

IV.H.2 Novel Theoretical and Experimental Approaches for Understanding and Optimizing Hydrogen-Sorbent Interactions in Metal Organic Framework Materials

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Objectives

- Develop a comprehensive understanding of how small molecules (e.g. H₂) bind inside metal organic framework (MOF) materials, using experimental methods (infrared [IR] and Raman spectroscopy) and theoretical tools (first-principles density functional theory).
- Develop an accurate model for the kinetics and diffusion of molecular hydrogen and gas mixtures through MOF materials.
- Devise approaches to increase the binding energy and uptake of molecular hydrogen in MOF materials to the required 20 kJ/mol by designing new MOFs with tailored, unsaturated metal clusters or catalytic centers.

Technical Barriers

- MOFs of very high surface area have been developed by making use of long ligands and suitable metal nodes, but great challenges remain in achieving sufficiently high hydrogen binding energies (the highest Q_{st} values are still below 15 kJ/mol and low porosity is usually associated with high Q_{st}) that will lead to high H₂ uptake at room temperature.
- The microscopic nature of the interaction between gas molecules and the MOF network is difficult to extract from spectroscopy alone (without theoretical modeling), although much information on the adsorption sites and relaxation of the MOF network is reflected in both IR and Raman spectra. Many MOFs are also sensitive to

water vapor, which may complicate adsorption studies, requiring in some cases H₂O co-adsorption studies.

- First-principles spin-polarized simulations of interesting MOFs with magnetic atoms (Fe, Ni, Co) and the effective inclusion of temperature and dynamical effects are not yet possible in our simulations, as van der Waals density functional (vdW-DF) has not been extended for such cases.

Abstract

Hydrogen storage is a key challenge and the largest barrier to a hydrogen economy. Many hydrogen-storage materials have been investigated, e.g. transition-metal hydrides or light-element hydrides. MOF materials—metal-oxide clusters connected by organic ligands (e.g. linkers or pillars)—use a different approach. These structures are porous and have a huge effective surface area, making them ideal for H₂ storage through physisorption. Possible combinations of clusters and ligands are literally limitless and give hope that desired properties can be obtained by designing the “right” combination. MOF properties of interest are the hydrogen-storage capacity and the thermodynamics of the hydrogen adsorption/desorption. At high pressures or low temperatures, MOFs typically have a hydrogen-storage capacity of up to 5 wt% and a hydrogen binding energy of up to 10 kJ/mol. The overall aim is to increase both, as required for on-board applications, by designing improved metal clusters and linkers. To this end, it is necessary to understand how the hydrogen interacts with clusters and linkers. Our specific aim is to develop a fundamental mechanistic understanding of the interaction of H₂ in MOFs, using a combination of novel synthesis, theoretical analysis, and characterization. We combine high-pressure and low-temperature IR absorption and Raman measurements, adsorption isotherms, and isosteric heat of adsorption measurements with first-principles calculations based on vdW-DF. This provides insight into the role of unsaturated metal centers in enhancing molecular uptake, selective adsorption, and diffusion. The short-term impact of this work is that the control and understanding of common MOF systems makes it possible to determine the theoretical loading limits and stability of a specific class of materials. The long-term impact includes the development of (i) theoretical and experimental methods to gain a fundamental understanding of molecular interactions within these systems, and (ii) new classes of microporous MOFs with enhanced molecular binding.

Progress Report

Synthesis, structure characterization, and modification of MOFs: We have functionalized a bdc ligand in $\text{Zn}(\text{bdc})(\text{ted})_{0.5}$ by introducing hydroxyl and amino groups that lead to two related structures, $\text{Zn}(\text{bdc-OH})(\text{ted})_{0.5}$ and $\text{Zn}(\text{bdc-NH}_2)(\text{ted})_{0.5}$ (bdc = terephthalate, ted = triethylenediamine, bdc-OH = 2-hydroxyterephthalate, bdc-NH₂ = 2-aminoterephthalate). $\text{Zn}(\text{bdc})(\text{ted})_{0.5}$ can be considered a three-dimensional (3D) porous structure having three interlacing one-dimensional (1D) channels, while both $\text{Zn}(\text{bdc-OH})(\text{ted})_{0.5}$ and $\text{Zn}(\text{bdc-NH}_2)(\text{ted})_{0.5}$ contain only 1D open channels as a result of ligand functionalization. A notable decrease in surface area and pore size is observed in both compounds. Consequently, $\text{Zn}(\text{bdc})(\text{ted})_{0.5}$ takes up the highest amount of H₂ at low temperatures. However, the isosteric heats of hydrogen adsorption is higher in $\text{Zn}(\text{bdc-OH})(\text{ted})_{0.5}$ than in $\text{Zn}(\text{bdc})(\text{ted})_{0.5}$, suggesting a stronger H₂-framework interaction in the former.

Calculation of IR intensities of adsorbed H₂ in MOFs: Knowledge of the strengths and frequencies of the IR bands resulting from molecules adsorbed at varying adsorption sites is crucial for the correct interpretation of IR data. The calculation of frequencies is fairly straightforward, but the intensities have proved difficult or impossible to calculate for an IR inactive molecule like H₂ adsorbed in a large structure such as MOFs. This is because the dipole moments are only induced and small, and occupy a large volume. This is exacerbated by the fact that vibrations, rotations, and translations contribute strongly to the spectra. We have developed theoretical methods to tackle this problem and successfully applied them to the IR spectra of an important MOF (MOF-74). Our ability to do this substantially enhances our ability to use our now more powerful experimental/theoretical combination to unravel the complexities of H₂ adsorption in less understood structures.

H₂-H₂ interactions in MOF-74: We have identified H₂-H₂ interactions between near neighboring sites and next-near neighboring sites in MOF-74. Using our vdW-DF approach, we have shown that H₂ dipole moments and IR shifts are greatly affected by these interactions. We were able to detect these effects using IR absorption measurements of H₂ in MOF-74-M (M= Zn, Mg), as a function of temperature and pressure. A small shift (~ -30 cm⁻¹ with respect to the unperturbed H₂ molecule) is observed for the internal stretch frequency of H₂ adsorbed on the metal site at low loading. This contrasts the much larger shifts (~ -70 cm⁻¹) observed in previous studies of MOFs with unsaturated metal centers (including MOF-74) and the general assumption that the H₂ stretch shifts depend on adsorption energies. We show that larger shifts (~-70 cm⁻¹) do occur, but only when the next available site (“oxygen” site) is occupied. This larger shift originates from H₂-H₂ interactions on near neighboring sites, consistent with the short distance between H₂ in these two sites ~2.6 Å.

Improving computational tools: The original exchange-correlation functional vdW-DF showed slightly overestimated binding distances and underestimated binding energies. Before his untimely passing, Langreth and his group had refined this functional and developed a successor, i.e. vdW-DF2. We adapted this functional and tested it for gas adsorption in MOFs under the current DOE grant. We now use it to calculate nuclear positions, molecular binding sites, and IR spectra for gases adsorbed in MOFs; it is more accurate for calculations of gas adsorption in MOFs than vdW-DF. We implemented vdW-DF and vdW-DF2 in PWscf (part of QUANTUM-ESPRESSO), which is faster by a factor of 2–3 compared to our original implementation in ABINIT, resulting in much increased productivity. We also derived a formalism to calculate the vdW-DF stress tensor, allowing for a much more efficient structural optimization. With these new computational tools, we performed a purely theoretical study of the hydrogen-storage capacity of (H₂)₄CH₄ in MOFs and carbon nanotubes. While we find that MOFs cannot provide sufficient pressure to stabilize this extraordinary hydrogen-storage material at room temperature, we do find that carbon nanotubes have the potential to do so, with storage capacities of up to 20 wt%.

Future Directions

From a structure designing point of view, our future focus will be to incorporate a high density of functional groups (e.g. -OH, -Cl, -F, -NR₂) and metal clusters (e.g. Mg, Li) in MOF structures that have strong binding interactions with hydrogen and other targeted small molecules, while keeping the high porosity of the MOF framework.

Future theoretical work will focus on: (i) Our DFT calculations are performed with our vdW-DF exchange-correlation functional, including van der Waals forces—which are crucial for the description of H₂ physisorbed in MOF structure—seamlessly. Currently, vdW-DF cannot describe spin-polarized systems, excluding many interesting MOFs. We will work on finding suitable approximations for such systems, with applications to MOF74-Fe, MOF74-Co, and MOF74-Ni. (ii) For hydrogen storage in MOFs, not only the binding energy is important, but also the kinetics of hydrogen diffusion through the network. We plan to investigate H₂ diffusion barriers in MOFs from first-principles, using nudged-elastic-band calculations. These barriers will reveal previously inaccessible information about hydrogen kinetics and migration in MOFs. (iii) Currently, all simulations are strictly speaking performed at zero K. The effect of temperature can be included by performing first-principles molecular dynamics simulations. To this end, we will incorporate vdW-DF into a molecular dynamics code.

The methods and approaches developed here are directly applicable to study the interaction of many other small molecules such as CO, CO₂, N₂, H₂O, and CH₄ with

MOFs. We plan to apply our successful experiment/theory framework to study co-adsorption of CO₂, H₂O, and H₂ in MOFs with unsaturated metal centers for the purpose of gas sequestration of these molecules.

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