Advanced molecular simulations to accurately characterize Metal-Organic Frameworks

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Metal-organic frameworks (MOFs) are a unique class of porous crystalline materials which are made up by metal clusters connected by organic linkers. These materials can be synthesized with a large versatility and can easily be tuned both chemically and structurally [1]. They show great promise for different industrial applications such as separation, catalysis and storage.

In this work, the textural, thermal and mechanical properties of MOFs will be studied using force fields derived from first-principles molecular calculations on smaller building units. Textural properties, e.g. accessible surface area, are important for porous materials. Molecular dynamics simulations are used to determine the thermal expansion coefficients, whereas the mechanical properties at 0 K are studied by the determination of the full stiffness tensor. One spectacular property is the structural flexibility or so-called breathing phenomenon observed for some MOFs [2]. Recent studies have shown that a characterization of the anisotropic elastic behavior can predict this flexibility [3]. Molecular simulations are performed with YAFF [4], an in-house developed code based on force fields.

The methodology will be tested on the well-known MOF-5, which was synthesized for the first time by Yaghi [5]. Several theoretical and experimental results are available for this MOF, which allows for a direct validation of the obtained results. A second test case concerns the MIL-53(Al) material, belonging to a family of flexible frameworks that undergo a transition from large pore to narrow pore under mechanical pressure [6]. The simulations on these materials use in-house developed force fields [7,8] parametrized by means of Density Functional Theory (DFT) calculations.

In a second step, the test set is expanded. To this end a series of ab initio parametrized force fields are generated with QuickFF [9]. The required input consists of DFT calculations on non-periodic clusters representing the metal clusters and organic linkers respectively. The proposed characterization will be applied to this extended set of MOFs. If possible, structure-property relations will be identified to allow for a more rationalized design of high-performance MOFs.

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