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Structural and Optical Response of Complex Mixed Gas Dynamics in Rare Earth Metal-Organic Frameworks

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Abstract and Motivation

Rare Earth 2,5-dihydroxyterephthalic acid (RE-DOBDC) metal organic frameworks (MOFs) with the composition $RE_{12}(\mu_3\text{-}OH)_{16}(C_8O_6H_4)_8(C_8O_6H_5)_4$ (RE=Y,Eu,Tb,Yb), have demonstrated a unique and strong optical response to the presence of acid gases for varying applications. Here, ground state density functional theory (DFT) methods are used to investigate the underlying mechanisms of interactions of acid gases within the RE-MOF frameworks at the atomistic level. Individual gas molecules are calculated to have varying binding energies and interaction types with the RE-MOF framework, indicating binding site selectivity. To highlight RE-MOF response to industrial environments, mixtures of multiple acid gases (SO_2, NO_2, and H_2O) are investigated at various concentrations. The *ab initio* molecular dynamic (AIMD) trajectories are investigated for direct competitive adsorption with the pore structure of RE-DOBDC MOF, providing additional insight into adsorption selectivity for more complex and realistic mixed gas environments.

Computational Methodology

- Spin polarized ground state geometries and ab initio molecular dynamics calculated using Density Functional Theory (DFT) as implemented in the Vienna Ab initio Simulation Package (VASP).
- Calculation parameters:
  - Plane wave basis set.
  - Projector augmented wave potentials.
  - Exchange correlation functional of Perdew-Burke-Ernzerhof designed for solids (PBEsol).
- Calculated Optical Absorption

$$\alpha_\sigma(\varepsilon) = \sum_{\sigma,ij} f_{\sigma,ij}\delta(\varepsilon - \varepsilon_{\sigma,ij})$$

- Transition Oscillator Strength

$$f_{\sigma,ij} = |\vec{D}_{\sigma,ij}|\frac{4\pi m_e \omega_{ij}}{3\hbar e^2}$$

- Transition Dipole Moment

$$\vec{D}_{\sigma,ij} = e\int \varphi_{\sigma,i}^{KS^*}\vec{r}\varphi_{\sigma,j}^{KS}d\vec{r}$$

- One Electron Kohn-Sham Equation

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + v_{eff}(r)\right)\phi_i(r) = \varepsilon_i\phi_i(r)$$

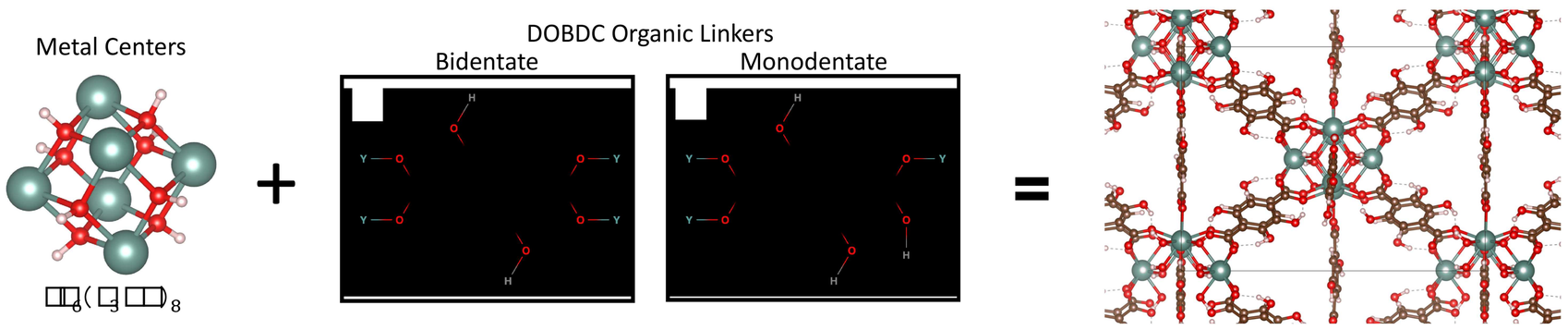
Conclusions

- Multiple binding sites exist at unsaturated metal sites and linker positions. Binding energies of individual gases indicate a selectivity of $SO_2 \approx H_2O > NO_2$.
- In humid NOx environments H_2O preferentially binds to metal sites and NOx binds to organic ligands.
- NOx exposure decreases photoluminescence in all synthesized RE-DOBDC MOFs due to interaction with DOBDC ligands.
- The percentage of intramolecular Hydrogen bonds produce a shift in the calculated optical properties of Y-DOBDC.
- Ab initio molecular dynamic trajectories are used to study complex acid gas mixtures in nanoconfined pore spaces.

Future Work

- Predicting new unsynthesized RE-DOBDC MOFs for acid gas separation and sensing.
- Analyzing new gas species formed via reaction due to complex gas mixtures.
- Identifying impact of nanoconfinement on gas interactions due to size of MOF pore.
- Provide large data sets, generated from ab initio molecular dynamic trajectories, for machine learning analysis.

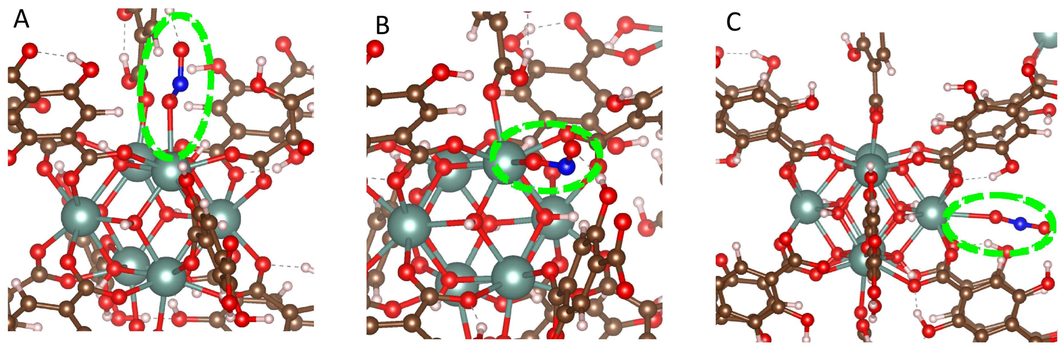
Introduction to MOFs and RE-DOBDC MOFs



39 Y Yttrium 88.906	57 La Lanthanum 138.905	58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.243	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.055	71 Lu Lutetium 174.967

Acid Gas Binding Energies in RE-DOBDC MOFs

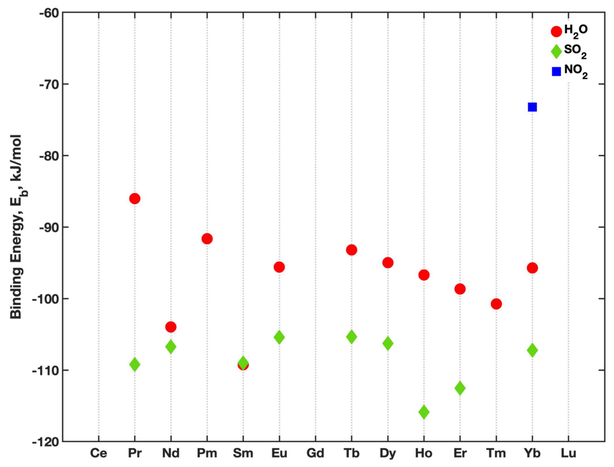
Rare Earth Metal Gas Adsorption Sites



Binding Energy: -70.27 kJ/mol

Binding Energy: -62.52 kJ/mol

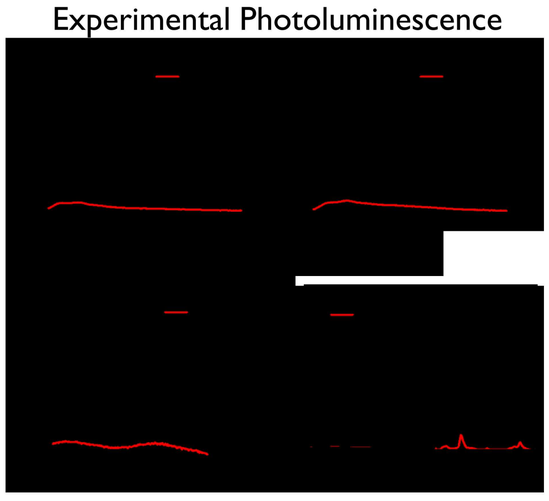
Binding Energy: -21.87 kJ/mol



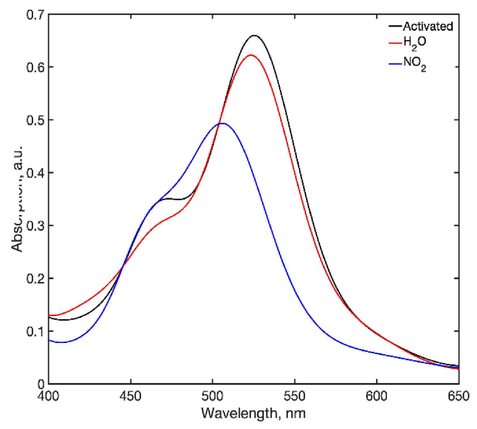
- Gas adsorption energies are dependent on metal location and local coordination environment.

Photoluminescence Quenching of RE-DOBDC MOFs in Humid NO_x

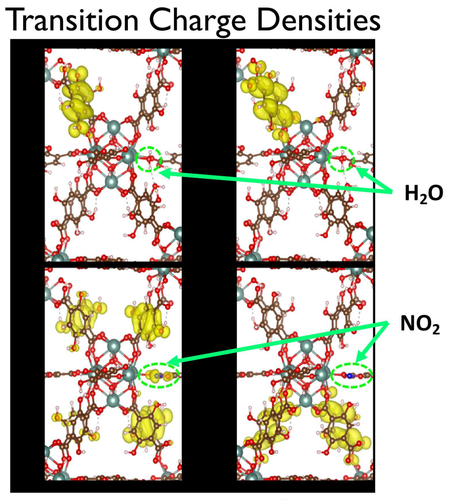
Experimental Photoluminescence



Calculated Optical Absorption



Transition Charge Densities

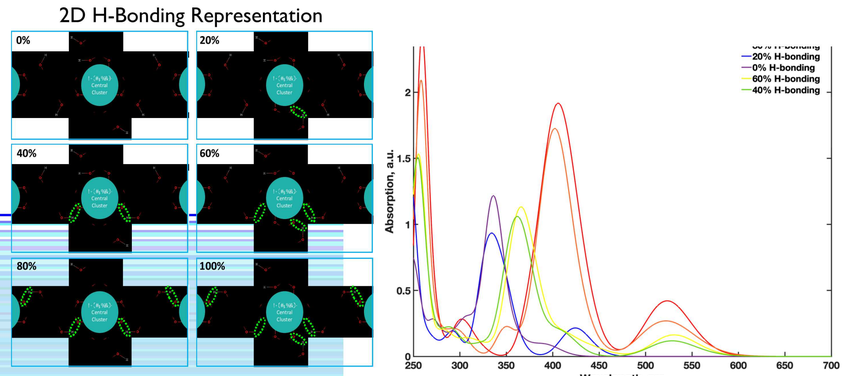


- Intrinsic RE-DOBDC MOF photoluminescence is reduced only upon exposure to NO_x.

Hydrogen Bonding in Y-DOBDC

H-Bonding (%)	Optimized Lattice Parameters a (Å)	b (Å)	c (Å)	Volume (Å^3)	ρ (g/cm^3)	Total Energy (eV)	H Bonds	Band Gap (eV)
0	14.88	14.86	21.36	4724	1.299	-1953.34	0	1.93
20	15.47	15.46	20.95	5013	1.224	-1953.09	4	1.80
40	15.45	15.44	20.97	5004	1.227	-1955.22	8	1.15
60	15.45	15.43	20.95	4996	1.229	-1957.57	10	1.21
80	15.44	15.43	21.00	5004	1.227	-1960.02	16	1.18
100	15.44	15.43	20.97	4996	1.229	-1962.03	20	1.25
Expt[a]	15.14	15.14	21.39	4904	-	-	-	-

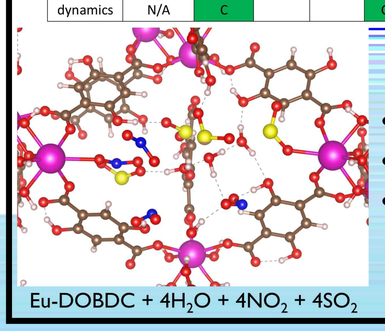
2D H-Bonding Representation



- H-bonding required to maintain measured geometry.
- Increased H-bonding induces red shift of primary optical absorption.

Mixed Acid Gas Dynamics

System	Activated	12 H_2O	12 NO_2	12 SO_2	H_2O	NO_2	SO_2	H_2O NO_2 SO_2	4 H_2O 4 NO_2 4 SO_2	6 H_2O 6 NO_2	6 H_2O 6 SO_2	6 NO_2 6 SO_2	H_2O NO_2	H_2O SO_2	NO_2 SO_2
Y optimize	C	C	R	C	C	C	C	C	R	R	R	R	C	R	R
heating	N/A	C		C	C	C	C	C					C		
dynamics	N/A	C		R	C	R	C	R					R		
Eu optimize	C	C	C	R	C	C	C	C	C	R	C	C	C	C	C
heating	N/A	C	C		C	C	C	C	C		C	C	C	C	C
dynamics	N/A	C	C		C	C	C	C	C		C	C	C	C	C
Tb optimize	C	C	C	C	C	C	C	C	C	R	C	C	C	C	C
heating	N/A	C	R	C	C	C	C	R	R		C	R	R	C	C
dynamics	N/A	R		R	C	C	C				R			C	C
Yb optimize	C	C	C	C	C	C	C	C	C	R	C	C	C	R	C
heating	N/A	C	R	R	C	C	C	R	R		R	R	R		R
dynamics	N/A	C			C	C	C								



Eu-DOBDC + $4H_2O$ + $4NO_2$ + $4SO_2$

- Complex Gas Interactions.
- Selectivity due to metal choice.
- New gas interactions due to pore confinement.

References

1. Vogel, D. J., Nenoff, T. M., Rimsza, J. M., Tuned Hydrogen Bonding in Rare Earth MOFs for Design of Optical and Electronic Properties. **2019,** *ACS Appl. Mater. Interfaces, submitted*
2. Sava Gallis, D. F., Vogel, D.J., Vincent, G.A., Rimsza, J. M., Nenoff, T. M., NOx Adsorption and Optical Detection in Rare Earth Metal Organic Frameworks, *ACS Appl. Mater. Interfaces*. **2019**, 11, 43270-43277.
3. Vogel, D. J., Sava Gallis, D. F., Nenoff, T. M., Rimsza, J. M., Structure and electronic properties of rare earth DOBDC metal-organic-frameworks. *Phys. Chem. Chem. Phys*., **2019**, 21, 23085-23093.

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