Modeling Fluxionality and Off-Stoichiometric Restructuring at Electrochemical Interfaces

Zisheng Zhang,[a] Philippe Sautet,[a,b] Anastassia N. Alexandrova[a,b,*]

[a]Dept. of Chemistry and Biochemistry, [b]California NanoSystem Institute, University of California, Los Angeles, Los Angeles, CA. 90095
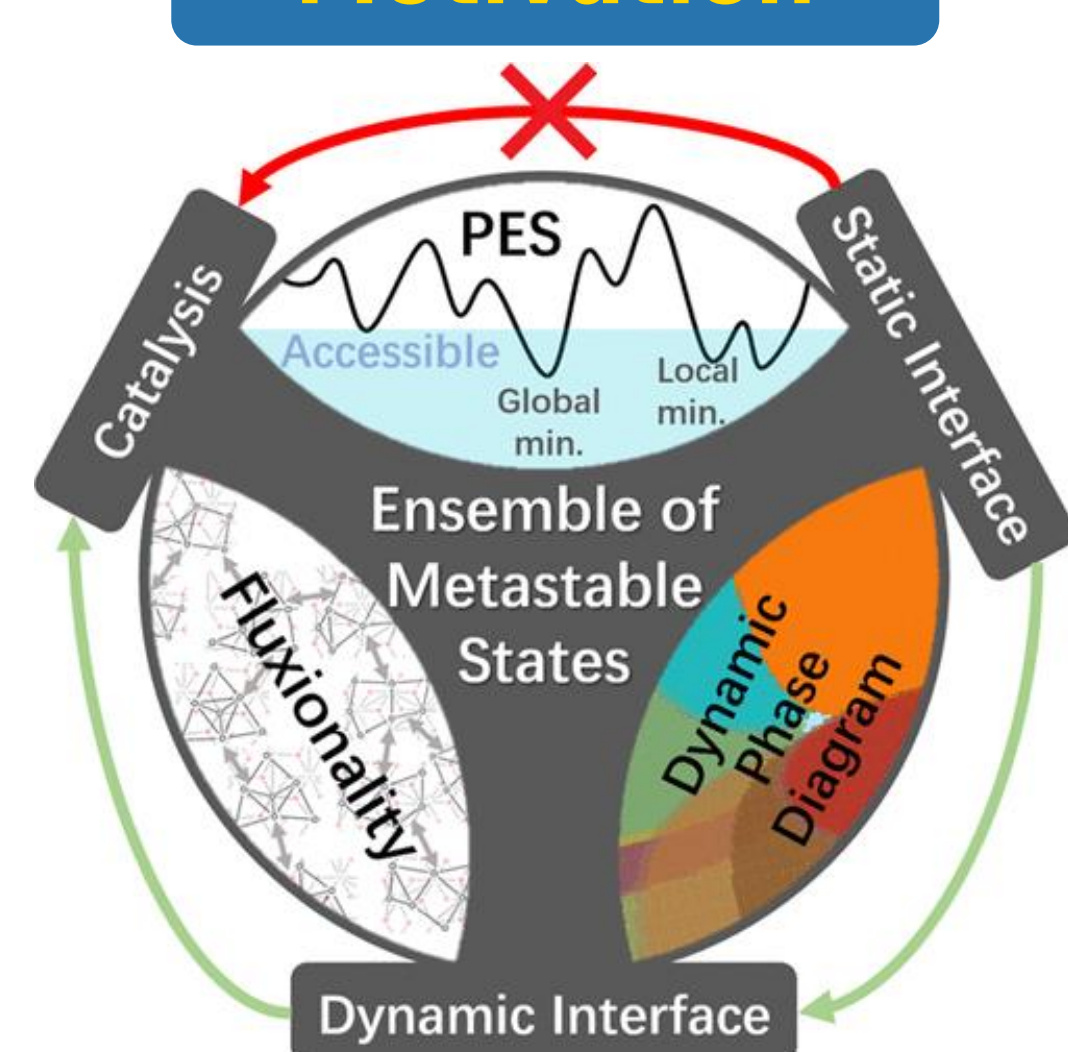
Motivation

Many heterogeneous catalysts have been shown to become fluxional and dynamic under rxn conditions.[1] To model them correctly, we need to consider:

- Isomeric configurations
- Off-stoichiometric restructurings
- Varying coverage of adsorbates
- Different adsorbate configurations

Electrocatalysts operating at room T have extra factors to consider:

- Narrower distribution of states
- Effect of electrode potential and the electric double layer

Methods

In this collection of our recent works, we applied a combination of state-of-the-art computational methods to address the complexities mentioned in "Motivation":

- Global optimization search for global and local minima
- Grand canonical treatment for varying composition and adsorbate coverages
  Grand Canonical Genetic Algorithm **(GCGA)** as implemented in our open-source package, GOCIA (Global Optimizer for Clusters & Interfaces & Adsorbates).
  The optimization objective is the grand canonical free energy:

$$\Omega_{stoi} = G_{slab_{non-stoi}} - G_{slab_{ref}} - \sum_i \mu_i$$

- Grand canonical treatment for electrons
  DFT and linearized Poisson-Boltzmann model for electrolytes
  Electronic free energy under the constant capacity approximation:

$$\Omega_{el}(U) = E(U) - q(U) \cdot U \approx E(U_0) - \frac{1}{2}C \cdot (U - U_0)^2$$
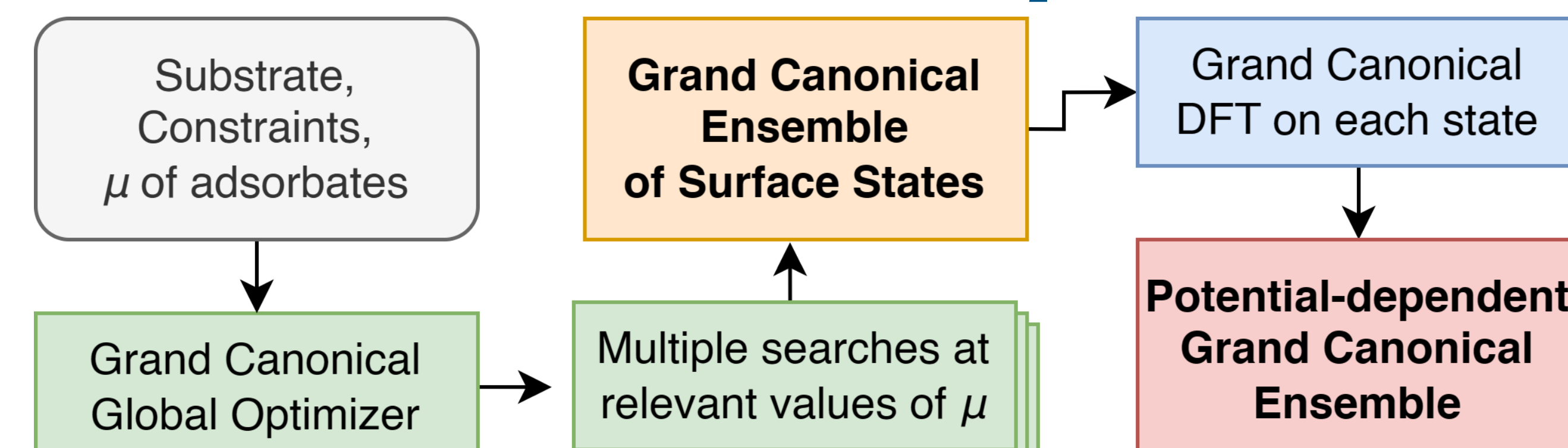
A **statistical ensemble representation** of the interface can be then constructed, including all chemically relevant metastable surface states (of diverse geometry and stoichiometry) and their dependence on the electrode potential.[1,2]

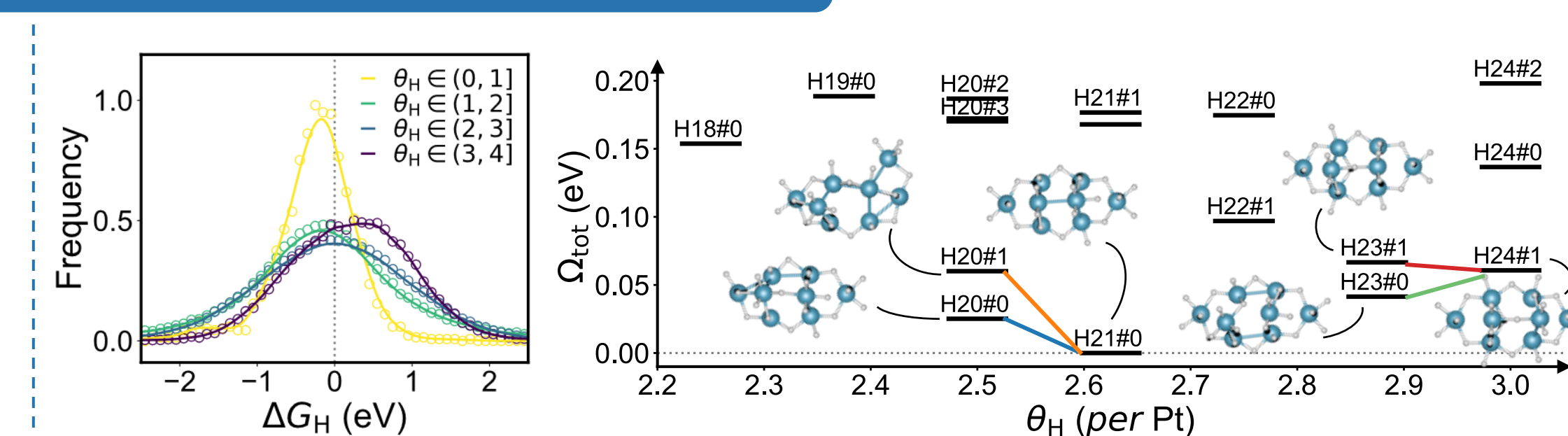## Hydride states govern HER on Pt clusters[3]
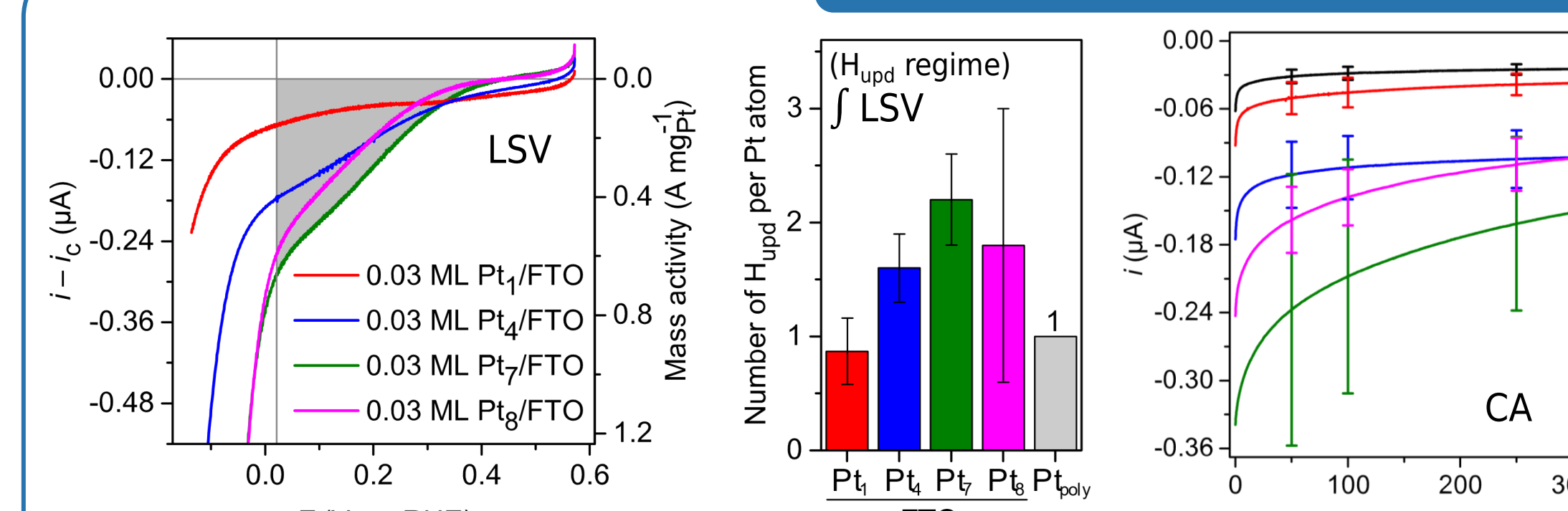
Size-selected cluster experiments by Anderson Group (UofU)
- HER activity: $Pt_8 > Pt_7 > Pt_4 > Pt_1$
- HER stability: $Pt_4 > Pt_8 > Pt_7 > Pt_1$
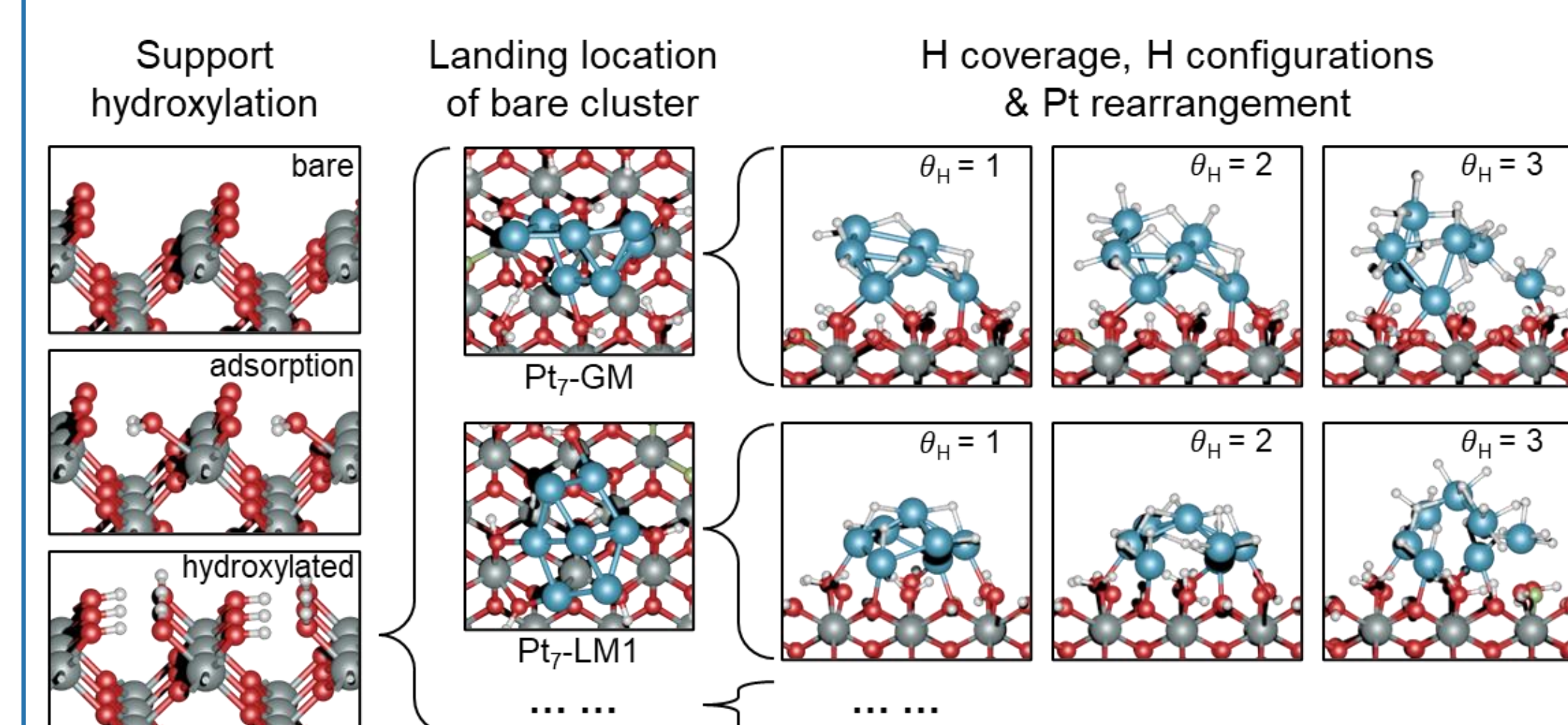
- Hydroxylation of the (100) termination in aqueous media
- Assuming clusters to stay at the landing location
- GCGA search: core reshaping and H coverage/configurations
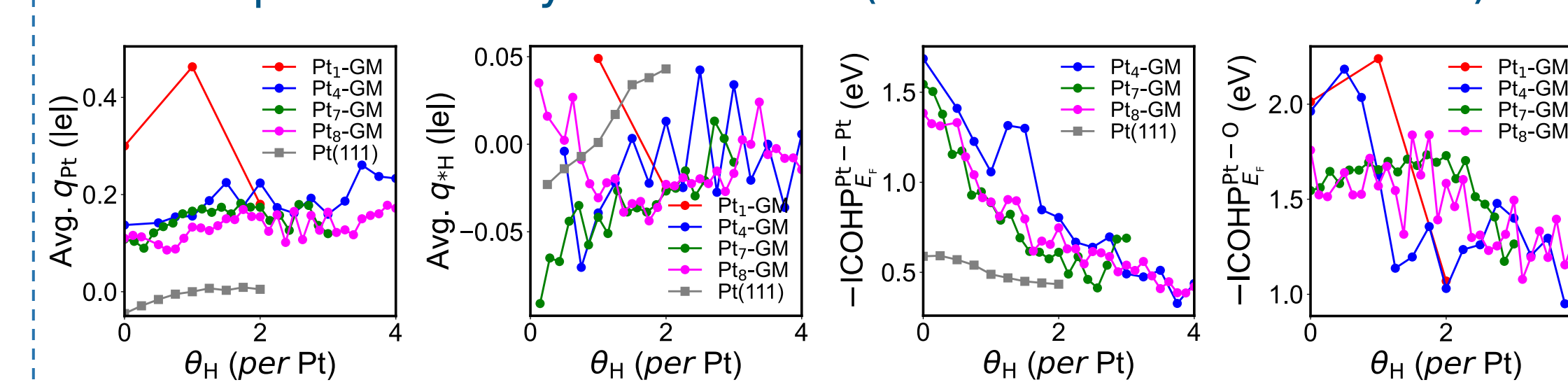
In the potential-dependent GC ensemble, we assume any two states from neighboring H coverage can make a HER pathway.
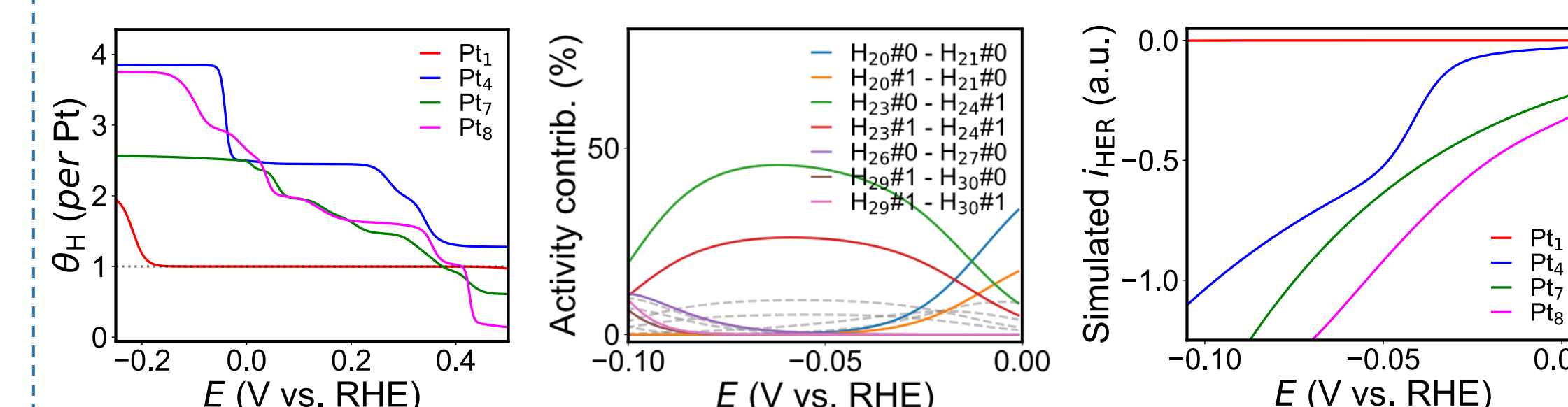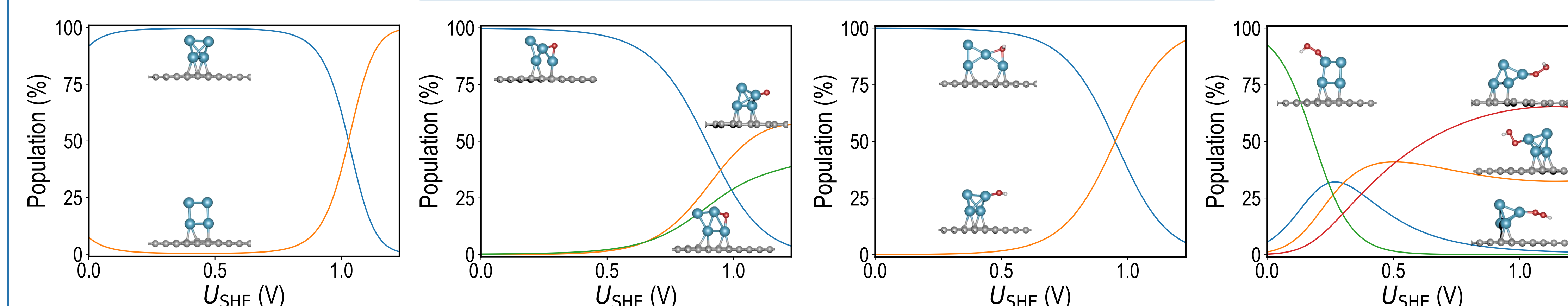

Kinetic model considering both population and pair-wise HER energetics of the states.[2]

Active species are hydride states (formed before HER onset)

Destabilization: cluster-support outcompeting intra-cluster int.

## Fluxionality reshapes the activity volcano[4]

- Clusters reshape to adapt to different adsorbates, with inconsistent binding sites and bonding modes, **breaking the LSR**.
- **Adsorbate-dependent** fluxionality causes overall binding strengthening, making Ag/Au better and Pt/Pd worse at ORR.
- **Potential-dependent fluxionality** shifts the isomeric distribution differently for every reaction intermediate as U varies
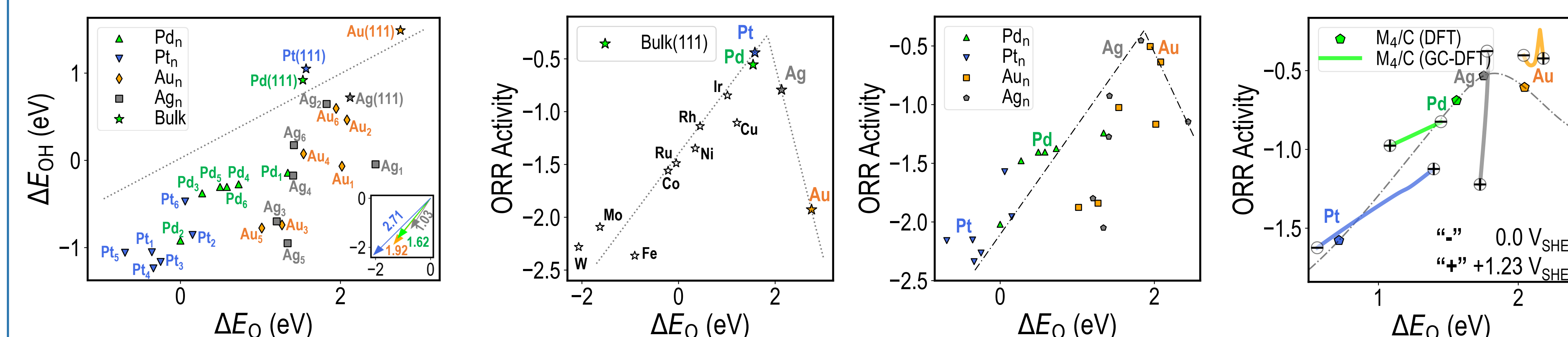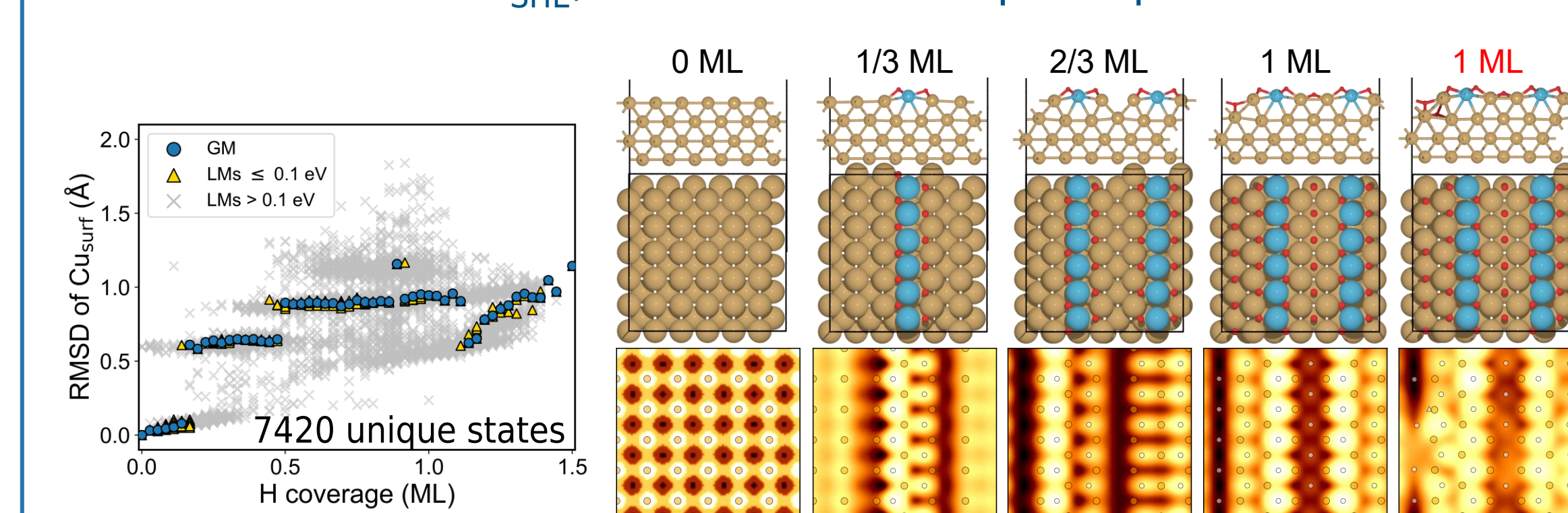

- The **ORR activity volcano** is therefore reshaped into a bumpy landscape, non-linearly dependent on the electrode potential
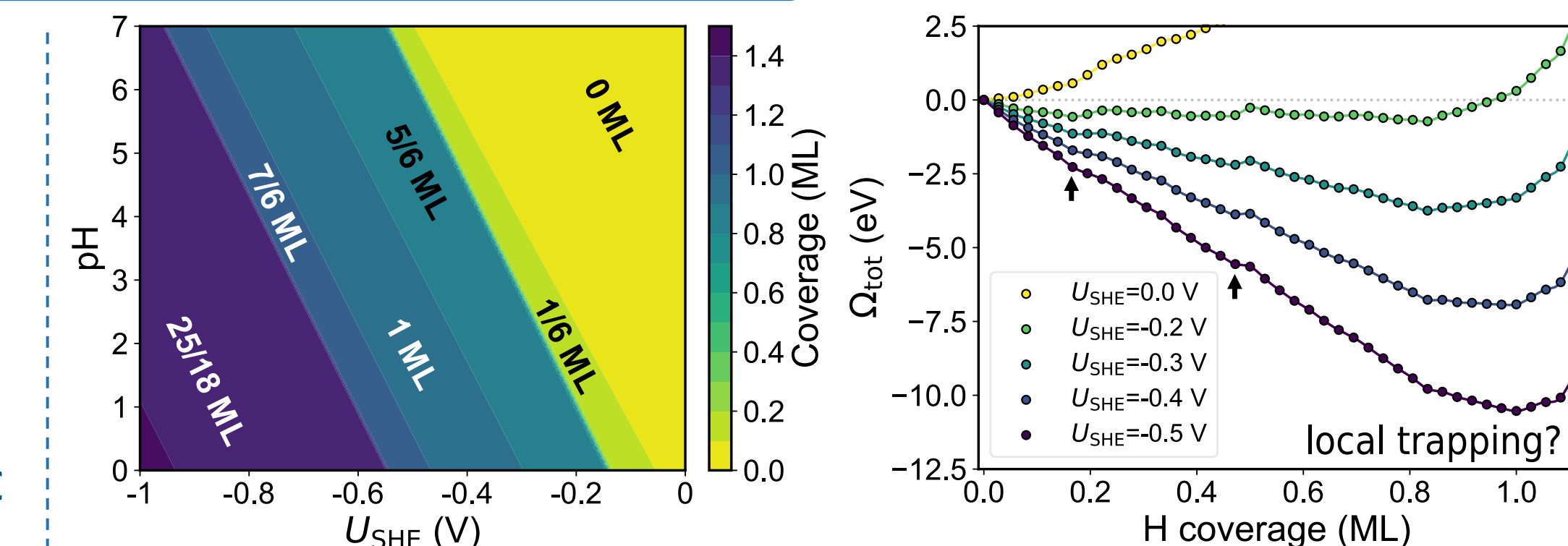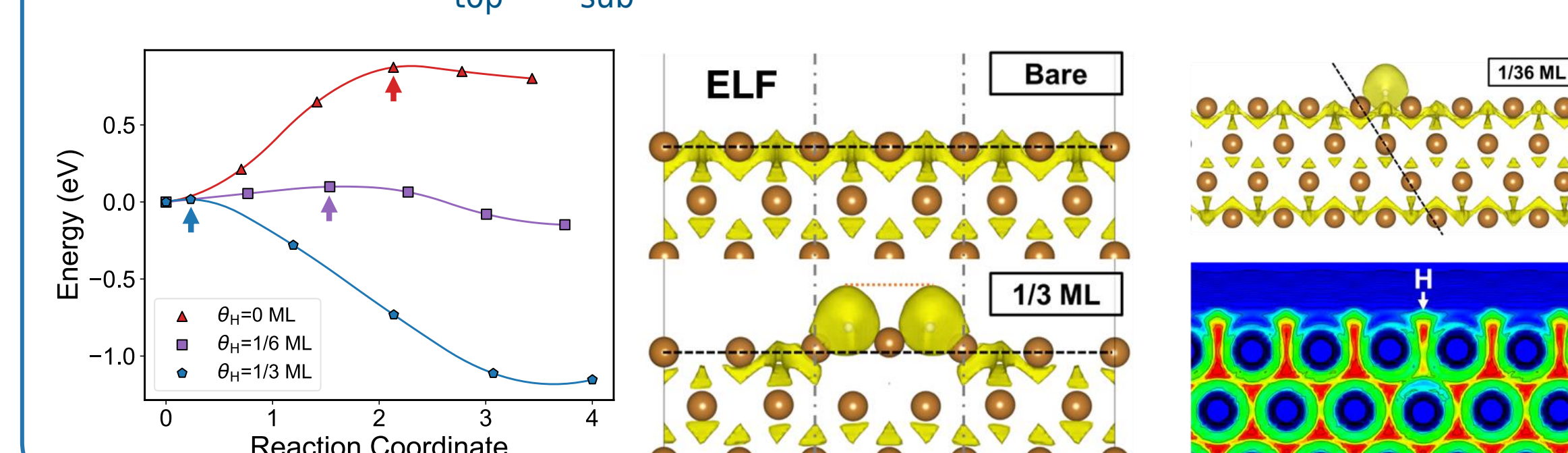- The apex shifts to the under-binding regions (Ag/Au) in the bulk volcano!

Adsorbate-induced surface restructuring[5]
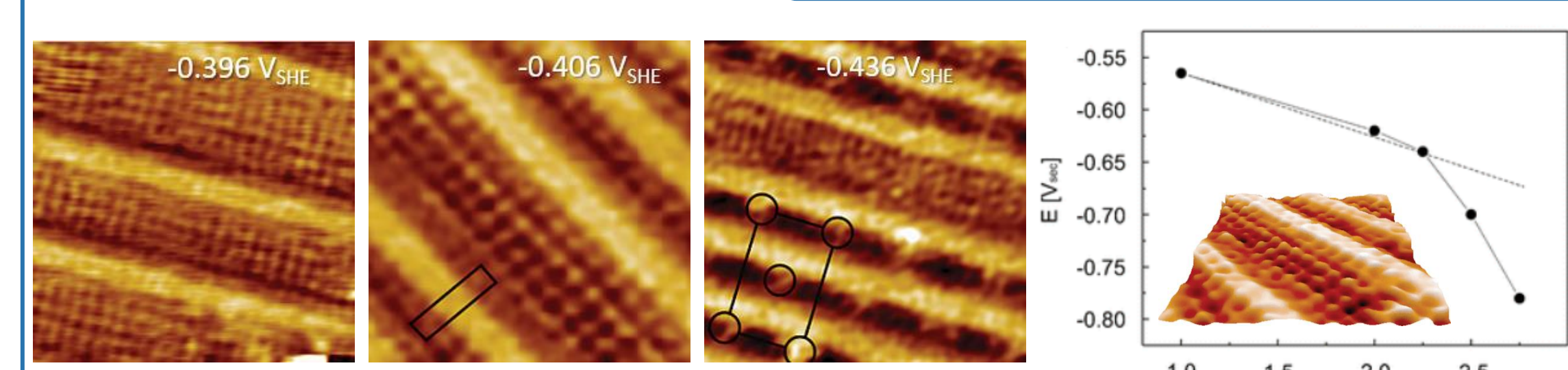
In situ STM showed **stripe formation** on **Cu(100)** in acidic media at c.a. -0.4 V_{SHE}, with a non-linear pH-dependence.
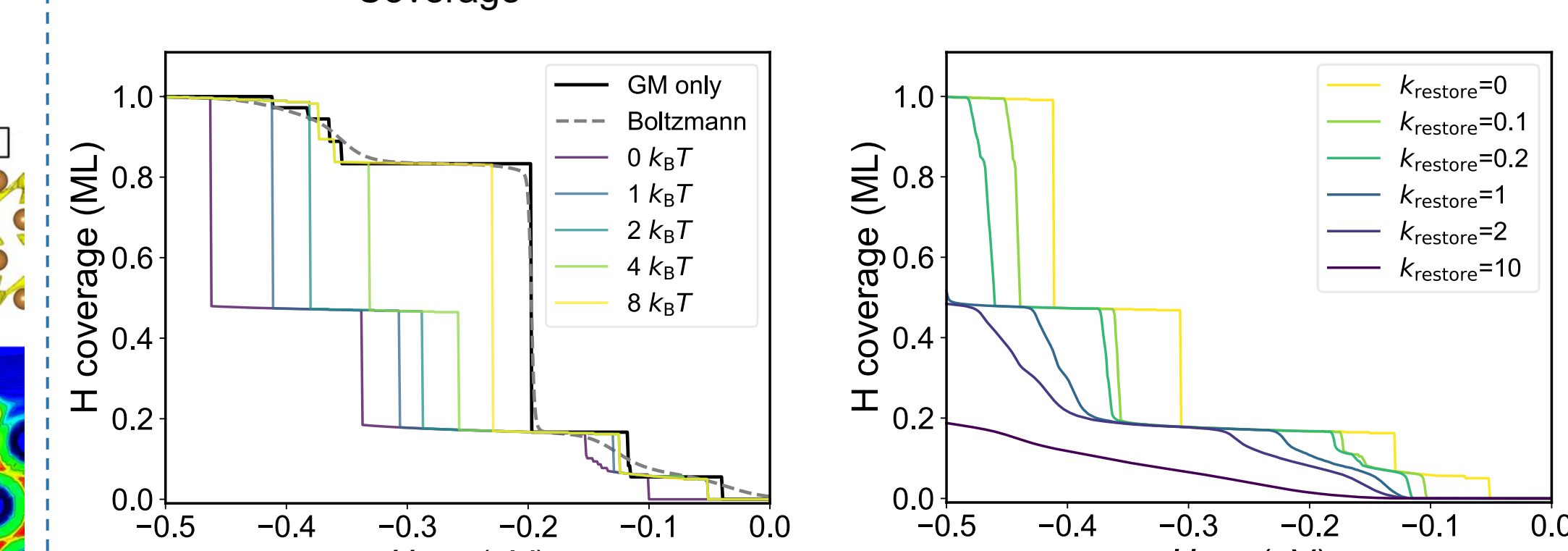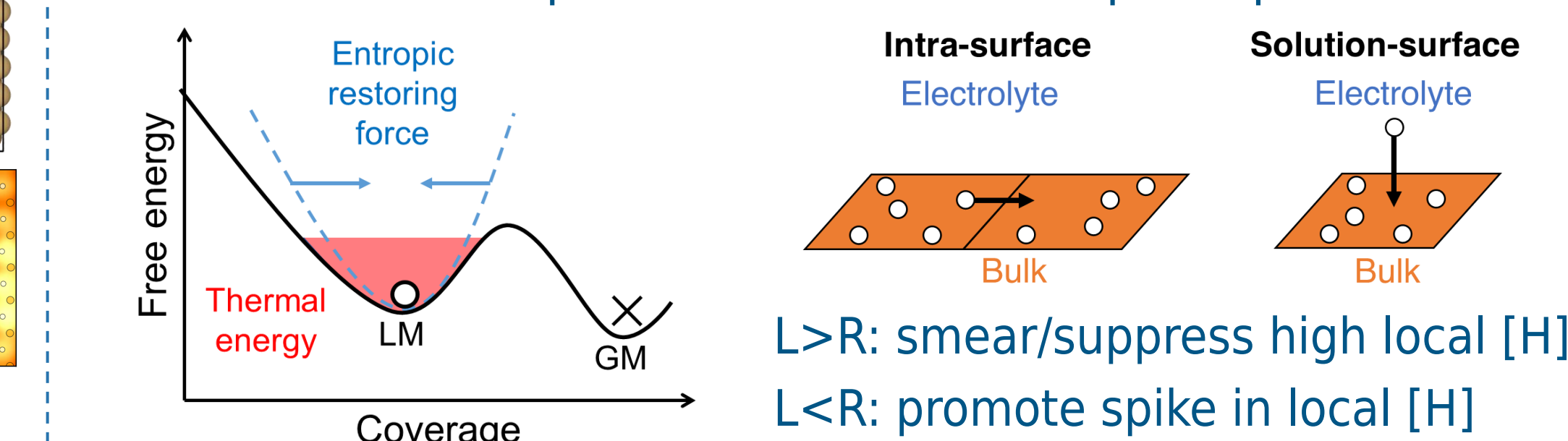

- Row-shifting restructuring is observed only at high θ_H.
- *H weakens Cu_{top}-Cu_{sub} and stabilize the trifold site

Consider extra factors to recover the physics
- Finite thermal energy -> trapping in metastable θ_H
- Collective entropic force -> non-linear pH-dependence

L>R: smear/suppress high local [H]
L<R: promote spike in local [H]

Summary

- We develop a statistical ensemble representation of fluxional electrocatalysts & computational tools to efficiently sample the PES.
- The potential- and adsorbate-dependent fluxionality can routinely break catalyst design principles based on linear scaling relations.
- Adsorbate coverage influences the reactivity of subnano clusters, effectively changing the nature of active sites for electrochemistry.
- Even bulk metal surfaces can undergo dramatic restructuring under coverage of the simplest adsorbate H.

[1] Z. Zhang, B. Zandkarimi and A. N. Alexandrova, Acc. Chem. Res., 2020, 53, 447–458. [2] Z. Zhang, Z.-H. Cui, E. Jimenez-Izal, P. Sautet and A. N. Alexandrova, ACS Catal., 2020, 10, 13867–13877. [3]. Z. Zhang, T. Masubuchi, P. Sautet, S. L. Anderson and A. N. Alexandrova, 2023, under review. Preprint: 10.26434/chemrxiv-2022-ssh9n [4] Z. Zhang, B. Zandkarimi, J. Munarriz, C. E. Dickerson and A. N. Alexandrova, ChemCatChem, 2022, 14, e202200345. [5]. Z. Zhang, Z. Wei, P. Sautet and A. N. Alexandrova, J. Am. Chem. Soc., 2022, 144, 19284–19293.