

# **Nanoporous Materials Genome Center All-Hands Meeting**

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October 18 & 19, 2014 | University of Minnesota

# Nanoporous Materials Genome Center All-Hands Meeting

October 18 & 19, 2014 | University of Minnesota

**Location:** The Saint Paul Hotel  
350 Market Street, St. Paul, MN 55102  
800-292-9292 [www.saintpaulhotel.com](http://www.saintpaulhotel.com)

## Saturday, October 18, 2014

- 8:00 am** Continental Breakfast Buffet, Foyer, James J. Hill Room
- 8:30 am** Meeting begins in the James J. Hill Room
- 8:35 am Welcome and update on the center, Ilja Siepmann
- 8:45 am BES Program Officers, Mark Pederson & Larry Rahn
- 9:00 am** **Materials Genome and Large-scale Screening of Nanoporous Materials**
- 9:00 am Predictive Materials Discovery: Finding Optimal Zeolites for Challenging Separation and Chemical Conversions  
Peng Bai, Chris Knight, Michael Deem, Michael Tsapatsis, and Ilja Siepmann
- 9:15 am An Efficient Method to Search MOF Databases: Pre-Combustion CO<sub>2</sub> Capture  
Yongchul Greg Chung, Diego A. Gomez-Gualdrón, and Randall Q. Snurr
- 9:30 am Evaluation of DFT functional performance for the prediction of MOF ground state structure  
Dalar Nazarian and David Sholl
- 9:45 am Small Molecule Binding in the M-MOF-74 Series  
Gregory Mann, Bess Vlasisavljevich, Kyuho Lee, Jeff Neaton, and Berend Smit
- 10:00 pm Computational Screening of MOFs with Open Metal Sites for Adsorption and Catalysis Applications  
Konstantinos Vogiatzis, Emmanuel Haldoupis, J. Ilja Siepmann, and Laura Gagliardi
- 10:15 am Prediction of High Deliverable Capacity Metal-Organic Frameworks with an Evolutionary Algorithm  
Yi Bao, Richard L. Martin, Cory Simon, Maciej Haranczyk, Berend Smit, and Michael W. Deem
- 10:30 am The Nanoporous Materials Genome on the World Wide Web  
Emmanuel Haldoupis, Daniel Gunter, Maciej Haranczyk, and J. Ilja Siepmann
- 10:45 am Questions and discussion
- 11:00 am** **Coffee Break**
- 11:20 am** **Synthesis and Properties of Functional Nanoporous Materials**
- 11:20 am Metal-Organic Magnets  
Lucy E. Darago, Eric D. Bloch, Dianne J. Xiao, Julia Oktawiec, Joel S. Miller, and Jeffrey R. Long
- 11:35 am Decomposing Chemical Warfare Agents Utilizing Metal-Organic Frameworks  
Joseph E. Mondloch, Michael J. Katz, William C. Isley, Pritha Ghosh, Peilin Liao, Randall Q. Snurr, Christopher J. Cramer, Joseph T. Hupp, and Omar K. Farha
- 11:50 am The Synergy Between Anion Photoelectron Spectroscopy and Theory  
Jacob Graham, Allyson Buytendyk, Joe Gould, and Kit Bowen
- 12:05 pm Questions and discussion
- 12:30 pm** **Buffet Lunch and Discussion of Collaborative Research Projects, Summit Room**  
Junior Researchers, Members of the Advisory Board, Guests, and BES Program Officers
- Principal Investigator Lunch, Archbishop Ireland Room**  
Principal Investigators

- 1:30 pm Advances in Computational Methods for Nanoporous Materials**
- 1:30 pm A New Theoretical Framework for Implementing Self-Interaction Corrections into DFT with DFT Scaling  
Mark Pederson
- 1:45 pm Beyond Energies: Molecular Geometries as Metrics for Assessing Electronic Structure Approaches for Intermolecular Interactions  
Jonathon Witte, Jeffrey Neaton, and Martin Head-Gordon
- 2:00 pm Force Fields for Fe-MOF-74  
Laura Fernandez, Bo Wang, and Donald G. Truhlar
- 2:15 pm The Projection-Based WFT-in-DFT Embedding Method: Application to Organometallic and Condensed-Phase Systems  
Taylor Barnes, Pengfei Huo, Jason Goodpaster, Jakub Kaminski, Oleg Borodin, Thomas Miller III
- 2:30 pm Evaluation of Force Field Performance for High-Throughput Screening of Gas Uptake in MOFs  
Jesse McDaniel, Song Li, Emmanouil Tyllianakis, Randall Snurr, JR Schmidt
- 2:45 pm Deconstructing Hydrogen-Bond Networks in Confined Zeolitic-Imidazolate Frameworks: Implications for Water-Alcohol Separation  
Chun-Hung Wang and Aurora Clark
- 3:00 pm Decomposing Hydrogen Bond Dynamics into Multiscale Components – Implications for Synthesis and Catalytic Schemes of Nanoporous Materials  
Tiecheng Zhou and Aurora Clark
- 3:15 pm Questions and Discussion
- 3:30 pm Coffee Break**
- 3:50 pm Understanding Nanoporous Materials**
- 3:50 pm Mechanism of Oxidation of C<sub>2</sub>H<sub>6</sub> to C<sub>2</sub>H<sub>5</sub>OH at Iron(IV)–Oxo Sites in Magnesium-Diluted Fe<sub>2</sub>(dobdc)  
Pragya Verma, Konstantinos D. Vogiatzis, Nora Planas, Joshua Borycz, Dianne Xiao, Jeffrey R. Long, Laura Gagliardi, and Donald G. Truhlar
- 4:05 pm Periodic DFT Study of the Preferential Location of Germanium, Aluminium and Gallium in the UTL and IPC-2a Zeolites  
Samuel Odoh, Michael Deem, and Laura Gagliardi
- 4:20 pm Defining the Proton Topology of the Zr<sub>6</sub>-Based Metal–Organic Framework NU-1000  
Nora Planas, Joseph E. Mondloch, Samat Tussupbayev, Joshua Borycz, Christopher J Cramer, Joseph T. Hupp, Omar K. Farha, and Laura Gagliardi
- 4:35 pm Development of Transferable Potentials for Phase Equilibria Force Field for Hydrogen Sulfide and Adsorption in All-silica Zeolites  
Mansi S. Shah, Michael Tsapatsis, and J. Ilja Siepmann
- 4:50 pm Predictions on the organophosphate hydrolysis of nerve agents catalyzed by NU-1000  
William Isley III and Christopher J. Cramer
- 5:05 pm Metal Organic Framework Based Vehicle for Nitric Oxide Delivery  
Revati Kumar, Tanping Li, and Kiara Taylor-Edinbyrd
- 5:20 pm Molecule Models for Spin-Crossover, Catalysis, and Proton Conduction in Metal Organic Frameworks  
Zack Terranova, Jordi Cirera, and Francesco Paesani
- 5:35 pm Questions and Discussion
- 6:00 pm Dinner in the Market Street Café, lower level of the hotel**
- 7:30 pm Poster Session – Summit Room**
- 9:30 pm End of Poster Session**

**Sunday, October 19, 2014**

- 8:00 am** Continental Breakfast Buffet, Foyer, James J. Hill Room
- 8:30 am** Meeting begins in the James J. Hill Room
- 8:30 am Welcome from Director
- 8:40 am** **Breakout Sessions**
- Session I: Benchmarking of electronic structure software and of density functionals for nanoporous materials  
Promenade Ballroom North
- Session II: Enhancing the Nanoporous Materials Genome WWW Interface and Database  
Promenade Ballroom South
- Session III: New Research Challenges for the NMGC  
J.J. Hill Room
- 9:25 am Switch Sessions
- 10:10 am** **Coffee Break**
- 10:30 am Reports from Sessions I, II & III and Discussion  
J.J. Hill Room
- 11:30 am Small working groups to draft reports and small group discussions of projects for year 3
- 12:00 pm** **Box Lunches Delivered to foyer of James J. Hill Room**
- 1:00pm** **Adjourn**

**Nanoporous Materials Genome Center All-Hands Meeting**  
**Poster Session**  
**October 18, 2014 | 7:30 pm – 9:30 pm**  
**Saint Paul Hotel, Summit Room**

Presenters of odd-numbered abstracts are kindly requested to stay near their posters during the first hour and presenters of even-numbered abstracts are kindly request to stay near their posters during the second hour.

1. Predictive Materials Discovery: Finding Optimal Zeolites for Challenging Separation and Catalysis Problems  
Peng Bai, Chris Knight, Michael Deem, Michael Tsapatsis, and Ilja Siepmann
2. Prediction of High Deliverable Capacity Metal-Organic Frameworks with an Evolutionary Algorithm  
Yi Bao, Richard L. Martin, Cory Smith, Maciej Haranczyk, Berend Smit and Michael W. Deem
3. Embedding Methodologies for Electrochemistry: Oxidative Decomposition of Lithium-Ion Battery Solvents  
Taylor Barnes, Jakub Kaminski, Oleg Borodin, and Thomas Miller III
4. A computational study of water behavior in two Zr<sub>6</sub>-Based Metal Organic-Frameworks, UiO-66 and NU-1000  
Varinia Bernales, David Semrouni, Emmanuel Haldoupis, Joshua Borycz, Joe Hupp, Omar Farha, Randy Snurr and Laura Gagliardi
5. The Electronic Structure of Nitrosyl Metal Catecholates  
Gary D. Bondarevsky, Laura Gagliardi, and Randall Snurr
6. CO<sub>2</sub> Adsorption in M-IRMOF10 (M=Mg, Ca, Fe, Cu, Zn, Ge, Sr, Cd, Sn, Ba)  
Joshua Borycz, Davide Tiana, Emmanuel Haldoupis and Ilja Siepmann, Laura Gagliardi
7. Predicting Kinetic Separation of Light Gases in a Flexible Porous Organic Cage Crystal Using Transition State Theory  
Jeffrey Camp and David Sholl
8. An Efficient Method to Search MOF Databases: Pre-Combustion CO<sub>2</sub> Capture  
Yongchul Greg Chung, Diego A. Gomez-Gualdrón, and Randall Q. Snurr
9. Metal-Organic Magnets  
Lucy E. Darago, Eric D. Bloch, Dianne J. Xiao, Julia Oktawiec, Joel S. Miller, and Jeffrey R. Long
10. Understanding bulk properties of metal-organic frameworks using lattice models  
Kathryn Deeg, Bess Vlasisavljevich, Sondre K. Schnell, Stephen Whitlam, and Berend Smit

11. Molecular Sieve Nanosheets  
Neel Rangnekar, Meera Shete, Kumar Varoon Agrawal, Berna Topuz, Prashant Kumar, Issam Ismail, Bahman Elyassi, Christopher W. Macosko, Lorraine Francis, K. Andre Mkhoyan, Benjamin Stottrup, and Michael Tsapatsis
12. Force Fields for Fe-MOF-74  
Laura E. Fernandez, Bo Wang, and Donald G. Truhlar
13. Photoelectron Spectra of Porphyrin Anions: a Preliminary Test for Theory  
Jacob Graham, Allyson Buytendyk, Julian Gould, and Kit Bowen
14. The Nanoporous Materials Genome on the World Wide Web  
Emmanuel Haldoupis, Daniel Gunter, Maciej Haranczyk, and J. Ilja Siepmann
15. Predictions on the organophosphate hydrolysis of nerve agents catalyzed by NU-1000  
William Isley III, and Christopher J. Cramer
16. Solvent-Assisted Linker Exchange and Transmetalation: Alternatives to the De Novo Synthesis of Unattainable Metal–Organic Frameworks  
Olga Karagiari, Wojciech Bury, Amy A. Sarjeant, Charlotte L. Stern, Marianne B. Lalonde, Emmanuel Tylianakis, David Fairen-Jimenez, Christopher E. Wilmer, Omar K. Farha, and Joseph T. Hupp
17. Small Molecule Binding in the M-MOF-74 Series  
Gregory Mann, Bess Vlasisavljevich, Kyuho Lee, Jeff Neaton, and Berend Smit
18. Evaluation of force field performance for high-throughput screening of gas uptake in MOFs  
Jesse McDaniel, Song Li, Emmanouil Tyllianakis, Randall Snurr, JR Schmidt
19. Decomposing Chemical Warfare Agents Utilizing Metal-Organic Frameworks  
Joseph E. Mondloch, Michael J. Katz, William C. Isley, Pritha Ghosh, Peilin Liao, Randall Q. Snurr, Christopher J. Cramer, Joseph T. Hupp, and Omar K. Farha
20. Evaluation of DFT functional performance for the prediction of MOF ground state structure  
Dalar Nazarian and David Sholl
21. Periodic DFT Study of the Preferential Location of Germanium, Aluminium and Gallium in the UTL and IPC-2a Zeolites  
Samuel Odoh, Michael Deem, and Laura Gagliardi
22. Development of Transferable Potentials for Phase Equilibria Force Field for Hydrogen Sulfide and Adsorption in All-silica Zeolites  
Mansi S. Shah, Michael Tsapatsis, and J. Ilja Siepmann
23. Transferable Force Field for gas adsorption in Na-exchanged zeolites  
Huilian Shi, Emmanuel Haldoupis, Peng Bai, Michael Tsapatsis, Ilja Siepmann, and Laura Gagliardi

24. Finding materials for vehicular methane storage  
Cory M. Simon, Rocio Mercado, Jihan Kim, Diego A. Gomez-Gualdron, Jeffrey S. Camp, Yongchul G. Chung, Richard L. Martin, Michael W. Deem, Dan Gunter, Maciej Haranczyk, David S. Sholl, Randall Q. Snurr, and Berend Smit
25. Molecule Models for Spin-Crossover, Catalysis, and Proton Conduction in MOFs  
Zack Terranova, Jordi Cirera, and Francesco Paesani
26. Defining the Proton Topology of the Zr<sub>6</sub>-Based Metal–Organic Framework NU-1000  
Nora Planas, Joseph E. Mondloch, Samat Tussupbayev, Joshua Borycz, Christopher J Cramer, Joseph T. Hupp, Omar K. Farha, and Laura Gagliardi
27. *Ab Initio* Force Field Development for Coordinatively Unsaturated Metal–Organic Frameworks  
Mary Van Vleet and JR Schmidt
28. Mechanism of Oxidation of C<sub>2</sub>H<sub>6</sub> to C<sub>2</sub>H<sub>5</sub>OH at Iron(IV)–Oxo Sites in Magnesium-Diluted Fe<sub>2</sub>(dobdc)  
Pragya Verma, Konstantinos D. Vogiatzis, Nora Planas, Joshua Borycz, Dianne Xiao, Jeffrey R. Long, Laura Gagliardi, and Donald G. Truhlar
29. Computational screening of MOFs with Open Metal Sites for Adsorption and Catalysis Applications  
Konstantinos Vogiatzis, Emmanuel Haldoupis, J. Ilja Siepmann, and Laura Gagliardi
30. Deconstructing Hydrogen-Bond Networks in Confined Zeolitic-Imidazolate Frameworks: Implications for Water-Alcohol Separation  
Chun-Hung Wang and Aurora Clark
31. Beyond Energies: Molecular Geometries as Metrics for Assessing Electronic Structure Approaches for Intermolecular Interactions  
Jonathon Witte, Jeffrey Neaton, and Martin Head-Gordon
32. Decomposing hydrogen bond dynamics into multiscale components – Implications for synthesis and catalytic schemes of nanoporous materials  
Tiecheng Zhou and Aurora Clark

# **Abstracts**

Listed in alphabetical order of first author's name

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# Predictive Materials Discovery: Finding Optimal Zeolites for Challenging Separations and Chemical Conversions

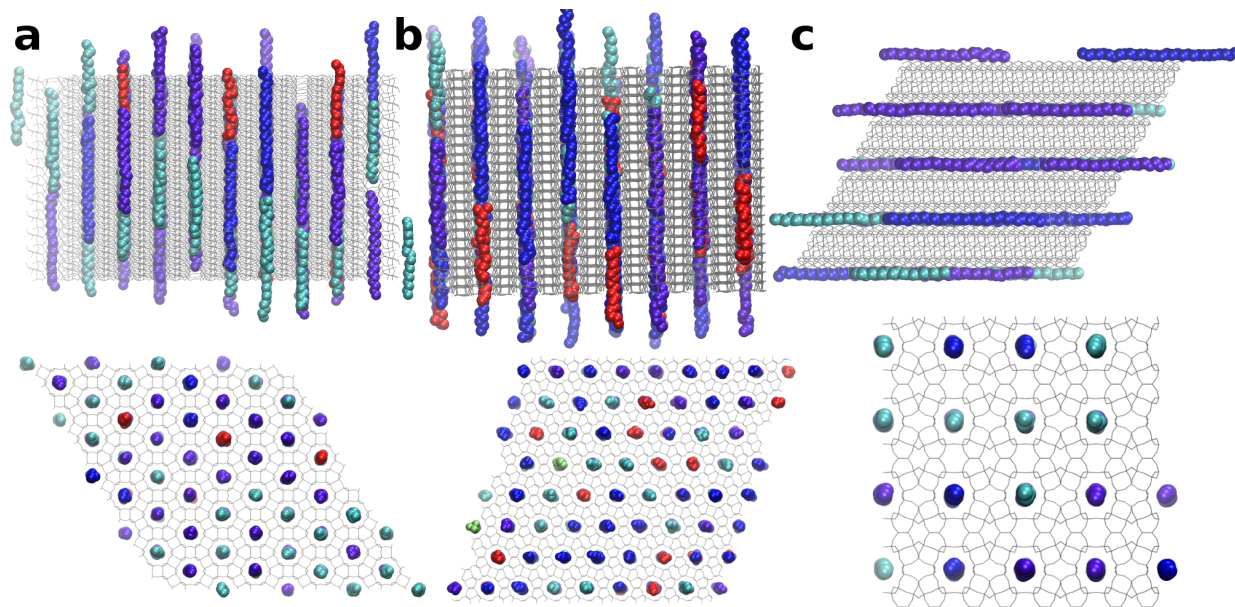
Peng Bai<sup>a</sup>, Chris Knight<sup>b</sup>, Michael W. Deem<sup>c</sup>, Michael Tsapatsis<sup>a</sup>, and J. Ilja Siepmann<sup>a</sup>

<sup>a</sup>Departments of Chemistry and of Chemical Engineering and Materials Science and Chemical Theory Center, University of Minnesota

<sup>b</sup>Leadership Computing Facility, Argonne National Laboratory

<sup>c</sup>Departments of Bioengineering and of Physics and Astronomy, Rice University

Zeolites play numerous important roles in modern petroleum refineries and have the potential to advance the production of fuels and chemical feedstocks from renewable resources. The performance of a zeolite as separation medium and catalyst depends on its framework structure and the type or location of active sites. To date, 213 framework types have been synthesized and >330000 thermodynamically accessible zeolite structures have been predicted. Hence, identification of optimal zeolites for a given application from the large pool of candidate structures is attractive for accelerating the pace of materials discovery. Here we identify, through a large-scale, multi-step computational screening process, promising zeolite structures for two energy-related applications: (i) with the ability to purify ethanol beyond the ethanol/water azeotropic concentration in a single separation step from fermentation broths and (ii) with up to two orders of magnitude better adsorption capability than current technology for linear and slightly branched alkanes with 18-30 carbon atoms encountered in petroleum refining. These results demonstrate that predictive modeling and data-driven science can now be applied to solve some of the most challenging separation problems involving highly non-ideal mixtures and highly articulated compounds.



Snapshots of representative sorbate configurations obtained for adsorption from a liquid phase containing an equimolar hydrocarbon mixture at  $T = 573$  K and  $p = 3$  MPa. Views facing (top row) and along (bottom row) the main channel axis are shown for (a) ATO, (b) MTW, and (c) PCOD 8113534. Zeolite frameworks are depicted as gray lines, and C18, C24, C30, (2C17 and 4C17), and 22C16 molecules as cyan, purple, blue, red, and green spheres, respectively.

# Prediction of High Deliverable Capacity Metal-Organic Frameworks with an Evolutionary Algorithm

Yi Bao<sup>a</sup>, Richard L. Martin<sup>b</sup>, Cory Simon<sup>c</sup>,

Maciej Haranczyk<sup>b</sup>, Berend Smit<sup>c</sup>, Michael W. Deem<sup>a, d</sup>

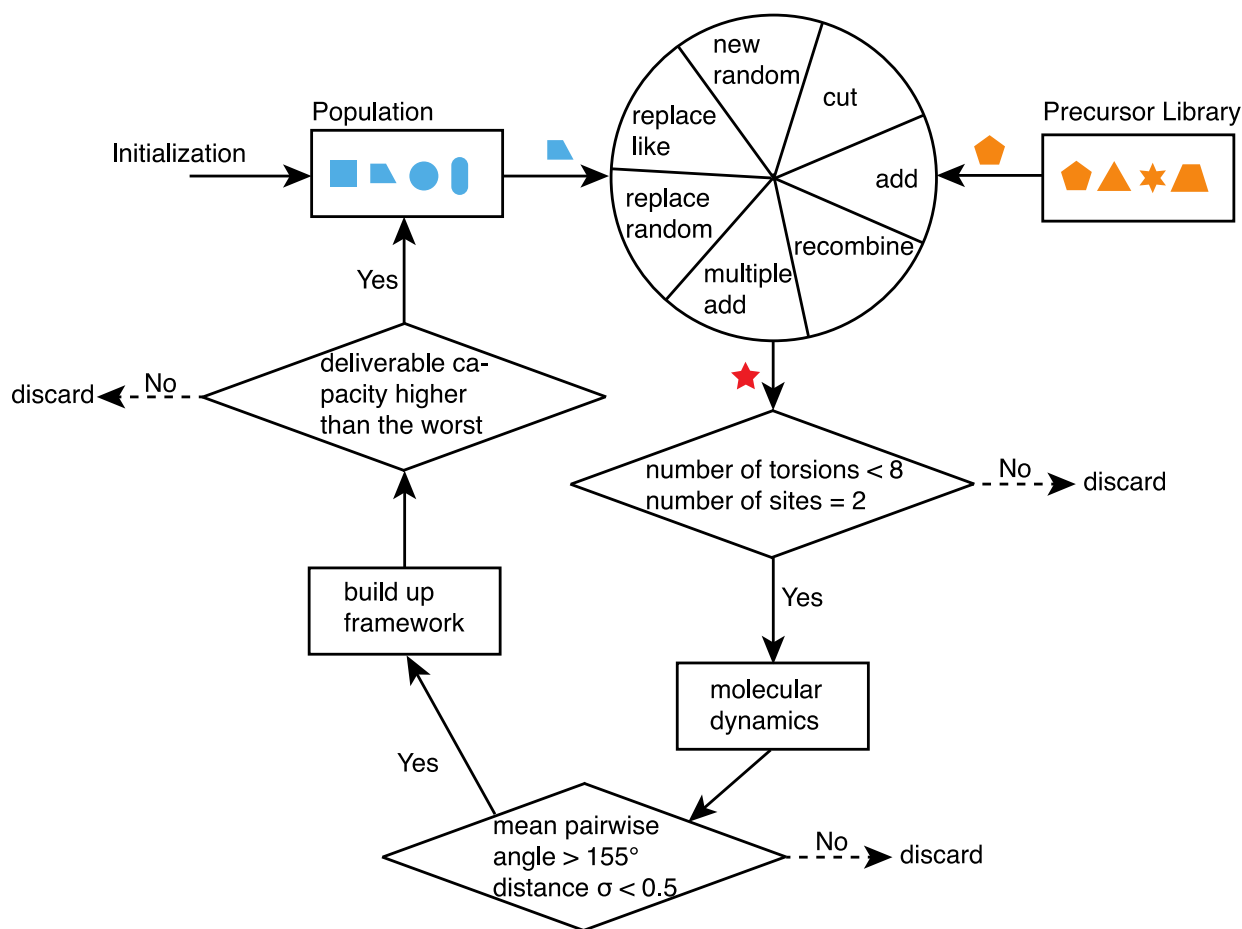
<sup>a</sup>Department of Physics and Astronomy, Rice University

<sup>b</sup>Computational Research Division, Lawrence Berkeley National Laboratory

<sup>c</sup>Department of Chemical & Biomolecular Engineering, University of California, Berkeley

<sup>d</sup>Department of Bioengineering, Rice University

Metal organic frameworks (MOFs) are actively being explored as potential adsorbed natural gas storage materials for small vehicles. We here describe an *in silico* procedure to identify high methane deliverable capacity MOFs. We efficiently search the composition and conformation space of organic linkers for nine MOF networks, finding a total of 48 predicted materials with higher predicted deliverable capacity (at 65 bar storage, 5.8 bar depletion, and 298 K) than MOF-5 in four of the nine networks.



# Embedding Methodologies for Electrochemistry: Oxidative Decomposition of Lithium-Ion Battery Solvents

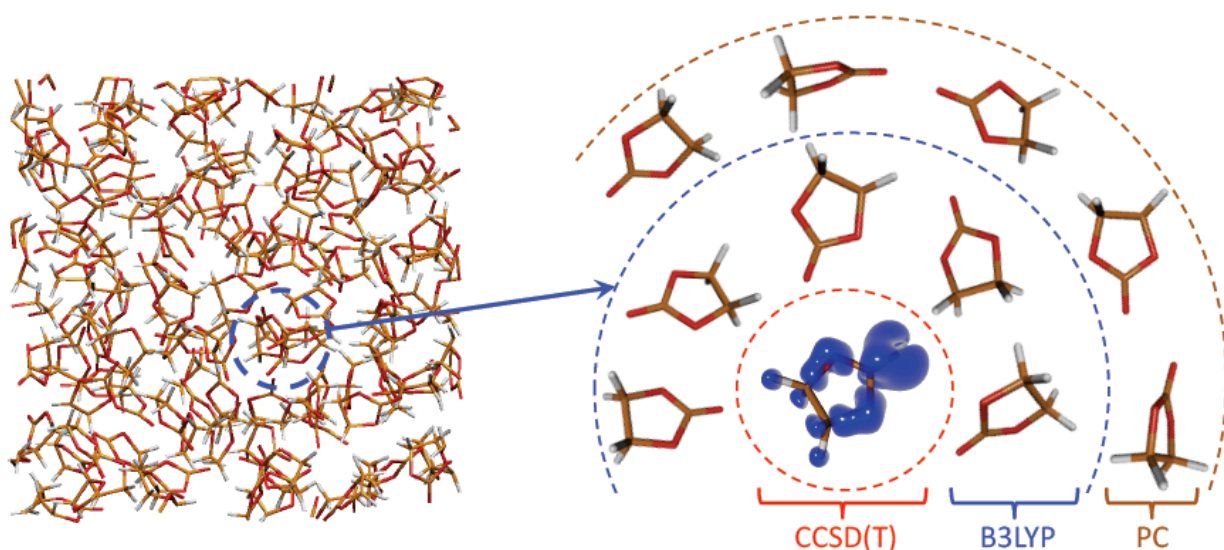
Taylor Barnes<sup>a</sup>, Jakub Kaminski<sup>b</sup>, Oleg Borodin<sup>c</sup>, Thomas Miller III<sup>a</sup>

<sup>a</sup>Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125

<sup>b</sup>Department of Mathematics, University of California, Los Angeles, CA 90095

<sup>c</sup>U.S. Army Research Laboratory, Electrochemistry Branch, Sensors & Electron Devices Directorate, 2800 Powder Mill Road, Adelphi, MD 20783

A central challenge in the refinement of lithium-ion batteries is to avoid cathode-induced oxidative decomposition of electrolyte solvents, such as ethylene carbonate (EC) and dimethyl carbonate (DMC). We study the oxidation potentials of neat EC, neat DMC, and 1:1 mixtures of EC and DMC using our newly developed projection-based embedding method, which we demonstrate to be capable of correcting qualitative inaccuracies exhibited by conventional Kohn-Sham density functional theory (DFT) methods. Our wavefunction-in-DFT embedding approach enables accurate calculation of the vertical ionization energy (IE) of individual molecules at the CCSD(T) level of theory, while explicitly accounting for the solvent using a combination of DFT and molecular mechanics interactions. We find that the ensemble-averaged distributions of IEs are consistent with a linear response interpretation of the statistics of the solvent configurations, enabling determination of both the intrinsic adiabatic oxidation potential of the solvents and the corresponding solvent reorganization energies. Interestingly, we demonstrate large contributions to the solvation properties of DMC from quadrupolar interactions, resulting in a much larger solvent reorganization energy than that predicted using dielectric continuum models. This insight into the nature of DMC intermolecular interactions supports an improved understanding of the solvation structure of ions in lithium-ion batteries.



**Figure:** Summary of the embedding strategy. First, equilibrium solvent configurations are generated using classical MD simulations. Then, embedding calculations are performed to determine the vertical IE of each configuration.

# The Projection-Based WFT-in-DFT Embedding Method: Application to Organometallic and Condensed-Phase Systems

Taylor Barnes<sup>a</sup>, Pengfei Huo<sup>a</sup>, Jason Goodpaster<sup>b</sup>, Jakub Kaminski<sup>c</sup>, Oleg Borodin<sup>d</sup>,  
Thomas Miller III<sup>a</sup>

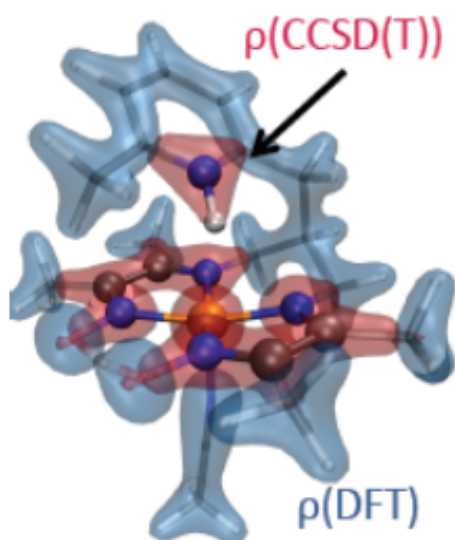
<sup>a</sup>Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125

<sup>b</sup>Department of Chemistry, University of California, Berkeley, CA 94720

<sup>c</sup>Department of Mathematics, University of California, Los Angeles, CA 90095

<sup>d</sup>U.S. Army Research Laboratory, Electrochemistry Branch, Sensors & Electron Devices Directorate, 2800 Powder Mill Road, Adelphi, MD 20783

The computational cost of performing accurate *ab initio* wavefunction theory (WFT) calculations on condensed-phase systems has motivated the development of numerous methods to partition the description of large systems into smaller subsystem calculations. These methods typically describe the interactions between subsystems in an approximate way, often requiring the introduction of fictitious link-atoms between covalently bound subsystems. Our recently developed projection-based WFT-in-DFT embedding method avoids these problems by accounting for interactions between subsystems at the DFT level, without any of the approximations common among other WFT-in-DFT embedding methods. We demonstrate the successful application of this method to challenging problems, including the organometallic catalysis of hydrogen evolution and the condensed-phase oxidation of battery solvents. Our results establish the applicability of the projection-based WFT-in-DFT embedding method to complex, condensed-phase systems, such as metal organic frameworks.



**Figure:** Application of the projection-based WFT-in-DFT embedding method to a cobalt-based catalyst for hydrogen evolution. The red region, which includes the cobalt atom, is treated at the CCSD(T) level of theory, while the remainder of the system is treated at the DFT level of theory. Because of the numerically exact DFT-level treatment of the interactions between subsystems, link-atoms are not necessary for the subsystem calculations.

A computational study of water behavior in two Zr<sub>6</sub>-Based Metal Organic-Frameworks, UiO-66 and NU-1000.

**Varinia Bernales<sup>a</sup>, David Semrouni<sup>a</sup>, Emmanuel Haldoupis<sup>a</sup>, Joshua Borycz<sup>a</sup>, Joe Hupp<sup>b</sup>  
Omar Farha<sup>b</sup>, Randy Snurr<sup>c</sup> and Laura Gagliardi<sup>a</sup>**

<sup>a</sup> Department of Chemistry, University of Minnesota – Twin Cities

<sup>b</sup> Department of Chemistry, Northwestern University

<sup>c</sup> Department of Chemical and Biological Engineering, Northwestern University

Zr<sub>6</sub>-based Metal Organic-frameworks (MOFs) are considered chemically and thermally stable (up to 500 °C) materials. [1] Recently, it was reported that UiO-67 collapses when water vapor is introduced, unlike to its isorecticular analog UiO-66. [2] This shows that the presence of water in the pores of a MOF can lead to instabilities (e.g. hydrolysis and/or capillary force) in the material. These instabilities may lead to a loss of its crystallinity. [3] In this work, we examined the adsorption and diffusion behavior of water in two Zr-based MOFs. We used molecular simulations with available force fields, such as UFF/DREIDING, combined with different set of charges obtained from periodic DFT calculations. As a first step we aim to investigate the reliability of the available force fields and point charge assignment methods for the study of water (solvent) behavior in these systems and subsequently to develop more realistic force fields using quantum chemical calculations.

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[1] *J. Am. Chem. Soc.*, **2008**, 130, 13850-13851.

[2] *J. Mater. Chem., A*, **2013**, 1, 5642-5650.

[3] *Chem. Commun.*, **2014**, **50**, 8944-8946.

## The Electronic Structure of Nitrosyl Metal Catecholates

**Gary D. Bondarevsky<sup>a</sup>, Laura Gagliardi<sup>a</sup>, and Randall Snurr<sup>b</sup>**

a. Department of Chemistry, University of Minnesota

b. Department of Chemical and Biological Engineering, Northwestern University

Metal organic frameworks (MOFs) are composed of metal centers and organic linker molecules in a crystalline structure. MOFs have a nanoporous structure that is highly tunable in size by adjusting the metal nodes or organic ligands. The metal nodes can be anything from a single metal atom to larger polyoxometalate nodes. The organic linker must be a polydentate linker able to connect multiple nodes. Unlike many materials, MOFs can be used for many different applications by varying the metal centers or the organic linkers. The MOF can be tuned to specific applications such as catalysis or gas storage, which are important for energy applications. One such modification has been made to include a catecholate group within the organic linker. The catecholate group can be metallated with various divalent transition metals such as  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Zn}^{2+}$ . These metal–catecholates can be used to bind NO within the MOF. Nitric oxide (NO) is an environmental contaminant present in flue gas produced from power plants; therefore, it is advantageous to bind NO to reduce the pollution from power plants. The electronic structure and binding of NO to the various metal–catecholate systems have been investigated by density functional theory (DFT), and complete active space self-consistent field (CASSCF) followed by second order perturbation theory (CASPT2) methods. Results will be presented on the Mn and Fe systems.

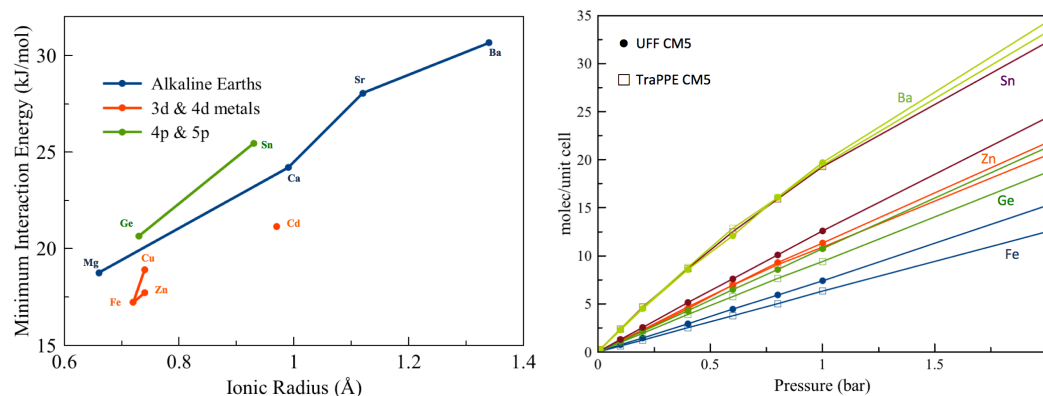
## CO<sub>2</sub> Adsorption in M-IRMOF10 (M=Mg, Ca, Fe, Cu, Zn, Ge, Sr, Cd, Sn, Ba)

Joshua Borycz<sup>a</sup>, Davide Tiana<sup>b</sup>, Emmanuel Haldoupis<sup>a</sup>, Ilja Siepmann<sup>a</sup>, Laura Gagliardi<sup>a</sup>

<sup>a</sup>Department of Chemistry, University of Minnesota

<sup>b</sup>Department of Chemistry, University of Bath

Metal-organic frameworks (MOFs) have been studied extensively for the application of flue gas separation because of their tunability, structural stability, and large surface area. IRMOF10 is one of the most well studied structures,<sup>1,2</sup> and contains saturated tetrahedral Zn<sub>4</sub>O nodes and biphenyl dicarboxylate linkers that form a cubic unit cell. The effect of changing the metal within this MOF topology has been studied computationally,<sup>3</sup> but the change in its affinity towards CO<sub>2</sub> has never been probed. To study the CO<sub>2</sub> interactions within the M-IRMOF10 series, periodic density functional theory (DFT) was used to optimize the structures of each MOF and compute point charges. Clusters centering on the metal node were then designed and used to compute potential energy curves (PECs) that maximize the interaction of CO<sub>2</sub> with each metal, with PBE0-D3. These reference curves were then used to fit parameters for each metal. TraPPE parameters were used for all interactions apart from the metals. The results indicate that the 3d metals (Ca<sup>2+</sup>, Fe<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>) each have very weak interaction with CO<sub>2</sub>. For heavier ions like Sn<sup>2+</sup> and Ba<sup>2+</sup> the increase in adsorption of CO<sub>2</sub> at low pressure is more noticeable (Figure 1). Both UFF and this newly derived force field can capture this behavior reasonably well.



**Figure 1:** On the left, minimum energy (kJ/mol) versus ionic radius (Å) of the metal center within the IRMOF10 cluster. On the right, low pressure CO<sub>2</sub> adsorption isotherms with pure UFF and the TraPPE/parameterized metal force field developed in this work.

1. Yang, Q.; Zhong, C.; Chen, J.-F. *Computational Study of CO<sub>2</sub> Storage in Metal–Organic Frameworks*, *J. Phys. Chem. C*, 112, 5, 2008, 1562-1569.
2. Hicks, J. M.; Desgranges, C.; Delhommelle, J. *Characterization and Comparison of the Performance of IRMOF-1, IRMOF-8, and IRMOF-10 for CO<sub>2</sub> Adsorption in the Subcritical and Supercritical Regimes*, *J. Phys. Chem. C*, 116, 43, 2012, 22938-22946.
3. Yang, L.-M.; Ravindran, P.; Vajeeston, P.; Tilsted, M. *Ab initio investigations on the crystal structure, formation enthalpy, electronic, structure, chemical bonding, and optical properties of experimentally synthesized isorecticular metal-organic framework-10 and its analogues: M-IRMOF-10 (M=Zn, Cd, Be, Mg, Ca, Sr, Ba)*, *R. Soc. Chem. Adv.*, 2, 2012, 1618-1631.

# The Synergy Between Anion Photoelectron Spectroscopy and Theory

**Jacob Graham<sup>a</sup>, Allyson Buytendyk<sup>a</sup>, Julian Gould<sup>a,b</sup>, Kit Bowen<sup>a</sup>**

<sup>a</sup>Department of Chemistry, Johns Hopkins University, Baltimore, MD 21218, USA

Together, anion photoelectron spectroscopy and theory are a synergetic combination. Since negative ion photoelectron spectroscopy provides electronic structure information about the mass-selected anion's neutral counterpart, as well as the energetic relationship between the anion and its corresponding neutral, it is a powerful tool for benchmarking and validating theoretical calculations. Here, the essential capabilities of anion photoelectron (photodetachment) spectroscopy are summarized, several examples of synergy between anion photoelectron spectroscopy and theory are reviewed, preliminary photoelectron and theoretical work on several porphyrin anions is presented, and plans for future studies are discussed. At this very early stage of our work, porphyrins are seen as primitive models of metal organic frameworks (MOF's). As next steps, we plan to generate anions of small MOF's or fragments of MOF's in the gas phase by bringing together metal atoms and organic linkers in our anion beam source, mass-selecting the species of interest, measuring their photoelectron spectra, and conducting complimentary calculations. Additionally, we will explore bringing anionic MOF's into the gas phase, where they can be photodetached, by electro-spraying MOF nanocrystals.

<sup>b</sup>J. Gould, supported by a JHU Greer Fellowship, thanks M. R. Pederson and Chad Hoyer for help with DFT and CASSCF calculations, respectively.



# Predicting Kinetic Separation of Light Gases in a Flexible Porous Organic Cage Crystal Using Transition State Theory

**Jeffrey Camp and David Sholl**

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Porous molecular crystals are comprised of discrete molecules that crystallize in the solid state without intermolecular covalent or coordination bonds. Recently, experiments have demonstrated that a novel class of cage-shaped porous molecular crystals can be used to separate mixtures of noble gases. Using numerically efficient transition state theory methods, we have quantified the substantial influence of framework flexibility on diffusion in these materials. These results were used to predict the membrane selectivity of porous organic cages for light gases in the Henry's regime.

## An Efficient Method to Search MOF Databases: Pre-combustion CO<sub>2</sub> Capture

**Yongchul G. Chung, Diego A. Gomez-Gualdron, Randall Q. Snurr**

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We have developed a genetic algorithm (GA) that can efficiently extract essential structure-property information from a database of nanoporous materials, and we have applied it to CO<sub>2</sub> capture from the effluent gas stream of a coal gasification process (so-called pre-combustion CO<sub>2</sub> capture).

First, GCMC simulations with a 50:50 CO<sub>2</sub>/H<sub>2</sub> mixture at 313 K were carried out for a genetically diverse set of 100 hypothetical MOF (hMOF) structures to evaluate their fitness metrics, such as selectivity and working capacity. Based on the GCMC simulation results, a new generation of hypothetical MOFs was created by carrying out genetic operations on the genes of the hMOFs to maximize selectivity, working capacity, and an adsorbent selection criterion (selectivity multiplied by working capacity). This completes a “generation” in the GA search strategy, and GCMC simulations were subsequently carried out for the new generation of hMOFs. The process was repeated for 10 generations.

We found that the GA can help to find top performing MOFs at a fraction of the computational cost (~1/100) when compared with a “brute-force” method and can effectively maximize different types of fitness metrics, such as selectivity of CO<sub>2</sub>/H<sub>2</sub> and working capacity of CO<sub>2</sub>, for a given set of hypothetical MOF structures. GA search also revealed a combination of textural properties in MOFs that can maximize CO<sub>2</sub> working capacity for pre-combustion CO<sub>2</sub> capture. Such MOFs have an optimal range of void fraction (0.8 – 0.87), gravimetric surface area (3600 – 4700 m<sup>2</sup>/g), largest cavity diameter (8.2 – 11.7 Å), and pore limiting diameter (6.6 – 11.3 Å). To test the transferability of the identified textural properties and the fitness metric, we searched the CoRE MOF database<sup>1</sup> to find a MOF (IMP-9) that matches the above combination of textural properties. Subsequent GCMC simulations on IMP-9 showed that the MOF has a very high CO<sub>2</sub> working capacity (> 15 mol/kg) as predicted.

<sup>1</sup> Y.G. Chung, J. Camp, M. Haranczyk, B.J. Sikora, W. Bury, V. Krungleviciute, T. Yildirim, O. K. Farha, D.S. Sholl, R.Q. Snurr, “Computation-Ready, Experimental (CoRE) Metal-Organic Frameworks: A Tool to Enable High-Throughput Screening of Nanoporous Crystals,” *Chemistry of Materials*, accepted

## Metal-Organic Magnets

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Jeffrey R. Long<sup>a</sup>**

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Metal-organic materials afford access to synthetic tunability and rational property design unmatched by traditional inorganic solid-state materials. Porous metal-organic frameworks in particular lend themselves towards applications benefiting from electronic or magnetic response to guest molecules. Toward this end, we present several metal-organic frameworks that effectively separate O<sub>2</sub>/ N<sub>2</sub> mixtures and exhibit reversible changes in magnetic behavior upon binding and release of O<sub>2</sub>. In addition, we more generally investigate magnetic behavior as a function of guest molecule identity in metal-organic frameworks. Beyond response to guest molecules, metal-organic frameworks offer a unique opportunity to design magnetic materials synthetically tuned to exhibit hard or soft magnetism. Current magnetic metal-organic frameworks are limited in applications due to their low magnetic transition temperatures. Inclusion of organic radical moieties in metal-organic frameworks increases the density of magnetic moments within the framework, promoting high magnetic transition temperatures. Design of new organic radical-based metal-organic frameworks will be discussed, with potential secondary functions such as response to guest molecules, conductivity, or light-sensitivity also considered.

# Understanding bulk properties of metal-organic frameworks using lattice models

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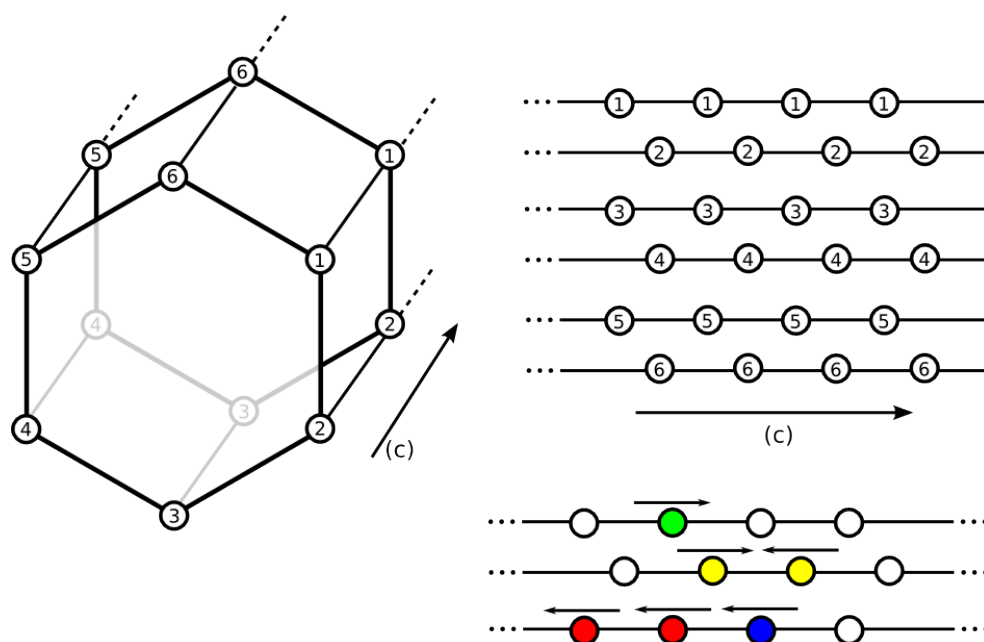
<sup>b</sup>Department of Chemical and Biological Engineering, UC Berkeley

<sup>c</sup>Molecular Foundry, Lawrence Berkeley National Laboratory

<sup>d</sup>Materials Sciences Division, Lawrence Berkeley National Laboratory

M-MOF-74 materials and their derivatives are promising candidates for carbon capture, with exceptional capacity for CO<sub>2</sub> adsorption and separation of CO<sub>2</sub> from H<sub>2</sub> or N<sub>2</sub>. We have used lattice models to understand two important properties of MOF-74 variants: (1) formation of the M-MOF-74 framework and (2) the mechanism of CO<sub>2</sub> adsorption in the diamine-appended mmen-M<sub>2</sub>(dobpdc) (mmen = *N,N'*-dimethylethylenediamine; M = Mg, Mn, Fe, Co, Zn; dobpdc<sup>4-</sup> = 4,4'-dioxidobiphenyl-3,3'-dicarboxylate).

First, we use a lattice model for the formation of the M-MOF-74 series and Monte Carlo simulations to investigate why MOF-74 crystals grow anisotropically to form needle-shaped crystals. We compute free energy barriers to nucleation and aim to demonstrate the contributions of geometry and energetics to MOF-74's anisotropic growth. Second, we use a lattice model to predict the unusual step-shaped CO<sub>2</sub> adsorption isotherms in mmen-M<sub>2</sub>(dobpdc) and compare two proposed mechanisms for CO<sub>2</sub> adsorption. We show that only the mechanism in which adsorption occurs via insertion into the metal-N bond results in an isotherm consistent with experiment.



## Molecular Sieve Nanosheets

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It is important to lower the cost of biofuel production to increase its competitiveness with conventional fuels. Current separation processes in biorefinery impose a major cost in biofuel production. Membrane-based separation is widely considered as one of the most promising low cost alternatives to conventional energy-intensive industrial separations, however, high cost and difficulties in scale-up constrain their wide-spread commercial application. To address these issues, we recently demonstrated a new concept to synthesize membranes using layered (2D) zeolites [1]. The fabrication method consists of exfoliation of lamellar zeolites to the constituent nanosheets and forming well-packed nanosheets on porous substrates using filtration. The pores perpendicular to the monolayers selectively transport target molecules through the membrane [1].

Our recent simulations showed hydrophobic silicalite-1 zeolite is selective for alcohols separation from water [2]. This finding encouraged us to investigate the growth of hydrophobic silicalite-1 zeolite membrane on porous supports.

In this poster, we demonstrate a step forward to quantitative transfer of the nanosheets monolayer to silicon wafers through dispersion at the air-water interface in a Langmuir-trough. In short, acid treatment of nanosheets facilitated partial removal of the long-chain organic structure-directing agent (OSDA) and allowed the formation of stable suspensions in ethanol. Nanosheets from these suspensions were introduced at the air-water interface in a Langmuir-trough. Compression of the interface led to a well-packed monolayer which was transferred on silicon wafers using a horizontal lifting technique, also known as Langmuir-Schaefer deposition. The performance of hydrophobic membranes made using zeolite nanosheet seed layer vs. large zeolite crystals seed layer will be investigated. This will provide a better understanding of the effect of zeolite microstructure and hydrophobicity on the membranes performance for alcohols separation from water.

[1] K. Varoon, X.Y. Zhang, B. Elyassi, D.D. Brewer, M. Gettel, S. Kumar, J.A. Lee, S. Maheshwari, A. Mittal, C.Y. Sung, M. Cococcioni, L.F. Francis, A.V. McCormick, K.A. Mkhoyan, M. Tsapatsis, *Science*, 2011, 333, 72-75.

[2] P. Bai, M. Tsapatsis, and J.I. Siepmann, *Langmuir*, 2012, 28, 15566-15576.

## Force Fields for Fe-MOF-74

**Laura E. Fernandez<sup>a</sup>, Bo Wang<sup>a</sup>, Donald G. Truhlar<sup>a</sup>**

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The structure and thermodynamic properties of metal-organic frameworks (MOFs) are an active area of scientific inquiry due to their actual and potential cost-effective industrial applications in gas storage, separations, and catalysis. Molecular mechanics provides an efficient approach to model material properties to materials properties for tailoring them to meet specific practical application needs or for screening them for potential applications.. However, most molecular mechanics calculations involve several terms terms that do not reproduce the true contributions to the energy that they nominally represent; such methods can work only by cancellation of errors. By designing force fields with better physical underpinnings, we hoe to increase the transferability of parametrizations.

Previous studies of Fe-MOF-74 have shown that quantum mechanical (QM) calculations on an 88-atom cluster model allows for accurate calculation of the interaction between the MOF and adsorbed ethane or ethylene.<sup>1</sup> We have compared various interaction energies of molecular mechanics (MM) and QM/MM calculations to the QM calculations. In this work we compare the energy decomposition of the binding energy between Fe-MOF-74 and ethane and ethylene adsorbates. This decomposition involves taking a close look at the static Coulomb, static exchange, dispersion-like, repulsion, and polarization terms and cross terms. Our initial study has involved an in depth analysis into the electrostatics and dispersion-like terms. For the electrostatics we utilize screened electrostatics<sup>2,3</sup> and for the dispersion-like terms we utilize the dispersionless density functional theory (dIDF) developed by Pernal et al.<sup>4</sup> in 2009; and we further develop both methods to be used on Fe.

1. Verma, P.; Xu, X.; Truhlar, D. G., Adsorption on Fe-MOF-74 for C1-C3 Hydrocarbon Separation. *The Journal of Physical Chemistry C* **2013**, *117*, 12648-12660.
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4. Pernal, K.; Podeszwa, R.; Patkowski, K.; Szalewicz, K., Dispersionless Density Functional Theory. *Physical Review Letters* **2009**, *103*, no. 263201.

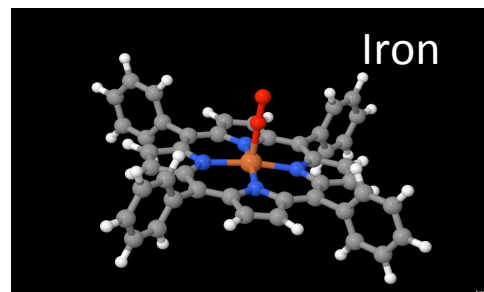
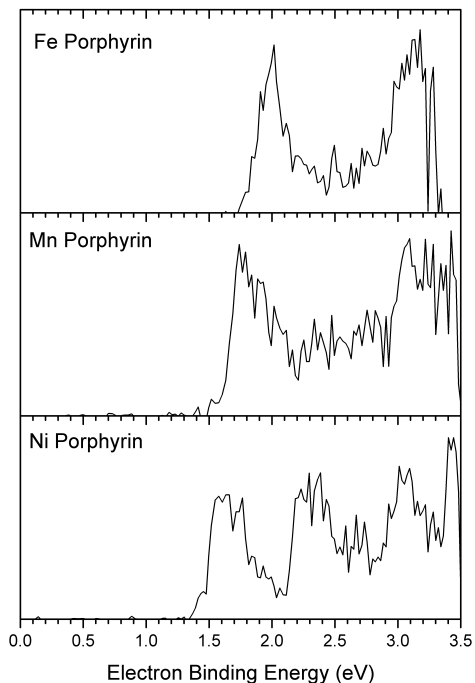
# Photoelectron Spectra of Porphyrin Anions: a Preliminary Test for Theory

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Porphyrins can be viewed as a representative descriptor for metal organic frameworks. Being able to bring porphyrins or even better, significant portions of MOFs themselves, into the gas phase as anions would allow the electronic structure of their neutral counterparts to be directly assessed through anion photoelectron spectroscopy. This electronic structure information could then be used to validate DFT, with and without SIC, or higher-level calculations such as GASSCF, for these systems and provide navigational beacons for improving such calculations. Other possibilities may include experimental quantification of spin-dependent interactions between open metal centers and adsorbed gas molecules. Although multiply-negatively charged porphyrins have been generated by electrospray ion sources, these anions are unsuitable for investigating the electronic structure of the anion's corresponding neutral. Using laser-prepared photo-ejected electrons from a metal target and a supersonic jet, we have very recently prepared singly-charged porphyrin parent anions (with several metal centers) and measured their photoelectron spectra. This work can be extended in the future to provide a pathway for studying the electronic structure properties of well-defined MOFs units in the gas phase. Electron detachment spectra from the anion have been calculated using PBE-GGA, NRLMOL and very large Gaussian-orbital basis sets and there is relatively good agreement between theory and experiment. For example, for Fe, NRLMOL finds a doublet-triplet and doublet-singlet electron detachment energy of 2.11 and 3.09 eV respectively. Similarly for Ni the two lowest electron detachment energies for each spin are found to be 1.54 and 2.68 eV for the double-singlet and doublet-triplet electron detachment respectively. In addition to bare porphyrins, computational results for other porphyrins with weakly bound FM/AF adsorbed O<sub>2</sub> and CO<sub>2</sub> molecules are presented. Prospects for experimental measurements will be discussed.

<sup>b</sup>J. Gould, supported by a JHU Greer fellowship, thanks M.R. Pederson and Chad Hoyer for help with DFT and CASSCF calculation respectively.



## The Nanoporous Materials Genome on the World Wide Web

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Metal-organic frameworks (MOFs), zeolites and other nanoporous materials are potentially useful for many energy-relevant or technologically important processes, such as adsorption, catalysis, sensing, and drug delivery. Over the past few years, a huge number of new nanoporous structures have been synthesized experimentally or predicted computationally. The computational design and properties prediction for these nanoporous materials offer a high-payoff opportunity. Several large-scale computational studies of these materials have demonstrated the feasibility of identifying high-performing candidate materials for various applications, and these studies have also generated large property data sets. The goal of the Nanoporous Materials Genome Center (NMGC) is to discover and study these novel nanoporous materials. Additionally, the NMGC aims to provide a repository of experimental and hypothetical structures and associated properties for the rapidly growing scientific communities that are interested in these materials. In order to accomplish these goals, the NMGC has partnered with the Materials Project (<https://materialsproject.org>) at Lawrence Berkeley National Laboratory in order to produce a state-of the art web interface for a comprehensive database of nanoporous materials and their properties. The search functionality of the web interface is built around a visual representation of the stored properties. One of the available ways to search for materials is by choosing two properties, from an ever-expanding list, to be plotted against each other. This allows for the selection of a group of materials within a range of desired target values and the observation of useful trends. The properties and structures of a group of selected materials can then be extracted for further analysis by the user or by a list of available online tools. This effort aims to make research more effective, consistent and transparent by collecting data from various research groups and eventually expedite the discovery of new high performing nanoporous materials while expanding the knowledge around them.



# Predictions on the organophosphate hydrolysis of nerve agents catalyzed by NU-1000

**William C. Isley III and Christopher J. Cramer**

Department of Chemistry, University of Minnesota

Chemical warfare agents (*e.g.*, GD and VX) containing phosphate ester bonds are among the most toxic chemicals known to mankind. Thus for some applications, rapid destruction of agents is essential. Here we report theoretical predictions on a carefully chosen metal-organic framework (MOF) material featuring high porosity and exceptional chemical stability that is extraordinarily effective for the degradation of nerve agents and their simulants.<sup>1</sup> Computational models point to Lewis acidic Zr<sup>IV</sup> ions as the active site and to their accessibility as a defining element of their efficacy.

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<sup>1</sup> Joseph Mondloch, Michael Katz, William Isley III, Pritha Gosh, Peilin Liao, Wojciech Bury, George Wagner, Morgan Hall, Jared DeCoste, Gregory Peterson, Randall Snurr, Christopher Cramer, Joe Hupp, Omar Farha. *Decomposing Chemical Warfare Agents Utilizing Metal-Organic Frameworks*. Submitted 2014.

# Solvent-Assisted Linker Exchange and Transmetalation: Alternatives to the De Novo Synthesis of Unattainable Metal–Organic Frameworks

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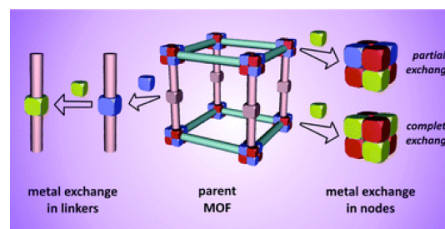
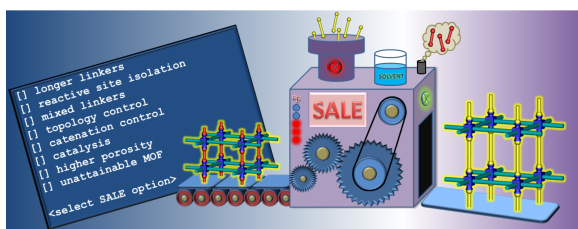
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Metal-organic frameworks (MOFs) have attracted considerable attention as potential candidates for the performance of many useful applications, ranging from gas storage and separation to catalysis and sensing. Unfortunately, obtaining a desired MOF structure that is tailored to perform a specific application is often not trivial, as *de novo* synthesis may present challenges such as formation of undesirable (*e.g.*, catenated) topologies, low solubility of precursors, and loss of functionality of sensitive network components. Solvent-assisted linker exchange (SALE) and transmetalation are two facile to implement strategies for circumventing these setbacks; their use has already led to the generation of a variety of MOF materials previously unobtainable by one-pot synthetic methods. SALE and transmetalation are heterogeneous reactions of parent MOF crystals with concentrated solutions of organic linkers and inorganic metal salts, respectively, that lead to the replacement of the linkers or metal nodes within the parent MOFs by the desired components, while the overall framework topology is preserved. This poster presents applications of these invaluable synthetic tools to replace linkers in chemically robust MOFs, synthesize MOFs that are energetically “unfavorable”, extend MOF cages by longer linker incorporation, and endow MOFs with permanent and persistent porosity.

This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Separations and Analysis Program under Award Number DE-FG02-08ER15967, not the NMGP. Organocatalysis applications of ZIFs, not described in the poster, were supported by the NMGP.



## Metal organic framework based vehicle for nitric oxide delivery

**Revati Kumar<sup>a</sup>, Tanping Li<sup>a</sup>, Kiara Taylor-Edinbyrd<sup>a</sup>,**

<sup>a</sup>Department of Chemistry, Louisiana State University

The use of copper based metal organic frameworks (MOFs) as a vehicle for the delivery of nitric oxide, a molecule with biomedical applications including anti-angina medication, is being explored. Recent preliminary experiments [*J. Am. Chem. Soc.*, **2012**, *134*, 3330-3333] have shown that the MOF Cu<sub>3</sub>(BTC)<sub>2</sub> can be used to catalyze the release of nitric oxide from chemically stored S-nitrosocysteine, an RSNO species, in a slow and sustained manner. We present the results of our computational investigations to gain insight into the mechanism in the complex MOF environment as well as factors that can affect the release of the chemically stored nitric oxide, have been carried out. These include electronic structure studies of representative clusters as well as condensed phase simulations, using classical force-fields, to understand the effect of the MOF environment (with bound copper ions) on the RSNO species compared to the case of free copper ion catalysts in solution.

## Small Molecule Binding in the M-MOF-74 Series

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In order to use density functional theory (DFT) to reliably treat small molecule binding at open metal sites in metal-organic frameworks (MOFs), techniques must be employed that consider effects of the strong electron correlation present at the metal centers. The density functional theory plus U (DFT+U) formalism provides an efficient means to compute the energies and electronic properties of such systems. If the appropriate value for the parameter U is chosen, excellent agreement with experiment can often be achieved, but how can we select this parameter for diverse systems in a systematic manner? In recent years, the implementation of an *ab initio* “linear response” method to calculate U has provided an alternative to the empirical strategies previously employed. This method has been shown to reproduce previous results for the binding of CO<sub>2</sub> in Co-MOF-74, and is being applied to the rest of the M-MOF-74 series (M=Mg, Mn, Fe, Co, Ni Cu, and Zn), aiming to improve the accuracy of calculated binding energies in these and similar systems. The method also permits the computational study of diverse MOFs containing transition metals for which empirically-derived U parameters are not available.

The significant van der Waals interactions between guest molecules and organic linkers are often not properly accounted for in standard DFT functionals; however, researchers have developed functionals with this in mind. For the M-MOF-74 series, CO<sub>2</sub>, methane, and water binding energies were compared using four van der Waals corrected functionals: opt88, opt86b, vdW-DF2, and rev-vdW-DF2. The opt88 and opt86b functionals over-bind guests but give reasonable geometries. Binding energies computed at the vdW-DF2 and rev-vdW-DF2 levels of theory are improved; however, vdW-DF2 overestimates bond distances.

# Evaluation of force field performance for high-throughput screening of gas uptake in MOFs

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High-throughput computational techniques have been increasingly used to screen large numbers of MOFs for their gas adsorption properties, in attempts to discover the best performing experimentally documented MOFs, design high-performing hypothetical MOF structures, or glean quantitative structure-property relationships describing general trends in gas uptake. The predictions of all of these studies, however, critically depend on the accuracy of the force field used to model all inter-molecular interactions between MOFs and adsorbates. In this study, we compute CO<sub>2</sub> and CH<sub>4</sub> adsorption in a database of 424 MOFs, comparing the predictions of standard force fields to those of our entirely first principles derived force fields which are based on symmetry-adapted perturbation theory. This comparison allows for the assessment of standard force fields to reliably characterize MOFs in high-throughput screening applications, while providing important insight into the quantitative role of polarization and dispersion interactions in determining gas uptake in MOFs.

## Decomposing Chemical Warfare Agents Utilizing Metal–Organic Frameworks

**Joseph E. Mondloch<sup>a\*</sup>, Michael J. Katz<sup>a\*</sup>, William C. Isley<sup>b\*\*</sup>, Pritha Ghosh<sup>c\*</sup>, Peilin Liao<sup>c\*</sup>, Randall Q. Snurr<sup>c\*</sup>, Christopher J. Cramer<sup>b\*\*</sup>, Joseph T. Hupp<sup>a\*</sup>, and Omar K. Farha<sup>a\*</sup>**

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Chemical warfare agents (*e.g.*, GD and VX) containing phosphate ester bonds are among the most toxic chemicals known to mankind. Recent global military events, such as the conflict and disarmament in Syria, have brought into sharp focus the need to find effective strategies for the rapid destruction of these banned chemicals. Solutions are needed for immediate personal protection (*e.g.*, the filtration and catalytic destruction of air borne versions of agents), bulk destruction of chemical weapon stockpiles, protection (via coating) of clothing, equipment, and buildings, and containment of agent spills. G agents, for example, act in insidious fashion—*inhibiting the enzyme acetylcholine esterase, and thereby causing loss of control of muscles, including pulmonary muscles. Ensuing oxygen deprivation causes brain damage and death within a few minutes. Thus for some applications, destruction of agents within a few minutes or less is essential. Here we report a carefully chosen metal–organic framework (MOF) material featuring high porosity and exceptional chemical stability that is extraordinarily effective for the degradation of nerve agents and their simulants. Experimental and computational evidence point to Lewis acidic Zr<sup>IV</sup> ions as the active site and to their superb accessibility as a defining element of their efficacy.*

\*Work at Northwestern University on the experimental investigation of nerve agent hydrolysis was supported by the Defense Threat Reduction Agency (grant HDTRA1-10-1-0023), not the NMGC. \*\*Theoretical studies at the UMN of NU-1000 and its hydrolysis activity were supported by the NMGC.

# Evaluation of DFT functional performance for the prediction of MOF ground state structure

**Dalar Nazarian and David Sholl**

School of Chemical & Biomolecular Engineering, Georgia Institute of Technology

We discuss the development of a methodology to benchmark DFT functional performance for the prediction of porous metal-organic framework (MOF) ground state structure. Our inclusion criteria for the test set used in this study yielded a chemically diverse test set of 24 MOFs with reliable experimental crystal structure data. These 24 MOFs were DFT energy minimized with GGA (PBE, PW91), meta-GGA (M06-L, MN12-L), and dispersion corrected (vdw-DF2, DFT-D2, DFT-D3) functionals. The DFT ground state structures of our MOF test set computed with each of these functionals were compared to experimental structure data obtained from the Cambridge Structure Database. The accuracy of each functional was assessed by comparison to experimental lattice parameters, bond lengths, bond angles, torsion angles, and pore descriptors including the largest cavity diameter and pore limiting diameter. The results demonstrate that DFT is a reliable predictor of MOF ground state structure.

# Periodic DFT Study of the Preferential Location of Germanium, Aluminium and Gallium in the UTL and IPC-2a Zeolites

**Samuel O. Odoh,<sup>a</sup> Michael W. Deem,<sup>b</sup> and Laura Gagliardi<sup>a</sup>**

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The preferential location of Ge in the double four-membered rings (D4R) of zeolite UTL has been examined with periodic density functional theory calculations. Our computations show that, Ge atoms are preferentially sited at the T1 and T2 atoms in the D4R cages with the preference for siting Ge atoms at the D4R sites over other T atom sites in UTL increasing as more Si atoms are replaced by Ge. In addition to this replication of experimental results, there are two interesting findings. First, comparison to Al and Ga show some correspondence between the atomic radii of these elements, the oxygen-centred T-O-T angles and the site preferences. Second, comparison of Ge atom siting in UTL to zeolite IPC-2a shows that the single four-membered ring (S4R) sites in the latter are not the most favourable sites.



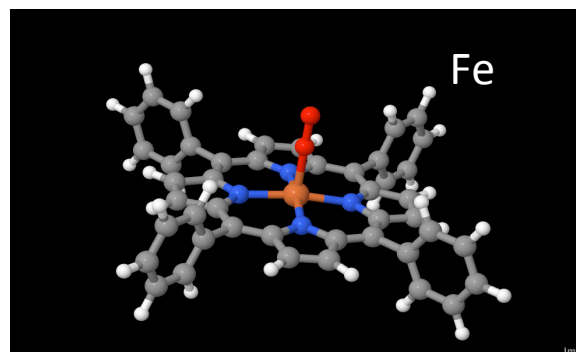
# A New Theoretical Framework for Implementing Self-Interaction Corrections into DFT with DFT Scaling

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Advances in approximations to the density-functional theory have primarily focused upon improvements based upon the gradients of spin densities. While such functionals have been highly successful and well used, an early paper concluded by noting that neither LDA or GGA functionals could account for the long-range part of the exchange-correlation hole because of the self-interaction error[1]. An approach to addressing this issue has been inclusion of some percentage of exact exchange, which improves the asymptotic behavior of the potential. Another means for implementing the self-interaction correction (SIC) and recovering an asymptotically exact effective potential is due to Perdew and Zunger and dates back to 1981. However the explicit orbital dependence, or alternatively unitary non-invariance, associated with this formulation leads to large increases in computational costs due to the need to solve the localization equations for SIC[2]. In recent work[3] a size-extensive unitarily invariant reformulation of the self-interaction correction has been introduced by constructing the SIC functional in terms of orbitals that are explicitly dependent on the single-particle density matrix but depend parametrically on a set of quasi-classical electronic positions that can be optimized along with the atomic positions of a given molecule. An overview of this method will be provided along with a summary of recent calculations on small molecules. A possible correspondence between the resulting quasi-classical electronic positions and Lewis structures will be offered along with a discussion of why DFT-based scaling can be achieved within this “Fermi-Orbital SIC”. Possible applications of this method to systems containing open metal centers will be discussed based upon the known need for such corrections to some problems in the field of molecular magnetism and on the need for describing proper dissociation of ionic systems. Possibilities for determining and experimentally validating the level shifts and changes in chemical hardness, due to FO-SIC, in a system containing an open metal center and gas molecule will be discussed. Thanks to the Bowen group for discussions on Photodetachment of electrons from molecules.



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[2] M.R. Pederson, R.A. Heaton and C.C. Lin, *J. Chem. Phys.* **80**, 1972 (1984).

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# Development of Transferable Potentials for Phase Equilibria Force Field for Hydrogen Sulfide and Adsorption in All-silica Zeolites

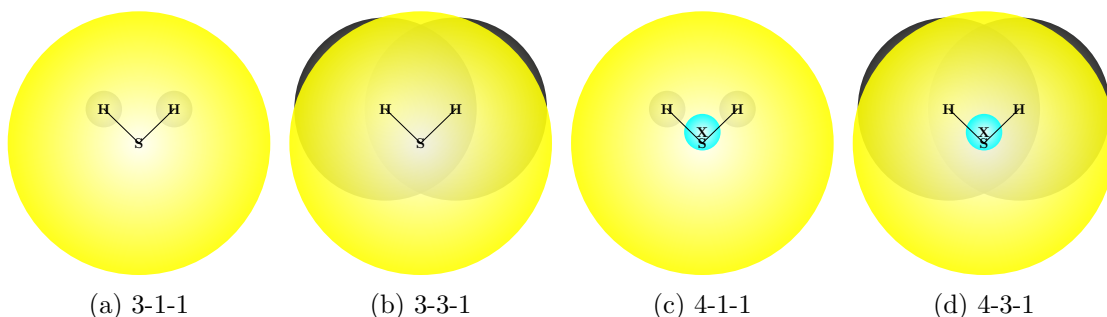
Mansi S. Shah<sup>a,b</sup>, Michael Tsapatsis<sup>a</sup>, and J. Ilja Siepmann<sup>a,b,c</sup>

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Hydrogen sulfide is a very hazardous chemical and is of paramount concern to industries dealing with it as regards the health, safety, and environment. The objective of our work is to find an optimum adsorbent for separating H<sub>2</sub>S from natural gas mixtures. As a first step towards attaining this objective, the transferable potentials for phase equilibria (TraPPE) force field is extended to H<sub>2</sub>S.



Models with three and four interaction sites were investigated that place partial charges either on the positions of the nuclei or along the H-S-H bisector for the negative partial charge and use Lennard-Jones sites on either only the sulfur or on all three atoms. The initial parameter screen focused on reproducing the experimental vapor–liquid coexistence curve of H<sub>2</sub>S and its liquid-phase dielectric constant. The model was further refined by considering the binary vapor–liquid equilibria of the H<sub>2</sub>S – CH<sub>4</sub> and H<sub>2</sub>S – CO<sub>2</sub> mixtures where other species were described by the TraPPE–EH and TraPPE force fields. The new H<sub>2</sub>S model was used to compute pure and binary adsorption isotherms of H<sub>2</sub>S and CH<sub>4</sub> in a few all-silica zeolites.

## Transferable force field for gas adsorption in Na-exchanged zeolites

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Zeolites have shown great potential for applications in many processes related to gas adsorption, separation, and catalysis. Their properties can be fine-tuned by adjusting the structure topologies and chemical compositions (Si/Al ratio and type of cation). The ability to identify optimal materials for a given application computationally is hence very desirable, but the quality of the predictions is often limited by the availability of accurate, transferable force fields. The recently developed TraPPE-zeo force field, parametrized against experimental adsorption isotherms, shows great performance for a variety of molecules in all silica zeolites<sup>1</sup>. We extended this force field to Na-exchanged zeolites based on first-principle calculations. The atomic charges for framework atoms were calculated using the LoProp method<sup>2</sup> and were found to be in good agreement with the existing values from TraPPE-zeo. The interaction between Na and O atoms of the zeolite framework were captured using the Buckingham potential with parameters fitted to PBE-D2 relative energies. The TraPPE-zeo LJ parameters for Si and O (Si-O-Si) were adopted and also applied to Al and O (Si-O-Al). The LJ parameters of Na were fitted to vdW-DF/CC<sup>3</sup> energies of the CO<sub>2</sub>/NaY system. The transferability of the new force field to other gas molecules, such as CH<sub>4</sub>, H<sub>2</sub>O, and H<sub>2</sub>S, was tested by comparing the predicted interaction energies with vdW-DF/CC results and by comparing the predicted adsorption isotherms with available experimental results.

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## Finding materials for vehicular methane storage

**Cory M. Simon,<sup>a</sup> Rocio Mercado,<sup>b</sup> Jihan Kim,<sup>c</sup> Diego A. Gomez-Gualdron,<sup>d</sup> Jeffrey S. Camp,<sup>e</sup> Yongchul G. Chung,<sup>d</sup> Richard L. Martin,<sup>f</sup> Michael W. Deem,<sup>g</sup> Dan Gunter,<sup>f</sup> Maciej Haranczyk,<sup>f</sup> David S. Sholl,<sup>e</sup> Randall Q. Snurr,<sup>d</sup> and Berend Smit<sup>a,b,h</sup>**

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Natural gas, which is mostly methane, is an attractive alternative to petroleum as a transportation fuel because of the increasing supply and possibly lower emissions of greenhouse gases and other pollutants. The main technological obstacle for the replacement of gasoline with natural gas is the comparatively low volumetric energy density of natural gas. An alternative densification strategy for natural gas is to pack the fuel tank with a porous material, such that exploiting the van der Waals attractions between methane and the framework atoms leads to a density competitive with compressed natural gas (CNG) but at a lower storage pressure. One of the exciting aspects of advanced nanoporous materials is that by combining different molecular building blocks, researchers have obtained an unprecedented chemical and geometrical tunability of nanoporous materials. Millions of different materials can, in principle, be synthesized by combining different molecular building blocks in varying topologies. However, in practice, only a small set of the possible materials will ever be synthesized and tested as natural gas adsorbents due to limits on time and resources. We illustrate how various computational methods can be used to search this vast space of potential structures for high-performing natural gas adsorbents for use in vehicular fuel tanks. Drawing upon recent reports of large databases of existing and predicted nanoporous materials generated *in silico*, we have collected and compared on a consistent basis the methane uptake in over 650,000 materials based on the results of molecular simulation.

# Molecular Models for Spin-Crossover, Catalysis, and Proton Conduction in Metal Organic Frameworks

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The rational design of new multifunctional metal-organic frameworks (MOFs) is entirely dependent on understanding how the frameworks respond to external stimuli, how guest molecules behave inside the pores and interact with the framework, and how the local electronic structure of the metal centers change upon guest adsorption or distortion of the framework. Here we provide insight into i) the electronic and structural properties of MOFs that exhibit SCO behavior; ii) how framework flexibility affects catalysis and dynamics, and iii) proton conduction in chemically different MOFs, all of which are of considerable interest for possible applications in future fuel cell technologies. Characterizing both structural and dynamical properties of MOFs and their guests requires a physically realistic description of the thermodynamic and kinetic properties collectively described by the force field parameters. We discuss the development and application of advanced search heuristics and a novel hybrid Monte Carlo/MD method that builds upon the ligand field molecular mechanics approach.

# Defining the Proton Topology of the Zr<sub>6</sub>-Based Metal–Organic Framework

NU-1000

**Nora Planas,<sup>a</sup> Joseph E. Mondloch,<sup>b</sup> Samat Tussupbayev,<sup>a</sup> Joshua Borycz,<sup>a</sup> Christopher J Cramer,<sup>a</sup> Joseph T. Hupp,<sup>b</sup> Omar K. Farha,<sup>b,c</sup> and Laura Gagliardi<sup>a</sup>**

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Metal–organic frameworks (MOFs) constructed from Zr<sub>6</sub>-based nodes have recently received considerable attention given their exceptional thermal, chemical, and mechanical stability. Because of this, the structural diversity of Zr<sub>6</sub>-based MOFs has expanded considerably and in turn given rise to difficulty in their precise characterization. In particular it has been difficult to assign precisely where protons (needed for charge balance) reside on some Zr<sub>6</sub>-based nodes. Elucidating the precise proton topologies in Zr<sub>6</sub>-based MOFs will have wide ranging implications in defining their chemical reactivity, acid/base characteristics, conductivity and chemical catalysis. Here we have used a combined quantum mechanical and experimental approach to elucidate the precise proton topology of the Zr<sub>6</sub>-based framework NU-1000. Our data indicate that the mixed node topology, [Zr<sub>6</sub>(μ<sub>3</sub>-O)<sub>4</sub>(μ<sub>3</sub>-OH)<sub>4</sub>(OH)<sub>4</sub>(OH<sub>2</sub>)<sub>4</sub>]<sub>8</sub><sup>+</sup>, is preferred and simultaneously rule out five alternative node topologies.

# *Ab Initio* Force Field Development for Coordinatively Unsaturated Metal-Organic Frameworks

Mary Van Vleet<sup>a</sup> and J.R. Schmidt<sup>a</sup>

<sup>a</sup>Theoretical Chemistry Institute and Department of Chemistry, University of Wisconsin-Madison

We have previously developed accurate and transferable *ab initio* force fields based on symmetry-adapted perturbation theory (SAPT) for a wide range of chemical systems including small molecules, metal organic frameworks (MOFs), neat organic liquids, and ionic liquids. We find that our methodology yields physically motivated parameters that are exceptionally transferable between diverse systems, largely due to the one-to-one correspondence between force field terms and the explicit energy decomposition given by SAPT. We are now in the processes of extending our methodology to investigate strongly interacting systems (i.e. metal-ligand binding) where SAPT problematically underestimates interaction energies. Using the M-MOF-74 series as a case study, we have found that localized molecular orbital energy decomposition analysis (LMOEDA) applied to super-molecular, DFT-based interaction energy calculations, correctly predicts metal-ligand binding energies. Furthermore, the LMOEDA decomposition scheme results in a consistent energy decomposition compared to SAPT, such that LMOEDA and SAPT calculations can be combined together yield accurate force field parameters. By introducing new force field terms to account for short-range exchange and induction effects, we use LMO-EDA interaction calculations in conjunction with previously determined SAPT-based force field parameters to develop force fields for the M-MOF-74 system. These force fields are applied to predicting CO<sub>2</sub> adsorption isotherms in the M-MOF-74 series with good success.

Mechanism of Oxidation of C<sub>2</sub>H<sub>6</sub> to C<sub>2</sub>H<sub>5</sub>OH  
at Iron(IV)–Oxo Sites in Magnesium-Diluted Fe<sub>2</sub>(dobdc)

Pragya Verma<sup>a,d</sup>, Konstantinos D. Vogiatzis<sup>a,d</sup>, Nora Planas<sup>a,d,e</sup>, Joshua Borycz<sup>a,d</sup>, Dianne Xiao<sup>b,d</sup>,  
Jeffrey R. Long<sup>b,c,d</sup>, Laura Gagliardi<sup>a,d,\*</sup>, and Donald G. Truhlar<sup>a,d,\*</sup>

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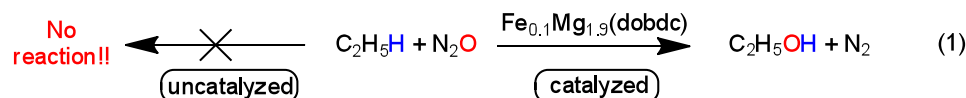
<sup>b</sup>. Department of Chemistry, University of California, Berkeley, California, 94720, USA

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<sup>e</sup>. Department of Chemistry, University of Wisconsin-Eau Claire, Eau Claire, Wisconsin, 54702, USA.

The MOF-74 metal–organic framework (MOF) contains a high density of open Fe metal sites, such as sites with five-coordinate Mg(II) or Fe(II) ions, and it has been shown to be useful for applications such as gas separation and catalysis. The organic linker in MOF-74 is dobdc<sup>4-</sup> = 2,5–dioxido–1,4–benzenedicarboxylate. Its catalytic properties include hydroxylation of phenol by pure Fe<sub>2</sub>(dobdc) and hydroxylation of ethane by its magnesium-diluted analogue, Fe<sub>0.1</sub>Mg<sub>1.9</sub>(dobdc). In an earlier work, the latter reaction has been proposed to occur through a redox mechanism involving the formation of fleeting iron(IV)–oxo species;<sup>1</sup> that work showed that MOFs could mimic the chemistry found in several Fe-containing heme and non-heme enzymes and synthetic complexes for activating strong C–H bonds. In this work, we present a theoretical study of a member of this class of reaction, wherein the catalytic material, Fe<sub>0.1</sub>Mg<sub>1.9</sub>(dobdc), activates the strong C–H bonds of ethane. Kohn-Sham density functional theory calculations with Minnesota functionals have been performed to characterize the electronic structure of key species and to unravel the detailed mechanism of the catalytic cycle. The strong C–H bonds of ethane have been demonstrated to be activated by the highly reactive iron(IV)–oxo (*S* = 2) intermediate generated after the oxidation of redox active Fe(II) sites by nitrous oxide. The proposed mechanistic pathway involves three key transition states with the highest activation barrier corresponding to the transfer of oxygen from N<sub>2</sub>O to the Fe(II) center. The uncatalyzed reaction, where nitrous oxide directly oxidizes ethane to ethanol, is also investigated (Scheme 1). The activation barrier for the uncatalyzed reaction is 230 kJ/mol higher than the reaction catalyzed by the iron(IV)–oxo intermediate, which clearly indicates that the formation of the iron(IV)–oxo intermediate is crucial for the reaction to occur.



**Scheme 1.** The two reactions investigated in this work.

1. Xiao, Bloch, Mason, Queen, Hudson, Planas, Borycz, Dzubak, Verma, Lee, Bonino, Crocellà, Yano, Bordiga, Truhlar, Gagliardi, Brown, Long. Oxidation of ethane to ethanol by N<sub>2</sub>O in a metal–organic framework with coordinatively unsaturated iron(II) sites. *Nature Chem.* **6** (2014) 590.



# Computational screening of MOFs with Open Metal Sites for Adsorption and Catalysis Applications

**Konstantinos D. Vogiatzis<sup>1</sup>, Emmanuel Haldoupis<sup>1</sup>, J. Ilja Siepmann<sup>1,2</sup>, Laura Gagliardi<sup>1</sup>**

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Metal-organic frameworks containing undercoordinated metal centers are promising for adsorption and catalytic applications. The open-metal site can selectively adsorb gas molecules and can thus be used for gas separation applications. In addition, the coordinatively unsaturated metal cations can be used as catalytic centers for various reactions.

More than 37,000 1D, 2D and 3D MOF structures have been deposited into the Cambridge Crystallographic Data Centre (CCDC). Recently, a **Computationally Ready Experimental (CoRE)** MOF database [1] has been compiled which includes more than 5000 3D structures. Our interest is to detect materials within this database with undercoordinated metal cations. For an efficient data mining on the CoRE database, we have developed a computational tool for the identification of open metal sites. The computational screening of MOFs is based on the characterization of the first coordination sphere of the metal centers and on their accessibility from guest molecules. A statistical analysis of the CoRE database is provided. This tool is transferable to other databases of materials.

The applicability of the data mining tool is demonstrated with two examples. The first is the identification of Mg-containing MOFs with exposed metal sites for CO<sub>2</sub> adsorption studies. The choice of MOFs with Mg centers was based on the exceptional good CO<sub>2</sub> capacity of Mg between the isostructural M<sub>2</sub>(dobdc) series (M = Mg, Fe, Ni, Co, Cu, Zn). [2] We identified 51 MOFs with unsaturated magnesium sites and assessed their affinity towards CO<sub>2</sub> by computing binding energies using periodic DFT calculations. The second application is the identification of Fe-MOFs which can potentially stabilize the highly reactive iron(IV)-oxo intermediate. Recently, the catalytic behavior of the Fe-diluted Mg<sub>2</sub>(dobdc) MOF has been attributed to such intermediate. [3] 41 MOF structures with coordinatively unsaturated iron centers were found. In order to limit our selection, additional criteria were taken into consideration, such as the spin state of iron, number of atoms coordinated to the metal, symmetry of the coordination sphere of iron and geometrical hindrance from the surrounding linkers constituting the pore. Finally, 5 out of 41 frameworks are selected for further investigation on the stability of the iron(IV)-oxo intermediate by means of electronic structure theory.

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# Deconstructing Hydrogen-Bond Networks in Confined Zeolitic-Imidazolate Frameworks: Implications for Water-Alcohol Separation

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The hydrogen-bond networks of water, methanol, ethanol, and their binary mixtures adsorbed in nanoporous zeolitic imidazolate framework (ZIF-8, ZIF-20, and ZIF-22) by grand-canonical Monte Carlo (GCMC) simulations are analyzed and compared to their bulk liquid counterparts. These include the geodesic distribution (the shortest H-bond pathways between molecular vertices), the average Euclidean length, and the adsorbate-adsorbate and adsorbate-adsorbent distributions of H-bonds. Ongoing molecular dynamics simulations will study the role of hydrophobicity and confinement upon the hydrogen bond dynamics so as to elucidate whether dynamic properties influence selectivity. The orientation and binding energy of the adsorbate to the interior of the material in extremely dilute concentration are currently being evaluated by DFT calculation. In combination, these studies will describe how the H-bond networks are altered by different hydrophobicity/hydrophilicity, pore size, surface area, and accessible volume when going from the bulk to the confined environment. By understanding H-bond network of water-alcohol mixture in nanoporous materials, better biofuel purification criteria can be better developed.

# Beyond Energies: Molecular Geometries as Metrics for Assessing Electronic Structure Approaches for Intermolecular Interactions

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Electronic structure approaches have traditionally been benchmarked exclusively on the basis of energy-centric metrics. Decades ago, when computational constraints restricted the focus of research to small single molecules, this approach was adequate. In recent years, systems of interacting molecules have become computationally accessible, and so there has been a shift in the focus of the literature. There has not, however, been a concomitant shift in metrics. The potential energy surfaces associated with non-covalently-interacting systems are often very soft along intermolecular degrees of freedom, and so an energy-centric metric is no longer sufficient. We have thus explored the idea of utilizing some form of metric related to geometry.

On a diverse series of non-covalently-interacting systems of different sizes, from the water dimer to the coronene dimer, we have evaluated a variety of electronic structure approximations with respect to their abilities to reproduce coupled-cluster-level geometries. Specifically, we have examined Hartree-Fock, second-order Møller-Plesset perturbation theory (MP2), attenuated MP2, scaled MP2, and a number of density functionals, many of which incorporate some form of empirical or nonempirical van der Waals correction.

We have found a number of trends that transcend system size and interaction type. For instance, functionals incorporating VV10 nonlocal correlation tend to yield highly accurate geometries;  $\omega$ B97X-V and B97M-V in particular stand out. We have established that intermolecular distance, as measured by, e.g., the center-of-mass separation of two molecules, is the geometric parameter that deviates most profoundly among the various methods. This property of the equilibrium intermolecular separation, coupled with its accessibility via a small series of well-defined single-point calculations, makes it an ideal metric for the development and evaluation of electronic structure methods.

# Decomposing Hydrogen Bond Dynamics into Multiscale Components - Implications for Synthesis and Catalytic Schemes of Nanoporous Materials

Tiecheng Zhou<sup>a</sup> and Aurora Clark<sup>a</sup>

<sup>a</sup>Department of Chemistry and the Materials Science and Engineering Department  
Washington State University

The synthetic tunability of nanoporous materials, such as zeolites and MOFs, make them promising materials in industry for separation, storage, catalysis, and drug delivery. These materials are often prepared in hydrothermal conditions and recent work has illustrated how the use of co-solvents can manipulate the free energies of solvation of growing MOF crystallites<sup>1</sup> and thus may impact the end topologies created<sup>2</sup>. Further, many applications utilize these materials with a solvent. In both scenarios, the organization and dynamics of the solvent impact reactivity of the material and thus robust algorithms are required to quantify both solvent response to the material, as well as predict future reactive properties under varying solution phase conditions. In the case of protic systems, it is well established that the hydrogen bond network changes dramatically in the confined space of a nanoporous material. Many nanoporous materials are also somewhat hydrophobic, which also can influence the organization and dynamics of the solvent (or adsorbate). We are particularly interested in whether the hydrophobic effect can be quantified based on the dynamics of the H-bond networks in the nanoporous materials using Molecular Dynamics simulations and Network Analysis<sup>3</sup>. However, the use of a numerical cutoff in MD to separate the H-bonded pairs and non-bonded pairs will inevitably lead to the transient artifacts (transient bonds and transient breaks). A dynamics-based correction scheme<sup>4</sup> is introduced to recover these artifacts and to decompose the H-bond lifetime of water into multiscale components in terms of the breaking/reforming mechanisms in the molecular level. The short time scale of the H-bond lifetime of water is dominated by libration ( $\sim 50$  fs), and the long time scale is dominated by H-bond switch ( $\sim 0.1$ -2 ps) (Figure 1). The hydrophobic effect of the nanoporous materials can then be characterized by how much these dynamical components are altered relative to the corresponding bulk properties. This algorithm may enable rational control of the internal properties of nanoporous materials by changing the hydrophobic environment within the pores.

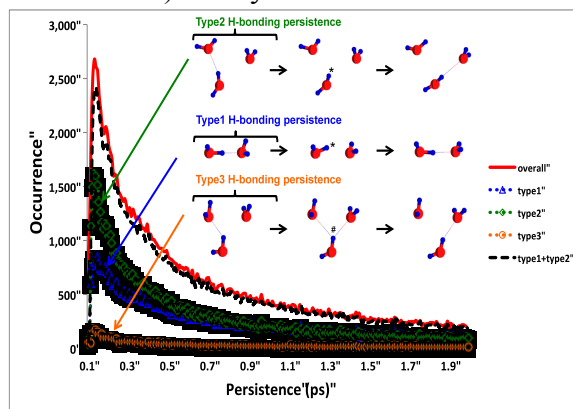


Figure 1. Lifetime of H-bond decomposed into different H-bond breakage mechanisms. Derived from corrected H-bond networks.

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4. Ozkanlar, A.; Zhou, T.; Clark, A. E. *Journal of Chemical Physics* *submitted*.

**NMGC All-Hands Meeting Attendees  
Saint Paul Hotel, St. Paul, MN  
October 18-19, 2014**

Advisory Board Member				
Joachim	Sauer	Humboldt-Universitaet zu Berlin	Advisory Board	
Department of Energy Program Officers				
Mark	Pederson	US Department of Energy	Program Officer	
Larry	Rahn	US Department of Energy	Program Officer	
Investigators				
Ilja	Siepmann	University of Minnesota	Principal Investigator	
Kit	Bowen	The Johns Hopkins University	Co-Investigator	
Aurora	Clark	Washington State University	Co-Investigator	
Chris	Cramer	University of Minnesota	Co-Investigator	
Michael	Deem	Rice University	Co-Investigator	
Laura	Gagliardi	University of Minnesota	Co-Investigator	
Maciej	Haranczyk	Lawrence Berkeley National Laboratory	Co-Investigator	
Martin	Head-Gordon	University of California, Berkeley	Co-Investigator	
Joseph	Hupp	Northwestern University	Co-Investigator	
Jeff	Long	University of California, Berkeley	Co-Investigator	
David	Sholl	Georgia Tech	Co-Investigator	
Berend	Smit	University of California, Berkeley	Co-Investigator	
Randy	Snurr	Northwestern University	Co-Investigator	
Don	Truhlar	University of Minnesota	Co-Investigator	
Michael	Tsapatsis	University of Minnesota	Co-Investigator	
Junior Researchers				
Peng	Bai	University of Minnesota, Siepmann/Tsapatsis Groups	Graduate Student	
Yi	Bao	Rice University, Deem Group	Graduate Student	
Varinia	Bernales	University of Minnesota, Gagliardi Group	Postdoc	
Gary	Bondarevsky	University of Minnesota, Gagliardi Group	Graduate Student	
Joshua	Borycz	University of Minnesota, Gagliardi Group	Graduate Student	
Jeff	Camp	Georgia Tech, Sholl Group	Graduate Student	
Yongchul Greg	Chung	Northwestern University, Snurr Group	Postdoc	
Lucy	Darago	University of California, Berkeley, Long Group	Graduate Student	
Katie	Deeg	University of California, Berkeley, Smit Group	Graduate Student	
Bahman	Elyassi	University of Minnesota, Tsapatsis Group	Postdoc	
Laura	Fernandez	University of Minnesota, Truhlar Group	Postdoc	
Jacob	Graham	The Johns Hopkins University	Graduate Student	

**NMGC All-Hands Meeting Attendees**  
**Saint Paul Hotel, St. Paul, MN**  
**October 18-19, 2014**

Emmaneul	Haldoupis	University of Minnesota, Gagliardi/Siepmann Groups	Postdoc
William	Isley	University of Minnesota, Cramer Group	Graduate Student
Olga	Kargiardi	Northwestern University, Hupp Group	Graduate Student
Aaron	League	University of Minnesota, Cramer Group	Graduate Student
Wei-Guang	Liu	University of Minnesota, Truhlar Group	Postdoc
Greg	Mann	University of California, Berkeley, Smit Group	Graduate Student
Rocio	Mercado	University of California, Berkeley, Smit Group	Graduate Student
Dalar	Nazarian	Georgia Tech, Sholl Group	Graduate Student
Samuel	Odoh	University of Minnesota, Gagliardi Group	Postdoc
Mansi	Shah	University of Minnesota, Siepmann/Tsapatsis Groups	Graduate Student
Huilian	Shi	University of Minnesota, Gagliardi Group	Graduate Student
Jeff	Sung	University of Minnesota, Siepmann Group	Graduate Student
Samat	Tussupbayev	University of Minnesota, Cramer Group	Postdoc
Pragya	Verma	University of Minnesota, Truhlar Group	Graduate Student
Bess	Vlaisavljevich	University of California, Berkeley, Smit Group	Postdoc
Konstantinos	Vogiatzis	University of Minnesota, Gagliardi Group	Postdoc
Bo	Wang	University of Minnesota, Truhlar Group	Graduate Student
Chun-hung	Wang	Washington State University, Clark Group	Graduate Student
Jon	Witte	UC Berkeley, Head-Gordon Group	Graduate Student
Tiecheng	Zhou	Washington State University, Clark Group	Graduate Student
<b>Guests</b>			
Taylor	Barnes	California Institute of Technology, Tom Miller Group, Graduate Student	
Richard	Baumer	Dow Chemical Company	
Omar	Farha	Northwestern University	
Daniel	Gunter	Lawrence Berkeley National Laboratory	
Christopher	Knight	Argonne National Laboratory	
Revati	Kumar	Louisiana State University	
Jesse	McDaniel	University of Wisconsin, Madison, JR Schmidt Group, Graduate Student	
Joe	Mondloch	University of Wisconsin, Stevens Point (previously in Hupp Group)	
Peter	Nickias	Dow Chemical Company	
Zack	Terranova	University of California, San Diego, Paesani Group, Postdoc	
Cathy	Tway	Dow Chemical Company	
Mary	Van Vleet	University of Wisconsin, Madison, JR Schmidt Group, Graduate Student	

# Acknowledgment

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