

First-Principles Investigation of Functionalized Metal-Organic-Frameworks for Energy Efficent CO₂ Capture

Aseem Rajan Kshirsagar¹, Jing Li², Claudio Attaccalite², Roberta Poloni¹ ¹Univ. Grenoble Alpes, CNRS, Grenoble-INP, SIMaP, Grenoble, France ²Institut Néel, Grenoble, France



trans

electron

electron

Introduction: Efficient technologies for CO₂ capture and its sequestration can be vital in mitigating the problem of climate change arising from increasing atmospheric CO₂ levels. Metal Organic Frameworks (MOFs) are promising crystalline solids with high porosity and affinity for CO₂ due to strong interaction with metal modes. Here, we study MOFs functionalized with photo-isomerizing azobenzene molecules for light-stimulated capture and release of CO₂. The structure of photo-isomerizing azo functionalizations can be changed (*trans* to *cis* and viceversa) with light stimulus in order to sterically block-unblock the metal nodes of MOF interacting with CO_2 , to achieve efficient capture and release of CO₂. We shed light on 1) role of structure of embedded molecules on adsorption, 2) calculation and tuning of the optical spectra of functionalized MOFs to increase the photo-stationary yield of embedded isomers, to increase the efficiency of O_2 capture.

Absorbance

Background and initial study

Current work and future directions





a) Potential energy surface of *cis* structure, b) relaxed structures of two *cis* configurations [E(cis1) – E(cis2) = 111 meV]

Using DFT and classical NVT simulations, we find that the mechanism behind the reversible capture is (un)blocking of metal node by *cis* (*trans*) isomer².



Calculated optical spectra

• azobenzene:



• PCN-123 ligand



Benchmarking our calculation methods with azobenzene and PCN-123 ligand, we attempt, further, to calculate the absorption spectra of the PCN-123 by considering only fragments of the MOF and using QM/MM approach to incorporate the effects of the rest of the MOF environment.



Absorption spectra of trans PCN-123 fragment 1 as a function of dielectric constant of the MOF environment

• Improvement at DFT level using **ESP charges of atoms in MM part** Benchmarking the methodology using more expensive periodic calculations (because of large unit cells and high number of atoms)

Future Directions



1. Park et al. Journal of the American Chemical Society 2011, 134. 2. Yang, Kshirsagar et al. *Chemistry-A European Journal* (accepted). 3. Bléger et al. Journal of the American Chemical Society 2012, 134. 4. Li et al. *Physical Reviews B* 2018, 97. 5. Muller et al. Chemistry-A European Journal 2017, 27.

This PhD project is funded by ANR-15-CE06-0003-01. Computational resources granted by GENCI (under the CINES grant number A0020907211), CIMENT (froggy infrastructure) and Ohio Supercomputer Center (OSC) were used. We thank all these agencies for their support.