

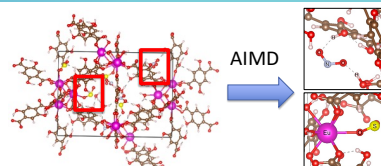
# Mechanisms of Competitive Adsorption and Reactivity of Acid Gases in RE-DOBDC MOFs

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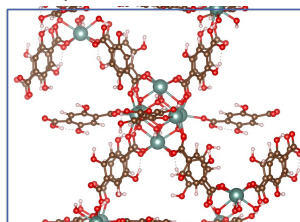
## Introduction

- Acid gases are commonly found in complex chemical streams, and metal-organic frameworks (MOFs) are being evaluated for their separation and removal [1,2]
- Ab initio* molecular dynamics (AIMD) are applied to identify fundamental acid gas-framework interactions in *ternary gas mixtures*
- Results are used to design new materials for acid gas separation and adsorption based on binding energies and reactive intermediates identified via AIMD trajectories
- Provides a road map for the application of advance computation for materials design



## Ab initio Electronic Structure Methods

- Vienna *ab initio* Simulation Package (VASP)
- Generalized Gradient approximation with PBEsol functional [3]
- Plane wave basis set with Projector Augmented Wave (PAW) pseudopotentials
- Dispersion corrections treated by DFT-D3 method with Becke-Johnson Damping
- AIMD protocol: NVE thermalization at 300 K followed by NVT for 10 ps [4,5]
- 4 H<sub>2</sub>O, 4 NO<sub>2</sub> and 4 SO<sub>2</sub> molecules in MOF
- Three unique geometries generated with PACKMOL
- Three geometries calculated at 300 K, one at 500 K and 700 K



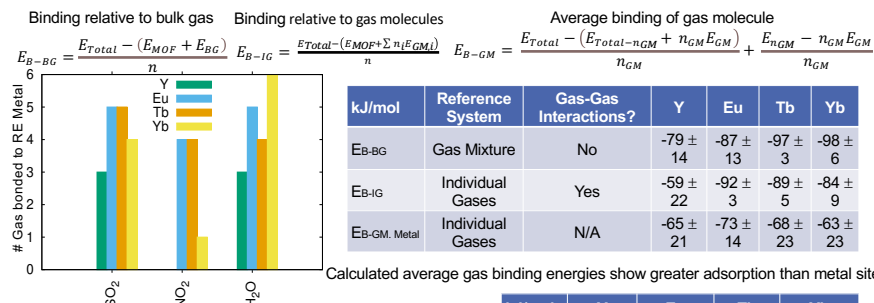
Y-DOBDC Unit Cell Model

Atom Colors: O (red), H (white), C (brown), Y\* (teal)  
\*can be substituted for any RE metal

### 5 simulations for 4 DOBDC MOF structures

Rare Earth Metal	Simulations/RE (#)	Configurations (#)	Temperature (K)
Eu, Tb, Y, Yb	3	3	300
	1	1	500
	1	1	700

## Average System Adsorption



- Simulations show MOFs have selective adsorption, even with similar average adsorption energies
- Eu and Tb has strongest SO<sub>2</sub> adsorption
- NO<sub>2</sub> has large variability; strongest in Yb, though not with metal site
- HONO, formed from NO<sub>2</sub> deprotonation reaction, has much smaller adsorption than NO<sub>2</sub>
- H<sub>2</sub>O binds most to metal sites and has largest adsorption energy

kJ/mol	Y	Eu	Tb	Yb
H <sub>2</sub> O	-45 ± 27	-115 ± 7	-112 ± 3	-95 ± 16
NO <sub>2</sub>	-65 ± 70	-93 ± 8	-71 ± 5	-148 ± 78
HONO	-22 ± 41	-29 ± 22	-10 ± 23	-19 ± 12
SO <sub>2</sub>	-61 ± 31	-102 ± 27	-98 ± 7	-59 ± 9
Average	-53 ± 8	-83 ± 46	-89 ± 28	-57 ± 40

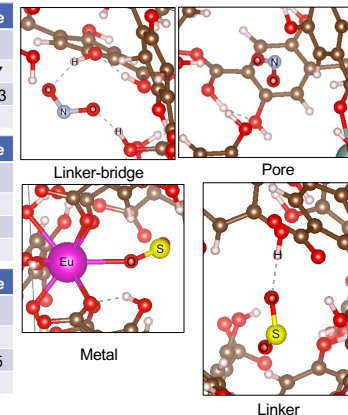
Average calculated Adsorption Energies

## Adsorption Site Analysis

Simulations revealed four common adsorption sites that have different MOF-Gas interactions

$$E_{B-BG} = E_{Total} - (E_{MOF} + E_{GM})$$

kJ/mol	Y	Eu	Tb	Yb	Average
H <sub>2</sub> O Pore	0.4	-0.2	3	8	3 ± 3
H <sub>2</sub> O Linker	-50	-87	-60	-41	-60 ± 17
H <sub>2</sub> O Linker-Bridge	-74	-130	-31	-111	-112 ± 23
H <sub>2</sub> O Metal	-88	-91	-93	-88	-90 ± 2
NO <sub>2</sub> Pore	-15	-34	-18	-29	-24 ± 8
NO <sub>2</sub> Linker	-44	-63	-53	-41	-50 ± 9
NO <sub>2</sub> Linker-Bridge	-44	-66	-68	-50	-58 ± 9
NO <sub>2</sub> Metal	-46	-69	-47	-42	-51 ± 11
SO <sub>2</sub> Pore	-20	-17	-17	-21	-19 ± 2
SO <sub>2</sub> Linker	-65	-71	-69	-69	-69 ± 3
SO <sub>2</sub> Linker-Bridge	-22	-89	-49	-85	-61 ± 25
SO <sub>2</sub> Metal	-61	-66	-65	-60	-63 ± 3



Calculated Adsorption Energies

## Temperature Effects

	kJ/mol	Y		Eu		Tb		Yb	
Temp (K)	500	700	500	700	500	700	500	700	
EB-Mix	-86	-60	-90	-50	-41	-73	-53	-53	
EB-Ind	-74	N/A	-89	-10	-18	N/A	-35	-38	
H <sub>2</sub> O	-107	-95	-113	-11	64	-54	-83	-206	
NO <sub>2</sub>	-101	-27	-63	61	-10	-89	71	-1	
HONO	-74	-32	-32	N/A	N/A	17	-160	11	
SO <sub>2</sub>	-91	-24	-125	44	19	-33	-16	-14	

- Average adsorption energies decrease with increasing temperature
- Adsorption energies depend on molecule configuration in MOF
- Strong adsorption energies at 500K

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## Conclusions

- Ab initio* molecular dynamics simulations of multi-component acid gas mixtures were used to identify reactivity of acid gases with metal and linker sites
- Calculated average adsorption energies were similar for all MOFs despite having different metal-site adsorption
- Nanoconfinement inside MOF *lowers* average adsorption energy
- Adsorption site analysis shows that linker-gas interactions can be greater than metal-gas interactions, especially if they are able to create multiple hydrogen bonds
- Higher temperature simulations show stable adsorption up to 700K
- Future work: Investigating MOF degradation pathways, looking at effect of functional groups on MOFs**

## References

- Sava Gallis, D.F., D.J. Vogel, G.A. Vincent, J.M. Rimsza, and T.M. Nenoff. *ACS Appl. Mater. Interfaces* 11, 46 (2019): 43270-43277. 2. Qiu, Shun, Ming Xue, and Guangshan Zhu. *Chem. Soc. Rev.* 43, 36 (2014): 6136-6140. 3. Vogel, D.J., D.F. Sava Gallis, T.M. Nenoff, and J.M. Rimsza. *Phys. Chem. Chem. Phys.* 21, 41 (2019): 23085-23093. 4. Parkes, M.V., J.A. Greathouse, D.B. Hart, D.F. Sava Gallis, and T.M. Nenoff. *Phys. Chem. Chem. Phys.* 18, 16 (2016): 11528-11538. 5. Vogel, D.J., J.M. Rimsza, and T.M. Nenoff. *Angewandte Chemie* 133, 20 (2021): 11615-11623. 6. Vogel, D.J., Z.R. Lee, C.A. Hanson, S.E. Henkelis, C.M. Smith, T.M. Nenoff, D.A. Dixon, and J.M. Rimsza. *J. Phys. Chem. C* 124, 49 (2020): 26801-26813.

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