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# Entrapment of Volatile Organic Compounds in MOF UiO-66: An *ab initio* molecular dynamics study

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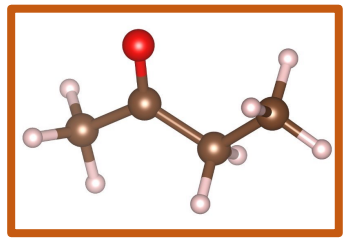
# Introduction

- Metal Organic Frameworks (MOF) have been shown to be effective for Volatile Organic Compound (VOCs) absorption
- MOFs have been used in the food industry for food preservation and ripening

Nong, Wenqian, et al. "Metal-organic framework-based materials: Synthesis, stability and applications in food safety and preservation." *ES Food and Agroforestry*, 2020.

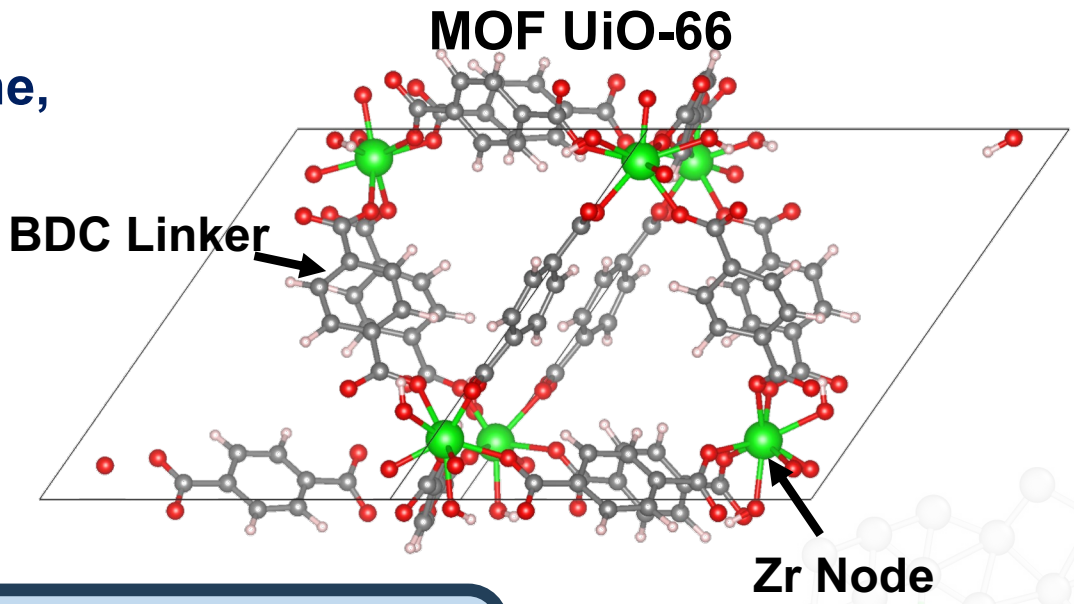


2-Butanone Molecule

- VOCs are harmful gas chemicals such as 2-butanone, which is often found in the breath of lung cancer patients

Fu, Xiao-An, et al. "Noninvasive detection of lung cancer using exhaled breath." *Cancer Medicine*, vol. 3, no. 1, 20 Nov. 2013, pp. 174–181.

- UiO-66 is well known for its use in gas capture.
  - Composed on $Zr_6O_4(\mu_3\text{-}OH)_4$ nodes and BDC linkers

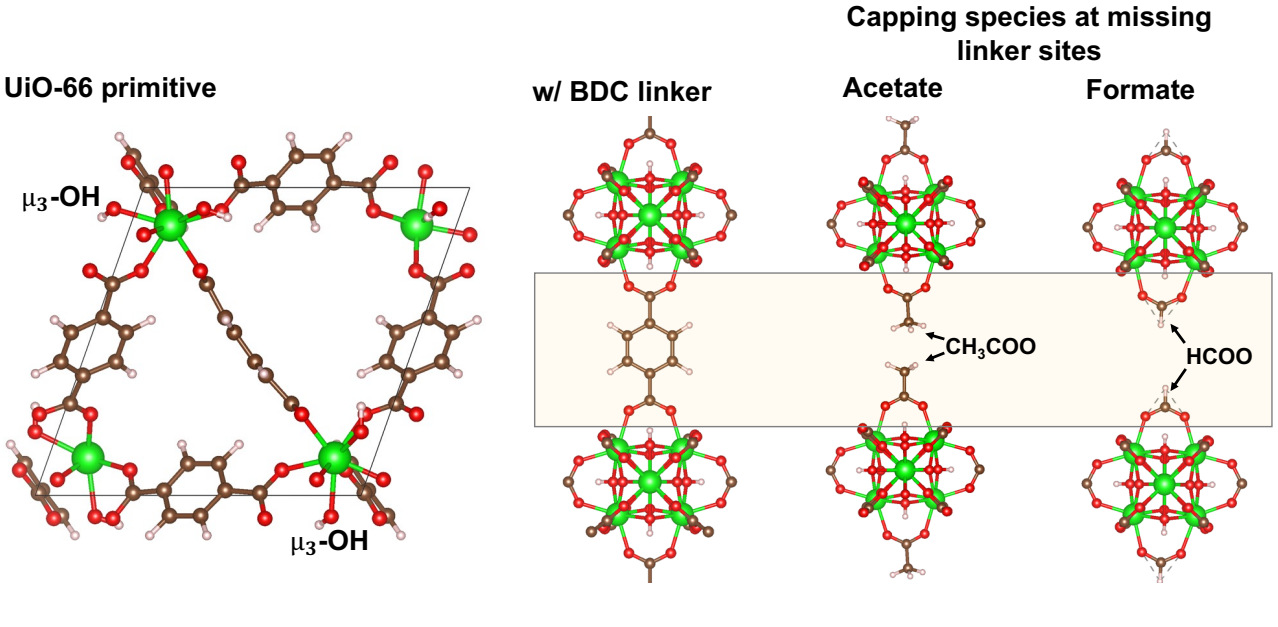


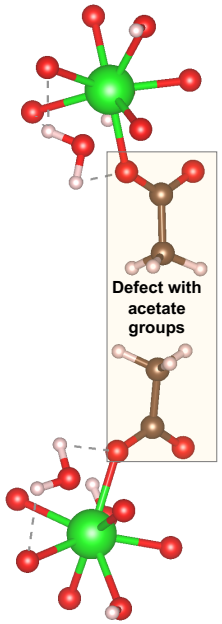

**Can UiO-66 Be used for 2-Butanone absorption?**

# Outline

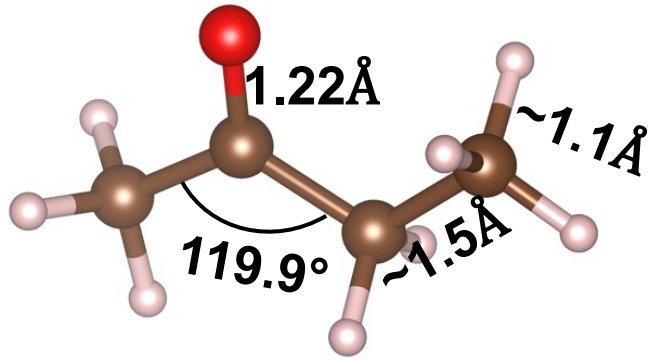
- **Methodology and simulation details**
  - Difference between pristine and defective UiO-66
  - AIMD simulations
  - Energy formulations
- **Results**
  - Energetics of defective UiO-66
  - Energetics of butanone/UiO-66 interactions and structures

# Initial structures and simulation protocols




**2-butanone: $CH_3C(O)CH_2CH_3$**




Energy minimized using UFF

Vermoortele F, Bueken B. Synthesis modulation as a tool to increase the catalytic activity of metal-organic frameworks: the unique case of UiO-66(Zr). J Am Chem Soc. 2013 Aug

1. ***Ab initio* molecular dynamics (AIMD) was performed using the Vienna *ab initio* simulation package (VASP)**
2. **Simulations performed at 300 K**
3. **1fs per iteration for 10 ps (10K iterations)**
4. **NPT ensemble: Langevin thermostat and Parrinello–Rahman Barostat**

# Formulations and simulation design

**1.** **Defect formation energy :** $\Delta E_{Defect-Formation}(T,t) = \frac{\Delta E_{Defective-MOF}(T,t)}{N_{Defect}} - \frac{\overline{E_{Pristine-MOF}(T)}}{N_{MOF}}$

Choudhuri, D. and Rinehart, A.J., 2024. Interaction between water and point defects inside volume-constrained α-quartz: An ab initio molecular dynamics study at 300 K. *Journal of Applied Physics*, *135*(16).

**2.** **Butanone/UiO-66 Interaction energy**

Vogel DJ, Rimsza JM, Nenoff TM. Prediction of Reactive Nitrous Acid Formation in Rare-Earth MOFs via ab initio Molecular Dynamics. Angew Chem Int Ed Engl. 2021 May 10;60(20)

**2a.** **Interaction energy with pristine UiO-66:** $\Delta E^{Pristine}_{Interaction}(T,t) = \Delta E^{Pristine}_{butanone}(T,t) - \overline{E_{Pristine-MOF}(T)} - m \times \overline{E_{butanone}(T)}$

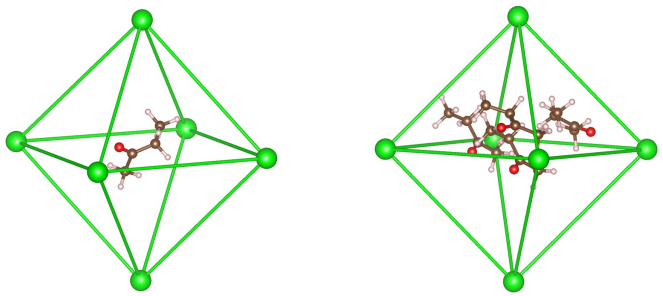
**2b.** **Interaction energy with defective UiO-66:** $\Delta E^{Defect}_{Interaction}(T,t) = \Delta E^{Defect}_{butanone}(T,t) - \overline{E_{Defective-MOF}(T)} - m \times \overline{E_{butanone}(T)}$

*Overbar represents time averaged quantities

**3.** **Four different loading conditions were employed:**

a) 1 molecule (mol.) of Butanone *w* and *w/o* defects

b) 4 molecules of Butanone *w* and *w/o* defects



# Outline

- Methodology and simulation details
  - Difference between pristine and defective UiO-66
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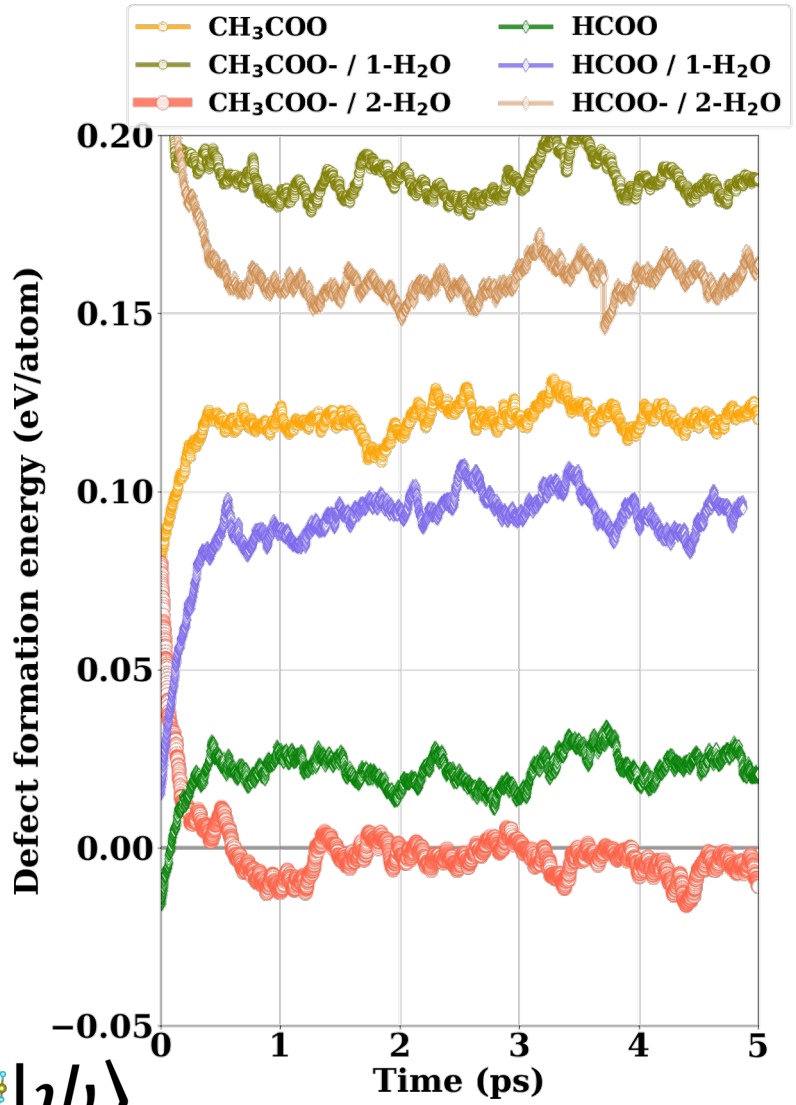
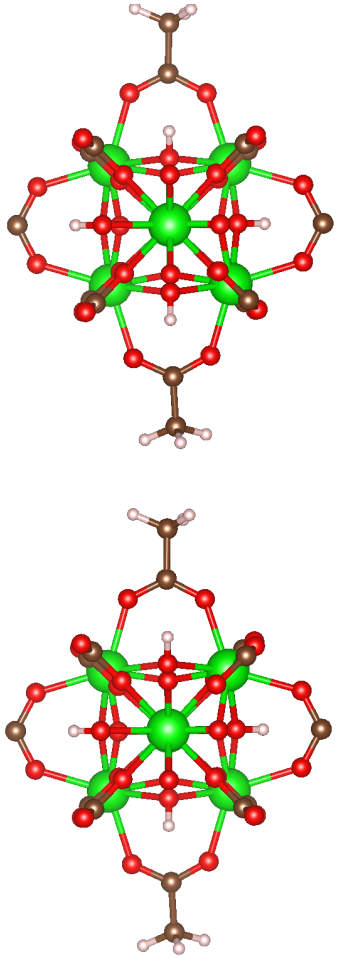
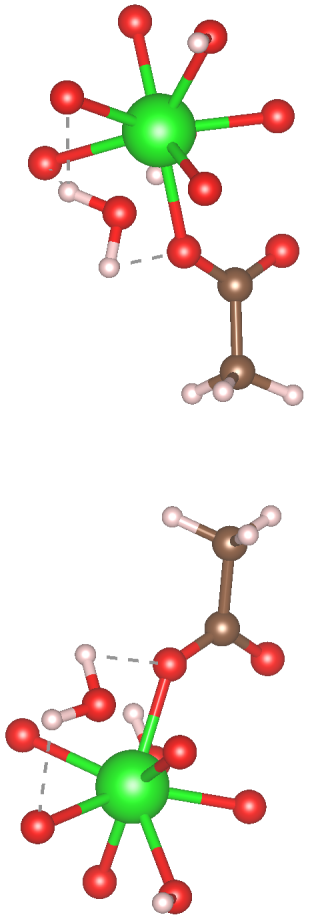
- **Results**
  - **Energetics of defective UiO-66: selection of stable defects**
  - **Energetics of butanone/UiO-66 interactions and structures**

# Determination of energetically favorable defects at 300 K

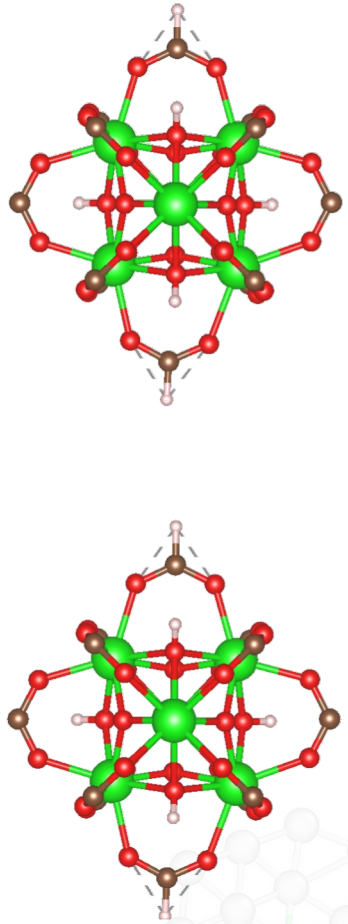


Defect with Acetate Group Cappers



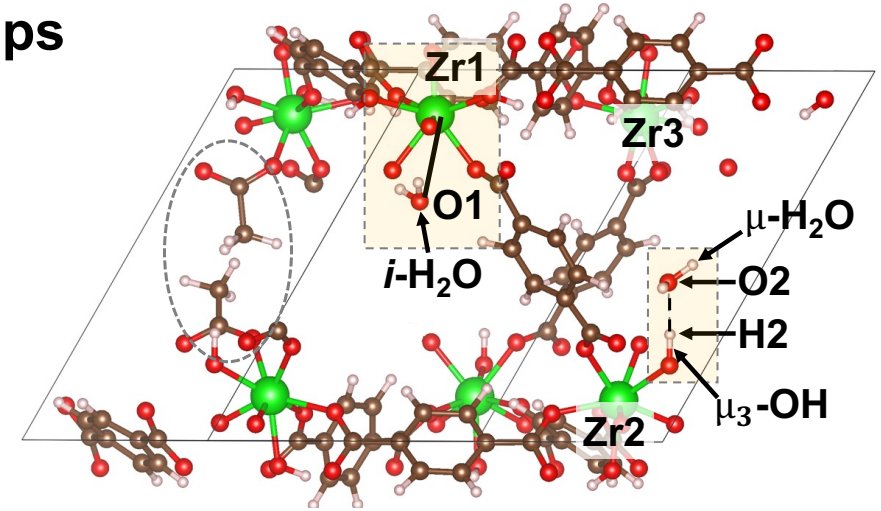
Defect with Acetate Group Cappers + 2-$H_2O$

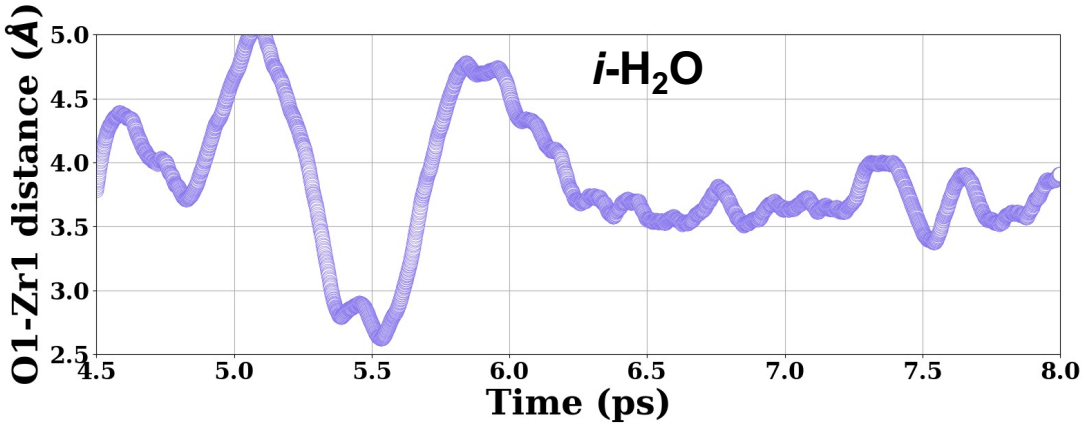


Defect with Formate group Cappers

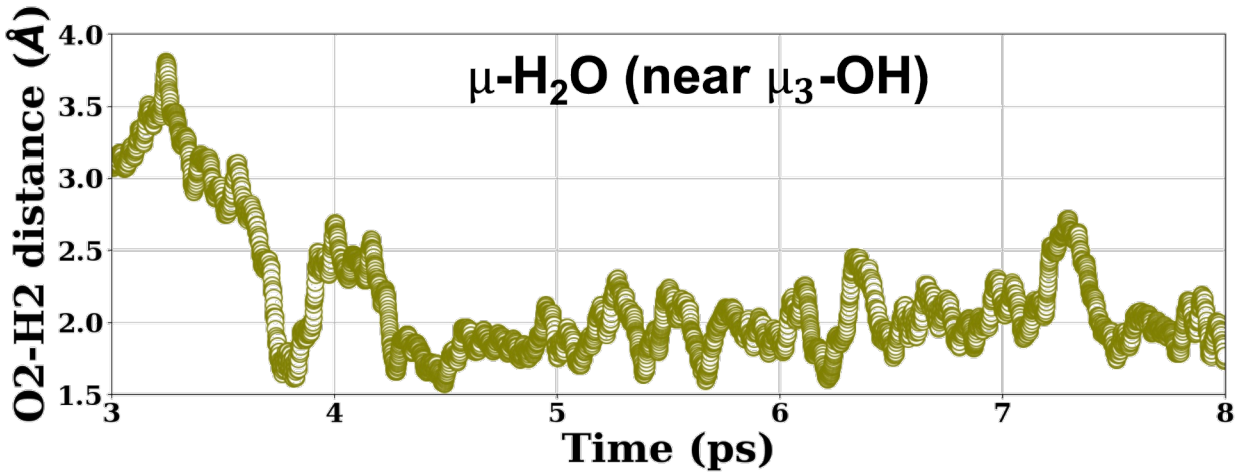
# Characterization of energetically favorable defect

8ps




**The Defect structure was stabilized by 2-H2O Molecules**

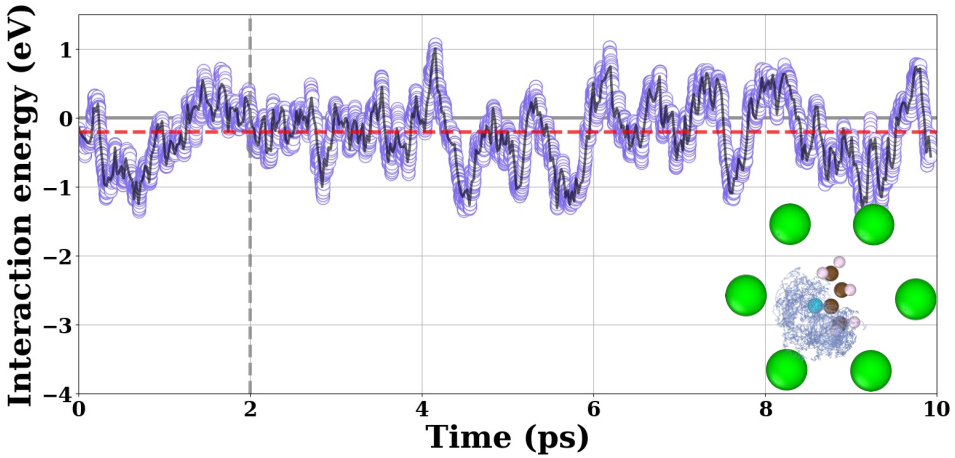



**μ-$H_2O$ forms a hydrogen bond with $\mu_3$-OH and moves outside of the octahedral interstitial cage after 4.3 ps.**

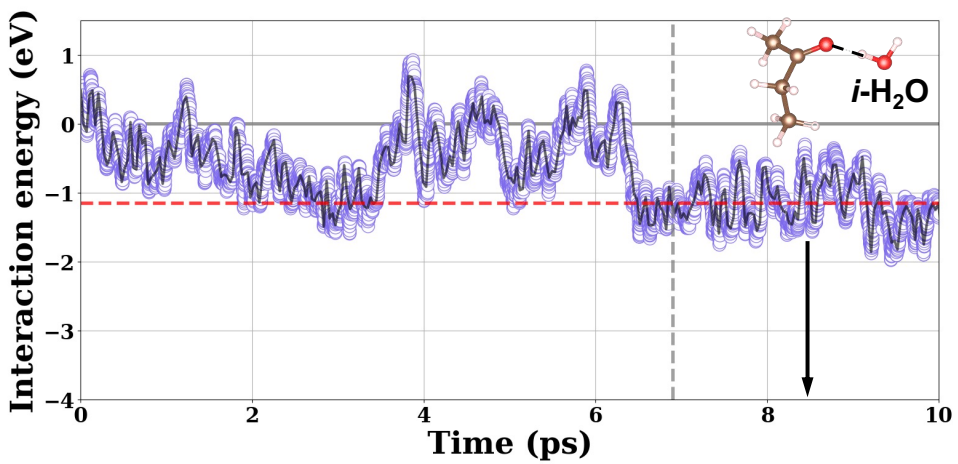
***i*-H2O stabilizes interstitially near Zr1 Node within 6.5 ps.**

# Comparison of interaction energies

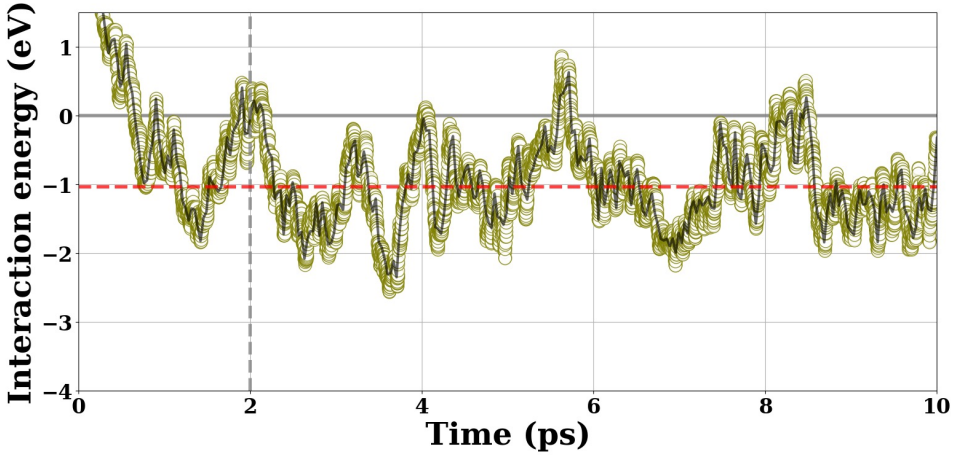
1 mol. of 2-butanone



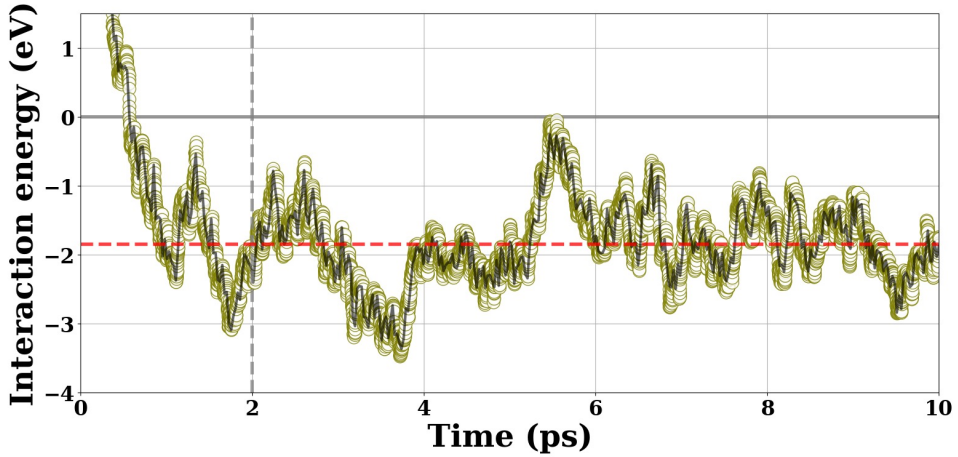

1 mol. with "$CH_3COO^-$ / 2-$H_2O$" defect



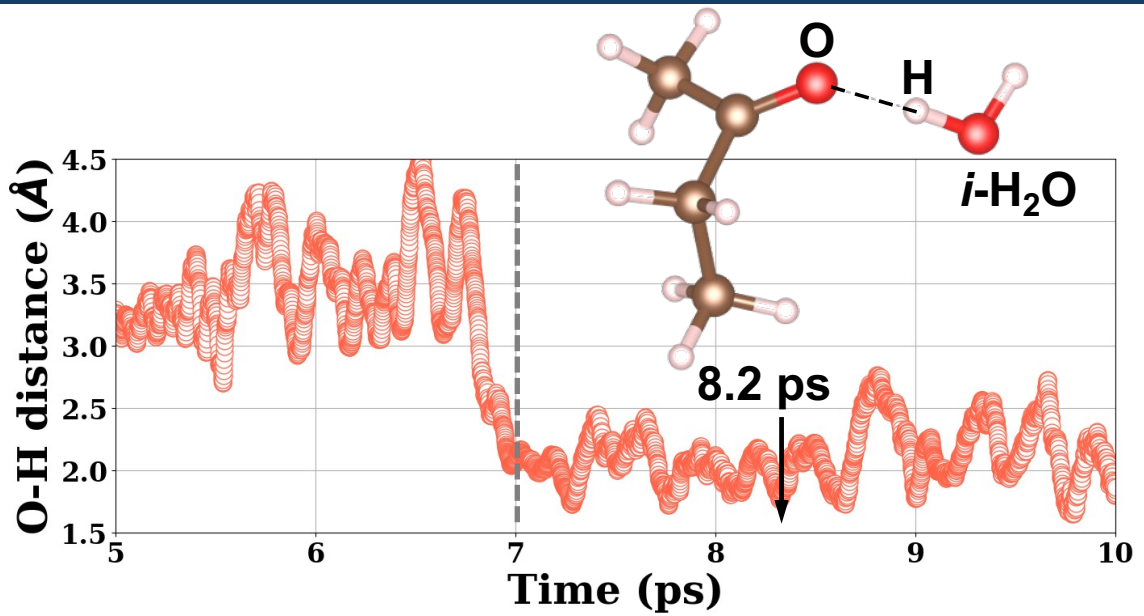

4 mol. of 2-butanone

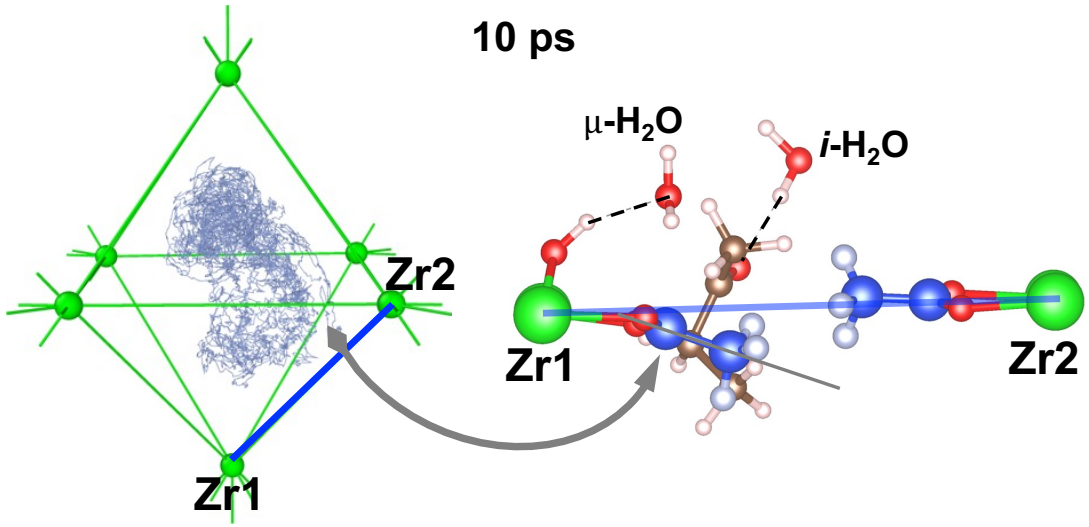



4 mol. with "$CH_3COO^-$ / 2-$H_2O$" defect



# Defect interactions at 300K: 1 mol. of Butanone loading



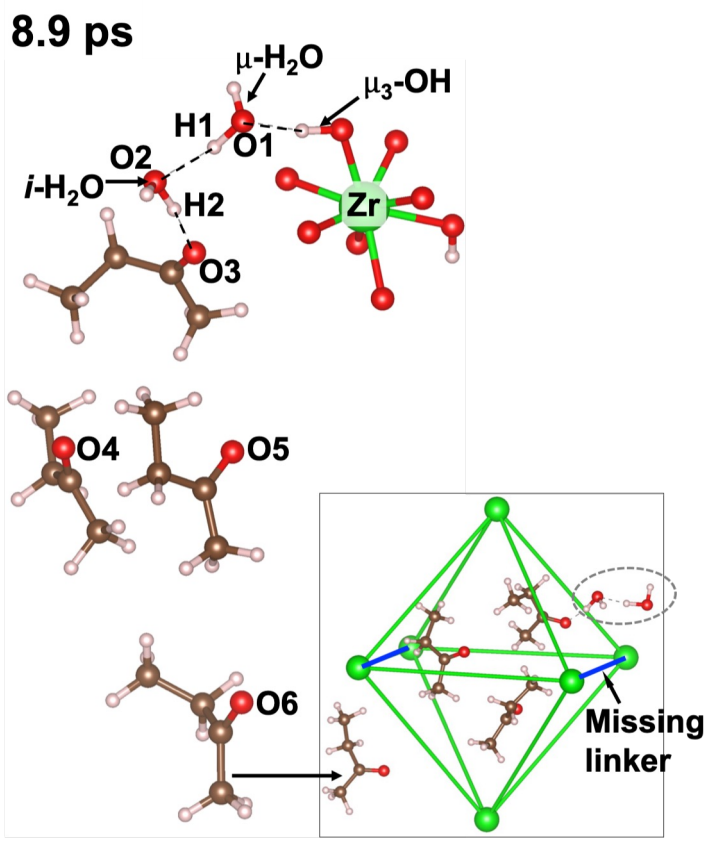



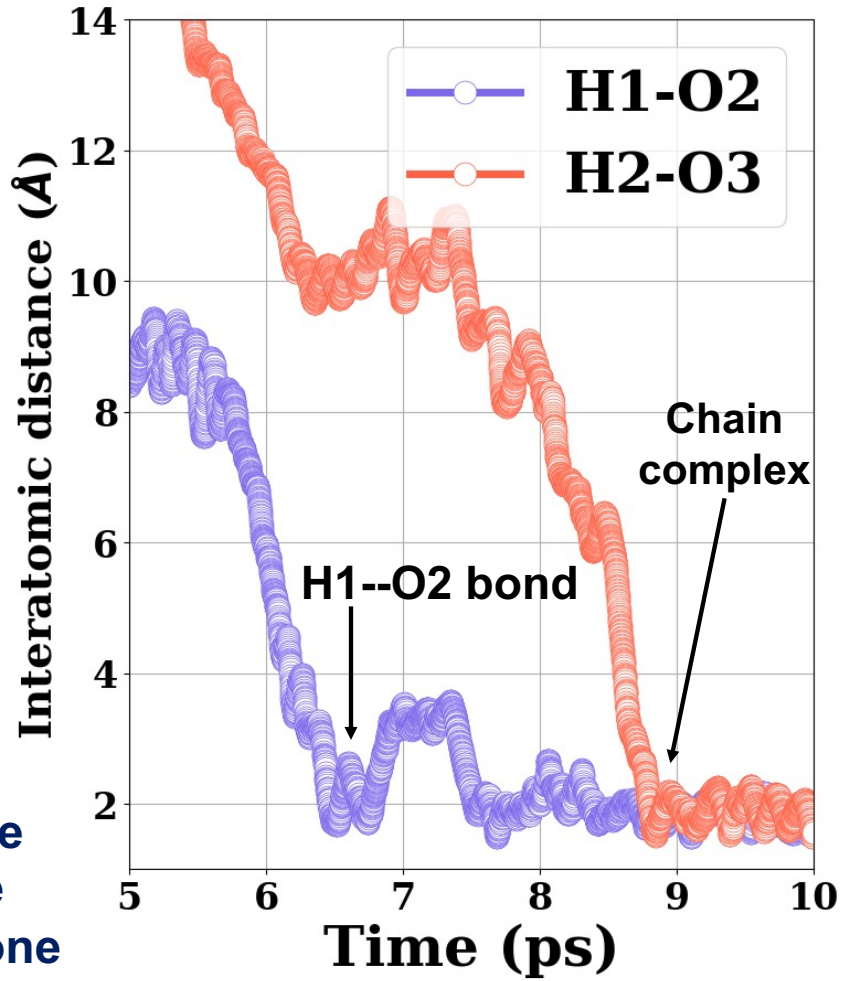

The butanone molecule diffuses out of the cage and stabilizes through a hydrogen bond formed between the butanone and *i*-H2O after roughly 7 ps

Defect acetate capping groups are flexible and are distorted as the butanone moves

These extra degrees of freedom may facilitate the 2-Butanone molecule's diffusion

# Defect interactions at 300K: 4 molecules of 2-Butanone loading




A chain complex comprising hydrogen bonds between $\mu_3$-OH, $\mu$-$H_2O$, $i$-$H_2O$ and butanone forms after 9ps.

Chain complex formation mediated by defects may be used to capture 2-Butanone

Repulsion forces (not caused by the distant $H_2O$s) or the flexible acetate cappers may have caused a butanone to be ejected from the cell

# Summary

**AIMD simulations at 300K indicated that 2-butanone will favorably interact with defective UiO-66 MOF.**

1. **Formation of hydrogen bonded complexes between water and butanone molecules is observed in the defect MOF. Increasing the number of butanone molecules inside MOF cages/pores enhances such bond formation**
2. **Diffusion of 2-butanone molecules out of the octahedral cage was observed, potentially due to the flexible defect structure**

**Thus, our AIMD simulations predict that butanone based VOCs can be trapped within the octahedral cages of defective UiO-66.**

# Thank you!