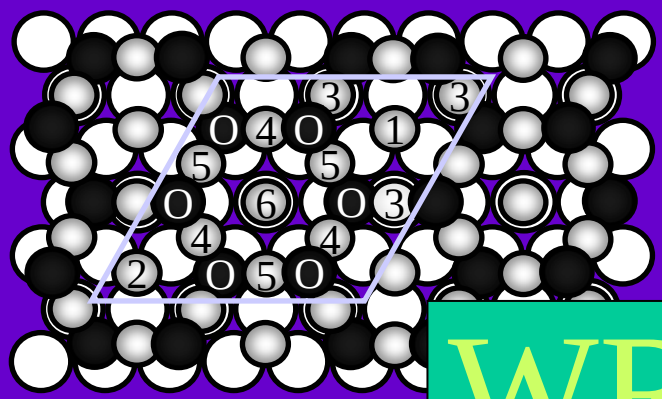
Experiment Theory



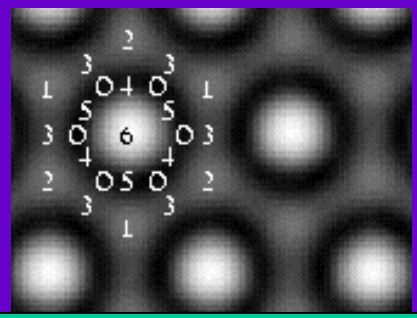


$Ag(111)+p(4x4)Ag_2O$

Ag_2O

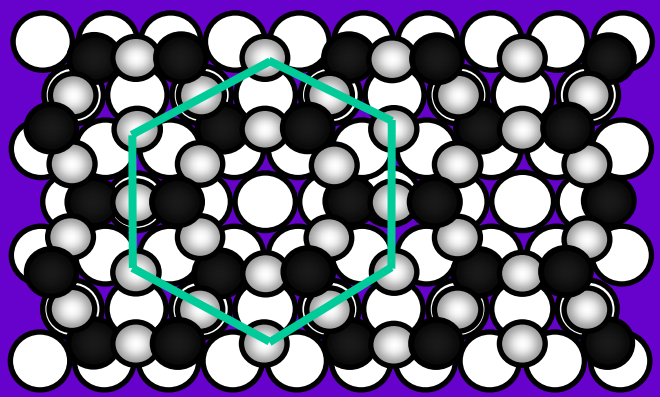


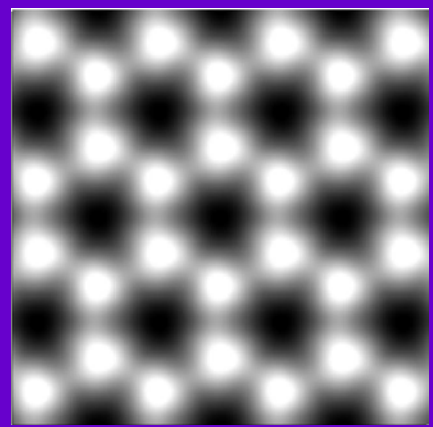
Simulations



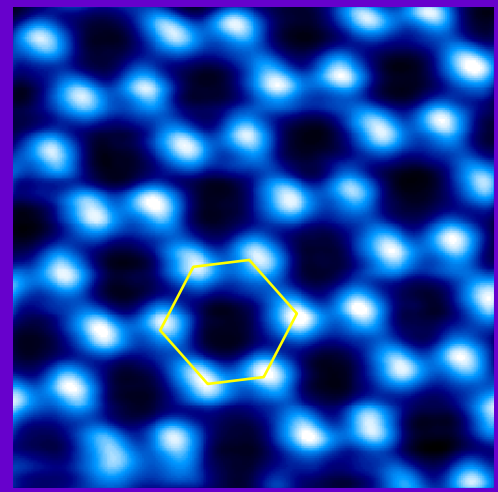
WRONG?

$Ag_{1.83}O$





Experimental



C.I. Carlisle et al, PRL (00)

Conclusions

- STM simulations is a “mature” field:
  - Most of the experimental features can be well reproduced

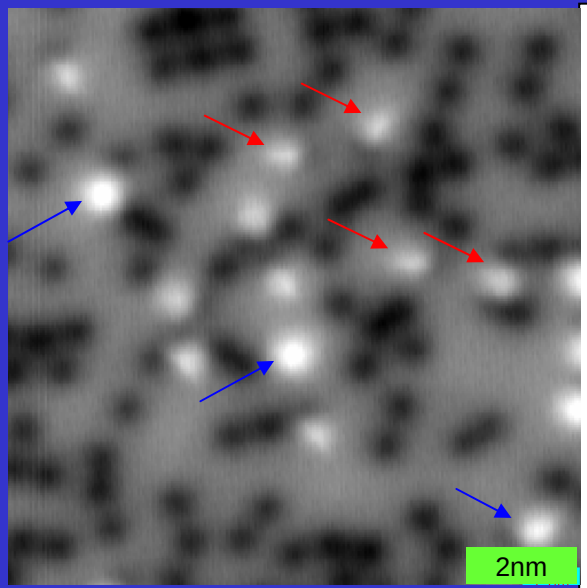
- STM simulations can be a very useful tool for structure analysis, but not always !!
  - Different models may yield the same image

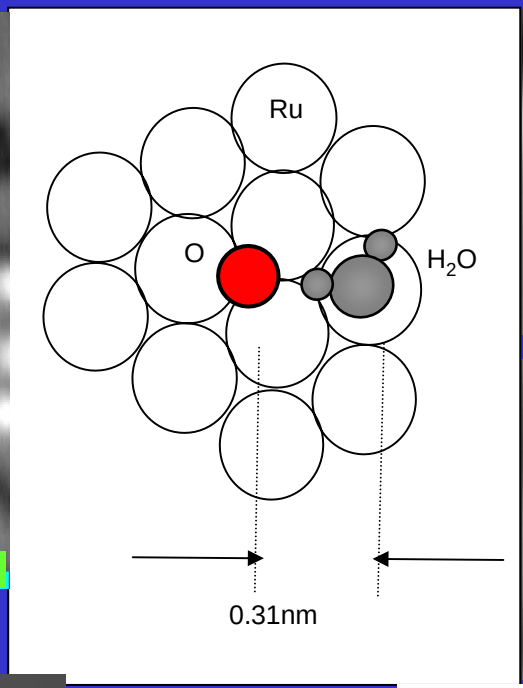
- Take care with:
  - Convergence parameters: # atoms/k-points
  - Tip modelling
  - Using normal exp. images for comparison

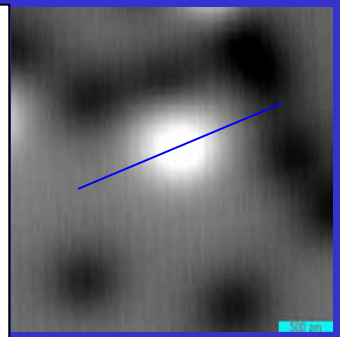
Acknowledgements

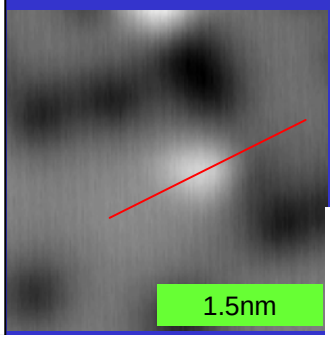
Theory: **M.-L. Bocquet , P. Sautet**
IRC-CNRS, Villerbaune & ENS de Lyon
$Pd+H_2O$: A.Michaelides (Cambridge University, UK)
P. J. Feibelman (SNL, Alburqueque, USA)
T. Mitsui, E. Fomin, M. Rose and M. Salmeron
(LBNL, Berkeley, USA)
$Ru+H_2O$: A. Mugarza, T. Shimizu, D. Ogletree, M. Salmeron
(LBNL, Berkeley, USA)
Ag_2O: C.I. Carlisle, M. Webb, A.Alavi & D. King
(Cambridge University, UK)
CO+O: J. Méndez (ICMM-CSIC)
S.H. Kim, J. Wintterlin, G. Ertl (FHI, Berlin)
Y_3Si_5: C. Rogero, J.A. Martín Gago (ICMM-CSIC)
Rh+NO: K. Flipse, C. Poppa and J. Haagelard (Holland)

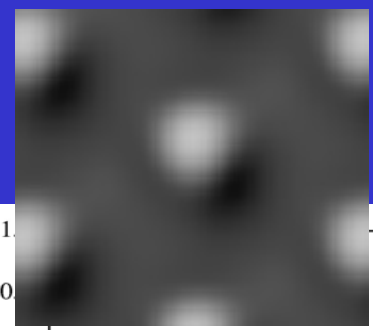
Species before Water Desorption (surface oxygen precovered)

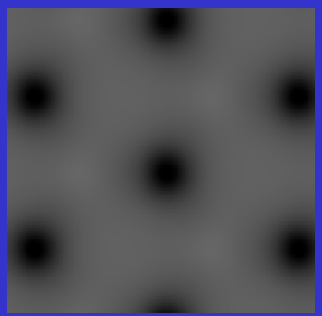


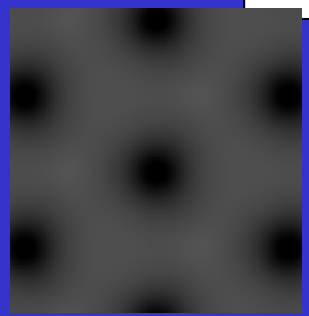






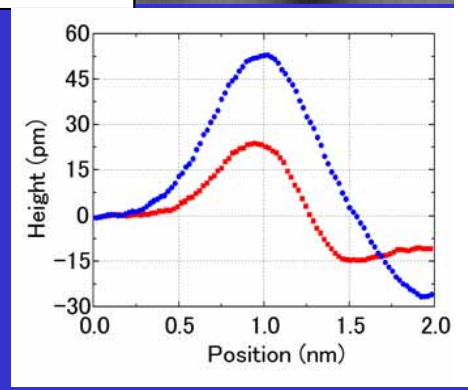


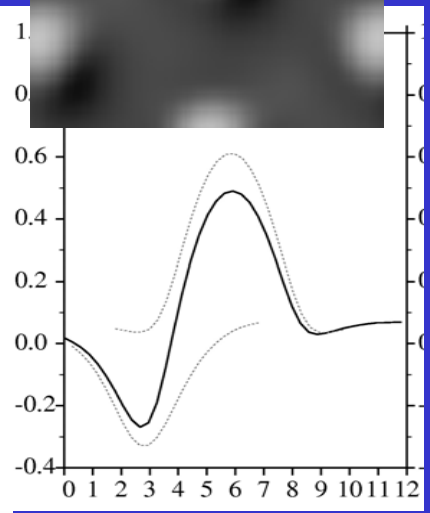




W(110) tip
C=0.43 A

W(111) tip
C=0.29





Green's Functions

Definition:

$$F(E,k_{par}) = E*S(k_{par})-H(k_{par})$$

$$G(E,k_{par})*F(E,k_{par})=I$$

Projection onto PLs i,j:

$$G_{ij} = (F^{-1})_{ij}$$

$$T_{ij} = G_{ij} (G_{jj})^{-1}$$

Sequential Stacking (Dyson):

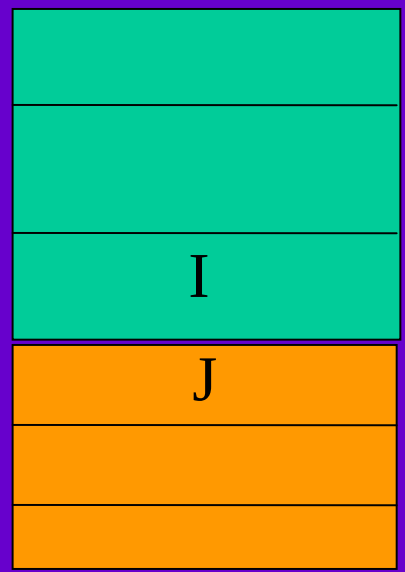
$$T_{IJ} = -G^{0}_{II} F_{IJ}$$

$$\Sigma_{JJ} = F_{JI} T_{IJ}$$

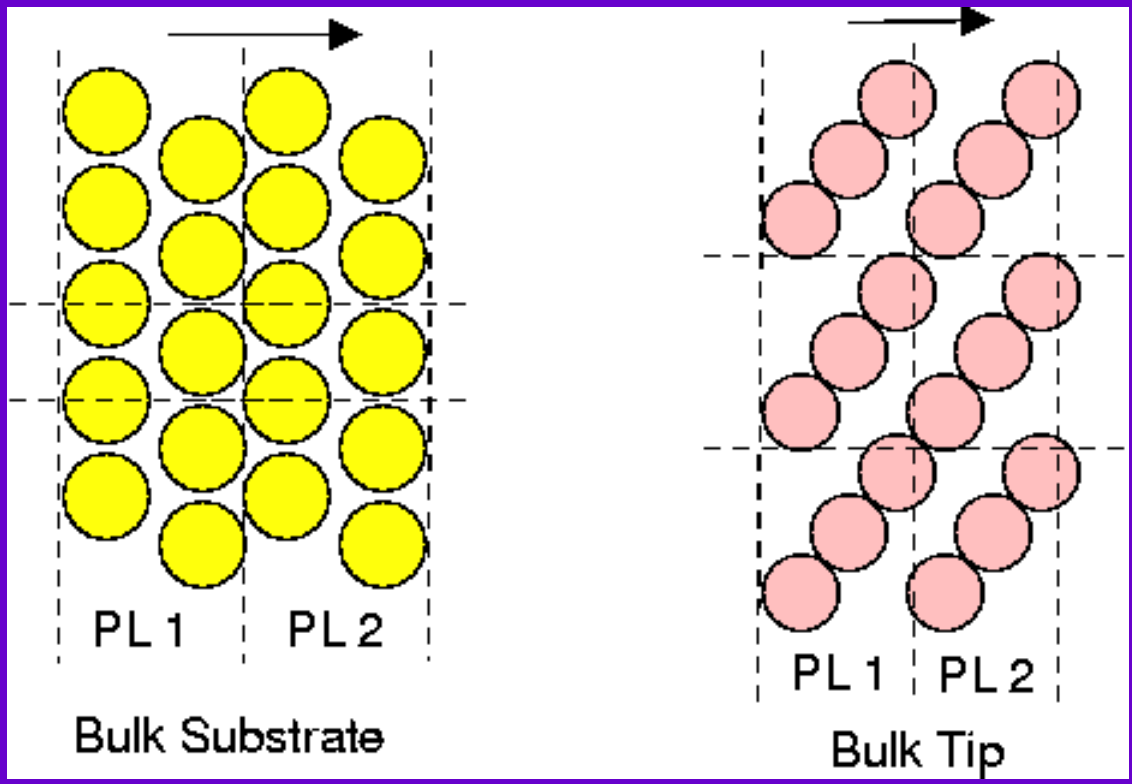
$$G_{JJ} = (G^{0}_{JJ} + \Sigma_{JJ})^{-1}$$

SGFM (Moliner):

$$G_{ij} = G^{0}_{ij} + T^{0}_{iI}(G_{IJ}-G^{0}_{IJ})T^{0}_{Jj}$$

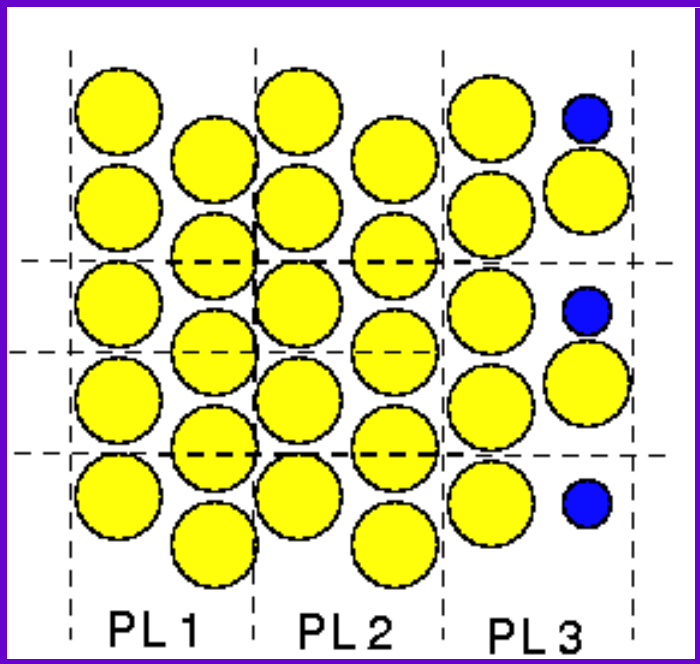


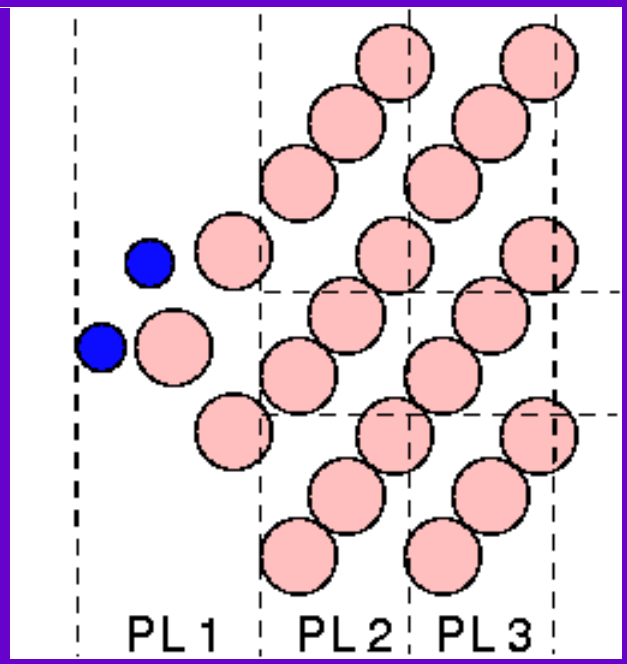
Bulk Stacking



$-G_{b+/-}$, $T_{b+/-}$, $k_{perp}(E)$, U_{kperp}

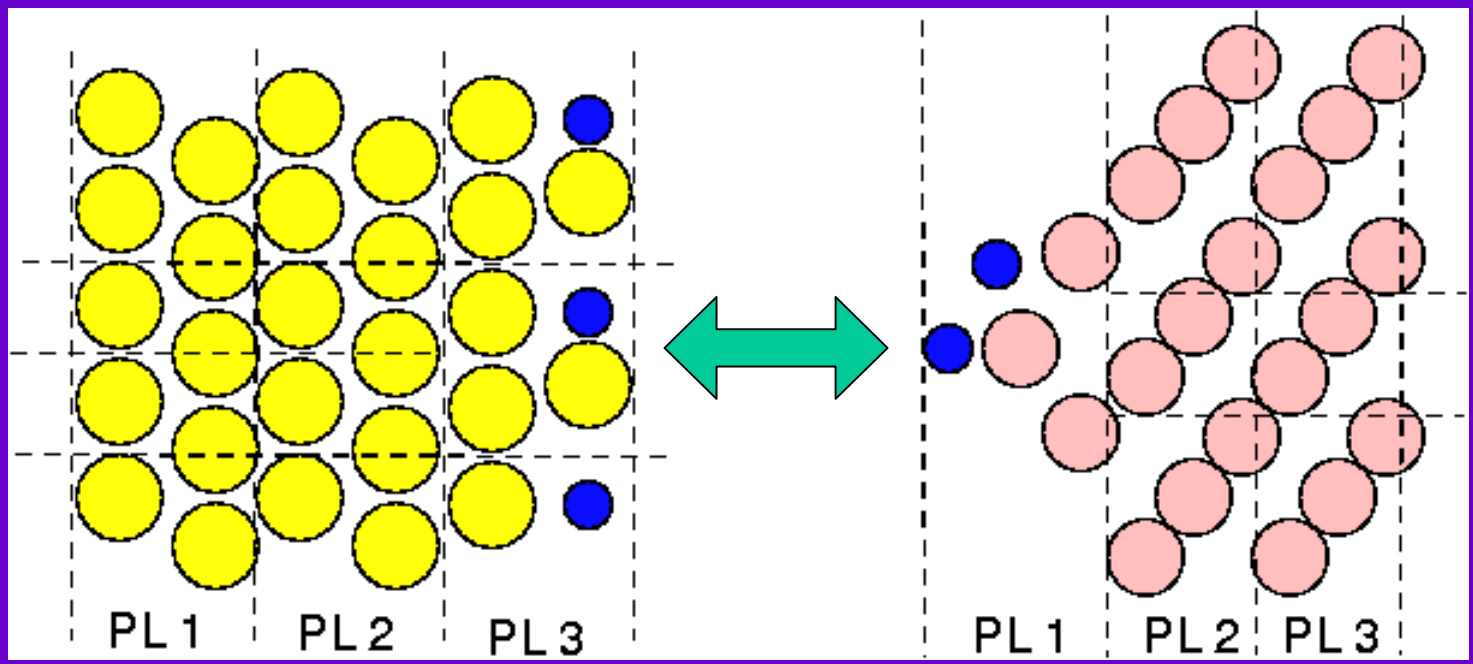
Surfaces





Surface (Localized) States?

Tip-Sample Interaction



First Order: $G_{JJ}=G^{0}_{JJ} => G_{IJ} = T_{IJ} * G^{0}_{JJ}$

2nd order tunneling events neglected

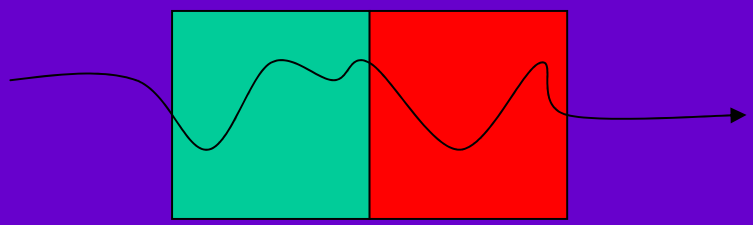
Current Formula

$$I(V) = \Sigma_{kpar} \int dE\ \sigma(E,V,kpar)\ f_{tip}(E-eV) f_{subs}(E)$$

-Landauer-Büttiker:

Links eigenstates at the bulk electrodes

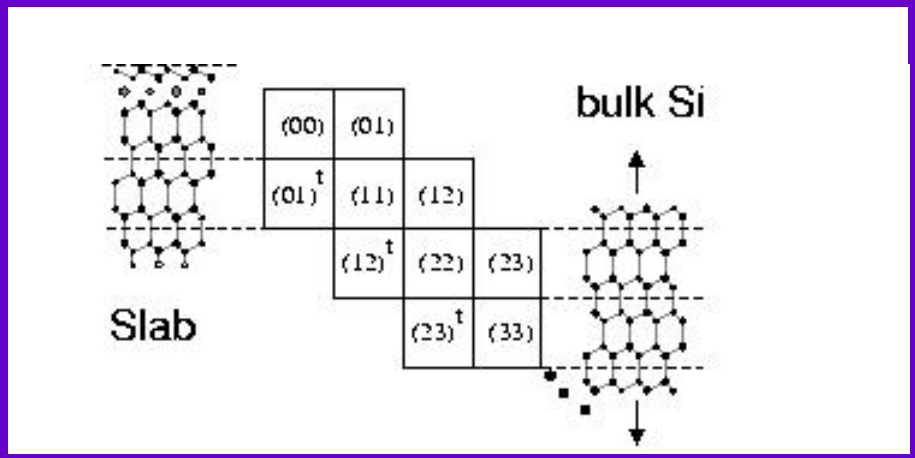
Green's Functions (Todorov,Datta):

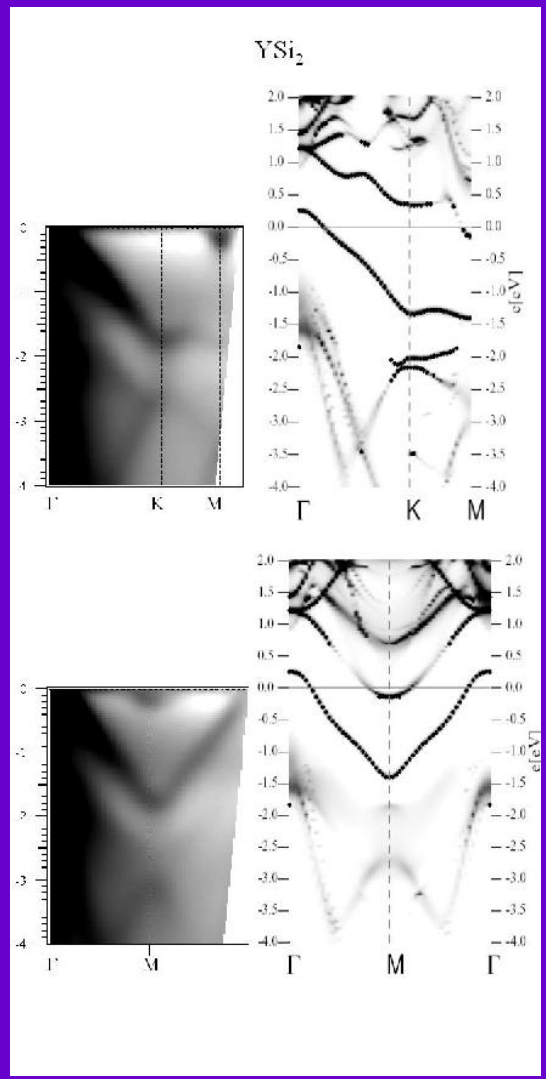


Subspace of propagative states

DFT (siesta)

- Do self-consistency by pieces





Some Key Issues

- k-sampling

- E_i
  Required for integration but induces damping
  Want to skip surface states?

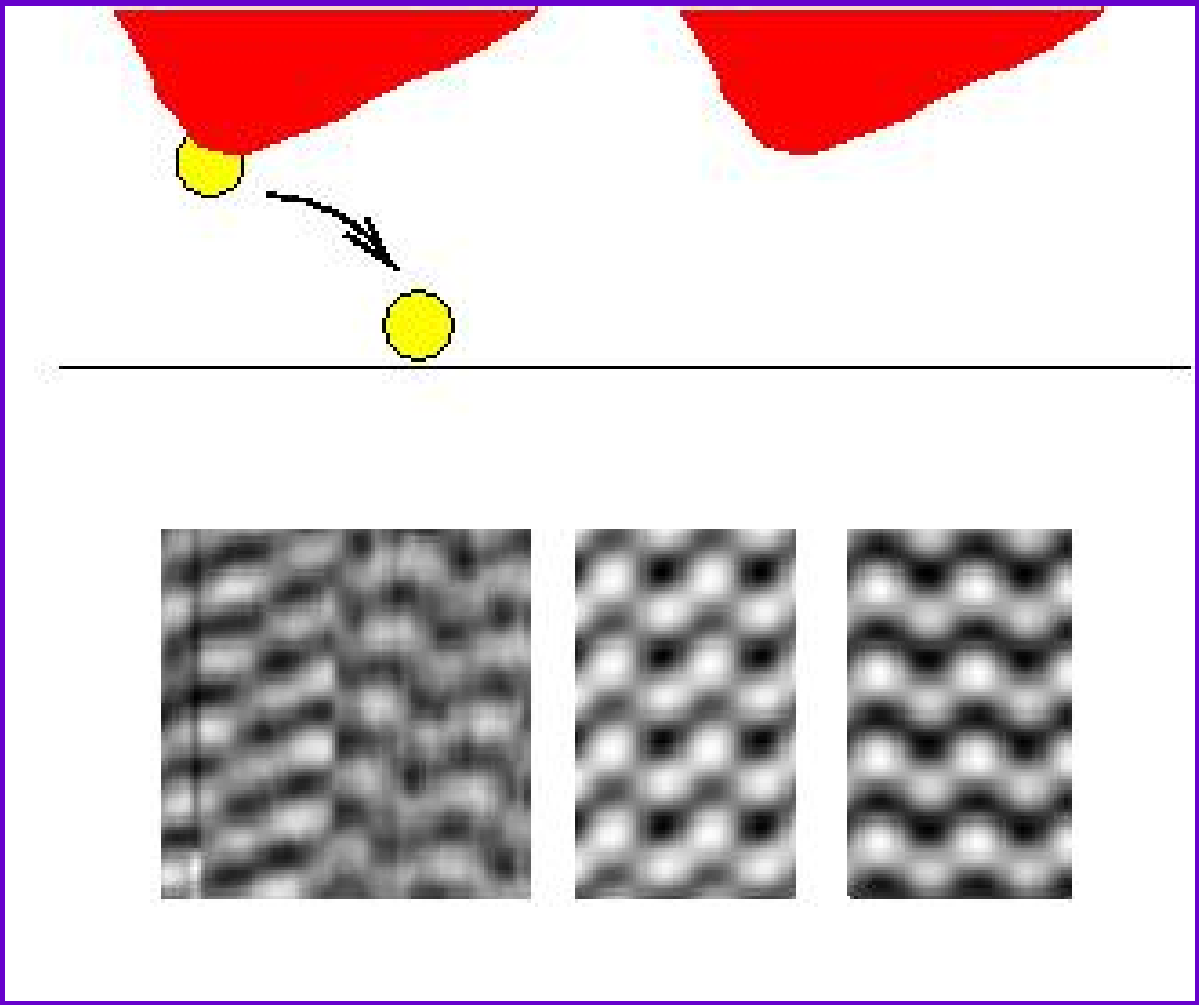
- **I** : $N_E \times N_{PL} \times N_{kc} \times (N_{AO},N_G)^2$
  # atoms > 1000 ; $N_{AO} x N_G < 1000$ => Fast

- **DM** : $N_E \times N_{PL}^2 \times N_{kc} \times (N_{AO},N_G)^2$

- Loops: bias , energy , spin , pixels, z_{tip} , topography
  => save/allocate dynamically

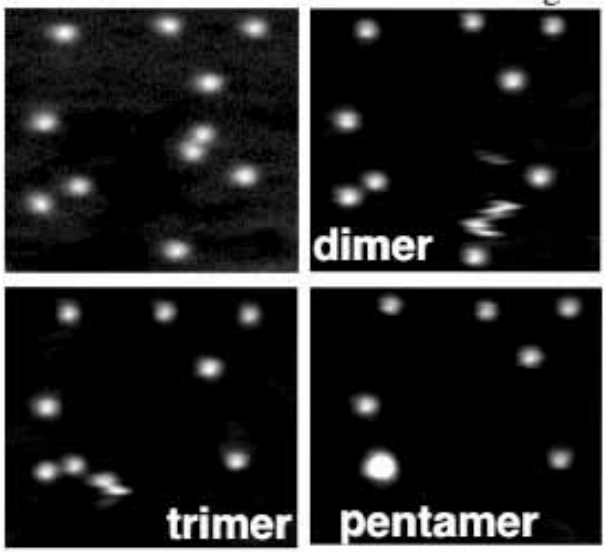
- AO basis small => Corrugations within a factor 2

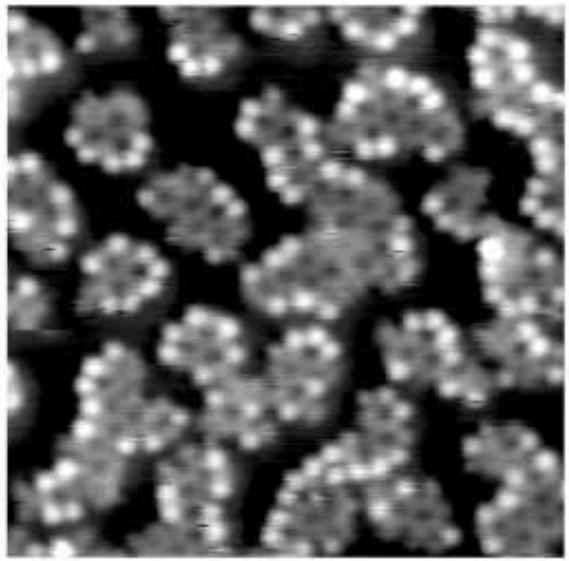
Tip effects



Water on Pd(111)

Monomer diffusion and clustering





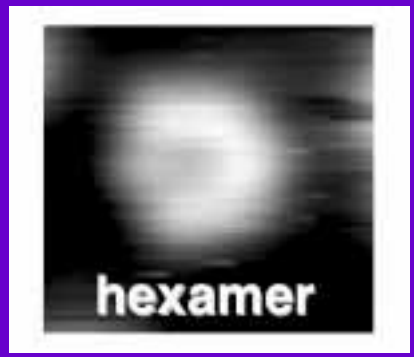
Hexamers forming honeycombs at 40K.
Bright molecules at edges:
dangling H bonds ?

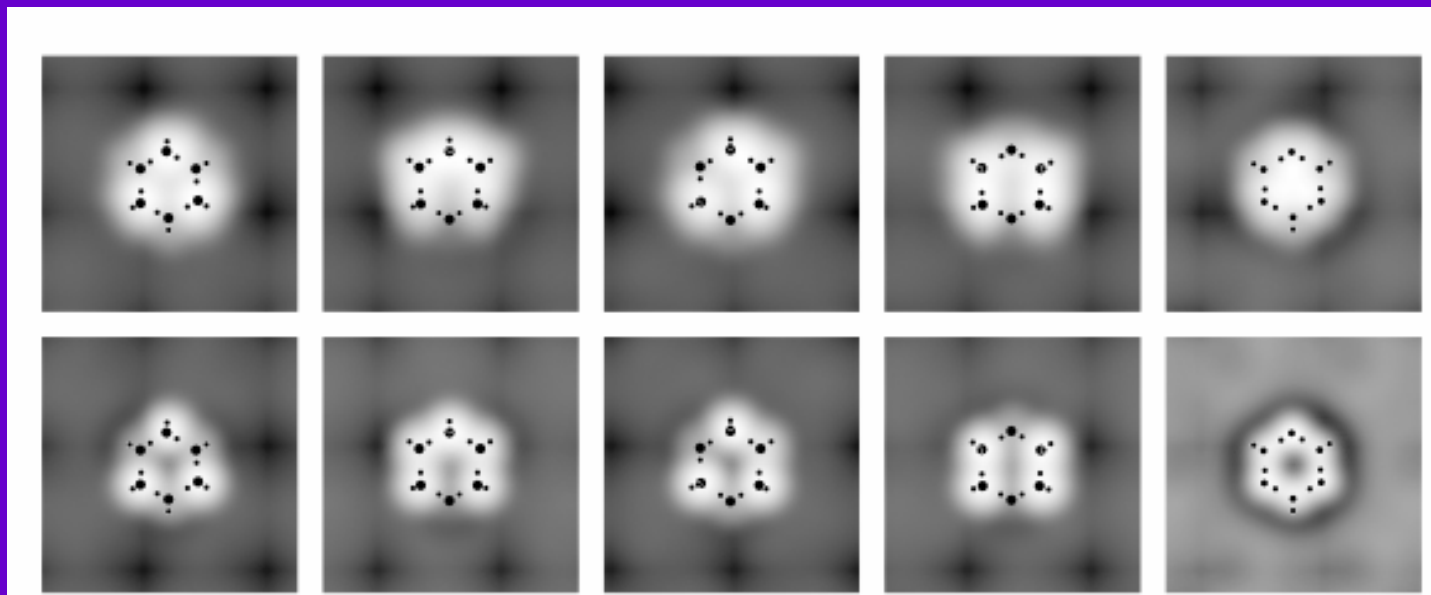
diffusion coefficient

- **monomer ~ 2.30 x 10^{-3} Å²/s**
- **dimer > 50 Å²/s**
- **trimer, tetramer ~ 1.02 Å²/s**

T. Mitsui et al, Science (02)

Hexamers





W(111) tip

Pt(111) tip