Ab initio parametrized force field for the flexible metal organic framework MIL-53(Al)

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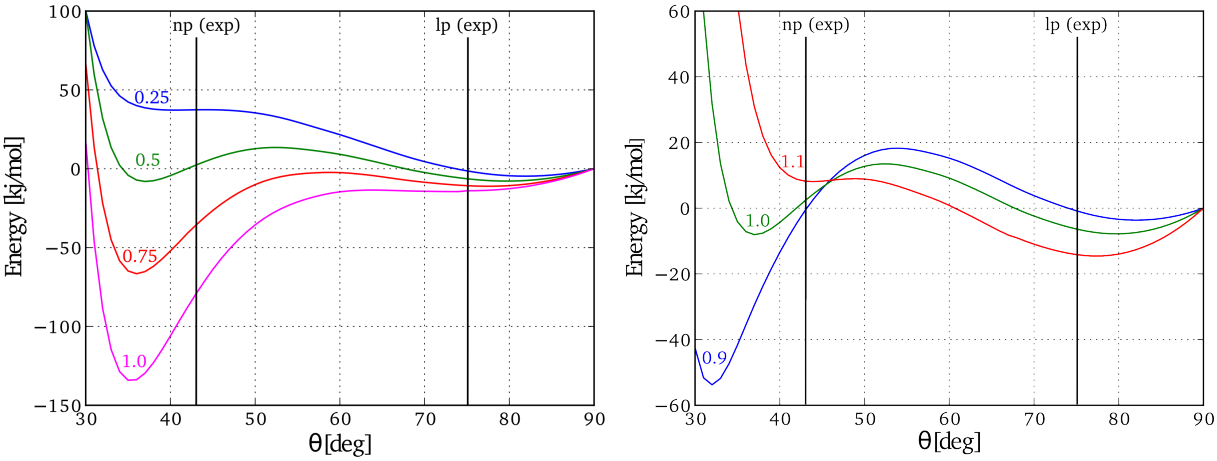
A force field is proposed for the flexible metal-organic framework MIL-53(Al), which is calibrated using density functional theory calculations on non-periodic clusters[1]. The force field has three main contributions: an electrostatic term based on atomic charges derived with a modified Hirshfeld-I method, a van der Waals (vdW) term with parameters taken from the MM3 model [2] and a valence force field whose parameters were estimated with a new methodology that uses the gradients and Hessian matrix elements retrieved from non-periodic cluster calculations.



(a) Rescaling epsilons (a) Rescaling sigmas

***Figure 1**: Energy profiles of the breathing mode after uniformly rescaling (a) the vdW-interaction strength (b) the vdW radii by a factor indicated above each curve. The experimental lines of lp and np are taken from Ref. 3*

The new force field, predicts geometries and cell parameters that compare well with the experimental values both for the large and narrow pore phases. The energy profile along the breathing mode of the empty material (Fig. 1) reveals the existence of two minima, which confirms the intrinsic bistable behaviour of the MIL-53. Even without the stimulus of external guest molecules the material may transform from the large pore (lp) to the narrow pore (np) phase [3]. The relative stability of the two phases critically depends on the vdW parameters and MM3 dispersion interaction has the tendency to overstabilize the np phase.

[1] Vanduyfhuys et al., *submitted to J. Chem.Theory Comput.*
[2] Allinger et al. *J. Am. Chem. Soc.* **1989**, 111, 8551
[3] Liu et al. *J. Am. Chem. Soc.* **2008**, 120, 11813