How does water move in MOF-303 and MOF-333?

Diffusion of water in the metal-organic frameworks MOF-303 and MOF-333

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In Short

- Several billion people live in water-stressed regions, emphasizing the need for innovative solutions; modern metal-organic frameworks offer exciting opportunities for adsorbing water from air;
- We plan to use density functional theory (DFT) to investigate diffusion of water in the two metal-organic frameworks MOF-303 and MOF-333;
- This project will guide and accelerate the knowledge-driven design of water harvesting materials and devices.

It is of utmost importance to address the intensifying global water crisis, given the large populations living in water-stressed regions.[1] The existing solutions, such as water transfer and desalination, come with high costs and environmental consequences, hindering their widespread adoption. However, the invention of water-harvesting metal-organic frameworks (MOFs) presents a promising avenue.[2] These porous materials are able to efficiently collect and release atmospheric water. MOF-based water harvesting devices demonstrate operational flexibility across diverse temperature and humidity ranges and require minimal maintenance while producing clean drinking water.[3]

In recent years, significant endeavors have been dedicated to unraveling the crystal structures of water-harvesting MOFs and understanding of their chemical properties, resulting in a more profound comprehension of their performance. Studies have revealed that the metal oxide clusters/nodes are responsible for the MOF stability, while the organic linkers determine the water capture behaviour.[4,5] Additionally, it has been shown that substituting the organic linker results in tunable MOF systems with varying moisture uptake and adsorption properties.[4,6] Moreover, the introduction of vinyl groups into the PZDC linker increased the pore size and water uptake by 50%.[5] These advancements in linker design represent significant steps towards more efficient and versatile water collection. A MOF-303-based device demonstrated the ability to harvest 1.3 liters of water for 1 kg of MOF in one day with no energy but sunlight. Under extreme conditions in the Mojave Desert, it collected 0.7 L $\cdot$ kg MOF^{-1} $\cdot$ day^{-1} of clean water without electricity.[7] While this quantity can partially meet the daily water requirements of an individual, it falls short for household and agricultural needs. To drive advancements in water-harvesting materials, it is crucial to not only gain an understanding of water adsorption but also to comprehend the motion of water molecules within the MOF.

That is why we will study water within MOFs and aim to gain insights into the diffusion of water molecules. This project comprises two main parts. In the first part, we plan to investigate water adsorption and diffusion in the MOFs, MOF-303 and MOF-333, using DFT. This involves conducting structure optimizations, performing Hessian calculations, and employing NEB transition structure searches. The second part of the project aims to achieve chemical accuracy by using hybrid MP2:DFT calculations and CCSD(T) corrections. This is important to reach a level of accuracy which allows for theory-guided, reliable predictions.

Throughout the project, the obtained results will be compared with available experimental data from the collaborative group of Prof. Dr. Yaghi based at UC Berkley. This will verify the reliability and accuracy of our findings. Additionally, we collaborate with Prof. Dr. Gagliardi's group from UC Chicago. The combination of their molecular dynamics simulations with our results will help to establish a comprehensive understanding of water diffusion in MOFs. The obtained results will further be used as input for Grand Canonical Monte Carlo (GCMC) and kinetic Monte Carlo (kMC) methods. The project's ultimate goal is to contribute to developing improved water-harvesting materials and gain a comprehensive understanding of the molecular-level phenomena involved.

In the first year, we will conduct the first part of the project on MOF-303, see Figure 1. Based on test calculations using VASP on HLRN resources with specific settings (PBE+D3(BJ), 520 and 850 eV cutoff, Γ-point, normal and hard POTCARs), we have determined that the total amount of the computational resources will be approximately 10.5M core hours.

More Information

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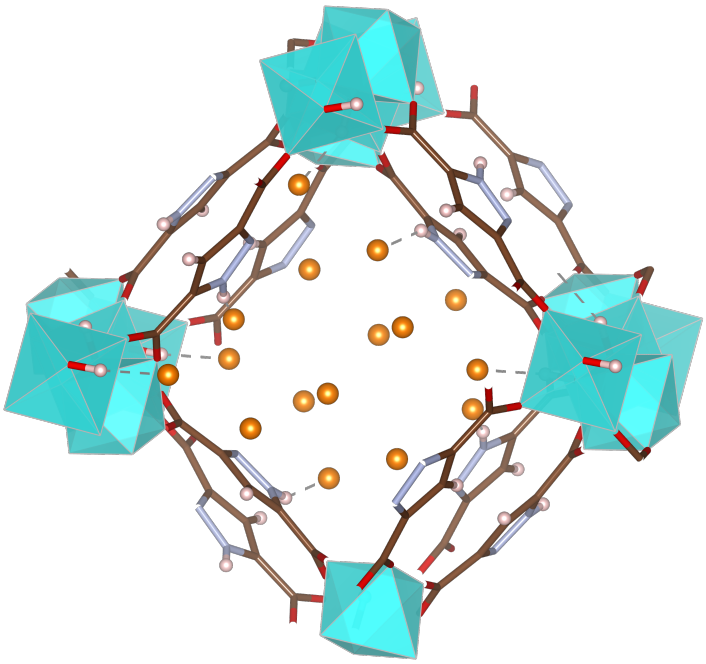

Figure 1: *Experimental structure of water-loaded MOF-303. Colour code: O of water – orange spheres, O of the MOF – red vertices, C – brown vertices, N – blue vertices, H - white spheres, AlO_6 - light blue octahedra.*

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