Ultrafast Surface Chemistry and Catalysis using Soft X-rays at LCLS

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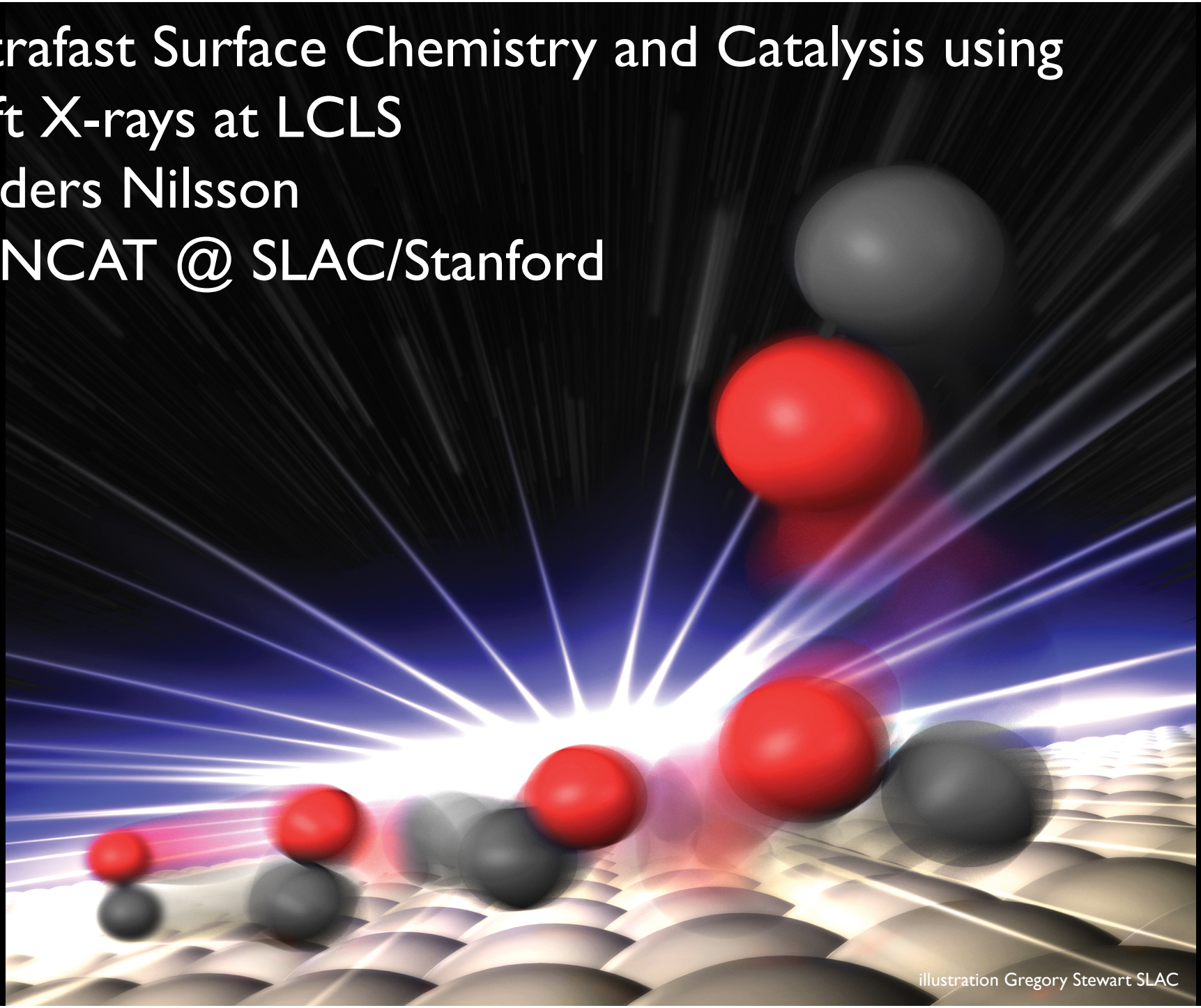

Collaboration

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

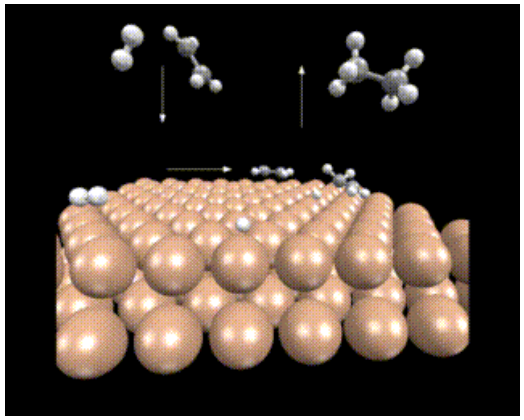
Office of Basic Energy Sciences

Ammonia feeds the world; Fertilizers

1-2 % of the global energy consumption

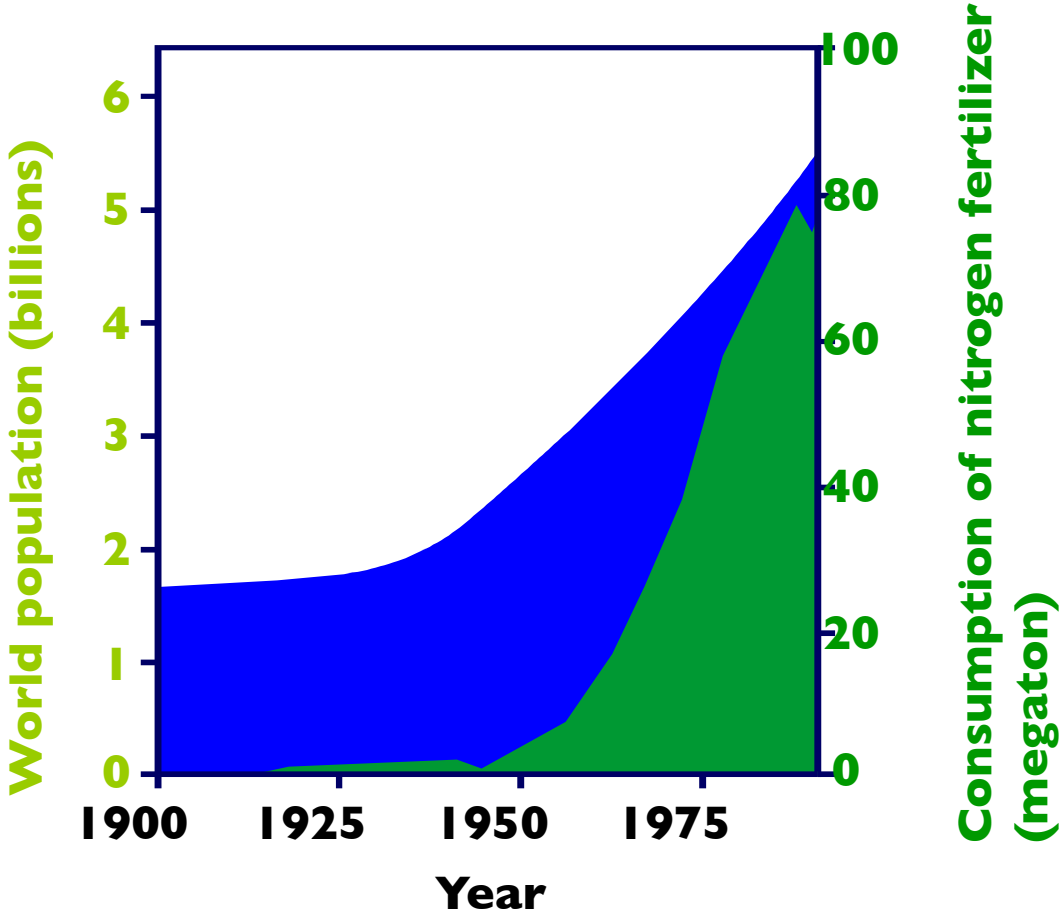
$N_2 + 3H_2 \leftrightarrows 2NH_3$

Haber Bosch Process



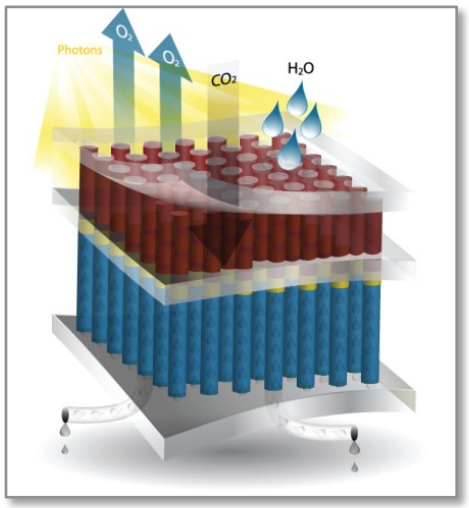
Catalysis

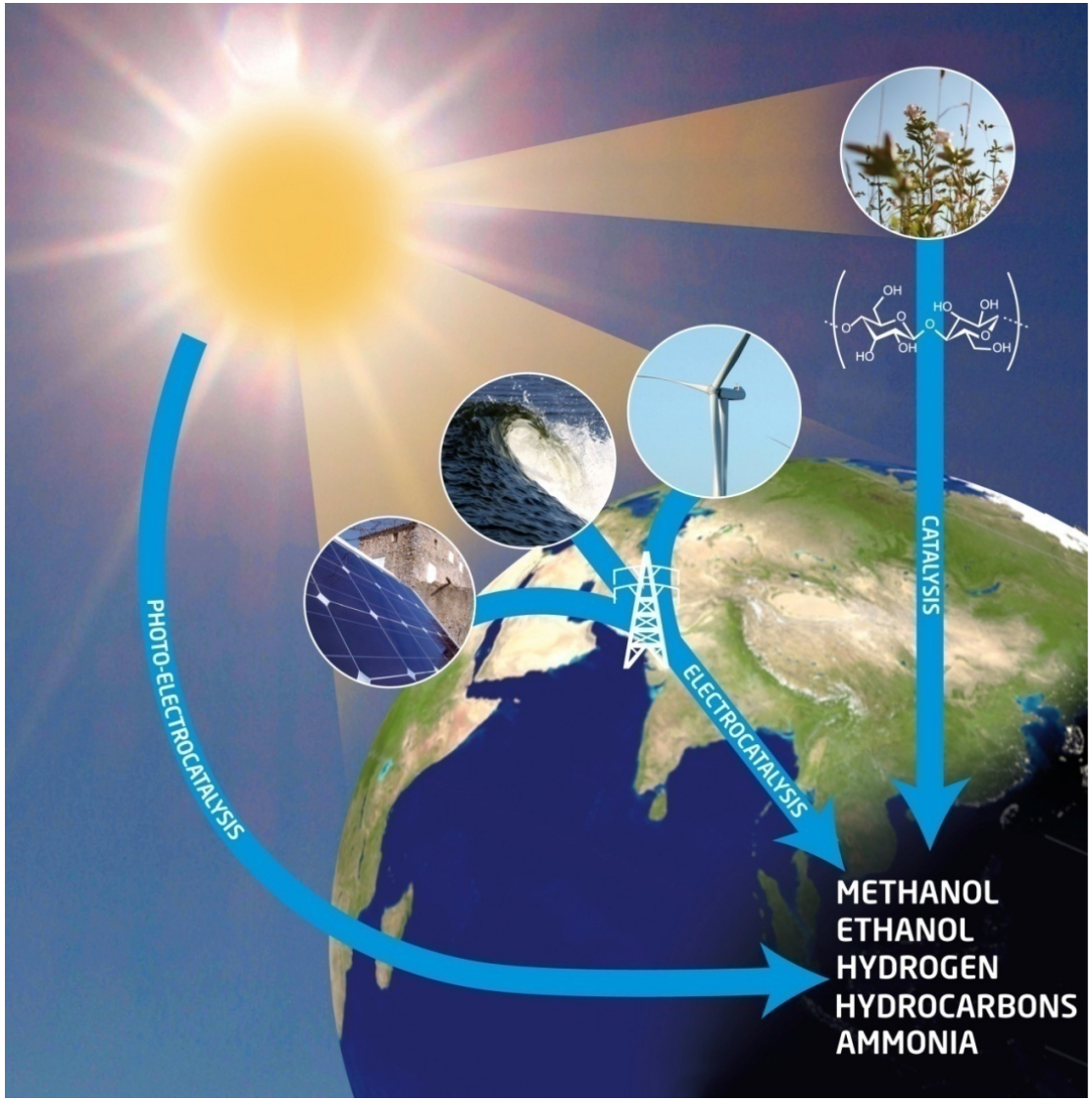
Nobelprize 1918 and 2007



Sustainable fuels

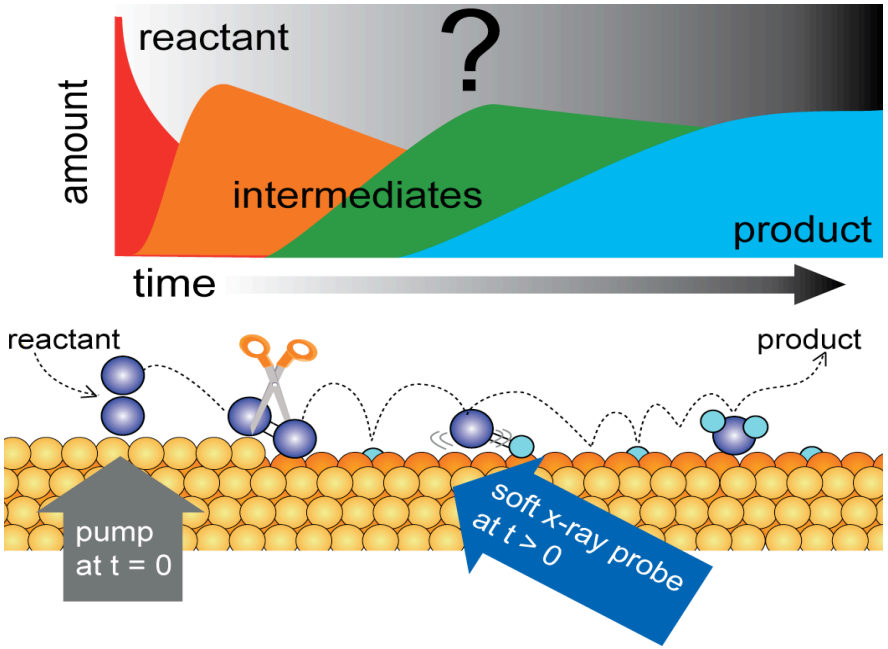
Catalysis is key
Biomass → fuels
Electricity → fuels
Direct sunlight → fuels
(artificial photosynthesis)
Novel catalysts needed
Made from Earth abundant materials

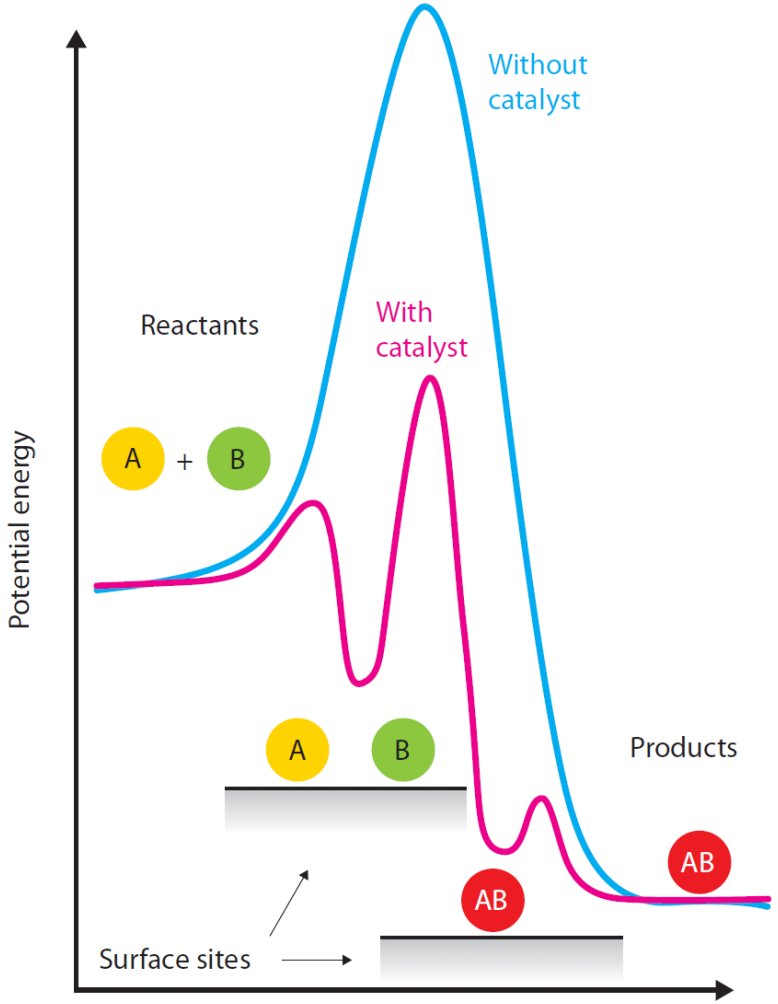




The Catalyst Challenge

Understanding reaction mechanism and dynamics





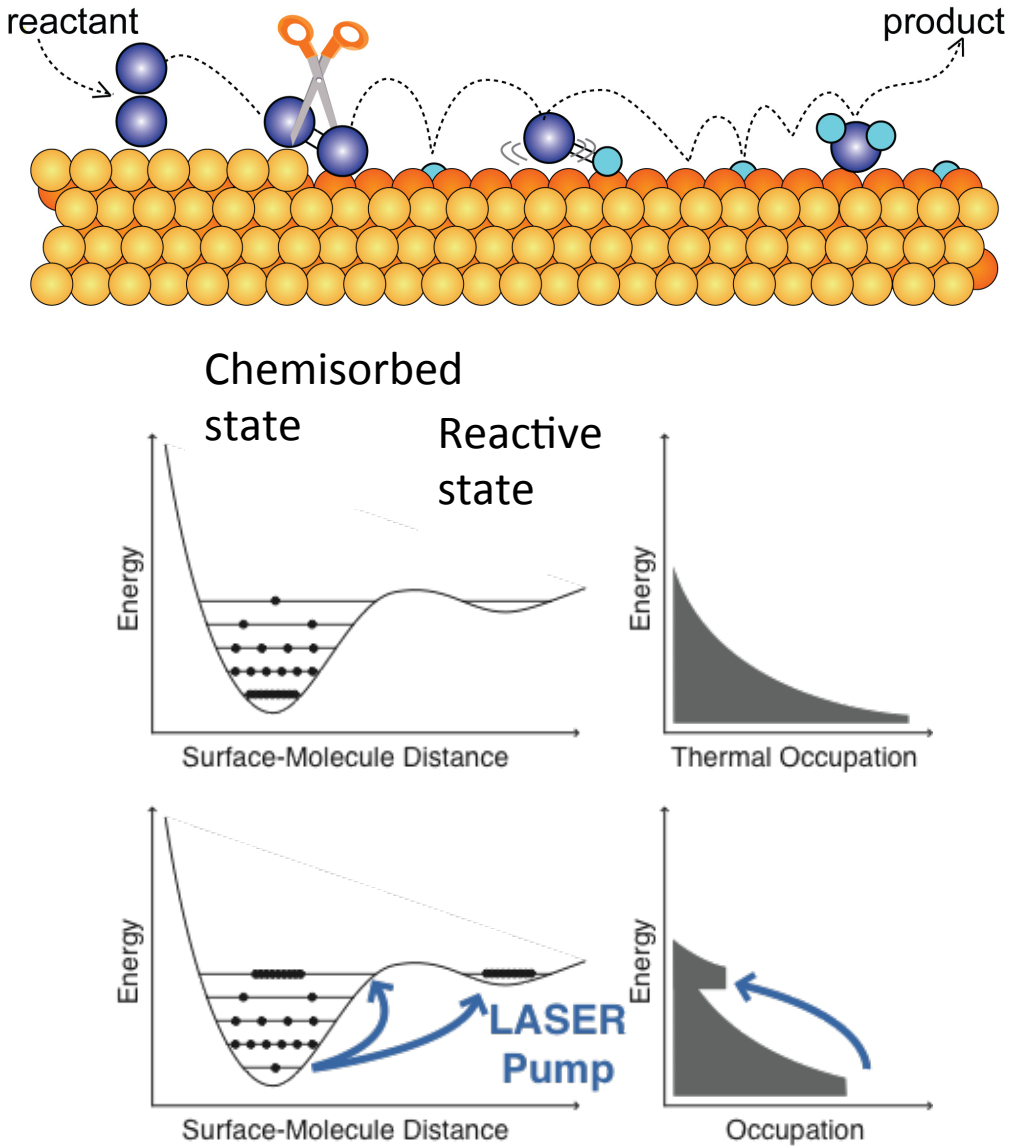
Probing the Reactive State in Catalysis

Most important catalytic reactions are driven by thermal processes

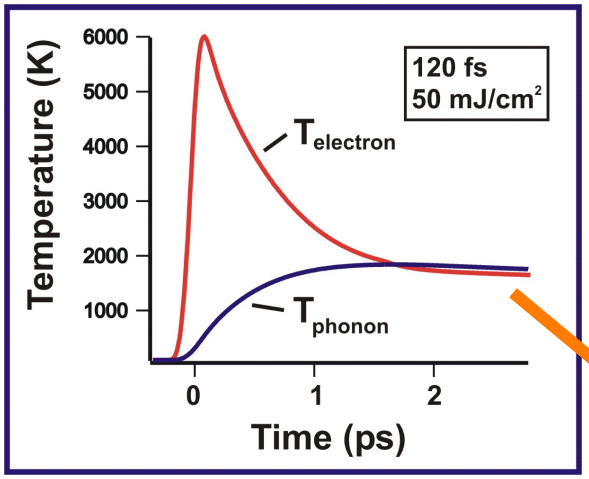
The number of turn-over events at each active site at a given time is extremely low

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



LCLS pump-probe experiments
400 nm fs-laser induced desorption of CO from Ru(0001)



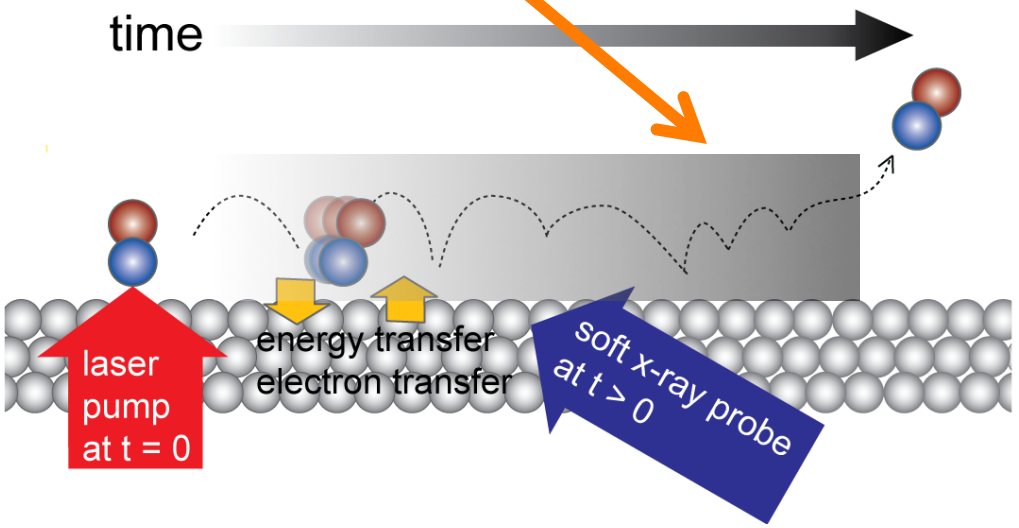
400 nm fs-laser pump

⇩

<1ps electronic excitation

⇩

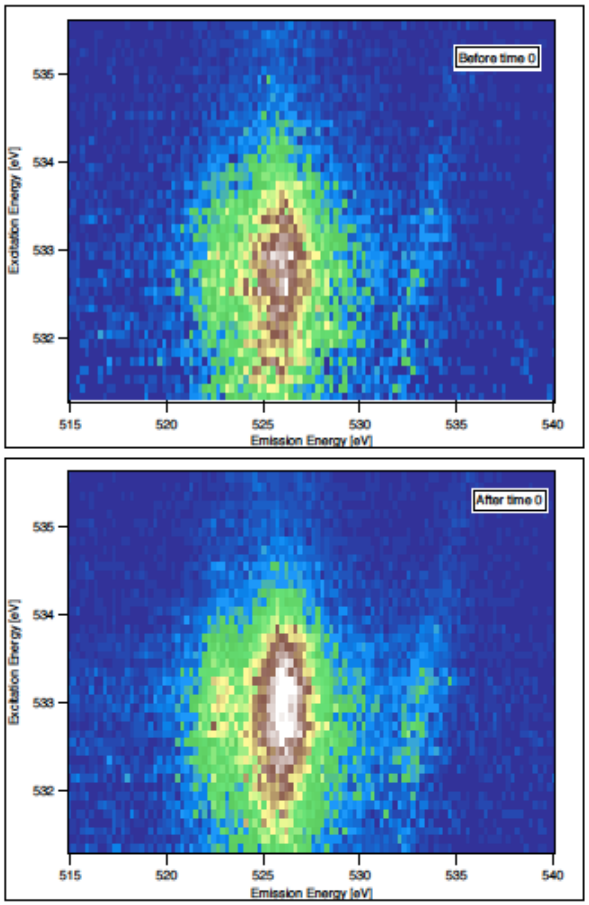
>1ps phononic excitation



Previous ultrafast study: C-O vibration (SFG)

This work: Ru-C-O electronic structure (X-ray spectroscopy)

Experimental Set-up
Full RIXS plane

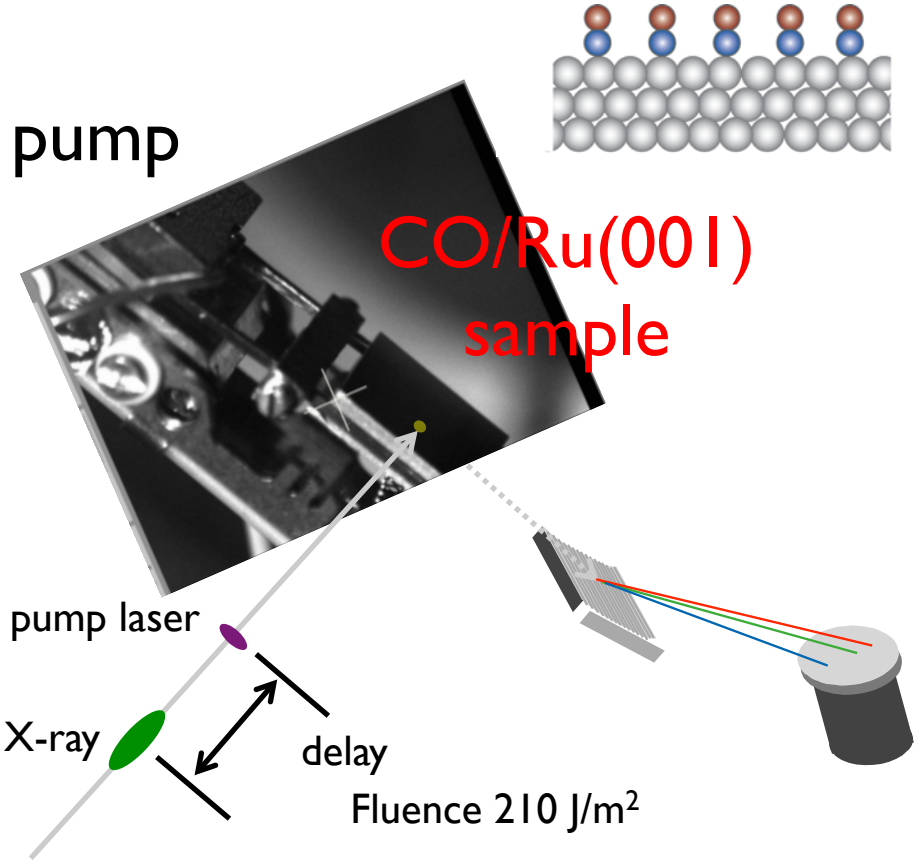


FEL photon energy

x-ray emission energy

before pump

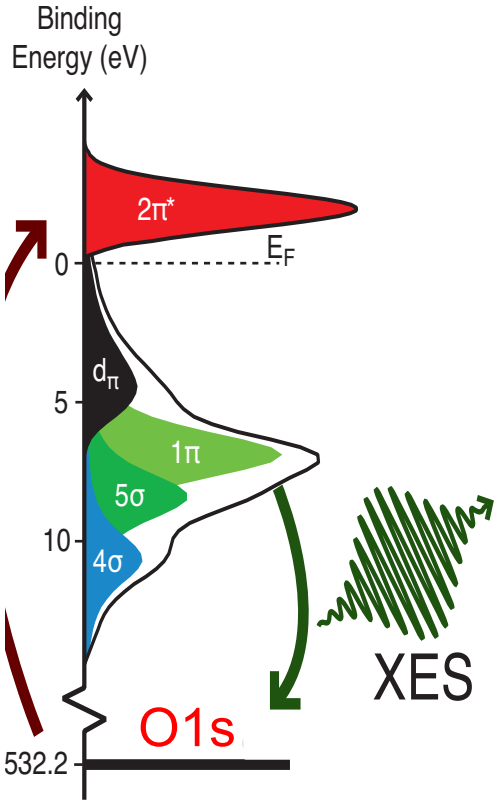
after pump

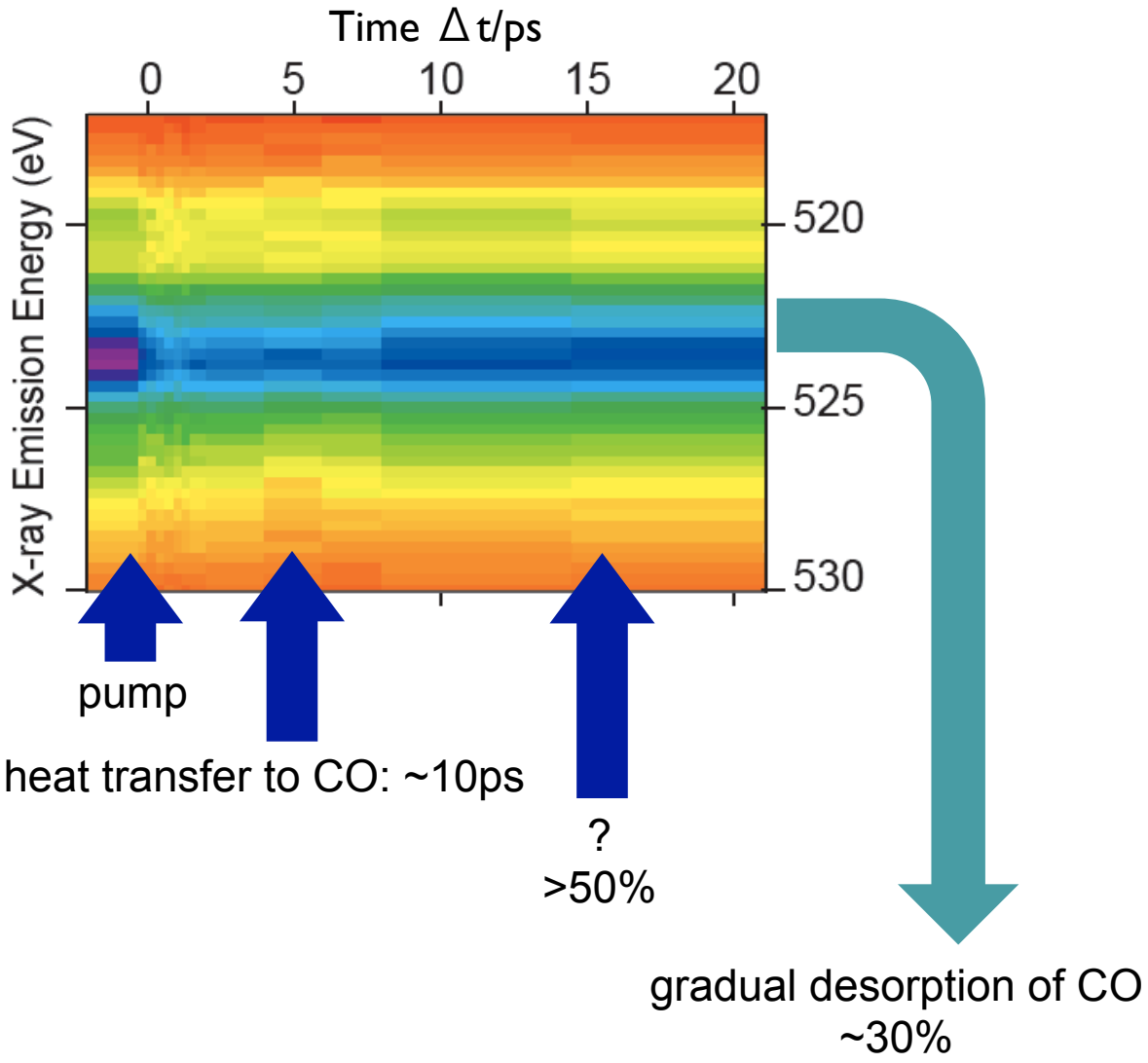


Pump-Probe delays between 100 fs to 20 ps
≈ 200-300 fs time resolution

J. Electron Spectr. **187** (2013) 9

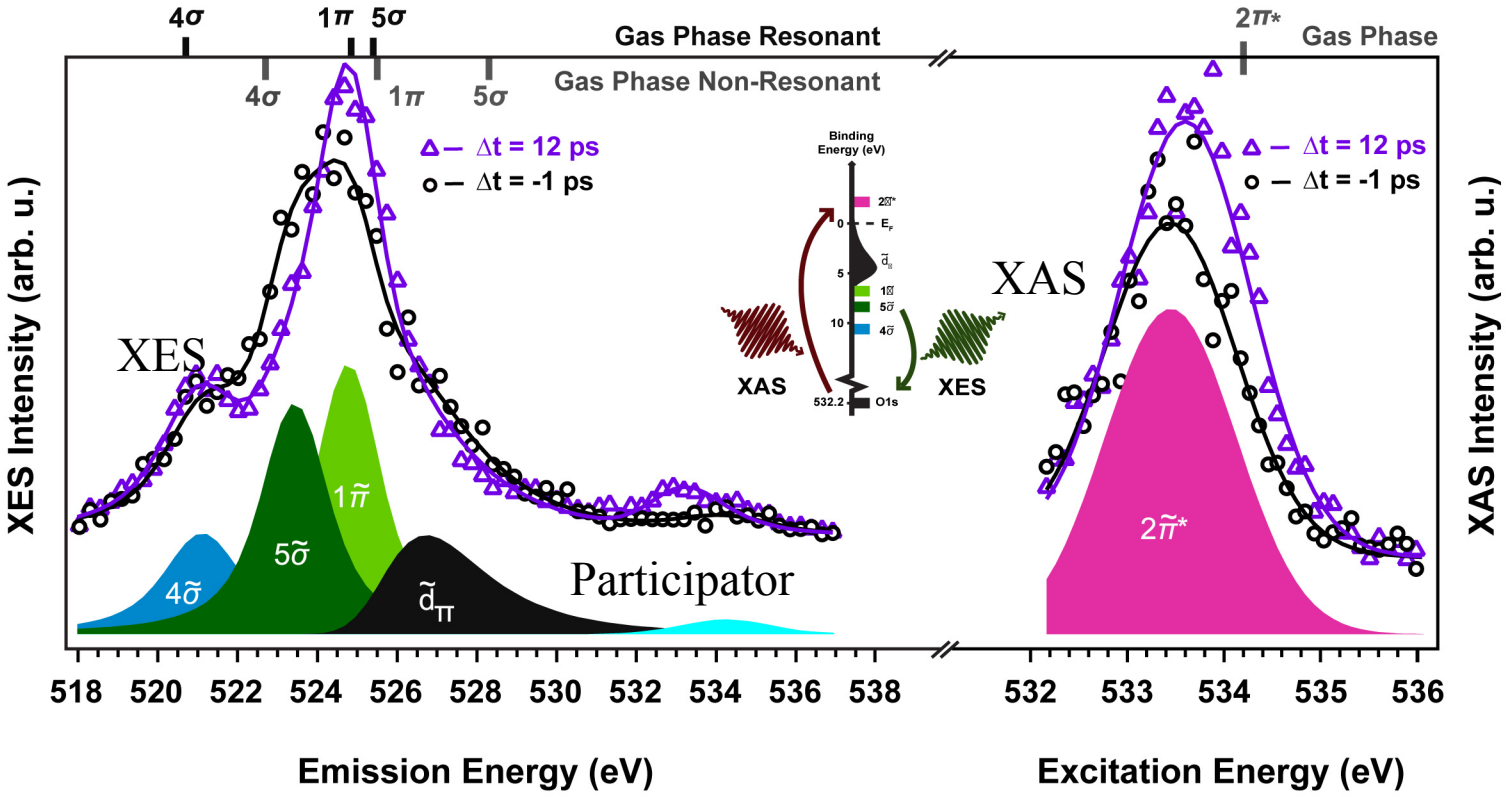
LCLS pump-probe experiments
X-ray emission and X-ray absorption spectrscopy





J. Electron Spectr. **187** (2013) 9

Before and After Pump

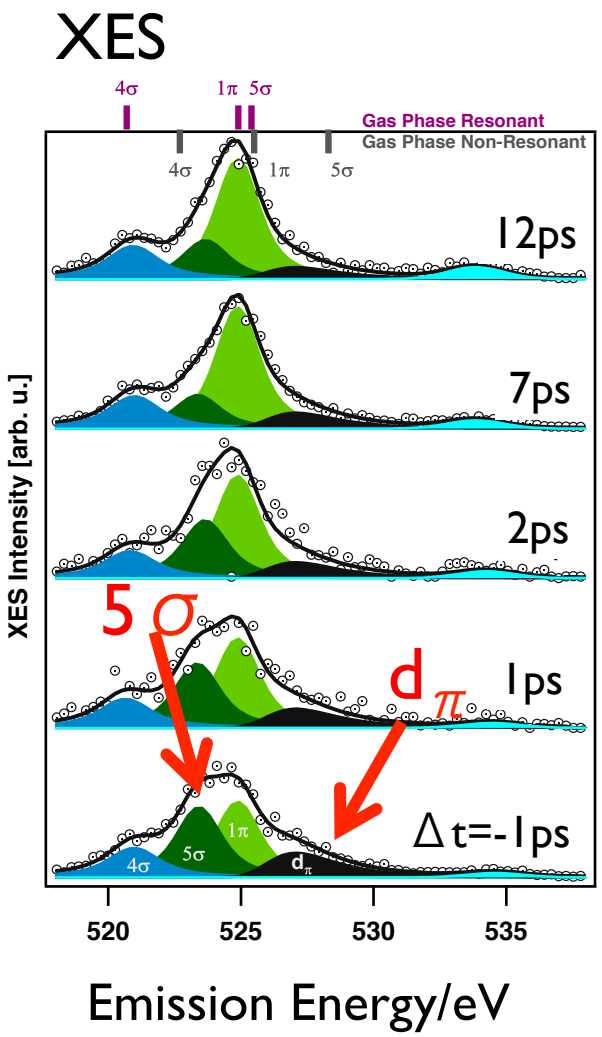


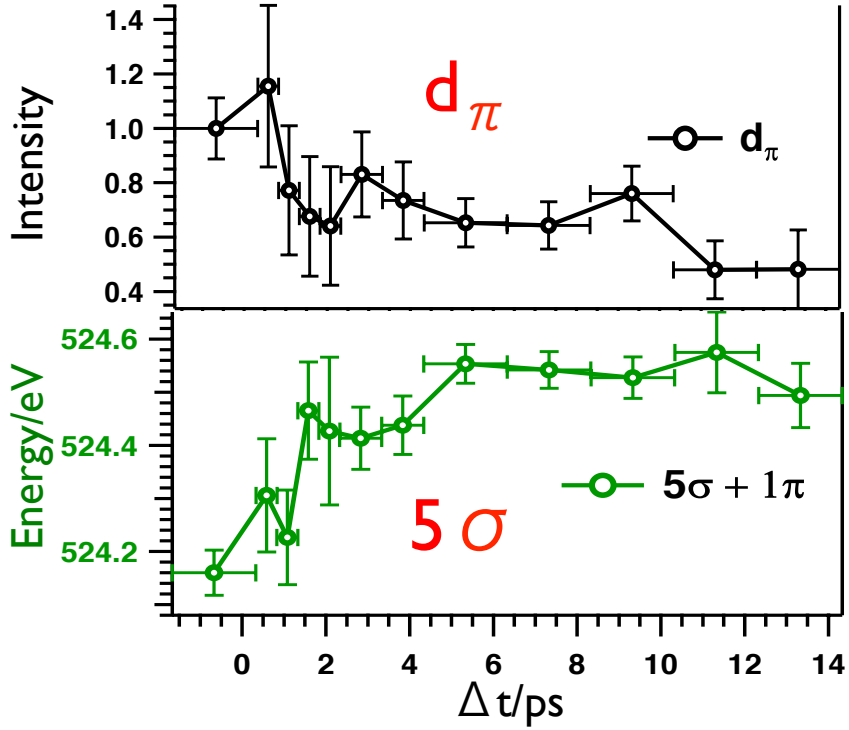
Shifts towards gas phase (resonant)
d_π looses itensity
Participator increases in intensity –
- less connection to surface

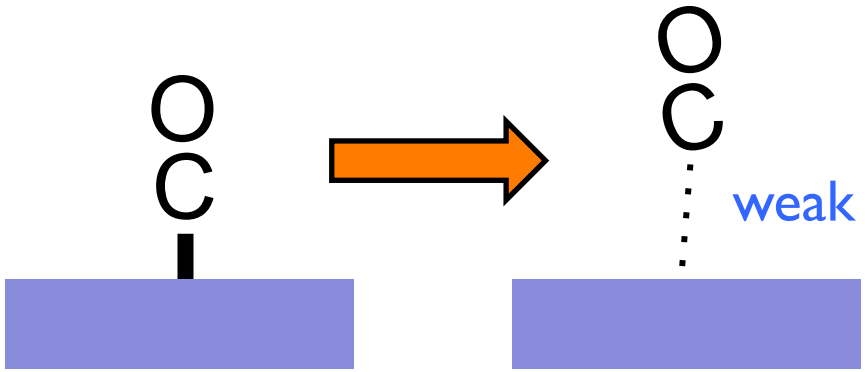
π* shifts towards
gas phase position

Science **339**, 1302 (2013)

CO desorption from Ru(0001)
Pump-probe XES

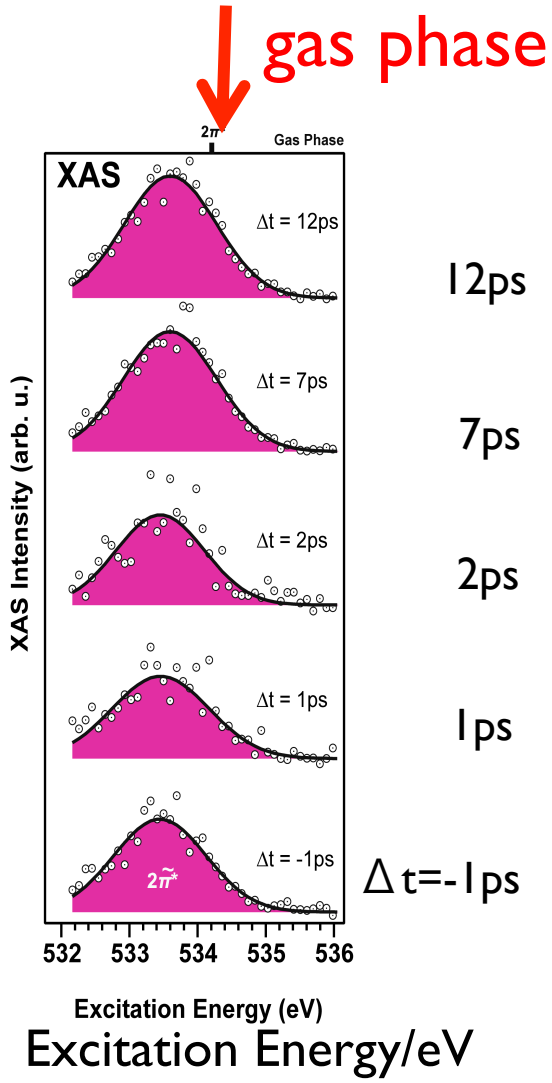


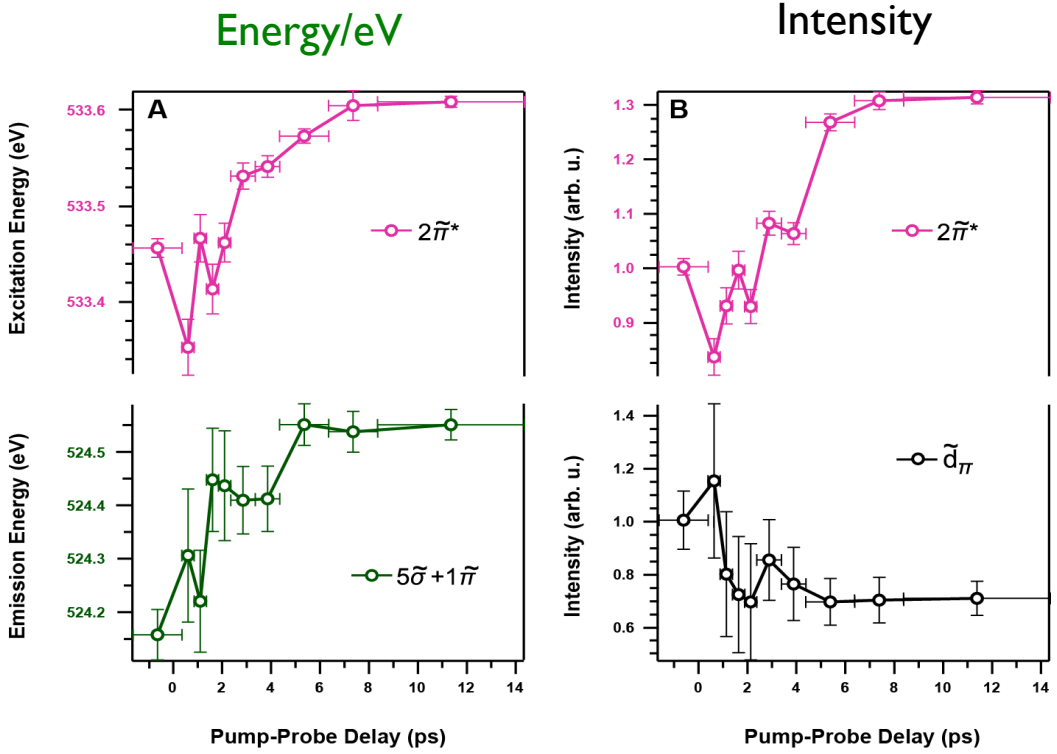


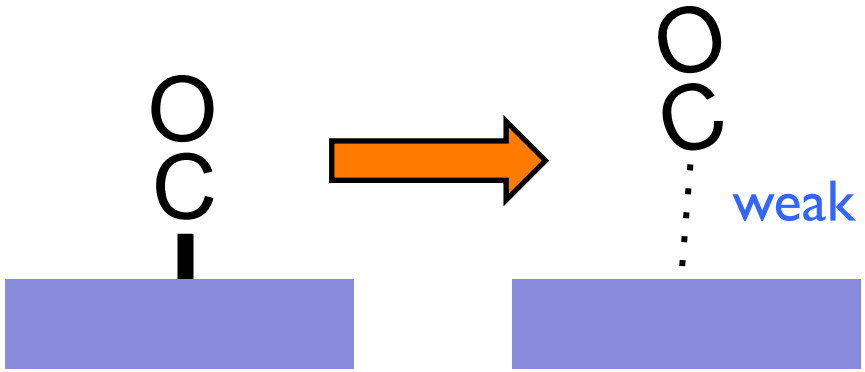


Science **339**, 1302 (2013)

CO desorption from Ru(0001)
Pump-probe XAS







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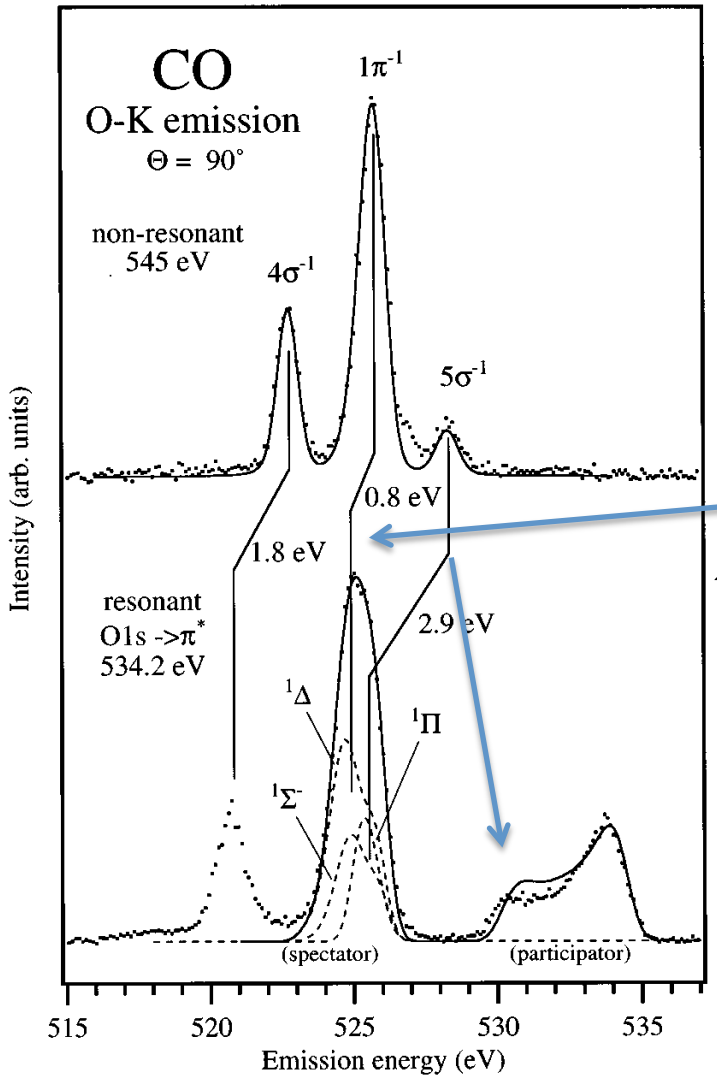
Resonant and non-resonant excitation in gas phase



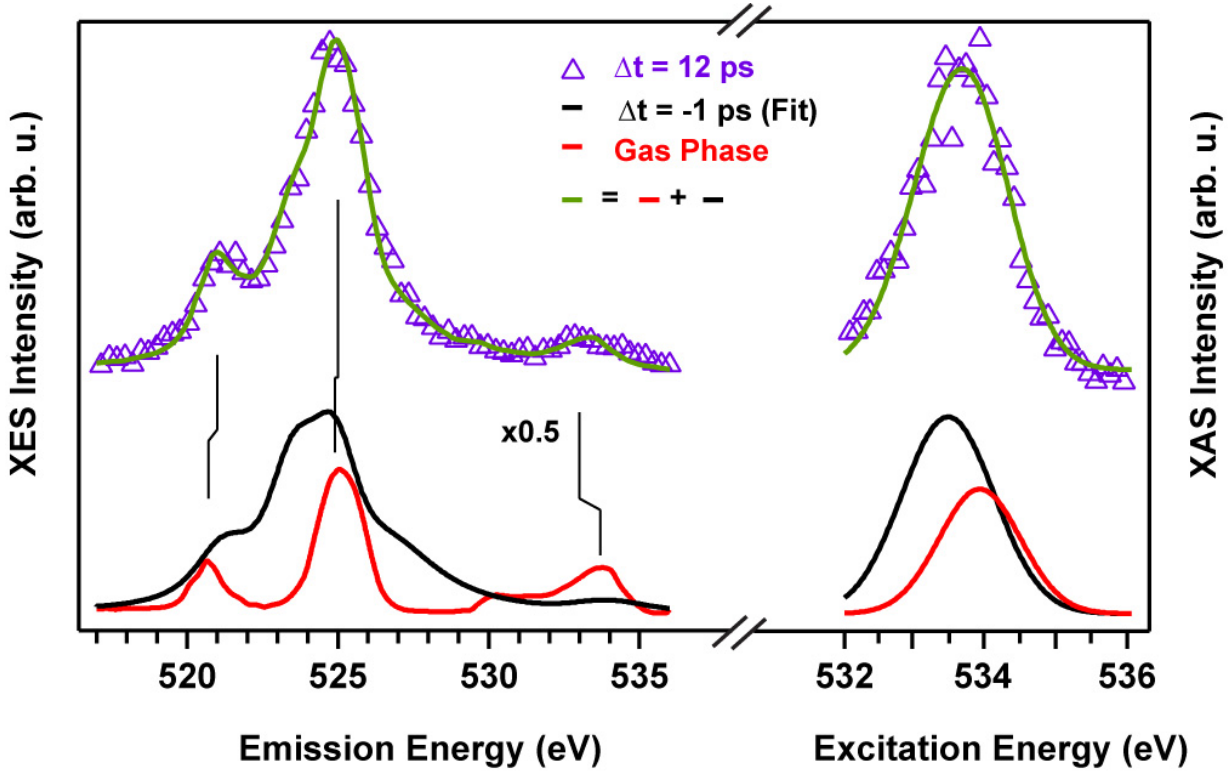
Decay from
O1s $^{-1}$

Spectator shifts due to presence of $2\pi^*$ electron

Decay from
O1s $^{-1}$ $2\pi^{*1}$

P. Skytt et al., Phys. Rev. A **55** (1997) 134

Fit Using Chemisorbed and Gas Phase Resonant Excitation

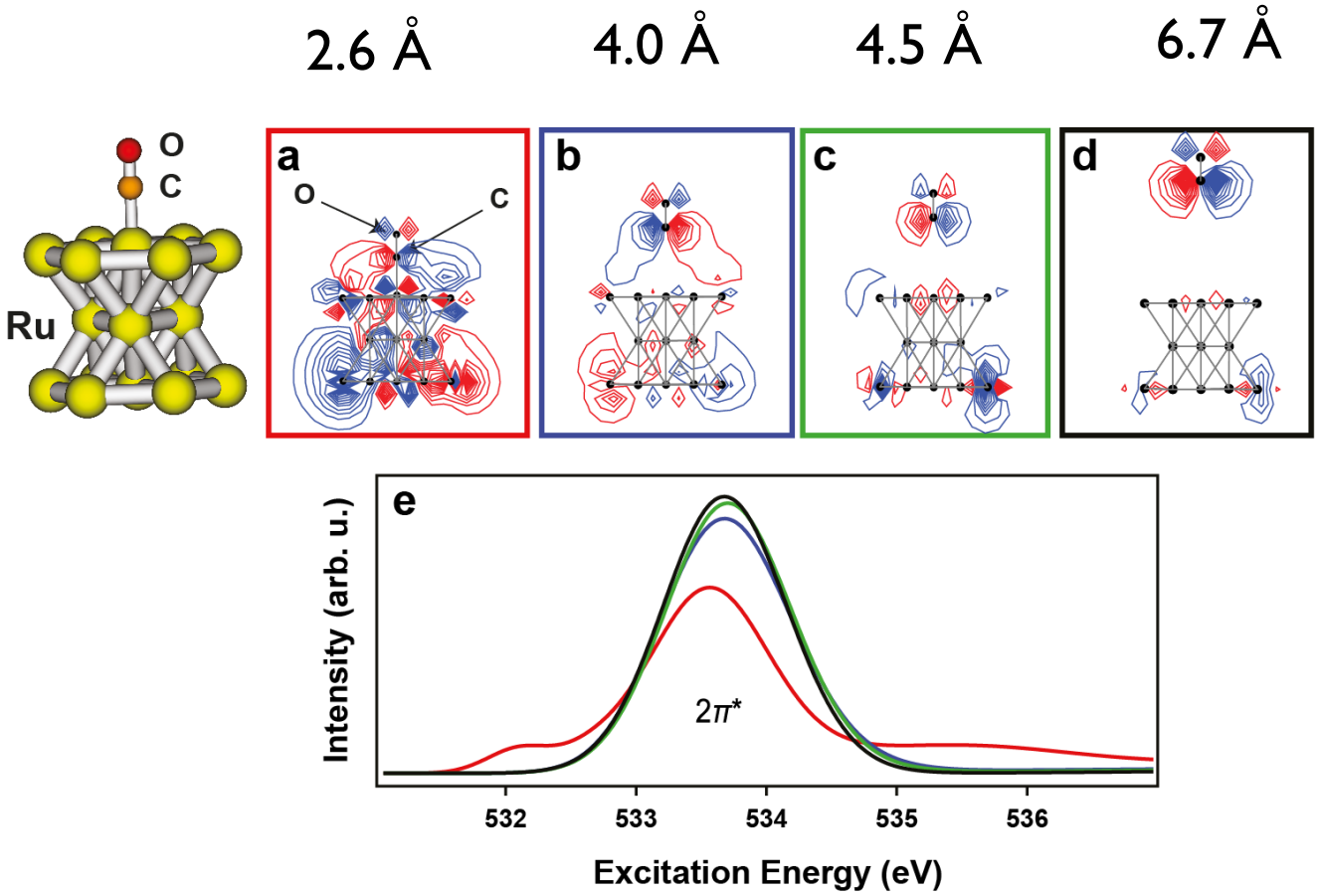


70% unpumped + 30% gas phase
But gas phase:
4σ: 0.3 eV smaller shift (1.8 eV)
1π: 0.1 eV smaller shift (0.8 eV)
Participator: -0.5 eV and x0.5

XAS 70% + 30%
Gas phase π* -0.3 eV

Science **339**, 1302 (2013)

Computed 2π* Excited States



Excited 2π* state delocalized to even long CO molecule distance

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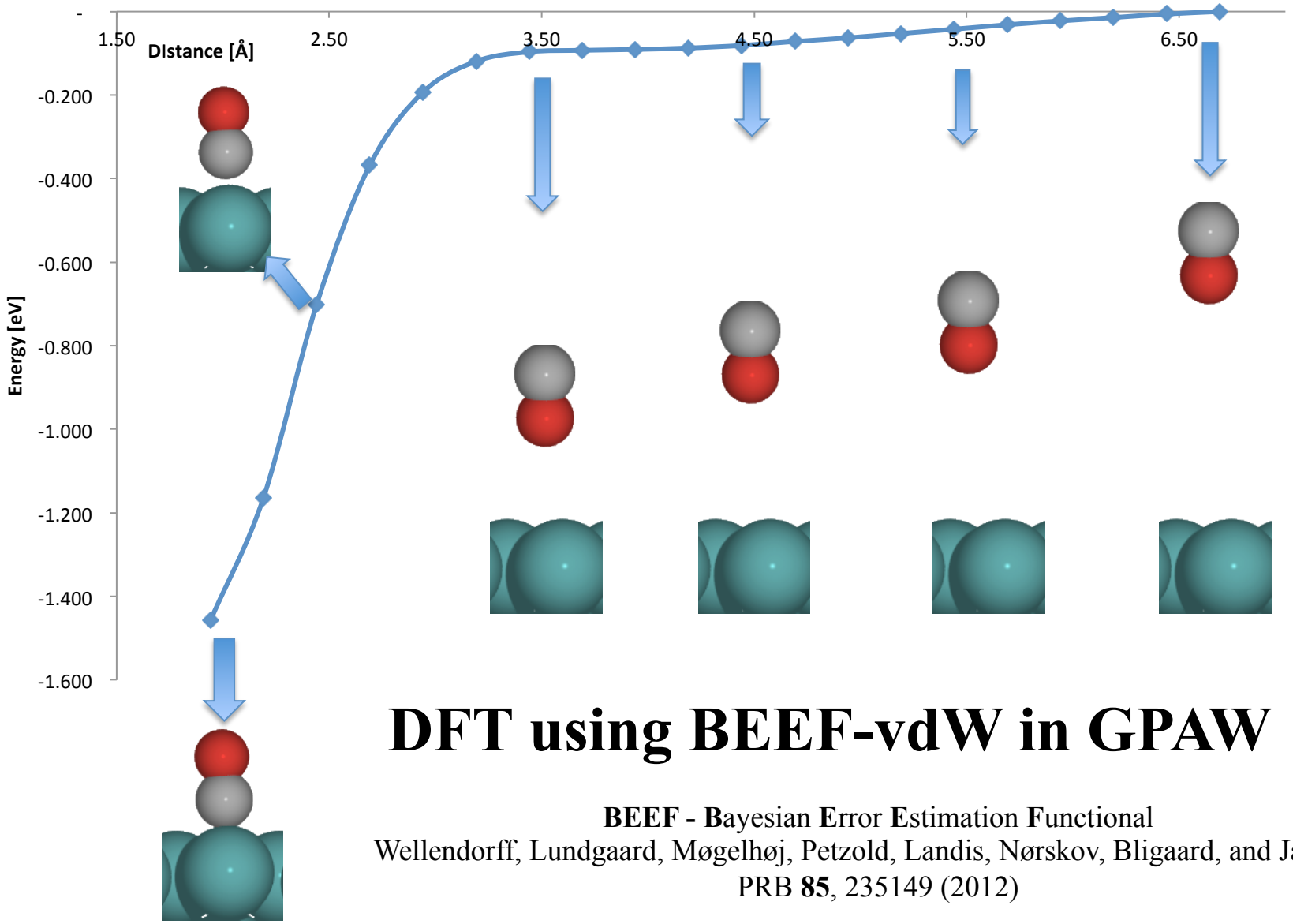
Minimum Energy Path in Desorption

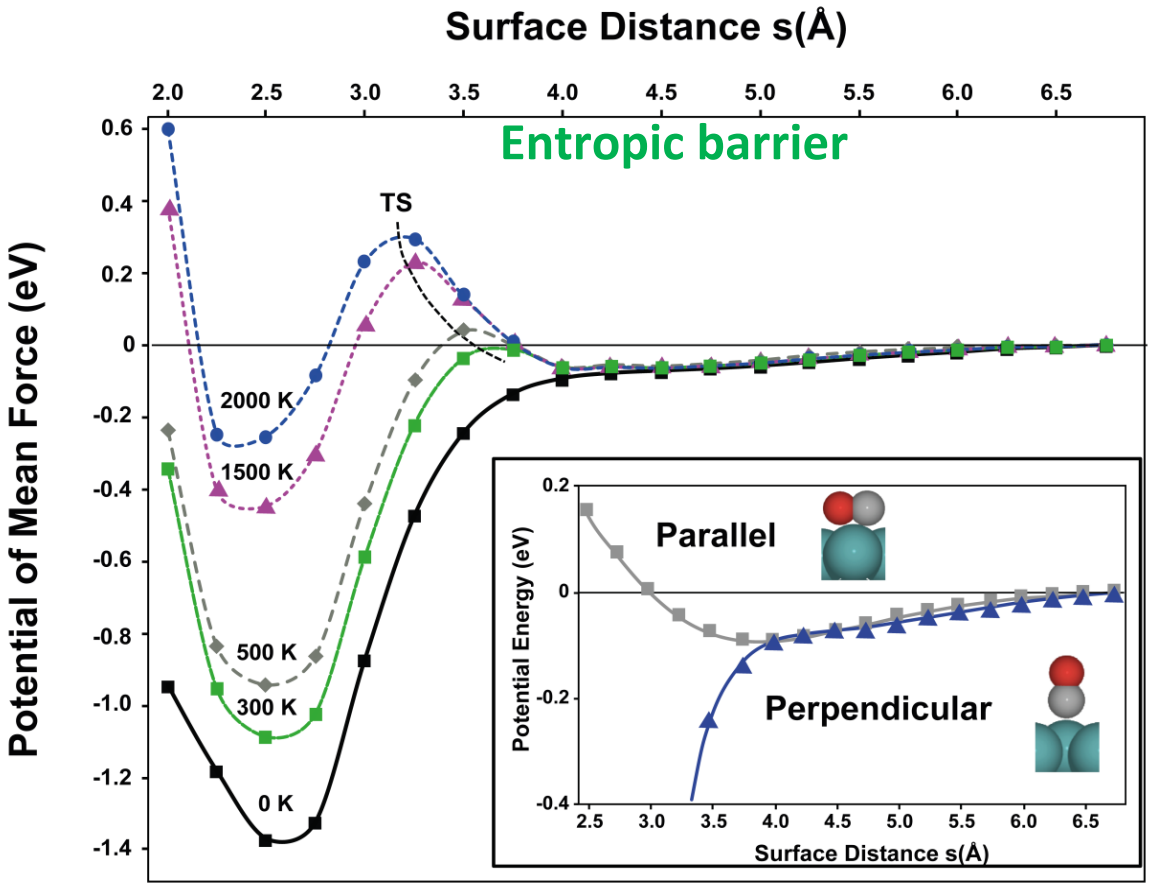


DFT using BEEF-vdW in GPAW

BEEF - Bayesian **E**rror **E**stimation **F**unctional
Wellendorff, Lundgaard, Møgelhøj, Petzold, Landis, Nørskov, Bligaard, and Jacobsen
PRB **85**, 235149 (2012)

Science **339**, 1302 (2013)

Potential of Mean Force

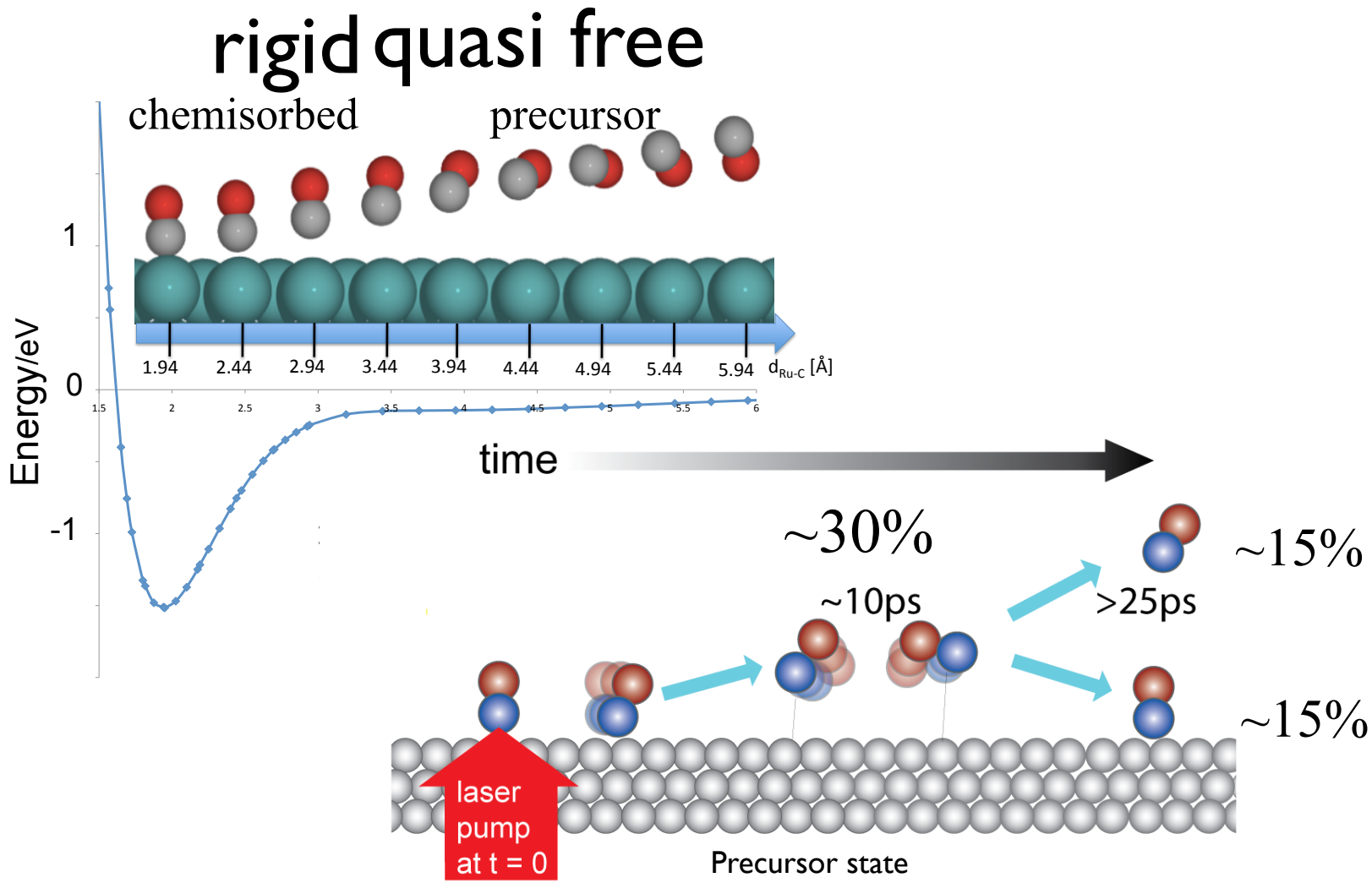


- Large difference in entropy between chemisorbed state (perpendicular only) and molecules in plateau (free to rotate)
- Compute potential of mean force, $W(s)$, to estimate free energy
- Temperature-dependent entropic barrier
- **Two wells: chemisorbed and precursor state to desorption (and adsorption)**

Originally developed by D. J. Doren, J. C. Tully, Langmuir **4**, 256 (1988), J. Chem. Phys. **94**, 8428 (1991)

Science **339**, 1302 (2013)

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



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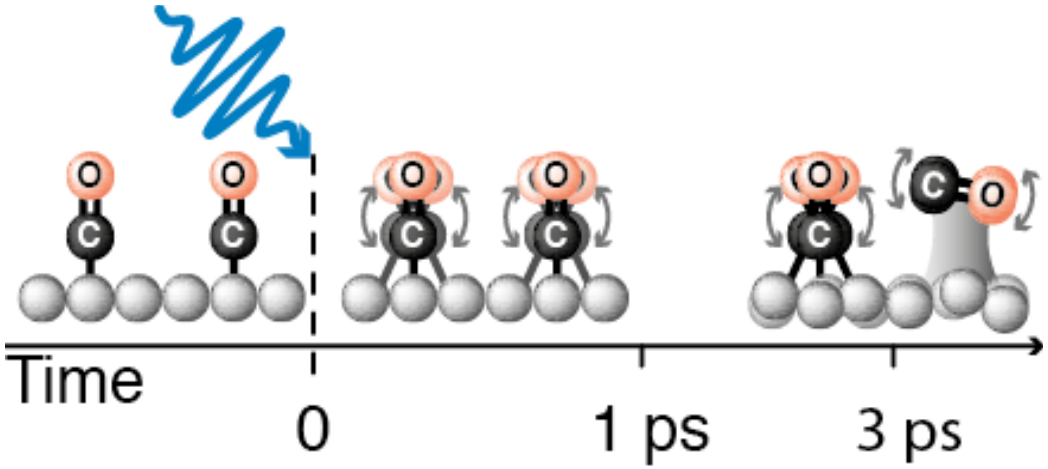
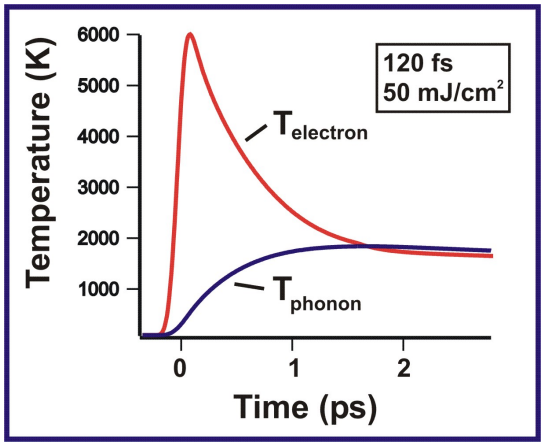
Times scales and temperature





<1ps frustrated rotations

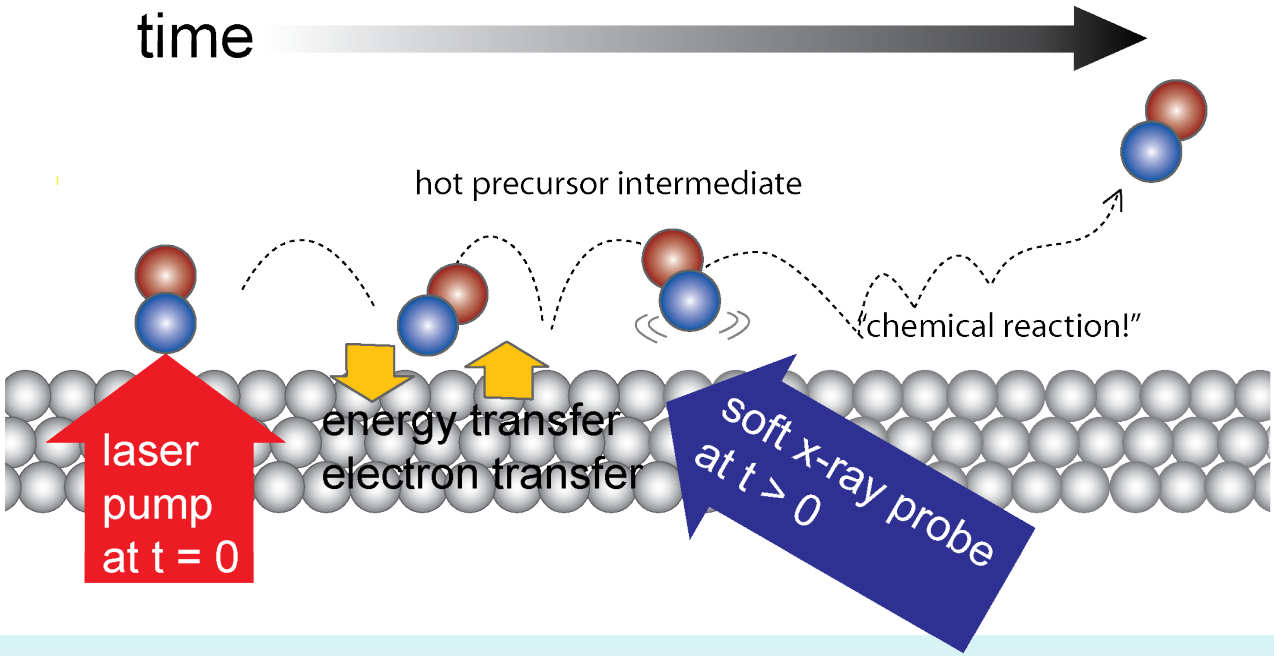
Hot electron driven

>3ps moving to presursor

Phonon driven

Phys. Rev. Lett. **110** (2013) 186101

New Era in Catalysis



- First surface chemical reaction with LCLS
- Proof of principle

Precursor to CO desorption in a weakened surface chemical bond

Transition State with CO—O interaction in CO oxidation

- H+CO → HCO, Fischer-Tropsch, ammonia synthesis, etc.
- Higher pressure (~100 torr), solid-liquid interfaces, photocatalysis
- Shorter FEL pulses, THz radiation control (LCLS 2)
- "Chemist's dream"