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Chemically Accurate *Ab Initio* Prediction of Adsorption Thermodynamics and Isotherms in Metal–Organic Frameworks

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Current environmental and energy challenges necessitate the development of advanced nanoporous adsorbents, making predictive atomistic modeling essential for both materials design and process integration. The key descriptor is the gas-surface interaction strength, expressed most fundamentally as the adsorption Gibbs free energy, which determines the adsorption isotherm, i.e., the equilibrium uptake as a function of gas pressure at fixed temperature. To be meaningful, predictions must achieve chemical accuracy (±4 kJ mol^{-1}),[a] requiring both a reliable potential-energy surface and rigorous statistical-mechanical sampling of the relevant configurational space.

Here we focus on two MOFs proposed for CO_2 capture – Mg_2(dobdc) (CPO-27-Mg/MOF-74) and CALF-20 – and show how chemical accuracy can be achieved by going beyond standard periodic DFT+D workflows. We first compute periodic DFT+D adsorption energetics and then add high-level correlation corrections using periodic MP2 together with CCSD(T) corrections evaluated on adsorption-site cluster models, yielding chemically accurate adsorption energies at equilibrium structures.[a-e] Adsorption entropies and Gibbs free energies are then obtained by local sampling of this surface via vibrational partition functions that include quantum nuclear effects and anharmonicity. To capture coverage-dependent nonlocal effects, we account for lateral adsorbate-adsorbate interactions either through a mean-field (Bragg-Williams) isotherm model or via a nonisolated-site treatment in which additional intermolecular modes augment the adsorbed-state partition function, thereby substantially improving adsorption entropies and Gibbs free energies. For CALF-20, the resulting ab initio isotherms and heats of adsorption reproduce experiment within chemical accuracy and agree with independent GCMC simulations based on a newly parametrized force field, providing a triple cross-validation across ab initio thermodynamics, GCMC simulations, and experiment.[e]

References:

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