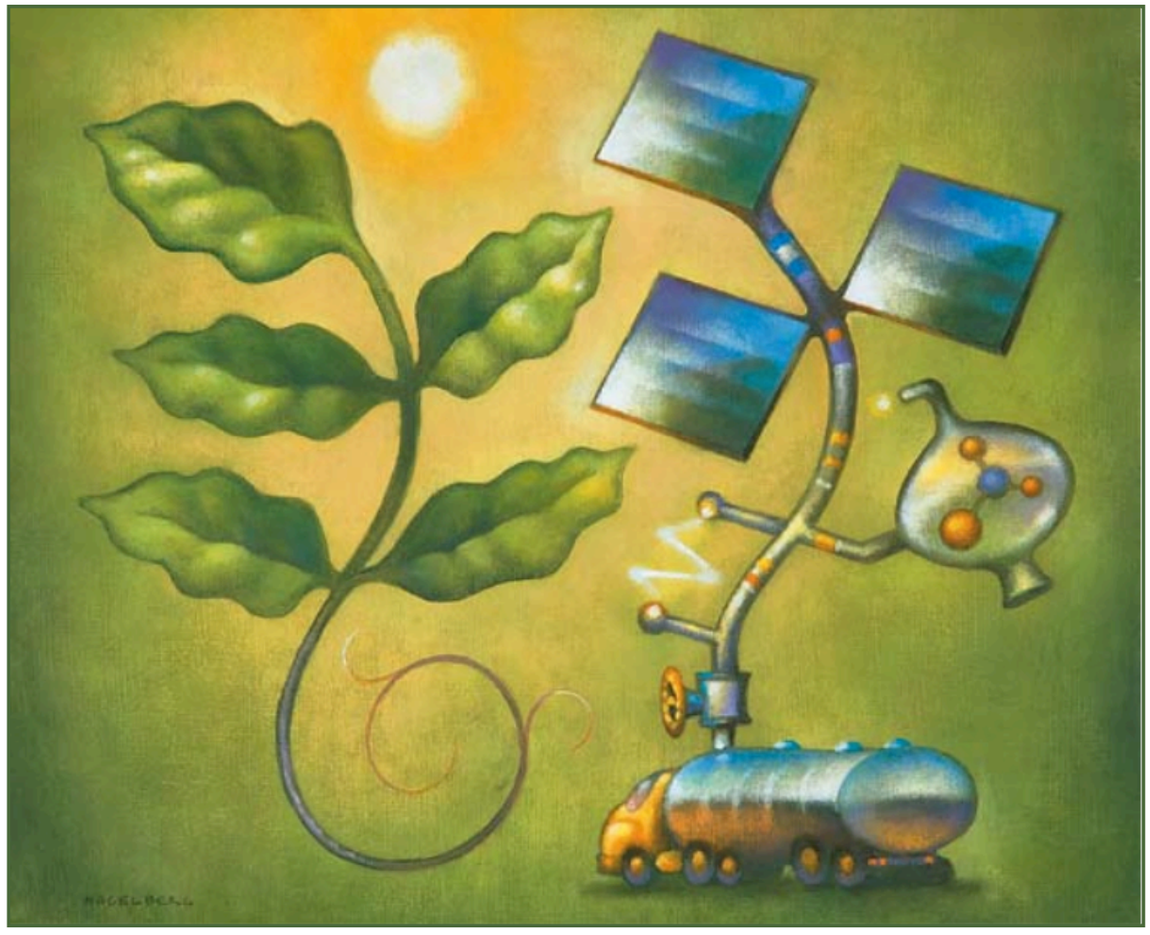
Computational Catalysis

& its applications to renewable energies



Stefano Fabris

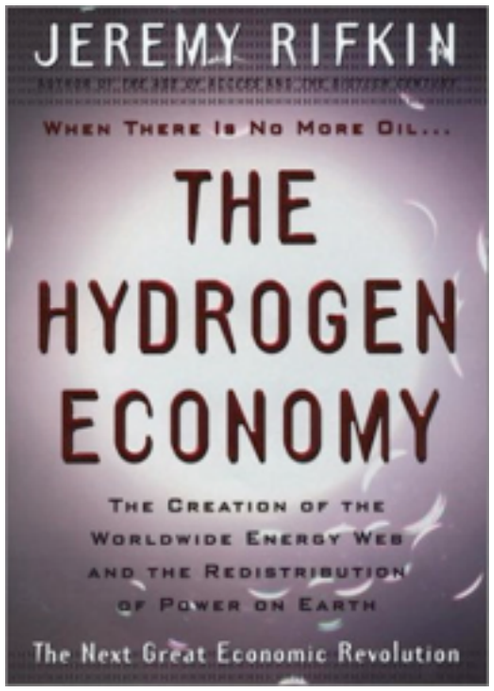
CNR-IOM DEMOCRITOS Simulation Center

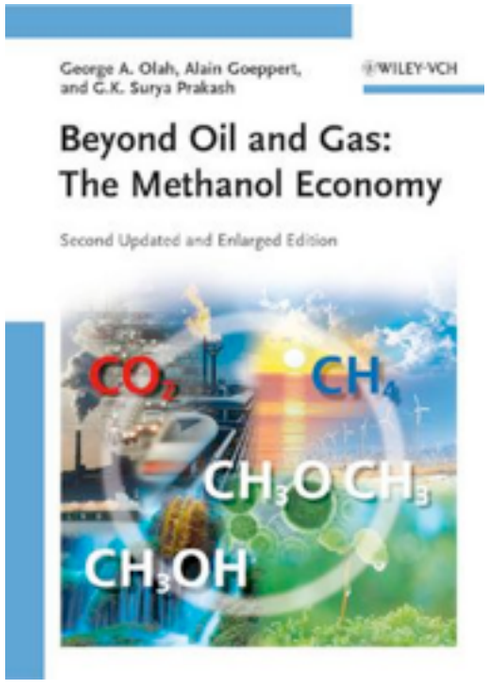
SISSA - Scuola Internazionale Superiore di Studi Avanzati - Trieste - ITALY

Computational Catalysis

& its applications to renewable energies

Technologies limited by the lack of stable, efficient, and selective catalysts





Solar fuels: conversion of solar energy into chemical energy

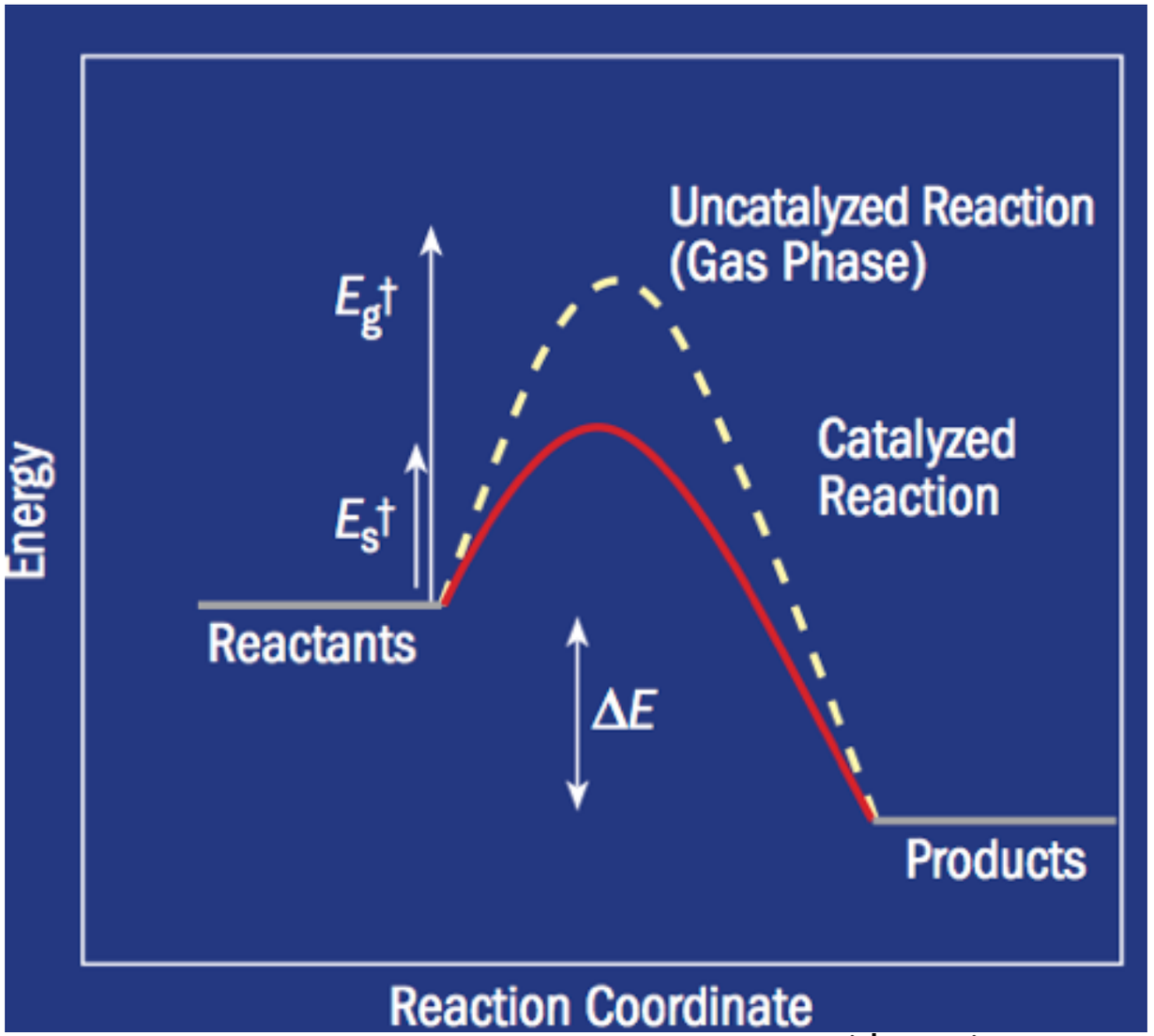
Fuel cells: electrodes, production and purification of H2, ...

Energy storage: batteries, ...

Catalysis: general principles

Catalyst: material that can control the rate of a chemical reaction

ACTIVITY: it alters the kinetics and thermodynamic of the reaction leading to *high rate*



www.scidacreview.org

Catalysis: general principles

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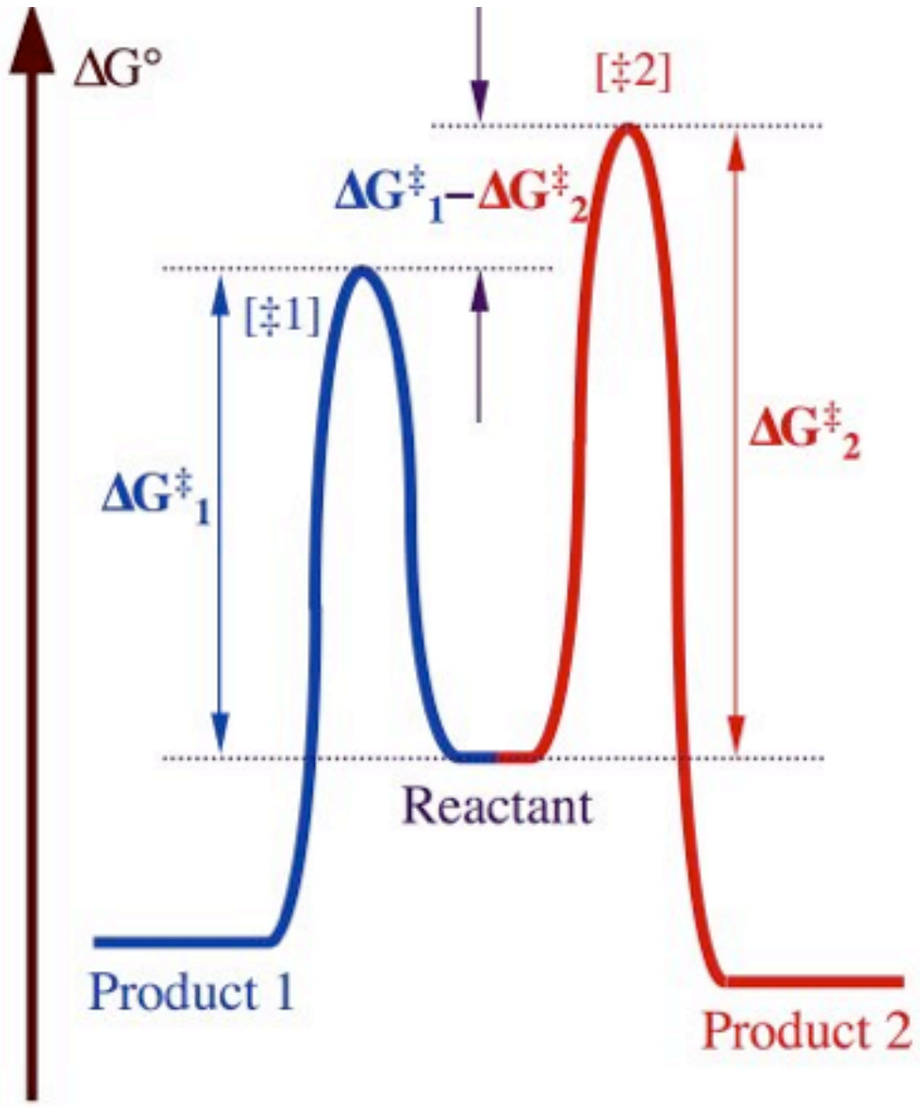

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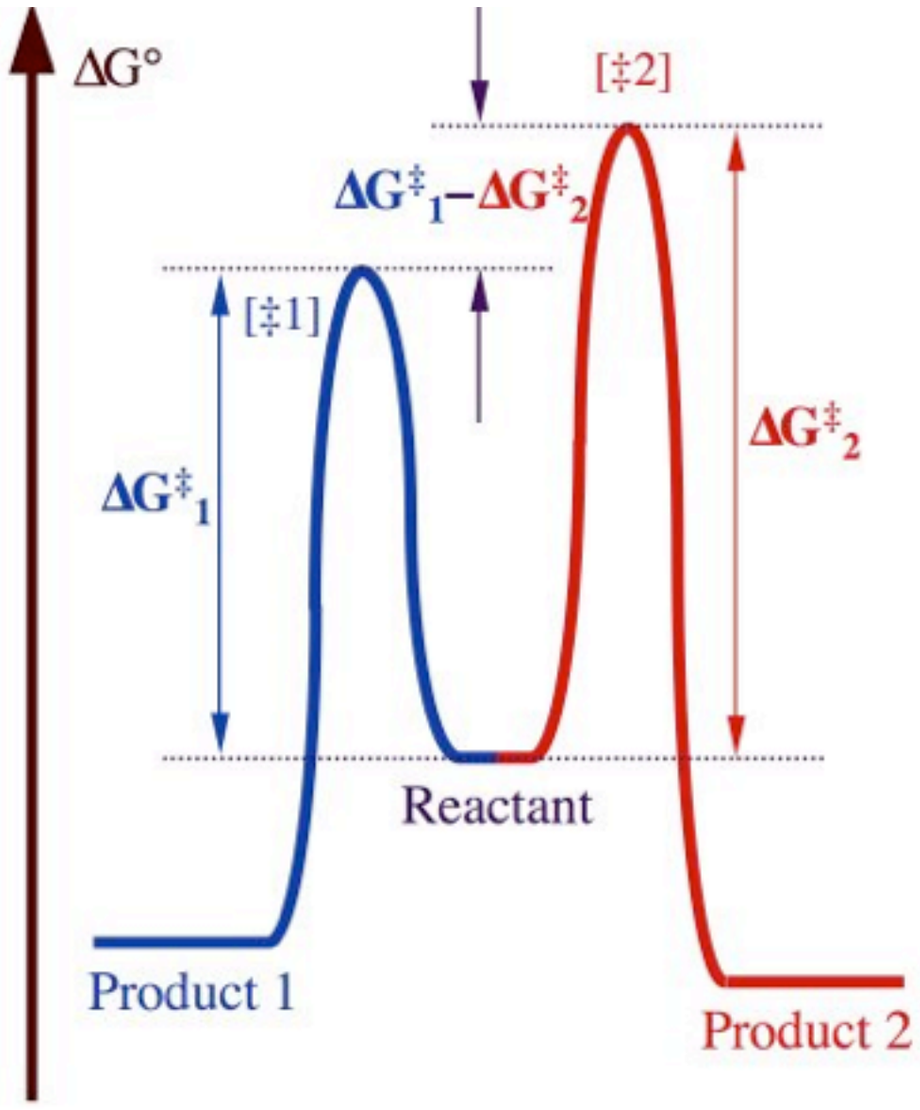


MATERIALS SCIENCE CHALLENGE

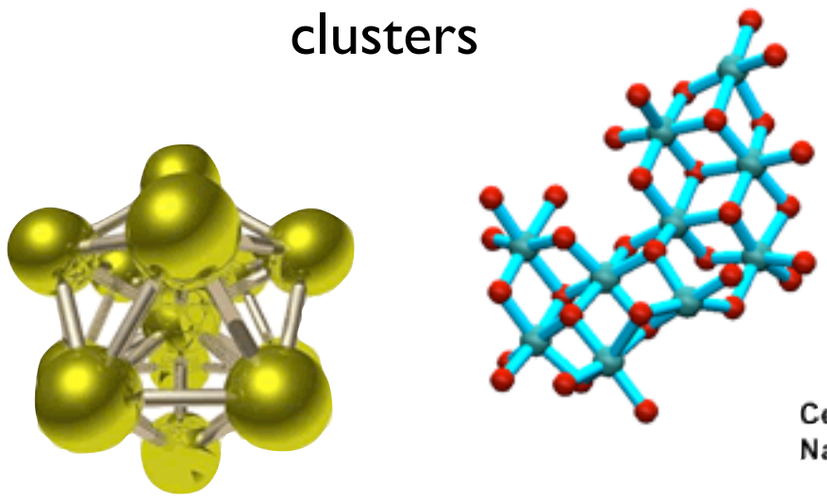
Finding materials that optimally comply with these principles

Length scales of Catalysis

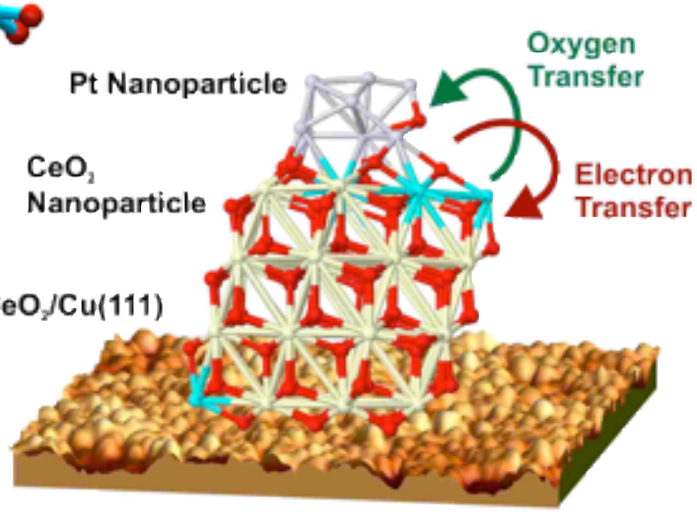
Catalysis spans a wide range of length scales

single-metal atom

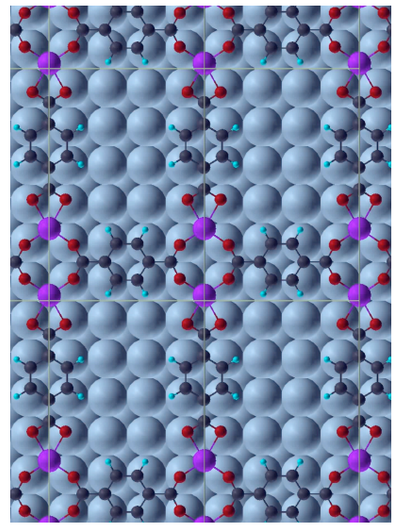
metal/oxide/... clusters



supported heterogeneous NP



extended crystalline surfaces



Homogeneous

Heterogeneous

1 nm

10 nm

Length scales of Catalysis

Catalysis spans a wide range of length scales

single-metal atom

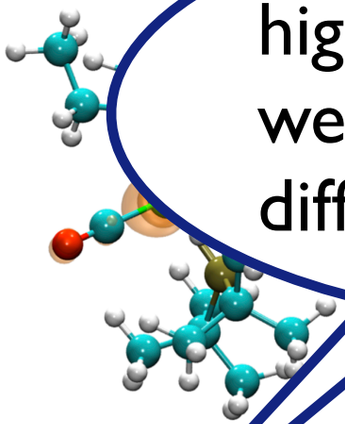
metal/oxide/... clusters

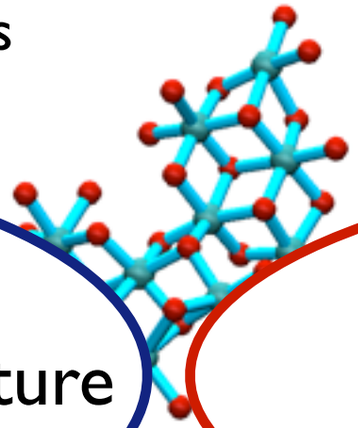
supported heterogeneous NP

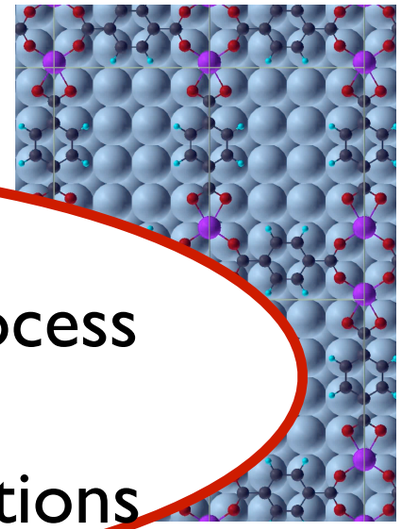
extended crystalline surfaces

high selectivity
well-determined structure
difficult to immobilize

lower selectivity
easier synthesis and process
difficult to characterize
stable in reaction conditions







Homogeneous

Heterogeneous

1 nm

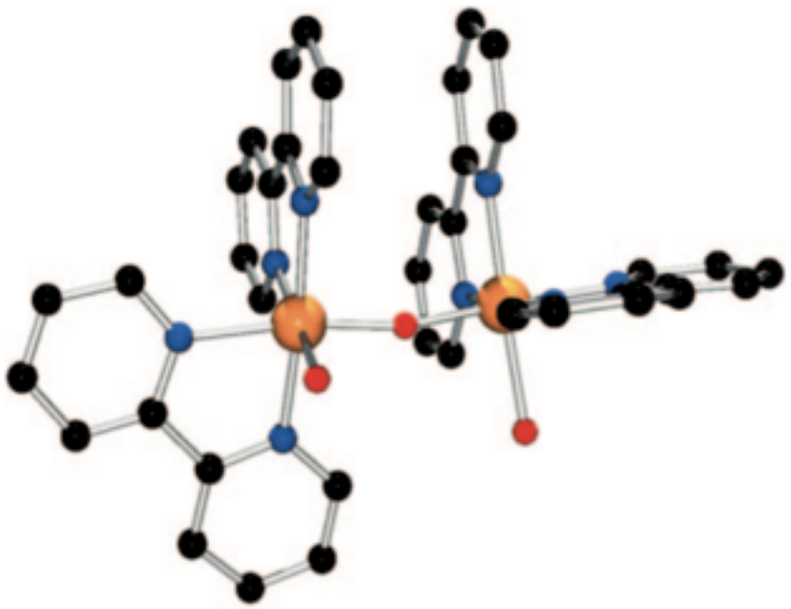
10 nm

Ex: Water oxidation catalysts

WOx is one of the main bottlenecks in the conversion and storage of solar energy into chemical fuels

Homogeneous

Single- and multi-center TM-based catalysts
(Ru, Ir, Co, Mn)



"Blue dimer" (T. Meyer 1982)

STRUCTURE AND FUNCTION

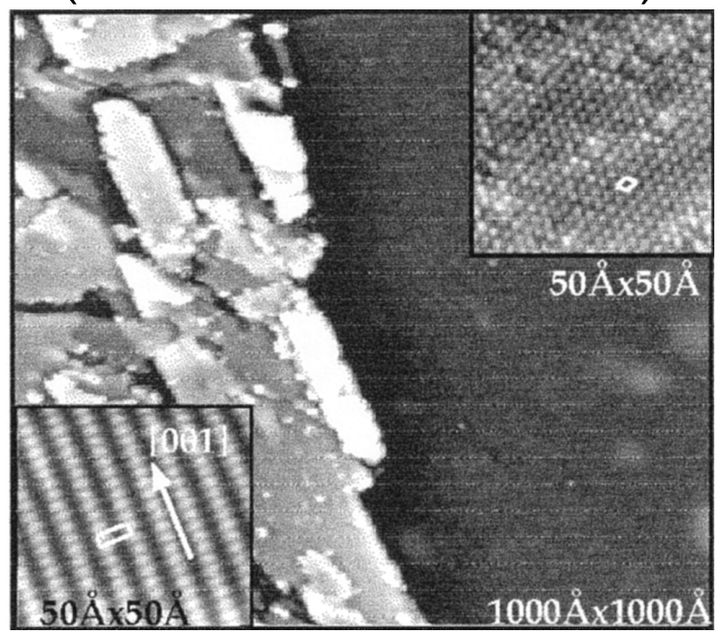
Well characterized - mechanisms of reactions

STABILITY

Short-lived due to ligand oxidation

Heterogeneous

Metal-oxide reducible catalysts
(RuO_2, IrO_2, Co_3O_4, ...)



RuO_2(110 and 0001) under UHV

STABILITY

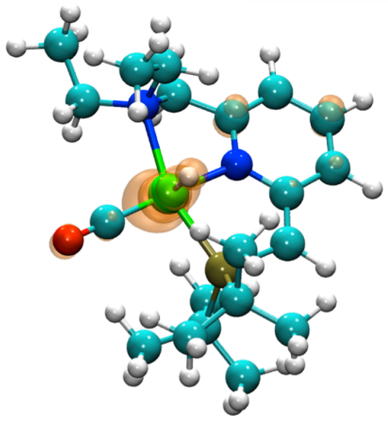
Combine robustness and efficiency
Stable under suitable pH conditions

STRUCTURE AND ~~FUNCTION~~

Structure and composition of the active sites?
Surface of the catalyst under reaction conditions?

Computational Catalysis

Traditionally addressed both



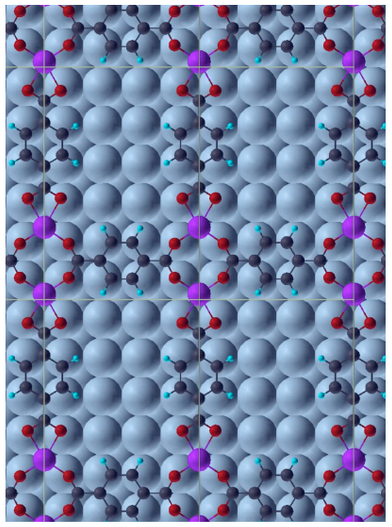
single-metal atom

Homogeneous

extended crystalline surfaces

Heterogeneous

simplified models of real catalyst's surfaces



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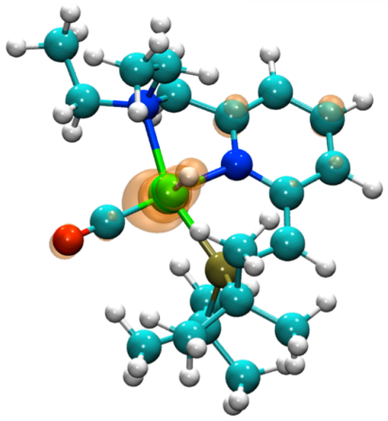

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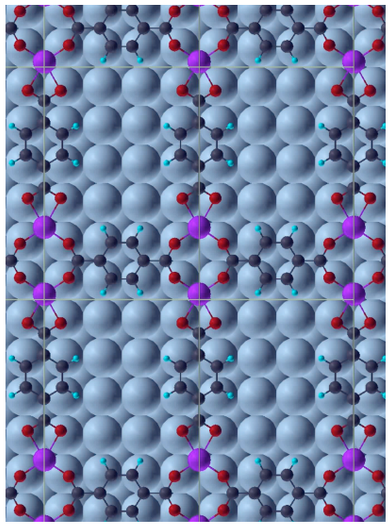
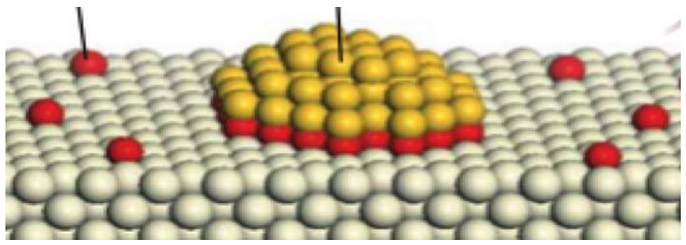
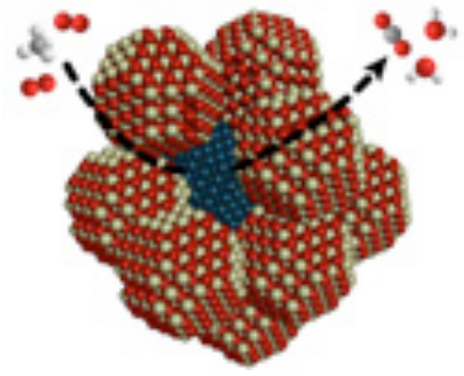


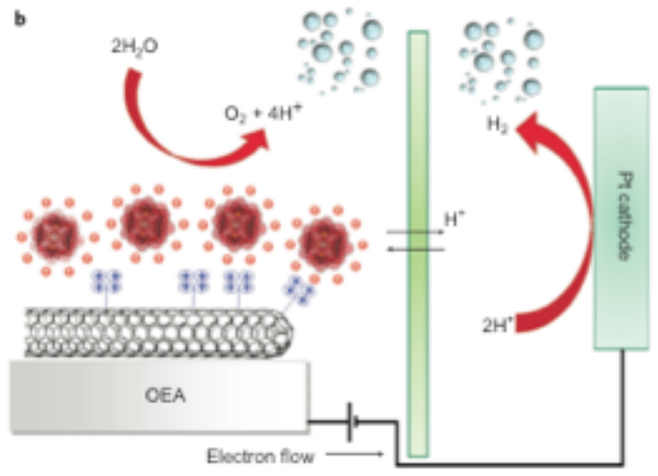
Current trend towards more complex systems:



supported sub-nm clusters



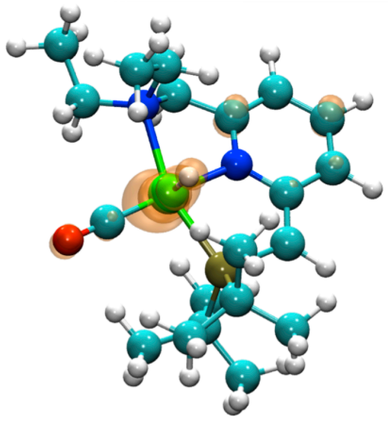
core-shell nanoparticles



functionalized surfaces

Computational Catalysis

Traditionally addressed both



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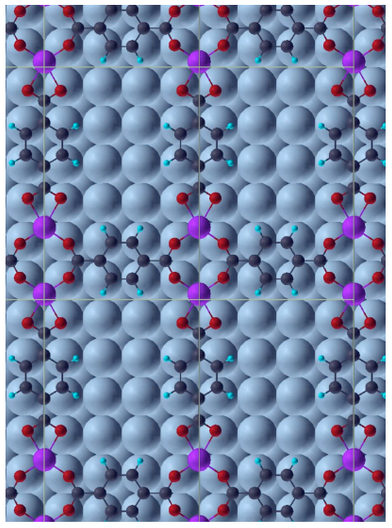

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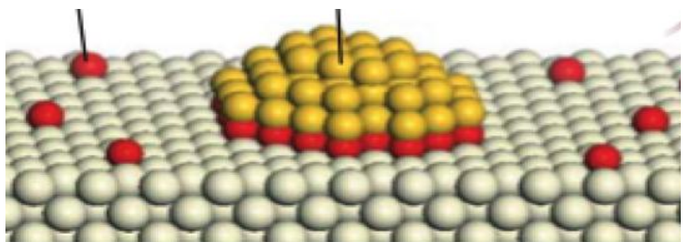

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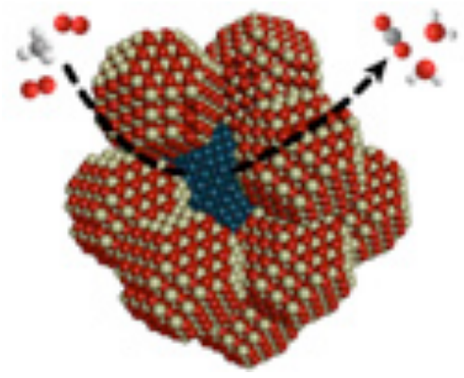

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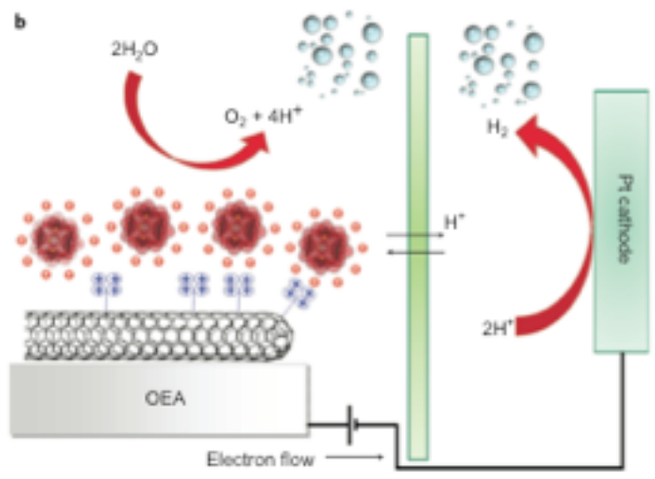
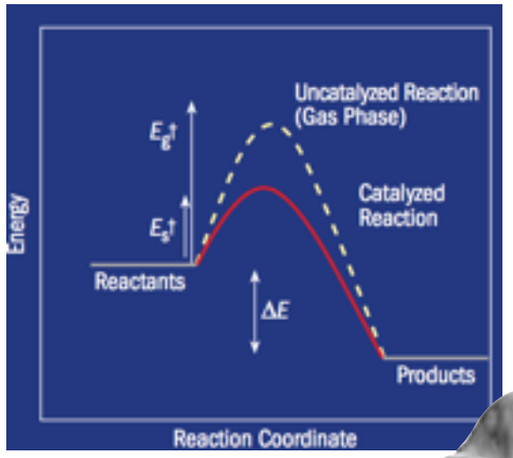


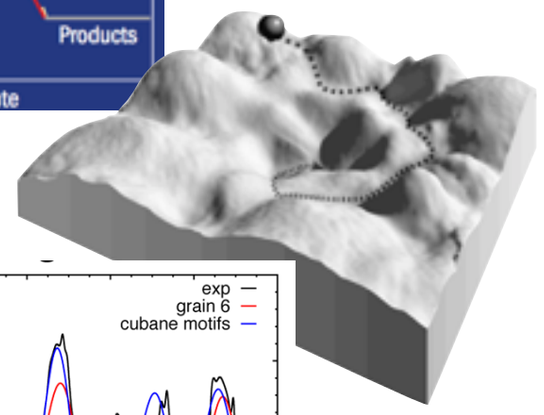
functionalized surfaces

New materials synthesized in the context of renewable materials belong to these classes

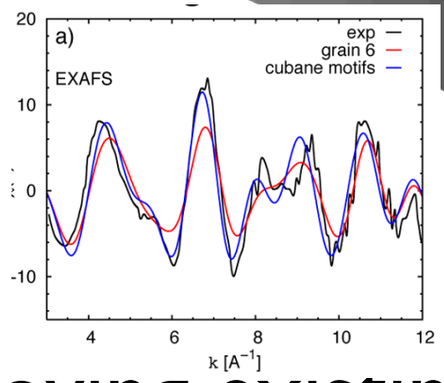
Challenges for Comp. Catalysis?

Materials and processes for renewable energy questions&challenges for computational catalysis

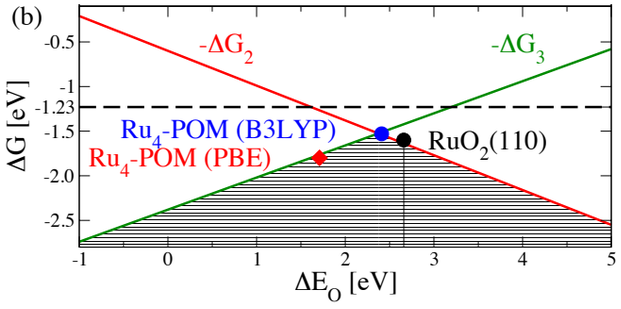


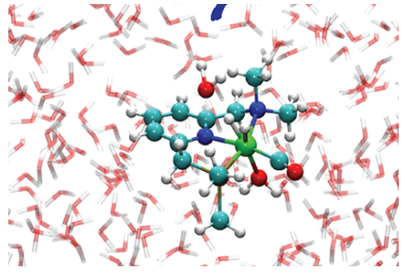


- How to determine the activation energy?
- How to identify the reaction mechanism?
- Catalyst characterization (experiment)
- Effects of chemical environment (gas and liquid)?



- How to find new catalysts or guidelines for improving existing ones?
- Electrochemistry?





Techniques and approaches

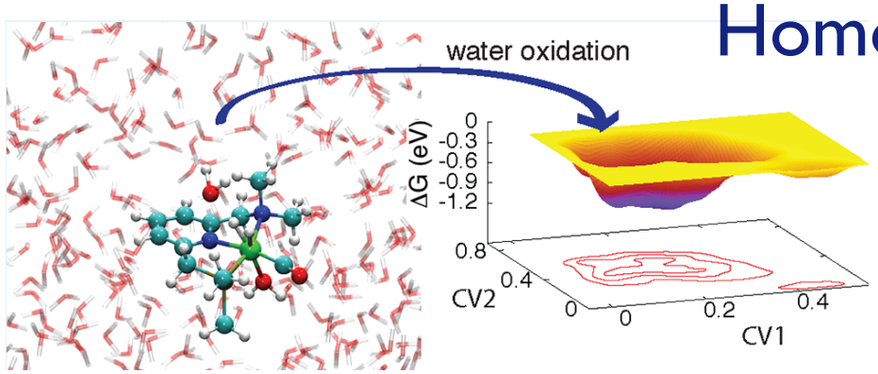
- [x] DFT, plane waves and pseudopotentials
- [x] Total energy and electronic structure
- [x] Interatomic Forces & Molecular Dynamics
- [x] Computational spectroscopy & link to experiment

- [ ] Simulating rare (activated) events
  - Minimum energy paths - NEB
  - Beyond MD - Metadynamics

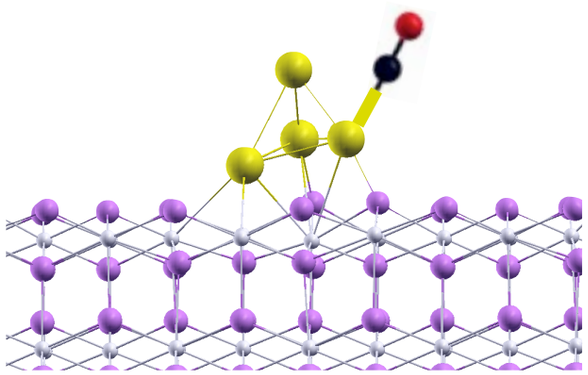
- [ ] Screening techniques for finding new catalysts
  - Reaction descriptors - Volcano plots
  - Materials informatics

Examples

Homogeneous, reaction mechanism, role of environment

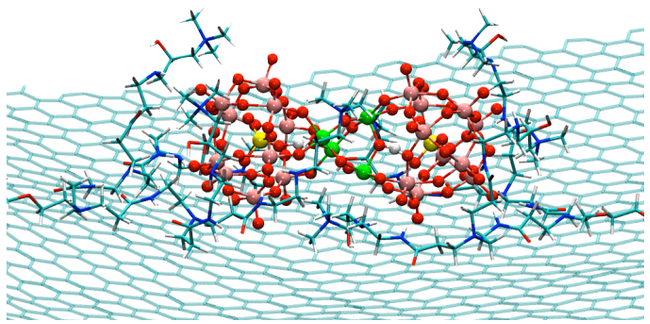


C. Ma, S. Piccinin, and SF
Reaction mechanisms of water splitting and H2 evolution by a Ru(II)-pincer complex identified with ab-initio metadynamics in explicit solvent
ACS Catalysis 2, 1500 (2012)



Heterogeneous, sub-nm supported, characterization, role of support

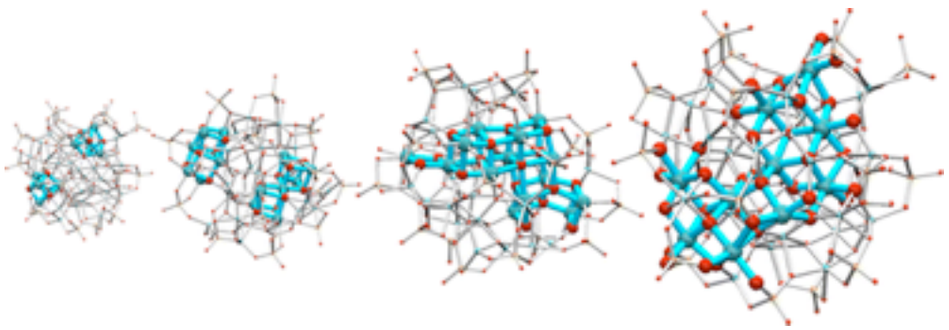
M. Farnesi Camellone and SF
Reaction Mechanisms for the CO Oxidation on Au/CeO2 catalysts: Activity of Substitutional Au3+/Au+ Cations and Deactivation of Supported Au+ Adatoms
J. Am. Chem. Soc. 131, 10473 (2009)



Homogeneous/Heterogeneous, functionalized surfaces, characterization, reaction mechanism, role of environment

S. Piccinin, A. Sartorel, G. Aquilanti, A. Goldoni, M. Bonchio, and SF
Water Oxidation Surface mechanisms replicated by a totally inorganic tetraruthenium-oxo complex
Submitted

Heterogeneous, characterization, structure prediction



H. L. Hu, S. Piccinin, A. Laio, and SF
Atomistic Structure of Cobalt-Phosphate Nanoparticles for Catalytic Water Oxidation
to appear in ACS Nano (2012)

Techniques and approaches

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based on modified FORCES

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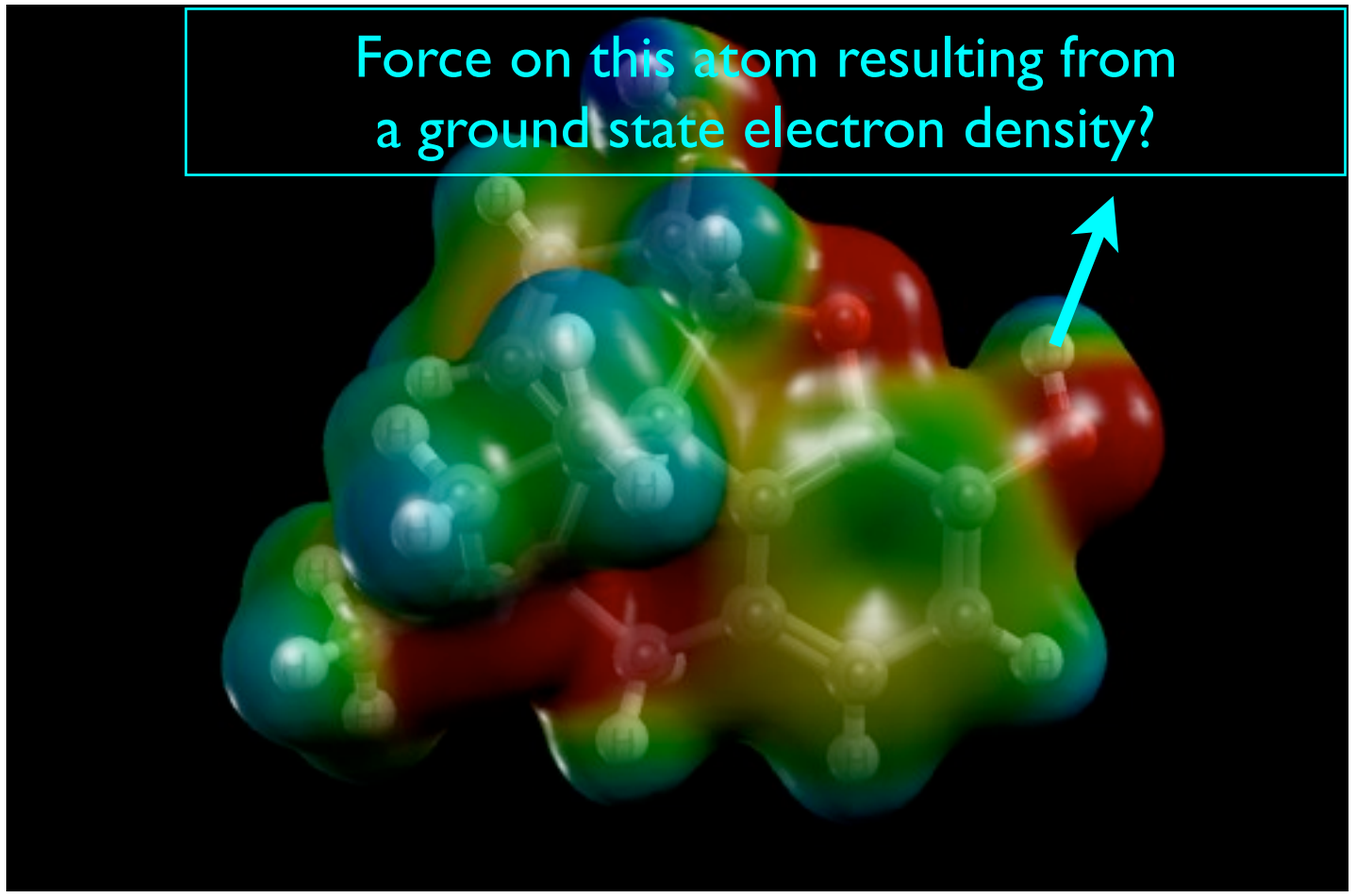
  - Reaction descriptors - Volcano plots
  - Materials informatics

Ab-initio interatomic forces

Interatomic forces are central in computational catalysis (rare events, reactions ...)



Hellmann-Feynman theorem

Energy variations are second order in the electron density

$$\mathbf{F}_I = -\frac{\partial E}{\partial \mathbf{R}_I} = \left\langle \Psi_{\mathbf{R}} \middle| \frac{\partial H}{\partial \mathbf{R}_I} \middle| \Psi_{\mathbf{R}} \right\rangle$$

Interatomic forces can be calculated on the basis of the ground state density only

- Simulating rare (activated) events
  - Minimum energy paths - NEB
  - Beyond MD - Metadynamics

based on modified FORCES

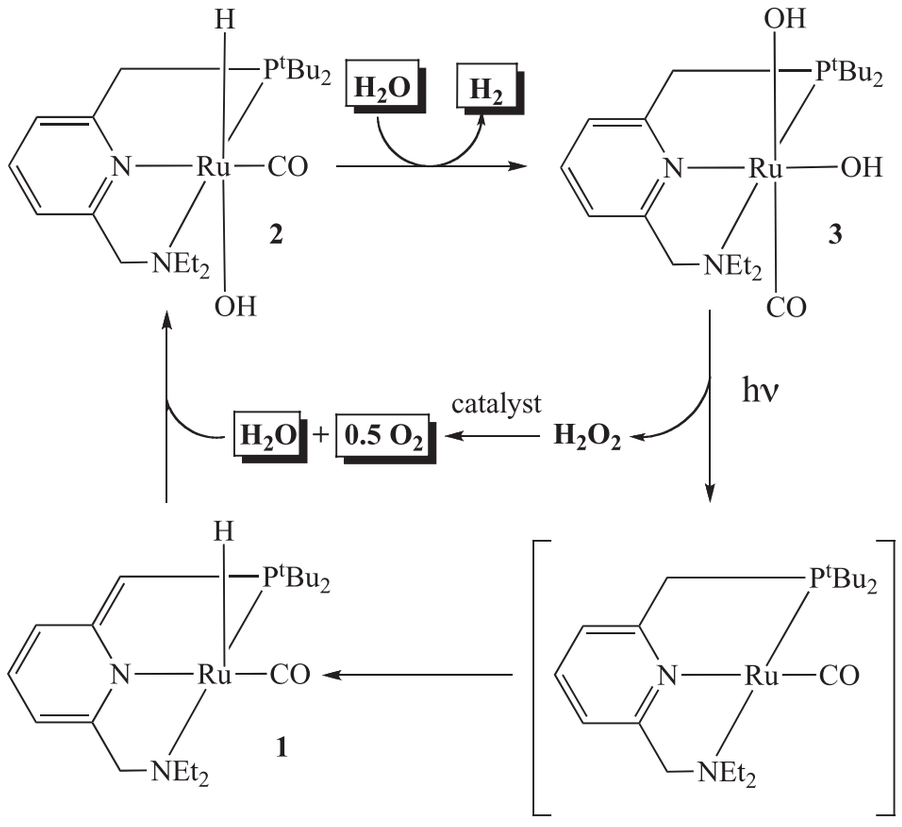
Ab-initio MD?

3 APRIL 2009 VOL 324 SCIENCE

Science
AAAS

Consecutive Thermal H_2 and Light-Induced O_2 Evolution from Water Promoted by a Metal Complex

Stephan W. Kohl,[1] Lev Weiner,[2] Leonid Schwartsburd,[1] Leonid Konstantinovski,[2] Linda J. W. Shimon,[2] Yehoshoa Ben-David,[1] Mark A. Iron,[2] David Milstein[1]*



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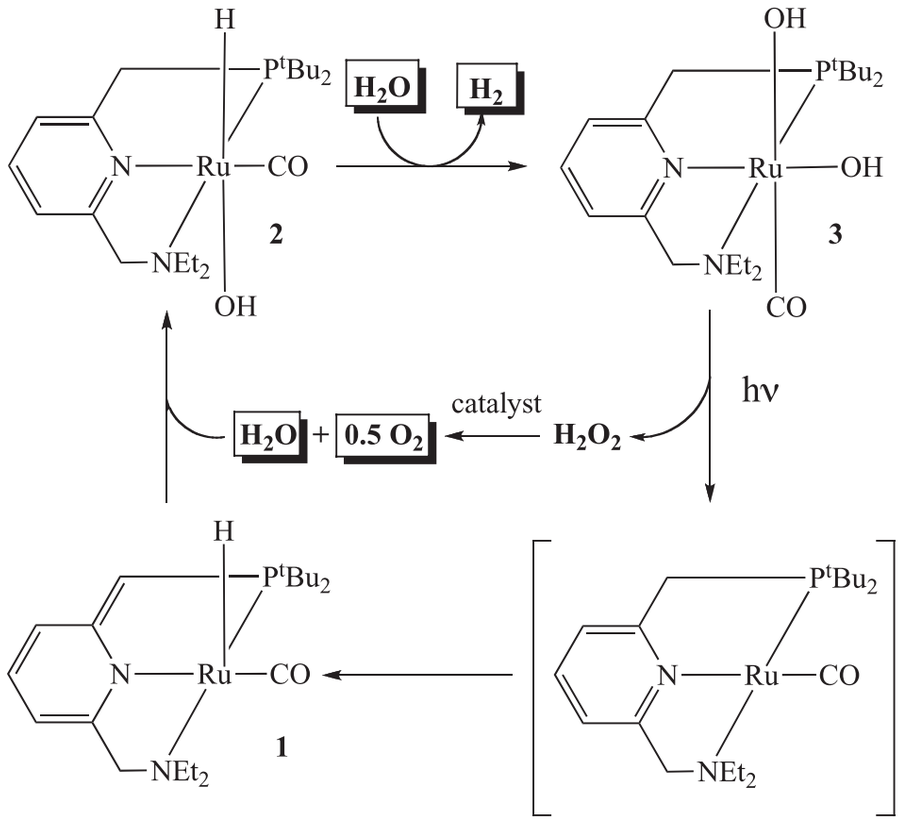


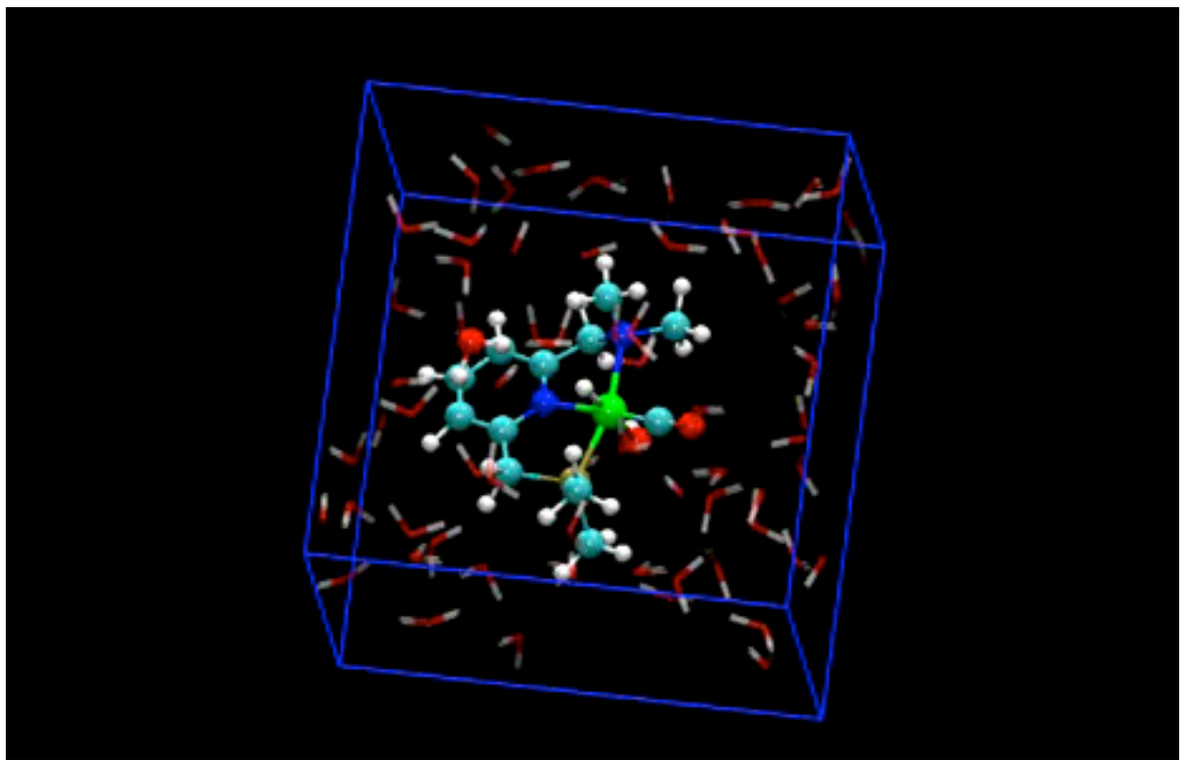
ACS Catalysis

Research Article

pubs.acs.org/acscatalysis

Reaction Mechanisms of Water Splitting and H_2 Evolution by a Ru(II)-Pincer Complex Identified with Ab Initio Metadynamics Simulations

Changru Ma,[†] Simone Piccinin,[‡,†] and Stefano Fabris*[,‡,†,§]



Ab-initio MD of reactants

... and wait for reaction to occour

Ab-initio MD?

3 APRIL 2009 VOL 324 SCIENCE

Science
AAAS

Consecutive Thermal H_2 and Light-Induced O_2 Evolution from Water Promoted by a Metal Complex

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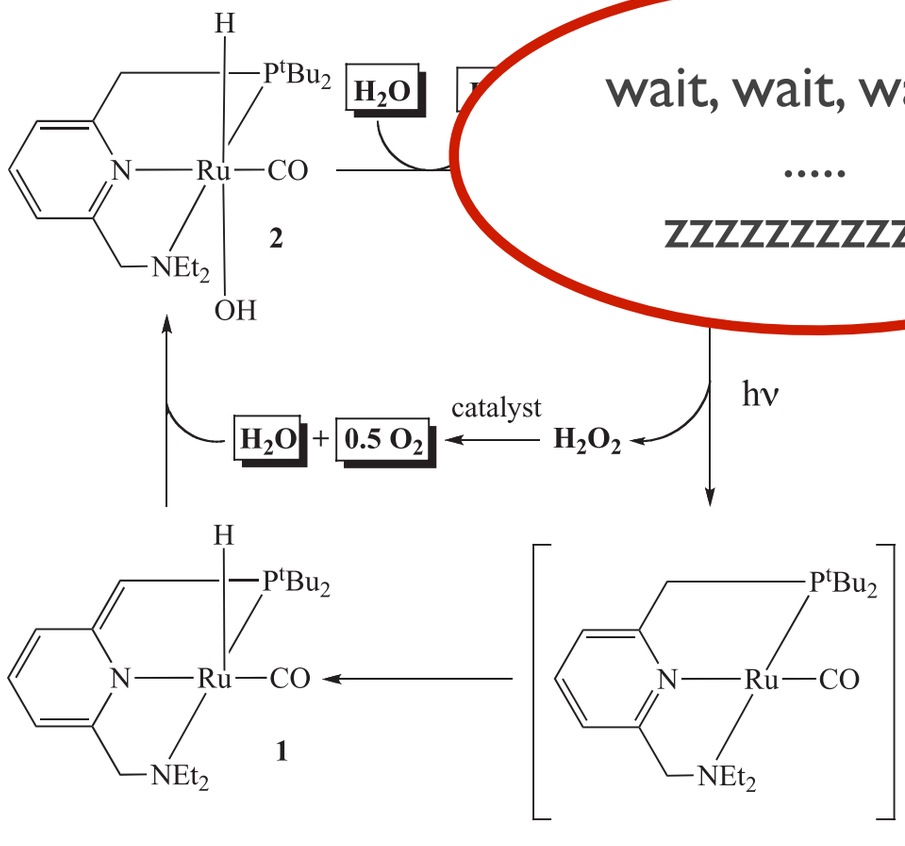

wait, wait, wait, ...

.....

ZZZZZZZZZZZ

Research Article

pubs.acs.org/acscatalysis

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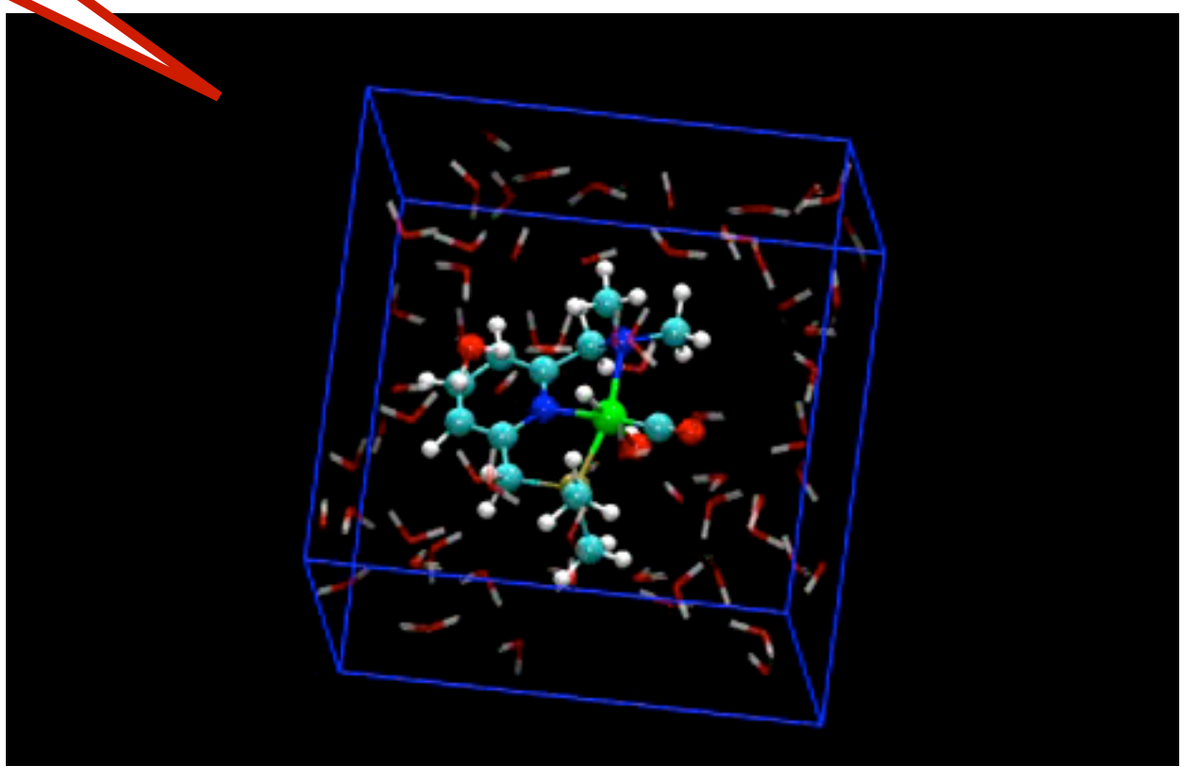
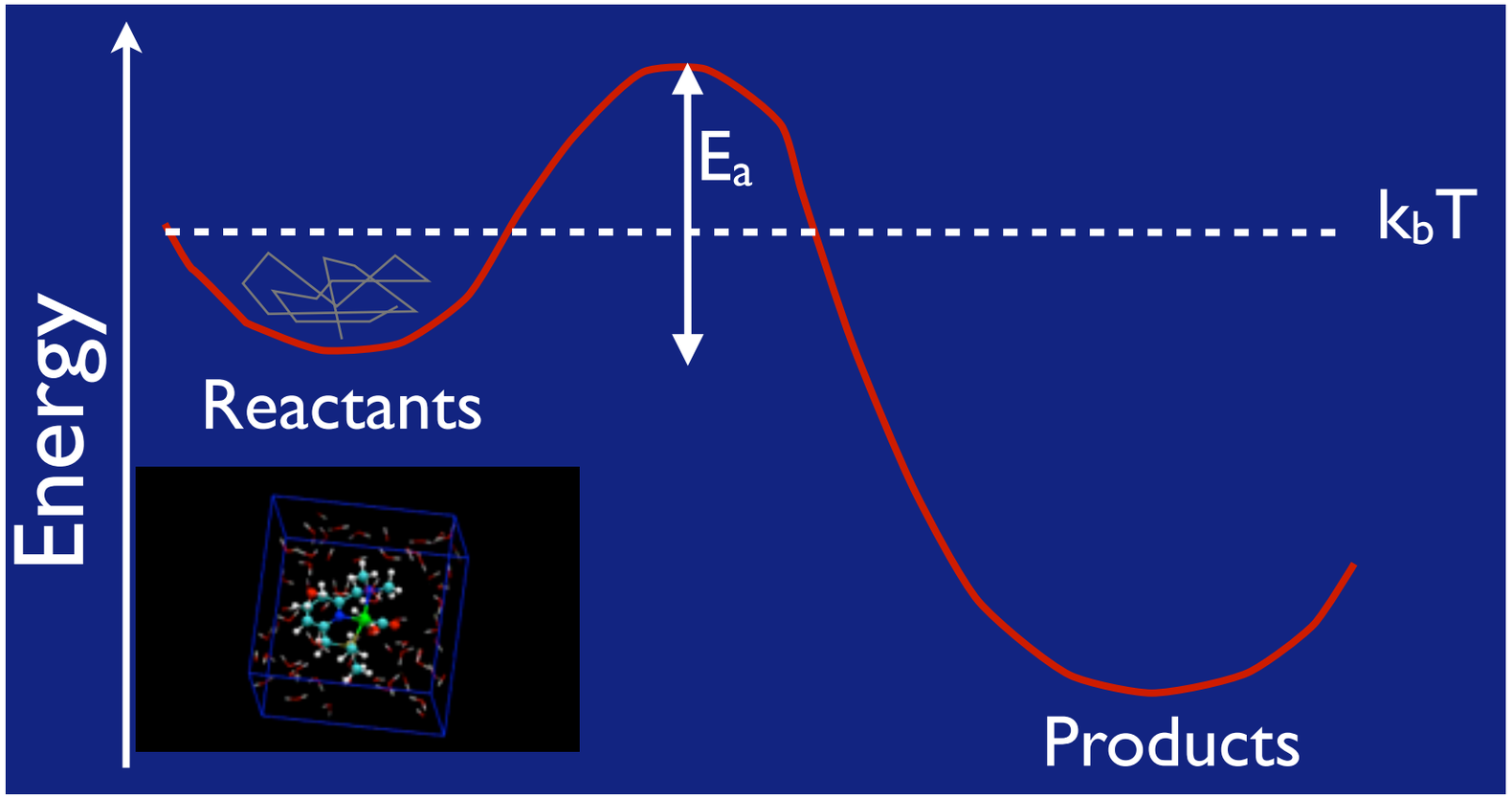


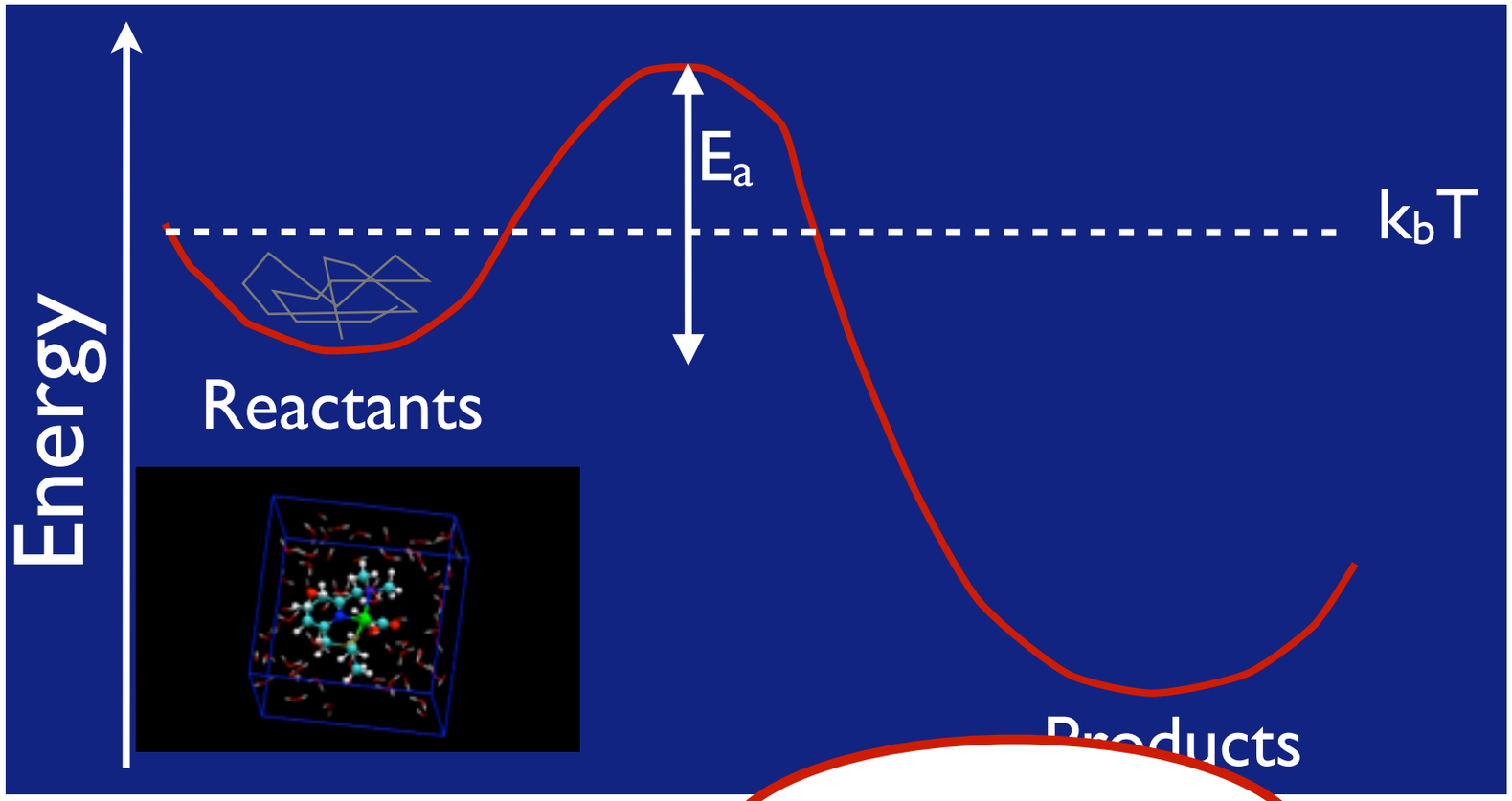
Ab-initio MD of reactants

... and wait for reaction to occour

Rare events: Arrhenius

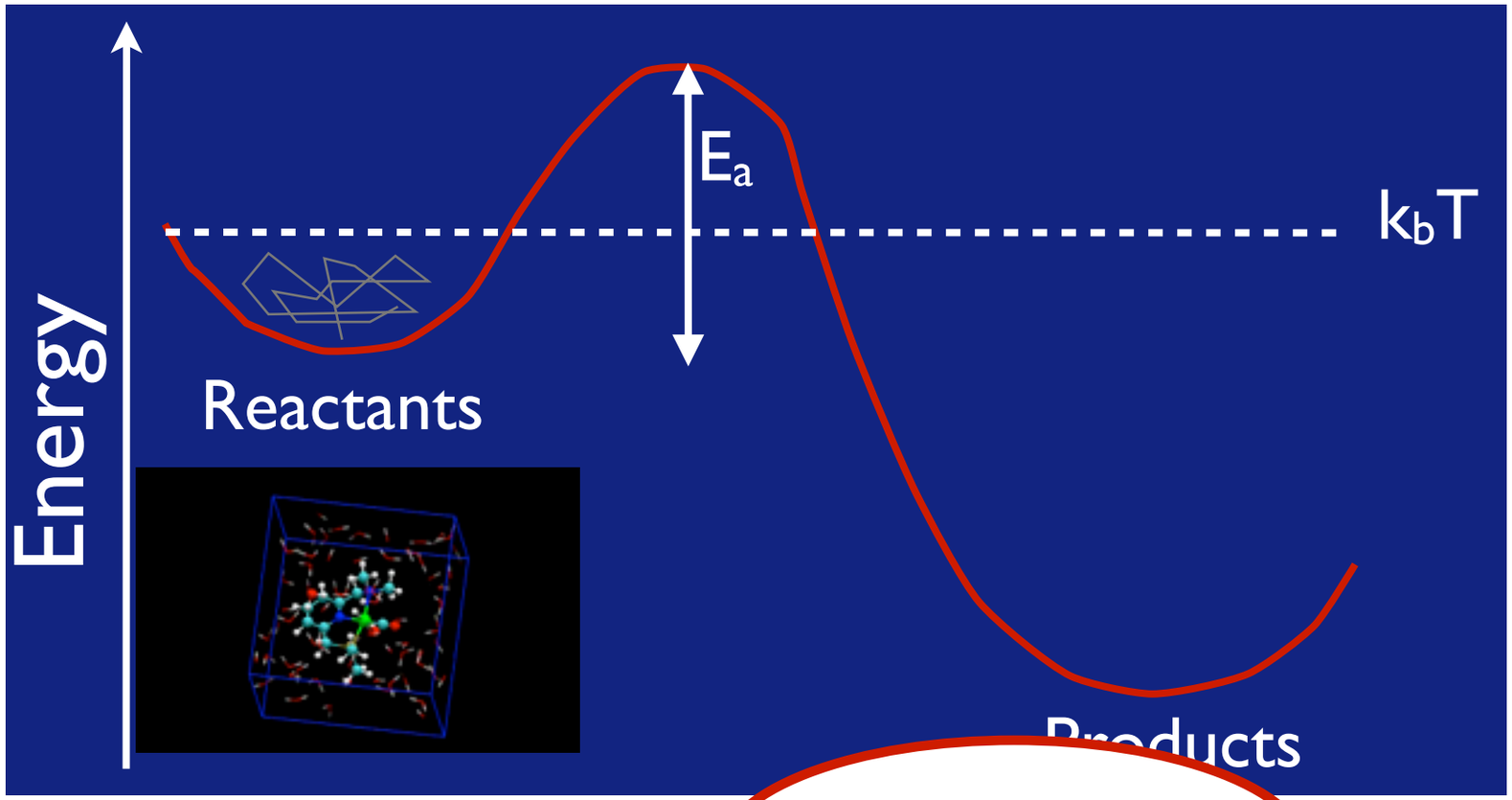


Rare events: Arrhenius



Dynamics display oscillations about the equilibrium $\nu_0 \propto \sqrt{\frac{d^2V}{dx^2}}$

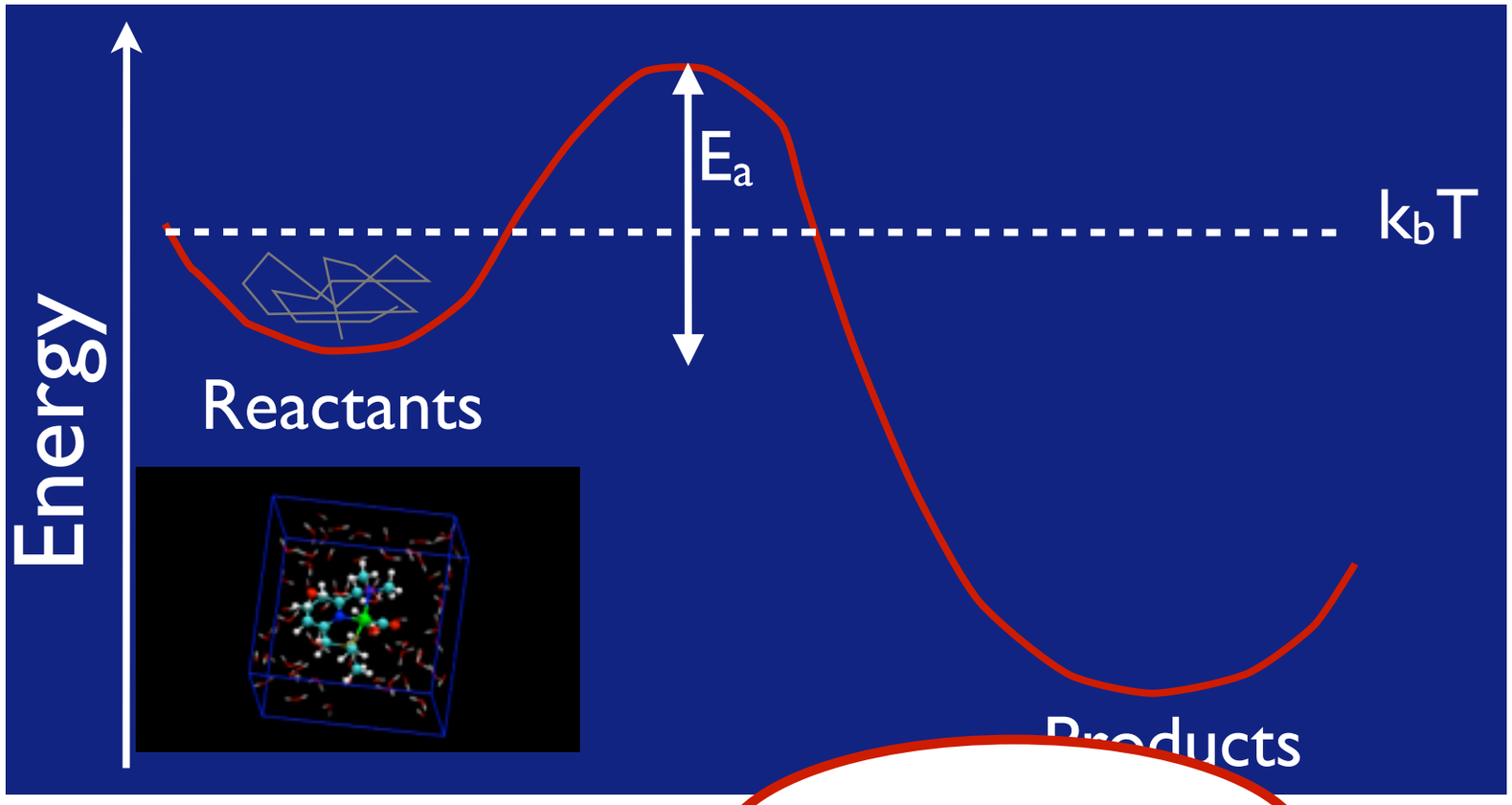
Rare events: Arrhenius



Dynamics display oscillations about the equilibrium $\nu_0 \propto \sqrt{\frac{d^2V}{dx^2}}$

Finite probability of transition for each attempt $e^{-\frac{E_a}{k_b T}}$

Rare events: Arrhenius



Dynamics display oscillations about the equilibrium

# of attempts / s

$$\nu_0 \propto \sqrt{\frac{d^2 V}{dx^2}}$$

Finite probability of transition for each

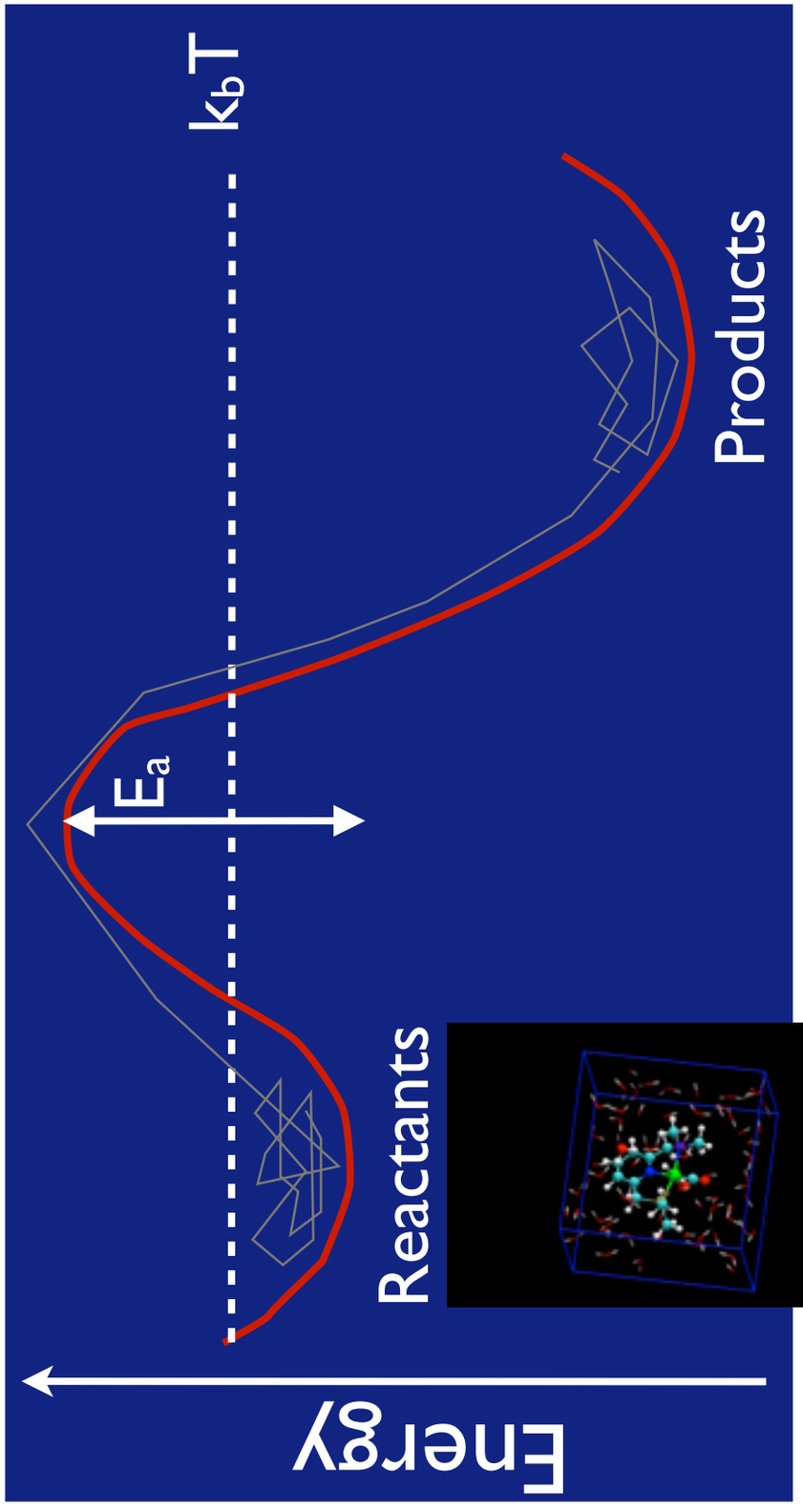
$$e^{-\frac{E_a}{k_b T}}$$

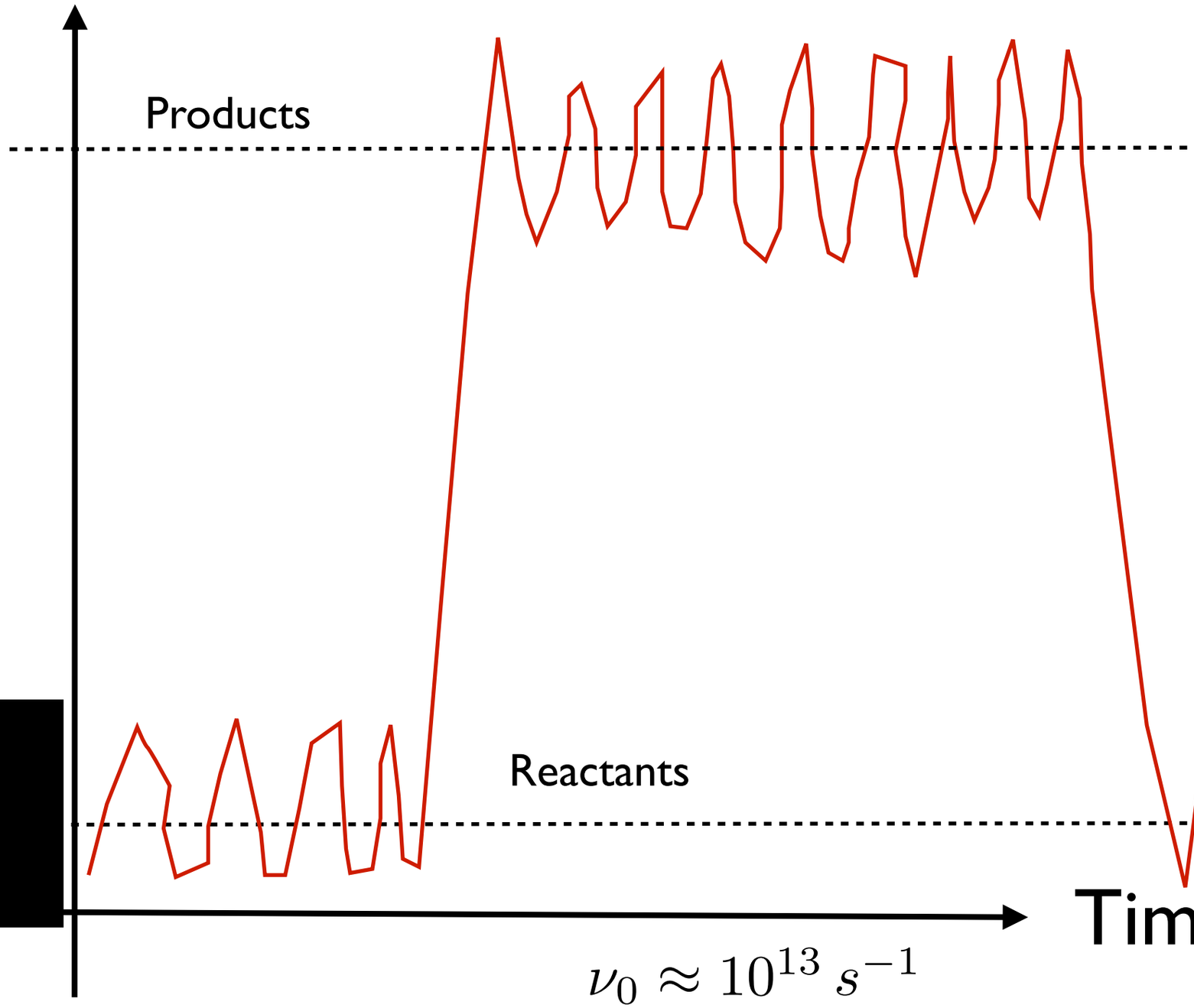
rate constant
Arrhenius

Number of transitions per unit of time

$$k = \nu_0 \, e^{-\frac{E_a}{k_b T}}$$

Rare events





$$k = \nu_0 \, e^{-\frac{E_a}{k_b T}}$$

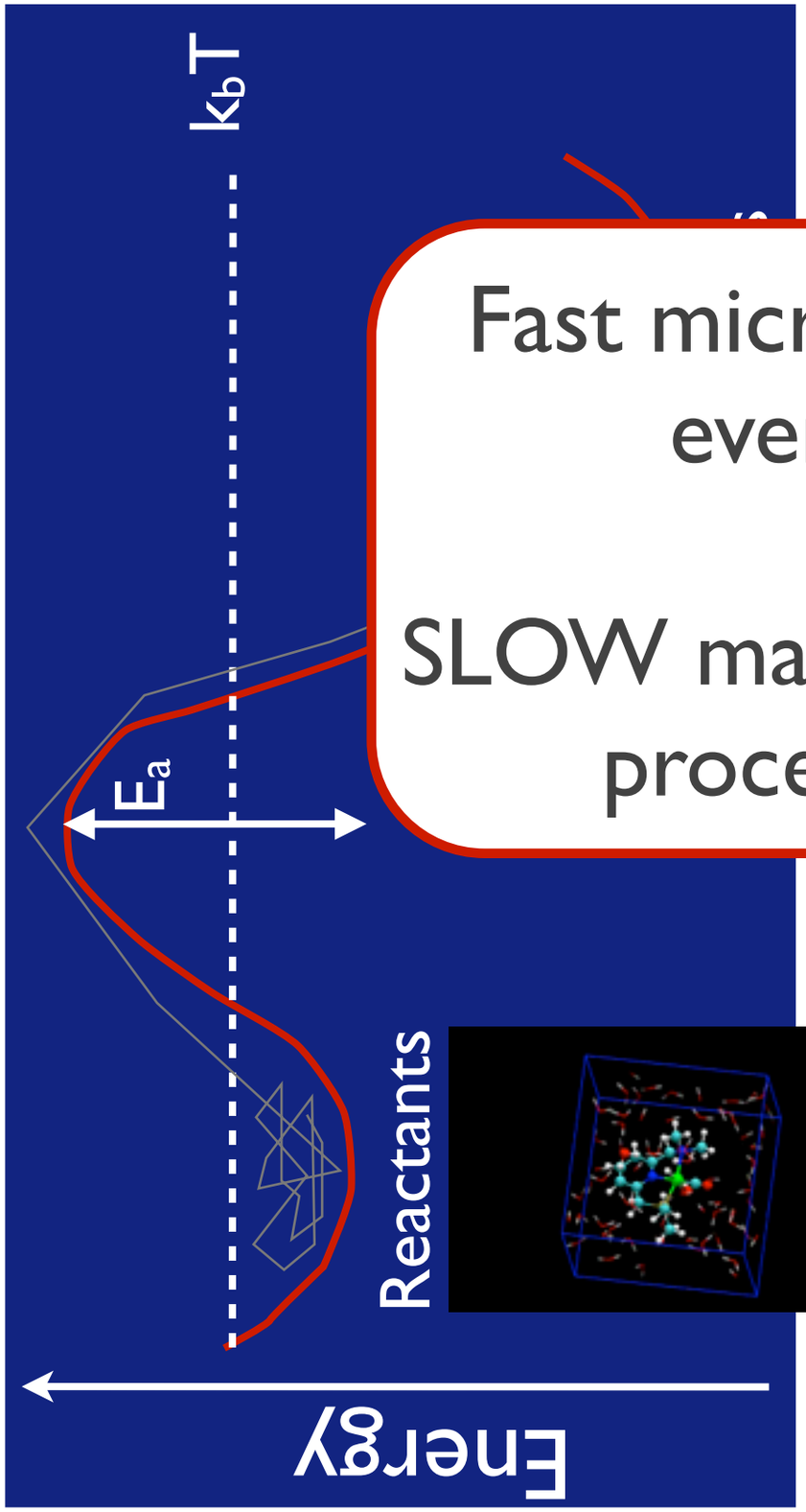
$$\nu_0 \approx 10^{13}\, s^{-1}$$
$$E_a = 0.75eV$$
$$T = 300K$$

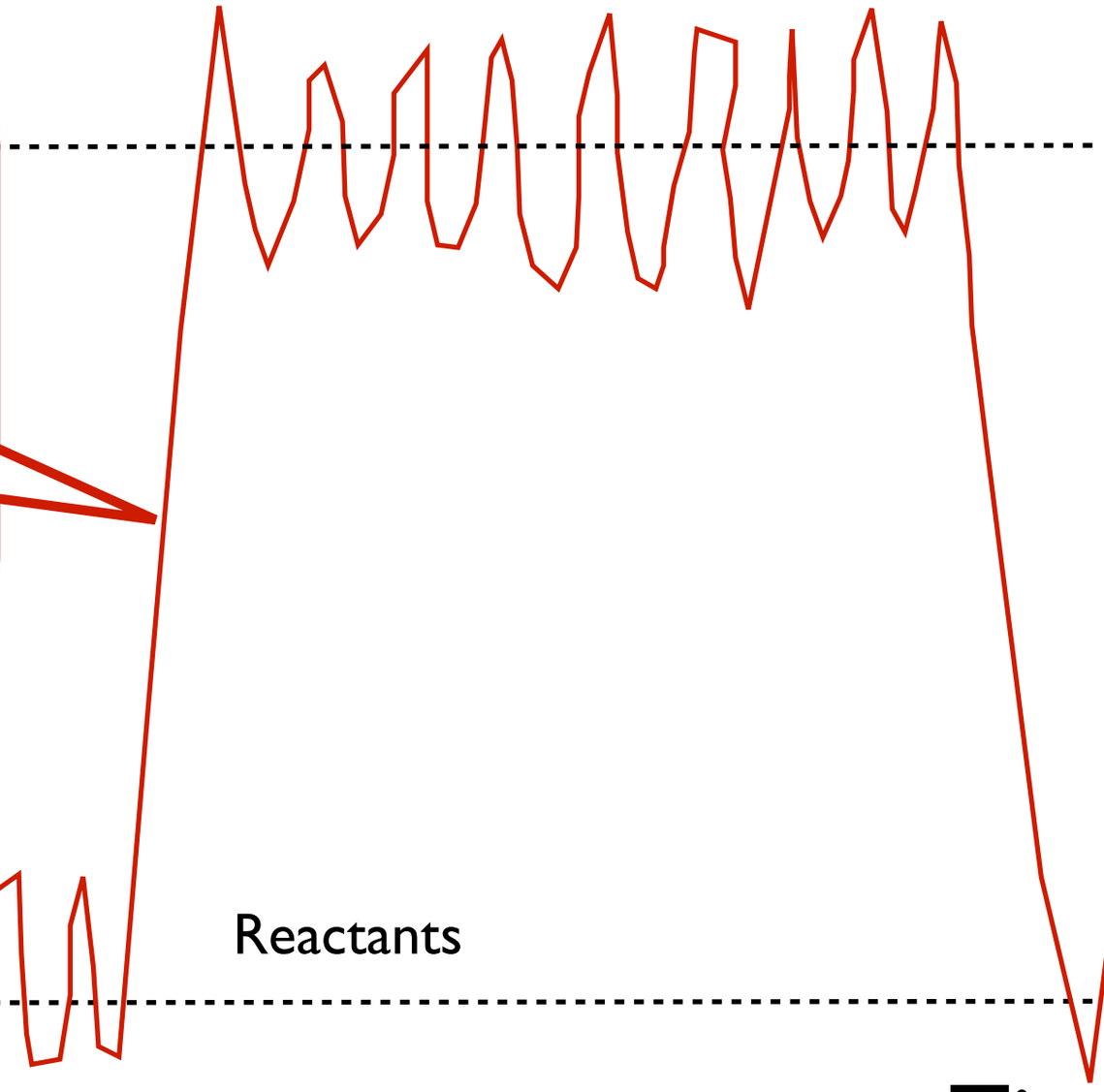
$$k \approx 1\, s^{-1}$$

Rare events

Fast microscopic events

SLOW macroscopic processes





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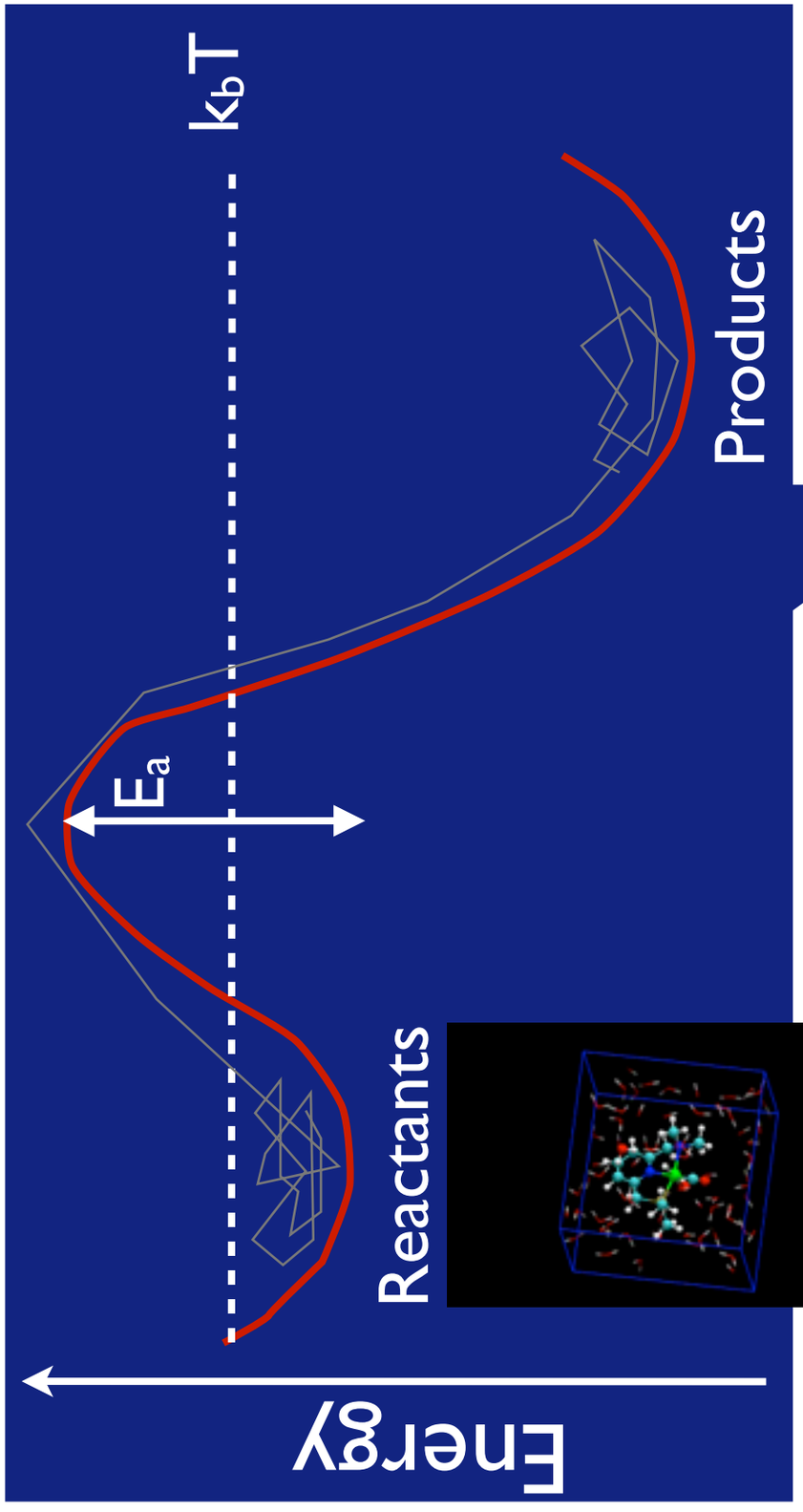

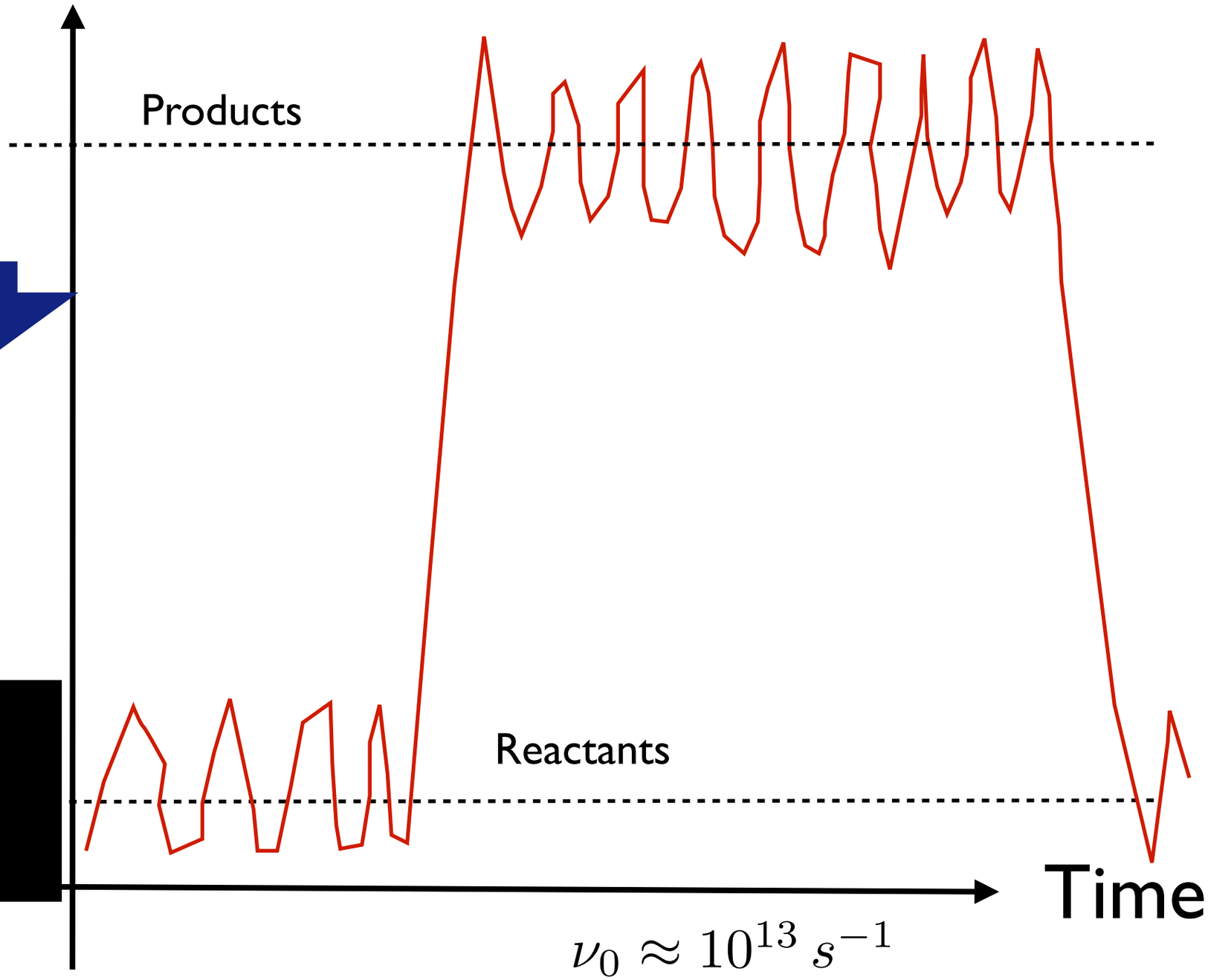

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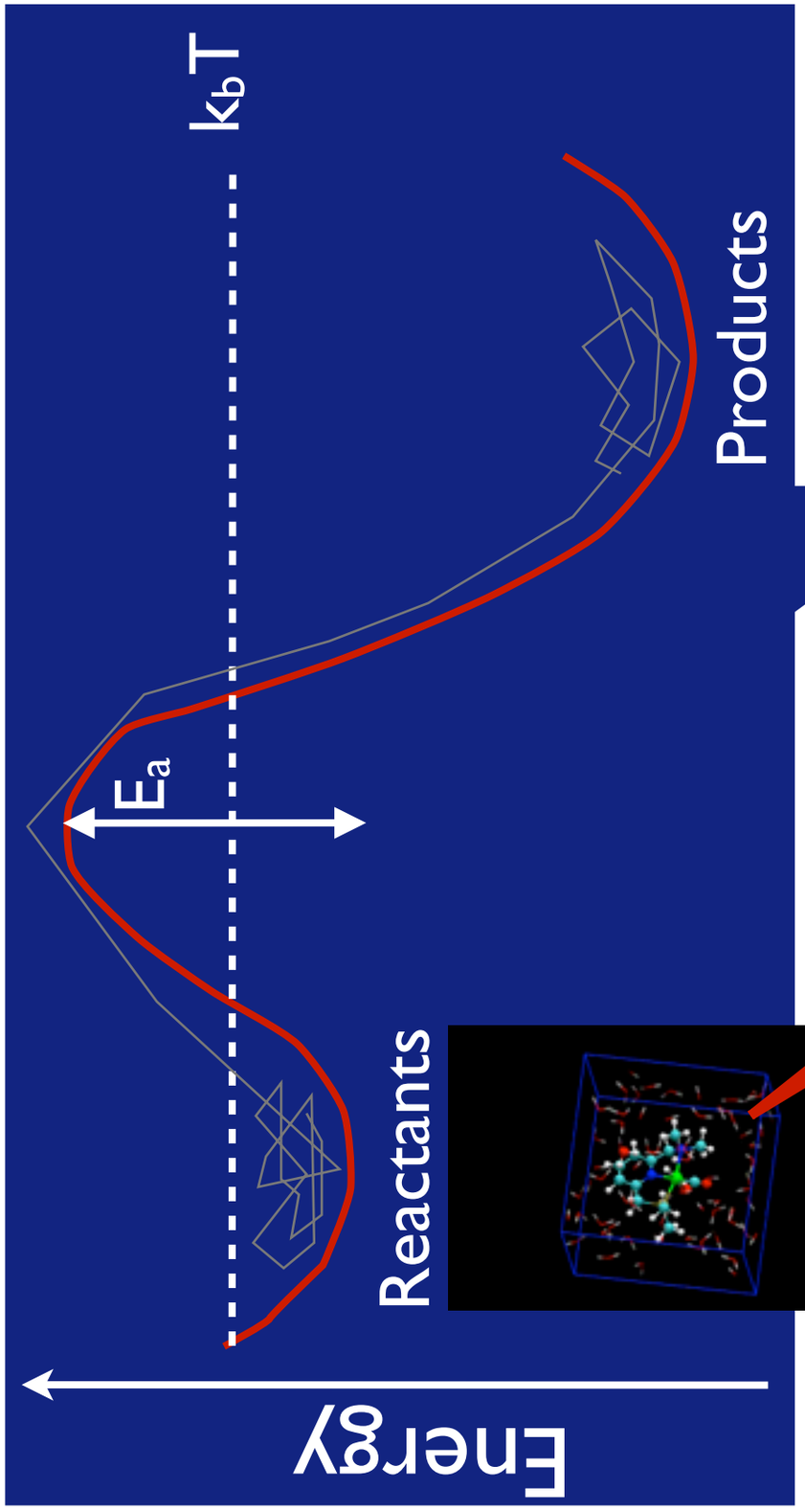
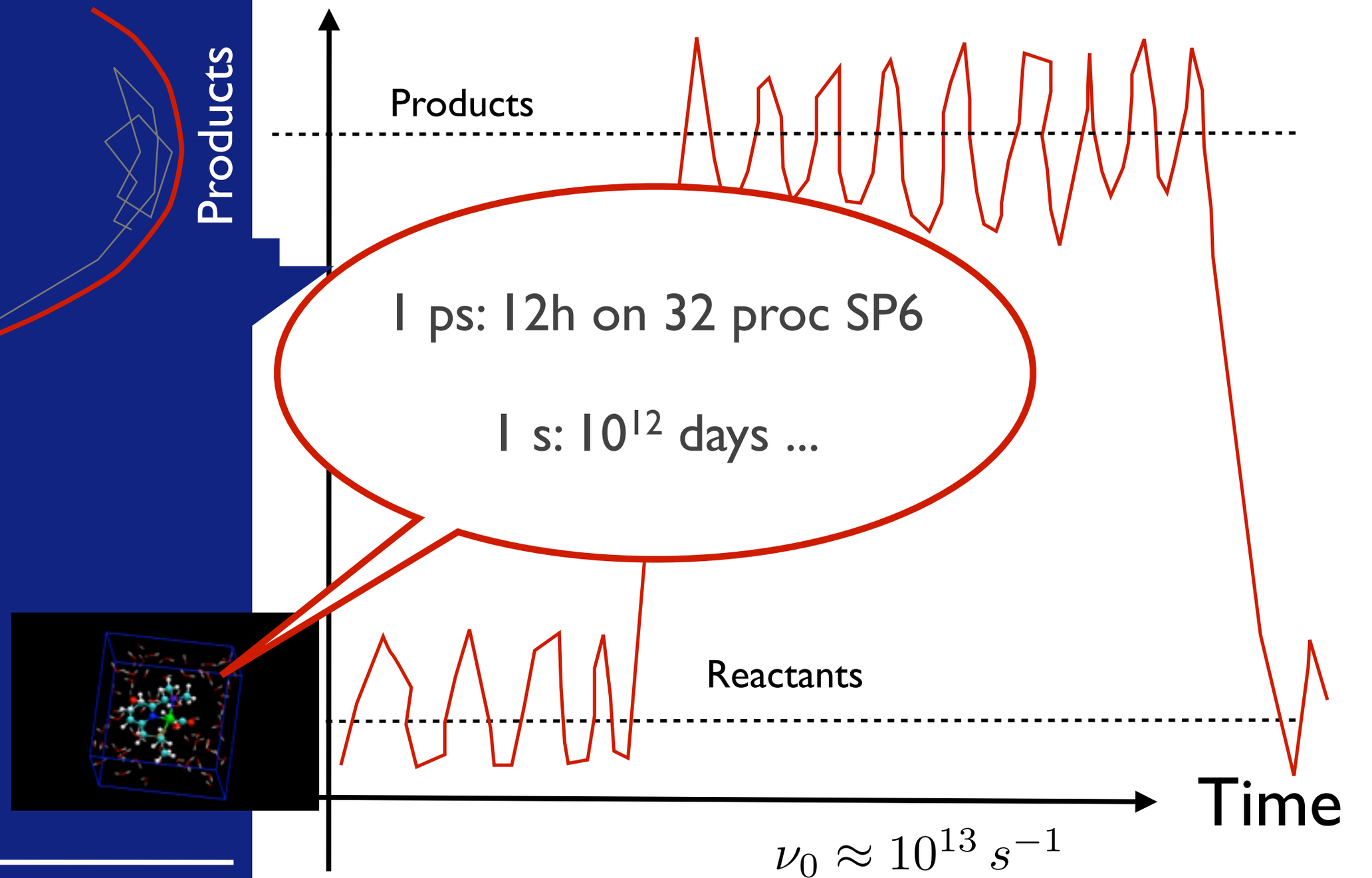
time-step~0.1 fs ; 1 transition in 10^{16} MD steps

Reaction rates NOT compatible with MD time scales

Rare events





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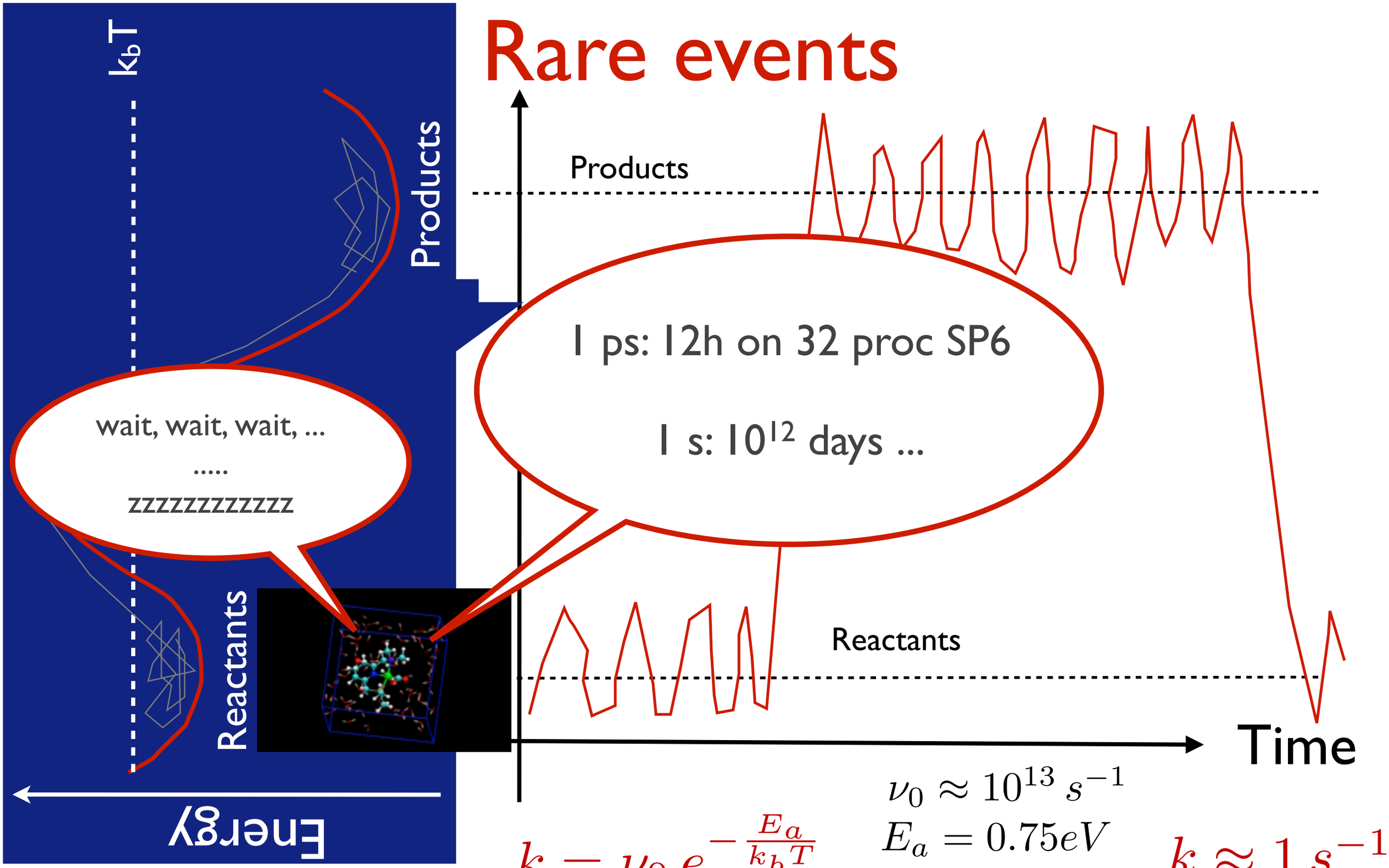

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time-step~0.1 fs ; 1 transition in 10^{16} MD steps

Reaction rates NOT compatible with MD time scales

Thermally activated processes

& relevance to renewable energies materials

Diffusion (e.g. I3- ions in DSSC, proton diffusion in electrolytic cells, Li in batteries, FC...)

Chemical reactions (e.g.CO oxidation, NOx reduction, steam reforming, WGS, ...)

Electron injection at interfaces (e. g. DSSC, electrodes for water OX, ...)

Carrier concentration in semiconductors (e.g.photoexitation, exitons...)

Carrier conductivity in insulators (e.g. charge percolation in DSSC, ...)

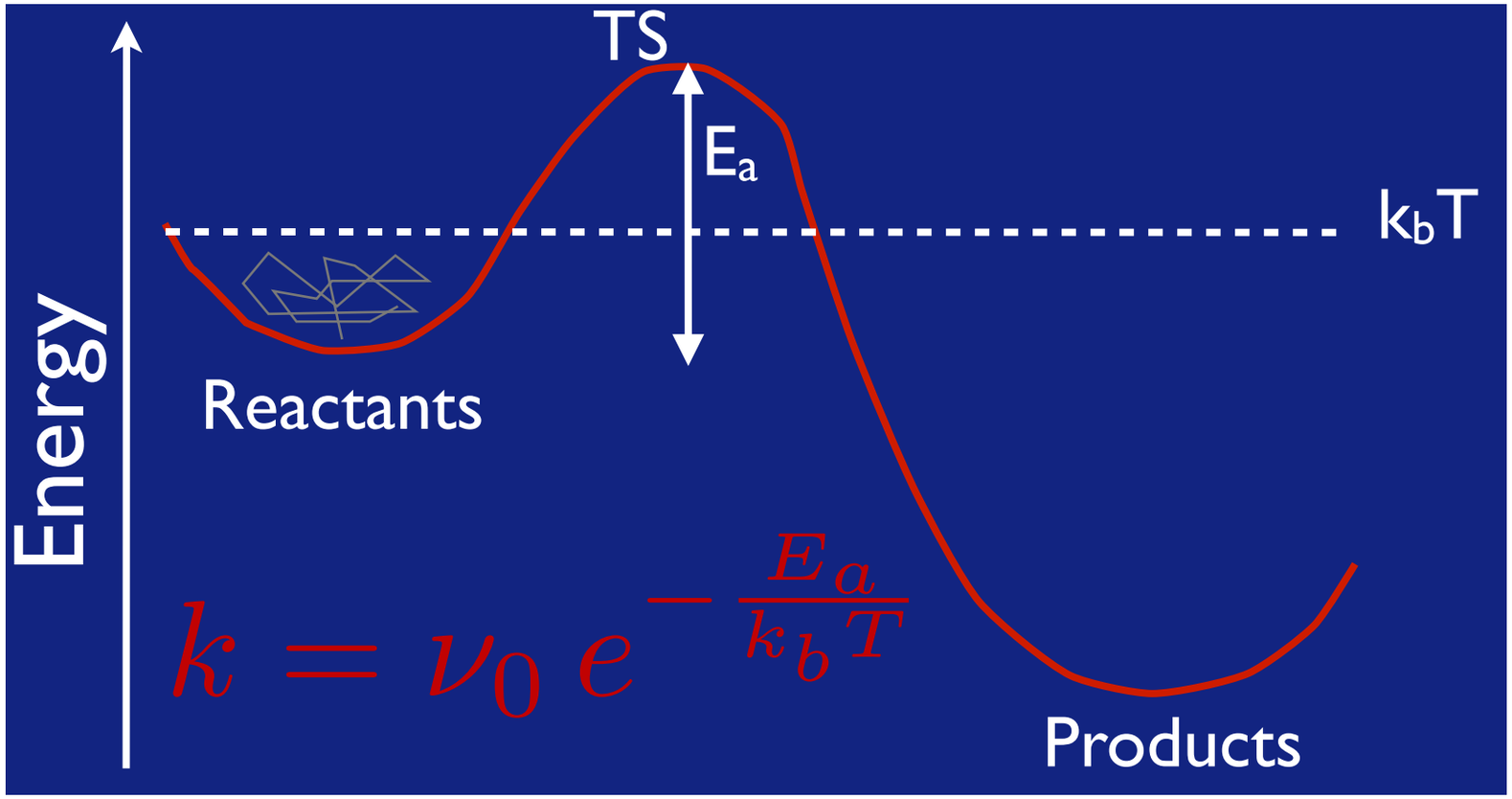
Materials growth, ...

Numerical modeling of ***rare events*** requires methods beyond MD

Taking advantage of statistical mechanics

Harmonic Transition State Theory

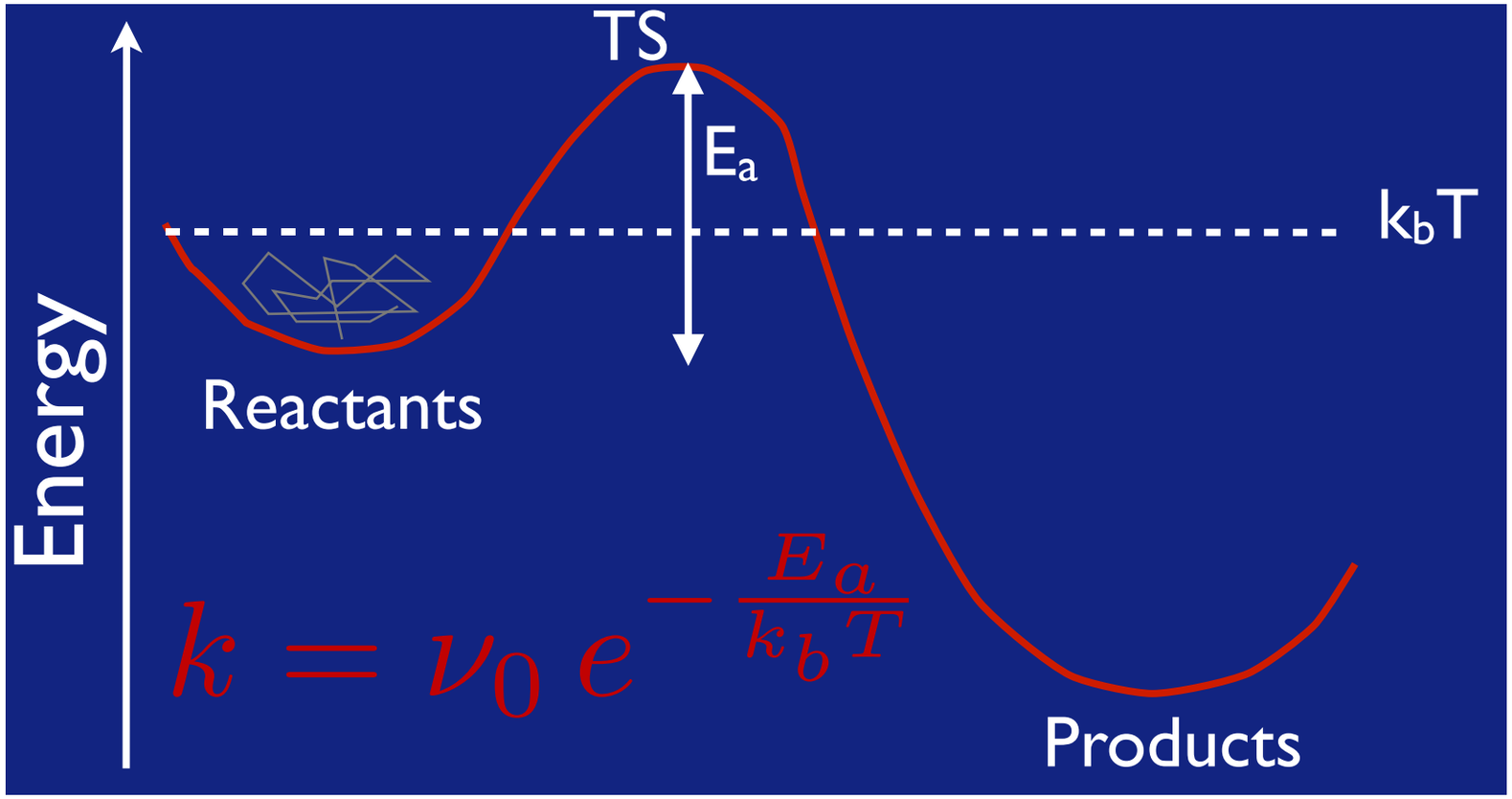
The rate of the process can be estimated using statistical mechanics



We need to determine ν_0, TS, and E_a

Harmonic Transition State Theory

The rate of the process can be estimated using statistical mechanics



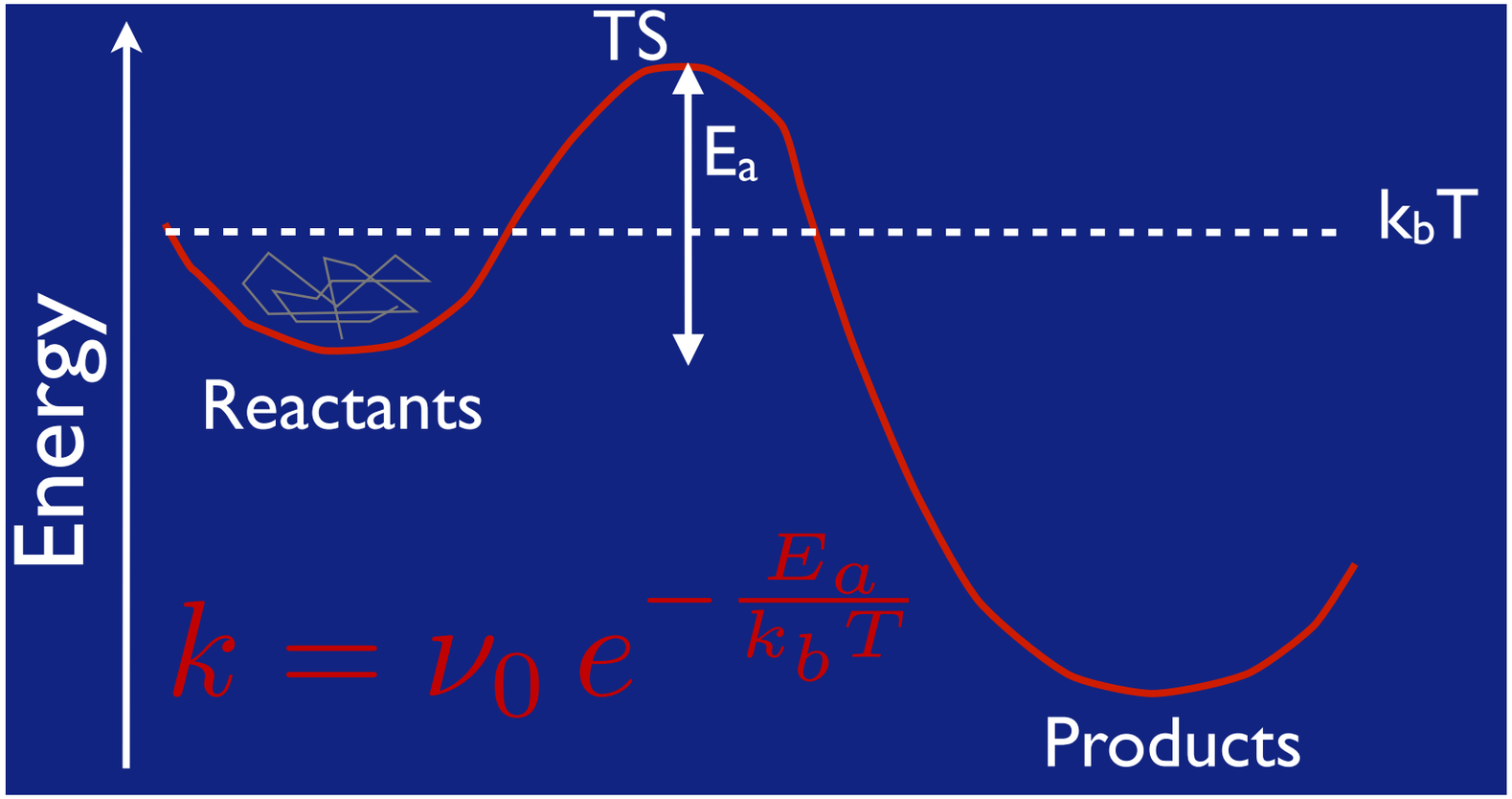
We need to determine ν_0, TS, and E_a

In TST ν_0 is approximated as $\nu_0 \approx \frac{\prod_{i=1}^{3N} \nu_i^{\text{reactants}}}{\prod_{i=1}^{3N-1} \nu_i^{TS}}$

EASY

Harmonic Transition State Theory

The rate of the process can be estimated using statistical mechanics



need to determine ν_0, TS, and E_a

all V'=0
all V"<0 but one

Identify the **TS**

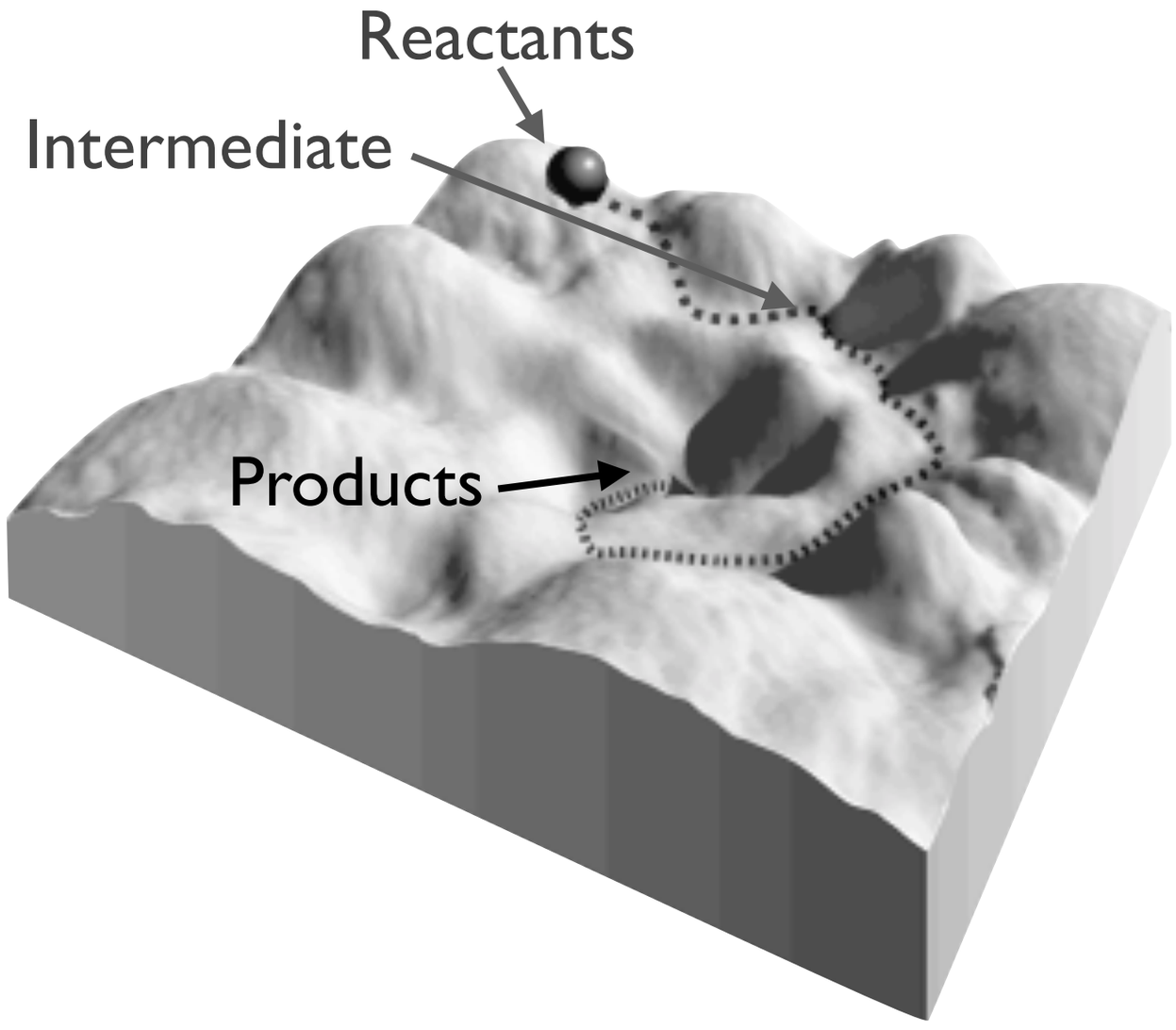
VERY HARD TASK

proximated as $\nu_0 \approx \frac{\prod_{i=1}^{3N} \nu_i^{\text{reactants}}}{\prod_{i=1}^{3N-1} \nu_i^{TS}}$

EASY

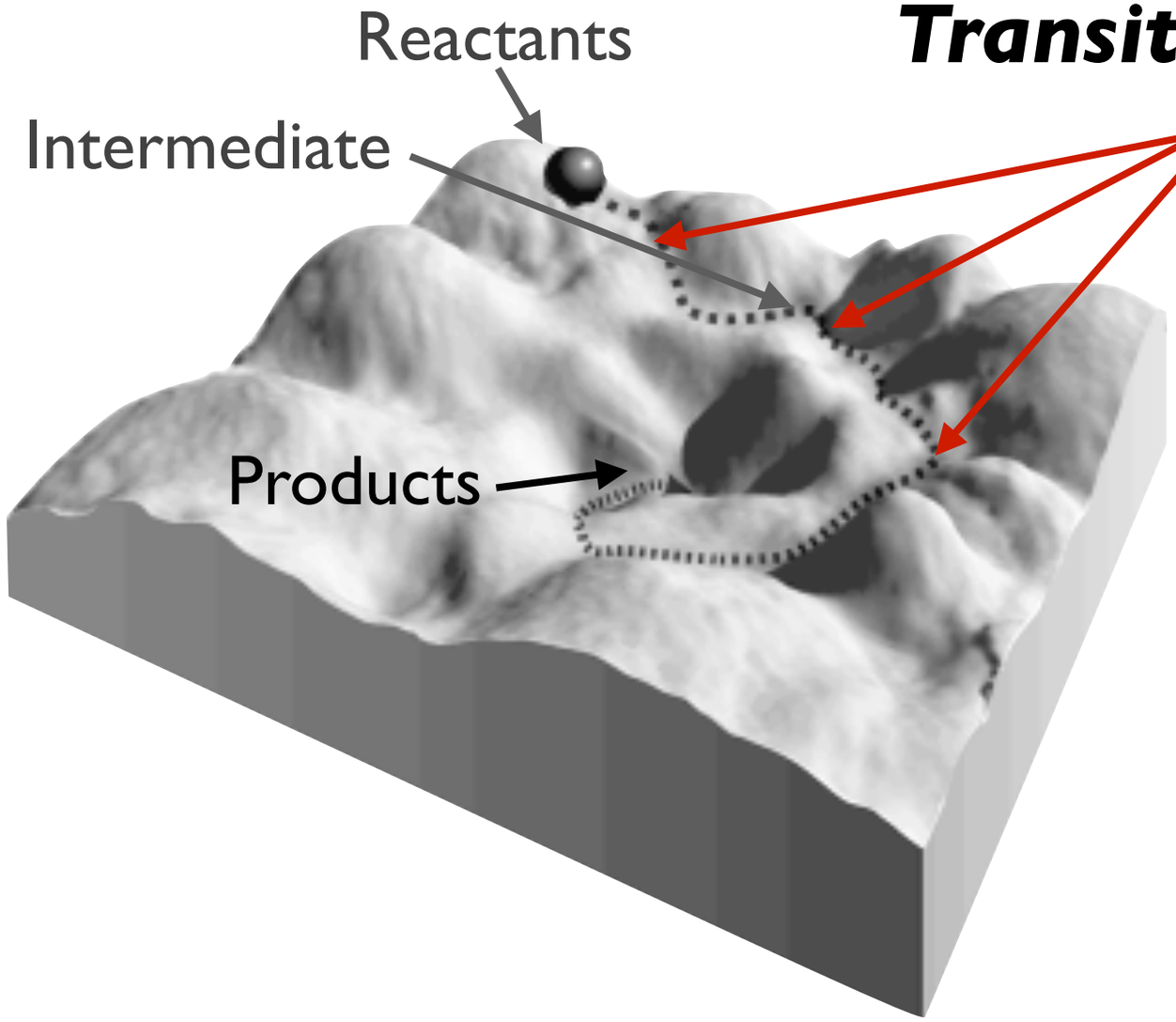
Identifying the TS

Exploring energy landscapes: Unknown and often multidimensional



Identifying the TS

Exploring energy landscapes: Unknown and often multidimensional

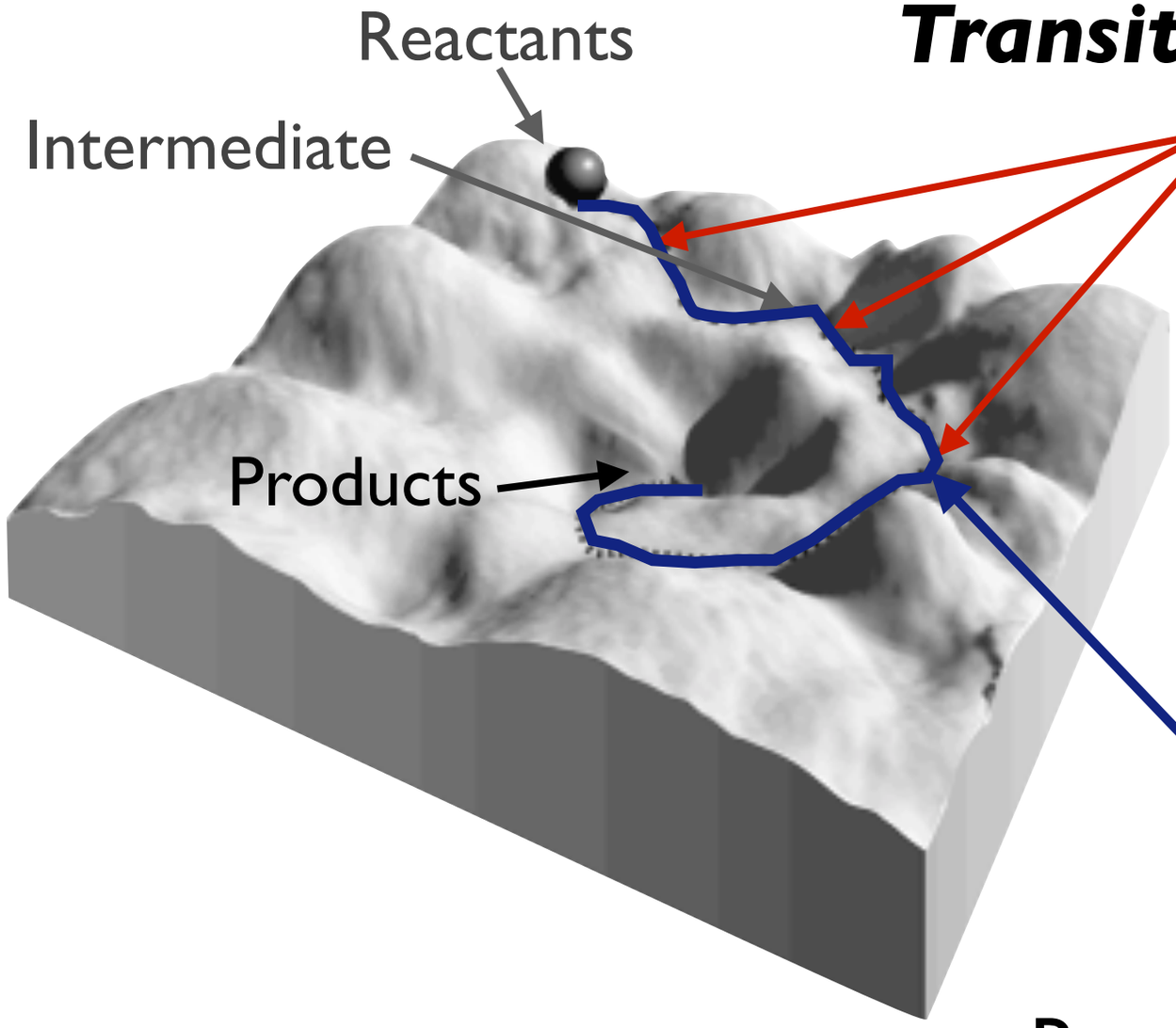


Transition States* = *saddle points

there may be more than one TS!

Identifying the TS

Exploring energy landscapes: Unknown and often multidimensional



Transition States* = *saddle points

there may be more than one TS!

Minimum Energy Path

Reaction path with the highest rate

It crosses the TS with the minimum Ea

Exploring energy landscapes

- Nudged Elastic Band (NEB)

Method for finding the MEP between IS (reactants) and FS (products) based on the calculation of atomic forces.

G.Mills and H.Jonsson, Phys. Rev. Lett. 72, 1124 (1994)
G.Henkelman and H.Jonsson, J. Chem. Phys. 133, 9978 (2000)

- Meta-dynamics (available in PLUMED)

Method for calculating the free energy landscape, unknown products, ... based on a biased dynamics in the space of a set of CVs.

A. Laio and M. Parrinello, PNAS 99, 12562 (2002)

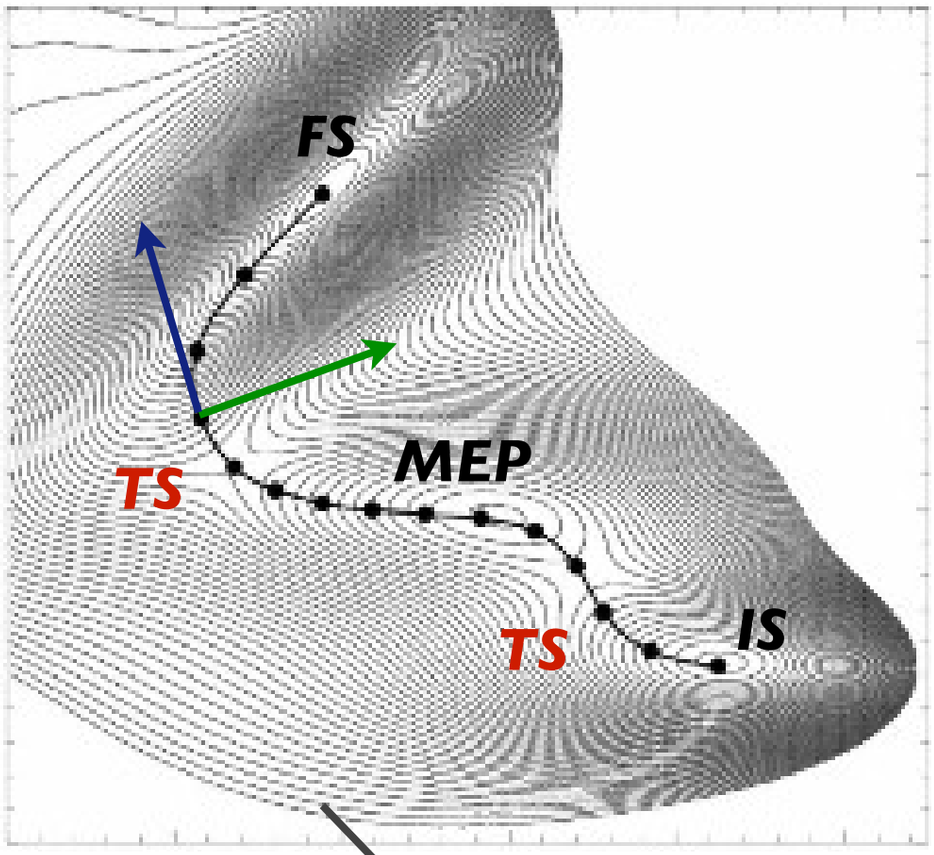
- Constrained minimization

- ...

Nudged Elastic Band - NEB

*Method for finding the **MEP** between IS (reactants) and FS (products) based on the calculation of atomic forces*

!! MUST KNOW IS AND FS !!



Minimum Energy Path

- Path with maximum rate
- Crosses all saddle points with minimum Ea
- Components of the forces ORTHOGONAL to the path are zero

!! E(Ri) is NOT known !!
MUST be sampled with single point calculations

Nudged Elastic Band - NEB

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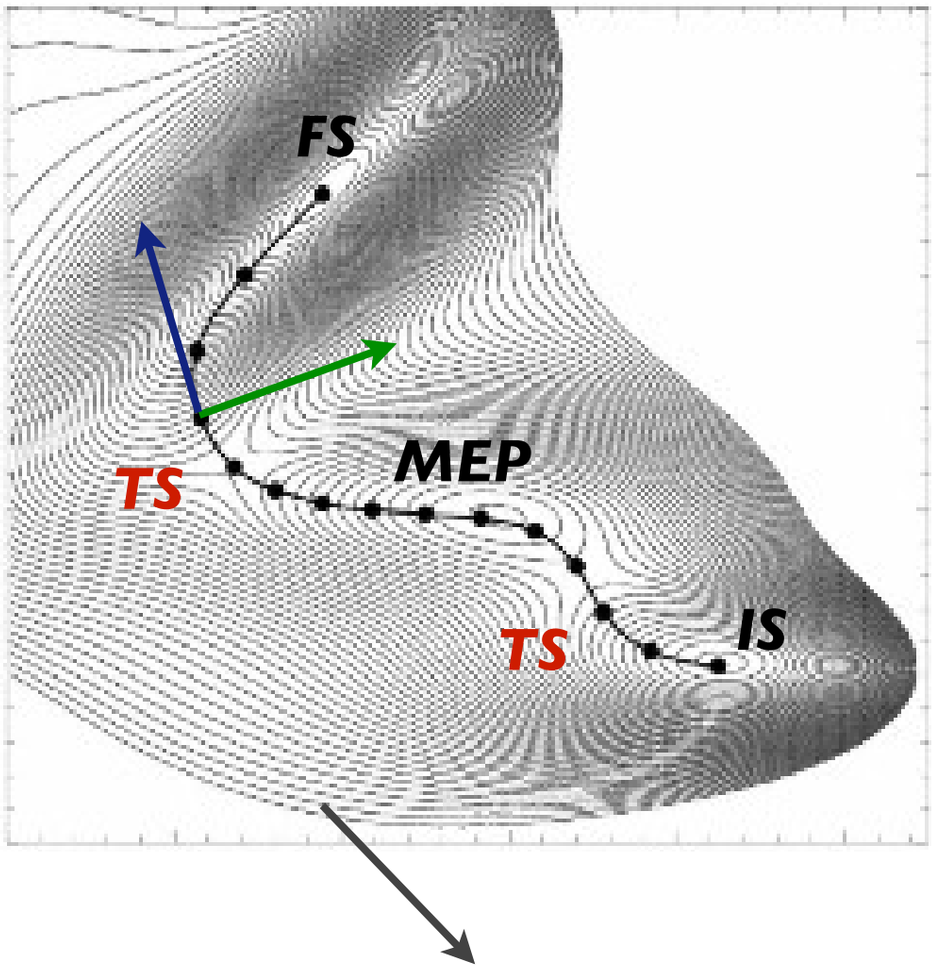

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Minimum Energy Path

- Path with maximum rate
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$$\mathbf{f}_{\parallel}^{i} = -\langle \nabla E(\mathbf{R}^{i}) \,|\tau^{i}\rangle \; \tau^{i}$$

$$\mathbf{f}_{\perp}^{i} = -(\nabla E(\mathbf{R}^{i}) \; - \; \langle \nabla E(\mathbf{R}^{i}) \,|\tau^{i}\rangle \; \tau^{i})$$

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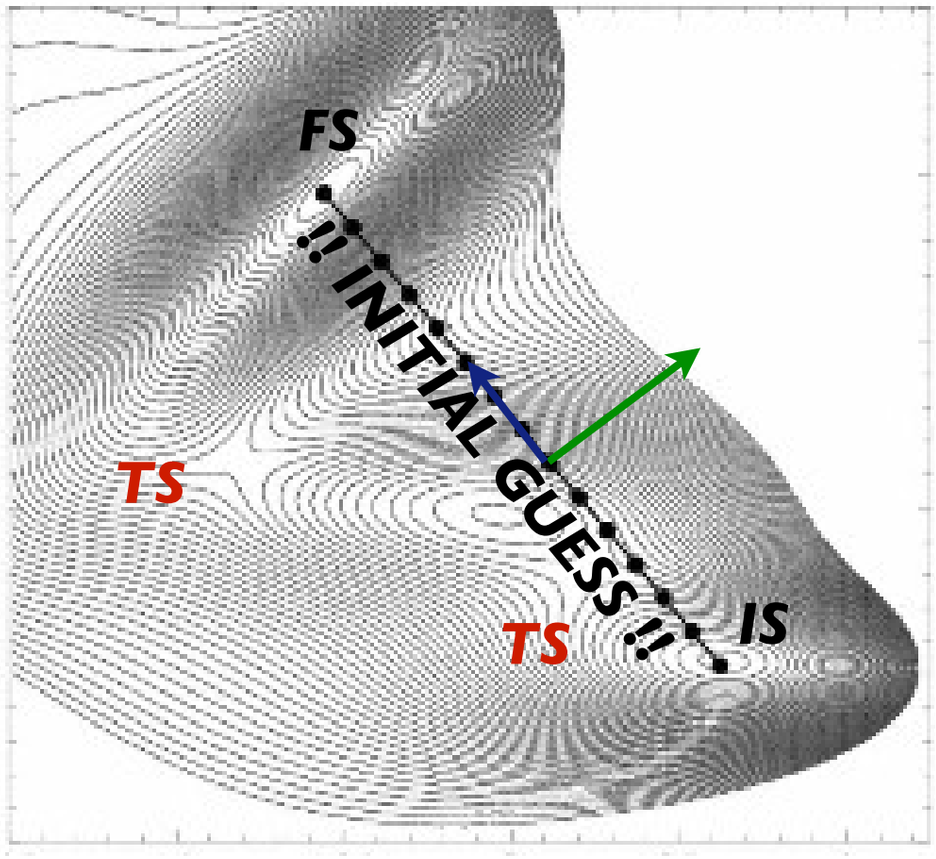

NEB condition

Components of the forces ORTHOGONAL to the path are zero

- Build a set of n replicas of the system connecting the IS and FS
- Calculate parallel and perpendicular components of the forces along the path

$$\mathbf{f}^i_{\parallel} = -\langle \nabla E(\mathbf{R}^i) \,|\tau^i\rangle \; \tau^i$$

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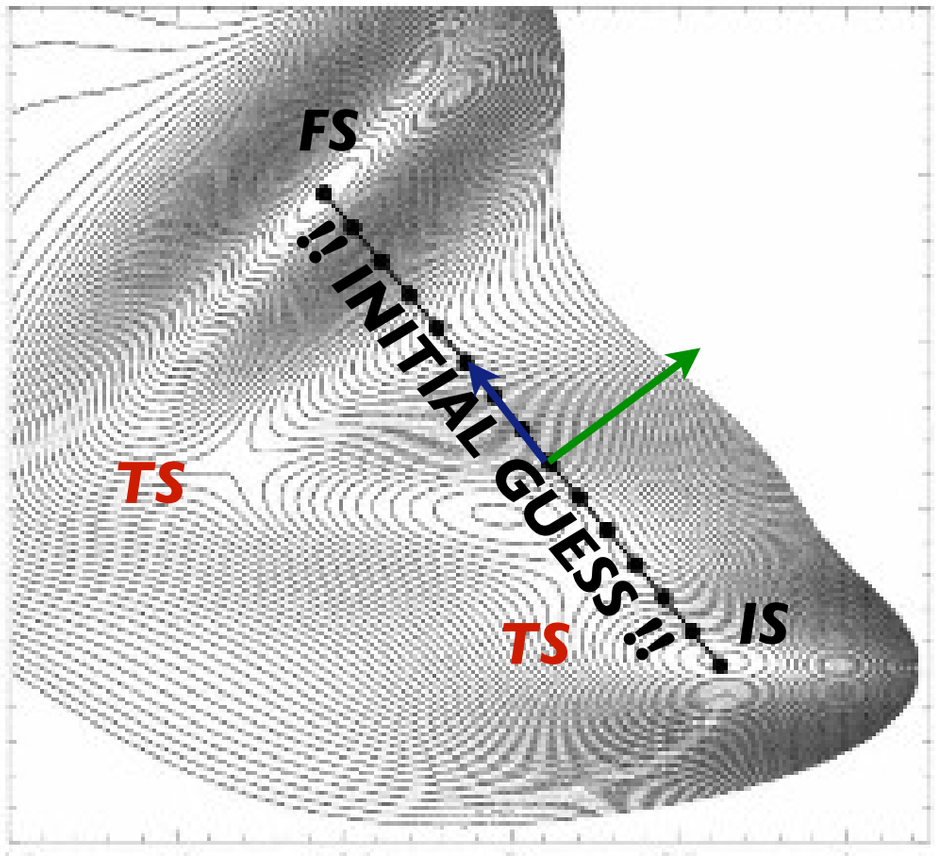

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- Add an harmonic interaction acting between adjacent images along path

$$\mathbf{F}^{i} = \mathbf{f}_{\perp}^{i} \; - \; \langle \nabla \left(\frac{1}{2} K \left(\mathbf{R}^{i} - \mathbf{R}^{i-1} \right)^{2} \right) \; | \tau^{i} \rangle \; \tau^{i}$$

Nudged Elastic Band - NEB

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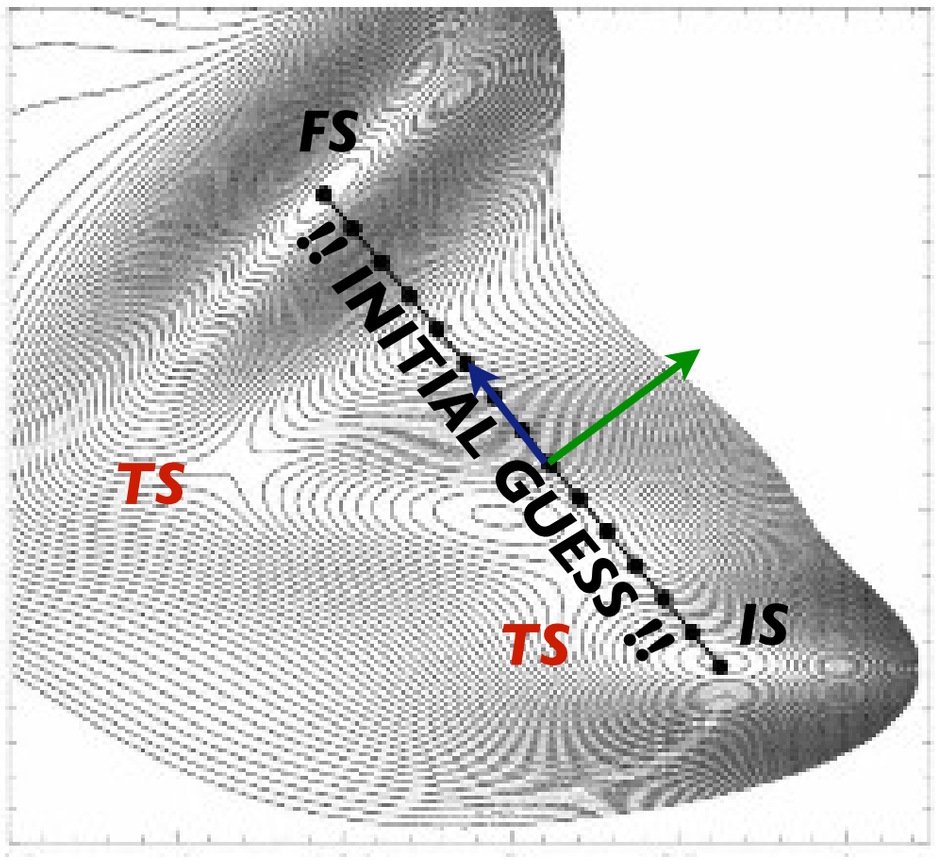

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Components of the forces ORTHOGONAL to the path are zero

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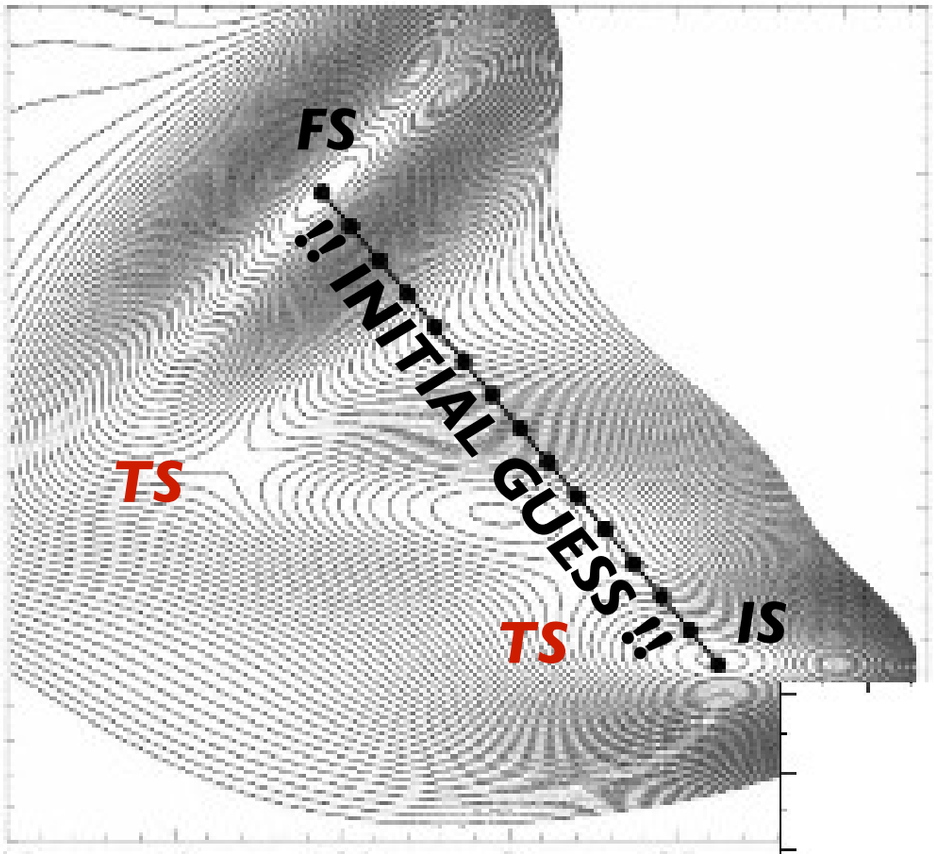
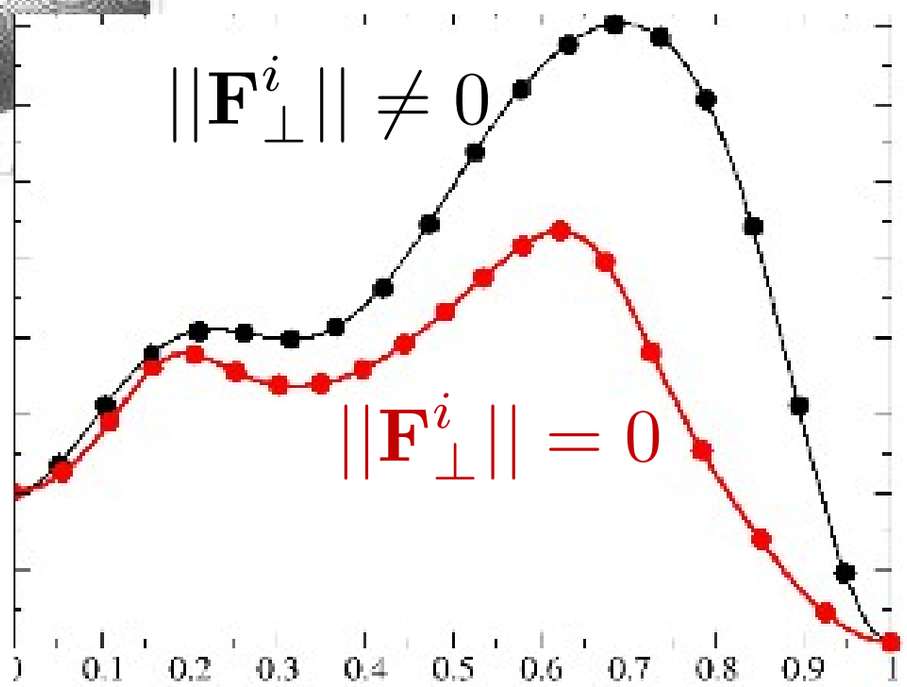
- Impose MEP condition $\quad ||\mathbf{F}_{\perp}^{i}|| = 0$

Nudged Elastic Band - NEB

*Method for finding the **MEP** between IS (reactants) and FS (products) based on the calculation of atomic forces*





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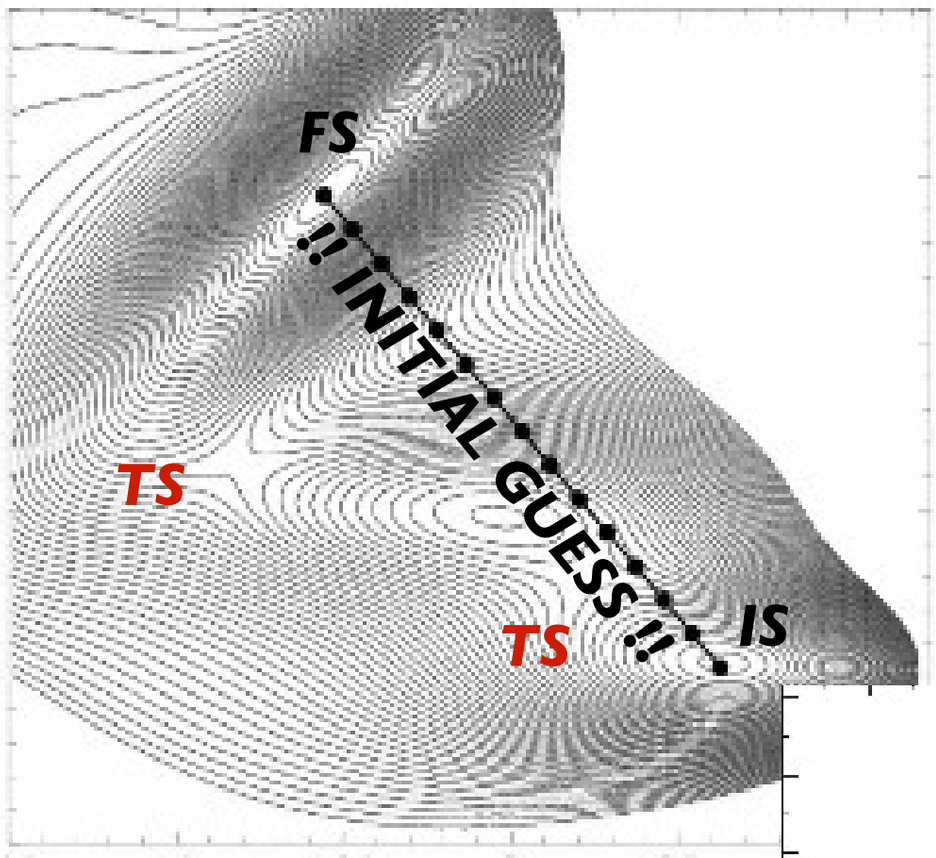
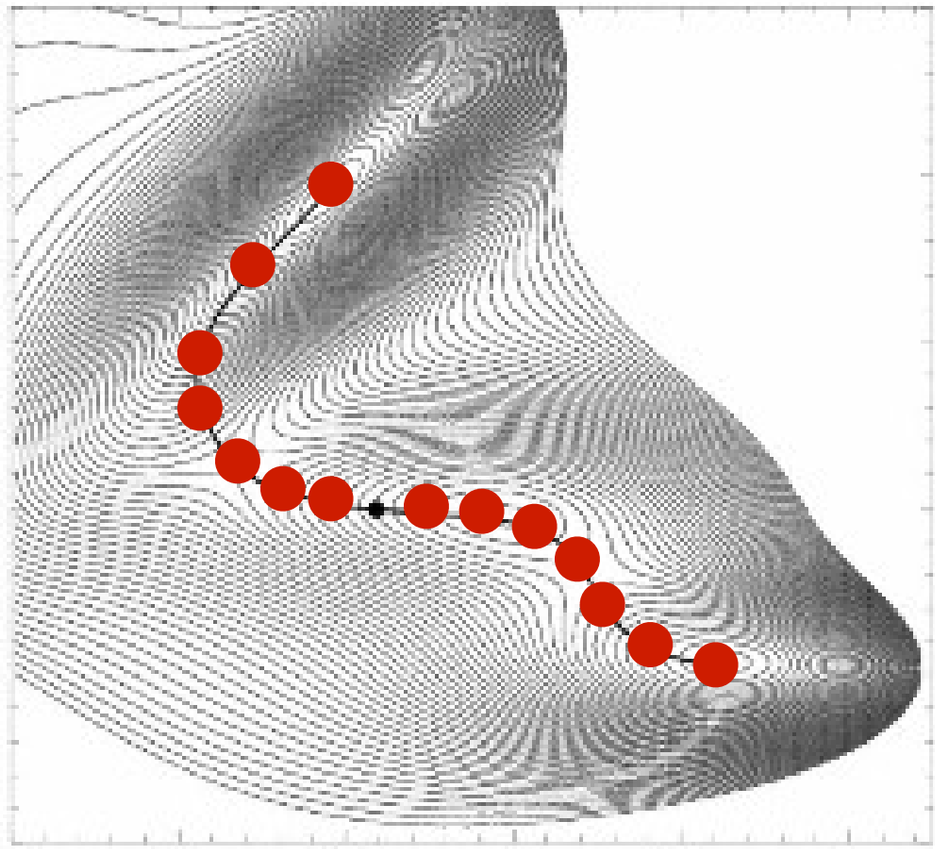
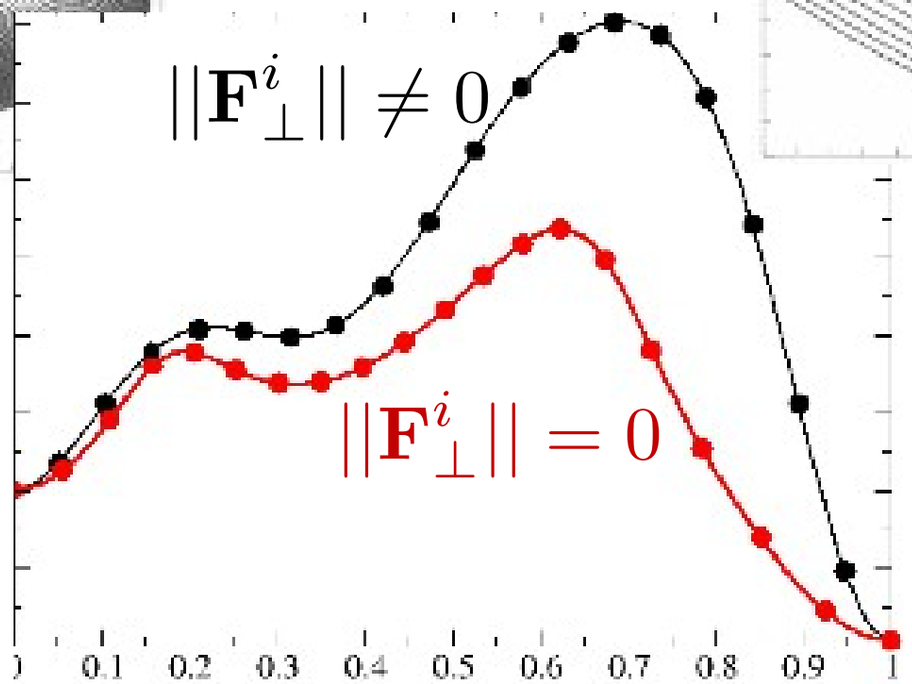


PATH DYNAMICS

$$||\mathbf{F}^i_\perp|| = 0$$





NEB @QE

Notes | Changes | Files | Associated Tracker Items | Tags

Files	FileSize	Downloads	Md5 Hash
pwcond-5.0.1.tar.gz	121296	2497	
atomic-5.0.tar.gz	2348770	4076	
PHonon-5.0.2.tar.gz	1115310	408	0978887ad083903baf16709ce3cf0328
xspectra-5.0.tar.gz	2168600	1667	
pwcond-5.0.tar.gz	118978	3596	
tddfpt-5.0.tar.gz	3193486	3719	
atomic-5.0.1.tar.gz	2347148	2779	
PWgui-5.0.1.tgz	1221946	1154	
PHonon-5.0.tar.gz	1058047	4569	
neb-5.0.tar.gz	282091	3911	
xspectra-5.0.1.tar.gz	2168611	1096	
PWgui-5.0.tgz	1228689	1750	
PHonon-5.0.1.tar.gz	1053933	2880	
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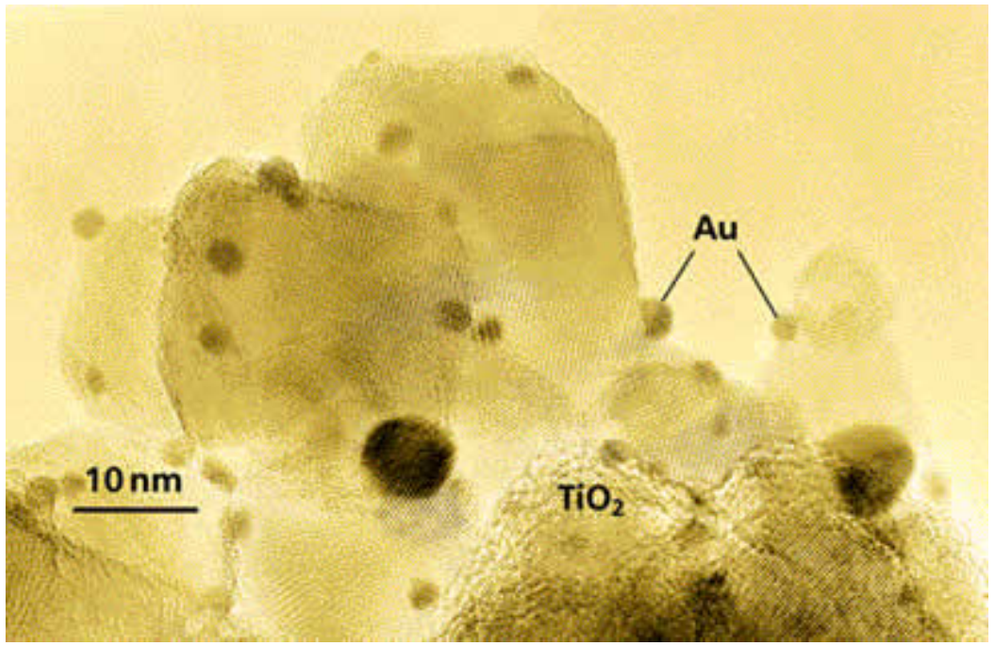
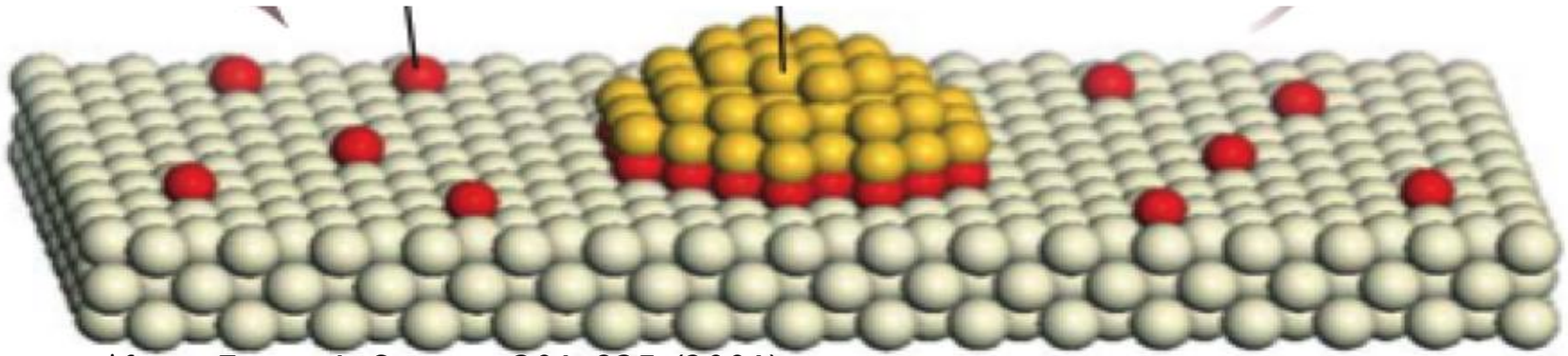
PWgui-5.0.2.tgz	1230959	529	c93ebb301ff657b2737664ca77ee6770
plugins_list-5.0.1	844	643	cee73c09ebc1b7664bad5bdee40a64c5
neb-5.0.1.tar.gz	282306	2559	
tddfpt-5.0.2.tar.gz	6965590	663	f1d844a110ad113b2d797e3157d7a00d
tddfpt-5.0.1.tar.gz	7120668	2770	
XSpectra-5.0.2.tar.gz	2168615	299	634b2364d8c4f487761177c6ab3d2dd1
atomic-5.0.2.tar.gz	2340420	698	4bda54a136468fbeed06ed5ee10037bc
espresso-5.0.tar.gz	16558830	8651	
pwcond-5.0.2.tar.gz	201307	198	107c8bd84c495ad8e85154193ccaeb79
espresso-5.0.2.tar.gz	17001783	895	d8b0d7ac3ddbfe0a656ec1501a2a4688
espresso-5.0.1.tar.gz	16572110	5187	0a280604d738d312e881a97b3b3dfbb1
neb-5.0.2.tar.gz	285154	259	5ae778fe2ae033d15182778f5f4f6334
plumed-1.3-qe.tar.gz	11729604	53	88c8468aec16347bef513972c35eba11

Metals at reducible oxides

Catalyst class that promotes a wide range of redox reactions

- ENERGY: H_2 production, HC reforming, ...
- ENVIRONMENT: gas sensing, gas purification, ...
- DEVICES: fuel cells, photocatalysts, ...





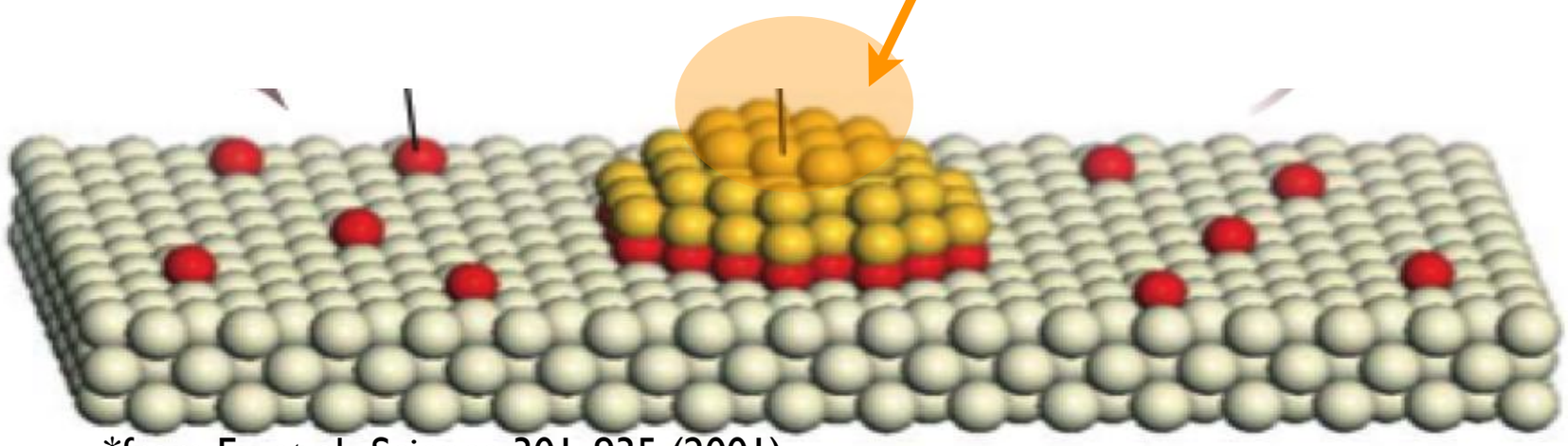
*from Fu et al., Science 301, 935 (2001)

Reactivity controlled by several factors

Metals at reducible oxides

Metal

composition, size, shape, charge state
supported vs. dispersed, ...



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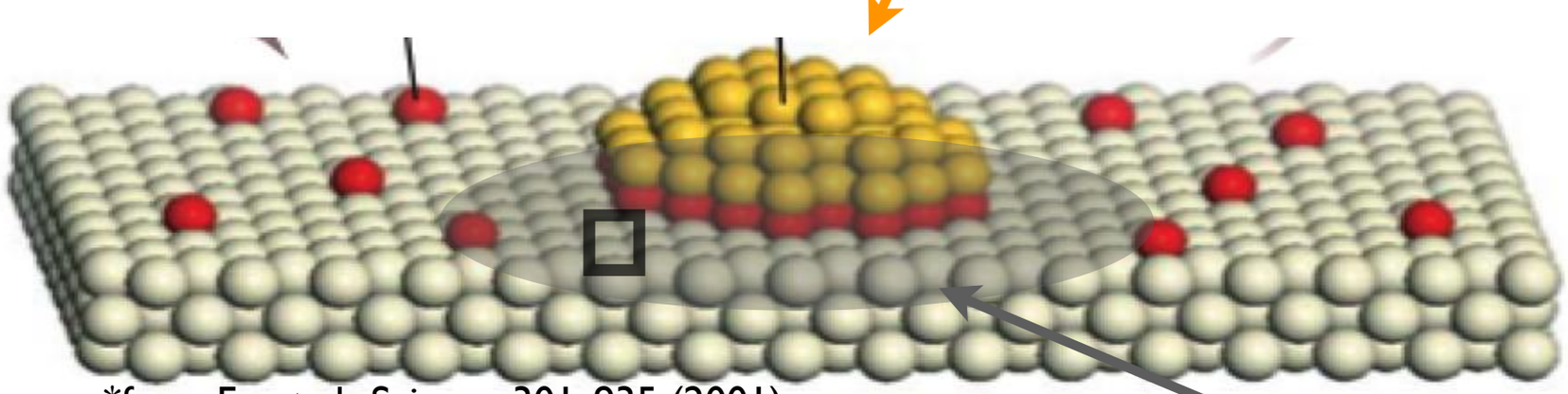

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$$CeO_2 \rightleftharpoons CeO_{(2-x)} + \frac{x}{2}O_2$$

***Support**: active role*
supply of lattice O, stabilization/dispersion/activation of M

Reactivity controlled by several factors

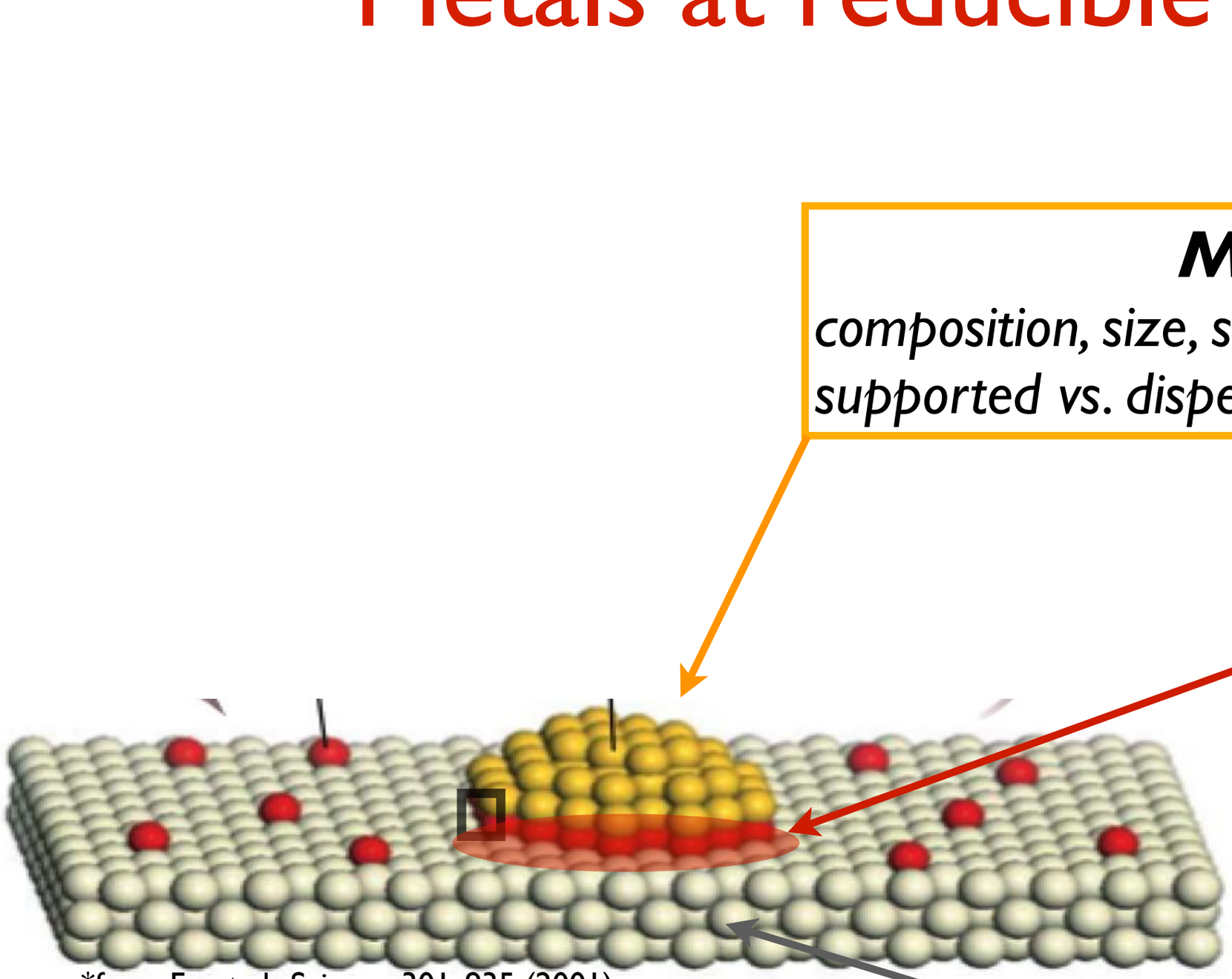
Metals at reducible oxides

Metal

composition, size, shape, charge state
supported vs. dispersed, ...

Interface

charge transfer,
adsorbate spillover,
encapsulation, ...



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Support: *active role*
supply of lattice O, stabilization/dispersion/activation of M

Reactivity controlled by several factors

Metals at reducible oxides

Environment

Oxidative/reducing
dynamics during reaction
segregations, clustering, ...

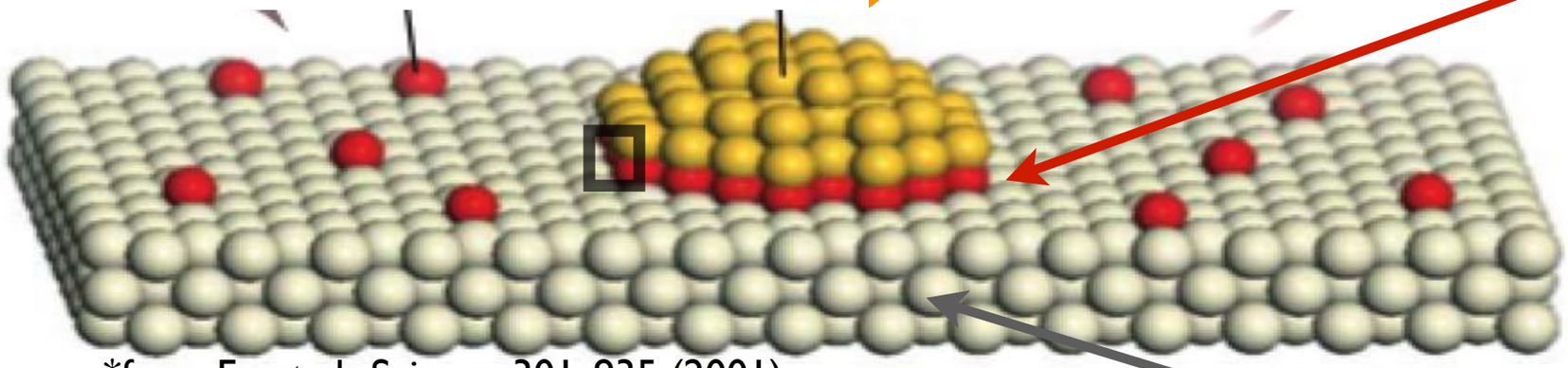
p, T

Metal

composition, size, shape, charge state
supported vs. dispersed, ...

Interface

charge transfer,
adsorbate spillover,
encapsulation, ...



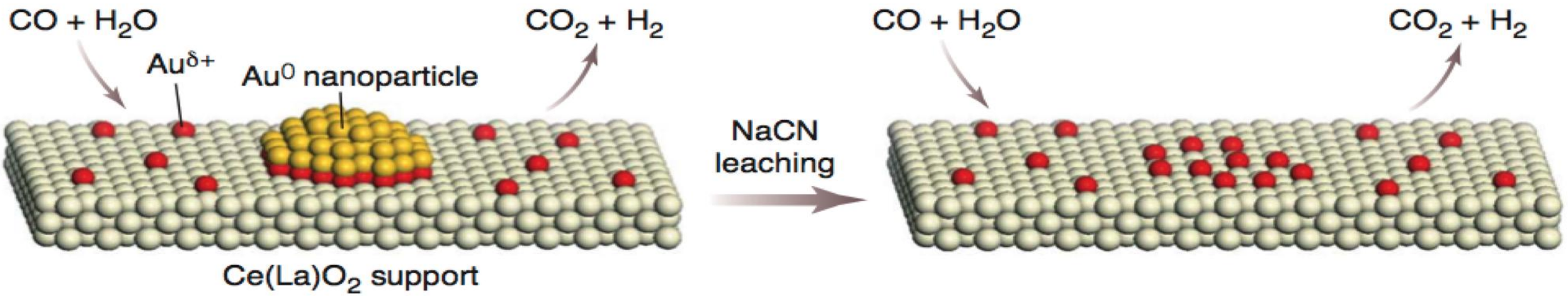
*from Fu et al., Science 301, 935 (2001)

$$CeO_2 \rightleftharpoons CeO_{(2-x)} + \frac{x}{2}O_2$$

Support: *active role*
supply of lattice O, stabilization/dispersion/activation of M

Reactivity controlled by several factors

Which are the active species on supported catalysts?



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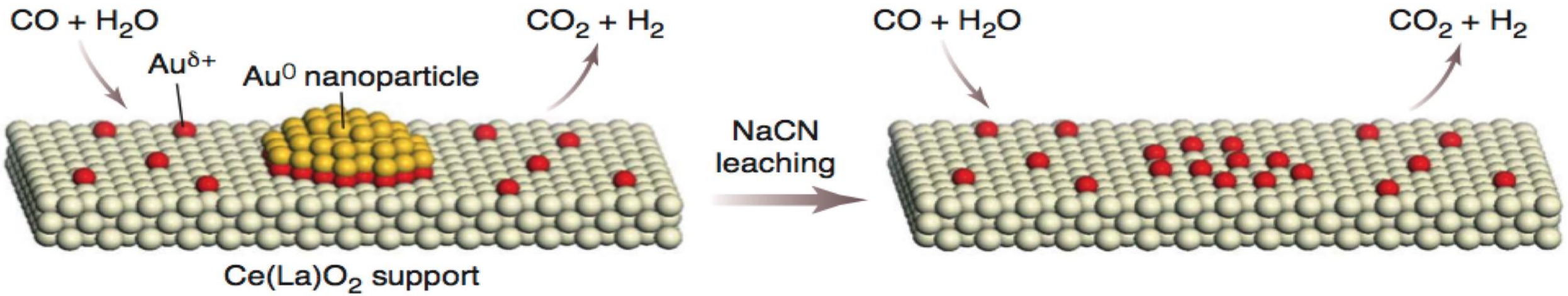

Water Gas Shift reaction

Fu et al., Science 2005: active species are isolated Au^{d+}

Rodriguez et al., xxx: no, they are neutral or negative Au species

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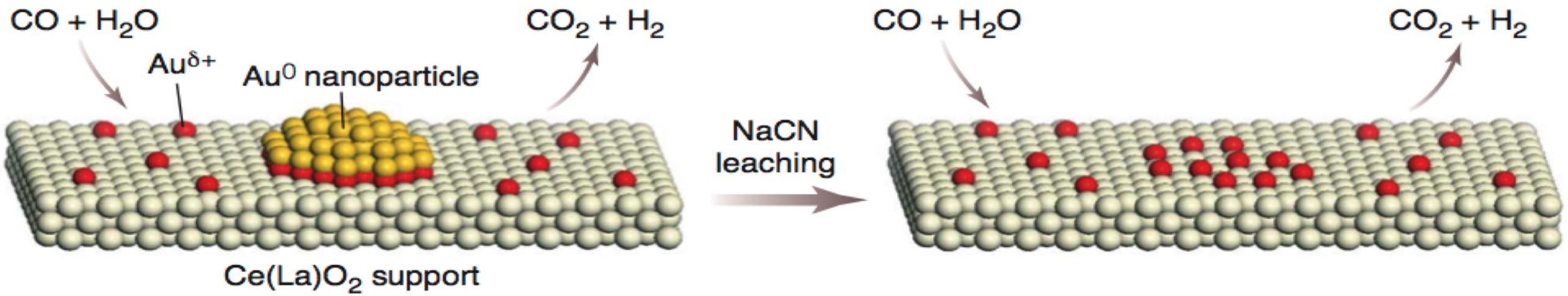


Water Gas Shift reaction

Fu et al., Science 2005: active species are isolated Au^{d+}

Rodriguez et al., xxx: no, they are neutral or negative Au species

CO oxidation

Guzman et al., JACS 2005: active species are isolated Au^{3+} or Au^{+}

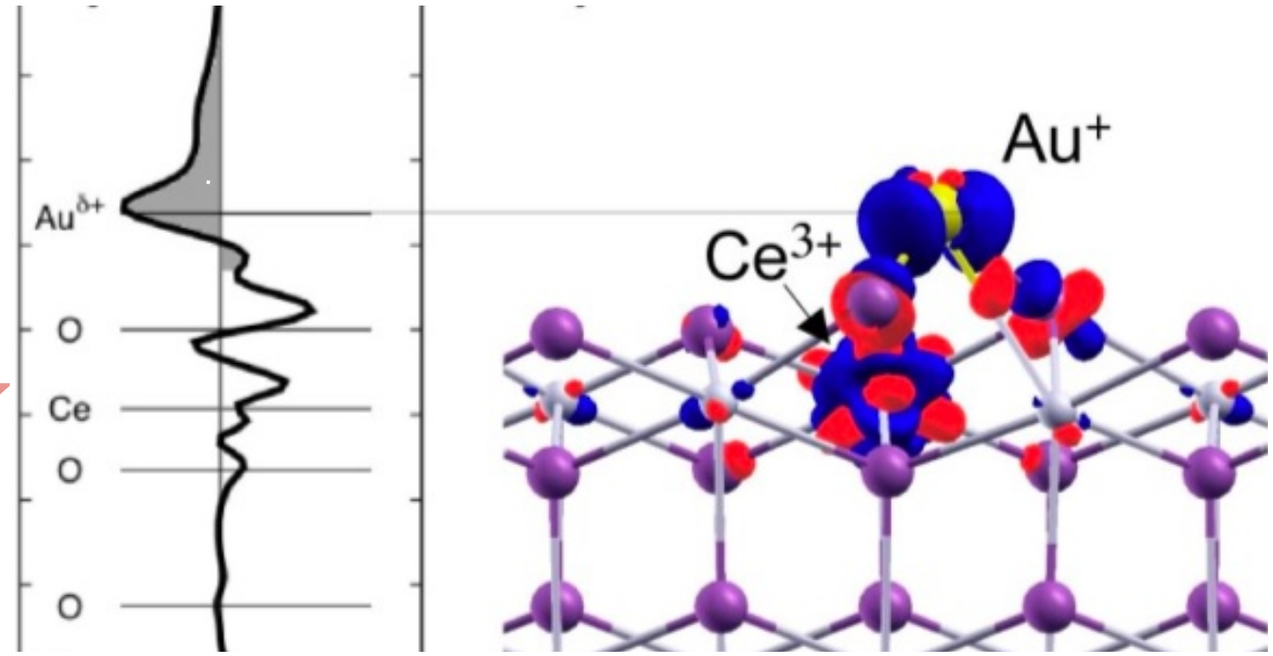
Supported Au ionic species

Charge transfer and electron localization effects at the metal/oxide interface

Au+ species in oxidizing conditions (CO ox)

~1 e

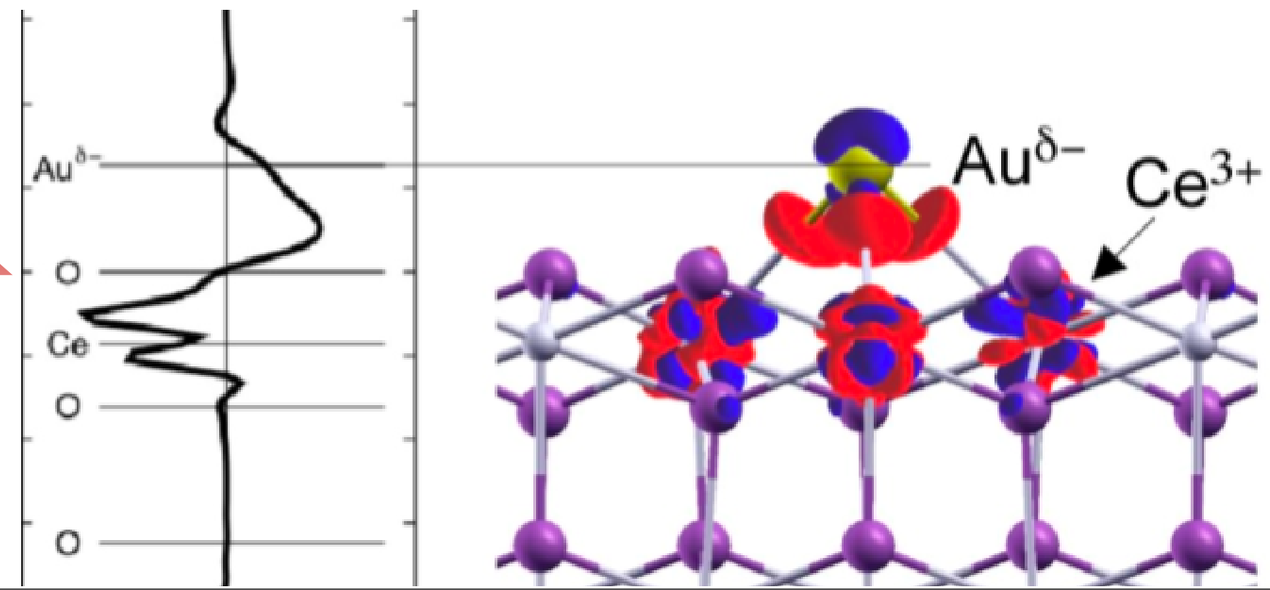
E(ads)
-1.18 eV



Au- species in reducing conditions (WGS)

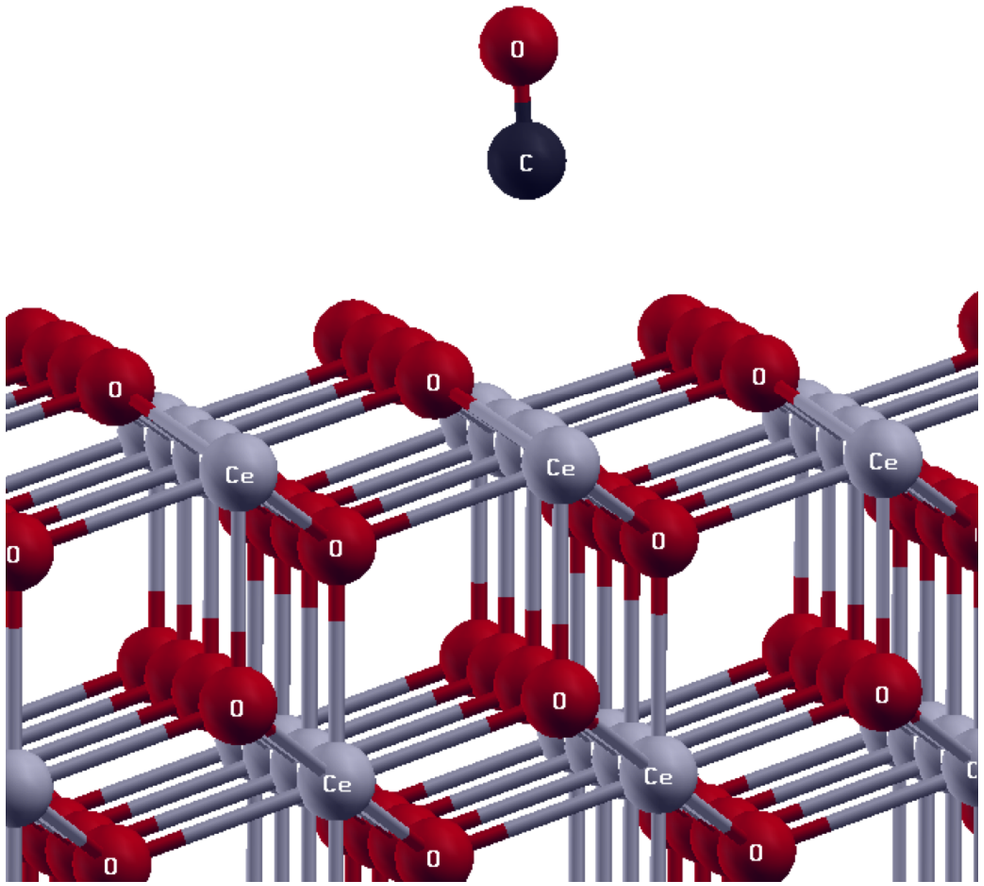
~1 e

E(ads)
-2.29 eV



Stabilization of reaction intermediates

1) CO weakly bind to the stoichiometric CeO2 (111) surface



- Eads = -0.17 eV

	E_b	Ce-C	C-O	Ref.
GGA+U	0.17 eV	2.86 Å	1.14 Å	
GGA+U	0.26 eV	2.88 Å		a)
GGA	0.17 eV	2.88 Å	1.16 Å	b)

a) Nolan *et al.*, JPCB 110, 16600 (2006)
b) Yang *et al.*, CPL 396, 384 (2004)

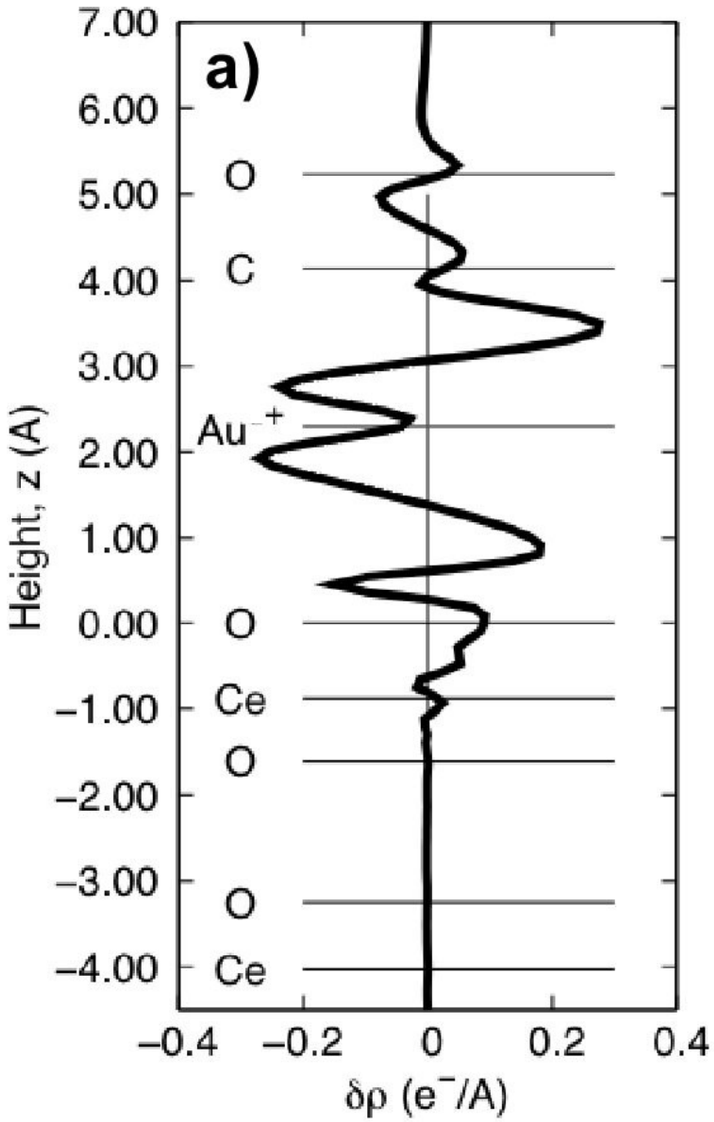
Metal particles required to form stable CO adsorbates on the CeO2 (111) surface

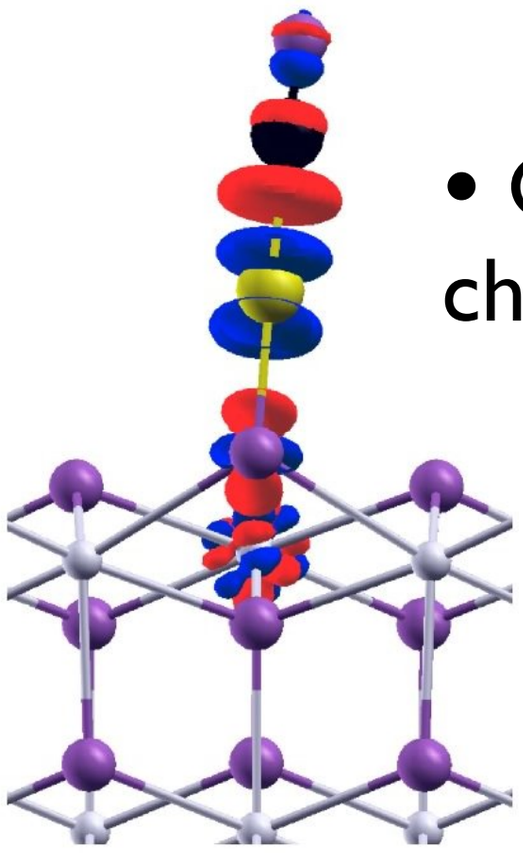
M. Huang and SF, J. Phys. Chem. C 112, 8643 (2008)

CO adsorption on ionic Au

1) CO weakly binds to the stoichiometric CeO2 (111) surface

2) CO strongly binds to the Au^{+} scpecies supported by CeO2 (111)





- Eads = -2.48 eV
- CO adsorption drives further charge depletion of Au+ adsorbate

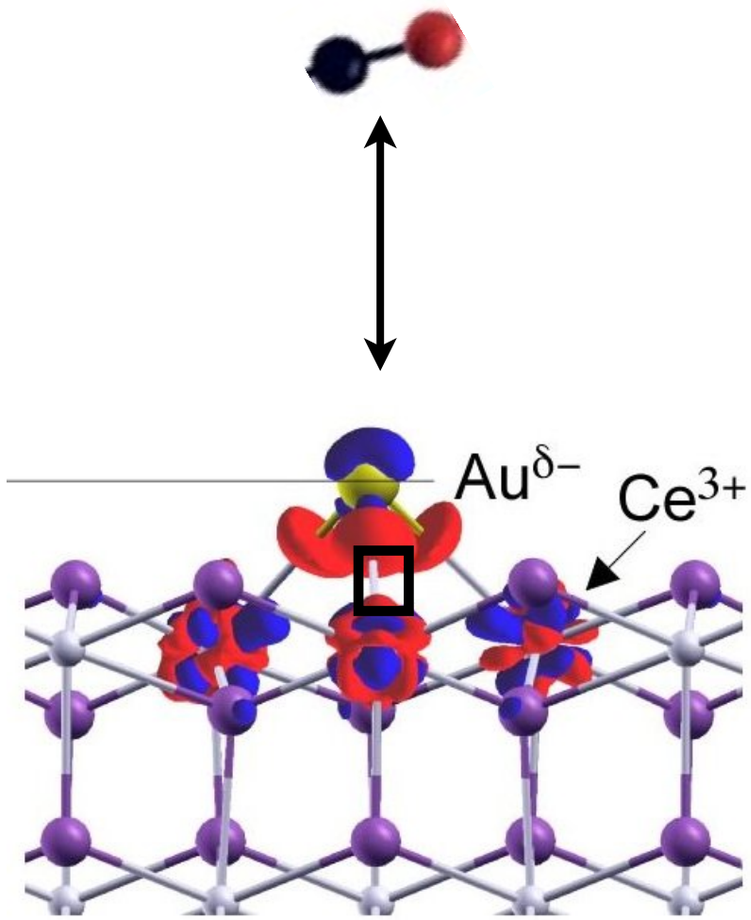
M. Farnesi Camellone and SF, J. Am. Chem. Soc.131, 10473 (2009)

CO adsorption on ionic Au

1) CO weakly bind to the stoichiometric CeO2 (111) surface

2) CO strongly bind to the Au+ species supported by CeO2 (111)

3) CO does not bind to Au- species supported by CeO2 (111)



- Repulsive interaction between CO and Au- species

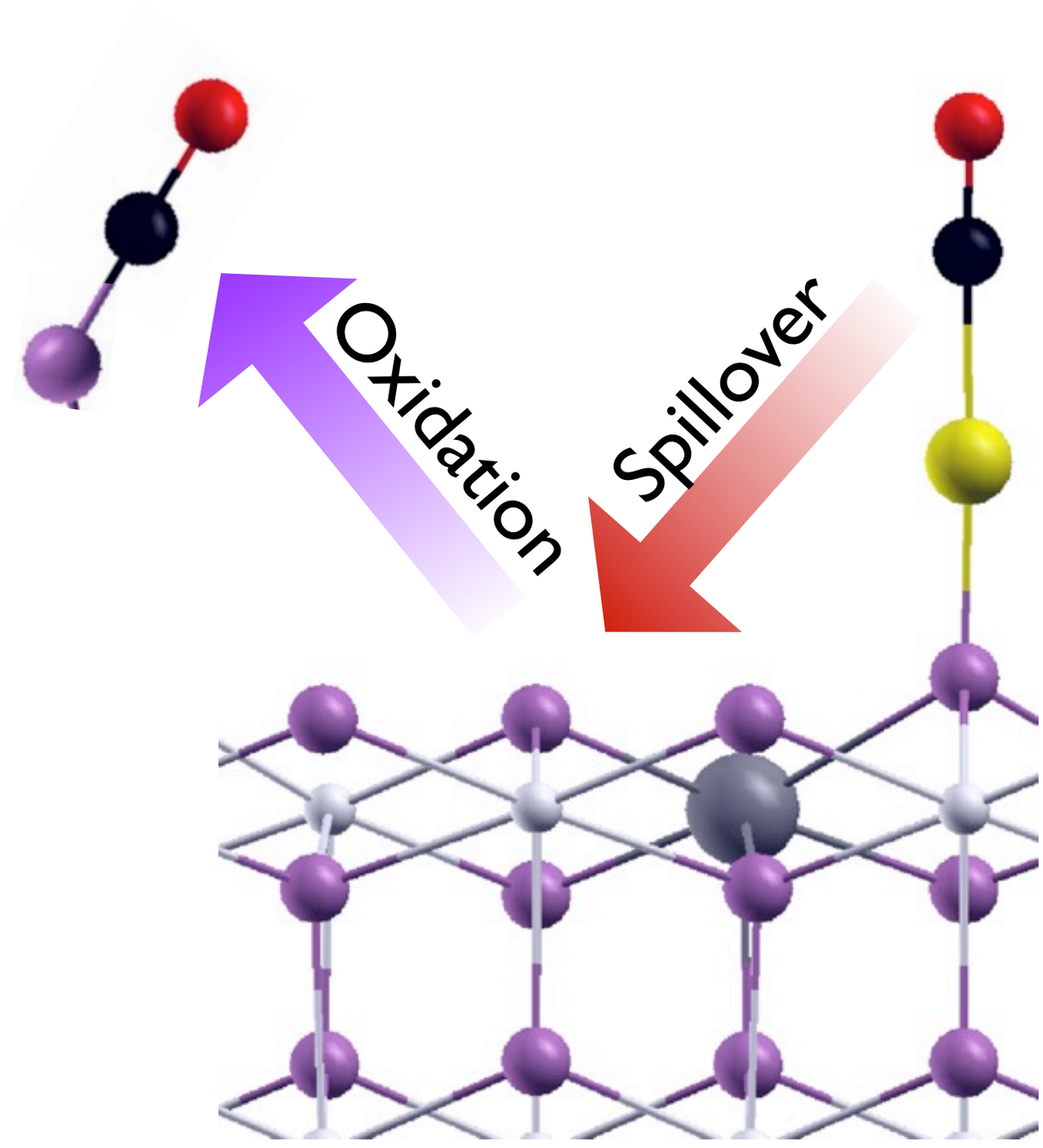
- Supported Au- species prevents CO adsorption

- Au- species prevents also O2 adsorption

M. Farnesi Camellone and SF, J. Am. Chem. Soc.131, 10473 (2009)

CO oxidation via O buffering of the oxide support

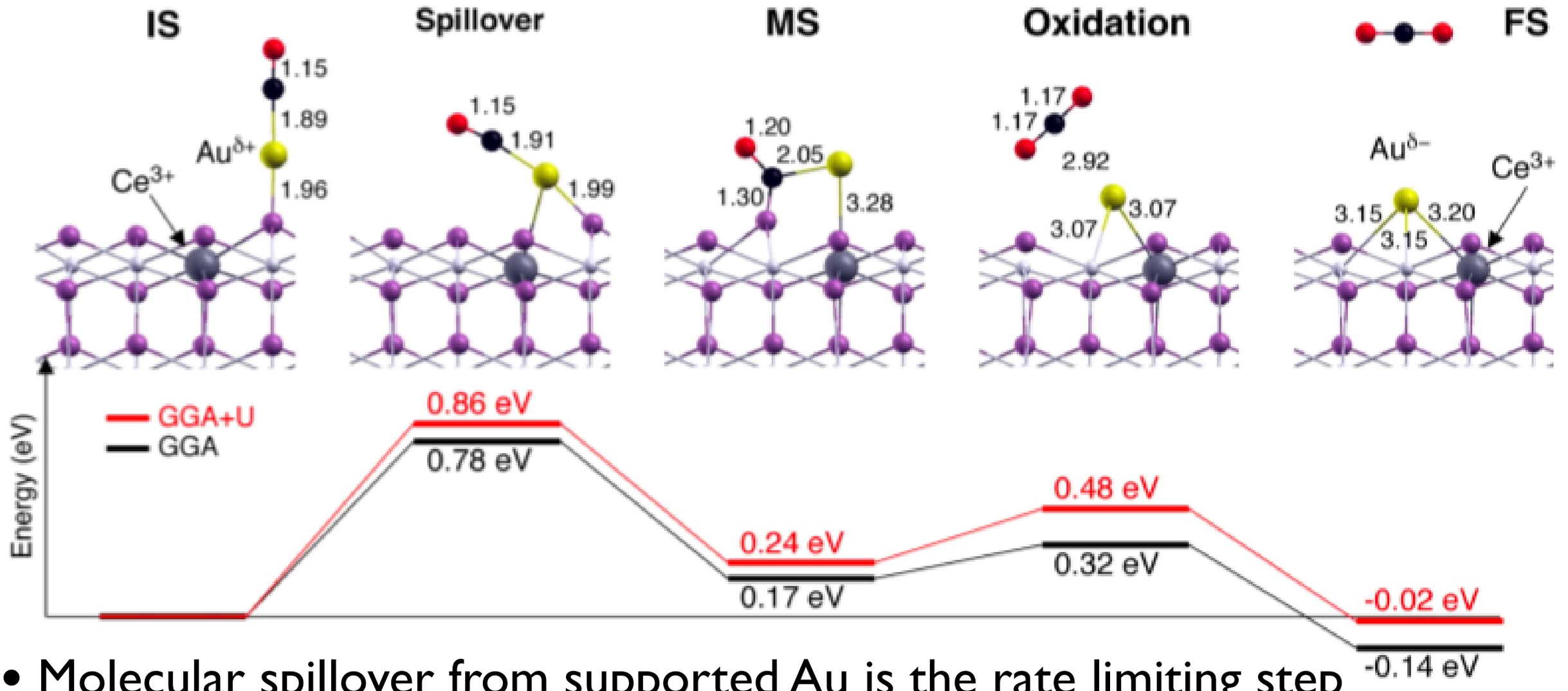
Are these Au^+ species relevant for CO oxidation?



1. Adsorbate diffusion to oxide surface (spillover)

2. Oxidation via lattice O and O vacancy formation

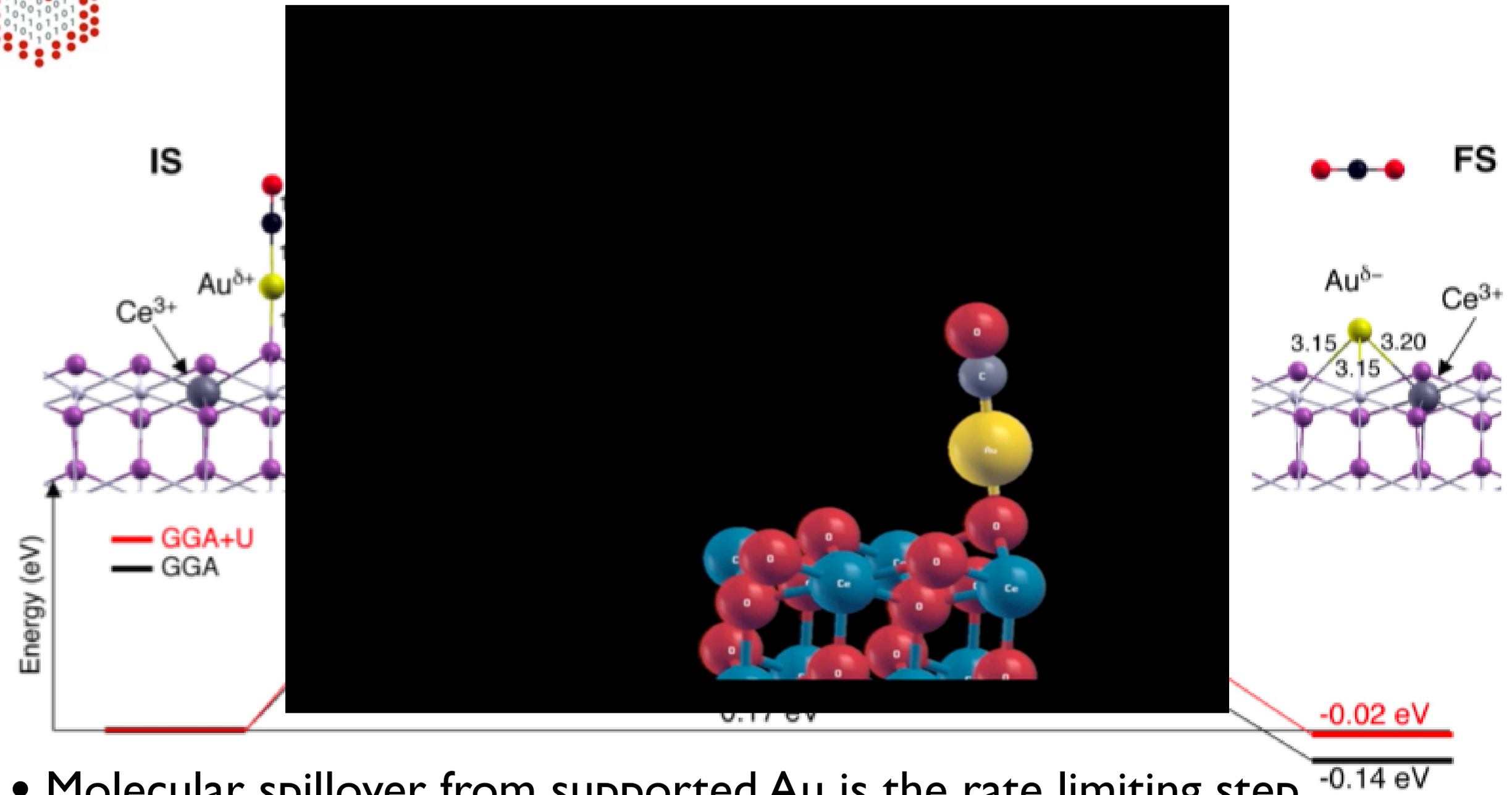
MEP for CO oxidation



- Molecular spillover from supported Au is the rate limiting step
- O vacancy formed during reaction attracts supported Au
- Charge reorganization and catalyst deactivation
- Results independent on the U parameter

Au+ species promotes CO oxidation but readily turns into inactive Au-

M. Farnesi and SF, J. Am. Chem. Soc. 131, 10473 (2009)



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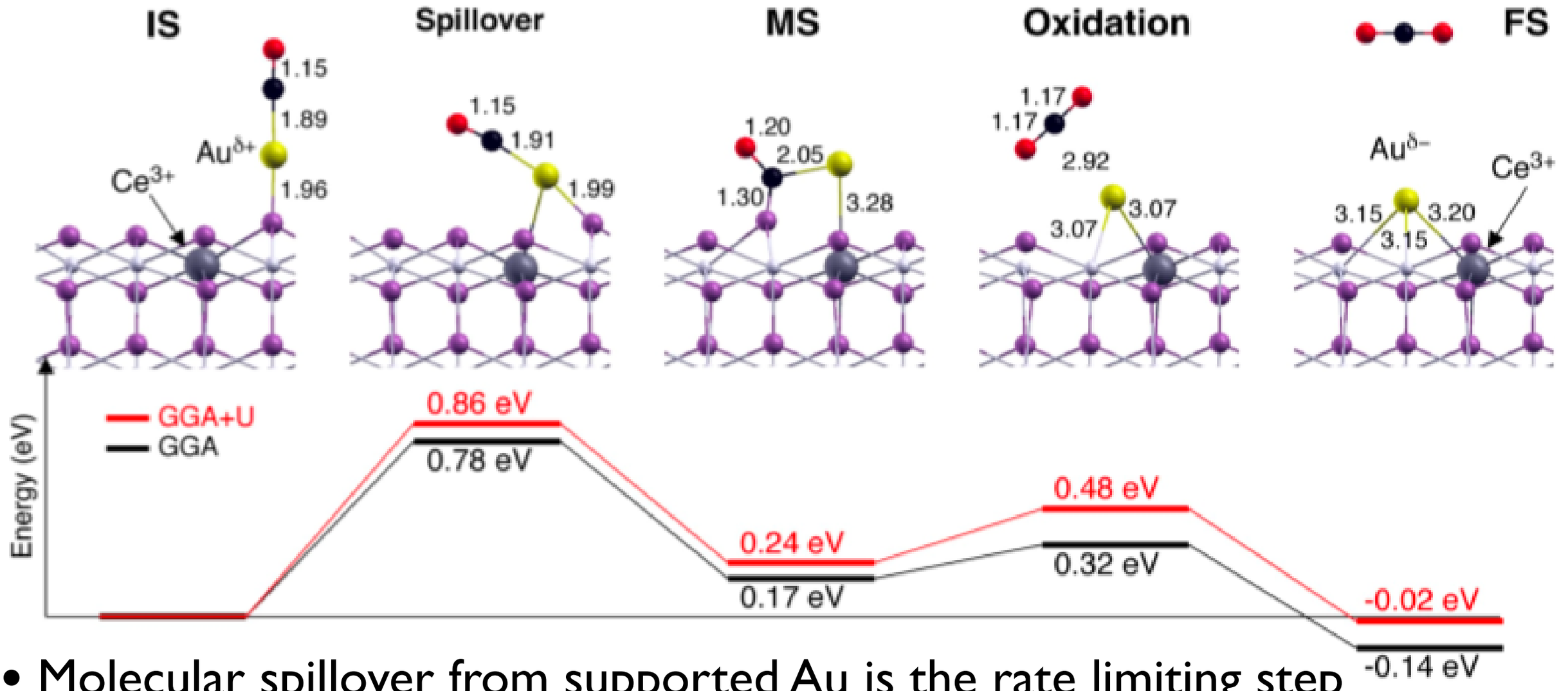

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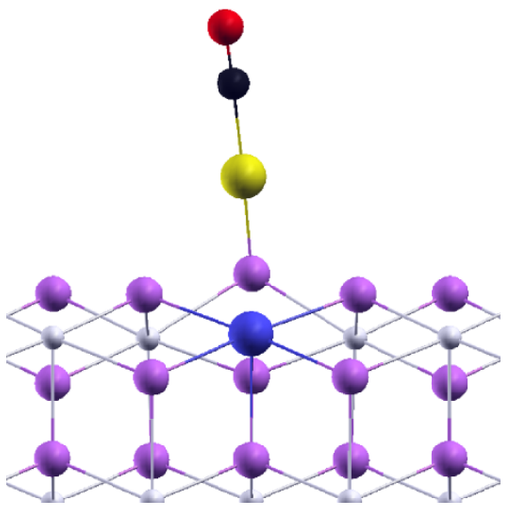
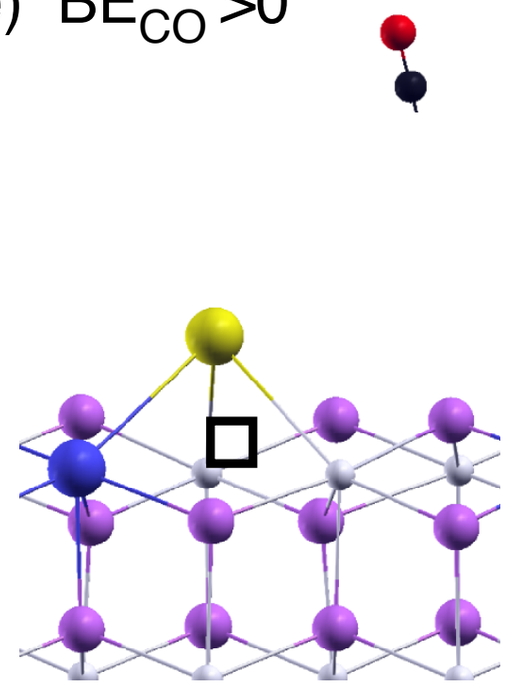
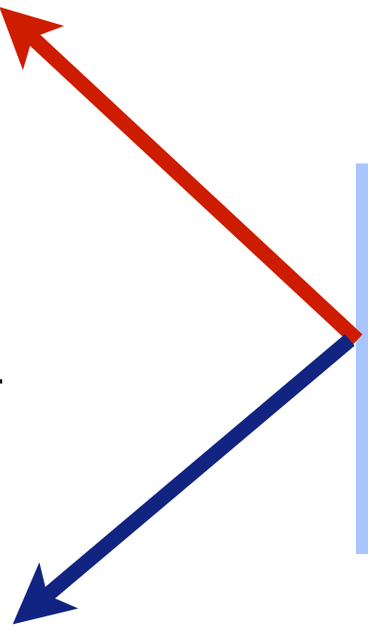
Stability of adsorbates

	$CO\text{-}Au_1$	$CO\text{-}Au_2$	$CO\text{-}Au_3$	$CO\text{-}Au_4$
$Au@CeO_2$	a) BE_{CO}=-2.48 eV 			
$Au@CeO_{2-x}$	e) BE_{CO} >0 			



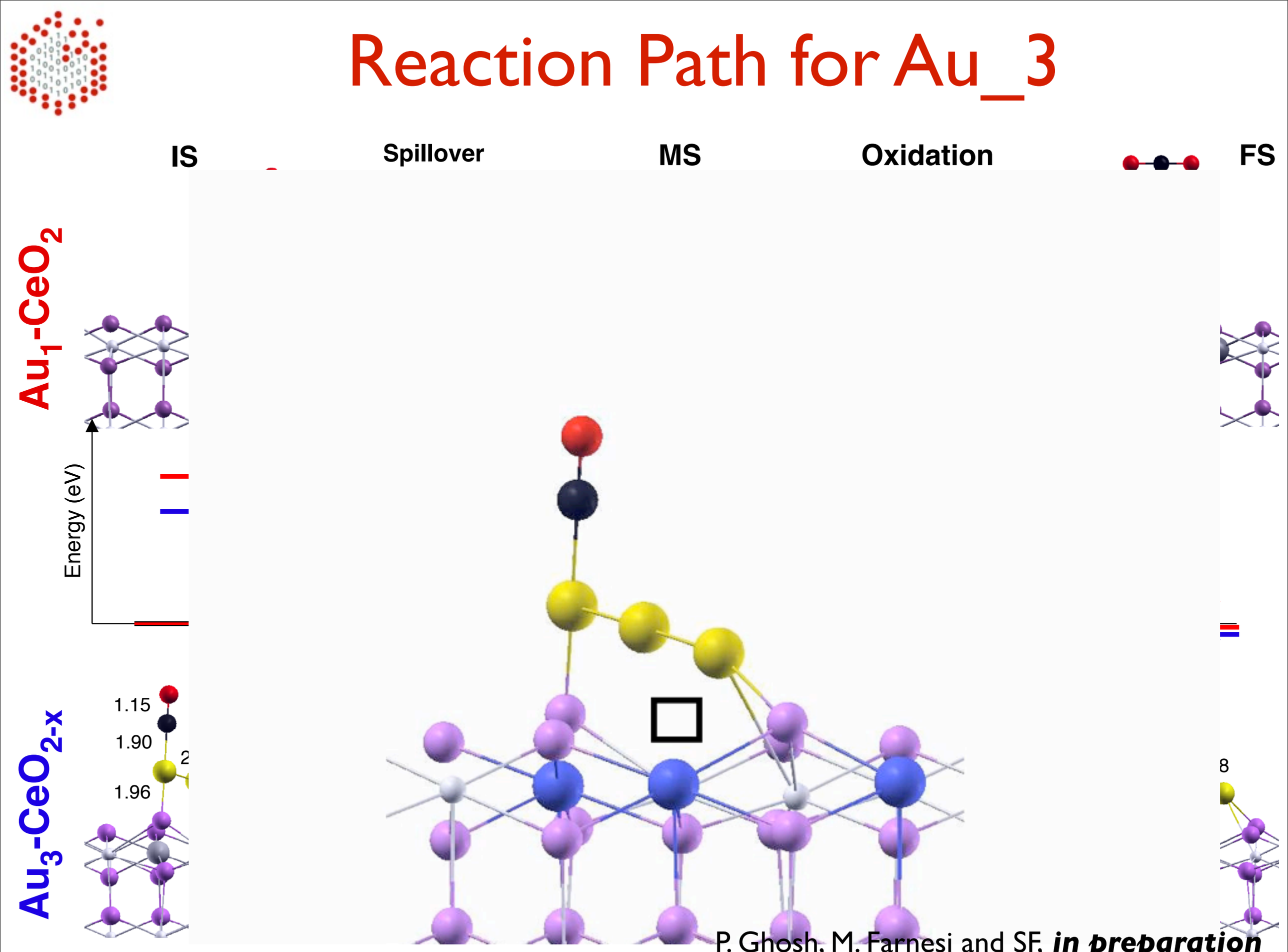
Au_1

Strong preferential binding of CO to Au@CeO2

Stability of adsorbates

	CO-Au$_1$	**CO-Au$_2$**	**CO-Au$_3$**	**CO-Au$_4$**
Au@CeO$_2$	a) BE_{CO}=-2.48 eV	b) BE_{CO}=-1.24 eV	c) BE_{CO}=-1.02 eV	d) BE_{CO}=-1.08 eV
Au@CeO$_{2-x}$	e) BE_{CO} >0	f) BE_{CO}=-1.60 eV	g) BE_{CO}=-1.80 eV	h) BE_{CO}=-1.14 eV

Reaction Path for Au_3



P. Ghosh, M. Farnesi and SF, ***in preparation***

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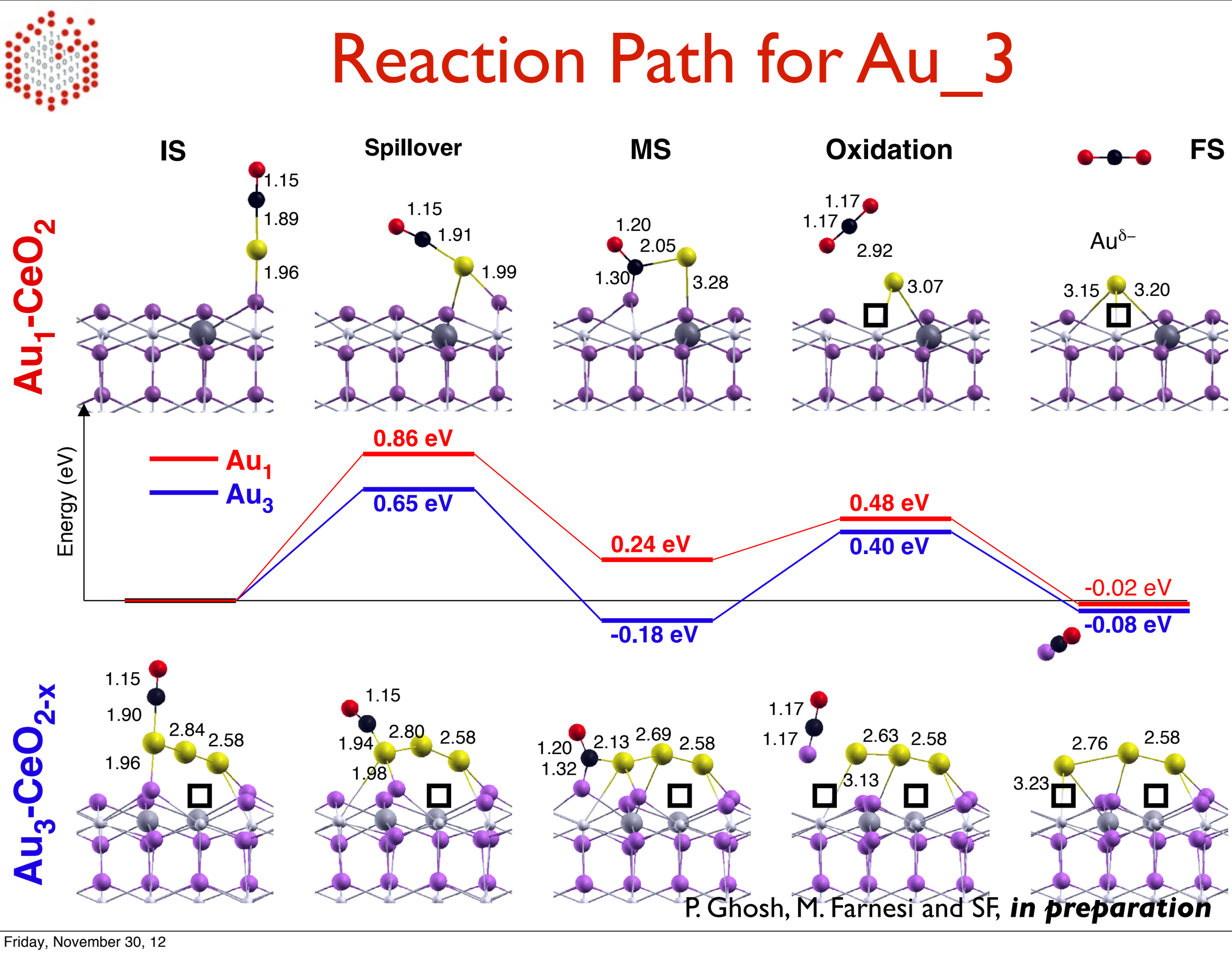

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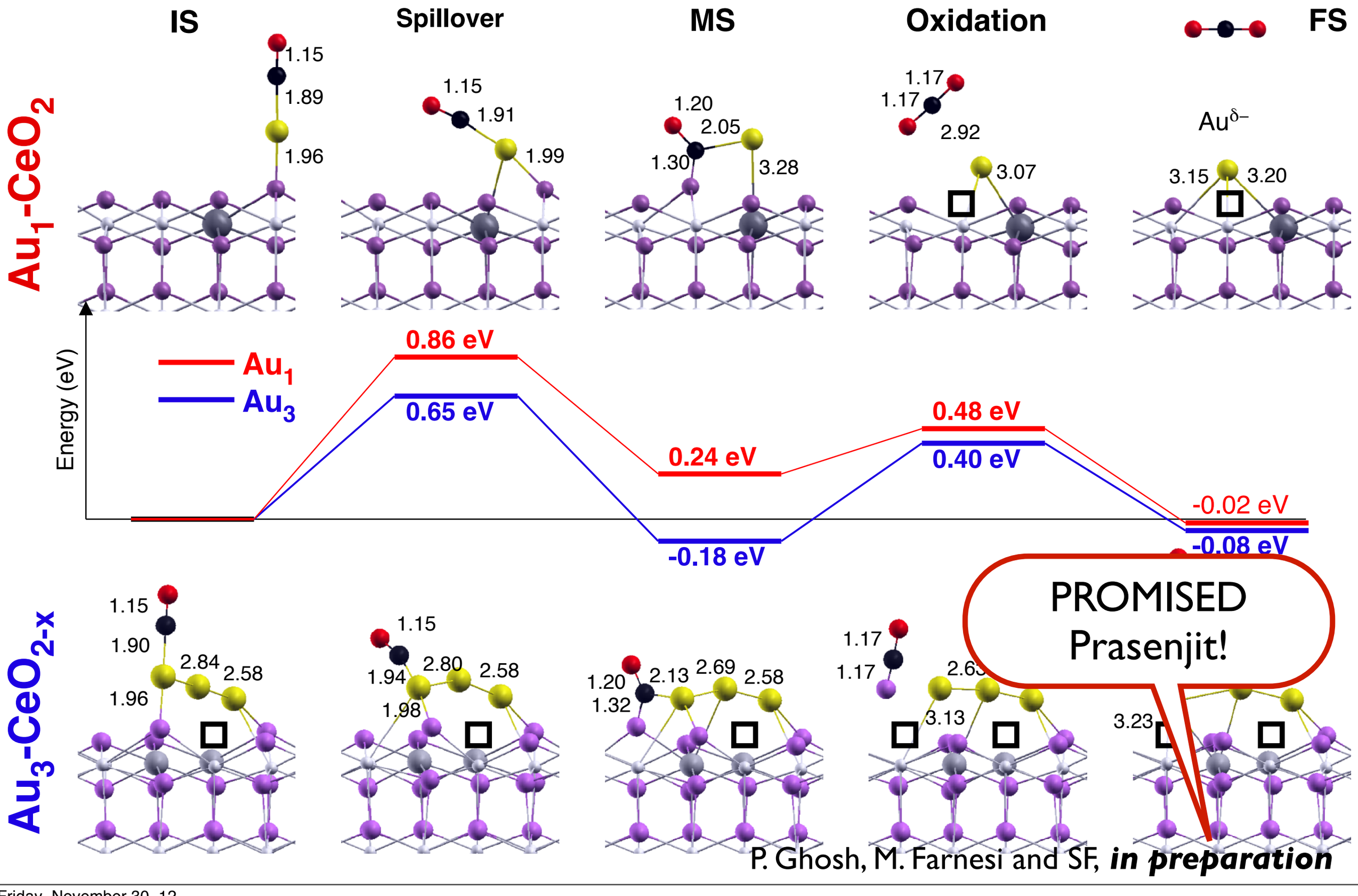

P. Ghosh, M. Farnesi and SF, ***in preparation***

Exploring energy landscapes

- Nudged Elastic Band (NEB)

Method for finding the MEP between IS (reactants) and FS (products) based on the calculation of atomic forces.

- Meta-dynamics (available in PLUMED)

Method for calculating the free energy landscape, unknown products, ... based on a biased dynamics in the space of a set of CVs.

A. Laio and M. Parrinello, PNAS 99, 12562 (2002)

Metadynamics

Simulating rare (activated) events without knowledge of the final state is even more challenging!

Ex: the formation of the O-O bond during water oxidation

$$2H_2O \rightarrow 4H^+ + 4e^- + O_2$$

$$4H^+ + 4e^- \rightarrow H_2$$

Metadynamics

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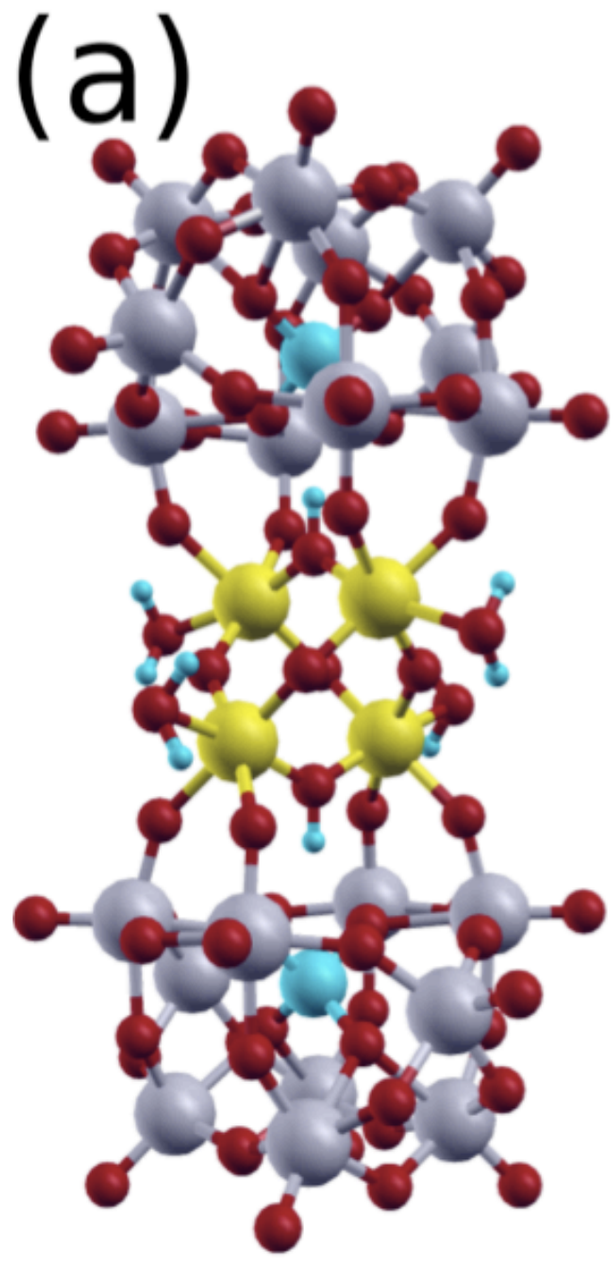
Polyoxometalate Embedding of a Tetraruthenium(IV)-oxo-core by Template-Directed Metalation of $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$: A Totally Inorganic Oxygen-Evolving Catalyst

Andrea Sartorel,*,‡ Mauro Carraro,‡ Gianfranco Scorrano,‡ Rita De Zorzi,†
Silvano Geremia,*,† Neal D. McDaniel,|| Stefan Bernhard,|| and Marcella Bonchio*,‡

ITM-CNR and Department of Chemical Sciences, University of Padova, via F. Marzolo 1, 35131 Padova, Italy, Centro di Eccellenza di Biocristallografia, Dipartimento di Scienze Chimiche, Università di Trieste, via L. Giorgieri 1, 34127 Trieste, Italy, and Department of Chemistry, Princeton University, Princeton, New Jersey 08544

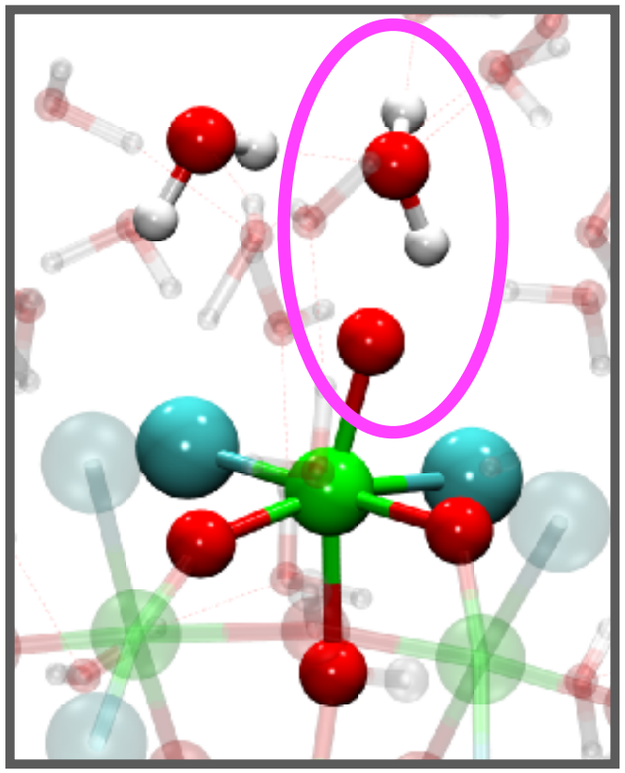


One of the most efficient and stable catalysts reported so far

Working mechanism? Relevant intermediates?
How does water split and an O2 molecule form?
Which are the thermodynamic and kinetic origin of this high efficiency and stability?
Is it possible to improve them? How?

Sartorel et al. JACS 130, 5006 (2008)
Geletii et al. Angew. Chem. Int. Ed. 47, 3896 (2008)

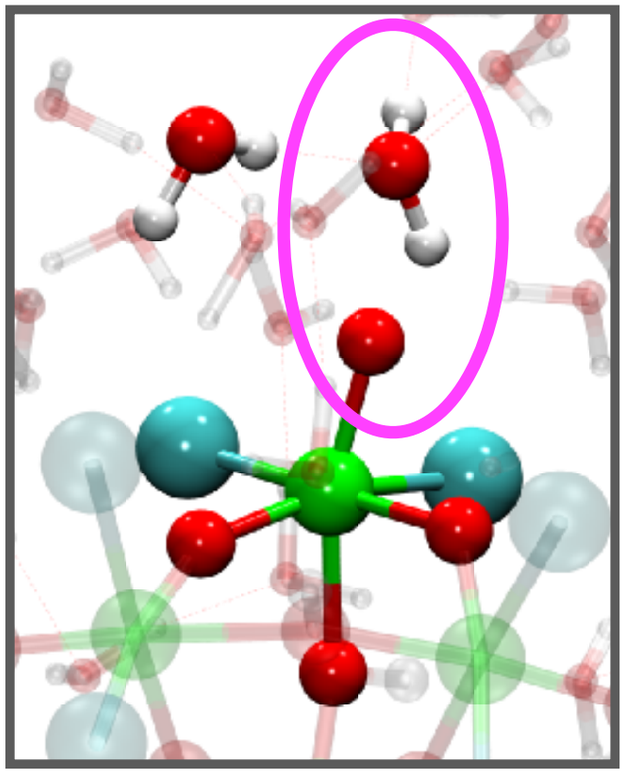
How is molecular O2 formed?



From the solvent?

- ✳nucleophilic attack of RuVI=O termination
- ✳The water that splits is from the solvent
- ✳<u>Catalyst is not damaged and can be reactivated</u>

How is molecular O2 formed?



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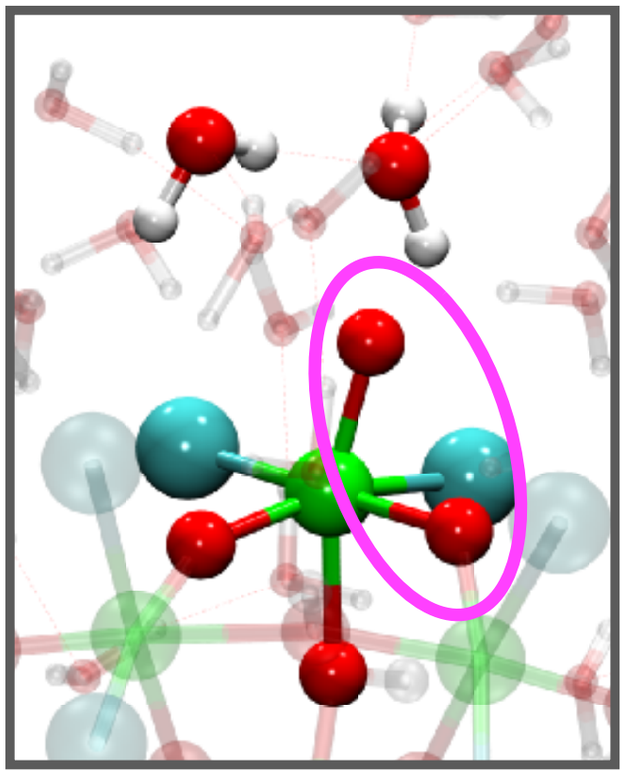
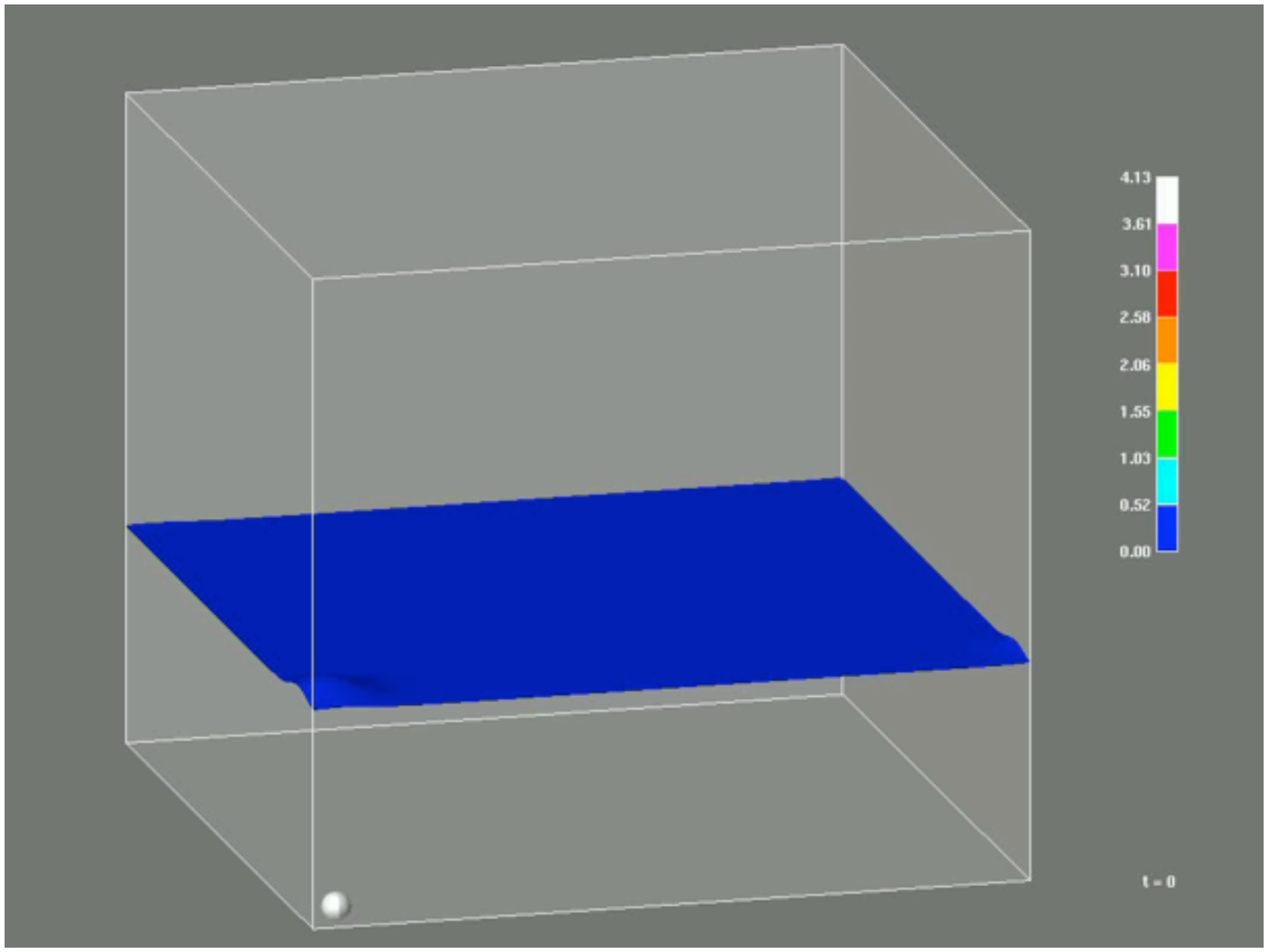


From an O of the oxide core?

- ✳RuVI=O termination attacks the oxide cluster
- ✳Intermolecular mechanism without participation of water from the solvent
- ✳The water that splits is ligated
- ✳<u>Catalyst is damaged and needs to be repared</u>

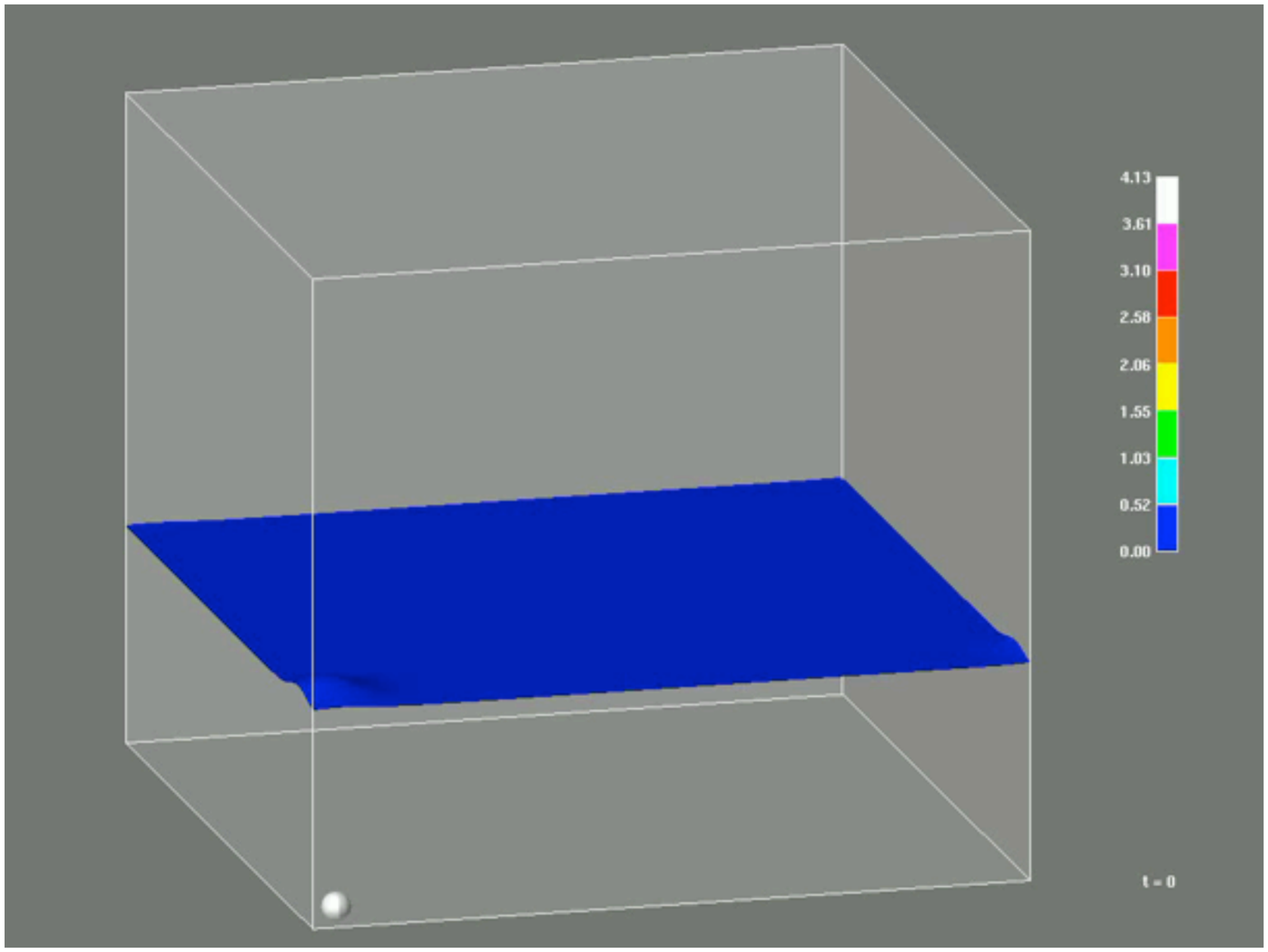
Metadynamics



- Technique for accelerating rare events and reconstructing the free energy
- Technique for escaping free energy minima
- Efficient exploration of configuration space
- Knowledge of final state is not required
- Biased and history-dependent MD

A. Laio and M. Parrinello, PNAS 99, 12562 (2002)

Metadynamics



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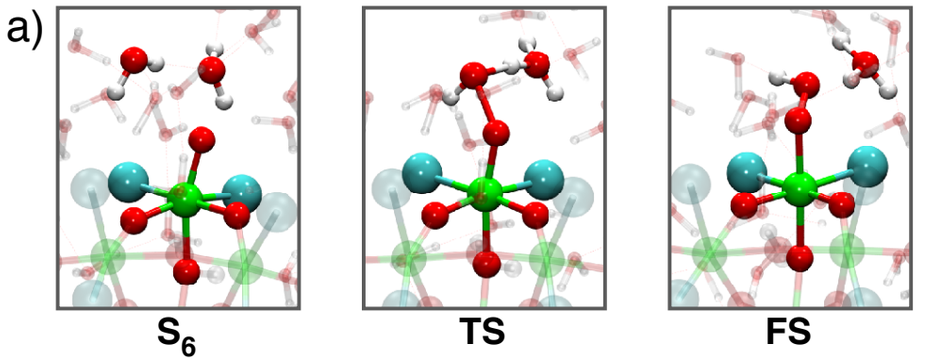
- Efficient explorati
- Knowledge c equired
- Biased and his pendent MD

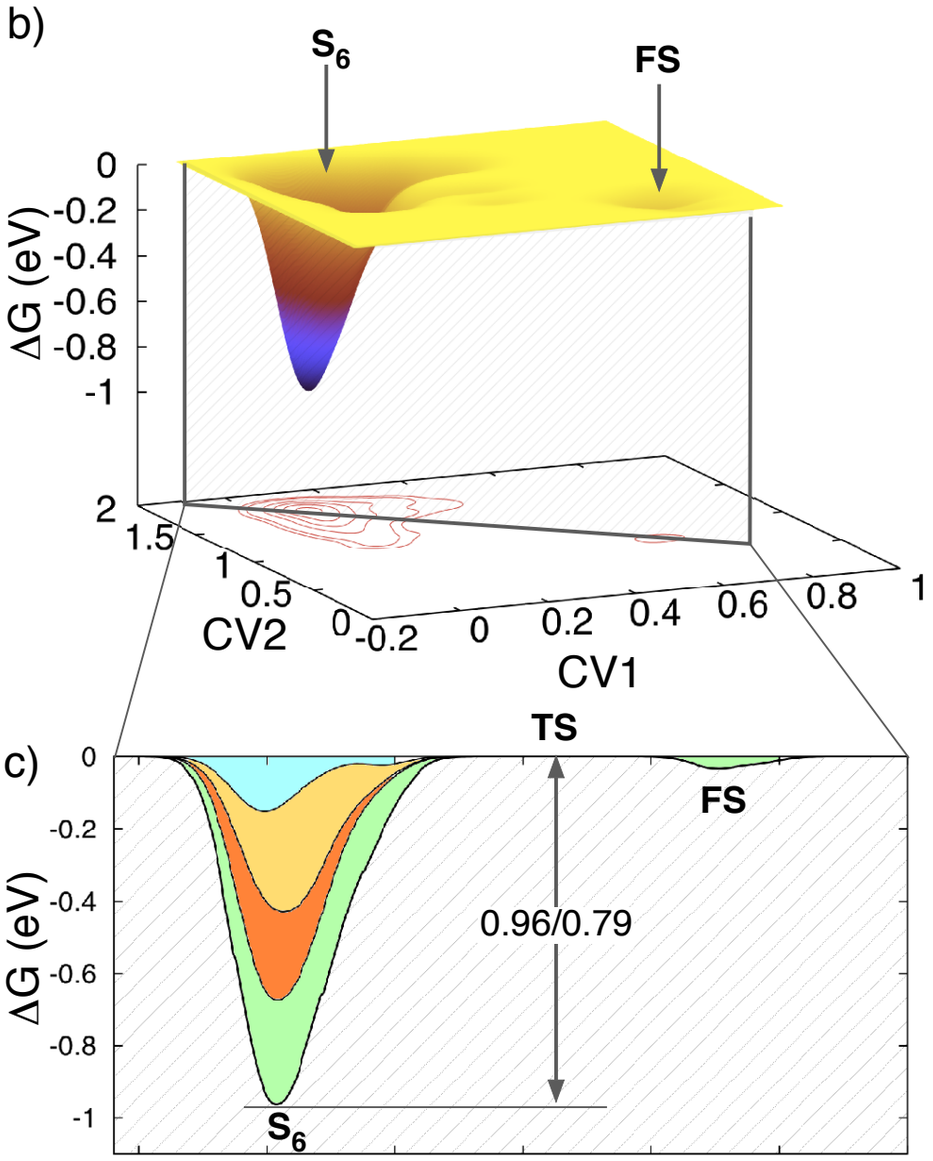
MODIFIED forces again ...
HOW? Find out at the afternnon lab

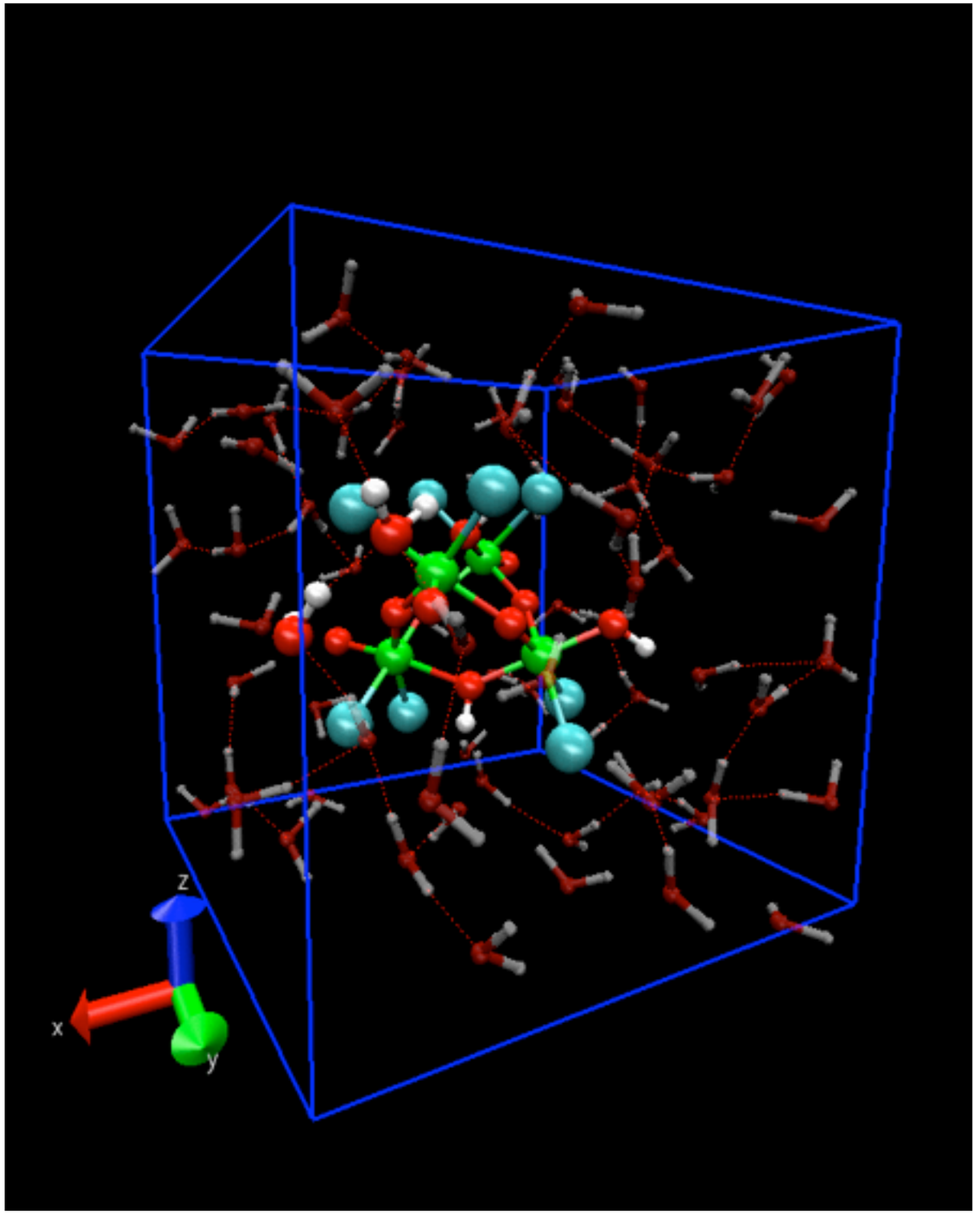
A. Laio and M. Parrinello, PNAS 99, 12562 (2002)

Metadynamics

Reaction mechanism for water oxidation and O2 formation?







S. Piccinin, A. Sartorel, G. Aquilanti, A. Goldoni, M. Bonchio, and SF, submitted

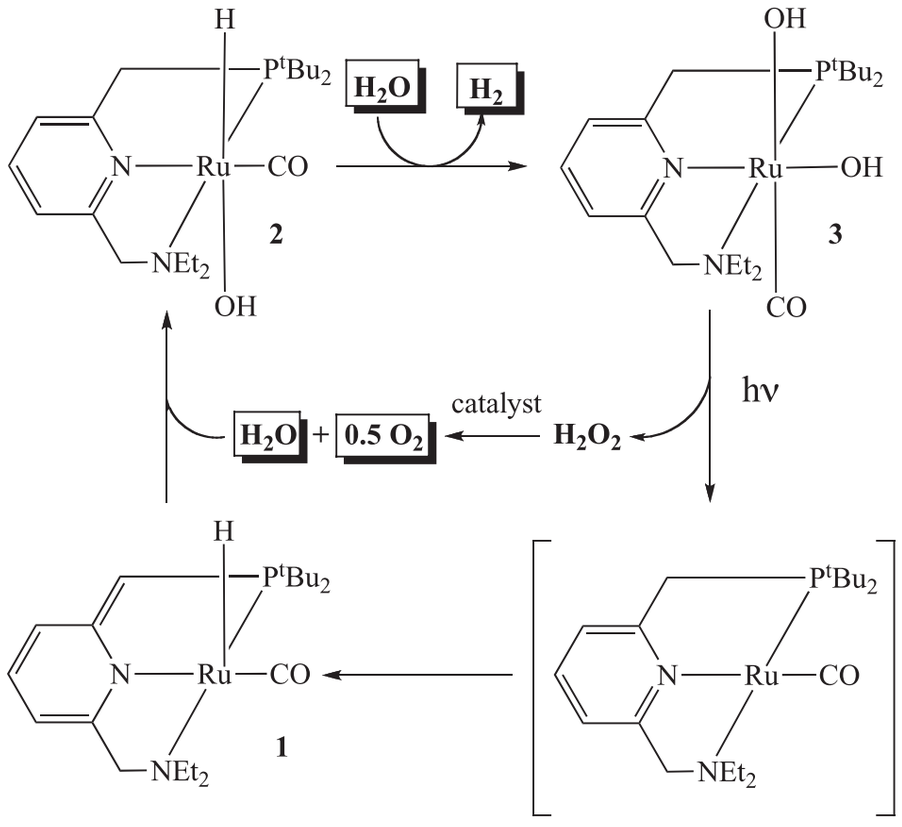
Ab-initio MD?

3 APRIL 2009 VOL 324 SCIENCE

Science
AAAS

Consecutive Thermal H_2 and Light-Induced O_2 Evolution from Water Promoted by a Metal Complex

Stephan W. Kohl,[1] Lev Weiner,[2] Leonid Schwartsburd,[1] Leonid Konstantinovski,[2] Linda J. W. Shimon,[2] Yehoshoa Ben-David,[1] Mark A. Iron,[2] David Milstein[1]*



Ab-initio MD of reactants

... and wait for reaction to occour

Ab-initio MD?

3 APRIL 2009 VOL 324 SCIENCE

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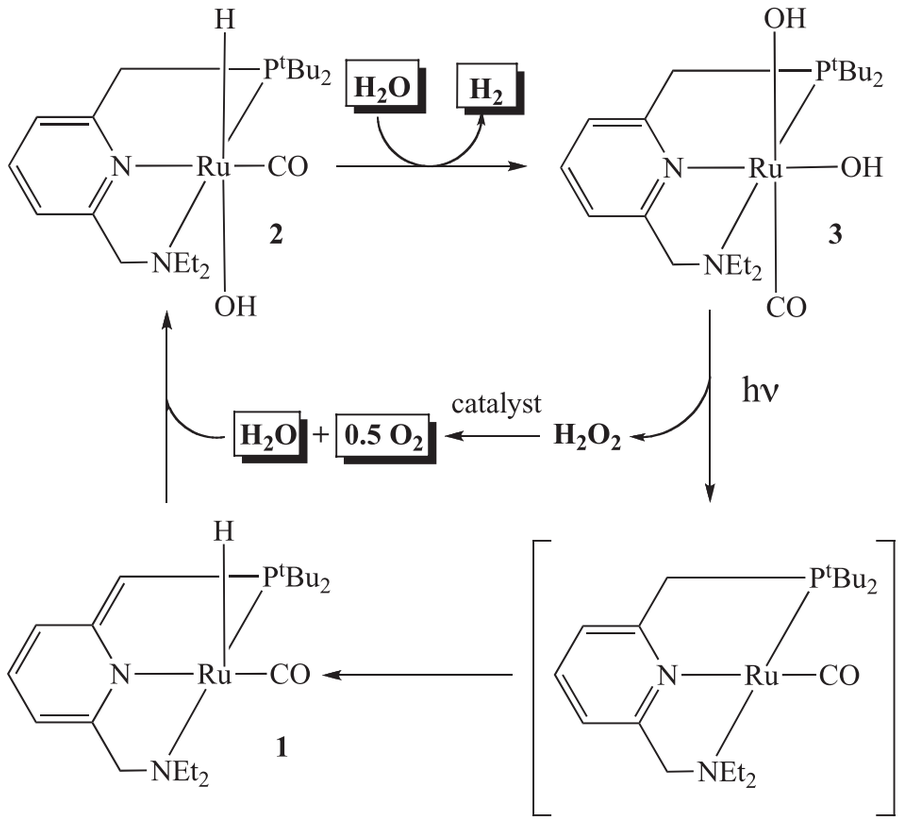
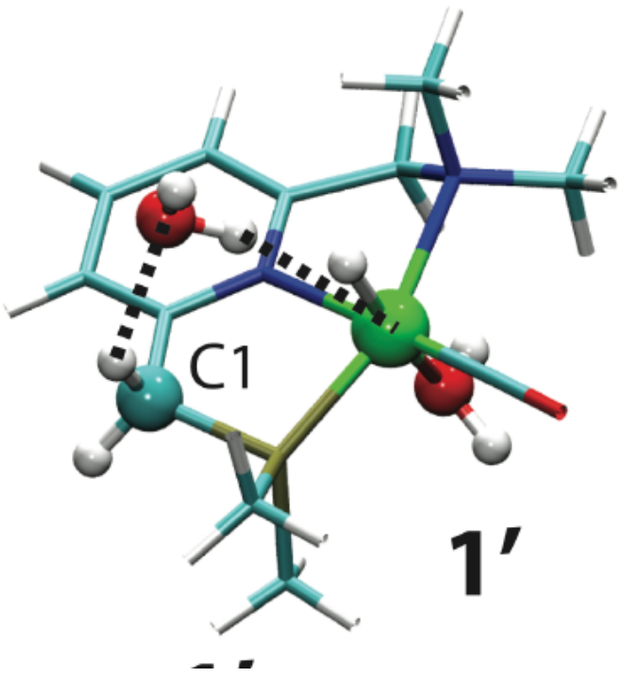


Ab-initio MD of reactants

... and wait for reaction to occour

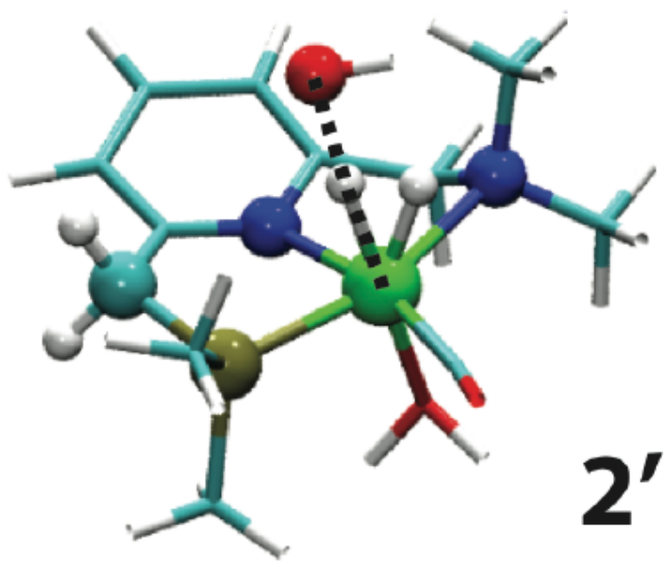
NOPE
USE METADYNAMICS

How is molecular H2 formed?



Intramolecular proton transfer?

- ✳ Ligand dearomatization
- ✳ Proton transfer assisted by bridging water



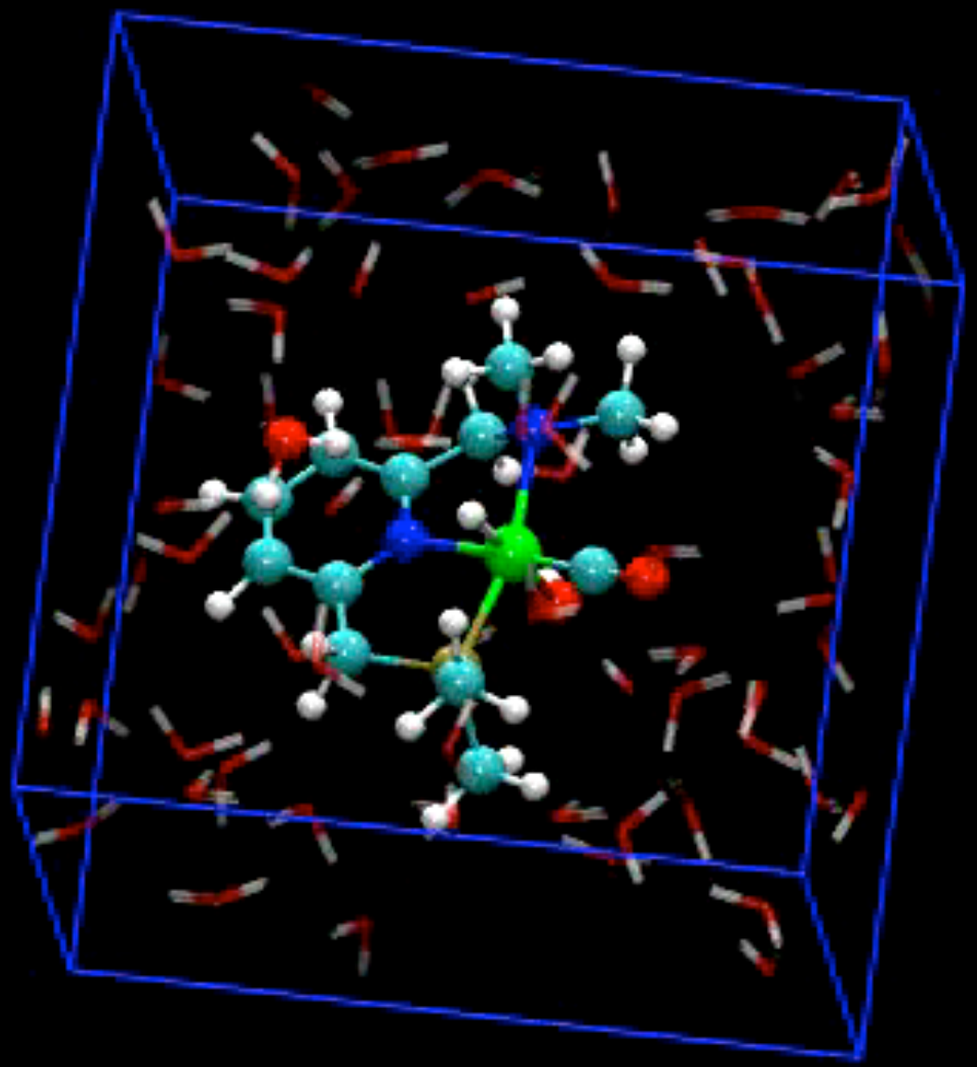
From the solvent?

- ✳ Splitting of a solvent water molecule @ Ru
- ✳ Ligand aromatization unaffected

Free energy surfaces as a function of the CVs defined as coordination numbers of Ru, O, and H

How is molecular H2 formed?

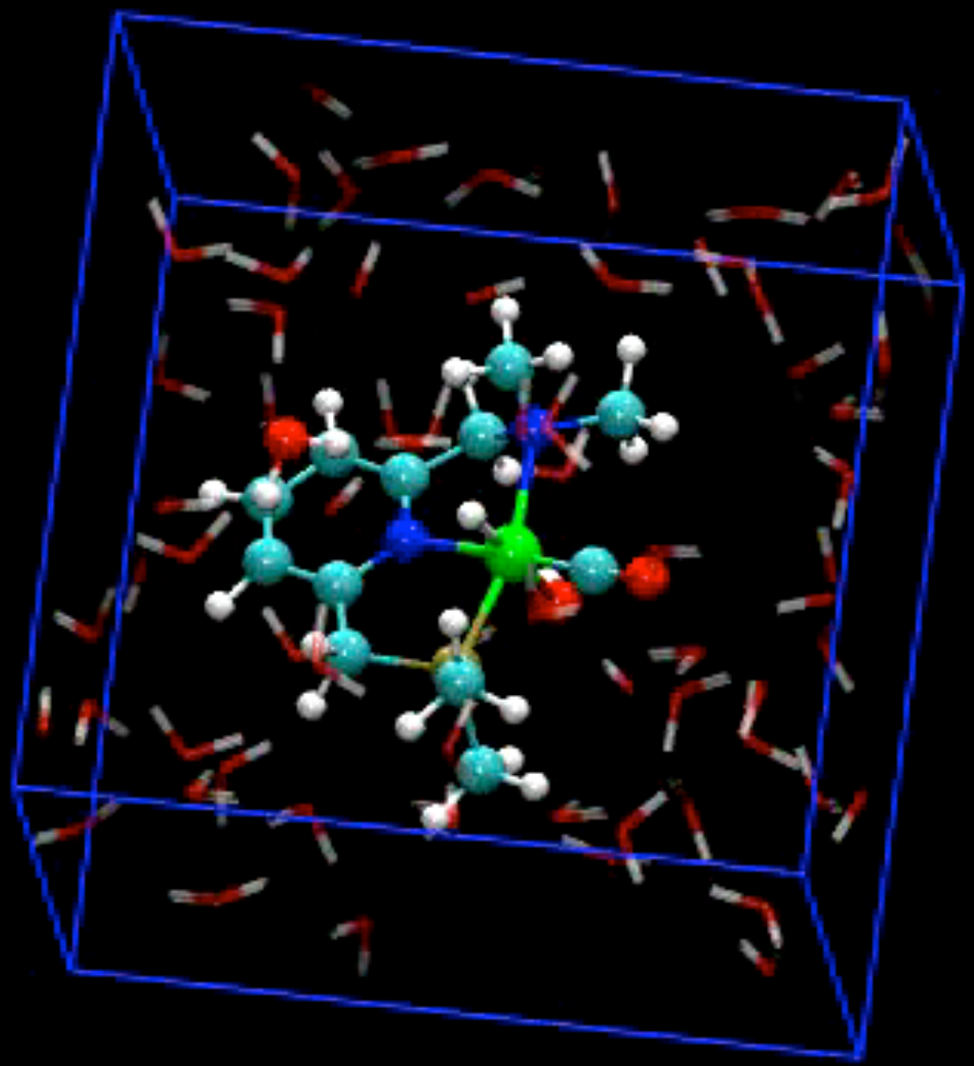
Plain Molecular Dynamics



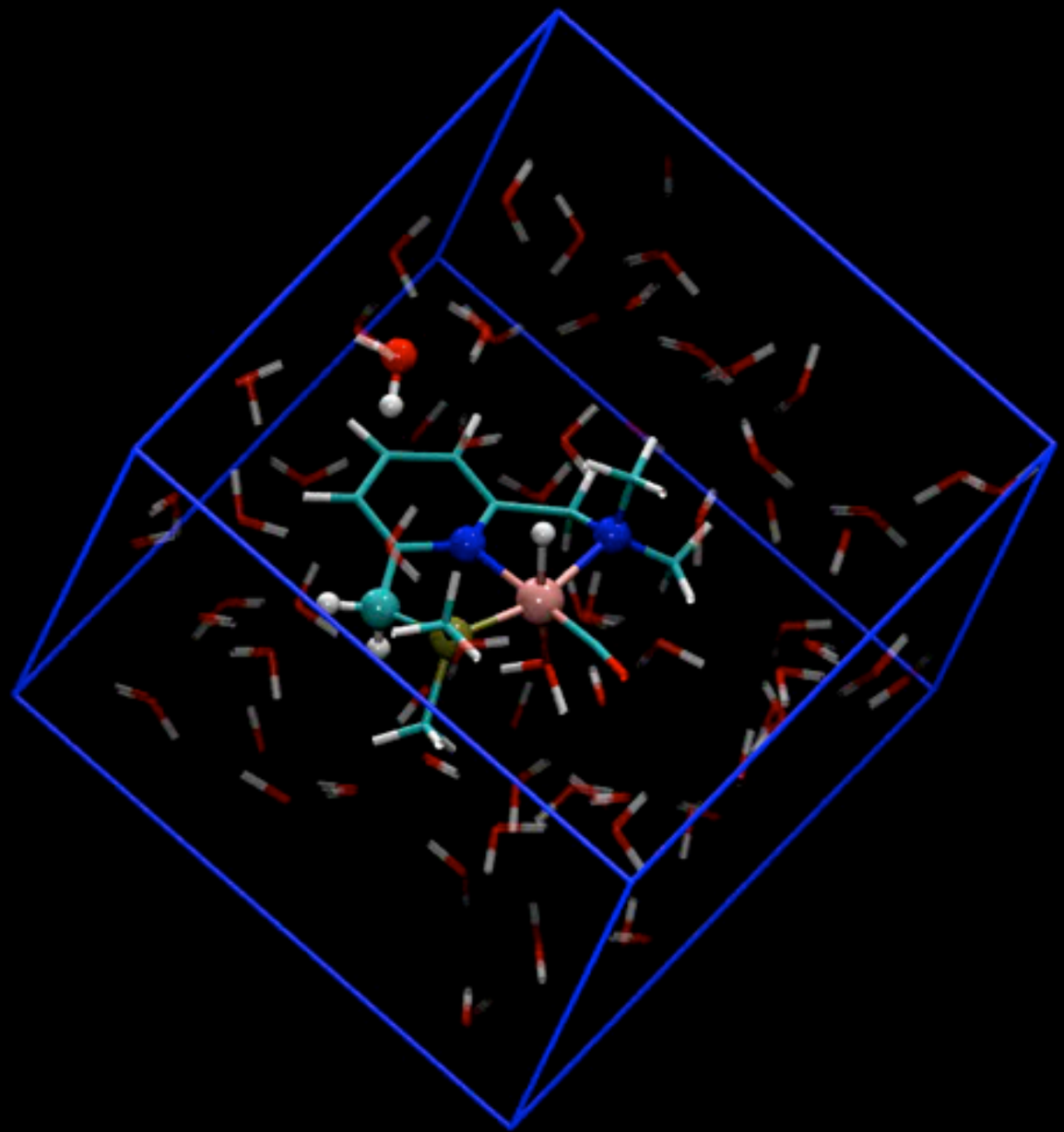
Metadynamics

How is molecular H2 formed?

Plain Molecular Dynamics



Metadynamics



ACS Catalysis

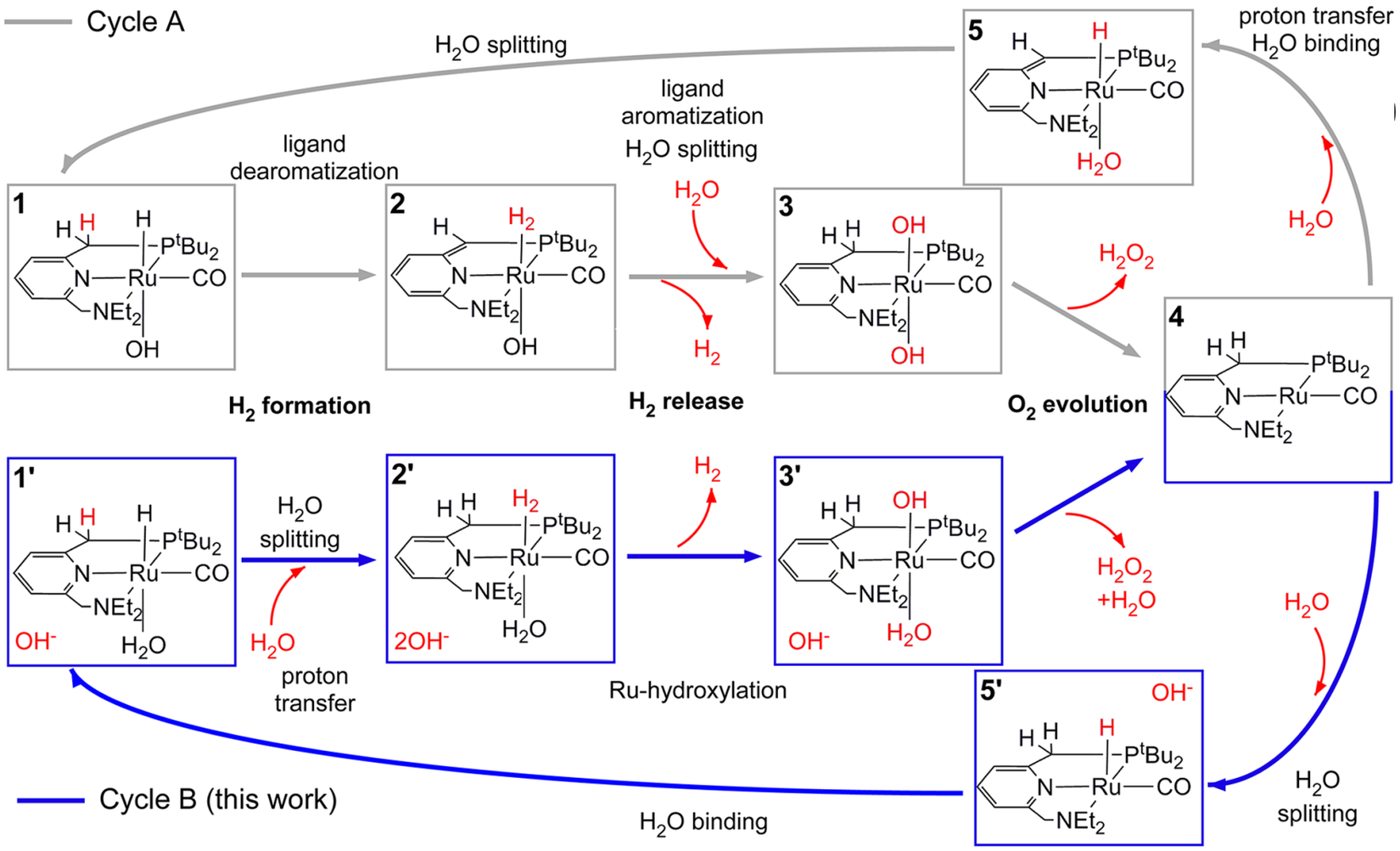
Research Article

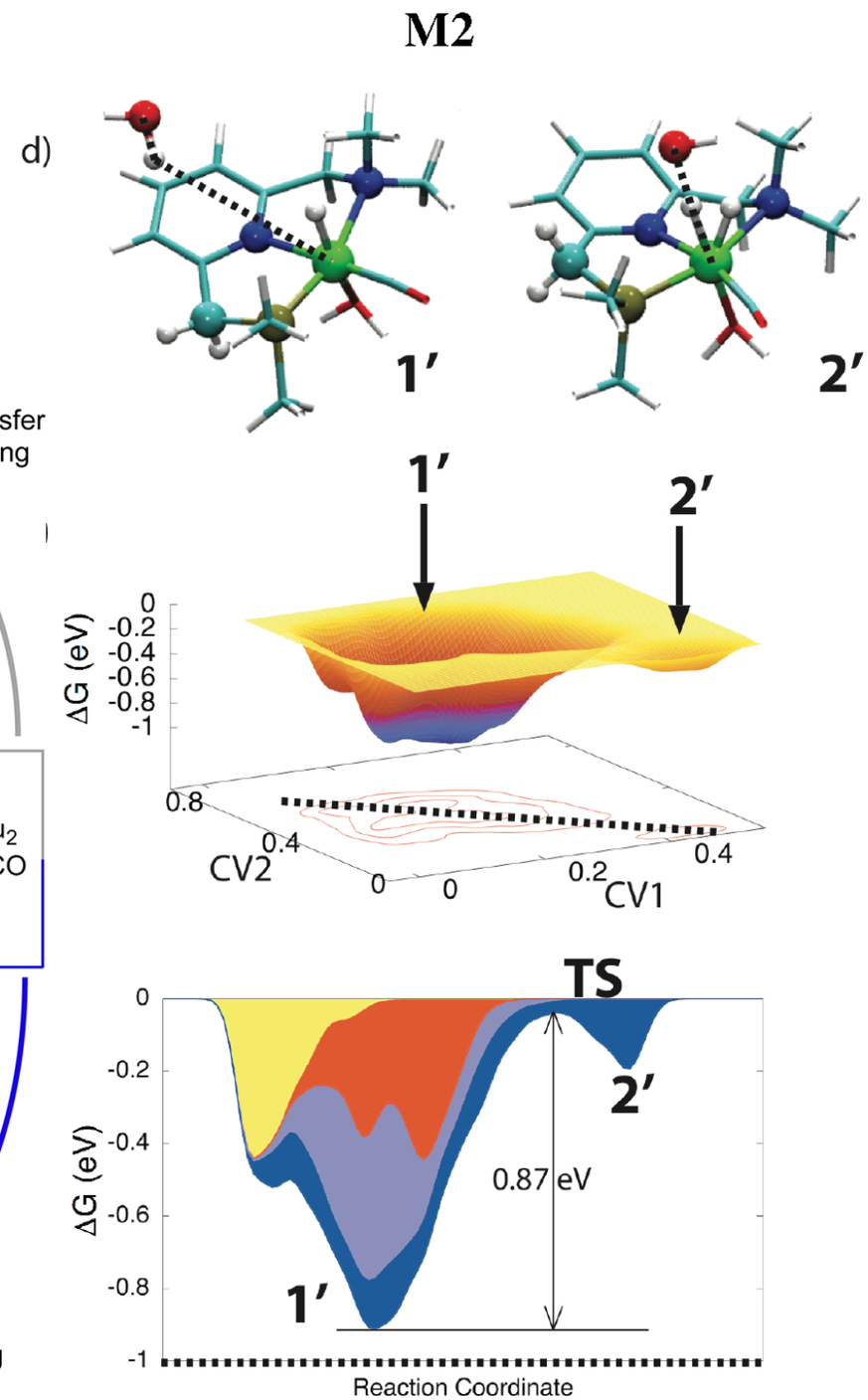
pubs.acs.org/acscatalysis

Reaction Mechanisms of Water Splitting and H_2 Evolution by a Ru(II)-Pincer Complex Identified with Ab Initio Metadynamics Simulations

Changru Ma,[†] Simone Piccinin,[‡,†] and Stefano Fabris*[,‡,†,§]

Scheme 2. Proposed Catalytic Cycles for Water Splitting Catalyzed by the Ru(II)−Pincer





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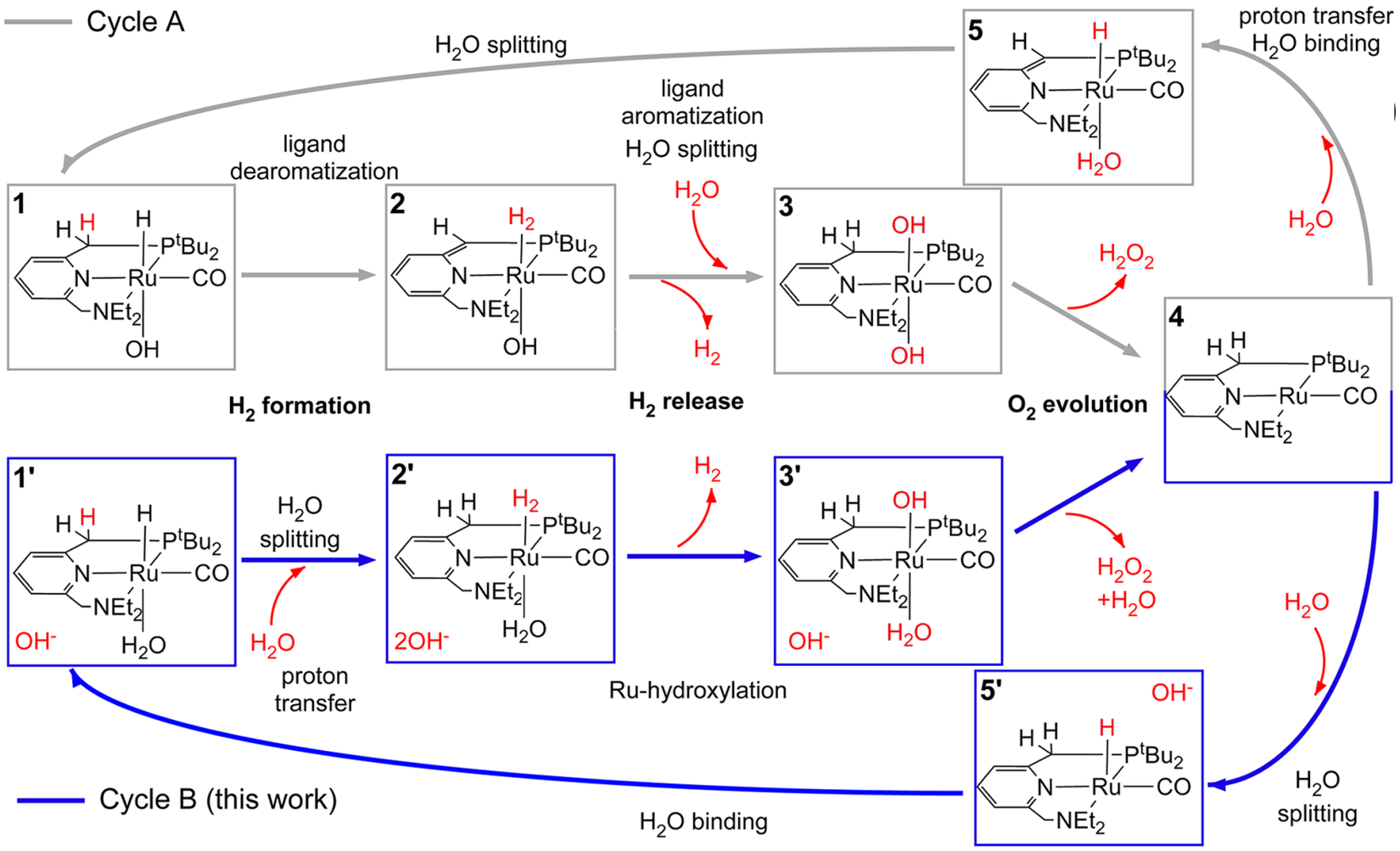
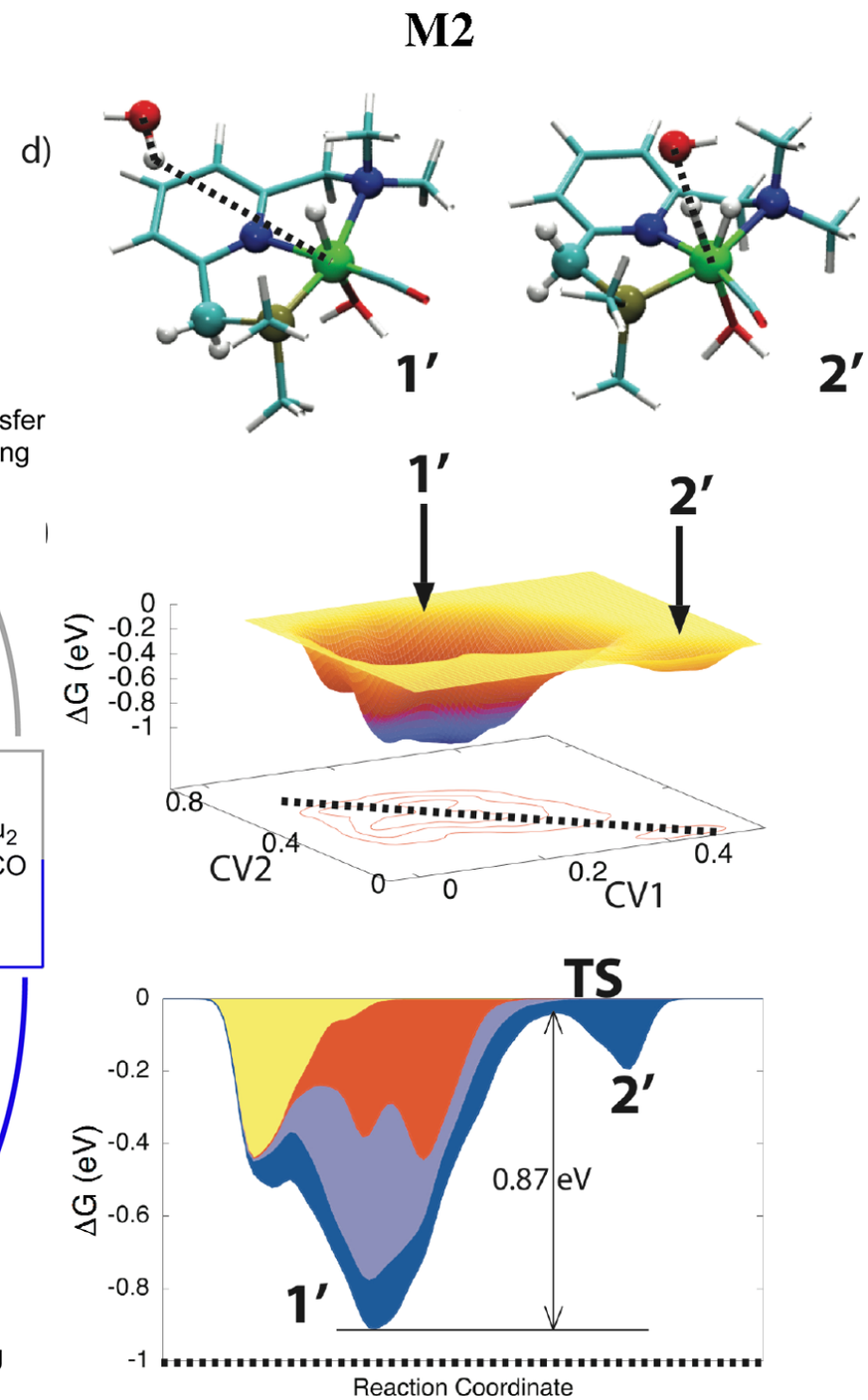
Changru Ma,[†] Simone Piccinin,[‡,†] and Stefano Fabris*[,‡,†,§]

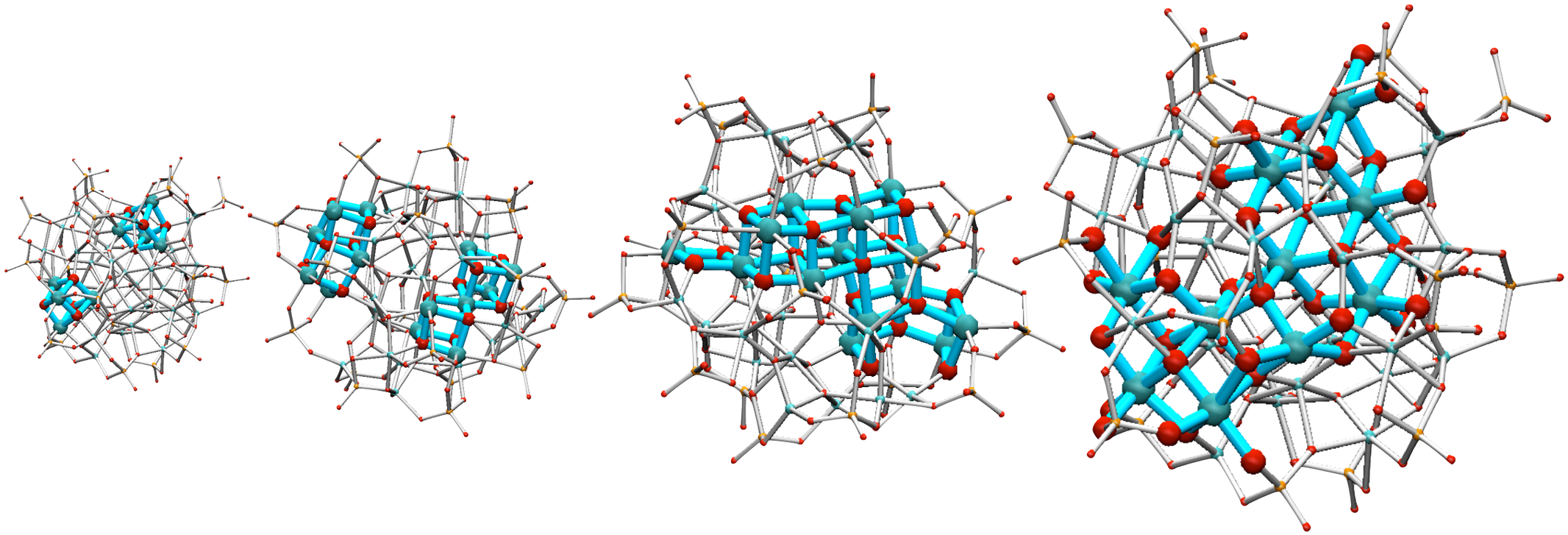
Scheme 2. Proposed Catalytic Cycles for Water Splitting Catalyzed by the Ru(II)−Pincer





Importance of an explicit description of the solvent for a predictive modeling of chemical reactions that involve the active participation of the solvent.

Atomistic Structure of Cobalt-Oxide Nanoparticles for Catalytic Water Oxidation



Co-oxides water-oxidation catalysts

Novel class of materials based on Co oxide and other earth abundant elements

Science
AAAS

In Situ Formation of an Oxygen-Evolving Catalyst in Neutral Water Containing Phosphate and Co^{2+}

Matthew W. Kanan and Daniel G. Nocera*

Credit: Dan Nocera

STABILITY - No degradation

COST - Based on earth-abundant elements

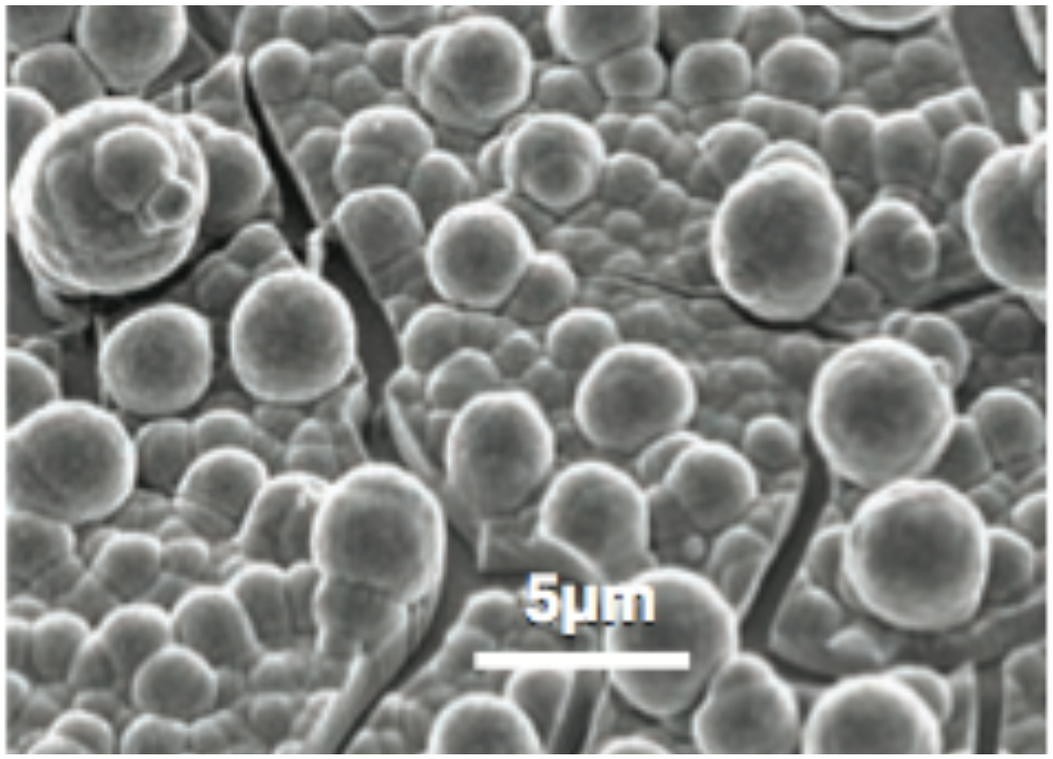
EFFICIENCY - Low overpotential, high TOF

STRUCTURE - FUNCTION

Design guidelines

Co oxides as WOC

Novel class of materials based on Co oxide and other earth abundant elements

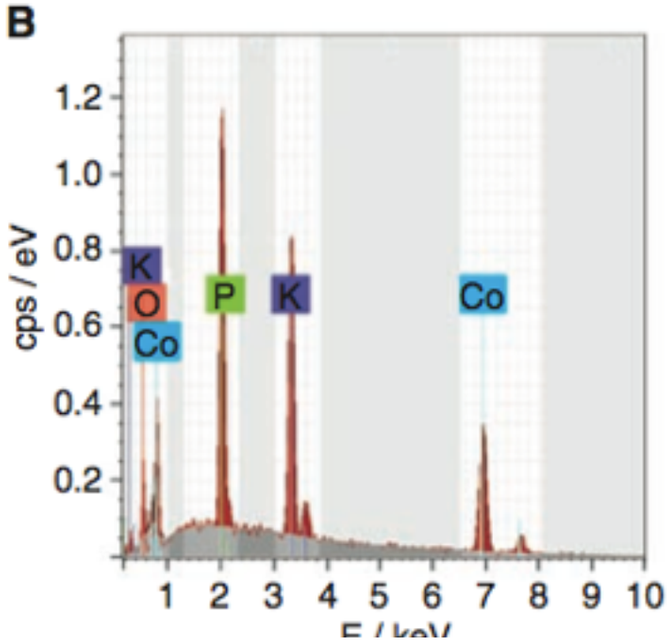


• Self-assembles on conductive substrates via electrolysis from a phosphate-buffered Co2+ solution.

• Formation and operation require a very low overpotential (0.28-0.41 V), room temperature and neutral pH

Exact composition: not known. Exact structure: not known

Kanan and Nocera, Science 321, 1072 (2008)



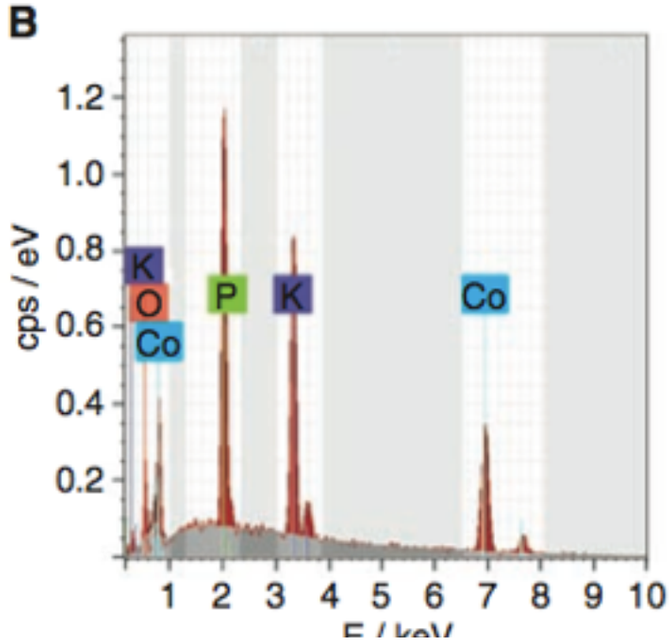
Structure and composition

X-ray diffraction: amorphous Co-oxide;
No sign of long-range crystalline phases

EDX: it is not a pure Co oxide
Co:P:K ratio is roughly 2:1:1

Kanan and Nocera, Science 321, 1072 (2008)

Structure and composition



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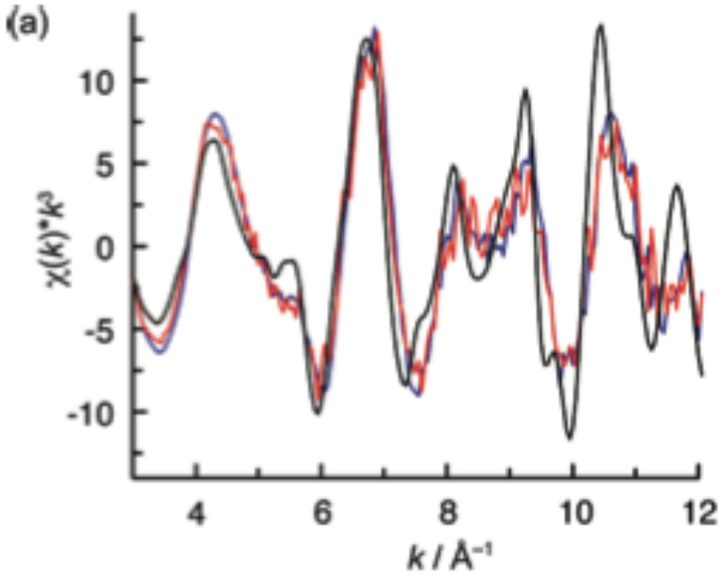
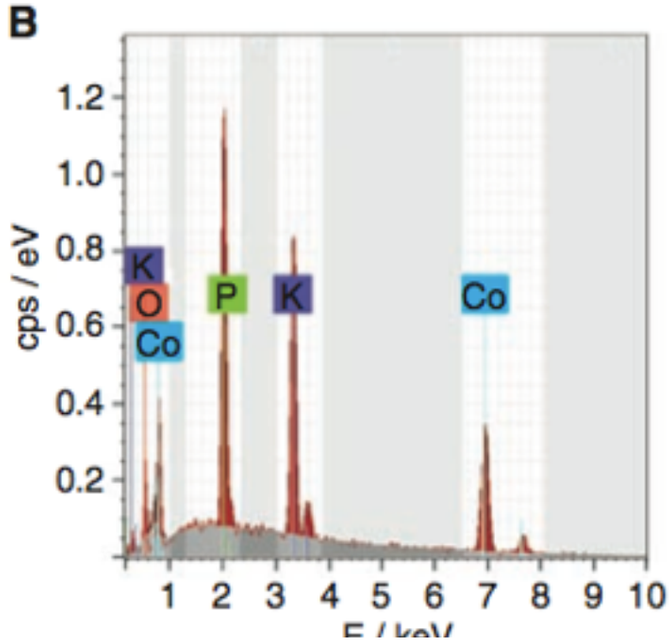


EXAFS discrete multi cobalt-oxo molecular units

?arranged into an amorphous network?

Structure and composition



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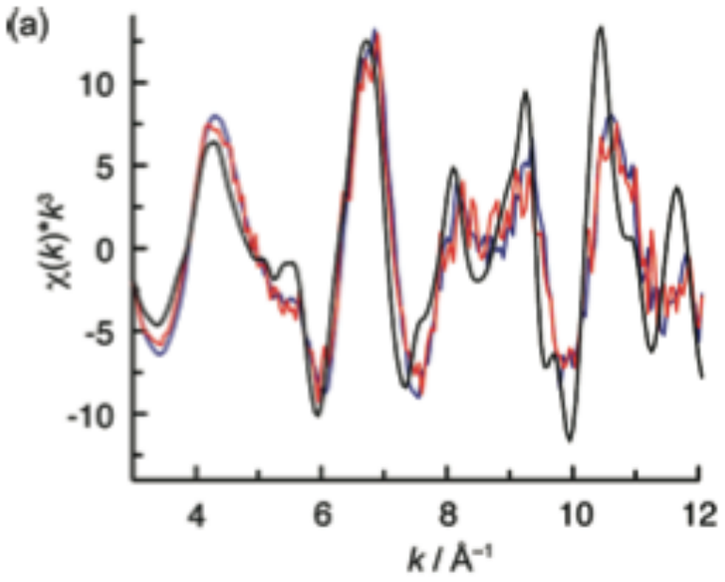

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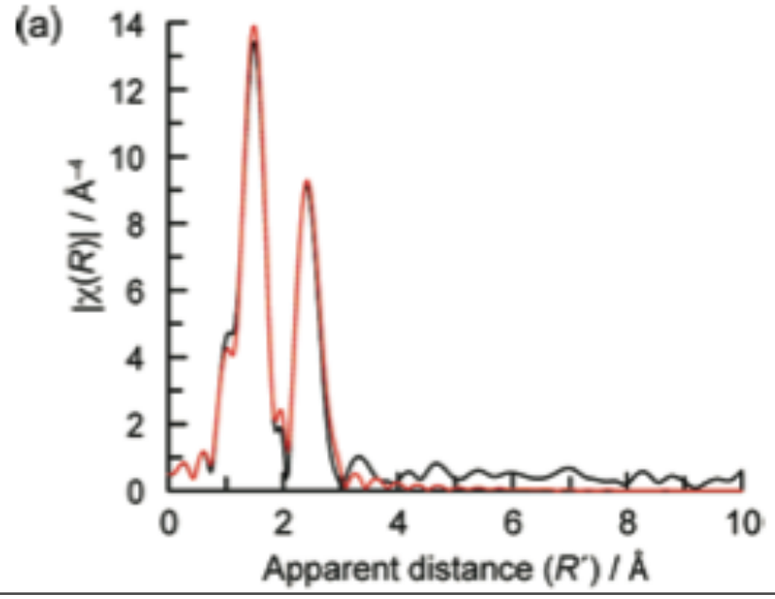
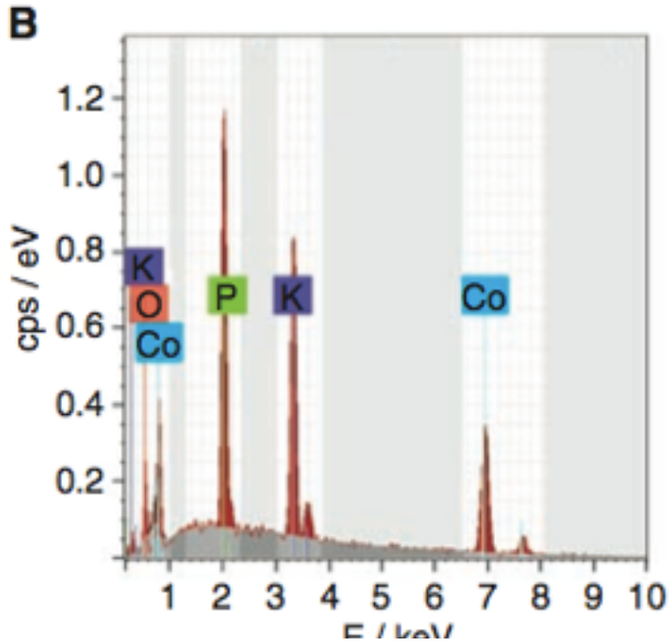
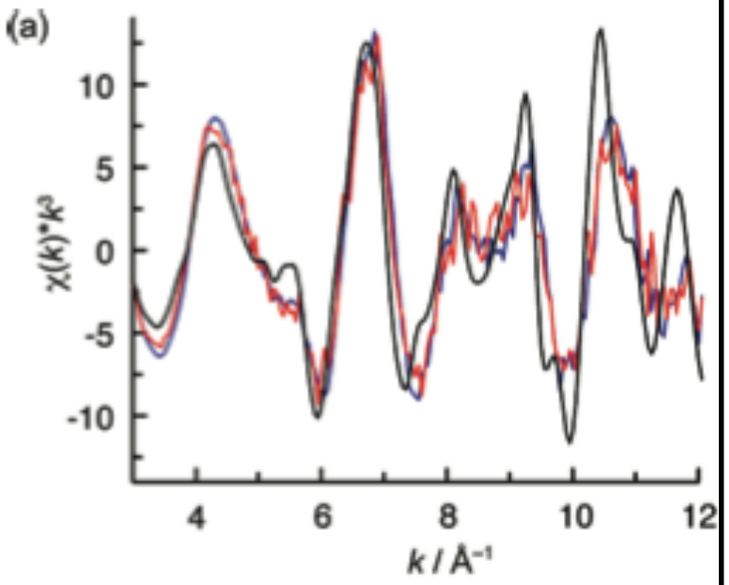
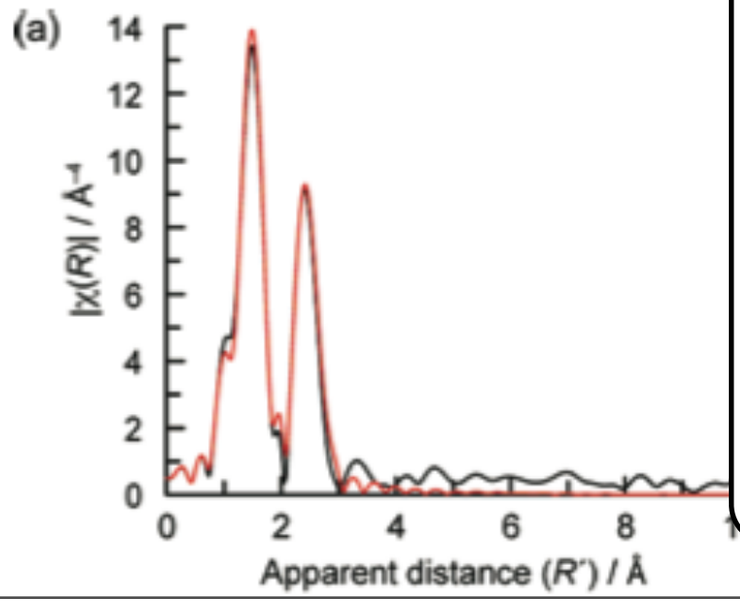


Fourier-transformed EXAFS:
Order at short and medium range
Short range: CoO6 octahedra
Medium range? difficult interpretation

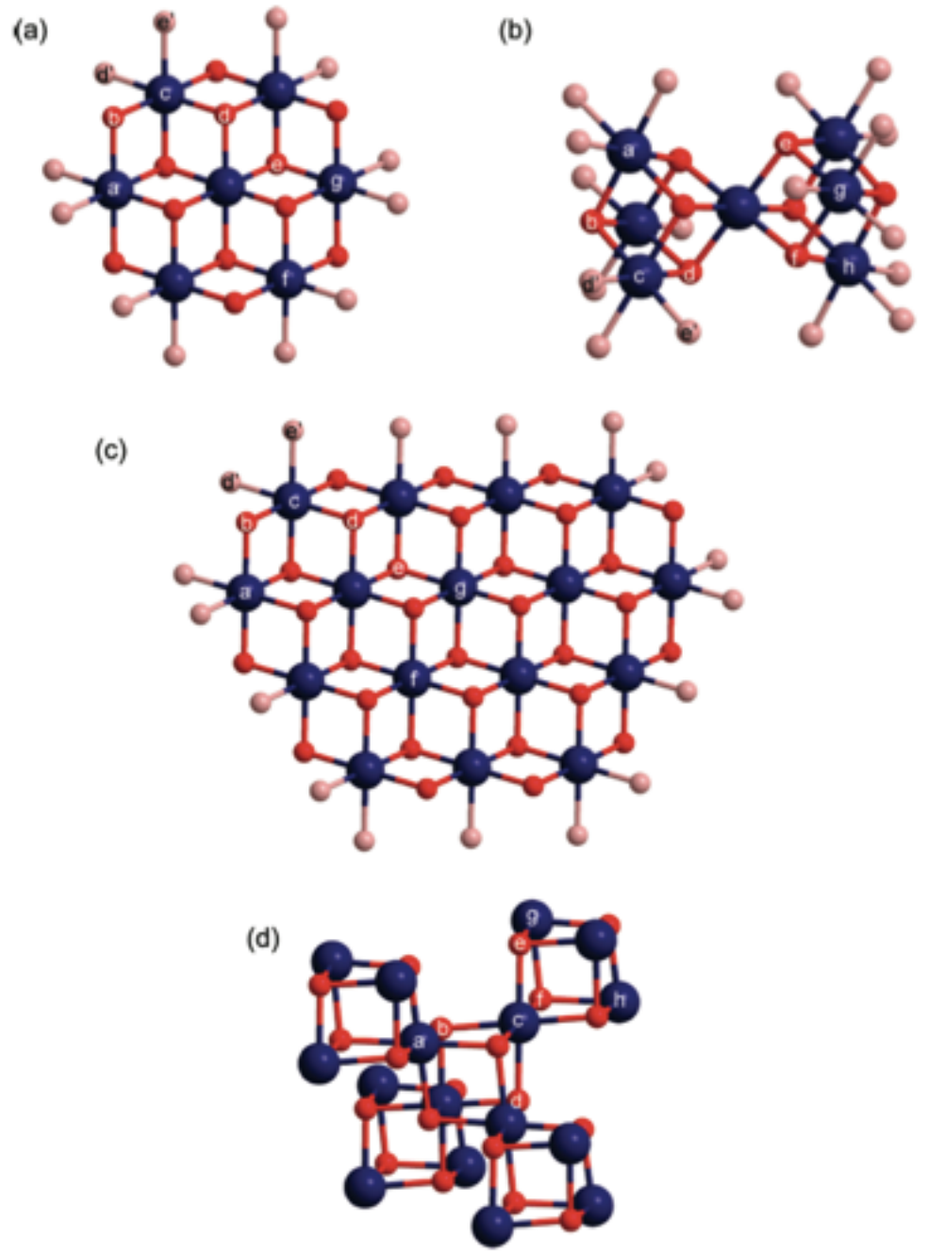
M.W. Kanan et al., JACS 132, 13692 (2010)
M. Risch et al., JACS 131, 6936 (2009)







Tentative models compatible with EXAFS



Complete and incomplete cobalt-oxo cubane motifs or layered CoO6 octahedra

Structure-function relationship

Reliable structural and compositional models of the catalyst are missing

GOAL

predict the first realistic structural model of amorphous Co-Pi

(no assumptions from experimental data, besides the chemical composition of the grains)

STRUCTURE → ***FUNCTION***

Knowing the catalyst's structure will open the way for clarifying the reaction mechanisms

Computational approach

STRUCTURAL SEARCH

Metadynamics

(shell model)

STRUCTURE OPTIMIZATION

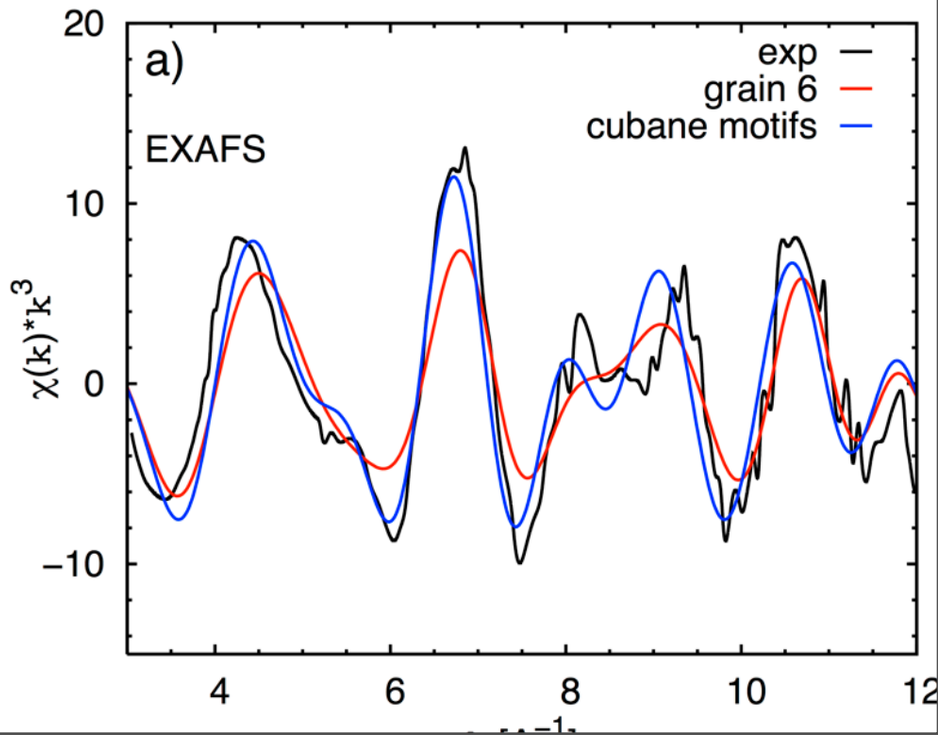
DFT

STRUCTURE VALIDATION

EXAFS simulation

Comparison with exp

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + v_{\text{eff}}(\mathbf{r})\right)\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r})$$

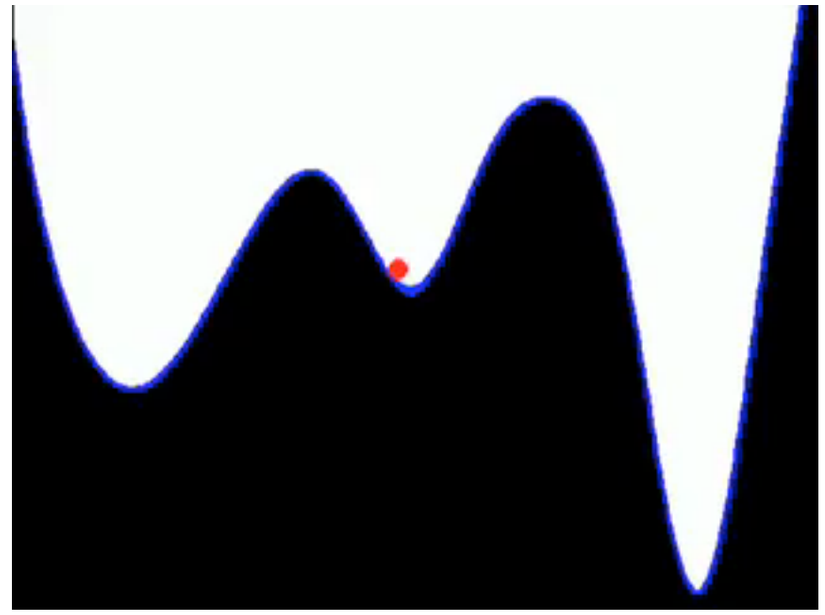


Computational approach

STRUCTURAL SEARCH

Metadynamics

(shell model)



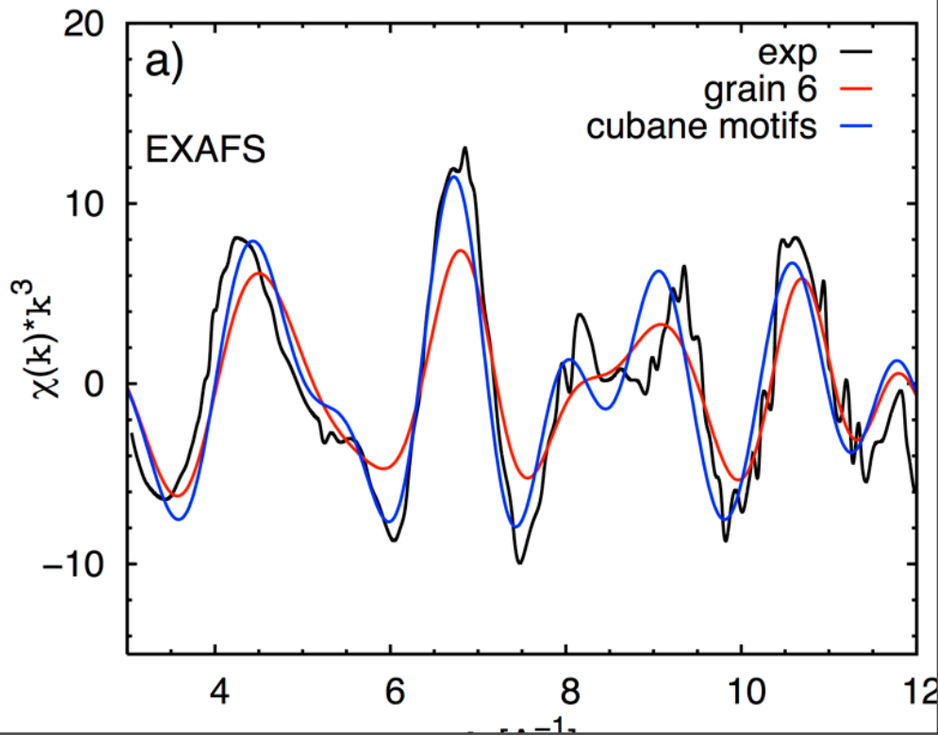
STRUCTURE OPTIMIZATION

DFT

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + v_{\text{eff}}(\mathbf{r})\right)\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r})$$

STRUCTURE VALIDATION

EXAFS simulation



Comparison with exp

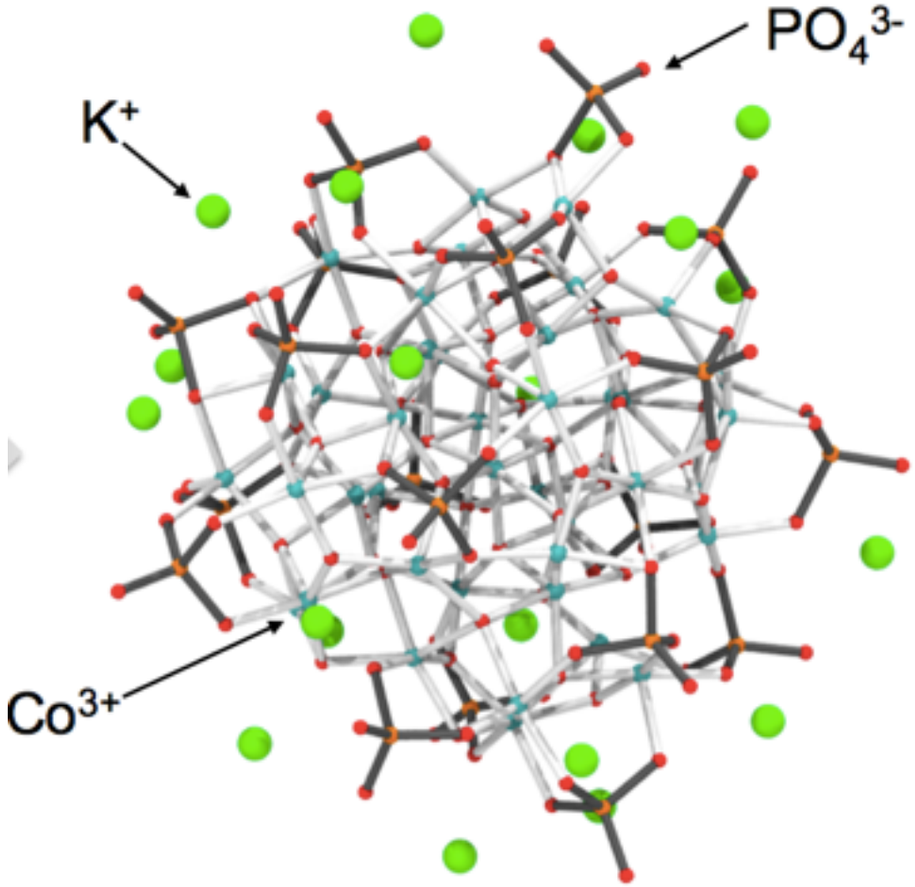
Computational approach

Model Nanoparticles

$Co_{40}P_{20}K_{20}O_{120}$ stoichiometry

(EDX ~2:1:1 ratio for Co:P:K)

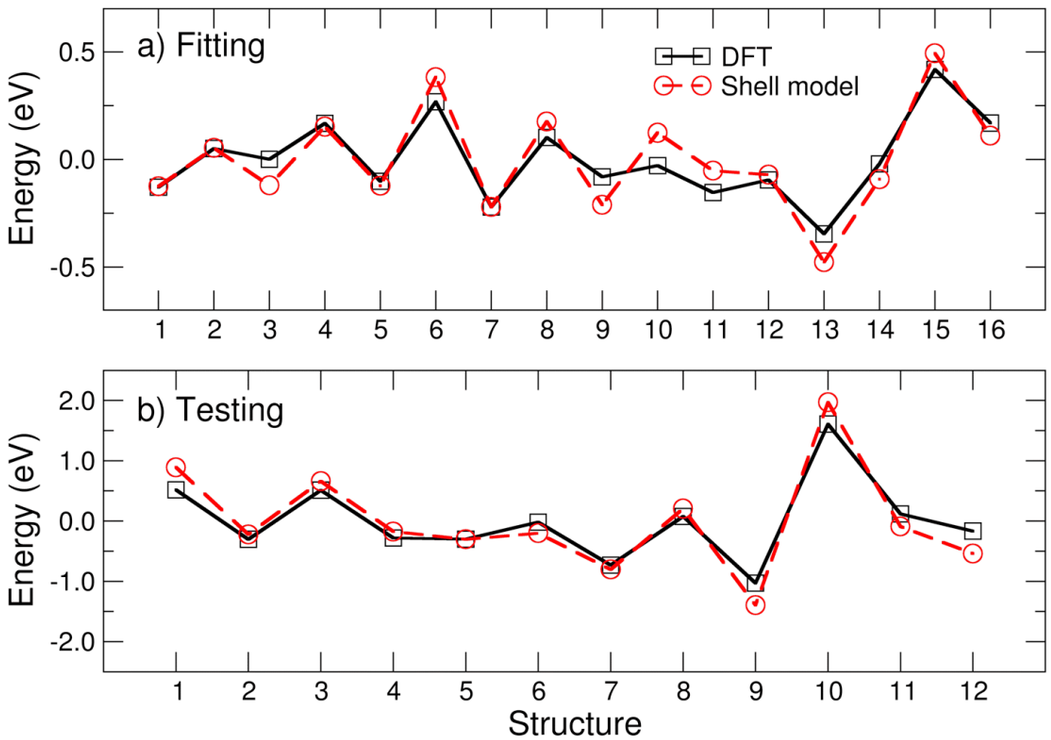
Initial random position of atoms



Empirical Shell-model for CoPi

Fitting to DFT-PBE total energy differences for Co3O4 and KPO4

Energetics and structure of CoPi



Computational approach

Metadynamics simulations *(shell model)*

2 CV sampling the atomic environment around the Co sites

CV1: coordination number of Co with respect to O ions

CV2: number of Co ions bridging between a pair of O ions

DLPOLY and PLUMED codes

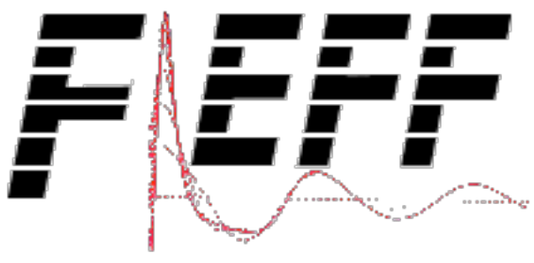
Structural optimization with DFT

Plane-wave pseudopotential approach

Structural optimization of shell-model predictions

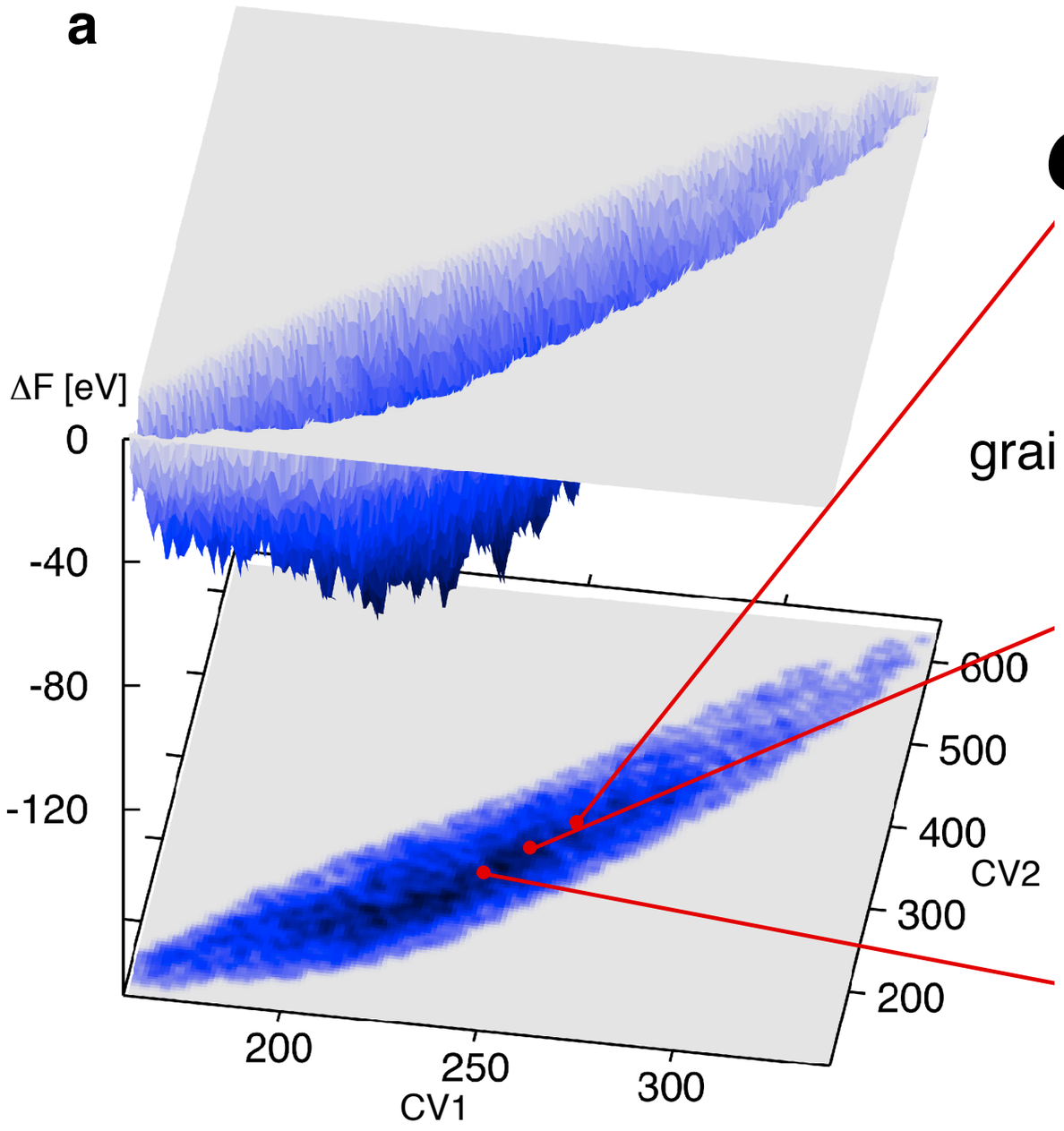
Simulated EXAFS

Ab-initio multiple scattering simulation - FEFF code



Metadynamics simulations - I

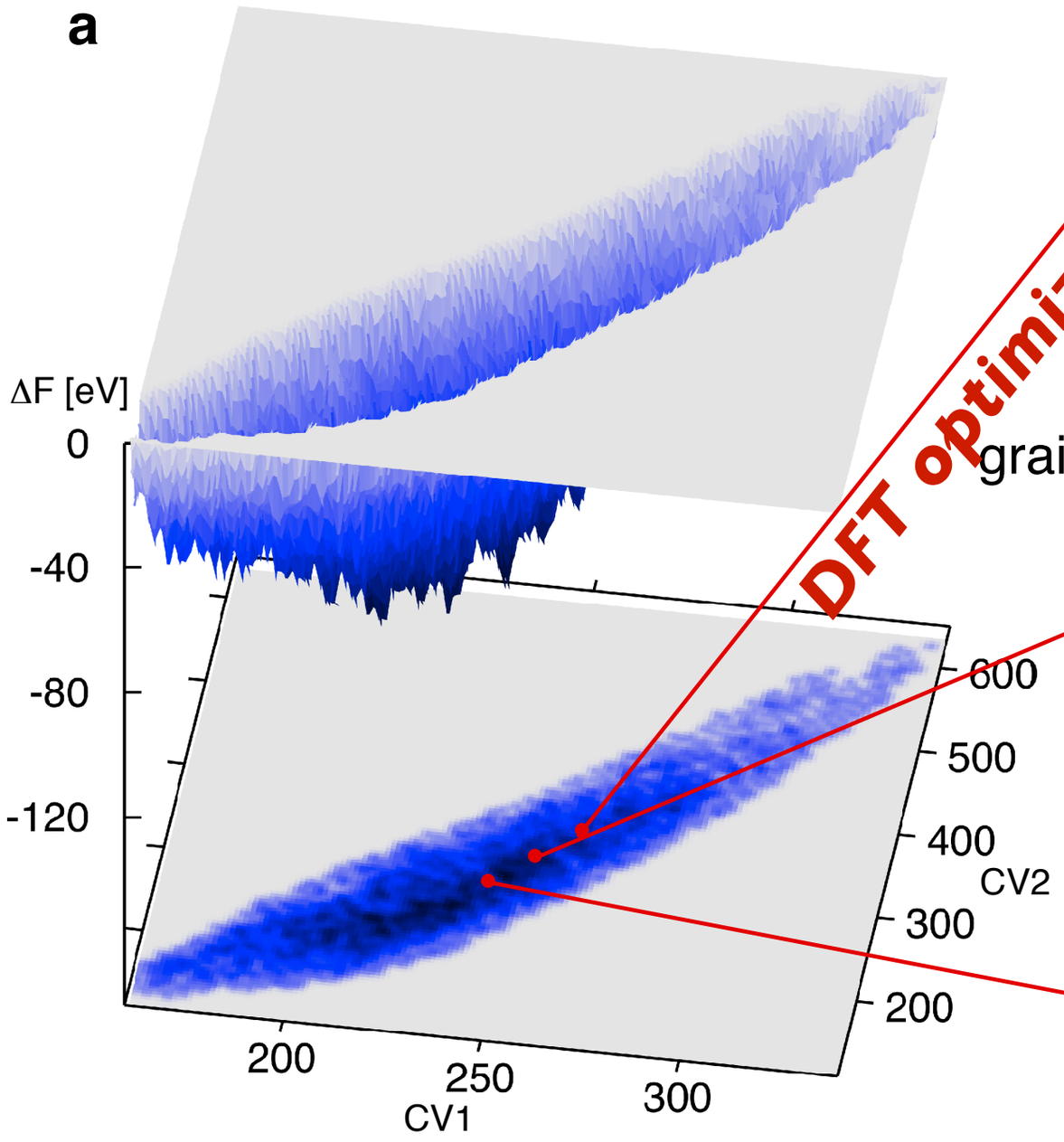
Free energy of NP in the configurational domain spanned by CV1 and CV2



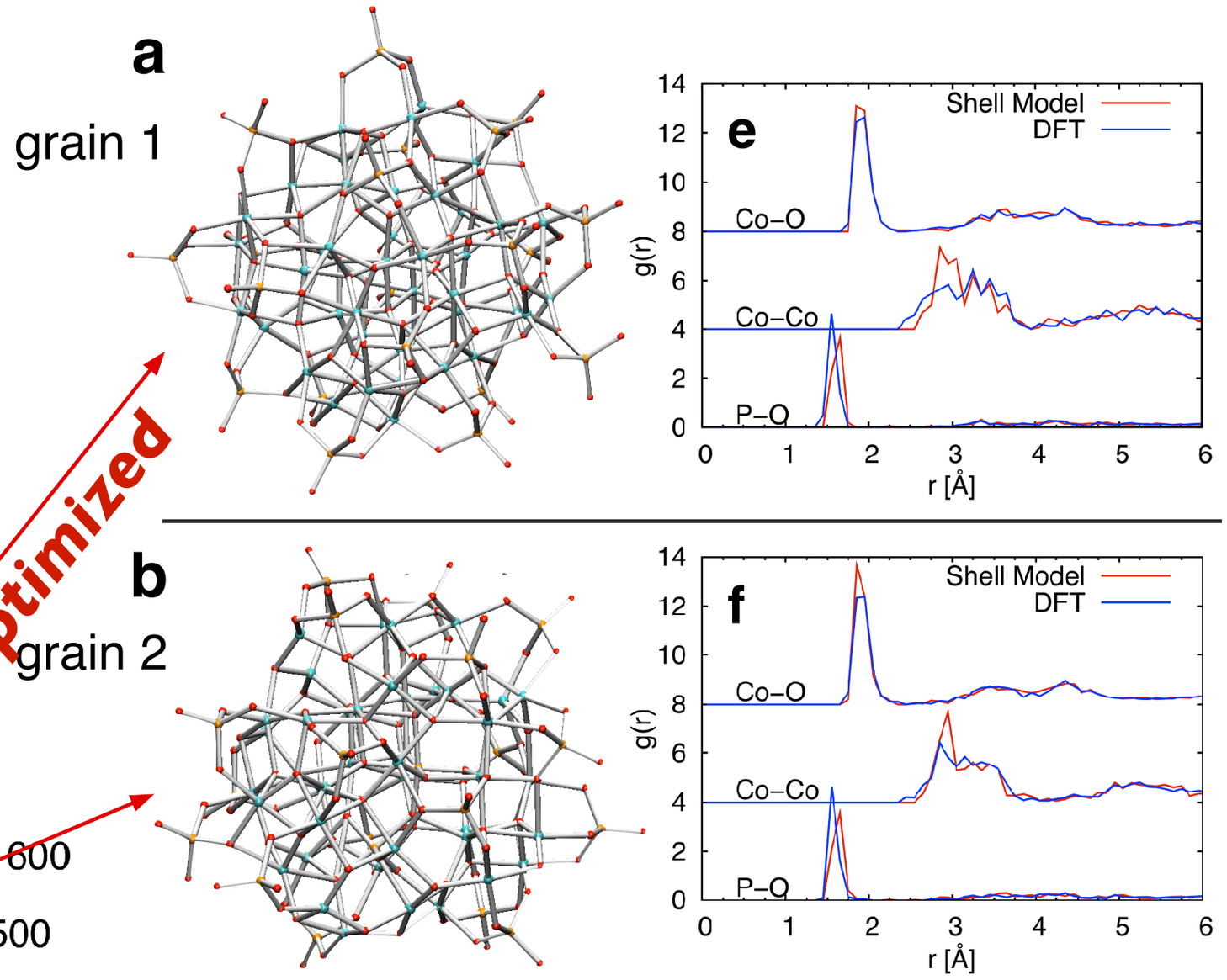
Clear low-energy basin

COMPACT STRUCTURES

Identifies a large number of low-energy amorphous structures

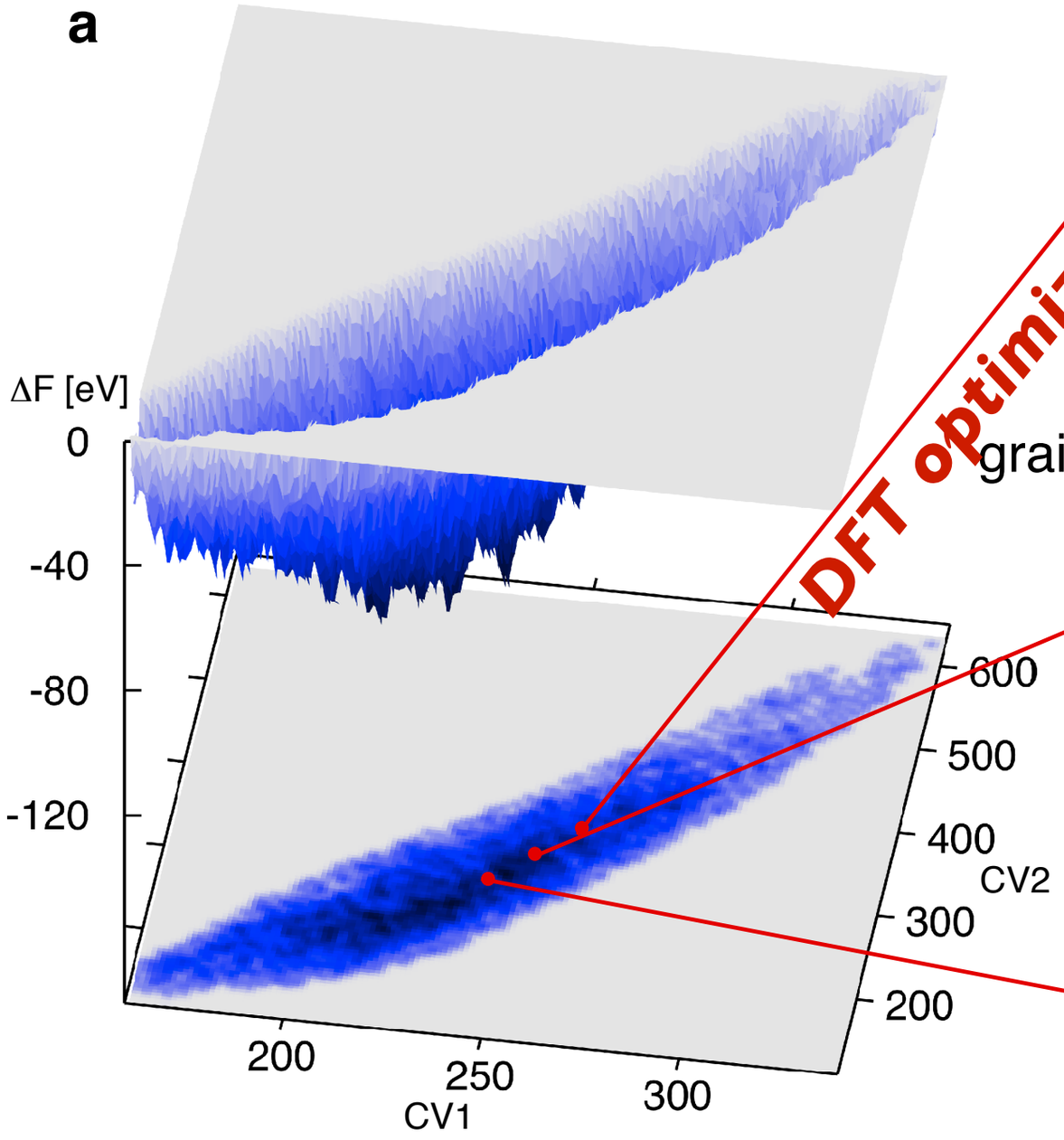


DFT optimized



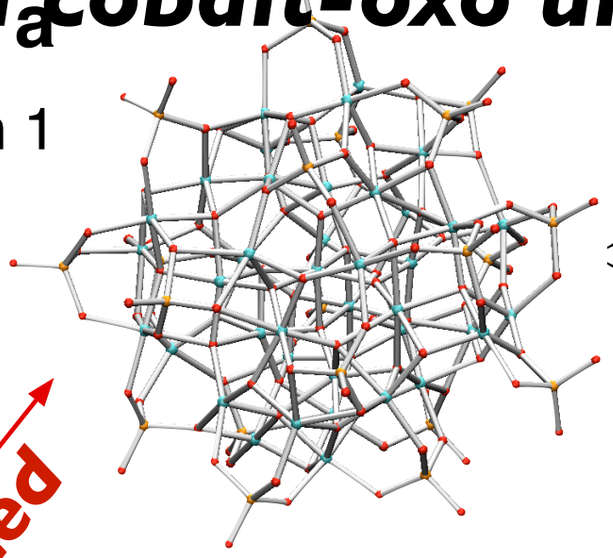
X. Hu, S. Piccinin, A. Laio, and SF, ACS Nano (2012)

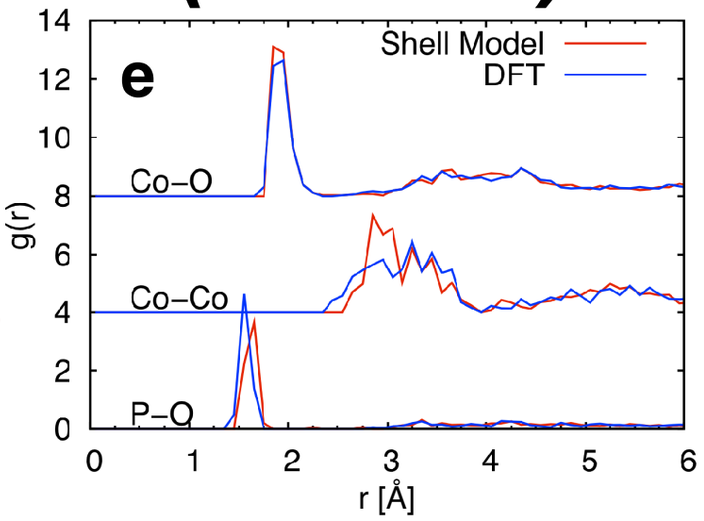
Predominant six and five-fold coordination by oxygen ions in interlinked octahedral cobalt-oxo units (XAS OK)



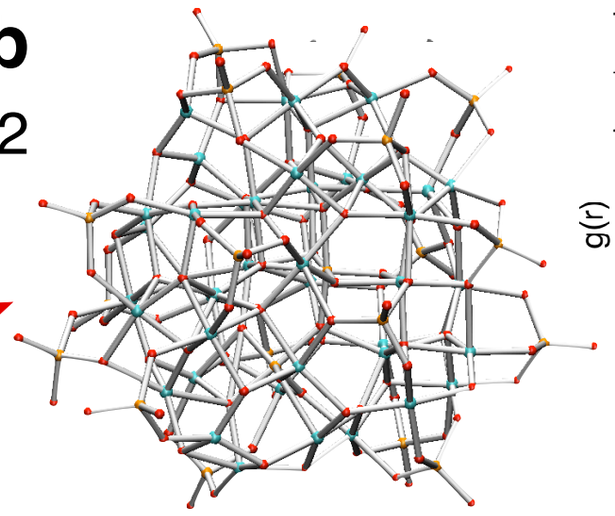
DFT optimized

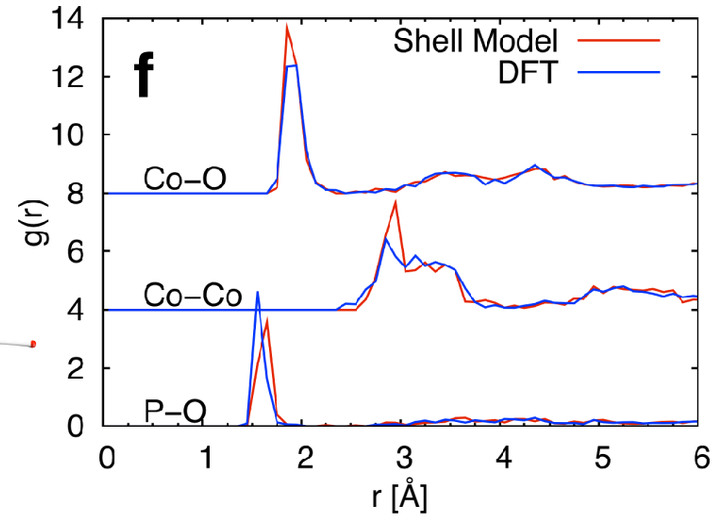
a
grain 1



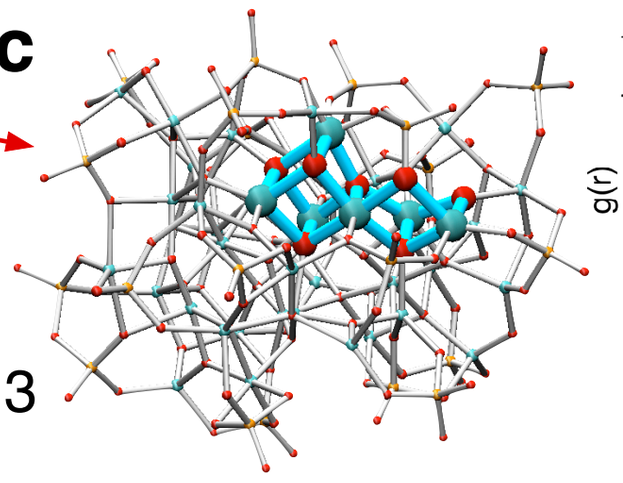


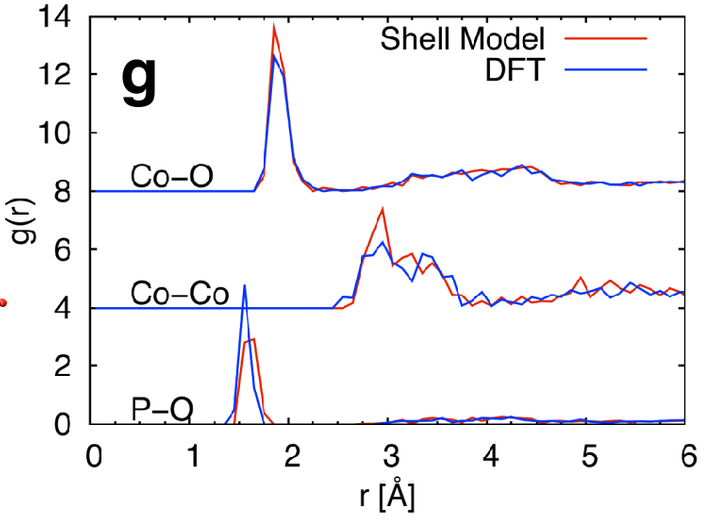
b
grain 2





c
grain 3





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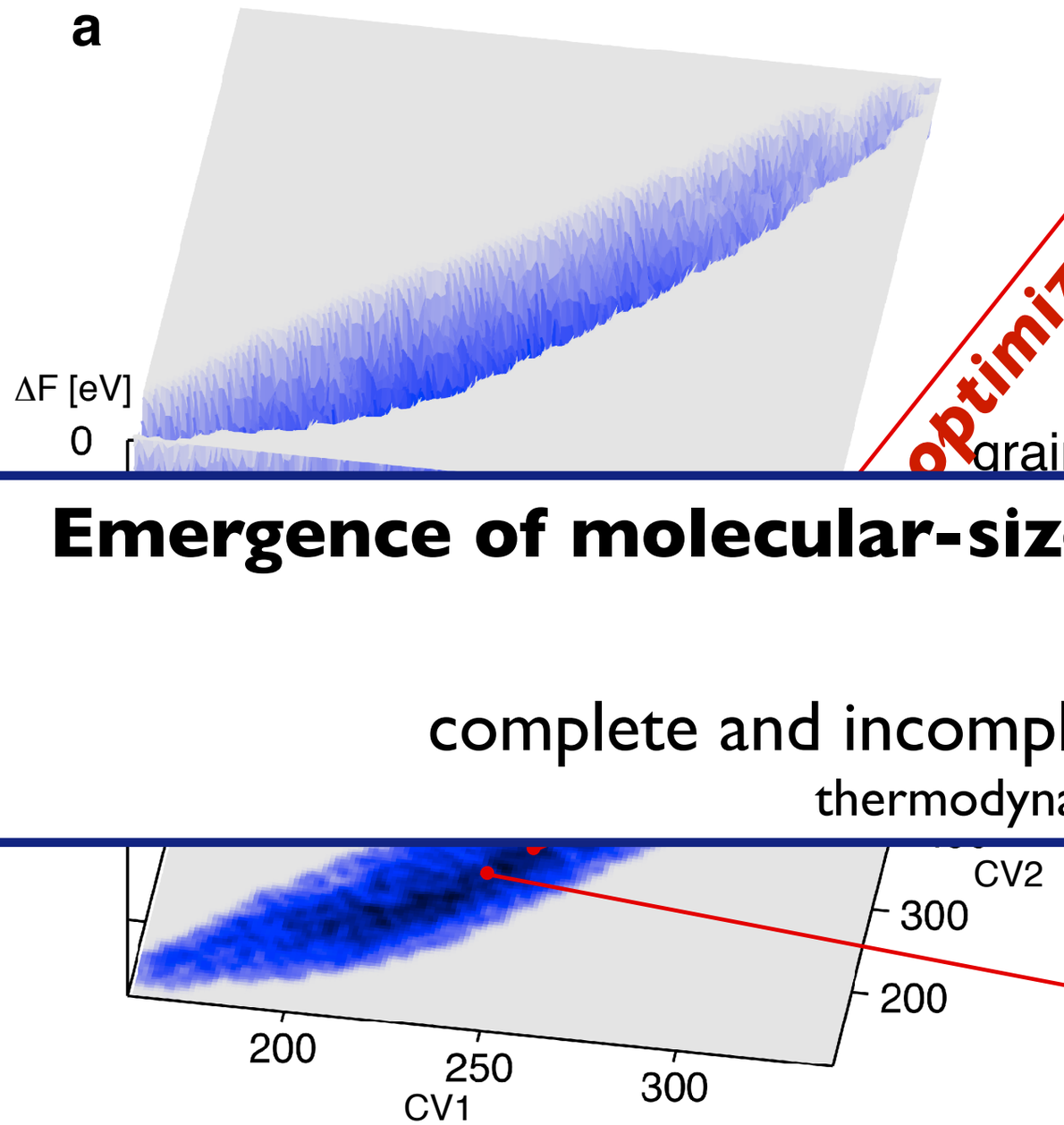
Predominant six and five-fold coordination by oxygen ions in interlinked octahedral cobalt-oxo units (XAS OK)

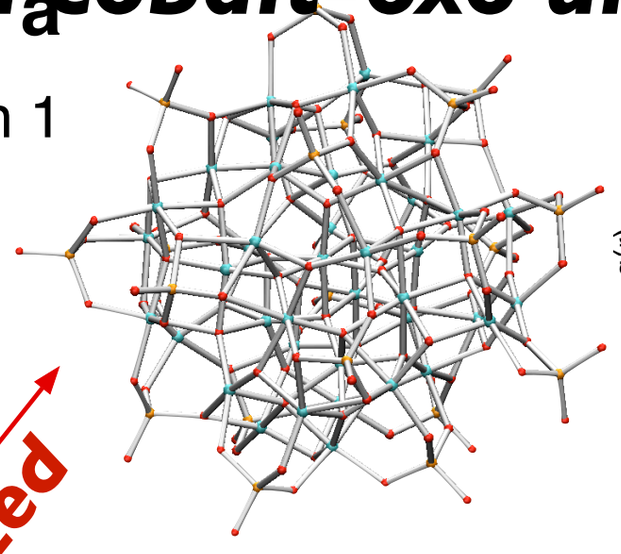
Emergence of molecular-sized crystallites in disordered NP

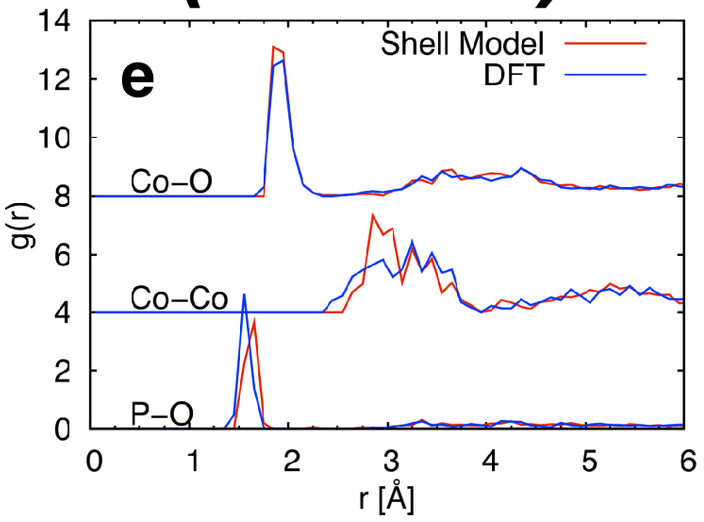
complete and incomplete Co4O4 cubane motifs

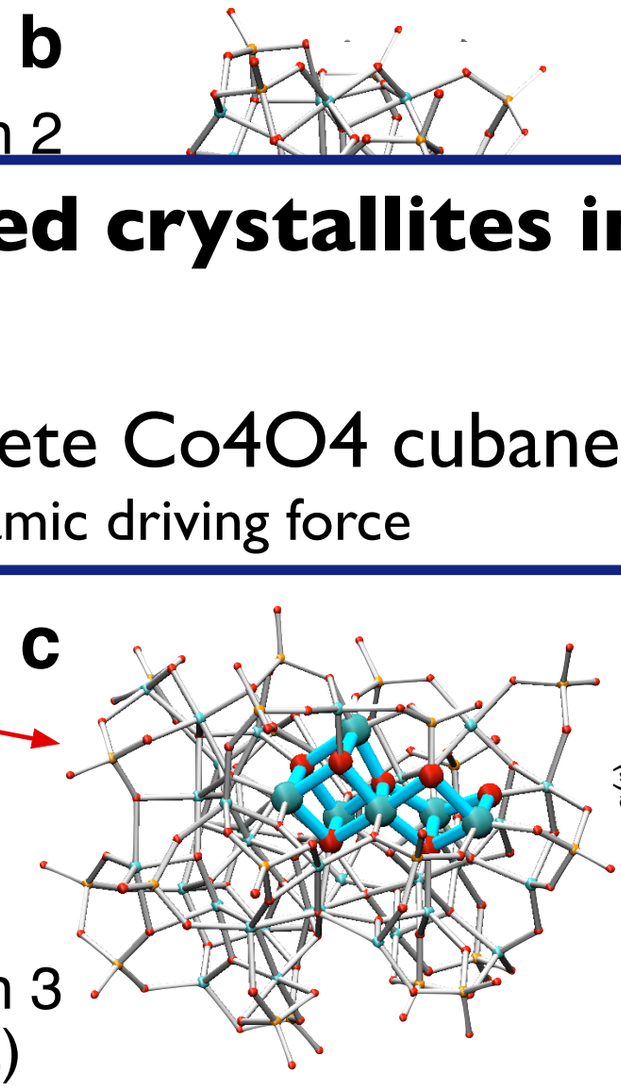
thermodynamic driving force

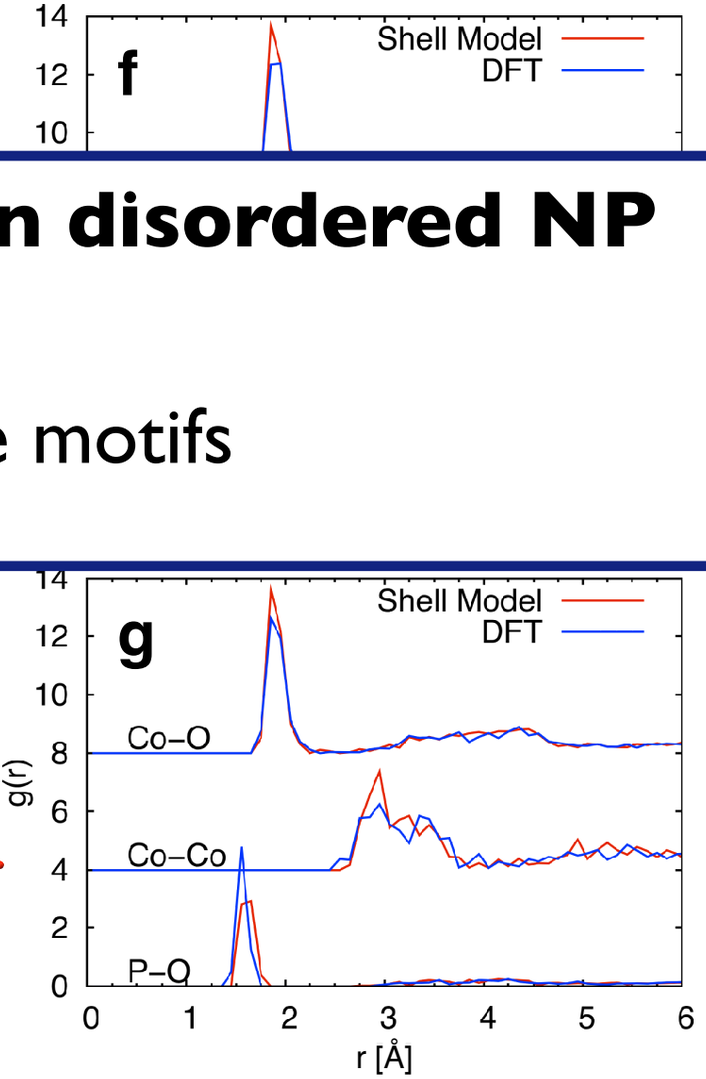


optimized









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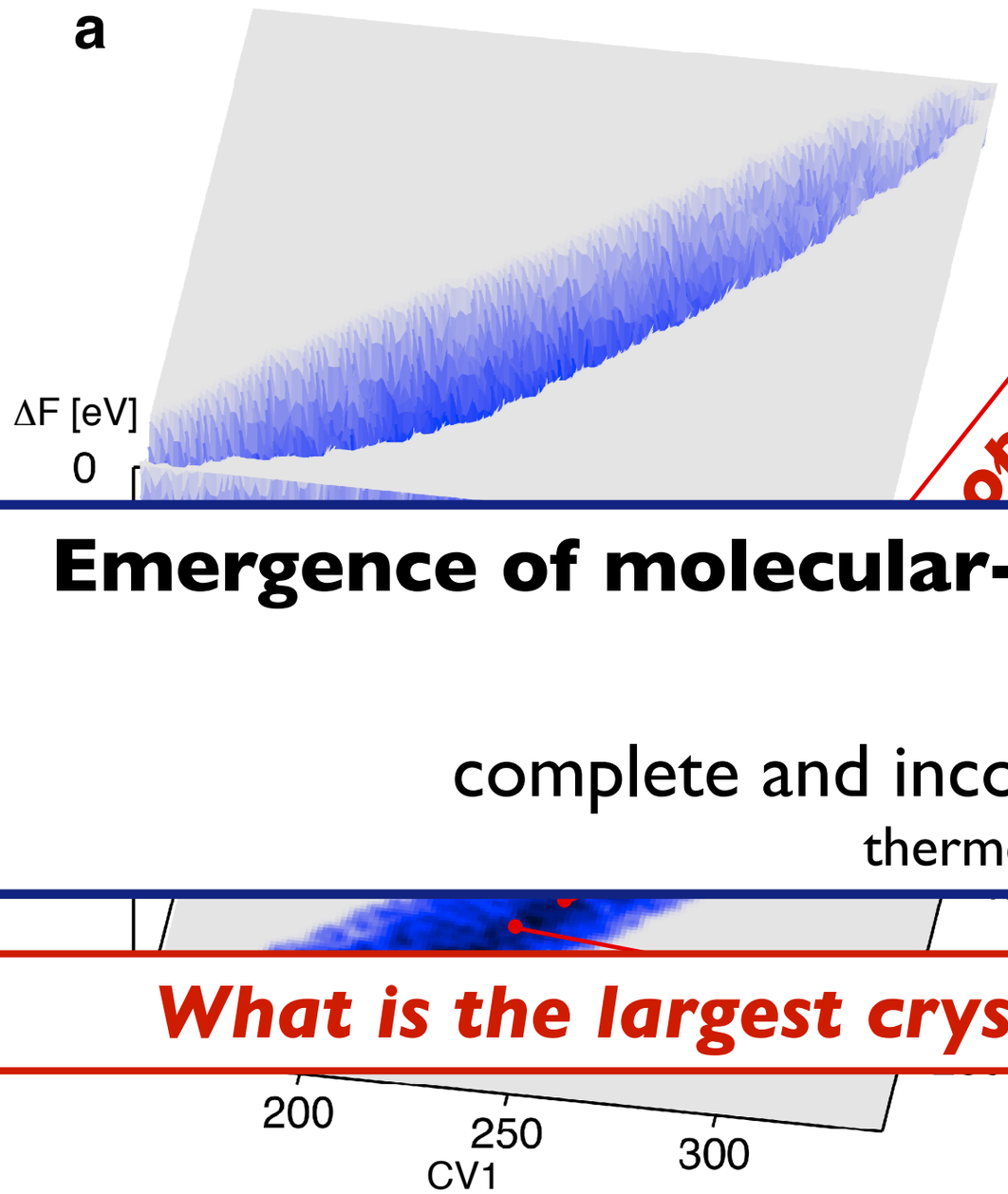
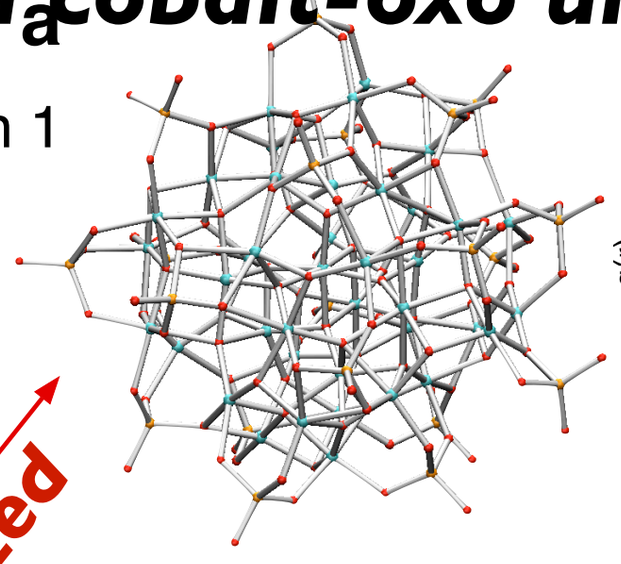
Emergence of molecular-sized crystallites in disordered NP

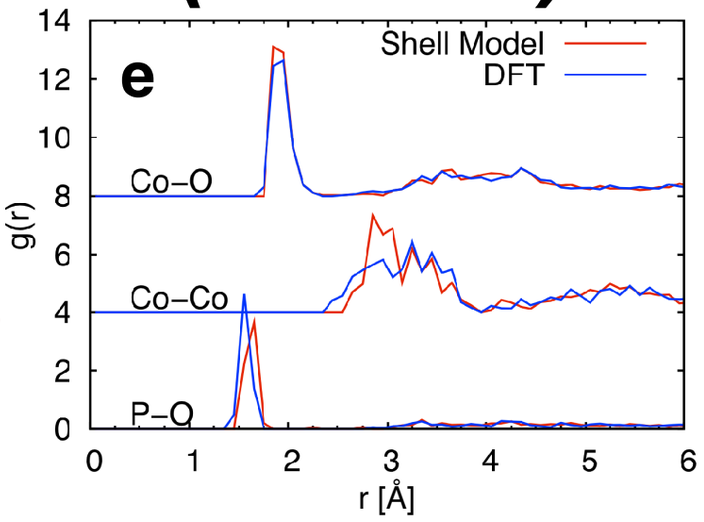
complete and incomplete Co4O4 cubane motifs

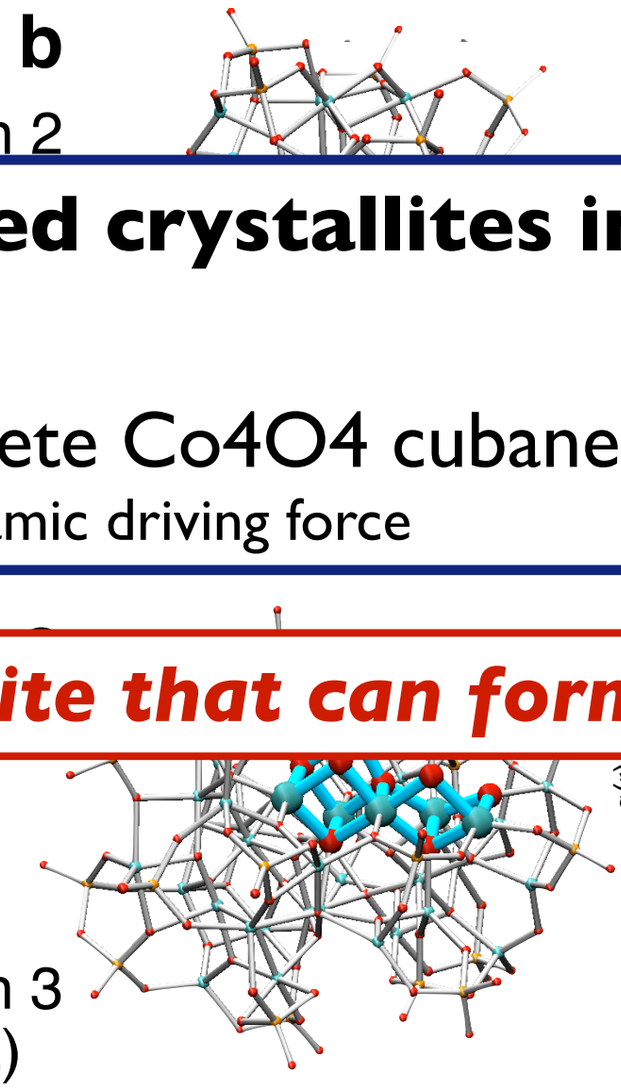
thermodynamic driving force

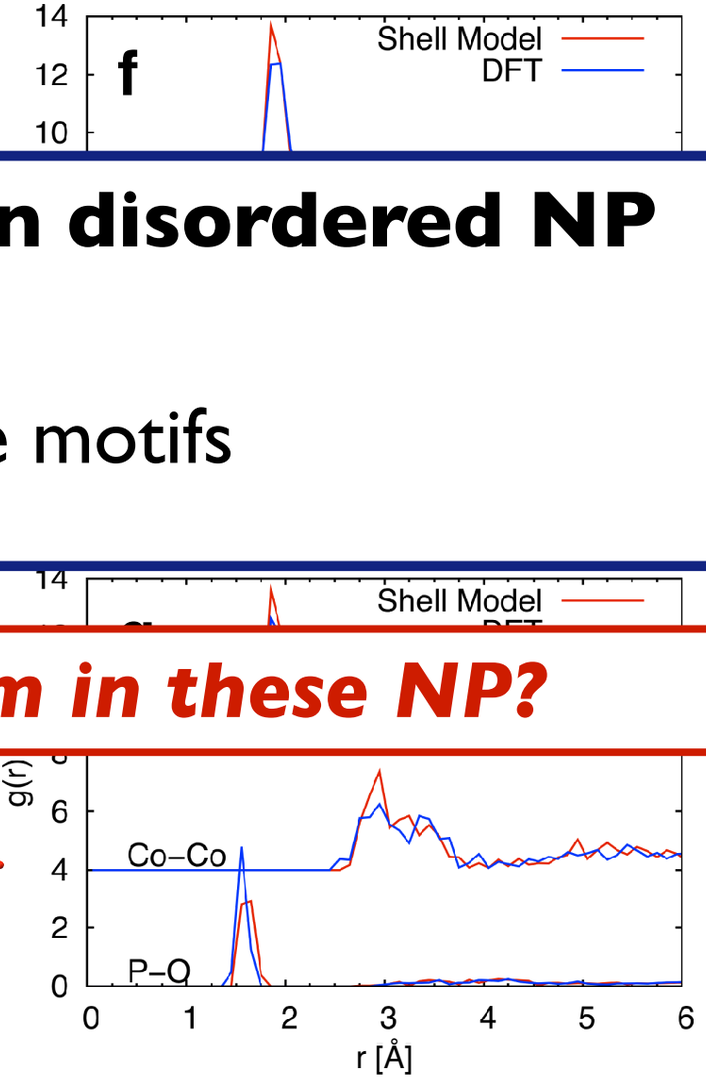
What is the largest crystallite that can form in these NP?











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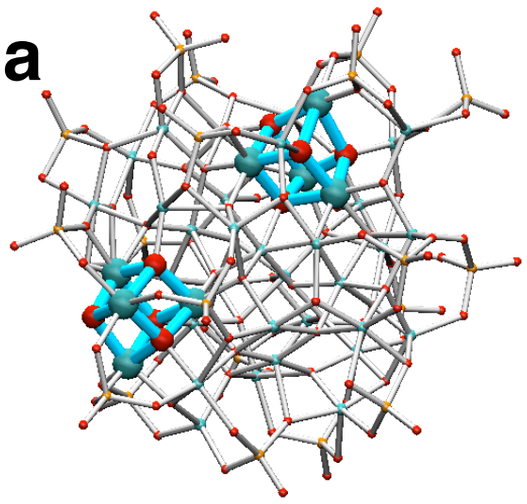
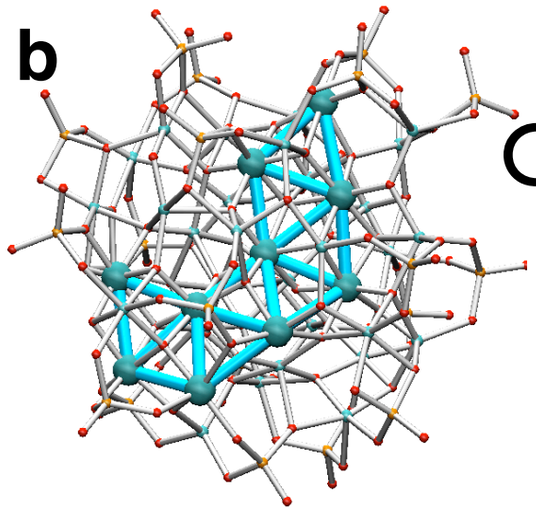
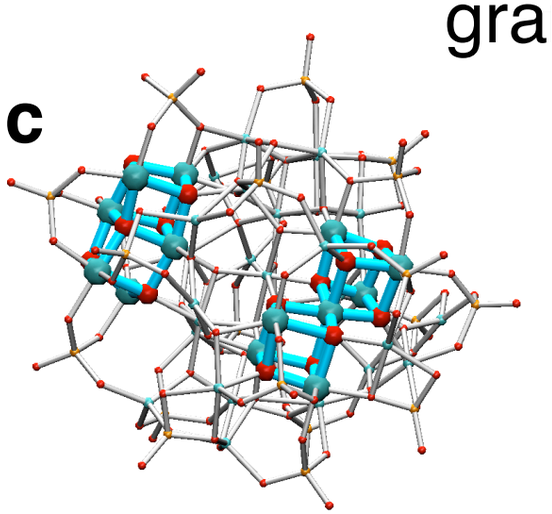
Stability of larger cubane crystallites?

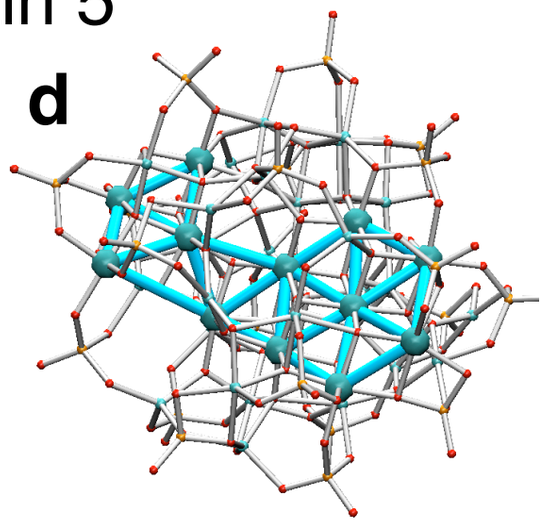
grain 4



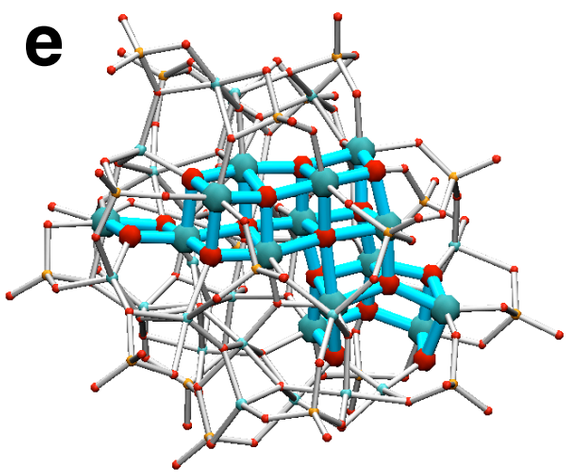


grain 5





grain 6



Metadynamics I

CV1 & CV2: short-range Co atomic environment

Metadynamics II

CV3: medium-range Co atomic environment

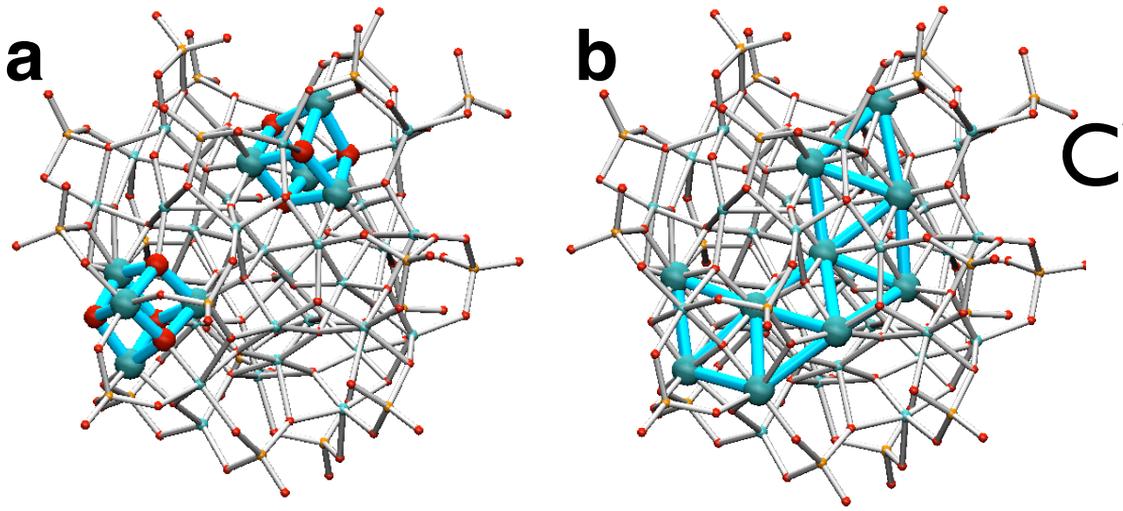
MOLECULAR-SIZE crystallites

- Common building block: bis-oxo-bridged Co centers
- Layered structures (edge-sharing CoO6 octahedra) + in corner- and face-sharing cubane units

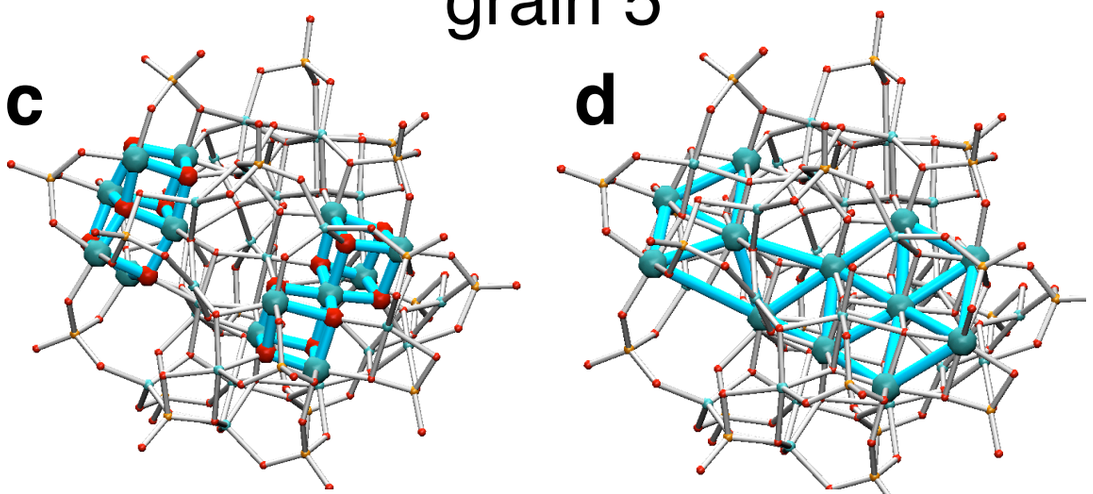
Layered and cubane motifs coexist in the crystallites

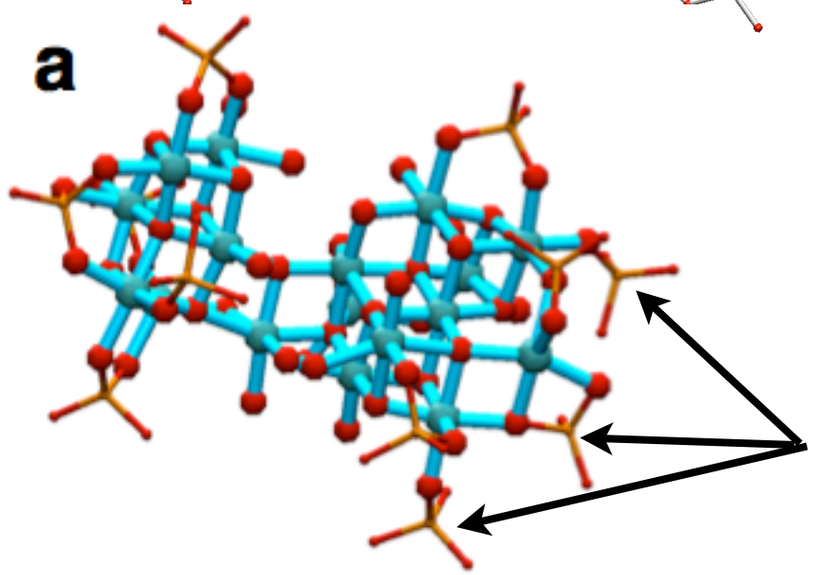
Stability of larger cubane crystallites?

grain 4



grain 5





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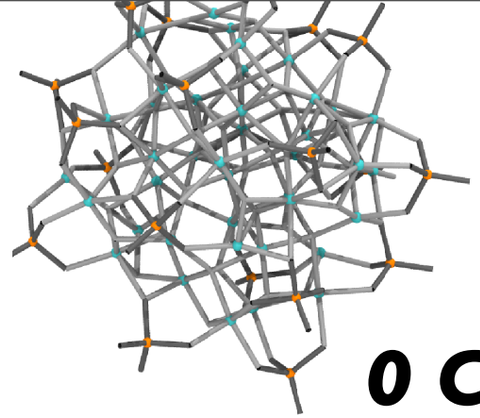
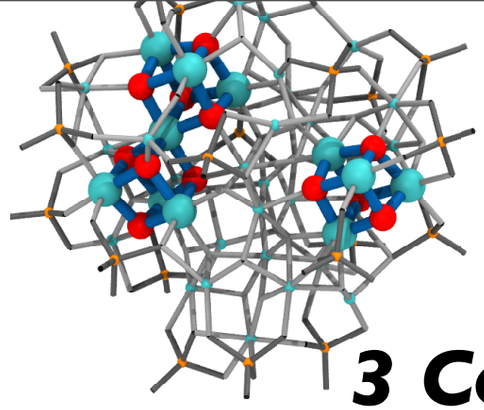
- Layered structures (edge-sharing CoO6 octahedra) + in corner- and face-sharing cubane units

Layered and cubane motifs coexist in the crystallites

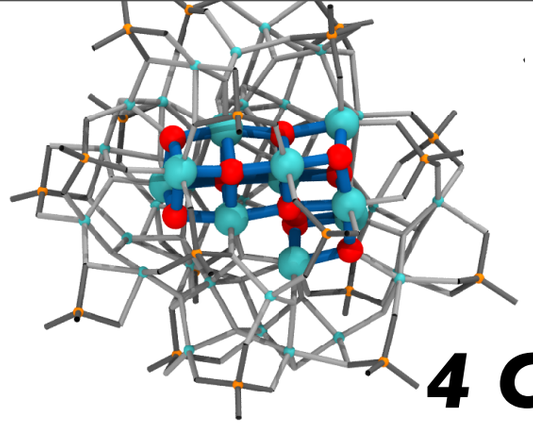
Phosphate groups terminate crystalline edges



0 Co_4O_4



3 Co_4O_4



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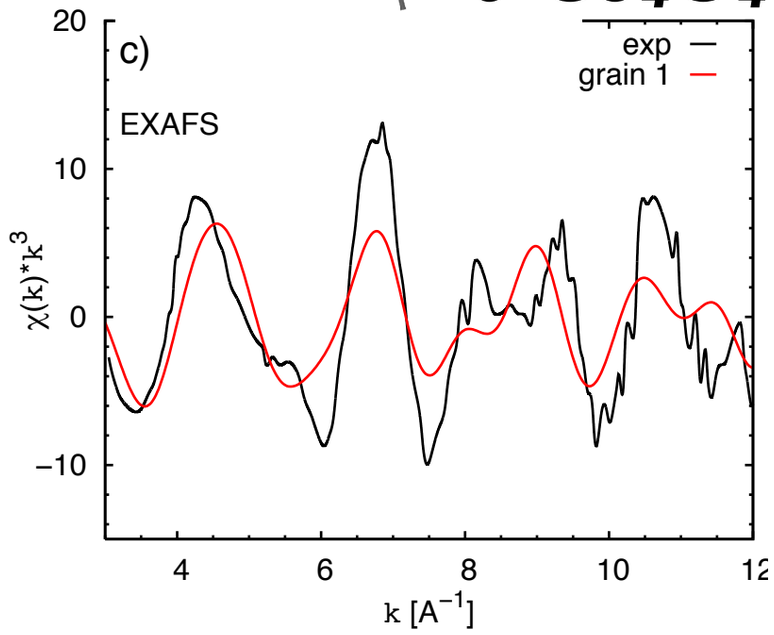
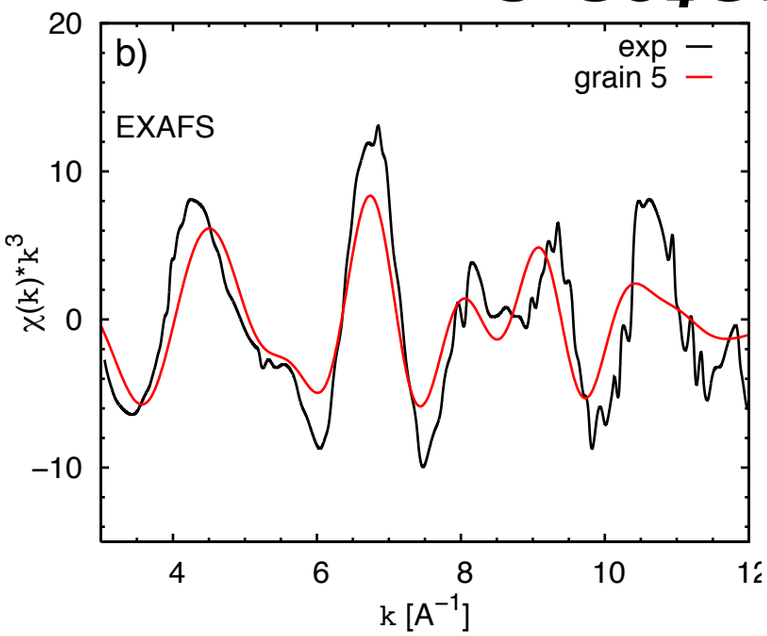
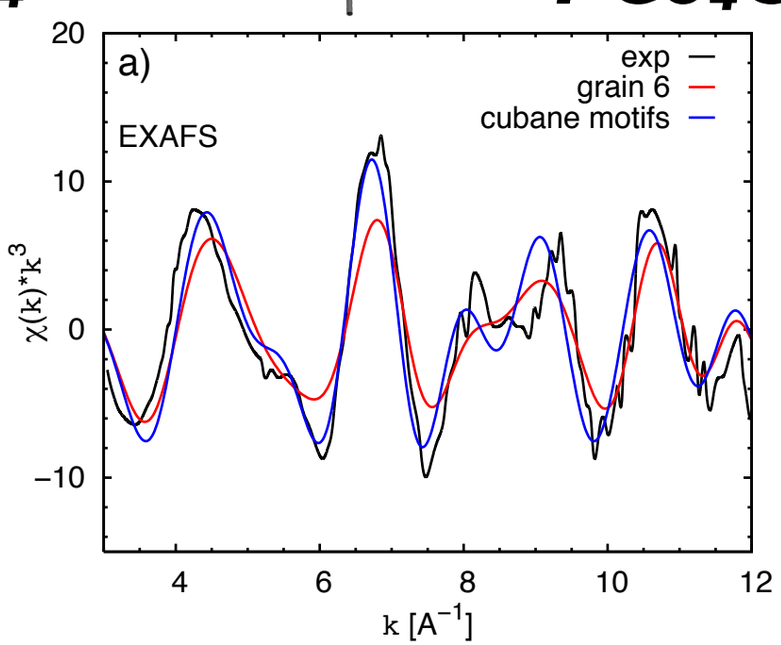
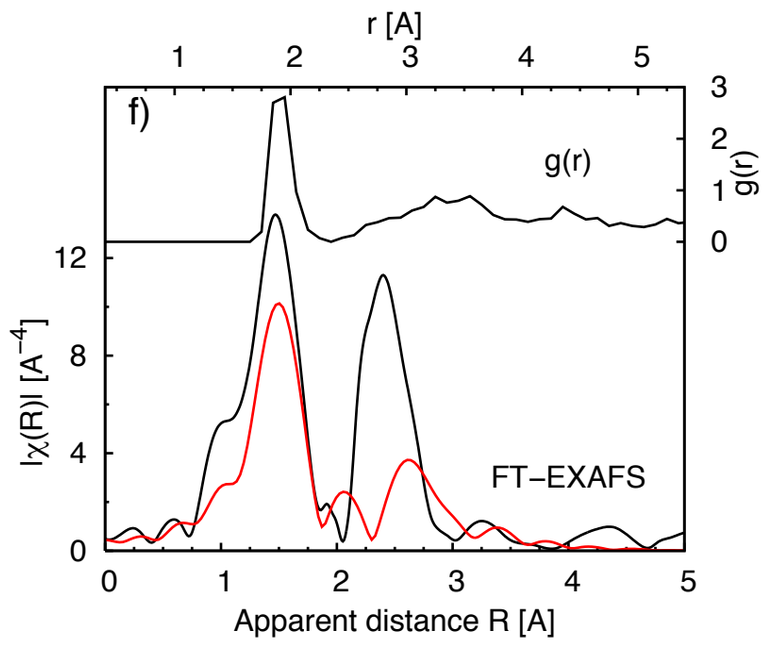
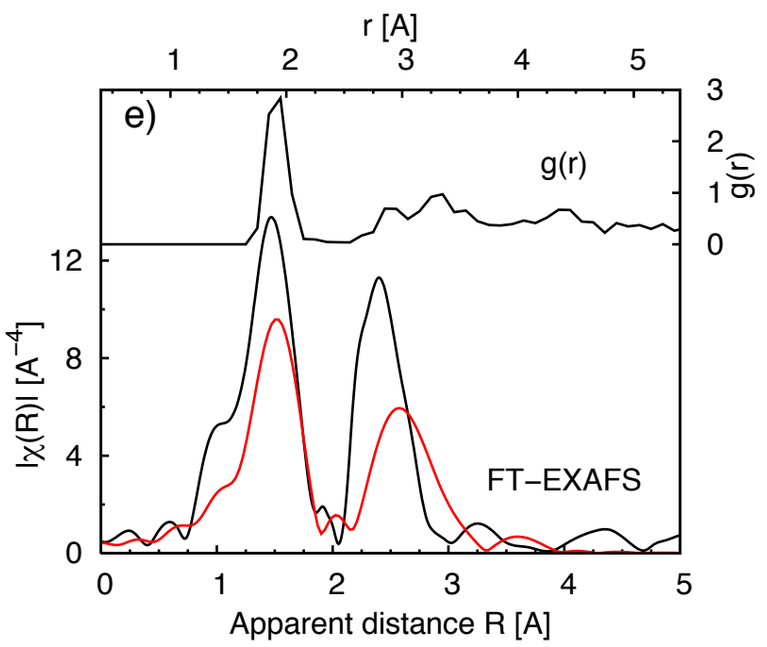
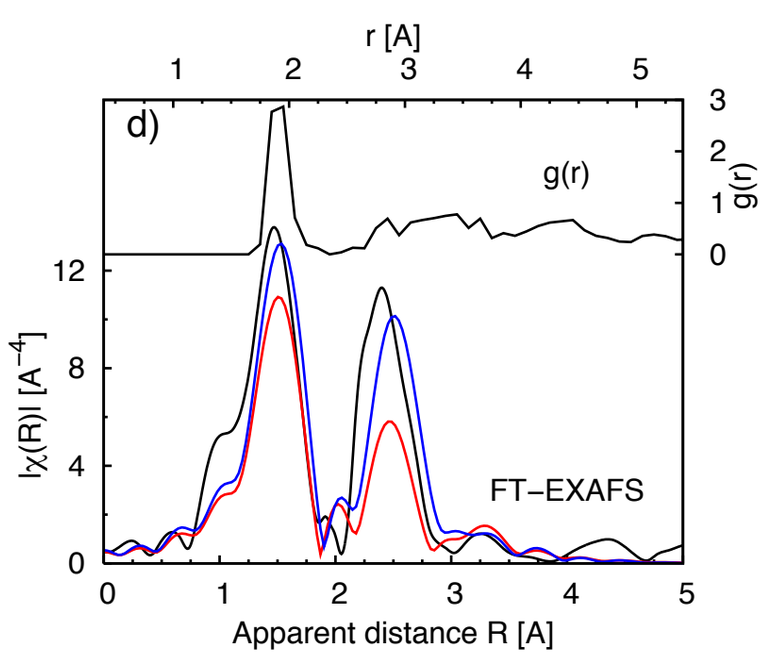




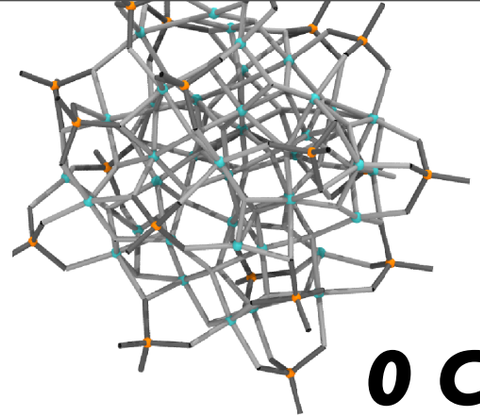




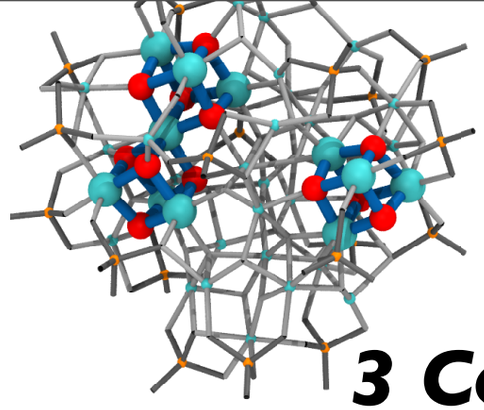




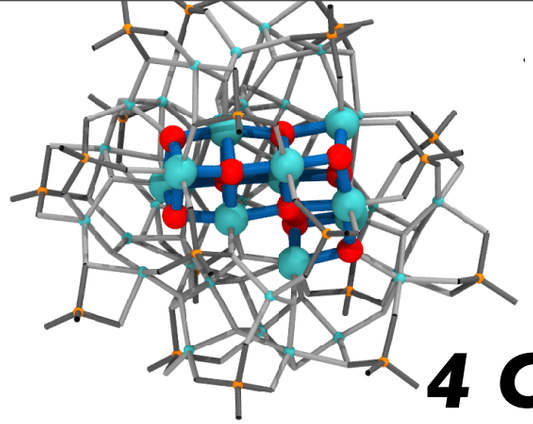
The larger the number of Co4O4 motifs-the better the agreement



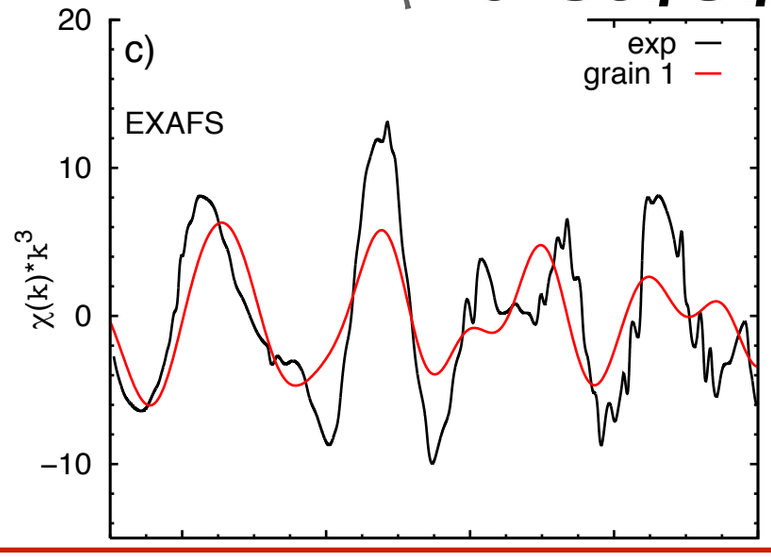
0 Co_4O_4

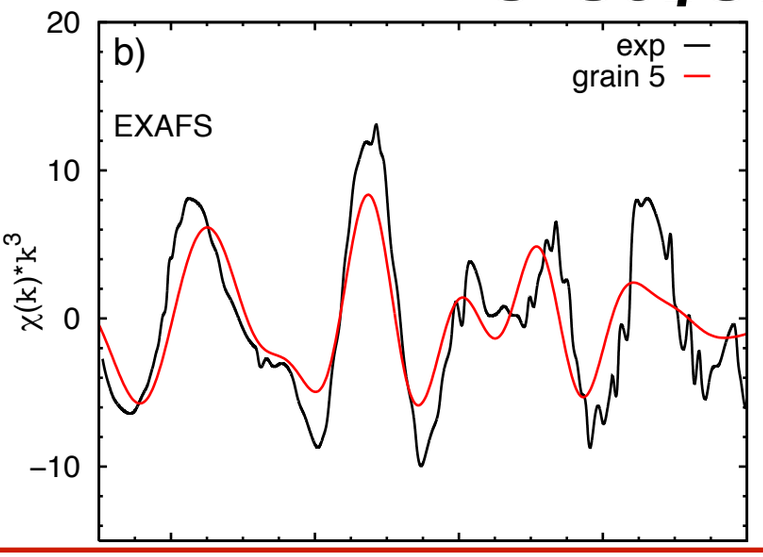


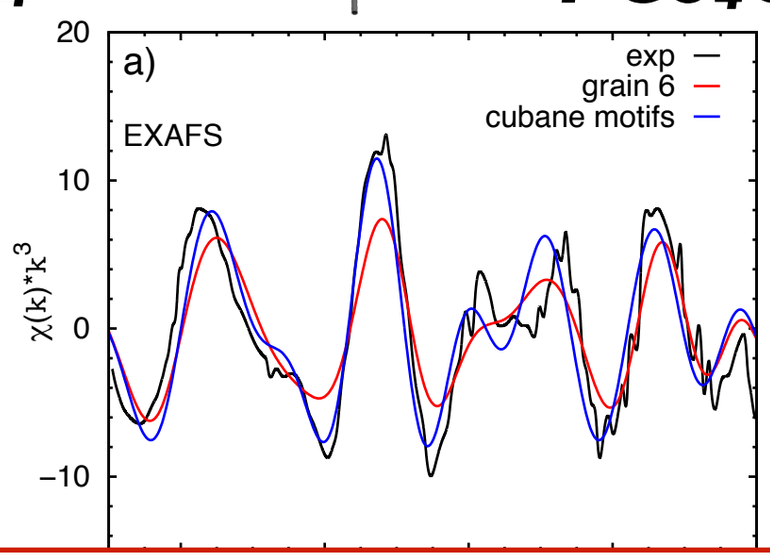
3 Co_4O_4



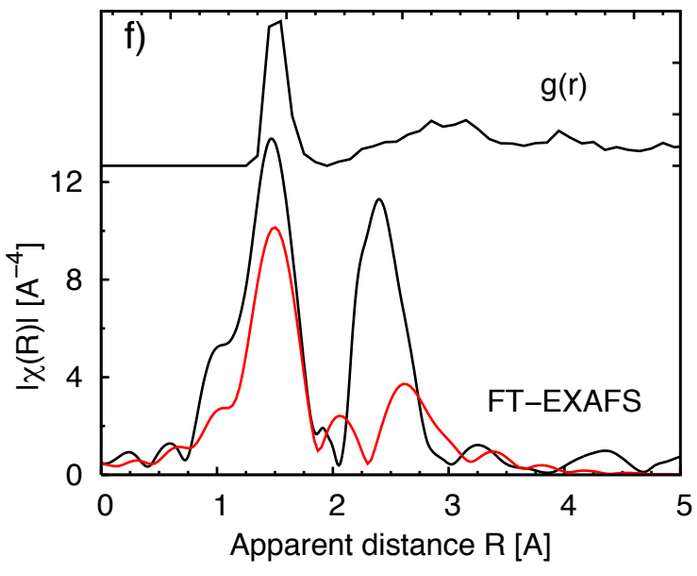
4 Co_4O_4

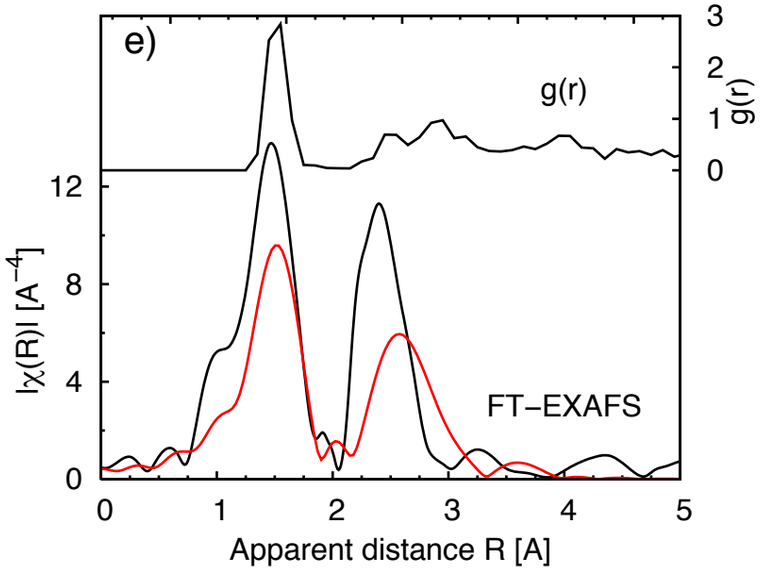


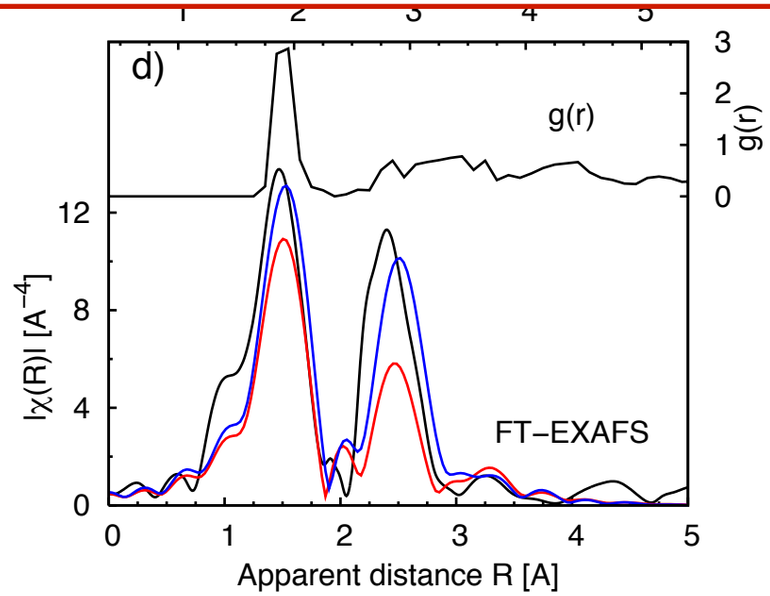




Regions of our nanoparticles abundant in Co4O4+phosphate well reproduce all known exp features of CoPi







The larger the number of Co4O4 motifs-the better the agreement

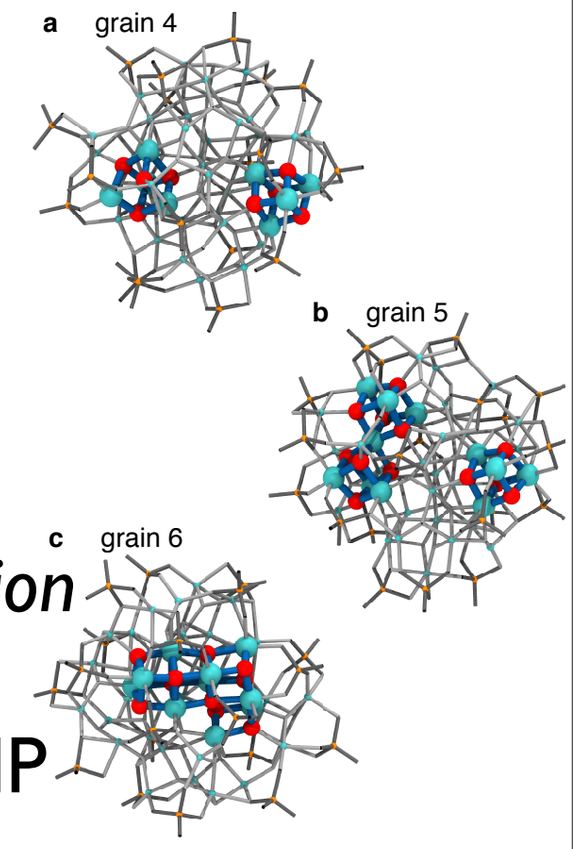
Conclusions

First realistic structural model of amorphous CoO-Pi nanoparticles

* Emergence and stability of molecular-sized crystallites in disordered NP

* Crystallites: bis-oxo bridged Co centers - Co4O4 motifs sharing faces/corners

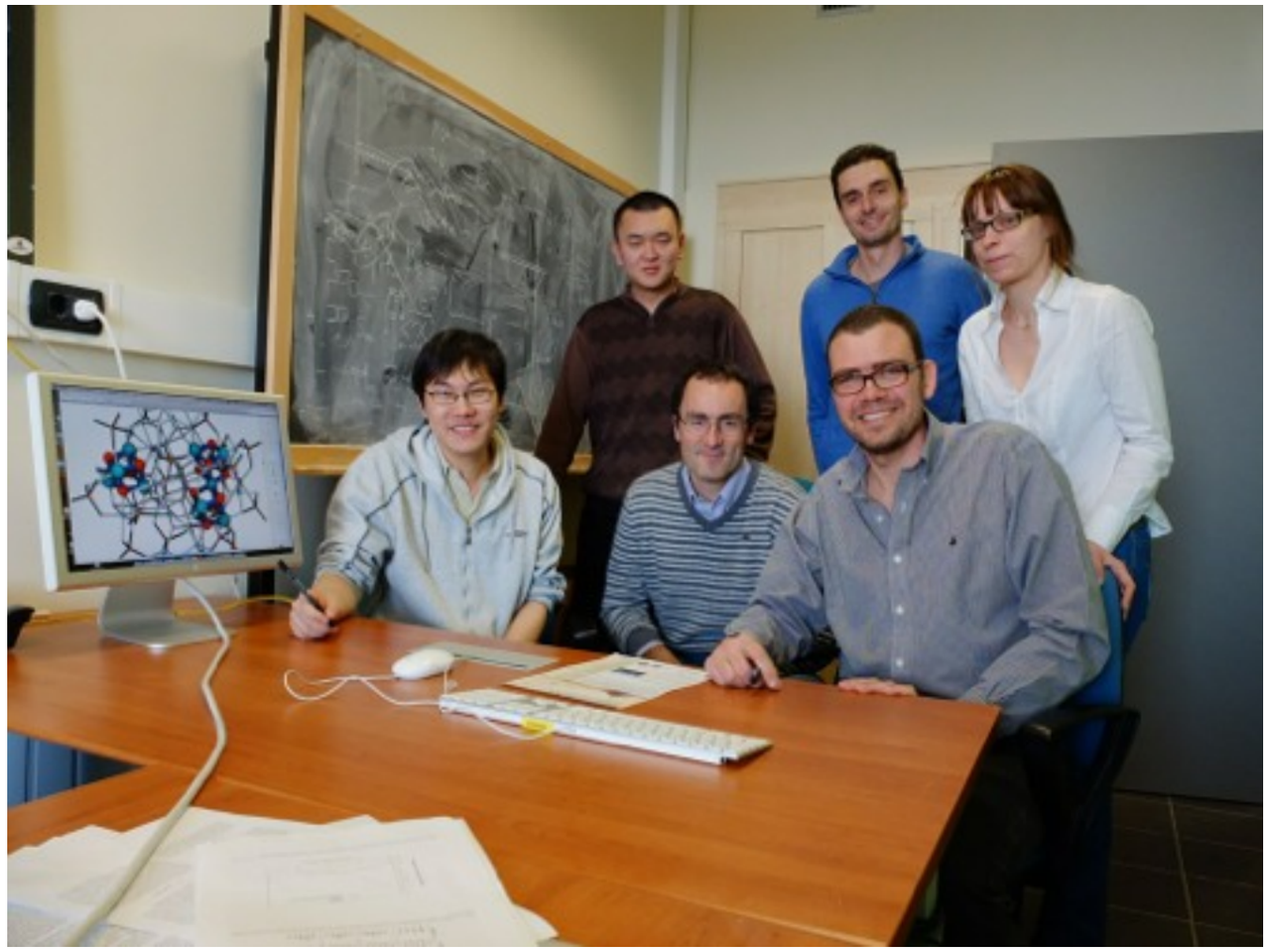
* Co4O4 crystallites
  - *stable up to high T*
  - *always expose cobalt sites at the grain surface*
  - *incorporate at least one phosphate group at cubane termination*



* Good agreement with exp displayed only by cubane-rich NP

Cubane-rich portion of our amorphous nanoparticles are reliable structural models of the Co-Pi catalyst surface

Thanks



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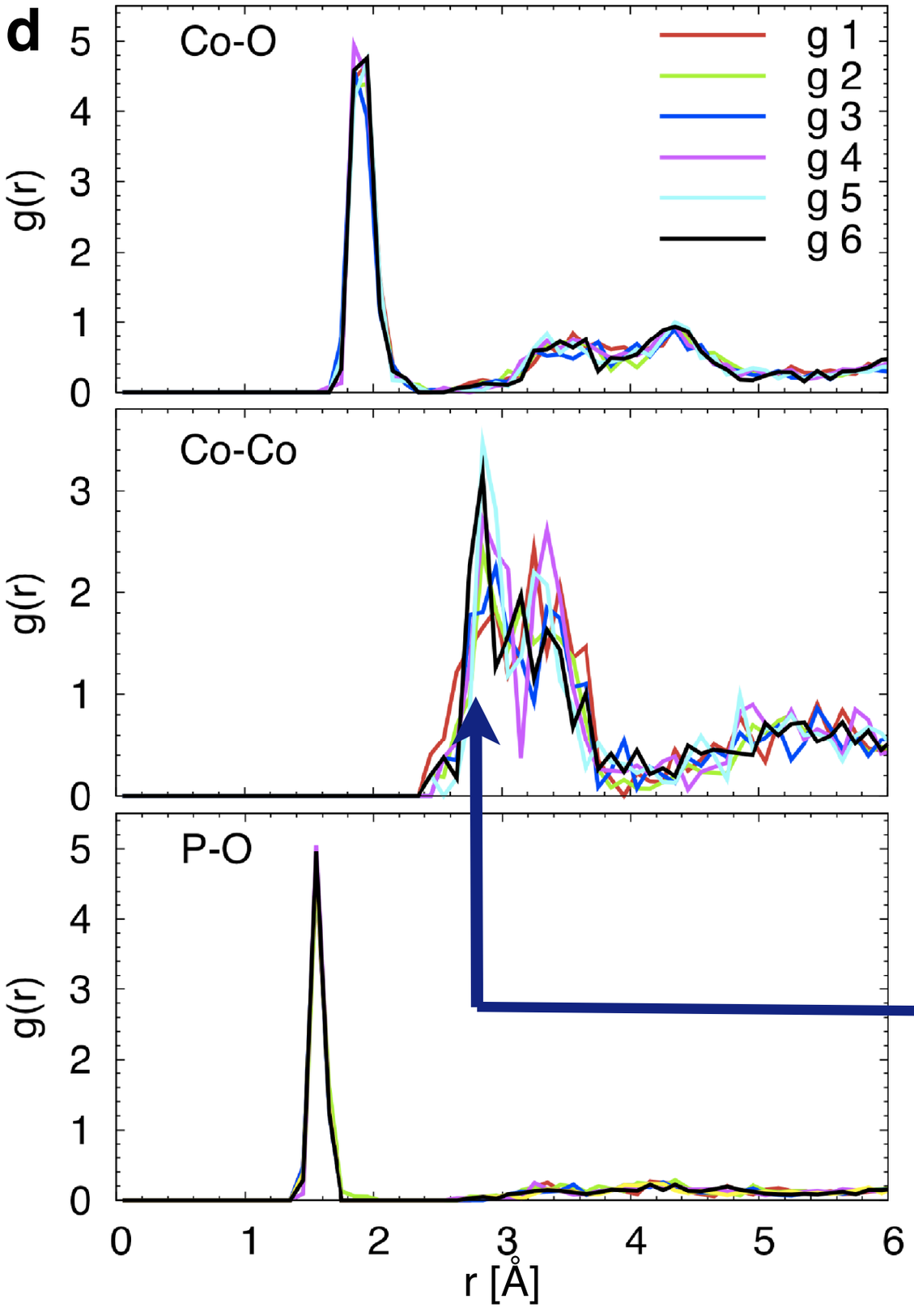
FUNDING

FP7- Marie Curie Program
IIT - Italian Institute of Technology
PRACE Partnership for Advanced Computing in Europe
ISCRA & CINECA supercomputing center
COST action CM1104

Local structure around Co ions



Co-O distance

2.0 Å (1.89 Å - EXAFS)

Co coordination number

5.4 (5.2-6 EXAFS)

!Independent on Co4O4 units!

Broad peak in Co-Co RDF

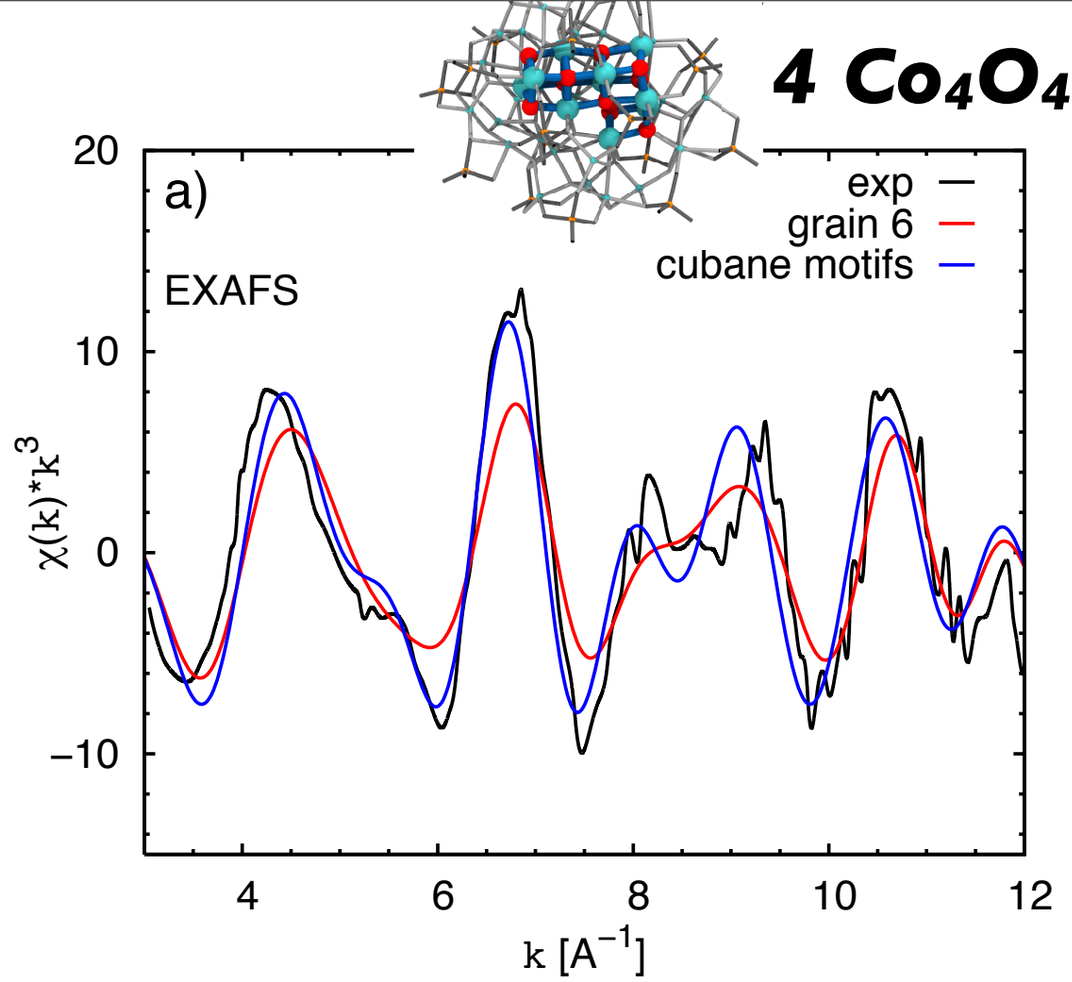
No clear first shell - compatible with FT-EXAFS?

Co4O4 motifs should display a sharp peak at 2.8 Å?

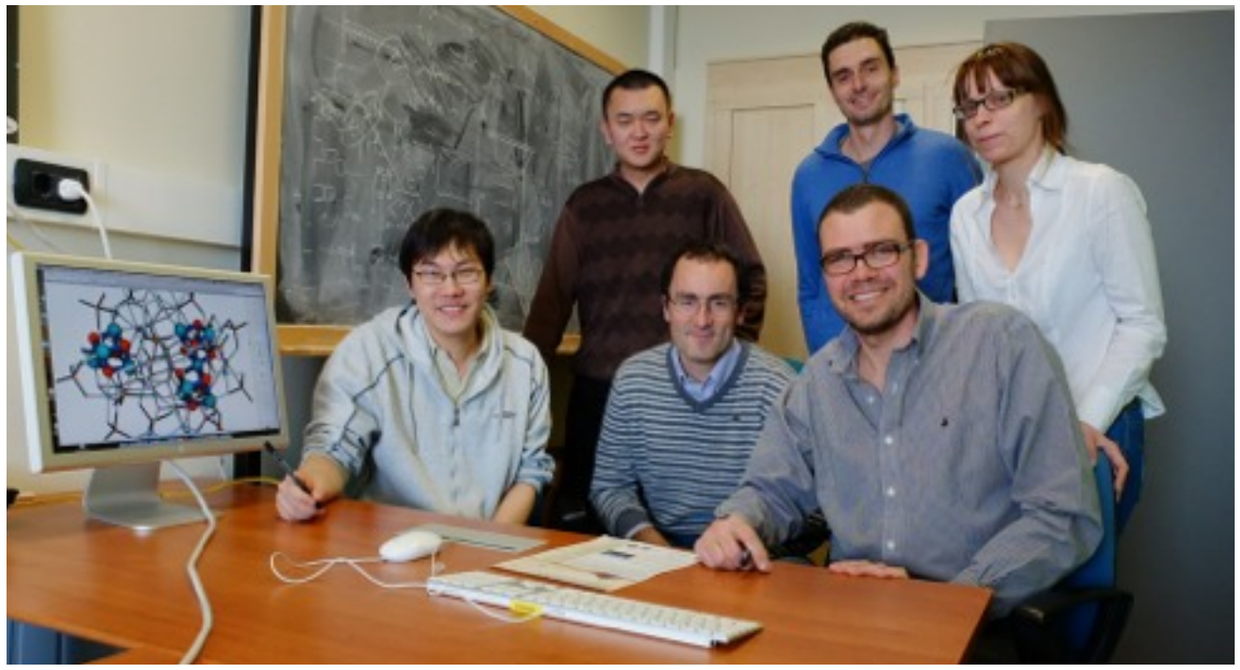
Simulated EXAFS

Sharp peak in Co-O g(r)
strong Co-O vector in EXAFS

Broad peak in Co-Co g(r)
strong Co-O vector in EXAFS



Thanks



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