Entrapment of Volatile Organic Compounds in Defective UiO-66 Metal-Organic-Framework: *Ab Initio* Molecular Dynamics Simulations at 300K

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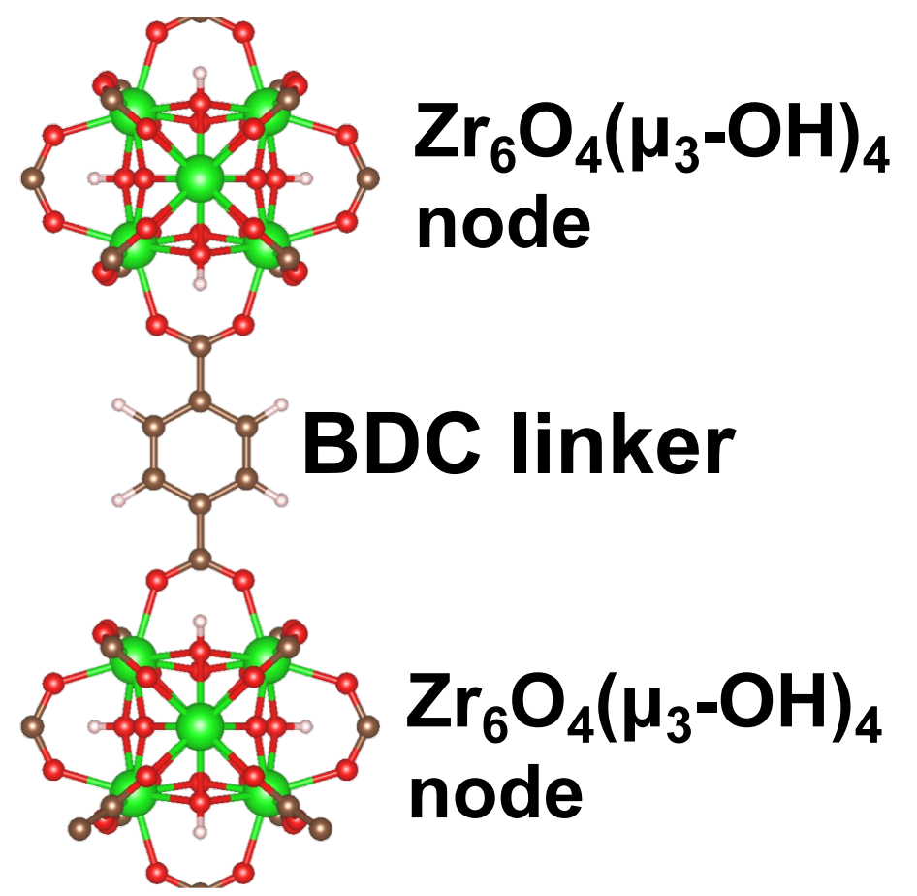
Introduction

Volatile organic compounds (VOC), e.g. 2-butanone ($CH_3C(O)CH_2CH_3$), are produced by various pathogens and metabolic pathways. They have the potential to be used as a diagnostic tool, ***if they are trapped within the cages/pores of hybrid organic-inorganic Metal-Organic-Frameworks (MOFs).***



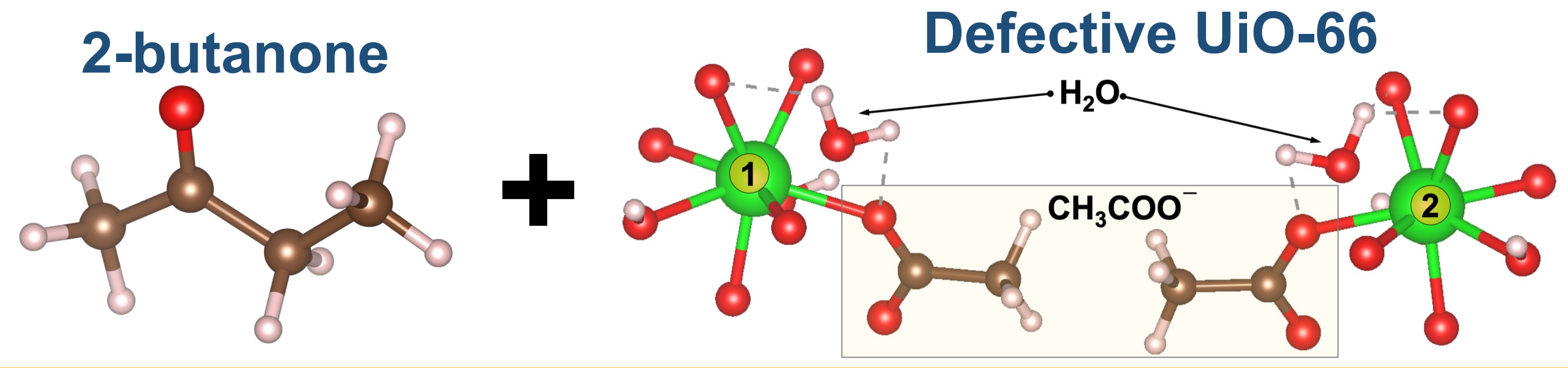
UiO-66 is a well-known MOF that forms 3D structure with larger octahedral and smaller tetrahedral cages. The edges of each cage comprise $Zr_6O_4(\mu_3\text{-}OH)_4$ nodes and 1,4 benzenedicarboxylate (BDC) linkers [1].

UiO-66 are very effective in gas storage and separation, detection and decomposition of warfare agents, drug delivery and catalysis [1,2,3]. Recently, it was revealed that defective UiO-66, with missing linkers, can show enhanced gas storage and separation capabilities compared to pristine structures [4].

Defective UiO-66 forms when chemical modulators are used for their synthesis. Here, the missing linker sites are capped with acetate ($CH3COO^-$) groups, along with collocated water (H_2O) molecules near $Zr_6O_4(\mu_3\text{-}OH)_4$ nodes [4].

Research Objective

Investigate the chemical interaction between 2-butanone and defective UiO-66 MOF with capping acetates and collocated H_2O molecules.



Computational Approach

Ab initio molecular dynamics (AIMD) was performed using the Vienna ab initio simulation package (VASP) that employs the projector augmented plane-wave (PAW) method and utilized Perdew–Burke–Ernzerhof (GGA-PBE) parameterization to describe the electron exchange correlation functional.

All simulations employed Born–Oppenheimer dynamics to compute atomic forces by using isobaric-isothermal ensemble. Equations of motions were integrated using 1femtosecond time step. Long-range van der Waals interactions were incorporated using the DFT-D2 method developed by Gimme [5].

The time-volution of interaction energy, between 2-butanone and MOF, was quantified at 300K using the expression [2]:

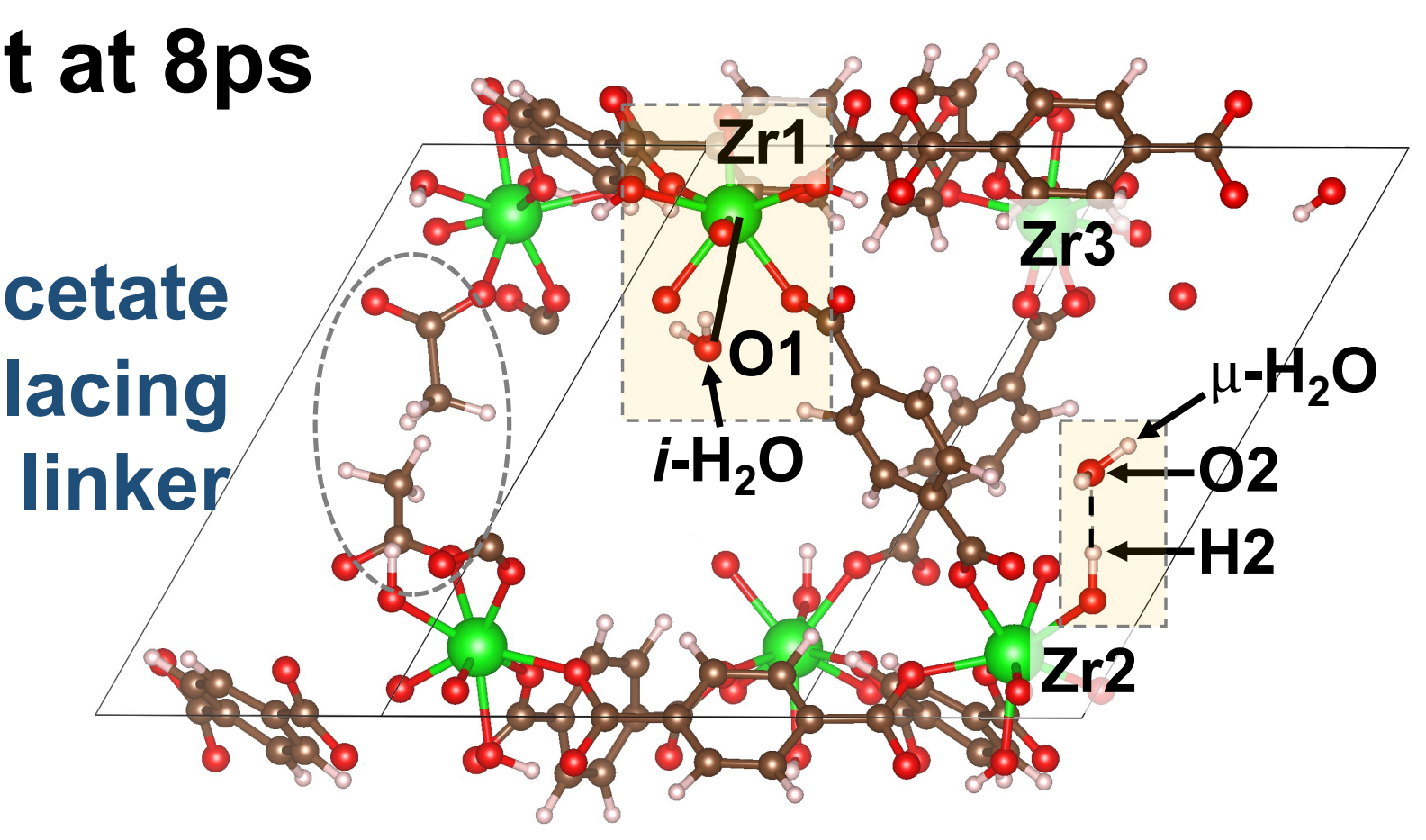
$$\Delta E^{Interaction}_{MOF+VOC+water}(t) = \Delta E^{t}_{Defective-MOF+VOC} - \Delta E^{Time\ Avg}_{defective-MOF} - n\times\Delta E^{Time\ Avg.}_{VOC},$$

where, $\Delta E^{t}_{Defective-MOF+VOC}$ is the supercell energy; $\Delta E^{Time\ Avg}_{defective-MOF}$ and $\Delta E^{Time\ Avg.}_{VOC}$ are time-averaged energies of defective MOF (without VOC) and only 2-butanone, respectively; and n is the number of VOC molecules in the simulation cell.

Results and Discussion

Structure of defective MOF at 300K

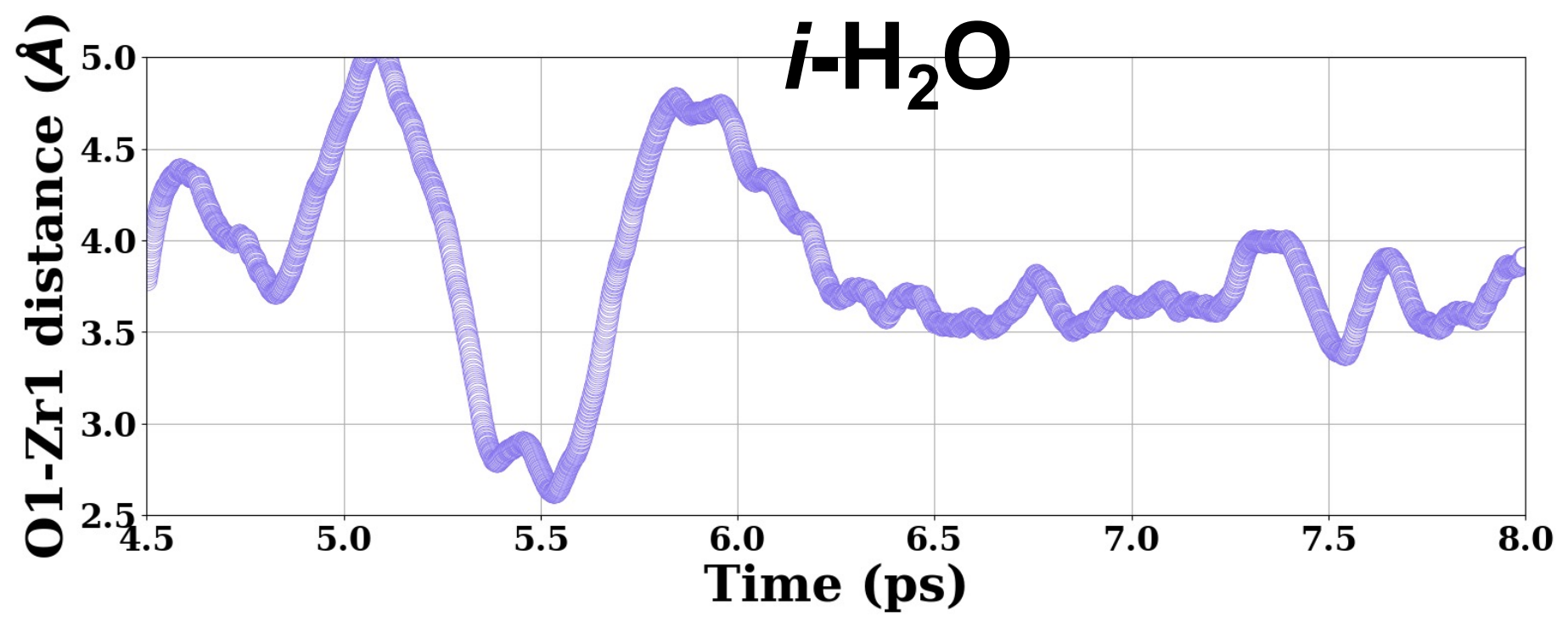
Snapshot at 8ps

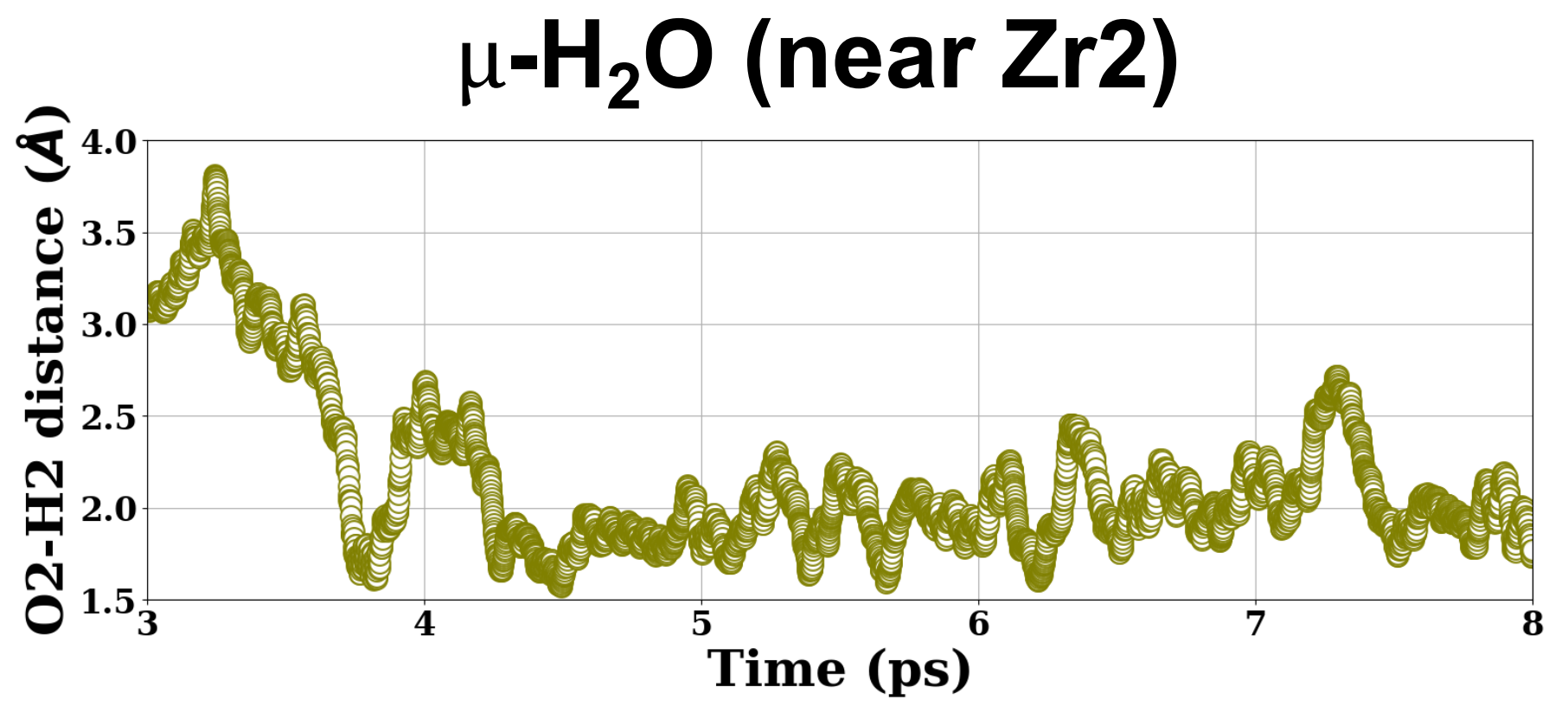


Two acetate caps replacing BDC linker

Defect structure is stabilized by two water molecules located *(i)* within the octahedral interstitial cage and near a node-Zr (marked as i-H_2O); and, *(ii)* near a μ-OH (marked as μ−H_2O)

Time-resolved interatomic distance obtained from AIMD simulations





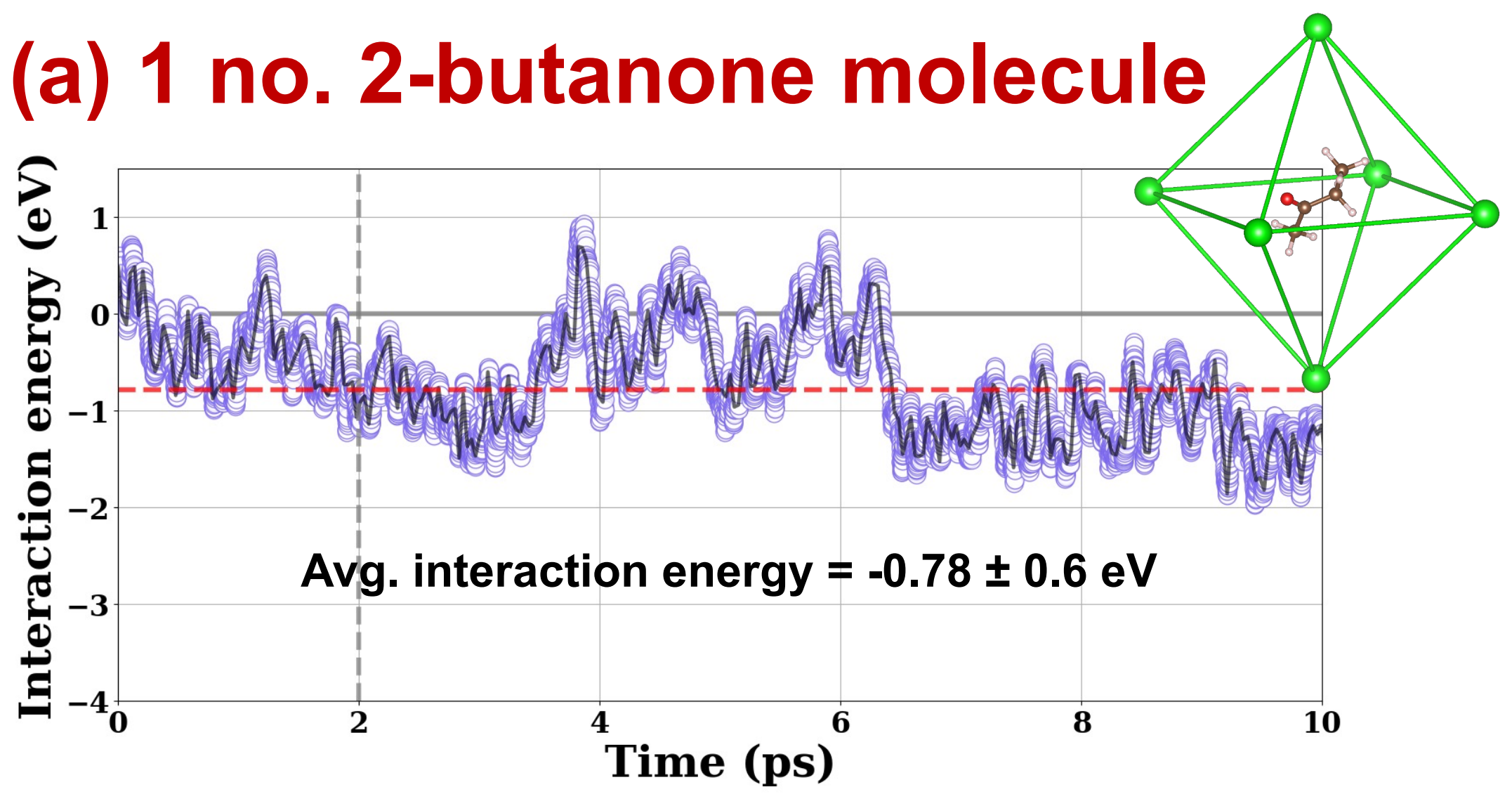
Effect of isothermal annealing at 300K on the location of H_2O molecules

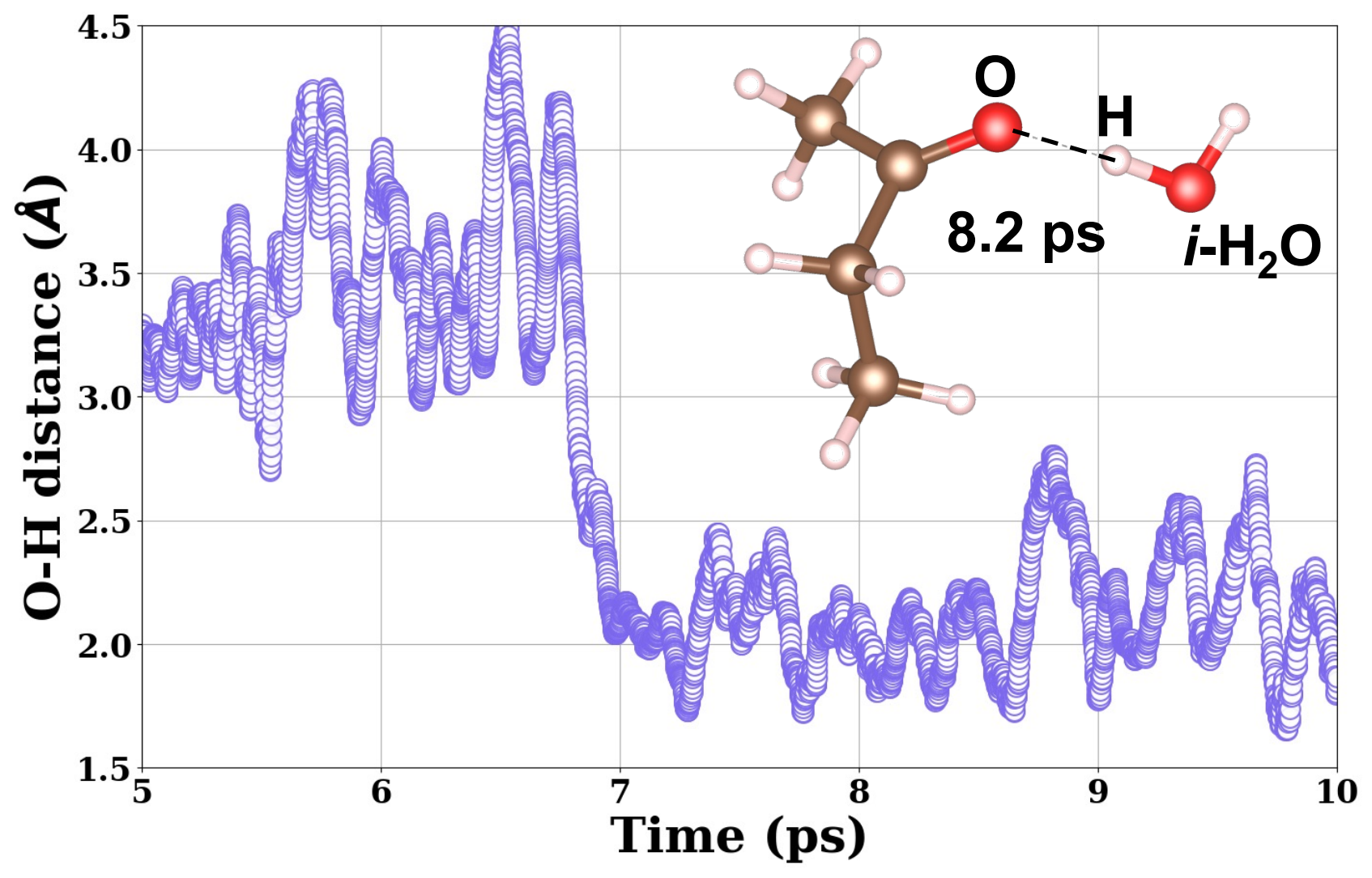
i-H_2O quickly locates itself near a Zr atom (marked as Zr1) at the $Zr_6O_4(\mu_3\text{-}OH)_4$ nodes within ~6.5ps. The new location was different from that of the initial structure.

μ-H_2O forms a hydrogen bond with μ-OH, i.e. O2-H2. This μ-site was located outside of octahedral interstitial cage. μ-H_2O did not move away from the Zr atoms (as was placed the initial configuration), but moved to the adjoining octahedral cage.

Interaction of 1 and 4 no. 2-butanone with defective UiO-66 MOF at 300K

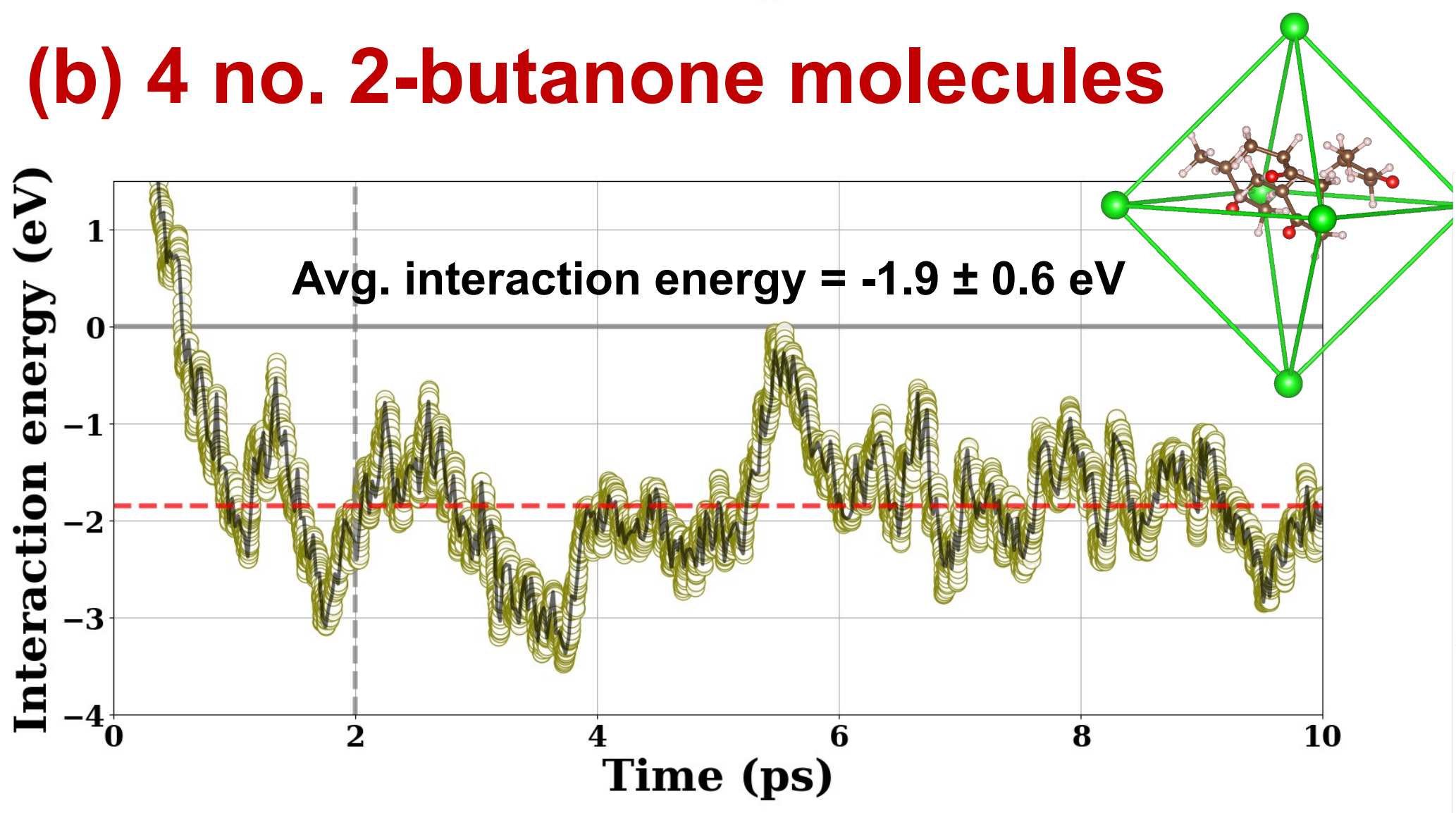
(a) 1 no. 2-butanone molecule





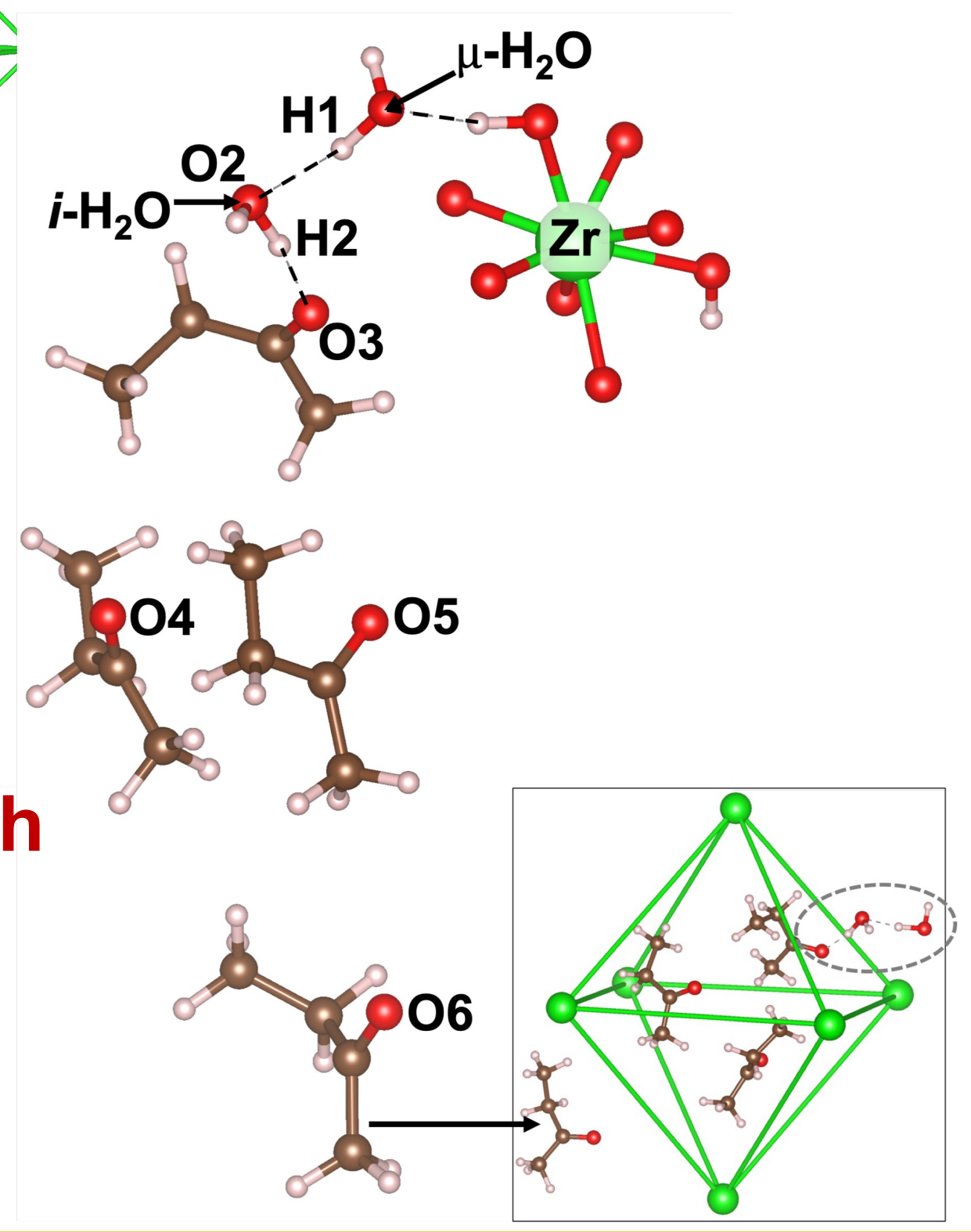
- Butanone forms a persistent hydrogen bond with *i*-H_2O after thermally driven motions drive them closer around 7ps.
- This further lowers the interaction energy to ~1.2eV
- Butanone does not interact with μ-H_2O
- Butanone remains trapped inside the octahedral cage

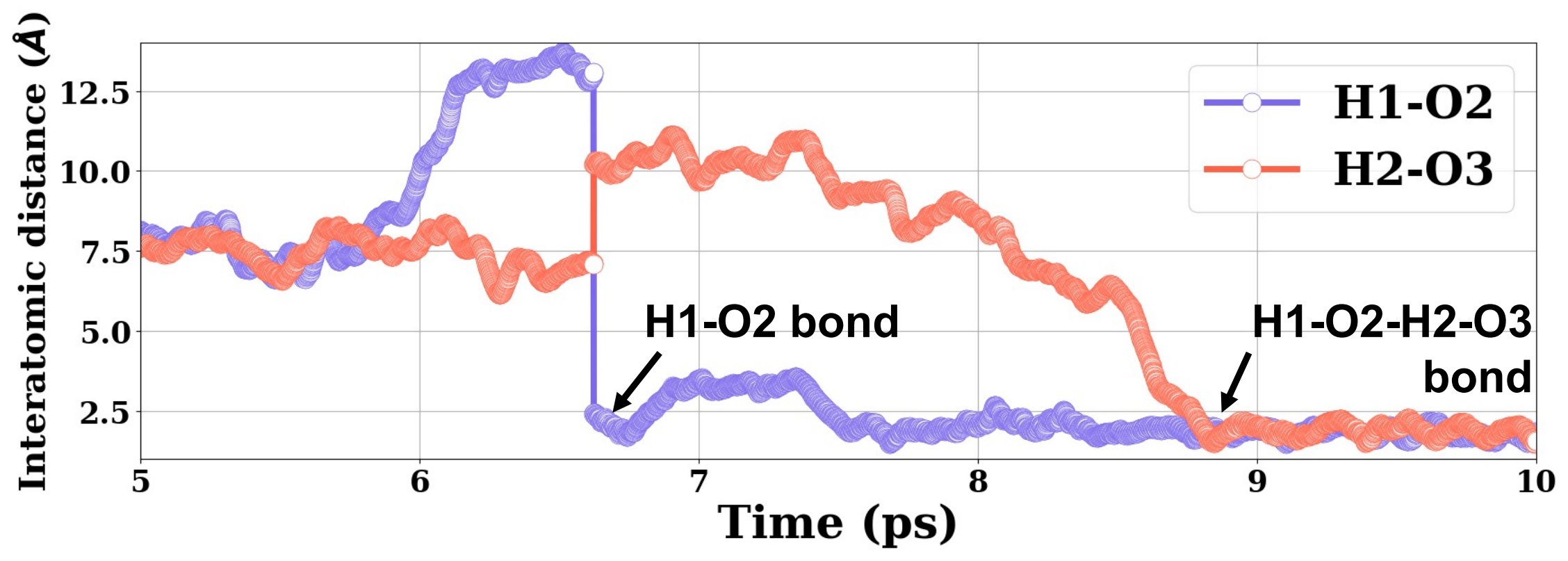
(b) 4 no. 2-butanone molecules



1. 4-butanone interacts more favorably with defective UiO-66 than 1-butanone
2. The former shows negative interaction after temperature convergence at ~2ps

Snapshot at 8.9ps





- One out of four butanone molecule forms a hydrogen bonded complex with both *i*-H_2O and μ-H_2O.
- The mobile *i*-H_2O first forms a bond with relatively static μ-H_2O ~6.9ps, then butanone bonds with *i*-H_2O ~8.9ps
- Not all four 2-butanone molecules remain trapped inside the cage. They tend to diffuses out of the cage.

Summary

AIMD simulations at 300K indicated that 2-butanone will favorably interact with defective UiO-66 MOF. This beneficial effect was caused by:

1. Forming hydrogen bonded complexes between water and 2-butanone molecules
2. Increasing 2-butanone within the MOF cages/pores enhances such bond formation
3. Diffusion of 2-butanone molecules out of the octahedral cage

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

References

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