CENTER FOR MOLECULAR MODELING

HPC UGENT

VSC Vlaams Supercomputer Centrum

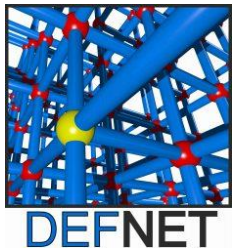
Modeling nanoporous materials at the nanoscale: the role of high performance computing in materials science

Chiara Caratelli

HPC-UGent User Meeting - 28 Jan 2019

http://molmod.ugent.be

erc



EOS THE EXCELLENCE OF SCIENCE

fwo

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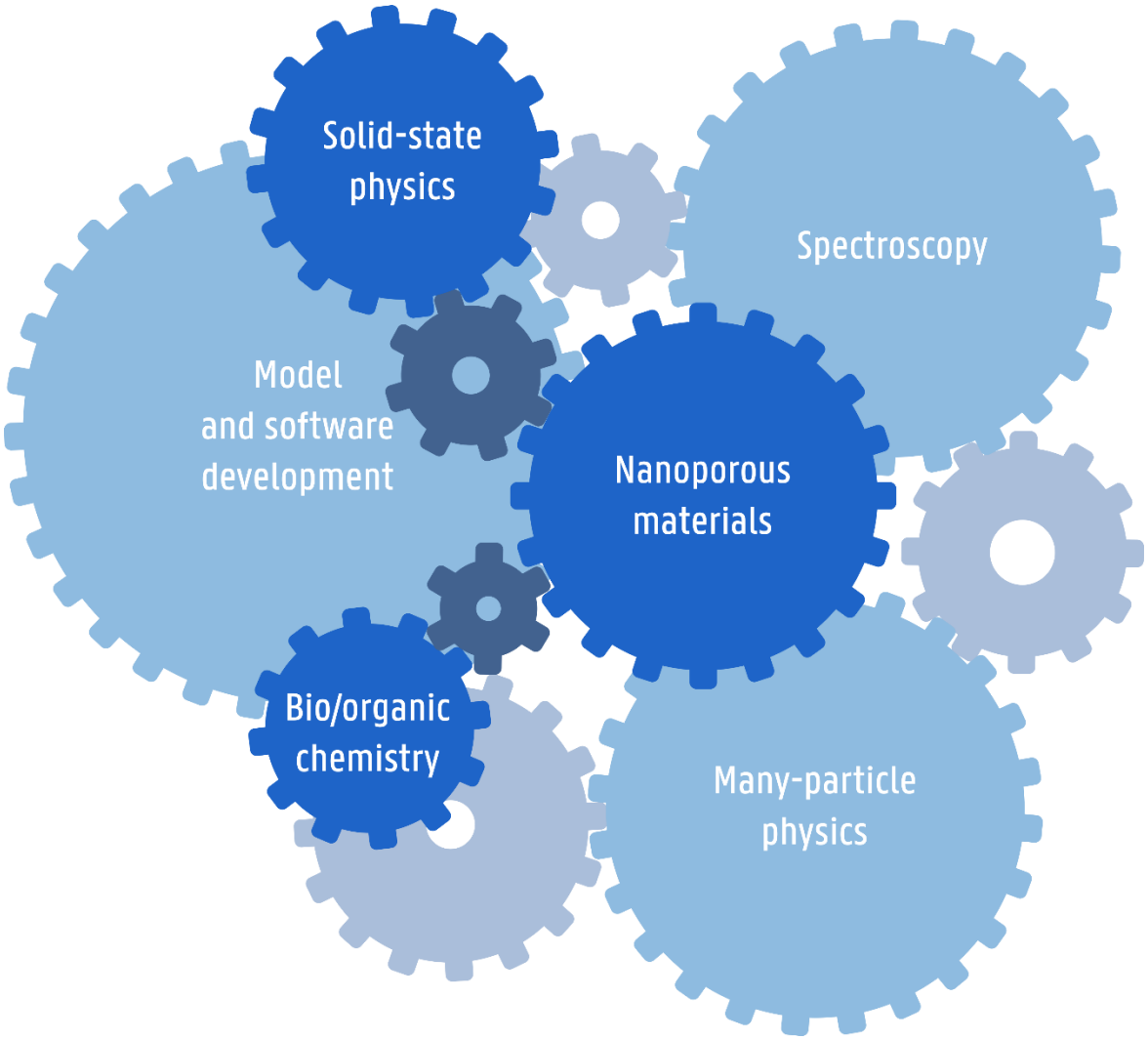
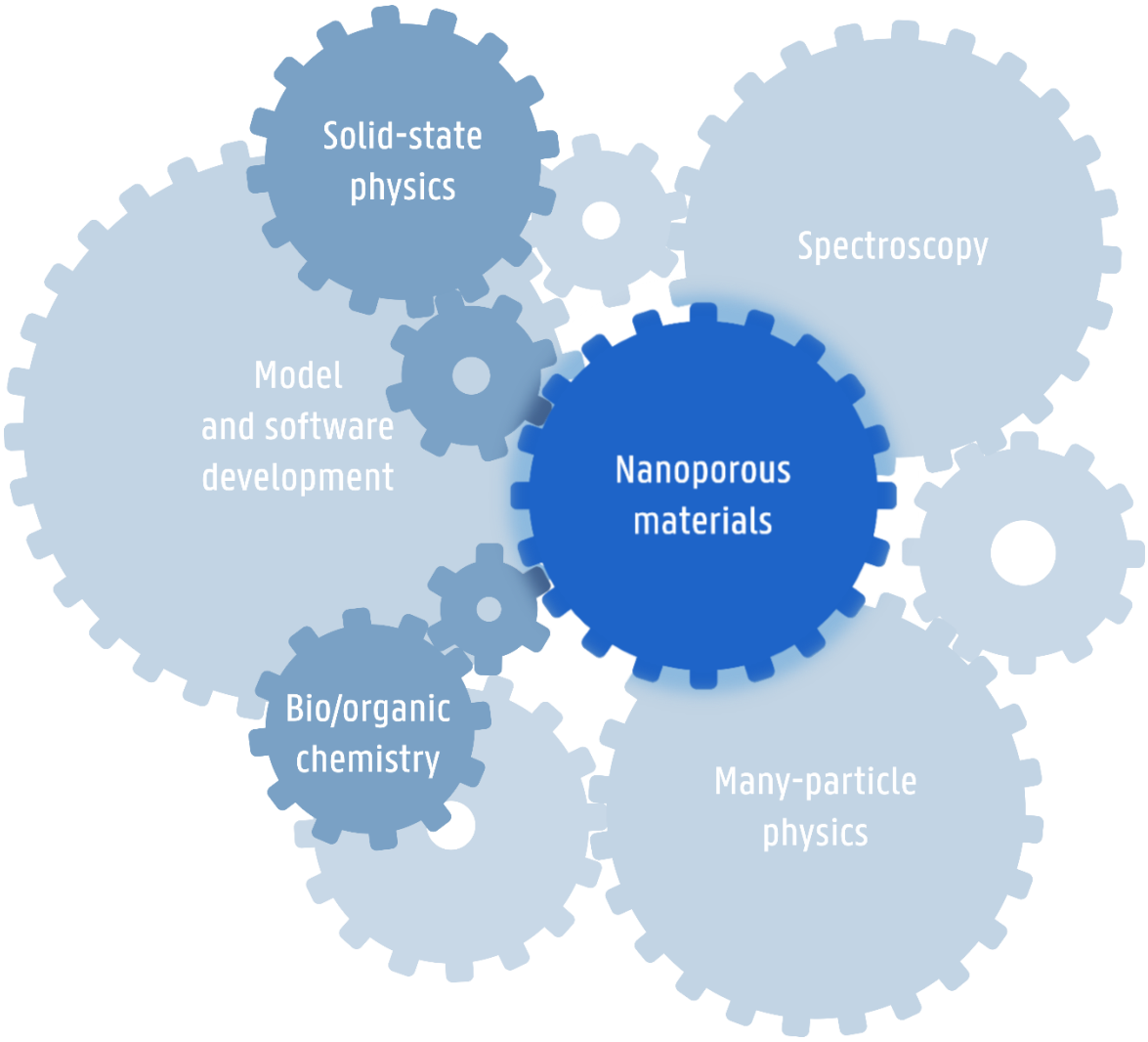
Frontier research in six major areas



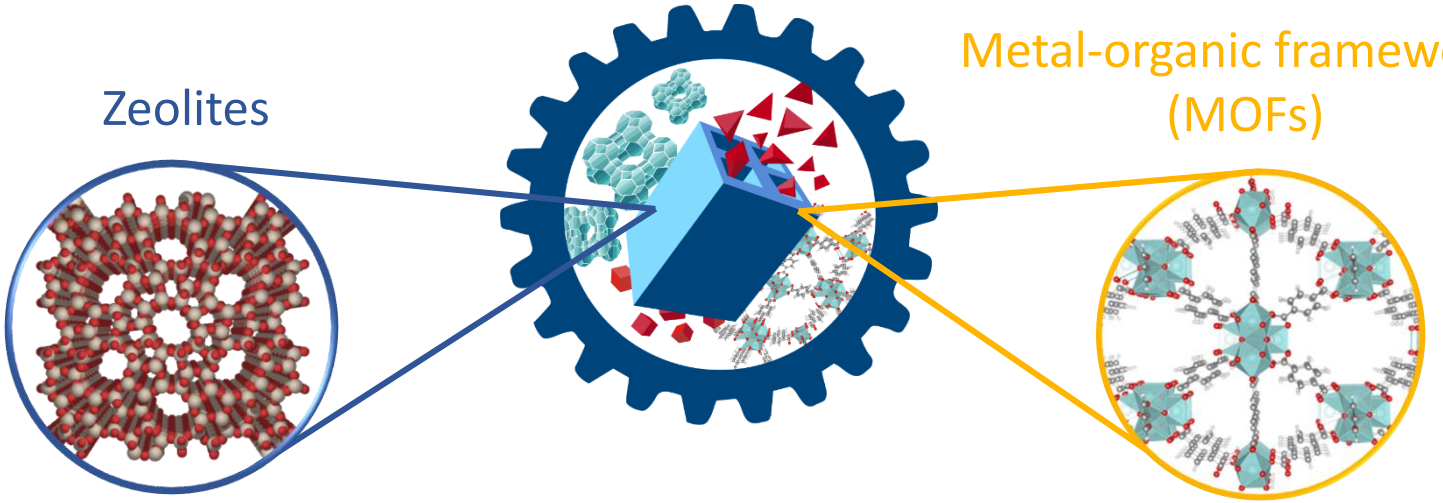
Research is conducted by a multidisciplinary team of physicists, chemists, and engineers

Frontier research in six major areas



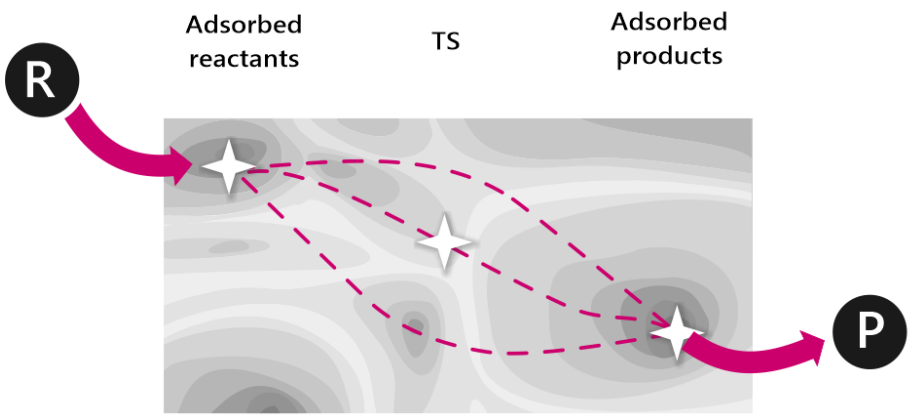
Research is conducted by a multidisciplinary team of physicists, chemists, and engineers

Chemical transformations and catalysis in nanoporous materials



Following complex chemical reactions with **operando** *in silico* techniques

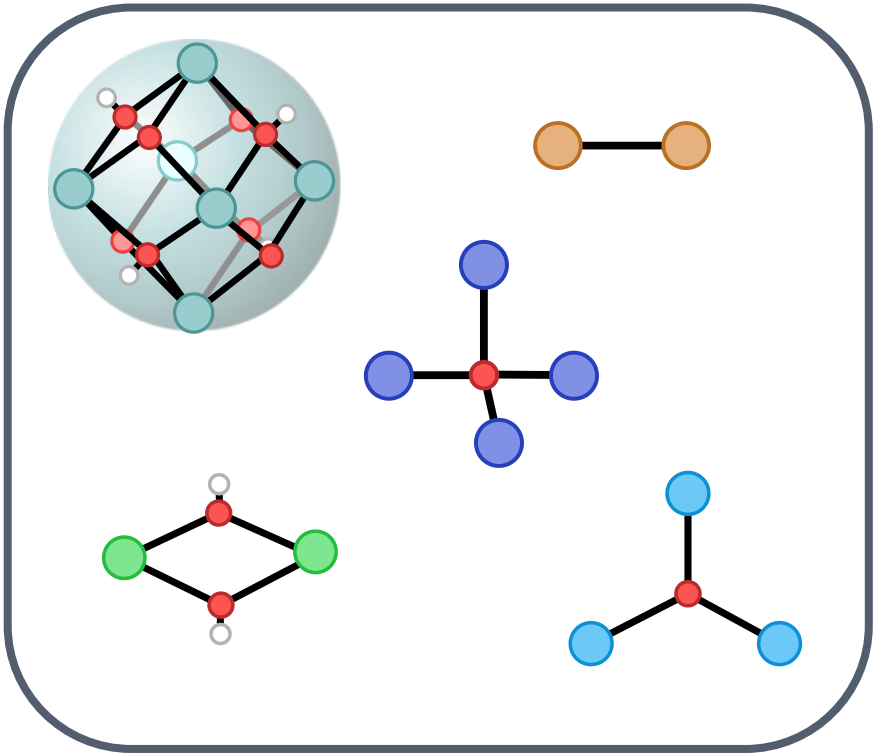
Molecular dynamics



Metal-organic frameworks are hybrid materials

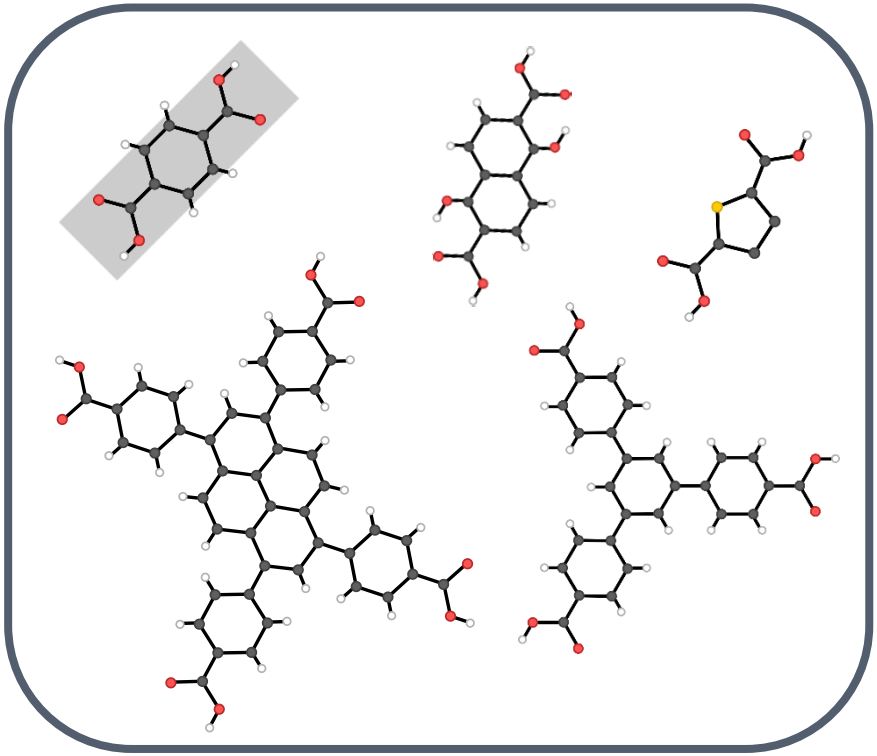
Inorganic chemistry

Metal ions or clusters

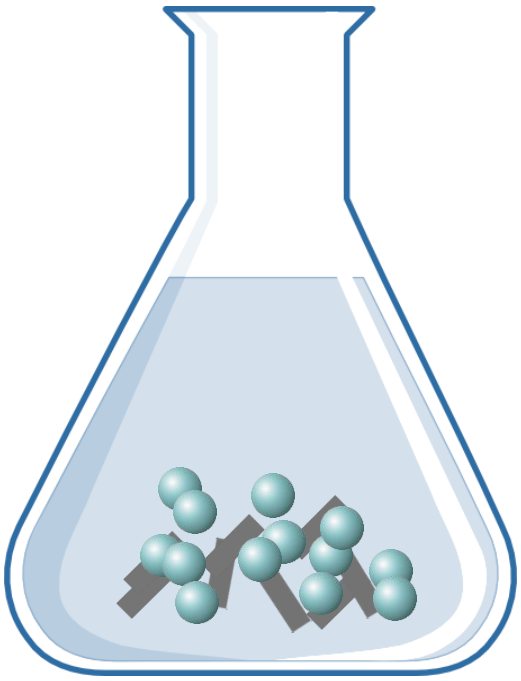


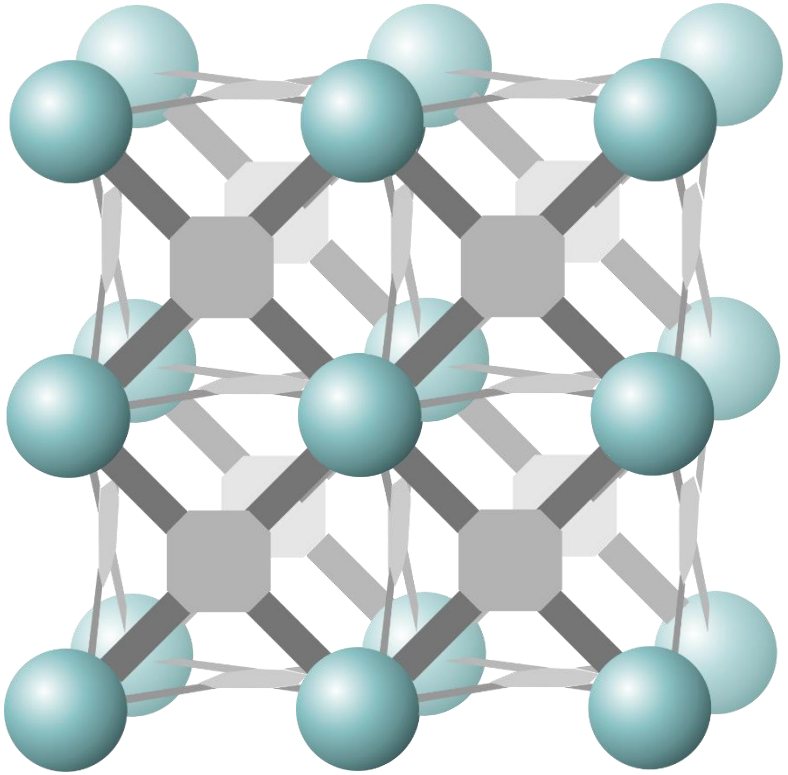
Organic chemistry

Organic molecules

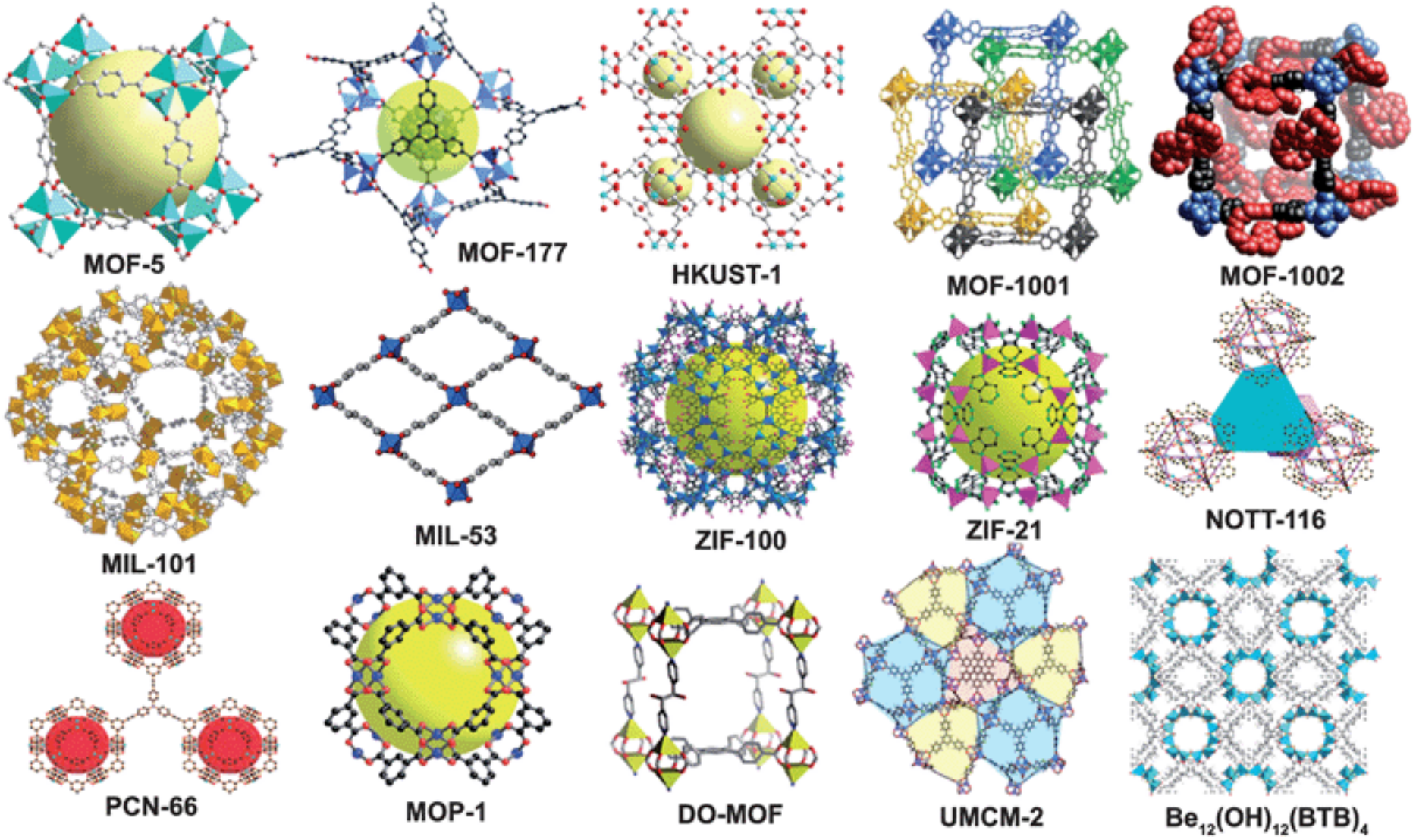


Metal-organic frameworks are hybrid materials

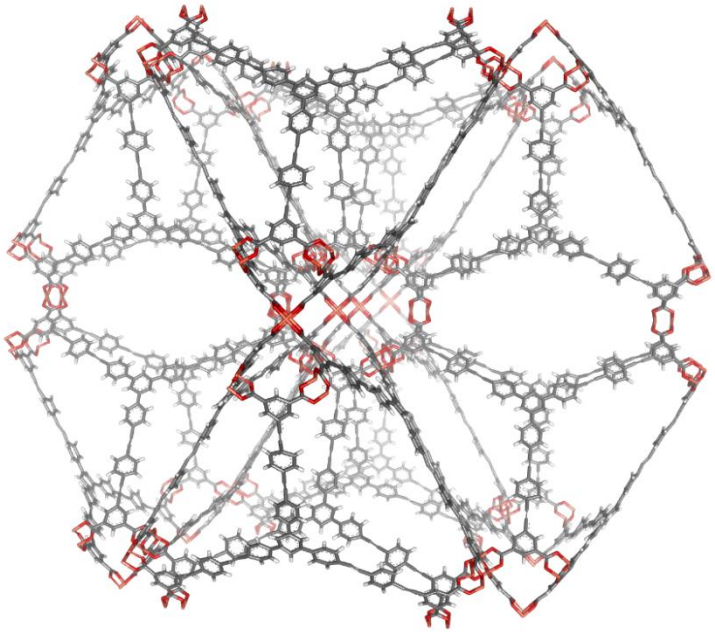




More than 10000 distinct MOF structures exist!



MOFs exhibit many attractive properties, such as their high porosity

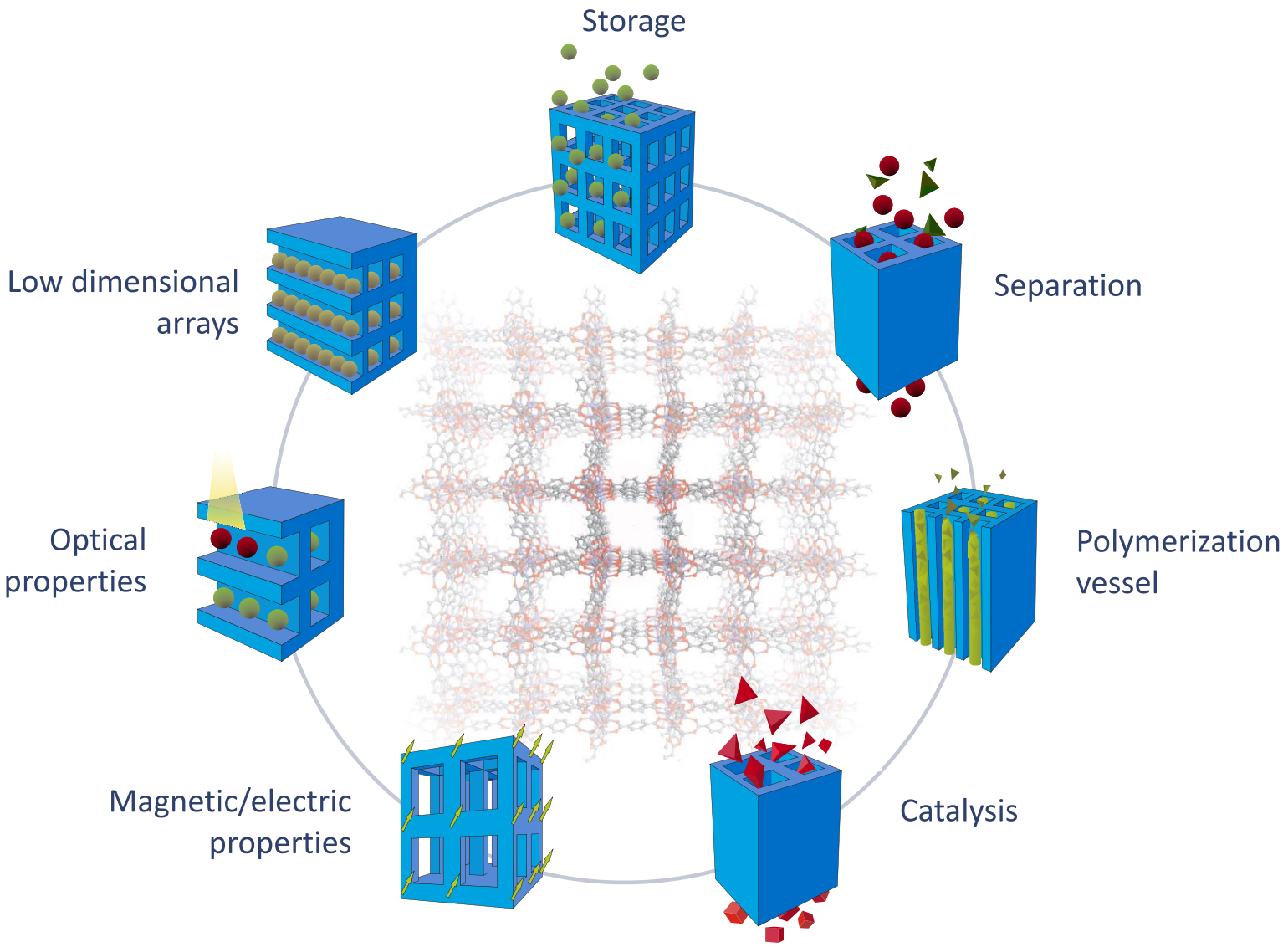


NU-110: 4.4 ml g^{-1} pore volume
7140 m^2 g^{-1} surface area

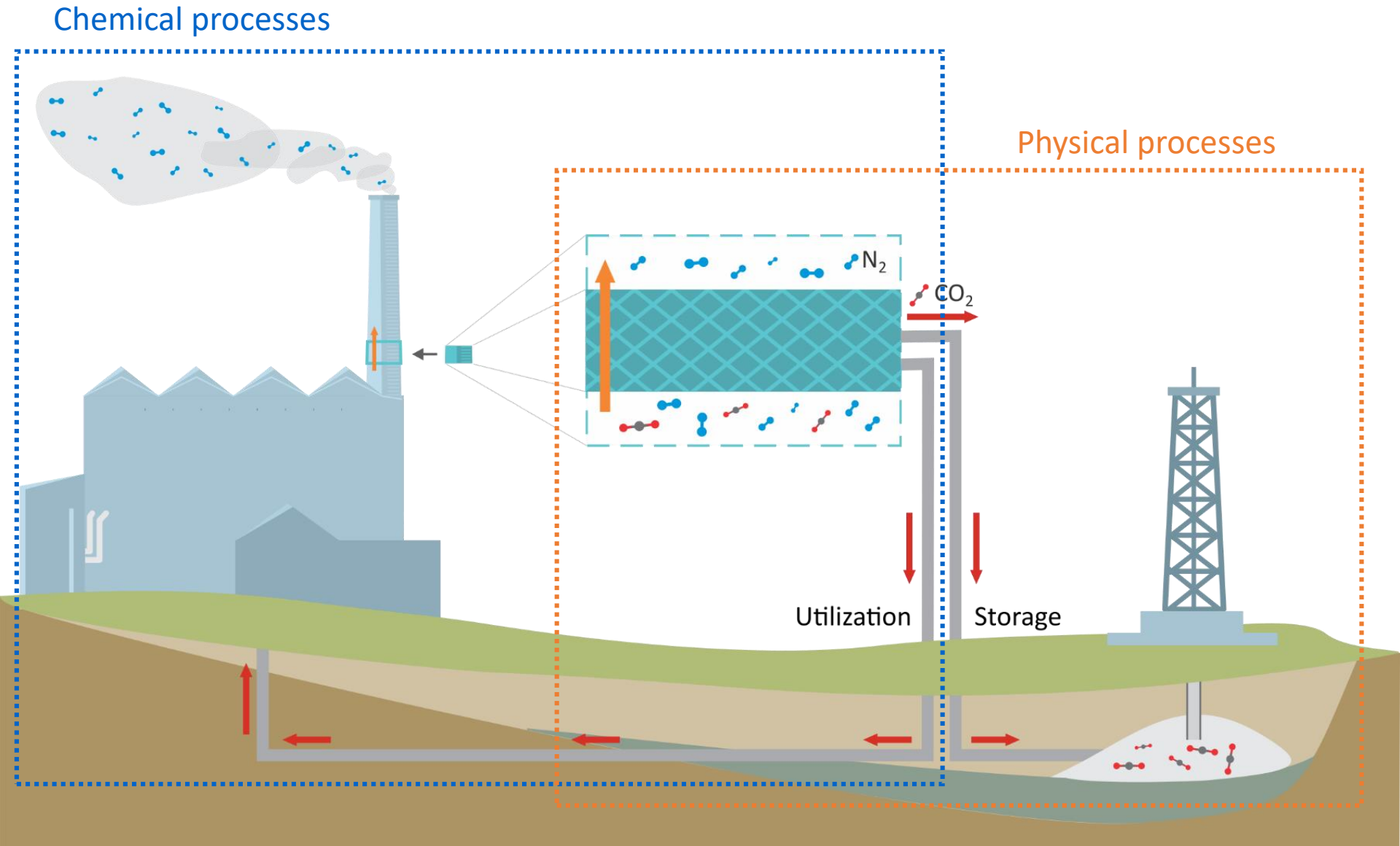
~ 40 g of NU-110 has the same surface area as all the 160 floors of the Burj Khalifa

J. Hupp *et al.*, *J. Am. Chem. Soc.* **134** (36): 15016-15021, **2012**

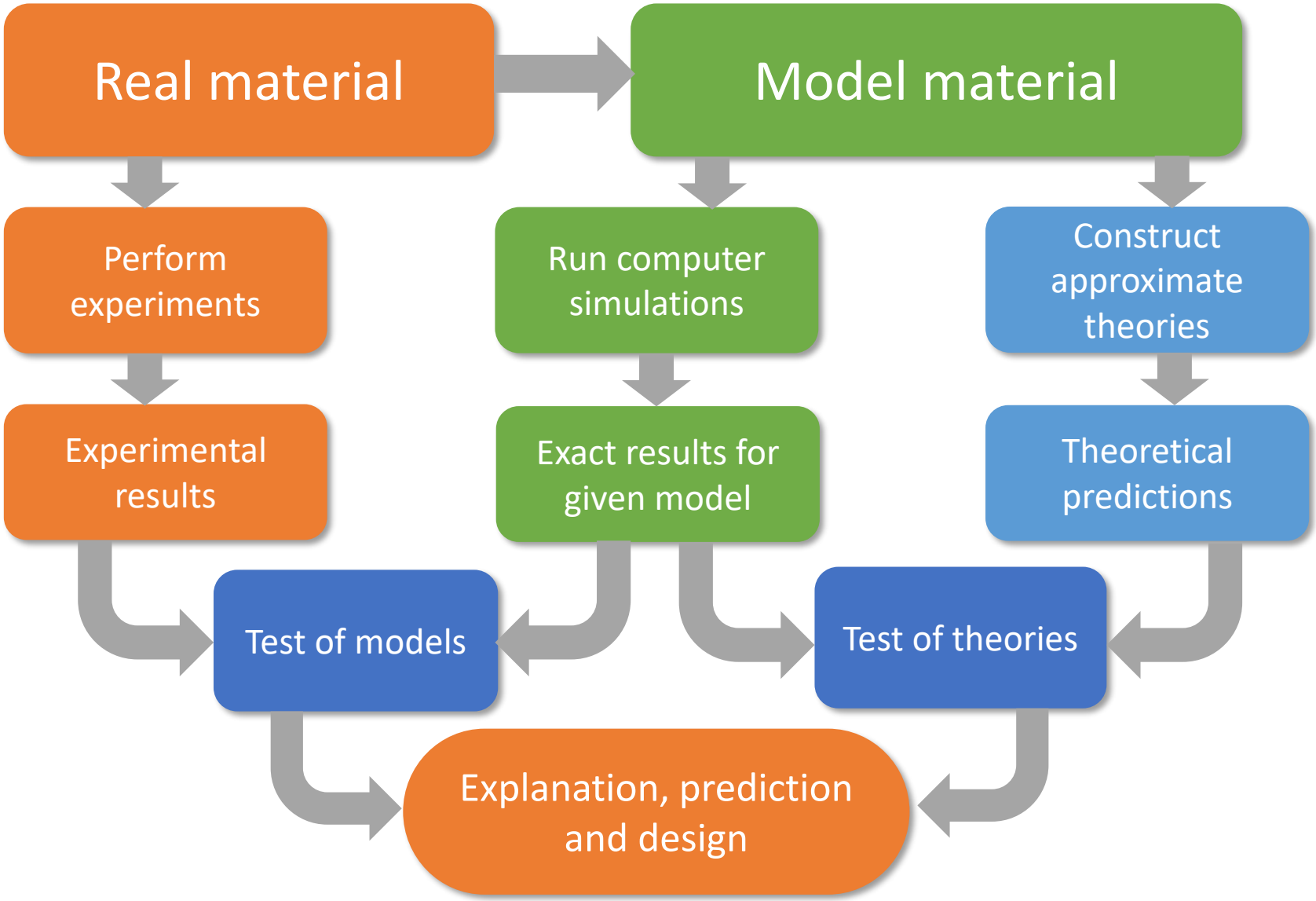
This gives rise to a large variety of possible MOF applications



Chemical and physical processes in MOFs



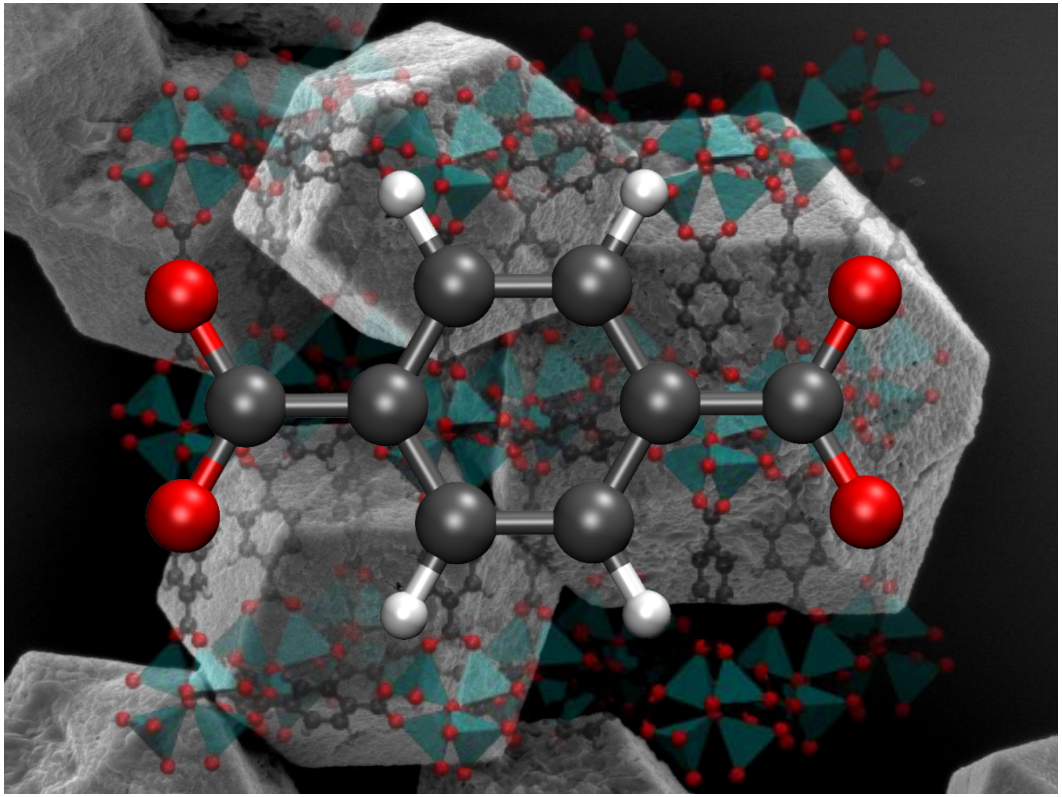
How does molecular modeling fit in?

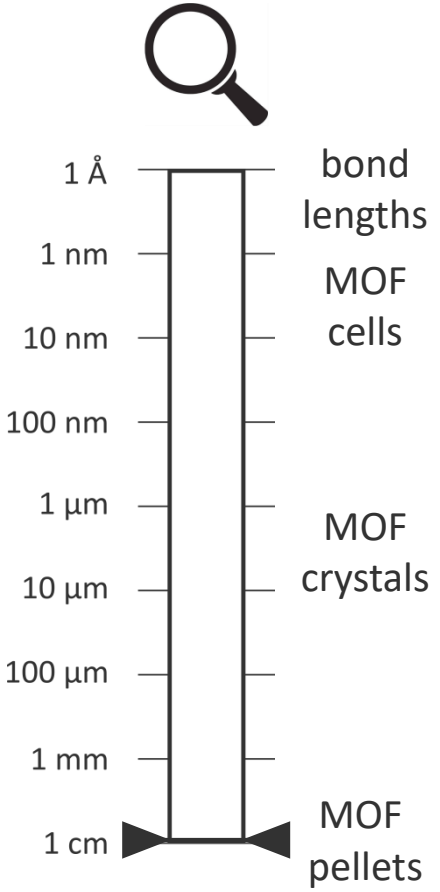


M.P. Allen and D.J. Tildesley, *Computer simulations of liquids*, **1989**

Computational modeling at the nanoscale

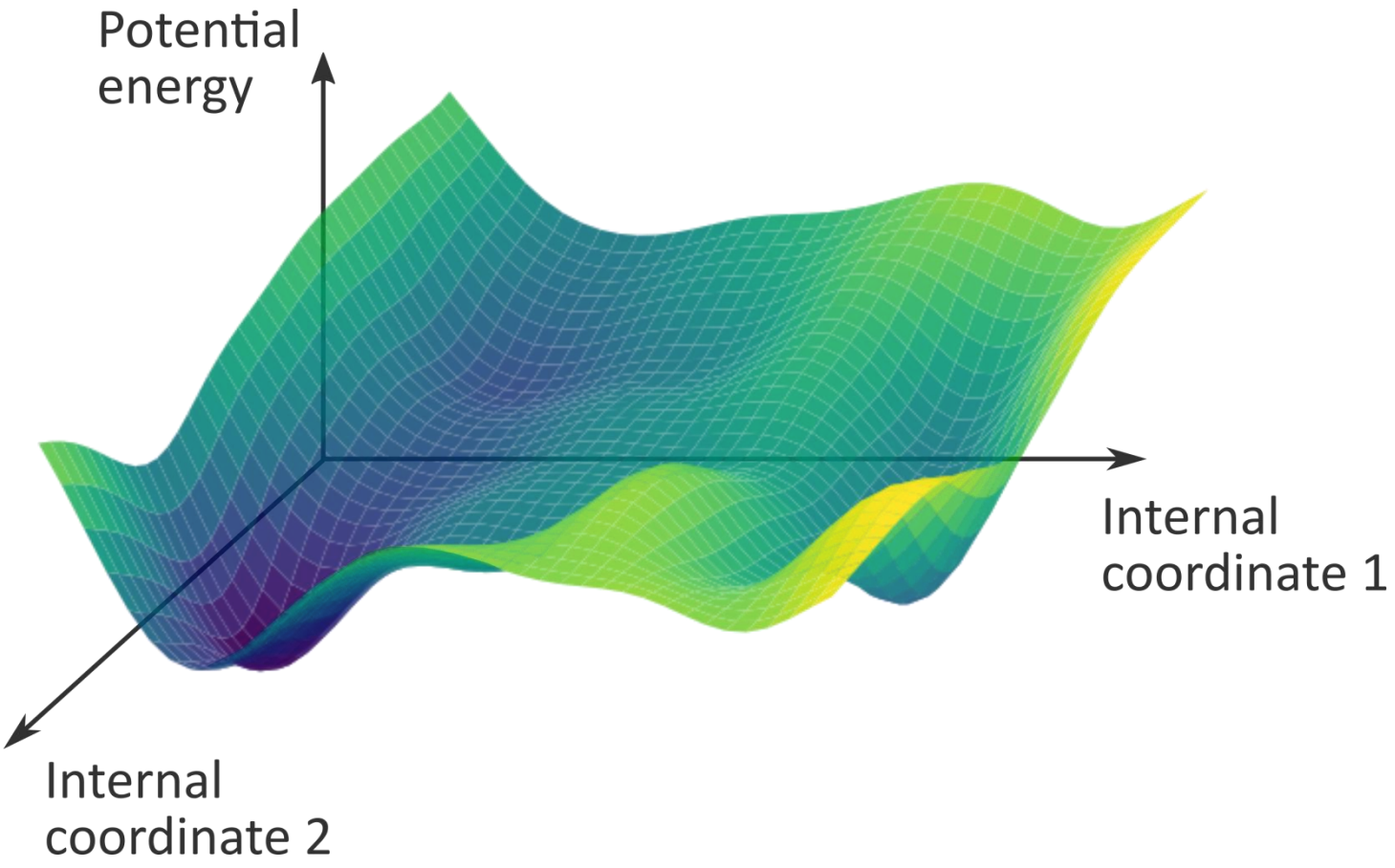
The macroscopic properties of a material are determined by the fundamental interactions on the nanoscale



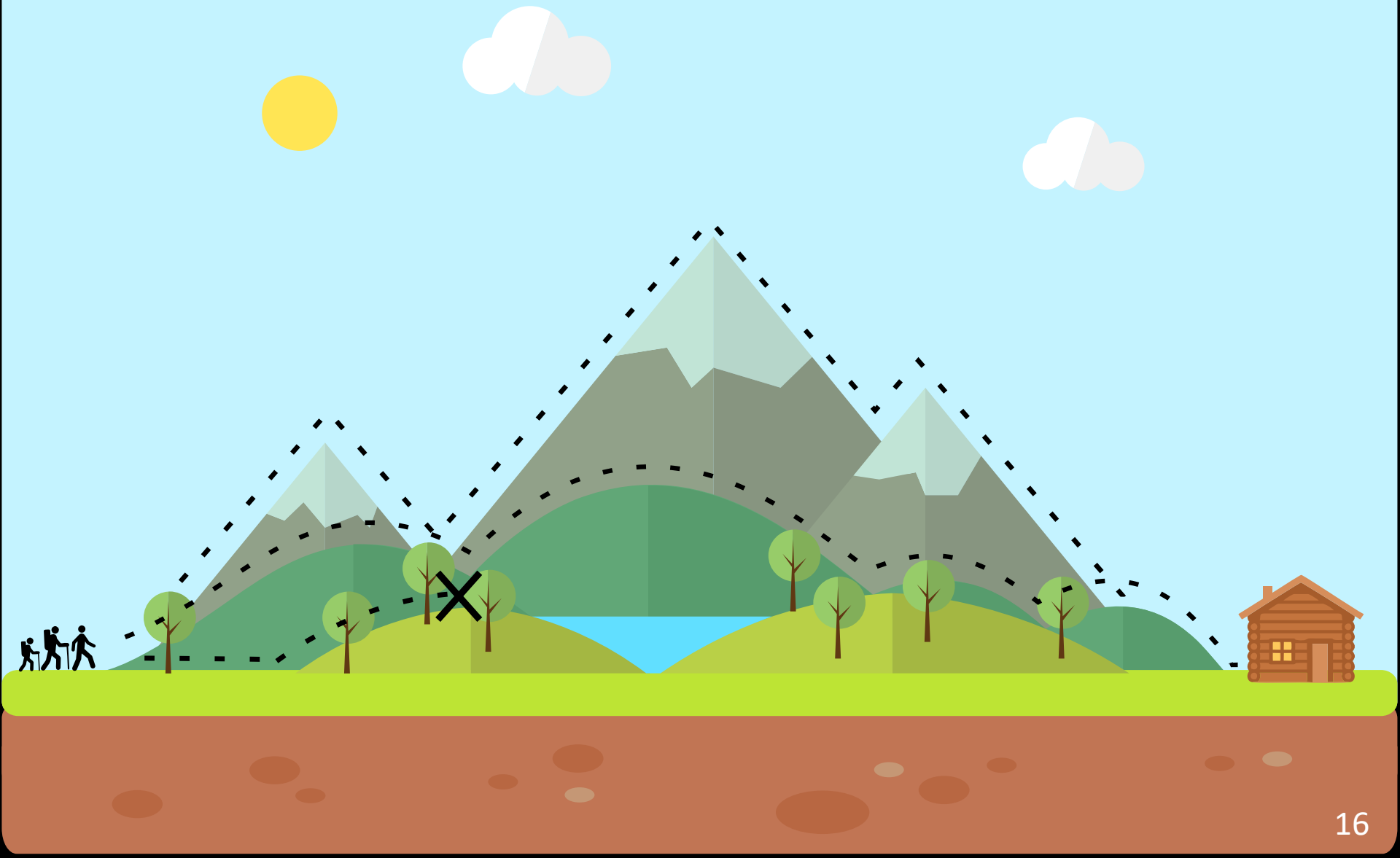


The potential energy is a central quantity

The PES determines the energy of a system as a function of a well-chosen set of parameters, e.g. the nuclear coordinates



Which path is the easiest?



Which path is the easiest?

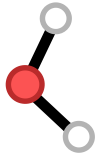
The PES is a highly dimensional function

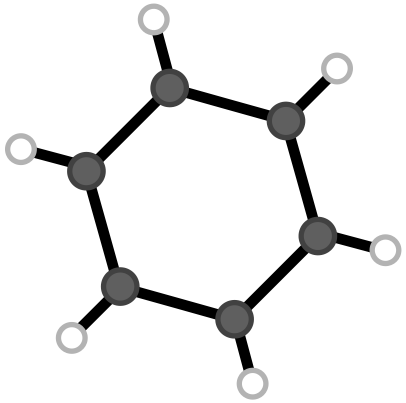
Oxygen molecule

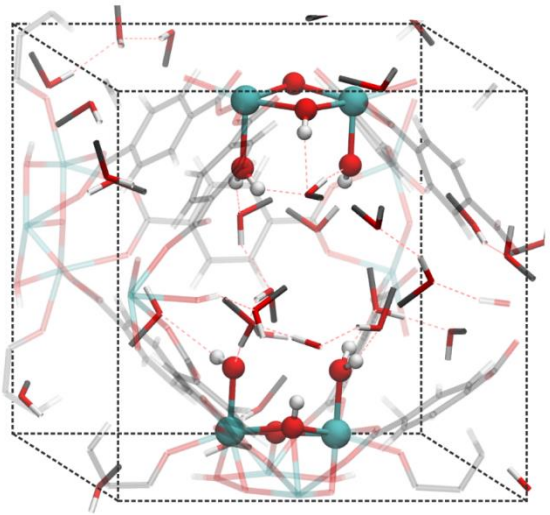
Water

Benzene

Small simulation cell



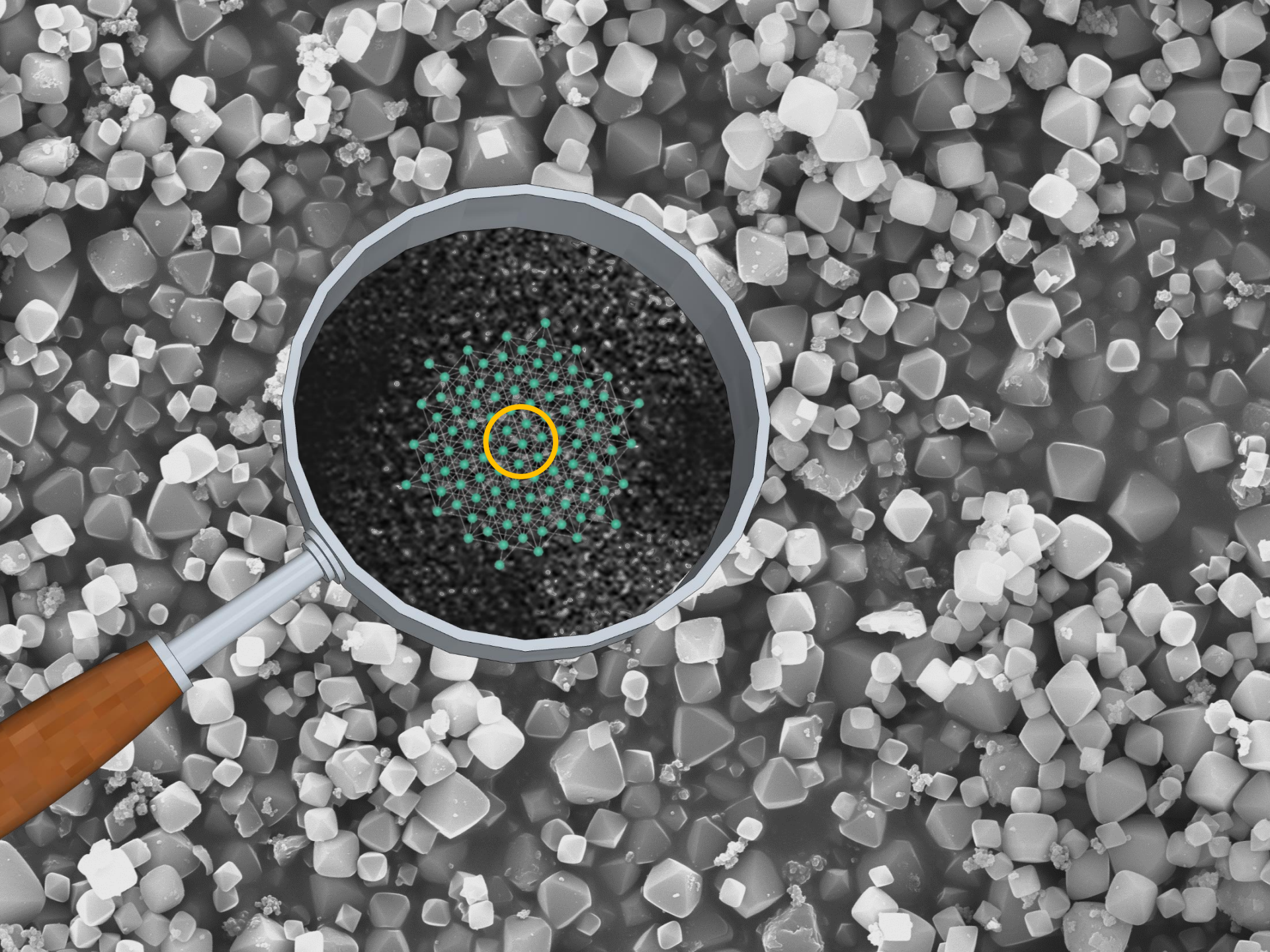




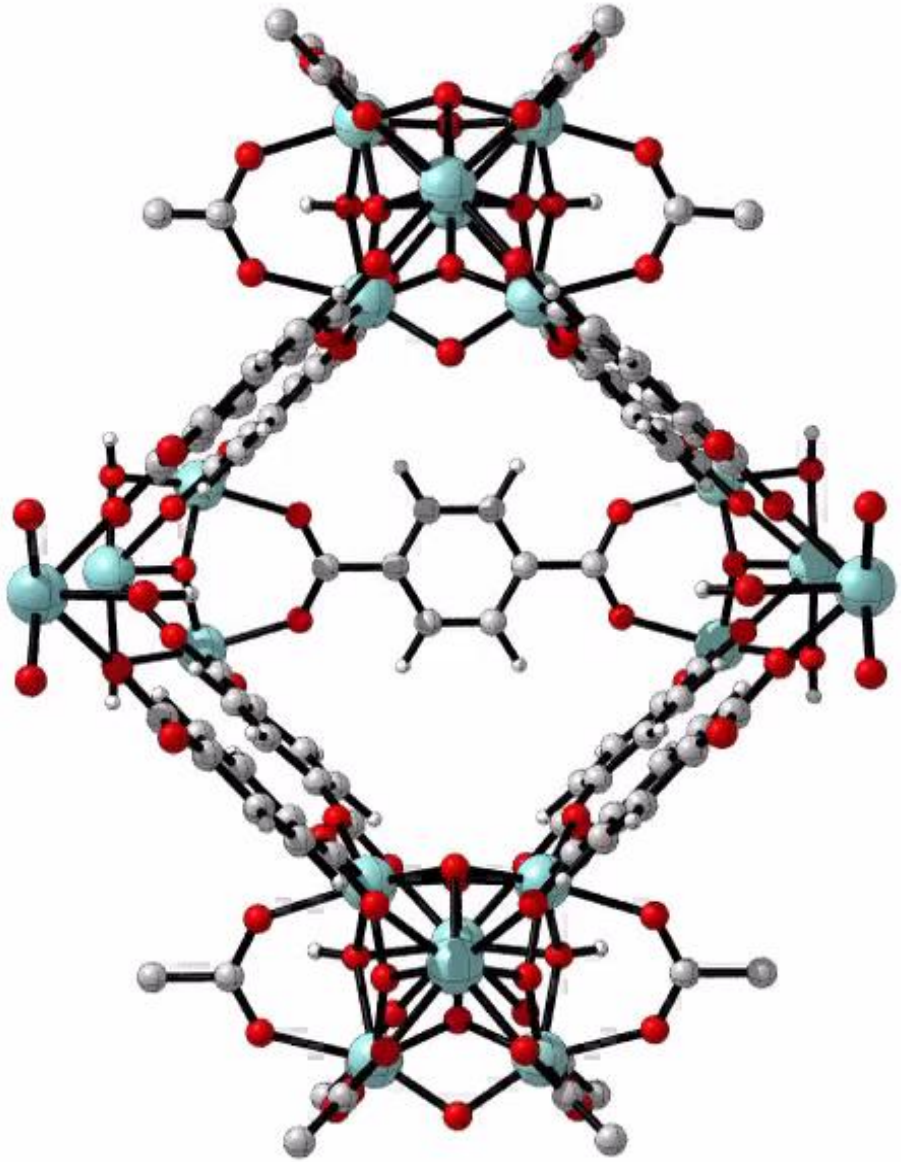
R^N: N = 1 N = 3 N = 30 N > 1000 !!

Number of atoms

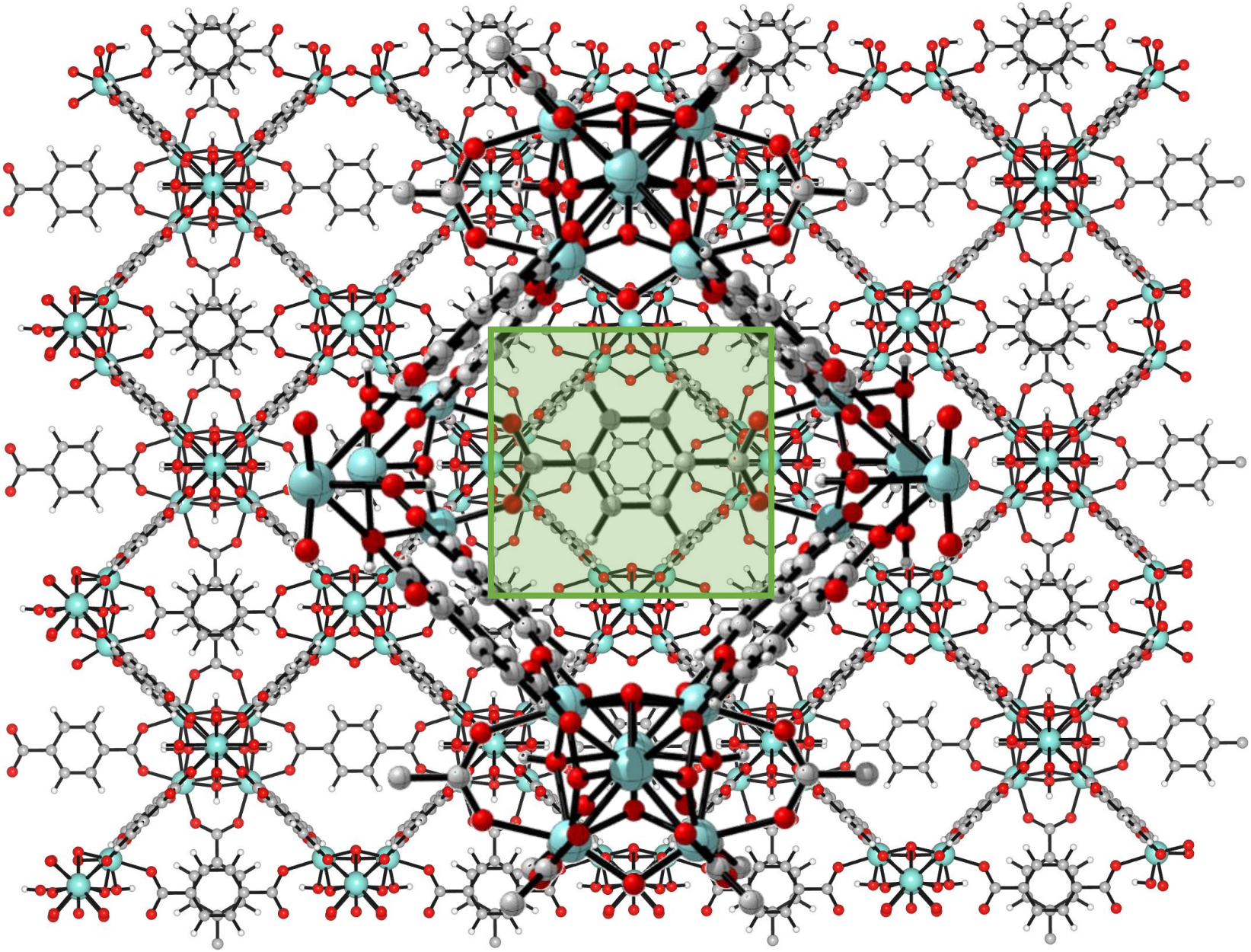
The complexity of the PES dramatically increases with the number of atoms



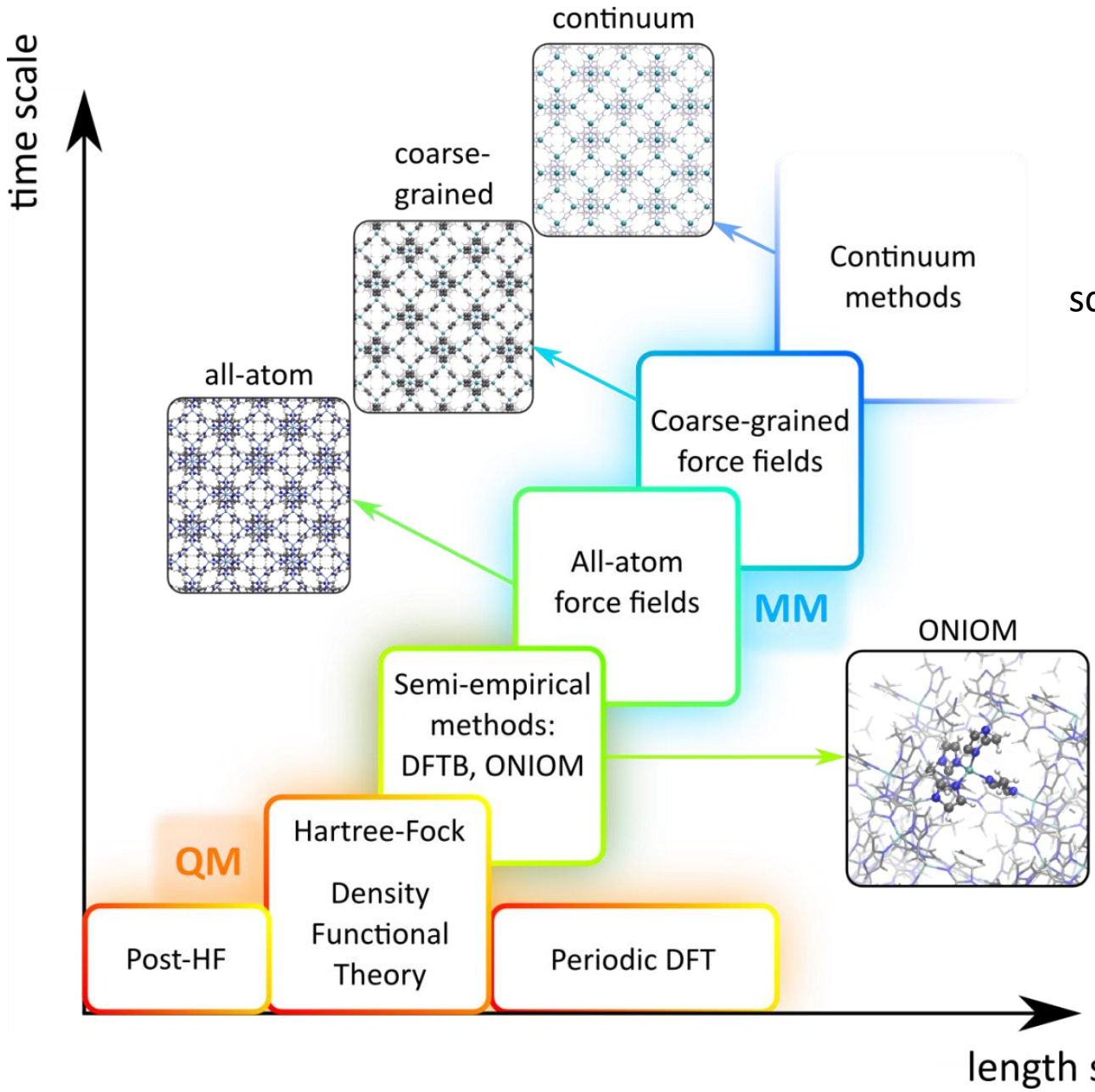
Towards operando description



Towards operando description



Molecular modeling methods



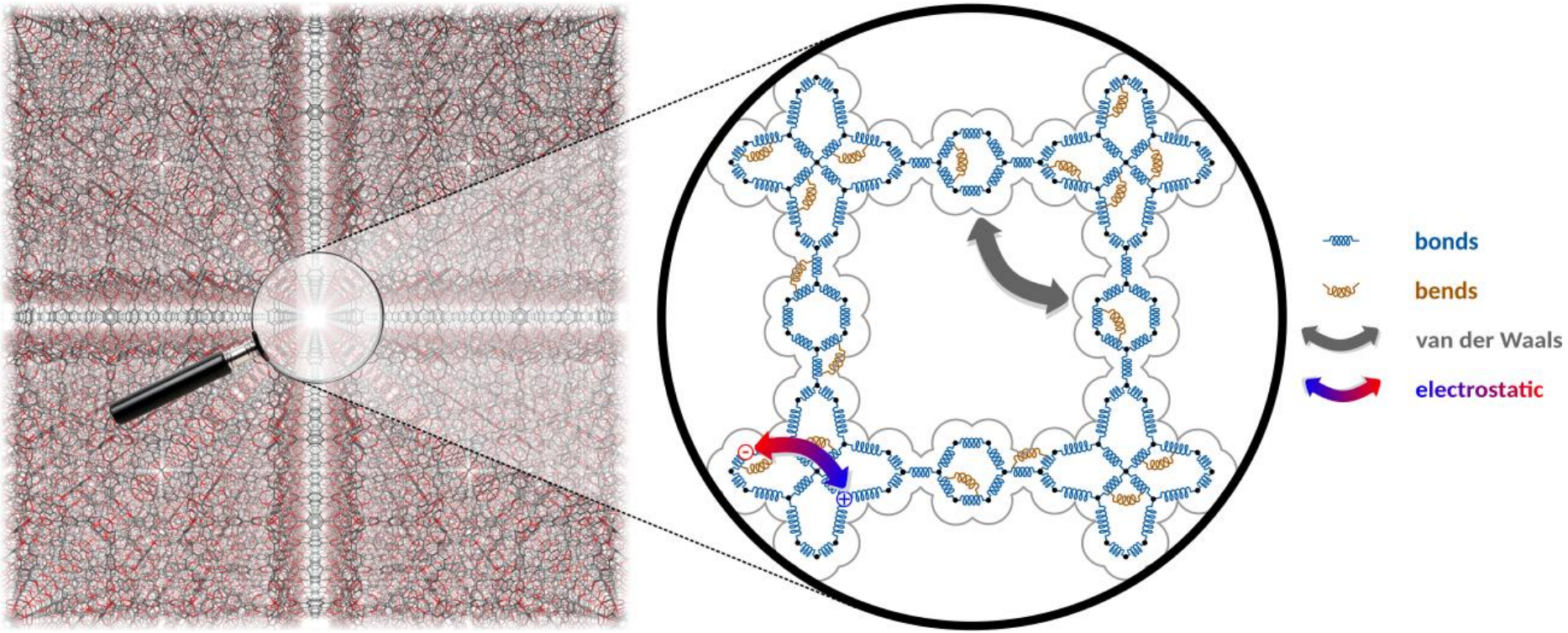
The selection of the appropriate model depends on the time and length scale of the phenomena under study

Quantum mechanical approach: the Schrödinger equation

Time-independent Schrödinger equation

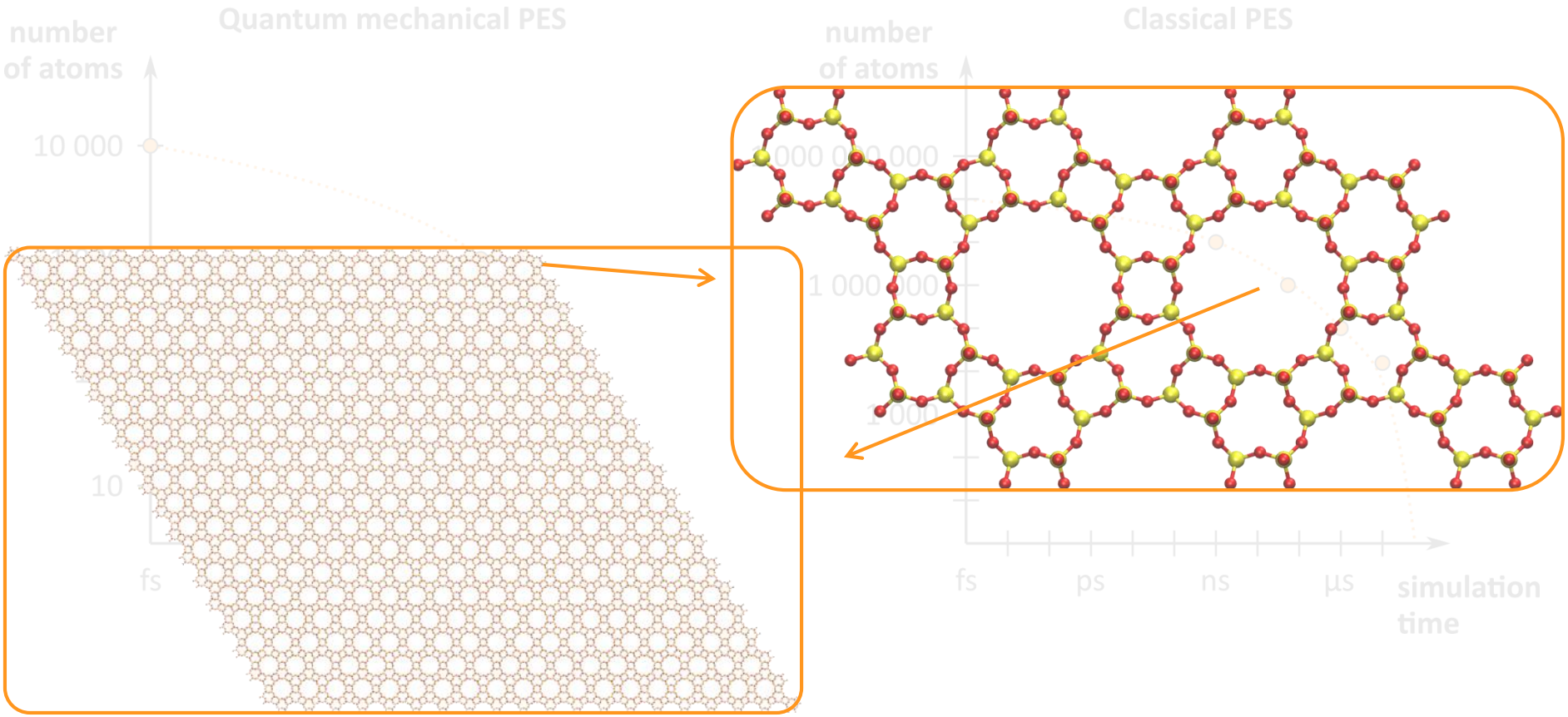
$$\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$$

Classical approach: force fields

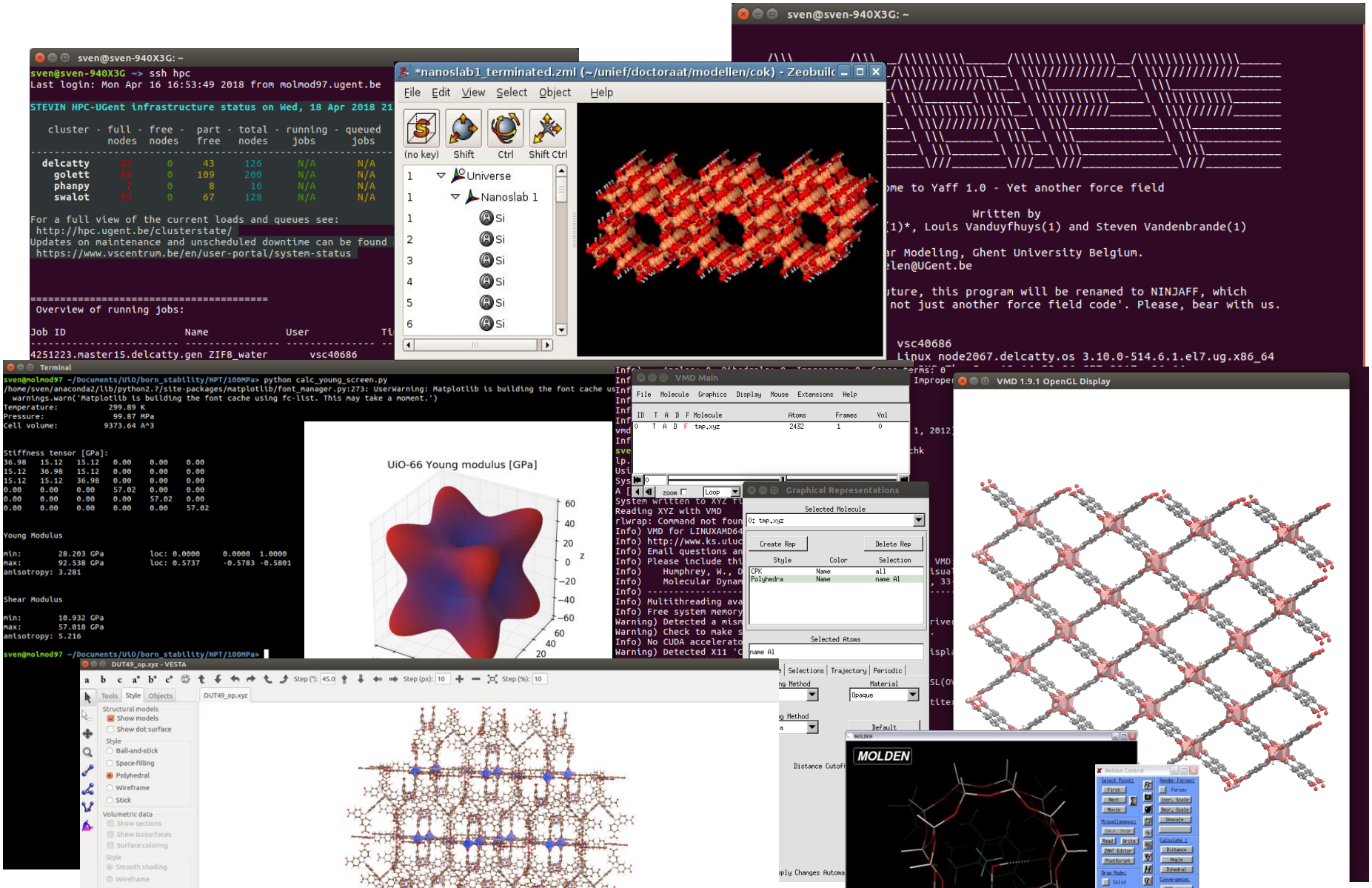


Molecules are described as a set of classical spheres and springs which imitate the interactions provided by quantum chemistry laws

How large are the systems we can model today?

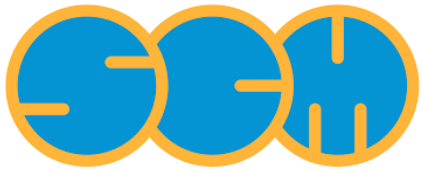


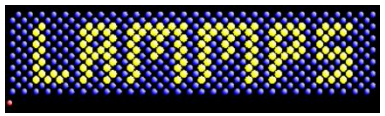
Access to large-scale computer programs



Access to large-scale computer programs

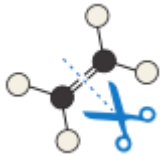
Licenses for
major simulation packages



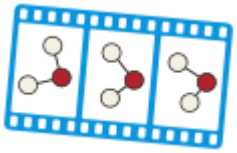


Dedicated in house developed software
Made available open source at
https://molmod.ugent.be/software

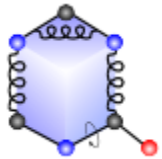
Zeobuilder



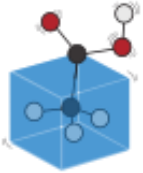
HiPart



MD-Tracks



QuickFF

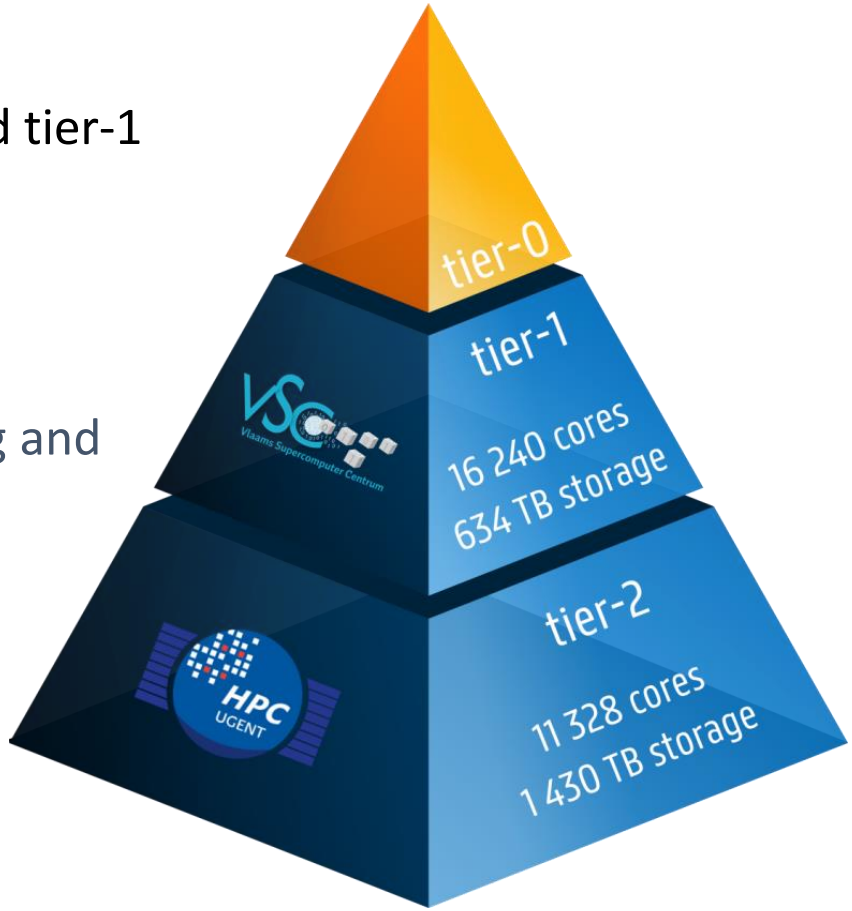


TAMkin

Yaff, MolMod, Con3F, …

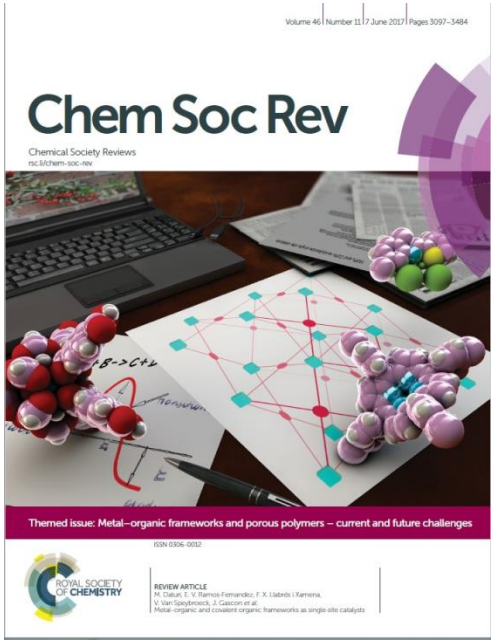
Access to large-scale computer facilities: the HPC

- CMM is one of the largest users of tier-2 and tier-1 HPC
- 35 frequent users
- A lot of number-crunching
- Heavily involved in pilot-user phases: testing and benchmarking codes/clusters
- Pushing machines to their limits
- Co-investor in central HPC infrastructure



High-end infrastructure necessary to stay competitive in our research field

Fundamental role of HPC in highly competitive research



nature chemistry

Structure–performance descriptors and the role of Lewis acidity in the methanol-to-propylene process

Irina Yarulina, Kristof De Wispelaere, Simon Bailleul, Joris Goetze, Mike Radersma, Edy Abou-Hamad, Ina Vollmer, Maarten Goesten, Brahim Mezari, Emiel J. M. Hensen, Juan S. Martínez-Espín, Magnus Morten, Sharon Mitchell, Javier Perez-Ramirez, Unni Olsbye, Bert M. Weckhuysen, Veronique Van Speybroeck, Freek Kapteijn & Jorge Gascon

Nature Chemistry **10**, 804–812 (2018) | Download Citation

nature COMMUNICATIONS

Article | OPEN | Published: 15 January 2018

Thermodynamic insight into stimuli-responsive behaviour of soft porous crystals

L. Vanduyfhuys, S. M. J. Rogge, J. Wieme, S. Vandenbrande, G. Maurin, M. Waroquier & Speybroeck

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nature materials

Design of zeolite by inverse sigma transformation

Elke Verheyen[1], Lennart Joos[2], Kristof Van Havenbergh[3], Eric Breynaert[1], Nataliia Kasian[1,4], Elena Gobechiya[1], Kristof Houthoofd[1], Charlotte Martineau[5], Manuel Hinterstein[6], Francis Taulelle[5] Veronique Van Speybroeck[2], Michel Waroquier[2], Sara Bals[3], Gustaaf Van Tendeloo[3], Christine E. A. Kirschhock[1]* and Johan A. Martens[1]

SHARE

RESEARCH ARTICLE

Reproducibility in density functional theory calculations of solids

Kurt Lejaeghere[1,*], Gustav Bihlmayer[2], Torbjörn Björkman[3,4], Peter Blaha[5], Stefan Blügel[2], Volker Blum[6], Damien Caliste[7,8], Ivano E. Castelli[9], Stewart J. Clark[10], Andrea Dal Corso[11], Stefano de Gironcoli[11], Thierry Deutsch[7,8], John Kay Dewhurst[12], Igor Di Marco[13], Claudia Draxl[14,15], Marcin Dułak[16], Olle Eriksson[13], José A. Flores-Livas[12], Kevin F. Garrity[17], Luigi Genovese[7,8], Paolo Giannozzi[18],

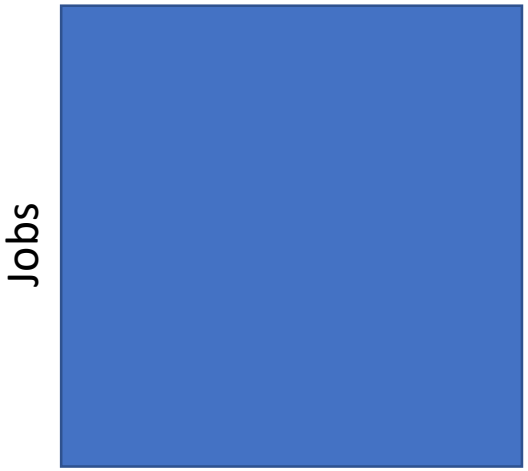
Different types of jobs

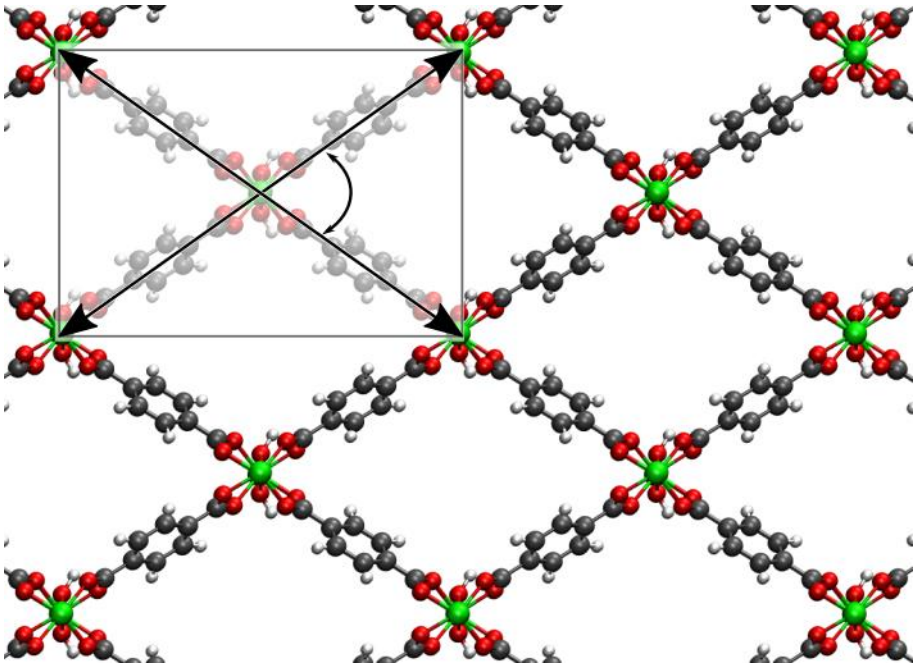
job type 1: **large static calculations**

limiting factor: RAM memory

e.g. RPA on 76-atom MOF – 26 TB, 2800 cores

J. Wieme, K. Lejaeghere et al., *Nat. Commun*. **2018**





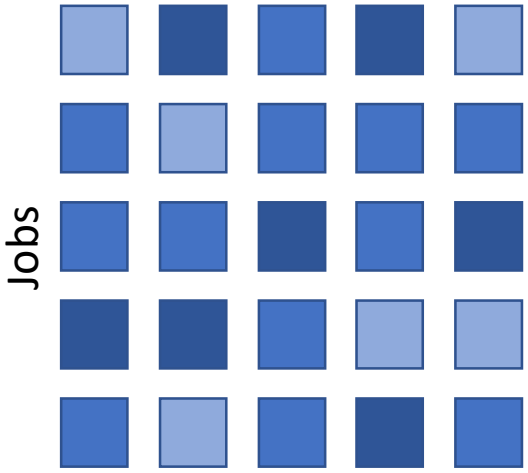
Different types of jobs

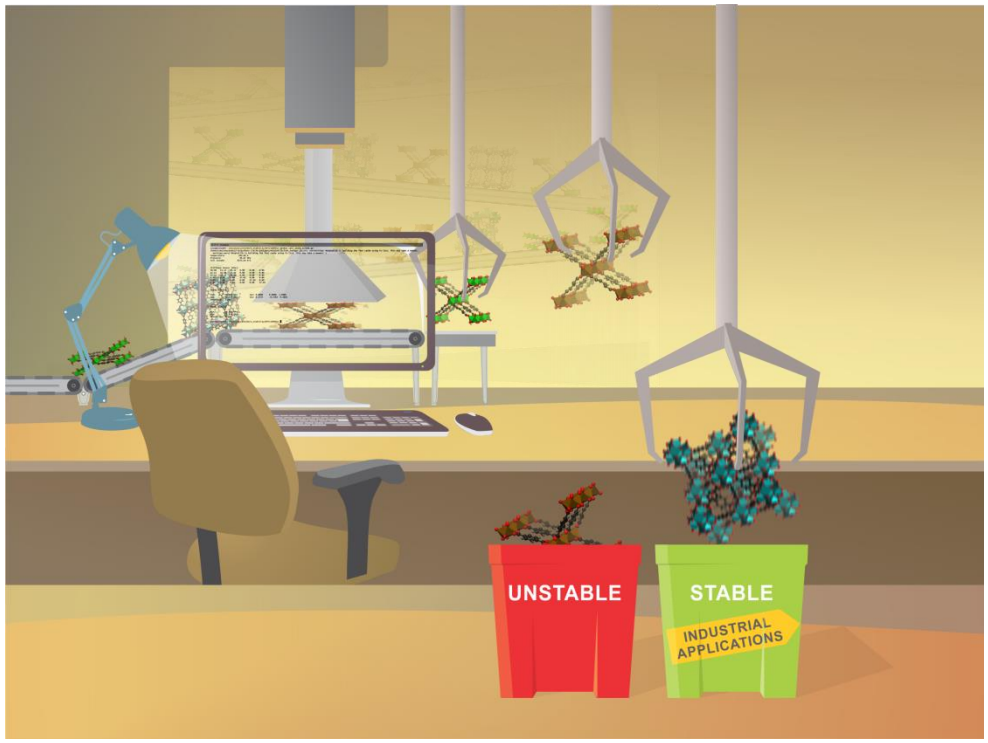
job type 2: **high-throughput calculations**

limiting factor: core hours + storage

e.g. high-throughput simulations on 14 MOFs
576 core hours (x700), 78 GB storage

P.Z. Moghadam, S.M.J. Rogge et al.,
Joule, **2019**, in revision.





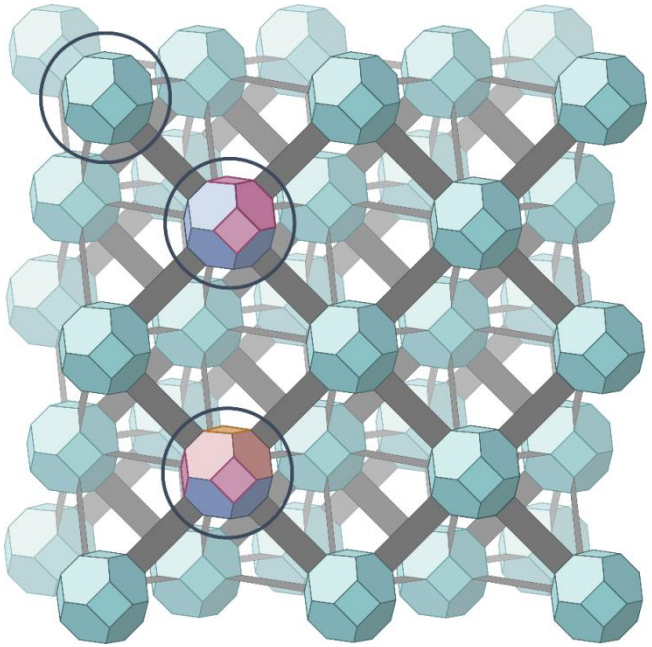
Different types of jobs

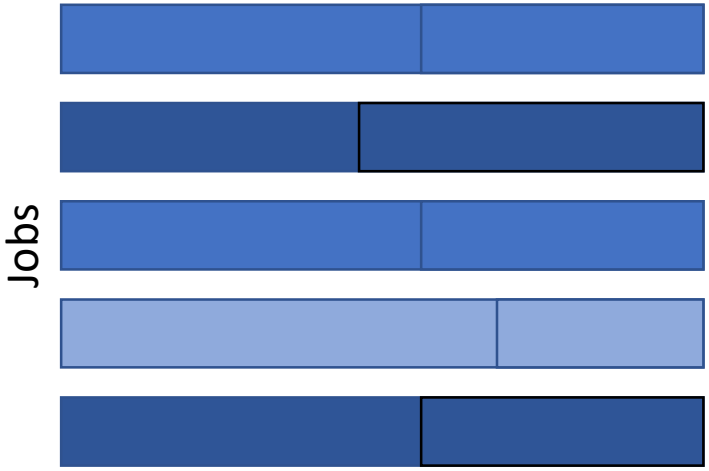
job type 3: **dynamic calculations**

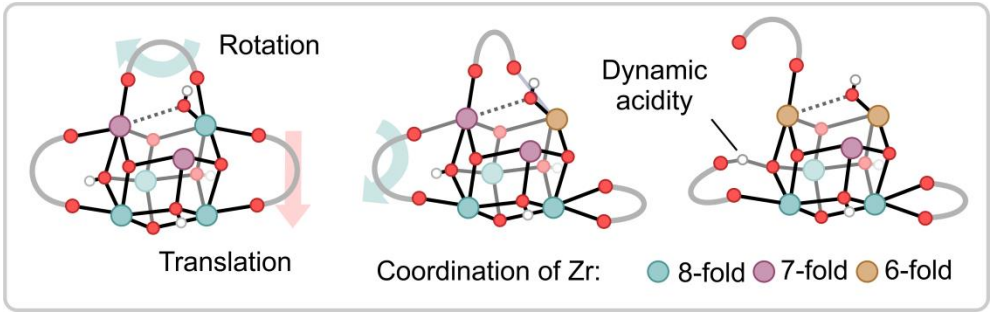
limiting factor: wall time + storage

e.g. dynamic behavior of UiO-66
[50k steps, 16k core hours, 8 GB] x 36

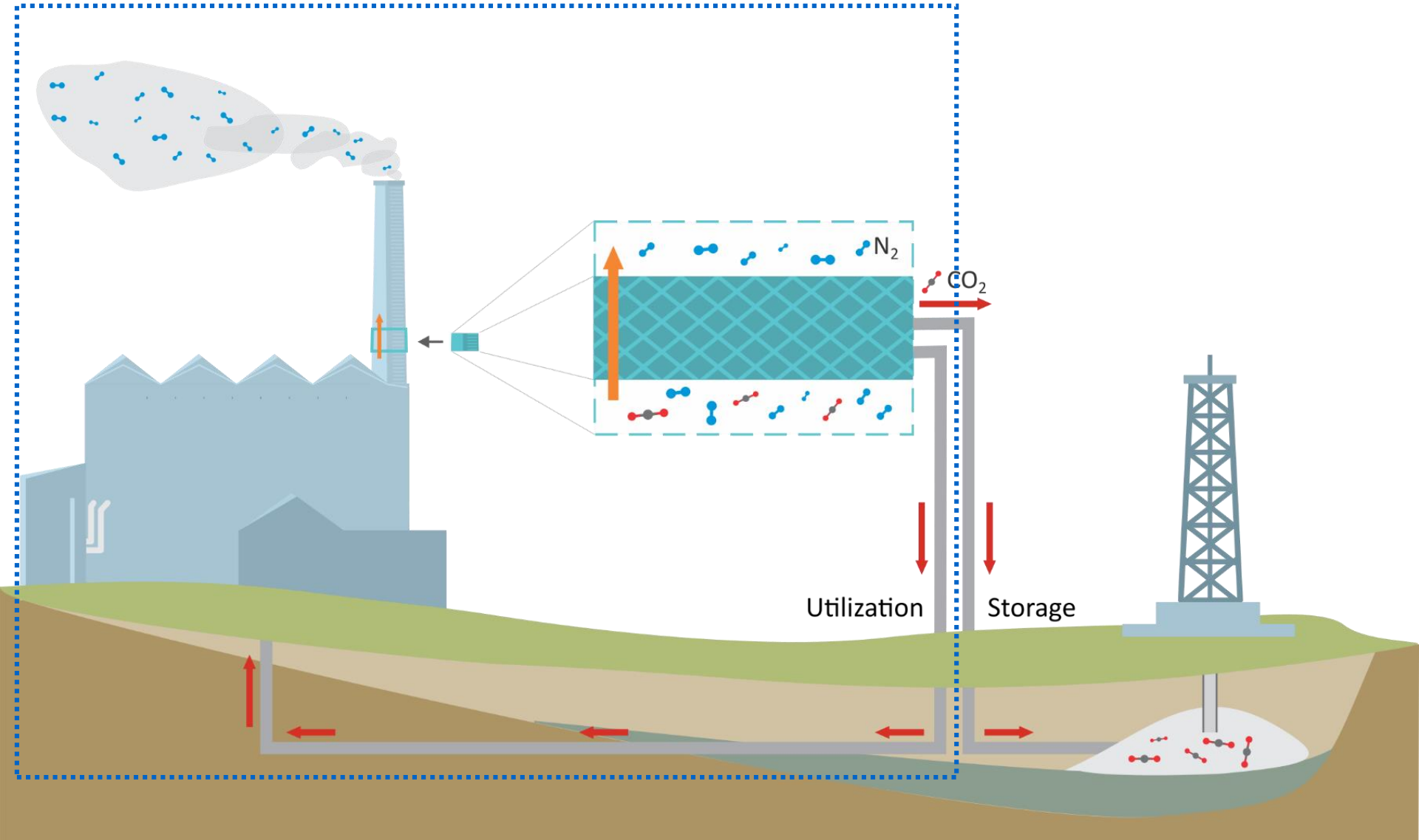
J. Hajek, et al. *Chemical Science*, **2018**



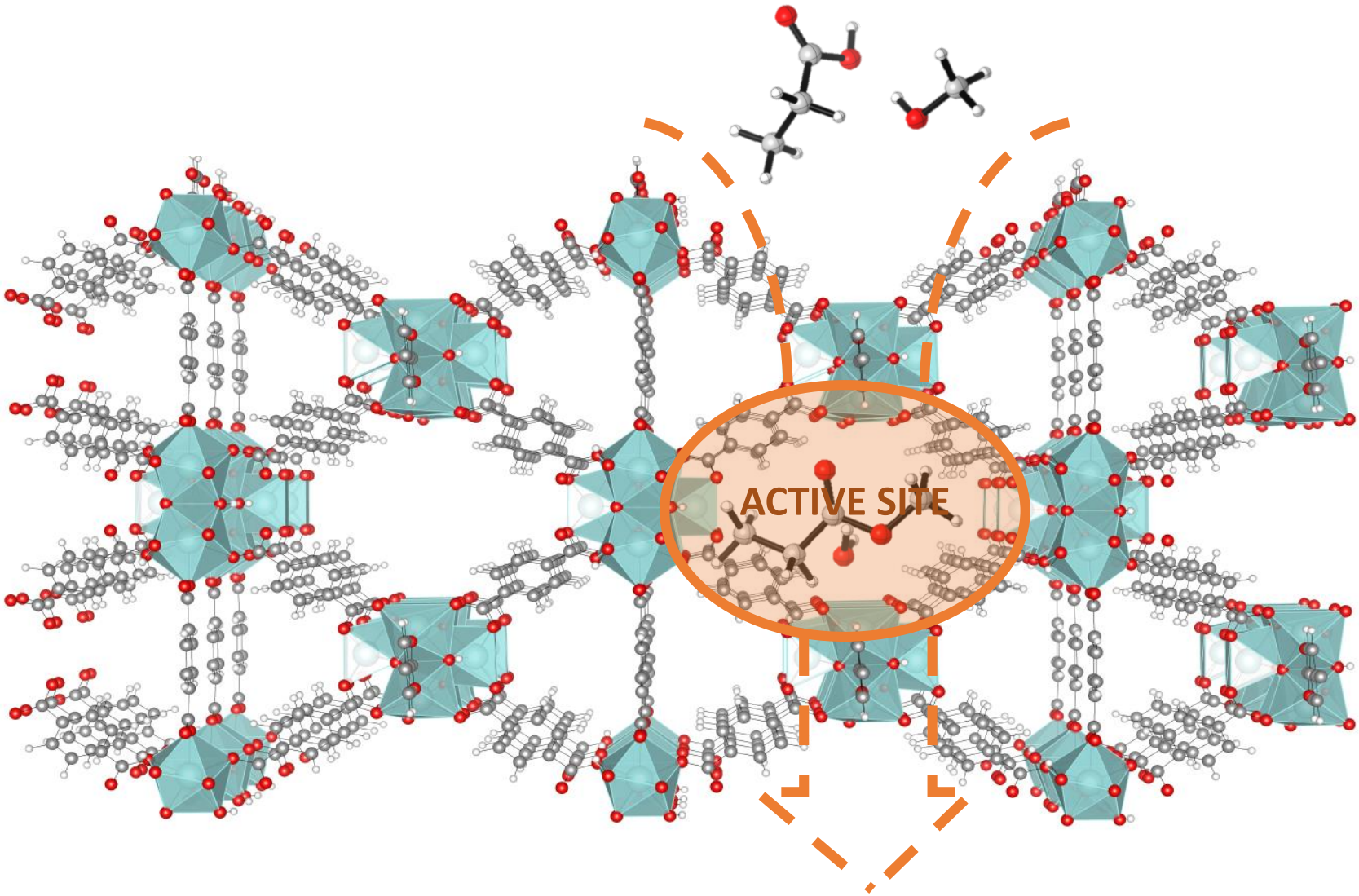




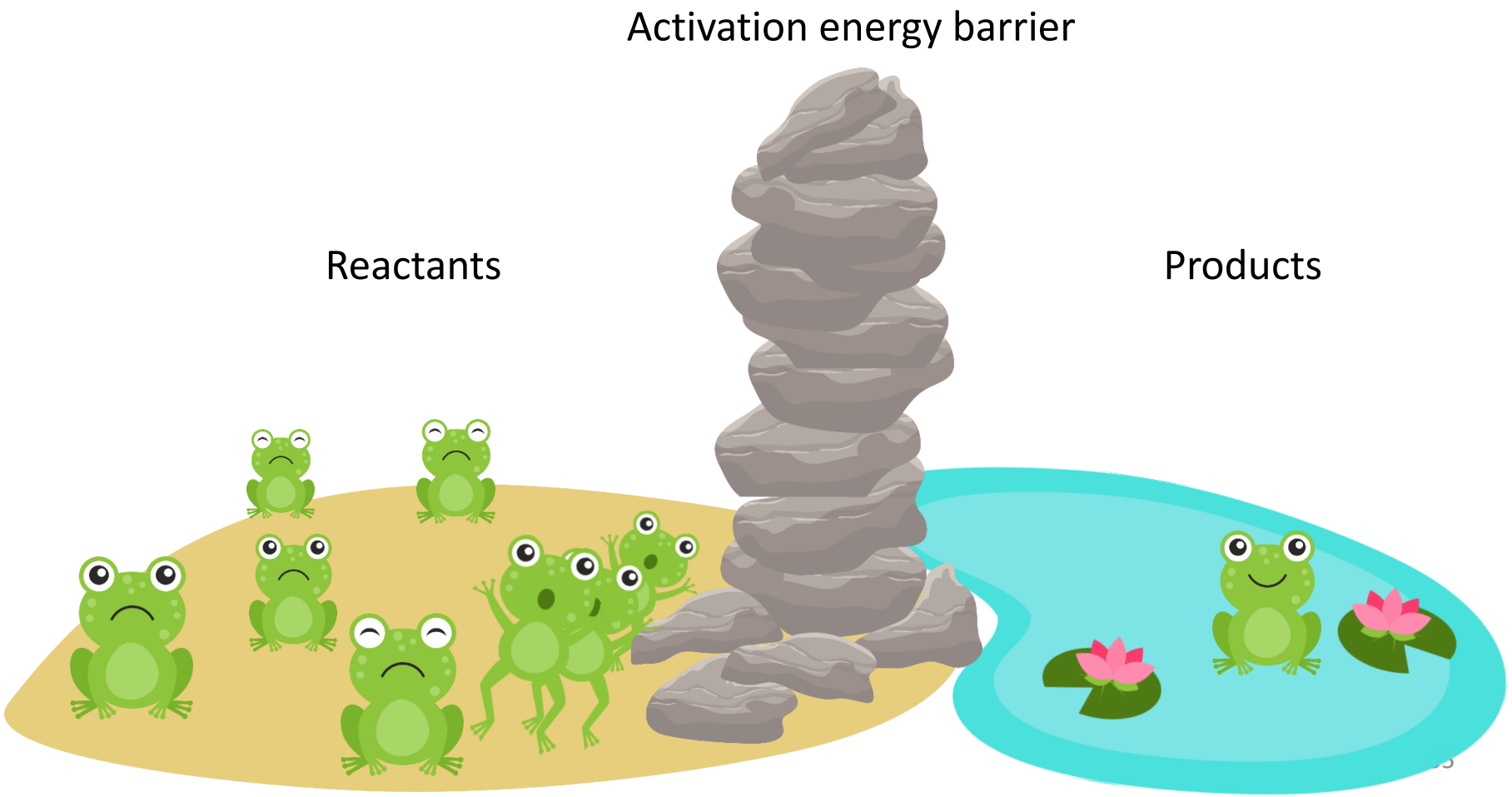
Chemical processes in MOFs



Catalysis in MOFs



Reaction without a catalyst

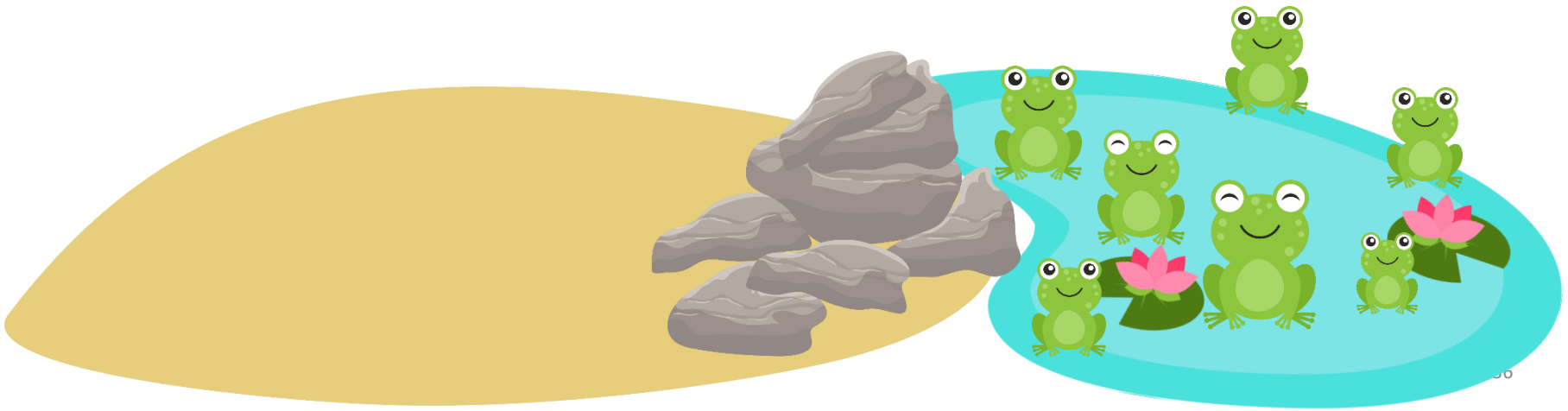


Reaction with a catalyst

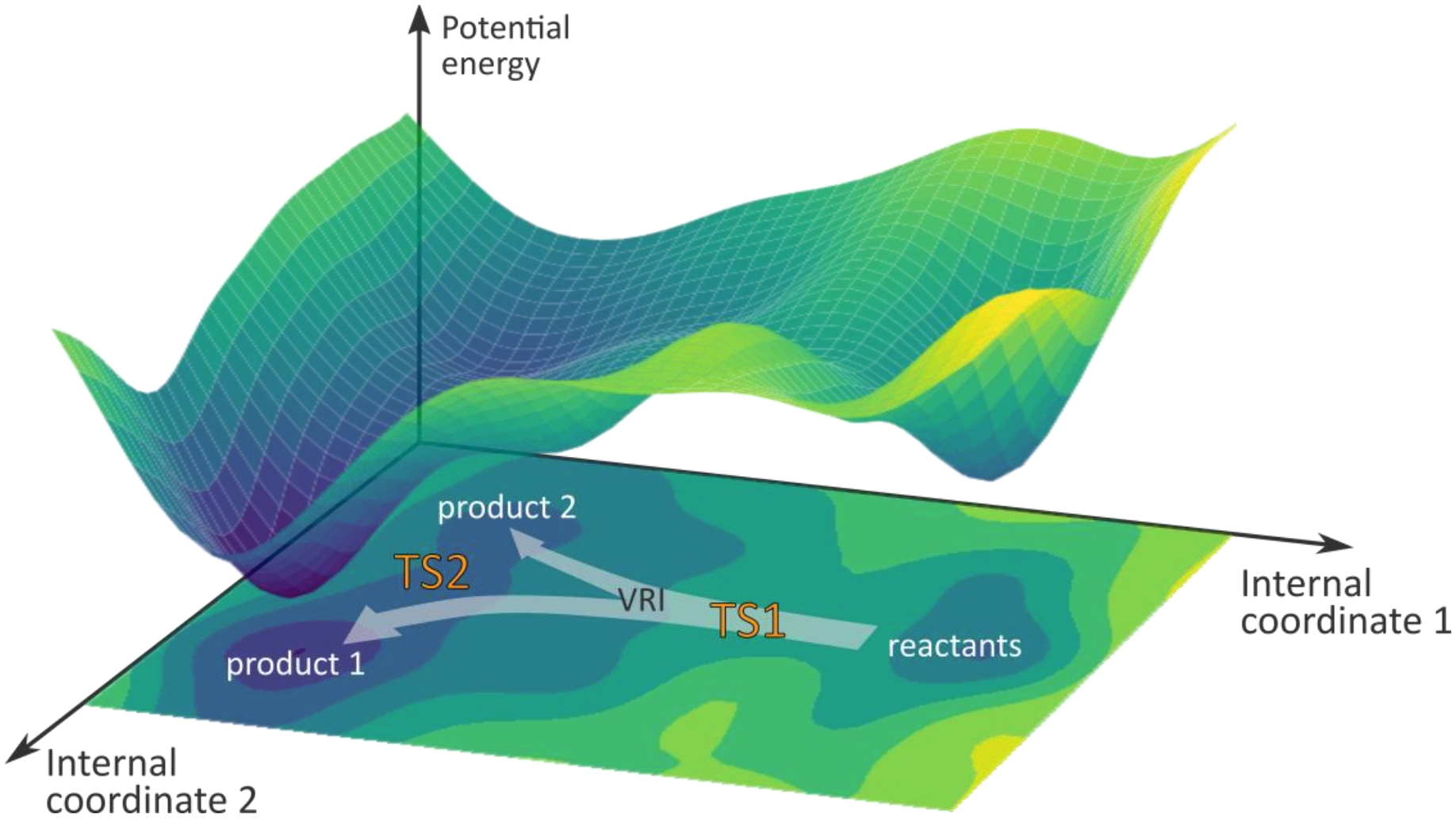
Activation energy barrier

Reactants

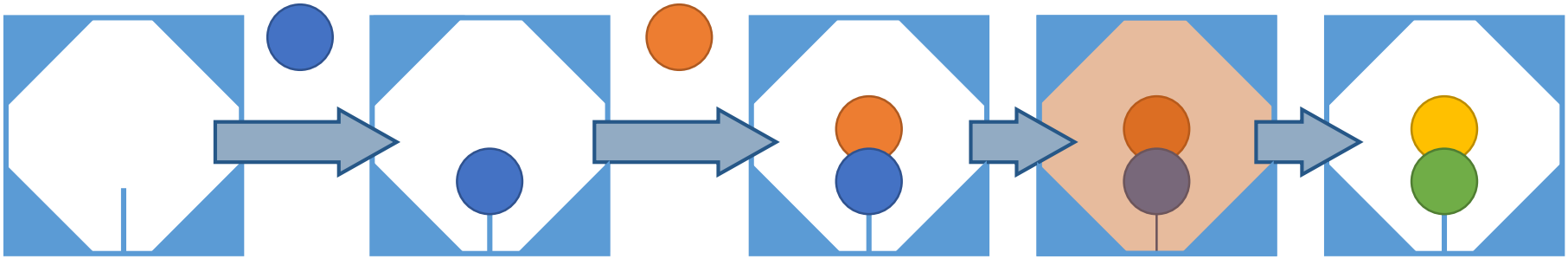
Products

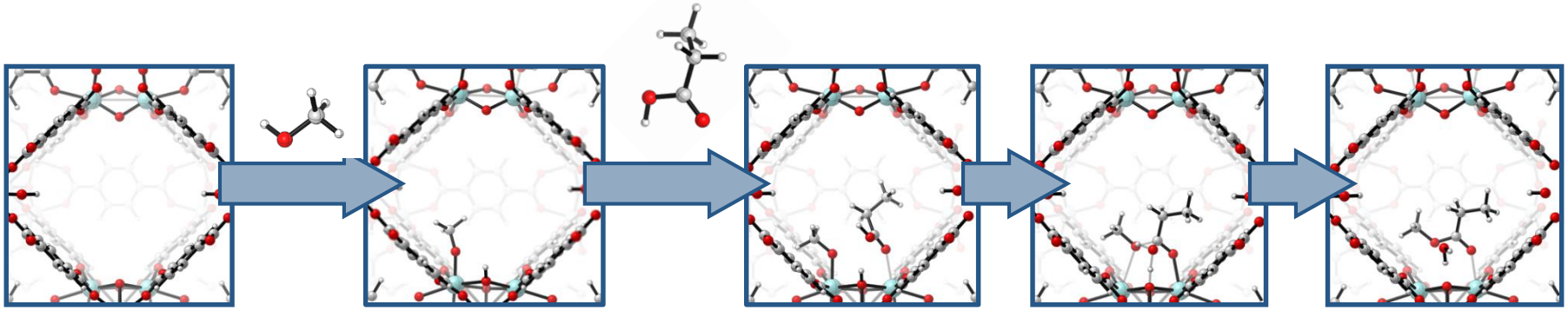


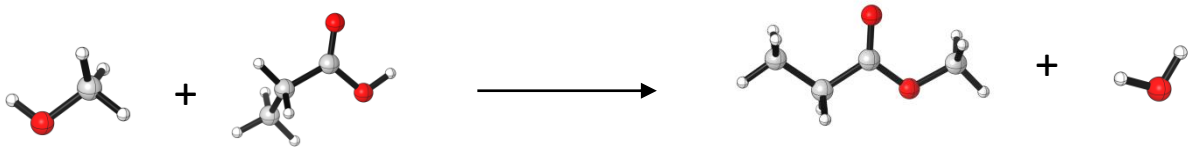
A catalytic reaction: a path between different minima on the PES



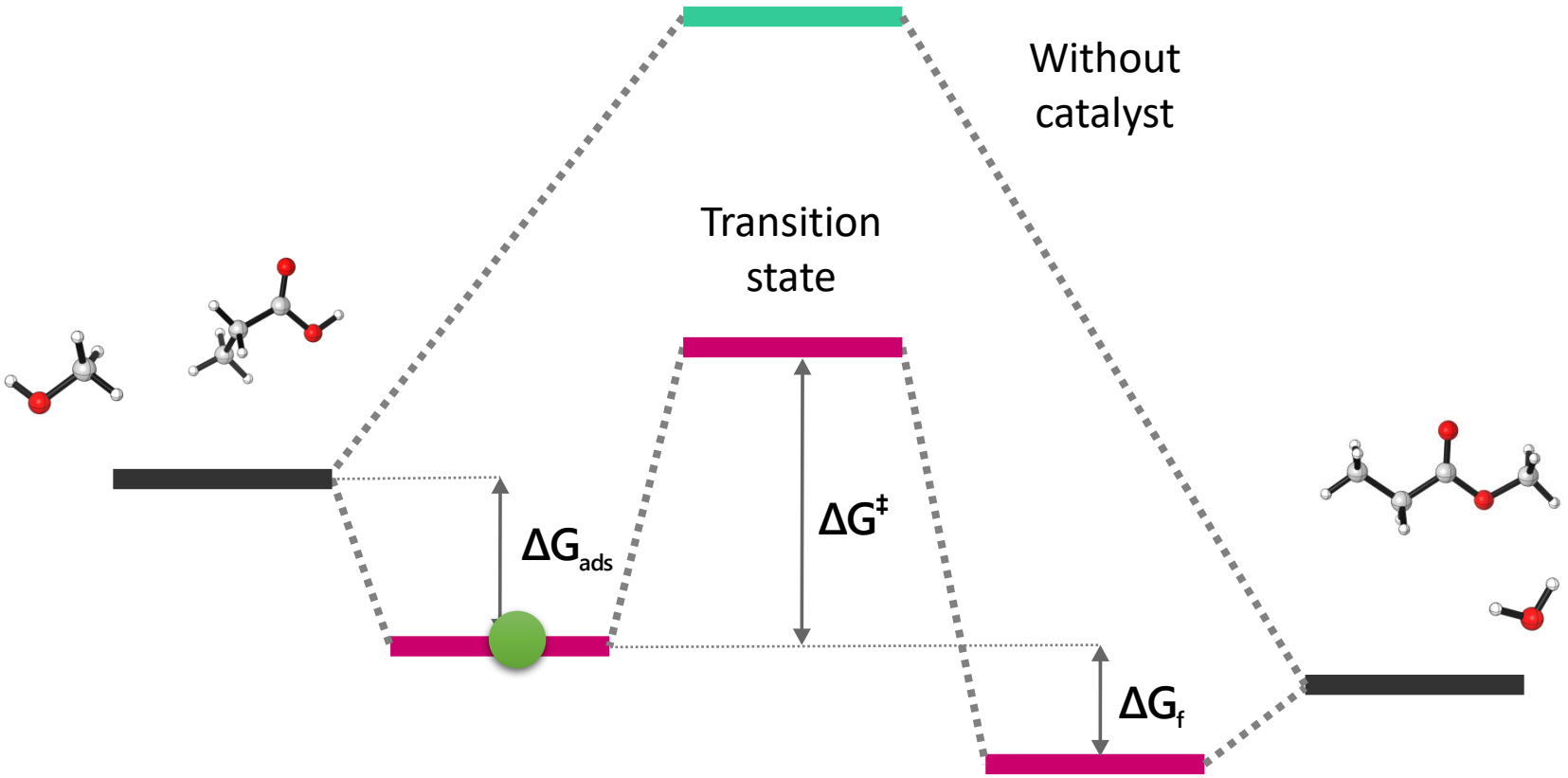
A catalytic reaction in nanoporous materials



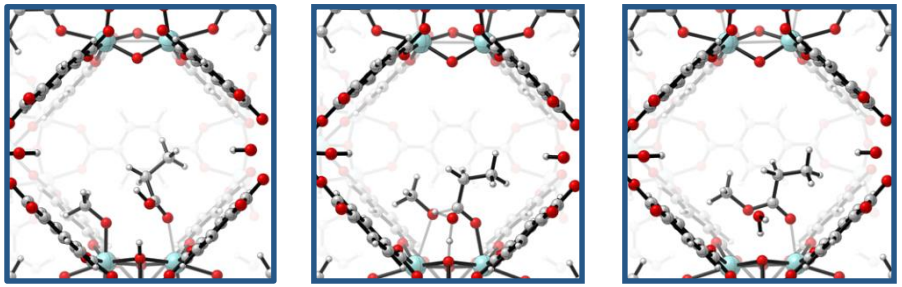




Construction of a free energy diagram

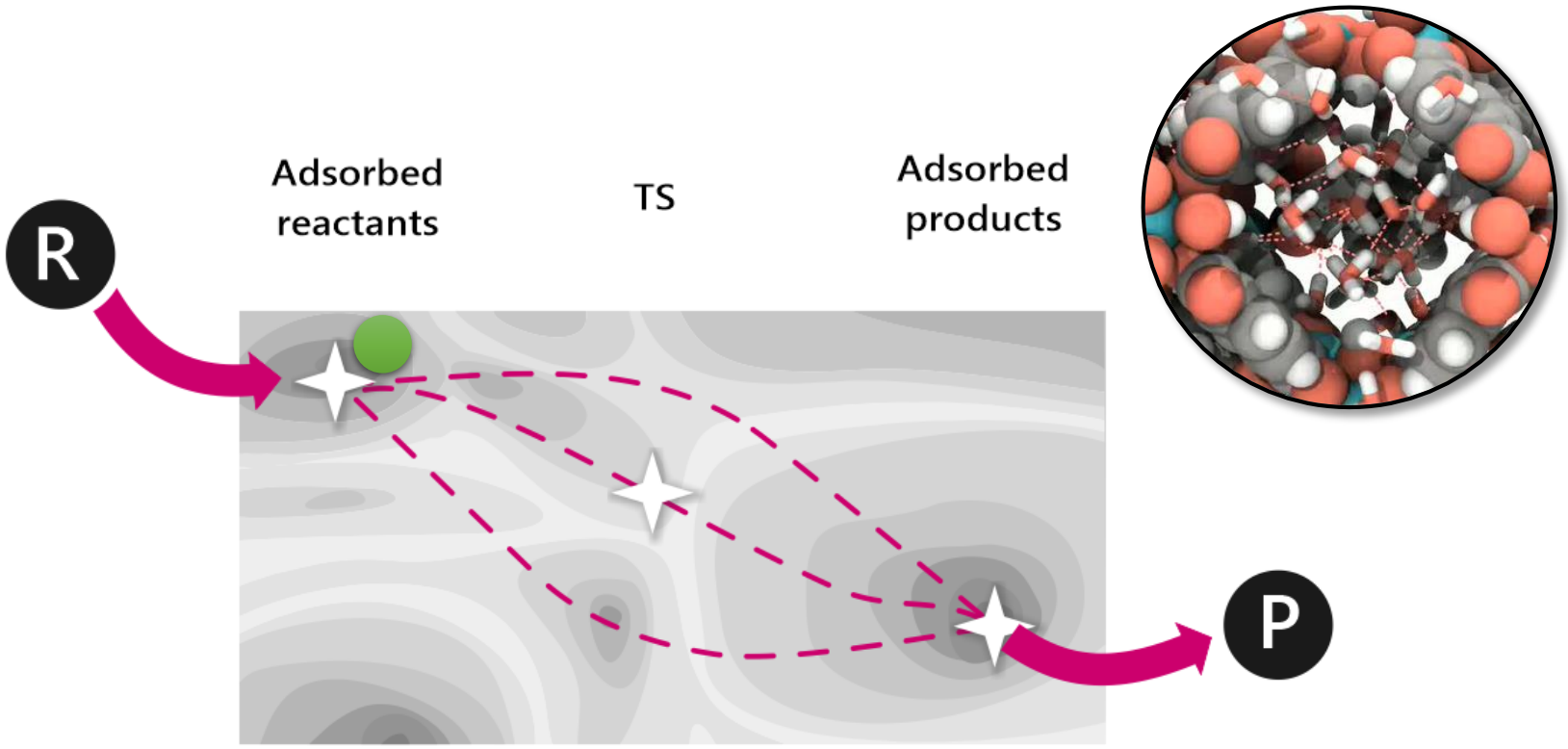


Adsorbed
reactants



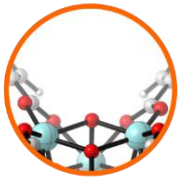
Adsorbed
products

Molecular dynamics methods allow to explore the PES

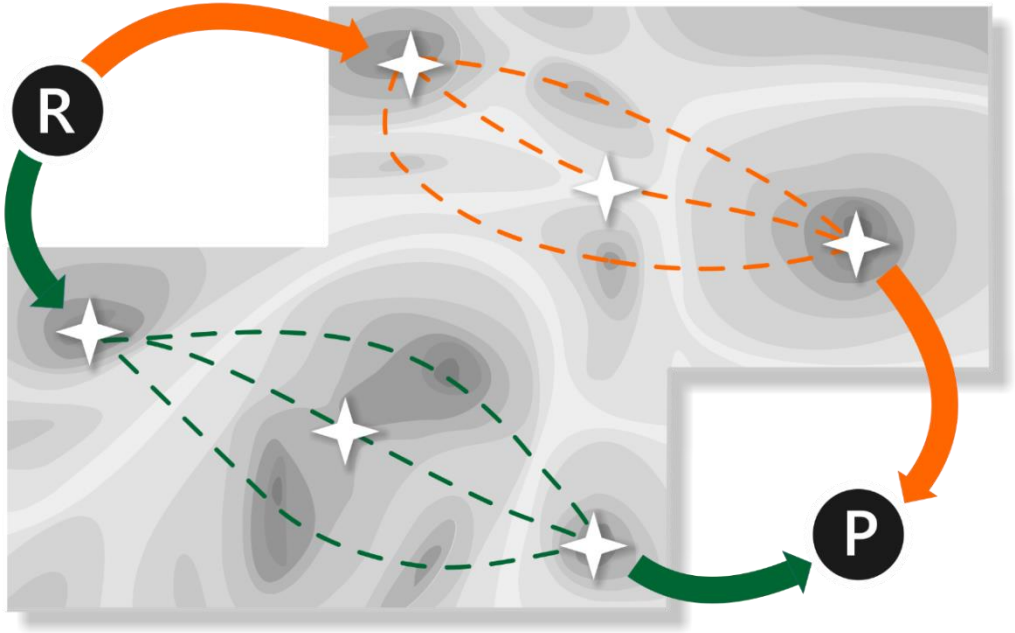


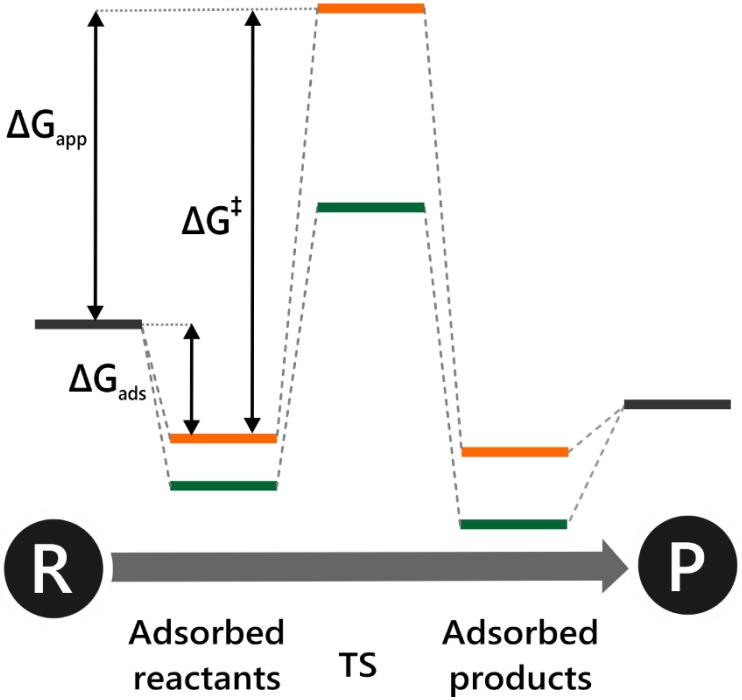
Exploring the free energy surface at operating conditions
using molecular dynamics methods

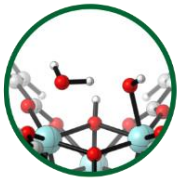
Two main approaches to study reactions



Active
Site 1

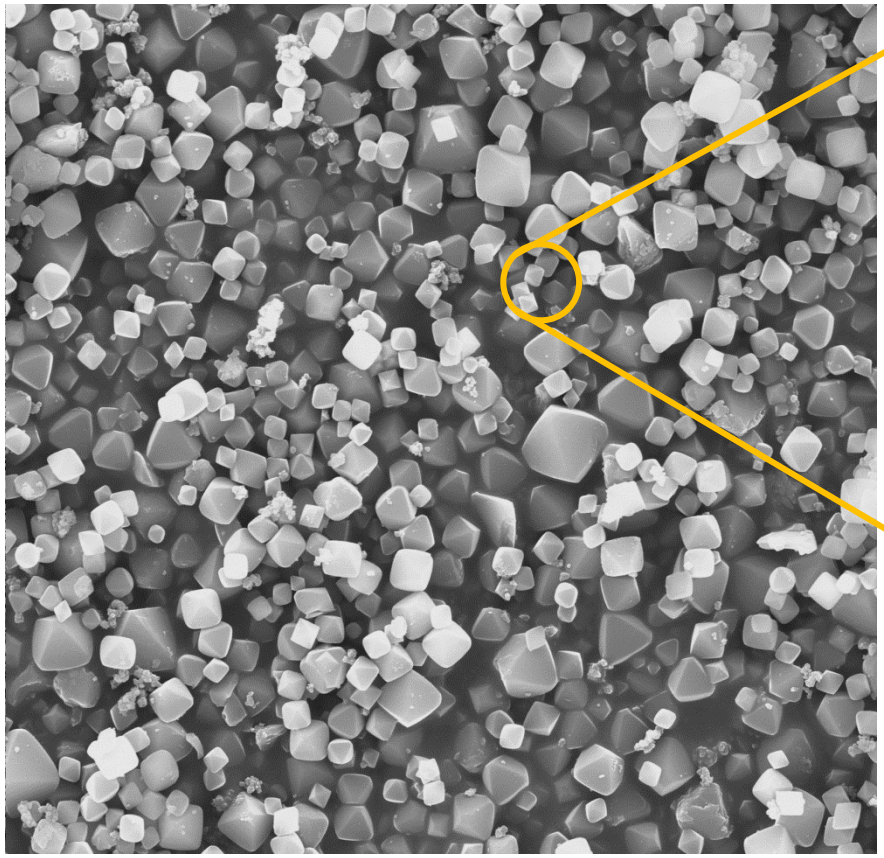


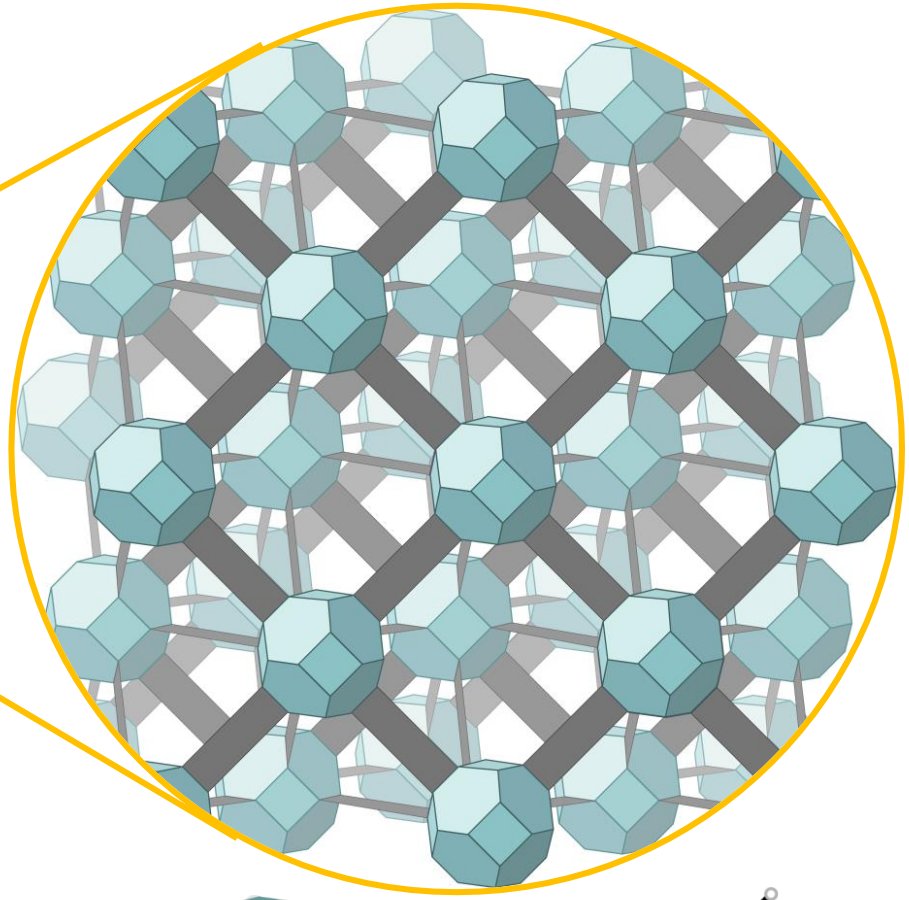


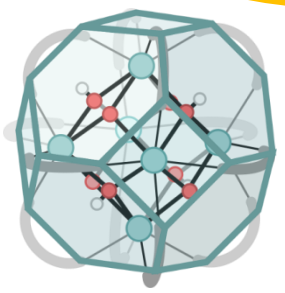


Active
Site 2

UiO-66

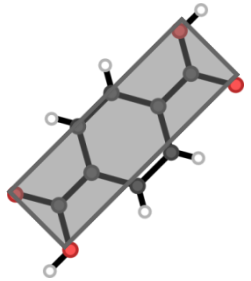






$[Zr_6O_4(OH)_4]^{12+}$

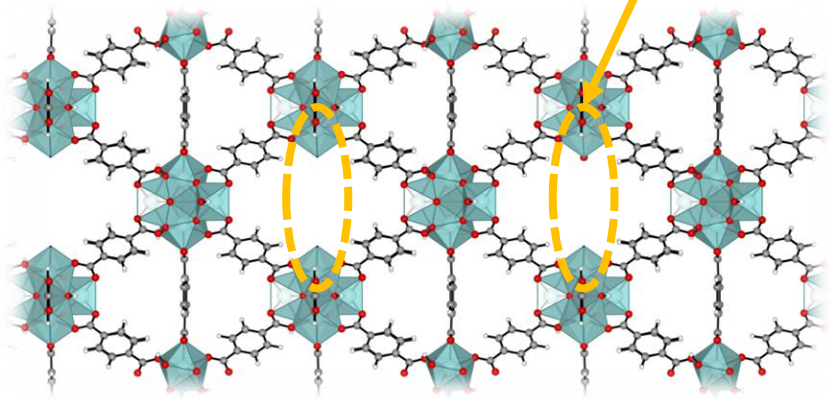
+

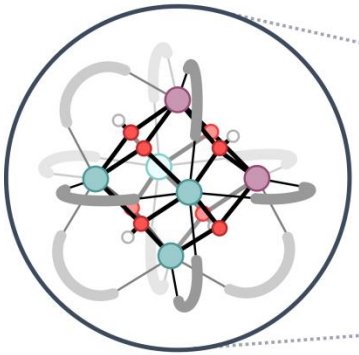


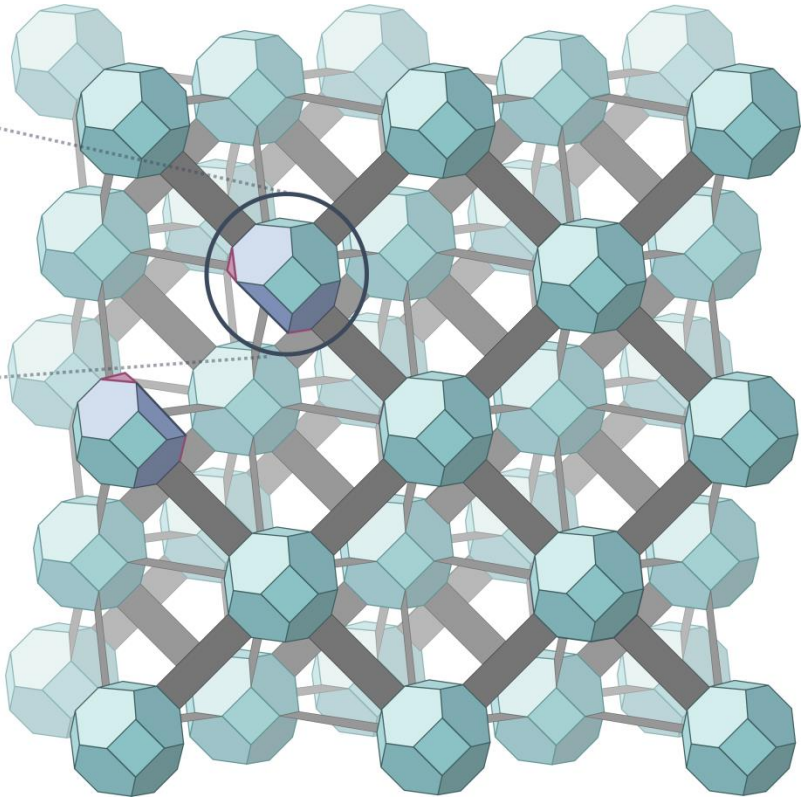
$[C_6H_4(CO_2)_2]^{2-}$

Point defects

Missing linker defects







Dehydration

250 – 300 °C

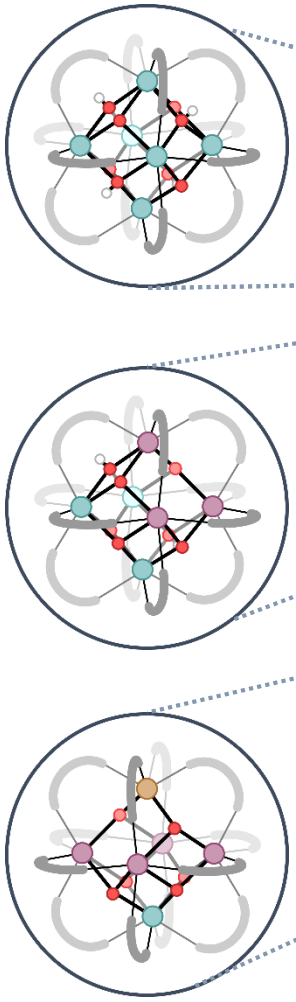
Pristine brick
$Zr_6O_4(OH)_4$

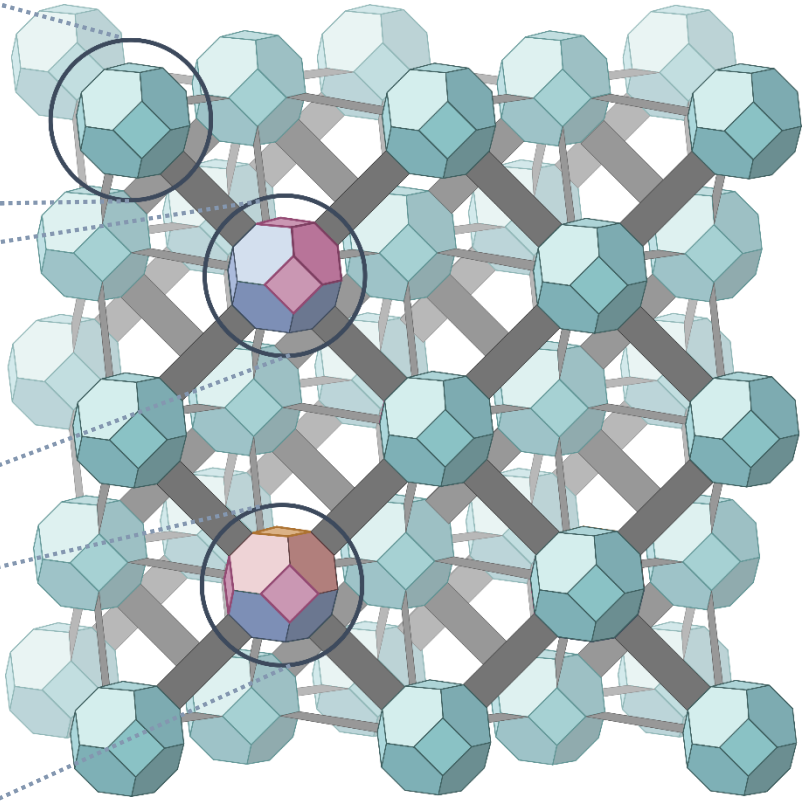
- H_2O

Partly dehydrated brick
$Zr_6O_5(OH)_2$

- H_2O

Fully dehydrated brick
Zr_6O_6

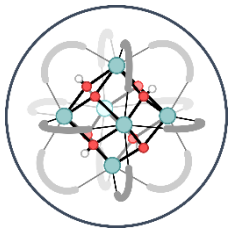




Coordination of Zr

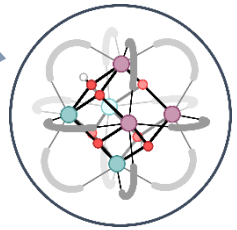
- 8-fold
- 7-fold
- 6-fold

Dehydration mechanism



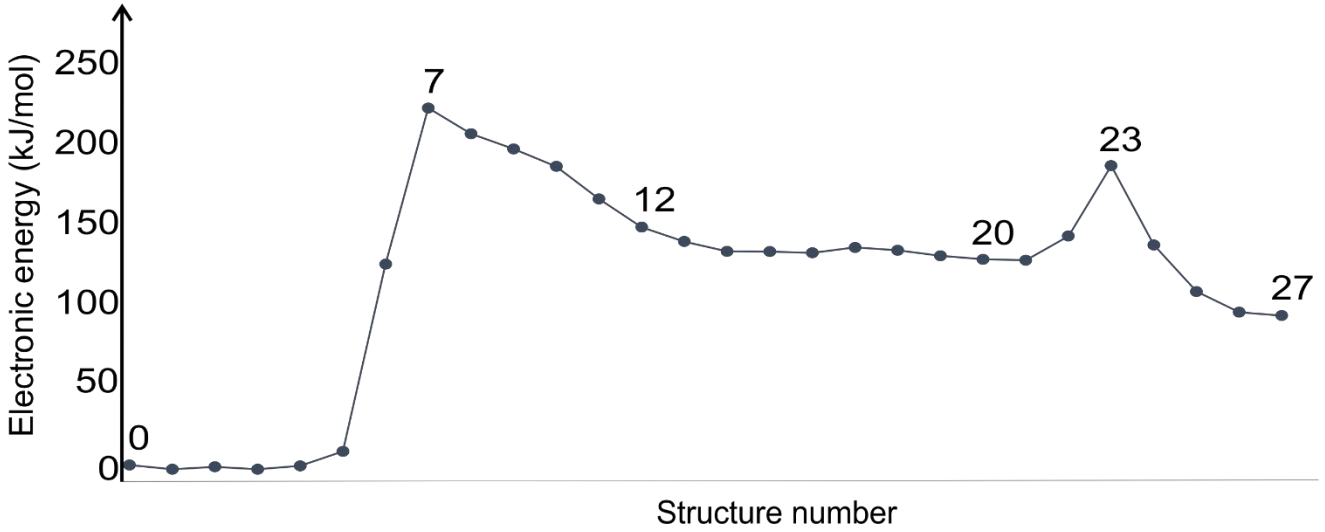
Pristine brick
$Zr_6O_4(OH)_4$

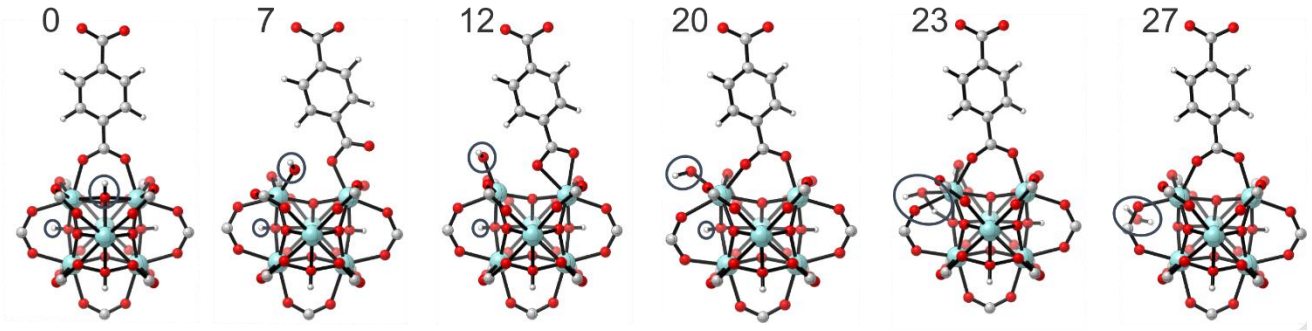
- H_2O



Partly dehydrated brick
$Zr_6O_5(OH)_2$

Method: Nudged elastic band

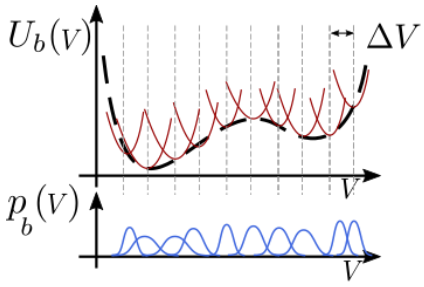


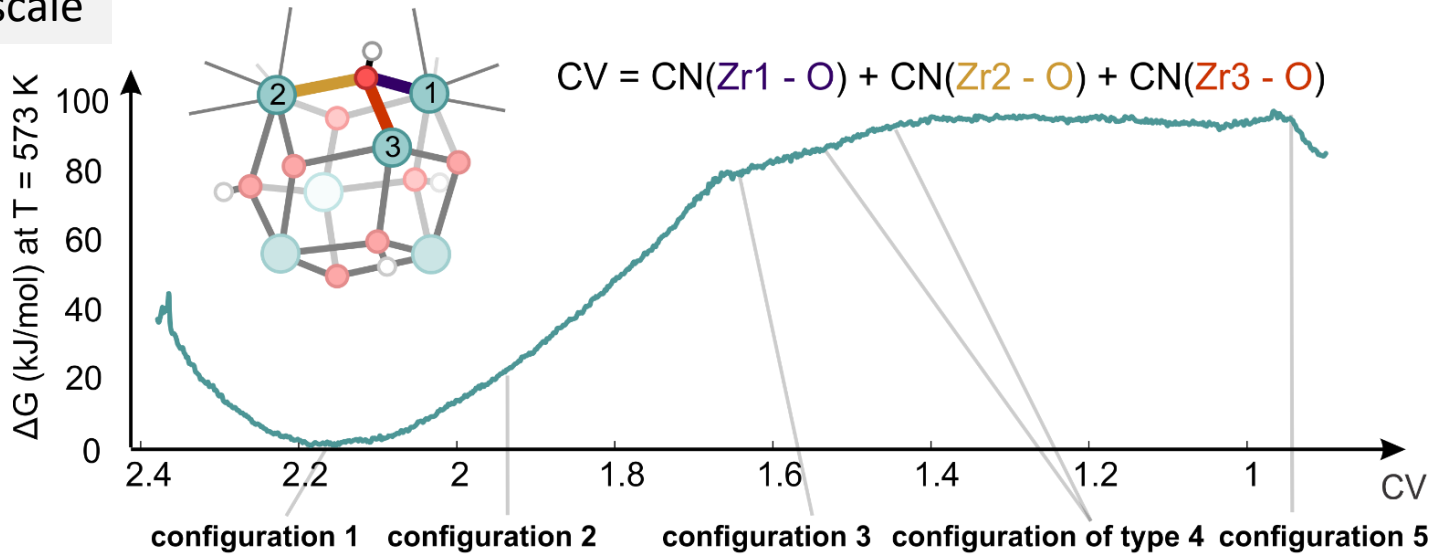


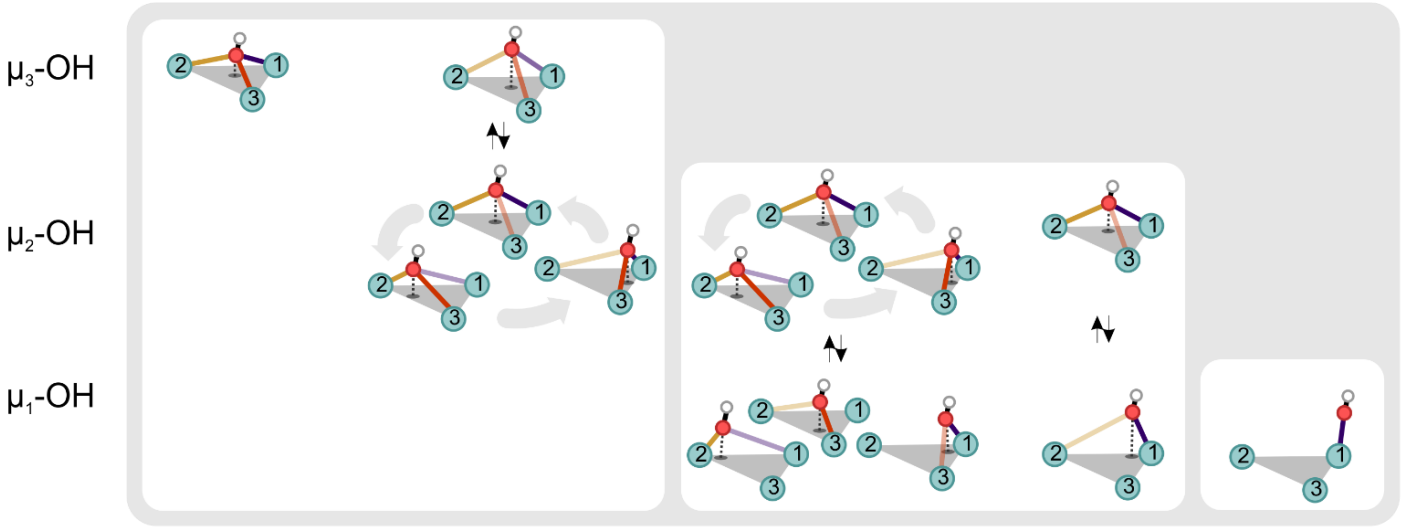
J. Hajek *et al.*, *Chemical Science*, **2018**

Job type 3
Dynamic calculations
with extended
time and/or length scale

Dynamic nature of UiO-66







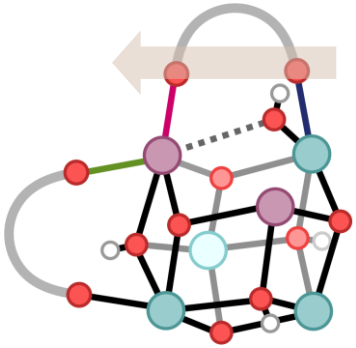
J. Hajek *et al.*, *Chemical Science*, **2018**

Job type 3
Dynamic calculations with extended time and/or length scale

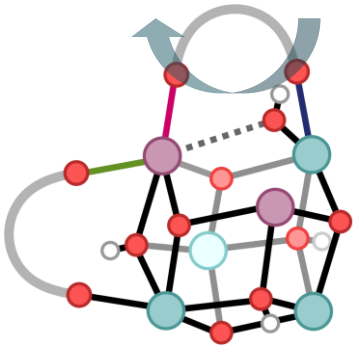
Dynamic nature of UiO-66

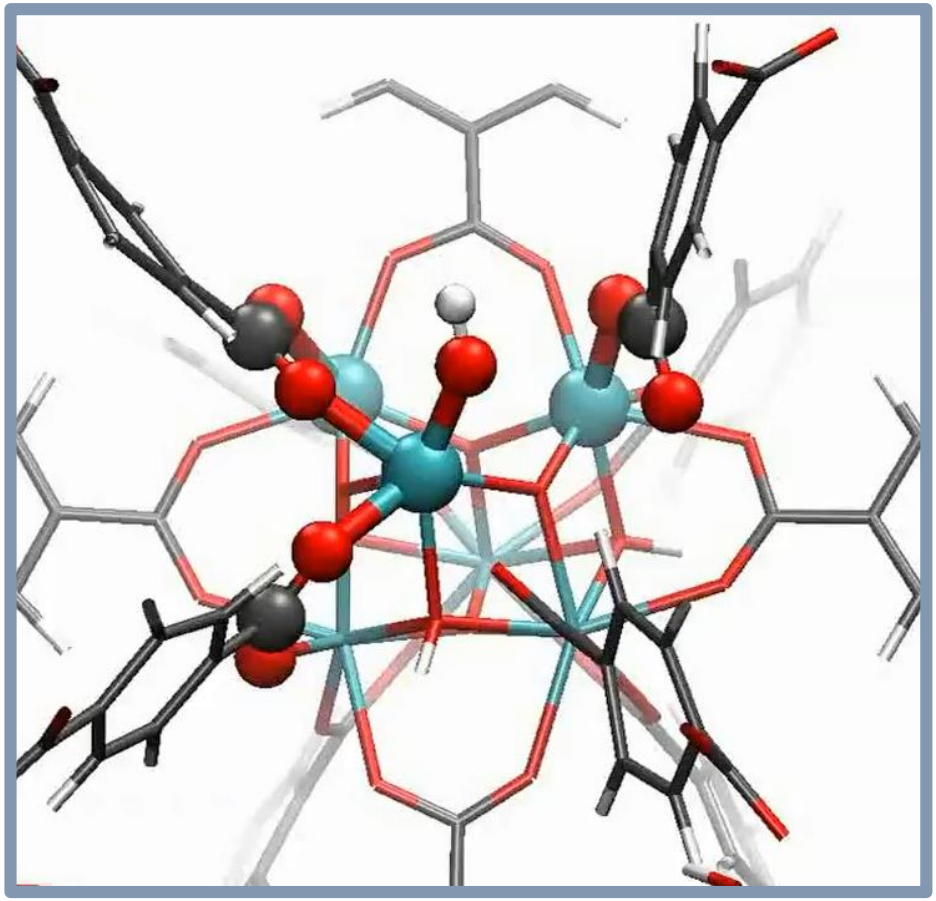
Method: Umbrella sampling, CV = 0.9

Translation



Rotation

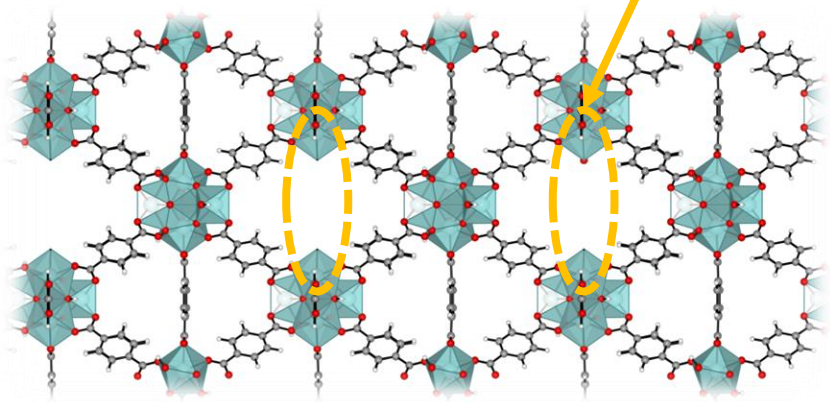


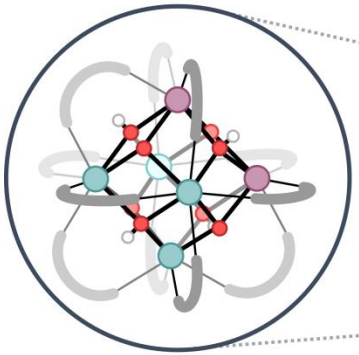


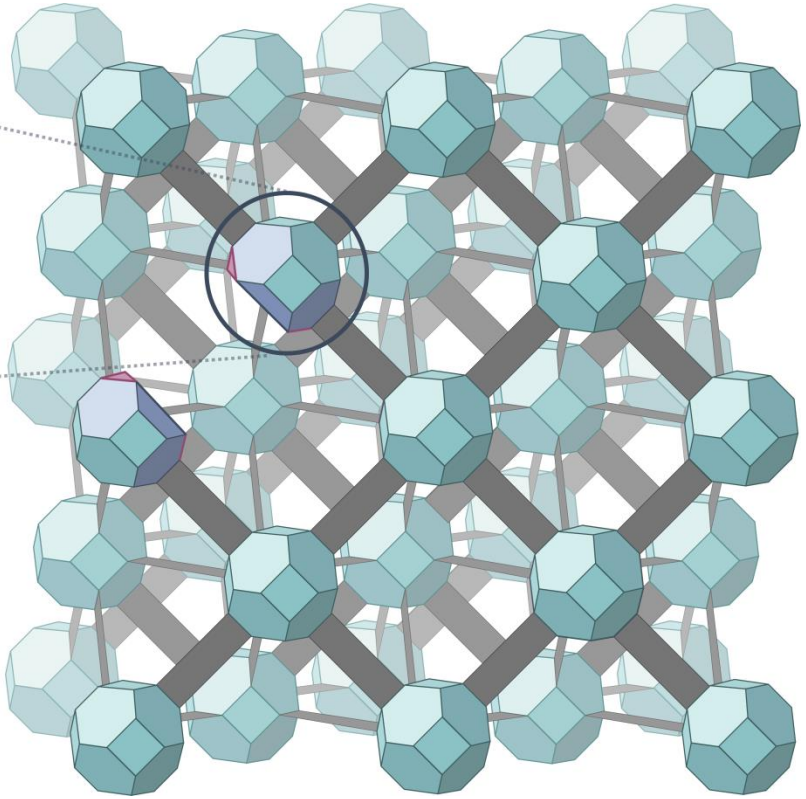
J. Hajek *et al.*, *Chemical Science*, **2018**

Point defects

Missing linker defects



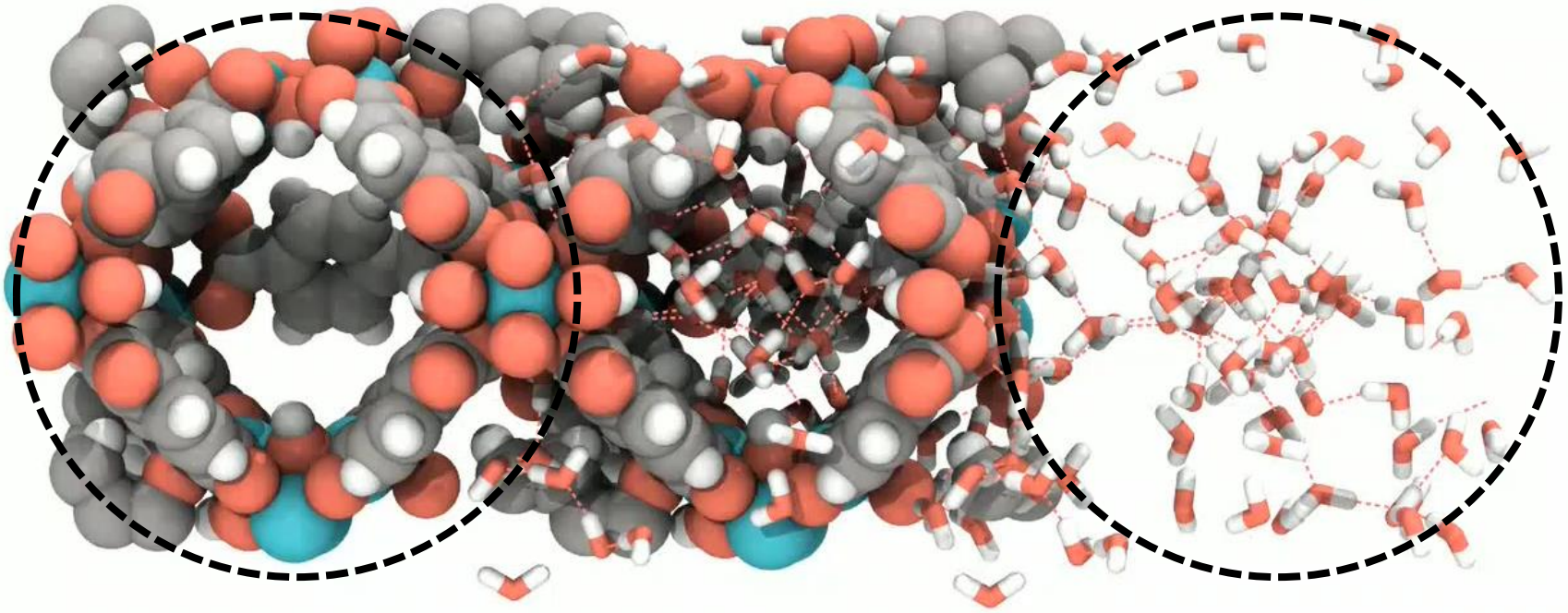




Interaction between material and solvent

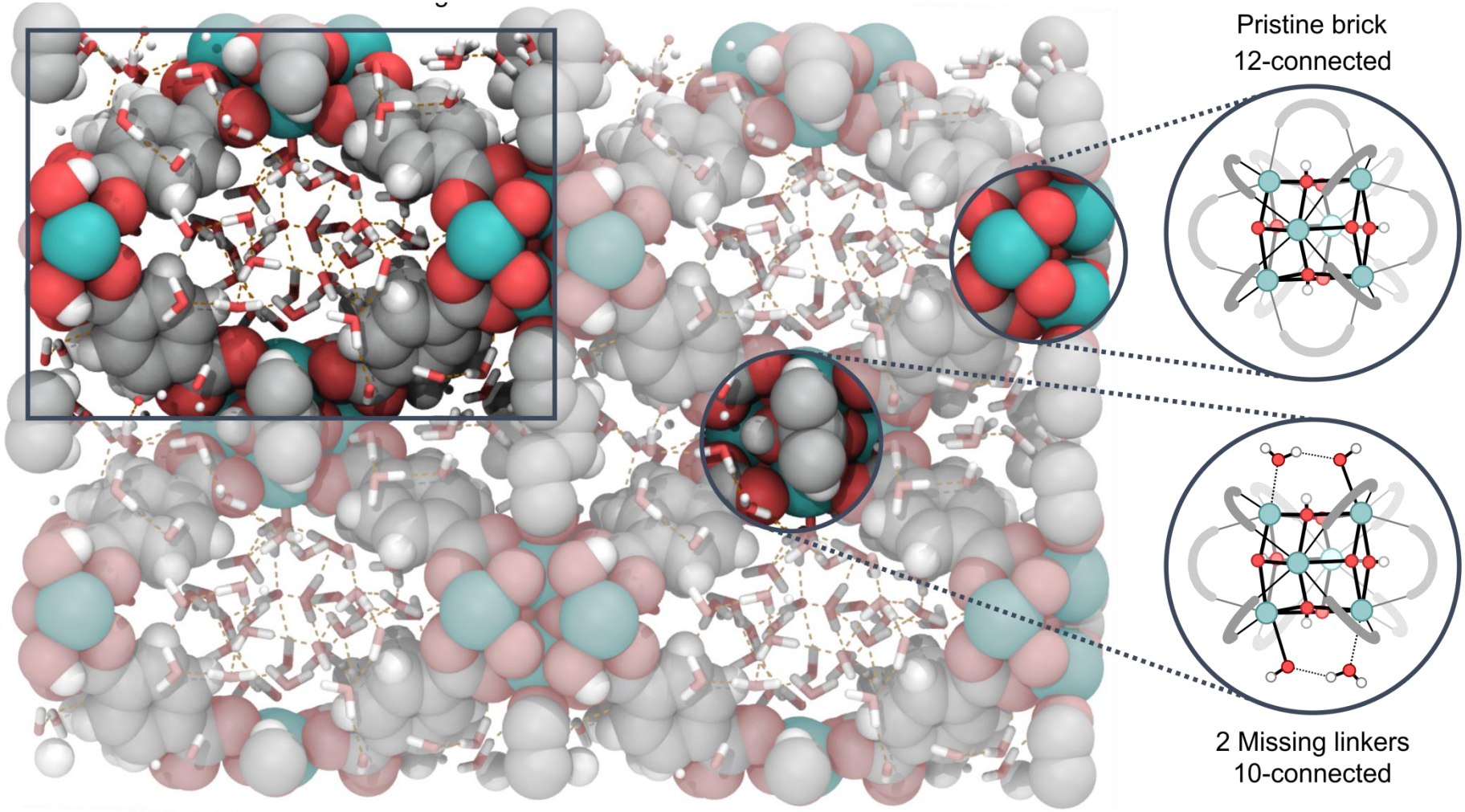
Job type 3
Dynamic calculations
with extended
time and/or length scale

Ab initio MD simulation, PBE-D3, T = 298 K, p = 1 atm

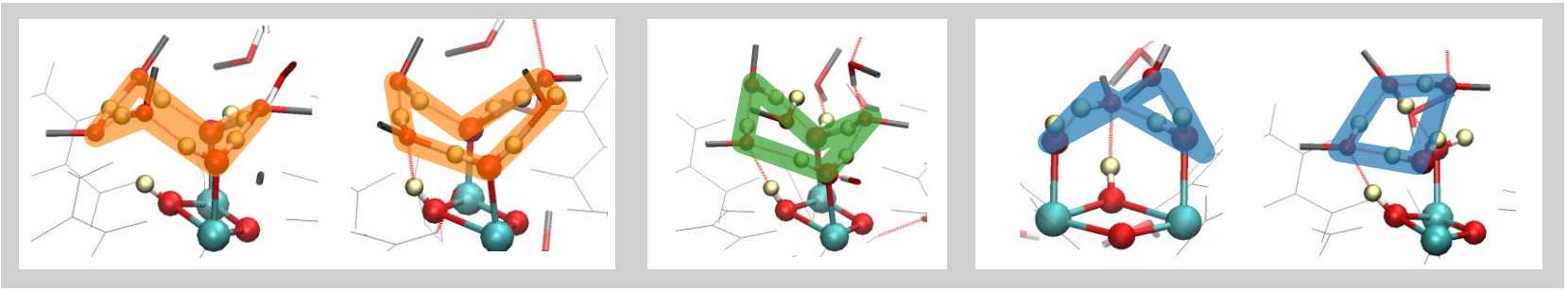


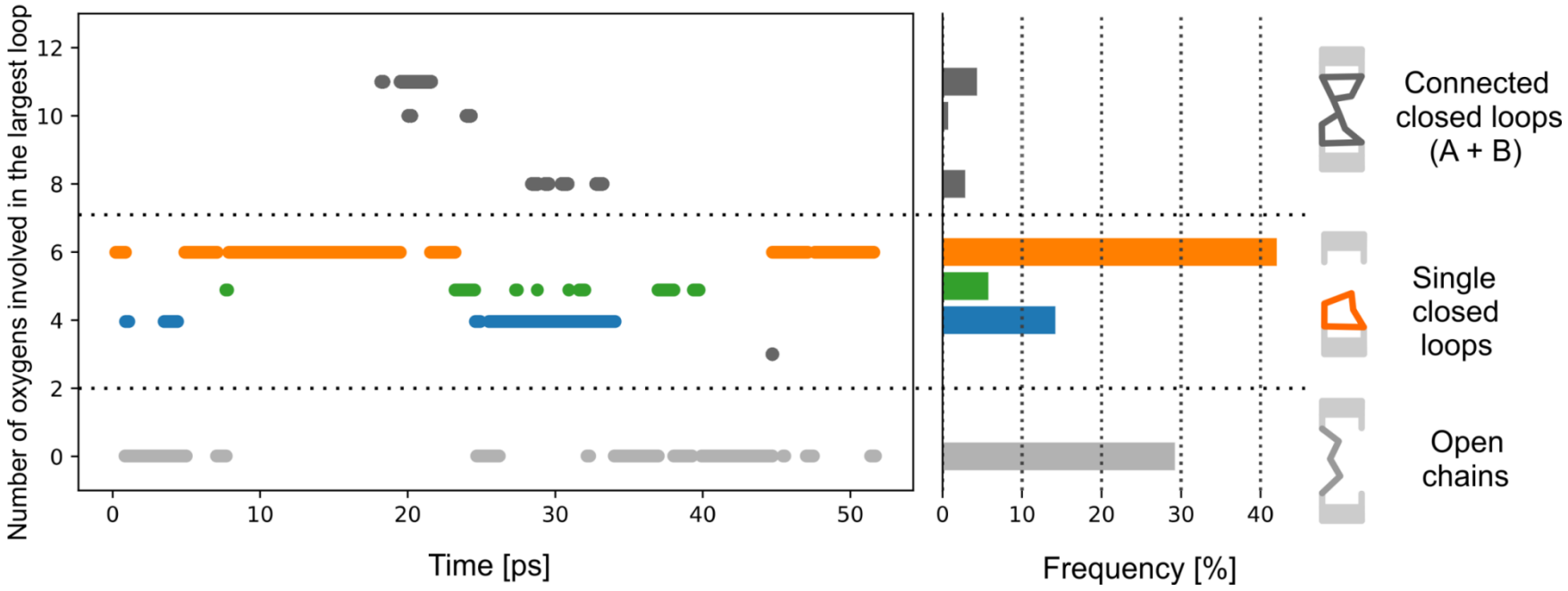
Material | Solvated material | Solvent

Interaction between material and solvent



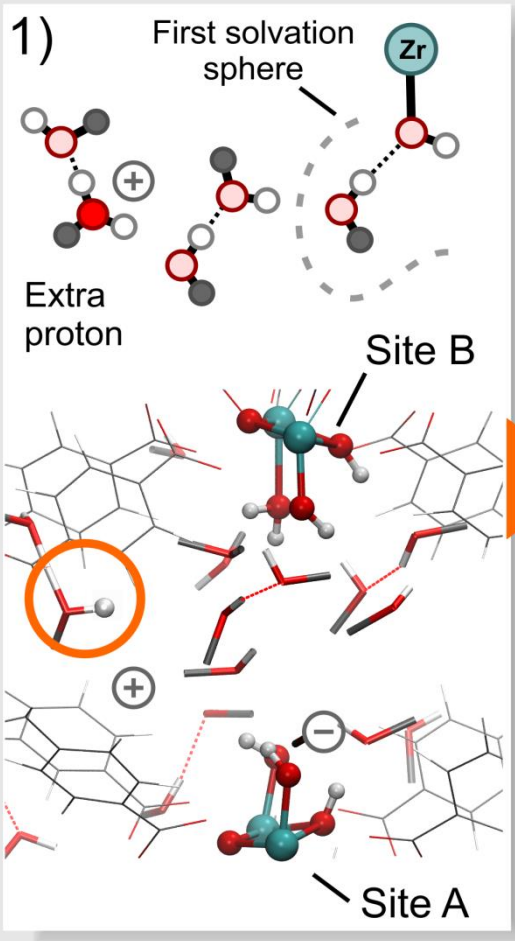
Hydrogen bond configuration





C. Caratelli *et al.*, *ChemPhysChem*, **2017**

Proton transport in solvent

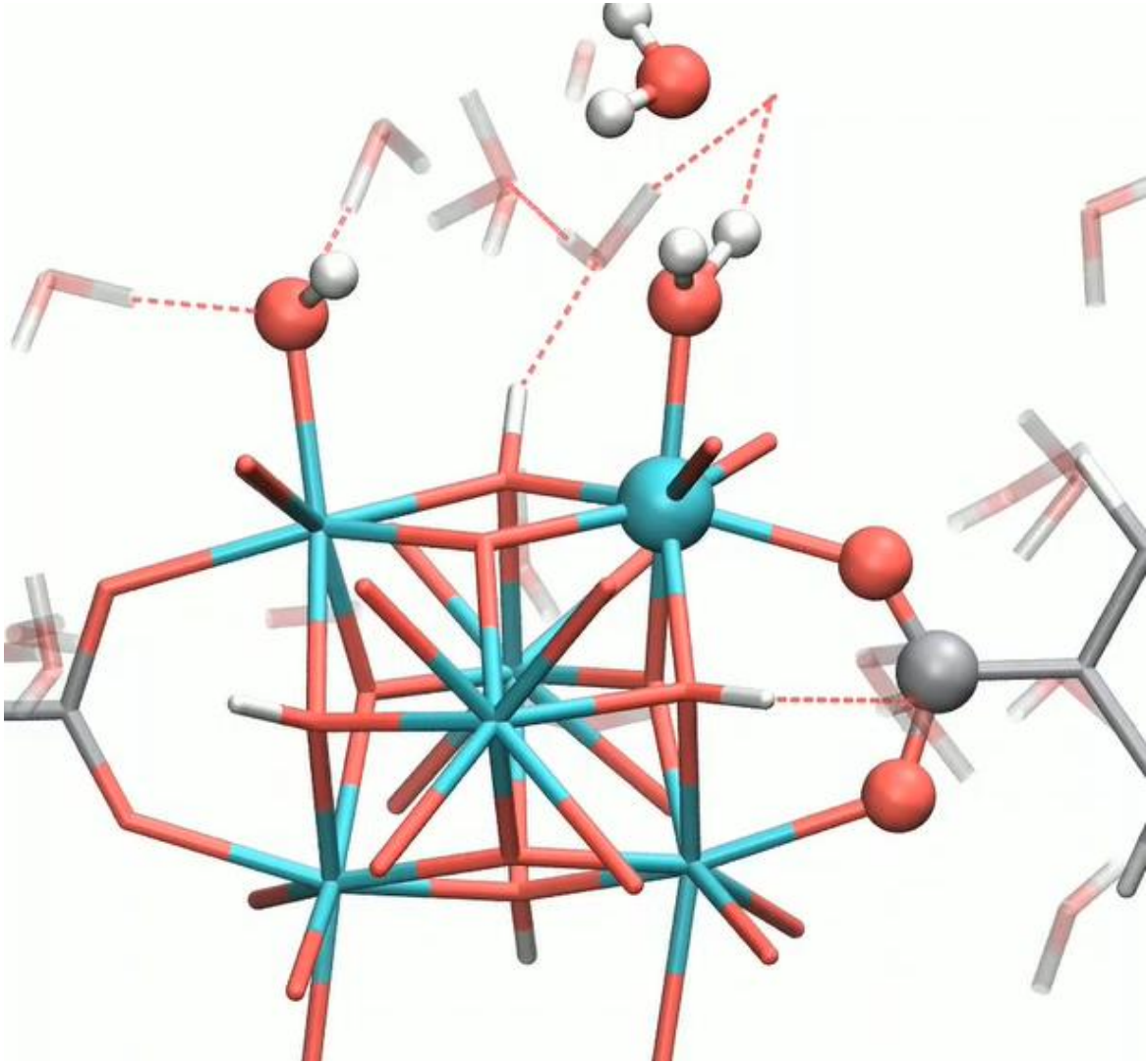


C. Caratelli *et al.*, *ChemPhysChem*, **2017**

Advanced MD: metadynamics

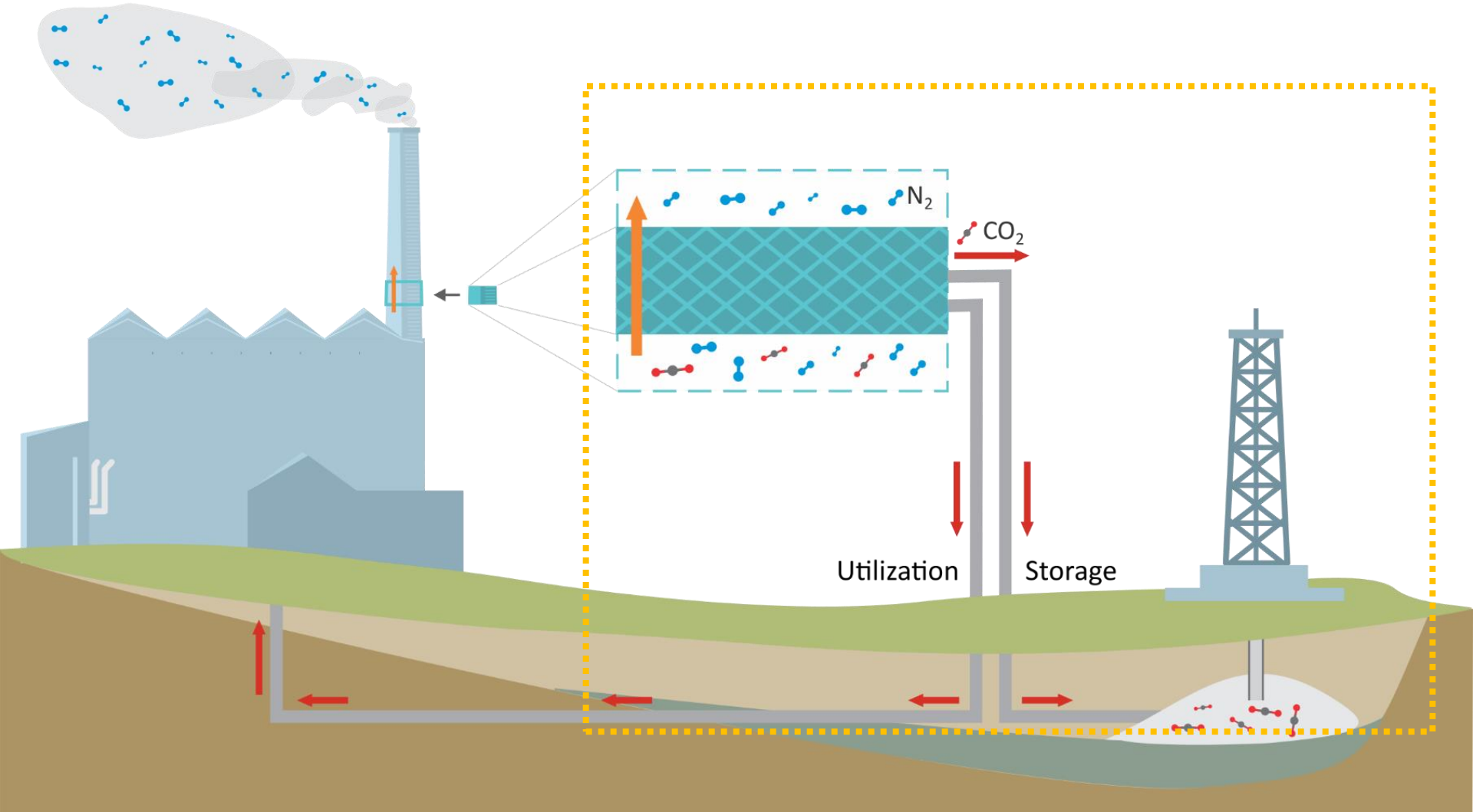
Metadynamics
T = 298 K, p = 1 atm
CP2K

$$CV = \sum_{i=1}^{n} \frac{1 - \left(\frac{r_i}{r_0}\right)^n}{1 - \left(\frac{r_i}{r_0}\right)^m}$$



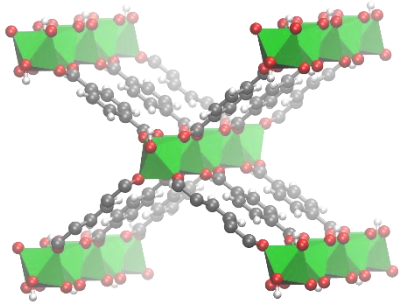
C. Caratelli *et al.*, *Chemical Science, in preparation*

Physical transformations in nanoporous materials



Physical transformations in MOFs: pressure as a stimulus

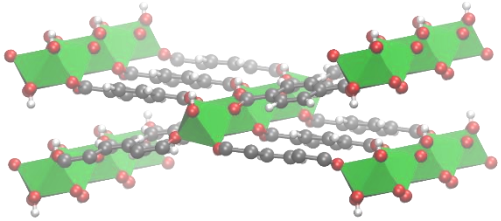
Large pore (LP)

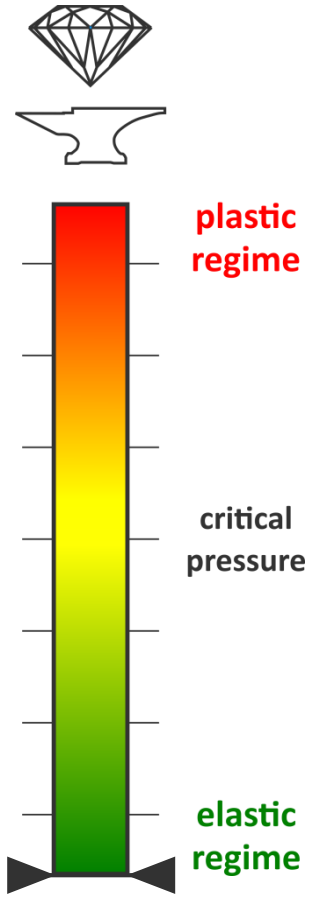


pressure ⟶

⟵ temperature

Closed pore (CP)



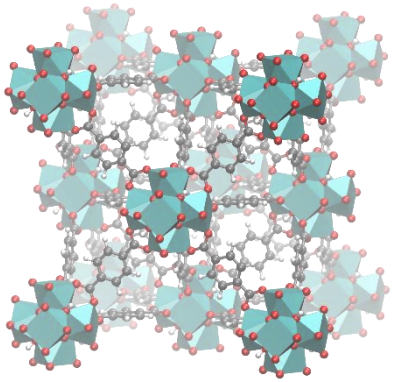


Flexible MOFs, such as MIL-53(Al), undergo single-crystal-to-single-crystal phase transitions already at low pressures (< 100 MPa)

S.M.J. Rogge *et al.*, *Acc. Chem. Res.* **51** (1): 138-148, **2018**

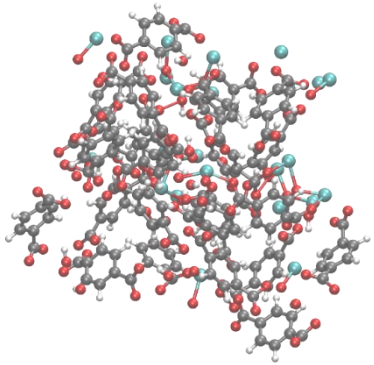
Physical transformations in MOFs: pressure as a stimulus

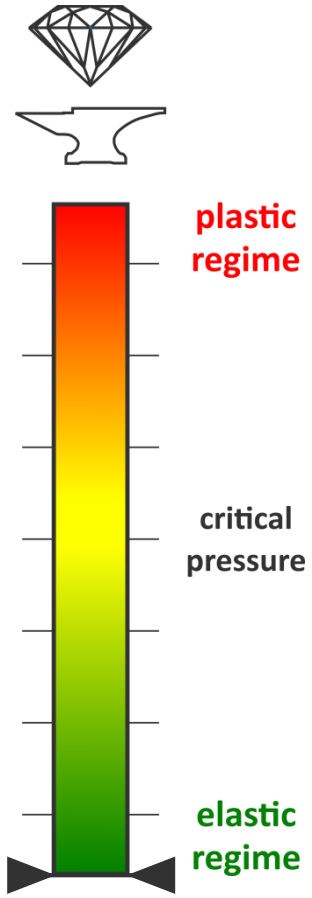
Crystalline



pressure →

Amorphous



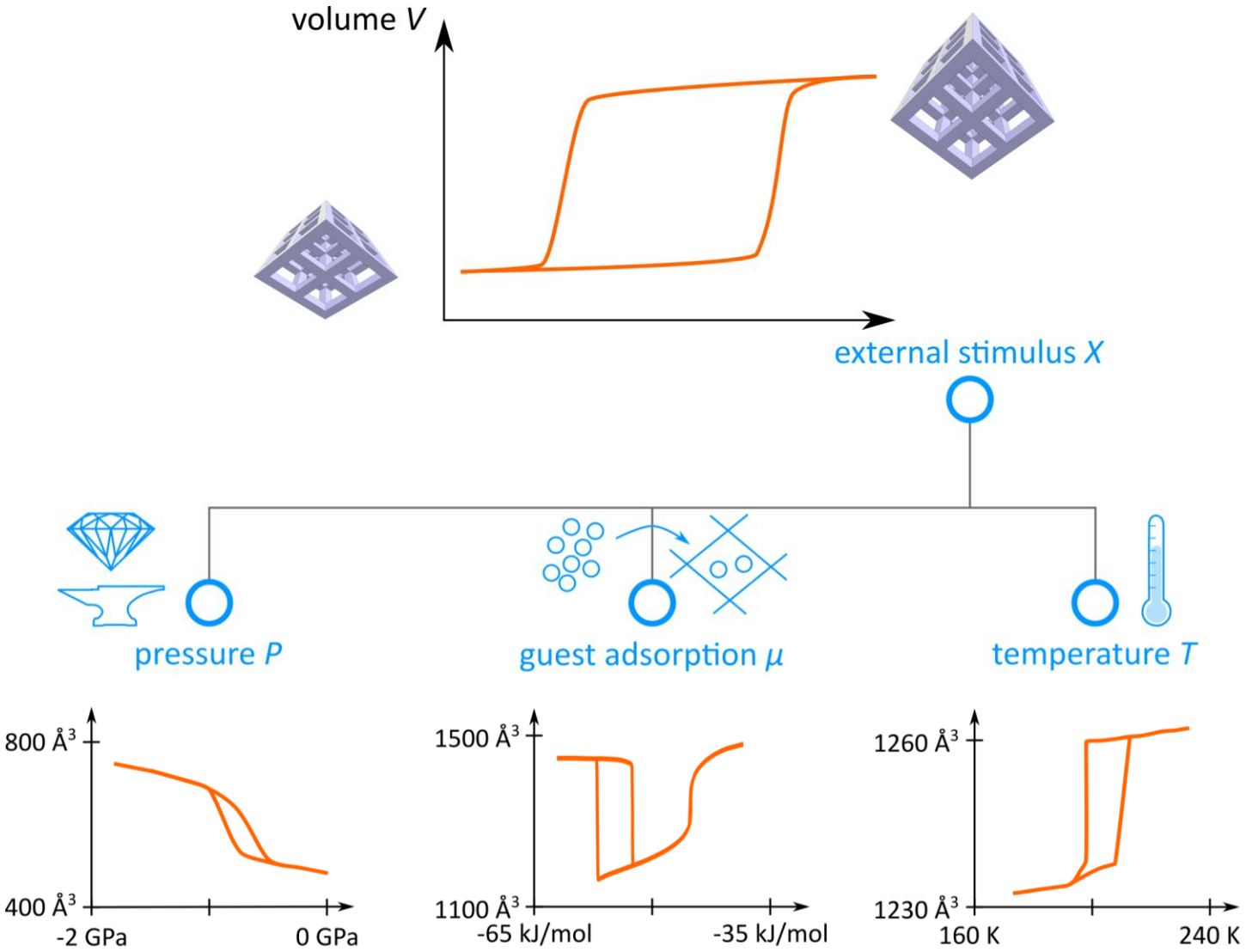


Rigid MOFs, such as UiO-66(Zr), undergo single-crystal-to-amorphous transitions only at elevated pressures (> 100 MPa)

S.M.J. Rogge *et al.*, *Acc. Chem. Res.* **51** (1): 138-148, **2018**

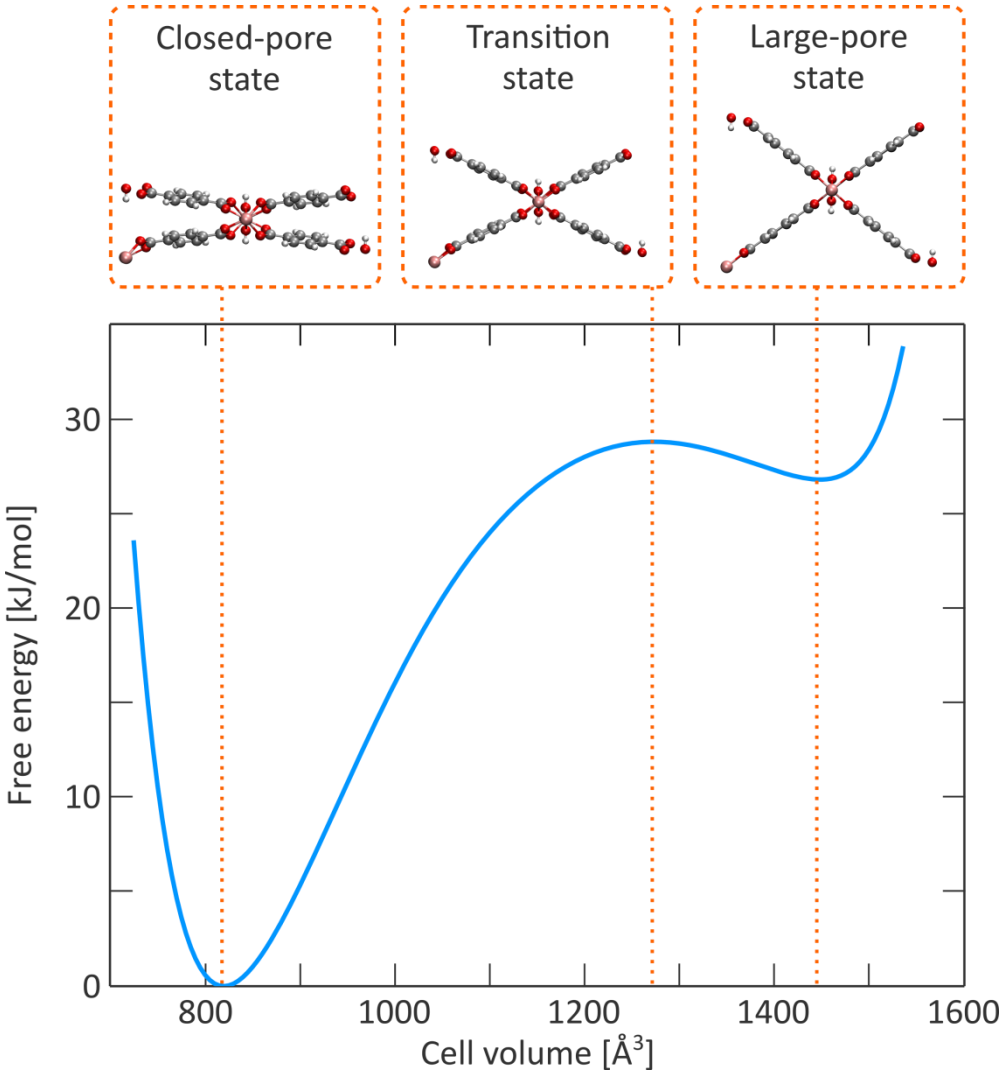
Physical transformations in MOFs: other stimuli

Experimental investigation of flexibility



L. Vanduyfhuys *et al.*, *Nat. Commun.* **9**: 204, **2018**

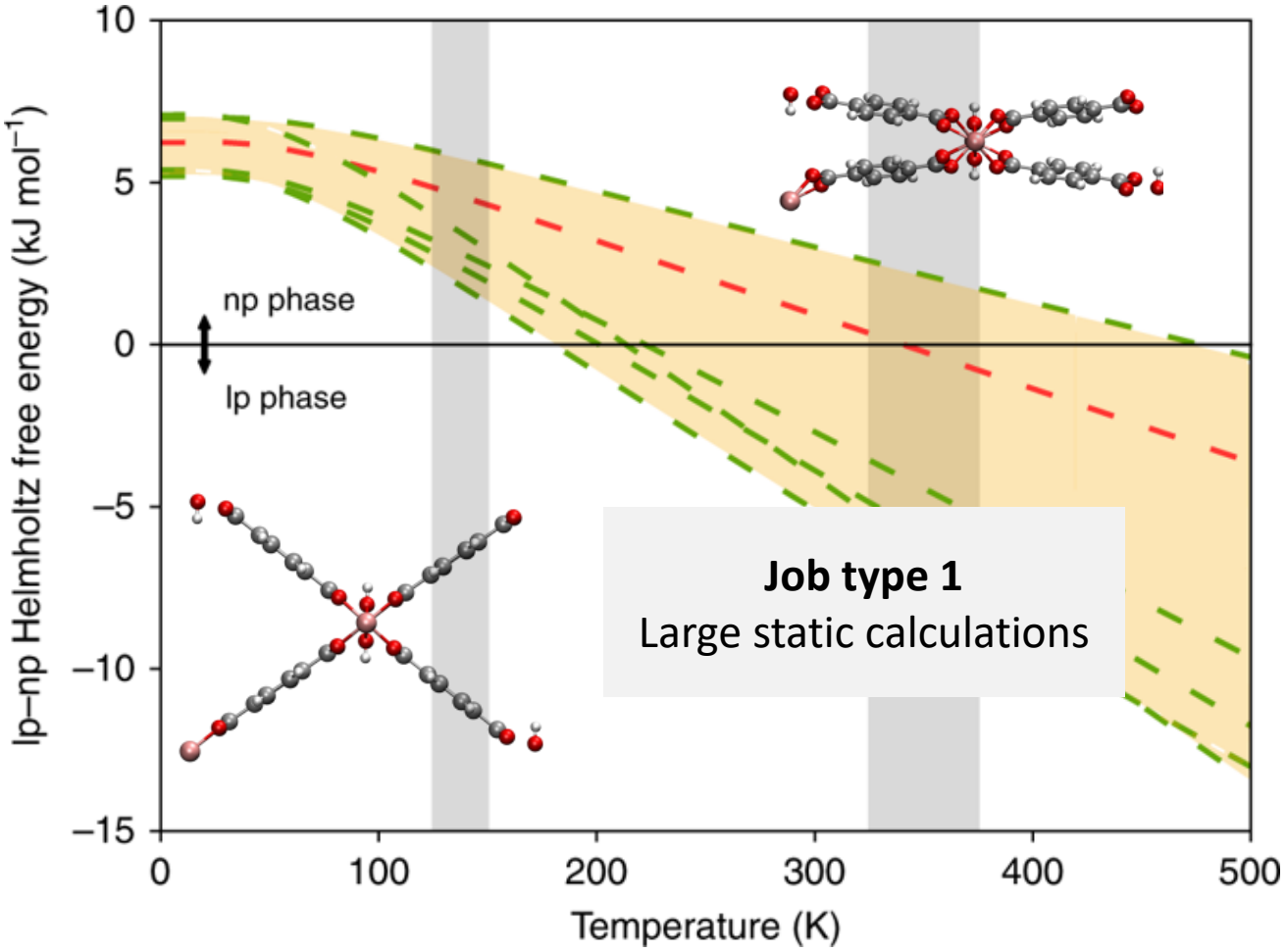
Physical transformations in MOFs are activated processes, requiring enhanced sampling methods



R. Demuynck *et al.*, *J. Chem. Theory Comput.* **13** (12): 5861-5873, **2017**

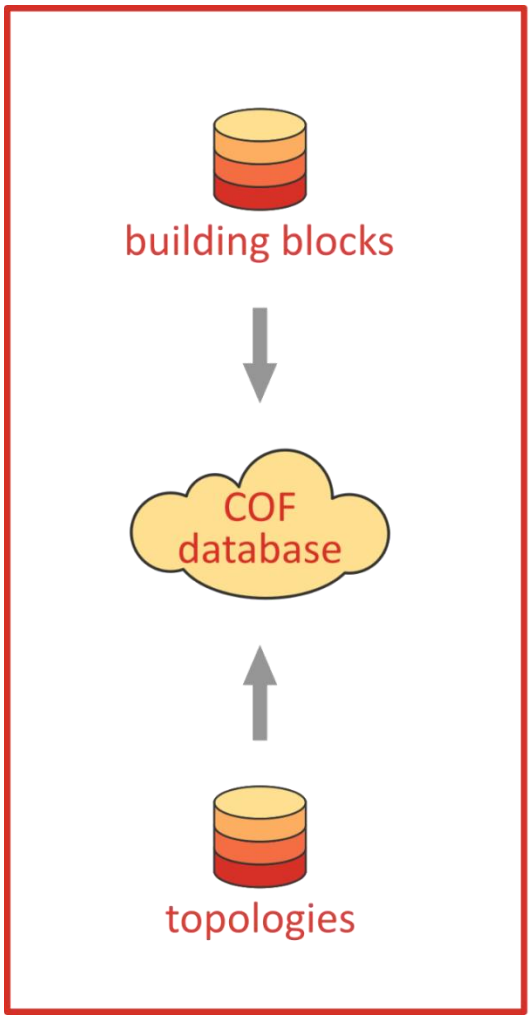
A proper description of the PES is crucial to obtain quantitative results

Random phase approximation (RPA) to the correlation energy
to quantitatively predict the transition temperature in MIL-53(Al)



J. Wieme *et al.*, *Nat. Commun.* **9**: 4899, **2018**

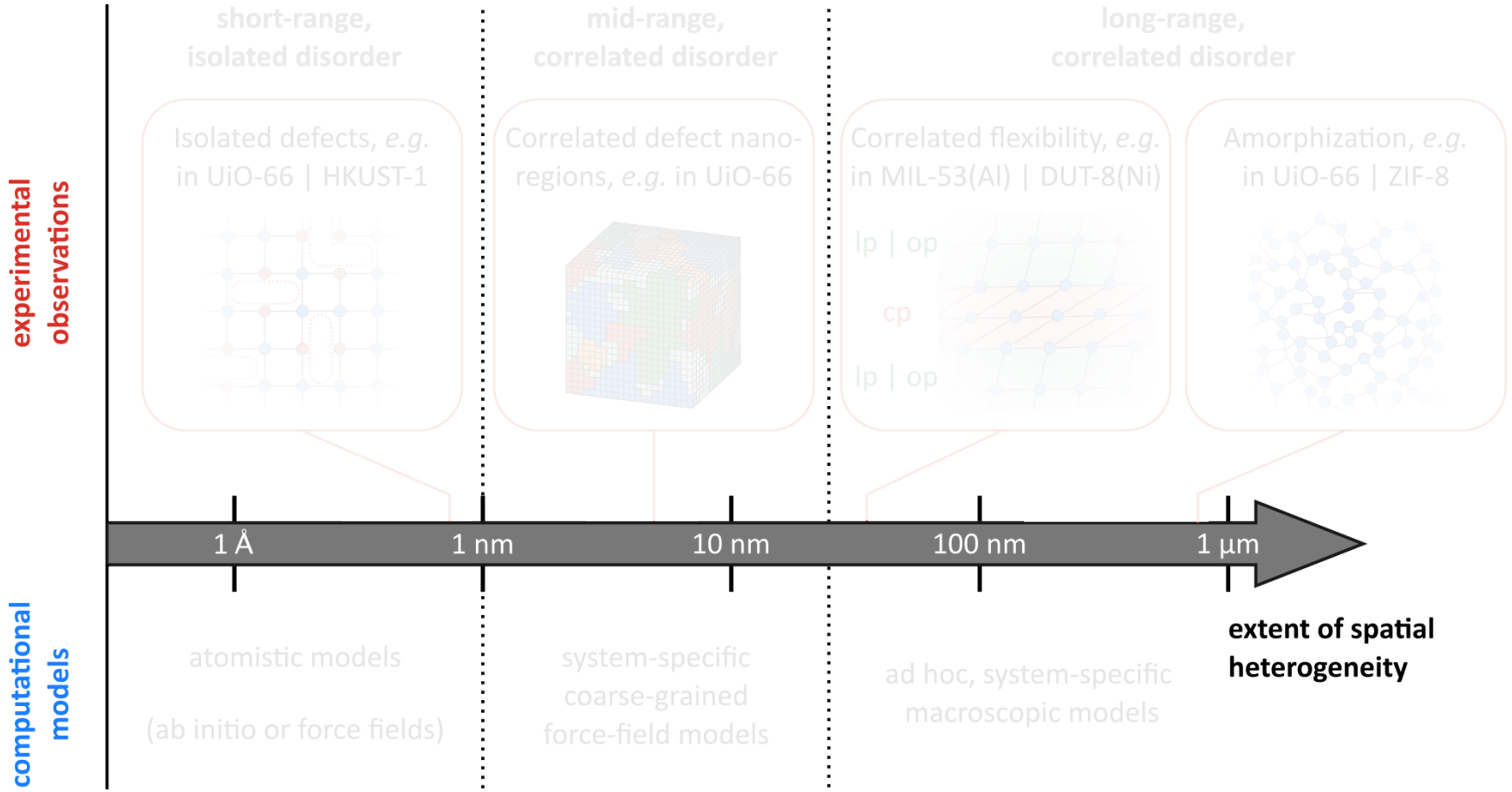
High-throughput screening of MOFs and COFs



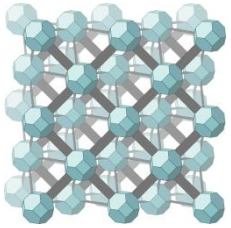
Job type 2
High-throughput calculations

J. De Vos *et al.*, *in preparation*

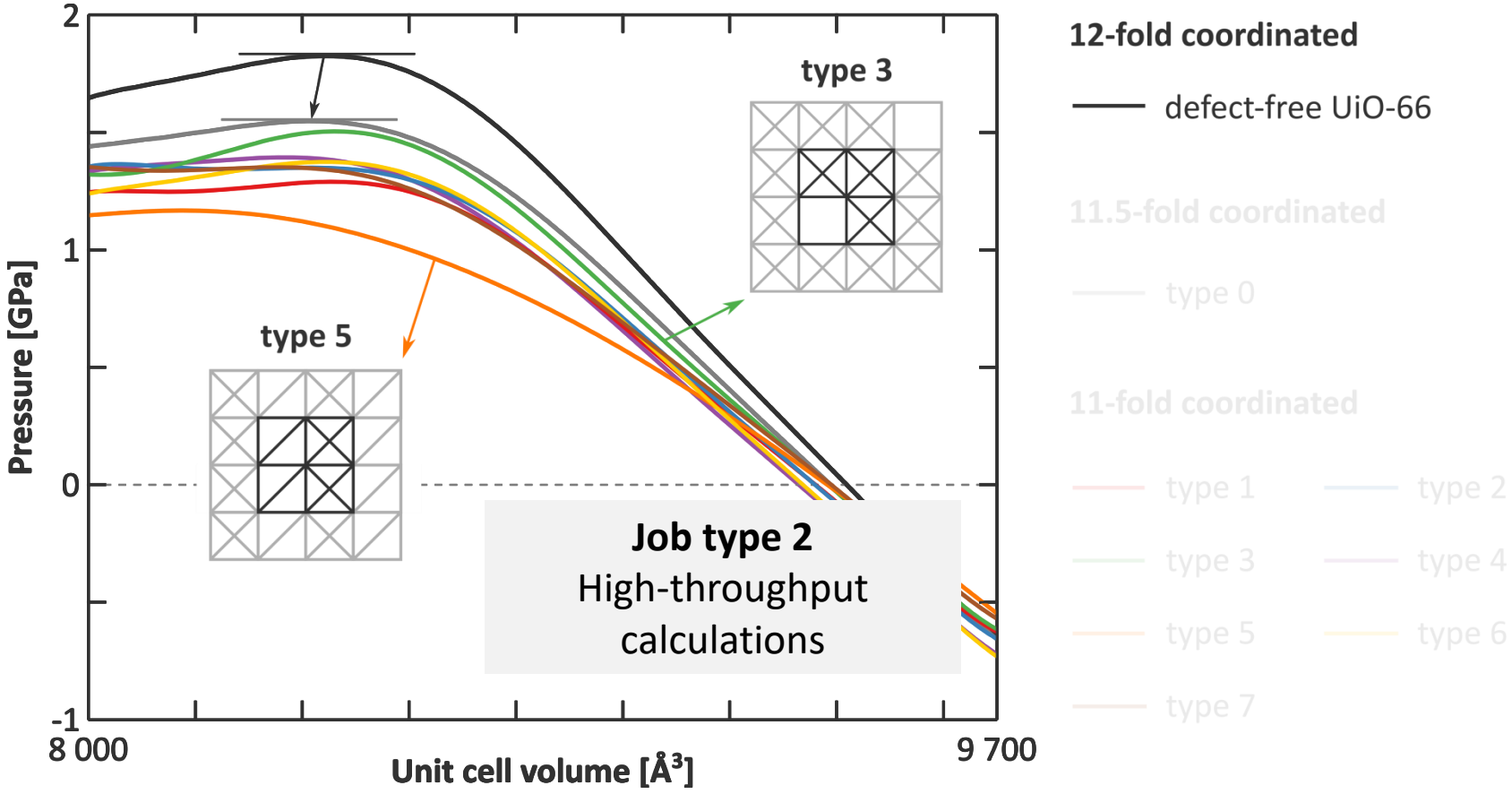
Different types of spatial disorder are inherently present in MOFs



To model the different types of short-range spatial disorder, nanometer-sized unit cells are sufficient



Impact of defects on the mechanical stability of UiO-66(Zr)



S.M.J. Rogge *et al.*, *Chem. Mater.* **28** (16): 5721-5732, **2016**

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Dr. Julianna Hajek

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Thank you for your attention!

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