X-ray Photon Correlation Spectroscopy at Surfaces : Challenges and Opportunities for in-situ Surface and Electrochemistry Studies.

January 10th, 2012
X-ray Interface Science Workshop
Advanced Photon Source
Argonne National Laboratory

Michael S Pierce
Department of Physics,
Rochester Institute of Technology

Collaborators:

Hoydoo You[1]
Alec Sandy[3]
Vladimir Komanicky[2]
Daniel Hennessy[1]
Andi Barbour[1]
Jun-Dar Su[3]
Kee-Chul Chang[1]
Joseph Strzalka[3]
Chenhui Zhu[1]

1) Materials Science Division, Argonne National Laboratory
2) Faculty of Sciences, Safarik University, Slovakia
3) Advanced Light Source, Argonne National Laboratory

[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

[2)]Work at Safarik U. is supported by Slovak grant VEGA 1/0138/10 and VVCE-0058-007.

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 and more facilities!

- 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 just beyond our reach)?
- What becomes possible in the future?

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).

CAUTION
X-RAY RADIATION
CAUTION
X-RAY RADIATION

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

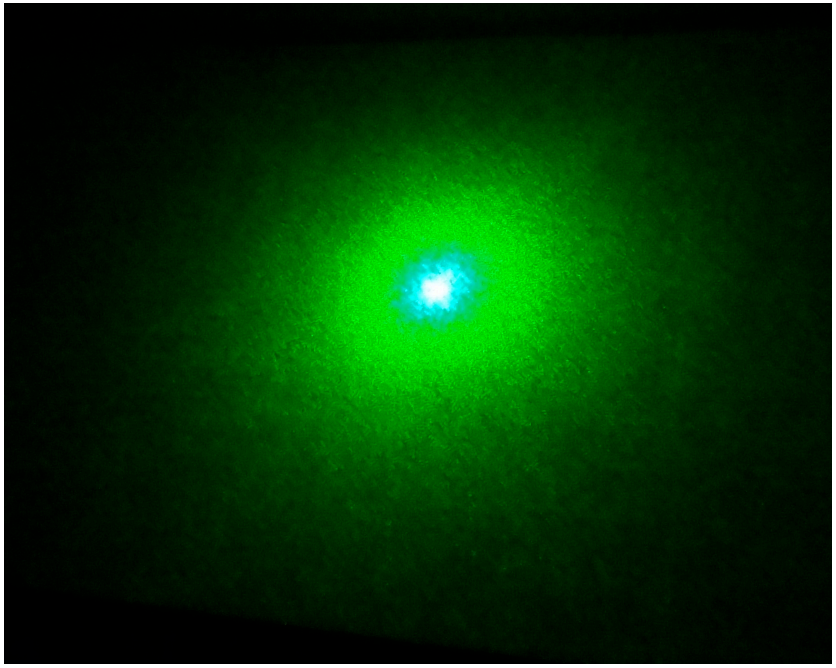
XPCS from films, interfaces, 2-d structures, and surfaces

Developments in Synchrotron and Detector Science

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

What is Coherent Scattering?
What is XPCS?

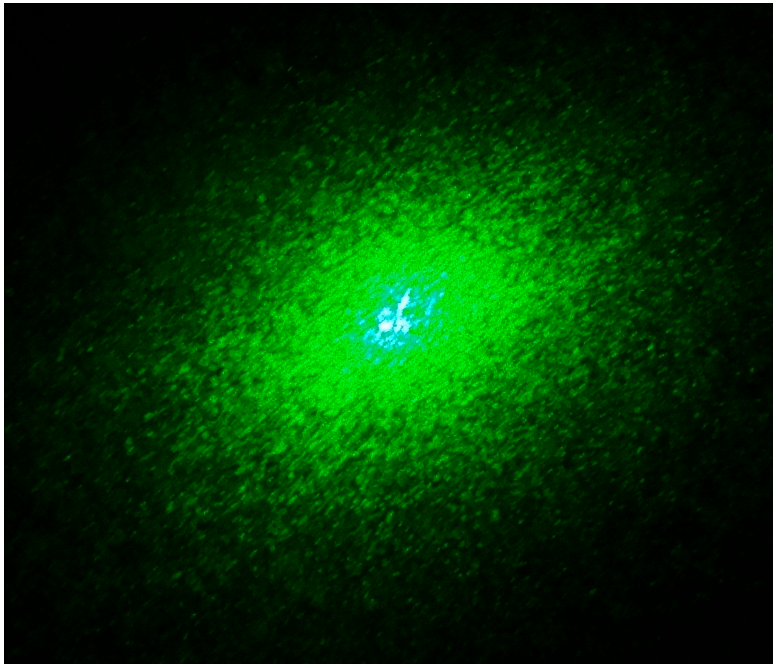
Low Coherence



Short range order: size, intensity, position, shape, etc…

State changes, intensity changes.
In equilibrium, intensity constant.

High Coherence

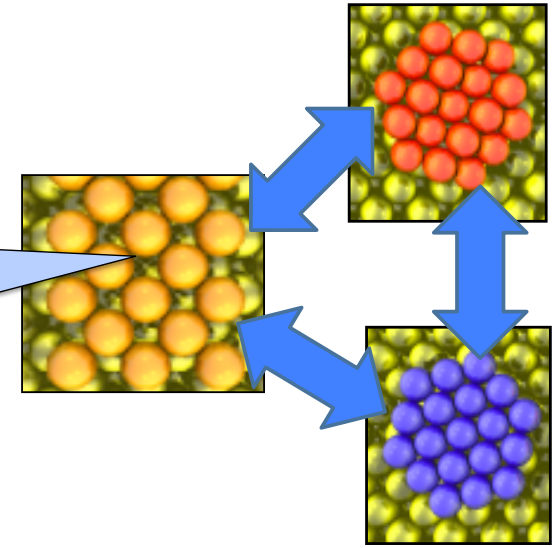


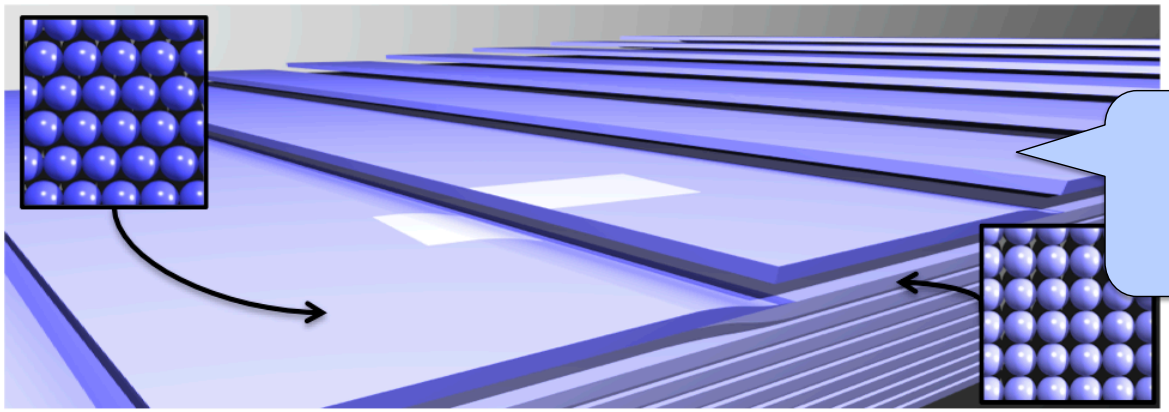
All of that, plus information about the "long range" over the illuminated area.

As the state changes, the intensity changes. But in quasi-equilibrium, the position and intensity of the speckles fluctuate.

What have we studied? (successfully)

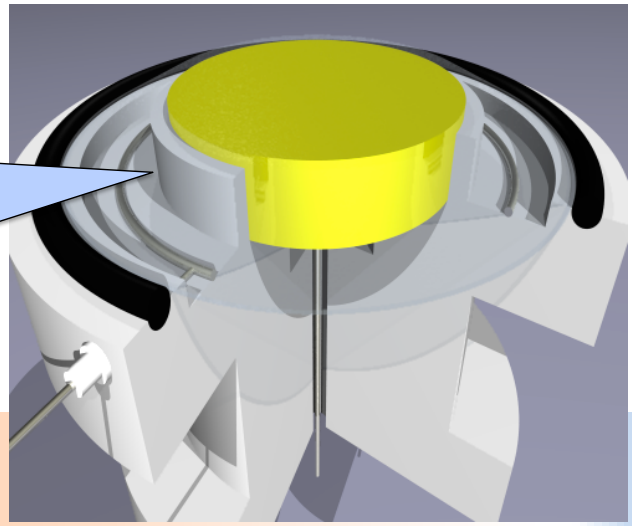
• Au (001) surface in vacuum, over a large temperature range. The local surface phase will vary, and that rate of variation is temperature dependent.





• Sublimation effects on Pt (001) surface in vacuum at very high temperature.

• Au (001) and Au (111) in electrolyte. We can study the effects of solution, impurities, and applied potential on surface dynamics.



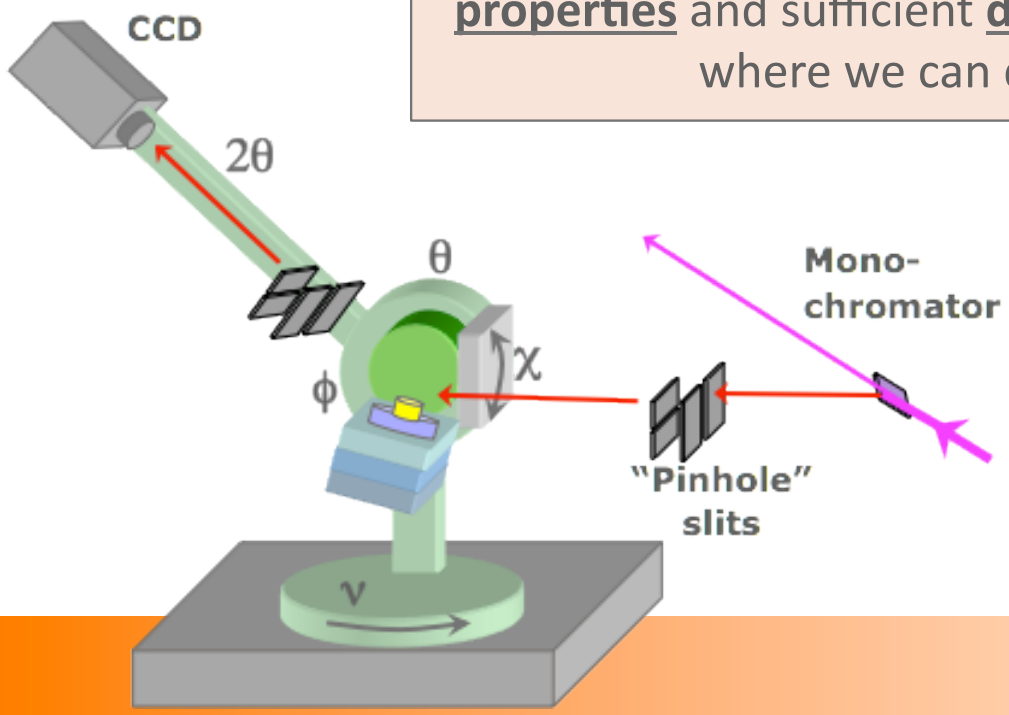
Experiments done at Advanced Photon Source, Beamline 8-ID

- 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 **diffractometer** limit where we can do this.



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

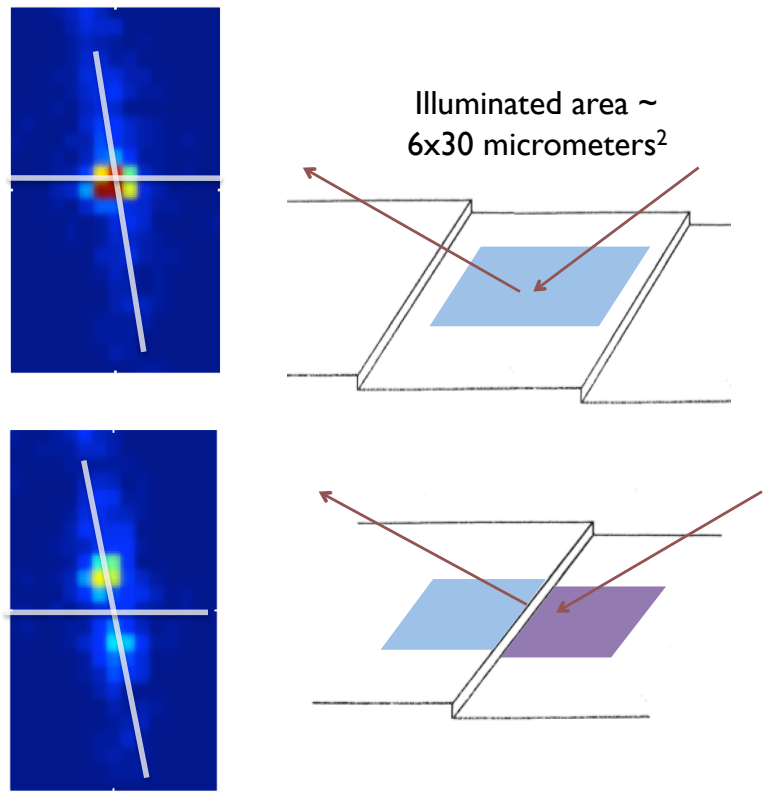
~ 10^{10} x-rays/sec on sample
~ 10^{3} – 10^{4} x-rays/sec as signal
Typically 1-30 sec exposures/image
and 1-3 hours of data at a time.

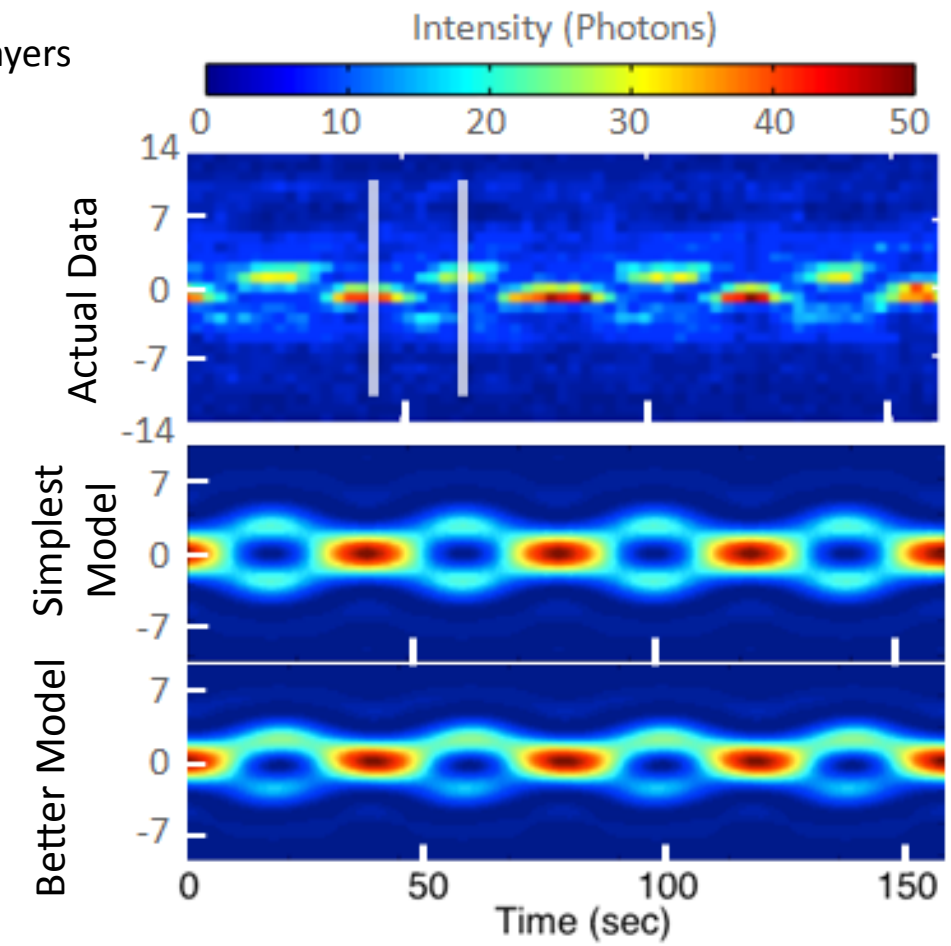
R·I·T

Platinum (001) Surface Step-Flow

We can model the observed oscillation

At the (001) condition for an FCC, you find that layers ½ unit cell apart interfere destructively.



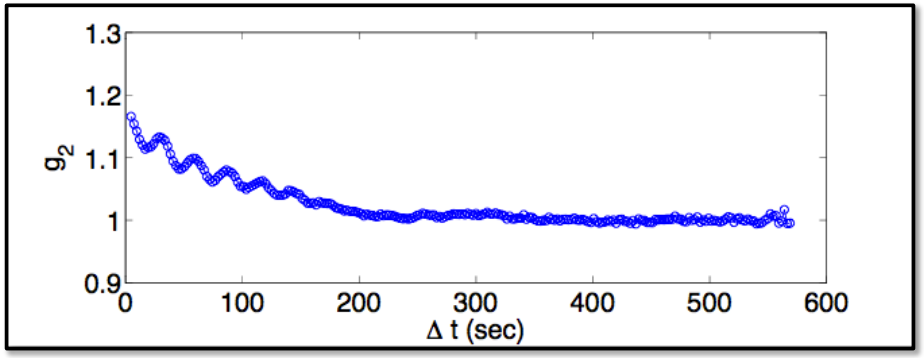


The rate of oscillation can be used to measure the vapor pressure of Pt.

M.S. Pierce, et al. Applied Physics Letters 99, 121910 (2011).

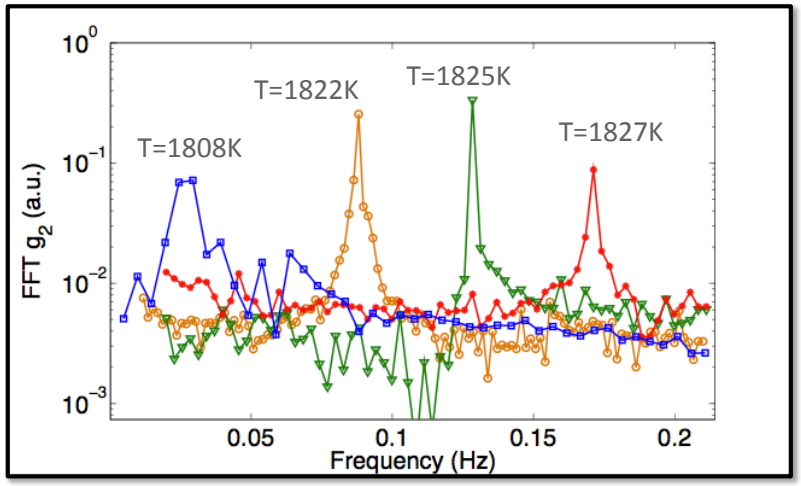
R·I·T

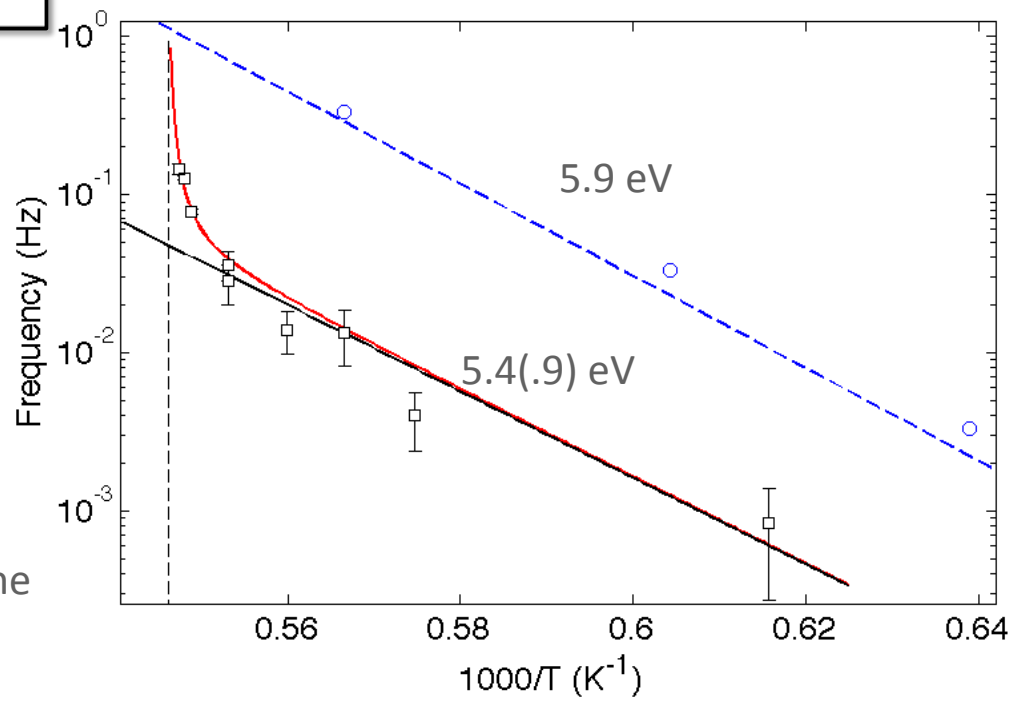
Platinum (001) Surface Step-Flow



Is it real? What can you do with the temperature?

We have several records of oscillations at different temperatures.



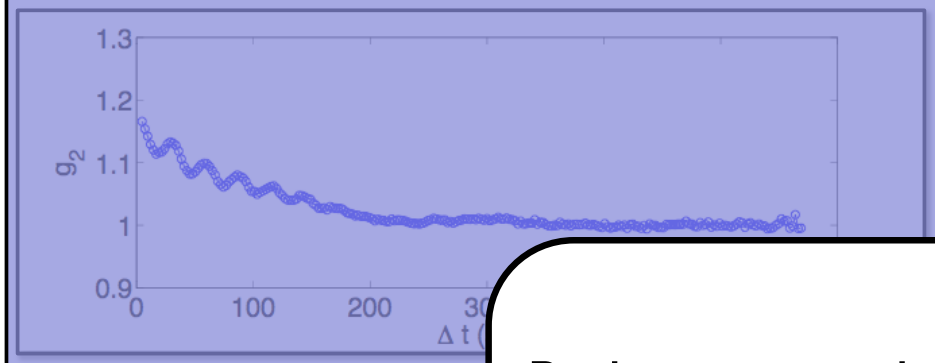


By plotting the temperature dependence of the frequencies, we obtain the known heat of sublimation! What better verification?

M.S. Pierce, et al. Applied Physics Letters 99, 121910 (2011).

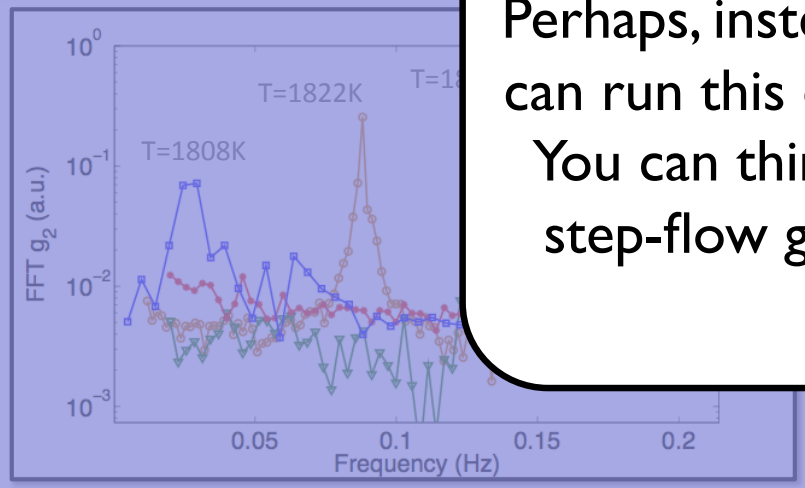
R·I·T

Platinum (001) Surface Step-Flow

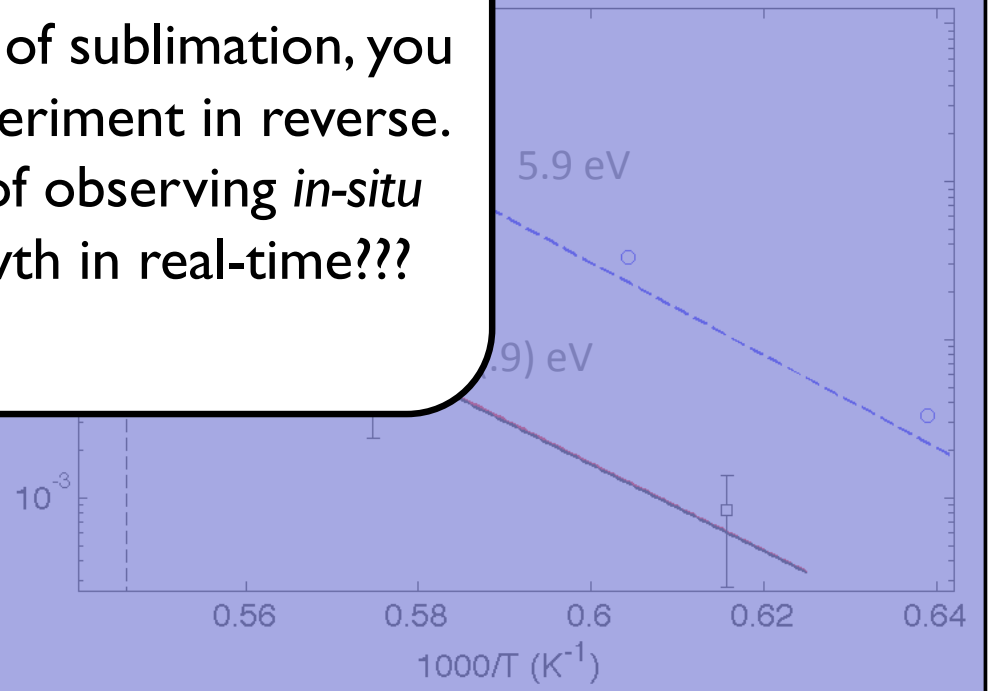


Is it real? What can you do with the temperature?

We have several records of oscillations at different temperatures.



Perhaps, instead of sublimation, you can run this experiment in reverse. You can think of observing *in-situ* step-flow growth in real-time???



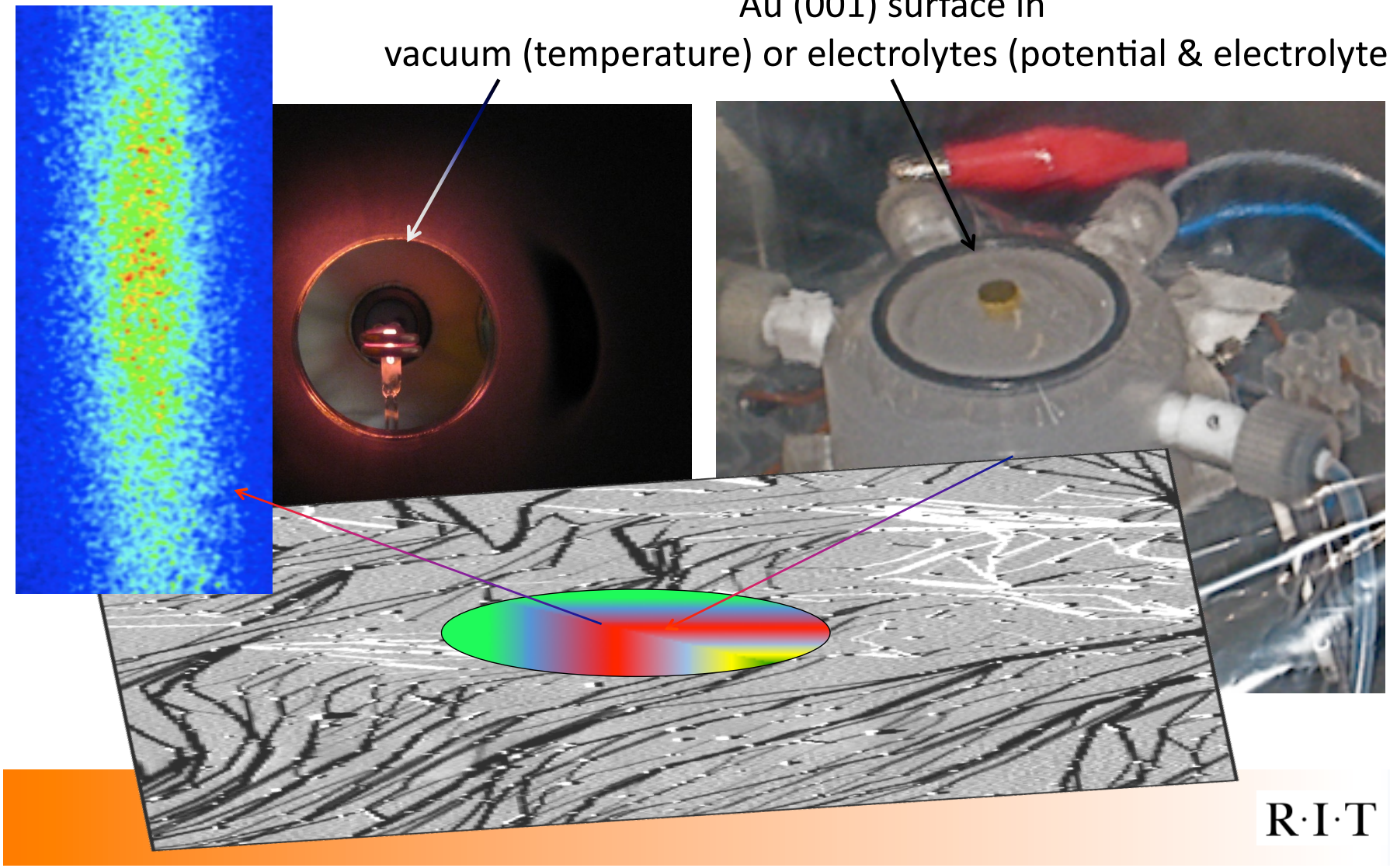
By plotting the temperature dependence of the frequencies, we obtain the known heat of sublimation! What better verification?

M.S. Pierce, et al. Applied Physics Letters 99, 121910 (2011).

R·I·T

Coherent Surface Scattering from Au (001)

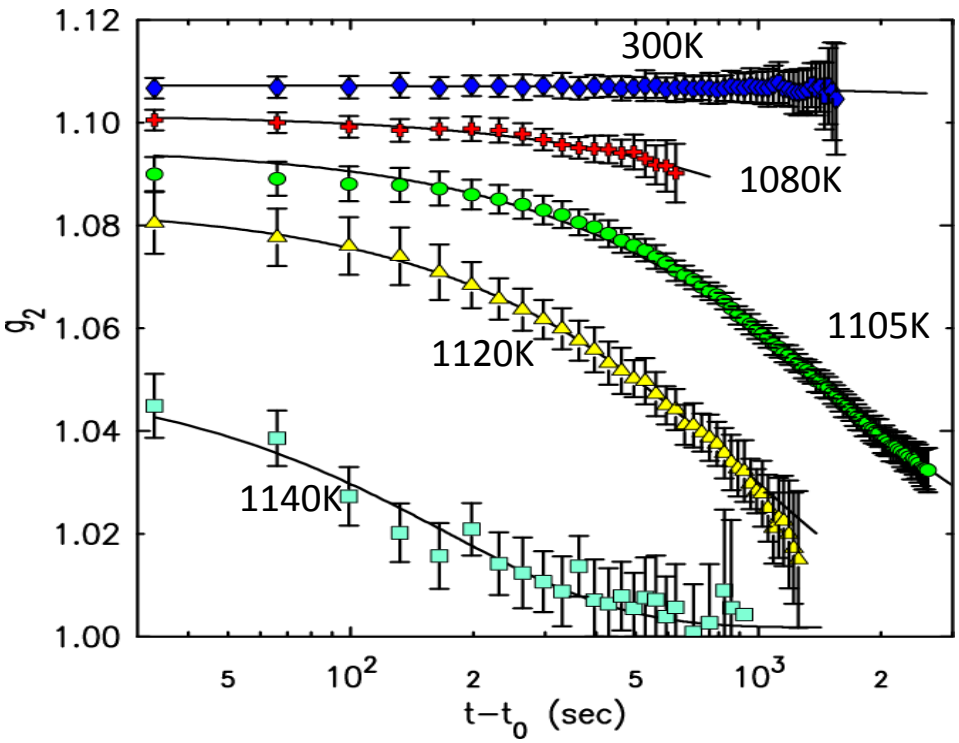
Au (001) surface in
vacuum (temperature) or electrolytes (potential & electrolyte)

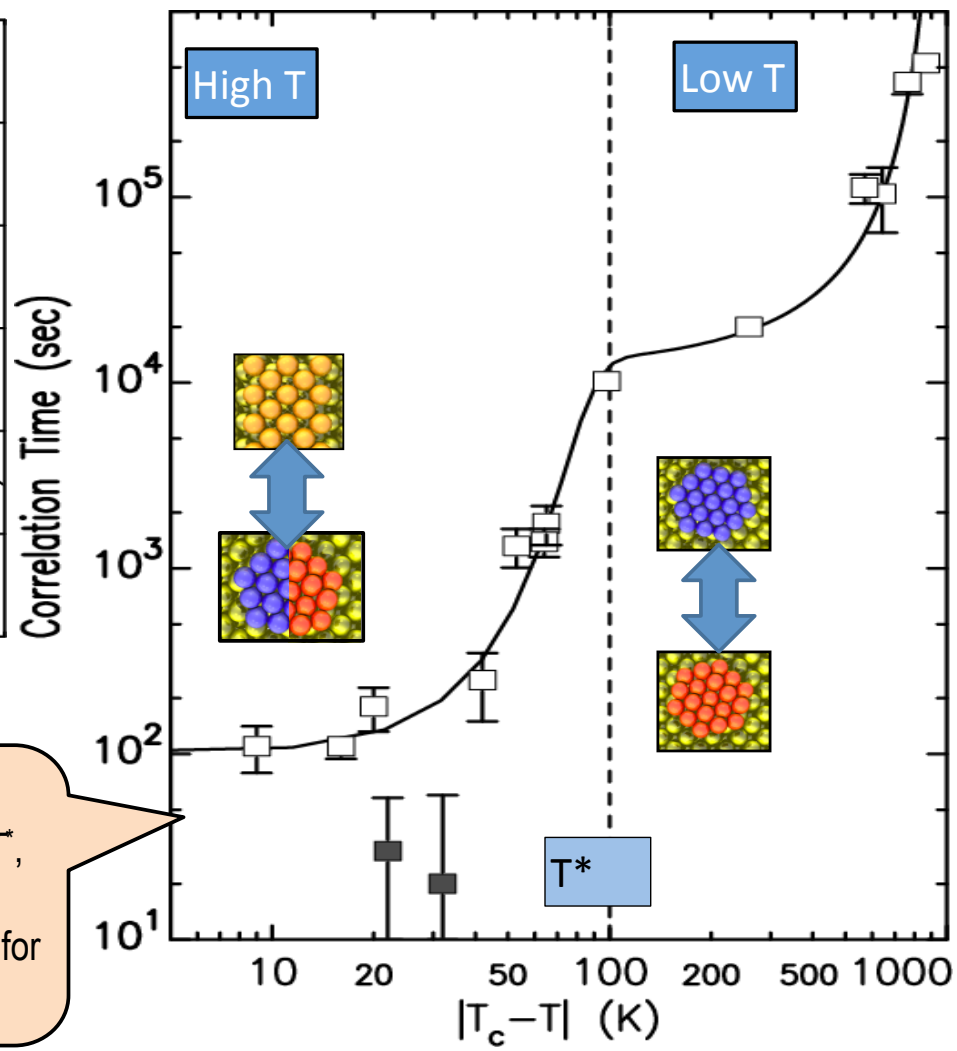


R·I·T

Two different time scale regimes

$$\frac{1}{\tau} = \nu_1 e^{-\alpha (T_c - T)^2 / T_c T} + \nu_2 e^{-E_a / kT}$$





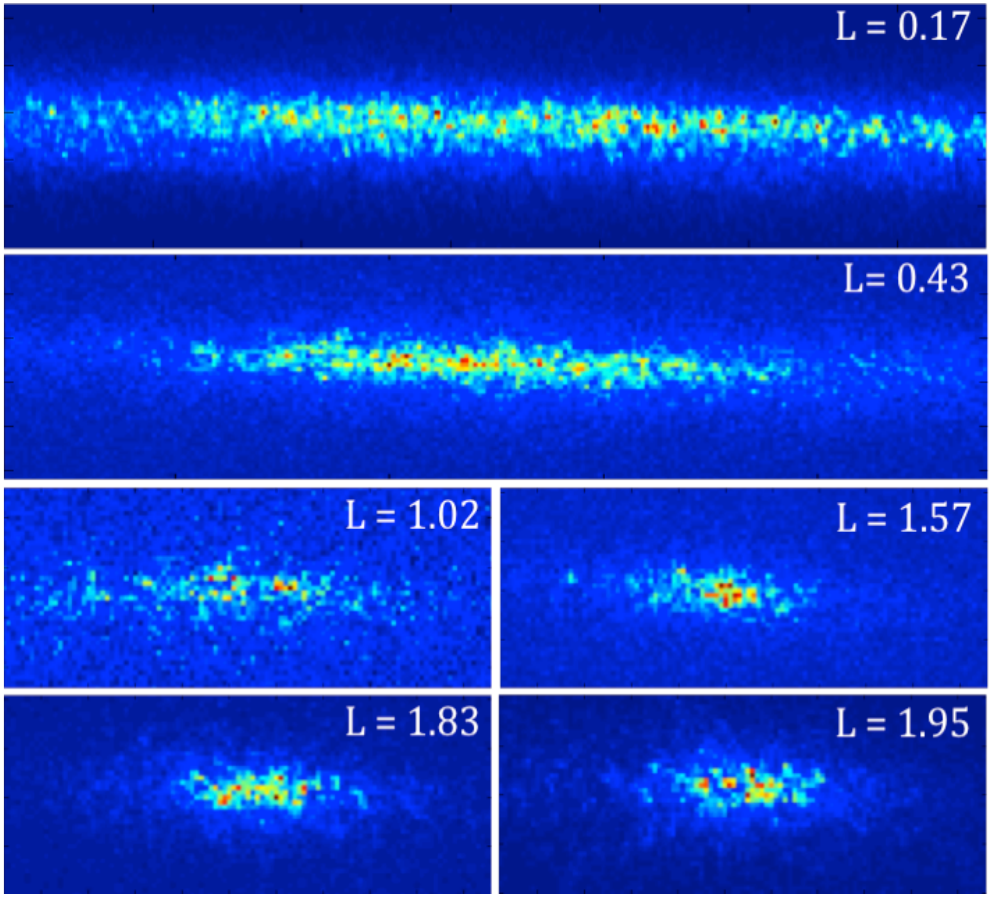
Duration (τ) vs. temperature (T). Below T^*, the speckles are mainly from rearrangements of the hex boundaries. Above T^*, atomic motions are dominated by the hex-to-square transitions. Sublimation is not as important here as it will be for Platinum.

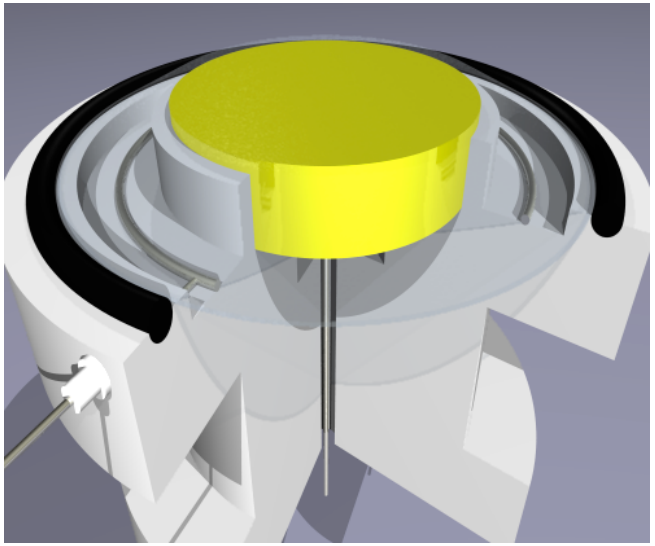
M.S. Pierce, et al. Physical Review Letters 103, 155501 (2009).

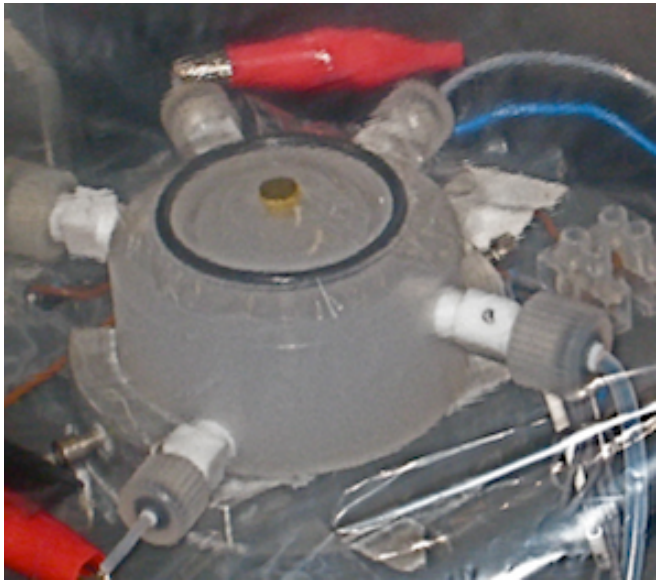
R·I·T

Electrochemical Studies

Moving from vacuum, to something closer to the "real-systems, in real-time" with Au (001) in 0.1M HClO4



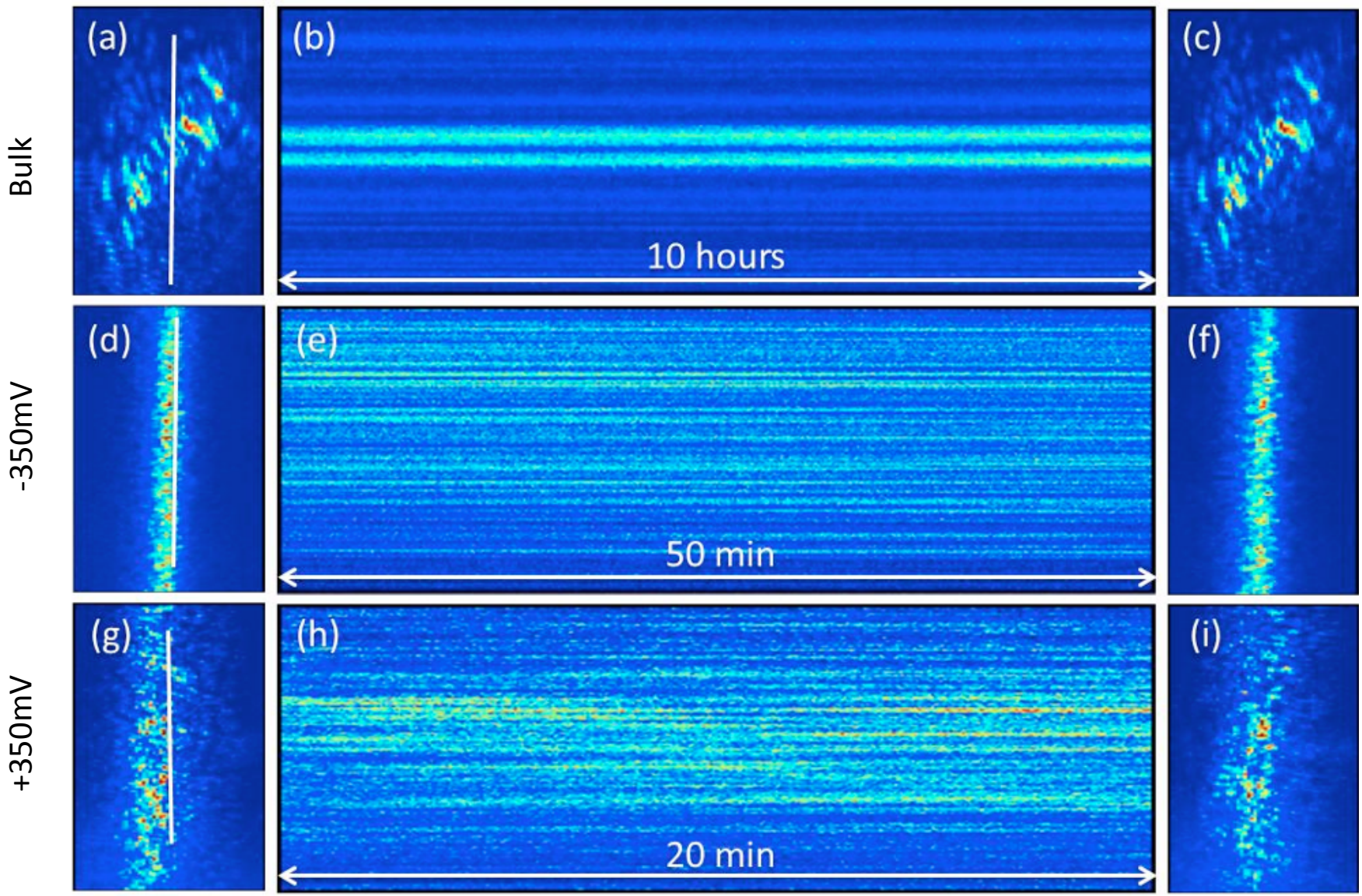




M.S. Pierce, et al. Electrochemical Society Transactions 35, 71 (2011).

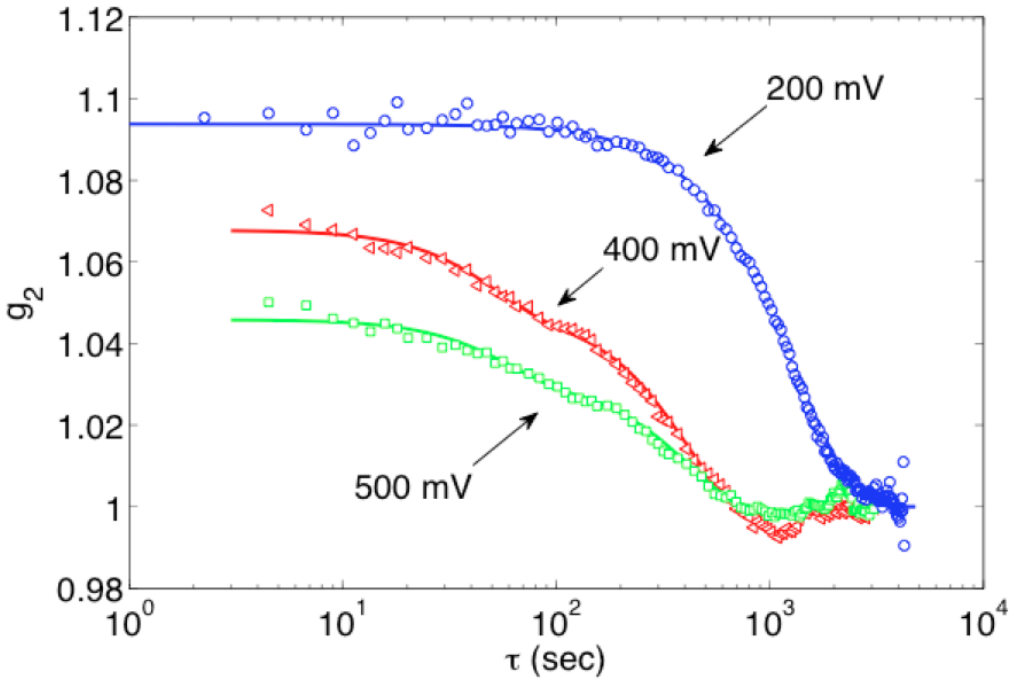
R·I·T

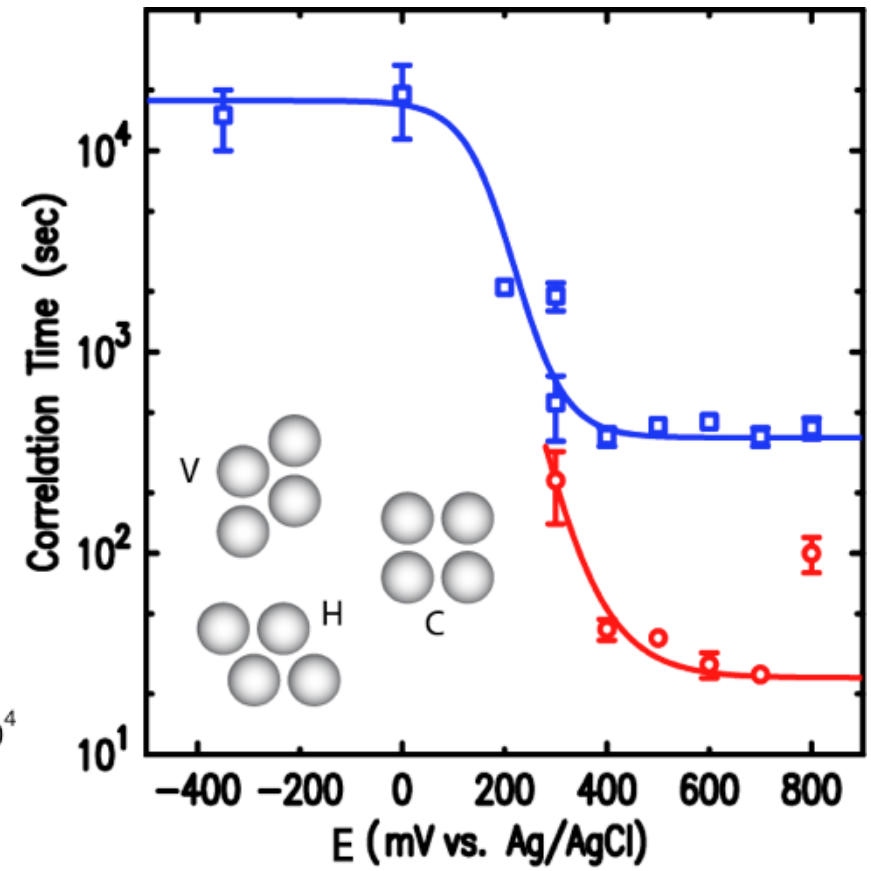
Au (001), in 0.1M HClO4. Three different conditions:



Au(001) in 0.1M HClO4 Dynamics

Measured at L = 0.17





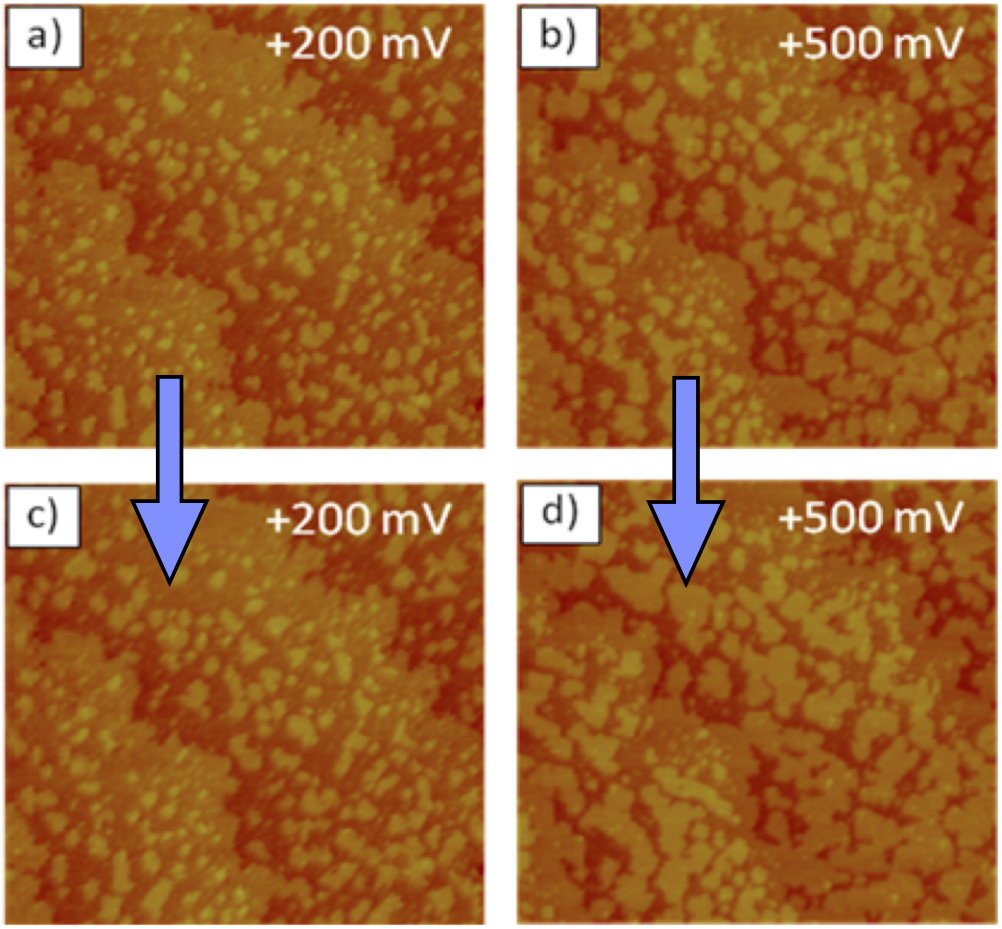
Very slow evolution at low applied potenials.
Increasing evolution rate as the potential is increased.
Eventually 2 different time constants can be seen.

M.S. Pierce, et al. Submitted to JACS, late 2011.

R·I·T

What are these dynamics?

10-15 minutes elapses...



.4 x .4 micometer^2

We cannot invert our images directly using lensless microscopy techniques.

But we can perform some in-situ electrochemical STM for comparison.

200mV shows little evolution, but 500mV shows substantial change.

Without going into too much detail, we have a series of different electrolyte (both different chemicals and concentrations).

Stronger interaction -> faster timescales

We think for a given condition, the slower dynamics is due to hex domain and edge fluctuation, while the faster timescale is due to hex <-> 1x1 transitions.

You, Pierce, and Komanicky, submitted to Electrochemica Acta (2011).

R·I·T

What can we do in the future?

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

Thank You!

1) More Light! (and make it tunable!)

2) Large, strong, stable diffractometer, preferably 6-circle

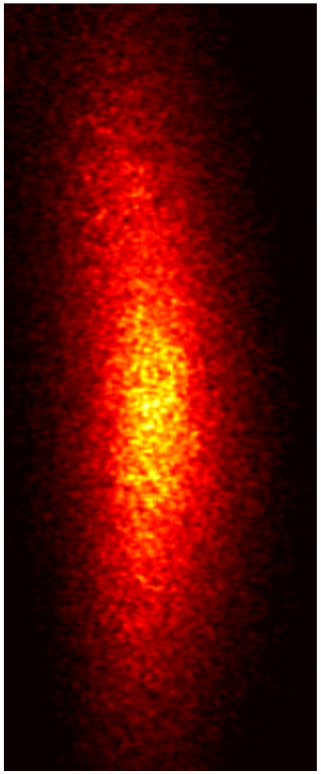
3) Temperature control (hot & cold)

4) Gas injection and analysis

5) "Plug and Play" for smaller sample cells (electrochemical for instance)

6) Long diffraction arm for speckle resolution

7) Detectors: smaller pixels, faster readout, more dynamic range!



I'm very happy to be here and will be happy to answer questions. For in-depth discussion, do not hesitate to contact me at : mspsps@rit.edu