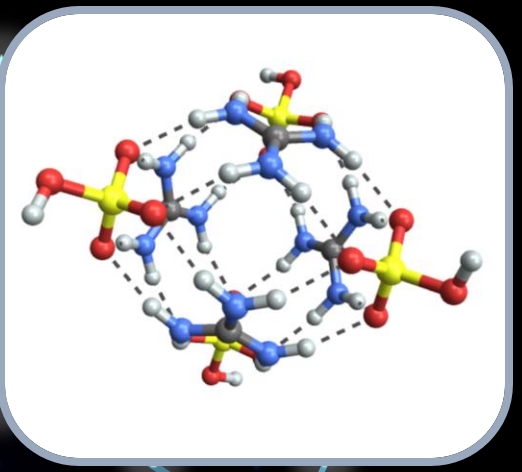
Quantum Chemical Modelling of Atmospheric Molecular Clusters



Enhanced by Machine Learning

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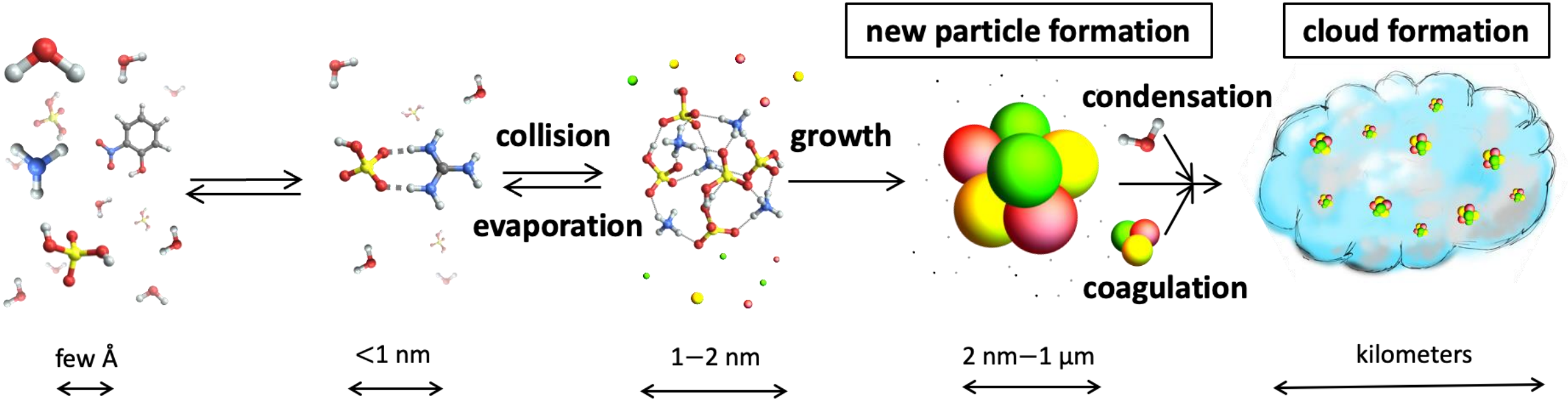
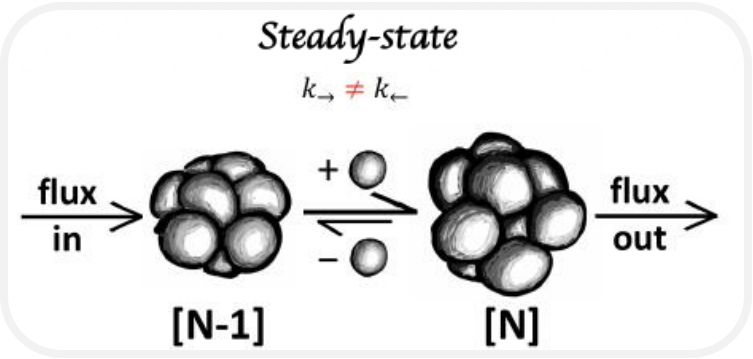
Denmark DK

New Particle Formation (NPF)

- **Aerosols - tiny particles dispersed in the air**
  - source of uncertainty in climate modelling [IPCC report 2021]
  - **Primary aerosols** (emmited to the atmosphere, e.g. soot, pollen)
  - **Secondary aerosols** (gas-to-particle formation = NPF)



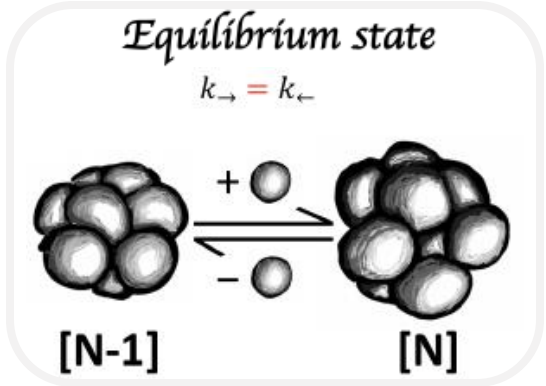
How do we model NPF?

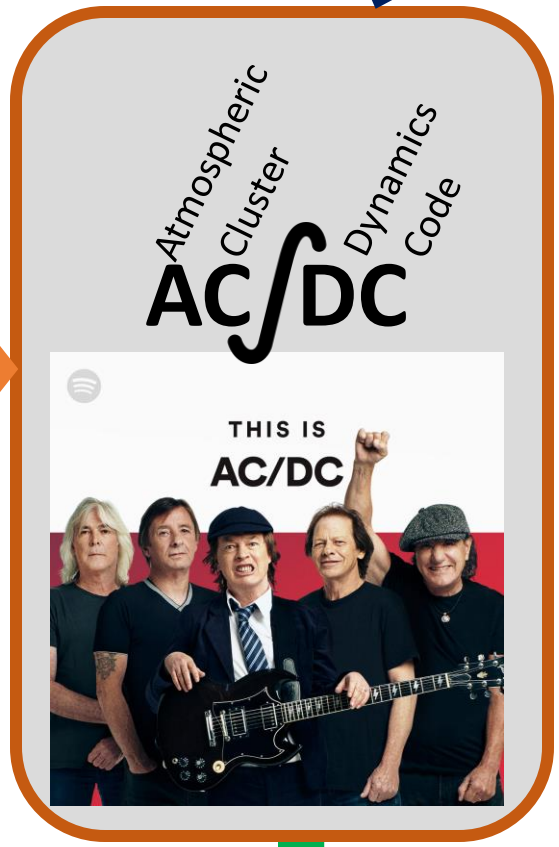


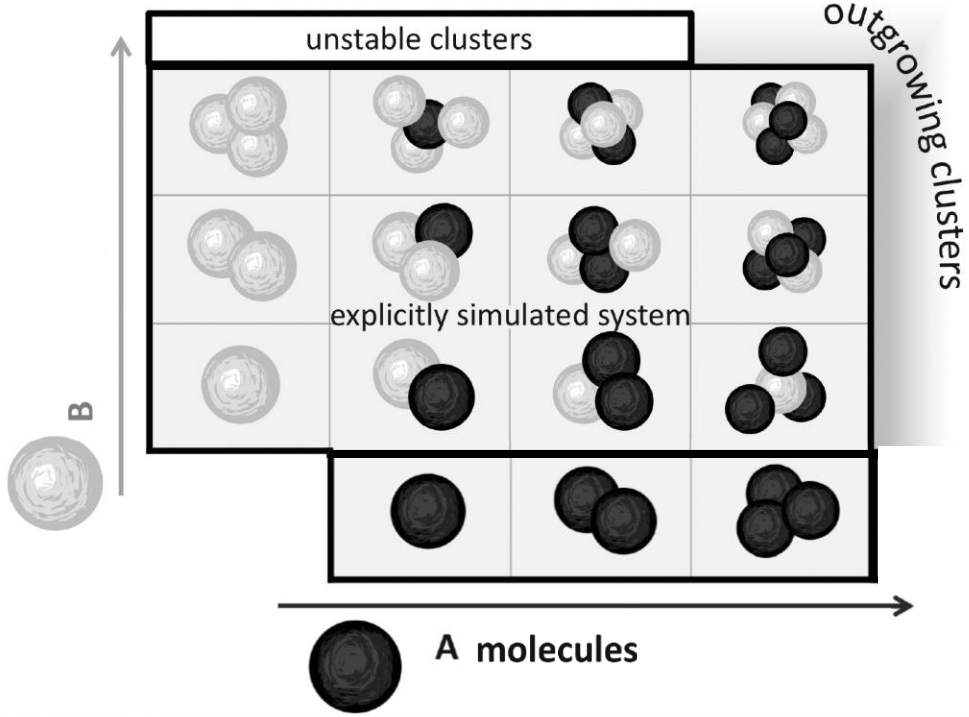
$k_{\rightarrow} \equiv \beta$: collision rate
(from kinetic gas theory)

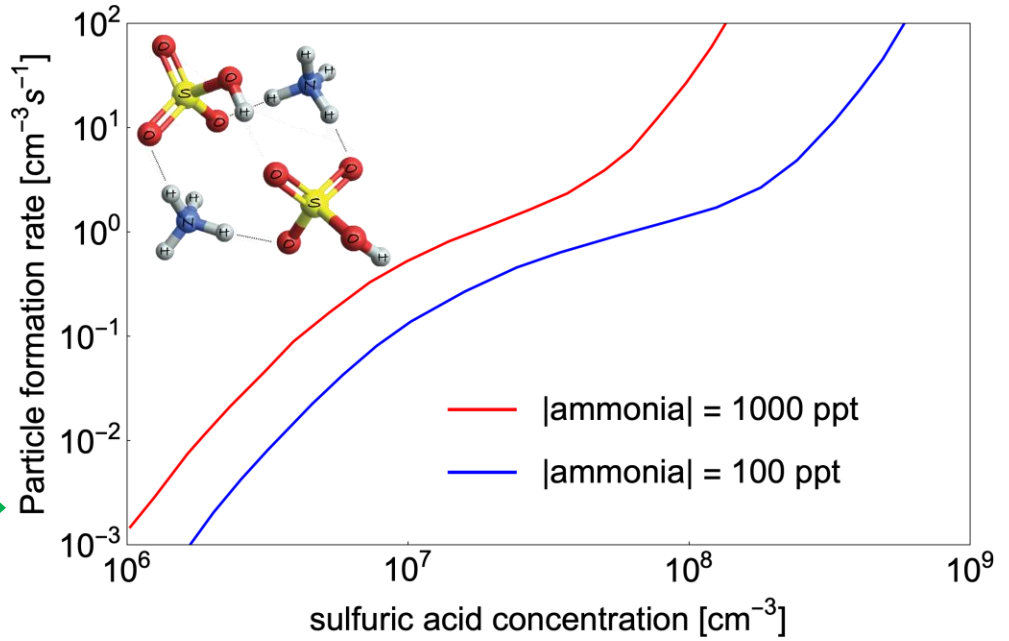
$k_{\leftarrow} \equiv \gamma$: evaporation rate
(from stat. thermodynamics)

$$\gamma = \beta \cdot p \cdot e^{-\Delta G/kT}$$







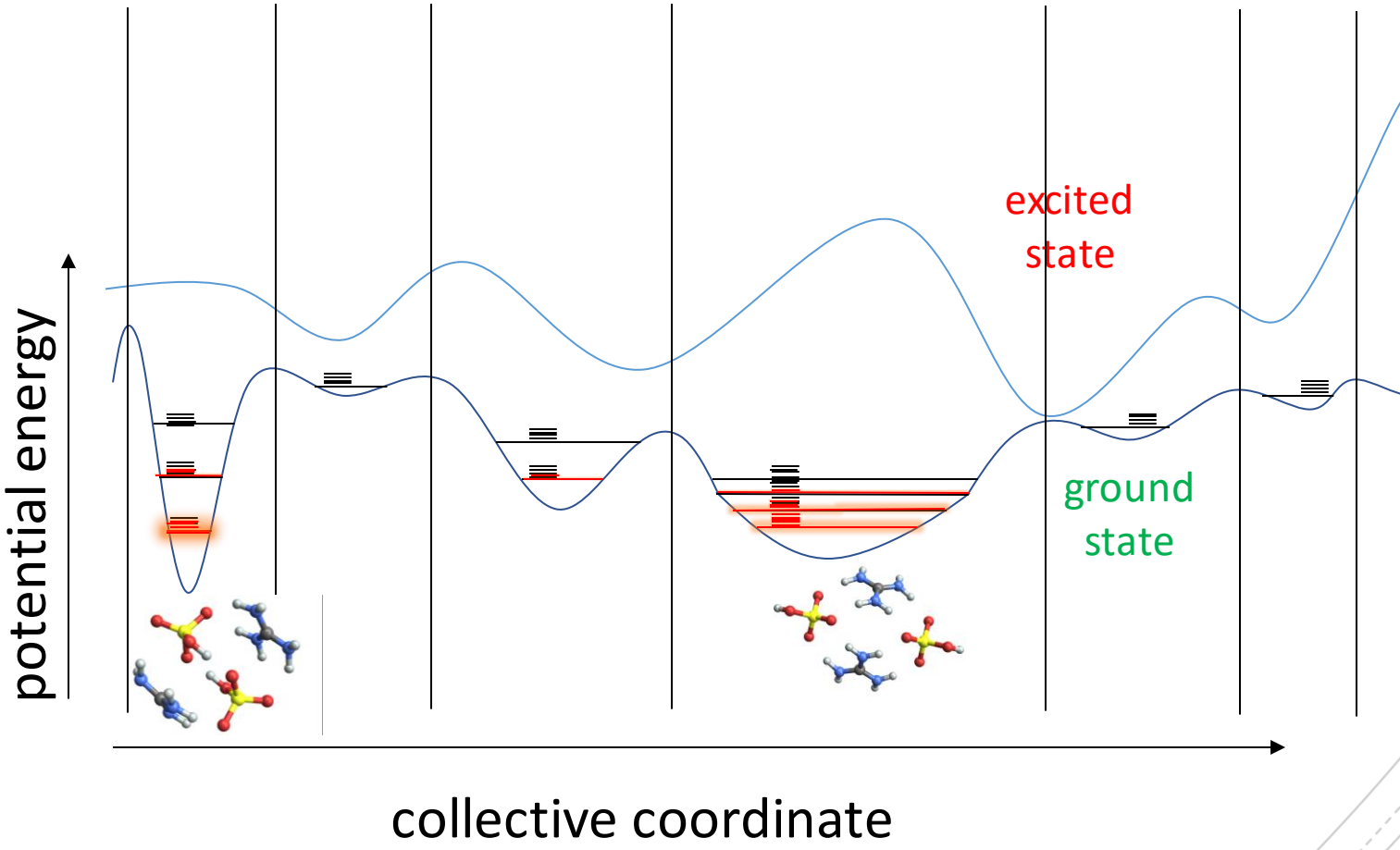


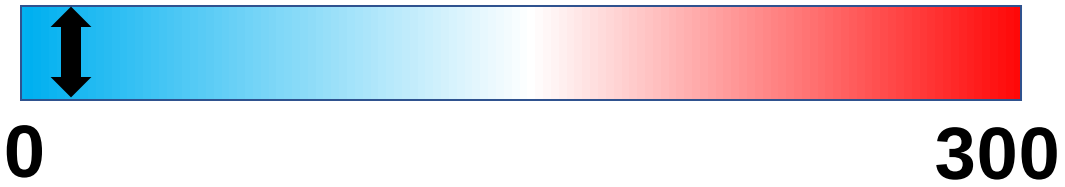
Configurational sampling

[Kubečka *et al.*, JPC, 2018]

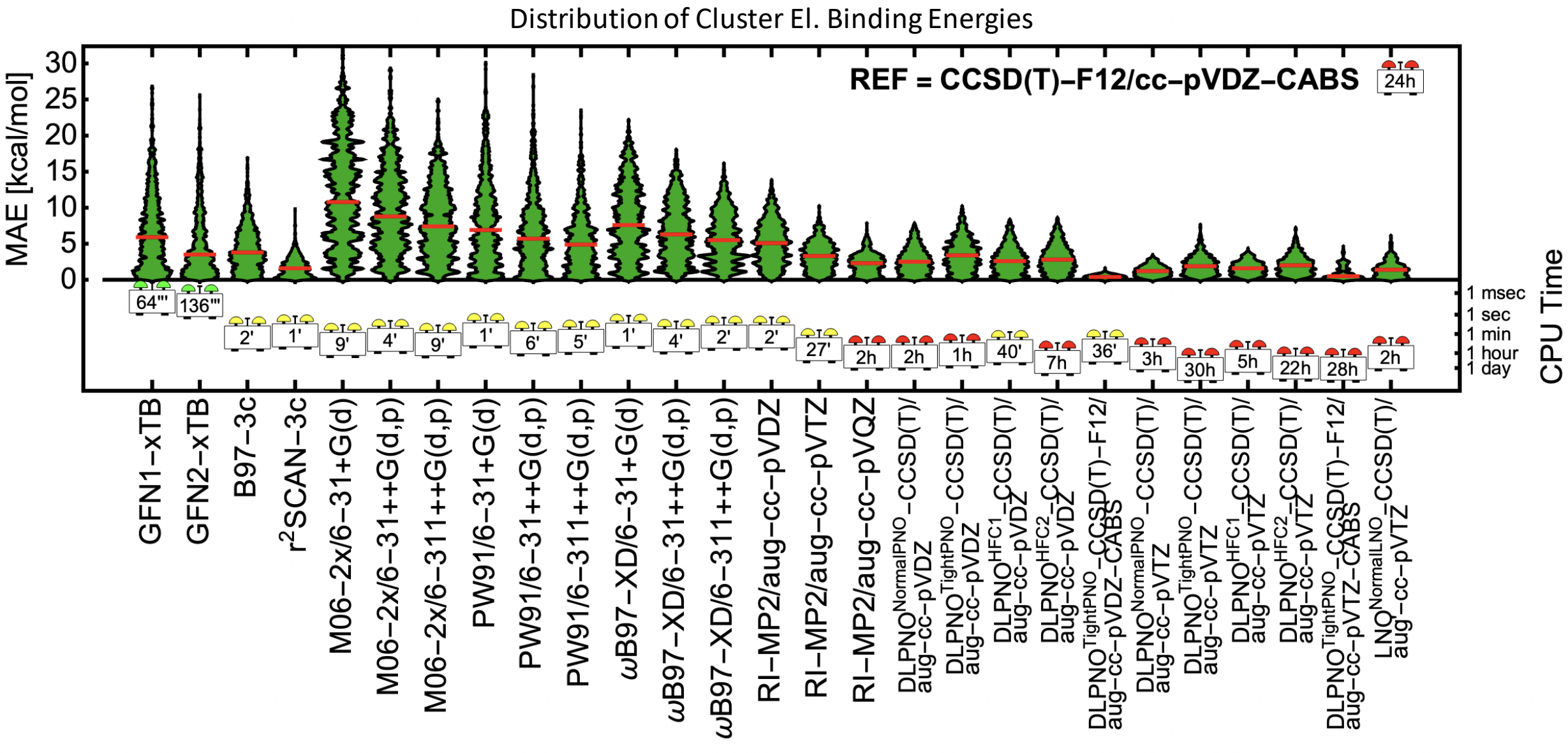
Computational Tools for Molecular Clusters

[Kubečka *et al.*, ACS Ω, 2023]





Benchmarking methods

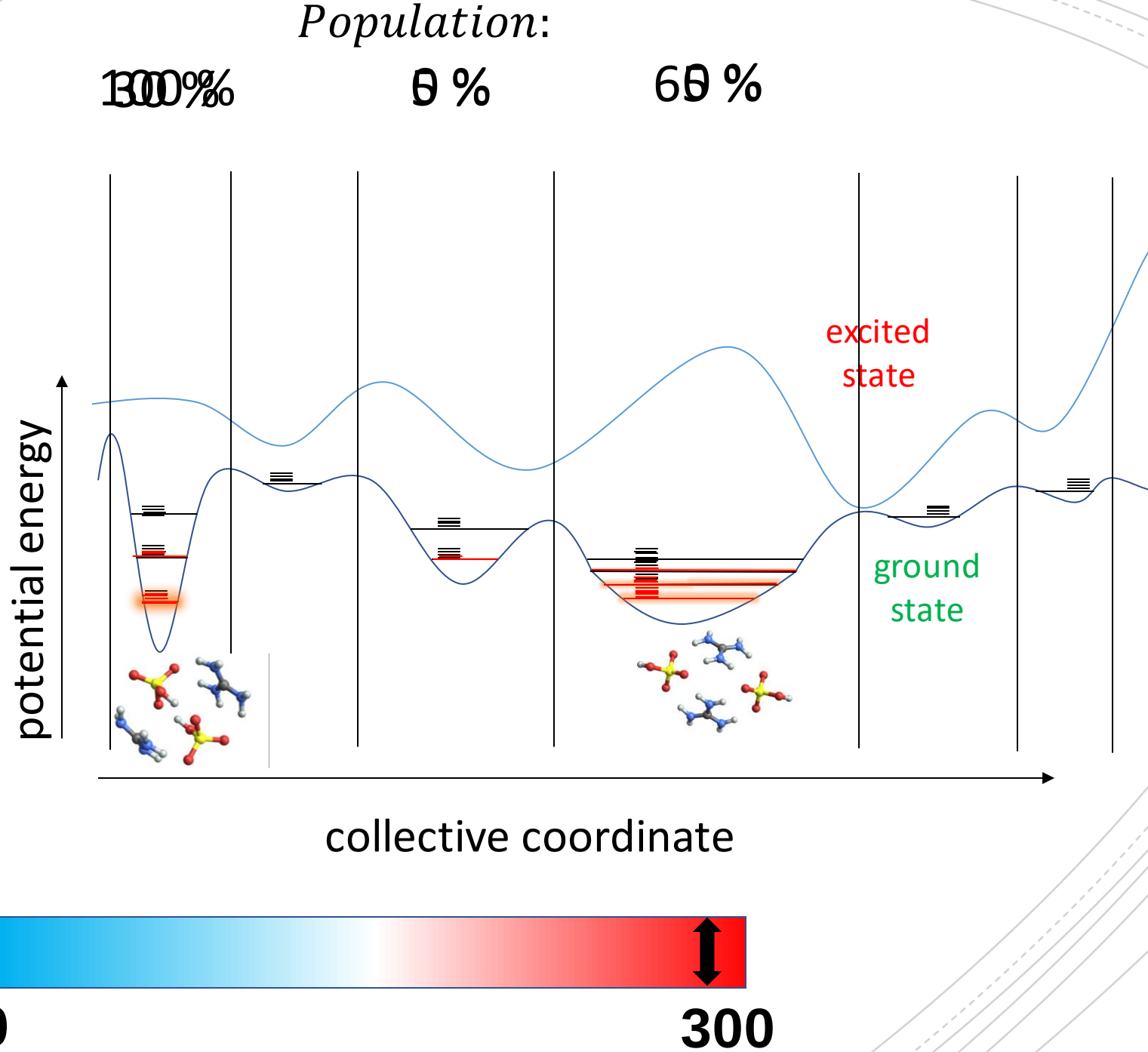


Configurational sampling

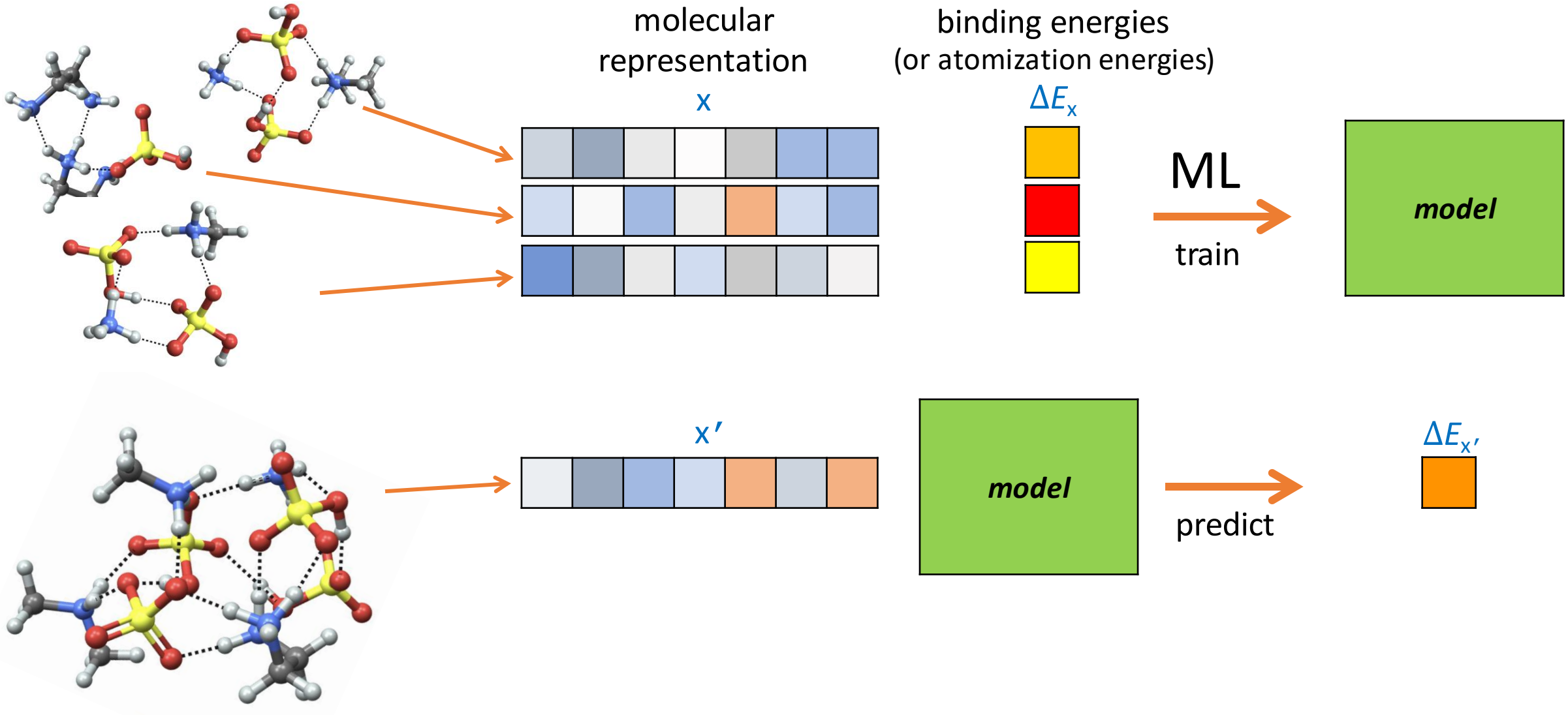
[Kubečka *et al.*, JPC, 2018]

Computational Tools for Molecular Clusters

[Kubečka *et al.*, ACS Ω, 2023]

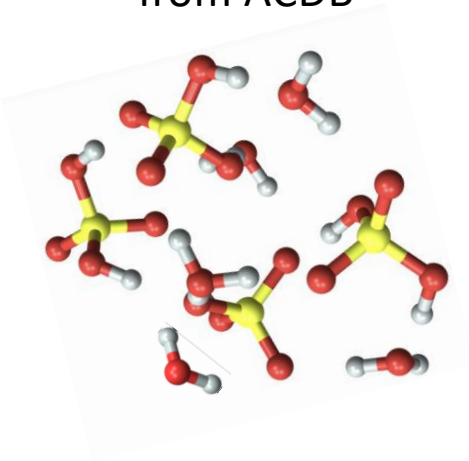


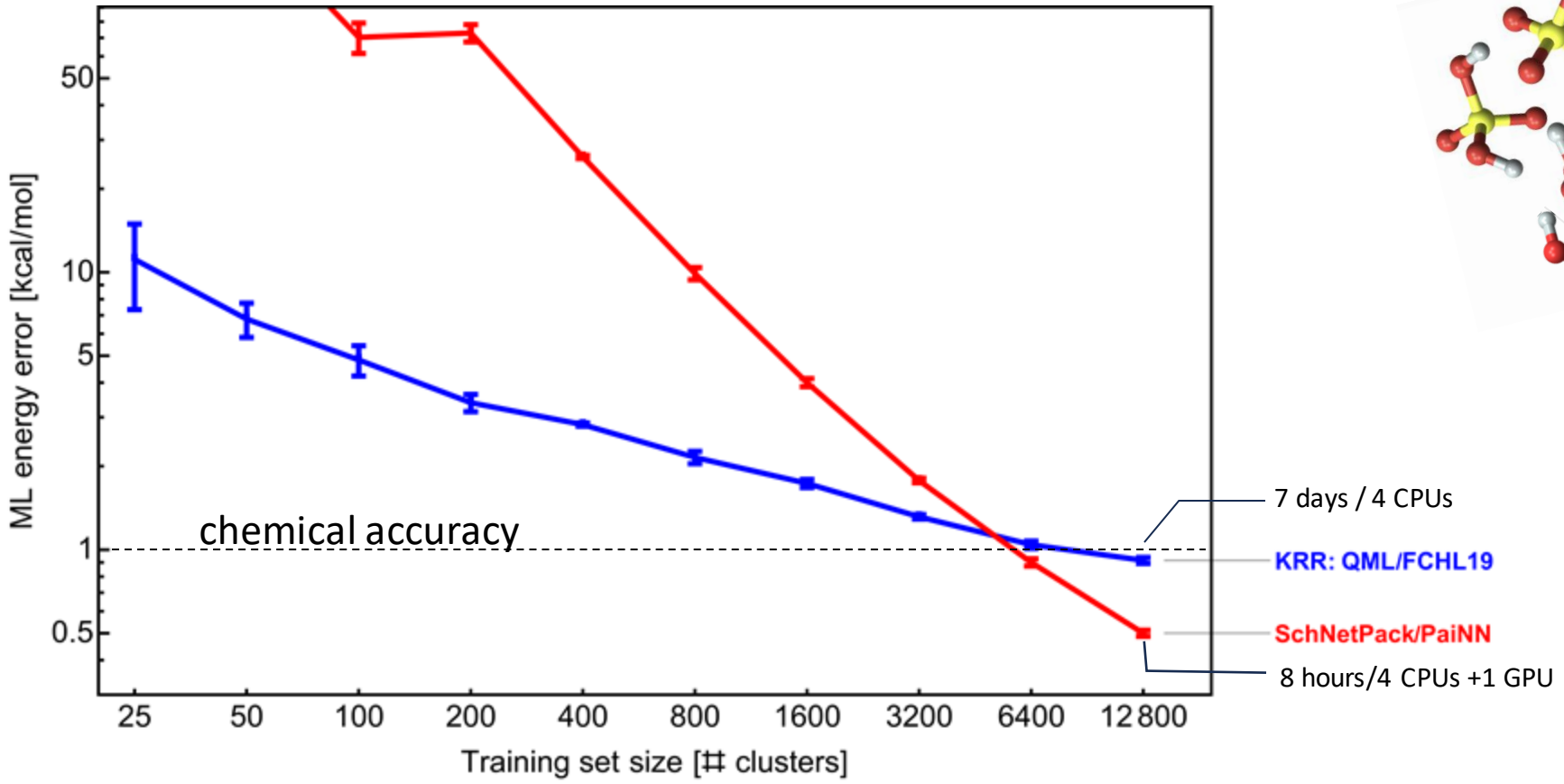
Machine Learning (e.g. GPR, KRR, or NN)



Accuracy of ML methods

Tested on 17k data
of sulfuric acid and water
from ACDB





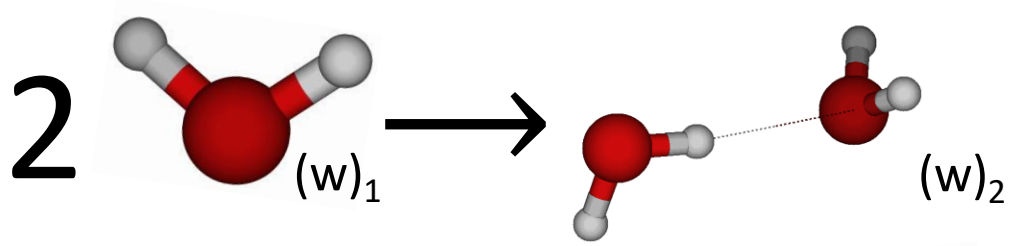
PREDICTION
4000 structures
just 3 min

Are the QC methods themselves accurate?!

DLPNO^{NormalPNO}-CCSD(T)/aug-cc-pVTZ//ωB97X-D/6-31++G(d,p)
+ vibrational anharmonicity scaling factor 0.996
+ low vibrational frequency treatment with cutoff of 100 cm^{-1}
+ monomer rotational symmetry correction
+ multi low-energy minima treatment

Reactional Free Energy

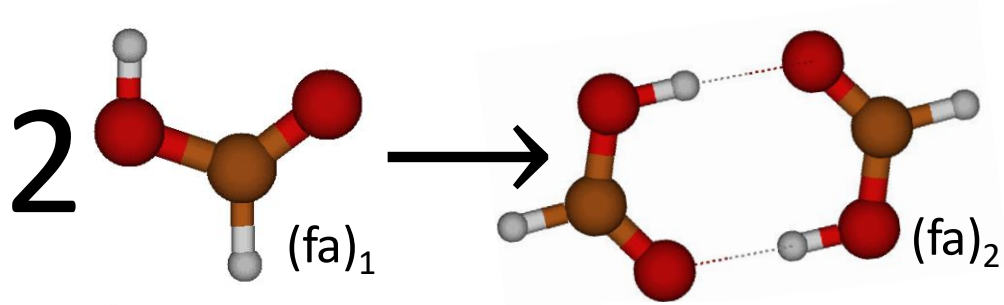
Water dimerization:



THEORY: +**3.19** kcal/mol

EXP: **+3.15** ± 0.12 kcal/mol
[Auwera et al., J.Chem.Phys. (2007)]

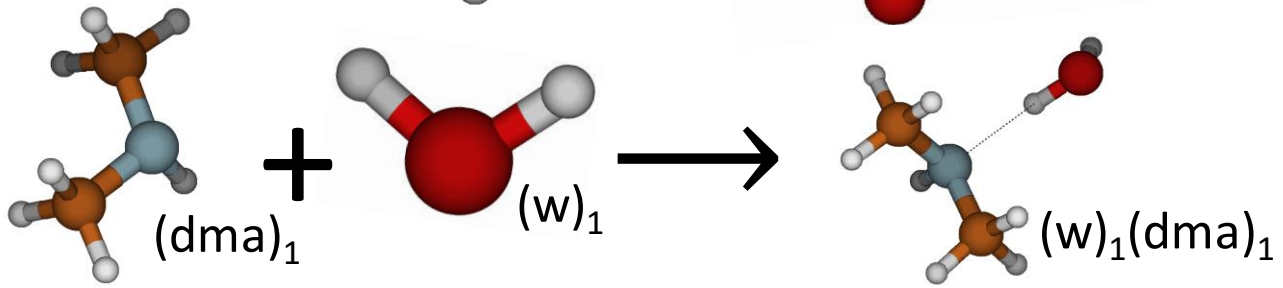
Formic acid dimerization:



THEORY: **−3.33** kcal/mol

EXP: **−3.31** ± 0.04 kcal/mol
[Rocher-Casterline et al., J.Chem.Phys. (2011)]

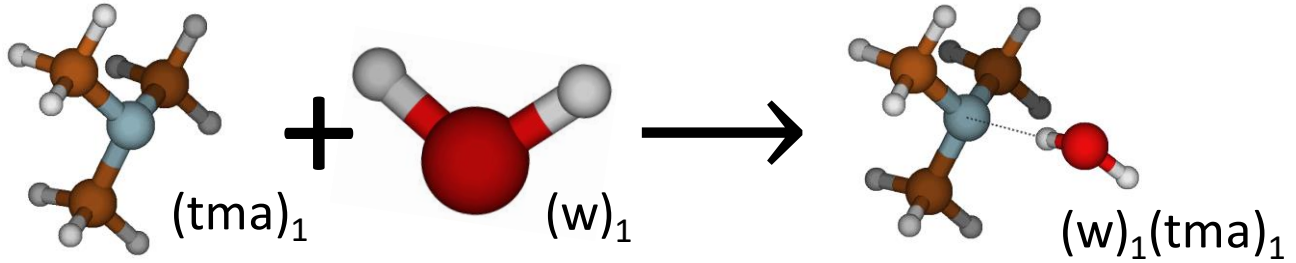
Dimethylamine hydration:



THEORY: +**1.91** kcal/mol

EXP: **+1.19** ± 0.04 kcal/mol
[Kjærsgaard et al., J.Phys.Chem.A (2020)]

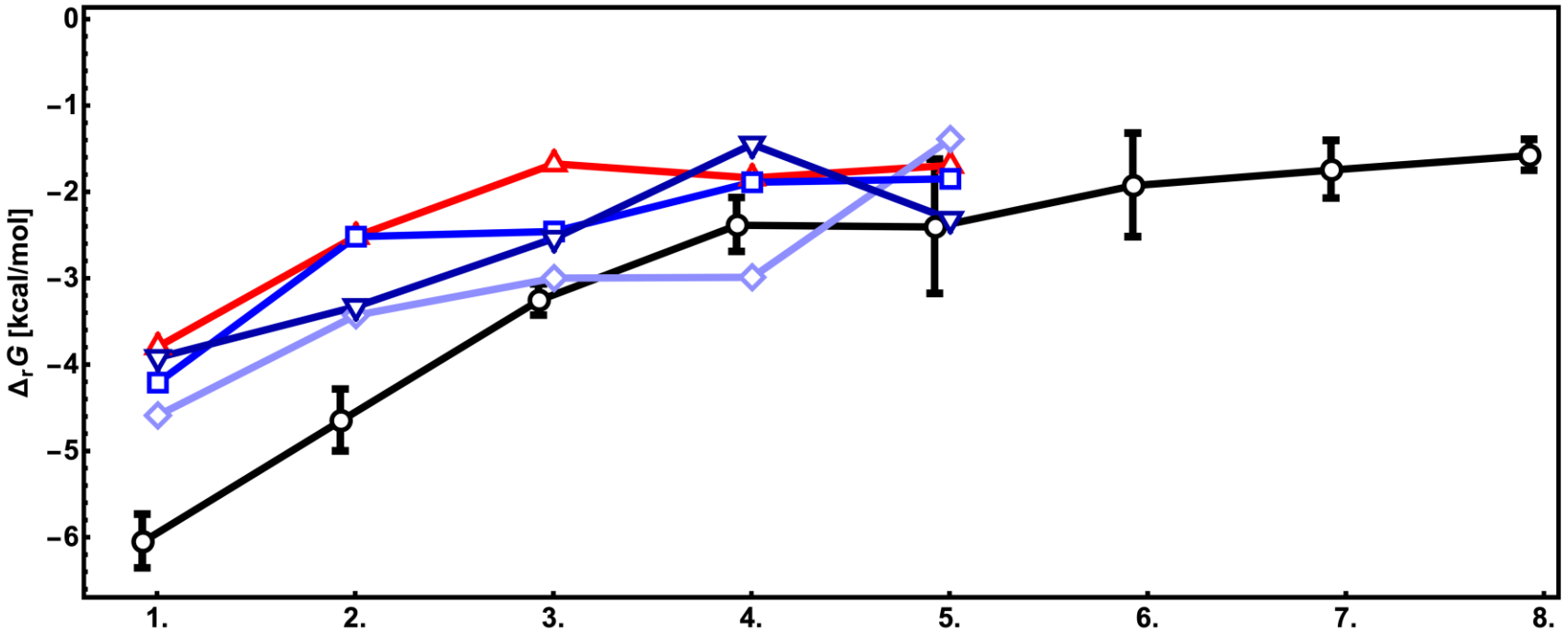
Trimethylamine hydration:



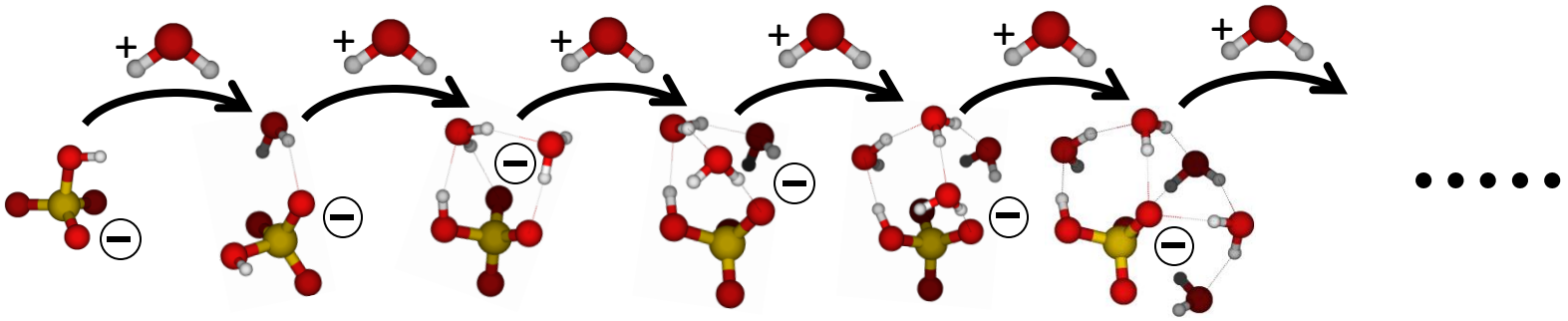
THEORY: +**1.30** kcal/mol

EXP: **+0.91** ± 0.04 kcal/mol
[Kjærsgaard et al., J.Phys.Chem.A (2020)]

Bisulfate hydration



Experiment [Froyed and Lovejoy, *J.Phys.Chem.A* (2003)]



Potential errors in predictions

- ACDC simulation:

  (ACDB data)

100 ppb NH_3

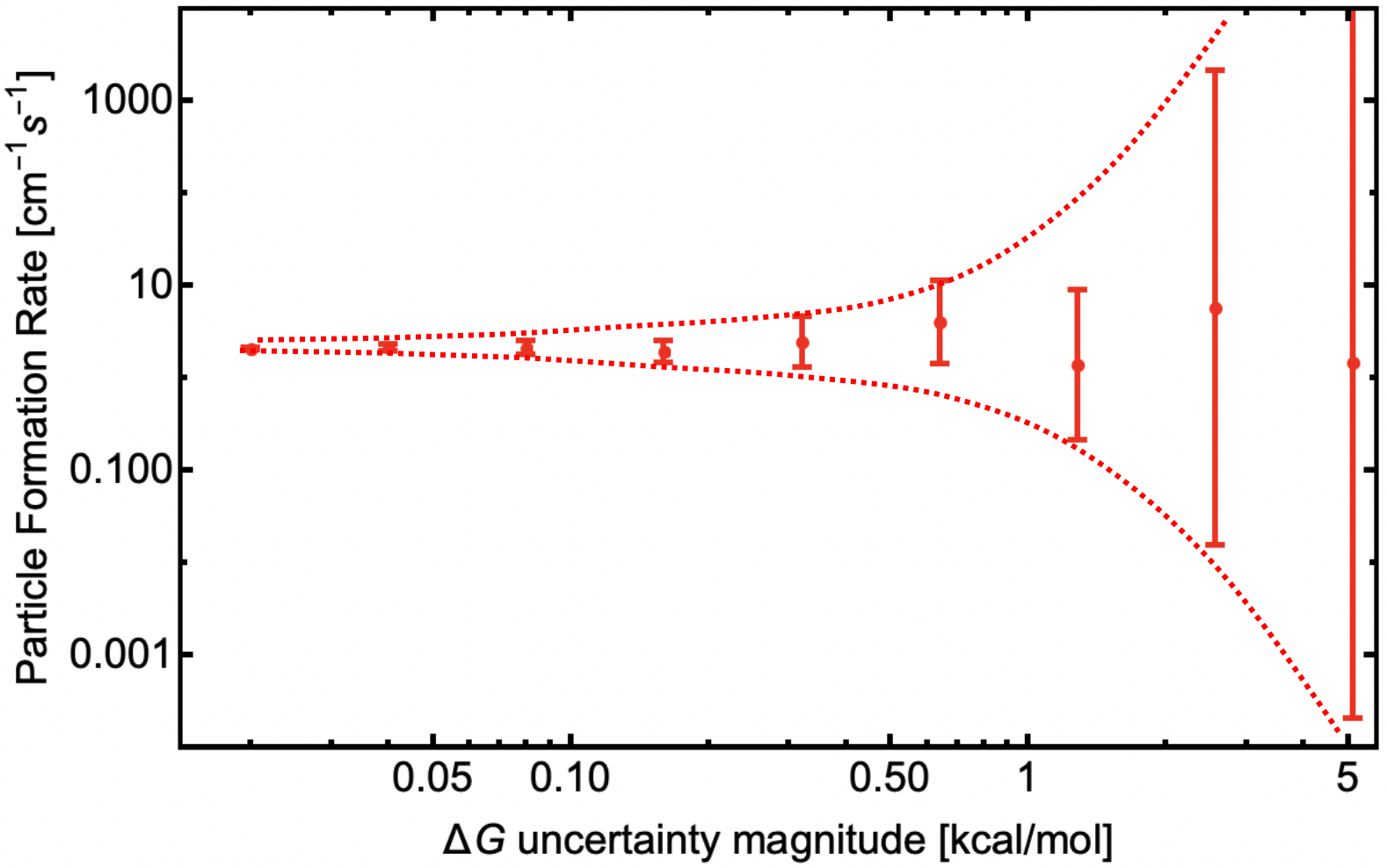
(≈10^{12} cm^{-3} NH_3)

+

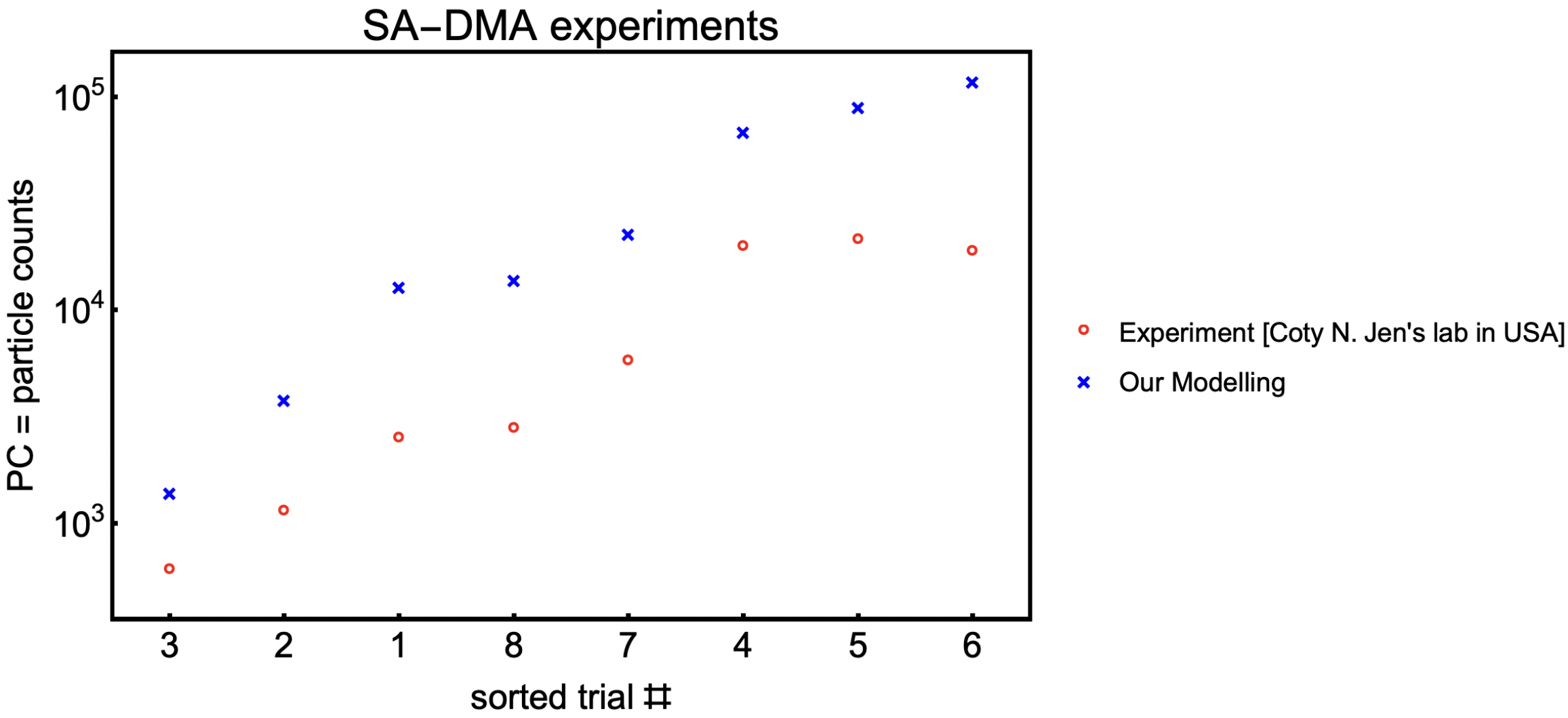
10^8 cm^{-3} H_2SO_4

----------298.15 K----------

~2 particles·cm^{-3}·s^{-1}

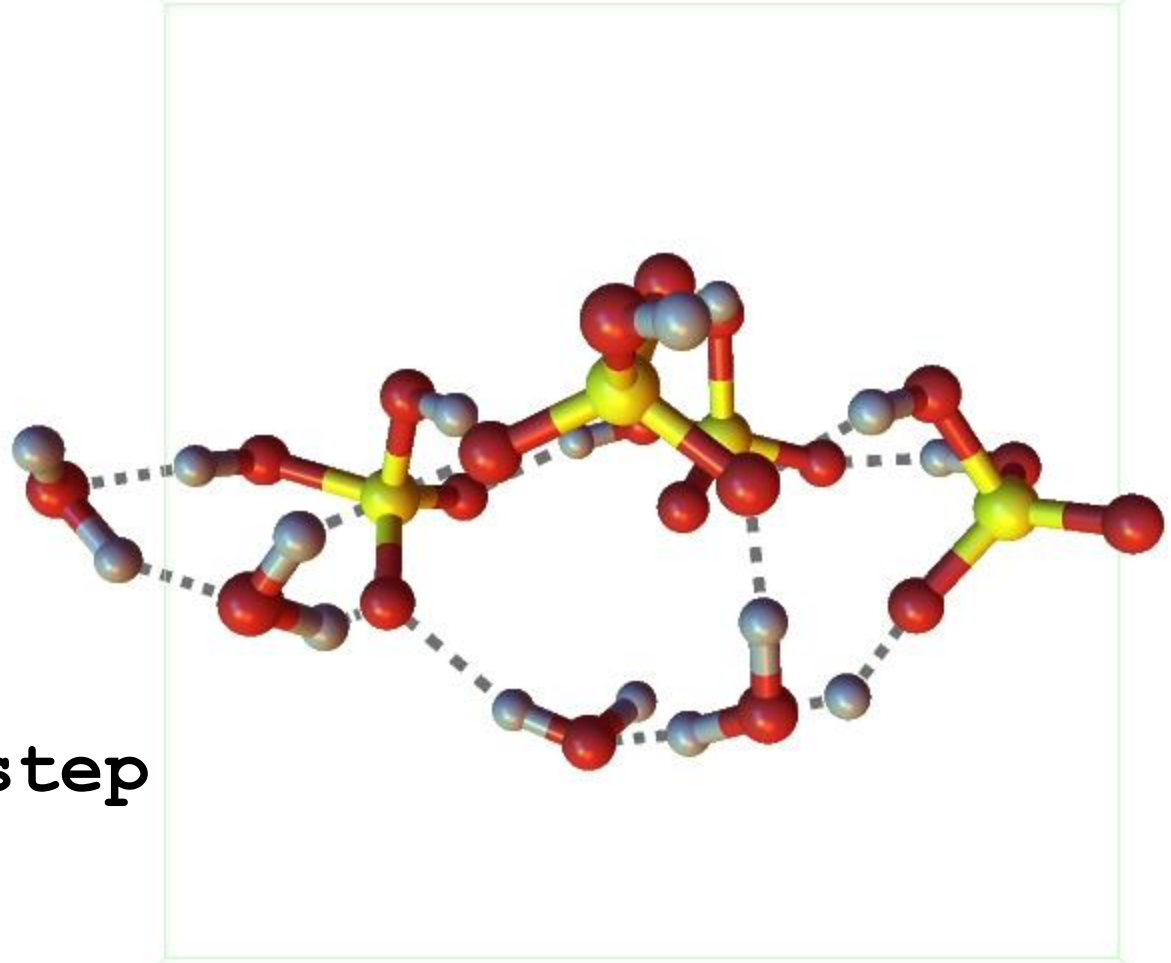


Systematic Error for Strongly Binding Clusters



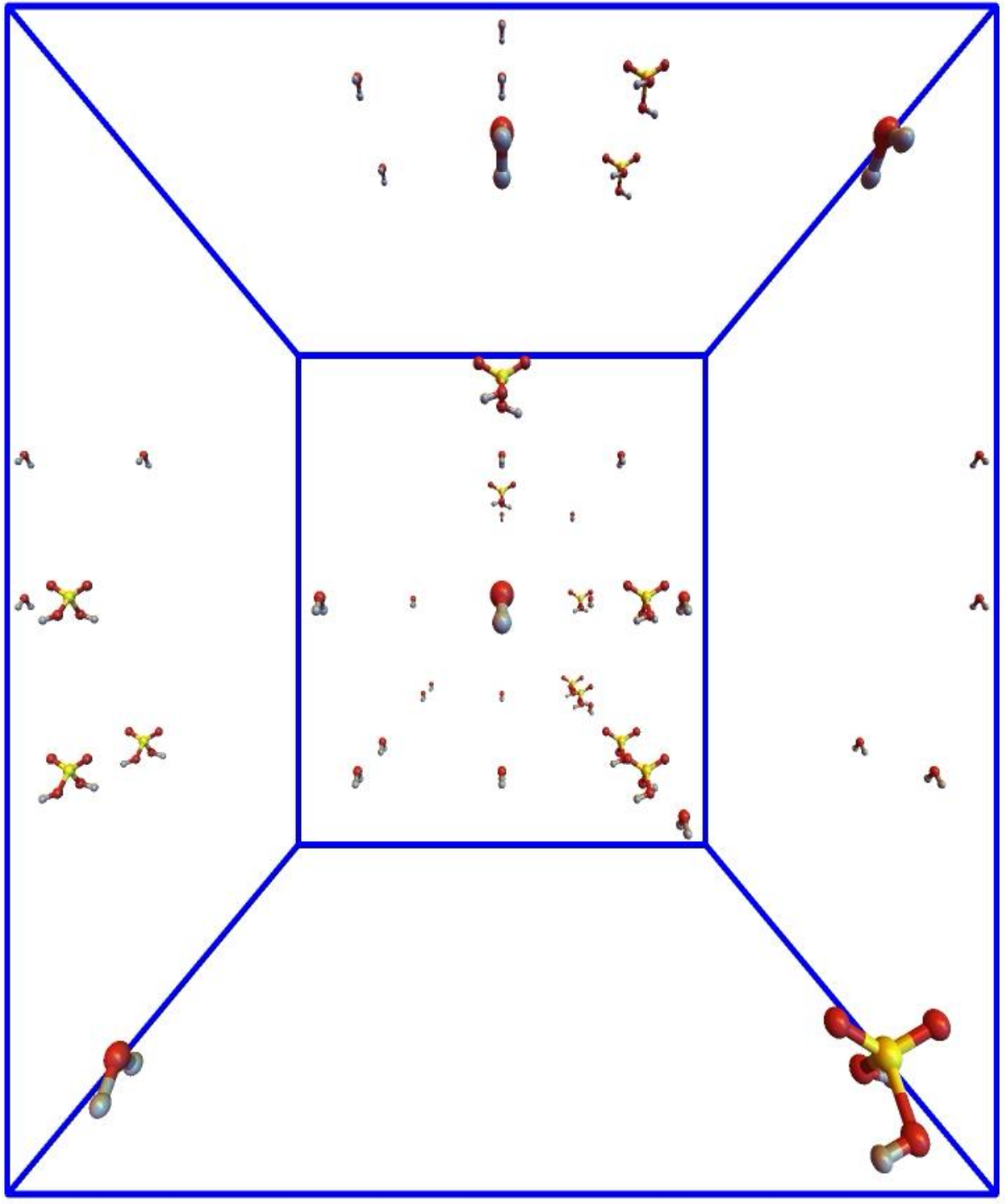
Simulating CLUSTER

- **Level = DFT via NN**
  ωB97X-D/6-31++G(d,p)
- **System = 4×(H_2SO_4)**
  4×(H_2O)
- **MD = Langevin (300 K)**
  1 fs integration step
  0.1 ns simulation



Simulation BOX

- **Level = DFT via NN**
  ωB97X-D/6-31++G(d,p)
- **Box = 40×40×40 Å^3**
- **System = 10×(H_2SO_4)**
  10×(H_2O)
- **MD = Langevin (300 K)**
  1 fs integration step
  1 ns simulation



Conclusion and Outlook

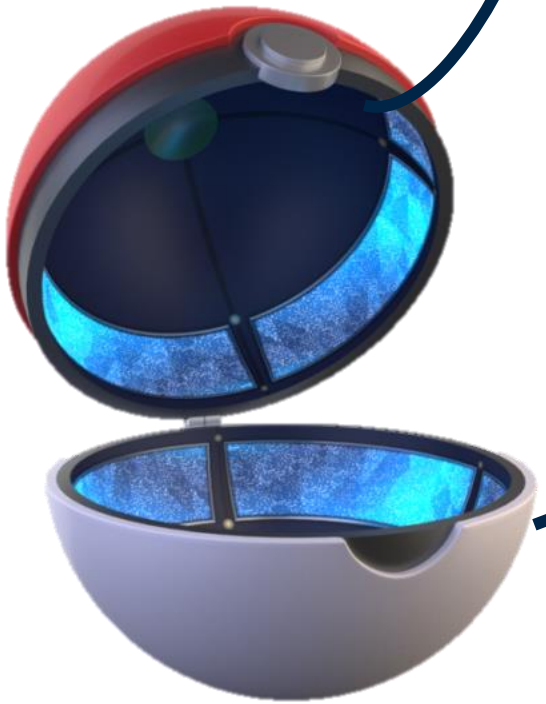
- Atmospheric NPF
- QC + Configurational Sampling of Molecular Clusters
- (Conformational) Entropy Needs To Be Addressed Now!

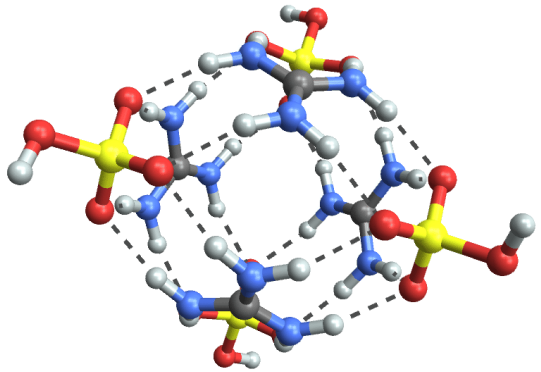
TAKE HOME MESSAGE:

Funded by the European Union

Thank you

Center for Chemistry of Clouds





Gotta CATCH'em all!

CAtCh

Computational Atmospheric Chemistry

From left to right: Haide Wu, Daniel Ayoubi, Yosef Knattrup, Jakub Kubečka, Morten Engsvang, Jonas Elm, Andreas Buchgraitz Jensen, Jakob Lund, Astrid Nørskov Pedersen

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