

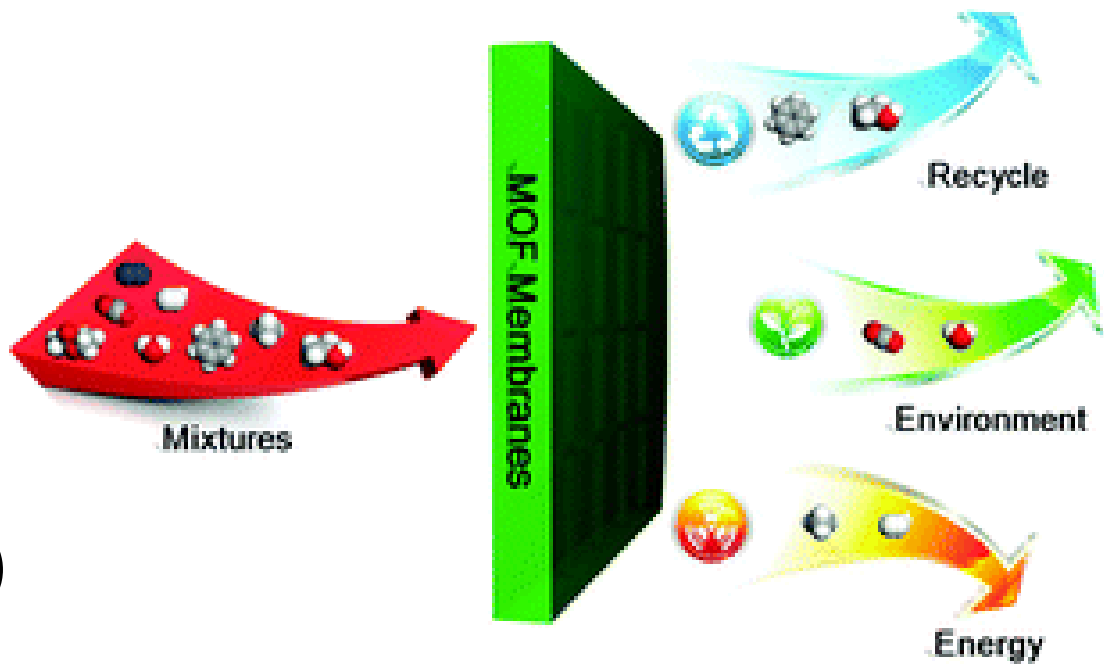
Mechanisms of Competitive Adsorption and Reactivity of Acid Gases in RE-DOBDC MOFs

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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]
- Porous materials for acid gas separation need to be robust during exposure to multicomponent gas streams
- Density functional theory (DFT) and *ab initio* molecular dynamics (AIMD) are applied to identify fundamental acid gas-framework interactions in *tertiary 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



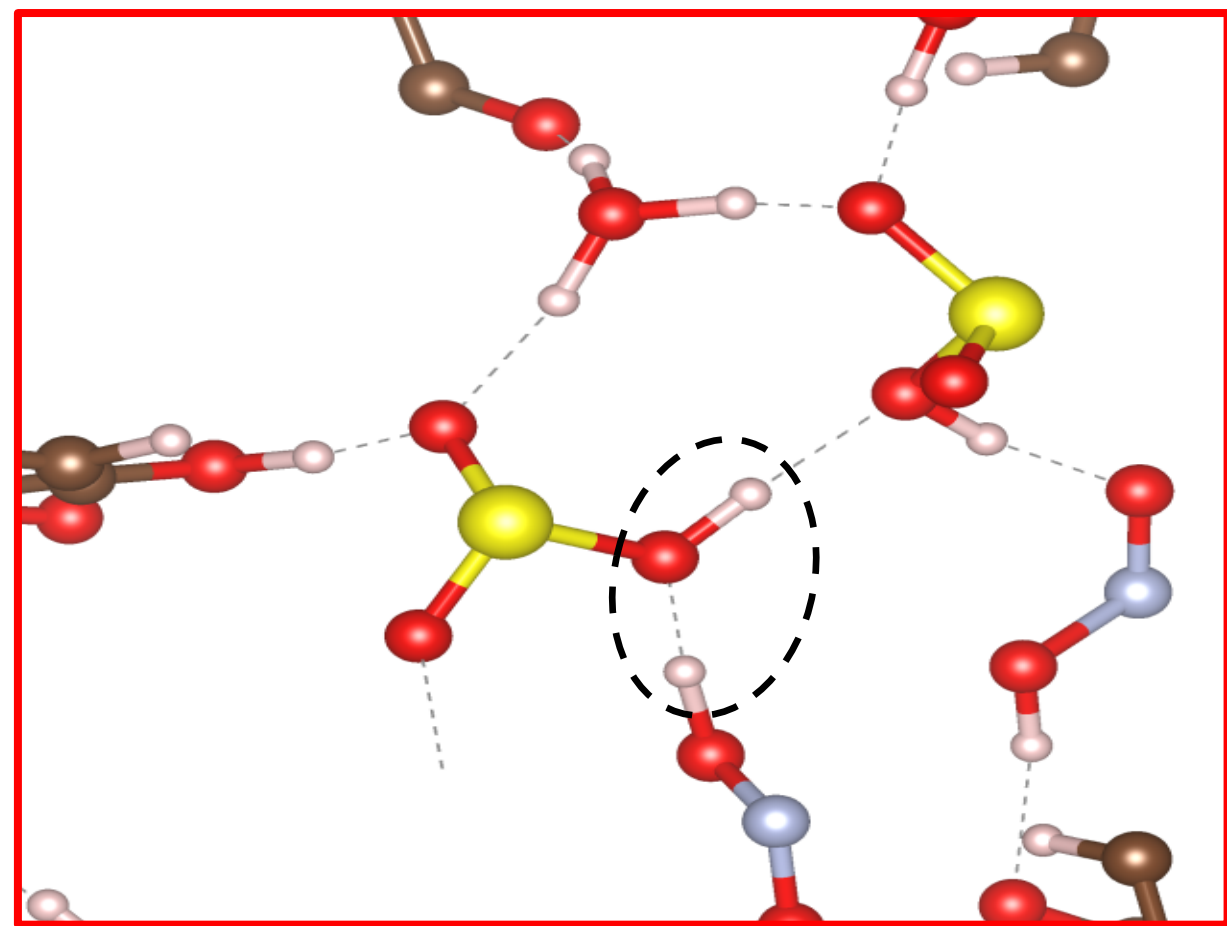
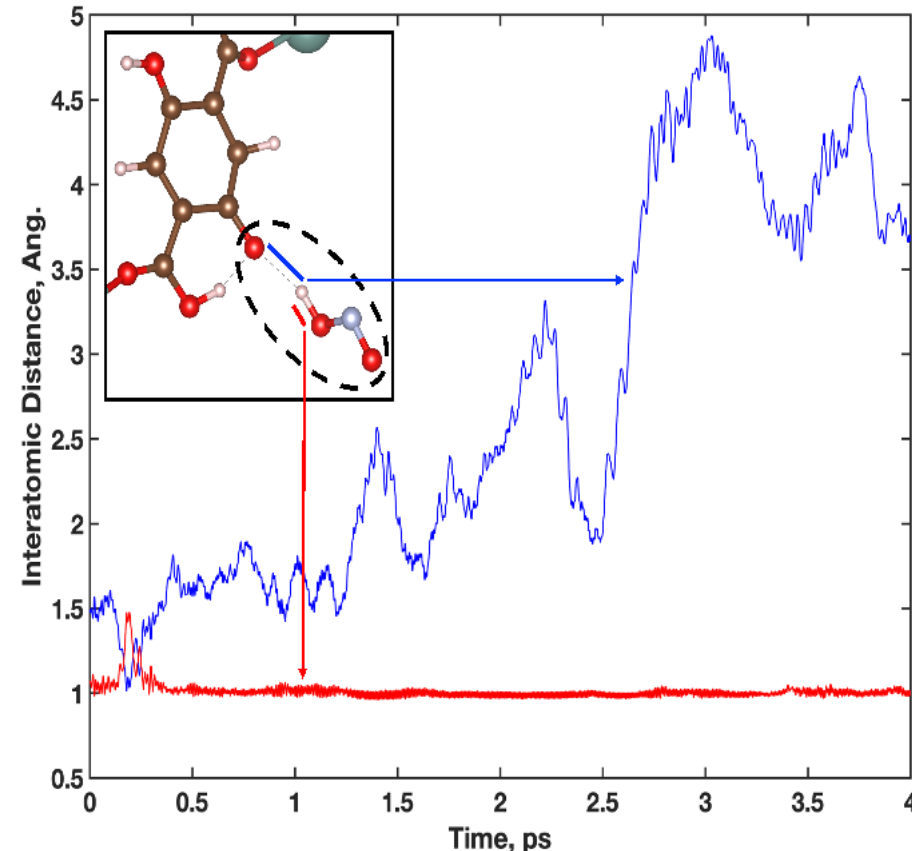
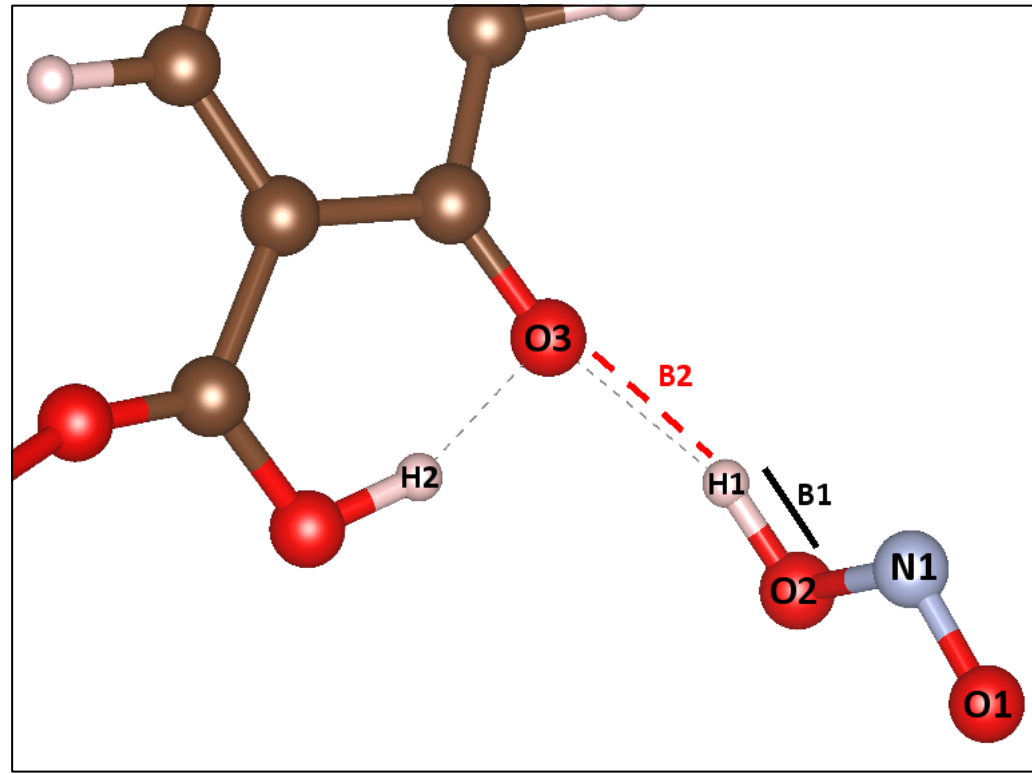
Formation of Secondary Gas Species

- Multiple secondary gas species are spontaneously formed in the MOF pore
- NO₂ is the most reactive of the gases investigated
- HONO accounted for 60% of intermediate species, and formed at low and high gas loadings
- Additional species formed: N₂O₄, H₃O⁺, SO₃²⁻, HSO₃⁻

RE Metal	Gas Mixture			
	12 NO ₂	6NO ₂ + 6H ₂ O	6NO ₂ + 6SO ₂	4NO ₂ + 4H ₂ O + 4SO ₂
Eu	HONO, N ₂ O ₄ , nitro nitrate	HONO, N ₂ O ₄	HONO	HONO, HSO ₃ ⁻ , H ₃ O ⁺
Tb	HONO, N ₂ O ₄ , nitro	HONO, H ₃ O ⁺	HONO	HONO
Y	HONO, N ₂ O ₄ , nitro	HONO	HONO, SO ₃ ²⁻ , NO	HONO, nitrate
Yb	HONO, nitro	HONO	Nitro	HONO
	NO ₂	NO ₂ + H ₂ O	NO ₂ + SO ₂	NO ₂ + H ₂ O + SO ₂
Eu	HONO	HONO	HONO	-
Tb	HONO	HONO	HONO	-
Y	HONO	HONO	HONO	-
Yb	HONO	HONO	-	-
	H ₂ O	12 H ₂ O	H ₂ O + SO ₂	6 H ₂ O + 6 SO ₂
				SO ₂
				12 SO ₂
Eu	-	-	-	-
Tb	-	-	-	-
Y	-	-	-	-
Yb	-	-	-	-

Reaction Mechanisms

- HONO formation is via deprotonation of the DOBDC linker. No reaction with a second gas molecule is necessary
- SO₂ based intermediate formation requires reactions with additional confined gas molecules

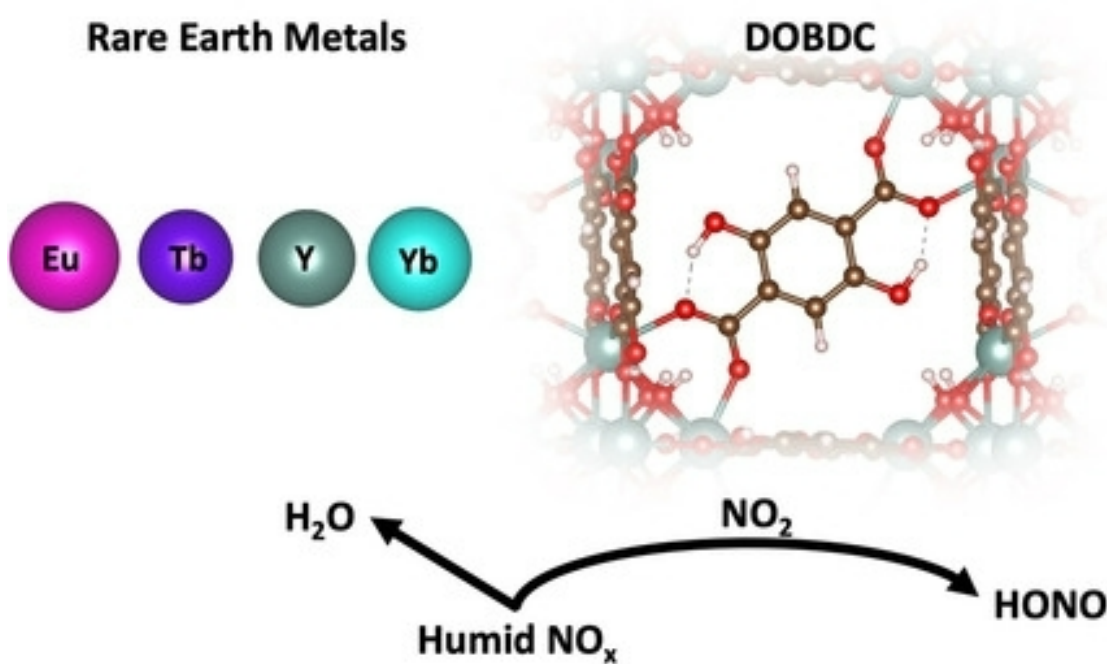


Deprotonation of the linker is an initial degradation mechanism.

Atom Colors: O (red), H (white), S (yellow), C (brown), N (blue)

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
- Dynamic competitive gas binding results in SO₂ and H₂O binding on metal sites providing resistance to framework degradation
- NO₂ reacting with the linker and forming secondary gas species, including a new HONO formation mechanism, was due to deprotonation of the linker
- Additional, potentially damaging, intermediate gas molecules were identified: HSO₃⁻, N₂O₄, H₃O⁺
- Similar *ab initio* molecular dynamic methodologies can be applied for further evaluation of the impact of multicompetent gases on MOF framework stability and acid gas separation for future material design
- Future work: Application of *ab initio* molecular dynamic methods for simulated mixed acid gas adsorption in MOFs to predict selectivity with increasingly complex gas mixtures.**



References

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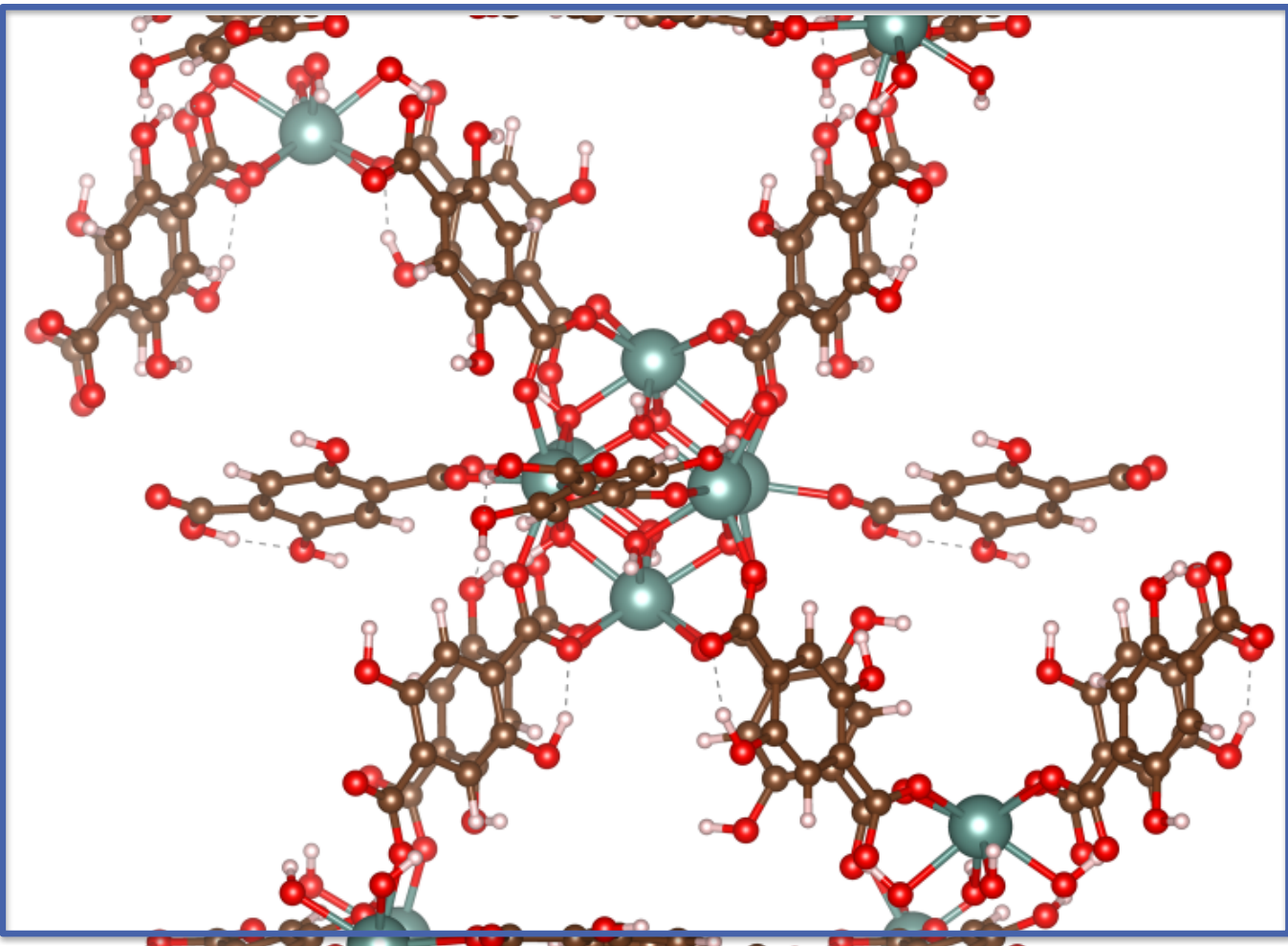
Acknowledgements

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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 at 300 K for 15 ps [4,5]



Y-DOBDC Unit Cell Model

Atom Colors: O (red), H (white), C (brown), Y* (teal)

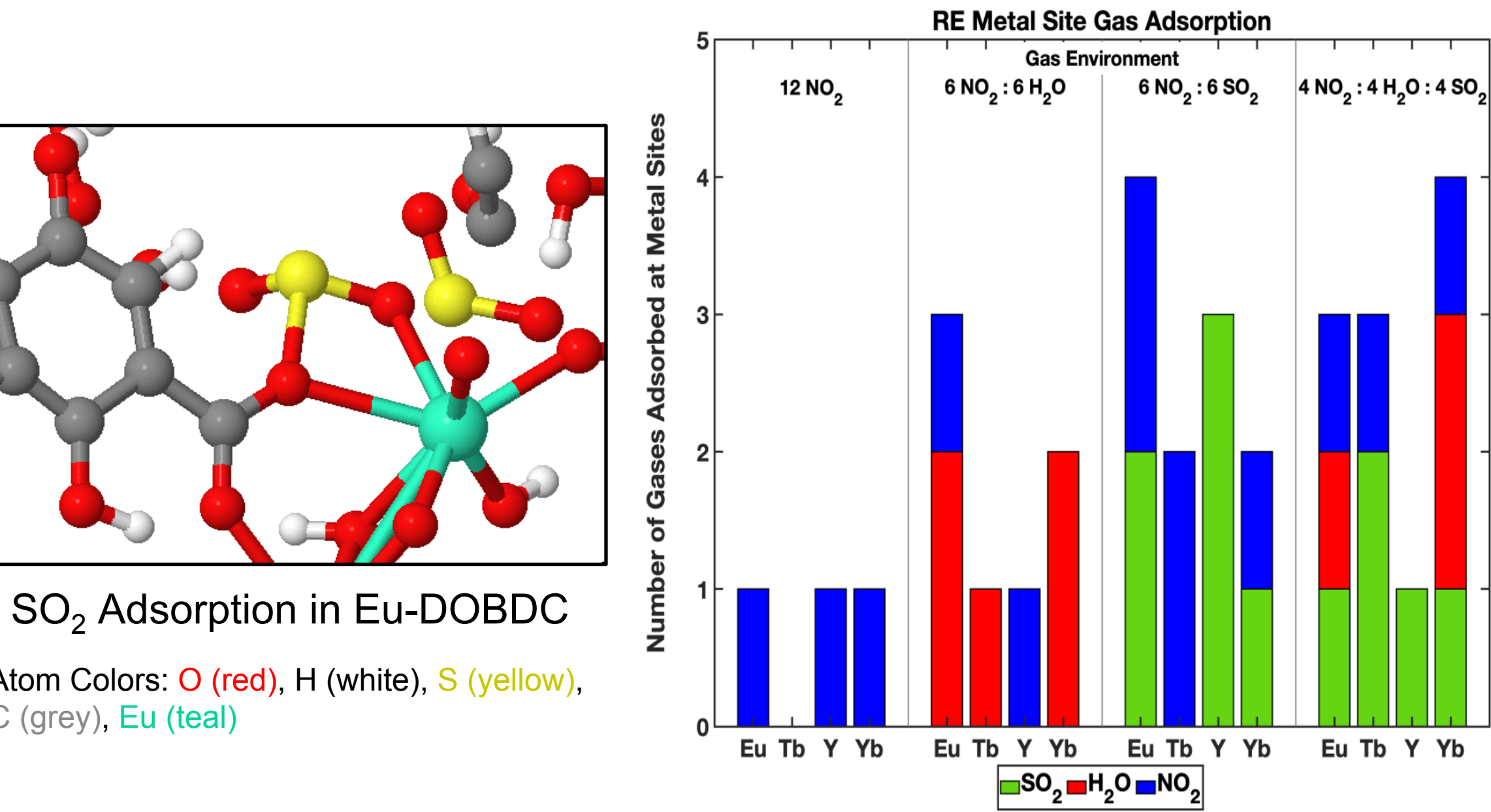
*can be substituted for any RE metal

14 gas compositions in 4 DOBDC MOF structures = 56 unique simulations

Rare Earth Metal	Gas Molecules (#)	Gas Composition
Eu, Tb, Y, Yb	1	H ₂ O or NO ₂ or SO ₂
	12	H ₂ O or NO ₂ or SO ₂
	2	1:1 H ₂ O:NO ₂ 1:1 NO ₂ :SO ₂ 1:1 H ₂ O:SO ₂
	12	6:6 H ₂ O:NO ₂ 6:6 NO ₂ :SO ₂ 6:6 H ₂ O:SO ₂
	3	1:1:1 H ₂ O:NO ₂ :SO ₂
	12	4:4:4 H ₂ O:NO ₂ :SO ₂

Competitive Binding

Dynamic competitive gas binding identifies preferential binding of SO₂ over NO₂ and H₂O in binary and tertiary gas mixtures.

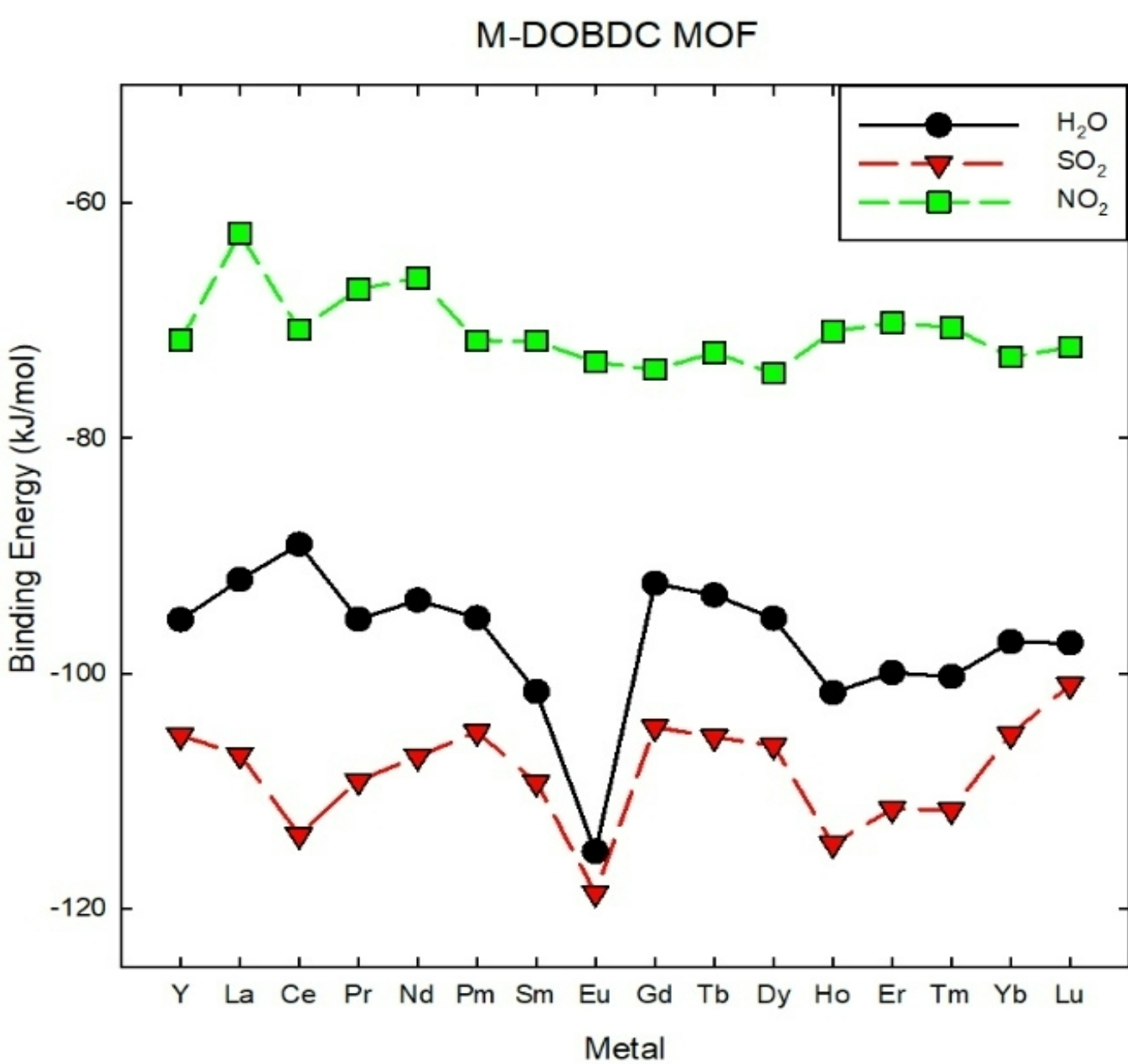


SO₂ Adsorption in Eu-DOBDC

Atom Colors: O (red), H (white), S (yellow), C (grey), Eu (teal)

Gas Composition	Binding Ratio	Binding Preference
NO ₂ :H ₂ O	2:5	H ₂ O
NO ₂ :SO ₂	5:6	SO ₂
NO ₂ :H ₂ O:SO ₂	3:3:5	SO ₂

$$E_{Int,Gas} = E_{MOF+Gas} - (E_{MOF} + E_{Gas})$$



Static calculated gas binding energies follows a NO₂ < H₂O < SO₂ trend. [6]