Empty host breathing profiles of MIL-53 type frameworks with various cations at the nodal points

Louis Vanduyfhuys, Toon Verstraelen, Matthias Vandichel, An Ghysels, Michel Waroquier, Veronique Van Speybroeck

Center for Molecular Modeling, Ghent University, Technologiepark 903, 9052 Zwijnaarde, veronique.vanspeybroeck@ugent.be

Some Metal-organic frameworks (MOFs) show an intriguing flexible behavior, in which the pores can open or close upon external stimuli such as temperature, gas and liquid exposure, etc. This breathing behavior has been most extensively studied to date for the MIL-53 type framework which was originally characterized by Férey and co-workers.[1] Recently, we developed an ab initio parametrized force field for the MIL-53(Al) framework, which enabled us to calculate the energy profile along the breathing mode of the empty material, which revealed the existence of two minima corresponding to the large and narrow pore phase.[2] Indeed Liu et al. showed experimentally the intrinsic bistable behavior of the material and also Walker et al. showed the existence of two minima by means of first principle calculations.[3,4] The MIL-53 series of materials has been synthesized with a series of cations at the nodal points (Al, Cr, Fe, Ga, Sc and In) and interesting differences in the breathing behavior of these materials were observed, which could not only be observed in terms of the hydration with trapped water molecules.[5-8] Clearly the size and the electronic structure of the metal play also a crucial role. To unravel these features, we calculated free energy profiles of the empty host along the breathing angle using Density Functional Theory calculations including an empirical dispersion term and using the Nudged Elastic Band methodology for MIL-53 materials bearing Cr, Al, Ga and In at the nodal points. In parallel we extended our force field to other metals which allowed us to also construct similar profiles. The latter simulations do have the advantage that they allow to provide insight into the relative magnitude of the various energy contributions (covalent, electrostatic, dispersion,…). This study gives a deeper understanding in the intrinsic bistable behavior of MIL-53 type materials.

[1] Loiseau, T et al. *Chem. Eur. J.* **2004**, 10, 1373-1382; [2] Vanduyfhuys, L et al., submitted to *J. Chem. Theory Comput*. **2012**; [3] Liu, Y., J. H. Her et al., *J. Am. Chem. Soc.* **2008**, 130, 11813-11818; [4] Walker, A. M. et al., *Ang. Chem. Int. Ed.* , 2010, 49(41): 7501-7503; [5] Serre C et al. *J. Am. Chem. Soc.* **2002**, 124, 13519-13526; [6] Whitfield, TR et al. J *Solid State Sci.* **2005,** 7, 1096-1103; [7] Millange, F et al. *Chem. Commun.* **2008**, 4732-4734; [8] Volkringer, C. et al. *Dalton Trans.* **2009**, 2241-2249