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Simulation of low-pressure noble gas adsorption in nanoporous framework materials

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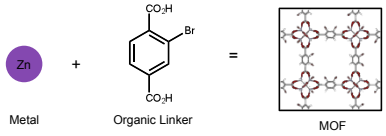
Introduction

Metal-organic frameworks (MOFs) are a type of nanoporous framework material comprised of metal oxide centers connected by organic linker molecules. MOFs have exceptionally high gas storage capacity and high gas uptake at very low pressures due to their high surface area (>4000 m^2/g) and low density (<1g/cm^3). Additionally, with appropriate choice of building materials MOF properties can be tuned to preferentially adsorb and store specific gases.



Small quantities of noble gases are present in the atmosphere, yet their separation from air, purification, and detection are important to a variety of processes. Adsorption of noble gases has proven difficult since they are known to adsorb onto surfaces by van der Waals interactions. MOFs represent a new class of sorbent materials that are capable of preferentially detecting and capturing specific these and other weakly interacting gases. We investigated halogenated MOFs as detectors of noble gases, and the effects of increasing polarizability on noble gas adsorption.

Gas	Concentration In Air
Argon	9340 ppm
Krypton	1.1 ppm
Xenon	0.09 ppm
Radon	--
Nitrogen	78.09%

The current study uses grand canonical Monte Carlo simulations to determine Henry's constants, adsorption energies, and adsorption isotherms for noble gases and halogenated MOFs at low pressures and room temperature.

Model

MOFs are modeled as rigid frameworks whose atoms are held fixed at their crystallographic positions. MOF atoms are modeled using the universal force field and charges from Zu *et al*[1]. A single-site Lennard-Jones model is used for the noble gases and a three-site model including charge is used for N_2.

MOF	Chemical Formula	Surface Area [m^2/g]	% Free Volume
IRMOF1	$Zn_4O(CO_2\text{-}C_6H_4\text{-}CO_2)_3$	3280	78.8
IRMOF2 - F	$Zn_4O(CO_2\text{-}C_6H_3F\text{-}CO_2)_3$	3236	78.6
IRMOF2 - Cl	$Zn_4O(CO_2\text{-}C_6H_3Cl\text{-}CO_2)_3$	3208	77.2
IRMOF2 - Br	$Zn_4O(CO_2\text{-}C_6H_3Br\text{-}CO_2)_3$	2828	76.4
IRMOF2 - I	$Zn_4O(CO_2\text{-}C_6H_3I\text{-}CO_2)_3$	2538	75.5

Surface areas and free volumes calculated using the Connelly surface method[2]

Method

Grand canonical Monte Carlo simulations were performed in the μVT ensemble using the MCCCS Towhee Code[3]. Translational, rotational, particle insertion and deletion, and particle swap moves were performed. Simulations were performed at 292K for pressures between ~ 0.001 atm and ~ 2.5 atm. The following properties were calculated:

Henry's constant – a measure of the distribution between an infinitely dilute gas in the gas phase and the gas adsorbed onto a MOF's surface

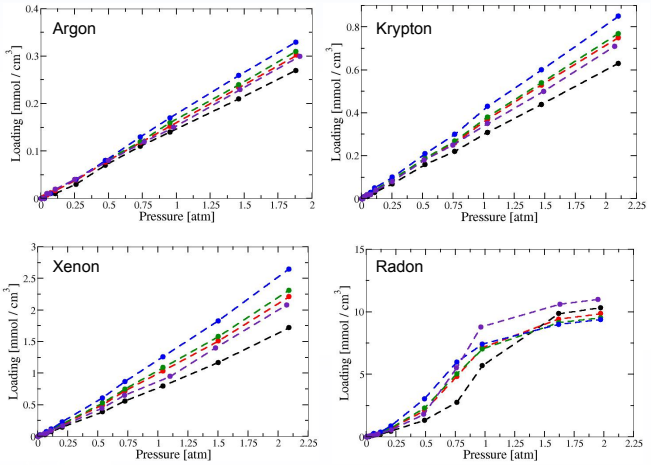
Adsorption Energy – the energy released upon adsorption of an infinitely dilute gas onto a MOF

Adsorption Isotherm – the amount of gas adsorbed onto the surface of a MOF as a function of pressure for a given temperature

Results

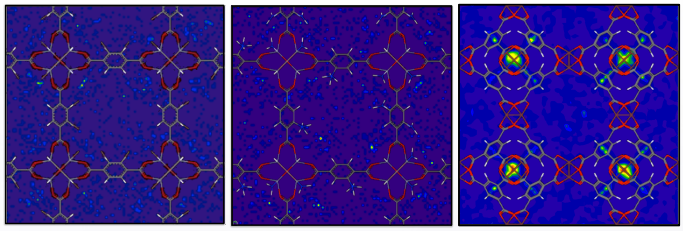
Adsorption Isotherms

- MOFs functionalized with halogens have a greater affinity for noble gases than IRMOF1
- At higher pressures, gas uptake correlates with halogen polarizability: I > Br > Cl > F
- Halogenated MOFs have the strongest affinity for radon compared to other noble gases



2-D Density Plots for Kr at P ~ 2 atm

- Adsorption sites in IRMOF2-I (near carboxylate groups) are representative of the halogenated series
- Amine functionalization shifts the adsorption into the pore
- Enhanced gas adsorption is seen by MOFs with open metal sites and small cavities, such as Cu-BTC



IRMOF2 - I | IRMOF3 | Cu-BTC

Adsorption Properties

MOF	Henry's Constant [mmol/cm^3 - atm]					Adsorption Energy [kJ/mol]					Selectivity			
	Ar	Kr	N_2	Xe	Rn	Ar	Kr	N_2	Xe	Rn	Ar/N_2	Kr/N_2	Xe/N_2	Rn/N_2
IRMOF2 - F	0.14	0.29	0.13	0.73	2.20	-8.10	-10.27	-8.12	-13.43	-16.67	1.13	2.29	5.72	17.22
IRMOF2 - Cl	0.16	0.36	0.14	0.88	2.76	-8.48	-10.98	-8.52	-14.3	-17.63	1.12	2.47	6.12	19.11
IRMOF2 - Br	0.16	0.37	0.15	0.93	3.32	-8.42	-11.0	-8.42	-14.24	-17.57	1.12	2.50	6.30	22.63
IRMOF2 - I	0.18	0.39	0.16	0.99	3.57	-8.63	-11.79	-8.47	-14.62	-18.57	1.11	2.47	6.31	22.72

Conclusions

In summary, Monte Carlo simulations are an efficient method for predicting trends of gas adsorption in MOFs. In general, MOFs functionalized with halogens have a greater affinity for noble gases than IRMOF-1. Gas uptake at higher pressure correlates with halogen polarizability, but these trends are less apparent in the low pressure regime. Additionally, halogenated MOFs are slightly selective for noble gases over nitrogen (a proxy for air).

References

[1] Q. Zu, C. Zhong, *J. Phys. Chem. C* 2010, 114, 5035-5042

[2] Accelrys Material Studios

[3] M.G. Martin, B. Chen, C.D. Wick, J.J. Potoff, J.M. Stubbs, J.I. Siepmann, MCCCS Towhee,http://towhee.sourceforge.net.

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