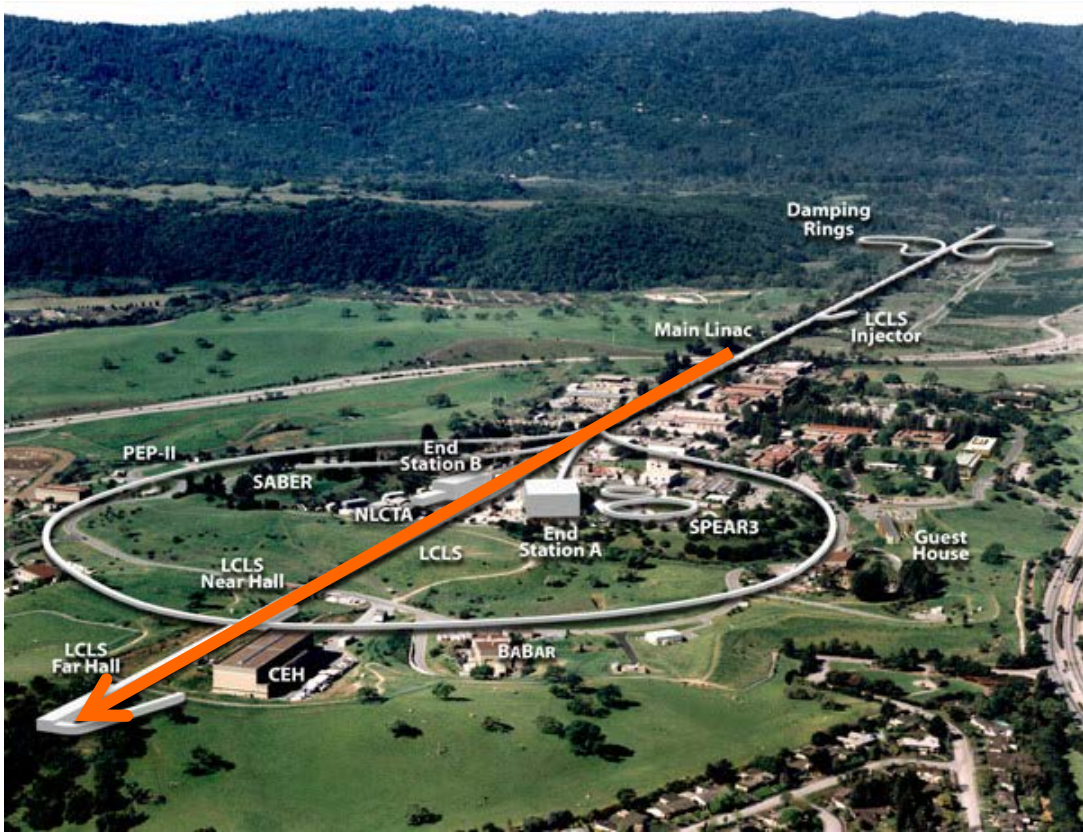
Linac Coherent Light Source (LCLS) X-ray Free-Electron Laser

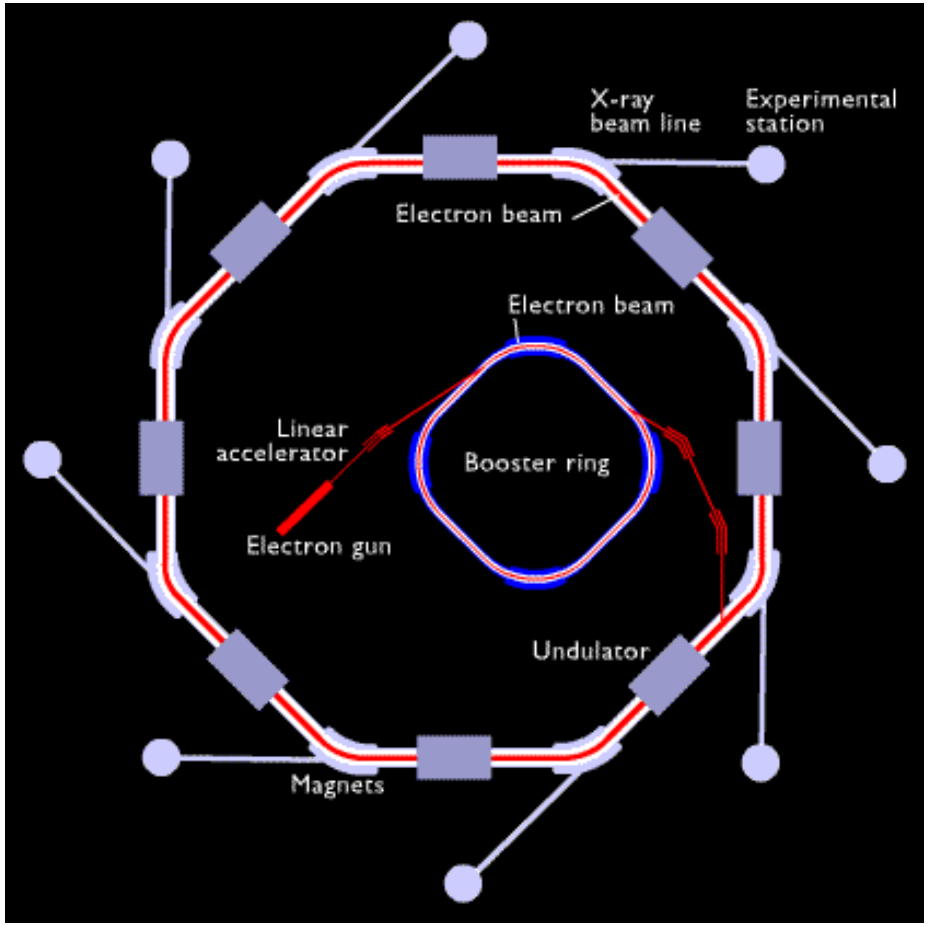
- Electron Energy: **15 GeV**
- Photon Energy: **0.5-10 keV**
- Pulse length: **5-500 fs**
- Flux: **10^{12}**
- Frequency: **120 Hz**
- E. Bandwidth: **0.1-2%**
- Machine Length: **2 km**



The worlds first x-ray laser
Linac Coherent Light Source (LCLS)

Synchrotron Radiation - How is it Produced and Used?

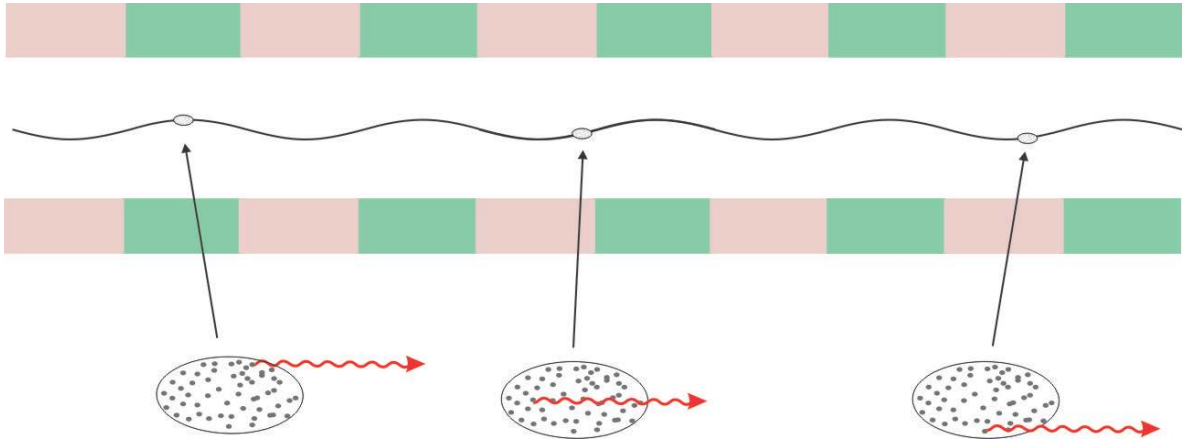
- **Electron gun produces electrons**
- **Storage ring circulates electrons**
- **Synchrotron radiation produced where electron path is bent**

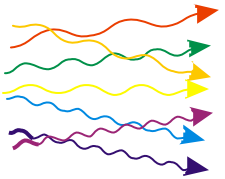


beam lines transport radiation into experimental stations or "hutches" where instrumentation is available for experiments

Synchrotron radiation from undulator in storage ring

Electron bunch is “stored” in ring and used over and over…..
Magnets cause electrons to wiggle





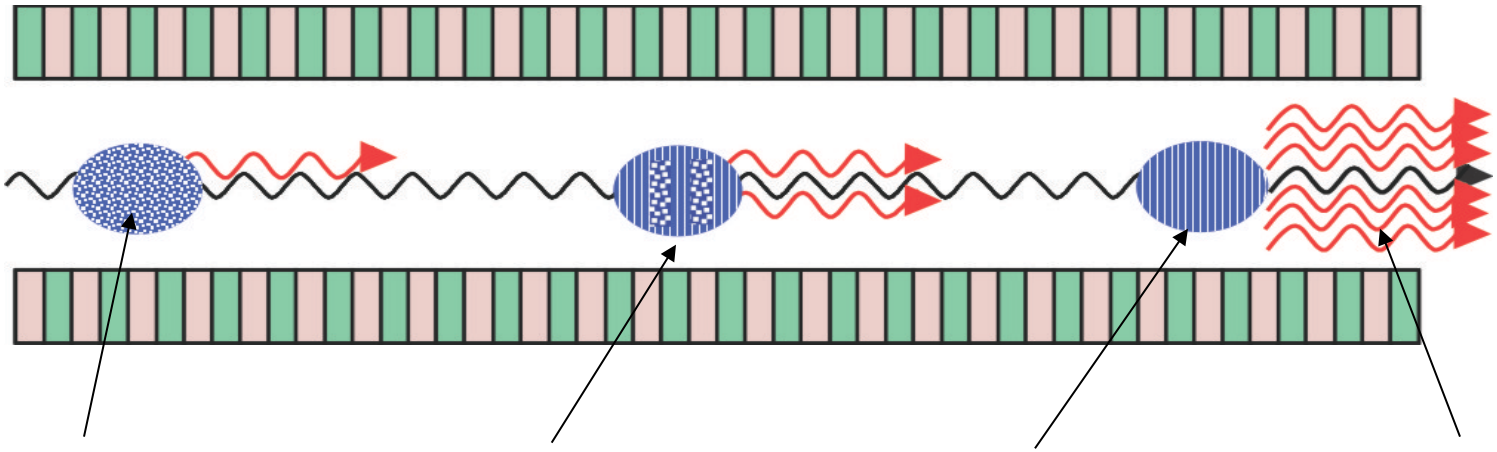
electron bunch
~ 1cm long

Each bunch contains $N_e \sim 10^9$ electrons
…but electrons emit spontaneously
photons not coherent

Intensity limited by independent photon emission – scales as N_e

Concept of a free electron x-ray laser

- Replace storage ring by a linear accelerator
  allows compression of electron bunch – use once, then throw away
- Send electron bunch through a very long undulator



very short bunch length micrometers

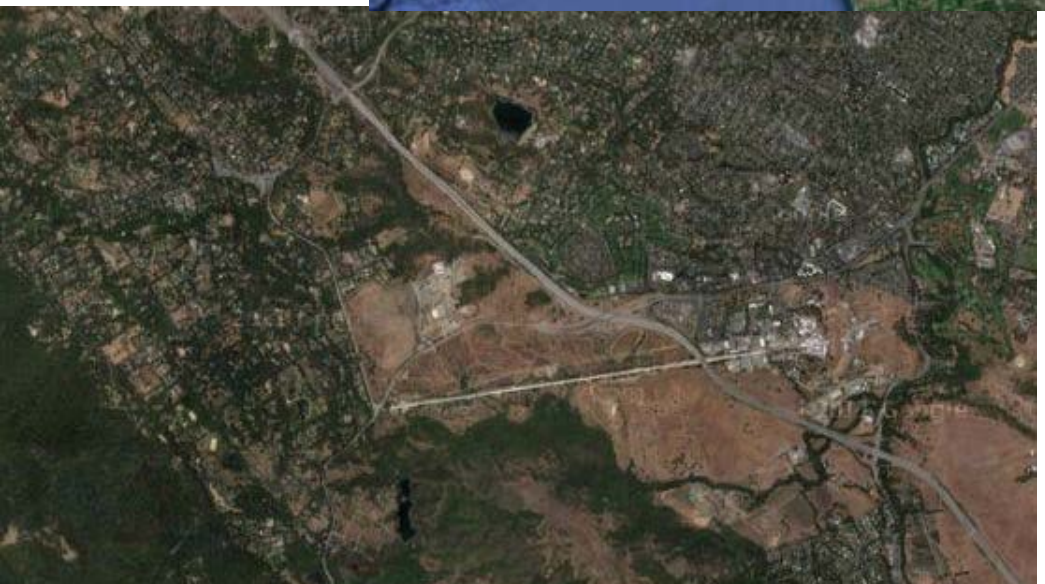
spontaneous photons from back of bunch create order

ordered electrons enhance **stimulated** photon emission

amplified photons completely coherent

Intensity scales as N_e^2 or increased by 10^9

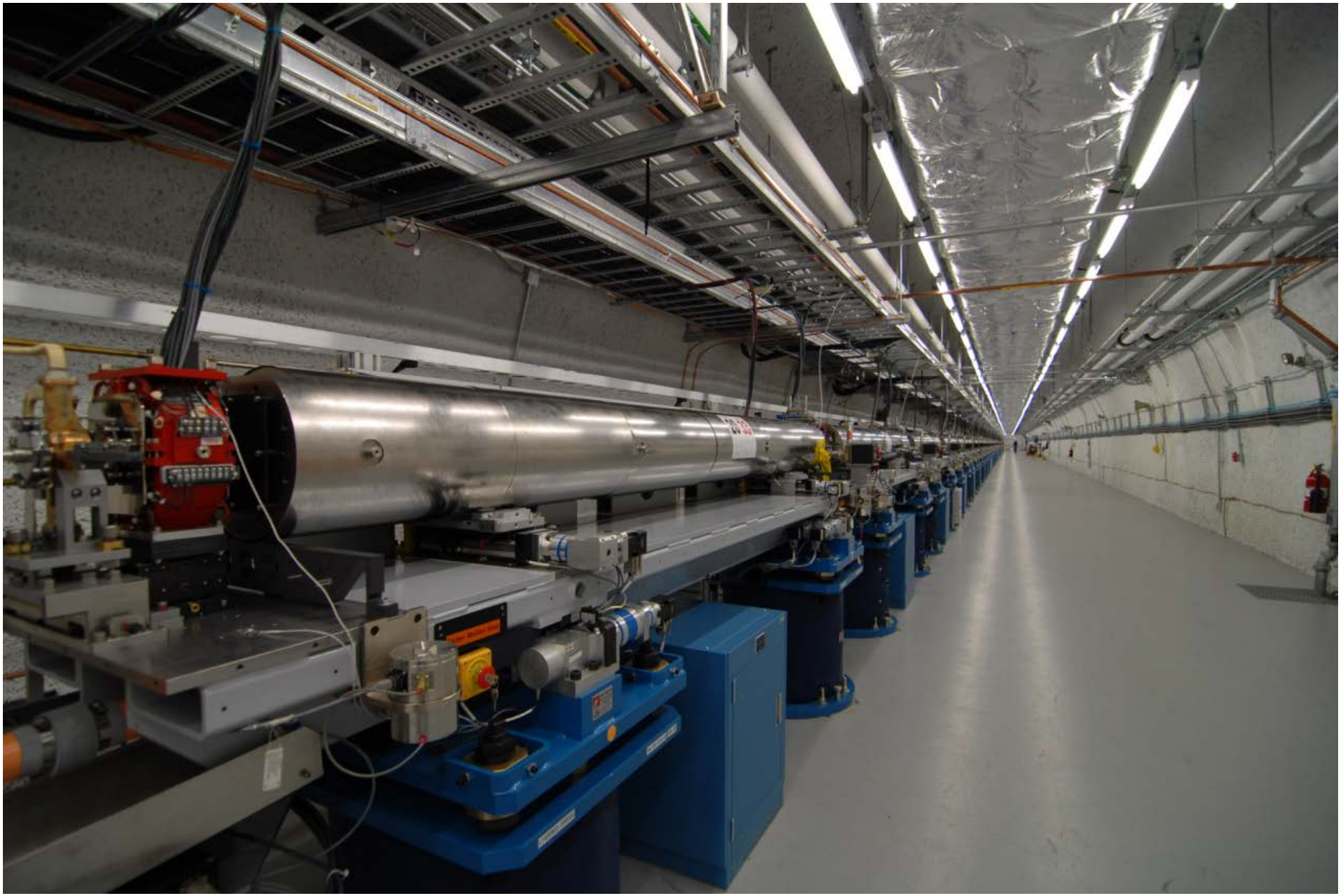
San Francisco Bay area



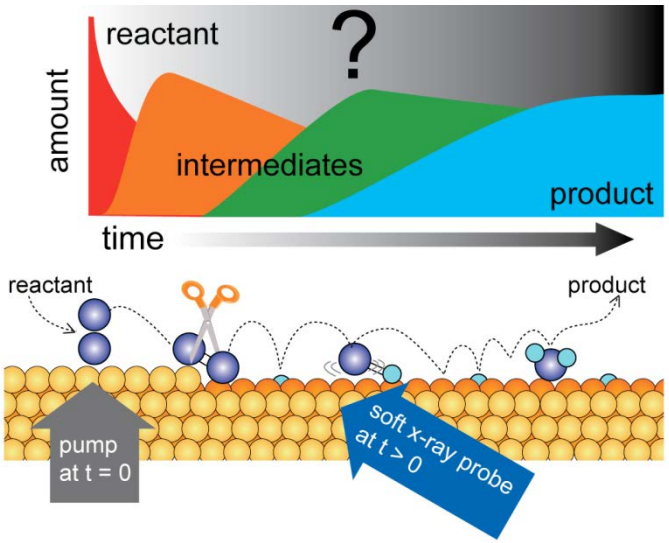
Golden Gate Bridge

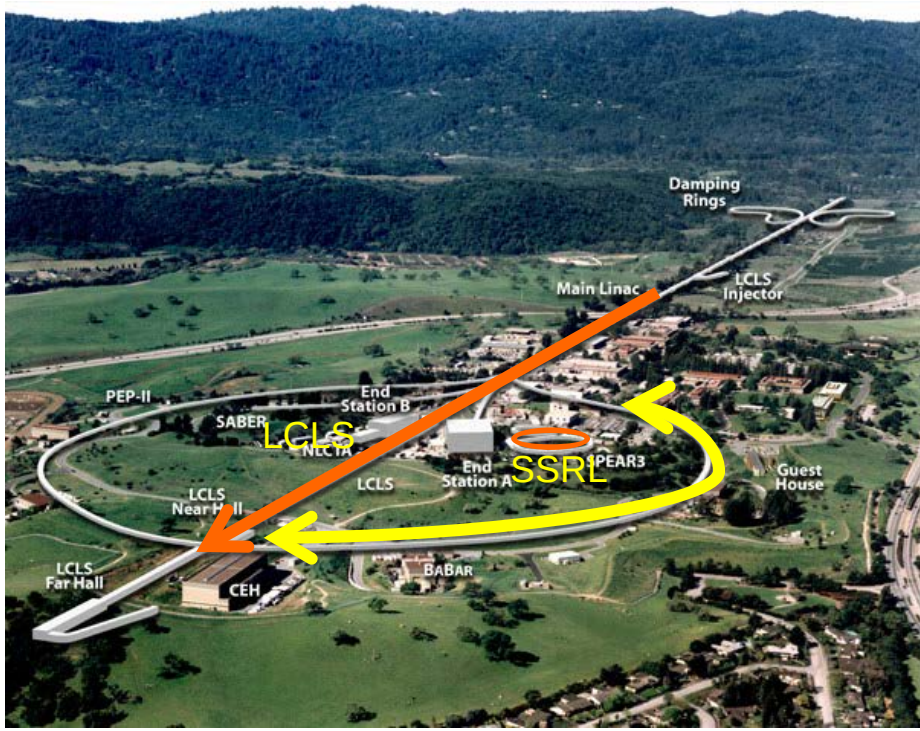
LINAC

132 meters of FEL undulators



Real-Time Observation of Surface Bond-Breaking with an X-ray Laser





Dell'Angela et al., Science **339**, 1302 (2013)

Collaboration






Toyli Anniyev, Martin Beye, Ryan Coffee, Martina Dell'Angela, Alexander Föhlisch, Jörgen Gladh, Tetsuo Katayama, Sarp Kaya, Oleg Krupin, Andreas Møgelhøj, Anders Nilsson, Dennis Nordlund, Jens Nørskov, Hirohito Ogasawara, Henrik Öberg, Henrik Öström, Lars GM Pettersson, William F Schlotter, Jonas A Sellberg, Florian Sorgenfrei, Joshua J Turner, Martin Wolf, Wilfried Wurth

University of Hamburg and CFEL, Stockholm University, Helmholtz-Zentrum Berlin, Fritz Haber Institute, SLAC (LCLS, SIMES, SSRL, SUNCAT)

Dell'Angela et al., Science **339**, 1302 (2013); Beye et al., PRL **110**, 186101 (2013)

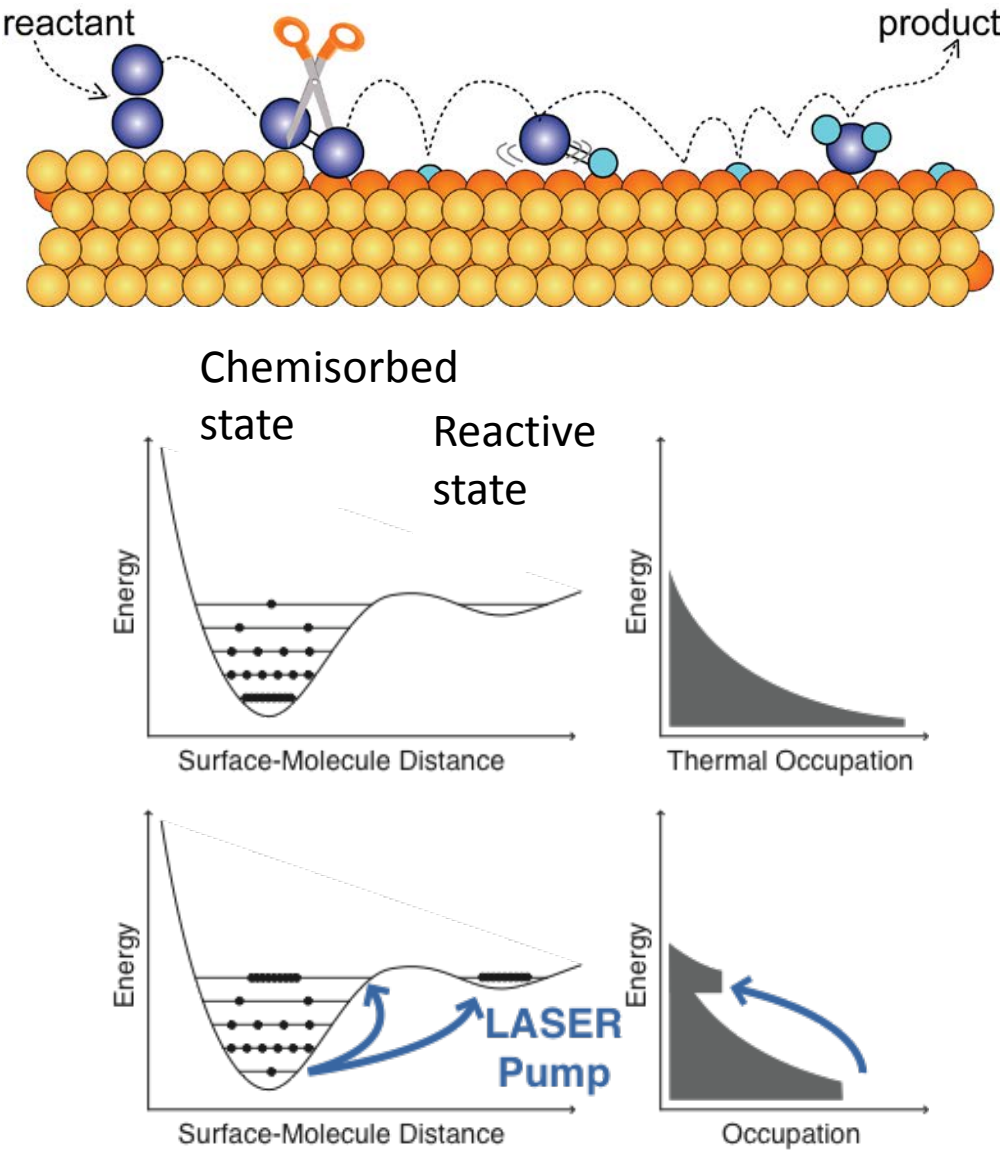
Probing the Reactive State in Catalysis

Most important catalytic reactions are driven by thermal processes

The number of turn-over events at each active site at a given time is extremely low

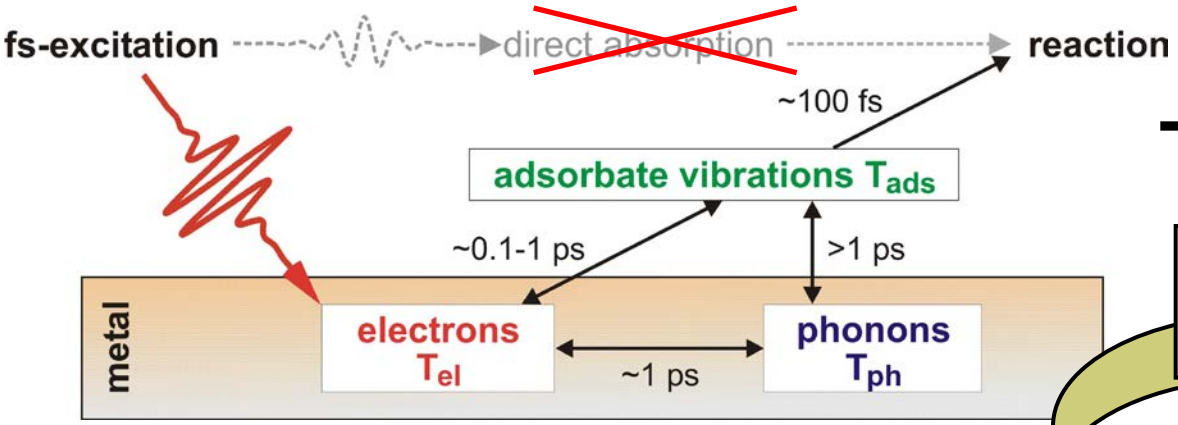
The Boltzmann energy distribution gives only few molecules to be in a reactive state

Ultrafast laser-induced heating leads to orders of magnitude higher population of the reactive state which can now be probed with ultrafast methods



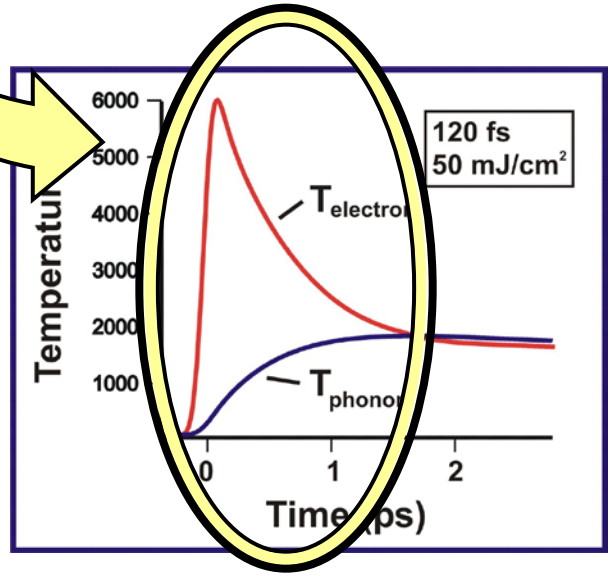
Femtochemistry through laser excitation

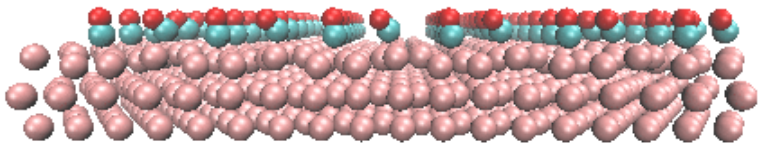
Mechanisms and time scales of energy transfer after optical excitation



→ substrate-mediated excitations dominate

transient non-equilibrium with $T_{el} >> T_{ph}$





LCLS pump-probe experiments: Targets

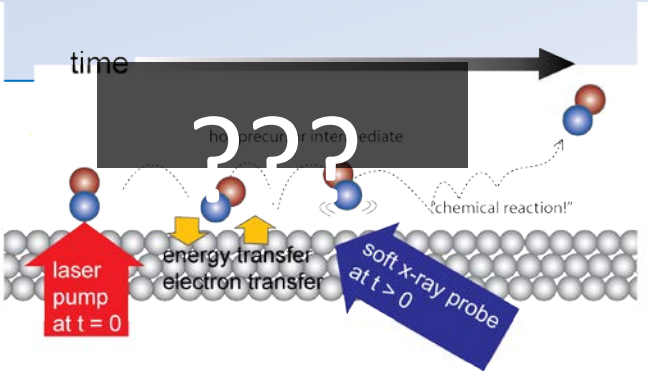
Use new femtosecond free-electron x-ray laser (LCLS or XFEL) to:
Measure electronic structure changes on a femtosecond timescale as reaction proceeds
Identify intermediates experimentally through x-ray spectroscopy – couple to theory
Concerted start of reaction using femtosecond laser heating or terahertz radiation

First experiment:

Proof of principle: Laser-induced desorption of CO/Ru(0001) – well-known system
Measure valence electronic structure time-resolved using x-ray spectroscopies

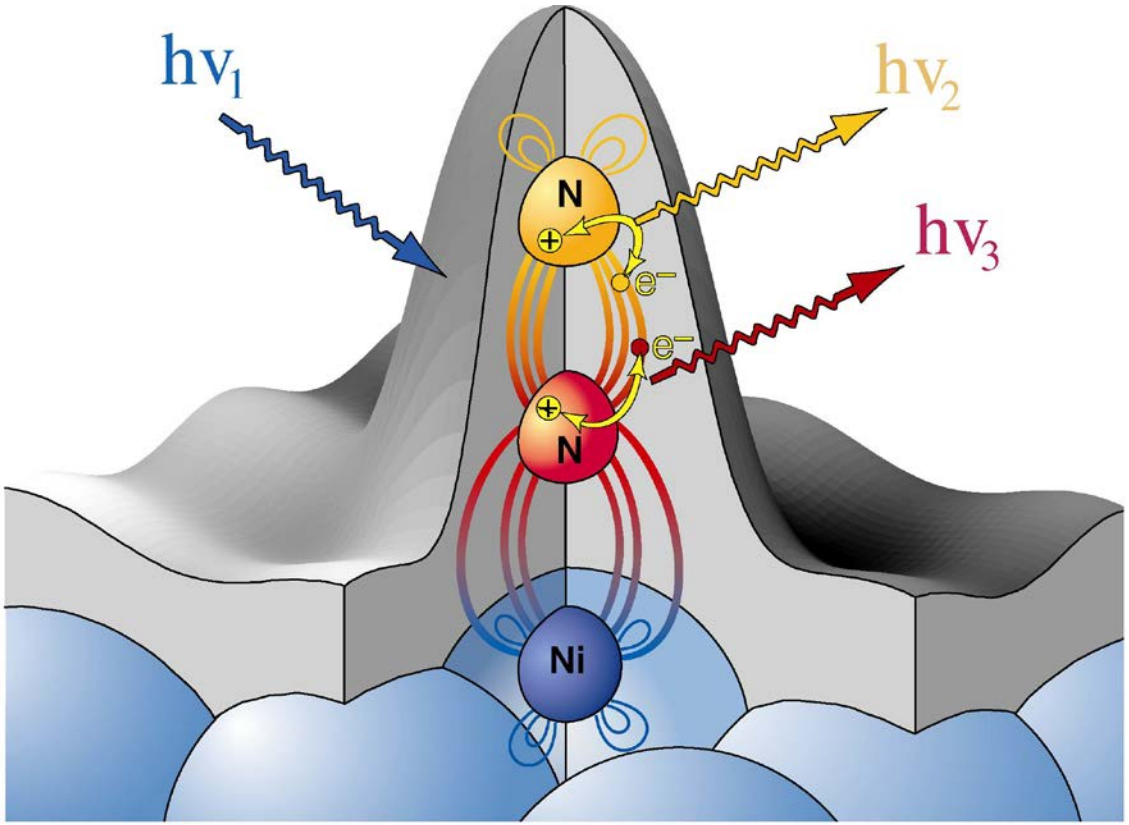
Planned:

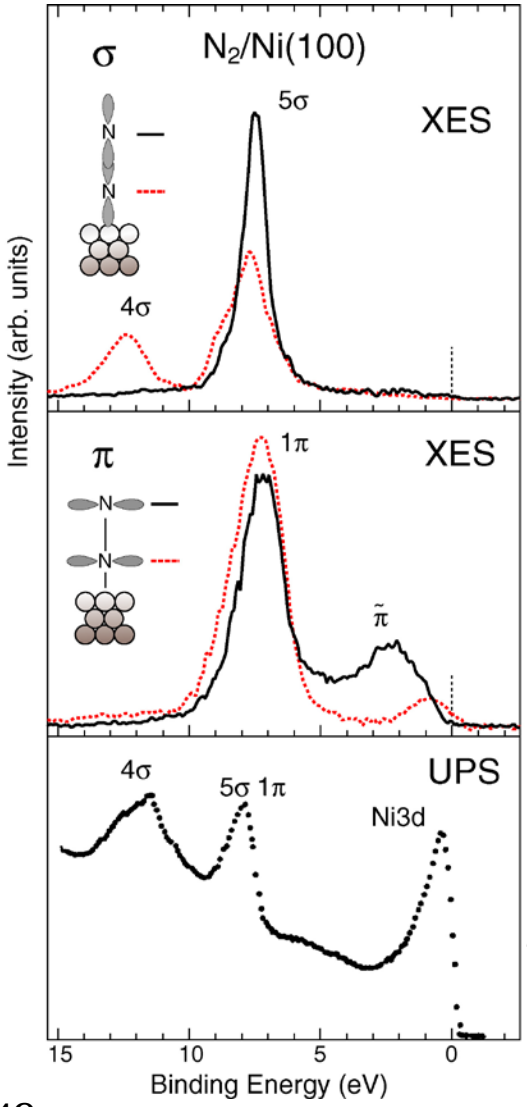
Fischer-Tropsch $CO + H_2 \rightarrow C_xH_y + H_2O$ Iron based catalyst
Methanol production
Higher pressures (<100 torr)



X-ray Emission Spectroscopy

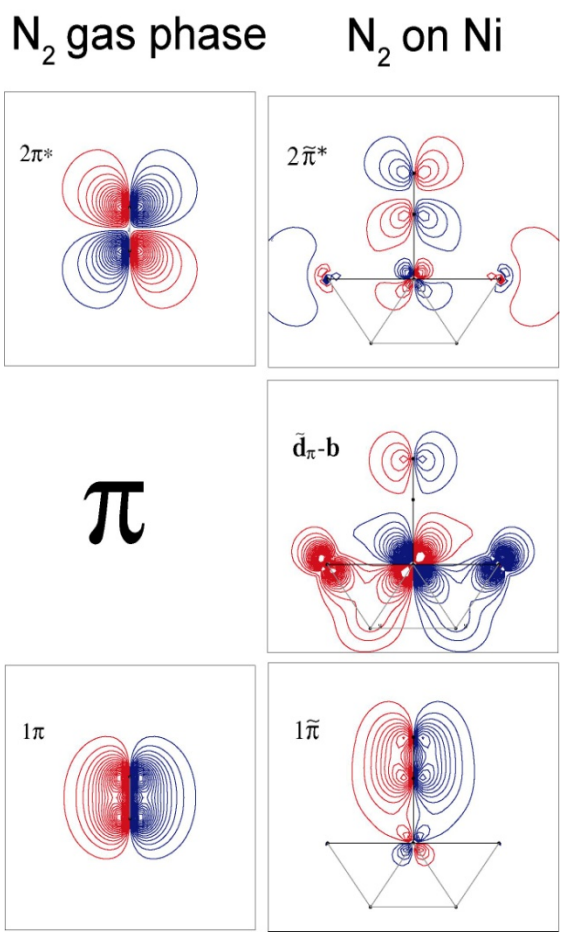
Atom-specific probing



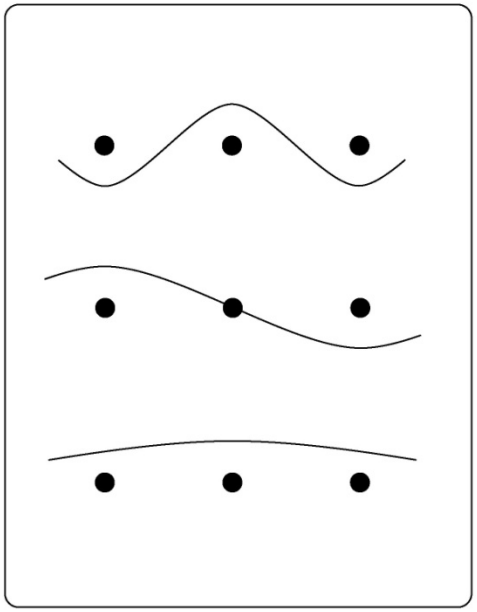


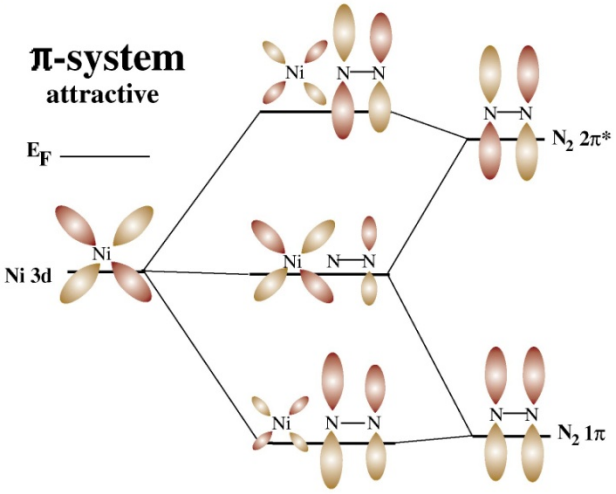
Phys. Rev. Lett. **78** (1997) 2847, *Surf. Sci. Reps.* **55** (2004) 49.

π–Orbital Interaction



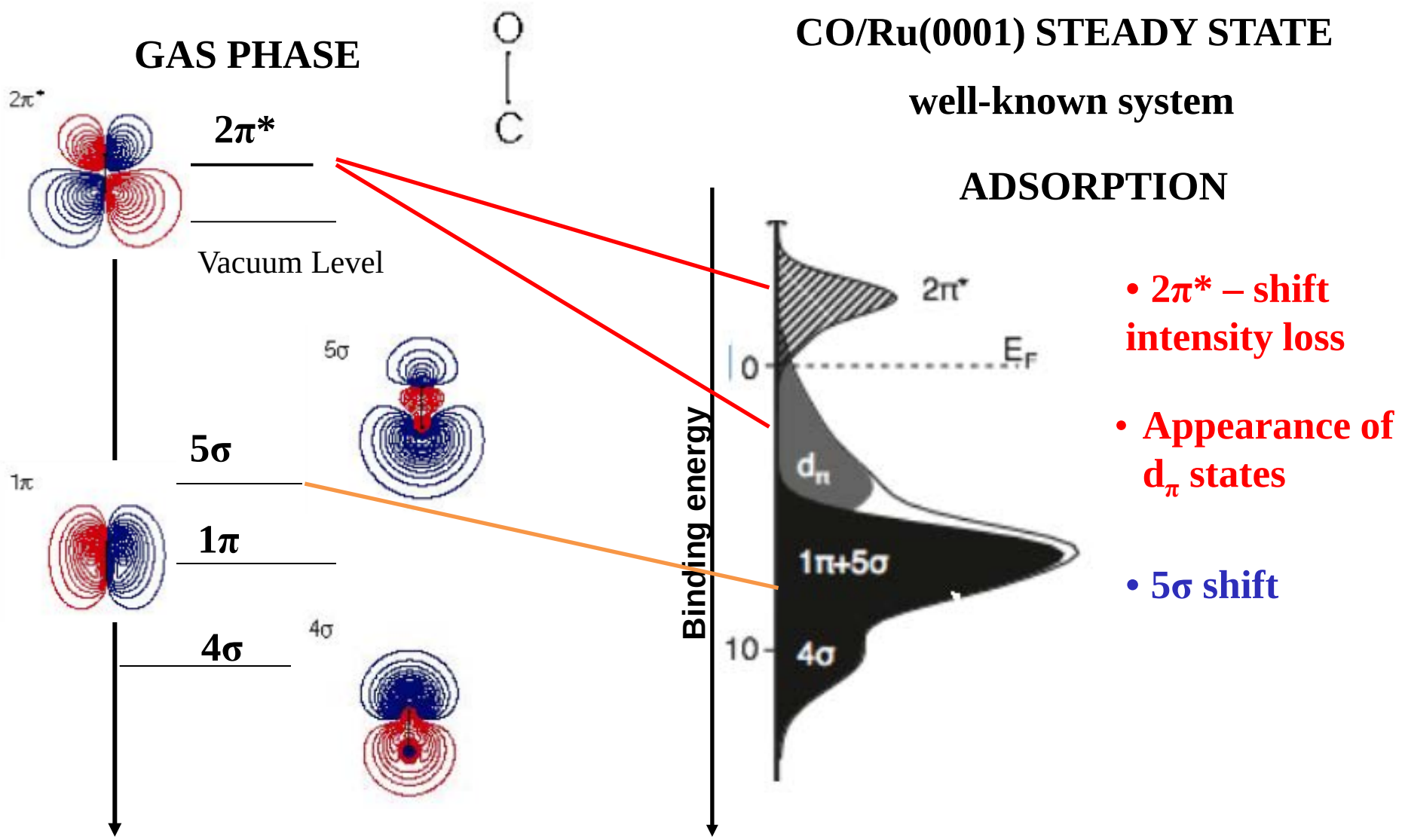
Allylic Configuration
π-Orbital structure of 3 atoms





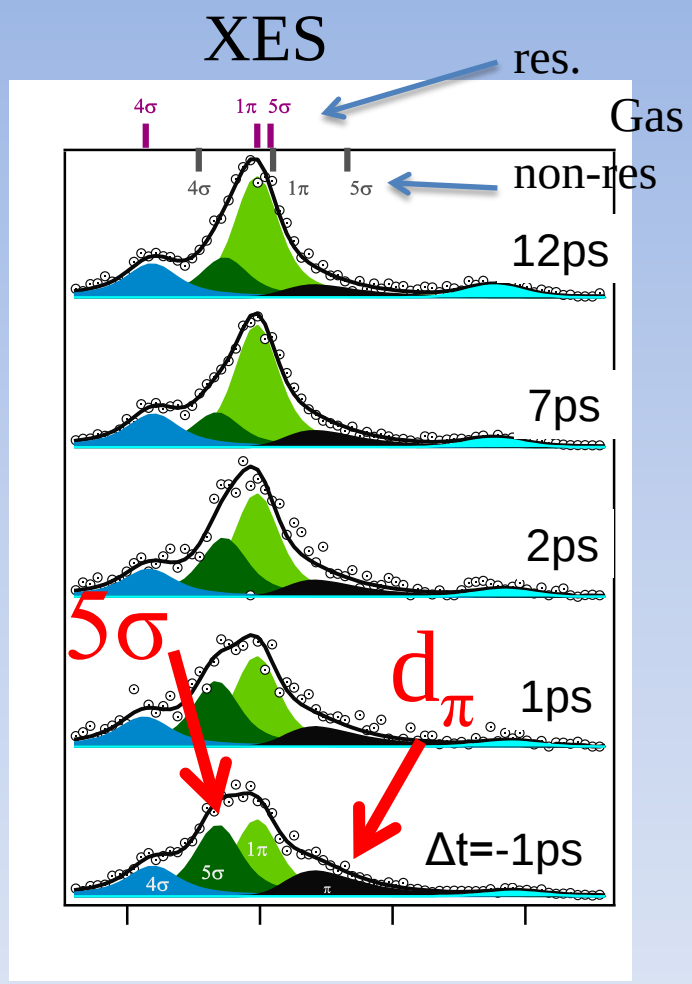
Nilsson and Pettersson, Surf. Sci. Reps. 55, 49 (2004).

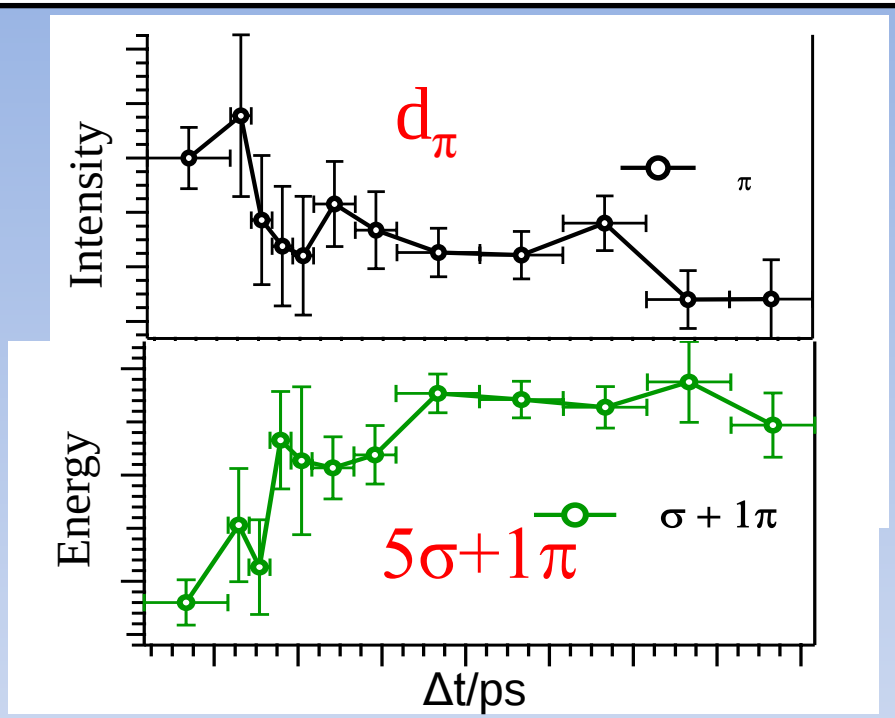
Valence-Electronic Changes upon Adsorption

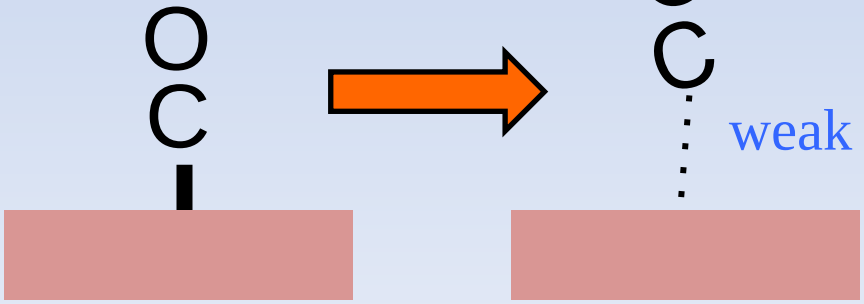


A. Föhlisch, et al. J. Chem. Phys. **121**, 4848 (2004).

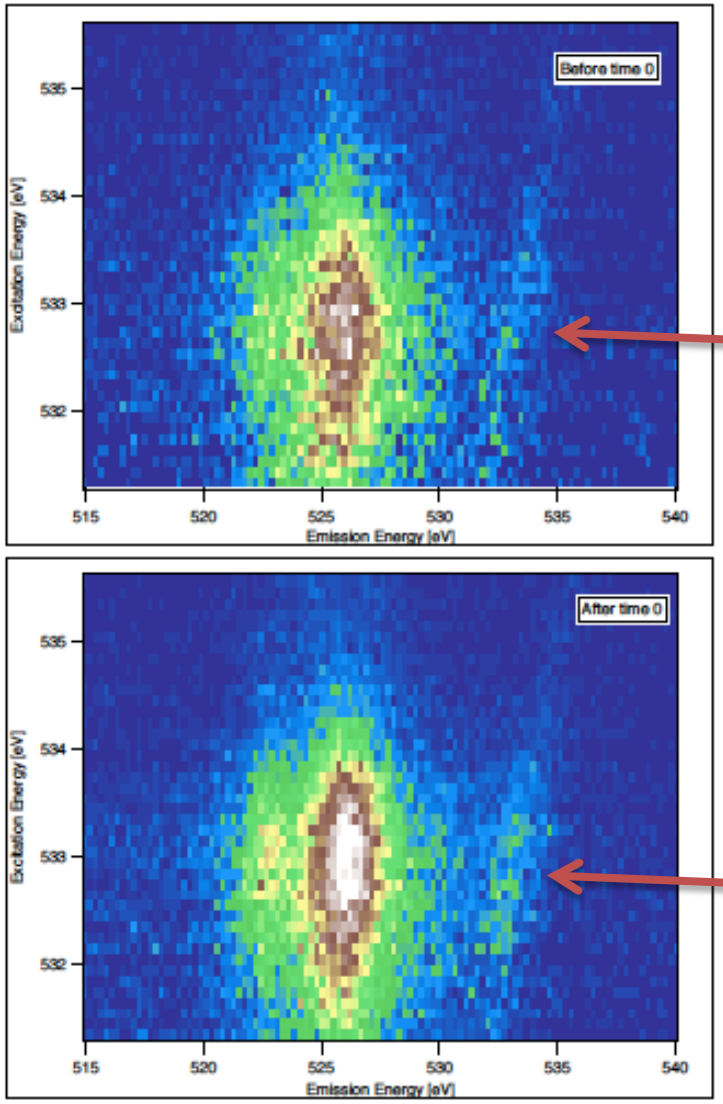
CO Desorption from Ru(0001)
Pump-probe XES







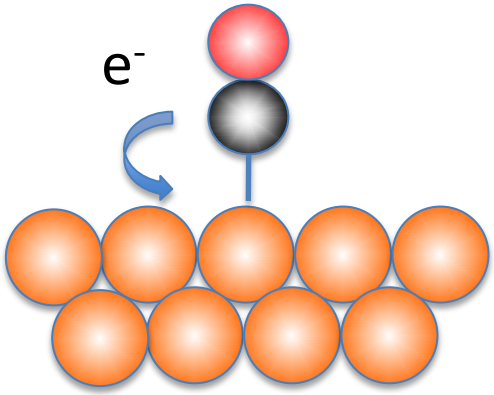
Participator Peak



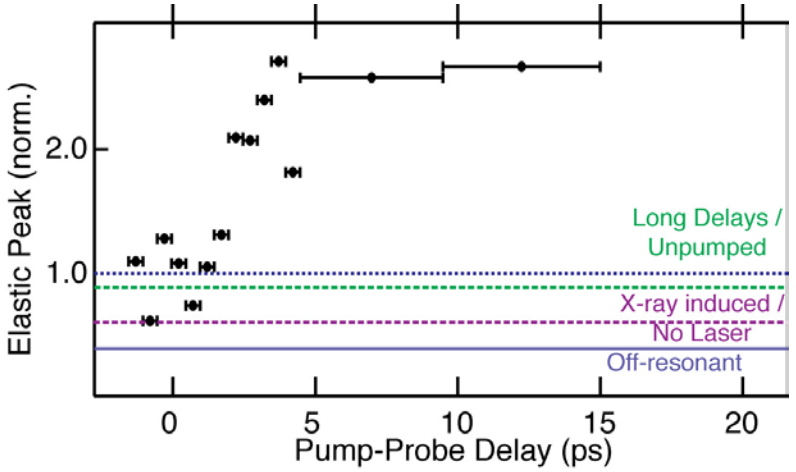
RIXS plot

Elastic peak is the recombination of excited electron

Before pump

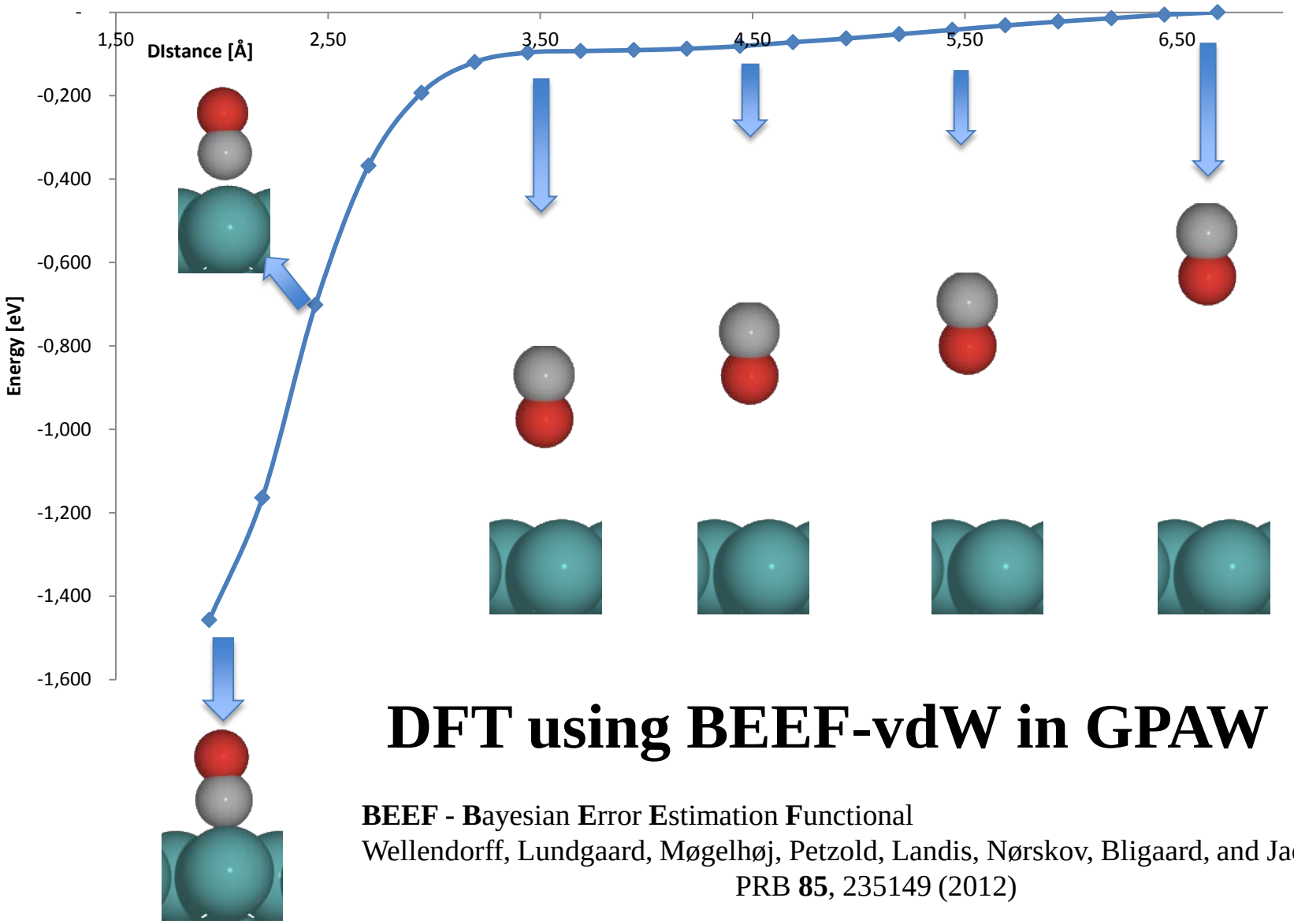


After 5 ps



Slower electron transfer of excited electron
Excited electron can go back: ~ same energy

Minimum Energy Path in Desorption



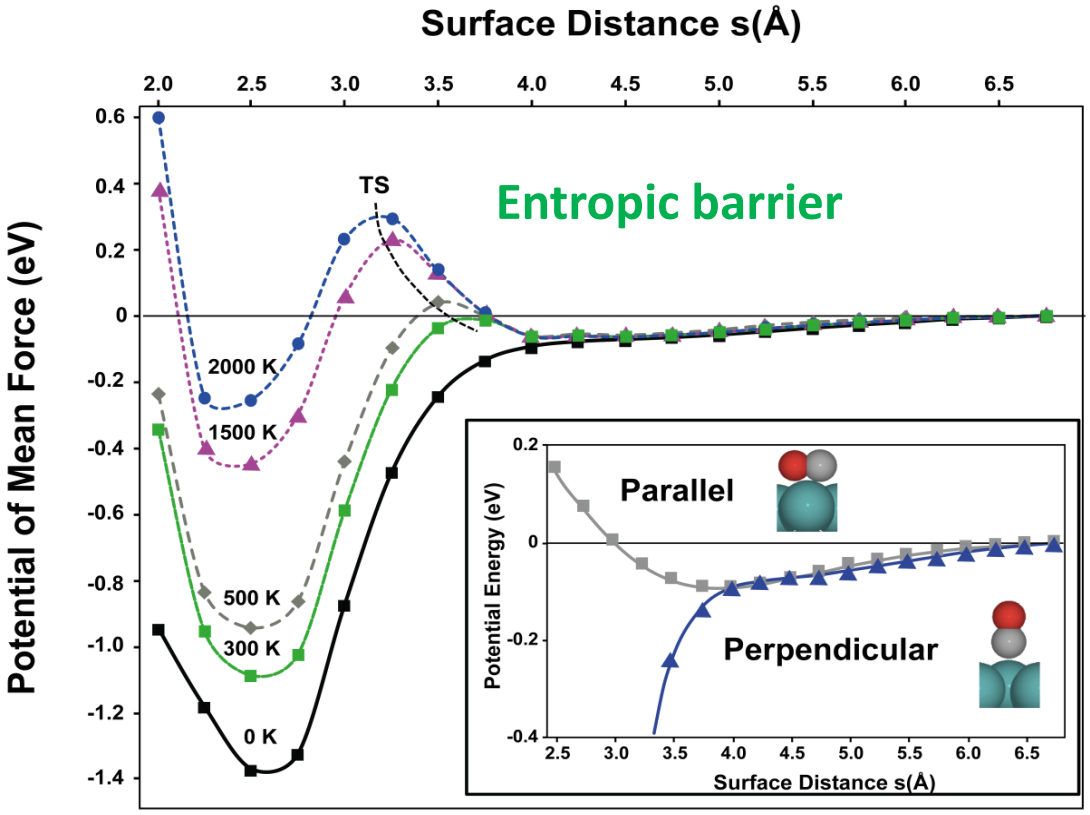
DFT using BEEF-vdW in GPAW

BEEF - Bayesian **E**rror **E**stimation **F**unctional

Wellendorff, Lundgaard, Møgelhøj, Petzold, Landis, Nørskov, Bligaard, and Jacobsen

PRB **85**, 235149 (2012)

Potential of Mean Force



$$W(s) = -k_B T \ln(g(s)) + k_B T \ln(g(\infty))$$

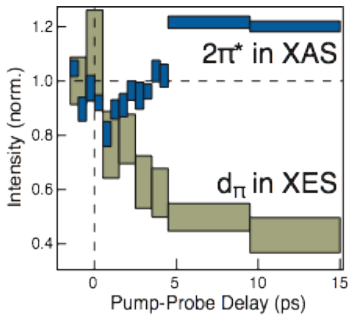
$$g(s) = \Gamma^{-1} \int e^{-\frac{V(s,\mathbf{q})}{\mathbf{k_B} T}} d\mathbf{q}$$

$$g(s) = \Gamma^{-1} \int e^{-\frac{V_0(s)+2V_{trans}(s,x)+V_{rot1}(s,\theta)+V_{rot2}(s,v)}{\mathbf{k_B} T}} dx d\theta dv = \Gamma^{-1} g^{2}{}_{trans}(s) g_{rot1}(s) g_{rot2}(s)$$

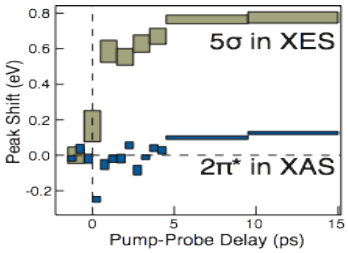
- Large difference in entropy between chemisorbed state (perpendicular only) and molecules in plateau (free to rotate)
- Compute potential of mean force, $W(s)$, to estimate free energy
- Temperature-dependent entropic barrier
- **Two wells: chemisorbed and precursor state to desorption (and adsorption)**

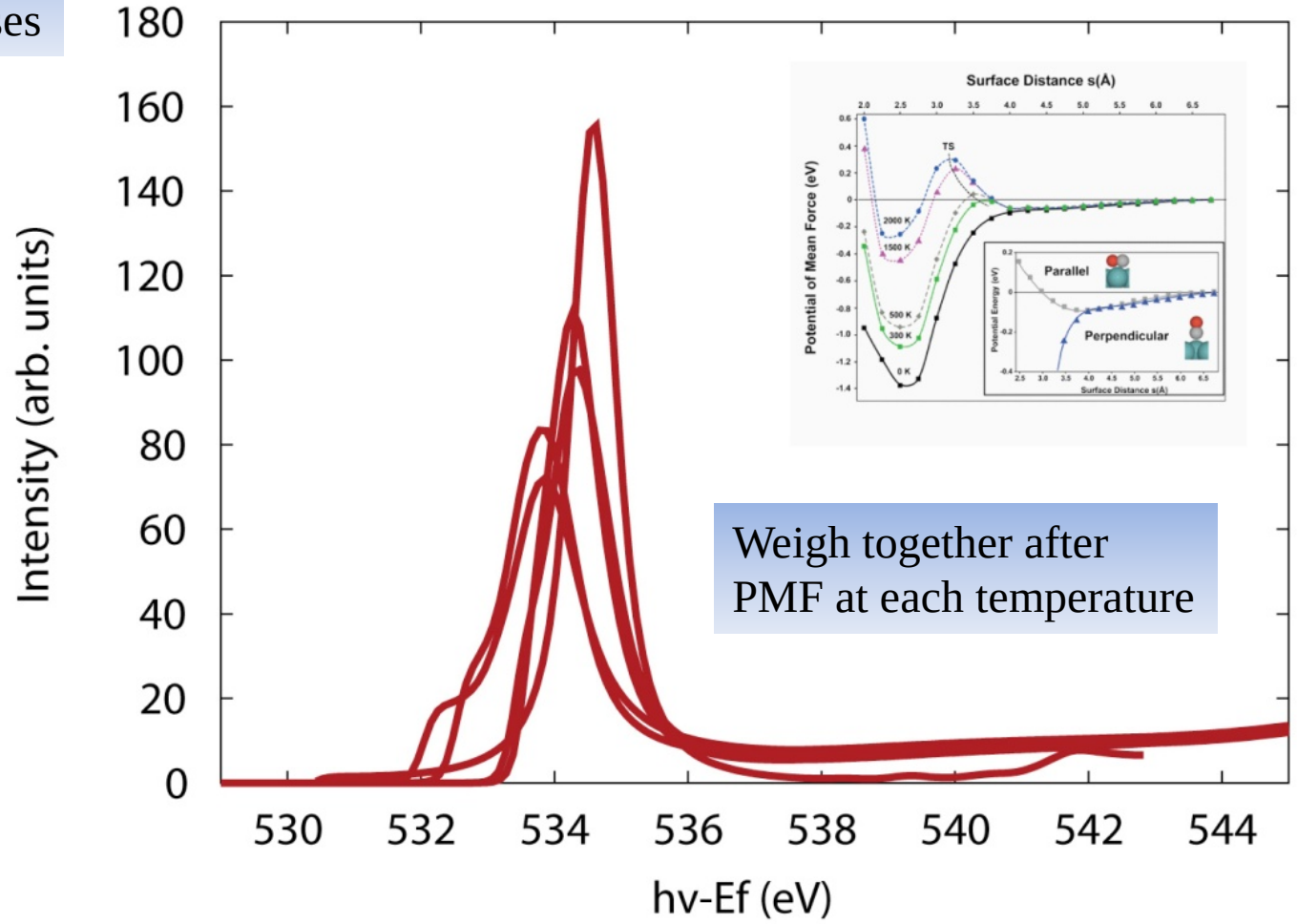
Computed XAS CO/Ru(0001)

Experiment:
2π* intensity increases



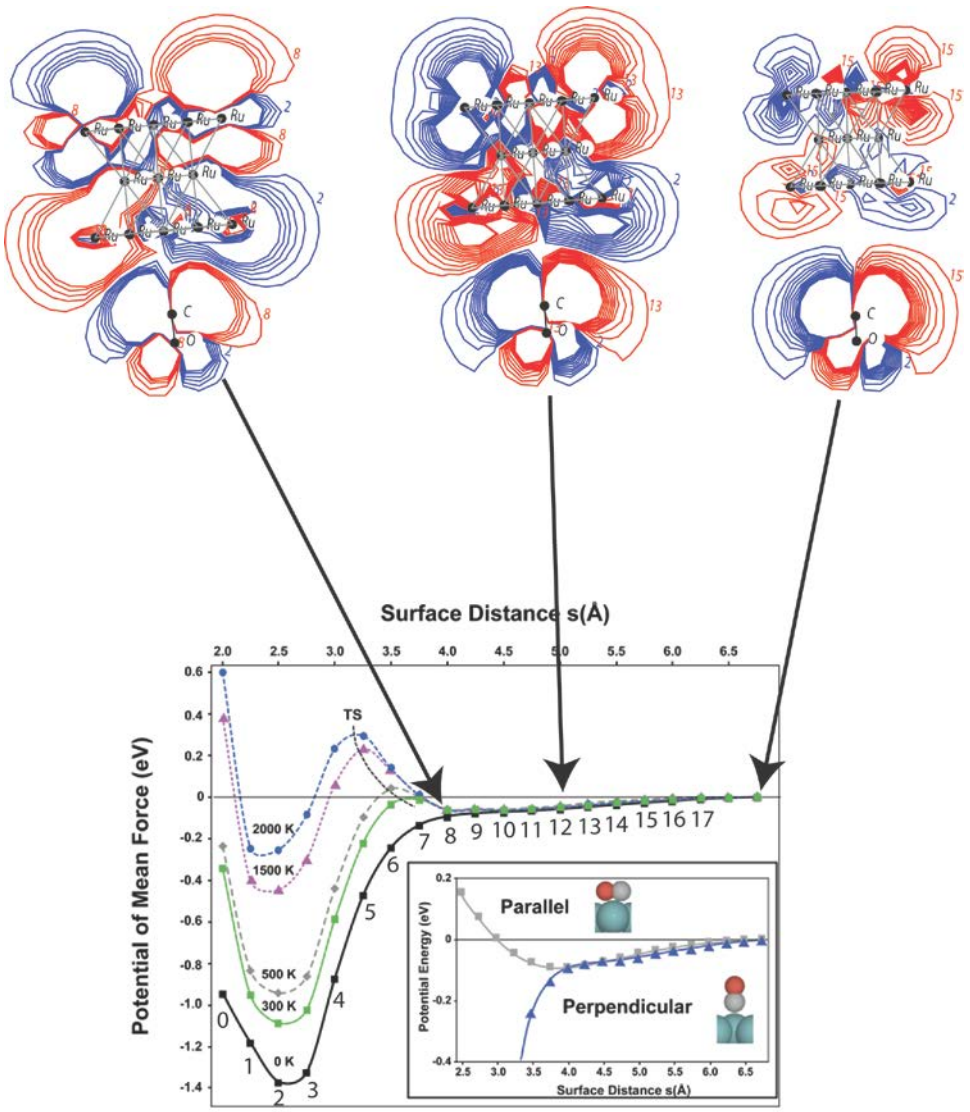
Experiment:
2π* moves to higher energy





Weigh together after PMF at each temperature

Core-excited 2π* in Precursor State



Excitation done resonantly in XES to minimize shake-up

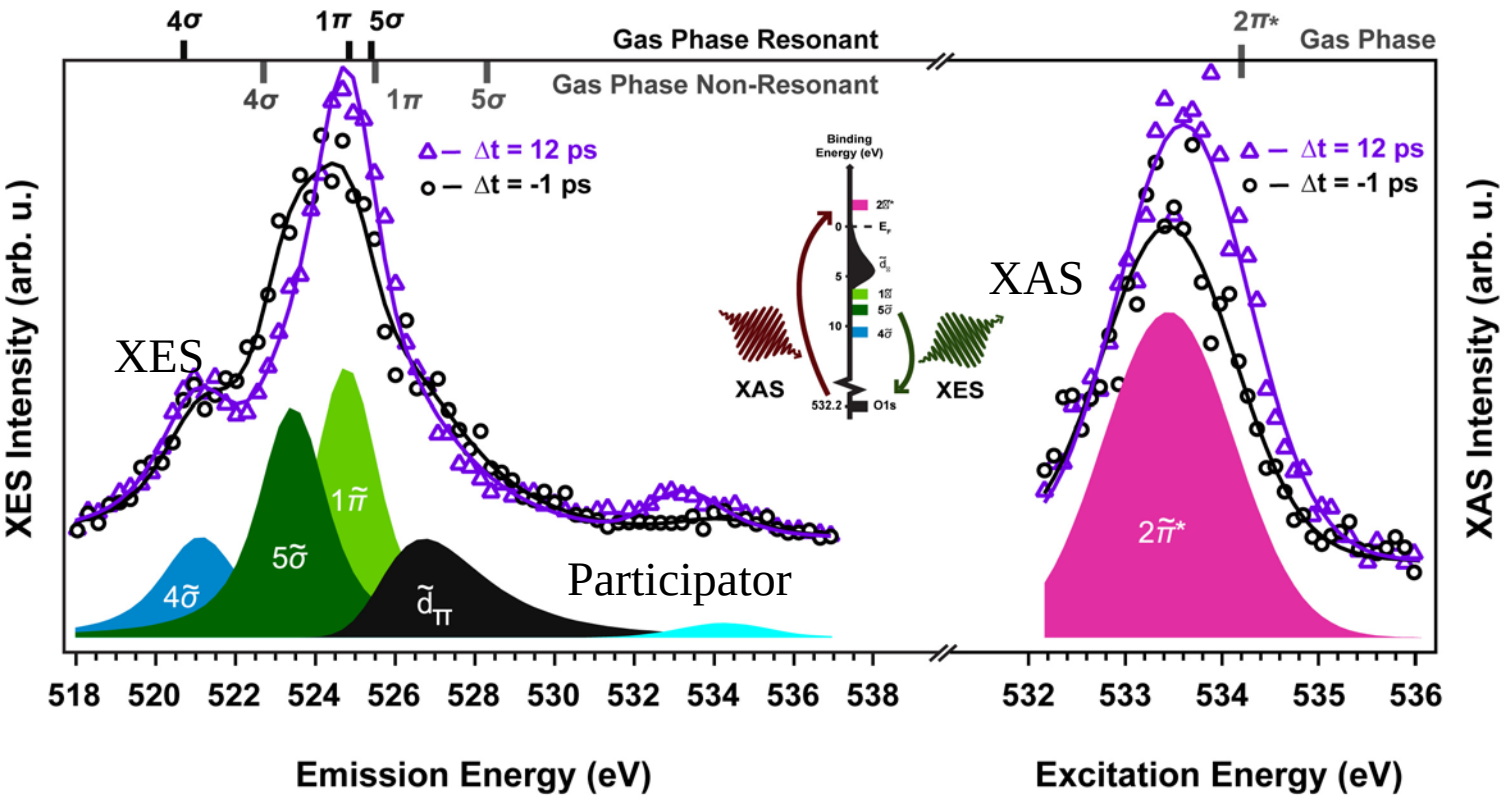
Chemisorbed: excited electron delocalizes and does not affect the decay

Gas phase: excited electron is localized, causes shifts and enhanced participator decay

Core-excited state is extended → some delocalization in precursor state

Smaller shifts, less participator

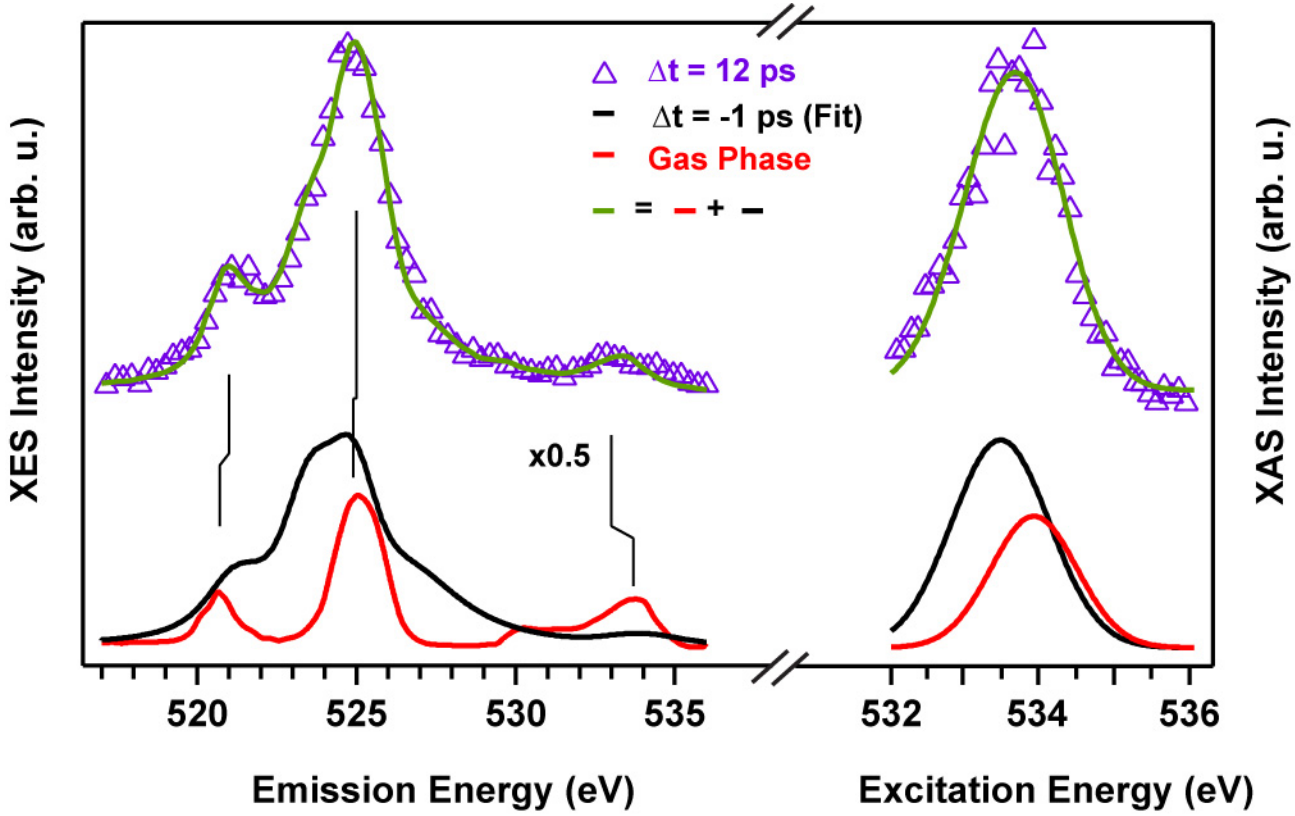
Before and After Pump



Shifts towards gas phase (resonant)
d_π looses itensity
Participator increases in intensity –
- less connection to surface

π* shifts towards gas phase position

Fit Using Chemisorbed and Gas Phase Resonant Excitation

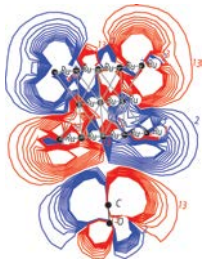


Consistent with ~30% in outer well (precursor) with extended π* state not fully localized on molecule
(Smaller shifts, lower participator intensity)

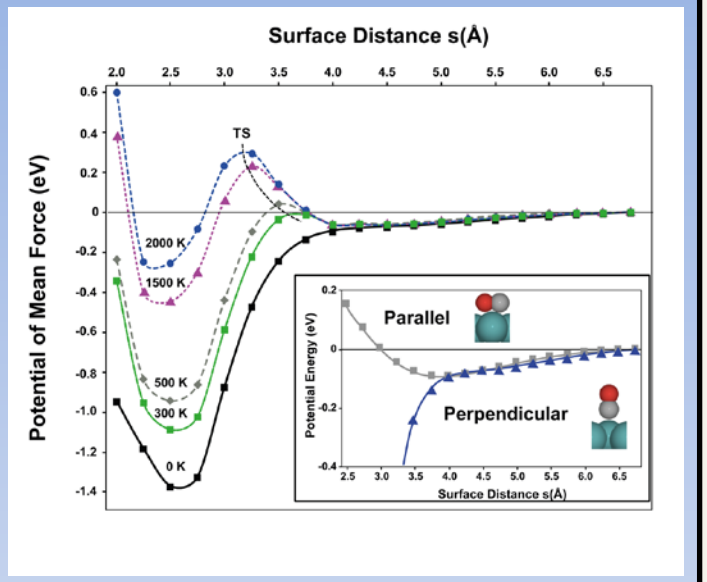
From SFG ~50% return to chemisorbed as the surface cools off
(Bonn et al. PRL**84** 4653 (2000))

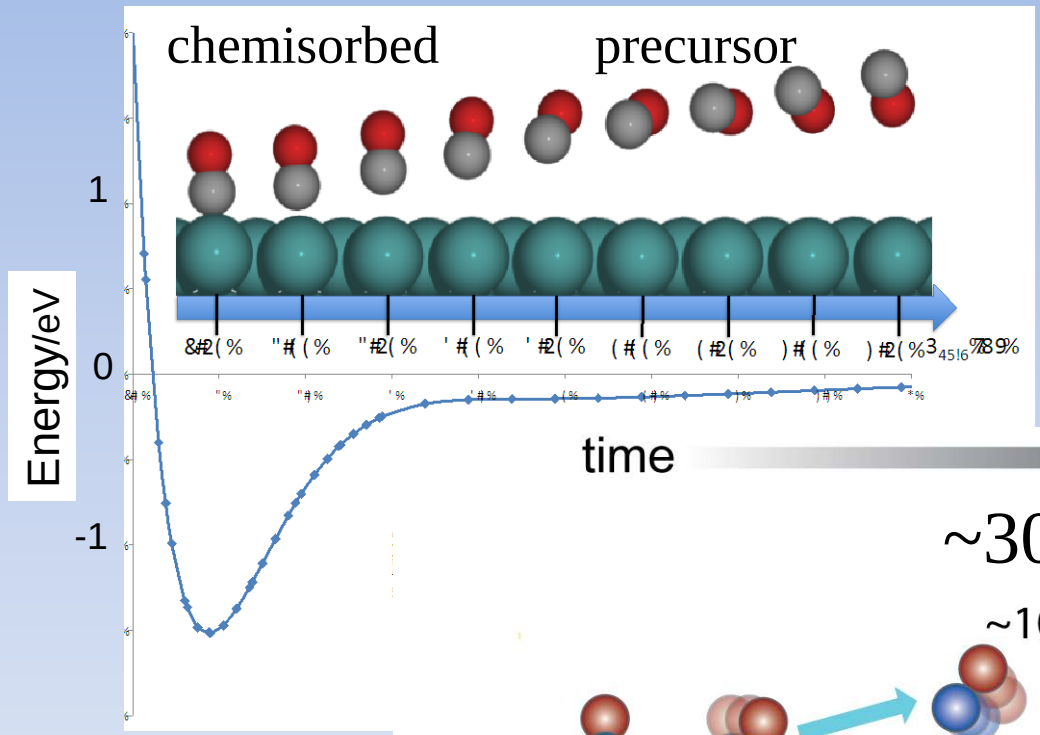
70% unpumped + 30% gas phase
But gas phase:
4σ: 0.3 eV smaller shift (1.8 eV)
1π: 0.1 eV smaller shift (0.8 eV)
Participator: -0.5 eV and x0.5

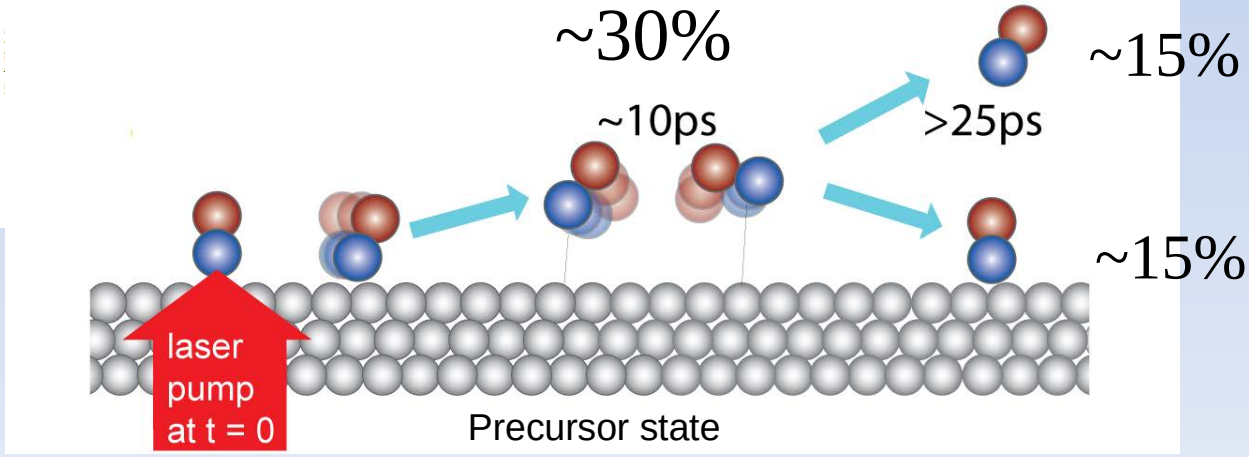
XAS 70% + 30%
Gas phase π* -0.3 eV



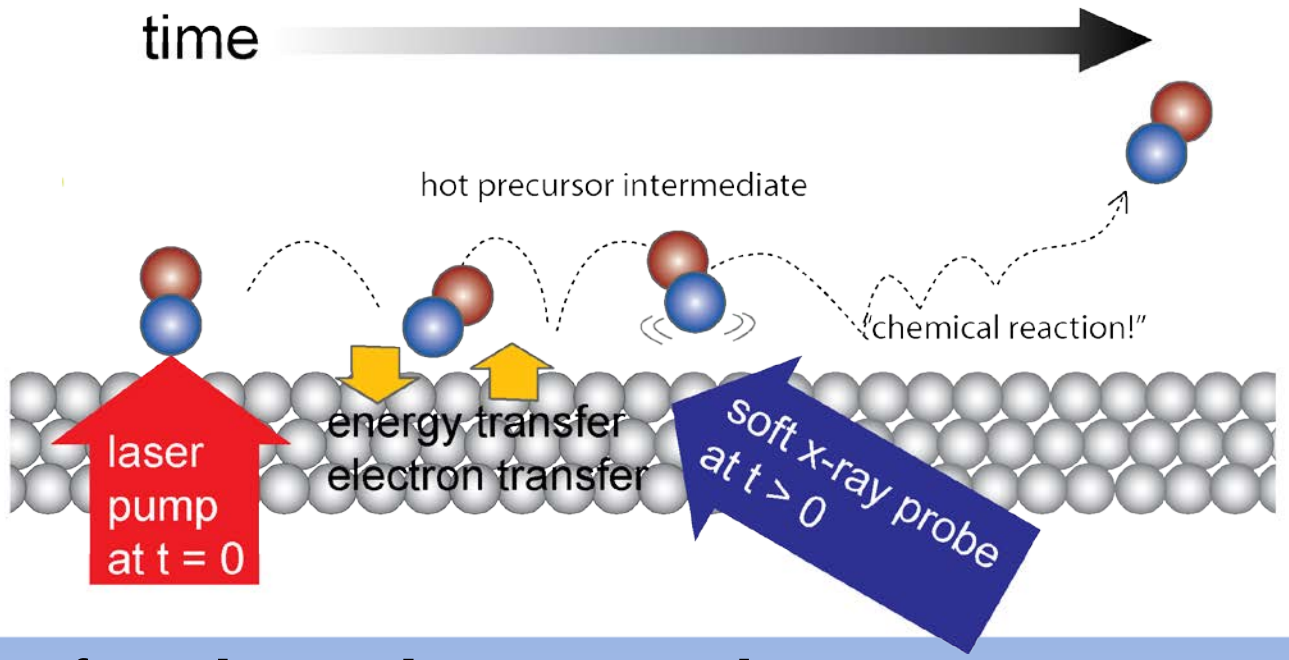
CO Desorption from Ru(0001): Weakly Bound Precursor State







Conclusions



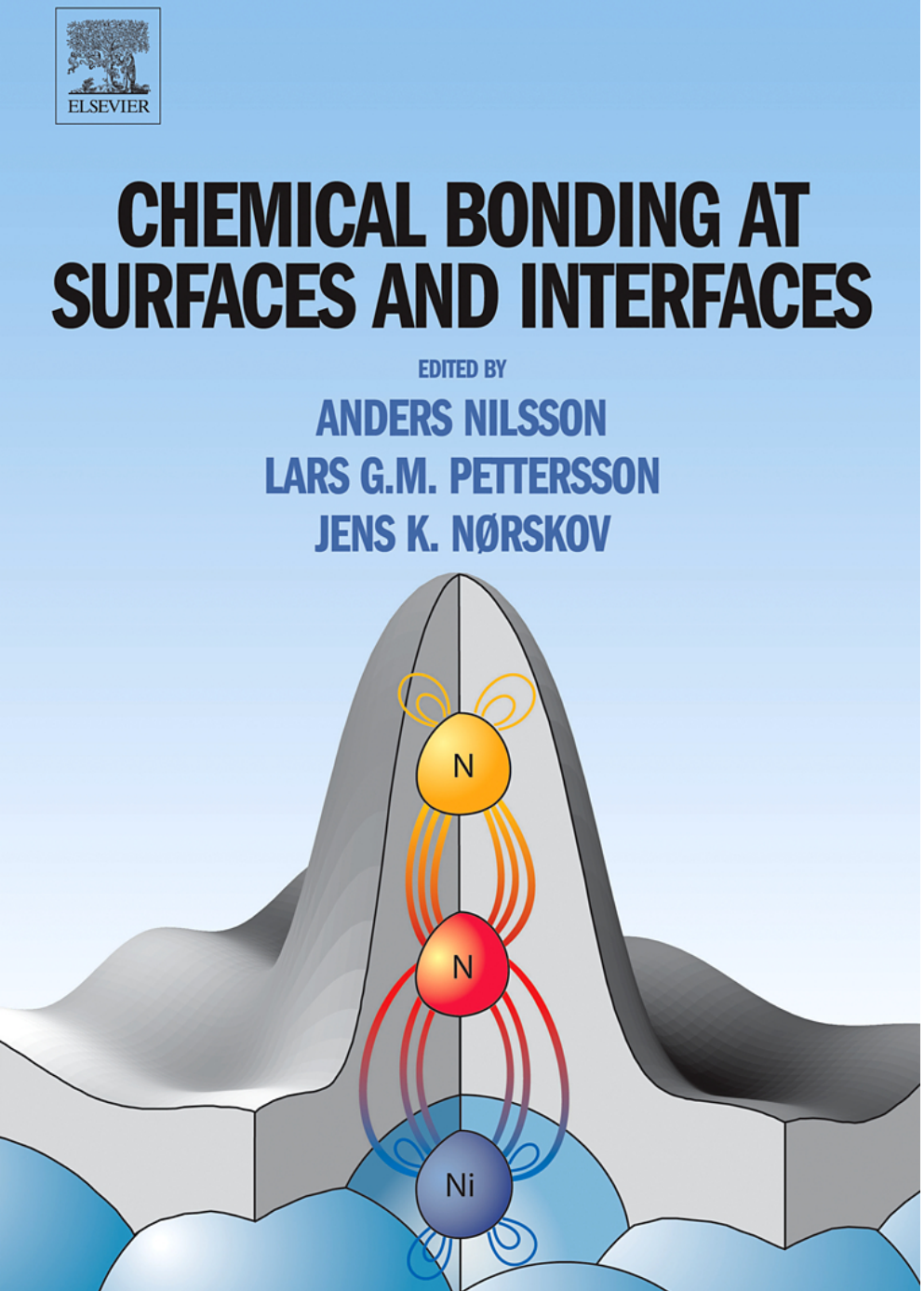
- First surface chemical reaction with LCLS
- Proof of principle

Observation of two different excitations of CO

Strong coupling to motion parallel to the surface; early times

Precursor to desorption in a weakened surface chemical bond

- CO+O/Ru(0001) → CO_2, H+CO → HCO, Fischer-Tropsch,…
- Higher pressure (~100 torr), photon in – photon out
- Shorter FEL pulses, THz radiation control (LCLS 2)
- "Chemist's dream"



Elsevier (2008)

1. **Woodruff**, *Surface Structure*
2. **Nilsson & Pettersson**, *Bonding*
3. **Luntz**, *Dynamics*
4. **Bligaard & Nørskov**, *Heterogeneous Catalysis*
5. **Bent**, *Semiconductor surface chemistry*
6. **Strasser & Ogasawara**, *Electrochemistry*
7. **Brown, Trainor & Chaka**, *Geochemistry*