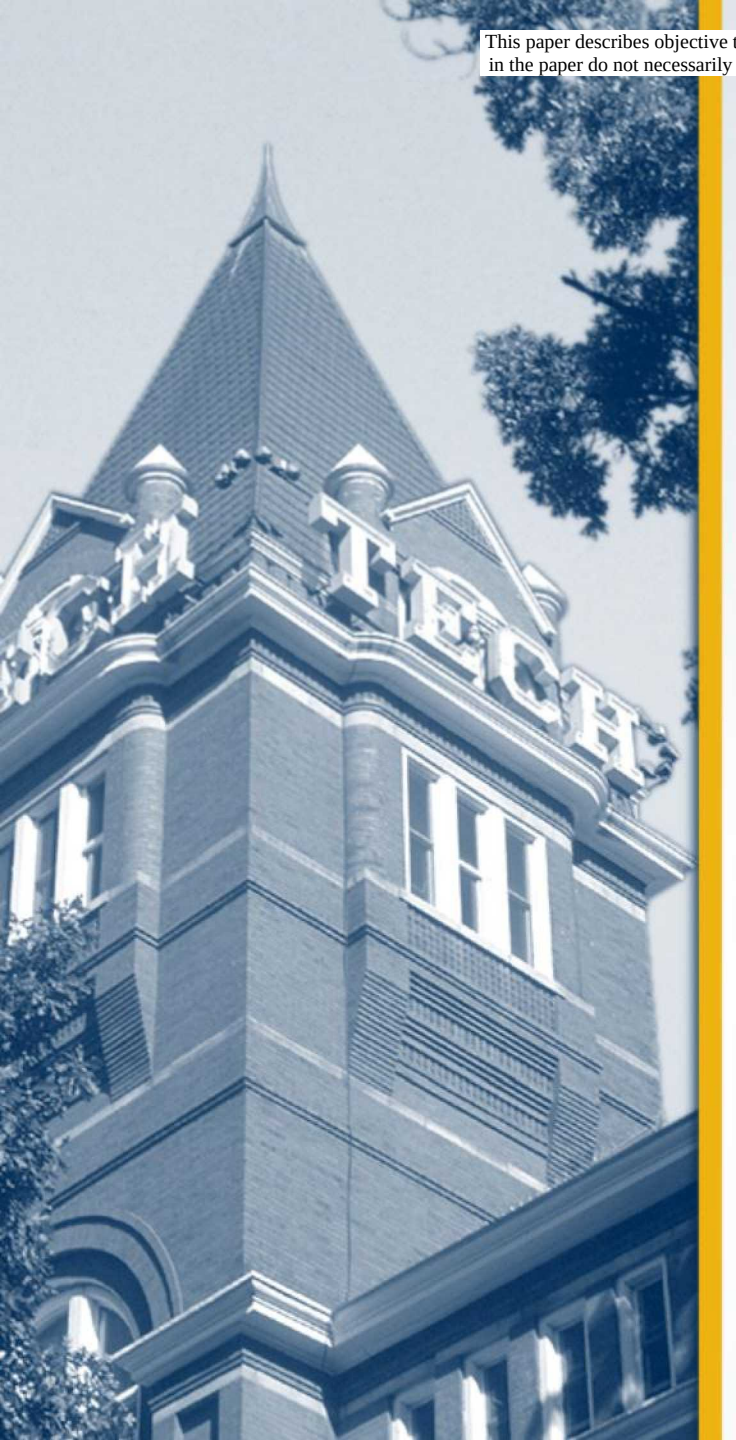

SAND2018-11266C

18AIChE
Annual Meeting, Pittsburgh, PA

Using Computer Simulations to Select Simulants for Capture of Chemical Warfare Agents in Nanoporous Materials by Adsorption

Mayank Agrawal, Dorina F. Sava Gallis, Jeffery A. Greathouse, and David S. Sholl

November 1st, 2018

Presentation by

Mayank Agrawal

In collaboration with

Sandia National Laboratories

Georgia Institute of Technology

This work is supported by the Laboratory Directed Research and Development Program at Sandia National Laboratories. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525. The views expressed in this article do not necessarily represent the views of the U.S. Department of Energy or the United States Government. Approved under Sand No SAND2018-8753 PE.

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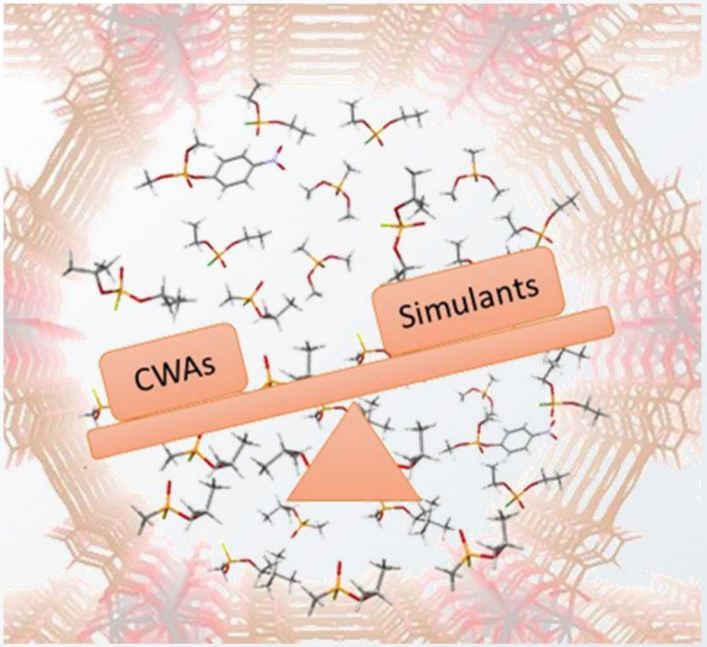
Introduction

- Nerve agents: extremely toxic synthetic chemicals which can be dispersed as a gas, liquid or aerosol
  - Tokyo subway station gas attack, 1995
  - Syria gas attacks in 2013 and 2018
- Use of simulant molecules instead of real agents in experiments to study and compare the activity of any adsorbent material due to toxicity of CWAs
- Recent work to simulate a large library of MOFs for CWA removal under humid conditions[1]
- However, no detailed comparison between CWAs and simulants for adsorption processes
- We use Metal-Organic Frameworks (MOFs) to compare adsorption properties of CWAs with simulants in nanoporous materials



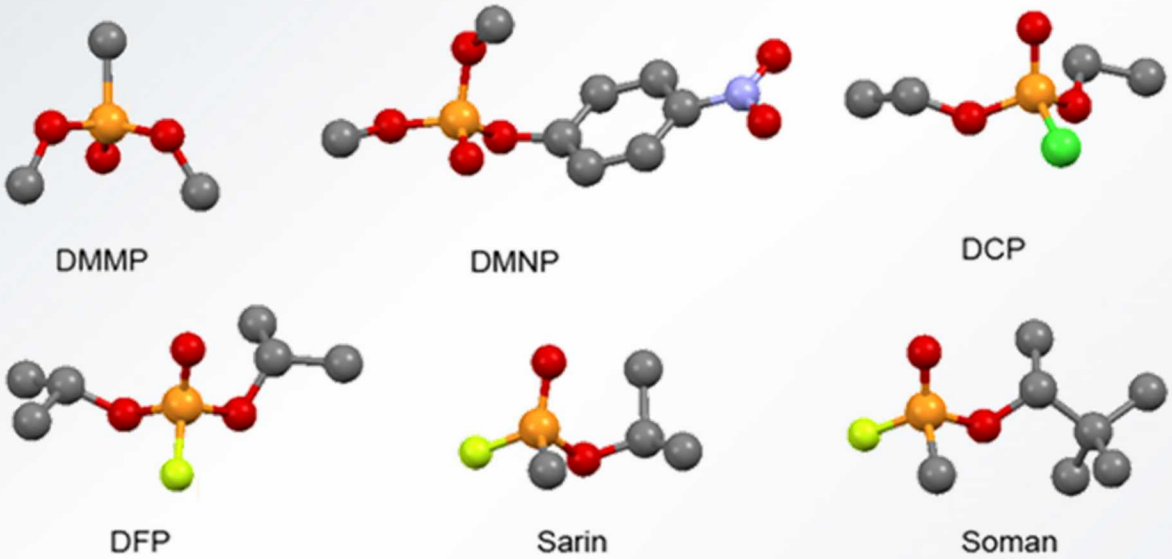
[1]*Matito-Martos, I et al. Chem. Mater., 2018, 30, 4571-4579*
[2]*Agrawal, M et al., J. Phys. Chem. C, 2018 (submitted)*

Objectives

- Prediction of adsorption properties of CWAs and simulants in a library of thousands of MOFs using molecular simulations
- To address the question of whether simulants for CWAs are truly similar to CWAs in terms of their adsorption properties
- Probing the sensitivity of our results to newly DFT derived FF to draw robust conclusions

Materials

- Adsorbents: CoRE MOF database[3], a collection of >2900 experimental reported MOFs with high quality charges assigned to the frameworks
- Adsorbates:
  - CWAs: Sarin and Soman
  - Simulants: DMMP, DMNP, DCP and DFP



[3]*Chung, Y. G. et al. Chem. Mater. 26, 6185–6192 (2014)*

Simulation Methods

- Force-field derivation
  - Derived from dispersion-corrected DFT calculations[4,5]
  - VASP package, PBE-D3 functional, 10^{-6} energy cutoff
  - DFT interaction energies of configurations are obtained using

$$E_{ads} = E_{adsorbate-MOF} - (E_{adsorbate} + E_{MOF})$$

  - Energies obtained above are fitted to Lennard-Jones potential of a force-field, where $\varepsilon_{ij}^{*} = \sqrt{\varepsilon_i(C_1\varepsilon_j)}$, $\sigma_{ij}^{*} = \frac{\sigma_i + C_2\sigma_j}{2}$, and i, j are subscripts for MOF and adsorbate atoms respectively

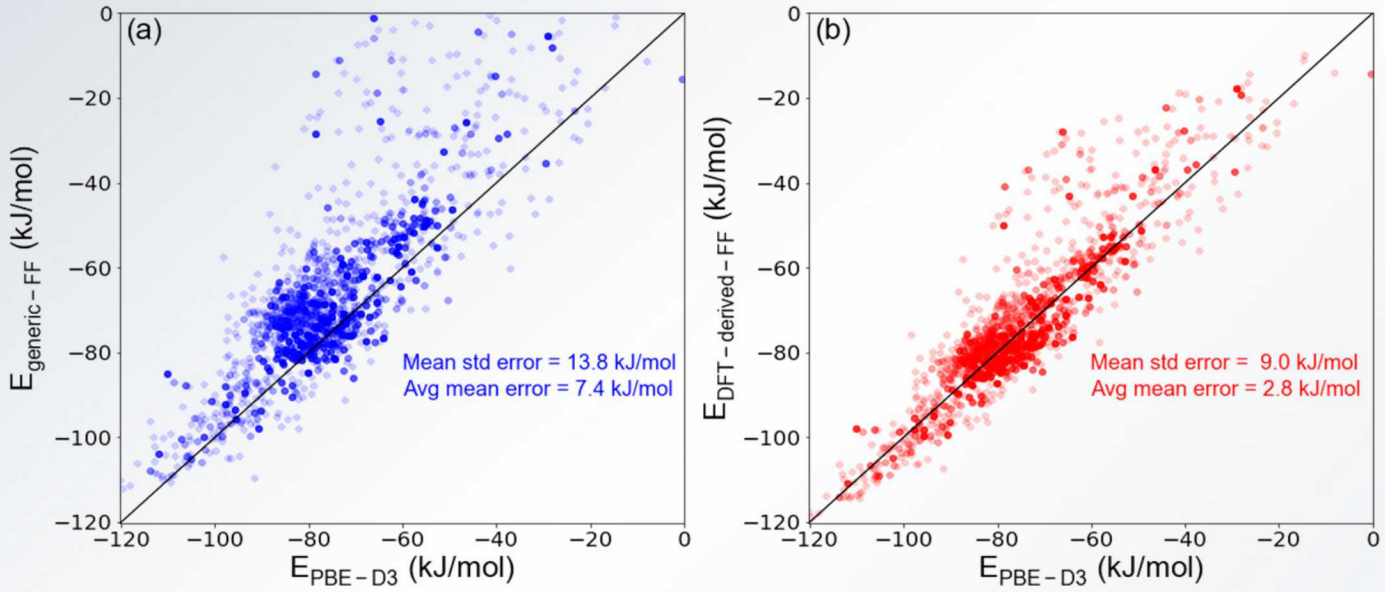
$$E_{LJ}(r_{ij}) = \sum 4\varepsilon_{ij}^{*}\left[\left(\frac{\sigma_{ij}^{*}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}^{*}}{r_{ij}}\right)^{6}\right]$$

- Adsorption properties calculations
  - RASPA package, Monte-Carlo simulations
  - Widom insertion method
  - 10^6 MC cycles

[4] *Fang, H. et al. J. Phys. Chem. C 116, 10692–10701 (2012)*
[5] *Kulkarni, A. R. & Sholl. D.S. J. Phys. Chem. C 117, 7519–7525 (2013)*

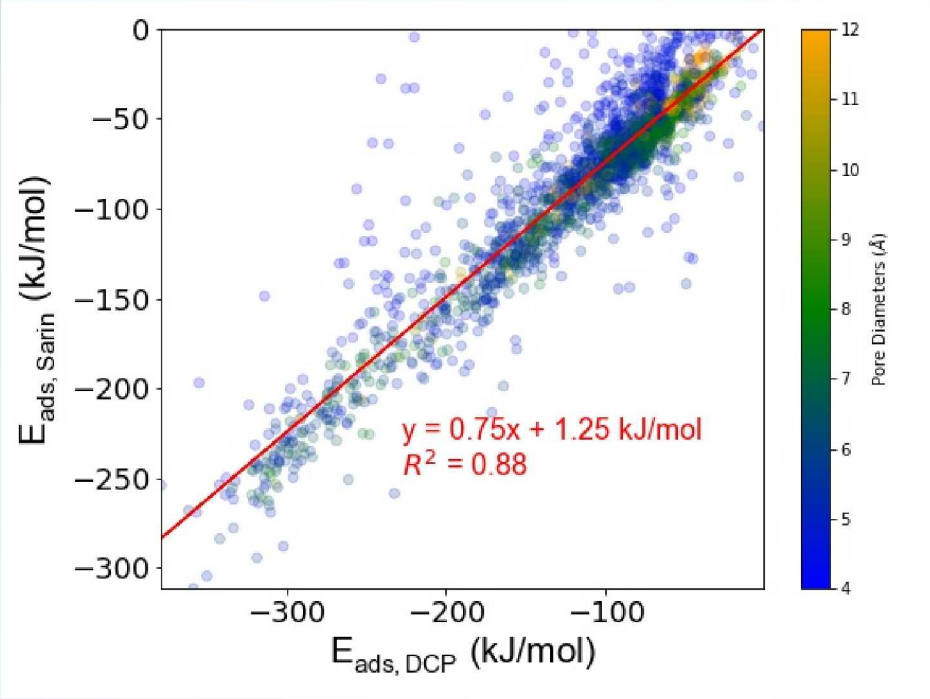
DFT-derived FF vs Generic FF

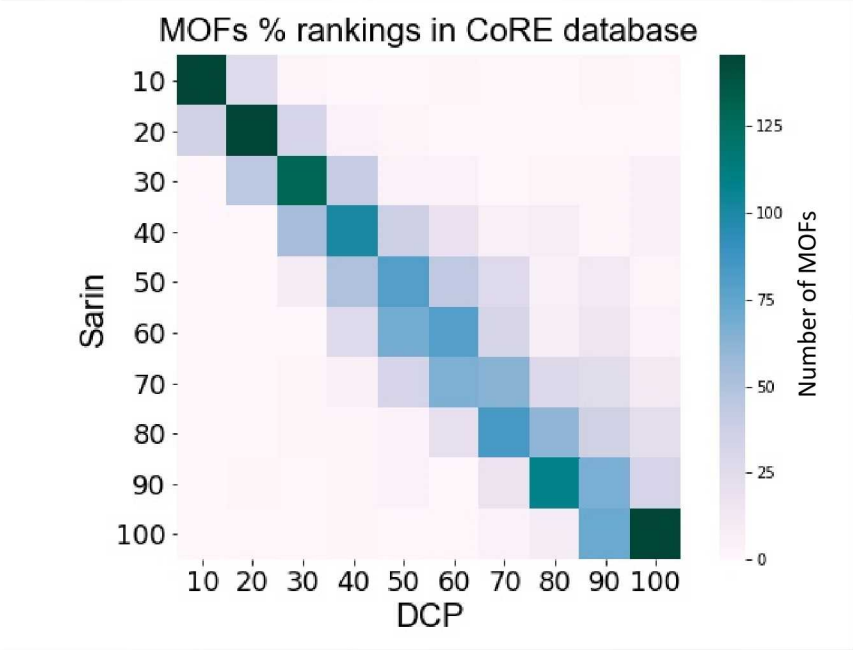
Interaction energies of 3000 configurations of 6 molecules in UiO-66



- Generic FF is reasonable, but DFT-derived FF is more accurate
- TraPPE force field is used as generic FF
- Results calculated using DFT-derived FF are shown primarily in the following slides

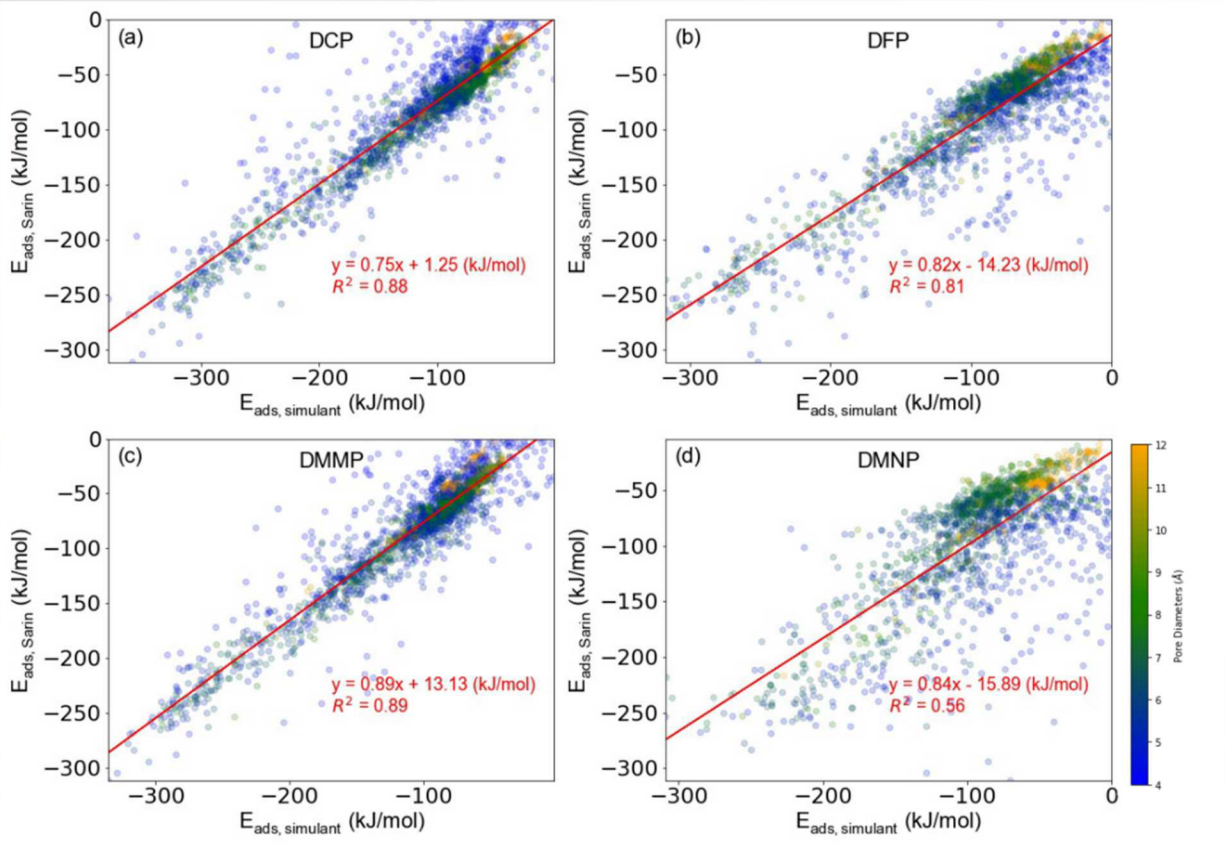
Heats of Adsorption: Sarin vs DCP





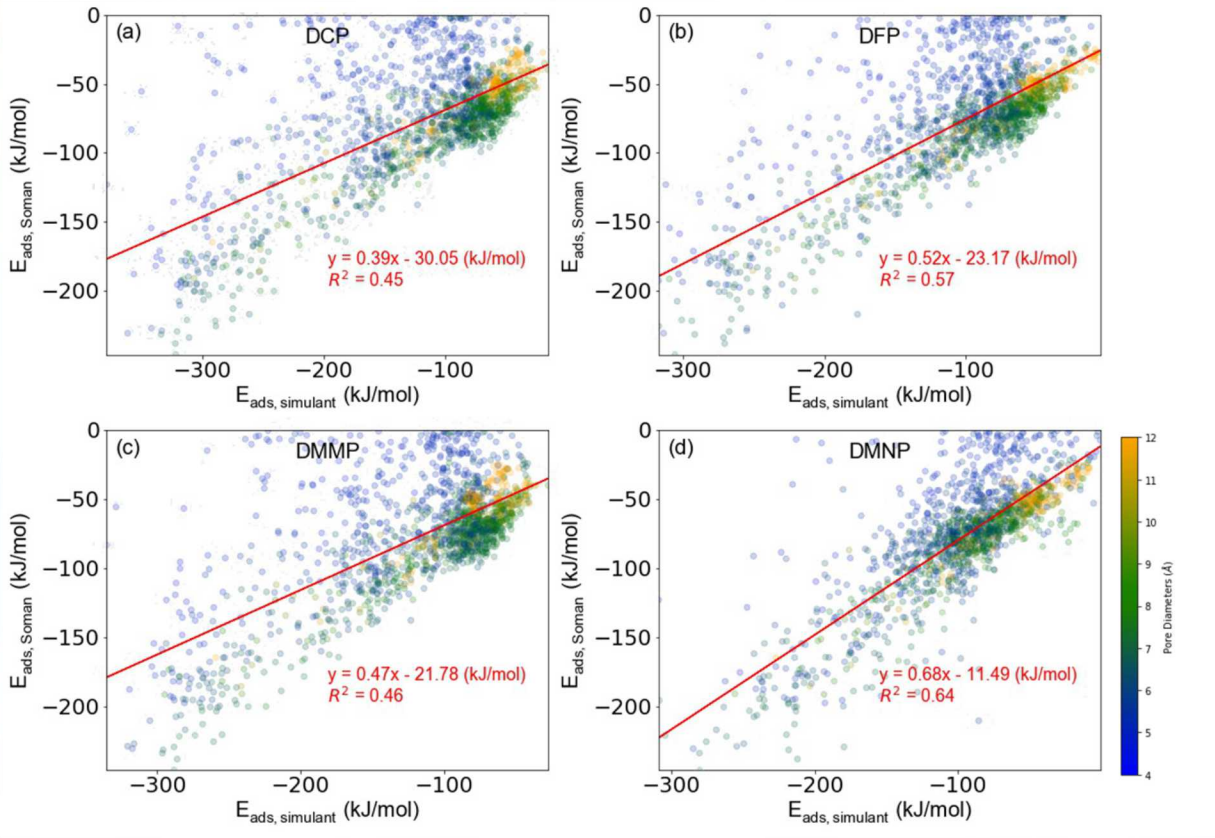
- Data is shown adsorption properties of Sarin and DCP in >2900 MOFs using DFT-derived FF
- DCP is able to predict Sarin's adsorption properties in CoRE MOF database within 10% error for most MOFs
- Heat of adsorption at zero loading is used as metric for adsorption affinity

Heats of Adsorption: Sarin vs Simulants



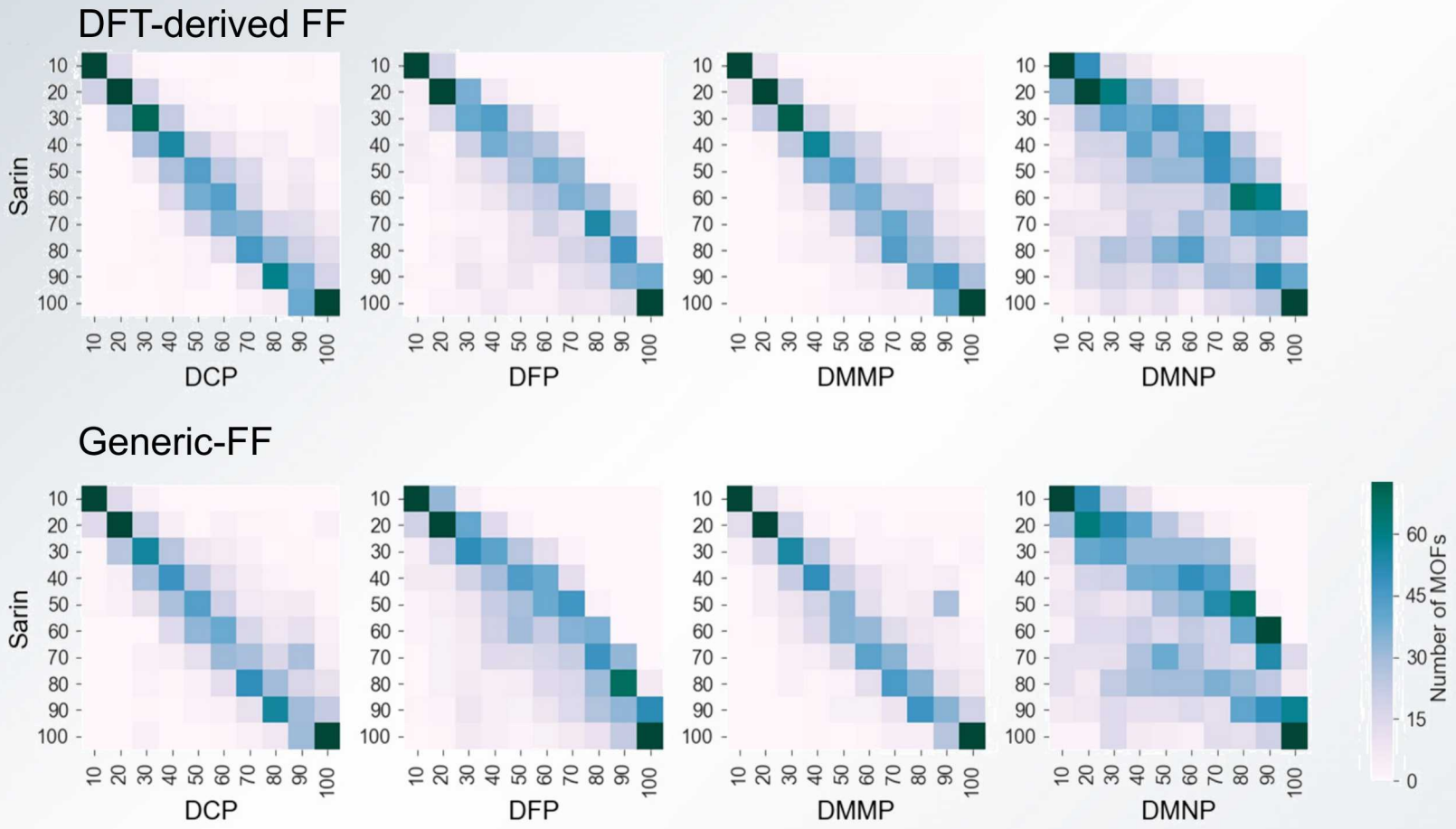
- High performing MOFs' pore diameters are in the range of 6-9 Å
- DCP and DMMP are the closest to Sarin

Heats of Adsorption: Soman vs Simulants



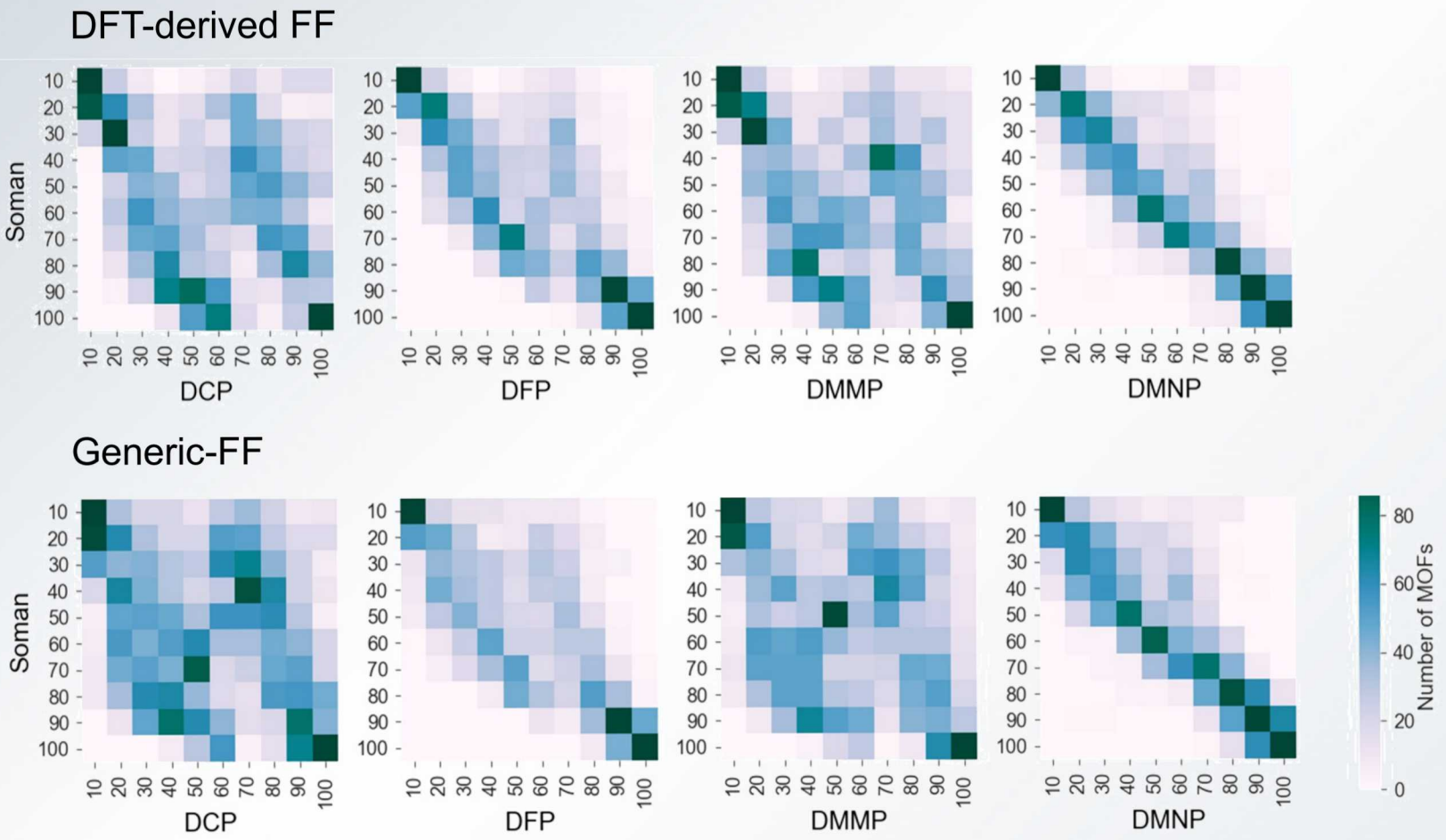
- No simulant is able to very closely predict Soman's adsorption properties
- DMNP is the closest to Soman among all simulants

Correlation Between MOFs Rankings: Sarin vs Simulants



- DCP and DMMP are able to best predict MOF rankings for Sarin based on adsorption properties
- The above conclusion is same using both force-fields

Correlation Between MOFs Rankings: Soman vs Simulants



- DMNP is the only simulant that is able to closely predict MOF rankings for Soman based on adsorption properties
- The above conclusion is same using both force-fields

Conclusions

- Of the simulants studied, DCP and DMMP are the best suited simulants to predict adsorption behavior of Sarin in nanoporous materials
- Of the simulants studied, DMNP is best suited to predict Soman's adsorption behavior in nanoporous materials
- Our DFT-derived FF is performing better than generic FF in predicting interaction energies of CWAs and simulants in MOFs, however, generic FFs are also well suited to predict qualitative adsorption behavior of CWAs and simulants
- Our predictions of the best simulant for each CWA are independent of the force-field used in the simulations

Acknowledgement

Sholl Research Group

Sandia National Laboratories

Funding Source: Sandia LDRD

Sandia National Laboratories

Georgia Tech

Thank you

Georgia Tech

Extra Slide 1

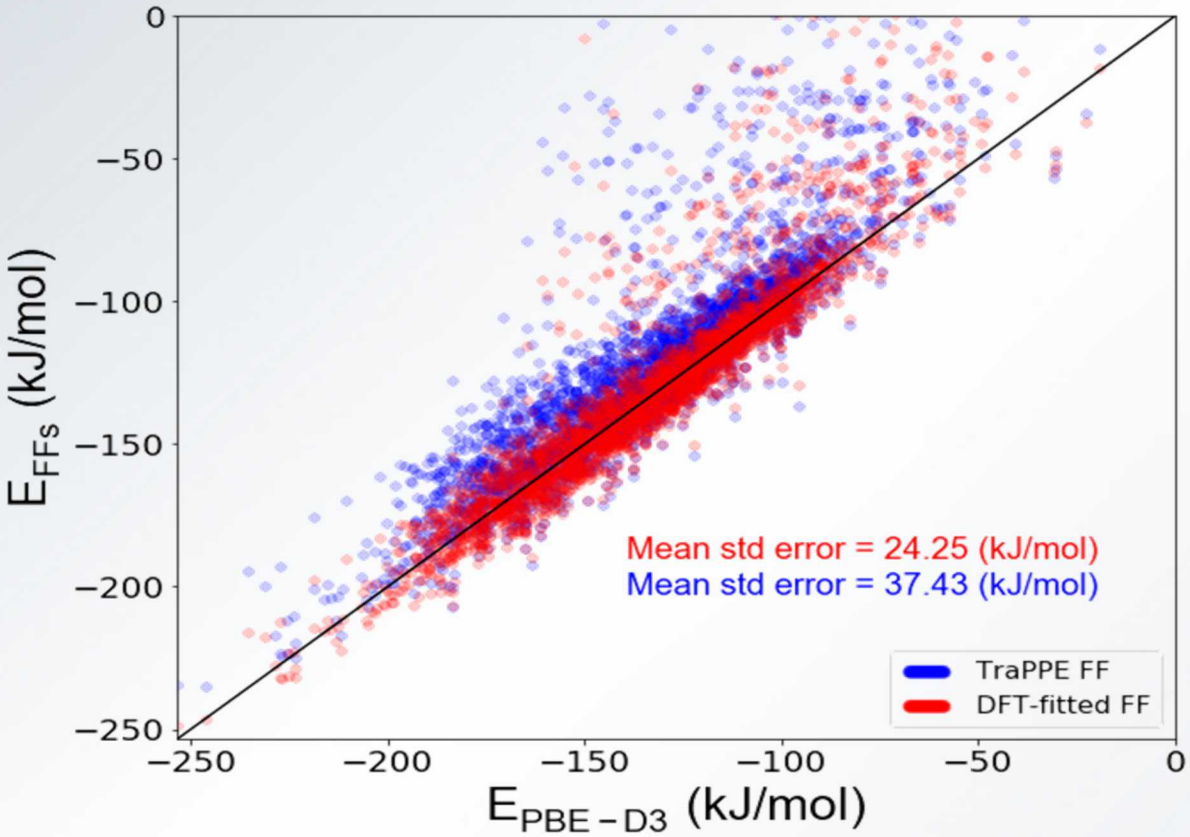


Figure E1: A parity plot between interaction energies calculated using classical force fields and quantum chemistry calculations using (a) a generic FF and (b) a DFT-derived FF for all CWAs and simulants adsorbed in 5 randomly selected MOFs from the database

Extra Slide 2

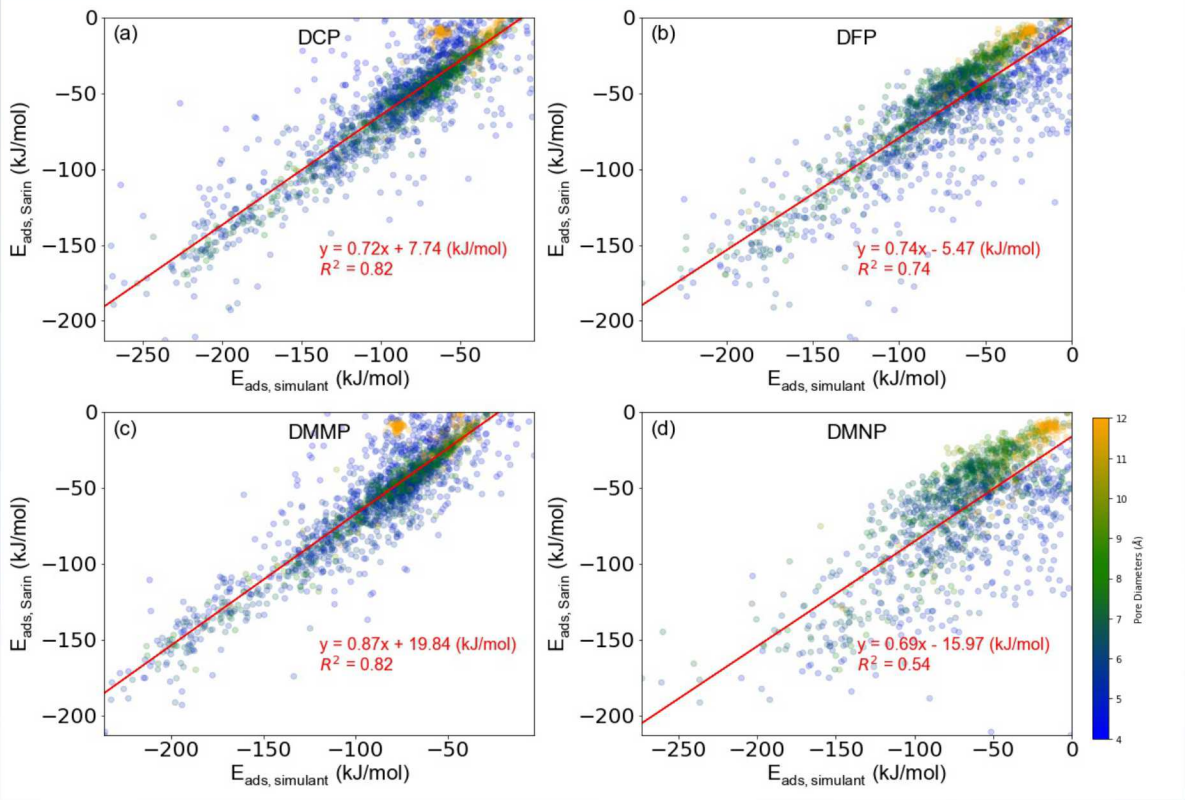


Figure E2: Heat of adsorption of Sarin compared to simulants, (a) DCP, (b) DFP, (c) DMMP, and (d) DMNP using generic FF

- High performing MOFs pore diameters are in the range of 6-10 Å
- DCP and DMMP are the closest to Sarin

Extra Slide 3

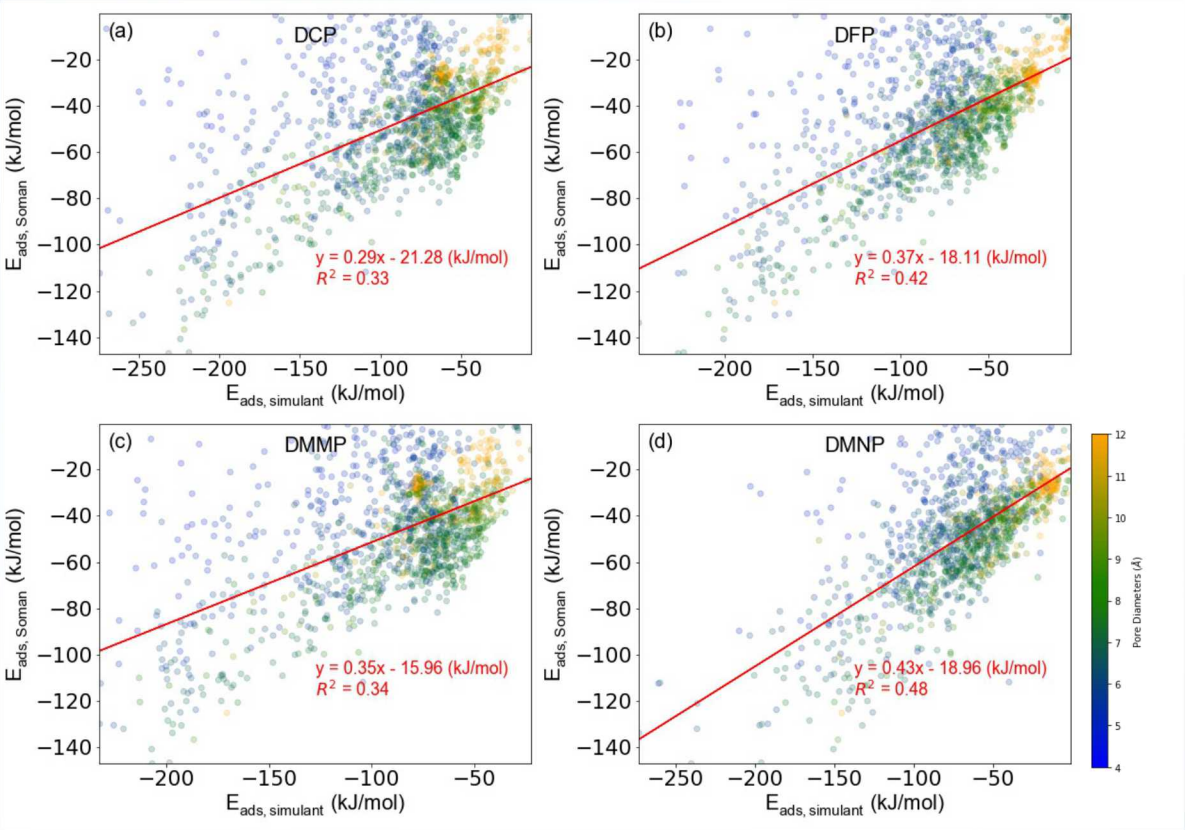
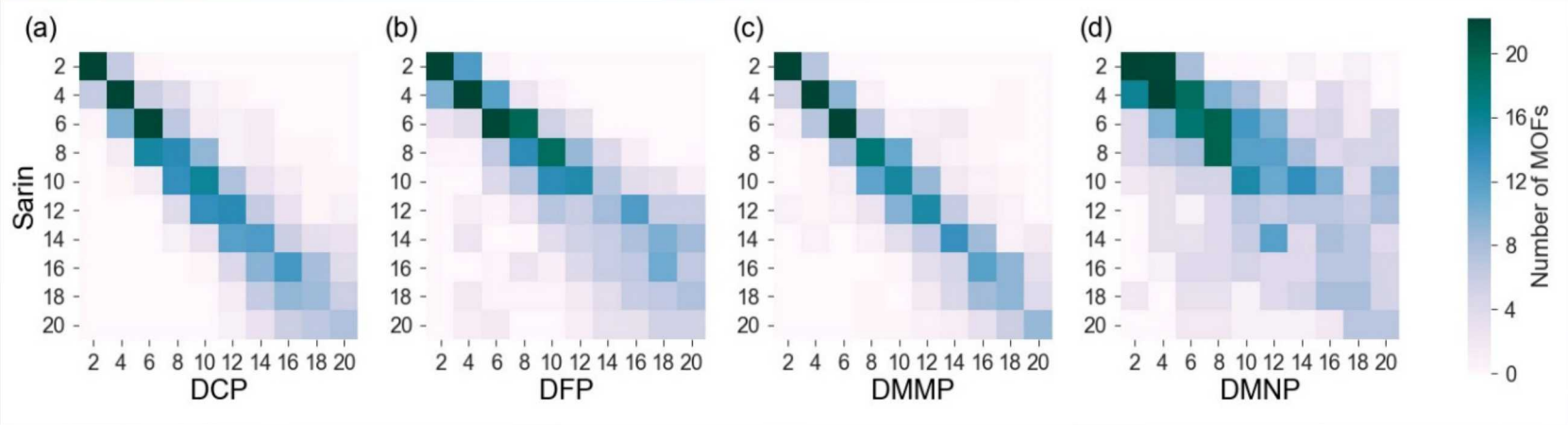


Figure E3: Heat of adsorption of Soman compared to simulants, (a) DCP, (b) DFP, (c) DMMP, and (d) DMNP using generic FF

- No simulant is able to very closely predict Soman's adsorption properties
- DMNP is the closest to Soman among all simulants

Correlation Between MOFs Rankings: CWAs vs Simulants for top 20% MOFs

For Sarin



For Soman