Progress Report

Grant (DE-FG02-11ER16283) entitled 'Bridging the Gap Between Quantum Chemistry and Classical Simulations for CO_2 Capture'

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Summary of work accomplished:

We have developed a systematic procedure to generate transferable force fields to simulate the behavior of CO_2 in open-metal-site metal organic frameworks using high-level quantum chemical calculations. Monte Carlo simulations based on an ab initio force field for CO_2 in the Mg_2(dobpdc) material have been employed to describe the interactions of CO_2 with open metals. Our study has shed some light on the interpretation of thermodynamic data of flue gas in Mg_2(dobpdc). This force field accurately describes the chemistry of the open metal sites, and is transferable to other structures.

We have also characterized the mechanism of carbon dioxide adsorption in the amine-functionalized metal-organic framework mmen-Mg_2(dobpdc) by quantum chemical calculations. The material is predicted to present a two amine to two CO_2 stoichiometry with a higher capacity and weaker CO_2 binding energy than that of the two to one stoichiometry observed in most amine-functionalized adsorbents. We have explained this behavior in the form of a hydrogen-bonded complex, involving two carbamic acid moieties resulting from the adsorption of CO_2 onto the secondary amines.

With a combination of quantum chemical methods and classical simulation techniques, we are currently investigating different metal organic frameworks having the general formula M_2(dobpdc), where M is a first-row transition metal. We are also considering different guests, including CO_2, CO, O_2, N_2, H_2S, SO_2, methane, and ethane. The goal is to predict if there is a material that will be selective for one or more specific guests and, critically, to explain *why* by understanding the specific chemical interactions that are occurring.

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List of publications that acknowledge support

- Dzubak, L.-C. Lin, J. Kim, J. A. Swisher, R. Poloni, S. N. Maximoff, B. Smit, L. Gagliardi *Ab initio Carbon Capture in Open-Site Metal Organic Frameworks* Nature Chemistry 4, 810-816 (2012)
- N. Planas, A. L. Dzubak, R. Poloni, L.-C.Lin, A. McManus, T. M. McDonald, J. B. Neaton, J. R. Long, B. Smit and L. Gagliardi *The Mechanism of Carbon Dioxide Adsorption in an Alkylamine-Functionalized Metal-Organic Framework* J. Am. Chem. Soc., under review (2013)