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First Principles Studies of Structural, Molecular Adsorption, and Spectroscopic Properties
of Metal-Organic Frameworks

by

Alex Smith

A dissertation submitted in partial satisfaction of the

requirements for the degree of

Doctor of Philosophy

in

Physics

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor Jeffrey B. Neaton, Chair

Professor Steven G. Louie

Professor Mark Asta

Summer 2024

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Abstract

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Doctor of Philosophy in Physics

University of California, Berkeley

Professor Jeffrey B. Neaton, Chair

Metal-organic frameworks (MOFs) are a class of crystalline materials with broad diversity in their chemical compositions and geometries which give rise to a high degree of tunability of their properties, and many possible applications. Because a broad range of synthetic modifications to MOFs are possible, computational methods are invaluable in guiding experimental studies to understand the relationship between a given structure and chemistry and its material properties. In this work, we use first principles electronic structure calculations to calculate low energy geometries, nuclear magnetic resonance (NMR) chemical shifts, and binding energetics of MOFs that adsorb CO_2 and O_2 . Our calculations explain experiments indicating that the presence of SO_2 degrades the performance of diamine-appended $\text{Mg}_2(\text{dobpdc})$, a promising class of MOF for carbon capture, with some appended diamines but not others. Additionally, we show that we can capture trends in O_2 binding in a computationally challenging family of MOFs, the BTTri MOFs, that contain open-shell transition metal atoms. We predict that by modifying the halide in BTTri we can obtain binding energies that are ideal for industrial separations of O_2 .

In order to better understand the mechanism of cooperative CO_2 adsorption in diamine-appended $\text{Mg}_2(\text{dobpdc})$, we extend a statistical mechanics model to understand the role of defects, steric hindrance, and mixtures of diamines on CO_2 adsorption isotherms and isobars. This work shows that cooperative uptake is robust in the presence of defects as long as the cooperative interaction which promotes CO_2 binding at adjacent diamine sites is sufficiently strong. We also rationalize experimentally observed double stepped isotherms, and develop a way of understanding how the ratio of mixed diamine systems can be chosen to target a specific pressure at which CO_2 will be bound to the MOF.

We benchmark the performance of van der Waals corrected density functionals in layered MOFs and layered perovskites, showing that recently developed functionals are able to accurately predict lattice constants for hybrid layered materials. Our calculations also highlight

the impact of the lattice constants on calculated observables like the exfoliation energy and the fundamental gap, and demonstrate that care must be taken in including van der Waals corrections in these challenging systems.

Finally, with ab initio many-body perturbation theory we predict the structure and spectroscopic properties of Zn-MFU-4l including electron-hole interactions and accounting for zero-point vibrational effects, and show how modifications to the anion in the framework can reduce both the fundamental gap and the optical gap, and we provide an explanation for previously seen trends in optical experiments on Zn-MFU-4l.

To my parents

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Acknowledgments

I can still remember my excitement about having gotten into grad school, which came after several weeks of rejection and dejection when I wondered if I would get in anywhere. It's funny to look back on how little I knew about condensed matter physics at the time, but even so, a course in solid state physics made me think it would be a fun field to learn more about. I knew little about what I wanted to do besides knowing that I wanted to do density functional theory calculations in solids. I am lucky that I ended up working with my advisor, Jeff Neaton, because his group studies such a wide range of materials and uses a wide range of methods, so that I've been able to learn about and develop interests for so many things that I hadn't even heard about when I started at Berkeley. I am very grateful for Jeff's mentorship and for his being open to helping us pursue our interests. I have learned a lot from Jeff about how to do research, how to think about what projects are worth investing time in, and how to collaborate with people from a range of different backgrounds.

The group dynamics have been great, and everyone has been so friendly, especially when I first joined the group. I am grateful that Jung-Hoon Lee, Florian Brown-Altvater, and Sebastian Reyes-Lillo were willing to help me out as I got started learning about metal-organic frameworks even though they had already left Berkeley. My office mate when I first joined, Sophie Weber, showed me a lot of kindness, helped me troubleshoot things in VASP, and helped me adjust to doing research in the group. Jonah Haber gave me a lot of his time explaining the fundamentals of DFT and many-body perturbation theory, and I'm grateful that he was so generous with his time and knowledge to share it with me and with so many other people who joined the group. He and Marina Filip were great companions to near daily trips to local restaurants for lunch in 2019, and also helped me get comfortable with the group. Stephanie Mack was such an important part of making the group fun to be in when I first joined, and has given me a lot of valuable advice. In these early, in person, times in the group, I also spent a lot of time learning from and explaining things to Will De Snoo and Eric Taw. We were all somewhat new, but had a great mix of complementary backgrounds that helped us get up to speed quickly. Eric had a few months advantage on us, and was invaluable in helping us understand MOFs.

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Among my friends, Josh Wakefield and Adam Black have had the largest impact on my grad school experience. Perhaps they are the reason I went to grad school in the first place,

since until I had met them, getting a Ph.D., not to mention in physics, wasn't on my radar since I had not known people who went that route. They have been great friends since my first days and weeks of college, and I have learned so much math and physics from them. I still think back fondly of our late nights doing physics homework until the early hours of the morning, of finding new places on campus to work from, and of anxiously preparing for exams and getting some of the most impressive equation sheets I have ever seen on a single piece of paper. I took solid state physics because Josh signed up for the course, and I thought his copy of Ashcroft and Mermin looked cool, so I signed up too, and learned about this field that I have come to find so interesting. Josh and Adam's passion for math encouraged me to take a full year of analysis rather than just taking the math methods course, and while I do not remember many proofs from it, I benefited a lot from taking a proof based math class that taught me a lot of skills that paid off in physics as well. (I still can not fully figure out why I took a full year of it though). I am glad that I have been able to stay in such close contact with Josh and Adam, and our shared experiences at our different grad programs have been helpful in navigating the experience. I am glad that we have been able to keep in contact with a good group of friends, also including Warren Mo and George Liu, who I always enjoy talking to, especially since they have experiences so outside math and physics research.

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Chapter 1

Introduction

Condensed matter physics [1] deals with a wide range of systems and phenomena, and it has played a tremendous role in contributing to the advances in technology of the last 100 years. In doing so, it has had a profound influence on society via transforming the way we work, communicate, and seek entertainment. Much of condensed matter physics investigates materials in the solid state. There is a long history of humans using naturally occurring materials like gemstones and metals for their aesthetics and also for tools. People managed to do incredible things in shaping and transmuting the materials nature gave them in giving rise to fields like mineralogy and metallurgy. As our technology and scientific understanding have improved, we have been able to build upon the long history of using materials to transform our society. The field of solid state physics has given us transistors, photovoltaics, batteries, and so much more. These advances in particular have helped improve our ability to do solid state physics: nowadays, computers are so much faster than they were during the early days of the digital computer that we can do numerical calculations simulating solids that yield a better understanding of what gives rise to their properties, guiding further research. Shortly after the dawn of quantum mechanics, physicists and chemists set the stage for studying the properties of electrons in solids with early work on model Hamiltonians and numerical calculations on simple enough systems for the computers at the time. Their tremendous effort led to insights into the problems of condensed matter physics of their day, and informed and guided the present numeric work that would have been impossible with the technology of earlier times.

This dissertation draws on modern computational condensed matter physics to calculate and understand the properties of metal-organic frameworks (MOFs) from first principles, that is from the quantum mechanics of their constituent electrons and nuclei. MOFs are a fascinating emerging class of crystalline materials composed of a lattice of metal complexes or nodes connected by organic linkers. Figures 1.1 and 1.2 show two example MOFs that we study. Figure 1.1 shows a MOF with ordered 1D periodic arrays of metal nodes that span the material, while Figure 1.2 shows a MOF that has isolated metal nodes that are 0D units. These two structures highlight how MOFs are an unusual sort of solid and motivate how they might be rationalized both in the context of organic gas-phase molecular systems

and of inorganic solid-state materials.

One application that has attracted much interest in MOFs is gas separations, which is reliant on gas adsorption, the process in which gas molecules bind to the surface of a material. There are many contexts in which such a process is useful. Our atmosphere is composed of many gas molecules, some of which can be harmful for the environment or for humans. Being able to selectively capture pollutants can enable a healthier environment and a higher quality of life. Other times, we want to capture gases like O_2 or N_2 or water for their industrial use. Capturing these gases in an energy-efficient manner could help improve our environment and lead to cheaper, more abundant, industrially useful gas separations. MOFs have the highest known internal surface area of any material, and they are a very diverse type of material, and outside of gas capture they are also studied for applications like energy storage, electronics, and optoelectronics. The fact that MOFs are highly tunable also makes them a unique platform for trying to probe the fundamental physics of correlated electron systems and magnetic systems.

In order to calculate the properties of these MOFs, we use first principles density functional theory (DFT) and many-body perturbation theory. With these two methods, we are able to calculate energetic, spectroscopic, and geometric observables of solids using the crystal structure and atomic types as input parameters. There are several approximations made, which are detailed in Chapter 2, but a key strength of these approaches is that they can be done with no (or in some cases minimal) empirical parameters or tuning. The lack of empiricism in the calculations enables us to attain deep understanding and to be predictive in cases where there have been no prior experiments, and it also allows the methods to be broadly applicable since they were not designed to be used on one specific MOF.

In this dissertation, we use DFT and many-body perturbation theory to study metal-organic frameworks that are being explored for gas adsorption and for optoelectronics. These methods will be explained in more detail in Chapter 2. Our work is carried out in close collaboration with experimentalists who synthesize and characterize the materials that we study. There are many challenges in carrying out first principles calculations for MOFs. MOFs have complex geometries with many atoms and large unit cells, making them computationally demanding for state of the art methods. In addition to the computational cost, MOFs can be difficult to characterize experimentally. Their properties are sensitive to their atomic-scale geometry, so structural determination is an important way that first principles methods can improve our understanding of how MOFs function. MOFs are an interesting class of materials to model because a range of different methods and levels of theory are required. First principles methods that can accurately calculate the ground state properties like total energies and optimize atomic positions are valuable for studying the relationship between the structure of the MOF and its properties, while ab-initio excited state methods are needed to understand the optical spectroscopy of the materials. More recently, machine learning and neural network interatomic potentials fit to first principles methods have also been used for these systems. Additionally, finite temperature effects can be important, whether they are reducing the band gap, determining the kinetics of gas adsorption, or modifying gas adsorption energies. Lattice models are useful in understanding the statistical mechanics of

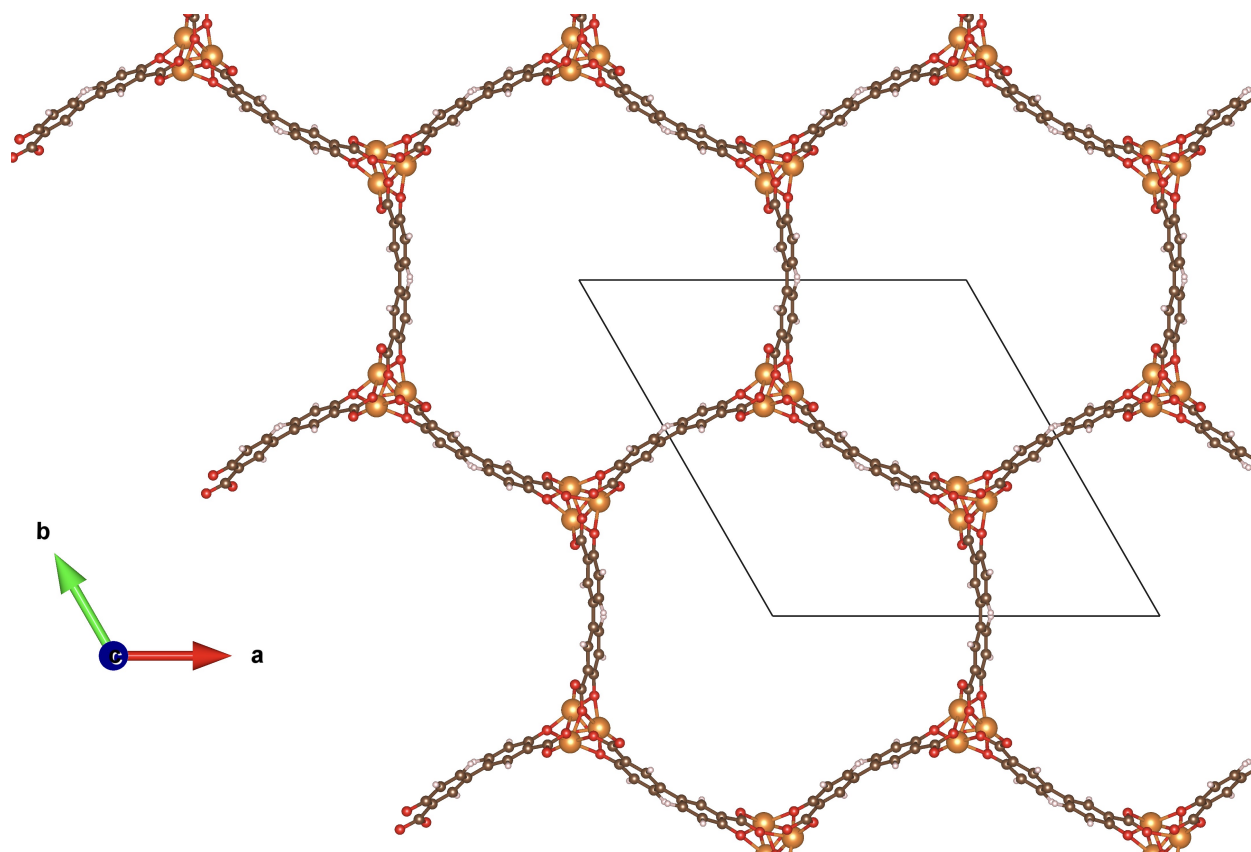


Figure 1.1: Supercell of $\text{Mg}_2(\text{dobpdc})$, also referred to as MOF-274. This MOF has hexagonal pores which are good for allowing gases to flow through. Additionally, the Mg sites are exposed, so they can bind gas molecules or functional groups. Mg - Orange, C - Brown, O - Red, H - White

MOFs in cases where an atomistic level of modeling would be impossible. This dissertation is organized as follows. After reviewing the methods that we use in Chapter 2, in Chapter 3, we discuss a study of SO_2 adsorption in a metal-organic framework which is synthesized to selectively bind CO_2 . SO_2 is present in some flue gas streams, and it can degrade the CO_2 capture if it competes with CO_2 at a molecular scale for binding sites. Experiments found that depending on how the MOF is functionalized, the uptake of CO_2 could be greatly hindered, or it could be relatively robust to SO_2 exposure. The calculations discussed in Chapter 3 detail our efforts to understand how SO_2 bound in different versions of the MOF. We calculate NMR chemical shifts for different candidate geometries, and compare them with experimental chemical shifts. We are able to show that the best performing functionalization involved the SO_2 binding in the pore of the MOF, rather than at the metal site where the CO_2 binds, explaining the degradation in performance relative to cases where the

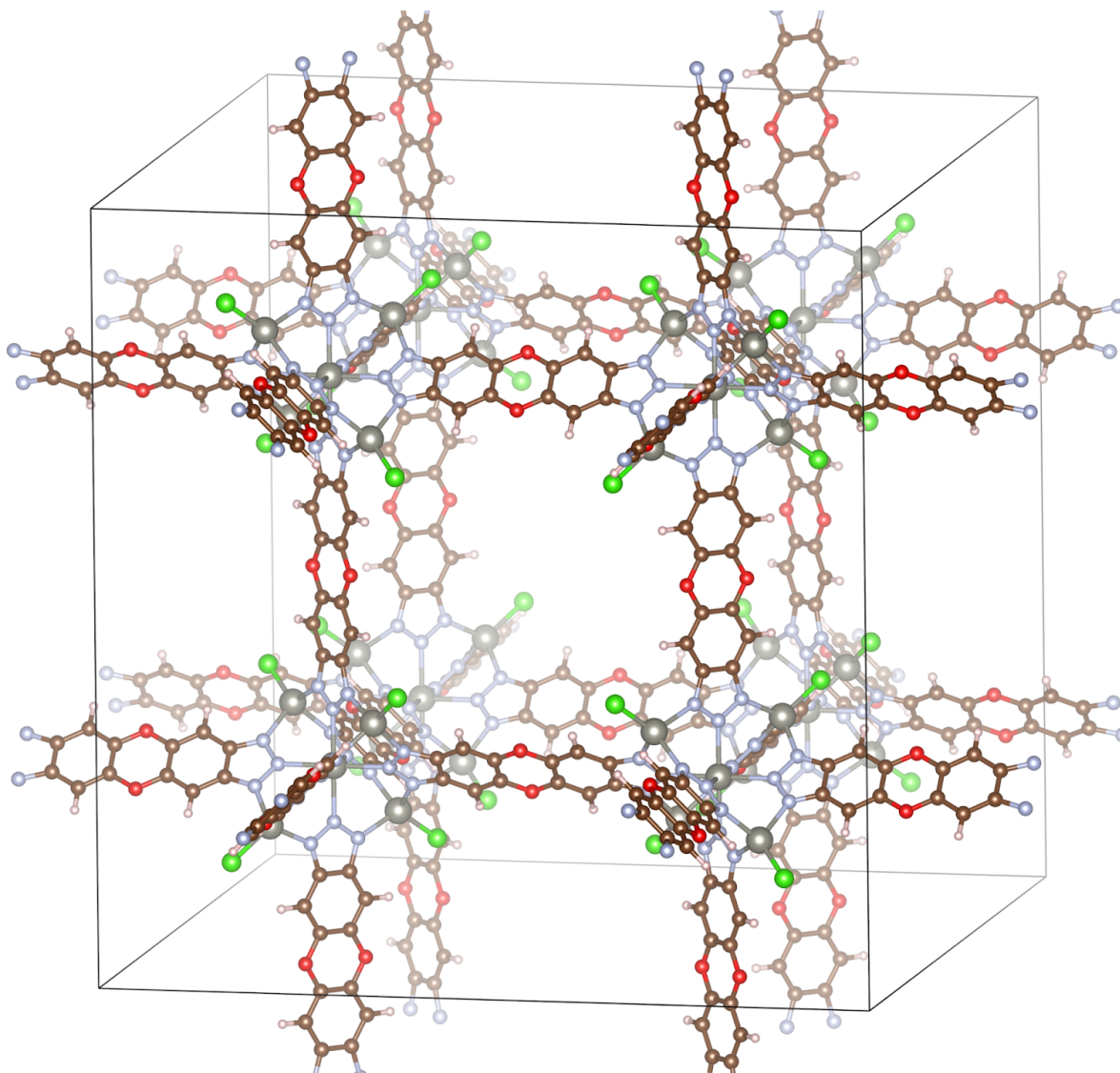


Figure 1.2: Supercell of ZnCl-MFU-4L. This MOF is studied for gas adsorption and for its optical properties. Zn -Grey, N - Light Blue, Cl - Green, C - Brown, O - Red, H - White

SO₂ preferred to insert where the CO₂ binds.

In Chapter 4, we discuss calculations of O₂ binding in a family of MOFs that is promising for O₂ capture. Comparing our first principles calculations with periodic boundary conditions calculations with those of finite clusters, we showed that DFT methods can accurately capture trends in O₂ binding seen experimentally both for periodic systems and clusters, and we predicted modifications to these MOFs that could improve O₂ uptake performance.

In Chapter 5, we introduce a statistical mechanics model that can capture the step-like isotherms and isobars in a MOF which cooperatively captures CO₂. This cooperative adsorption entails the adsorption of CO₂ to one binding site in the MOF that facilitates the adsorption of CO₂ to a neighboring site. While previous work [2] showed that a simple lattice model could be used to rationalize trends in the CO₂ adsorption isotherms and isobars, experimentally, it has been shown that isotherms and isobars can be more complicated and they can have multiple steps, they can be defect tolerant, and they can be tuned via a mixture of the amine groups which functionalize the MOF. Here, we extend prior statistical mechanics models and, using parameters taken from prior experiments and DFT calculations [2], show that double steps can be understood via steric hindrance between chains of CO₂, that cooperativity is defect tolerant, and that mixtures of amines behave like their average in the case of small clusters, and that large amine clusters give rise to double steps.

In Chapter 6, we study van der Waals interactions in layered MOFs and perovskites. van der Waals interactions are difficult to capture in DFT since most common approximations for the exchange-correlation energy are generally local or semi-local, so nonlocal correlations like the van der Waals interaction are not included. While different approaches for incorporating van der Waals interactions into exchange-correlation functionals have been developed, they can vary in their efficacy, depending on the material. van der Waals interactions are particularly important in layered solids because in the direction perpendicular to their layers they are weakly bound. While prior work [3–6] has studied van der Waals interactions in layered solids exfoliatable into 2D materials, here we focus on less studied systems, layered MOFs and layered hybrid organic-inorganic perovskites. These systems have strongly bonded metal-halide nodes, organic subunits, and substantial void space. They also have more complicated chemistries and geometries than standard layered solids like graphite or hexagonal boron nitride. Our work identifies the approximations for the van der Waals interaction in DFT that perform best for these systems. We also show how the lattice parameters impact the calculation of exfoliation energies and band gaps in these systems.

In Chapter 7, we use ab-initio many-body perturbation theory to compute the spectroscopic properties of a family of MOF which has attracted recent interest for white light emission [7]. Experimental work showed that the emission wavelength of these MOFs could be modified by changing the anion from Cl to Br to I [7]. These color changes were not associated with a change in the band gap or the optical absorption onset. Considering a range of different anions, we predict that while changing halides will not affect the optical absorption onset, introducing small organic anions can reduce the optical gap of the system. We provide an atomistic explanation for the previously observed phenomena, and predict modifications that could yield an even larger diversity of behavior than has already been

seen.

Finally, we conclude this dissertation with an outlook on future directions of this work.

Chapter 2

First Principles Electronic Structure Methods

2.1 Introduction

In this chapter, we review the theory underlying the first principles electronic structure methods used in this work. First principles calculations concern the non-empirical approximate solution to the many-electron Hamiltonian of a multi-electron atom, molecule, or solid. Most of this dissertation uses such electronic structure methods to calculate geometries and experimental observables for metal-organic frameworks. These calculations provide understanding by computing quantities inaccessible to experiments, help explain experimental results, and motivate future experiments by predicting properties of hypothetical materials. First principles theory is widely used in molecular and solid state systems to calculate their ground state and excited state properties. The calculations in this dissertation primarily use three codes that implement density functional theory (DFT) and ab-initio many body perturbation theory. VASP [8–10] and Quantum Espresso [11–13] are DFT codes used to calculate ground state properties like energies and forces, and BerkeleyGW [14–16] is a many body perturbation theory and Green’s function based code that is used to calculate excited state properties like electron removal energies and optical spectra. The documentation for those codes provides lots of background information on the numerical implementation of these theories, and also the theoretical background underpinning the work. The purpose of this chapter is to provide background on fundamental aspects of the underlying theory that are used in the rest of the dissertation, and to highlight important approximations that are made that can impact the results. Along the way, we briefly discuss some important fundamentals of solid state physics. There are many great books on these topics; some that I have found particularly useful include Kittel’s *Introduction to Solid State Physics* [17], Cohen and Louie’s *Fundamentals of Condensed Matter Physics* [18], Mattuck’s *A Guide to Feynman Diagrams in the Many-body Problem* [19], Martin’s *Electronic Structure* [20] and *Interacting Electrons* [21], Giustino’s *Materials Modelling using Density Functional Theory: Properties*

and Predictions [22], Fetter and Walecka's *Quantum Theory of Many-Particle Systems* [23], and Mahan's *Many-particle Physics* [24].

2.2 Many-electron Hamiltonian for Solids

The nuclei and electrons that make up a solid give rise to the wide diversity of phenomena solids demonstrate. Because the nuclei are much heavier than the electrons, typically one makes the Born-Oppenheimer approximation and considers the nuclear and electronic degrees of freedom separately. In this approximation, one treats the nuclei as having fixed coordinates, and then solves the quantum mechanical problem of the electrons separately. One gets an electronic Hamiltonian that is a function of the nuclear positions, $\vec{R}$, giving a time-independent Schrödinger equation that depends parametrically on the nuclear coordinates:

$$H(\vec{R})\Psi(\vec{r}, \vec{R}) = E(\vec{R})\Psi(\vec{r}, \vec{R}). \quad (2.1)$$

The electronic Hamiltonian has a term for the electron kinetic energy, and terms from the potential energy of the nuclei with the electrons, and the potential energy of the electrons interacting with each other,

$$V(\vec{r}_1, \vec{r}_2)_{e-e} = \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}, \quad (2.2)$$

where e is the charge of the electron. Over the past 100 years, many methods have been developed to tackle the challenges imposed by the electron-electron interaction. We will introduce the primary method used in solids, density functional theory (DFT) [25, 26]. In molecules, some other methods, such as Möller-Plesset Perturbation theory [27], coupled-cluster theory [28–30], and configuration interaction [31] are commonly used, but they are not used in this work. We will also discuss many-body perturbation theory [32], an excited-state Green's function based formalism that we use to calculate the band gap and optical properties of solids.

2.3 Kohn-Sham Density Functional Theory for Ground State Properties

Density functional theory approaches the many electron problem by finding the ground state electron density directly, without needing the wave function. It is commonly used in the Kohn-Sham framework in which the interacting electron problem is mapped to an auxiliary problem of non-interacting electrons that can be more easily solved. In practice we end up with a non-interacting Schrödinger equation which is similar in form to the Hartree-Fock equation, except it is interpreted as the single particle Schrödinger equation for an auxiliary

system whose ground state electron density and energy equal the true ground state electron density and energy, rather than the Hartree-Fock equation which arises from minimizing the energy with respect to a trial wave function. Following Ref [18], the Kohn-Sham Hamiltonian [26] can be written:

$$\left(\frac{-\hbar^2}{2m} \nabla^2 + V_{\text{ion}} + V_H + V_{xc} \right) \phi_i = \epsilon_i \phi_i, \quad (2.3)$$

where, ϕ_i are the single particle orbitals with single particle energies ϵ_i , and the fully interacting electron density, ρ , is given by

$$\rho(\vec{r}) = -e \sum_i |\phi_i(\vec{r})|^2 \quad (2.4)$$

where the sum runs over occupied states and $-e$ is the charge of an electron. The Hartree potential can therefore be expressed in terms of the density:

$$V_H(\vec{r}) = e^2 \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}', \quad (2.5)$$

V_{ion} is the electron-ion interaction, and

$$V_{xc}(\vec{r}) = \frac{\delta E_{xc}}{\delta \rho(\vec{r})} \quad (2.6)$$

is the functional derivative of the exchange-correlation energy.

The mapping between energy and density is based on the Hohenberg-Kohn theorems [25]. The Hohenberg-Kohn theorems allow one to formulate the interacting electron problem in terms of the density rather than the more complicated many-body wave-function. They state that for a system in an external potential, $v(\vec{r})$, which can be the potential from the ions in the case of a solid, the ground state energy can be written as

$$E_v[\rho] = \int v(\vec{r}) \rho(\vec{r}) d\vec{r} + F[\rho], \quad (2.7)$$

where $F[\rho]$ is a universal functional which does not depend on $v(\vec{r})$. The ground state energy, $E_v[\rho]$, is minimized for the ground state density of the interacting electron system. In the Kohn-Sham formalism, this ρ can be found from the single-particle orbitals of some auxiliary one-electron system that satisfies eqn. (2.3). This auxiliary system has energy given by

$$E_v[\rho] = \int v(\vec{r}) \rho(\vec{r}) d\vec{r} + T_s[\rho] + \frac{e^2}{2} \int \frac{\rho(\vec{r}) \rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' + E_{xc}[\rho]. \quad (2.8)$$

The exchange-correlation functional, $E_{xc}[\rho]$, is not known, so in practice, it is commonly approximated using numerically exact results from model systems. Typically, real physical

systems are best described by exchange-correlation energy approximations if the physical system is reasonably similar to the model system. For example, one of the most common early approximations for the exchange-correlation energy is the local density approximation (LDA) [33]. The local density approximation uses the uniform electron gas (UEG) as a model system with exchange and correlation energies that can be calculated exactly using numerical methods [34] and they lead to efficient parameterization schemes [33].

The uniform electron gas is a system which has the same electron density at all points in space, and a neutralizing background charge. While a molecule or solid may seem different from an electron gas, this approximation can end up being accurate, especially in solids, because in some simple solids the charge density is more slowly varying than isolated atoms. In the LDA the exchange-correlation energy just depends on the electron density at each point:

$$E_{xc,LDA} = \int \rho(\vec{r}) E_{UEG}(\rho(\vec{r})) d\vec{r}. \quad (2.9)$$

At each point in space, one assumes that the exchange-correlation energy coming from the charge density at that point equals the exchange-correlation energy of the uniform electron gas. The UEG has an exchange potential which can be written in a simple form,

$$v_x(\rho(\vec{r})) = \frac{-e^2}{\pi} (3\pi^2)^{1/2} \rho(\vec{r})^{1/3}. \quad (2.10)$$

The correlation potential, on the other hand, is more complicated, and different parameterizations are used, for example Perdew-Zunger [33], which uses numerically exact results from the UEG [34].

A natural extension of the local density approximation is to consider the exchange-correlation energy of a slowly varying electron gas instead. Generalized gradient approximations (GGAs) [35] depends on both the electron density and the gradient of the electron density. Similarly, one could consider high order derivatives of the electron density or the kinetic energy, but in practice, usually one stops at the GGA, or a meta-GGA [36].

The Hartree-Fock term has a spurious interaction of an electron with itself that is present in the Hartree potential. In Hartree-Fock, Fock exchange exactly cancels this self-interaction. In DFT, by contrast, rather than using Fock exchange (or exact exchange), one uses a local or semi-local approximation for the exchange energy. Thus, the self-interaction is no longer exactly cancelled. One natural way to try to deal with this issue would be to replace the approximate exchange with exact exchange. Such an approximation would be Hartree-Fock with an approximate correlation energy, and the Kohn-Sham equations would have an E_{xc} of the form:

$$E_{xc} = E_{x,HF} + E_{c,GGA} \quad (2.11)$$

with Fock exchange and semi-local correlation from a GGA. Empirically, such a functional does not perform well [37, 38], and instead most functionals which include exact exchange

(called hybrid functionals) either only include some fraction of exact exchange and some fraction of local or semi-local exchange [38], or they have the Coulomb potential screened by an error-function in the exchange term [39, 40]. A part of the success of the LDA compared with Hartree-Fock with LDA correlation is typically attributed to cancellation of errors. While there is some error in the local approximation to the exchange energy, it ends up getting in part cancelled by the error in the local approximation to the correlation energy. Thus, when one instead includes exact exchange, the cancellation of error is removed and the functional performs worse. A hybrid functional has an exchange-correlation energy like

$$E_{xc} = \alpha E_{x,HF} + (1 - \alpha) E_{x,GGA} + E_{c,GGA} \quad (2.12)$$

where α specifies the fraction of exact exchange used. Typical values for α range from 10-30% which empirically tends to lead to a good balance of exchange and correlation. See Ref. [38] for a discussion of why these values tend to work. Calculating exact exchange in solids is computationally demanding, so often hybrid functionals are not used.

In d- or f-electron systems, one can instead use a Hubbard U value to recover some of the physics of exact exchange at lower computational cost. The Hubbard U approach incorporates electron-electron interactions for those orbitals where its effect is largest: orbitals that are localized and located on the same atomic site. Valence d- and f-electrons are more localized than s and p electrons, so a Hubbard U is more commonly applied to them. The Hubbard U interaction adds a term $U_i N_{i,\uparrow} N_{i,\downarrow}$ to the energy of the system for the states i that are most strongly interacting (typically d states). The N_i are the number operators for up and down electrons, so this U_i penalizes double occupancy of orbitals. Often U_i is taken to be the same for all of the orbitals. This interaction only affects a subset of the states, but because it affects the charge density of these electrons, it indirectly modifies the electron density of the whole system via self-consistent cycles. Because the spin-state of the d-electrons depends on the difference in the exchange energy and crystal field splitting, larger values of U tend to stabilize high spin states, while lower values of U will be more likely to favor low spin states. We can see this since the U value penalizes double occupancy of the up and down orbitals of one of the electrons.

A final shortcoming of many approximations for the exchange-correlation energy is the neglect of non-local van der Waals (vdW) interactions [41, 42]. In a local or semi-local approximation, the only long range interactions that are included are those in the Hartree term. van der Waals interactions are non-local contributions to the correlation energy due to induced dipole moments in the system. At lowest order, they go like $1/R^6$ for neutral atoms, so one approach for including them is to take an LDA or GGA functional, and add a pairwise $1/R^6$ interaction which is parameterized for different types of atoms and a damping term to avoid double counting energy contributions at short distances. Such approaches are the D2 [43] or D3 methods [44, 45]. These are often successful in many solids where vdW interactions are important, such as layered solids and metal-organic frameworks

Another approach to including vdW interactions is to modify the correlation energy so that it takes into account correlations between two points in space that are well separated

[41, 42]. Such an approximation is used in the vdW-DF functionals [4, 6, 41, 46–52] and the VV10 functionals [53], and involves the addition of a non-local correlation functional,

$$E_c = \frac{1}{2} \int d\vec{r} d\vec{r}' \rho(\vec{r}) \rho(\vec{r}') \Phi[\rho](\vec{r}, \vec{r}'), \quad (2.13)$$

where $\Phi[\rho](\vec{r}, \vec{r}')$ is the non-local vdW kernel which describes the correlation energy between points $\vec{r}$ and $\vec{r}'$. The kernel Φ can be shown to have the form

$$\Phi[\rho](\vec{r}, \vec{r}') = \frac{-3}{\pi} \int_0^\infty du \frac{1}{\omega[\rho](\vec{r})^2 + u^2} \frac{1}{\omega[\rho](\vec{r}')^2 + u^2} \frac{f[\rho](|\vec{r} - \vec{r}'|, u)^2}{|\vec{r} - \vec{r}'|^6} \quad (2.14)$$

which can be derived by evaluating the energy of coupled harmonic oscillators at $\vec{r}$ and $\vec{r}'$ (see Ref [42] for more information). There are many different ways to parameterize these functionals which involve choice of ω and f . Two common approaches include the VV10 approach and the vdW-DF family.

These functionals have different parameterizations for the $\omega[\rho](\vec{r})^2$:

$$\omega[\rho](\vec{r})^2 = \frac{4\pi}{3} \rho + C \left| \frac{\nabla n}{n} \right|^4 \quad (2.15)$$

for VV10 [54] and

$$\omega[\rho](\vec{r})^2 = 4\pi^2 \left(\epsilon_{xc}^{LDA}(\rho) + Z \left| \frac{\nabla}{n^{7/6}} \right|^2 \right)^4 \quad (2.16)$$

for the vdW-DF functionals.¹ The function f has a more complicated form, and can be found in reference for the two methods. One can parameterize the parameters C and Z in these functionals by using model systems which interact with the vdW interaction, or by fitting the parameters empirically. These functionals greatly improve the performance of DFT calculations on the energies and geometries of systems that have significant van der Waals interactions. In Chapter 6 we will see an example of the greatly improved performance upon including vdW interactions for layered solids, and improvements on the original VV10 and vdW-DF functionals have made non-local vdW interactions even more quantitatively accurate than they were in the original implementations.

One important practical point in the numerical implementation of DFT and also other electronic structure methods is the choice of basis set to represent the wave functions and operators being computed. In this dissertation, we primarily study periodic solids. A periodic solid can be represented by a unit cell with a finite number of atoms that is infinitely repeated. The unit cell is represented with lattice vectors, $\vec{a}_1, \vec{a}_2$, and $\vec{a}_3$, and within each unit cell, the nuclei are located by a set of vectors, $\vec{\tau}_i$. Translation by

$$\vec{R}_{a,b,c} = a\vec{a}_1 + b\vec{a}_2 + c\vec{a}_3, \text{ with } a, b, c \in \mathbb{N} \quad (2.17)$$

¹Although of the many vdW-DF functionals, some have modifications to this form.

(and with $\vec{a}_1, \vec{a}_2$, and $\vec{a}_3$ not all in the same plane) yields an identical place in another cell. Because of periodicity, we can calculate the properties of a macroscopic material like diamond with a unit cell that only has two atoms. Reciprocal space plays an important role in periodic systems. Reciprocal lattice vectors satisfy

$$\vec{G}_{a,b,c} \cdot \vec{R}_{a,b,c} = 2\pi n, n \in \mathbb{N}. \quad (2.18)$$

Functions which have the periodicity of the lattice, meaning $f(\vec{r}) = f(\vec{r} + \vec{R}_{a,b,c})$, can be expressed in a Fourier sum over the reciprocal lattice vectors:

$$f(\vec{r}) = \sum_{a,b,c} c_{a,b,c} e^{i\vec{G}_{a,b,c} \cdot \vec{r}}. \quad (2.19)$$

Bloch's theorem is an important result for wave functions in periodic potentials which says that such wave functions can be written as

$$\Psi_{\vec{k}}(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} u_{\vec{k}}(\vec{r}) \quad \text{with } u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r} + \vec{R}_{a,b,c}). \quad (2.20)$$

The function $u_{\vec{k}}(\vec{r})$ has the periodicity of the lattice, and translating $\Psi_{\vec{k}}$ by a $\vec{R}_{a,b,c}$ incurs a phase of $e^{i\vec{k} \cdot \vec{R}_{a,b,c}}$. The $u_{\vec{k}}(\vec{r})$ can be expanded in a Fourier sum over the reciprocal lattice vectors:

$$u_{\vec{k}}(\vec{r}) = \sum_{\vec{G}} C_{\vec{k},\vec{G}} e^{i(\vec{k} + \vec{G}) \cdot \vec{r}}. \quad (2.21)$$

In practice, one chooses a discrete grid of points to sample reciprocal space. Integrals over the first Brillouin zone

$$\int f(\vec{k}) d\vec{k} \quad (2.22)$$

are instead written as a sum

$$\frac{1}{N} \sum_{\vec{k}_i} f(\vec{k}_i) \quad (2.23)$$

where N is the number of points sampled, and $\vec{k}_i$ are the grid points chosen, typically a uniformly spaced grid. Often, one can reduce the number of grid points due to the crystal having spacegroup symmetries. The number of points needed to converge the sum is an important parameter in periodic boundary condition calculations. One must increase the number of points until the quantity of interest (often the total energy) is converged to within some threshold.

Many periodic boundary condition DFT codes also use a plane wave basis set, as in eqn. (2.21). One chooses a cutoff point in the magnitude of $\vec{G}$ vectors that enter in the expansion

so that the sum involves a finite number of basis functions. This cutoff is another important convergence parameter, and one must increase the cutoff value until whatever quantity one is calculating is converged. Such a basis is computationally convenient, because it makes evaluating some of the matrix elements of the Hamiltonian very efficient. Plane waves are also a complete basis, and can be made systematically more accurate by increasing the cutoff value.

One drawback of plane waves is that wave functions that are highly localized or have high frequency oscillations in real space (like those for the core electrons) require very high cutoff values for the plane wave expansion. Pseudopotentials are used to address this issue and allow smaller sized basis sets to be used. One typically makes the frozen core approximation in which some electrons are treated as core electrons whose density will not change in the calculation. These core densities are taken from all electron calculations on isolated atoms. Additionally, these all electron calculations are done to find the effective potential (the pseudopotential) of the valence electrons coming from the protons in the nucleus and the core electrons. Pseudopotentials can be transferable, and there are many publicly available pseudopotentials for most of the atoms on the periodic table, and they are typically transferable between different systems with the same types of atoms. These two approximations both reduce the number of electrons that have to be included in the calculation, and also allow for a smaller plane wave basis set. All of the electrons can be included in solids, although such calculations typically include a different basis set. Calculations with Gaussian orbitals [55–57] can better capture localized states near the nucleus, and they tend to need fewer basis functions, so the number of basis functions per electron can be lower. The full potential LAPW method [58, 59] uses a mixed basis set where the core electrons are treated with a set of localized basis functions, and the valence electrons are treated with plane waves. Ref. [60] compares the accuracy with these different approximations, and finds that while full potential LAPW tend to be the most accurate, the other approaches are able to get similar quality results with a lower cost.

In later sections of the introduction, we will discuss how the outputs of density functional theory calculations, the charge-density, total energies, and Kohn-Sham states can be used to calculate a range of quantities of interest for electronic systems.

2.4 Ab-initio Many body perturbation theory

Many body perturbation theory [32] is another formalism for solving the electronic structure problem. In principle, one can use it to calculate the charge density and ground state of an electronic system, but it is most often used for calculating the excited state properties of a system. The two main excited state properties that we calculate are the fundamental gap, and the optical absorption spectrum. The fundamental gap is the difference between the lowest unoccupied and highest occupied states in the system. Optical absorption can occur below the fundamental gap due to excitonic effects, which are discussed later. The GW method allows one to calculate the fundamental gap, and the Bethe-Salpeter equation (BSE)

allows one to calculate the impact of excitonic effects and leads to an optical absorption spectrum. Refs. [15, 16, 21] detail these methods and their practical implementations. We will briefly discuss the formalisms, and highlight some key points associated with their practical use in solids.

Hedin's Equations

We follow the treatment of many body perturbation theory in Refs. [21] and [18]. The single particle Green's function is one of the central quantities of many body perturbation theory. It is defined by

$$G(\vec{r}_1, t_1; \vec{r}_2, t_2) = -i \langle 0 | T [\psi(\vec{r}_1, t_1) \psi(\vec{r}_2, t_2)^\dagger] | 0 \rangle \quad (2.24)$$

where $|0\rangle$ is the exact ground state wave function, T is the time ordering operator, and $\psi(\vec{r}, t)$ destroys a particle at $\vec{r}$ and time t while $\psi(\vec{r}, t)^\dagger$ creates a particle at $\vec{r}$ and time t . The single particle Green's function, G , can be calculated from a non-interacting Green's function, G_0 , with Dyson's equation:

$$G = G_0 + G_0 \Sigma G. \quad (2.25)$$

Σ is the self-energy, which is the central quantity that we are interested in calculating. The non-interacting Green's function can be written as

$$G_0(\vec{r}, \vec{r}', \omega) = \sum_{n, \vec{k}} \frac{\phi_{n\vec{k}}^*(\vec{r}) \phi_{n\vec{k}}(\vec{r}')}{\omega - E_{n, \vec{k}}}. \quad (2.26)$$

The poles of G_0 equal the non-interacting particle energies. In this work, we use the Kohn-Sham eigensystem from DFT calculations for the non-interacting particle energies. If we Fourier transform to the time domain, we get that

$$G_0(\vec{r}, \vec{r}', t) = \sum_{n, \vec{k}} \phi_{n\vec{k}}^*(\vec{r}) \phi_{n\vec{k}}(\vec{r}') e^{-iE_{n, \vec{k}} t} \quad (2.27)$$

where $t = t_2 - t_1$ since our system is invariant under time translation. This expression is reminiscent of the time evolution from elementary quantum mechanics, where there's an $e^{-iEt/\hbar}$ phase factor for the eigenstates of the time-independent Schrödinger equation. These non-interacting particles have infinite lifetime because the exponential is not damped. When we go from G_0 to G , we can get both a shift in the energy levels, which comes from the real part of Σ , and a finite lifetime, which comes from the imaginary part of Σ . One can see these changes from Dyson's equation which gives:

$$G \sim (\omega - E_{n, \vec{k}} - \Sigma)^{-1} \quad (2.28)$$

so that the time domain G goes like

$$G \sim e^{-i(E_{n,\vec{k}} + \text{Re}[\Sigma])t - \text{Im}[\Sigma]t} \quad (2.29)$$

which has a finite lifetime and a quasiparticle energy renormalized by the real part of the self-energy. The GW method is based on Hedin's equations [32], which is a set of self-consistent equations for the interacting Green's function. They are

$$\Sigma_{xc}(1, 2) = iG(1, \bar{4})W(1^+, \bar{3})\Gamma(\bar{4}, 2; \bar{3}) \quad (2.30)$$

$$W(1, 2) = V_c(1, 2) + V_c(1, \bar{3})P(\bar{3}, \bar{4})W(\bar{4}, 2) \quad (2.31)$$

$$P(1, 2) = -iG(1, \bar{3})G(\bar{4}, 1)\Gamma(\bar{3}, \bar{4}; 2) \quad (2.32)$$

$$G(1, 2) = G_0(1, 2) + G_0(1, \bar{3})\Sigma(\bar{3}, \bar{4})G(\bar{4}, 2). \quad (2.33)$$

There is an additional equation for Γ , but we do not reproduce it here because vertex corrections (non-trivial terms in Γ) will be neglected. We use the notation of Ref. [21] where $\bar{X}$ indicates that a variable is integrated against, and the variables X in each of these equations stands for spatial, spin, and time coordinates (for example, $1 = (\sigma_1, x_1, y_1, z_1, t_1)$). W is the screened Coulomb interaction, V_c is the bare Coulomb interaction, P is the irreducible polarizability, and Γ is set to a δ function in the GW approximation, which gets its name from the approximation for the self-energy:

$$\Sigma = iGW. \quad (2.34)$$

This expression corresponds to the first term of an expansion of Σ in W . The screened Coulomb interaction is a key component of Hedin's equations. In solids, screening can be somewhat large, so that the screened Coulomb interaction is a good deal weaker than the bare Coulomb interaction. They are related by

$$W = \epsilon^{-1}V_c \quad (2.35)$$

$$\epsilon^{-1} = 1 - V_c P \quad (2.36)$$

$$(2.37)$$

V_c is the Coulomb interaction, given by eqn (2.2). Common semiconductors can have macroscopic dielectric constants of around 10. Because W is weaker than V_c , an expansion in W is a good alternative to an expansion in V_c for perturbation theory.

The GW Approximation in Practice

In the GW approximation, the Green's function, G , and the screened Coulomb interaction, W , are taken from the initial DFT calculation and are typically not updated with self-consistent cycles in what is called a G_0W_0 calculation. GW is currently the best performing method that is commonly used for the calculation of the fundamental gaps in solids. We can write the Fock exchange contribution to the self-energy as

$$\Sigma_X = iGV_c$$

where V_c is the bare Coulomb interaction. Thus, we can see that GW includes the exchange self-energy and the screening contributes to the correlation component of the self-energy.

In order to perform a GW calculation, one first does a DFT calculation to get Kohn-Sham wave-functions, $\phi_{n,\vec{k}}$ and eigenvalues, $E_{n,\vec{k}}$. These can be used to compute the polarizability within the random phase approximation (RPA),

$$P(\vec{r}, \vec{r}', \omega) = \sum_{ij} (f_i - f_j) \frac{\phi_i^*(\vec{r}) \phi_j(\vec{r}) \phi_j^*(\vec{r}') \phi_i(\vec{r}')}{\epsilon_i - \epsilon_j + \hbar\omega + i\hbar\alpha}. \quad (2.38)$$

This sum is over occupied and unoccupied states, and f is the Fermi-Dirac occupation function evaluated at energy ϵ_i . An important convergence parameter is the number of empty states that are used, which requires doing a DFT calculation with many empty states, and then calculating the dielectric function. From P , one can calculate the dielectric function with:

$$\epsilon = 1 - V_c P. \quad (2.39)$$

Then, one constructs the screened Coulomb interaction, W_0 , with

$$W_0 = \epsilon^{-1} V_c, \quad (2.40)$$

where $\epsilon^{-1} = \epsilon^{-1}(\vec{q}, \omega)$ is a matrix. The non-interacting Green's function, G_0 is given by

$$G_0(\vec{r}, \vec{r}', \omega) = \sum_{n,\vec{k}} \frac{\phi_{n\vec{k}}^*(\vec{r}) \phi_{n\vec{k}}(\vec{r}')}{\omega - E_{n,\vec{k}}}, \quad (2.41)$$

and then by calculating the convolution of G_0 and W_0 , one gets the self energy, $\Sigma(\omega)$. Dyson's equation gives us a Schrödinger like equation, with the self-energy replacing V_{xc} from the DFT Kohn-Sham equations:

$$\left(\frac{-\hbar^2}{2m} \nabla^2 + V_{\text{ion}} + V_H + \Sigma(E_i^{QP}) \right) \phi_i^{QP} = \epsilon_i^{QP} \phi_i^{QP}. \quad (2.42)$$

We can then compute the quasiparticle energy via first-order perturbation theory as:

$$E_i^{QP} = E_i^{MF} - \langle \phi_i | \Sigma(E) - \Sigma(E)^{MF} | \phi_i \rangle \quad (2.43)$$

where $\Sigma(E)^{MF}$ is taken to be V_{xc} for DFT starting points. We use BerkeleyGW [14] for our GW calculations, and more implementation details can be found in Ref. [14]. Note that the DFT wave functions and eigenvalues enter into our expressions for P and Σ , so that different functionals might produce different results. For example, over/under-estimating the fundamental gap at the DFT level can lead to less/more screening in P by making the denominator smaller in the case of over estimation and larger in the case of under-estimation,

which will impact W and Σ . There has been recent work trying to either improve the starting point [40, 61] or to do self-consistent GW calculations that do not depend on the starting point [62–65]. In addition to the number of empty states in the calculation of P being an important convergence parameter, one must also check convergence with respect to the plane wave cutoff and k-grid in the wave functions, the cutoff kinetic energy for the vectors, $\vec{G}$, that are the basis for ϵ in reciprocal space, and the number of bands summed over in the self-energy evaluation.

The ab-initio Bethe-Salpeter Equation approach for solids

After an electron from the valence band is excited to the conduction band, it can interact with the positively charged hole that it left behind. This interaction between opposite charges is screened by the other electrons and is attractive, so the optical gap is lower than the band gap. Here we will discuss the inclusion of electron-hole interactions in computing two-particle neutral excitations using the Bethe-Salpeter equation (BSE) [16, 66–70]. The BSE can be written in reciprocal space as

$$(E_{c\vec{k}} - E_{v\vec{k}})A_{v\vec{k}}^S + \sum_{v'c'\vec{k}'} \langle v\vec{k} | K^{eh} | v'c'\vec{k}' \rangle A_{v\vec{k}}^S = \Omega^S A_{v\vec{k}}^S. \quad (2.44)$$

In the Tamm-Dancoff approximation to the BSE, $E_{c\vec{k}}$ and $E_{v\vec{k}}$ are the GW-corrected quasi-particle energies of conduction band and valence band states, $A_{v\vec{k}}^S$ is the exciton wave-function, Ω^S is the exciton energy for the excitonic state $|S\rangle$, and K^{eh} is the electron-hole kernel which is composed of a bare exchange and statically-screened direct interaction. Without the electron-hole kernel, one gets the independent particle eigenstates which just have eigenvalues equal to the difference of the quasiparticle states. Solving this eigenvalue problem yields a set of eigenvalues and eigenvectors that represent the excitonic states of the system. Important convergence parameters for the BSE are similar to those of GW calculations, but also include the number of bands used to expand the excitonic wave function. These include some number of bands above and below the valence band maximum, and one must ensure that the absorption spectrum is converged with respect to the number of bands chosen.

Using these, we can calculate the imaginary part of the dielectric function, ϵ_2 which is related to the optical absorption coefficient, η , as follows

$$\epsilon_2 = 2nk \quad (2.45)$$

$$\eta = \frac{2\omega k}{c} = \frac{\omega \epsilon_2}{2nc} \quad (2.46)$$

$$(2.47)$$

where n and k come from the complex index of refraction,

$$N = n + ik = \sqrt{\epsilon_1 + i\epsilon_2}. \quad (2.48)$$

The imaginary part of the dielectric function, ϵ_2 , can be evaluated without excitonic effects

$$\epsilon_2(\omega) = \frac{16\pi^2 e^2}{\omega^2} \sum_{v\vec{k}} |\vec{e} \cdot \langle v\vec{k} | \vec{v} | c\vec{k} \rangle|^2 \delta(\omega - E_{c\vec{k}} + E_{v\vec{k}}) \quad (2.49)$$

or with excitonic effects

$$\epsilon_2(\omega) = \frac{16\pi^2 e^2}{\omega^2} \sum_S |\vec{e} \cdot \langle 0 | \vec{v} | S \rangle|^2 \delta(\omega - \Omega_S). \quad (2.50)$$

2.5 Observables of Interest

Electronic structure theory calculations are used for a variety of purposes. One common use of electronic structure theory is trying to understand experimental results. For these cases, being able to calculate observables from experimental characterization techniques can be helpful for identifying what part of the system is responsible for the experimental signal. Another common use is trying to predict properties of materials that haven't yet been synthesized. In this work, we use DFT and many-body perturbation theory to calculate ground state geometries, binding energies of adsorbed molecules, phonon frequencies, fundamental gaps, and optical absorption spectra. For these calculations, one must first determine what sort of geometry the hypothetical material might have² and then if it has the desired properties. The fundamental quantities that one gets out of a DFT calculation are the ground state charge density and energy. Additionally, one gets a mean field single particle eigensystem, the Kohn-Sham (KS) states; while these KS wave-functions don't rigorously correspond to the quasiparticle states in the system, they are typically close enough for them to be useful for G_0W_0 calculations or density functional perturbation theory [71–73] calculations (called DFPT). From these computed quantities, one gets access to a wide range of properties. The forces on the ions are related to the derivative of the total energy with respect to atomic displacements. The Hellman-Feynman theorem allows one to calculate these forces using the ground state expectation value of the derivative of the Hamiltonian with respect to displacements of the nuclear coordinates [22, 73]. Thus, one can calculate forces on ions using DFT calculations. Using the forces, one can find the DFT predicted most stable geometry by using a gradient descent minimization algorithm, perform molecular dynamics calculations at finite temperature, and calculate the phonon frequencies and eigenvectors using the derivative of the forces.

Using the phonon frequencies, one can calculate the IR and Raman spectra as well [18, 22]. These spectroscopic techniques depend on the Born effective charges, $Z_{\alpha ij}^*$, and the static

²Typically one also wants to estimate how likely such a material is to be stable and synthesizable, although the latter is often difficult.

Raman tensor, $\mathcal{R}_{ijk\alpha}$, which can be formulated as partial derivatives of the total energy, E :

$$Z_{\alpha ij}^* = \frac{\partial^2 E}{\partial \mathcal{E}_i \partial R_{\alpha j}} \quad (2.51)$$

$$\mathcal{R}_{ijk\alpha} = \frac{\partial Z_{\alpha jk}}{\partial \mathcal{E}_i} \quad (2.52)$$

where $\mathcal{E}_i$ is an electric field in direction i , and $R_{\alpha j}$ is a displacement of atom α in the j direction. These quantities can be computed via finite-differences, or with DFPT.

Nuclear magnetic resonance (NMR) is another spectroscopic technique that one can calculate using DFT [74–76]. It involves calculating the response of the electrons to an external magnetic field, and DFPT can be used to calculate the induced current from the magnetic field, which allows one to find the NMR chemical shift.

Phonons in Solids

Phonons are collective excitations of lattice vibrations in a material and they can be understood to lowest order as arising out of a harmonic approximation for the potential energy of a crystal. Higher order terms beyond the harmonic approximation, called anharmonic effects, are important for properties like thermal expansion, thermal transport, and other properties, but we will limit our discussion to harmonic phonons.

We will follow Cohen and Louie [18] in the discussion of phonons. We first assume the Born-Oppenheimer approximation, in which we assume that the wave-function of the electronic and nuclear components of the system can be separated because the electronic degrees of freedom respond very quickly to changes in the nuclear positions. When we Taylor expand the Hamiltonian of the ionic degrees of freedom about the equilibrium positions of the ions, we get

$$U = U_0 + \frac{1}{2} \sum_{n,\alpha,n',\alpha'} \frac{\partial^2 U}{\partial \xi_n^\alpha \partial \xi_{n'}^{\alpha'}} \xi_n^\alpha \xi_{n'}^{\alpha'} \quad (2.53)$$

to lowest non-zero order. Here, we have used $\alpha = x, y, z$ to give the Cartesian directions the atom is displaced in, while n is a composite index for the l, j pair that denotes the cell and atom within that cell. We denote the crystal lattice with lattice vectors $\vec{a}_1, \vec{a}_2, \vec{a}_3$. We write the origin of the unit cell as

$$\vec{R}_l^0 = a\vec{a}_1 + b\vec{a}_2 + c\vec{a}_3 \text{ for } a, b, c \in \mathbb{Z}. \quad (2.54)$$

We let $\vec{\tau}_j^0$ be the equilibrium position of the j th ion in the unit cell. Then, we write the equilibrium positions of all of the atoms in the crystal as

$$\vec{R}_{l,j}^0 = \vec{R}_l^0 + \vec{\tau}_j^0. \quad (2.55)$$

Displacement away from these equilibrium positions is denoted by $\vec{\xi}_{l,j}(t)$, so that we write the time dependent positions of the ions as

$$\vec{R}_{l,j}(t) = \vec{R}_{l,j}^0 + \vec{\xi}_{l,j}(t). \quad (2.56)$$

Each of these configurations $\vec{R}_{l,j}$ has an associated potential energy, $U(\vec{R}_{l,j})$, that can be computed using a DFT calculations, for example. At equilibrium, the forces on each ion, given by the first derivative, $\frac{\partial U}{\partial \xi_{lj}} = 0$, for all of the atomic displacements ξ_{lj} .

We can calculate these second derivatives in DFT using finite differences [22, 77] or DFPT [71–73]. Our calculations use the finite differences approach, in which the second derivatives are calculating by manually displacing each of the atoms a small amount, calculating the forces in the displaced geometries, and then using the definition of the derivative to calculate the second derivative. It is very important to converge total energies to a high precision since the second derivatives involve very small differences in total energies, so we need our numerical accuracy to be high. After we have the force constants, we can find the phonon frequencies and eigenvalues by diagonalizing the dynamical matrix, which is a matrix of the force constants in the solid Fourier transformed to reciprocal space and divided by the square root of the product of the mass of the two atoms that component describes the coupling between.

Useful quantities can be calculated from the phonons, such as the zero point and thermal energy and the phonon specific heat. As in the case of the quantum harmonic oscillator, we can write the phonon Hamiltonian in terms of creation and annihilation operators like

$$H_{\text{ph}} = \sum_{\lambda \vec{q}} \hbar \omega_{\lambda \vec{q}} \left(a_{\lambda \vec{q}}^\dagger a_{\lambda \vec{q}} + \frac{1}{2} \right) \quad (2.57)$$

where we have phonon eigenvalues $\omega_{\lambda \vec{q}}$ for phonon branch λ (which run from 1 to $3N$ at wavevector $\vec{q}$). With this form of the Hamiltonian, we can see that in the harmonic approximation, the phonon system is a system of non-interacting vibrational modes. We can calculate the zero point energy just as we would for the simple quantum harmonic oscillator:

$$E_{\text{ZPE}} = \langle 0 | H_{\text{ph}} | 0 \rangle \quad (2.58)$$

where $|0\rangle$ is the ground state of the phonon system which has occupation 0. As in the quantum harmonic oscillator, we get $\frac{1}{2}\hbar\omega$ per mode:

$$E_{\text{ZPE}} = \frac{1}{2} \sum_{\lambda \vec{q}} \hbar \omega_{\lambda \vec{q}}. \quad (2.59)$$

Phonons are bosons, so their thermal occupations can be determined using the Bose-Einstein distribution:

$$\langle n(E, T) \rangle = \frac{1}{e^{\frac{E}{k_B T}} - 1} \quad (2.60)$$

where $\langle n(E, T) \rangle$ is the occupation number of a state with energy E at temperature T and k_B is Boltzmann's constant. Thus, to find the thermal energy, we need to find the energy of a system with $\langle n(\hbar\omega_{\lambda, \vec{q}}, T) \rangle$. The thermal energy for such a state is

$$E_{\text{TE}} = \sum_{\lambda \vec{q}} \langle n(\hbar\omega_{\lambda, \vec{q}}, T) \rangle \hbar\omega_{\lambda \vec{q}}, \quad (2.61)$$

where the ZPE has been subtracted away so we get the energy just from the thermal motion. Similarly, one can find the heat capacity using $\frac{\partial U}{\partial T}$ at constant volume or pressure with $U = E_{\text{ZPE}} + E_{\text{TE}}$.

Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) is an experimental technique that can probe the chemical environment of the atoms and molecular species in a sample. In NMR, one studies which frequencies of an applied magnetic field causes the nuclear spins to flip. These frequencies are sensitive to the type of nucleus and its environment. An external magnetic field induces an electronic current around an atom which creates its own magnetic field that opposes the external field, so that the NMR experiment is sensitive to the electron density around each nuclei. Thus, different chemical species will give rise to different external fields which can excite the nuclear spins. The chemical shift, which is defined by

$$\delta = \frac{\nu - \nu_{\text{ref}}}{\nu_{\text{ref}}} \quad (2.62)$$

expresses the resonance frequency of the nuclei in the sample relative to some reference compound. The referencing is done so that comparisons can be made across different experimental set ups. δ is the observable that we are interested in calculating using density functional theory so that we can compare chemical shifts from computationally determined geometries with experimental chemical shifts. Refs. [74–76] discuss the calculation of NMR chemical shifts with DFPT. Here, we will sketch some of the key steps. In order to calculate δ , we need to calculate the chemical shielding tensor, σ_{ij} , which is defined as

$$B_j^{\text{in}} = -\sigma_{ij} B_i. \quad (2.63)$$

This tensor relates the applied magnetic field and the magnetic field that it induces from the electronic motion. Then, the chemical shift is given by

$$\delta_{ij} = \sigma_{ij}^{\text{ref}} - \sigma_{ij} \quad (2.64)$$

where each of these quantities are evaluated at each of the nuclear positions and σ_{ij}^{ref} is the calculated reference chemical shielding tensor for that specific nuclei. We can calculate the induced magnetic field using equations that are familiar from classical electrodynamics:

$$\vec{B}_{\text{ind}}(\vec{r}) = \frac{1}{c} \int d^3 \vec{r}' \vec{J}_{\text{ind}}(\vec{r}') \times \frac{\vec{r} - \vec{r}'}{|\vec{r} - \vec{r}'|^3} \quad (2.65)$$

where c is the speed of light. This induced magnetic field depends only on the induced current, $\vec{J}_{\text{ind}}$, which we can calculate from DFPT. We need to calculate the expectation value of the current operator,

$$\vec{J}_{\text{ind}}(\vec{r}) = \vec{J}_p(\vec{r}) + \vec{J}_d(\vec{r}) \quad (2.66)$$

$$\vec{J}_p(\vec{r}) = -\frac{\vec{p}|\vec{r}\rangle\langle\vec{r}| + |\vec{r}\rangle\langle\vec{r}|\vec{p}}{2} \quad (2.67)$$

$$\vec{J}_d(\vec{r}) = -\frac{A\vec{r}}{c}|\vec{r}\rangle\langle\vec{r}|, \quad (2.68)$$

in the presence of the perturbing magnetic field. $\vec{J}_p$ and $\vec{J}_d$ are the paramagnetic and diamagnetic current operators, respectively. Both terms can be generated via of the quantum mechanical probability current operator which is

$$\vec{J} = \frac{1}{2}(\psi^*\vec{v}\psi + \psi\vec{v}\psi^*) \quad (2.69)$$

with the velocity operator given by $\vec{v} = \vec{p} - \frac{q}{c}\vec{A}$ in an external magnetic field, $|\vec{r}\rangle$ is a position eigenfunction with $\langle\vec{r}|\psi\rangle = \psi(\vec{r})$, and ψ is a Kohn-Sham state. $\vec{A}$ is the vector potential, which can be written as

$$\vec{A} = \vec{B} \times \vec{r}. \quad (2.70)$$

Calculating the induced current with DFPT involves computing the first order change in the Kohn-Sham states due to the external magnetic field and then evaluating the expectation value of these current operators.

The output from such a calculation is the chemical shielding tensor. The NMR experiment captures the isotropic part of the chemical shielding tensor, so we calculate the chemical shift by taking the trace of the chemical shielding tensor, and then subtracting that value from a reference value. There can be some subtleties involved in the referencing. For example, our work involves C^{13} chemical shift calculations. The C^{13} reference is the molecular crystal adamantane. Adamantane rotates a lot on the experimental time scale, so the NMR signal gets averaged across the different chemical environments. One way around this issue is to do an NMR experiment on a system that has many carbon environments which do not have such averaging, find these peaks relative to that of adamantane, then do a DFT calculation on the system with many carbon environments. The cocaine molecule, $\text{C}_{17}\text{H}_{21}\text{NO}_4$ happens to have many different C environments, so it was chosen experimentally. DFT calculations on cocaine were done previously [78]. By plotting the DFT chemical shifts for cocaine vs. the experimental chemical shifts for cocaine, a linear fit can extract the adamantane reference shift value as the y-intercept (because that is the point where the cocaine chemical shift is 0). For N^{15} the glycine molecule can be used, and such referencing tricks are not needed. Important convergence parameters include the convergence criterion in the DFT total energies which must be more strict than typical ground state calculations because derivatives are taken, and the step size for the finite differences derivative in k-space used in the calculation.

Electron-Phonon Coupling

Electron-phonon coupling describes how electronic energy levels change with atomic distortions of the lattice. Electron-phonon coupling can be calculated with DFPT [71–73] or with frozen phonons [77]. Ref. [73] provides a comprehensive summary of first principles electron-phonon coupling calculations. In Chapter 7, we use electron-phonon calculations to compute the change in the Kohn-Sham and GW fundamental gaps in a MOF with strong electron-phonon coupling. We follow Refs. [18] and [73] to summarize key aspects of electron-phonon coupling. The potential that the electrons feel, $V(\vec{r})$, changes as the lattice vibrates. For small displacements, we can Taylor expand $V(\vec{r})$ around the equilibrium positions of the atoms, $\vec{R}_l^a$:

$$V(\vec{r}, t) \approx \sum_{l,a} \left[V_a(\vec{r} - \vec{R}_l^a) + \delta \vec{R}_l^a \cdot \nabla_{\vec{r}} V_a(\vec{r} - \vec{R}_l^a) \right] \quad (2.71)$$

The last term in the sum,

$$\sum_{l,a} \delta \vec{R}_l^a \cdot \nabla_{\vec{r}} V_a(\vec{r} - \vec{R}_l^a), \quad (2.72)$$

is the lowest order term in the electron-phonon interaction. We can use the representation of atomic displacements in terms of phonon creation and annihilation operators to write this expression as:

$$H_{\text{e-ph}} = \frac{1}{N_p} \sum_{\vec{k}, \vec{q}, mn\nu} g_{mn\nu}(\vec{k}, \vec{q}) c_{m\vec{k}+\vec{q}}^\dagger c_{n\vec{k}} (a_{\vec{q}\nu} + a_{-\vec{q}\nu}^\dagger) \quad (2.73)$$

where

$$g_{mn\nu}(\vec{k}, \vec{q}) = \left\langle u_{m\vec{k}+\vec{q}} \left| \frac{\partial V}{\partial \tau_{\vec{q}\nu}} \right| u_{n\vec{k}} \right\rangle \quad (2.74)$$

is the electron-phonon matrix element, $\tau_{\vec{q}\nu}$ is a displacement of phonon ν with wavevector $\vec{q}$, and $u_{n\vec{k}}$ are the cell-periodic parts of the Bloch states. It describes scattering from state $|u_{n\vec{k}}\rangle$ into state $|u_{m\vec{k}+\vec{q}}\rangle$ by the displacement $\tau_{\vec{q}\nu}$. $g_{mn\nu}$ can be calculated via DFPT [71–73] and by finite differences [77].

We are interested in electron-phonon coupling because of its impact on the fundamental band gap of a material. Electron-phonon coupling tends to decrease the band gap of a material. This result can be seen intuitively by a generic perturbation theory argument [73]. Consider a non-degenerate conduction band minimum with energy E_c . If we want to find the change to E_c with the inclusion of electron-phonon coupling, we would have an expression from standard perturbation theory like

$$\Delta E_c = \sum_{m \neq c} \frac{|\langle m | \frac{\partial V}{\partial \tau} | c \rangle|^2}{E_c - E_m}.$$

A similar argument to the valence band maximum with energy E_v gives

$$\Delta E_v = \sum_{m \neq c} \frac{|\langle m | \frac{\partial V}{\partial \tau} | v \rangle|^2}{E_v - E_m}.$$

E_c will be decreased because the sum over state $|m\rangle$ will have its largest contribution for nearby conduction band states which all have higher energies than E_c (valence band states are separated enough in energy that the energy denominator is small for them). Thus, the denominator will be negative for the conduction band states, while the numerator is non-negative, so that the conduction band energy will decrease. Similarly, E_v , will be increases because the largest contribution to the sum comes from valence band states that are close in energy to E_v , all of which are lower in energy than E_v , so that the denominator is positive for the largest contributions, so electron-phonon coupling will tend to increase the valence band energy. As a result, the valence band energies move up and the conduction band energies move down.

In our work, we calculate the impact of phonons on the band gap by freezing in phonon modes. This approach [77] is more economical for our large system size. It involves a Monte Carlo sampling of phonon displacements. We also use the “special displacement method” [79]. This approach is similar to Monte Carlo sampling except it only involves finding the band gap after one set of displacements. In the Monte Carlo approach, we calculate the phonon spectrum and then make 100 displacements of the atomic positions based on the phonon modes. See Ref. [77] for more discussion. Following that review article, we introduce Monte Carlo sampling for electron-phonon coupling. In this approach, we use Monte Carlo sampling to sum contributions to the expectation value of an operator, A , at some lattice temperature, T :

$$A(T) = \frac{1}{\mathcal{Z}} \sum_k \langle \chi_k(\vec{R}) | A(\vec{R}) | \chi_k(\vec{R}) \rangle e^{\frac{-E}{k_B T}}.$$

Here, χ_k are the nuclear wave-functions in the Born-Oppenheimer approximation, wherein it is assumed that the total nuclear and electronic wave-functions can be written as a product of nuclear and electronic wave-functions, and $\vec{R}$ represents all of the nuclear coordinates. We can evaluate this sum using Monte Carlo methods by first making the harmonic approximation, in which the nuclear wave-functions, χ_k , are replaced with the harmonic phonon wave-functions, $\Phi_{\nu, \vec{q}}(\vec{u})$. Then, $A(T)$ can be re-written as

$$A(T) = \frac{1}{\mathcal{Z}} \sum_{\nu, \vec{q}} \langle \Phi_{\nu, \vec{q}}(\vec{u}) | A(\vec{u}) | \Phi_{\nu, \vec{q}}(\vec{u}) \rangle e^{\frac{-E}{k_B T}}$$

or

$$A(T) = \int d\vec{u} |\Phi(\vec{u}, T)|^2 A(\vec{u}),$$

where

$$|\Phi(\vec{u}, T)\rangle|^2 = \Pi_{\nu, \vec{q}} \frac{e^{-u_{\nu, \vec{q}}/2\sigma_{\nu, \vec{q}}^2}}{\sqrt{2\pi\sigma_{\nu, \vec{q}}^2}(\vec{u})}$$

and

$$\sigma_{\nu, \vec{q}} = \frac{1}{2\omega_{\nu, \vec{q}}} \coth\left(\frac{\omega_{\nu, \vec{q}}}{2k_B T}\right).$$

Monte Carlo sampling is done by treating $|\Phi(\vec{u}, T)|^2$ as the probability distribution of the nuclear degrees of freedom, and the integral over the atomic displacements is replaced with a sum of N atomic displacements chosen to satisfy the distribution given by $|\Phi|^2$. We approximate

$$A(T) \approx \frac{1}{N} \sum_{n=1}^N A(\vec{u}_n),$$

and often 100-1000 samples are needed for convergence. Our work using Monte Carlo sampling is in Chapter 7.

Chapter 3

Understanding SO₂ Adsorption in dmpn-Mg₂(dobpdc)

3.1 Introduction

Diamine-appended MOFs, one of which is shown in Figure 3.1 have diamines bound to open metal sites in MOFs. In this study, we consider amines bound to Mg₂(dobpdc), shown in Figure 1.1. Early experiments [80] showed that appended diamines to Mg₂(dobpdc) led to step-shaped isotherms due to cooperative interactions between neighboring CO₂ binding sites along the c-axis of the MOF. These isotherms have a pressure at which the MOF goes from no CO₂ bound to full CO₂ bound in a narrow pressure swing. We study the dmpn- and e2-appended versions of Mg₂(dobpdc). Figures 3.2 and 3.3 show what the dmpn and e2 organic molecules look like when bound to the MOF. Many diamine-appended MOFs are able to capture CO₂ with step-shaped isotherms, and different diamines have been shown to modify the pressure at which the step occurs [81]. Another important aspect of the tunability of the functionalization of these MOFs is the ability to choose diamines that are able to capture CO₂ in the presence of other gas molecules, such as water and SO₂, which are present in the exhaust of coal-fired power plants. Experiments found that dmpn-Mg₂(dobpdc) was able to maintain its CO₂ capture performance in the presence of humid SO₂ much better than e2-Mg₂(dobpdc), but it was not well understood why the dmpn-appended framework performed better. Single crystals were not synthesizable after humid SO₂ exposure, so experimental methods were not able to provide insight into the binding geometries of the two frameworks after humid SO₂ exposure.

This work was a part of a collaboration with experimentalists who synthesized and characterized the MOF. That work is published in Ref. [82]. Parts of that work are reprinted with permission from J. Am. Chem. Soc. 2022, 144, 43, 19849–19860. Copyright 2022 American Chemical Society. Our collaborators had found that diamine-appended Mg₂(dobpdc) had different CO₂ adsorption performance after being exposed to SO₂. Figure 3.1 shows the unit cell with the dmpn diamine appended to Mg₂(dobpdc). SO₂ is present in the exhaust of

coal-fired power plants that $\text{dmpn-Mg}_2(\text{dobpdc})$ is well suited to capture CO_2 from, so performance after SO_2 exposure was an important metric to evaluate. They studied diamines **e2** and **dmpn**, which are shown in Figures 3.2 and 3.3. They found that after SO_2 exposure and subsequent heating of the material to remove the SO_2 , the maximum CO_2 uptake in these diamine-appended MOFs decreased from the original uptake to 77% for **dmpn** and 39% for **e2**. Because they were unable to get single crystals of these materials, and because there is significant disorder in the pore of the MOFs, they were unable to use x-ray diffraction to get a crystal structure to investigate why the CO_2 capacity was degraded. They had evidence that the amines were detaching from the MOF after SO_2 exposure: **dmpn** went from 98% loading to 89%, while **e2** went from 98% loading to 52% loading. In order to get an atomistic understanding of the differences in amine volatilization, we compared ^{15}N chemical shifts from NMR experiments and from DFT calculations to understand how the SO_2 was binding in these systems. NMR chemical shifts are sensitive to changes in the local chemical environment of the nitrogens on the diamines, and can inform whether the SO_2 coordinates with the nitrogen that was closer to the Mg site, or if it was closer to the nitrogen that was in the pore. We used a wide range of candidate binding geometries and SO_2 species, did DFT geometry optimizations, and then DFT chemical shift calculations to compare with experiments. We outline the generation of the geometries and the details of our DFT calculations in the next section. Since humid SO_2 was used experimentally, we considered products of H_2O and SO_2 . We considered SO_2 , HSO_3^- , and SO_3^{2-} . We found that the most stable product was HSO_3^- , and that for **dmpn**, the HSO_3^- coordinated with the amine group in the pore of the MOF, while for the other diamines, the HSO_3^- coordinated with the Mg and the amine group bound to the Mg. From these results, we could see that the **dmpn** was more stable after SO_2 exposure and then removal since the SO_2 exposure did not break the Mg-N bond that held the **dmpn** to the MOF. In contrast, for **e2** the Mg-N bond was disrupted by the SO_2 exposure, so that after the SO_2 was desorbed, some of the diamines were stripped away from the framework as well.

3.2 Methods and Candidate Geometry Generation

First-principles DFT calculations were performed to study the structures resulting from adsorption of humid SO_2 in $\text{dmpn-Mg}_2(\text{dobpdc})$ and $\text{e-2-Mg}_2(\text{dobpdc})$. The Vienna ab initio Simulation Package (VASP) code [8–10] was utilized with a plane-wave basis and projector augmented-wave (PAW) [83, 84] pseudopotentials. The van der Waals (vdW) dispersion interactions were accounted for by using the vdW-DF2 [47, 50, 51] exchange-correlation functional as implemented in VASP. All calculations used (i) a $1 \times 1 \times 4$ k-point grid, (ii) a 1000 eV plane-wave cutoff energy, and (iii) a 10^{-8} eV self-consistency convergence threshold in the total energy. Two valence electrons were explicitly treated for Mg ($3s^2$), 6 for O ($2s^2 2p^4$), 5 for N ($2s^2 2p^3$), 4 for C ($2s^2 2p^2$), and 1 for H ($1s^1$). All structural relaxations used a Gaussian smearing of electronic occupations of 0.05 eV [85]. Ions were relaxed until the Hellmann-Feynman forces were less than 0.01 eV/Å.

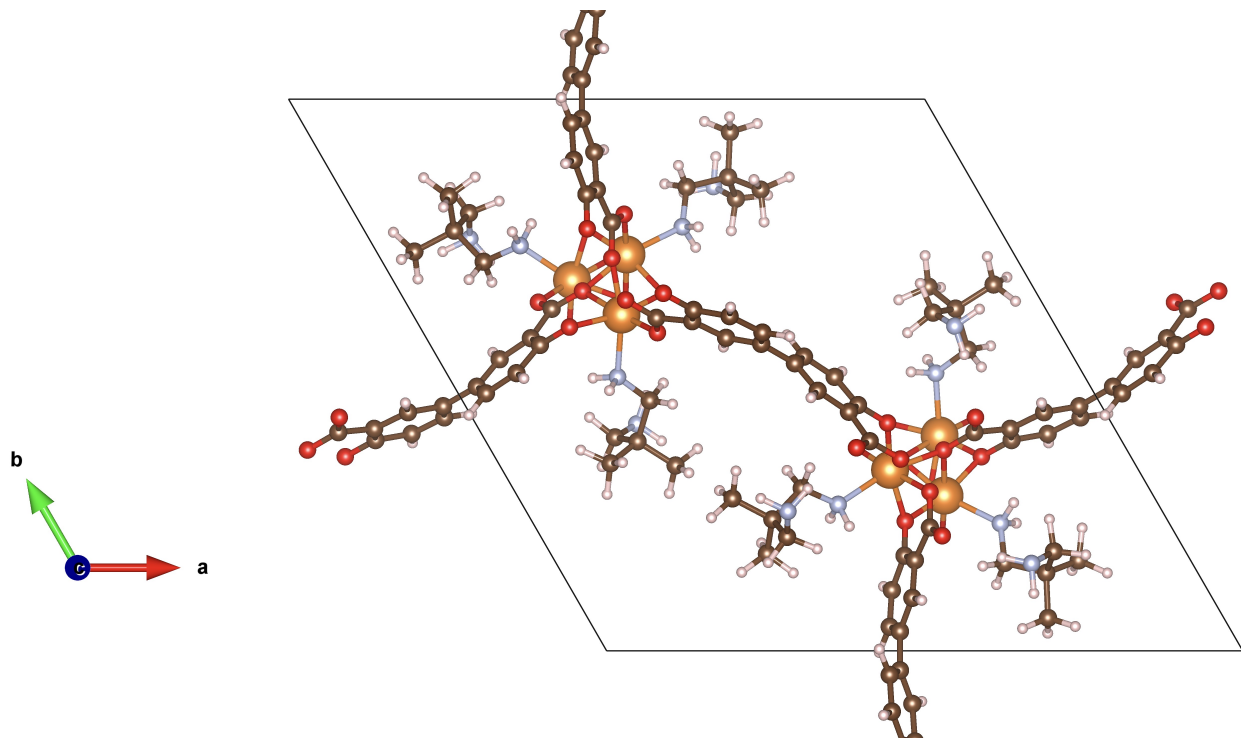


Figure 3.1: Unit cell of $\text{dmpn-Mg}_2(\text{dobpdc})$. Mg - Orange, N - Light Blue, C - Brown, O - Red, H - White

To compute SO_2 product binding energies (see Table 3.3), ionic and lattice relaxation on $\text{dmpn-Mg}_2(\text{dobpdc})$ ($E_{\text{dmpn-MOF}}$) and $\text{e-2-Mg}_2(\text{dobpdc})$ ($E_{\text{e2-MOF}}$) was first performed without any SO_2 products. These relaxations started from crystal structures taken from prior work [78]. The $\text{dmpn-Mg}_2(\text{dobpdc})$ structure came from a modified version of the structure for $\text{m-2-m-Zn}_2(\text{dobpdc})$ ($\text{m-2-m} = \text{N,N'-dimethylethylenediamine}$) [81] where the m-2-m diamine was replaced by dmpn and Zn^{2+} with Mg^{2+} . This modified starting structure, upon relaxation, has been shown to yield CO_2 binding energies and geometries for $\text{dmpn-Mg}_2(\text{dobpdc})$ that are in good agreement with experiment [78], and thus was chosen as a suitable starting structure for the calculations here. Structural relaxation of $\text{dmpn-Mg}_2(\text{dobpdc})$ was also performed with adsorbed HSO_3^- , SO_3^{2-} , or SO_2 ($E_{\text{dmpn-MOF-X}}$) and on $\text{e-2-Mg}_2(\text{dobpdc})$ with adsorbed HSO_3^- ($E_{\text{e2-MOF-HSO}_3^-}$). When charged species were adsorbed, the overall system was made neutral by adding hydrogens to the nitrogen that interacted with the charged small molecules. The energy of isolated gas-phase SO_2 (E_{SO_2}) and H_2O ($E_{\text{H}_2\text{O}}$) were also calculated by relaxing the species in the gas phase in a $15 \times 15 \times 15$ Åcell. All relaxations used the vdW-DF2 functional. Binding energies (E_B) were

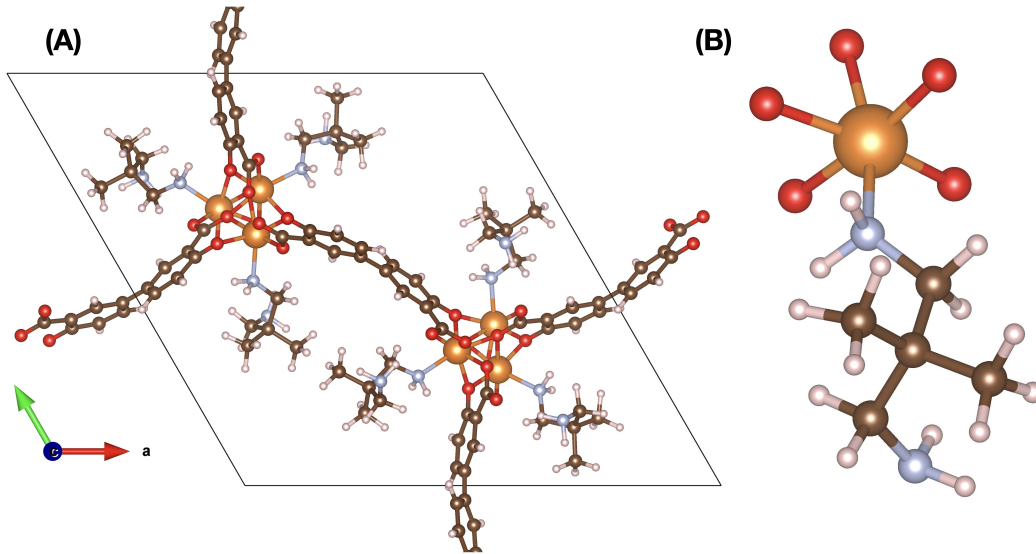


Figure 3.2: (A) Unit cell of $\text{dmpn-Mg}_2(\text{dobpdc})$ and (B) $\text{dmpn-Mg}_2(\text{dobpdc})$ with framework atoms removed for clarity. Mg - Orange, N - Light Blue, C - Brown, O - Red, H - White

computed by:

$$E_B = E_{\text{dmpn/e2-MOF-X}} - (E_{\text{dmpn/e2-MOF}} + E_{\text{SO}_2} + E_{\text{H}_2\text{O}}). \quad (3.1)$$

Isotropic NMR chemical shielding values (δ_{iso}) were computed using the linear response method of Yates, Pickard, and Mauri implemented in VASP [74–76] according to the following equation:

$$\delta_{\text{iso}} = -(\delta_{\text{iso-DFT}} - \delta_{\text{ref-DFT}}), \quad (3.2)$$

where $\delta_{\text{ref-DFT}}$ is a reference value from the ^{15}N DFT chemical shifts of glycine from prior work [78]. NMR chemical shifts were calculated using the vdW-DF2 functional with a vdW-DF2 relaxed structure. It was found that the NMR chemical shifts derived for the original cell

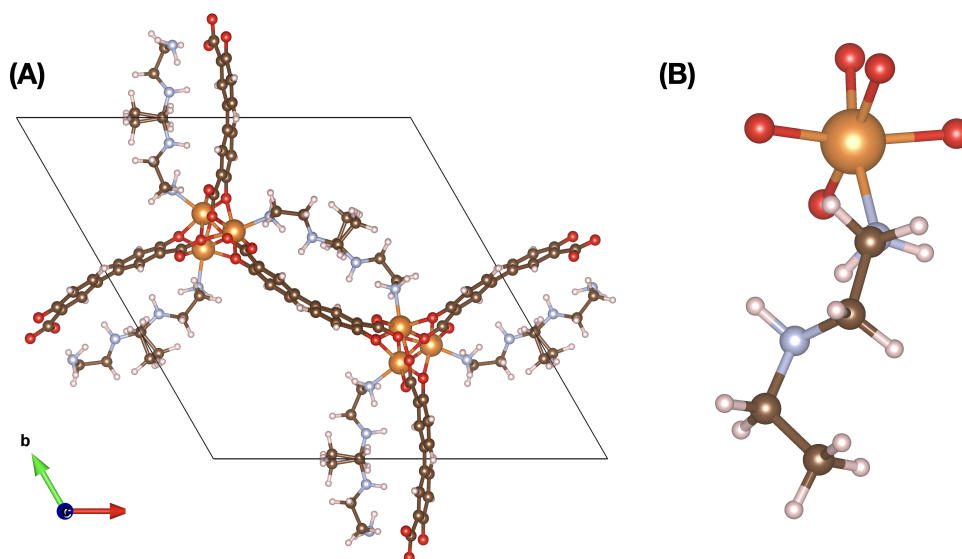


Figure 3.3: (A) Unit cell of $\text{e2-Mg}_2(\text{dobpdc})$ and (B) $\text{e2-Mg}_2(\text{dobpdc})$ with framework atoms removed for clarity. Mg - Orange, N - Light Blue, C - Brown, O - Red, H - White

volume of the $\text{m-2-m-Zn}_2(\text{dobpdc})$ structure modified to $\text{dmpn-Mg}_2(\text{dobpdc})$ were similar to those determined for the relaxed cell volume, and as such, the cell volume was not relaxed for any structures in the course of predicting the NMR chemical shifts to reduce computational time, an acceptable approximation.

To ensure that the chosen functional did not have a significant impact on predicted NMR chemical shifts, four sets of calculations were performed to determine the NMR chemical shifts, all starting from the vdW-DF2-relaxed HSO_3^- structure of $\text{dmpn-Mg}_2(\text{dobpdc})$. We also computed NMR shifts for the vdW-DF2 relaxed structure using the PBE exchange-correlation functional [35] for comparison. In the third and fourth calculations, the vdW-DF2 relaxed structure was used as the initial set of atomic positions for a PBE geometry optimization, and the resulting structure was subject to NMR calculations using vdW-DF2 or PBE, respectively. All PBE calculations used the reference ^{15}N shift of glycine, as was

used in the experimental ^{15}N spectra as well as prior work from prior work [78]. The results, presented in Figure 3.4, illustrate that the functional used to relax the structure or calculate the chemical shifts affects the calculated values by no more than ~ 3 ppm.

Additionally, symmetry was not enforced on these structures, so the diamine and HSO_3^- orientation may differ as a result of the six unique metal sites within the unit cell of the framework. As such, there are six distinct lines for each nitrogen in Figure 3.4. Independent of whether the structure was relaxed with PBE or vdW-DF2, the calculated chemical shifts for a given nitrogen atom differ by no more than 7 ppm if the same functional is used. Note that a typical error of 6.3 ppm between DFT-predicted and experimental ^{15}N shifts has been observed in previous studies on CO_2 adsorption in diamine- $\text{Mg}_2(\text{dobpdc})$ materials [78]. Overall, this analysis suggests that the choice of functional should not significantly affect the NMR chemical shifts calculated here, and that deviations in computationally predicted shifts are reasonable given with the previously observed error in these systems. All further calculations discussed below were carried out using the vdW-DF2 relaxed structures and vdW-DF2 to compute chemical shifts.

^{15}N NMR chemical shifts were calculated for several hypothetical structures formed upon humid SO_2 uptake in $\text{dmpn-Mg}_2(\text{dobpdc})$ with different binding modes. Figure 3.5 shows these geometries. See below for a discussion of how these geometries were generated.

While there are many local minima in the potential energy landscape of these geometries, we show in Figure 3.6 that the chemical shift depends more on the binding mode and species of SO_2 than it does on the exact geometry that is chosen since the chemical shifts for the pore and metal bound nitrogens are similar across all 5 of these different geometries. Thus, the NMR calculations are insensitive to small differences in the geometries, but are able to distinguish between different binding modes.

All candidate structures in Figure 3.7 for $\text{e-2-Mg}_2(\text{dobpdc})$ were generated by adding various SO_2 products to an initial diamine- $\text{Mg}_2(\text{dobpdc})$ geometry and subsequently relaxing the structure. See below for more details on the generation of these geometries

Generation of Candidate Geometries

Humid SO_2 leads to different possible species that could bind in the pore of the MOF. We considered a water + SO_2 product, HSO_3^- , and also the SO_2 molecule by itself interacting with the MOF. The geometries with HSO_3^- involved adding a hydrogen to the amine group closest to the HSO_3^- for charge balancing, and the SO_2 geometries involved inserting the SO_2 at different sites in the MOF. SO_3^{2-} is another possible speciation, but that would require a 2 : 1 SO_2 product : amine ratio, and experiments observed that there was a 1 : 1 ratio.

Single crystals of the SO_2 bound system couldn't be synthesized, so we had to use prior single crystal x-ray diffraction data from related systems to generate our geometries. The starting $\text{dmpn-Mg}_2(\text{dobpdc})$ structure was derived from the known structure of $\text{m-2-m-Zn}_2(\text{dobpdc})$ [81], by replacing m-2-m with dmpn and Zn^{2+} ions with Mg^{2+} ions [78]. Because we did not know how dmpn would orient itself in the pore of the MOF, we did initial molecular dynamics calculations to get a suitable initial geometry of the dmpn attached to the

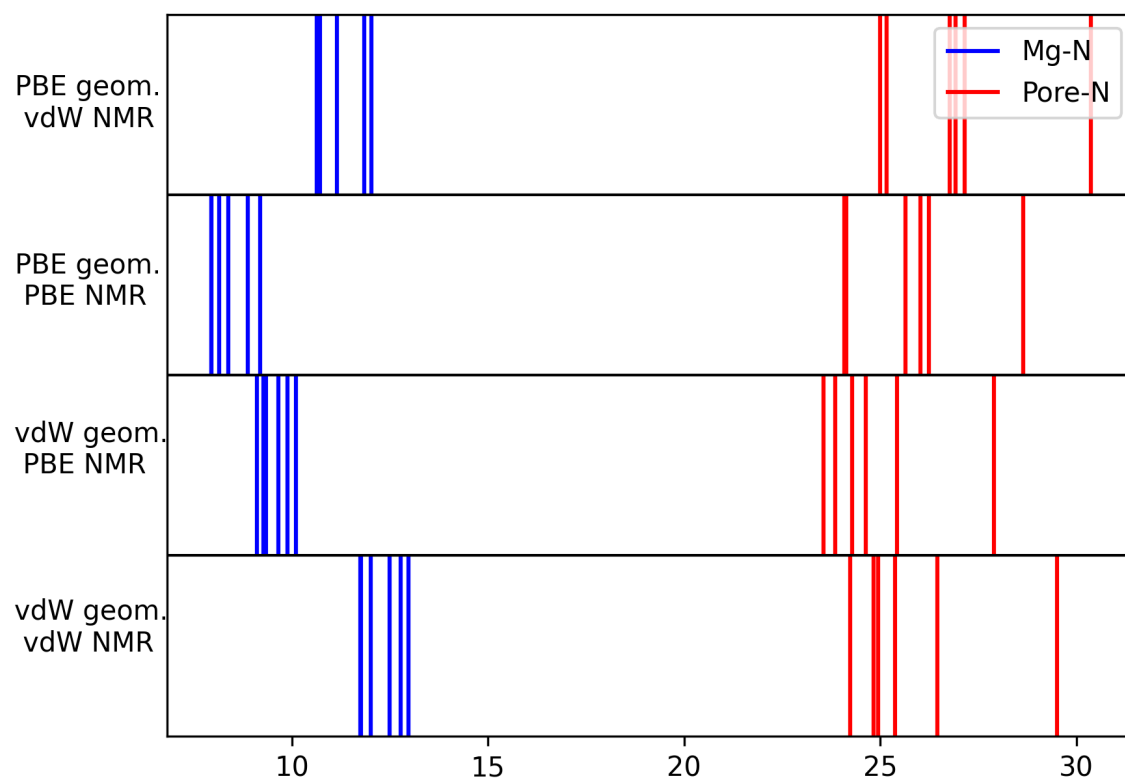


Figure 3.4: Chemical shifts calculated with PBE and vdW-DF2 functionals on PBE and vdW-DF2 relaxed geometries. For the same geometry, there's a slight difference when calculating the chemical shifts with vdW-DF2 or PBE. Similarly, there's a slight difference when using the same functional on the two different geometries. In any cases, the predicted chemical shifts are within a few ppm of each other for the same binding mode with either functional.

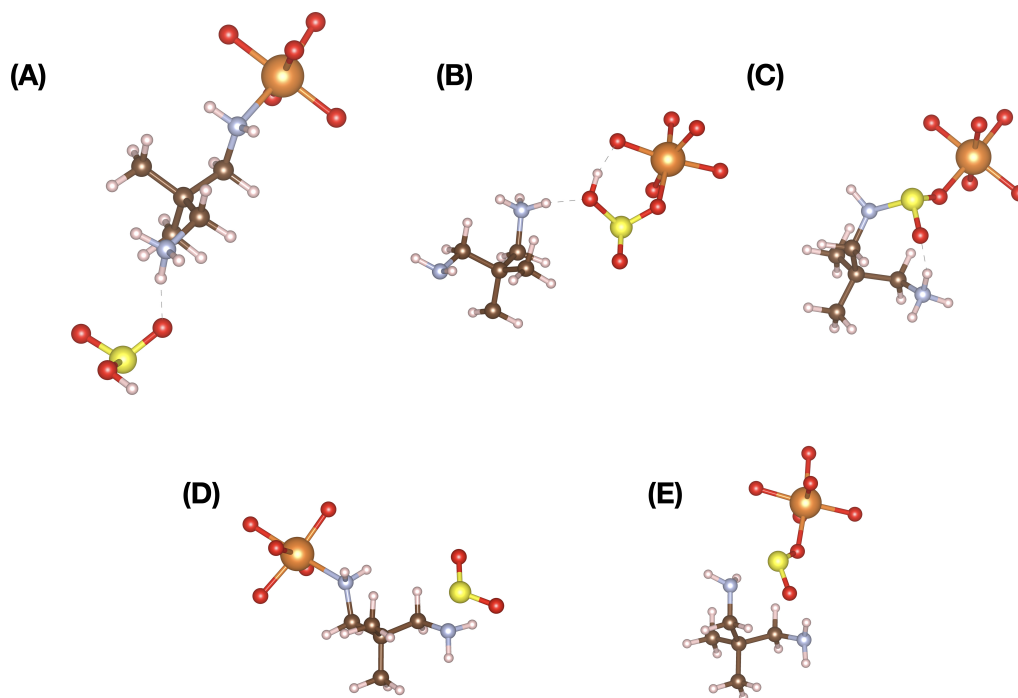


Figure 3.5: Fragment of DFT Relaxed Crystal Structures with $\text{dmpn-Mg}_2(\text{dobpdc})$ and (A) HSO_3^- coordinating with the pore nitrogen, (B) HSO_3^- coordinating with the metal nitrogen, (C) SO_2 bound to Mg with proton transfer from metal nitrogen to pore nitrogen an ammonium carbamate chain like geometry, (D) SO_2 in the pore of the framework, and (E) SO_2 bound to Mg. Framework atoms are removed for visual clarity. Mg - Orange, N - Light Blue, C - Brown, O - Red, S - Yellow, H - White

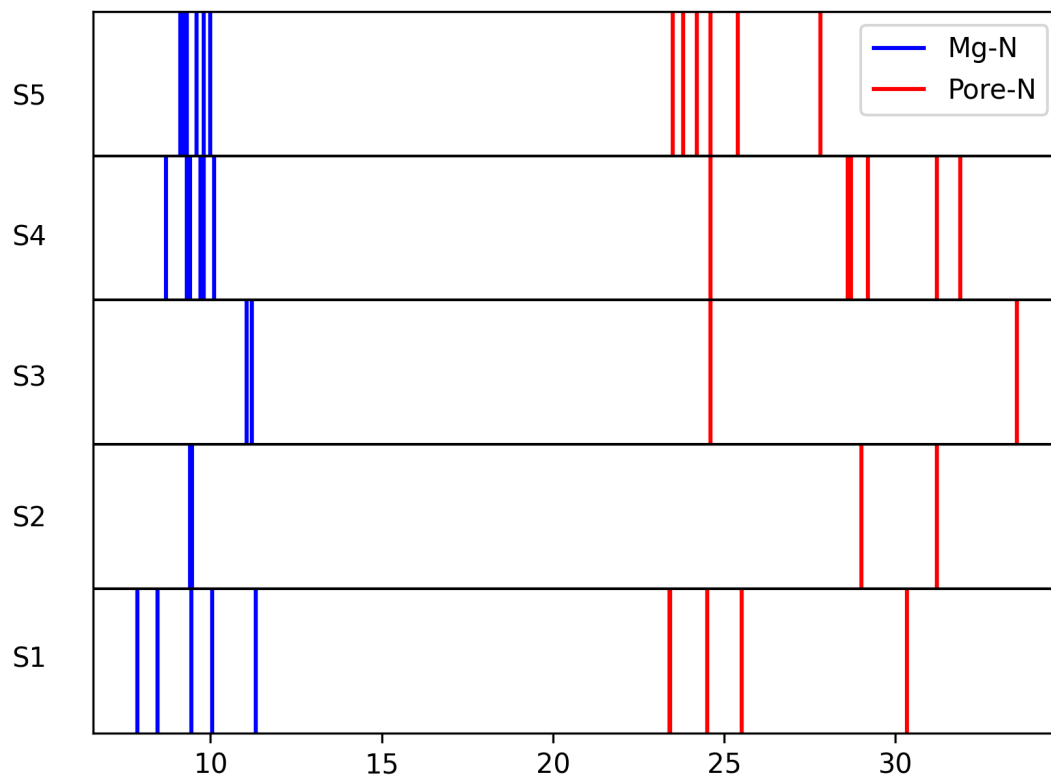


Figure 3.6: ^{15}N chemical shifts for HSO_3^- binding to the pore nitrogen with different local minima. We generated 5 different geometries; two geometries (S2 and S3) were symmetrized so that they have fewer distinct N environments, leading to fewer shifts. The other geometries didn't have the 6 dmpn-HSO_3^- being equivalent, so there's a small spread in the chemical shifts. For all of the different geometries, we can see that the nitrogen bound to the metal always has a chemical shift in the 8-12 ppm range, while the N in the pore has a chemical shift in the 25-31 ppm range.

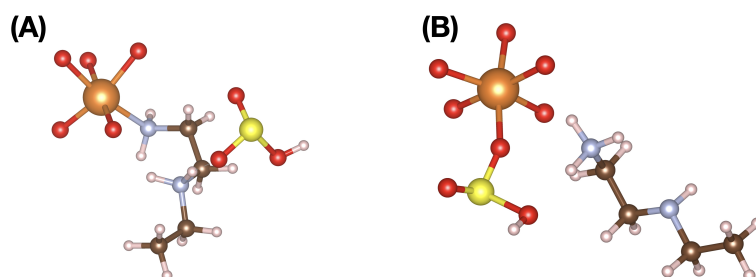


Figure 3.7: Fragment of DFT Relaxed Crystal Structures with $\text{e2-Mg}_2(\text{dobpdc})$ and (A) HSO_3^- coordinating with the pore nitrogen, (B) HSO_3^- coordinating with the metal nitrogen. Framework atoms are removed for visual clarity. Mg - Orange, N - Light Blue, C - Brown, O - Red, S - Yellow, H - White

MOF. This initial geometry then had different SO_2 species added to the framework. We considered 5 different binding modes, 2 with HSO_3^- , and two with SO_2 . Figure 3.5 shows the different binding modes that we considered. The HSO_3^- geometries involved the placement of HSO_3^- to coordinate with one of the two amine groups. Diamine-appended $\text{Mg}_2(\text{dobpdc})$ has one amine group bound to the framework at the Mg site, while the other amine is free in the pore of the MOF. Thus, we labeled these geometries “pore N” and “metal N” based on which amine the HSO_3^- was coordinating with. The “metal N” geometry involved inserting the HSO_3^- in between the Mg and dmpn, while the “pore N” involved having the HSO_3^- coordinate in the pore of the MOF near the dmpn. Thus, the “pore N” geometries had more possible configurations, so in Figure 3.6 we compared the results of different ways to initialize the “pore N” geometries, and we see that since NMR chemical shifts are similar when there is a similar chemical environment, the chemical shifts for those different “pore N” geometries are similar to each other. This figure also helps us confirm that for the other geometries, small changes in the conformations across the many local minima in the potential energy surface of these flexible functional groups will not have a large impact on the computed chemical shifts.

After determining that HSO_3^- was the most likely water + SO_2 product to form, we only generated HSO_3^- in the e2- $\text{Mg}_2(\text{dobpdc})$ framework. These geometries, shown in Figure 3.7, involve HSO_3^- inserting between the Mg and e2 (the “metal N”), or involve the HSO_3^- coordinating with the amine group in the pore (the “pore N”). We started from a previously calculated e2- $\text{Mg}_2(\text{dobpdc})$ geometry in Ref. [86], and inserted the HSO_3^- in those two sites.

3.3 Results

Table 3.3 shows the results for our NMR chemical shift and binding energy calculations with the dmpn diamine. The experimental chemical ^{15}N chemical shifts for dmpn- $\text{Mg}_2(\text{dobpdc})$ after humid SO_2 exposure show peaks at 13 ppm and 30 ppm (see Ref. [82]). Thus, we

SO_2 species	Metal N Shift (ppm)	Pore N Shift (ppm)	Binding Energy (kJ/mol)
HSO_3^- , pore N	12	27	-148
HSO_3^- , metal N	32	5	-98
SO_2 , chain	128	28	-63
SO_2 , pore N	14	69	-70
SO_2 , metal N	81	19	-53

Table 3.1: Chemical shifts for the nitrogen at the Mg site and in the pore for the dmpn-appended framework. We also have binding energies for the different binding modes.

can see that in addition to having the most favorable binding energy, the “ HSO_3^- , pore N”

geometry has chemical shifts that are closest to experiment. We can see that the other HSO₃[−] geometry, which has the HSO₃[−] between the Mg and the N has similar chemical shifts, although its binding energy is much less favorable, so we can conclude that the most likely geometry is HSO₃[−] binding to the amine group that is in the pore when the diamine is dmpn. Based on the result that the HSO₃[−] is most likely to coordinate with dmpn’s amine group that is in the pore, we can understand the experimental result showing that dmpn-Mg₂(dobpdc) has few of the dmpn molecules detach from the framework after the MOF is regenerated. If HSO₃[−] were bound between the Mg and the dmpn, then regenerating the MOF and removing the HSO₃[−] would be more likely to remove the dmpn since it is not bound to the MOF at the Mg site. Since the HSO₃[−] coordinates with the pore nitrogen, it does not disrupt the Mg-dmpn bond, so that the HSO₃[−] can be removed from the framework without removing the dmpn as well.

To investigate the poorer performance of e2-Mg₂(dobpdc) after humid SO₂ exposure, we did similar calculations with HSO₃[−] binding between the Mg and N, or with the amine group that is in the pore. Table 3.3 shows our results. We can see that the chemical shifts for the HSO₃[−] bound between the Mg and the N are in better agreement with experiment than the structure with HSO₃[−] bound on the pore side of the e2.

Binding Mode	Metal N Shift (ppm)	Pore N Shift (ppm)
HSO ₃ [−] , pore N	17	58
HSO ₃ [−] , metal N	34	52
Experimental Result	33	46

Table 3.2: Chemical shifts for the nitrogen at the Mg site and in the pore for the e2-appended framework.

From this result, we can see that e2 is susceptible to the amines being removed after humid SO₂ exposure because the HSO₃[−] inserts between the framework and the e2, meaning that after the system is heated and the HSO₃[−] is desorbed, the e2 is already detached from the framework and is free to leave as well.

3.4 Conclusions

We found that some of our proposed geometries agreed with experimental NMR chemical shifts, suggesting that we were able to generate structure which had similar chemical environments as the experimental system. Additionally, we were able to rule out different binding modes and SO₂ species since those structures had chemical shifts that were much too far from the experimental signals to be consistent. We were able to explain that dmpn experiences less degradation after SO₂ exposure than e2 because the HSO₃[−] binds with the nitrogen that is in the pore rather than the nitrogen that bound to the MOF’s metal site, as it does in e2. Additionally, HSO₃[−] does not interfere with CO₂ adsorption at the metal site,

so that $\text{dmpn-Mg}_2(\text{dobpdc})$ can be exposed to both humid SO_2 and CO_2 , and not have the CO_2 binding site get taken by the SO_2 . Our results help explain the superior performance of $\text{dmpn-Mg}_2(\text{dobpdc})$ compared to $\text{e2-Mg}_2(\text{dobpdc})$, by showing how the different HSO_3^- binding geometries enable $\text{dmpn-Mg}_2(\text{dobpdc})$ to lose less dmpn after regeneration, and to keep its CO_2 binding site open.

Chapter 4

Tuning O₂ Adsorption in BTTri MOFs

4.1 Introduction

In the previous section, we studied SO₂ adsorption in diamine appended Mg₂(dobpdc) to investigate how SO₂ affected CO₂ capture performance in those systems. In this section, we use DFT calculations to study how modifications to a different class of MOFs can improve O₂ capture performance. Efficient O₂ separations is important because many industrial applications require purified O₂. This work highlights the ways that DFT calculations can be predictive in guiding experimental efforts, while in the previous section we used DFT to help explain experimental results. This work was published in Ref. [87]. Parts of that work are reproduced from Ref. [87] with permission from the Royal Society of Chemistry. We study modifications to the MOFs M-BTT [88], M-BTTri [89], and M-BTP [90]. The BTT and BTTri MOFs have been previously synthesized, but the BTP MOFs are hypothetical. Figure 4.1 shows a supercell of Co-BTTri. These MOFs have metal nodes with four metals bridged by a halide, and coordinate with 5 membered azolate rings which can have 2 (-BTP), 3 (-BTTri), or 4 (-BTT) nitrogens per ring. The metals can be substituted with many different 2+ transition metal ions, so that one can tune O₂ adsorption by modifying the metal and the linker. Additionally, we will show that hypothetical frameworks with the Cl replaced with other halides further tunes the binding energies.

Because of this tunability, this family of MOFs has been widely studied and have shown promise for their O₂ adsorption properties [87]. They tend to have binding energies that are close to the -45 kJ/mol target, and have a high number of binding sites per unit volume compared to other MOFs studied for O₂ adsorption. Additionally, there are known O₂ binding energies for Cr-BTT (-65 kJ/mol) and Co-BTTri (-34 kJ/mol), so that we can validate the accuracy of our calculations by comparing them with previously characterized materials. Previous works have used DFT calculations to predict O₂ binding energies [91–93] to open metal sites in MOFs. We note that open-shell transition metal systems pose a

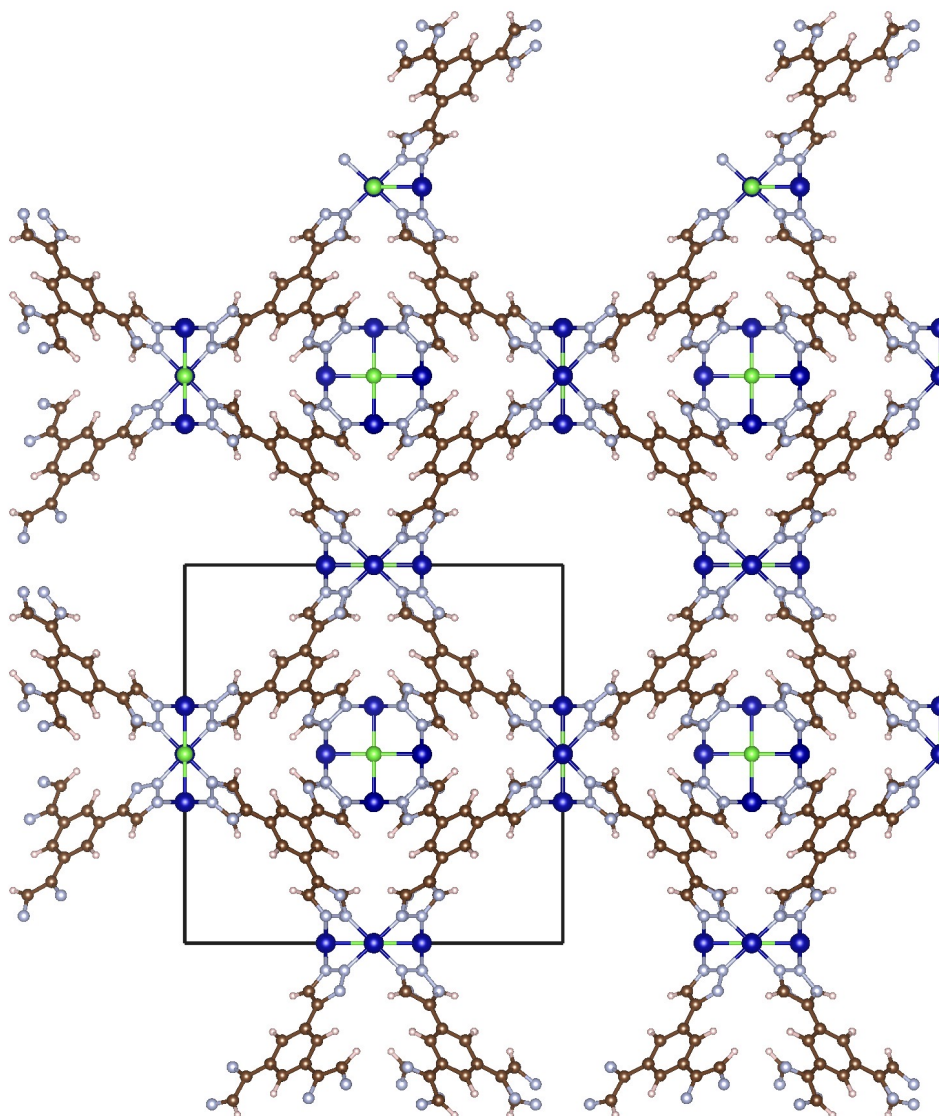


Figure 4.1: Supercell of Co-BTTRI-Cl. The BTT and BTP versions of the MOF have either 2 or 4 nitrogens in the azolate ring instead of the 3 in BTTRI. Co - Dark Blue, N - Light Blue, C - Brown, O - Red, Cl, Light Green, H - White

challenge for DFT calculations, as standard functionals can fail to adequately treat exchange and correlation effects associated with states having localized d orbital character. As such, it is common to utilize hybrid functionals or Hubbard U corrections [92], which can lead to improved treatments of electron-electron interactions, and we utilize this approach here.

4.2 Methods

We performed DFT geometry optimizations to obtain binding energies for variants of M₃[(M₄X)₃(benzenetrisazolate)₈]₂ (M = Cr, Mn, Co; X = F, Cl, Br). Here, benzenetrisazolate = BTT³⁻, BTTri³⁻, BTP³⁻, or BDTriP³⁻. A plane-wave basis and projector augmented-wave (PAW) [83, 94] pseudopotentials within the Vienna ab initio Simulation Package (VASP) were used [8–10, 84]. Effects of long-range dispersion interactions using the DFT-D3 correction [44] with Becke-Johnson damping were used [45], which took into account the transition metal onsite interactions using a Hubbard U value in the Dudarev approach [95–97] chosen based on reported transition metal oxides calculations [98]. O₂ binding energies, ΔE_{O_2} were calculated using

$$4\Delta E_{O_2} = E_{\text{MOF-O}_2} - (E_{\text{MOF}} + 4E_{O_2}) \quad (4.1)$$

where $E_{\text{MOF-O}_2}$ is the energy of the framework with bound O₂, E_{MOF} is the energy of the framework, and E_{O_2} is the energy of free O₂.

In particular, we considered binding of four O₂ molecules to the exposed metal centers in the cubic unit cell. Figures 4.2 and 4.3 show the binding sites with and without O₂. We calculated zero point and thermal energy contributions for Co-BTTri with Γ point phonon calculations where only the oxygens, oxygen-bound metals, and the atoms bound to oxygen-bound metals were displaced to reduce the time required for the calculation. The final zero point and thermal energy correction was 11.5 meV (1.11 kJ/mol).

Our structural relaxations used a Γ point sampling of the Brillouin zone, the gamma point only VASP binary, and a 600-eV plane-wave energy cutoff energy. We used spin-polarized calculations with the initial transition metal spin chosen to match the expected spin-state. The unit cell shape, unit cell volume, and the ions were relaxed until the Hellman-Feynman forces were less than 0.01 eV/Å. To account for Pulay stress due to a changing cell shape, we successively converged calculations from their last set of lattice vectors and atomic positions until the forces were converged after just a single ionic step.

We initialized our geometries with the reported experimental structure of Co-BTTri [89] and replaced the metal, ligand, and/or halogen accordingly. As a structure is also reported for Cr-BTT [88], we computed the O₂ binding energy in Cr-BTT based on initialized experimental atomic positions, as well as coordinates from Co-BTTri, with Co replaced with Cr and BTTri replaced with BTT. While generating O₂-bound structures, there can be some freedom regarding the orientation of the bound O₂. To illustrate the effect of the M–O–O angle on the O₂ binding energy, we performed calculations on Cr-BTT with the O₂ oriented

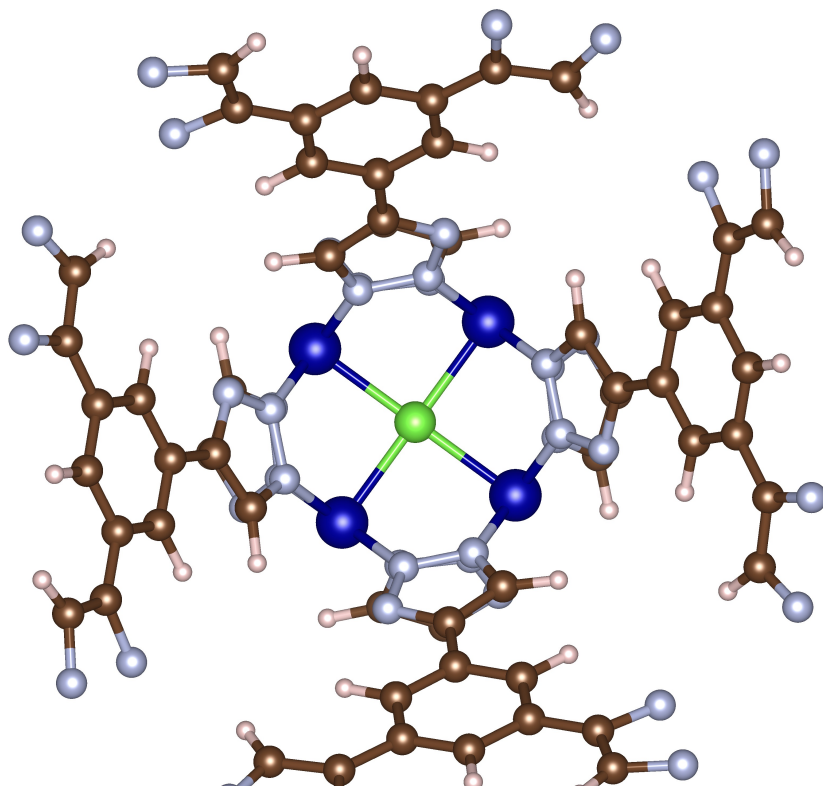


Figure 4.2: Geometry of the four open-metal sites per metal node in Co-BTTRI. Co - Dark Blue, N - Light Blue, C - Brown, O - Red, Cl, Light Green, H - White

side-on, end-on at 45° , and end-on at 180° . Both end-on binding modes results in binding energies of 57 kJ/mol, while the side-on mode was 5 kJ/mol lower in energy.

A final important consideration when computing binding energies in these frameworks is how to balance the charge in the system. The experimental system contains disordered pore-dwelling cations in order to charge balance the anionic framework. Past computational studies have charge balanced by protonating one nitrogen on the azolate per metal node [99, 100]. This approach makes geometry optimization converge faster relative to incorporating pore-dwelling cations to charge balance. We note, however, that when protonating nitrogen atoms of the ligand, the electronic structure of the coordinatively unsaturated metal sites could be directly affected, thereby influencing O₂ binding. As a result, we used a positive neutralizing background charge. Future work could consider incorporating pore-dwelling cations, but such a system will exhibit many local minima on the potential energy surface.

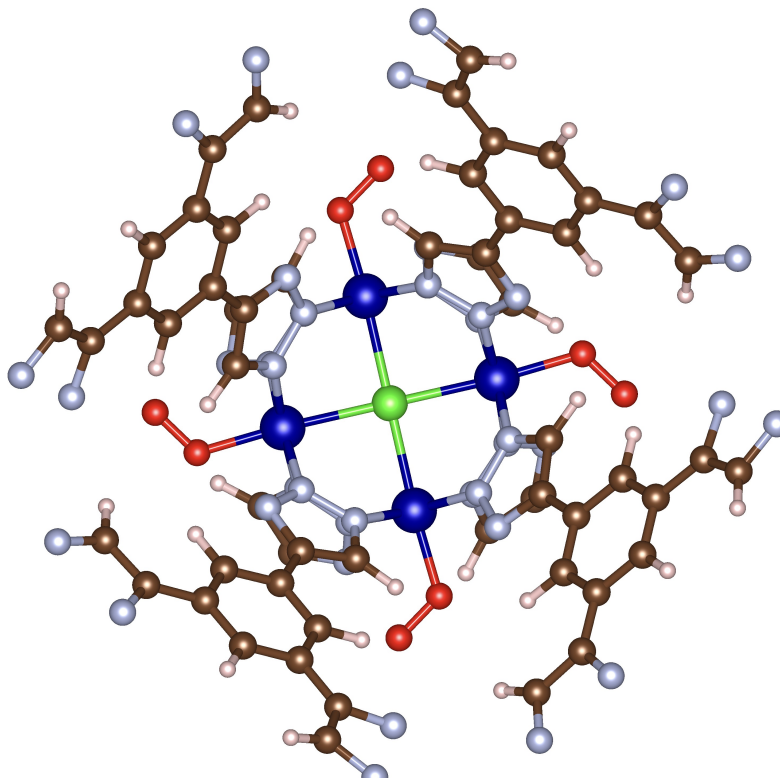


Figure 4.3: O₂ binding geometry in Co-BTTRI. Co - Dark Blue, N - Light Blue, C - Brown, O - Red, Cl, Light Green, H - White

4.3 Results and Conclusions

Table 4.3 has the results of our DFT calculations for the binding energy of O₂ with different linkers and halogens, and the metal fixed to Co.

Linker	F BE (kJ/mol)	Cl BE (kJ/mol)	Br BE (kJ/mol)	I BE (kJ/mol)
BTT	25.1	29.0	31.7	38.6
BTTRI	33.3	39.7	45.5	53.7
BTP	44.5	53.3	-	70.2

Table 4.1: Binding energies (BE) with different anions, X, and different linkers, L, in Co-L-X. Co-BTP-Br's geometry optimization did not converge, so no binding energy is reported.

Table 4.3 has the results of our DFT calculations for the O₂ binding energies with different metals and linkers, and Cl as the halogen.

Linker	Co BE (kJ/mol)	Cr BE (kJ/mol)	Mn BE (kJ/mol)
BTT	31.4	58.9	23.7
BTTri	39.7	60.3	23.6
BTP	53.3	101.3	40.8

Table 4.2: Binding energies (BE) with metals M, and different linkers, L, in M-L-Cl.

Experimental O₂ binding energies have been found for Cr-BTT [87, 88] and Co-BTTri [87, 89]. These experimental values are -65 kJ/mol for Cr-BTT and -34 kJ/mol for Co-BTTri. We can see that for our choice of the Hubbard U parameter, which was taken from the Materials Project [98] based on fitting to transition metal oxide formation energies [101], we are within 5-10 kJ/mol of the experimental binding energies. Additionally, our calculations get the binding energy trends across the different metals and linkers for those that have known experimental values. We note, however, that the calculated binding energies depend sensitively on the choice of the U value. This result was found in Ref. [99] for O₂ systems. Ref. [102] showed a smaller dependence on the U value in CO₂ adsorption in transition metal systems. O₂ binding often occurs via reduction of the O₂ when an electron is transferred from the transition metal to the O₂. This electron transfer means that the choice of the U value will have a larger impact on the binding energy than it does in CO₂ adsorption where there is no electron transfer.

A binding energy of -45 kJ/mol is best in terms of the energy efficiency of binding and unbinding O₂ [87]. We can see from our results that Mn-BTP and Co-BTP could end up having a binding energy in this range. Additionally, Co-BTTri-Br, Co-BTTri-I, Co-BTP-F, and Co-BTP-Cl could end up having binding energies close to -45 kJ/mol based on our calculations. Should the binding energies for some of these systems be found, we could use the trends that we found, which show that for fixed linker and halide, the binding energies follow Mn < Co < Cr, and for fixed linker and metal, the binding energies increase as the size of the halide increases. For fixed metal and halide, we see that binding energies increase BTT < BTTri < BTP.

Chapter 5

vdW Interactions in MOFs and Layered Perovskites

5.1 Introduction

In the previous chapters, we discussed calculations involving systems in which vdW interactions are important, and also in which there were open shell transition metals for which we used Hubbard U corrections. These systems have been the subject of prior benchmarking, [86, 99, 102] and our choice of functionals was based on those works. Another class of materials for which benchmarking studies have been performed is layered solids [4–6]. These benchmarking studies primarily focused on simpler inorganic layered solids like graphite, hexagonal boron nitride, and transition metal dichalcogenides (TMDs). They found that SCAN+rVV10, rev-vdW-DF2, vdW-DF-cx, and vdW-DF3-opt1 in particular perform best for these layered solids. Here, we expand these studies and consider vdW functionals in layered “hybrid” organic-inorganic systems which have a larger diversity of chemical bonding environments than previous benchmarking studies considered. We also discuss the impact of Hubbard U values on changing the lattice parameters for hybrid magnetic layered systems, and study the impact of the choice of pseudopotentials on the results.

Hybrid organic-inorganic materials have been important forefront materials due to the potential to tune their properties by leveraging insight from both inorganic and organic materials. Two large classes of hybrid materials include metal-organic frameworks and hybrid organic-inorganic perovskites. As discussed in earlier chapters, many metal-organic frameworks of interest are bulk solids that are studied for applications like gas separations due to their porous structures [87, 103], but another large group of metal-organic frameworks are quasi-2D metal-organic frameworks. These materials have attracted interest for a mix of their electronic and magnetic properties. Recent interest in quasi-2D metal-organic frameworks include for use as hard magnets [104, 105], the ability to be tunable platforms for studying novel magnetic interactions and electron correlation [106–108], the discovery of unconventional superconductivity [109], and as supercapacitors due to their ability to contain

intercalated ions [110]. Hybrid organic-inorganic perovskites are derived from the crystal structure of inorganic perovskites with the ABX_3 stoichiometry where the A site cations are replaced with organic molecules. These structures can range from the hybrid 3D perovskite (MA)PbI₃ (MA = CH₃NH₃⁺) [111], to layered 2D perovskites like (HIS)PbBr₄ (HIS = C₅H₁₁N₃) [112], to 0D perovskites [113]. Hybrid 3D perovskites have attracted a lot of interest over the past decade as high performing semiconductors for photovoltaic applications [111, 114–119], while lower dimensional hybrid perovskites have shown promise as white light emitters [112, 120].

Layered solids are materials with two dimensional layers that weakly interact with neighboring layers via van der Waals interactions (vdW). Because of their reliance on vdW interactions, accurately capturing their structural parameters with ab-initio density functional theory (DFT) [25, 26] calculations requires an accurate approximation for the non-local vdW interactions in a material. Commonly used exchange-correlation functionals in DFT like the local density approximation (LDA) [33] and the generalized gradient approximation (GGA) [35] only contain information about the electron density at one point in space (in the case of the LDA) or the electron density and gradient of the density at one point in space (in the case of GGAs). Such approximations neglect long-range electron correlation. Two main approaches have been employed to include the effects of vdW interactions. One approach, which is computationally less demanding, is pairwise methods like the Grimme D3 [43–45] and Tkatchenko-Scheffler [121, 122] approaches. Another approach involves modifying the exchange-correlation energy used in DFT to include a carefully constructed non-local correlation term. This approach is employed in the vdW-DF [4, 6, 41, 46–52, 123] family of functionals as well as the VV10 [53, 124–126] family of functionals.

Past benchmarking work has shown that the inclusion of pairwise or non-local vdW corrections greatly improves the accuracy of predicted lattice constants in layered solids [4–6]. This past work focused on inorganic layered solids such as graphite, hexagonal boron nitride, and transition metal-dichalcogenides. While hybrid organic-inorganic layered solids like layered metal-organic frameworks and organic-inorganic perovskites share similarities with these layered inorganic solids, the addition of organic molecules to their structure adds structural complexity and also potentially poses challenges for the design of approximations to vdW interactions. Some approximations for the vdW interaction perform well for layered solids, but perform poorly for molecular crystals composed of organic molecules [6], making benchmarking in organic-inorganic perovskites which have inorganic metal-halide layers and layers of cationic organic molecules a useful way of evaluating the degree to which the inclusion of organic molecules makes structural prediction difficult with existing vdW corrections. One prior study looked at complex organic-inorganic perovskites, Ref. [127], but it did not include the non-local vdW-DF and rVV10 functionals. That study found that PBE-D3, PBE-D3(BJ), and PBE-TS performed well in predicting the lattice constants of 0D, 1D, and 2D hybrid perovskites.

Additionally, past benchmarking has primarily focused on layered solids which have closed shell ions. Many layered metal-organic frameworks have unpaired spins with localized electrons on 3d ions. Such electrons typically require methods like the Hubbard U [128–130]

correction to approximately model the properties of the localized d electrons. Fewer studies have systematically looked at the impact of the inclusion of spin and a Hubbard U value in determining the lattice constants of layered solids. The interlayer spacing in magnetic layered solids is an important material parameter since it affects the degree to which spins in different layers interact with each other. Past experimental studies [106] on the magnetic layered metal-organic framework $\text{NiX}_2(\text{pyz})_2$ $\text{X} = \{\text{Cl}, \text{Br}, \text{I}\}$ where ($\text{pyz} = \text{C}_4\text{H}_4\text{N}_2$) have found that the change in interlayer spacing due to the size of the halogen affects the degree to which the magnetic structure is 2 or 3 dimensional; this sensitivity to the interlayer spacing means that over- or under-predicting the lattice constants in a DFT calculation can affect the magnetic properties of similar materials. To examine the impact of the choice of Hubbard U value on structural parameters, for the magnetic materials in this study, we compared lattice parameters with a range of Hubbard U values.

Finally, the choice of pseudopotentials one uses can affect predicted materials properties. We study the impact of using three common choices for the type of pseudopotentials on the predicted lattice parameters, including norm-conserving pseudopotentials [131] from Pseudojdo [132], ultrasoft pseudopotentials [133, 134] from the Rutgers-GBRV database [135], and projector-augmented wave pseudopotentials [83, 94] from VASP [8–10, 84]. We follow past benchmarking studies [6] which use PBE pseudopotentials for all calculations.

5.2 Methods

To study the impact of the choice of pseudopotential and also the way the Hubbard U correction is implemented in different codes, we perform DFT calculations with the Vienna ab-initio Simulation Package (VASP) and with Quantum Espresso (QE) [11–13]. Our VASP calculations use a 650 eV planewave cutoff and a $2 \times 2 \times 2$ sampling of the Brillouin zone. We use PAW pseudopotentials generated with the PBE functional for all calculations, explicitly including $1s^1$ for H, $2s^2 2p^2$ for C, $2s^2 2p^3$ for N, and $3s^2 3p^5$ for Cl. We perform lattice and ionic optimization until the internal forces are less than $0.01 \text{ eV}/\text{\AA}$, and have a total energies are converged to within 10^{-8} eV . We perform collinear spin-polarized calculations with magnetic ordering set according to experimental magnetic data, [136], which indicates that the spins in $\text{CrCl}_2(\text{pyz})_2$ to be aligned with each other.

Our QE calculations use either norm-conserving pseudopotentials from Pseudojdo or ultrasoft pseudopotentials from the Rutgers-GBRV database. Both sets of pseudopotentials are generated with the PBE functional. Both the norm-conserving pseudopotentials and the ultrasoft pseudopotentials explicitly include the following electrons as valence electrons: $1s^1$ for H, $2s^2 2p^2$ for C, $2s^2 2p^3$ for N, $3s^2 3p^5$ for Cl, $4s^2 4p^5$ for Br, $5s^2 5p^5$ for I, $3s^2 3p^6 4s^1 3d^4$ for V, $3s^2 3p^6 4s^1 3d^5$ for Cr, $3s^2 3p^6 4s^1 3d^9$ for Ni, and $6s^2 5d^1 06p^2$ Pb. All QE calculations include a $2 \times 2 \times 2$ k-grid, a 0.001 Ry/Bohr force threshold ($0.02571 \text{ eV/\AA}$), a 10^{-4} Ry Marzari-Vanderbilt smearing [137], a 84 Ry plane wave energy cutoff, and a 10^{-8} Ry scf stopping criteria. For our QE calculations on $\text{MX}_2(\text{pyz})_2$ for $\text{M} = \{\text{Cr}, \text{Ni}, \text{V}\}$ and $\text{X} = \{\text{Cl}, \text{Br}, \text{I}\}$ we use a Hubbard U of $U = 3.7 \text{ eV}$ for Cr, $U = 4.5 \text{ eV}$ for Ni, and $U = 3.25 \text{ eV}$ for V, again chosen based

on Ref. [98]. We perform collinear spin-polarized calculations with magnetic ordering set according to experimental magnetic data [106, 108, 136]. For $\text{CrCl}_2(\text{pyz})_2$, we initialize the Cr spins to be aligned with each other, while for $\text{NiX}_2(\text{pyz})_2$, $\text{X} = \{\text{Cl}, \text{Br}, \text{I}\}$ and $\text{VCl}_2(\text{pyz})_2$ we initialize the Ni or V spins to be anti-aligned with each other.

All of our geometry optimizations were performed with the different functionals by starting from the same crystal structure. For $\text{CrCl}_2(\text{pyz})_2$, we use Ref. [136], and for $\text{NiX}_2(\text{pyz})_2$ we use Ref [106] to generate our structures. For $\text{VCl}_2(\text{pyz})_2$ we use Ref. [136] with Cr replaced with V to generate our initial structure. In our VASP calculations we use a $2 \times 2 \times 1$ supercell, while in our QE calculations we use a $\sqrt{2} \times \sqrt{2} \times 1$ structure for increased computational efficiency. For $(\text{HIS})\text{PbBr}_4$, we used the 300 K structure from Ref. [112].

Kohn-Sham band gaps in $(\text{HIS})\text{PbBr}_4$ were calculated with Quantum Espresso, using the same computational set up as used in the geometry optimizations. We computed the same band gaps with the vdW-corrected functionals and also with PBE to confirm that changes in band gap were due geometrical changes rather than changes to the exchange-correlation functional. We also calculated the band gap for some of the systems using HSE06 [39] as further confirmation for the impact of the geometry on the band gap. We used a coarse $2 \times 2 \times 2$ k-grid when calculating the band gaps because our primary goal was to analyze trends in the differences in the eigenvalues with different geometries, rather than trying to get quantitative agreement with experiment results. Given the experimental lattice parameters are all on the order of 10 Å in $(\text{HIS})\text{PbBr}_4$, it is also reasonable to assume that the Γ point Kohn-Sham band gap will be similar to the Kohn-Sham band gap on a denser k-grid in $(\text{HIS})\text{PbBr}_4$.

5.3 Crystal Structures

$\text{MX}_2(\text{pyz})_2$ Family

$\text{MX}_2(\text{pyz})_2$ is a family of layered metal-organic frameworks with M a 2+ or 3+ metal, X a halogen, and $\text{pyz} = \text{pyrazine}$. It makes up a structure consisting of octahedrons of MX_2N_4 with the nitrogens in the octahedra being a part of pyrazine molecules that bridge the metal sites. Figure 5.1 shows an example of the $\text{CrCl}_2(\text{pyz})_2$ structural motif. The pyrazine molecules have rotational freedom, and experimental crystal structures are unable to distinguish between different rotational orientations of the pyrazine, although it has been speculated based on steric hindrance arguments that the pyrazines should be oriented in a “propeller” like manner in which each of the pyrazines are oriented in the same direction, as in Figure 5.1. Prior DFT calculations [138] have confirmed that this structure is lowest in energy. We perform all of our calculations on the propeller structure. Such a structure can be obtained with a 46 atom cell consisting of just two formula units. In order to properly allow for antiferromagnetism between metal sites in the same plane, one must use a supercell. The smallest supercell that permits two metal sites in the same plane is of dimension $\sqrt{2} \times \sqrt{2} \times 1$. A $2 \times 2 \times 1$ supercell like in Figure 5.1 also permits AFM in-plane interactions, but it requires 184 atoms, which is a good deal more computationally demanding.

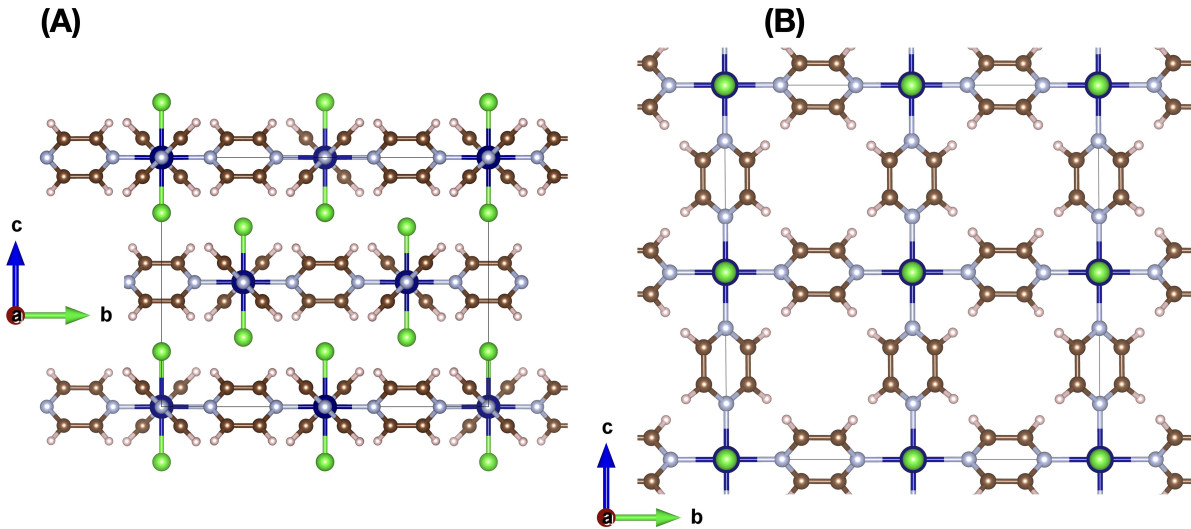


Figure 5.1: Crystal structure of $\text{CrCl}_2(\text{pyz})_2$ as viewed perpendicular from the a-c plane (A) and the a-b plane (B). Colors of atoms are Cr - Dark Blue, Cl - Green, N - Light blue, C - brown, H - white.

$\text{CrCl}_2(\text{pyz})_2$ has been found to have Cr 3+ where there is an electron delocalized across the two pyrazines in the formula unit using prior DFT calculations [136]. This electron delocalization on the pyrazines gives rise to high conductivity values [136], and also causes there to be unpaired spin density on the pyrazines. The Cr-pyrazine magnetic interaction is anti-ferromagnetic, so that along a Cr-pyrazine-Cr chain, the Cr have ferromagnetic interactions in an overall ferrimagnetic structure [136]. $\text{NiX}_2(\text{pyz})_2$ with $\text{X} = \{\text{Cl}, \text{Br}, \text{I}\}$ has Ni in the nominally 2+ oxidation state, so there are not any electrons delocalized across the pyrazine. This 2+ oxidation state is what one might expect from simple octet rule considerations for $\text{MX}_2(\text{pyz})_2$ since pyrazine is neutral, and X have 1- charges. With some transition metals, like Cr [136] or Ti [108], the M site is 3+ instead and there's a cationic metal node and anionic pyrazine linkers. The Ni material has anti-ferromagnetic interactions in plane due to superexchange across the pyrazine. Both the Cr and Ni materials have weak out of plane magnetic interactions; however, the Ni material has been found to go from quasi-2D magnetic ordering to 3D magnetic ordering upon changing Cl to I [106]. We assume ferromagnetic ordering between Cr sites out of plane and between Ni sites out of plane for simplicity. Such an approximation should have minimal impact on the predicted lattice constants because of the weak interplane magnetic coupling [106]. $\text{VCl}_2(\text{pyz})_2$ [108] has similar properties as $\text{NiCl}_2(\text{pyz})_2$, and we include it in our study because it has reported lattice parameters at 120 K and at 300 K, allowing us to compare our 0 K lattice parameters with lower temperature measurements.

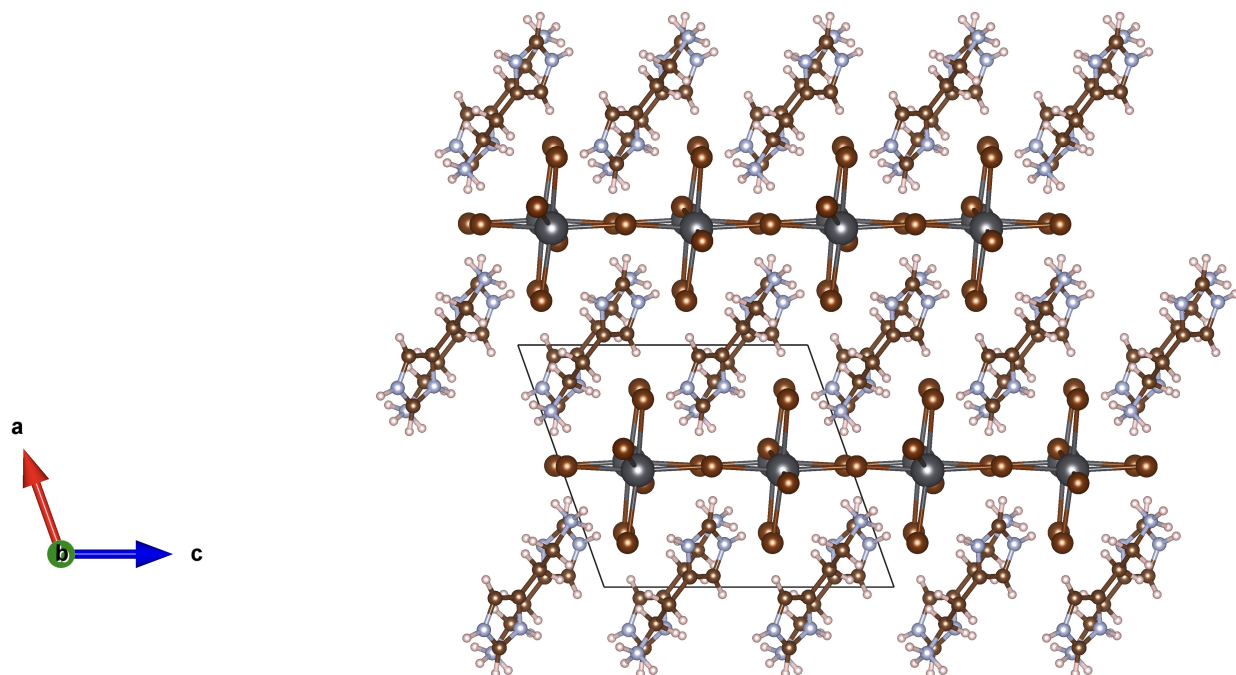


Figure 5.2: Crystal structure of (HIS)PbBr₄. Primitive cell indicated with black lines. Colors of atoms are Pb - Gray, Br - Brown, N - Light blue, C - brown, H - white.

Hybrid organic-inorganic perovskites

We consider the hybrid organic-inorganic perovskite (HIS)PbBr₄ (HIS = histammonium), with an anionic inorganic layer of PbBr₄ and histammonium cations separating adjacent layers and charge balancing the anionic inorganic layer. Figure 5.2 shows the structure of (HIS)PbBr₄.

Overall, our benchmarking study includes six hybrid organic-inorganic crystals, five metal-organic frameworks, and one perovskite derived system. The metal-organic frameworks have strong covalent bonds in the a-b plane and weak vdW interactions between layers in the c direction, while the perovskite has a mix of structural features, including strongly bound PbBr₄ layers which weakly coordinate with the histammonium cations. The histammonium cation interacts in the a-b plane by nonbonding vdW interactions, and there's also electrostatic interactions between the cationic and anionic layers.

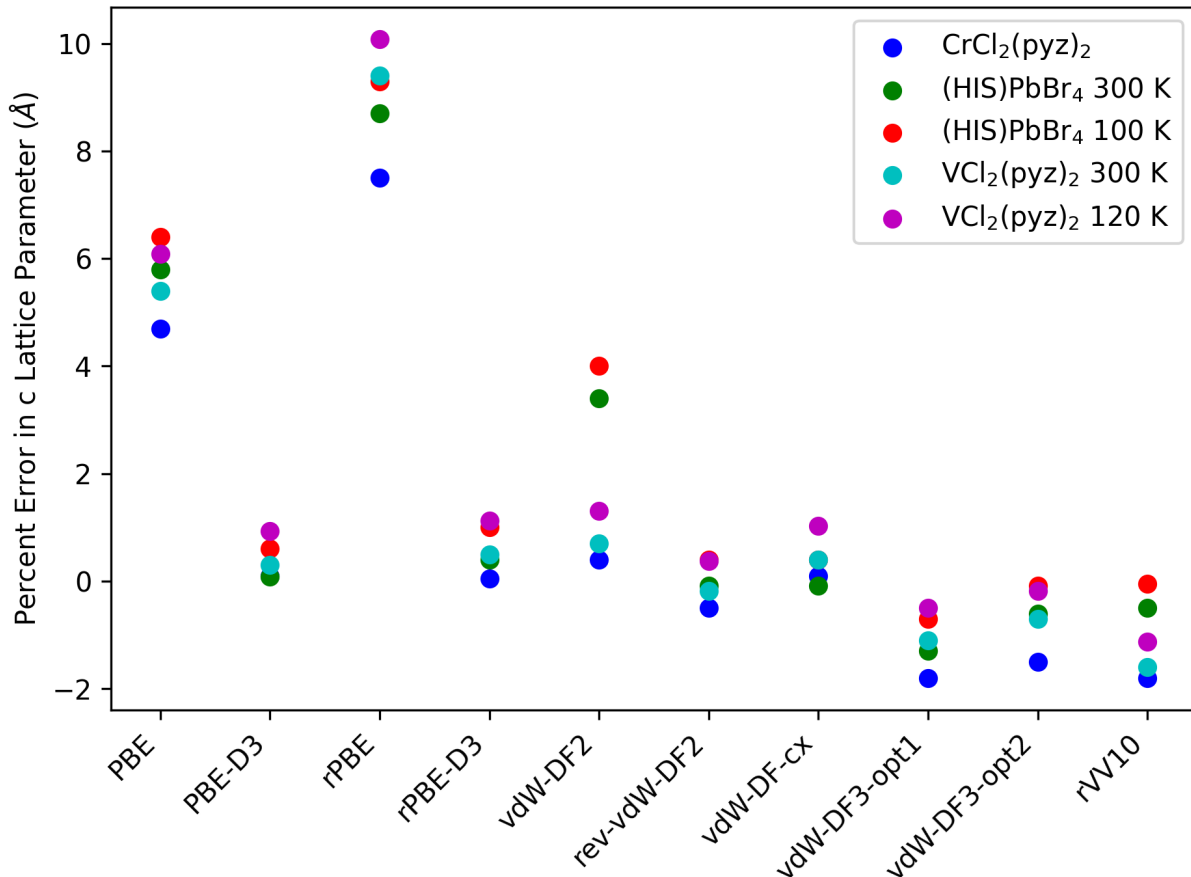


Figure 5.3: Deviations in the interplane lattice vector for different functionals on $\text{CrCl}_2(\text{pyz})_2$ at room temperature, $\text{VCl}_2(\text{pyz})_2$ at 120 K and 300 K, and $(\text{HIS})\text{PbBr}_4$ at 100 K and 300 K. Experimental values taken from Refs. [108, 112, 136].

5.4 Results

Lattice Parameters

We can see from Figures 5.3 and 5.4 that for these systems, the out of plane lattice constant shows similar trends with different functionals. Appendix B tabulates our calculated lattice parameters.

The GGAs rPBE [139] and PBE, lead to largest lattice vectors, as expected since they do not account for vdW interactions and PBE tends to overestimate lattice constants of solids [140]. Pairwise Grimme D3 methods with both PBE and rPBE lead to reduced lattice parameters and volume and show similar results. Both PBE-D3 and rPBE-D3 show similar

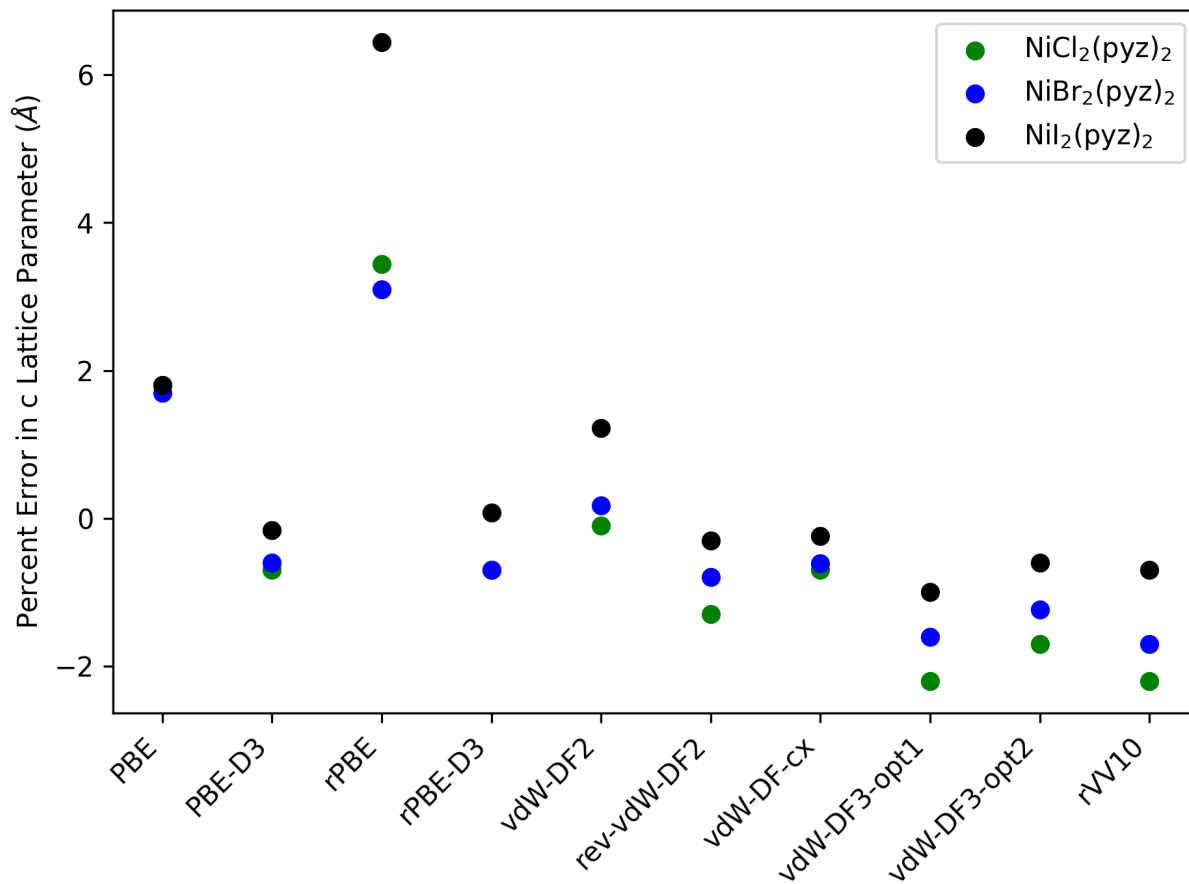


Figure 5.4: Deviations in the interplane lattice vector for different functionals on NiCl₂(pyz)₂, NiBr₂(pyz)₂, NiI₂(pyz)₂ at room temperature for NiCl₂(pyz)₂ and NiBr₂(pyz)₂, and at 100 K for NiI₂(pyz)₂. Experimental values taken from Ref [106].

performance to vdW-DF-cx [48] and rev-vdW-DF2. [52] These four approximations have the lowest errors when compared to room temperature lattice constants, although at 100 K in (HIS)PbBr₄ [112] and 120 K in VCl₂(pyz)₂[108] they have c lattice constants that are too large. vdW-DF3-opt1 [6], vdW-DF3-opt2 [6], and rVV10 [53] consistently predict the smallest lattice constants, and they tend to give similar results to each other, with deviations from experiment that are less than 1%. While slightly overestimating that lattice parameters, PBE-D3, rev-vdW-DF2, and vdW-DF-cx also have percent errors around 1% of lower. For the two structures for which we have low temperature experimental data lattice constants, the performance of vdW-DF3-opt1, vdW-DF3-op2, and rVV10 is improved compared to the 300 K data because of the reduced thermal expansion. In (HIS)PbBr₄ at 100 K, all functionals which include the vdW interaction either via an explicit correlation functional or via pairwise interaction, are within 1% of the experimental out of plane lattice parameters except for vdW-DF2, which is 4% too large. Similarly, for VCl₂(pyz)₂ at 120 K, all functionals are within 1% of the experimental c lattice vector except for rPBE-D3 (which is 1.1% too large) and vdW-DF2 (which is 1.3% too large). In contrast, PBE and rPBE are 6.5% and 9.4% too large compared to 100 K experimental values in (HIS)PbBr₄ and 6% and 10% too large compared to 120 K experimental values in VCl₂(pyz)₂. For the systems studied, we can see three groupings of vdW corrected functionals based on their relative lattice parameters: vdW-DF2 predicts the largest c lattice parameter, PBE-D3, rPBE-D3, vdW-DF-cx, and rev-vdW-DF2 predict intermediate c lattice parameters, and rVV10, vdW-DF3-opt1, and vdW-DF3-opt2 are the smallest c lattice parameters. The experimental results tend to be somewhere around those of the second and third groups of functionals, depending on the material. While PBE-D3 and rPBE-D3 lead to nearly identical results to vdW-DF-cx for CrCl₂(pyz)₂, they differ by 1% for the a- and b-lattice parameters, illustrating that while the choice of functional is most important for the c-axis, the in-plane directions with strong covalent bonds are also affected by the choice of vdW approximation.

5.5 Exfoliation Energies for CrCl₂(pyz)₂

Exfoliation energies are defined as the energy required to separate layers of the bulk phase material to end up with just a single layer [141]. Values around 2-5 kJ/mol Å² are typical for materials that can be exfoliated to just a single layer, so computational determination of exfoliation energies can help guide experimental efforts toward materials which are more likely to be able to be exfoliated. Experimental realization of single layer CrCl₂(pyz)₂ has attracted theoretical interest [105, 138, 142] due to the bulk phase's high conductivity and ferrimagnetic behavior, but thus far it has not been successfully exfoliated. We calculate the exfoliation energy using the equation [141]

$$E_{ex} = (E_{\text{single}} - E_{\text{bulk}}/2)/SA \quad (5.1)$$

where E_{ex} , E_{single} , and E_{bulk} are the exfoliation, single layer, and bulk energies, respectively, and SA is the surface area of the cell that the calculation is done in. We divide E_{bulk} by 2

because there are two layers in the bulk unit cell. We calculate the surface area of the layered structure by multiplying the a and b lattice vectors, and we calculate the single layer energy by relaxing a single layer of $\text{CrCl}_2(\text{pyz})_2$ in a cell with expanded c -axis to act as vacuum. We use a c -axis length that is twice the bulk phase lattice c lattice vector length (approximately 20 Angstrom).

While it is not known experimentally if this crystal can be exfoliated, this quantity has recently been calculated [138] as $0.22 \text{ J/m}^2 = 1.32 \text{ kJ/mol } \text{\AA}^2$ using PBE-D2 [43], and in Ref. [142] it was calculated as $0.1 \text{ J/m}^2 = 0.602 \text{ kJ/mol } \text{\AA}^2$. They were interested in the electronic and magnetic properties of the hypothetical single layered system. They compare this energy favorably to CrI_3 , which has an exfoliation energy of $1.81 \text{ kJ/mol } \text{\AA}^2$, and can be exfoliated [143]. CrI_3 is an interesting layered magnetic system, and this family of MOFs would be interesting if they could be exfoliated since they show a range of magnetic and electronic behaviors as the metals [108, 136] or the halides [106] are modified. Prior work in Ref. [3] found that on a set of TMDs, graphite, and h-BN, vdW-DF-1 and vdW-DF-2 provided lower exfoliations than the RPA [42] best estimate of the exfoliation energy in TMDs, while for graphite they were very close to the RPA estimate, and for h-BN they were above the estimate. In their study, PBE-D2 consistently had worse exfoliation energies than the vdW-DF methods. On a similar set of materials SCAN+rVV10 [5] and rev-vdW-DF2 [4] additionally perform well compared to RPA reference values. More recent benchmarking [6] found that the newer vdW-DF3-opt1 also is one of the best performers compared to RPA reference values. Here, we calculate the exfoliation energy in $\text{CrCl}_2(\text{pyz})_2$ with different approximations for the vdW interaction, and find a variation of $1.43\text{-}1.90 \text{ kJ/mol } \text{\AA}^2$ with the different methods, a variance of 24%. While these values are higher than the previous PBE-D2 results, $\text{CrCl}_2(\text{pyz})_2$, we also calculate it with PBE-D2 and get $1.56 \text{ kJ/mol } \text{\AA}^2$, which is close to the value in Ref. [138]. Even if the larger values were more accurate with experiments, $\text{CrCl}_2(\text{pyz})_2$ might still be able to be exfoliated. We note that in Ref. [138] and Ref. [142], they gradually increased the interlayer distance to calculate the exfoliation energy, which could explain why our values are similar, but slightly different.

Figure 5.5 shows the results of our calculations. Larger positive exfoliation energies correspond to systems where the interlayer binding energy is strongest, meaning it is hardest to separate the layers. We can see that the non-local vdW methods tend to have larger exfoliation energies than the pairwise D3 method, and that the results don't exactly follow the trends from the calculated lattice parameters. While vdW-DF2 was 0.5% larger than the experimental c lattice vector and vdW-DF3-opt1 was 1.8% smaller than the experimental c lattice vector, both have similarly large exfoliation energies. Thus, it is not simply the case that the functionals with the smallest lattice parameters lead to the largest exfoliation energies. These results are consistent with Ref. [86] which found a similar ordering of the binding energies of CO_2 in diamine appended MOFs when calculated with these functionals. Thus, our exfoliation energy results show similar trends to total energy differences calculated in a different context and different type of system. Based on the performance of vdW-DF3-opt1 in Ref. [6], our best estimate for the exfoliation energy of $\text{CrCl}_2(\text{pyz})_2$ is $1.9 \text{ kJ/mol } \text{\AA}^2$, which is only slightly larger than the $1.81 \text{ kJ/mol } \text{\AA}^2$ reported for CrI_3 , so perhaps

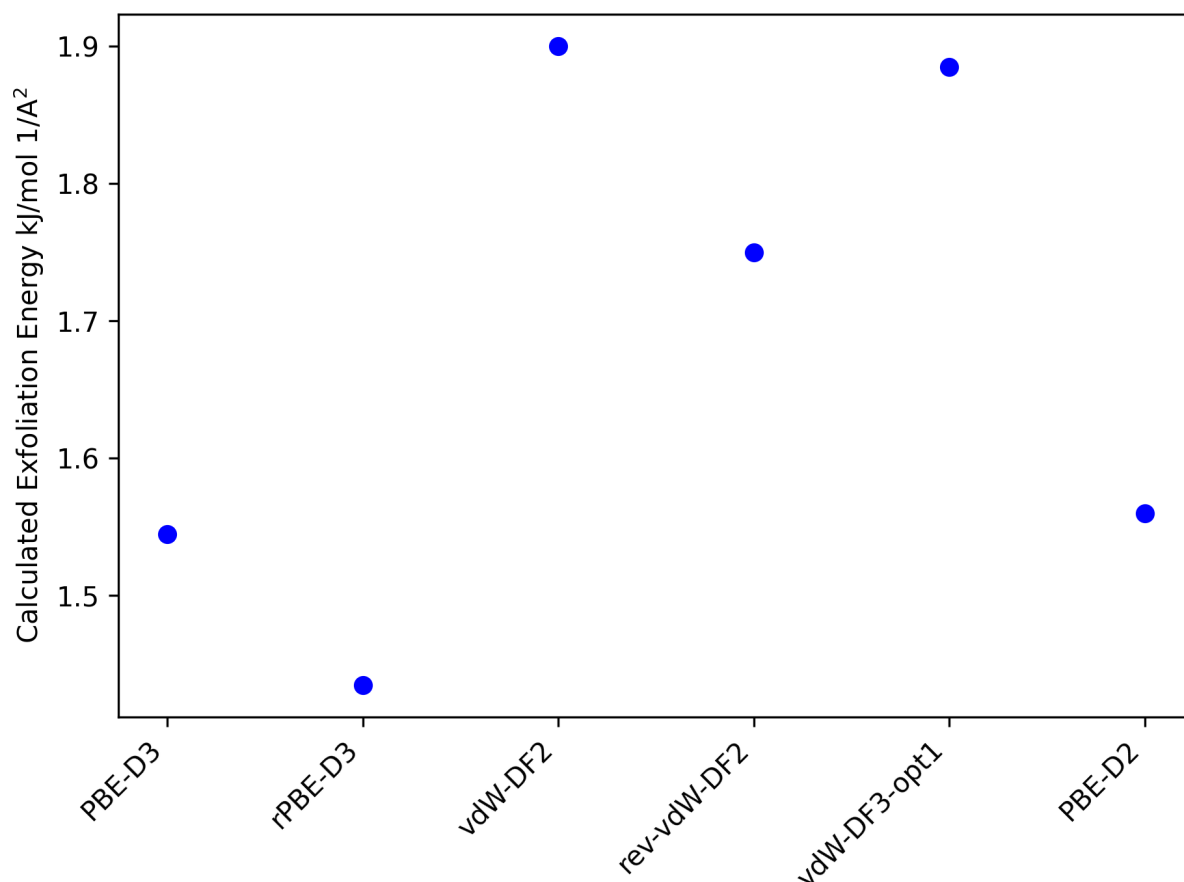


Figure 5.5: Exfoliation energies in $\text{CrCl}_2(\text{pyz})_2$ calculated with different vdW corrections.

$\text{CrCl}_2(\text{pyz})_2$ can be exfoliated.

5.6 Electronic Structure: Kohn-Sham Fundamental Gaps in $(\text{HIS})\text{PbBr}_4$

Figure 5.6 compares the band gaps of $(\text{HIS})\text{PbBr}_4$ computed with different geometries which came from relaxation with different exchange-correlation functionals. It has previously been noticed that in 1D perovskites the choice of the exchange-correlation functional can have a large impact on the lattice parameters of the system, and these changes in the lattice parameters can have a large impact on the Kohn-Sham fundamental gap [113]. Our results look at a wider range of approximations for the vdW interaction, and they include more modern developments in vdW corrected functionals. While the difference between the highest

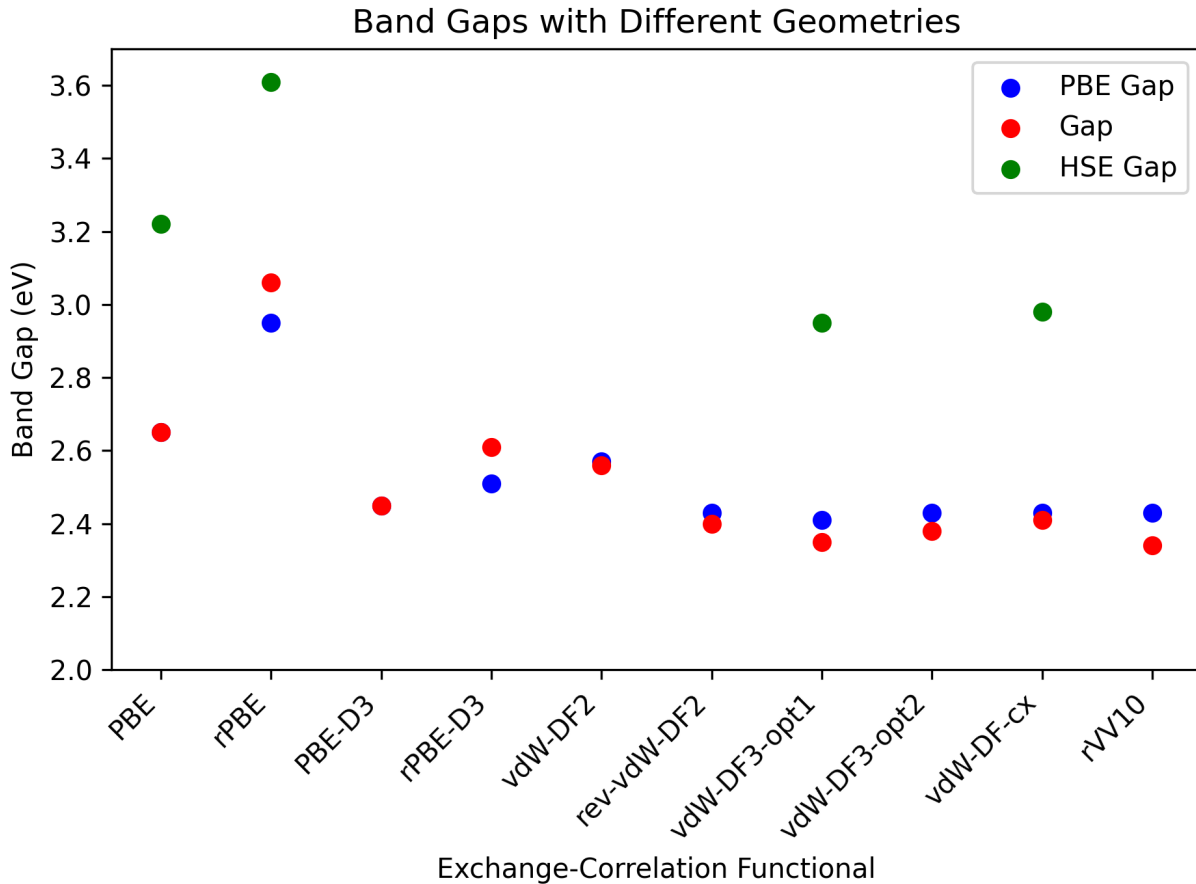


Figure 5.6: (HIS)PbBr₄ Band Gaps Calculated with the vdW functional, PBE, and HSE on geometries relaxed with the functionals on the horizontal axis.

occupied and lowest unoccupied Kohn-Sham states is not a good quantitative prediction of the fundamental gap in a solid, often trends in the Kohn-Sham fundamental gap agree with experimental data, and other ab-initio methods like GW can provide quantitative prediction of the fundamental gap in solids. We do not do GW calculations on all of these geometries because of the computational cost.

For each structure that we relaxed, we computed the band gap in two ways: with the exchange-correlation functional used to relax the geometry, and also with PBE. For a select few geometries we also performed HSE fundamental gap calculations to confirm that the trends with PBE still hold with HSE. We can see that for most of the geometries, the PBE and vdW-corrected exchange-correlation functionals lead to very similar band gaps; this result is expected since vdW-corrected functionals use LDA or GGA local and semi-local exchange correlation in the short range, and the long-range contributions in the vdW

correlation energy does not have a large impact on the fundamental gap. rPBE and rVV10 (which uses PW86r exchange) show somewhat larger deviations, but even so they are within around 0.1 eV of the PBE band gap. A similar result was found in Ref. [113].

If we compare the PBE band gaps across the different structures, we can see that the lattice parameters can have a large impact on the computed band gap, with the PBE band gaps ranging from 2.43 eV to 2.95 eV, a 21% variation in the computed band gap. With HSE, we see a similar trend, with band gaps ranging from 2.95 eV to 3.61 eV, a 22% variation in the calculated gaps for (HIS)PbBr₄. Additionally, we can see a clear trend that the functionals which predict the largest lattice parameters have the largest band gaps. Figure 5.6 plots the band gaps vs. lattice parameter distance, with the lattice parameters coming from each of the functionals we tested.

These results show a sensitive dependence of the band gap on the lattice parameters, and a GGA functional without vdW corrections will be insufficient to get accurate lattice parameters. This result is in line with similar trends in 1D-perovskites [113]. Fortunately, we find that modern methods we studied here for capturing the vdW interaction perform well compared to the 100 K experimental lattice parameters, as all but two vdW corrections (vdW-DF2 and rPBE-D3) tested were within 1% of the experimental lattice parameters. While we have shown that some functionals, such as vdW-DF3-opt1/2 and rVV10, tend to have smaller lattice vectors than others, such as PBE-D3, rPBE-D3, and vdW-DF2, across MX₂(pyz)₂ and (HIS)PbBr₄, all of these methods show significant improvements compared to relaxations with PBE and rPBE. Often the electronic structure of a system is computed without relaxing the lattice parameters using the geometry from XRD experiments. However, when this is not possible or advised, vdW interactions need to be included to get an accurate structure. Even though the layers of (HIS)PbBr₄ are weakly interacting with each other, the band gap of the bulk material changes as the layer separation changes. For example, we observe that the PBE lattice constant differs from that of PBE-D3 by around 5% and the PBE band gap calculated on those two structures differs by around 5% as well, which while not a large difference, can be important if one wants to get as accurate of a prediction as possible.

5.7 Effect of Pseudopotentials

Table 5.1 compares the lattice parameters of CrCl₂(pyz)₂ with $U = 3.7$ eV and with GBRV ultra soft pseudopotentials compared with Pseudodojo norm-conserving pseudopotentials. Both sets of pseudopotentials are generated with PBE. In the ab-plane there is minimal variation in the lattice parameters with pseudopotentials, just about 0.4%. For the out of plane lattice parameters, some functionals like rVV10, vdW-DF3-opt1, and vdW-DF3-opt2 see essentially no change when the pseudopotential is changed. The PBE out of plane lattice parameter differs by 3.4% between the two pseudopotentials.

Functional	a (Å)	b (Å)	c (Å)	Functional	a (Å)	b (Å)	c (Å)
PBE	9.94	9.95	11.74	PBE	9.90	9.92	11.34
PBE-D3	9.88	9.91	10.91	PBE-D3	9.85	9.88	10.84
rPBE-D3	9.92	9.95	10.92	rPBE-D3	9.89	9.92	10.83
vdW-DF2	10.04	10.06	11.00	vdW-DF2	10.05	10.07	10.87
rev-vdW-DF2	9.85	9.88	10.81	rev-vdW-DF2	9.82	9.85	10.77
vdW-DF3-opt1	9.79	9.83	10.64	vdW-DF3-opt1	9.76	9.80	10.63
vdW-DF3-opt2	9.82	9.87	10.66	vdW-DF3-opt2	9.80	9.84	10.66
rVV10	9.89	9.94	10.66	rVV10	9.90	9.93	10.63

Table 5.1: Lattice parameters of $\text{CrCl}_2(\text{pyz})_2$ with GBRV ultrasoft pseudopotentials (left) and Psuedojo norm conserving pseudopotentials (right) calculated with Quantum Espresso and different vdW approximations.

5.8 Effect of Hubbard U

Table 5.2 compares the lattice parameters of $\text{CrCl}_2(\text{pyz})_2$ with $U = 0$ eV and $U = 3.7$ eV on Cr with a range of vdW corrections, calculated in VASP With $U = 3.7$ eV, for all vdW corrections the ab-plane lattice parameters are consistently larger and the c lattice parameter is consistently smaller than those with $U = 0$. The out of plane lattice parameter is about 0.5% smaller with $U = 3.7$ eV compared to the $U = 0$ eV calculations with all functionals studied. The ab-lattice parameter is about 1% larger with $U = 3.7$ eV compared with $U = 0$ eV calculations.

Functional	a (Å)	b (Å)	c (Å)	Functional	a (Å)	b (Å)	c (Å)
PBE-D3	13.96	13.96	10.66	PBE-D3	13.86	13.86	10.73
rev-vdW-DF2	13.94	13.94	10.65	rev-vdW-DF2	13.79	13.79	10.70
vdW-DF2	14.20	14.20	10.80	vdW-DF2	14.07	14.07	10.86
vdW-DF-cx	13.93	13.92	10.74	vdW-DF-cx	13.76	13.77	10.81

Table 5.2: Lattice parameters of $\text{CrCl}_2(\text{pyz})_2$ calculated with VASP using PAW pseudopotentials and a Hubbard U of 3.7 eV (left) and 0 eV (right). These calculations are in a 2x2x1 cell, so the a and b lattice vectors are longer than the ones in Table 5.1, which used a $\sqrt{2}\times\sqrt{2}\times 1$ cell.

5.9 Conclusion

We have performed calculations for a select number of approximations for the van der Waals interaction in solids. We find they are, in some cases, in quantitative agreement with respect to experimental lattice parameters in both metal-organic frameworks and in hybrid organic-inorganic perovskites. The different functionals lead to large variations in DFT calculated exfoliation energies and gaps, so one must be careful with which functional is used for geometry optimization. Experimental exfoliation energies of CrCl_2 would help clarify which functionals perform best for predicting its exfoliation energies. Fortunately, for structural properties and DFT gaps, the vdW approximations, while showing some variation, give much better agreement with experiment than PBE and rPBE, which do not include long range correlation. PBE-D3, rVV10, rev-vdW-DF2, vdW-DF-cx, vdW-DF3-opt1, and vdW-DF3-opt2 tend to have the best agreement with experimental low temperature lattice parameters in our study. Additionally, we have shown that the choice of pseudopotentials and Hubbard U for open shell systems can have similar impacts on the geometry as the choice of van der Waals functional where deviations in the lattice parameters of around 1-3% can be seen between different geometries calculated with the same vdW functional and different U values or pseudopotentials, and similarly deviations in the lattice parameters of around 1-3% can be seen with calculations with the same U value and pseudopotential but a different vdW functional. Prior works [99, 102] showed that the choice of Hubbard U alongside a vdW correction can have a small impact in CO_2 binding to transition metals, but a large impact in O_2 binding to transition metals, with the difference coming from some amount of electron transfer in the case of O_2 , but none in CO_2 . Thus, the chemistry of the material can have a strong impact on how much the choice of U value will have on the predicted properties.

Chapter 6

Modelling Cooperative Adsorption in Amine-Appended Metal-Organic Frameworks

In Chapter 3 we discussed calculations relevant to the impact of SO_2 on CO_2 capture performance in diamine-appended $\text{Mg}_2(\text{dobpdc})$ MOFs. These amine-appended MOFs exhibit novel step-shaped isotherms [78, 80, 81, 103, 144, 145]. Here, we develop a model of features of these isotherms arising from more complex interactions in the MOFs than nearest neighbor cooperative bonding interactions.

The step-shaped isotherms associated with CO_2 adsorption in diamine-appended $\text{Mg}_2(\text{dobpdc})$ (MOF-274) is an advantage over materials with Langmuir adsorption behavior because for step-shaped isotherms the change in working capacity across a small pressure swing is much larger. For the most part in these systems, the steps stem from 1D ammonium carbamate chains that form cooperatively along the c -axis of the MOF. The binding of one CO_2 promotes additional binding at neighboring sites along the c -axis, giving rise to the cooperative behavior. Recent studies have shown how step-shaped isotherms can have a single or a double step depending on the size of the amine [145, 146], and the size of the pore of the MOF [145, 147]. These results have suggested that steric energetic penalties may play a role in double-stepped isotherms, but previous modelling did not incorporate steric hindrance in the a - b plane [2]. Additionally, recent unpublished experiments have shown that the introduction of monoamines, which cannot form ammonium carbamate chains because they have only one amine group, does not inhibit step-shaped adsorption, even with large concentrations of defect sites. This result indicates that diamine-appended MOFs have robust cooperative adsorption, even in the presence of defects.

In what follows, we extend a prior lattice model of cooperative adsorption to include defect sites and show that depending on how large the cooperative binding energy is in diamine-appended MOF-274, cooperative adsorption can persist even with only $\sim 2 - 5$ consecutive diamine sites along the c -axis, rationalizing the experimental studies. We further study systems of 1D chains with a mixture of diamines to understand the impact of the diamine

cluster sizes and CO₂ binding affinities on the isotherms. We show that large clusters of amines yield double stepped isotherms, while for smaller clusters we get single steps with a step at the same temperature/pressure for isobars/isotherms corresponding to that expected for a single amine with a binding energy equivalent to a weighted average of the two amines' binding energies.

6.1 Lattice Model

In what follows, we introduce some of the basics of the statistical mechanics of lattice models of gaseous adsorption, and then discuss a previous model and the modifications we make.

Gas adsorption¹ is a process in which gas molecules bind to the surface of a material. There is a long history of studying gas adsorption, and recently MOFs have attracted a lot of interest for their novel adsorption behavior. In principle, MOFs are appealing for gas adsorption because they have large pores, and high surface areas, and they have tunable components so that specific gas molecules can be targeted for adsorption.

One of the simplest models for gas adsorption is the Langmuir model [148, 149]. An isotherm or isobar of adsorption tells us how many gas molecules are bound to the system as we change the temperature or pressure of the system while keeping the other parameter fixed. It is straightforward to derive the Langmuir isotherm. Consider a system which has N sites which can bind a molecule with energy $-E$ (E is positive so that the system lowers its energy when the molecule binds). The sites do not interact with each other, and there is assumed to be a bath of an ideal gas molecule at chemical potential μ . The grand partition function of the system is given by

$$\mathcal{Z} = \sum_n \binom{N}{n} e^{-\beta En + \beta \mu n} \quad (6.1)$$

where our sum is over all possible numbers of adsorbed molecules, n , and $\beta = \frac{1}{k_B T}$. There are $\binom{N}{n}$ ways to distribute these molecules across the N sites, all with identical energies. We can then perform the summation via

$$\mathcal{Z} = \sum_{n=0}^N \binom{N}{n} (e^{\beta(\mu-E)})^n = (1 + e^{\beta(\mu-E)})^N \quad (6.2)$$

with the binomial theorem. The grand potential per site, $\omega = \Omega/N$, is then given by

$$\omega = \frac{\Omega}{N} = \frac{-k_B T}{N} \log(\mathcal{Z}) = \frac{-k_B T}{N} \log((1 + e^{\beta(\mu-E)})^N) \quad (6.3)$$

$$= -k_B T \log(1 + e^{\beta(\mu-E)}) \quad (6.4)$$

¹Not absorption!

The average value of the number of gas molecules adsorbed per site, $\langle n \rangle$, is given by

$$\langle n \rangle = \frac{1}{N\mathcal{Z}} \sum_n n \binom{N}{n} e^{-\beta En + \beta \mu n}, \quad (6.5)$$

which can be obtained with a partial derivative of ω ,

$$\langle n \rangle = -\frac{\partial \omega}{\partial \mu}, \quad (6.6)$$

giving an average particle number of:

$$\langle n \rangle = \frac{k_b T}{N\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \mu} = \frac{k_b T}{N\mathcal{Z}} N (1 + e^{\beta(\mu-E)})^{N-1} \beta e^{\beta(\mu-E)} \quad (6.7)$$

$$= \frac{(1 + e^{\beta(\mu-E)})^{N-1} e^{\beta(\mu-E)}}{(1 + e^{\beta(\mu-E)})^N} \quad (6.8)$$

$$= \frac{e^{\beta(\mu-E)}}{1 + e^{\beta(\mu-E)}}. \quad (6.9)$$

This equation is commonly written as

$$\langle n \rangle = \frac{x}{1 + x} \quad (6.10)$$

with $x = e^{\beta(\mu-E)}$. In equilibrium, the chemical potential of the adsorbed gas equals the chemical potential of the gas of molecules. Thus, we can use the expression for the chemical potential of an ideal gas of molecules with temperature T , $\beta = (k_B T)^{-1}$ at pressure P , i.e.,

$$e^{\beta \mu} = \beta P \Lambda^3 \quad (6.11)$$

with $\Lambda = \sqrt{\frac{2\pi\hbar^2}{mk_B T}}$ the thermal deBroglie wavelength to convert the chemical potential to a pressure in order to calculate an isotherm. Isotherms can be calculated by varying the pressure for a fixed temperature. Taking P as the independent variable and expressing $\langle n \rangle$ in terms of P ,

$$\langle n \rangle = \frac{e^{\beta \mu} e^{-\beta E}}{1 + e^{\beta \mu} e^{-\beta E}} = \frac{\beta P \Lambda^3 e^{-\beta E}}{1 + \beta P \Lambda^3 e^{-\beta E}} \quad (6.12)$$

$$= \frac{P}{P_0(T) + P} \quad (6.13)$$

with

$$P_0(T) = \frac{e^{\beta E}}{\beta \Lambda^3} \quad (6.14)$$

At lower temperatures in the Langmuir isobar more of the gas is adsorbed because the ground state is one in which every site has a gas molecule. Similarly, at higher pressures in the isotherm, more of the gas is adsorbed because more gas molecules are present. These general trends at high and low temperature and high and low pressures hold for many gas adsorption systems. An isobar at higher pressures will have most of the gas uptake at higher temperatures, while an isobar at lower pressures will have most of the gas uptake at lower temperatures.

In cooperative adsorption, neighboring sites interact with each other and facilitate further binding. Therefore, to model cooperative adsorption, we must extend the model introduced above to include interactions. The simplest model would be a 1D Ising model with nearest-neighbor interactions. We first note how the Hamiltonian for the Langmuir independent particle limit can be written as

$$H_L = \sum_{n=0}^N -\sigma_n E, \quad (6.15)$$

where

$$\sigma_n = \begin{cases} 1 & \text{site } n \text{ occupied} \\ 0 & \text{site } n \text{ unoccupied} \end{cases} \quad (6.16)$$

is of the same form as a 1D Ising model, namely

$$H_I = \sum_{n=0}^N -J\sigma_n\sigma_{n+1} - \sum_{n=0}^N \sigma_n B \quad (6.17)$$

where $J = 0$. In the Ising model, one typically lets the spin states be $+1$ and -1 ; if we define the Langmuir σ_n sites as $\frac{1}{2}(1 + \sigma_{\text{Ising}})$ then the two models map to each other with an appropriate redefinition of B as the energy gained upon gas adsorption in the case of the Langmuir model. Here, we introduce an effective J for cooperative adsorption, assuming a periodic system where sites $N + 1$ and 0 are equivalent can be thought of as a simple model for a 1D adsorbate that again has nearest neighbor cooperative interactions which are given by J . This model can be solved using the transfer matrix method, which appears in many textbooks [150, 151].

In the transfer matrix method, one writes the partition function as a product of matrices. Historically, this was first done in Ref. [152]. The total Ising partition function is:

$$Z = \sum_{\sigma_1} \sum_{\sigma_2} \dots \sum_{\sigma_N} e^{\beta \sum_{n=0}^N -J\sigma_n\sigma_{n+1} - \sum_{n=0}^N \sigma_n B}. \quad (6.18)$$

where here σ_n is -1 for spin down and $+1$ for spin up. We can rewrite this as a summation of matrix elements of the transfer matrix, defined as

$$T = \begin{pmatrix} e^{\beta(J+B)} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta(J+B)} \end{pmatrix}. \quad (6.19)$$

This is a 2x2 matrix since σ can take on two values. With the transfer matrix, the partition function becomes

$$Z = \sum_{s_1} \sum_{s_2} \cdots \sum_{s_N} \langle s_1 | T | s_2 \rangle \langle s_2 | T | s_3 \rangle \langle s_3 | \cdots \langle s_{N-1} | T | s_N \rangle \quad (6.20)$$

where the vectors $|s_i\rangle$ are

$$|s_i\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{ for } \sigma_i = 1, \quad (6.21)$$

$$|s_i\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \text{ for } \sigma_i = -1. \quad (6.22)$$

The 2x2 matrix T gives all Boltzmann weights possible between neighboring spins. For example, if $\sigma_2 = 1$ and $\sigma_3 = -1$, this would select one of the off-diagonals of T , $e^{-\beta J}$. The other components of the matrix can be found in a similar manner. One then gets that

$$Z = \text{Tr}[T^N] \quad (6.23)$$

$$= \lambda_+^N + \lambda_-^N \quad (6.24)$$

where $\lambda_{\pm}$ gives the larger and smaller eigenvalue. Applying the transfer matrix method to the 1D Ising model yields

$$m = \frac{\sinh(\beta B)}{\cosh^2(\beta B) - 2e^{-2\beta J} \sinh(2\beta J)} \quad (6.25)$$

where m is the magnetization per site, and other thermodynamic quantities of interest can be found from Z . Early work [153] noted the connection between the Ising model and the lattice gas model, which is a gas adsorption problem in which neighboring gas sites interact with each other with repulsive interactions.

6.2 Chain Polymerization Model for Cooperative Adsorption

In Ref. [2], a model similar to the 1D Ising model was introduced for cooperative adsorption, except each site can bind CO_2 3 different ways, leading to 3 states on each site. Refs. [154, 155] applied this approach earlier in the context of models for polymerization, and provide some useful additional context. They discuss the connection between models for chain polymerization and the Ising model due to the very similar forms of the Hamiltonians that model them. In $\text{Mg}_2(\text{dobpdc})$, a CO_2 binding to one site interacts with CO_2 molecules that bind nearby, and these cooperative interactions give rise to ammonium carbamate chains

along the c-axis of the MOF. Each lattice site has 3 binding modes, which correspond to CO₂ participating in ammonium carbamate chains, CO₂ bound as the end point of a carbamate chain, which only has ammonium carbamate to its left or right, but not both, and finally, CO₂ bound in a way that does not involve ammonium carbamate chain formation, so this mode just has a singly bound CO₂ that is not interacting with its neighbors. These binding modes have energies E_{int} , E_{end} , and E_1 , respectively. The grand partition function for the model can be written as a vector,

$$\bar{\mathcal{Z}}_N = \begin{pmatrix} \mathcal{Z}_N^u \\ \mathcal{Z}_N^p \end{pmatrix}, \quad (6.26)$$

which has components $\mathcal{Z}_N^u$, the partition function of a model with N sites, the last of which is not a part of an ammonium carbamate chain, and $\mathcal{Z}_N^p$ which represents the partition function of a model with N sites, the last of which is a part of an ammonium carbamate chain. In order to go from $\bar{\mathcal{Z}}_N$ to $\bar{\mathcal{Z}}_{N+1}$, one multiplies by the transfer matrix T , given by

$$T = \begin{pmatrix} 1 + K_1 & K_{\text{end}} \\ K_{\text{end}} & K_{\text{int}} \end{pmatrix} \quad (6.27)$$

where the $K_\alpha = \gamma\beta PV_\alpha \exp(-\beta E_\alpha)$ where γ is a fit parameter which characterizes the internal partition function of a binding mode (see below for further discussion), V_α is the volume accessible to CO₂ in each binding mode, and E_α is the binding energy of each mode. P is the pressure of the gas, and $\beta = (k_B T)^{-1}$. One then sets the boundary condition that $\mathcal{Z}_1^u = 1 + K_1$ and $\mathcal{Z}_1^p = K_{\text{end}}$ because the first site will have either no CO₂ or a singly bound CO₂ not involved in ammonium carbamate formation (so that $\mathcal{Z}_1^u$ has the weights for no CO₂ bound or a singly bound CO₂), or it will have an ammonium carbamate chain end site (so that $\mathcal{Z}_1^p$ will have the weight of a CO₂ bound as the end point of an ammonium carbamate). Then, we can write

$$\mathcal{Z}_N^u = \begin{pmatrix} 1 & 0 \end{pmatrix} T^N \begin{pmatrix} 1 \\ 0 \end{pmatrix}. \quad (6.28)$$

We can calculate this partition function exactly for small N by doing repeated matrix-matrix products, but for large N , it is helpful to decompose T in terms of its eigenvalues like

$$T = Q\Lambda Q^{-1} \quad (6.29)$$

where Λ is a matrix with the eigenvalues of T on the diagonal, and Q is a matrix with the eigenvectors of T as its columns (with column i of Q corresponding to the eigenvector of the eigenvalue i in the diagonal matrix Λ). Then, using

$$T^N = (Q\Lambda Q^{-1})^N \quad (6.30)$$

$$= Q\Lambda Q^{-1}Q\Lambda Q^{-1}Q\Lambda Q^{-1} \dots Q\Lambda Q^{-1} \quad (6.31)$$

$$= Q\Lambda^N Q^{-1} \quad (6.32)$$

we can more easily obtain an expression for T^N since a diagonal matrix is easier to exponentiate. Then, one finds that [2, 154, 155]

$$\mathcal{Z}_N^u = \frac{\lambda_+^N(1 + K_1 - \lambda_-) + \lambda_-^N(\lambda_+ - 1 - K_1)}{\lambda_+ - \lambda_-} \quad (6.33)$$

where λ_+ and λ_- are the larger and the smaller of the eigenvalues of T . This expression gives the partition function for a system with maximum size N . We will see later how it gives the same result as if we introduce a defect transfer matrix, D . In the limit $N \rightarrow \infty$, we get

$$\mathcal{Z}_N^u \rightarrow \lambda_+^N \quad (6.34)$$

so that the grand potential per site, ω can be written

$$\omega = -k_b T \log(\lambda_+) \quad (6.35)$$

in the thermodynamic limit.

One can then calculate the adsorbed CO_2 concentration with

$$\langle n \rangle(P, T) = -\beta P \frac{\partial \omega}{\partial P}. \quad (6.36)$$

We can see this result using an equivalent form of the grand potential from Ref. [2]

$$\omega = \sum_{n_1, n_{\text{int}}, n_{\text{end}}} K_1^{n_1} K_{\text{end}}^{n_{\text{end}}} K_{\text{int}}^{n_{\text{int}}} \Gamma(n_1, n_{\text{int}}, n_{\text{end}}) \quad (6.37)$$

where Γ is the number of ways to arrange all of these sites. This expression depends on P only through the K_α , and one can show that

$$\frac{\partial(K_\alpha^N)}{\partial P} = N K_\alpha^{N-1} K_\alpha * \frac{1}{P} = N K_\alpha^N * \frac{1}{P}, \quad (6.38)$$

so that the P partial derivative will bring down the N_α for each state and then multiplication by P restores that factor.

6.3 Finite Chains of Ammonium Carbamate

Finite chains of ammonium carbamate, separated by “defects” where no CO_2 is adsorbed can be studied using eqn. (6.33). We introduce a defect transfer matrix,

$$D = \begin{pmatrix} 1 & 1 \\ 0 & 0 \end{pmatrix} \quad (6.39)$$

which when multiplied by T will force a chain to be finite since it zeroes out the $\mathcal{Z}_n^p$ on the next site. By replacing 1 with a K_1 -like term, one could also allow the defects to bind singly bound CO_2 . Similarly, one could instead use the matrix

$$D_2 = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \quad (6.40)$$

to further prevent the last site from being involved in ammonium carbamate since that would eliminate the $\mathcal{Z}_{N-1}^p$ component of the restricted partition function. The matrices D and D_2 as defined above some useful properties, namely $D^2 = D$ and $D_2^2 = D_2$; both are projectors. This property is important physically since we do not allow multiple defects in a row to modify the partition function in our model, so $TD^N = TD$. Additionally, for a generic matrix,

$$A = \begin{pmatrix} a & b \\ c & d \end{pmatrix} \quad (6.41)$$

DAD , DA , and AD have the same eigenvalues, $\lambda = a + c, 0$. (Note that this property holds for D_2 with $\lambda = a$). Then, if we want N sites to be accessible with defects on both sites, we can construct the partition function as $DT^N D$. In the case of $N = 1$, we would expect Langmuir adsorption. Indeed, finding $\langle n \rangle$ for DTD yields

$$\langle n \rangle = \frac{P}{C + P} \quad (6.42)$$

with C depending on temperature, which is the same functional form as Langmuir adsorption in eqn. (6.10). We note that eqn. (6.33) for $N = 1$ also gives:

$$\mathcal{Z}_1 = \frac{\lambda_+(1 + K_1 - \lambda_-) + \lambda_-(\lambda_+ - 1 - K_1)}{\lambda_+ - \lambda_-} \quad (6.43)$$

$$= \frac{(\lambda_+ - \lambda_-)(1 + K_1)}{\lambda_+ - \lambda_-} \quad (6.44)$$

$$= 1 + K_1 \quad (6.45)$$

so that

$$\omega = -k_B T \log(1 + K_1) \quad (6.46)$$

$$\langle n \rangle = -\beta P (-k_B T \frac{\partial \log(1 + K_1)}{\partial P}) = \frac{P}{1 + K_1} \frac{\partial K_1}{\partial P} \quad (6.47)$$

$$= \frac{K_1}{1 + K_1} \quad (6.48)$$

$$= \frac{\beta P V_1 e^{-\beta E_1}}{1 + \beta P V_1 e^{-\beta E_1}} = \frac{P}{C + P} \quad (6.49)$$

which is the Langmuir form. In the above, we let $K_1 = \beta P V_1 e^{-\beta E_1}$ and $C = \frac{e^{\beta E_1}}{\beta V_1}$ which agrees with eqn (6.14) after taking into account the translational degrees of freedom of the adsorbate as in Ref. [2], leading to a factor of $V_1 \Lambda^{-3}$ in the denominator.

More generally, since the largest eigenvalue of $T^N D$ equals $T_{11}^N + T_{12}^N$ and eqn. (6.28) gives $\mathcal{Z}_n = T_{11}^N$, our results using the largest eigenvalue of $T^N D$ are similar to those using eqn. (6.33), except we also include a term with T_{12}^N . This T_{12}^N term in the sum comes from allowing the amine site to bind CO_2 in the singly bound state, and also in the ammonium carbamate chain end point state. For example, while $\mathcal{Z}_1 = 1 + K_1$ using eqn. (6.33), we use $\mathcal{Z}_1 = 1 + K_1 + K_{\text{end}}$, meaning our single site can have CO_2 bound in either the singly or end point only configuration. If we instead used D_2 , then we would get the same result as eqn. (6.28) where $\mathcal{Z}_N = T_{11}^N$. Both choices for the defect transfer matrix are valid, and represent cases where we want the site adjacent to a defect to be able to bind CO_2 in the singly bound or the ammonium carbamate end point configurations.

We choose D rather than D_2 because we are interested in cases with $N \sim 5$ where our boundary sites should be allowed to be carbamate chain end point sites. For the Langmuir case, the choice of D or D_2 would depend on whether or not in the physical system the chain end point configuration is possible without any neighbors being a part of an ammonium carbamate chain. Without detailed knowledge of the kinetic process that govern cooperative adsorption in this class of MOF, it is unclear if CO_2 first inserts in the end chain configuration with no neighbors as a part of a chain, or if some other process with different energetics happens first before chains start forming.

6.4 Mixed Amines

We can use this framework and consider models with amines which have different CO_2 binding energies in different patterns by using two transfer matrices, T_1 and T_2 which have the same form as eqn. (6.27), but with their own K_α weights corresponding to their own sets of CO_2 binding energies. Then, if we want a pattern of n diamines of amine 1 and m diamines of amine 2, we construct a transfer matrix

$$T = T_1^n T_2^m, \quad (6.50)$$

and solve it using the same methods as the original model. For large n or large m , symbolically doing the matrix product can be difficult, so either an eigendecomposition or numerical implementation is faster. We use a numerical implementation.

6.5 Two Lane Model

The model described above is referred to as a “one lane model” in Ref. [2], and they also introduce a two lane model which can capture effects that depend on diamines’ neighbors across the pore of the MOF. Figure 6.1 shows the pore of the MOF, which has 6 1D chains

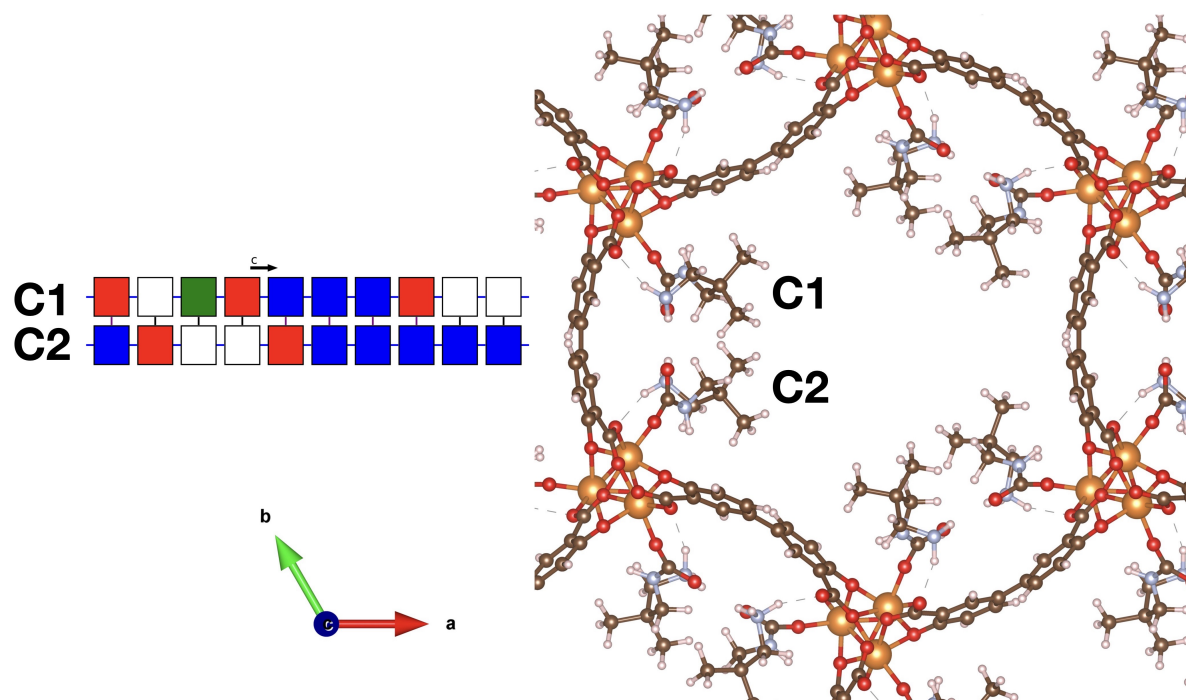


Figure 6.1: Example of diamine-appended MOF with ammonium carbamate chain. There are 6 “lanes,” which are 1D chains along the c -axis. The one lane model considers just a single chain, C1, while the two lane model considers the interactions between chains C1 and C2 which are closest to each other in the pore. On the left, we have an example configuration in the two lane model. Red squares are chain end sites, blue squares are chain internal sites, green squares are singly bound CO_2 , and empty squares have no CO_2 . Purple lines between the two chains indicate when the E_{ab} penalty would be applied because adjacent sites on C1 and C2 have CO_2 on them.

that are referred to as lanes. Most of the effects can be understood in terms of a one lane model since the dominant interactions involve ammonium carbamate, which can only form along the c -axis. To explore interactions in the a - b plane, we construct a minimal model which involves 2 1D chains that can interact with each other along the a - b plane.

Ref. [2] also details a two lane model in the context of understanding adsorption of carbamic acid species, which bridge the a - b plane. Here, we consider steric energy penalties in the a - b plane. In any case, such models have restricted partition functions that have four

components,

$$\begin{pmatrix} \mathcal{Z}_N^{L,u;R,u} \\ \mathcal{Z}_N^{L,u;R,p} \\ \mathcal{Z}_N^{L,p;R,u} \\ \mathcal{Z}_N^{L,p;R,p} \end{pmatrix} \quad (6.51)$$

where $\mathcal{Z}_N^{L,u;R,u}$ corresponds to the left chain having its N th site not in an ammonium carbamate and its right chain also not in an ammonium carbamate. The other components correspond to the 3 other cases for the left and right chain being a combination of participating and not participating in ammonium carbamates. The transfer matrix can be obtained via inspection (by seeing what K_α weights have to be added to get the next restricted partition function from the previous one). It equals

$$\begin{pmatrix} 1 + 2K_1 + K_d^2 & K_e(1 + K_1) & K_e(1 + K_1) & K_e^2 \\ K_e(1 + K_1) & K_i(1 + K_1) & K_e^2 & K_i K_e \\ K_e(1 + K_1) & K_e^2 & K_i(1 + K_1) & K_i K_e \\ K_e^2 & K_i K_e & K_i K_e & K_i^2 \end{pmatrix}. \quad (6.52)$$

Using this transfer matrix, we calculate ω and $\langle n \rangle$. Finally, we introduce an energy penalty for having the N th site of the left and right being involved in ammonium carbamate. We want all elements $\mathcal{Z}_N^{L,p;R,p}$ to be penalized by an energy E_{ab} which is the energy penalty for neighboring sites to be occupied. Physically, this would correspond to neighboring diamines in the a-b plane interacting with each other in a way that reduces the CO₂ binding energy. We want all of our

$$\mathcal{Z}_N^{L,p;R,p} \rightarrow \mathcal{Z}_N^{L,p;R,p} e^{-\beta E_{ab}}. \quad (6.53)$$

This term models a steric energy penalty wherein the cooperative driving force is reduced in bulky amines which “get in each other’s way” of facile CO₂ binding to an adjacent site in the a-b plane. Figure 6.1 has an example of a MOF where pairs of diamines are close to each other in the a-b plane. Less bulky amine molecules have minimal effect on each other, but bulkier amines can prevent their neighbor from having more energetically favorable configurations after CO₂ binding. We can introduce this change by adding a term $e^{-\beta E_{ab}}$ to the last row of the two lane transfer matrix in 6.52 because

$$\mathcal{Z}_N^{L,p;R,p} = \sum_i T_{4i} \mathcal{Z}_i^{N-1}. \quad (6.54)$$

6.6 Internal Partition Function Free Parameter

Ref. [2] has a free parameter (see the Errata in that paper) that plays an important role in determining the step position. Table 6.1 shows the step position for different values of the free parameter, γ .

Isotherm Temp (K)	Step P, $\gamma_1 = 11 * 10^{-3}$	Step P, $\gamma_2 = 4.25 * 10^{-3}$	Expt. Step P
298	0.1	0.25	< 0.25
313	0.5	1	1-5
323	1.4	4	1-20
348	13.75	35	5-20
373	100	250	100
393	410	1150	300
405	900	2300	1000

Table 6.1: Step pressures in mbar. Experimental step pressures from Ref. [81]. γ_1 was chosen so that the step position at 373 K matched experiment, and γ_2 was chosen so that the step position at 298 K matched. Binding energies were chosen based on the experimental values in Ref. [81], and the volume parameters are the same as those in Ref. [2].

We can see that γ chosen has a large impact on the predicted step position. Even so, when we fit the parameter to agree with the step at 373 K, the rest of the step positions are similar to the experimental ones at other temperatures, so that we are able to capture trends in the isotherms.

6.7 Discussion

The model from Ref. [2] has 6 parameters that correspond to experimental observables, and one parameter which is treated as a fitting parameter that is related to the internal partition of the bound CO_2 . While in principle one could have a γ_i for each binding mode, Ref. [2] only uses one. Since the step is dominated by the energetics and internal degrees of freedom of the carbamate chain binding mode, it is reasonable to only use a single γ which corresponds to that mode. In addition to E_1 , E_{int} , and E_{end} , we have V_1 , V_{int} , and V_{end} which are the volumes accessible of the bound CO_2 in the single, carbamate chain internal, and carbamate chain end configurations. The accessible volume refers to an estimate of the translational freedom of the CO_2 molecule in each binding mode. These accessible volumes were estimated in Ref. [2]. In the case of a-b plane interactions, we have an energy penalty E_{ab} associated with steric hindrance between CO_2 molecules bound at adjacent sites. The fitting parameter in the model comes from the internal degrees of freedom of bound CO_2 , and it is treated as a fit parameter by setting it so the experimental step-positions at different temperatures and pressures are reproduced. See Table 6.1 to see how we determined the fit parameter. Experimentally, different diamines, for example with varying alkanes or functional groups, with similar binding energies can have different step positions due to their different entropies. Our fit parameter is able to capture this effect by moving the step in the isotherms/isobars. At zero CO_2 loading and at full CO_2 loading, the configurational entropy is zero since there

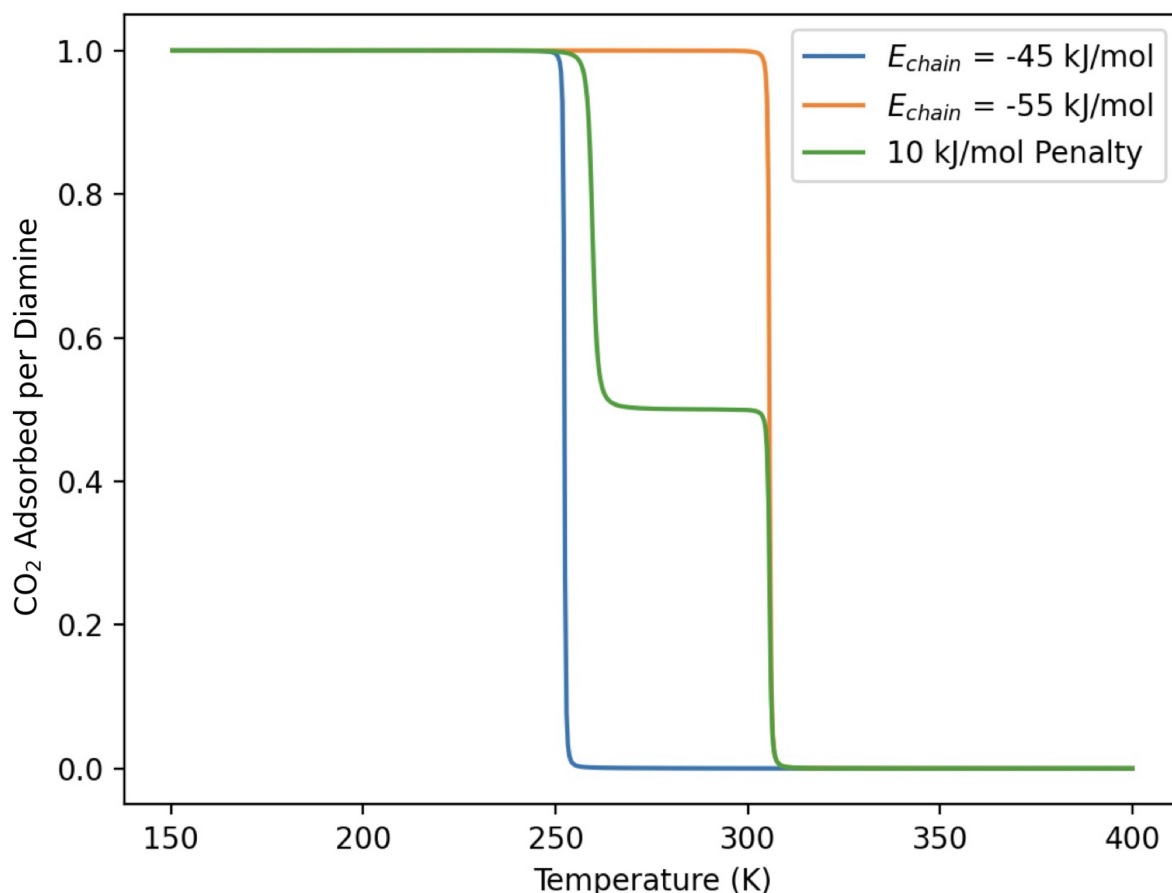


Figure 6.2: Isobar at 200 mbar comparing systems with no steric hindrance and a -45 kJ/mol ammonium carbamate binding energy (blue), a -55 kJ/mol ammonium carbamate binding energy (orange), and a -55 kJ/mol ammonium carbamate binding energy with a 10 kJ/mol steric hindrance if sites which are adjacent on two different chains are occupied.

is only one way to arrange no or full CO_2 onto the binding sites. Thus, all of the entropy at full loading comes from the internal degrees of freedom of the amines, so that our fit parameter is able to empirically capture entropic effects.

First, we discuss the results of the results of the two lane model with steric hindrance. Figure 6.2 shows an example isobar at 200 mbar calculated with $E_{int} = -45$ kJ/mol, and $E_{ab} = 10$ kJ/mol. Additionally, we plot two isotherms, one with $E_{ab} = 0$ and $E_{int} = -55$ kJ/mol, and another with $E_{ab} = 0$ and $E_{int} = -45$ kJ/mol. We can see that when we add steric hindrance we end up with a double stepped isobar that can be understood with the first step happening at the pressure that the single step would be without any steric hindrance

penalty, and the second step happening in a similar position to where the step would be if E_{int} were reduced from the first isotherm by E_{ab} . This picture is consistent with half of the CO₂ first binding to form one chain along one of the lanes in the pore of the MOF without incurring any energy penalty due to their empty neighboring sites, and the rest of the CO₂ binding to the other chain with their binding energy reduced by the steric hindrance energy penalty.

From this result, we see that a model which includes steric hindrance can explain double stepped isotherms, and also the model enables us to interpret experimental isotherms to estimate how large the steric hindrance penalty is. Previous work [2, 81, 86] has found that the trend between the step position and the ammonium carbamate binding energy, follows the functional form of the Clausius-Clapeyron relation:

$$P_{\text{step}}(T) = P_0 e^{\frac{H_{\text{step}}}{R}(\frac{1}{T_0} - \frac{1}{T})} \quad (6.55)$$

where R is the ideal gas constant, and H_{step} is the binding energy. If one knows the step at T_0 is P_0 , then one can estimate the step at some other temperature T using this relation. By fitting this functional form to the first and second step positions we can determine the steric hindrance energy penalty.

Now, we turn to the defect model. Figure 6.3 shows an example isotherm at 300 K with $E_{int} = -55$ kJ/mol and a maximum ammonium carbamate chain length going from $N = 1$ to 10. For $N = 1$ we recover Langmuir adsorption since the binding is independent at each site, and the functional form for our isotherm also ends up being identical to that of Langmuir adsorption, as discussed in the Methods section. For these parameter values, there is little uptake in the Langmuir regime. For $1 < N \leq 3$, there's a broad adsorption step that is more cooperative than Langmuir adsorption, but not nearly as sharp as the isotherms for $N \geq 5$. Figure 6.4 shows isotherms with the same set of parameters for chain lengths 10-100, and the infinite chain. We can see that for these parameters, the isotherm is very similar to the infinite chain.

For larger binding energies, we can get much faster convergence to the infinite chain limit. Figure 6.5 shows a system with E_{int} of -65 kJ/mol, and the same other parameters as the isotherms in Figure 6.3. Now, the non-cooperative Langmuir model shows about 80% capacity achieved within this pressure range, and with only 2 amine sites that can interact cooperatively with each other we get a step. Two amine sites are the minimum number of sites required to form ammonium carbamate because the CO₂ interacts with two amines along the c-axis when it forms ammonium carbamate. The step pressure of the infinite chain with these parameters at 300 K is 3 mbar; Ref. [81] shows that around 300 K and even higher temperatures there can be steps around 1-5 mbar for five diamines (see the Supplementary Information). They estimate binding enthalpies in the -78 - -100 kJ/mol range, which is similar to the interaction energy that we are using.

Given that only a few cooperative sites are needed provided that the E_{int} is sufficiently strong, we can see that the infinite connectivity along the pore of Mg₂(dobpdc) actually is

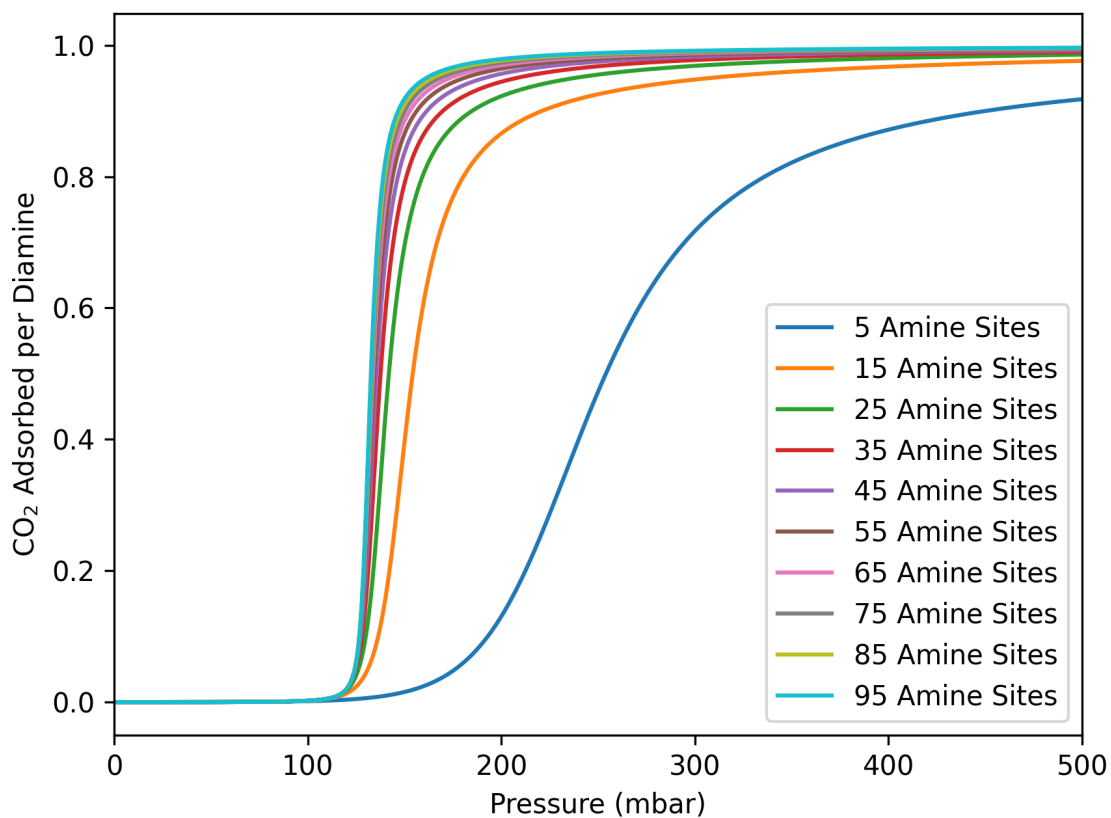


Figure 6.3: Isotherm at 300 K comparing systems with an ammonium carbamate binding energy of -55 kJ/mol, which are limited to different maximum chain lengths, N , with transfer matrix $T^N D$.

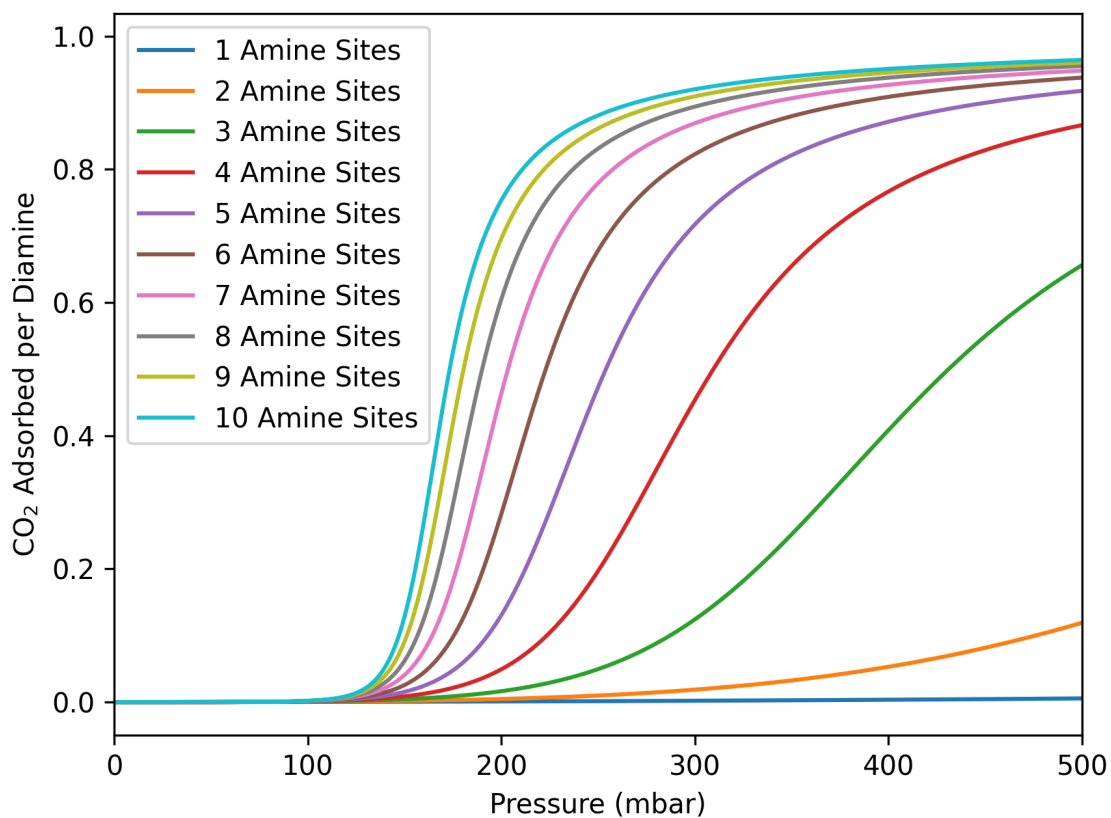


Figure 6.4: Isotherm at 300 K comparing for systems with an ammonium carbamate binding energy of -55 kJ/mol, which are limited to different maximum chain lengths, N , with transfer matrix $T^N D$.

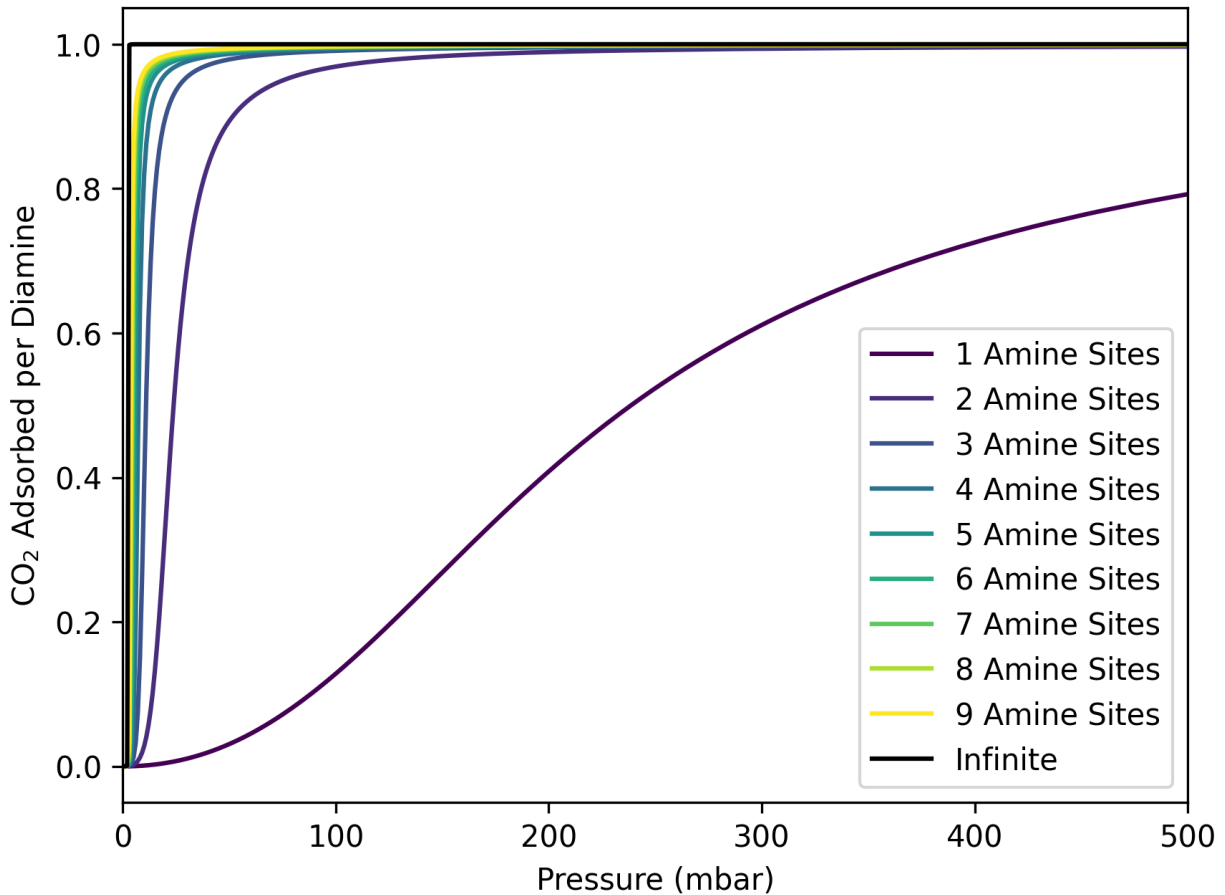


Figure 6.5: Isotherm comparison for systems with an ammonium carbamate binding energy of -65 kJ/mol, which are limited to different maximum chain lengths, N , with transfer matrix $T^N D$.

not needed to observe step-shaped isotherms. Instead, isolated metal nodes, like those in CoBTri [89] or Zn-MFU-4l [156] could also host cooperative adsorption, provided that the degree of cooperativity, defined by the gain in energy associated with binding at an adjacent site, is strong enough. Another system which shows cooperative adsorption is O_2 binding to hemoglobin. In hemoglobin, binding of O_2 to one site causes a structural reorganization that promote O_2 binding at the 3 neighboring sites, thus hemoglobin has non-Langmuir adsorption with only 4 binding sites [157].

In the case with mixed amines, we study systems with different distributions of amines to understand trends in their isotherms. We consider having two types of diamines which bind CO_2 in the ammonium carbamate chain with binding energies of -55 kJ/mol and -52.5 kJ/mol. For simplicity, we assume that the singly bound CO_2 binding energy is the same for

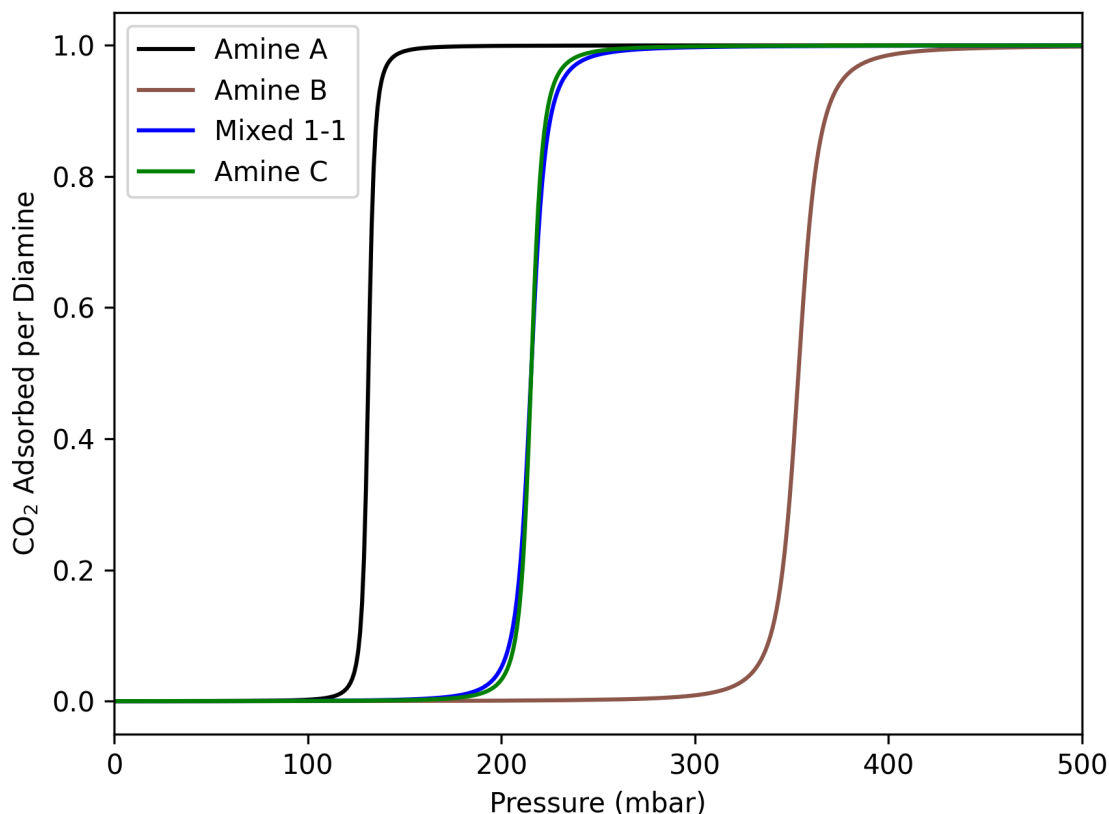


Figure 6.6: Isotherm with alternating pattern of amines A (with a cooperative binding energy of -55 kJ/mol) and B (with a cooperative binding energy of -52.5 kJ/mol). Amine C has a cooperative binding energy of -53.75 , and its step coincides very well with the pattern of alternating amines A and B.

both amines, and we follow Ref. [2] in assuming that a carbamate chain end site has binding energy of $0.8 \cdot E_{int}$ where E_{int} is the binding energy of CO_2 in an ammonium carbamate chain.

Figures 6.6 and 6.7 show isotherms with small clusters, which have patterns of 1 of amine A and 1 of amine B, and large clusters, which have patterns of 50 of amine A and 50 of amine B. In the case of small clusters, we get just a single step, whereas in the case of large clusters, we get a double step. Figure 6.6 also shows three additional isotherms for single amine systems: a system that is all amine A, a system that is all amine B, and a system that is a third amine whose ammonium carbamate chain binding energy is the average of the binding energies of amine A and amine B. We can see that the single step with small clusters

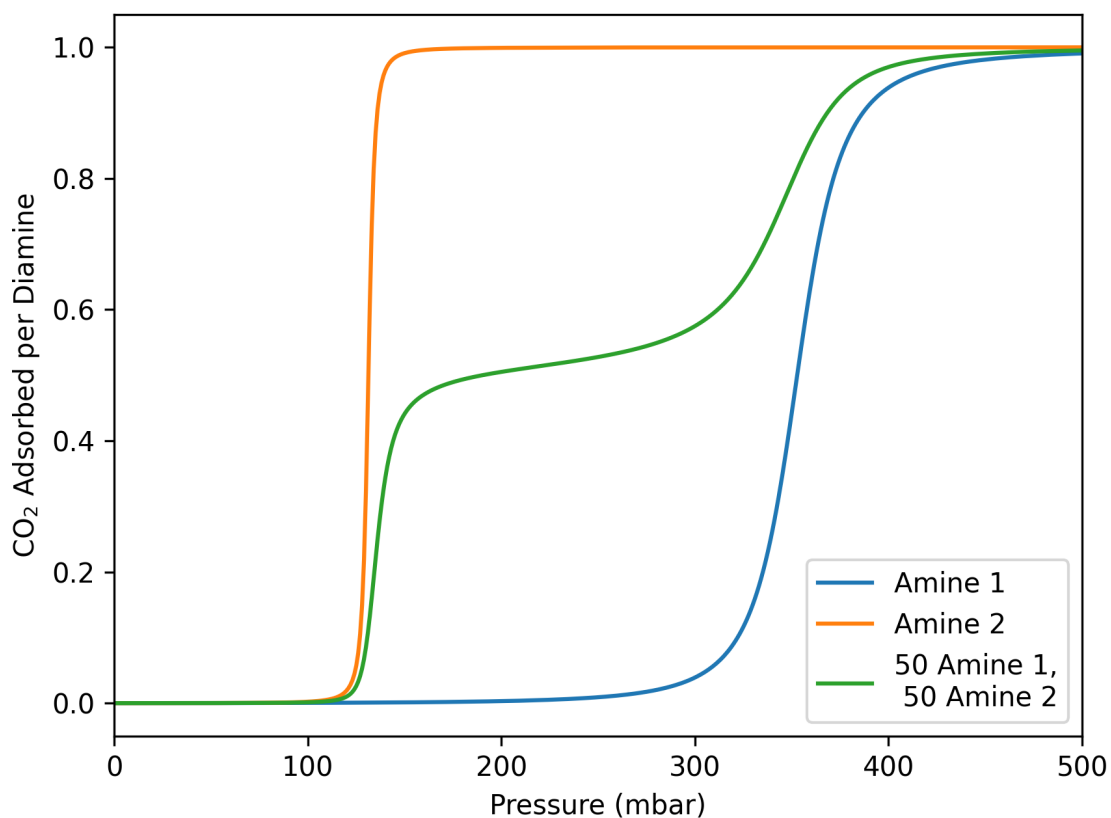


Figure 6.7: Isotherm at 300 K comparing CO₂ adsorption with single amines patterns (blue - $E_{\text{int}} = -55$ kJ/mol, orange - $E_{\text{int}} = -52.5$ kJ/mol) and a pattern with 50 of the blue amine and 50 of the orange amine.

matches the single step of amine C, while the double step with large clusters matches the single steps of pure phase amine A and amine B.

For small clusters, we vary the ratio of amine 1 and amine 2 to study how that affects the single step that we get. Figures 6.6 and 6.8 have alternating amines shown in Figure 6.6 and patterns of N_a of amine A and N_b of amine B for N_a and N_b less than 6 shown in Figure 6.8. These results show that we can tune the step position by varying the ratios and distributions of the amines. Table 6.7 shows results for different ratios that for a small cluster with N_a of amine A and N_b of amine B, we get a single step that is at the same position as a hypothetical system that consists of a single amine whose ammonium carbamate binding energy equalled the weighted average of amine A and amine B's binding energies:

$$E_b = \frac{N_a E_A + N_b E_b}{N_a + N_b}. \quad (6.56)$$

Pattern	Single Amine Binding Energy with Same Step (kJ/mol)
1-1	-53.75
1-2	-53.33
2-1	-54.16
1-3	-53.125
3-1	-54.375

Table 6.2: Pattern of N_a - N_b corresponds to N_a of amine A followed by N_b of amine B. For each of these, we used eqn. (6.56) to find a single amine which had the same step as that pattern. Plots of the isotherms are in Appendix A.

Finally, we assess the transition between single and double steps to more quantitatively understand the role of cluster size in determining the shape of the isotherms. Figure 6.9 shows that as we get to cluster sizes of 8-15 amines in a row, we transition from broad single steps to broad double steps.

6.8 Conclusion

We showed that modifications to a previous model enabled an understanding of more complicated features in CO₂ uptake curves in MOF-274. We showed that a steric penalty can generate double stepped isotherms/isobars. Since bulky amines can result in such an energy penalty, it can plausibly explain double steps in these systems.

Our model for cooperative adsorption associated with ammonium carbamate chain formation in finite clusters provides some energetic parameters that can be compared with computational predictions of cooperative adsorption to estimate how steep the isotherm might be in such finite systems. A more challenging task is to design materials with strong

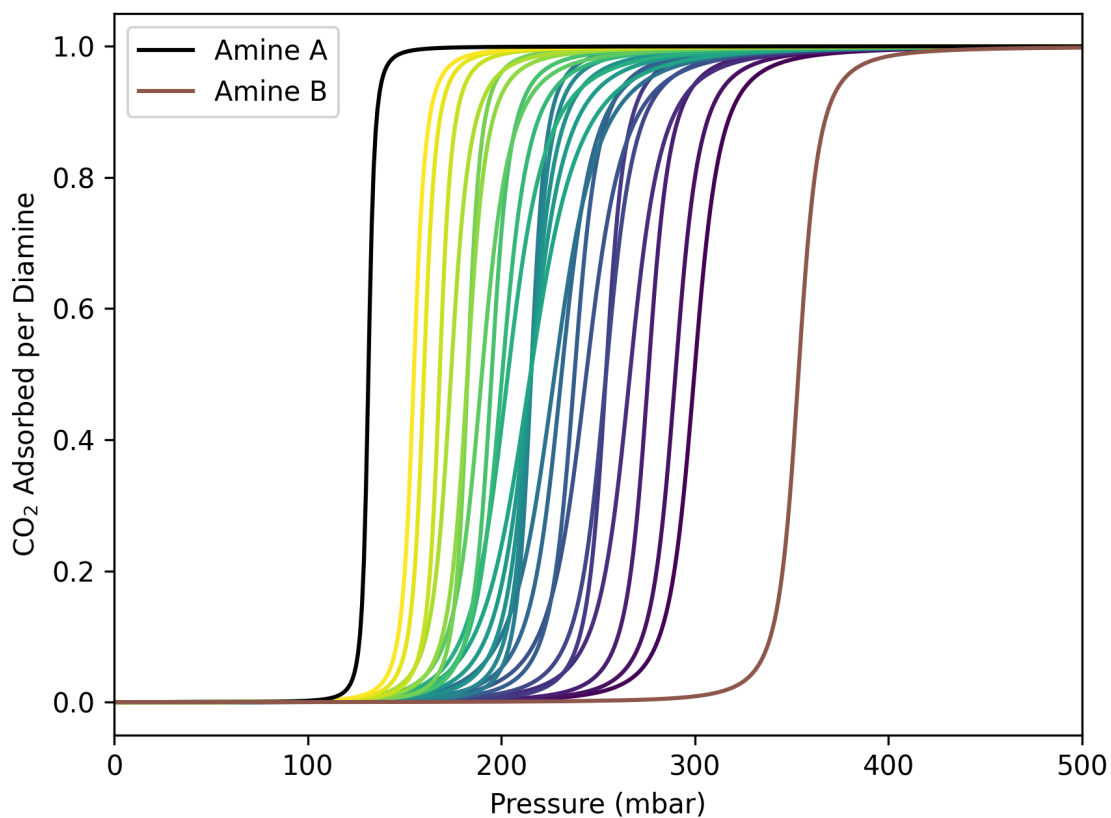


Figure 6.8: Isotherm at 300 K comparing CO₂ adsorption with single amines (black - $E_{\text{int}} = -55$ kJ/mol, brown - $E_{\text{int}} = -52.5$ kJ/mol) and a pattern with ratios of amine a to amine b of $N_a : N_a$ with $1 \leq (a, b) \leq 5$. The colors go from light yellow for lower values of N_b/N_a to dark purple for higher values of N_b/N_a .

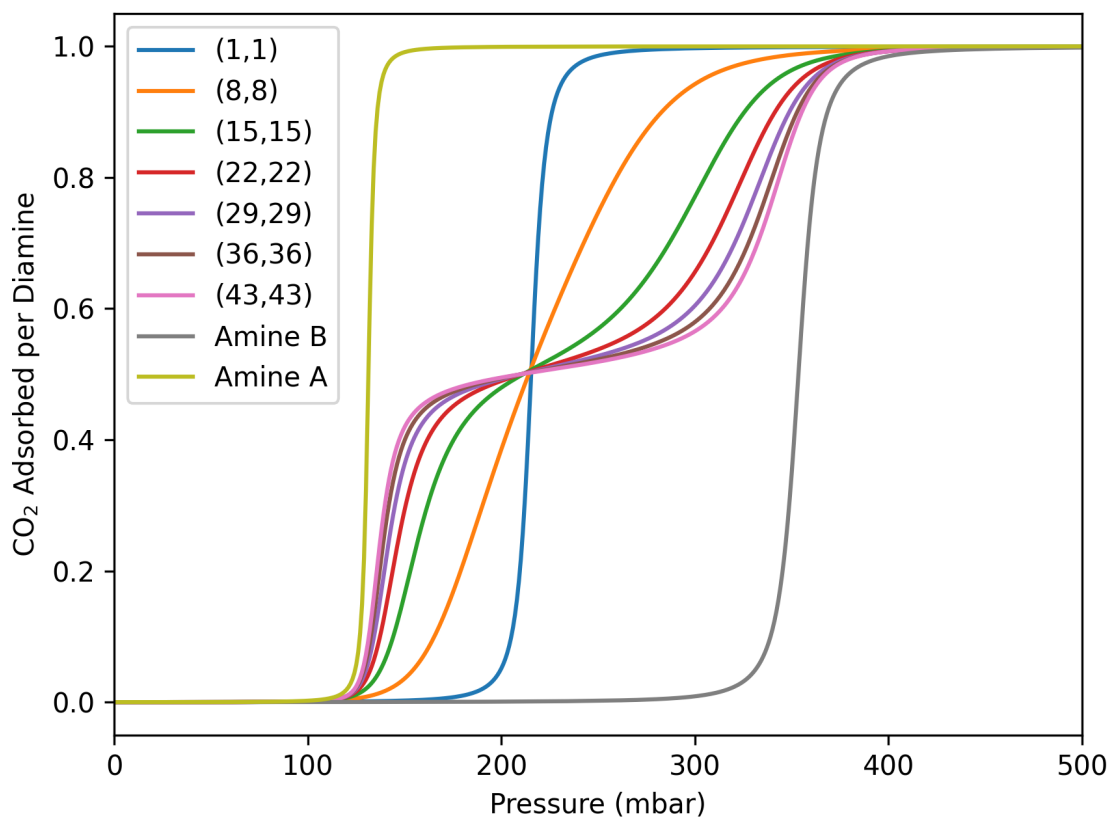


Figure 6.9: Isotherm at 300 K comparing CO₂ adsorption with single amines A (cooperative binding energy -55 kJ/mol) and B (cooperative binding energy -52.5 kJ/mol) and a pattern with (N_a, N_b) of amines A and B.

enough E_{int} terms, but precedent from the case of hemoglobin [157] suggests that it could be possible. Additionally, CoBBTA [158] has been shown to have negative cooperativity due to electron density changes after gas adsorption. Such electronic changes in systems without charge transfer between the metal and the gas might be less likely, but perhaps a structural change upon binding could promote adsorption. Phase change MOFs [159] are cooperative due to a phase transition that increases the pore size after gas adsorption, allowing more gas molecules to find. Ref. [159] found that a simple model which was a Langmuir model with different number of sites in the small- and large-pore versions of the MOF captured cooperative behavior in those systems. Thus, those systems didn't involve local geometric changes enhancing subsequent binding.

For mixed amines, we showed that single or double steps can be rationalized in terms of the size of the clusters of the two amines. Additionally, we showed with equation (6.56) that the ratio of the amines can be used to target specific step positions for different gas adsorption applications by choosing an appropriate ratio of the two amines.

Chapter 7

Tuning the Electronic Structure of Zn-MFU-4l

7.1 Introduction

The metal-organic framework $(M_5X_4)(BTDD)_3$, or MFU-4l, with M being a metal cation node and X an anion, is a MOF family, first synthesized in 2011 [160], that is an extended pore analog of MFU-4 which was first synthesized in 2009 [161]. MFU-4l MOFs have been explored for tunable gas adsorption [156, 160, 162–165], whereby different metals [156, 163–174] and anions [163, 165, 168] can controllably alter the binding energy of guest gas molecules to the metal node of MFU-4l MOFs. Other work on MFU-4l has studied its potential for catalysis due to the ability to replace the Zn with catalytically active metals into the framework [162, 166, 170–174].

Recently, tunable light emission was reported for Zn-MFU-4l via changing the halogen from Cl to Br to I [7]. This work was motivated by recent results reporting MOFs to be promising for white-light emission [175–182]. Zn-MFU-4l is a good candidate material for further exploration since it has a high degree of tunability that has been reported in experiments targeting gas adsorption and catalysis applications, and its 0-D metal-halide nodes are chemically similar to those of lower dimensional metal-halide perovskites that have shown promise for white light emission [112, 183, 184]. Additionally, metal-organic frameworks with large pores like Zn-MFU-4l can incorporate guest dye molecules which further tune the emitted light frequencies [7, 177].

The optical properties of MOFs and other porous materials have attracted a lot of attention for a range of applications including white-light emission and also, as a part of photovoltaic devices [185], as chemical sensors [186–188] for light induced guest molecule desorption [189], and for enabling the design of novel donor-acceptor optically active structures [190–192]. Within all of these different types of applications, a wide range of modifications to MOF structures have been studied both experimentally and theoretically to optimize their performance [185, 186, 193–196].

Among optically active MOFs, Zn-MFU-4l has some key advantages. The MFU-4l family of MOFs is highly tunable: the compatibility of different anions with this structure that has been previously reported motivates a more systematic study of Zn-MFU-4l’s electronic structure and optical properties. Other MOFs that have shown promise for white light emission typically have rare-earth ions or Pb or Cd based metal-nodes [179, 181, 197]. Zn based white light emitting materials have an advantage of being less toxic and environmentally damaging. Another advantage of the MFU-4l family of MOF for white light emission is that the large pores can accommodate guest molecules that are optically active, enabling even further tunability.

Whereas prior work [7] reports optical gaps of 3.39, 3.41, and 3.43 eV for ZnCl-MFU-4l, ZnBr-MFU-4l, and ZnI-MFU-4l, respectively, emission is peaked at 2.7 eV for ZnCl-MFU-4l and ZnBr-MFU-4l and 2.9 eV for ZnI-MFU-4l. In the solid-state the H₂BTDD organic linker has an optical gap of 3.5 eV, and exhibits emission centered at 2.4 and 3.2 eV, suggesting that the light emission in Zn-MFU-4l is more sensitive to the halogen than absorption (which is apparently dominated by the H₂BTDD linker). The detailed origin of the halogen anion-dependent shift in emission and the prospects for greater tunability of this MOF for optoelectronic applications remain unknown. Ab initio calculations would therefore be of great value in this context to increase our understanding of the absorption and emission properties of MFU-4l MOFs, and to predict promising modifications.

Ab initio many-body perturbation theory calculations within the GW approximation [14, 15, 32, 198] [41–45] and the Bethe-Salpeter equation (BSE) [16, 66–70, 199] approach have been successful in quantitatively understanding the quasiparticle band structure and optical excitations of materials ranging from the III-V semiconductors [200] to materials with heavy elements [201–205] or hybrid organic-inorganic components, [203–205] low dimensionality, [206–210], defects [211–213], and organic systems [214–216]. A range of methods have been used to study the optical properties of MOFs, although GW/BSE calculations of MOFs are relatively rare [217, 218]. A previous calculation of MOF-5 [217] reported that the GW approximation increases the band gap of MOFs rather significantly compared to DFT calculations, which is in line with past results in organic semiconductors [214–216]. Additionally, Ref. [217] reported a large exciton binding energy of 3.5 eV. Other calculations of the optical properties of MOFs have typically relied on doing DFT calculations with GGA [219] or hybrid functionals [219]. These calculations involve a mix of cluster calculations [219] and full periodic calculations [218].

In MFU-4, the smaller pore version of the MFU-4l family of MOFs, previous DFT calculations [219] on both periodic systems and clusters demonstrated a reduction in band gap via substitution of Zn with Co, which led to the introduction of an unoccupied Co state lower in energy than the linker-based conduction band minimum in Zn-MFU. Based on the recent experimental reports of tunable light emission via anion substitution [7], we focus here on the impact of further anion substitutions on the optical properties of Zn-MFU-4l.

In this work, we use DFT with semi-local and hybrid functionals and ab initio many-body perturbation theory to compute the electronic structure and optical properties of Zn-MFU-4l with nine different anions, including H, the halogens F, Cl, Br, and I, and four small

organic moieties, $-\text{CH}_3$ (Me), $-\text{SCH}_3$ (SMe_2), $-\text{N}(\text{CH}_3)_2$ (NMe_2), and $-\text{OC}_6\text{H}_5$ (Ph). Our GW calculations demonstrate that substituting $\text{N}(\text{CH}_3)_2$ and OC_6H_5 into the structure lowers the fundamental band gap of the system by as much as 1 eV, while all other anions leave the gap largely unchanged, as the band extrema are dominated by the BTDD organic linker character. Using ab initio GW-BSE calculations, we show that introducing organic anions $\text{N}(\text{CH}_3)_2$ leads to the emergence of low-lying charge transfer excitons, while OC_6H_5 anions do not. $\text{N}(\text{CH}_3)_2$ substitutions lead to a reduction in the optical gap due to the introduction of charge transfer excitons with small, but non-negligible, oscillator strength, while OC_6H_5 feature charge transfer excitons with negligible impact on the linear absorption spectrum. This result highlights the sensitive dependence of the anion geometry and molecular orbitals on the ability of an anion to have charge transfer excitons which have higher oscillator strengths. Additionally, our analysis shows that they can facilitate anion-sensitive emission. Our DFT and ab initio GW-BSE calculations, taken together, illustrate how anions in Zn-MFU-4l can be used to tune its optoelectronic properties into a range relevant to applications.

7.2 Methods

DFT

We first relax the structure of ZnCl-MFU-4l using density functional theory (DFT) with the rev-vdW-DF2 exchange-correlation functional [52], starting from experimentally-determined room-temperature structures from x-ray diffraction [160]. Our DFT calculations are performed using the Quantum Espresso [11–13] code using norm-conserving scalar relativistic pseudopotentials from Pseudodojo [132] using the “standard” accuracy setting. These explicitly include 3s, 3p, 4d and 4s electrons for Zn, 2p and 2s electrons for N, C, and O, 1s electrons for H, 3s and 3p electrons for Cl, 4s and 4p electrons for Br, and 5s and 5p electrons for I. We use a plane wave basis and a 96 Ry plane wave energy cutoff, a $1\text{e-}8$ Ry scf convergence threshold, a $1\text{e-}3$ Ry/Bohr force convergence threshold, and $2\times 2\times 2$ k-grid to sample the Brillouin zone (BZ). Our BZ integrations are performed using the Marzari-Vanderbilt [137] smearing approach with a smearing parameter of 0.0001 Ry. Starting with our relaxed structure ZnCl-MFU-4l, we replace Cl with different anions, and then re-optimize the lattice parameters and atomic positions in the same manner. We calculate the density of states using rev-vdW-DF2 with the same $2\times 2\times 2$ k-grid and smearing. We also use a hybrid functional, HSE06 [39], for computing electronic structure with fixed lattice parameters computed with rev-vdW-DF2. For HSE density of states calculations, we used the same convergence parameters and k-grid as with rev-vdW-DF2, and for the Fock operator we use an energy cutoff of 150 Ry and only sample the gamma point, which is sufficient for our study due to the limited band dispersion in this material. For ZnBr-MFU-4l and ZnI-MFU-4l we perform all calculations with spin-orbit coupling using fully relativistic pseudopotentials from Pseudodojo.

GW

To compute fundamental gaps, exciton energies, and optical spectra, we use ab initio many-body perturbation theory within the GW approximation and the Bethe-Salpeter equation (BSE) approach. We use the BerkeleyGW code [14–16] for these calculations. We perform G0W0 calculations using a DFT-PBE [35] starting point, which we refer to below as G0W0@PBE. Our DFT-PBE calculation uses a 90 Ry plane wave cutoff and a gamma-point only k-grid with a scf convergence threshold of 1e-10 Ry. For Cl, we construct the static dielectric matrix using 2097 bands (including 410 occupied bands) and a 25 Ry cutoff for the dielectric matrix. Our self-energy calculation also includes 2097 unoccupied bands. We use the static remainder approach to accelerate convergence in the Coulomb hole sum over empty states. Our BSE calculations use 32 valence bands and 31 conduction bands, and the cutoff for the bare Coulomb interaction is set to 35 Ry in the calculation of the BSE kernel.

Phonons

We calculate the phonon spectrum of ZnCl-MFU-4l using VASP [8–10, 84]. We use the PBE-D3 [43–45] functional with a 1000 eV planewave cutoff, a 2x2x2 k-grid, and PAW pseudopotentials generated by VASP. These pseudopotentials explicitly include the following electrons: $2s^22p^2$ with 4 electrons for C, $2s^22p^3$ with 5 electrons for N, $2s^22p^4$ with 6 electrons for O, $3d^{10}4s^2$ with 12 electrons for Zn, and $1s^1$ with 1 electron for H. We relax the lattice vectors and the atomic positions until the forces are below 0.0001 eV/Angstrom. We calculate the second order force constants using VASP’s finite difference method with a displacement size of 0.015 Angstrom.

Electron-phonon coupling

We calculate electron phonon coupling using the finite differences method [77] as implemented in VASP. We use the ZG special displacement method [79] and Monte Carlo sampling [77] to calculate the change in the band gap due to zero point motion and thermal effects. For ZnCl-MFU-4l, we use the ZG special displacement method to generate phonon mode displaced structures for 0, 100, 200, 300, and 500 K structures, and for ZnNMe₂-MFU-4l, we use Monte Carlo sampling with 100 structures to calculate the zero point renormalization. For ZnNMe₂-MFU-4l, we only calculate the zero point motion contribution because we found that for ZnCl-MFU-4l the zero point contribution to the band gap reduction was much larger than the finite temperature effects.

7.3 Results

The structure of ZnCl-MFU-4l is shown in Figure 7.1. The MFU-4l family of MOFs has a pentanuclear metal node consisting of a central metal surrounded by four other metals which are ionically bonded with charge balancing anions. These metals are coordinated with

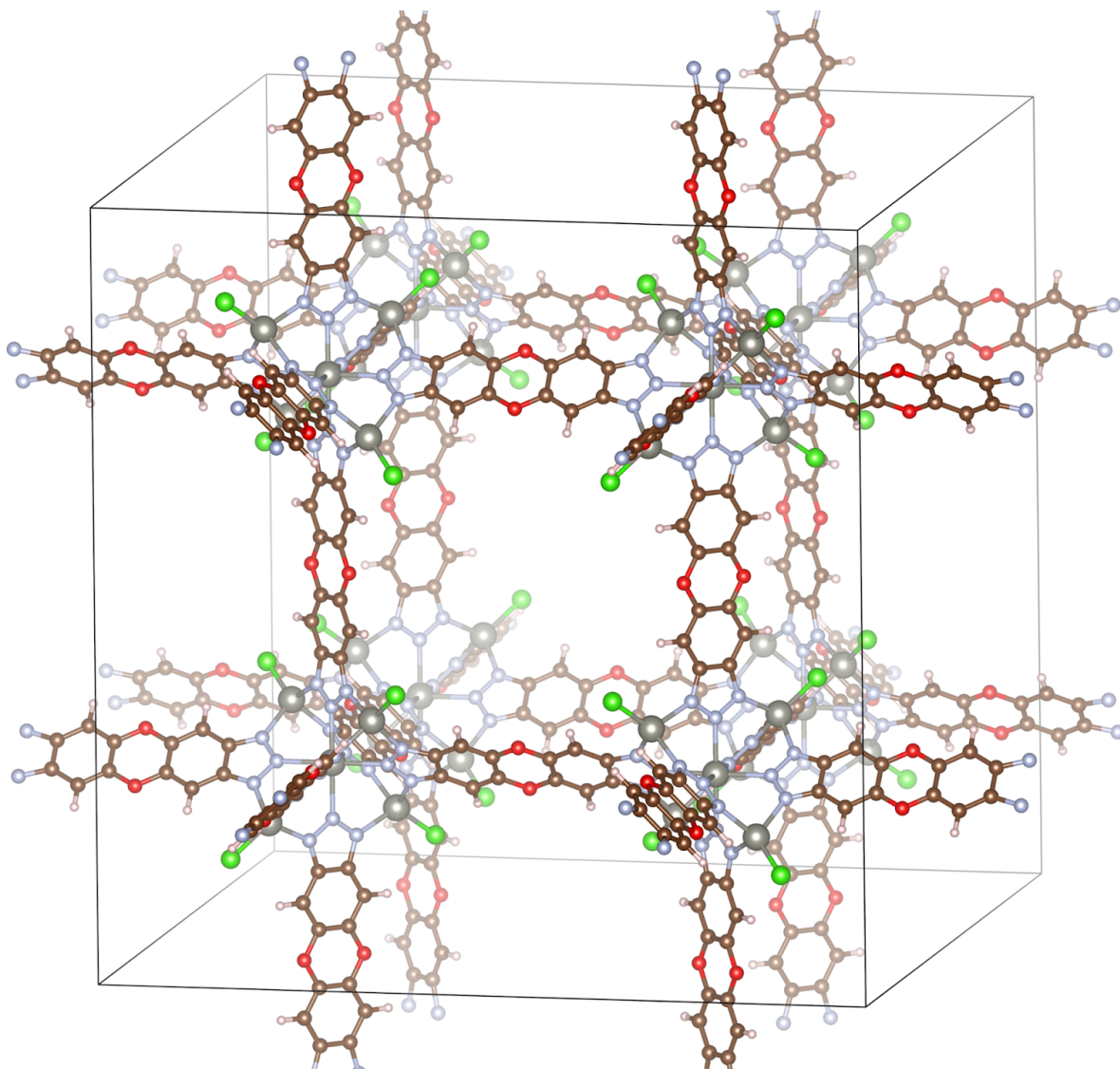


Figure 7.1: Supercell of ZnCl-MFU-4l. Zn -Grey, N - Light Blue, Cl - Green, C - Brown, O - Red, H - White

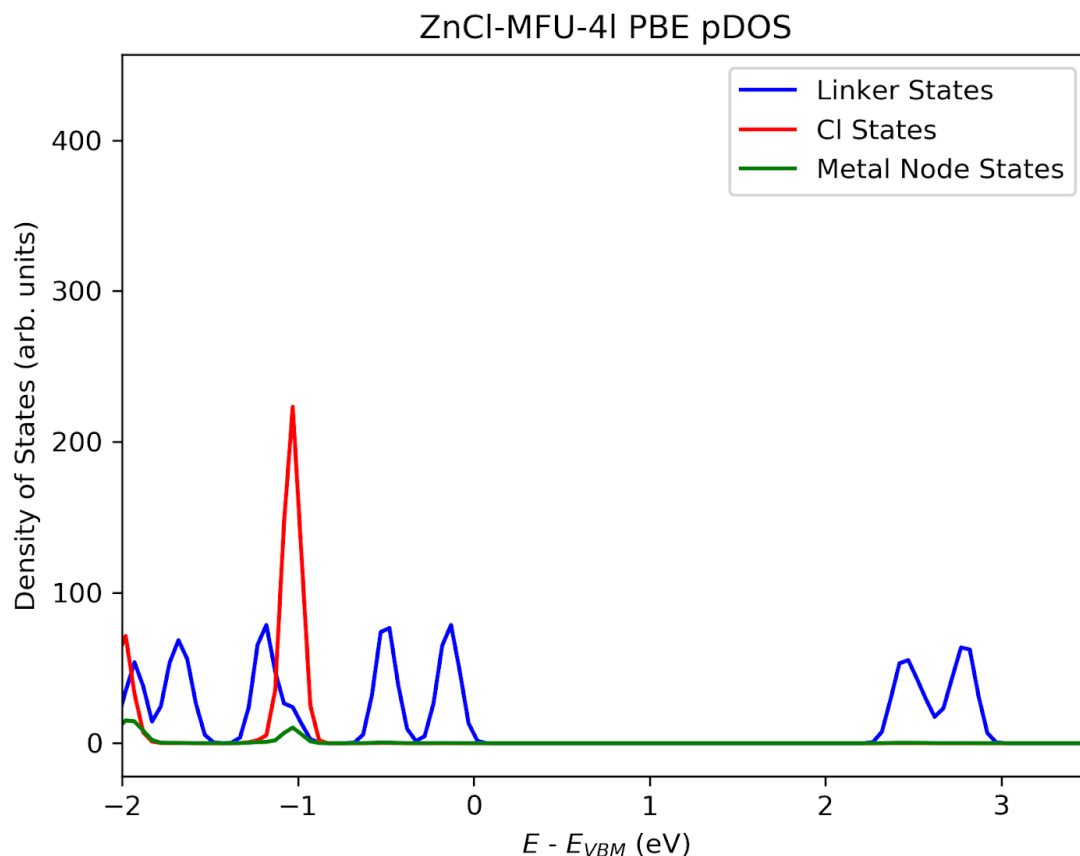


Figure 7.2: Projected density of states of ZnCl-MFU-4l with the PBE functional.

BTDD (bis(1H-1,2,3-triazolo[4,5-b],[40 ,50 -i])dibenzo[1,4]dioxin 2-) organic linkers via the nitrogens on the triazoles. In our study, we focus on Zn-MFU-4l, with Zn as the metal node, and in what follows we vary the anion to include H, halogens, and small organic anions. The Zn-MFU-4l crystalline framework takes up the space group $Fm\bar{3}m$, and has lattice parameter of 22.11 Å in the DFT-PBE-D3 relaxed structure, which deviates by 0.6% from the primitive cell lattice parameter of 21.96 Å reported in Ref [160]. The Zn-Cl bond in the DFT-PBE-D3 relaxed structure is 2.17 Å, and the Cl is 3.0, 3.6, 4.1 Å from the nearest H, N, and C on the organic linker.

Electronic structure of ZnCl-MFU-4l

Figure 7.2 has the density of states (DOS) for ZnCl-MFU-4l calculated with DFT-PBE. From the projected DOS, we can see that the valence band maximum (VBM) and conduction band

minimum (CBM) both have organic linker based states which are separated by 2.5 eV. Thus, at the DFT-PBE level, we compute a fundamental band gap of 2.5 eV associated with $\pi - \pi^*$ transitions on the organic linker.

The Cl states are 1 eV below the valence band maximum in our DFT-PBE calculations, suggesting that light absorption at the band edges does not involve states of Cl character. We compare the band gap and the relative position of the Cl state to the valence band maximum with DFT-PBE, DFT-HSE, and G0W0@PBE in Tables 7.1 and 7.2.

Anion	PBE (eV)	HSE (eV)	G0W0@PBE (eV)
Cl	-1.0	-1.5	-2.6
SMe	0.6	0.3	-0.8
NMe ₂	1.4	1.2	0.7
Ph	0.75	0.73	0.2

Table 7.1: Anion state relative to highest occupied organic linker state in ZnX-MFU-4l calculated with PBE, HSE, and GW.

Method	ZnCl-MFU-4l Fundamental Gap (eV)
PBE	2.5
HSE	3.1
PBE@G0W0	5.8

Table 7.2: ZnCl-MFU-4l Fundamental Gap calculated with PBE, HSE, and G0W0 with a PBE starting point.

As expected, the DFT-HSE and G0W0@PBE gaps are significantly larger than the gap computed with DFT-PBE. For many inorganic systems, the DFT-HSE and GW band gaps can be fortuitously similar to each other, but ZnCl-MFU-4l has localized molecular-like electronic frontier states which lead to the DFT-HSE band gap to be significantly underestimated compared to the G0W0@PBE gap. The DFT-HSE and G0W0@PBE calculations also demonstrate that the energy of the Cl state relative to the valence band maximum depends on the level of theory used. While with DFT-HSE the Cl state is around -1.5 eV below the valence band maximum, with G0W0@PBE the Cl state is -2.6 eV below the VBM. Thus, we can see that both G0W0@PBE and DFT-HSE alter the electronic structure more than a rigid shift of all of the bands. Spectroscopic measurements of ZnCl-MFU-4l have focused on its optical gap, and therefore we turn to computing its exciton energies with the ab initio GW-BSE method. We find a lowest exciton energy of 3.8 eV, with an exciton binding energy of 2.0 eV. A previous experiment found the room temperature optical gap of ZnCl-MFU-4l to be 3.4 eV [7] which is within about 10% of our clamped-nuclei zero-temperature result.

Given exciton-phonon coupling effects are neglected in our results, our overestimation of the gap is not unexpected. Previous *ab initio* GW-BSE calculations on a similar MOF [217], MOF-5, also yielded a strong renormalization of the electronic gap (from 3.57 eV with PBE to 8.12 with eVGW@PBE) and a large exciton binding energy of 3.5 eV.

To better understand zero-point and finite-temperature vibrational effects on these excited states, we also calculate the impact of phonons on the electronic gap. We use the special displacement method [79] to generate structures with atoms displaced based on our calculated phonon frequencies and eigenvectors. Table 7.3 shows our results for the fundamental gap including zero point and thermal effects from the Z-G special displacement method. At

Temperature (K)	Band Gap (eV)	VBM (eV)	CBM (eV)
Clamped Ions	2.52	-4.16	-1.63
0	2.06	-3.96	-1.90
100	2.05	-3.97	-1.92
200	1.99	-3.95	-1.95
300	1.92	-3.95	-1.95
500	1.77	-3.86	-2.09

Table 7.3: Band gaps of ZnCl-MFU-4l with clamped ions, and with zero point and thermal motion taken into account with the ZG special displacement method.

the PBE level, we find that the band gap of ZnCl-MFU-4l is reduced from 2.52 eV in the static structure to 2.06 eV at 0 K with zero point renormalization. Then, at 100, 200, and 300 K the band gap is reduced to 2.05 eV, 1.99 eV, and 1.92 eV. This trend suggests that the highest frequency phonons couple most strongly to the electronic states since thermal activation of the lower frequency modes has comparatively little impact on the band gap. Organic molecular crystals have shown similar behavior [220, 221]. This large renormalization of the electronic gap of ZnCl-MFU-4l reflects a strong coupling of phonons to organic linker states, which would be consistent with our GW/BSE optical gap of ZnCl-MFU-4l being overestimated due to the neglect of electron-phonon and exciton-phonon coupling in the GW and BSE calculations. A G0W0@PBE calculation on the ZG displaced geometry for 0 K yields a gap of 5.2 eV, showing an even larger reduction at the GW level.

Our analysis of the phonons show several with strong coupling to the ZnCl-MFU-4l frontier states in the range of 19.7 meV to 37 meV. In more detail, the mode with energy 19.7 meV involves mainly motion of the Zn, with some organic linker motion; the modes from 20 meV - 22.6 meV feature mainly organic linker displacements with some Zn displacement; the modes at 23.4 meV involve the central Zn, peripheral Zn, and the organic linker; the modes from 23.6 meV - 26.4 meV emphasize the peripheral Zn and the organic linker; the mode at 26.4 meV involve relative motion of the central Zn, the peripheral Zn and organic linker, and Cl; the modes at 26.7 meV feature mainly organic linker motion with some peripheral Zn motion; and the modes from 28.9 meV - 36.7 meV are primarily peripheral Zn

and N on the organic linker modes. Thus, of the modes near in energy to 25 meV that couple strongly to the frontier states, the Zn and organic linker are mainly involved in the motion, which is inconsistent with the experimental conclusion that Zn-Br modes in ZnBr-MFU-4l couple strongly to the lowest exciton which they claim is on the Zn-Br metal node. While their analysis was for the Br version of the MOF, they suggest that it should hold for the Cl and I versions as well. Given that we get similar electronic structures for the Cl and Br versions of the MOF, it is reasonable to think that the electron-phonon coupling should be similar in character for these two halide substitutions.

Electronic structure with other monoatomic anions

In Ref. [7], the authors found that replacing the Cl or Br with I led to an increase in the energy of light emitted from ZnX-MFU-4l. They attribute the absorption of light to the linker based states since the optical gap is unchanged for Cl, Br, and I versions of ZnX-MFU-4l. A comparison of the emission spectrum of the molecular crystal H₂BTDD linker and ZnBr-MFU-4l provided evidence that light emission in ZnBr-MFU-4l originates with recombination of excitons involving the metal node. Additionally, an analysis of the lineshape of the emission spectrum is consistent with a 25 meV vibrational mode coupling strongly to the exciton, which was speculated to be of the energy scale of metal-anion Raman modes, further suggesting emission from the metal node.

Our results for the density of states of ZnX-MFU-4l with $X = \{H, F, Cl, Br, I\}$ are consistent with the reported optical absorption experimental results for the three halides. For all X, we find qualitatively similar DOS with the VBM and CBM originating from linker based states. The primary difference with X is that the energies associated with anion states shift relative to the VBM, as can be seen in Table 7.4. We compute the same DFT-PBE

Anion	$E_{\text{anion}} - E_{\text{linker, occupied}}$	IP (eV)	PBE Kohn-Sham Gap(eV)
F	-1.2	-9.3	2.5
Cl	-1.0	-8.8	2.5
Br	-0.6	-8.5	2.5
I	0.0	-7.7	2.5
H	-0.8	-7.2	2.5
SMe	0.6	-6.9	1.9
Me	-0.5	-6.7	2.5
NMe ₂	1.4	-5.8	1.0

Table 7.4: Difference between highest occupied anion state and highest occupied linker states, as calculated with PBE. At the PBE level NMe₂ and SMe have occupied anion states higher in energy than the highest occupied linker states, leading to a reduction in the fundamental gap. Tables 7.1 and 7.5 shows that at the G_0W_0 level, only the NMe₂ and Ph anion states remain above the linker states.

fundamental gap for all X of 2.5 eV, consistent with the experimental report that the optical absorption onset being at the same energy for all of the halides in the experiment.

To rationalize these trends, we have calculated the highest occupied molecular orbital calculated from a calculation of gas phase Na-X. We find that the calculated highest occupied molecular orbital from Na-X follows the same trend as the measured ionization potentials, and also that anions with the least negative ionization potentials show the anion state closest to the VBM. ZnI-MFU-4l comes closest to having the I state cross the VBM, but it ends up right at the linker VBM states.

Electronic structure with other anions

From the trends computed for H and halogen anions, the gas-phase ionization potential is an indicator of where anion states may be positioned relative to the valence band edge. To examine whether the anion might introduce states above the valence band edge, we perform calculations for additional organic anions which have not yet been experimentally studied in this material, including Me = $-\text{CH}_3$, SMe = $-\text{SCH}_3$, NMe₂ = $-\text{N}(\text{CH}_3)_2$, Ph = $-\text{OC}_6\text{H}_5$, all of which have smaller ionization potentials than the halogens we have considered so far. These anions are also chosen for their relatively small size (for computational efficiency and to ensure they could fit in the pore of the MOF) and similarity to previously synthesized modifications to the anion in the MFU-4l family of MOFs [168]. Table 7.4 compares the band gap, anion level relative to the VBM, and highest occupied molecular orbitals calculated from Na-X for X = (CH₃, SCH₃, N(CH₃)₂, OC₆H₅).

We perform more computationally-efficient PBE and HSE calculations, as well as more rigorous GW calculations, on the systems with anions which yielded smaller fundamental gaps than -Cl at the PBE and HSE levels. Our results are in Table 7.1 and Table 7.5. We find that at the PBE and HSE level, SMe, NMe₂, and Ph anions generate states in the linker gap, just above the highest-occupied linker state, lowering the ZnCl-MFU-4l fundamental gap. With GW corrections, we find that this trend persists for NMe₂ and Ph, although the SMe anion states lie below the highest-occupied linker state after GW corrections. The Me anion does not contribute states in the gap at any of the levels of theory. A comparison of the difference in the energy of the highest occupied anion states versus the highest occupied linker states in Table 7.1 shows that from Cl to SMe to NMe₂, the G0W0 orbital energy of the highest occupied anion states gets renormalized by -1.6 eV for Cl, -1.4 eV for SMe, and -0.7 eV for NMe₂. Thus, the anions with the more localized states are reduced the most relative to the organic linker states in our GW calculations. Based on these results and our calculated gas phase ionization potentials of the anions, we can conclude that organic anions with low ionization potentials and delocalized electronic states are promising for reducing the band gap of Zn-MFU-4l.

While the GW calculations lower the energy of the Cl and SMe states relative to the VBM by 1.6 eV and 1.4 eV compared to PBE, respectively, the shifts for NMe₂ and Ph are smaller going from PBE to GW. For NMe₂, the NMe₂ state is 0.7 eV closer to the VBM with GW than with PBE, and with Ph the Ph state is 0.55 eV closer to the VBM with GW

than with PBE. These results suggest that the more localized states on Cl and SMe have a larger decrease in their energy upon going from PBE to GW than NMe₂ and Ph have.

Even though SMe does not introduce an anion state higher in energy than the highest occupied linker state, it still modestly reduces the band gap of ZnCl-MFU-4l from 5.8 eV to 5.65 eV in our G₀W₀ calculation. We can understand this change based on the increased dielectric constant of SMe which is 1.58 compared to 1.52 for ZnCl-MFU-4l (see Table 7.5). Ph, which has the largest dielectric constant of 1.67, causes the linker-linker gap to get reduced to 5.5 eV, giving further support to this trend. To explore the impact of anion substitutions on

Anion	ϵ_∞	PBE Gap (eV)	G ₀ W ₀ Gap (eV)	Linker-Linker Gap (eV)	Exciton Binding Energy (eV)
Cl	1.52	2.50	5.80	5.8	2.0
SMe	1.58	1.88	5.65	5.65	1.30
NMe ₂	1.59	1.01	4.87	5.65	1.4
Ph	1.66	1.60	5.30	5.49	1.7

Table 7.5: Results from G₀W₀ calculations on Zn-MFU-4l-X for different anions. The linker-linker gap is the G₀W₀ energy gap between the highest occupied and lowest unoccupied organic linker states. For Cl and SMe the linker-linker gap equals the fundamental gap because the linker states are at the band extrema. SMe has a higher dielectric constant leading to a slightly reduced gap. For NMe₂ and Ph, the linker-linker gap varies due to different dielectric constants, but also the fundamental gaps are reduced from the linker-linker gap because there are occupied anion states higher in energy than the highest occupied linker states. The NMe₂ anion state gives rise to bright charge-transfer excitons, while the Ph state does not.

the optical gap of MFU-4l MOFs, we perform ab initio BSE calculations on ZnCl-MFU-4l, with SMe, Ph, and NMe₂ anions. Table 7.5 summarizes our results, and Figures 7.3 and 7.4 in show the linear optical absorption spectrum calculated from our BSE results for these materials. ZnCl-MFU-4l has the largest exciton binding energy of 2.0 eV, while SMe and NMe₂ have exciton binding energies of 1.3 eV and 1.4 eV. While ZnCl-MFU-4l and SMe have a strong absorption feature associated with the linker-linker transition, NMe₂ also has a weak absorption peak associated with NMe₂-linker transitions. Thus, we can see that the introduction of NMe₂ both reduces the fundamental gap of ZnCl-MFU-4l and also introduces a charge-transfer exciton with small but non-negligible oscillator strength. Given that experimental results suggest strong electron-phonon coupling influences the optical properties of ZnX-MFU-4l where X is a halogen, it's possible that electron-phonon coupling in NMe₂ could increase the oscillator strength of the NMe₂-linker transition. Ph, on the other hand, does not lead to a charge transfer exciton with a noticeable oscillator strength. Calculations looking at band gap renormalization in NMe₂ using 100 phonon displaced geometries found a reduction in the band gap from 1.1 eV to 0.73 eV with a standard deviation of 0.12 eV

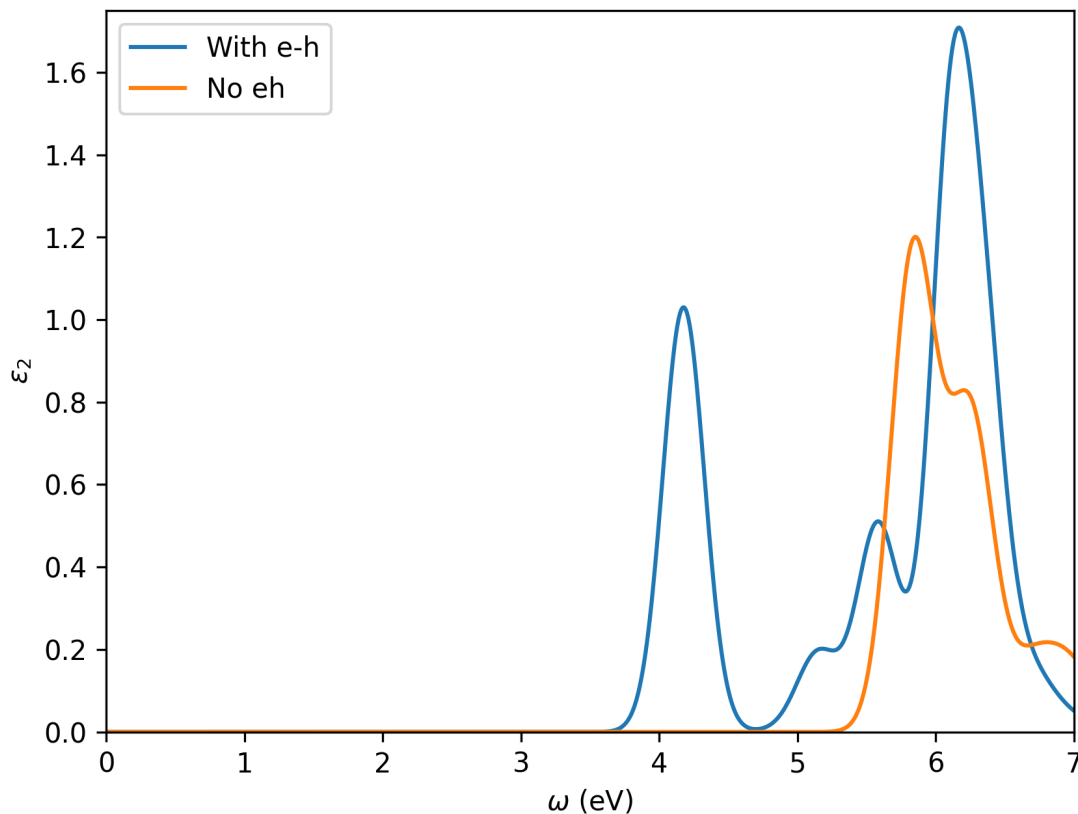


Figure 7.3: Imaginary part of the dielectric function for ZnCl-MFU-4l calculated with and without excitonic effects.

at 0 K with zero point motion taken into account. See Figure 7.5 for the distribution of band gaps calculated from our 100 phonon displaced geometries. Table 7.5 reports a PBE fundamental gap of 1.01. The difference between these two gaps stems from further geometry optimization done to get forces low enough for phonon calculations.

7.4 Discussion

Based on our results, we expect modest changes in the optical absorption onset with different organic anion substitutions. SMe and Ph slightly reduce the gap between linker states in the MOF due to increased dielectric screening, but they also lead to slightly smaller exciton binding energies, so that the optical absorption onset is nearly unchanged in our calculations

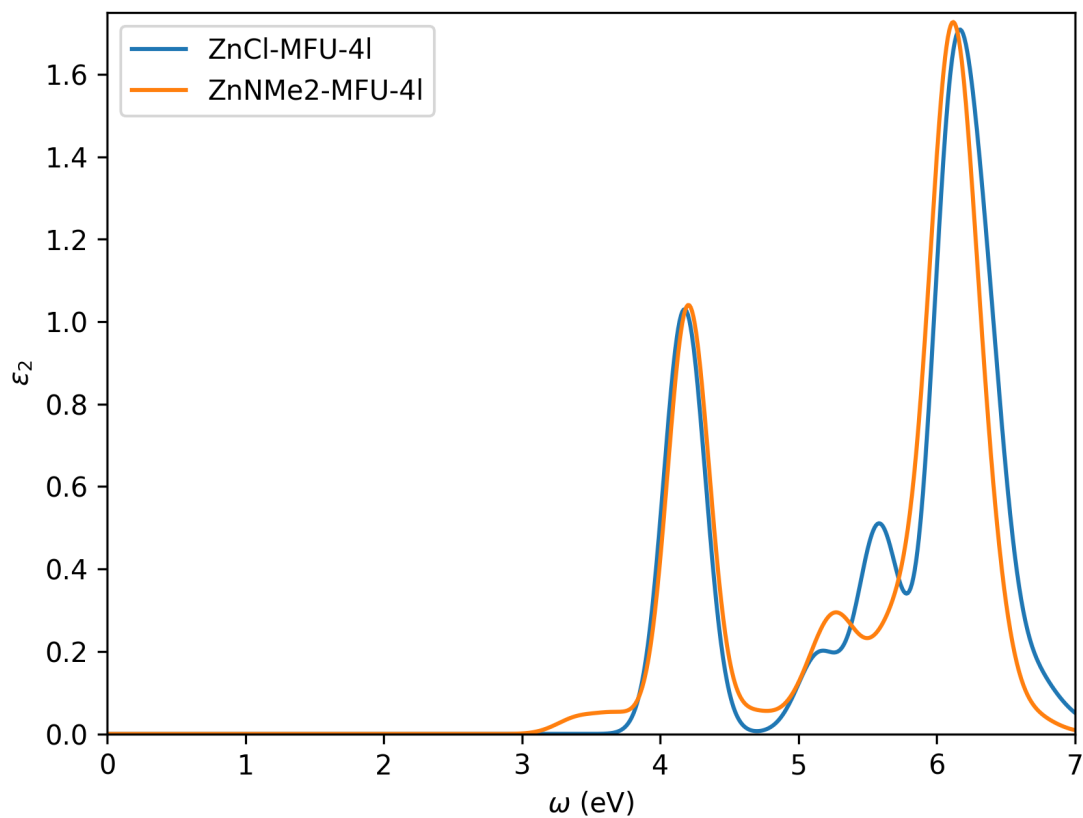


Figure 7.4: Imaginary part of the dielectric function for ZnCl-MFU-4l compared with ZnNMe₂ MFU-4l. While the spectra are largely similar at higher energies, NMe₂ introduces a charge-transfer exciton with non-zero oscillator strength at lower energies.

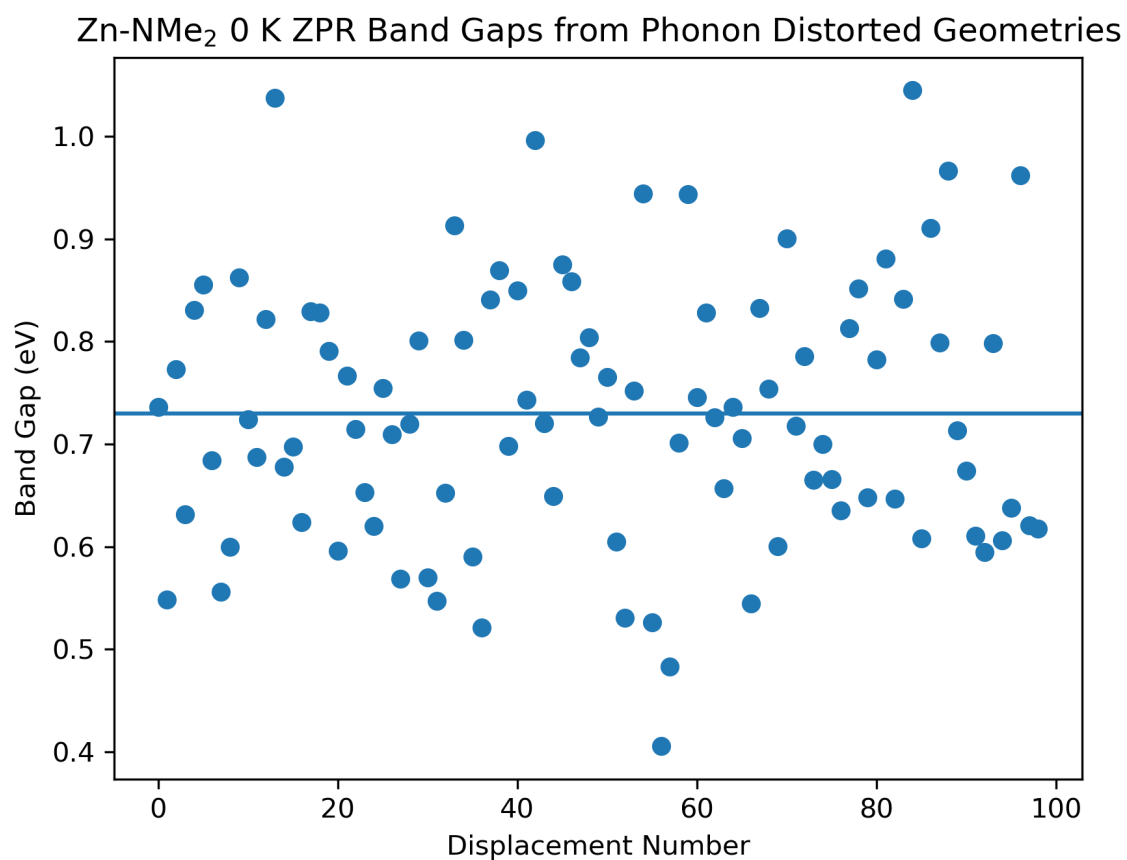


Figure 7.5: PBE fundamental Gap of Zn-NMe₂ calculated in 100 phonon distorted geometries to estimate the 0 K fundamental gap including ZPR. The horizontal line denotes the average value of 0.73 eV.

with these two anions. While Ph does lower the fundamental gap of the material because the highest occupied Ph state is higher in energy than the highest occupied linker state, the oscillator strength between the Ph state and the linker conduction band states is small and the linear optical response of the material with this anion is largely unchanged compared to the Cl version of the MOF. For NMe₂, on the other hand, the fundamental gap is reduced and a charge transfer exciton with non-negligible oscillator strength emerges that leads to a shoulder feature in the linear optical absorption spectrum. These results suggest that organic anions with ionization potentials that are low in magnitude and which are close enough to the organic linker could modify the optical absorption properties of the MOF even further. Large organic anions might be able to have van der Waals interactions with the organic linker and create more orbital overlap due to their proximity to the linker. Other organic anions with more delocalized states could have orbital overlap with the N on the linker, like NMe₂ does.

Our calculations provide new insight into the light emission properties of Zn-MFU-4l. While past experiments have been interpreted as showing support for self-trapped excitons on the metal-anion sites, our calculations of the phonon frequencies in this material are not consistent with that interpretation. The experimentally determined phonon frequencies that couple most strongly to the excitons feature relative motion between the Zn sites and the organic linker, with limited involvement of the Cl anion. Further work is needed to fully understand the mechanism of light emission in this material. In any case, experimentally it has been shown that modifying the anion can change the centroid of emitted light even if the optical absorption spectrum is unchanged; given that we are able to modify the absorption spectrum with the introduction of NMe₂, it is likely that the emission properties with that anion would be different than that of the halide version of the MOF.

7.5 Conclusion

We have shown that anion substitutions in Zn-MFU-4l can modify its band gap via moving the energies of the anion states and modifying the dielectric screening in the material. One organic anion, NMe₂, generates charge transfer excitons which create a shoulder feature in the linear optical absorption spectrum due to non-negligible oscillator strength between the organic anion and the organic linker. Our results suggest that looking for organic anions with low magnitude ionization potentials and the ability to have orbital overlap with the organic linker can modify the absorption properties of the MFU-4l family of MOFs. Additionally, given that going from ZnCl-MFU-4l to ZnI-MFU-4l leads to an increase in the energy of emitted light in experiments even without changing the absorption spectra, it is plausible that anions which increase the anion highest occupied level even more than I does will change the energy of emitted light even more than I does. Thus, organic anions which don't modify the absorption spectrum like Ph or SMe might still be able to modify the emission spectrum of MFU-4l MOFs. Because MFU-4l MOFs can be synthesized with different anions on different metal sites, broader emission spectra could be obtained via a

material with a mixture of different anions that led to emission at different energies. We have also shown that DFT with semilocal or hybrid functionals is not able to adequately capture the qualitative features of the density of states of Zn-MFU-4l as a function of different anions; PBE and HSE predicted that SMe would introduce a state in between the linker based VBM and CBM, in contrast to G0W0@PBE. Our calculations demonstrate an ability to tune the electronic and optical properties of Zn-MFU-4l beyond what has previously been reported from experiments, and suggest that in addition to looking at modifying the metal site and adding guest molecules in the pore, substituting halides for organic anions can be a promising and experimentally accessible way to modify the electronic and optical properties of Zn-MFU-4l.

Chapter 8

Outlook

My dissertation research covered a range of topics related to gas adsorption and the electronic structure of metal-organic frameworks. MOFs are a challenging class of materials for electronic structure theory methods because they have large unit cells, making the computational cost high; additionally, van der Waals interactions are important for capturing small energetic differences, and some MOFs are magnetic and have open-shell transition metals. The high computational cost means that it can be difficult to use higher accuracy methods like hybrid functionals or wave-function based methods [56, 57, 222–224]. Additionally, many MOFs can have structural disorder, solvent molecules in their pores, or difficult to resolve crystal structures from x-ray diffraction data. More experimental characterization of MOFs could help validate which methods are most accurate in these materials. Improvements in their synthesis could yield better crystal structures to use as input for first principles calculations, and could also facilitate more accurate experimental measurements, which could be used to validate calculations. For MOFs with well characterized geometries, one way to improve the computational predictive power in MOFs would be to develop approximations that speed up the calculation of these methods, such as ACE [225] which makes hybrid calculations faster, or stochastic methods for GW [226, 227] or MP2 [27, 222]. Similarly, methods like CCSD [29, 30] for solids are currently not computationally tractable enough in complex solids with many atoms, but increases in computing power and algorithm design will likely make more powerful methods feasible in large unit cells. Work in neural network potentials, such as work that I contributed to in Ref. [228], help speed up total energy and force calculations, and ML approaches can be combined with higher accuracy methods [229] to get temperature dependent properties. Additionally, the field of machine learning can also help with other methods, like GW [230].

Even so, as computing power increases, the size of systems we try to tackle increases as well. For example, DFT and GW on inorganic systems that were once state of the art [15] can be done in under a minute today, but DFT and GW calculations are still rather expensive in MOFs. I would imagine that eventually, the GW calculations done in this dissertation and hybrid calculations that had to be replaced with PBE + U calculations because hybrid calculations were too slow, will be somewhat routine in such large systems,

but with MOFs, the level of complexity can increase quickly. For example, in Chapter 7, we studied the optical properties of Zn-MFU-4l as we modified the anion; one other promising experimental route to modifying the optical properties of that material is using other organic molecules in the pore of the MOF. Adding in a molecule to the pore would increase the atom count, and give rise to much more geometric complexity. Similarly, to study the light emission in that material, excited state forces [231] could be employed, but currently these calculations would be challenging given the system size. Even so, excited state force calculations can be improved upon by including nuclear quantum effects [232, 233] where things like conical intersections [234] are important. Such calculations are primarily done today on small molecule systems. One could imagine that over time, these methods that are computationally infeasible in MOFs today might be possible, and one might still want more accuracy and fewer approximations. Our ambitions for the accuracy and the level of theory of the physics included in our calculations increase as our computing power and algorithms improve. I hope our ambitions will always outpace our computational capabilities.

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Appendix A

Plots of Small Clusters of Two Amines

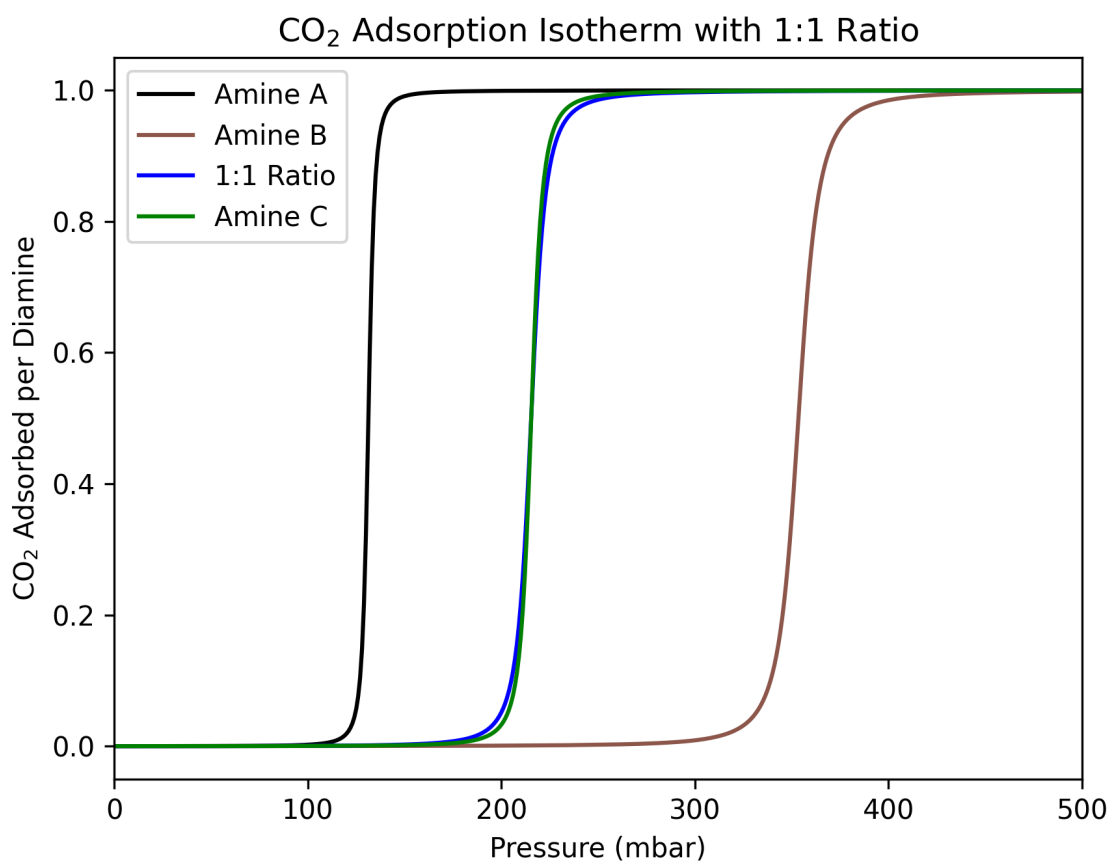


Figure A.1: Isotherm with alternating pattern of amines A (with a cooperative binding energy of -55 kJ/mol) and B (with a cooperative binding energy of -52.5 kJ/mol). Amine C has a cooperative binding energy of -53.75 , and its step coincides very well with the pattern of alternating amines A and B.

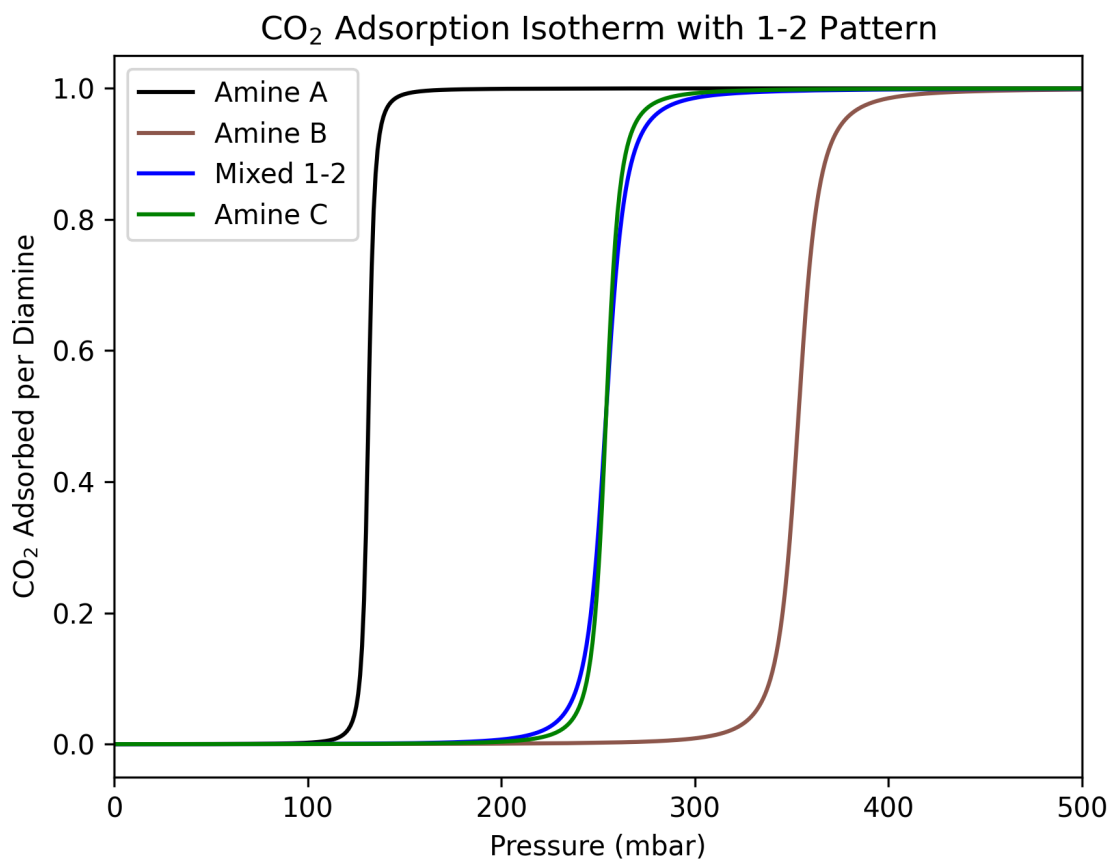


Figure A.2: Isotherm with pattern of 1 of amine A (with a cooperative binding energy of -55 kJ/mol) and 2 of amine B (with a cooperative binding energy of -52.5 kJ/mol). Amine C has a cooperative binding energy of -53.33, and its step coincides very well with the pattern of alternating amines A and B.

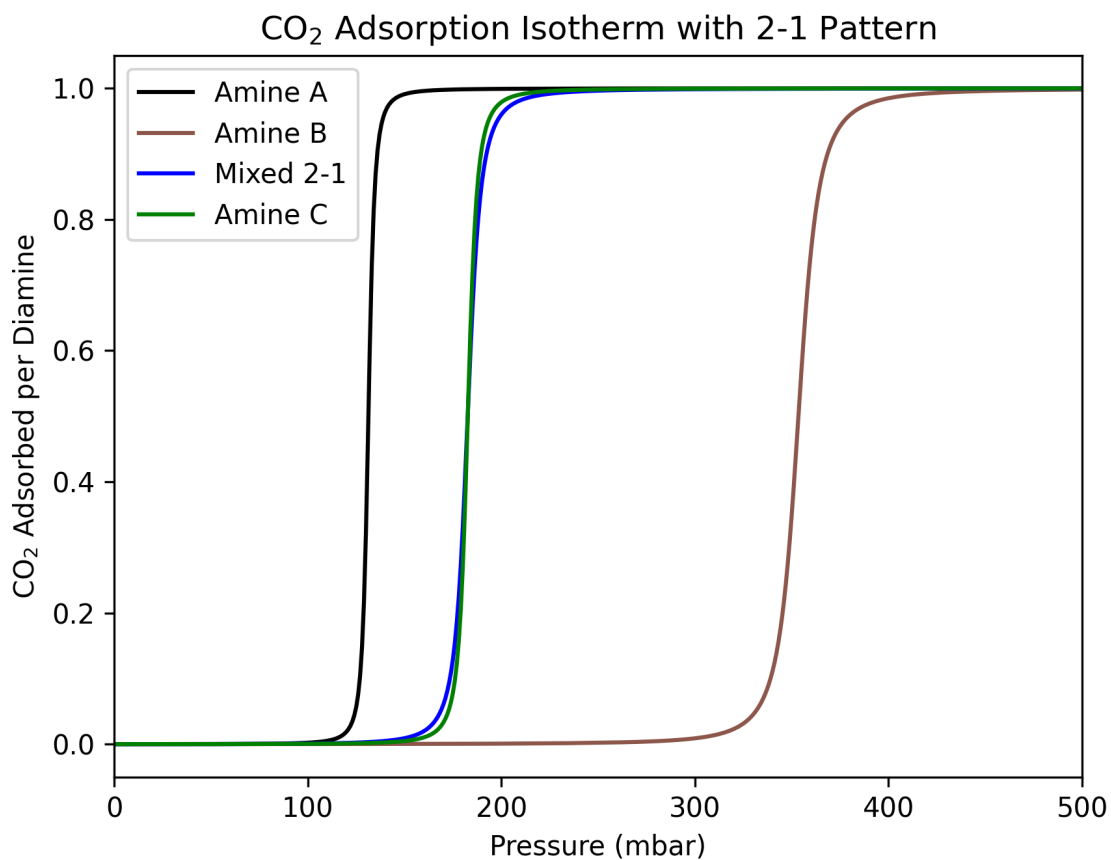


Figure A.3: Isotherm with pattern of 2 of amine A (with a cooperative binding energy of -55 kJ/mol) and 1 of amine B (with a cooperative binding energy of -52.5 kJ/mol). Amine C has a cooperative binding energy of -54.16, and its step coincides very well with the pattern of alternating amines A and B.

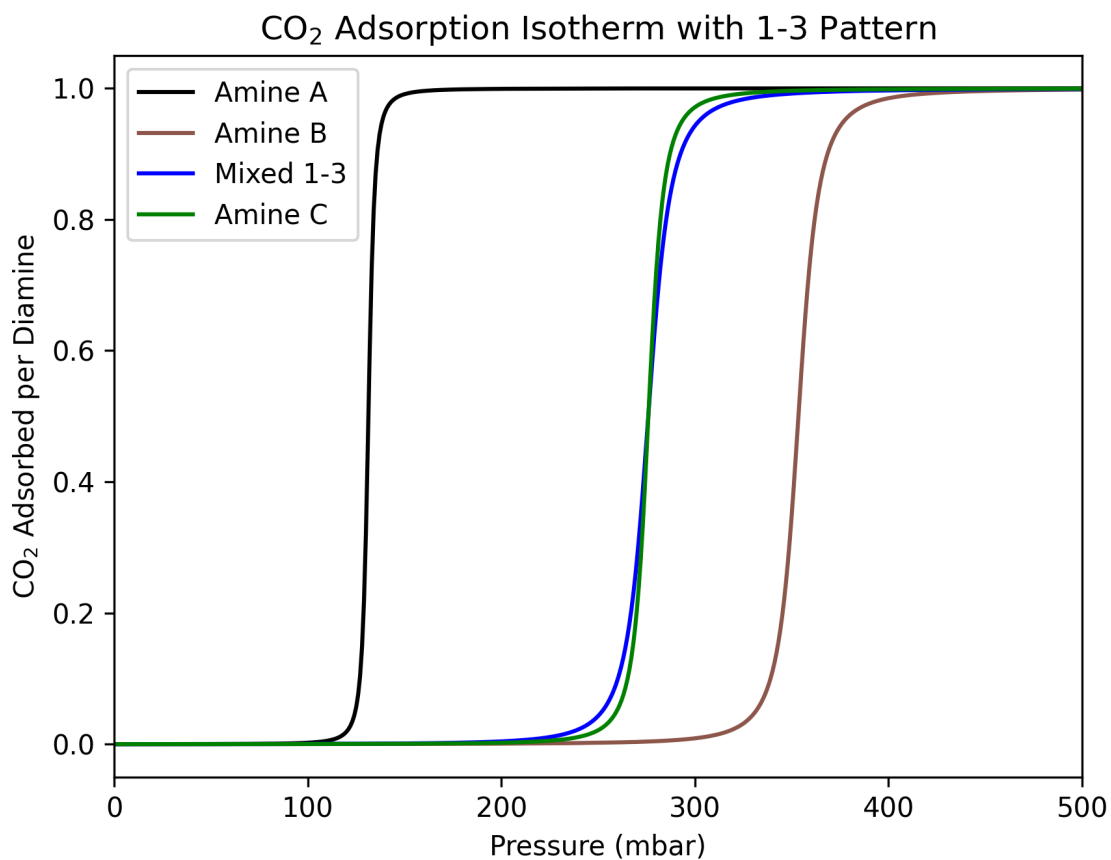


Figure A.4: Isotherm with pattern of 1 of amine A (with a cooperative binding energy of -55 kJ/mol) and 2 of amine B (with a cooperative binding energy of -52.5 kJ/mol). Amine C has a cooperative binding energy of -53.125, and its step coincides very well with the pattern of alternating amines A and B.

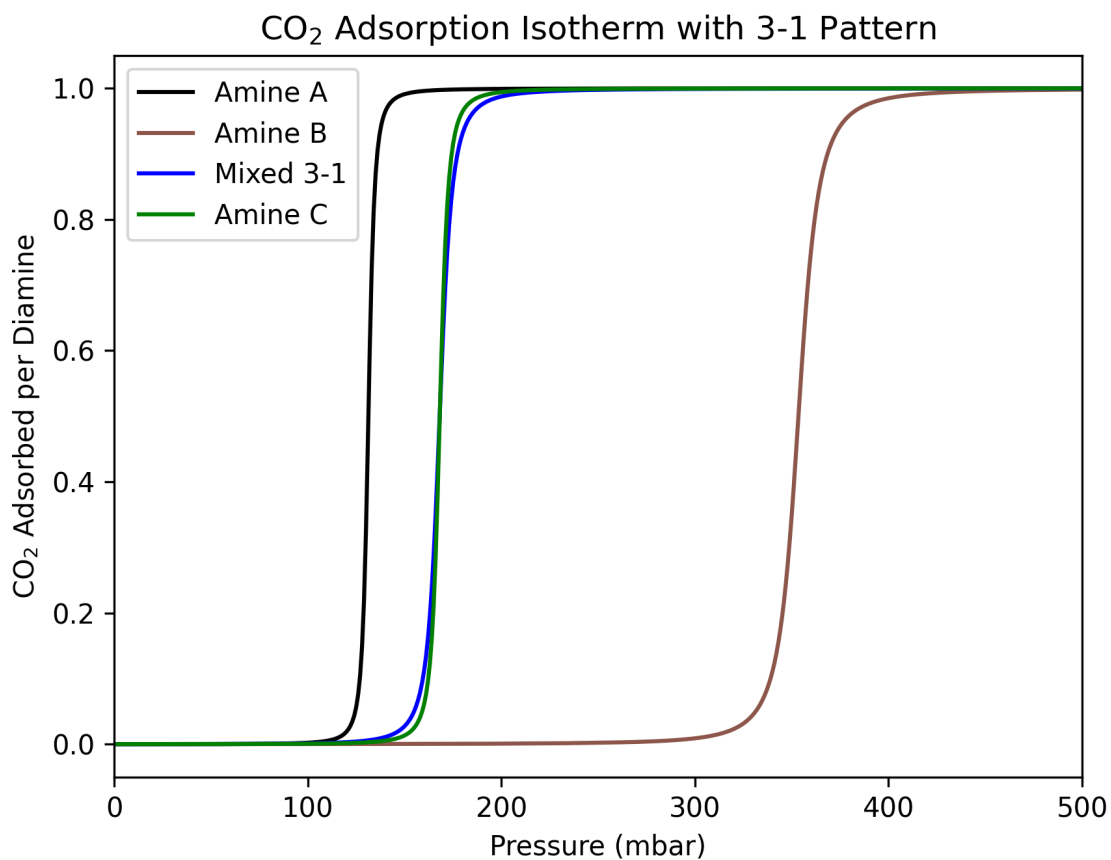


Figure A.5: Isotherm with pattern of 1 of amine A (with a cooperative binding energy of -55 kJ/mol) and 2 of amine B (with a cooperative binding energy of -52.5 kJ/mol). Amine C has a cooperative binding energy of -54.375, and its step coincides very well with the pattern of alternating amines A and B.

Appendix B

vdW Bechmarking Data

Functional	a (Å)	b (Å)	c (Å)
PBE	9.90	9.92	11.34
rPBE	10.85	10.85	11.64
PBE-D3	9.85	9.88	10.84
rPBE-D3	9.89	9.92	10.93
vdW-DF2	10.05	10.07	10.87
rev-vdW-DF2	9.82	9.85	10.77
vdW-DF-cx	9.78	9.81	10.84
vdW-DF3-opt1	9.76	9.80	10.63
vdW-DF3-opt2	9.80	9.84	10.66
rVV10	9.89	9.93	10.63

Table B.1: Lattice Parameters of $\sqrt{2}\times\sqrt{2}\times 1$ supercell of $\text{CrCl}_2(\text{pyz})_2$ calculated with different functionals. The experimental c lattice parameter from Ref. [136] at ambient conditions is 10.825 Å

Functional	a (Å)	b (Å)	c (Å)
PBE	9.95	9.97	10.94
PBE-D3	9.89	9.93	10.66
rPBE-D3	9.93	9.96	10.66
vdW-DF2	10.08	10.11	10.72
rev-vdW-DF2	9.84	9.87	10.6
vdW-DF-cx	9.8	9.84	10.66
vdW-DF3-opt1	9.77	9.8	10.5
vdW-DF3-opt2	9.81	9.85	10.55
rVV10	9.92	9.96	10.5

Table B.2: Lattice Parameters of $\sqrt{2} \times \sqrt{2} \times 1$ supercell of $\text{NiCl}_2(\text{pyz})_2$ calculated with different functionals. The experimental c lattice parameter from Ref. [106] at 298 K is 10.74 Å

Functional	a (Å)	b (Å)	c (Å)
PBE	10.01	10	11.51
PBE-D3	9.95	9.95	11.24
rPBE	10.19	10.18	11.67
rPBE-D3	10	9.99	11.23
vdW-DF2	10.14	10.14	11.33
rev-vdW-DF2	9.88	9.88	11.22
vdW-DF-cx	9.84	9.85	11.24
vdW-DF3-opt1	9.811	9.82	11.13
vdW-DF3-opt2	9.85	9.86	11.17
rVV10	9.96	9.98	11.11

Table B.3: Lattice Parameters of $\sqrt{2} \times \sqrt{2} \times 1$ supercell of $\text{NiBr}_2(\text{pyz})_2$ calculated with different functionals. The experimental c lattice parameter from Ref. [106] at 298 K is 11.31 Å

Functional	a (Å)	b (Å)	c (Å)
PBE	10.05	10.04	12.48
PBE-D3	9.98	9.97	12.23
rPBE	10.2	10.2	13.04
rPBE-D3	10.03	10.02	12.26
vdW-DF2	10.16	10.16	12.4
rev-vdW-DF2	9.91	9.9	12.21
vdW-DF-cx	9.87	9.87	12.22
vdW-DF3-opt1	9.85	9.84	12.12
vdW-DF3-opt2	9.88	9.88	12.17
rVV10	9.99	9.99	12.16

Table B.4: Lattice Parameters of $\sqrt{2} \times \sqrt{2} \times 1$ supercell of $\text{NiI}_2(\text{pyz})_2$ calculated with different functionals. The experimental c lattice parameter from Ref. [106] at 100 K is 12.25 Å

Functional	a (Å)	b (Å)	c (Å)
PBE	10.099	10.11	11.32
PBE-D3	10.03	10.05	10.77
rPBE	10.27968291	10.29267607	11.74569536
rPBE-D3	10.07	10.09	10.79
vdW-DF2	10.27	10.29	10.81
rev-vdW-DF2	9.99	10.02	10.71
vdW-DF-cx	9.95	9.98	10.78
vdW-DF3-opt1	9.92	9.94	10.61
vdW-DF3-opt2	9.97	9.99	10.65
rVV10	10.08	10.1	10.55

Table B.5: Lattice Parameters of $\sqrt{2} \times \sqrt{2} \times 1$ supercell of $\text{VCl}_2(\text{pyz})_2$ calculated with different functionals. The experimental c lattice parameter from Ref. [108] at 120 K is 10.67 Å

Functional	a (Å)	b (Å)	c (Å)
PBE	11.22	11.84	11.97
PBE-D3	10.61	11.54	12.00
rPBE	11.53	12.05	12.56
rPBE-D3	10.65	11.63	12.21
vdW-DF2	10.97	11.86	12.21
rev-vdW-DF2	10.59	11.52	11.97
vdW-DF-cx	10.59	11.51	11.93
vdW-DF3-opt1	10.46	11.39	11.88
vdW-DF3-opt2	10.53	11.46	11.95
rVV10	10.54	11.51	12.02

Table B.6: Lattice Parameters of (HIS)PbBr₄ calculated with different functionals. The experimental a lattice parameter from Ref. [112] at 100 K is 10.54 Å. (Note that what they define as the a lattice parameters is the out of plane lattice parameter which we refer to as the c lattice parameter in the main text.)