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UNDERSTANDING HYDROGEN STORAGE IN METAL–ORGANIC FRAMEWORKS USING MASSIVELY PARALLEL ELECTRONIC STRUCTURE CALCULATIONS

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EXECUTIVE SUMMARY

Hydrogen has the potential to be a major green-energy source, but for use as a fuel, it requires efficient storage materials for retaining and releasing hydrogen in large quantities. Metal–organic frameworks (MOFs) are one such possible material, and their hydrogen storage potential and microscopic properties need further investigation. Toward that end, we performed first-principles quantum-mechanical molecular-dynamics calculations to understand the behavior of hydrogen inside MOFs. We included the effect of quantum nuclear motions, which are critical for the properties of hydrogen, the lightest element. These challenging calculations are only possible on large-scale and massively parallel computational platforms such as Blue Waters. The knowledge gained from our studies informs the materials research community as to the fundamental reasons underlying the properties of hydrogen in MOFs, and, potentially, how we may improve the chemical composition of MOFs for hydrogen storage.

RESEARCH CHALLENGE

We used large-scale and accurate quantum-mechanical calculations on an important class of porous hydrogen storage materials: metal–organic frameworks (MOFs). Hydrogen has a strong potential to be a source of green energy, but, as a fuel it requires efficient storage materials that retain and release a great deal of hydrogen. We studied the properties of hydrogen inside MOFs to understand their physical properties and potentially how to improve MOFs to deliver increased hydrogen storage. We simulated hydrogen inside of MOFs at the atomistic scale
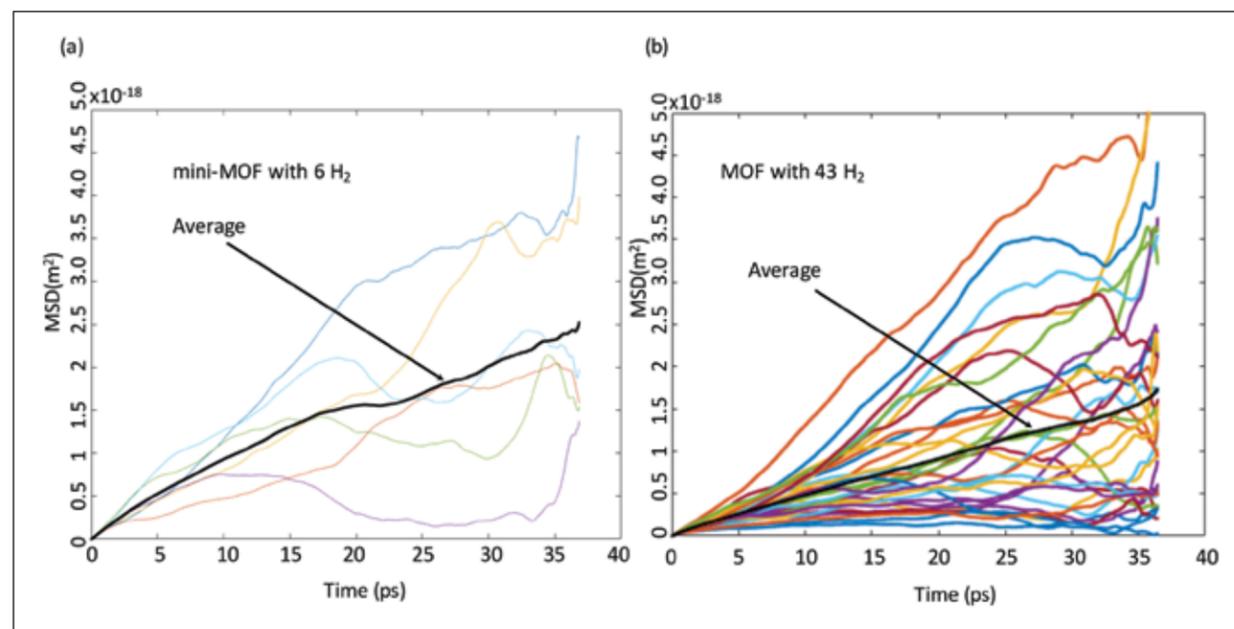

Figure 1: Mean square displacement at 77K of the centers of mass of the H_2 molecules as a function of elapsed simulation time. For both the mini-MOF and full MOF, each colored curve represents a unique H_2 molecule in the simulation cell. The black curve is the average over all the H_2. The slope of the average curve is a direct measure of the diffusion coefficient for H_2. The diffusion coefficient (D) for the mini-MOF is approximately $1x10^{-8}$ m^2/s and for the full MOF it is $8x10^{-9}$ m^2/s. Both values are very close to prior simulation results of $7x10^{-9}$ m^2/s where the simulation parameters were fitted to experimental databases [2].
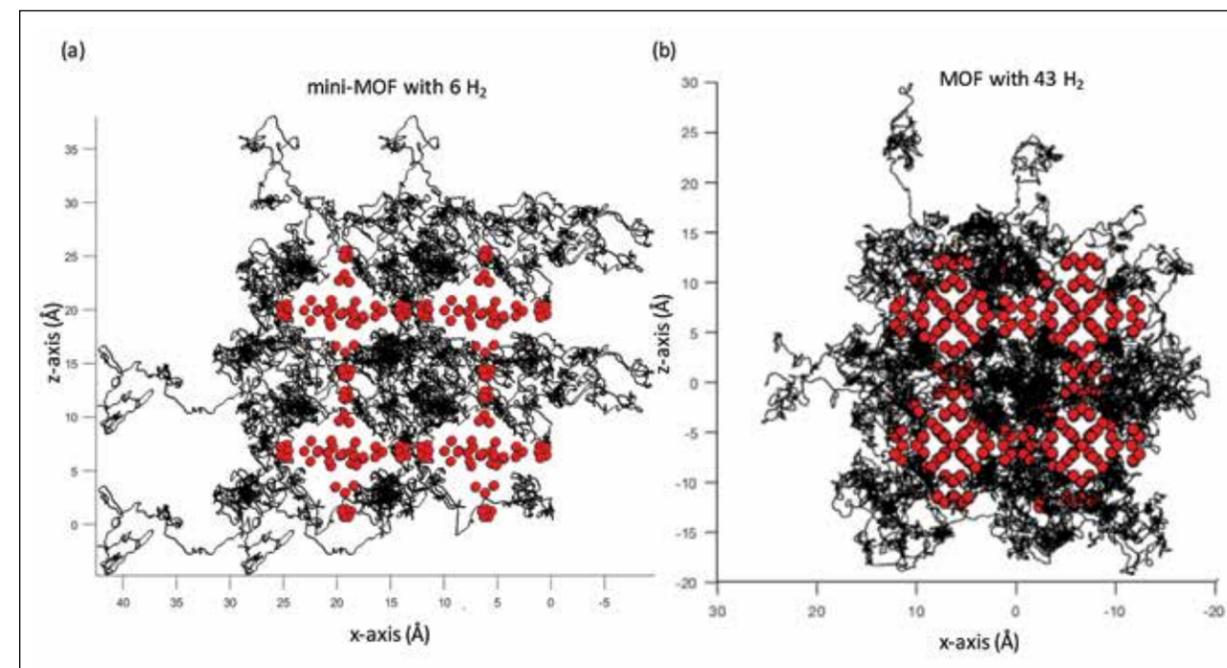

Figure 2: A 2D projection of the MOF backbone atoms (in red) along with the trajectories followed by the center of mass of each H_2 molecule diffusing in (a) the mini-MOF, and (b) the full MOF at 77K. Periodic boundary conditions were imposed to extend the trajectories to neighboring unit cells.

using accurate first-principles quantum-mechanical simulations based on Density Function Theory (DFT). We aim to understand the binding and dynamics of light elements such as hydrogen inside MOFs.

METHODS & CODES

Answering the above questions requires an accurate quantum-mechanical simulation at finite temperature. The method must work beyond the harmonic approximation because hydrogen motion can be diffusive and highly anharmonic. Due to the use of complex ligands chelated to metal ions and the metal ions themselves, standard pairwise force fields can be problematic in describing the energetics, and parameterizing a more transferable model is both time consuming and difficult. We employed the Car–Parrinello Molecular Dynamics simulation technique (CPAIMD), which allows the nuclei to move on the Born–Oppenheimer energy surface provided by plane wave-based DFT. By including the electronic degrees of freedom (valence) explicitly, we bypassed force field difficulties.

RESULTS & IMPACT

We spent the majority of the 2017 calendar year performing molecular dynamics simulations of a MOF (the zinc-containing "MOF-5" material) using our OpenAtom first-principles molecular dynamics software. We first obtained simulation on a smaller 1/8-sized subsection of the full MOF (denoted as mini-MOF) and then compared the results with the full MOF. The full MOF simulation has in excess of 510 atoms per simulation cell with a large amount of "vacuum" (voids) in the structure to provide room for hydrogen diffusion, and a large internal surface area for hydrogen adsorption. The smaller size of the mini-MOF allows us to run very long molecular dynamics simulations and benchmark the results carefully. We studied the dynamics of 43 hydrogen molecules inside this metal–organic molecular system for the full MOF; we studied the diffusion of six H_2 molecules for the mini-MOF. We performed our simulations at 77K and 300K for both systems to understand the effect of temperature on hydrogen diffusion. Fig. 1 shows a comparison at 77K of the mini-MOF and full MOF mean square displacement versus time delay; the slope of a linear fit gives us the diffusion coefficient. Fig. 2 shows a 2D projection of the MOF backbone atoms (in red) along with the trajectories followed by the center of mass for each H_2 molecule diffusing in (a) the mini-MOF, and (b) the full MOF at 77K. Both simulations are long enough to show significant diffusion of the H_2 molecules and thus are statistically meaningful.

WHY BLUE WATERS

Massively parallel electronic structure calculations require tightly coupled computing nodes due to intense communication loads: electron waves are delocalized over the entire system so all parts of the system end up interacting with each other. For the MOF system of interest, the CPAIDM simulations already require a massively parallel calculation with many hundreds of nodes.