Diffusion and adsorption of aromatic guests in MOFs studied by ab initio and force field simulations including lattice dynamics

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Introduction

About a decade ago, a new class of nanoporous molecular systems known as metal-organic frameworks (MOFs) were introduced by the group of Yaghi [1]. One of the most attractive features of MOFs is its very high surface area, e.g. up to 5.640 m^2/g for MOF177 [2]. Their high surface area makes them a very promising class of materials for hydrogen storage [3]. Other applications can be found in catalysis [4] and gas separation. Recently it was shown that Metal-Organic Frameworks could be successfully used as selective adsorbents for the extremely difficult and industrially relevant separations of mixed C8 alkylaromatic compounds [5,6].

Another remarkable property of MOFs, is its high framework flexibility [7]. The strong interactions between the framework and host molecules, make the MOF prone to drastic volume changes. An example of such a MOF is MIL-53 (Figure 1) for which cases have been reported of volume change as high as 40 % [8]. Another interesting consequence of the framework flexibility is the phenomenon of pore breathing. Due to the interaction with guest molecules, the complete framework is able to expand and shrink.

Since MOFs are periodic structures with rather large unit cells (cell parameters are of the order of 10 Å, a full ab initio calculation is readily demanding with the modern computer systems. Therefore force fields are used to perform molecular dynamics simulations. In this study, we wish to develop such a force field for MIL-53 based on

first principles. Our main goal is to develop a force field able to reproduce the geometry. We will also investigate the simulated infrared spectrum and the ability to simulate the breathing phenomenon.

Theoretical Method

The parameters of the force field are derived from ab initio calculations on smaller clusters. The periodic unit cell is divided in two clusters (Figure 1) which are representative for the periodic structure of the MIL-53. In order te determine the non-bonding interactions of the force field a proper description of the charges is needed. Simply using the charges of the clusters is not viable, as this would yield periodic unit cells which are not neutral. Instead a method based on charge transfers over each bonds is used, also called bond increments [9]. The bond increments were calculated to reproduce the ab initio electrostatic potential (ESP) as good as possible. The oxygen atoms connected to the metal center are largely screened by the linkers and therefore the ESP method is not appropriate to describe these charges. For these atoms the Hirshfeld-I partitioning scheme was used and the bond increments were determined to reproduce these charges as good as possible. The Van der Waals parameters were taken from literature [10].

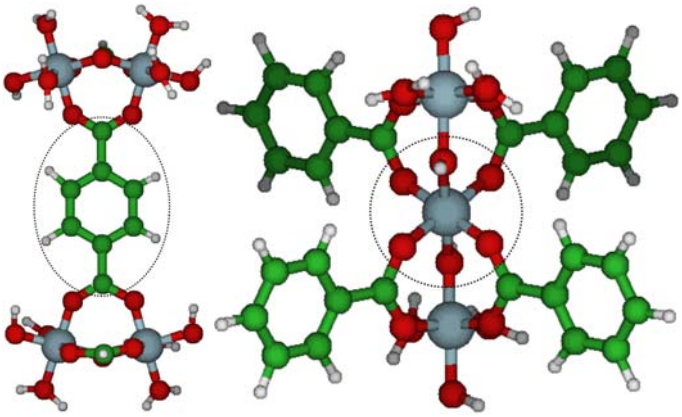

Figure 1 : Clusters cut from the MIL-53 structure and used to derive parameters for the force field.

The parameters of the bonding interactions (bonds, bends, torsions, ...) were calculated to reproduce the ab initio Hessian. For both clusters, we equated the ab initio Hessian (the expected values) with the force field Hessian. The latter is a function of all the force field terms present in the cluster. Since not all Hessian elements and force field terms of the clusters are relevant for the periodic structure,

only those that are relevant are selected and used to construct one set of equations from which all the relevant parameters can be calculated. Every force field term that contains at least one atom from the core is included.

Computational Details

To characterize the ab initio PES, we performed geometry optimizations and frequency calculations using density functional theory. From these calculations, the ab initio Hessian can be calculated. The B3LYP exchange correlation functional was chosen for its known success in reproducing the experimental geometry. The 6-31G(d,p) basis set was used for all atoms. All calculations were performed with the Gaussian03 program package. The force field fitting was performed using the in-house developed MMFit and MolMod packages. Molecular dynamics (MD) simulations were done with the CP2K program. Finally, for the processing of the MD simulation data, we used the MD-Tracks package [11].

Results and Discussion

At first instance the newly generated force field was used to optimize the structure of MIL-53. The results in shown in figure 3.

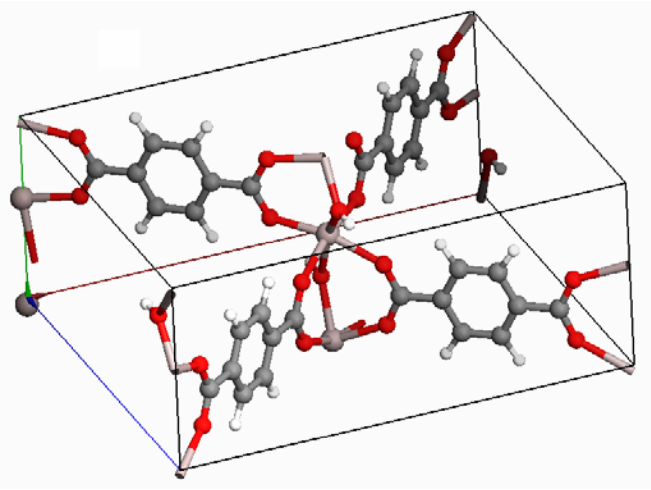

Figure 2 : Optimized structure of the MIL-53 using the newly generated force field.

The cell parameters after optimization are determined as a=16.79, b=7.08, c= 13.77 Å. These are slightly different than the experimentally determined values using XRD : a=16.24, b=6.64, c= 13.49 Å. By performing NPT simulations at 1bar and 300K the agreement becomes slightly better. Also infrared spectra were determined using

NPT simulations. During the NPT simulation, the breathing mode of MIL-53 was also observed at a frequency of 6.7 1/cm. In a next step the newly derived force field will be used to study the adsorption of aromatic guests in the MIL-53 pore system.

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