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

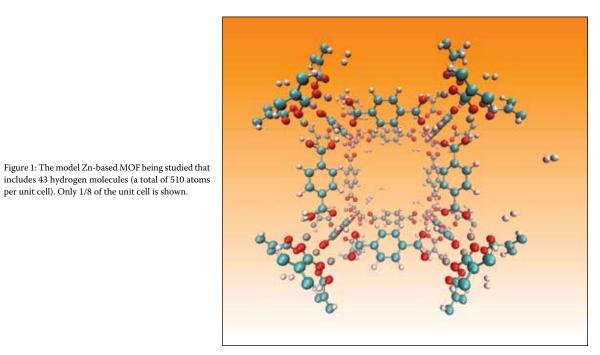## EXECUTIVE SUMMARY

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 potential storage materials, and their hydrogen storage potential and microscopic properties need further investigation. We perform first-principles quantum-mechanical molecular dynamics calculations to understand the behavior of hydrogen inside MOFs. We include the effect of quantum nuclear motions, which are critical for the properties of hydrogen, the lightest atomic element. These challenging calculations are only possible on large-scale and tightly coupled 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 use 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 green energy source, but as a fuel it requires efficient storage materials that retain and release a great deal of hydrogen as desired. We study the properties of hydrogen inside MOFs to understand their physical properties and potentially how to improve MOFs to deliver improved hydrogen storage. We simulate hydrogen inside of MOFs at the atomistic scale using accurate first-principles quantum-mechanical simulations based on density functional theory. In addition to large-scale molecular dynamics simulations of the diffusion and dynamics of hydrogen inside MOFs, we describe the atomic nuclei in the entire system quantum mechanically via a path integral formalism. The effects due to the quantum fluctuations of the nuclear degrees of freedom are critical for understanding the binding and dynamics of light elements such as hydrogen.

Figure 1: The model Zn-based MOF being studied that includes 43 hydrogen molecules (a total of 510 atoms per unit cell). Only 1/8 of the unit cell is shown.

METHODS & CODES

Answering the above questions requires an accurate quantum-mechanical simulation method at finite temperature. The method must work beyond the harmonic approximation as 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 employ the Path Integral Car–Parrinello Molecular Dynamics simulation technique (PI-CPAIMD), which allows the nuclei to move on the Born–Oppenheimer energy surface provided by plane wave-based Density Function Theory (DFT) and includes quantum effects via Feynman Path Integrals. By including the (valence) electronic degrees of freedom explicitly, we bypass force-field difficulties; by employing path integrals, nuclear quantum effects are treated in a completely general way and are converged with a single parameter.

The use of the PI-CPAIMD method and the high-quality results it delivers requires highly scalable software, developed by us under NSF support (NSF SI2 grants ACI-1339804 and ACI-1339715), and named OpenAtom. CPAIMD, which simulates classical mechanics of the nuclei moving on the DFT-derived energy surface, has a computational workload scaling as N^3 where N is the number of atoms in the simulation. Adding Path integrals, the computational cost increases by the factor P to PN^3 where P is the number of "beads" used to discretize the Feynman path integral: Typically, P ranges between 20 and 80, which is a significant increase in computational requirements. As one can imagine, the computational cost requires petascale resources, and a supercomputer such as Blue Waters is needed to carry out this work. Work on Blue Waters is supported by NSF PRAC grant OAC-1614491.

RESULTS & IMPACT

In the first year of our PRAC project on Blue Waters, we have spent the majority of the time studying a model MOF system with hydrogen to understand the behavior of the system and its various timescales. Fig. 1 illustrates the unit cell of the MOF crystal with hydrogen molecules inside. A smaller version of the MOF was carefully studied with CPAIMD long simulations, which permitted us to obtain preliminary results. Fig. 2 shows the results of the CPAIMD simulations (without quantum effects) for the hydrogen probability distribution inside the MOF when the system is at 300°K: The hydrogen molecules spend most of their times in the "voids" (corner regions) away from the MOF backbone, signaling weak binding to the MOF backbone at these temperatures and potentially rapid diffusion. Other measures of diffusion (e.g., the hydrogen diffusion coefficient) are in good agreement with prior results, giving us confidence that the benchmarking has been successful in producing physically accurate and important results. The next step is to perform CPAIMD simulations with the full larger MOF system and then to turn on quantum nuclear effects
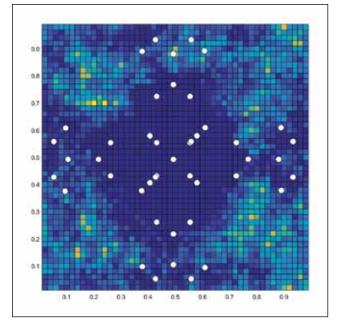

Figure 2: Preliminary heatmap of hydrogen diffusion inside the small MOF model system. The heatmap shows the averaged probability distribution of finding hydrogen atoms inside the MOF at 300°K. The backbone of the MOF itself is shown in white while the colormap shows hydrogen probability density with brighter colors indicating higher probabilities (linear scale).

via the path integral approach to understand how the quantum effects modify the behavior of hydrogen inside the MOF.

Successful modeling of the behavior of hydrogen inside MOFs will provide valuable information to the community of materials and energy researchers, in academia as well as at national and industrial labs, regarding the underlying reasons for the performance of these materials. Chemical modifications of the MOF structure can then be explored using such simulations to help design improved hydrogen storage performance.

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 CPAIMD simulations already require a massively parallel calculation with many hundreds of nodes. The inclusion of nuclear quantum effects, however, means that only a tightly coupled petascale computer such as Blue Waters is capable of delivering results on a reasonable (one- to two-year) timescale.