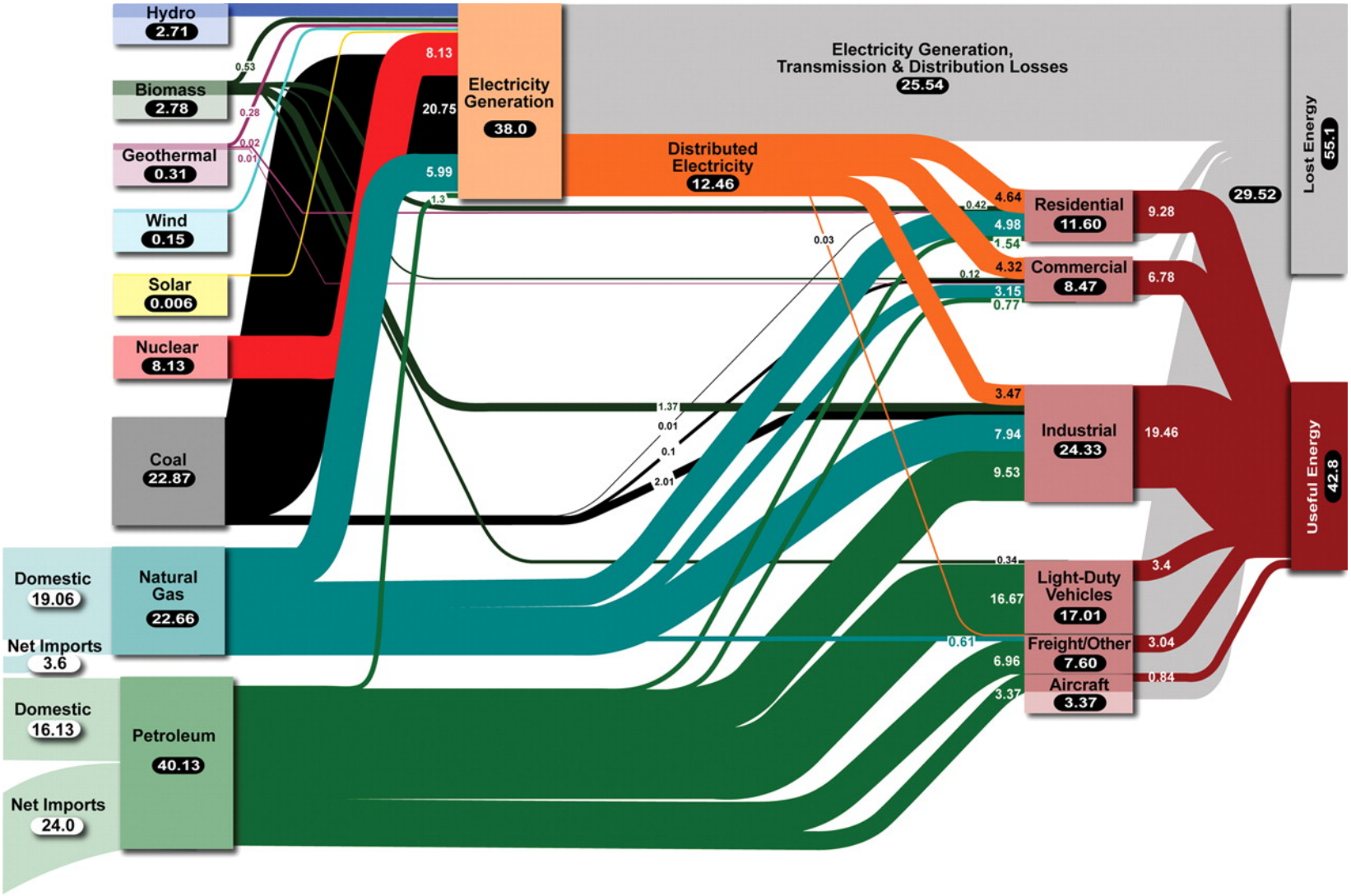
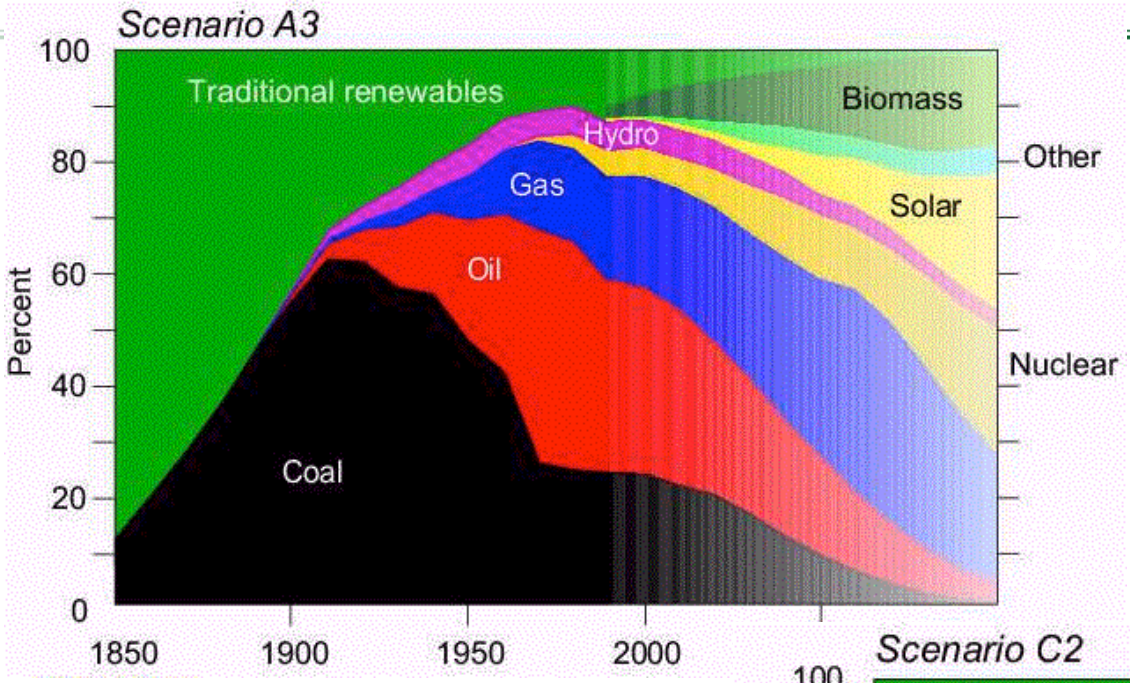
Introduction: energy sources and uses

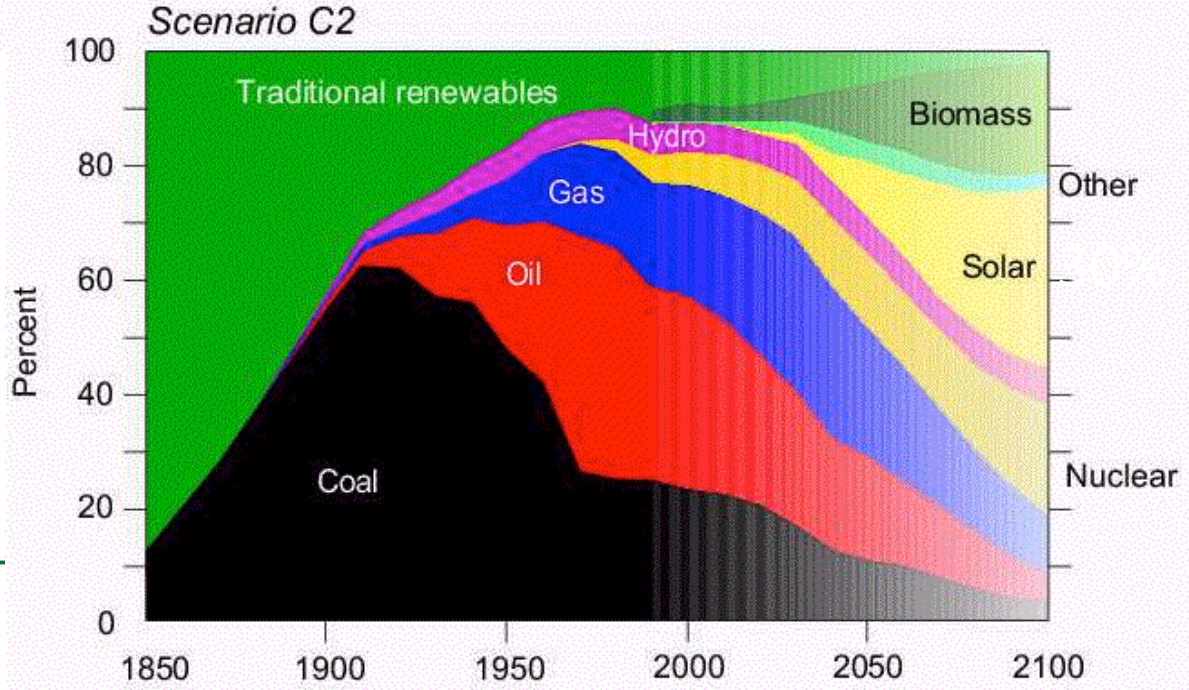


The challenge of sustainable energy sources



New Materials: key to better devices (more stable, more efficient)

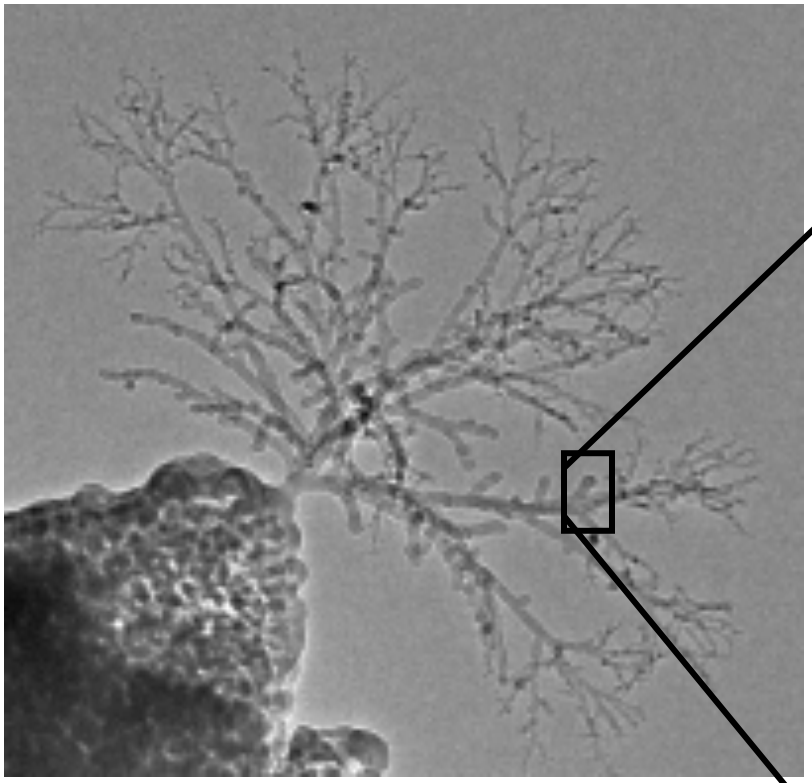
E.D. Cubuk, B. Malone, G. Tritsaris, B. Onat

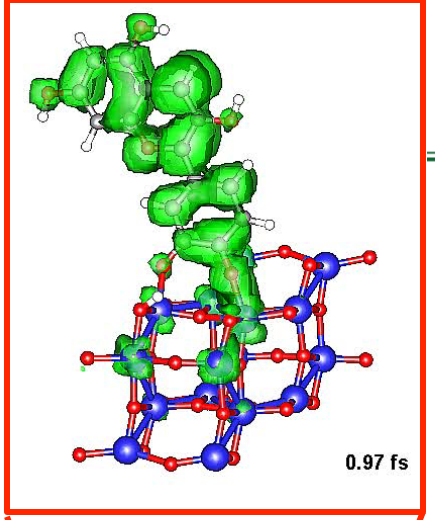


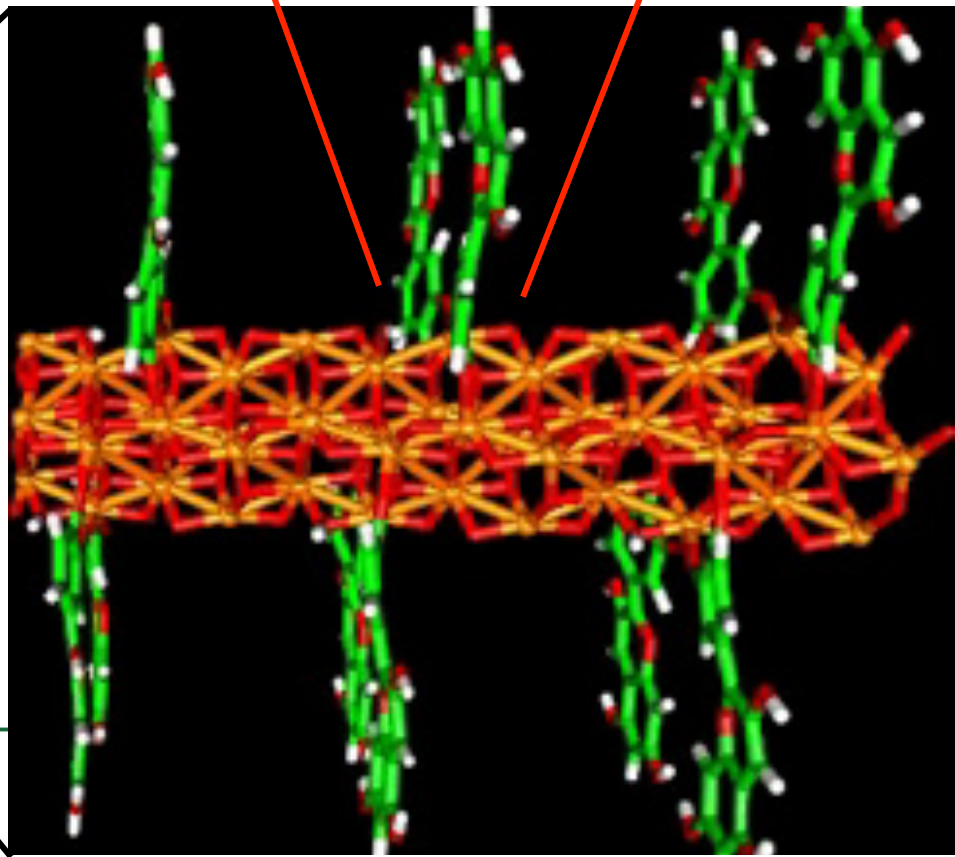
Source: Report of Inter-Governmental Panel on Climate Change

S. Meng *et al*.

Artificial Nano Tree (based on QM simulations)



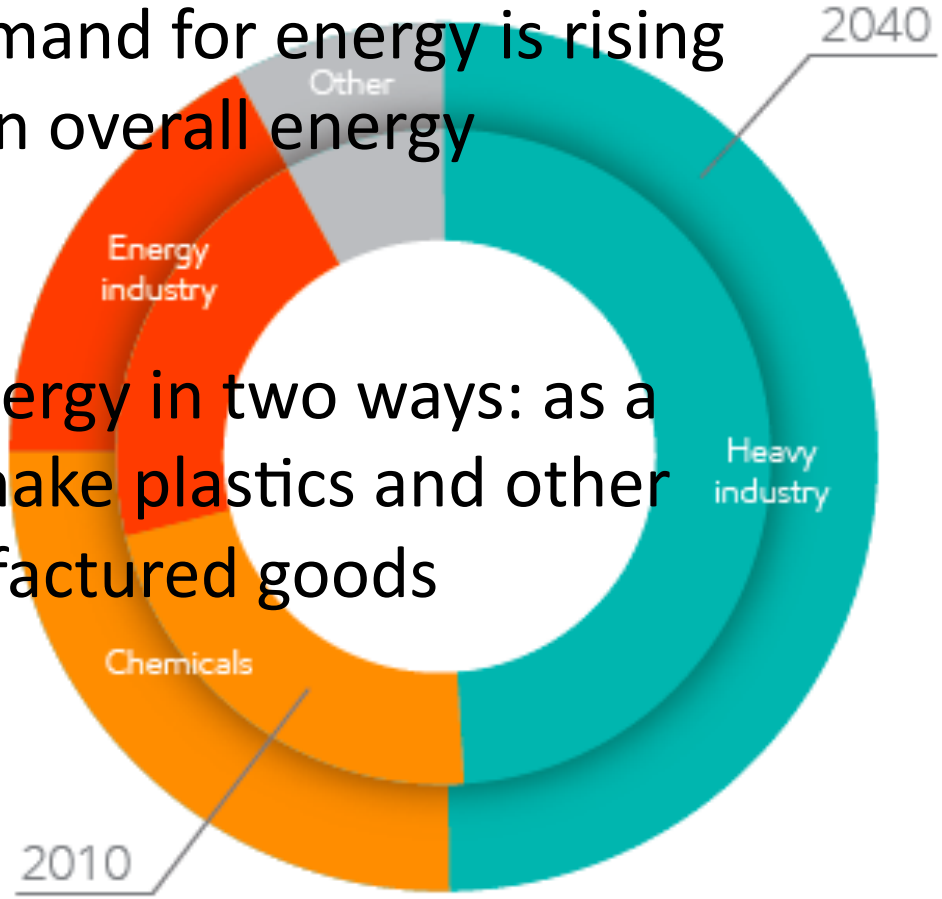




Motivation: Growing role of Chemical production in Industrial Energy demand

Global industrial energy use also is driven by the chemicals sector, where demand for energy is rising about 50 percent faster than overall energy demand.

Chemical companies use energy in two ways: as a fuel and as a feedstock to make plastics and other products essential to manufactured goods

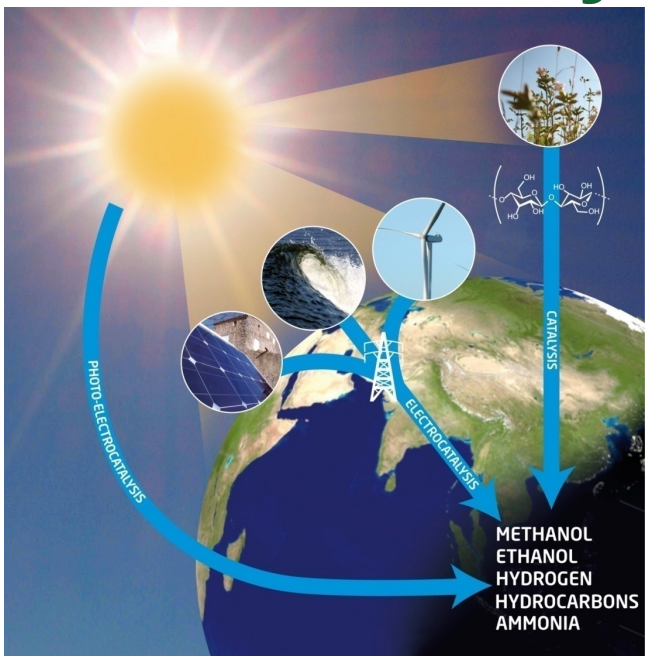


EXXONMOBIL, "The Outlook for Energy 2040" (2014).

Need for catalysis research:

Chemical production relies on catalysis

- Catalysis for sustainable energy
- Catalysis for sustainable chemicals
- Optimization of existing industry

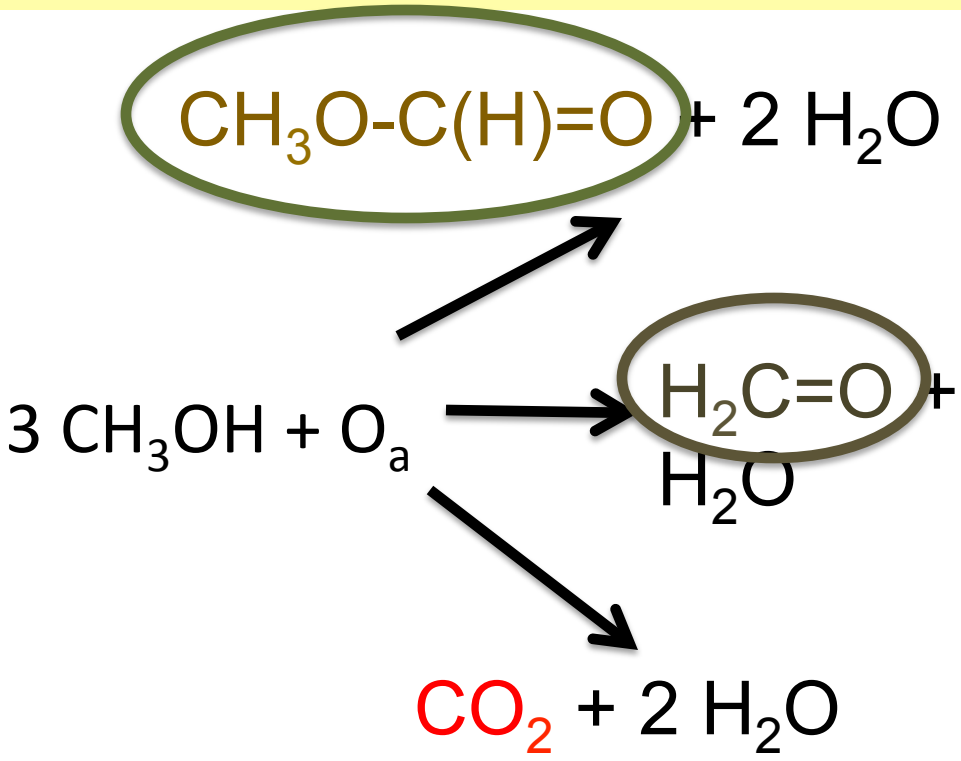


Reduction in energy cost using catalysis

- ***Increase selectivity*** **— get the product you want with little or no waste**

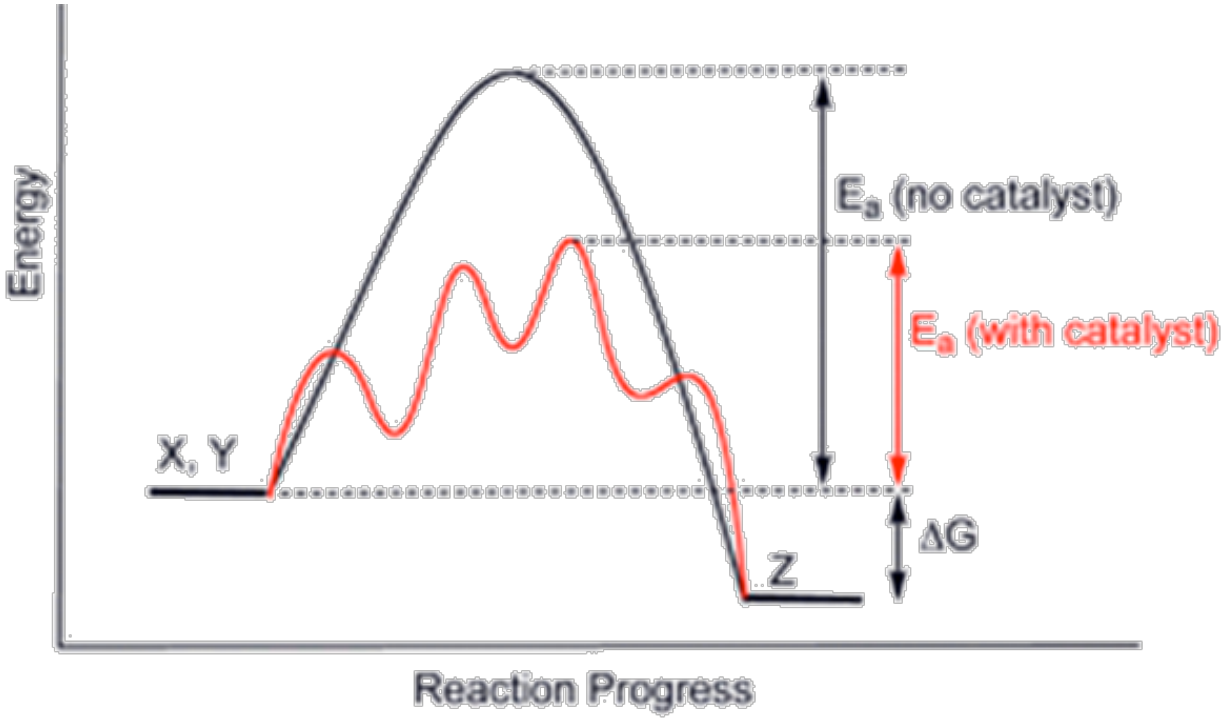
Its all about ***kinetics!***

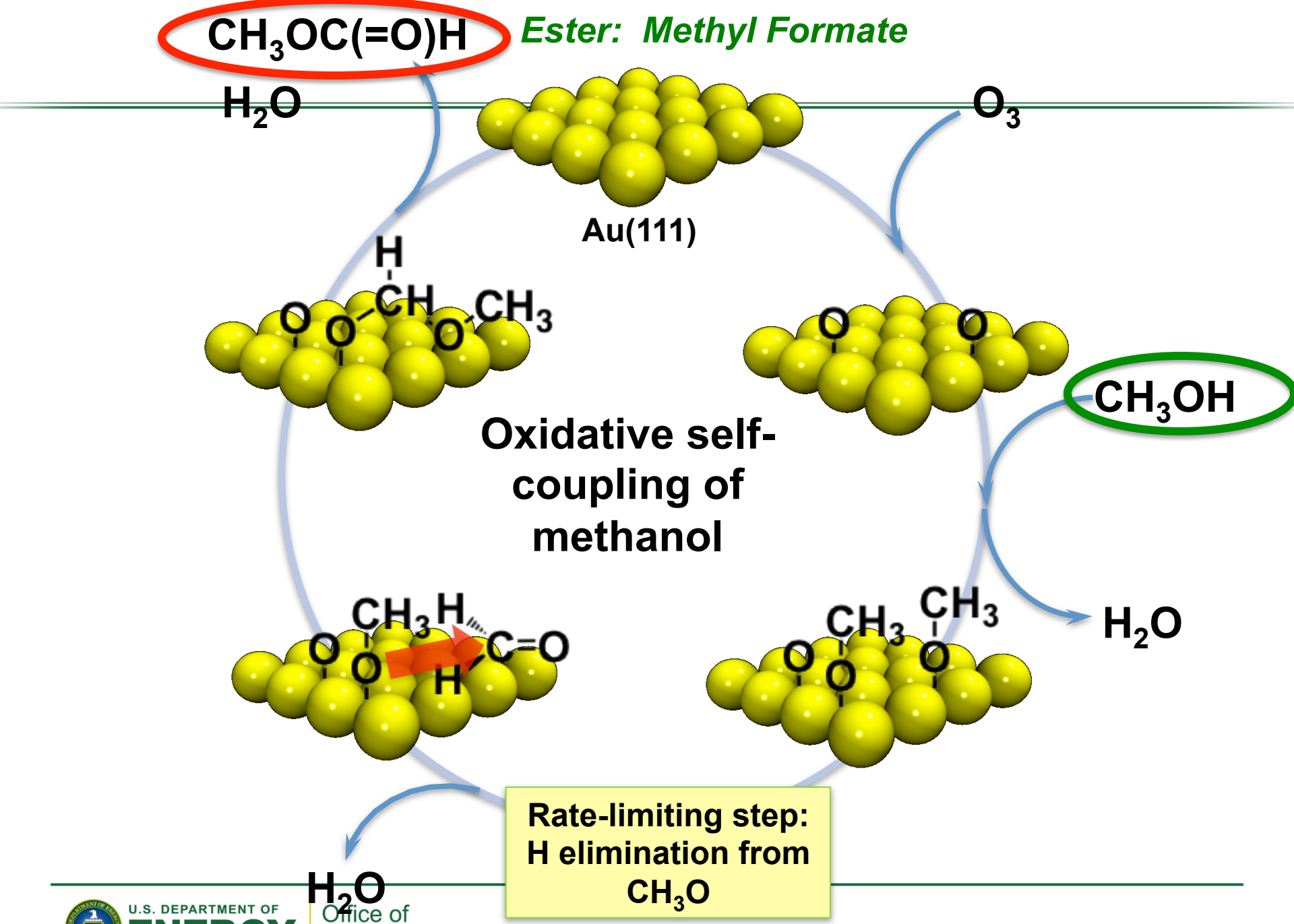
Example: Methanol oxidation on Ag or Au



Catalysis: Modification of kinetics via introducing intermediate steps

- Increase ***rate***
- ***Lower*** operating ***temperature*** (save energy)





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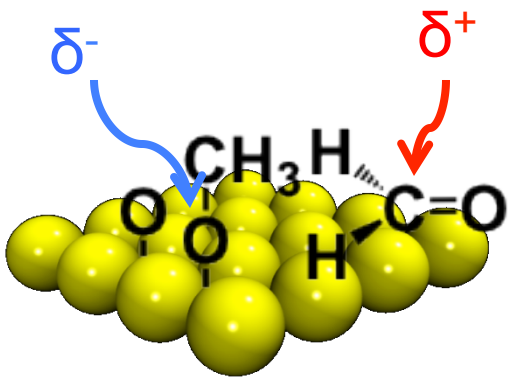
Xu, B., Liu, X., Haubrich, J., Madix, R. & Friend, C. Angew. Chem., Int. Ed. 48, 4206—4209 (2009).

Generalization: Guiding principle for designing new reactions



Electron distribution leads to reaction of negatively polarized species with positively charged one

Prediction: Any molecule with electron-deficient carbon should react with OCH_3 on O/Au surface (e.g. CO or NR_2

EFRC Participants:

Harvard:

C.M Friend, E. Kaxiras, D. Bell, J. Hoffman, R. Madix

Tufts: M. Flytzani-Stephanopoulos,

Fritz Haber Inst. (Berlin): A. Tkatchenko

U. Kansas F. Tao

LBNL: M. Salmeron

LLNL: J. Biener

Collaborators:

CNR (Rome): S. Succi, G. Falcucci

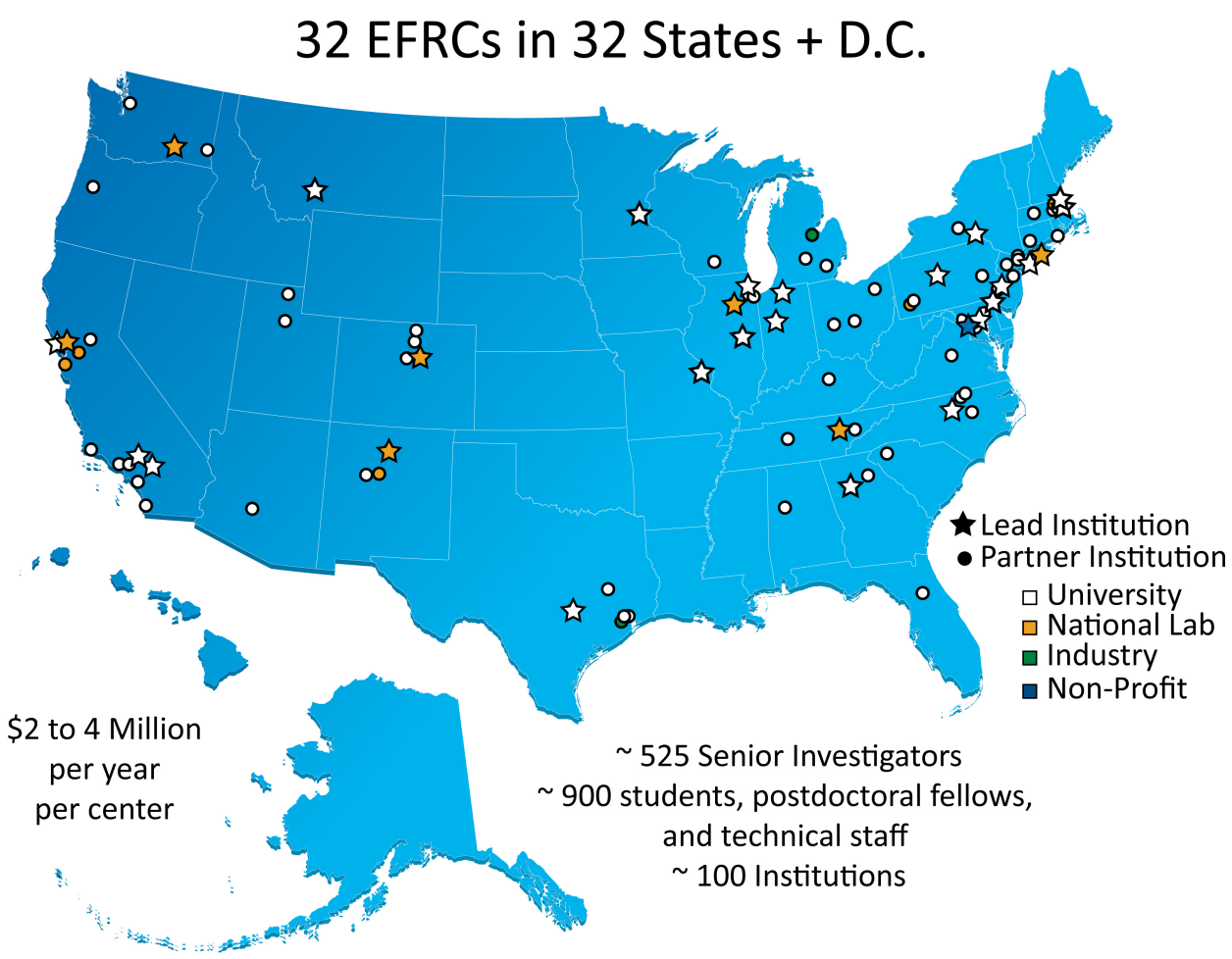
U. St. Louis: R. Fushima

BNL: Y. Zhu

EXA Corp: S. Melcionna

Goal: Develop design principles for increasing selectivity and lower operation temperatures to reduce energy expenditure

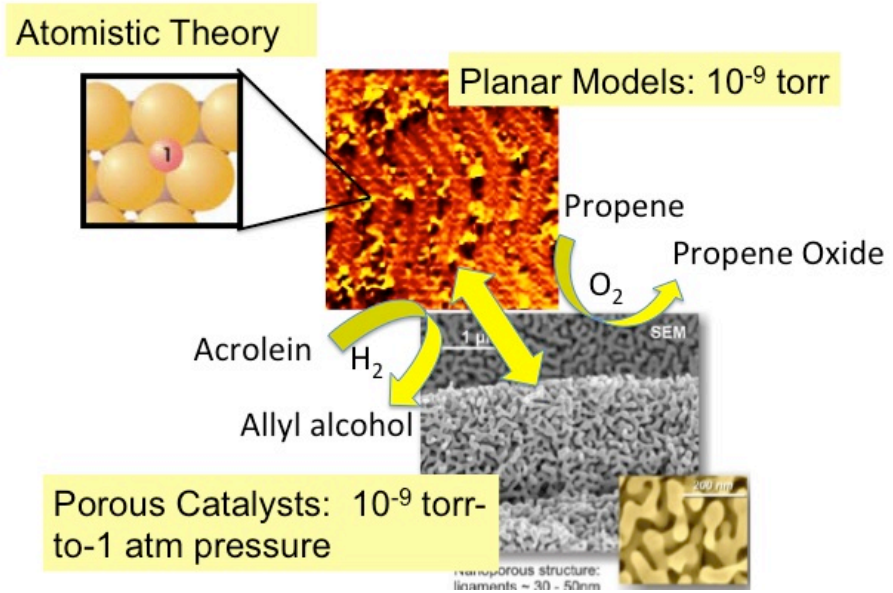
The DOE EFRC Program



The Office of Basic Energy Sciences in the U.S. Department of Energy's Office of Science established the Energy Frontier Research Center (EFRC) program, to accelerate such transformative discovery, combining the talents and creativity of our national scientific workforce with a powerful new generation of tools for penetrating, understanding, and manipulating matter on the atomic and molecular scales.

Integrated Mesoscale Structures of Sustainable Catalysis (IMASC)
Director: Cynthia Friend (Harvard University)

EFRC mission statement:
To develop a fundamental understanding of how to design and use novel mesoporous catalyst architectures for sustainable conversion and production of platform chemicals through selective oxidation and selective hydrogenation



RESEARCH PLAN

Principles for designing catalytic processes that will reduce energy consumption in producing chemical production will be constructed using advanced experiment and theory. Porous catalyst architectures will be studied under a wide range of conditions in order to optimize production of most desirable products.

U.S. DEPARTMENT OF ENERGY | Office of Science

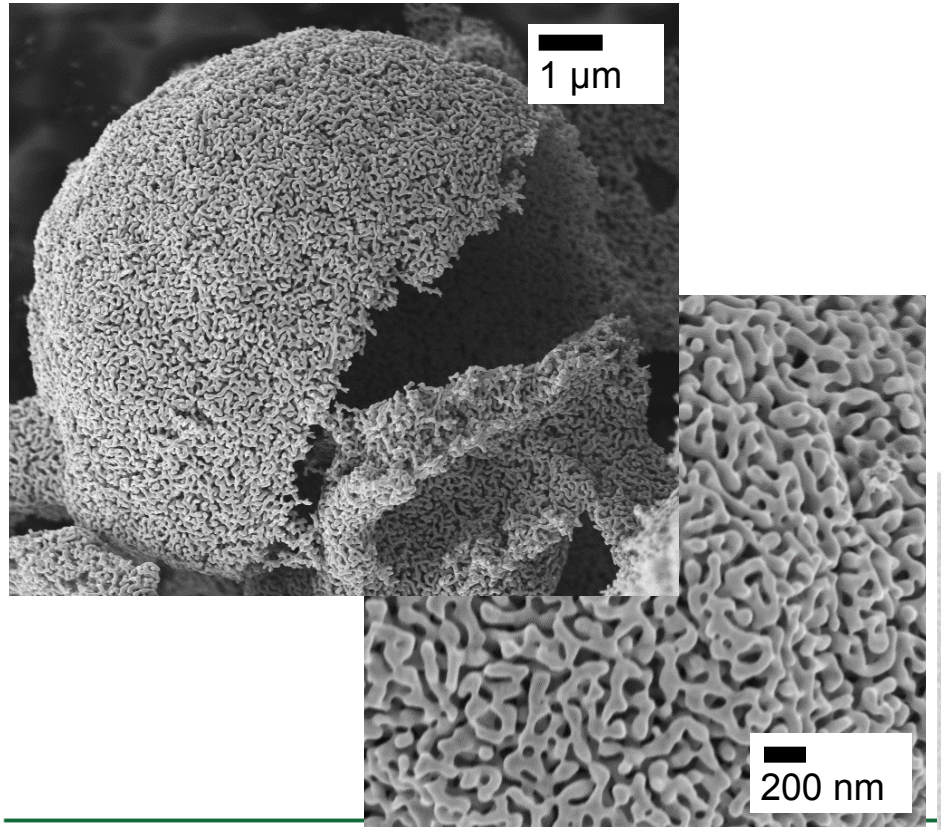
BERKELEY LAB

LAWRENCE LIVERMORE NATIONAL LABORATORY

Nanoporous Au: Dilute Ag/Au alloys exploit ability of Ag to dissociate O_2

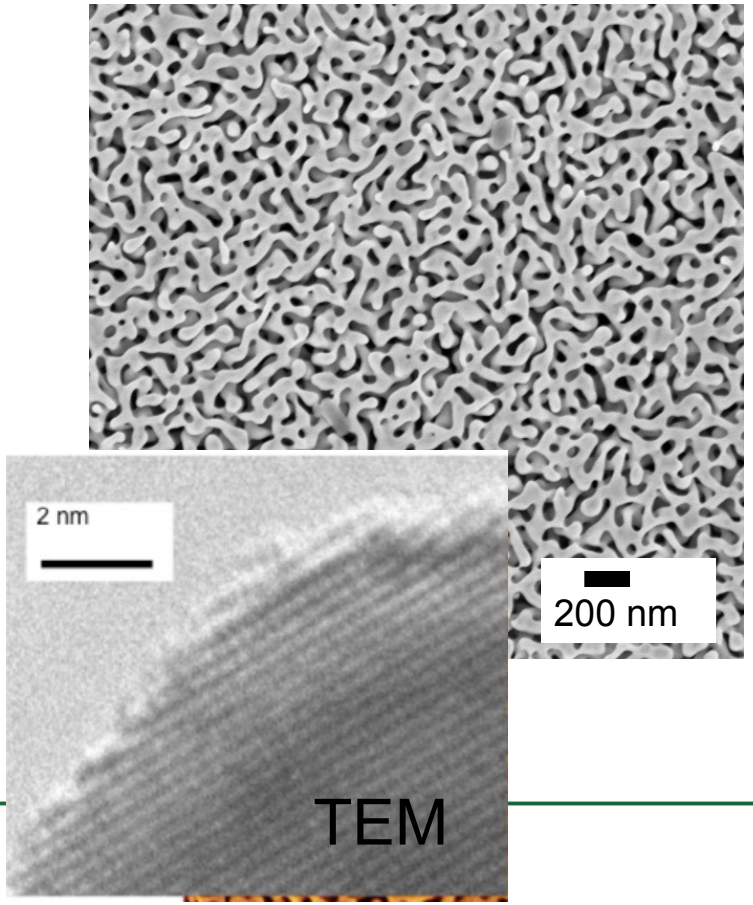
Nanoporous Au Microspheres

1-3 at% Ag (EDS)

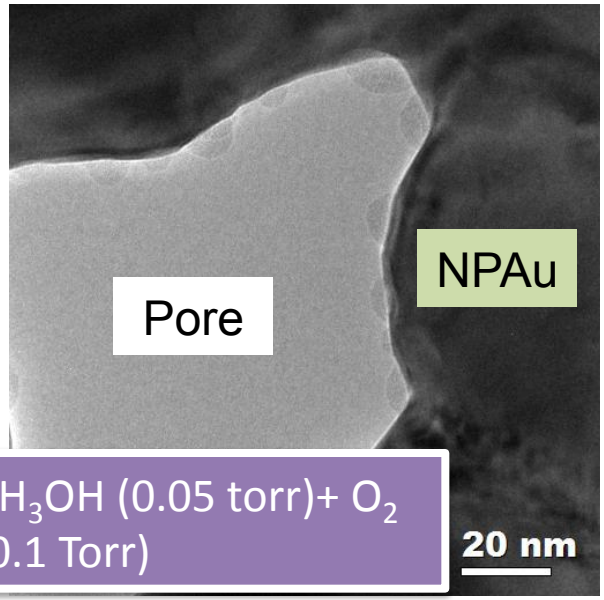


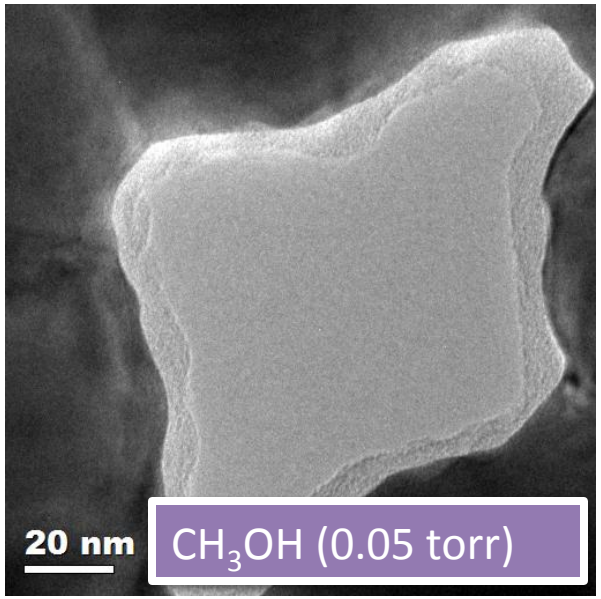
Nanoporous Au Ingots

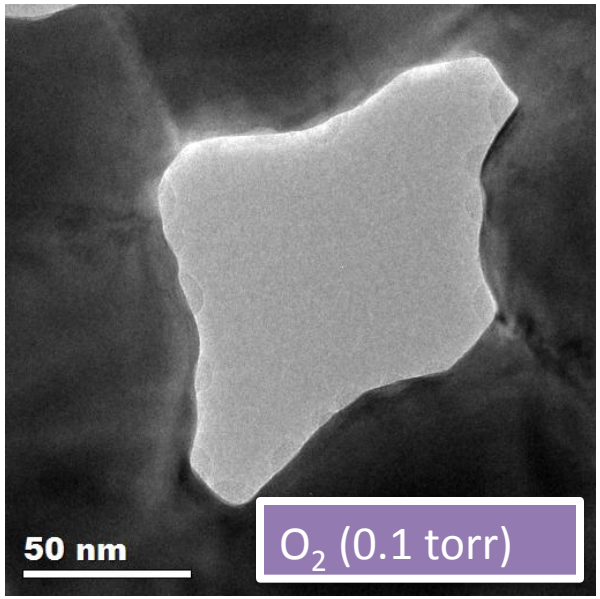
1-3 at% Ag (EDS)

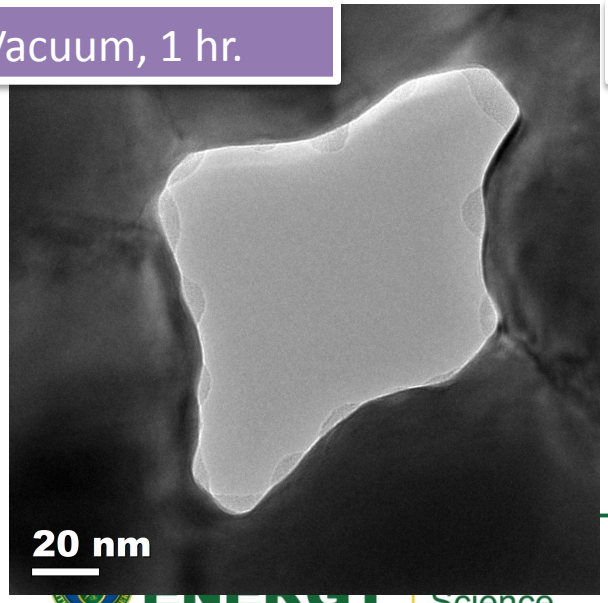


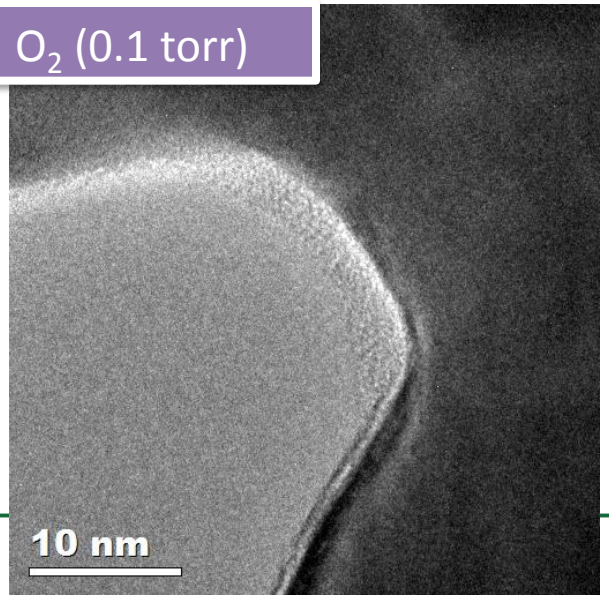
Environmental TEM shows dynamic nature of catalyst: $CH_3OH + O_2$ on npAu

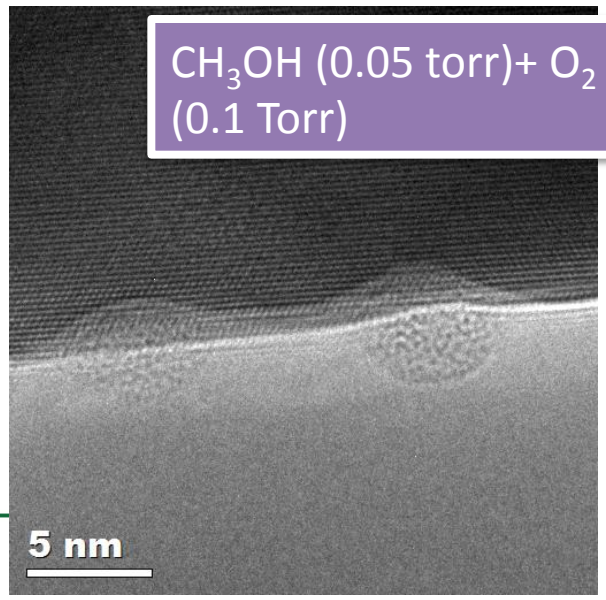






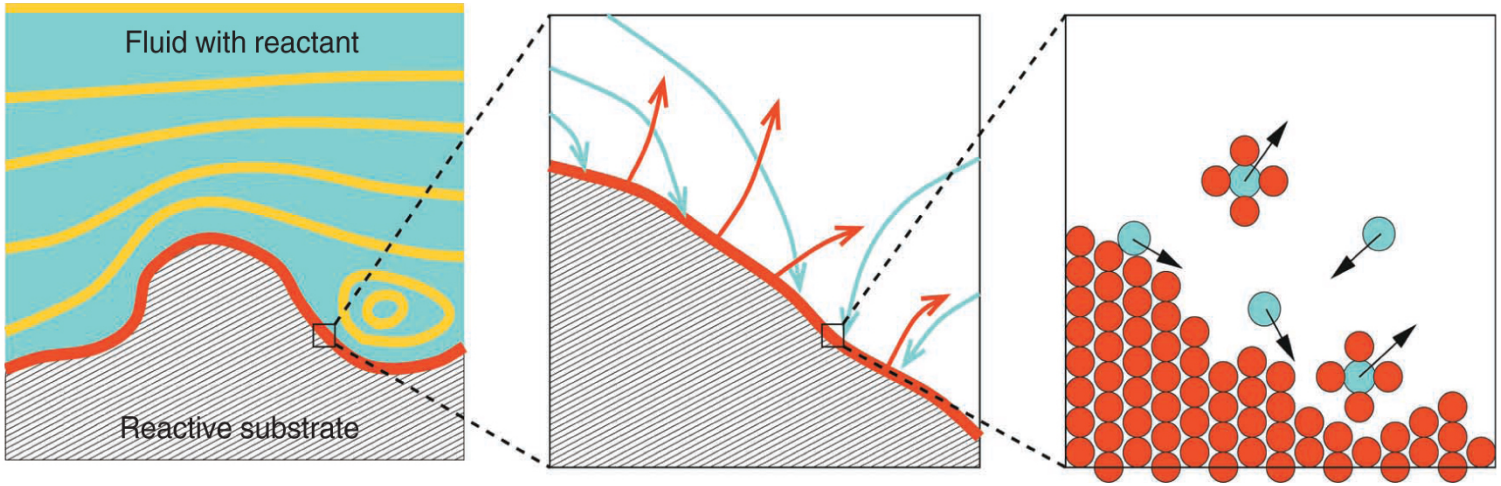






The role of theory: "Multiscale modeling of complex chemical systems"

Macroscopic → Mesoscopic → Microscopic

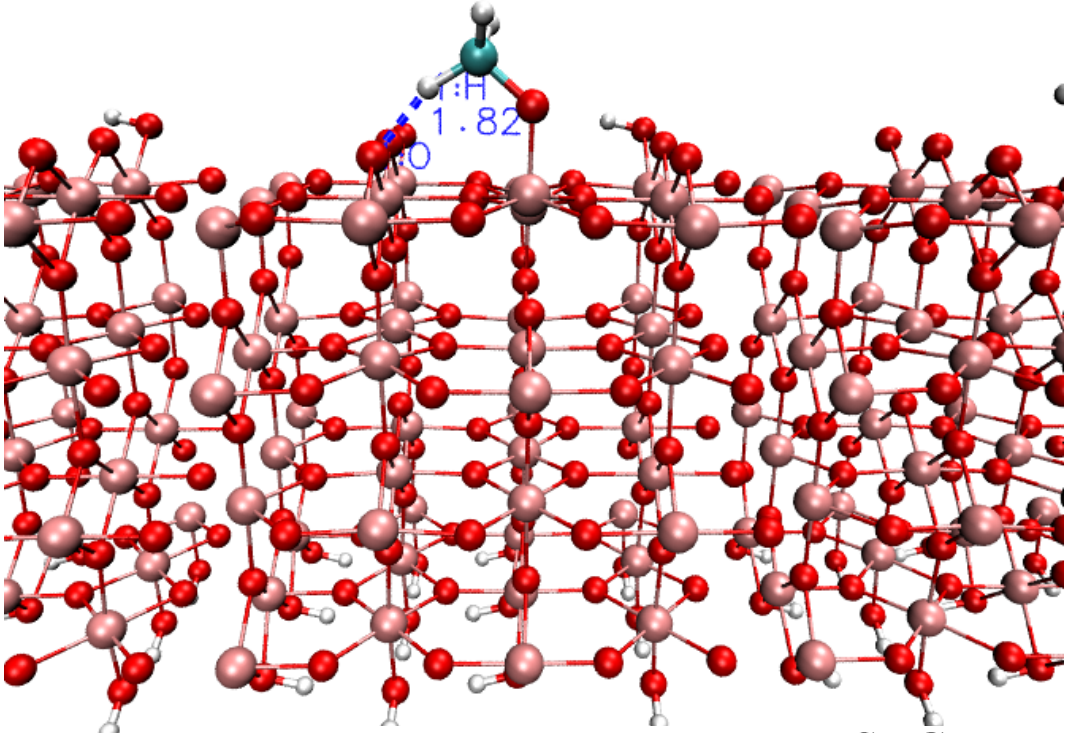


Prof. Sauro Succi
Applied Computation 274:
Computational modeling of fluids and soft matter

Methoxy splitting on TiO_2 surface

- **Formaldehyde was photochemically produced from methoxy on TiO_2 (110) surface**

$$CH_3O_{(a)} + O_{(a/br)} + h^+ \rightarrow H_2CO_{(a)} + OH_{(a/br)}$$

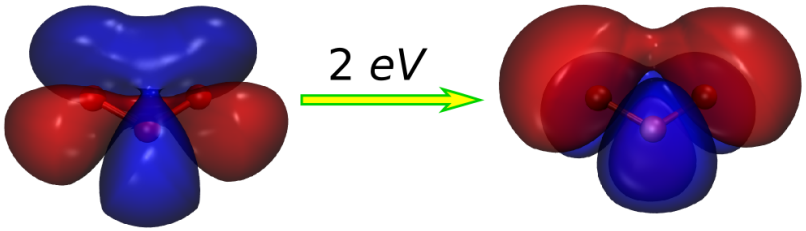


D. Vinichenko
G. Kolesov
G. Tritsaris
O. Granas
R. Hoyt

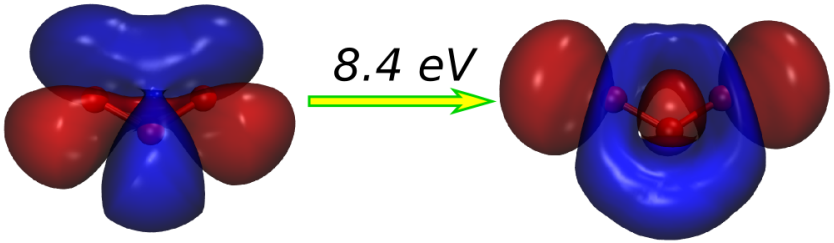
Phillips, K. R., Jensen, S. C., Baron, M., Li, S.-C. & Friend, C. M. Sequential photo-oxidation of methanol to methyl formate on TiO2 (110). *Journal of the American Chemical Society* **135**, 574–577 (2013).

Example: ozone photolysis

- Excitation HOMO to LUMO: slow dissociation

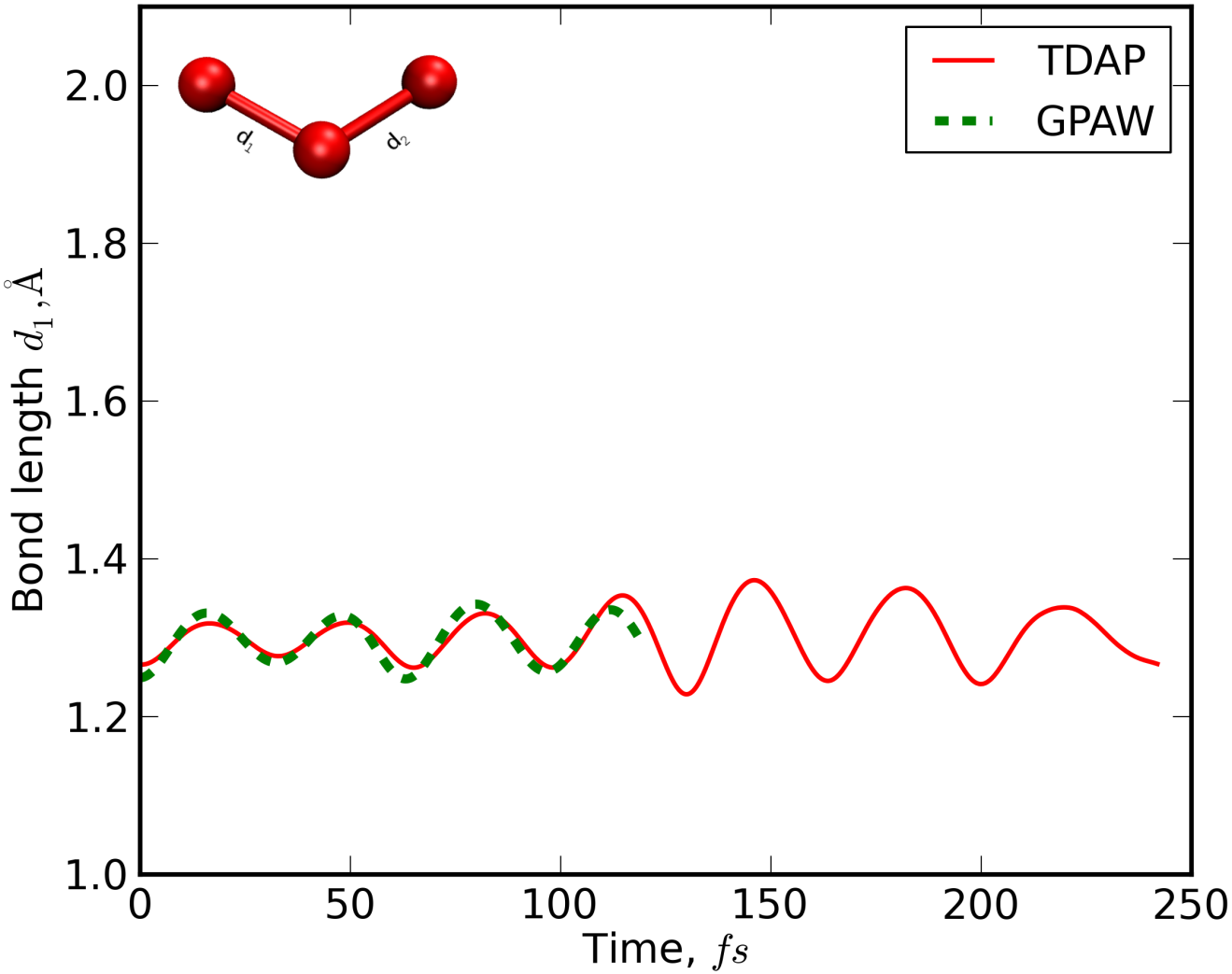


- Excitation HOMO to LUMO+1: quick dissociation

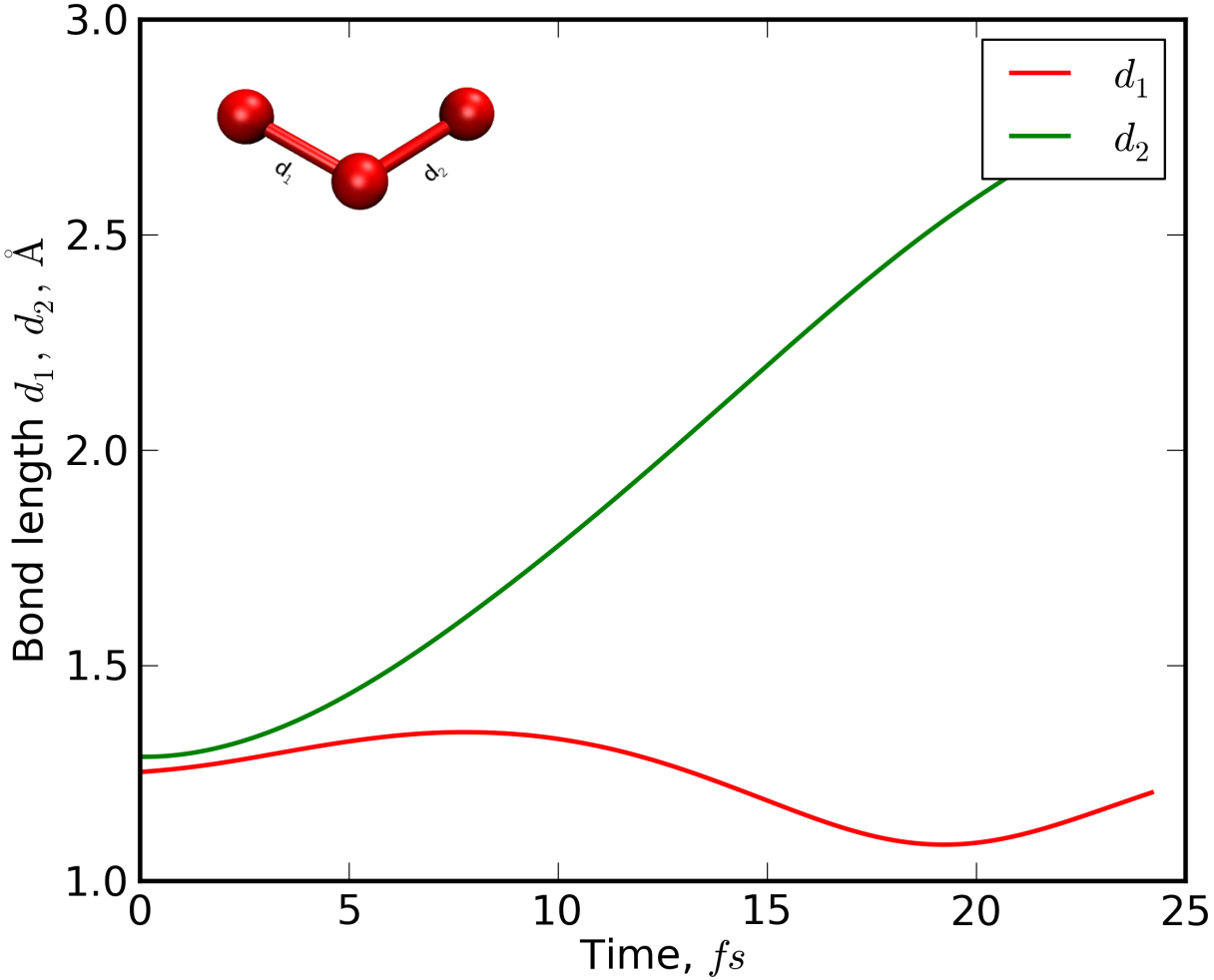


Matsumi, Y. & Kawasaki, M. Photolysis of atmospheric ozone in the ultraviolet region. *Chemical reviews* **103**, 4767–4782 (2003).

Wrong excitation (visible light)



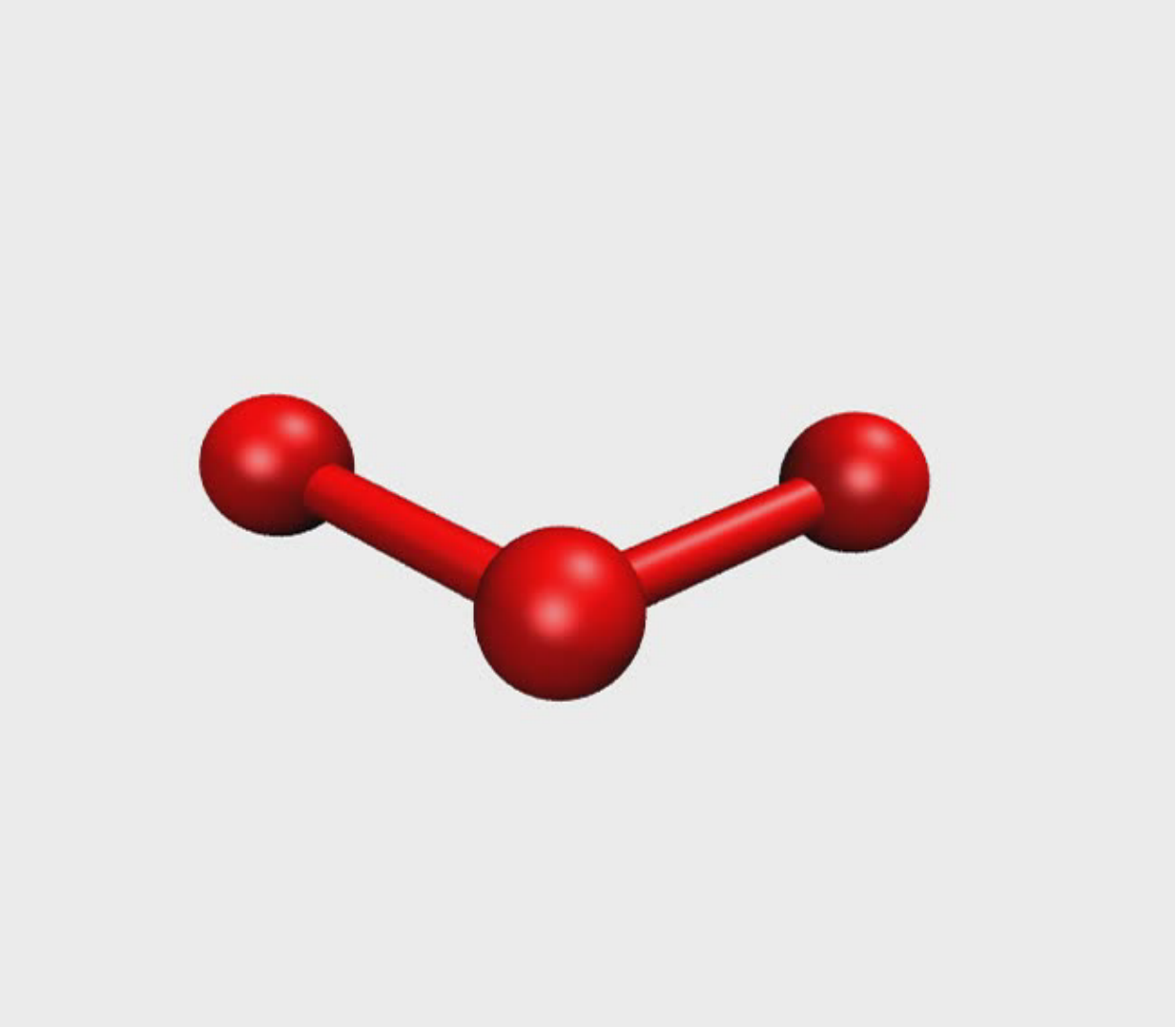
Right excitation (UV light)



2nd excited state trajectory

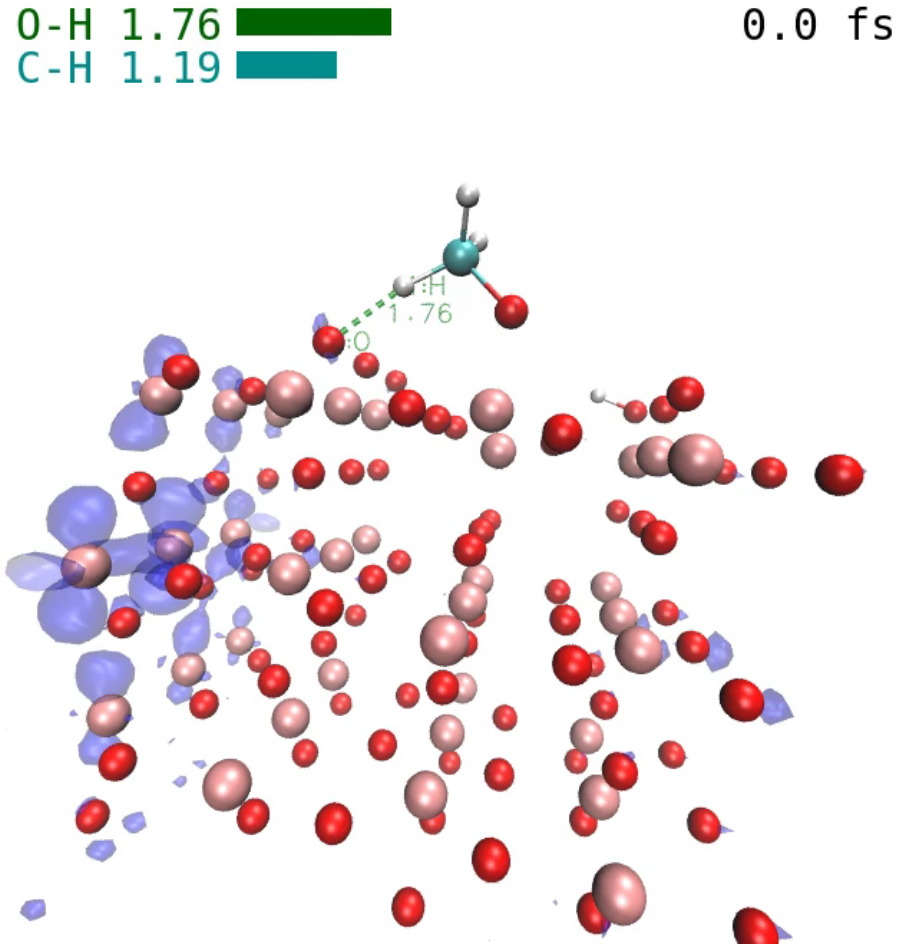
- **Movie:**

o3split.mov

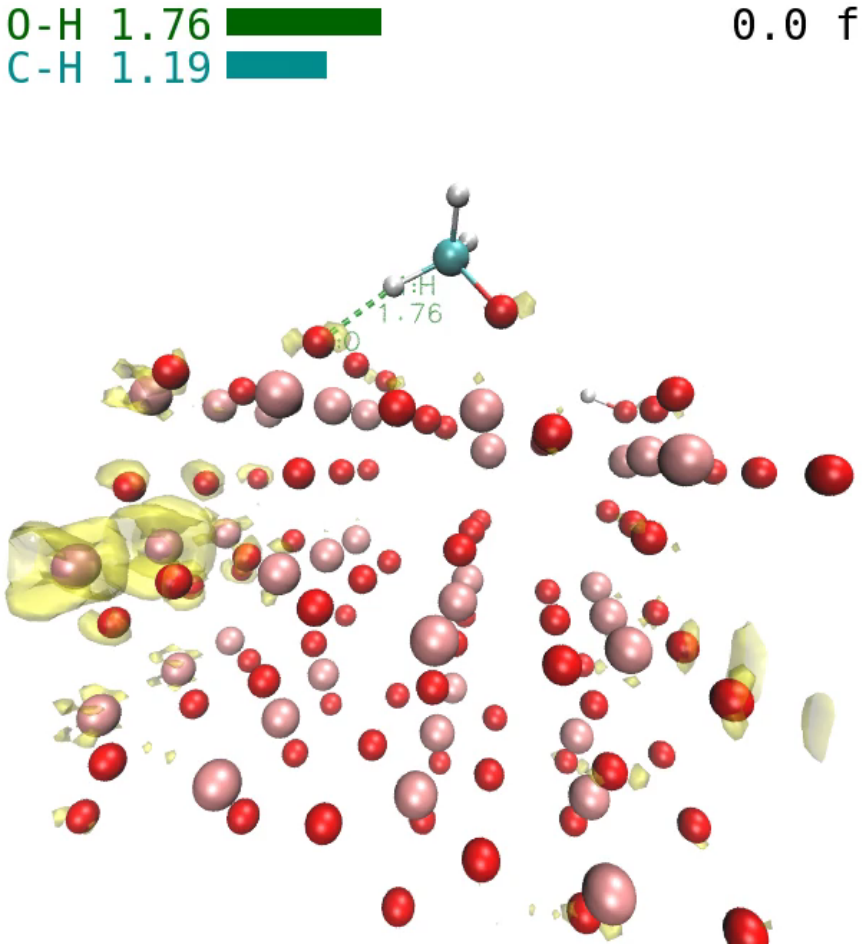


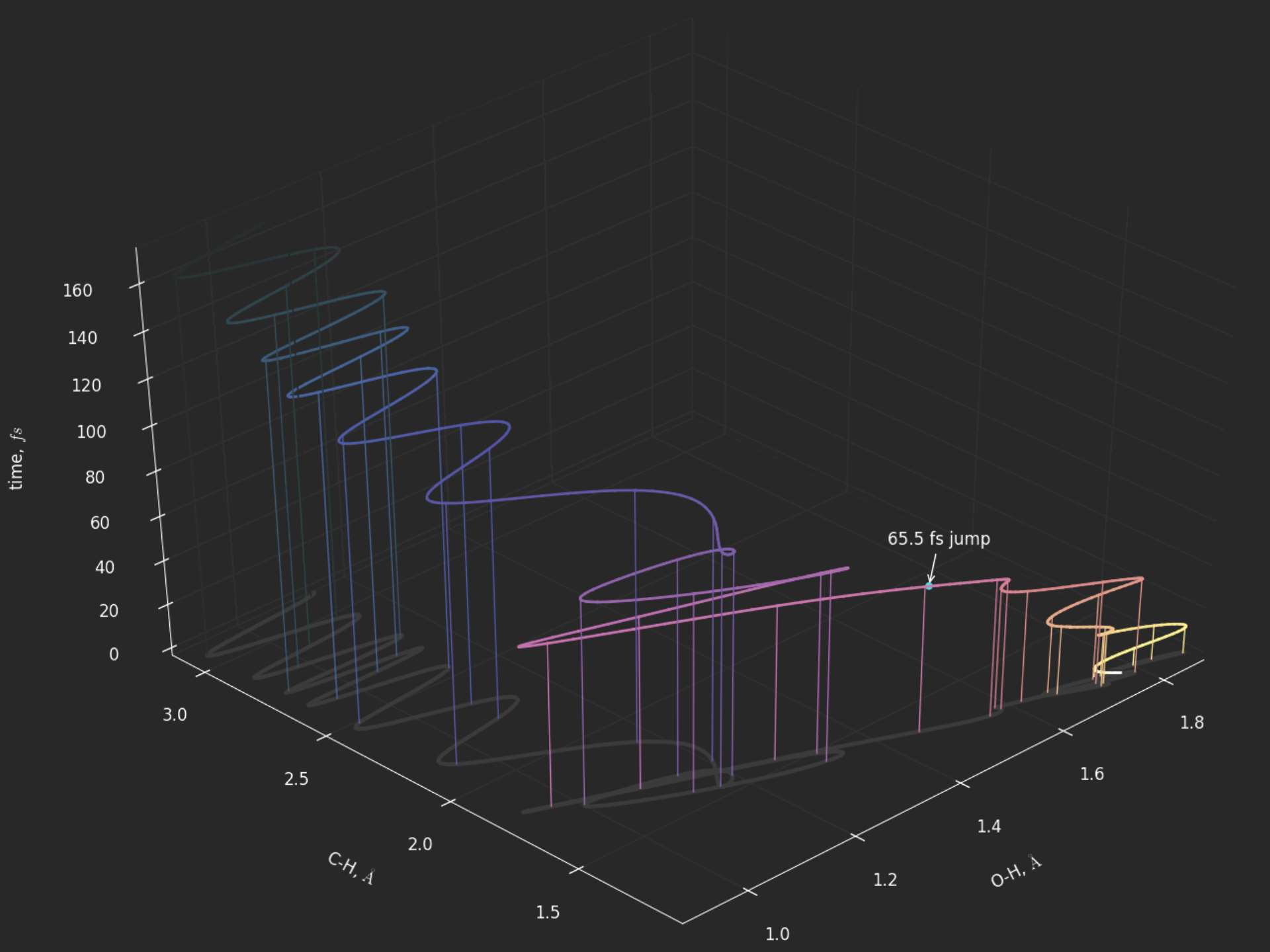
TDDFT trajectory:

Electron



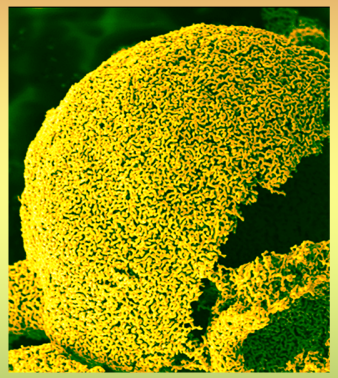
Hole




time, fs
160
140
120
100
80
60
40
20
0
65.5 fs jump
3.0
2.5
2.0
1.5
C-H, Å
1.0
1.2
1.4
1.6
1.8
O-H, Å

Integrated Mesoscale Architectures for Sustainable Catalysis (IMASC)

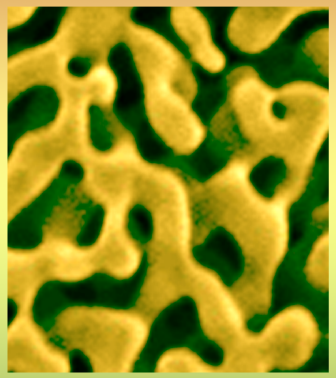
understanding kinetics



selective oxidation and hydrogenation reactions

10^{-9} torr → 1 atm

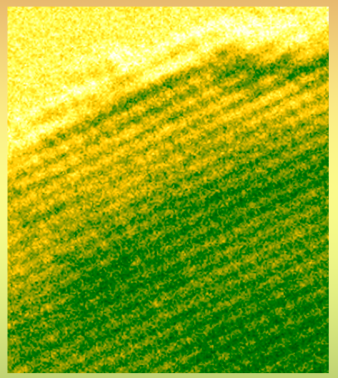
building innovative catalytic architectures



multi-scale computational modeling

atomistic → macroscopic

improved reaction selectivity



sustainable catalytic systems

efficient and benign by-products

decreased fuel consumption