Opportunities for nanoscale dynamics in APS-MBA

Linda Young
APS-MBA Upgrade Workshop
Argonne National Laboratory
21-22 Oct 2013

Outline

- Why is APS a mecca for timing experiments ?
- Grand challenge science: direct and control matter
  - Quantum materials : ps-microscopy of nanoscale dynamics
  - Chemical dynamics : single nanoparticle dynamic chemical imaging
- Report on SLAC and BESSY-VSR

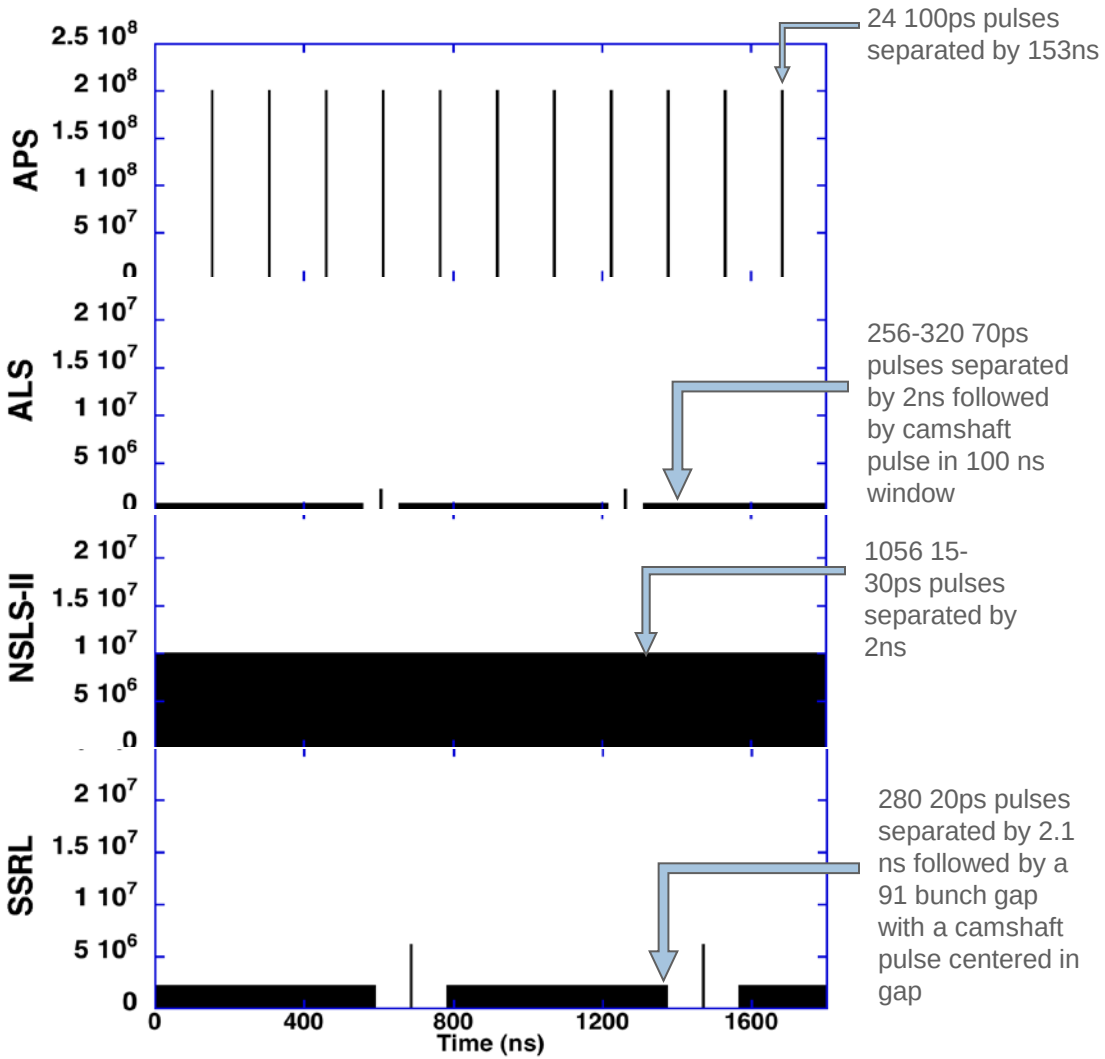
Large circumference storage rings always win for timing

Simultaneous high average brightness and high single pulse brightness.

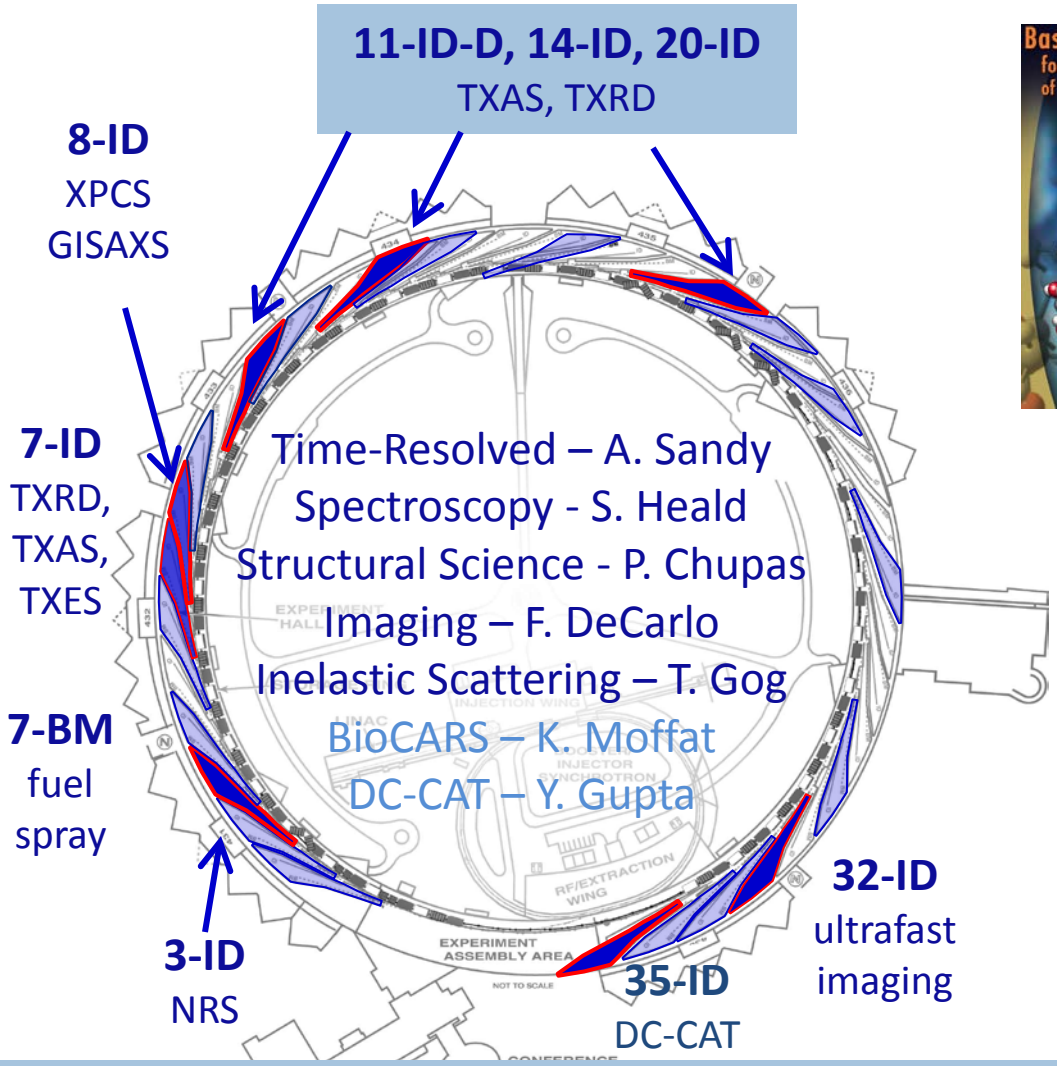
Large intervals between pulses enable
- mechanical chopping of x-rays
- sample relaxation
- sample replenishment
- pixel detector gating

100% of x-ray pulses are useful in pump-probe or pump-probe•probe•probe configurations

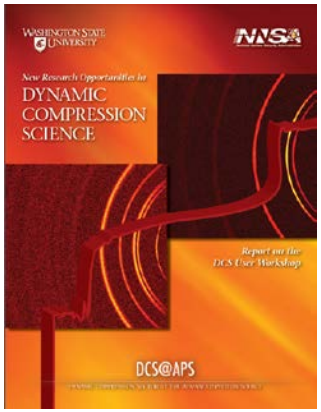
Transient species can be probed with same fidelity as ground state.



Diverse timing community has developed at the APS



DOE Basic Needs Reports



Dynamic Compression Sector – commissioning mid-2014

Unique APS features: single-shot phase contrast imaging, 4 dedicated laser-pump/x-ray probe stations, > 10^{10} x-rays/pulse for time-resolved diffraction

MBA lattice design – October 1 revision

MBA: 6 GeV, 200 mA, 80 pm, flexible timing modes
Present: 7 GeV, 100 mA, 3 nm, flexible timing modes

Quantity	Symbol	Range	Units
Total current	I	200	mA
Number of bunches	N_b	48-324	
Bunch rate	f_b	13-88	MHz
Rms bunch duration	σ_t	70-18	ps

48 bunch mode: x, x' = 7.4 µm, 5.7 µrad
y, y' = 10.9 µm, 3.8 µrad

Michael Borland – white paper on APS website

Back to Basics

To direct and control matter at the quantum, atomic and molecular level.

2007 BESAC Grand Challenge Report

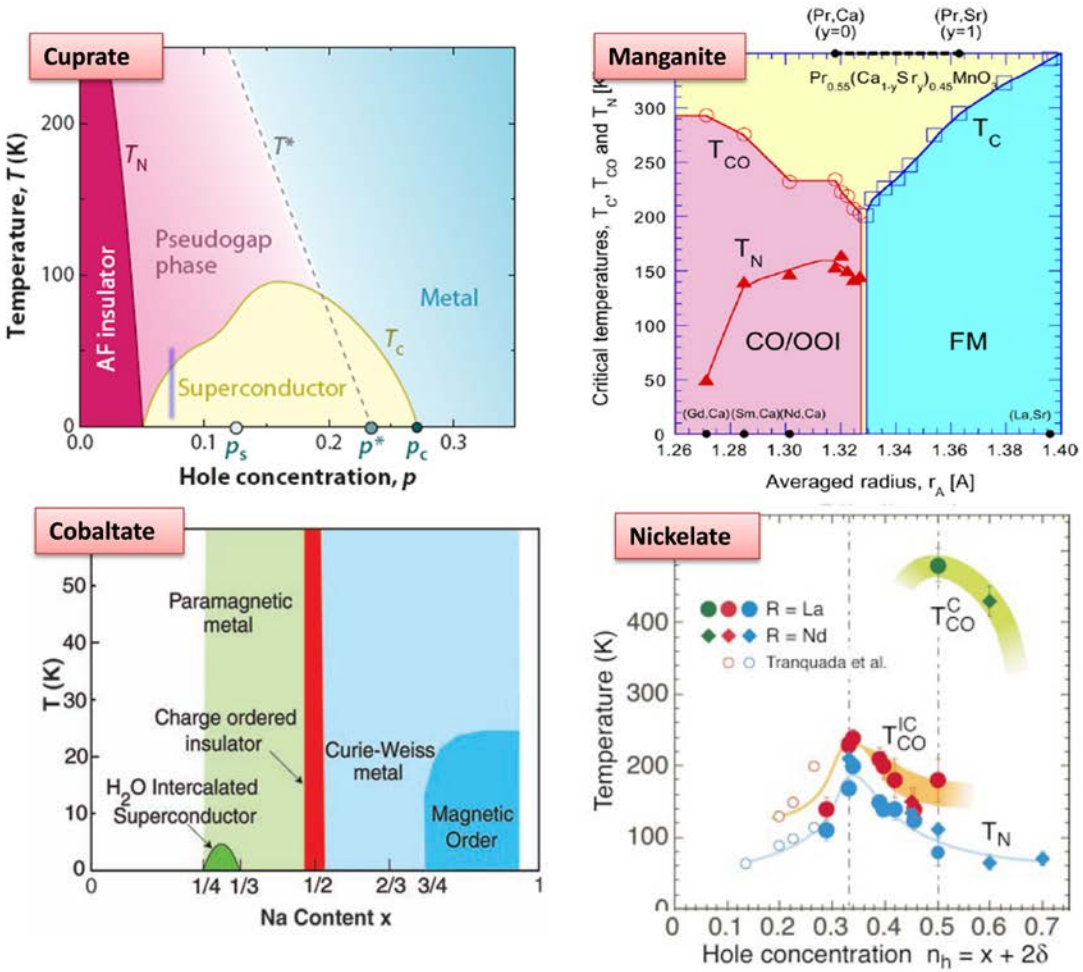
Quantum materials

How do complex phenomena emerge from simple ingredients?

National Academies Press
CMMP 2010

Quantum Materials

Can we understand and control the emergence of collective behavior in strongly correlated multiparticle systems?



Quantum Material - Nickelate

Nickelate: $La_{1.75}Sr_{0.25}NiO_4$

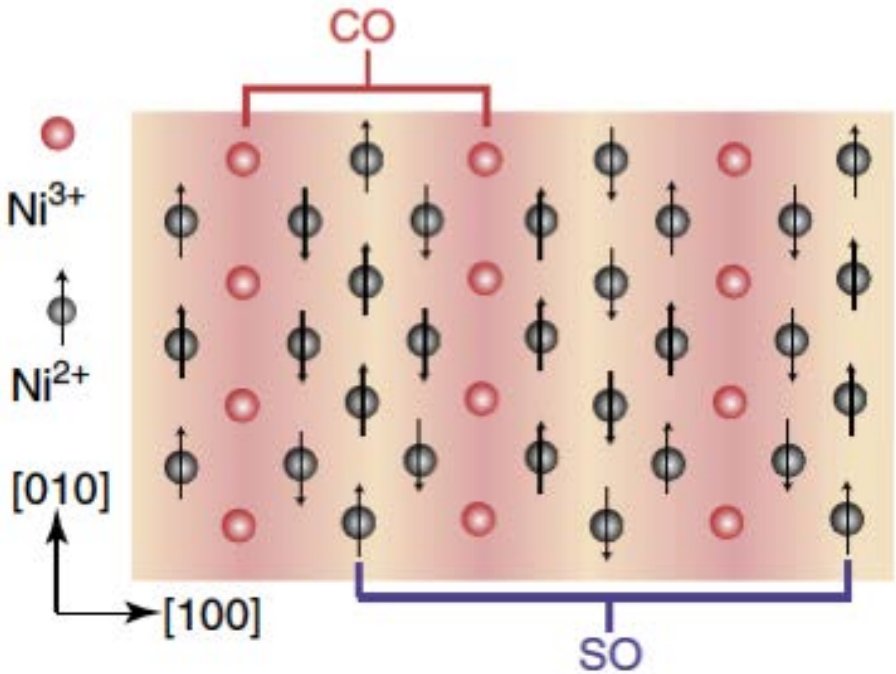
Electronic order on nm length scales

Charges & spins form regular patterns to minimize total energy

Manipulate charge order with light

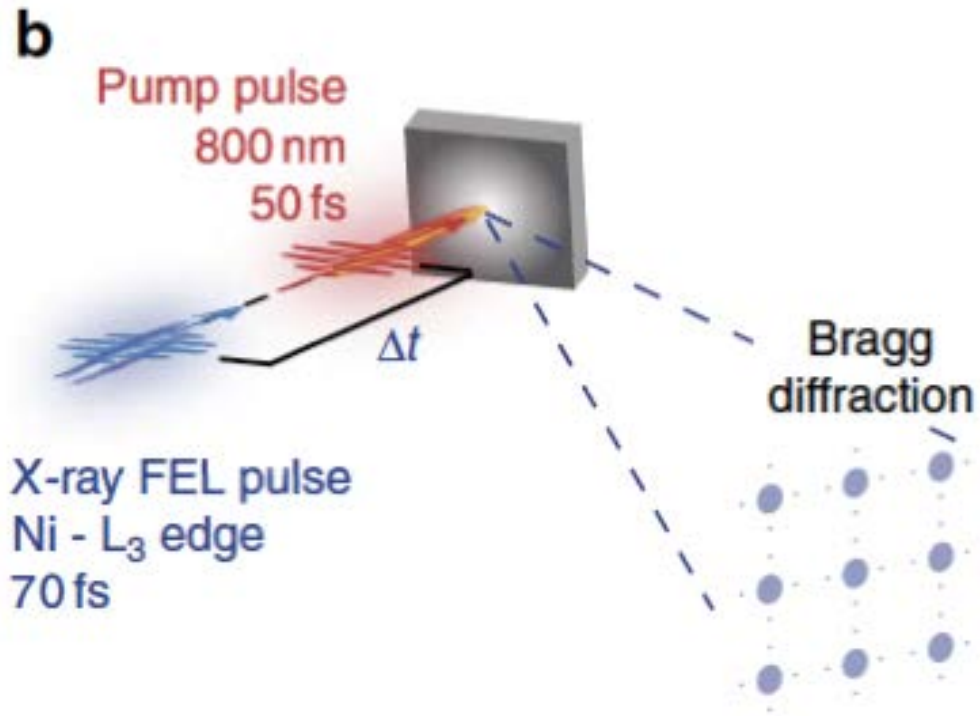
Probe charge order dynamics with x-ray diffraction & optical reflectivity

Compare light-induced vs thermal phase change

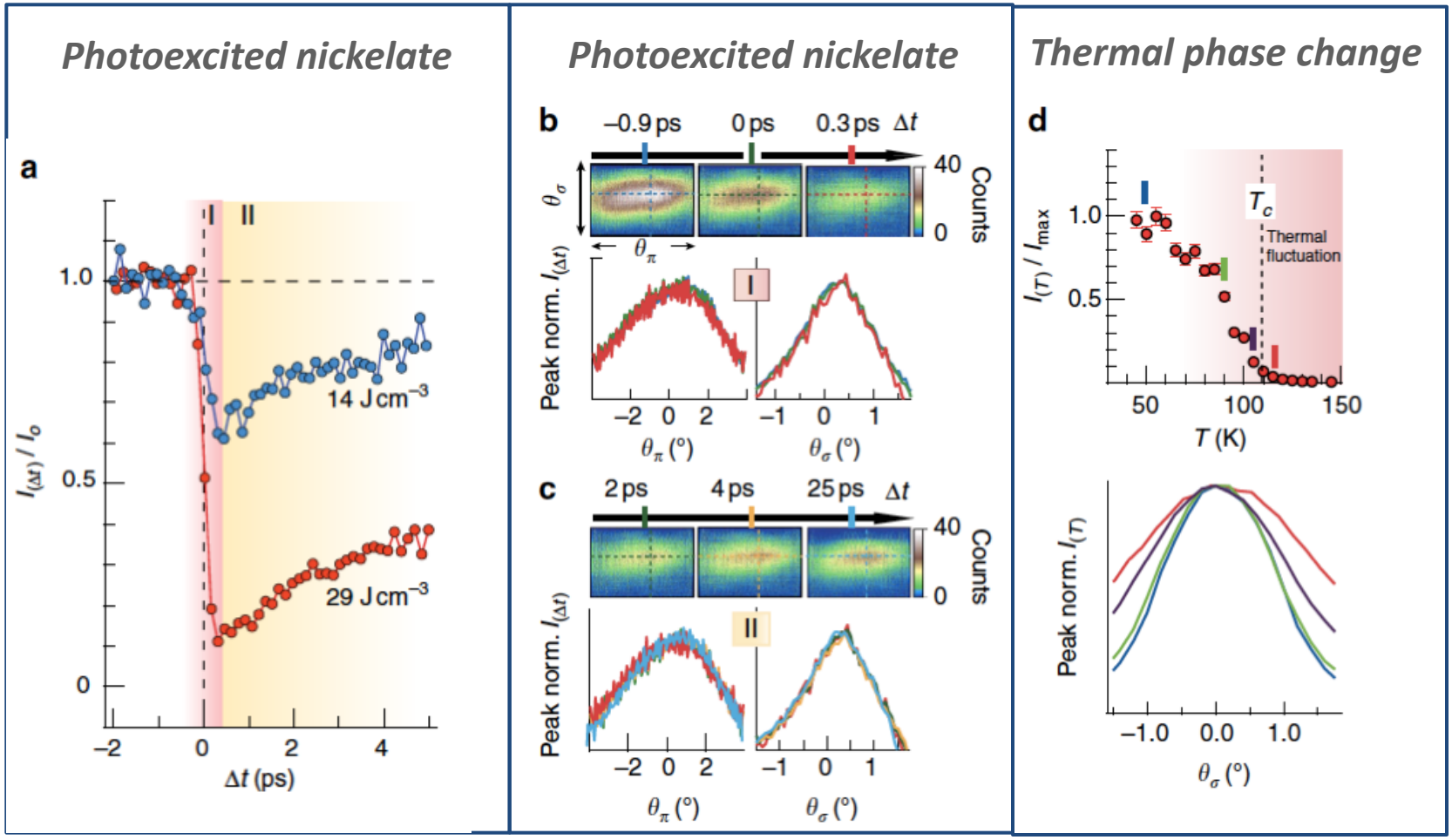


W. S. Lee et al., Nat Comm **3**, 838 (2012)

Observing charge order with resonant diffraction @ LCLS



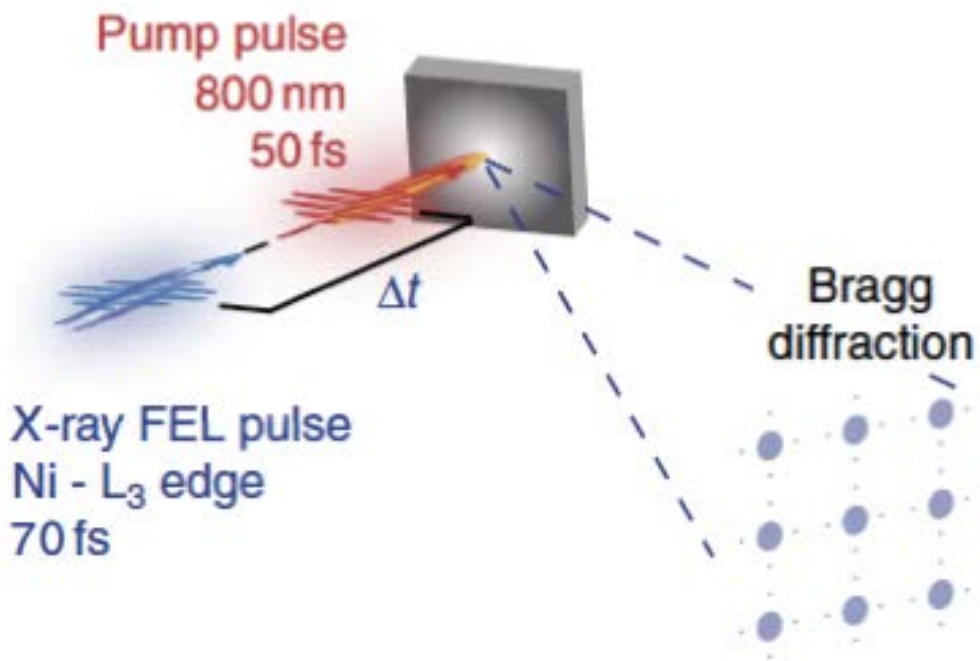
Light-induced Charge Order dynamics: Timescales



CO recovery timescales measured by XRD: τ_{fast} = 2 ps, τ_{slow} = 57 ps

CO melting by temperature rise leads to different long range ordered state

Observing charge order with resonant diffraction @ LCLS



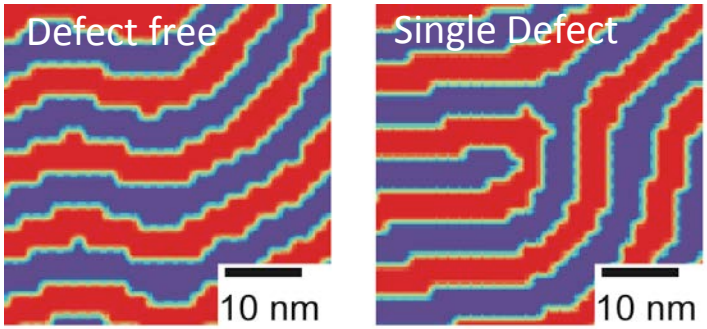
X-ray fluence ~0.5 mJ/cm^2/pulse
300 X 300 μm^2 target
Fraction of LCLS pulse energy used ~ 10^{-3}-10^{-4}
Number of shots per time step ~ 40
Repetition rate 120 Hz

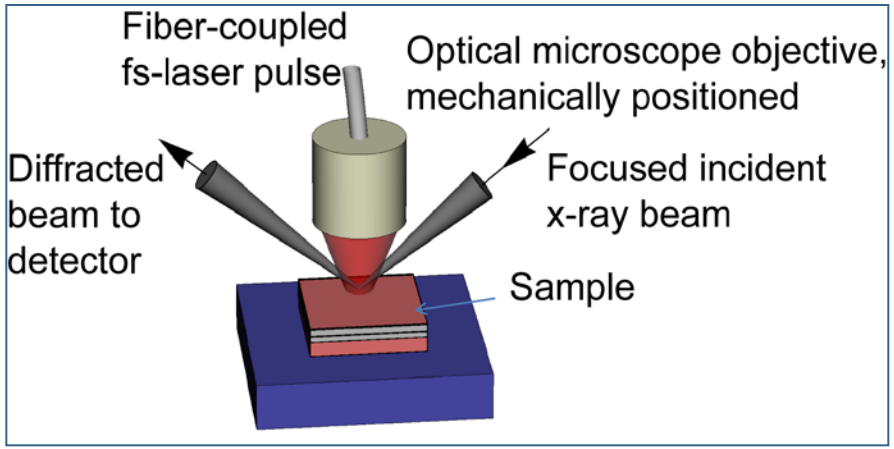
Repetive measurement, linear x-ray probe, ps timescale

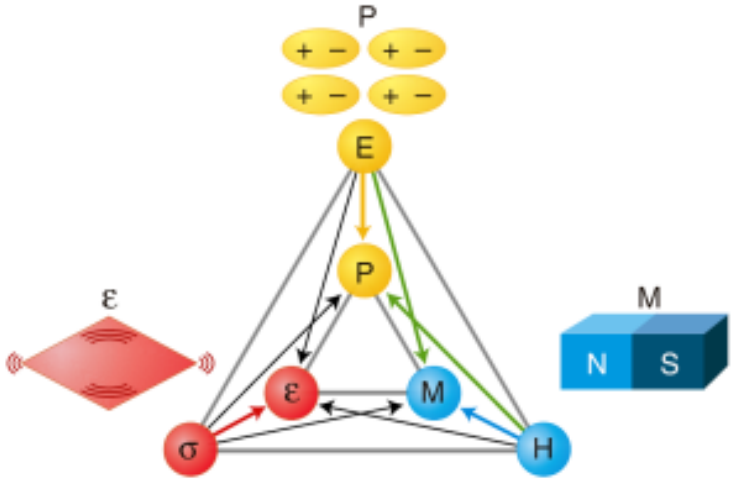
Beyond macroscopic averages to microscopic dynamics

Repetitive measurement, linear x-ray probe, ps timescale, nanofocused

Time-resolved microscopy on the nanoscale @ APS/MBA







N. A. Spaldin & M. Fiebig,
Science 309, 391 (2005)

Increased nanofocused brightness yields ~100x signal

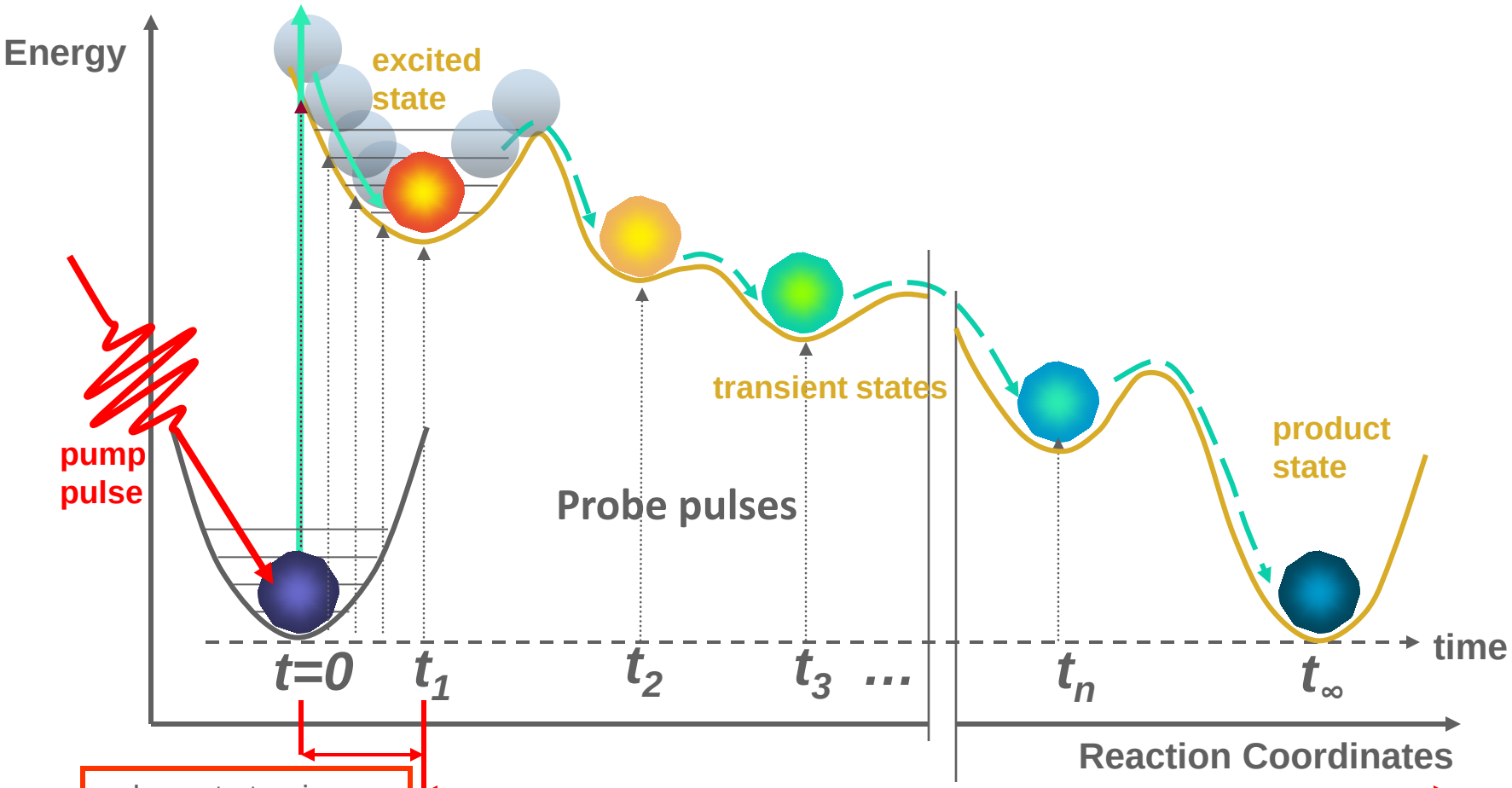
Atomic motion governed by speed of sound ~ 1 nm/ps.

Chemical dynamics

Repetitive measurement, linear x-ray probe, ps timescale, ultrastable, nanofocused

Chemistry

Dream: to see molecules during the course of a chemical reaction

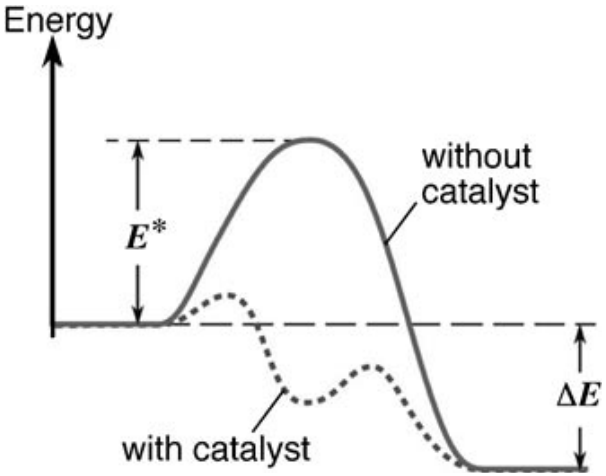


coherent atomic motions on fs to ps time scales

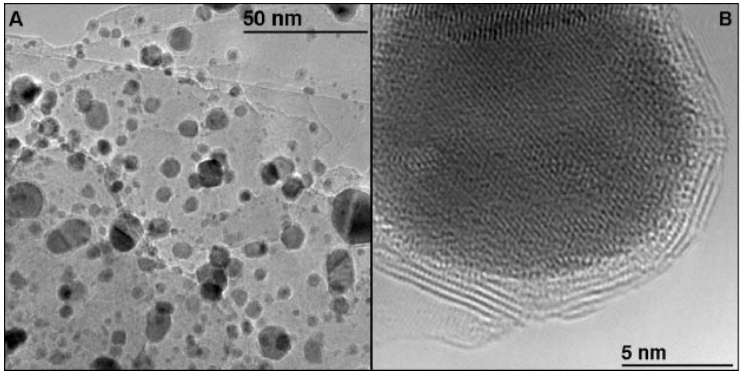
incoherent atomic motions leading to discrete thermally equilibrated transient states on ps to s time scales →"molecular snapshots"

Catalysis – on the nanoscale – understand the transition state

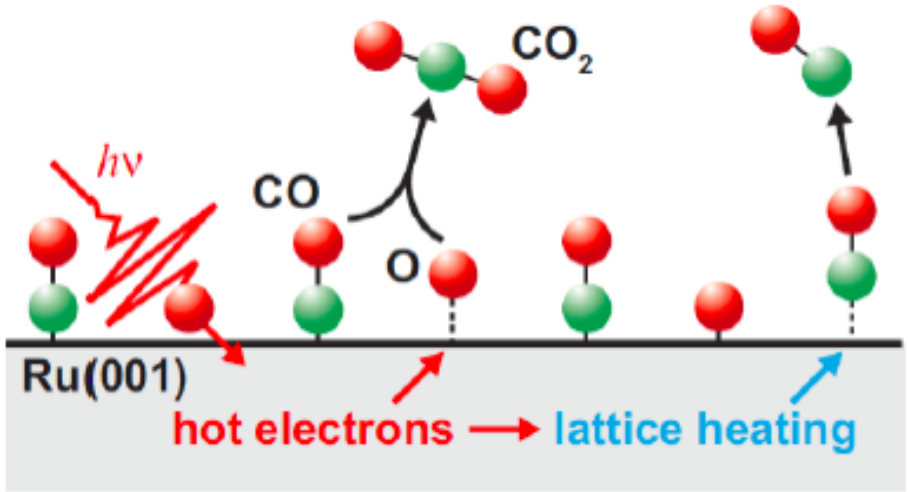
Nobel Prize 2007
"for his studies of chemical processes on solid surfaces"



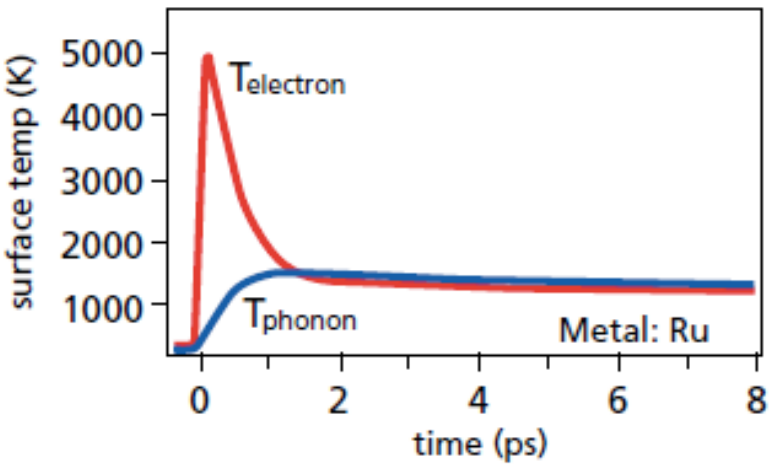
Ru catalyst
for ammonia synthesis



Surface catalysis triggered by lasers – CO on Ru



From Swiss FEL science case



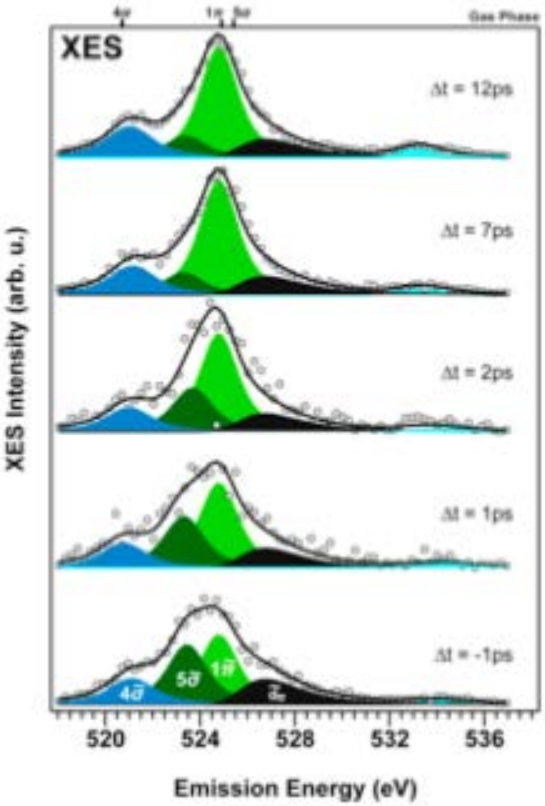
Electron-lattice equilibration in ~1-2 ps.

Experiment at LCLS: X-rays: 60 Hz, 10^{10} x-rays/pulse (1µJ) , 50x1800 µm
Optical: 30 Hz, 400 nm, 350 µJ, 100 µm

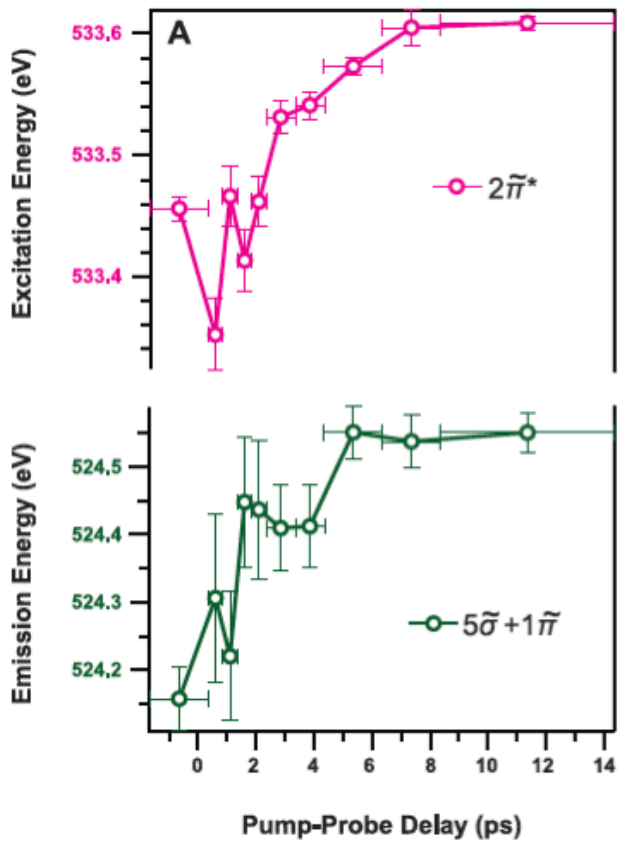
Dell' Angela *et al.*, Science **339**, 1303 (2013)

First observation of time evolution of valence electron states involved in bond breaking @ LCLS

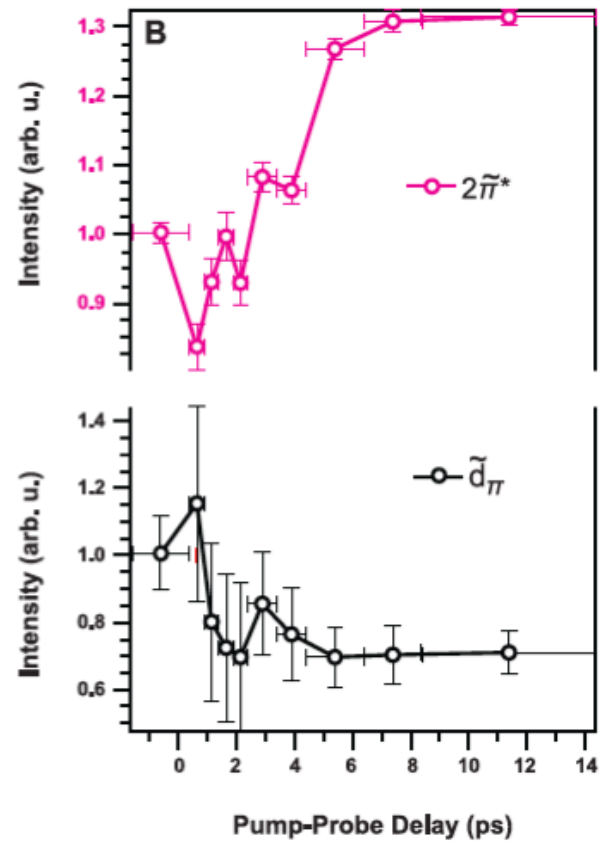
X-ray Emission Spectra



Energy Shifts



Intensity Changes



Energy shifts consistent with metal-CO bond weakening – on few ps timescale.

Dell' Angela *et al.*, Science **339**, 1303 (2013)

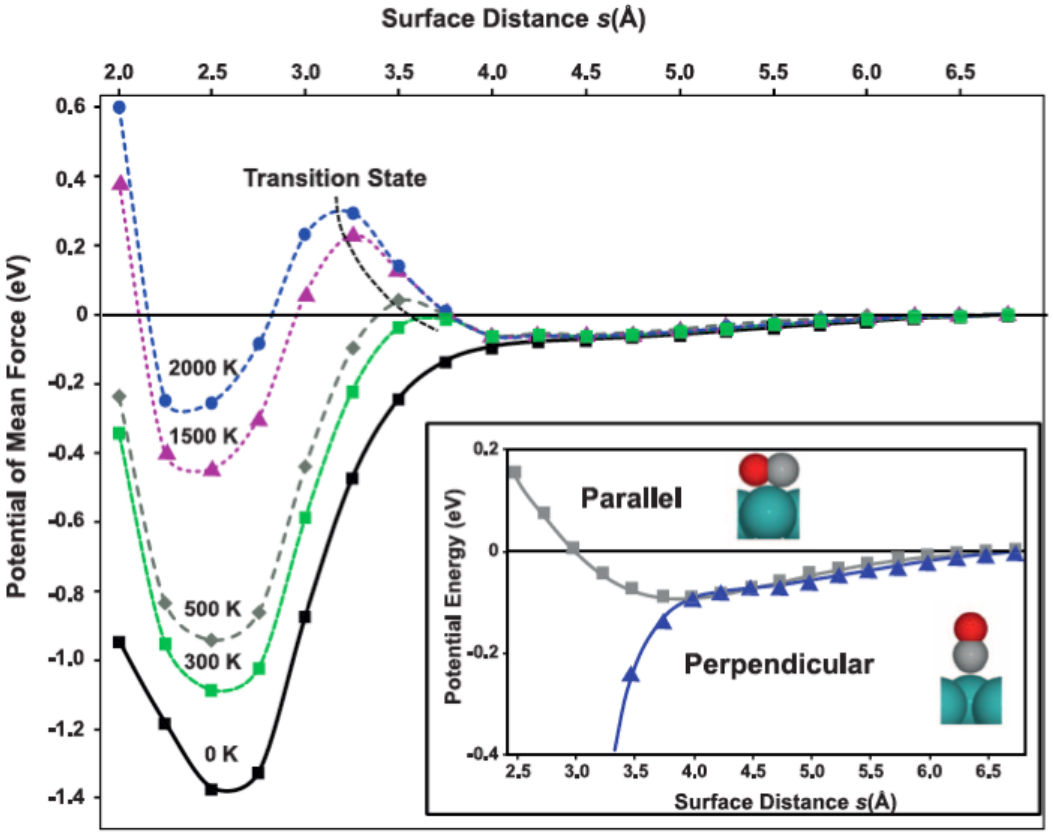
What is happening?

Equilibrium is chemisorbed state.

Transient spectra can not be explained by thermal population of ground state.

Temperature increase creates two minima in the potential: the chemisorption minimum and another a precursor state.

Identify a precursor state as a "loose transition state" with CO roaming the Ru surface.



Theory by Jens Norskov, L. G. M. Peterson and co-workers

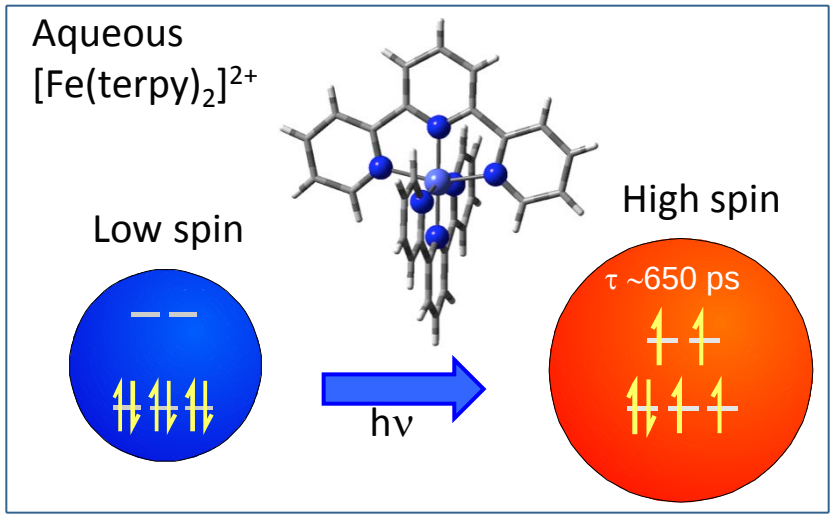
Transient precursor state observed by XAS + XES on ps timescales

Adapted from W. Wurth

Dell' Angela *et al.*, Science **339**, 1303 (2013)

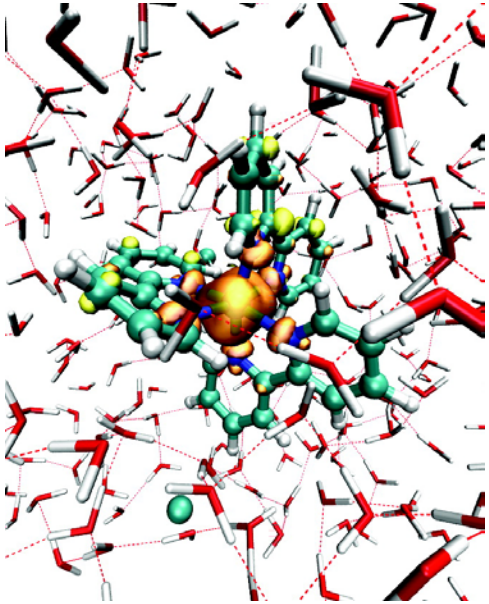
APS has developed high repetition rate capabilities for simultaneous x-ray absorption, emission, scattering characterization of transient species

Demo on Fe spin-crossover system



Local atomic and electronic coordinates for transient species of >100 ps lifetime via simultaneous XAS, XES, RIXS, XDS.

K. Haldrup et al., *J.Phys Chem.* ***A116,*** *9878 (2012)*
G. Vanko et al, *JESRP* ***188****, 166 (2013)*



- Solvent shells of ground low-spin and long-lived (650 ps) high spin states are different!
- 2 water molecules are expelled from the solvent shell upon expansion of the molecule in the HS state

But few ps timescales typical for dynamics of ligand substitution, solvent caging …

A.M. March et al., RSI (2011)

Dynamic chemical imaging on single nanoparticles

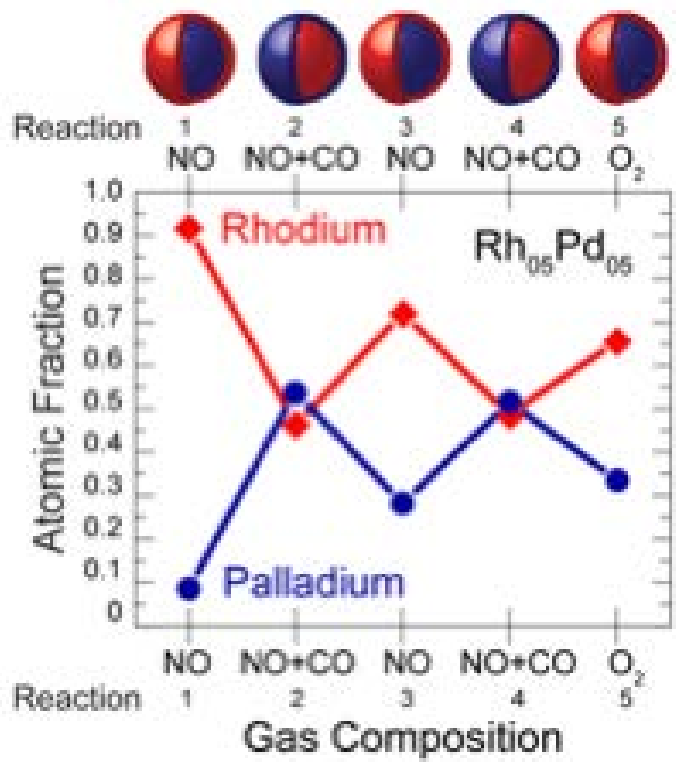
Can image single nanoparticles

3D-lattice dynamics imaged in laser pump/x-ray probe using coherent Bragg diffraction @ LCLS
Clark et al, Science (2013)

Acoustic phonon oscillations on picosecond timescales – matching adsorbate & ligand dynamics

Add suite of x-ray spectroscopic, scattering techniques to give chemical information.

Observe core-shell nanoparticles restructuring under catalytic conditions



F. Tao et al. *Science* **322**,932 (2008)
M. Salmeron & G. Somorjai

High-Repetition-Rate Picosecond Science Workshops in October 2013 – aimed at filling in the 1-100 ps gap.

SLAC/SSRL: Scientific Opportunities using High Repetition Rate X-ray Sources with 1-10 ps Bunch Length

Aaron Lindenberg, Kelly Gaffney, Anders Nilsson, David Reis, Phil Bucksbaum, Mariano Trigo (Stanford/SLAC), Philip Wernet (Helmholtz Zentrum Berlin), Oliver Gessner (LBNL), Christian Bressler (XFEL), Martin Meedom Nielsen (TU-Denmark)

BESSY-VSR: The variable pulse length synchrotron radiation source

Alexander Fohlisch (Helmholtz Zentrum Berlin), Majed Chergui (EPFL), Simone Techert (Gottingen), Nils Huse (DESY), Wilfried Wurth (Hamburg), Hermann Durr (SLAC), Stefan Eisebitt (TU-Berlin), Matias Bargheer (Potsdam)

Summary

- The MBA lattice improves APS as the premier site for x-ray timing experiments. Timing capabilities go along with high brightness as a feature of the circumference.

- Pump-probe techniques are central to BESAC grand challenge of directing and controlling matter at the level of electrons, atoms and molecules.

- Exciting new classes of experiments enabled by combination of high brightness and picosecond timescales
    - Microscopic view of nanoscale dynamics in quantum materials
    - Single nanoparticle dynamic chemical imaging

- From heroic to systematic … relative to XFELs, APS is comparable in flux and superior in stability, tuning and efficient use of x-rays as a simply-understood, linear response probe of matter.

- Highly experienced user community eager and ready for an ultrastable, widely tunable, polarized, high average flux, high brightness, picosecond x-ray source.