Han-sur-Lesse Winterschool
November 26, 2024

Computational Spectroscopy & Catalysis

it is all about models and your expectations

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Outline & Learning Outcomes

- Catalysis, Models and Accuracy

1

  - There is always a model/method combination that gives you "right" number
  - Expert bias exists and limits one's imagination

- The Predictive Theory of Catalysis

2

  - We can construct a framework, but everything depends on everything
  - Many uncertainties (structural, performance, definitions…)
  - Kinetics need to be expressed through thermodynamics. Why would it?

- Computational Spectroscopy

3

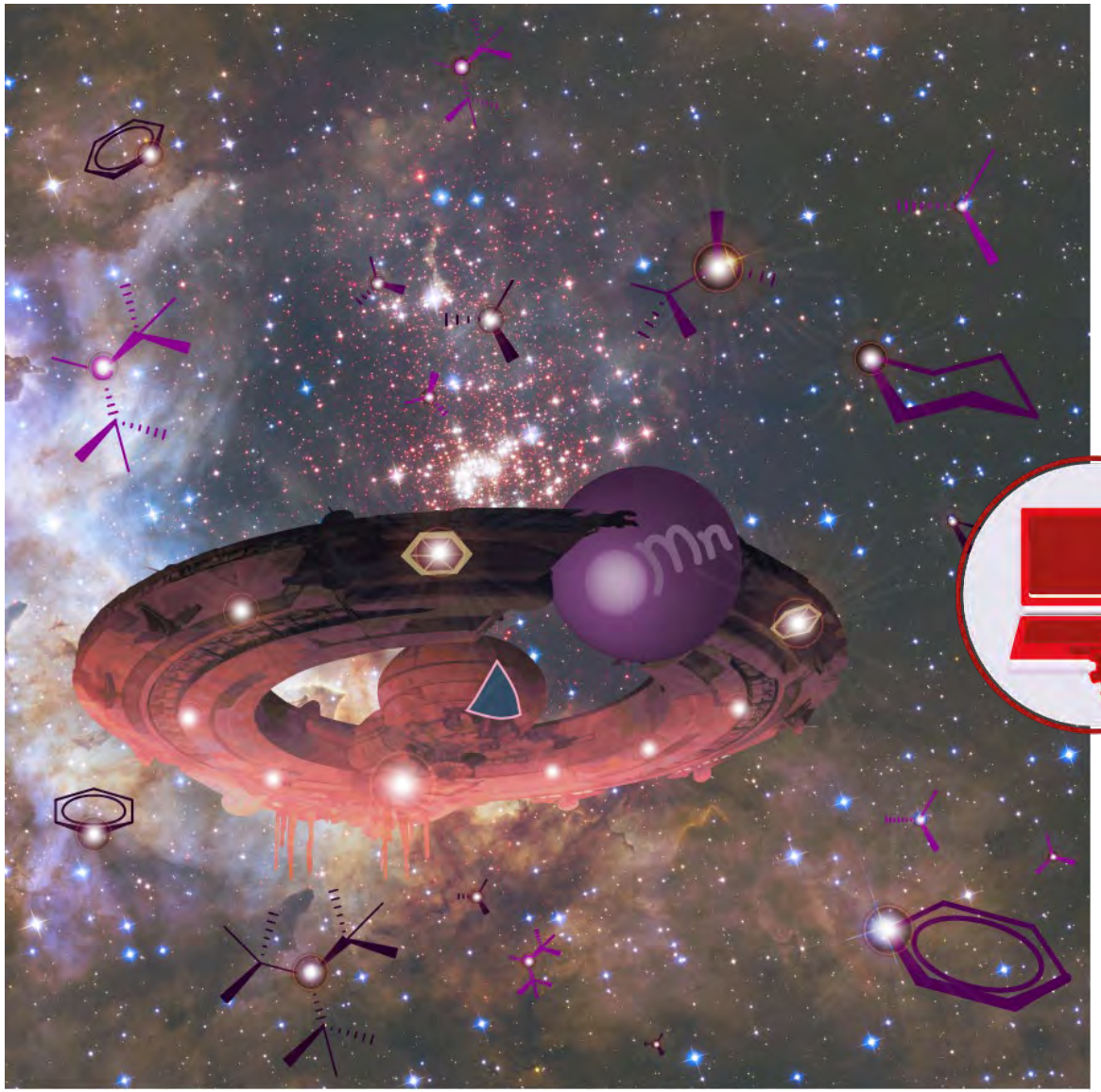
  - If we know the structure, we can predict spectra
  - Mapping spectroscopic fingerprints to address the structural problem
  - If it looks like a duck, swims like a duck, and quacks like a duck… and it does not matter what your experimental friend thinks it is.

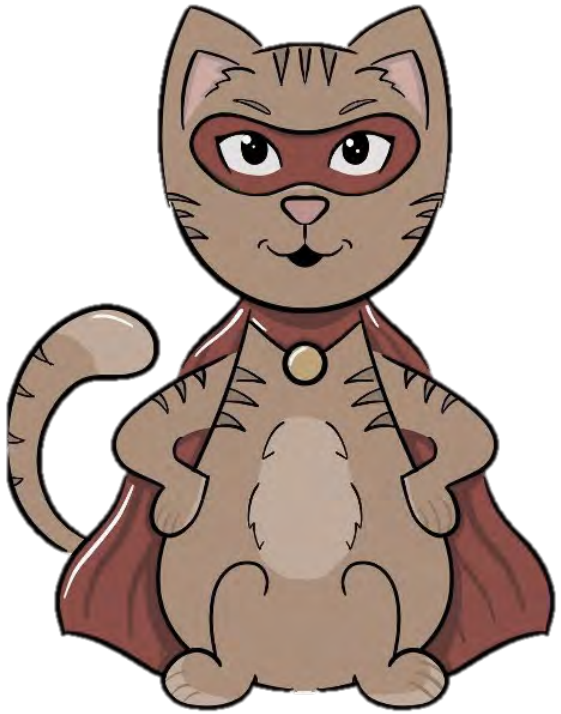
- Exploring PES and Catalyst Descriptors

4

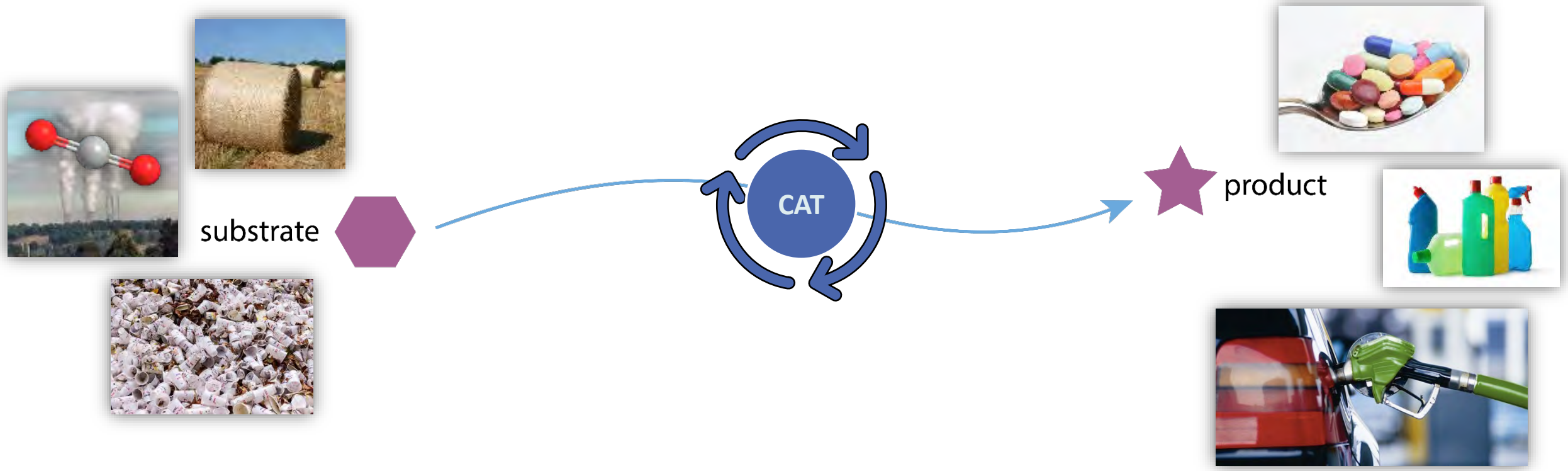
  - Shut up and calculate! (automation helps fight anxiety)
  - Working with the data rather than with results
  - We may need new representations

Searching the chemistry space for a supercat!



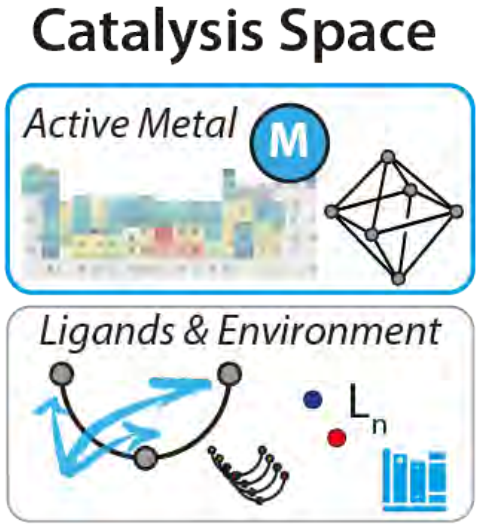


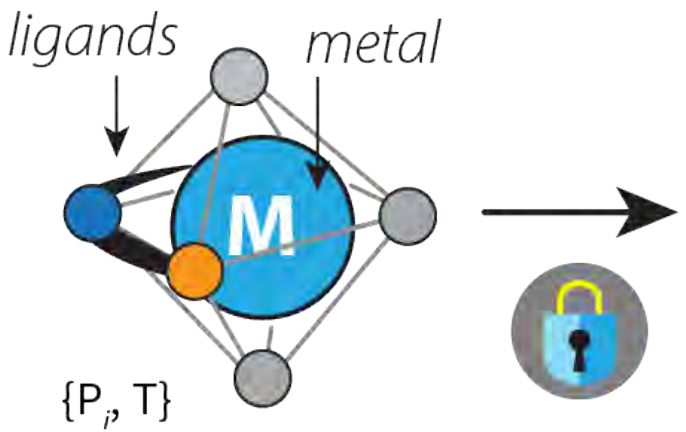
KPIs for SuperCat: What exactly are we looking for?

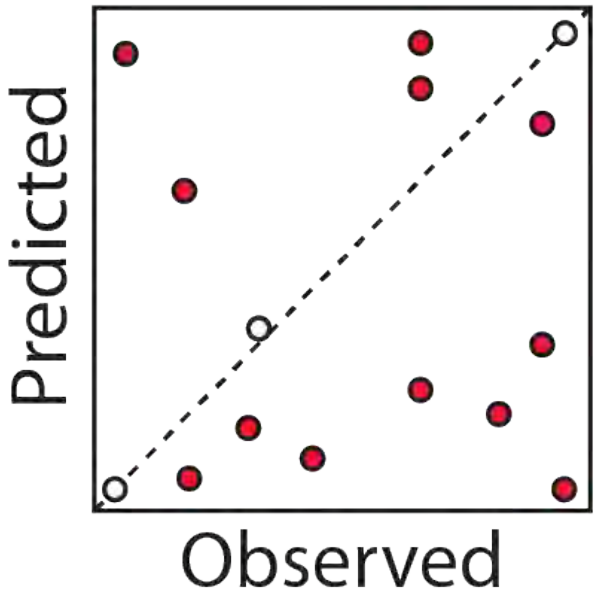


- Chemical entity that will accelerate right chemical conversion
- Does the right chemistry: provides a favorable path from S to P
- Efficient and selective: does not engage in other chemistry
- We have to be able to make it and make it work

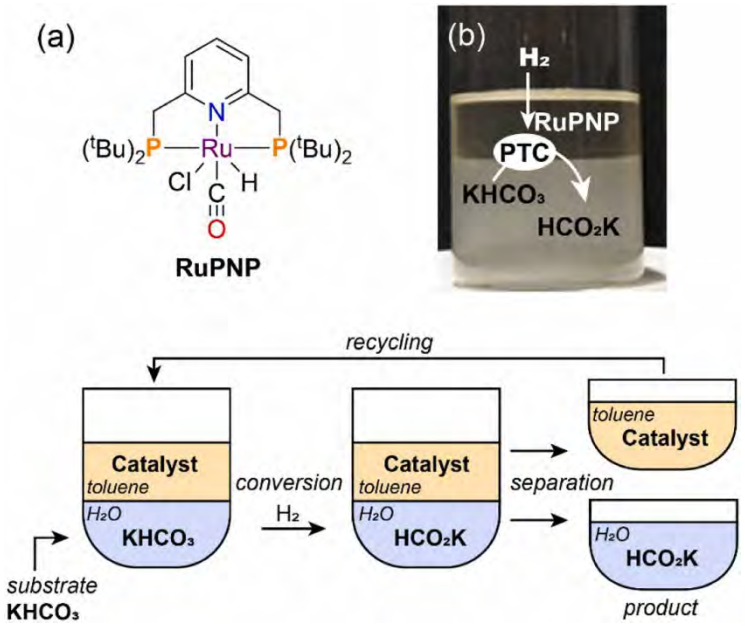
Navigating the catalysis space

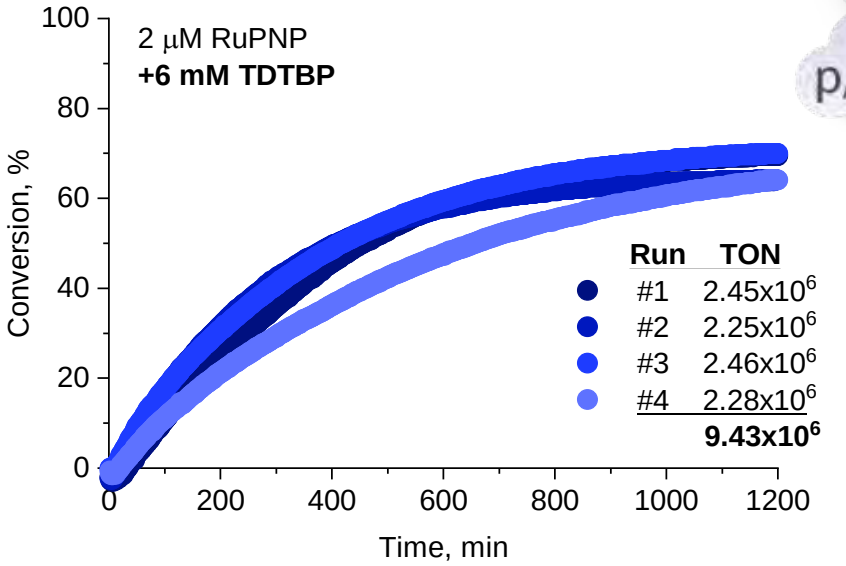




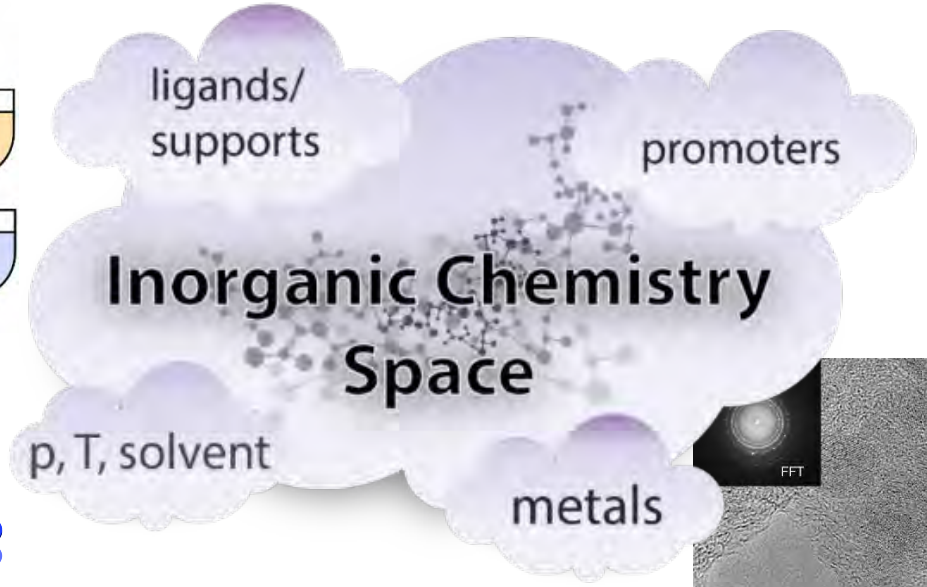


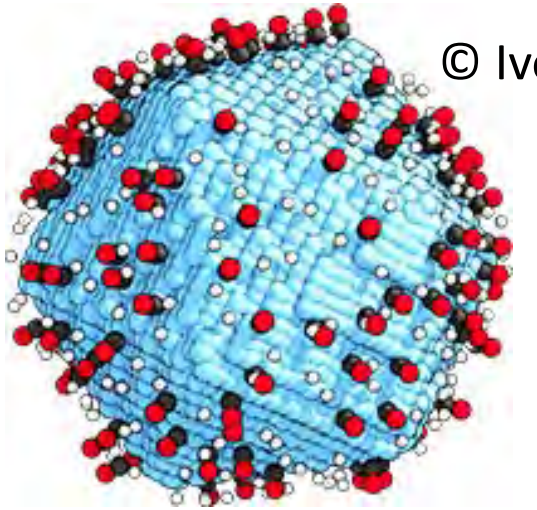
The complexity of catalysis





J. CO2 Util. **2024**, *81*, 102718





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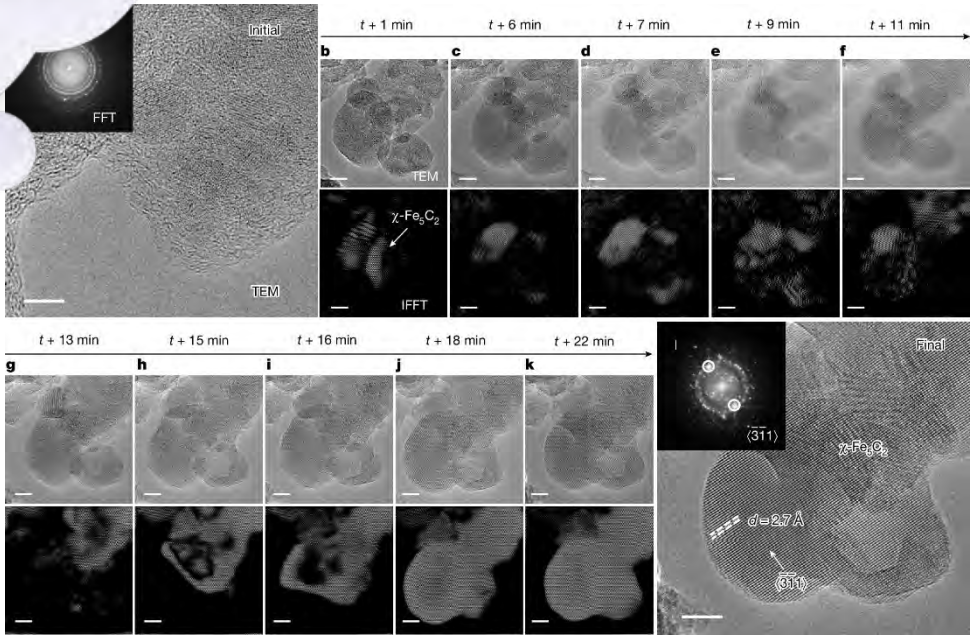
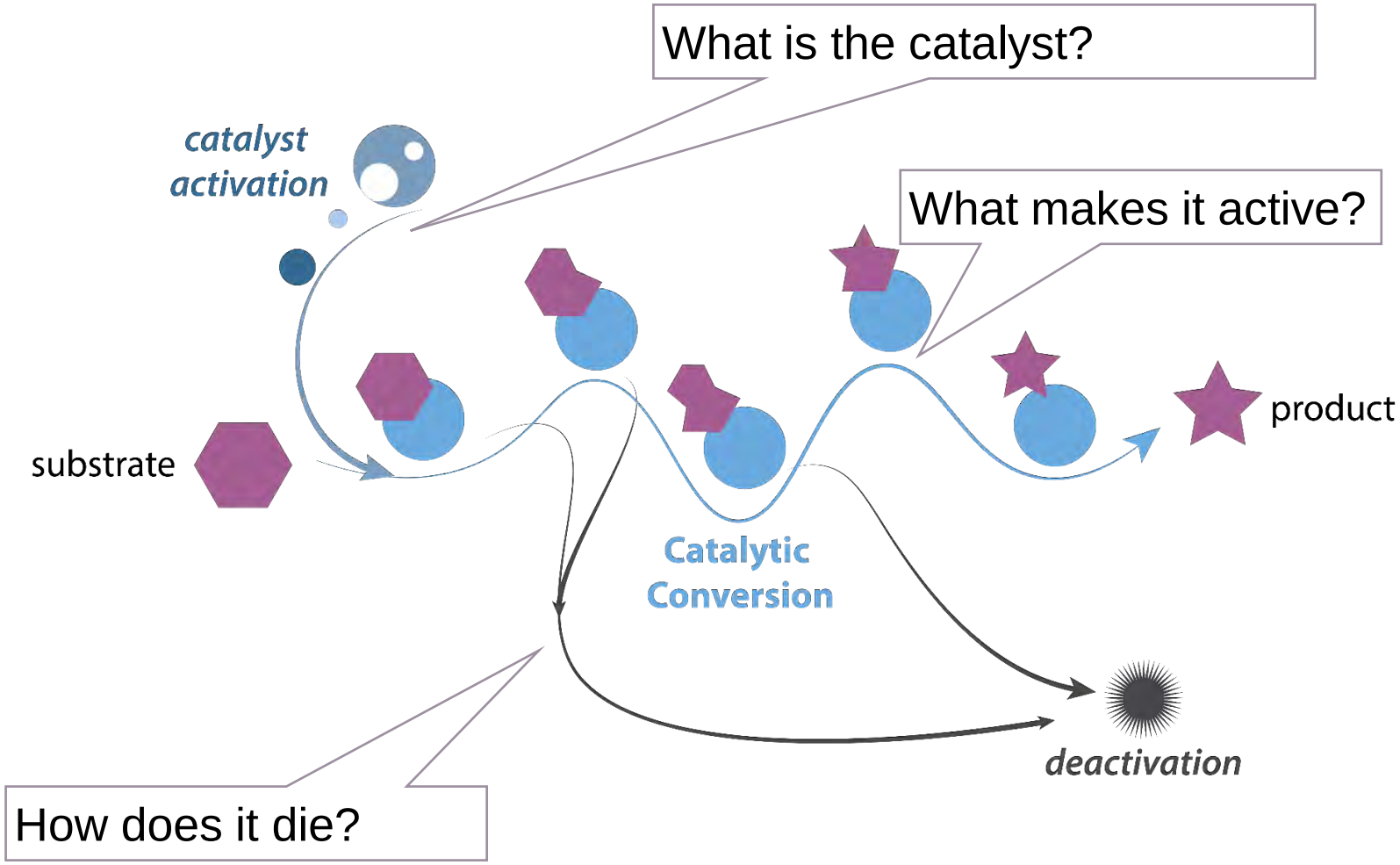
Wang et al (also IF)
Nature **2024**, *635*, 102



Molecular definition of a catalyst

- Catalytic entity / active site is formed in situ / evolves during the reaction
- The catalyst is defined by the nature of pre-catalyst and reaction conditions
- Common problem for homogeneous and heterogeneous catalysis



Vogt, Weckhysen, *Nat. Rev. Chem.* **2022**, *6*, 89
Yang, Filonenko, EAP, *ChemCommun* **2023**, *59*, 1757

Models and Methods in Catalysis

Catalysis – the dynamic black box

- What is(are) the active site(s)?
- What is the mechanism?
- What can we do to improve the process?

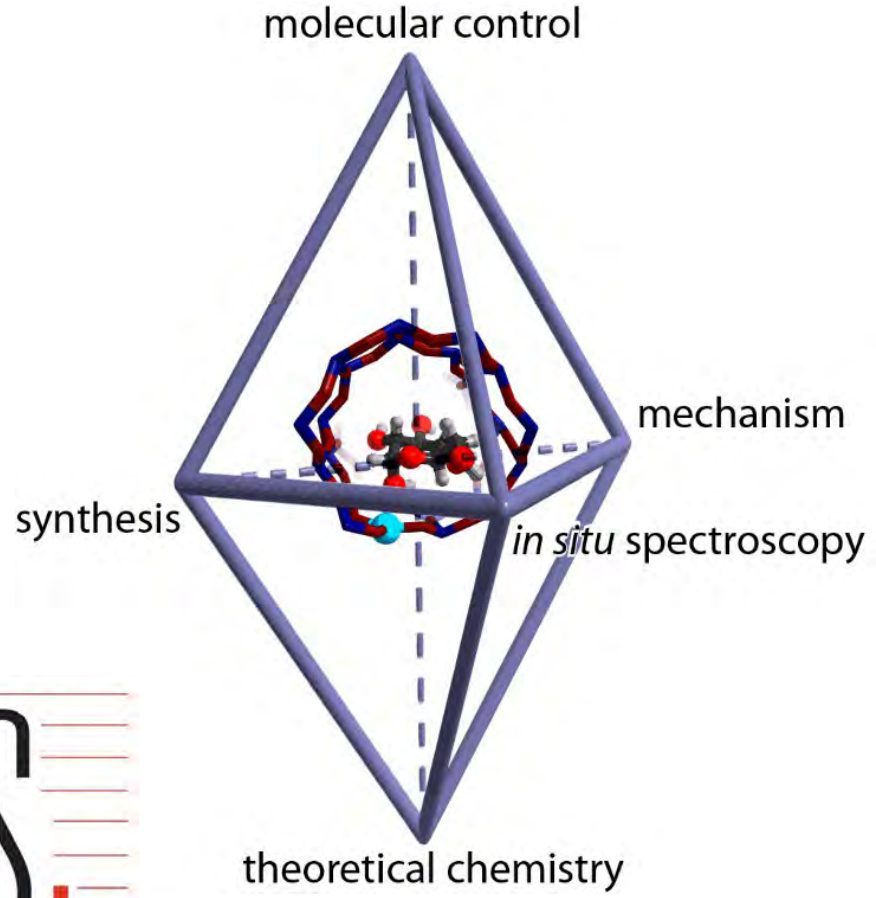
substrate

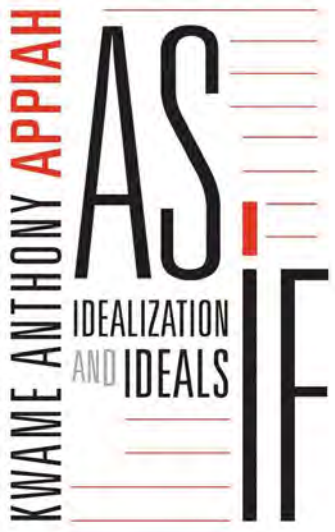
catalyst

product

Definitions: Modeling and Simulations

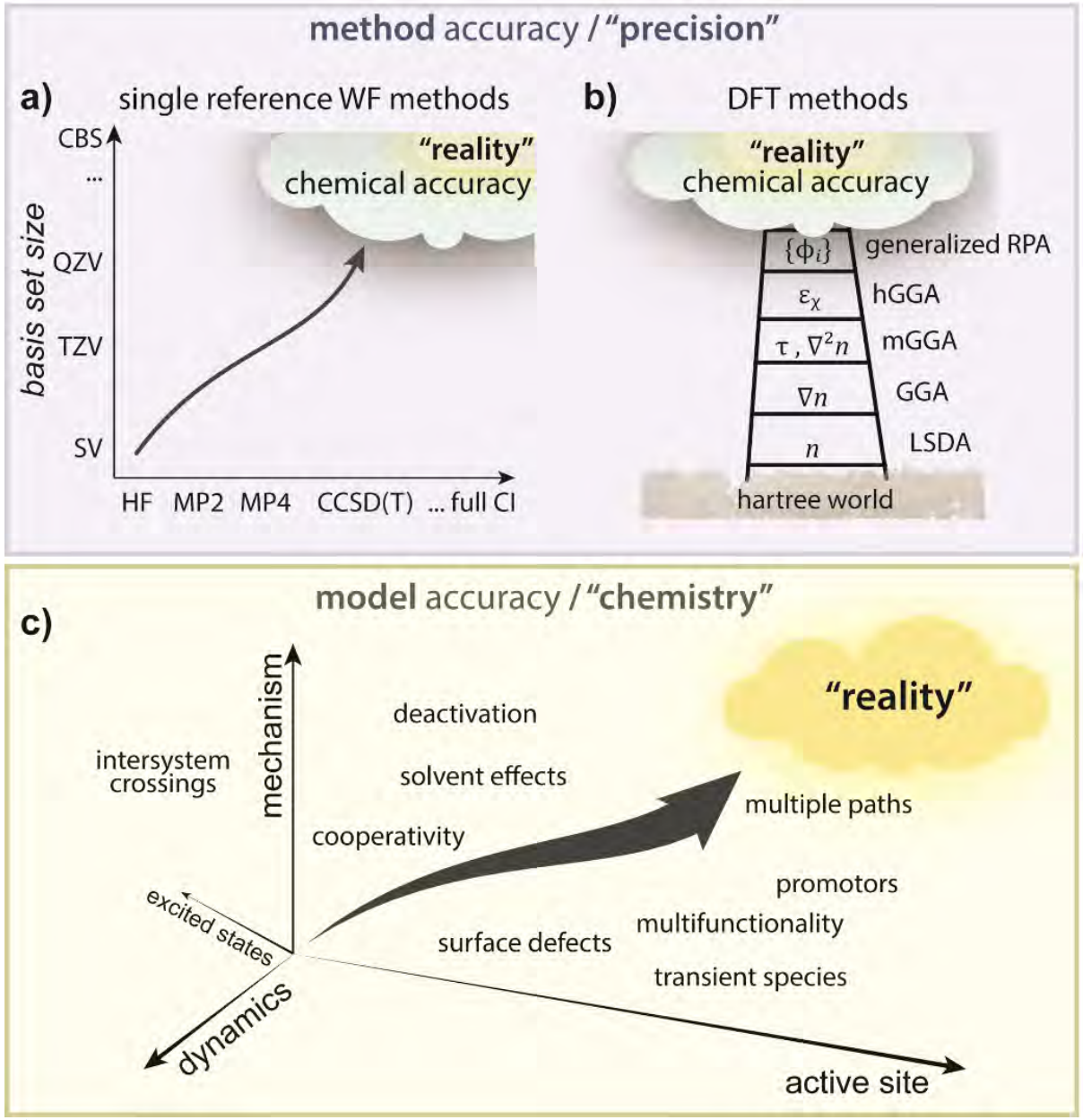
- A **model** is an idealization of real behavior - that is an approximate description based on empirical and/or physical reasoning.
- Both experimentalists and theoreticians operate with models
- A **simulation** is a study of the response of a modeled system found by subjecting **models** to inputs and constraints that simulate real events.
- A **simulation** does not mimic reality, rather it mimics a **model** of reality.





K.A. Appiah, *As If: Idelaisation and Ideals*, **2017**

Computational Chemistry & Accuracy



- The accuracy of a **simulation** depends on many factors, some involving the **simulation** method itself (accuracy in solving sets of equations, for example).
- Often, however, the biggest errors in a **simulation**, at least with respect to how well it describes a real system, are the inadequacies of the **models** upon which the **simulation** is based.
- Thus, one cannot separate **simulations** from the underlying **models**.

EAP, *ACS Catal.* **2017**, *7*, 4230
E.G. Lewars, Computational Chemistry, Springer, **2011**.

How do we define a model

Identify the Problem

Identify the input/output

Identify the mechanism

Target the precision

Construct model

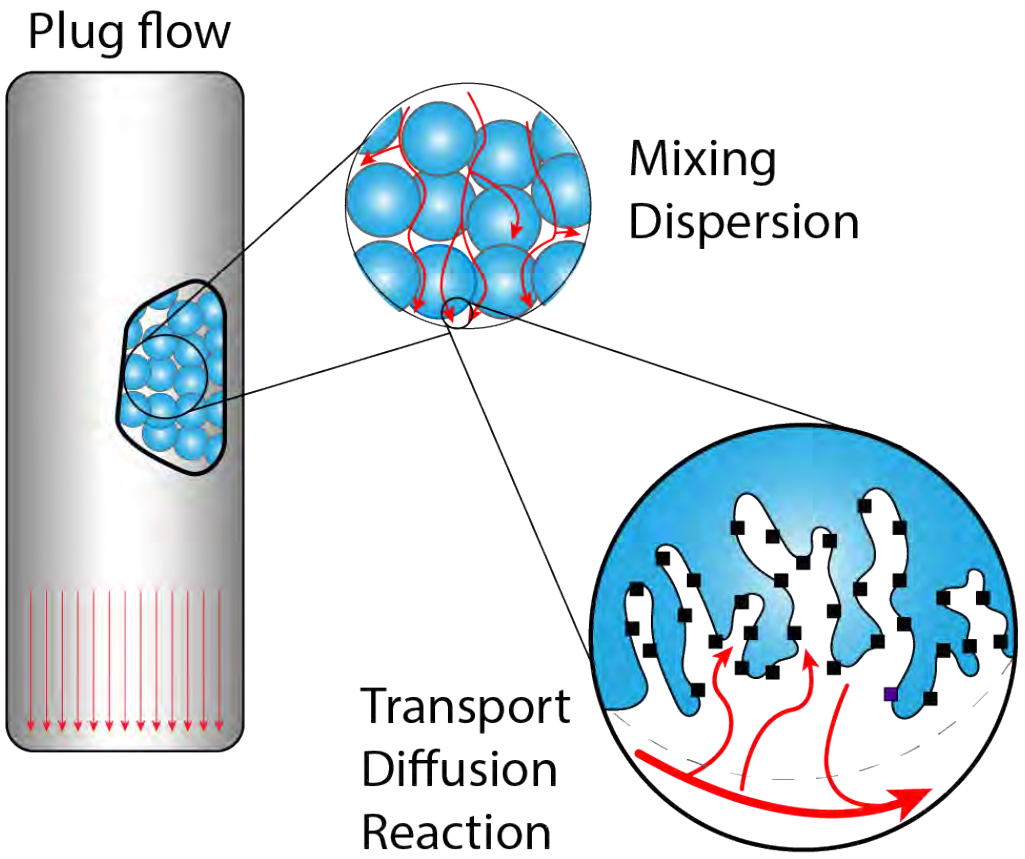
Select method/code

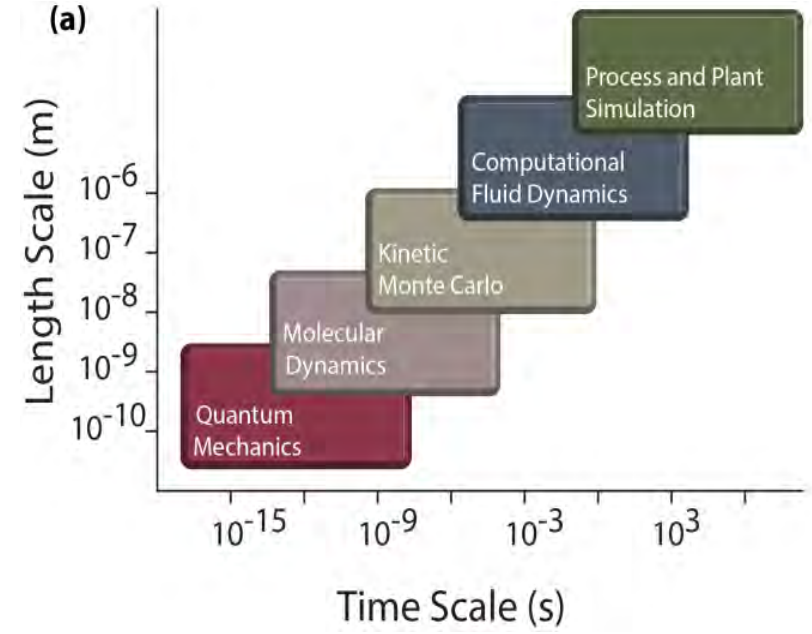
Run simulation

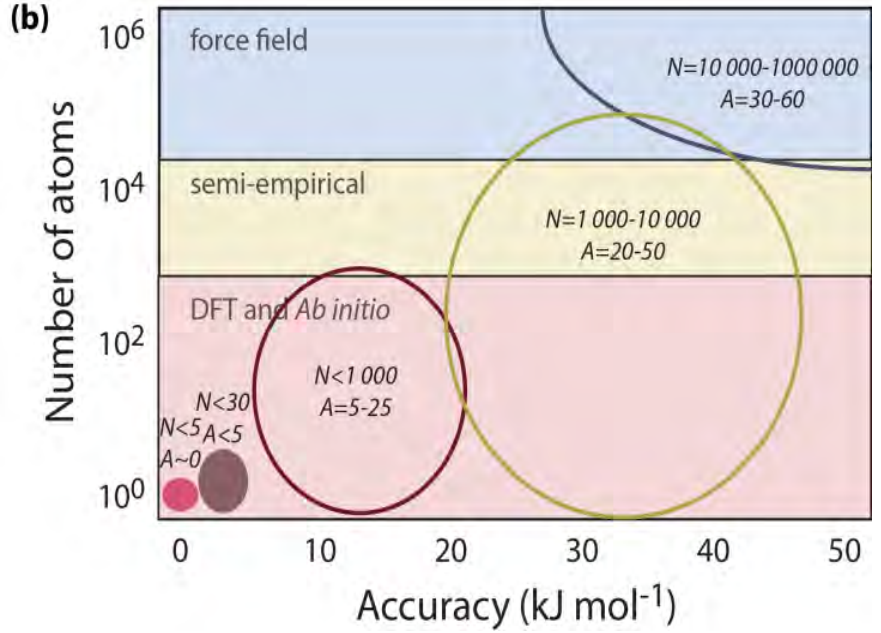
Use results

re- Formulate hypothesis

Accuracy and scales

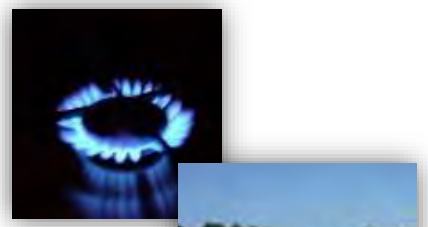






EAP & Hensen *"Computational approach to chemical reactivity of metal organic frameworks"* in F.X. Llabrés i Xamena, J. Gascón (eds.), *Metal Organic Frameworks as Heterogeneous Catalysts*, Chapter 6, RSC Catalysis Series No.12, Royal Society of Chemistry, **2013**.

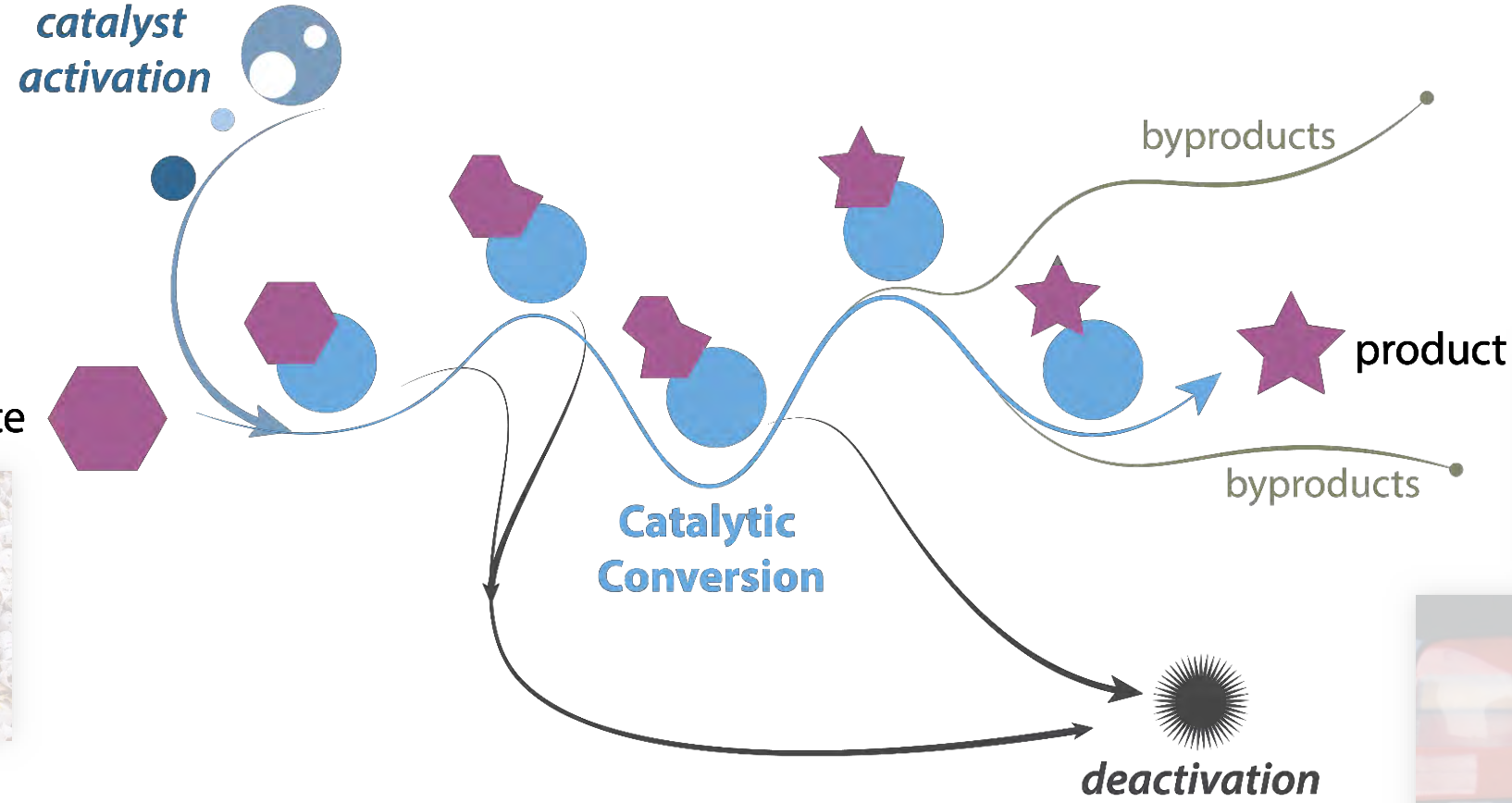
Dealing with chemical complexity of catalytic conversions



substrate

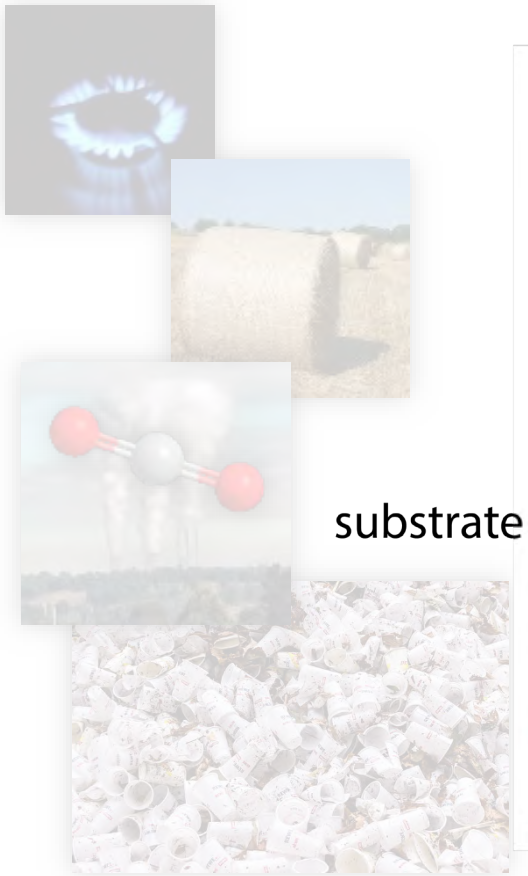
product

Dealing with complexity of catalytic conversions



Everything depends on everything

$$state = \boldsymbol{f}(chem. = \{structure, catalyst, PES, \dots\}, conditions = \{solvent, T, P, ci \dots)$$



catalyst
precursors, promotors, etc...

byproducts

substrate

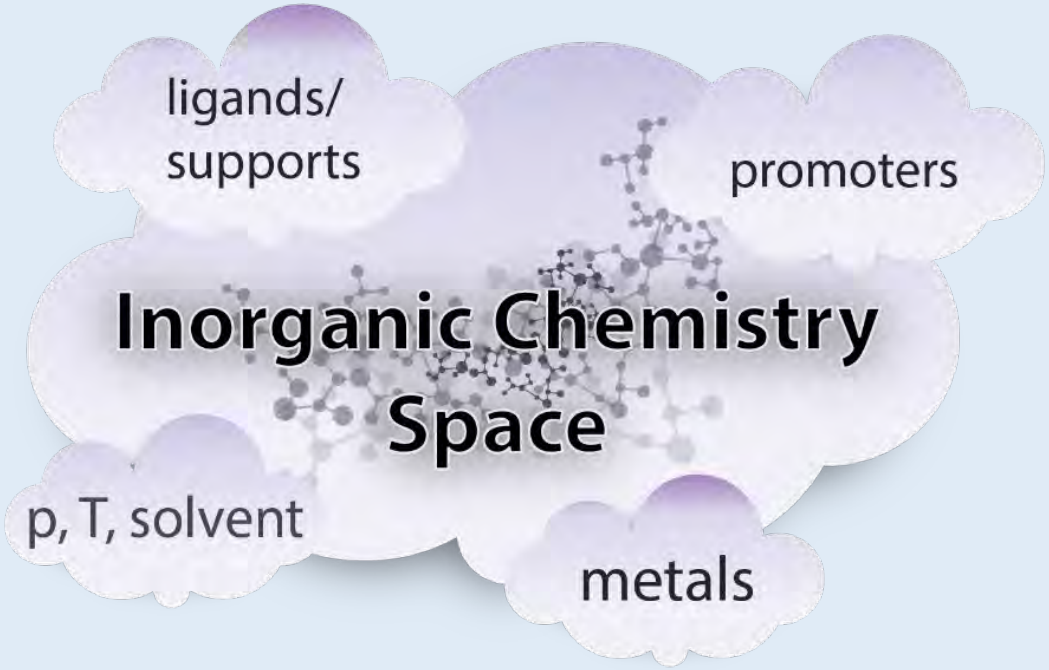
product

deactivation

TU Delft

Chemistry out of equilibrium

Catalysis



Reaction networks

ICT & Data science

- **We need to develop multiscale models**
- **We need to learn how to navigate chemistry space**
- **We need to link chemistry and condition spaces**

Chem. Soc. Rev. **2018**, 47, 8307; *Chem. Rev.* **2019**, *119*, 2453

2

Predictive Theory in Catalysis

DFT and Microkinetic Frameworks

Predictive theory in catalysis

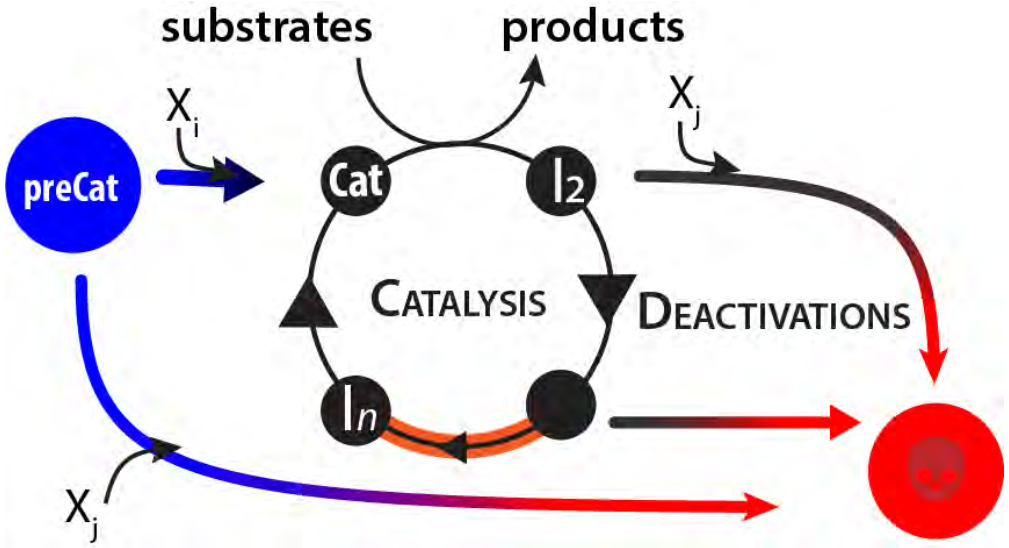
Quantum Chemistry

Transition State Theory

Mechanism

Micro-kinetic model

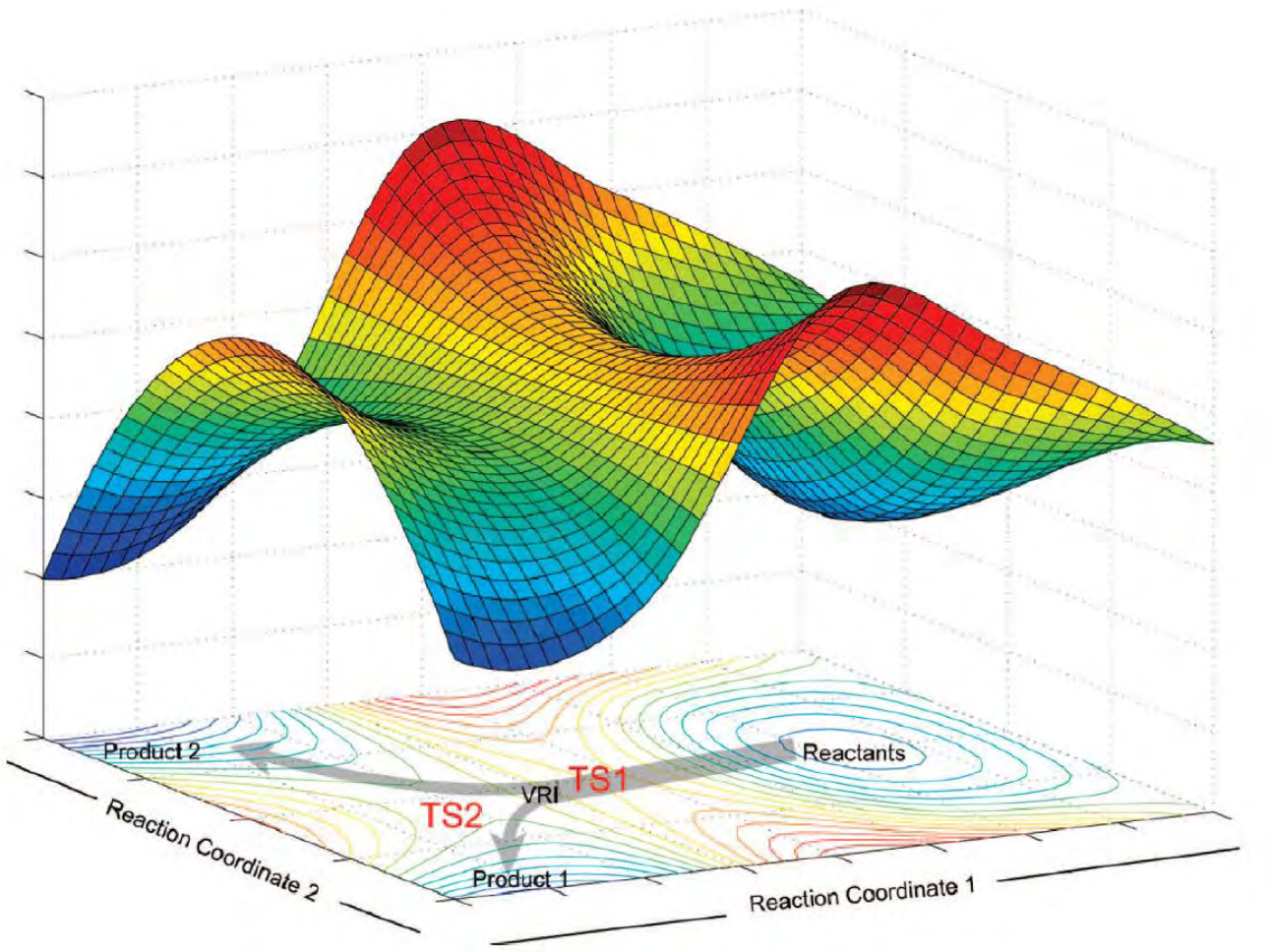
Final Kinetics

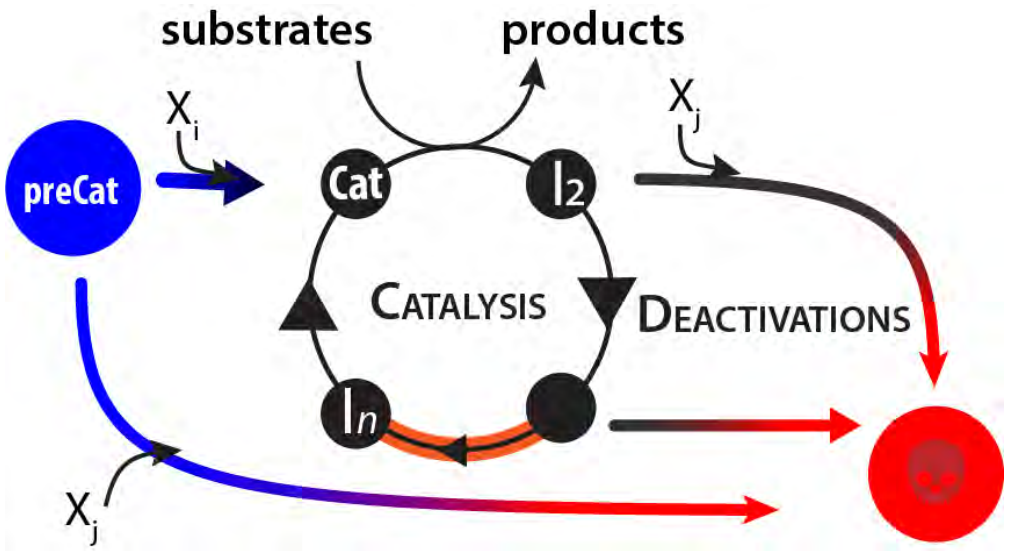


$$r_i = k_{\mathrm{f},i} \prod_{j=1, n_j<0}^{j=N} C_j^{-n_j} - k_{\mathrm{r},i} \prod_{j=1, n_j>0}^{j=N} C_j^{n_j}$$

$$k = \frac{k_B T}{h} e^{-\Delta G^{\ddagger}/RT}$$

Mechanism, PES and DFT

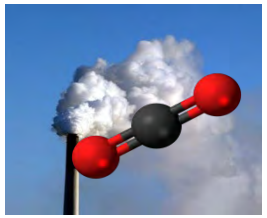




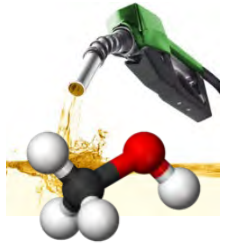
$$r_i = k_{\mathrm{f},i} \prod_{j=1,n_j<0}^{j=N} C_j^{-n_j} - k_{\mathrm{r},i} \prod_{j=1,n_j>0}^{j=N} C_j^{n_j}$$

$$k = \frac{k_B T}{h} e^{-\Delta G^{\ddagger}/RT}$$

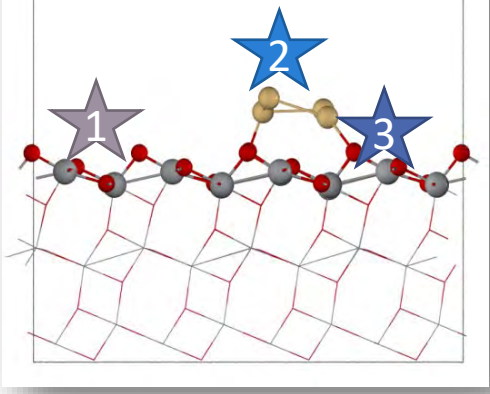
Heterogeneous catalysis (gas-solid interface)

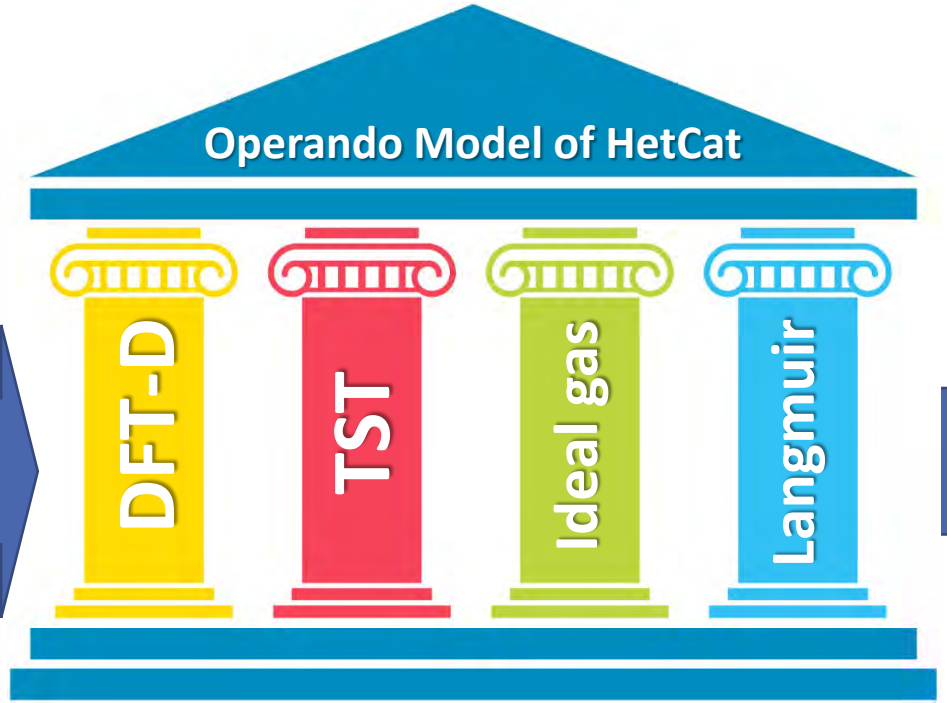


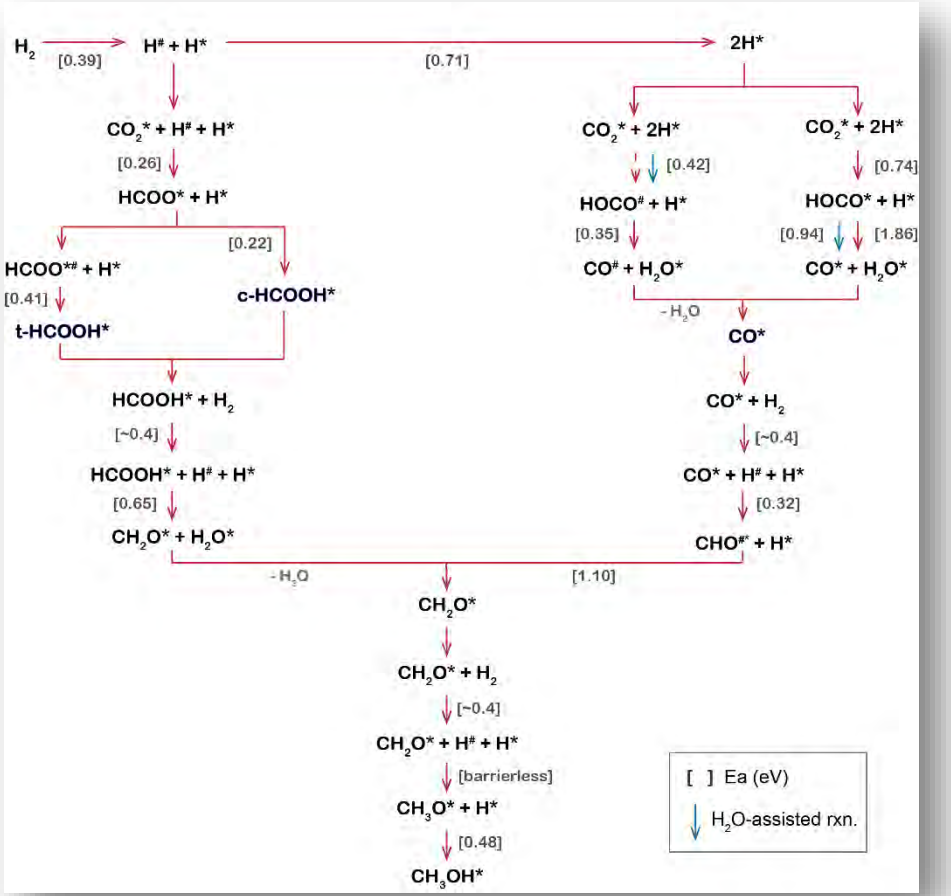
$$CO_2 + 3H_2 \xrightarrow{M_{NP}/oxide} CH_3OH + H_2O$$



Define a model:
Cd_4/TiO_2

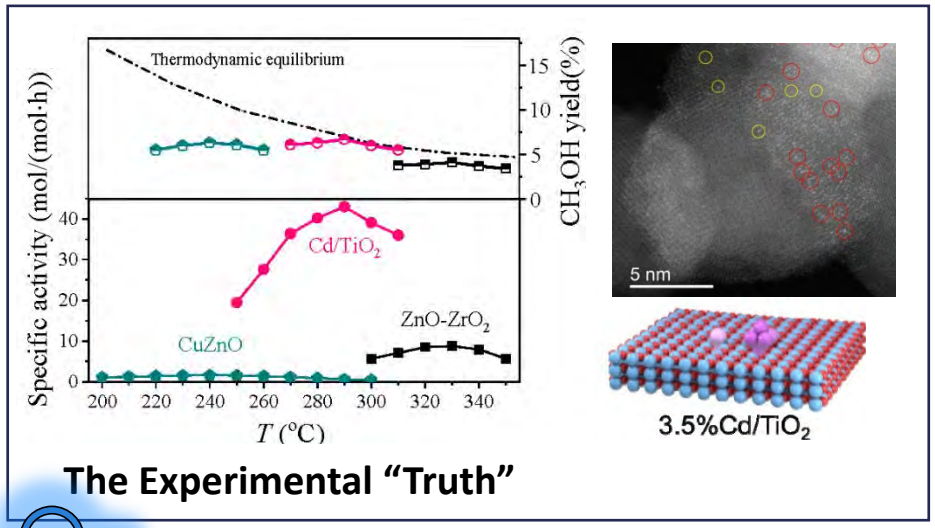




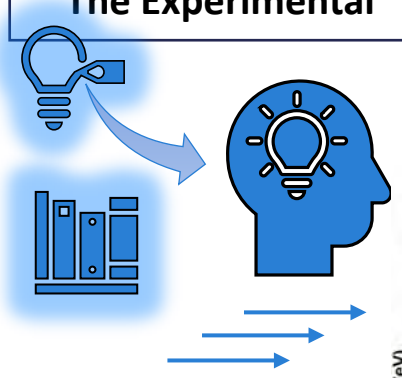


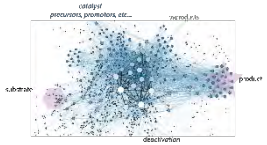
With Jittima Meeprasert, Dapeng Sun, Guanna Li
ChemCatChem **2022**, *14*, e202101646; *Chin. J. Catal.* **2022**, *43*, 761

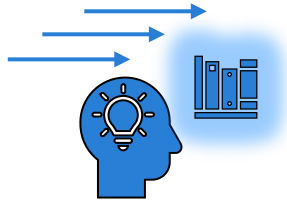
From mechanism to kinetic model



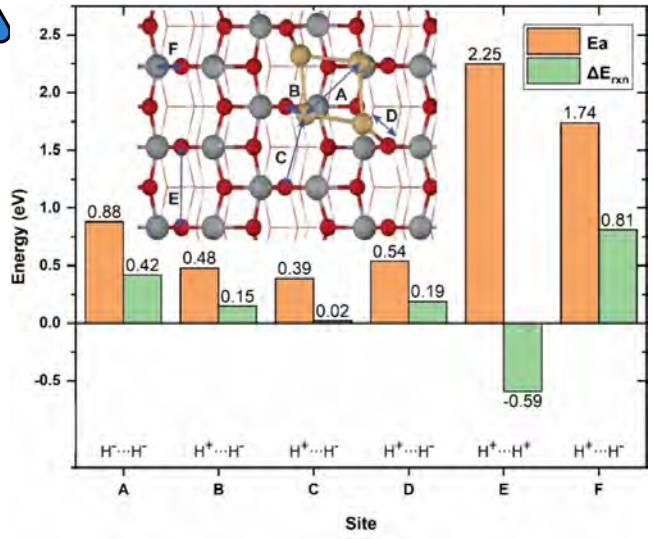
The Experimental "Truth"



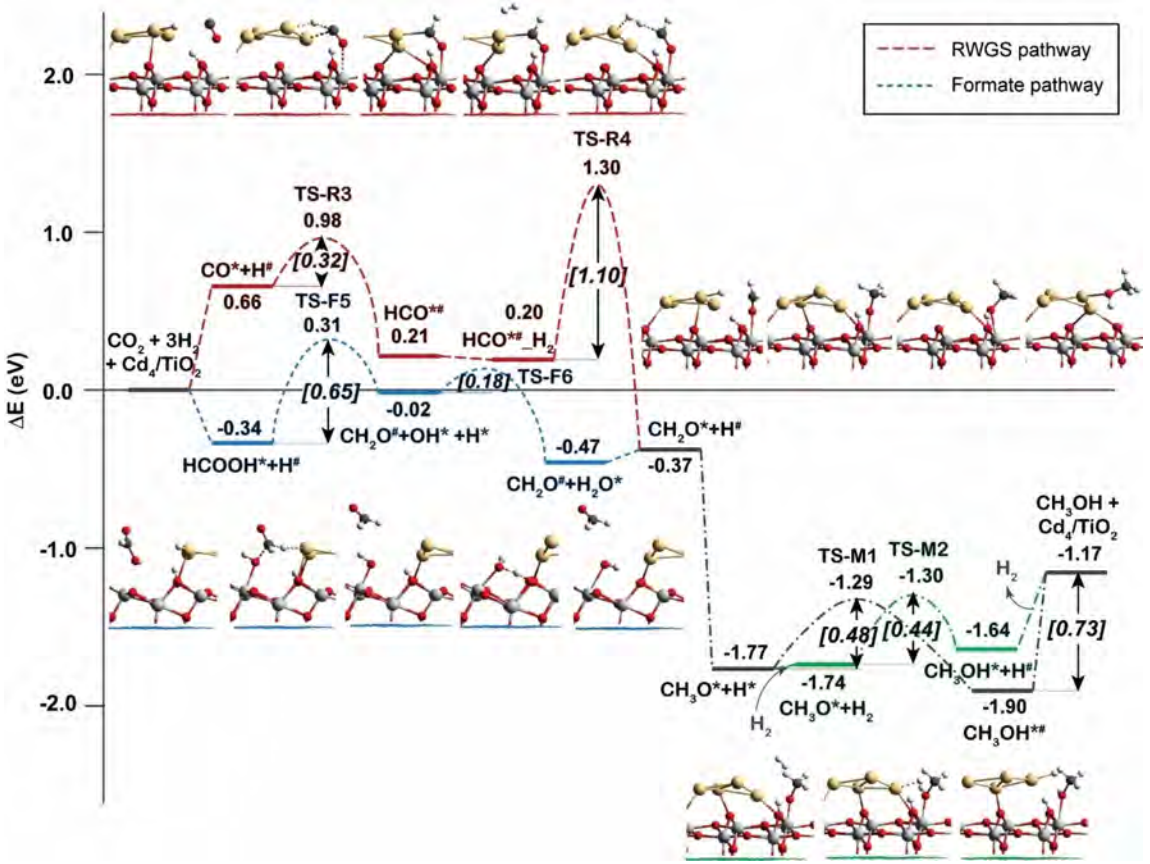




Catalyst Model & DFT Calculations



Mechanism & Reaction Energy Profile



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ChemCatChem **2022**, *14*, e202101646; *Chin. J. Catal.* **2022**, *43*, 761

MKM Operando Model of a HetCat process

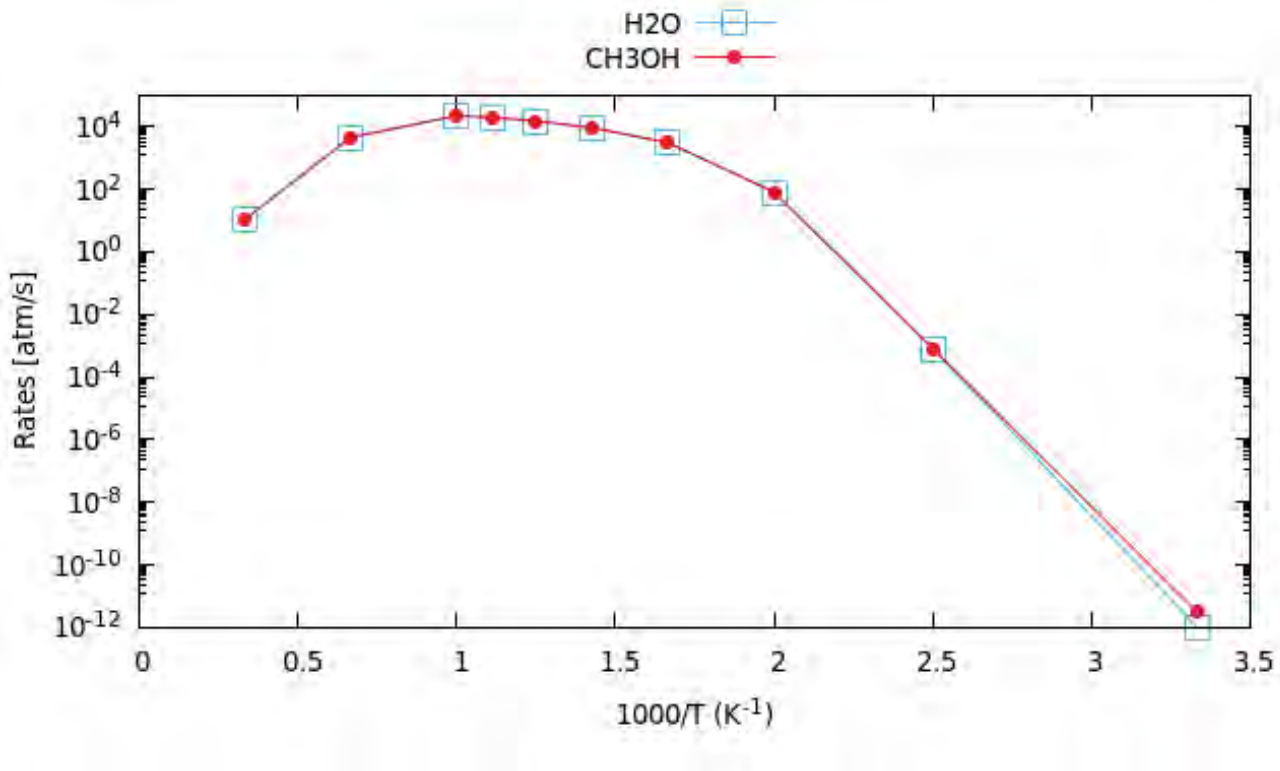
$$r_i = k_{f,i} \prod_{j=1,n_j<0}^{j=N} C_j^{-n_j} - k_{f,i} \prod_{j=1,n_j>0}^{j=N} C_j^{n_j}$$

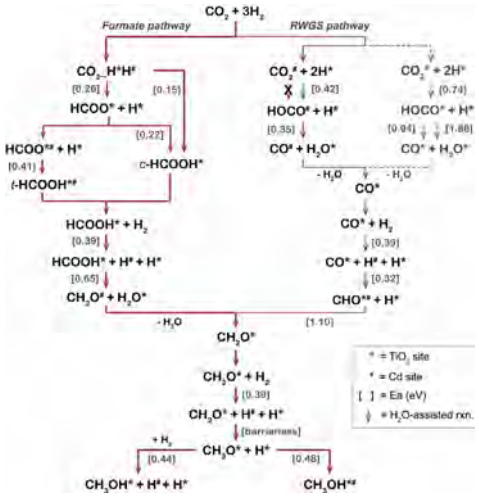
$$k = \frac{k_B T}{h} e^{-\Delta G^{\ddagger}/RT}$$

$$G^{o}(X_i)_{gas} = E(X_i)_{0,DFT} + \varepsilon_{i,ZPE} + H_{i,corr} + T(S_{tot,i}) \quad \Big| \quad T, P_{tot}$$

$\underbrace{\Sigma\varepsilon_{int} + k_B T}$ $\underbrace{S_t + S_v + S_r + S_e}$

$$CO_2 + 3H_2 \xrightarrow{Cd_4/TiO_2} CH_3OH + H_2O$$





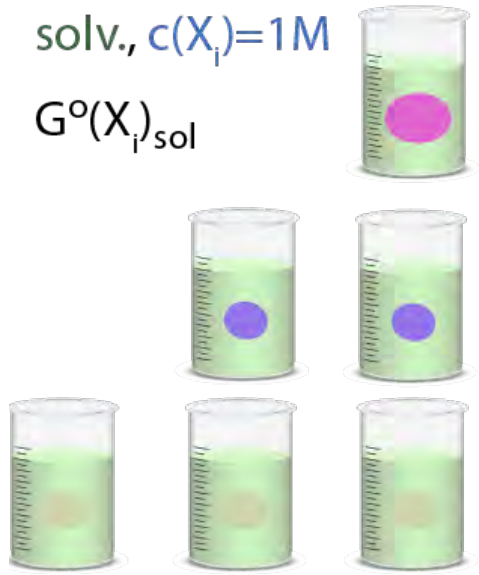
- **Ideal gas approximation**
- Intrinsic reactivity is condition-independent

With Jittima Meeprasert, Guanna Li, J. Wang, C. Li
ChemCatChem **2022**, *14*, e202101646

MKM and more complex systems

DFT calculations:
- Intrinsic reactivity
- Molecules in vacuum

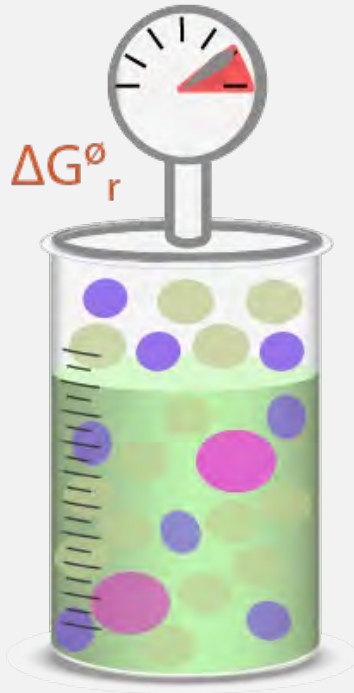
Implicit (PCM) solvent:
- Polarized continuum
- Ideal solution



Real solultion (COSMO-RS)

$\Delta G^{ø}_r$ (solv., T, P_{tot}, a_i)

$f(p,T,c_i,$ solvent)



- Real solvent = reactive mixture
- Reactive System
- Multiphase, multicomponent

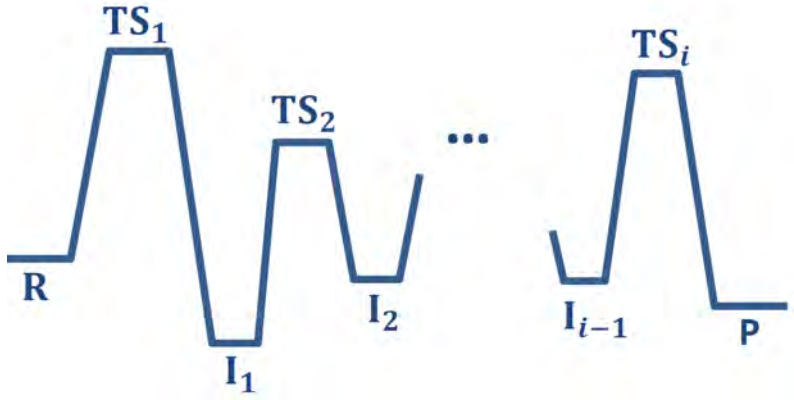
$$G°_{gas} = E_{DFT} + H_{corr} + TS_{gas}$$

$$G°_{sol} = G°_{gas} + G_{i,S}$$

Kulyaev, **EAP**, *ChemCatChem* ***2020***, *10.1002/cctc.201901911*

Condition-dependencies in kinetics of liquid phase catalysis

$$R \xrightarrow{k} P$$



$$\frac{d[R]}{dt} = -k_1[R] + k_{-1}[I_1]$$

$$\frac{d[I_1]}{dt} = k_1[R] - k_{-1}[I_1] - k_2[I_1] + k_{-2}[I_2]$$

$$\vdots$$

$$\frac{d[P]}{dt} = k_i[I_{i-1}] - k_{-i}[P]$$

Quantum Chemistry

Transition State Theory

Dynamic Solvation model

$$k_i = \frac{kT}{h} K_j^{\neq} =$$

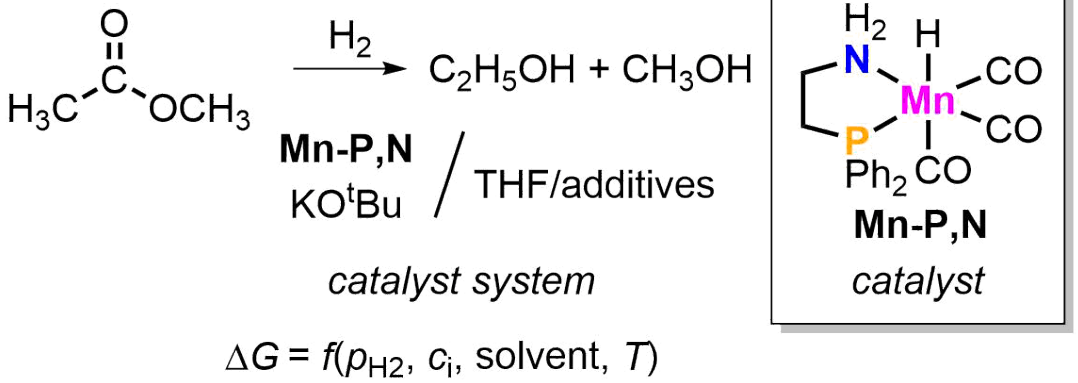
$$= \frac{kT}{h} K_{j0}^{\neq} \cdot \frac{\prod_i \gamma_{ij}^{\alpha_i}}{\gamma_j^{\neq}} =$$

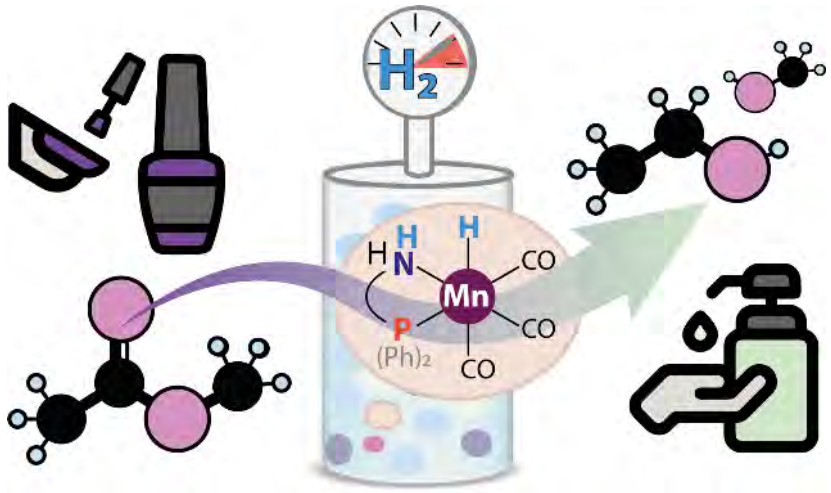
$$= \frac{kT}{h} \exp\left(-\frac{\Delta G_{sol}^{\neq} + RT ln(\frac{\prod_i \gamma_{ij}^{\alpha_i}}{\gamma_j^{\neq}})}{RT} \right)$$

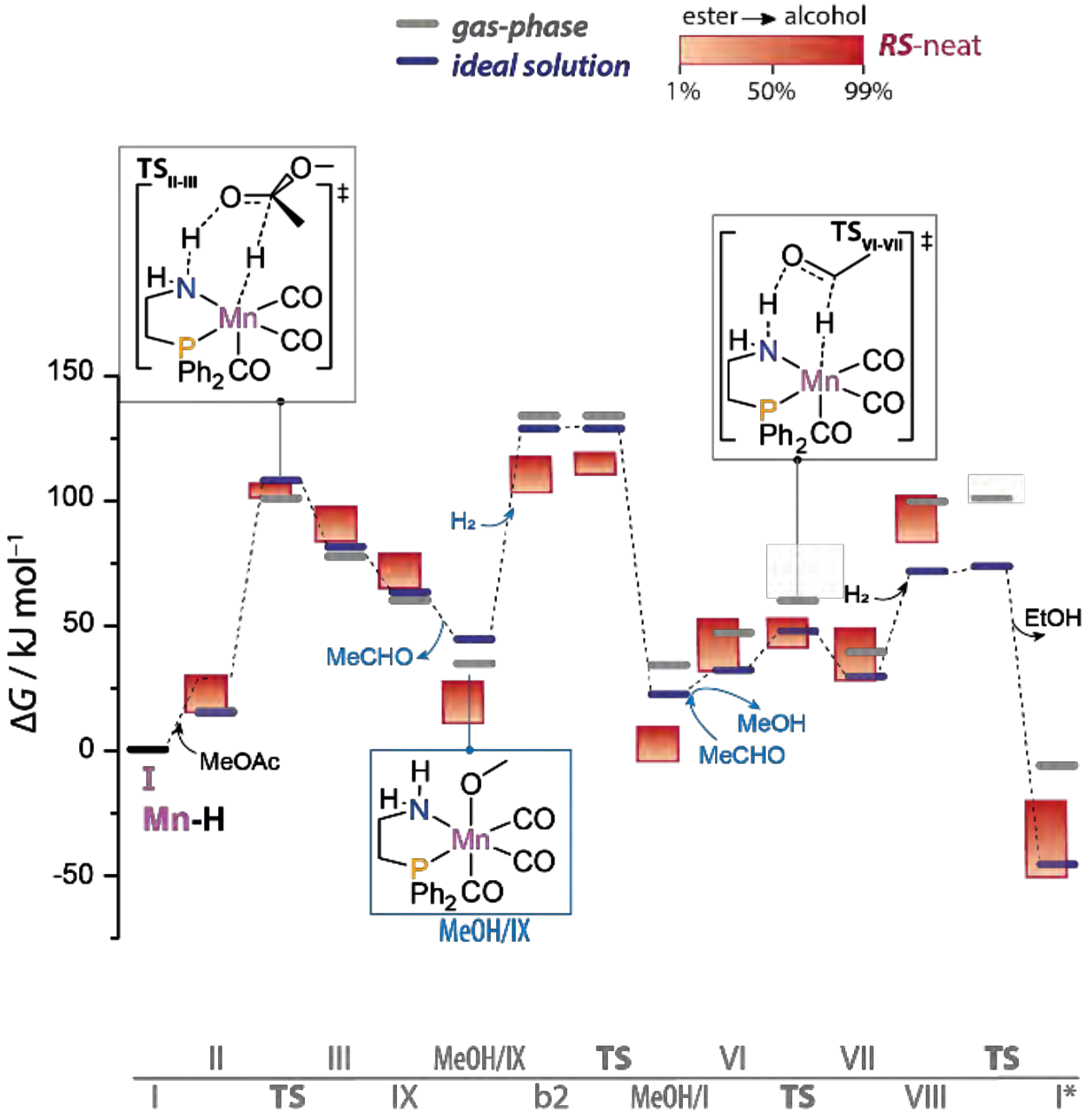
$$\Delta G_r(\text{solv.}, T, P_{tot}, \underbrace{a_i}_{f(p,T,c_i,\text{solvent})})$$

O. N. Temkin, *Homogeneous Catalysis with Metal Complexes: Kinetic Aspects and Mechanisms,* 2012, Wiley.

Ester hydrogenation as a relevant example



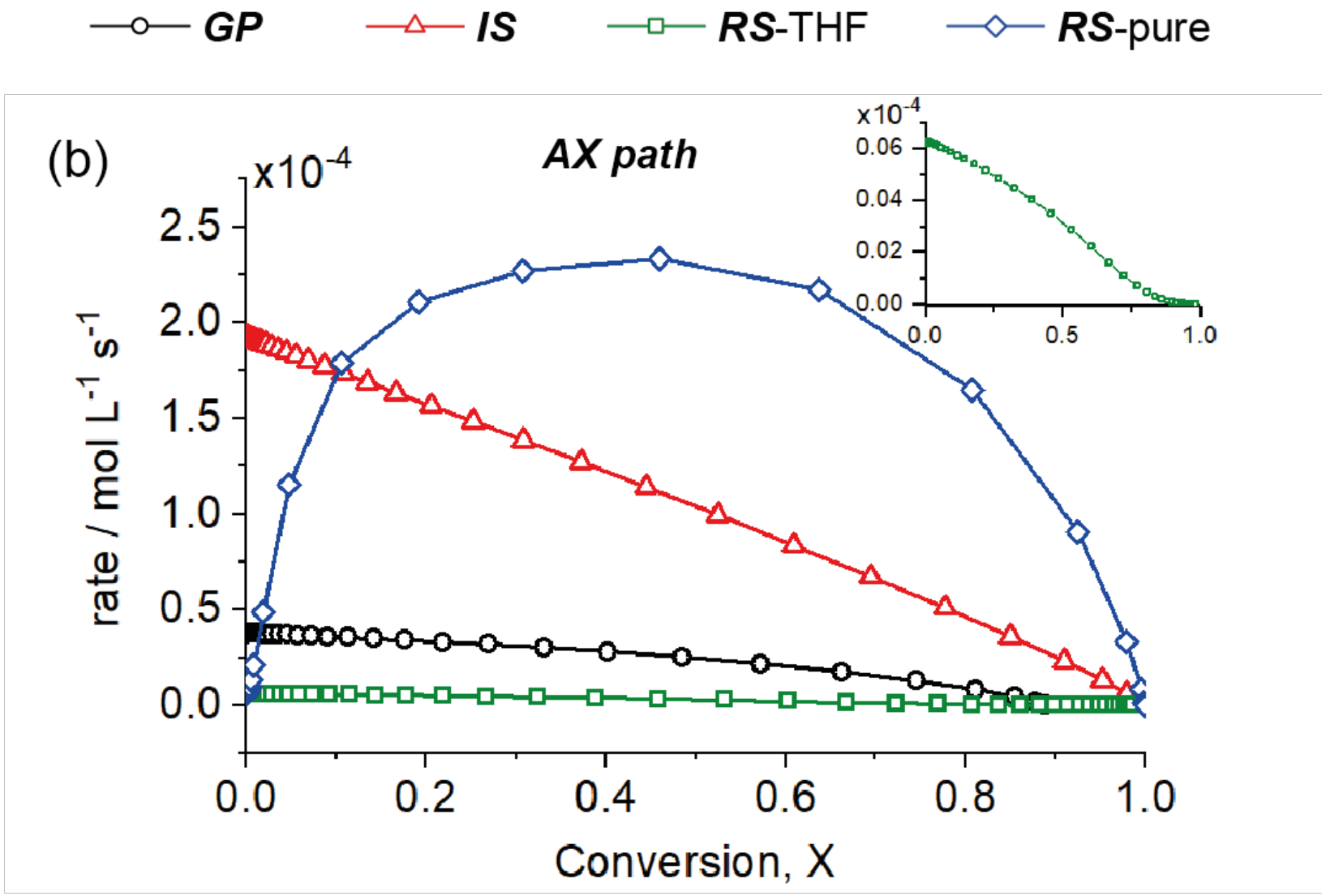




With A. Krieger, P. Kulyaev, D. Sun, submitted

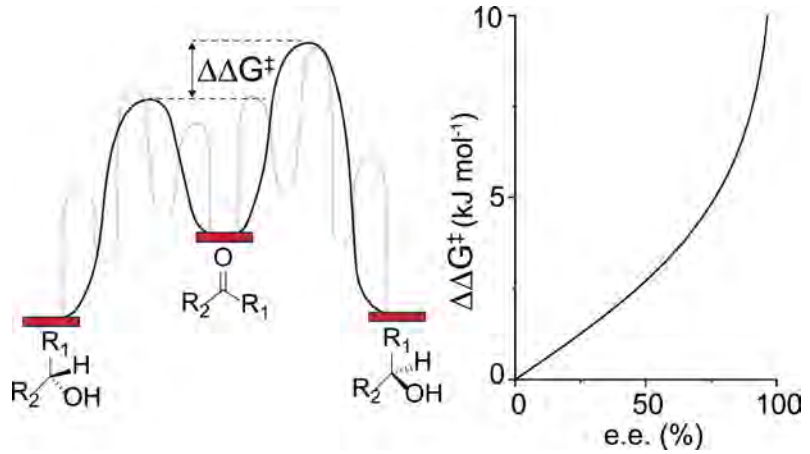
Condition-dependencies in kinetics of HomCat

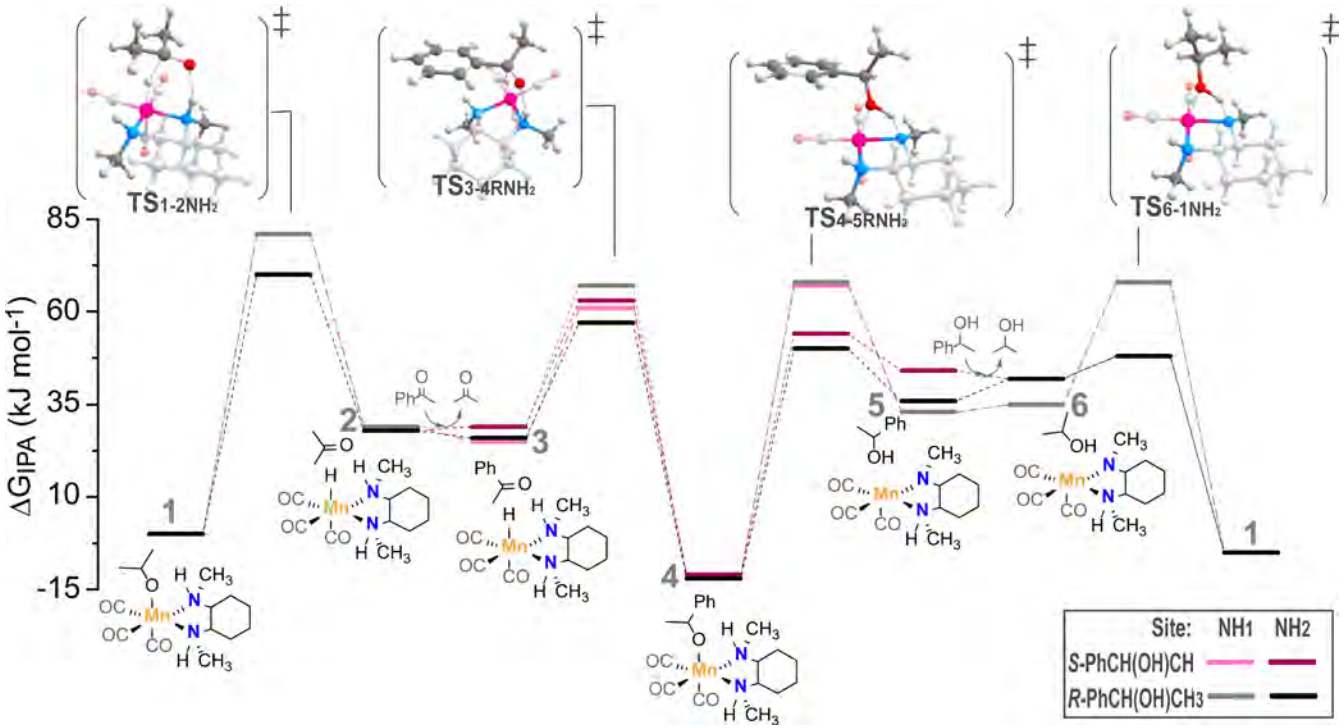
- Intrinsic reactivity is condition-independent
- PES depends on compositions and concentrations
- HetCat: lateral interactions

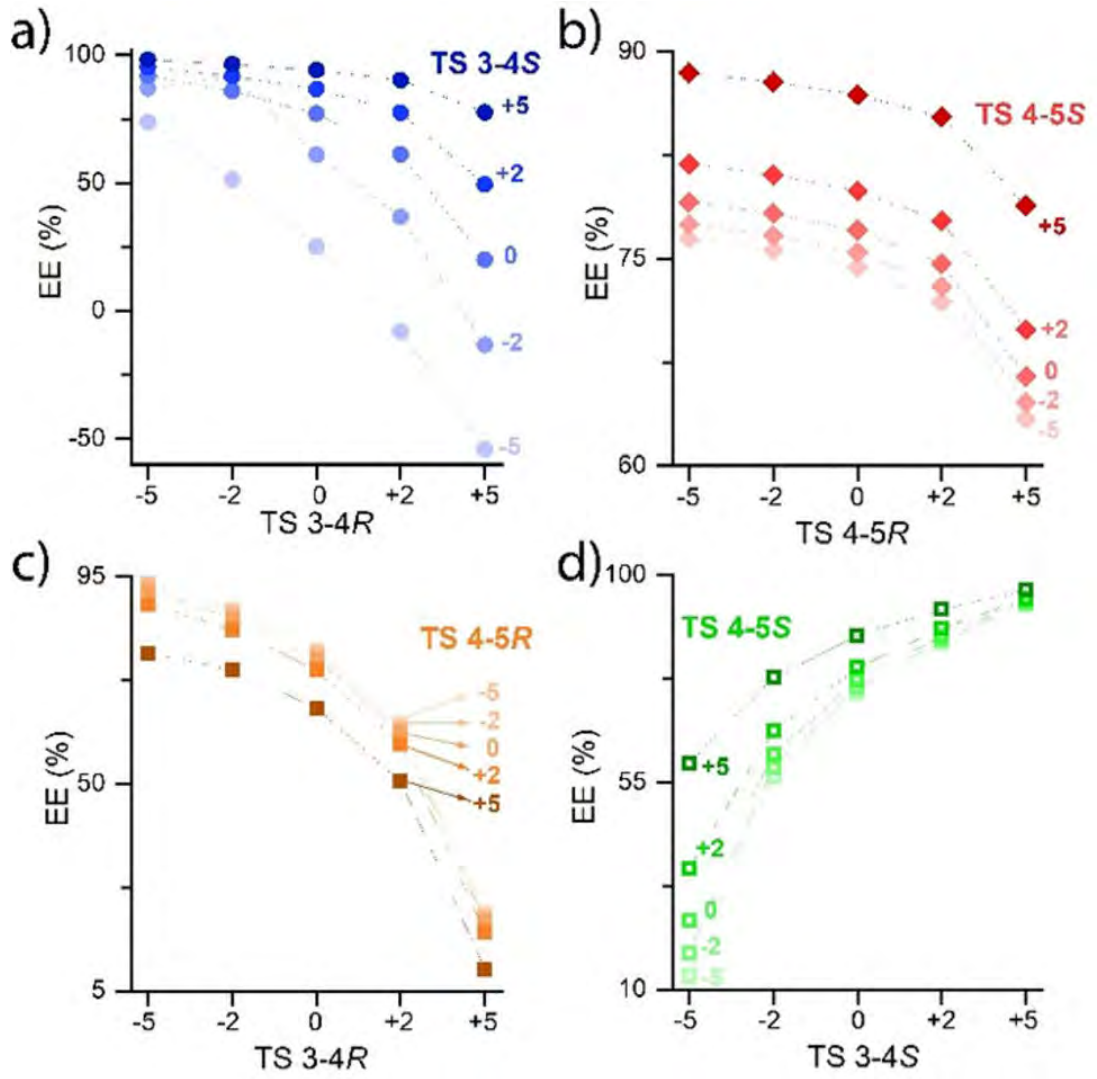


A. M. Krieger, P. Kuliaev, F.Q. Armstrong Hall, D. Sun, **EAP**, *JPC C* **2020**, *124*, 26990

What about errors in our energies?



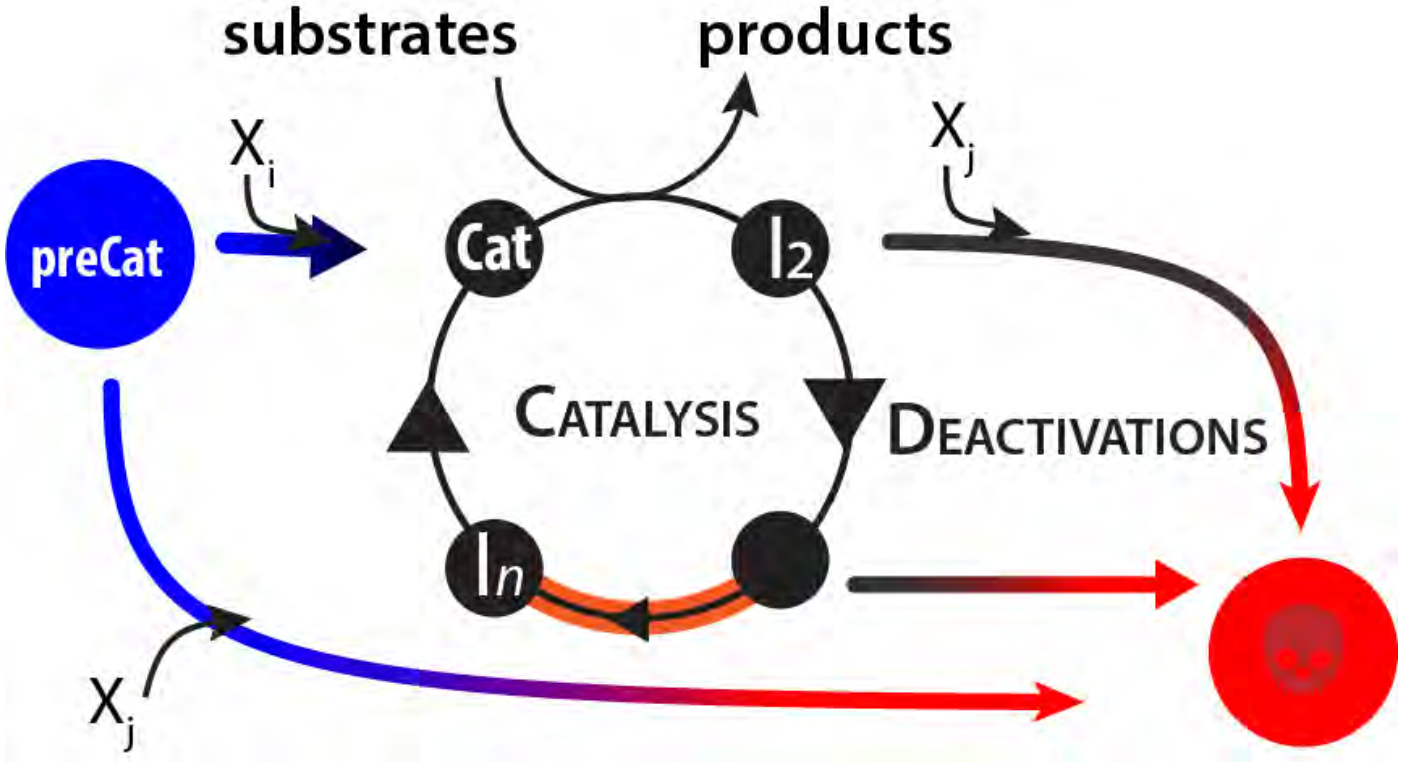




A. M. Krieger, **EAP**, *ChemCatChem* **2021**, *13*, 3517

Everything depends on everything… should we give up?

Once again: the predictive model of a catalytic process



$$r_i = k_{\mathrm{f},i} \prod_{j=1,n_j<0}^{j=N} C_j^{-n_j} - k_{\mathrm{r},i} \prod_{j=1,n_j>0}^{j=N} C_j^{n_j}$$

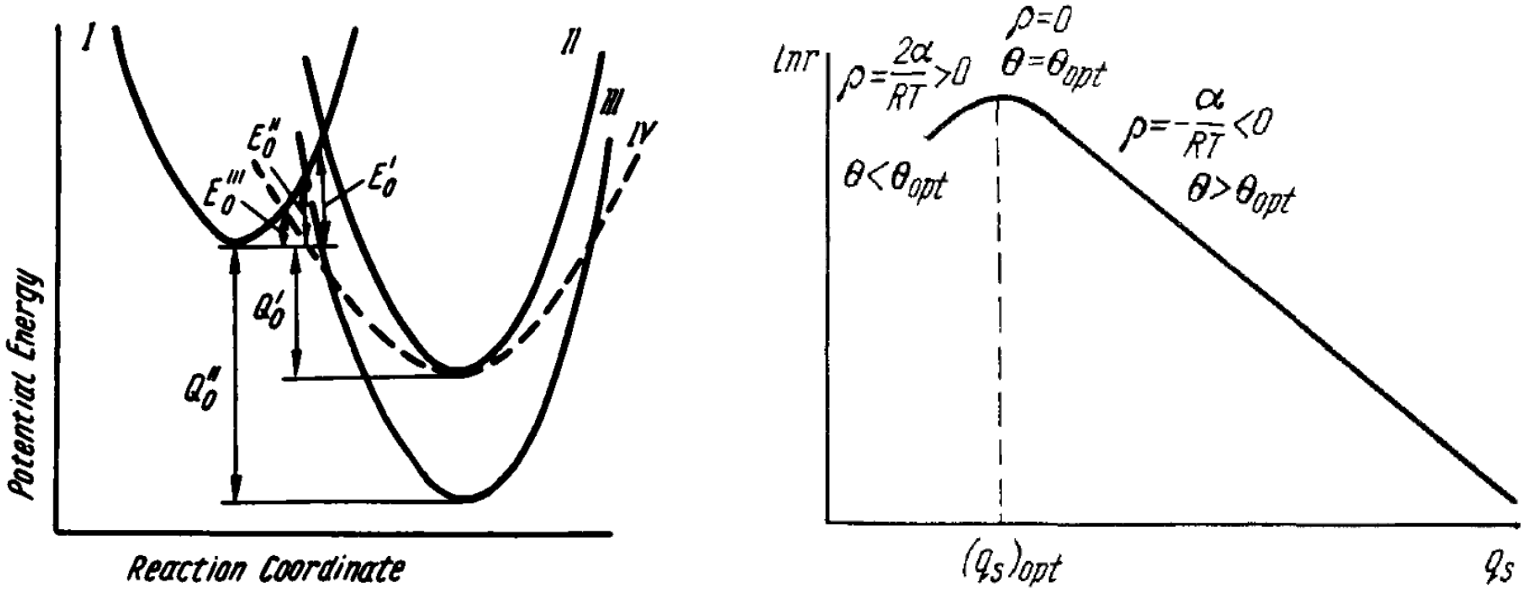
$$k = \frac{k_B T}{h} e^{-\Delta G^{\ddagger}/RT}$$

- Unrealistic to compute or measure all barriers for all paths and all catalysts
- Minor errors in energy calculations give major effects
- Condition-dependencies of the reates?
- Let's look at a single **rate-determining step**!
- Let's **reduce a kinetic problem to thermodynamics**!

(Bell)-Brønsted–(Evans)–Polanyi-(Semenov)-(Temkin)

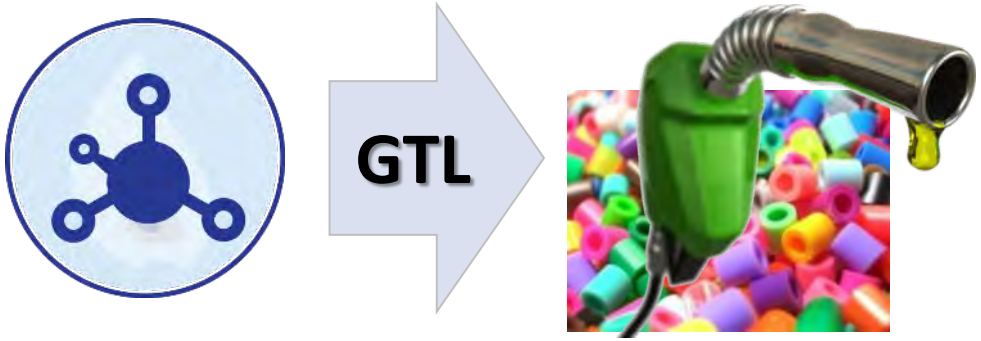
The Brönsted - Polanyi - Semenov - Temkin Relation

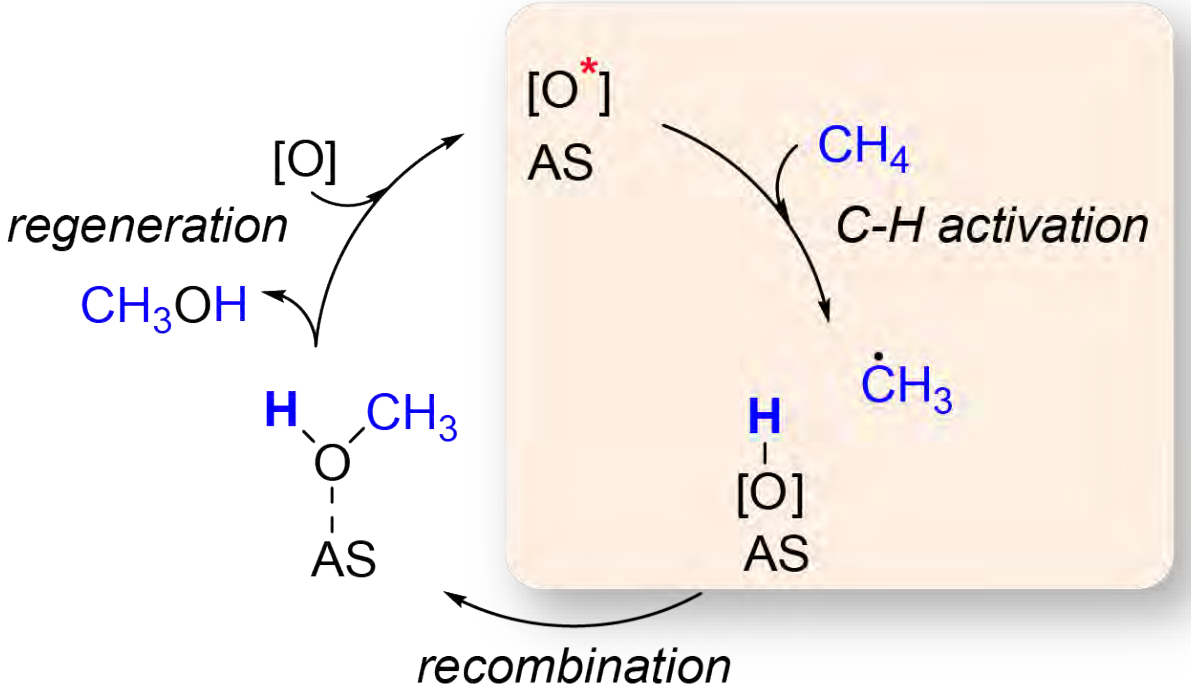
It is accepted that kinetic problems may not be solved by the methods of thermodynamics for the latter do not consider time dependences. Nevertheless, relationships between thermodynamic and rate characterisctics of reactions do exist under definite conditions, usually when ions or radicals participate in a process. The



G.I. Golodets, *Stud. Surf. Sci. Catal.* Vol. 15, **1983**

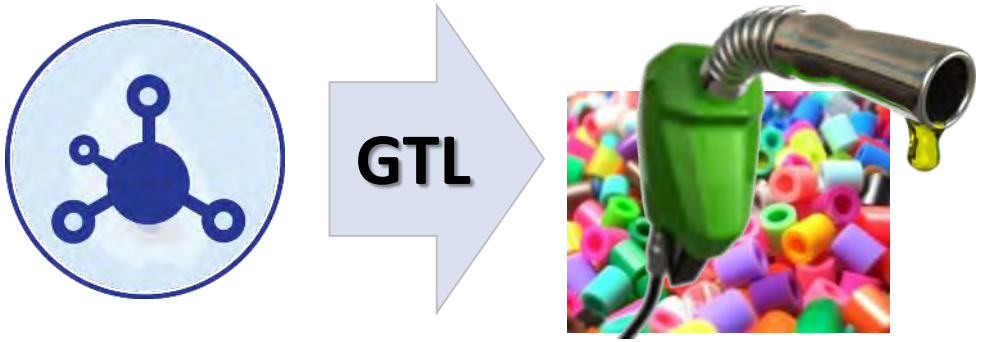
Looking for activity descriptors: CH_4 activation as a model

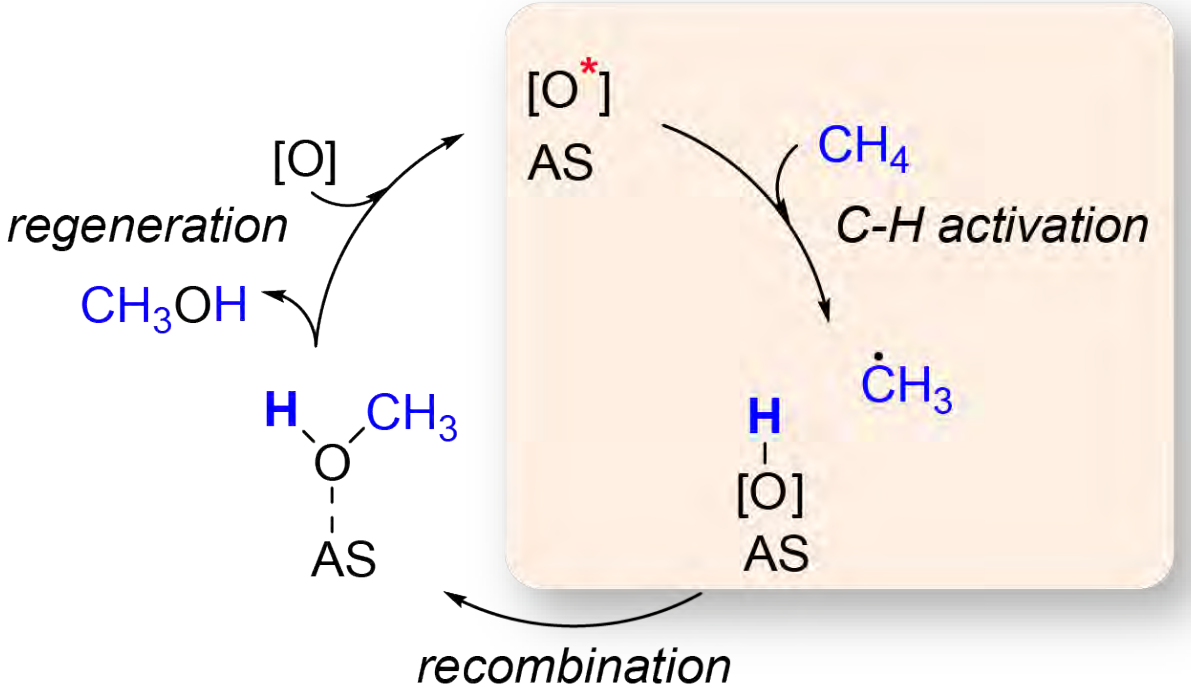


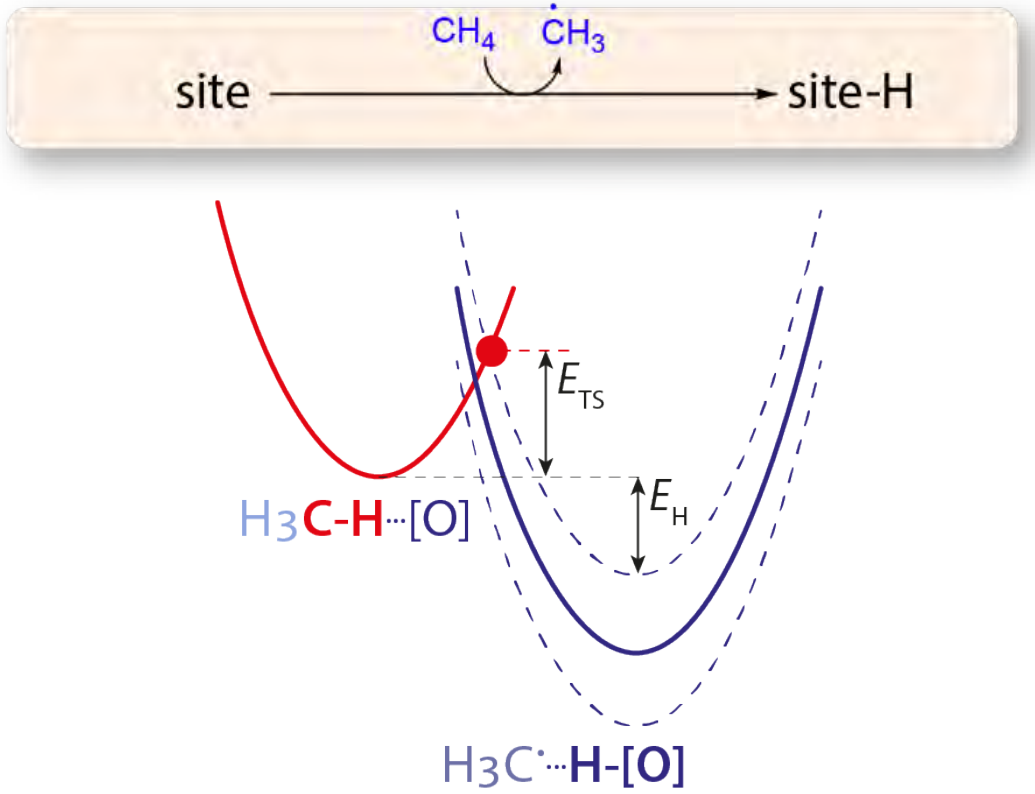


G.I. Golodets, *Stud. Surf. Sci. Catal.* Vol. 15, **1983**
Olivos-Suarez, Szécsényi, Ruiz-Martinez, **EAP**, Gascon, *ACS Catal.* **2016**, *6*, 2965
Latimer, Kulkarni, Aljama, Montoya, Yoo, Tsai, Abild-Pedersen, Studt, Nørskov *Nat. Mater.* **2017**, *16*, 225

Looking for activity descriptors: CH_4 activation as a model







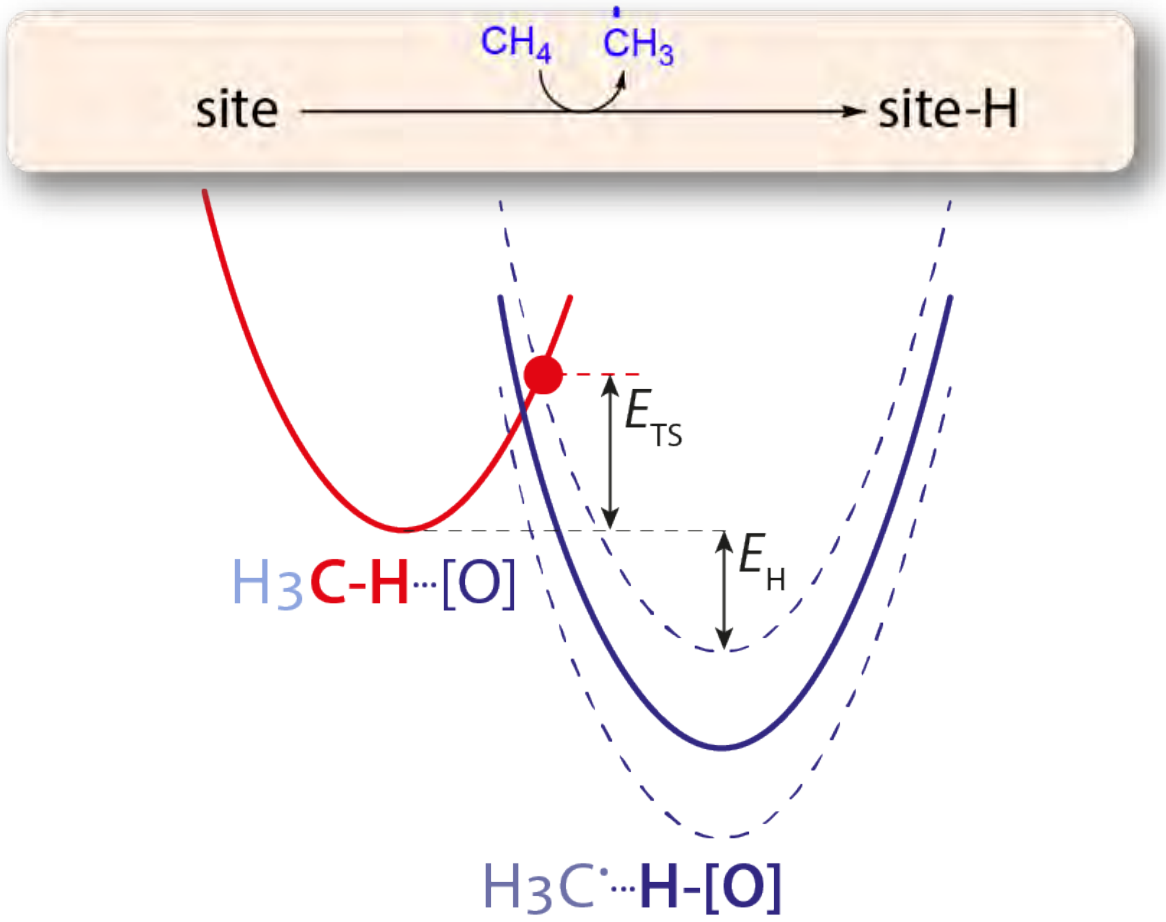
Activity ~ E_H ~ OH bond energy

G.I. Golodets, *Stud. Surf. Sci. Catal.* Vol. 15, **1983**

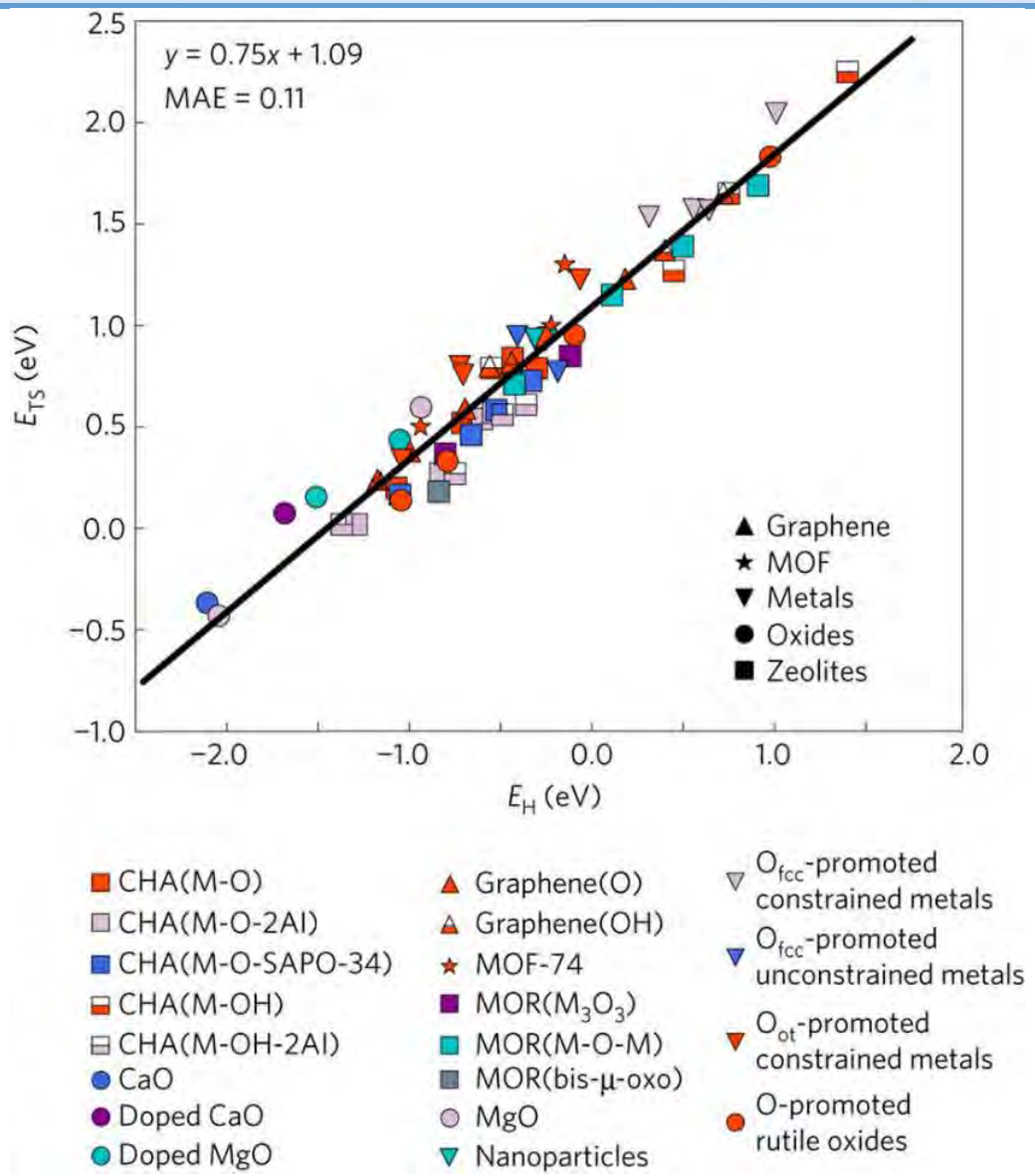
Olivos-Suarez, Szécsényi, Ruiz-Martinez, **EAP**, Gascon, *ACS Catal.* **2016**, *6*, 2965

Latimer, Kulkarni, Aljama, Montoya, Yoo, Tsai, Abild-Pedersen, Studt, Nørskov *Nat. Mater.* **2017**, *16*, 225

Property-Activity Relationships



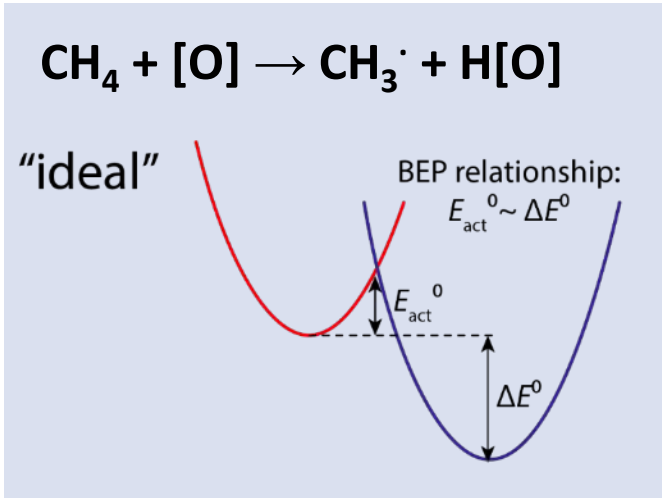
E_H ~ energy of adding **H·**; OH bond energy

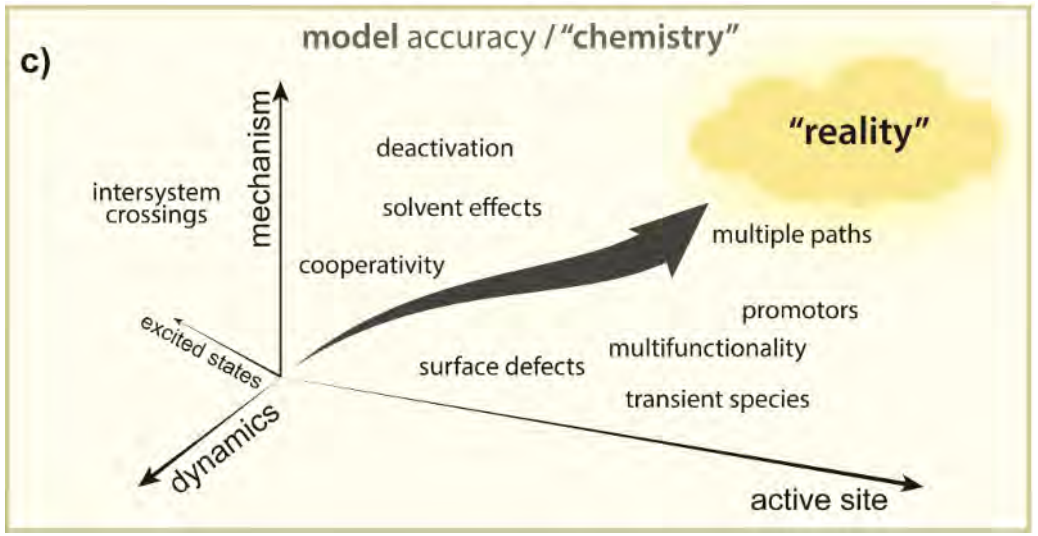


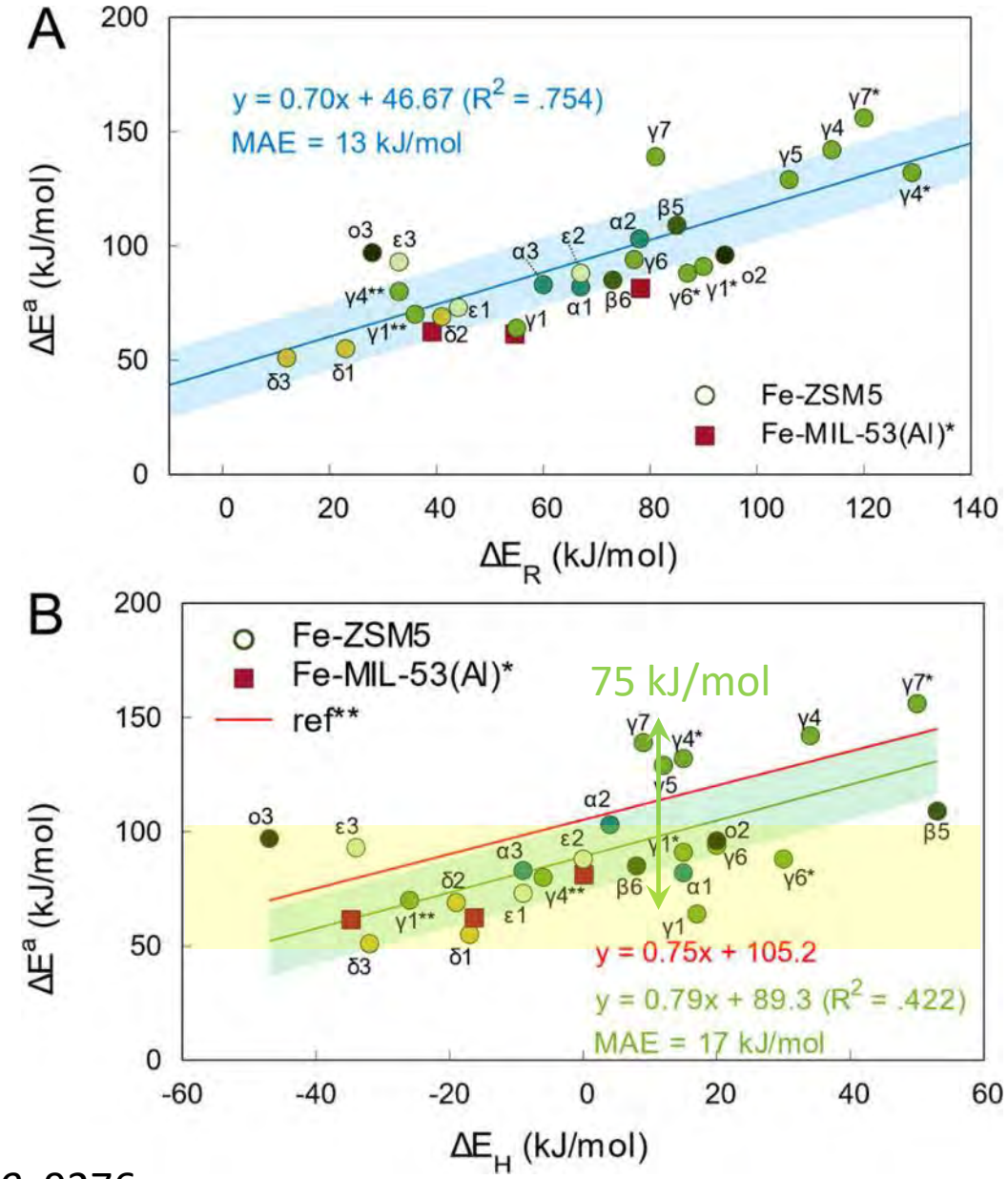
Latimer, Kulkarni, Aljama, Montoya, Yoo, Tsai, Abild-Pedersen, Studt, Nørskov *Nat. Mater.* **2017**, *16*, 225

Thermodynamic activity descriptors for catalysis

$CH_4 + [O] \rightarrow CH_3^{\cdot} + H[O]$



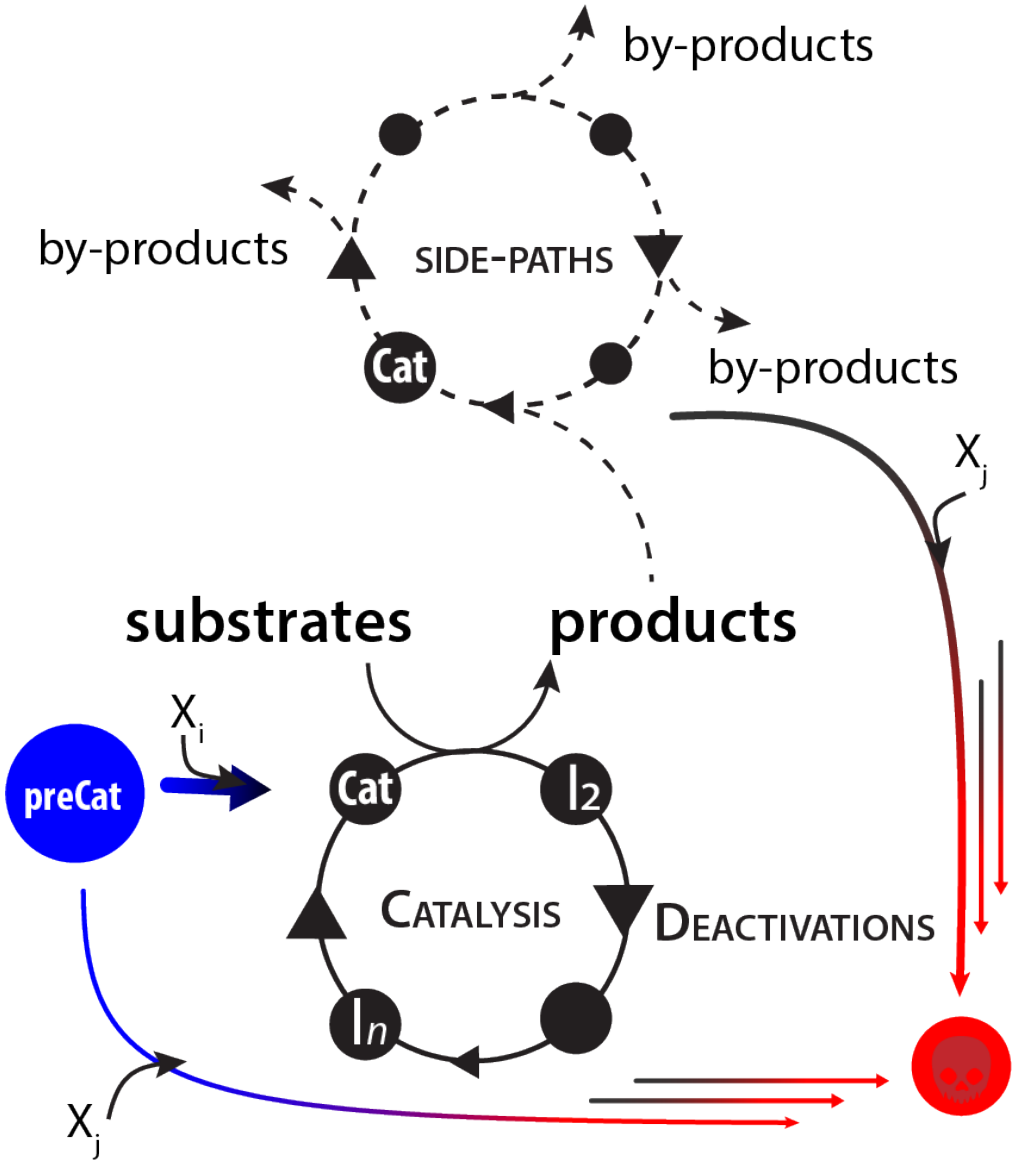




EAP, *ACS Catal.* **2017**, *7*, 4230

Szécsényi, Khramenkova, Chernyshov, Li, Gascon, EAP, *ACS Catal.* **2019**, *9*, 9276

It is not a single step…



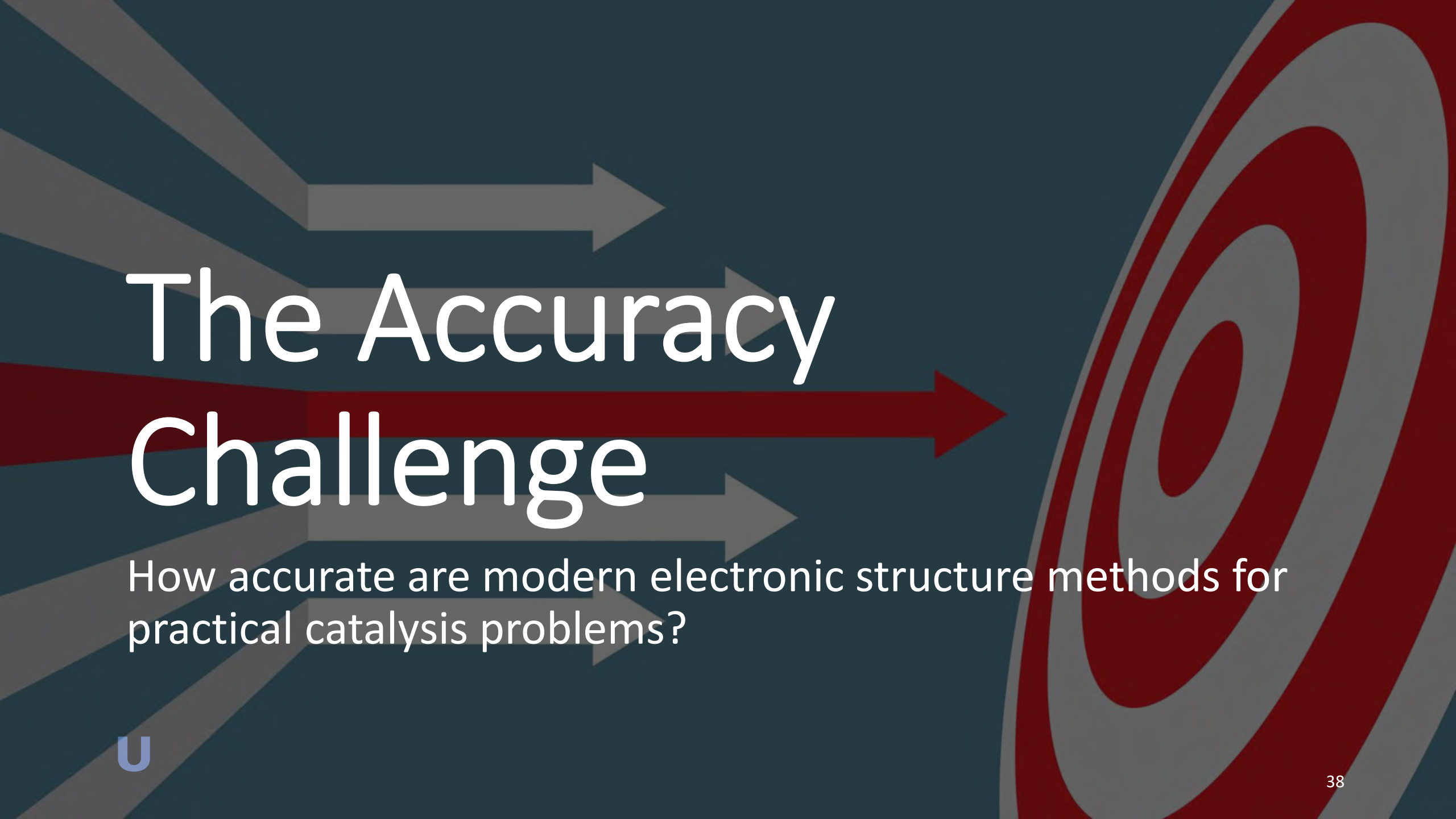
See e.g. Szécsényi, Li, Gascon, **EAP**, *ACS Catal.* **2018**, *8*, 7961

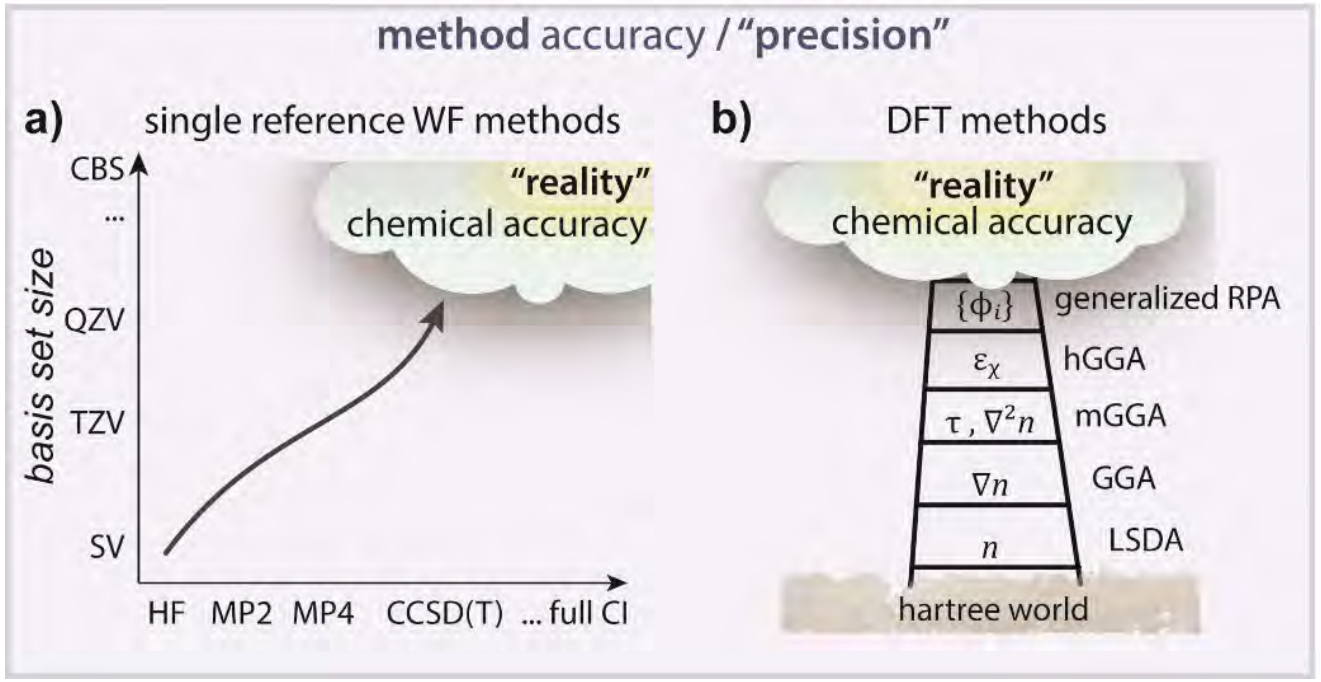
Summary #1: Predictive theory for catalyst design

- Catalysis: everything depends on everything!
- Accuracy is key for predictive modeling in chemistry and catalysis
- Kinetic problem of complex reaction networks
- We always operate with models, which are incomplete
- Key question is to figure out what “feature” is important
- We need to **assume** possible active sites & mechanisms

The Accuracy Challenge

How accurate are modern electronic structure methods for practical catalysis problems?





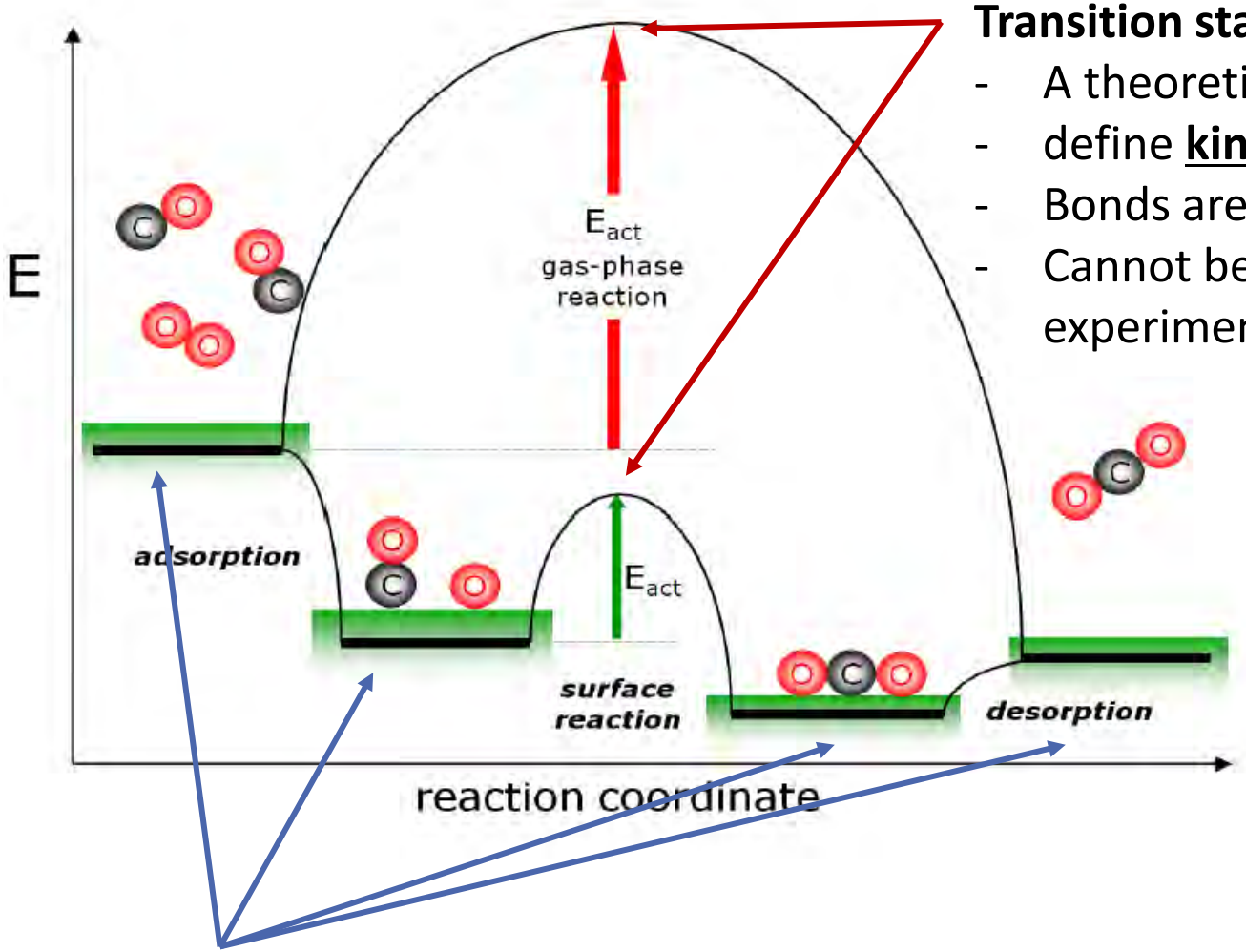
Computational Spectroscopy & Catalysis

Method accuracy in computational catalysis

Is our theory good enough?

EAP, *ACS Catal.* **2017**, *7*, 4230

Potential energy surface & experimental chemistry

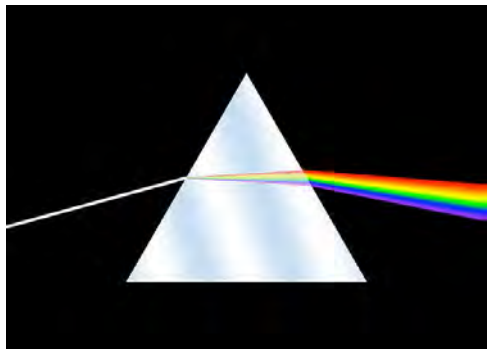


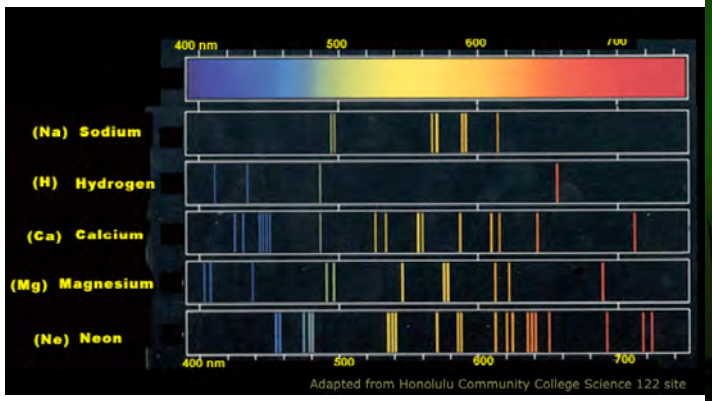
Transition states:

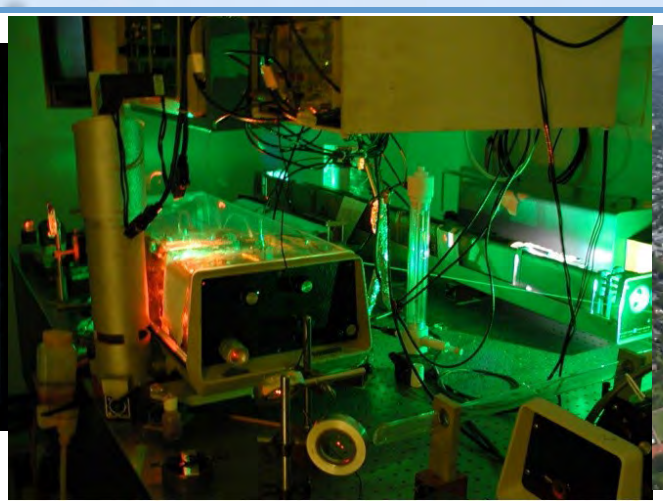
- A theoretical construct
- define **kinetics**
- Bonds are semi-broken/formed
- Cannot be probed directly with an experiment.

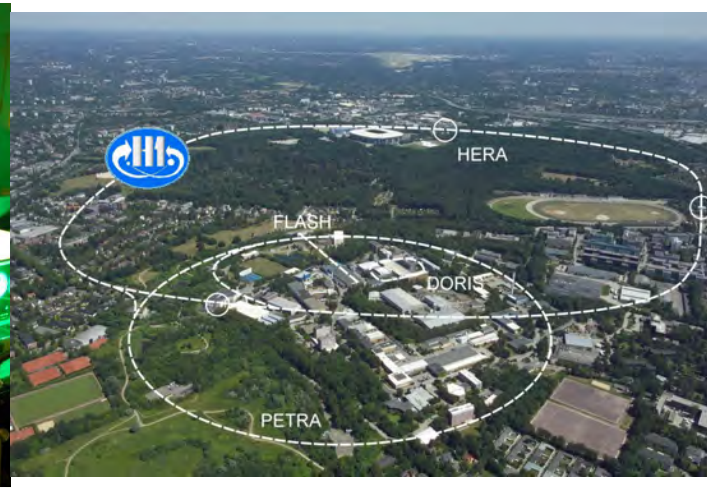
Intermediates / stable states:

- can be directly characterized by physico-chemical methods
- define **thermodynamics** (overall, elementary steps)
- contain intact bonds => thermodynamics ~ change in bond energies





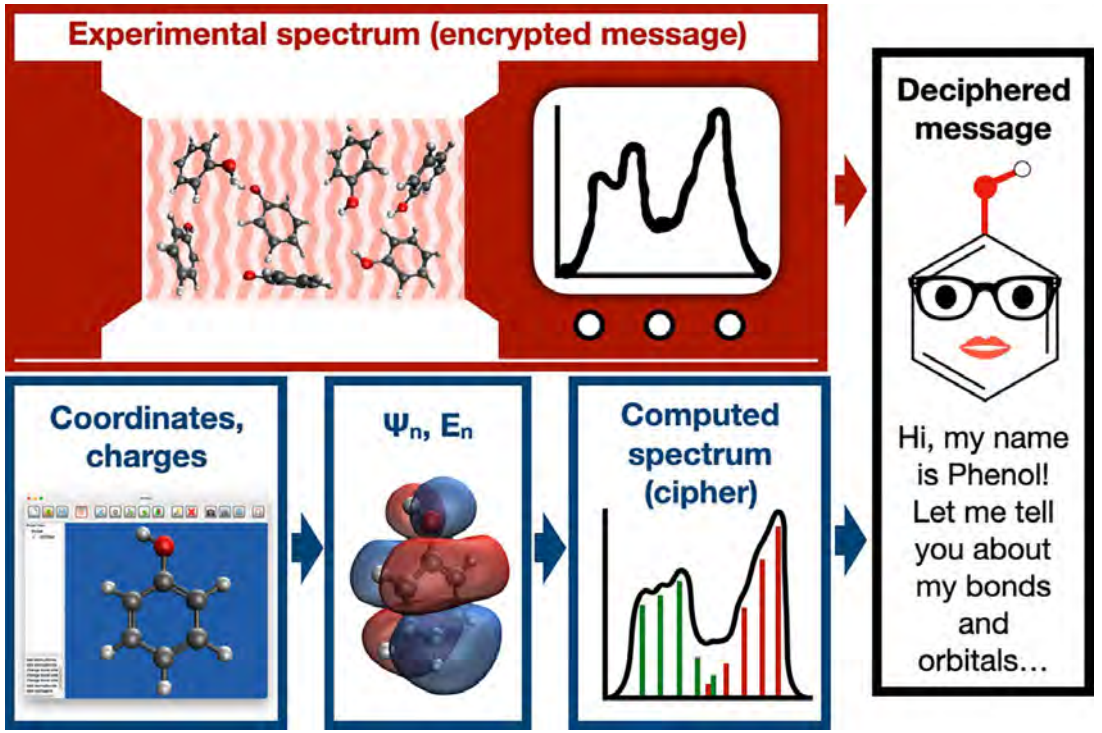




- Light + material = spectrum

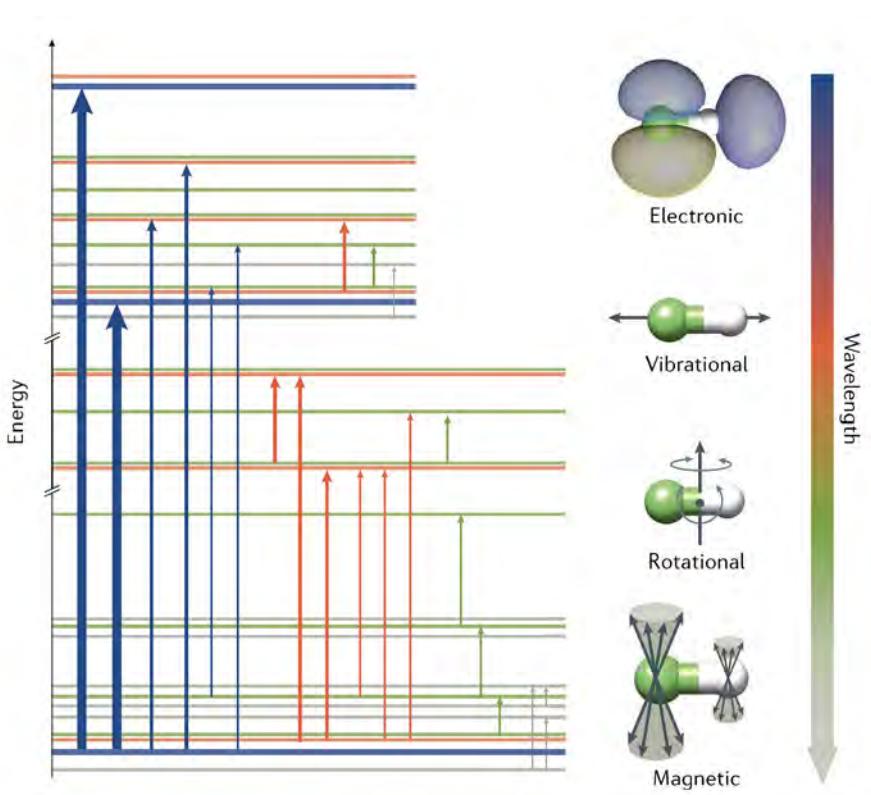
- The spectrum is the response of material to the irradiation

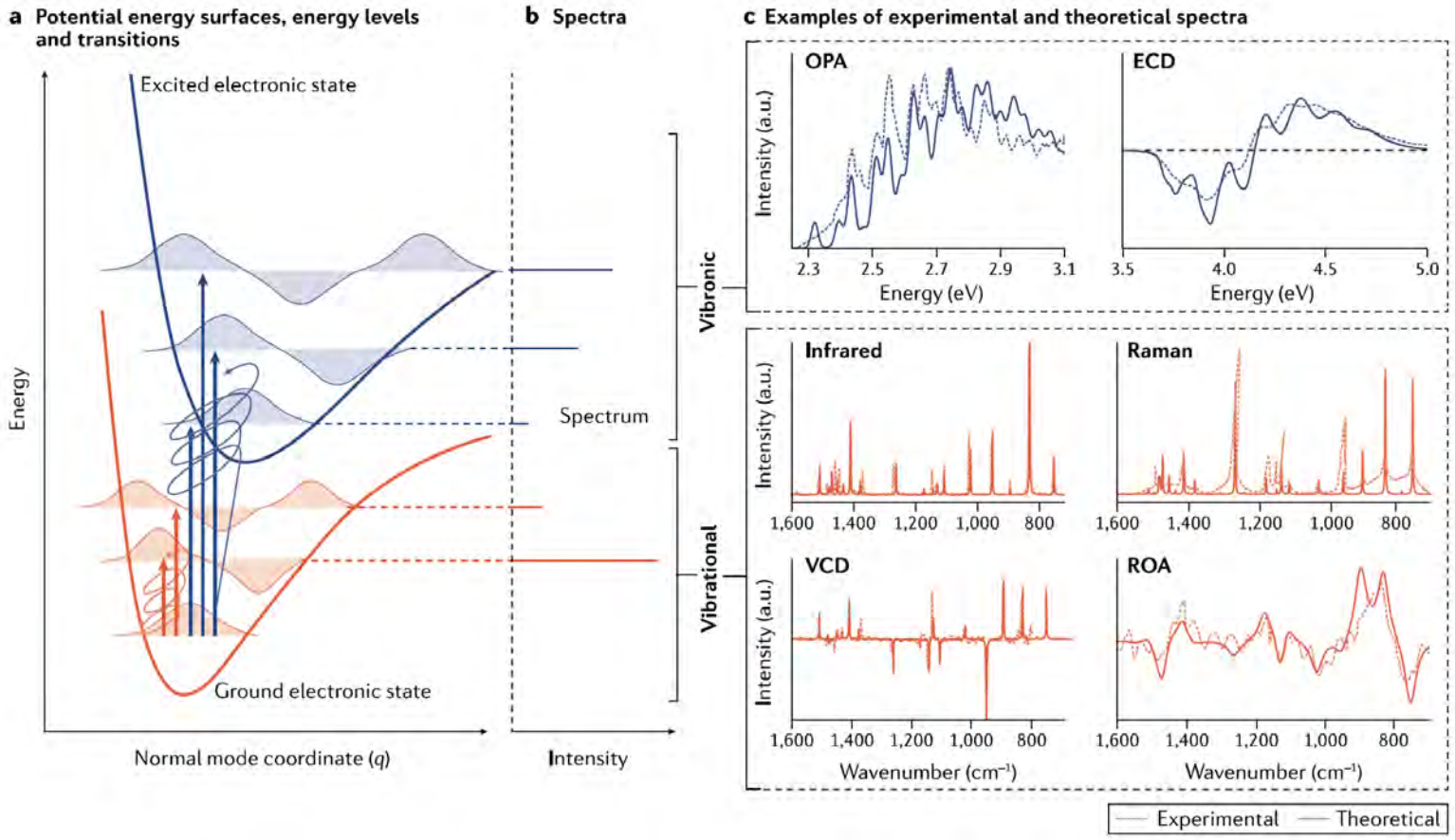
- The theory is a key for deciphering the message



A. I. Krylov, Q-Chem workshop, 2024

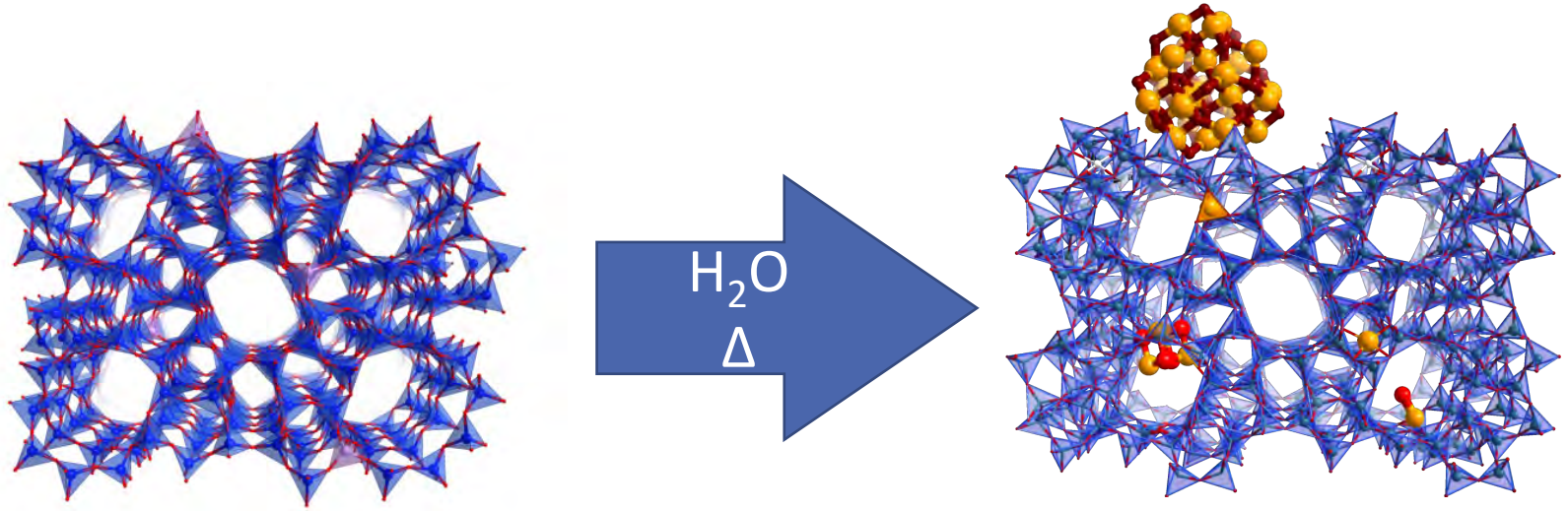
DFT and Characterization: *Computational Spectroscopy*





Puzarini et al, *Nat. Rev. | Methods Primers* **2021**, *1*, 38

The structural problem of ZeoCAT: a computational approach



Key assumptions:

- Perfect crystallinity
- Homogeneous speciation
- DFT is good enough

The conventional workflow:

- Expert proposes structures
- Calculate structures & energies with DFT: *PES at vacuum / 0K*
- **Compute spectroscopic signatures**
- Add conditions via ab initio thermodynamic analysis: *Free energies*

Overview of the approach: G. Li, **EAP**, *ChemCatChem* **2018**,*11,* 134
Cu: G. Li, P. Vassilev, M. Sanchez-Sanchez, J. Lercher, E.J.M. Hensen, **EAP**, *J. Catal.* **2016**, *338*, 305
Al: C. Liu, G. Li, E.J.M. Hensen, **EAP**, *ACS Catal.* **2015**, *5* ,7024
Mo: G. Li, I. Vollmer, C. Liu, J. Gascon, **EAP**, *ACS Catal.* **2019**, *9*, 8731

“Sample” preparation for catalyst characterization

- **Experiment:**
  - Sample – Spectrometer – Response - Spectrum
- **Theory:**
  - Model – “Spectrometer” (perturbation) – Response – Spectral data

1. FTIR

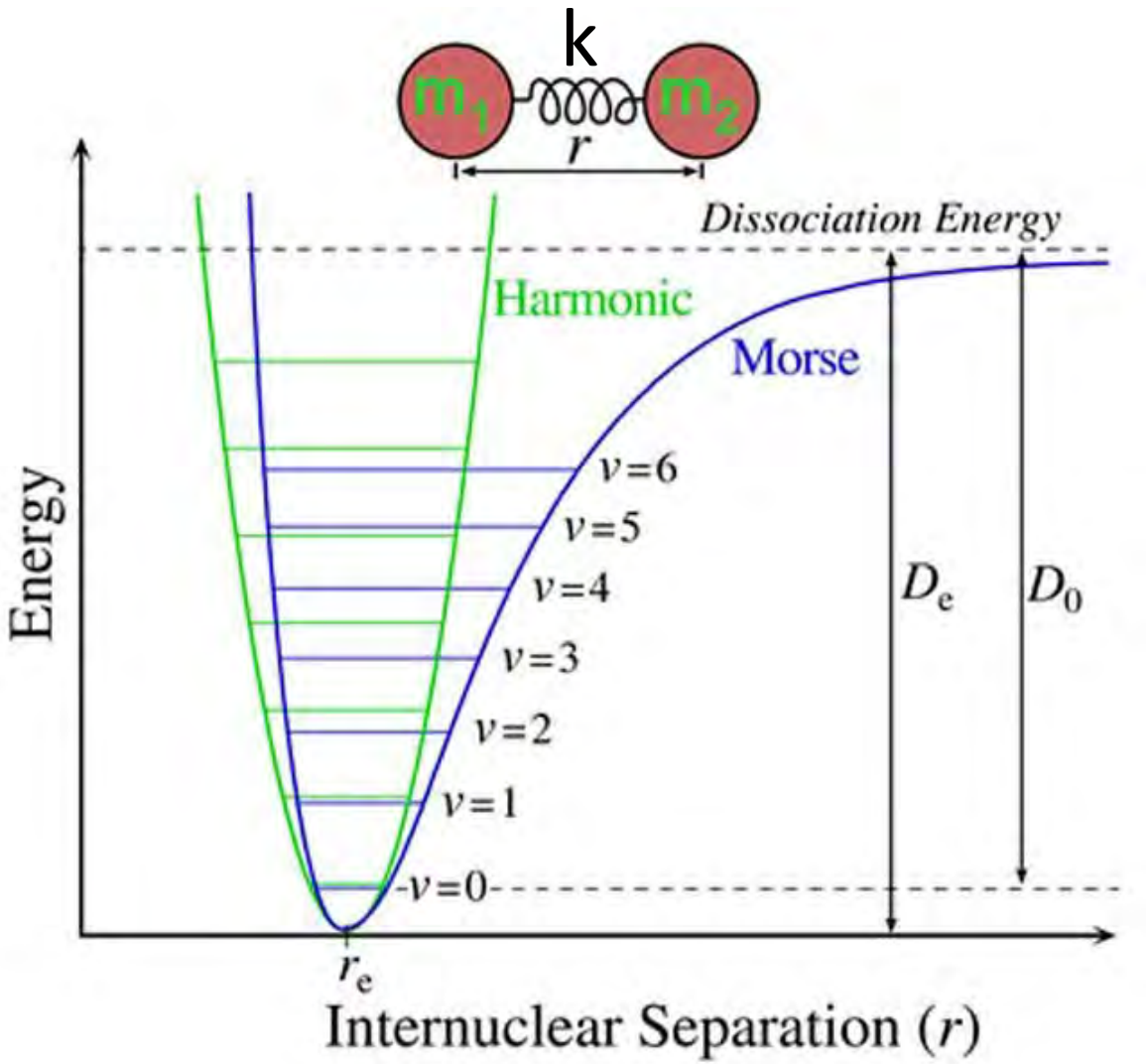
2. SS NMR

3. Uv-DRS

4. XANES/EXAFS

5. What else?

FTIR: harmonic approximation



Molecule = atomic dipole oscillator

Force constant: $d^2E/dx^2 = k$

Vib. frequency: $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$;

Reduced mass: $\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$

Intensity ~ change in dipole moment

FTIR: harmonic approximation

Vib. frequency:

$$\nu = \frac{1}{2\pi}\sqrt{\varepsilon}$$

Make a small displacement of each atom: ±x; ±y; ±z

Optimized geometry

$$\mathbf{H} = \begin{pmatrix} \frac{\partial^2 E}{\sqrt{m_1}\sqrt{m_1}\partial q_1 \partial q_1} & \cdots & \frac{\partial^2 E}{\sqrt{m_n}\sqrt{m_1}\partial q_n \partial q_1} \\ \vdots & \ddots & \vdots \\ \frac{\partial^2 E}{\sqrt{m_1}\sqrt{m_n}\partial q_1 \partial q_n} & \cdots & \frac{\partial^2 E}{\sqrt{m_n}\sqrt{m_n}\partial q_n \partial q_n} \end{pmatrix}$$

Hessian matrix

Output: harmonic freqs

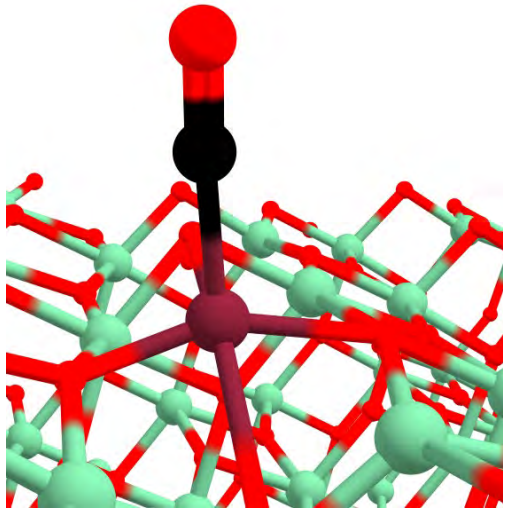
30: 1895.23 cm**-1
31: 2204.75 cm**-1
32: 2212.35 cm**-1
33: 2213.98 cm**-1
34: 2225.94 cm**-1
35: 2296.40 cm**-1

$k_1, k_2 \ldots k_n$

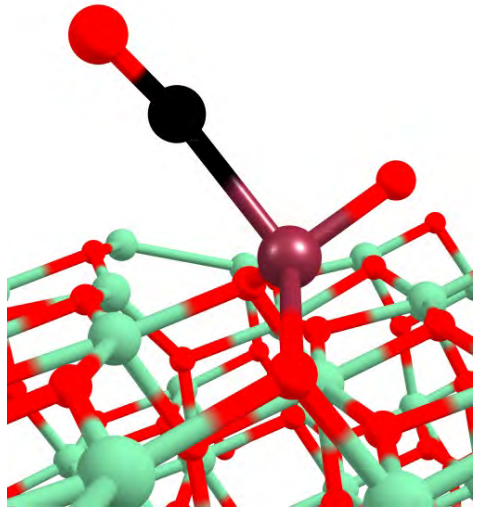
Total $3 \times N_{atoms}$ eigenvalues

Accuracy and the comparison with experiment

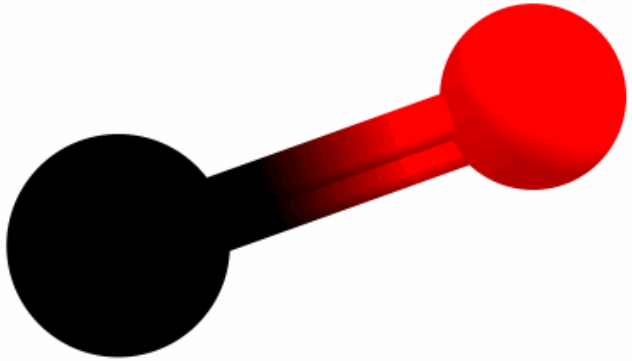
- Calculated harmonic vibrational frequencies systematically deviate from experimental vibrational frequencies.



$CO@Re/TiO_2$



$CO@ReO/TiO_2$



$$k_{scaling} = \frac{\nu_{\mathbf{exp.}}(CO_{\text{gas-phase}})}{\nu_{\mathbf{DFT}}(CO_{\text{gas-phase}})}$$

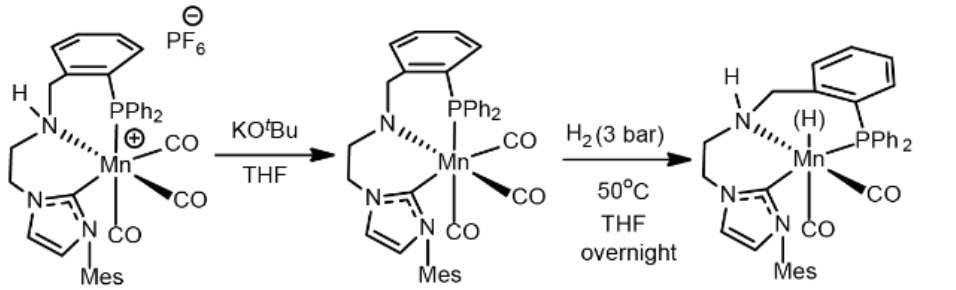
$\nu_{DFT}(CO_{ads})$

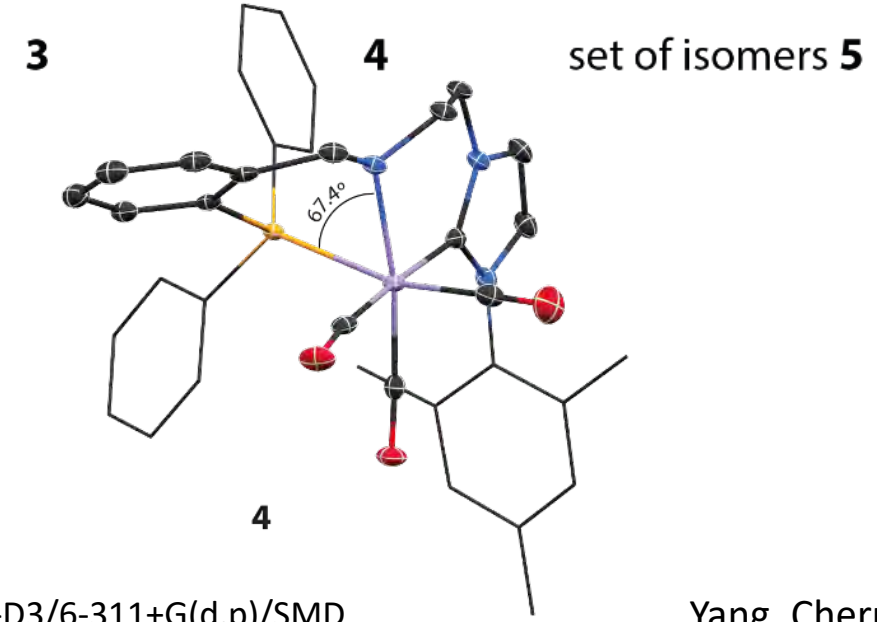
$\nu_{DFT}(CO_{ads})$

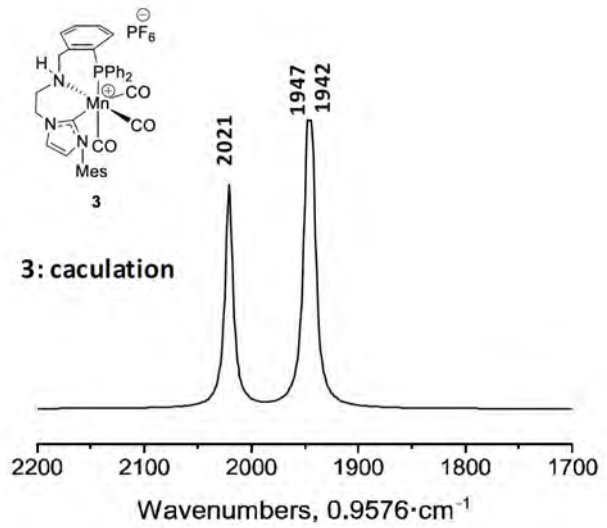
$$^{\mathbf{CORR}}\nu_{DFT}(CO_{ads}) = k_{scaling} \times \nu_{DFT}(CO_{ads})$$

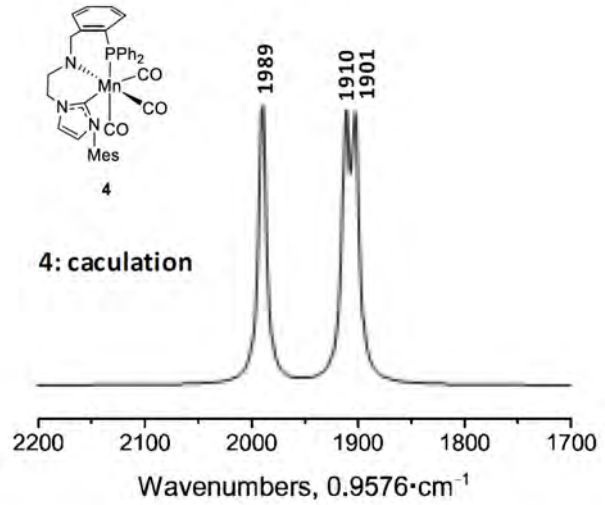
FTIR characterization of Mn(I) transformations

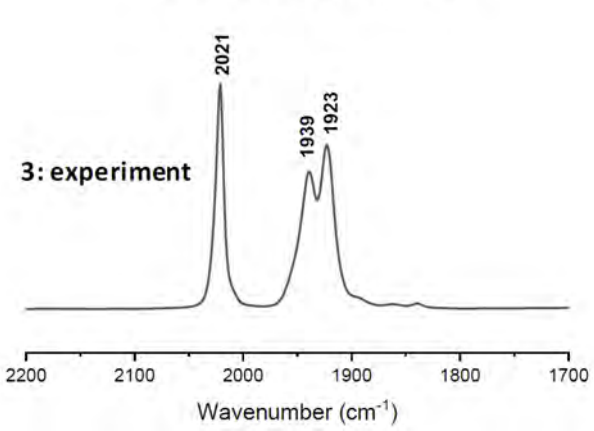
- **HomCat**: molecularly defined
- High model accuracy
- Theory vs. Experiment: ±20 cm^{-1}

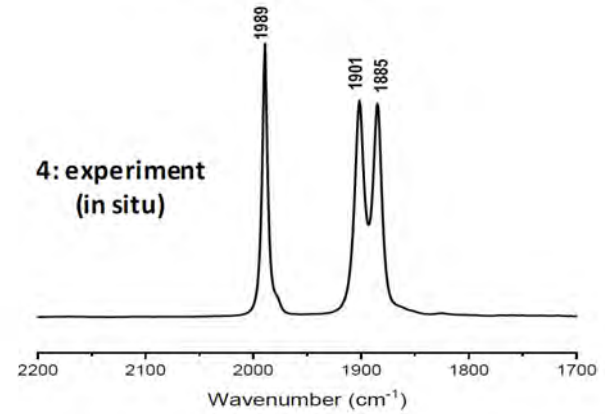








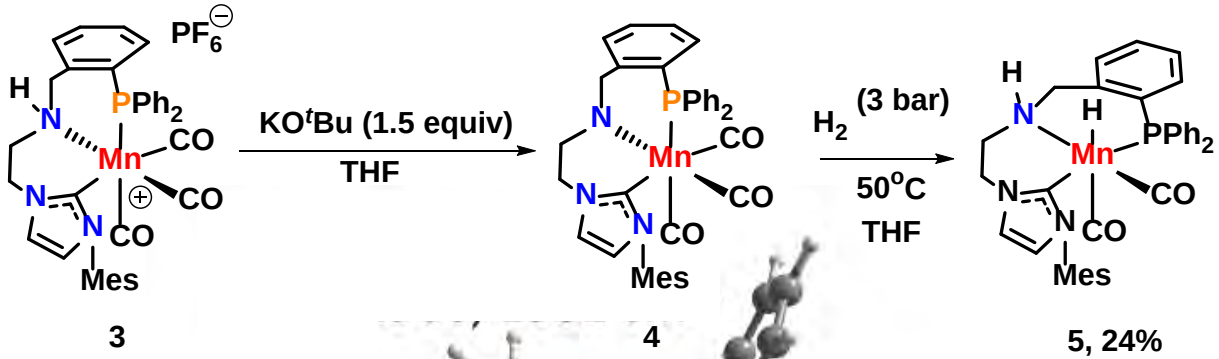




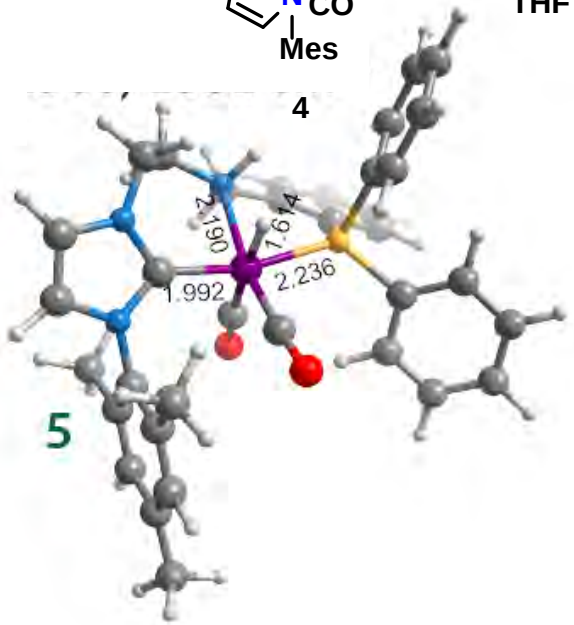
PBE0-D3/6-311+G(d,p)/SMD

Yang, Chernyshov, van Schendel, Weber, Müller, Filonenko, ***EAP***, *Nat. Commun.* **2021**, *12*, 12

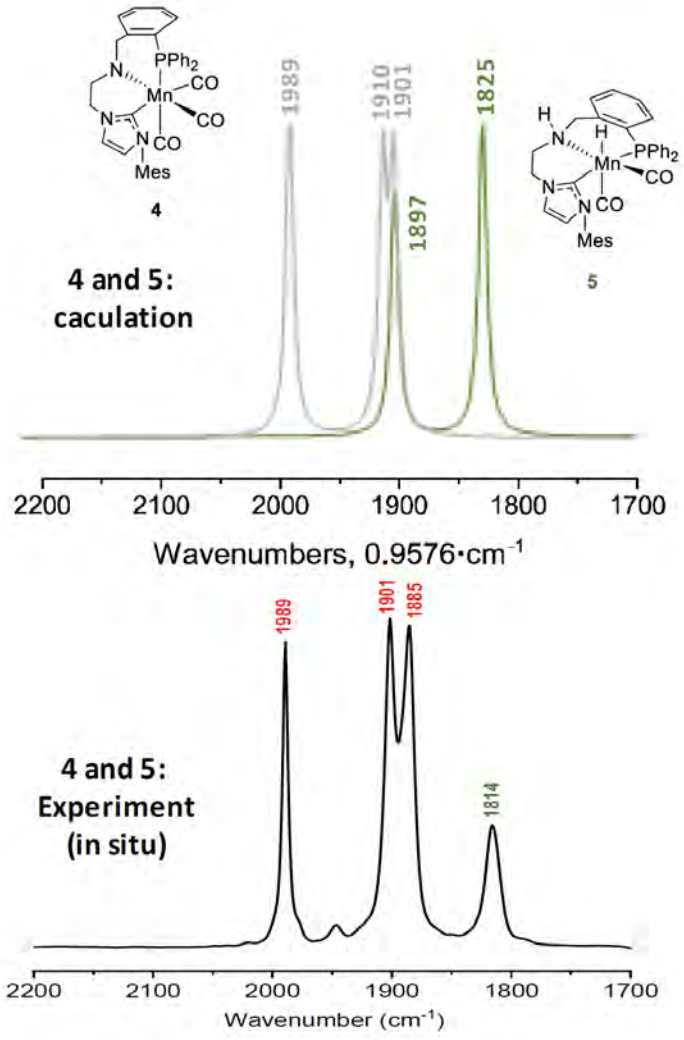
Theory helps rationalize the experiment



3 4 5, 24%



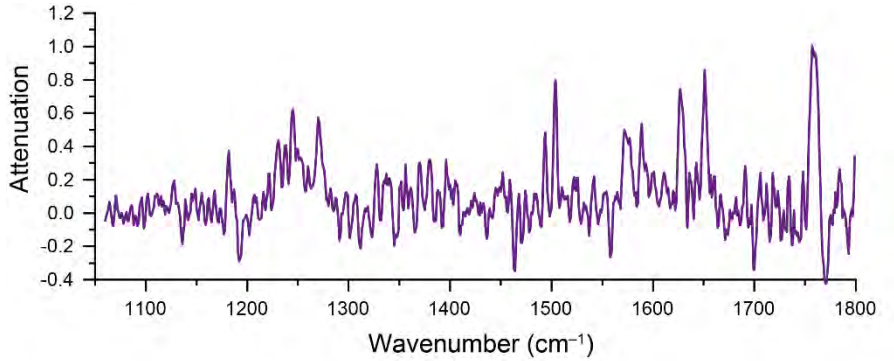
Complex	Experiment hydride (ppm)	Caculated hydride (ppm)
5	-3.46, -3.49	-3.38

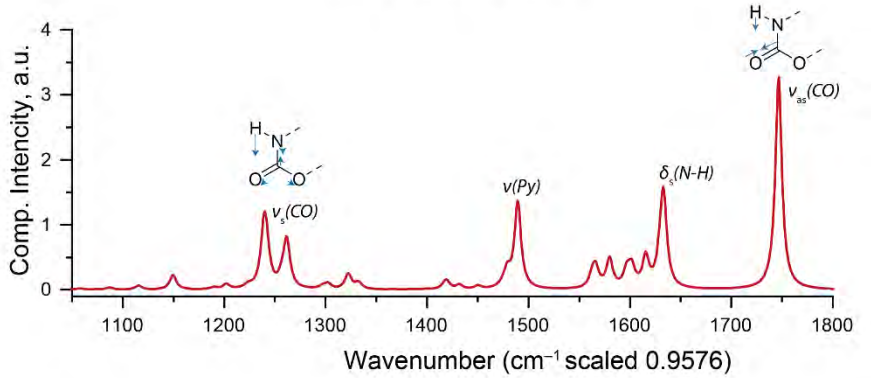


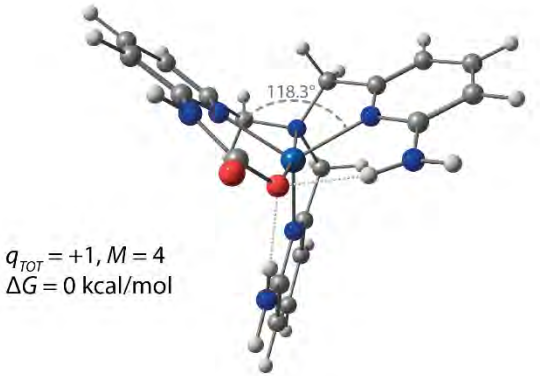
Yang, Chernyshov, van Schendel, Weber, Müller, Filonenko, ***EAP***, *Nat. Commun.* **2021**, *12*, 12

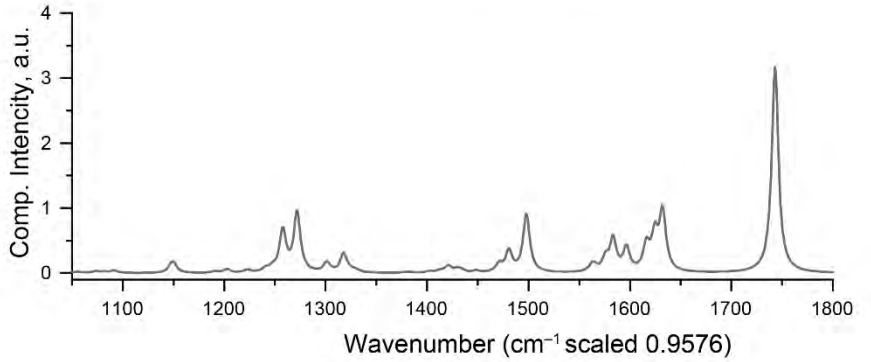
A few more successful examples: #2 - electrochemistry

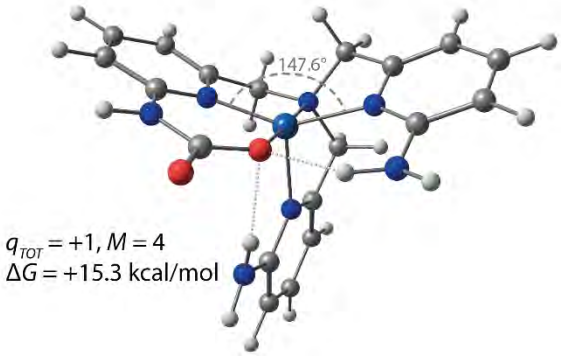
CO_2 electroreduction
by HomCat
in situ monitoring by
IR-EC-MS





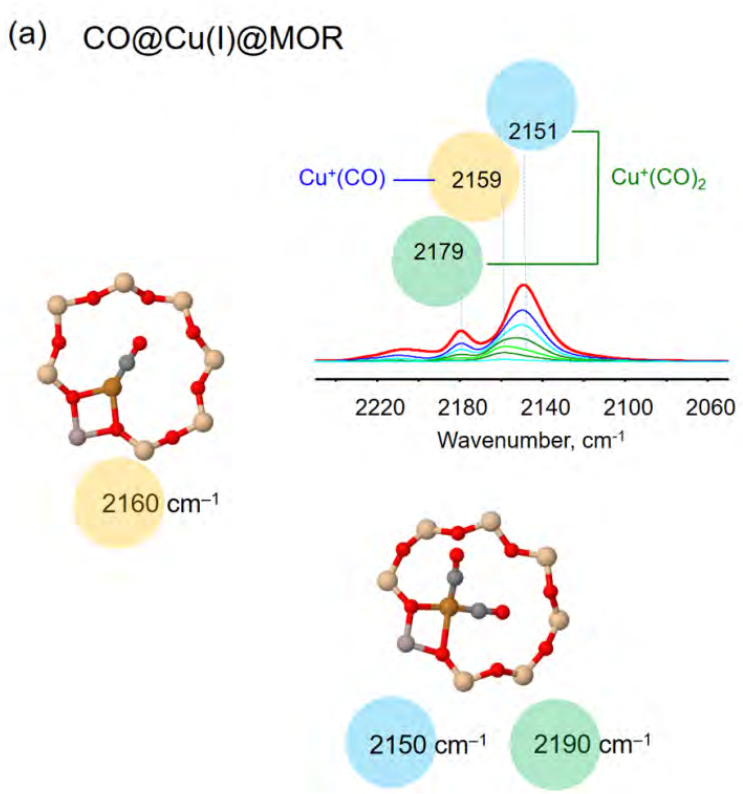


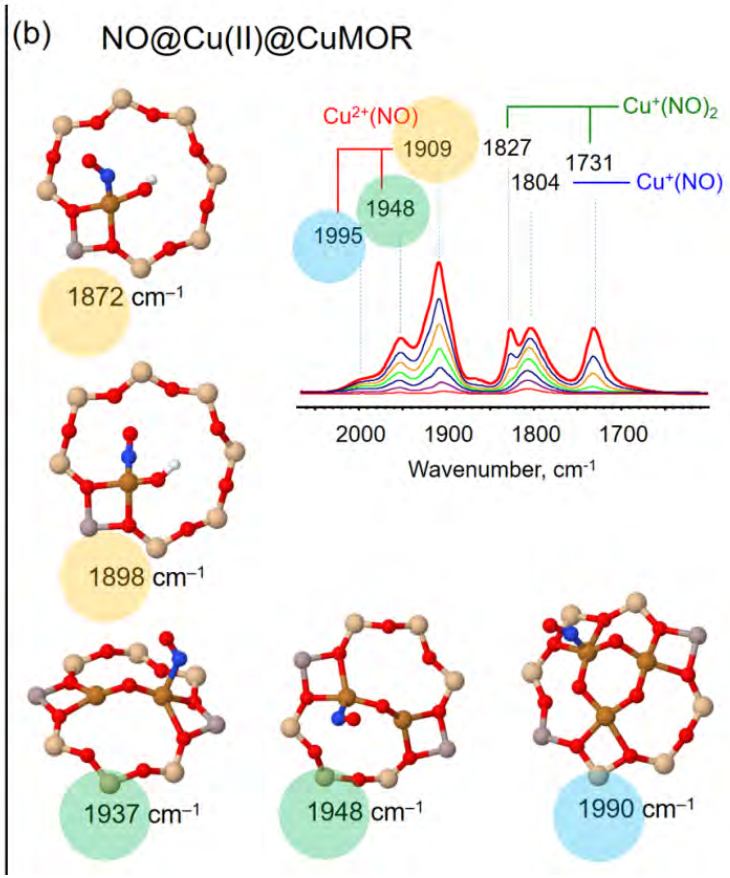




A. Bairagi, A.Y. Pereverzev, P. Tinnemans, EAP, J. Roithova, *JACS* **2024**, *146*, 5480

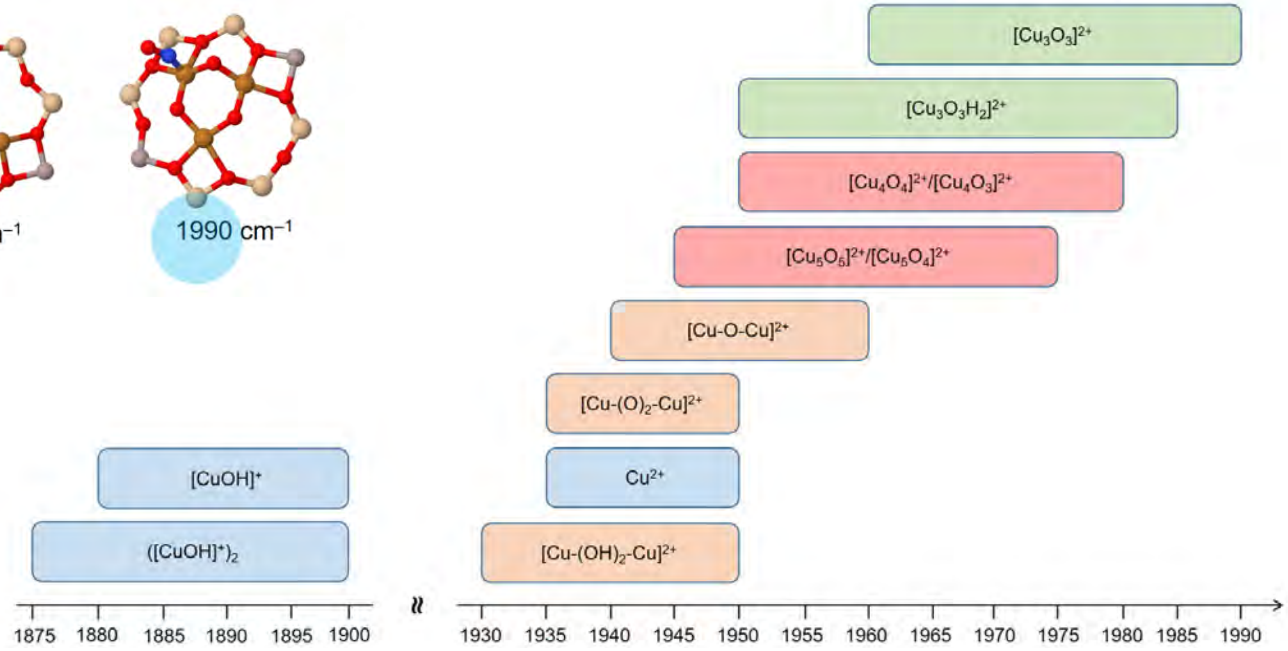
Probing Cu-sites in zeolites by CO and NO adsorption w/ FTIR and DFT





Computationally mapping the copper species by the spectroscopic signatures of their adsorption complexes w/ **NO**

Accurate prediction of the stretching modes of probe molecules



Palagin et al., JPCC, 2021

Beyond harmonic approximation

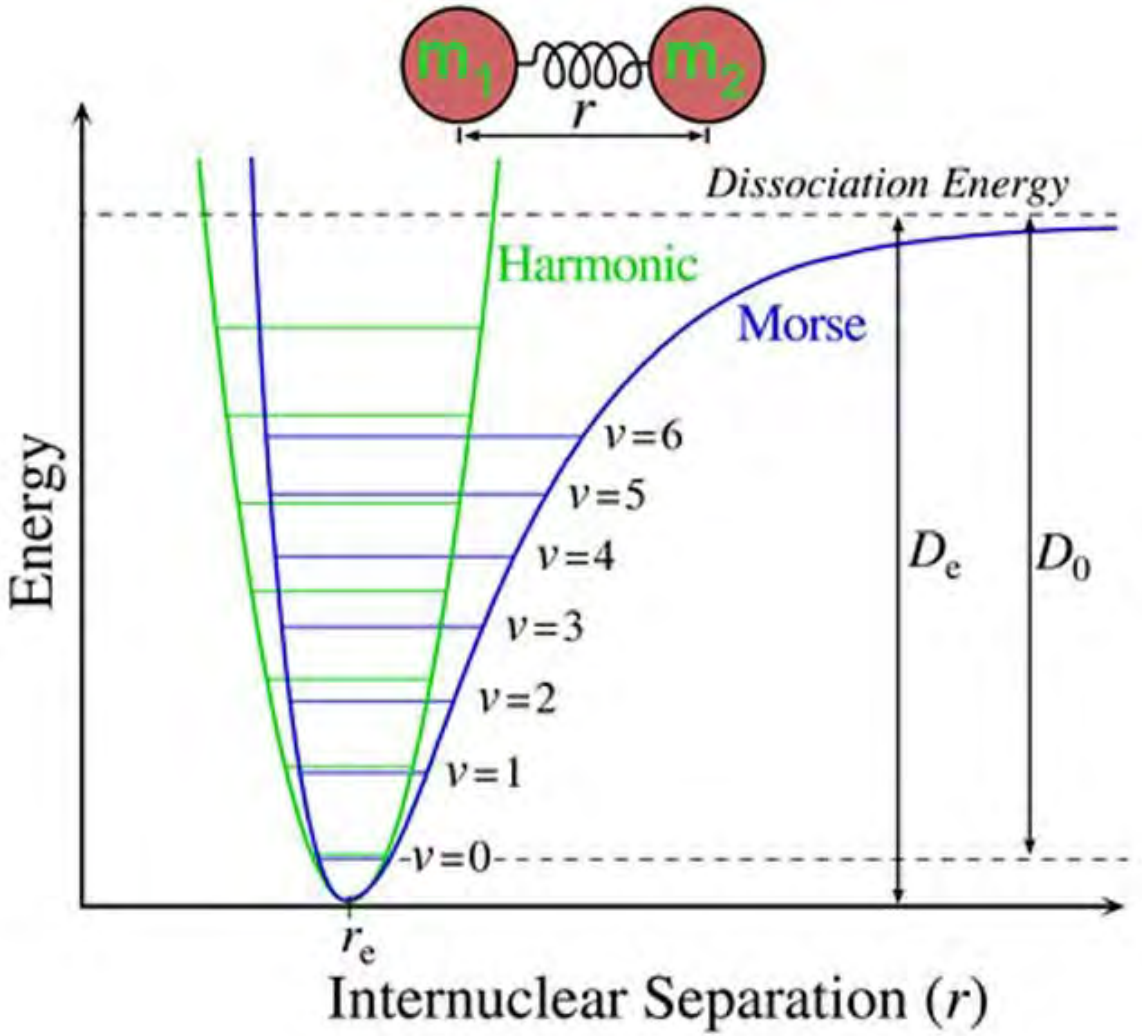
- The Harmonic Approximations is great and has proven to give good results

- But it is only an approximation, and any deviations from harmonic behavior won't be accounted for

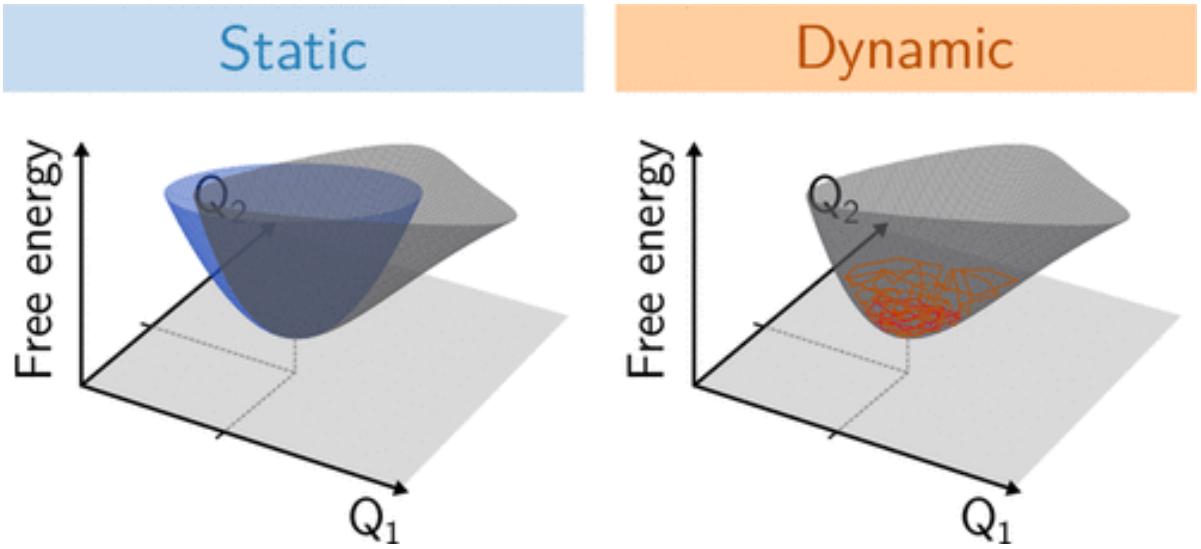
  a) Anharmonicity

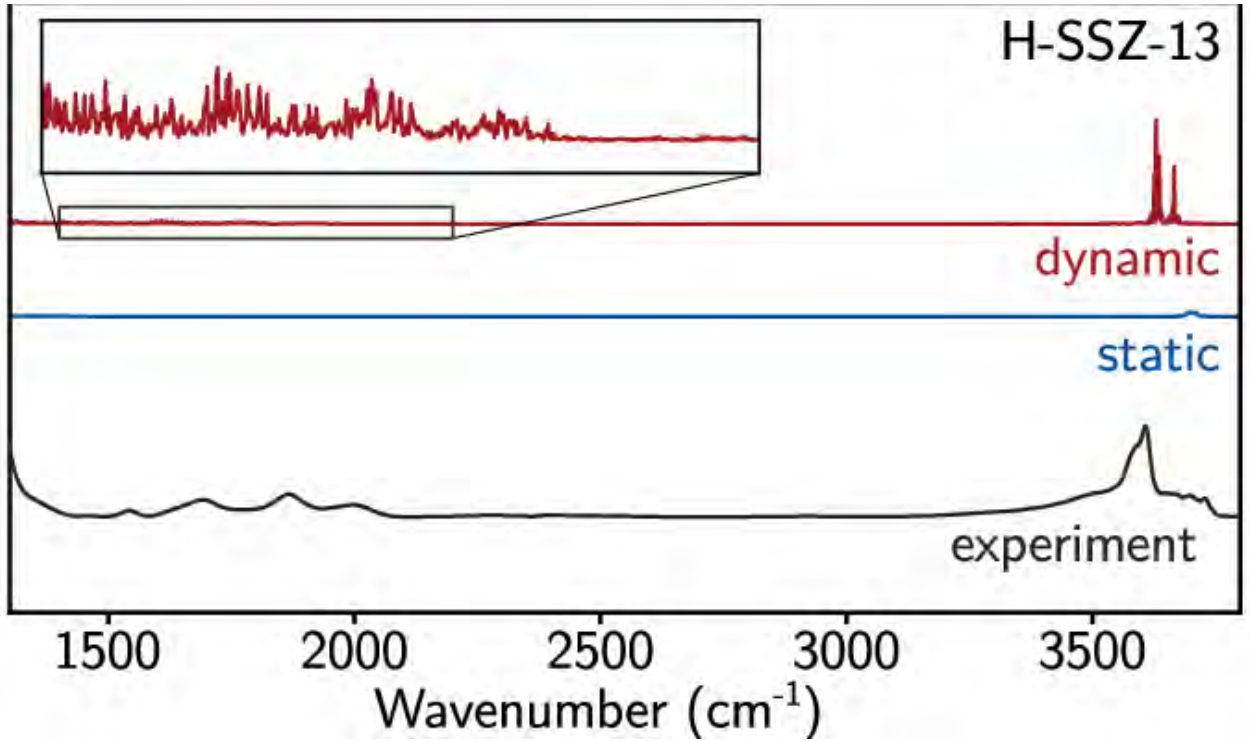
  b) Thermal effects

- Molecular dynamics can account for both!



How can MD predict IR spectra?





1. Run *ab initio* MD

2. Compute dipole moment at every *n*th step

3. Compute "dipole moment-time" autocorrelation functions

4. Obtain you beautiful IR spectrum!

$$A(\omega) \propto \int \langle \dot{\boldsymbol{\mu}}(\tau)\dot{\boldsymbol{\mu}}(t+\tau)\rangle_{\tau} \mathrm{e}^{-i\omega t}\mathrm{d}t.$$

Van Speybroeck et al., JCTC, 2023

Summary: FTIR computations

- **Harmonic approximation:**

+ Computationally inexpensive

+ Can provide accurate info on vibrational frequencies

- Only harmonic frequencies can be obtained

- No info on the thermal effects and line shape

- **Molecular dynamics:**

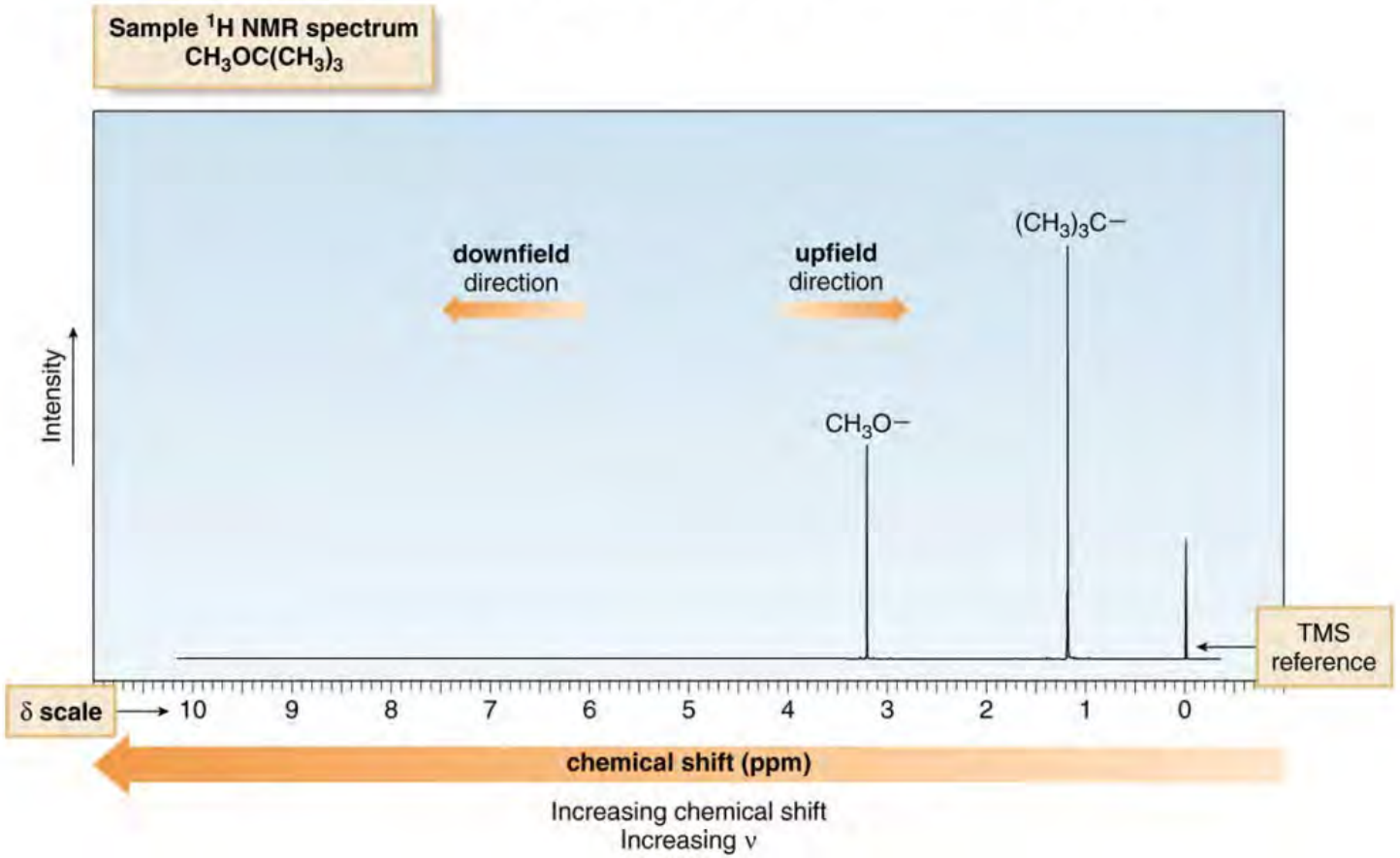
+ Correctly accounts anharmonicity and thermal effects

+ **Spectra** can be obtained

- Computationally expensive

- **If you know the structure, you can compute response**

- **An NMR spectrum is a plot of the intensity of a peak against its chemical shift, measured in parts per million (ppm).**



The chemical shift (δ) is an **observable quantity** that indicates the resonant frequency of a nucleus **relative to a standard reference.**

NMR from theoretician's perspective

- DFT calculates **absolute** nuclear shielding constants:

$$\boldsymbol{\sigma_{\alpha,\beta}} = \frac{\boldsymbol{\partial B_{\alpha}^{ind}}}{\boldsymbol{\partial B_{\beta}^{ext}}} =$$

- You need calculate an absolute shielding all with independent cartesian components (α, β):

$$\begin{matrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{matrix}$$

- Next: symmetrize & bring to principal axes ($\sigma_{xx} \leq \sigma_{yy} \leq \sigma_{zz}$):

$$\begin{matrix} \sigma_{xx} & 0 & 0 \\ 0 & \sigma_{yy} & 0 \\ 0 & 0 & \sigma_{zz} \end{matrix}$$

- Isotropic shielding constant = $\sigma_{iso} = (\sigma_{xx}+\sigma_{yy}+\sigma_{zz})/3$

From chemical shielding to chemical shifts

σ_{iso} (DFT) ??? δ_{iso} (DFT)

1. Using the reference.

$$\delta(\text{DFT}) = \sigma_{ref}(\text{DFT}) - \sigma(\text{DFT}) + \delta_{ref}(\text{EXP})$$

E.g. if you need to calculate some ^{1}H, ^{13}C or ^{29}Si shift, you can use TMS as a standard, and the formula will be:

$$\delta(\text{DFT}) = \sigma_{TMS}(\text{DFT}) - \sigma(\text{DFT})$$

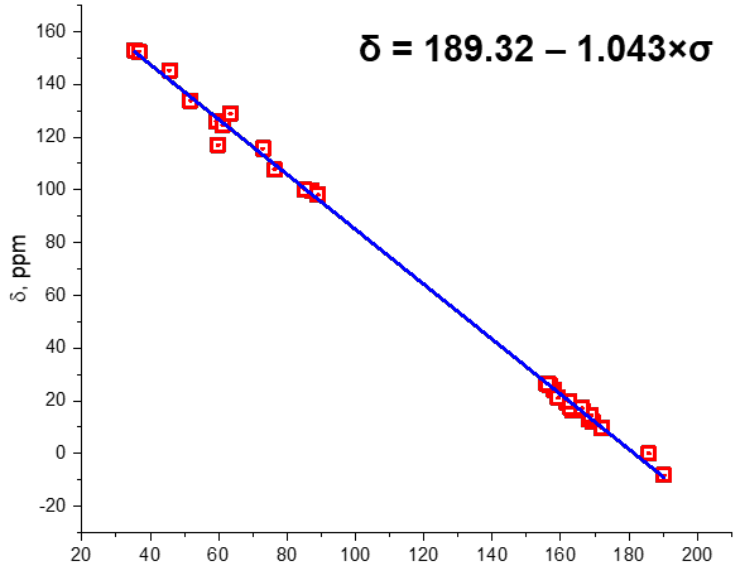
$(\delta(\text{TMS}) = 0)$

From chemical shielding to chemical shifts

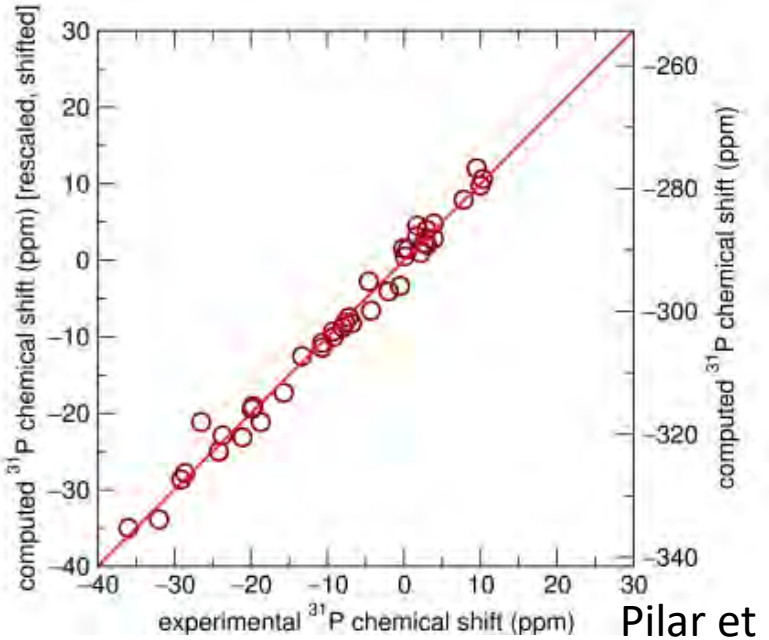
σ_{iso} (DFT) ⟷ ??? ⟷ δ_{iso} (DFT)

2. Plotting the calibration graph

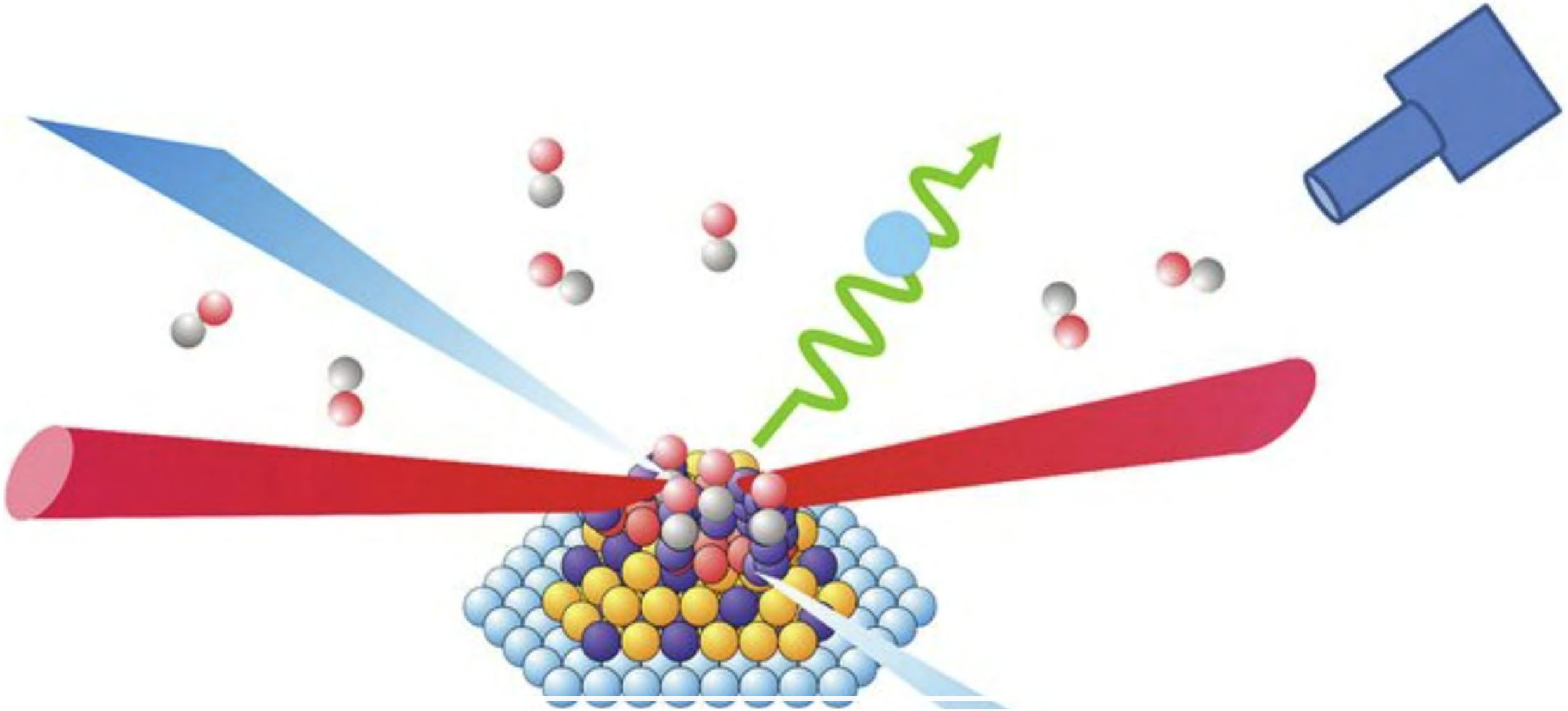
You need to calculate the series of reference compounds with the known chemical shifts to plot the correlation between the calculated **σ** and experimentally observed **δ** by equation $\delta = k \times \sigma + b$



Kolganov et al., PCCP, 2021



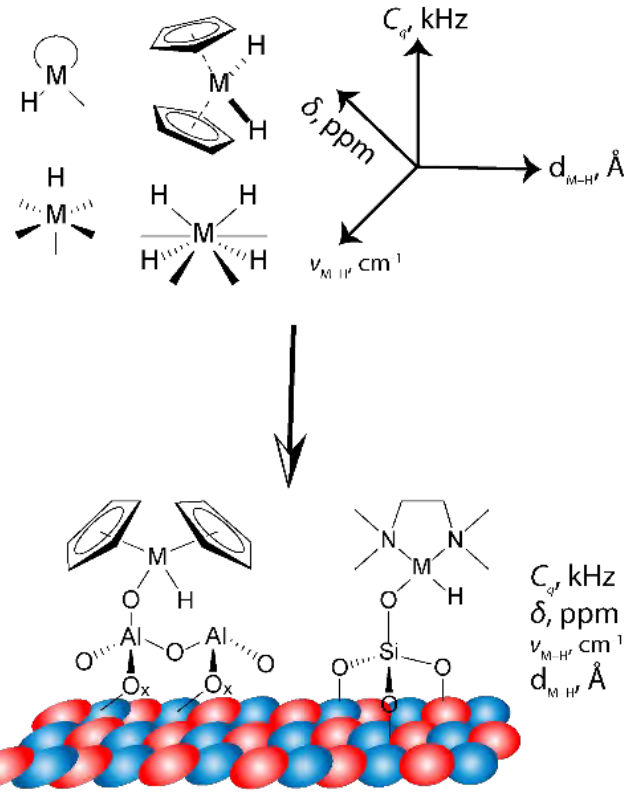
Pilar et al., PCCP, 2019

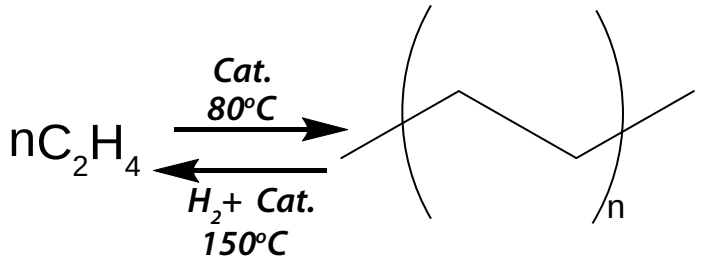


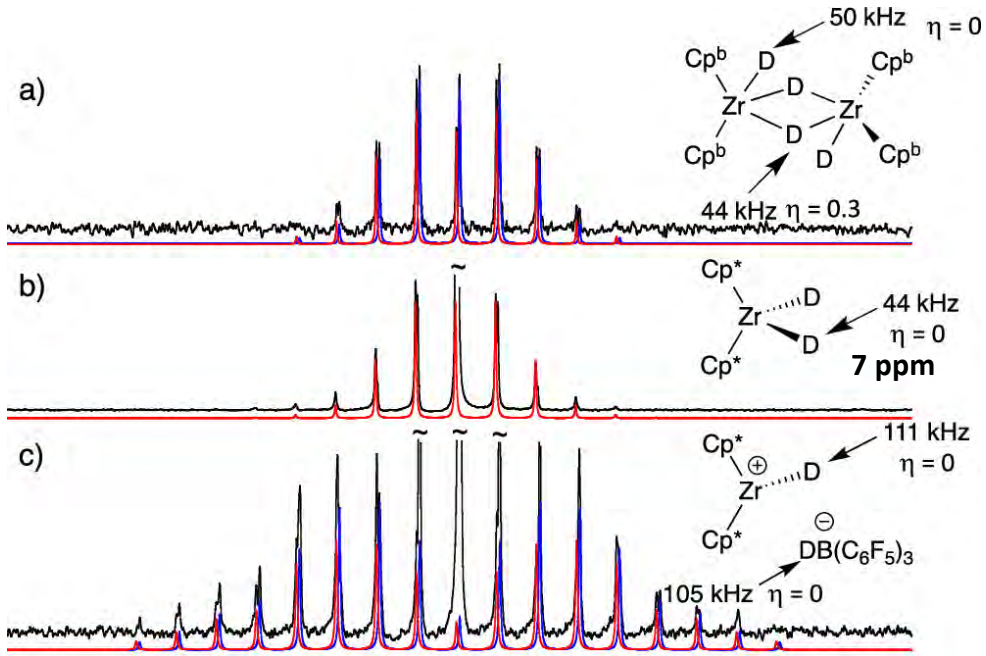
The Experiment Tells Us the Truth!

K. Föttinger and G. Rupprechter,
Acc. Chem. Res. **2014**, *47*, 3071

Experimentalists always know better, but…







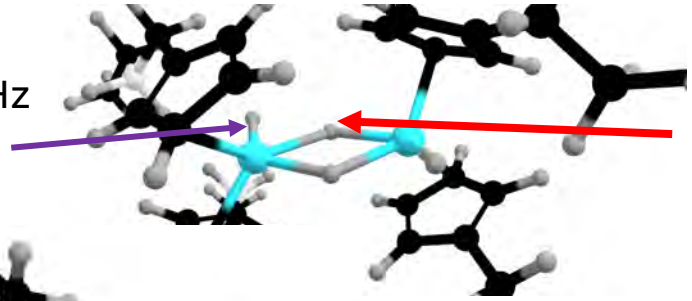
D. B. Culver, R.W. Dorn, A. Venkatesh, J. Meeprasert, A. J. Rossini, EAP, A. S. Lipton, G.R. Lief, M.P. Conley, *ACS Cent. Sci.* **2021**, *7*, 1225

NMR parameters calculations

Chemical shielding constants and EFG tensor eigenvalues: ORCA 5.0.4 software
Geometry optimization: PBEh-3c (PBE0-D3BJ/def2-mSVP)
NMR calculations: ωB97x-D4/def2-tZVPP

Theory

C_q = 49.1 kHz
η = 0.02

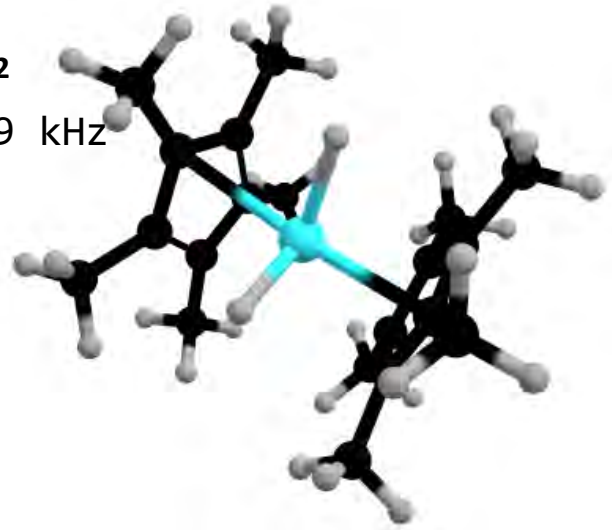


$(^{nBu}Cp_2ZrD_2)_2$

C_q = 44.8 kHz
η = 0.3

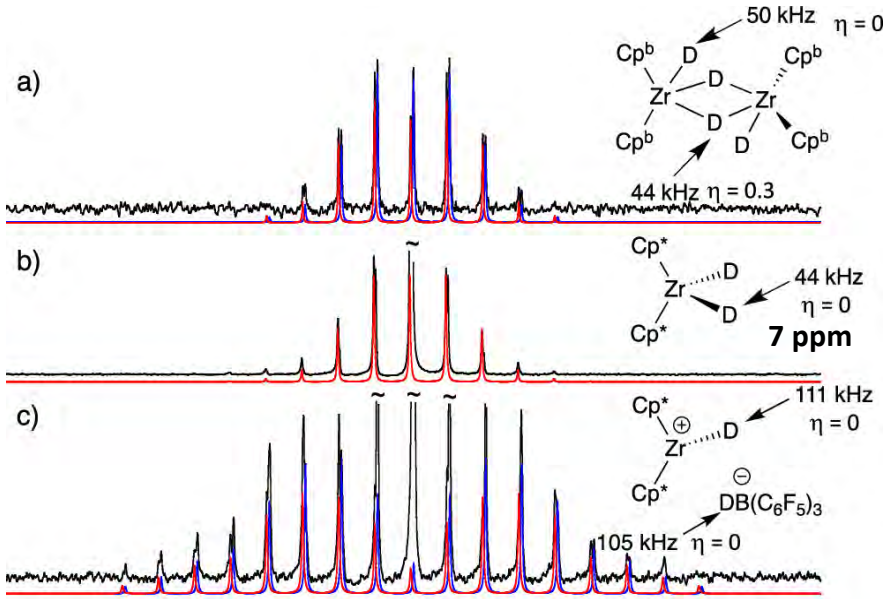
$Cp^*_2ZrD_2$

C_q = 44.9 kHz
η = 0.09

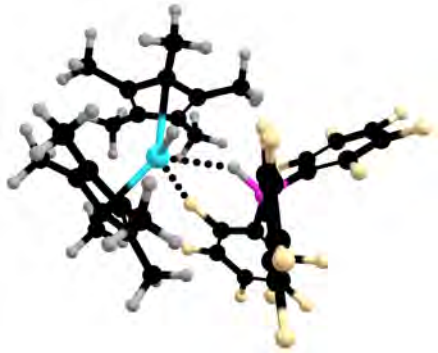


Our theory has a problem with matching parameters experimentalists assigned for the ionized Zr-H^+ species

Experiment



$Cp^*_2ZrD...DBPh^F_3$

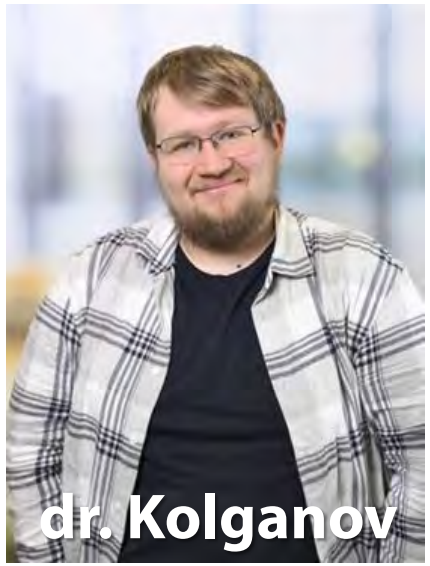


Zr-H

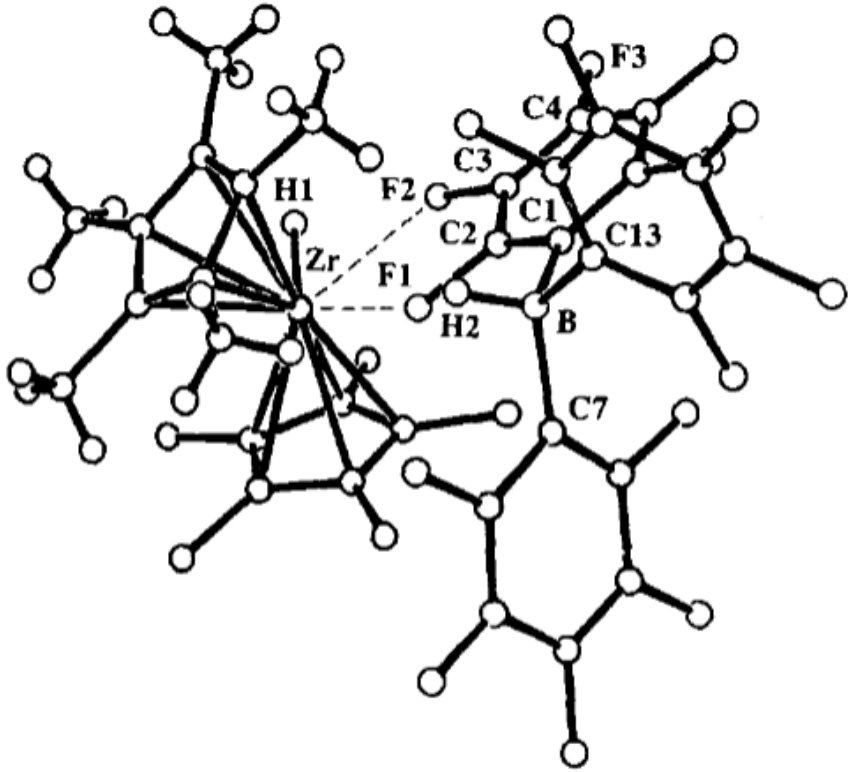
C_q = 52.9 kHz
η = 0.12

B-H

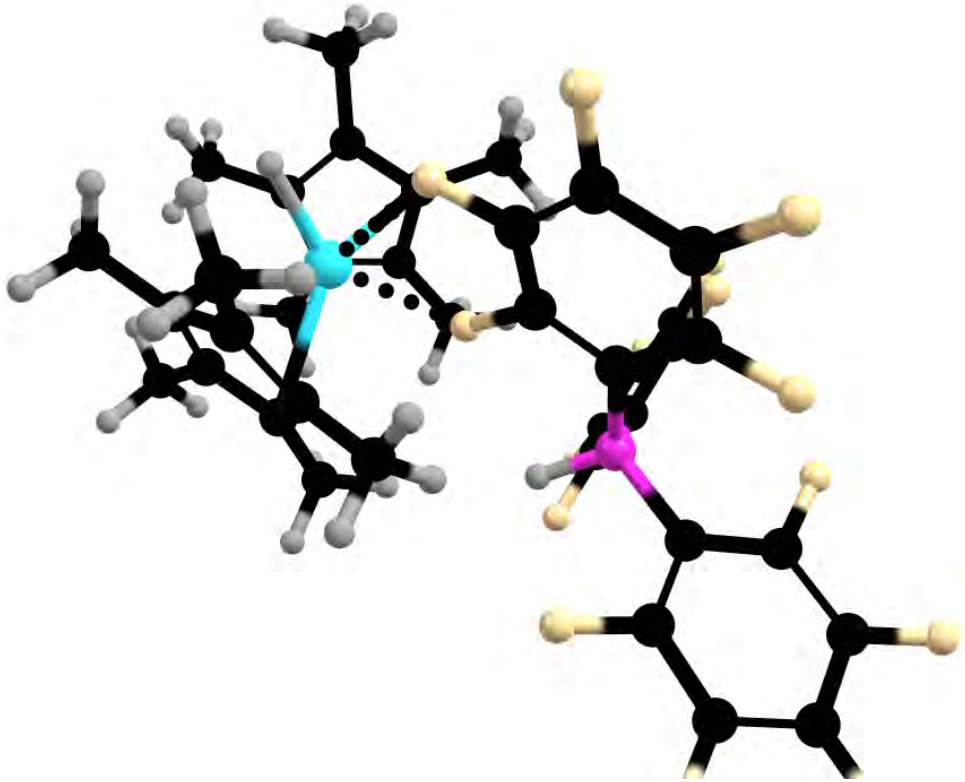
C_q = 118.9 kHz
η = 0.01



Our model



Crystal structure



Optimized geometry

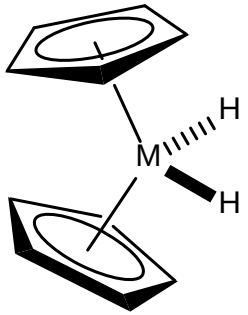
The Method Accuracy

Method	Cq(Zr-H$^+$) (kHz)	Cq(B-H)$^-$ (kHz)
Experiment	**111**	**105**
PBEh-3c//ωB97x-D4/def2-tZVPP	53	119
PBE0-D3BJ/def2-tZVP//ωB97x-D4/def2-tZVPP	48	126
PBE0-D3BJ/def2-tZVP//ωB97x-D4/def2-tZVPP (very tight geometry optimization)	48	126
PBE0-D3BJ/def2-tZVPP//ωB97x-D4/def2-tZVPP	48	127
PBE0-D3BJ/def2-tZVP//DLPNO-DSD-PBEP86/def2-tZVPP (Double hybrid functional)	50	127
PBE0-D3BJ/def2-tZVP//ωB97x-D4-DKH2/cc-pVTZ-DK (w/ relativistic DKH2 Hamiltonian)	54	127
pPBE-D3BJ/600 eV (in VASP – calculations carried out for molecular crystal)	48	122
PBE0-D3BJ/def2-tZVP//ωB97x-D4/def2-tZVPP (calculations for the geometry taken straight from the crystal structure, only –CH_3 position were optimized	23	256

All methods are “not working”.

Let’s try calculate C_q of other complexes, to see if the method works in general

Test set

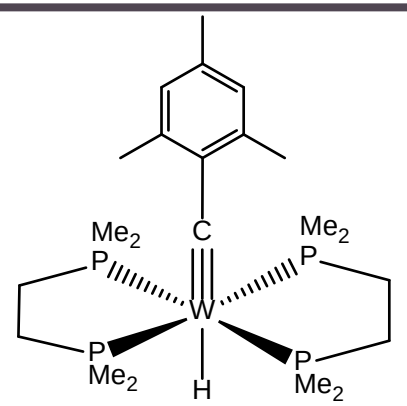


M = W, Mo

Wei, I. Y.; Fung, B. M. J. Chem. Phys. 1971,55,1486.

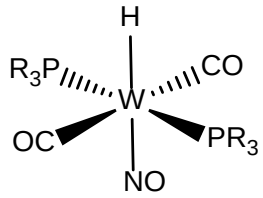
I have selected following hydride complexes with available experimental data in the test set

$Ru(pp_3)H_2$, $Os(pp_3)H_2$,
$[Ru(pp_3)H(H_2)]^+$, $[Cp^*(dppm)Ru(H_2)]^+$
V. I. Bakhmutov et al., Chem. Eur. J. 1999, 5, No. 11

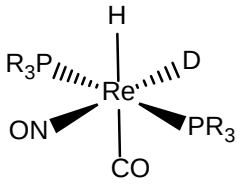


F. Zoue et al., JACS 2007, 129, 7195-7205

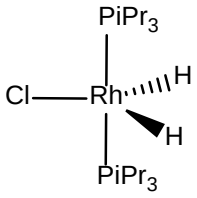
$HMn(CO)_5$
Ireland, P. S.; Olson, L. W.; Brown, T. L. JACS 1975, 97, 3548.

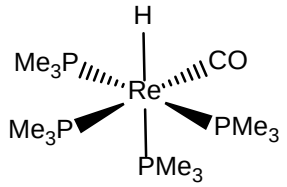


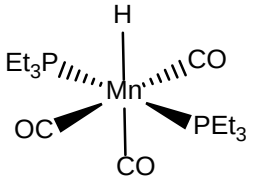
R = Me, Ph

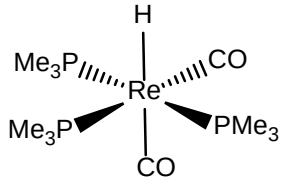


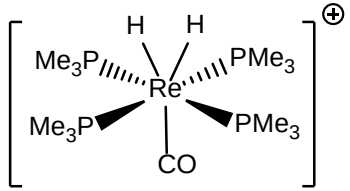
R = iPr, O-iPr, Me, Cy

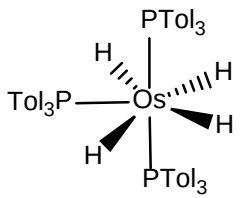


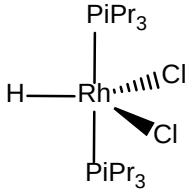


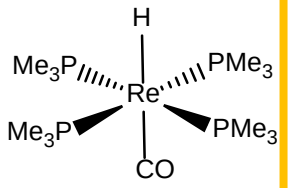


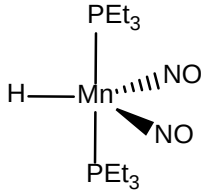


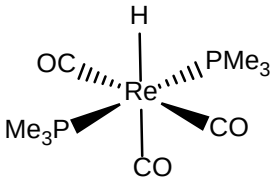


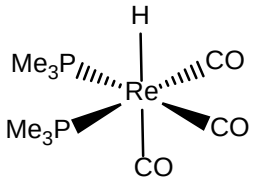


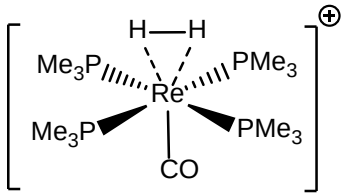


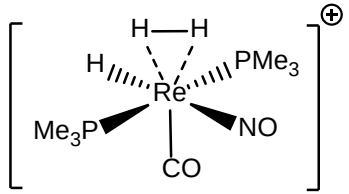






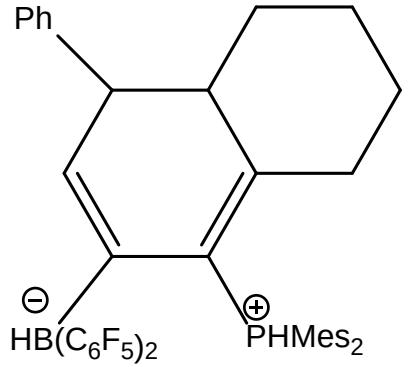






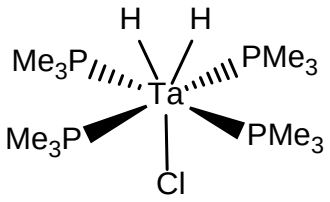
D. Nietlispach; V. I. Bakhmutov; H. Berke, JACS 1993, 115, 9191-9195

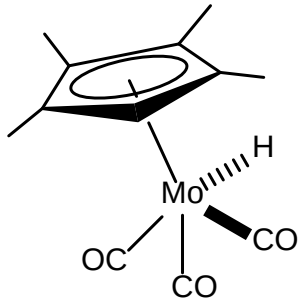
$Cp^*_2ZrH_2$, $(^{nBu}Cp_2ZrH_2)_2$,
$Cp^*_2ZrH...BH(C_6F_5)$
D. B. Culver et al.,
ACS Cent. Sci. 2021, 7, 1225−1231

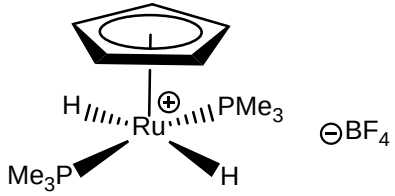


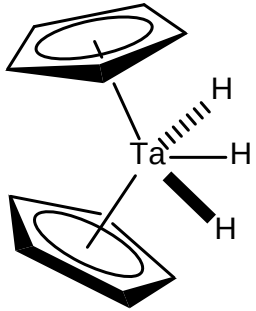
R. Knitch et al.,
ChemPhysChem 2019, 20, 1837– 1849

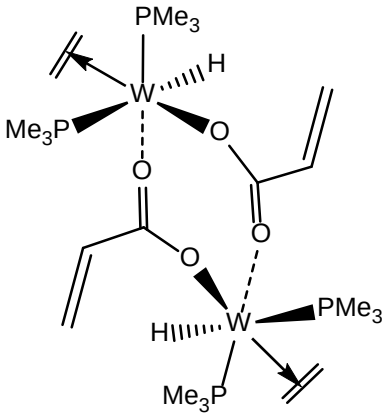
Additional molecules for a test set

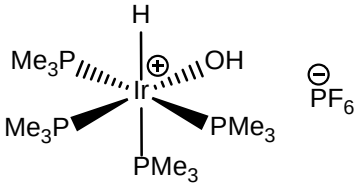




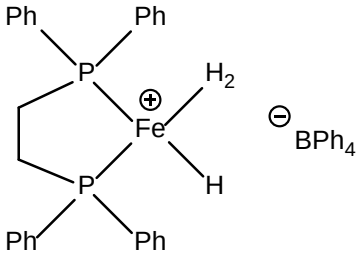




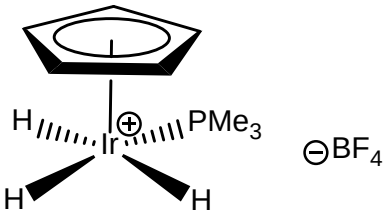


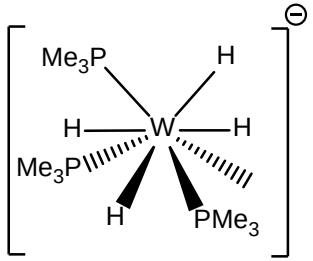


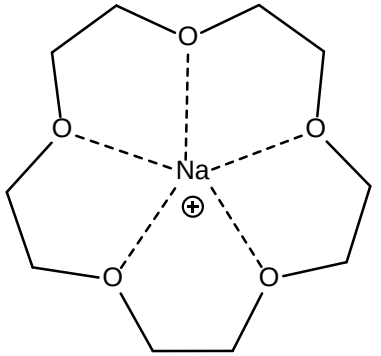
$WH_6P(^iPr_3)$

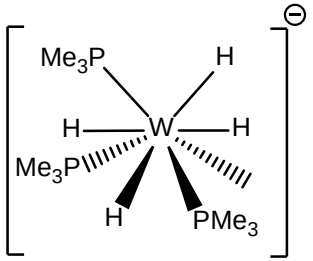


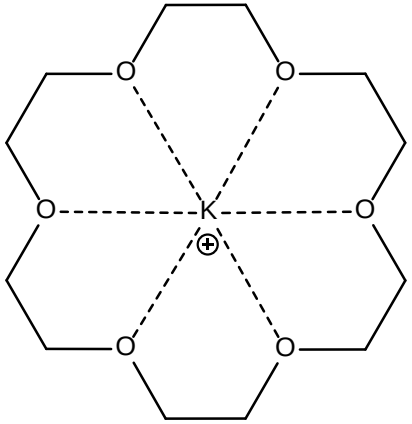
$ReH_5(PhPMe_2)_3$









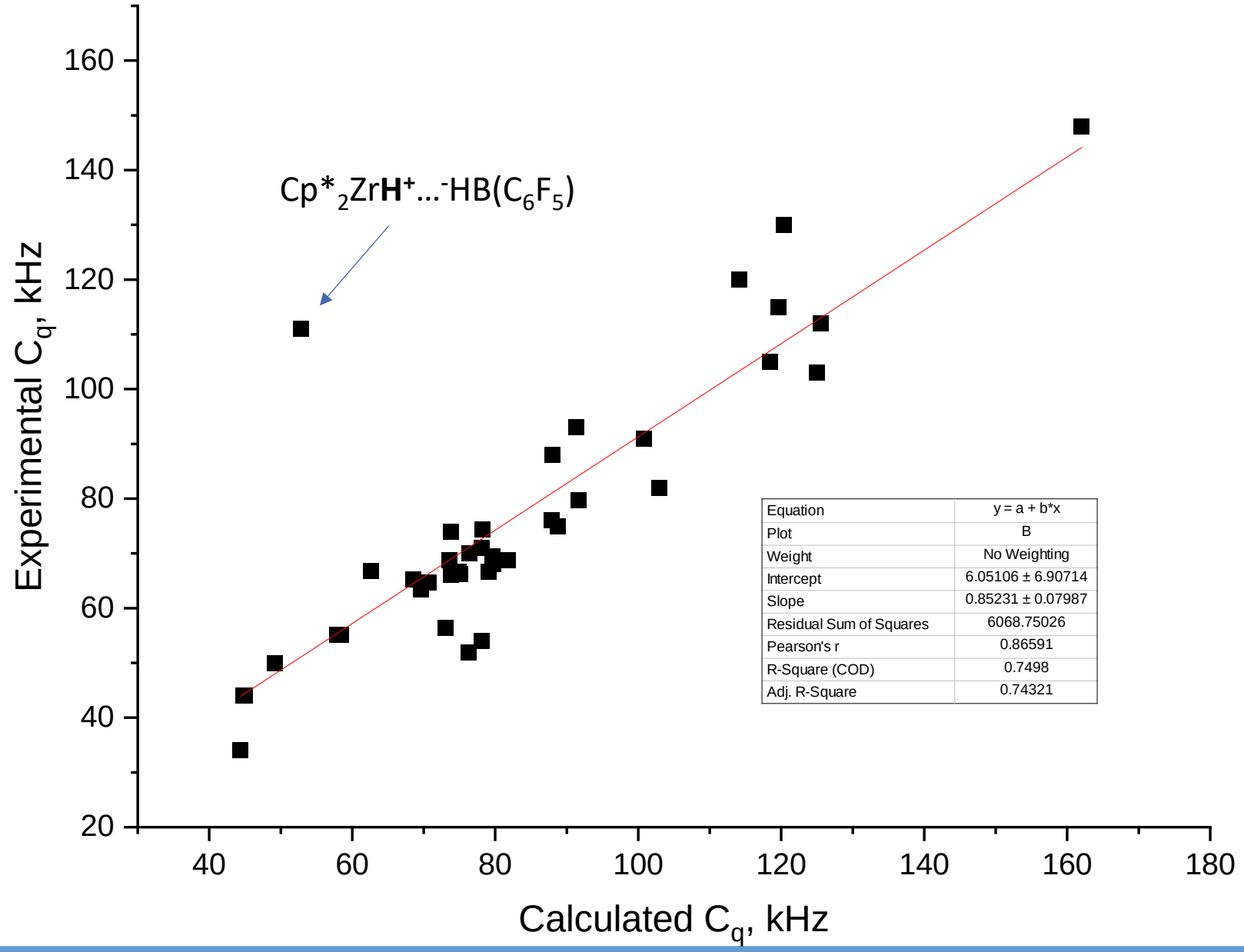


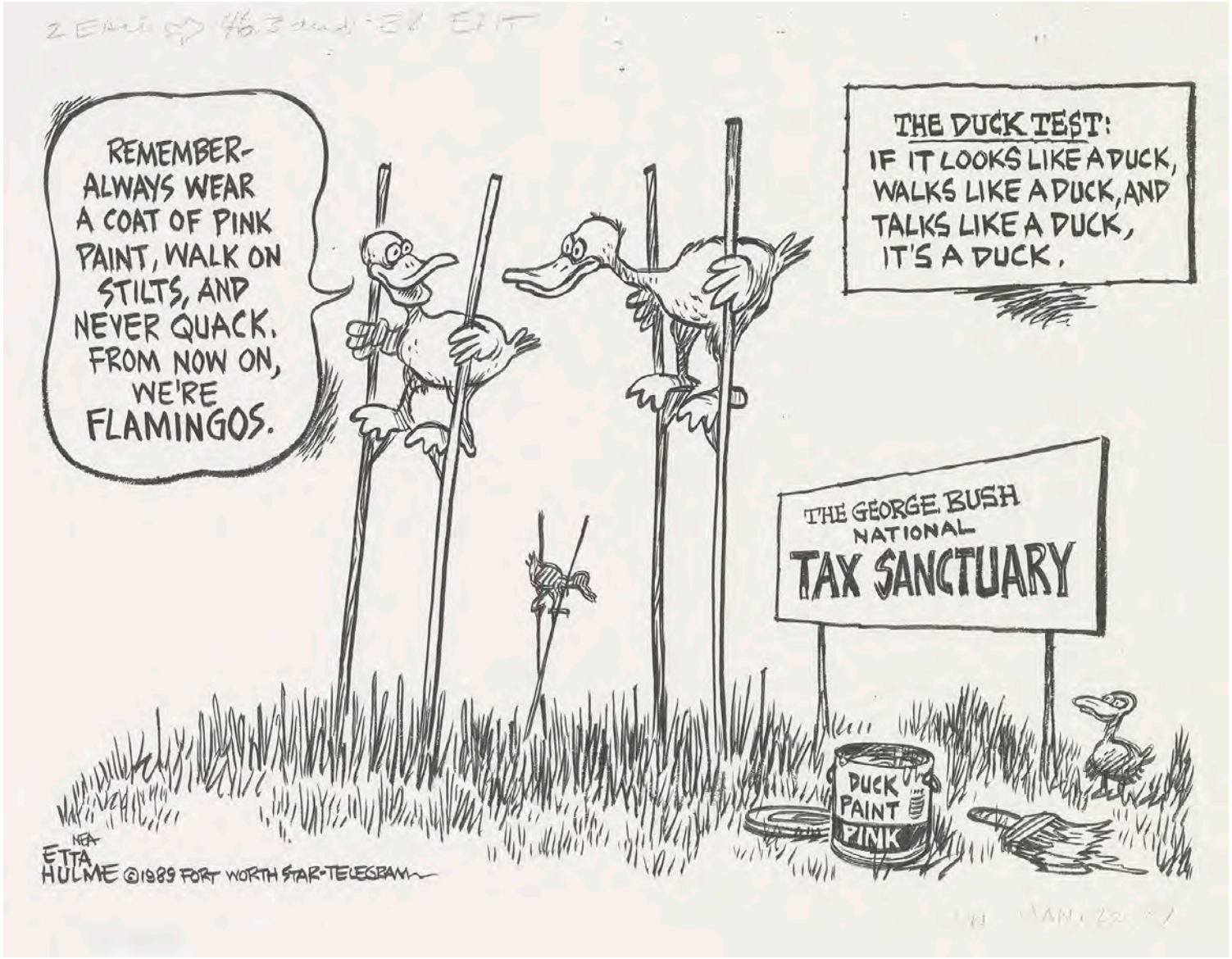
The data on M-H bond lengths were taken from:

R. Bau end M. Drabnis, Structures of transition metal hydrides determined by neutron diffraction; Inorg. Chim. Acta; 1997

Unfortunately, there is no data on the C_q of these complexes ☹

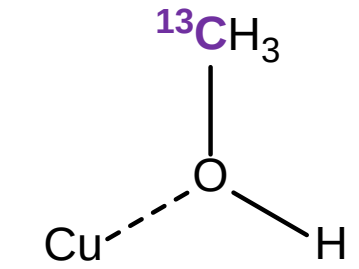
Parity plots



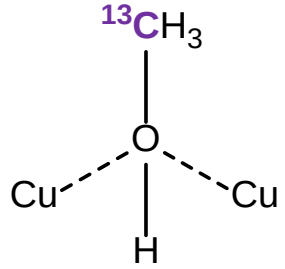

REMEMBER- ALWAYS WEAR A COAT OF PINK PAINT, WALK ON STILTS, AND NEVER QUACK. FROM NOW ON, WE'RE FLAMINGOS.
THE DUCK TEST: IF IT LOOKS LIKE A DUCK, WALKS LIKE A DUCK, AND TALKS LIKE A DUCK, IT'S A DUCK.
THE GEORGE BUSH NATIONAL TAX SANCTUARY
DUCK PAINT PINK
NEA ETTA HULME ©1989 FORT WORTH STAR-TELEGRAM

HetCat spectroscopy characterization – the case of ^{13}C NMR

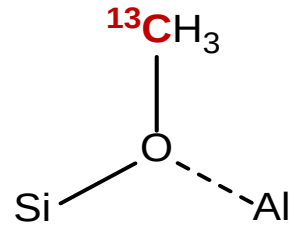
CH_4@Cu/H-ZSM-5



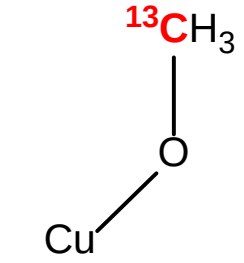
Sushkevich et al., 2019



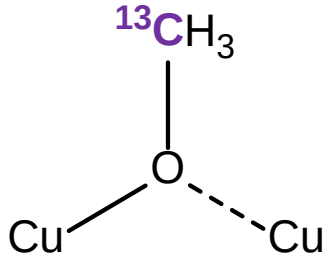
Kolganov et al., 2020



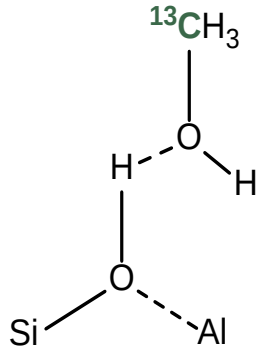
Narsimhan et al., 2015



Wu et al., 2019



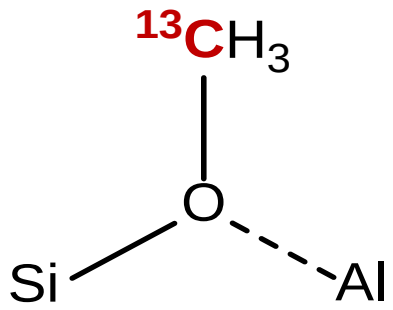
Narsimhan et al., 2015

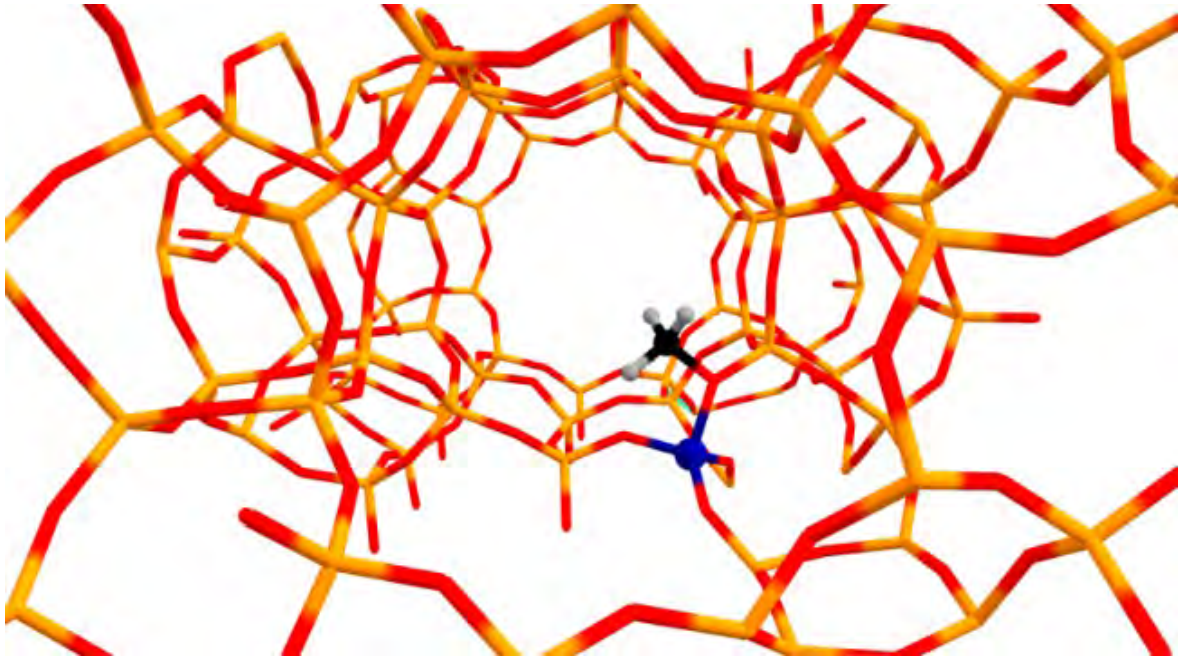


Narsimhan et al., 2015

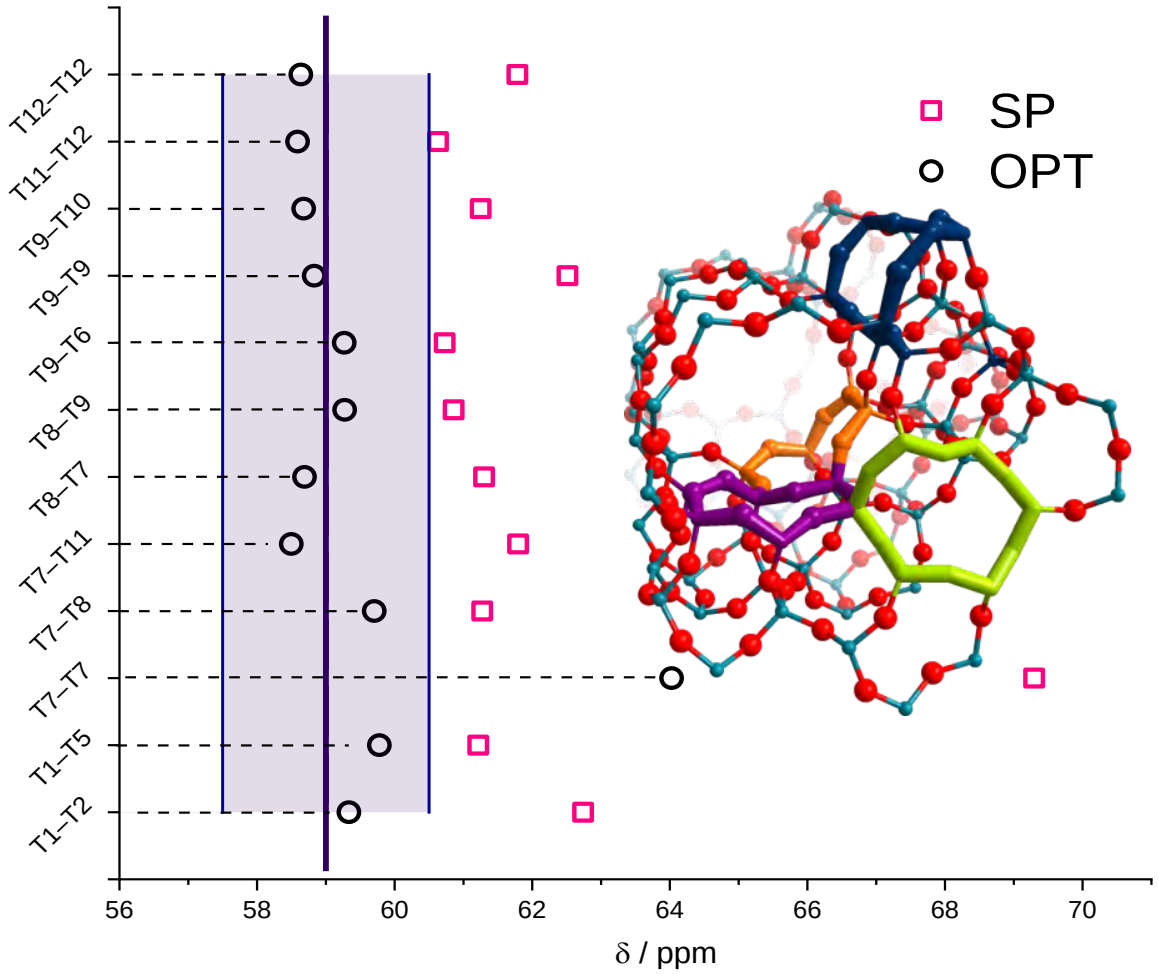
A. A. Kolganov, A. A. Gabrienko, S. A. Yashnik, **EAP**, A.G. Stepanov, *J. Phys. Chem. C* **2020**, *124*, 6242

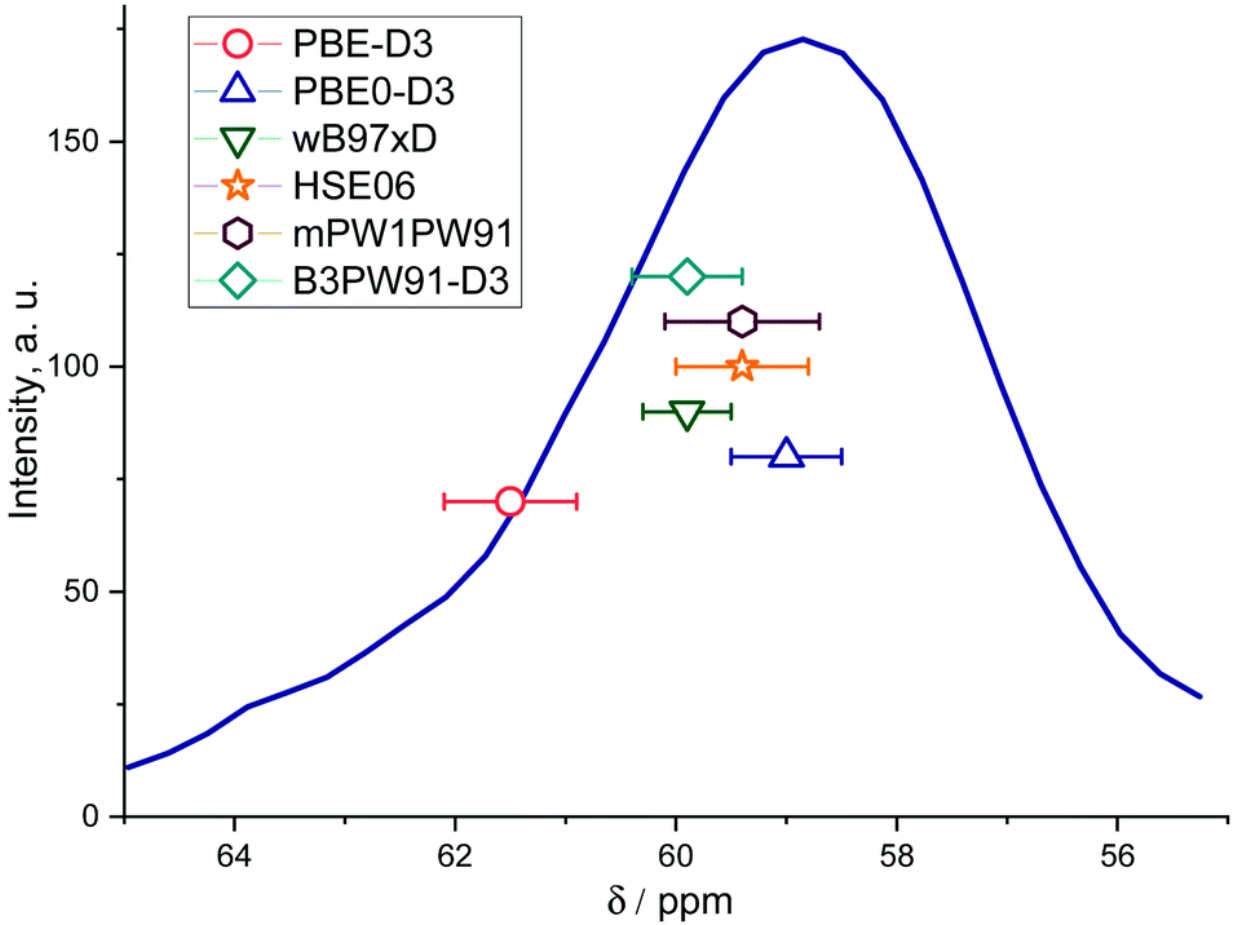
Let’s start with something we know for sure





Model and method accuracies

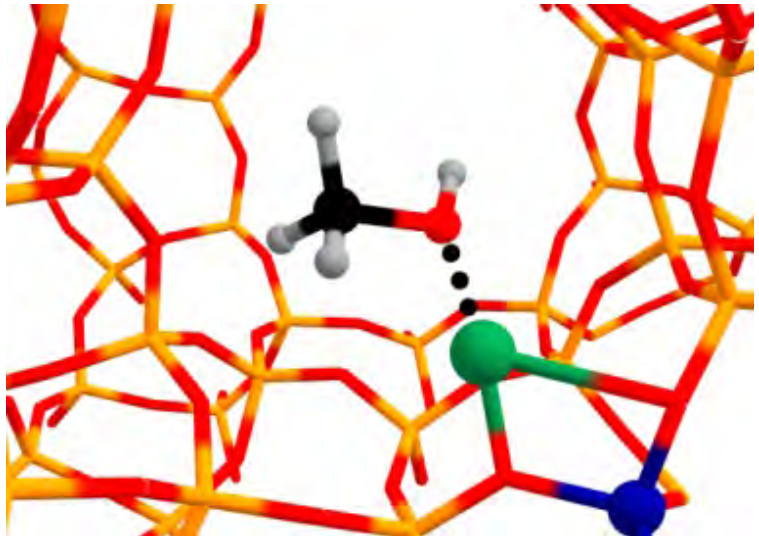




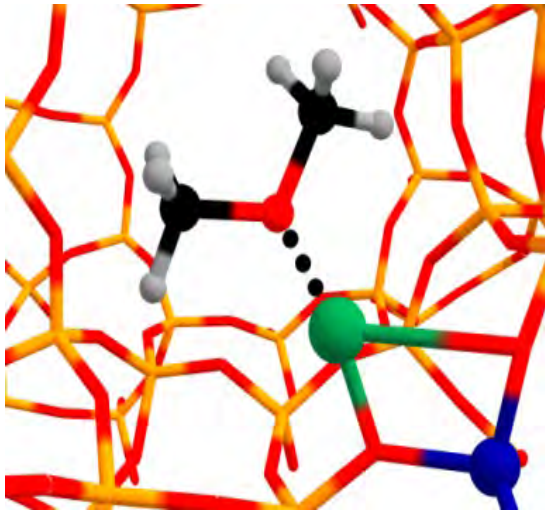
PBE0/aug-cc-pVDZ//PBE0/6-311G(d,p)

A. A. Kolganov, A. A. Gabrienko, I. Yu. Chernyshov, A.G. Stepanov, **EAP**, *PCCP* **2020**, *22*, 24004

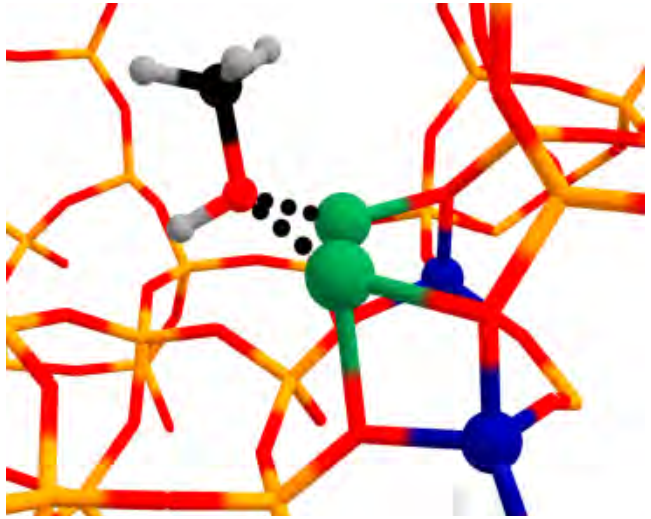
Products of CH_4 oxidation by CuZSM-5



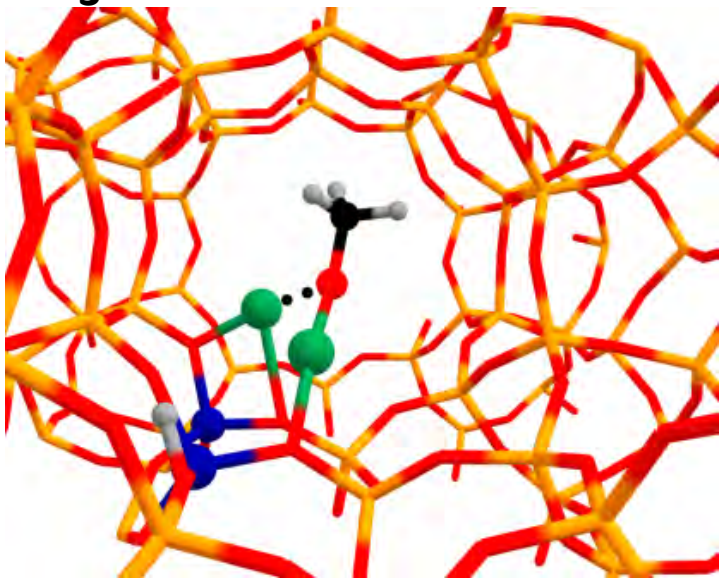
$Cu^+..CH_3OH$



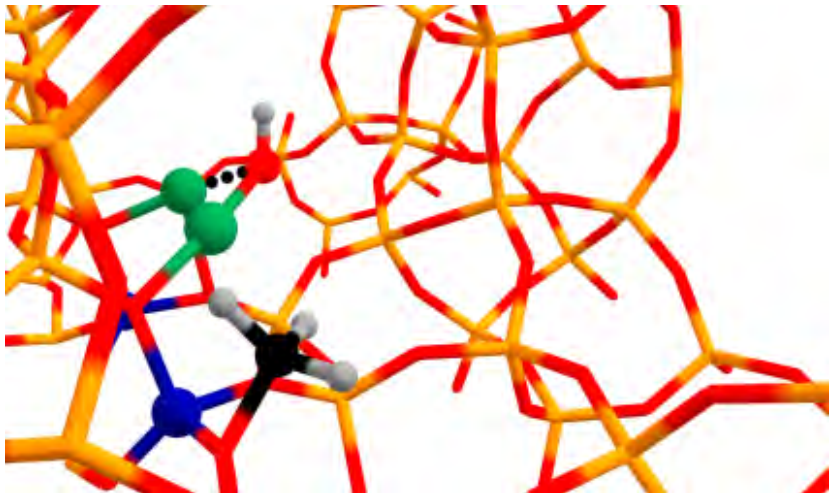
$Cu^+..CH_3OCH_3$



$[Cu(\mu\text{-}CH_3OH)Cu]^{2+}$

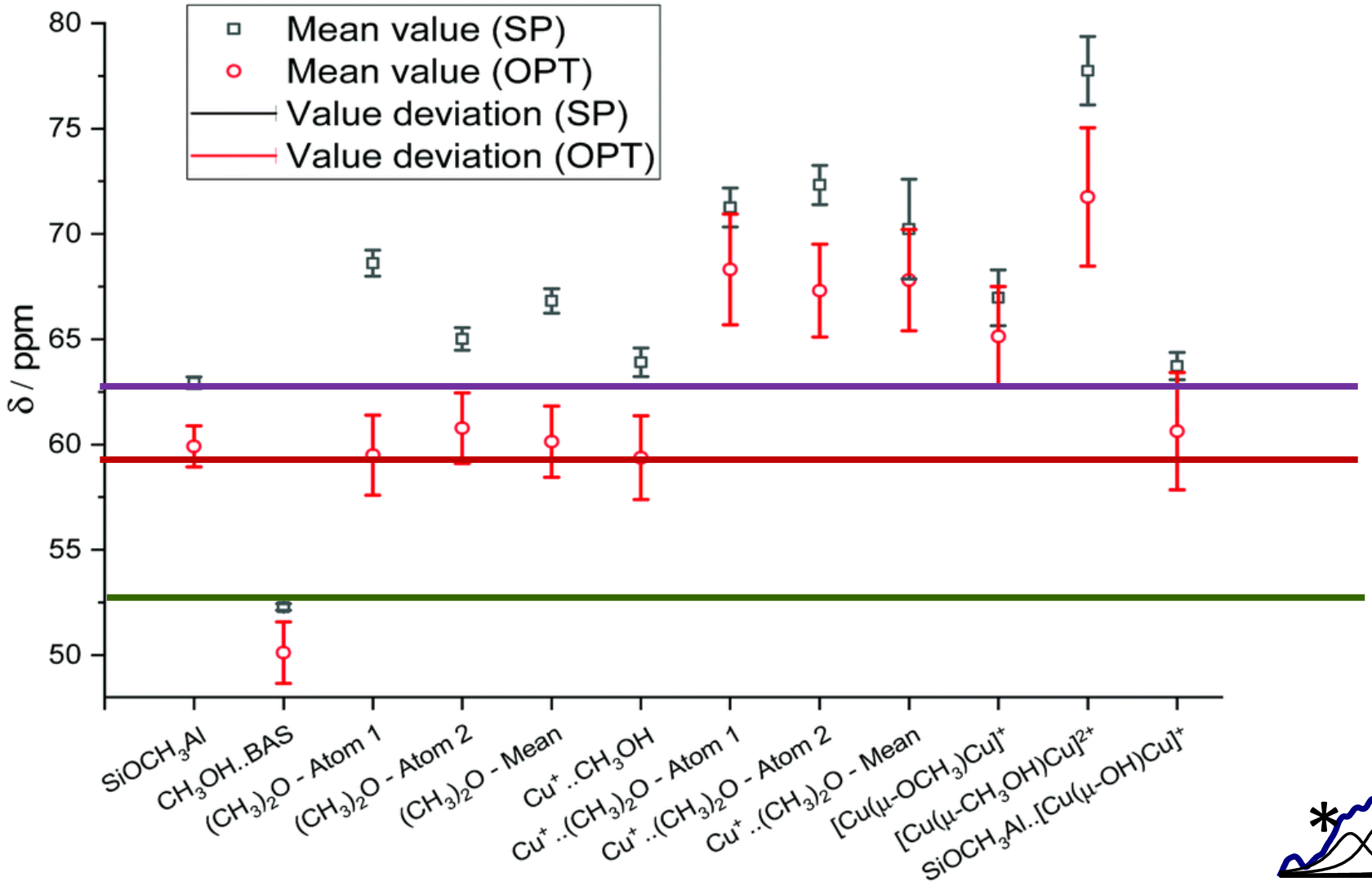


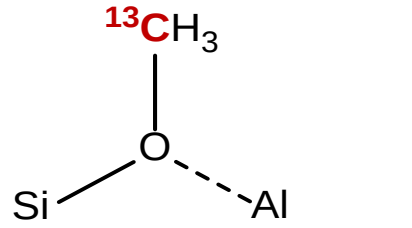
$[Cu(\mu\text{-}OCH_3)Cu]^{2+}$



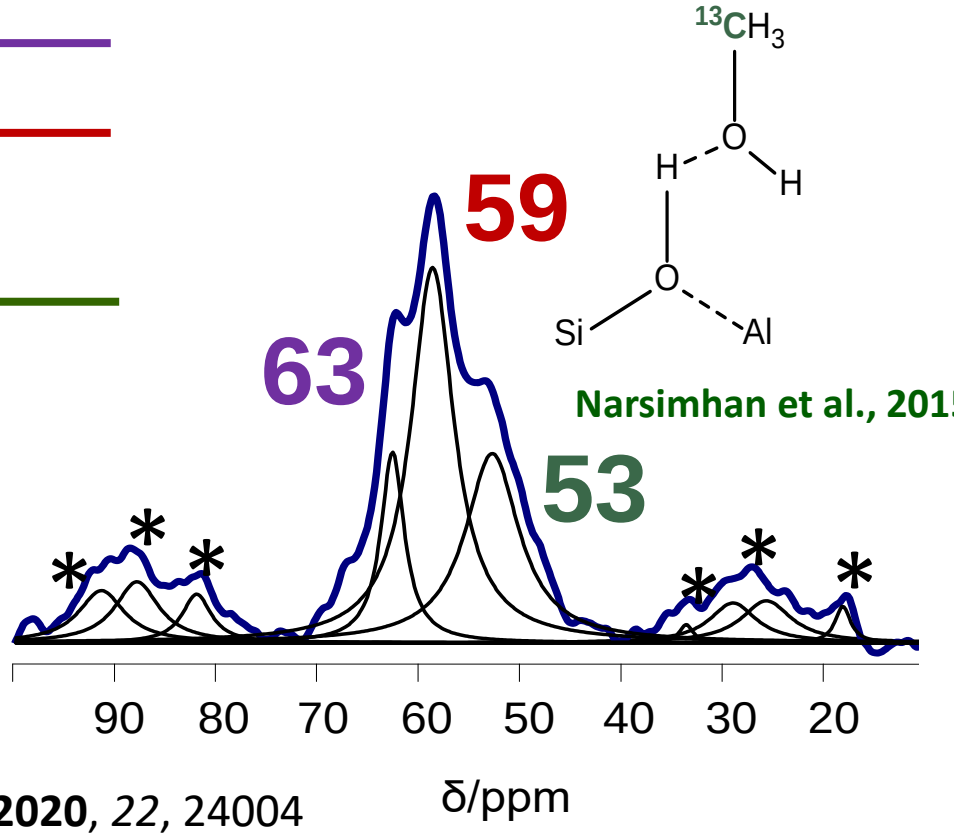
$Si(OCH_3)Al..\ [Cu(\mu\text{-}OH)Cu]^+$

Do we get theory supporting spectroscopy for Cu/ZSM-5?





Narsimhan et al., 2015

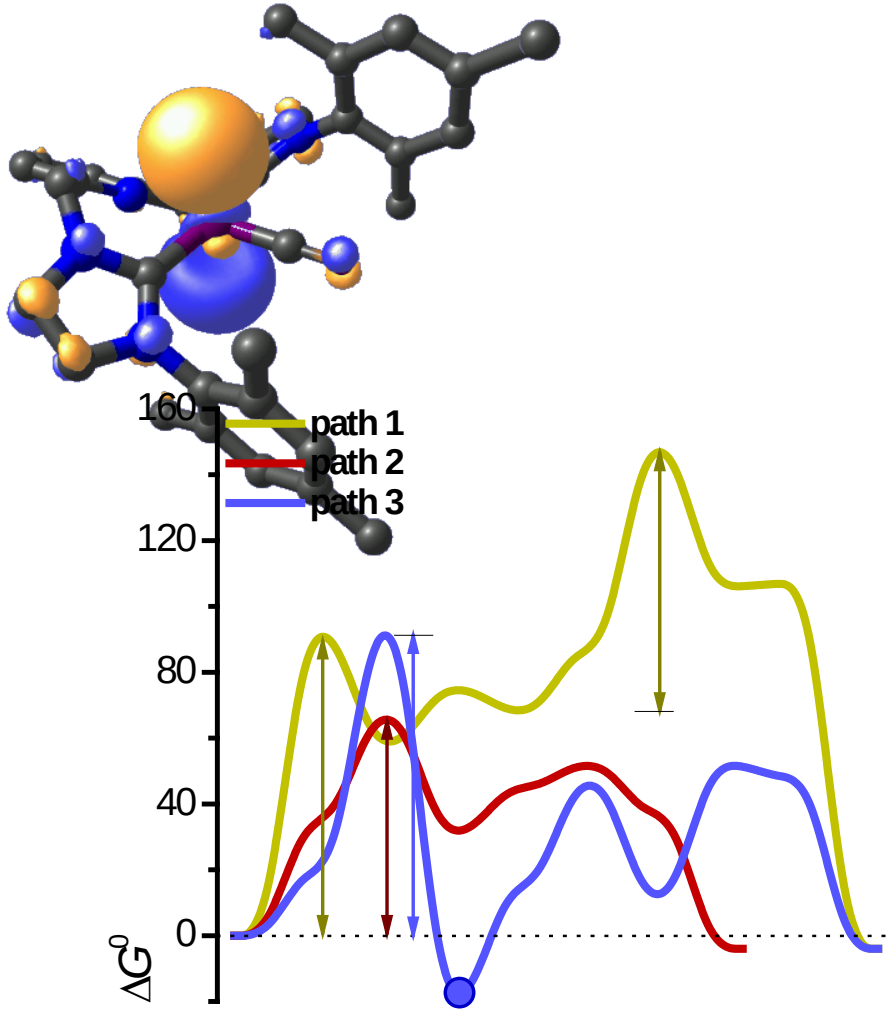


Narsimhan et al., 2015

A. A. Kolganov, A. A. Gabrienko, I. Yu. Chernyshov, A.G. Stepanov, **EAP**, *PCCP* **2020**, *22*, 24004

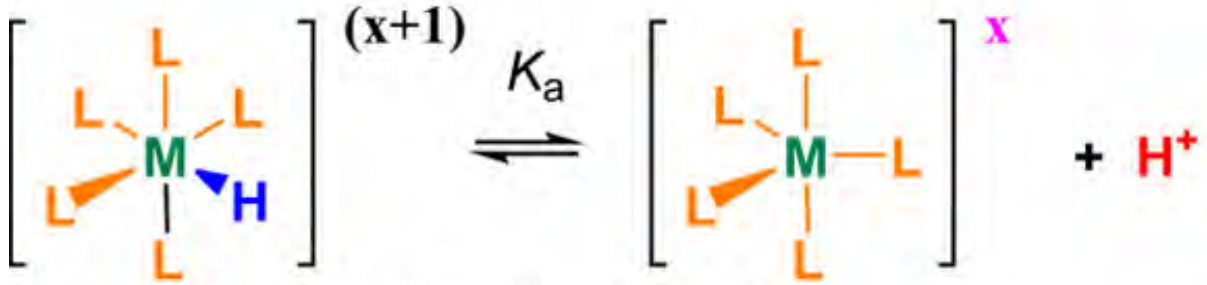
Reactivity predictions

How good are we with predicting reaction energetics?

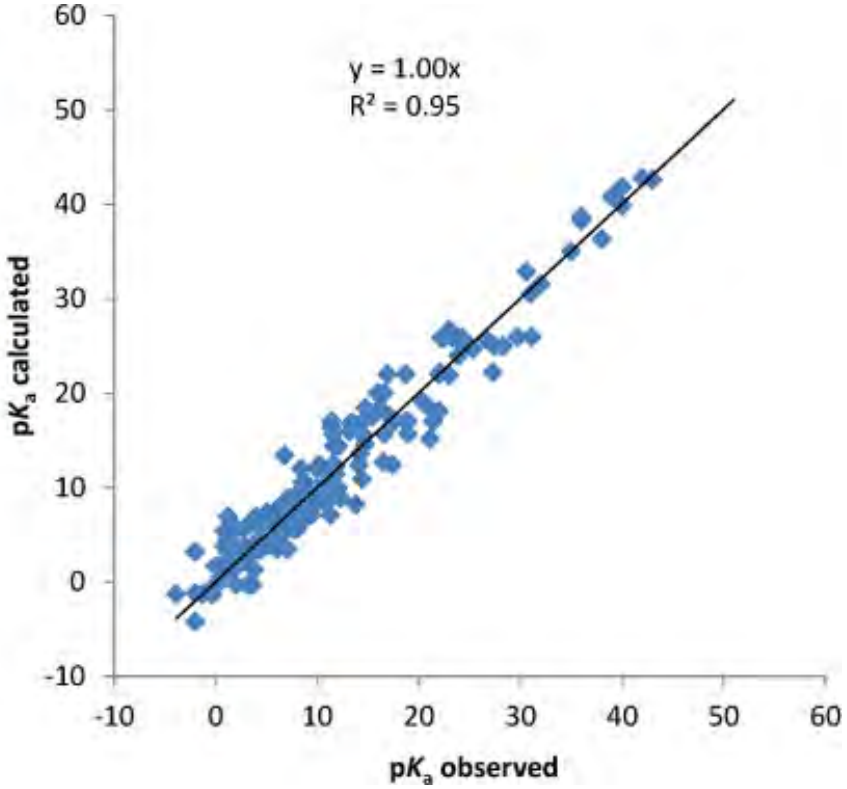


Let's try something simple: pKa calculations of TM hydride complexes!

$$pK_a(\text{M-H}) = \Sigma A_L + C_{charge} + C_{nd} + C_{d6}$$



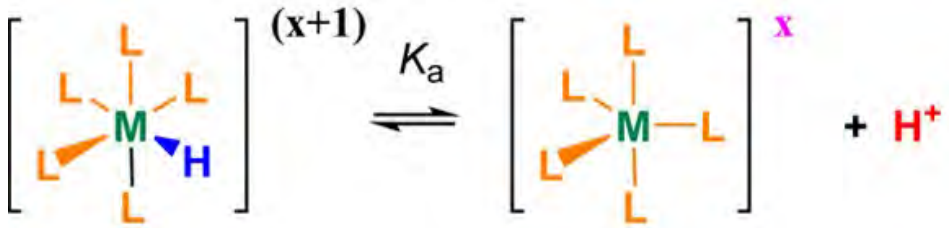
6	7	8	9	10
Cr	Mn	Fe	Co	Ni
Mo	Tc	Ru	Rh	Pd
W	Re	Os	Ir	Pt

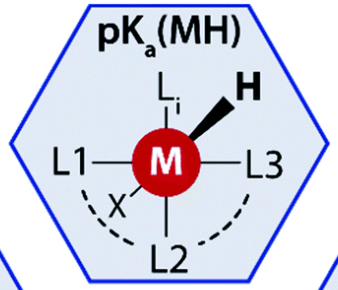


$$\Delta G^{\ominus} = -RT \ln K_a \approx 2.303 RT \, pK_a$$

R. H. Morris, J. Am. Chem. Soc. **2014**, *136*, 1948

pKa calculations of TM hydride complexes: can we do it fast?



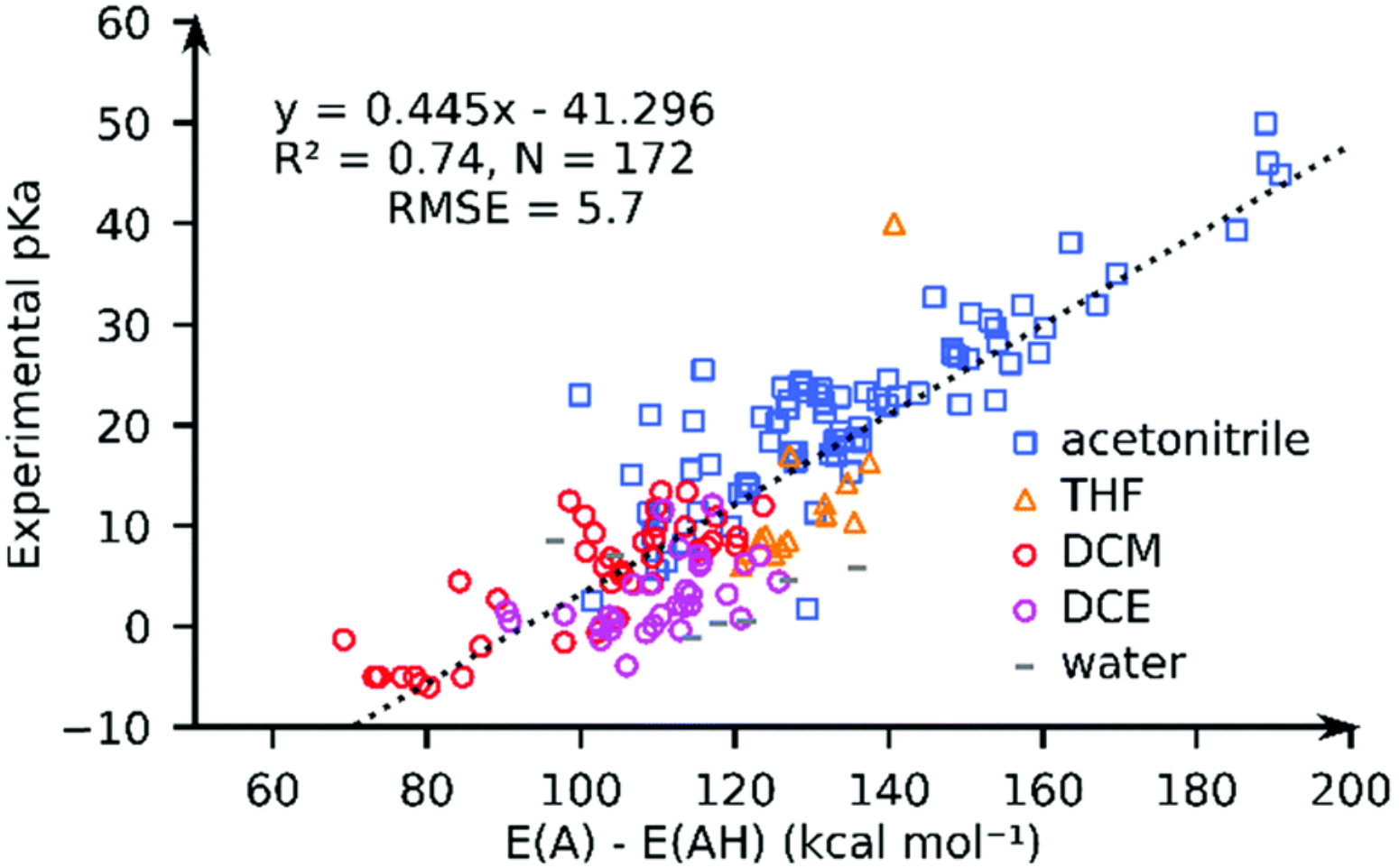


Dataset:
201 pK_a *values ranging from -6 to 50*

Solvents:
CH_3CN, PhCN, CH_2Cl_2, H_2O, DCE, THF

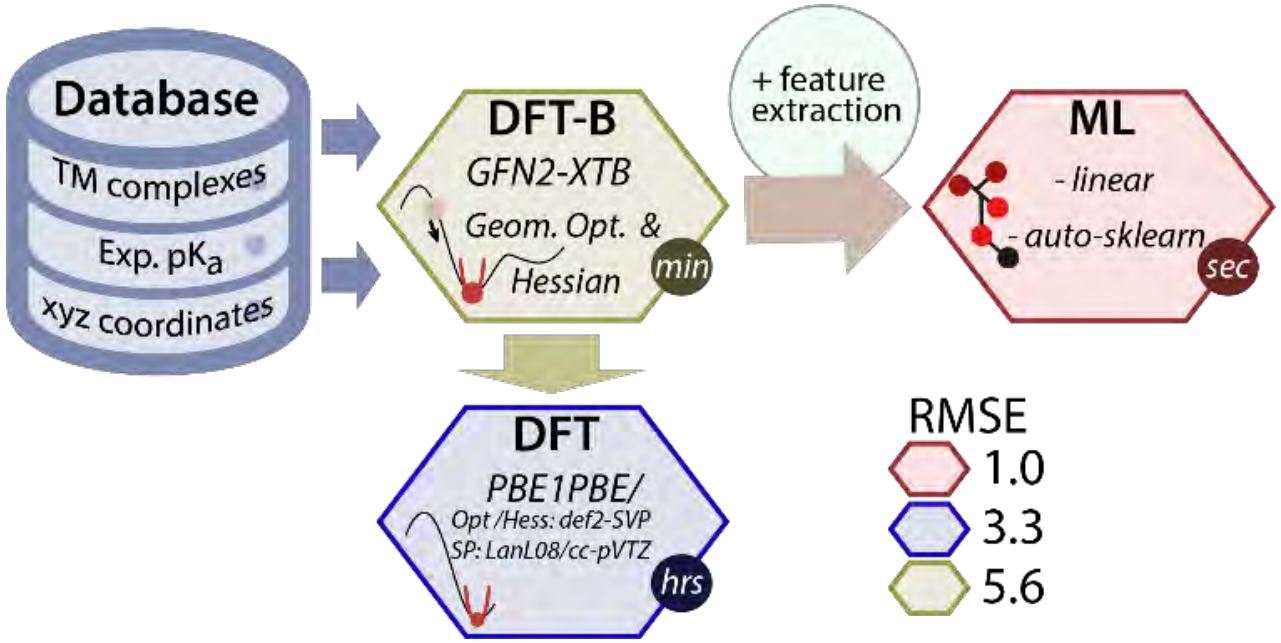
14 M types:
Cr, Mn, Fe, Co, Ni, Mo, Ru, Rh, Pd W, Re, Os, Ir, Pt

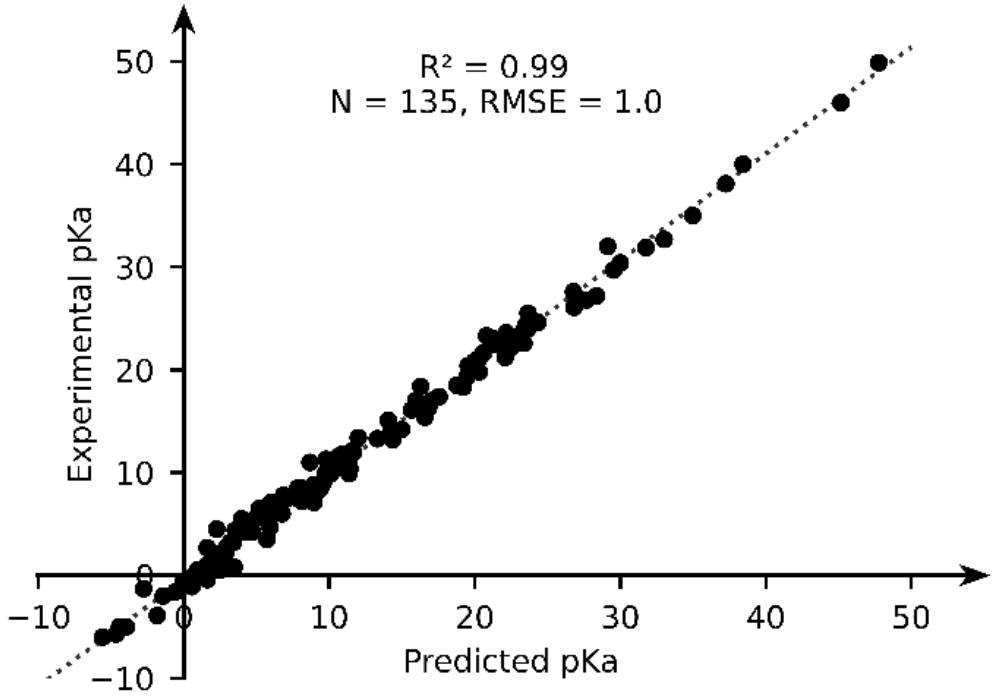
System sizes:
10 - 140 atoms



V. Sinha, J. J. Laan, **EAP**, *PCCP* **2021**, *23*, 2557

DATA+CompChem = PROFIT!!!



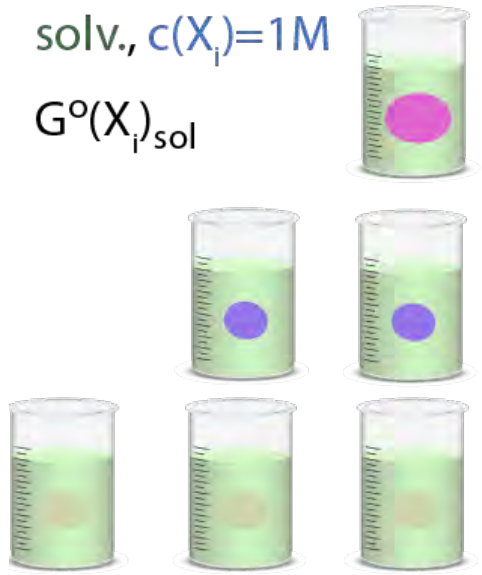


V. Sinha, J. J. Laan, **EAP**, *PCCP* **2021**, *23*, 2557

DFT calculations on reactions in the liquid phase: taking care of conditions

DFT calculations:
- Intrinsic reactivity
- Molecules in vacuum

Implicit (PCM) solvent:
- Polarized continuum
- Ideal solution



Real solultion (COSMO-RS)

$\Delta G^{ø}_r$ (solv., T, P_{tot}, a_i)

$f(p,T,c_i,$ solvent)

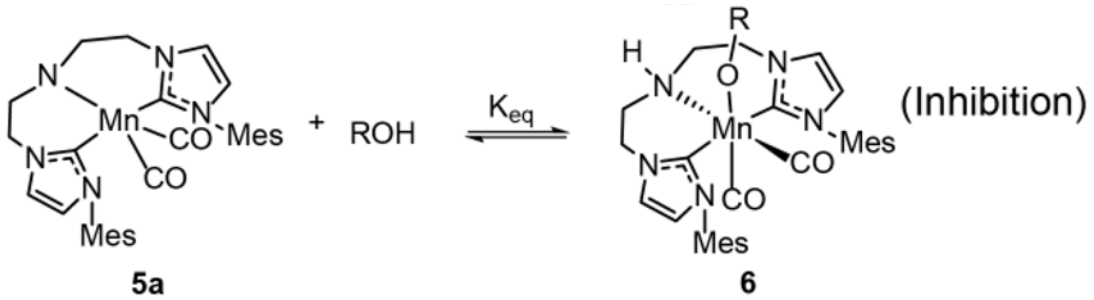
- Real solvent = reactive mixture
- Reactive System
- Multiphase, multicomponent

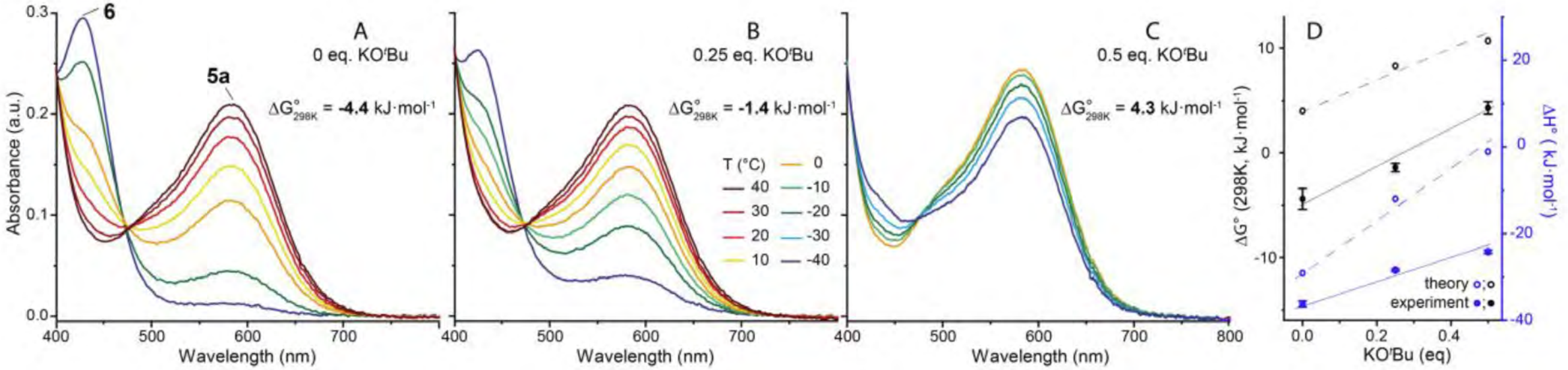
$$G°_{gas} = E_{DFT} + H_{corr} + TS_{gas}$$

$$G°_{sol} = G°_{gas} + G_{i,S}$$

Kulyaev, **EAP**, *ChemCatChem* ***2020***, *12*, 795

Additive changes the intrinsic thermodynamics





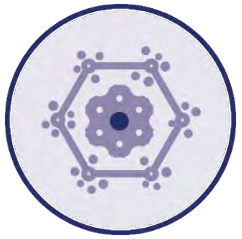
c(base) ↑

with W. Yang & G. Filonenko, *J. Am. Chem. Soc.* **2022**, 144, 8129

Summary #3: The Method Accuracy in CompCatal

- We've got robust tools to compute thermodynamics and spectroscopy features (if we are sure about the structure)
- If you know the structure, you'll have a high chance of having a good spectral signature. But usually, if the structure is known, then there is not much problem to start with.
- Still big problems with multireference systems
- Wrong structural model can give you the right answer, because of huge uncertainties/errors in experiment/theory

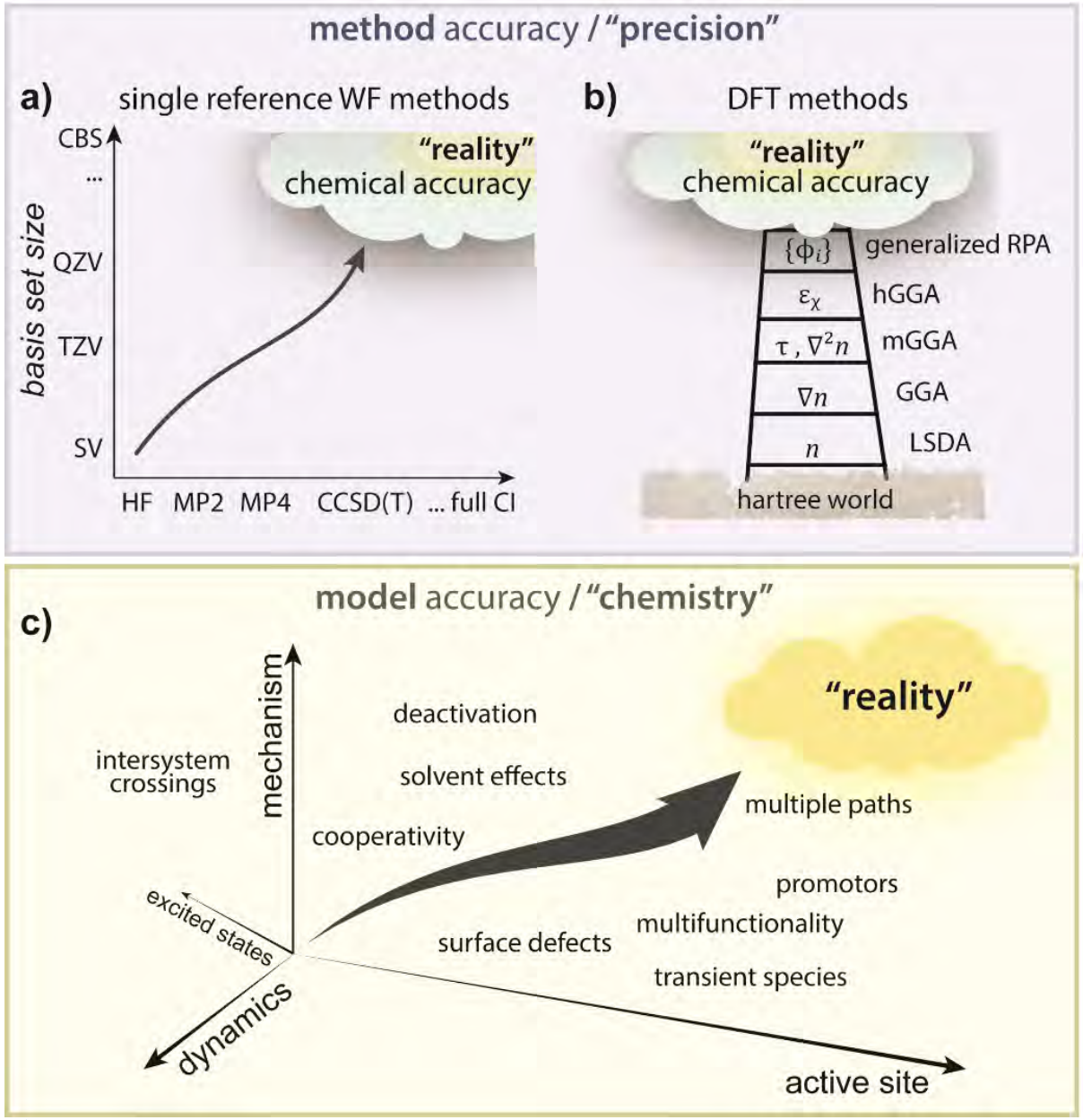
Computational **modelling in catalysis**

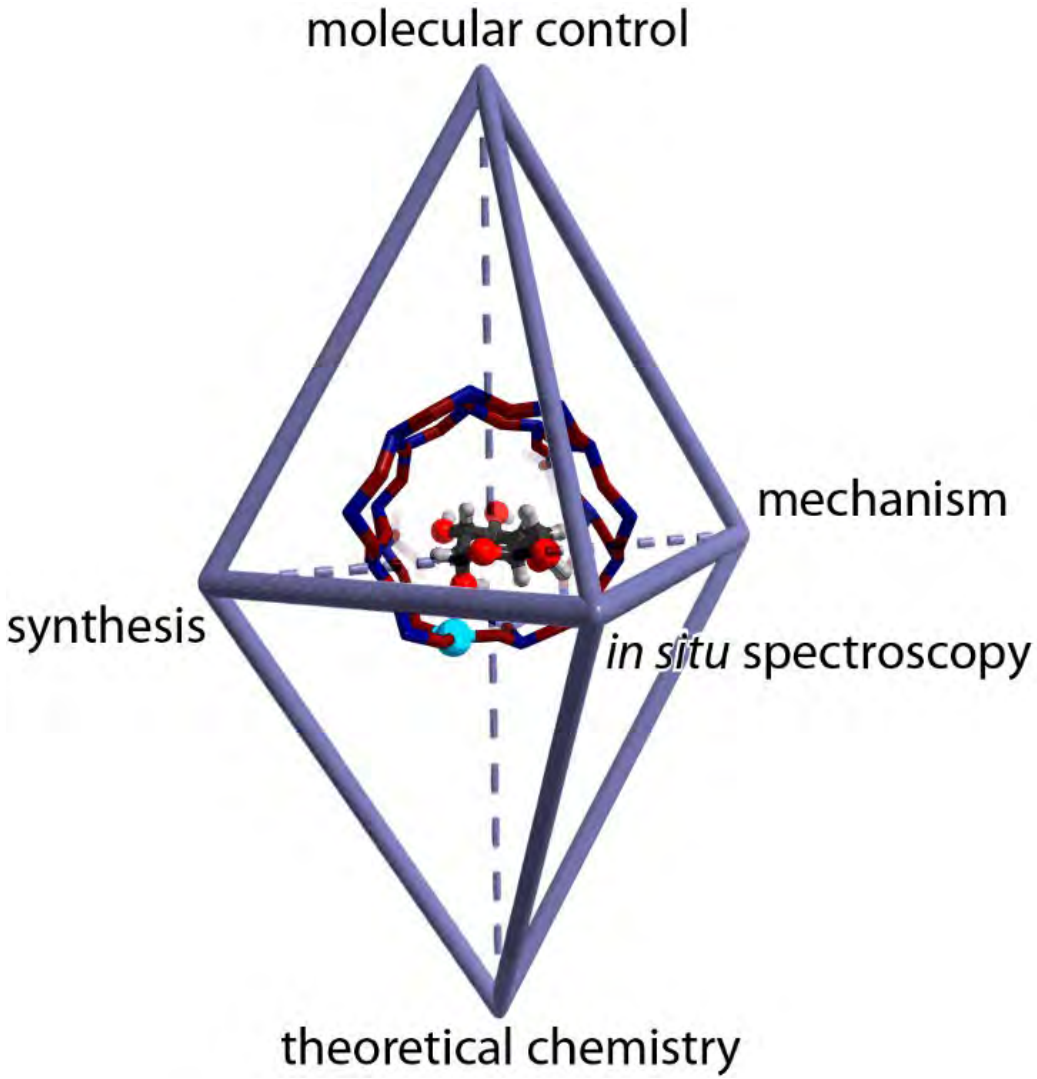


Model accuracy in computational catalysis

Are we certain about our model assumptions?

Computational Chemistry & Accuracy





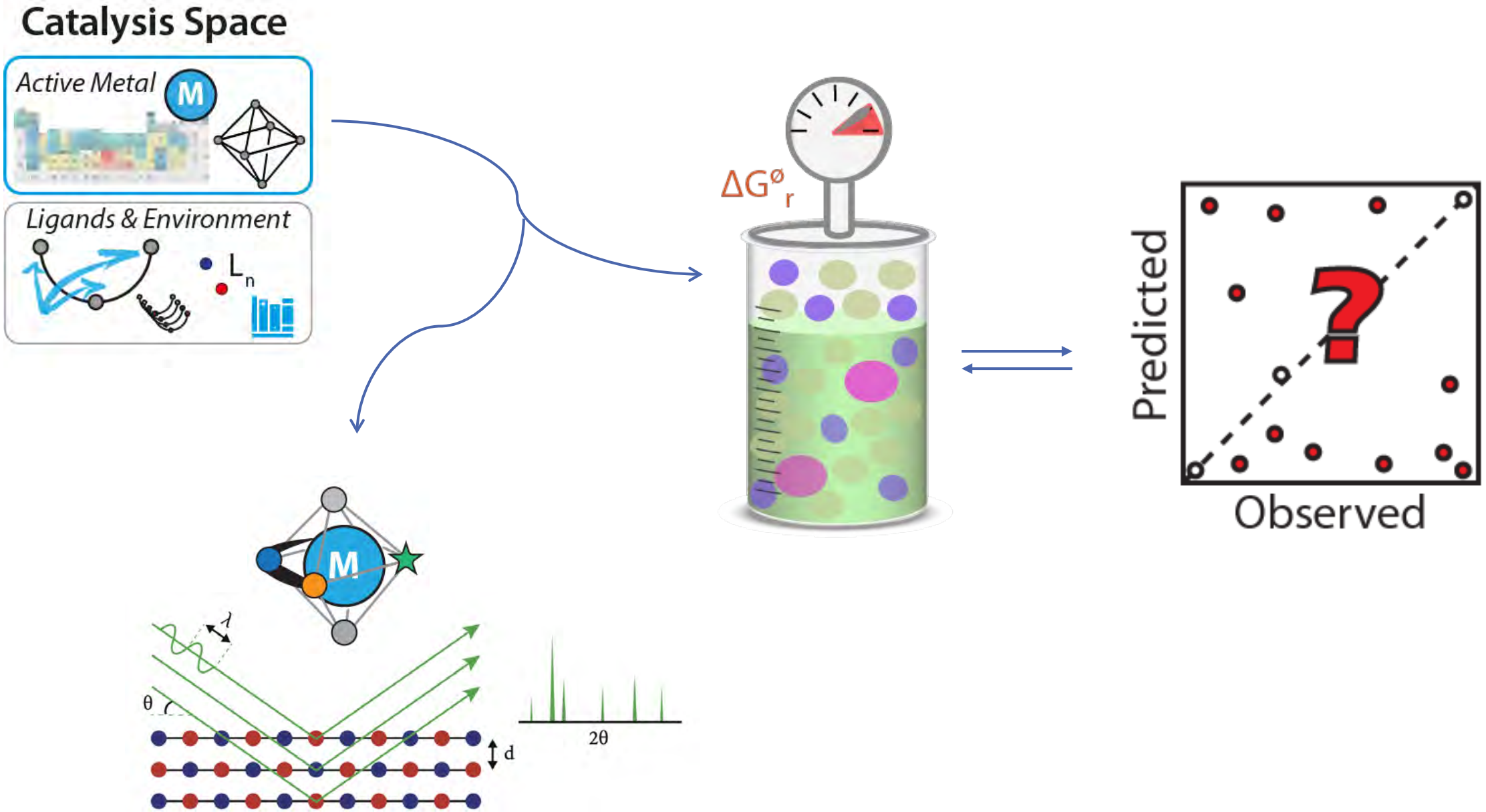
EAP, *ACS Catal.* **2017**, *7*, 4230

“Spherical cow moving with a speed of light”

Figure 1. Illustrative example of excessive reductionism in modeling. Despite being in a partial agreement (e.g., spectral features, patterns, and size) with the “experiment”, the model may not be adequate for the description of the key details within the catalytic system and its overall function.

EAP, *ACS Catal.* **2017**, *7*, 4230

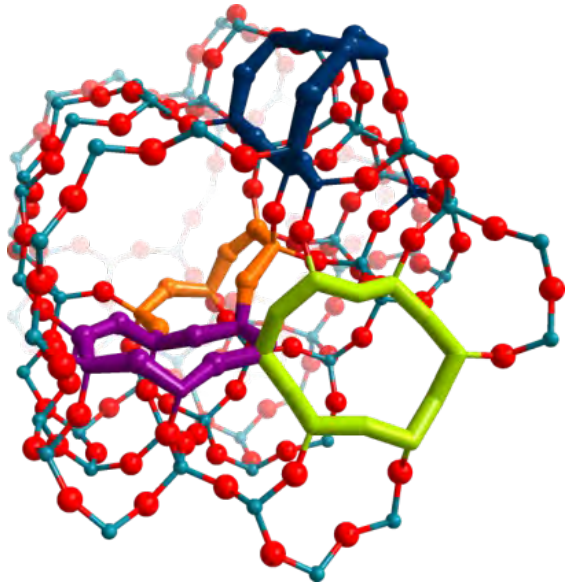
The Structural Problem in HomCat



The Structural Problem in HetCat

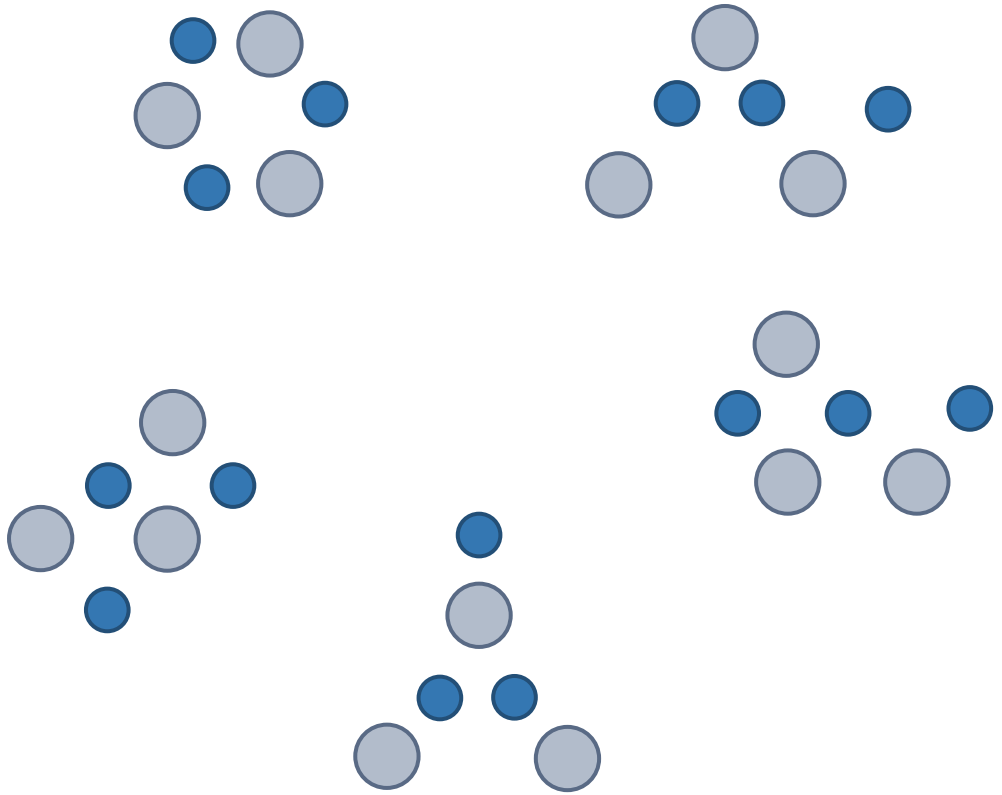
There are many possible stoichiometric combinations
Each combination has many possible configurations

MO

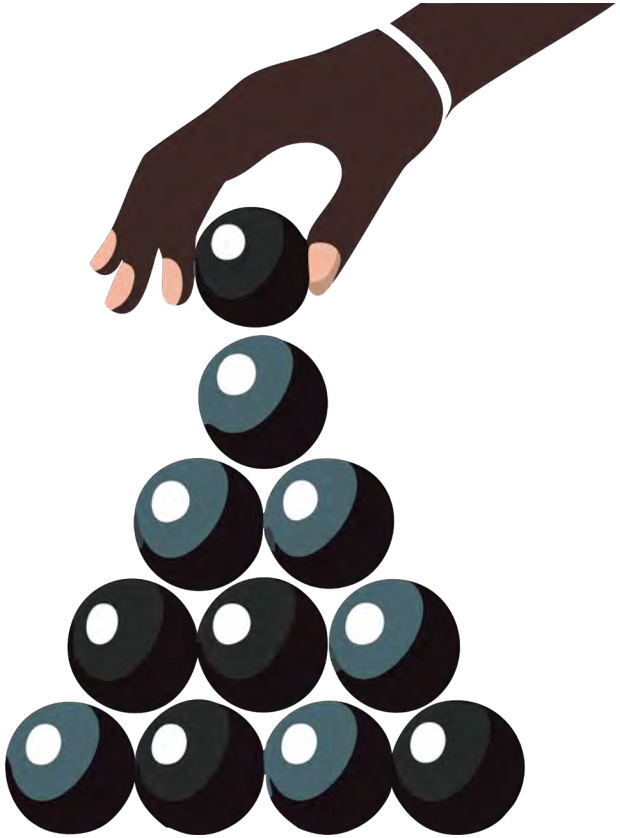


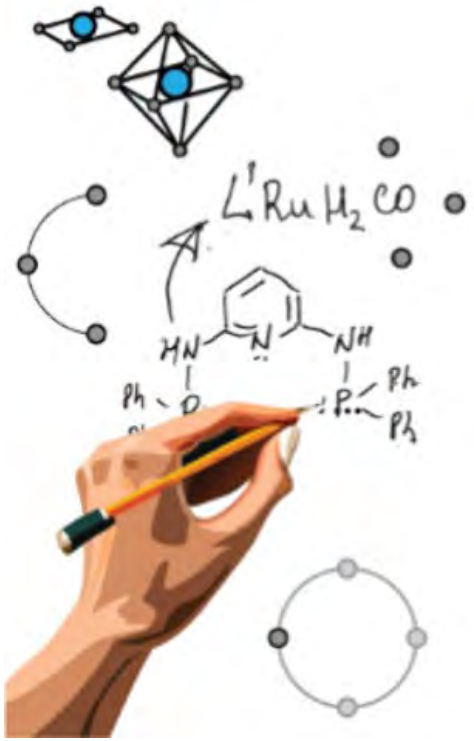
M_2O_2

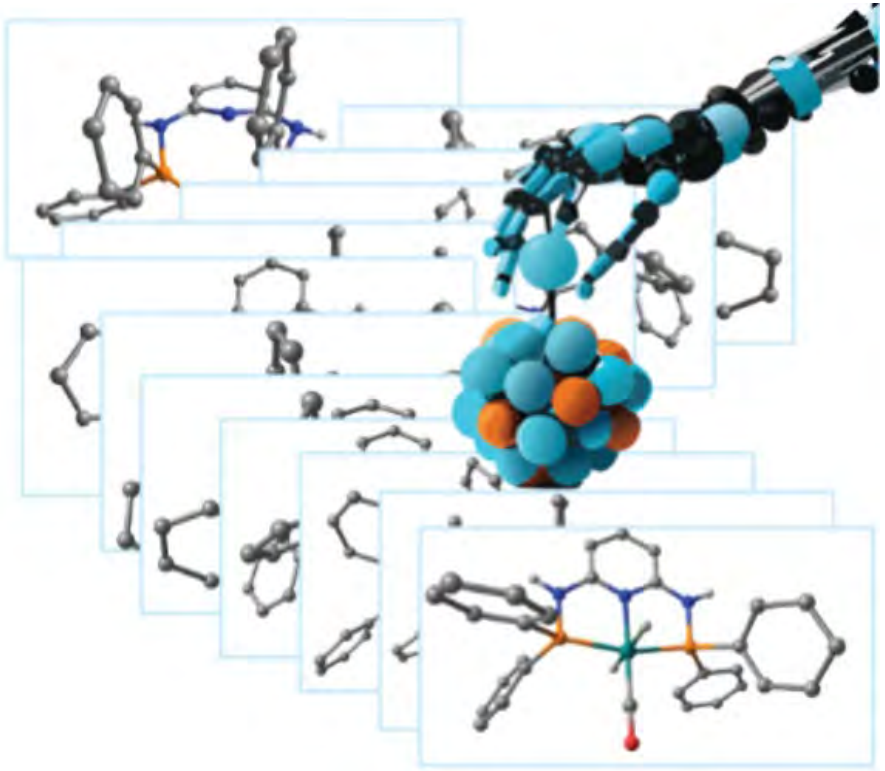
M_3O_3



How to get the structure right?



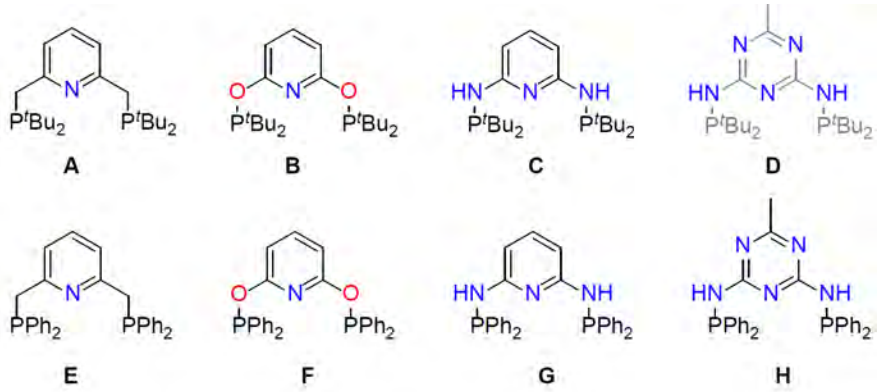


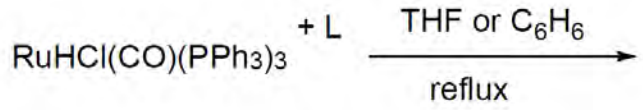


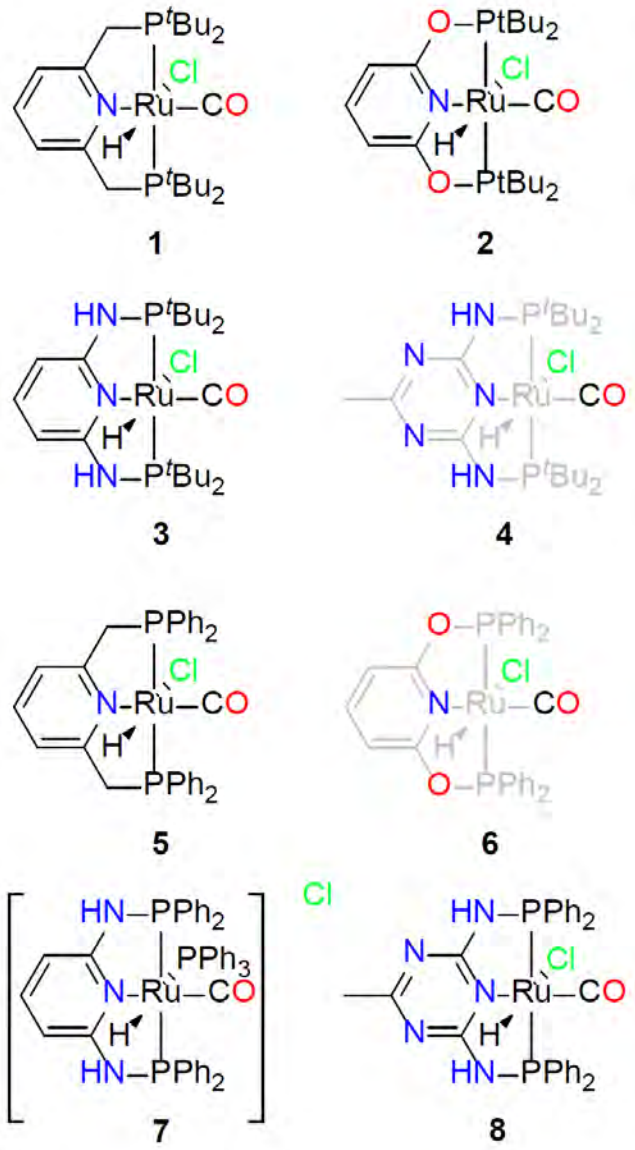
Defining the primary catalyst model

Engineers and Organometallic Chemistry

The practice of HomCat



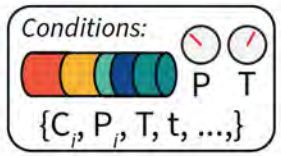


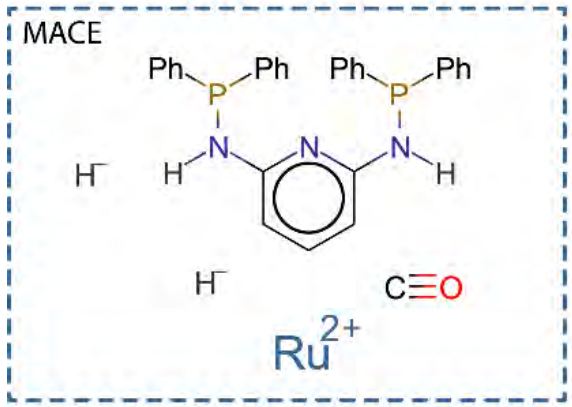


- No a priori knowledge on the exact coordination
- Structural uncertainty

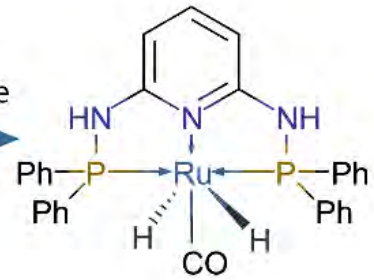
Experimental studies on bicarbonate hydrogenation by Ru pincers: *Catal. Sci. Technol.*, 2022,**12**, 2972
Green Chem., 2021,**23**, 8848

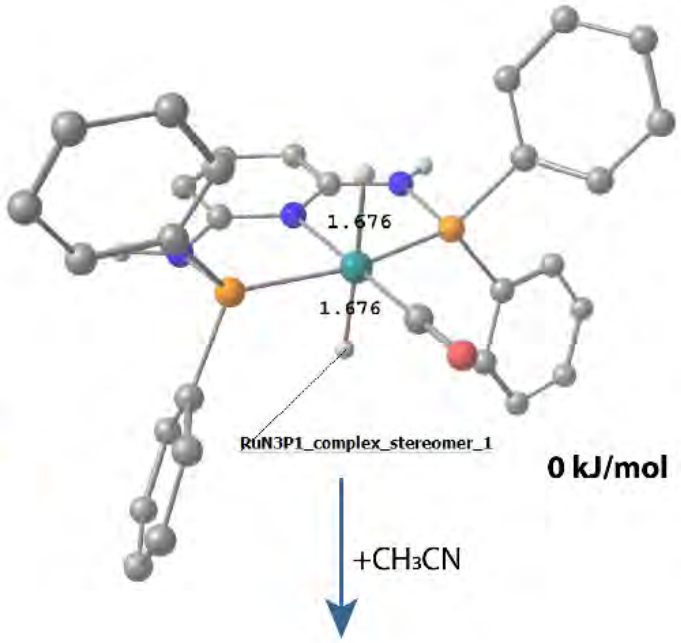
Initiating DFT worfklow





Expert knowledge



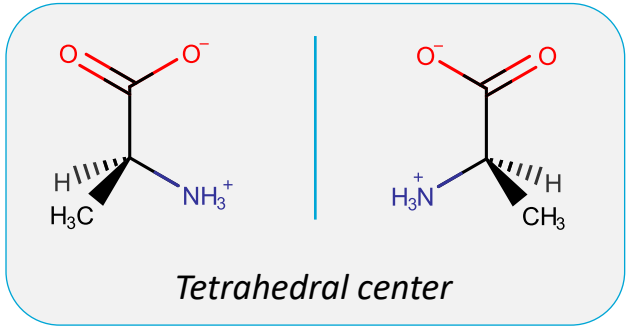


?

- Conventional DFT workflow poses quite some barrier for experimentalists (chemical engineers) to join in
- Much expert knowledge is necessary for building molecular models

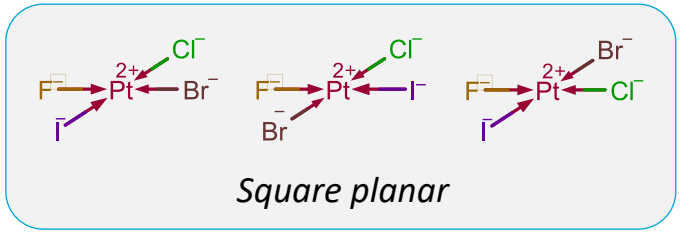
Cheminformatic routines

- Almost all operations use the graph representation of molecules:
  - Substructure search;
  - Stereomers generation;
  - Generation of 2D & 3D coordinates;
  - Descriptors generation, etc

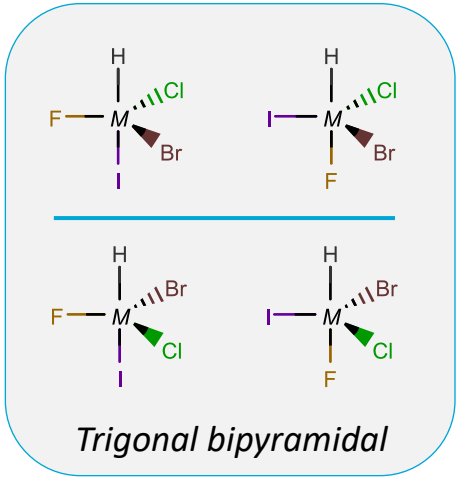


Tetrahedral center

- Stereochemistry: binary variable in organic, but not in coordination chemistry
  - 3, 18, 30 variants of ligand arrangement for *sqp*, *tbp*, *oct* complexes + hemilability

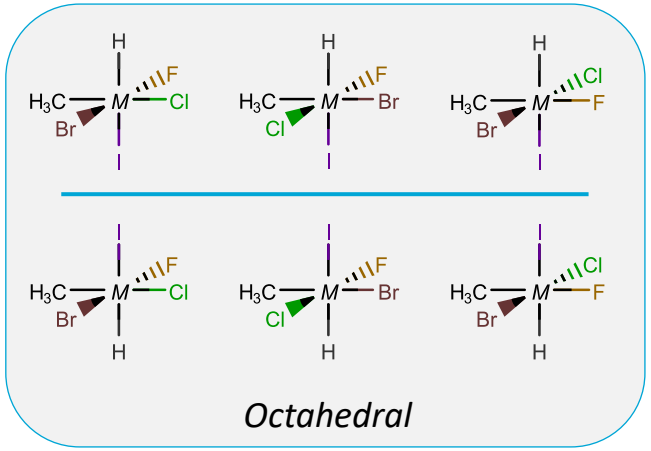


Square planar



Trigonal bipyramidal

… and 7 more pairs

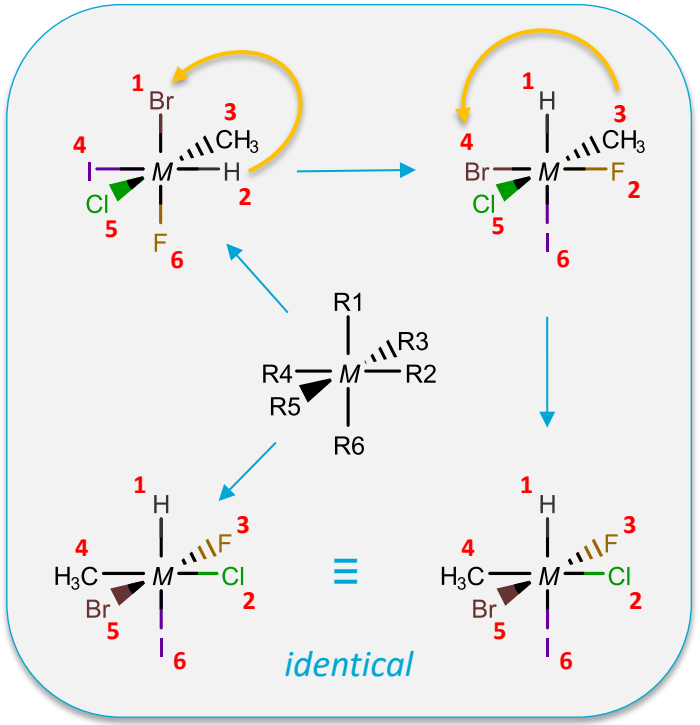


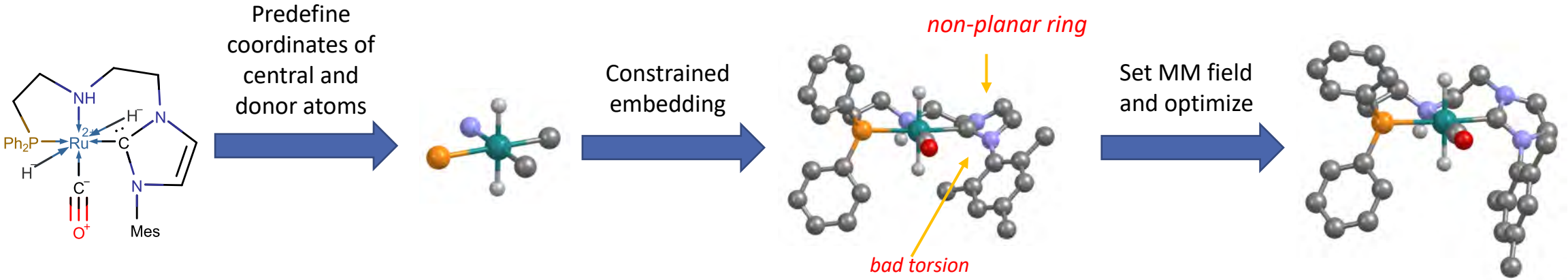
Octahedral

… and 12 more pairs

How to: compare stereomers & 2D→3D convert

- Compare complexes by unique SMILES:
  - If identical => continue
  - Otherwise => different
- Enumerate ligands by their 3D position (with atom map numbers)
- Try to superimpose two complexes:
  - If successful => identical
  - Otherwise => different

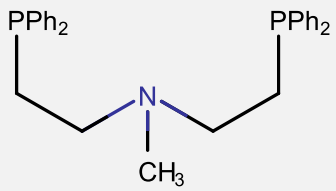




EPIC-MACE

Mn^+

Central atom



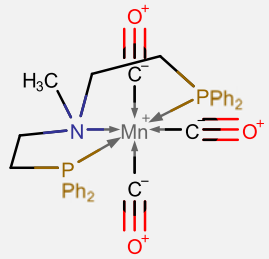
Main ligand

CO

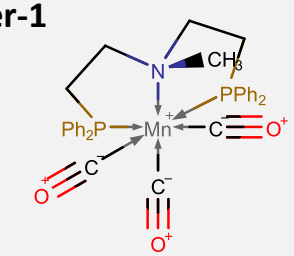
Auxiliary ligands

in situ

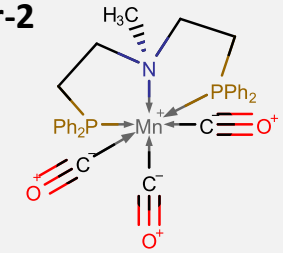
eq



mer-1



mer-2

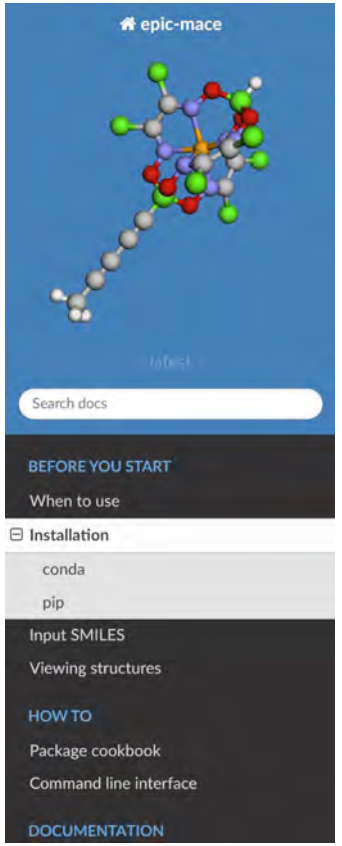


What it does:

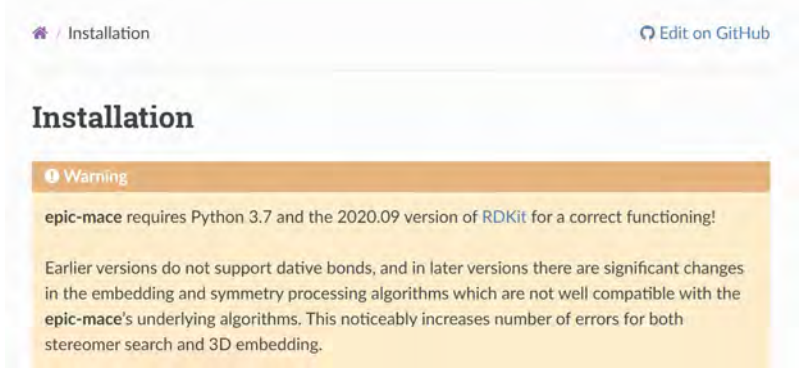
1. Generate all stereomers for given set of ligands
2. Make 3D coordinates

Acceptable limits:

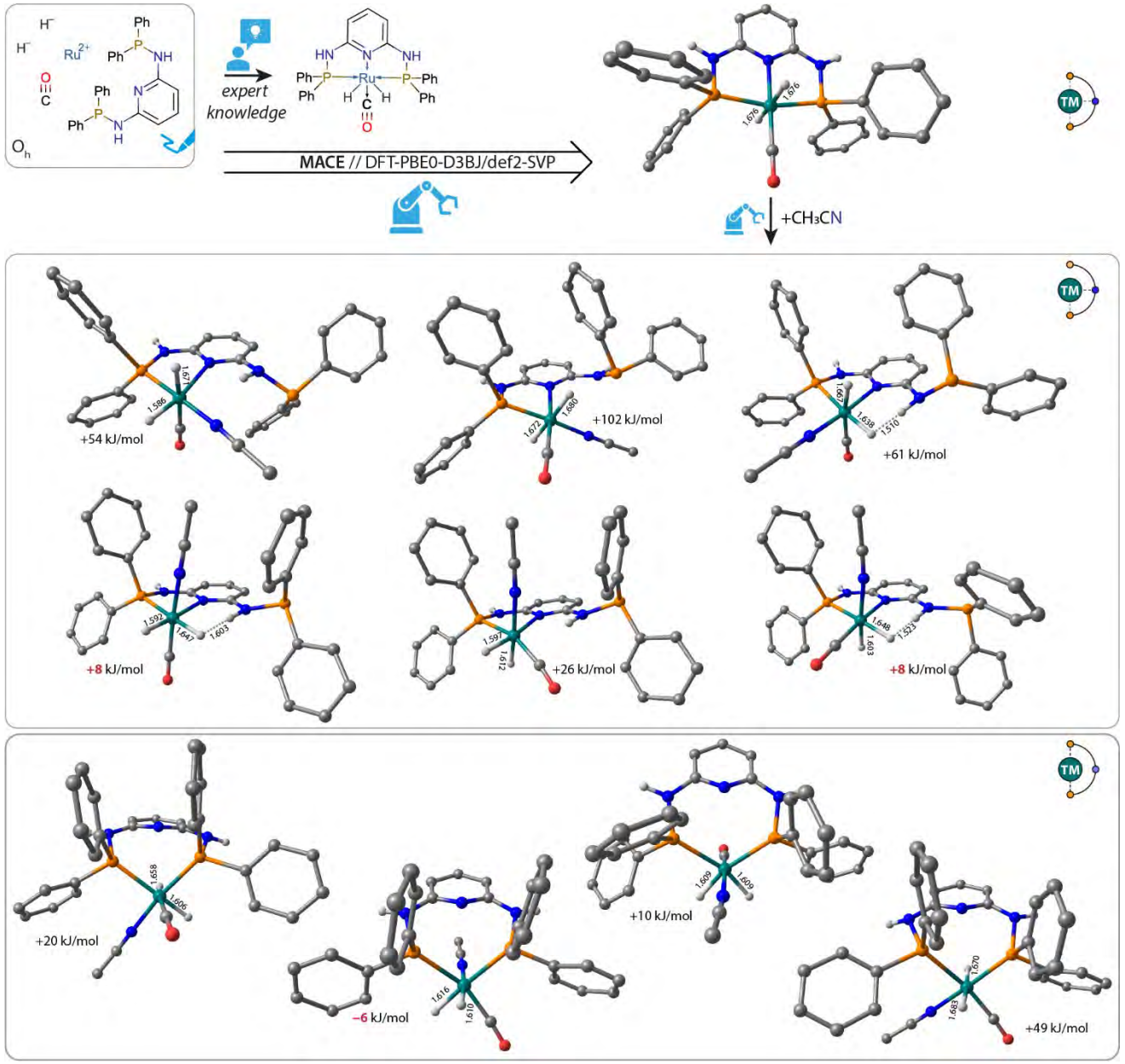
1. One central atom
2. No π-bonding (ferrocene, etc.)
3. Pre-defined donor atoms & Coordination polyhedron



Chernyshov, **EAP**, *JCTC* **2024**, *20*, 2313



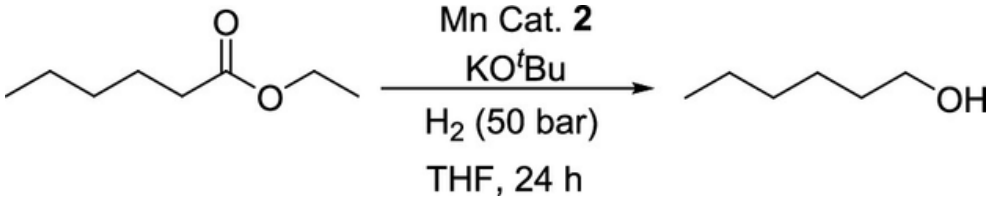
MACE: bias-free configuration explorer

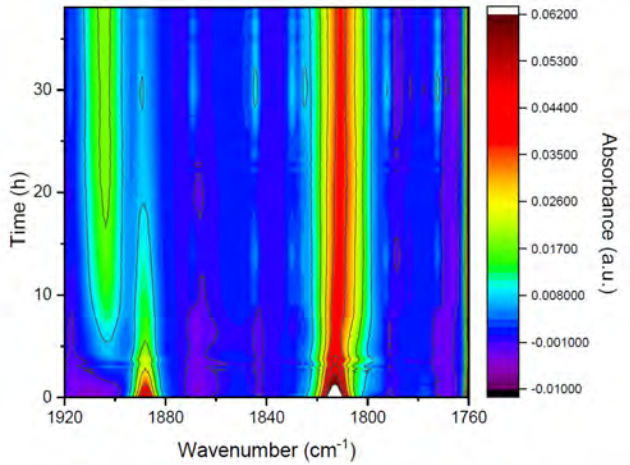


- Fully automated exploration structure construction
- New coordination mode identified
- Substrate-induced hemilability

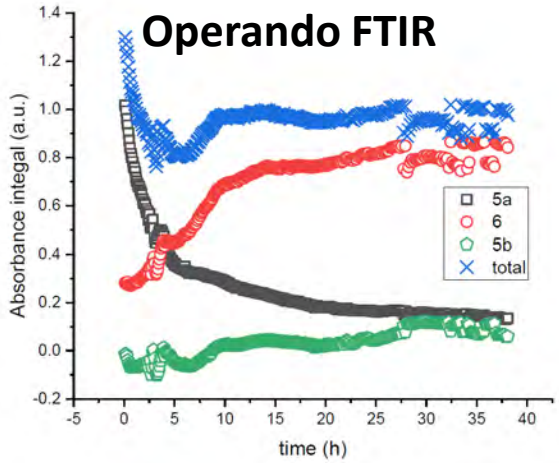
Chernyshov, **EAP**, *JCTC* **2024**, *20*, 2313

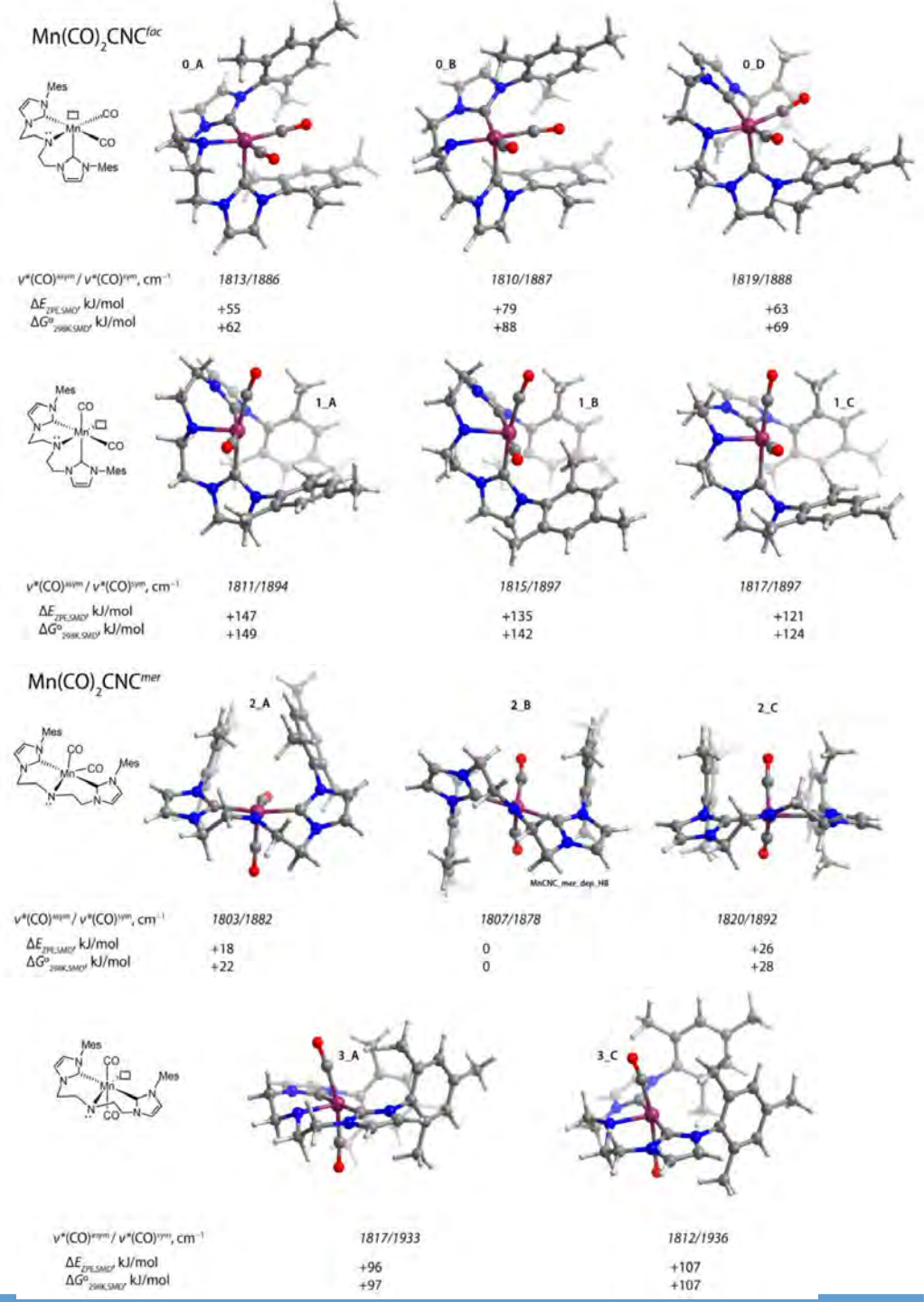
MACE: structural assignments





Operando FTIR

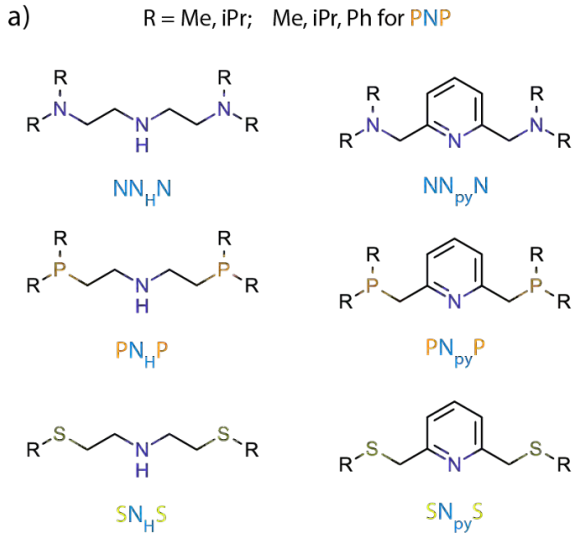


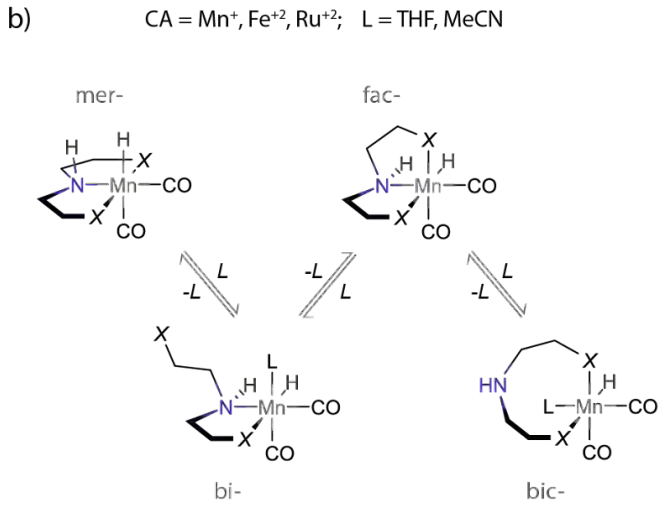


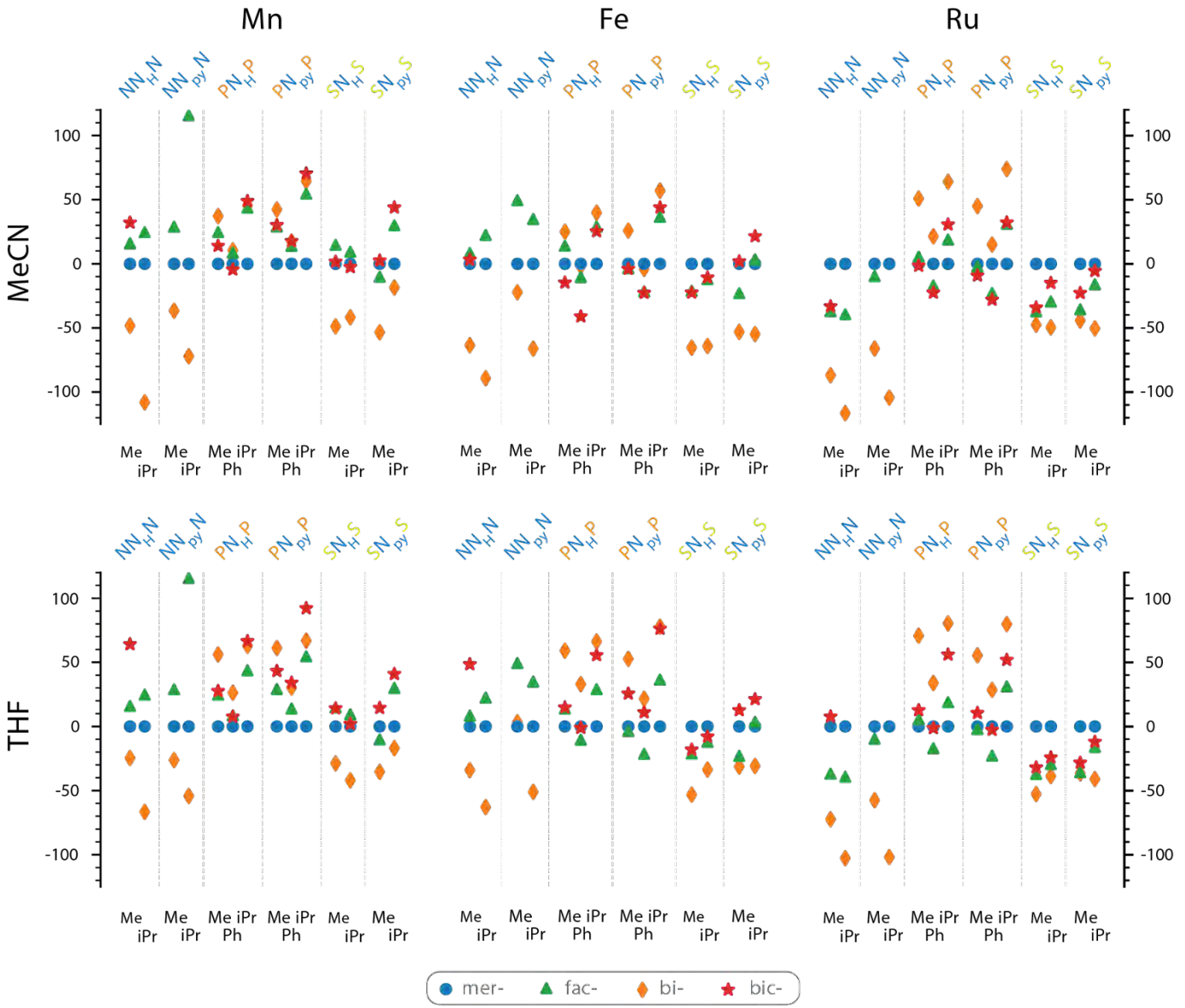
J. Am. Chem. Soc. **2022**, *144*, 8129

* scaled x0.9516
G16.C01-PBE1PBE-D3/6-311+G(d,p)/SMD(THF)

MACE: High-throughput exploration







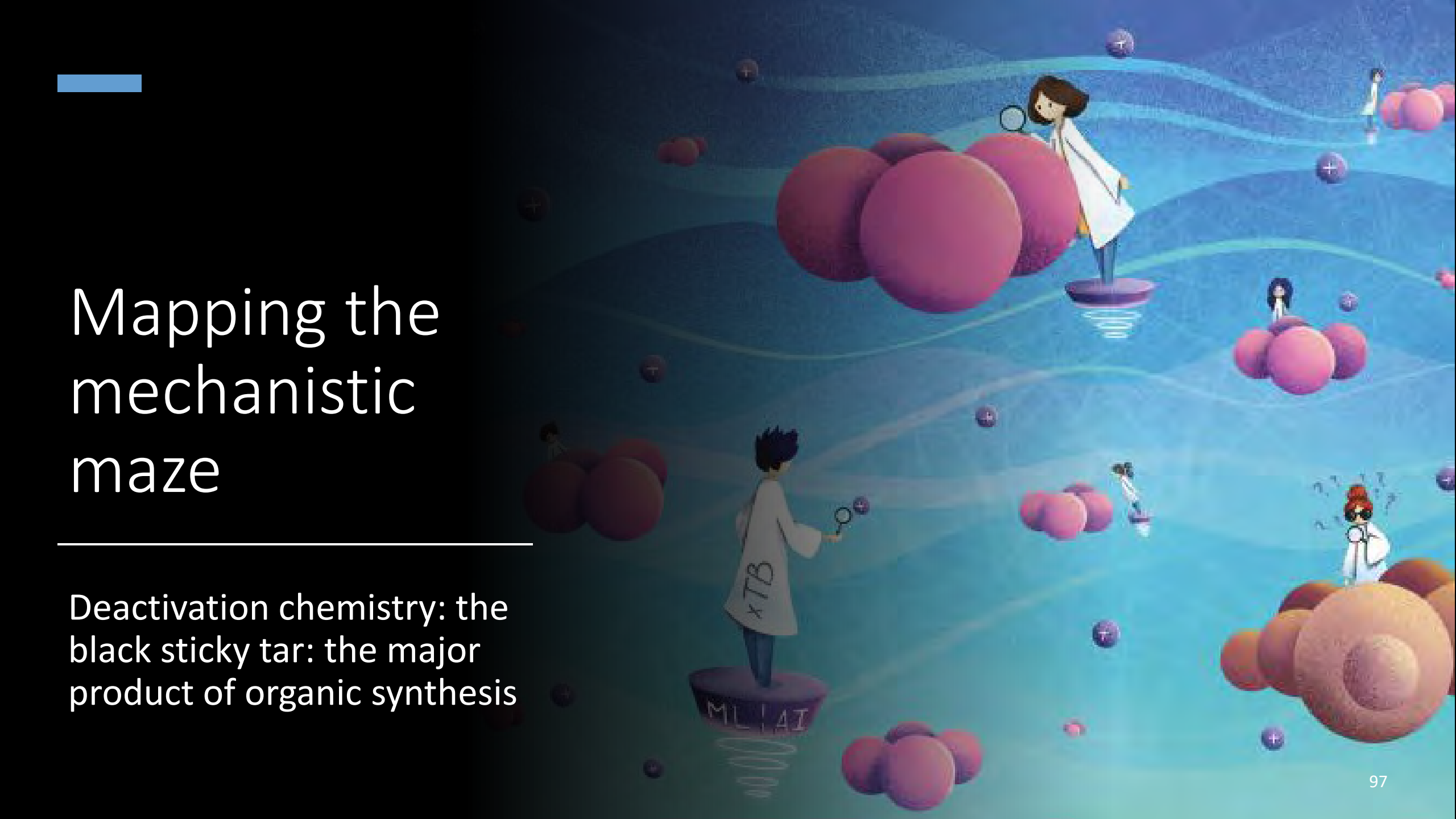
Chernyshov, **EAP**, *JCTC* **2024**, *20*, 2313

Summary: MACE

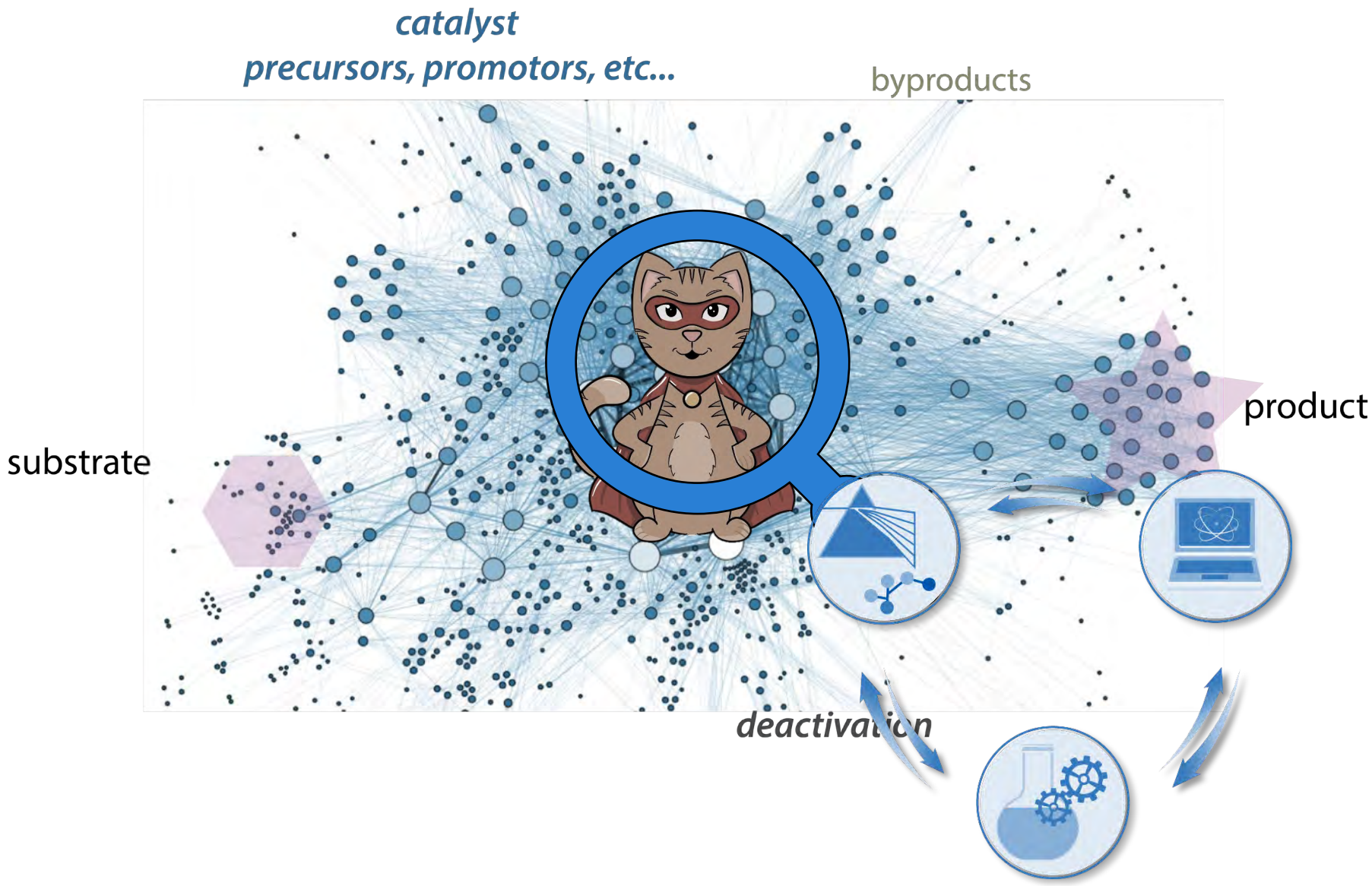
- Automated generation of organometallic scaffolds
- Intuition / expert-bias free coordination analysis
- Initial structure quality on par with that from expert with >15 years of experience
- Unresolved (yet) issues:
  - π-complexes
  - mononuclear only
  - limited coordination modes

Mapping the mechanistic maze

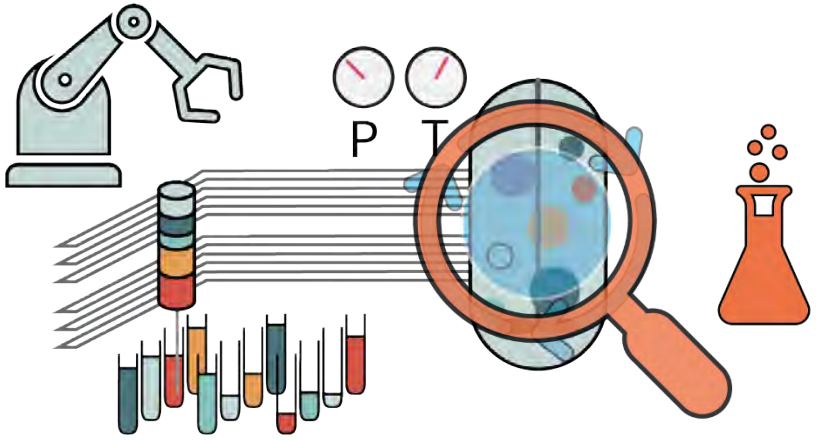
Deactivation chemistry: the black sticky tar: the major product of organic synthesis

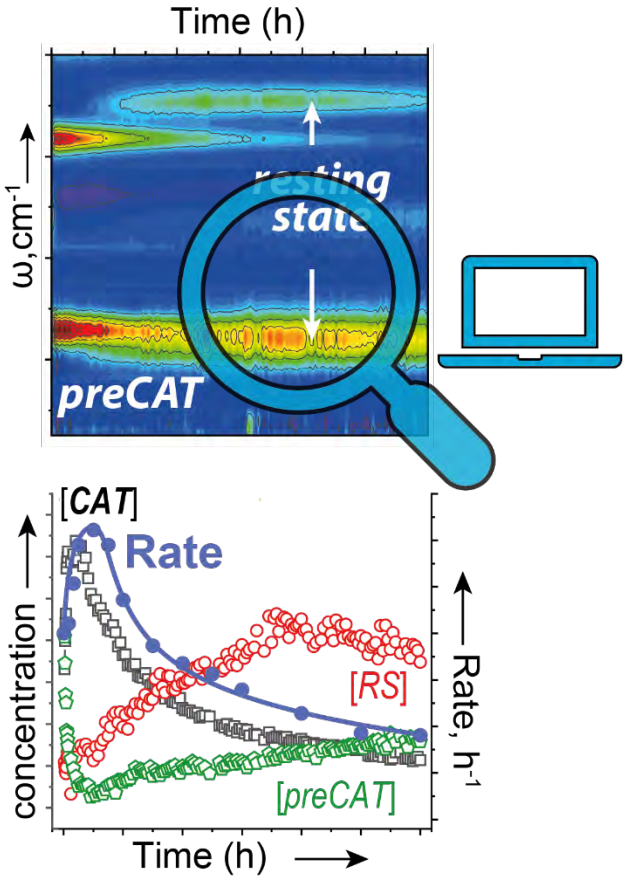


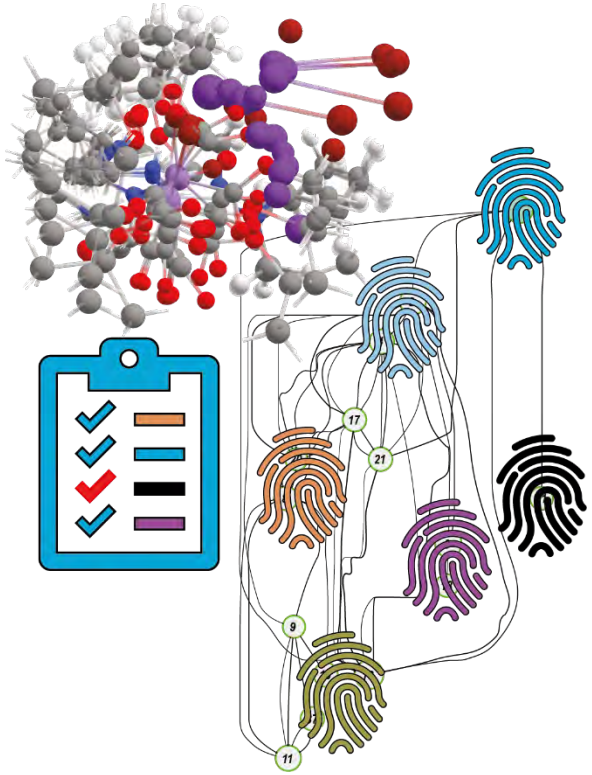
Automated in silico reactivity analysis: how it dies



Mapping chemistry in silico through automation





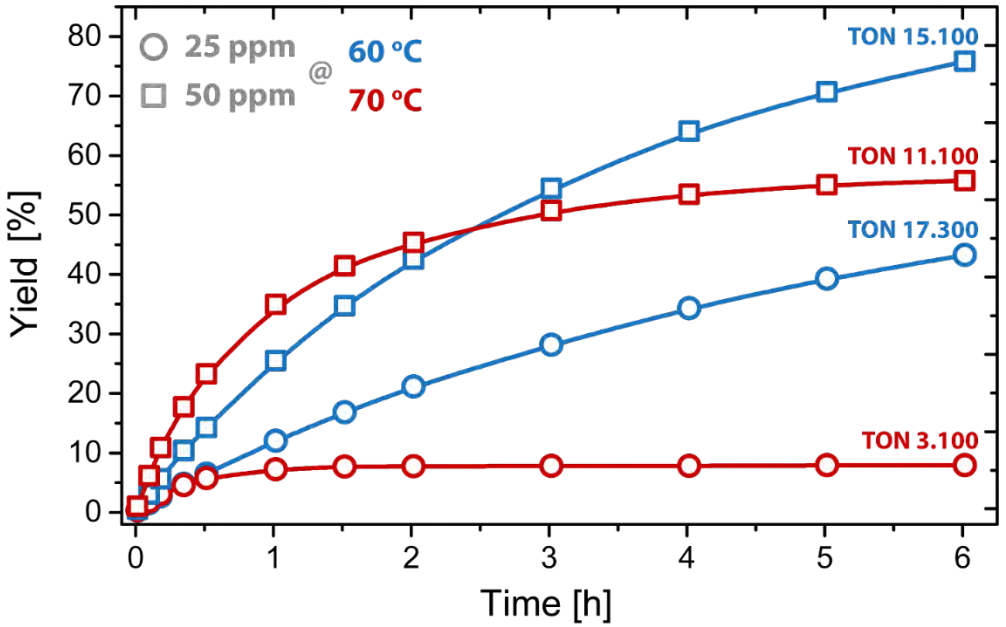


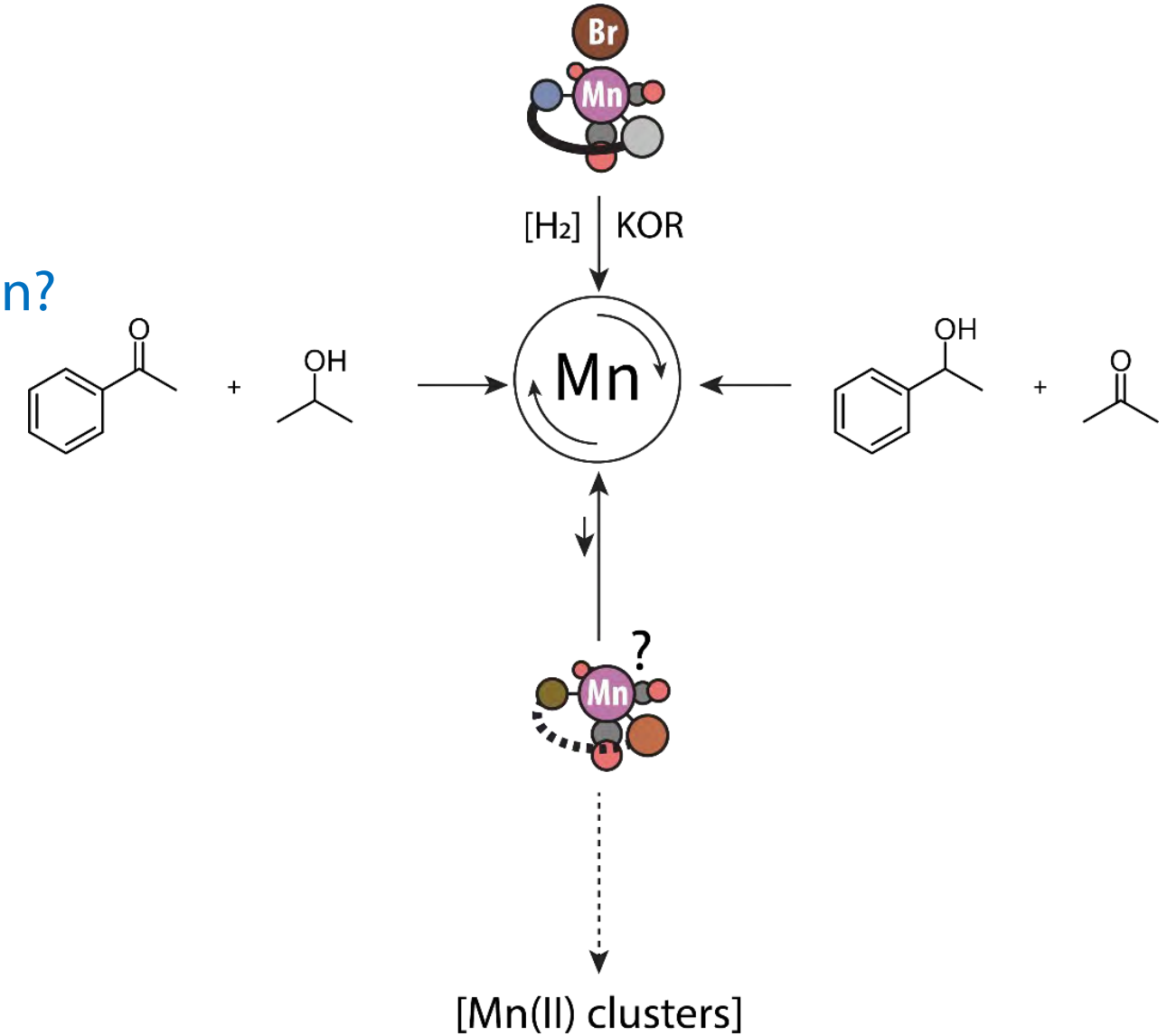
Key assumptions

- Reduce kinetic problem to thermodynamics
- No TS search, only minima
- More stable states – resting/deactivated states
- Meta-stable states – onset of deactivation/degradaton

Transfer hydrogenation with Mn(I) catalysts

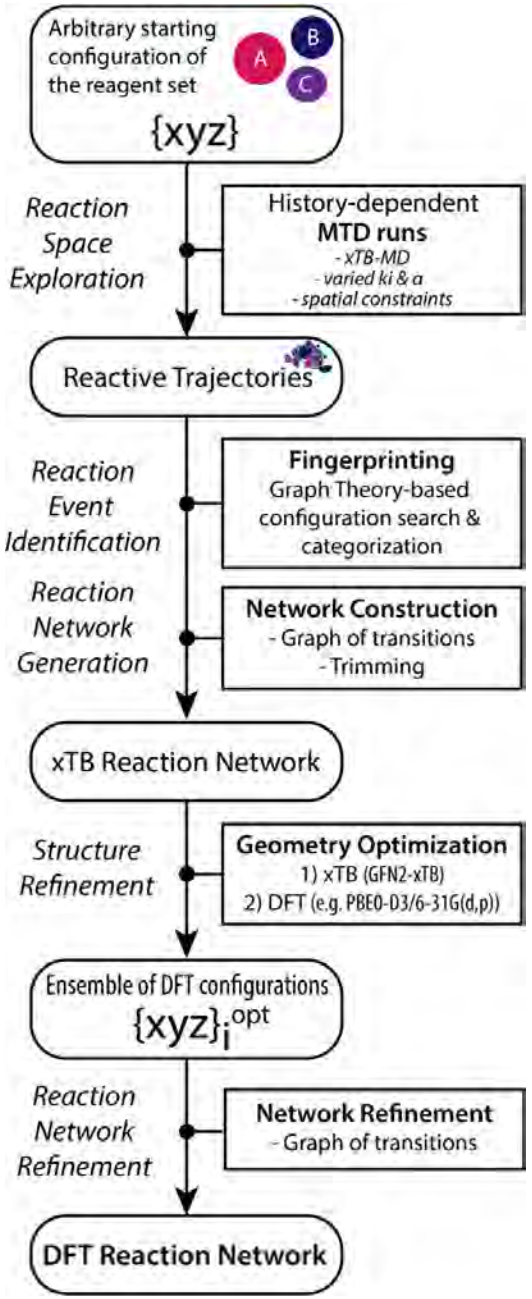
- Deactivation of best catalysts is most challenging to study
- Multiple, unresolved, activated paths
- Low concentration/rare event challenge
- Key question – what triggers the deactivation?

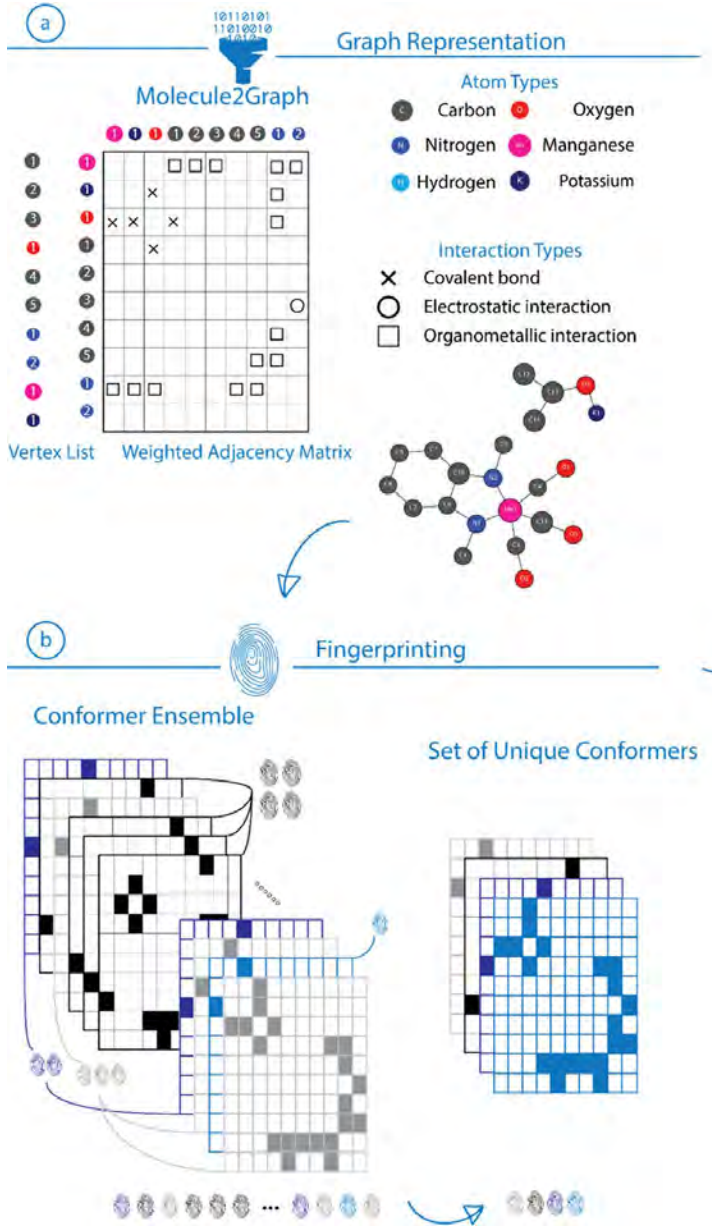


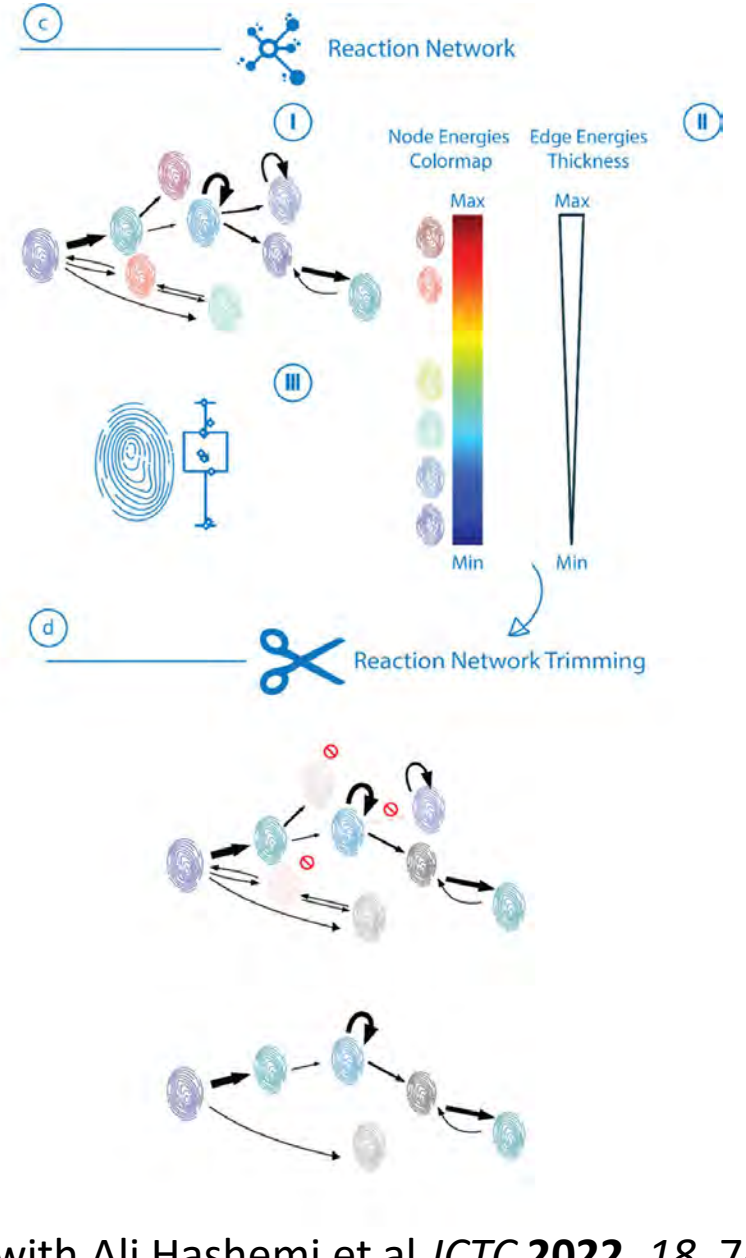


with van Putten et al, ChemCatChem **2019**, *11*, 5232

Expert bias-free in silico reactivity exploration: The **ReNeGate**

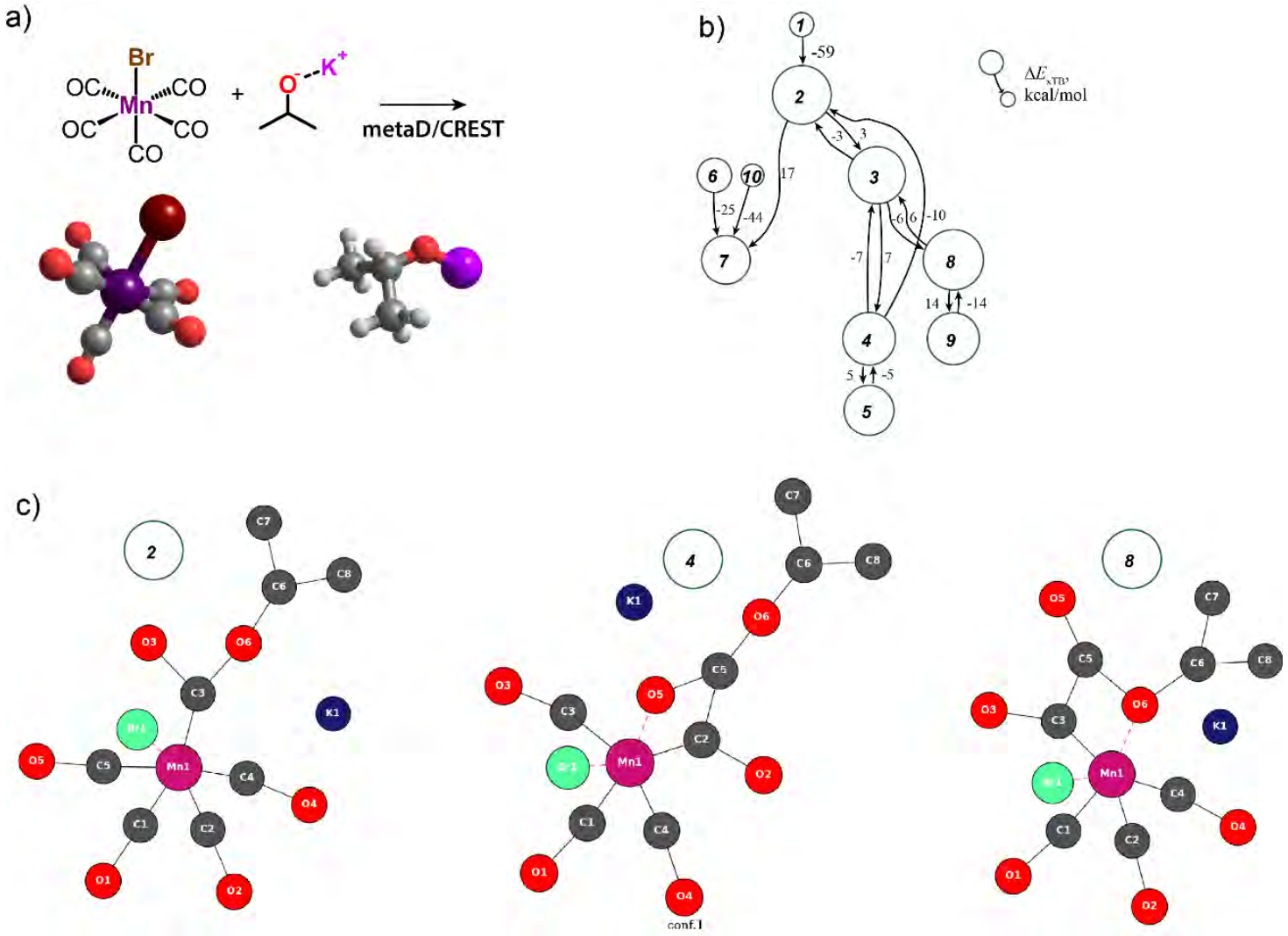






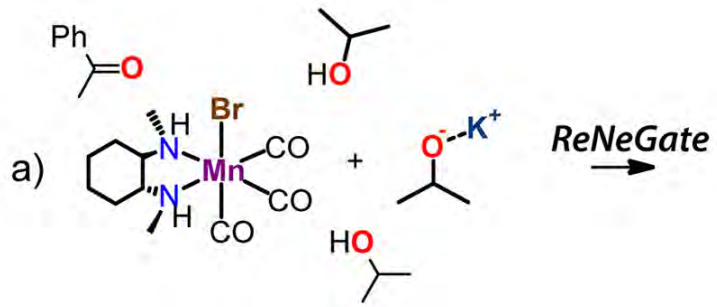
with Ali Hashemi et al *JCTC* **2022**, *18*, 7470

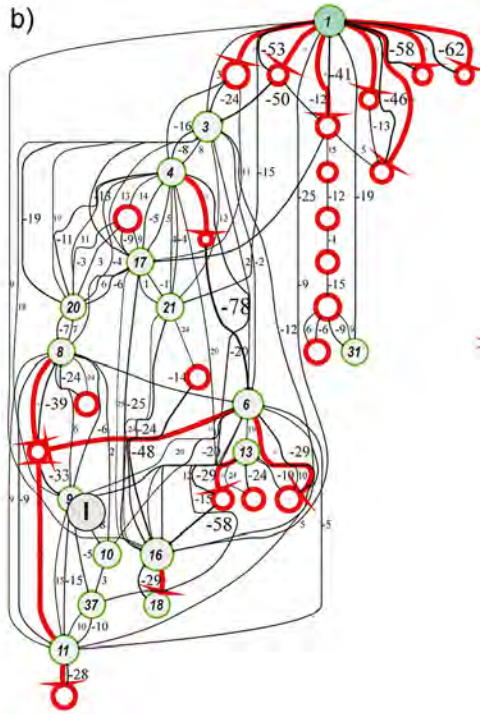
2D-MolGraphs to analyze reactive trajectories

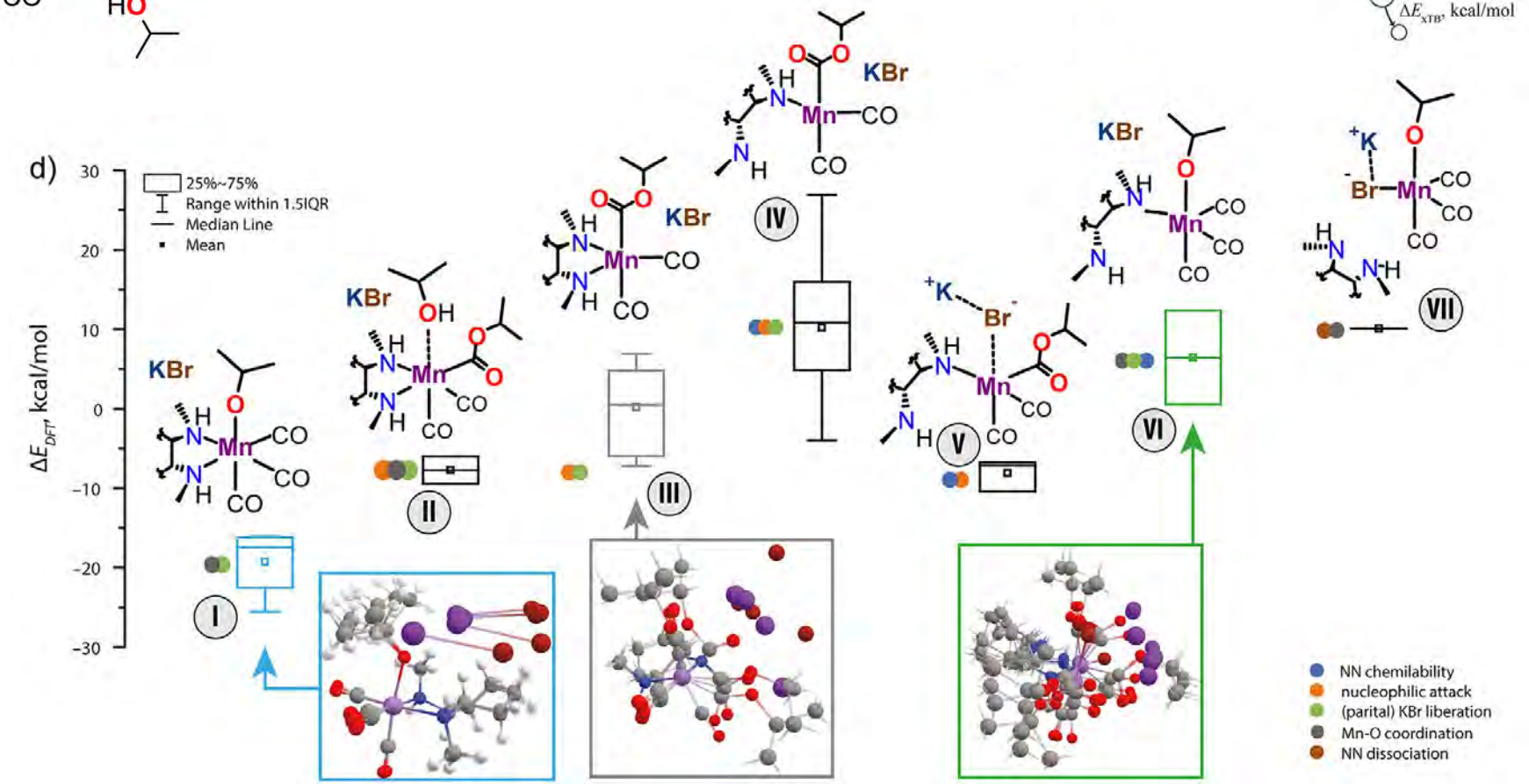


Topological 2D-Molecular Graphs: With Sana Bougueroua and Marie-Pierre Gaigeot (Université Paris-Saclay, Univ Evry)

A relevant model: $Mn(L^2)CO_3Br$ + KO^iPr + xHO^iPr







- **Nucleophilic attack on CO and ligand dissociation**

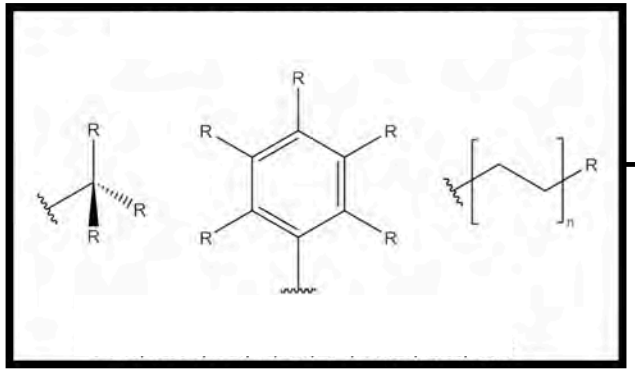
with Ali Hashemi et al *JCTC* **2022**, *18*, 7470

Exploring the space of catalysts

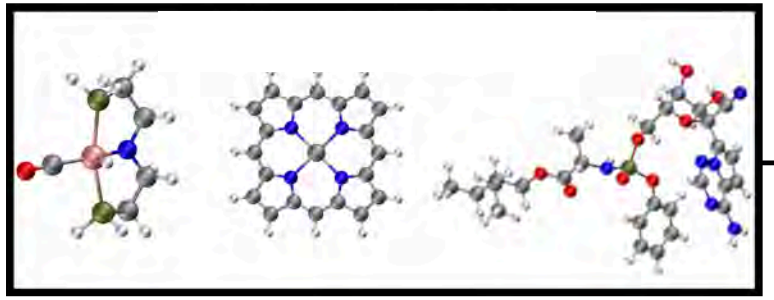
In silico HomCat screening

Quality comparable to xTB

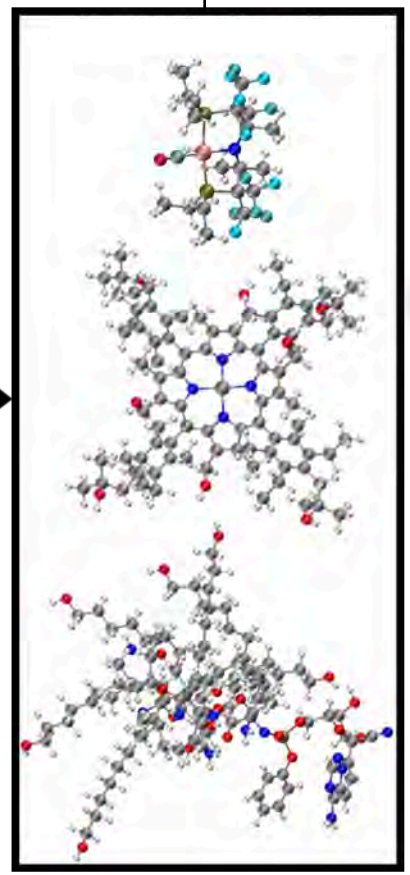
Library of ligands



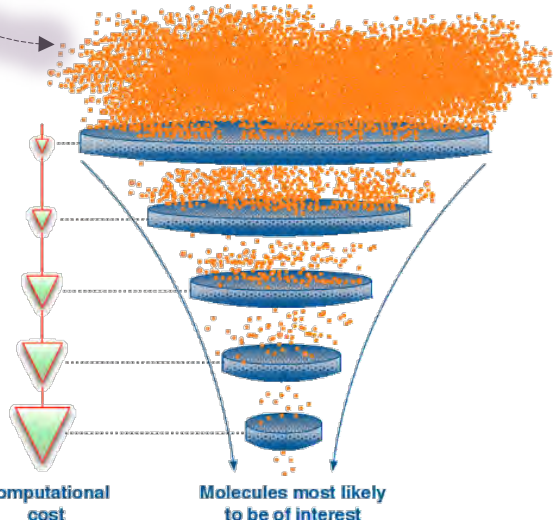
Library of scaffolds



ChemSpaX

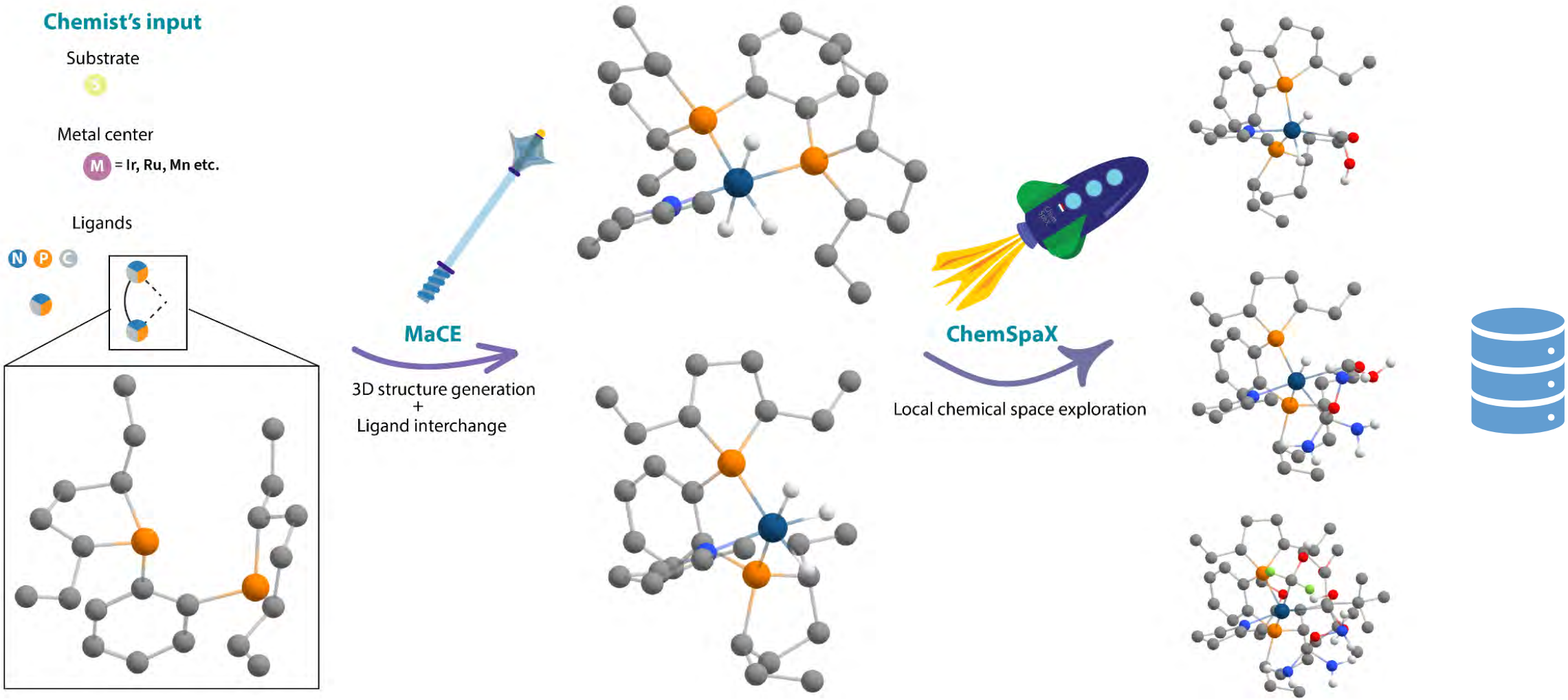


Library of functionalized complexes



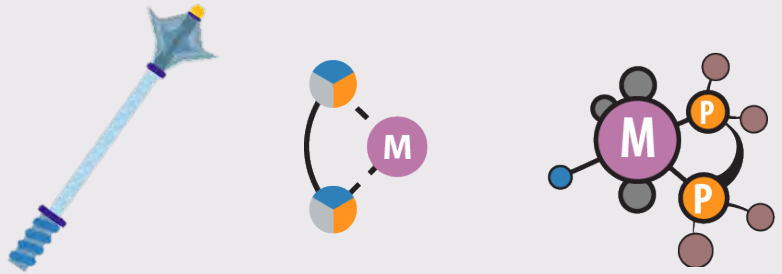
Kalikadien, EAP, Sinha, *Digital Discovery* **2022**, *1*, 8

In silico screening: MACE+ChemSpaX



OBELIX: Plugging things together

Catalyst structure generation
MACE

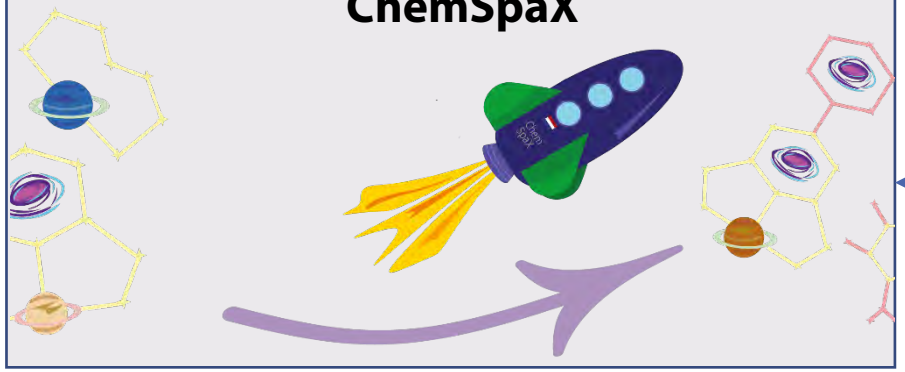


OBELIX

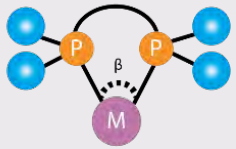
Conformer sampling
CREST

DFT optimization
Gaussian

Catalyst structure modification
ChemSpaX

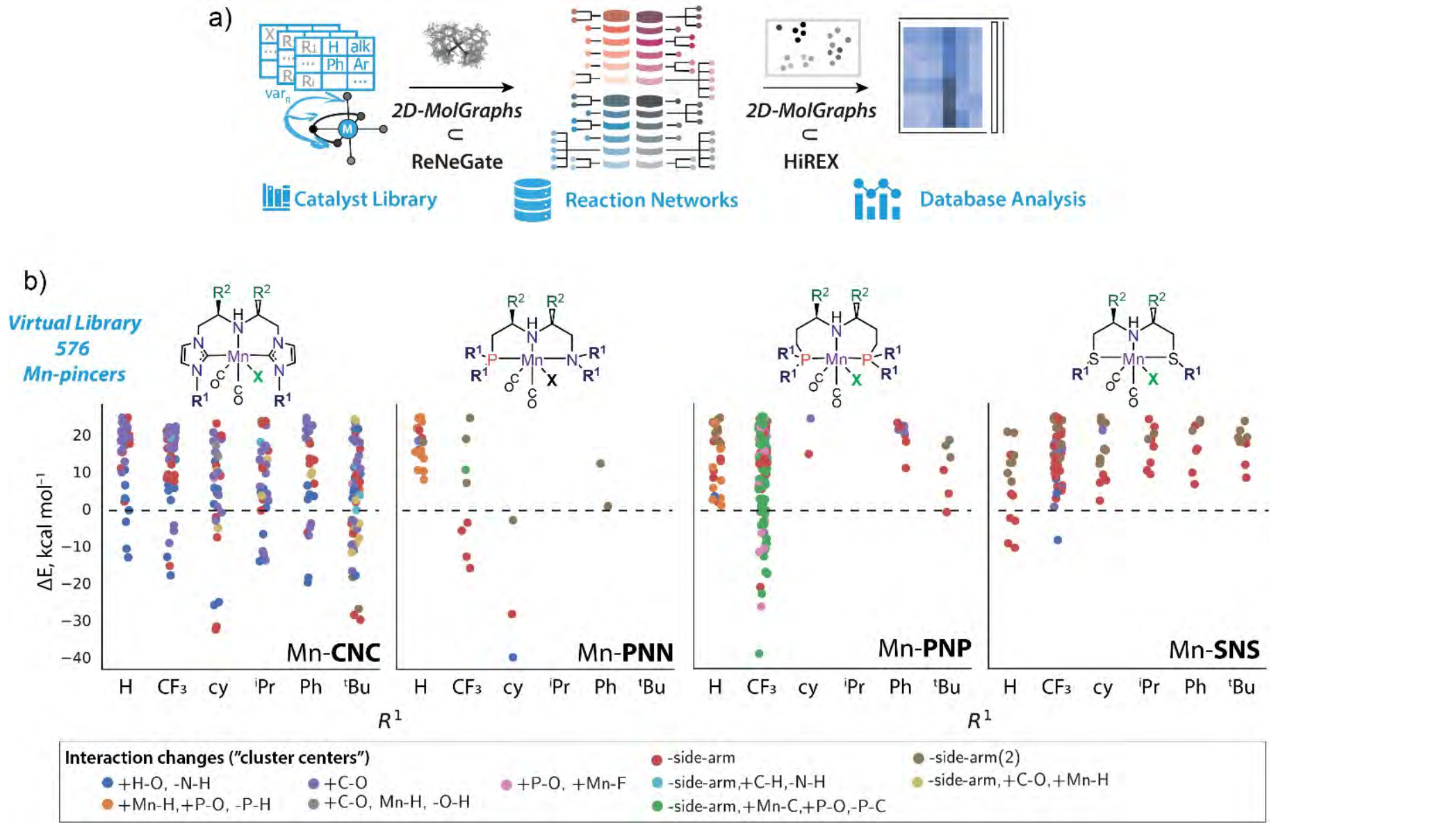


Descriptor calculation
Morfeus/in-house scripts



Kalikadien, Mirza, Najl Hossaini, Sreenithya, **EAP**, *ChemPlusChem* **2024**, DOI: 10.1002/cplu.202300702

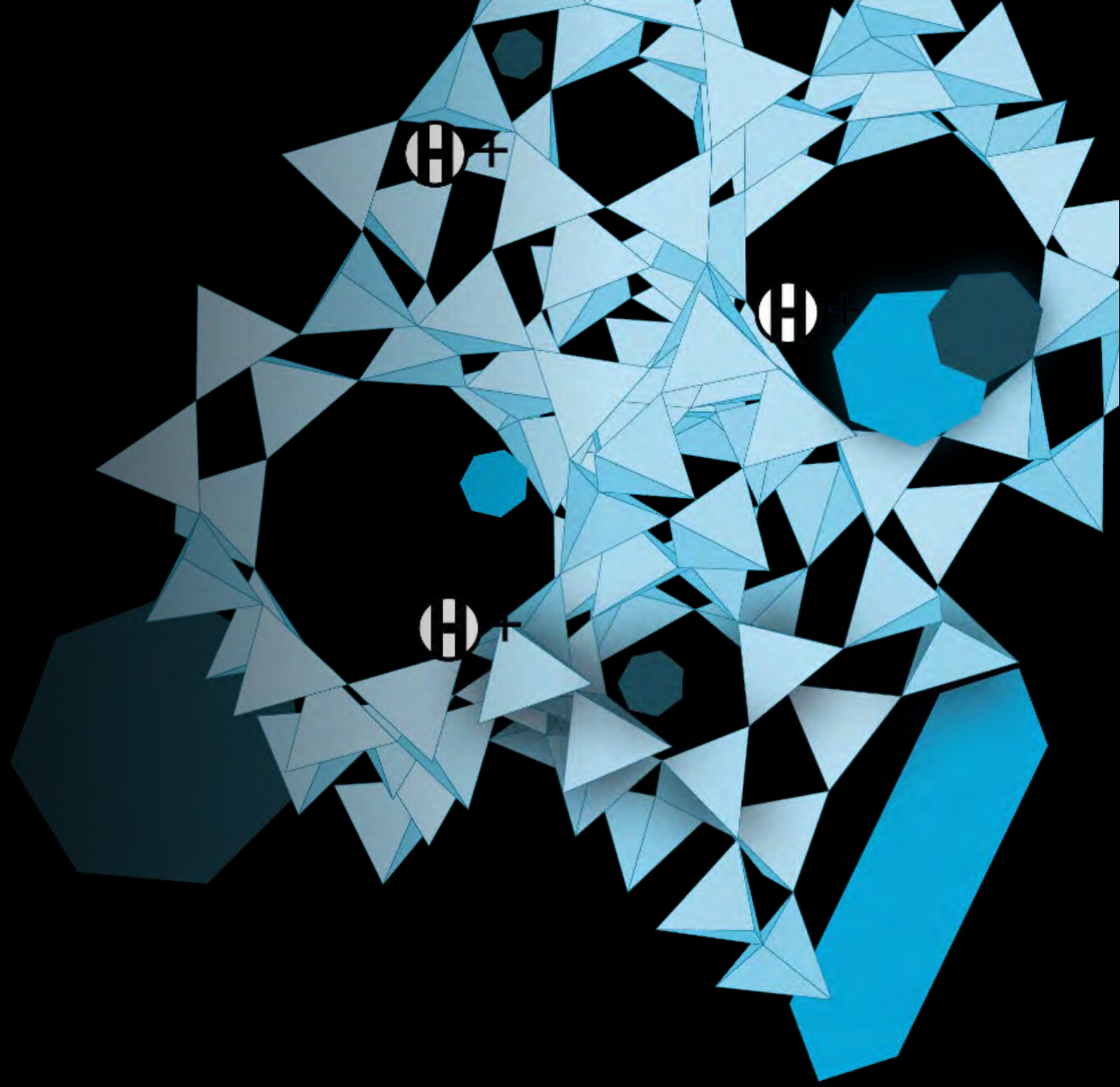
New reactivity explorations in HomCatal



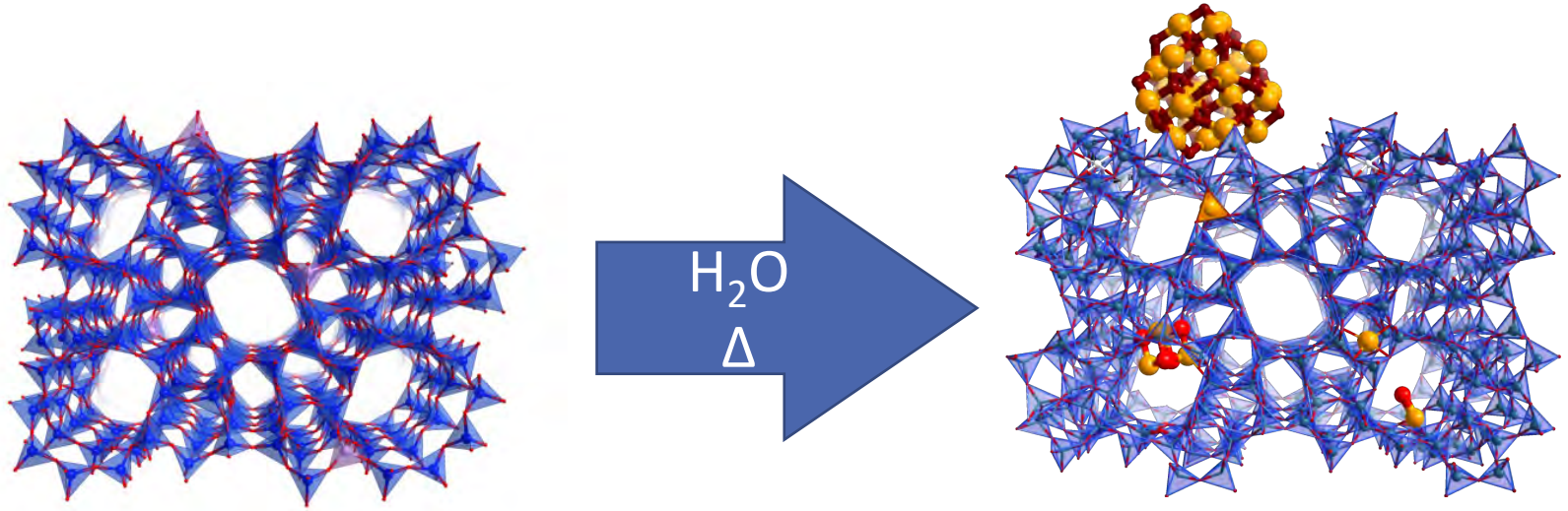
Hashemi, Bougueroua, Gaigeot, **EAP**, *J. Chem. Inf. Model.* **2023**, *63*, 6081

A few words about HetCat

The structural problem of zeolite catalysis



The structural problem of ZeoCAT: a computational approach



Key assumptions:

- Perfect crystallinity
- Homogeneous speciation
- DFT is good enough

The conventional workflow:

- Expert proposes structures
- Calculate structures & energies with DFT: *PES at vacuum / 0K*
- Add conditions via ab initio thermodynamic analysis: *Free energies*

Overview of the approach: G. Li, **EAP**, *ChemCatChem* **2018**,*11,* 134
Cu: G. Li, P. Vassilev, M. Sanchez-Sanchez, J. Lercher, E.J.M. Hensen, **EAP**, *J. Catal.* **2016**, *338*, 305
Al: C. Liu, G. Li, E.J.M. Hensen, **EAP**, *ACS Catal.* **2015**, *5* ,7024
Mo: G. Li, I. Vollmer, C. Liu, J. Gascon, **EAP**, *ACS Catal.* **2019**, *9*, 8731

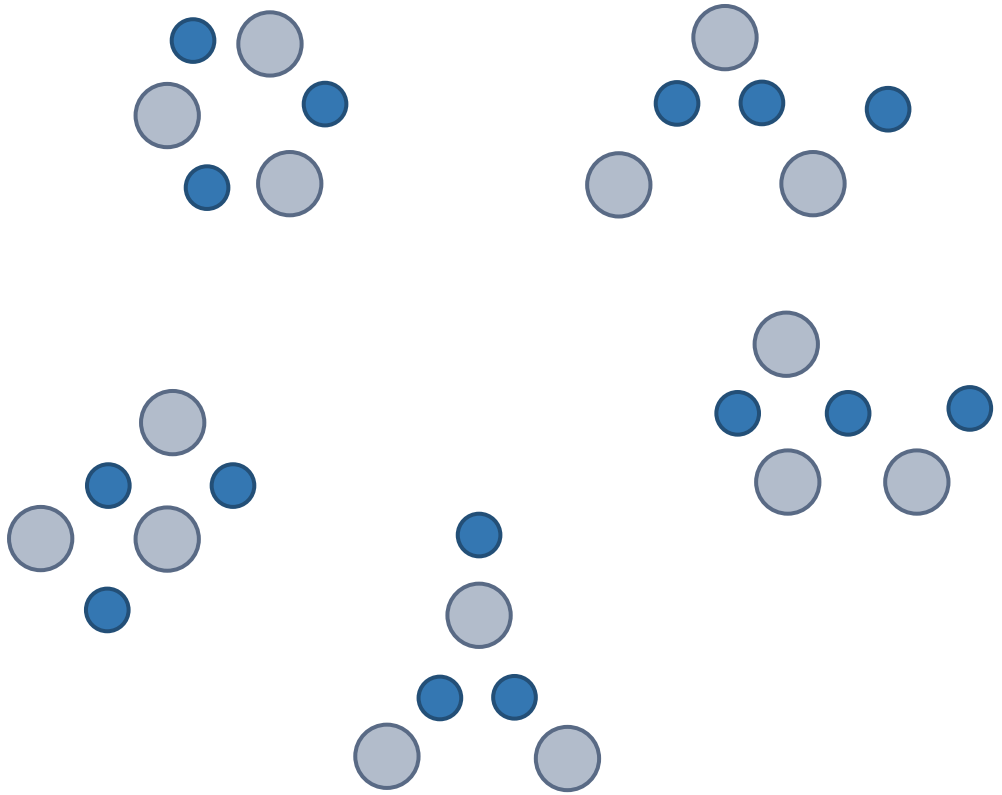
The Structural Problem

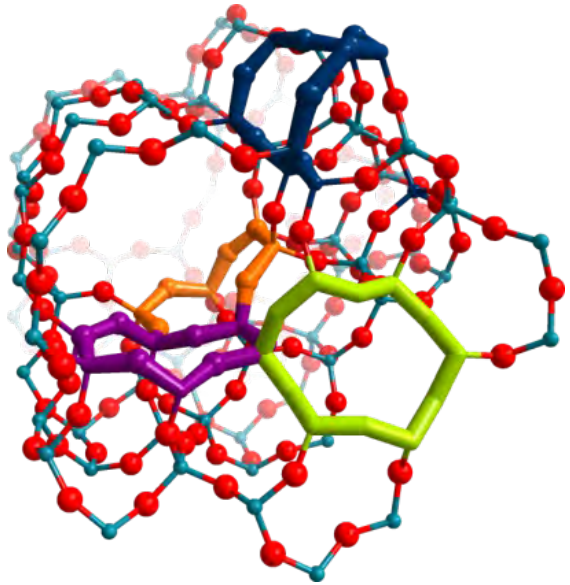
There are many possible stoichiometric combinations
Spectroscopy gives a signal, but experts assign it to some structure
Each combination has many possible configurations

MO

M_2O_2

M_3O_3



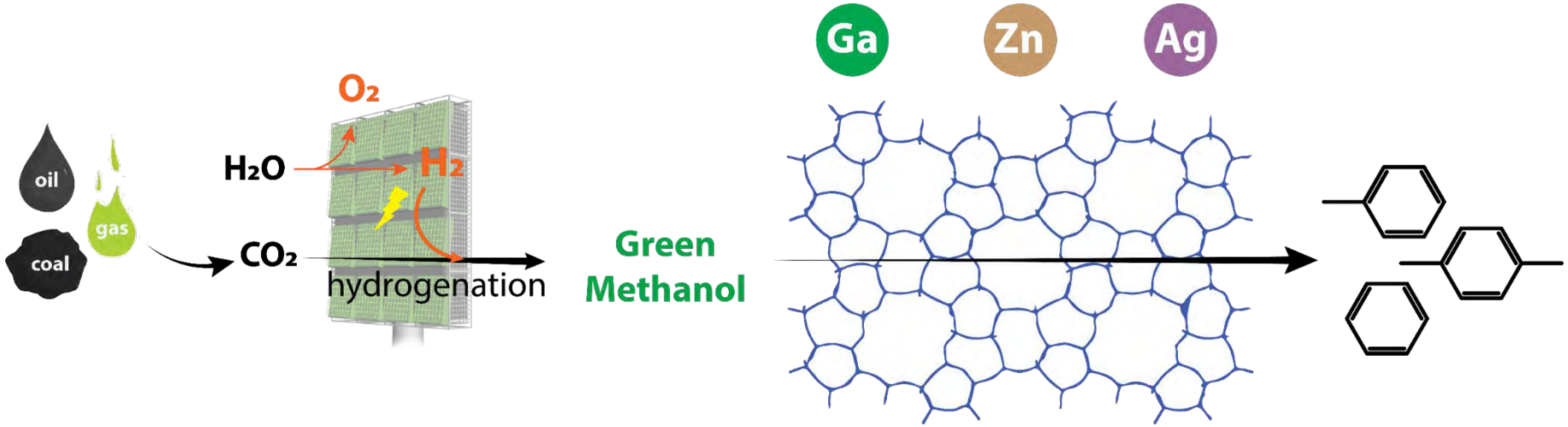


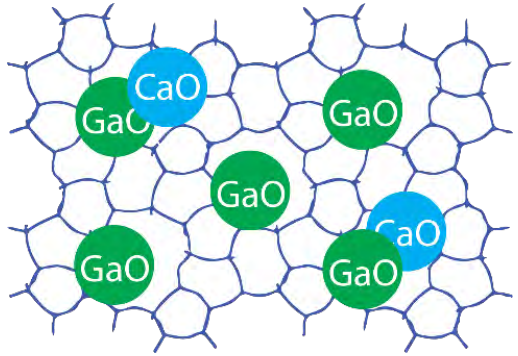
(Almost) bias-free approach to modeling HetCatal

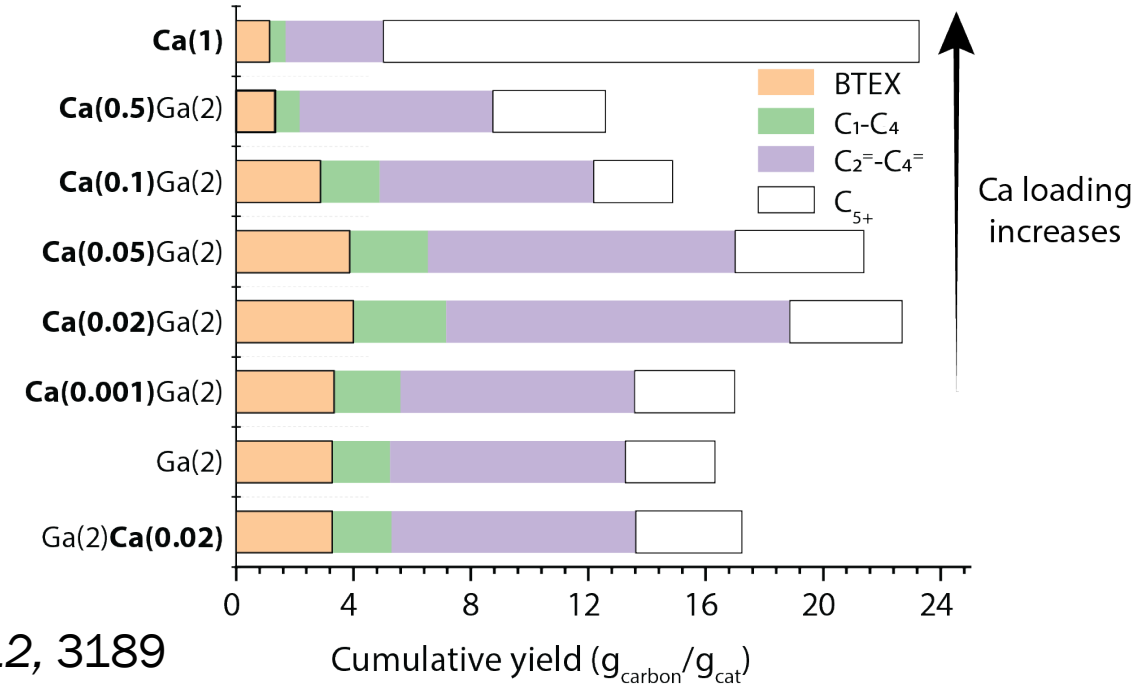
- Genetic Algorithm
  - Efficient when targeting global minima
  - Many versions available
  - Can be coupled with semiempirical methods
  - Ensembles are not accessible
  - Transitions/Conversions are beyond the scope

- aiMD + fingerprinting
  - Insights into interconversion
  - Following the rules of chemistry
  - Uncertainty w.r.t. exhaustiveness
  - CPU demanding
  - Analysis and structure extraction - challenge

Genetic algorithm: structures beyond the chemical intuition







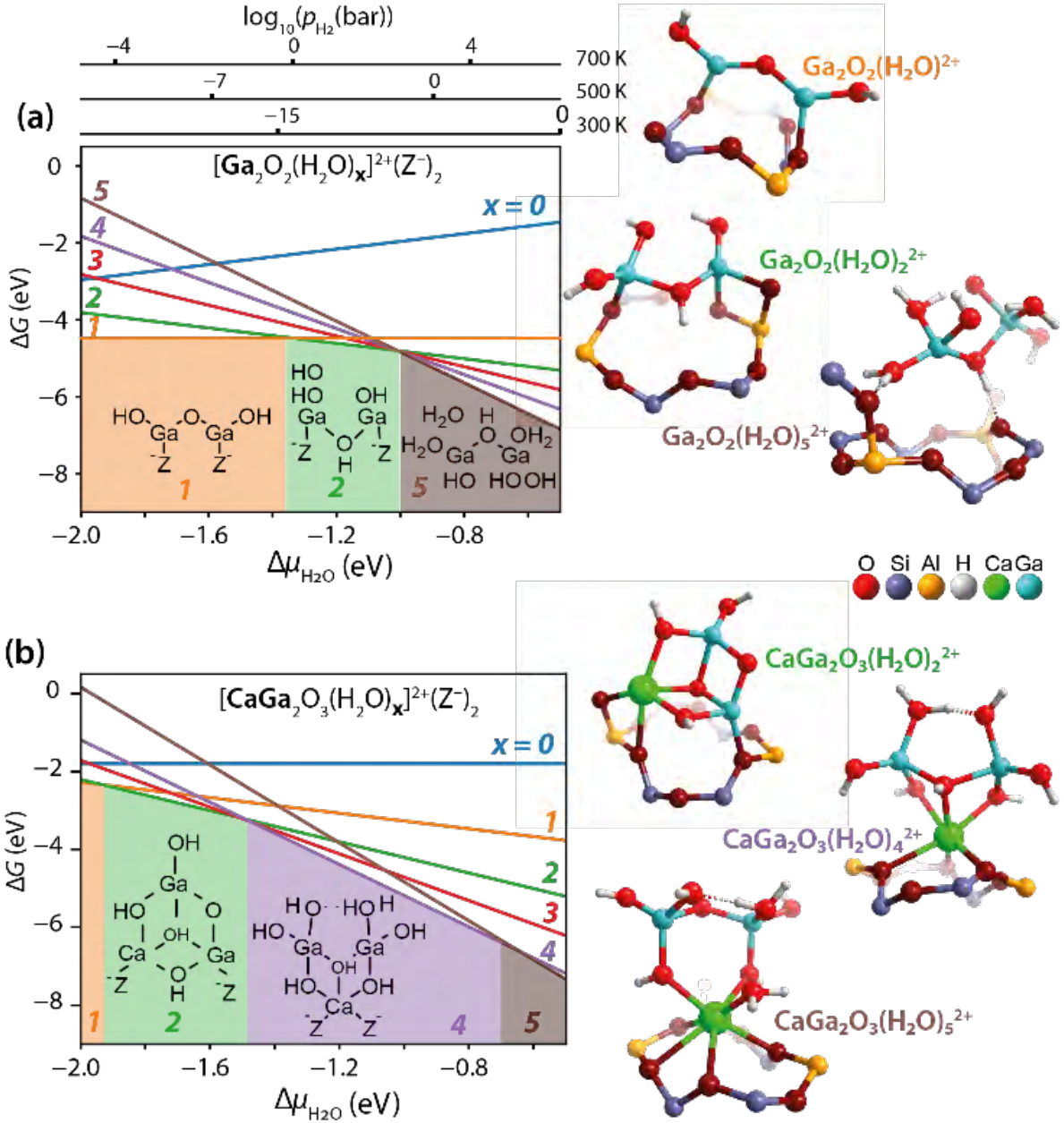
with Liu, Khramenkova, et al ACS Catal. **2022**, *12*, 3189

Genetic algorithm: structures beyond the chemical intuition

Configurational exploration
- Define stoichiometries
- Zeolite cluster model
- GA (xTB)

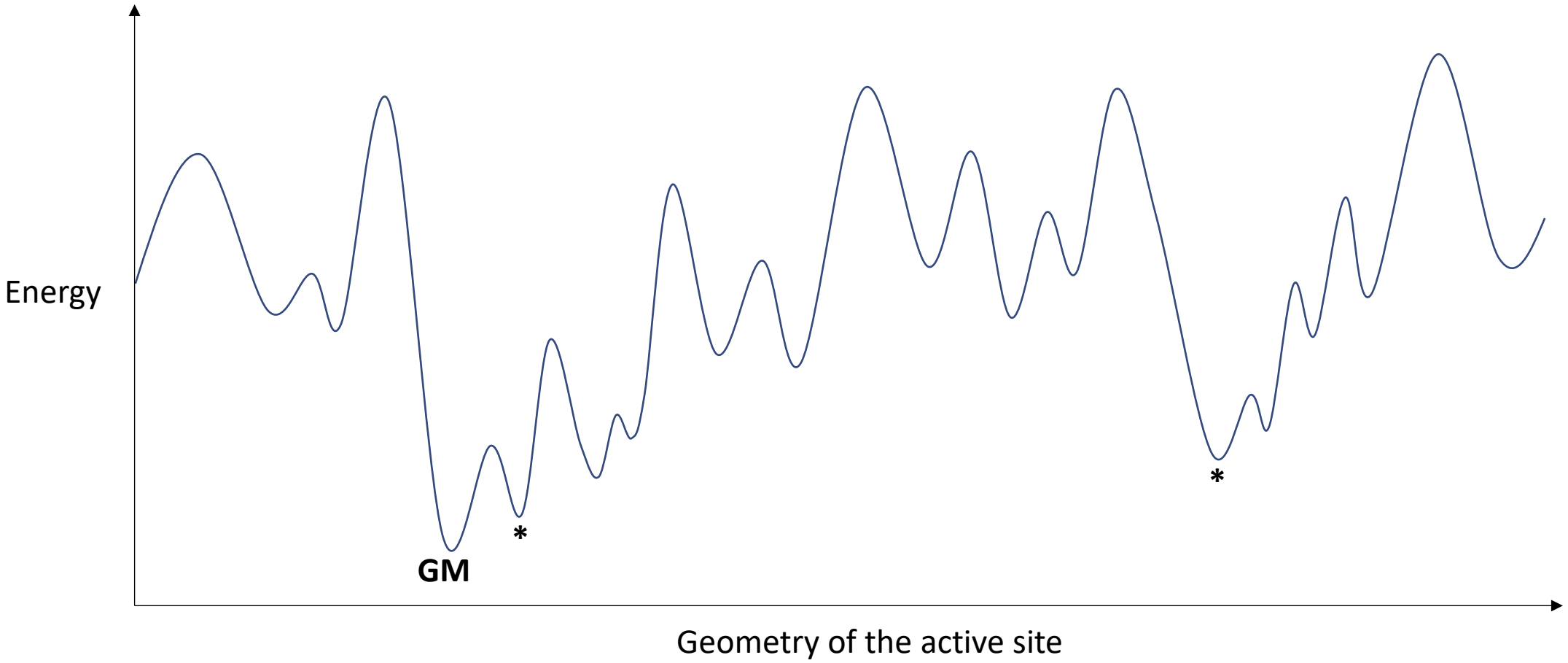
Structure refinement
- Periodic zeolite model
- PBE-D3

Operando model
- ab initio TD analysis



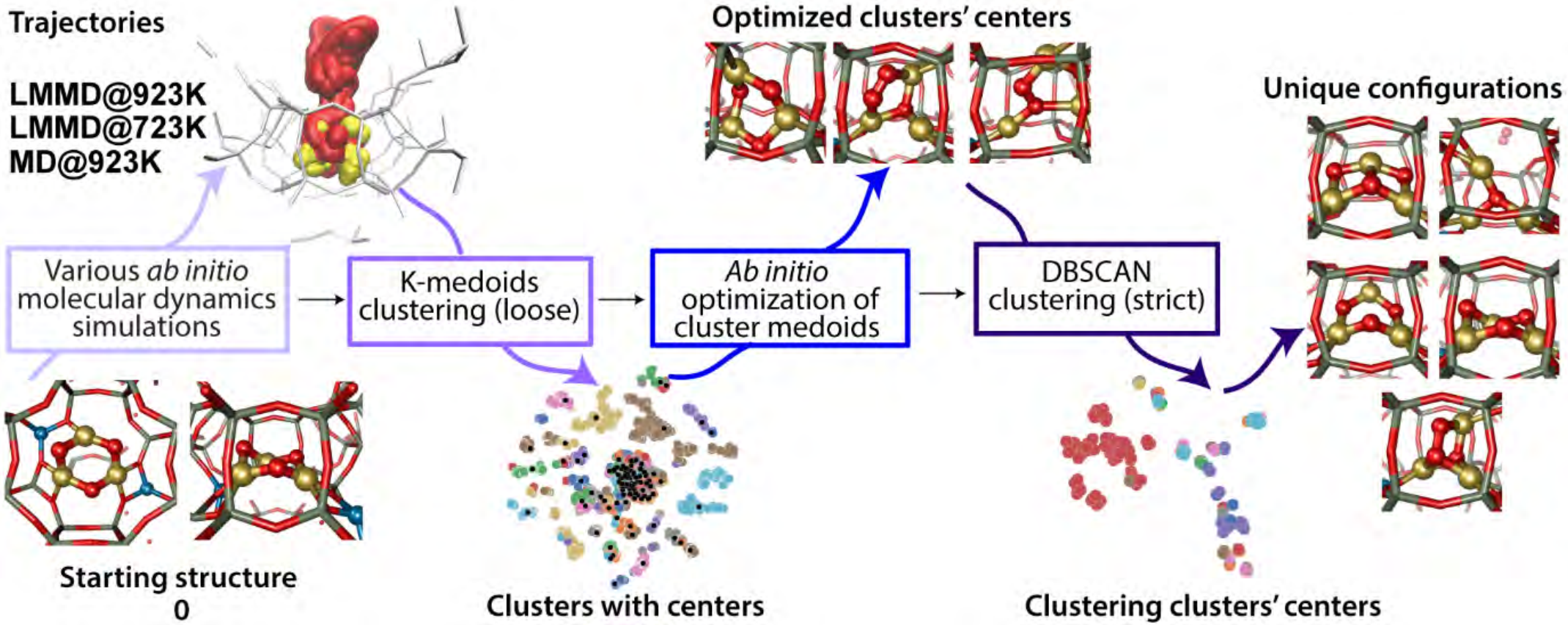
with Liu, Khramenkova, et al ACS Catal. **2022**, *12*, 3189

Dynamics and Ensembles



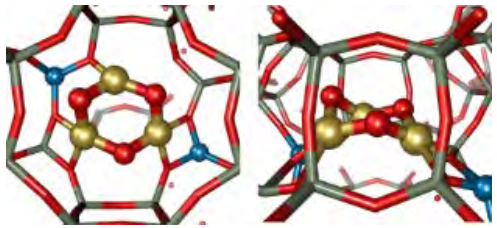
Dynamics and Ensembles

Elena Khramenkova

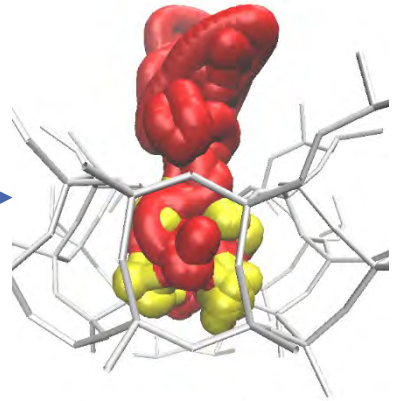


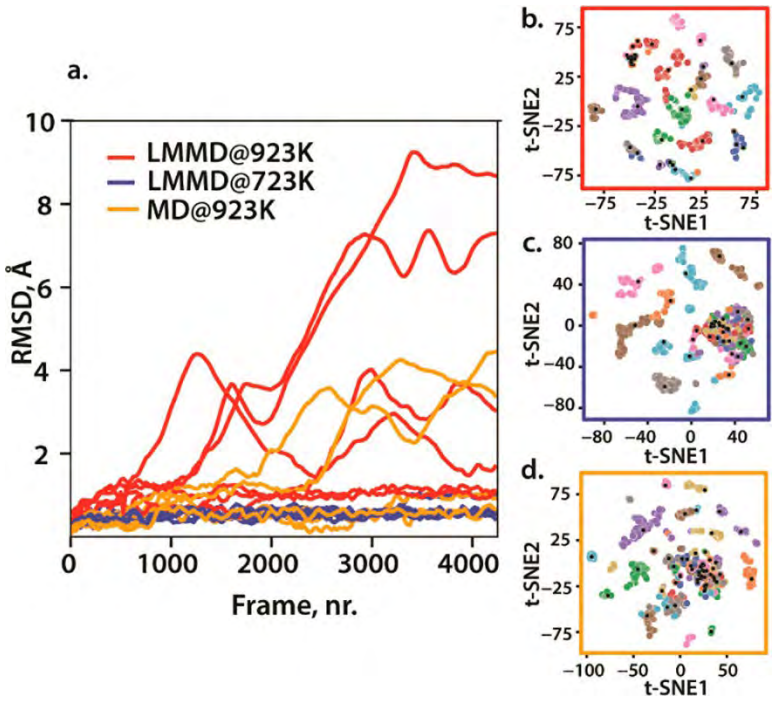
Khramenkova, Medvedev, Li, **EAP**, *J. Phys. Chem. Lett.* **2021**, *12, 10906*

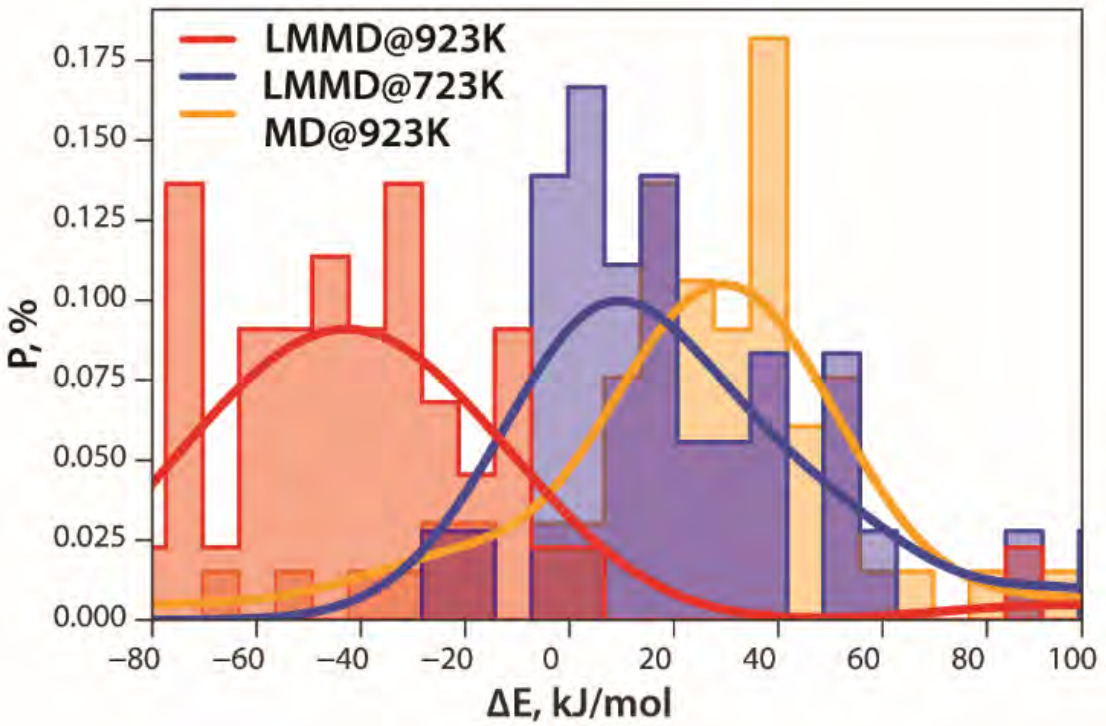
MD exploration of the configurational space



Low Mode aiMD

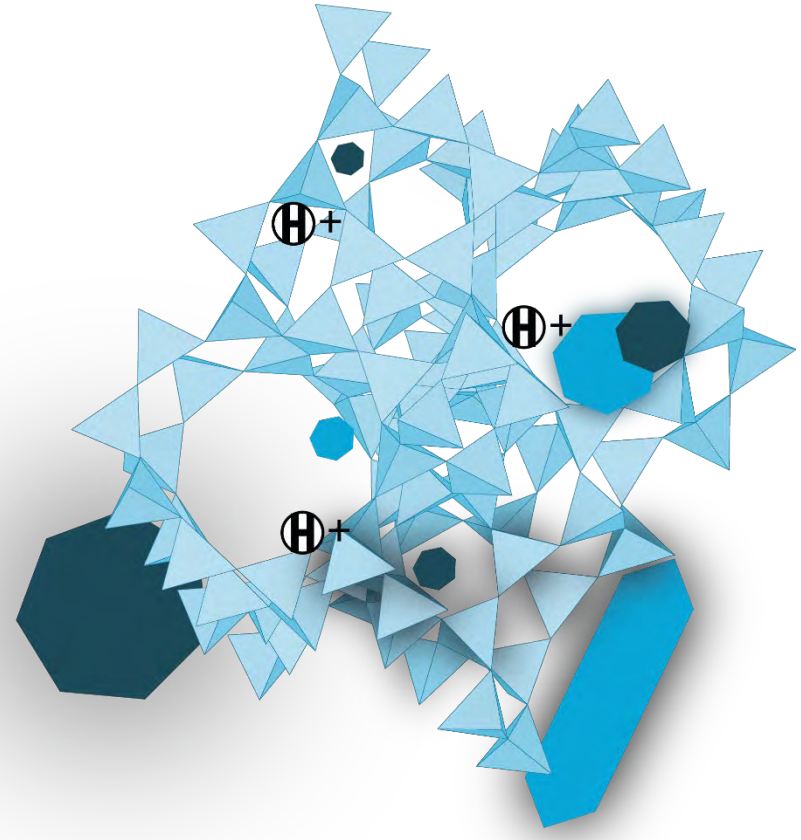


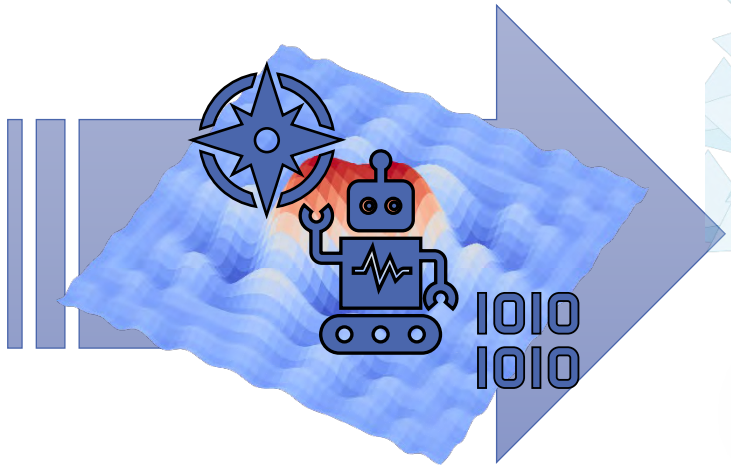


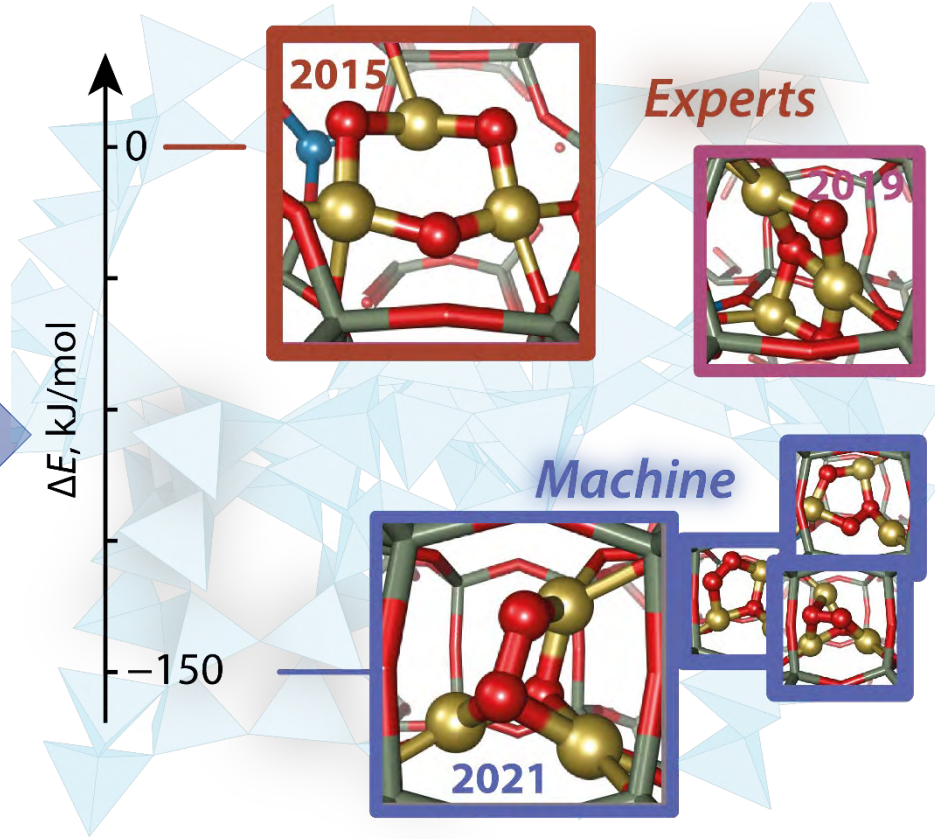


Khramenkova, Medvedev, Li, **EAP**, *J. Phys. Chem. Lett.* **2021**, *12, 10906*

Structural problem in catalysis

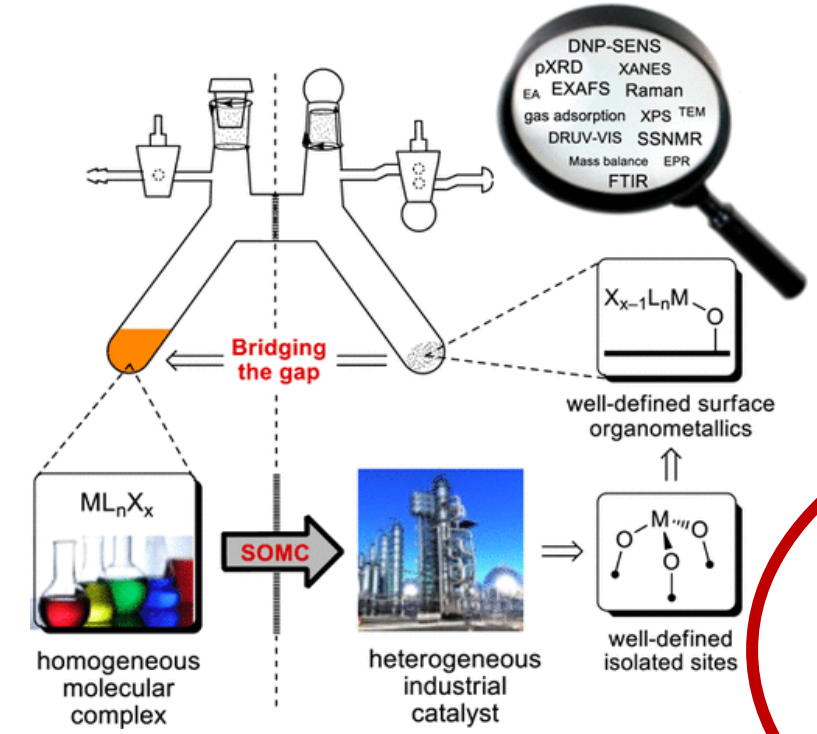




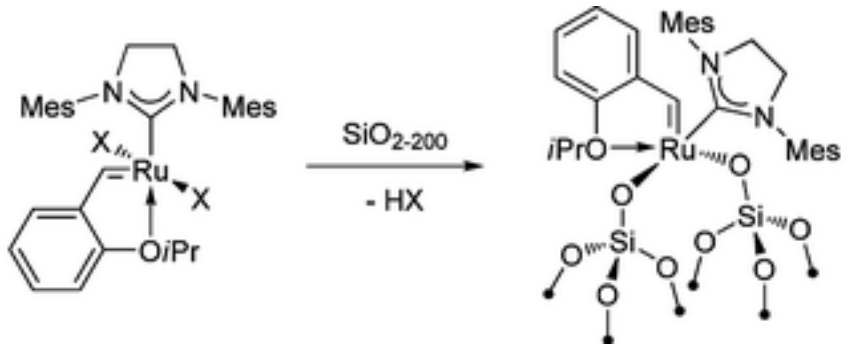


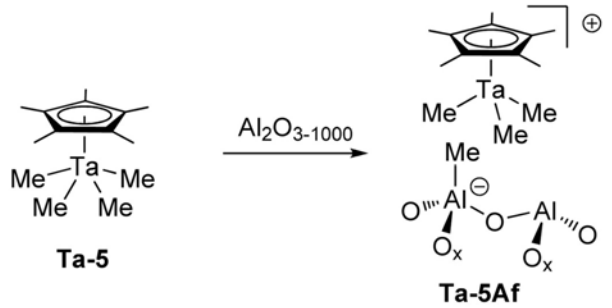
Expert bias free structural analysis of zeolite catalysts:
with Khramenkova, Li, Liu, Uslamin et al
J. Phys. Chem. Lett. **2021**, *12, 10906*
ACS Catal. **2022**, *12,* 3189
PCCP **2022**, *24*, 27047

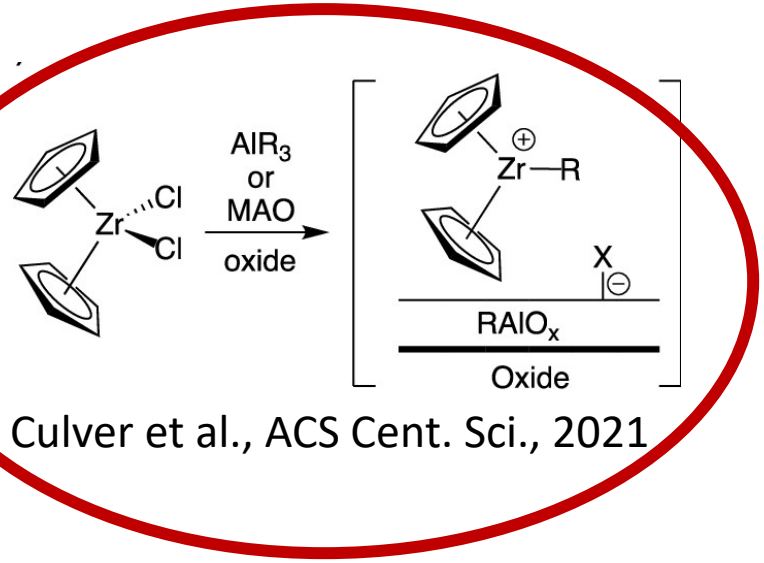
Organometallic Chemistry of Surfaces: challenges of all worlds



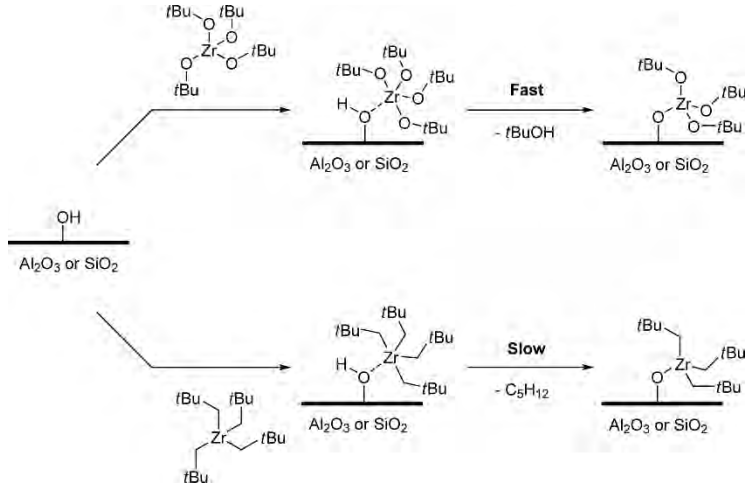
Coperet et al., Chem. Rev., 2016
10.1021/acs.chemrev.5b00373





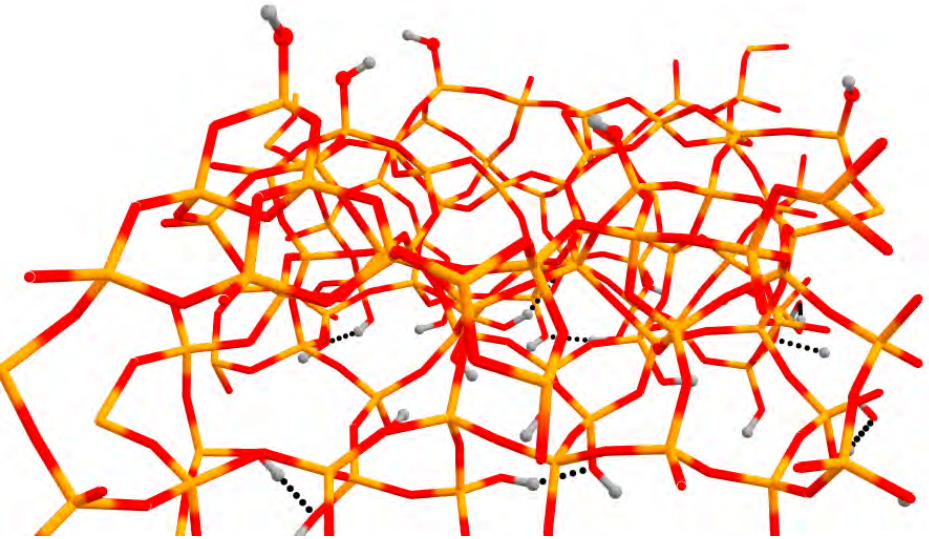


Culver et al., ACS Cent. Sci., 2021



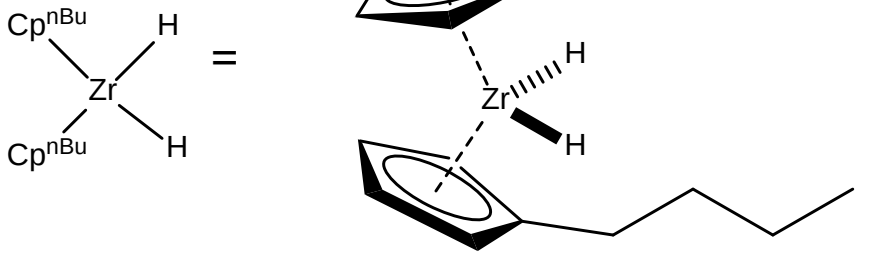
- Understanding surface chemistry of common supports
- All type of bonding – challenge for GO
- How dynamic are single-site catalysts?

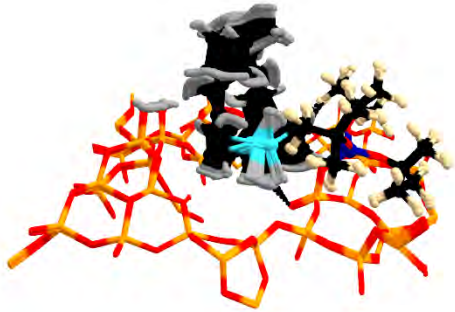
Overview of the studied systems

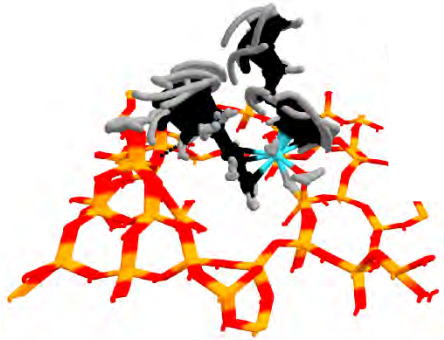


Amorphous silica (1OH/nm^2) model
$Si_{70}O_{194}(SiOH_{bottom})_{31}(SiOH_{surface})_5$

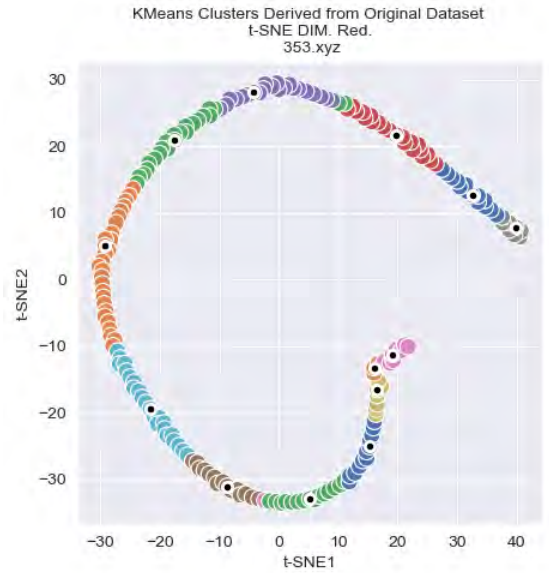
Taken from 10.1039/c6cp00602g

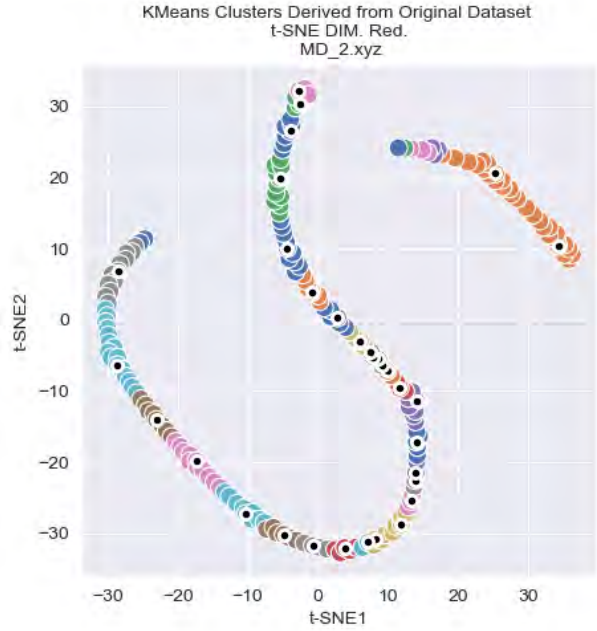




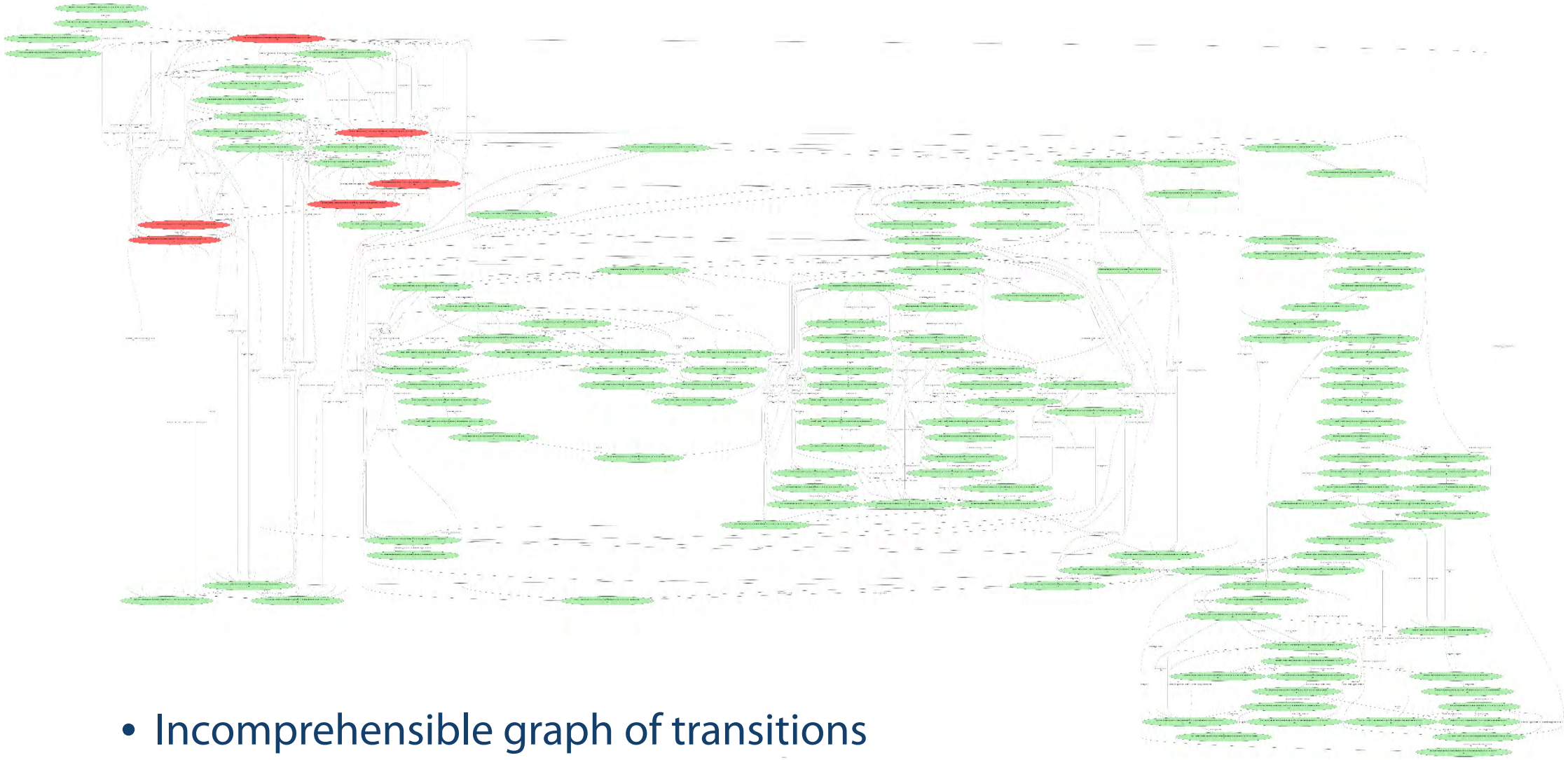


ab initio and velocity-softening molecular dynamics



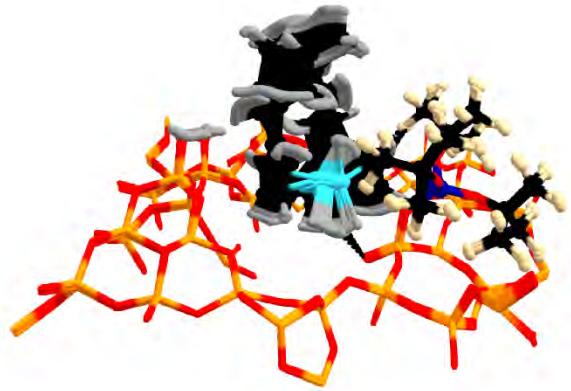


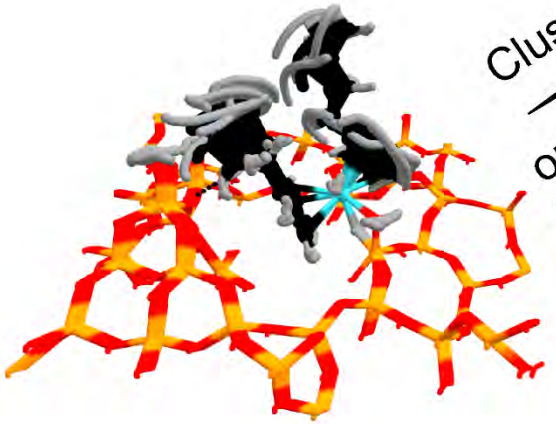
2D-MolGraph for structure elucidation & trajectory analysis



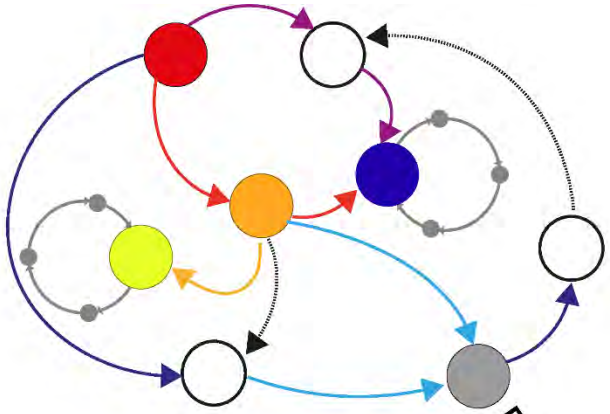
- Incomprehensible graph of transitions
- Work in progress
- More efficient than direct k-clustering

Dynamics of surface organometallic catalysts



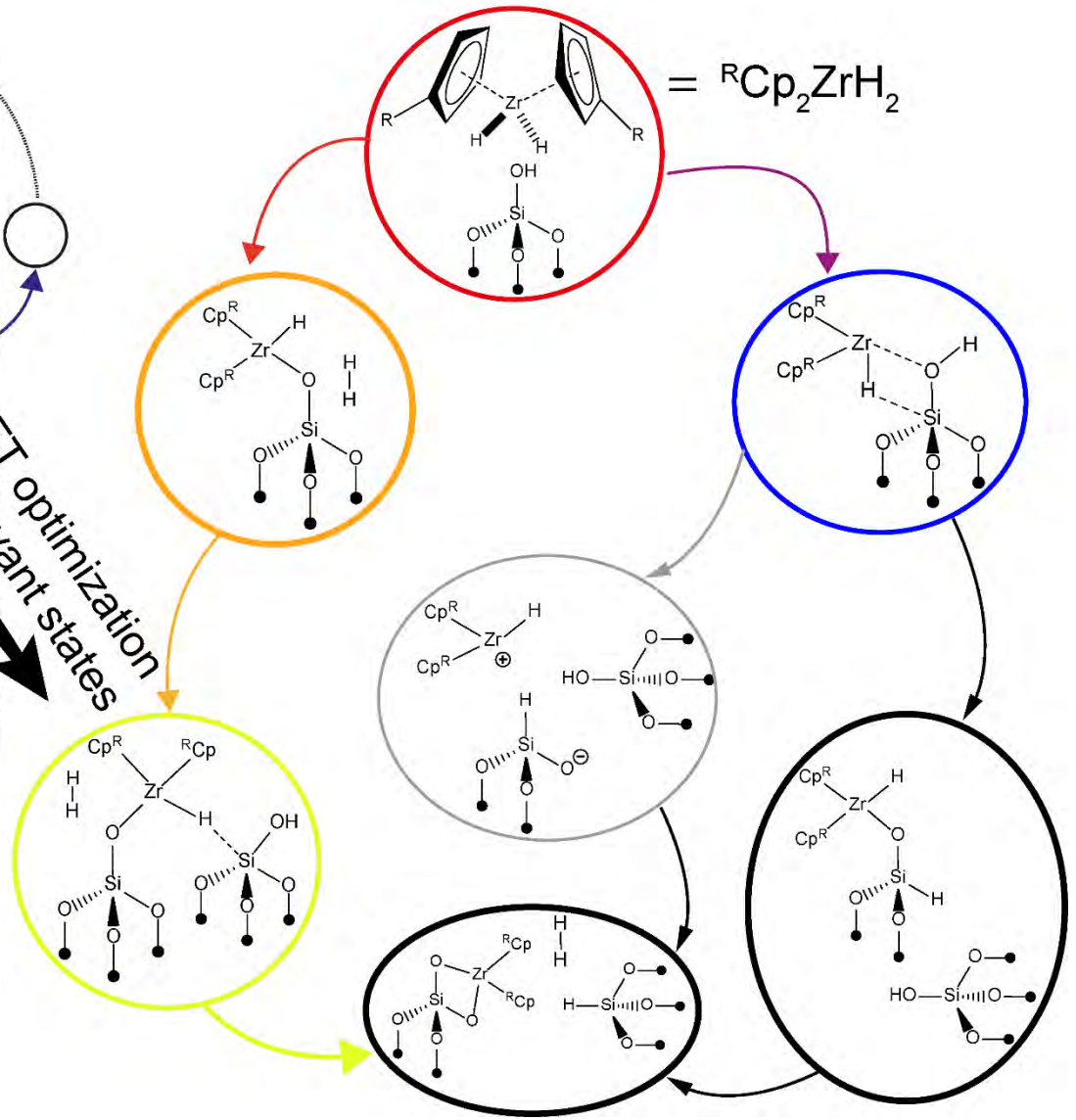


Clustering or graph theory-based analysis



DFT optimization of relevant states

Rationalization



ab initio and velocity-softening molecular dynamics

With Kolganov et al. *in preparation*

Summary

- Reducing the expert bias to address the structural uncertainty in catalysis
- Automation to bring theory and experiment together
- Integrated workflows
- High-throughput reactivity screening
- Operando modelling
  - Condition-dependencies
  - MKM
  - Ensembles and reaction networks