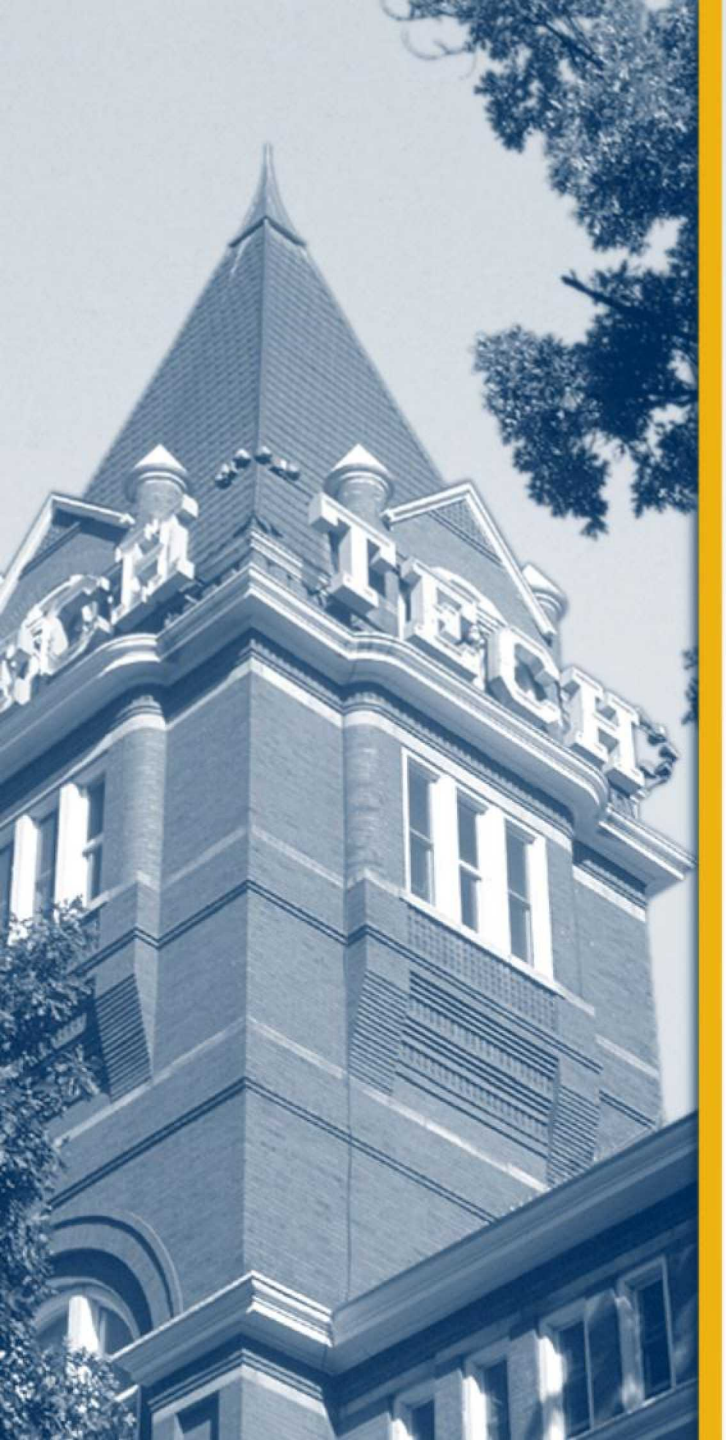

SAND2019-12808PE

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

October 22nd, 2019

Presentation by

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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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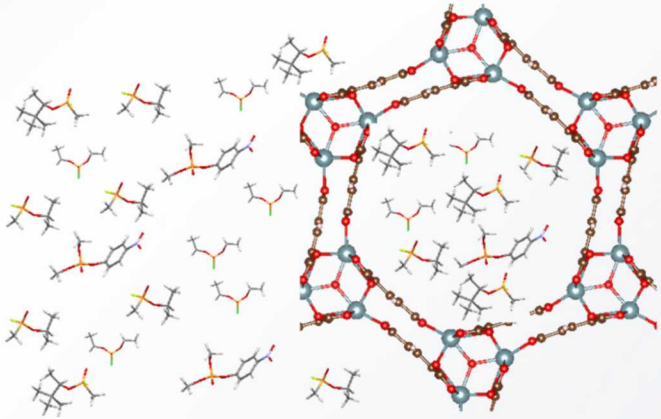
Introduction: Chemical Warfare Agents

- 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
- Capture of nerve agents using metal-organic frameworks (MOFs)
- 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
- However, no detailed comparison between CWAs and simulants for adsorption processes



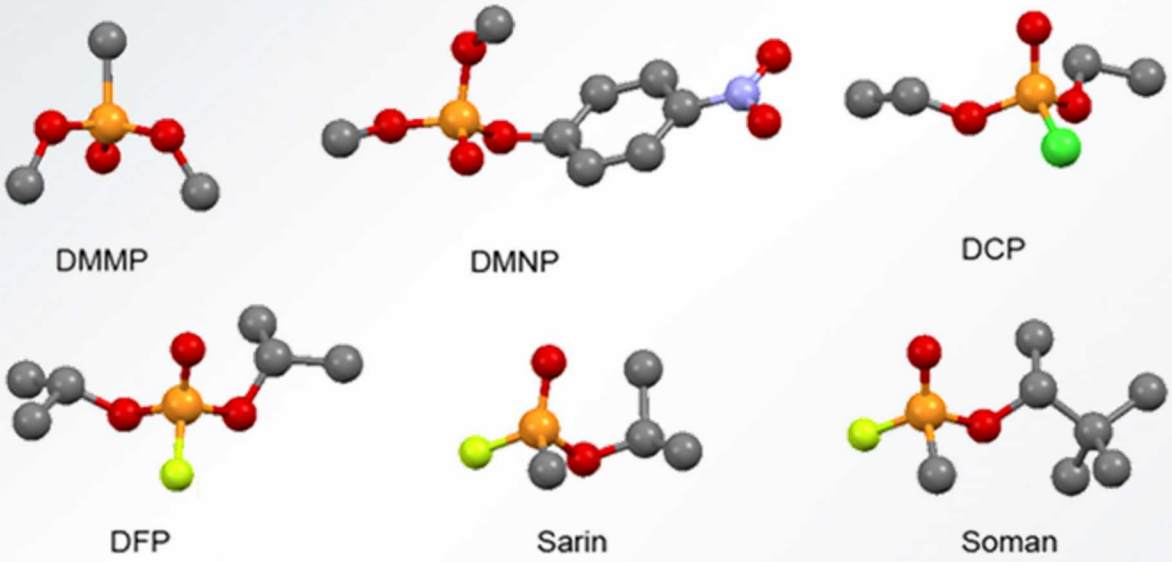
Objectives

- Prediction of adsorption and diffusion 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

Materials

- Adsorbents: CoRE MOFs database[1], 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



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

Simulation Methods

- Force-field derivation
  - VASP package, PBE-D3 functional, 10^{-6} eV 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

$$V = -\sum 4\varepsilon_{ij}^{*}\left[\left(\frac{\sigma_{ij}^{*}}{r}\right)^{12} - \left(\frac{\sigma_{ij}^{*}}{r}\right)^{6}\right] + k\frac{q_i q_j}{R_{ij}}$$

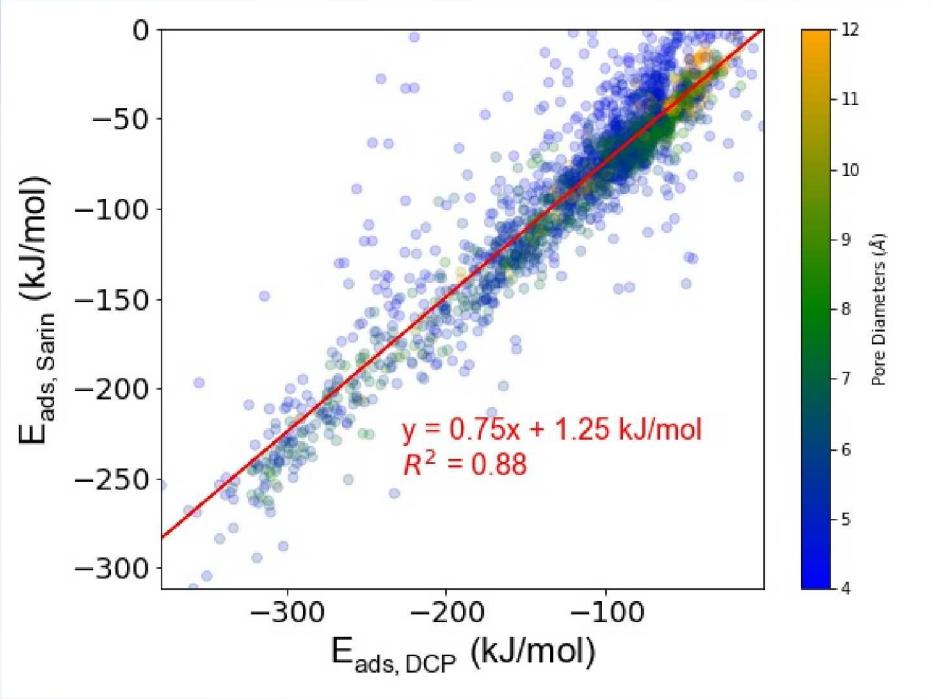
where, $\varepsilon_{ij}^{*} = \sqrt{\varepsilon_i(\boldsymbol{C_{1j}}\varepsilon_j)}$, $\sigma_{ij}^{*} = \frac{\sigma_i + \boldsymbol{C_{2j}}\sigma_j}{2}$ (Lorentz-Berthelot mixing rule),

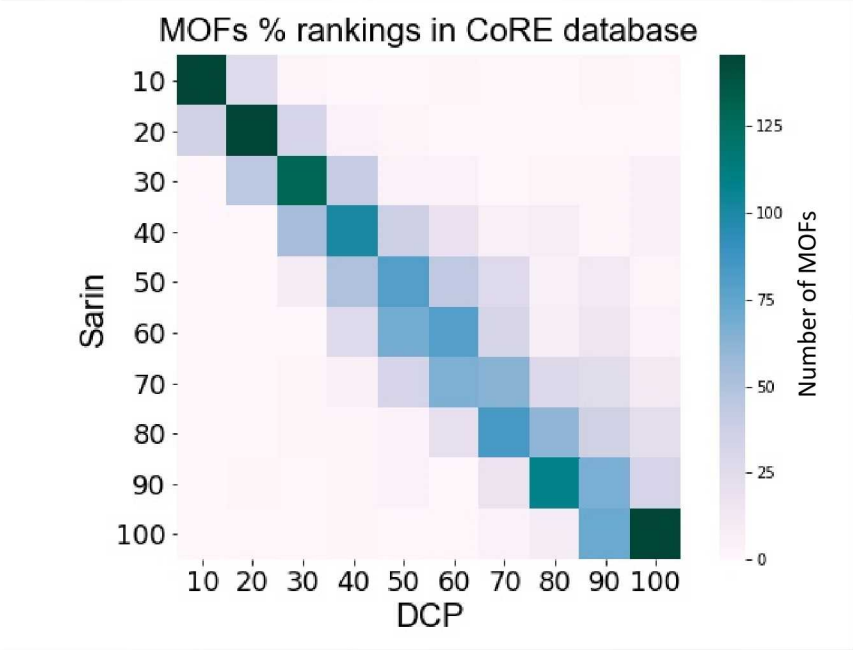
i and j are subscripts for MOF and adsorbate atoms respectively

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

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

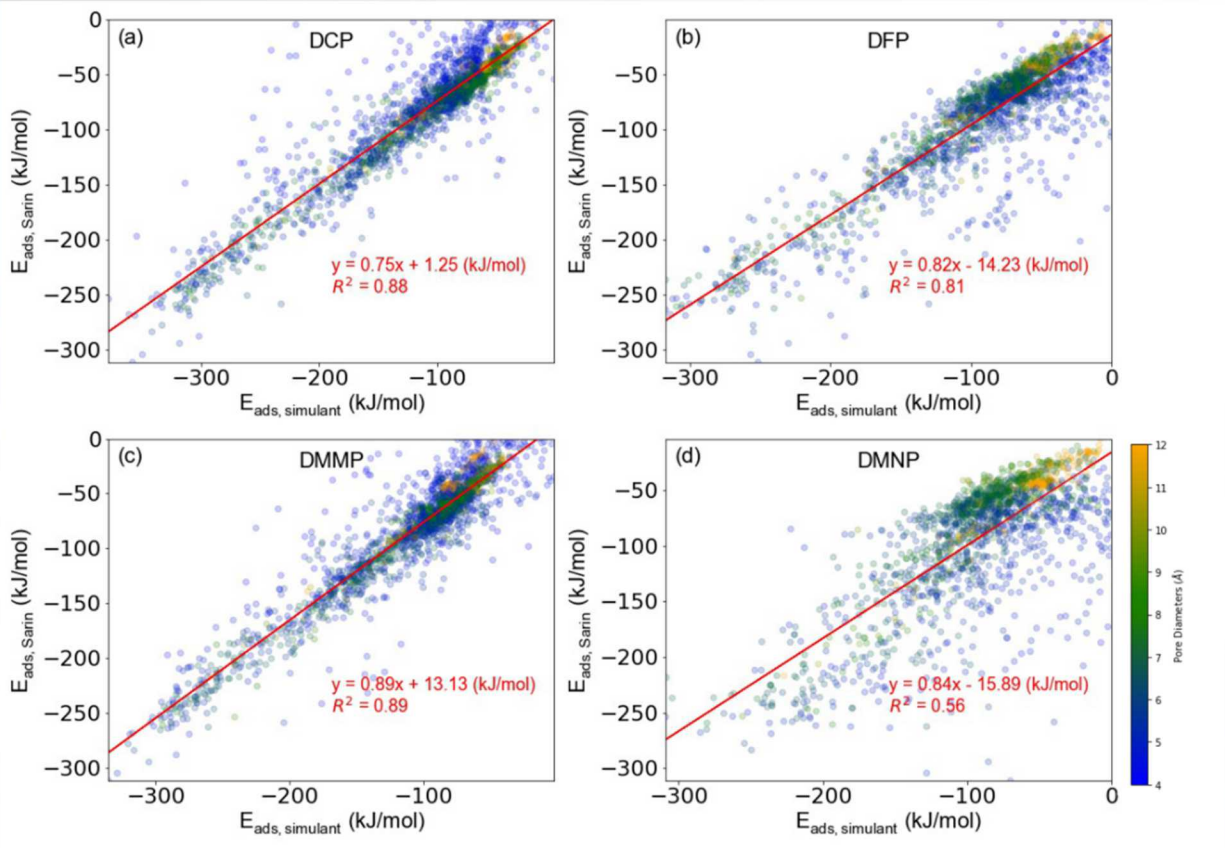
Heats of Adsorption: Sarin vs DCP





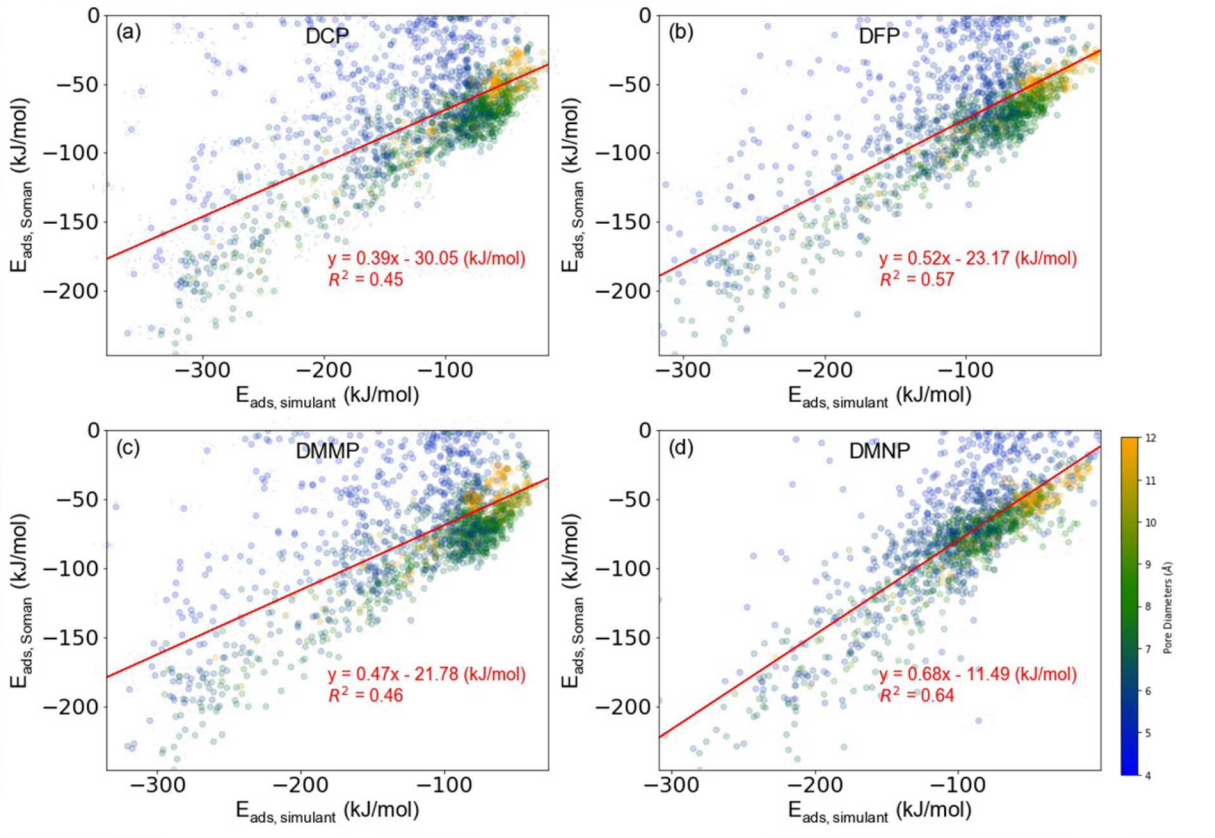
- Figures compares adsorption properties of Sarin and DCP in >2900 MOFs using DFT-derived FF
- DCP is able to predict Sarin's adsorption properties in CoRE database within 10% error for most MOFs

Heats of Adsorption: Sarin vs Simulants



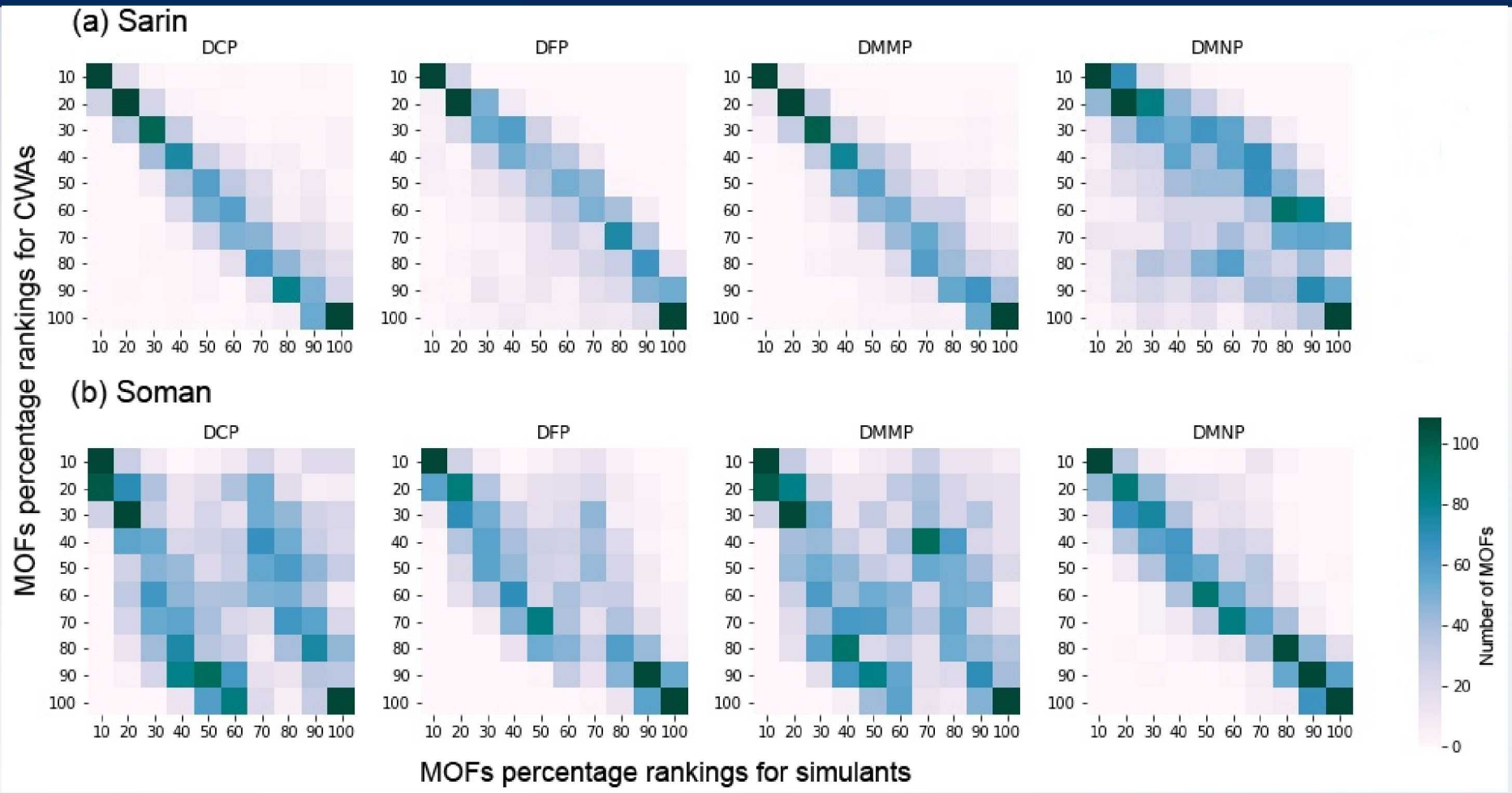
- High performing MOFs' pore diameters are in the range of 6-9 Å
- DCP and DMMP are the closest to Sarin

Heats of Adsorption: Soman vs Simulants



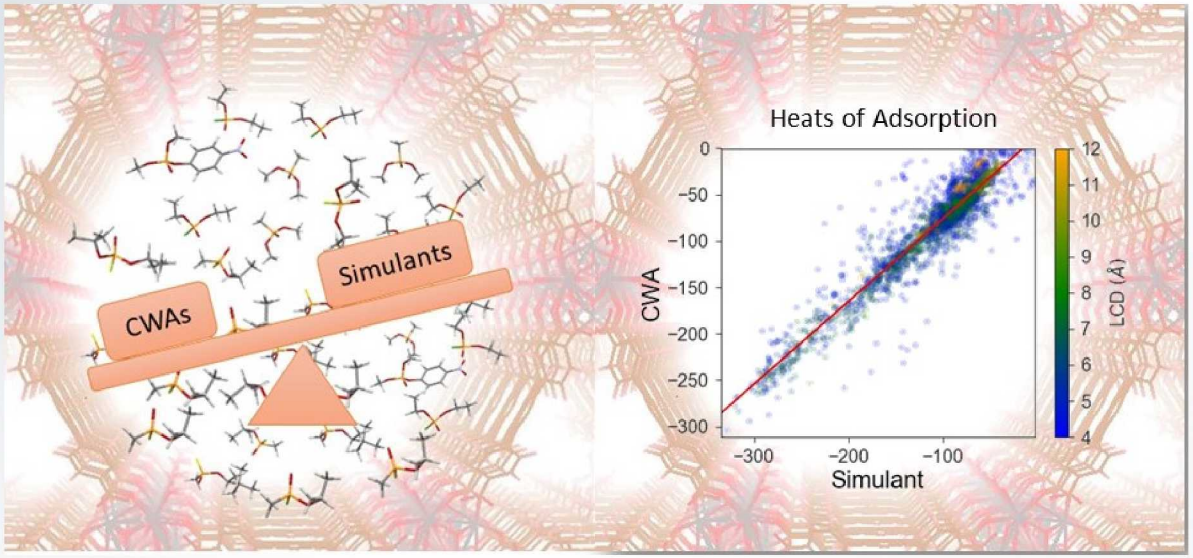
- No simulant is able to very closely predict Soman's adsorption properties
- DMNP is the closest to Soman among all simulants

Correlation Between MOFs Rankings: CWAs vs Simulants



- DCP and DMMP are able to best predict MOF rankings for Sarin based on adsorption properties
- DMNP is the only simulant that is able to closely predict MOF rankings for Soman based on adsorption properties

Summary: Adsorption of CWAs in MOFs



- DCP and DMMP are the best suited simulants to predict adsorption behavior of Sarin in nanoporous materials
- DMNP is the only simulant that is suited to predict Soman's adsorption behavior in nanoporous materials

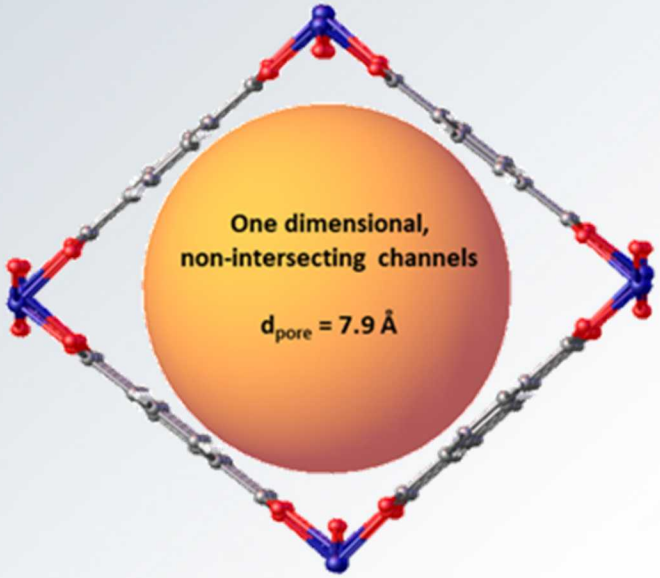
Diffusion of CWAs in MOFs

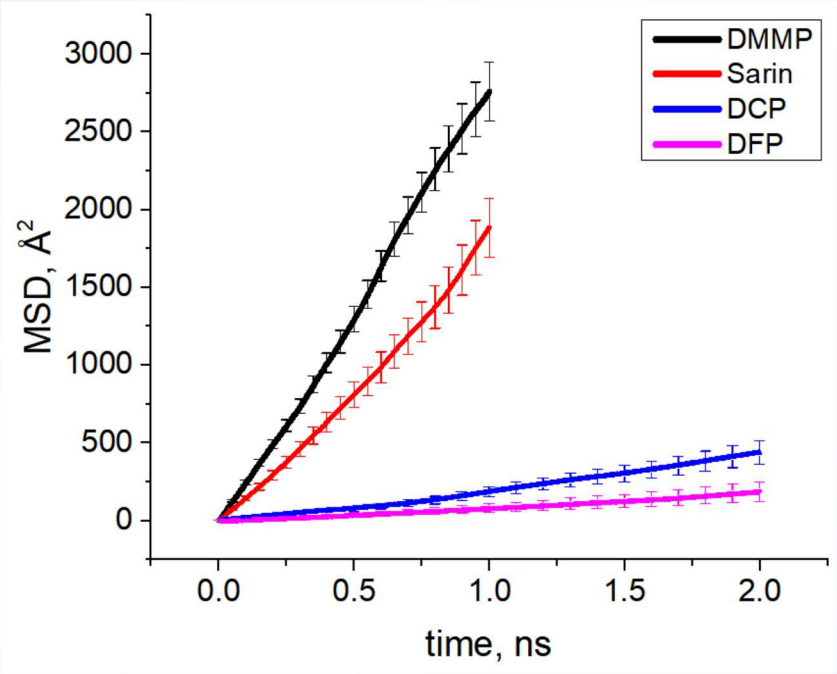
- To determine the kinetics of CWAs adsorption in MOFs, diffusion coefficients of these compounds in MOFs must be known

- We calculate diffusion of Sarin in four prototypical MOFs using classical simulations
  - MIL-47, ZIF-8, UiO-66, Cu-BTC

- Methods used:
  - Mean square displacements calculated using molecular dynamics for MIL-47
  - dcTST method using Umbrella sampling for other MOFs

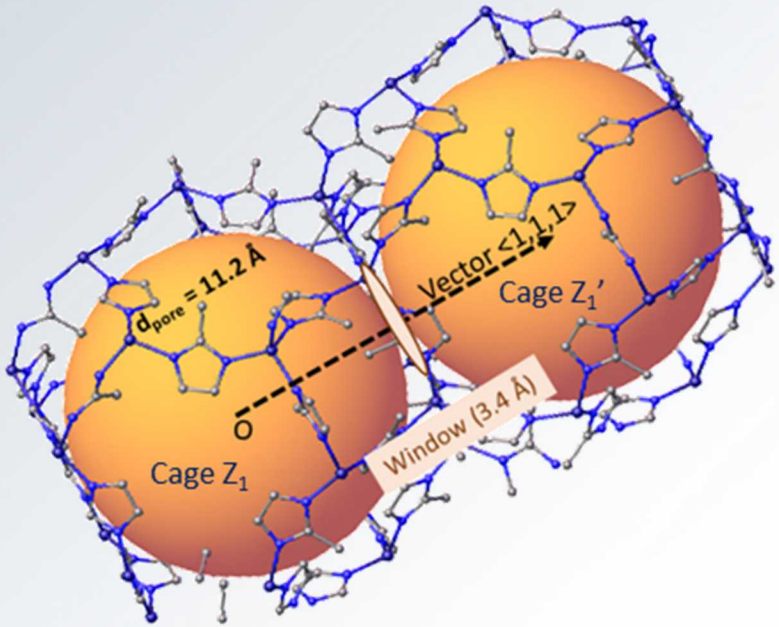
Diffusion in MIL-47

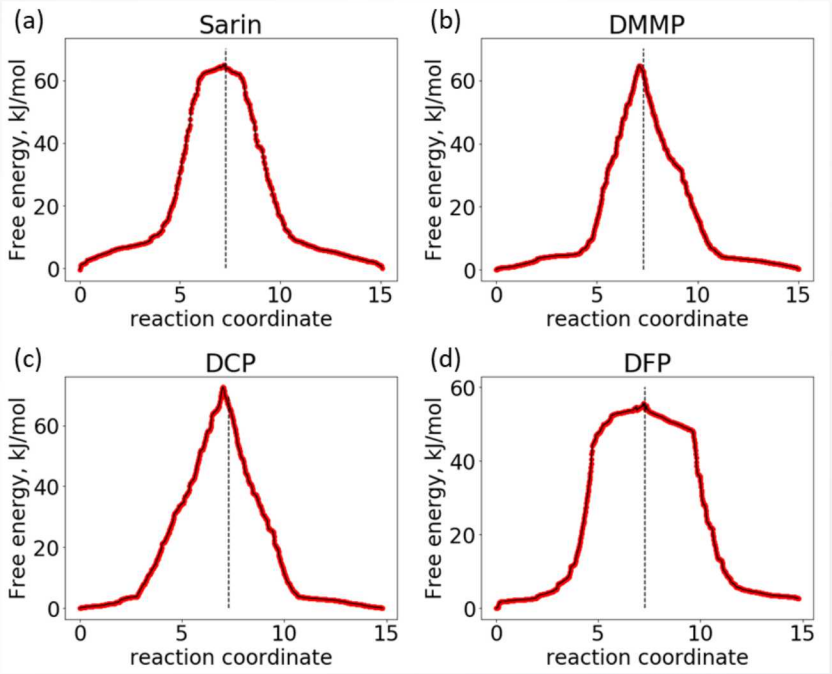




	Sarin	DMMP	DCP	DFP
$D_{300\ K}$ (cm^2/s)	2.2×10^{-5}	4.1×10^{-5}	1.7×10^{-6}	5.6×10^{-7}
$D_{400\ K}$ (cm^2/s)	4.7×10^{-5}	8.4×10^{-5}	6.3×10^{-6}	2.2×10^{-6}
$D_{500\ K}$ (cm^2/s)	8.3×10^{-5}	1.2×10^{-4}	1.2×10^{-5}	8.1×10^{-6}
E_A (kJ/mol)	8.2	6.4	12.3	16.3

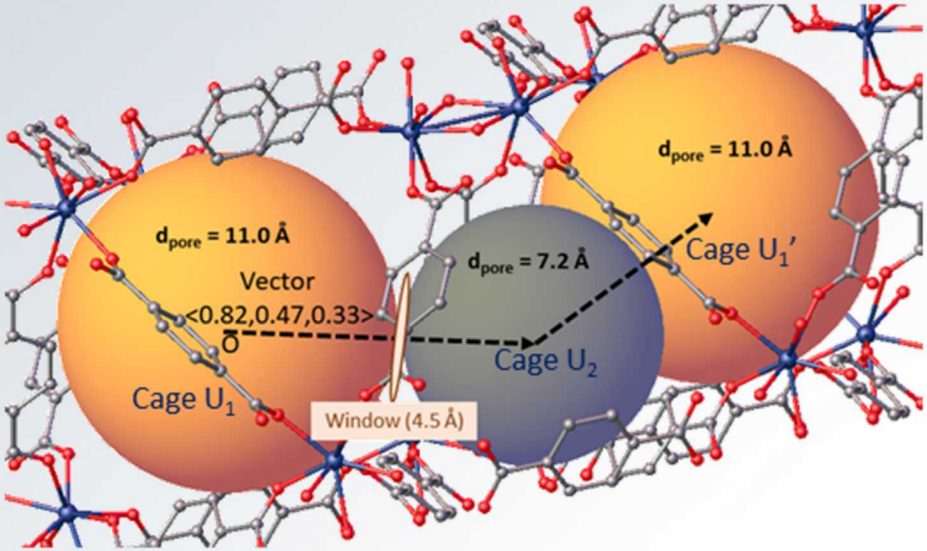
Diffusion in ZIF-8

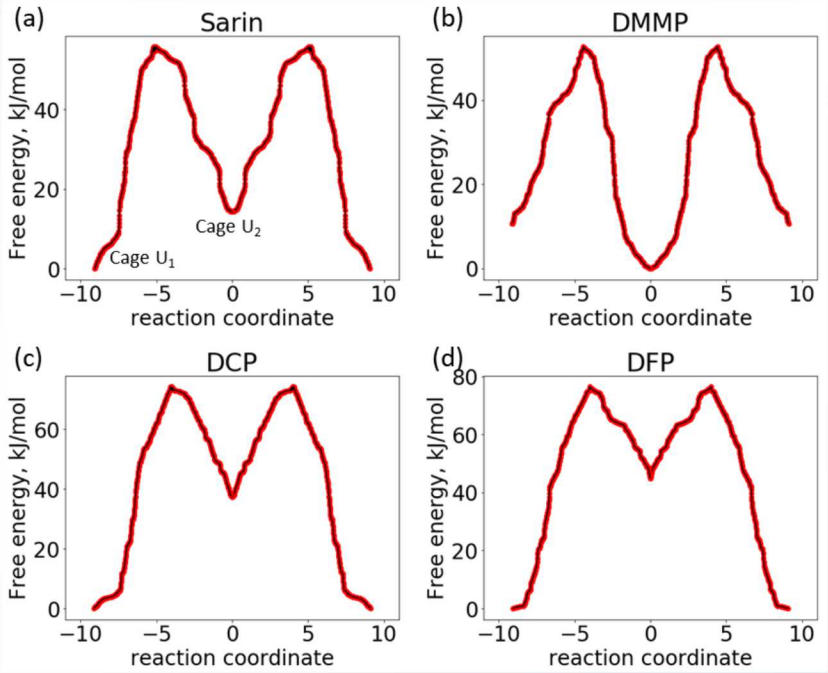




Molecule	Activation energy, kJ/mol	DCF	Diffusivity, cm^2/s
Sarin	66.0	0.85	5.44×10^{-14}
DMMP	64.7	0.89	4.81×10^{-14}
DCP	72.5	0.45	8.73×10^{-16}
DFP	54.7	0.31	1.15×10^{-12}

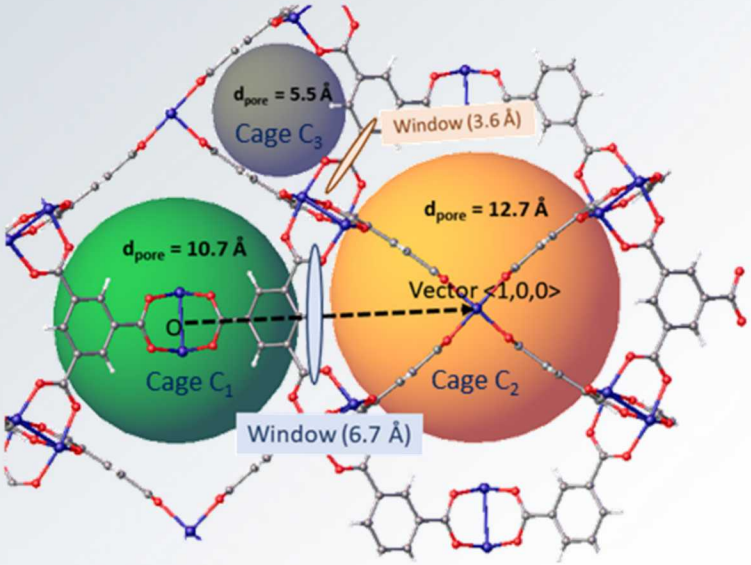
Diffusion in UiO-66

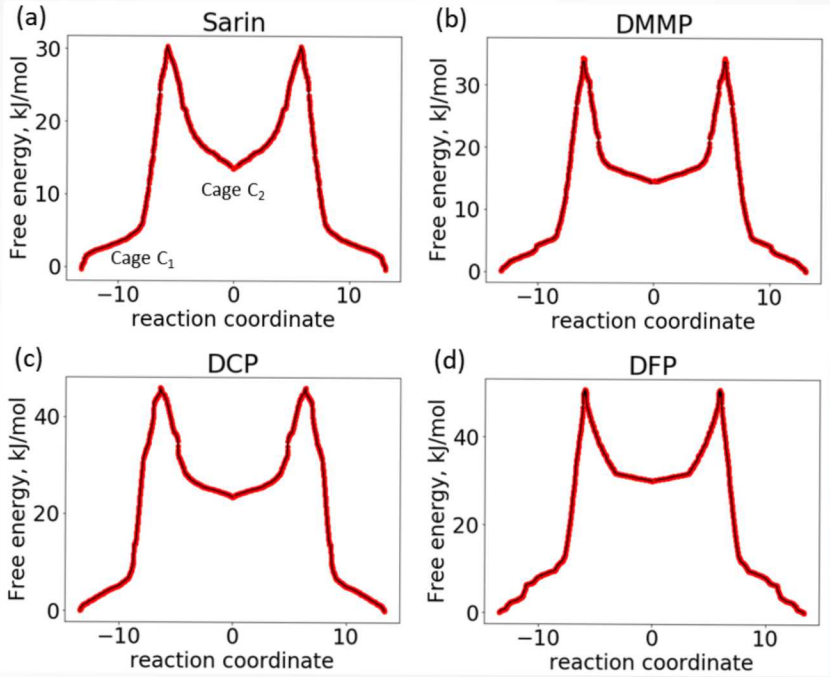




Molecule	$E_{A,U1-U2}$ kJ/mol	DCF_{U1-U2}	$E_{A,U2-U1}$ kJ/mol	DCF_{U2-U1}	D, cm^2/s
Sarin	53.2	0.024	37.4	0.027	4.3×10^{-13}
DMMP	45.8	0.038	56.1	0.032	1.6×10^{-13}
DCP	74.7	0.013	28.9	0.03	3.2×10^{-17}
DFP	76.3	0.008	35.2	0.017	1.2×10^{-17}

Diffusion in Cu-BTC





Molecule	$E_{A,C1-C2}$ kJ/mol	DCF_{C1-C2}	$E_{A,C2-C1}$ kJ/mol	DCF_{C2-C1}	D, cm^2/s
Sarin	30.3	1.21	17.3	1.15	5.4×10^{-8}
DMMP	33.8	1.32	23.1	1.31	1.3×10^{-8}
DCP	45.9	0.87	20.3	0.82	1.7×10^{-10}
DFP	50.6	0.81	16.4	0.86	1.4×10^{-11}

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Summary: Diffusion of CWAs in MOFs

Characteristic time for diffusion (in seconds) of sarin and simulants across 1 micron in different MOFs

Adsorbate	MIL-47	Cu-BTC	ZIF-8	UiO-66
Sarin	2.4×10^{-4}	2.2×10^{-2}	9.2×10^{4}	1.2×10^{4}
DMMP	1.2×10^{-4}	5.0×10^{-2}	1.0×10^{5}	3.1×10^{4}
DCP	2.9×10^{-3}	29	5.7×10^{6}	1.6×10^{8}
DFP	1.4×10^{-2}	1.8×10^{2}	4.3×10^{3}	4.2×10^{8}

- Sarin can diffuse throughout a one micron crystal in less than a second in MIL-47 and Cu-BTC but this process takes more than 3 hours in ZIF-8 and UiO-66
- DMMP is consistently the most similar in diffusivity of sarin for every MOF

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THANK YOU

Extra Slide 1

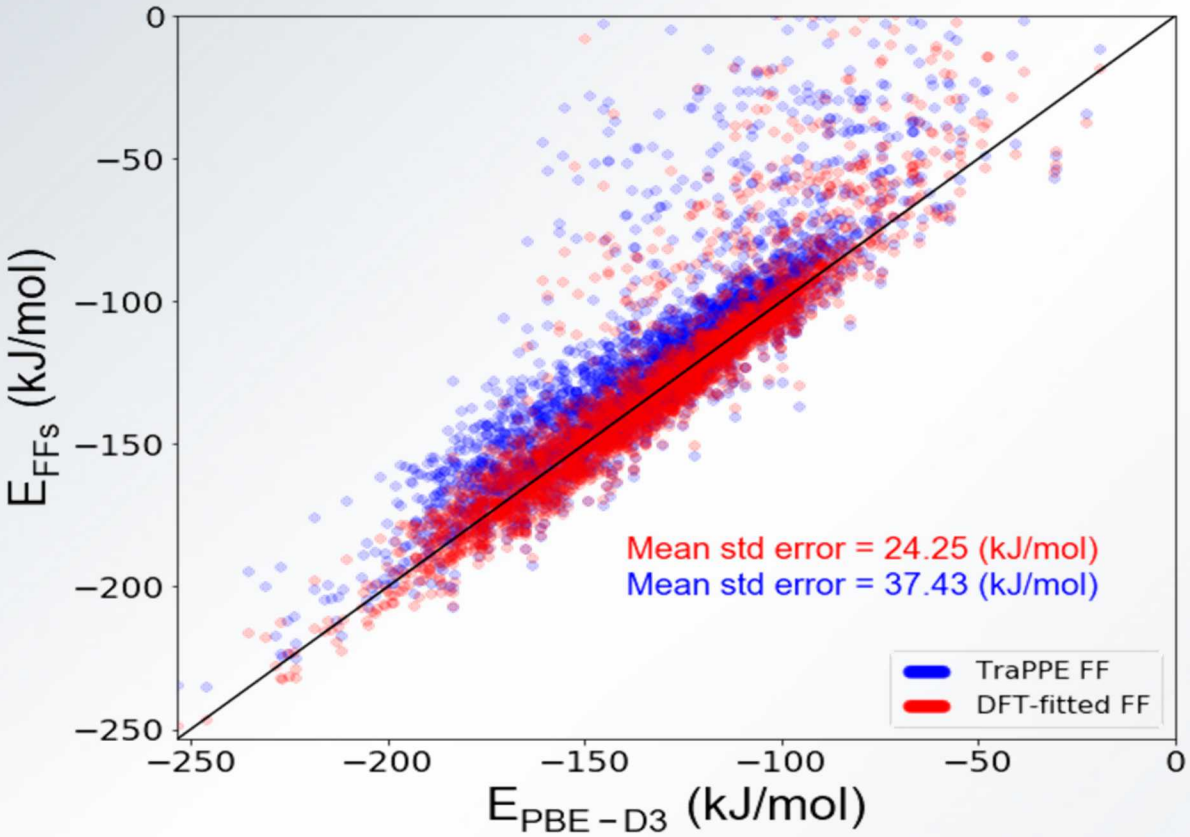


Figure E1: A parity plot between interaction energies calculated using classical force fields and quantum chemistry calculations using (a) a generic FF and (b) a DFT-derived FF for all CWAs and simulants adsorbed in 5 randomly selected MOFs from the database

Extra Slide 2

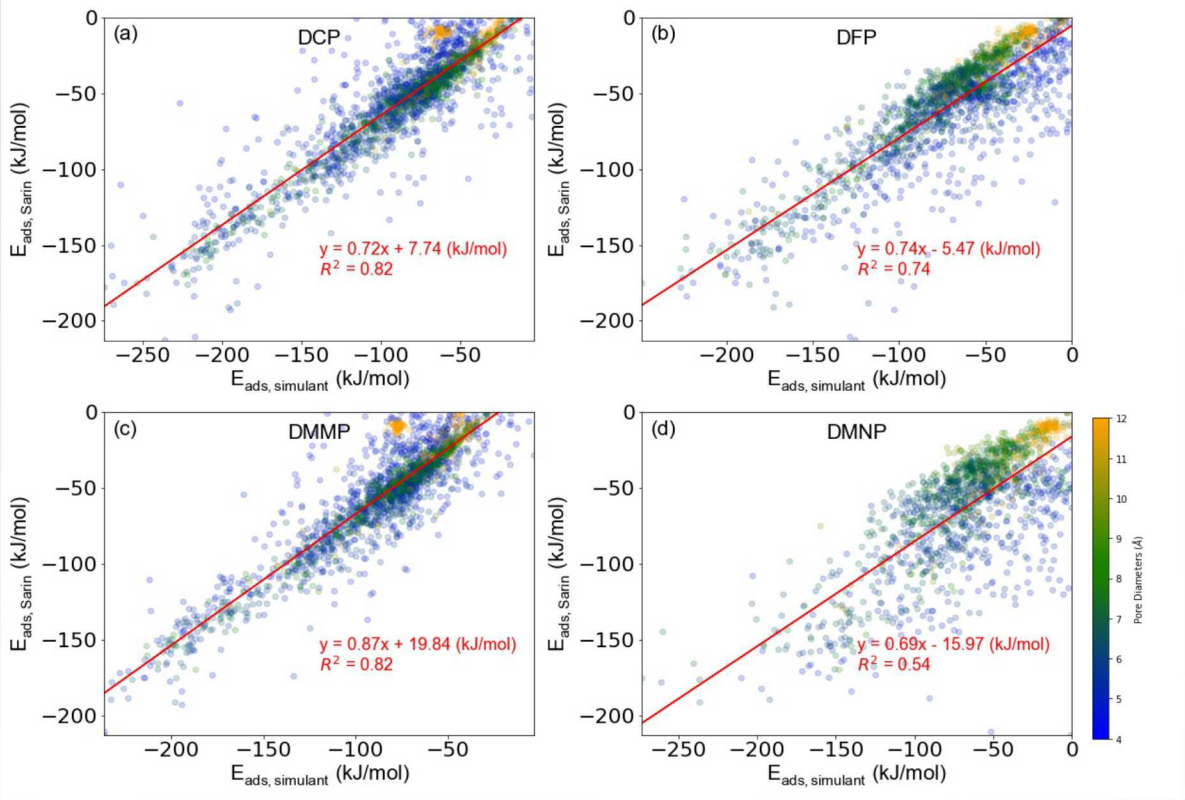


Figure E2: Heat of adsorption of Sarin compared to simulants, (a) DCP, (b) DFP, (c) DMMP, and (d) DMNP using generic FF

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

Extra Slide 3

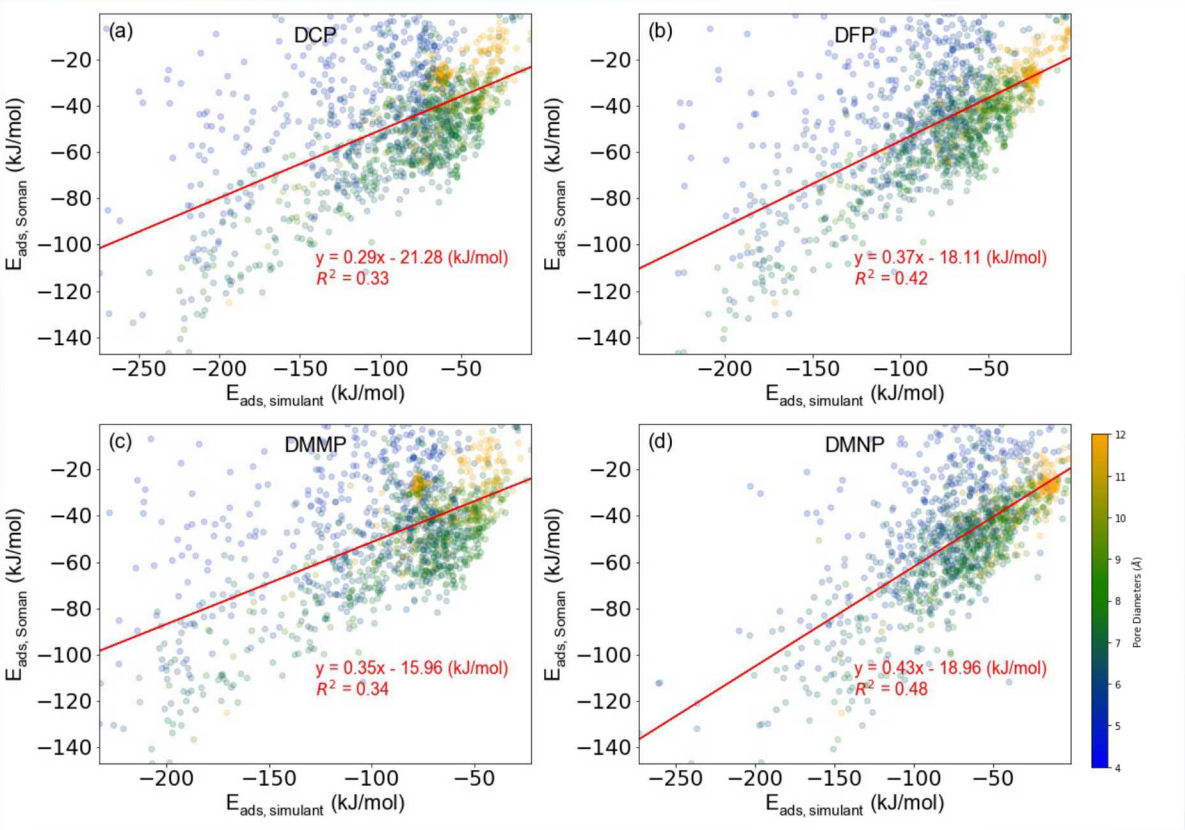
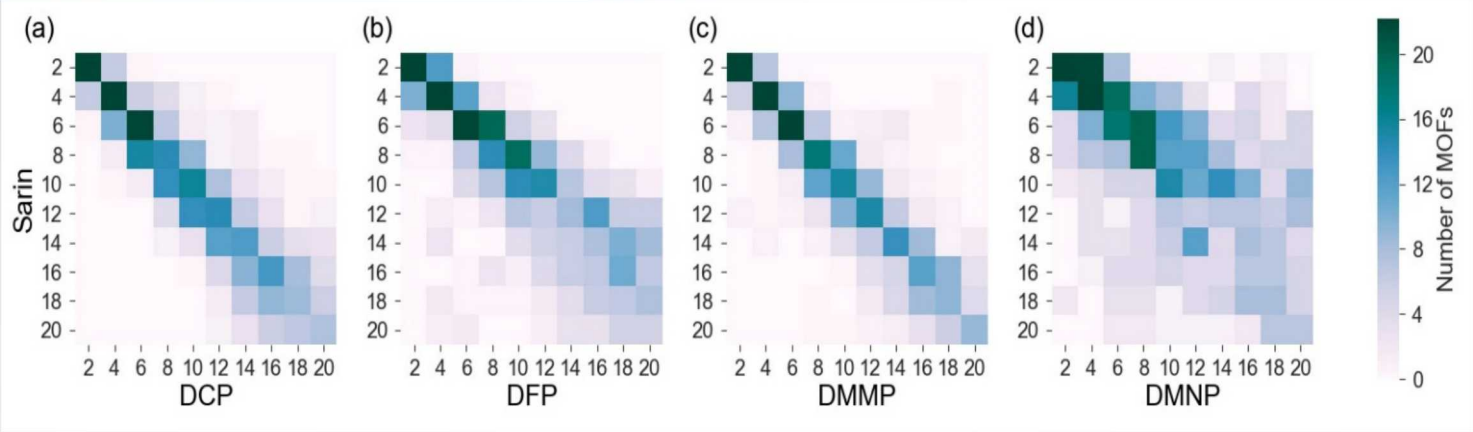


Figure E3: Heat of adsorption of Soman compared to simulants, (a) DCP, (b) DFP, (c) DMMP, and (d) DMNP using generic FF

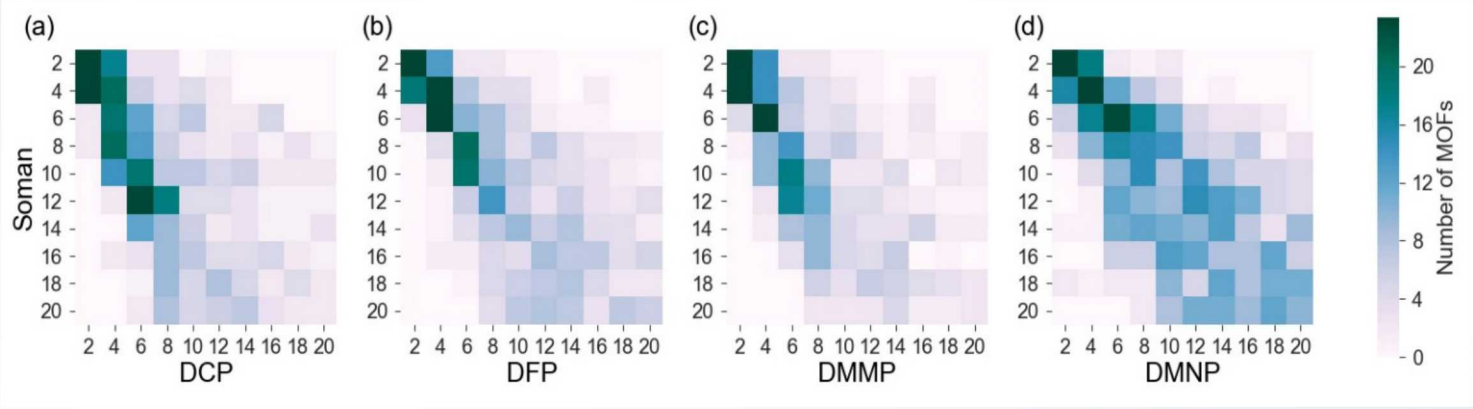
- No simulant is able to very closely predict Soman's adsorption properties
- DMNP is the closest to Soman among all simulants

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

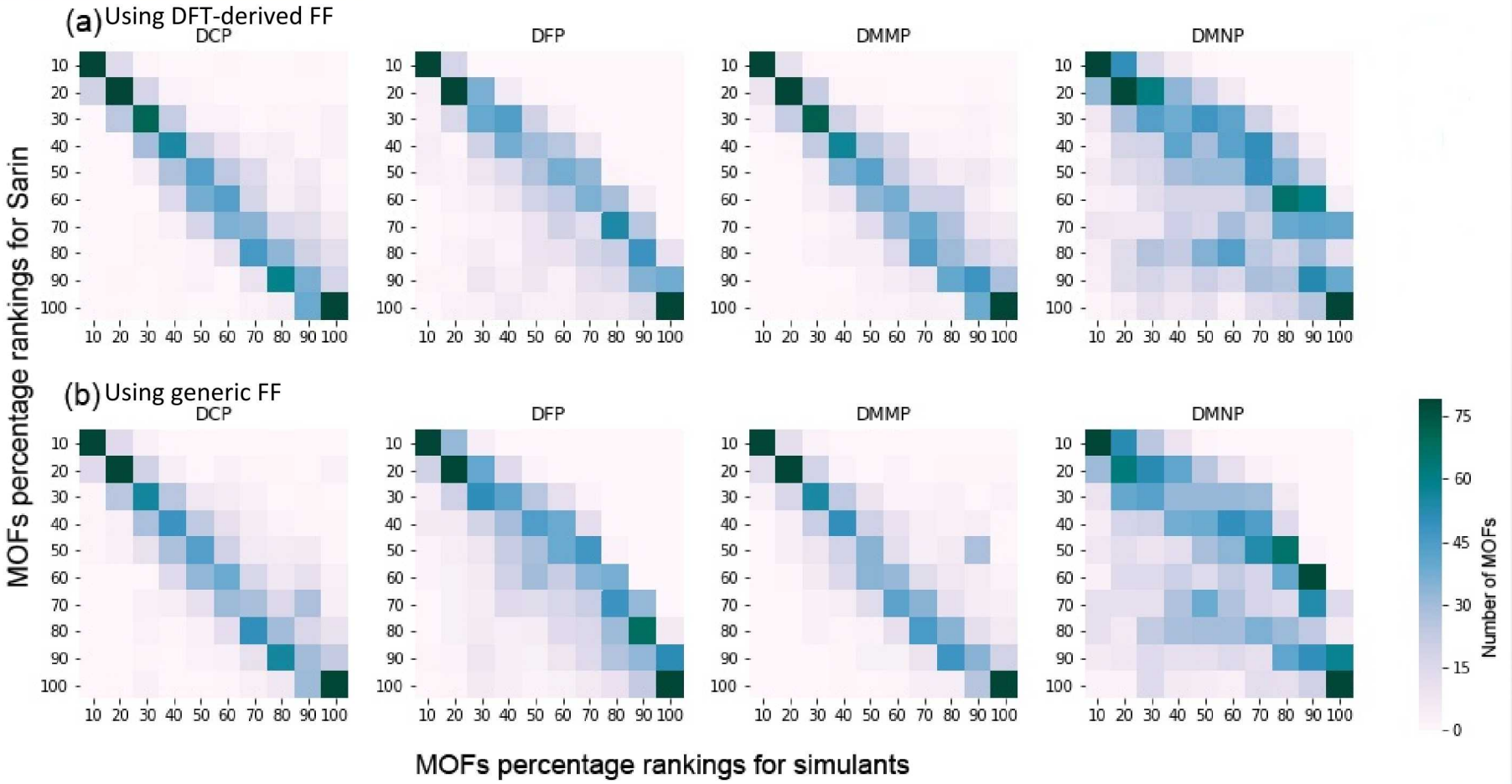
For Sarin



For Soman

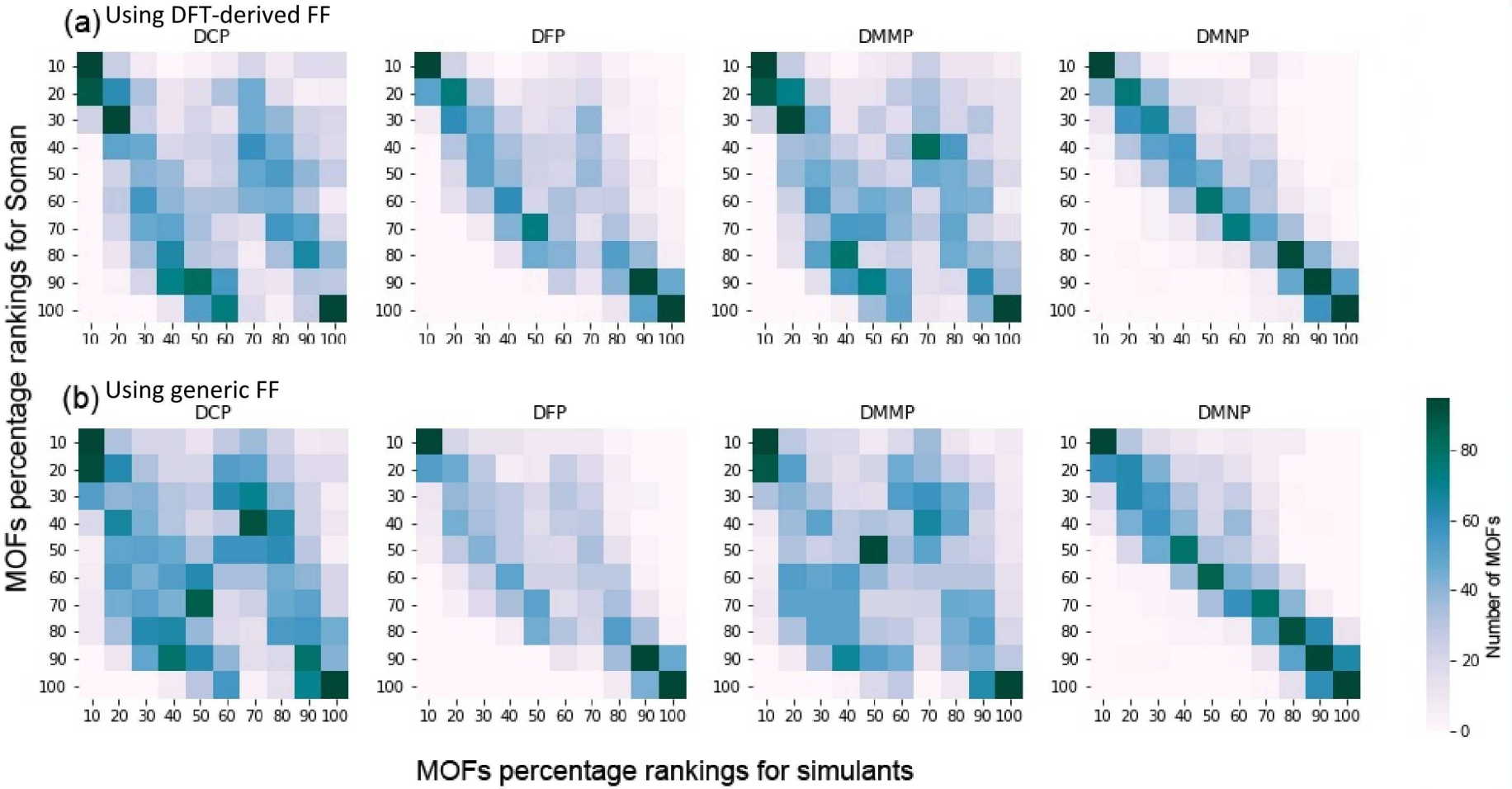


Correlation Between MOFs Rankings: Sarin vs Simulants



- DCP and DMMP are able to best predict MOFs ranking of Sarin based on adsorption properties
- DMNP is the only simulant that is able to closely predict MOFs ranking of Soman based on adsorption properties

Correlation Between MOFs Rankings: Soman vs Simulants



- Both generic and DFT-derived FFs show similar behaviors