Quantum Chemical Investigation of MOF-74-Mg-I and II as Proof of Concept to Reliable Dispersion Dominated Gas Adsorption Predictions

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Abstract

Metal-Organic Frameworks (MOFs) are a large family of synthetic hybrid compounds which have shown promising potential for uses in gas separation and storage. Comprised of interchangeable metal and organic linkers, the number of possible structures is immense and far from being exhausted. As such, looking for reliable means to efficiently probe the efficiency of these structures toward their many potential applications as well as to have a better understanding of the factors that influence their effectiveness in gas sorption applications, is of paramount importance from a chemical and materials engineering stand point. The application of electronic structure methods and, in particular, the use of computationally efficient theoretical approximations such as those provided by Density Functional Theory (DFT) allow for reliable quantum chemical investigation tools. DFT is well suited toward modeling MOFs thanks to its ability to predict equilibrium structures and corresponding energies for multi-electronic systems and, although via approximated implementations, its potential at describing intermolecular interactions dominated by dispersion forces. The MOF-74-M (M=metal) family constitutes an ideal framework to test these method's effectiveness in predicting adsorption due to its open metal sites; and since it has been synthesized with a variety of different metals, varying organic ligand lengths, and an assortment of functionalizations, it is a useful framework for testing the influences on molecular adsorption energies. The chosen MOF is the well-known MOF-74-Mg-I, a hollow hexagonal framework with Mg^{2+} vertices connected by 2,5-dihydroxy-terephthalte linkers, which is used as a benchmark to confirm known adsorption energies of N_2, CO, CO_2, CH_4, C_2H_6, and H_2O in the MOF-74-Mg-I cavity through the use of the plane-wave Quantum Espresso code. The work is further extended to describe original results obtained for the mentioned molecules in the similarly structured but larger pore MOF-74-Mg-II with respect to different molecular loadings. Results obtained via a fully periodic approach and via a molecular cluster approach are presented showing consistently higher binding energies for the larger pore MOF-74-Mg-II system than the smaller pore MOF-74-Mg-I.

Biosketch

Thomas Ripplinger is a second year graduate student in the Department of Chemistry at Michigan Tech. His research investigates the factors influencing long range and dispersive interactions in periodic materials.