



*Multiscale Modeling of Metal-Organic Frameworks*

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## Summary

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Metal-organic frameworks (MOFs), or porous coordination polymers, have gained considerable interest in the past two decades due to their potential in a plethora of technological applications. These nanoporous materials consist of metal nodes interconnected by organic linker molecules forming an extended network. MOF-materials containing open-metal sites (OMS) are promising materials for the adsorptive separation of olefin/paraffin mixtures. Current technologies for *e.g.*, ethylene/ethane separations rely on expensive high-pressure cryogenic distillations. Open-metal sites interact more strongly with olefins compared to paraffins, which can lead to higher adsorption selectivities. Kohn-Sham density functional theory (KS-DFT) calculations provide useful electronic insight into these adsorption processes. However, the associated molecular orbital interactions are often unknown.

Chapter 2 reports a KS molecular orbital analysis of water adsorption on the OMS of the MOF HKUST-1. Hybrid functionals show better agreement with experimental magnetic and electronic properties than generalized gradient approximated (GGA) functionals. Analysis of the molecular orbitals reveals a Jahn-Teller distortion upon water adsorption due to antibonding interactions between the Cu( $3d_{z^2}$ ) and the highest occupied molecular orbital of water in the A1 irreducible representation. Donor-acceptor interactions show that empty Cu( $4s$ ) and Cu( $4p_z$ )-orbitals on the opposite Cu-sites are populated, thereby explaining the reduced adsorption energy of the second adsorbed water molecule. A  $\sigma$ -bond is established between the two Cu-cations as was recently suggested using electron paramagnetic resonance.

HKUST-1 is, due to the open-metal site, an excellent candidate material for the adsorptive separation of ethylene/ethane mixtures. Knowledge of the multicomponent adsorption behavior is important to assess the full potential of the sorbent material. Measuring multicomponent adsorption isotherms experiment-

ally is rather challenging. Therefore, the ideal adsorbed solution theory (IAST) is widely used. Chapter 3 demonstrates that this theory breaks down in HKUST-1 for ethylene/ethane mixtures. Using KS-DFT molecular orbital analysis and an energy decomposition analysis scheme, a new force field potential is constructed that accounts for the donor-acceptor interactions between the open-metal site and ethylene that are missing in standard hydrocarbon force fields. The computed single component ethylene adsorption isotherm is in excellent agreement with the experimental adsorption isotherm in semi-logarithmic scale. By computing the multicomponent adsorption isotherms directly, it becomes clear that IAST fails at industrially relevant pressures. This suggests that a multiscale modeling approach is crucial in predicting complex adsorption behavior.

A key challenge for the commercialization of MOF-materials is to increase their mechanical stability. Therefore, an understanding of MOF mechanical properties is critical for their integration with technological applications. The majority of the reported mechanical properties are obtained from room temperature experiments or 0 Kelvin *ab initio* calculations. Typically, significant discrepancies are observed between the *ab initio* and room temperature values. An important reason for this discrepancy is temperature effects. Previously, thermomechanical properties of MOF-materials were unknown. Thermomechanical properties are not only important from an application perspective, such as in sensor devices and fixed-bed reactors, but also from a fundamental understanding of elasticity in MOFs.

In Chapter 4, state-of-the-art flexible force field models, which form an essential tool in predicting mechanical properties of MOFs, are reviewed. Various parameterization schemes, including the building block methodology and periodic phonons are discussed. Most (generic) force fields are able to reasonably reproduce lattice parameters, coefficients of thermal expansion and bulk moduli. However, there are still major challenges to overcome in order for force fields to be used to their full potential, such as the development of efficient sampling schemes.

Thermomechanical properties can be determined from knowledge of the variable-temperature elastic constants. Therefore, in Chapter 5, a new parameterization scheme is proposed that fits flexible force fields on the *ab initio* calculated elastic tensor. Furthermore, it is shown that framework flexibility has negligible influence on the adsorption and diffusion of small guest molecules in MIL-47(V).

Experimental thermomechanical and creep properties of HKUST-1 are presented in Chapter 6. Although HKUST-1 becomes denser due to negative thermal expansion, single crystal nanoindentations and dynamic mechanical analysis show a reduction of the Young's modulus and hardness upon increasing temperature. These findings are consistent with softening of the isothermal elastic constants calculated from classical molecular dynamics simulations. Creep analysis shows a large decrease of the aforementioned mechanical properties. These findings suggest that one has to rethink the use of HKUST-1 in technological applications.