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Competitive Adsorption and Reactive Chemical Species Identification in RE-DOBDC MOFs via AIMD

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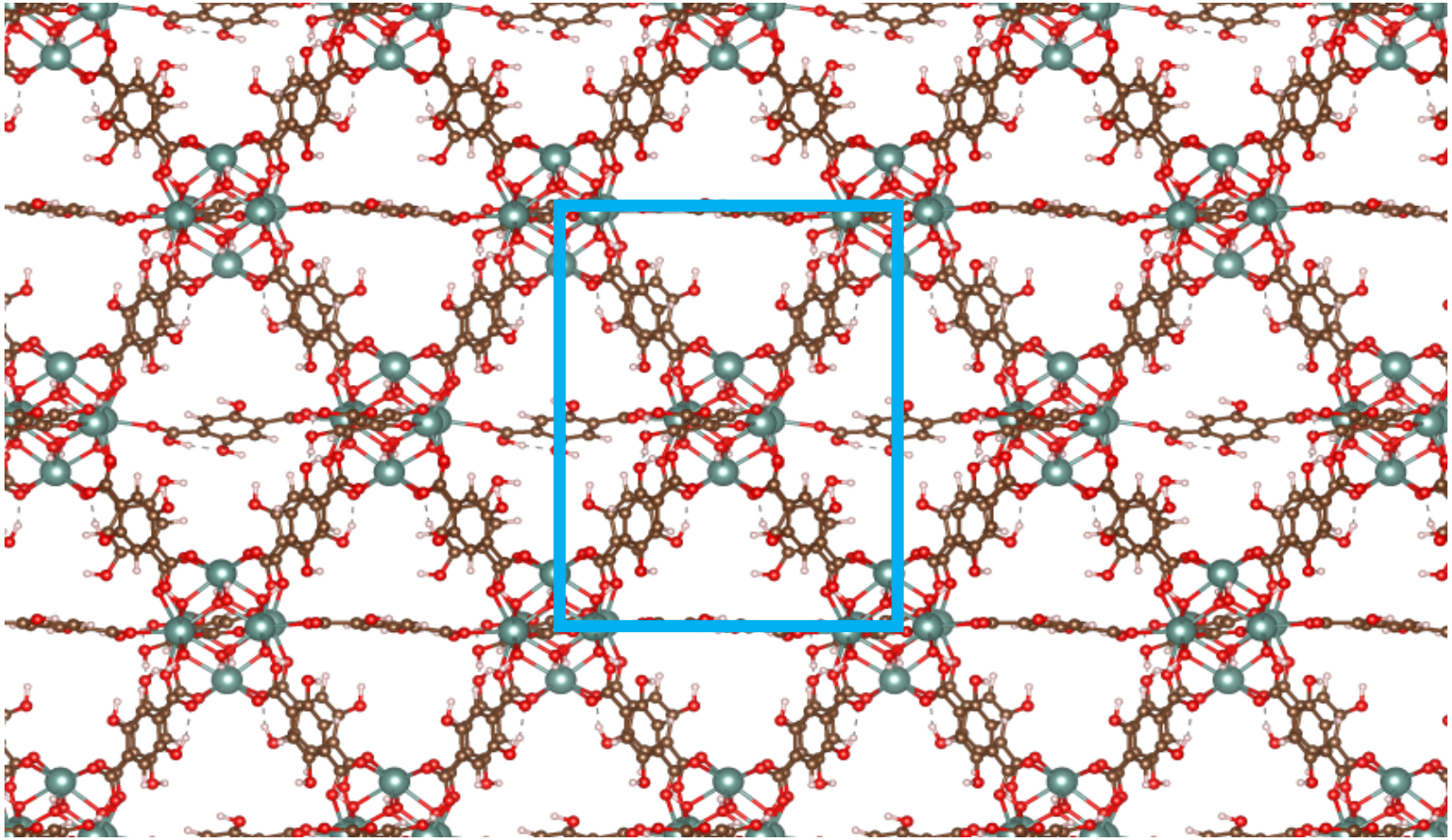
Understanding and Control of Acid Gas-Induced Evolution of Materials for Energy (UNCAGE-ME)
Energy Frontier Research Center

Introduction to Rare Earth DOBDC MOFs



Unit Cell[1] = $RE_{12}(\mu_3\text{-}OH)_{16}(C_8O_6H_4)_8(C_8O_6H_5)_4$ RE = Y, Eu, Tb, Yb

Acid Gas Environments

- Flue streams are chemically harsh and can degrade materials.
- Flue gas composition:
  13% CO_2, 6% H_2O, ~4% O_2, 50 ppm CO, 420 ppm NO_2, 420 ppm SO_2, and 76% N_2.[4]

Can we predict gas-MOF interactions and separations using advanced computational techniques?

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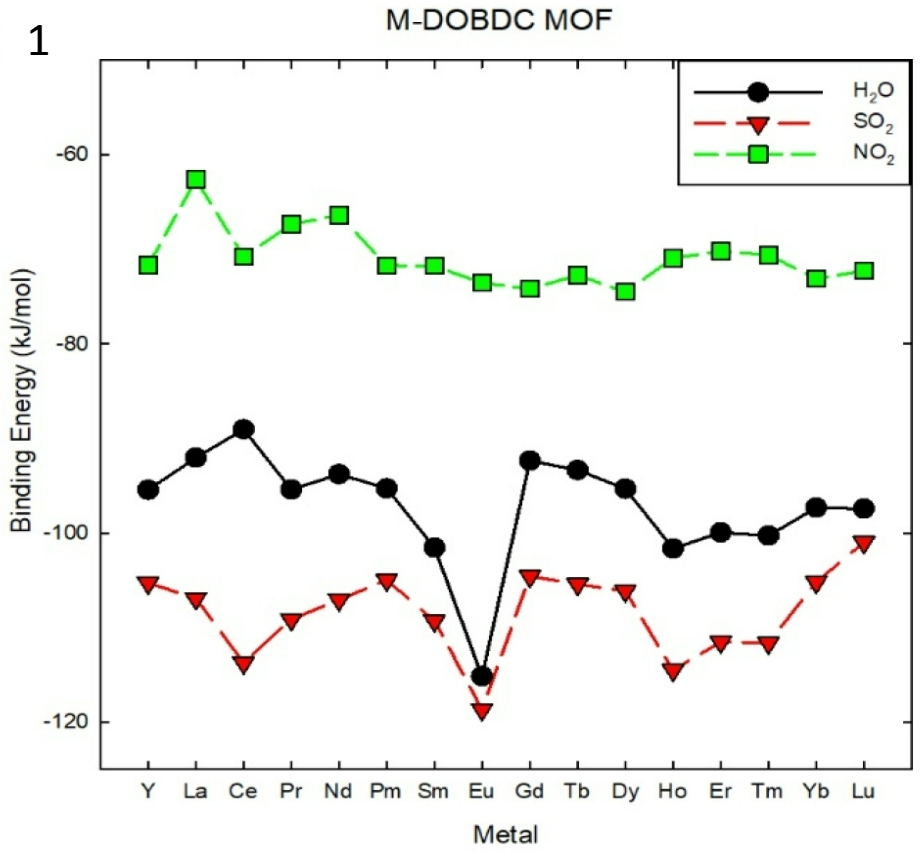
1. **Vogel, D.J.**, et al. *Phys. Chem. Chem. Phys.* **2019**, 21,23085
2. Sava Gallis, D.F., **Vogel, D.J.**, et al. *ACS Appl. Mater. Interfaces* **2019**, 11, 46, 43270
3. **Vogel, D.J.**, et al. *ACS Appl. Mater. Interfaces* **2020**, 12, 4, 4561
4. Rezaei, F. et al. *Energy Fuels* **2015**, 29(9), 5467

DFT Calculated Binding Energies and AIMD Gas Mixtures

Binding Energies Across Lanthanide Series



Specific RE metals and Gas Species

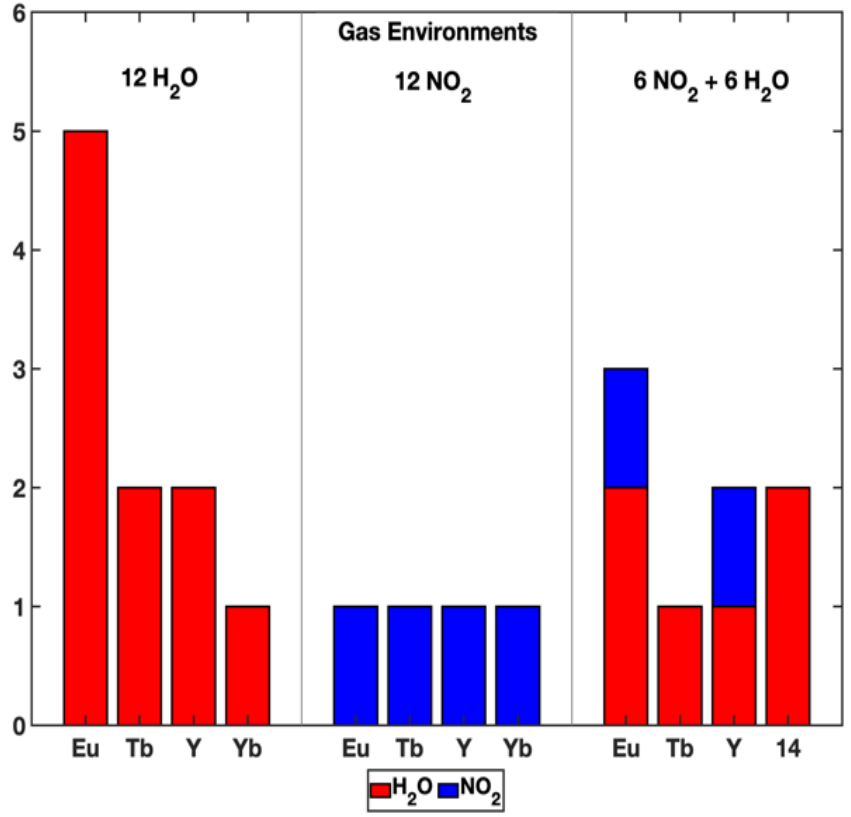
Rare Earth Metals	Gas Molecules (#)	Gas Composition
Eu, Tb, Y, Yb	1	H_2O or NO_2
Eu, Tb, Y, Yb	12	H_2O or NO_2
Eu, Tb, Y, Yb	2	$H_2O + NO_2$
Eu, Tb, Y, Yb	12	$6\ H_2O + 6\ NO_2$

- Calculated individual gas binding energies resulted in strength trends of $NO_2 < H_2O < SO_2$.
- In binary acid gas mixtures of humid NOx, H_2O expected to bind to metal sites and NO_2 to the MOF framework.
- Varying concentrations of H_2O and NO_2 provide greater gas-framework reactivity.

1. Vogel, D.J., et al. *J. Phys. Chem. C* **2020**, 124, 26801-26813
2. Vogel, D.J., et al *Angew. Chem. Int. Ed.* **2021** doi: 10.1002/anie.202102956

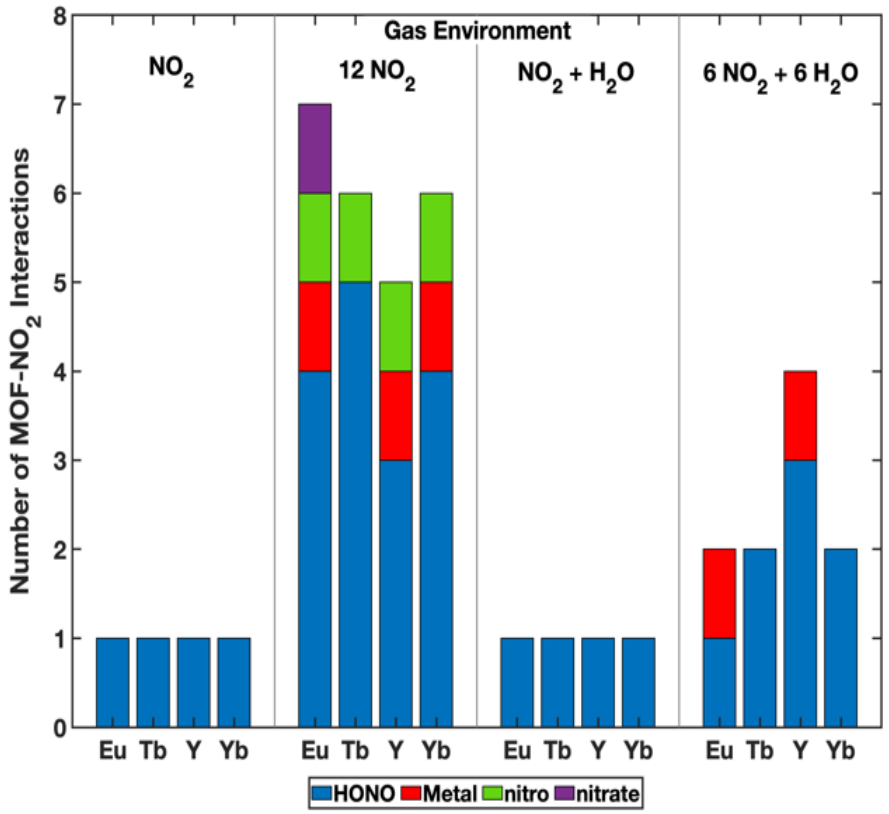
Competitive Adsorption of H_2O and NO_2 During AIMD

Gas Adsorption at RE Metal Sites



- H_2O binds more favorably to RE metal sites than NO_2
- Number of gas-metal binding follows pore volume trend.

NO_2 Interactions



- NO_2 interacts with DOBDC to form new species.
- HONO forms in all calculated AIMD trajectories.

Vogel, D.J., et al *Angew. Chem. Int. Ed.* **2021**
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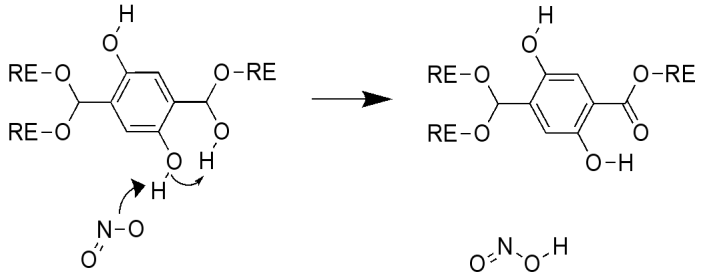
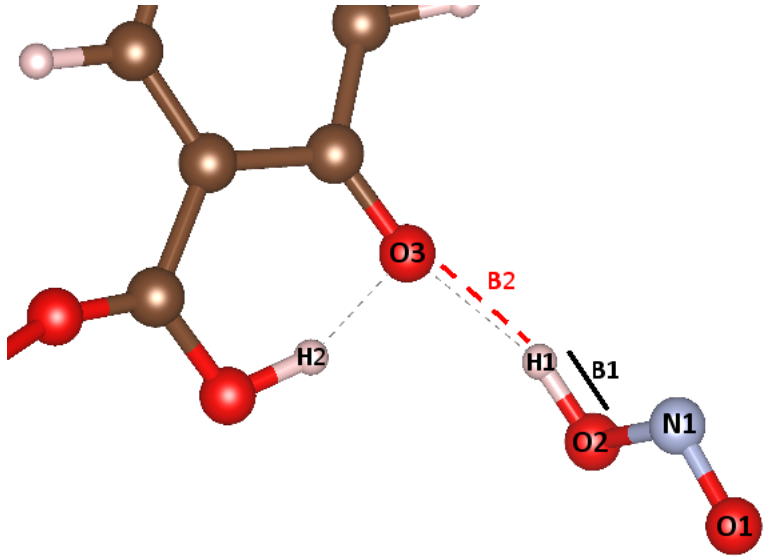
Reactive HONO Formation in RE-DOBDC MOFs

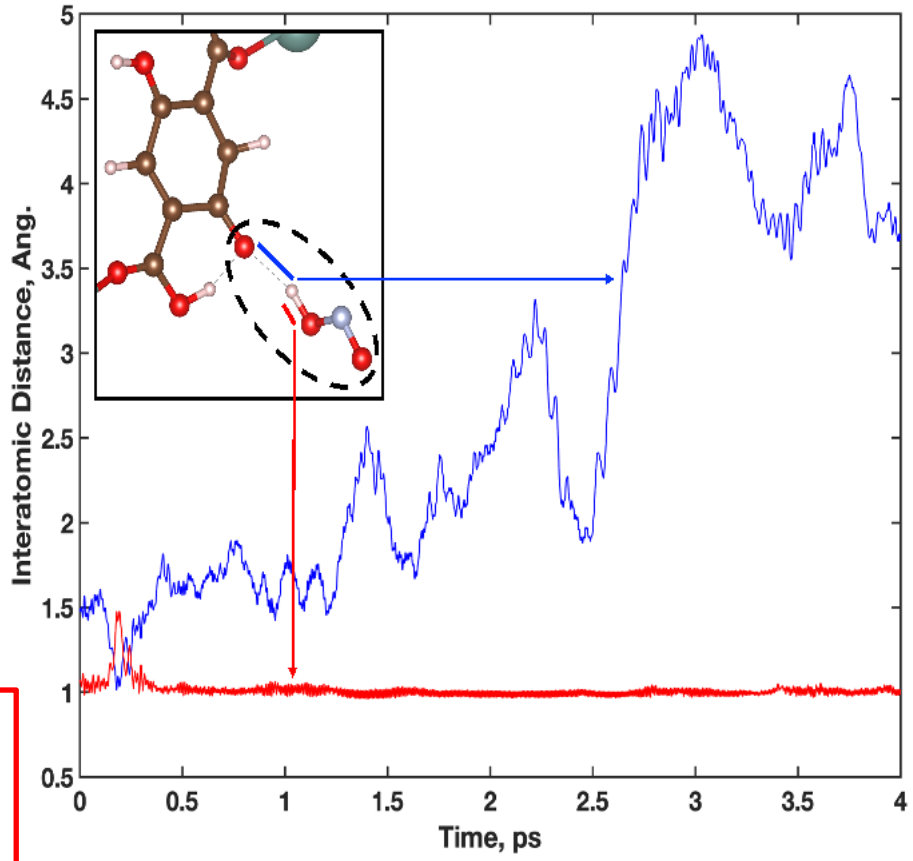
Reaction Scheme



Reaction Visual



H Atom Interaction Distances



- NO_2 interactions with DOBDC hydroxyl groups result in HONO formation.
- Monodentate DOBDC linkers have an extra hydroxyl group due to non bonded carboxyl O atom.
- Extra hydroxyl provides H atom to help facilitate HONO formation.

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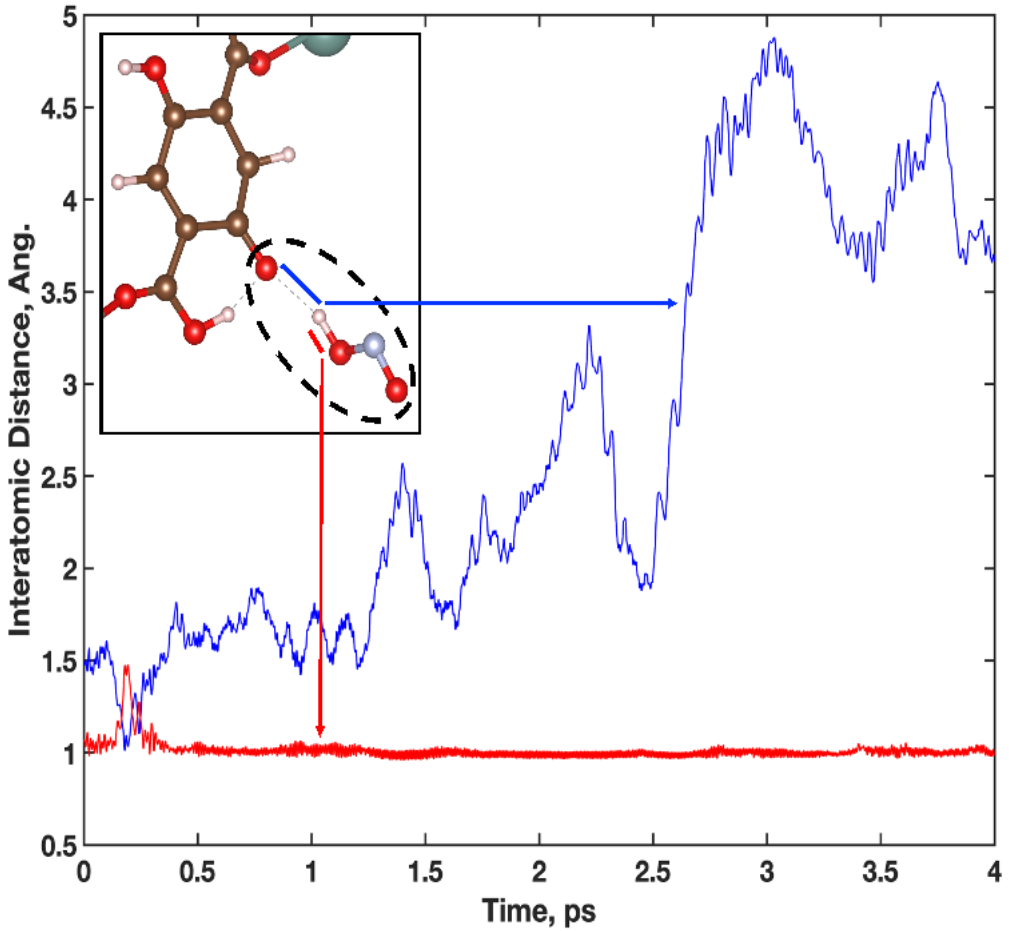
HONO Interaction Energies and Dissociation

H Atom Interaction Distances



Average HONO Binding Energy:

- 0.0-0.0125 ps: -0.86 eV
- 0.375-0.5 ps: -0.65 eV
- 2.6-2.8 ps: -0.47 eV

HONO Dissociation Energy

- 3.75 ps: -0.2 eV

- The interaction energy decreases as HONO forms and moves away from deprotonated O.
- The interaction energy of ~ -0.2 eV classifies the resulting HONO interaction as physisorption.

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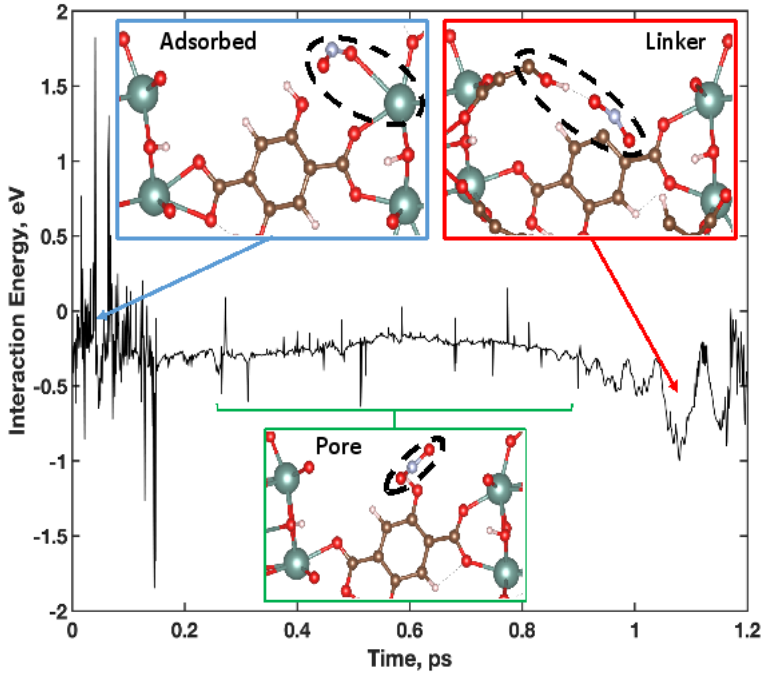
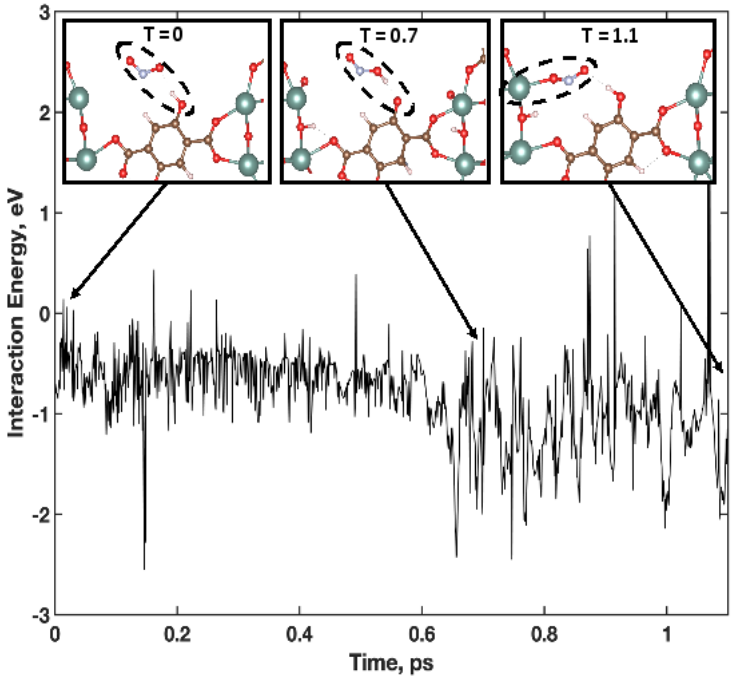
Strong NO_2-DOBDC Interactions

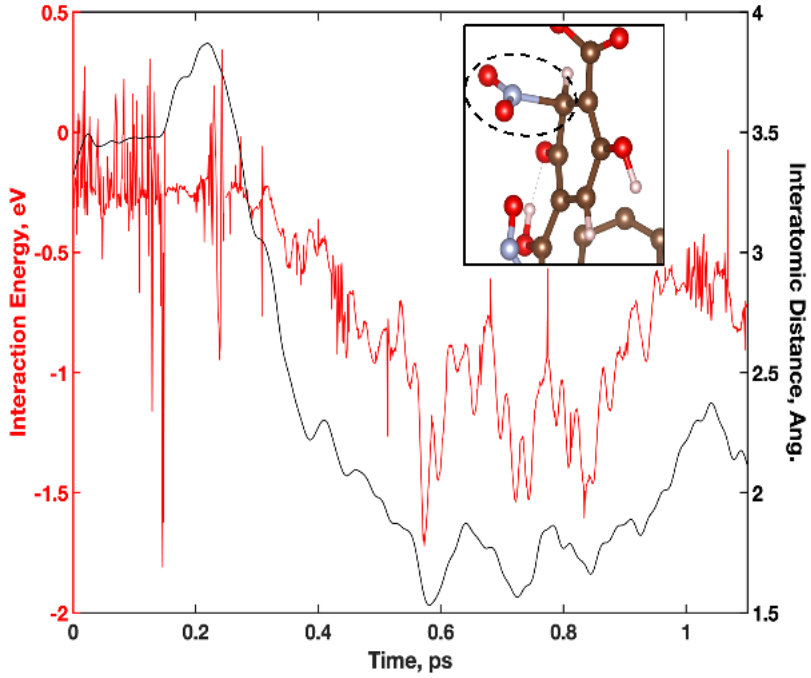
Desorption and Linker Interaction



Linker Interaction and Adsorption



Nitro Formation



- NO_2 interaction energies are dynamic along AIMD trajectories.
- Time dependent binding energies highlight NO_2-framework interactions are stronger than at metal sites.
- New nitro group formation is calculated to be strong and has been validated with experimental FTIR.

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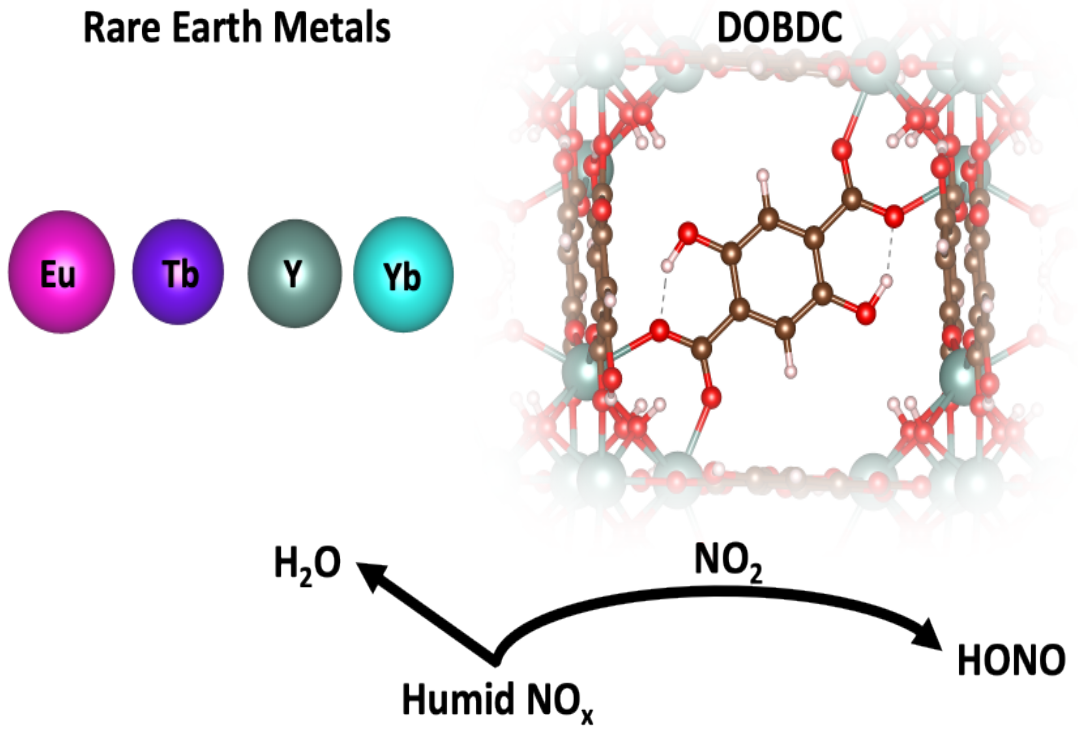
Conclusions

- *Ab initio* molecular dynamic simulations of humid NOx in RE-DOBDC MOFs highlights reactivity of acid gases at metal and linker sites.
- Predicted site selectivity of H2O-metal and NO2-linker is observed along AIMD trajectories.
- Multiple strong NO2 interactions were observed for desorption, adsorption, nitro formation, and linker interactions.
- New HONO formation mechanism has been identified, which is facilitated by unique DOBDC linker coordination.



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