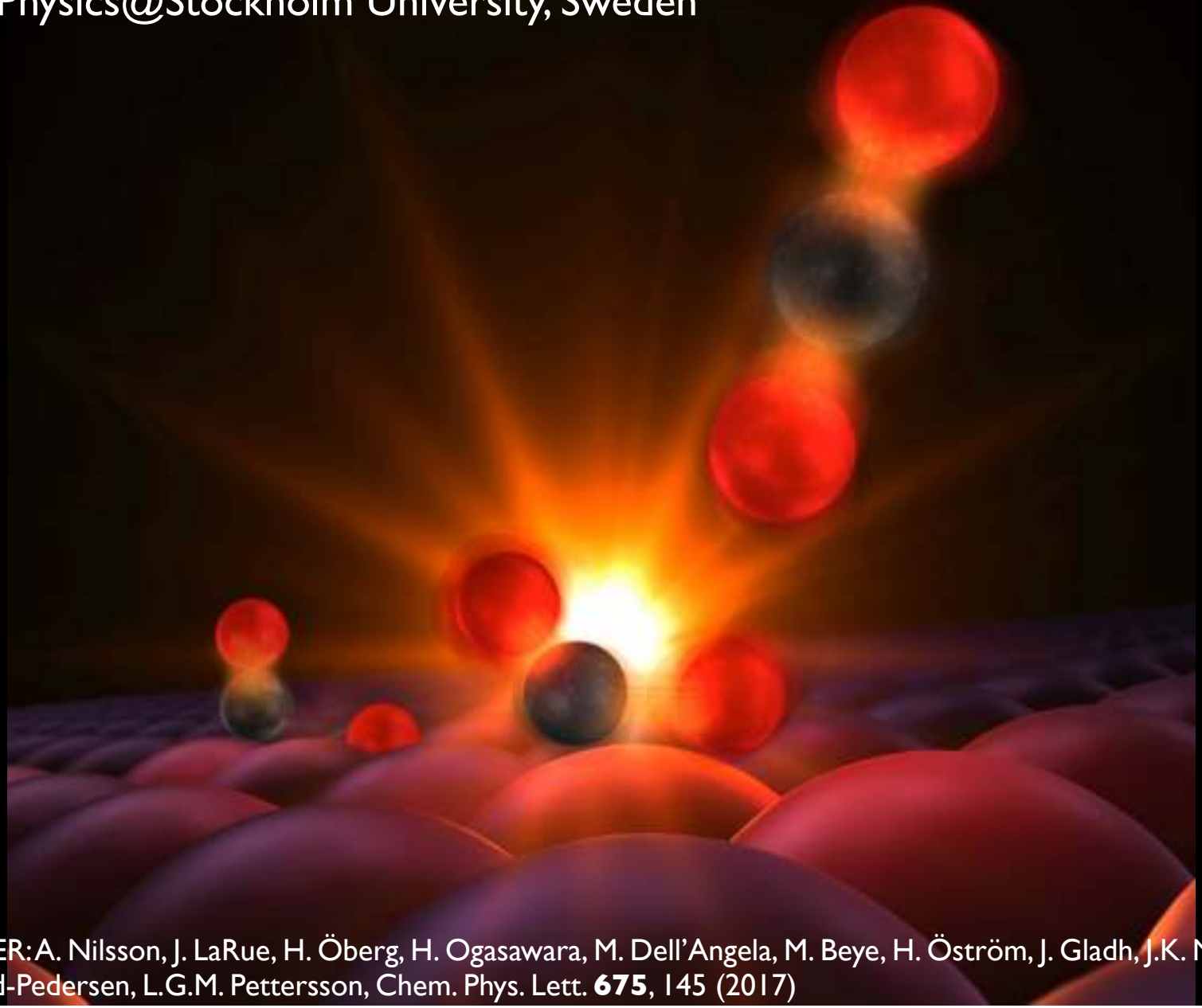
Ultrafast PES Opportunities in Surface Catalysis

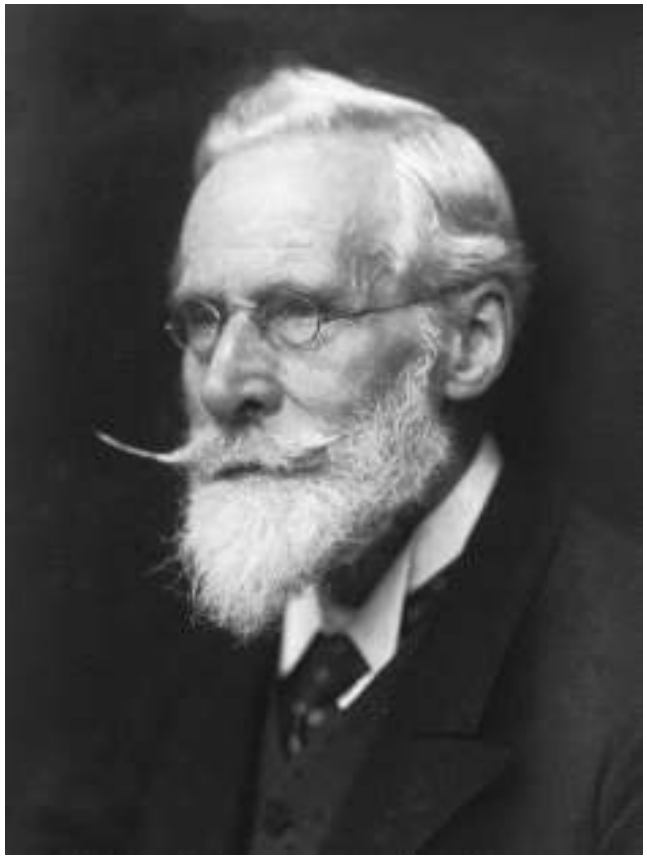
Peter Amann and Anders Nilsson
Chemical Physics@Stockholm University, Sweden



REVIEW PAPER: A. Nilsson, J. LaRue, H. Öberg, H. Ogasawara, M. Dell'Angela, M. Beye, H. Öström, J. Gladh, J.K. Nørskov, W. Wurth, F. Abild-Pedersen, L.G.M. Pettersson, Chem. Phys. Lett. **675**, 145 (2017)

The World is Doomed

In his installment talk as the incoming president of the British Academy of Sciences in 1898



Sir William Crookes (1832-1919)

There will be mass starvation due to lack of fertilizers

The Chemists need to Save Humanity!!!

T. Hager, *The Alchemy of Air*, Broadway Books, New York 2008.

The World is Doomed

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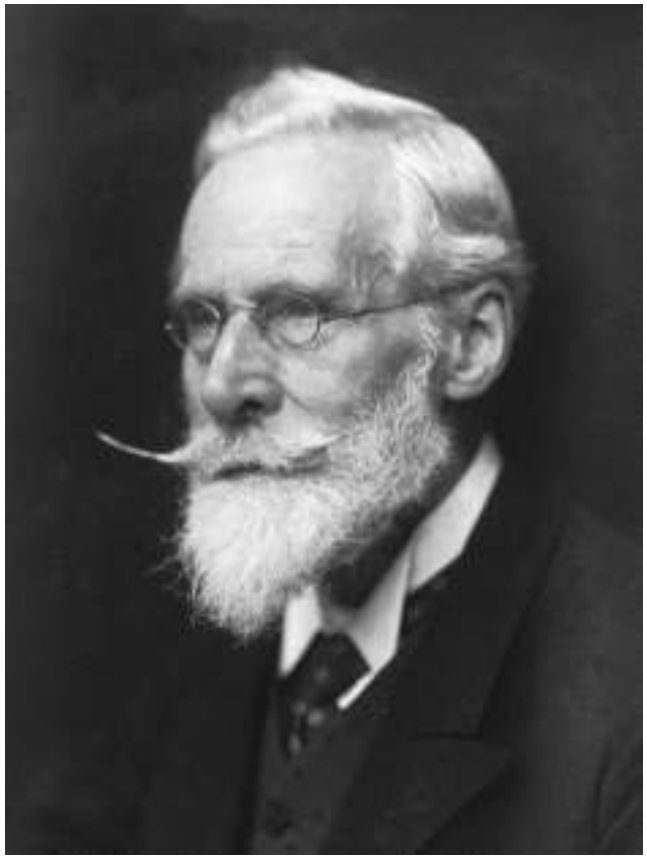

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The **Surface Scientists** need to Save Humanity!!!

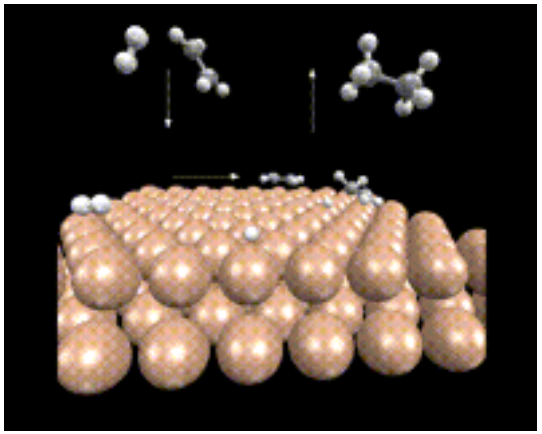
T. Hager, *The Alchemy of Air*, Broadway Books, New York 2008.

Ammonia feeds the world
Fertilizers

1-2 % of the global energy consumption
Saved 2-3 Billion peoples life

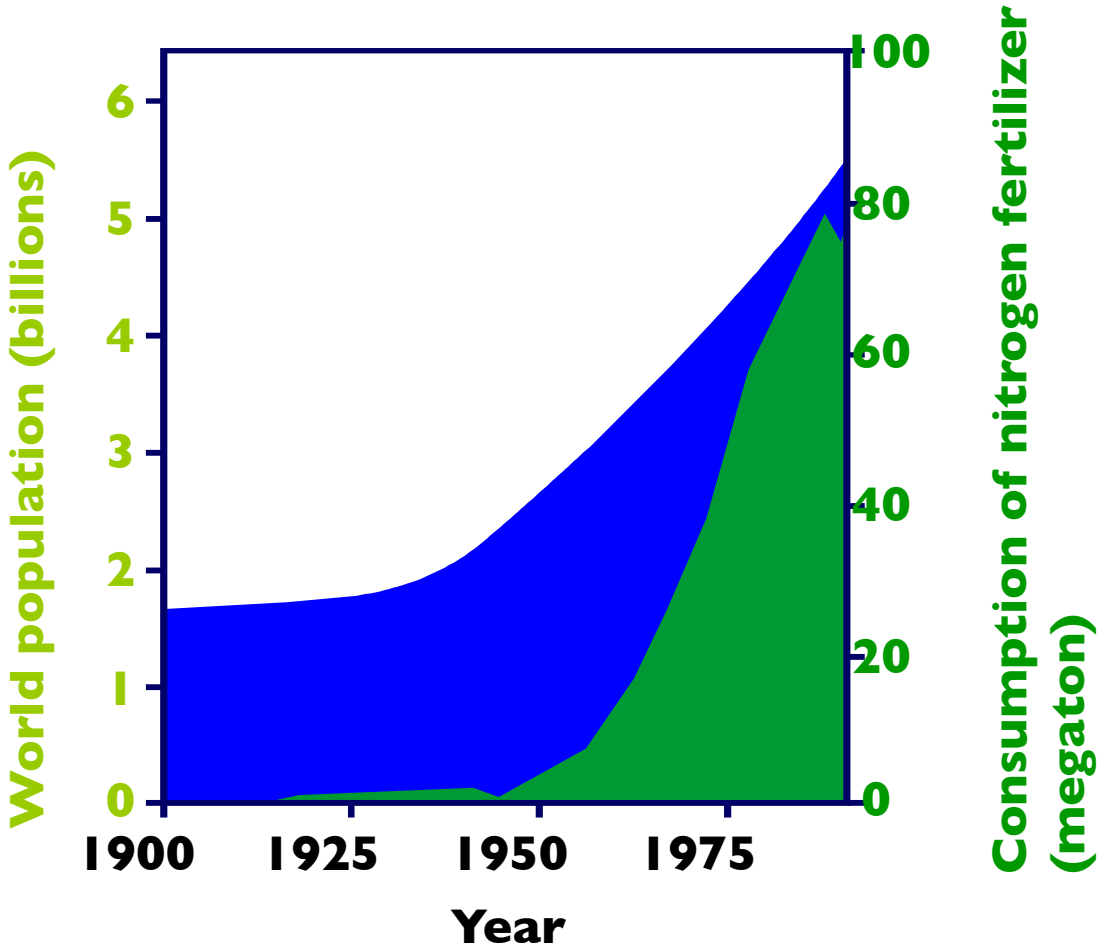
$$N_2 + 3H_2 \leftrightarrows 2NH_3$$

Haber Bosch Process

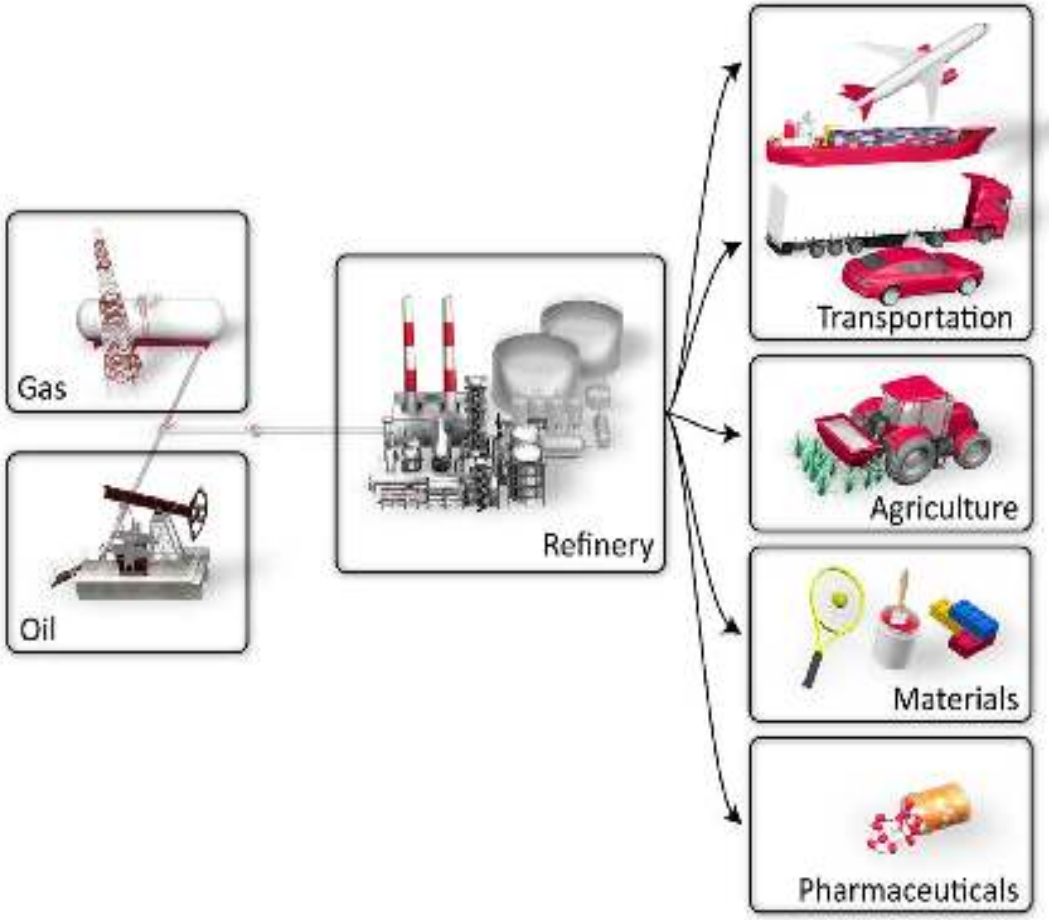


Surface Catalysis

Nobelprize 1918, 1933 and 2007



The fossil (20th) century



This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 820444

Image: Jakob Kibsgaard

The e-refinery

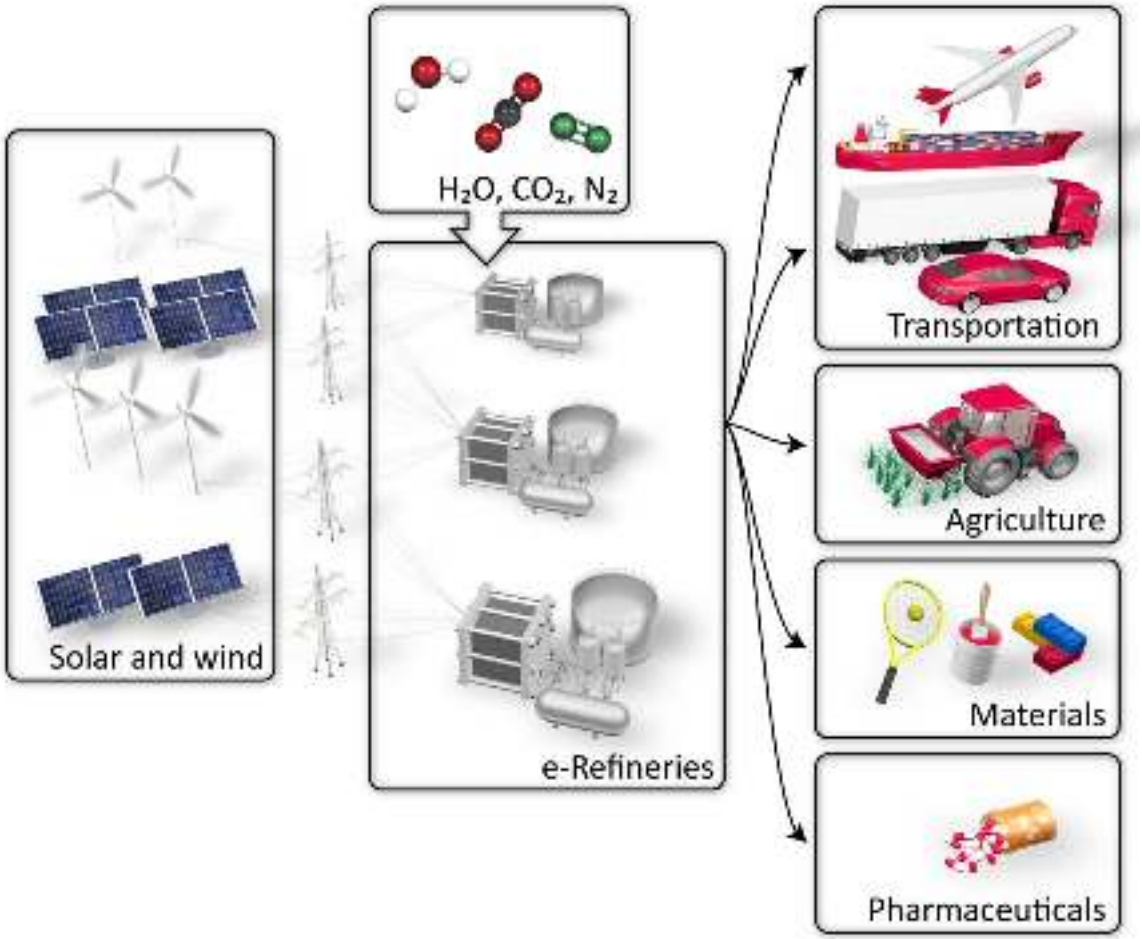


Image: Jakob Kibsgaard

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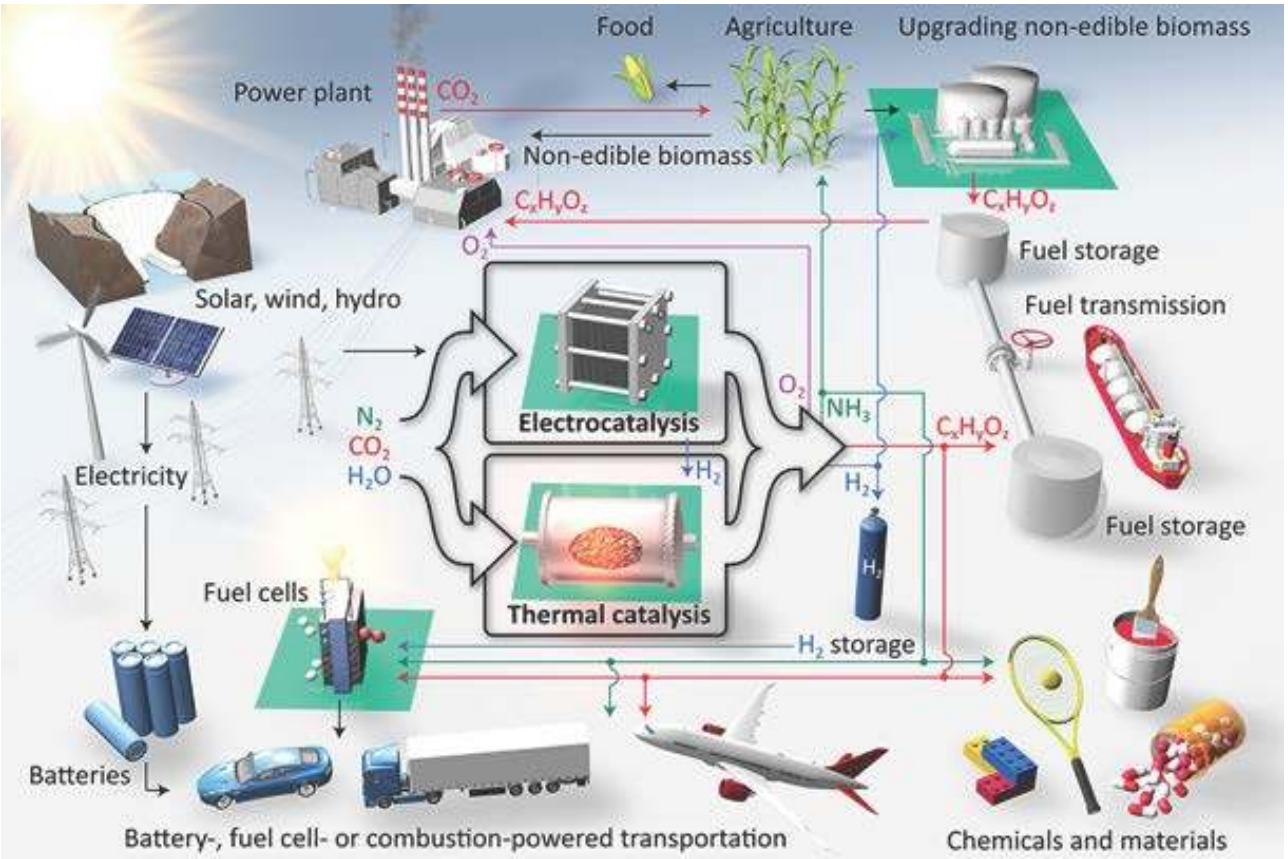
programme under grant agree

ENERGY X

A sustainable energy and chemical production scenario



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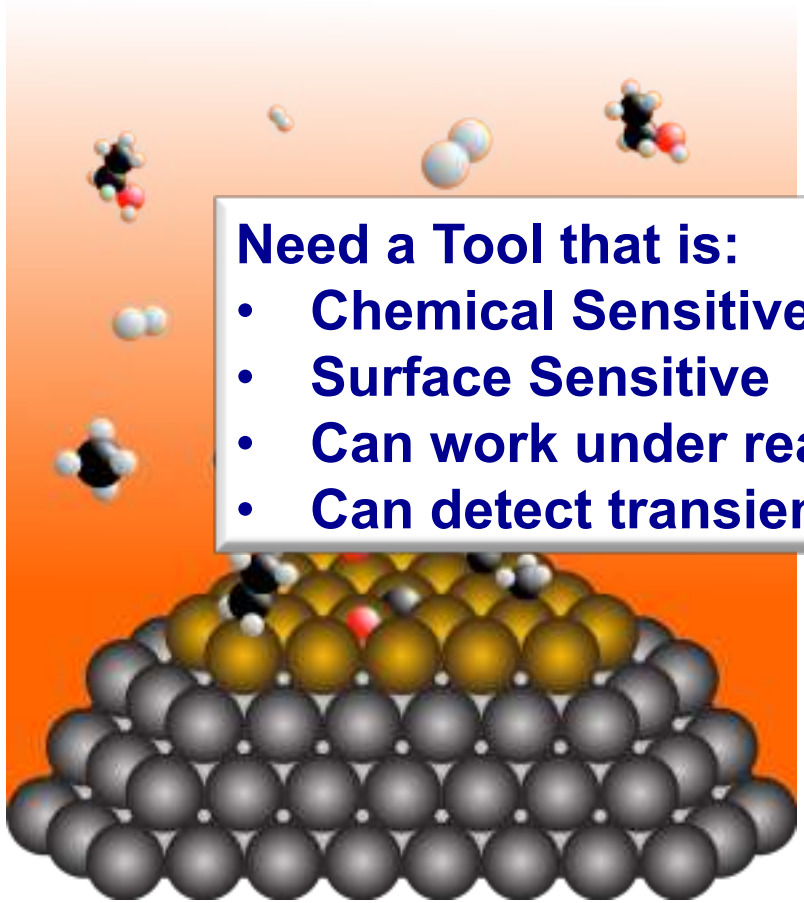
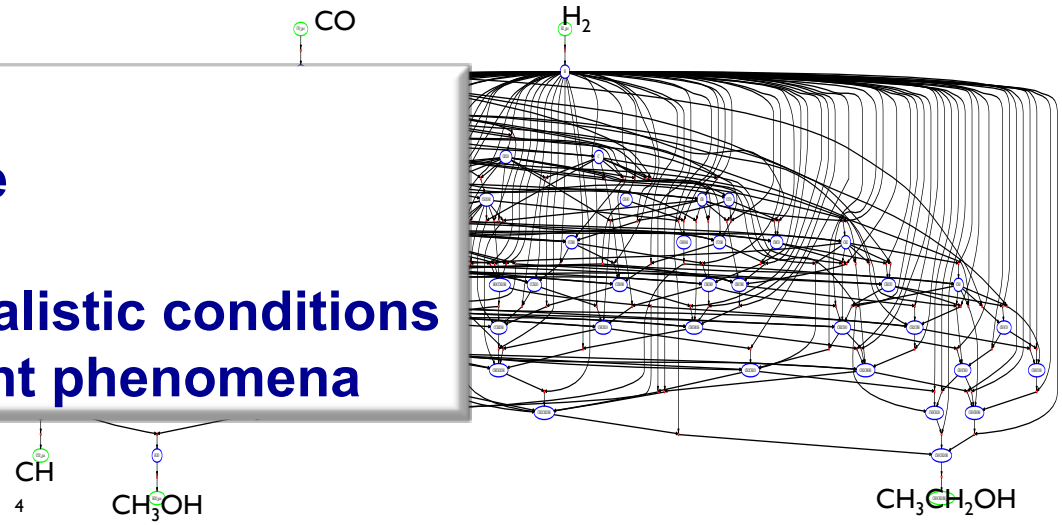
Catalysis: Dealing with complexity

CO hydrogenation to methane, methanol or ethanol



Need a Tool that is:

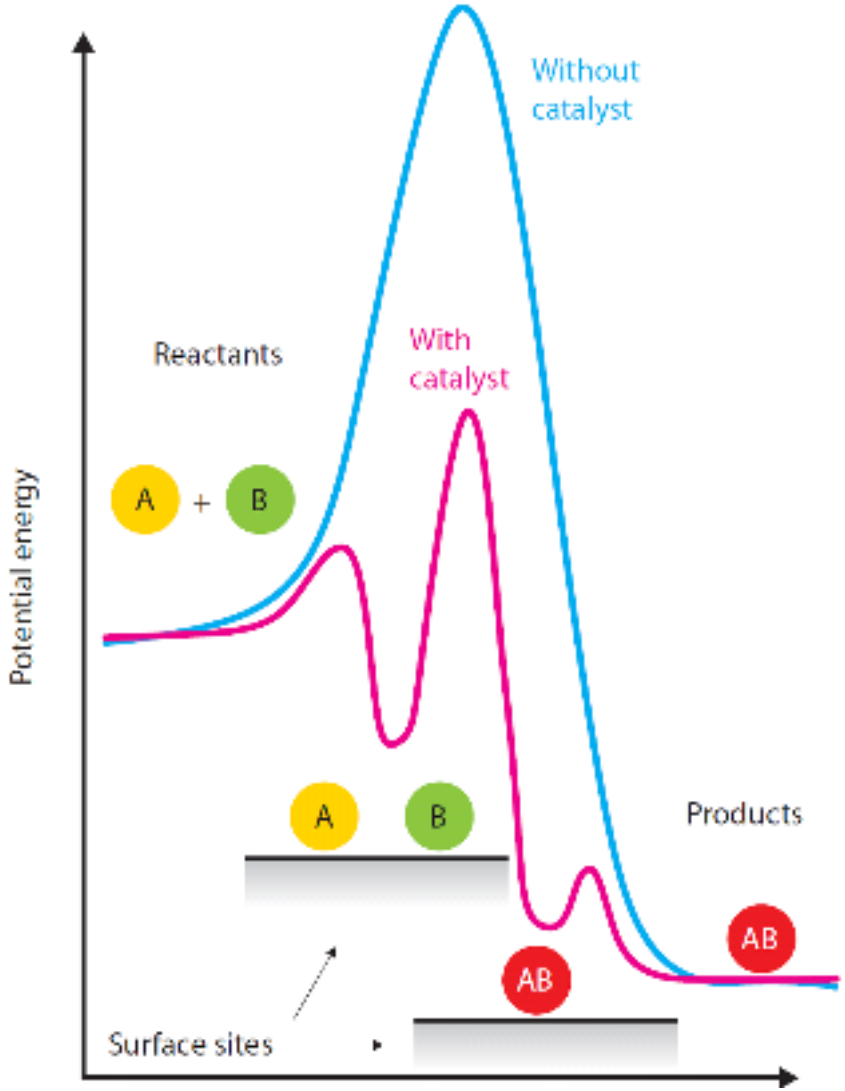
- **Chemical Sensitive**
- **Surface Sensitive**
- **Can work under realistic conditions**
- **Can detect transient phenomena**



Medford, Ulissi, Hummelshøj, Bligaard, Nørskov (2016)

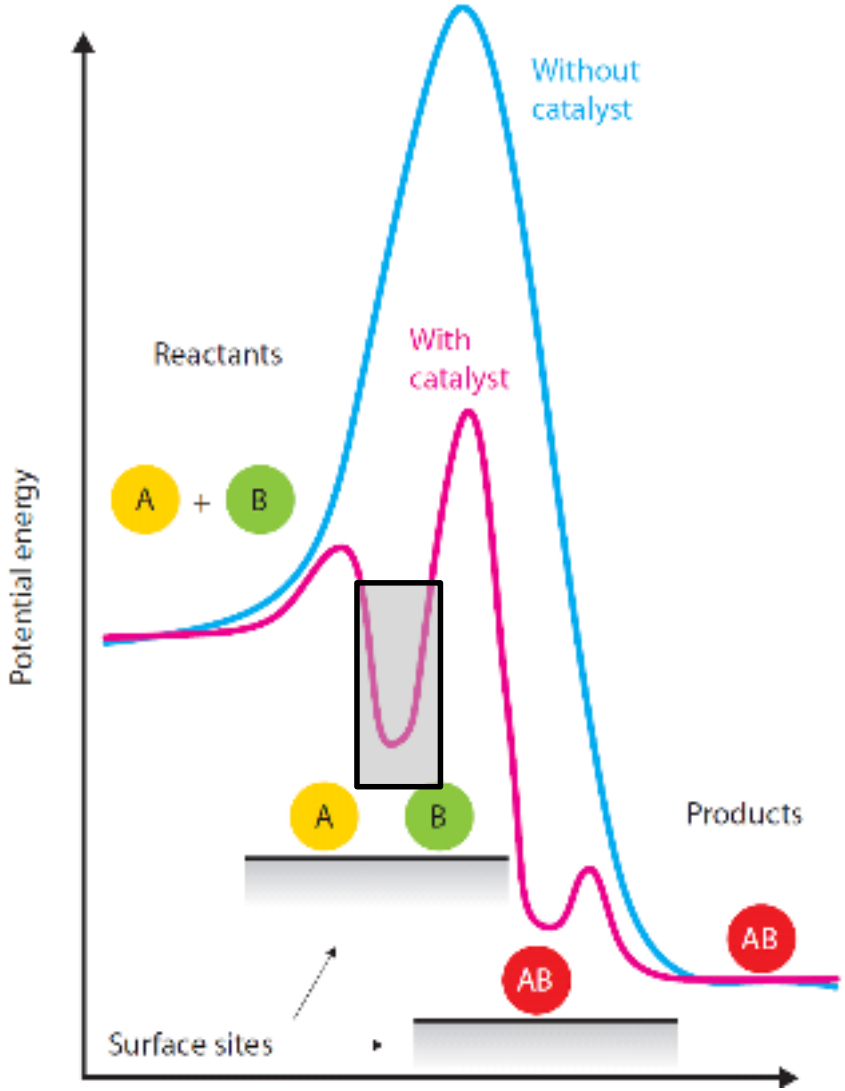
100+ species
200+ reactions
2000+ unique pathways

Fundamental Understanding of Catalysis



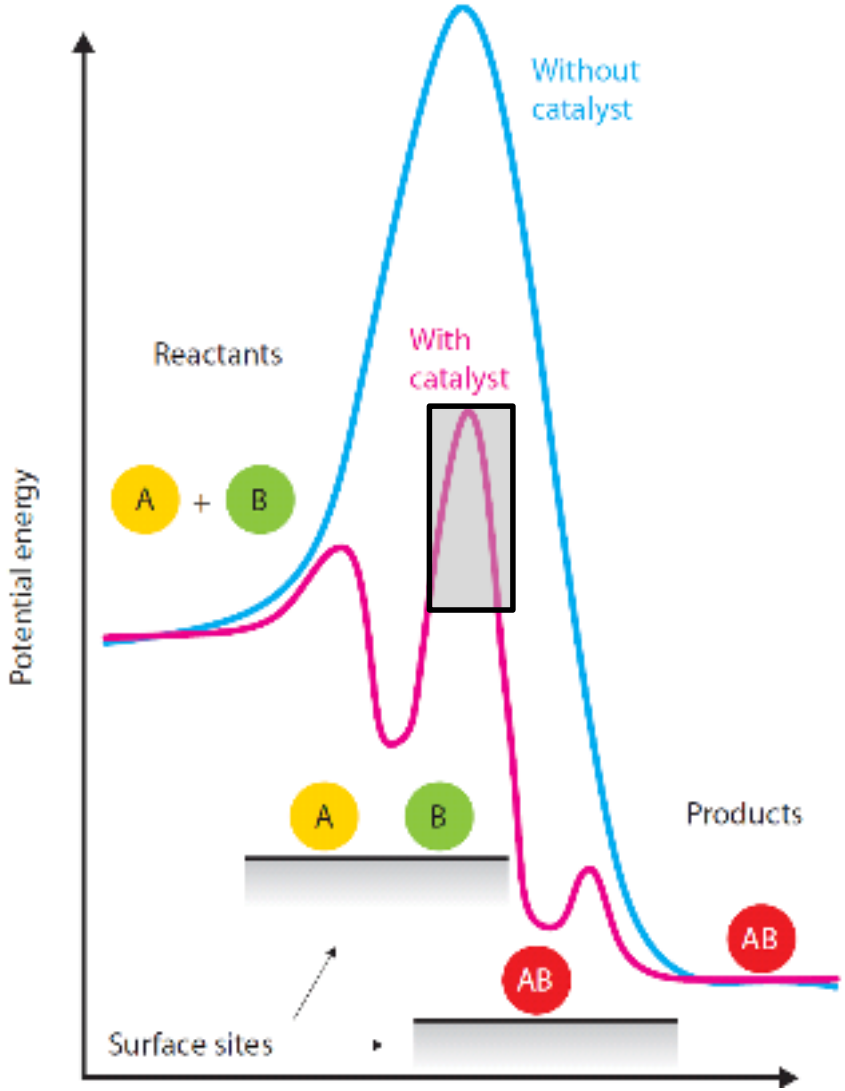
Courtesy I. Chorkendorff

Probing Intermediates ?



Courtesy I. Chorkendorff

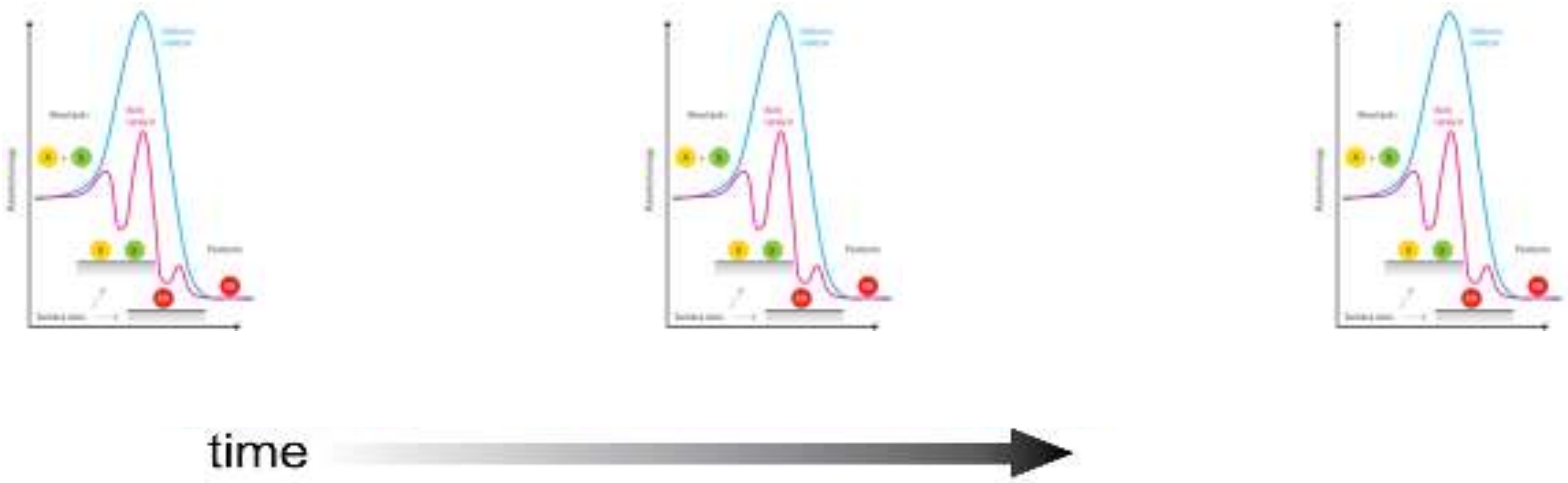
Probing Transition States ?



Courtesy I. Chorkendorff

Time Resolved Measurements

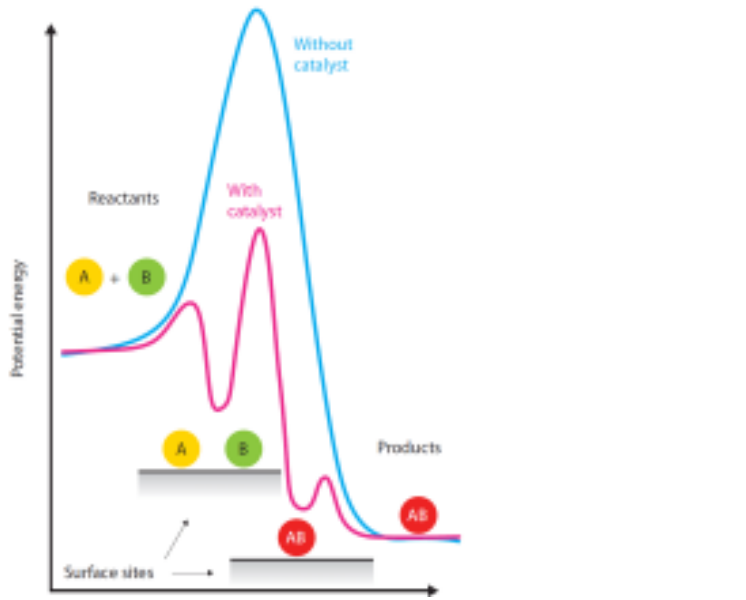
Kinetics: Macroscopic reaction rate
How often a reaction event is successful



Time Resolved Measurements

Kinetics: Macroscopic reaction rate
How often a reaction event is successful

Dynamics: Following movements of atoms, molecules and electrons,
Following reaction events in real time as they occurs



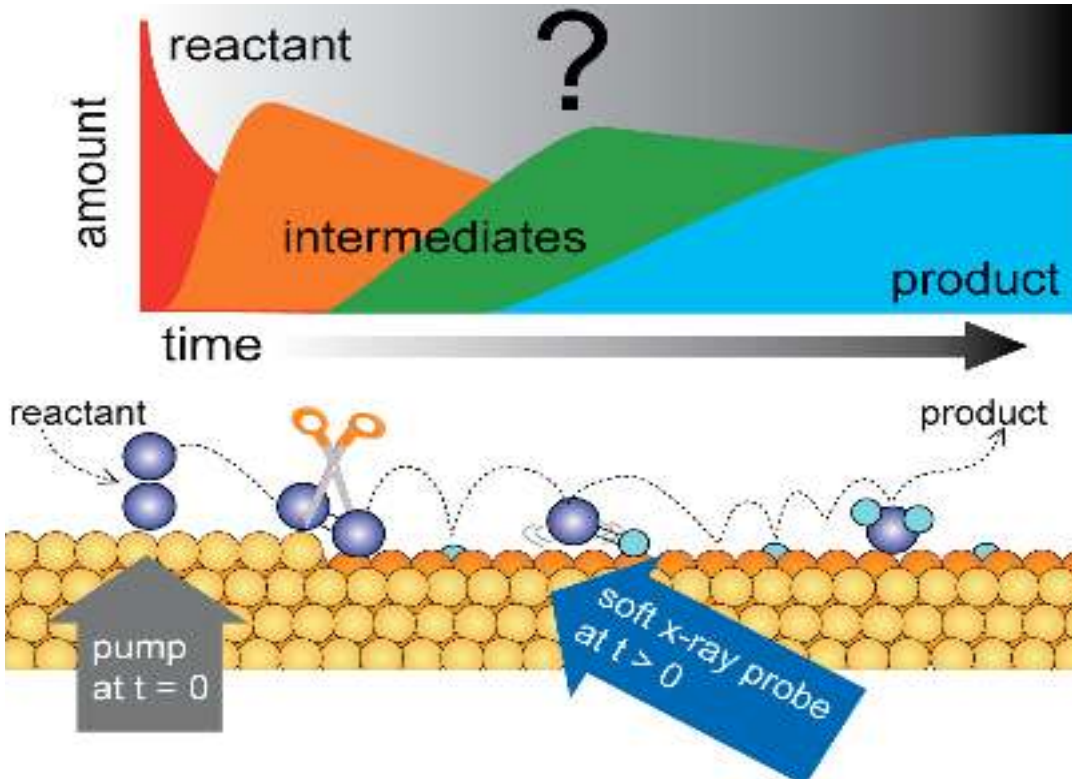
time

Time Resolved Measurements

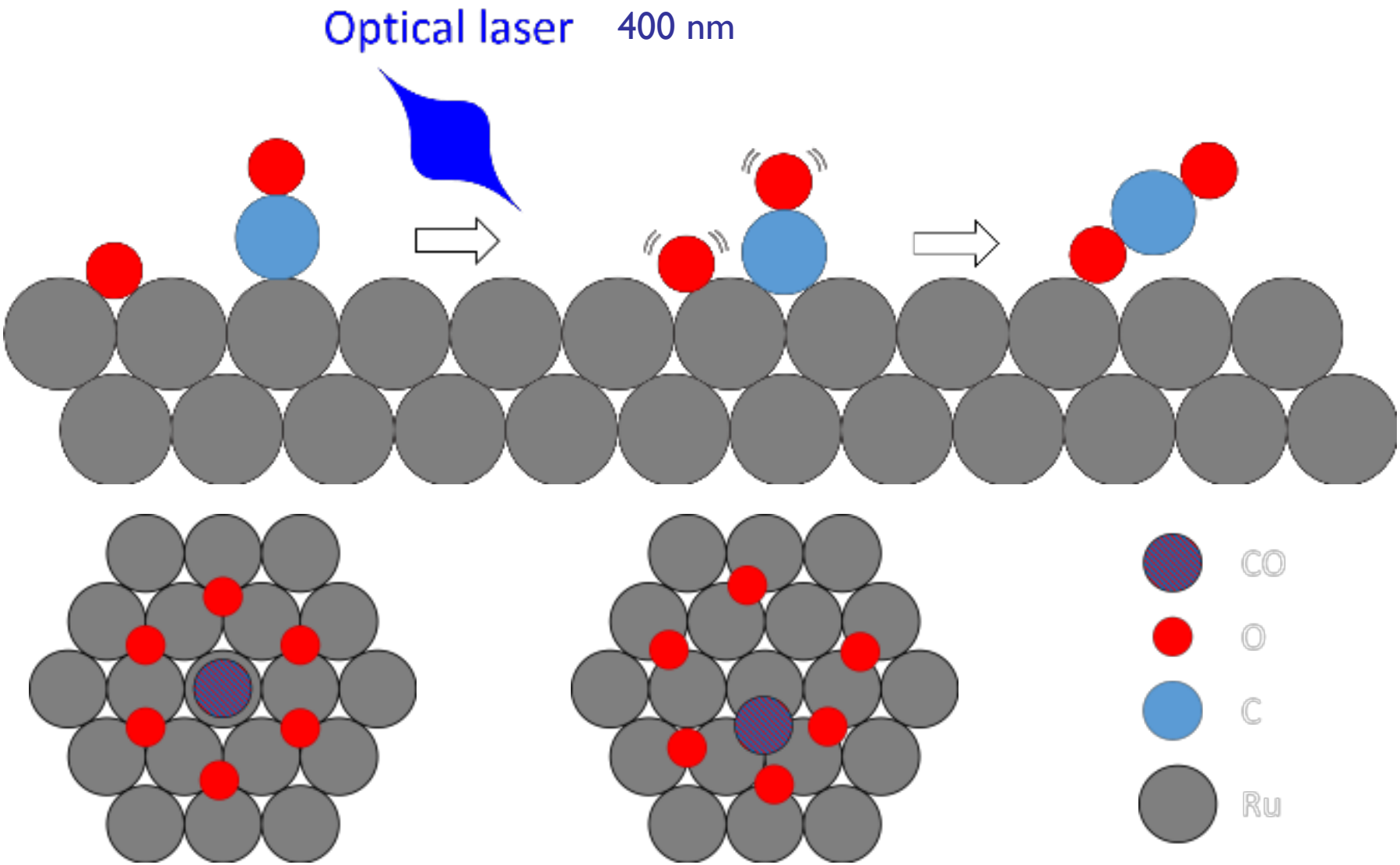
Kinetics: Macroscopic reaction rate
How often a reaction event is successful

Dynamics: Following movements of atoms, molecules and electrons,
Following reaction events in real time as they occurs

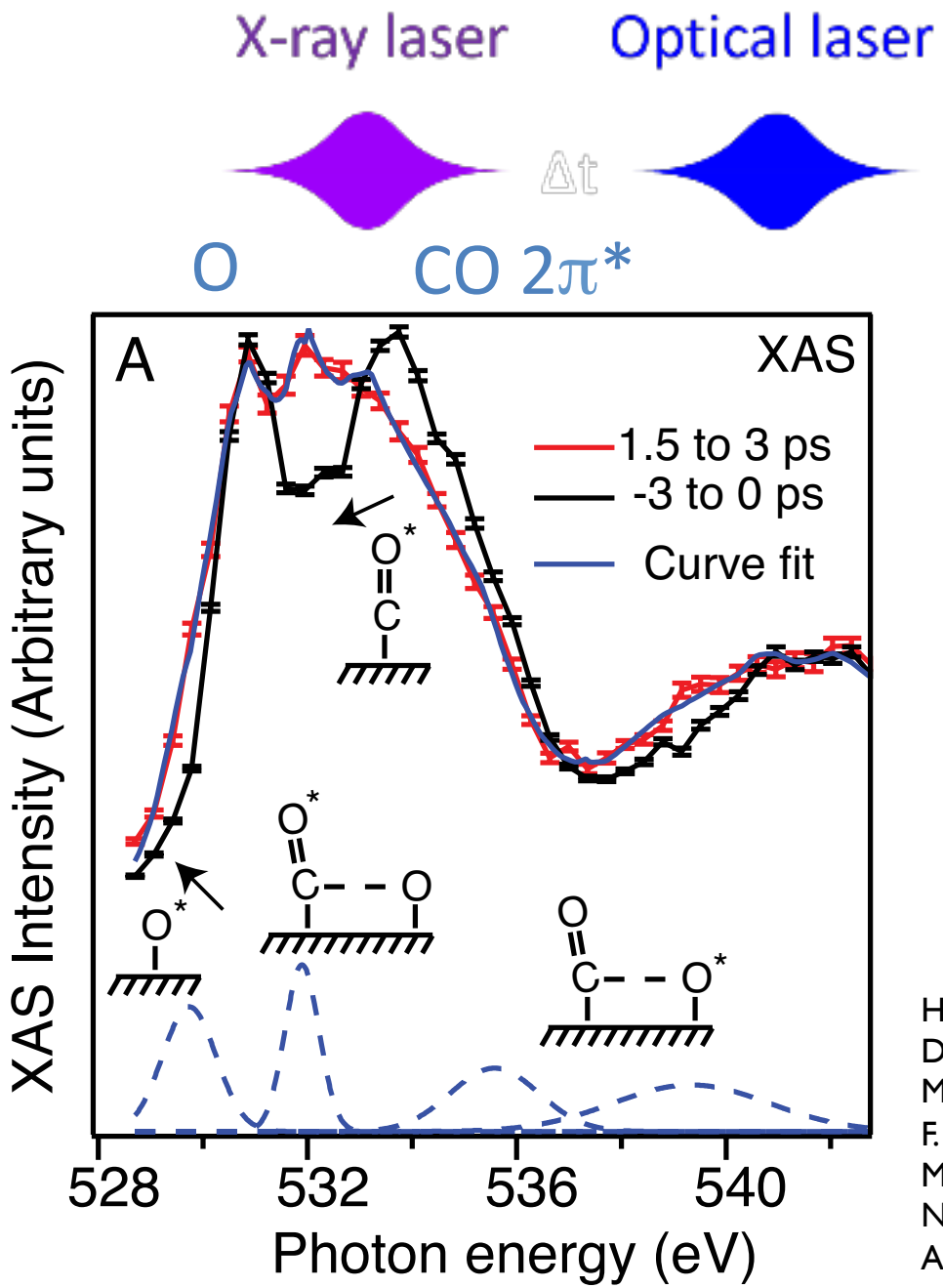
Pump: to start all reaction events simultaneous; optical lasers
Probe: probing the evolvement of the reaction at a specific time delay; x-rays

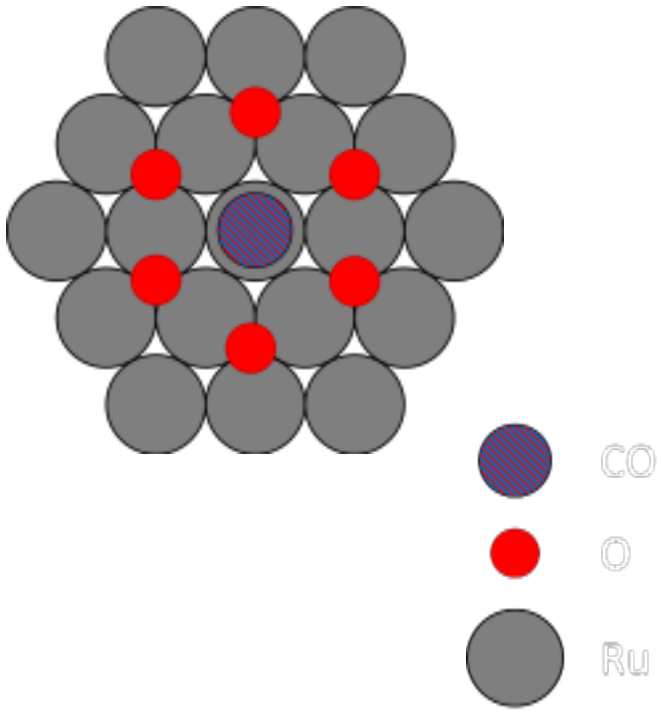


O and CO are both excited to produce CO_2
Observation of the Transition State
LCLS (O K) and FERMI (C K) experiments



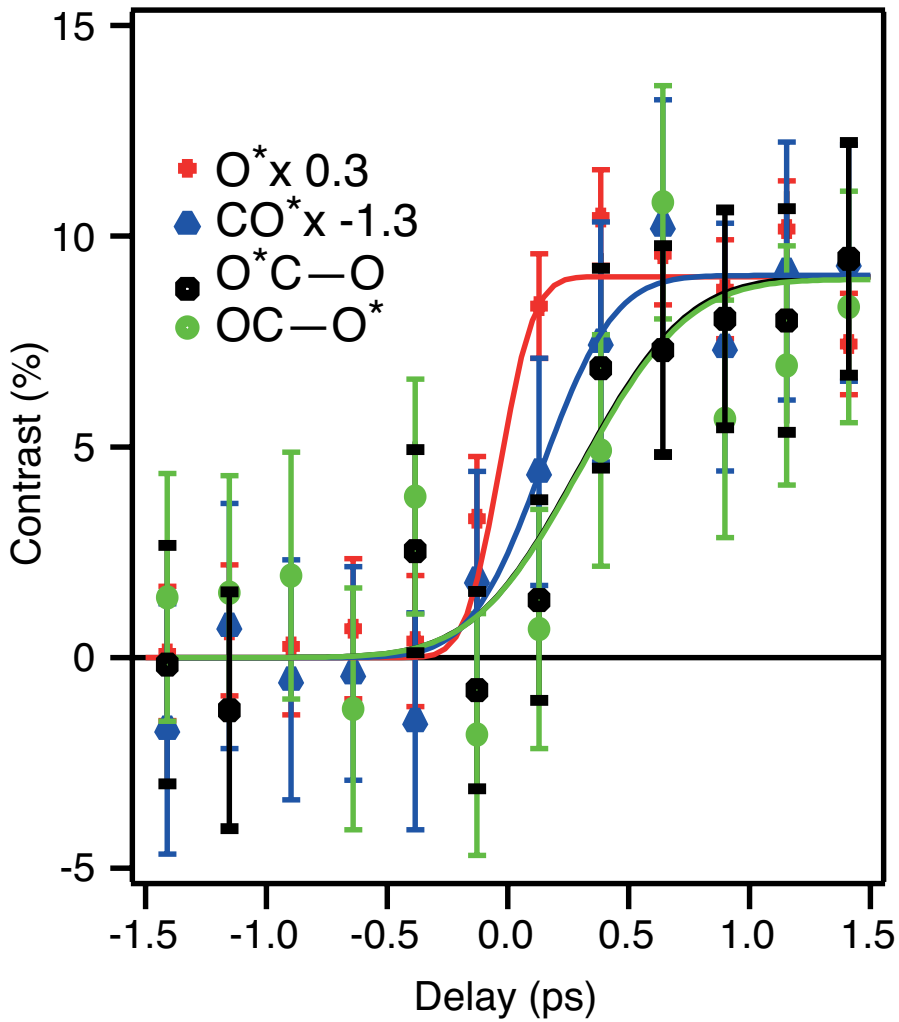
Pump-probe of CO oxidation





H. Öström H. Öström, H. Öberg, H. Xin, J. LaRue, M. Beye, M. Dell'Angela, J. Gladh, M. L. Ng, J. A. Sellberg, S. Kaya, G. Mercurio, D. Nordlund, M. Hantschmann, F. Hieke, D. Kühn, W. F. Schlotter, G. L. Dakovski, J. J. Turner, M. P. Minitti, A. Mitra, S. P. Moeller, A. Föhlisch, M. Wolf, W. Wurth, M. Persson, J. K. Nørskov, F. Abild-Pedersen, H. Ogasawara, L. G. M Pettersson, A. Nilsson, Science **347**, 978 (2015)

Transient Time Scales



- O activation 300 fs
- CO activation 500 fs
- Formation of *OC--O 800 fs
- Formation of OC---O* 800 fs

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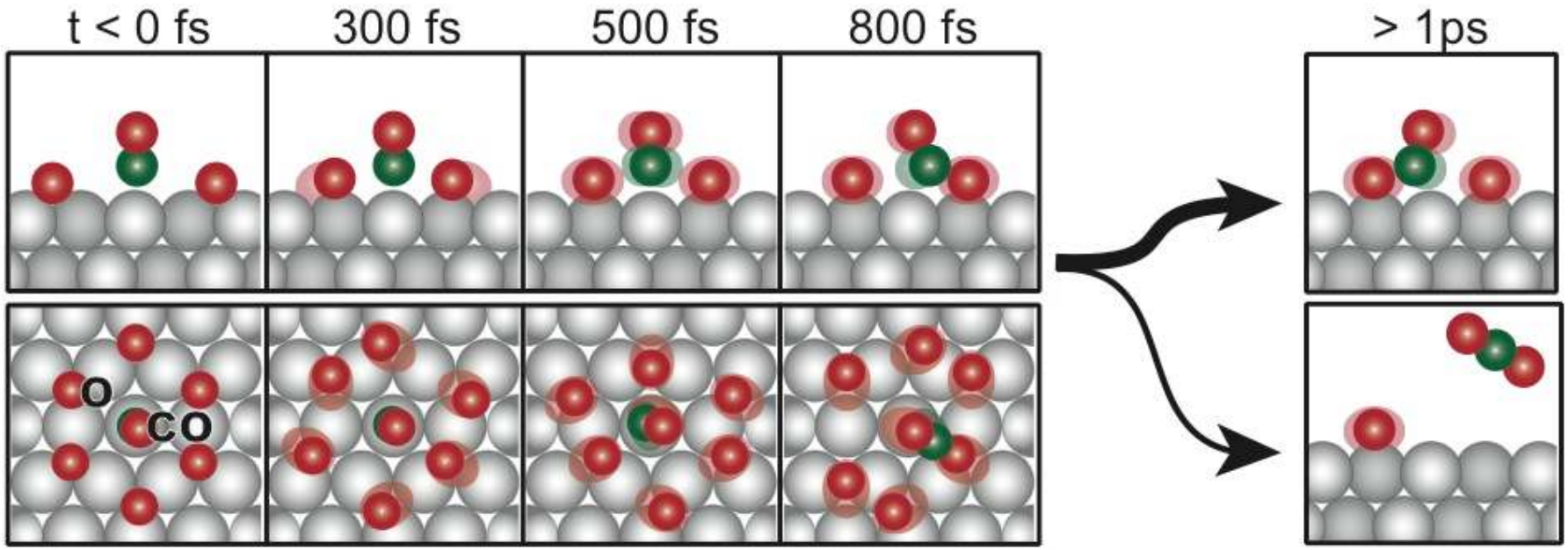
Mechanism



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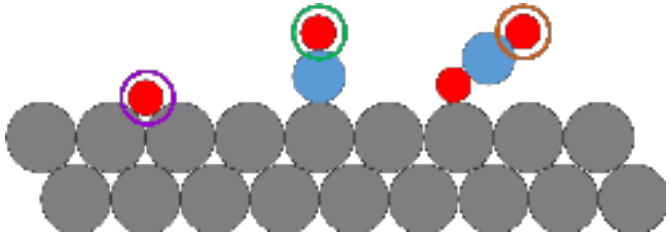
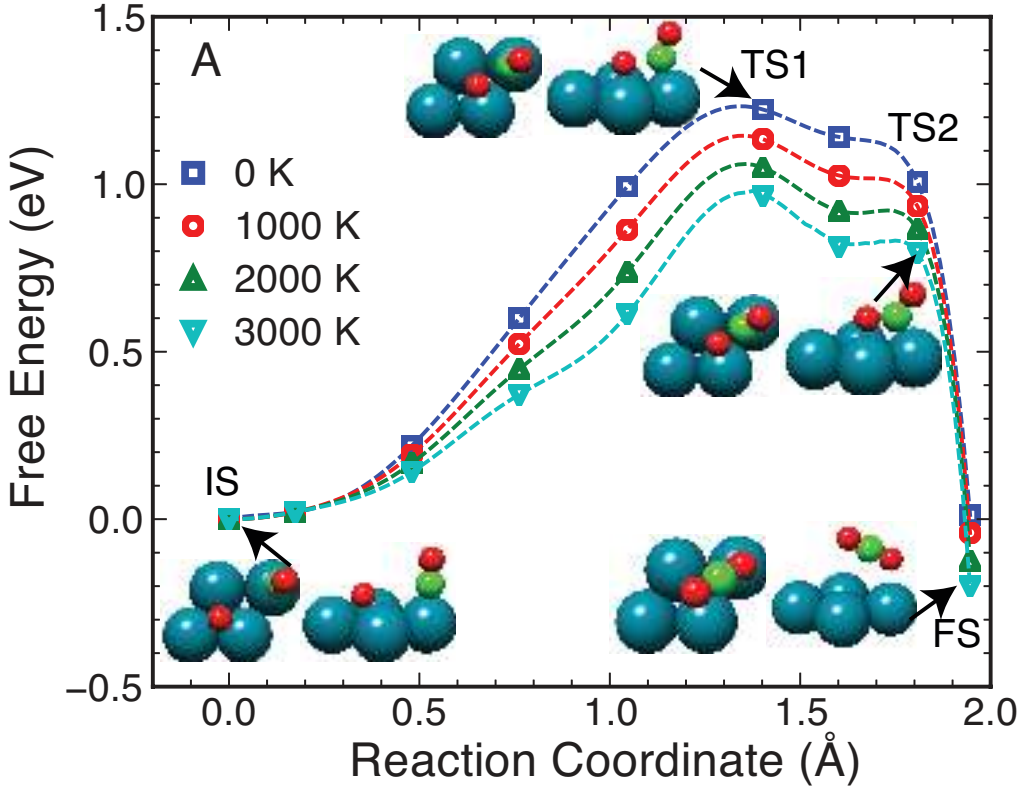
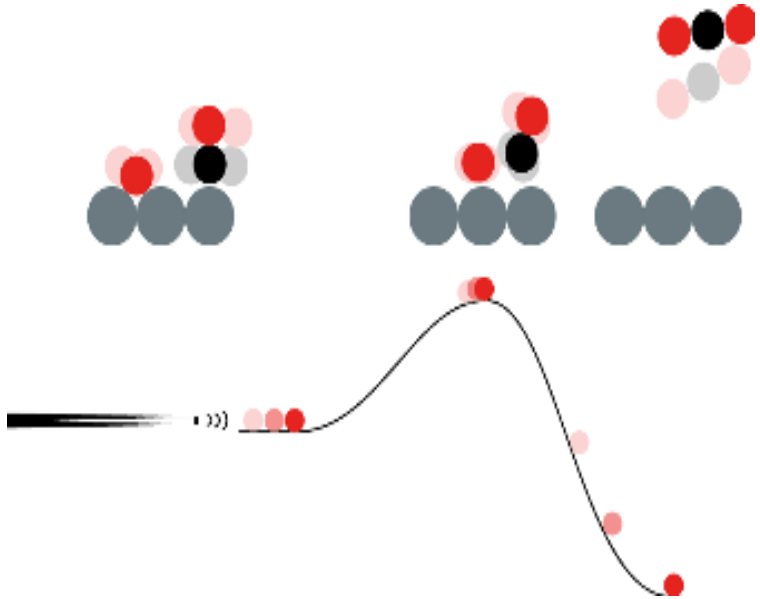
Ultrafast Observation of the Transition State Region in Catalytic CO Oxidation on Ru(0001)







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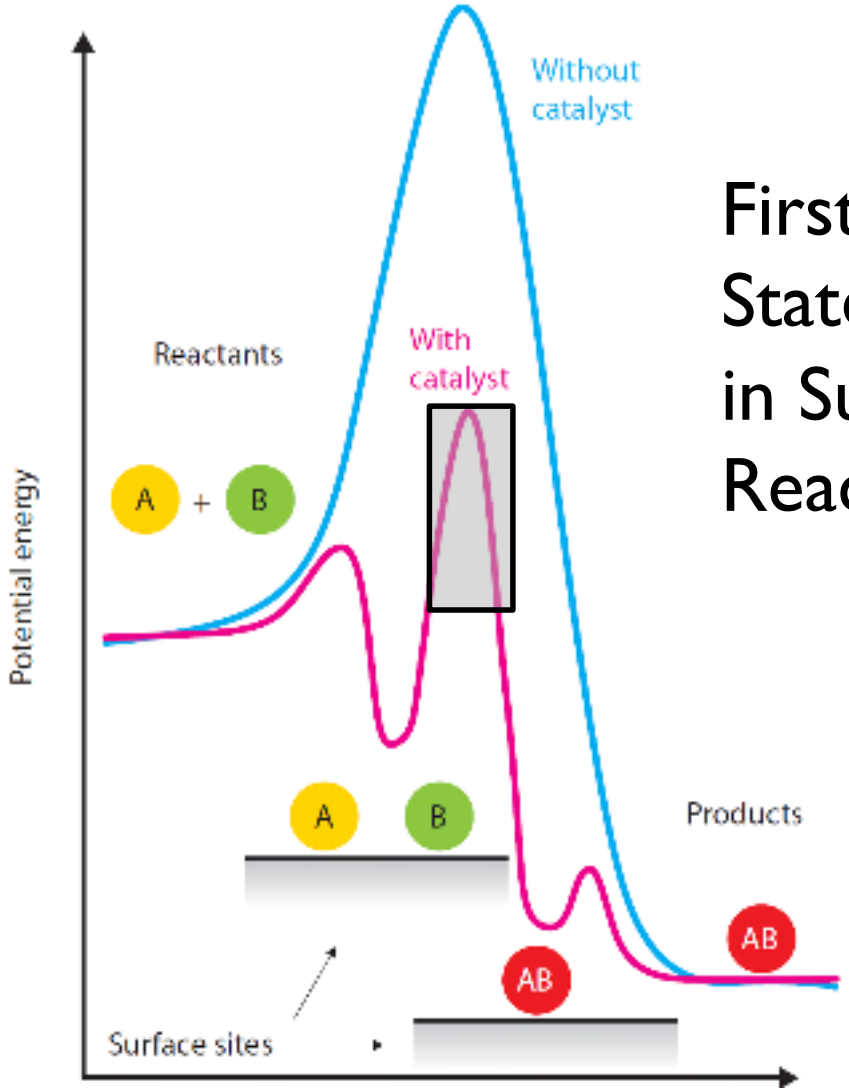
Probing Transition States



First time Transition State is Observed in Surface Chemical Reaction

Artificial Photosynthesis

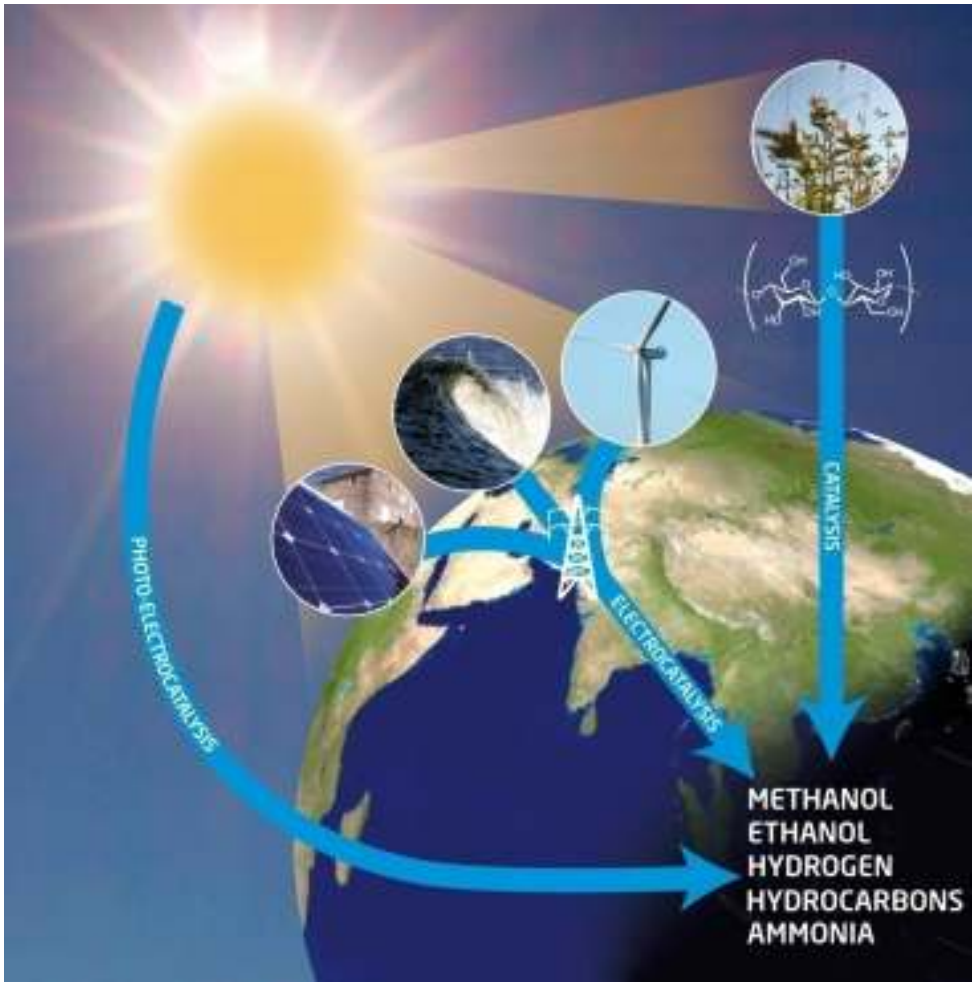
Reducing CO_2 to fuels and chemicals

One of the main challenges for the future

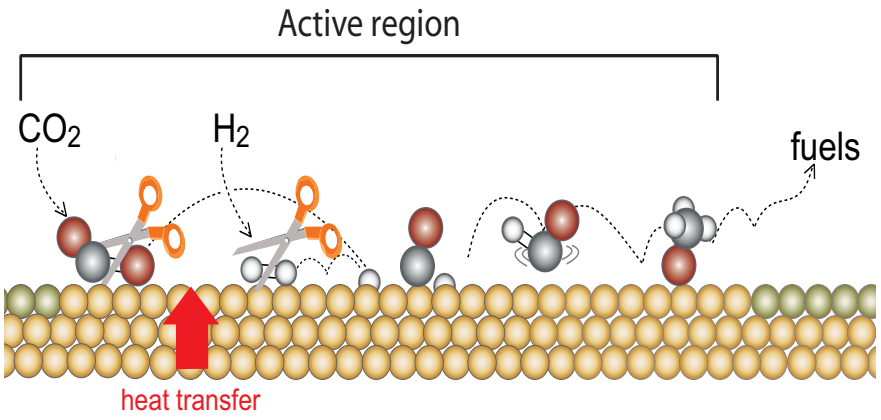
Photochemical

Electrochemical

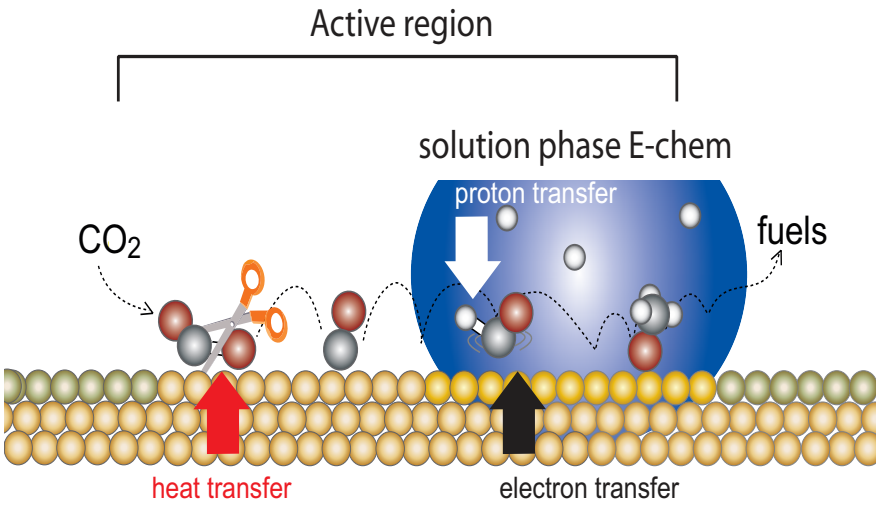
Chemical



Heat or Electron Transfers

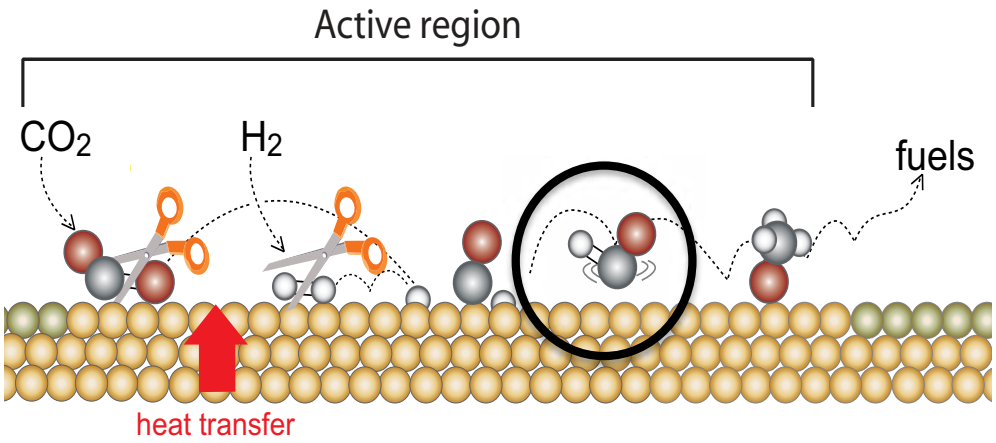


Thermal



Electrochemical

Can we see the most essential intermediate predicted by theory COH or HCO



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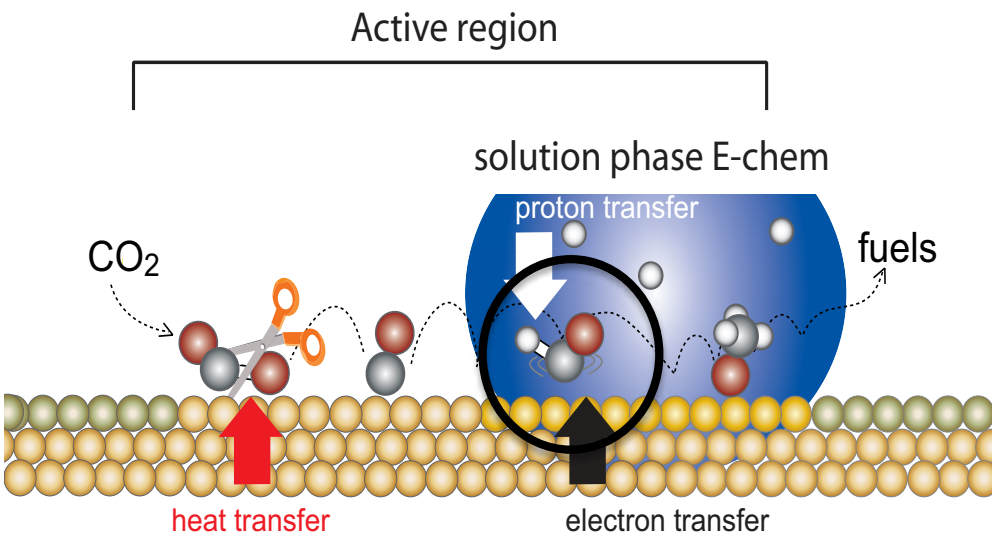
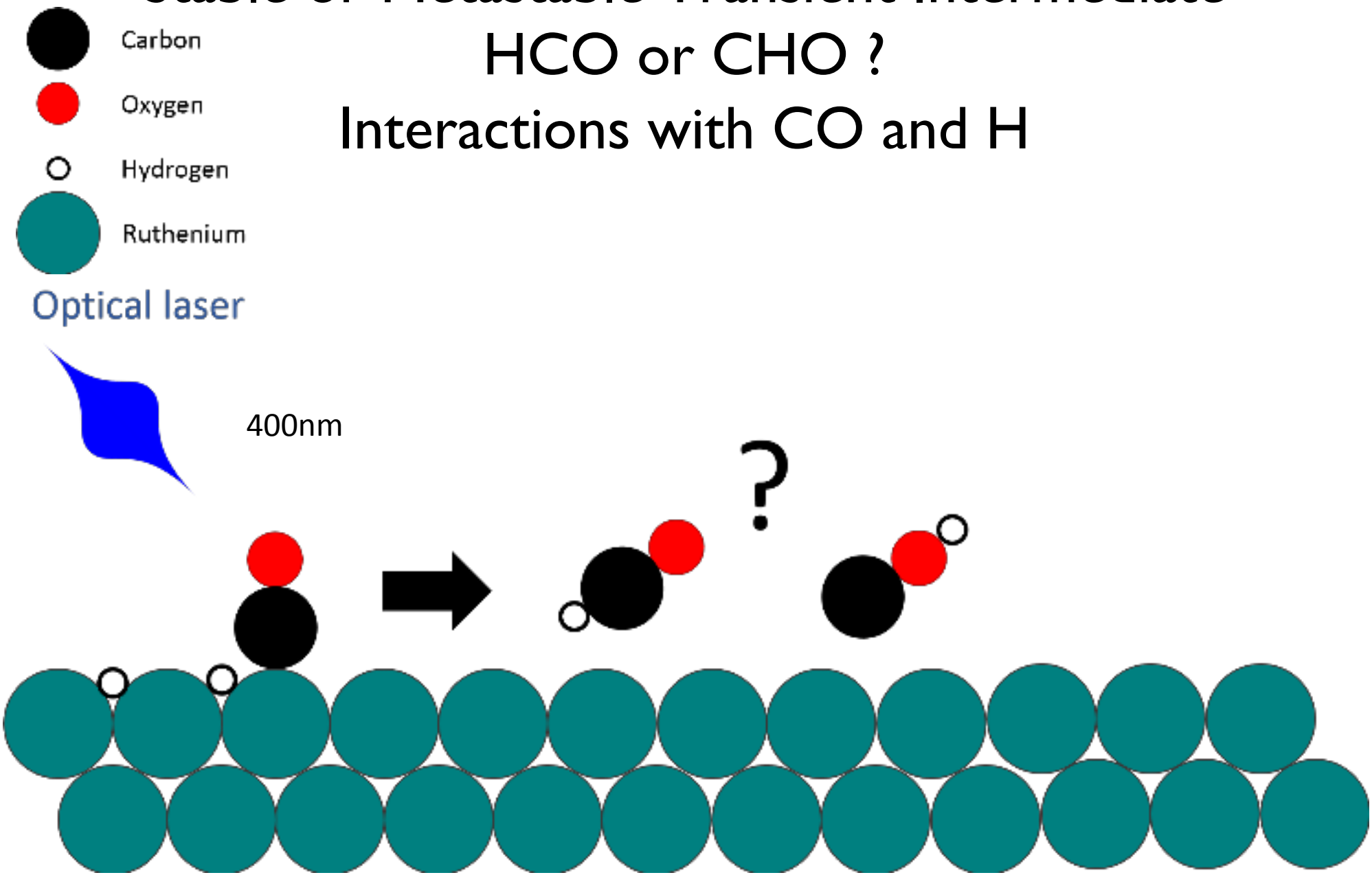
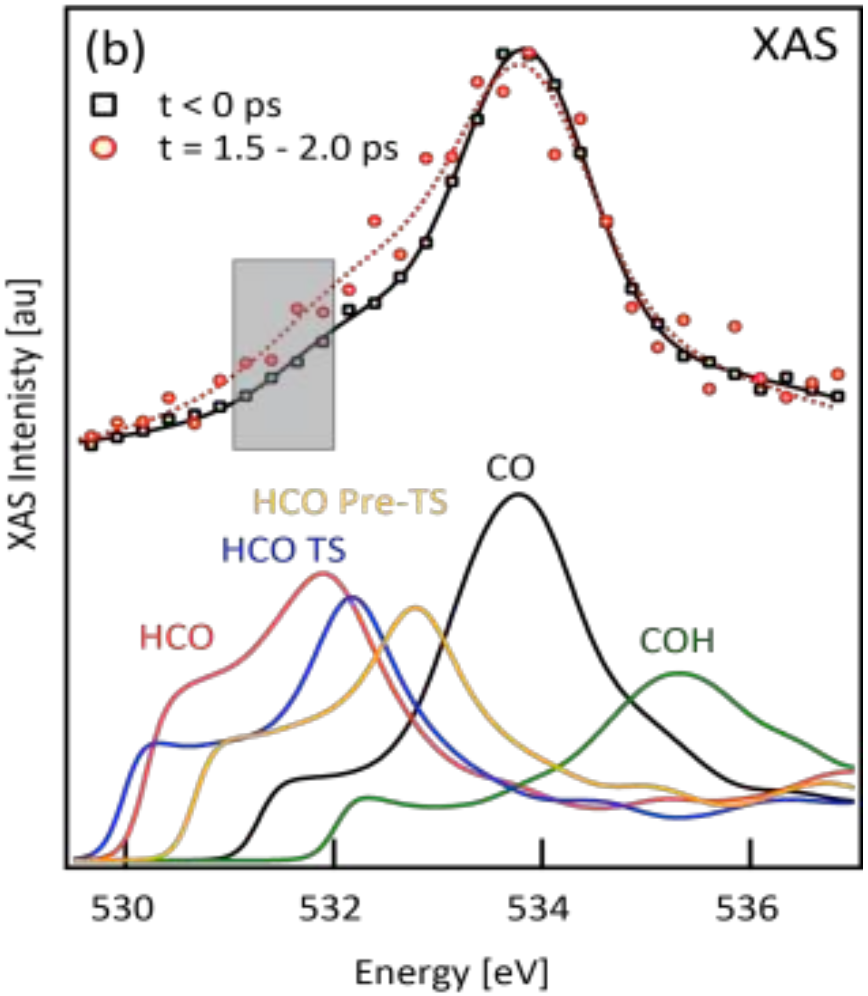


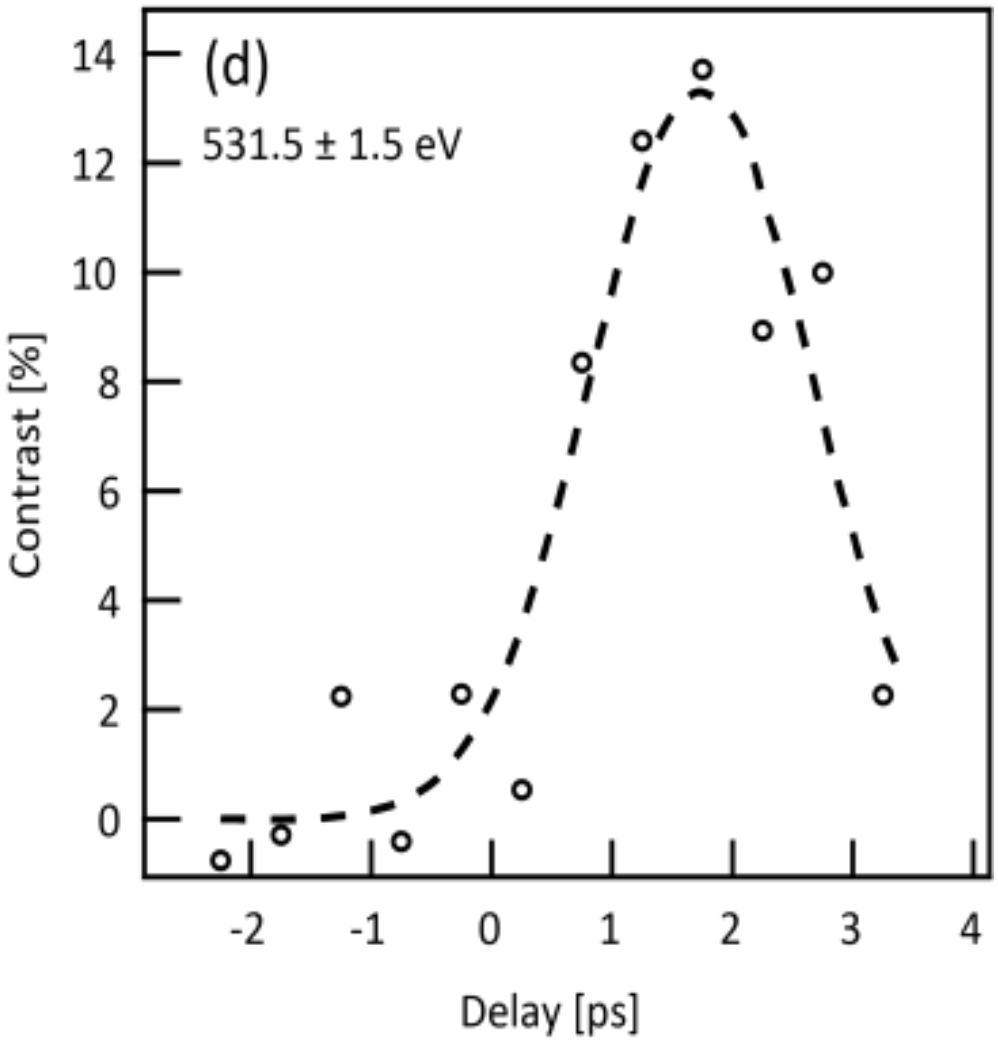
Electrochemical

Stable or Metastable Transient Intermediate
HCO or CHO ?
Interactions with CO and H



Fast time scales (t < 4 ps)





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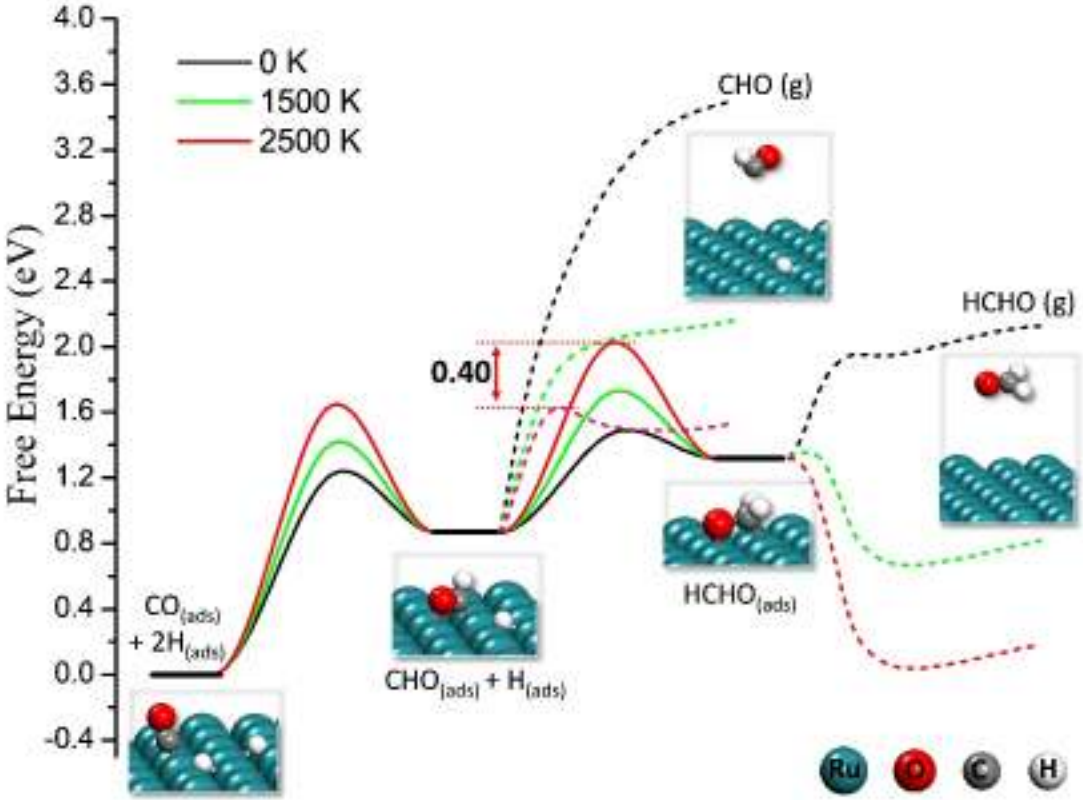
Free Energy Calculations CHO and CH_2O Formation



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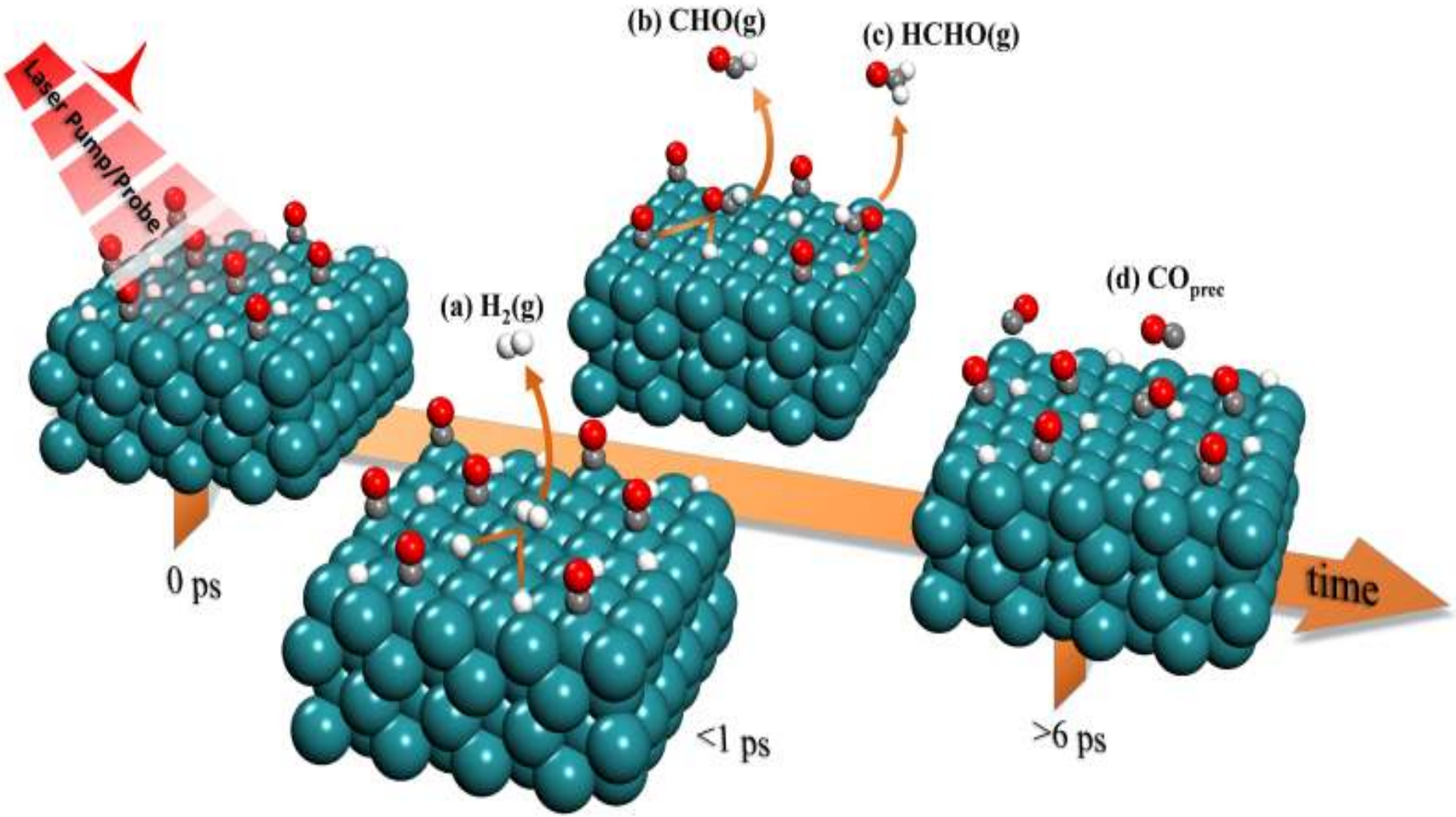

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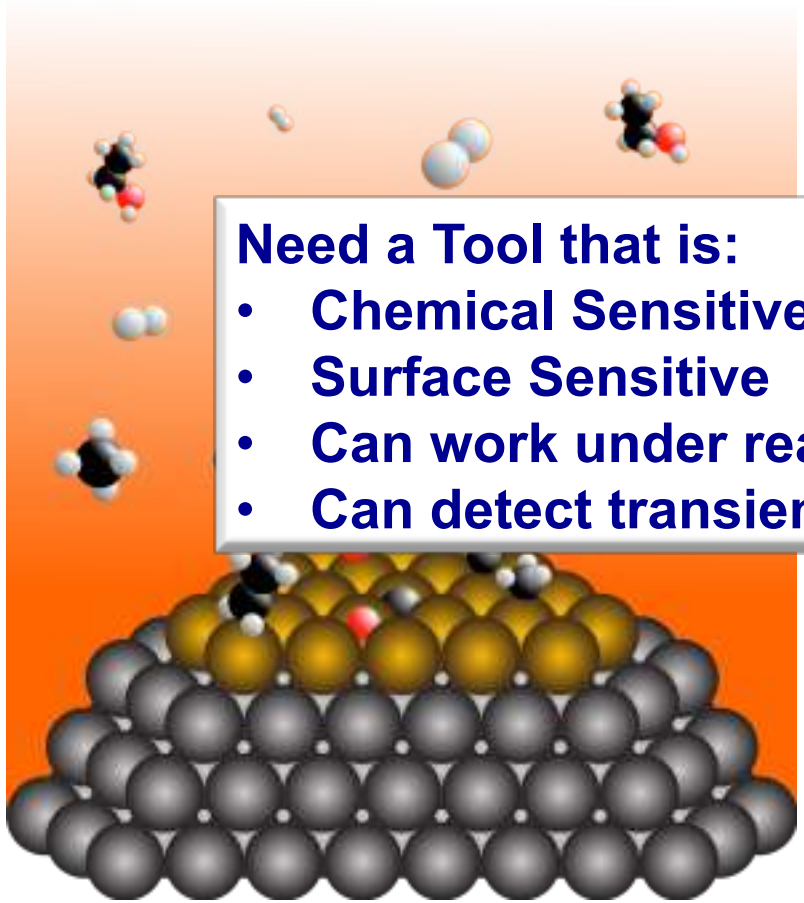
Catalysis: Dealing with complexity

CO hydrogenation to methane, methanol or ethanol



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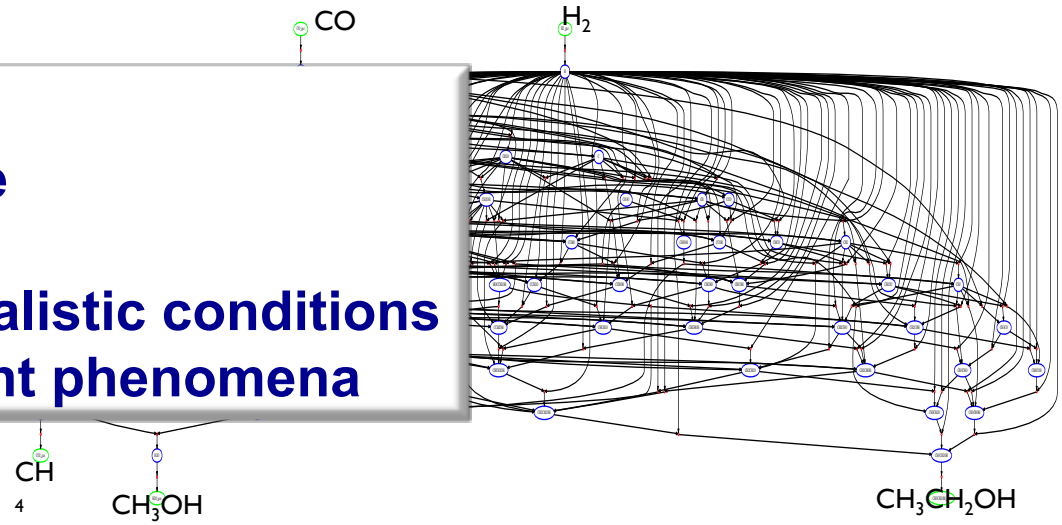
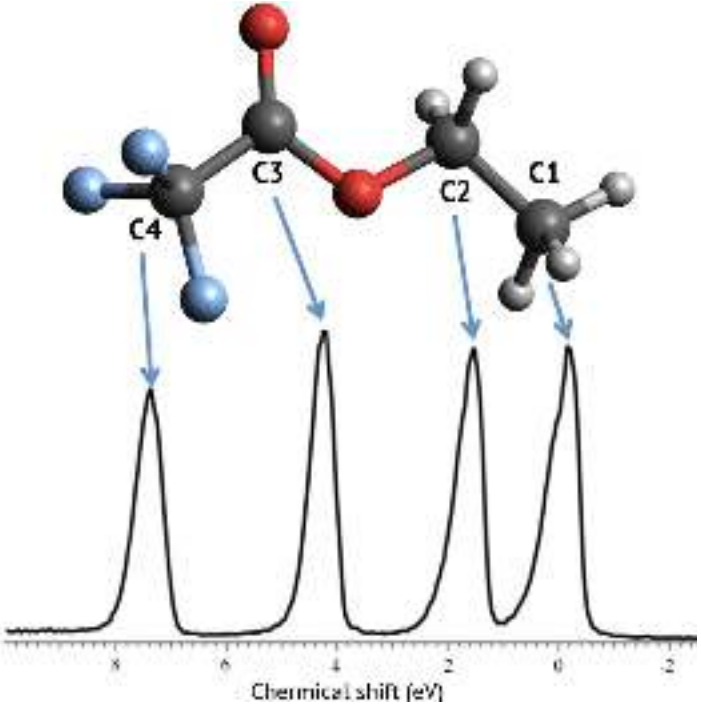


Medford, Ulissi, Hummelshøj, Bligaard, Nørskov (2016)

100+ species
200+ reactions
2000+ unique pathways

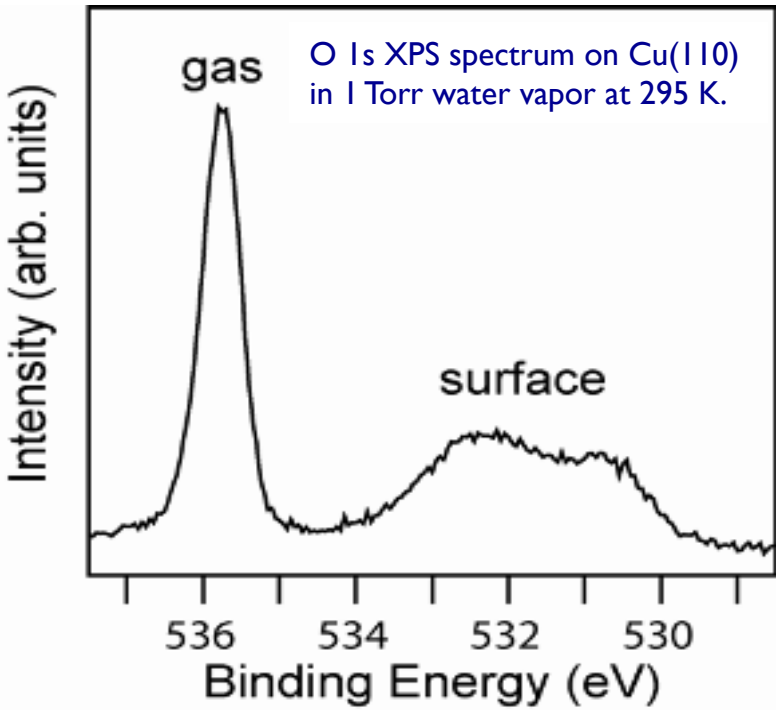
X-ray Photoelectron Spectroscopy (XPS)

Chemical sensitivity



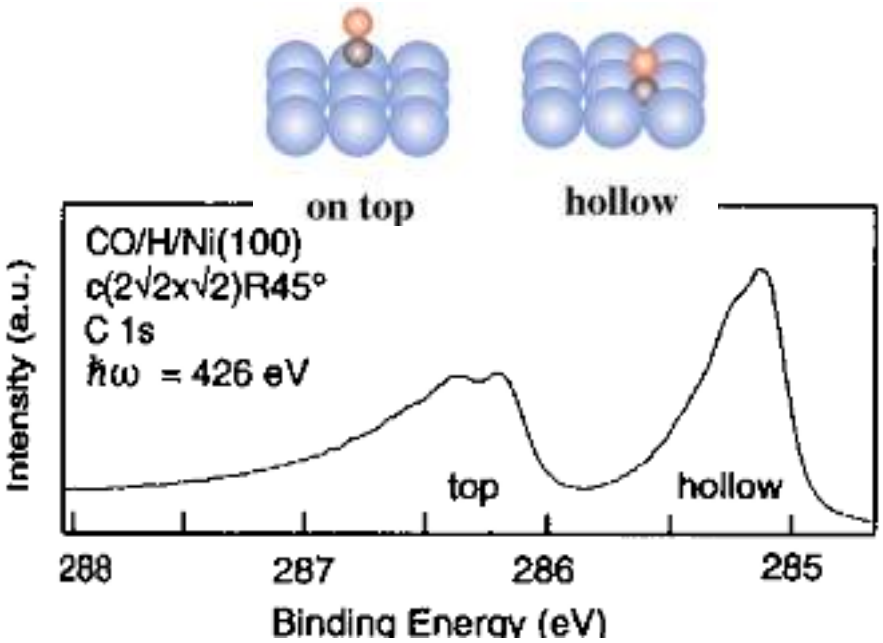
Delesma et al. ChemPhysChem 2018, 19, 169 – 174

Surface sensitivity

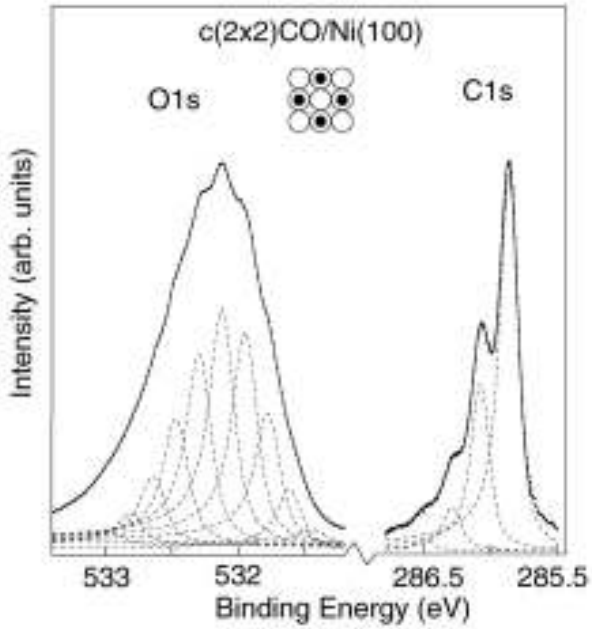


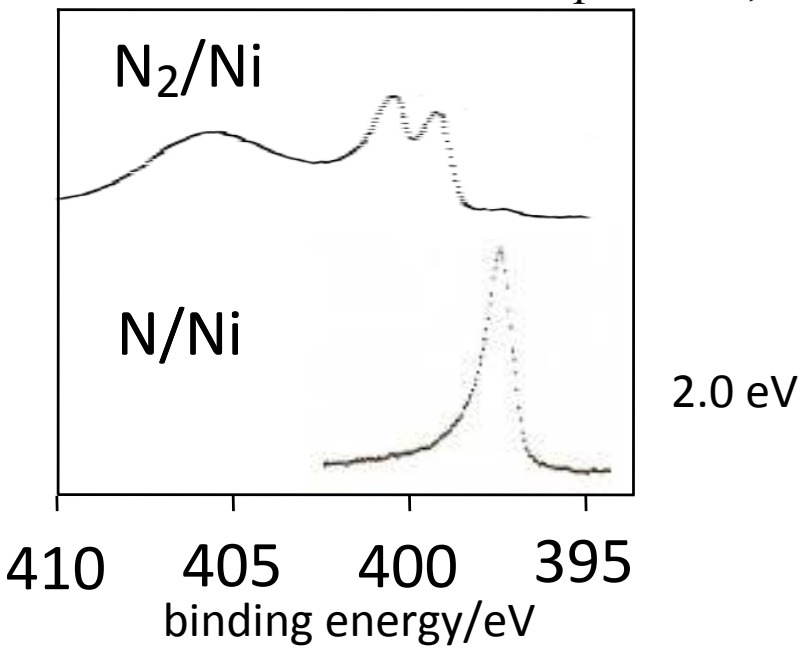
Yamamoto et al. J. Phys.: Condens. Matter **20** (2008) 184025 (14pp)

Core Level Shifts and Geometry

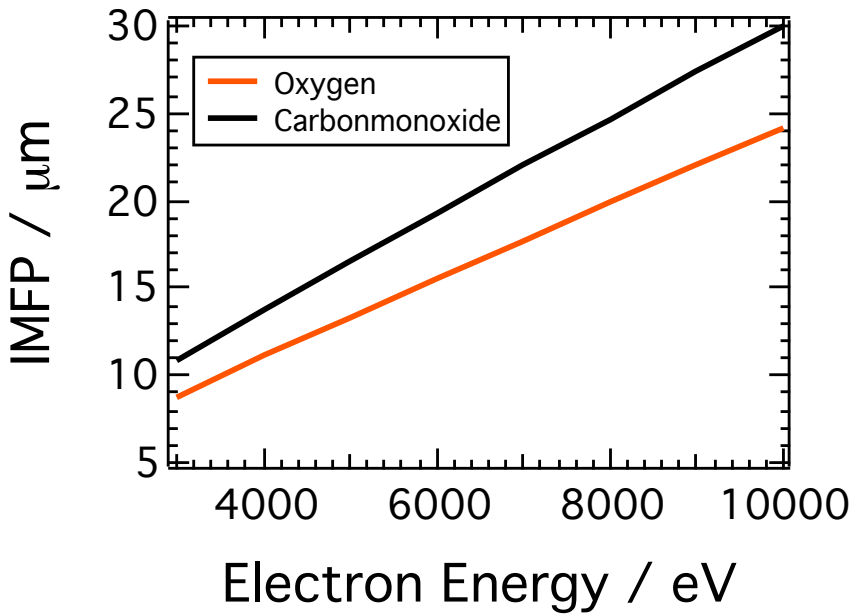


J. El spec. **126**, 3 (2002)



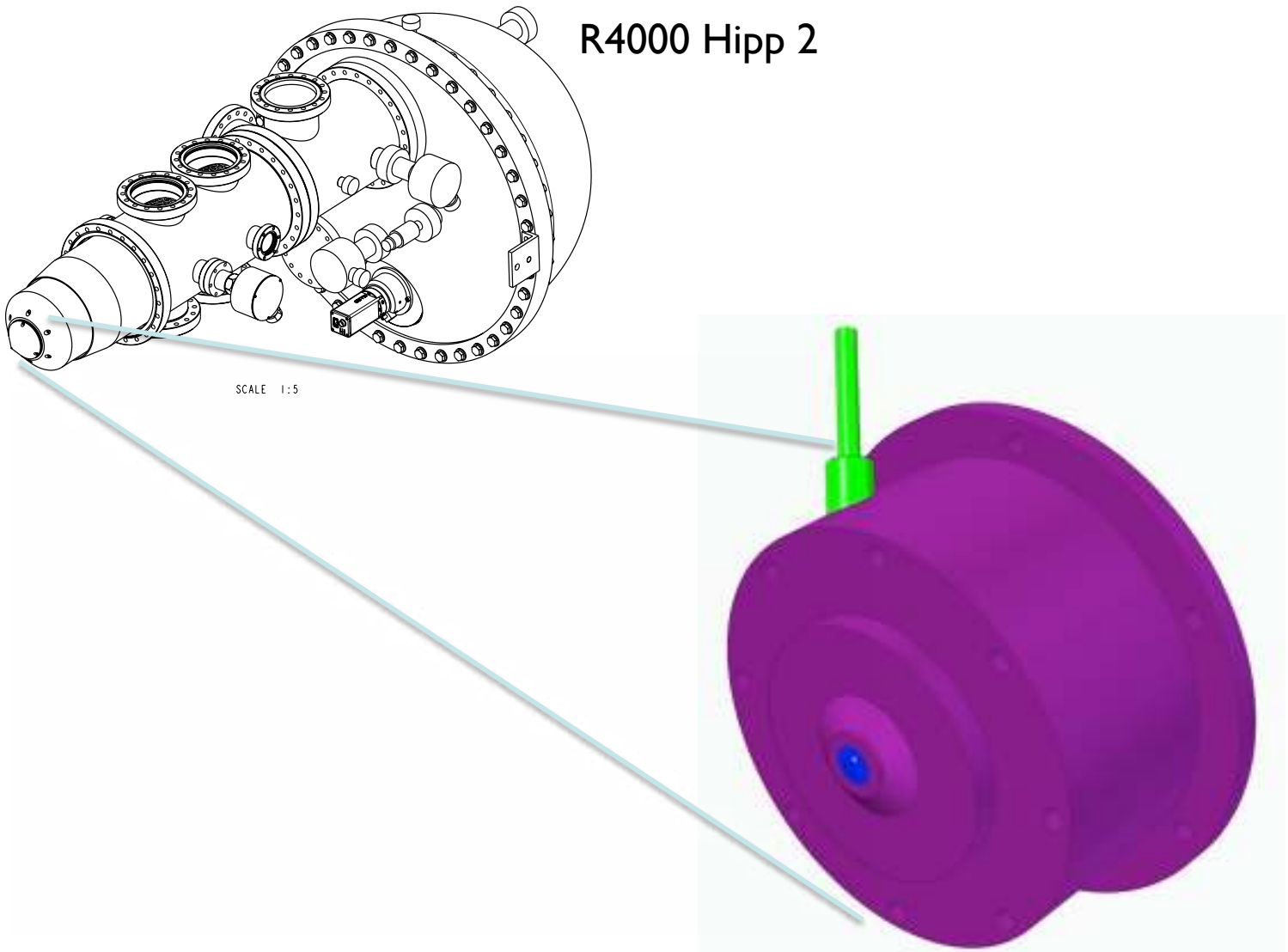


High pressure XPS



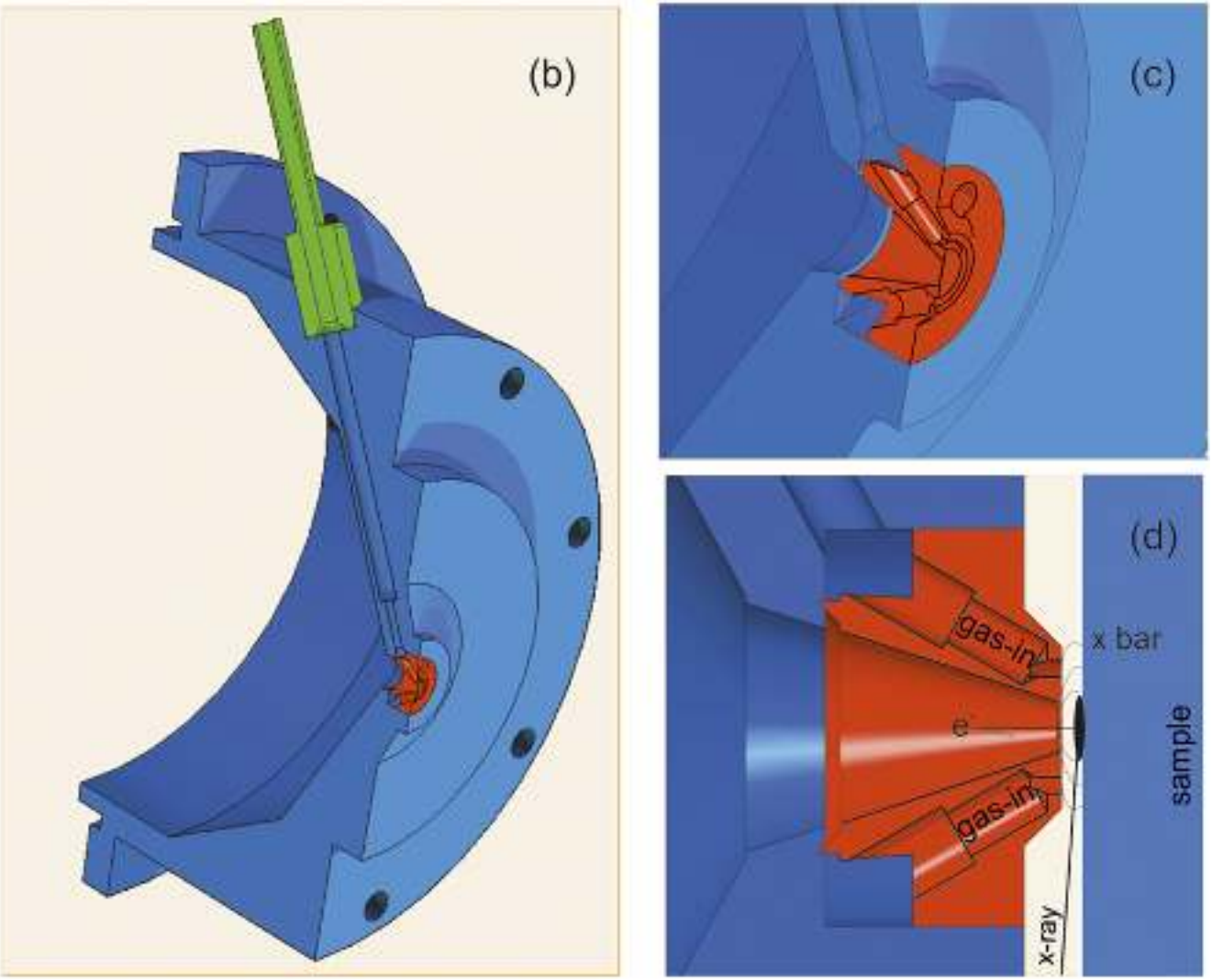
Mean free path of electrons in 1bar gas pressure

Conceptual design of the high-pressure region



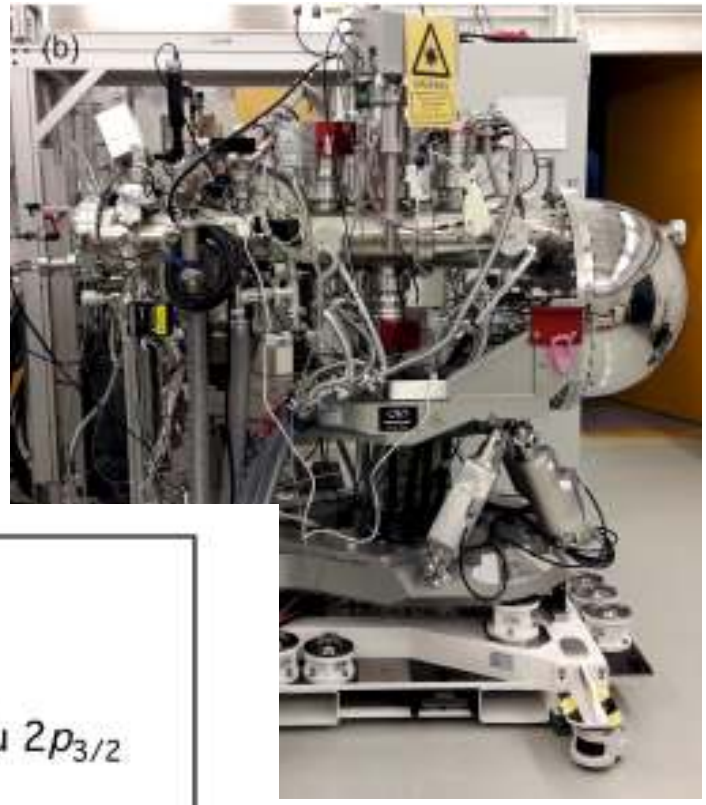
Amann et al. Review of Scientific Instruments, 90 103102, (2019)

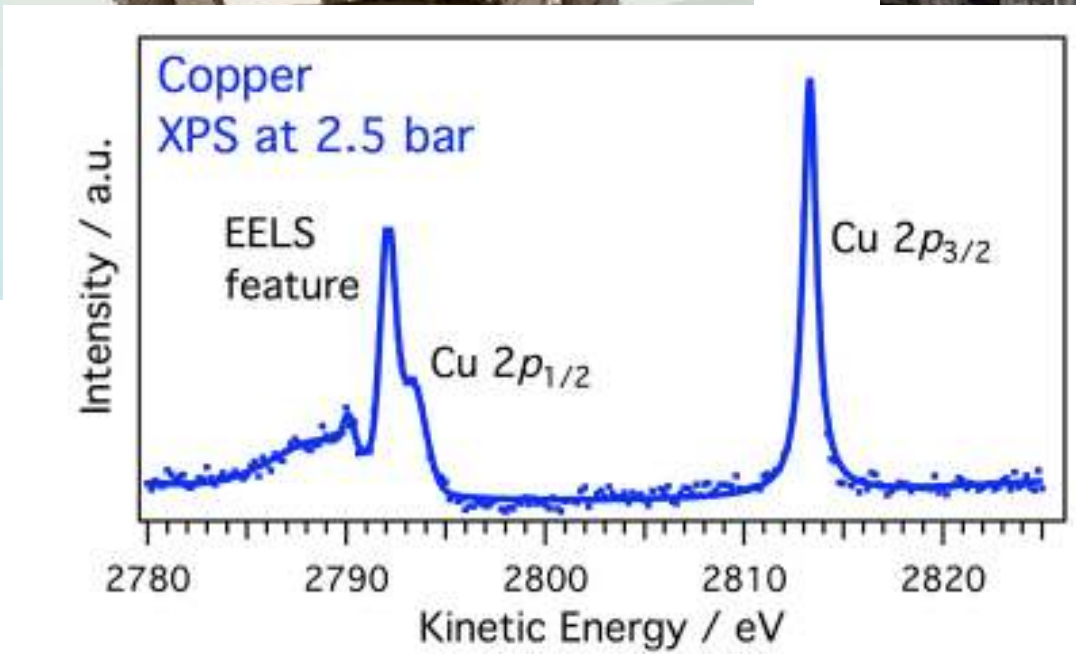
Conceptual design



Amann et al. Review of Scientific Instruments, 90 103102, (2019)

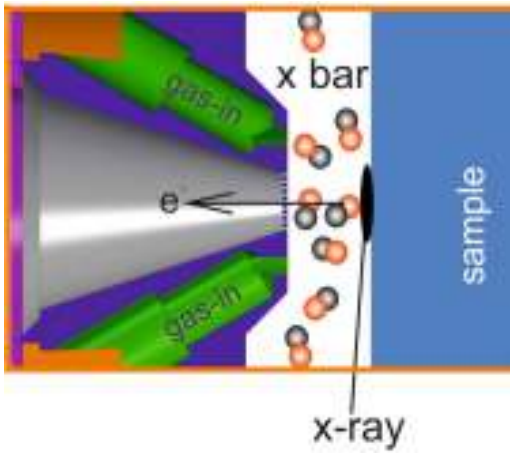
High pressure XPS - the POLARIS endstation

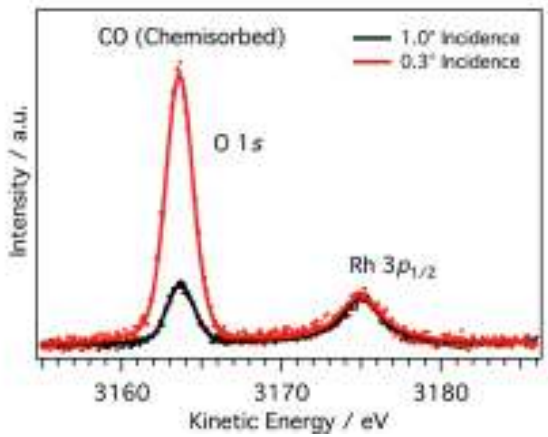




Amann et al. Review of Scientific Instruments, 90 103102, (2019)

Hard X-rays, grazing incidence, small divergence, AND … High Repetition Rate





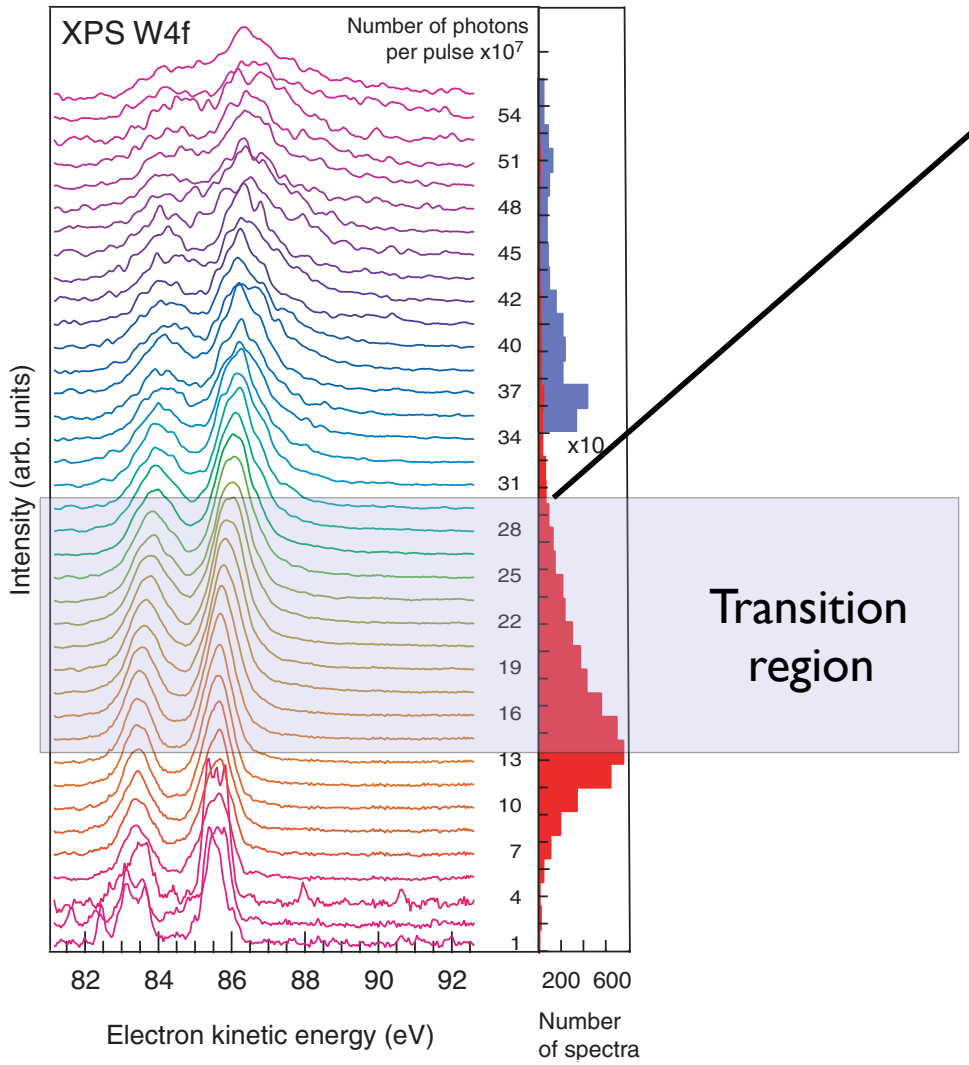
Amann et al. Review of Scientific Instruments, 90 103102, (2019)

Hard X-Rays …
to enhance the mean free path of the photo excited electrons

Grazing Incidence & Small Divergence…
to increase the surface sensitivity

High Repetition Rate …
to avoid space charge effect and to increase signal intensity

Time-resolved XPS at FLASH



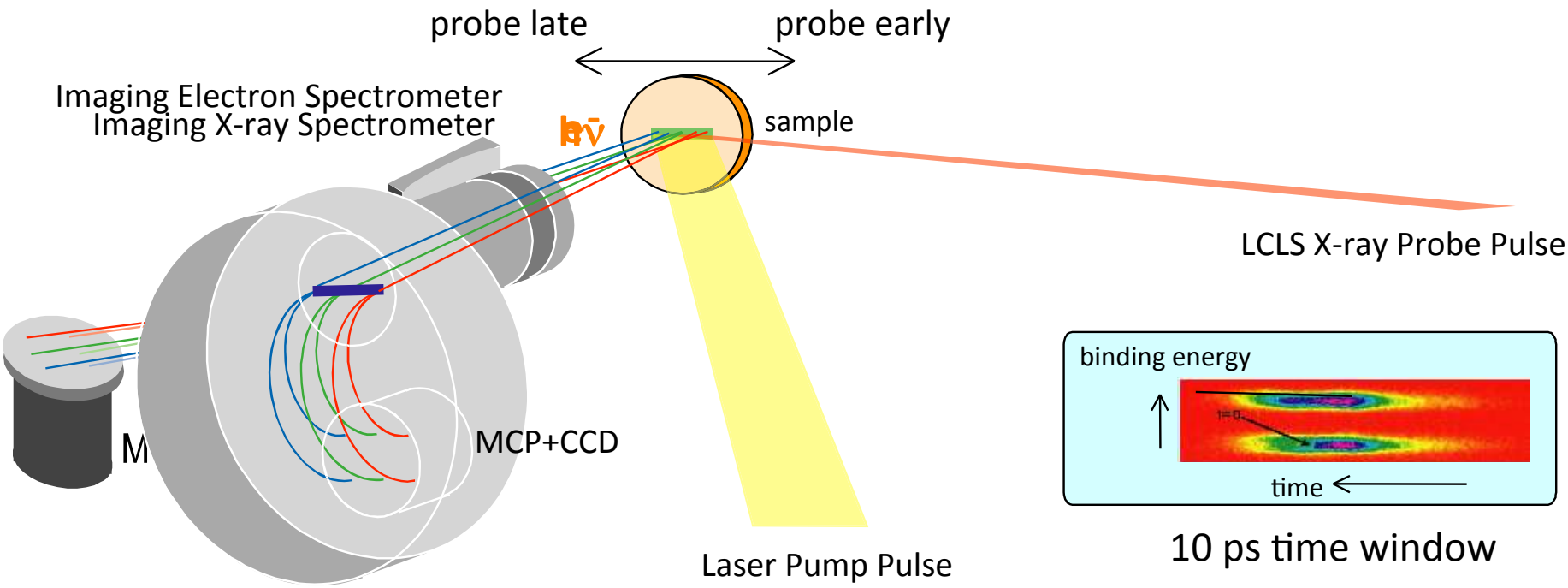
Not more than 10^7 photons/pulse

HPXPS at beamline P22: 10^{13} photons/s

→ Require high repetition rate

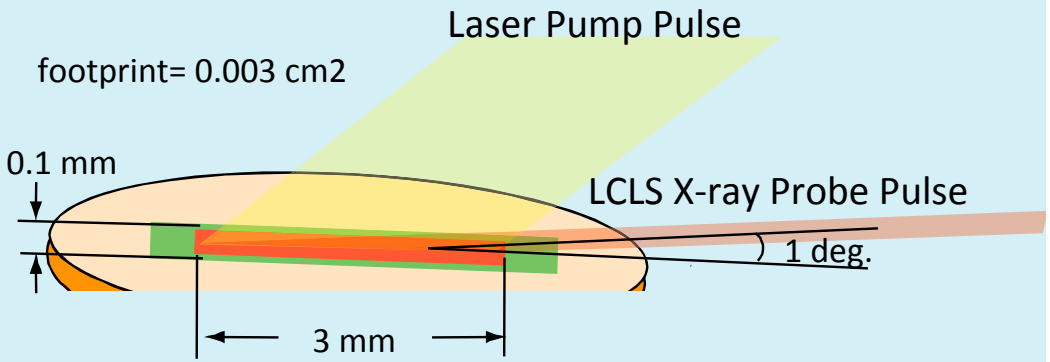
A. Pietzsch et al. New J. Phys. 10 033004 (2008)

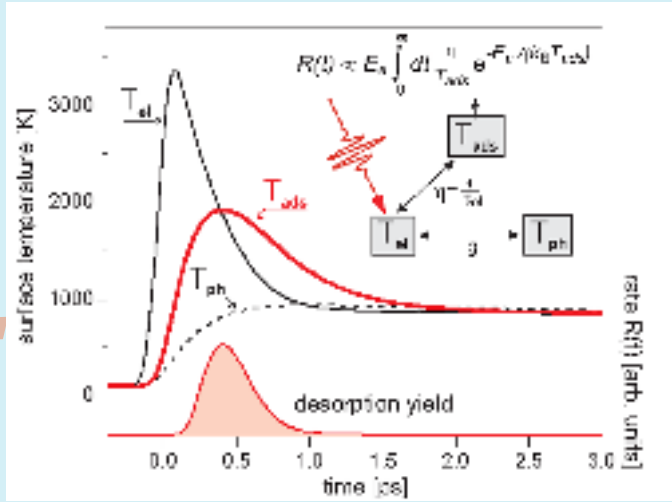
Measures complete time history around t=0 in single shot



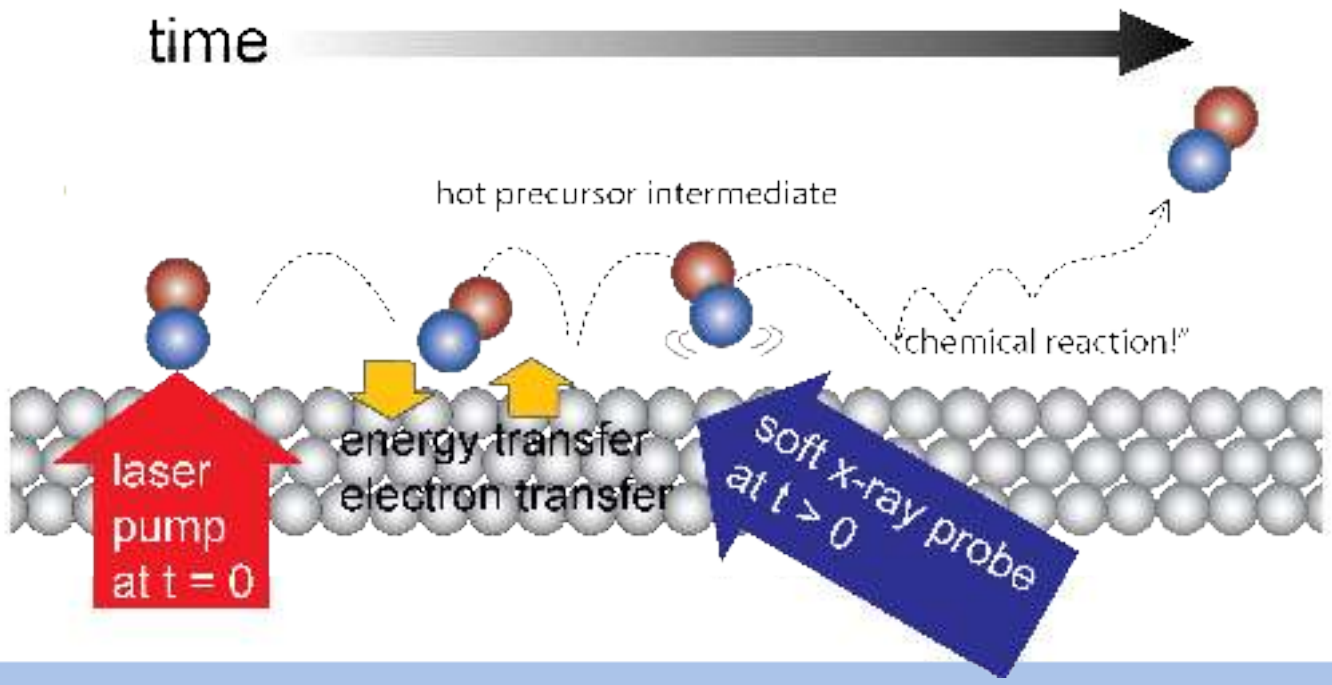
10 ps time window

required laser power: 1-10 μJ/pulse





New Era in Probing Catalysis



- First surface chemical reactions 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
- "Chemical Physicists dream"

Thanks to …
Anders Nilsson and the team at Stockholm University