Computer Modeling of CO_2 Capture in the Nanoporous Material ZIF-8

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Introduction

Figure 1. Smokestack Gas Emissions: An important Industrial Source of CO_2

CO2 Capture and Storage (CCS) represents a serious strategy to reduce CO_2 emissions in the global challenge of mitigating global warming. CCS involves scrubbing vast amounts of CO_2 from energy producing combustion processes (coal burning) and permanently storing it. Currently, large scale CCS is not practical because an energy and cost effective technology to scrub CO_2 from combustion flue streams has not been developed.

Metal Organic Frameworks for CO_2 Capture

Metal Organic Frameworks (MOFs) are materials which have recently been shown to display exciting promise for CO_2 capture (Science **2008**, *319*, 939). MOFs are nanoporous solids, meaning they have pores and cavities at the scale of molecules. These pores give some MOFs huge internal surface areas and the ability to reversibly capture vast amounts of CO_2, some as much as 83L of gas per 1L of material.

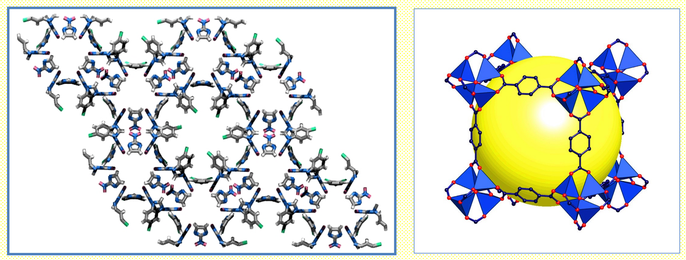

Figure 2. An Example of a Metal Organic Framework. An extended network is shown on the left and a unit cell is shown on the right, with the yellow ball representing a pore

MOFs could form the basis of a new energy efficient technology to scrub CO2 from the combustion flue stream of coal burning power plants (which are the world's biggest single source of CO_2).

The most serious limitation of MOFs for CO2 capture is that they are poisoned by water, a major combustion product, and other common combustion products.

Objectives

Recently, the Woo lab was able to show that computer simulations can predict the amount of CO_2 that is adsorbed by Metal Organic Frameworks and the location of the binding sites. (*Science* **330** ,650 (2010)). Unfortunately, very limited experimental data is available for water and other gases.

The goal of this work is to evaluate the how well these simulation techniques predict the nature of adsorption of benzene ,water and DMF, for which limited experimental data was recently acquired.

The long term goal of the lab's work is to use computer simulation to aid in the molecular design of new Metal Organic Frameworks for CO_2 capture.

Methodology

Molecular simulation has been found to be predictive of binding site localisation within a Metal Organic Framework. The geometry of the rigid ZIF-8 structure as well as that of the small molecules must be optimized using high accuracy Density Functional Theory calculations.

In order to explore the potential energy surface of the system being studied, several Grand Canonical Monte Carlo (GCMC) simulations are run, using molecular mechanics and in house developed scripts.

The Grand Canonical (GC) part inserts and deletes guest molecules, which reaches equilibrates with a gas reservoir at a given pressure. The Monte Carlo (MC) part of the code involves random samplings of the system based on thermodynamics at regular time steps. At each step, the new configuration of guest molecules within the rigid ZIF can either be accepted or not depending on thermodynamic criteria. It should however be noted that a less energetically favourable configuration always has a finite probability of being accepted. The statistical sampling of molecule positions gives binding data based on probability distributions.

Figure 3. A Step in a Typical GCMC Simulation for a Metal Organic Framework

Results

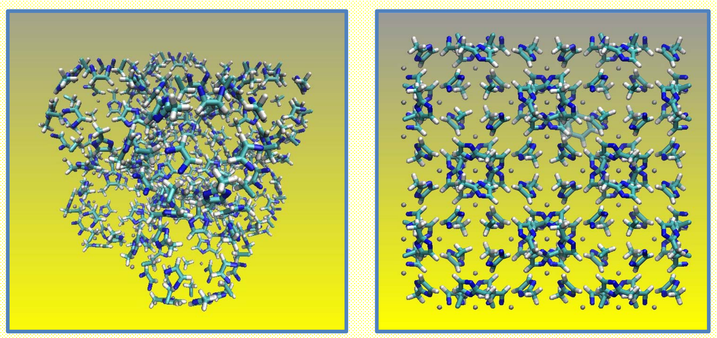

Figure 4. Rigid ZIF-8 Structure with DFT Geometry Optimized Hydrogen Atoms

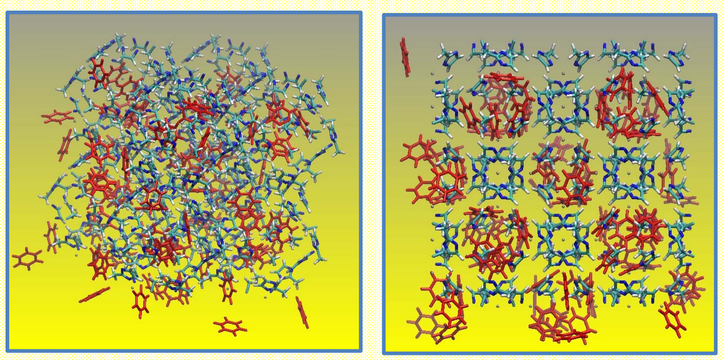

Figure 5. Example of Molecule adsorbed in a Framework Pore: Benzene Adsorbed in one of ZIF-8's Pores

Figure 5. Rigid ZIF-8 Structure with Adsorbed Benzene Molecules Isosurface & Probability Plots Show that Benzene Binds Preferentially Through its Carbon Atoms

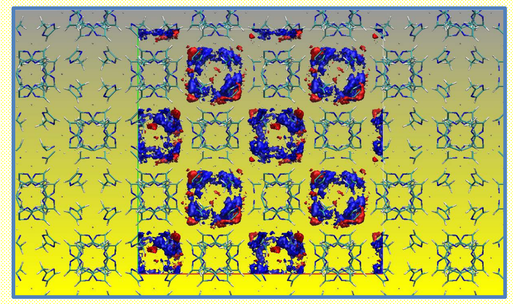

Figure 6. Rigid ZIF-8 Structure with Adsorbed DMF Molecules Overlayed Nitrogen (Blue) and Oxygen (Red) Probability Plots Show that DMF Molecules have Certain Favoured Binding Orientations

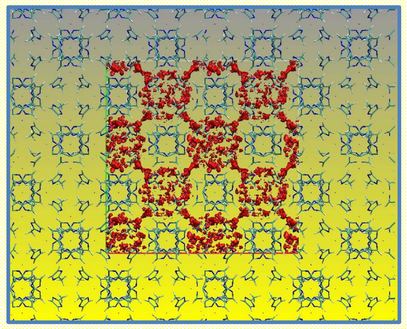

Figure 7. Rigid ZIF-8 Structure with Adsorbed Water Molecules Isosurface & Probability Plots Show that Water Molecules are much more in the Center of the Pore as well as Being Found in the Small Channels Separating ZIF-8 Unit Cells

Conclusion

The different isosurface and probability plots, which give a good idea of the possible binding sites within ZIF-8, depend strongly on the type of guest molecule being analyzed. This shows that binding is likely to differ depending on the guest molecule being adsorbed by the ZIF-8 Metal Organic Framework.

Future Work

This structural data could be used for comparison with experimental data in order to evaluate the accuracy of GCMC simulation for ZIF-8 analysis. Computational guest molecule uptake could also be compared to experimental guest molecule uptake.

References

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