Ligand Field Molecular Mechanics applied to MOFs

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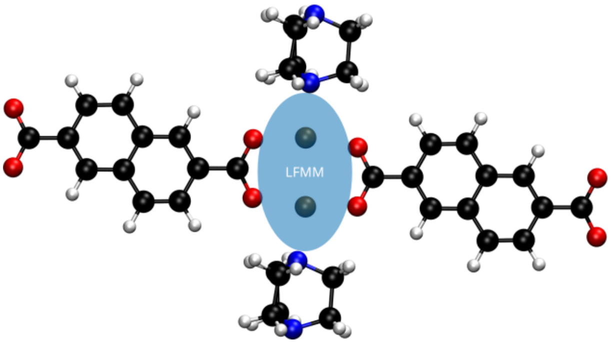
The observation of structural flexibility of certain Metal-Organic Frameworks (MOFs) triggered many theoretical investigations of these materials. The thermodynamics and kinetics of flexible MOFs can be difficult to model for various reasons: The role of the metal, conformational isomerism, dependence of the flexibility on the particle size and the role of dispersion interactions, to name only a few, are on their own already challenging for many methods. Combining these characteristics in one material challenges theoreticians to revisit their toolbox and combine tools and methods in new ways.

In our recent work [1] we apply Ligand Field Molecular Mechanics (LFMM) to perform molecular dynamics (MD) simulations of the pillared layer MOF $Ni_2(ndc)_2(dabco)$ (ndc=2,6-naphtalenedicarboxylate, dabco=1,4-diazabicyclo-[2,2,2]-octane), also known as DUT-8(Ni) [2]. This MOF shows pronounced stimuli-induced switching between a closed pore and an open pore phase upon ad- and desorption of certain gases and liquids accompanied by an enormous volume change of the unit cell [3]. The modelling of the flexible paddle wheel structure of this MOF is a very challenging task using standard density functional methods and even more so for classic force fields. By employing LFMM in combination with the general amber force field (GAFF) we modeled the loading of various guests (Nitrogen, carbon dioxide, dimethylether, methane, chlorinated methanes, methanol, ethanol and water) into the MOF to study the host-guest interactions and understand the characteristics of their adsorption inside the MOF.



LFMM is based on the calculation of the Ligand Field Stabilization Energy by use of the angular overlap model and is a well-established method that has been applied to the description of many transition metal complexes [4]. One of its distinct features is the applicability to model different spin states using only one set of parameters. Exploiting this, Paesani *et al.* introduced a hybrid Monte Carlo/MD method that allows switching of the spin state of each metal center individually during MD simulations [5].

Even though no spin state switching is experimentally observed in DUT-8(Ni) we hope that our investigation provokes others to also evaluate the applicability of LFMM and the concept of its use in the hybrid MC/MD scheme. Our goal is to extend our simulations to other flexible MOFs with dynamic spin state changes. A combination of LFMM and DFT simulations provides in our opinion a powerful toolbox for the description of many flexible MOFs, extending even to those with varying spin state.

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