Probing Surface Catalysis in Real Time

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Chemical Physics @ Stockholm University, Sweden

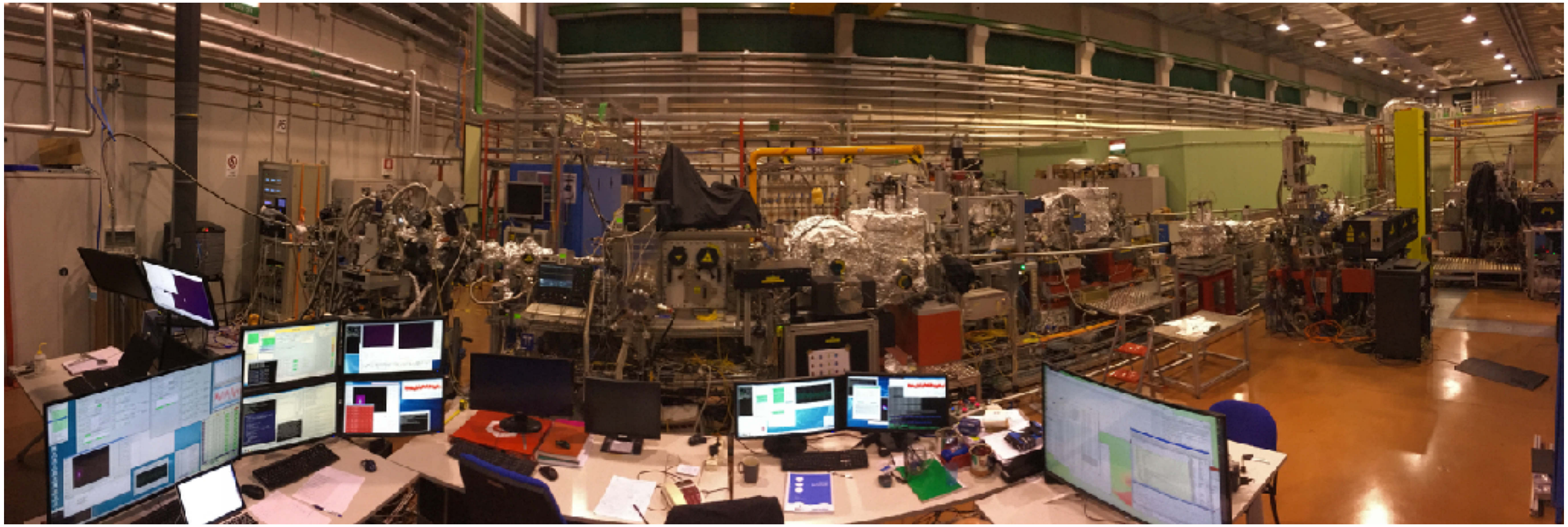
REVIEW PAPER: A. Nilsson, J. LaRue, H. Öberg, H. Ogasawara, M. Dell’Angela, M. Beye, H. Öström, J. Gladh, J.K. Nørskov, W. Wurth, F. Abild-Pedersen, L.G.M. Pettersson, Chem. Phys. Lett. **675**, 145 (2017)

Co-Workers for LCLS data

Jerry LaRue (Chapman University)
Lin Yu, May Ling Ng, Honliang Xin, Stefan Moeller, Dennis Nordlund, John Turner, Ryan Coffee, M. P. Minitti, Jens Nørskov, Frank Abild-Pedersen, Hirohito Ogasawara (Stanford/SLAC)
Martin Beye, Alexander Föhlisch (HZB Berlin)
Giuseppo Mercurio, Wilfried Wurth (DESY and Univ Hamburg)
Oleg Krejci, Henrik Öberg, Jörgen Gladh, Lars G. M. Pettersson, Henrik Öström, Simon Schreck, Matthew Weston (Fysikum, SU)
Jonas Sellberg (KTH, Stockholm)
Martin Wolf (FHI Berlin)

Denys Naumenko, Emanuele Pedersoli, Flavio Capotondi, Ivaylo Nikolov, Martina Dell’Angela, Roberto Costantini

Hirohito Ogasawara



Martin Beye, Piter Miedema

Jerry LaRue

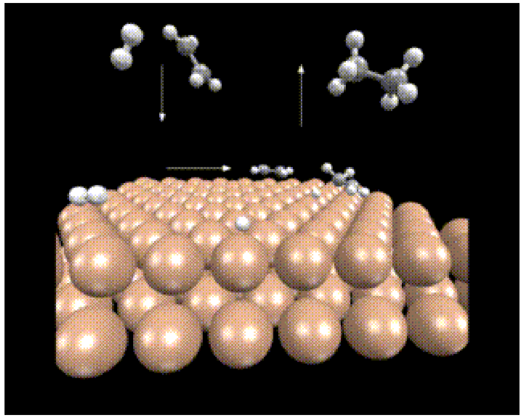
Anders Nilsson, Boyang Liu, Filippo Cavalca, Fivos Perakis, Hsin-Yi Wang, Jörgen Gladh, Matthew Weston, Sergey Koroidov, Simon Schreck

Ammonia feeds the world
Fertilizers

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

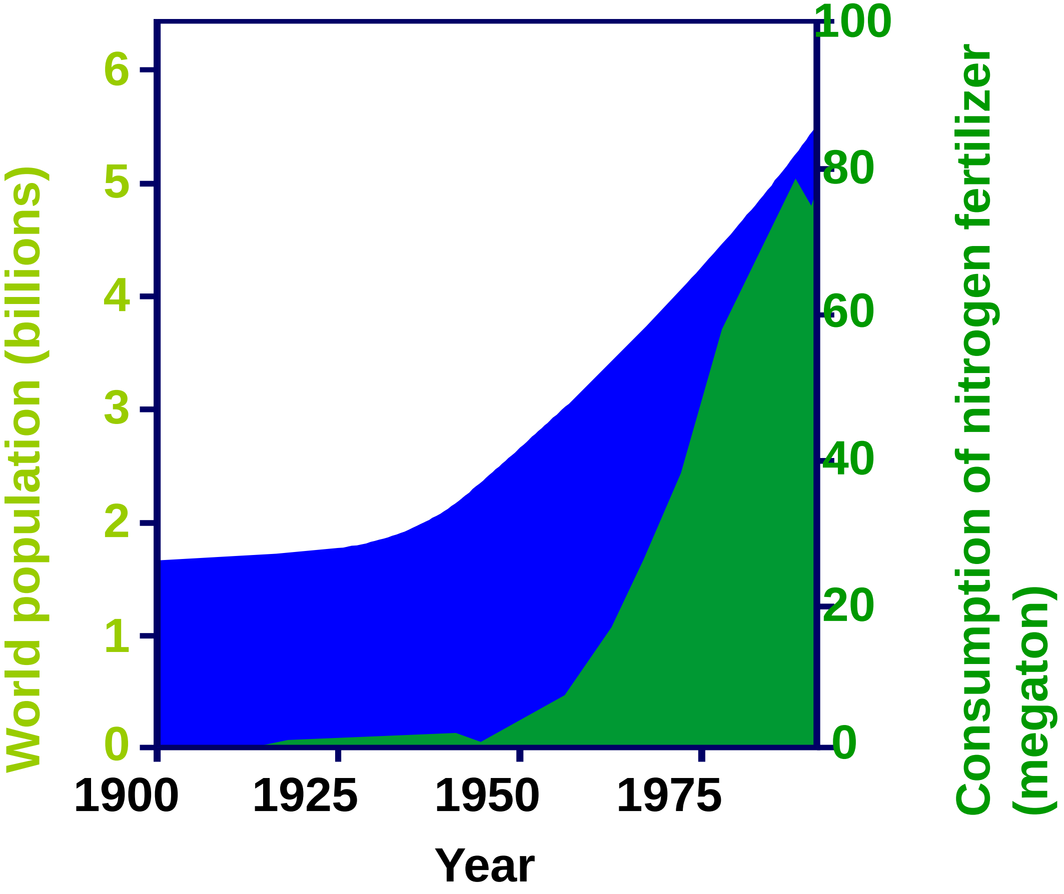
$N_2+3H_2 \leftrightarrows 2NH_3$

Haber Bosch Process



Surface Catalysis

Nobelprize 1918, 1933 and 2007



Sustainable fuels

Catalysis is key

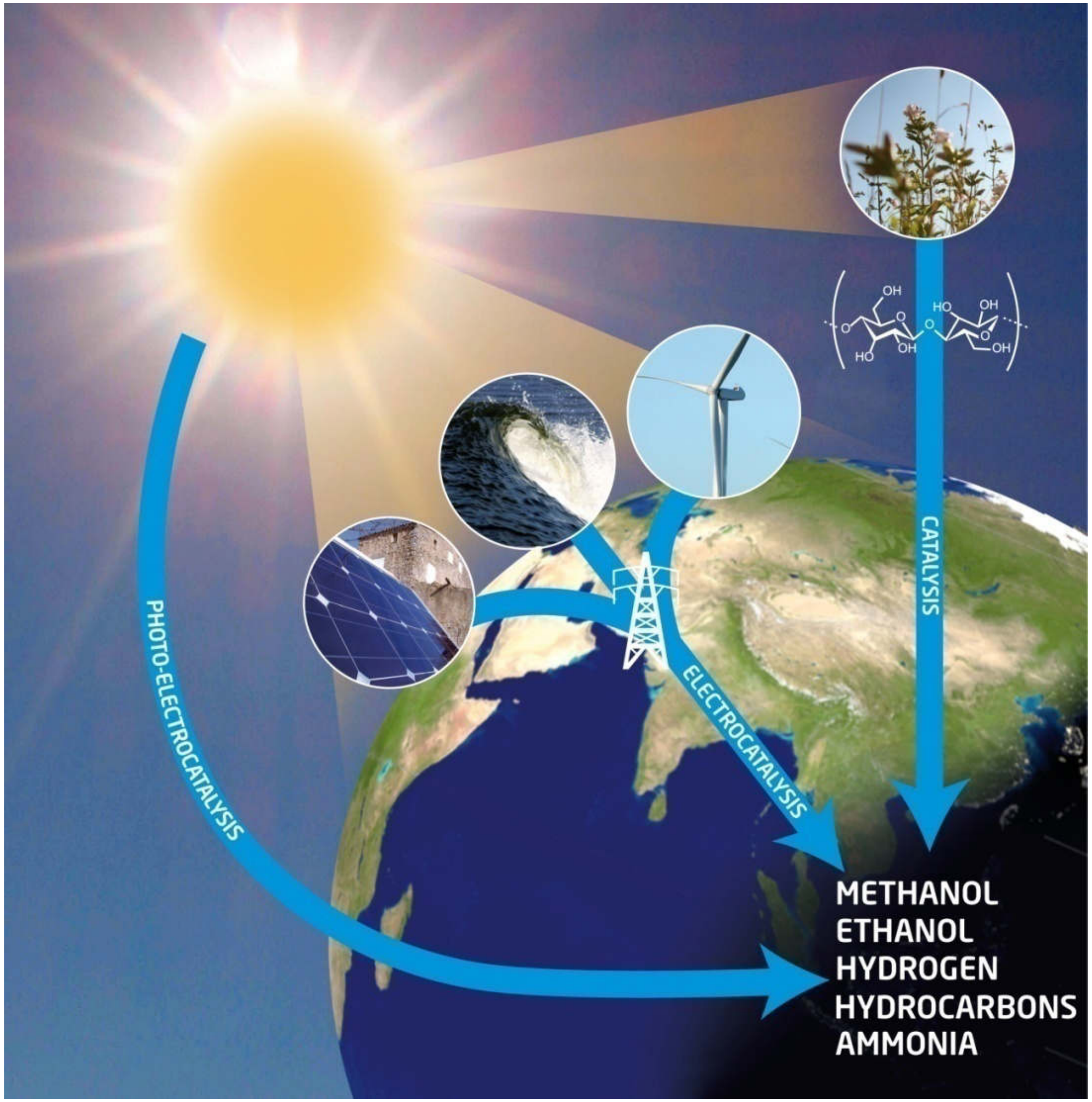
Biomass → fuels

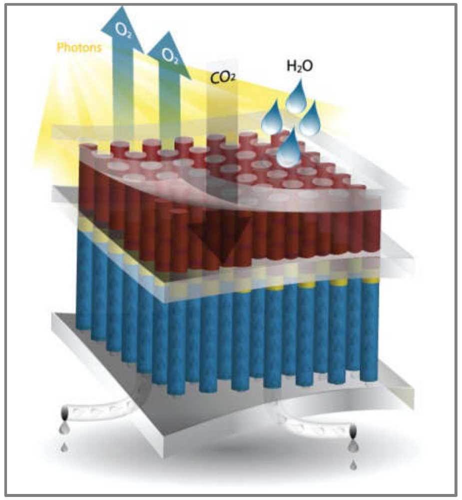
Electricity → fuels

Direct sunlight → fuels (artificial photosynthesis)

Novel catalysts needed

Made from Earth abundant materials

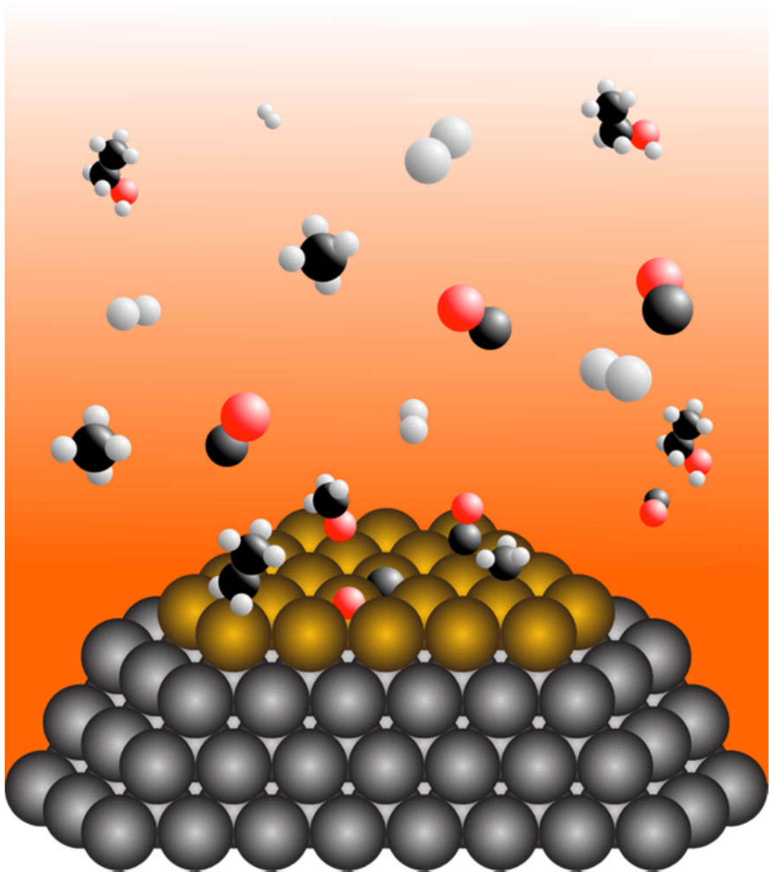


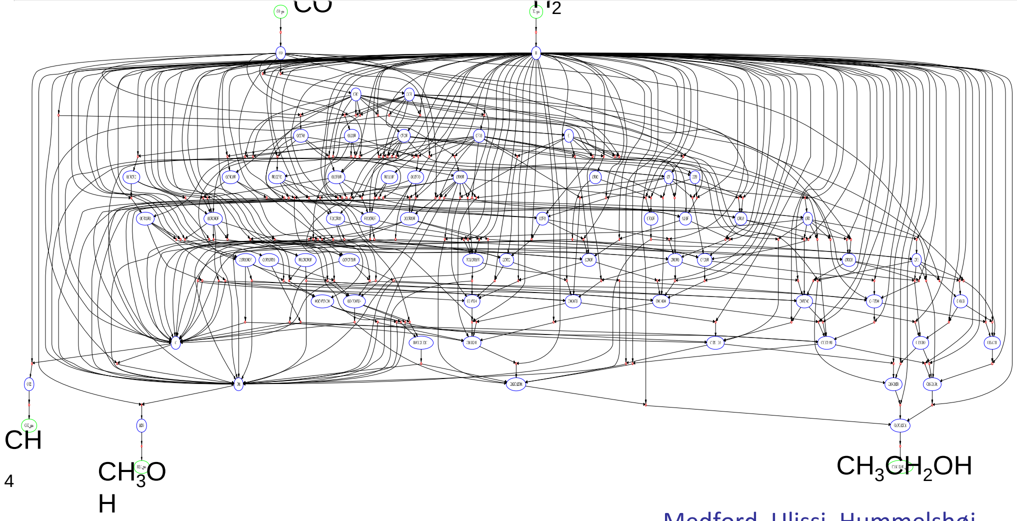


Catalysis: Dealing with complexity

Need a Tool that is:

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

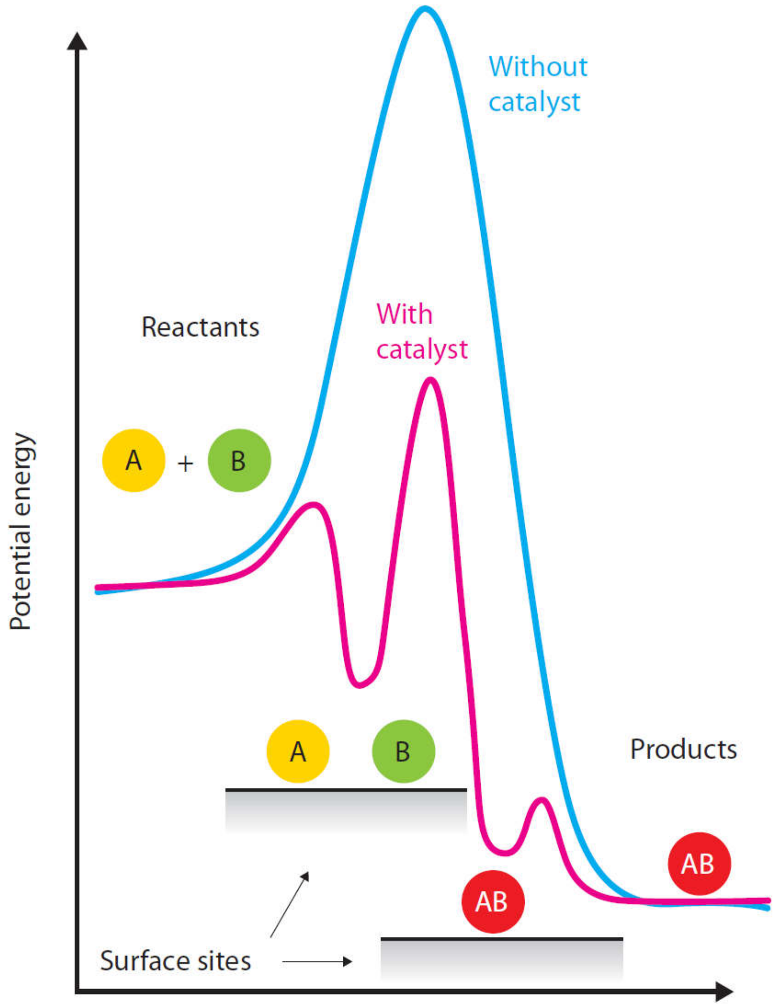




Medford, Ulissi, Hummelshøj, Bligaard, Nørskov (2016)

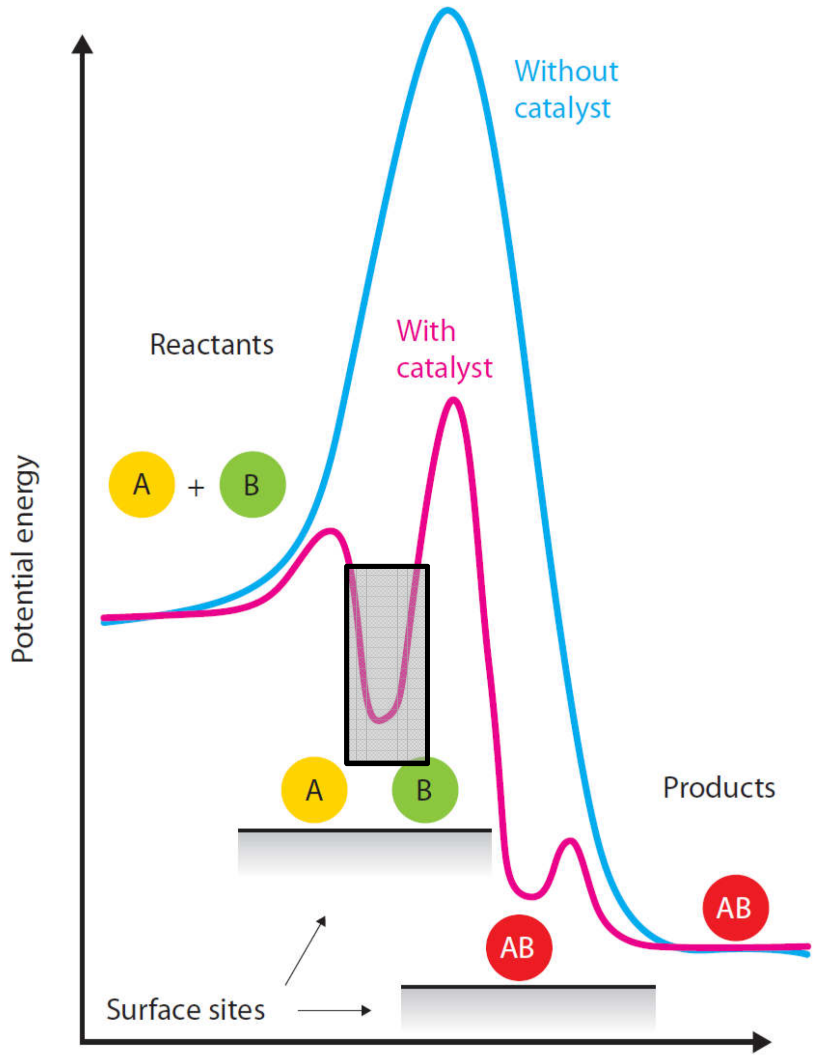
100+ species
200+ reactions
2000+ unique pathways

Fundamental Understanding of Catalysis



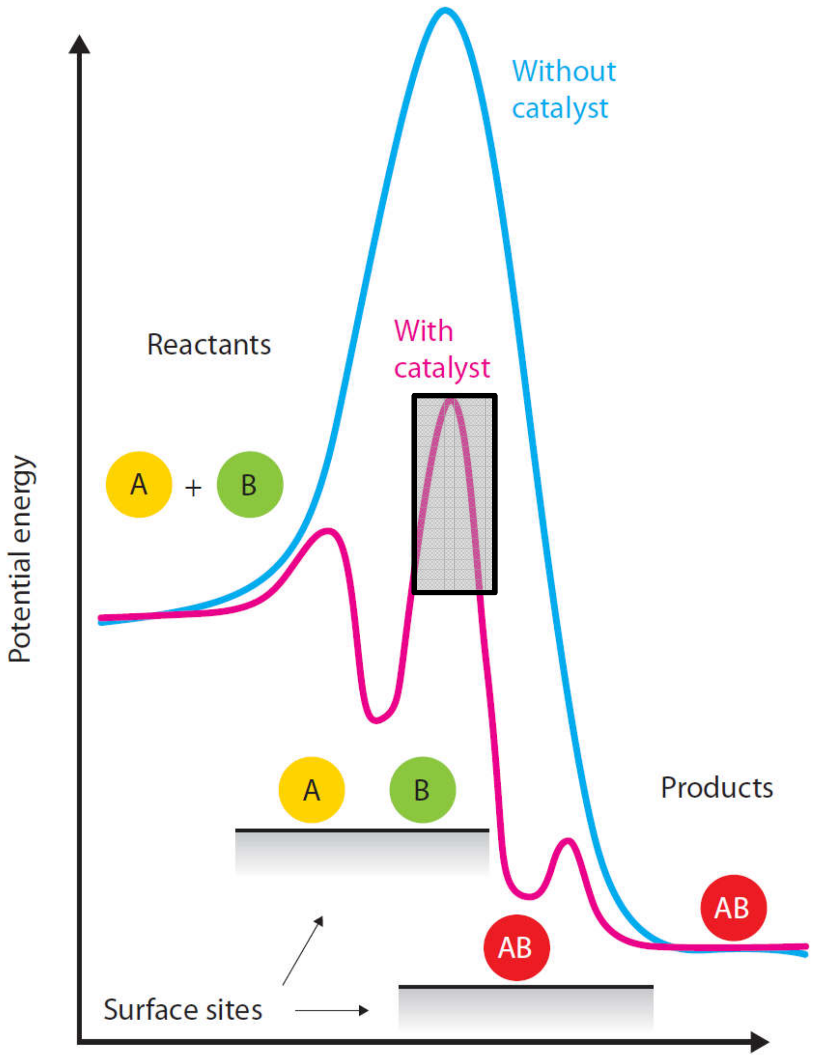
Courtesy I. Chorkendorff

Probing Intermediates ?



Courtesy I. Chorkendorff

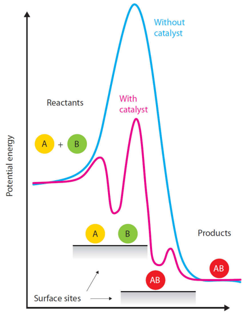
Probing Transition States ?

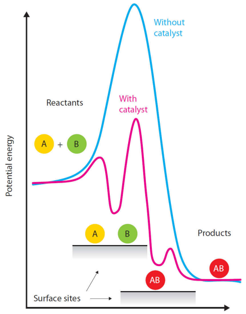


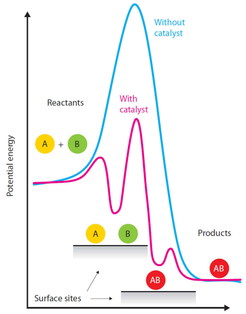
Courtesy I. Chorkendorff

Time Resolved Measurements

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





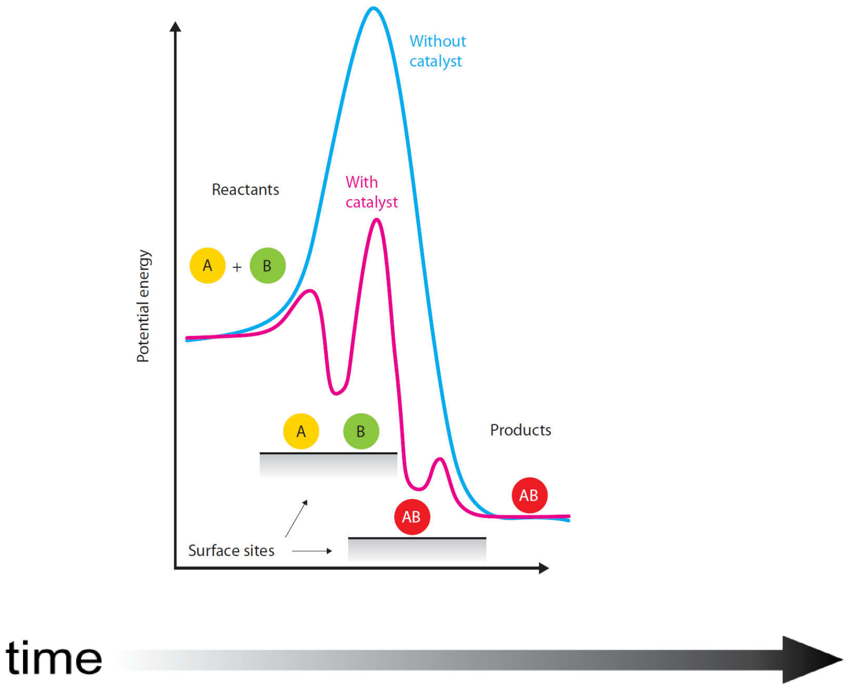


time

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

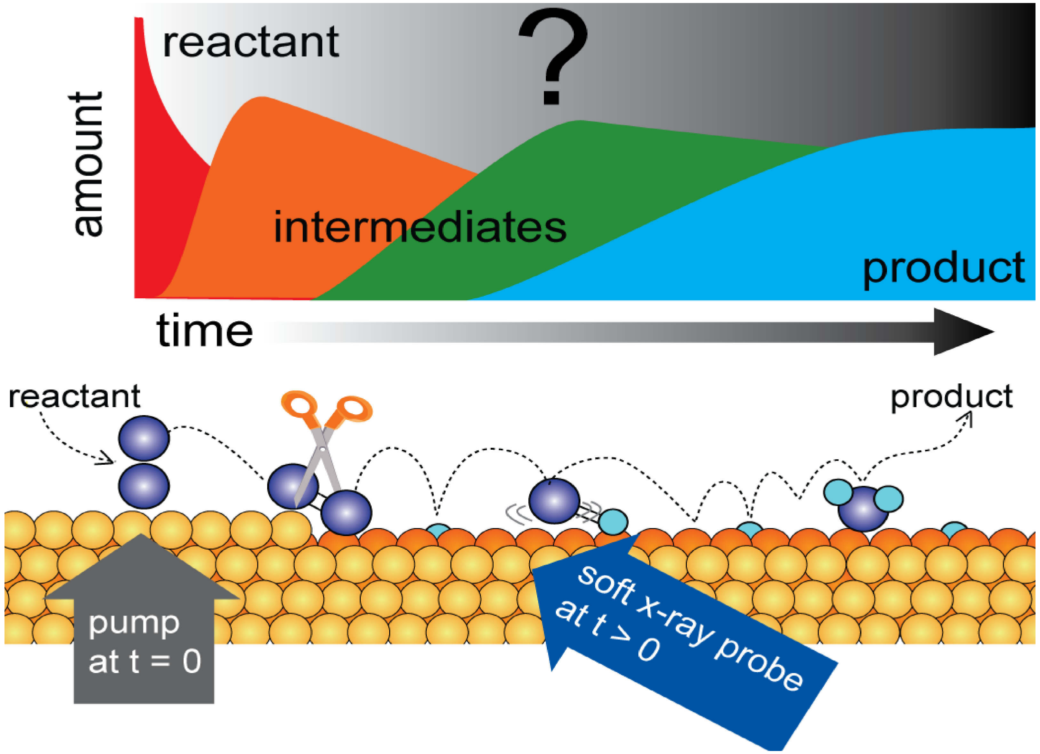


Time Resolved Measurements

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

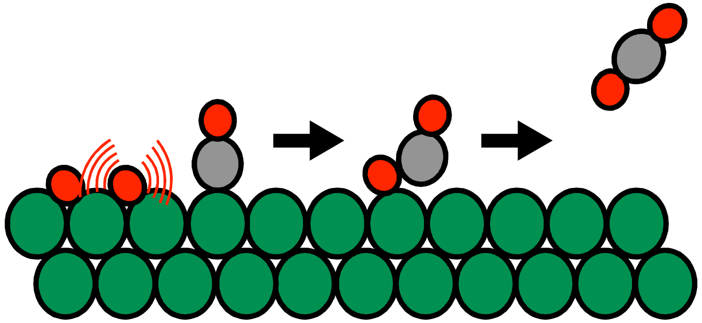
Dynamics: Following movements of atoms, molecules and electrons,
Following reaction events in real time as they occurs

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

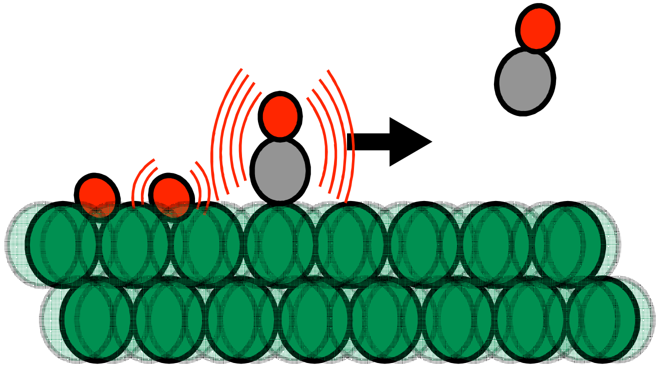


Atom Energy Selectivity Control

Can we direct the energy flow in catalysis?

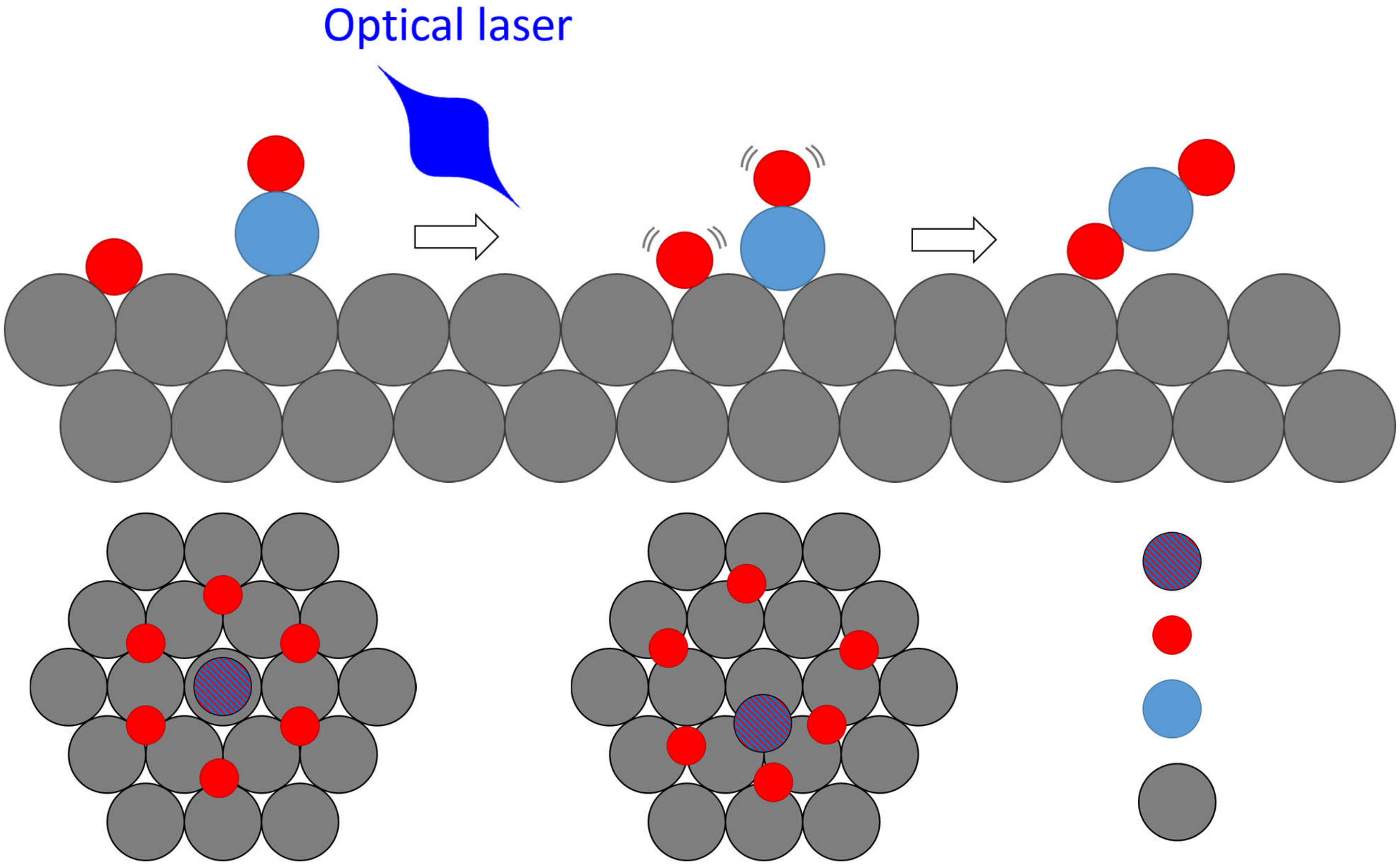


Selective Excitation on an Atomic Site



Thermal Energy Excites Everything

O and CO are both excited to produce CO_2
Observation of the Transition State



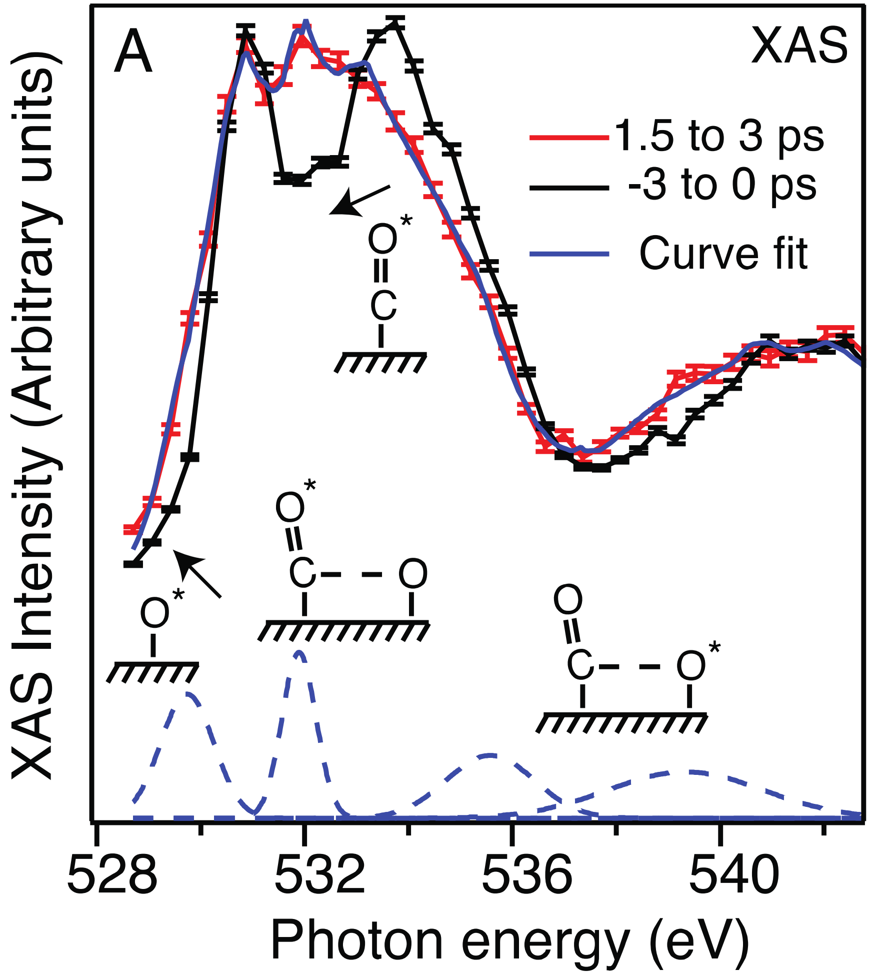
Pump-probe of CO oxidation

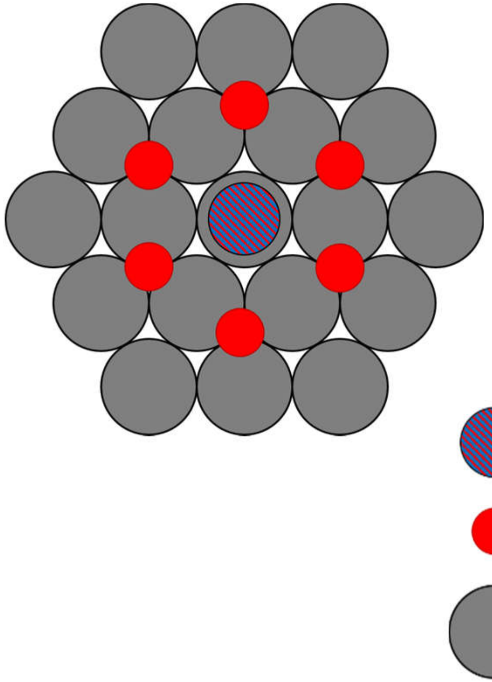
X-ray laser

Optical laser

O

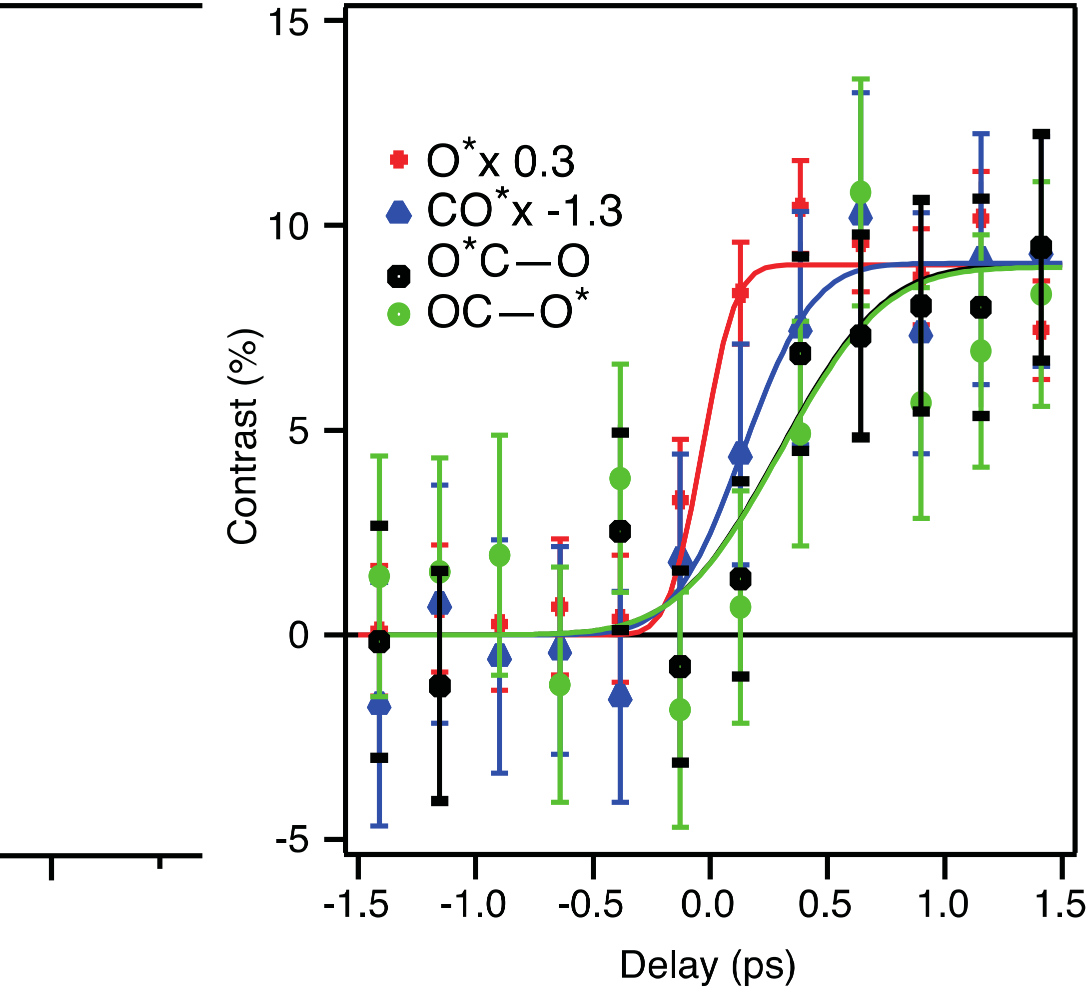
CO 2π*





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.

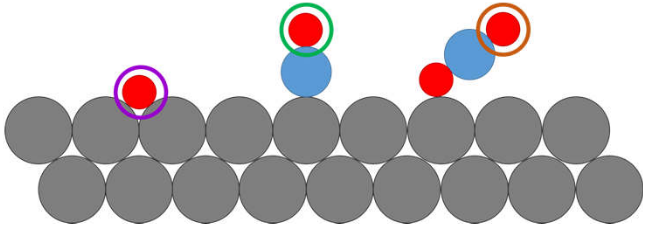
Transient Time Scales

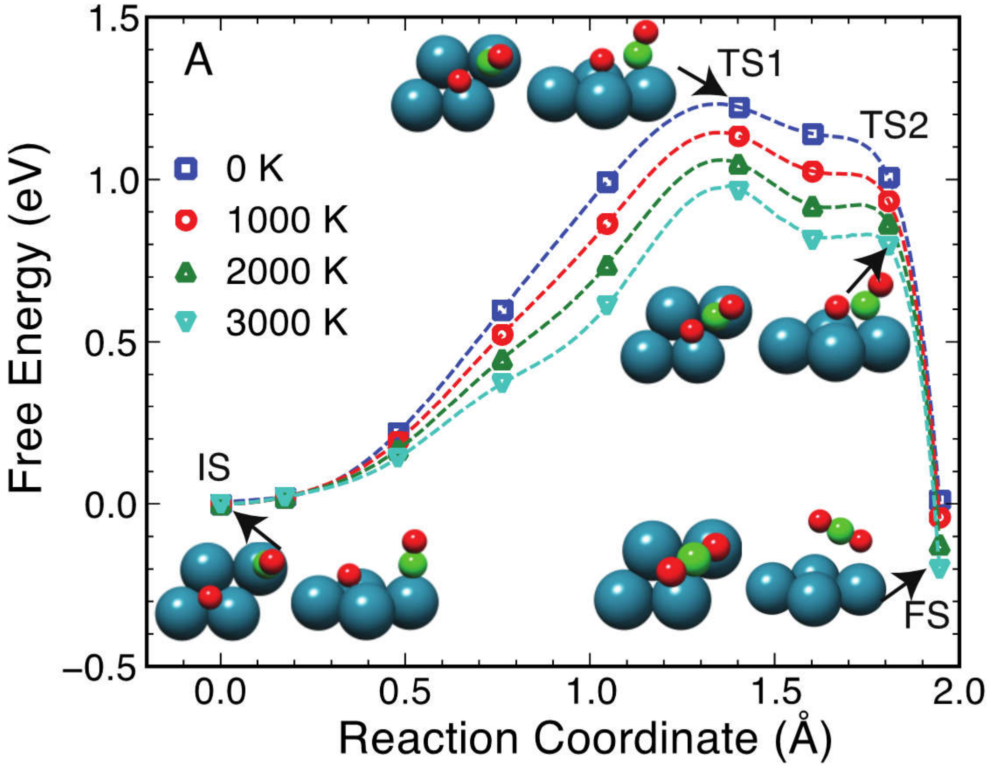


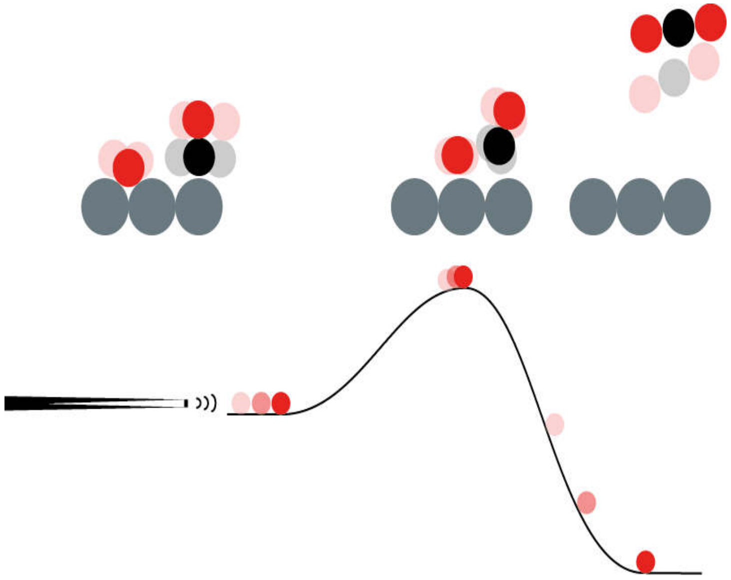
- O activation 300 fs
- CO activation 500 fs
- Formation of *OC--O 800 fs
- Formation of OC---O* 800 fs

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,

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







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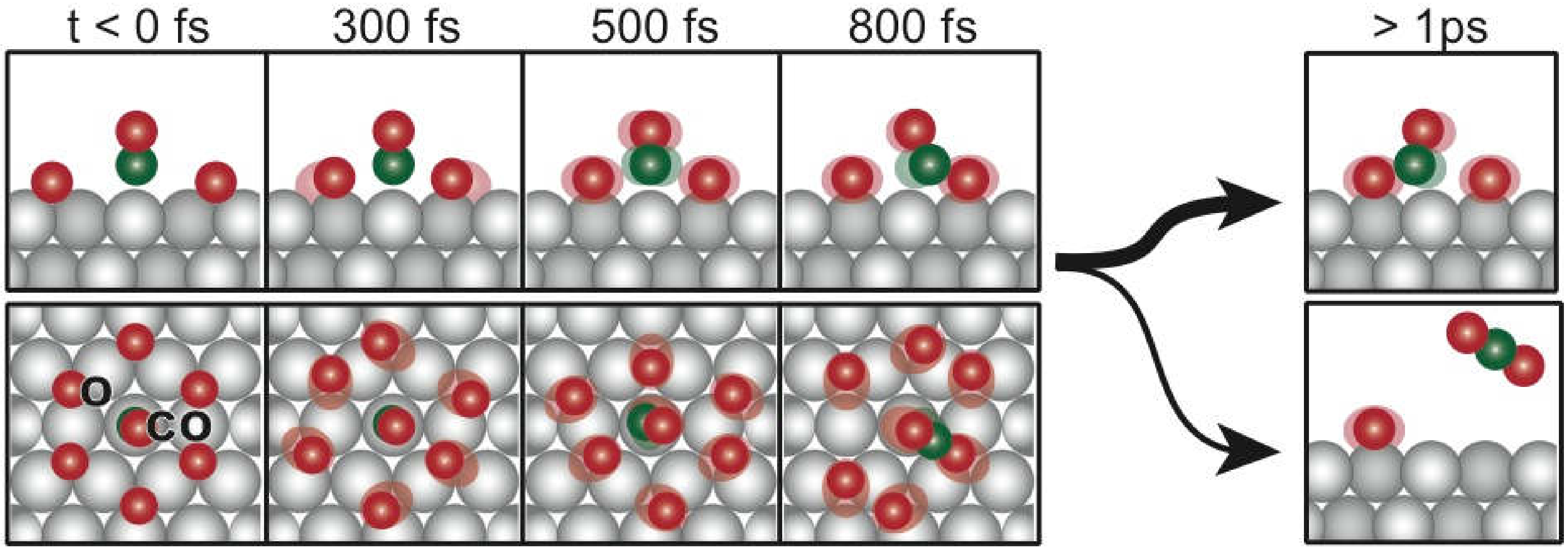
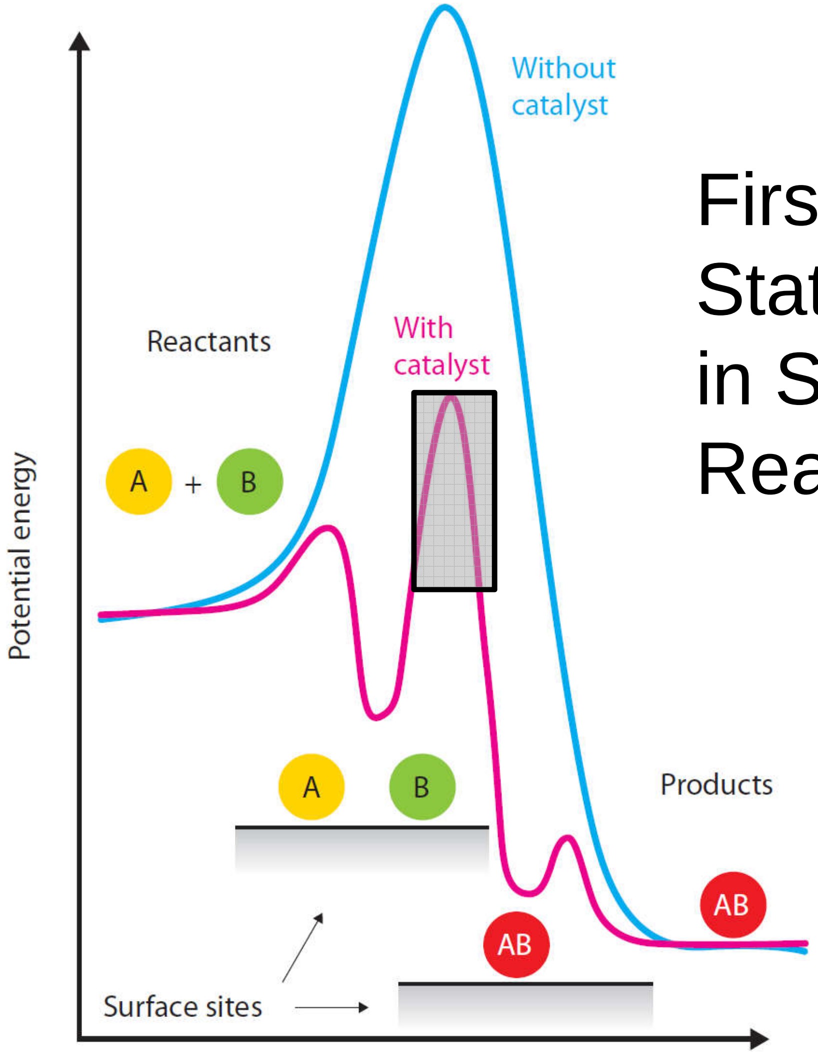
Mechanism



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,

☺Probing Transition States☺



First time Transition State is Observed in Surface Chemical Reaction

Artificial Photosynthesis

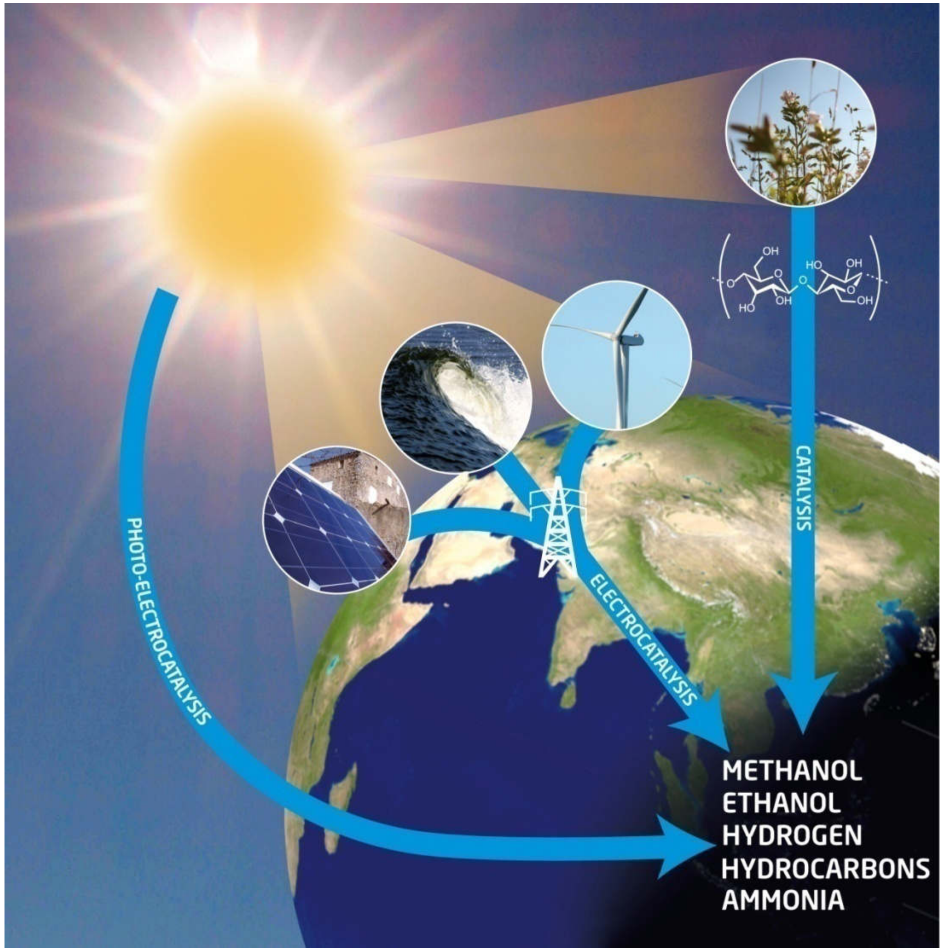
Reducing CO_2 to fuels and chemicals

One of the main challenges for the future

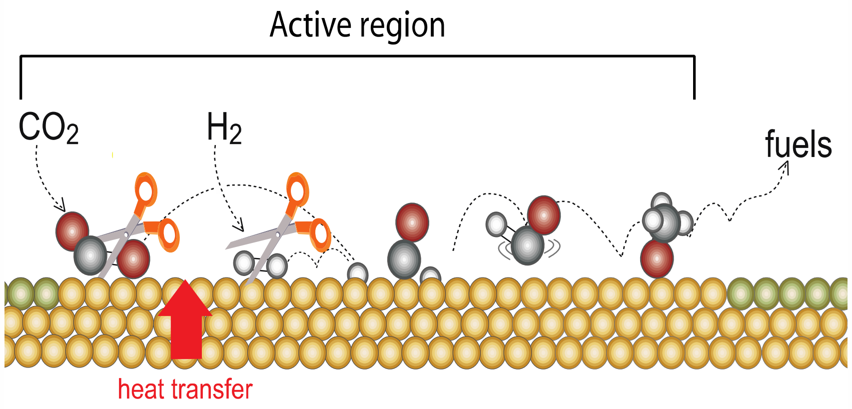
Photochemical

Electrochemical

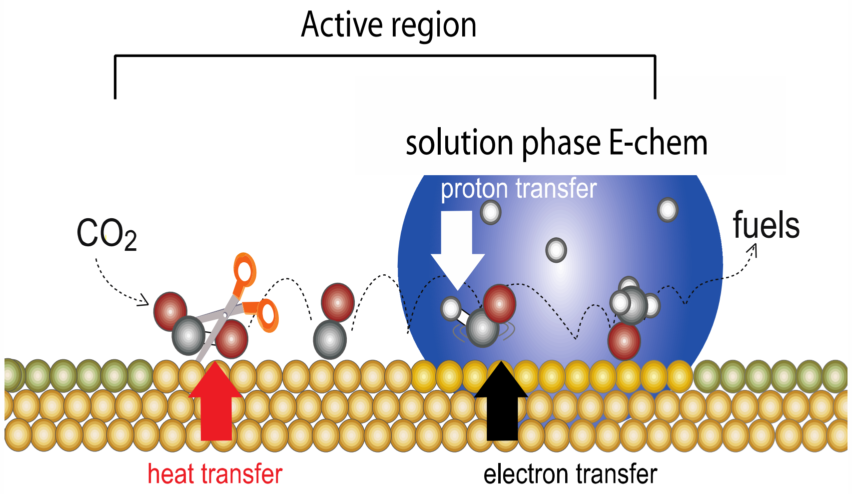
Chemical



Heat or Electron Transfers

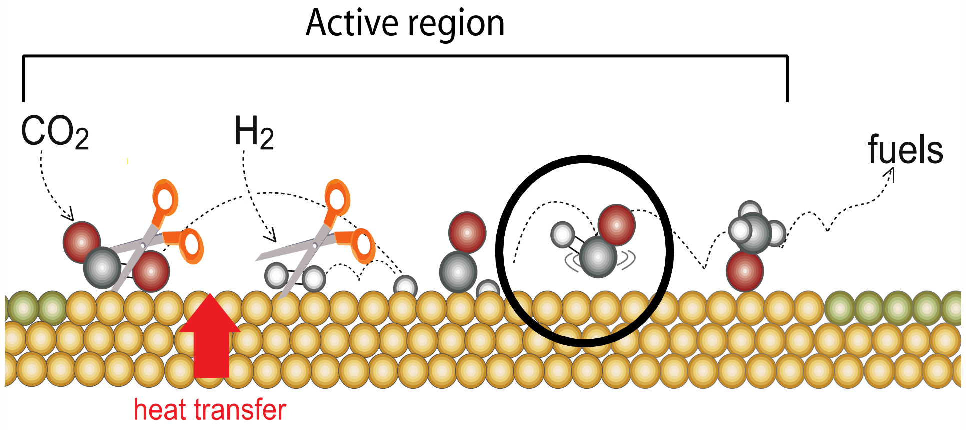


Thermal

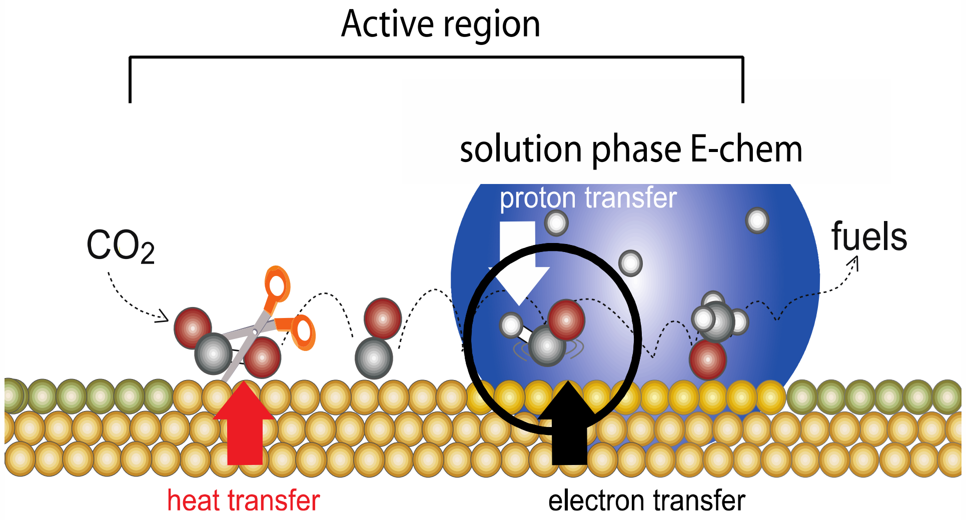


Electrochemical

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

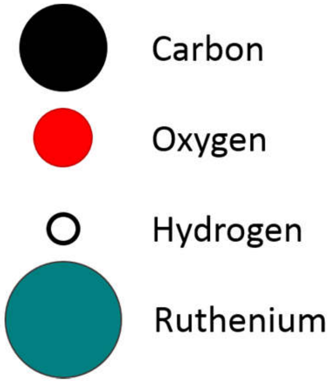


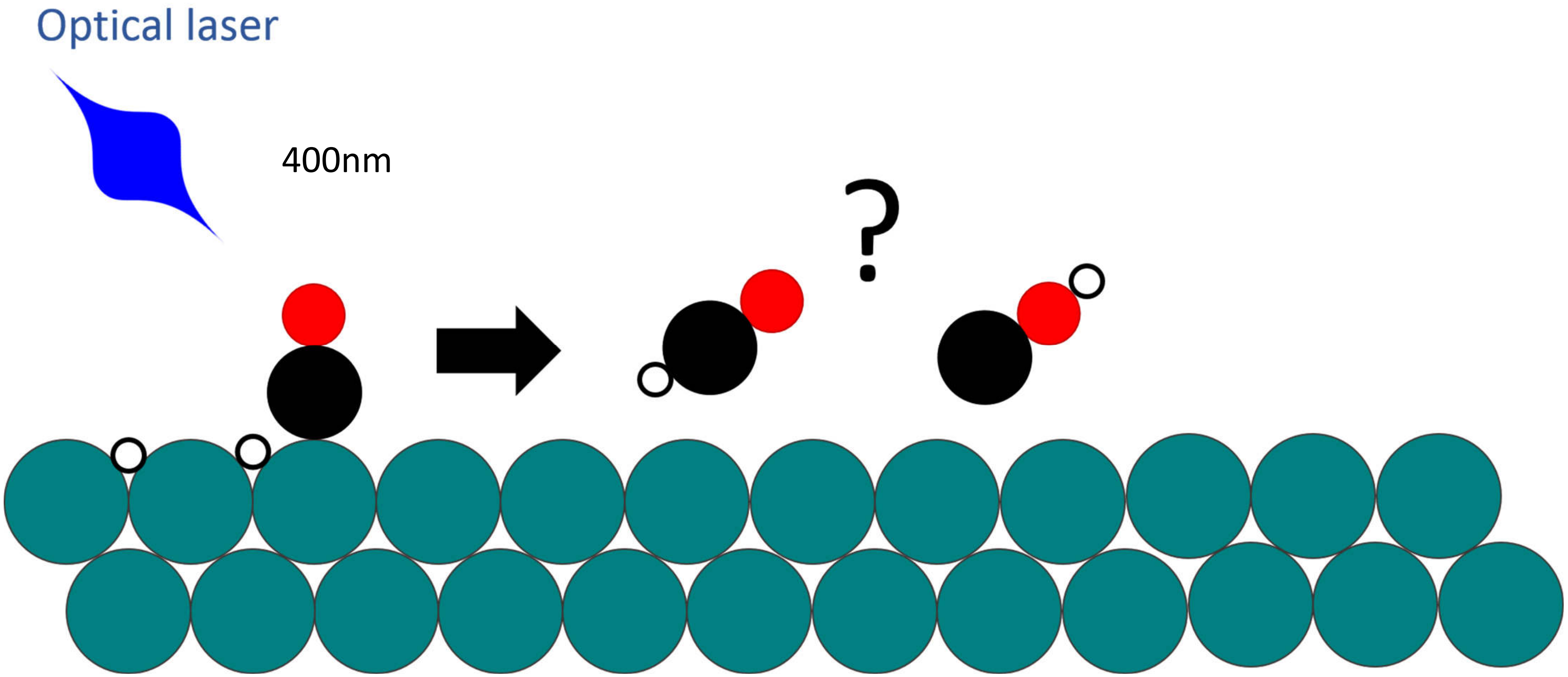
Thermal



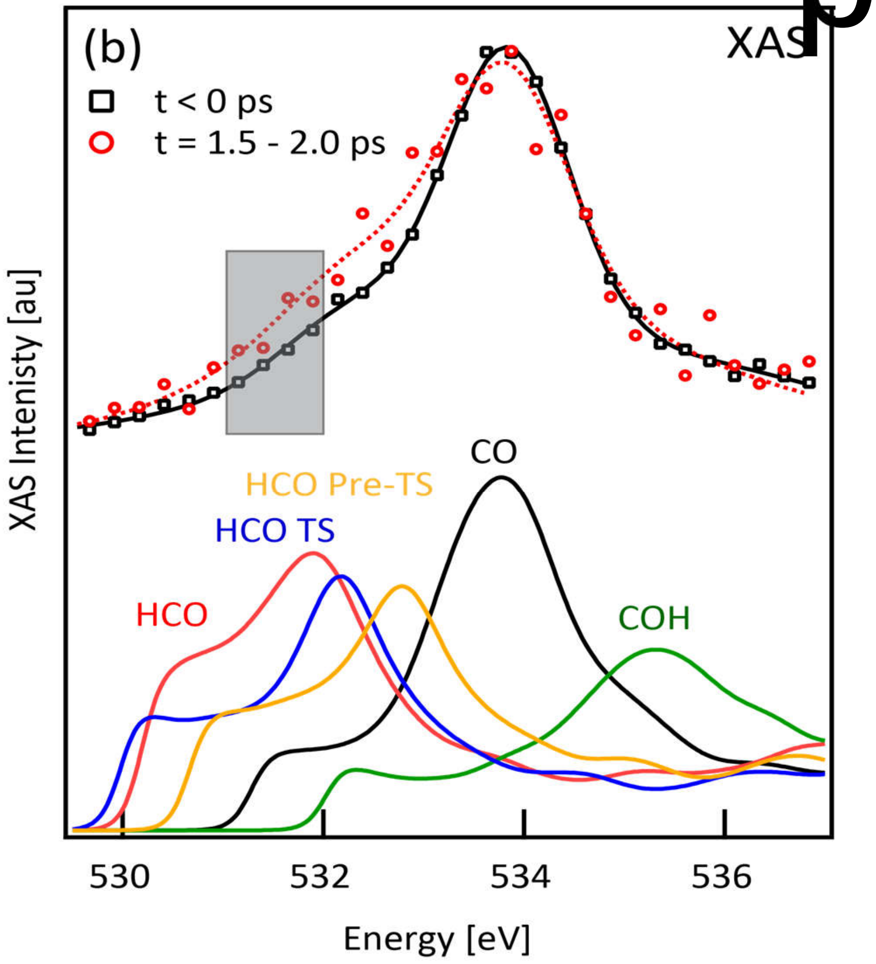
Electrochemical

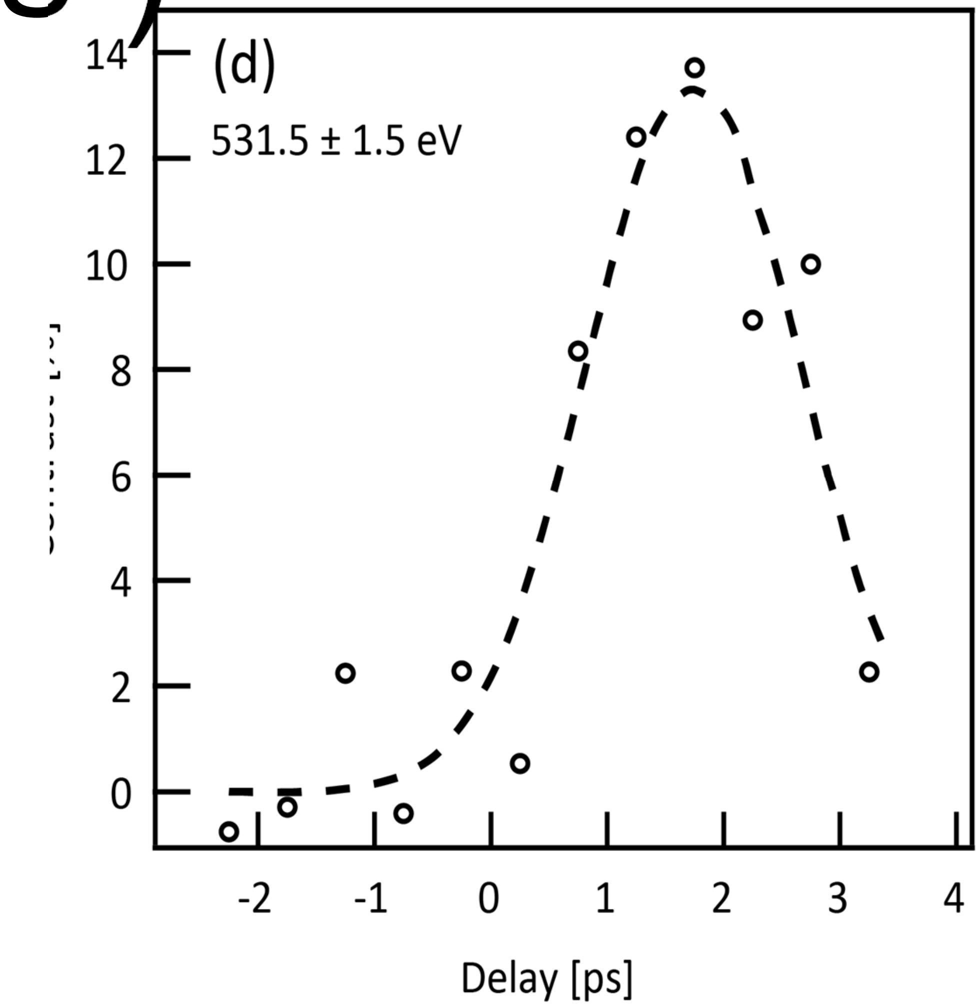
Stable or Metastable Transient Intermediate
HCO or CHO ?
Interactions with CO and H





Fast time scales (t < 4 ps)





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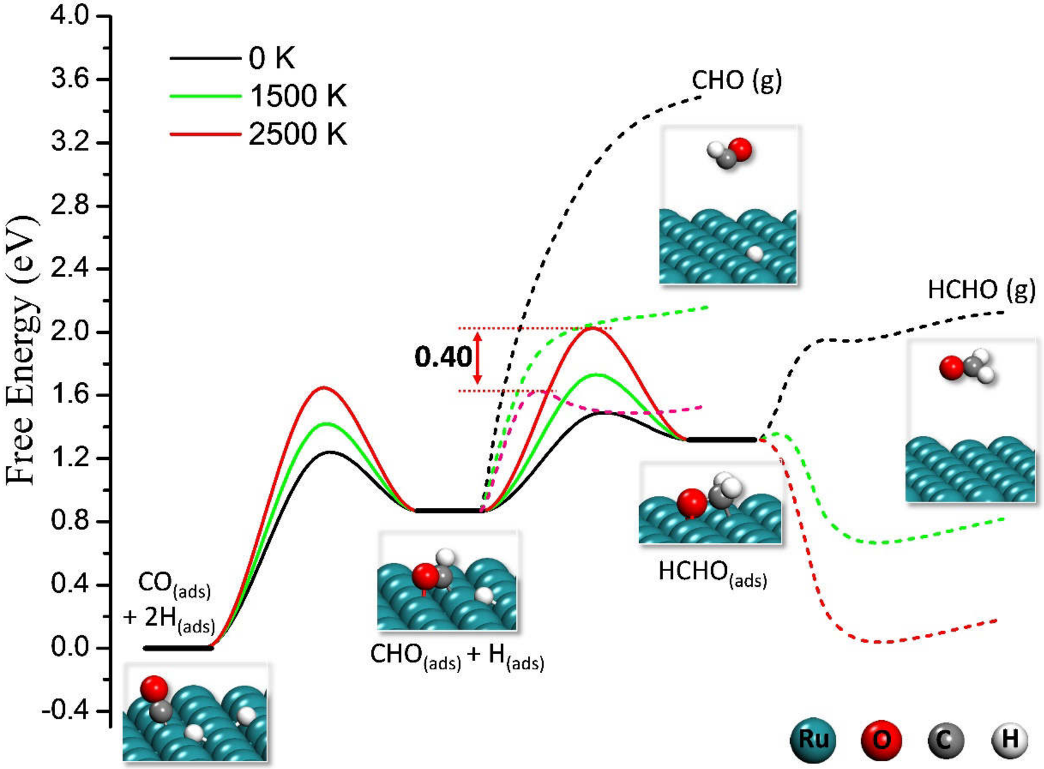
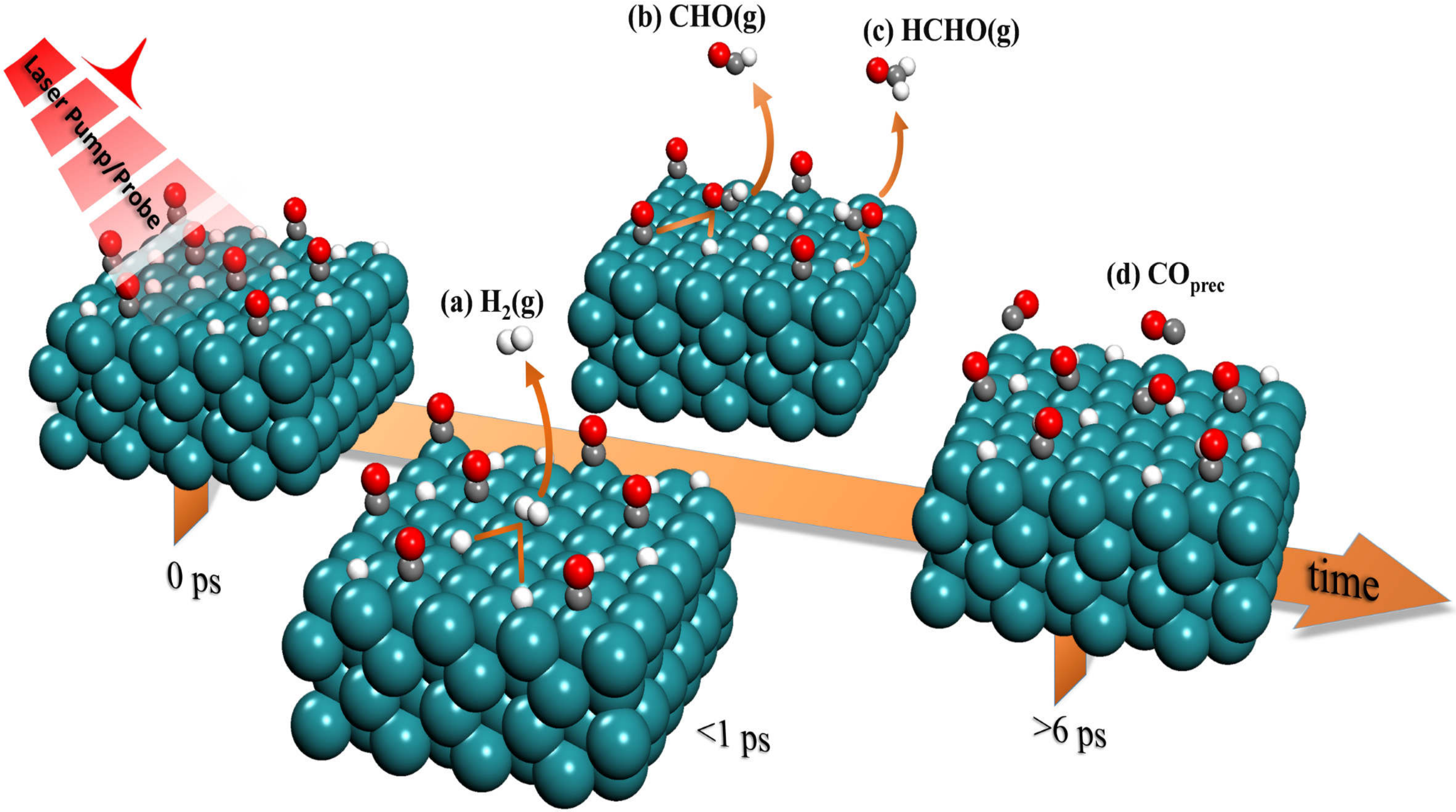
Free Energy Calculations CHO and CH_2O Formation



J. LaRue O. Krejci, L. Yu, M. Beye, M. L. Ng H. Öberg, H. Xin, G. Mercurio, S. Moeller, J. J. Turner, D. Nordlund, R. Coffee, M. P. Minitti, W. Wurth, L. G. M. Pettersson, H. Öström, A. Nilsson, F. Abild-Pedersen, H. Ogasawara, J. Phys. Chem. Lett **8**, 3820 (2017)

Mechanism



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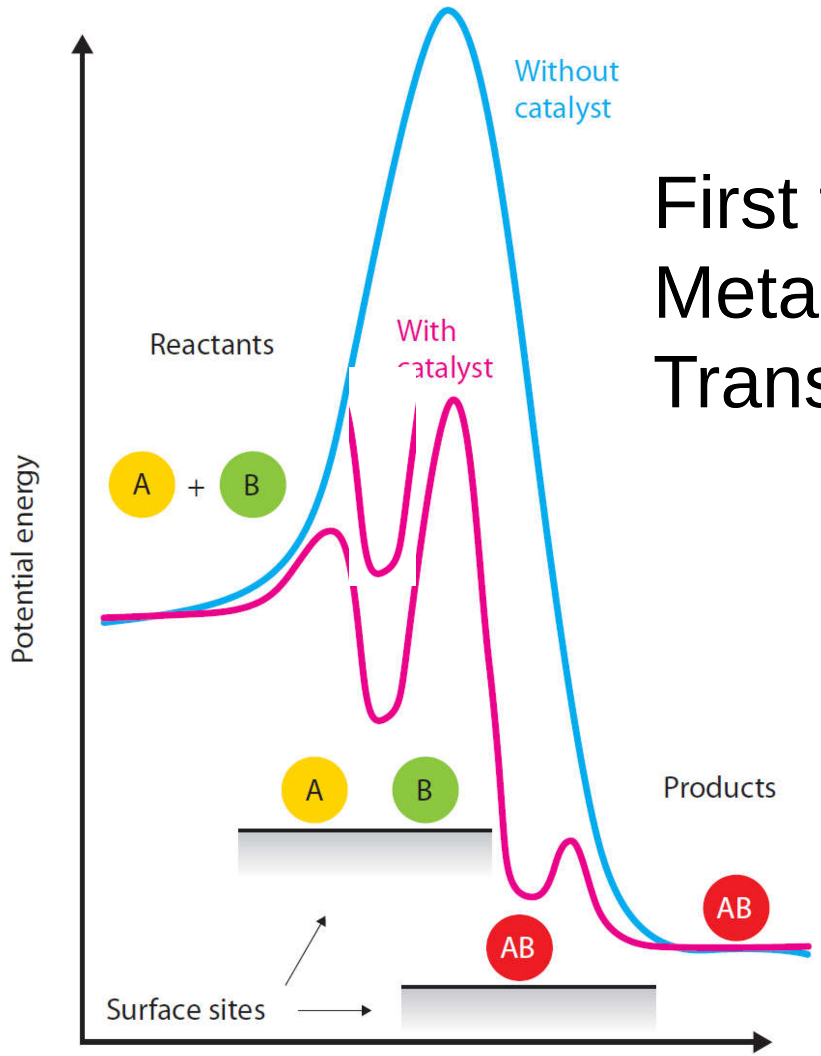
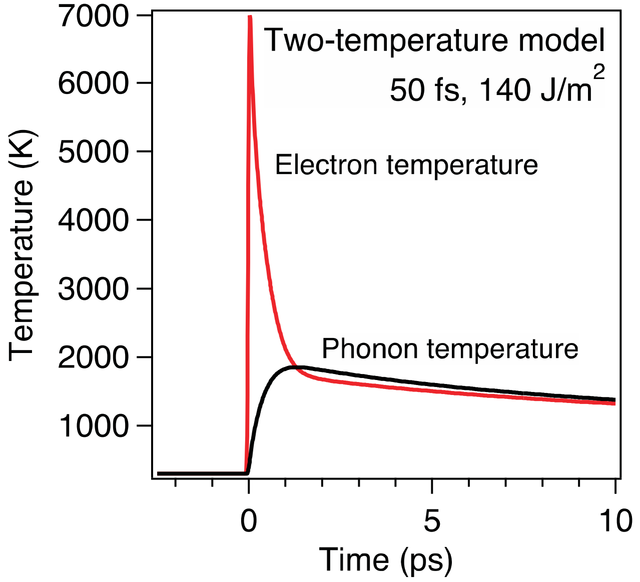
☺Probing Transient Intermediate☺

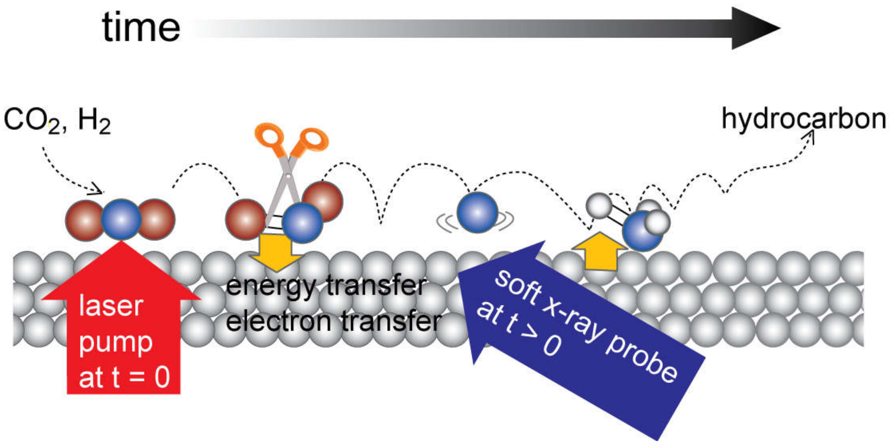


First time CHO is observe
Metastable
Transient Intermediate

400 nm fs-laser induced CO oxidation and hydrogenation on Ru(0001)

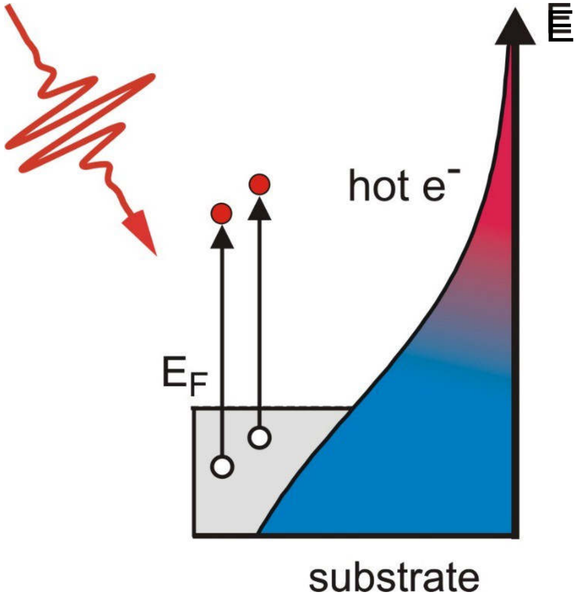


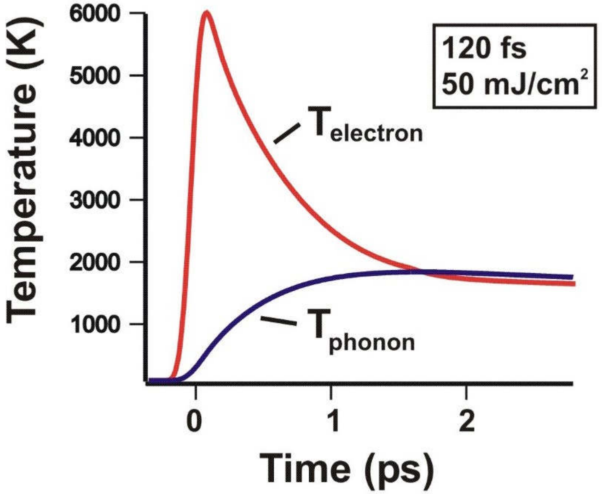
400 nm fs-laser pump
⇩
<1ps electronic excitation
⇩
>1ps phononic excitation



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)

Laser Stimulation





Substrate mediated processes

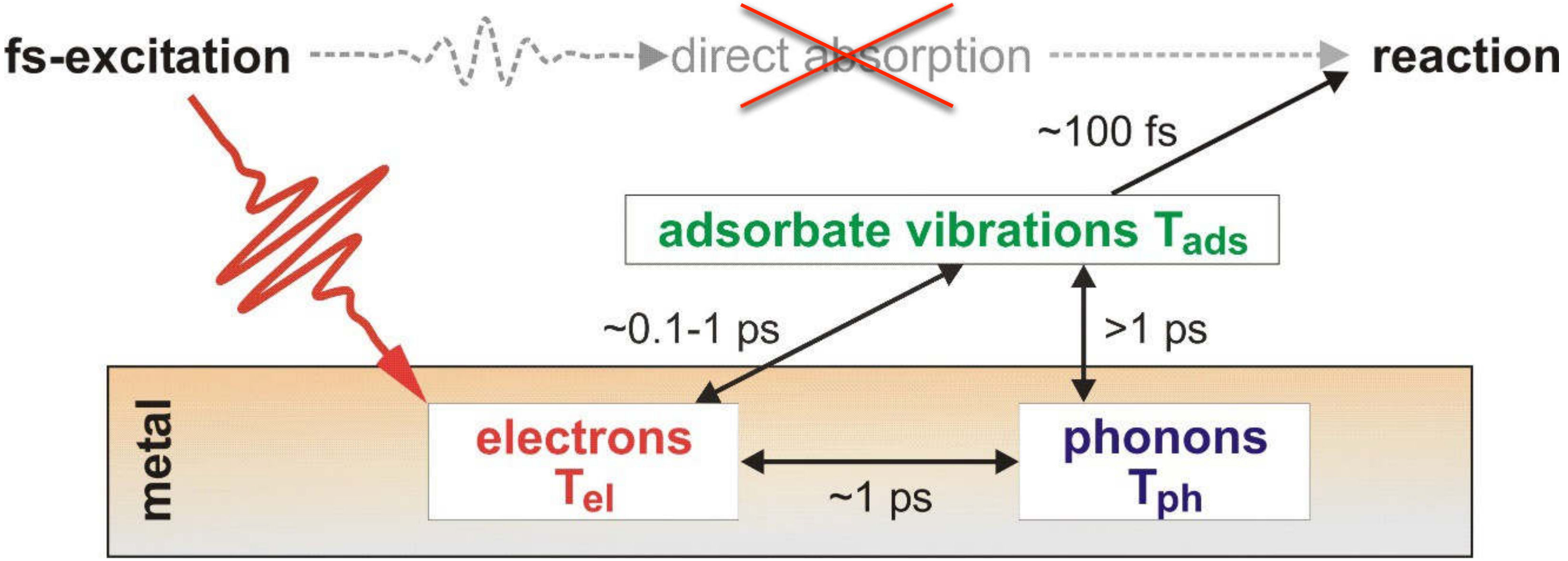
Role of…

? …Non-thermalized electrons

? …Thermalized electrons

? …Phonons

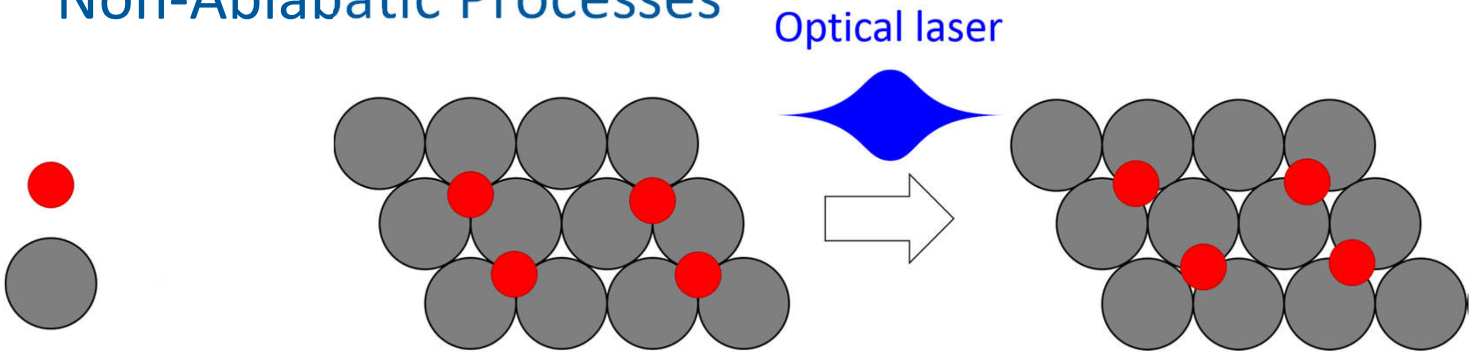
? Direct excitation of the adsorbates/reactants possible

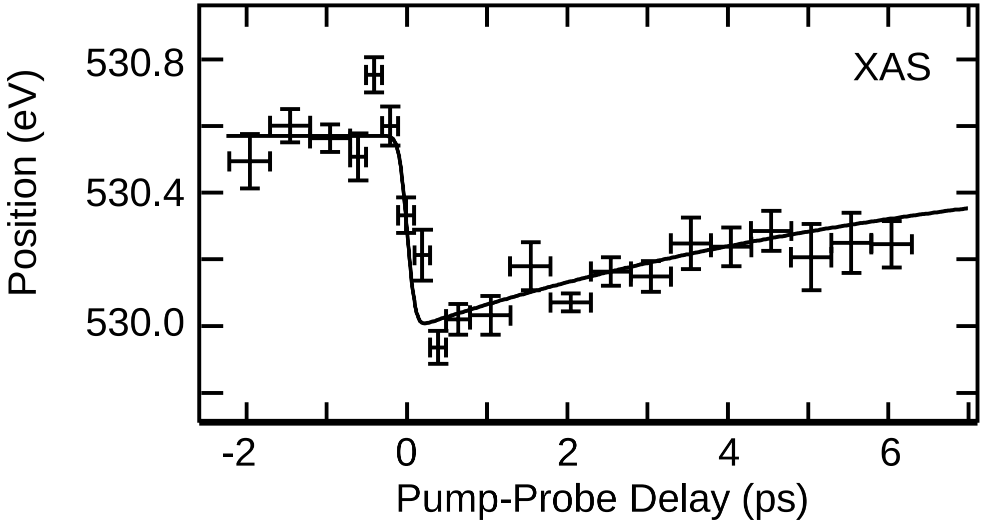


Frischkorn and Wolf, Chem. Rev., **106** (2006).

O/Ru

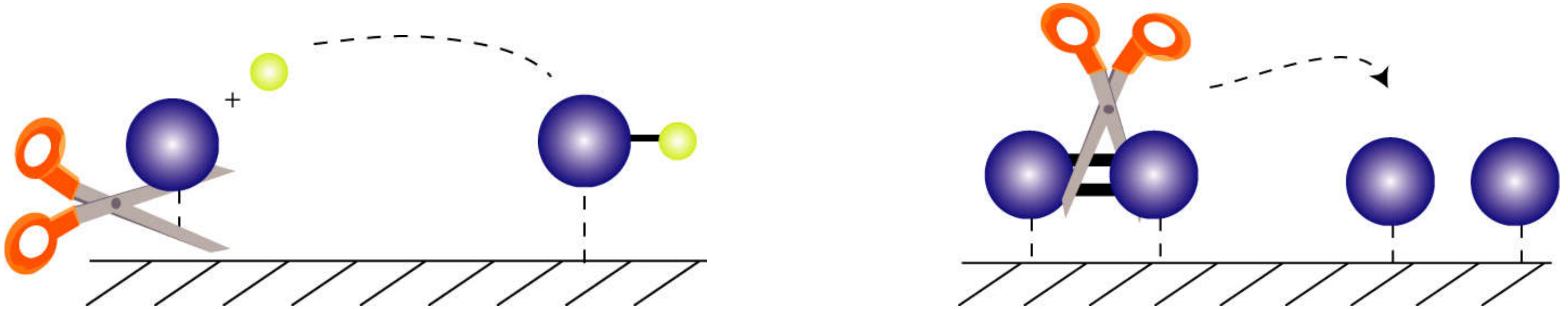
Very Fast Initial Rise – Equilibrated Hot Electrons or Non-Abiabatic Processes





M. Beye, H. Öberg, H. L. Xin, G. L. Dakovski, M. Dell'Angela, A. Föhlisch, J. Gladh, M. Hantschmann, F. Hieke, S. Kaya, D. Kühn, J. LaRue, G. Mercurio, M. P. Minitti, A. Mitra, S. P. Moeller, M. L. Ng, A. Nilsson, D. Nordlund, J. K. Nørskov, H. Öström, H. Ogasawara, M. Persson, W. F. Schlotter, J. A. Sellberg, M. Wolf, F. Abild-Pedersen, L. G. M Pettersson, W. Wurth, J. Phys. Chem. Lett. **7**, 3647 (2016)

General reactivity balance



Counter balance between atomic bond and molecular dissociation

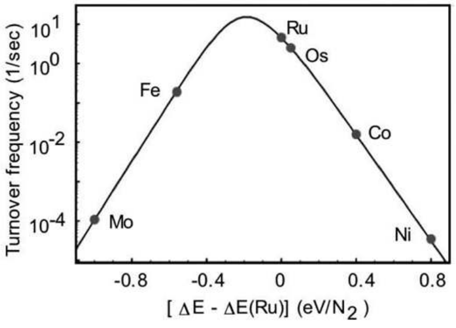
General for many processes of importance for energy production and vital for our industrial society

We need to obtain a fundamental understanding of these elementary reactions !!!

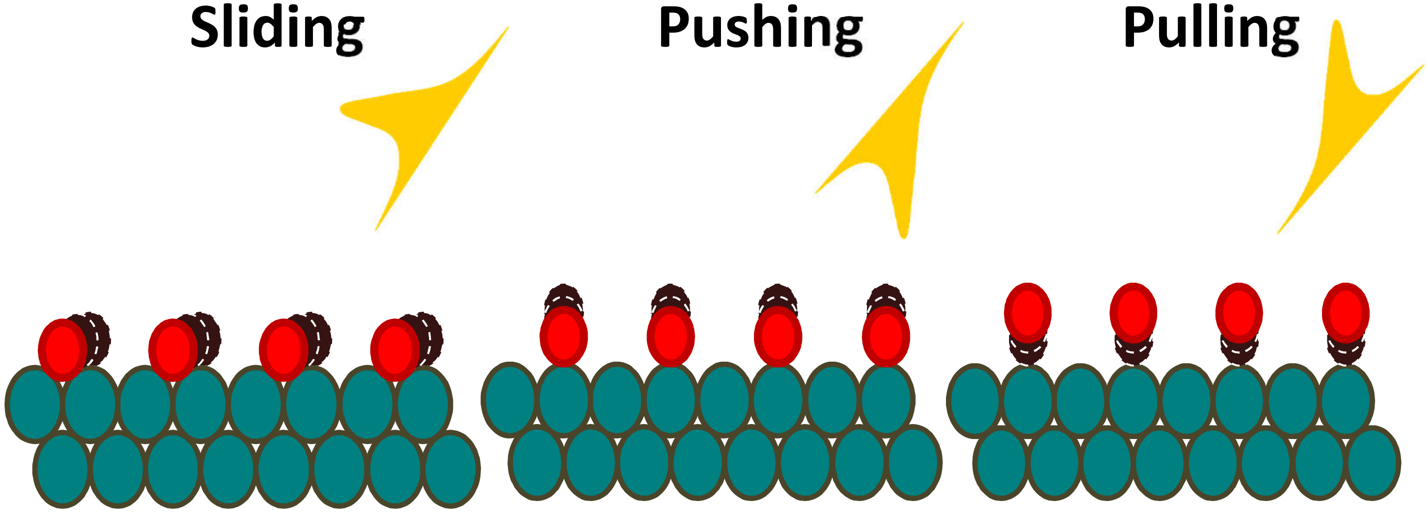
Can we find ways to overcome the fundamental limitation of this balance?

Coherent control to go beyond peak in vulcano?

Logatottir, Rod, Nørskov, Hammer, Dahl, Jacobsen, J. Catal. 197, 229 (2001)



Can we control reactivity by other means
First Experiment



THz radiation

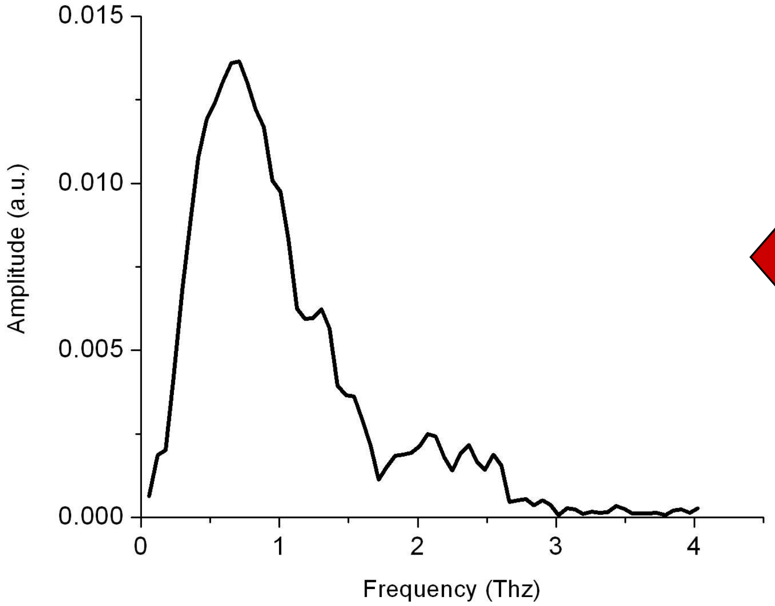
Sliding

Pushing

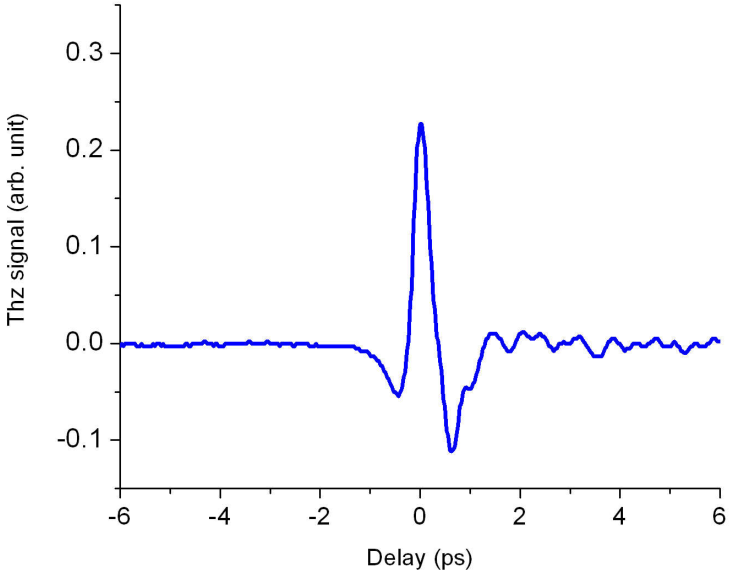
Pulling

Coherent THz generation by ultrafast laser pulses

broad band: freq. domain



Quasi-half cycle pulse: time domain

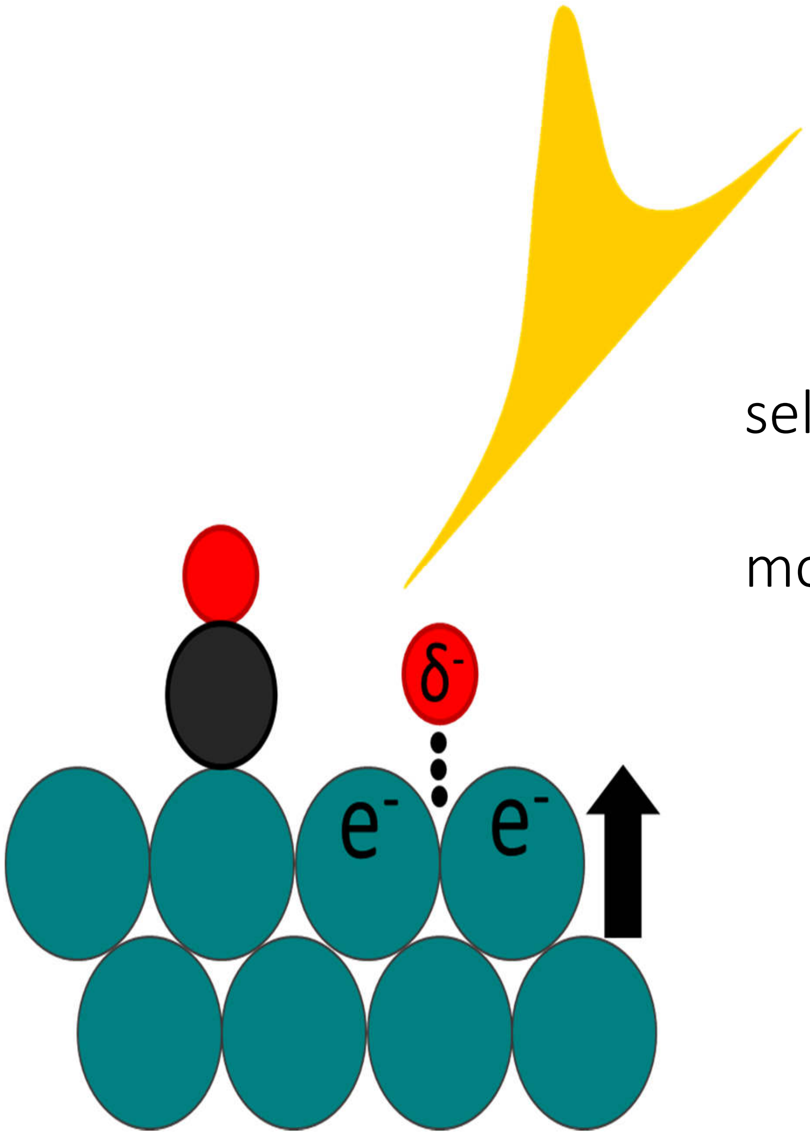


Femtosecond laser pulses are employed to generate THz pulses which have an extremely large bandwidth

Short THz pulses extend over only a few oscillation cycles are generated

H. Wein and A. Lindenberg, Phys. Rev. Lett. 103. 023902 (2009)

THz can induce CO oxidation



selectively exciting the O atom

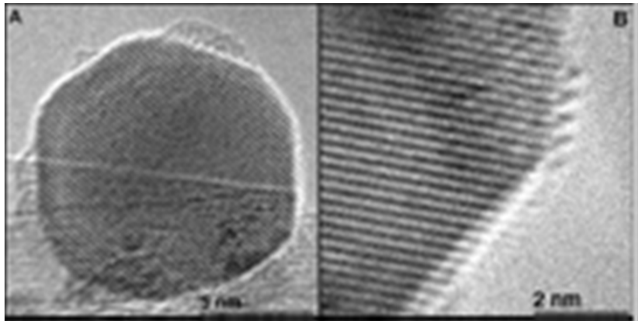
most likely through e⁻ polarization

J. LaRue et al. Phys. Rev. Lett. **115**, 036103 (2015)

Accessing Active Sites on Nanoparticles

Haber-Bosch

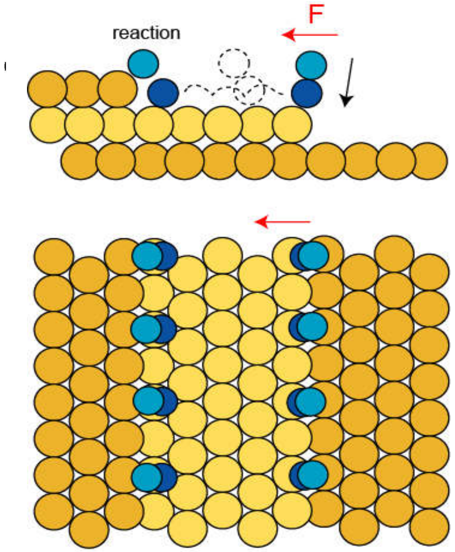
$$N_2 \;+\; 3H_2 \rightarrow 2NH_3$$



Hansen et.al. Science 294, 1508 (2001)

New Ru Catalyst

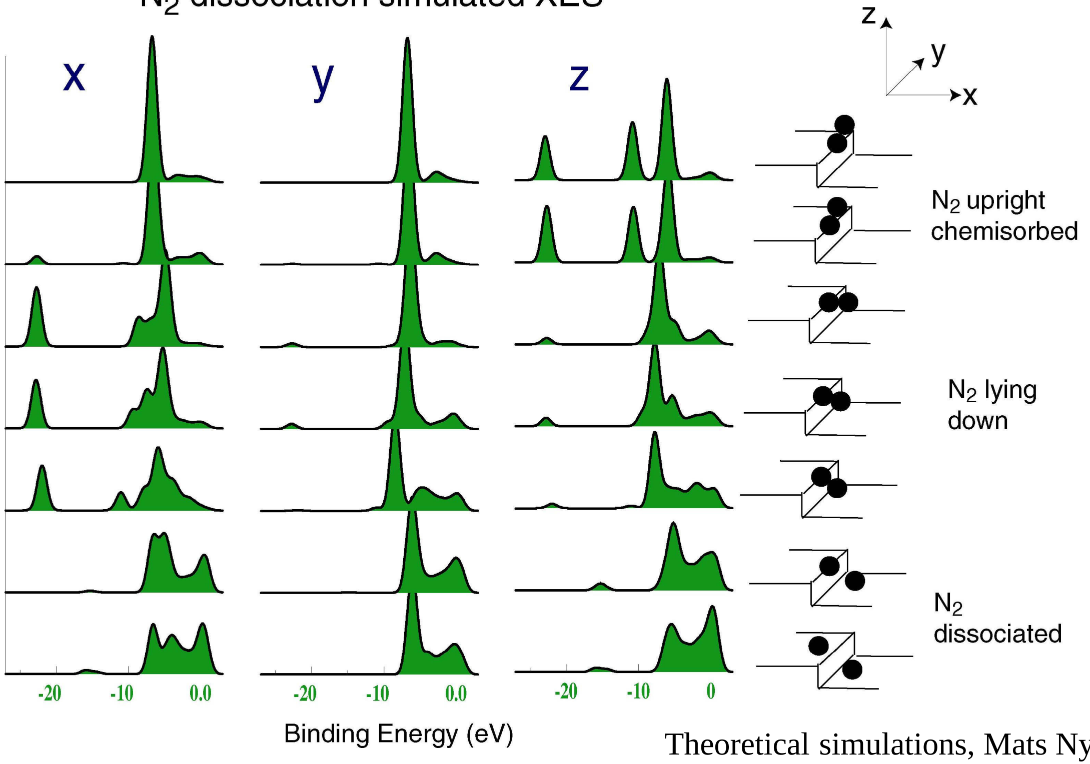
Active site at steps



diffusion barrier <50 meV

desorption barrier >500 meV

N_2 dissociation simulated XES



Both N atoms

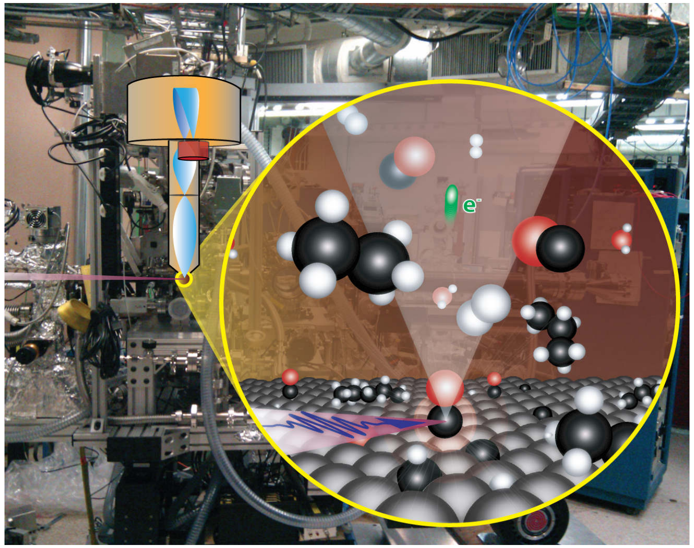
Theoretical simulations, Mats Nyberg, Stockholm University

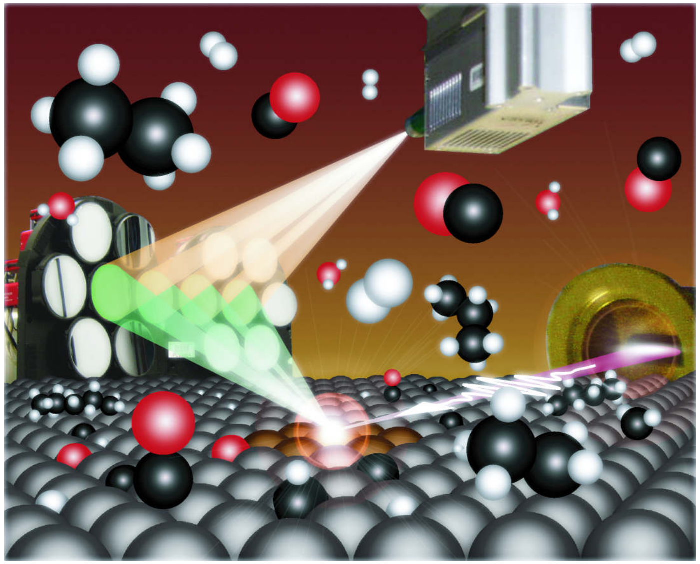
In-situ or In-operando

Record with ambient pressure XPS with 100 mbar

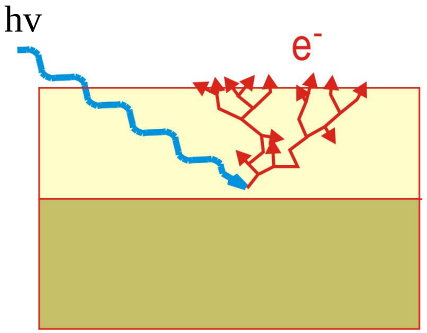
Hard x-ray ambient pressure XPS for 10 bar applications

In-situ Soft X-ray spectroscopy up to 1bar





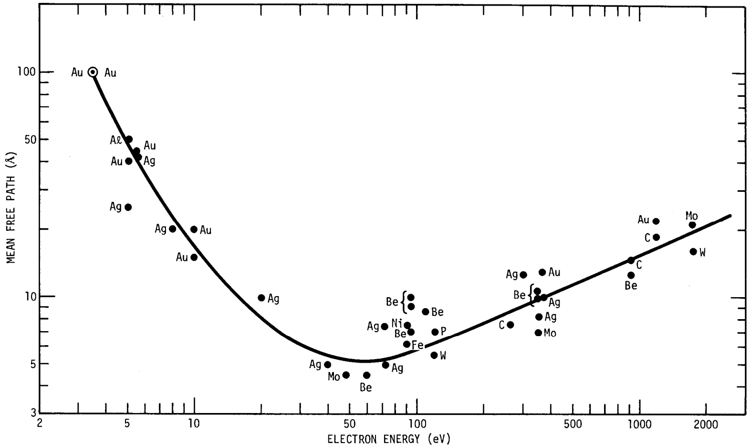
Core Level Electron Spectroscopy



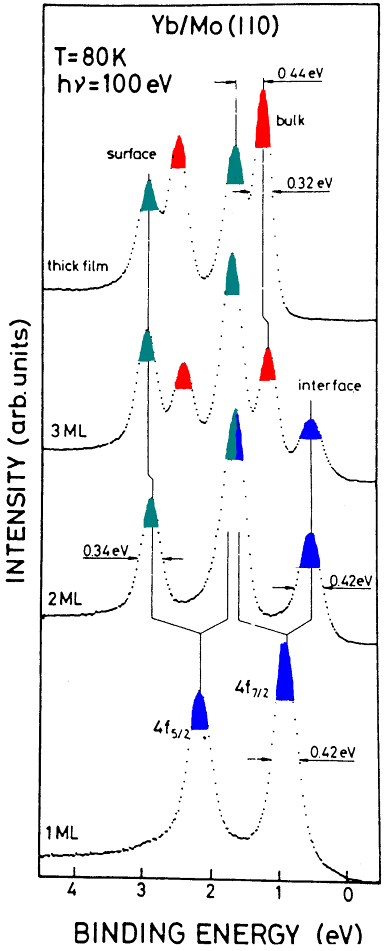
Electrons interact strongly

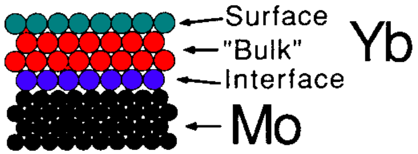
Surface Sensitivity

5-20 Å



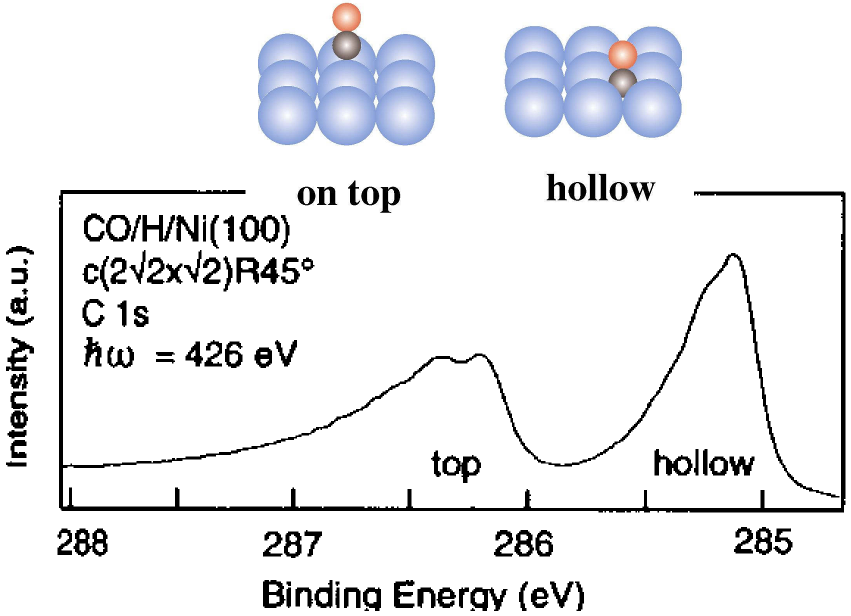
Dependent on electron kinetic energy

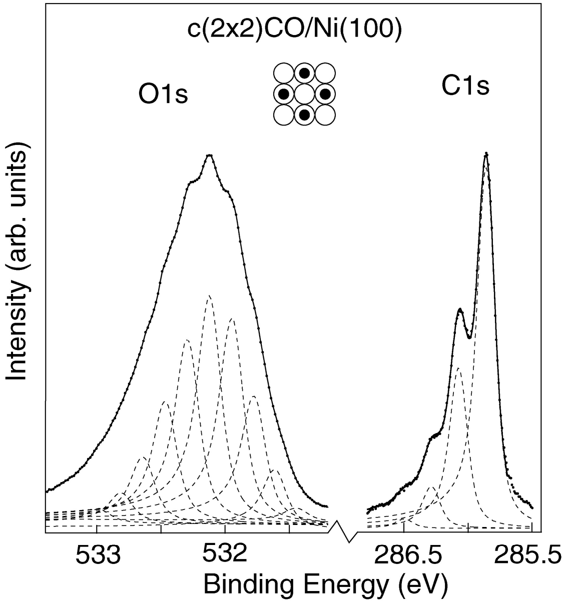




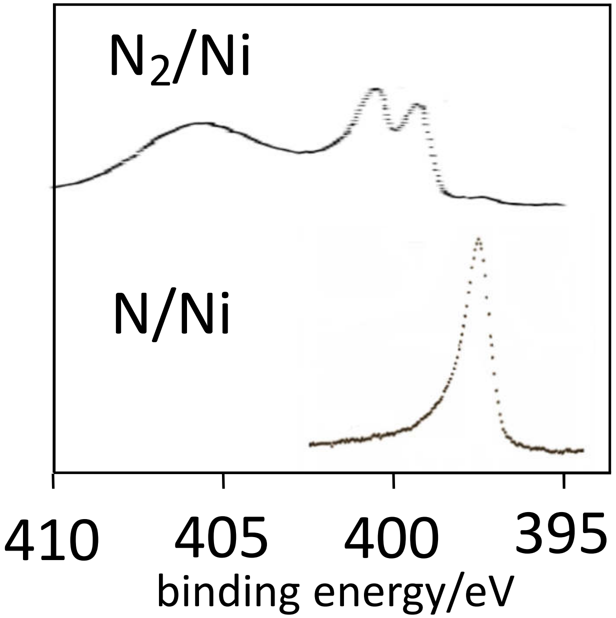
Mårtensson et. al. Phys. Rev. Lett. 60, 1731 (1988)

Core Level Shifts and Geometry

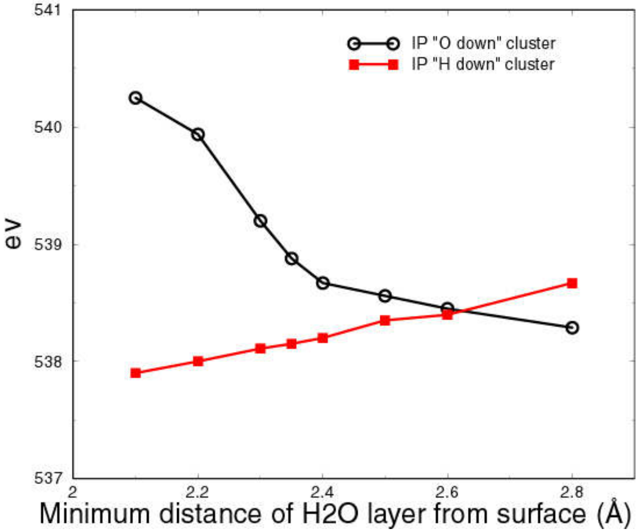




J. El spec. **126**, 3 (2002)



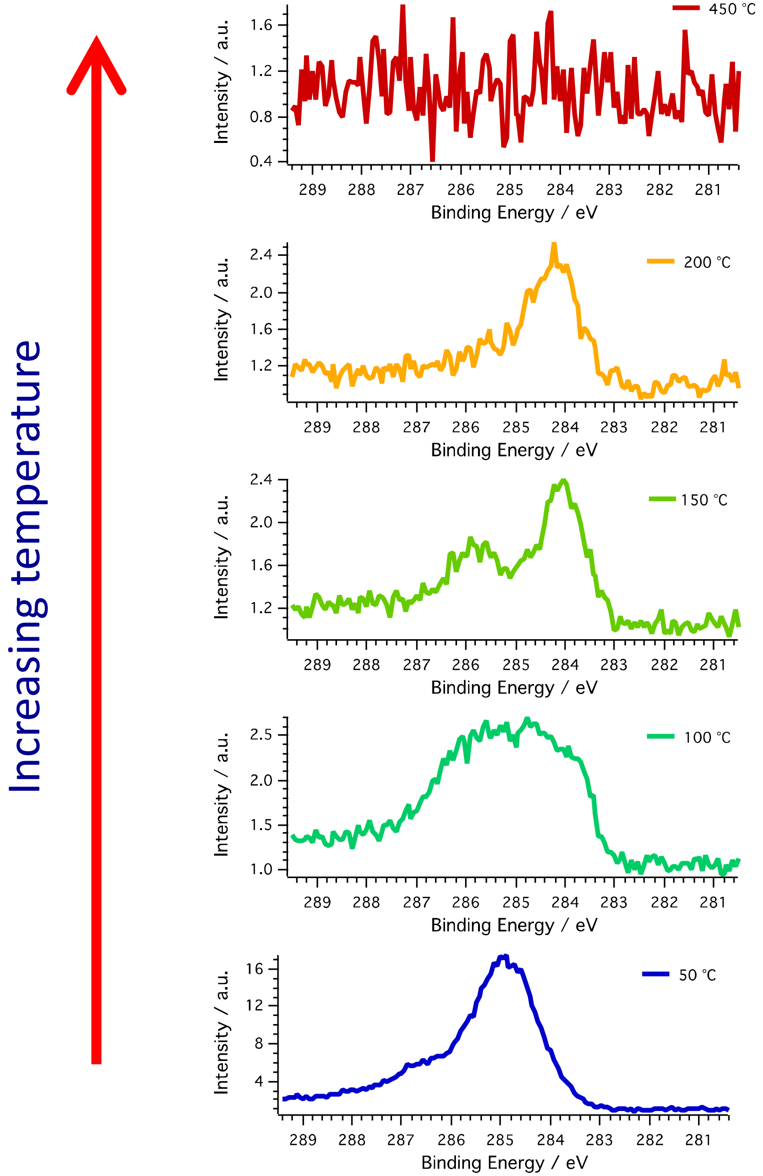
2.0 eV

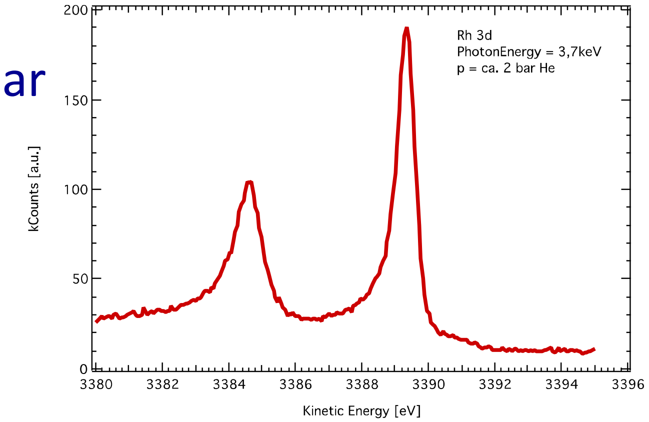


Phys.Rev.Lett. **89**, 276102 (2002)

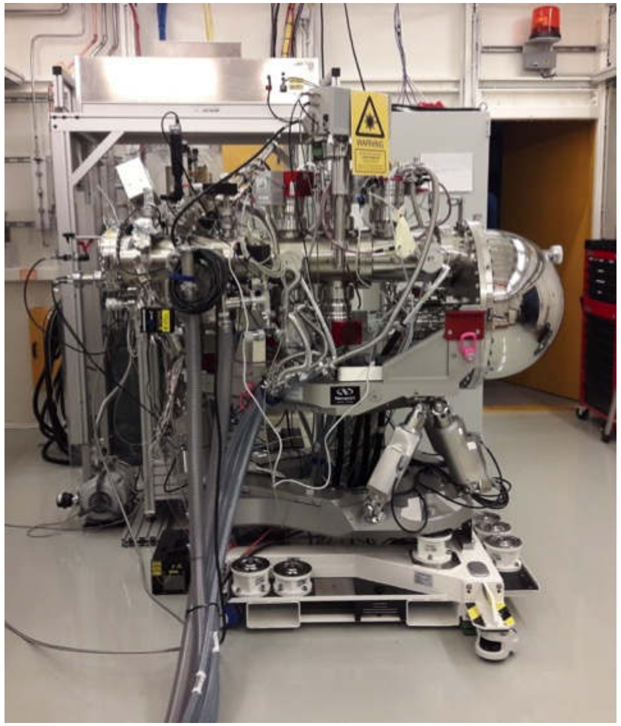
High Pressure XPS

First catalysis using CO_2 + H2 on Rh(111) at p = 160 mbar





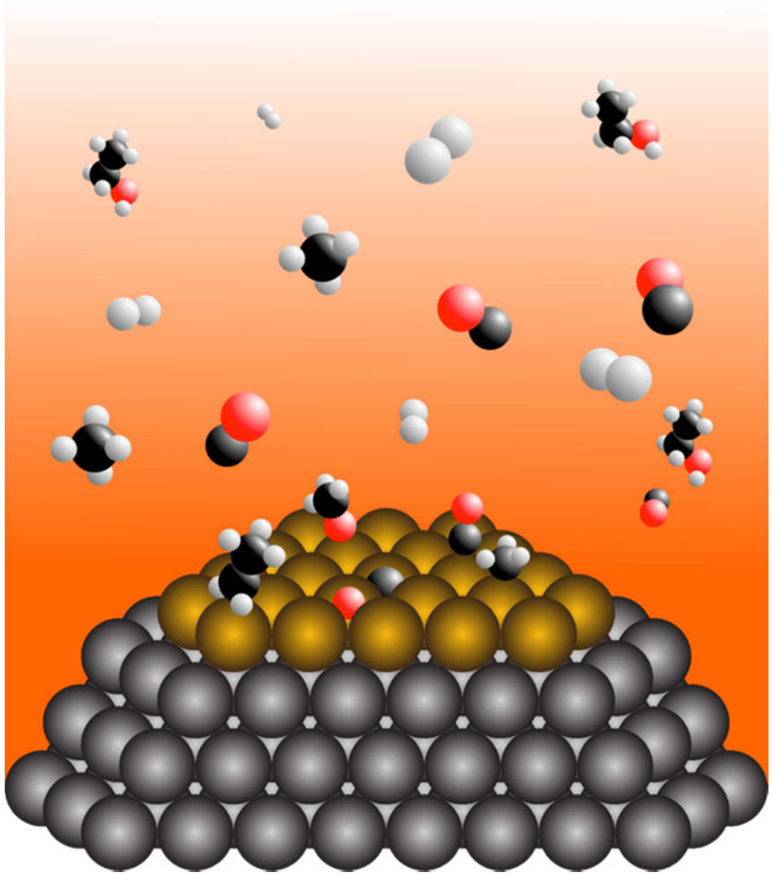
XPS @ 2,5 bar / 450 °C

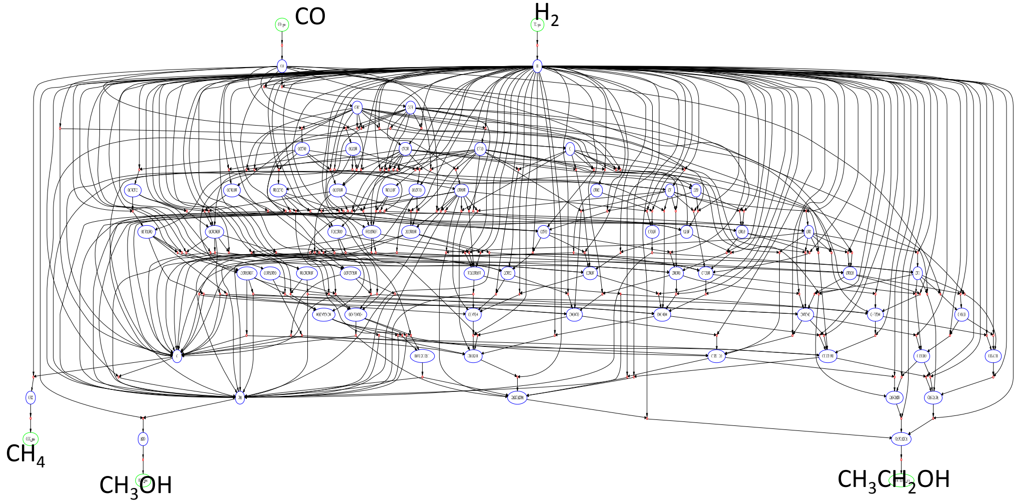


P. Amann et al. unpublished

Catalysis: Dealing with complexity

Need a Tool that is:
- **Chemical Sensitive**
- **Surface Sensitive**
- **Can work under realistic conditions**





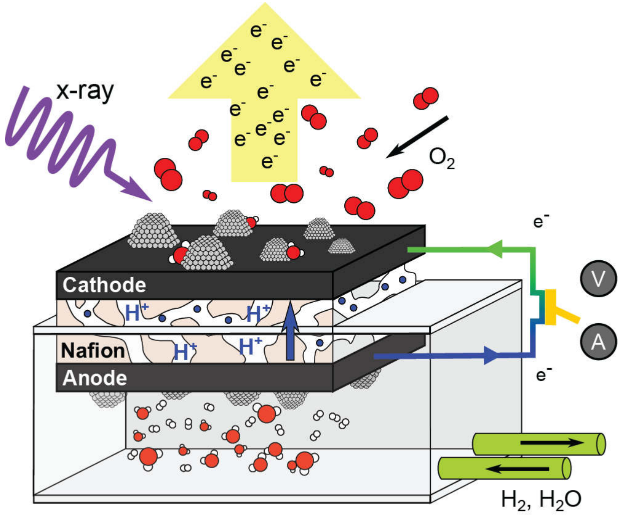
Medford, Ulissi, Hummelshøj,
Bligaard, Nørskov (2016)

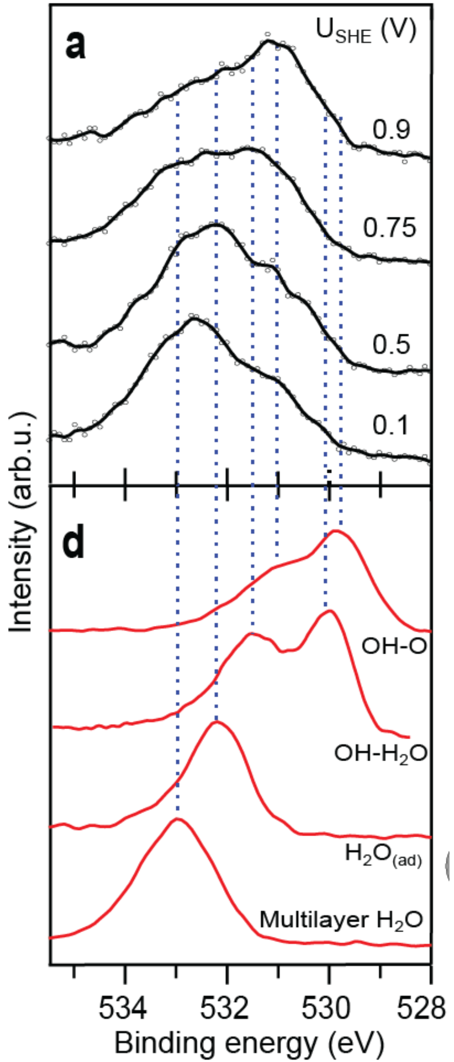
100+ species
200+ reactions
2000+ unique pathways

Electro Catalysis

XPS of operating PEMFC

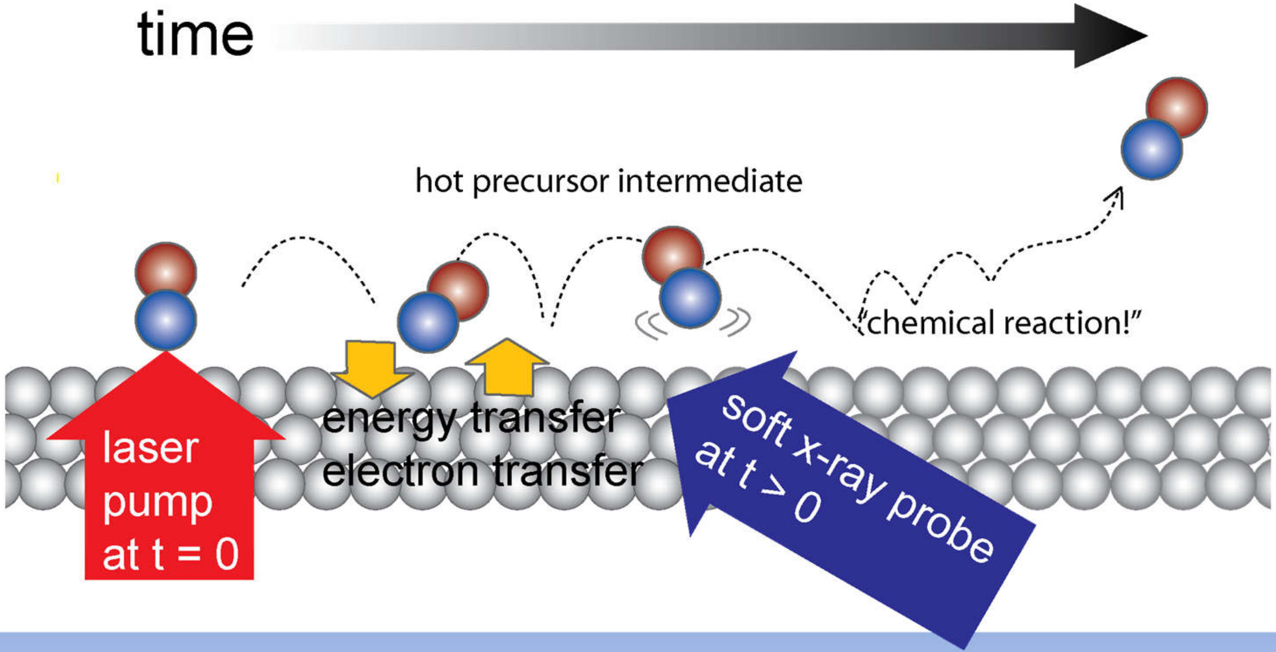
- direct observation of key O/OH intermediates
- Surface sensitivity
- complexity of nanoparticle surfaces
- Water splitting
- Artificial photosynthesis
- Batteries





H. S. Casalongue, S. Kaya, V. Viswanathan, D. J. Miller, D. Friebel, H. A. Hansen, J. K. Nørskov, A. Nilsson and H. Ogasawara, Nature Communication DOI 10.1038/ncomms3817

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"

Facility

- Soft x-ray undulator with monochromator $\Delta E \approx 0.2$ eV covering C, N, O K and 3d TM L-edges
- Variable polarization
- Dedicated station for XAS, RIXS with both UHV and operando
- Essential to develop efficient detection schemes
- Hard X-ray Line for High Pressure XPS
- Diffraction but this could be done at FXE
- Short pulses ≈ 1 fs to investigate electron dynamics
- THz pump
- Staff with knowledge in FEL science geared towards catalysis to support unexperienced FEL users