Argonne NATIONAL LABORATORY

XPCS on Surfaces : Challenges and Opportunities

Cornell University, CHESS
XDL Workshop 6, June 30th 2011

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U.S. DEPARTMENT OF ENERGY | Office of Science | Basic Energy Sciences

[1),3)]This work and the use of APS at ANL are supported by the U.S. Department of Energy, Basic Energy Sciences under contract DE-AC02-06CH11357

XPCS on Surfaces : Challenges and Opportunities

Macht doch den zweiten Fensterladen auch auf, damit mehr Licht hereinkomme.

Last words attributed to Johann Wolfgang von Goethe (as far back as letters from 1832).

Picture taken from Wikipedia

“Continuous” Operation Hard X-ray Light Sources

APS 8ID :	2.5×10^{11} photon/sec
ESRF :	1×10^{12} photon/sec
NSLSII :	5×10^{12} photon/sec (projected)
ERL :	5×10^{14} photon/sec (projected)

Bilderback, Brock, Dale, Finkelstein, Pfeifer, and Gruner, *New Journal of Physics* **12** 035011 (2010).

Ignoring obvious questions about:

- Detectors
- Flux vs. Coherence
- Beam Damage
- Etc…

XPCS on Surfaces : Challenges and Opportunities

In-situ XPCS from materials and hard matter surfaces has a great deal of promise. Especially with more light!

- What do we mean by surface XPCS? What led us to where we are now?
- What experiments have worked? Au and Pt: what have we learned?
- What hasn't worked (or, what's beyond our reach)?
- Given ~ 100 to 1000 fold increase in flux, what becomes possible?

Macht die Fensterladen auf, damit ich mehr Licht bekomme.

Last words attributed to Johann Wolfgang von Goethe (as far back as letters from 1832).

"Continuous" Operation Hard X-ray Light Sources

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What led to surface XPCS?
Well, surface XPCS!

Surface X-ray Scattering

Dynamic Light Scattering

XPCS from "bulk" or systems with volume

Coherent scattering from static surfaces

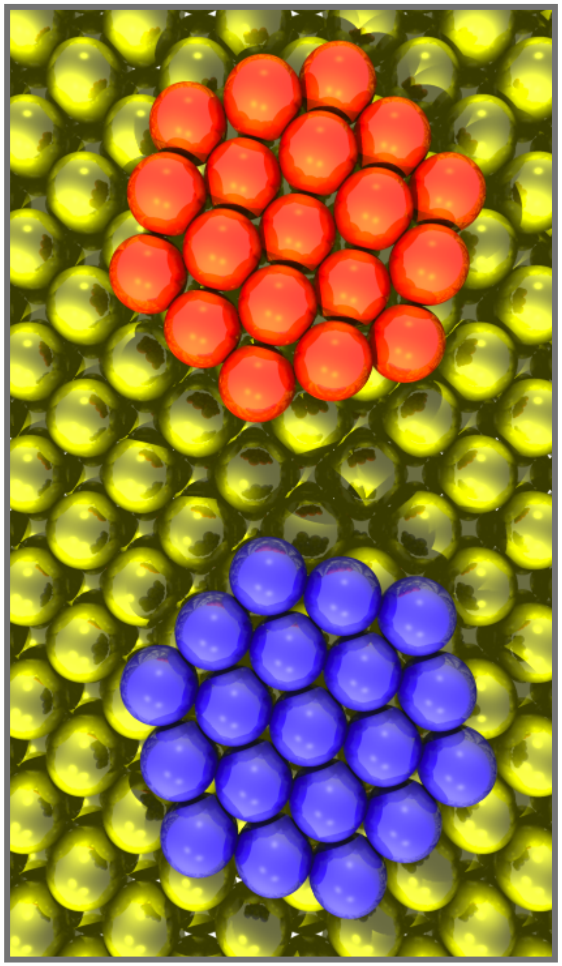
XPCS from films, interfaces, 2-d structures, and surfaces

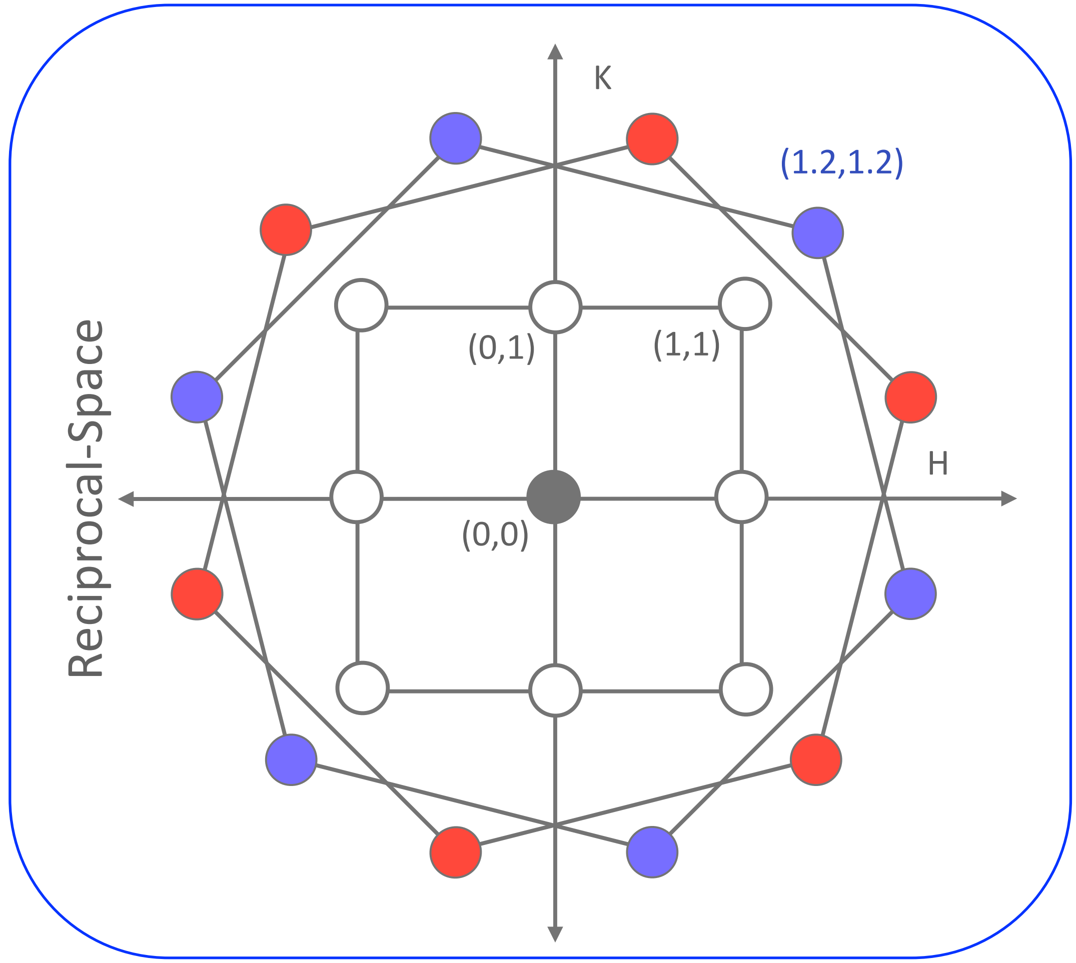
Surface X-ray Speckle: Atomic resolution (in at least one direction), driving towards in-situ application, faster time scales, lower Z, and higher Q.

Surface Scattering & Diffraction

Orient crystal and detector to satisfy the diffraction condition for the ordered surface lattice.

Real-Space





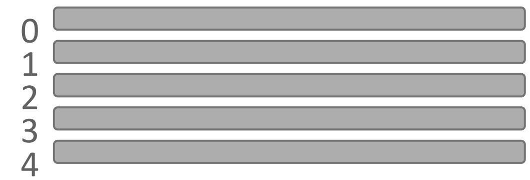
This is also a good place to mention that both Au (001) and Pt (001) surfaces reconstruct into a quasi-hexagonal pattern.

Specular Scattering from a (001) FCC Surface

$$S(L)\big|_{L=1} = \theta + e^{-i\pi L} + e^{-2i\pi L} + \cdots\big|_{L=1} = \theta + \frac{e^{-i\pi L}}{1-e^{-i\pi L}}\bigg|_{L=1} = \theta - \frac{1}{2}$$

ϑ is the relative density of the topmost layer

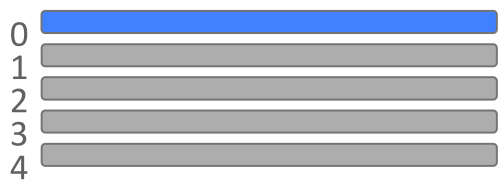
Bulk Truncation



$$f \propto e^{-i(0)\pi} + e^{-i\pi} + e^{-2\pi} + \ldots$$

$$f \propto 1 - 1/2 = 1/2$$

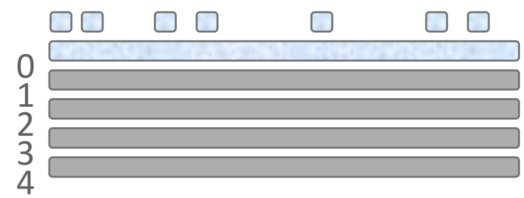
Reconstructed (quasi-hex)



$$f \propto 5/4\, e^{-i(0)} + 4/4\left(e^{-i\pi} + e^{-i2\pi} + \ldots\right)$$

$$f \propto 5/4 - 1/2 = 3/4$$

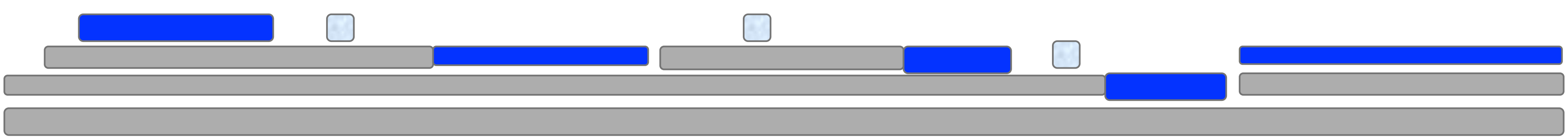
Unreconstructed



$$f \propto 1/4\, e^{i\pi} + e^{i(0)} + \left(e^{-i\pi} + e^{-i2\pi} + \ldots\right)$$

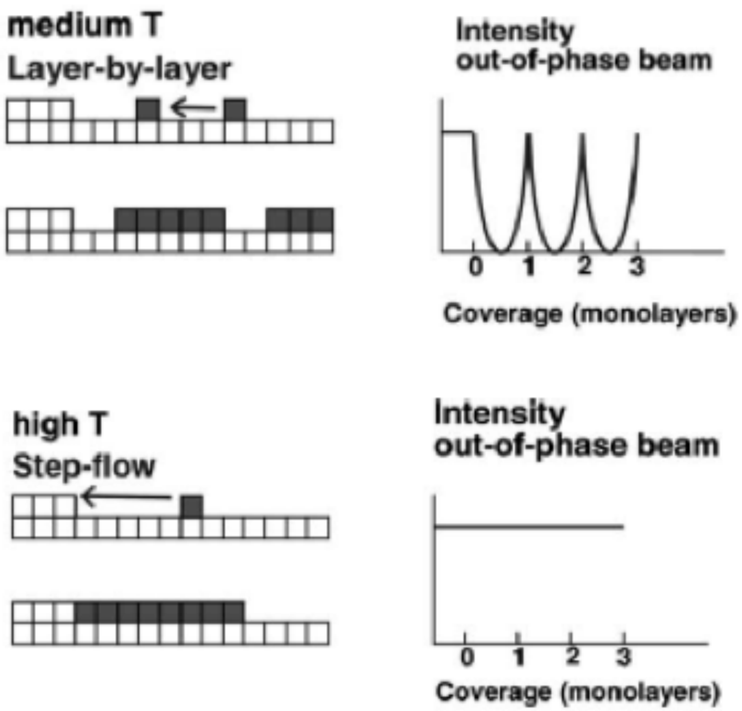
$$f \propto -1/4 + 1 - 1/2 = -1/4$$

Speckle : when the coherence length is long enough to interfere from lots of random variation.



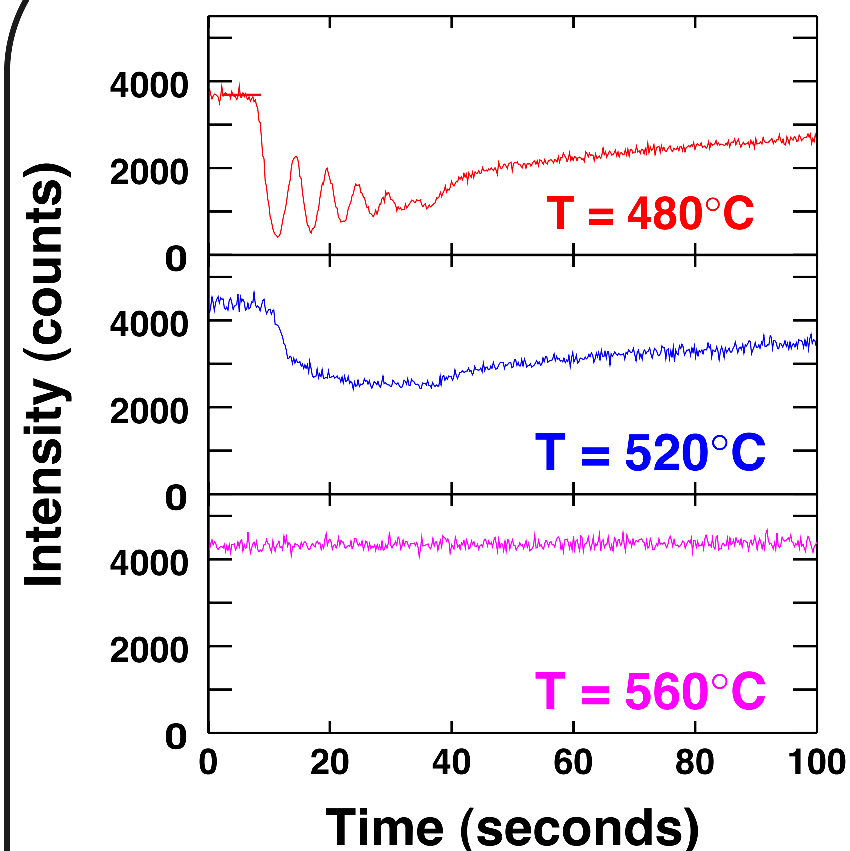
Time Resolved Surface X-ray Scattering : Growth Modes

Intensity equates to ordering



Steady-state and equilibrium fluctuations can't be easily seen with incoherent x-ray scattering.

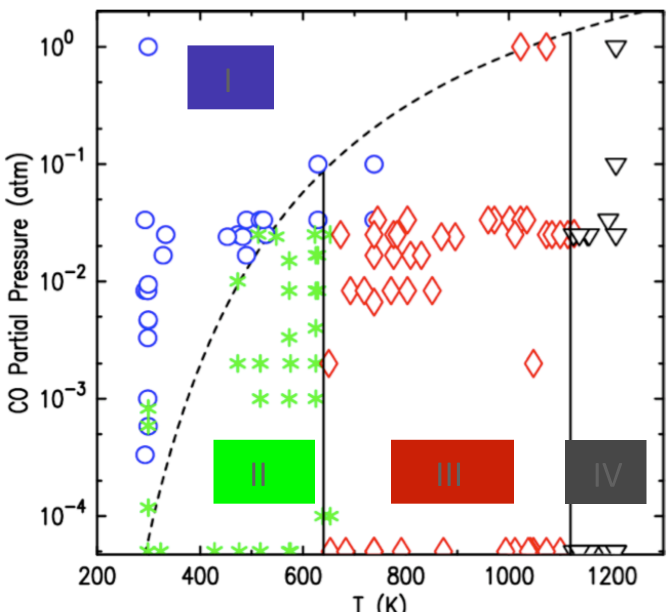
Layer by Layer ⇒ Step Flow



GaAs growth modes : P.H. Fuoss, et al : *Phys. Rev. Lett.*, **69** 2791 (1992).

Surface X-ray Scattering : Gas Phase Reaction Kinetics

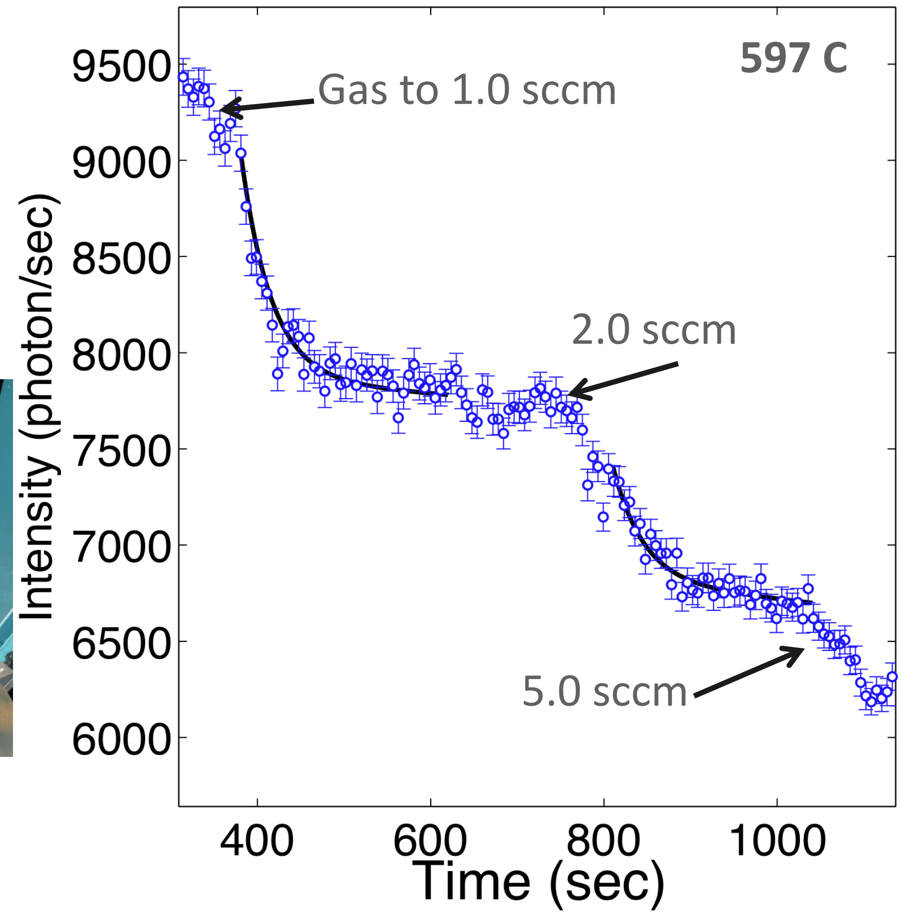
CO interaction with the Au (001) surface reconstruction. Pressure and Temperature both play a role and we are able to "dial in" the surface properties.



Steady-state and equilibrium fluctuations can't be easily seen with incoherent x-ray scattering.

Intensity measures "hex" vs. disordered (1x1)

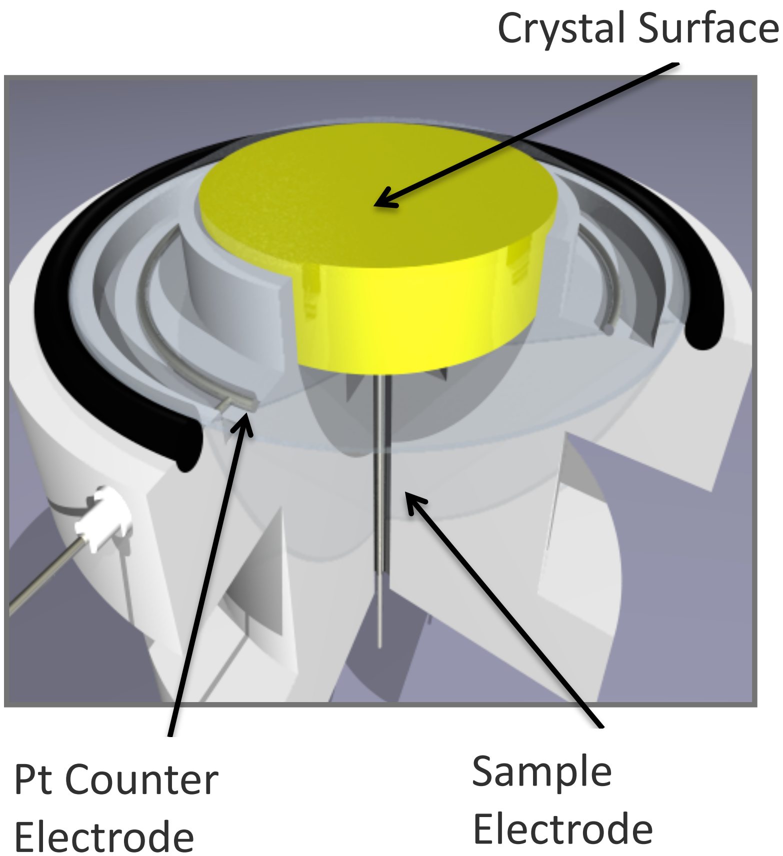
Gas at 0.5 sccm rate initially.



Lifting of the reconstruction as partial pressure is increased.

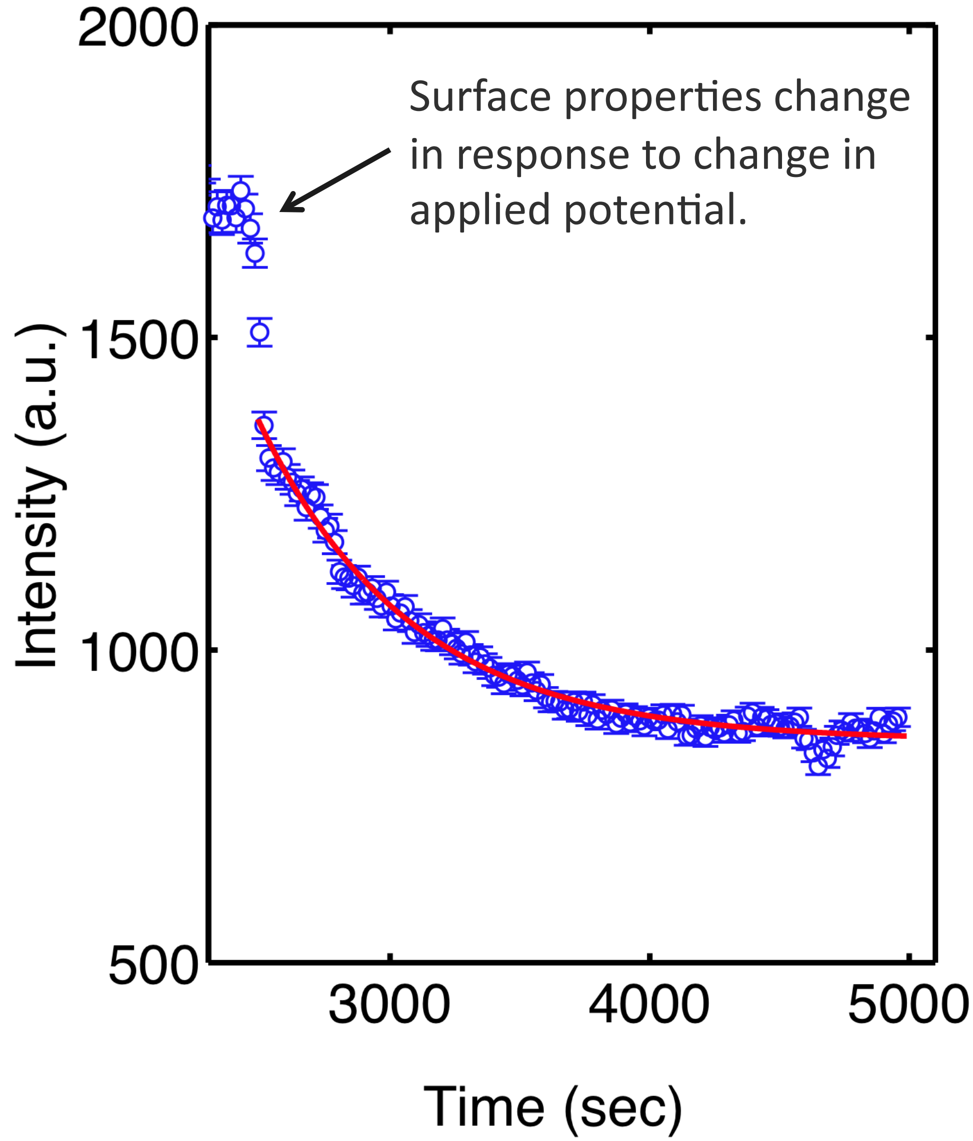
M.S. Pierce, K.C. Chang, D. Hennessy, V. Komanicky, A. Menzel, and Hoydoo You. J. Phys. Chem. C, **112** 2231 (2008).

Surface X-ray Scattering : In-Situ Electrochemistry



Steady-state and equilibrium fluctuations can't be easily seen with incoherent x-ray scattering.

Scattering at the (001) anti-Bragg condition.

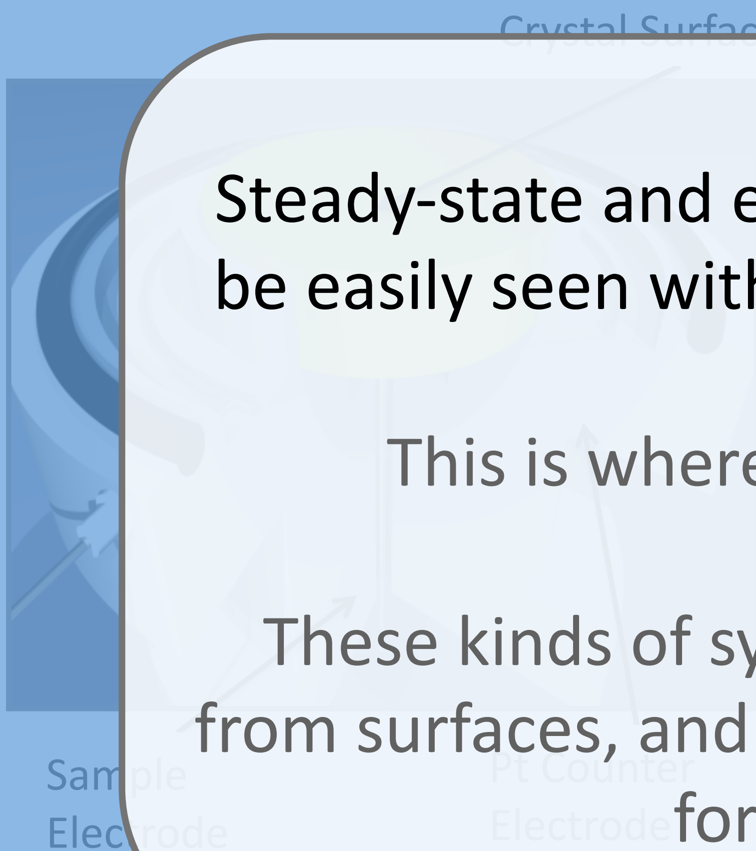


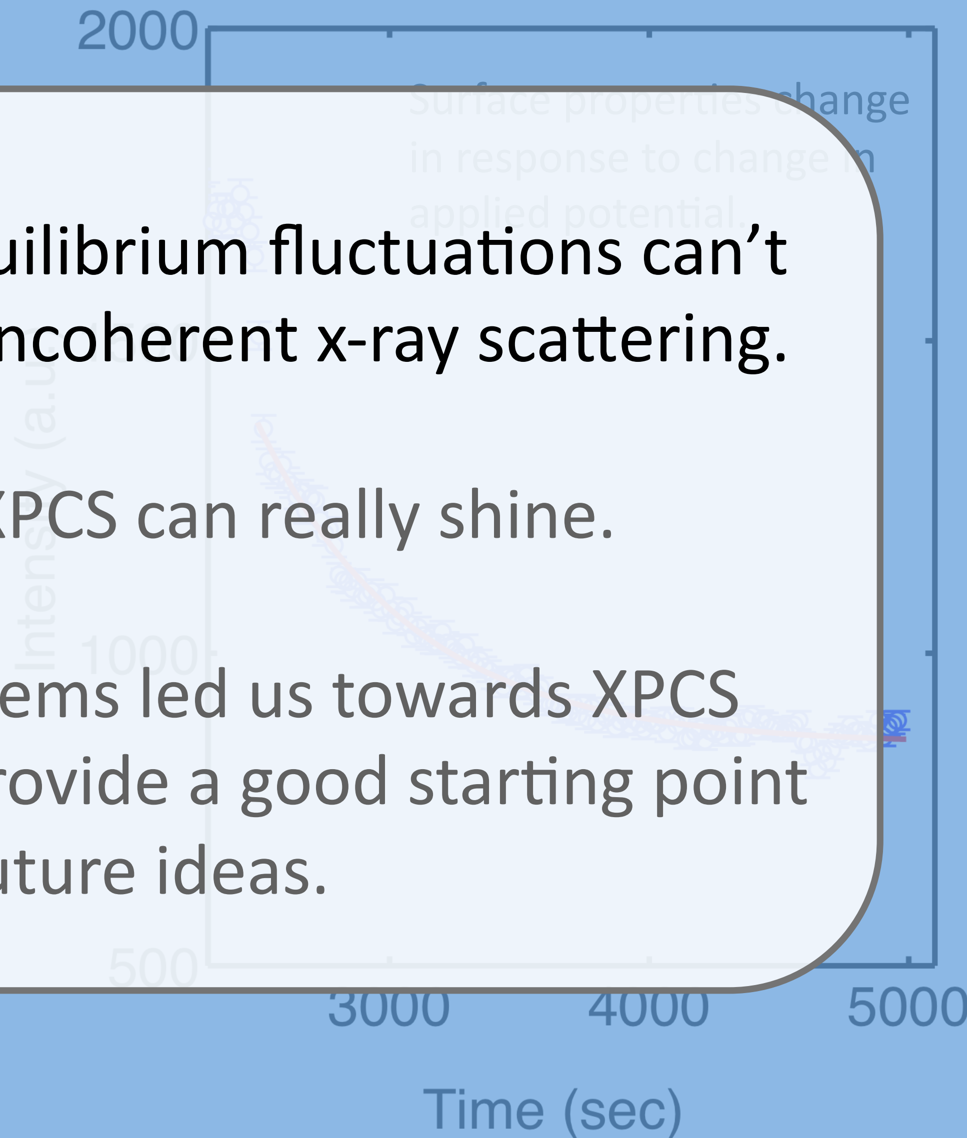
Time Resolved Surface X-ray Scattering : Electrochemistry

Steady-state and equilibrium fluctuations can't be easily seen with incoherent x-ray scattering.

This is where XPCS can really shine.

These kinds of systems led us towards XPCS from surfaces, and provide a good starting point for future ideas.





Steady-state and equilibrium fluctuations can't be easily seen with incoherent x-ray scattering.

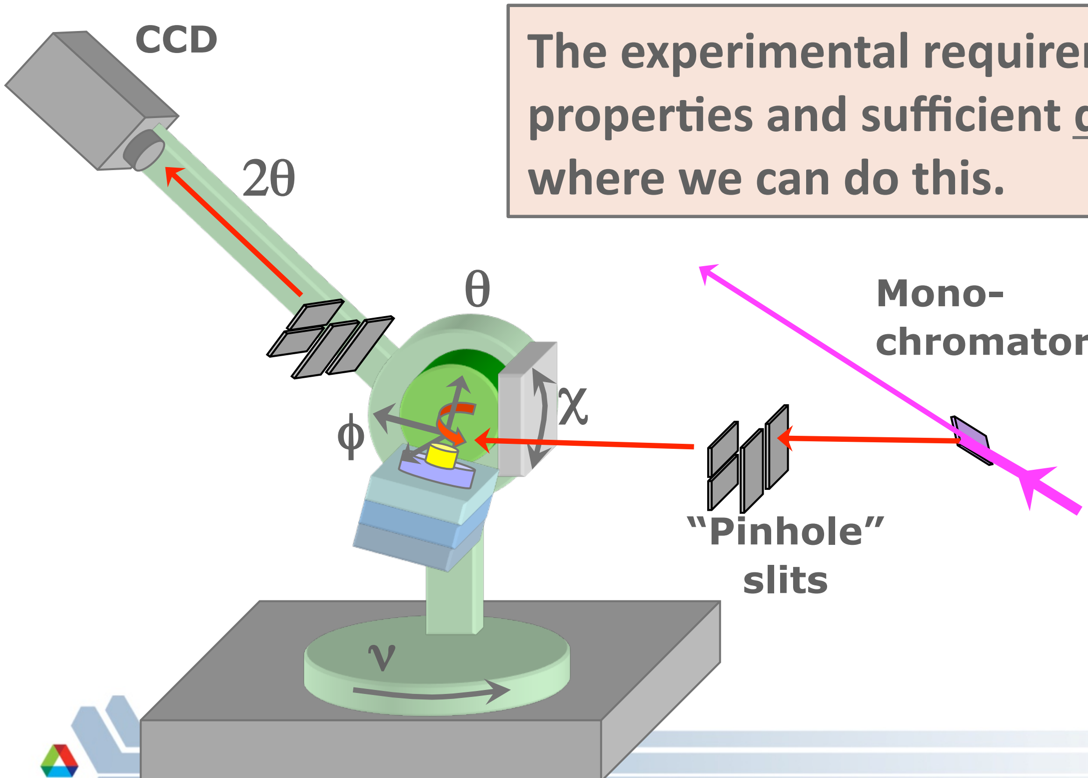
Experiments done at Advanced Photon Source, Beamline 8-ID

•High Z Material
•Long counting times (lots of patience).

•Be windows for x-ray transmission.
•Residual Gas Analyzer attached.
•RF induction heater used to control temperature.
•Lattice constant used to measure temperature.

•Thin layer of electrolyte.
•Solution can be varied.
•In-situ applied potential control.

The experimental requirements of photon properties and sufficient <u>diffractometer</u> limit where we can do this.



•Optimized Coherent Beamlime
•"Full" Diffractometer
•7.36 keV photons
•Slits : 6-10 (V) by 6-20 (H) microns

~ 10^{10} x-rays/sec on sample
~ $10^{3}-10^{4}$ x-rays/sec as signal
Typically 1-30 sec exposures/image
and 1-3 hours of data at a time.

Experiment and Coherence

•RF induction heater used to control temperature.
•Lattice constant used to measure temperature.
•High Z Material
•Long counting times (lots of patience).
•Be windows for x-ray transmission.
•Residual Gas Analyzer attached.

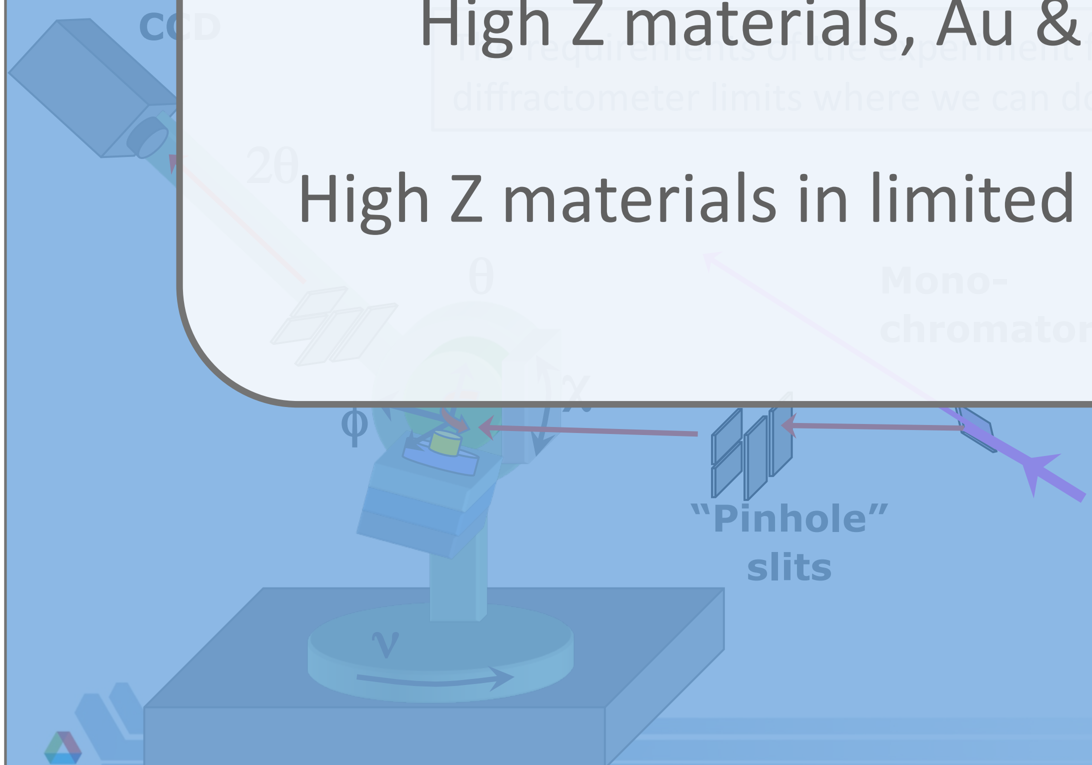
• What is "coherence."
• Why is it important to this experiment?

So what has worked so far?

High Z materials, Au & Pt, in vacuum.

High Z materials in limited *in-situ* application.

The requirements of the experiment for photon properties, intensity, and diffractometer limits where we can do this.



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~ 10^{10} x-rays/sec on sample
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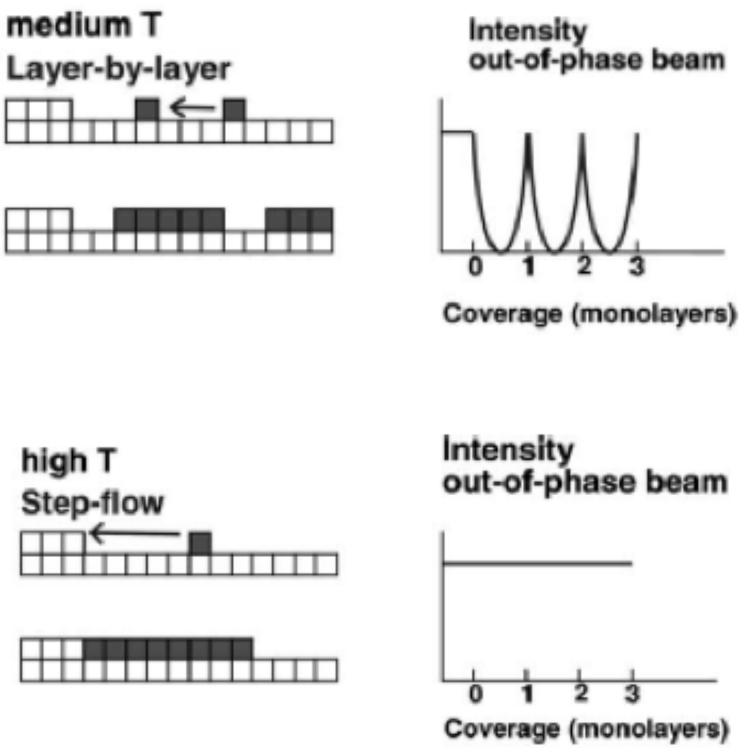
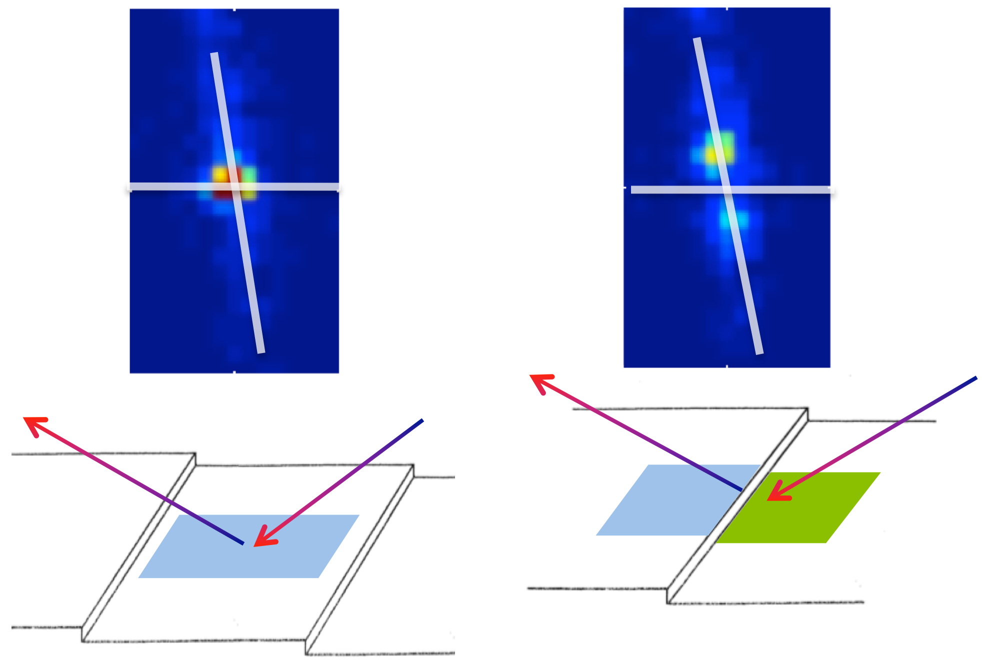
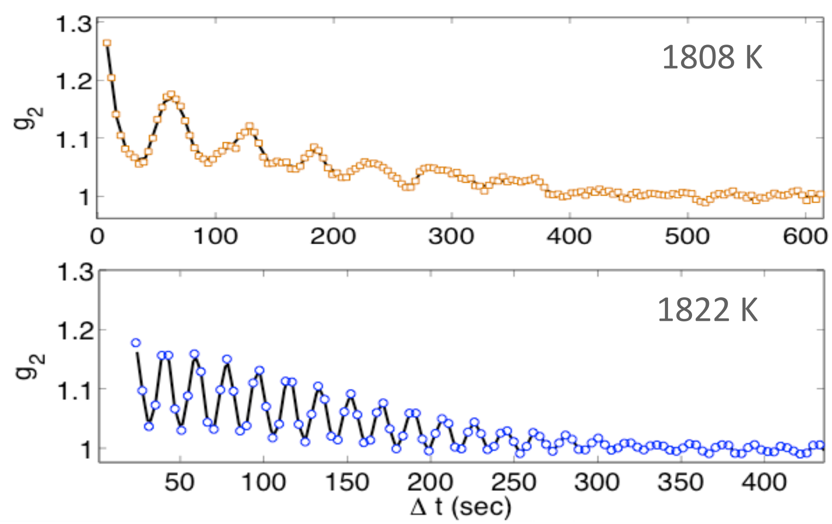
Typically 1-30 sec exposures/image and 1-3 hours of data at a time.

Coherent Surface X-ray Scattering 101

Pt (001) in vacuum at very high temperature, 1700-1830K, step-flow growth in reverse!







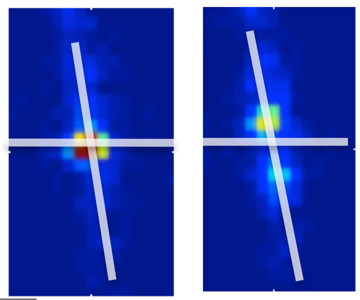
Slit size 6μm ✕ 6μm

Illuminated area: 6μm ✕ 30μm

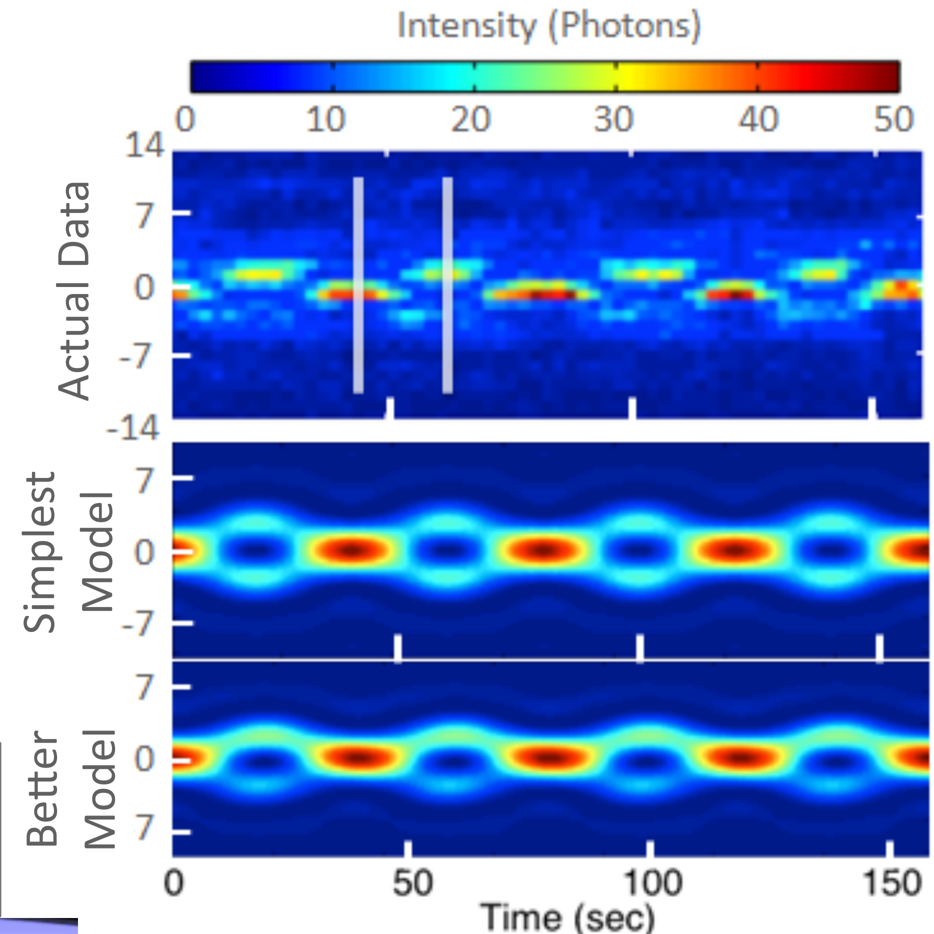
Pierce, Hennessy, Chang, Komanicky, You, submitted to *App. Phys. Lett.*

Pt (001) Step Flow

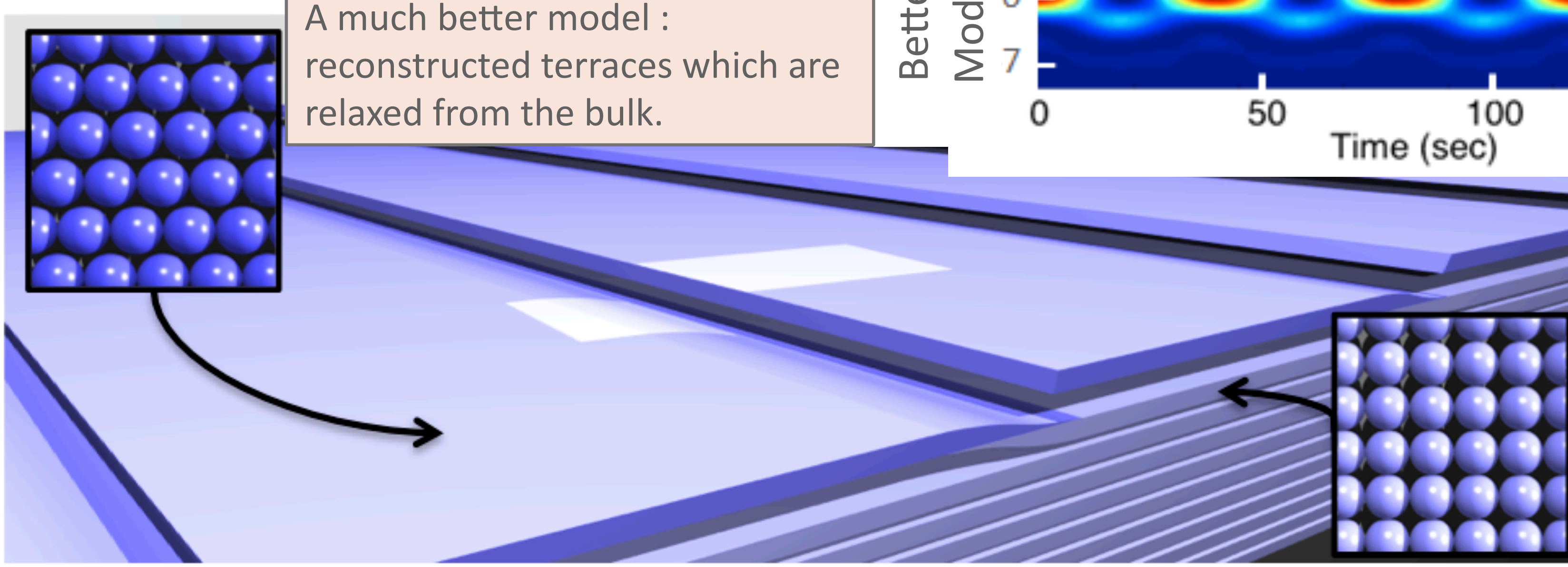
Two basic patterns which repeat with time.



Steps on a uniform surface, perfect bulk truncation.

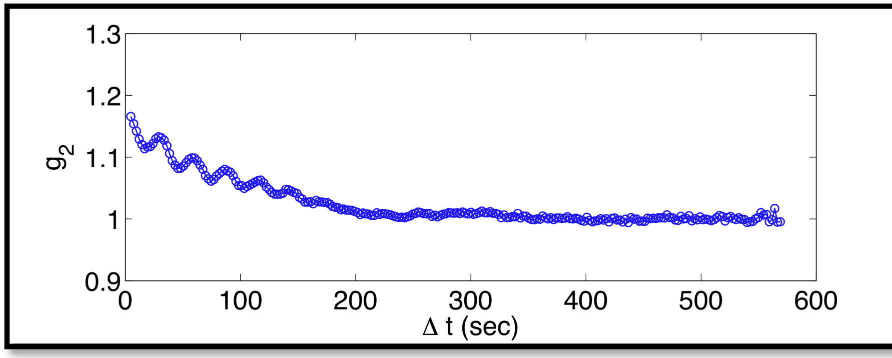


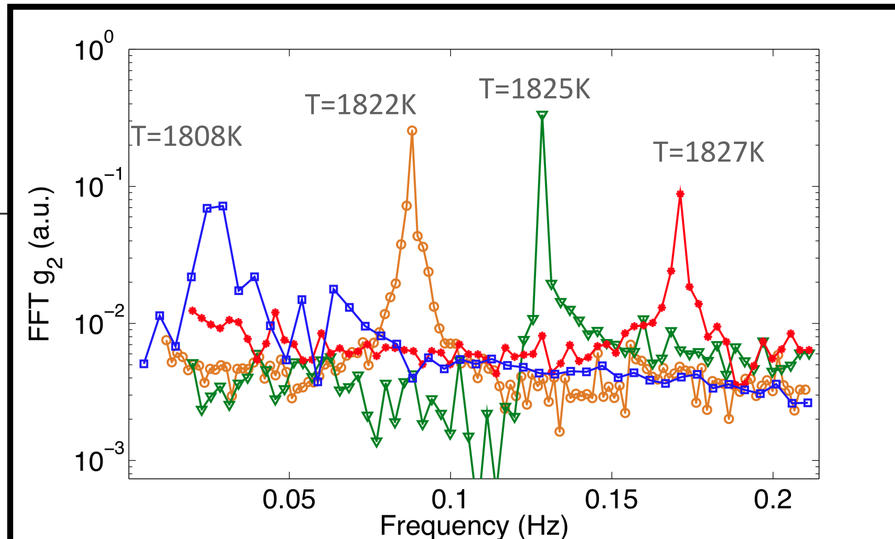
A much better model : reconstructed terraces which are relaxed from the bulk.

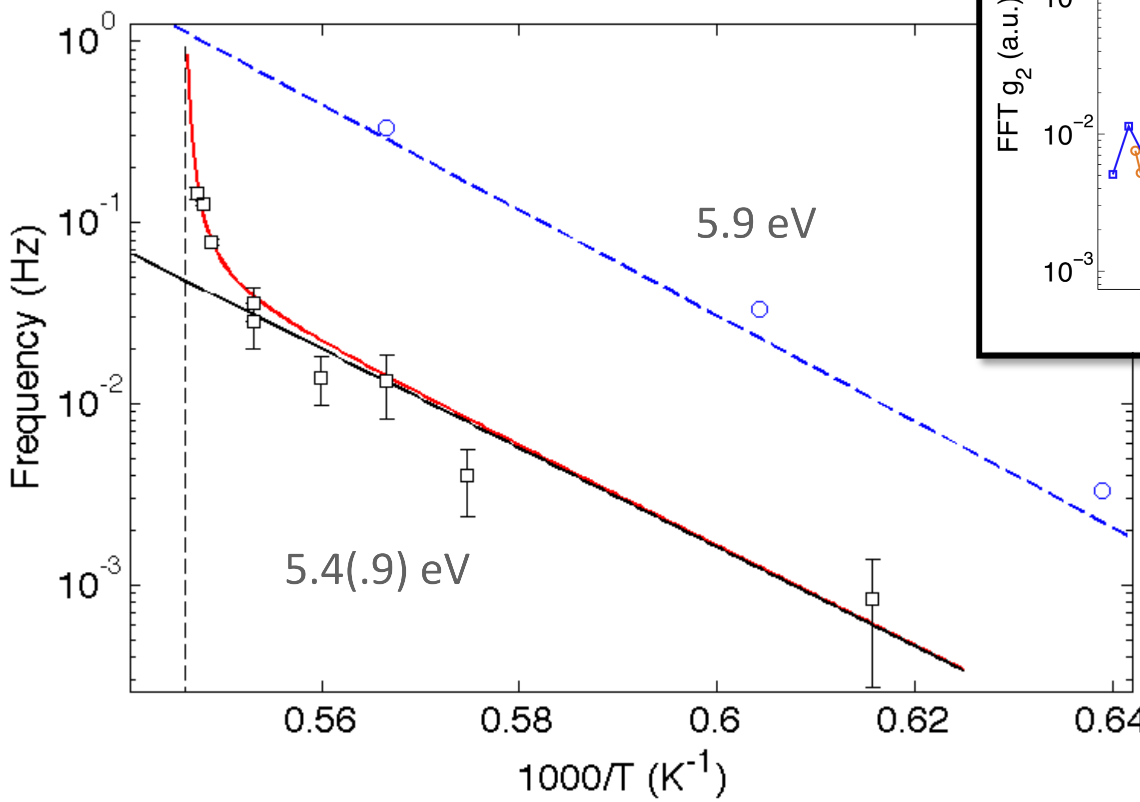


Pt (001) Step Flow

Is it real? What can you do with the temperature? We have several records of oscillations at different temperatures.



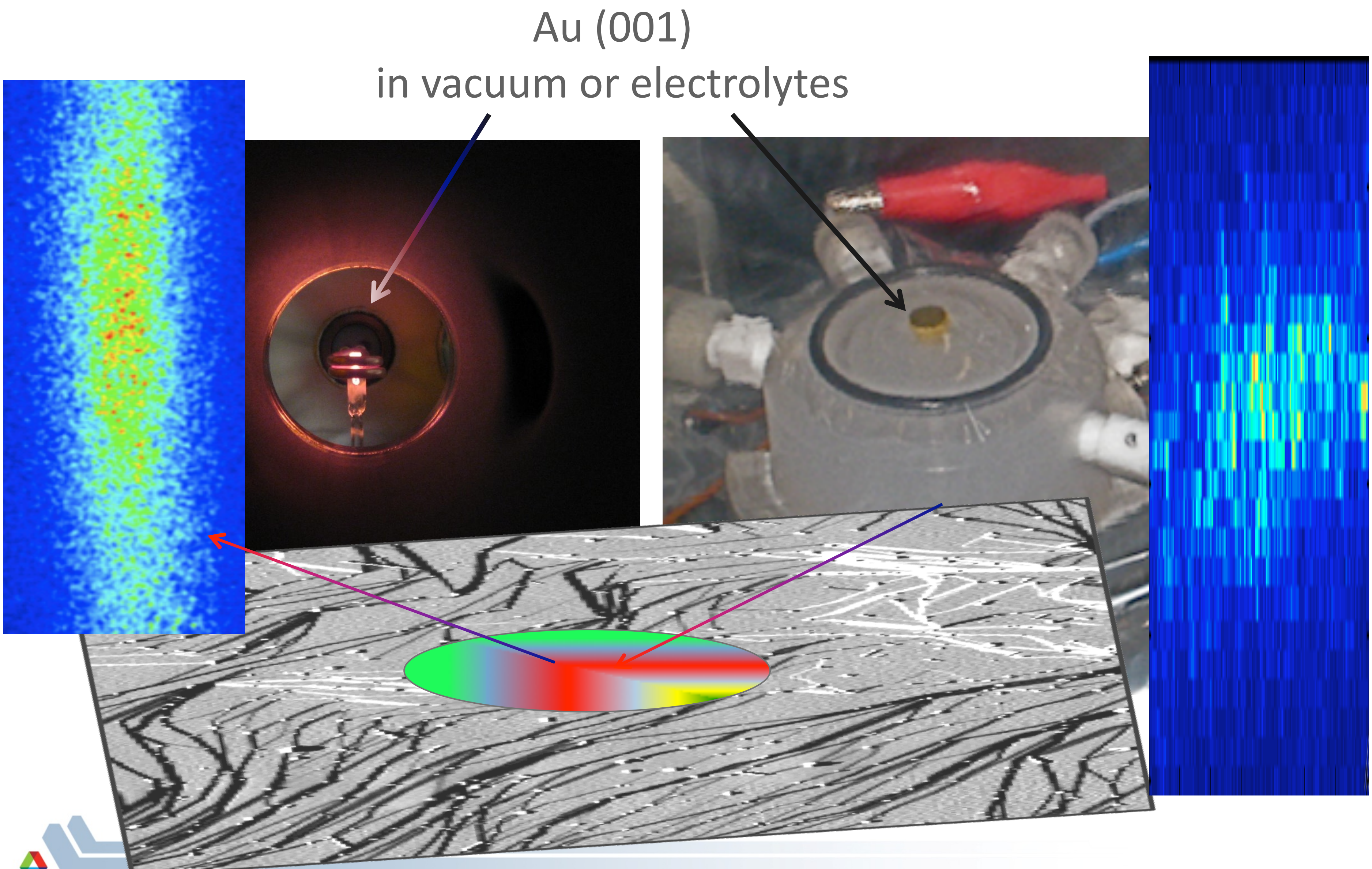




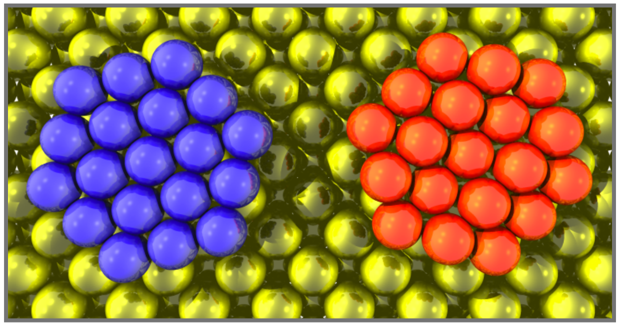
By plotting the temperature dependence of the frequencies, we obtain the known heat of sublimation! What better verification?

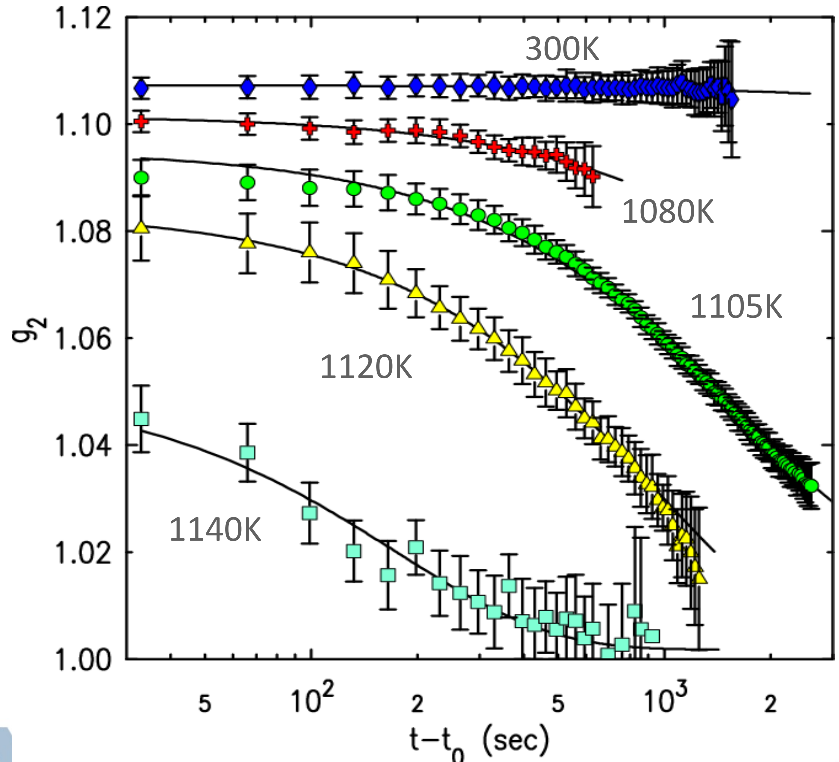
Pierce, Hennessy, Chang, Komanicky, You, submitted to *Applied Physics Letters*.

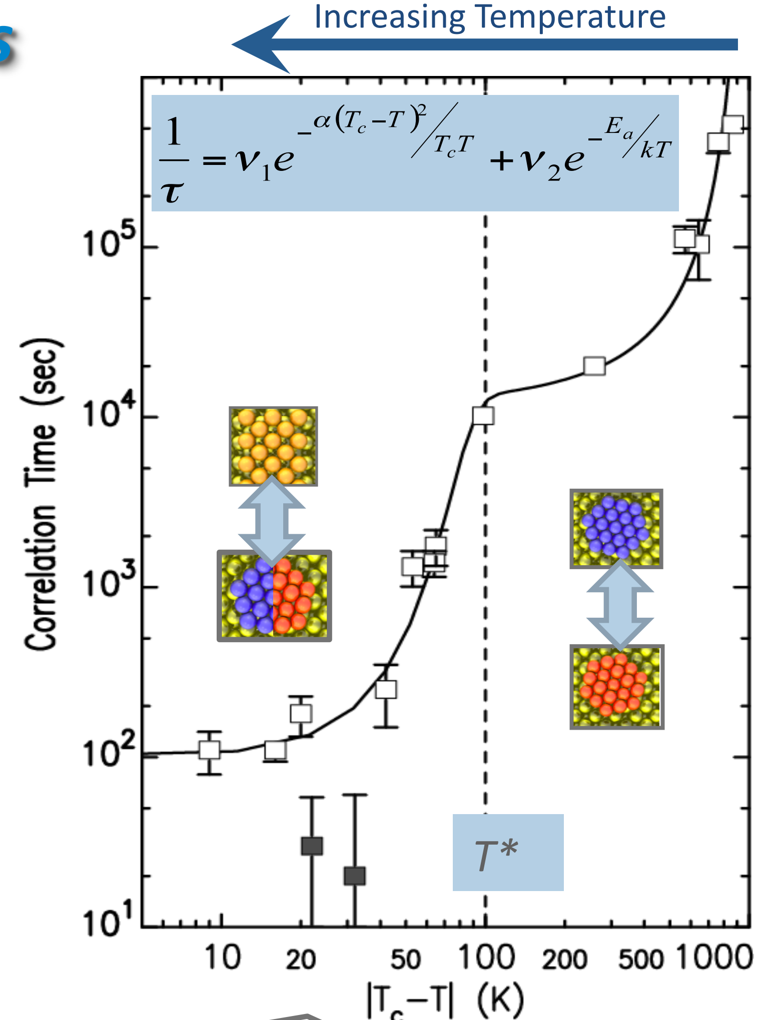
Coherent Surface X-ray Scattering 102



Au(001) reconstruction dynamics with X-ray Speckles (vacuum)



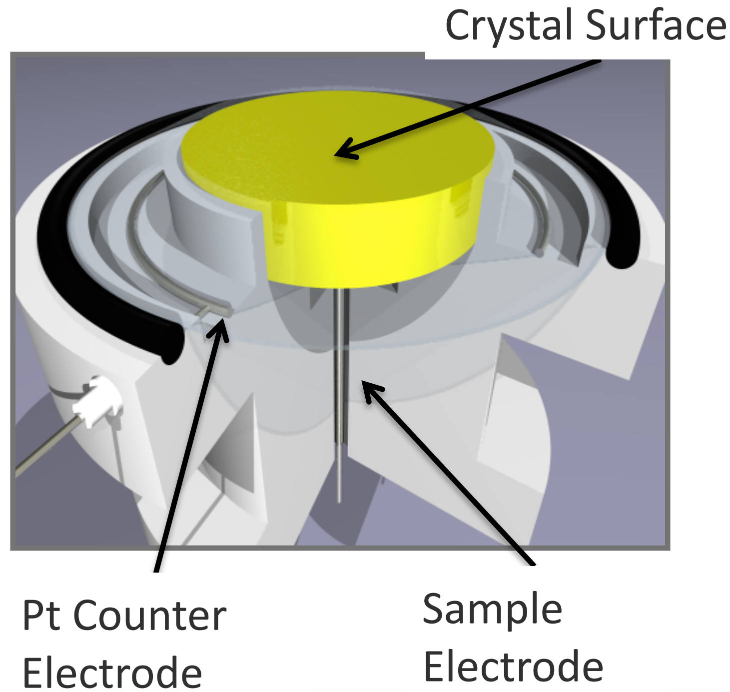


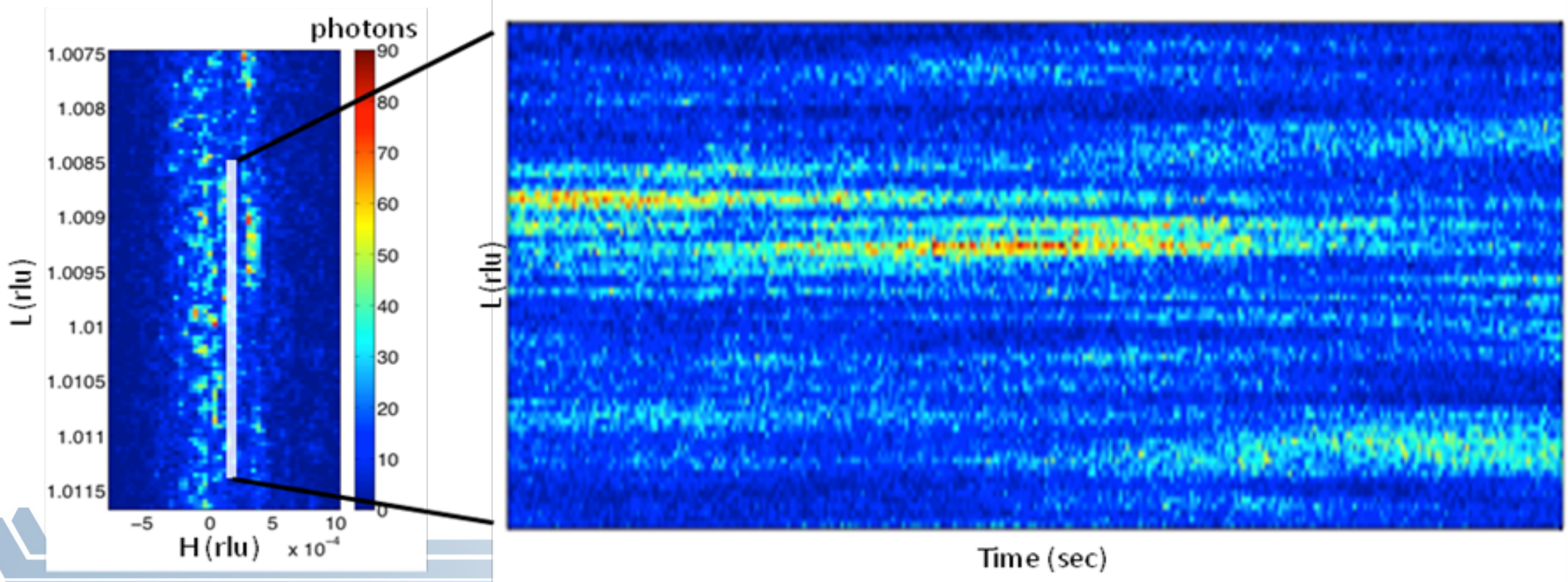


Duration (τ) vs. temperature (T). Below T^*, the speckles are mainly from rearrangements of the hex boundaries. Above T^*, atomic motions are dominated by the hex-to-square transitions.

Pierce, Chang, Hennessy, Komanicky, Sprung, Sandy, You *PRL 103* (2009) *165501*

Au (001) in $HClO_4$

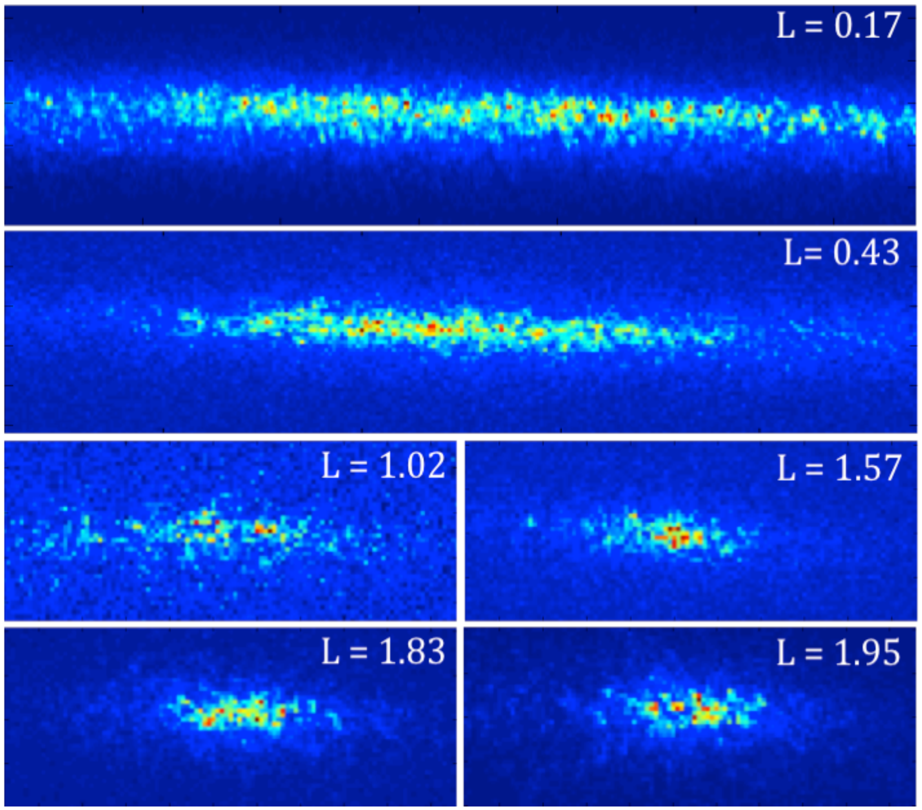




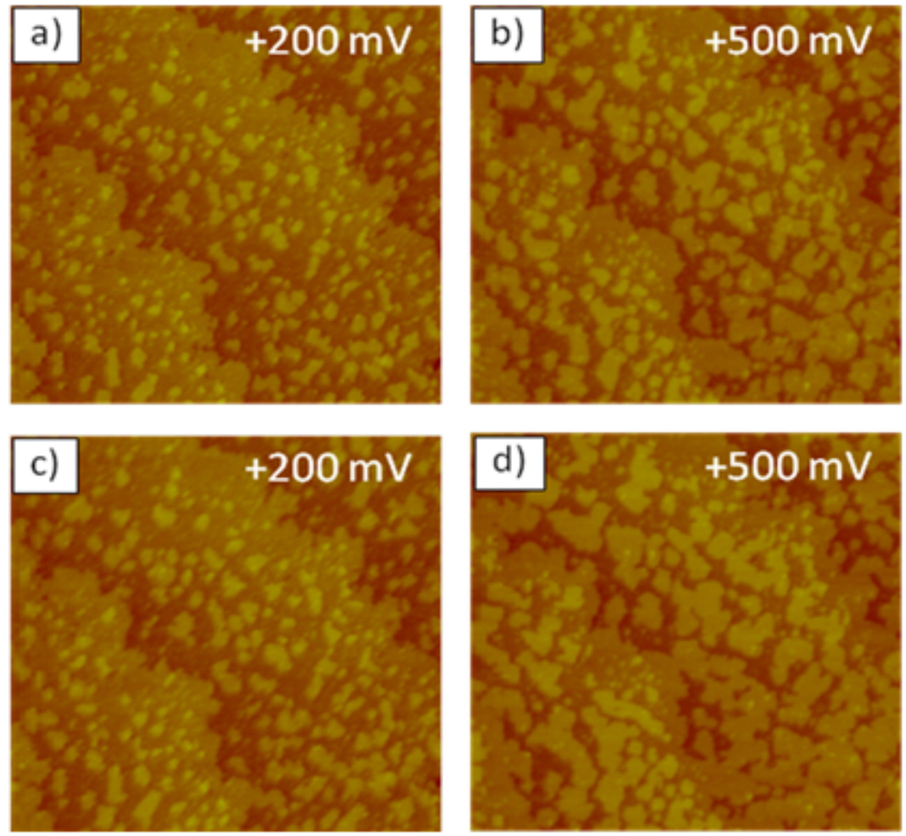
Specular Speckles: Au (001) in $HClO_4$ (aq)

Do we have enough light? Certainly enough to do science, but it's forcing us to conduct additional experiments in order to really understand this system.

In-situ XPCS



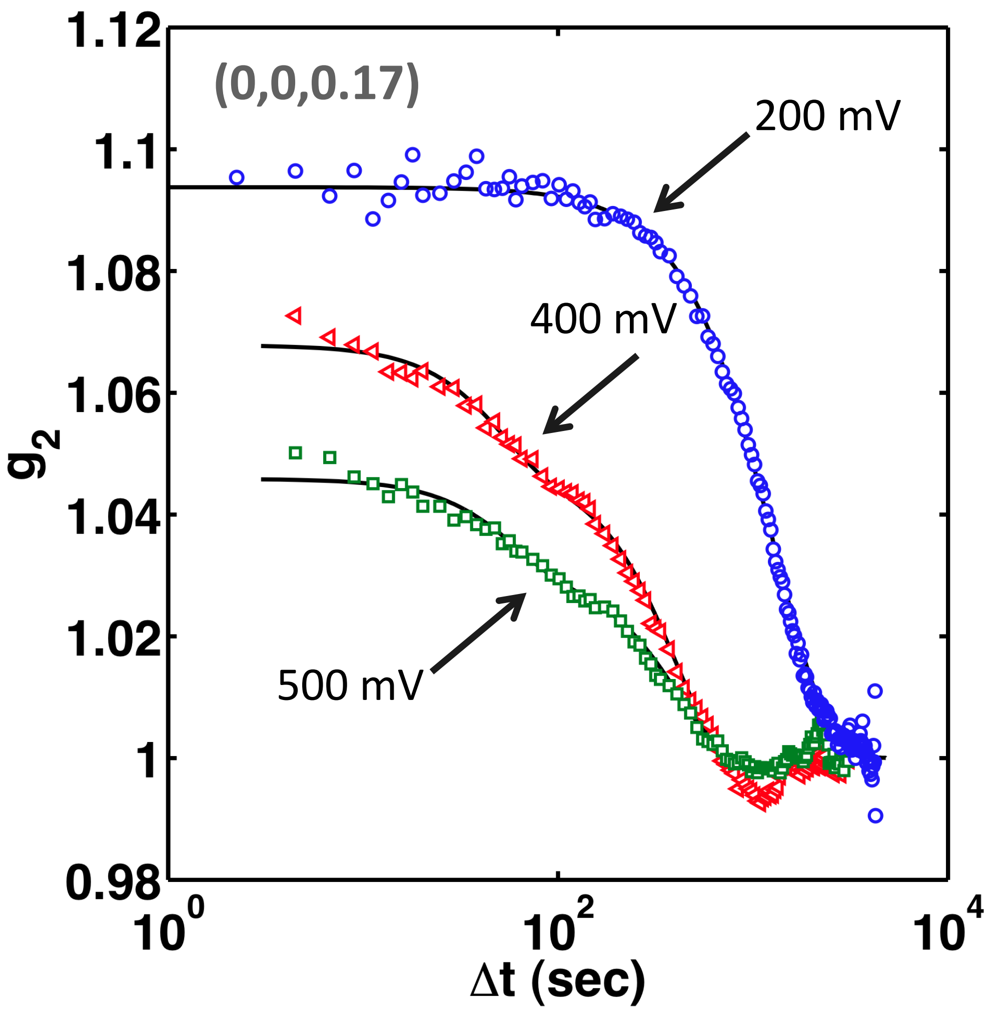
In-situ STM

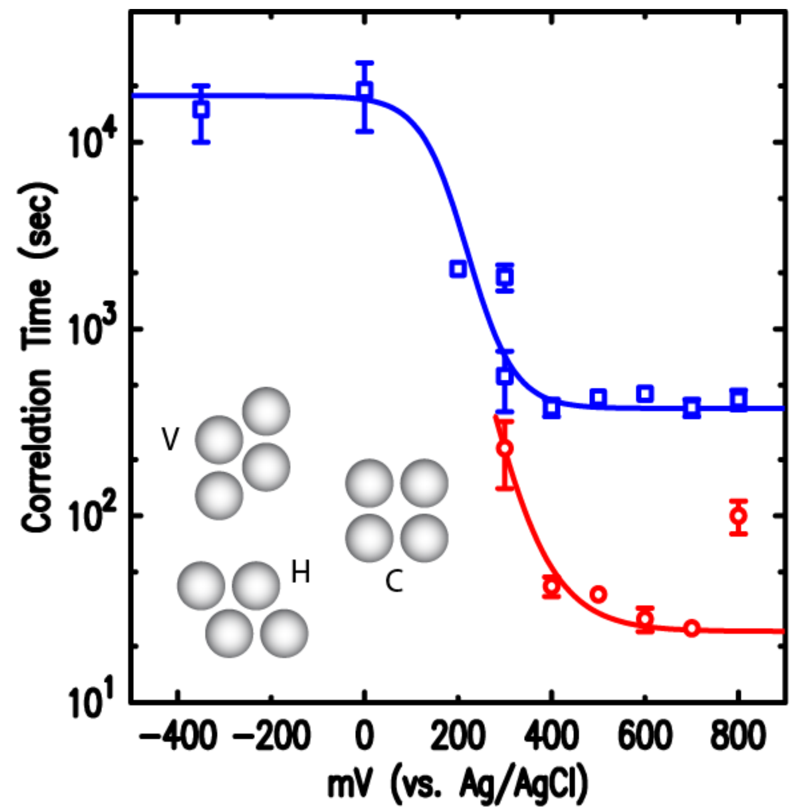


Each 400nm^2

Two time constants

q_z = 0.27 Å^{-1}





Pierce, Komanicky, Hennessy, Barbour, Su
Sandy, You, submitted to *J. Electrochemical Society.*

Speeding things up

What can we do with more light?

1) Look at systems with faster dynamics!
2) Study samples that do not scatter as strongly!
3) Study “real systems” in “real conditions” in “real time!”
4) Move towards a combination of dynamics AND imaging!

Lower Z : Not just Ag, Pd, Rh, Ru. Not just Cu, Ni, Co, Fe. Down to Si and Al?

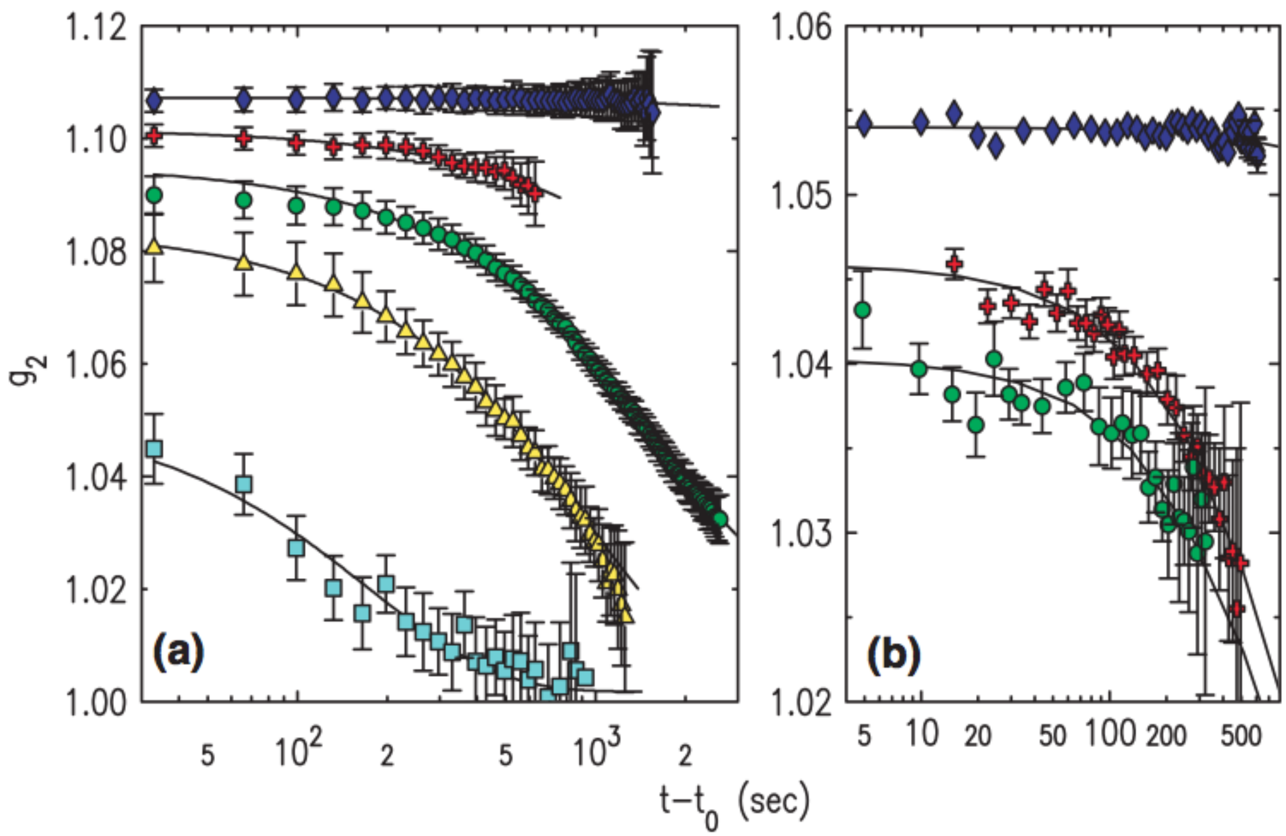
<u>In-situ studies of :</u>

Materials and Material Synthesis (Semi-conductor growth already shown)
Corrosion, Electroplating, Electrocatalysis and Energy Storage/Efficiency
Gas-phase Chemistry and Reactions
Surface Pattern Formation and Etching
Diffusion of Nano-Particles/Clusters on Surfaces
Alloy Chemical Migration/Separation (very often occurring at surface)
Geothermal Systems

Moving off-specular

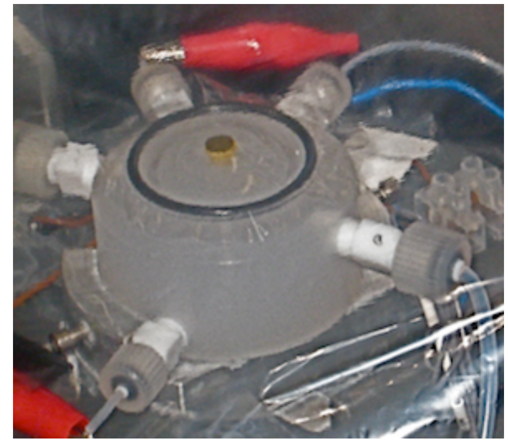
Au (001) at the (001) position.

Au (001) at the "hex" condition



Notice both the decrease in contrast and the increase in decay rate. Off-specular scattering presents additional challenges that increased coherent flux will greatly help!

Speeding up the electrolyte



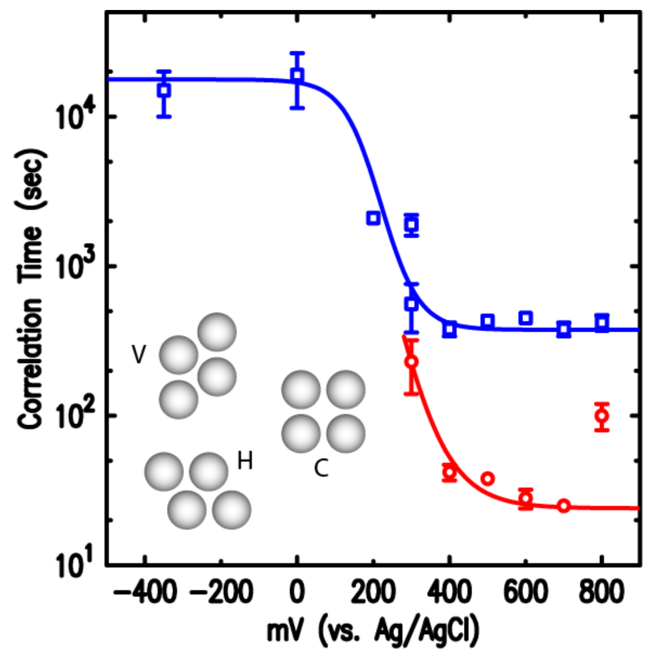
In the electrochemistry results presented, you may have already noticed that we have a drop in contrast and that the higher potential curves show an "upward" cusp. One easy thing we can do is to add a strongly interacting species to the electrolyte.

For instance, 1M $HClO_4$ + 0.1mM KI

In this case some of the dynamics appear to be too fast for us to currently measure.

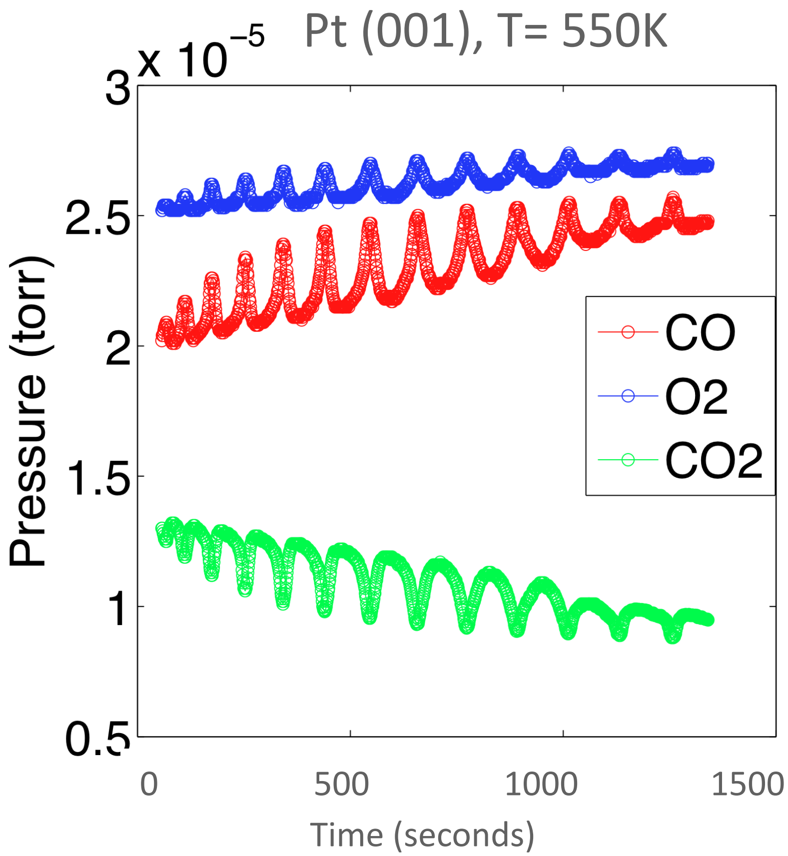
For instance: Gao and Weaver, *J. Phys. Chem.* **97**, 8685 (1993).

Non-equilibrium also becomes something one could tackle?

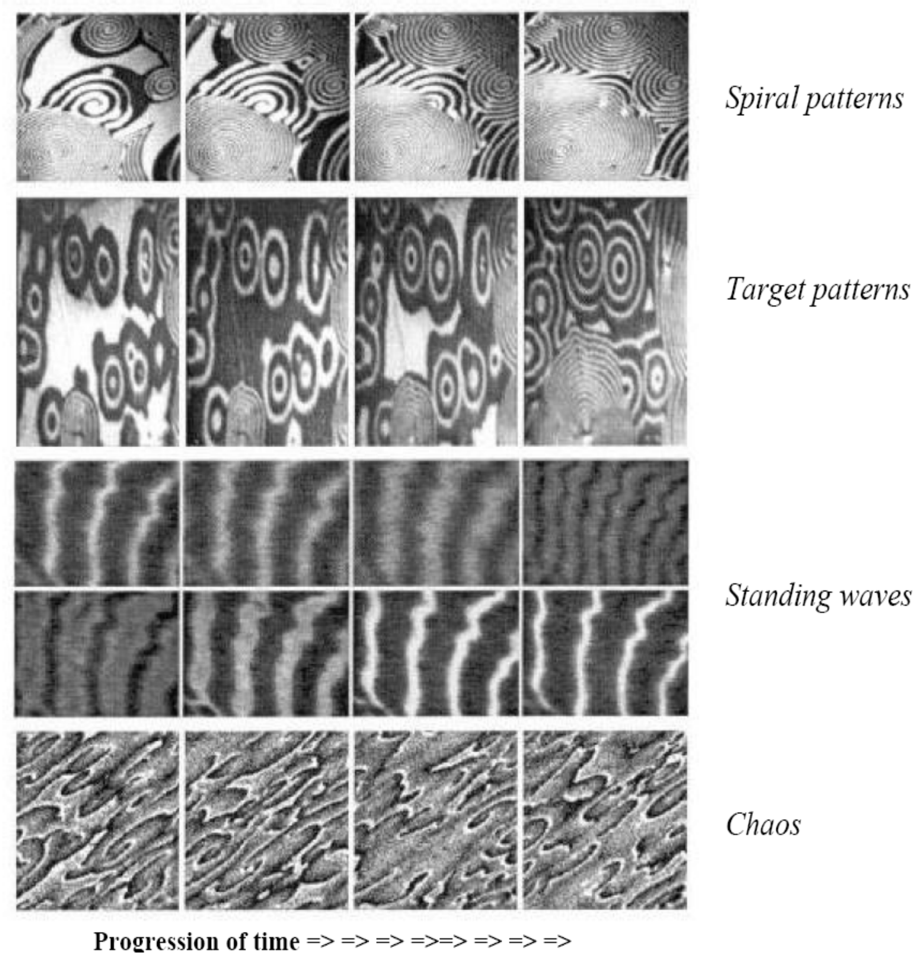


Gas-phase Reactions

CO oxidation "oscillations" on Pt (001)



Constant temperature and total pressure.

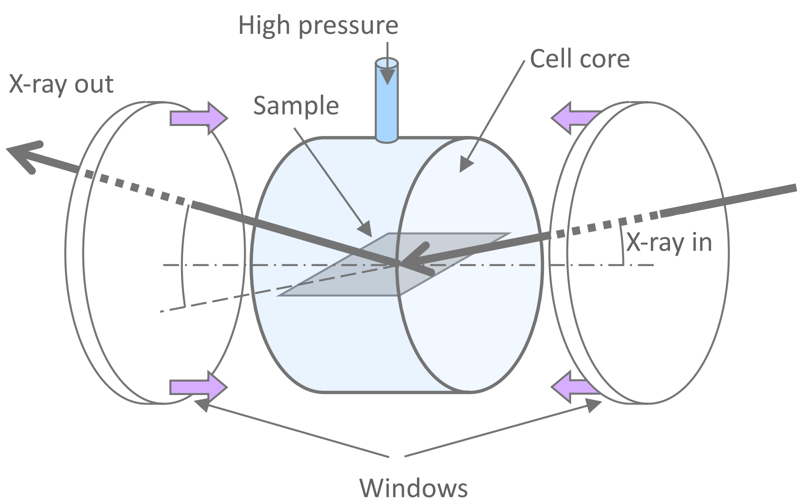


Platinum surfaces imaged by photoemission electron microscopy. Light and dark regions are associated with oxidized and reduced regions of the surface (From the Fritz-Haber-Institute of the Max-Planck-Society, www.fhi-berlin.mpg.de/surfimag).

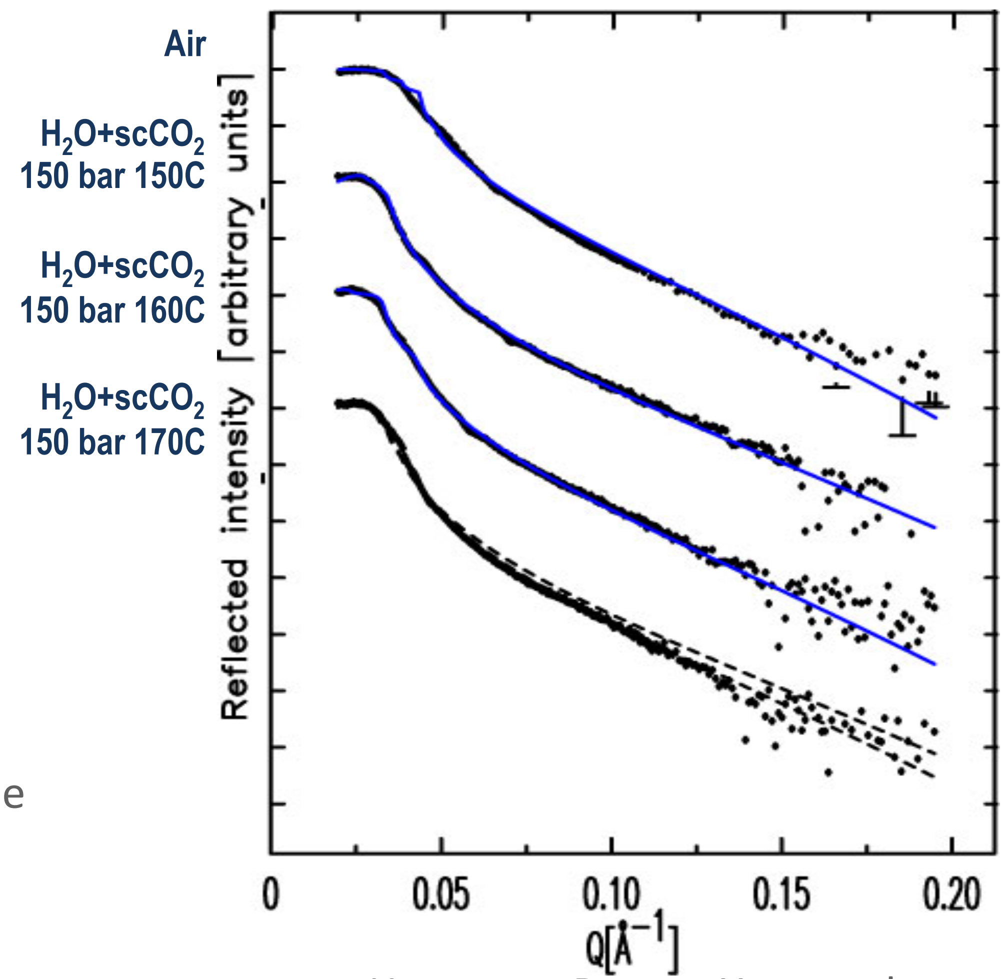
Ertl, G., P. R. Norton, and J. Rüstig, Phys. Rev. Lett. 49, 177 (1982).
Ertl, G. Science 254, 1750 (1991)

Solid-Fluid Interface Under Pressure: Supercritical CO2 and water on mineral surfaces

Roughening of mineral interfaces under supercritical CO_2 / H_2O



Orthoclase feldspar reflectivity:



•Orthoclase begins to dissolve in binary mixture above ≈163° C

Once equilibrium has been reached, is the surface static or still evolving? Reacting? Dissolving? This really will need a large increase in flux!

Hennessy, Bearat, You, et al in preparation.

Solid-Fluid Interface Under Pressure: Supercritical CO2 and water on mineral surfaces

More Light!

1-10 microns is a good range of sizes.
Smaller is also useful.

Timing requirements 1-10ms resolution
(though data output is a challenge)
Readout & Dynamic Range & Signal will set time.

10-20 keV is a good range.
Higher does have advantages, but I think the big
Payoff will be moving from 7-8 keV up to 11+ keV.

In-situ and high-Q mean a substantial amount of “real-estate”
at the diffractometer.

Hennessy, Bearat, You, et al
in preparation.

Summary

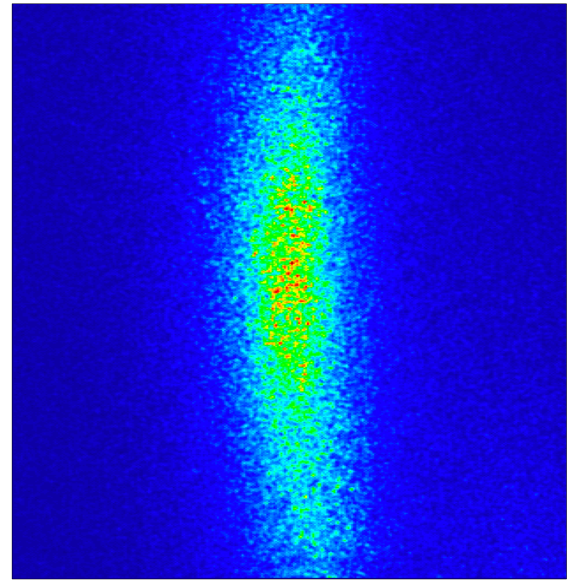
1) We have a x-ray technique that measures surface equilibrium dynamics.
2) High Z vacuum studies successful.
3) Simple high Z electrochemical studies successful.
4) Preliminary data obtained for the effect of NaI and KI. Promising, but also beginning to move out of our current range.
5) Gas-phase surface dynamics, promising, but definitely beyond our current experiments.

Future Work

6) Move to weaker scattering systems (metal-oxide on metal, or metal-oxides).
7) Push further in-situ study, current systems but faster timescales as well as new systems.

mpierce@anl.gov

Surface Speckles



Thank you!