# FMRI RET 2017-Theoretical Investigation of Hydrogen Sorption in Metal-organic Framework NOTT-101


Ileana Bermudez Luna [1], Douglas Franz[2], Dr. Tony Pham[2], Dr. Brian Space[2]

1. Gaither High School; 2. Department of Chemistry, University of South Florida


## Background

- The synthesis and characterization of metal-organic frameworks, or MOFs, is an increasingly popular and innovative field of investigation among the scientific community, due to their potential applications for solving environmental and industrial issues such as hydrogen ($H_2$) storage and carbon dioxide ($CO_2$) capture. MOFs are crystalline porous structures that are commonly synthesized by coordinating metal ions or clusters with organic ligands as linkers.
- The MOF NOTT-101 (NOTT = University of Nottingham) has been computationally investigated to determine its hydrogen sorption mechanism. It is an NbO (Niobium (II) Oxide) type MOF that contains binuclear Cu (II) paddlewheel nodes which are connected by L1 linkers (Figure 1).
- The focus of this research is to theoretically investigate the hydrogen sorption capacity in NOTT-101 by using grand canonical Monte Carlo (GCMC) simulations. Subsequently, the results will be compared with experimental adsorption measurements and neutron powder diffraction (NPD) data.

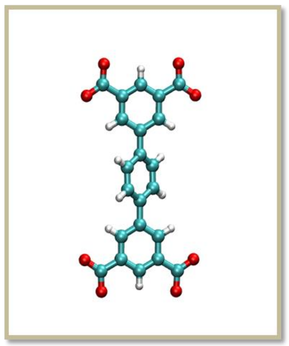


**Figure 1**. Single L1 organic linker. Atom colors: C = cyan, H = white, O = red.

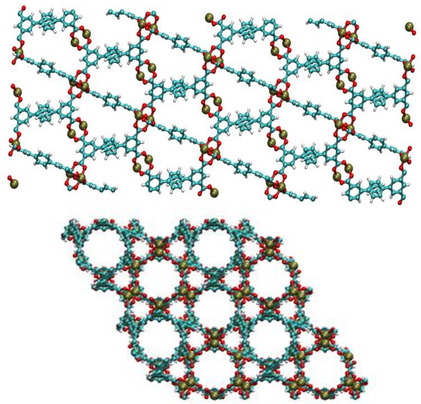


**Figure 2**. Different crystallographic views of NOTT-101 supercell. Atom colors: C = cyan, H = white, O = Red and Cu = tan.

## Objectives

**Obtain NOTT-101 X-Ray Crystal Structure.**

**MOF Parametrization and Perform Hydrogen Sorption Simulations Using GCMC.**

**Analyze and Compare Results from Simulations with Experimental Adsorption Measurements and NPD.**

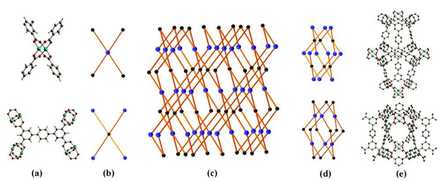



**Figure 3:** Views of (a) NOTT-101 nodes structures; (b) simplified 4-connect node; (c) NbO type framework; (d) and (e) structures of two types of cages [1].

## Approach

**Figure 4 (below)**. Chemically distinct atom labeled of NOTT-101. Atom colors: C = ivory, H = silver, O = red and Cu = mustard.

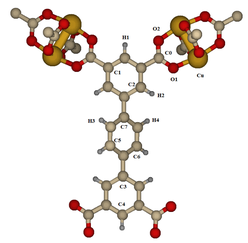
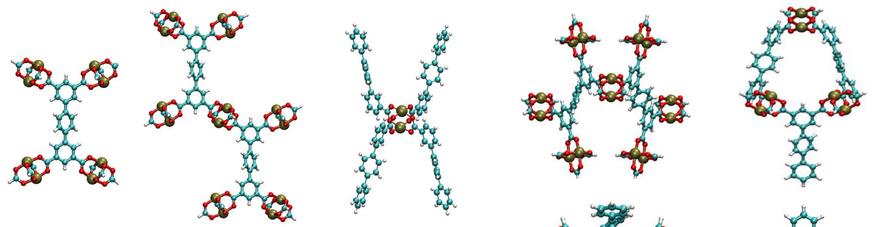


**Figure 5 (below)**. Representative fragments of NOTT-101. Atom colors: C = cyan, H = white, O = red and Cu = tan.

- Overlapped phenyl groups were discarded from the MOF structure.
- Chemically distinct atoms were identified. A total of fifteen of these atoms were found in NOTT-101 (Figure 4).
- Representative fragments were made with cap cut-off hydrogen atoms for better simulations (Figure 5).
- Single point quantum mechanical energy calculations were performed, followed by electrostatic potential fit to calculate partial charges (Table 1).
- The calculated charges were use to parameterize the MOF.
- GCMC simulations for hydrogen sorption were completed using three different models of increasing complexity: 1) Buch, 2) BSS and 3) BSSP (Figures 6).
- The collected data were analyzed and compared with experimental adsorption measurements and neutron diffraction (NPD) data (Figures 8 & 9).



## Results

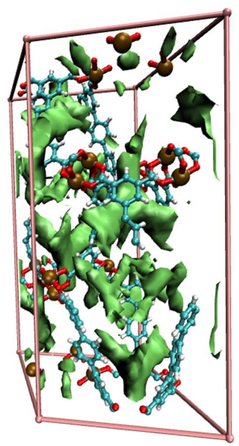


**Figure 6 (above)**. Perspective view through B axis of hydrogen sorption (green area) in NOTT-101. Atom colors: C = cyan, H = white, O = red and Cu = tan.

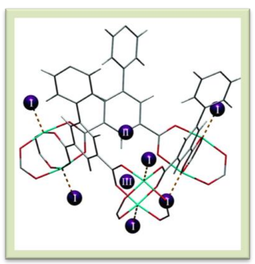





**Figure 7 (left)**. Experimental hydrogen sorption sites (I, II & III) in NOTT-101. Atom colors: C = black, H = white, O = red and Cu = turquoise[1].

**Table 1 (below)**. Partial charges for each chemically distinct atom.

| Atom ID | Partial Charge | Atom ID | Partial Charge |
|---|---|---|---|
| Cu | 1.12581 | C1 | -0.14787 |
| O1 | -0.74782 | C2 | -0.13069 |
| O2 | -0.74549 | C3 | 0.05790 |
| H1 | 0.17600 | C4 | -0.08540 |
| H2 | 0.16634 | C5 | -0.15787 |
| H3 | 0.14610 | C6 | -0.18925 |
| H4 | 0.13611 | C7 | 0.06374 |
| C0 | 0.96895 | | |

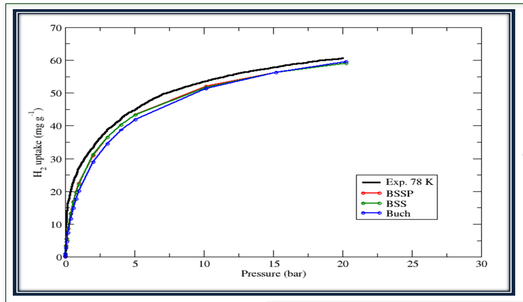



**Figure 8 (left)**. Simulated $H_2$ sorption isotherms at 78K in NOTT-101 compared with experimental ones.

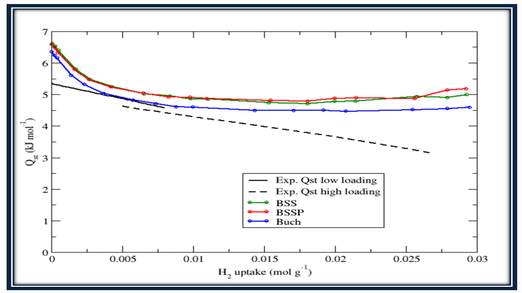



**Figure 9 (right)**. Isosteric heat of adsorption (Q*st*) for $H_2$ in NOTT-101 from simulations compared with experimental data .

## Conclusions

- The results obtained from simulations using the BSSP and BSS models found reasonable agreement with the corresponding experimental measurements for $H_2$ sorption in NOTT-101.
- The results for isosteric heat of adsorption simulations using Buch model shows very close values compared with the experimental data.
- These results confirmed the correlation between MOF modeling and experimental studies, as well as how utilizing explicit polarization in classical GCMC simulations can effectively reproduce experimental gas sorption behavior in these porous crystalline structures.
- This new technology also provides a new viable tool for elucidating gas sorption interaction mechanisms.

## References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## Acknowledgement


The author would like to thank Dr. Brian Space and all the students that are part of his lab, especially Douglas Franz (my mentor) and Dr. Tony Pham for all their patience and time. Also, the FMRI-RET for this great opportunity and the USF Research Computing and XSEDE for providing the computer resources for this research.