The use of STM & SXRD to study catalysis...
... at 'realistic' conditions

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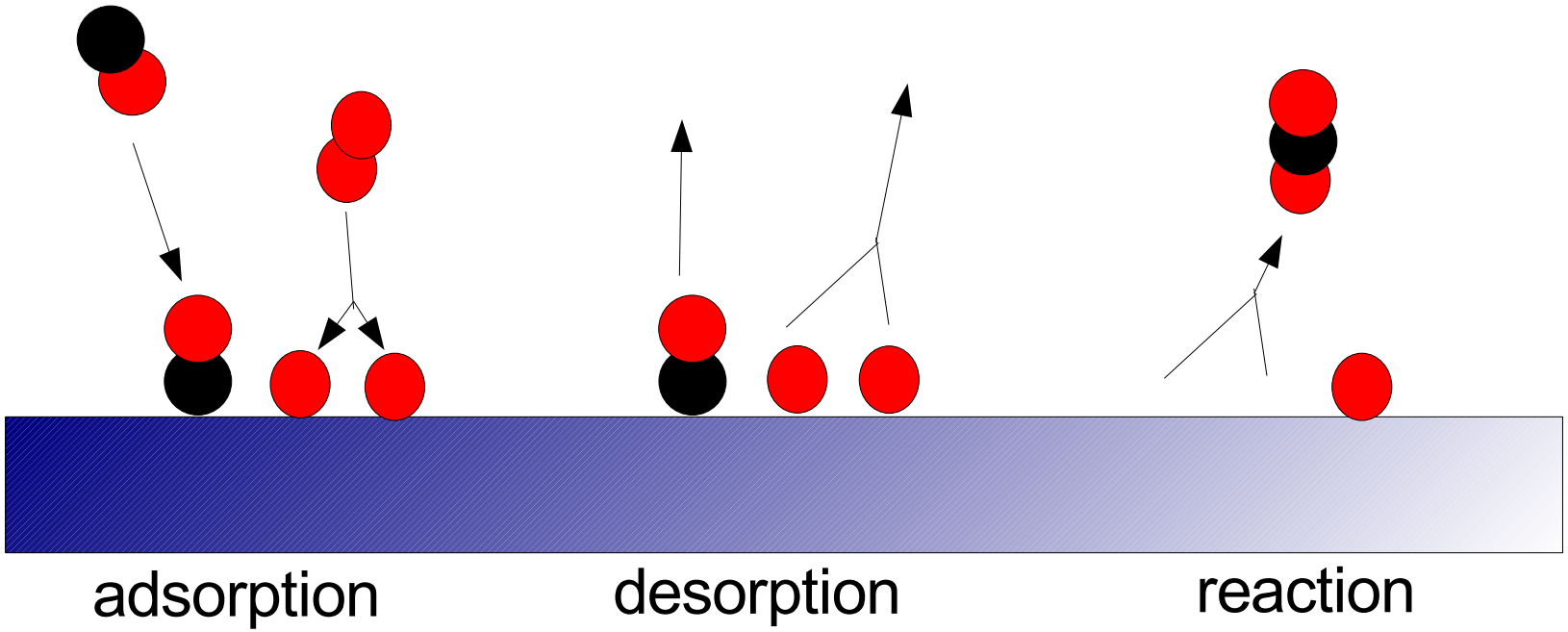
Outline

- The pressure gap
- The 'Reactor STM'
- **CO oxidation on platinum**
- Platinum in pure CO
- Pt(110) in CO+O2
- Pd(100) in CO+O2
- SXRD on Pt(110)

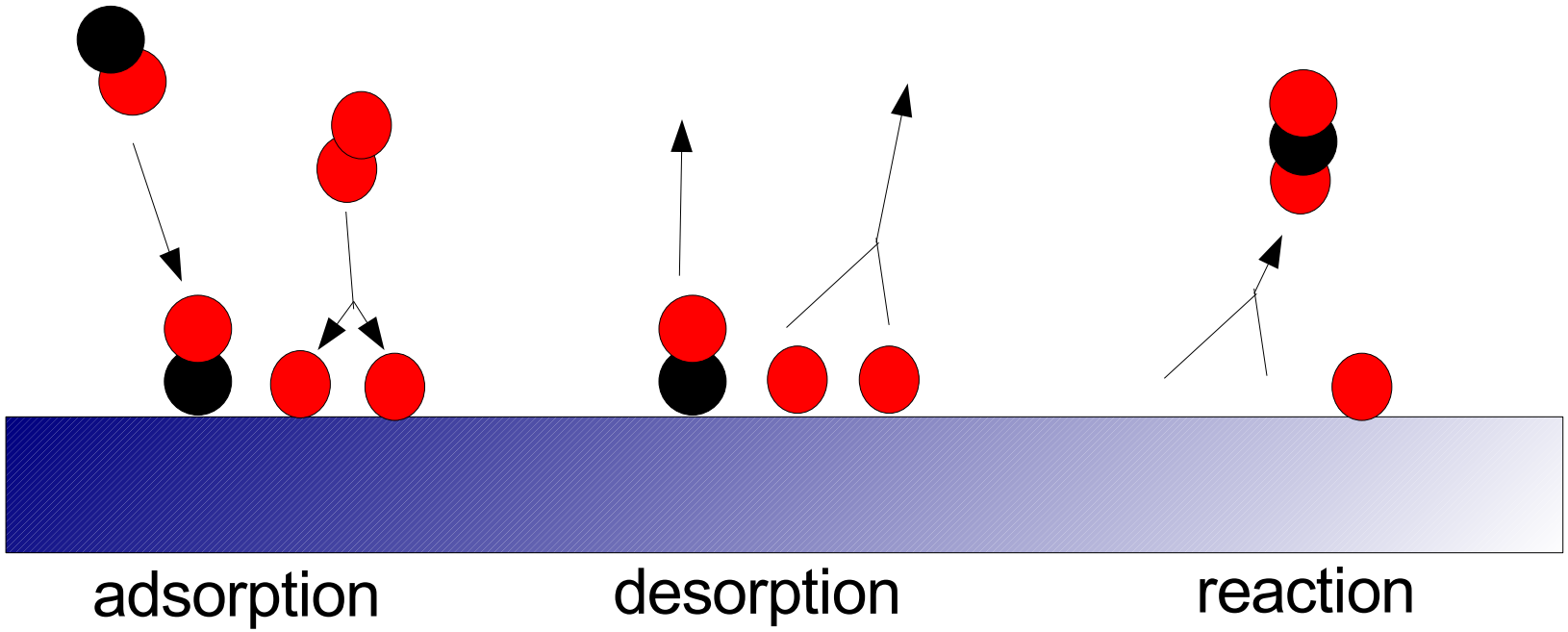
$$CO + \frac{1}{2} O_2 \rightarrow CO_2$$

Key question: What is the relation between surface structure and activity (and selectivity)

Langmuir-Hinshelwood



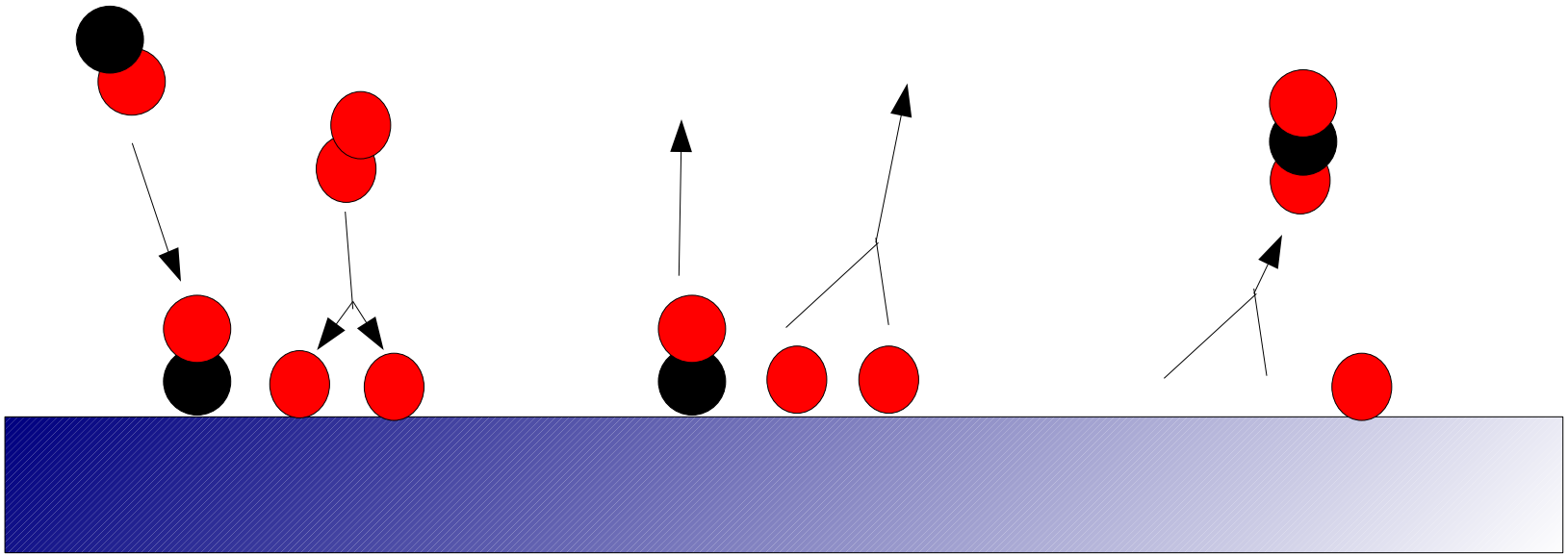
Langmuir-Hinshelwood



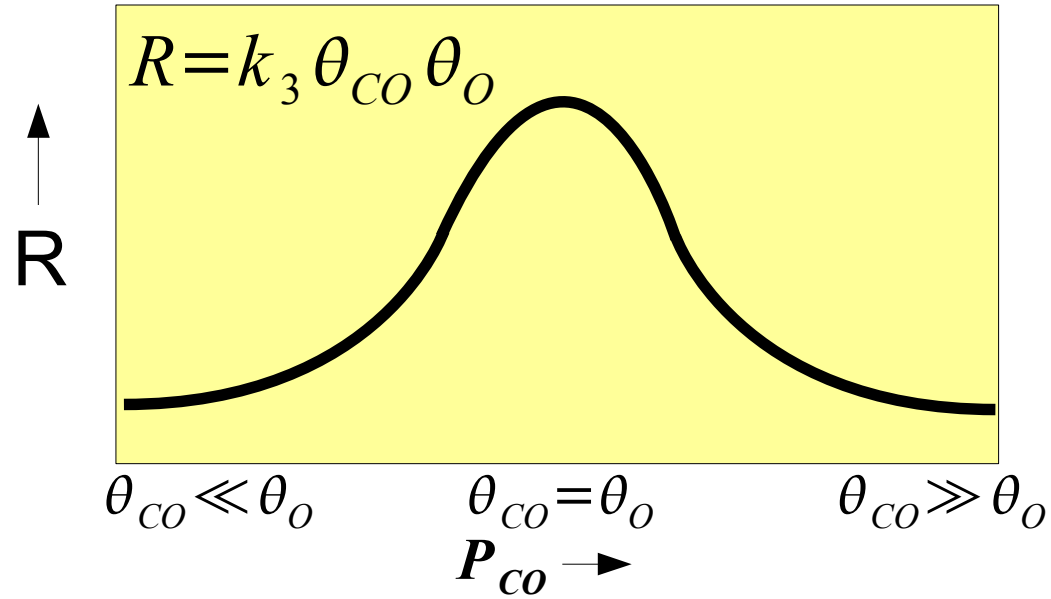
$$\frac{d\theta_{CO}}{dt} = k_1 P_{CO}(1-\theta_{CO}-\theta_O) - k_2\theta_{CO} - k_3\theta_{CO}\theta_O$$

$$\frac{d\theta_O}{dt} = k_4 P_{O_2}(1-\theta_{CO}-\theta_O)^2 - k_5\theta_O^2 - k_3\theta_{CO}\theta_O$$

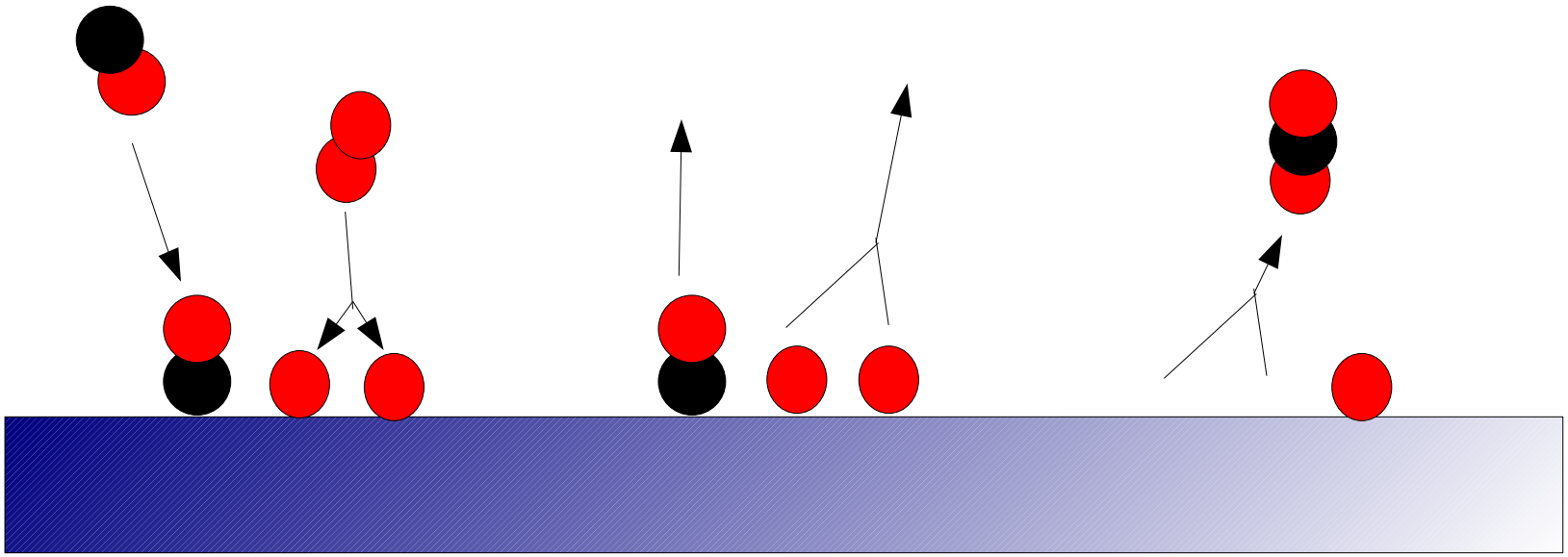
Langmuir-Hinshelwood



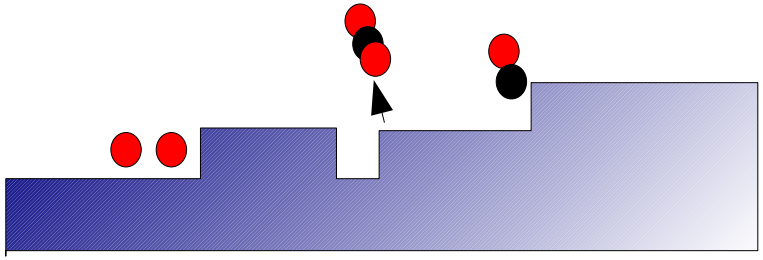
$$R = k_3 \frac{a\sqrt{P_{O_2}}\, b P_{CO}}{\left(a\sqrt{P_{O_2}} + b P_{CO} + 1\right)^2}$$



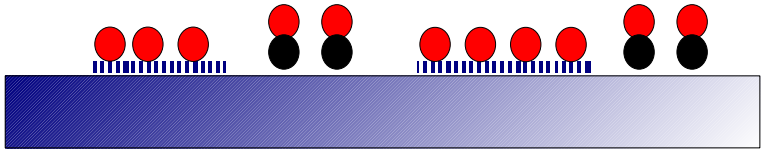
Langmuir-Hinshelwood



steps and defects

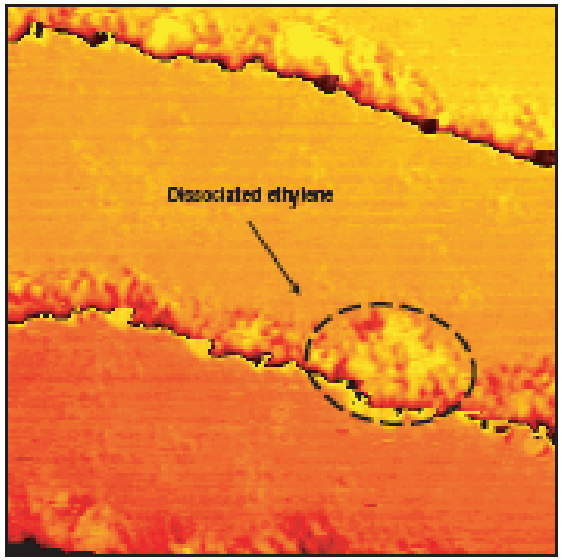


segregation & restructuring

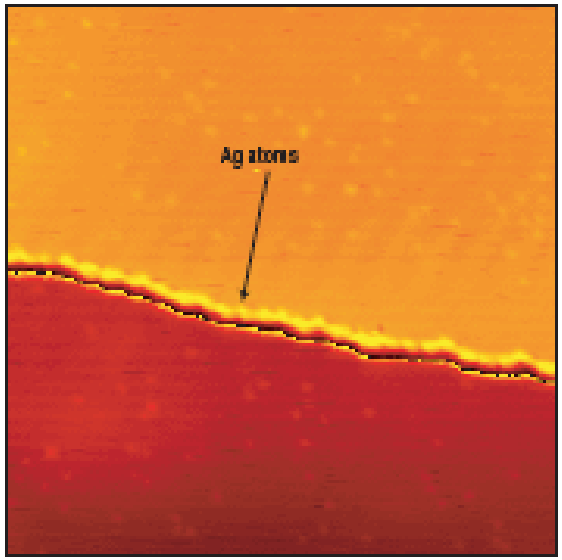


Decomposition at steps

a



b



Vang et al. Nature Materials 4 (2005) 160

Figure 1 Ethylene decomposition on Ni(111) and Ag/Ni(111). a, STM image (200 × 200 Å^2) of a Ni(111) surface after exposure to ethylene (10^{-8} torr; 100 s) at room temperature. A brim of decomposed ethylene is formed along the step edges. b, STM image (400 × 400 Å^2) of a Ni(111) surface with the step edges blocked by Ag atoms. No decomposition of ethylene is observed on this modified surface.

Wintterlin et al. Science 278 (1997) 1931

Reaction at adsorbate island edges

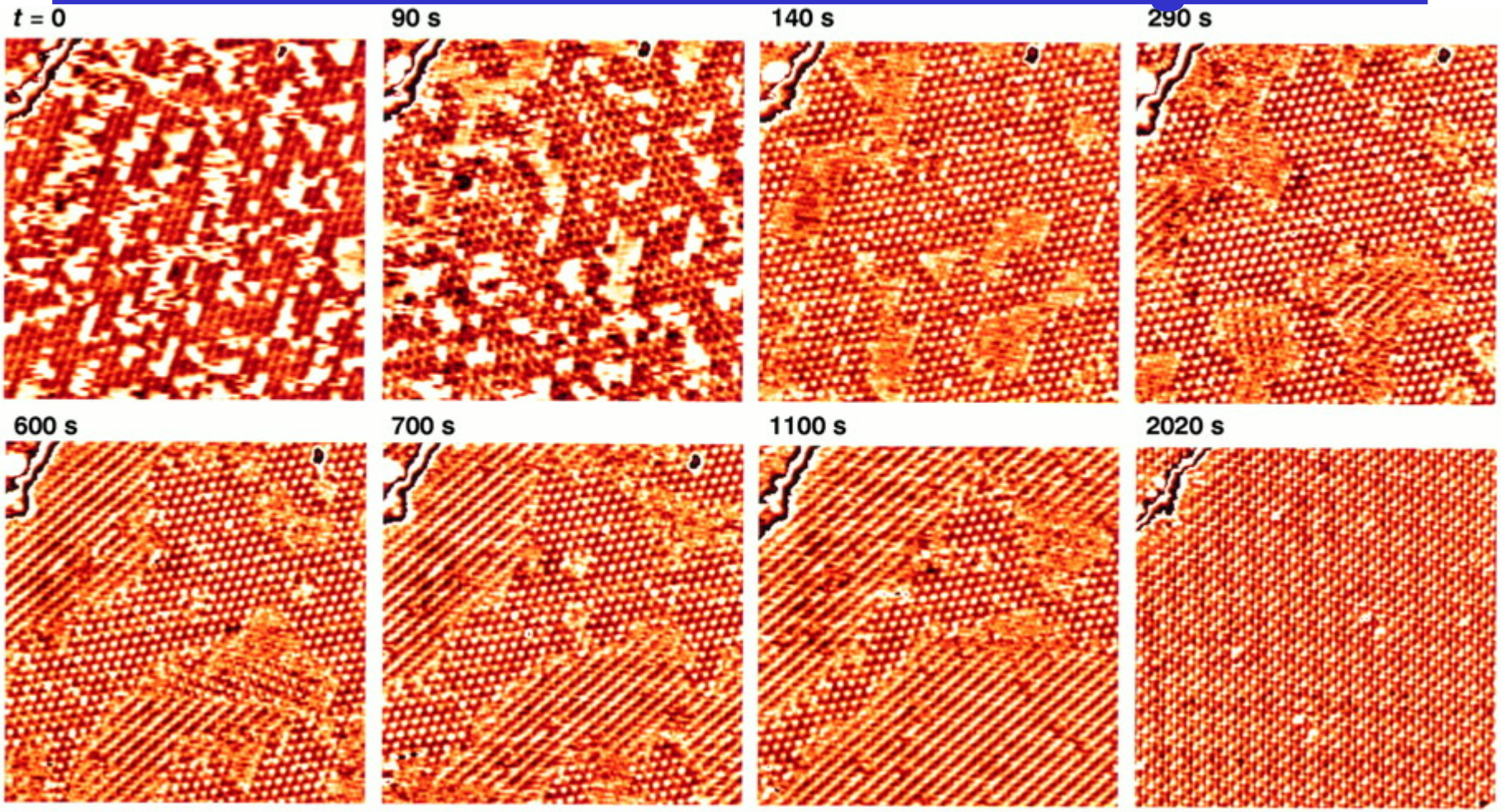
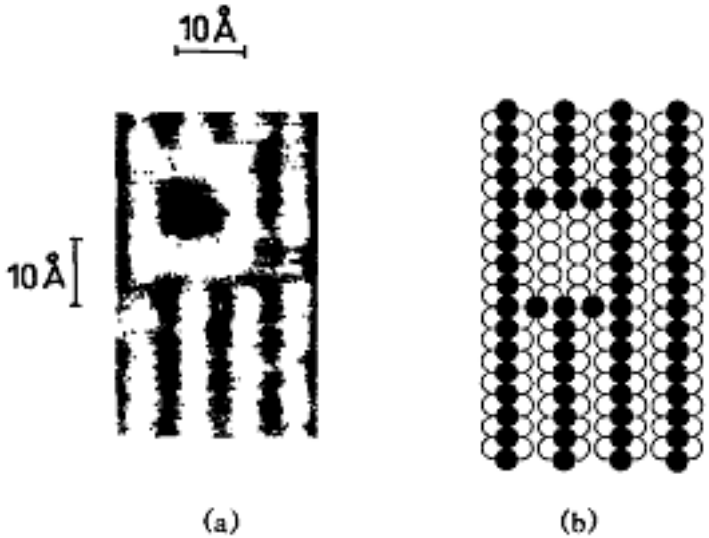


Figure 1. Series of STM images, recorded during reaction of adsorbed oxygen atoms with co-adsorbed CO molecules at 247 K, all from the same area of a Pt(111) crystal. Before the experiment, a submonolayer of oxygen atoms was prepared (by an exposure of 3 Langmuirs O_2 at 96 K, a short annealing to 298 K, and cooling to 247 K), and CO was continuously supplied from the gas phase ($P_{CO} = 5 \times 10^8$ mbar). At this pressure, the impingement rate of CO molecules is about 1 monolayer per 100 s, where the zero-coverage sticking coefficient on the empty and oxygen-covered surface is about 0.7 (8); the times refer to the start of the CO exposure. The structure at the upper left corner is an atomic step of the Pt surface. Image sizes, 180 Å by 170 Å; tunneling voltage (with respect to the sample), +0.5 V; tunneling current, 0.8 nA

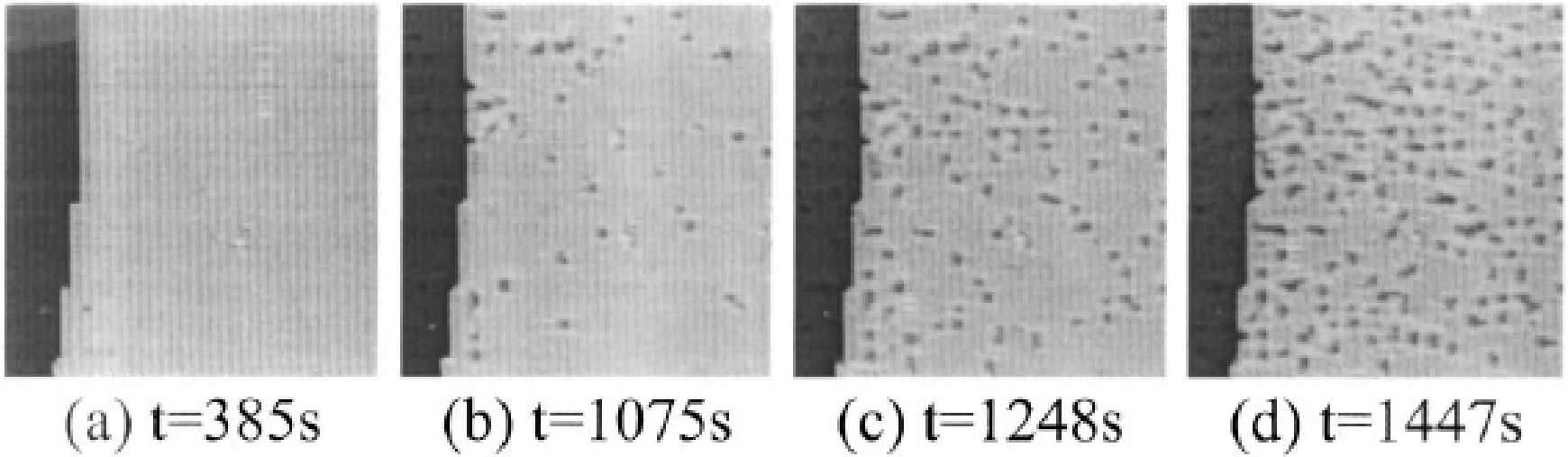
Adsorbate induced restructuring



Gritsch et at. (1989)

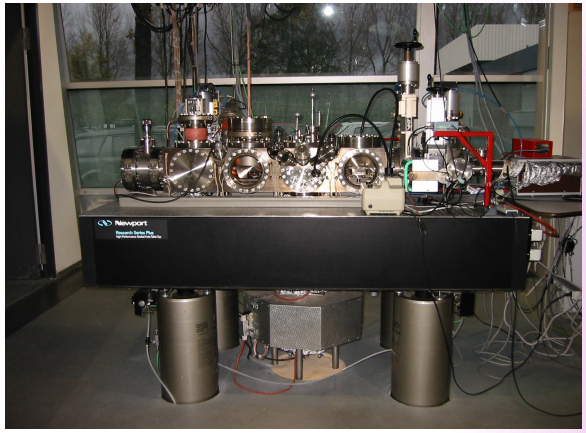
CO on Pt(110)

Thostrup et al. J.Chem. Phys. 118 (2003) 3724

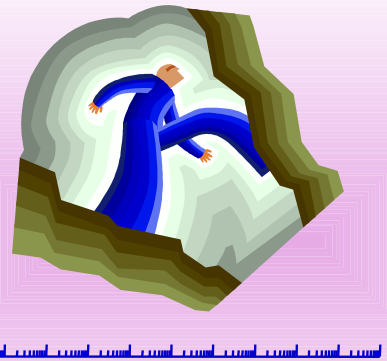


Bridging the pressure gap

Surface Science

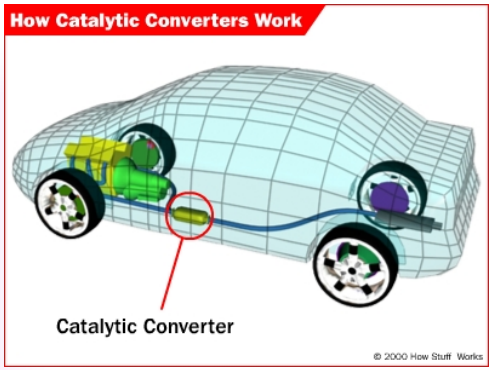


ultrahigh vacuum systems
(ultralow pressure):
-keeps the surface clean
-required by experimental
 techniques

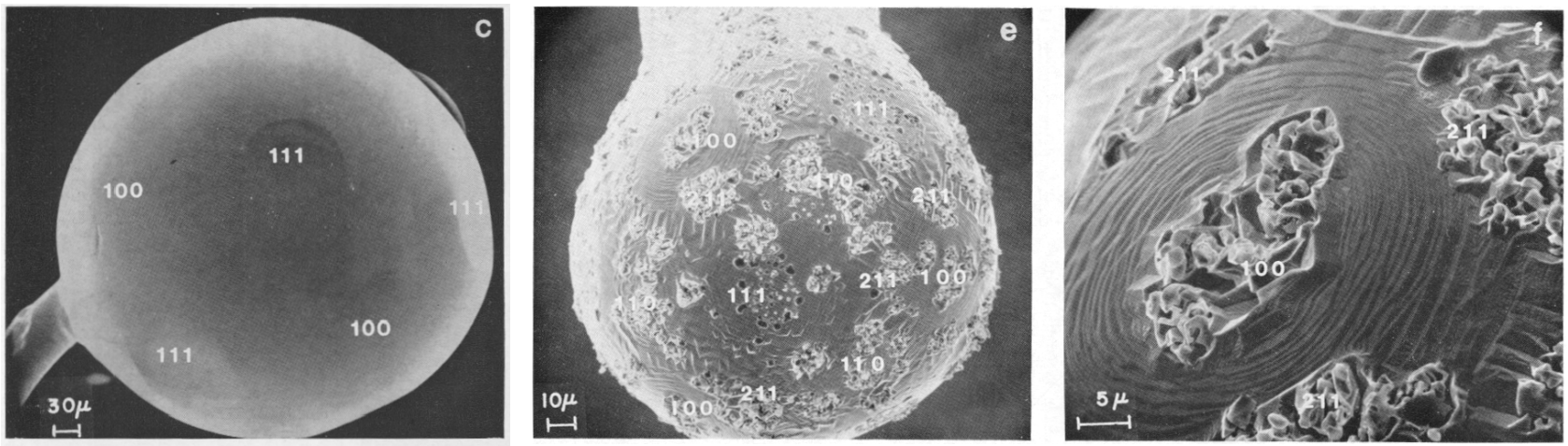


10^{-13} P (bar) 1.0

Catalysis



'ex-situ' electron microscopy

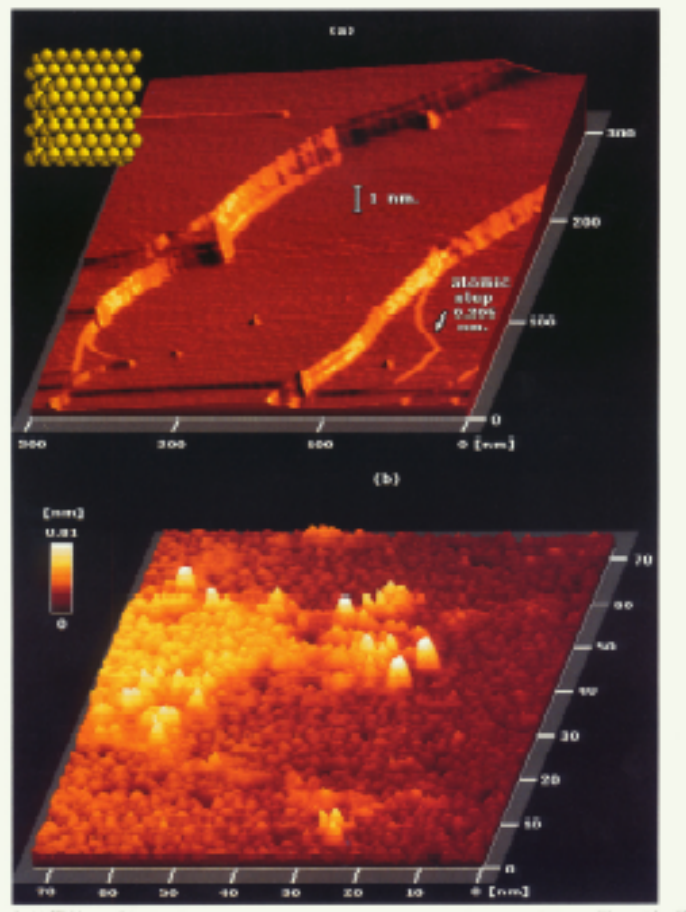


Platinum *before* and *after* exposure to $CO+O_2$

Flytzani-Stephanopoulos *et al.* ('77)

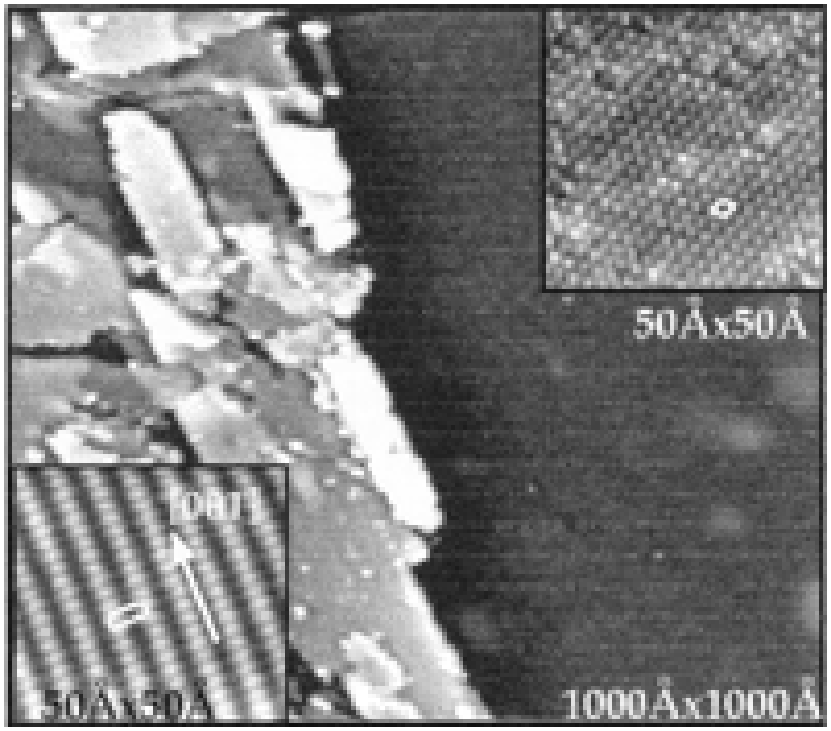
'ex-situ' STM

Co(0001) before & after CO/H2



Wilson & De Groot, J. Phys. Chem. 99 (1995) 7860

Ru(0001) after O2



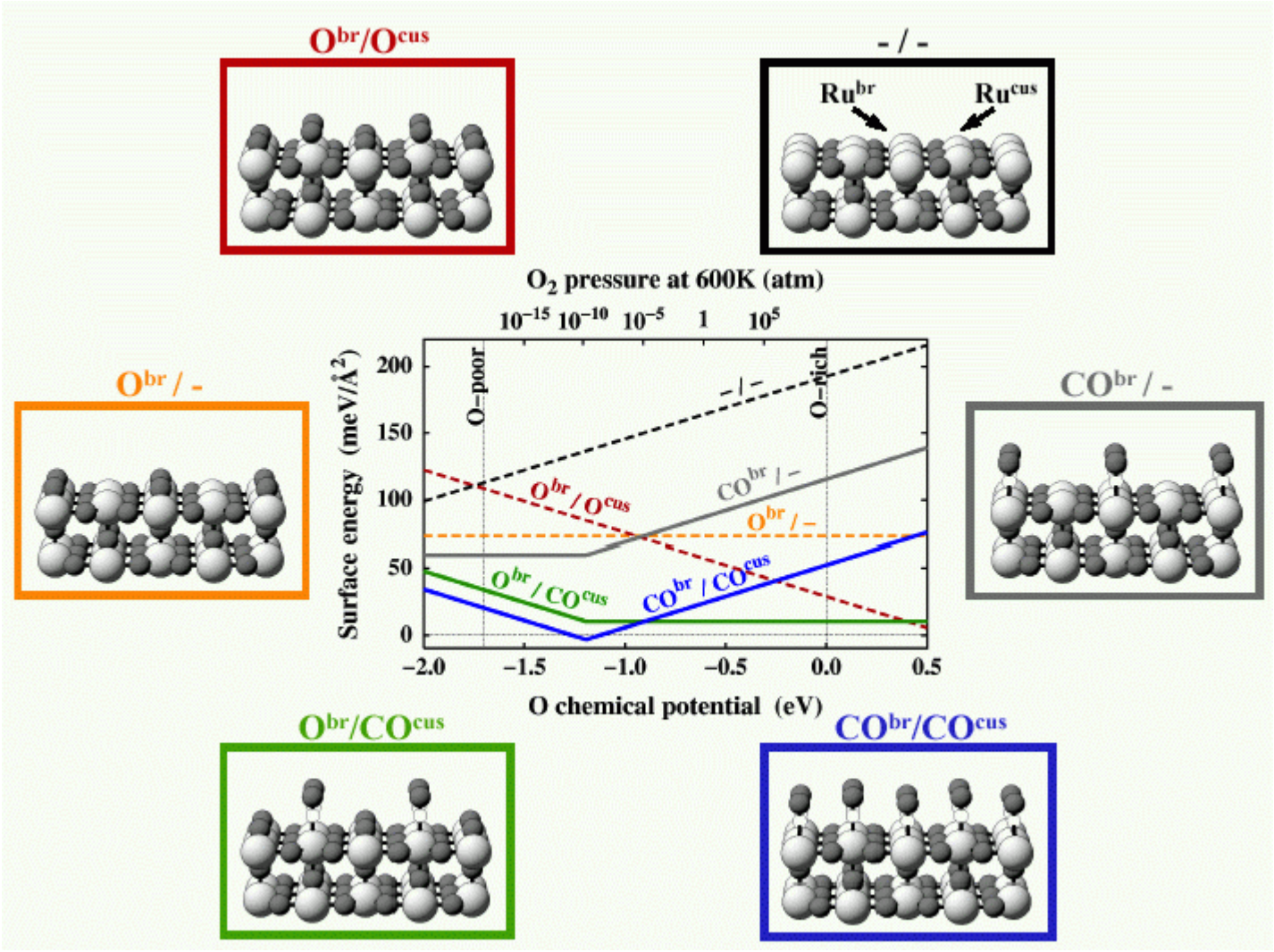
H. Over et al. , Science 287 (2000) 1474

Contribution of the gas phase

Chemical potential

$$kT \ln\left(\frac{p}{p^0}\right)$$

Ab initio calculations

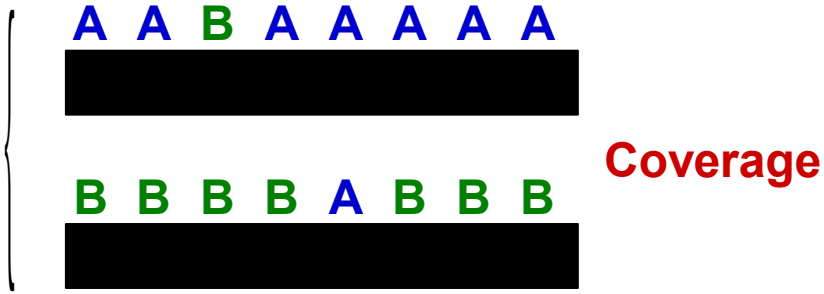


http://www.fhi-berlin.mpg.de

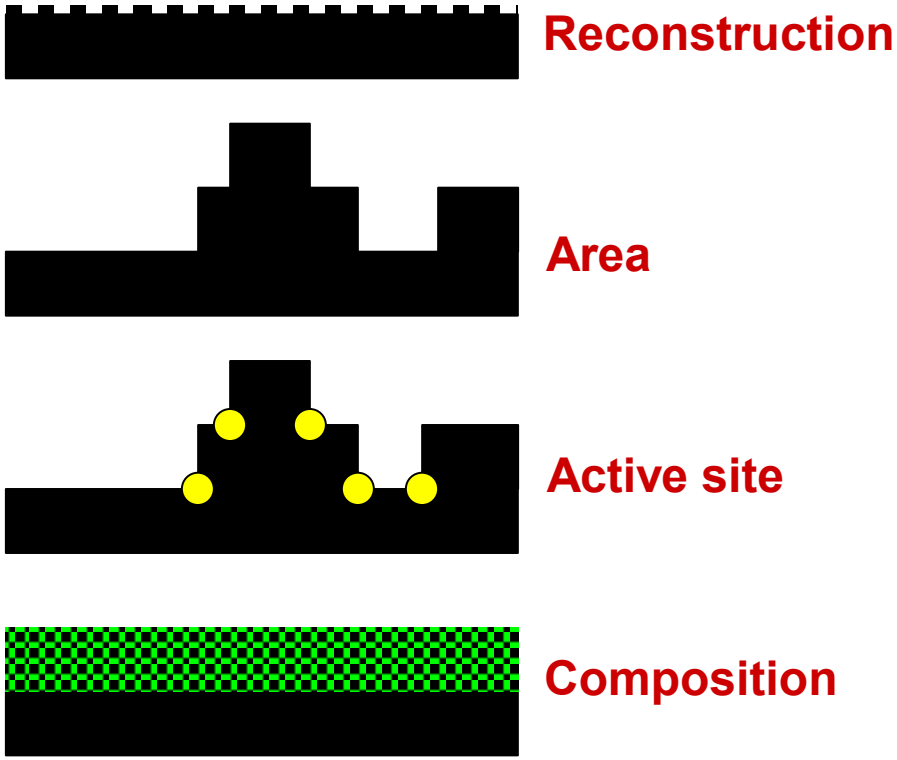
Reuter & Scheffler, PRB 68 (2003) 045407

Surface structure and reactivity

- During catalysis:
  surface structure and composition still the same?



- Changes of surface:
  cause or result of catalytic activity?



“High” pressure surface sensitive techniques

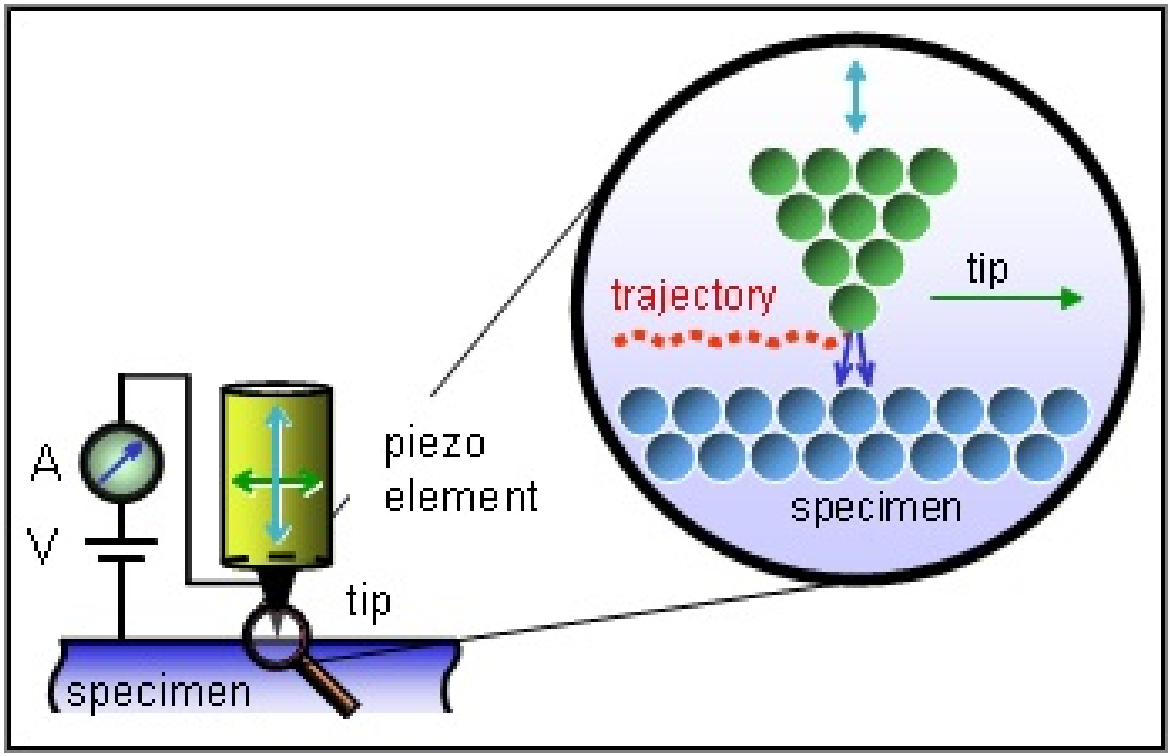
Increase operating pressure by differential pumping:

X-ray **P**hotoelectron **S**pectroscopy: composition, adsorbed species
Transmission **E**lectron **M**icroscopy: atomic structure, morphology
...

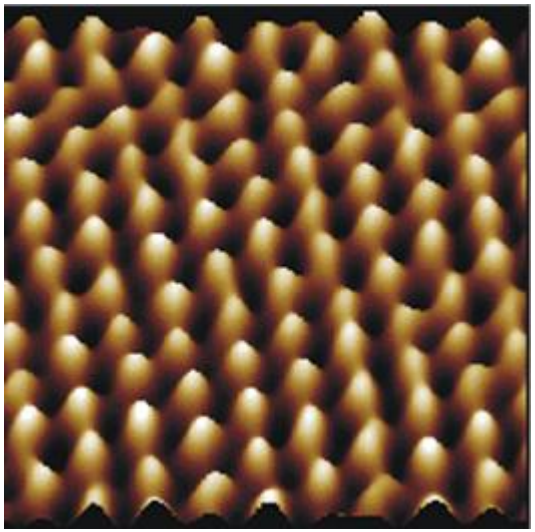
No a priori pressure limitation:

PM-RAIRS: vibrational spectroscopy
Sum **F**requency **G**eneration spectroscopy
Scanning **T**unneling **M**icroscopy: atomic structure, morphology
Surface **X**-**R**ay **D**iffraction: crystal structure, adsorbate structures
...

Scanning tunneling microscopy (STM)

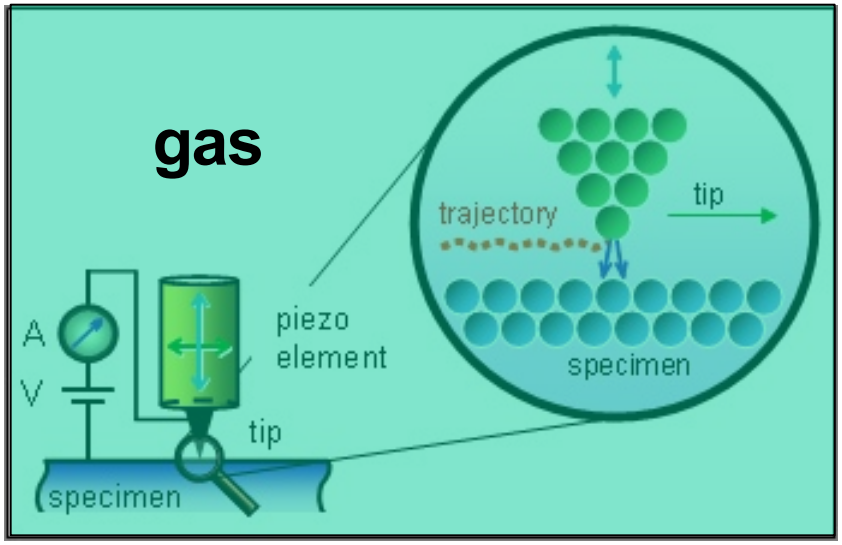


Carbon atoms of graphite



Using STM to bridge the pressure gap

Scanning tunneling microscope

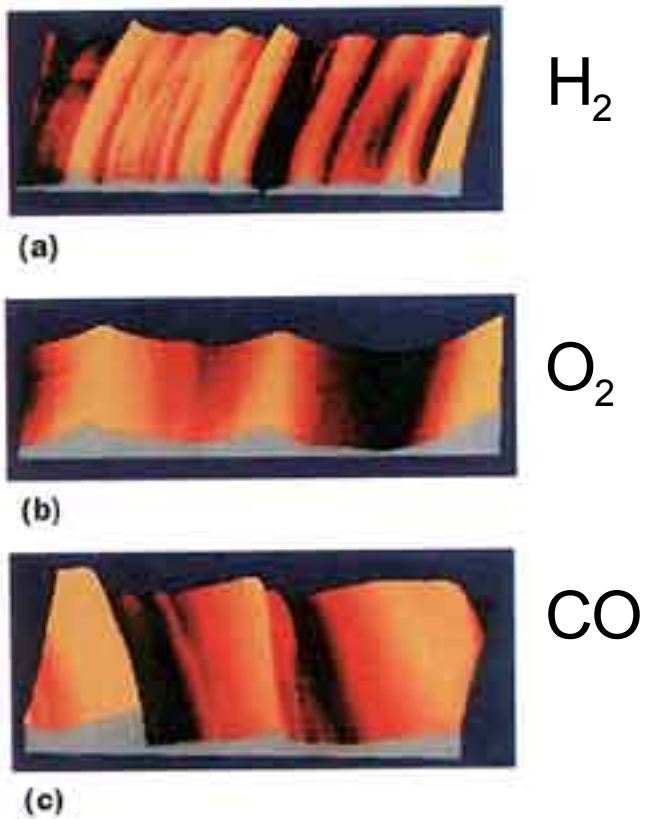


McIntyre (1992)
Laegsgaard (2001)
Kolmakov (2001)

Using STM to bridge the pressure gap

Pt(110)

Room temperature, P=1.6 bar



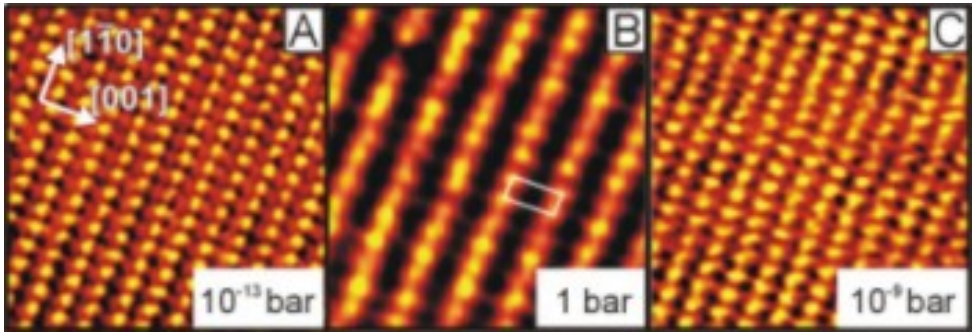
H_2

O_2

CO

B.J. McIntyre et al., *J.Vac.Sci.Technol. A, 11 (1993)*

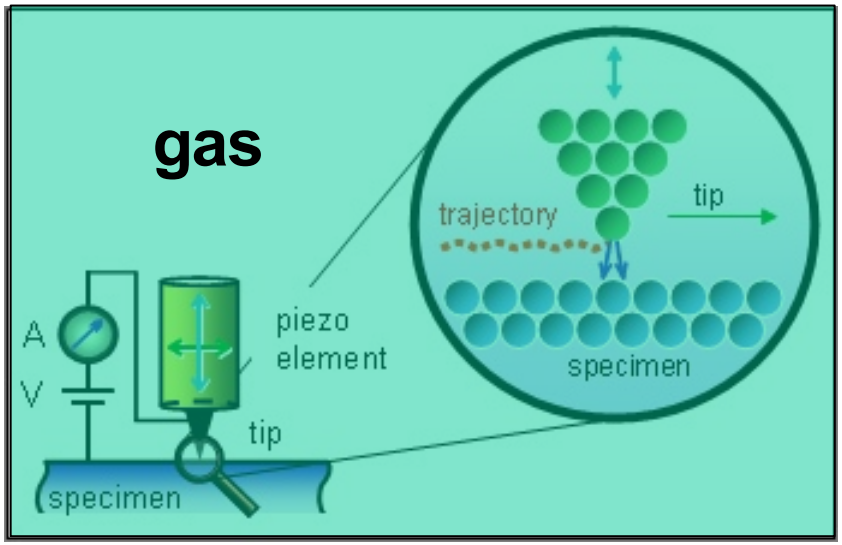
Cu(110) in hydrogen at 298K



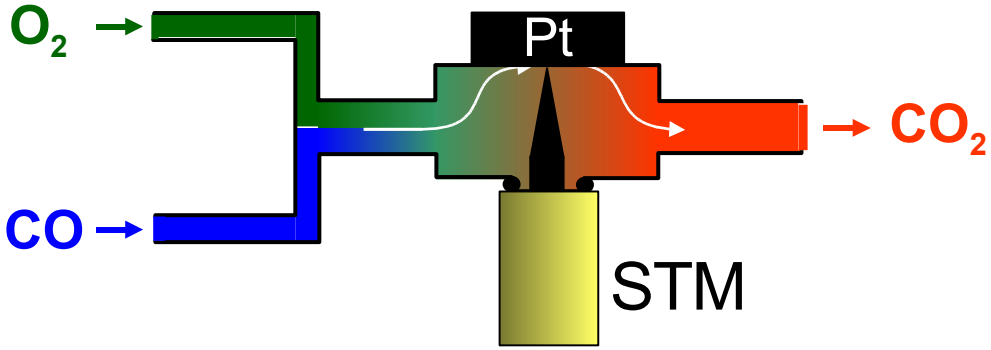
Osterlund et al. Phys. Rev. lett 86 (2001) 460

Using STM to bridge the pressure gap

Back filling UHV system



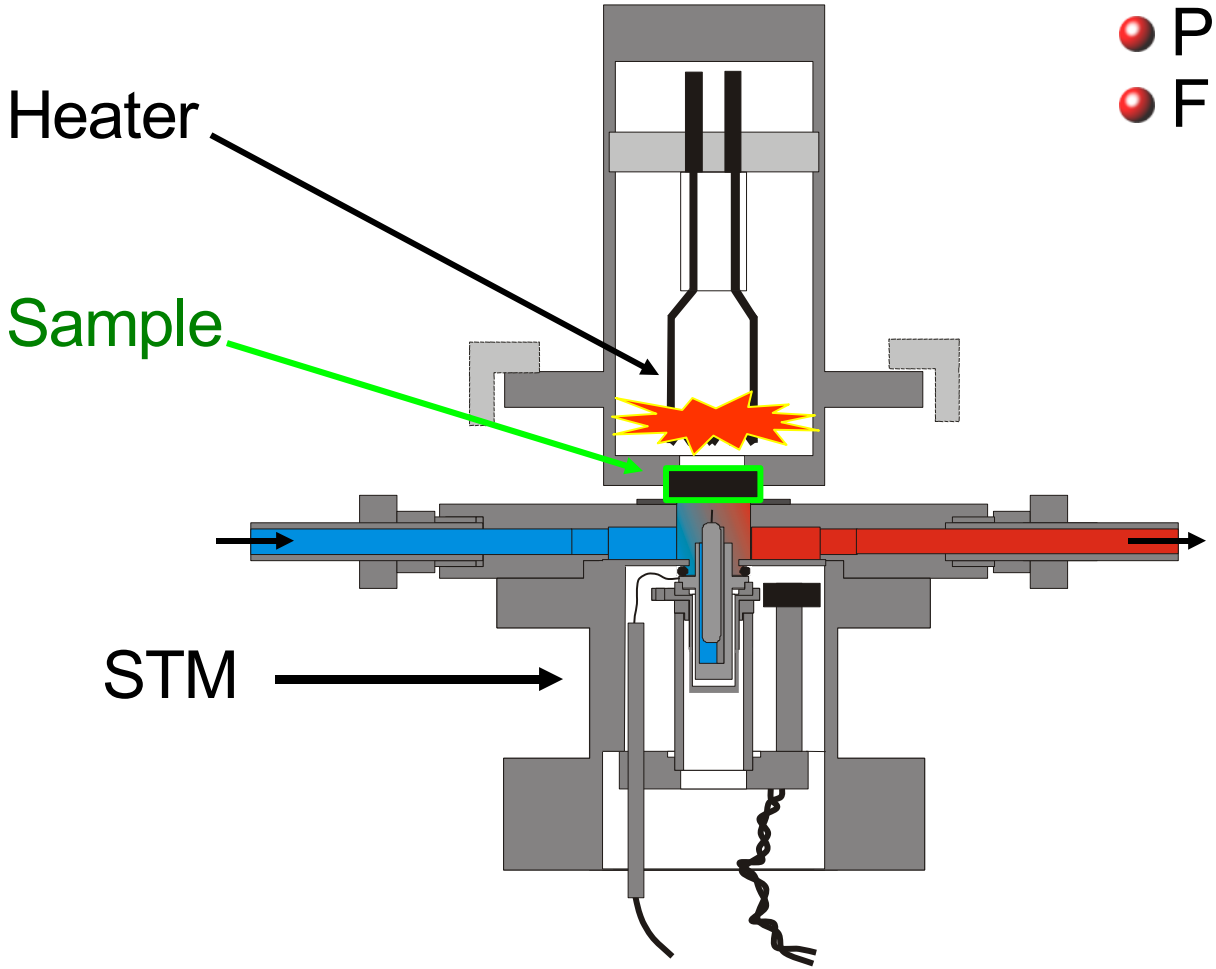
STM in a flow reactor



The 'Reactor STM'

Specs:

- T = 300 - 425 K
- P = UHV - 5 bar
- F = 0 - 10 ml/min



Rasmussen et al., *Rev.Sci.Instrum.* **69** (1998) 3879

The 'Reactor' STM

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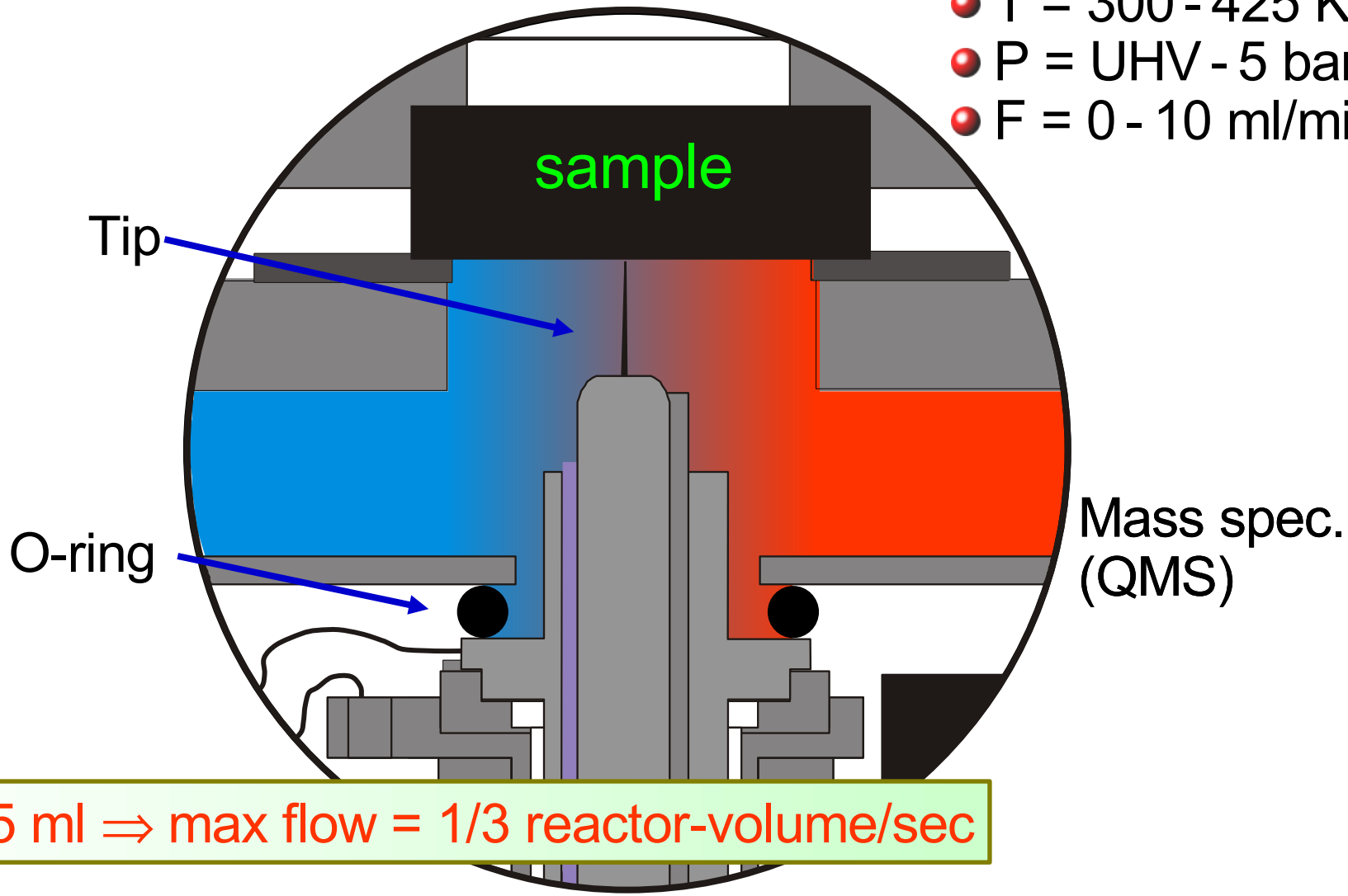
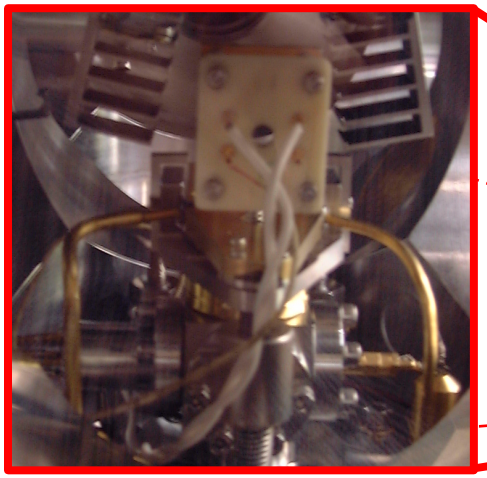
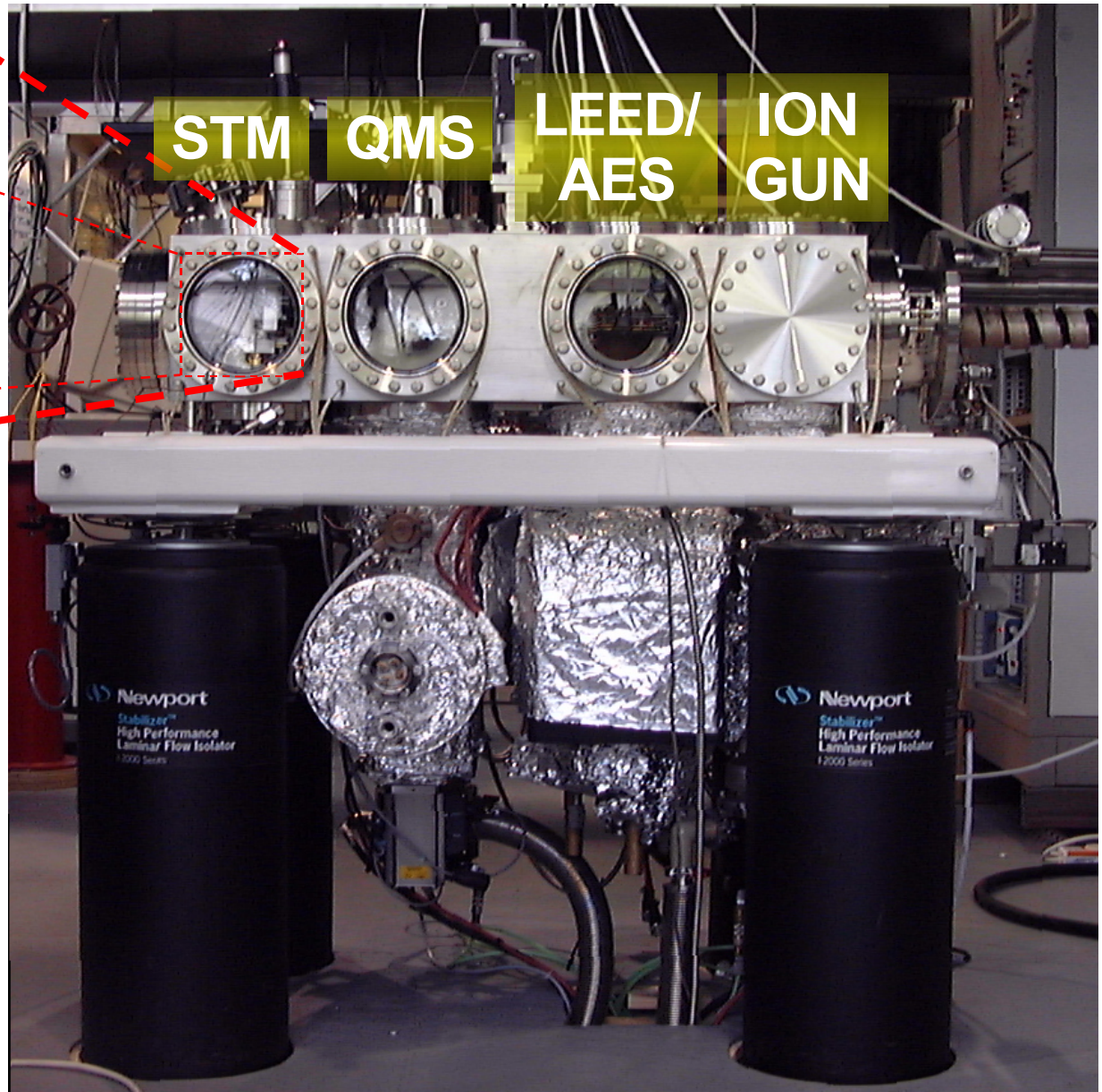
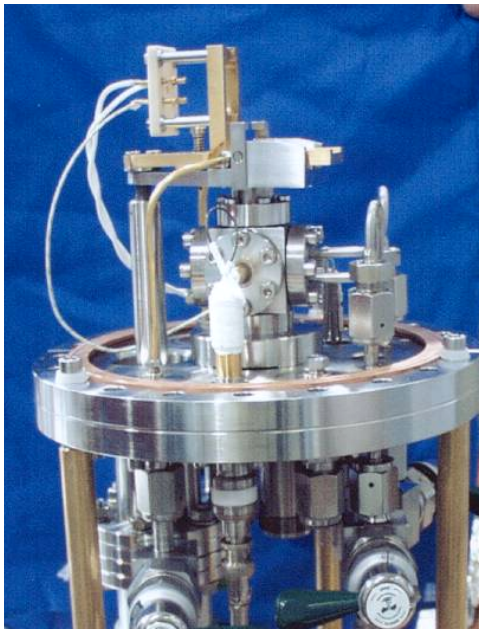


V=0.5 ml ⇒ max flow = 1/3 reactor-volume/sec

The 'Reactor' STM







CO on Pt(111)

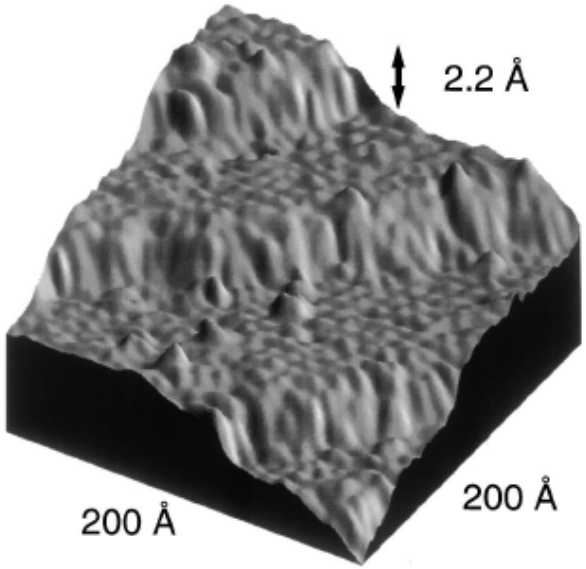
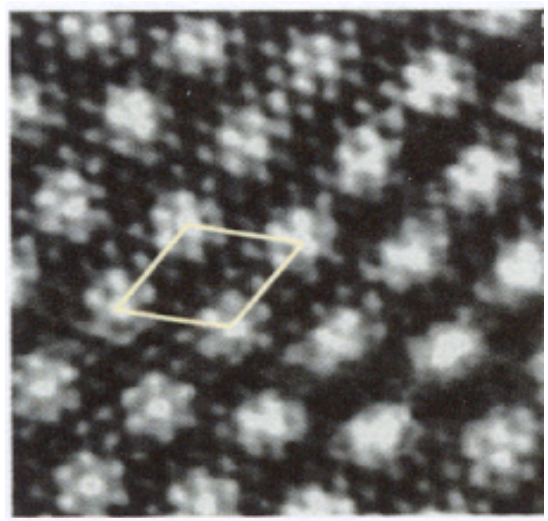
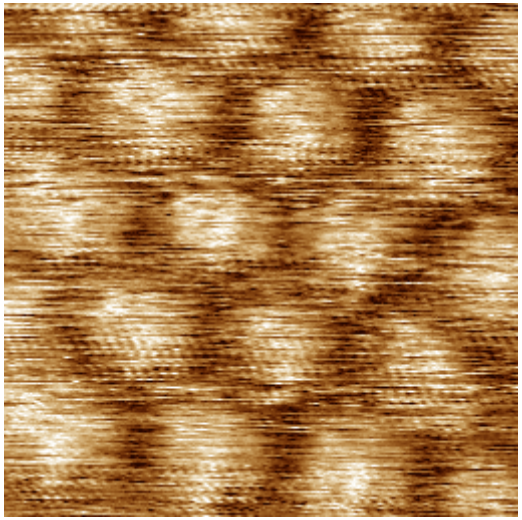
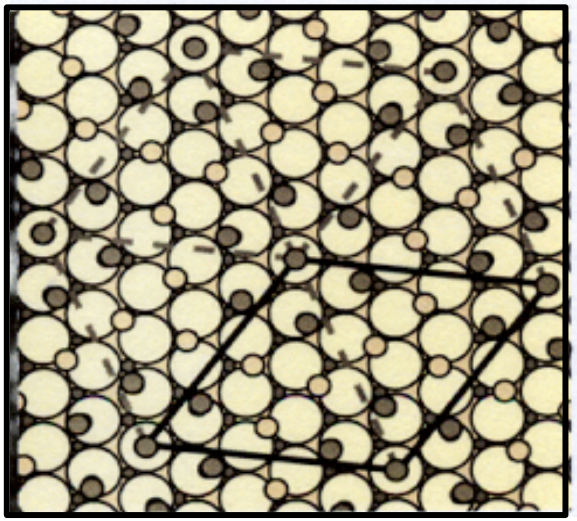


FIG. 1. 3D representation of an STM image obtained in 200 Torr CO. Image size is 200 Å × 200 Å, sample bias is +109 mV, and tunneling current 0.52 nA. Height scale is greatly exaggerated to display corrugation on the terraces. Hexagonal arrays of maxima can be observed on each terrace due to a CO monolayer forming a moiré structure. The alignment of the hexagonal array is the same in each terrace.

Jensen at al. PRL 80 (1998) 1228

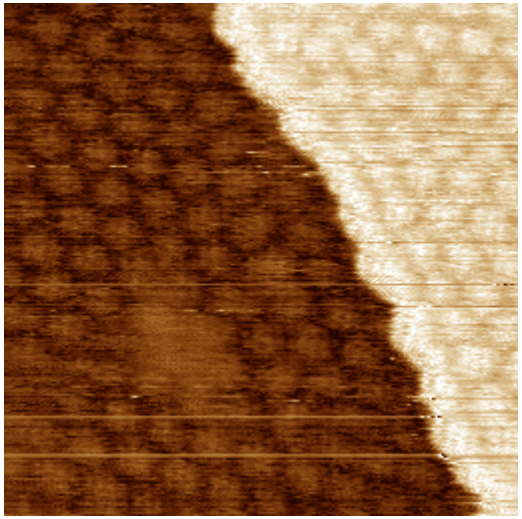






Vestergaard et al.,

PRL **88** (2002) 259601

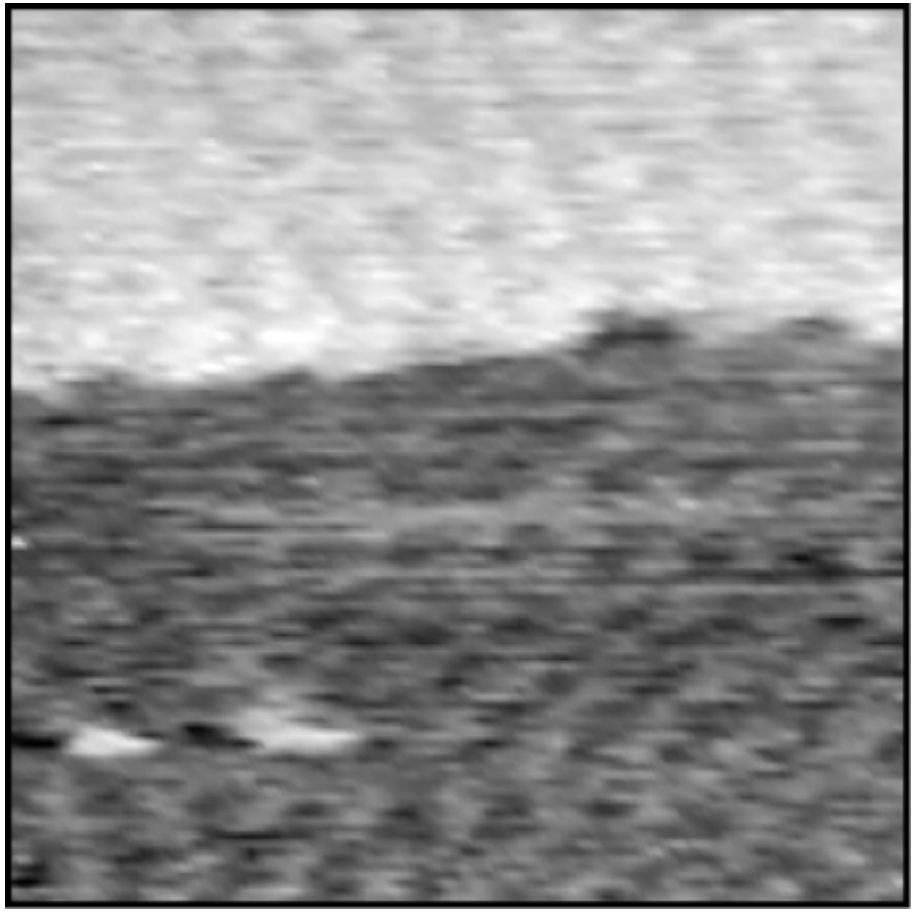


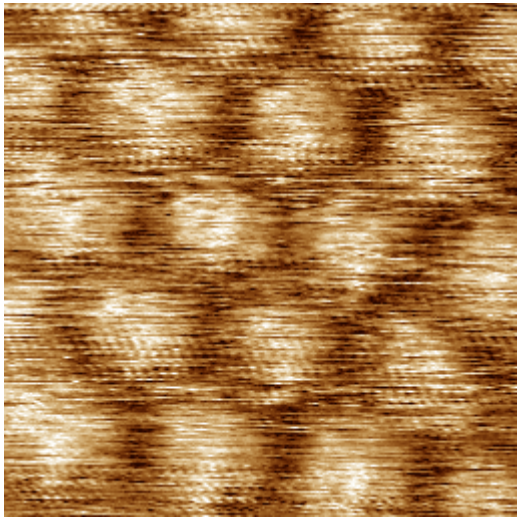
BH et al. Top. Catal. 36 (2005) 43

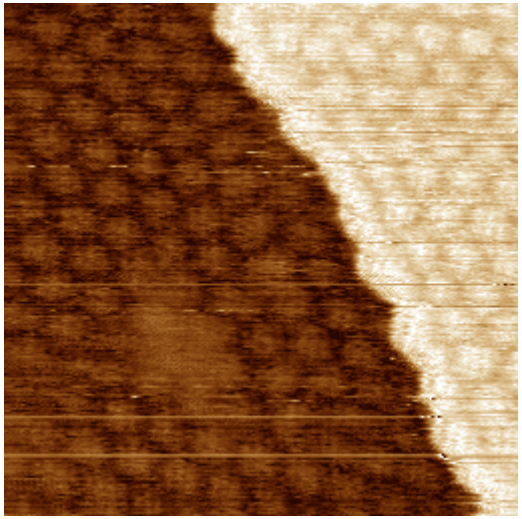
Moiré pattern: $\sqrt{19} \times \sqrt{19}\ R23.4^{\circ}$

CO overlayer structure!

Careful! gases are *never* 100% clean…

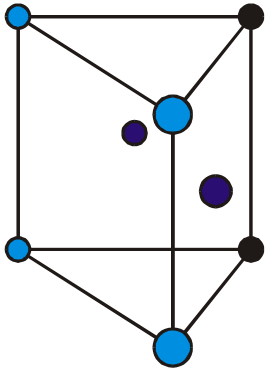




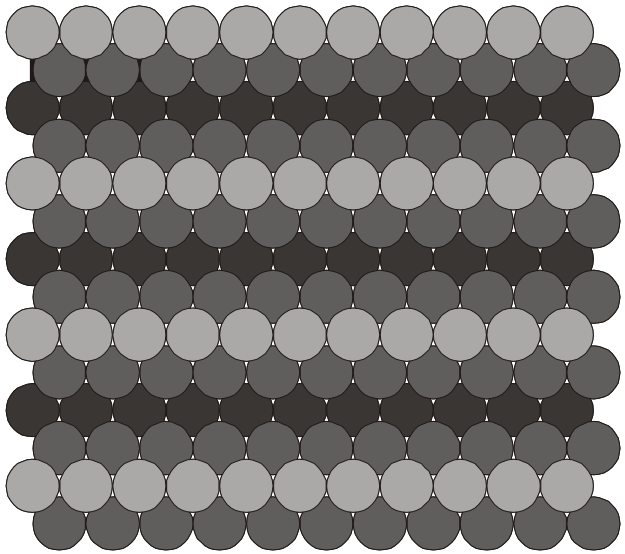


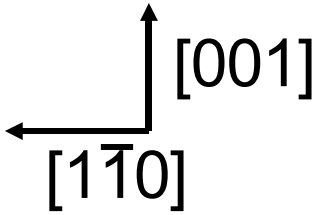
Pt(111) in 1 bar of 'pure' oxygen at 293K

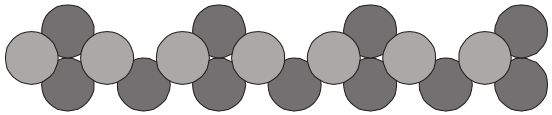
Pt(110): missing-row reconstruction



(1x2)-“missing row”

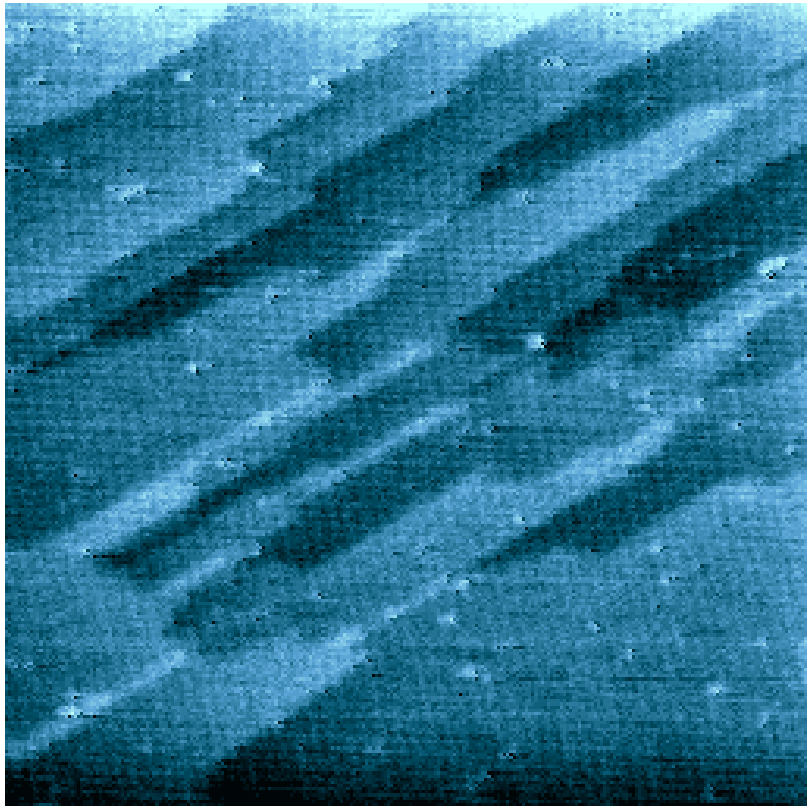


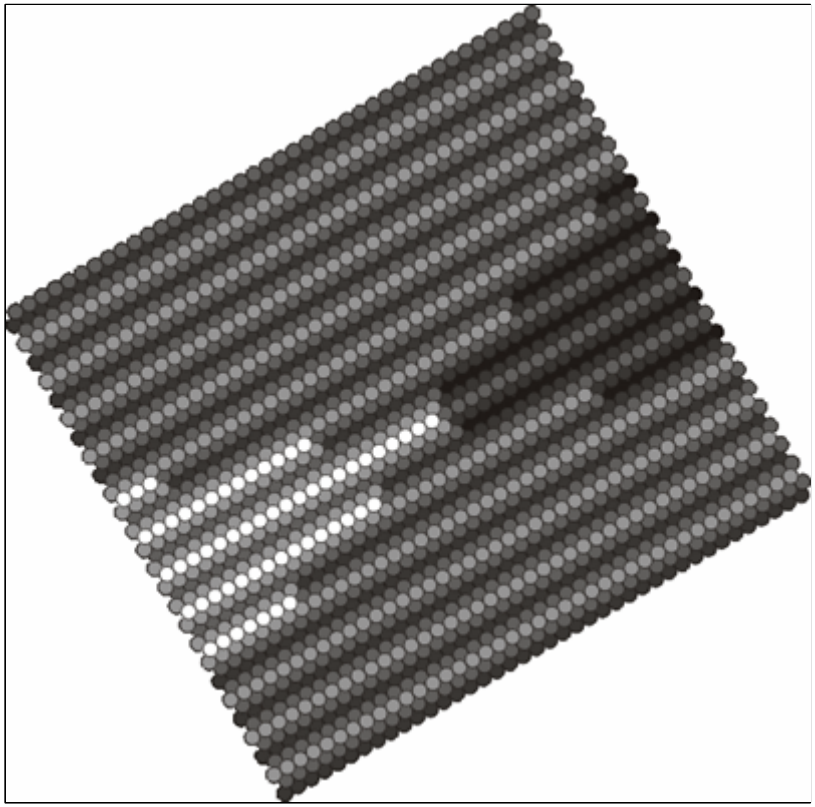




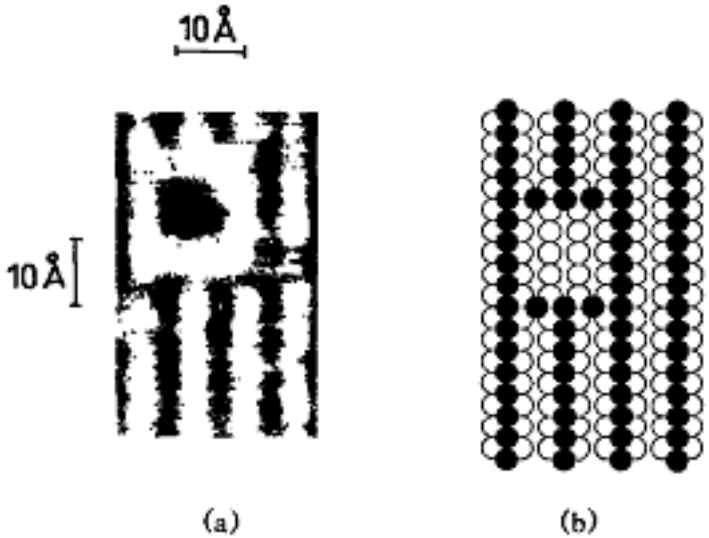
[001]

Step pattern: fish-scale structure





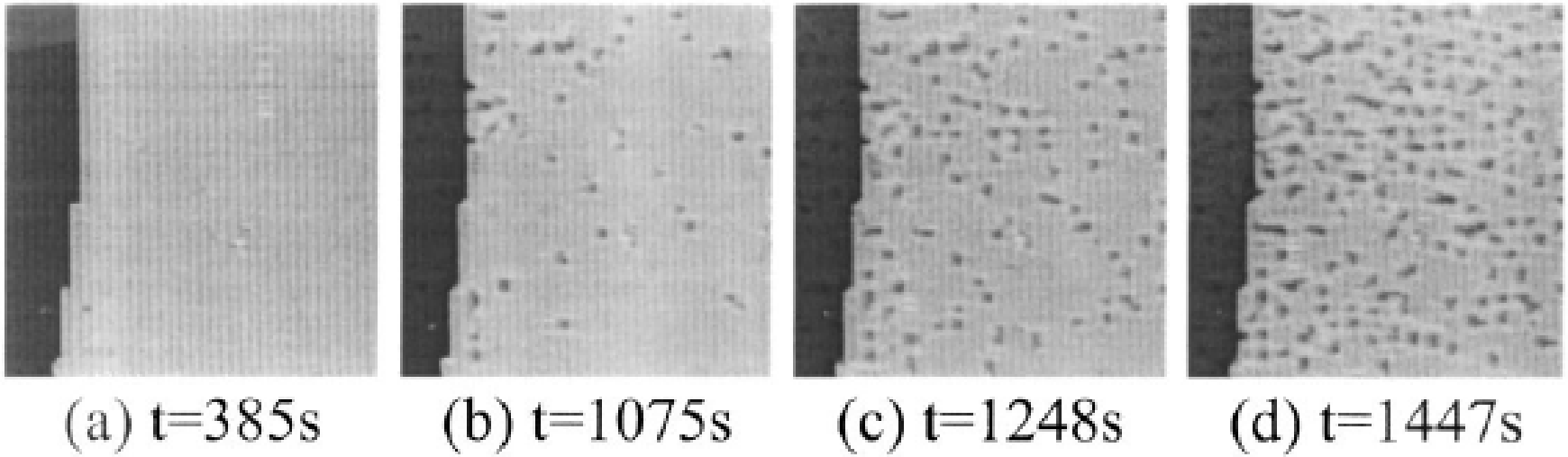
Adsorbate induced restructuring



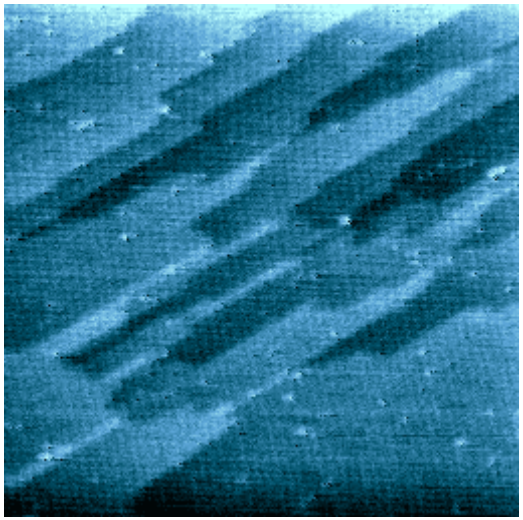
Gritsch et at. (1989)

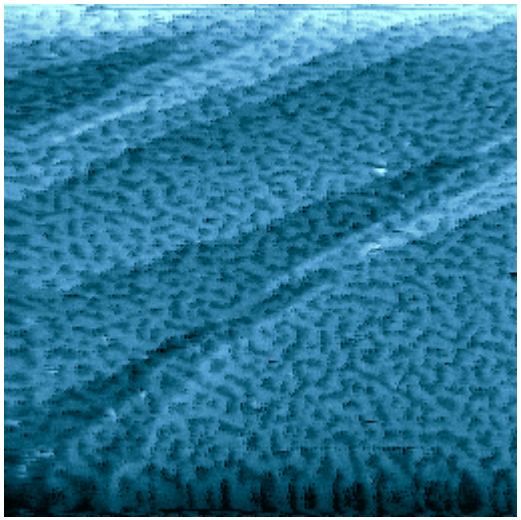
CO on Pt(110)

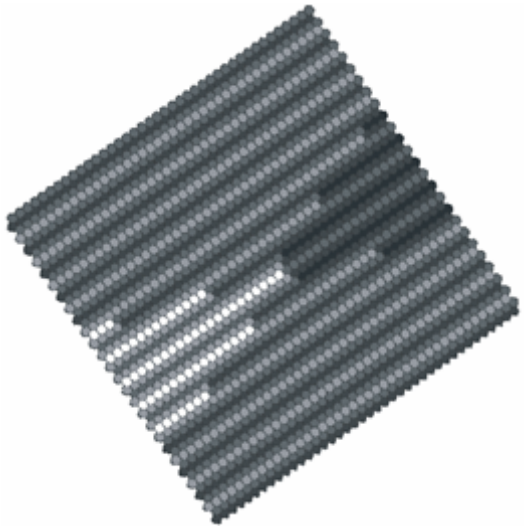
Thostrup et al. J.Chem. Phys. 118 (2003) 3724

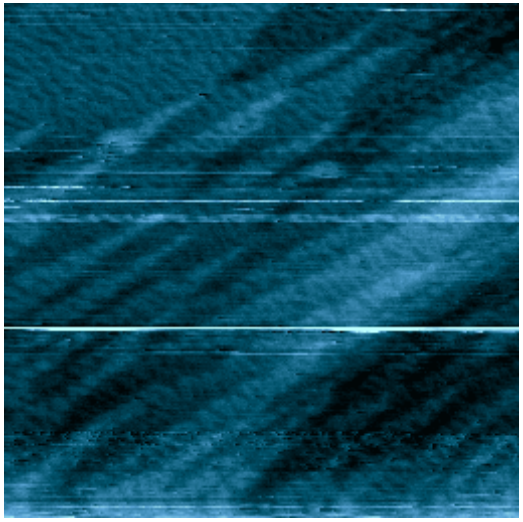


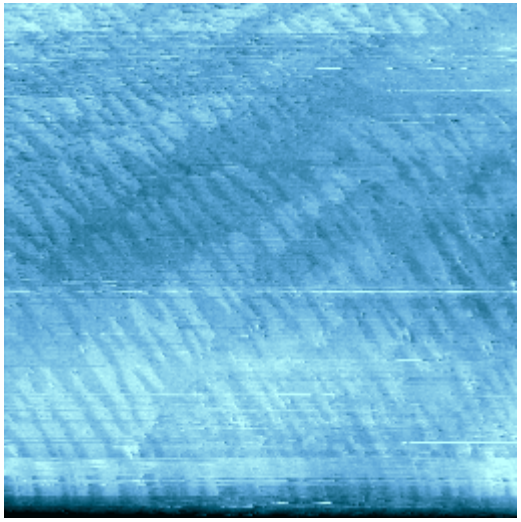
1x2 (‘fish scale’) → 1x1 (‘tiger skin’)

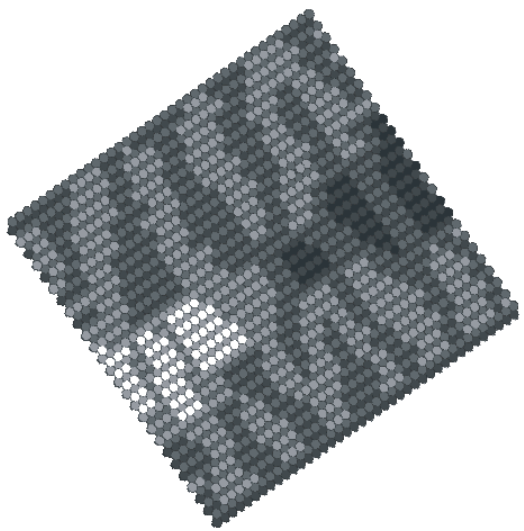






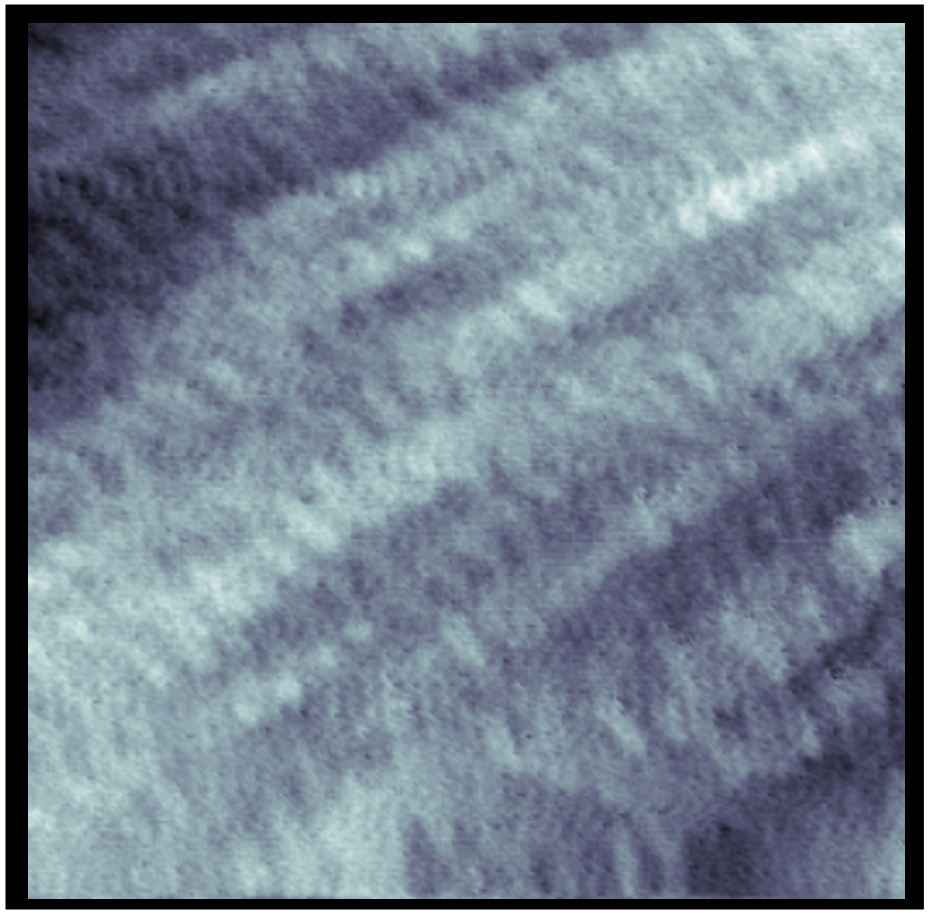






Platinum in flowing gas mixture: mainly CO

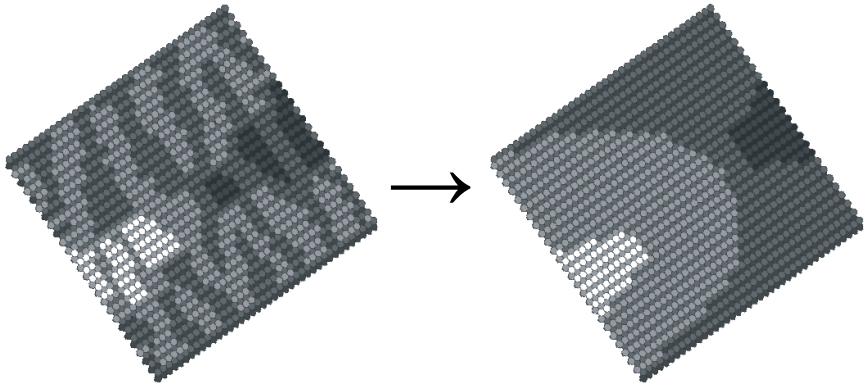
'fish scale'→'tiger skin' →smooth



Pt(110) in $Ar/O_2/CO$
T=425K
P_{tot}=1.25 bar

140 nm x 140 nm

8h:31min



Platinum in flowing gas mixture: mainly CO

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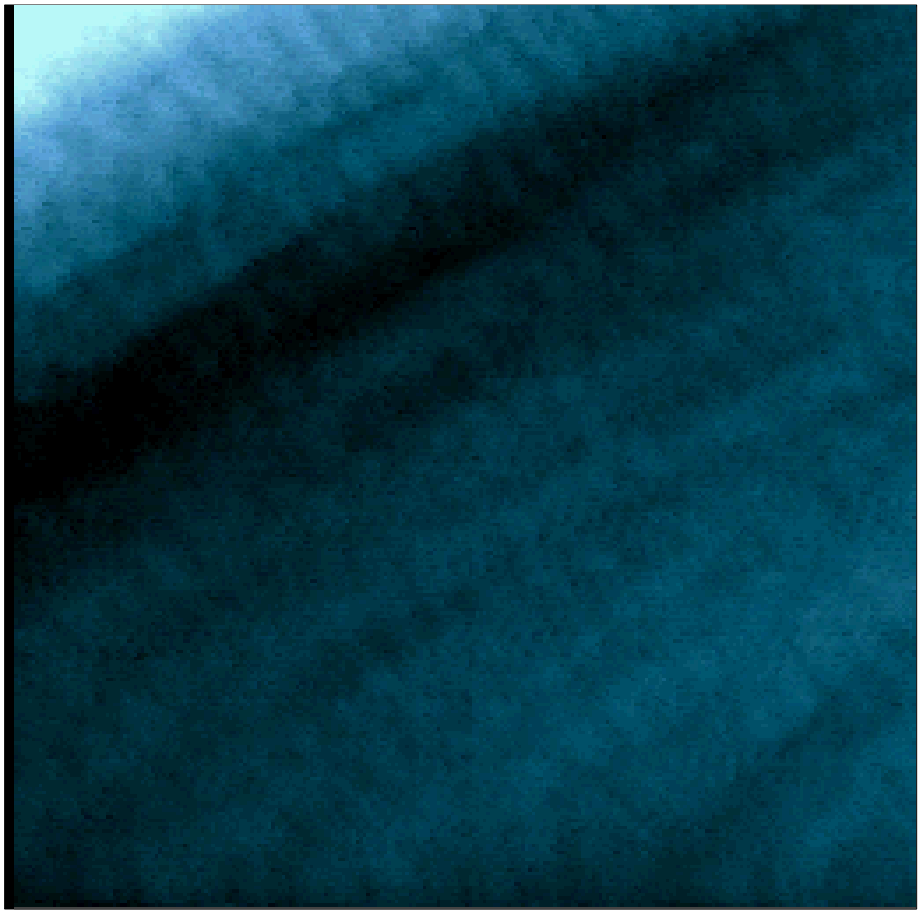

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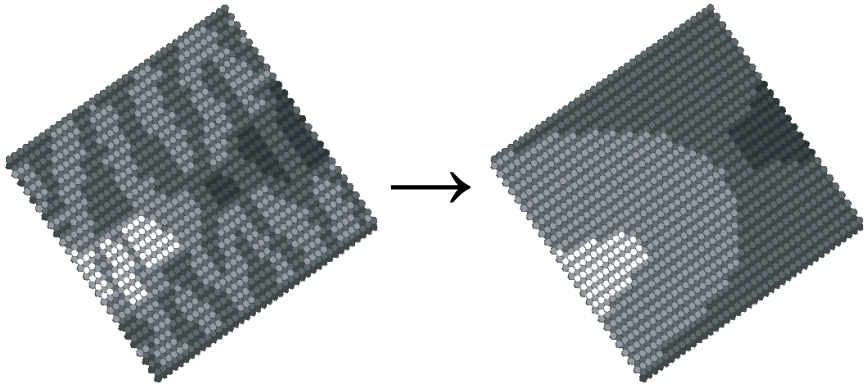
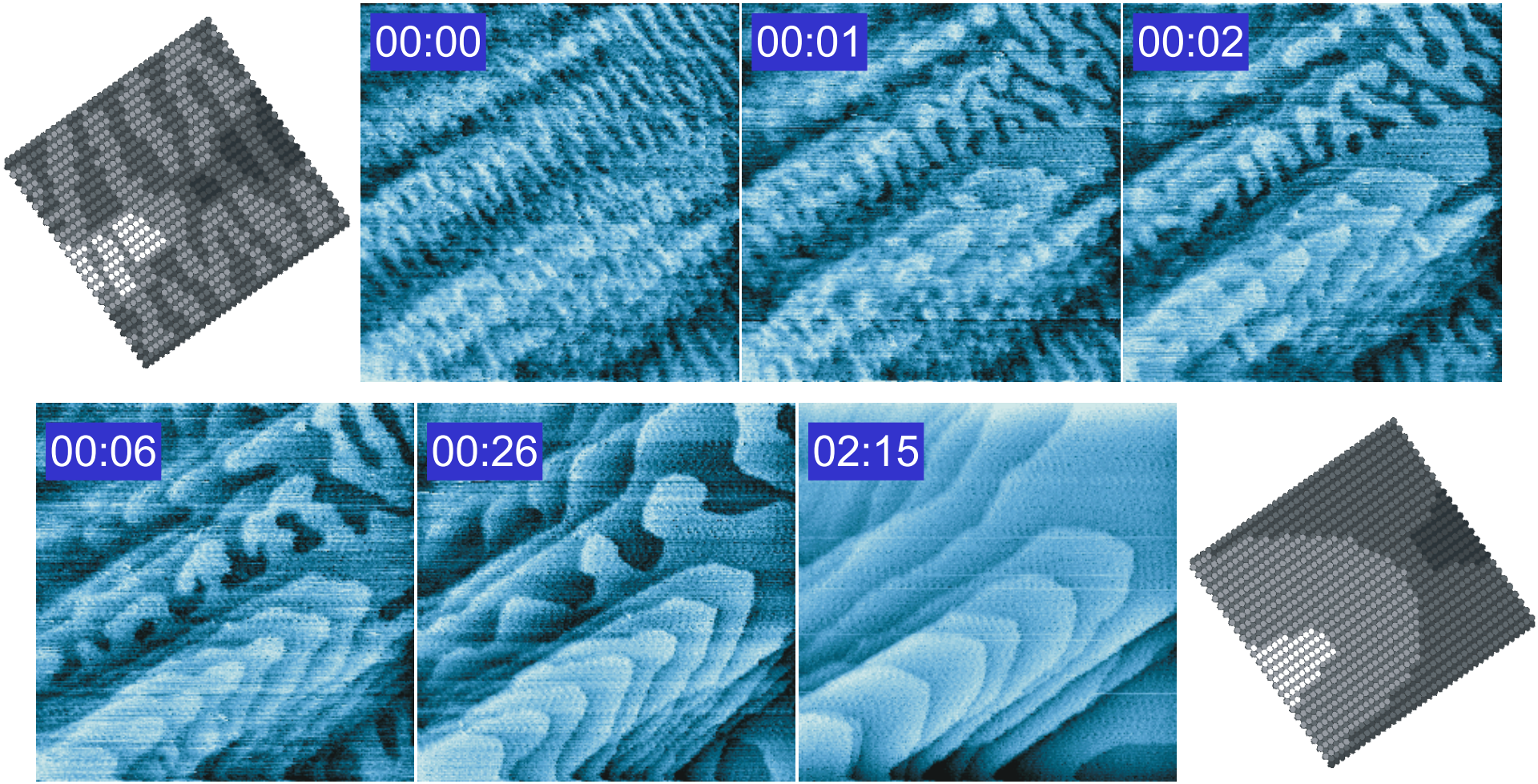


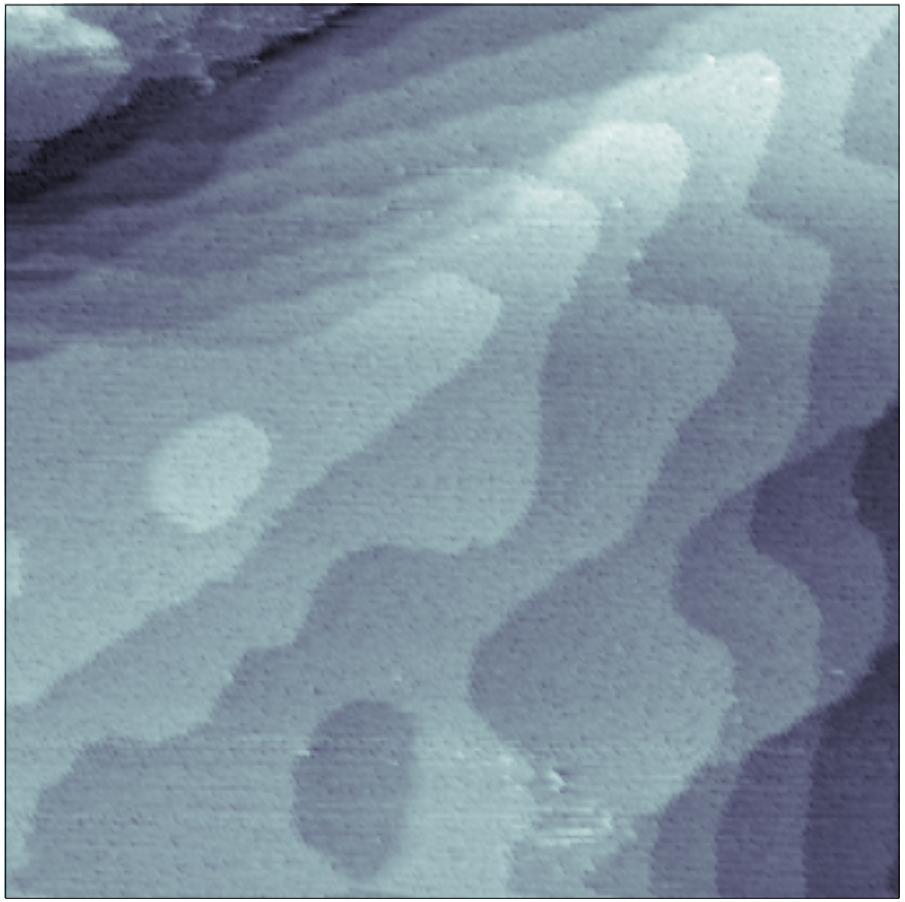
Platinum in flowing gas mixture: mainly CO

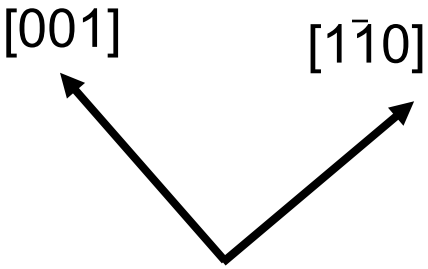
‘tiger skin’ →smooth



Platinum in flowing gas mixture: $CO + O_2$

P_{tot} = 0.5 bar
T = 425 K

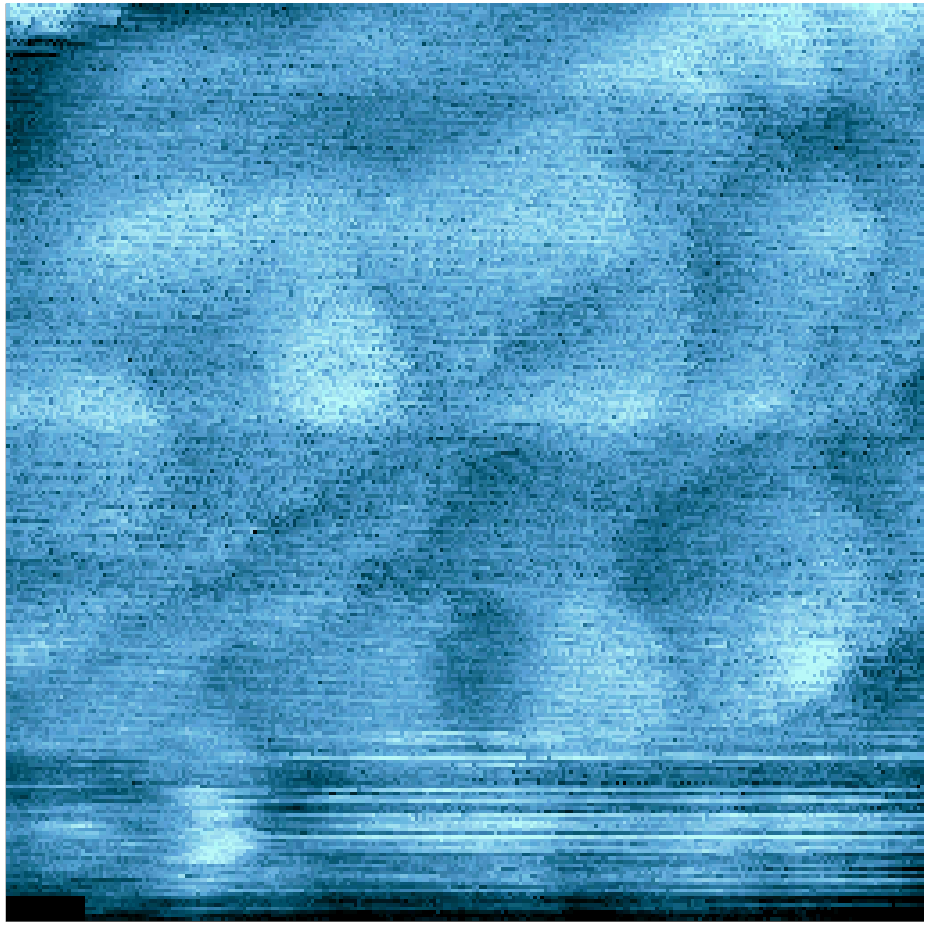


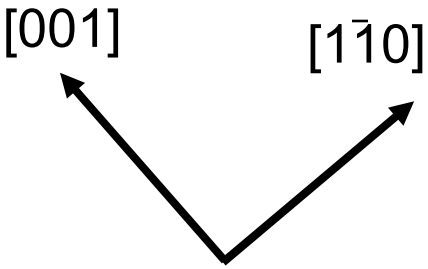


(140x140nm^2)
43 s/image

Platinum in flowing gas mixture: $CO + O_2$

P_{tot} = 0.5 bar
T = 425 K

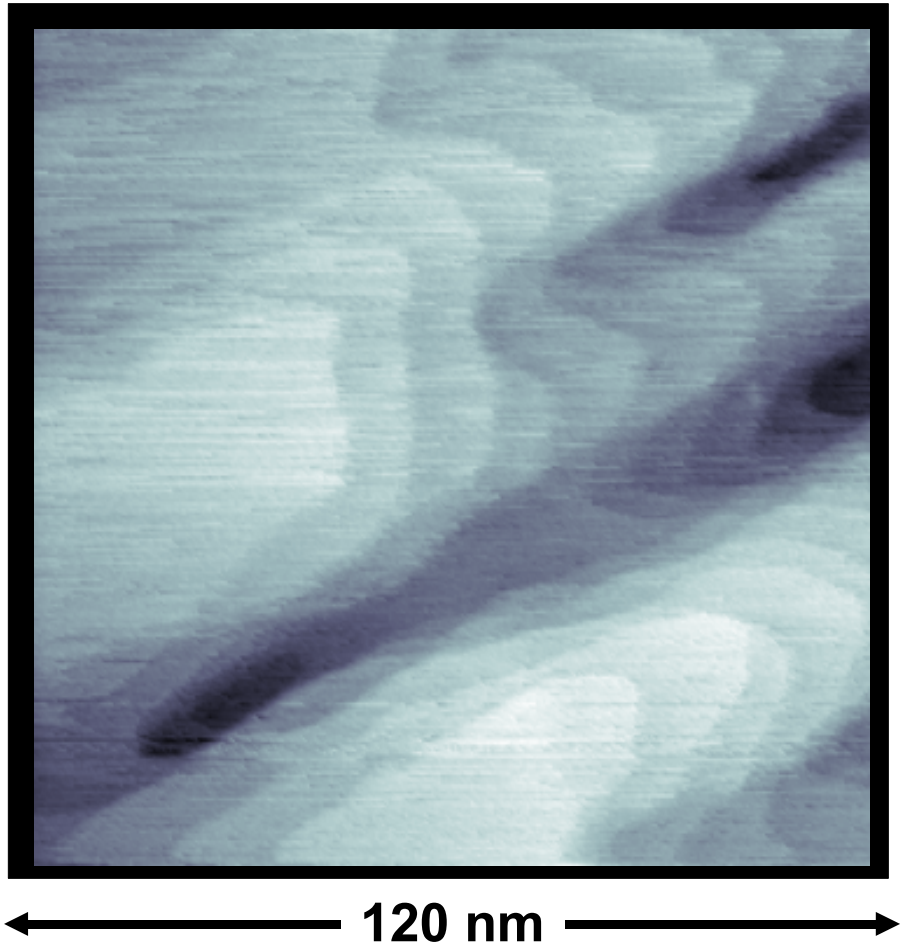


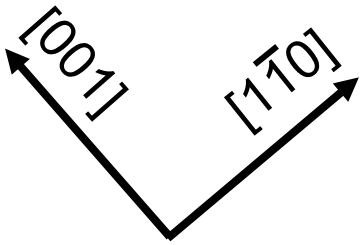


(140x140nm^2)
43 s/image

Platinum in flowing gas mixture: $CO + O_2$

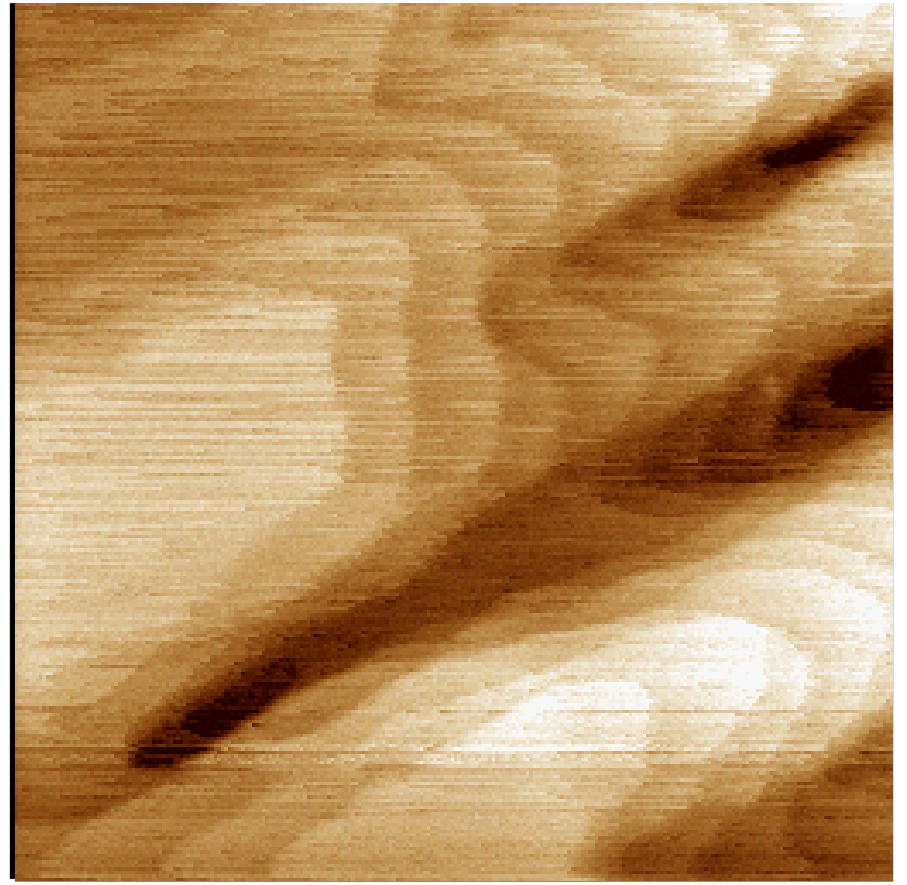
P_{tot} = 0.5 bar
T = 425 K
t_{total} = 3h:12m



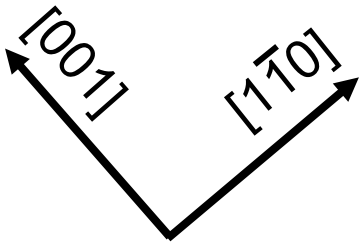


Platinum in flowing gas mixture: $CO + O_2$

P_{tot} = 0.5 bar
T = 425 K
t_{total} = 3h:12m

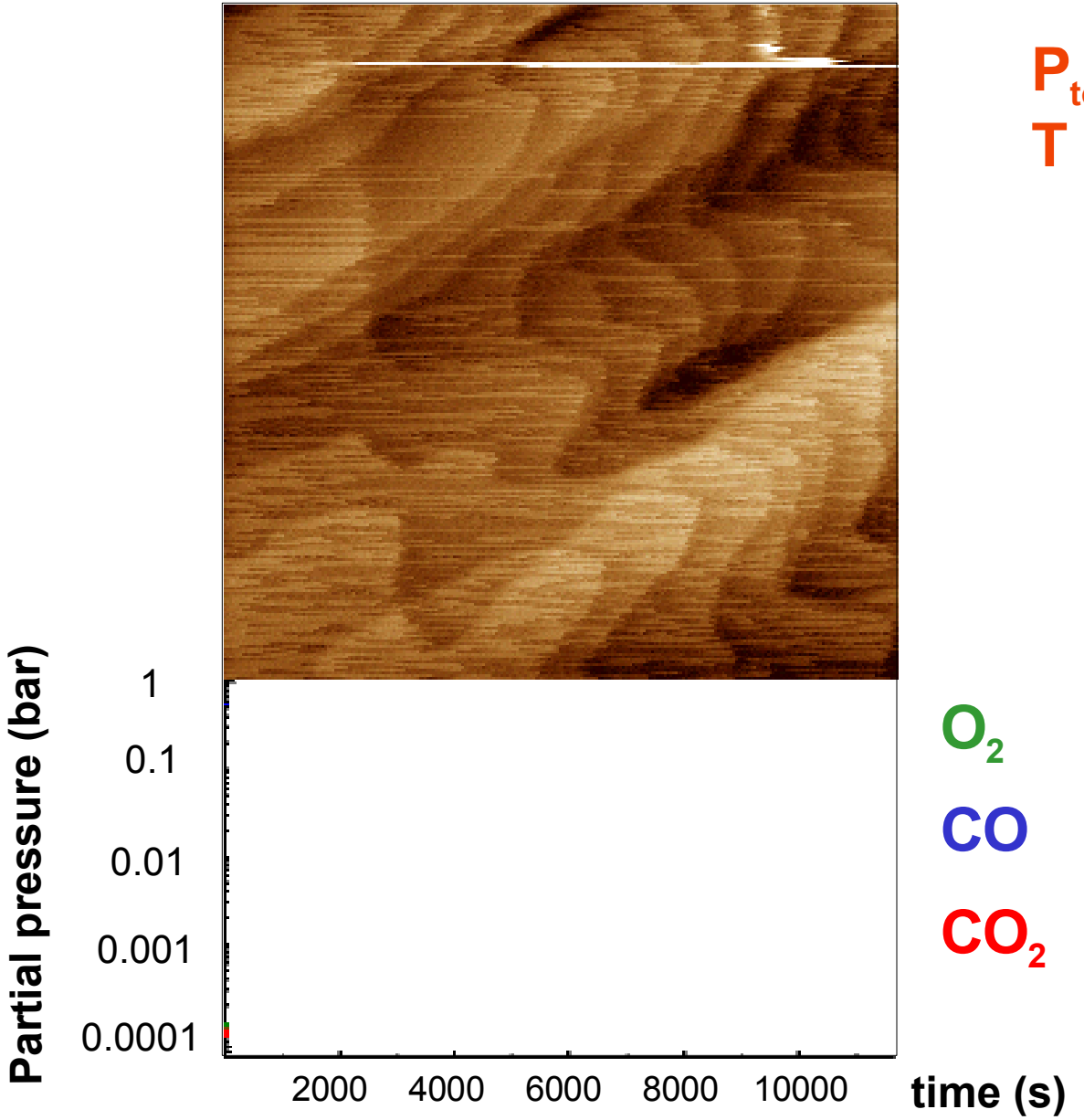


120 nm



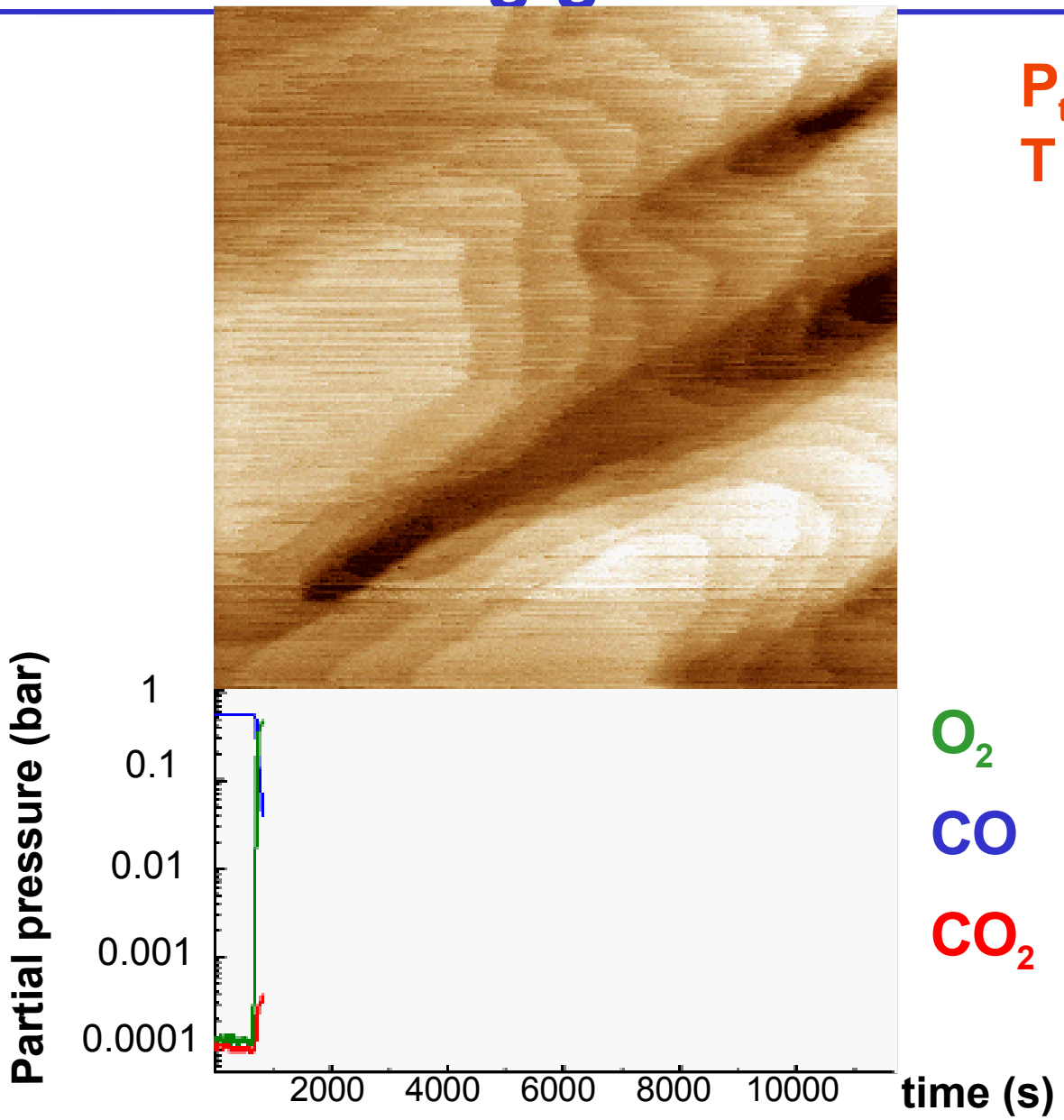
Platinum in flowing gas mixture: $CO + O_2$

$P_{tot} = 0.5$ bar
$T = 425$ K



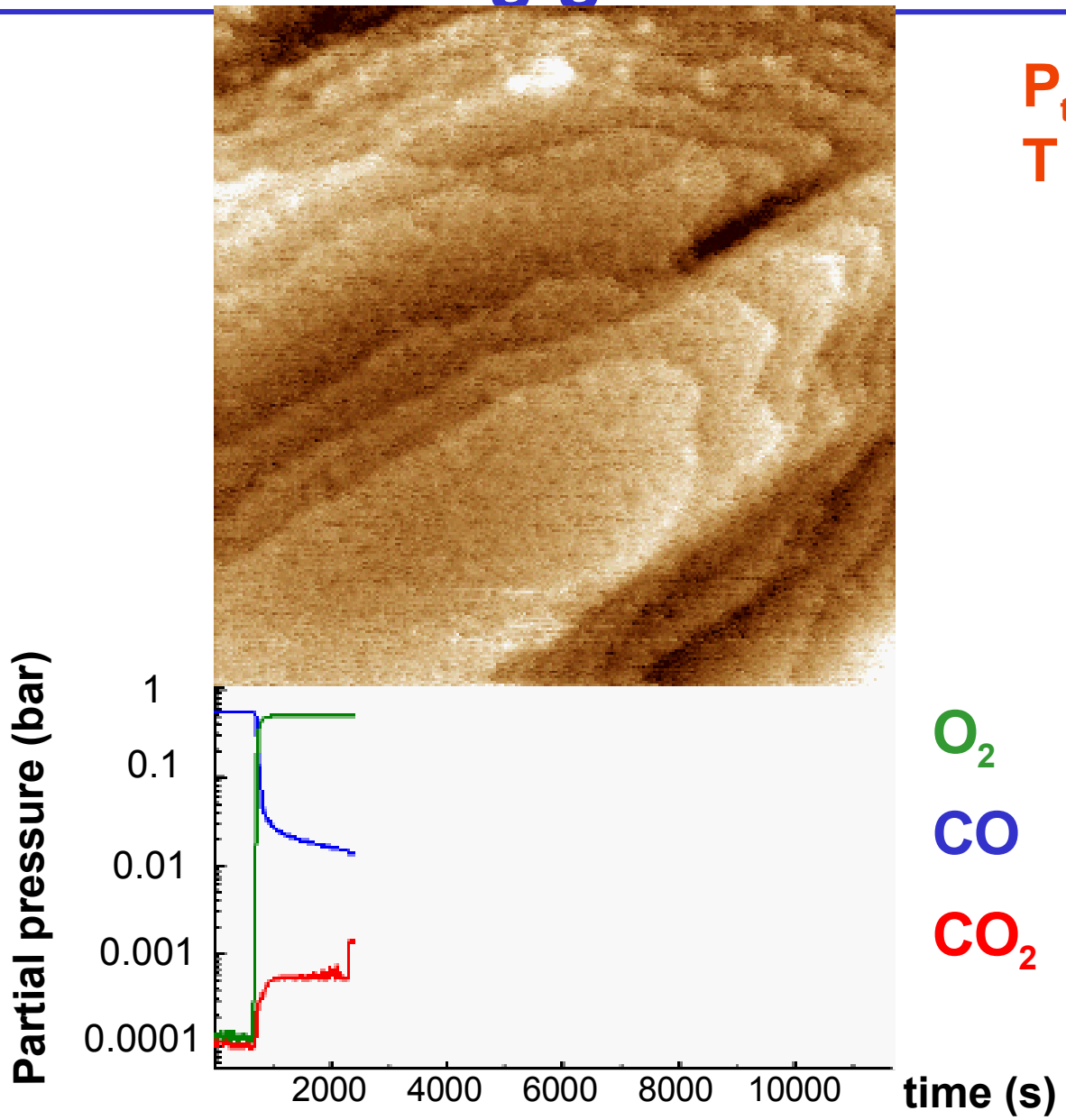
Platinum in flowing gas mixture: $CO + O_2$

P_{tot} = 0.5 bar
T = 425 K



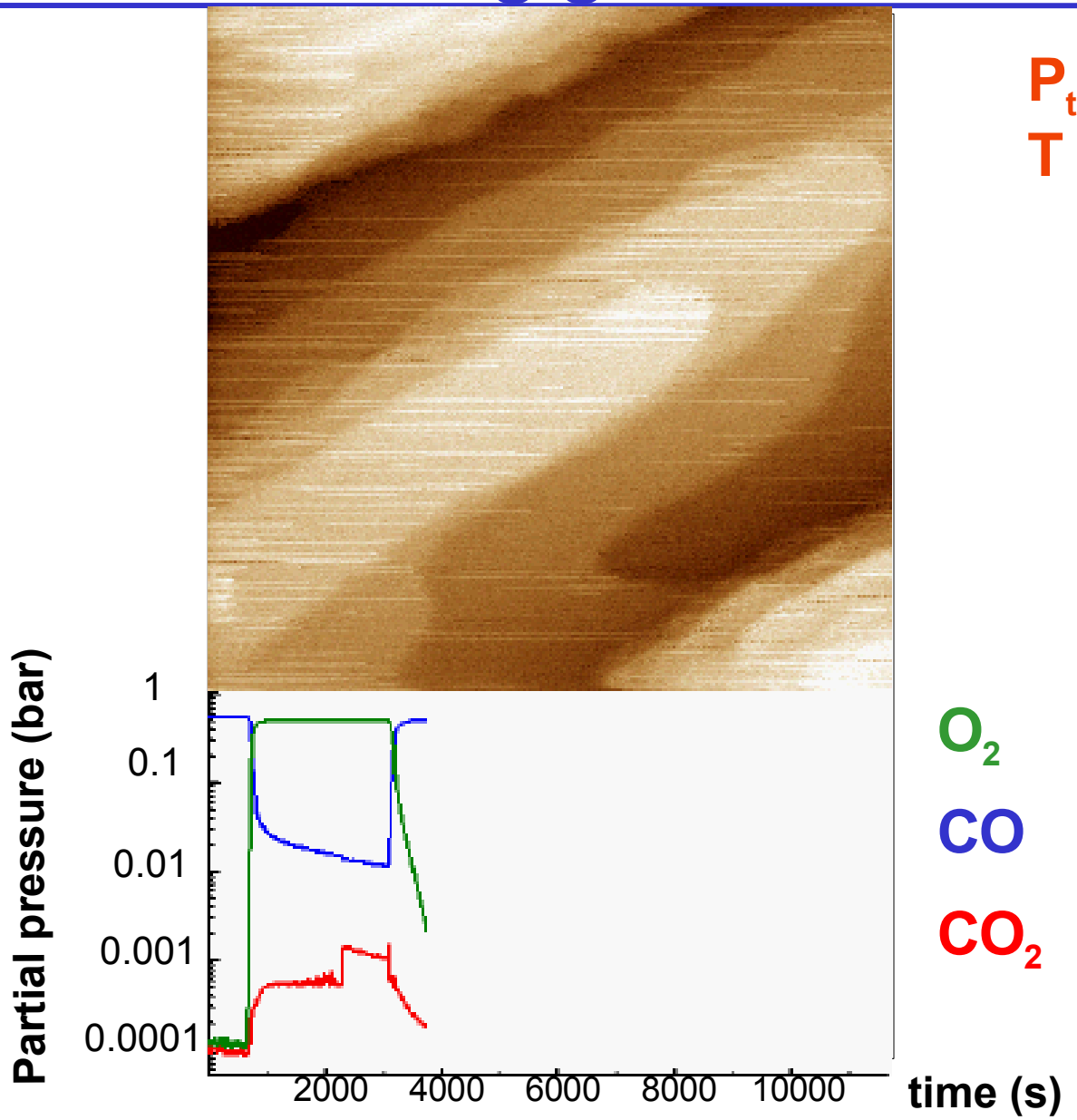
Platinum in flowing gas mixture: $CO + O_2$

$P_{tot} = 0.5$ bar
$T = 425$ K



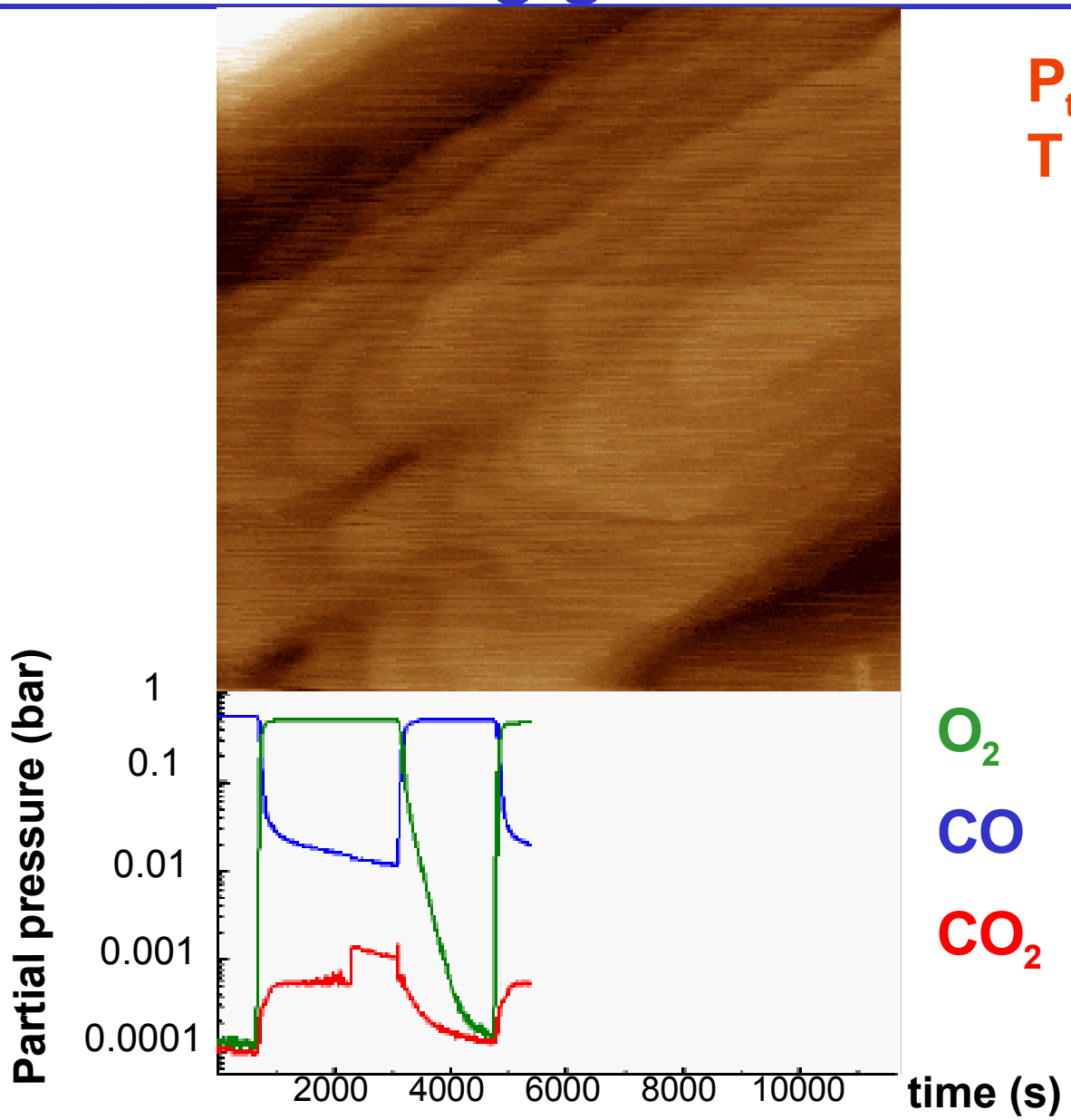
Platinum in flowing gas mixture: $CO + O_2$

P_{tot} = 0.5 bar
T = 425 K

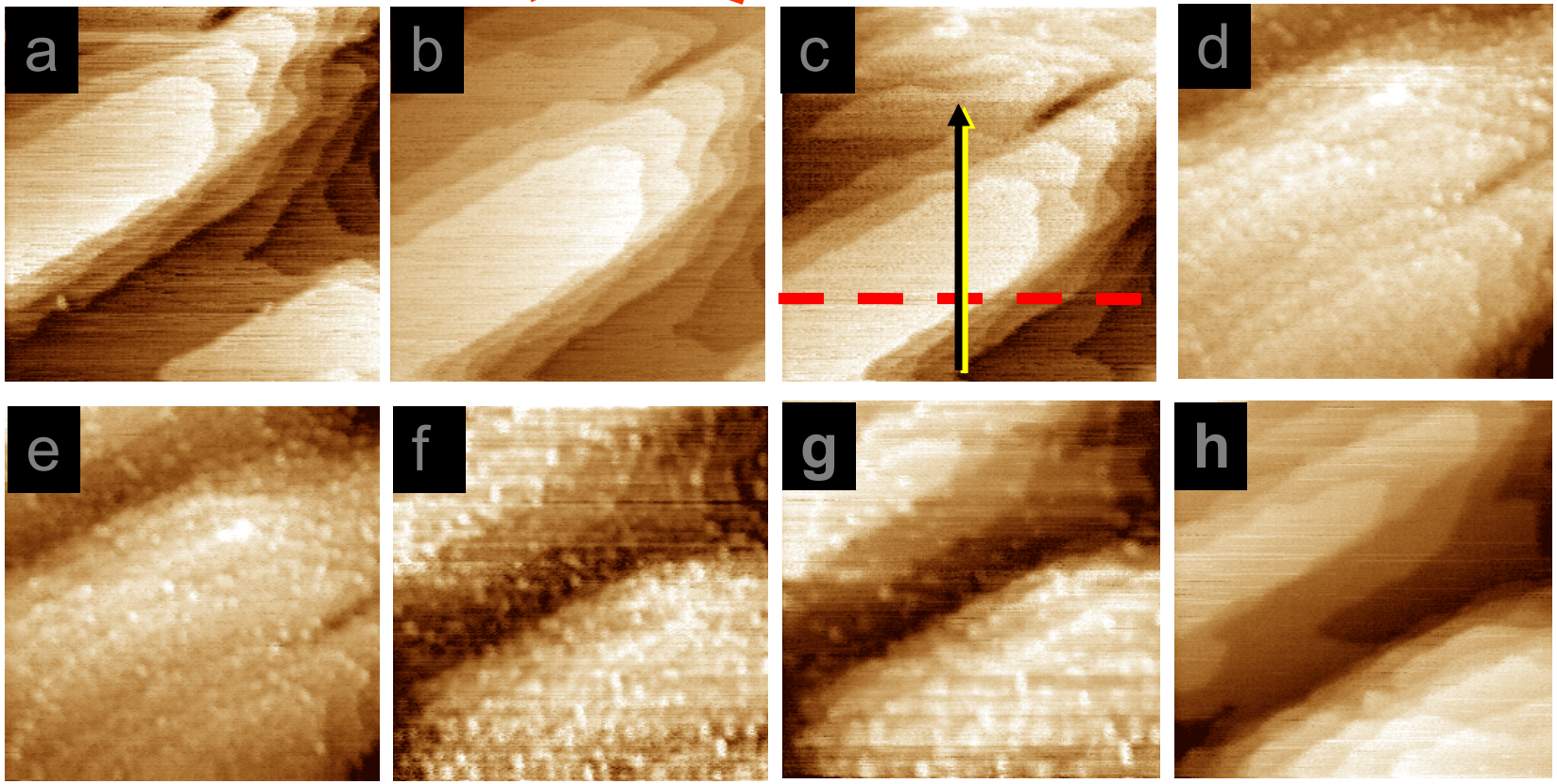


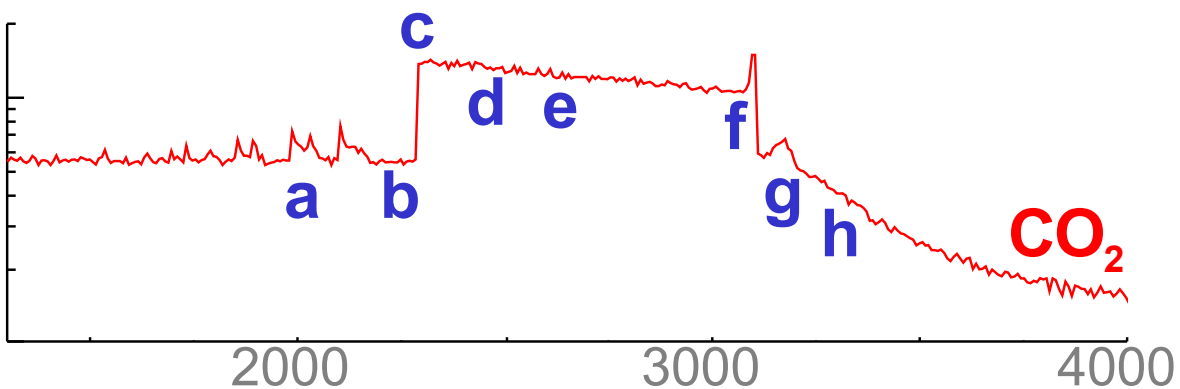
Platinum in flowing gas mixture: $CO + O_2$

P_{tot} = 0.5 bar
T = 425 K



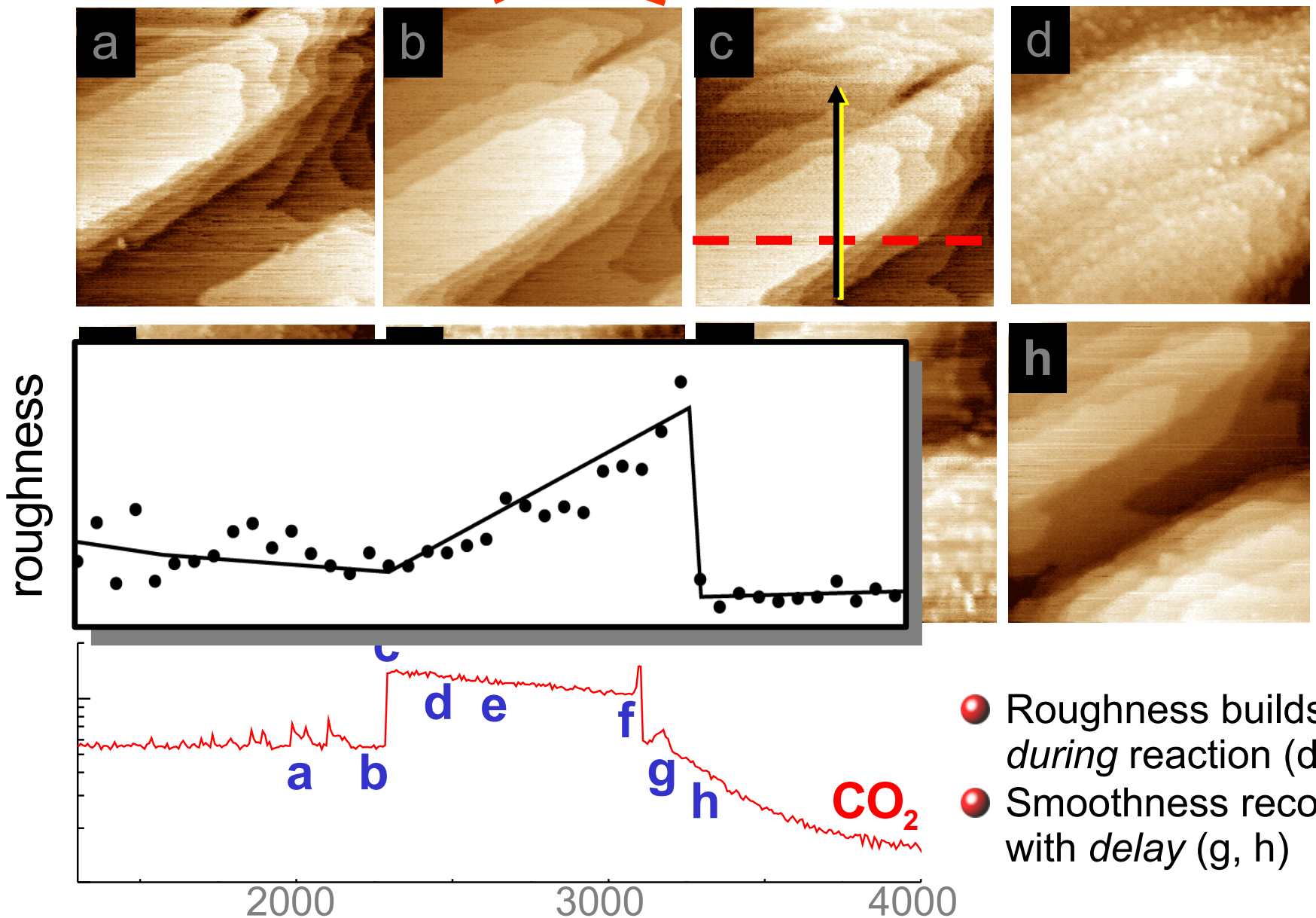
Roughness: ~~cause~~ or ~~effect~~?





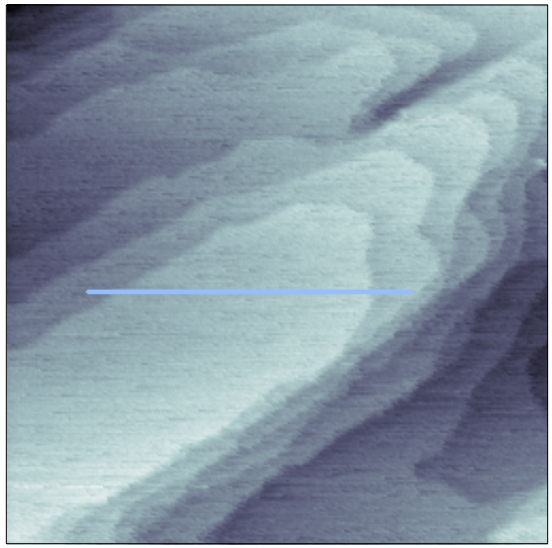
- Roughness builds up *during* reaction (d, e, f)
- Smoothness recovers with *delay* (g, h)

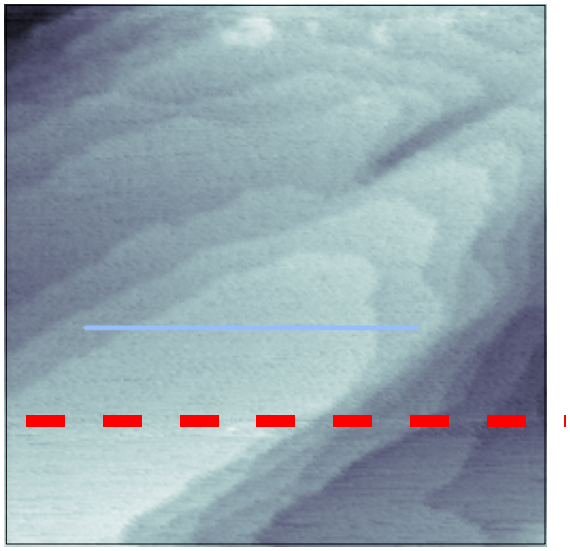
Roughness: ~~cause~~ or ~~effect~~?

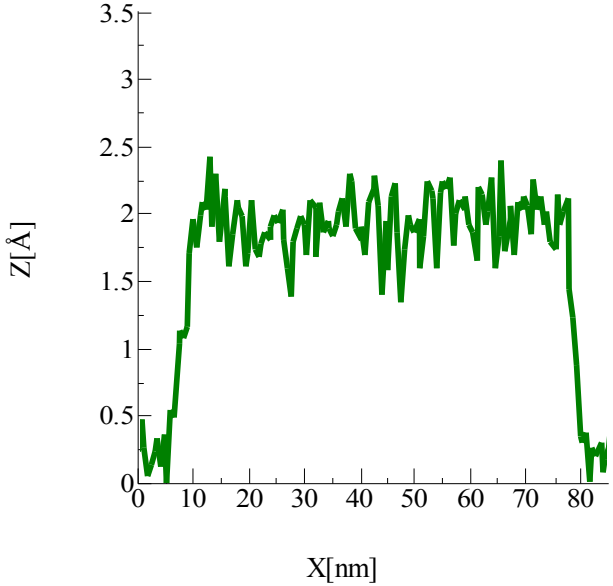


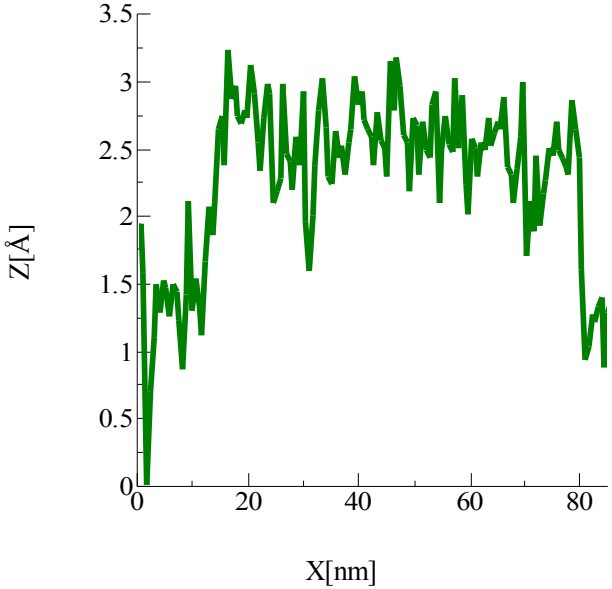
- Roughness builds up *during* reaction (d, e, f)
- Smoothness recovers with *delay* (g, h)

Switch from low to high activity

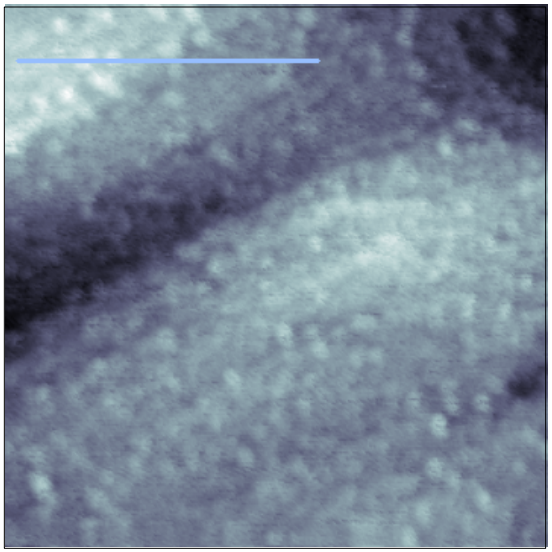


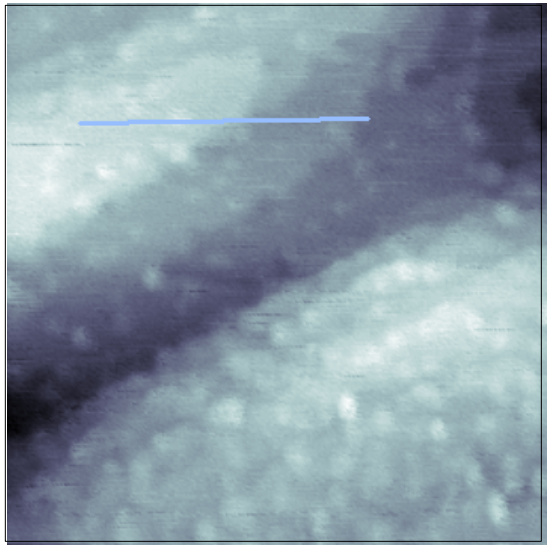


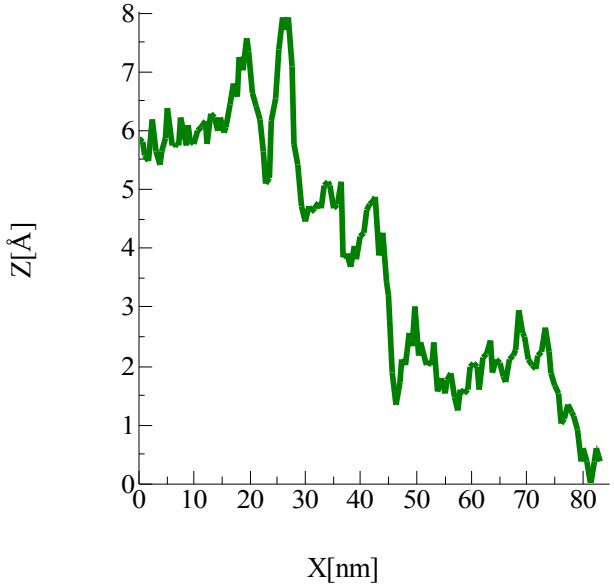


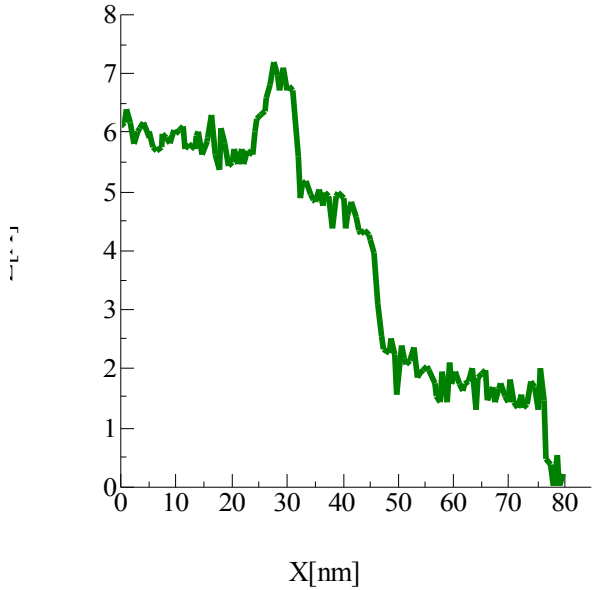


Switch from high to low activity

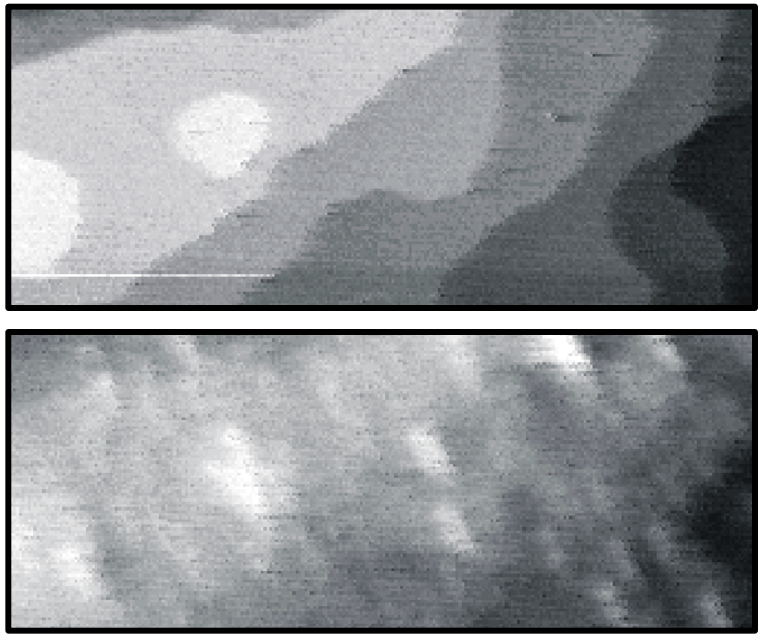


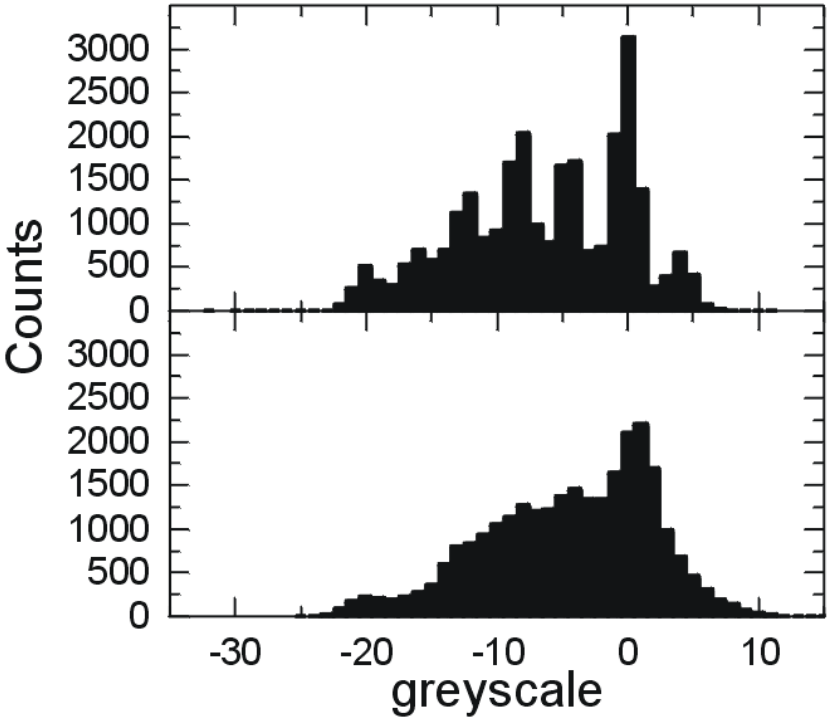


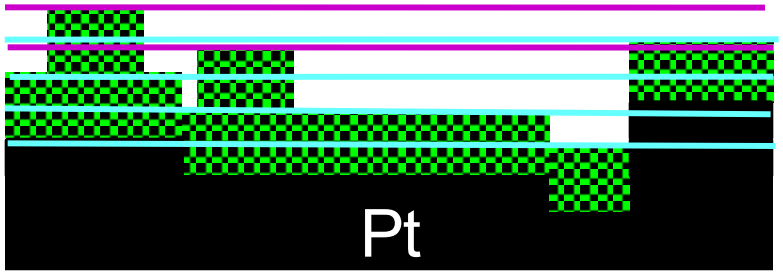




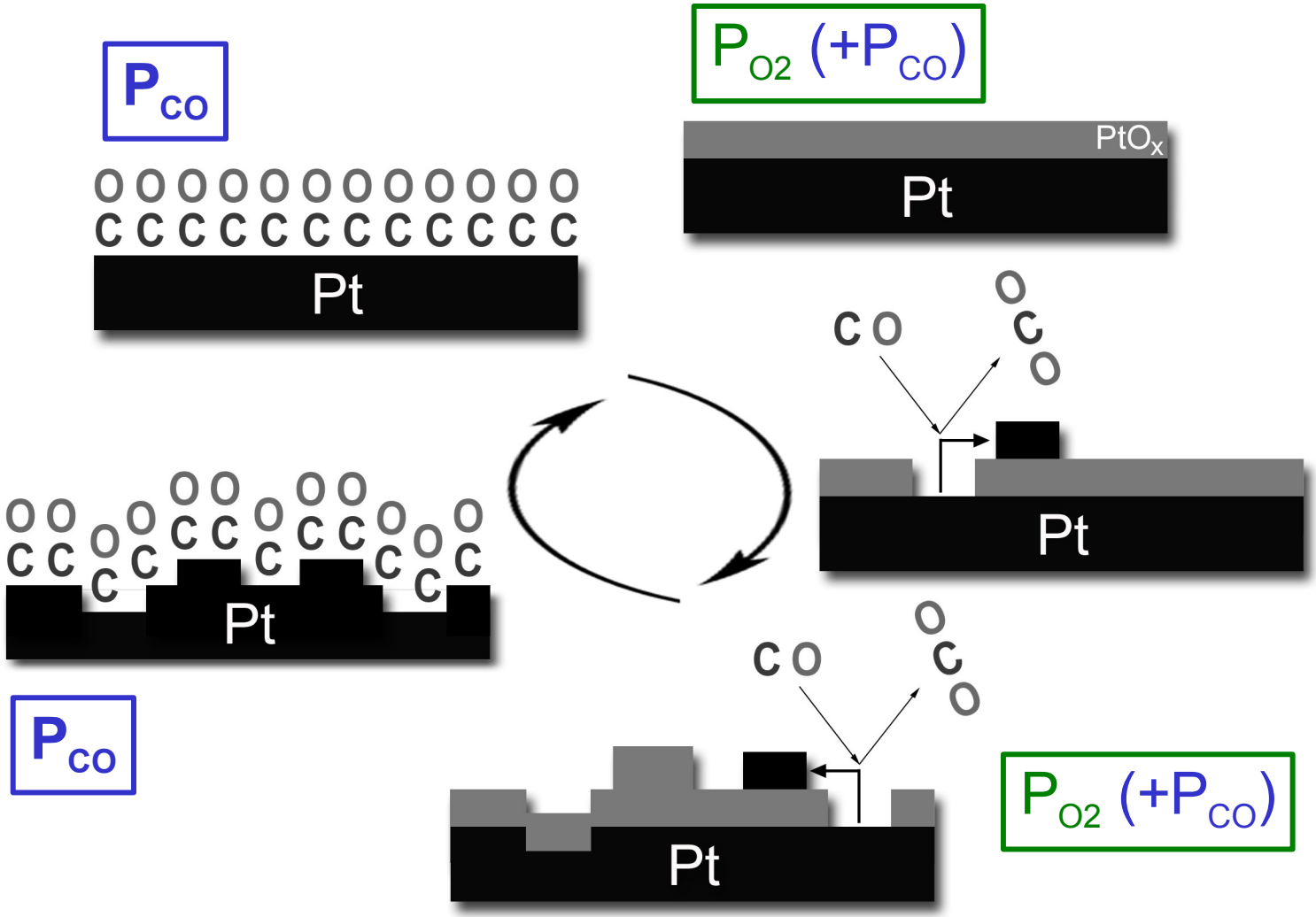
Height variations that are not Pt(110)



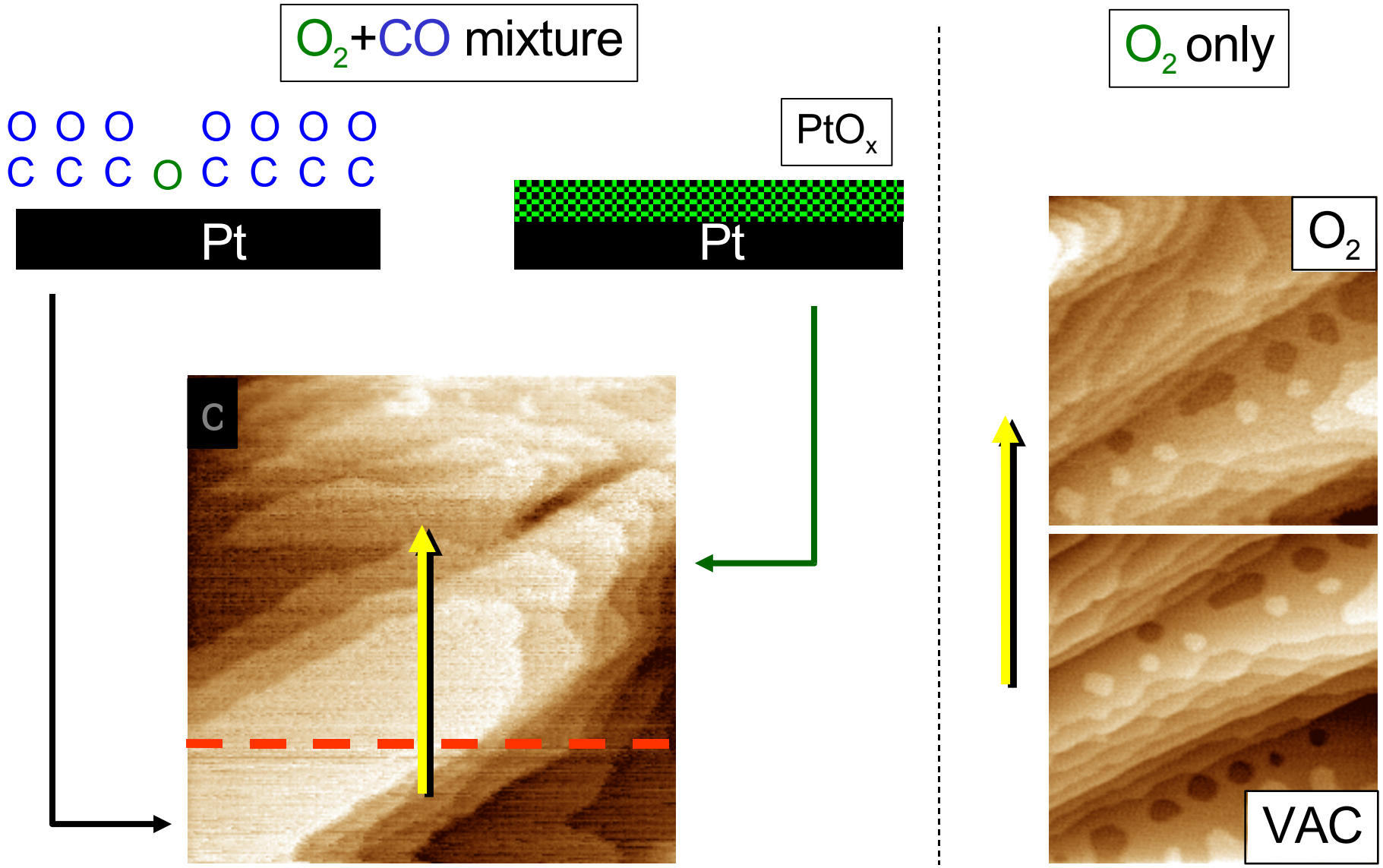




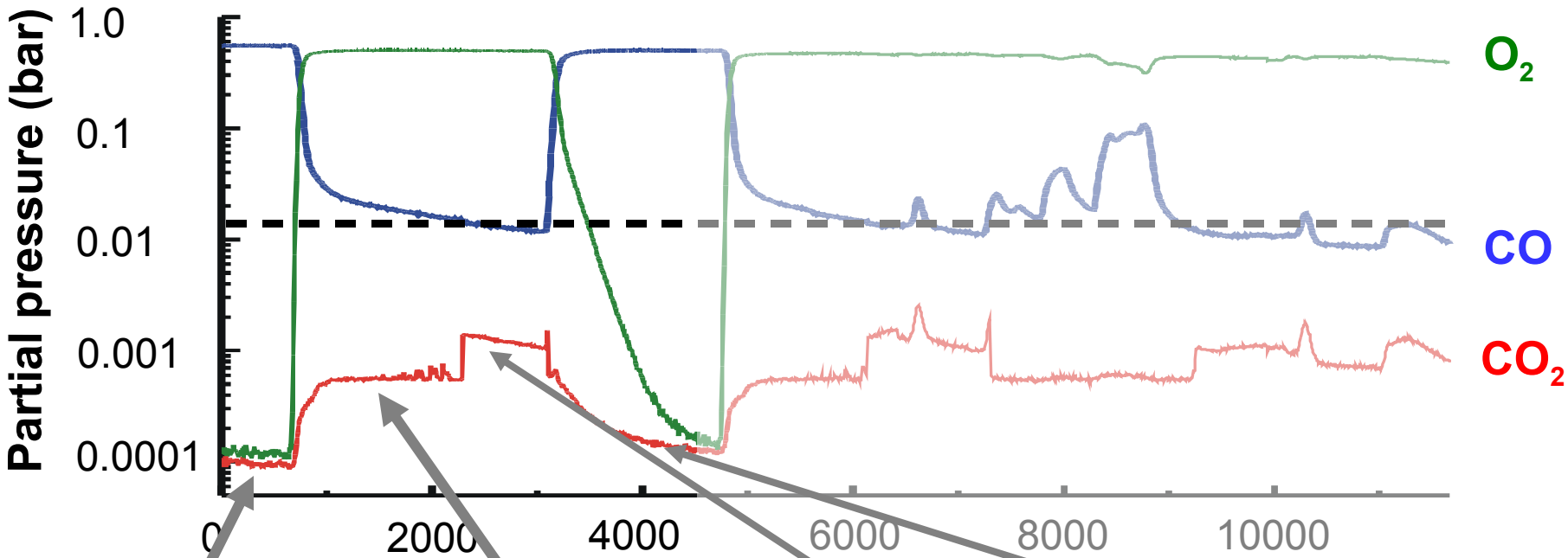
Mars-Van Krevelen reaction mechanism

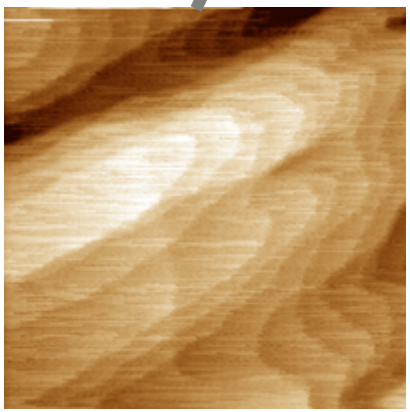


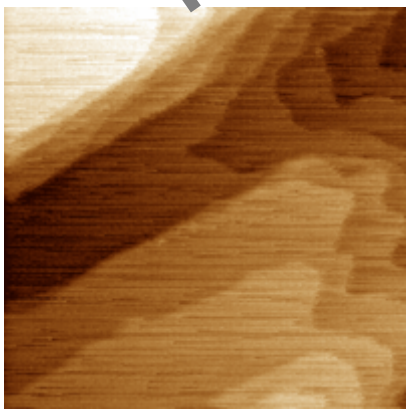
Surface oxide

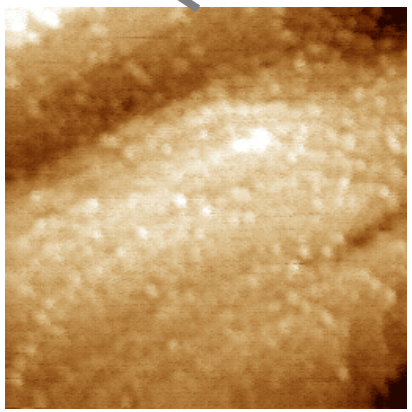


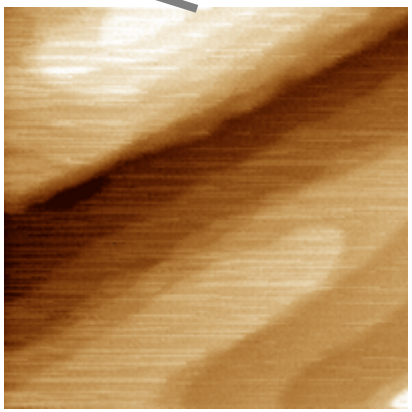
Platinum in flowing gas mixture: $CO + O_2$



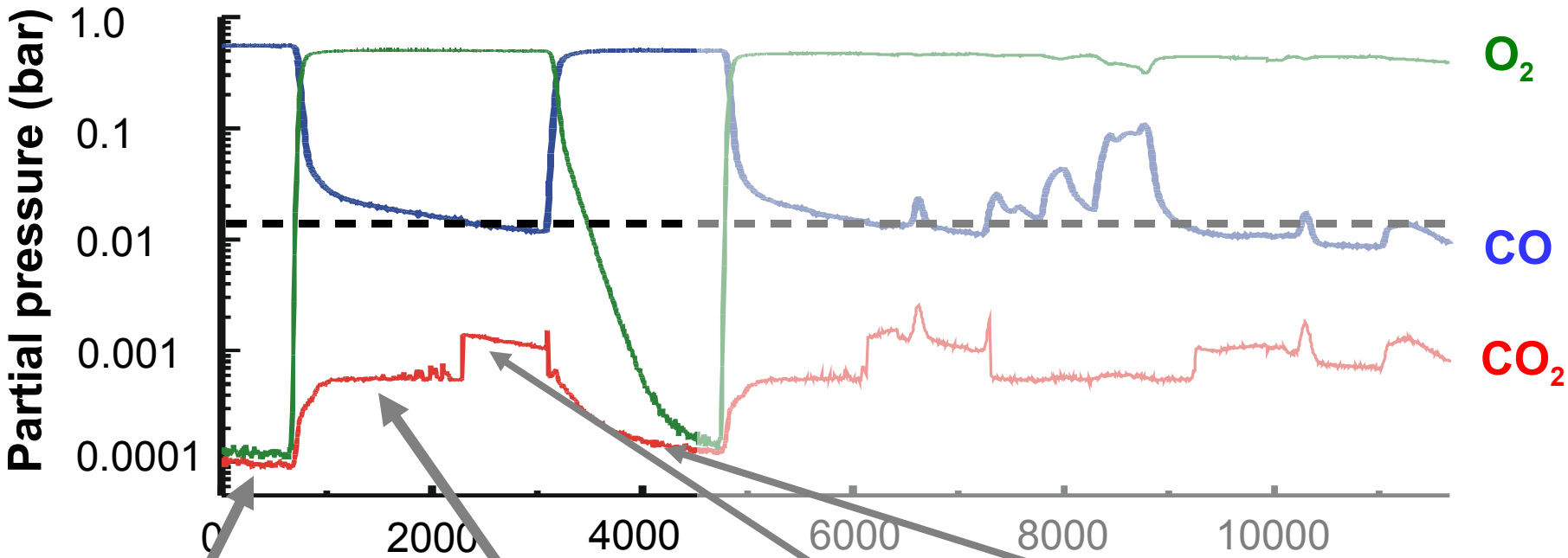


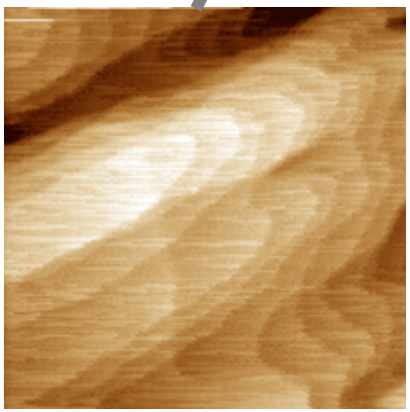


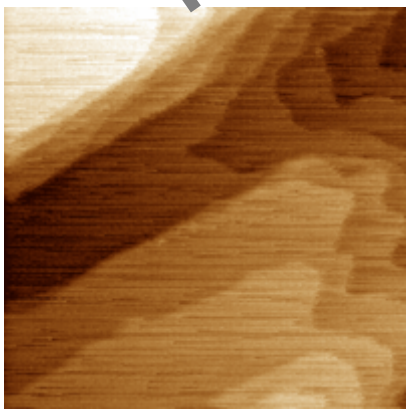


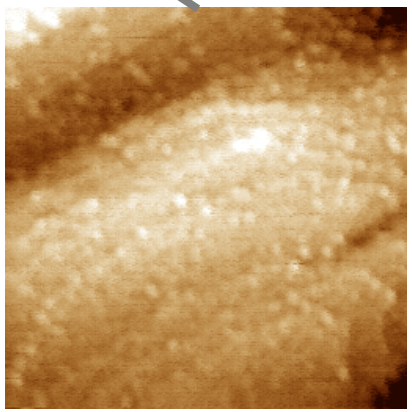


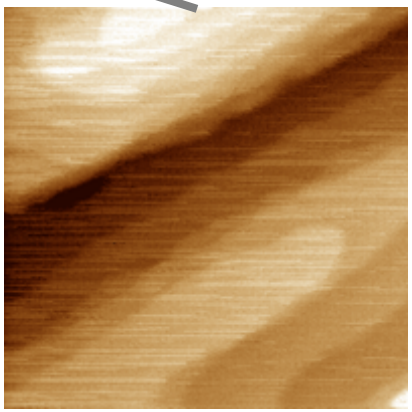
Platinum in flowing gas mixture: $CO + O_2$



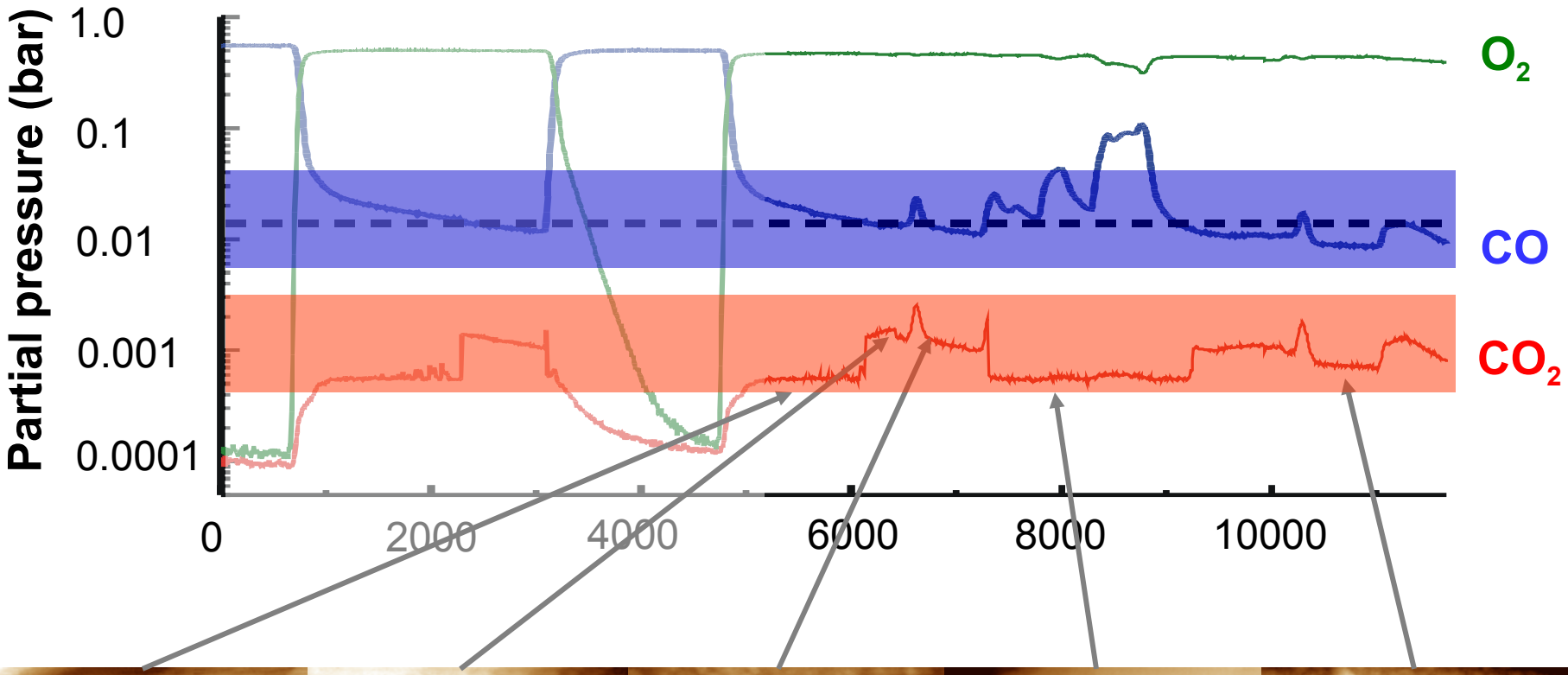


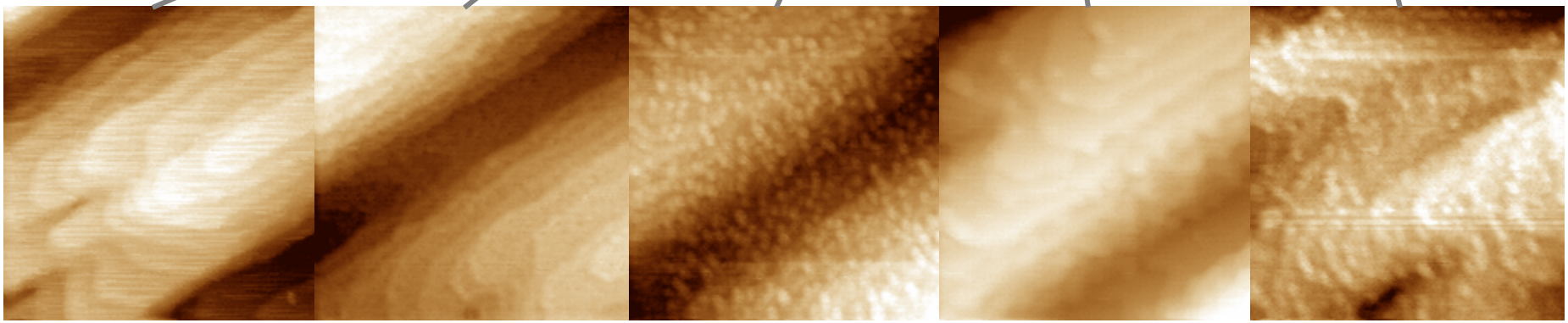




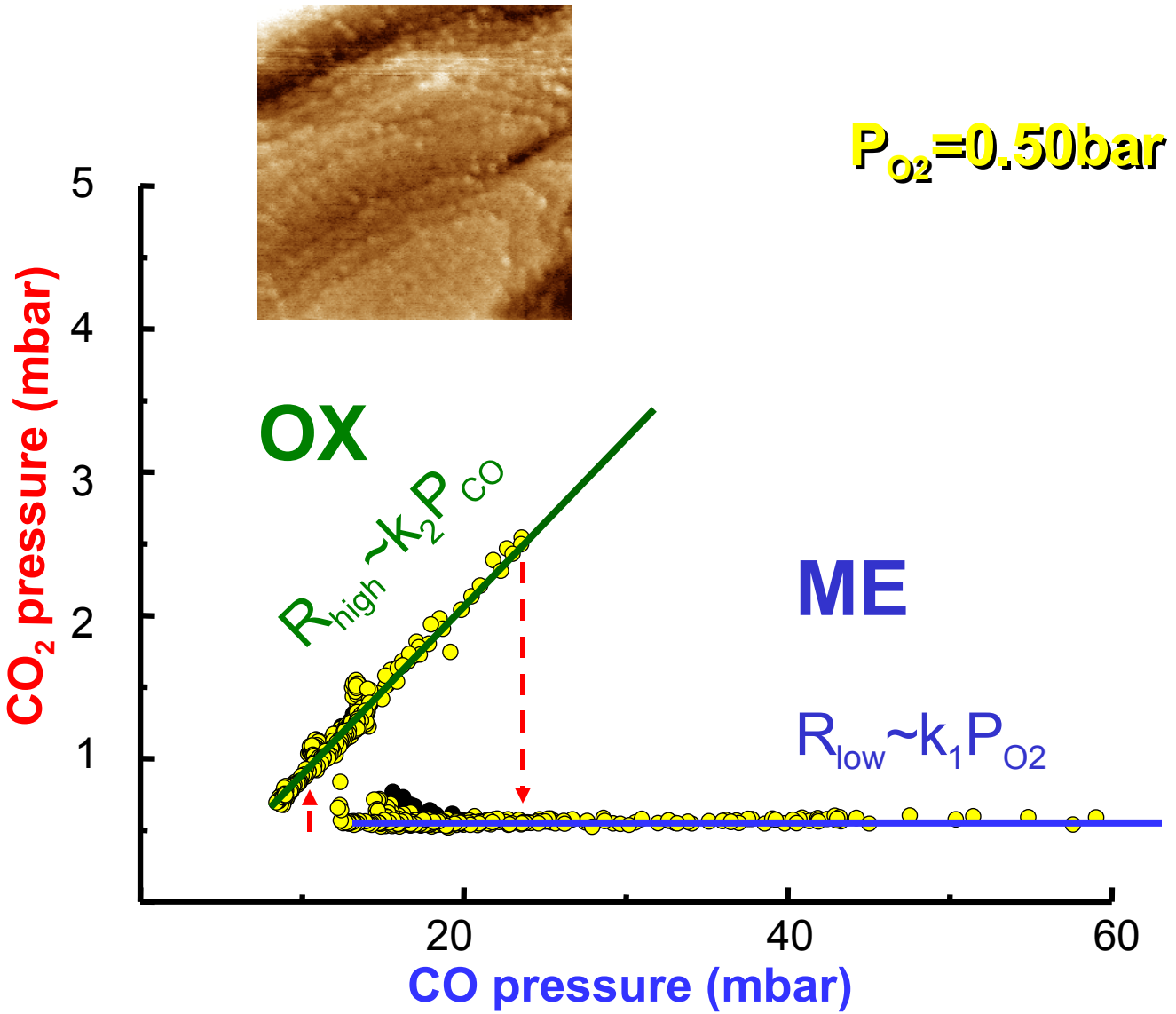


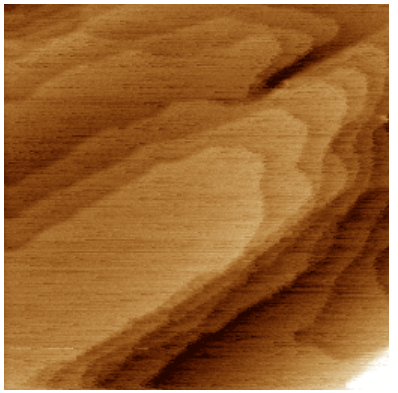
Platinum in flowing gas mixture: $CO + O_2$



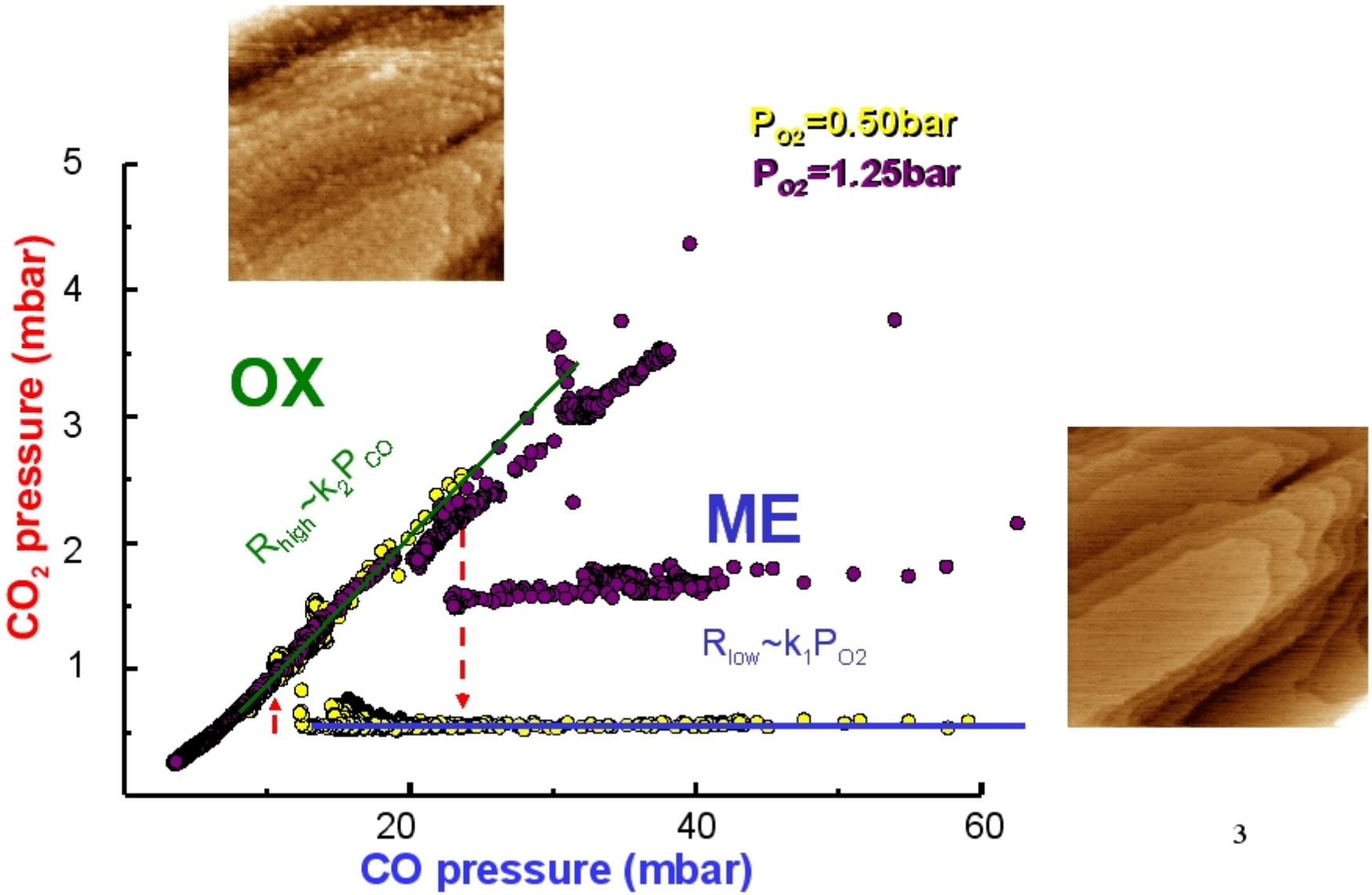


Quantitative relation between pressures

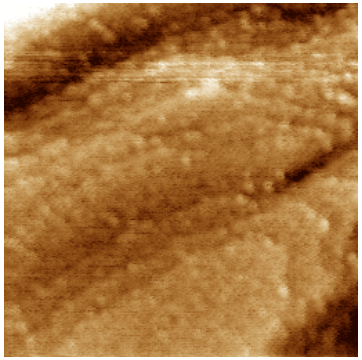


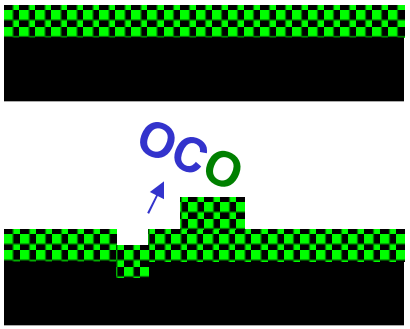


Quantitative relation between pressures

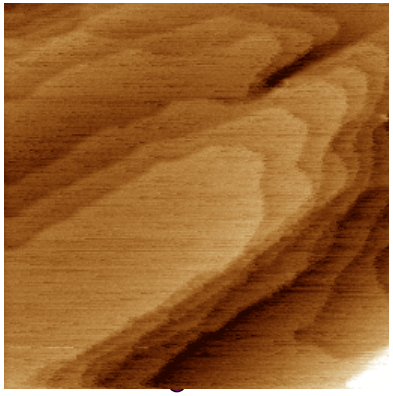


Quantitative relation between pressures





Two surfaces – two branches

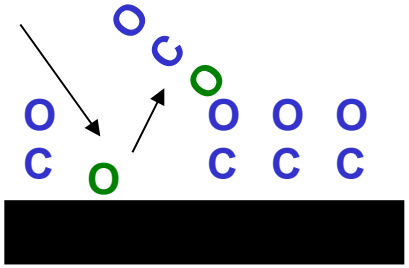


On both branches, CO_2 production depends

- … on the minority species
- … *not* on the roughness (structure)

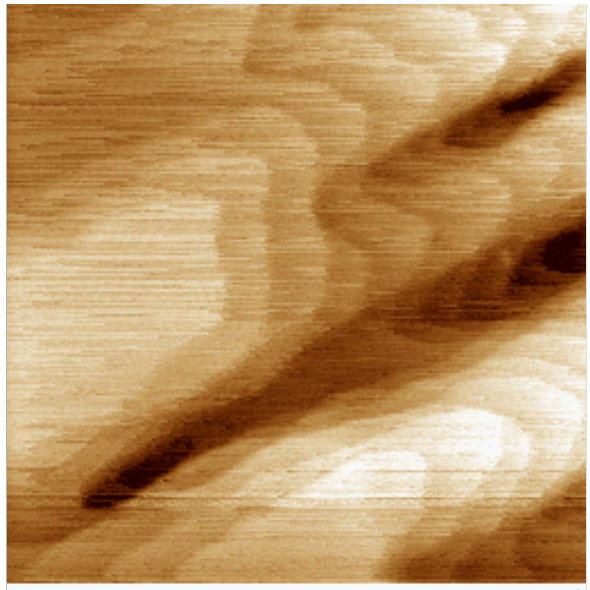
Switching also noticed on poly-Xtalline Pt, Ir, Pd

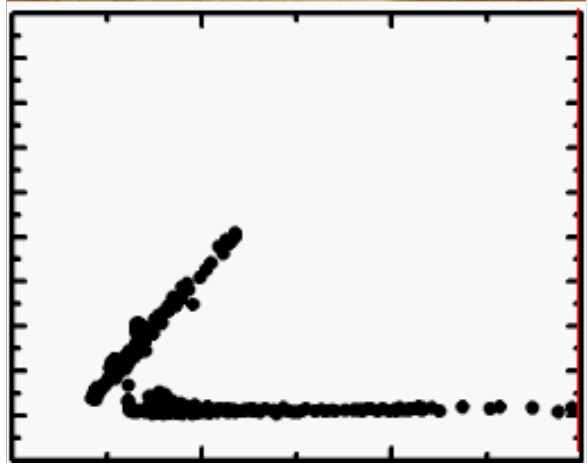
Turner et al., Surf.Sci. **109**, 310 (1981)

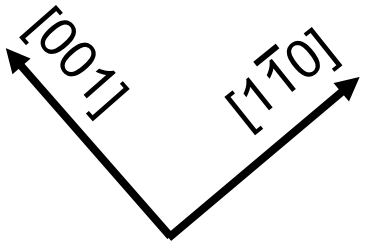


Platinum in flowing gas mixture: $CO + O_2$

P_{tot} = 0.5 bar
T = 425 K
t_{total} = 3h:12m

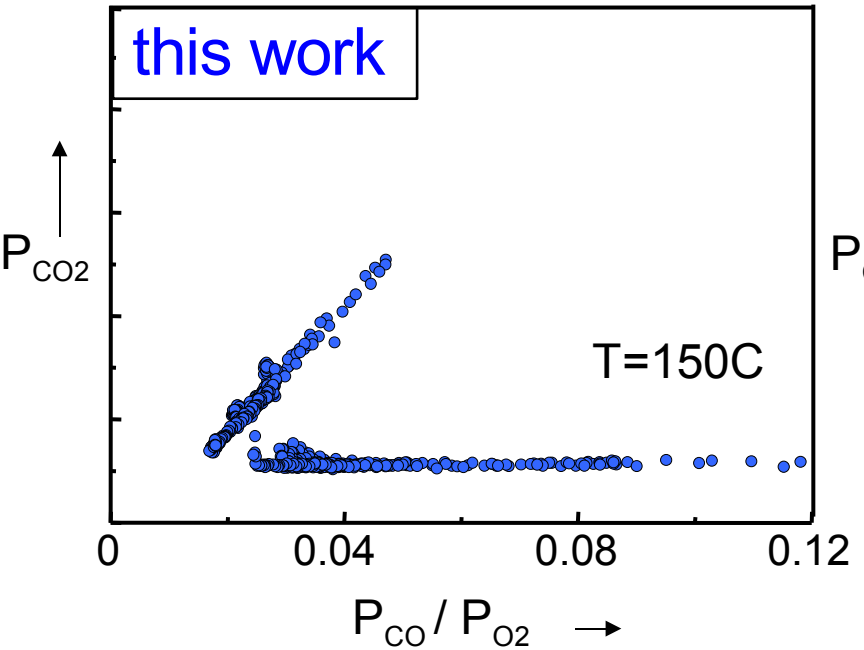




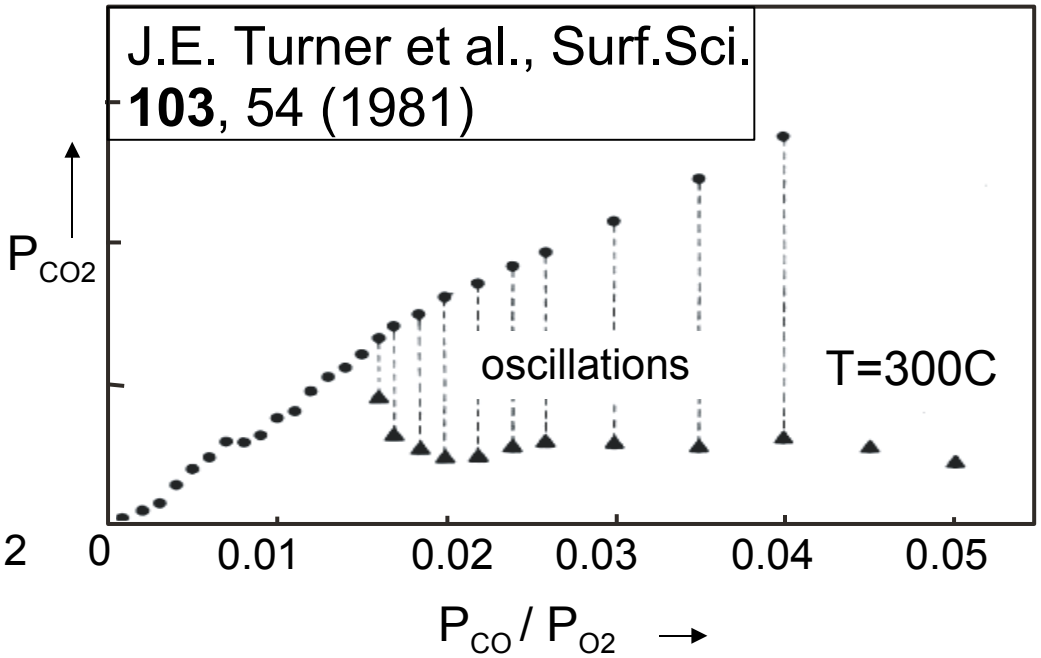


Comparison with 'real' catalysts…

Pt(110)

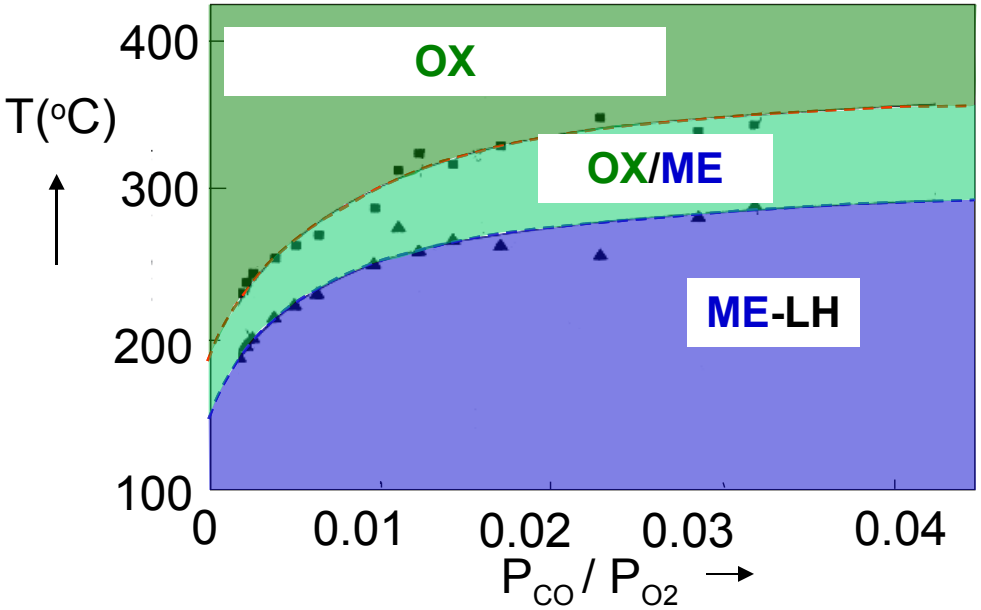


Polycrystalline Pt wires



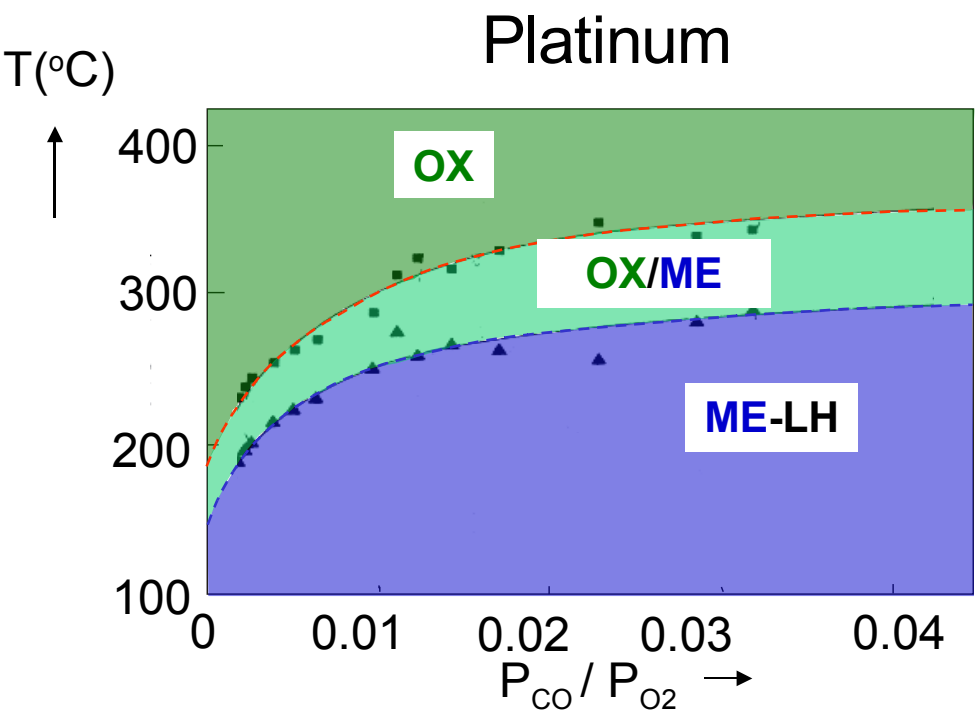
Turner et al. Surf. Sci. 103 (1981) 54, Surf. Sci. 109 (1981) 591

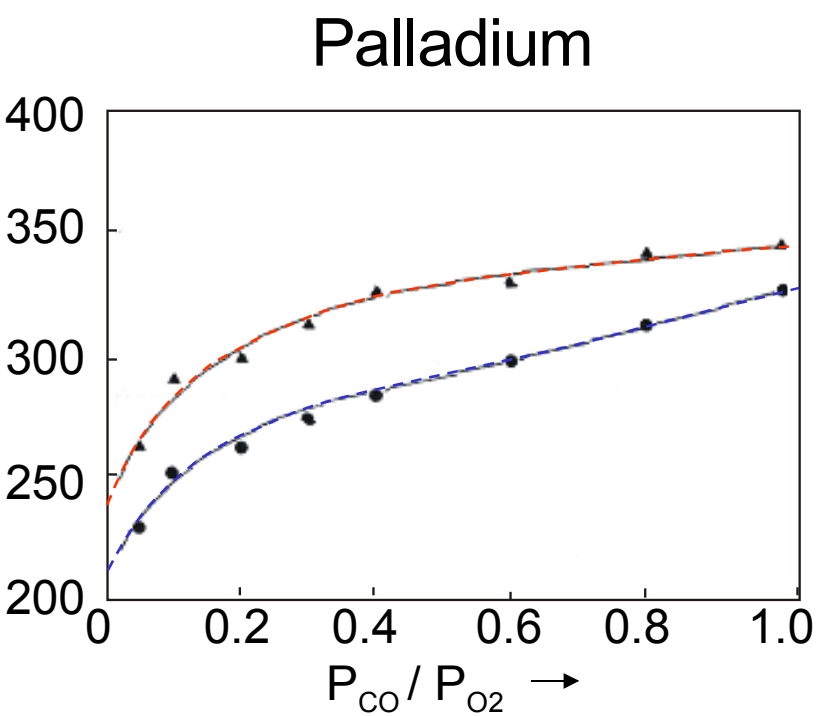
Comparison with 'real' catalysts…



J.E. Turner et al., Surf.Sci. **103**, 54 (1981)

Comparison with 'real' catalysts… Palladium



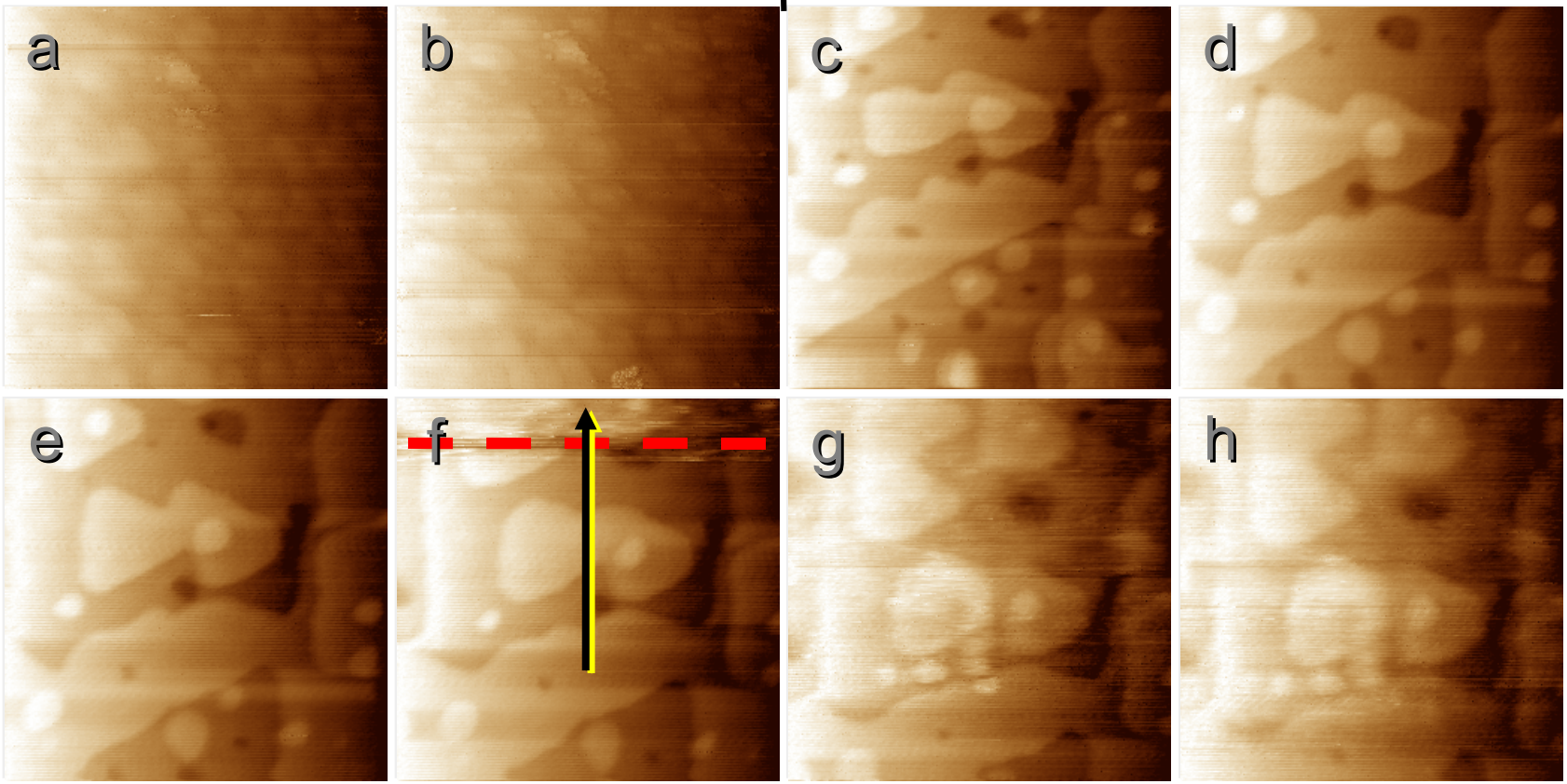


Turner et al. Surf. Sci. 103 (1981) 54, Surf. Sci. 109 (1981) 591

Pt(111) similar to Pt(110): ~~structural effects~~

P_{tot} = 1.25 bar T = 478 K

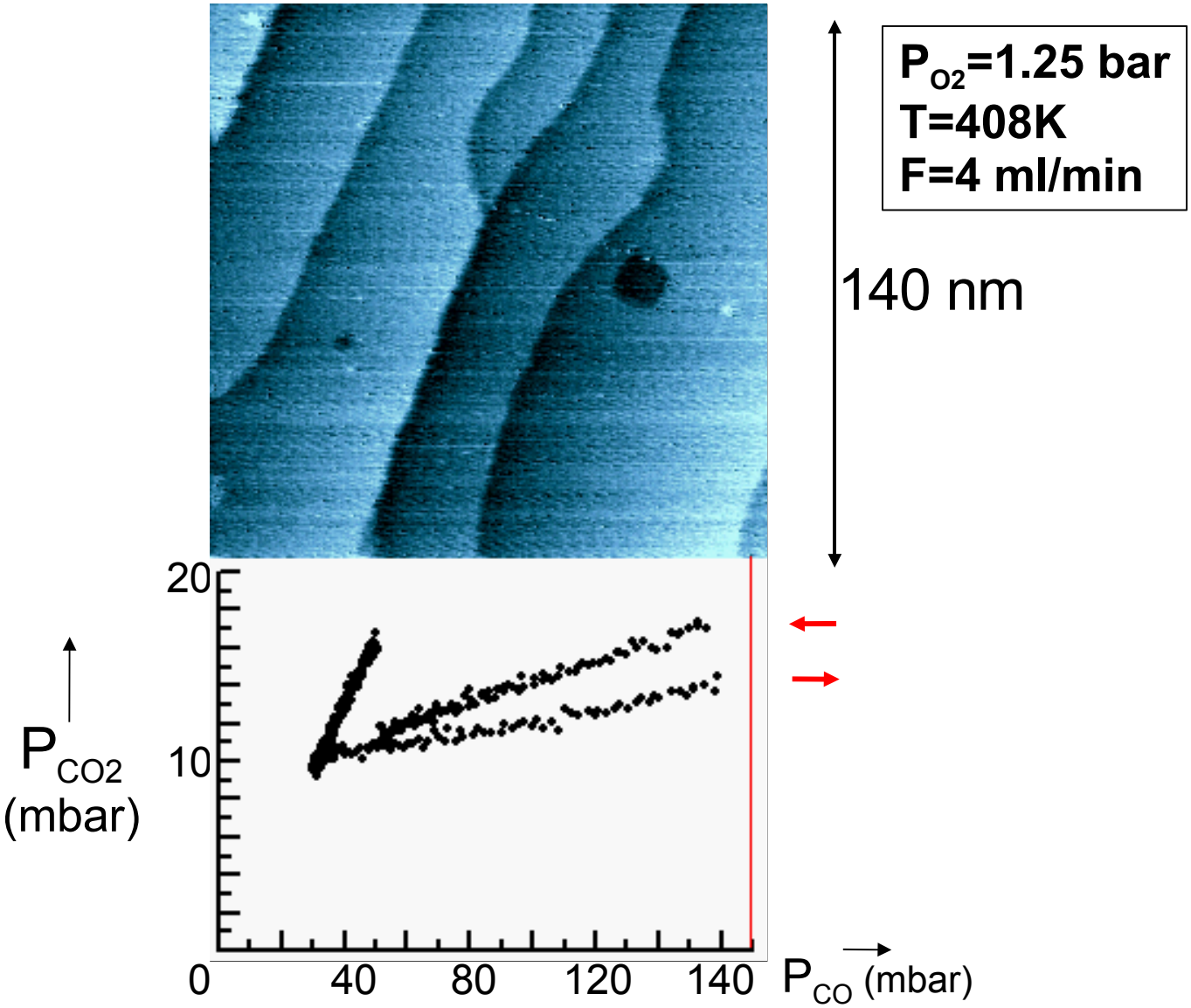
high reaction rate: oxide ← $P_{CO} < P_{th}$ | $P_{CO} > P_{th}$ → low reaction rate: metal



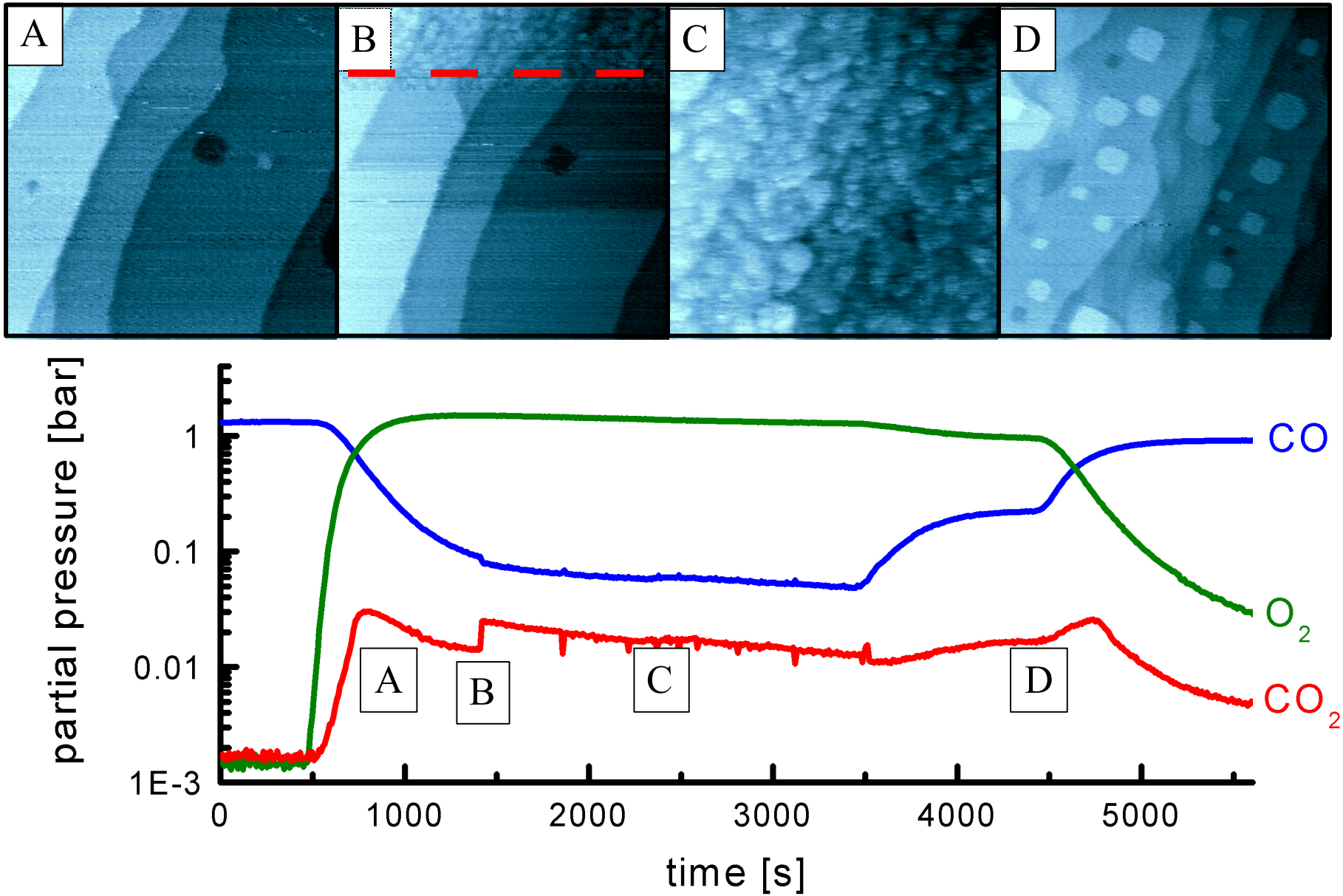
← 140 nm →

$P_{CO} < P_{th}$ → high reaction rate: oxide

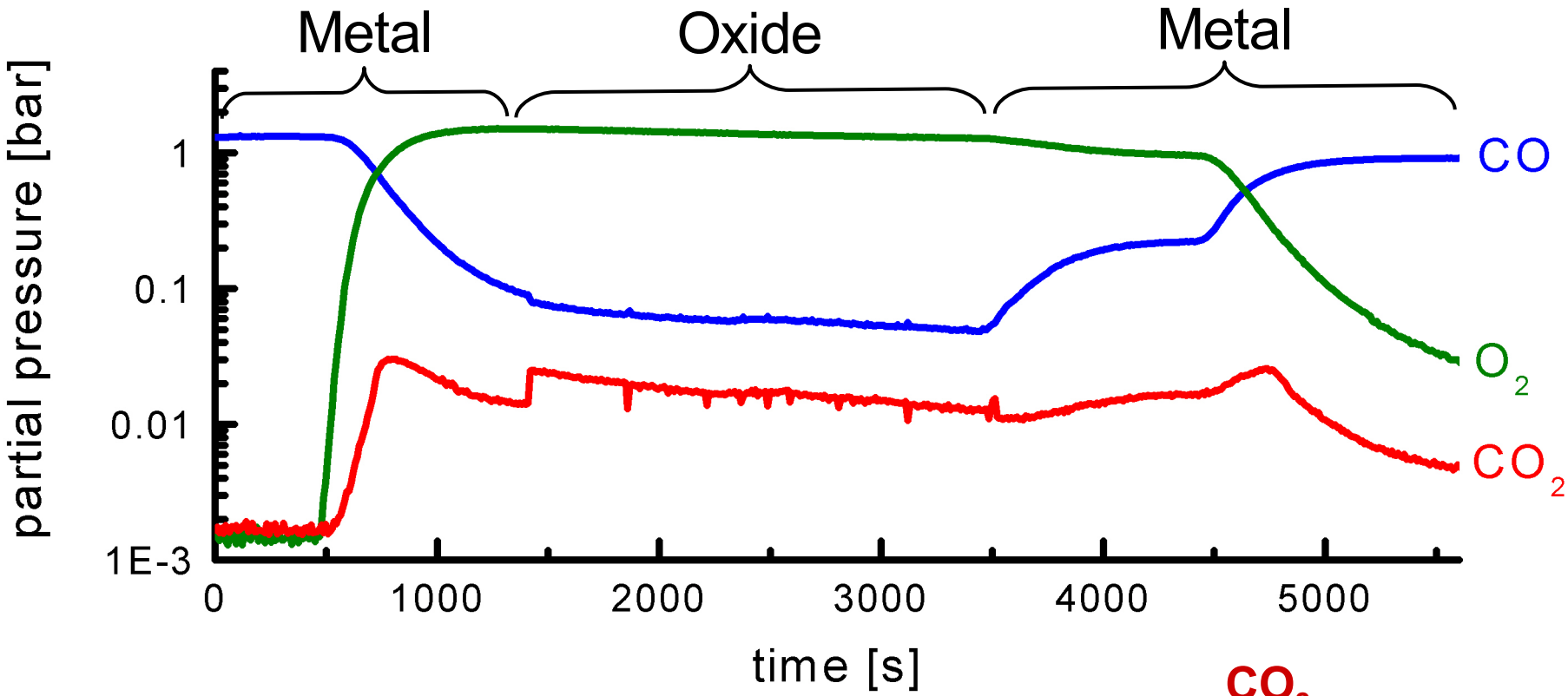
Pd(001): similar to Pt surfaces



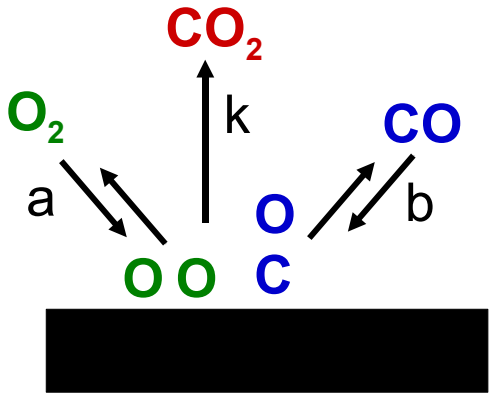
Pd(001) at 1.25 bar and 408K



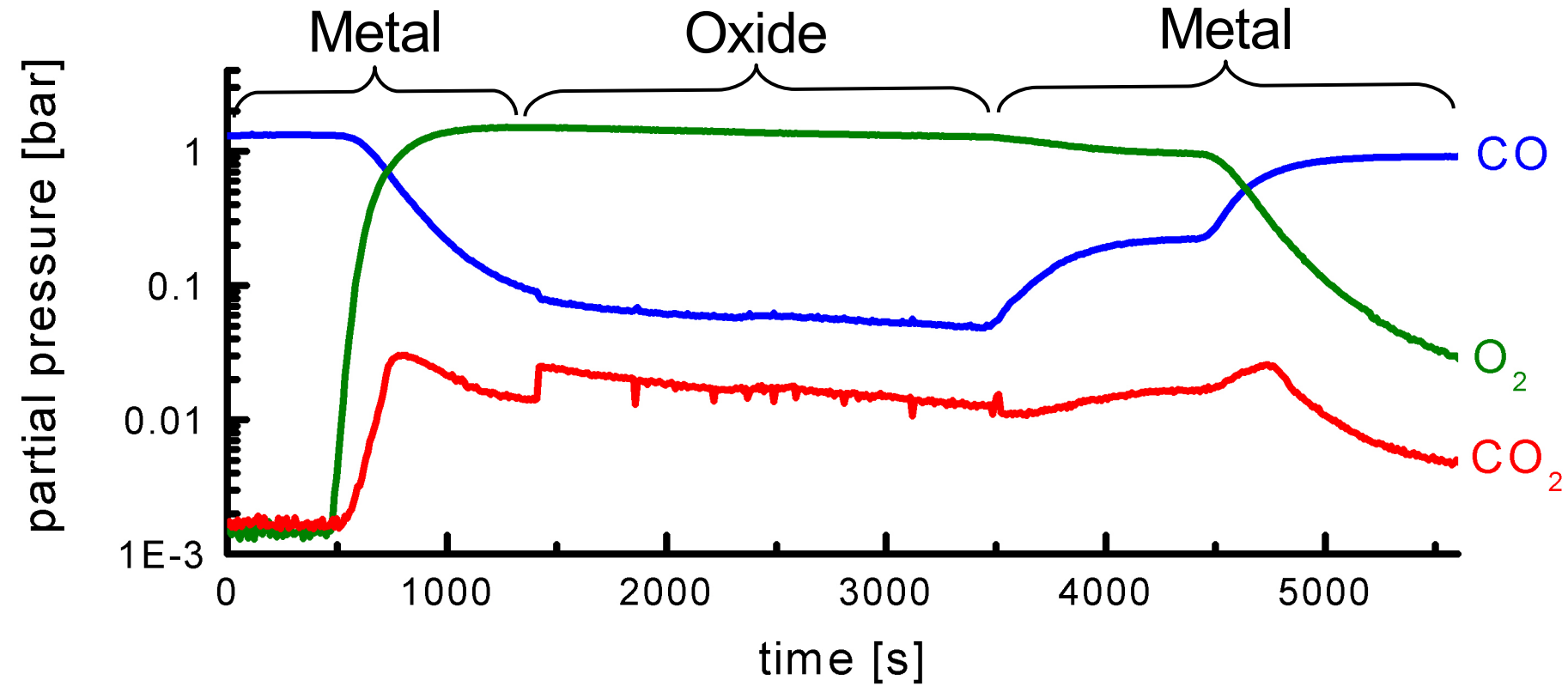
Langmuir-Hinshelwood kinetics

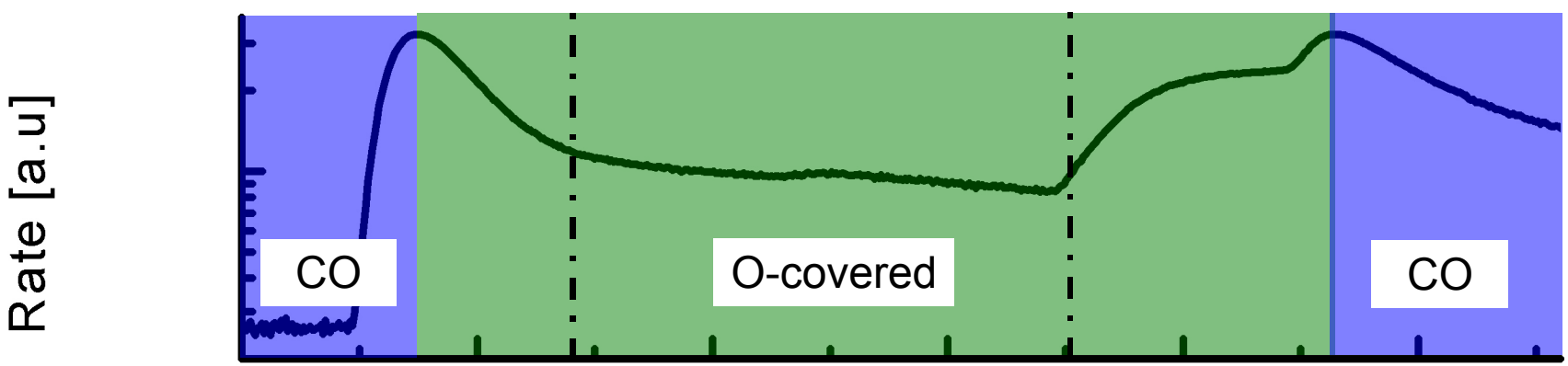


$$R_{LH} = k \cdot \theta_O \theta_{CO} = k \cdot \frac{a\sqrt{P_{O_2}}\, bP_{CO}}{\left(a\sqrt{P_{O_2}} + bP_{CO} + 1\right)^2}$$

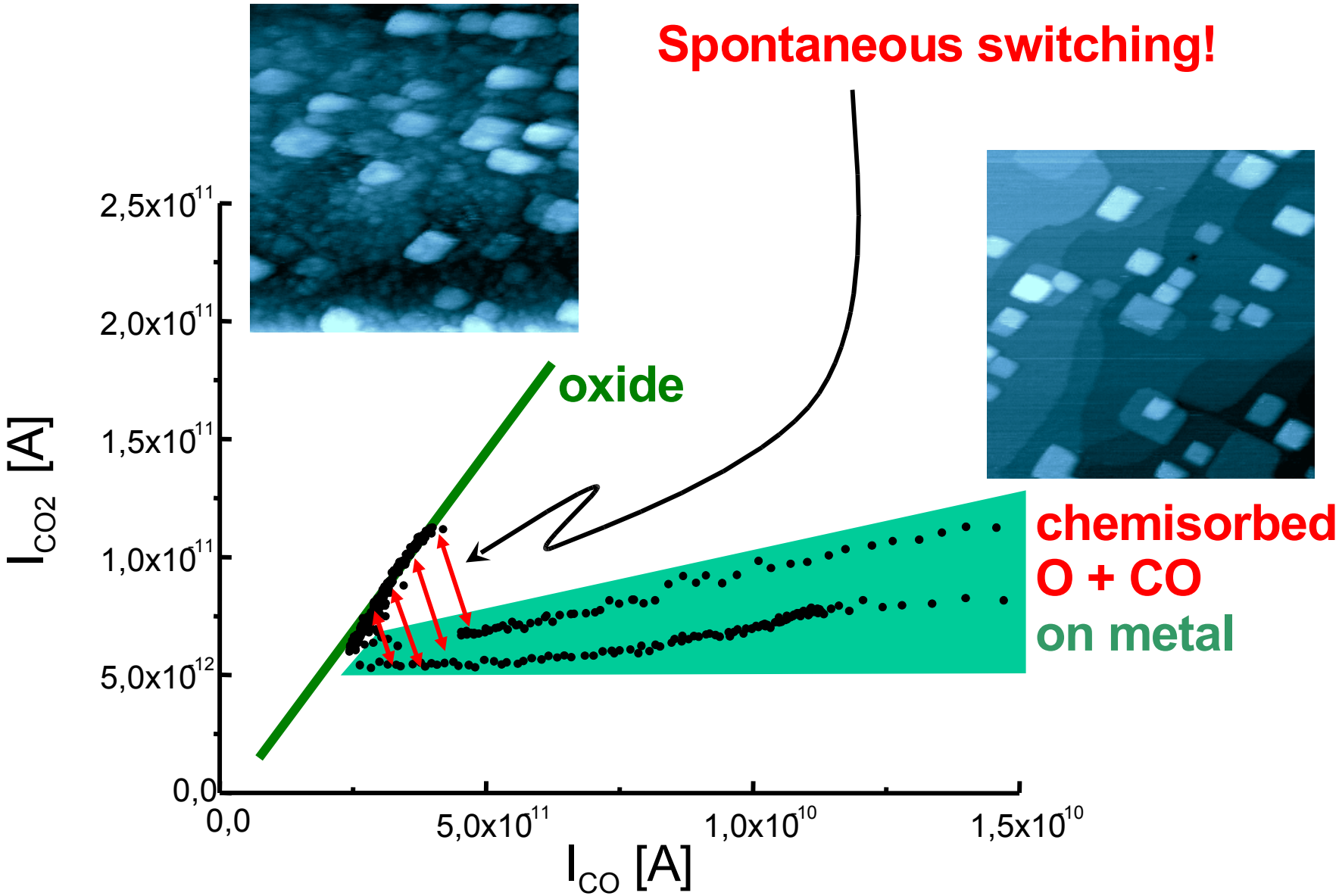


Langmuir-Hinshelwood kinetics

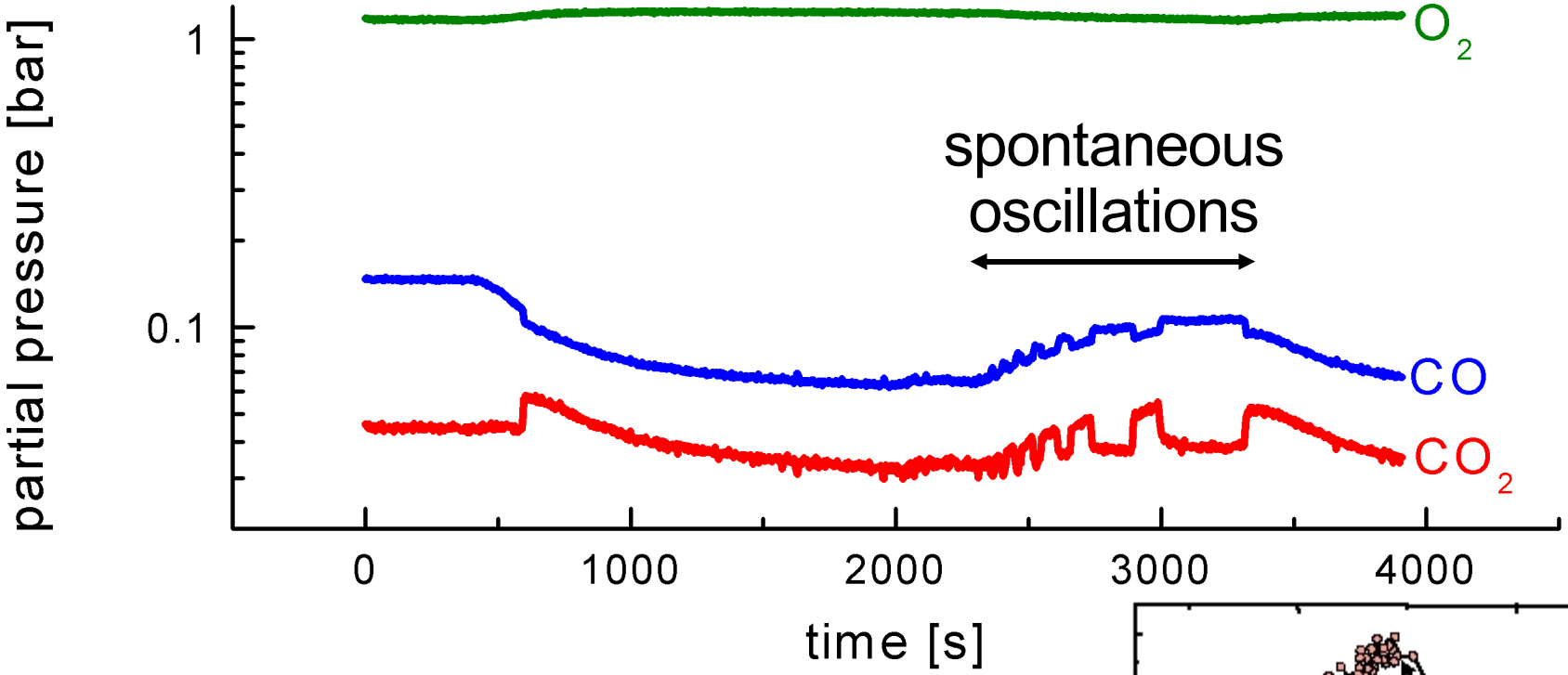


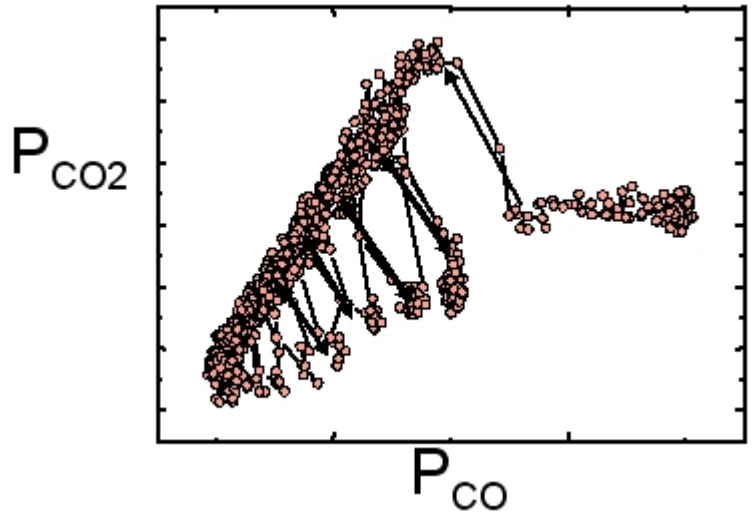


Bistability on Pd(001)

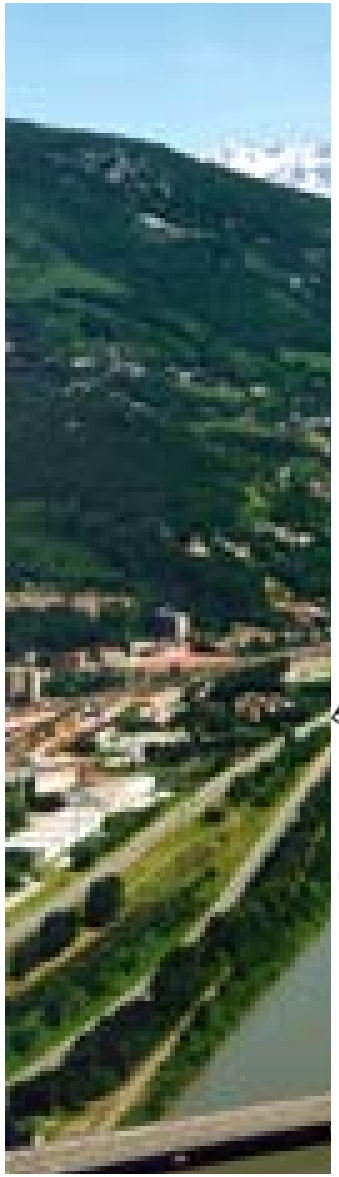


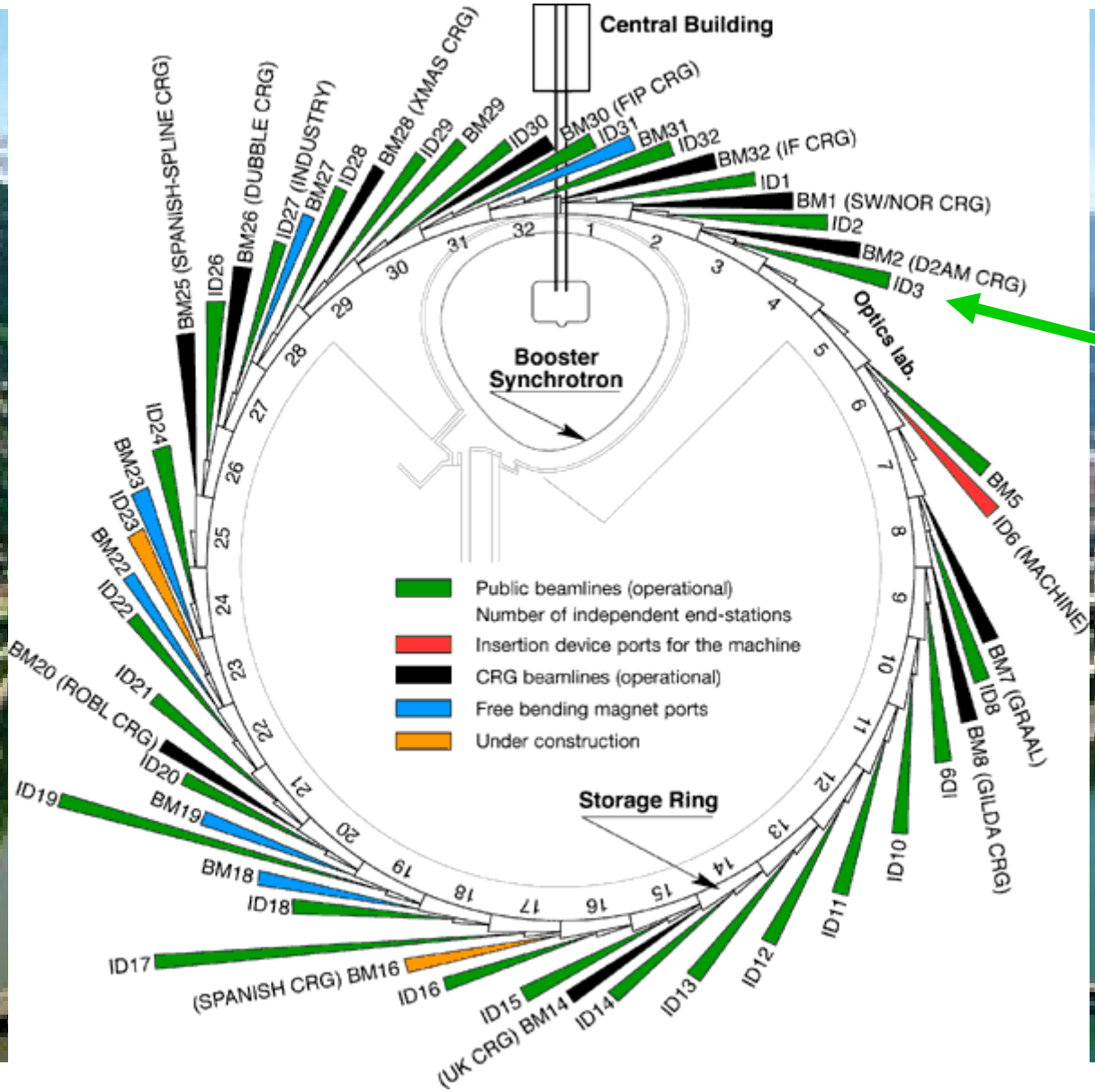
Bistability on Pd(001): Oscillations!

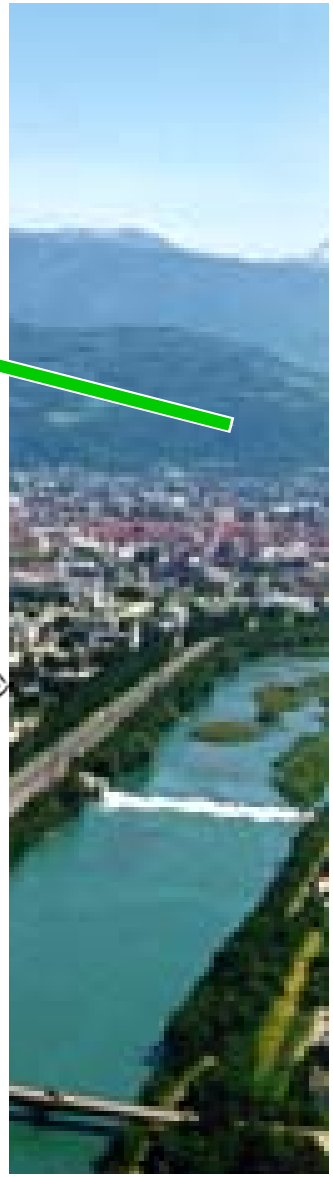




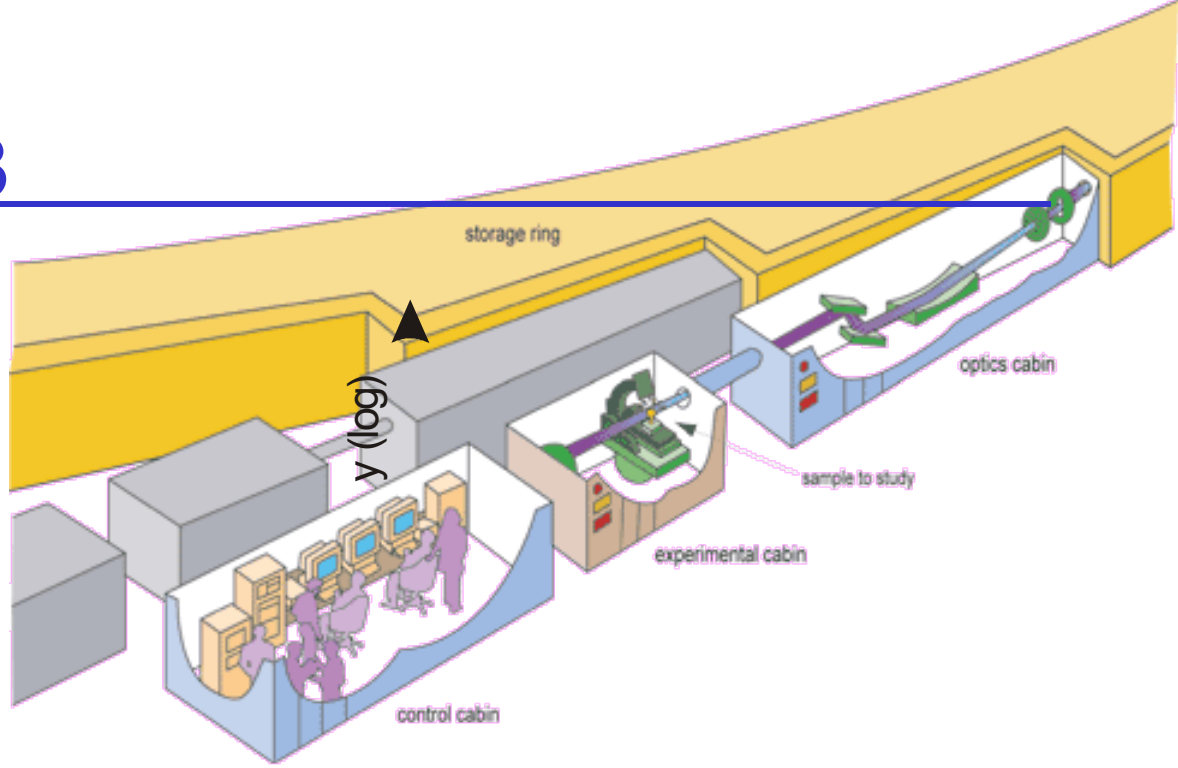
High-P Surface X-Ray Diffraction

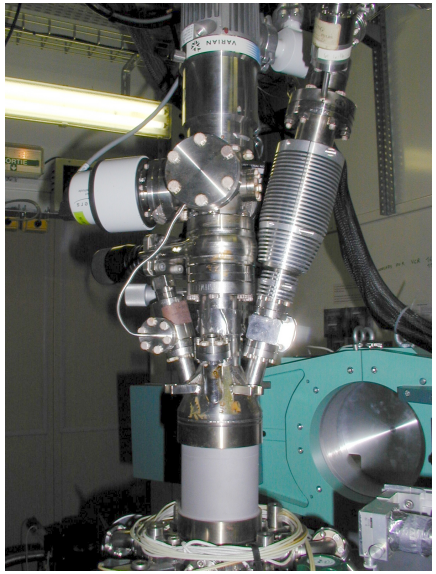


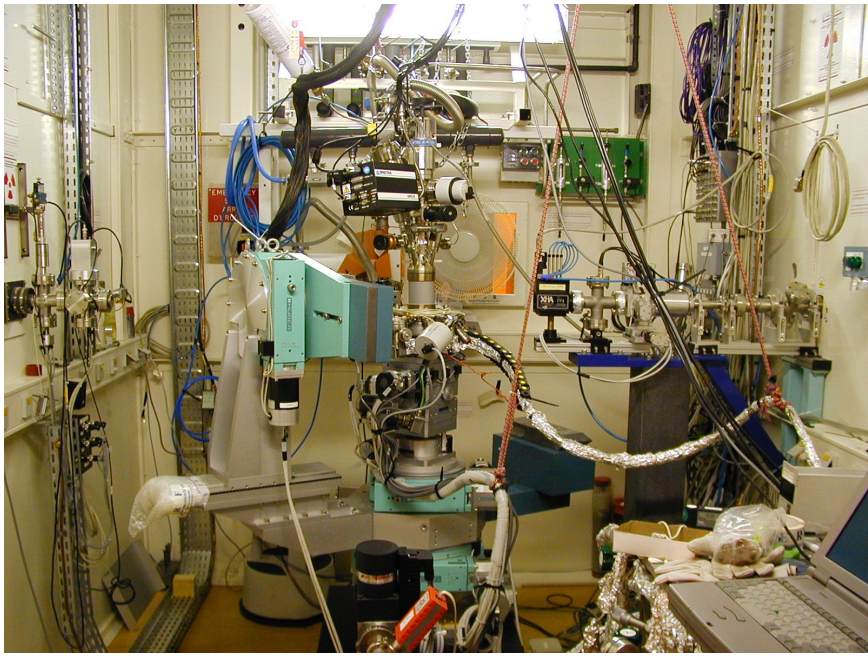




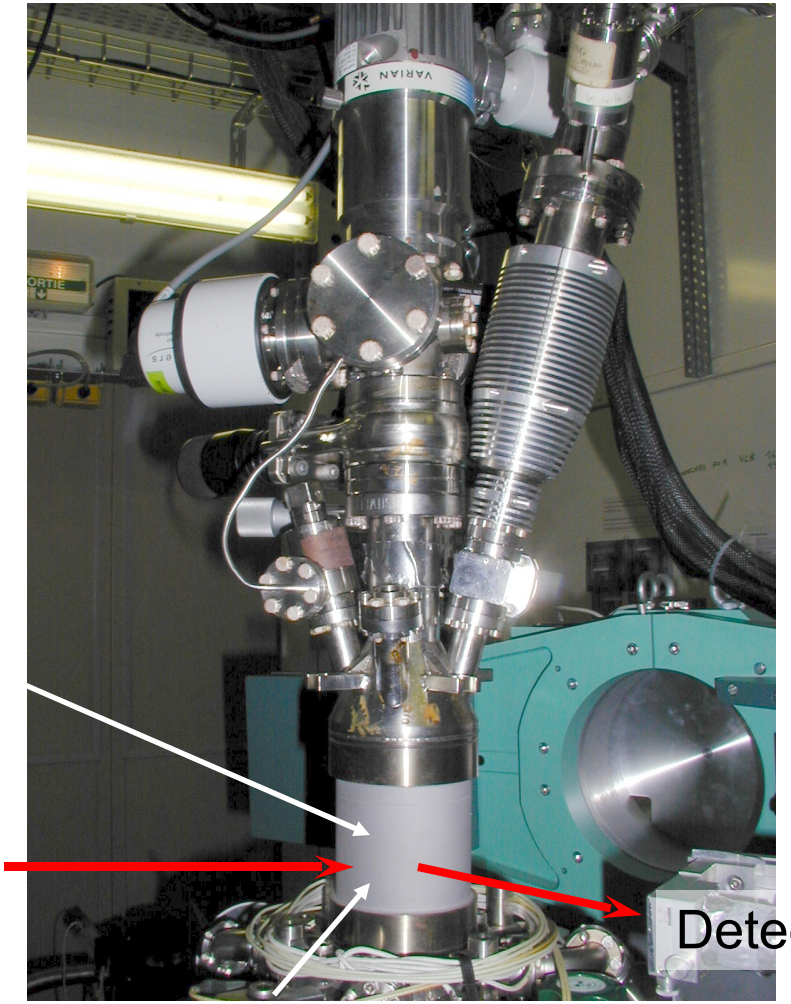
Beamline ID03







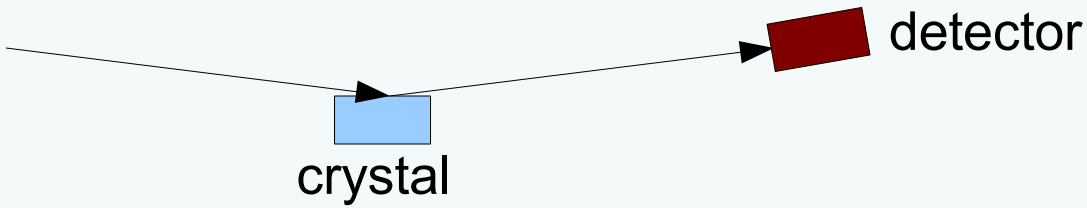
High-P Surface X-Ray Diffraction



ID03 Beamline:

- Base pressure 10^{-9} mbar
- Max pressure 2 bar
- 300 < T < 1200 K
- Reactor volume ~ 1 L
- On-line QMS

Diffraction and reciprocal lattice



Constructive interference of the x-ray wave with the atomic lattice of the crystal.

$$\boldsymbol{q} = \boldsymbol{k}' - \boldsymbol{k} \qquad \boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3$$

$$I \propto \left| F(\boldsymbol{q}) \sum_{n_1=-\infty}^{\infty} \sum_{n_2=-\infty}^{\infty} \sum_{n_3=-\infty}^{\infty} e^{i\boldsymbol{q}\cdot(n_1\boldsymbol{a}_1 + n_2\boldsymbol{a}_2 + n_3\boldsymbol{a}_3)} \right|^2$$

Laue condition for diffraction

$$I \neq 0 \text{ if } \quad \begin{aligned} \boldsymbol{q}\cdot\boldsymbol{a}_1 &= 2\pi h \\ \boldsymbol{q}\cdot\boldsymbol{a}_2 &= 2\pi k \\ \boldsymbol{q}\cdot\boldsymbol{a}_3 &= 2\pi l \end{aligned}$$

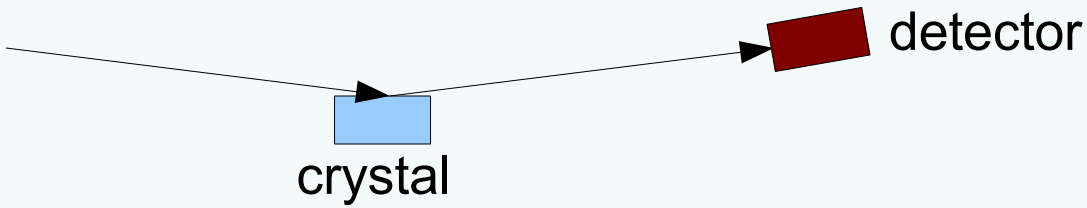
Reciprocal lattice vectors

$$\boldsymbol{q} = g_{hkl} = h\boldsymbol{b}_1 + k\boldsymbol{b}_2 + l\boldsymbol{b}_3$$

with $\boldsymbol{b}_i \cdot \boldsymbol{a}_j = 2\pi\delta_{ij}$

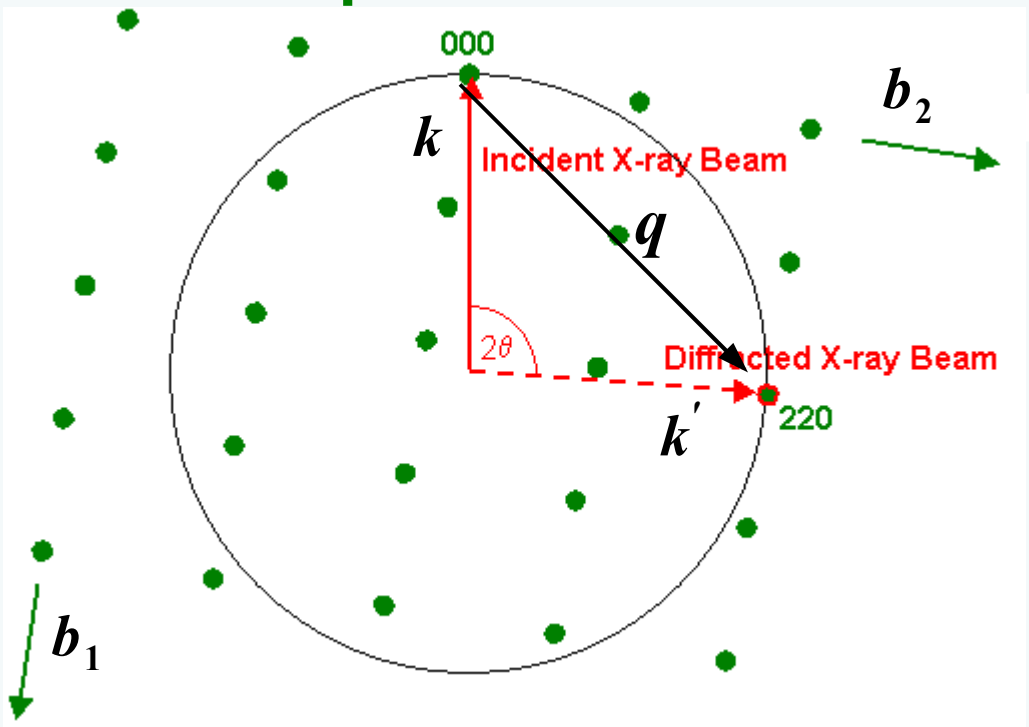
$$\boldsymbol{b}_1 = 2\pi \frac{\boldsymbol{a}_2 \times \boldsymbol{a}_3}{\boldsymbol{a}_1 \cdot \boldsymbol{a}_2 \times \boldsymbol{a}_3}$$

Diffraction and reciprocal lattice



Constructive interference of the x-ray wave with the atomic lattice of the crystal.

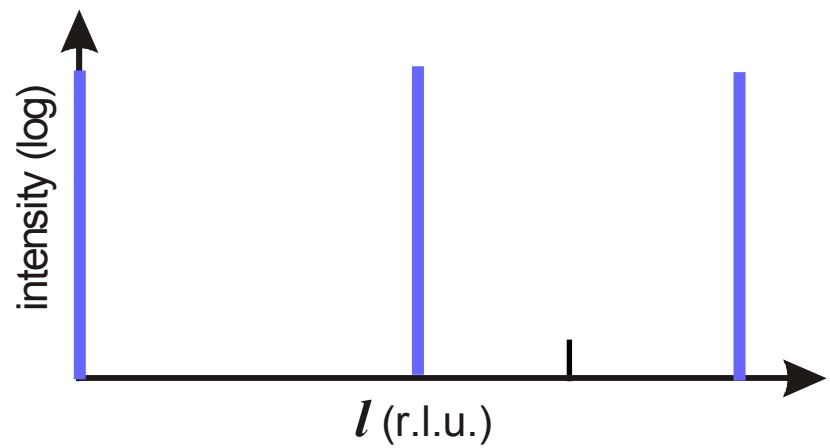
Ewald sphere construction

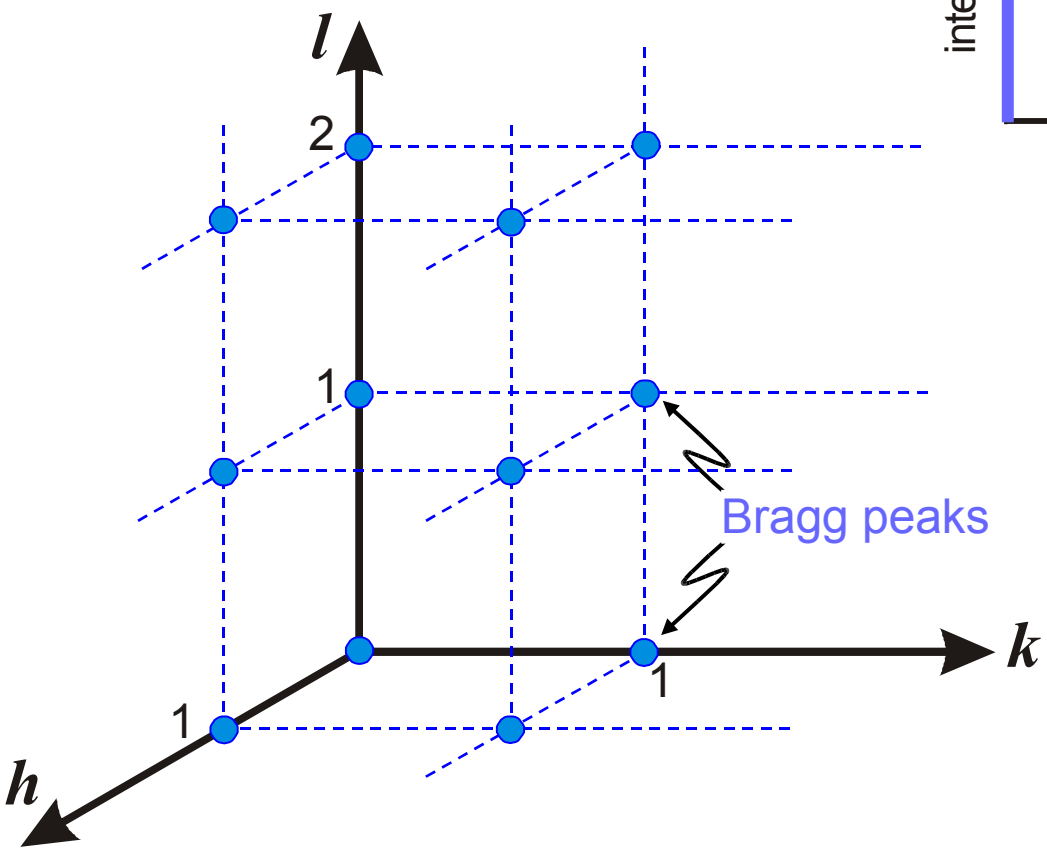


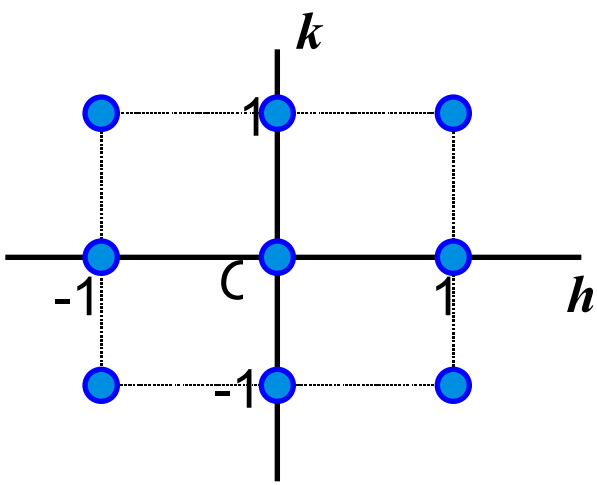
$$q = k' - k = h\,b_1 + k\,b_2 + l\,b_3$$

Reciprocal lattice

$$I \propto \left| F(\boldsymbol{q}) \sum_{n_1=-\infty}^{\infty} \sum_{n_2=-\infty}^{\infty} \sum_{n_3=-\infty}^{\infty} e^{i\boldsymbol{q}\cdot(n_1\boldsymbol{a}_1+n_2\boldsymbol{a}_2+n_3\boldsymbol{a}_3)} \right|^2$$

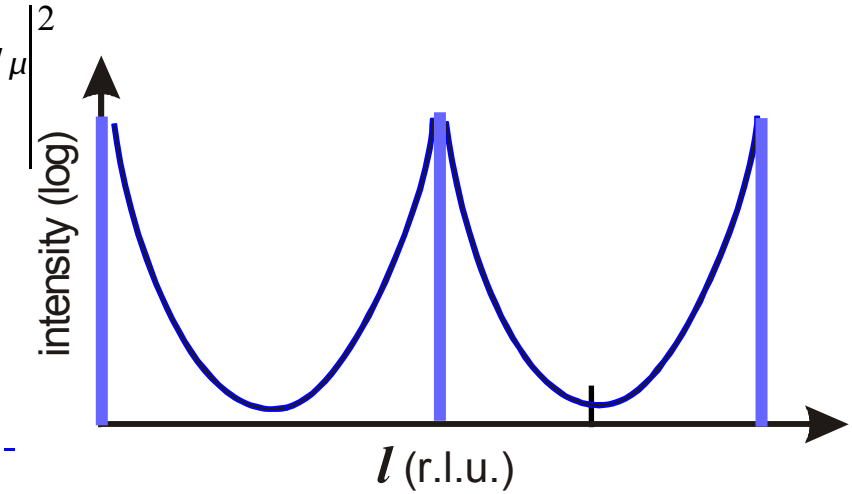


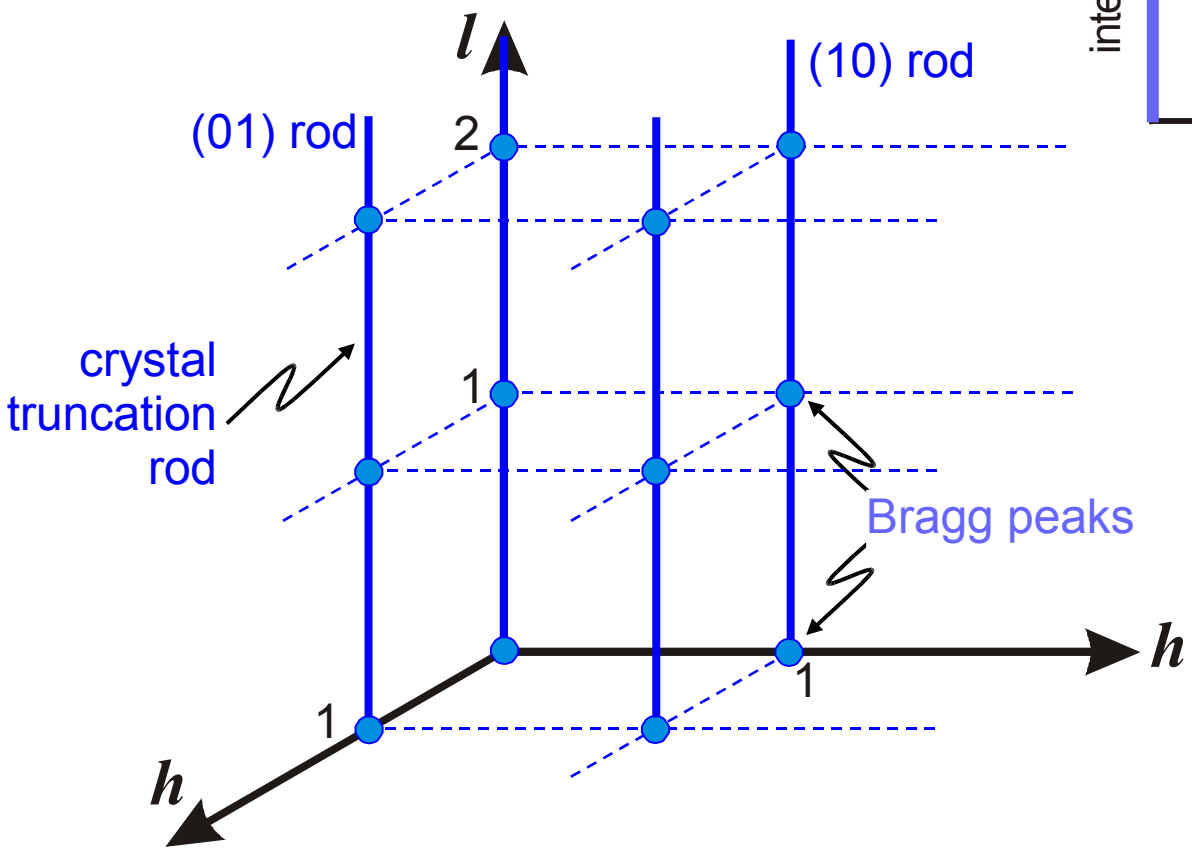


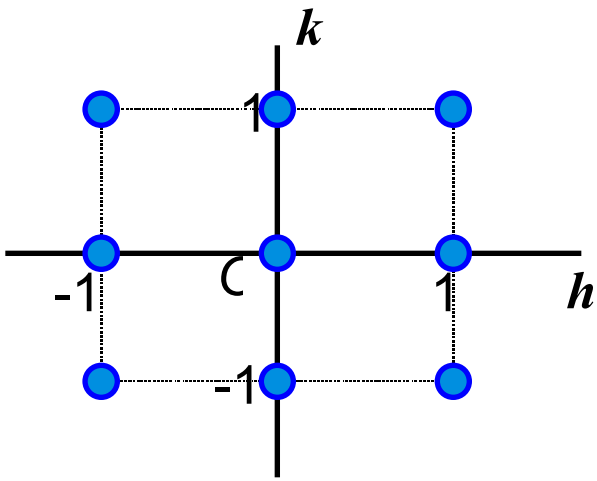


Crystal truncation rods

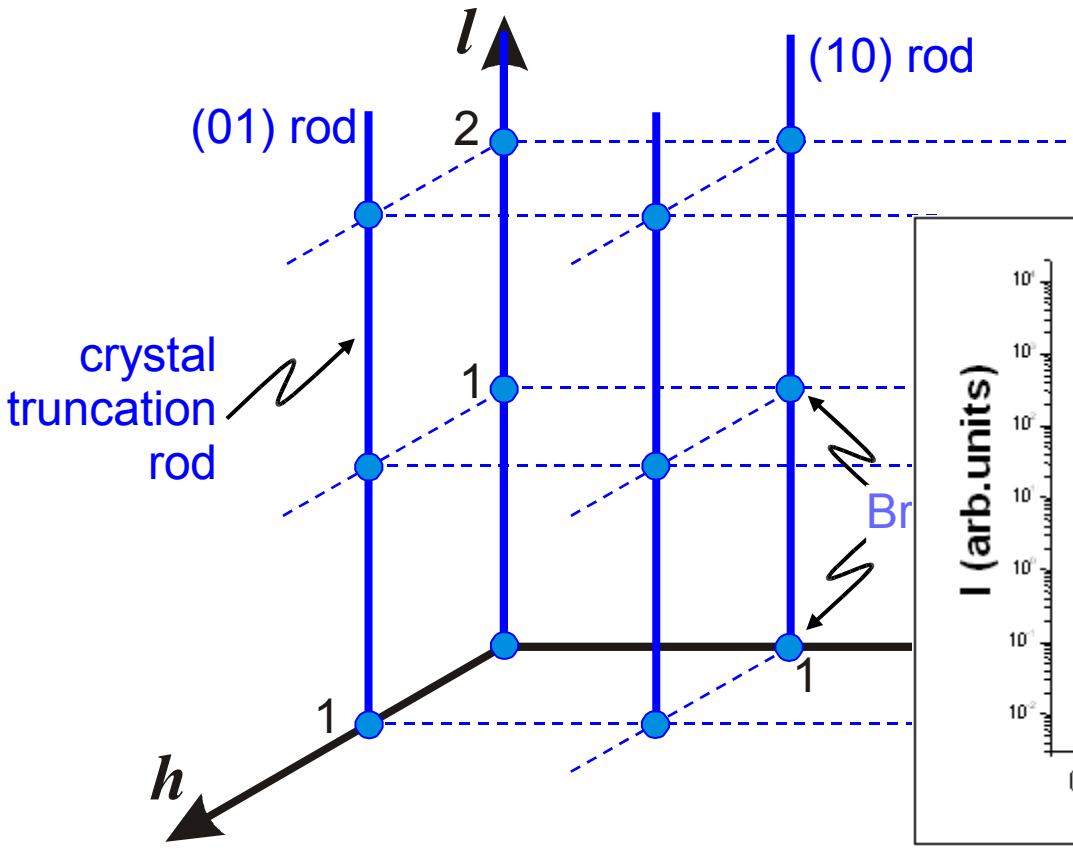
$$I \propto \left| F(\boldsymbol{q}) \sum_{n_1=-\infty}^{\infty} \sum_{n_2=-\infty}^{\infty} \sum_{n_3=-\infty}^{0} e^{i\boldsymbol{q}\cdot(n_1\boldsymbol{a}_1+n_2\boldsymbol{a}_2+n_3\boldsymbol{a}_3)} e^{\boldsymbol{a}_3/\mu} \right|^2$$

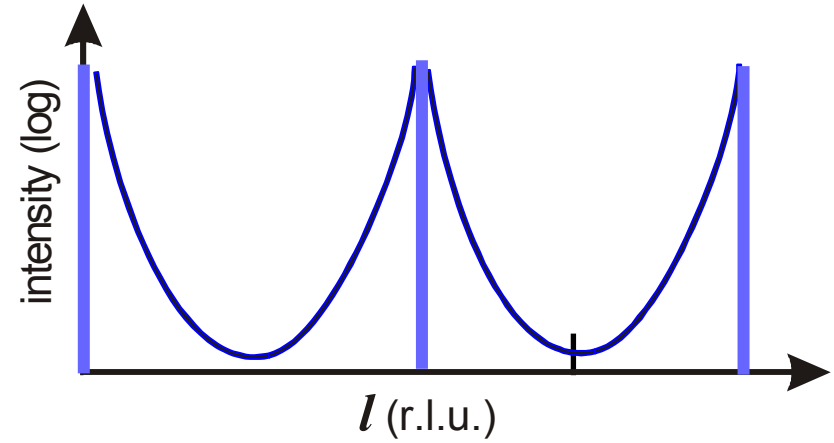


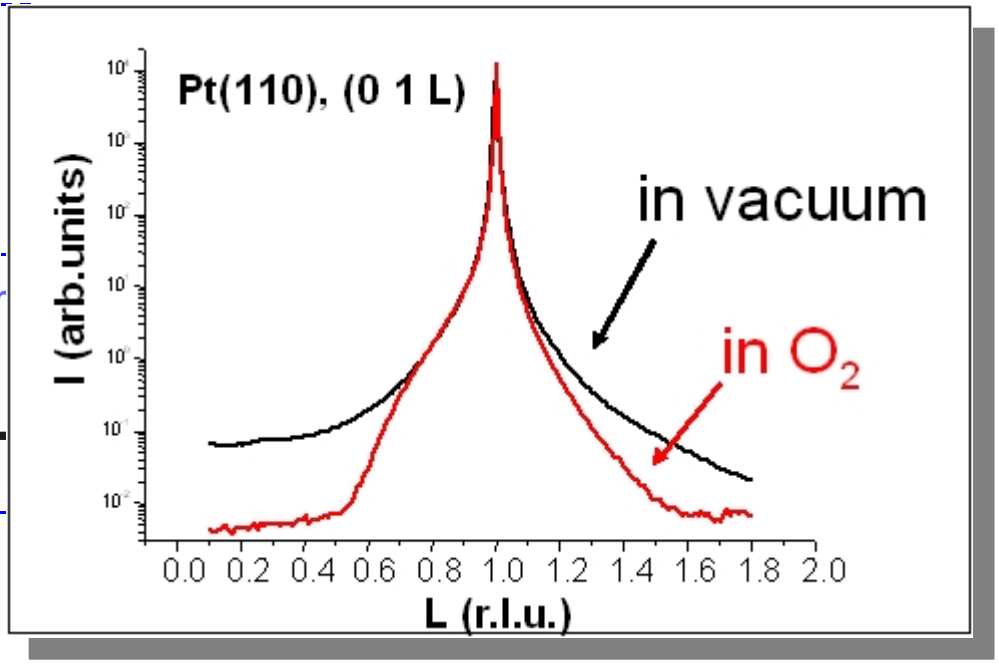




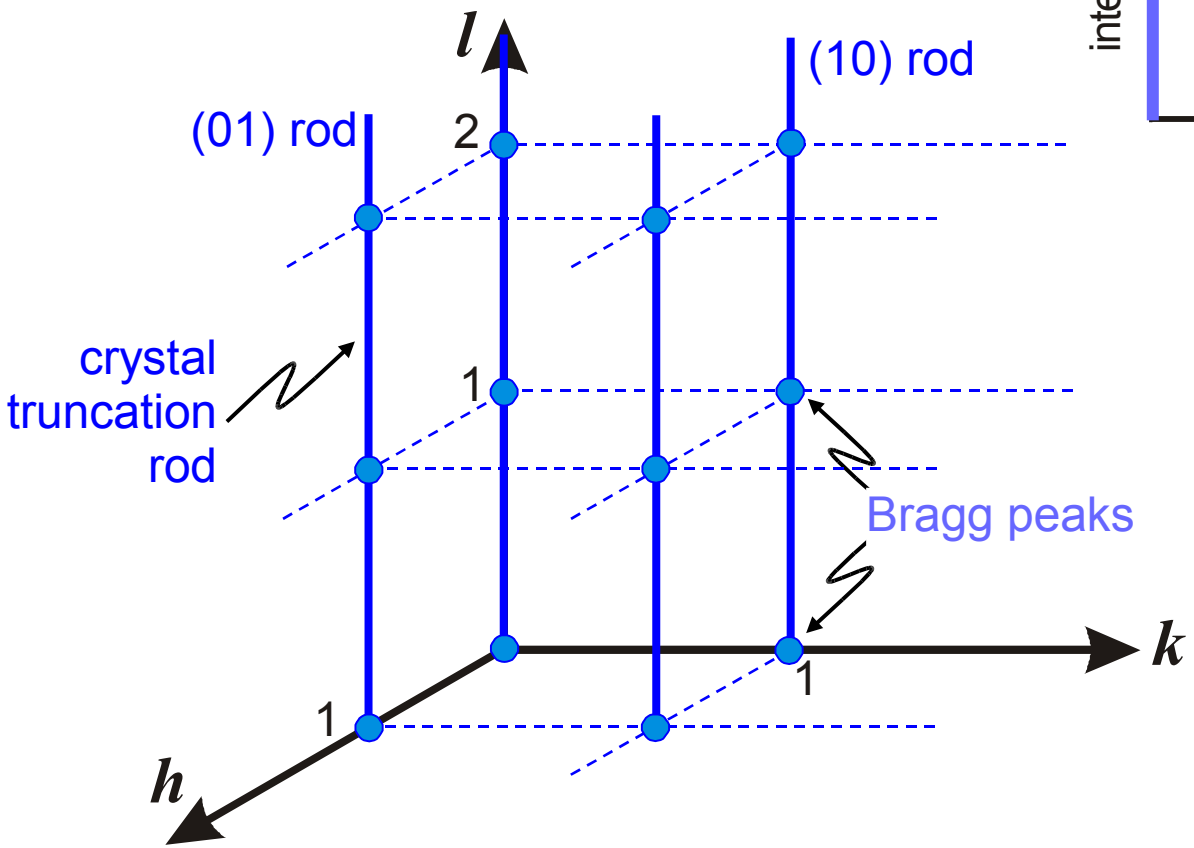
Crystal truncation rods

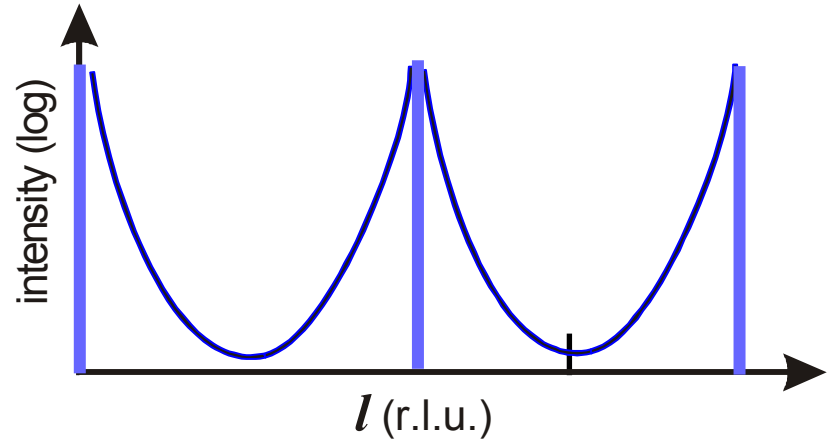


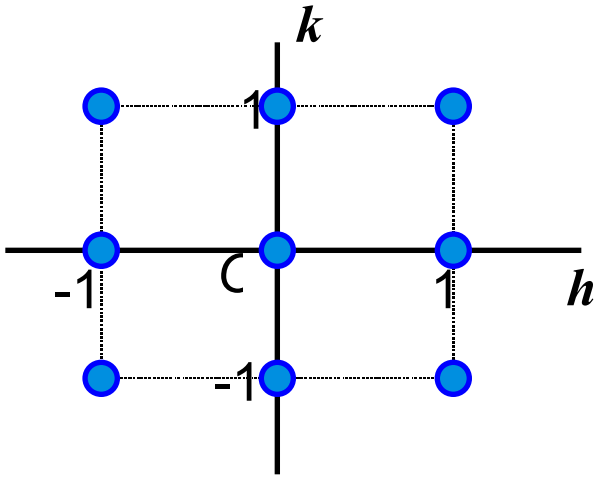




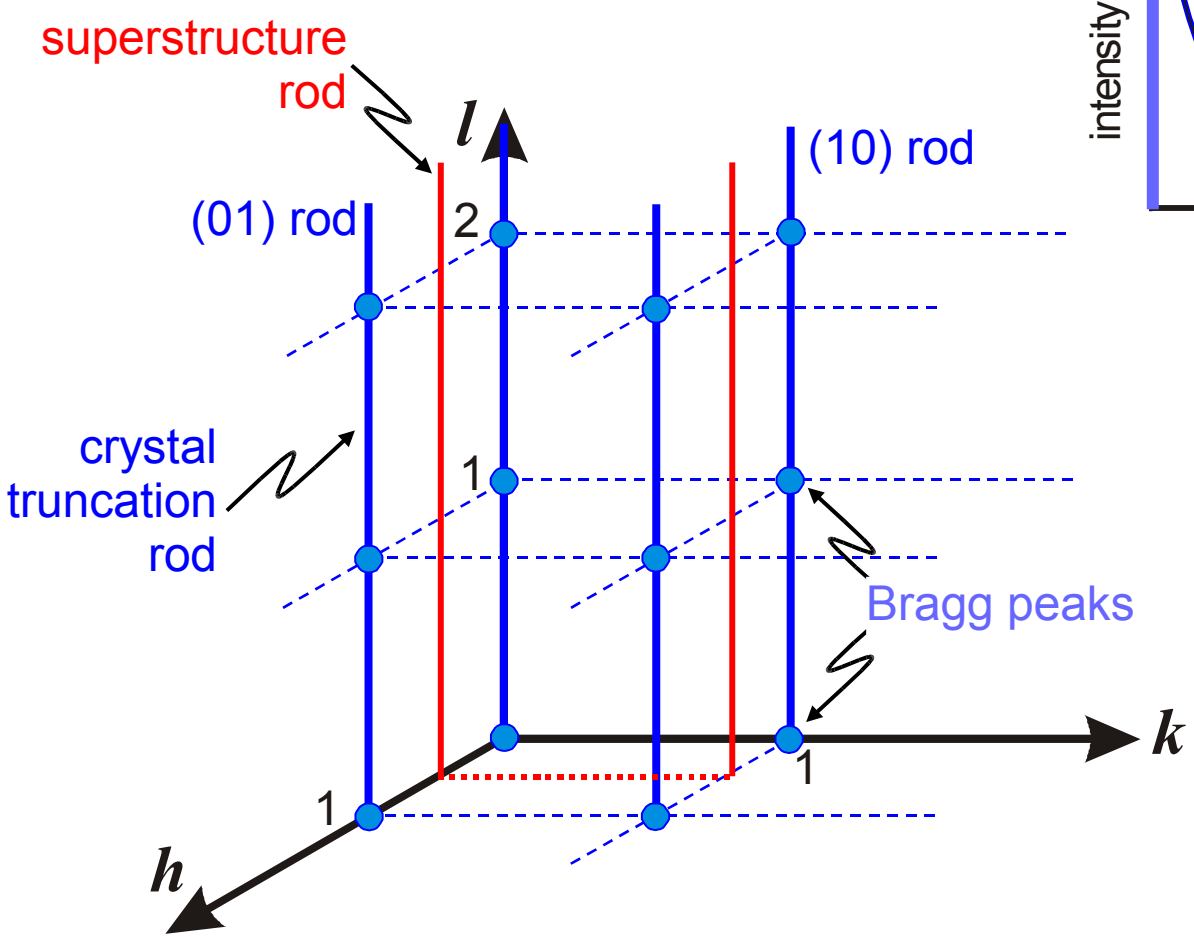
Crystal truncation rods

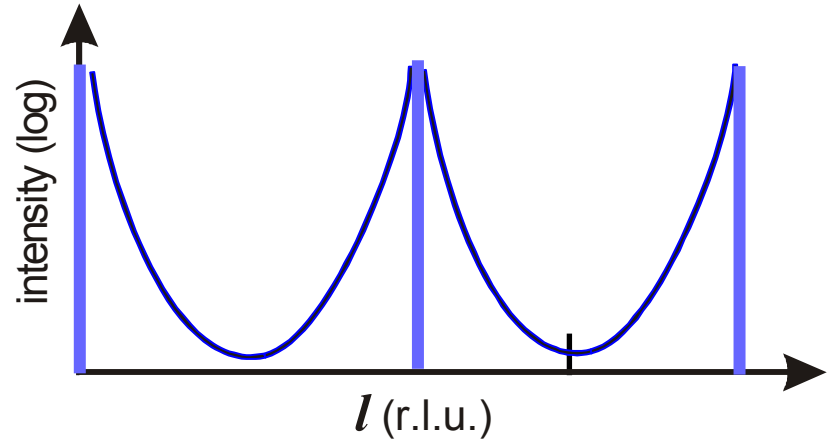


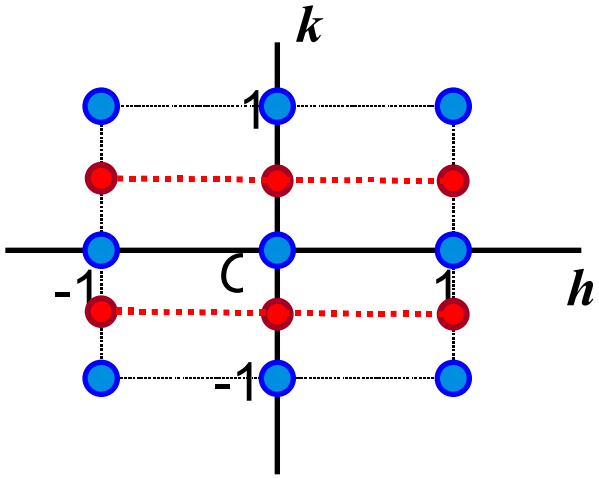




Crystal truncation rods

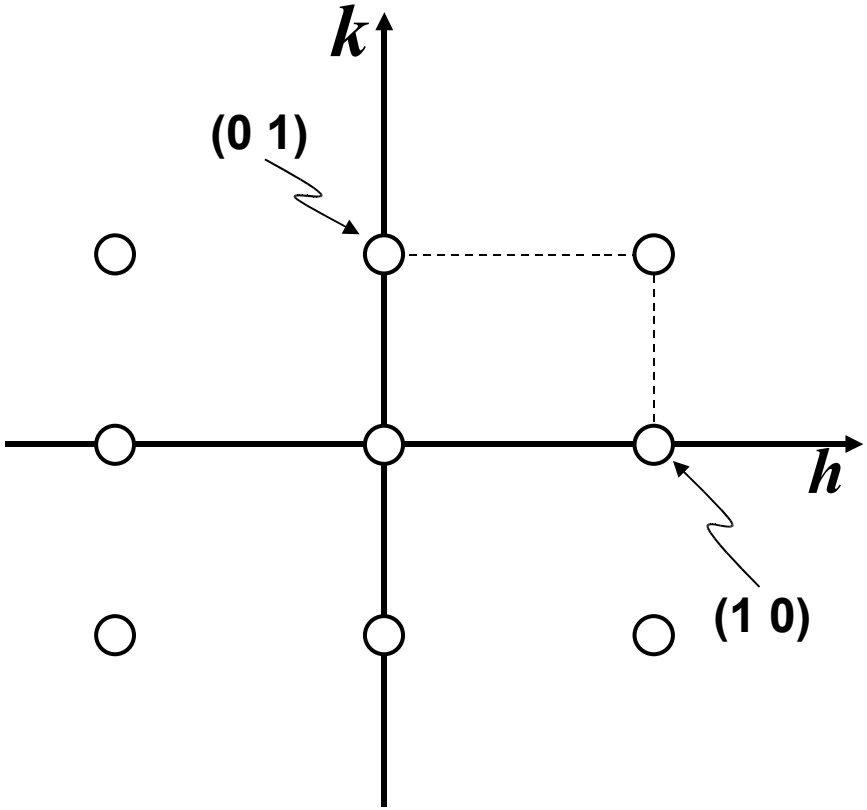


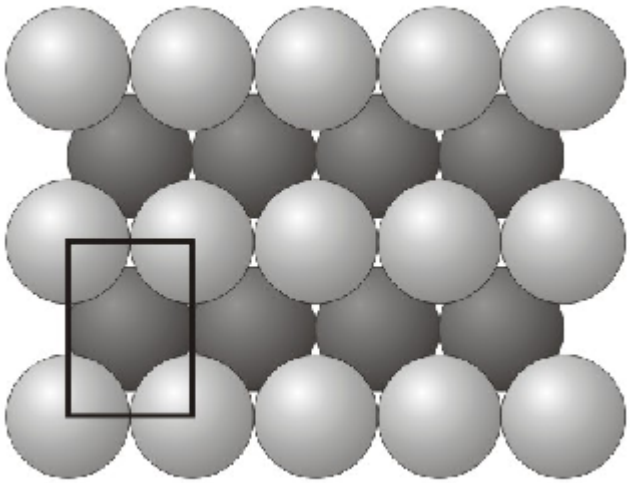




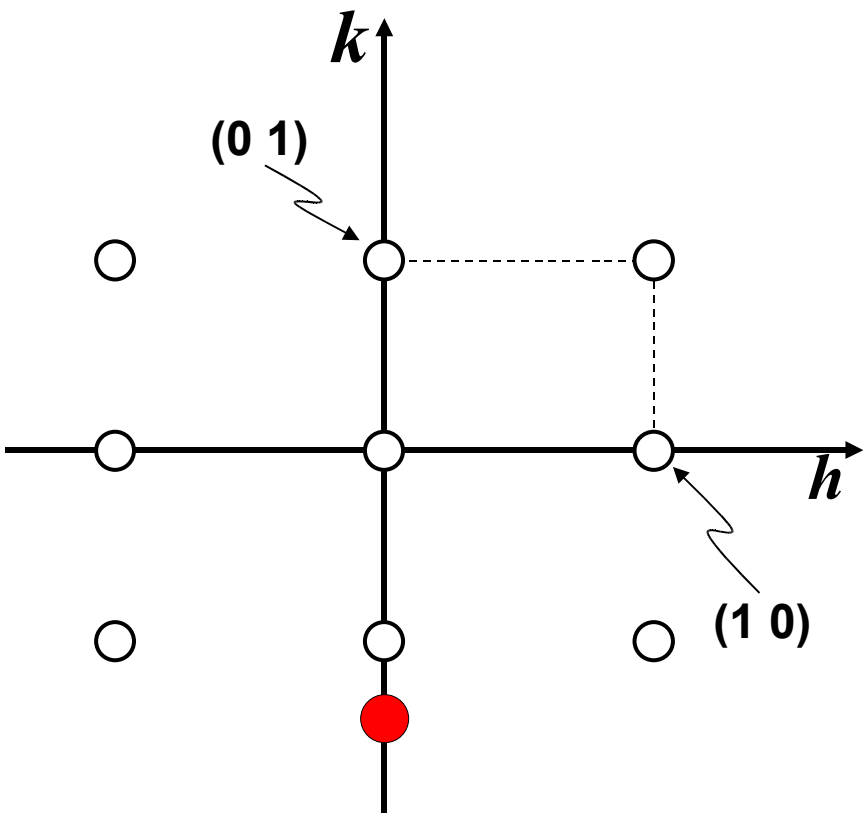
Unit cells and surface structures

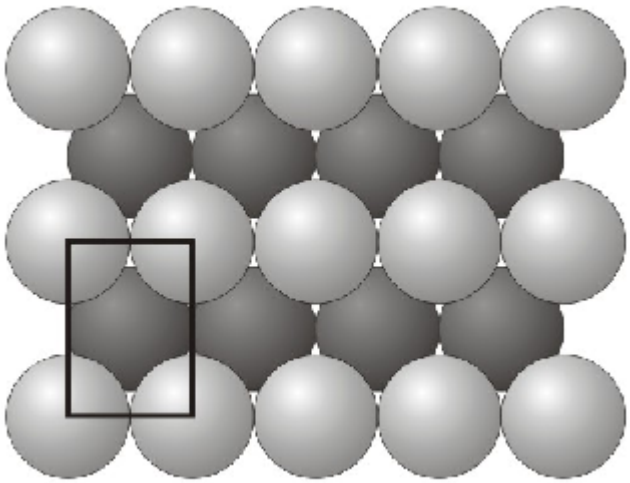
Pt(110) under 0.5 bar **CO** at 625 K

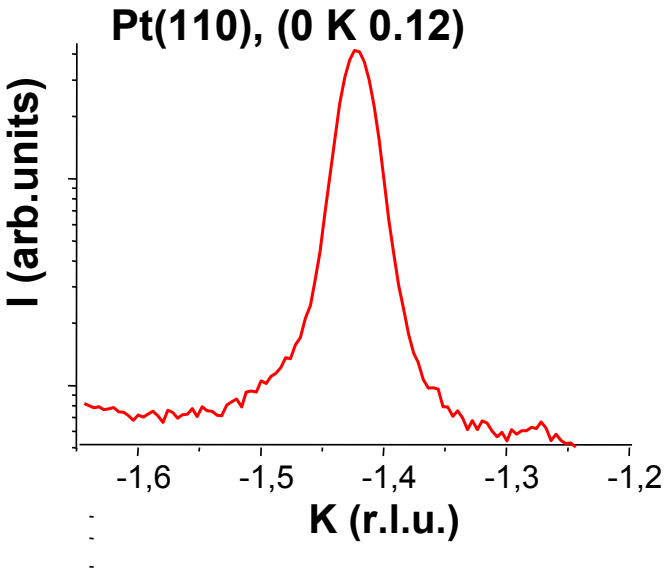




Unit cells and surface structures

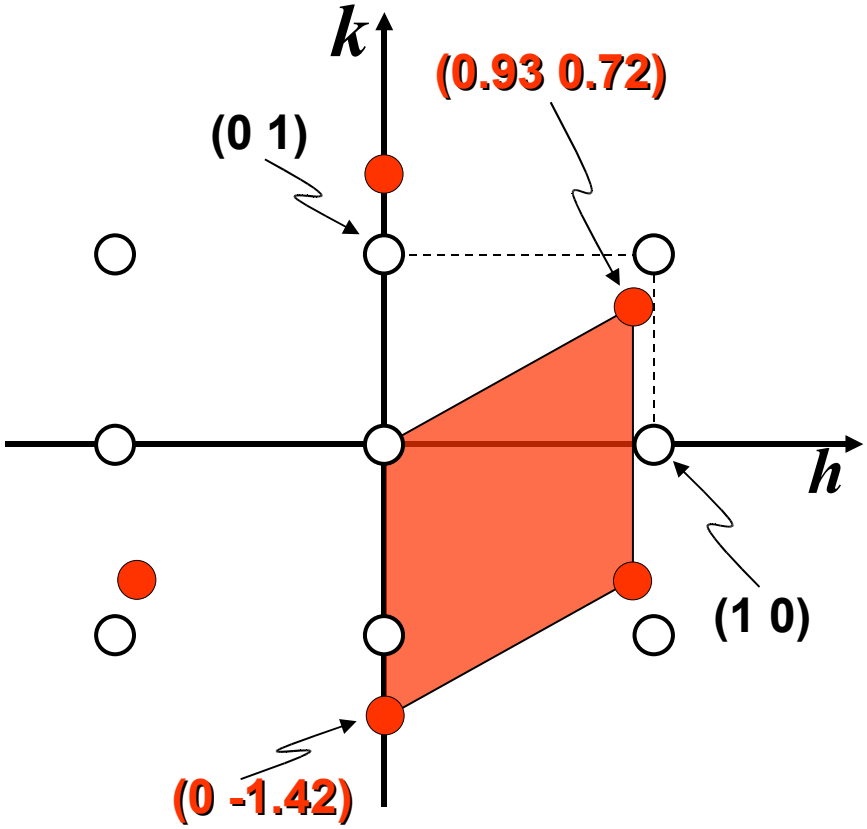


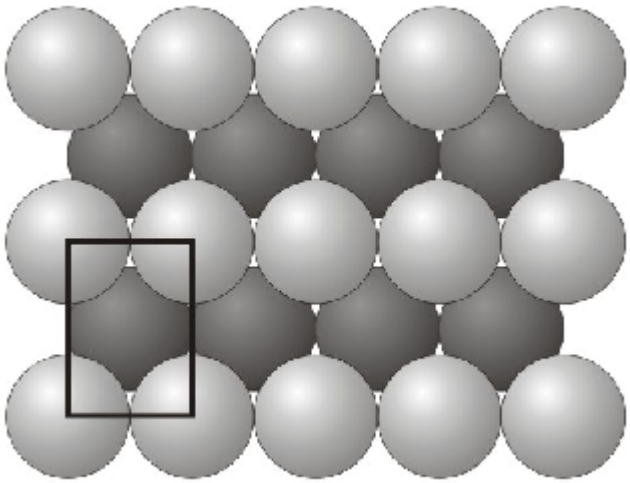


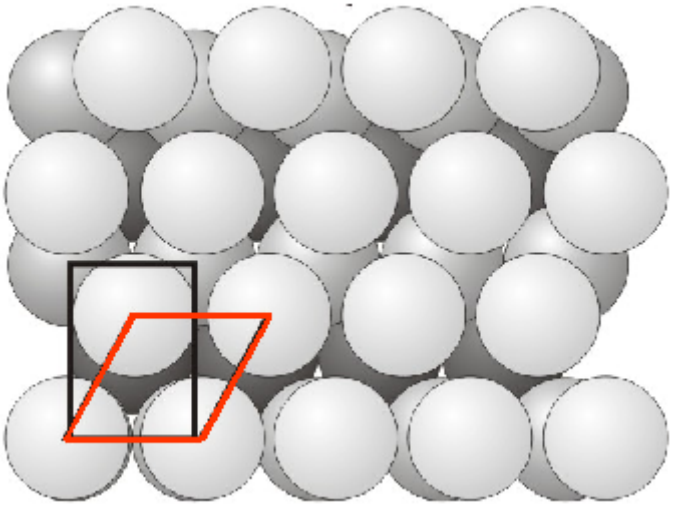


Pt(110) under 0.5 bar O_2 at 625 K

Unit cells and surface structures

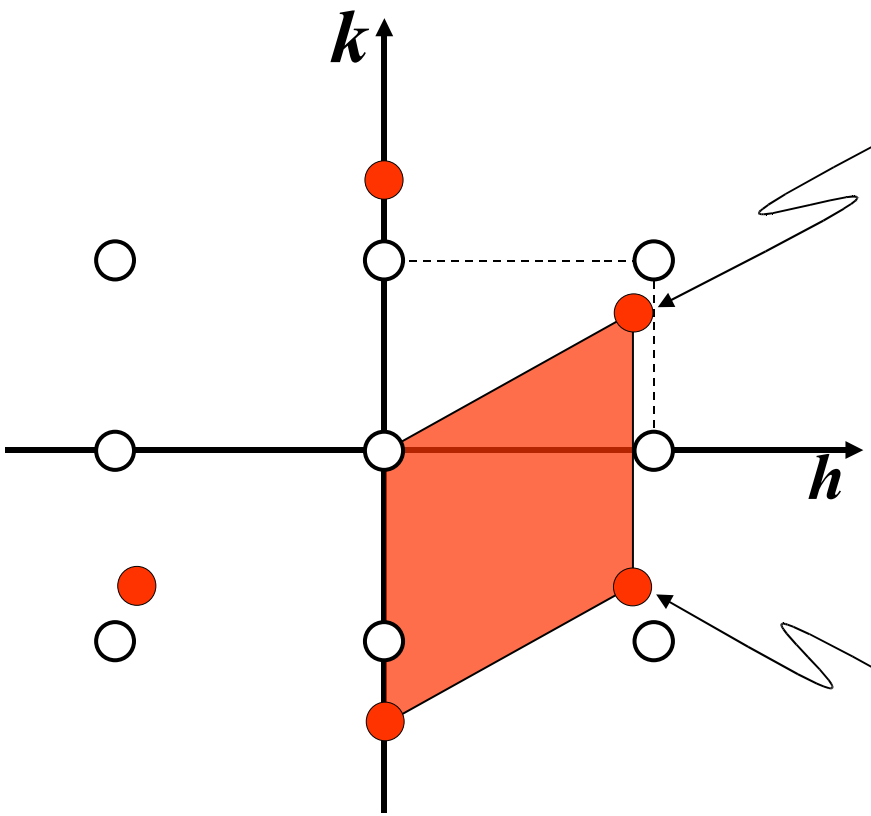


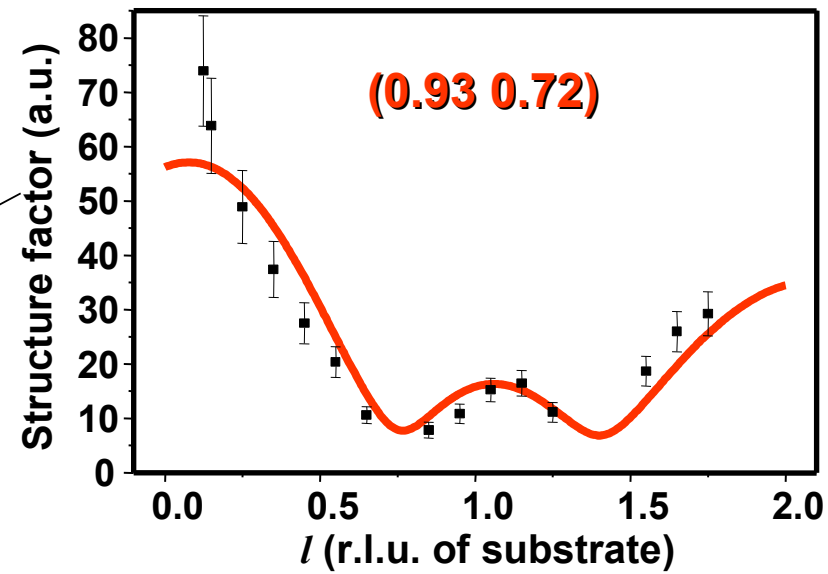


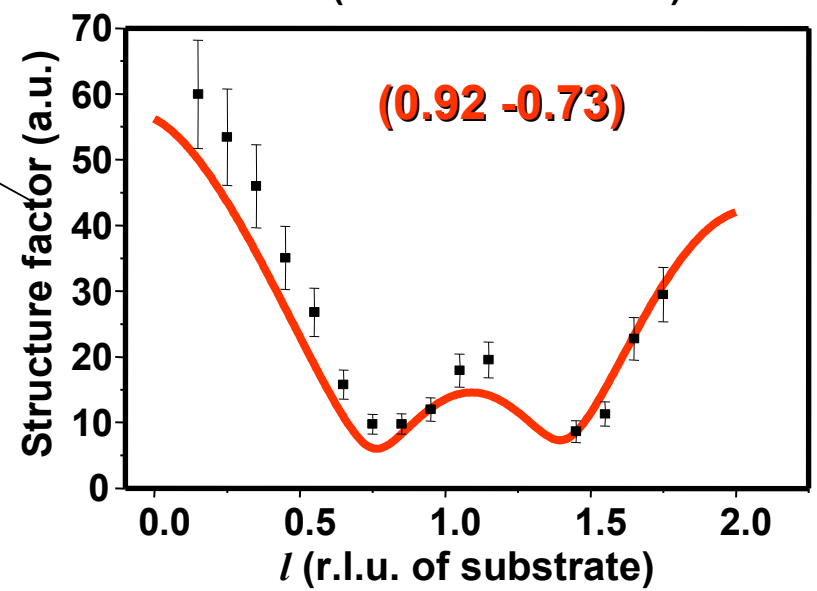


Pt(110) under 0.5 bar O_2 at 625 K

Unit cells and surface structures

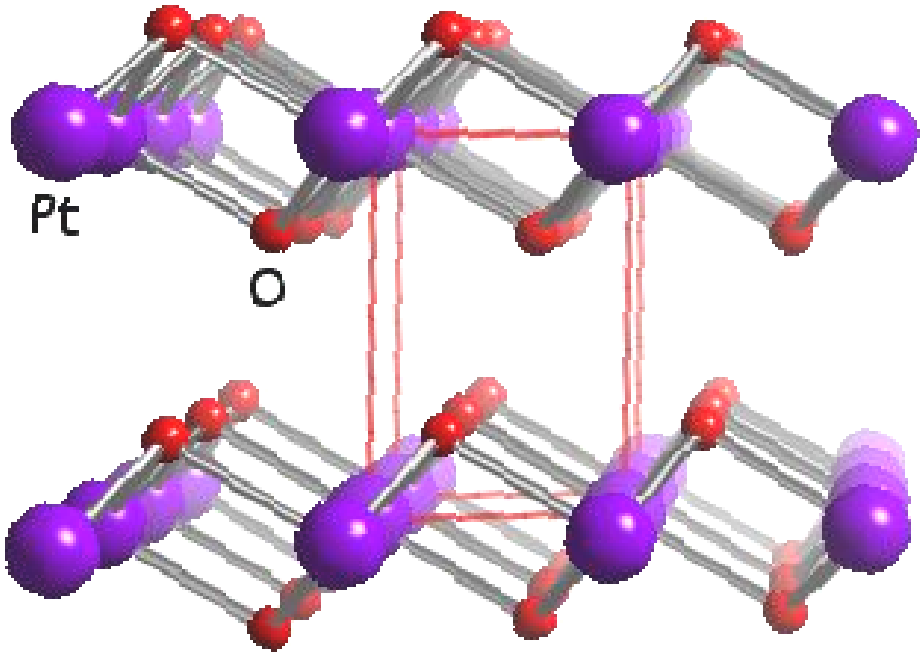




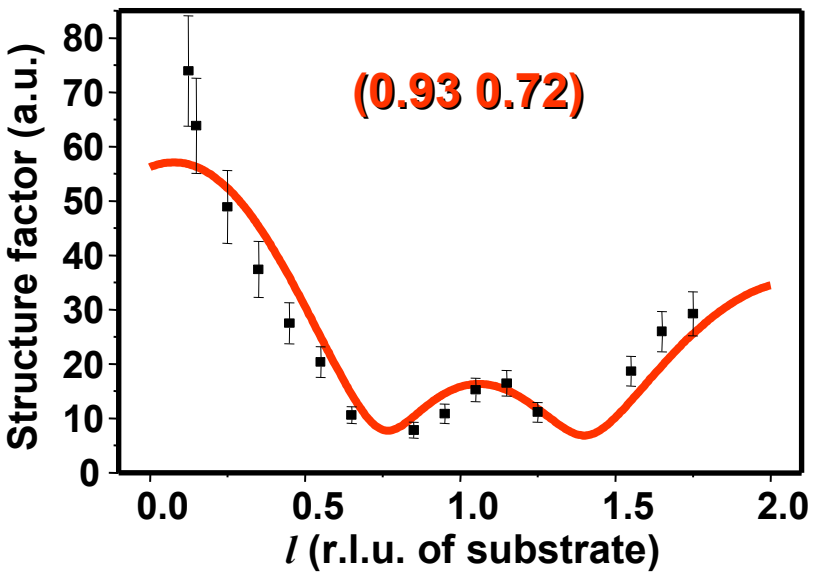


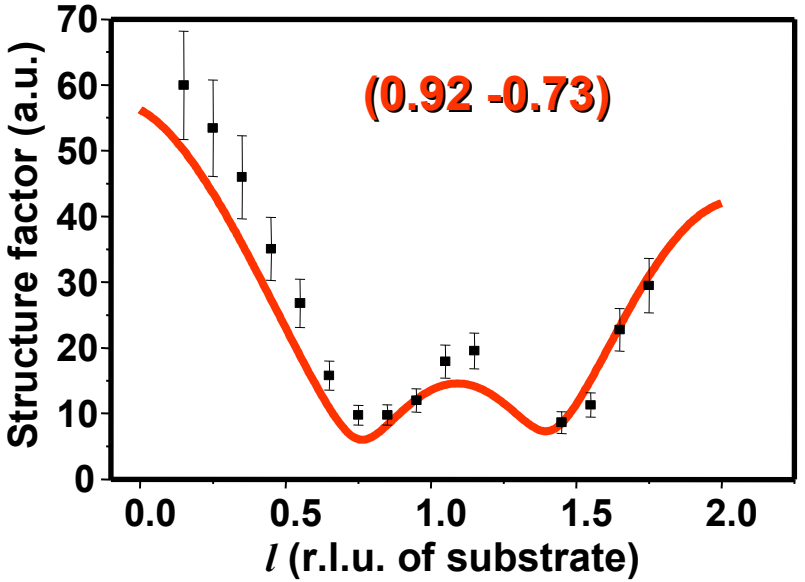
Fits: 2.6 monolayer PtO_2 film
laterally relaxed
vertically contracted

Unit cells and surface structures



webelements.com

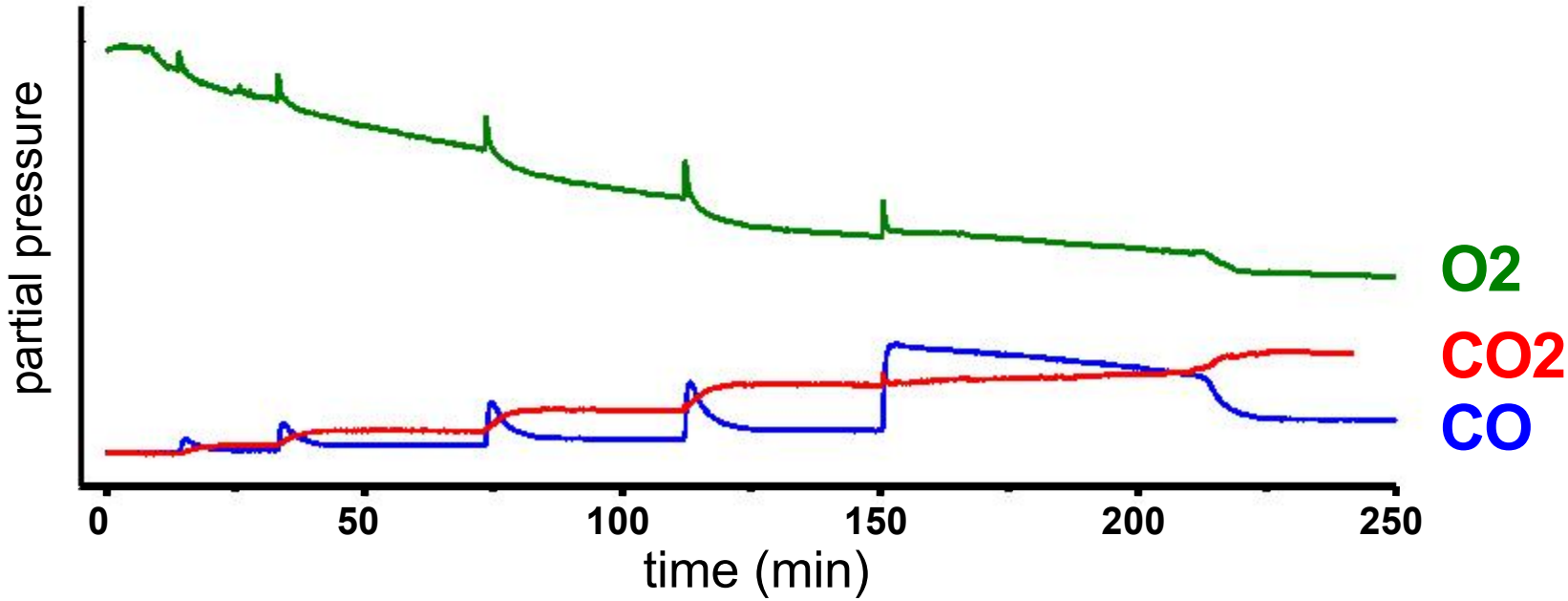




Fits: 2.6 monolayer PtO_2 film
laterally relaxed
vertically contracted

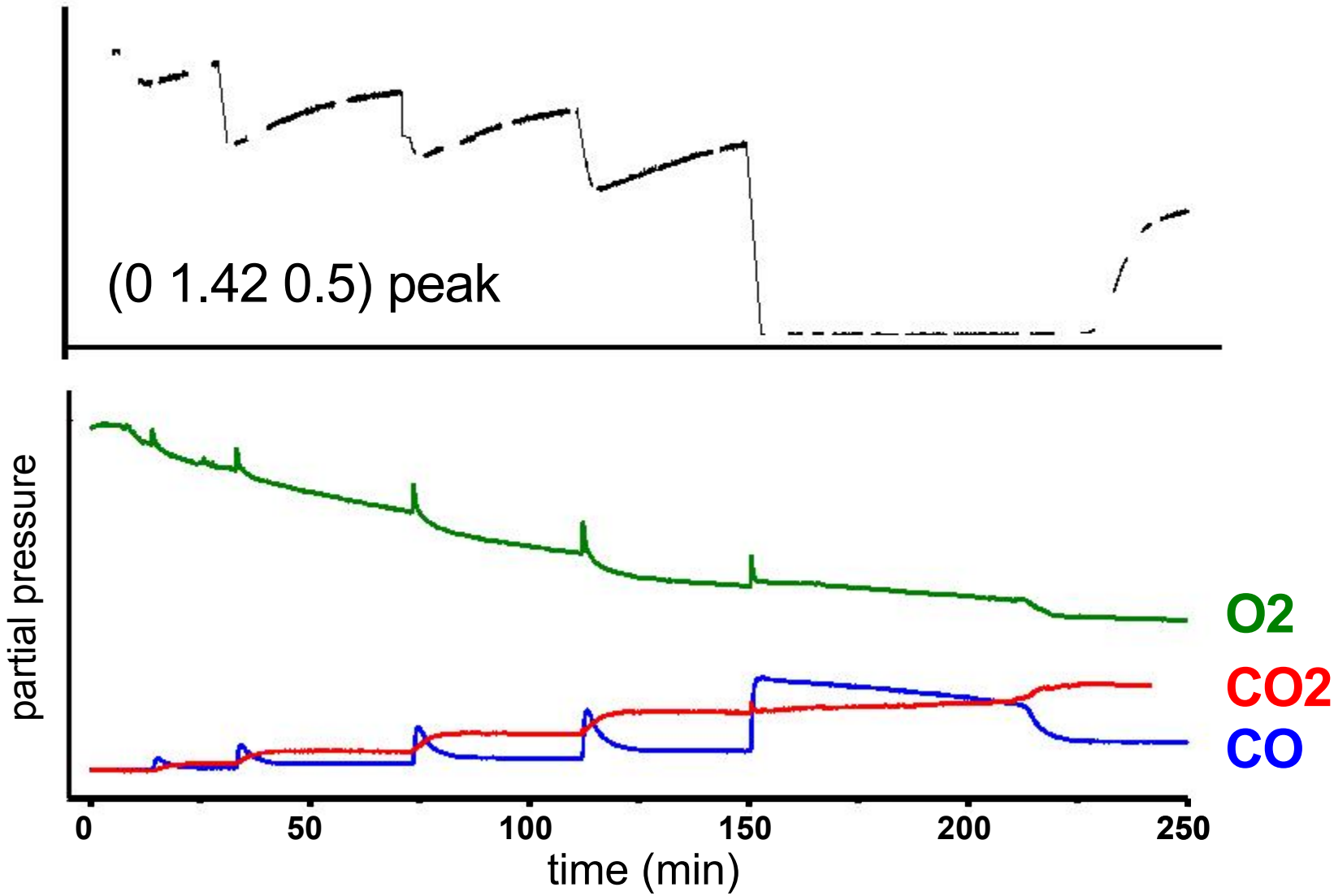
Pt(110): structure and reactivity

T = 625 K



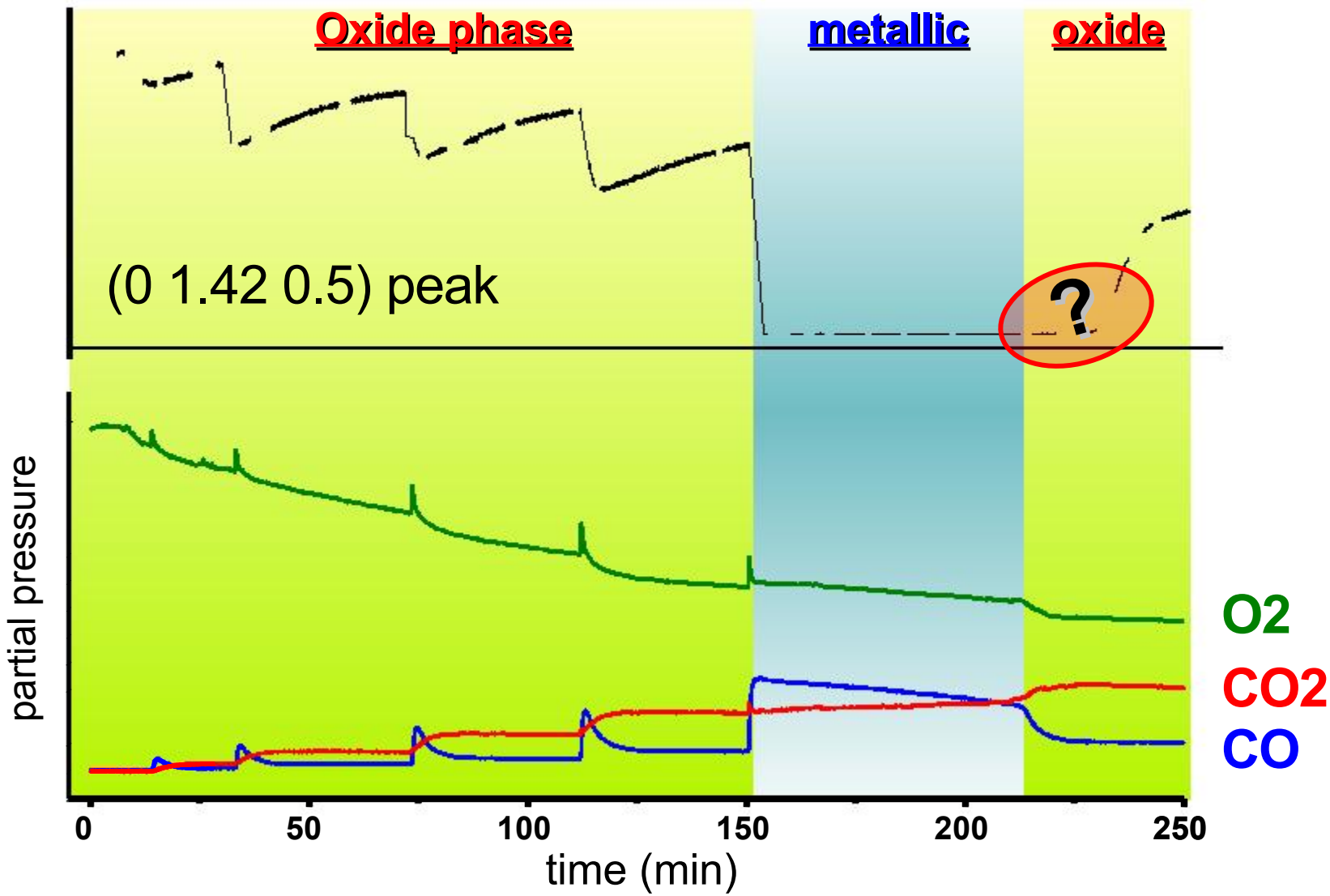
Pt(110): structure and reactivity

T = 625 K

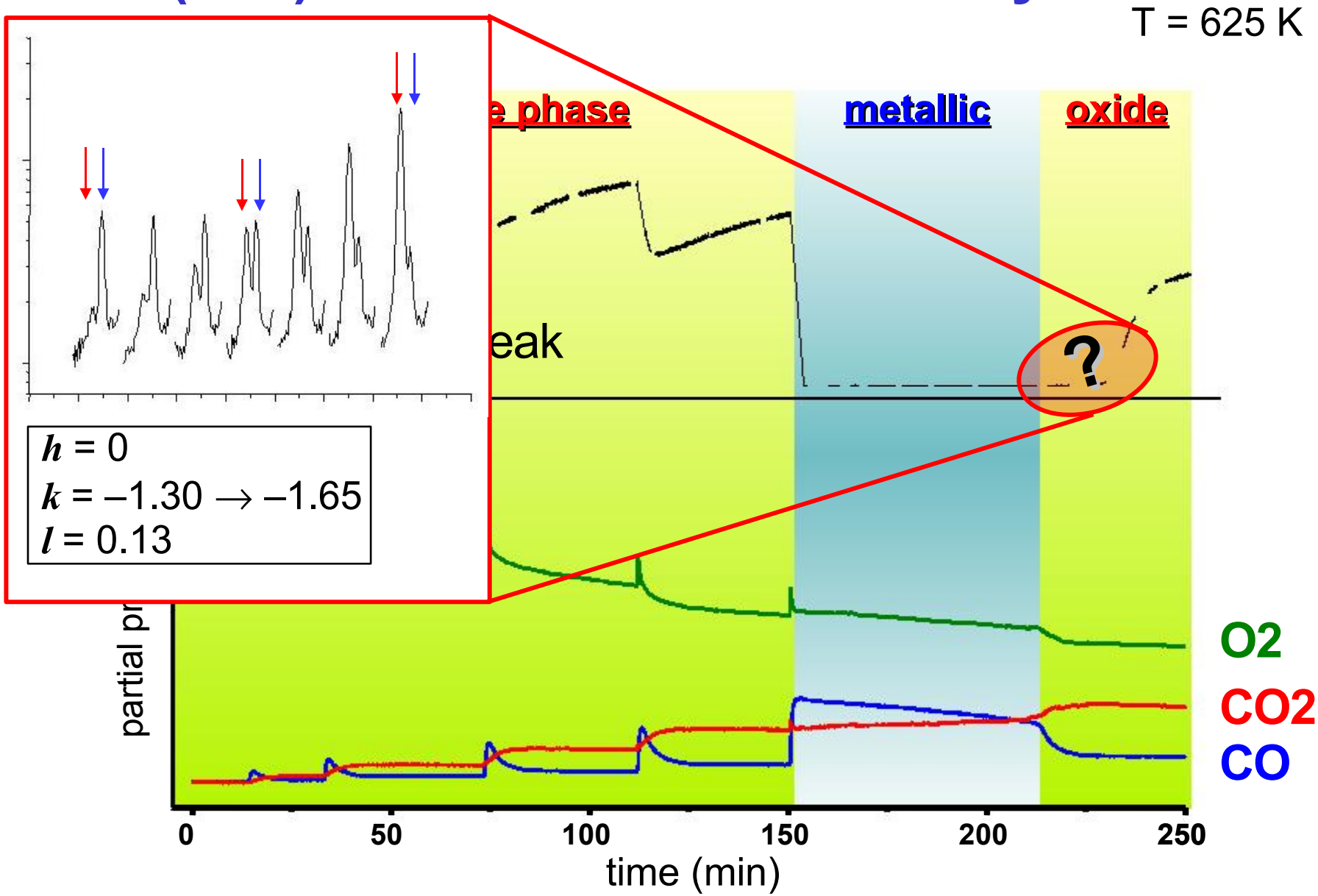


Pt(110): structure and reactivity

T = 625 K

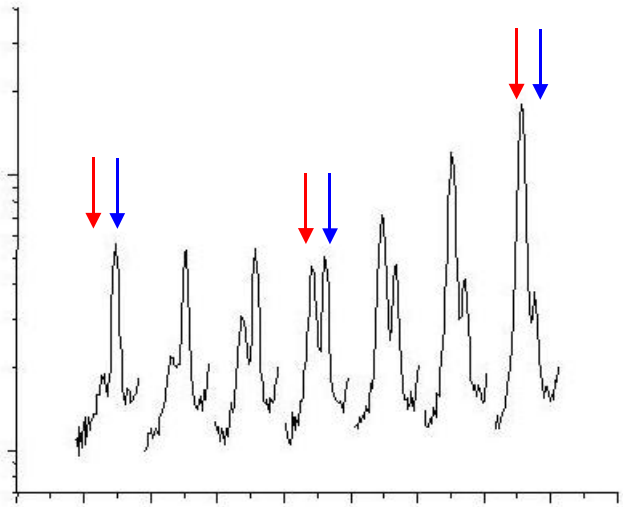


Pt(110): structure and reactivity

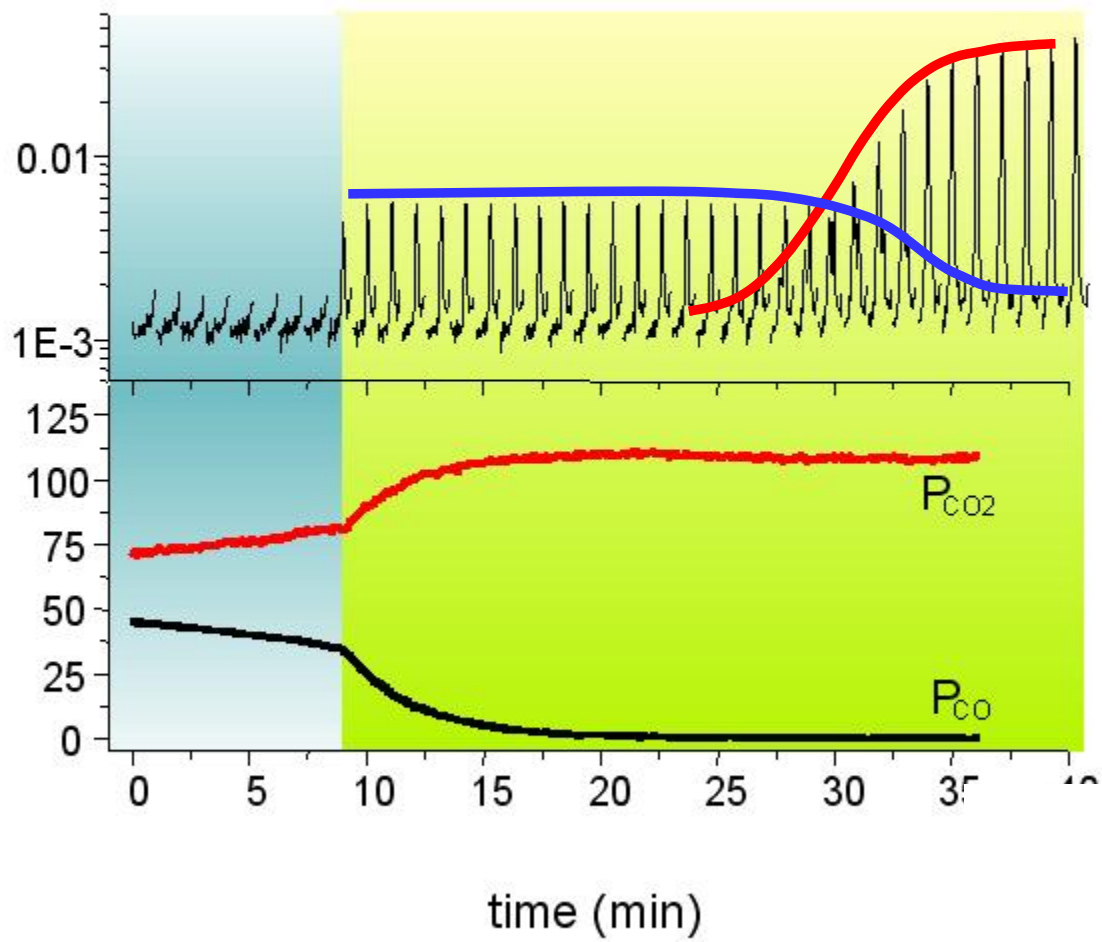


Pt(110): structure and reactivity

T = 625 K

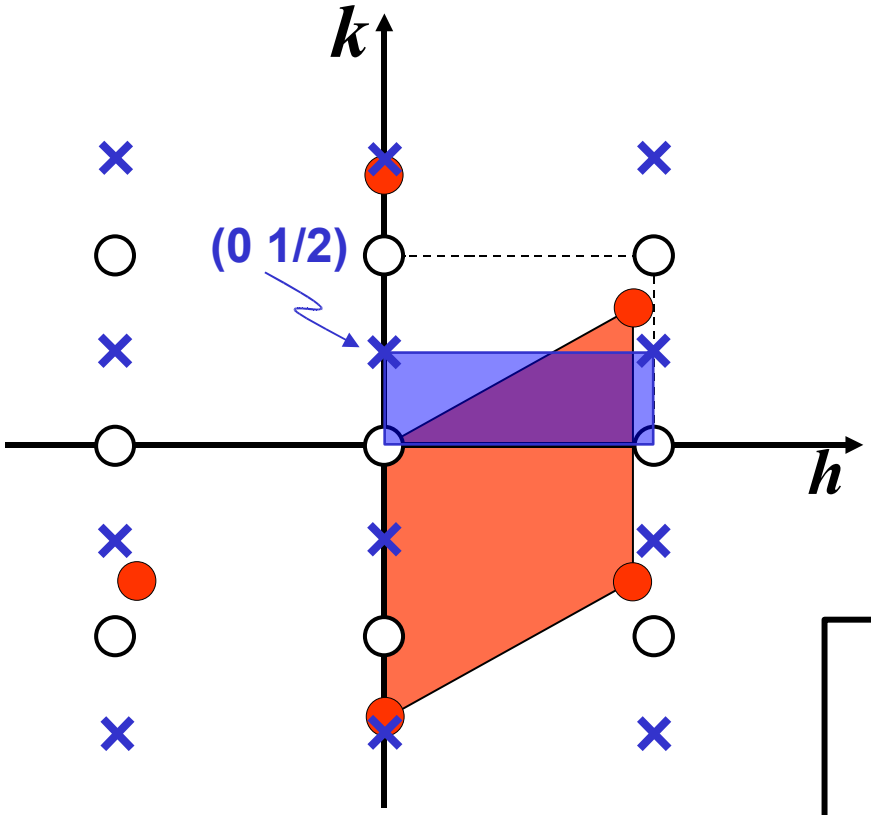


$h = 0$
$k = -1.30 \rightarrow -1.65$
$l = 0.13$

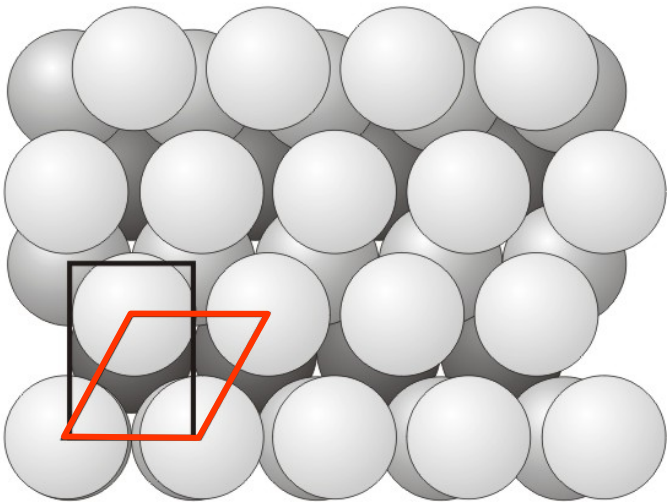


Again: unit cells and surface structures

Pt(110) under 0.5 bar of O_2/CO mixture (25:1) at 625 K



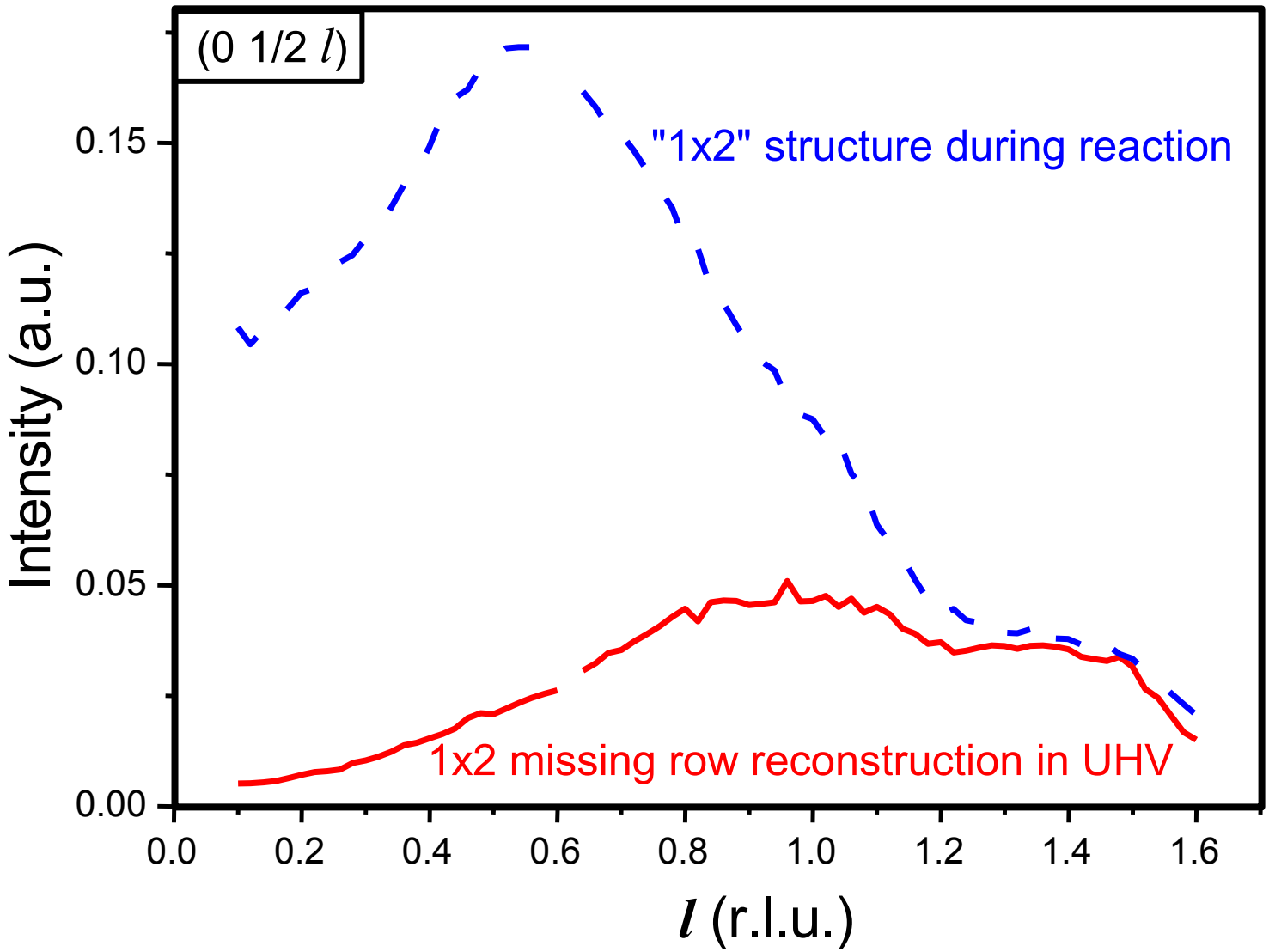
incommensurate structure



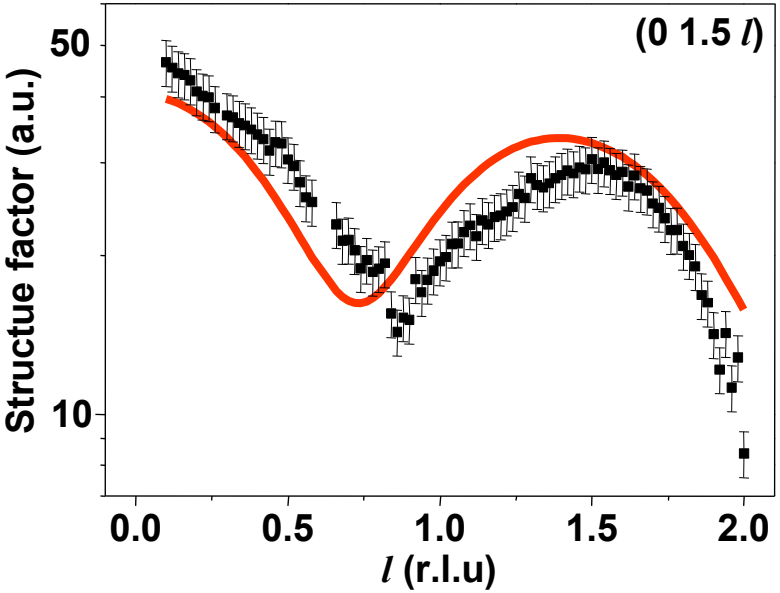
commensurate structure

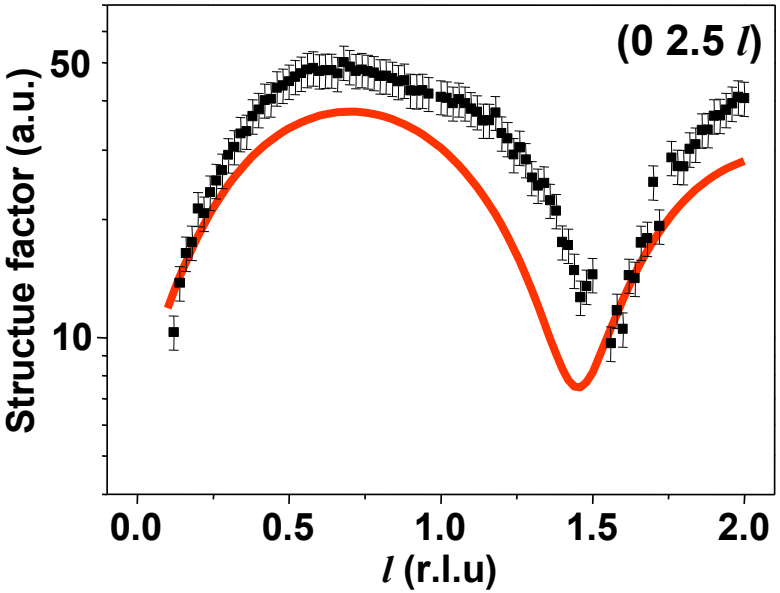
missing row?

High-P (1x2) is *not* MR-reconstruction!

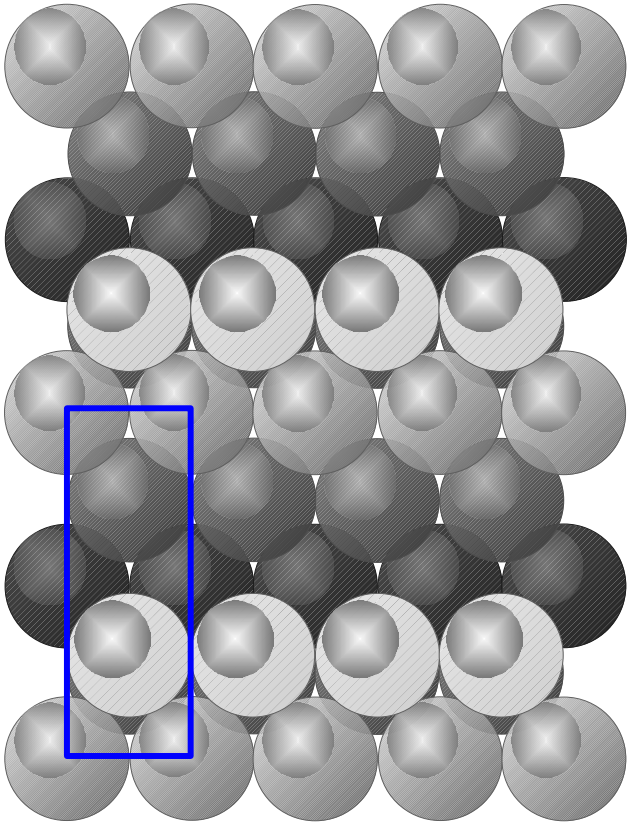


Commensurate oxide on Pt(110)





commensurate overlayer



CO-stabilized structure!!!

DFT by B. Hammer

SXRD on Pt(110)

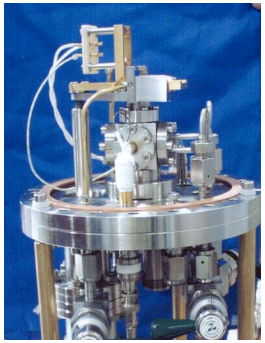
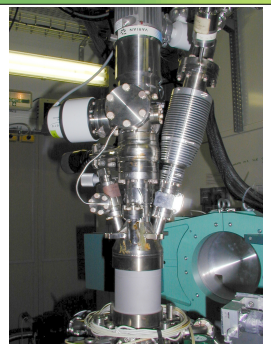
- **Similar to STM: During CO oxidation under O_2 rich conditions**

platinum oxide is the active phase

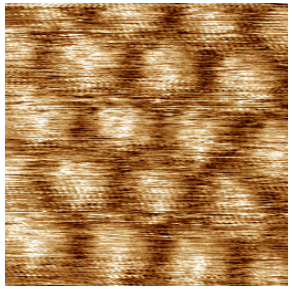
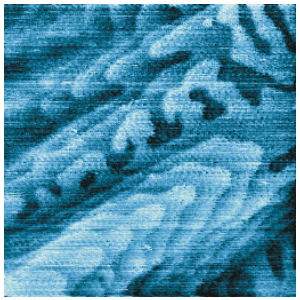
- ***2.6 monolayer of incommensurate PtO_2 like oxide in pure oxygen***
- ***1 monolayer of commensurate CO-stabilized (1x2) oxide during reaction***

SXRD: M.D. Ackermann et al, PRL 95 (2005) 255505

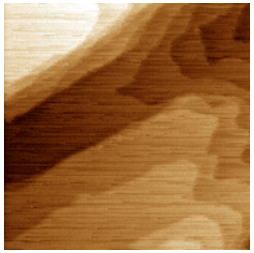
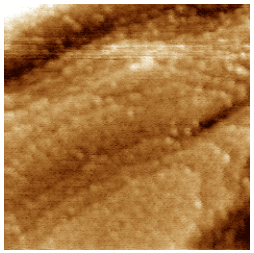
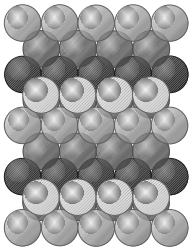
Summary

high pressure STM & SXRD

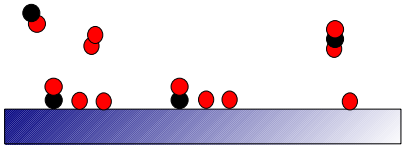
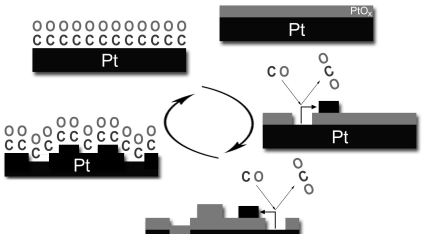



single gas: adsorbate structures & surface restructuring

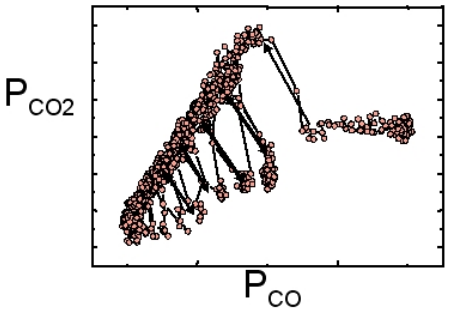




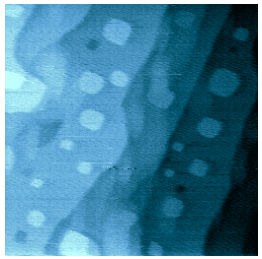
during CO oxidation: oxides more active

reaction mechanisms

oscillating reactions





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CO oxidation on Pt(110): scanning tunneling microscopy inside a flow reactor, B.L.M. Hendriksen and J.W.M. Frenken, Phys. Rev. Lett, **89**, 046101 (2002)

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Bistability and oscillations in CO oxidation studied with Scanning Tunnelling Microscopy inside a reactor, B.L.M. Hendriksen, S.C. Bobaru, J.W.M. Frenken, Catalysis Today 105 (2005) 234 (invited)

Structure and reactivity of surface oxides on Pt(110) during catalytic CO oxidation, M.D.Ackermann, T.M. Pedersen, B.L.M. Hendriksen, O. Robach, S. Bobaru, I. Popa, H. Kim, B. Hammer, S. Ferrer, J.W.M. Frenken, Phys. Rev. Lett. 95 (2005) 255505

www.physics.leidenuniv.nl/sections/cm/ip

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