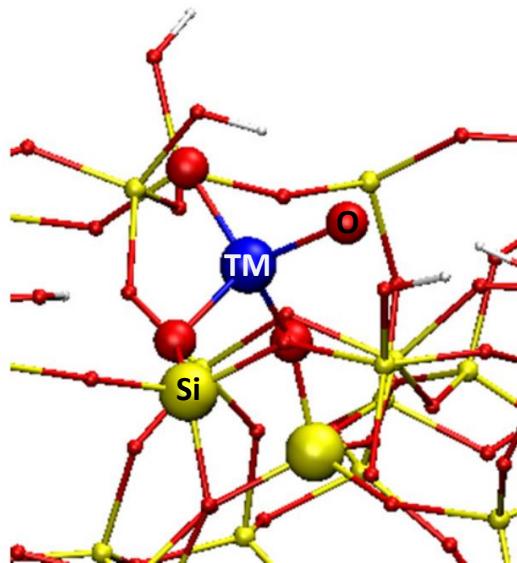


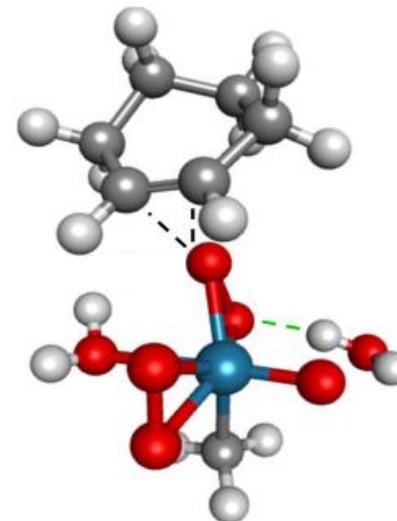
Understanding catalysts from first-principles: tackling challenges in modeling catalysts

Bryan R. Goldsmith

Fritz Haber Institute of the Max Planck Society
Berlin, Germany



dispersed metal ions
on amorphous SiO_2



$\text{CH}_3\text{ReO}_3 + \text{H}_2\text{O}_2 + \text{cyclohexene}$
in aqueous acetonitrile

Catalysis has a profound impact on everyday life

Commodity chemical production



Fertilizer

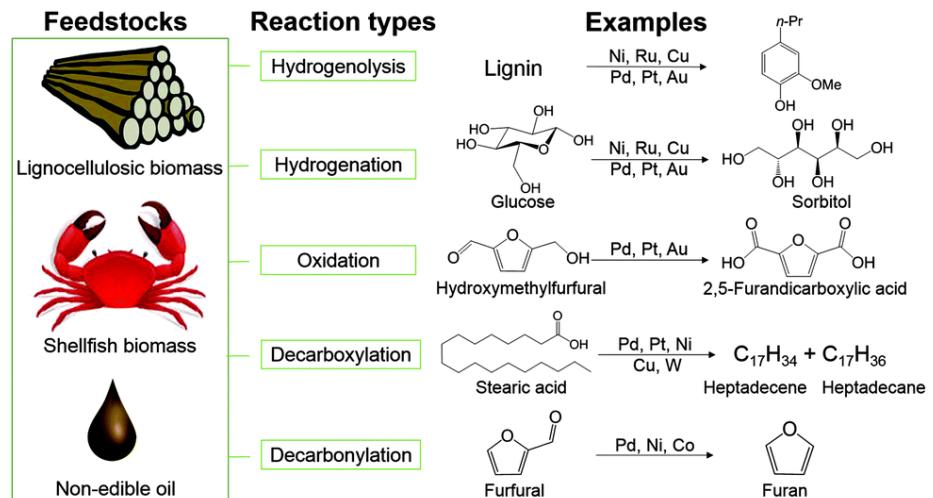


Synthesis of ammonia from its elements
Fritz Haber, Nobel Lecture (1920)

Pharmaceutical industry



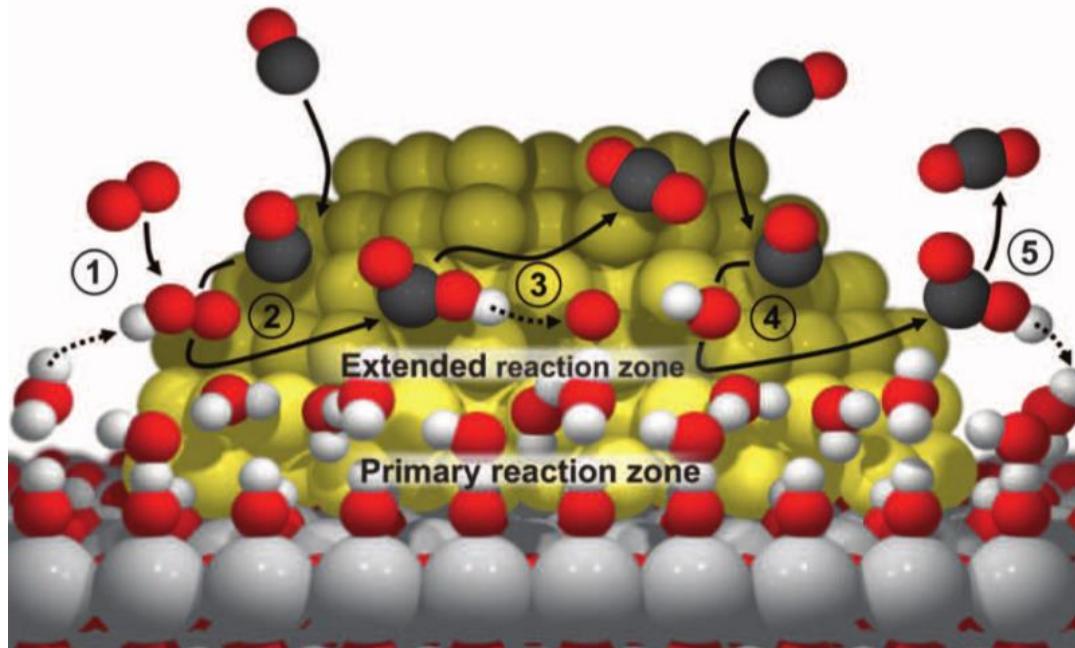
Value-added chemicals from biomass



Y. Wang , S. De, N. Yan,
Chem. Commun., 52, 6210 (2016)

Modeling can provide deep insights into catalysis

Gold nanoparticle on TiO_2 for CO oxidation



[1]

Experiments

Elementary step kinetics

In-situ reactivity

Structure

Chemisorption

Theory

Transition States

Intermediates

Structure

Dynamics

The dream: computer-aided catalyst design

Catalyst characterization

Computational spectroscopy

First-principles thermochemistry & kinetic parameters

First-principles microkinetic modeling

Catalyst design

Active sites

Reaction mechanism

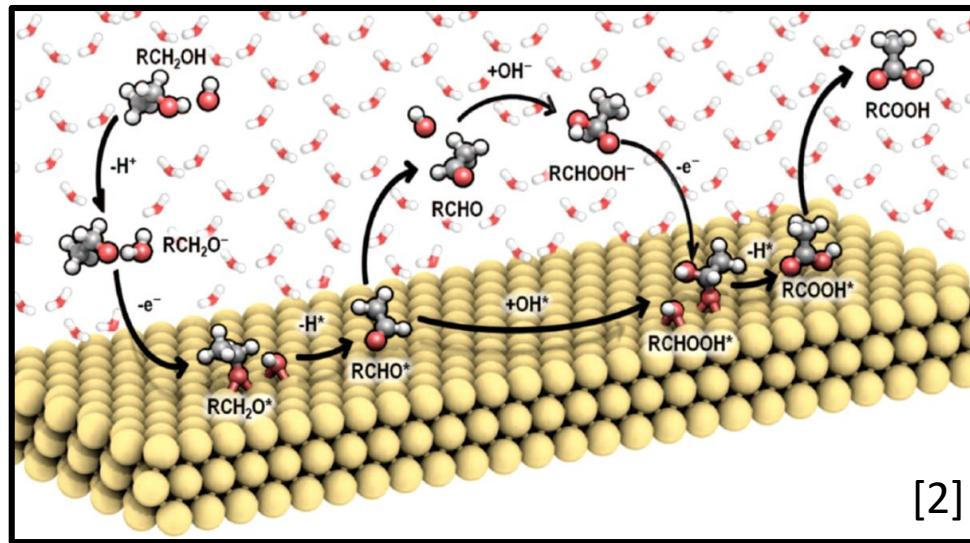
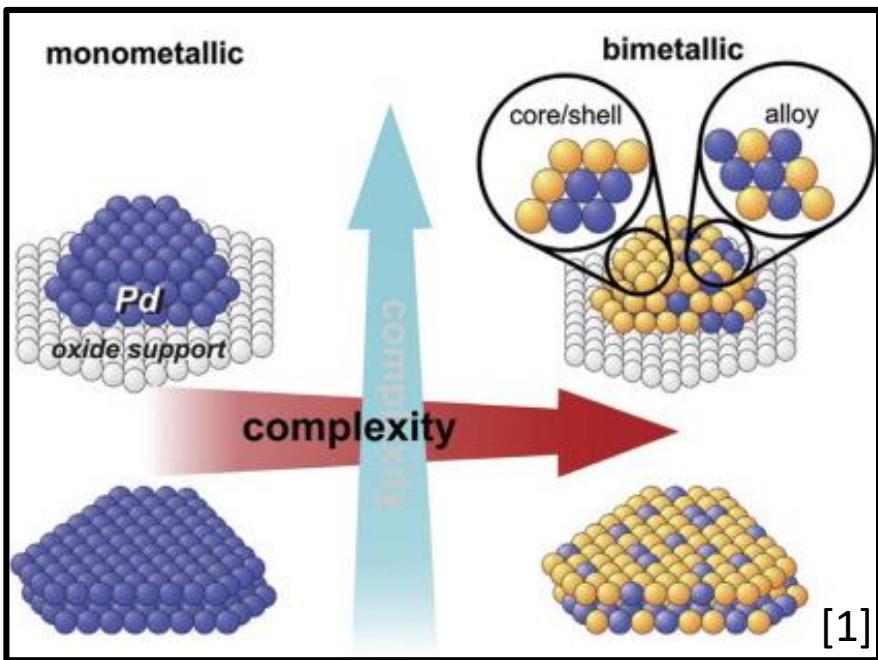
Mechanistic understanding

Descriptor

Computational screening

“Towards the computational design of solid catalysts”
J. K. Nørskov *et al.*, *Nat. Chem.* 1 (2009)

Many challenges remain for modeling catalysts



Representative models

Thermodynamics and kinetics
with chemical accuracy

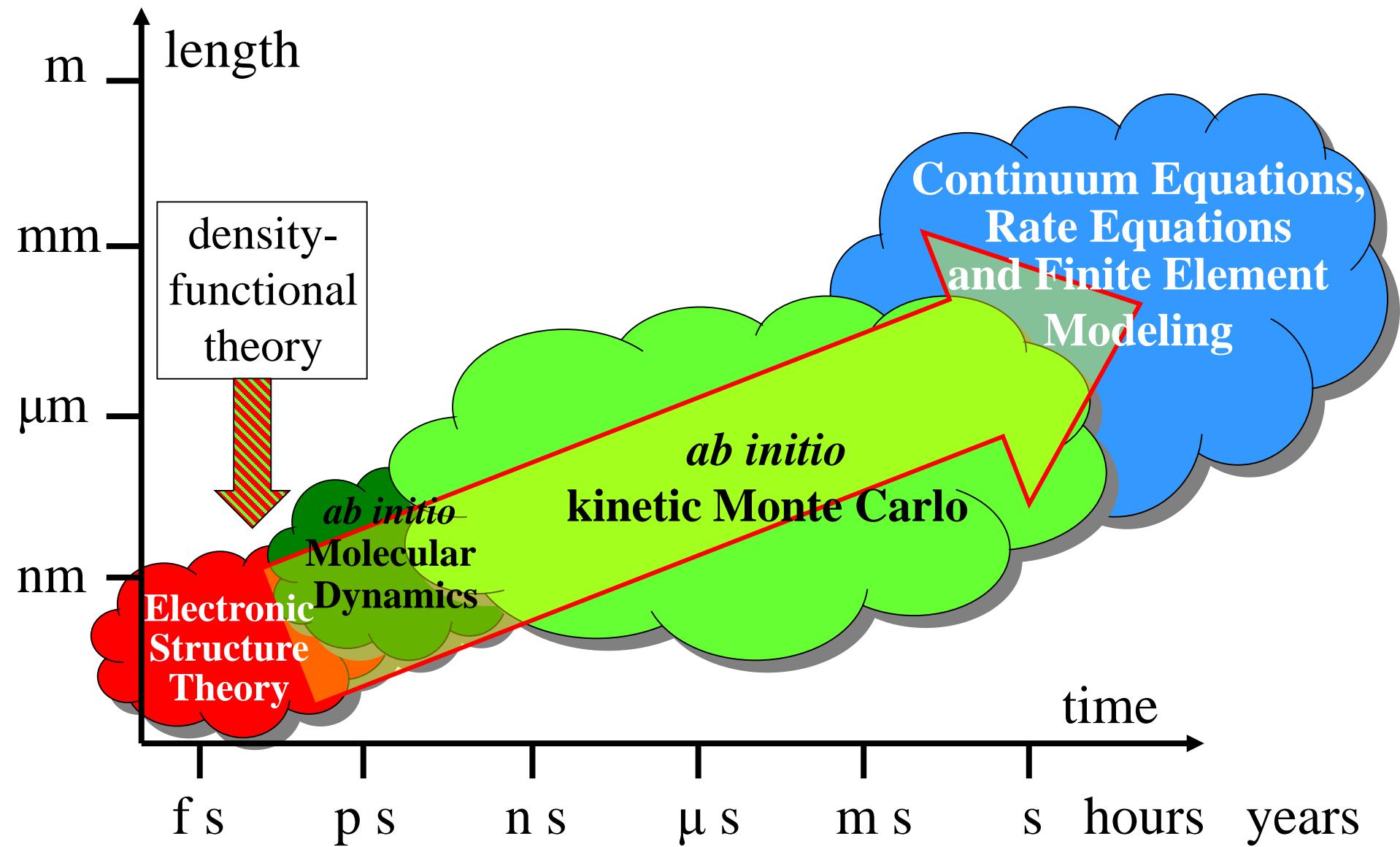
Complexity of solution

Liquid/solid interfaces

[1] G. Rupprechter and C. Weiland, *Nano Today* 2 (2007)

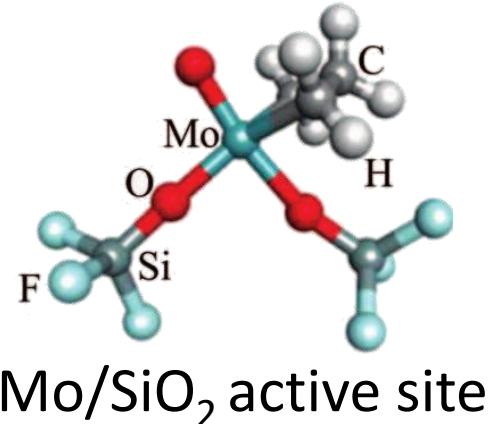
[2] B. N. Zope, D. D. Hibbitts, M. Neurock, R. J. Davis, *Science* 330 (2010)

Multi-scale approach for modeling catalysts

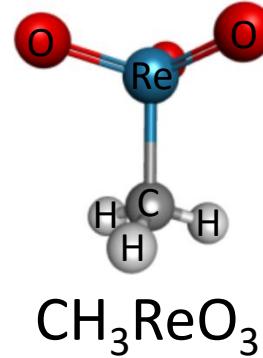


Outline. Three projects that help address the below challenges

Challenge 1: Modeling heterogeneity in reactivity of amorphous catalysts



Challenge 2: Understanding the importance of solvent during homogeneous catalysis

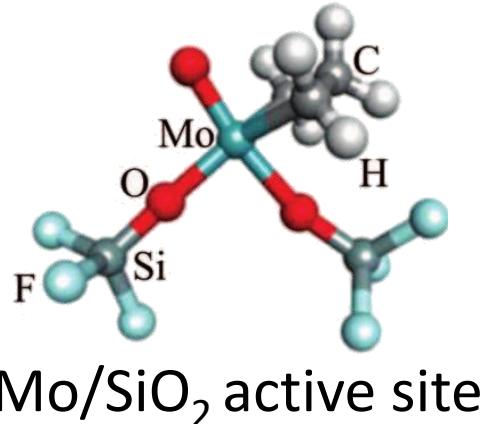


Challenge 3: Finding reliable descriptors of catalysts (and materials)

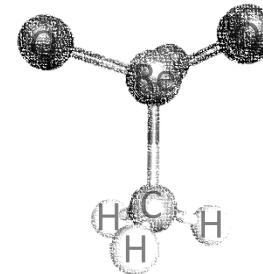


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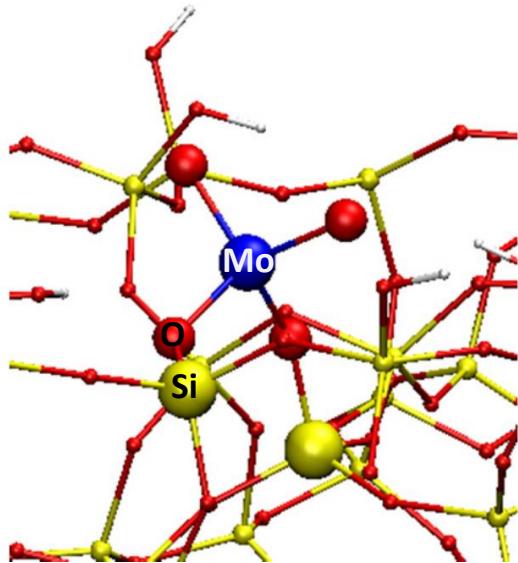


Challenge 3: Finding reliable descriptors of catalysts (and materials)



Amorphous catalysts are important
but not well-understood due to their disorder

Dispersed metal ions
on amorphous supports



Mo(VI) complex on SiO_2

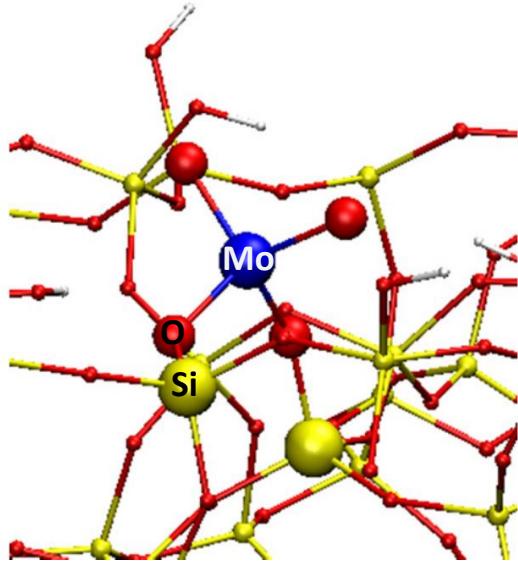
H. S. Taylor, *Proc. R. Soc. A* 108 (1925)

C. Yoon and D. Cocke, *J. Non-Crystalline Solids* 79 (1986)

B. Peters and S. L. Scott, *J. Chem. Phys.* 142 (2015)

Amorphous catalysts are important but not well-understood due to their disorder

Dispersed metal ions
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Challenges

- Lack of well-defined structure
- Diversity of catalyst site environments
- Preparation dependent properties

Mo(VI) complex on SiO_2

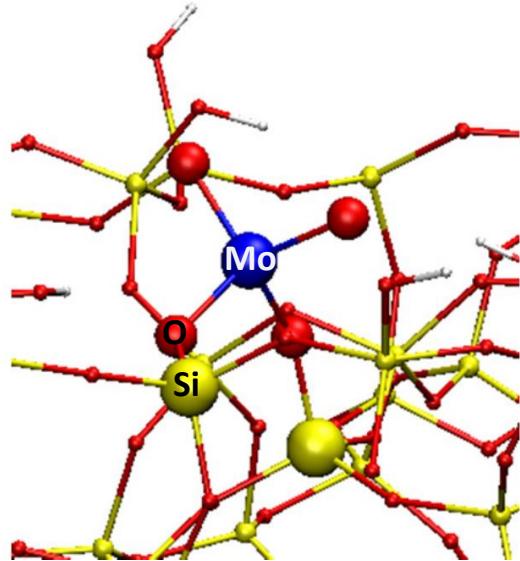
H. S. Taylor, *Proc. R. Soc. A* 108 (1925)

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Amorphous catalysts are important but not well-understood due to their disorder

Dispersed metal ions
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Mo(VI) complex on SiO_2

Challenges

Lack of well-defined structure

Diversity of catalyst site environments

Preparation dependent properties

Open questions

How do typical active and dead sites differ?

How to sample the distribution of sites?

How to build representative models?

H. S. Taylor, *Proc. R. Soc. A* 108 (1925)

C. Yoon and D. Cocke, *J. Non-Crystalline Solids* 79 (1986)

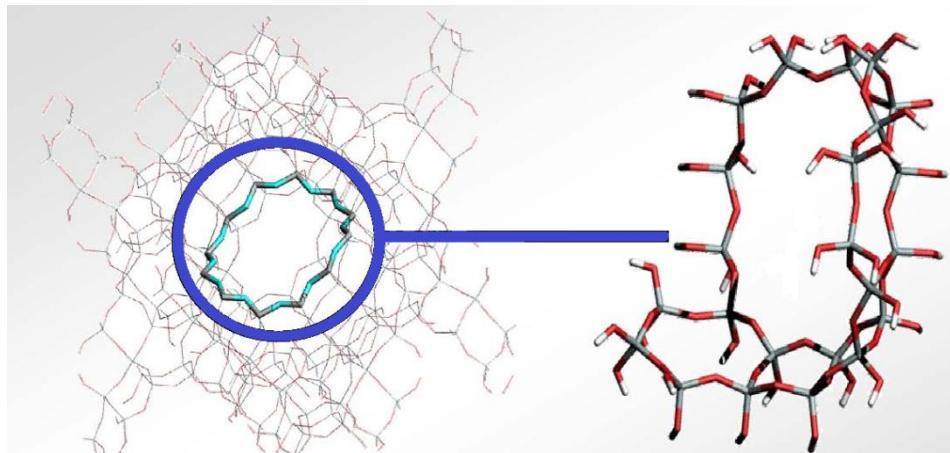
B. Peters and S. L. Scott, *J. Chem. Phys.* 142 (2015)

Typical modeling protocols for crystalline catalysts

from structure to properties

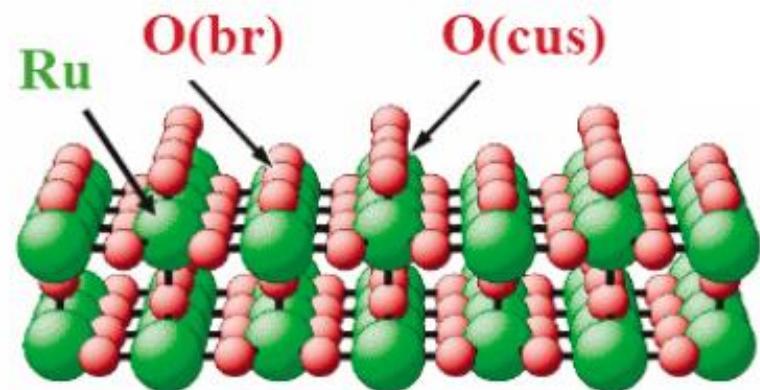
Cluster models

Real system



Cut, cap and constrain

Slab models

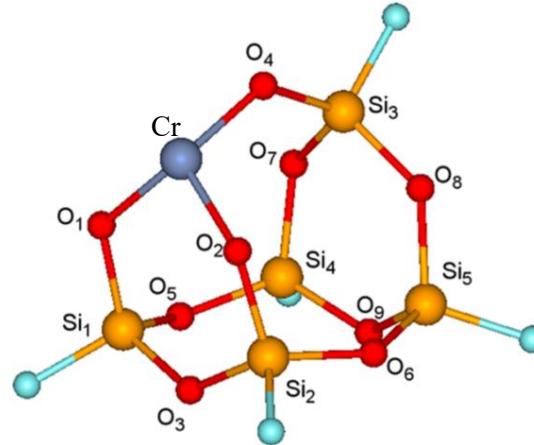
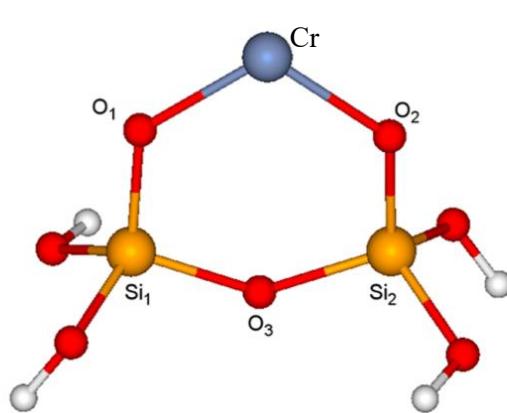


Under periodic
boundary conditions

Typical modeling protocols for amorphous catalysts

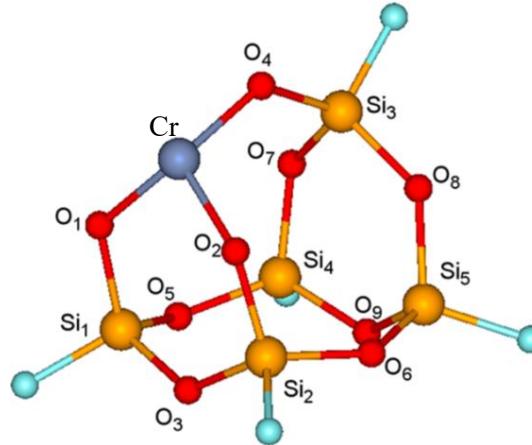
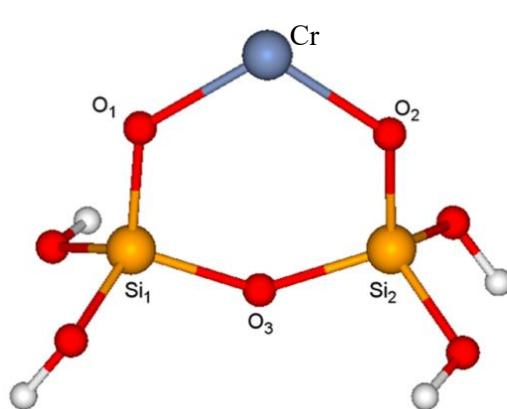
Typical modeling protocols for amorphous catalysts

Approach 1. Assume one or two cluster models capture main features

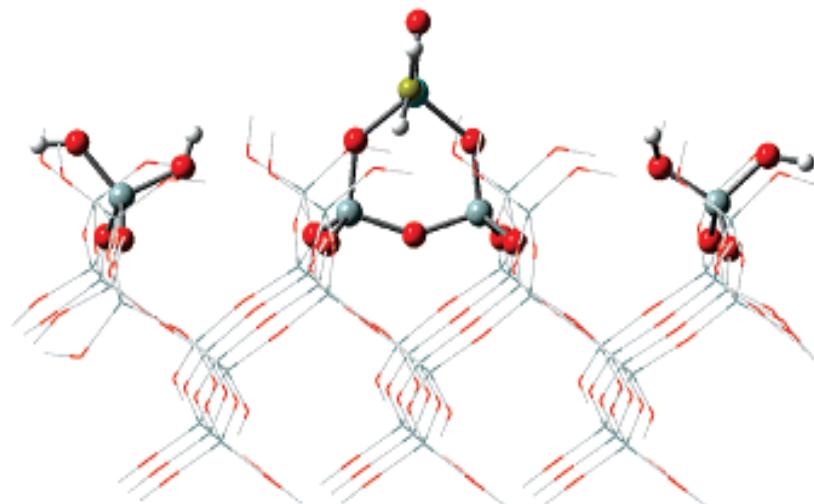
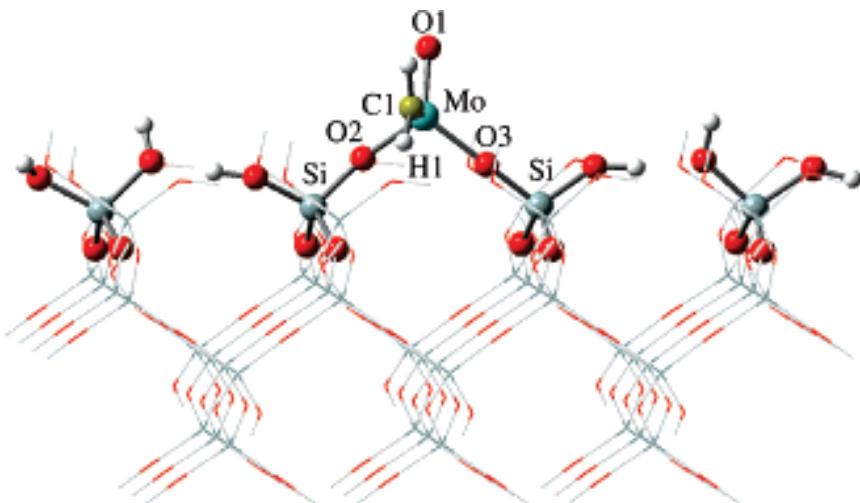


Typical modeling protocols for amorphous catalysts

Approach 1. Assume one or two cluster models capture main features

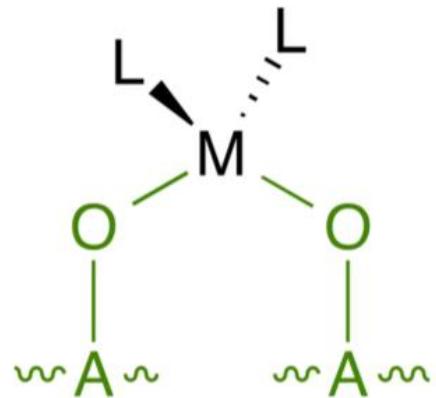


Approach 2. Use a crystalline slab as amorphous support surrogate



Goal: sample heterogeneity in reactivity
of amorphous catalysts

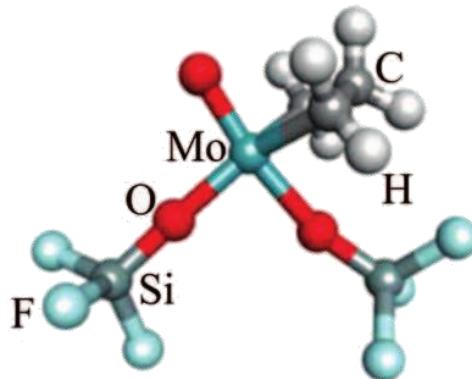
Our approach. Combine small cluster models with
a sequential quadratic programming algorithm



Goal: sample heterogeneity in reactivity
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Our approach. Combine small cluster models with
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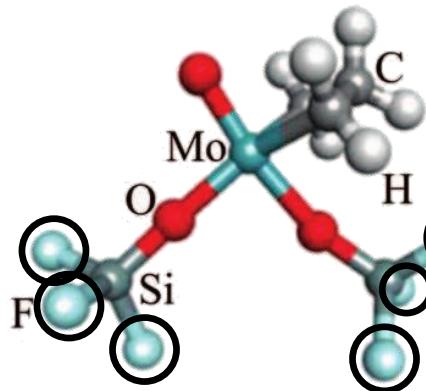
Mo/SiO₂ cluster model



Goal: sample heterogeneity in reactivity of amorphous catalysts

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Mo/SiO₂ cluster model

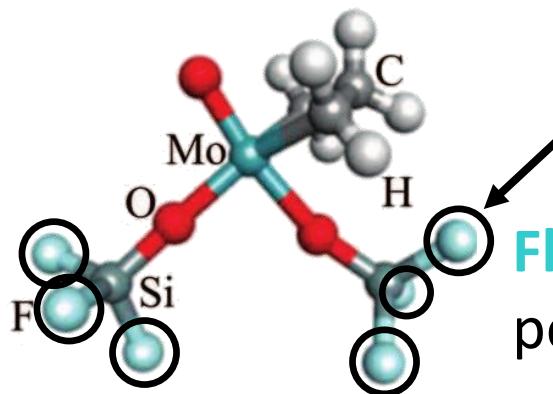


Fluorine = constrained
periphery atoms (x_p)

Goal: sample heterogeneity in reactivity of amorphous catalysts

Our approach. Combine small cluster models with
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Mo/SiO₂ cluster model



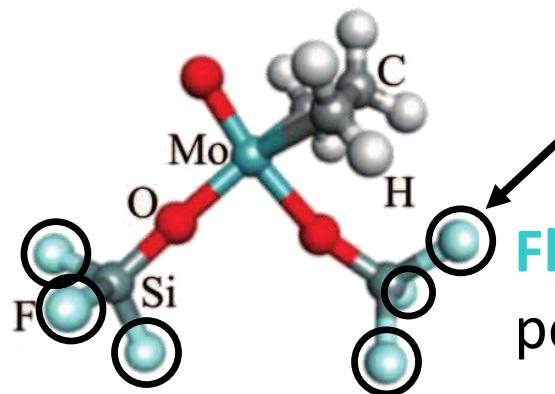
Where is the best place
to constrain the periphery atoms?

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Mo/SiO₂ cluster model



Where is the best place to constrain the periphery atoms?

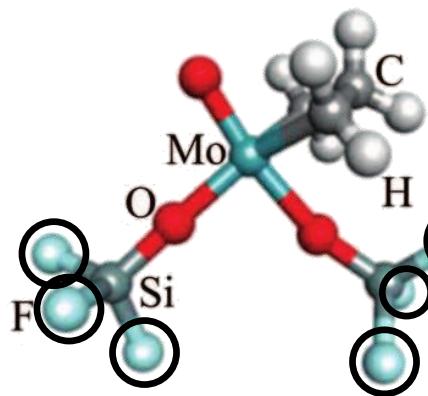
Fluorine = constrained periphery atoms (\mathbf{x}_p)

$$\min_{\mathbf{x}_p} E_{site}(\mathbf{x}_p) \text{ subject to } \Delta E^\ddagger(\mathbf{x}_p) = \Delta E^\ddagger$$

Goal: sample heterogeneity in reactivity of amorphous catalysts

Our approach. Combine small cluster models with a sequential quadratic programming algorithm

Mo/SiO₂ cluster model



Where is the best place to constrain the periphery atoms?

Fluorine = constrained periphery atoms (\mathbf{x}_p)

Position of periphery atoms

$$\min_{\mathbf{x}_p} E_{site}(\mathbf{x}_p) \text{ subject to } \Delta E^\ddagger(\mathbf{x}_p) = \Delta E^\ddagger$$

Energy of catalyst site

Activation energy

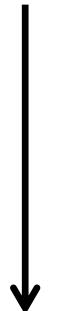
some value

Sample the lowest energy catalyst site
for each value of activation energy

$$\min_{\mathbf{x}_p} E_{site}(\mathbf{x}_p) \text{ subject to } \Delta E^\ddagger(\mathbf{x}_p) = \Delta E^\ddagger$$

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Sequential Quadratic
Programming

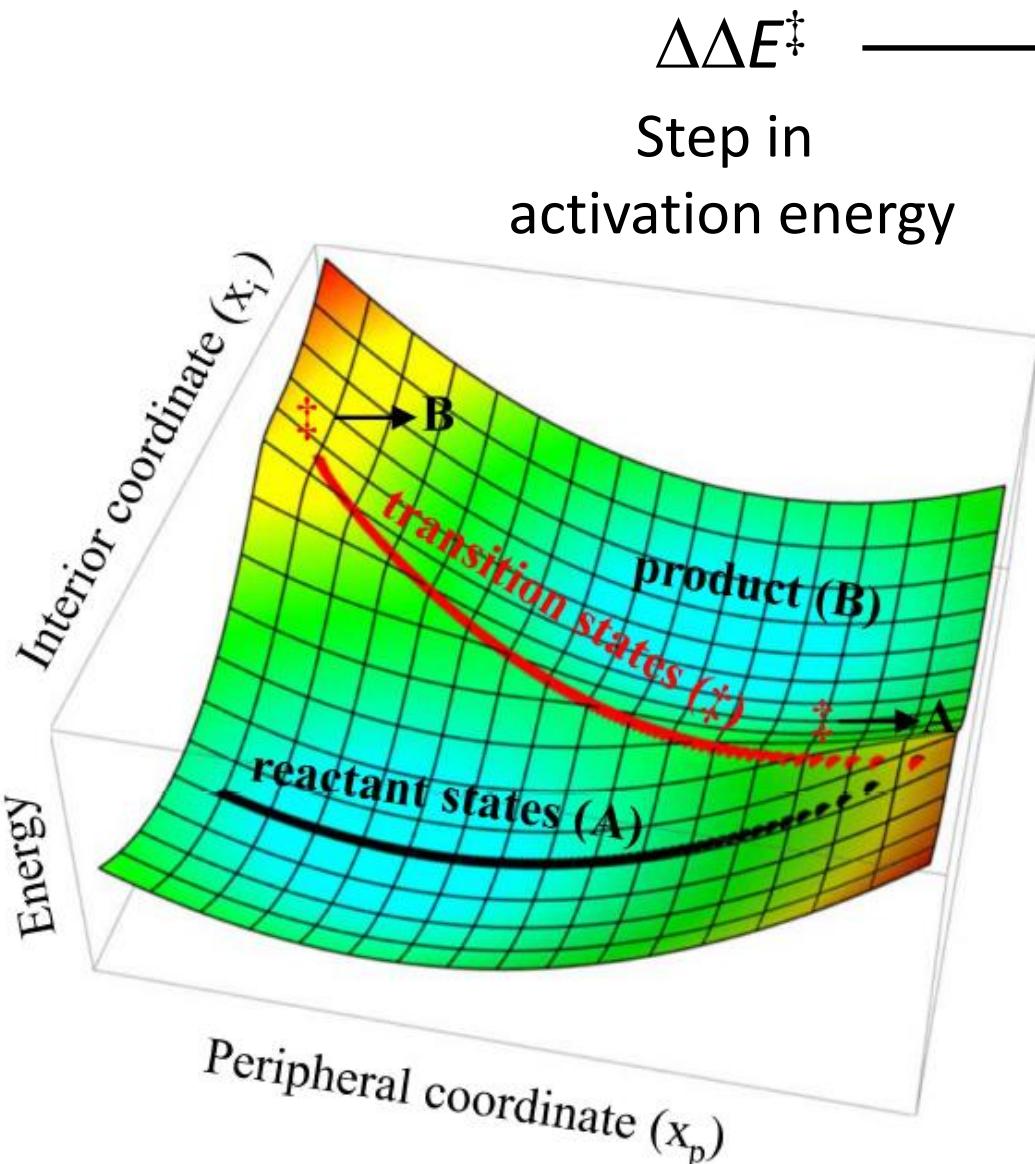
‘Dial’ the activation energy

Inverse design: property to structure

$$\Delta\Delta E^\ddagger \longrightarrow \Delta\mathbf{x}_p$$

Step in activation energy New catalyst site structure

Example of algorithm on model energy landscape



$$\Delta\Delta E^\ddagger$$

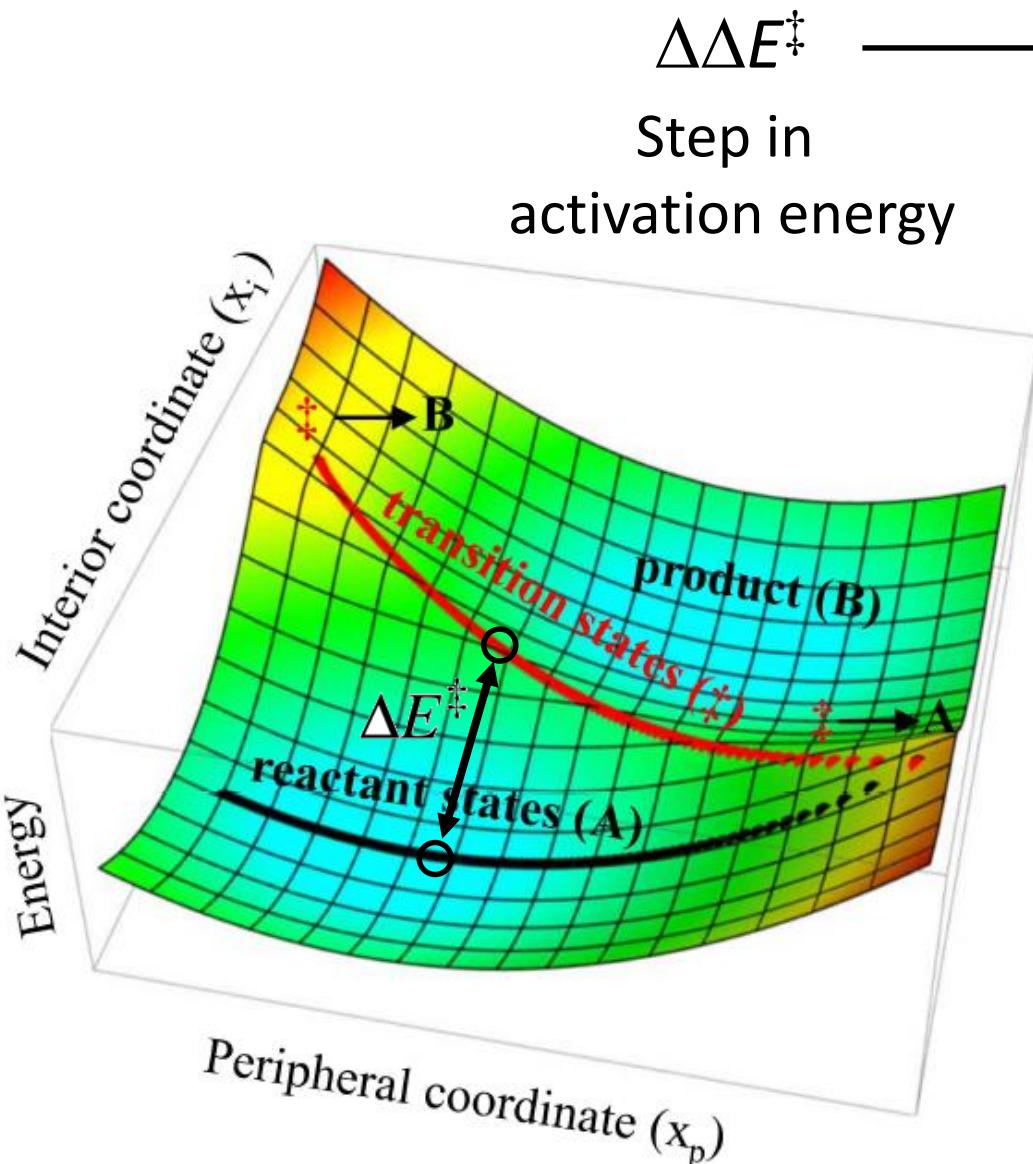
Step in
activation energy

$$\Delta \mathbf{x}_p$$

New catalyst
site structure

Sample the lowest energy site
for each value of ΔE^\ddagger

Example of algorithm on model energy landscape



$$\Delta\Delta E^\ddagger \longrightarrow \Delta x_p$$

Step in

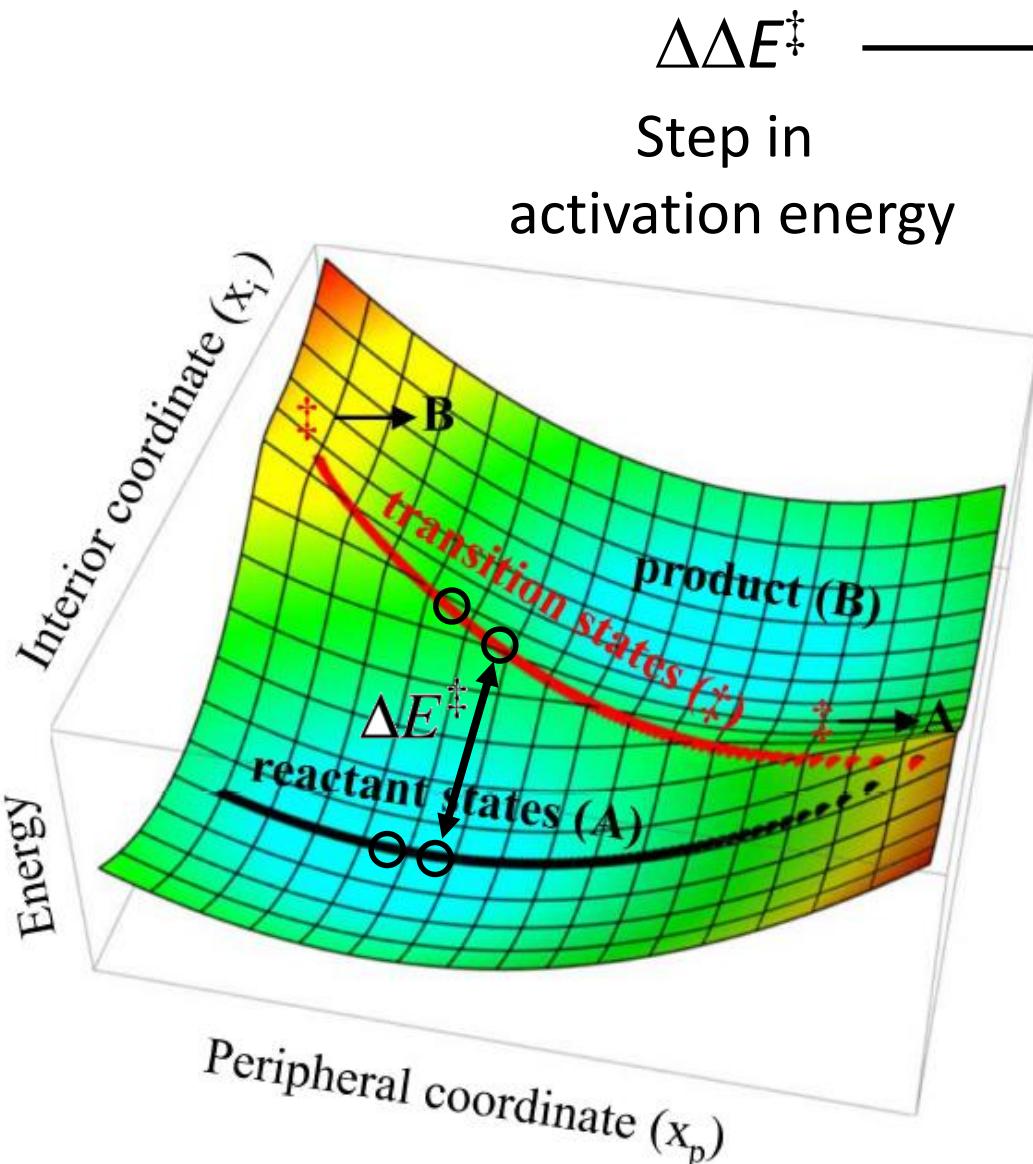
activation energy

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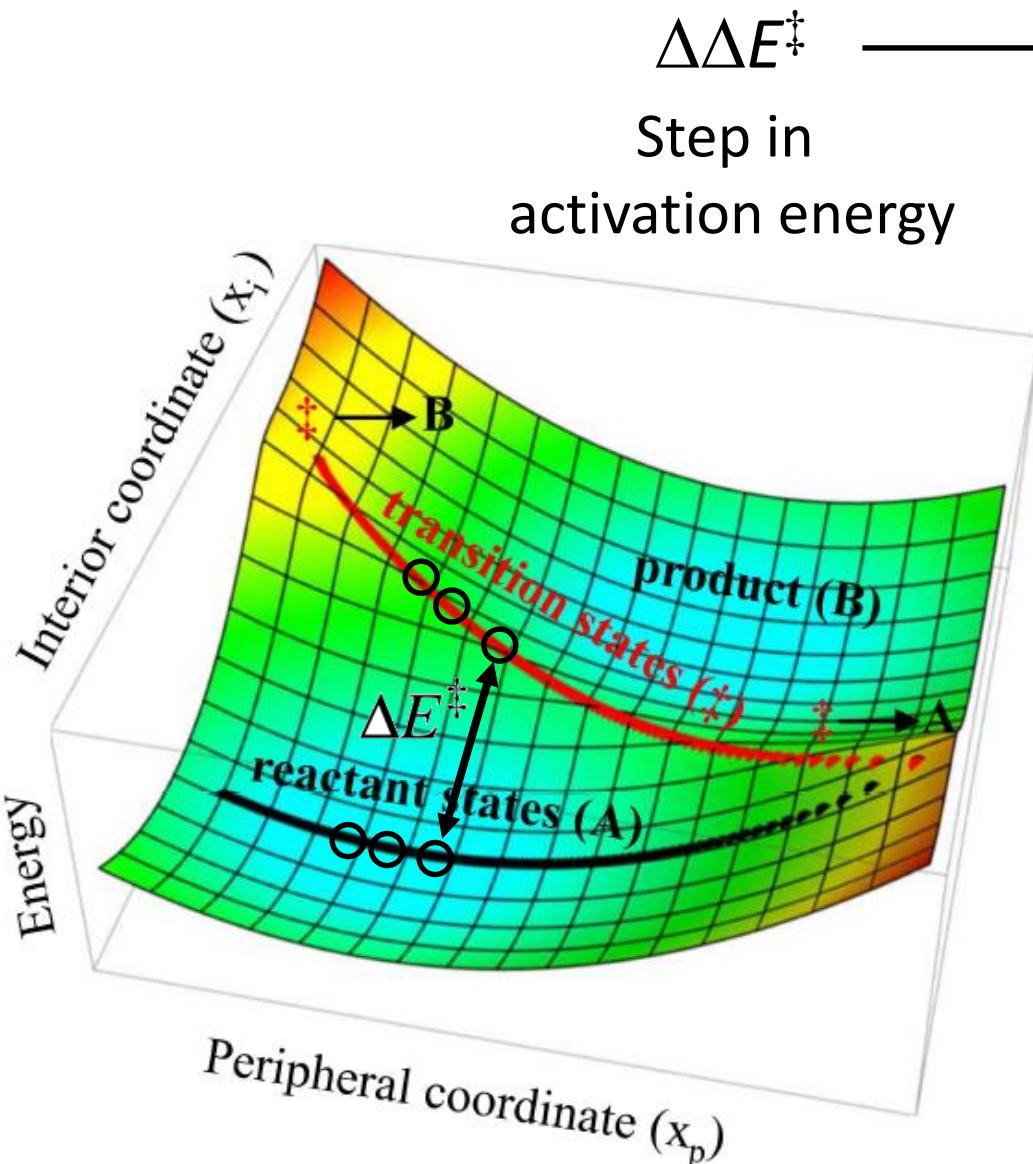


$\Delta\Delta E^\ddagger$ \longrightarrow Step in activation energy

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Example of algorithm on model energy landscape

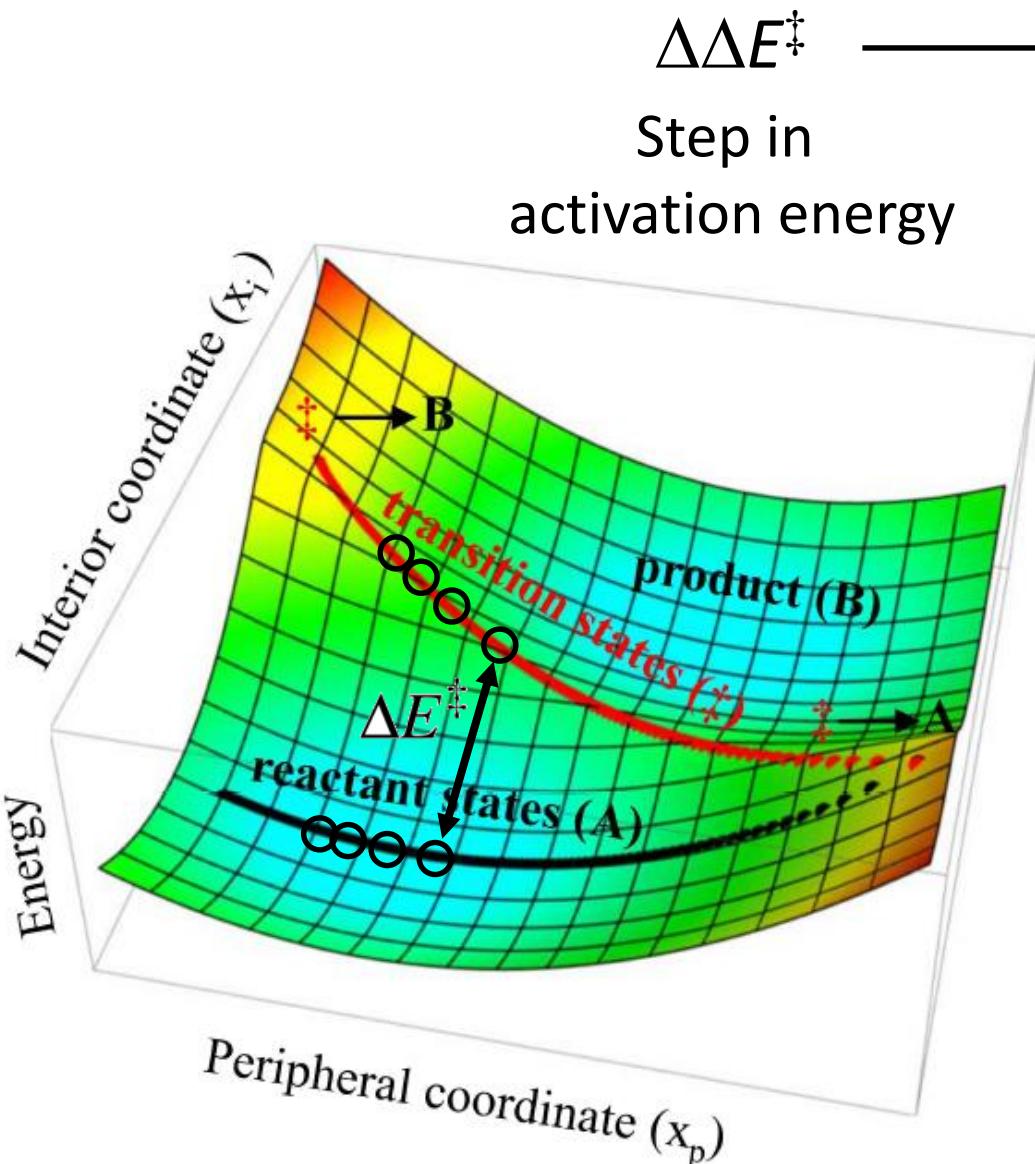


$\Delta\Delta E^\ddagger$
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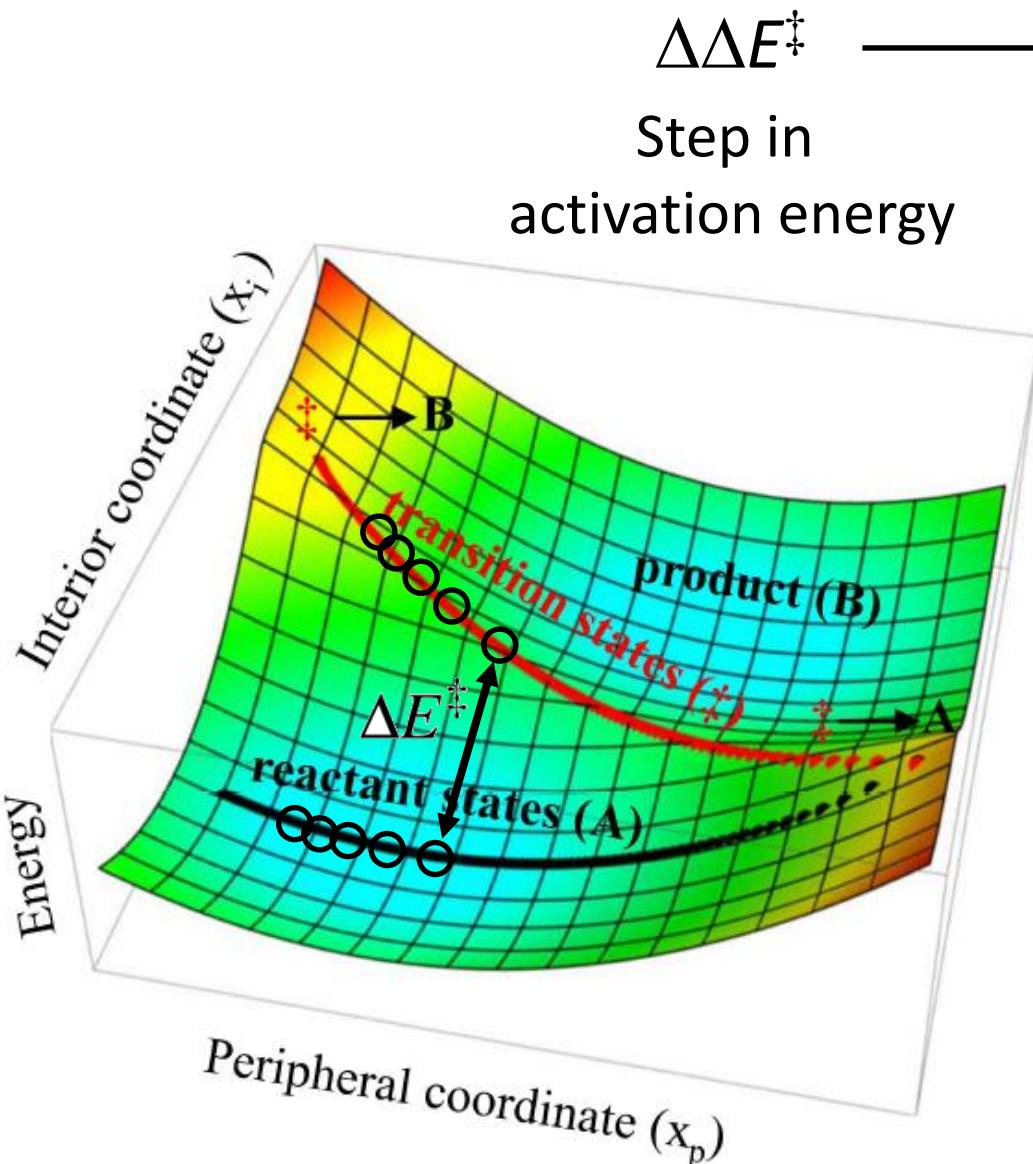


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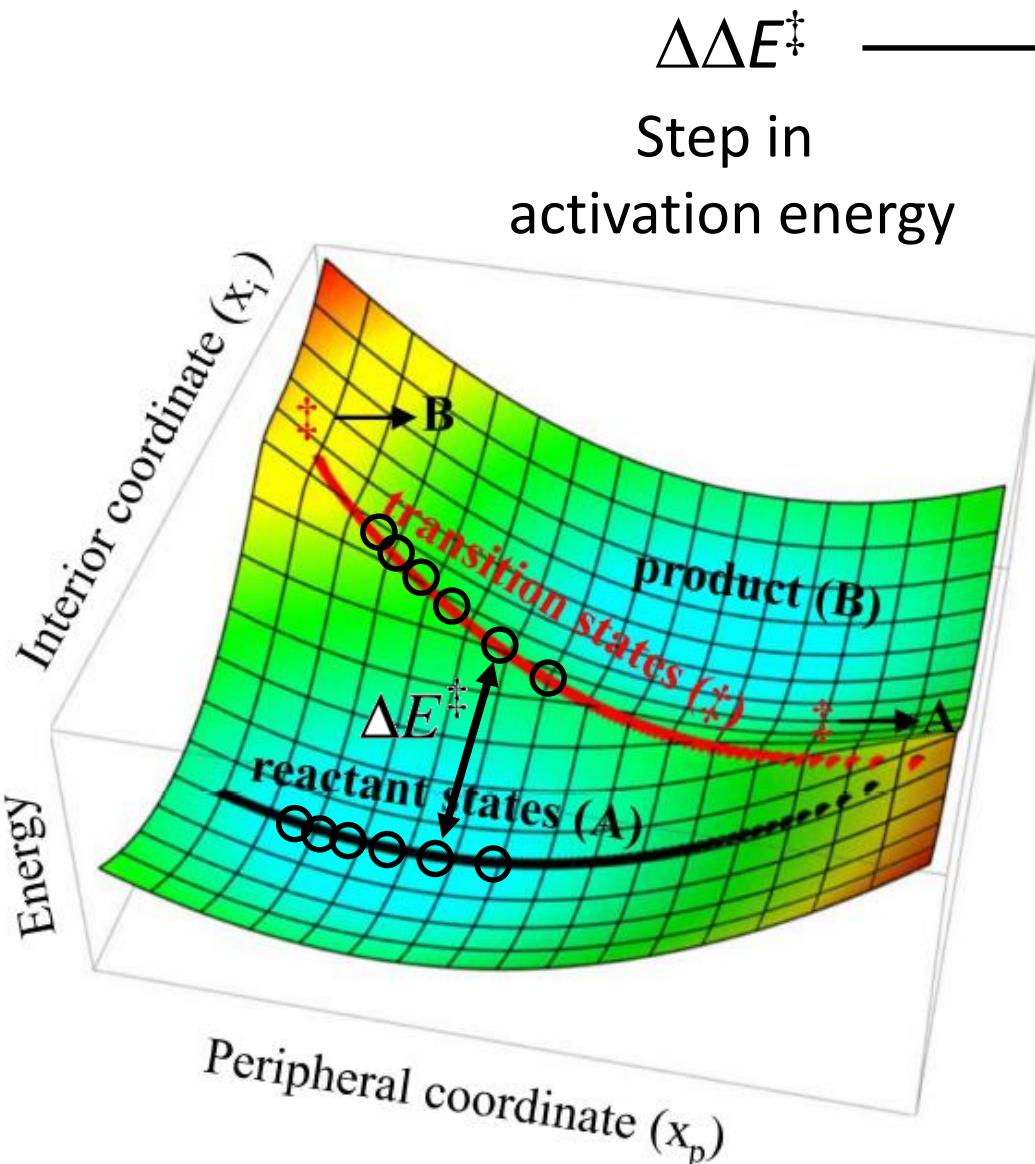


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$$\Delta\Delta E^\ddagger$$

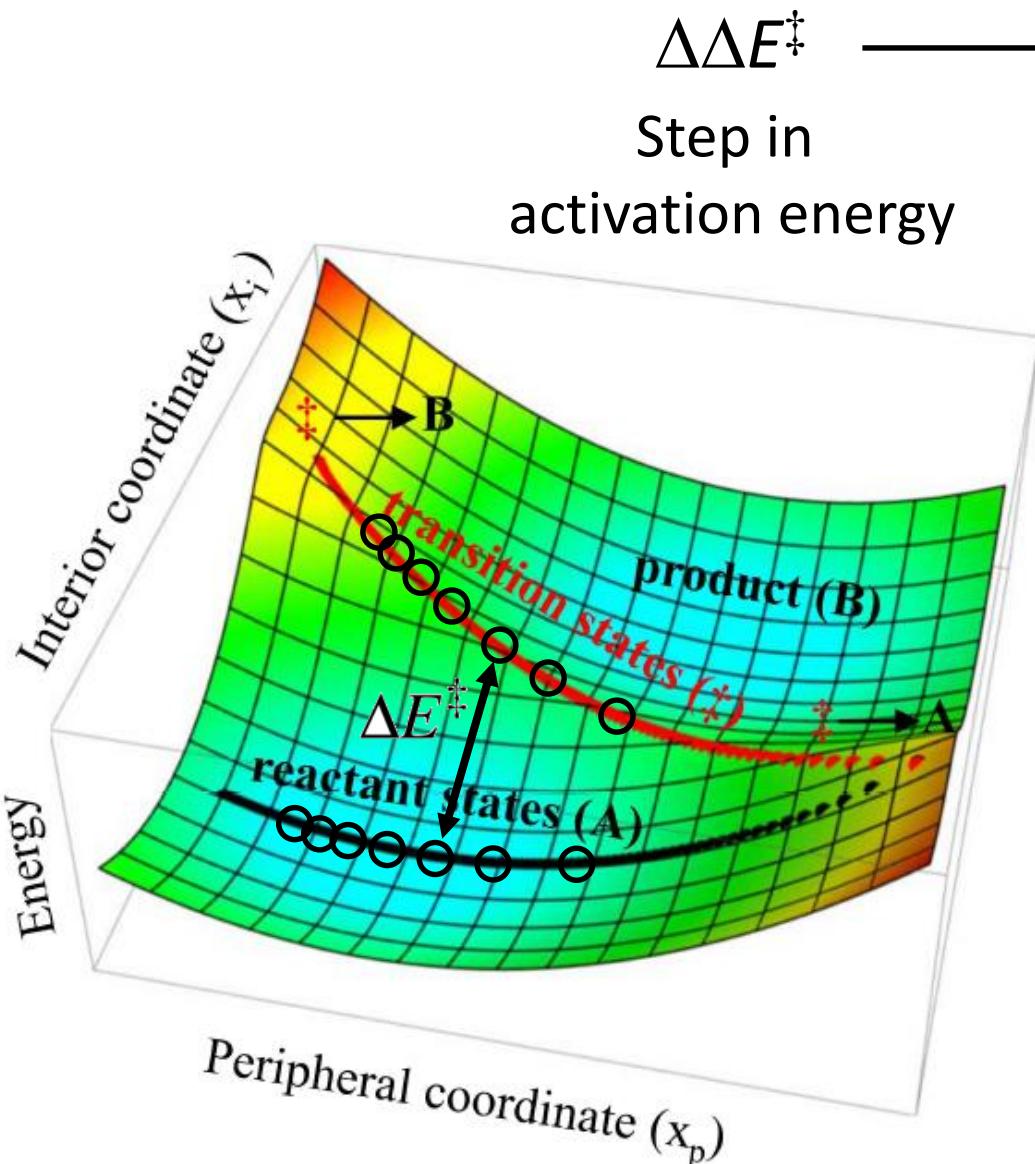
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$$\Delta \mathbf{x}_p$$

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Example of algorithm on model energy landscape

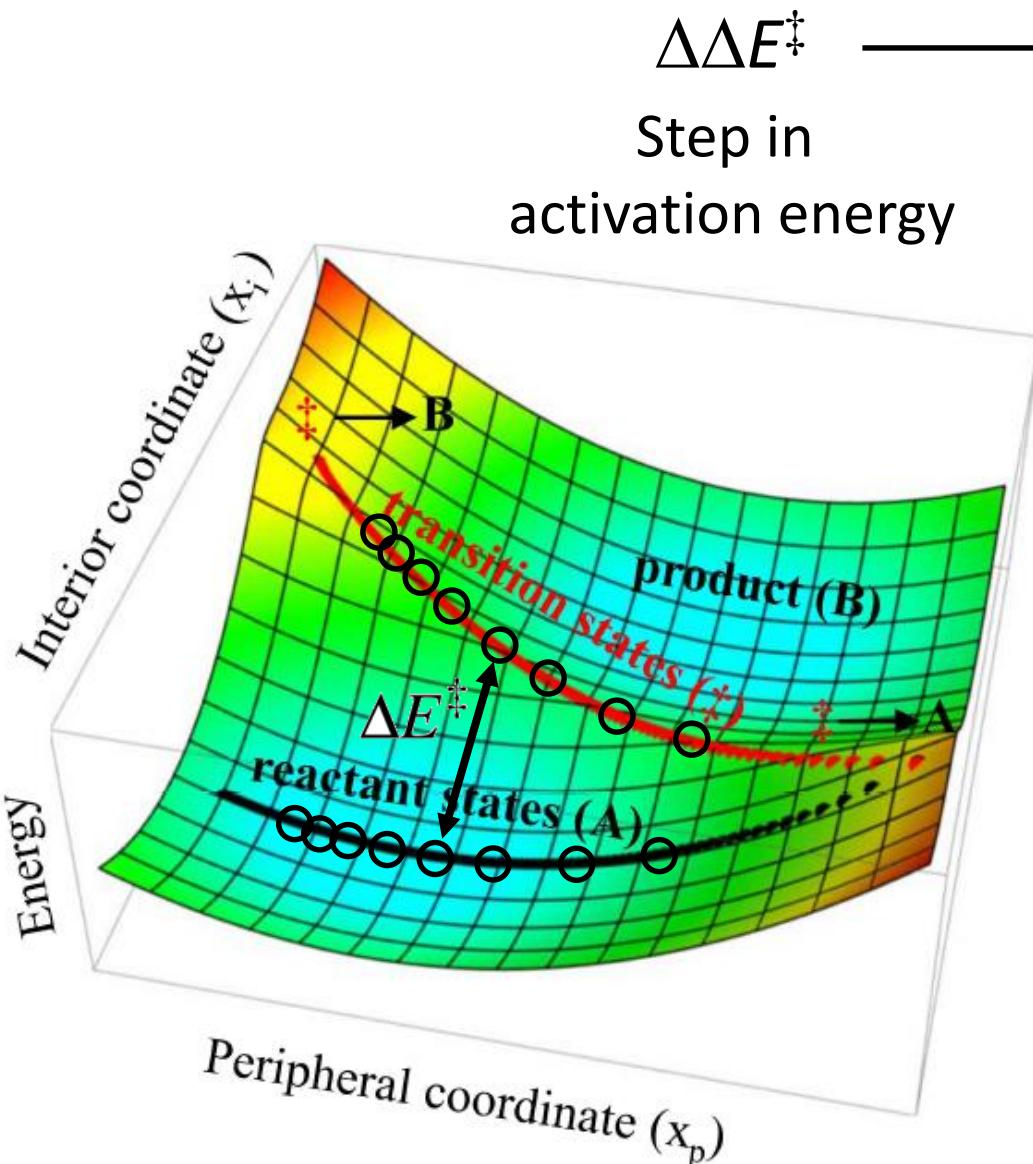


$\Delta\Delta E^\ddagger$
Step in
activation energy

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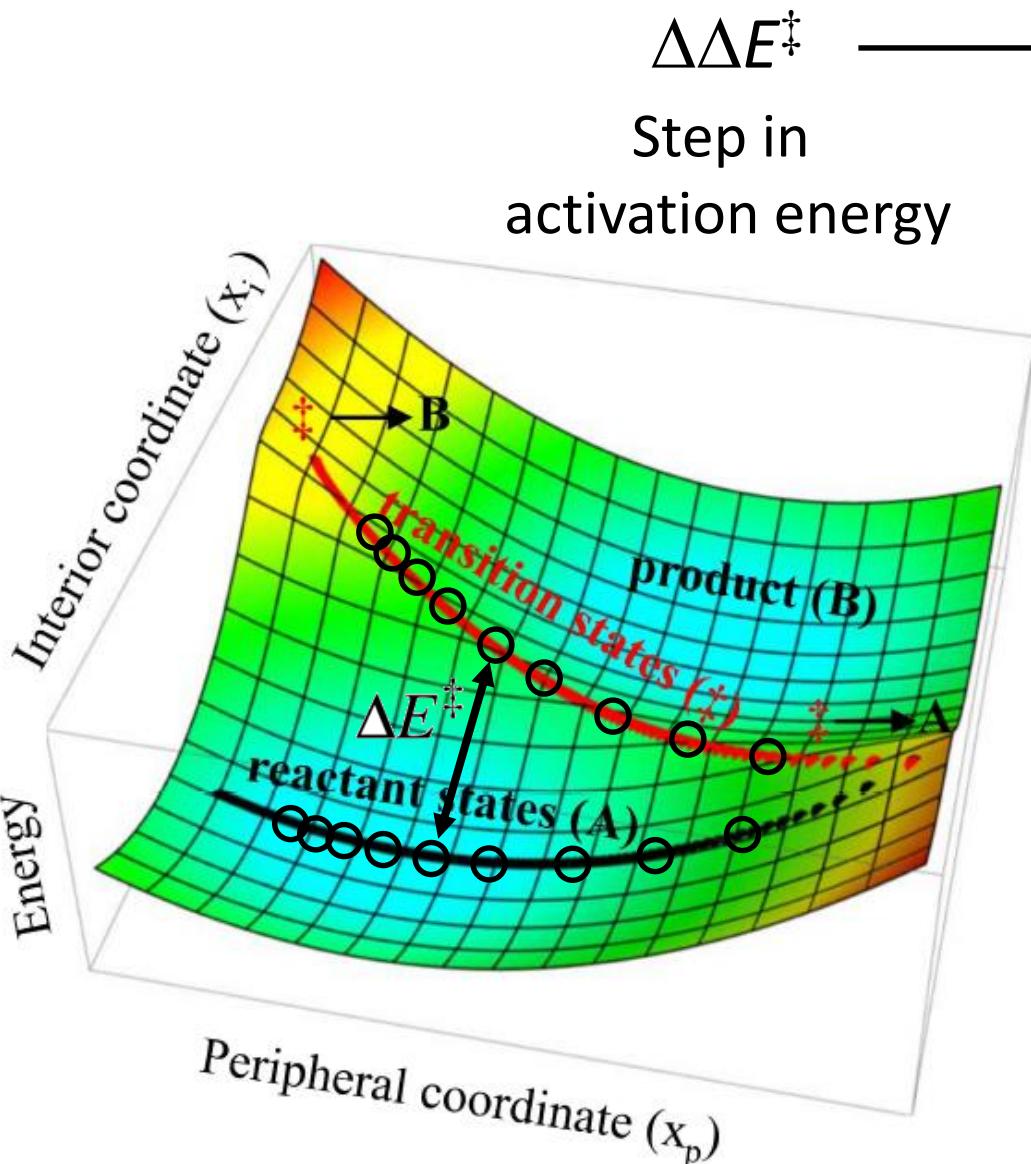


$\Delta\Delta E^\ddagger$ \longrightarrow Step in activation energy

$\Delta \mathbf{x}_p$
New catalyst site structure

Sample the lowest energy site for each value of ΔE^\ddagger

Example of algorithm on model energy landscape

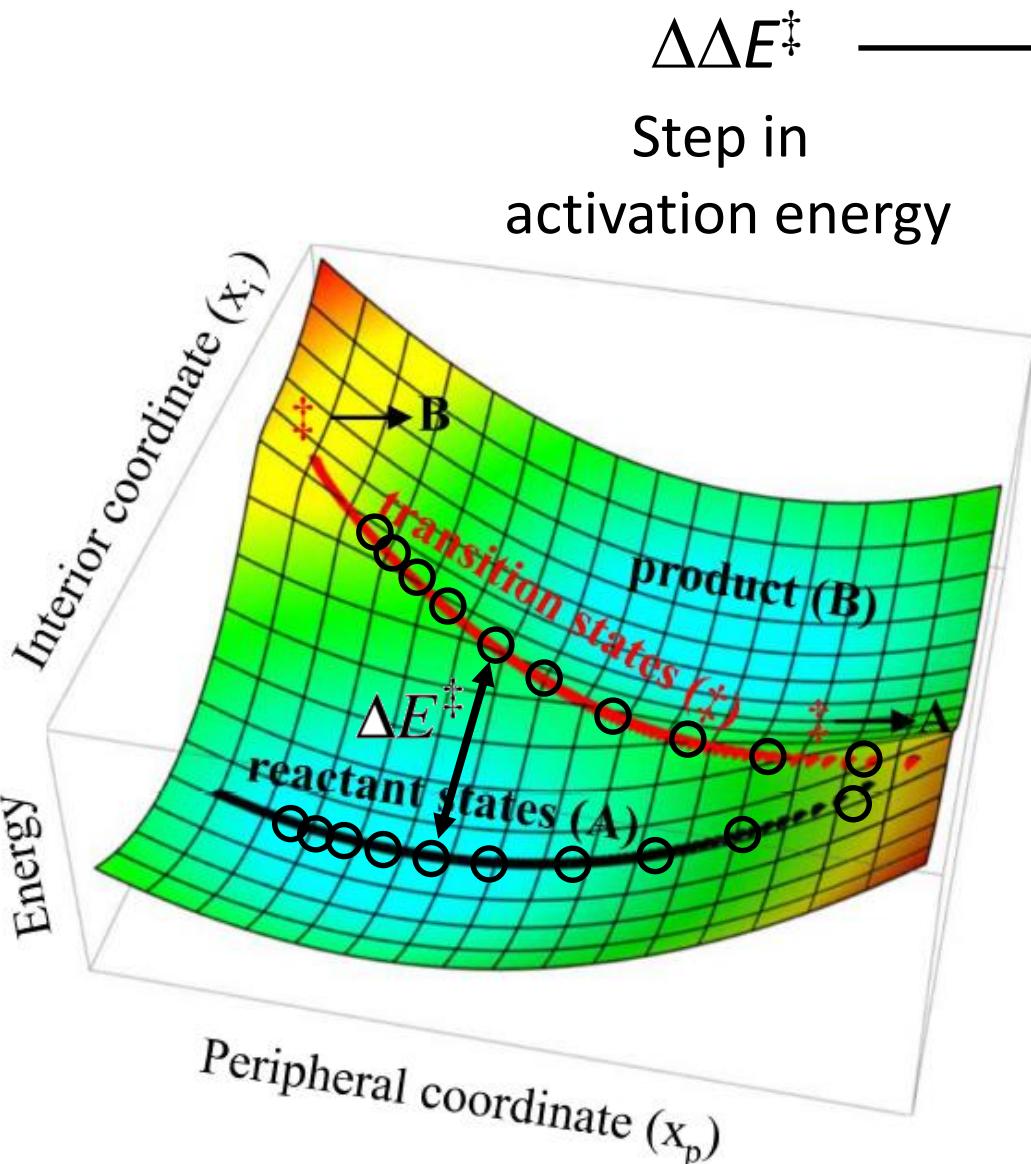


$\Delta\Delta E^\ddagger$ → Step in activation energy

$\Delta \mathbf{x}_p$ → New catalyst site structure

Sample the lowest energy site for each value of ΔE^\ddagger

Example of algorithm on model energy landscape

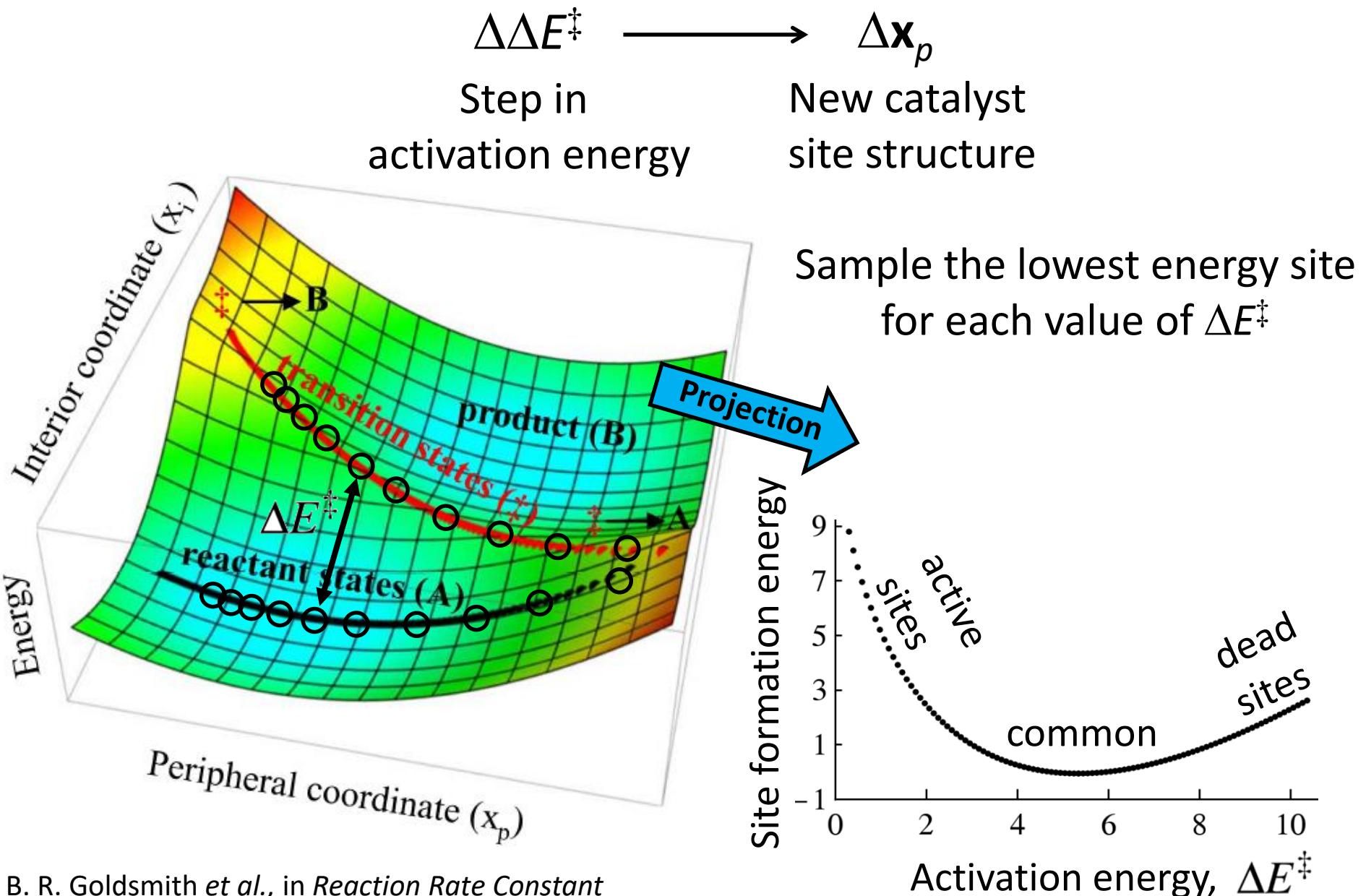


$\Delta\Delta E^\ddagger$ →
Step in
activation energy

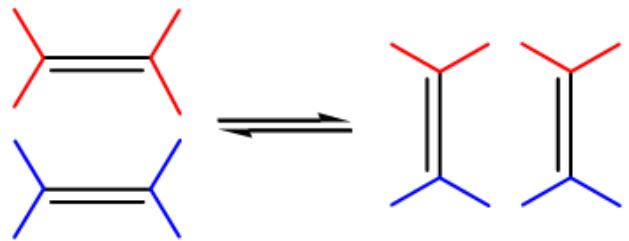
Δx_p
New catalyst
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Sample the lowest energy site
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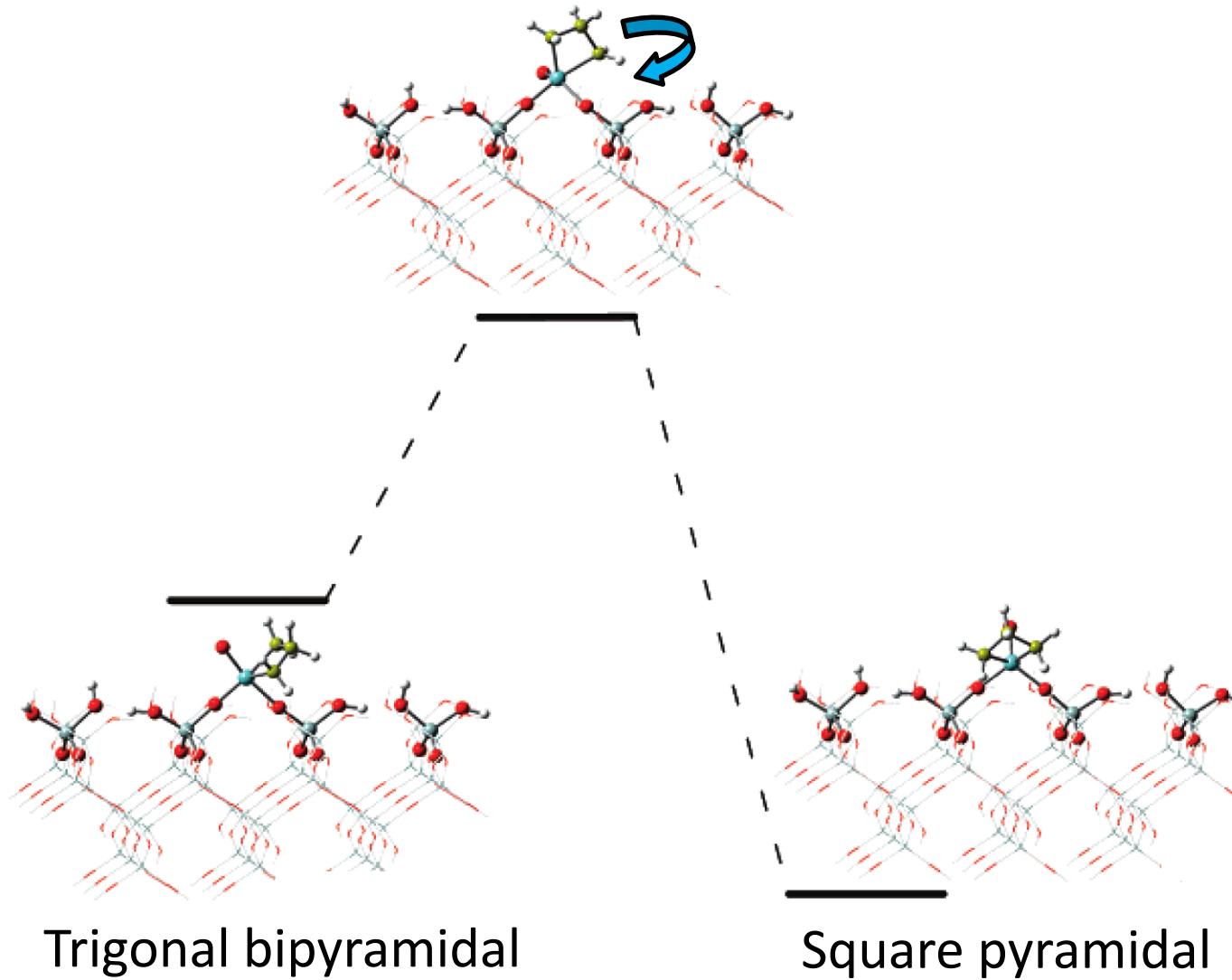


Ethene metathesis by isolated Mo(VI)/SiO₂



Ethene metathesis by isolated Mo(VI)/SiO₂

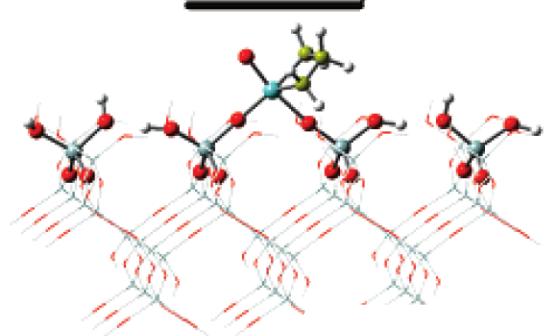
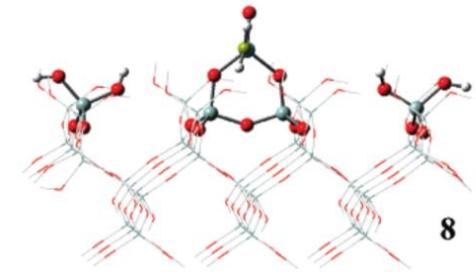
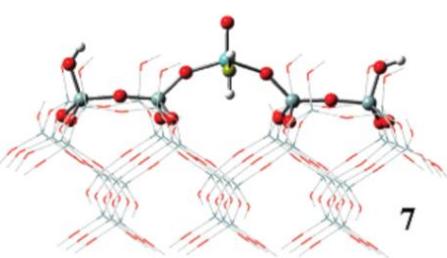
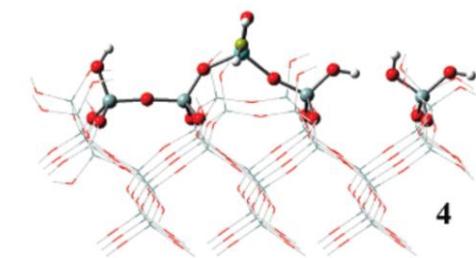
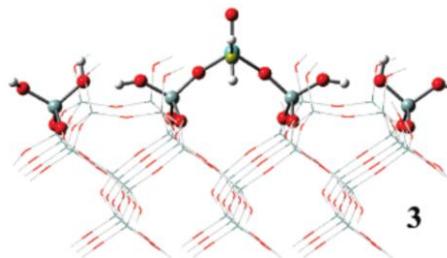
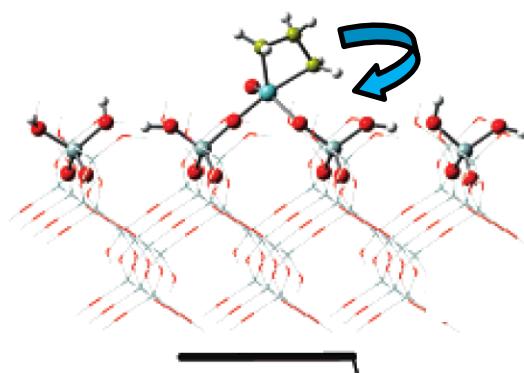
Metallacycle rotation



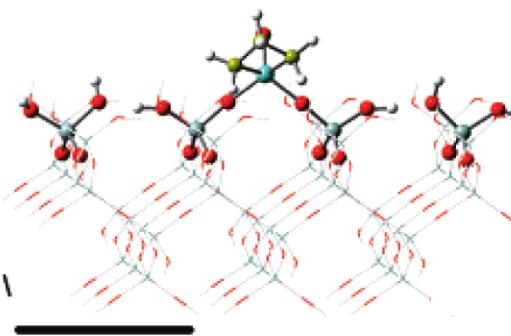
Ethene metathesis by isolated Mo(VI)/SiO₂

Metallacycle rotation

Examined structure-sensitivity
using 10 large models



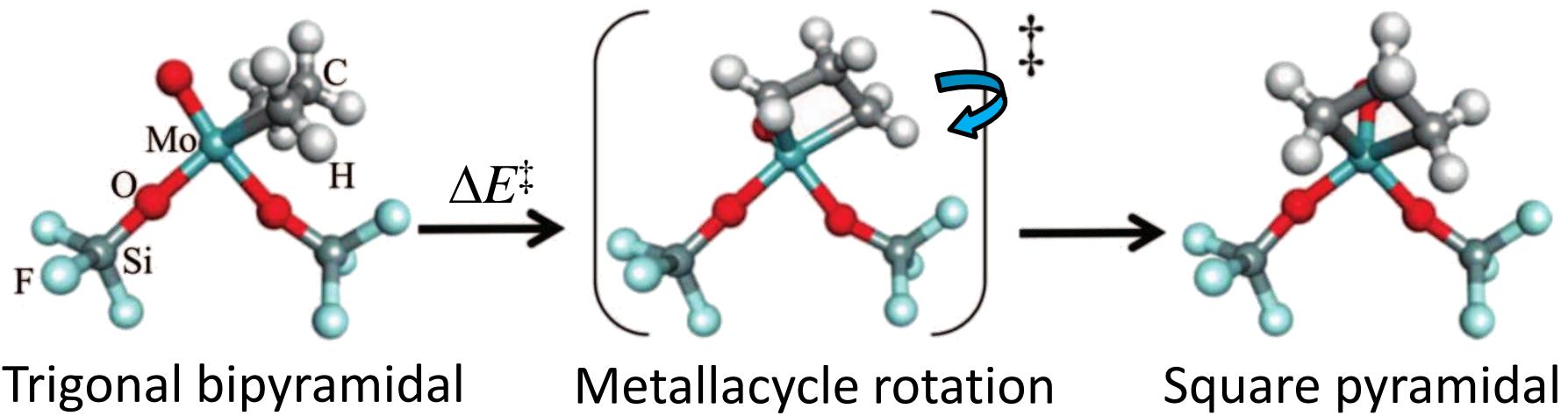
Trigonal bipyramidal



Square pyramidal

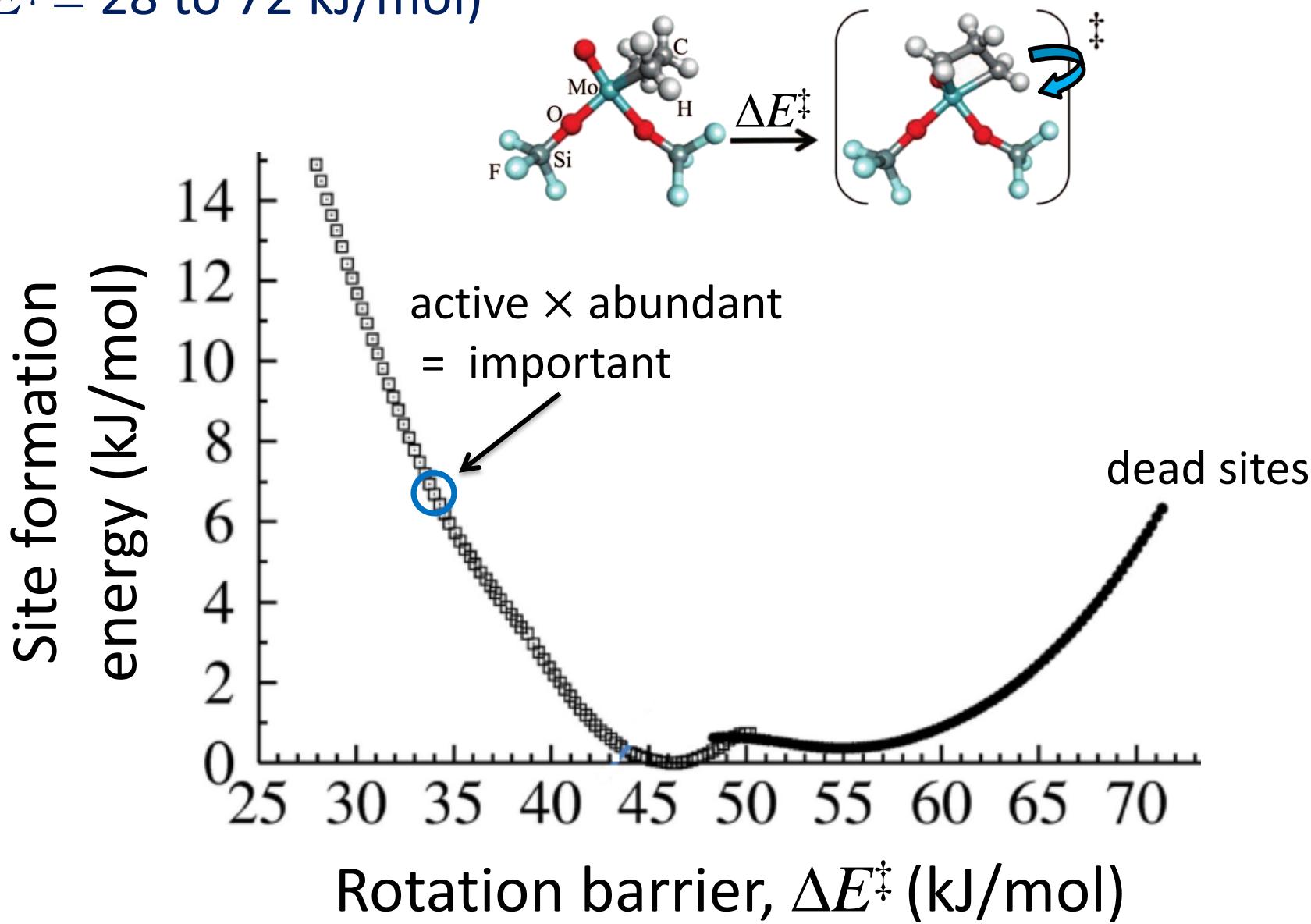
Examine structure-sensitivity toward metallacycle rotation

Our small cluster model for use with the algorithm

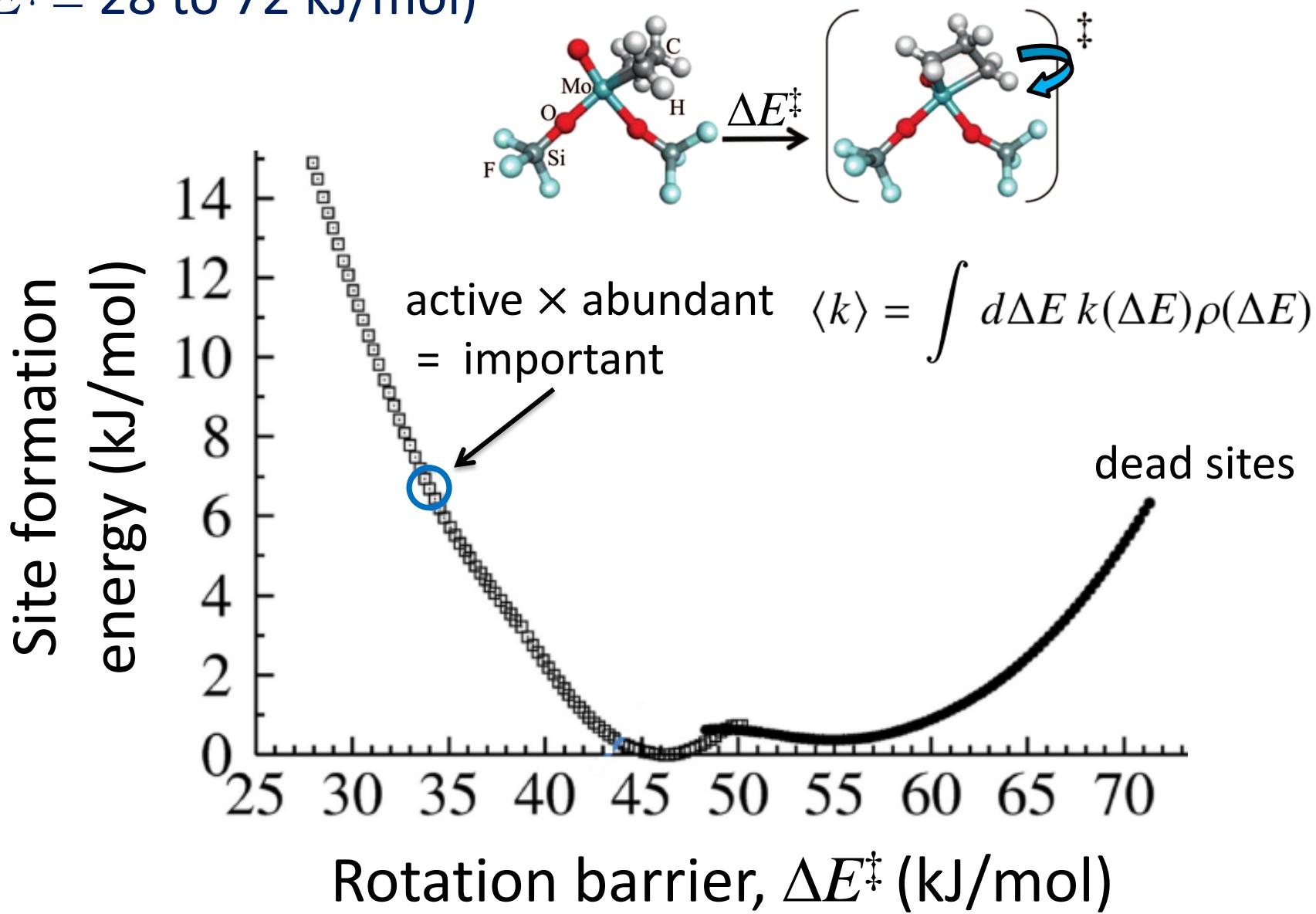


Six fluorine atoms = x_p = constrained atoms
for reactant, transition state, and product

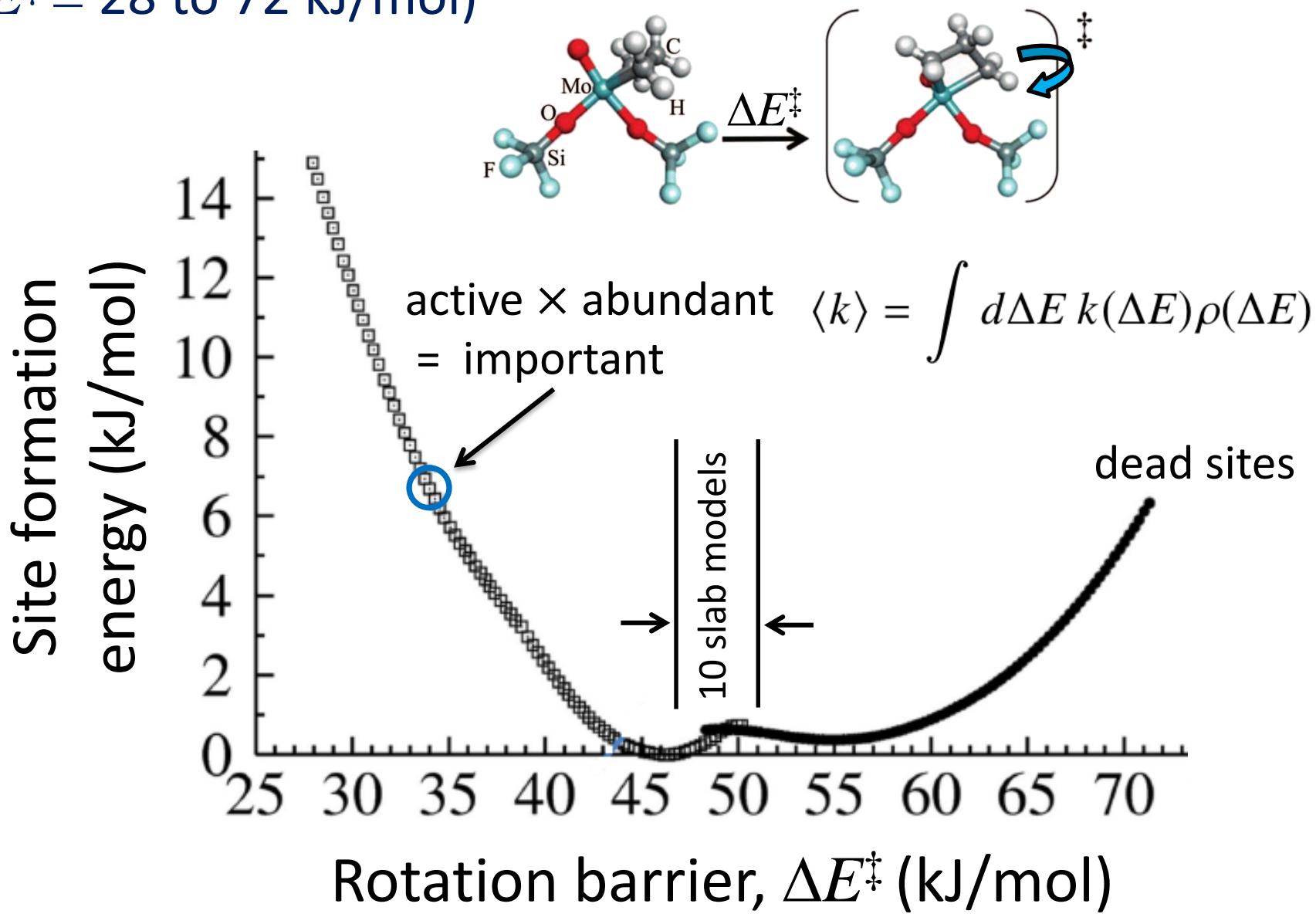
Wide range in the metallacycle rotation barrier exists
($\Delta E^\ddagger = 28$ to 72 kJ/mol)



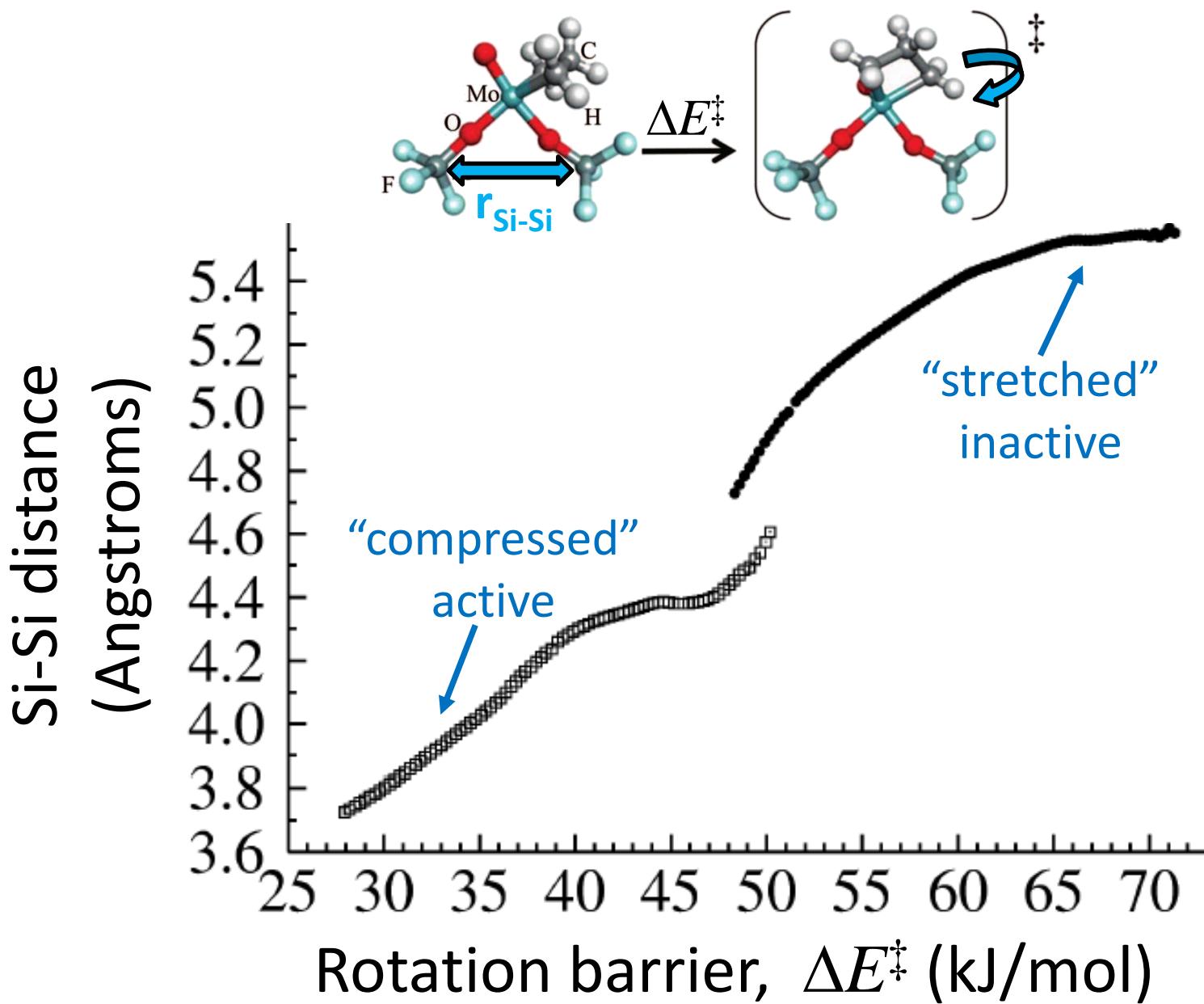
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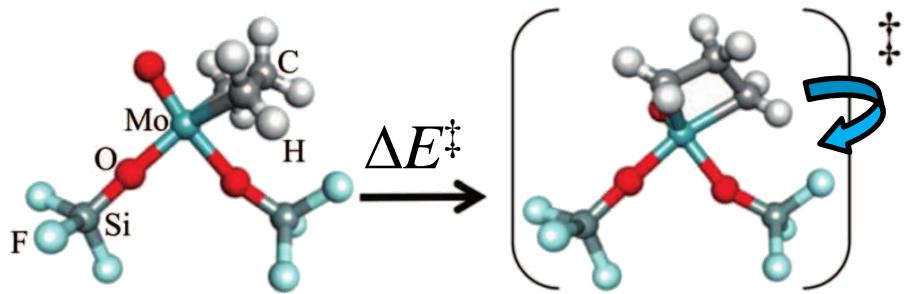


Identify structure-activity descriptors of catalyst sites

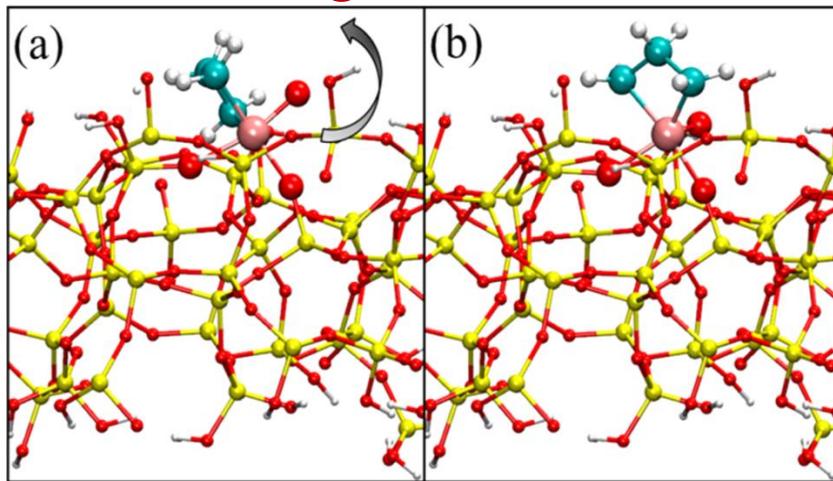


Compare one simple cluster model to five large slab models

One small cluster model

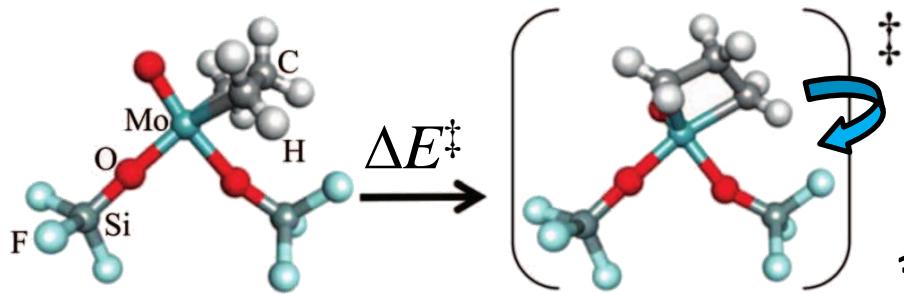


Five large slab models

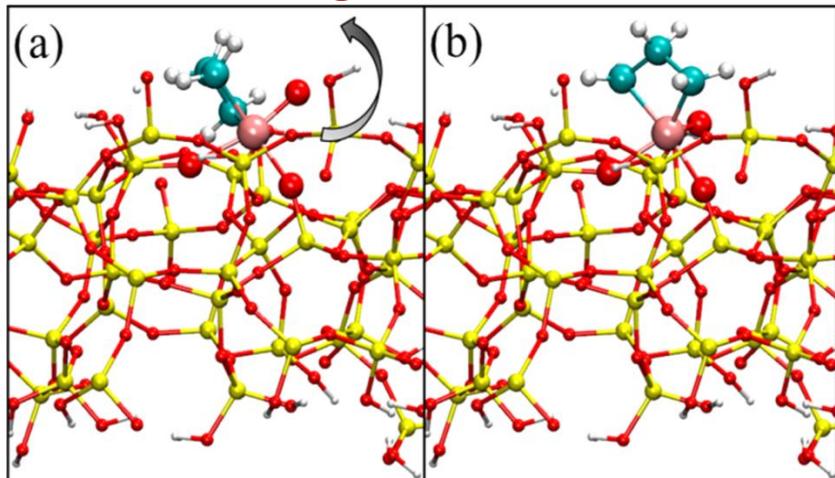


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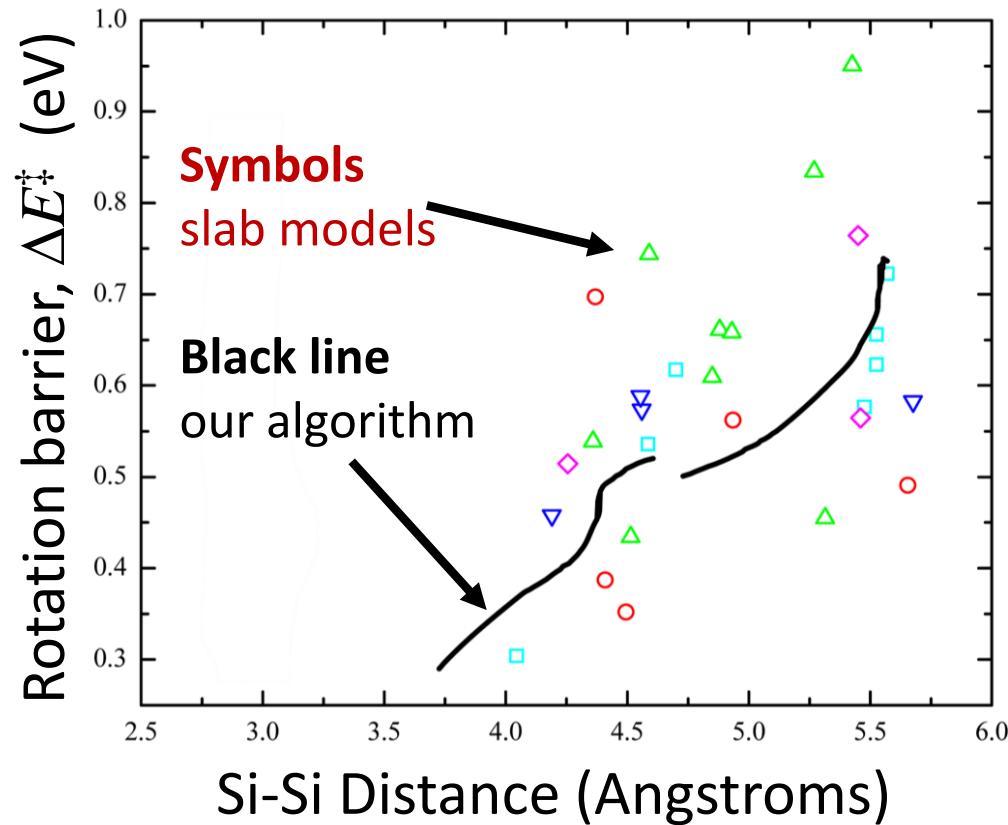
One small cluster model



Five large slab models

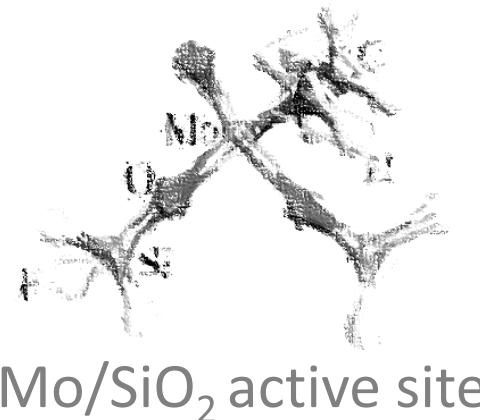


Small cluster model captures the trend and $\approx 90\%$ of the variance

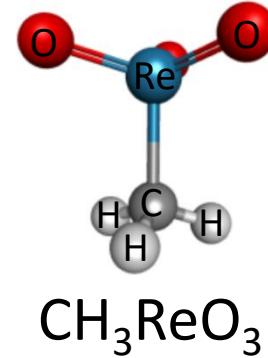


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Challenge 1: Modeling heterogeneity in reactivity of amorphous catalysts



Challenge 2: Understanding the importance of solvent during homogeneous catalysis



Challenge 3: Finding reliable descriptors of catalysts (and materials)



Homogeneous vs. amorphous catalysts

Amorphous catalytic solids

Diversity of active sites

Lack of long-range order

Less amenable to spectroscopy

Homogeneous catalysts

Single active site

Structurally well-defined

Amenable to spectroscopy

Solvent environment

Homogeneous vs. amorphous catalysts

Amorphous catalytic solids

Diversity of active sites

Lack of long-range order

Less amenable to spectroscopy

Homogeneous catalysts

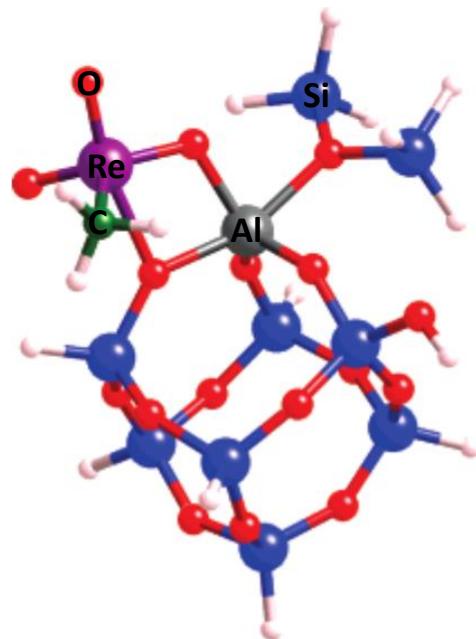
Single active site

Structurally well-defined

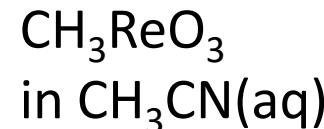
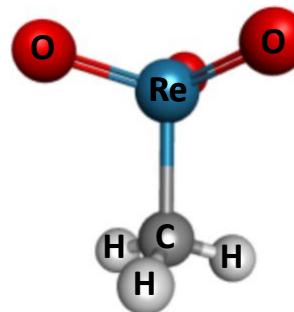
Amenable to spectroscopy

Solvent environment

Active alkene metathesis catalyst



Not active for alkene metathesis



Homogeneous vs. amorphous catalysts

Amorphous catalytic solids

Diversity of active sites

Lack of long-range order

Less amenable to spectroscopy

Homogeneous catalysts

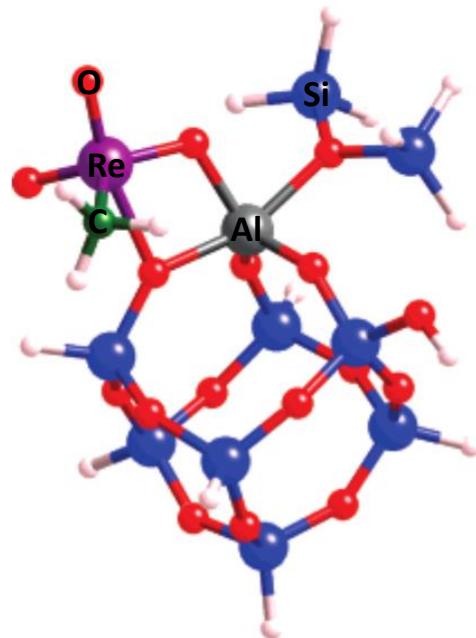
Single active site

Structurally well-defined

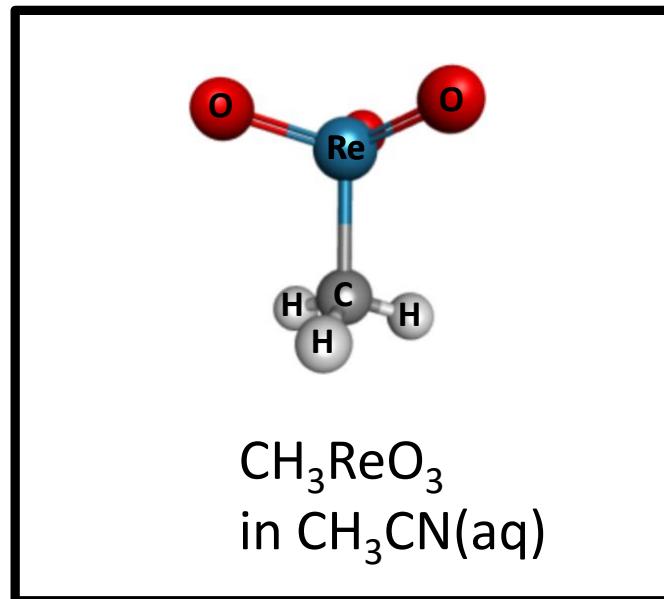
Amenable to spectroscopy

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Active alkene metathesis catalyst

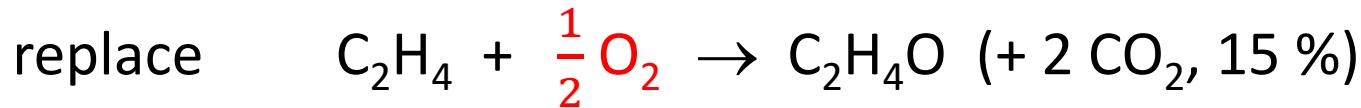


Very active for olefin epoxidation



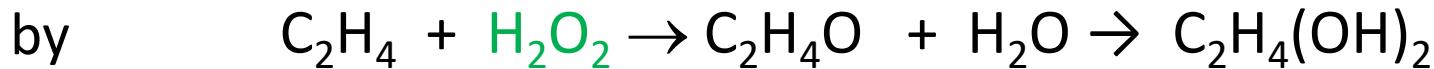
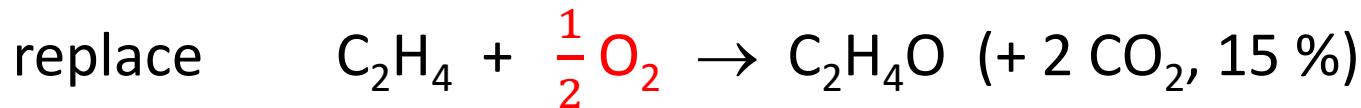
“Greening” the Ethylene Oxide Process

Ag/ α -Al₂O₃



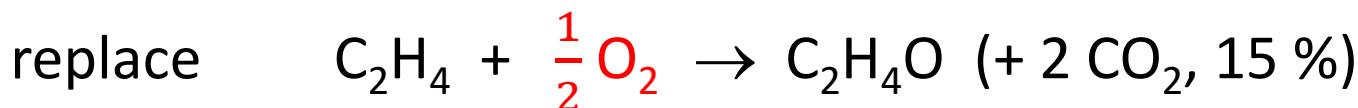
“Greening” the Ethylene Oxide Process

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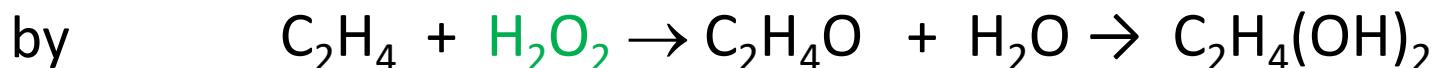


“Greening” the Ethylene Oxide Process

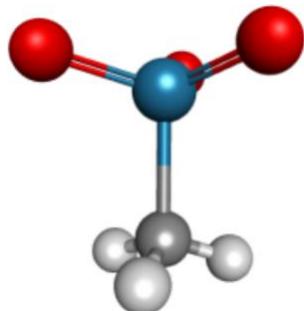
Ag/ α -Al₂O₃



CH₃ReO₃



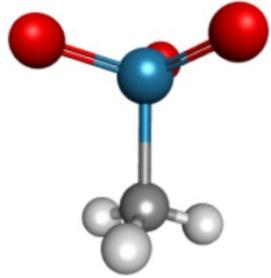
CH₃ReO₃ (MTO)



C₂H₄O selectivity ≈ 100 %
No H₂O₂ decomposition
Works with higher olefins (e.g., C₃H₆)

Homogeneous catalyst

Methyltrioxorhenium activates H₂O₂ for oxygen atom transfer

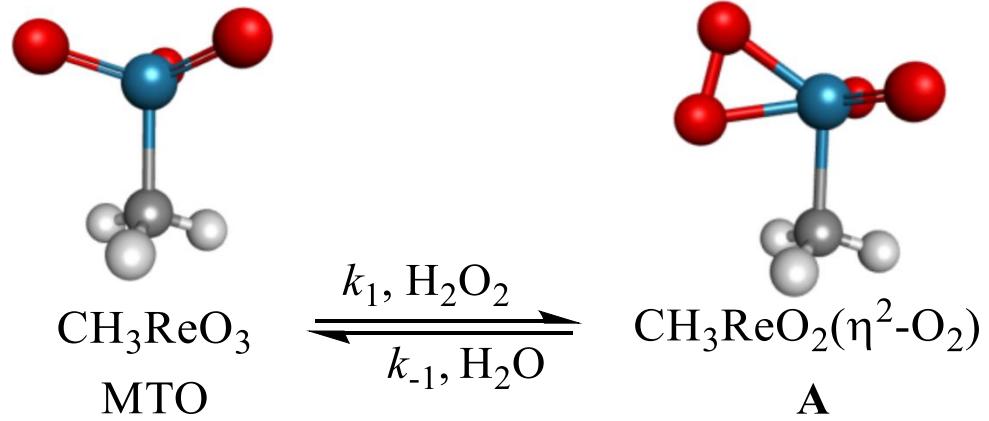


CH₃ReO₃
MTO

J. H. Espenson, *Chem. Comm.* 479 (1999)

W. A. Herrmann, R. W. Fischer, J. D. G. Correia, *J. Mol. Catal.* 94 (1994)

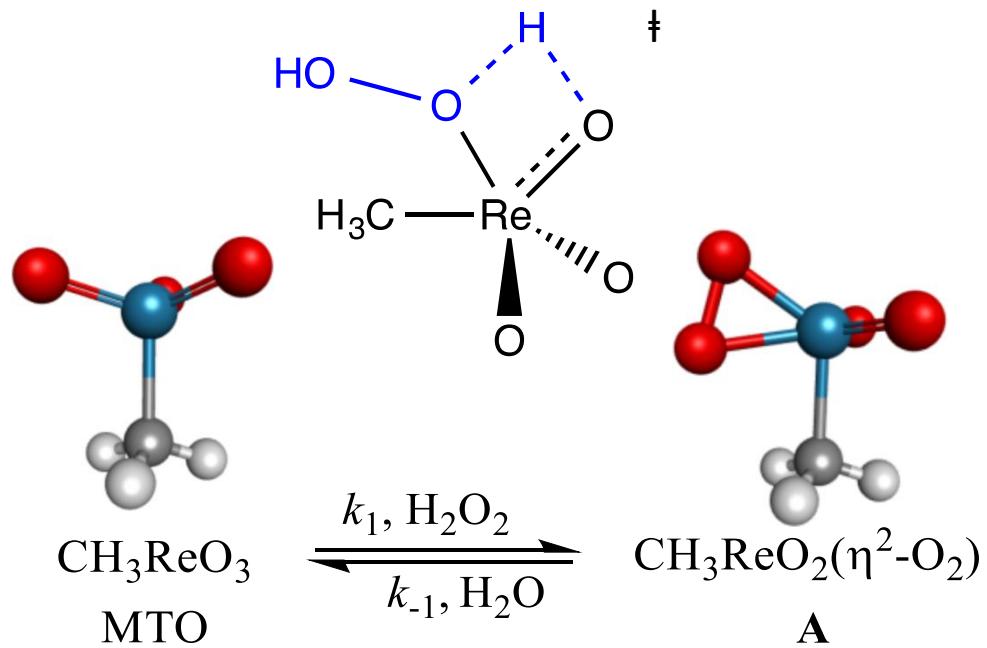
Methyltrioxorhenium activates H₂O₂ for oxygen atom transfer



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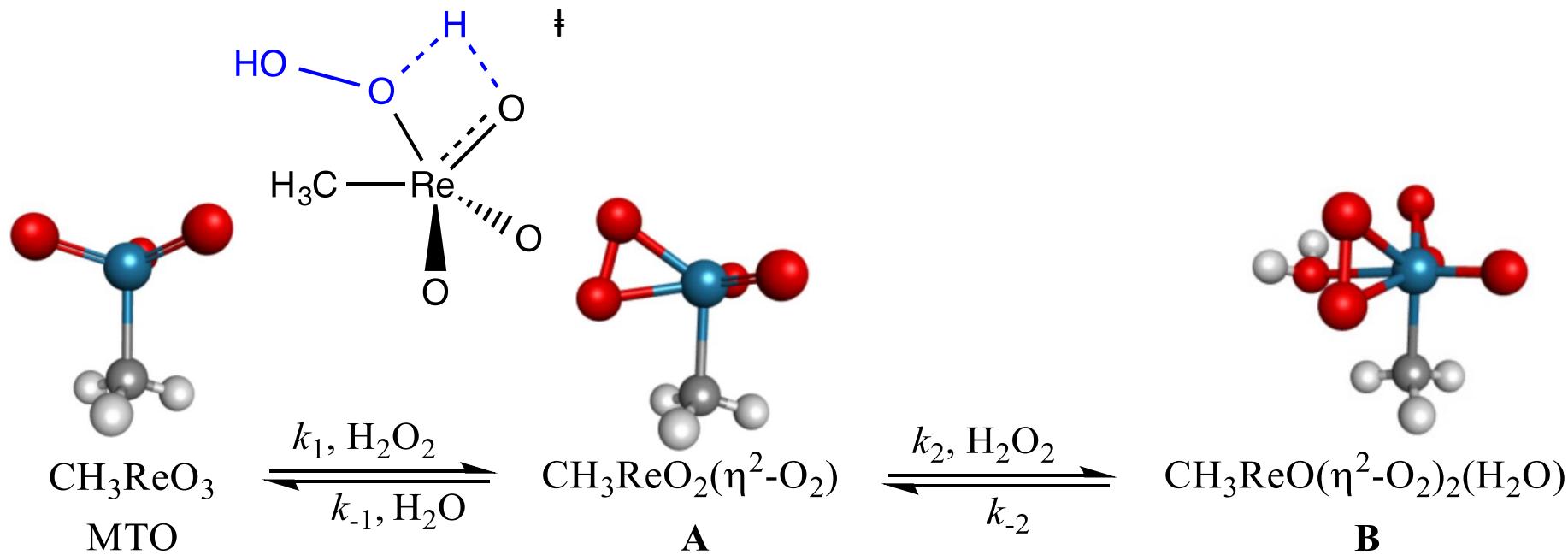
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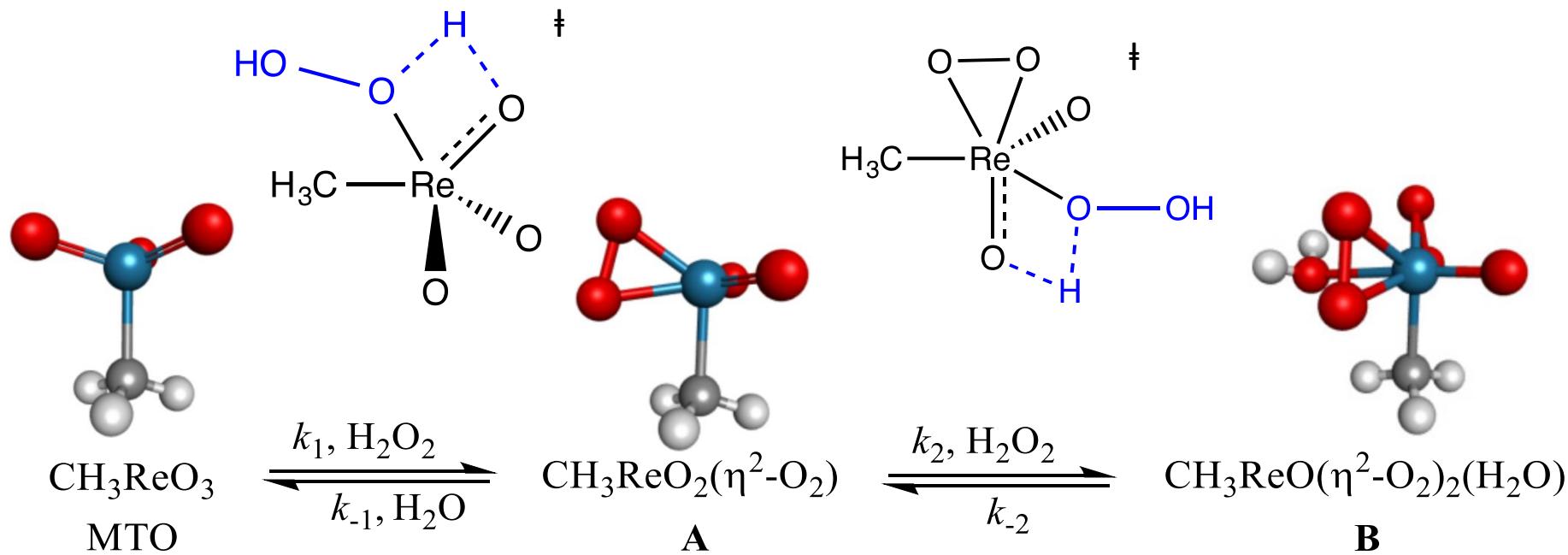
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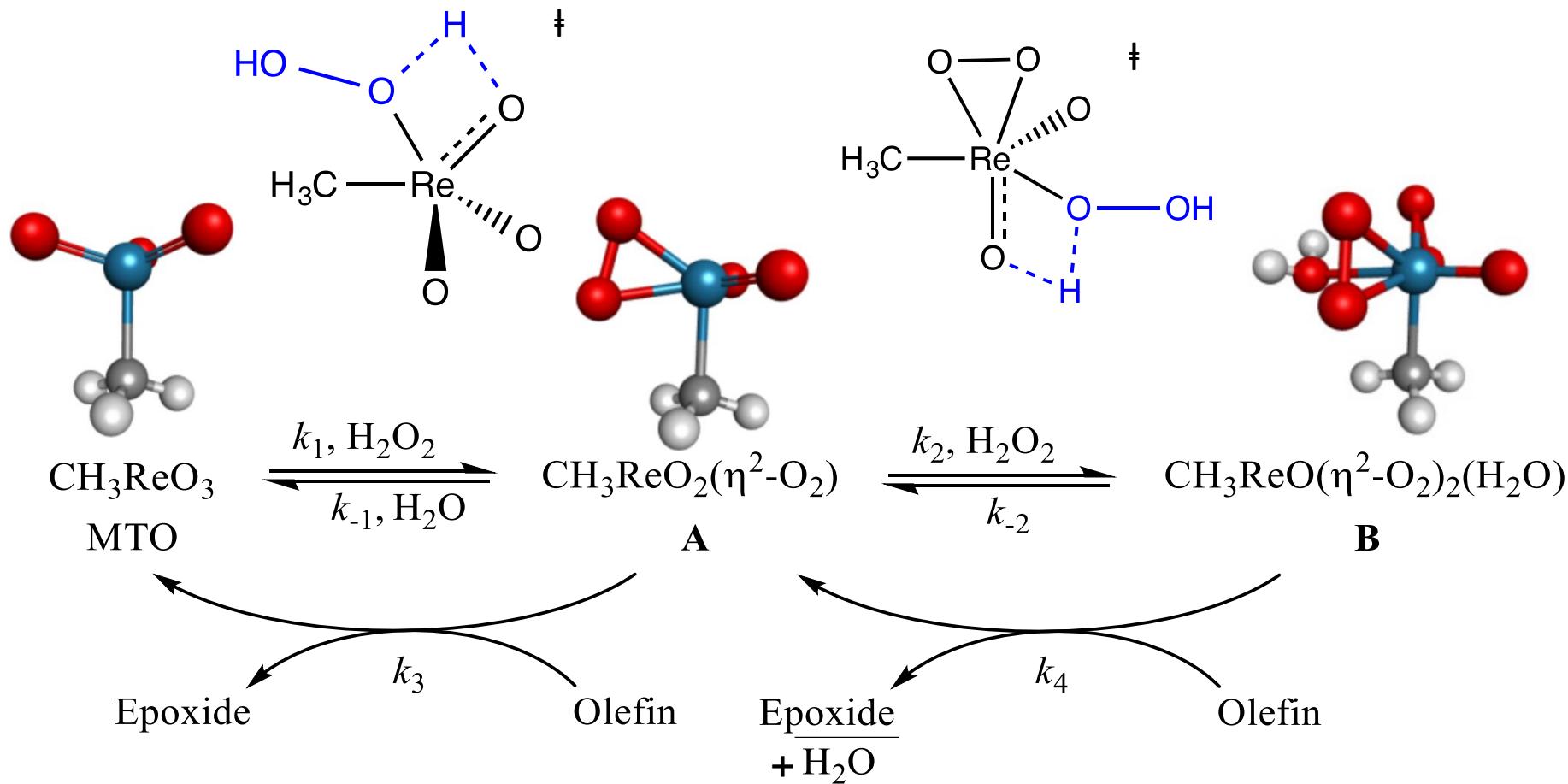
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J. H. Espenson, *Chem. Comm.* 479 (1999)

W. A. Herrmann, R. W. Fischer, J. D. G. Correia, *J. Mol. Catal.* 94 (1994)

Methyltrioxorhenium activates H_2O_2 for oxygen atom transfer

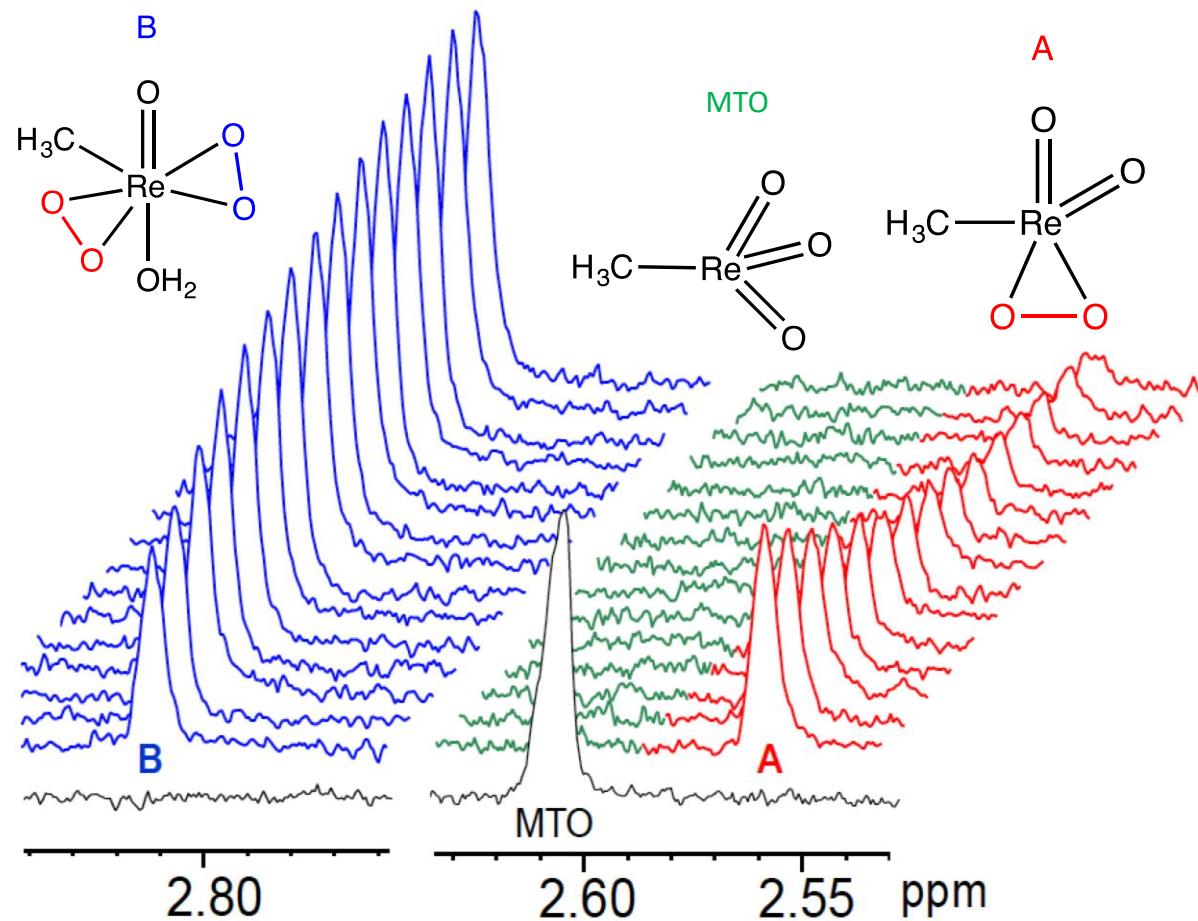
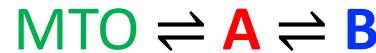


J. H. Espenson, *Chem. Comm.* 479 (1999)

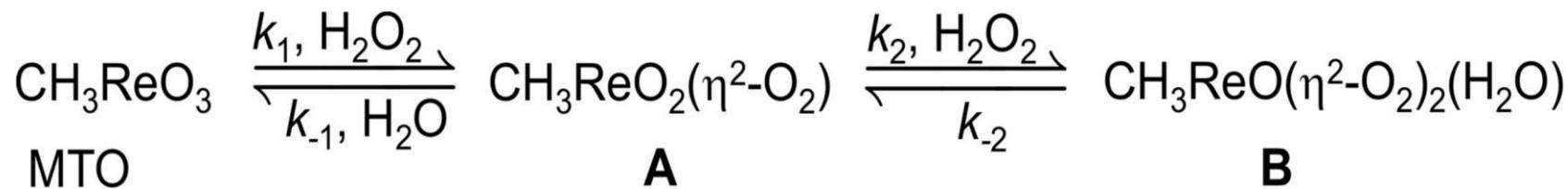
W. A. Herrmann, R. W. Fischer, J. D. G. Correia, *J. Mol. Catal.* 94 (1994)

The ‘clean’ spectra of MTO makes it amenable to kinetic studies

^1H NMR spectra recorded at 3 minute intervals, 23.0 °C



Many discrepancies remain between experiment and theory

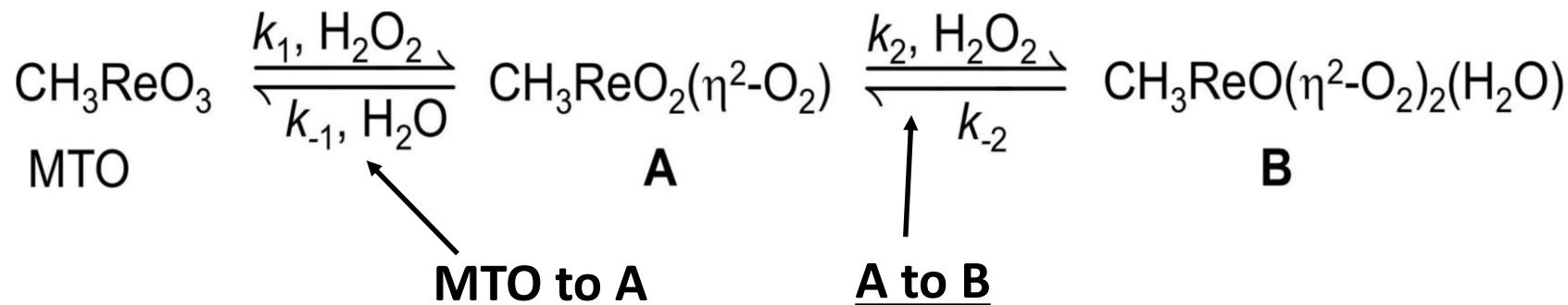


P. Gissakis *et al.*, *Angew. Chem. Int. Ed.* 37 (1998)

J. M. Gonzales, et al. *J. Am. Chem. Soc.*, 129 (2007)

B. R. Goldsmith *et al.*, *J. Am. Chem. Soc.* 137 (2015)

Many discrepancies remain between experiment and theory



Reaction parameters: ΔH₁, ΔS₁, ΔG₁ ΔH₂, ΔS₂, ΔG₂

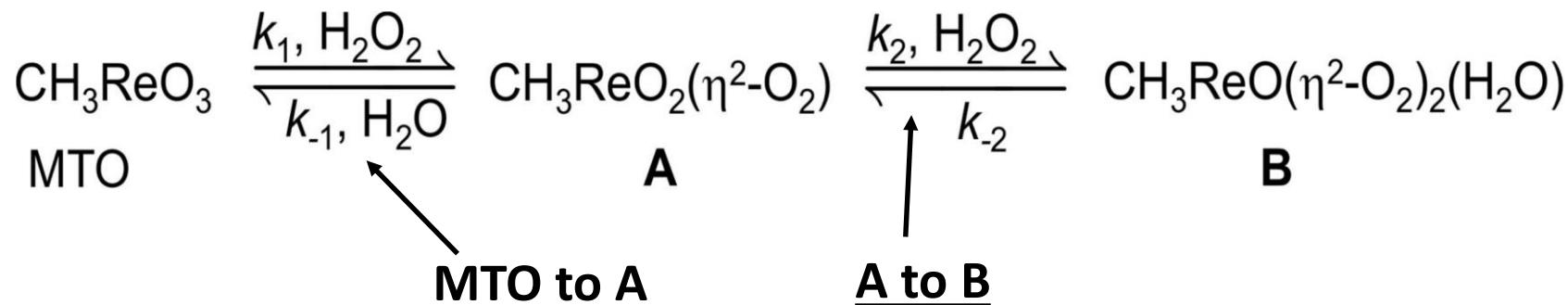
Activation parameters: ΔH₁[‡], ΔS₁[‡], ΔG₁[‡] ΔH₂[‡], ΔS₂[‡], ΔG₂[‡]

P. Gisdakis *et al.*, *Angew. Chem. Int. Ed.* 37 (1998)

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Reaction parameters: $\Delta H_1, \Delta S_1, \Delta G_1$ $\Delta H_2, \Delta S_2, \Delta G_2$

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Thermodynamics

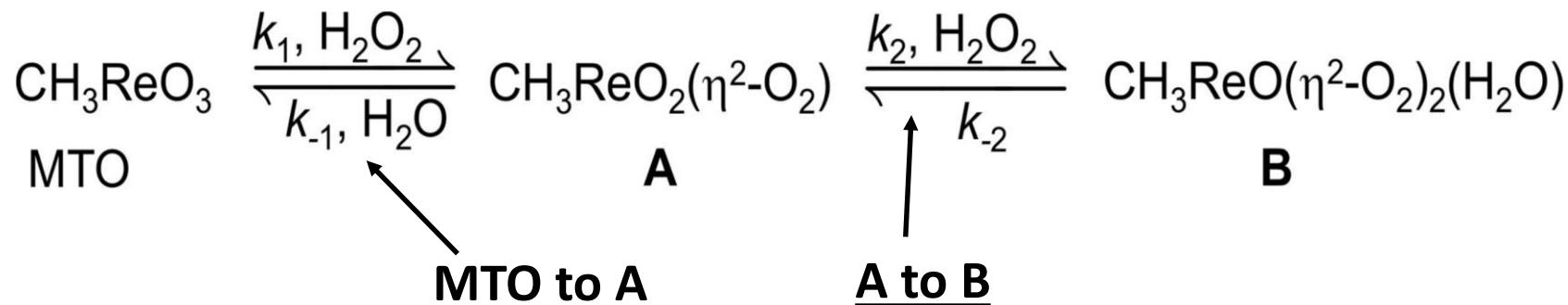
Calculated Experimental

P. Gisdakis *et al.*, *Angew. Chem. Int. Ed.* 37 (1998)

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Thermodynamics

Calculated Experimental

$\Delta H_1 > 0$

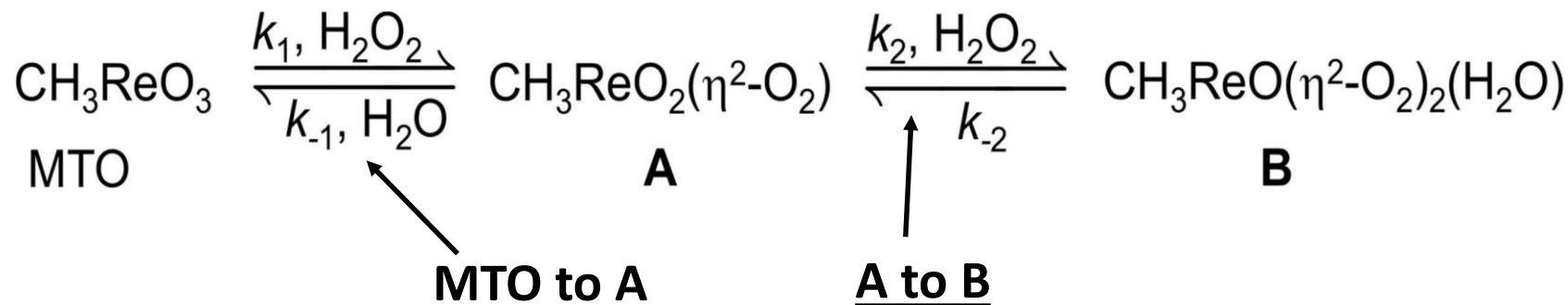
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Thermodynamics

Calculated Experimental

$\Delta H_1 > 0$ $\Delta H_1 < 0$

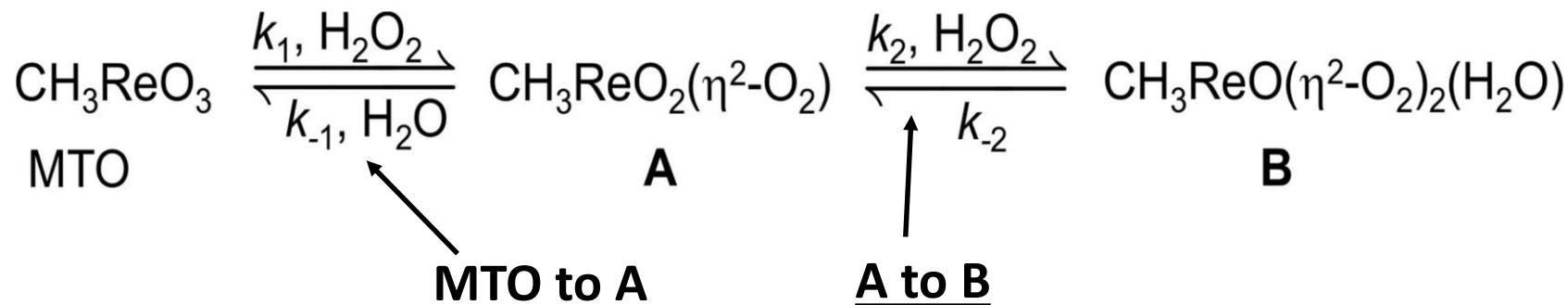
$\Delta S_1 < 0$ $\Delta S_1 > 0$

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J. M. Gonzales, *et al.* *J. Am. Chem. Soc.*, 129 (2007)

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Activation parameters: $\Delta H_1^\ddagger, \Delta S_1^\ddagger, \Delta G_1^\ddagger$ $\Delta H_2^\ddagger, \Delta S_2^\ddagger, \Delta G_2^\ddagger$

Thermodynamics

Calculated Experimental

$\Delta H_1 > 0$ $\Delta H_1 < 0$

$\Delta S_1 < 0$ $\Delta S_1 > 0$

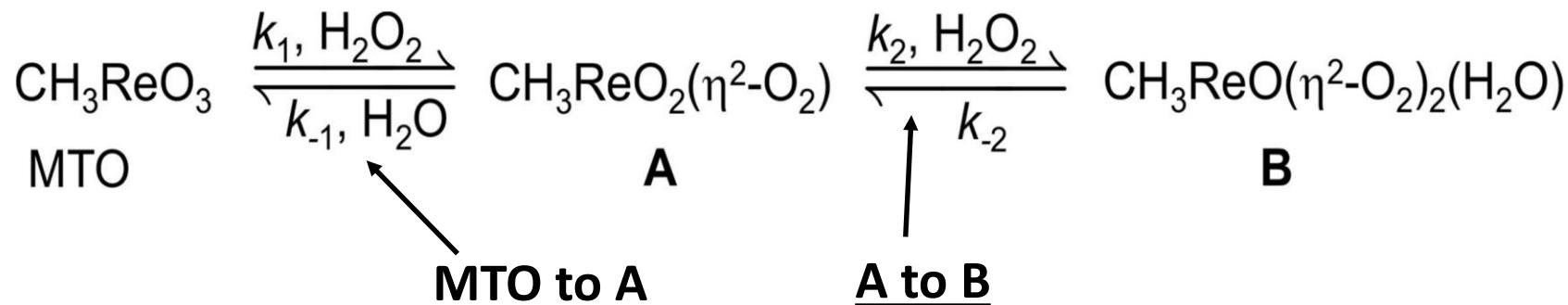
$\Delta G_1 > 0$ $\Delta G_1 < 0$

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Thermodynamics

Calculated Experimental

$\Delta H_1 > 0$ $\Delta H_1 < 0$

$\Delta S_1 < 0$ $\Delta S_1 > 0$

$\Delta G_1 > 0$ $\Delta G_1 < 0$

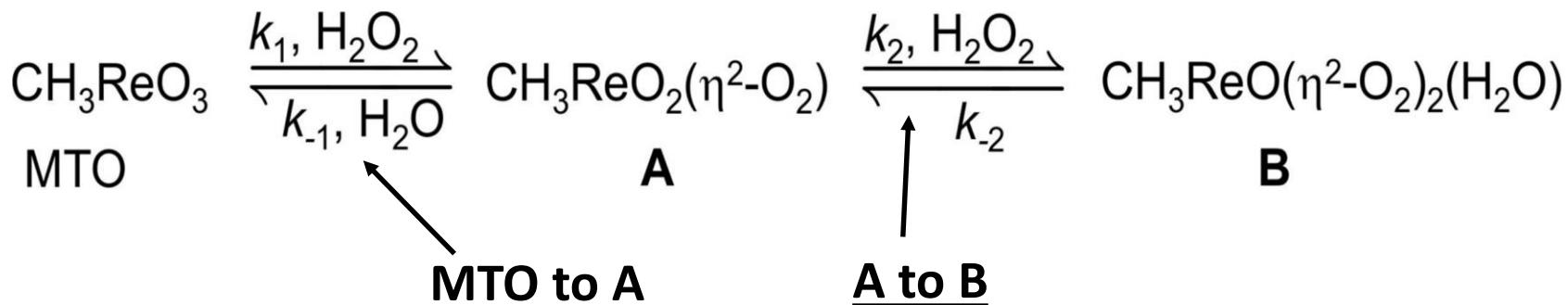
$\Delta G_1 > \Delta G_2$ $\Delta G_1 < \Delta G_2$

P. Gisdakis *et al.*, *Angew. Chem. Int. Ed.* 37 (1998)

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Thermodynamics

Calculated Experimental

$$\Delta H_1 > 0$$

$$\Delta S_1 < 0$$

$$\Delta G_1 > 0$$

$$\Delta G_1 > \Delta G_2$$

Kinetics

Calculated

$$\Delta H_1^\ddagger > 100 \text{ kJ mol}^{-1}$$

Experimental

$$\Delta H_1^\ddagger = 24.5 \text{ kJ mol}^{-1}$$

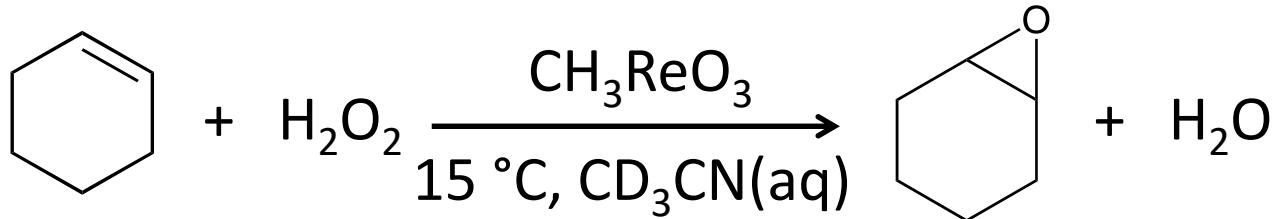
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B. R. Goldsmith *et al.*, *J. Am. Chem. Soc.* 137 (2015)

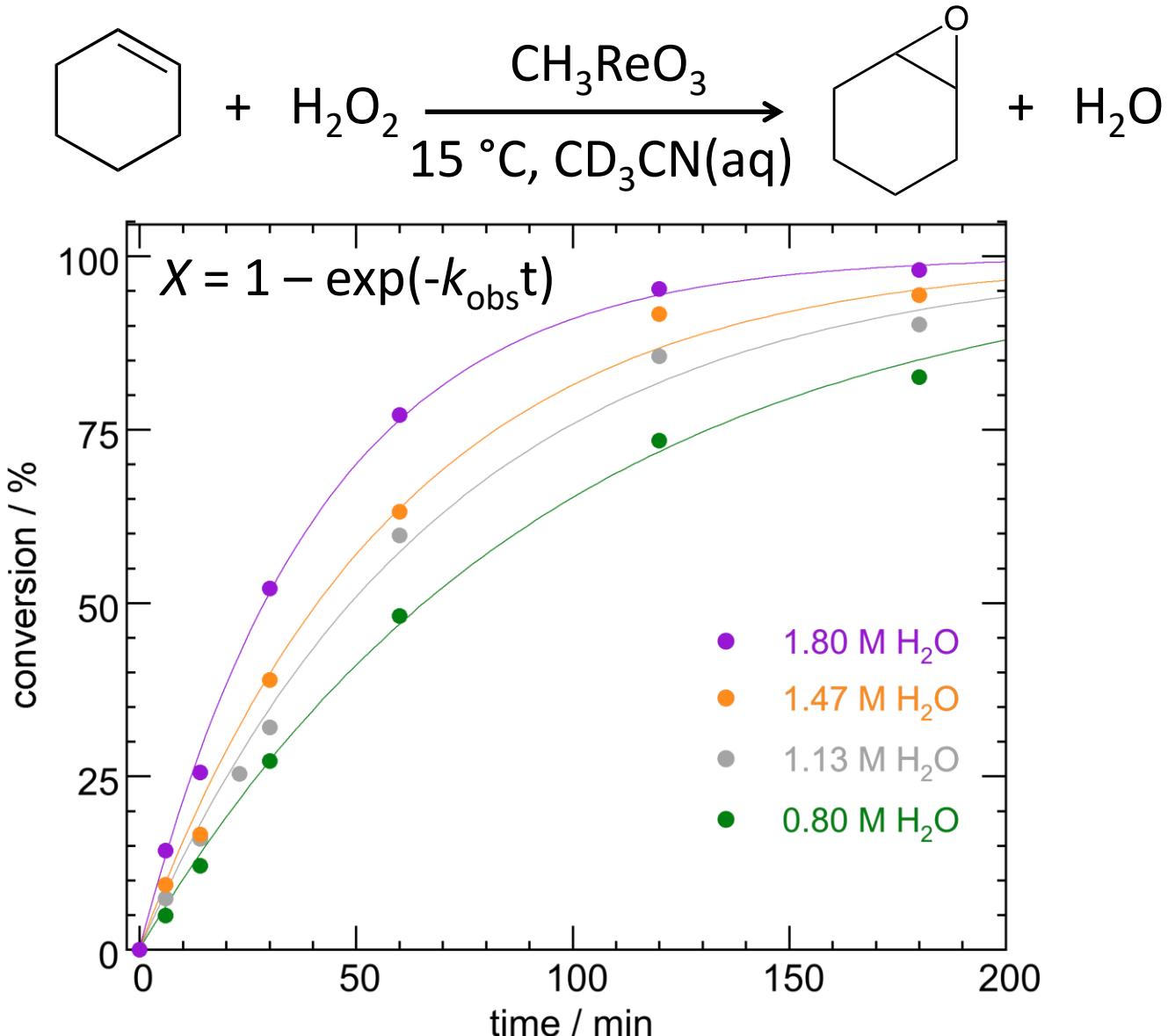
Trace water can be important in many reactions

The water dependence of MTO has not been explained



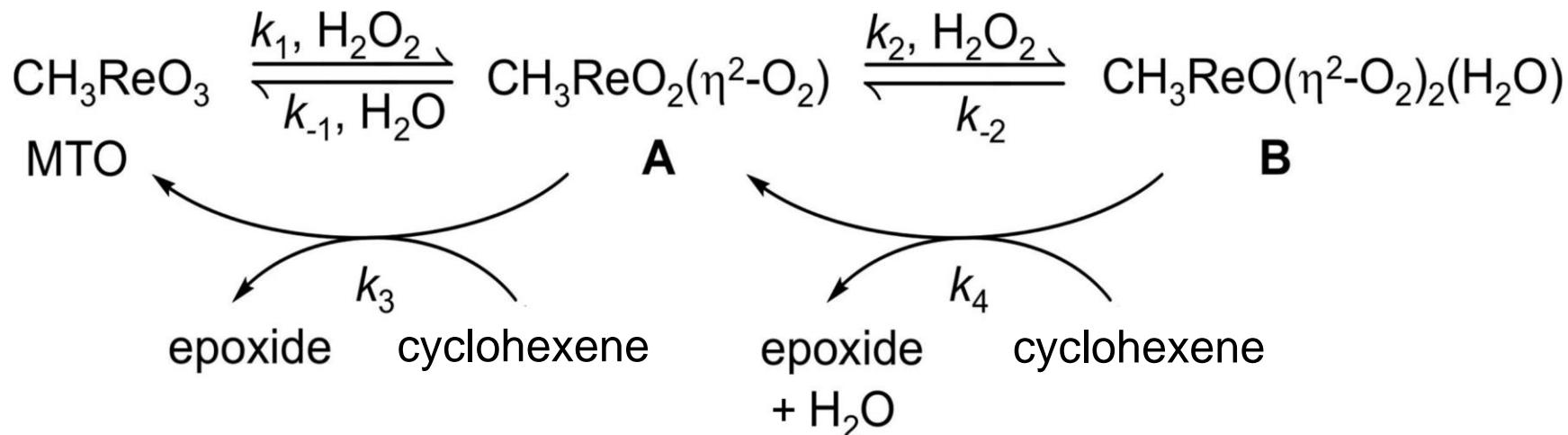
Trace water can be important in many reactions

The water dependence of MTO has not been explained



Goals

- 1) Fully characterize the thermodynamics and kinetics
- 2) Elucidate the importance of water



Methods

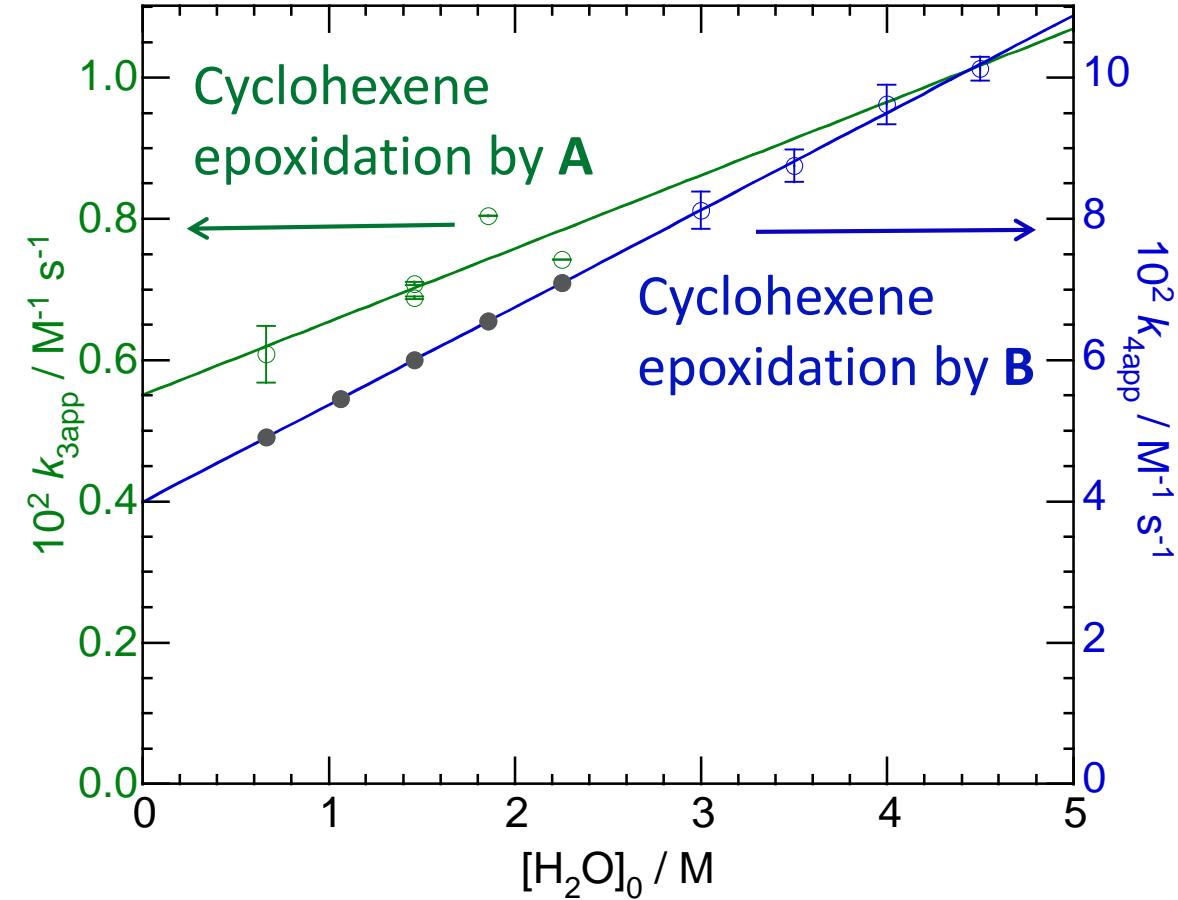
Density-functional theory

Microkinetic modeling

Experimental kinetic measurements

Cyclohexene epoxidation step has
only weak water acceleration

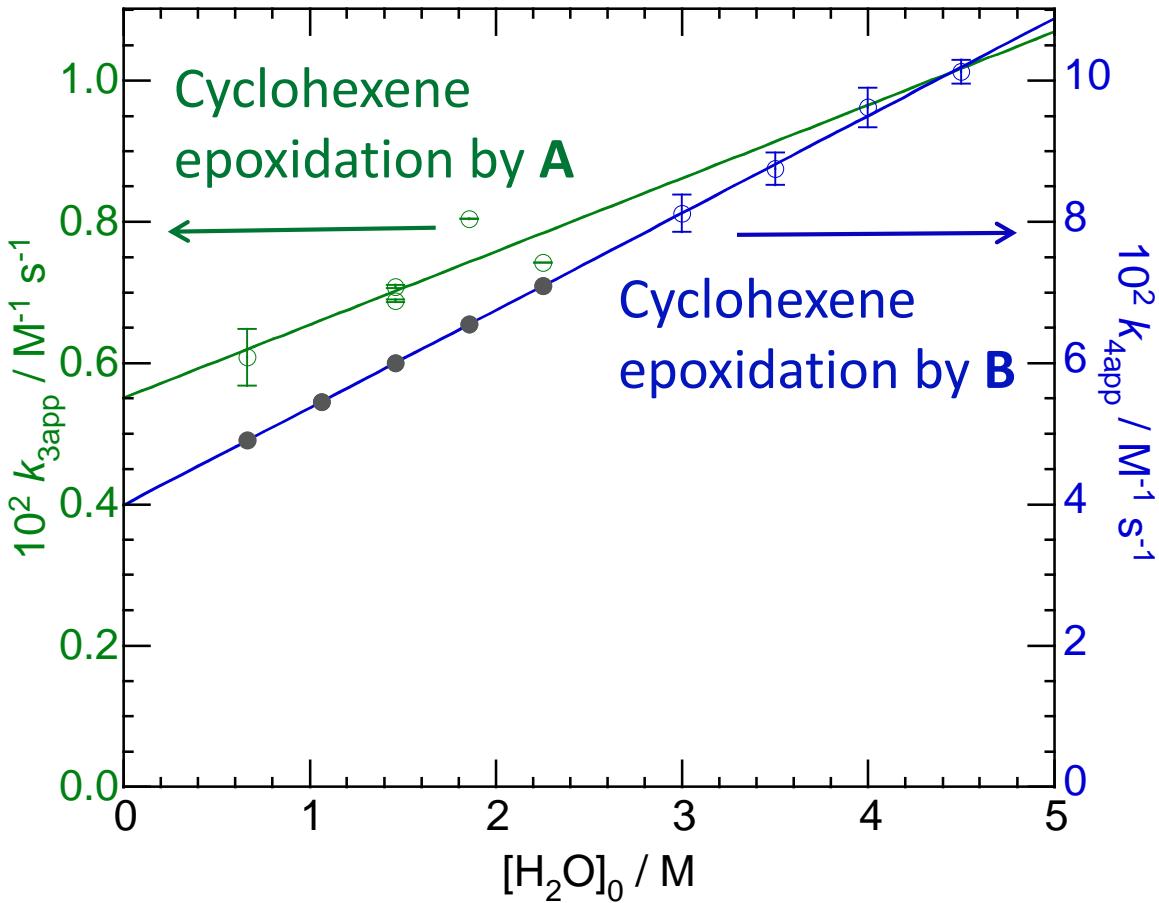
Experiments



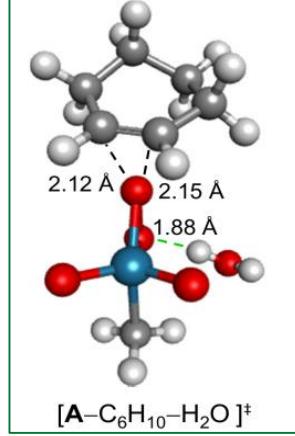
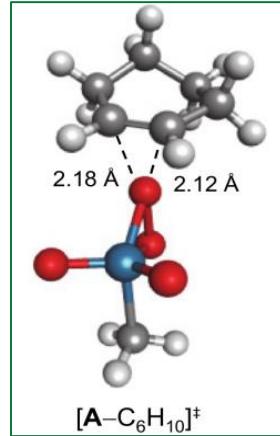
Cyclohexene epoxidation step has
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Theory

Experiments



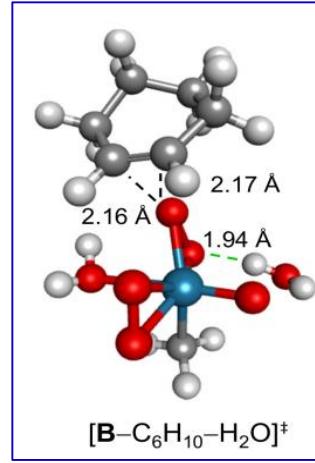
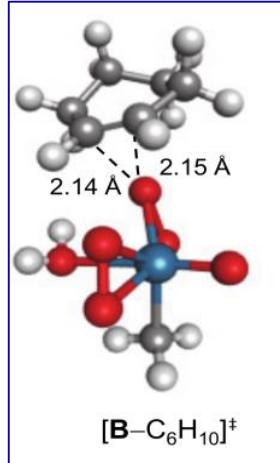
epoxidation by A



$$\Delta G^\ddagger = 118 \text{ kJ/mol}$$

$$\Delta G^\ddagger = 115 \text{ kJ/mol}$$

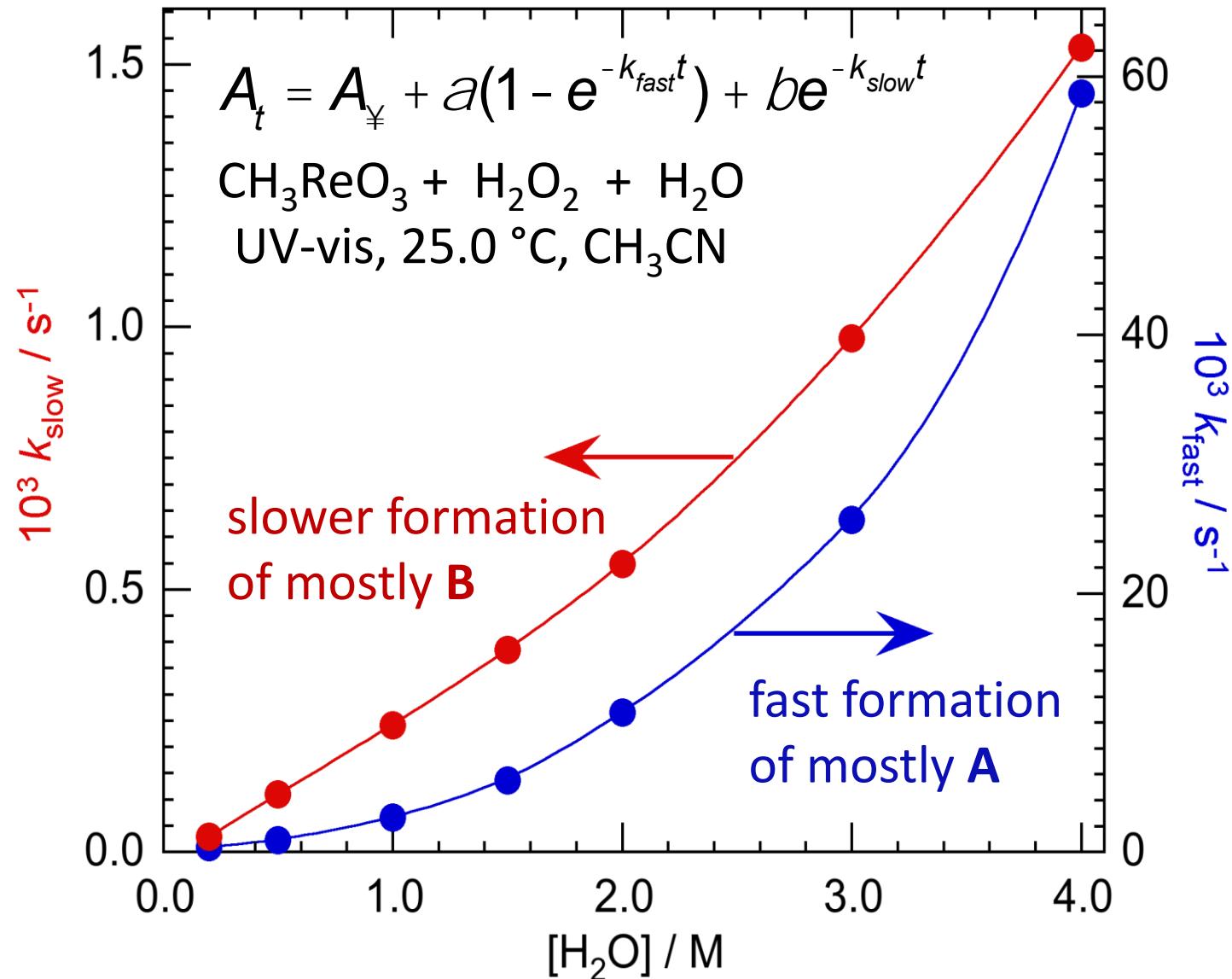
epoxidation by B



$$\Delta G^\ddagger = 96 \text{ kJ/mol}$$

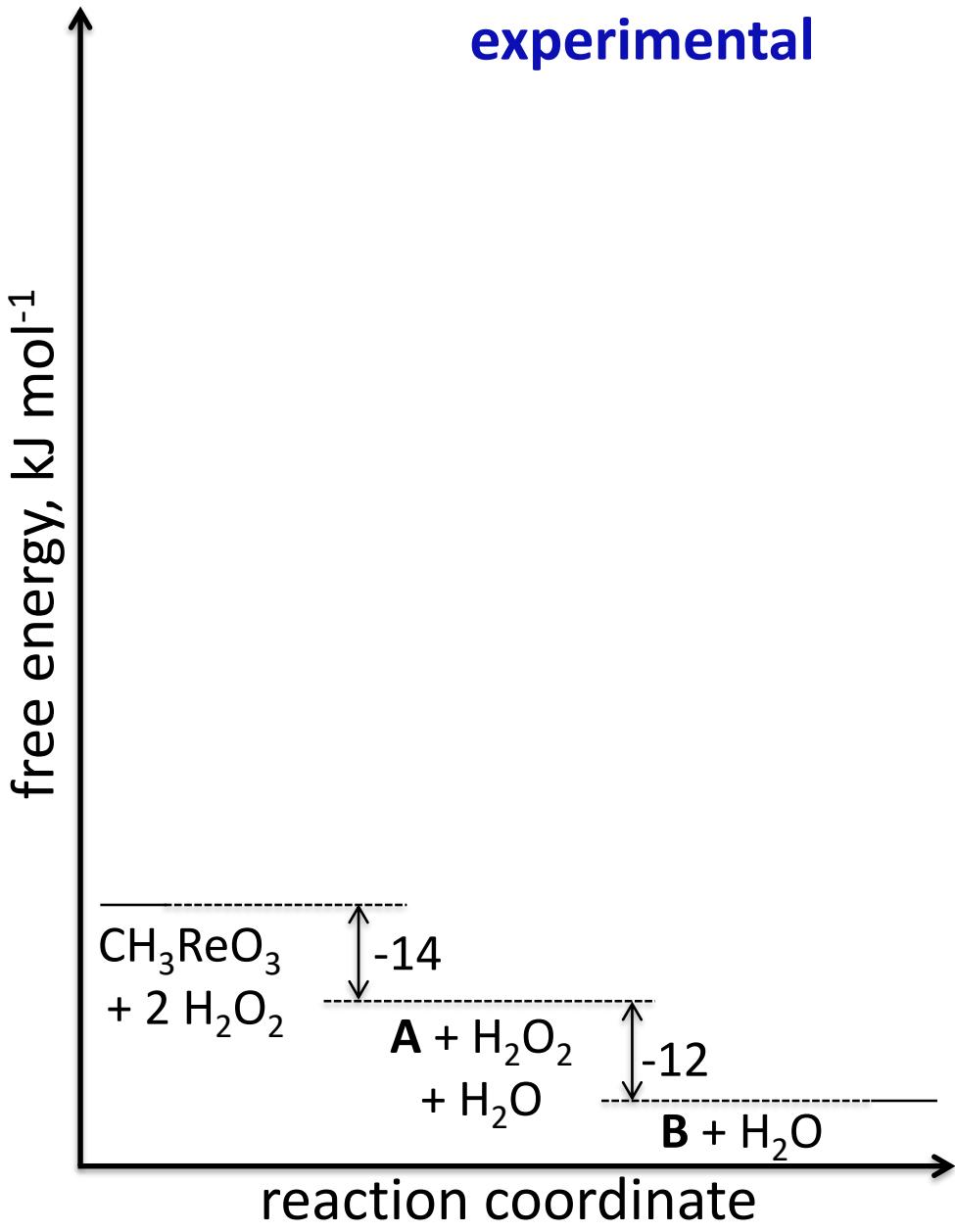
$$\Delta G^\ddagger = 94 \text{ kJ/mol}$$

Water dramatically accelerates the formation of species **A** and **B**, not the epoxidation step



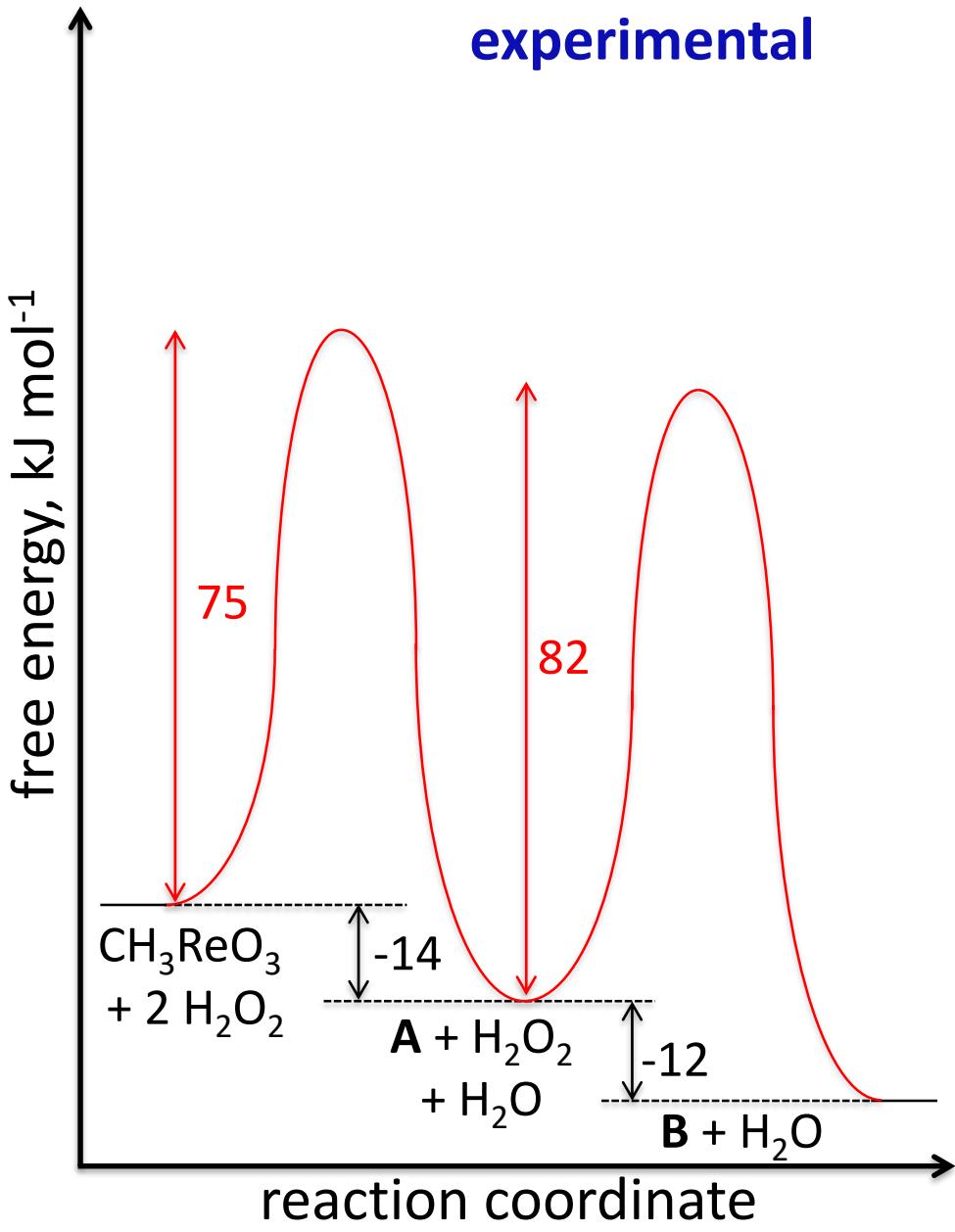
Free energy profiles for the formation of A and B

Free energy profiles for the formation of A and B

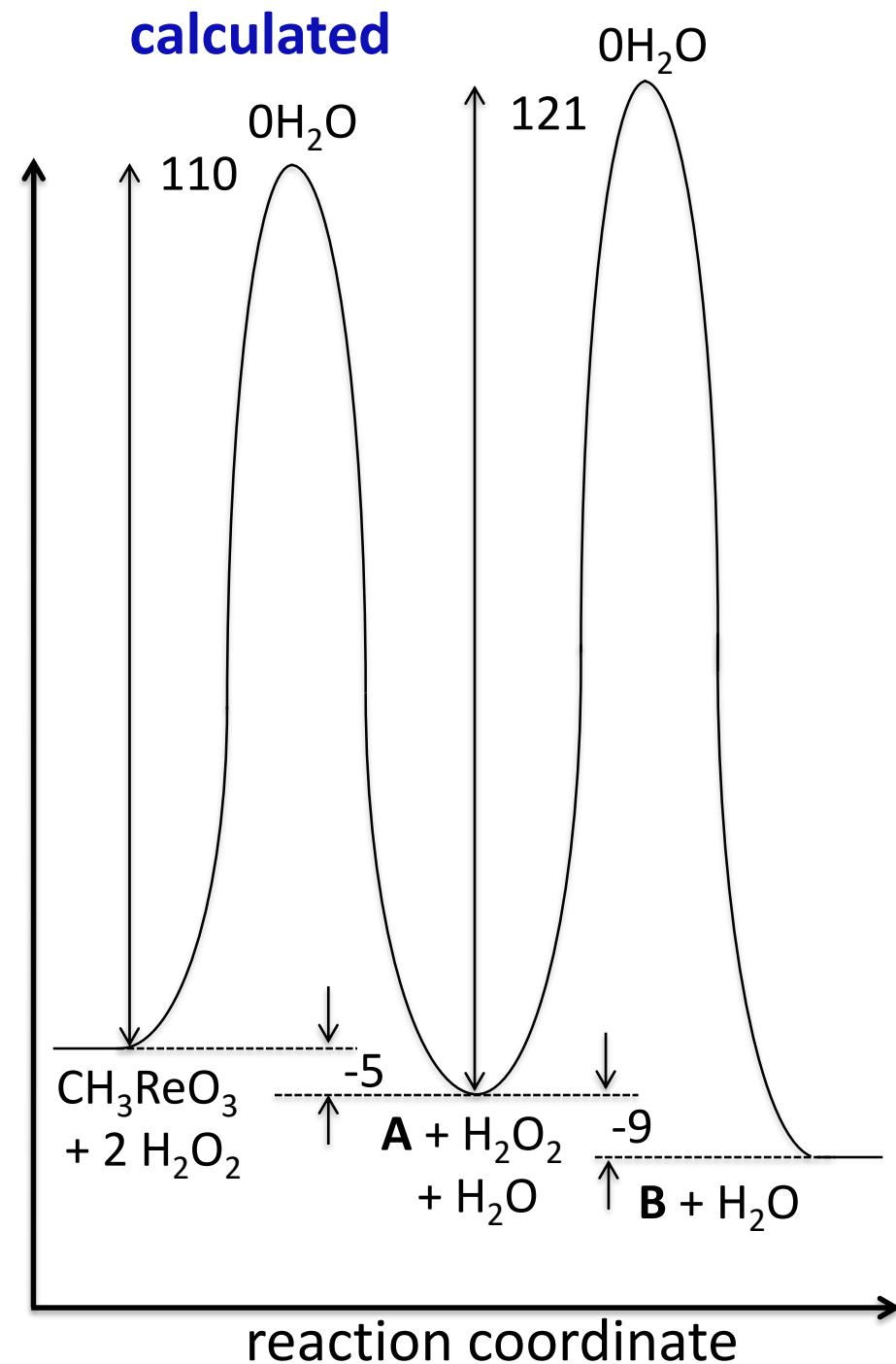
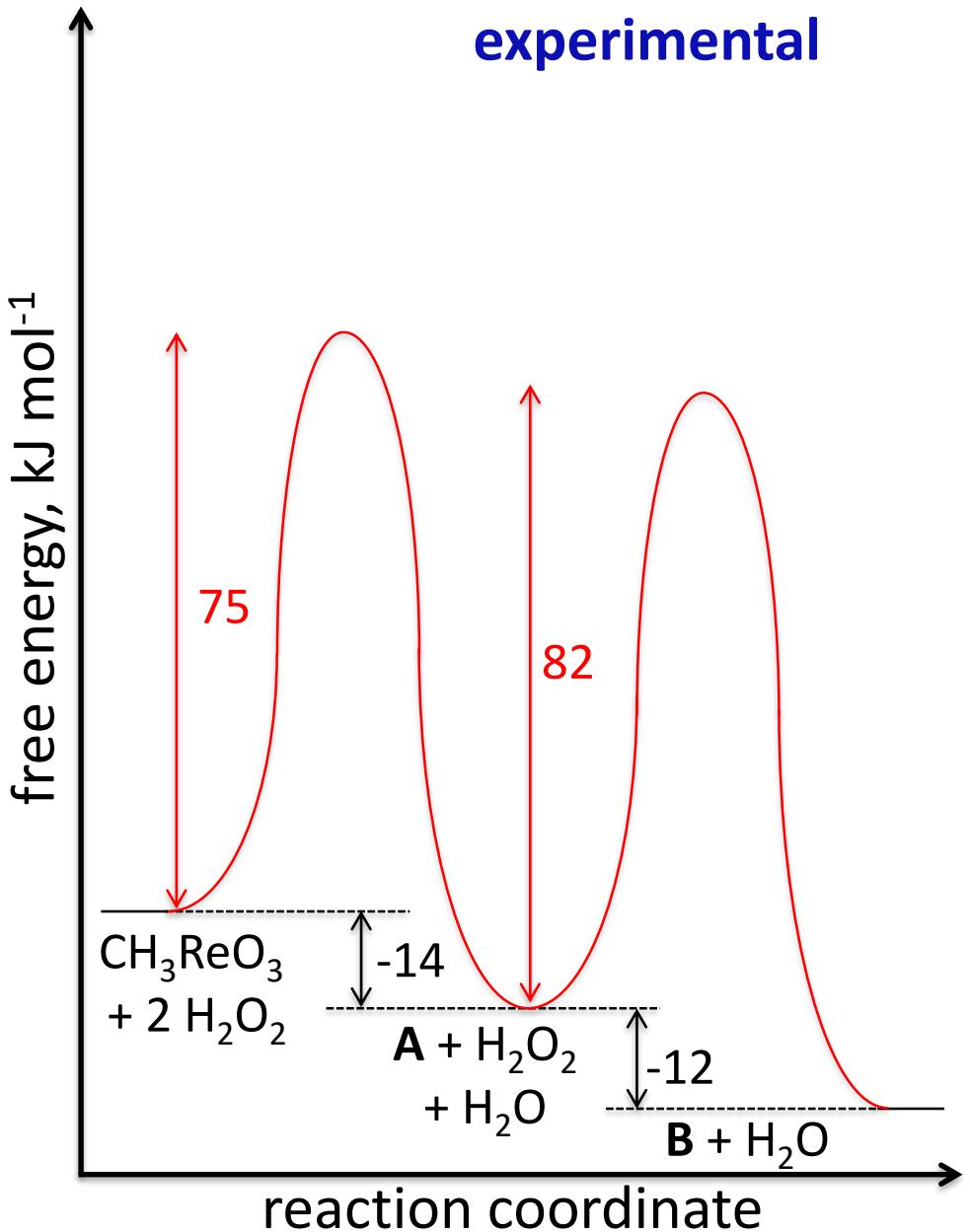


Free energy profiles for the formation of A and B

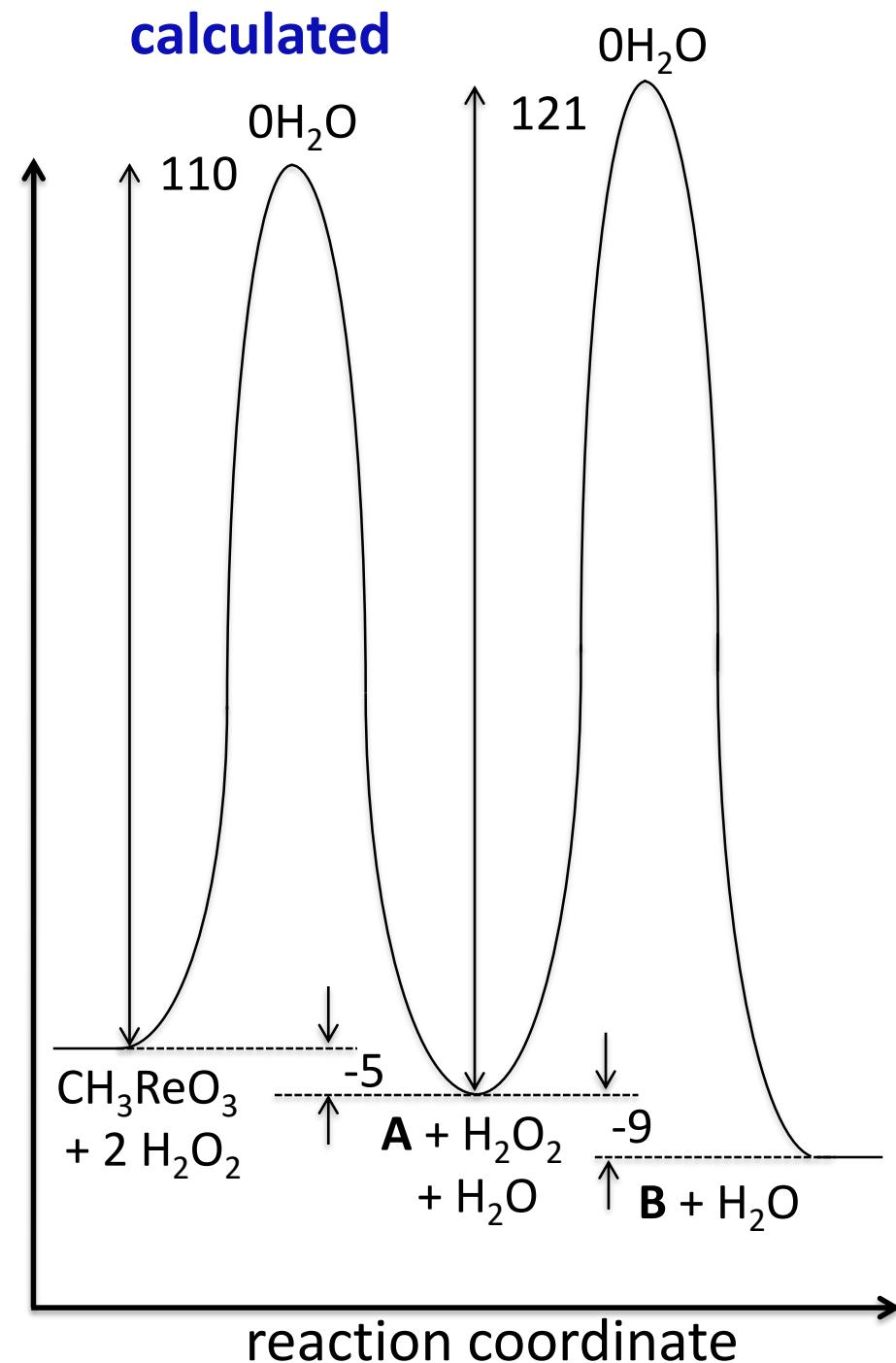
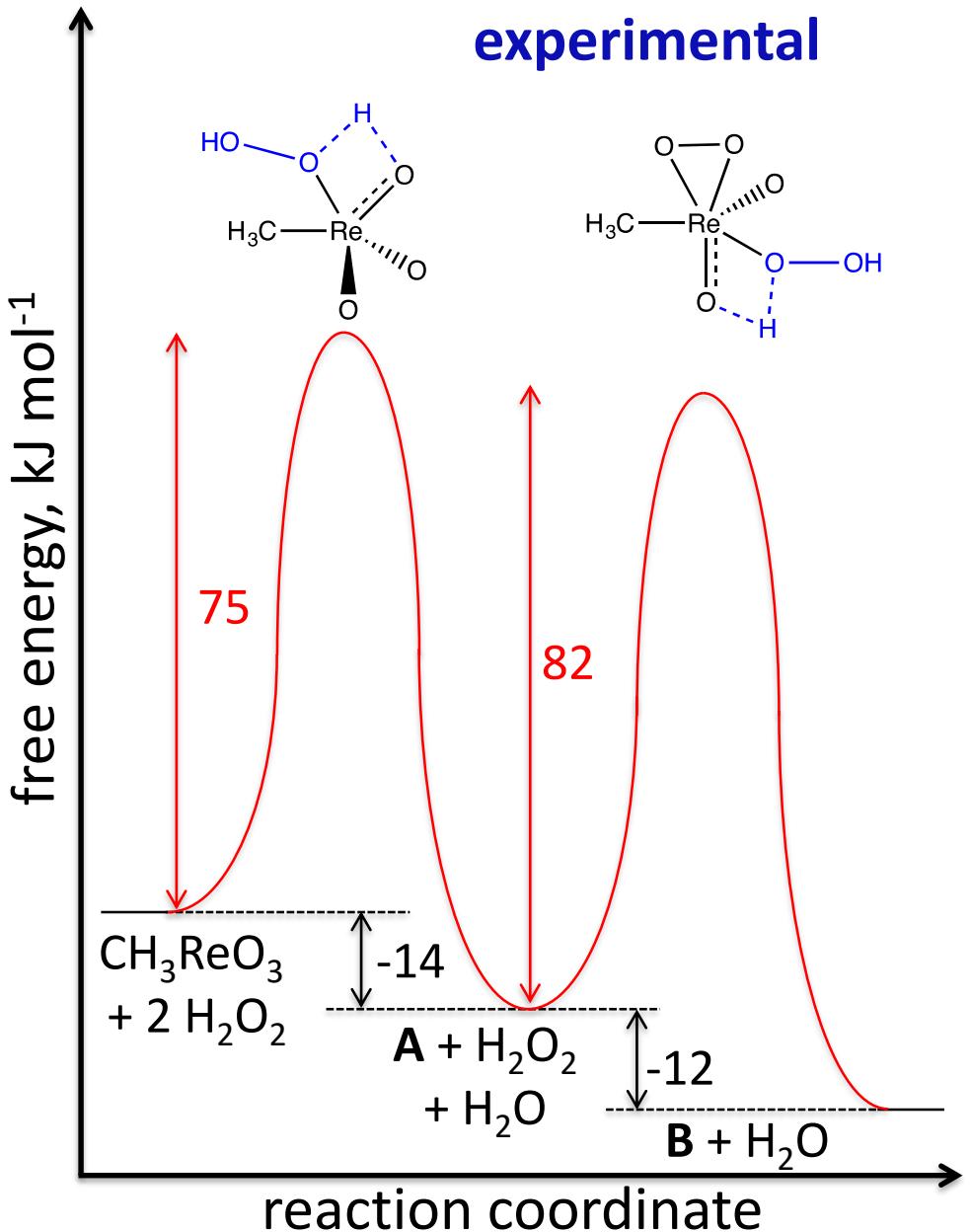
experimental



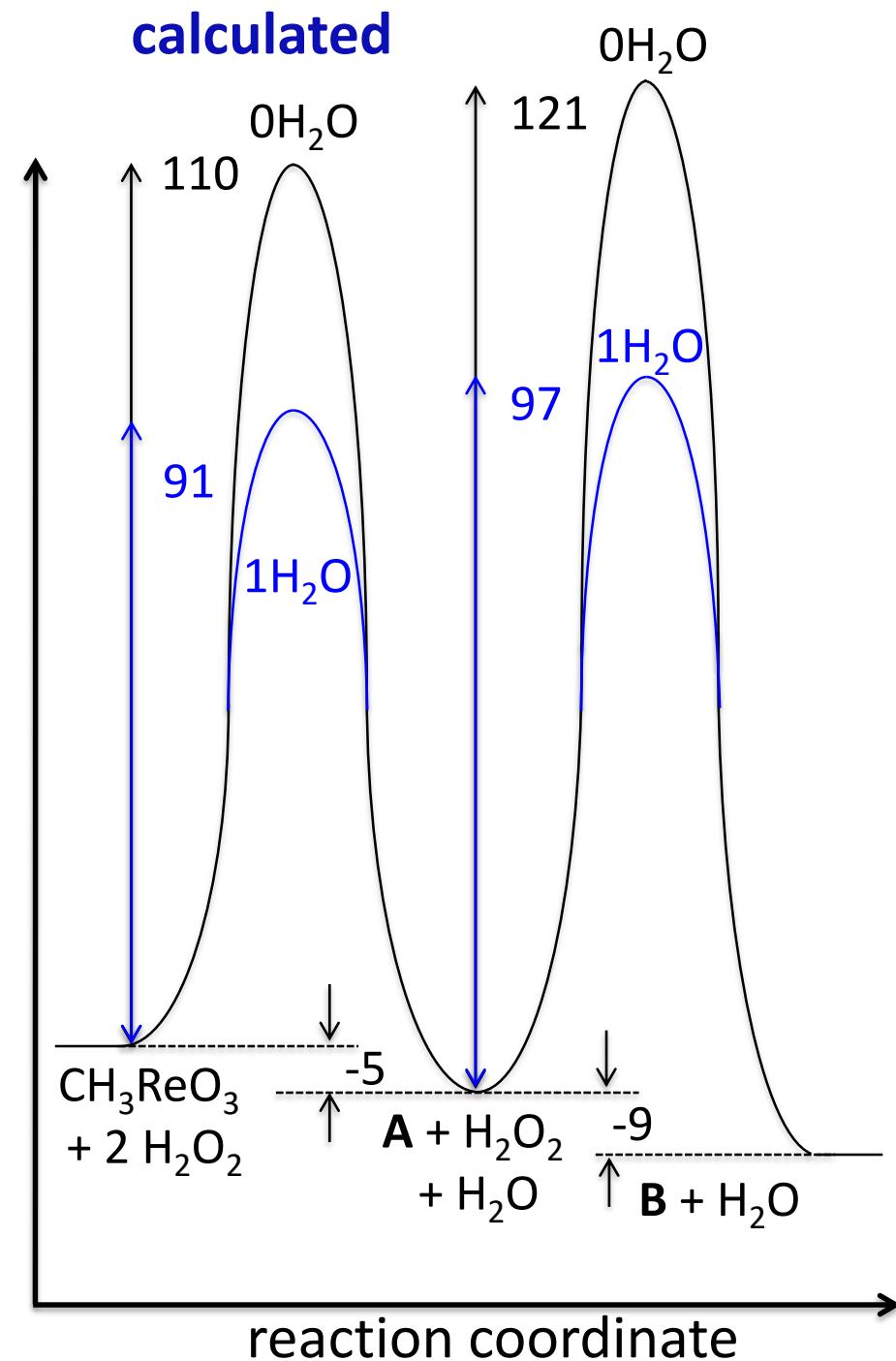
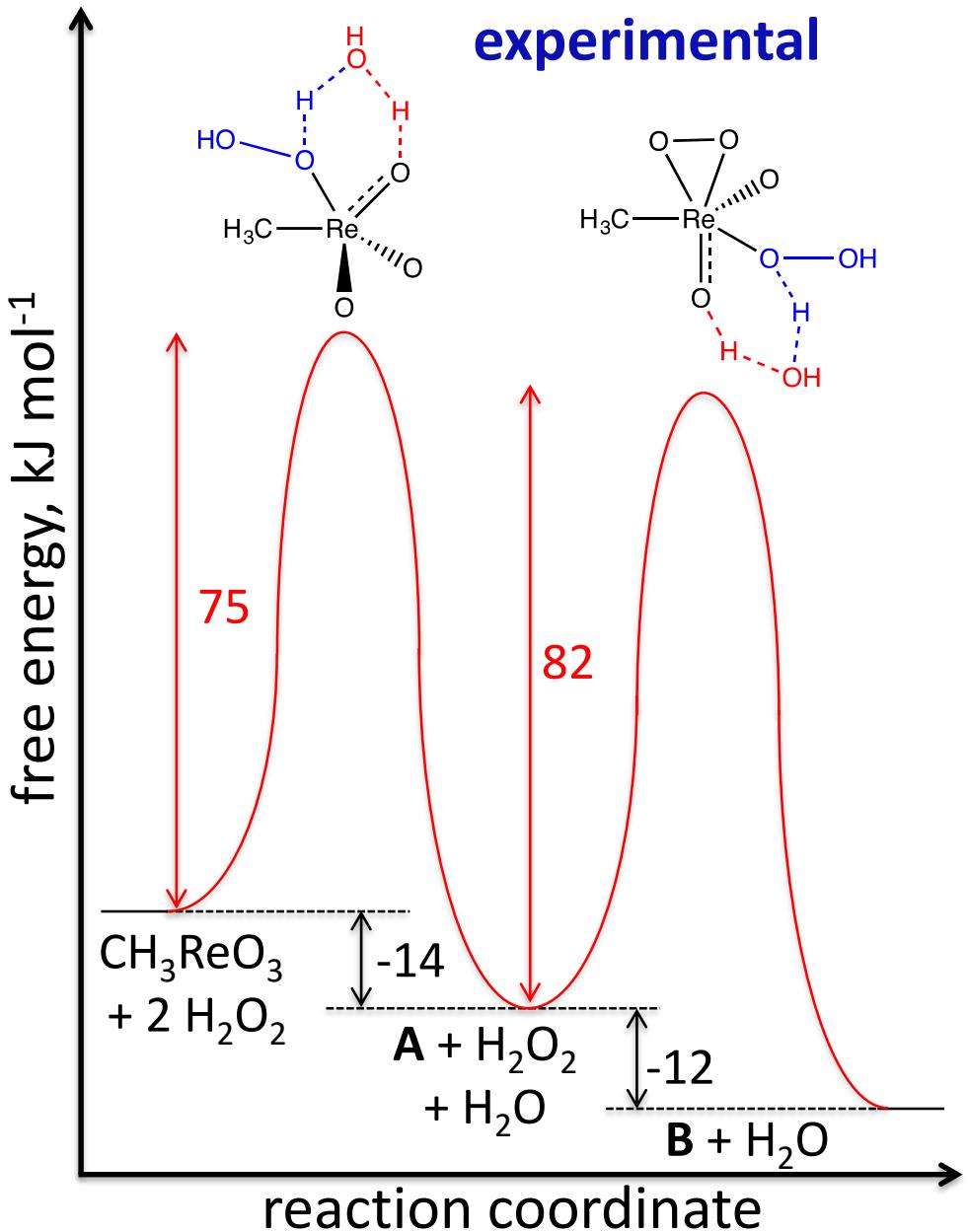
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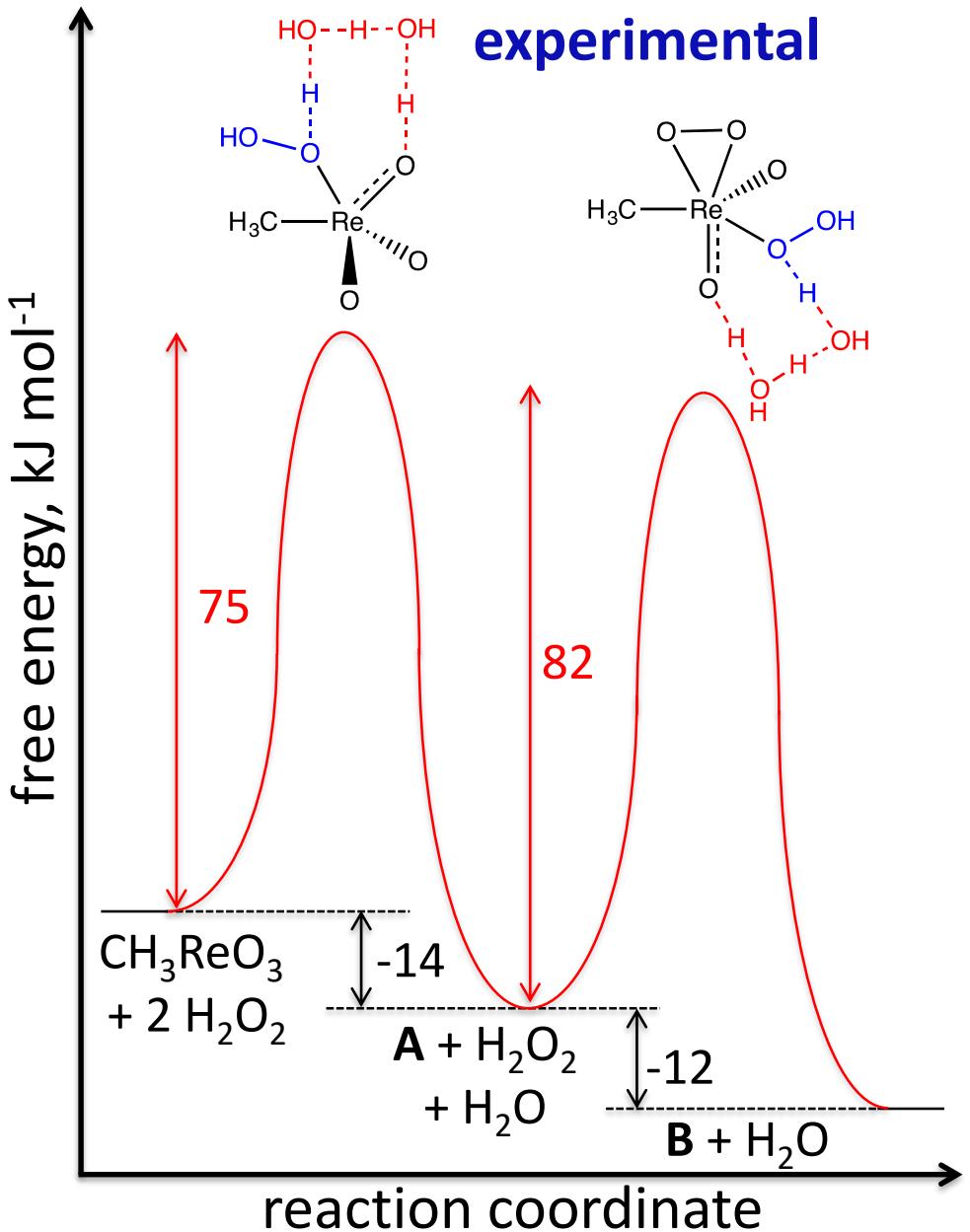
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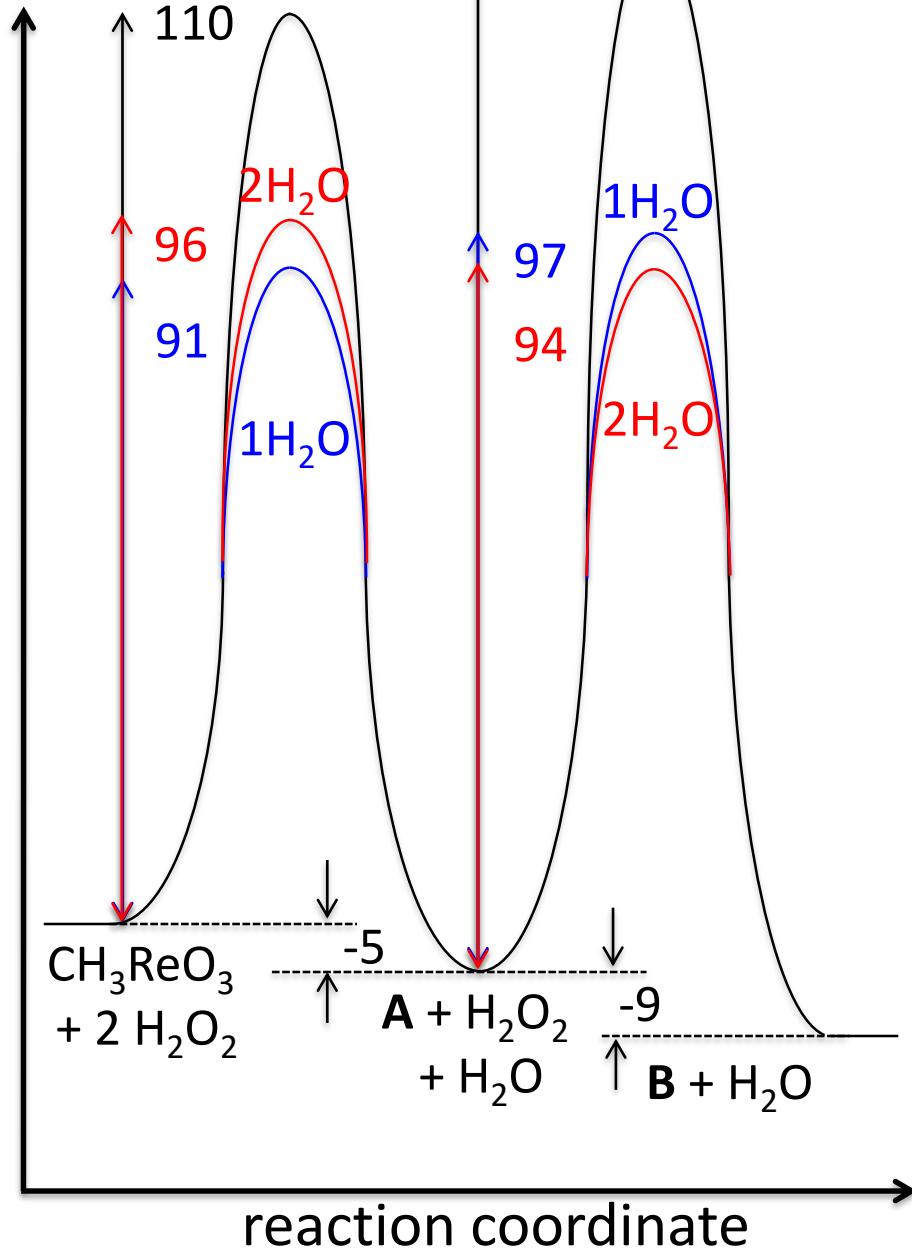
Free energy profiles for the formation of A and B



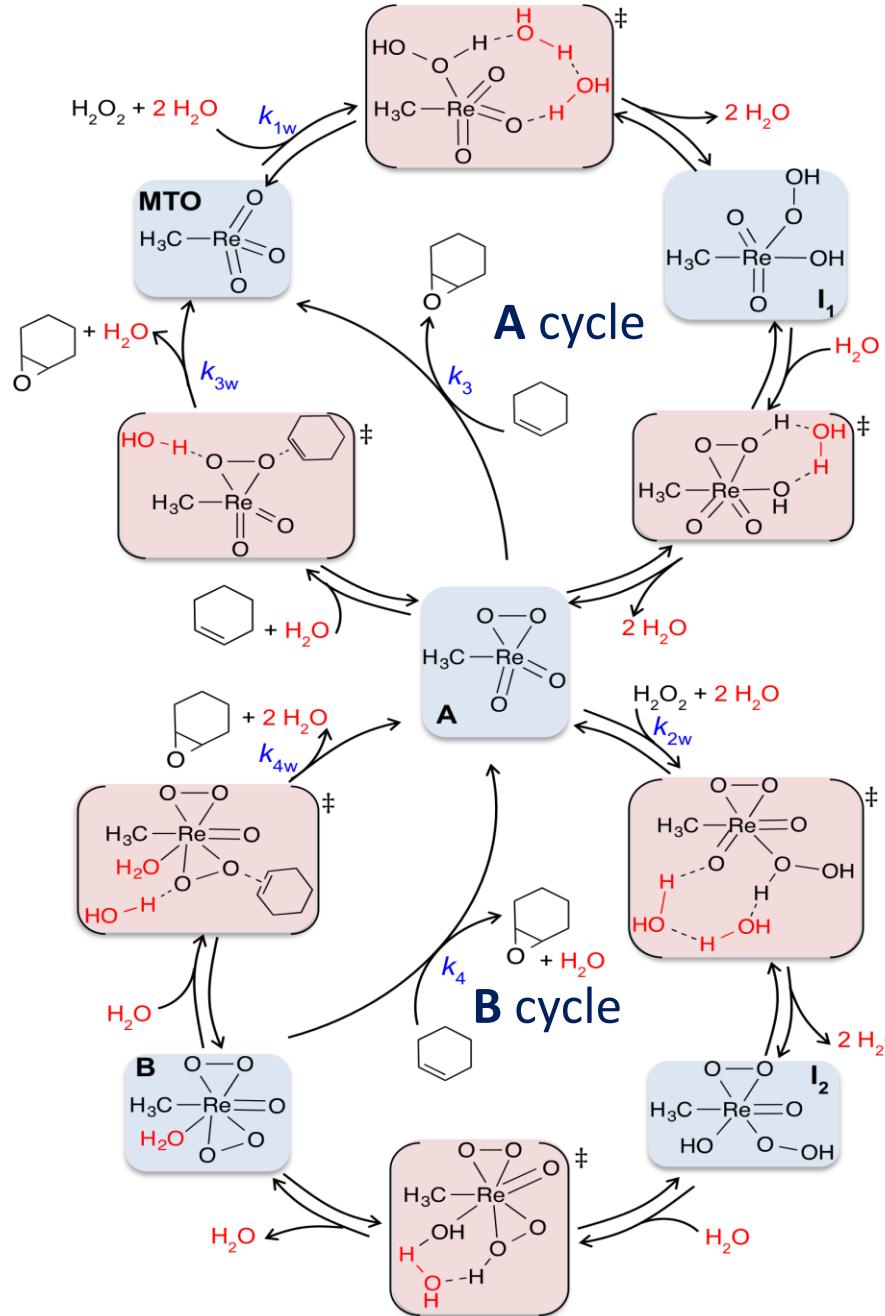
Free energy profiles for the formation of A and B



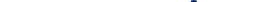
calculated



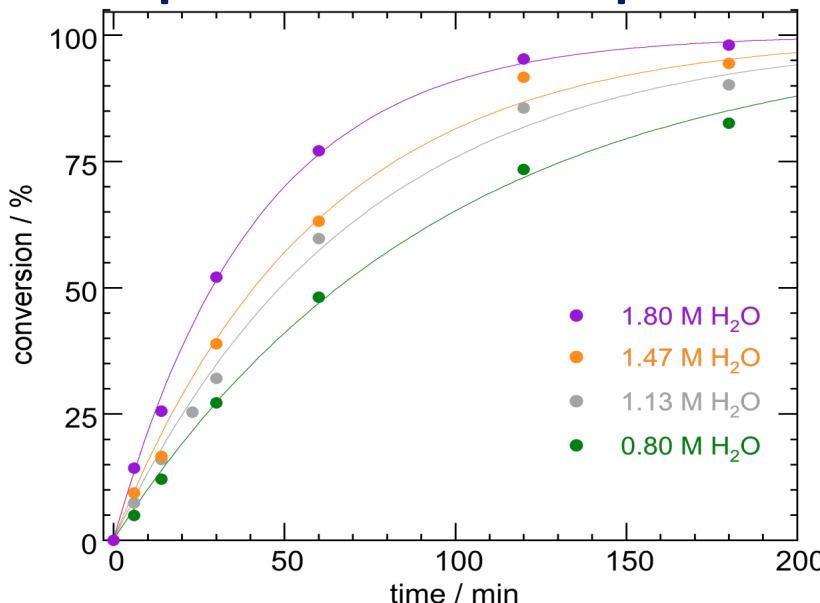
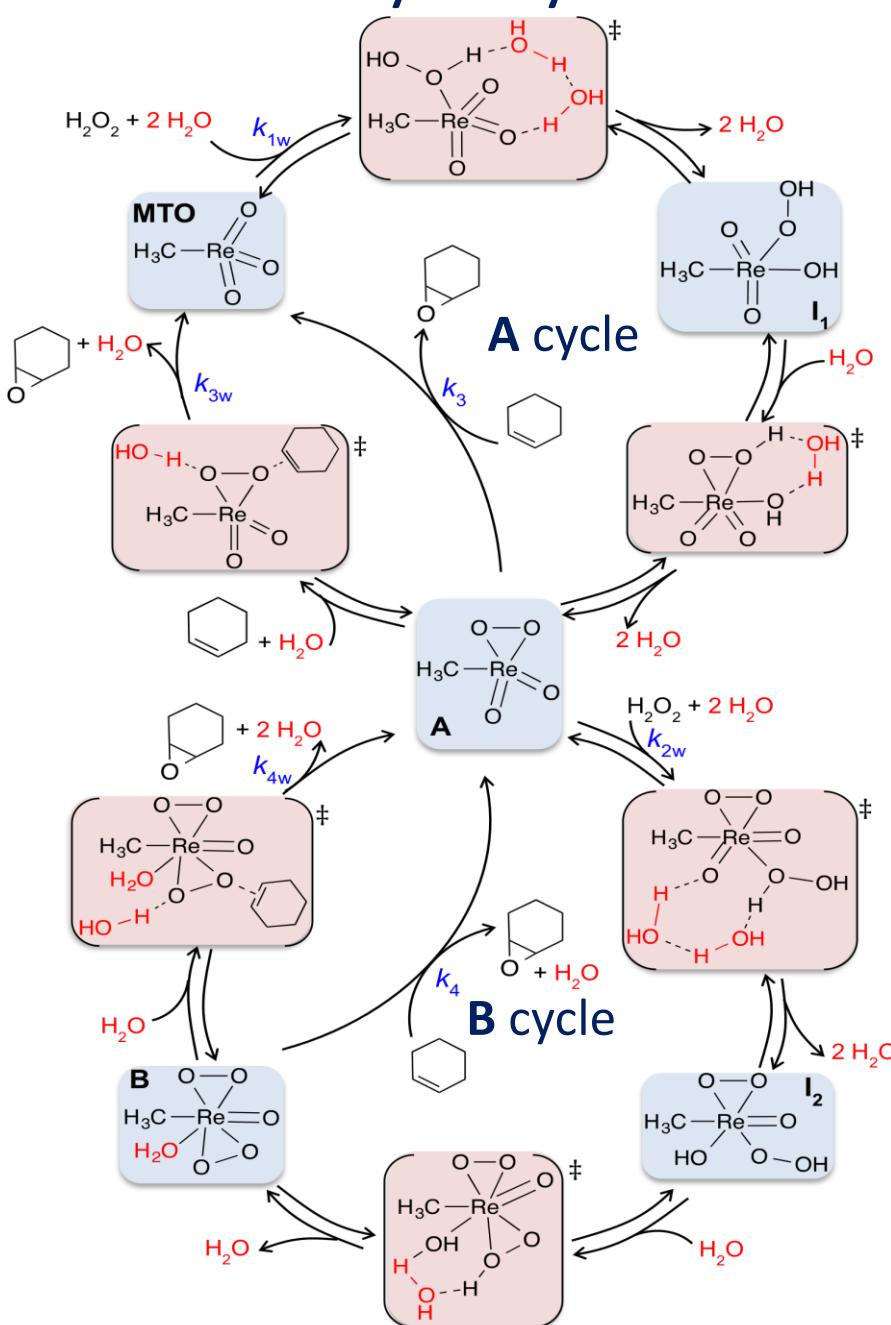
The full catalytic cycle and the importance of water



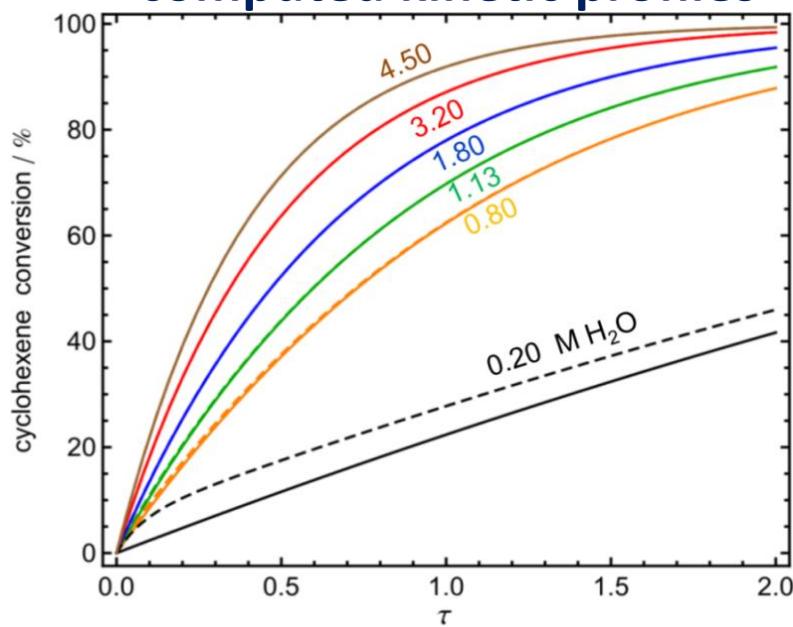
The full catalytic cycle and the importance of water



experimental kinetic profiles

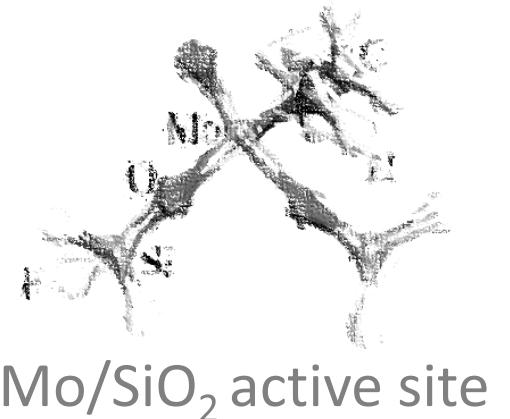


computed kinetic profiles

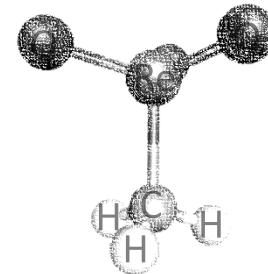


Outline. Three projects that help address the below challenges

Challenge 1: Modeling heterogeneity in reactivity of amorphous catalysts



Challenge 2: Understanding the importance of solvent during homogeneous catalysis



Challenge 3: Finding reliable descriptors of catalysts (and materials)



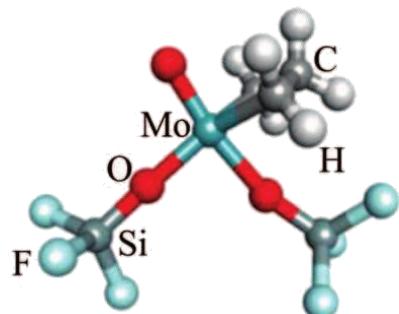
Can we reliably extract descriptors from such catalysts?

Catalyst characterization

Computational spectroscopy

First-principles thermochemistry & kinetic parameters

First-principles microkinetic modeling



Amorphous catalysts

Catalyst design

Active sites

Reaction mechanism

Mechanistic understanding

Descriptor

Homogeneous catalysts

Computational screening

Identifying physically meaningful *descriptors*
can help materials discovery

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can help materials discovery

Descriptor → Property

Descriptor = function(atomic or material features)

Identifying physically meaningful *descriptors*
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Descriptor → Property

Descriptor = function(atomic or material features)

Predict new materials

Increase understanding

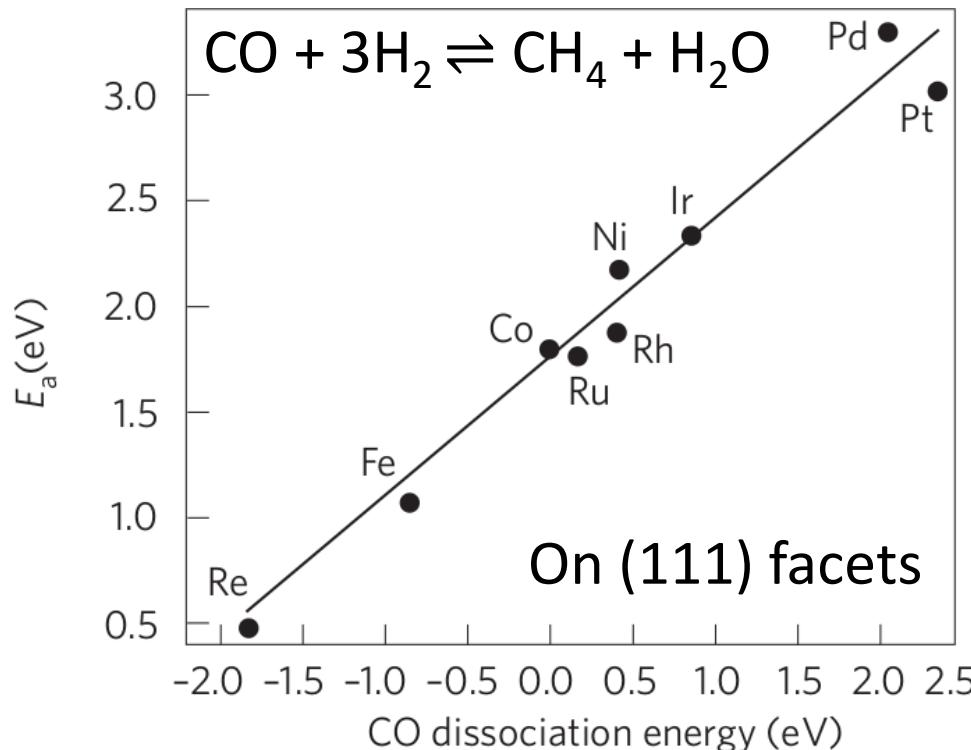
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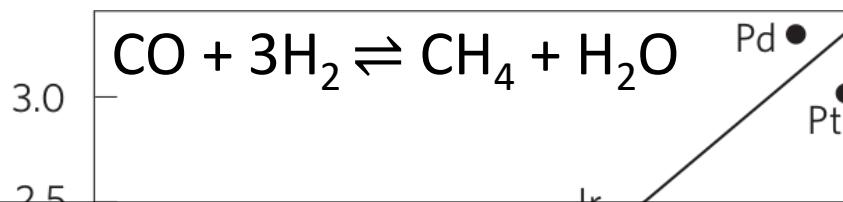
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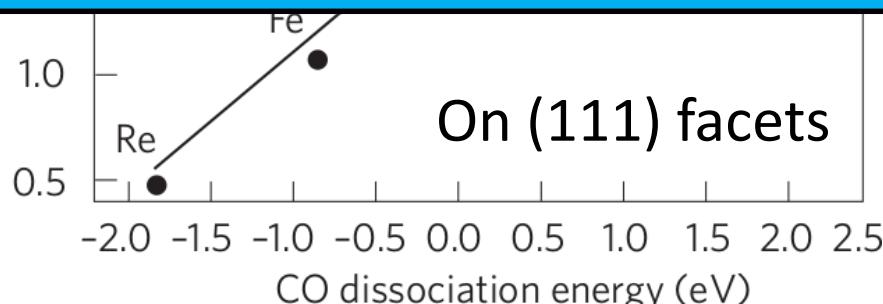
Descriptor = function(atomic or material features)

Predict new materials

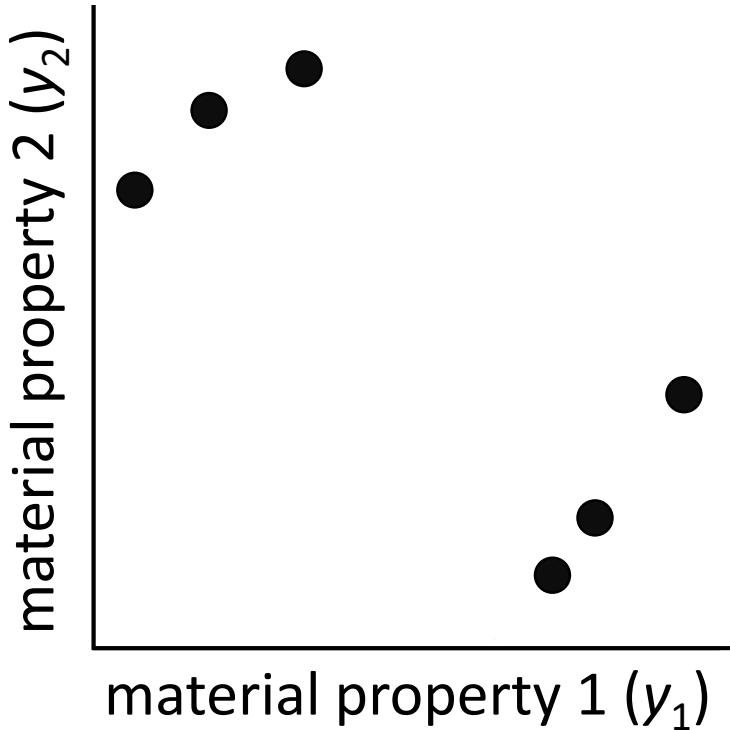
Increase understanding



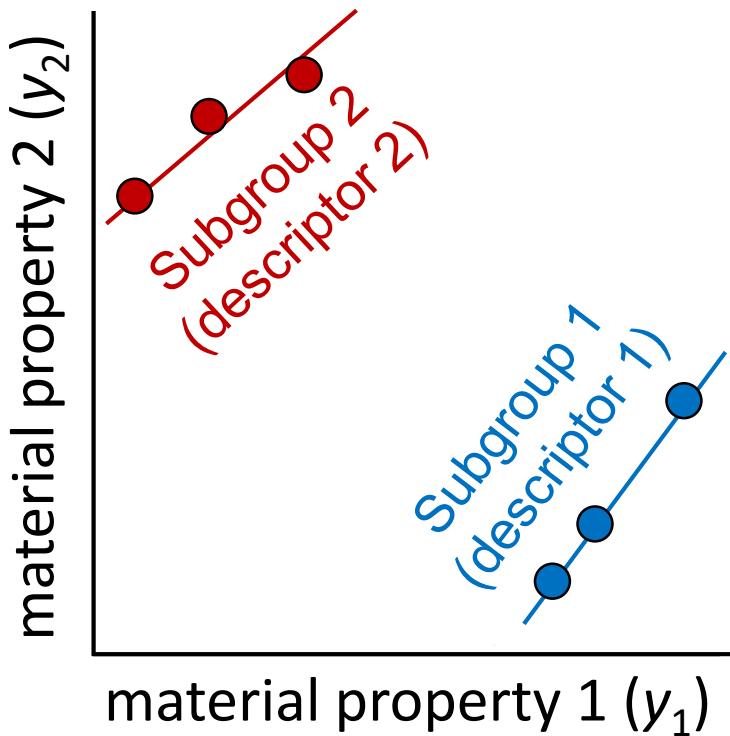
The development of data-mining tools
can facilitate the discovery of descriptors



Subgroup discovery:
find meaningful *local descriptors*
of a target property in materials-science data

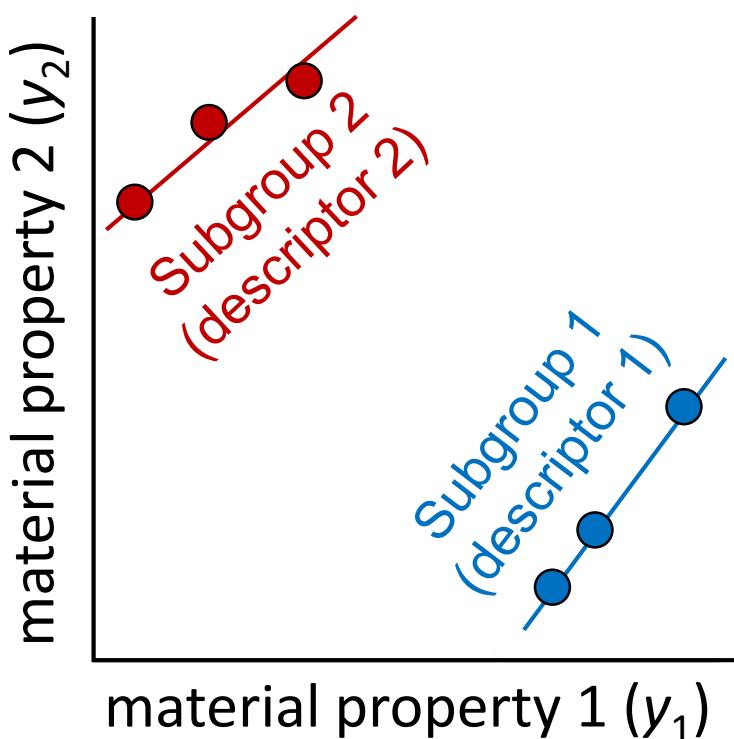


Subgroup discovery:
find meaningful *local descriptors*
of a target property in materials-science data



Subgroup discovery:

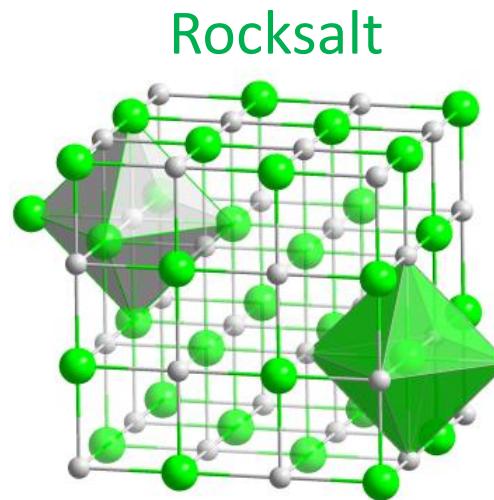
find meaningful *local descriptors*
of a target property in materials-science data



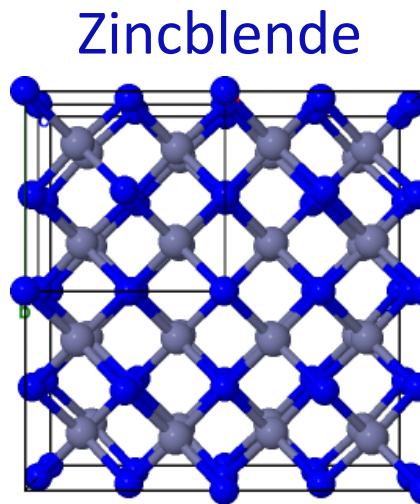
The periodic table has subgroups

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Find descriptors that predict crystal structures for the 82 octet AB-type materials

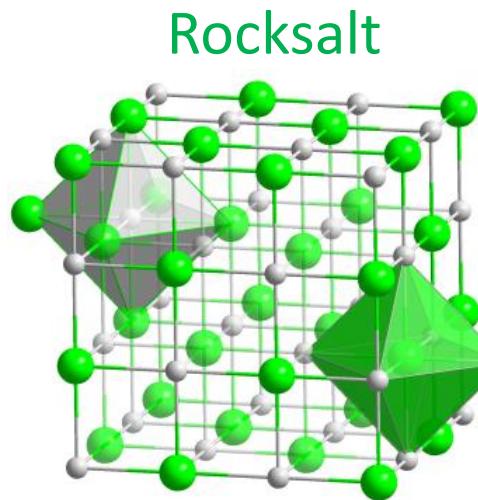


vs

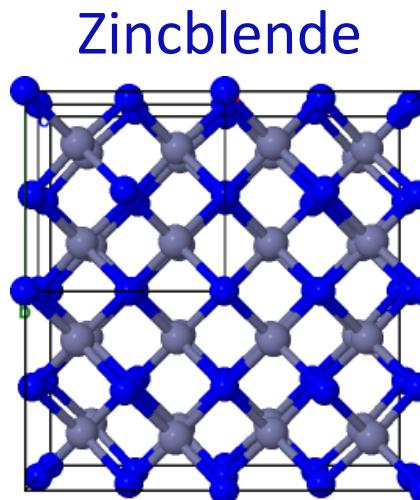


Target property
 $\text{sign}(E_{\text{rocksalt}} - E_{\text{zincblende}})$

Find descriptors that predict crystal structures for the 82 octet AB-type materials



vs



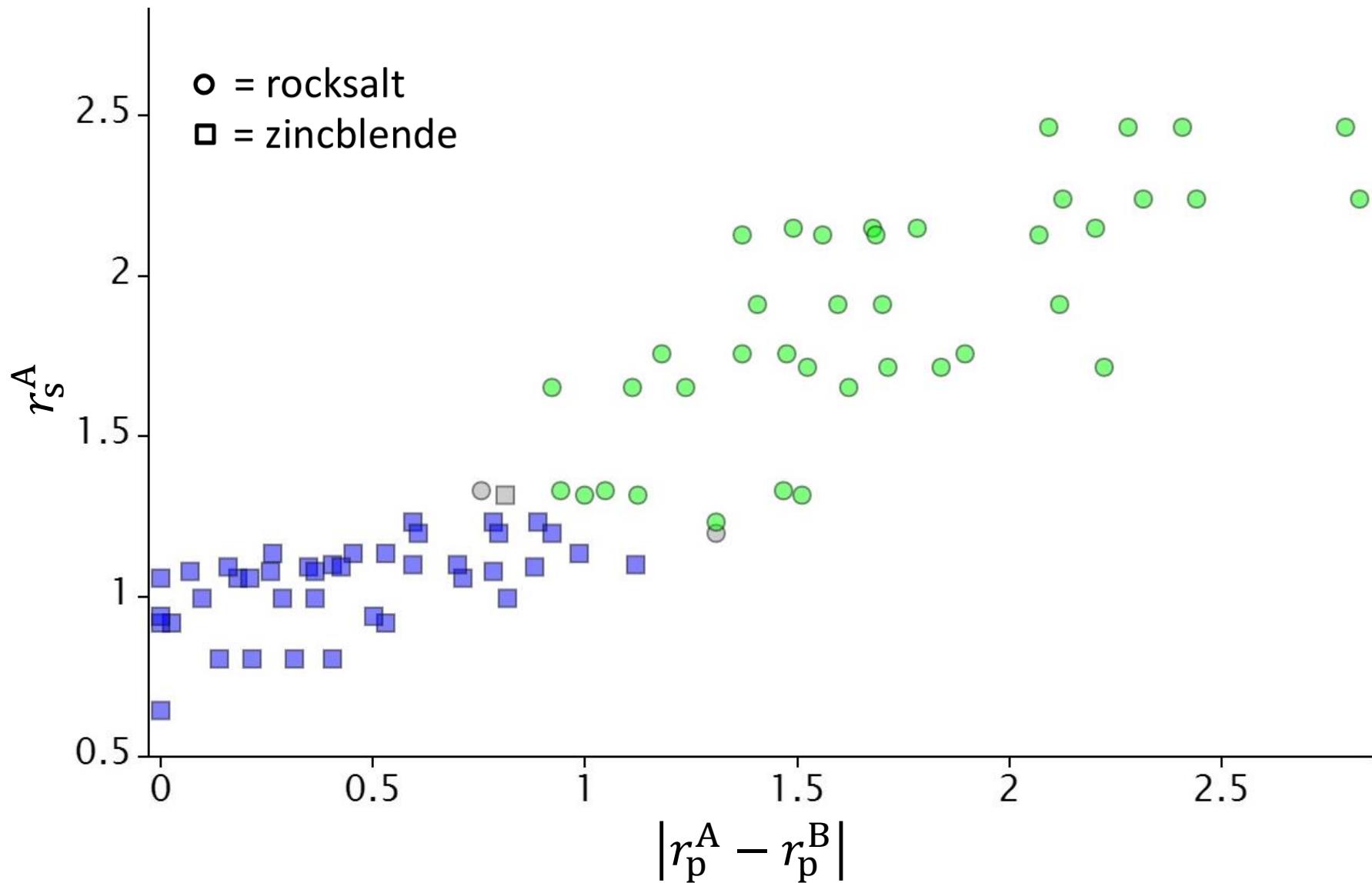
Target property

$$\text{sign}(E_{\text{rocksalt}} - E_{\text{zincblende}})$$

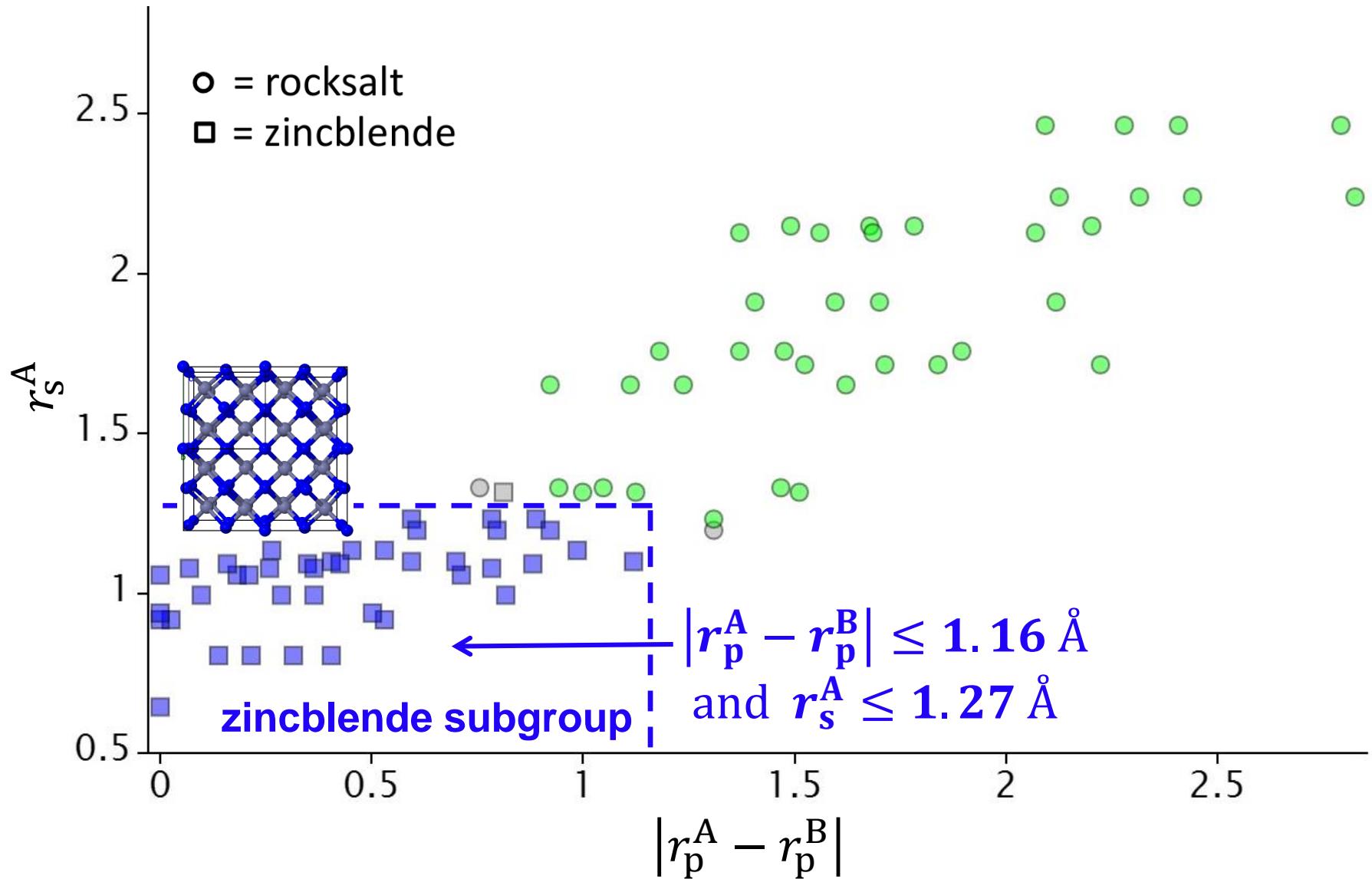
Input candidate descriptors into subgroup discovery from DFT calculations

- Radii of s , p , d orbitals of free atoms
- Electron affinity
- Ionization potential
-and many others

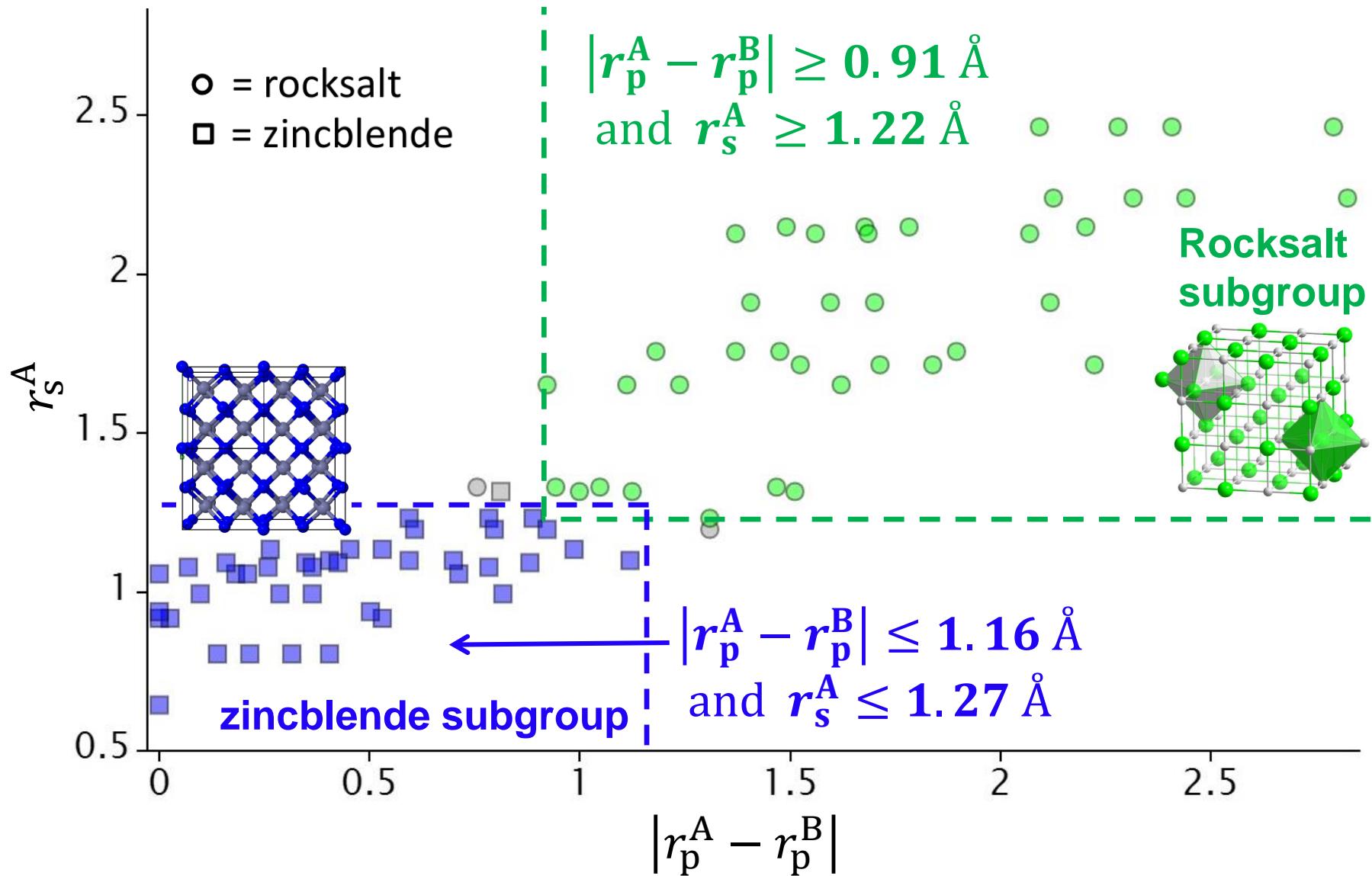
Subgroup discovery classifies 79 of the 82 compounds using a two-dimensional descriptor



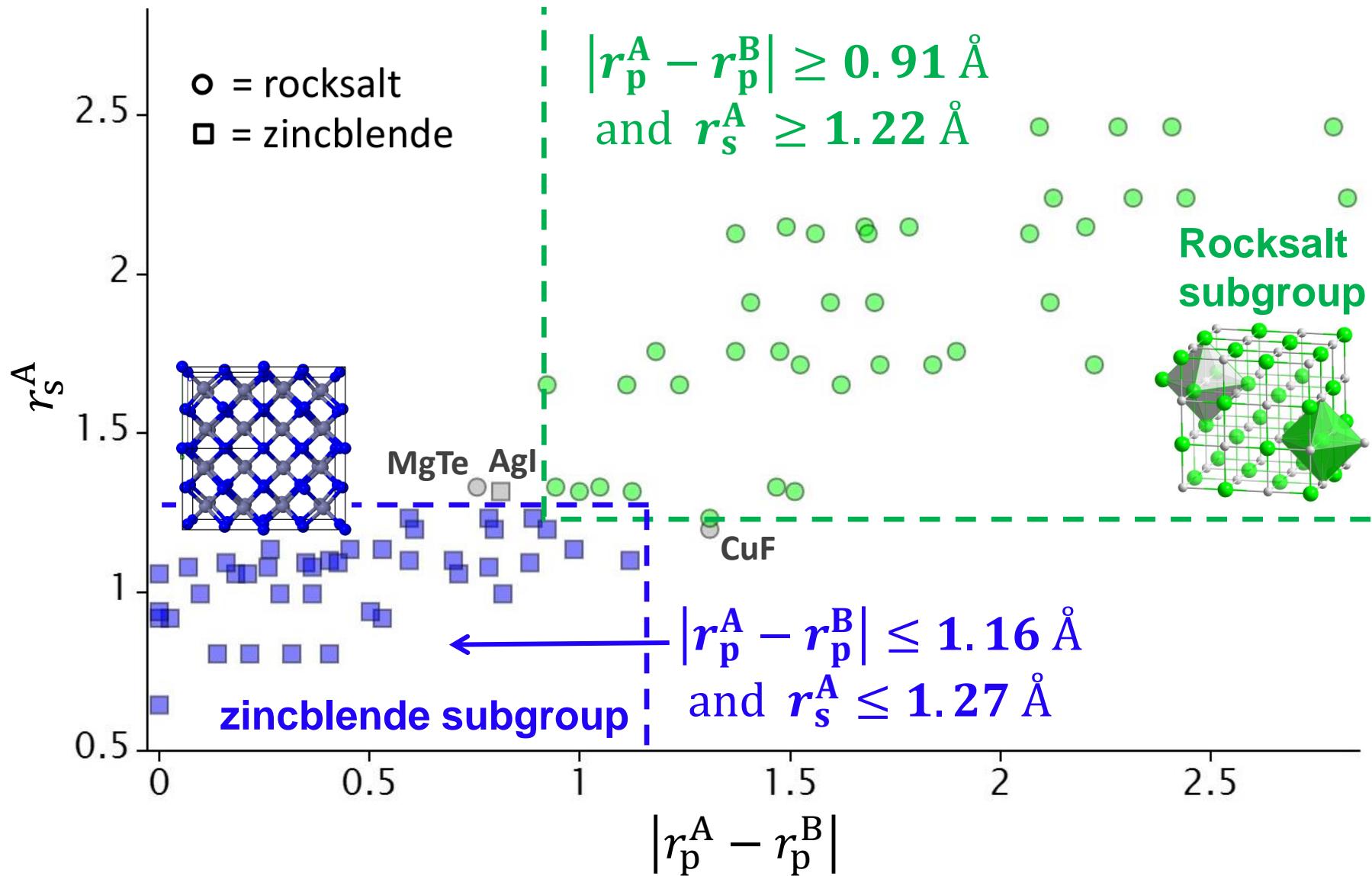
Subgroup discovery classifies 79 of the 82 compounds using a two-dimensional descriptor



Subgroup discovery classifies 79 of the 82 compounds using a two-dimensional descriptor



Subgroup discovery classifies 79 of the 82 compounds using a two-dimensional descriptor

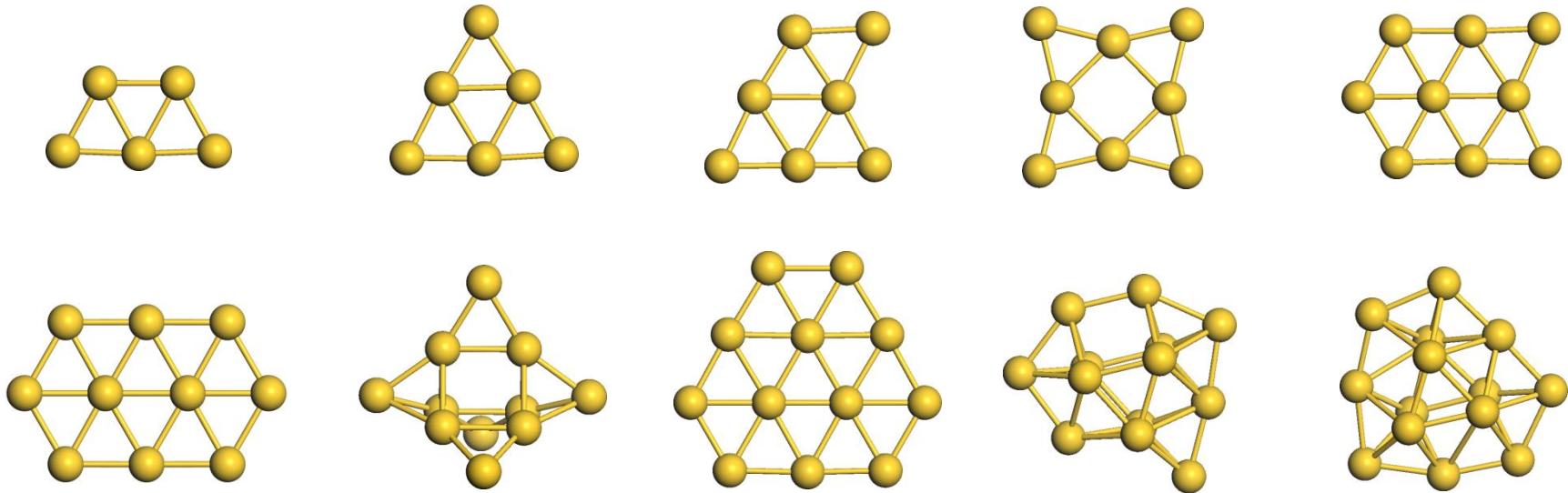


Subgroup discovery applied to gas-phase gold clusters

Gold clusters have interesting chemical and electronic properties

Examine 24,400 gold cluster configurations of sizes Au_5 - Au_{14}

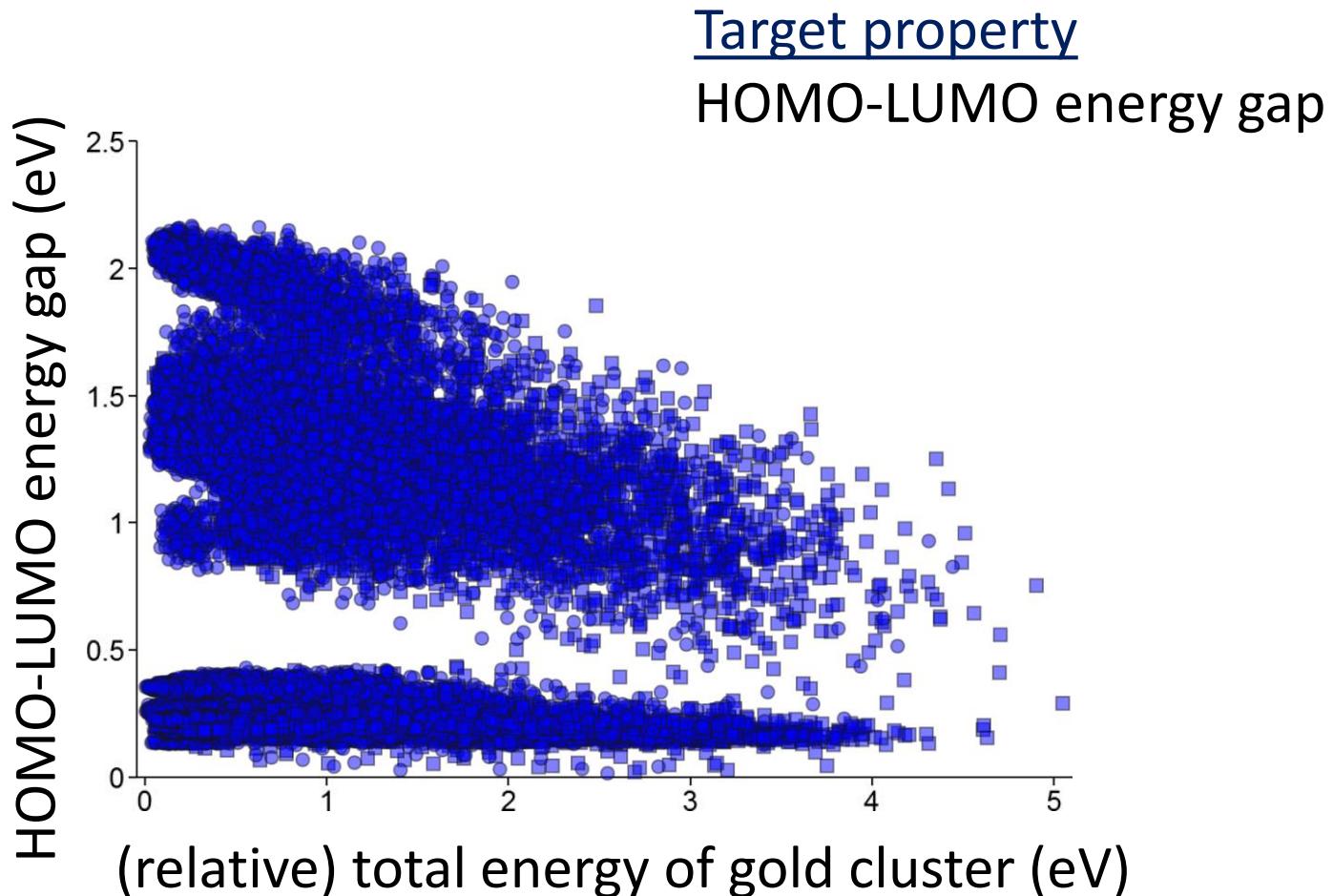
Snapshots of stable gold cluster configurations



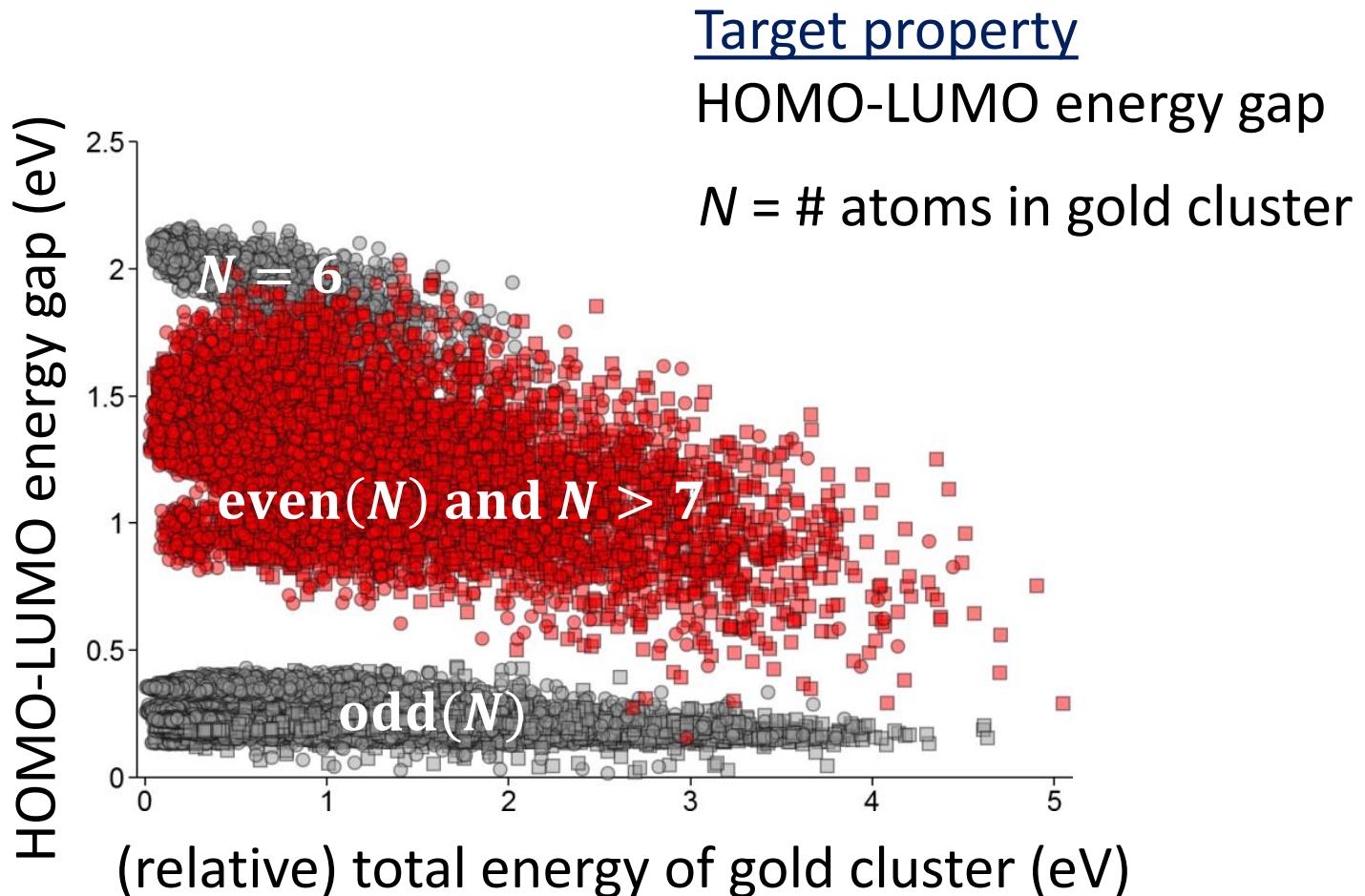
Rediscover simple insight about HOMO-LUMO gap

24,400 gold cluster configurations ($\text{Au}_5\text{-}\text{Au}_{14}$) in the gas phase

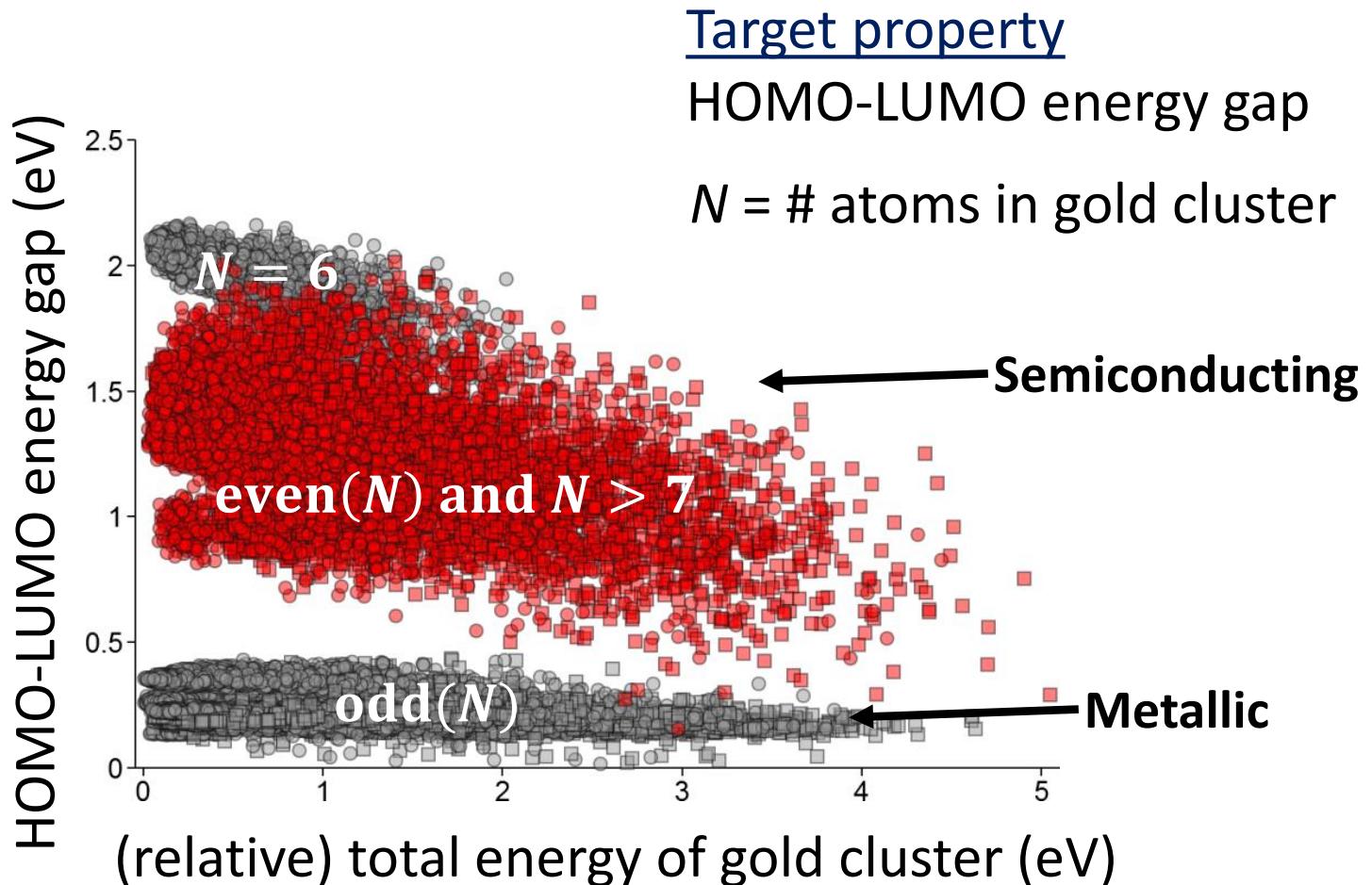
➤ 2,440 configurations per size



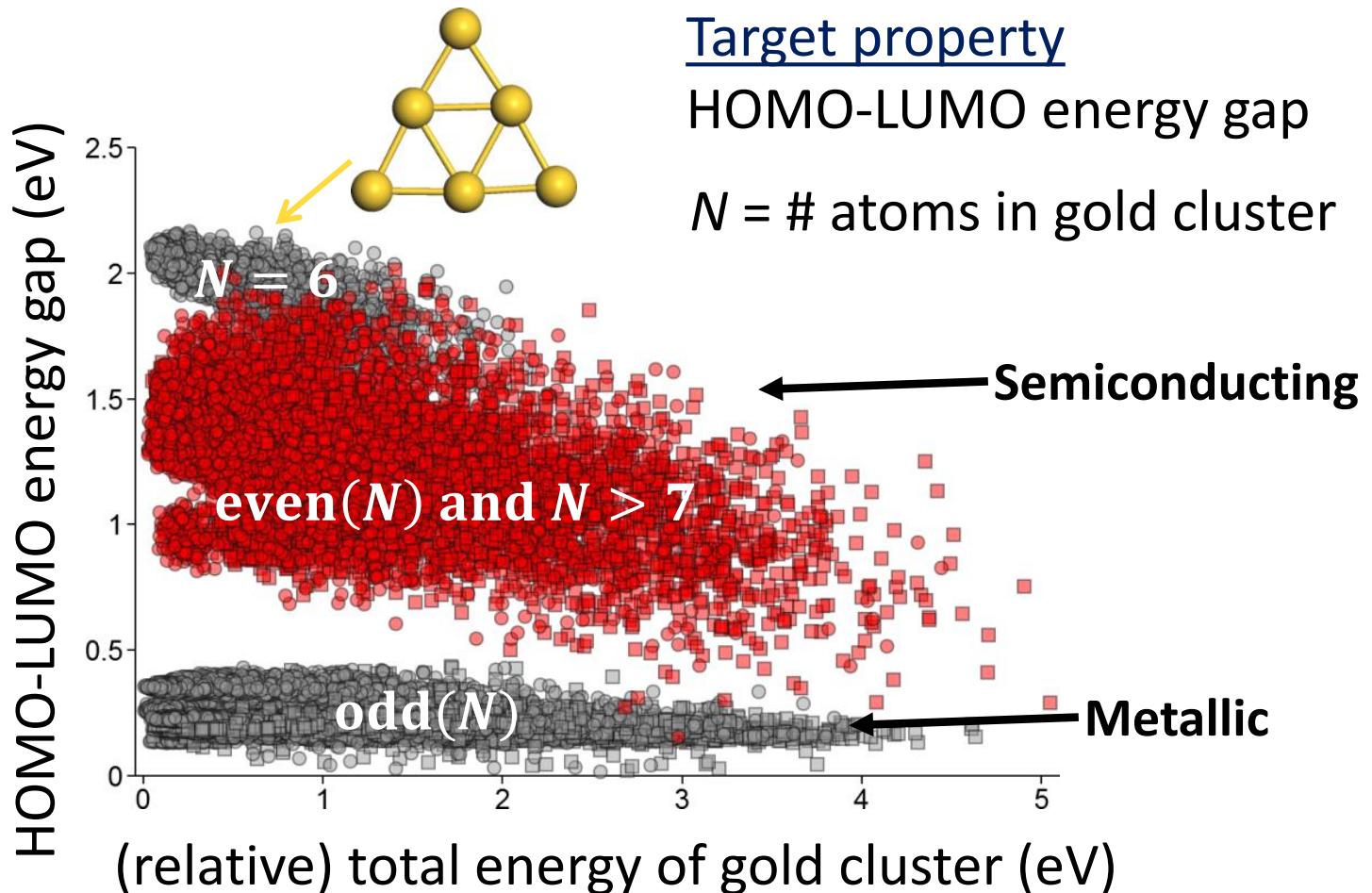
Three subgroups regarding
HOMO-LUMO gap are found



Three subgroups regarding
HOMO-LUMO gap are found



Three subgroups regarding HOMO-LUMO gap are found



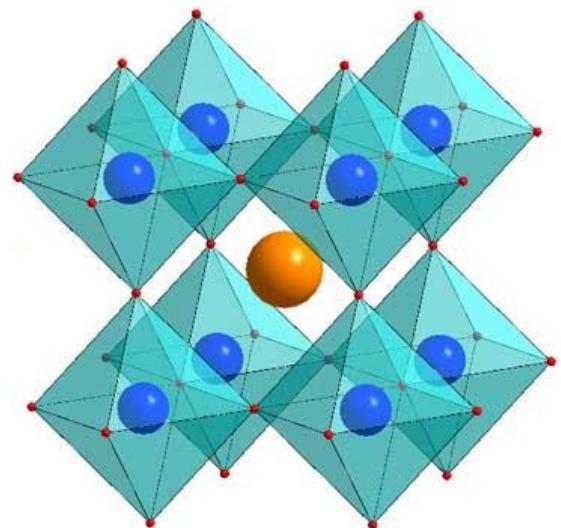
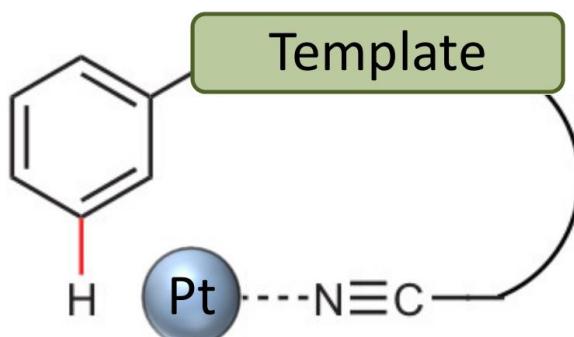
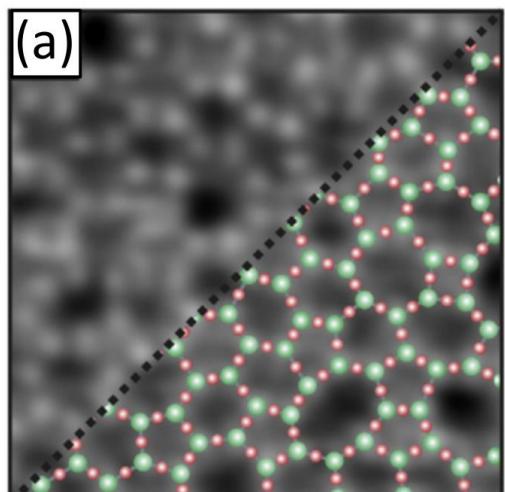
Toward accelerating computer-aided catalyst design

Plans to apply machine learning to other systems

Finding descriptors
of amorphous catalysts

Designing templates for
organometallic catalysts

Perovskite structure
prediction and reactivity



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and many others!



Alexander von Humboldt
Stiftung / Foundation



NOVEL MATERIALS DISCOVERY



Chemical Engineering Department,
UC Santa Barbara



Subgroup discovery tutorials
and other analytics tools are online
<https://www.nomad-coe.eu/>