Simulation and Software Development to Understand Interactions of Guest Molecules in Porous Materials

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Simulation and Software Development to Understand Interactions of Guest Molecules in Porous Materials

by

Douglas M. Franz

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy
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Date of Approval:
Jun 26, 2019

Keywords: air purification, gas sorption, metal-organic frameworks, porous materials, materials engineering, molecular simulation, monte carlo, molecular dynamics, electronic structure, quantum chemistry

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Dedication

To my wife, Ilona
Acknowledgments

I owe a tremendous debt of love to the people who have contributed to my life and goals through graduate school. My wife, Ilona, has stood by my side through thick and thin with a love that I am still learning to emulate. If it were not for you I would not be at this stage, writing the manuscript to complete a doctoral degree. I will be at your side for the rest of this crazy and short life we have to enjoy and look forward to what the future holds for us!

To my parents, Michelle and Mike Monroe, and sister Angel, thank you for years of nurturing and training that encouraged me to do my best and achieve what I once didn’t know was possible. Seeing me through many bright and dark days has certainly created an environment that allowed me to succeed. Pops and ma, thank you for years of patience and love, and celebrating life with me to the full! Angel, thank you for those awesome times when you taught me multiplication with stuffed animals in our household “classroom” (haha!) It definitely gave me a boost in pursuing a career in physical science.

To Dr. Brian Space – I couldn’t possibly have found a more encouraging, intelligent, professional and caring mentor. You truly have gone above and beyond for your students, as I have witnessed, and I feel especially blessed to have met you. My growth as a scientist and human has invariably been enhanced and directed by your existence. Words on a page will never do justice to the difference you’ve made in my life.

To Dr. Dean Martin, my undergraduate research mentor: I wouldn’t have even thought to go into graduate school if it had not been for your mentorship. I would not be where I am today without you. Having someone believe in me as you did propelled me to a place I am glad to have been.

To my committee members, Dr. Henry Woodcock, Dr. David Rogers, Dr. Inna Ponomareva, and Dr. Shengqian Ma, your support has been invaluable. It means a great deal to me that you all have given your time and thought to improve my graduate
education and point me in the right direction when needed. I am greatly enlivened by the positive experience I have had with you and look forward to knowing you as professional contacts in the future.

To the people who went through the ranks of graduate school ahead of me – Dr. Chris Cioce, one of my first mentors in the Space lab, although our intersecting time was short I am so grateful for your awesome personality and motivated spirit, giving me tours of Sandia National Labs and guiding my first commands with quantum chemistry software, we all miss you here! Dr. Katherine Forrest, who spent countless hours to guide my linux-neophyte self to full functionality; Dr. Tony Pham for his steadfast support and acceleration of my career by kindly including me on new research projects through the years;

My fellow Space cadets, some of the most generous and thoughtful people I have ever known: Adam Hogan, who is a genius of math, physics and programming with an effortless sense of humor and helped me to navigate the complexities of molecular physics; Brant Tudor, a great friend and constantly welcoming presence in our lab, not to mention probably the most well rounded academic in our lab; Matthew Mostrom who indulged me in stimulating conversation more than most people ever care to, who I count as a brother; Luciano Laratelli, who from the first moment of entering our lab made everything enjoyable – even if it was as grueling as perpetually calculating fugacity coefficients; Meagan Mulcair, a thoughtful, inquisitive person who I am glad to have met.

To the others in our lab who I had little time to get to know, I wish you the best of luck in your future endeavours! You are in good hands in the Space lab; my advice is amid all of the seeming daunting or menial requirements of the program, to allow your curiosity to guide you in research; this is at the heart of science!

You will all be dearly missed – indeed, you are my second family. I so much look forward to the success that is inevitable for all of you and knowing you for the rest of our lives – professionally and personally.
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Abstract

The effect of inclusion of explicit polarization is investigated through several theoretical studies of crystalline porous materials herein. In addition to the use of Monte Carlo simulation for such studies, a robust molecular dynamics software is presented which is suitable for analyzing time dependent properties of gases or other molecules in porous materials and other condensed phase systems. Metal-organic frameworks (MOFs) are the main focus of the work included here, a relatively young class of materials originally introduced in the early 1990s. These are usually three dimensional crystalline nanoporous materials that exhibit unique properties such as gas separation, storage and catalysis. They are synthesized by the combination of a metal ion e.g. Cu$^{2+}$ with an organic linker e.g. benzene dicarboxylate. They are a very popular topic of scientific research due to the diversity in possible structures and manifold utility – finding applications in electron transfer, sensing, drug release etc. Industrially, MOFs like HKUST-1 and others are on the global market for use in gas storage and separation in fuel cell and raw materials processing.

These materials are often ideal candidates for computer simulation owing to their crystalline nature – a very large atomic system (that is, moles of particles) can be understood by only evaluating one or a few unit cells of the MOF, usually less than 5,000 atoms, and macroscopic properties such as gas sorption capacity and diffusion coefficients can be calculated through extrapolation of atomistic interactions in a mathematically infinite lattice. The software developed by the space group as of 2005, Massively Parallel Monte Carlo (MPMC), allows for sophisticated calculation of repulsion dispersion, electrostatic and polarization energies. In this work, Monte Carlo Molecular Dynamics (MCMD) is introduced, which can hybridize both methods to explore the phase space of a system with ease and better efficiency, as well as explore the effects of MOF flexibility and dynamic properties which to-date are rarely studied.
Studies involving primarily CO$_2$, H$_2$ and CH$_4$ will be presented, but other gases investigated include C$_2$H$_2$, C$_2$H$_4$, C$_2$H$_6$, N$_2$, H$_2$O and others. Metal-organic materials with a wide variety of composition and structure will also be presented. Finally, features of the software MCMD will be presented for use by future studies.
Chapter 1

Introduction

The goal of classical molecular modeling is to achieve predictive or retrodictive power using mathematical models that agree with known experimental data and/or fundamental physical theory. Macroscopic utility can arise from a microscopic understanding of the way matter behaves, and computers provide a luxury of freedom to select the location, mass, speed and other properties of atoms before allowing a system to be governed by known physical laws. In general, molecular systems are treated as having a set of atoms each with centralized mass fixed to a point in space at the nucleus. These points bear numerical parameters which describe the chemical and physical properties of the atoms, which are used in model equations which emulate the true energetics of the system without the need to calculate observables from ab-initio quantum mechanics. That is to say, instead of computing the energy of a molecular system via the Schrödinger equation which depends on the number, position, mass and spin state of all electrons and nuclei, a well-fit model can be used to quickly evaluate the energy of the system via a sum of interactions from subsystems of pairs, triplets or more atoms.

There is no fundamental theorem that dictates or claims that any extant model perfectly agrees with the results that come about from solution of Schrödinger’s equation (in the complete basis set limit), but incremental improvements to existing models and the parameters used within them provides increasing confidence in the utility of molecular modeling for obtaining insights at the atomistic level. Likewise, there is no fundamental basis for trusting a pairwise, three-body, etc. summed potential to faithfully reproduce
the underlying quantum mechanics, since the true physics require a consideration of all particles at once.

The dominant paradigm of classical molecular modeling is the use of the Lennard-Jones functional form for repulsion/dispersion of electron clouds known to exist from shielding effects and Pauli exclusion, and Coulomb’s law for electrostatic interactions governed by the longer-range attraction/repulsion of charges. This is given by Eqn. 1.1,

\[ U_{LJ+ES} = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] + k \frac{q_i q_j}{r} \]  

Where \( \epsilon \) is a parameter defining the well-depth of the two-atom energy as a function of displacement, and \( \sigma \) defining where the distance at which the potential is zero (Fig. 1.1). \( r \) is the displacement of the nuclei, \( q_i \) the charge of atom \( i \), and \( q_j \) the charge of atom \( j \), and \( k \) is Coulomb’s constant. This is an obvious simplification of the true physics involved but is useful for having lower computational cost than full evaluation of the Schrödinger equation with large basis sets to describe the wavefunction of the system.

![Image of Lennard-Jones potentials for homonuclear Xe and Kr dimers.](image.png)

Figure 1.1: Comparison of Lennard–Jones potentials for homonuclear Xe and Kr dimers.

While the use of Lennard–Jones van der Waals interactions is the most commonly used form for classical modeling, there exist other forms to model repulsion/dispersion. Even with electrostatic contribution to the potential energy of the system, however, this type of classical modeling does not capture the effect of a changing electric field on moving molecules unless polarization is included explicitly. That is, introducing terms which
contribute to the total energy of the system based on evolution of dipoles can produce a more accurate simulation compared to reality. Electrodynami c effects are nonetheless rarely included because of difficulty in implementation and large computational cost. In a typical simulation like those presented in this work, the computational cost of polarization is 75-90% of the total. The bulk of this dissertation demonstrates the use of explicit polarization in modeling of porous materials with guest molecules and the improvement in accuracy (as measured by agreement with experimental data) obtained in doing so. Our research group has demonstrated the utility of polarization in Monte Carlo simulations for over a decade – a primary aim of my work was to contribute a code which could compute not only the energy emergent from explicit polarization of atoms but also the forces which govern molecular dynamics. This enables us to compute transport properties, such as diffusion and kinetic barriers, flexibility and phononic behavior.

Several examples of simulations of porous materials with gases will be presented herein, including parameterization methods and rationale for choosing certain parameters over others. The effect of polarization compared to the lack thereof will be addressed throughout. There is a guiding role in the collaborative engineering of porous materials that comes from insights gained through molecular modeling, and that too will be discussed.
Chapter 2

Accurate H₂ Sorption Modeling in the *rht*-MOF NOTT-112 Using Explicit Polarization

2.1 Note to Reader

This chapter contains content previously published in *Cryst. Growth Des.*, 2016, 16 (10), 6024–6032, and has been reproduced within the guidelines provided by the American Chemical Society.

2.2 Abstract

Hydrogen sorption was characterized theoretically in NOTT-112, an *rht*-metal-organic framework (MOF) that consists of Cu²⁺ ions coordinated to 1,3,5-tris(3',5'-dicarboxy[1,1'-biphenyl]-4-yl)benzene ligands. Grand canonical Monte Carlo (GCMC) simulations of H₂ sorption were performed using three different sorbate potentials of increasing complexity to elucidate the mechanism of interaction in NOTT-112. Reasonable agreement with the experimental H₂ sorption isotherms, isosteric heats of adsorption (*Q̂*ₘ), and H₂–Cu²⁺ distances were obtained with the model that includes explicit many-body polarization. This highlights the physical importance of induction in H₂ sorption in MOFs with open-metal sites. The two Cu²⁺ ions within the paddlewheels in NOTT-112 have distinct electrostatic profiles and sorption characteristics. The Cu²⁺ ions projecting into the cuboctahedral (cub–*O₈*) cage of the MOF are more electropositive than the Cu²⁺ ions projecting towards the organic linker, and therefore serve as the initial loading sites. Such a sorption mechanism has been shown to be sensitive and tunable *via* the magnitude of the metal charge. Simulated sorption onto the open-metal sites was compared with
extant experimental neutron powder diffraction (NPD) data in NOTT-112. Simulated annealing calculations on sorbates and analysis of the radial distribution function for H$_2$ sorbed about the Cu$^{2+}$ ions revealed metal–sorbate interaction distances that were in reasonable agreement with NPD data in NOTT-112 for the most realistic model. This study demonstrates how the inclusion of explicit polarization in classical GCMC simulation is able to reproduce experimental observables and elucidate the gas sorption behavior in a MOF possessing open-metal sites. Additionally, this study shows how careful modeling of the MOF–sorbate interactions can provide complementary atomistic resolution to data obtained from NPD measurements.

2.3 Introduction

Metal–organic frameworks (MOFs)\textsuperscript{1,2} are materials that comprise an increasingly innovative and interesting branch of “nano-architecture” that provides an abundance of demonstrated and foreseeable solutions to modern environmental and industrial problems, including H$_2$ storage\textsuperscript{3} and CO$_2$ capture and sequestration.\textsuperscript{4} These materials are synthesized by the self-assembly of metal ions (or metal ion clusters) and organic linkers to form highly organized and crystalline structures that are often porous.

While several MOFs, e.g., Mg-MOF-74\textsuperscript{5,6} and members of the SIFSIX platform\textsuperscript{7–9} have shown exceptional CO$_2$ selectivity and uptake, especially at room temperature and low pressures, another important but to-date less facile application of MOFs is H$_2$ storage,\textsuperscript{3,10–16} which is the focus in this study. It is notable that Mg-MOF-74 actually has high sorption capacity for H$_2$ (ca. 25 mg g$^{-1}$ at 77 K/1 atm)\textsuperscript{6} in addition to CO$_2$ (ca. 350 mg g$^{-1}$ at 298 K/1 atm).\textsuperscript{17–19} Although a material that can sorb H$_2$ quantitatively is desirable for industrial and environmental applications, the storage of H$_2$ remains a difficult problem due to the significantly weaker electronic interactions that H$_2$ makes with traditional sorbent materials compared to other gaseous sorbates. Molecular hydrogen is recognized as an excellent alternative energy carrier to traditional fuels because of its high energy output and the production of principally water upon combustion. Additionally, the heat of combustion by mass for H$_2$ is -141.9 kJ g$^{-1}$,\textsuperscript{20} compared to -47.8
The challenge is confining the gas to a usefully small volume. The ultimate U.S. Department of Energy (DOE) target for an on-board hydrogen storage system at near-ambient temperature and high pressures (e.g., 298 K, 100 bar) is 7.5 wt%. It is noteworthy that high pressures and a suitable container alone are not practical means of hydrogen storage or transport for fuel applications, so a robust medium that can physisorb the gas is desirable.

Evidence has shown that within certain bounds, MOFs with large pore sizes and 3-D carbon compounds, e.g., nanotubes and graphite ribbons, have high uptake for H₂ at high pressures. However, the presence of excessively large pores actually reverse the advantageous effect of physisorption at low pressures. Thus, MOFs with high surface area alone are of limited interest as the key to a productive H₂ storage material is strong specific interactions between the sorbate and sorbent. This implies that using intermolecular interactions, i.e., repulsion/dispersion, electrostatics, and polarization, in a concerted manner requires confined MOF spaces with appropriate chemistry for strong interactions. In other words, there is an optimal range of pore size for H₂ uptake in MOFs.

Tunability of MOF structures and selection of metal cation allows for further enhancement of sorption properties and this is explored herein. In terms of total H₂ uptake at low temperatures, rht-MOFs currently have some of the highest measured uptake capacities, surpassing 7.5 wt% at 77 K and high pressures, e.g., 10 to 80 atm. This study aims to contribute a greater depth of understanding of the structural and electronic chemical configurations that contribute most to hydrogen sorption in an rht-MOF, specifically through investigation of the simulated sorption capacity of hydrogen in NOTT-112.

Dehydrated NOTT-112 is a deep-purple crystalline solid comprised of Cu²⁺ paddlewheel nodes ([Cu₂(O₂CR)₄]) connected by 1,3,5-tris(3′,5′-dicarboxy[1,1′-biphenyl]-4-yl)benzene linkers, termed “H₆L” in Figure 2.1. When hydrated, the crystal is blue-colored. A unit cell of the MOF is shown in Figure 2.2. Characteristic of other MOFs in the rht (24-connected rhombicuboctahedra and 3-connected triangles) platform, the unit cell of this MOF contains three unique cages: cuboctahedron (cub-O₉), truncated tetrahedron (T–T₄), and truncated octahedron (T–O₉). The rims of these
The addition of Cu$^{2+}$ ions to the organic linker, termed H$_6$L, yields the self-assembled NOTT-112 crystal. The graphic for H$_6$L was reproduced from reference 15 within the guidelines provided by the Royal Society of Chemistry. Copyright 2009 Royal Society of Chemistry.

cages contain open-metal Cu$^{2+}$ sites which are typically the initial sorption sites for various guest molecules, such as H$_2$. Images of these cages are provided by Yan et al.\textsuperscript{15,16} and also in the Supporting Information (Figure S2) The rht-MOF platform represents an important and well-known family of MOFs that exhibit high porosity, stability, tunability, and open-metal sites.

Figure 2.2: A perspective view of a single desolvated unit cell of NOTT-112 along the $a$, $b$, or $c$ axis. Atom colors: Cu = brown; O = red; C = grey; H = white.
2.4 Methods

2.4.1 Atomic Coordinate Determination

The crystal structure of NOTT-112 as obtained through X-ray crystallography contains two configurations of the ligand with overlapping phenyl groups (Figure 2.3).\textsuperscript{15} This is similar to what was observed in the crystal structures for other \textit{rht}-MOFs.\textsuperscript{22,36} This “duplication” effect for the phenyl groups can be observed from X-ray diffraction data due to the symmetric periodicity of the crystal. One of these configurations with consistently rotated phenyl groups was selected for the parametrizations and simulations because only one indicated aromatic unit exists in the organic linker used to make the MOF. The specific orientations of these phenyl groups was deemed inconsequential for the simulations, although the actual crystal structure of NOTT-112 may have some asymmetry in these linker units under certain conditions. It is expected that the overall electronic effects of the angular difference is periodically equivalent. To confirm this, geometry optimizations of a series of linker fragments were performed, and it was observed that the selected phenyl rings (yellow in Figure 2.3) did not change conformation.

![Figure 2.3: The organic linker of NOTT-112 showing the overlapping phenyl groups as observed in the X-ray crystal structure of the MOF.\textsuperscript{15} The highlighted yellow phenyl units were kept for the parametrizations and simulations, while the corresponding overlapped phenyl groups were discarded. Atom colors: O = red; C = gray; H = white.](image-url)

\textsuperscript{15}
2.4.2 MOF Parametrization

Similar to parametrization methods used by our group and others previously, NOTT-112 was modeled with three types of parameters ascribed to the center of each atom (or site) in the three-dimensional Cartesian coordinate system: Coulombic partial charges, Lennard-Jones (LJ) 12–6 repulsion/dispersion terms and a polarizability parameter that becomes tensorial after interacting in a many-body fashion. Details for obtaining the requisite parameters are described below.

The partial charges were established from optimized NOTT-112 fragments using NWChem’s Hartree-Fock electrostatic potential surface algorithm with the 6-31G* basis set applied to all chemically distinct atoms. Additionally, charge calculations were performed using more expensive methods and basis sets for a model fragment (#3, Fig. S3(c)), and the resulting copper ion charges were in general lower in magnitude and closer together (Table S3 in Supporting Information). An example of a selected gas phase fragment is shown in Figure 2.4. The “cut-off” atoms (added as H) on all fragments were first optimized using the same level of theory and basis set. Peripheral atoms, e.g., H10 on some fragments and cut-off atoms, were not used for the parametrization because they are not sufficiently shielded as to produce a reasonable partial charge.

The charge parameters were calculated for eight different fragments to accurately establish an average partial charge for each chemically distinct atom. Fragments were used in place of calculating the electrostatic potential surface of the entire unit cell of the MOF because accurate quantum mechanical periodic partial charge calculations for such a large system (2,784 atoms including 96 Cu atoms) would be difficult if not unfeasible and has been shown to be unnecessary.

The partial charges for all chemically distinct atoms in the MOF and for the H\textsubscript{2} potentials are provided in the Supporting Information. All partial charges were calculated with and without LANL2DZ effective core potentials for Cu, with the latter yielding a more accurate H\textsubscript{2} sorption simulation compared to experiment. While the physically representative latter choice is most relevant, the earlier charges serve as a sensitivity test for H\textsubscript{2} sorption to the metals and are thus included to provide both chemical and
Figure 2.4: An example of a fragment of NOTT-112 that was selected for partial charge calculations with all chemically distinct atoms labeled. Atom colors: Cu = brown; O = red; C = grey; H = white.

modeling insights. The calculated partial charges for the Cu$^{2+}$ ions are presented in Table 2.1. All simulated thermodynamic data shown in this text are from the second charge parametrization.

Table 2.1: Partial charges for the Cu$^{2+}$ ions in NOTT-112. Averages and standard deviations for the partial charges calculated from eight different fragments using LANL2DZ ECP (param. 1) and no ECP (param. 2) for Cu are provided. Note, the partial charges for all other chemically distinct atoms in NOTT-112 are presented in the Supporting Information (Tables S1–S2).

<table>
<thead>
<tr>
<th>Atom ID</th>
<th># in unit-cell</th>
<th>$q$ (param. 1)</th>
<th>$q$ (param. 2)</th>
<th>Diff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuC</td>
<td>48</td>
<td>1.35 ± 0.06</td>
<td>1.56 ± 0.05</td>
<td>+0.21</td>
</tr>
<tr>
<td>CuL</td>
<td>48</td>
<td>0.86 ± 0.13</td>
<td>1.00 ± 0.08</td>
<td>+0.14</td>
</tr>
<tr>
<td>Diff.</td>
<td></td>
<td>0.49</td>
<td>0.56</td>
<td></td>
</tr>
</tbody>
</table>

In this MOF, it was observed through electronic structure calculations that CuC, the copper protruding into the cub–$O_h$ cage, exhibits a higher partial positive charge than CuL, itself facing inward toward the organic linker. This was evident for both methods of charge calculation but the magnitude of the Cu charges was greater when ECPs were not utilized. A comparison of the calculated partial charges for the Cu$^{2+}$ ions for one sample MOF fragment using different basis sets is provided in the Supporting Information (Table
It is interesting to note that the partial charges for both types of Cu$^{2+}$ ions were
lower in all cases where ECPs were used. Such a finding was also evident from electronic
structure calculations on the rht-MOF PCN-61.\(^{22,43}\) The copper charge differences were
inferred by Yan et al. through neutron powder diffraction (NPD) studies in NOTT-112.\(^{16}\) Here, the charge difference between the Cu sites was found to be approximately
0.5$e^-$, a substantially variant magnitude. Note that the differences in electropostivity
between the Cu$^{2+}$ ion is quite similar using both parametrizations, but the change in
absolute magnitude, itself leading to a more polar MOF, is an important design element
considering hydrogen sorption in this MOF. It is noteworthy that large differences in
the partial charges between the two chemically distinct Cu$^{2+}$ ions have been observed in
other rht-MOFs.\(^{22,34–36,43,51}\)

Repulsion/dispersion parameters for each atom type in the MOF were taken from the
Universal Force Field (UFF).\(^{52}\) These parameters from UFF have been widely used to
treat such interactions in many MOF–sorbate simulation studies,\(^{13,37,43,53–55}\) and have
been shown to reproduce H$_2$ sorption data in MOF-5 at a variety of temperatures
and pressures.\(^{38}\) The interactions between unlike species were governed by the Lorentz-
Bertholet mixing rules.\(^{52,56}\) The point polarizability parameters for all C, H, and O atoms
were taken from a carefully transferable set provided by van Duijnen and Swart,\(^{57}\) while
the polarizability for Cu$^{2+}$ was determined in reference 43 and used herein. All re-
pulsion/dispersion and polarizability parameters for the MOF atoms are given in the
Supporting Information (Table S6).

### 2.4.3 Simulation Details

GCMC simulations of H$_2$ sorption in NOTT-112 were performed with the Massively Par-
allel Monte Carlo (MPMC) code developed originally by Belof et al.\(^{58}\) and maintained
by our research group, with the potential energy function involving three components:
LJ 12–6 repulsion/dispersion, permanent electrostatics as calculated by Ewald summa-
tion,\(^{59}\) and Thole-Applequist many-body polarization.\(^{46,47,57,60}\) The sum of these energies
represents the total potential energy of a GCMC simulation state. Long-range correc-
tion terms were applied to compensate for calculations within the limited size simulation box (one MOF unit cell). Details on the programmatic procedures are provided in the Supporting Information.

GCMC equilibration simulations were performed in serial using Research Computing resources at the University of South Florida until an apparent energetic equilibrium was reached. Subsequent parallel calculations were performed (on the same system) with identical starting thermodynamic conditions to obtain converged average statistical mechanical quantities, e.g., total potential energy and particle number. Simulations of H$_2$ sorption were performed in NOTT-112 using three different models of increasing complexity: Buch, a single-site model that includes only repulsion/dispersion parameters; BSS, a five-site model that includes partial charges and LJ parameters; BSSP, a five-site model that includes point polarizabilities in addition to partial charges and LJ parameters. This was done to assess the importance that repulsion/dispersion, stationary electrostatic, and polarization interactions have on the H$_2$ sorption mechanism in NOTT-112. For simulations of D$_2$ sorption, here, the sorbate was modeled using an adaptation of the BSSP H$_2$ model by only adjusting the atomic mass and was not further developed (i.e., by fitting other parameters with experimental properties of D$_2$); the mass of the sorbate enters the GCMC calculations through the use of Feynman-Hibbs effective energies that capture quantum mechanical effects.

GCMC simulations of H$_2$ sorption in NOTT-112 were performed using the aforementioned MOF parameters to calculate the following:

- Total H$_2$ uptake at different state points (temperature & pressure).
- Isosteric heat of adsorption ($Q_{st}$) at different H$_2$ uptakes, including at the initial (~0 wt %) loading ($Q_{st}^0$).
- Radial distribution function ($g(r)$) of hydrogen molecules about the open-metal Cu$^{2+}$ sites.
- Induced dipole locations and magnitudes from the MOF–H$_2$ electronic interactions
- H$_2$/D$_2$ sorption distance from Cu$^{2+}$ ions including at the potential minimum obtained by simulated annealing.
• H₂ population density in the MOF by histogram analysis of equilibrated systems

2.5 Results and Discussion

2.5.1 Isotherms and Isosteric Heats of Adsorption

The hydrogen sorption isotherms are presented for experiment\textsuperscript{15} and simulations using the Buch, BSS, and BSSP models in NOTT-112 for pressures $\leq 1.0$ atm at 78 and 88 K in Figure 2.5. Note, the experimental and simulated H₂ uptakes are reported in units of absolute weight percent (wt %), which is defined as: 

$$\frac{\text{(Mass of H}_2\text{)}}{\text{(Mass of MOF} + \text{Mass of H}_2\text{)}} \times 100\%.$$ 

The theoretical isotherms shown in Figure 2.5 are based on simulations within the NOTT-112 potential energy surface where the MOF partial charges were calculated using the 6-31G$^*$ basis set for all atoms. Simulations using the model that includes explicit polarization (BSSP) produced isotherms that are in outstanding agreement with experiment for all state points considered. On the other hand, the BSS model, which includes permanent electrostatic interactions, generated isotherms that are notably lower than those for the BSSP model and therefore undersorb experiment for the considered pressure range at both temperatures. The single-site Buch model produced isotherms that are even lower for all state points considered. These results demonstrate the necessity of including polarization interactions in a classical simulation to reproduce experimental sorption measurements in a highly polar MOF.

The accuracy of the BSSP model at very low loading (e.g., 0.1 atm) is due to capturing the first sorption events in simulation, with H₂ sorbing onto the open-metal sites. This highlights the importance of polarization interactions for gaining an atomistic understanding of the sorption mechanism. It is also another example of how classical polarization is capable of quantitatively capturing this ostensible chemical phenomena.\textsuperscript{6,7,12,22,34–38,43,49}

Note, the error bars for all simulated state points considered are extremely small, with a maximum calculated error of $\pm 0.022$ wt %; thus, they have been omitted from the simulated isotherms for clarity.

It is notable that the electrostatic parameters derived using the 6-31G$^*$ basis set for all atoms, in contrast to those calculated using an effective core potential (ECP) for the
Figure 2.5: Simulated H\textsubscript{2} sorption isotherms in NOTT-112 compared with experiment (black) for the BSSP (red), BSS (green), and Buch (blue) models for pressures ≤ 1.0 atm at 77 K (circles) and 88 K (squares). The experimental data were taken from reference 15.

many-electron Cu\textsuperscript{2+} ions, yielded a higher partial positive charge on both chemically distinct Cu\textsuperscript{2+} ions and consequently higher simulated uptakes in NOTT-112, especially at low loading. The most important point to note here is that the overall magnitude of the Cu\textsuperscript{2+} partial charges is controlling sorption and not simply the ratio of the charges.

Figure 2.6: Isosteric heat of adsorption (Q\textsubscript{st}) for H\textsubscript{2} in NOTT-112 plotted as a function of loading. The experimental Q\textsubscript{st} values, taken from reference 15, are compared with those values that were determined from simulations using the BSSP (red), BSS (green), and Buch (blue) models.

A comparison of the experimental H\textsubscript{2} Q\textsubscript{st} values with those determined from simulations using the Buch, BSS, and BSSP models in NOTT-112 is provided in Figure 2.6. When comparing the results for the most realistic model (BSSP) with experiment, decent
agreement can be observed for most of the considered loading range (ca. \( \geq 0.3 \) wt %). Simulations using the Buch and BSS models produced \( Q_{st} \) values that underestimate experiment for the same loading range. Any deviations between experiment and simulation (considering the BSSP model) can be attributed to the difference in calculation method between experiment and the theoretical model. The experimental \( Q_{st} \) values are calculated using equation 3.2,\textsuperscript{64,65} and requires a large number of isotherm points at low loading to calculate the relevant derivatives.

\[
Q_{st} = kT^2 \frac{\partial \ln P}{\partial T}
\]

(2.1)

where \( k \) is the Boltzmann constant, \( P \) is the pressure, and \( T \) is the temperature. The theoretical \( Q_{st} \) are calculated in GCMC simulation by:\textsuperscript{66}

\[
Q_{st} = -\frac{\langle NU \rangle - \langle N \rangle \langle U \rangle}{\langle N^2 \rangle - \langle N \rangle^2} + kT
\]

(2.2)

where \( \langle \rangle \) indicates the ensemble average, \( N \) is the particle number, and \( U \) is the total potential energy.

For \( \text{H}_2 \) sorption in a MOF with \( rht \) topology, an initial loading \( Q_{st} \) within the range of 5.5 to 9.5 kJ mol\(^{-1} \) have been reported when considering both experimental data\textsuperscript{28,29,31–33} and simulation.\textsuperscript{22,34,35,43} As shown in Figure 2.6, the \( Q_{st} \) plot for the BSSP model is in very good agreement with experimental measurements for the second charge parametrization (6-31G* used for all atoms in partial charge calculations), except at low loading. It is clear that the magnitude of the copper charges heavily influence the mechanism of initial loading, and this is consistent with the first charge parametrization (\( \text{Cu}^{2+} \) ions treated with ECPs in partial charge calculations) giving proportionally lower sorption compared to using higher positive charge magnitudes for the \( \text{Cu}^{2+} \) ions. Implementation of higher levels of \textit{ab initio} theory, e.g., post-Hartree–Fock perturbation theory, would likely yield more accurate partial charges. As in all cases of computational research, calculative
efficiency must be balanced with maximization of accuracy and the amount of data produced. In this case, there is the need for overpolarized charges to represent MOF–MOF self polarization in the current modeling paradigm. Note, both charge parametrizations yielded a consistent sorption mechanism and reasonable models. Indeed, the first set of parameters yielded slightly better agreement with experiment at saturation with a lower initial $Q_{st}$. Nonetheless, careful modeling provides valid physical insights with atomistic resolution.

2.5.2 H$_2$ Sorption Sites

By neutron powder diffraction (NPD) experiments, Yan et al. discovered that the CuC ions are the primary H$_2$ sorption sites in NOTT-112. A CuC–D$_2$ interaction distance of 2.23(1) Å was observed from the NPD studies. The radial distribution function, $g(r)$, for the BSSP model about the CuC ions at 78 K and 0.10 atm reveals a clear peak from 2.2–3.0 Å (maxima at ca. 2.57 Å), which is indicative of H$_2$ sorbing onto those Cu$^{2+}$ ions in simulation (Figure 2.7). Indeed, examination of the modeled structure for the BSSP model in NOTT-112 confirmed that the H$_2$ molecules are sorbed onto the CuC ions at low loading as depicted in Figure 2.8(a). Thus, the simulations support the experimental finding that the CuC ions are the initial H$_2$ sorption sites in NOTT-112. The $g(r)$ for the BSS model shows slight sorption at the higher part of this range, while the Buch model, lacking explicit electrostatic interactions, entirely misses this contribution to the sorption mechanism. By not capturing this effect, the sorption at other sites is changed due to packing effects at higher pressures; the initial sorption sites influence subsequent sorption structure even when the energetics are correct in the other regions of the MOF.

This first definitive peak in the $g(r)$ about the CuC ions is entirely absent for the models that do not include explicit polarization effects, which suggests that polarization is the driving force for modeling the metal–sorbate interaction. This is not a unique observation as previous theoretical studies have shown, although what is novel in this case is that specific sorption distances associated with energy minima have been accurately modeled for H$_2$ and experimentally deduced for the D$_2$ molecular isotope.
Figure 2.7: Radial distribution function, g(r), of the center-of-mass (COM) of H\textsubscript{2} molecules about CuC for the BSSP (red), BSS (green), and Buch (blue) models in NOTT-112 at 78 K and 0.10 atm. The approximate CuC–COM distance for the primary and secondary sites are also indicated.

Deuterium was specifically used in the NPD experiments because it is more effective in elastic scattering than H\textsubscript{2} due to the presence of neutrons, which scatter from the nuclei of atoms.

The g(r) was also measured about the CuL ions in NOTT-112 for all three models at 78 K and 0.10 atm (Figure 2.9). These results reinforce the existence of sorption onto the primary sorption site (the CuC ions) in simulation, with a strong peak occurring at ca. 5.18 Å for the BSSP model only. In addition, a notable peak is evident at around 6.32 Å for all models; this peak corresponds to sorption onto the secondary sites in the MOF (described below). Interestingly, no peak was observed in the range of 2.2–3.0 Å about the CuL ions for all three models. This indicates the absence of sorption onto the CuL ions in simulation, even when explicit many-body polarization effects were included. This is in contrast with experimental results as NPD studies revealed that the D\textsubscript{2} molecules can sorb onto the CuL ions with a metal–sorbate distance of 2.41(1) Å.\textsuperscript{16} The lack of significant sorption onto the CuL ions in simulation could be attributed to the lower calculated partial positive charge for the CuL ions. Perhaps the positive charge for these Cu\textsuperscript{2+} ions is not high enough in magnitude to facilitate strong H\textsubscript{2}–metal interactions in simulation; a similar finding was observed in a MOF with open-metal sites in previous theoretical work.\textsuperscript{68}
Figure 2.8: The two quantitatively identified H\textsubscript{2} sorption sites in NOTT-112 from simulation: (a) sorption onto the CuC ion with a CuC–COM distance of \( \sim 2.57 \) Å; (b) and (c) sorption into the corner site of the truncated tetrahedron (\( T-T_d \)). Note, some of the atoms are truncated from the MOF for clarity. The H\textsubscript{2} molecule is shown in cyan. MOF atom colors: Cu = brown; O = red; C = grey; H = white.
This primary sorption site in NOTT-112 was further investigated by simulated annealing Monte Carlo using a D$_2$ model that is based on the BSSP potential, where only the atomic mass was set to 2.014 amu and the other parameters are left unchanged. The simulations were performed to match the experimental conditions for the NPD measurements (i.e., 0.5, 1.0, 1.5, and 2.0 D$_2$/Cu loading starting at 50 K). The resulting $g(r)$ about the CuC ions revealed that an interaction distance of $\sim$2.3–2.9 Å was obtained (see Supporting Information, Figure S12(a)), which is somewhat higher than what was obtained from NPD studies. It is reasonable to expect some discrepancy between the experimental and theoretical metal–sorbate distances, as the deuterium model used for the simulations herein was not rigorously developed under these extreme conditions. It has been shown that the mechanism of sorption for isotopes of hydrogen differs by thermal quantum effect properties, and induced electronic spin-state changes, which were not considered in these semi-classical simulations (via Feynman-Hibbs potential energy corrections).

It is notable that the strongest induced sorbate dipoles in simulation using the BSSP model correspond to sorption directly onto the CuC ions in the region described above; this correlates to the notable peak observed from 2.2–3.0 Å in the $g(r)$ about the CuC ions for the this model (Figure 2.7).
sorption mechanism is important not only for initial loading but also at higher pressures, as shown in Figure 2.10. Indeed, even at 1, 5, and 10 atm, polarization effects were still essential to capture the sorption of H$_2$ onto the CuC ions in NOTT-112 (Fig. 2.10). Radial distribution calculations for CuL under these conditions still did not show any significant sorption onto the CuL sites (see Fig. S14 in Supporting Information), further suggesting that the charge parameter plays a key role for sorption. To this effect, since experimental data$^{16}$ did suggest that some deuterium sorbs onto CuL (15% compared to CuC), a series of charge-variation tests were performed, where only the CuC and CuL charge parameters were changed. An equal or greater CuL charge resulted in sorption to the CuL site, although, the sorption to CuC is mostly lost as a result. The radial distributions and specific parameters can be found in Fig. S13 and Table S8 in the Supporting Information.

Figure 2.10: Radial distribution function, g(r), of the center-of-mass (COM) of H$_2$ molecules about CuC for the BSSP (red), BSS (green), and Buch (blue) models in NOTT-112 at 78 K and various pressures (1 atm = solid, 5 atm = dotted, 10 atm = dashed).

In NOTT-112, a secondary sorption site was observed in the corner of the $T$--$T_d$ cages (Figures 2.8(b) and 2.8(c)). This sorption site corresponds to the peak seen at approximately 5.18 and 6.32 Å in the g(r) about the CuC (Figure 2.7) and CuL ions (Figure 2.9), respectively, for all three H$_2$ potentials. The aforementioned distance about the CuL ion agrees well with the experimental distance reported for D$_2$ about this site.$^{16}$
Note, this sorption site has been observed for H$_2$ in a number of other \textit{rht}-MOFs through theoretical studies.$^{13,22,34,35,43}$

### 2.5.3 Simulated Annealing

Simulated annealing of the MOF–H$_2$ system was performed starting from several initial temperatures to assess the minimum energy landscape. Details of performing the simulated annealing calculations are provided in the Supporting Information. The resulting structures are characterized in terms of the Cu–COM energy-minimized distances in Table 2.2.

Table 2.2: Summary of the calculated CuC and CuL interaction distances for H$_2$ and D$_2$ (measuring about the center-of-mass (COM)) in NOTT-112 through simulated annealing studies. All sorbate molecules began \textit{ca.} 2.5 Å from the CuC or CuL ions, parallel to the Cu–Cu axis of the copper paddlewheels. The starting and ending temperatures (in K) and the number of Monte Carlo simulation steps ran for each simulated annealing calculation are provided. A qualitative description of the results are given relative to the sorption sites (site 1 = CuC ions, site 2 = $T$–$T_d$ cage.)

<table>
<thead>
<tr>
<th></th>
<th>Starting T (K)</th>
<th>Ending T (K)</th>
<th>Monte Carlo Steps (×1000)</th>
<th>Result</th>
<th>Cu–COM Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuC</td>
<td>20</td>
<td>5.58</td>
<td>444</td>
<td>stays at initial location</td>
<td>3.259</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>9.23</td>
<td>444</td>
<td>stays at initial location</td>
<td>2.990</td>
</tr>
<tr>
<td></td>
<td>77</td>
<td>14.83</td>
<td>391</td>
<td>moves to diff. site 1</td>
<td>2.844</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>29.55</td>
<td>449</td>
<td>moves to diff. site 1</td>
<td>2.628</td>
</tr>
<tr>
<td>CuL</td>
<td>20</td>
<td>6.88</td>
<td>246</td>
<td>moves to site 2</td>
<td>6.27</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>6.36</td>
<td>386</td>
<td>moves to site 2</td>
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</tr>
<tr>
<td></td>
<td>77</td>
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<td>386</td>
<td>moves to site 2</td>
<td>6.316</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>39.99</td>
<td>417</td>
<td>moves to diff. site 1</td>
<td>2.609</td>
</tr>
<tr>
<td>D$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuC</td>
<td>20</td>
<td>7.78</td>
<td>435</td>
<td>stays at initial location</td>
<td>2.837</td>
</tr>
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<td>stays at initial location</td>
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<tr>
<td></td>
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<td>457</td>
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<tr>
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<td>434</td>
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<tr>
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<td>40</td>
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<tr>
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<td>452</td>
<td>moves to site 2</td>
<td>6.07</td>
</tr>
</tbody>
</table>

The experimental NPD study for D$_2$ binding in NOTT-112 reports sorption onto the CuC and CuL ions, with interaction distances of 2.23(1) and 2.41(1) Å, respectively.$^{16}$ The experimental binding site for the latter was much less favored (representing about 15% on open-metal sorption) than the former. Sorption onto the CuL ions was not observed from the simulations in this work. This could be due to the lower partial positive charge
(relative to the CuC ions) that was calculated for these ions using the level of theory considered. If a higher electronic structure method was utilized, then perhaps more accurate partial charges could be obtained for the CuL ions, which in turn could result in capturing sorption onto such ions in simulation. It is somewhat atypical for an unequal affinity between Cu$^{2+}$ ions about the copper paddlewheels in MOFs of this type, but the structure and topology of NOTT-112 contributes to a lower electron density on the CuC ions (according to quantum mechanical calculations of the point partial charges) and thus a stronger interaction with H$_2$ for the these ions. Note, unlike in NOTT-112, the two Cu$^{2+}$ ions that make up the copper paddlewheels in HKUST-1 are equivalent; thus, there are equal affinities on both Cu$^{2+}$ ions in this MOF, which exhibits a Cu–D$_2$ distance of 2.39(1) Å according to NPD measurements.$^{71}$

In cases where the metal–sorbate interaction distance exceeded 6.0 Å, the sorbate molecule was found to localize to the secondary sorption site in the MOF, i.e., the corner of the $T$–$T_d$ cages as displayed in Figures 2.8(b) and 2.8(c). This was the case for nearly all simulated annealing calculations that started with the sorbate molecule (whether H$_2$ or D$_2$) positioned approximately 2.5 Å from the CuL ions (Table 2.2). Since the CuL ions were not favorable for sorbate binding within the present force field of NOTT-112, the sorbate molecules do not stay at these ions. It is interesting to note that the sorbate molecules mostly migrate to the corner of the $T$–$T_d$ cages for the energy minimum position rather than the CuC ions, which represents the global minimum in the system. It is expected that the H$_2$ or D$_2$ molecule is trapped at the $T$–$T_d$ cage because this site represents a local minima in the system. This could be due to the fact that the volume of this region is much larger than that for the primary binding site and not enough energy is available for the sorbate molecule to escape this energy basin. Note, the theoretical secondary site was discovered as a sorption site from the NPD experiments with a selectivity of 6% at a loading of 1 D$_2$/Cu.$^{16}$

For simulated annealing calculations where the H$_2$ or D$_2$ molecule was initially positioned near the CuC ions, the sorbate molecule either stayed in the region around their starting location or migrated to another CuC ion in the NOTT-112 system at the com-
pletion of the simulations (Table 2.2). Indeed, the sorbate molecules do not settle at different binding sites in the MOF when they are positioned near the global minimum to start the calculations. Reasonably short CuC–COM distances (typically less than 3.0 Å) were also obtained from these calculations. Further, it seems that utilizing a higher initial starting temperature causes the sorbate molecule to move to a different area of the MOF. This makes sense since a higher thermal energy allows the sorbate molecule to explore vast regions of the MOF in the simulated annealing process.

2.6 Conclusion

The world of MOFs gives experimental and theoretical researchers an exciting chance for collaborative design and development of these materials to target specific applications, such as H$_2$ storage and CO$_2$ capture and sequestration. The collective efforts in the physical production of new MOFs and the continual enhancement of computational methodology can help provide a better understanding of such materials. An ultimate goal is the synthesis of a material that can assist in reducing CO$_2$ emissions and therefore sustain human life in the future. There is indeed a pressing need for modern, rationally designed materials that can remediate human impact while facilitating inexpensive manufacturing processes. This kind of research aids the development of new materials that can effectively store and release hydrogen by increasing the depth of quantitative understanding of the microscopic interactions that cause macroscopic phenomena. In order to effectively design and evaluate these kinds of materials, software that can accurately model atomic-scale interactions using algorithms inspired by fundamental principles of chemistry and physics is an invaluable tool, and a pragmatic necessity when the components are particularly toxic and laboratory experiments are undesirable, e.g., with CO and HCN.

Here, the paramount role of polarization interactions for accurate modeling in a heterogeneous media was evident. The H$_2$ uptakes, $Q_{st}$ values, and binding sites have been accurately simulated in the $rht$-MOF NOTT-112. Simulations involving explicit many-body polarization produced observables that are in good agreement with the correspond-
ing experimental measurements in this MOF. Also, it was shown in this work that classical simulation was sufficient to capture the important chemical process in the sorbent, i.e., the interaction between the sorbate molecule and the open-metal site. Indeed, extensive (and expensive) quantum mechanical calculations were not needed to reproduce the metal–sorbate interaction. Further, the utility of neutron scattering techniques for sorption site determination in MOFs provides a useful empirical basis for the improvement and comparison of computational modeling and chemical theory.

High-throughput computational methods\textsuperscript{74} provide an excellent basis for initial screening for potentially effective sorbent materials. Further analysis on targeted compounds is meritable to infer the most effective route for synthesis, whether discovered theoretically or empirically. The subject of this study remains one of the best sorbents for H\textsubscript{2}.\textsuperscript{15} Experimental studies have shown that NOTT-112 is capable of sorbing 2.3 and 10.0 wt % of H\textsubscript{2} (absolute quantity) at 78 K/1 bar and 77 K/77 bar, respectively.

In closing, it is worth mentioning that the DOE initiative for efficient hydrogen storage remains a difficult challenge for the scientific and engineering communities. The ultimate goal of 7.5 wt % under near-ambient conditions\textsuperscript{21} is a target that has yet to be reached. This does not hinder many synthetic and computational chemists, however, as sorbents with higher H\textsubscript{2} uptake capacities are continually being discovered.\textsuperscript{3} It should be without question that scientific investigations in search of more energy efficient sources are meritable avenues of government support. In the process, not only do we produce solutions to optimally supply energy to a growing populace, but importantly (and often overlooked), we gain insights and discoveries that have potential to increase our breadth of understanding the materials and the world.

2.7 Acknowledgements

The authors acknowledge the National Science Foundation (Award No. CHE-1152362), including support from the Major Research Instrumentation Program (Award No. CHE-1531590), the computational resources that were made available by a XSEDE Grant (No. TG-DMR090028), and the use of the services provided by Research Computing at the
University of South Florida. We also thank Professor Martin Schröder and Dr. Sihai Yang for their clarifications on the H$_2$ sorption isotherms presented in reference 15.
Simulations of hydrogen, carbon dioxide, and small hydrocarbon sorption in a nitrogen-rich rht-metalorganic framework

3.1 Note to Reader

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3.2 Abstract

Grand canonical Monte Carlo (GCMC) simulations of gas sorption were performed in *rht*-MOF-9, a metal–organic framework (MOF) with *rht* topology consisting of Cu$^{2+}$ ions coordinated to 2,5,8-tris(3,5-dicarboxyphenylamino)-1,3,4,6,7,9,9b-heptaazaphenalene (TD-CPAH) ligands. This MOF is notable for the presence of open-metal copper sites and high nitrogen content on the linkers. *rht*-MOF-9 exhibits one of the highest experimental H$_2$ uptakes at 77 K/1 atm within the extant *rht*-MOF family (ca. 2.72 wt %) and also has strong affinity for CO$_2$ (5.83 mmol g$^{-1}$ at 298 K/1 atm). Our simulations, which include explicit many-body polarization interactions, accurately modeled macroscopic thermodynamic properties (e.g., sorption isotherms and isosteric heats of adsorption ($Q_{st}$)) as well as the binding sites for H$_2$, CO$_2$, CH$_4$, C$_2$H$_2$, C$_2$H$_4$, and C$_2$H$_6$ in the MOF. Four different binding sites were observed through analysis of the radial distribution function (g(r)) about the two chemically distinct Cu$^{2+}$ ions, simulated annealing calculations, and examination of the three-dimensional histogram showing the sites of occupancy: (1) at the Cu$^{2+}$ ion facing toward the center of the linker (CuL), (2) at the Cu$^{2+}$ ion facing
away from the center of linker (CuC), (3) nestled between three [Cu2(O2CR)4] units in the corner of the truncated tetrahedral (T–Td) cage and (4) straddling the copper nuclei parallel to the axis of the Cu–Cu bond within the T–Td cage. The low-loading (initial) binding site in the MOF is highly sensitive to the partial charges of the Cu2+ ions that were used for parametrization. It was discovered that most sorbates prefer to sorb onto or near the Cu2+ ions that exhibit the greater partial positive charge (i.e., at site 1). The simulated H2 and CO2 sorption results obtained using a polarizable potential for the respective sorbates are in good agreement with the corresponding experimental data, especially near ambient pressure. Simulations of gas sorption were also performed in rht-MOF-9 using nonpolarizable potentials for the individual sorbates; these include potentials from the TraPPE force field for most sorbates.

3.3 Introduction

Since the early 1990s, metal–organic frameworks (MOFs), a class of crystalline materials that are often porous, have been of rapidly increasing interest in the scientific and engineering communities.75 MOFs are three-dimensional structures composed of metal ions coordinated to organic ligands (also called “linkers”). The first reported MOF structure in the Cambridge Structural Database (CSD) dates back to 1978.76 Major advances have been made for utilizing MOFs for various applications, such as carbon dioxide (CO2) capture,4,5,7,17 hydrogen (H2) storage,3,10,11 gas separation,7,77 and catalysis.78–81

The computational study of MOFs is a recently emerging area of investigation. Predictive simulations of the sorption process in MOFs depend on accurate and thorough parametrizations of both the sorbate and sorbent. Using high levels of ab initio calculations, the properties of these materials can be fit to classical parameters to quantitatively reproduce physical phenomena. As models for the sorbate and sorbent continue to be developed,12,41,82 more accurate and efficient methods are introduced to reliably predict the sorption properties in porous materials. MOFs are ideally suited for computer simulation due to their crystalline and periodic nature. Macroscopic properties such as gas uptake isotherms, isosteric heat of sorption (Qst), and selectivity can be determined by
simulating very few to several unit cells of the crystal with a given sorbate model. There is still much room for growth in MOF modeling, however, as only a few accurate, transferable, and extensively tested potentials exist for small guest molecules, e.g., H₂, CO₂, N₂, and CH₄. In addition, parametrization of the material of interest remains a challenging and sometimes tedious problem to solve. For example, obtaining electrostatic parameters (i.e., partial charges) for the MOF can become difficult due to limitations in calculating the wavefunctions and accurate electrostatic potential surfaces (ESPs), especially if the system size is large. In spite of these problems, accurate prediction and retrodiction of MOF–sorbate interactions have been demonstrated to be invaluable for both validation of experimental measurements and elucidating gas sorption mechanisms.

The interest in MOFs is growing because the utility of these materials is manifold and their synthesis is very straightforward (usually involving a binary mixture of an organic ligand and metal cation in different solvents). In addition to the aforementioned uses of MOFs, highly selective gas separation involving other guest molecules (e.g., dyes, counterions, sensing, and photoinduced electron transfer have been reported. Further, the porous, thermodynamically sensitive, and sometimes flexible nature of MOFs make them an ideal candidate for various short- and long-term gas sorption and separation applications. Indeed, several MOFs have already been commercialized for remarkably high and reversible gas (especially CO₂) sequestration, selectivity, and storage.

The rht-MOF family is a relatively emerging and heavily studied class of MOFs in which the overall structure consists of three distinct cages: cuboctahedron (cub–O₈), truncated tetrahedron (T–T₄), and truncated octahedron (T–O₈). The first reported rht-MOF was rht-MOF-1, which was synthesized by Eddaoudi and co-workers in 2008. These MOFs have been used as platforms for gas storage, catalysis, and sensing among other applications. rht-MOFs are synthesized by the addition of a metal ion in the 2+ oxidation state to a C₃ symmetric ligand that is usually planar and contains three isophthalate groups on the edges. Since 2008, a large number of MOFs with rht
The judicious selection of the linker has been shown to change the pore volume, surface area, and sorption properties for various gases in \textit{rht}-MOFs.

Snurr and co-workers showed simulated H\textsubscript{2} sorption results in a variety of \textit{rht}-MOFs containing mainly carbon and hydrogen atoms within the central component of the linkers.\textsuperscript{23,110–112} They found that, in general, employing larger linkers resulted in greater excess uptakes at higher pressures. This is reasonable since a larger pore volume would allow more gas molecules to occupy the material under such conditions. In the earlier years of MOF synthesis, high priority was given to producing materials with increasingly high pore volume. However, it has been discovered that introducing charged or polar moieties within the material can significantly influence gas uptake, and MOFs with smaller pore volumes are capable of sorbing large amounts of gas at low pressures if synthesized with intentional chemical and physical intuition. Indeed, some MOFs, e.g., those within the “SIFSIX” family, are suited to sorb guest molecules in single pores with very high selectivity.\textsuperscript{7,113,114}

The unique geometry of the self-assembled crystals of \textit{rht}-MOFs allows for excellent tunability of the pore sizes and functionalities. These MOFs exhibit high uptake for various energy-related gases at low loading mostly due to the presence of open-metal sites. The introduction of nitrogen-rich regions on the linker can further increase MOF–sorbate interactions as demonstrated previously by several experimental groups.\textsuperscript{29,32,77,115–118} Over time through several theoretical studies,\textsuperscript{6,7,22,34–38,41–43,49,51,67,119,120} our group has shown that gas uptake in porous materials is not a simple function of pore volume or surface area. Rather, a careful analysis of the sorbent–sorbate interactions is needed to elucidate both the uptake capacity, and more importantly, the physical mechanism of gas sorption, especially when open-metal sites are involved. We note that simple introduction of nitrogen atoms on the linkers in MOFs does not necessarily improve selectivity or affinity for gases as shown by Mohamedali \textit{et al.}\textsuperscript{121} and Gao \textit{et al.}\textsuperscript{122,123} In general, a deeper chemical understanding is required to rationally design and predict MOFs with useful properties and simulation is an excellent way to obtain such insights.
Great efforts have been expended to develop a material that can store H$_2$ in high concentrations$^{124,125}$ because of its high energy density by mass,$^{20}$ and, contrary to most widely used fuels, produces only H$_2$O upon its combustion. While the U.S. Department of Energy (DOE) ultimate H$_2$ storage target of 7.5 wt % at ambient temperatures and high pressures$^{21}$ has yet to be attained and still seems far from reach, several materials have been synthesized that achieve $\sim$10 wt % of H$_2$ at colder temperatures and high pressures (e.g., 77 K and 60 atm),$^{15,16}$ and $\geq 2.5$ wt% at 77 K and 1 atm.$^{126-129}$

In 2010, the amount of energy-related CO$_2$ emission in the atmosphere reached an all-time high of 30.6 gigatonnes (roughly 4400 kg per person on earth) and global levels have nearly doubled since the early 1970s due to increasing use of fossil fuels in developing countries.$^{130}$ Thus, there is a pressing need for cost-effective, eco-friendly, and easily manufactured materials that can remove or mitigate the effects of CO$_2$ and other emitted gases on environmental stability and human health.$^{131}$ In addition, separation of CO$_2$ from other gases is desirable, especially in industrial processes where CO$_2$ is an unwanted byproduct. For example, CO$_2$ is known to poison the Li/MgO catalyst for methane (CH$_4$) to ethane (C$_2$H$_6$)/ethylene (C$_2$H$_4$) conversion.$^{77,132}$ Although it is important to remove CO$_2$ from flue gas emissions for industrial and environmental reasons, the motivation for CO$_2$ sequestration is inhibited because there are few scalable or popular uses for the compound itself. In the early years of research on porous materials for gas sorption, zeolites$^{133-136}$ were the primary material of interest for CO$_2$ separation because of their exceptional stability. As methods for synthesis and simulation of MOFs improve, many scientists are shifting their focus to such materials. Unlike zeolites (which are naturally occurring aluminosilicate minerals), MOFs can be synthesized systematically and rationally by careful selection of the metal cations and organic ligands to perform specific functions.$^2$

Since the chief component of natural gas is CH$_4$ (80–95%) and the impurities in this mixture are mainly C$_2$ hydrocarbons,$^{77}$ a material that can selectively sorb the latter over the former is desirable. Further, CH$_4$ is a fuel that burns cleaner than gasoline, thus making it a potential alternative for vehicular applications. CH$_4$ is also used in the
production of halomethanes, acetylene (C\(_2\)H\(_2\)) and other small molecules that serve as the building blocks for myriad useful chemicals like welding fuel, cleaning solvents, polymer plastics, and pharmaceuticals. Like CH\(_4\), the other C\(_2\) hydrocarbons considered in this study are useful as fuels and precursor molecules for diverse purposes, and therefore an efficient and reversible method of isolation and separation of these molecules is sought-after.

This work demonstrates the accuracy of some extensively tested polarizable and non-polarizable gas models (H\(_2\), CO\(_2\), and CH\(_4\))\(^{12,41,61,84,86,88}\) and promising effectiveness of newly developed polarizable models for C\(_2\)H\(_2\),\(^{137,138}\) C\(_2\)H\(_4\), and C\(_2\)H\(_6\) in \(rht\)-MOF-9 (Figure 3.1).\(^{77,118}\) This is a Cu\(^{2+}\)-based \(rht\)-MOF with an unconventional heptazine core connected to secondary amine groups in the triisophthalate linker. This MOF presently exhibits one of the highest H\(_2\) (ca. 2.72 wt% at 77 K/1.0 atm) and CO\(_2\) (ca. 5.83 mmol g\(^{-1}\) at 298 K/1.0 atm) uptakes within the extant \(rht\)-MOF family\(^{103}\) and is the first \(rht\)-MOF to feature a polycyclic central core.\(^{118}\)

Two groups have independently synthesized \(rht\)-MOF-9 (also known as Cu-TDPAH) in 2014, with both groups reporting their own distinct gas sorption measurements and crystal structure on the material.\(^{77,118}\) Interestingly, the 2,5,8-tris(3,5-dicarboxyphenylamino)-1,3,4,6,7,9,9b-heptaazaphenalene (TDCPAH) linker of this MOF contains coplanar angularly connected isophthalate groups,\(^{116}\) leading to a lower symmetry in the crystal structure compared to those \(rht\)-MOFs with coplanar linearly connected isophthalate groups, such as NOTT-112.\(^{15}\) Indeed, the crystal structure for NOTT-112 is cubic whereas that for \(rht\)-MOF-9 is tetragonal. In addition, the presence of nitrogen-rich centers on the linker resulted in greater affinity for various gases as compared with \(rht\)-MOFs containing mostly carbon and hydrogen atoms within their core (Figure 3.2).\(^{15,16,28}\) Moreover, Liu and co-workers have demonstrated the high selectivity of C\(_2\) hydrocarbons and CO\(_2\) over CH\(_4\) in \(rht\)-MOF-9.\(^{77}\)

This work aims to provide elucidation of the gas sorption mechanism and binding sites in \(rht\)-MOF-9 on an atomistic level using classical simulations. Of particular interest are the effects of the relative partial charges for the two chemically distinct Cu\(^{2+}\) ions about
the copper paddlewheels toward gas sorption: \textbf{CuC}, the Cu$^{2+}$ ion facing away from the center of the linker and located within the Cuboctahedral cage, and \textbf{CuL}, the Cu$^{2+}$ ion facing toward the center of the Linker and located within the T–T$_d$ and T–O$_h$ cages (see Figures 3.1 and 3.2).

### 3.4 Methods

The X-ray crystal structure for \textit{rht}-MOF-9 was taken from Eddaoudi et al.\textsuperscript{118} The system was purged of solvent molecules to obtain an empty crystal structure of the MOF to mimic experimental gas sorption conditions. All MOF atoms were treated as rigid for the simulations. Parameters from the Universal Force Field (UFF)\textsuperscript{52} were assigned to the sorbent atoms to model Lennard-Jones 12–6 repulsion/dispersion interactions.\textsuperscript{139,140} The Lorentz–Berthelot mixing rules\textsuperscript{56} were applied to handle the interactions between
Figure 3.2: A comparison of the copper paddlewheels and organic linkers (truncated for clarity) that comprise the frameworks in NOTT-112 (left) and rht-MOF-9 (right) with chemically distinct atom labels. Note, the introduction of electronegative N atoms on the linker for rht-MOF-9 results in enhanced gas sorption capacities relative to NOTT-112 (which contains only C and H atoms in the center of the linker). Atom colors: Cu = brown; C = grey; H = white; N = blue; O = red. Terminal atoms (where the system is truncated from the MOF) are marked with a red asterisk.

Unlike species. Scalar point polarizabilities were also given to the MOF atoms and such parameters were taken from the work of van Duijnen and Swart\textsuperscript{57} with the notable exception of that for Cu\textsuperscript{2+}, which was determined in previous work.\textsuperscript{43}

All MOF atoms were also treated with point partial charges to model stationary electrostatic interactions. The electrostatic parameters were obtained by averaging several instances of the partial charges of sufficiently buried chemically distinct atoms in 7 representative fragments of the MOF. These partial charges were calculated using ORCA\textsuperscript{141} with the Hartree–Fock (HF) method and 6-31G* basis sets for all atoms followed by the CHELPG fitting method.\textsuperscript{142,143} Prior to this, terminal H atoms on the fragments were optimized using the same level of theory. Note, while more modern electronic structure methods exist (e.g., density functional theory (DFT)), it has been extensively demonstrated that the HF/6-31G* level of theory produces efficient and accurate charge parameters for MOF modeling,\textsuperscript{6,7,22,34–36,42,43,51,67,119} especially due to the overpolarized nature of the basis set.\textsuperscript{144} Periodic quantum mechanical calculations for charge-fitting are also possible\textsuperscript{145,146} using softwares such as the Vienna \textit{ab initio} Simulation Package (VASP),\textsuperscript{147–149} but this was computationally prohibitive due to the large size of the unit.
cell of rht-MOF-9. More details regarding parametrization of the MOF, including figures of selected representational fragments, are provided in the ESI†.

Simulations of gas sorption in rht-MOF-9 were performed using grand canonical Monte Carlo (GCMC) methods,\textsuperscript{150} which is described more in detail in the ESI†. The total potential energy of the MOF–sorbate system was calculated as the sum of three contributions: (1) repulsion/dispersion interactions using the Lennard-Jones 12–6 potential\textsuperscript{139,140} (including long-range corrections),\textsuperscript{151} (2) permanent electrostatic interactions as calculated with Ewald summation\textsuperscript{59} of the point partial charges, and (3) many-body polarization interactions as calculated using a Thole–Applequist type method.\textsuperscript{46,47,57,152,153} In the case of H\textsubscript{2} sorption, fourth-order Feynmann–Hibbs quantum corrections\textsuperscript{62} were applied to the potential energy of the system.

In addition to the MOF, polarizable potentials were also used for all sorbates considered. The polarizable model employed for H\textsubscript{2} is the Belof Stern Space Polar (BSSP) model, which is a five–site model that has three polarizable sites.\textsuperscript{12} The analogous polarizable potential utilized for CO\textsubscript{2} is the CO\textsubscript{2}-PHAST* model, where PHAST stands for Potentials with High Accuracy, Speed, and Transferability and the * denotes the inclusion of explicit polarization.\textsuperscript{41} The polarizable model for CH\textsubscript{4} used herein, denoted Me-PHAST*, contains nine sites, five of which are polarizable.\textsuperscript{88} The polarizable C\textsubscript{2}H\textsubscript{2},\textsuperscript{137,138} C\textsubscript{2}H\textsubscript{4}, and C\textsubscript{2}H\textsubscript{6} models are four–, six–, and eight–site models, respectively, and all sites for these models contain polarizability parameters.

The electrostatic, nonpolarizable models used for H\textsubscript{2} are the three– and five–site Darkrim-Levesque (DL)\textsuperscript{84} and BSS\textsuperscript{12} models, respectively, while those for CO\textsubscript{2} are the analogous TraPPE\textsuperscript{86} and CO\textsubscript{2}-PHAST models,\textsuperscript{41} respectively. The individual nonpolarizable potentials for the hydrocarbons were also developed and employed herein (see ESI†); these models contain equal numbers of sites as their polarizable counterparts. Potentials that do not include electrostatic interactions (and therefore contain only Lennard-Jones parameters) were also considered for H\textsubscript{2}, CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{4}, and C\textsubscript{2}H\textsubscript{6}. Specifically, the potential developed by V. Buch was used for H\textsubscript{2} (referred to herein as Buch),\textsuperscript{61} whereas potentials from the TraPPE force field was used for CH\textsubscript{4},\textsuperscript{86} C\textsubscript{2}H\textsubscript{4},\textsuperscript{154} and C\textsubscript{2}H\textsubscript{6}.\textsuperscript{155}
In addition to gas uptake, the theoretical $Q_{st}$ values were calculated according to Equation 3.1, which involves fluctuations in the potential energy ($U$) and number of gas molecules ($N$) in the system in GCMC simulation:

$$Q_{st} = -\frac{\langle NU \rangle - \langle N \rangle \langle U \rangle}{\langle N^2 \rangle - \langle N \rangle^2} + kT$$  \hspace{1cm} (3.1)

Note, the typical method used to calculate $Q_{st}$ from experimental isotherm data is shown in equation 3.2, which involves a temperature derivative and therefore requires at least two isotherms collected at different temperatures in its computation (but is best represented when $>2$ isotherms are included).

$$Q_{st} = kT^2 \frac{\partial \ln P}{\partial T}$$  \hspace{1cm} (3.2)

All simulations were performed using Massively Parallel Monte Carlo (MPMC), a code developed and maintained by our group and available for download on GitHub under the GNU General Public License. While other classical programs exist for modeling porous materials, few contain the robust and fast algorithms for calculating the explicit many-body polarization energy contained in MPMC. Details for calculating all simulated observables considered in this study are provided in the ESI†. Most of the sorbate models used in this study were developed as described previously. The only exceptions are the polarizable models for $\text{C}_2\text{H}_4$ and $\text{C}_2\text{H}_6$; such potentials were developed by our group using a standard sorbate fitting procedure (see ESI† for details).
3.5 Results and Discussion

3.5.1 Summary

The modeled gas uptake and $Q_{st}$ for H$_2$ and CO$_2$ in rht-MOF-9 were remarkably accurate with respect to experiment for nearly all state points considered using the polarizable potentials for the respective sorbates. The polarizable models for CH$_4$ and C$_2$H$_n$ ($n = 2, 4, 6$) yielded useful information regarding the mechanism of gas sorption in the MOF, but the simulated uptakes and $Q_{st}$ values for these sorbates agreed less with the corresponding experimental measurements when compared to the agreement observed for H$_2$ and CO$_2$. We note that the polarizable H$_2$ and CO$_2$ models used herein have been extensively tested in a variety of porous materials. While the simulated hydrocarbon results shown here for rht-MOF-9 do not perfectly reproduce the experimental isotherms, the theoretical $Q_{st}$ values for these sorbates are nonetheless in decent agreement with the corresponding experimental $Q_{st}$ values. Thus, we still provide suggestions for the potential binding sites for these hydrocarbons in rht-MOF-9.

Overall, the quantitative hydrocarbon results can indicate the direction that needs to be taken for better model development. For example, it might be necessary to apply a scaling factor to the repulsion/dispersion parameters ($\sigma$ and $\epsilon$) used for the hydrocarbons, which has been shown to be useful in certain cases, especially for polarizable models of other small molecules. This is probably because of the dominance of repulsion/dispersion (van der Waals) energetics for hydrocarbon sorption compared to other gases (see ESI†, Figures S6, S13, S18, S25, S32, S39). To the best of our knowledge, although some C$_2$ hydrocarbon models have been developed to suit specific MOF force fields or reproduce vapor–liquid coexistence curves, there does not exist a robust and transferrable model of these gases for classical simulation in porous materials, especially one including explicit polarization. A summary of the major interaction distances of different sorbates about the primary binding site (site 1, described below) in rht-MOF-9 is presented in Figure 3.3.
Figure 3.3: The mean $g(r)$ distance of the nearest-neighbor peak for different sorbates about the CuL ions in rht-MOF-9 from simulations using polarizable potentials at 298 K (except H$_2$: 77 K). Strong open-metal physisorption is evident for H$_2$, C$_2$H$_2$, C$_2$H$_4$, and CO$_2$. Atom colors: H = white; C = black; O = red.

We note that the four identified binding sites for all sorbates in rht-MOF-9 as described later have been discovered experimentally via neutron powder diffraction (NPD) and X-ray crystallography and by theoretical methods (GCMC simulation and DFT energy calculations) for a number of other MOFs with copper paddlewheel units.$^{167-171}$ These correlations between experiment and theory will be discussed more in detail later. Simulated annealing (a process that lowers the system temperature as a function of simulation step until a desired minimum temperature is reached)$^{63}$ within the canonical (NVT) ensemble was performed for a single molecule of the individual sorbates in rht-MOF-9 with a starting temperature of 700 K and pressure of 0.1 atm. Quantitative (potential energies) and qualitative results (locations of annealed positions) for all considered models of each sorbate are displayed in Table 3.1. It is apparent from the simulated annealing calculations that all four sorption sites are represented as either local or absolute energy minima. This is not surprising given the fact that only one sorbate molecule can feasibly sorb onto one open-metal site (site 1 or 2) at a time (if it prefers that site) because of its strong affinity toward the highly charged Cu$^{+2}$ ions. Further, similar binding sites were observed for NOTT-112 (Fig. 3.2) in both experimental NPD$^{16}$ and simulation.$^{119}$ If one treats the magnitude of the final energies from Table 3.1 as approximations for the theoretical
Table 3.1: Simulated annealing results for different models of all sorbates in \textit{rht-MOF-9} from one-molecule simulations. All simulations were started at 700 K to ensure full exploration of the phase space before settling into a local or absolute energy minimum. The electrostatic (nonpolarizable) and polarizable models for the \textit{C}_2 hydrocarbons are denoted “Nonpolar” and “Polar”, respectively. \(T_f\) is the final temperature, \(U_f\) is the final averaged potential energy, and Exp. \(Q^0_{st}\) is the reported experimental \(Q_{st}\) at the lowest loading evaluated. The Result column lists the location of the simulated annealing position for the sorbate (sites 1, 2, 3, or 4, see main text). \(r_{CuC}\) and \(r_{CuL}\) represent the distance between the center-of-mass of the sorbate about the \(CuC\) and \(CuL\) ions, respectively, with the exception of the \(C_2\) hydrocarbon models for which \(r\) was determined by measuring about the C atoms. aFrom reference 118. bFrom reference 77.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
Model & \(T_f\) (K) & Steps (\(\times10^6\)) & \(U_f\) (kJ mol\(^{-1}\)) & Exp. \(Q^0_{st}\) (kJ mol\(^{-1}\)) & Result & \(r_{CuC}\) (Å) & \(r_{CuL}\) (Å) \\
\hline
\hline
H\(_2\) & 0.34 & 0.454 & -7.02 & 6.91\(^a\) & site 1 & — & 2.68 \\
BSSP & 0.13 & 2.703 & -31.2 & site 3 & — & 7.80 \\
BSS & 0.15 & 2.224 & -26.1 & site 3 & — & 5.81 \\
Buch & 0.28 & 0.404 & -9.75 & site 4 & 4.93 & 4.62 \\
DL & & & & & & & \\
\hline
\hline
CO\(_2\) & 1.25 & 1.679 & -29.0 & 37.9\(^a\)/33.8\(^b\) & site 2 & 3.25 & — \\
CO\(_2\)-PHAST & 4.13 & 0.463 & -32.8 & site 2 & 3.06 & — \\
CO\(_2\)-PHAST* & 0.90 & 1.752 & -22.3 & site 1 & — & 3.36 \\
TraPPE & & & & & & & \\
\hline
\hline
CH\(_4\) & 0.21 & 1.440 & -25.1 & 13.8\(^b\) & site 3 & — & 6.07 \\
Me-PHAST & 1.25 & 0.373 & -20.7 & site 4 & 5.39 & 4.68 \\
Me-PHAST* & 0.19 & 1.509 & -22.3 & site 3 & — & 6.12 \\
TraPPE & & & & & & & \\
\hline
\hline
C\(_2\)H\(_2\) & 0.86 & 1.646 & -29.4 & 23.5\(^b\) & site 2 & 2.63 & — \\
Nonpolar & 3.45 & 0.419 & -37.0 & site 2 & 2.73 & — \\
Polar & & & & & & & \\
\hline
\hline
C\(_2\)H\(_4\) & 0.49 & 1.446 & -27.8 & 45.0\(^b\) & site 4 & 4.77 & 5.75 \\
Nonpolar & 4.24 & 0.387 & -38.8 & site 2 & 2.62 & — \\
Polar & 0.24 & 1.963 & -24.2 & site 4 & 5.27 & 5.85 \\
TraPPE & & & & & & & \\
\hline
\hline
C\(_2\)H\(_6\) & 0.67 & 1.392 & -29.7 & 33.0\(^b\) & site 4 & 5.49 & 4.79 \\
Nonpolar & 1.70 & 0.402 & -29.8 & site 4 & 5.39 & 4.77 \\
Polar & 0.28 & 1.840 & -26.5 & site 4 & 5.15 & 5.88 \\
TraPPE & & & & & & & \\
\hline
\end{tabular}
\end{table}

\(Q_{st}\) at zero-loading (since there is only 1 gas particle in the simulation), such values are in close agreement with the experimental initial \(Q_{st}\) value for only the polarizable models for all sorbates with the exception of C\(_2\)H\(_2\). This demonstrates that models including explicit many-body polarization can more accurately reproduce important MOF–sorbate energetics at low loading.

### 3.5.2 Hydrogen

The H\(_2\) sorption isotherms in \textit{rht-MOF-9} at 77 and 87 K for experiment and four different H\(_2\) potentials are shown in Figure 3.4. All isotherms exhibit a Type I (or Langmuir) behavior,\(^{172}\) which is typical of gas sorption in a nanoporous material. At both temperatures, the isotherm for the polarizable BSSP model is in very good agreement with
Figure 3.4: H$_2$ sorption isotherms in rht-MOF-9 for experiment$^{118}$ and simulations using different models at (a) 77 K and (b) 87 K. Experiment = black, BSSP = red, BSS = green, Buch = blue, DL = brown.
experiment for most of the considered pressure range, especially at low loadings. The Buch model (which includes only repulsion/dispersion terms) notably undersorbs experiment at all state points considered. The BSS model (including repulsion/dispersion and electrostatic parameters) undersorbs experiment until about 0.6 atm at 77 K; the uptakes at pressures greater than this agreed very well with experiment. At 87 K, the isotherm for the BSS model slightly undersorbs experiment for all pressures considered. Simulation systems that do not include explicit polarization effects tend to have less MOF–sorbate interactions. The inclusion of polarization in simulation produces an attractive effect and generates better with the experimental uptake at low pressures.

It is apparent that only the polarizable BSSP model was able to capture the expected open-metal sorption onto the Cu$^{2+}$ ions in \textit{rht}-MOF-9 as shown by the very strong agreement between the experimental and calculated H$_2$ sorption data at low pressures. This is further demonstrated by the g(r) of the center-of-mass (COM) of H$_2$ molecules about the Cu$^{2+}$ ions at 77 K and 0.05 atm (Figure 3.5). Specifically, a large nearest-neighbor peak ranging from 2.27–3.03 Å was observed in the g(r) for the BSSP model about the CuL ions (Figure 3.5(b)), which represents a significant quantity of H$_2$ molecules sorbing onto these Cu$^{2+}$ ions. We note that such a peak is less pronounced when taking the g(r) about the CuC ions (Figure 3.5(a)). This is because the CuC ions exhibit a lower partial positive charge relative to the CuL ions in this MOF according to our calculations (Table S1).

As revealed in previous theoretical studies of gas sorption in \textit{rht}-MOFs, the sorbate molecule exhibits stronger interactions with the type of Cu$^{2+}$ ion having the greater partial positive charge. It appears that simulations using the DL model resulted in uptakes that overestimate experiment at both temperatures, especially at higher pressures (Figure 3.4). It is known that this potential can be overly attractive for simulations of H$_2$ sorption in MOFs. The fact that the DL model produced higher uptakes than the other models (especially BSSP) could be due to the inflated electrostatic energy that is associated with this model. Indeed, the magnitudes of the partial charges for this model are about 25% higher than those for the BSS and BSSP models (see ESI†, Table S3). Despite this increase in the
Figure 3.5: Radial distribution function (g(r)) of the center-of-mass (COM) of H₂ molecules about the (a) CuC ions and (b) CuL ions in rht-MOF-9 at 77 K and 0.05 atm for different models: BSSP = red, BSS = green, Buch = blue, DL = brown.

electrostatic energy, which leads to notably high H₂ uptakes, the DL model does not reproduce sorption onto the open-metal sites as well as the BSSP model (Figure 3.5).

The simulated Qₘ values for H₂ was calculated as before¹¹⁹ and it can seen that the results for the BSSP model are in very good agreement with experimental data for virtually all loadings considered (Figure 3.6). An initial Qₘ of 6–7 kJ mol⁻¹ is typical for H₂ sorption in MOFs with copper paddlewheel clusters.³ However, a range of values from 5.5–9.5 kJ mol⁻¹ has been reported for rht-MOFs in both experiment and simulation.²²,³⁴,³⁵,⁴³,¹⁰³ The Qₘ values for the nonpolarizable models agree less with experiment since they generally describe weaker MOF–H₂ interactions. The lack of contributions
Figure 3.6: Isosteric heat of adsorption ($Q_{st}$) for H$_2$ plotted against uptakes in $rht$-MOF-9 for experiment$^{118}$ and simulations using different models at 77 K. Experiment = black, BSSP = red, BSS = green, Buch = blue, DL = brown.

from many-body polarization is likely the cause for this. The Buch model produces lower $Q_{st}$ values than the BSS and DL models for all loadings considered, which could be due to the absence of electrostatic interactions. Nonetheless, all models were able to capture the expected monotonic decreasing trend of energy change as a function of loading, which suggests that the force field developed for $rht$-MOF-9 in this work accurately represents the energy landscape of the material. The slow decline of $Q_{st}$ as loading increases is a common result for both experimental and simulated measurements for MOFs with open-metal sites. This corresponds to H$_2$ sorbed at the global minimum at very low pressure (and thus a high $Q_{st}$) followed by sequential filling of the next favorable sorption sites in the MOF. When polarization is included in simulation, the most energetically favorable binding sites are the exposed Cu$^{2+}$ ions.

As demonstrated previously for other $rht$-MOFs,$^{22,34–36,43,119}$ the inclusion of explicit polarization is needed to accurately predict both the sorption isotherms and mechanism of sorbate binding. Indeed, only simulations with the polarizable BSSP model produce a strong interaction of H$_2$ with CuL, which corresponds to high induced dipoles and an energy minimum at that location. The simulations show that the primary sorption site of H$_2$ in $rht$-MOF-9 is located at the CuL ions (site 1, Figure 3.7), with a Cu$^{2+}$–COM(H$_2$) distance ranging from 2.27–3.03 Å as shown in Figure 3.5(b). This is characteristic of open-metal sorption as observed from simulation studies in other $rht$-MOFs$^{22,119}$ and
Figure 3.7: Molecular illustration of a H\textsubscript{2} molecule (cyan) sorbed at site 1, the primary sorption site in \textit{rht}-MOF-9, as viewed (a) down the b-axis and (b) rotated 90° in the crystallographic c direction. The H\textsubscript{2} molecule is sorbed onto the CuL ion. Note, site 2 (not shown) is on the “other” Cu\textsuperscript{2+} ion of the copper paddlewheel, which is colinear with this site and the copper atoms. Some MOF atoms are truncated for clarity. Atom colors: Cu = brown; C = grey; O = red; N = blue; H = white.

Experimental NPD in various Cu\textsuperscript{2+}-based MOFs\textsuperscript{16,167,175} For example, an interaction distance of 2.23 Å was discovered for D\textsubscript{2} sorbing onto the CuC ions in NOTT-112.\textsuperscript{16} In this case, binding was highly selective for CuC (85%) relative to CuL (< 15%), with a D\textsubscript{2}–metal distance of 2.41 Å observed about the latter.\textsuperscript{16} Distances of 2.39 and 2.50 Å was measured for D\textsubscript{2} sorbing onto the Cu\textsuperscript{2+} ions in HKUST-1\textsuperscript{167} and NOTT-101,\textsuperscript{175} respectively, through NPD studies. Recent theoretical studies of H\textsubscript{2} sorption in UTSA-20 revealed a Cu\textsuperscript{2+}–COM(H\textsubscript{2}) distance of 2.7 Å about the preferential Cu\textsuperscript{2+} ion.\textsuperscript{176}

Site 2 for the H\textsubscript{2} molecules in \textit{rht}-MOF-9 correspond to sorption onto the CuC ions. This site is less frequently occupied than the CuL ions at low loading due to the higher partial positive charge for the latter. Similar to previous computational studies on \textit{rht}-MOFs\textsuperscript{22,34–36,43,119} an energy minimum position for H\textsubscript{2} can be observed in the corner of the T–T\textsubscript{d} cage (site 3, Figure 3.8). This is also a major sorption site for the other molecules considered in this study and is demonstrated by histogram visualization in
the ESI† (Figures S4c, S10c, S15, S22c, S29c, S36c). This region is associated with the secondary broad peak in the g(r) about the CuL ion and is evident for all models considered (Figure 3.5(b)). This site has also been observed in NPD experiments for D₂ in NOTT-112,₁₆ HKUST-1,₁₆₇ and NOTT-101.₁₇₅ The g(r) plots for the electrostatic BSS and DL models reveal a consistent pattern in the distribution of H₂ sorption sites.

A few H₂ molecules can be seen sorbing onto the CuL ions with these models, but none were observed sorbing onto the CuC ions; this is in contrast to the results obtained using the BSSP model (Figure 3.5). The Buch model, which lacks electrostatic interactions, was not able to capture any sorption onto the open-metal sites. These trends are similar to those observed through g(r) analysis in NOTT-112.₁₁₉ Finally, some H₂ molecules were found to sorb at a fourth site by simulated annealing (using the DL model, Table 3.1). This H₂ sorption site has been observed experimentally in the case of NOTT-101 via NPD experiments.₁₇₅

Interestingly, the exchange of the organic linker in Cu²⁺-based MOFs (e.g., that used in NOTT-112₁₅,₁₆ compared to rht-MOF-9, see Figure 3.2) results in a selective switch in the binding site about the copper paddlewheels. By altering the central component of the hexatopic organic linker to include electronegative N atoms, the initial sorbate binding site changes from the Cu²⁺ ion facing the cub-Oₘ cage (CuC) (as observed in NOTT-112)¹¹⁹ to the other ion facing toward the center of the linker (CuL) (as observed in rht-MOF-9). It is likely that the presence of N atoms on the linker causes the electron density of the nearby CuL ions to decrease (and thereby increasing its partial positive charge) through an inductive effect. This charge sensitivity induced by linker selection has been observed for several other MOFs with copper paddlewheels, such as NOTT-112,¹¹⁹ rht-MOF-1,₁₆¹ MPAF-1,₁₆¹ Cu-TPBTM,₁₆¹ PCN-61,⁴₃,₁₆¹ and PCN-66,³⁶ as summarized in Table 3.2. The primary sorption site in these MOFs is located at the Cu²⁺ ion exhibiting the greater partial positive charge. Due to the different electronic environments of the Cu²⁺ ions in the paddlewheel clusters (and contrary to what may be hypothesized from these simulations in rht-MOF-9), very little sorption occurred inside the cub-Oₘ cage compared to the other cages. This highlights the importance of careful
Figure 3.8: Molecular illustration of a H₂ molecule (cyan) sorbed at site 3, a local minimum sorption region in \textit{rht}\textendash MOF-9, as viewed (a) from inside the cub\textendash\textit{O₇} cage and (b) horizontal to the copper paddlewheels (corresponding to Fig. 3.2). The H₂ molecule is sorbed within the corner of the T\textendash\textit{T₇} cage. The mesh radius around the atoms of the H₂ molecule is 2.0 Å, which corresponds to width of the broad secondary peak in Figure 3.5(b). Some MOF atoms are truncated for clarity. Atom colors: Cu = brown; C = grey; O = red; N = blue; H = white.
Table 3.2: Calculated partial charges for the Cu$^{2+}$ ions in selected MOFs containing copper paddlewheel units with different organic linkers. *Due to the structure of this MOF, there is no difference in the electronic environments of the Cu$^{2+}$ ions of the copper paddlewheels.

<table>
<thead>
<tr>
<th>Material</th>
<th>CuC $q$ ($e^-$)</th>
<th>CuL $q$ ($e^-$)</th>
<th>Primary H$_2$ Sorption Site</th>
<th>Diff. ($e^-$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>rht-MOF-9</td>
<td>1.31</td>
<td>1.44</td>
<td>CuL</td>
<td>0.13</td>
<td>This Work</td>
</tr>
<tr>
<td>rht-MOF-1</td>
<td>1.06</td>
<td>1.56</td>
<td>CuL</td>
<td>0.50</td>
<td>161</td>
</tr>
<tr>
<td>Cu-TPBTM</td>
<td>0.99</td>
<td>1.23</td>
<td>CuL</td>
<td>0.24</td>
<td>161</td>
</tr>
<tr>
<td>PCN-66</td>
<td>0.79</td>
<td>1.30</td>
<td>CuL</td>
<td>0.60</td>
<td>36</td>
</tr>
<tr>
<td>UTSA-20</td>
<td>0.89</td>
<td>1.32</td>
<td>CuL</td>
<td>0.43</td>
<td>176</td>
</tr>
<tr>
<td>rht-MOF-tri</td>
<td>0.95</td>
<td>1.64</td>
<td>CuL</td>
<td>0.69</td>
<td>177</td>
</tr>
<tr>
<td>NOTT-112</td>
<td>1.56</td>
<td>1.00</td>
<td>CuC</td>
<td>0.56</td>
<td>119</td>
</tr>
<tr>
<td>MPAF-1</td>
<td>1.58</td>
<td>1.00</td>
<td>CuC</td>
<td>0.58</td>
<td>161</td>
</tr>
<tr>
<td>PCN-61</td>
<td>1.44</td>
<td>0.87</td>
<td>CuC</td>
<td>0.57</td>
<td>43,161</td>
</tr>
<tr>
<td>HKUST-1*</td>
<td>1.13</td>
<td>1.13</td>
<td>Both</td>
<td>0.00</td>
<td>178</td>
</tr>
</tbody>
</table>

charge parametrization of the MOF atoms. On the basis of our theoretical results, we expect that the primary sorption sites for H$_2$ in rht-MOF-9 should correspond to the CuL ions as illustrated in Figure 3.7. There is not an equal preference for the sorbate molecules about both types of Cu$^{2+}$ ions.

### 3.5.3 Carbon Dioxide

rht-MOF-9 was systematically designed with enhanced CO$_2$ sorption in mind. It was demonstrated by Eddaoudi *et al.* that successive modifications to the organic linker improved CO$_2$ and H$_2$ uptake compared to rht-MOF-1 and rht-MOF-7). The introduction of N-rich regions in the linker has been shown to be an effective strategy to increase MOF–CO$_2$ interactions. The CO$_2$ sorption isotherms for two different experiments\(^77,118\) and three different CO$_2$ potentials at 298 K and pressures up to 1 atm are displayed in Figure 3.9. The isotherms for the electrostatic CO$_2$-PHAST and polarizable CO$_2$-PHAST* models are in better agreement with the two experiments than that for the TraPPE model at most state points considered, with the main exception being at low pressures (< 0.3 atm) for the polarizable potential. It appears that the inclusion of polarization leads to significant oversorption at low pressures relative to experiment. This is attributed to the fact that our simulations captured a very strong interaction between the Cu$^{2+}$ ions and the CO$_2$ molecules compared to what is physically obtained in experiment. This could be a consequence of the high partial positive charges used for the Cu$^{2+}$ ions in the MOF force field. Decreasing the magnitude of the these charges will
Figure 3.9: CO$_2$ sorption isotherms in *rht*-MOF-9 for two different experiments$^{77,118}$ and simulations using different models at 298 K. Experiment (Eddaoudi *et al.* = solid black, experiment (Liu *et al.*) = dashed black, CO$_2$-PHAST* = red, CO$_2$-PHAST = blue, TraPPE = brown.

likely lead to closer agreement with the experiments at low pressures. We note that a similar shape in the simulated CO$_2$ sorption isotherm was observed in *rht*-MOF-7 using this potential.$^{34}$ This shape is characteristic of CO$_2$ molecules sorbing initially onto the open-metal sites until they are saturated; afterward, the sorbate molecules fill the less energetically favorable sites in the MOF.

Electrostatic interactions play a significant role in the CO$_2$ sorption mechanism in *rht*-MOF-9 as compared to H$_2$, where this notable oversorption relative to experiment at low pressures was not observed for the polarizable BSSP model (Figure 3.4). The averaged contributions from each component of the total potential energy as a function of pressure are shown in the ESI† (Fig. S13). Not surprisingly, the absolute magnitudes of the potential energy from polarization for the CO$_2$-PHAST* model is greater than that for repulsion-dispersion interactions for pressures up to 0.4 atm. Interestingly, for the polarizable model, the uptakes at higher pressures are lower than those for the non-polarizable potentials, suggesting that a repulsive effect is produced from intramolecular dipole interactions at higher loadings. This could also be due to polarization leading to a favorable ordering effect of the sorbate molecules in the MOF.

The g(r) of CO$_2$ carbon atoms about both types of Cu$^{2+}$ ions in *rht*-MOF-9 at 298 K and 0.05 atm are shown in Figure 3.10. It is clear from this figure that the CO$_2$
Figure 3.10: Radial distribution function \(g(r)\) of the \(\text{CO}_2\) carbon atoms about the (a) \(\text{CuC}\) ions and (b) \(\text{CuL}\) ions in \(rht\)-MOF-9 at 298 K and 0.05 atm for different models: \(\text{CO}_2\text{-PHAST}^* = \text{red, CO}_2\text{-PHAST} = \text{blue, TraPPE} = \text{brown.}\)

Molecules exhibit strong binding onto \(\text{CuL}\) as indicated by a distinct nearest-neighbor peak about these ions for all models (Figure 3.10(b)). Specifically, a favorable interaction exists between the electronegative O atom of the sorbate and the highly positive charged \(\text{CuL}\) ions. The magnitude of the nearest-neighbor peak is largest for the \(\text{CO}_2\text{-PHAST}^*\) model, thus indicating that the inclusion of polarization leads to a greater number of \(\text{CO}_2\) molecules sorbing onto the open-metal sites. A small nearest-neighbor peak was observed in the \(g(r)\) about the \(\text{CuC}\) ions for all models (Figure 3.10(a)), which implies weaker \(\text{CO}_2\)-metal interactions since the partial positive charge is lower for this ion.
The modeled CO\(_2\) binding site about the Cu\(^{2+}\) ions in \(\text{rht-MOF-9}\) is similar to what has been observed through experimental NPD and \textit{ab initio} calculations of CO\(_2\) in HKUST-1.\(^{169}\) Also, binding was detected in the corner of the T–\(T_d\) cage (site 3), which was also observed through NPD studies of HKUST-1.\(^{169}\) As with H\(_2\), the CO\(_2\)–metal interaction is best captured when explicit polarization is implemented in simulation. The widely used TraPPE model\(^86\) for CO\(_2\) does not adequately model gas uptake in this MOF at pressures greater than 0.2 atm (Figure 3.9). At 1 atm, the uptakes for the TraPPE model overestimates the experimental data of Liu \textit{et al.}\(^77\) and Eddaoudi \textit{et al.}\(^118\) by approximately 27\% and 43\%, respectively. Although the TraPPE model is highly popular for use in general CO\(_2\) modeling, it can produce isotherms that notably oversorb experimental results for a variety of porous materials as demonstrated by our group\(^{34,41}\) and others.\(^{82,135,136,179–181}\) In addition, it is shown in Figure 3.10(b) that simulations using the TraPPE model yield the smallest nearest-neighbor peak about the CuL ions, which indicates that this model does not reproduce sorption onto the open-metal sites in this MOF all that greatly. On the basis of our results, we emphasize that the CO\(_2\)-PHAST and CO\(_2\)-PHAST\(^*\) potentials could be better choices for use in materials simulation due to their superior accuracy and transferability.\(^7,36,67,137,138,162–164\)

The simulated \(Q_{st}\) values for CO\(_2\) as a function of loading for the three different CO\(_2\) potentials are compared with the two experimental results\(^77,118\) in Figure 3.11. As aforementioned, the experimental curves are calculated using a finite-difference approximation to the Clausius–Clapeyron equation using at least two isotherms at different temperatures as in equation 3.2.\(^64,65\) On the other hand, the \(Q_{st}\) values in GCMC simulation are calculated from fluctuations in the particle number and potential energy \textit{via} equation 3.1.\(^66\) As in the case of H\(_2\) and other sorbates considered in this work, the polarizable CO\(_2\)-PHAST\(^*\) model best reproduces the experimental \(Q_{st}\) values within the considered loading range. The shape of the \(Q_{st}\) plot for CO\(_2\)-PHAST\(^*\) is notably different from that for the other models as it exhibits a steep decline at low loadings before plateauing at around 17 wt %. This shape is analogous to the experimental data reported by Eddaoudi \textit{et al.}, although the theoretical \(Q_{st}\) is higher than those within both reported experimen-
Figure 3.11: Isosteric heat of adsorption ($Q_{st}$) for CO$_2$ plotted against uptakes in $rht$-MOF-9 for two different experiments$^{77,118}$ and simulations using different models at 298 K. Experiment (Eddaoudi et al.) = solid black, experiment (Liu et al.) = dashed black, CO$_2$-PHAST$^*$ = red, CO$_2$-PHAST = blue, TraPPE = brown.

It can be observed that the nonpolarizable CO$_2$-PHAST and TraPPE models generate $Q_{st}$ values that are nearly constant for all loadings considered. This is in contrast to experiment as these theoretical $Q_{st}$ plots do not display the monotonic decreasing behavior. Thus, simulations using these electrostatic models do not provide an accurate representation of CO$_2$ molecules sorbing onto the open-metal sites.

### 3.5.4 Hydrocarbons

Adsorption simulation results for CH$_4$, C$_2$H$_2$, C$_2$H$_4$, and C$_2$H$_6$ in $rht$-MOF-9 compared with experiment at 298 K and pressures up to 1 atm were obtained. The main sorption site for all hydrocarbons considered is site 3, which is located in the corner of the T–$T_d$ cage. This site corresponds to the broad peak in the $g(r)$ about the Cu$^{2+}$ ions for these gases. The heavier molecules (C$_2$H$_4$ and C$_2$H$_6$) also had strong interaction at site 4; an illustration of C$_2$H$_6$ sorbed at this site is given in Figure 3.12. The polarizable models for C$_2$H$_2$ and C$_2$H$_4$ exhibited very strong interaction with the CuL ions (site 1) as well as some interaction with CuC (site 2), but those for CH$_4$ and C$_2$H$_6$ (which are more spherical in terms of van der Waal volume) lacked such interactions with the Cu$^{2+}$ ions,
Figure 3.12: Molecular illustration of a C$_2$H$_6$ molecule sorbed at site 4 in rht-MOF-9, where the sorbate aligns along the copper paddlewheel, with its C–C bond axis (semi-)parallel to the Cu–Cu axis. Note, C$_2$H$_6$ is shown here as opposed to H$_2$ (Figures 3.7 and 3.8) to demonstrate the “straddling” effect observed in simulation. Strong electrostatic interactions between corresponding opposite charges (C$_{\delta^-}$ with Cu$_{\delta^+}$ and H$_{\delta^+}$ with O$_{\delta^-}$) likely produce this effect. The two different views (a and (b)) are rotations of the same system. Some MOF atoms are truncated for clarity. Atom colors: Cu = brown; C = grey; O = red; N = blue; H = white.

preferring sites 3 and 4, respectively. All sorbates considered in this work (including H$_2$ and CO$_2$) frequently occupied the cavity in the corner of the T–T$_d$ cage (site 3). The newer hydrocarbon models (C$_2$H$_4$ and C$_2$H$_6$) tend to produce isotherms that oversorb with respect to the TraPPE models and experiment. However, in general, the polarizable models for the C$_2$ hydrocarbons produced $Q_{st}$ values that are in closer agreement with experiment, suggesting correct energetics between the MOF and gases. The cause of the oversorption compared to experiment for these hydrocarbons could be attributed to the inflated repulsion/dispersion energy in intramolecular interactions. Nonetheless, it is expected that the sorption sites for the hydrocarbons in rht-MOF-9 are similar to those for H$_2$ and CO$_2$, primarily due to the seemingly universal binding properties of the well-known desolvated copper paddlewheel secondary building units (SBUs) featured in rht-MOFs.31
3.6 Conclusion

A simulation study of gas sorption in \textit{rht}-MOF-9 was presented in this work. A quantitative and atomistic description of gas sorption in a porous material can provide detailed insights into the rational design of new materials for use in current and future applications. This work supports the notion that MOFs containing open-metal sites can provide an ideal chemical environment to facilitate strong MOF–sorbate interactions. Further, it was shown that the choice of the organic linker for a given metal counterpart can alter the resulting MOF environment in such a way that the electron density differs from one metal ion to the other. In NOTT-112, which contains only C and H atoms in center of the linker, the CuC ions exhibit a greater partial position charge than the CuL ions, and therefore represent the initial loading sites. However, the introduction of N atoms in the center of the linker, as in the case of \textit{rht}-MOF-9, causes the positive charge of the CuL ions to increase, which in turn leads to CuL being the primary sorption site. Broadly speaking, the use of linkers containing N-rich regions, as opposed to one containing only C and H, changes the mechanism of gas sorption in a marked and potentially useful way.

The polarizable H\textsubscript{2} and CO\textsubscript{2} models used in this work have been thoroughly tested and proven useful for accurate simulations of gas sorption in a wide range of porous materials. Overall, it is clear from this work and others that the BSS/BSSP models\textsuperscript{12} and CO\textsubscript{2}-PHAST/CO\textsubscript{2}-PHAST* models\textsuperscript{41} could predict gas sorption properties in porous materials more accurately than other widely used potentials, such as Buch\textsuperscript{61} and DL\textsuperscript{84} for H\textsubscript{2} and TraPPE for CO\textsubscript{2}\textsuperscript{86}. It is noteworthy that obtaining accurate and transferable models for small hydrocarbons remains a difficult problem. A reason for this is perhaps that the energetics for simulating these hydrocarbons in MOFs is heavily dominated by repulsion/displacement interactions, which was modeled using the Lennard-Jones potential in this work. This potential is considered by some to be the simplest model for repulsion/displacement interactions and among the cheapest computationally. Other more complicated methods for acquiring the repulsion/displacement energy without quantum mechanical energy calculations have been
such methods are worthy of consideration for site parametrization in chemical modeling, especially in the case of the hydrocarbons investigated here.

Additionally, different MOF parameters could be considered for calculating the Lennard-Jones potential, e.g. DREIDING and OPLS, with the latter being specifically designed for organic systems. Methods for calculating the electrostatic and polarization energies for periodic systems are based heavily on chemical and physical theory, while the Lennard-Jones potential originated as an empirical fit of observed atomic interactions. In general, repulsion/dispersion (or van der Waals) interactions remain the most nebulous and difficult to implement in a transferable fashion.

We have found that including explicit polarization for modeling H$_2$ and CO$_2$ sorption in rht-MOF-9 yields the most accurate results with respect to experiment for the material. However, since hydrocarbon sorption in this MOF is dominated by repulsion/dispersion interactions, the addition of polarization led to simulated isotherms that notably overestimated the experimental data for these gases. Nonetheless, the theoretical determination of the binding sites is clearly demonstrated through the use of explicit polarization. Particularly, polarization was requisite to reproduce sorption onto the open-metal sites in classical GCMC simulation.

The future of MOF modeling is practically unlimited due to the innumerable possible synthetic structures and high demand for cheaper and more efficient management of various gases and gas mixtures. In addition, the opportunity to contribute to ongoing effort for environmental remediation must not be overlooked. Indeed, great strides have already been taken in that direction using MOFs, especially with regards to CO$_2$ capture and sequestration. That considered, there is still a need to test the stability of various MOFs for gas sorption over many cycles to make them viable for long-term and industrial use. For the anticipated benefits of new research in porous materials, the effort in synthesis and simulation is well-spent. On the basis of the results displayed herein, the best design strategy to employ for enhanced gas sorption in porous materials may be optimizing a chemical environment that favors high induced dipoles, as the strongest binding sites in simulation and experiment occurs where the calculated dipoles have
the highest magnitude. While van der Waals energetics tend to dominate the sorption phase space, the role of emergent polarization from differing electron densities cannot be overlooked. In the case of $rht$-MOF-9, the use of a linker with a “rough” electronic surface (from alternating N and C atoms) and resulting inorganic complex produced a favorable environment for the sorbate molecules. Ultimately, a harmony between linkers with variant charge distributions and robustness needs to be attained.
Chapter 4

Quantum mechanical / Molecular mechanical (QM/MM) partial charge calculation of HKUST-1

4.1 Abstract

Quantum Mechanical / Molecular Mechanical (QM/MM) hybrid calculations were performed using an interface between Q-Chem and CHARMM softwares to determine net atomic charge parameters for use in metal-organic framework simulations. The subject of interest in this case was HKUST-1, a metal-organic framework consisting of binuclear copper paddlewheel building blocks and phenyl organic linkers. The charge parametrization method is validated by comparing QM/MM results with more traditional methods in Monte Carlo simulations of H\textsubscript{2} sorption in this material. It has been demonstrated that no significant difference exists for the final calculated charge-values, as well as the simulation results for H\textsubscript{2} uptake and heat of adsorption (Q\textsubscript{st}) under various thermodynamic conditions.

4.2 Introduction

Quantum Mechanical / Molecular Mechanical (QM/MM) computational methods have been applied to various fields in simulation science, most generally the study of biochemical systems on the atomic scale. A succinct introduction to the purpose and historical development of QM/MM methods was provided by Woodcock et al., and modeling procedures using CHARMM (Chemistry at Harvard Macromolecular Mechanics)\textsuperscript{191,192} and Q-Chem\textsuperscript{193–196} were introduced in 2007.
This work entails the use of these two softwares in tandem to approach the problem of point-charge parametrization for chemical modeling with a higher level of flexibility, realism, and efficiency. Compared to more traditional methods, for example fragmentation coupled with gas-phase QM calculations, QM/MM methods can greatly speed up the process of parametrization. Here, the well studied material HKUST-1, a metal-organic framework (MOF), is assigned point-charge parameters using QM/MM methods employed by CHARMM and Q-Chem. In this modeling paradigm, the use of fragments is unneeded, as the crystalline, periodic material can be treated with computational efficiency in the limit of long-range electronic interactions using MM, along with accurate QM calculations in a small volume of interest containing chemically distinct atoms (Fig. 4.1).

Thus the periodicity of these systems (MOFs) makes them a good candidate for utilization of QM/MM calculations for assignment of charge parameters for simulation in other codes, for example Massively Parallel Monte Carlo (MPMC), developed by Belof et al., LAMMPS, and others.

Here, calculated charge parameters are compared using different levels of theory and basis sets, and some charge parametrizations are used in MPMC simulations to test H\textsubscript{2} sorption in HKUST-1 compared with experiment.

4.3 Methods

The overarching principle of QM/MM calculation is simple in nature, and involves the redefinition of the Hamiltonian operator into 3 distinct partial Hamiltonians:

\[ \hat{H}_{\text{eff}} = \hat{H}_{\text{QM}} + \hat{H}_{\text{MM}} + \hat{H}_{\text{QM/MM}} \] (4.1)

The effective system was built according to the effective Hamiltonian split into 3 components as in Eqn. 4.1. The QM region was a 60-atom building block of HKUST-1 that contained all chemically distinct atoms in the material (Fig. 4.1, of which there are
Figure 4.1: HKUST-1 fragment used for QM calculations, with chemically distinct atoms labeled. Since the crystalline MOF system is periodic, these 6 atom types can be treated as having equivalent chemical environments extending to the macroscopic limit. Cu = brown; O = red; C = grey; H = white.

6: copper, oxygen, three chemically unique carbons, and hydrogen. In this fragment, 9 atoms (capped hydrogens) are treated with QM/MM hybridized energy calculation while the inner 51 atoms are treated with pure QM theory. The symmetry of the system assuming no impurities is what allows for simplified parametrization later for chemical modeling. The QM/MM hybrid region consists of the bonds that connect the QM region to the rest of the chemical system, which in this case consisted of capped hydrogen atoms where C-C bonds would normally occur. Finally, the MM region was a large set of conjoined unit-cells of the central cell in the 3 cartesian directions generating a 3x3x3 block. Point charges were assigned to the MM atoms using the VASP\textsuperscript{147} charges calculated previously.\textsuperscript{201} Thus 27 total unit cells were present, effectively surrounding the QM region. The total system therefore consists of 16,857 atoms (16,848 from unit cells plus 9 additional QM/MM atoms on the border of the primary fragment). Only the Merz-Kollman ESP net atomic charges were selected (not ground-state Mulliken charges). Of these, only the internal atom charges were selected and averaged for the final parameter definition (as in Table 4.2). In the case of C1, C2, C3, and H, only the three center-most...
Figure 4.2: Periodic unit-cell of HKUST-1 as determined by X-ray crystallography data, viewed with perspective. The cubic cell contains 624 atoms. Cu = brown; O = red; C = grey; H = white.

atoms were selected and their charges were averaged, ignoring more peripheral atoms which were close to the cut-off hydrogen atoms. Likewise with the innermost 6 O atoms. Finally, all 6 Cu atoms were considered in the final average.

With the first component of the project complete, the resulting charges were utilized in Monte-Carlo simulations (which include classical electrostatic energy calculations using atomic charge parameters) to test the validity of the results in a real system, compared to experimental data. Specifically, the VASP,\textsuperscript{147,201} Fragmentation,\textsuperscript{201} and average of QM/MM charges (results from table 4.2) were tested. Three different isotherms were considered: 303K, 318K, and 333K, at 0-500atm, matching experimental conditions.\textsuperscript{200}

Similar to previous studies,\textsuperscript{34–36,43,202} the Massively Parallel Monte Carlo\textsuperscript{58} simulations consisted of $\sim 5 \times 10^5 - 2 \times 10^6$ energy calculation steps until equilibration, calculating system energy for a 1x1x1 unit cell of HKUST-1 populated with H$_2$ molecules using three different models: Buch\textsuperscript{61} (only repulsion-dispersion forces), BSS\textsuperscript{12,49,60} (including electrostatics), and BSSP\textsuperscript{46,47} (also including explicit polarization). For the BSSP model, a Feynman-Hibbs correction was applied to the system energy. Mathematical descriptions
of the modeling methods in MPMC are provided in former work\textsuperscript{12,34,49,58,60,202} and are ommitted here for brevity.

![Diagram](image)

Figure 4.3: Modeling scheme showing different thermodynamic conditions and modeling techniques considered. For each modeling paradigm, pressures of 0.1 - 500 atm were simulated at the following points: 0.1, 0.5, 1, 10, 20, 50, 100, 200, 300, 400 and 500 atm.

4.4 Results

Original work by Wang et al.\textsuperscript{201} set the template for using CHARMM and Q-Chem for QM/MM charge calculation for the atoms in HKUST-1. For this project, the methods were duplicated. The original charges obtained were as follows:

Table 4.1: List of calculated charges from various computational methods. The first column represents the more traditional fragmentation method, the second represents results from VASP\textsuperscript{147} periodic quantum code, and the remaining columns represent QM/MM calculations according to the procedures described herein, using different levels of theory.

<table>
<thead>
<tr>
<th>Basis sets</th>
<th>Theory</th>
<th>6-31G* Frags/HF</th>
<th>7 VASP\textsuperscript{147}</th>
<th>6-31G* HF</th>
<th>6-31G* BLYP</th>
<th>6-31G* wB97XD</th>
<th>6-31G* M06-2X</th>
<th>6-31G* PBE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>1.081670</td>
<td>0.920150</td>
<td>1.145440</td>
<td>1.199546</td>
<td>1.234695</td>
<td>1.01153</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>-0.725384</td>
<td>-0.575880</td>
<td>-0.815980</td>
<td>-0.677630</td>
<td>-0.701410</td>
<td>-0.626030</td>
<td>-0.628570</td>
<td></td>
</tr>
<tr>
<td>C1</td>
<td>0.934740</td>
<td>0.662900</td>
<td>0.902850</td>
<td>0.723940</td>
<td>0.730410</td>
<td>0.730410</td>
<td>0.705330</td>
<td></td>
</tr>
<tr>
<td>C2</td>
<td>-0.212440</td>
<td>-0.279710</td>
<td>-0.166120</td>
<td>-0.119660</td>
<td>-0.171910</td>
<td>-0.261880</td>
<td>-0.094180</td>
<td></td>
</tr>
<tr>
<td>C3</td>
<td>0.009510</td>
<td>0.107800</td>
<td>0.010270</td>
<td>0.040330</td>
<td>0.079610</td>
<td>0.318330</td>
<td>-0.031940</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>0.178570</td>
<td>0.197330</td>
<td>0.228300</td>
<td>0.178300</td>
<td>0.201700</td>
<td>0.218380</td>
<td>0.128520</td>
<td></td>
</tr>
</tbody>
</table>

The original results can be compared with the QM/MM results obtained in this work (the attempt to reproduce the results):

Table 4.2: QM/MM resulting charges from this work.

<table>
<thead>
<tr>
<th>Basis sets</th>
<th>6-31G* Frags/HF</th>
<th>7 VASP\textsuperscript{147}</th>
<th>6-31G* HF</th>
<th>6-31G* BLYP</th>
<th>6-31G* wB97XD</th>
<th>6-31G* M06-2X</th>
<th>6-31G* PBE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>–</td>
<td>–</td>
<td>1.36334</td>
<td>1.12889</td>
<td>1.18081</td>
<td>1.21269</td>
<td>–</td>
</tr>
<tr>
<td>O</td>
<td>–</td>
<td>–</td>
<td>-0.82715</td>
<td>-0.69669</td>
<td>-0.70983</td>
<td>-0.71964</td>
<td>–</td>
</tr>
<tr>
<td>C1</td>
<td>–</td>
<td>–</td>
<td>1.03045</td>
<td>0.88246</td>
<td>0.87889</td>
<td>0.87536</td>
<td>–</td>
</tr>
<tr>
<td>C2</td>
<td>–</td>
<td>–</td>
<td>-0.11102</td>
<td>-0.08918</td>
<td>-0.06143</td>
<td>-0.04219</td>
<td>–</td>
</tr>
<tr>
<td>C3</td>
<td>–</td>
<td>–</td>
<td>-0.14211</td>
<td>-0.11189</td>
<td>-0.15560</td>
<td>-0.17726</td>
<td>–</td>
</tr>
<tr>
<td>H</td>
<td>–</td>
<td>–</td>
<td>0.21631</td>
<td>0.16425</td>
<td>0.18778</td>
<td>0.19193</td>
<td>–</td>
</tr>
</tbody>
</table>
Finally, average atom-charges for the relevant QM/MM methods were obtained and compared with original work:

Table 4.3: Average atomic charge parameters (in e\(^{-}\)) from 4 levels of theory (HF, B3LYP, wB97XD, M06-2X) with 6-31G* basis sets, comparing original work (Tab. 4.1) and this one (Tab. 4.2) The "Avg. q, here" column represents the charge parameter used for the "QM/MM method" MPMC simulations later in this text.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Avg. q, original(^{201})</th>
<th>Avg. q, here</th>
<th>Diff., e(^{-})</th>
<th>% Diff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>1.24 ± 0.10</td>
<td>1.22 ± 0.10</td>
<td>-0.02</td>
<td>-1.3%</td>
</tr>
<tr>
<td>O</td>
<td>-0.71 ± 0.08</td>
<td>-0.74 ± 0.06</td>
<td>-0.03</td>
<td>4.7%</td>
</tr>
<tr>
<td>Cl</td>
<td>0.77 ± 0.09</td>
<td>0.92 ± 0.08</td>
<td>0.14</td>
<td>18.8%</td>
</tr>
<tr>
<td>C2</td>
<td>-0.18 ± 0.06</td>
<td>-0.08 ± 0.03</td>
<td>0.10</td>
<td>-57.8%</td>
</tr>
<tr>
<td>C3</td>
<td>0.11 ± 0.14</td>
<td>-0.15 ± 0.03</td>
<td>-0.26</td>
<td>-230.8%</td>
</tr>
<tr>
<td>H</td>
<td>0.21 ± 0.02</td>
<td>0.19 ± 0.02</td>
<td>-0.02</td>
<td>-8.0%</td>
</tr>
</tbody>
</table>

Two more methods were used to calculate charge parameters which were not included in Table 4.2 because they were not performed in the original work and thus not suitable for direct comparison. These were (a) HF using the STO-3G basis sets, and (b) B3LYP using the 6-31G(d) basis sets. For (a), the resulting Cu charge was 0.56e\(^{-}\), and for (b), it was 1.21e\(^{-}\). HF calculation with what is considered one of the most primitive basis sets (STO-3G) yielded a very different charge value for Cu, while method (b) was very similar to the average of the four others considered in the averages in Table 4.3.

Monte Carlo Simulation H\(_2\) uptake isotherms for 303K, 318K, and 333K compared to experimental data are presented in figures 4.4, 4.5, 4.6, respectively, as in the scheme in Fig. 4.3.

4.5 Discussion

4.5.1 Charges

The results in table 4.3 demonstrate a reasonable agreement of charge values for the QM/MM calculations compared with original work.\(^{201}\) Small deviations appear in the final charge magnitudes, especially for C3 (by 0.26e\(^{-}\)), which suggests that the volume around this atom in the MOF lattice may be involved in a steady resonant shift in electron density. In general, the Merz-Kollman ESP net atomic charge for this atom hovers around zero (tables 4.1 and 4.2), changing sign sometimes depending on level of theory and basis.
set used. Similar results for secondary phenyl carbons in an rht-MOF have been obtained before, e.g. in NOTT-112.\textsuperscript{202}

Other slight changes in the final charge results can be attributed to slightly different Q-Chem input conditions. In the original work, in specific cases, the xc\_grid parameter was changed from the default value. Additionally, Gaussian blur representations of charge distribution for the MM region (rather than point charge approximations) were used. In this work, both of these parameters were not considered, as the primary goal was to duplicate the initial procedure and validate the results compared to other dependable (though more difficult) methods for charge parametrization.

The differences presented in table 4.3 are for averages of the 4 levels of theory used for each atom type. The individual methods varied in from original work by HF \textless B3LYP \textless wB97XD \textless M06-2X, in order of increasing total charge magnitude difference (i.e. difference of original Cu to new Cu charge, C1, C2, etc.).

### 4.5.2 Validation

It is apparent in figures 4.4, 4.5, and 4.6 that the 3 methods of charge parametrization (Fragmentation, VASP, and QM/MM) yield nearly identical H\textsubscript{2} uptake results in HKUST-1, regardless of thermodynamic conditions. This serves as a direct validation of the QM/MM method, as the fragmentation and VASP methods have been extensively used and verified for computer modeling of chemical systems.\textsuperscript{12,34,35,37,38,51}

No difference is expected when using the Buch model, as electrostatics are not considered in the energy calculation. However, in the BSS and BSSP models, charge parameters effect total energy and thus equilibrated H\textsubscript{2} uptake. The yielded charges for the QM/MM method were in good agreement with the other methods and the net result in simulations in most cases is indifferentiable at high pressure. While the simulated uptakes do not wholly agree with experiment at very high pressure (> 5MPa, or 50atm), the parametrization methods show self-consistency. It is notable, however, that at lower pressures (< 5MPa), the simulation isotherms are in very good agreement with experiment, which means that the generally most important (initial loading) energetic interactions of H\textsubscript{2}
with the MOF are being captured by simulation. At high pressure, HKUST-1 is known to deform ("breathe") from its characteristic desolvated crystal structure,\textsuperscript{203} which can allow higher H\textsubscript{2} uptake than the MPMC simulation allows, because in it the MOF atoms are fixed in space. This may be an explanation for the characteristically systematic error in figures 4.4, 4.5, and 4.6. This is evident not only in the high-pressure deviation of simulation from experiment, but also by contrast, the increasing accuracy of simulation with increasing temperature. Thus it can be inferred that for higher temperatures (\(~333\)K) it is likely that the structure of HKUST-1 is more consistent with the fixed system used in these experiments.

4.6 Conclusion

It has been shown that QM/MM calculation of charge densities using a Q-Chem / CHARMM interface is an accurate and facile method with respect to more traditional methods, specifically fragmentation and VASP\textsuperscript{147} calculations. The efficiency of QM/MM calculation for these purposes makes further development of charge parametrization a valuable pursuit. In this work, MM atoms were treated as point charges – in the future, utilizing the Gaussian-blur functionality of Q-Chem would expectedly yield a closer approximation to an accurate charge-density field rather than point charge approximation in the MM. This certainly is an avenue of improvement for future work, although it is remarkable that the point-charge MM approximation used here yields accurate results. Moreover, implementation of an iterative, programmed procedure for QM/MM point-charge parametrization is desirable for full optimization of the method. In this case, the goal would be to use a set of "guess" charges for the relevant MM field (in this case VASP charges were used) in order to calculate the charges in the QM region, and then use those QM charges for the new MM field, and re-calculate the QM charges until self-consistency is reached, i.e. by some minimum energy difference or Merz-Kollman net atomic charge difference (Fig. 4.2).
Figure 4.4: H$_2$ uptake as a function of pressure in HKUST-1. Here, experiment$^{200}$ is compared with the BSSP, BSS, and Buch simulation models (in vertical order downwards) at 303K.
Figure 4.5: H₂ uptake as a function of pressure in HKUST-1. Here, experiment²⁰⁰ is compared with the BSSP, BSS, and Buch simulation models (in vertical order downwards) at 318K.
Figure 4.6: \( \text{H}_2 \) uptake as a function of pressure in HKUST-1. Here, experiment\textsuperscript{200} is compared with the BSSP, BSS, and Buch simulation models (in vertical order downwards) at 333K.
Chapter 5

Classical and electronic structure studies of KIKDOZ

5.1 Introduction

The material classified as KIKDOZ in the Cambridge Crystal Structure Database (Deposition number 947383) is a metal-organic framework originally reported in 2013. Figure 5.1 shows the 2x2x2 supercell used for simulation down the a, b, and c crystal axes. It features a pyrazole linker with Cd$^{2+}$ ions staggered between SiF$_6^{2-}$ clusters. The formula unit of the hydrated form is (C$_{20}$H$_{28}$CdF$_6$N$_8$Si$_6$)$\cdot$nH$_2$O. The material gained our attention because of reported water and carbon dioxide sorption properties. In this chapter, results from electronic structure and classical simulations for KIKDOZ are reported.

5.2 KIKDOZ

5.2.1 Methods

Similar to previous chapters, MCMD software was used to run Grand Canonical Monte Carlo simulations to determine the simulate uptake of various gases in KIKDOZ. The repulsion-dispersion interactions were treated with the Lennard-Jones pair potential with Lorentz-Berthelot mixing rules using the universal force field.

A single unit cell was treated with periodic DFT (revPBE XC functional; DFTD3 pair potential; MOLOPT basis sets) to calculate ESP followed by RESP charge-fit using CP2K software to determine partial charges on each atom. The periodic DFT charges are displayed in table 5.1 along with charges obtained by another method: average charges computed by Hartree-Fock treatment of representative fragments using the 6-31G* basis
Figure 5.1: The KIKDOZ supercell displayed in the a, b, and c crystal basis directions. Atom colors: C: cyan, N: blue, H: white, F: green, Si: yellow, Cd: gray
Table 5.1: Charges obtained for each atom (following the labeling in the published .cif file) using two different methods.

<table>
<thead>
<tr>
<th>Atom Label</th>
<th>CP2K (e⁻)</th>
<th>Fragment (e⁻)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>1.13</td>
<td>1.02</td>
</tr>
<tr>
<td>Si</td>
<td>1.31</td>
<td>1.69</td>
</tr>
<tr>
<td>F1</td>
<td>-0.49</td>
<td>-0.55</td>
</tr>
<tr>
<td>F2</td>
<td>-0.48</td>
<td>-0.6</td>
</tr>
<tr>
<td>F3</td>
<td>-0.51</td>
<td>-0.61</td>
</tr>
<tr>
<td>C1</td>
<td>-0.3</td>
<td>0.12</td>
</tr>
<tr>
<td>C2</td>
<td>0.23</td>
<td>0.15</td>
</tr>
<tr>
<td>C3</td>
<td>-0.17</td>
<td>-0.09</td>
</tr>
<tr>
<td>C4</td>
<td>0.19</td>
<td>0.06</td>
</tr>
<tr>
<td>C5</td>
<td>-0.44</td>
<td>0.12</td>
</tr>
<tr>
<td>C6</td>
<td>-0.48</td>
<td>0.05</td>
</tr>
<tr>
<td>C7</td>
<td>0.29</td>
<td>0.22</td>
</tr>
<tr>
<td>C8</td>
<td>-0.11</td>
<td>-0.1</td>
</tr>
<tr>
<td>C9</td>
<td>0.17</td>
<td>0.13</td>
</tr>
<tr>
<td>C10</td>
<td>-0.38</td>
<td>0.06</td>
</tr>
<tr>
<td>N1</td>
<td>-0.39</td>
<td>-0.39</td>
</tr>
<tr>
<td>N2</td>
<td>-0.15</td>
<td>-0.15</td>
</tr>
<tr>
<td>N3</td>
<td>-0.33</td>
<td>-0.42</td>
</tr>
<tr>
<td>N4</td>
<td>-0.24</td>
<td>-0.24</td>
</tr>
<tr>
<td>H2</td>
<td>0.35</td>
<td>0.34</td>
</tr>
<tr>
<td>H4</td>
<td>0.39</td>
<td>0.38</td>
</tr>
<tr>
<td>H1</td>
<td>0.11</td>
<td>-0.01</td>
</tr>
<tr>
<td>H5</td>
<td>0.15</td>
<td>0</td>
</tr>
<tr>
<td>H6</td>
<td>0.15</td>
<td>0.02</td>
</tr>
<tr>
<td>H10</td>
<td>0.13</td>
<td>0.02</td>
</tr>
</tbody>
</table>

set for all atoms and LANL2DZ ECP for Cd, using NWChem software. These latter charges were obtained by Katherine Forrest. The charges obtained by both methods are in general agreement and no significant difference was observed by applying the two different sets in simulation. For polarizable simulations, all exponentially damped polarizabilities were obtained from the work of van Duijnen and Swart except Cd, which was obtained using a combination of Orca and MPMC. Note, all the parameters in a simulation-ready file are available in the source code for MCMD on github.

In order to compute fugacity for each state point in GCMC simulations, a built-in function was used depending on the gas, temperature, and pressure being simulated for $N_2$, $H_2$, $CO_2$, and $CH_4$. All other gases were treated with the ideal gas approximation for fugacity (where $P = f$).
5.2.2 Results

The GCMC equilibrium uptakes for various gases (and models) are presented in Fig. 5.2 for non-polarizable models. It is clear that the gas with highest gravimetric uptake for the unpolarized models is H$_2$O. Interestingly, when explicit polarization is activated in simulations (using compatible polarizable models), the uptake for H$_2$O decreases dramatically (Fig. 5.3). The same was observed for the polarizable model for CO$_2$ (Fig. 5.4). Since the polarization energy is rigorously negative, this is a counterintuitive result, as one would think that sorption would increase with polarization yielding a lower potential. Nonetheless, the inclusion of polarization produces initial binding sites for the molecules which restrict access by other molecules through steric hindering, resulting in a lower overall uptake at equilibrium. This has important consequences for molecular modeling in general. Besides this, it is likely that the TIP3P and TIP4P models exhibit a higher uptake do to their inflated partial charges which are meant to produce a realistic water density at STP. The charges produce an unrealistic dipole (∼2.35 D) whereas the known experimental dipole under these conditions is ∼1.85 D.

Figure 5.2: Simulated equilibrium gas uptakes in KIKDOZ at 1 atm and 273 K (blue) or 298 K (red) in mmol/g, from GCMC simulation.

The isosteric heat of CO$_2$ as a function of gas loading is presented for the four models considered in Fig. 5.5. There is an obvious uptrend for all models (although it does not have a very large slope). This indicates some cooperative loading, as CO$_2$ – CO$_2$ interactions produce a more favorable energetic environment at higher loadings.
Simulated annealing was performed to determine the binding site of a single CO$_2$-PHAST* molecule within the porous framework. Starting at 600 K (which essentially would allow any physically reasonable molecular motion), the system was cooled to ~63 K as the energy minimized. The observed binding site was a coordination of the C$_{CO2}$ atom with the F$_{MOF}$ atom with an interaction distance of 3.61 Å. The F atom was F3, which exhibits the highest magnitude charge from the above ESP calculations. While the molecule coordinates to the SIFSIX cluster in this manner, there are even closer inter-
actions between the O$_{CO2}$ and H$_{MOF}$ atoms with distances of 2.46 – 3.04 Å, suggesting strong interactions between CO$_2$ molecules and the methyl groups in the MOF lattice. There were also C$_{CO2}$ – N$_{MOF}$ interactions observed at 3.39 and 3.41 Å, likely owing to the negative charges residing on the N$_{MOF}$ atoms. The binding site is shown in Fig. 5.6 and has an interaction energy of -25.2 kJ/mol as calculated using the polarizable potential energy function.
6.1 Note to Reader

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6.2 Abstract

Grand canonical Monte Carlo (GCMC) simulations of carbon dioxide (CO₂) and acetylene (C₂H₂) sorption were performed in MPM-1-Cl and MPM-1-Br, two robust molecular porous materials (MPMs) that were synthesized by the addition of adenine to CuX₂ (X = Cl or Br) by solvent diffusion. Previous experimental studies revealed that both MPMs are selective for C₂H₂ over CO₂ [Xie, D, et al. (2017) *CIESC J.*, 68, 154–162]. Simulations in MPM-1-Cl and MPM-1-Br were carried out using polarizable and non-polarizable potentials of the respective sorbates; this was done to investigate the role of explicit induction on the gas sorption mechanism in these materials. The calculated sorption isotherms and isosteric heat of adsorption (Qst) values for both sorbates are in reasonable agreement with the corresponding experimental measurements, with simulations using the polarizable models producing the closest overall agreement. The modeled CO₂ binding site in both MPMs was discovered as sorption between the halide ions of two adjacent [Cu₂(adenine)₄X₂]²⁺ (X = Cl, Br) units. In the case of C₂H₂, it was found...
that the sorbate molecule prefers to align along the X–Cu–Cu–X axis of the copper paddlewheels such that each H atom of the C$_2$H$_2$ molecule can interact favorably with the coordinated X$^-$ ions. The simulations revealed that both MPMs exhibit stronger interactions with C$_2$H$_2$ than CO$_2$, which is consistent with experimental findings. The effect of halogen substitution toward CO$_2$ and C$_2$H$_2$ sorption in two isostructural MPMs was also elucidated in our theoretical studies.

6.3 Introduction

Metal–organic materials (MOMs) are a class of synthesized, often porous, and crystalline materials that have comprised the focus of a large amount of experimental and theoretical studies for the past few decades.$^{75,76,103}$ The application of MOMs is very diverse and has become essentially ubiquitous in scientific research, ranging from gas sorption,$^{3–5,7,10,11,14,15,17,67,103,119,175,176,208}$ separation,$^{7,209,210}$ catalysis,$^{78–81}$ sensing,$^{93,94}$ photoinduced electron transfer,$^{95–98}$ and biological uses.$^{211,212}$ The major reason for this is that there are conceivably infinite variations of MOM structures that can be synthesized by altering their component metal ions, organic linkers, secondary building units (SBUs),$^{2,31}$ solvents, and thermodynamic or physical conditions.

This study focuses on explaining the sorption properties of CO$_2$ and C$_2$H$_2$ in two isostructural porous materials. A method that separates these gases facilely from a mixture is highly sought for since CO$_2$ is one of the main contaminants in C$_2$H$_2$. The latter is an important feedstock chemical that is used for myriad products, such as pharmaceuticals, plastics, and fuels. There is also a growing need for technology that can mitigate the effects that CO$_2$ has on the environment. Indeed, the detrimental results of excess atmospheric CO$_2$ are both already observed and predicted to propagate in human health and the environment if steps are not taken to combat it.$^{131}$ A material that can effectively sorb and/or separate these two gases is therefore desirable and an understanding of the mechanism of such properties in candidate materials can pave the way for better, safer, and cheaper porous materials.
Recent studies involved examining C$_2$H$_2$/CO$_2$ separation in hybrid ultramicroporous materials (HUMs), a subclass of MOMs that combine ultramicropores with strong electrostatics from inorganic anions that line the pore surface. The materials of interest in this particular study are classified as molecular porous materials (MPMs), a class of molecular solids that are held together through weak noncovalent interactions (e.g., hydrogen bonding) as opposed to the conventional fully covalently bonded interactions found in most MOMs. The combination of adenine and Cu$^{+2}$ salts of Cl and Br forms self-assembled [Cu$_2$(adenine)$_4$Cl$_2$]Cl$_2$ and [Cu$_2$(adenine)$_4$Br$_2$]Br$_2$, known as MPM-1-Cl and MPM-1-Br, respectively. Orthographic views of the 1 × 1 × 2 supercell of MPM-1-Br are shown in Figure 6.1.

The syntheses of MPM-1-Cl and MPM-1-Br are reported in references and, respectively. Both MPMs feature an interesting hydrogen-bonding network in which (1) four hydrogen atoms from four different adenine linkers are hydrogen-bonded to a single halide ion and (2) an adenine linker from one [Cu$_2$(adenine)$_4$]$^{4+}$ unit exhibits hydrogen-bonding contacts with an adenine linker from another unit. Unlike most MOMs that contain dinuclear copper paddlewheel clusters, these MPMs contain halogen atoms bonded to the Cu$^{2+}$ ions of the copper paddlewheels at the axial position to create a saturated metal center. The two MPMs have a minor kink in the X–Cu–Cu–X (X = Cl or Br) motif such that the angle is not 180°. Previous theoretical studies on MPMs involved comparing the CO$_2$ and H$_2$ sorption mechanism in MPM-1-Cl and MPM-1-TIFSIX, with latter containing TiF$_6^{2−}$ ions in place of the halide ions. Overall, MPMs are of interest due to their thermal and water stability as well as their ease of synthesis compared to most MOMs. When these attributes are combined with their decent gas sorption and separation properties, MPMs could be good and interesting candidates for materials research.

The purpose of this study is to elucidate (with atomistic resolution) the sorption properties of CO$_2$ and C$_2$H$_2$ in the isostructural MPM-1-Cl and MPM-1-Br analogues. Insights into the reason for why both MPMs prefer C$_2$H$_2$ over CO$_2$ will be obtained. Another interest of this work is examining how the electronic environment (and thus
MPM–sorbate interaction) is effected by the use of a different halogen in the material. It will be shown that the van der Waals radius of the halogen and its polarizability play a key role in determining the location of the favorable sorption site and the energetics of binding in the material. To our knowledge, this is the first study reporting simulations of acetylene in these materials, as well as being the first theoretical study of MPM-1-Br.

6.4 Methods

The potential energy function for MPM-1-Cl was developed by our group in previous work\textsuperscript{216} and utilized herein. The crystal structure for MPM-1-Br was obtained from reference\textsuperscript{215}. For all simulations in both MPMs, the sorbent atoms were treated as rigid to accommodate a constant volume ensemble system. This approximation is especially valid when phononic effects are minor.\textsuperscript{12} As with previous work on MPM-1-Cl,\textsuperscript{216} all atoms of MPM-1-Br were given Lennard-Jones 12–6 parameters, point partial charges, and scalar point polarizabilities to model repulsion/dispersion, stationary electrostatic, and explicit polarization, respectively. The Lennard-Jones parameters for all MPM atoms were taken from the Universal Force Field (UFF),\textsuperscript{52} while the exponentially-damped polarizabilities for all atoms other than Cu were obtained from van Duijnen et al.\textsuperscript{57} The polarizability parameter for Cu\textsuperscript{2+} was determined in reference\textsuperscript{43} and used herein. The point partial charges for the chemically unique atoms were determined by averaging atomic charges computed \textit{via a least squares fit}\textsuperscript{143} to the electrostatic potential surface of representative MPM fragments generated by quantum mechanical calculations using NWChem.\textsuperscript{48}

The potentials used for CO\textsubscript{2} were the nonpolarizable CO\textsubscript{2}-PHAST\textsuperscript{41} and TraPPE\textsuperscript{86} models and the polarizable CO\textsubscript{2}-PHAST* model.\textsuperscript{41} C\textsubscript{2}H\textsubscript{2}-PHAST and C\textsubscript{2}H\textsubscript{2}-PHAST*\textsuperscript{137,138} were used to simulate C\textsubscript{2}H\textsubscript{2} sorption in both MPMs; the * denotes the inclusion of explicit polarization. Simulations of CO\textsubscript{2} and C\textsubscript{2}H\textsubscript{2} sorption in MPM-1-Cl and MPM-1-Br were performed using grand canonical Monte Carlo (GCMC) methods.\textsuperscript{150} The sorption simulations, theoretical isosteric heat of adsorption (\(Q_{st}\)) calculation, binding site analysis, etc. were carried out using the codes developed by our group.\textsuperscript{58,160} Further details of
performing the simulations and parametrizations are presented in the Supporting Information.

Simulated Annealing was performed using the polarizable models for CO$_2$ and C$_2$H$_2$ in both MPMs to determine the binding energy for each gas in each material. This is a computational method which involves a normal Monte Carlo procedure (using the MPM with a single sorbate molecule) which is tempered by reducing temperature with each accepted perturbation. As temperature decreases, the guest molecule settles into an energy minima, whose magnitude can be compared to $Q_{st}$ near zero loading.

6.5 Summary of Experimental Data

6.5.1 C$_2$H$_2$ Uptake

C$_2$H$_2$ uptake in MPM-1-Cl and MPM-1-Br was experimentally measured by Xie et al. at 273 and 298 K and pressures up to 1 atm; the resulting isotherms (as estimated from reference) are shown in Figure 6.2(a). It can be observed that as the pressure increases at 273 K, the Cl variant exhibits mildly greater affinity for C$_2$H$_2$ than the Br analogue. This could be due to the Cl$^-$ ions having a smaller ionic radius than Br$^-$, resulting in a slightly larger pore volume in MPM-1-Cl. This increased accessible volume in MPM-1-Cl relative to MPM-1-Br can allow for greater number of C$_2$H$_2$ molecules to occupy the pore space in the material at conditions approaching saturation.

Interestingly, the relative uptake trend is reversed at 298 K: MPM-1-Br shows slightly greater affinity for C$_2$H$_2$ compared to MPM-1-Cl for all pressures considered at this temperature. The observed phenomenon may be caused by the increased kinetic energy of the C$_2$H$_2$ molecules and the Br variant at higher temperatures. This permits the C$_2$H$_2$ molecules to diffuse through and collide with MPM-1-Br at a greater rate than at 273 K. Since Br is heavier than Cl, the Br$^-$ ions likely vibrate more slowly than the Cl$^-$ ions, thus making MPM-1-Br more rigid. When the C$_2$H$_2$ molecules are moving more quickly at higher temperatures, the favorable geometry of the MPM-1-Br framework is less flexible, whereas the higher kinetic energy of gas molecules may induce a slightly unfavorable conformational change for the Cl analogue. This is further emphasized from
the fact that the primary binding site discovered for C$_2$H$_2$ in MPM-1-Br has a lower potential energy and closer distance to the Cu paddlewheel than the analogous site in MPM-1-Cl; this will be explained below in section IV.C.

6.5.2 CO$_2$ Uptake

Xie et al. also measured CO$_2$ sorption in MPM-1-Cl and MPM-1-Br under the same conditions as C$_2$H$_2$; these isotherms are presented in Figure 6.2(b). We note that Zaworotko’s group also reported CO$_2$ sorption data in the Cl analogue previously. It can be seen that MPM-1-Cl sorbs a greater quantity of CO$_2$ for nearly all state points considered. This phenomenon may be explained by Cl exhibiting a higher electronegativity than Br, which allows for greater electrostatic interactions between the halide ion and the CO$_2$ molecule. Although CO$_2$ has no permanent dipole moment in the bulk, it displays high induced dipoles when interacting with the MPM framework. The interaction between the Cl$^-$ ion and the partial positive carbon atom of the CO$_2$ molecule is fortified with a greater electronegativity compared to Br$^-$. Our electronic structure calculations in both MPMs confirmed that the magnitude of the partial negative charges of the Cl$^-$ ions in MPM-1-Cl are greater than those for the Br$^-$ ions in MPM-1-Br.

6.5.3 Isosteric Heats of Adsorption

Xie et al. derived the experimental $Q_{st}$ values for C$_2$H$_2$ and CO$_2$ in MPM-1-Cl and MPM-1-Br by applying the virial method to the corresponding experimental isotherms. These $Q_{st}$ values are plotted as a function of gas loading in Figure 6.3. For both MPMs, the $Q_{st}$ for C$_2$H$_2$ is higher than that for CO$_2$ at all loadings considered, thus indicating that these two MPMs display greater preference for C$_2$H$_2$ over CO$_2$. Table 6.1 provides a summary of the zero-loading $Q_{st}$ values ($Q_{st}^0$) for C$_2$H$_2$ and CO$_2$ in both MPMs.

With regards to C$_2$H$_2$, MPM-1-Cl exhibits a $Q_{st}^0$ value of 28.57 kJ mol$^{-1}$, while that for MPM-1-Br is 25.05 kJ mol$^{-1}$. This suggests that MPM-1-Cl displays a more favorable initial loading site for C$_2$H$_2$ than MPM-1-Br according to experiment. The C$_2$H$_2$ $Q_{st}$ plot for MPM-1-Cl exhibits an expected decrease in $Q_{st}$ with each successive C$_2$H$_2$ molecule.
sorbed in the MPM at low loading; however, after \( \sim 1.5 \text{ mmol g}^{-1} \) loading is reached, the \( Q_{st} \) values begin to increase and eventually surpass the \( Q_{st}^0 \) value. The analogous plot for MPM-1-Br shows that the \( Q_{st} \) continually increases as the loading increases. Overall, for both MPMs, the increase in \( Q_{st} \) as a function of loading could be due to a combination of MPM–sorbate and cooperative sorbate–sorbate interactions.\(^{216,219}\) Interestingly, while the experimentally reported \( Q_{st} \) for MPM-1-Br is higher than that of MPM-1-Cl near 1 atm, the reported uptake is higher for MPM-1-Cl at that pressure. We believe this could be due to the empirical fitting method employed to obtain \( Q_{st} \) values from experimental isotherms. This is discussed in more detail in section 4.1.3.

The \( Q_{st}^0 \) value for CO\(_2\) in MPM-1-Cl and MPM-1-Br is 23.76 and 21.61 kJ mol\(^{-1}\), respectively. Further, the CO\(_2\) \( Q_{st} \) for MPM-1-Cl is greater than that for MPM-1-Br across the considered loading range. This implies that CO\(_2\) sorption is more favorable in MPM-1-Cl than MPM-1-Br, presumably due to the greater electronegativity and calculated partial negative charge of the Cl\(^-\) ion as explained in the previous subsection. Interestingly, the CO\(_2\) \( Q_{st} \) plot for MPM-1-Cl shows the same behavior as the C\(_2\)H\(_2\) \( Q_{st} \) plot for MPM-1-Br. Likewise, the shape of the \( Q_{st} \) plot for CO\(_2\) in MPM-1-Br is similar to that for the C\(_2\)H\(_2\) \( Q_{st} \) plot for MPM-1-Cl. As with C\(_2\)H\(_2\), both MPMs exhibit increasing \( Q_{st} \) with increasing loading in their CO\(_2\) \( Q_{st} \) plots, which indicates that CO\(_2\)–CO\(_2\) interactions are favorable in these materials.

### 6.6 Simulation Results and Discussion

#### 6.6.1 C\(_2\)H\(_2\) Sorption

The experimental and simulated C\(_2\)H\(_2\) sorption isotherms in MPM-1-Cl at 273 and 298 K are displayed in Figure 6.4(a). At 273 K, the calculated uptakes for the nonpolarizable C\(_2\)H\(_2\)-PHAST and polarizable C\(_2\)H\(_2\)-PHAST* models are in good agreement with experiment at pressures of 0.05 atm and lower. At higher pressures, however, the simulated uptakes for both potentials are significantly higher than experiment. At 298 K, both models generated sorption isotherms that show very good agreement with experiment for pressures up to 0.2 atm, while they notably oversorb experiment at greater pressures.
The fact that the simulated uptakes for the two potentials are in close agreement with experiment at low pressures for both temperatures suggest proper modeling of the initial C$_2$H$_2$ binding sites in this material. The significant oversorption compared to experiment implies that the simulations produced inflated sorbate–sorbate interactions in the MPM relative to what is physically captured in experiment, which could be attributed to inadequacies in the present C$_2$H$_2$ potentials. It can be observed that the polarizable model produced uptakes that are somewhat closer to experiment at higher pressures.

Figure 6.5(a) shows the simulated C$_2$H$_2$ sorption isotherms in MPM-1-Br at 273 and 298 K compared to experiment. As with MPM-1-Cl, simulations using the C$_2$H$_2$-PHAST and C$_2$H$_2$-PHAST* models in MPM-1-Br at both temperatures generally produced uptakes that are in good agreement with experiment at low pressures and those that are remarkably higher than experiment at higher pressures. Both models yielded comparable isotherms in MPM-1-Br at 273 K, with uptakes that are in closer agreement with experiment as the pressure approaches 1 atm. This could be a consequence of the material reaching C$_2$H$_2$ saturation under these conditions. At 298 K, the uptakes for the C$_2$H$_2$-PHAST* model is in better agreement with experiment at pressures lower than 0.1 atm.

As shown in Table 6.1, the experimental C$_2$H$_2$ uptakes for MPM-1-Br at both temperatures are higher than those for MPM-1-Cl at low pressures (0.05 atm), whereas such uptakes for the former are lower than those for the latter at higher pressures (1.0 atm). This trend is consistent with what was observed in the simulations when utilizing both C$_2$H$_2$ potentials. Therefore, MPM-1-Br exhibits greater interactions with the C$_2$H$_2$ molecules than MPM-1-Cl at low loadings, which could be explained by the Br$^-$ ions having a larger polarizability and van der Waals parameters than Cl$^-$ ions (see Supporting Information, Table S2). Nevertheless, at higher pressures, MPM-1-Br displays lower C$_2$H$_2$ uptake than the Cl analogue because less accessible space is available in the material under these conditions due to the larger ionic radius of the Br$^-$ ions. Indeed, the shape of the simulated C$_2$H$_2$ sorption isotherms for MPM-1-Br suggests that the material is near C$_2$H$_2$ saturation at ca. 3.5 mmol g$^{-1}$ loading.
The simulated C$_2$H$_2$ $Q_{st}$ values for MPM-1-Cl and MPM-1-Br are compared with their corresponding experimental $Q_{st}$ plots in Figures 6.6(a) and 6.7(a), respectively. It can be observed that simulations using the two models captured the apparent increase in $Q_{st}$ as the loading increases for both MPMs. This shape is consistent with the experimental C$_2$H$_2$ $Q_{st}$ plot for MPM-1-Br. Overall, the trend in the simulated $Q_{st}$ values for MPM-1-Cl and MPM-1-Br support the experimental observation that both MPMs tend to facilitate C$_2$H$_2$ sorption such that initially loaded molecules tend to cooperatively interact with each other to lower the potential energy of subsequent guest molecules, thereby leading to enhanced sorbate–sorbate interactions at higher loadings. When considering all loadings, both models produced $Q_{st}$ values that are within the vicinity of experiment for both MPMs.

The theoretical $Q^0_{st}$ value for the C$_2$H$_2$-PHAST and C$_2$H$_2$-PHAST* models in MPM-1-Cl are 25.49 and 25.65 kJ mol$^{-1}$, respectively, which are lower than the corresponding experimental value of 28.57 kJ mol$^{-1}$ (Table 6.1). Simulations in MPM-1-Br yielded $Q^0_{st}$ values of 30.61 and 27.55 kJ mol$^{-1}$ for the nonpolarizable and polarizable models, respectively, which are higher than the experimental value for this MPM (25.05 kJ mol$^{-1}$). In general, our simulations suggest that MPM-1-Br exhibits a higher $Q^0_{st}$ value for C$_2$H$_2$ than MPM-1-Cl, whereas the opposite trend is observed according to experiment. From a molecular point of view, it is expected that MPM-1-Br would display a greater affinity for C$_2$H$_2$ due to the higher polarizability of the Br$^-$ ions. Such an effect is probably captured in our simulations that include both implicit and explicit polarization. This behavior is not reflected in the reported experimental C$_2$H$_2$ $Q_{st}$ for both MPMs even though the experimental isotherms at both temperatures suggest that MPM-1-Br outperforms MPM-1-Cl for C$_2$H$_2$ uptake at low pressures (see Table 6.1). It is notable that the experimental $Q_{st}$ values are derived from an empirical fitting procedure on the measured sorption isotherms, whereas the theoretical values are obtained directly from GCMC simulation. We could therefore attribute the discrepancy in the relative $Q^0_{st}$ trend between experiment and simulation to the empirical fitting that was implemented to extract the experimental $Q_{st}$ values.
6.6.2 CO₂ Sorption

The simulated CO₂ uptakes for three different potentials (CO₂-PHAST, CO₂-PHAST*, and TraPPE) in MPM-1-Cl at 273 and 298 K are shown in Figure 6.4(b). The isotherms produced by the CO₂-PHAST and TraPPE models oversorb experiment for nearly all state points considered. On the other hand, the isotherms for the CO₂-PHAST* model are in excellent agreement with experiment across the considered pressure range at both temperatures. The strong agreement between the experimental and simulated isotherms for the CO₂-PHAST* model demonstrates that this potential is highly accurate for simulations in heterogeneous media. The TraPPE model yielded the highest calculated CO₂ uptakes in MPM-1-Cl out of all models. Indeed, at 273 K, the calculated uptakes for this model are > 1.5 mmol g⁻¹ higher than experiment at pressures of 0.2 atm and beyond. Although the TraPPE model is widely used, it has been shown to generate isotherms that notably oversorb experiment in many porous materials.

The CO₂-PHAST* model yielded the lowest CO₂ uptakes in MPM-1-Cl out of all models for all considered state points even though it includes explicit many-body polarization. Generally, the theoretical gas uptake in MOMs increases with increasing terms in the potential energy function. This was not the case here as the CO₂-PHAST model gives uptakes that are higher than those for its polarizable counterpart. It is predicted that the inclusion of polarization produces a favorable sorbate ordering effect in this MPM, which causes the CO₂ uptake to decrease compared to when only stationary electrostatic interactions are considered. A similar phenomenon was observed from theoretical studies in a HUM. We note that CO₂ sorption in MPM-1-Cl was investigated previously through GCMC simulations using only the CO₂-PHAST* model. Herein, we show the results that were obtained using different CO₂ potentials in this material.

A comparison of the experimental and simulated CO₂ sorption isotherms for the three different potentials in MPM-1-Br at 273 and 298 K is presented in Figure 6.5(b). The results for the three models in this MPM are consistent with that for MPM-1-Cl. Notably, the isotherms for the TraPPE model significantly oversorb experiment at both temperatures. The amount of oversorption for this model is generally proportional to the
pressure. The CO\textsubscript{2}-PHAST model produces the next highest calculated CO\textsubscript{2} uptakes for all pressures, followed by the CO\textsubscript{2}-PHAST* model. As observed in MPM-1-Cl, the CO\textsubscript{2}-PHAST* model yields uptakes that are in very good agreement with experiment for all pressures at both temperatures, thus further illustrating the accuracy of this potential for simulation CO\textsubscript{2} sorption in porous materials. The isotherm for the nonpolarizable CO\textsubscript{2}-PHAST model is in good agreement with experiment at 298 K, but somewhat oversorbs experiment at 273 K. The increase in temperature may provide enough kinetic energy to decrease electrostatic interactions between the Br\textsuperscript{-} ions and the CO\textsubscript{2} molecule; this could explain why the CO\textsubscript{2}-PHAST model shows better agreement with experiment at the higher temperature.

As shown in Table 6.1, the experimental atmospheric CO\textsubscript{2} uptakes in MPM-1-Br at 273 and 298 K are 2.54 and 1.56 mmol g\textsuperscript{-1}, respectively. The corresponding values for MPM-1-Cl are 3.50 and 1.97 mmol g\textsuperscript{-1}, respectively, which are higher than those for MPM-1-Br. Our simulations confirmed the experimental finding that the CO\textsubscript{2} uptakes under these thermodynamic conditions are greater for MPM-1-Cl than MPM-1-Br; this is true regardless of the CO\textsubscript{2} potential that was used. It is expected that CO\textsubscript{2} sorption in these MPMs is governed by electrostatic interactions between the halide ion and the positively charged carbon atom of the CO\textsubscript{2} molecule. MPM-1-Br displays weaker interactions with the CO\textsubscript{2} molecules than MPM-1-Cl, probably due to the lower calculated partial negative charges for the Br\textsuperscript{-} ions compared to the Cl\textsuperscript{-} ions (see Supporting Information, Table S1). Lower magnitudes for the partial negative charge of the halide ion will result in decreased electrostatic interactions with the CO\textsubscript{2} molecule.

Simulations using the CO\textsubscript{2} EPM\textsuperscript{220} model were also performed. The results were comparable to those of CO\textsubscript{2}-PHAST, in that they oversorbed with respect to experiment especially at higher pressures. Overall, the polarizable CO\textsubscript{2}-PHAST* model agreed most with experimental data, and binding sites are thus discussed below primarily from results using that model.

The simulated CO\textsubscript{2} values for the CO\textsubscript{2}-PHAST, CO\textsubscript{2}-PHAST*, and TraPPE models for MPM-1-Cl and MPM-1-Br are displayed in Figures 6.6(b) and 6.7(b), respectively.
According to our simulations, the relative trend in the magnitude of the CO$_2$ $Q_{st}$ values in both MPMs is: TraPPE > CO$_2$-PHAST > CO$_2$-PHAST*. This is consistent with the pattern that was observed for the simulated uptakes for the three models in both MPMs. The simulated $Q_{st}$ values for the CO$_2$-PHAST and CO$_2$-PHAST* models in MPM-1-Cl are in good agreement with experiment as well as each other for all considered loadings. The TraPPE model $Q_{st}$ values for this MPM are somewhat higher than experiment across the loading range. The $Q_{st}$ plots for all models in MPM-1-Cl show increasing $Q_{st}$ with higher loadings, which is consistent with the shape for the experimental plot. Therefore, our simulations captured the expected cooperative CO$_2$–CO$_2$ interactions in this MPM.

In MPM-1-Br, the $Q_{st}$ values for all models are consistently higher than experiment for all loadings, with values produced by the polarizable CO$_2$-PHAST* model being closer to experiment. The experimental $Q_{st}$ values in this MPM begins to increase when the material is partially saturated at ~1.0 mmol g$^{-1}$ loading, indicating cooperativity between the CO$_2$ molecules under these conditions. Unlike in MPM-1-Cl, the $Q_{st}$ plot for all three models in MPM-1-Br does not show much signs of sorbate–sorbate cooperativity in the material. Rather, the theoretical $Q_{st}$ values slightly decreases with increasing CO$_2$ uptake, as does the experiment. In addition, the simulated $Q_{st}$ plots level off at a loading of ~0.4 mmol g$^{-1}$, but there is neither a sustained or defined increasing trend in $Q_{st}$ as the uptakes continue to increase.

The calculated $Q^0_{st}$ values for all three potentials in both MPMs are summarized in Table 6.1. The $Q^0_{st}$ values produced by the CO$_2$-PHAST, CO$_2$-PHAST*, and TraPPE models in MPM-1-Cl are 24.33, 22.77 and 26.22 kJ mol$^{-1}$, respectively, whereas the analogous quantities for the three potentials in MPM-1-Br are 25.57, 25.02 and 25.40 kJ mol$^{-1}$, respectively. Simulations using the CO$_2$-PHAST and CO$_2$-PHAST* potentials suggest that the MPM–CO$_2$ interaction is greater for MPM-1-Br than MPM-1-Cl. This is in contrast to what was observed for experiment as the empirical $Q^0_{st}$ value for CO$_2$ is higher for MPM-1-Cl than MPM-1-Br. A potential reason for why our simulations generated a higher initial loading CO$_2$ $Q_{st}$ value for MPM-1-Br is explained in next section where the binding sites are discussed.
6.6.3 Binding Sites

Pham et al.\textsuperscript{216} reported a binding site for CO\textsubscript{2} in MPM-1-Cl in which the sorbate molecule aligns between two chlorine atoms, one that is bound to the copper paddlewheel complex and another which forms hydrogen-bonding interactions with four hydrogen atoms of two different adenine linkers. Interestingly, this site was minimally observed for simulations in MPM-1-Br. Indeed, the main binding site for CO\textsubscript{2} in MPM-1-Br was actually between two Br atoms that are coordinated to the Cu\textsuperscript{2+} ions of two different [Cu\textsubscript{2}(adenine)\textsubscript{4}Br\textsubscript{2}]\textsuperscript{2+} complexes (Figure 6.8(b)). Notably, the positively charged carbon atom of the CO\textsubscript{2} molecule can interact with two electronegative Br\textsuperscript{−} ions simultaneously. We also observed this site in MPM-1-Cl for the simulations reported herein (Figure 6.8(a)). The larger van der Waals radius of the Br\textsuperscript{−} ions causes this region to be more favorable for the CO\textsubscript{2} molecules in MPM-1-Br than in MPM-1-Cl. This is because the larger size of the bromide ions will result in greater close-fitting interactions with the sorbate molecules. The CO\textsubscript{2} molecule will exhibit a lower potential energy in the attractive well-depth potential region of both Br atoms as a result of the larger ionic radius. This could explain why the CO\textsubscript{2}-PHAST and CO\textsubscript{2}-PHAST* models produced CO\textsubscript{2} Q\textsubscript{st} values that are greater for MPM-1-Br.

The electrostatic and electrodynamic (polarizable) effects serve to attract the positively charged carbon center of the CO\textsubscript{2} molecule. The Lennard-Jones mixed σ parameter for Br–C used herein is \textasciitilde3.6 Å, and the measured Br–C\textsubscript{CO\textsubscript{2}} distance at the primary binding site is \textasciitilde3.2 Å. The expected repulsion of the CO\textsubscript{2} carbon atom is therefore counteracted by the attraction of the oxygen atoms on the molecule, which (being further away from the Br atoms) reside in the well-depth region of the dispersive potential. In addition, the calculated partial charge for this particular Br atom is -0.51 e\textsuperscript{−}, which is slightly lower in magnitude than that for the analogous Cl atom in MPM-1-Cl (-0.57 e\textsuperscript{−}) (see Supporting Information, Table S1). While the lower partial negative charge results in a weaker attraction between the halogen and the CO\textsubscript{2} carbon atom, it also reduces the repulsion experienced by each electronegative oxygen atom on the sorbate. The net effect
of all these interactions is a “balancing act” between the Br$^-$ ions in MPM-1-Br, which is a unique feature compared to the Cl analog.

MPM-1-Cl is able to sorb more CO$_2$ overall than MPM-1-Br as demonstrated through both experimental measurements$^{213}$ and simulation (Figures 6.4 and 6.5). This could be due to the higher magnitude of the partial negative charge of the Cl$^-$ ion as mentioned above. Electrostatic interactions are especially important for CO$_2$ sorption in both MPMs. It appears that the Coulombic attraction between the electropositive carbon atom of the CO$_2$ molecule and the halide ion increases with increasing partial negative charge of the anion. Further, the Cl$^-$ ions tend to attract more electron density from the guest molecules via dispersive forces than the Br$^-$ ions due to having a higher electronegativity.

The primary binding site for C$_2$H$_2$ in both MPM-1-Cl and MPM-1-Br is located near the copper paddlewheel complex, where the sorbate molecule orients parallel to the X–Cu–Cu–X axis (Figure 6.9). At this site, the center-of-mass (COM) of the C$_2$H$_2$ molecule is positioned approximately 5.5 and 5.2 Å away from the geometric center of the Cu$^{2+}$ ions in MPM-1-Cl and MPM-1-Br, respectively. This particular alignment of the C$_2$H$_2$ molecule about the copper paddlewheels allows the positively charged H atom on both sides of the sorbate to interact with the electronegative halide ions that are coordinated to the Cu$^{2+}$ ions. The negatively charged COM of the C$_2$H$_2$ molecule can also interact somewhat with the Cu$^{2+}$ ions of the copper paddlewheels.

Overall, there are more concurrent interactions between the C$_2$H$_2$ molecule and the framework about the primary binding site in both MPMs relative to that for CO$_2$. Indeed, at the primary binding site, the C$_2$H$_2$ molecule exhibits two H···X$^-$ and two COM(C$_2$H$_2$)···Cu$^{2+}$ interactions. On the other hand, there are only two C(CO$_2$)···X$^-$ interactions for CO$_2$ at the favorable binding site for this sorbate in both MPMs. The greater simultaneous interactions for C$_2$H$_2$ in MPM-1-X could explain why both MPMs display greater affinity and selectivity for C$_2$H$_2$ than CO$_2$. We note that the longer COM(C$_2$H$_2$)···Cu$^{2+}$ distance for MPM-1-Cl results in slightly weaker affinity at this site relative to MPM-1-Br, thus potentially explaining why our simulations produced lower initial C$_2$H$_2$ $Q_{st}$ values for the Cl analogue.
The results for binding energy calculations via Simulated annealing are presented in Table 6.2. It is clear from these simulations that both materials favor C$_2$H$_2$ over CO$_2$ (measured as a single molecule competition), in agreement with experimental data. The binding sites corresponding to an energy minimum discovered through these simulations were the same as those shown in Figures 6.8 & 6.9. As observed in the results for $Q_{st}$, the binding energies for MPM-1-Br in simulation are higher than those of MPM-1-Cl. Again, this is likely due to the higher polarizability of Br used in these simulations.

6.7 Conclusion

This study aimed to elucidate the CO$_2$ and C$_2$H$_2$ sorption properties and mechanisms in two isostructural MPMs, MPM-1-Cl and MPM-1-Br. Our simulations revealed that MPM-1-Cl exhibits a better overall sorption capacity for both gases than MPM-1-Br, which is consistent with the experimental measurements reported by Xie et al.$^{213}$ This could be due to a combination of larger accessible space in the Cl analogue at higher pressures (a consequence of the smaller ionic radius for Cl$^-$) and/or the fact that Cl is more electronegative than Br, which affords greater electrostatic interactions with the sorbate. At low loadings, however, the simulations suggest that MPM-1-Br is slightly more favorable toward both sorbates than MPM-1-Cl. We attribute this to the higher polarizability and van der Waals parameters for the Br$^-$ ions. Notably, repulsion/dispersion interactions could dominate the sorption mechanism at such loadings.

It was discovered through our simulations that the primary binding site for C$_2$H$_2$ and CO$_2$ in both MPMs are notably different between the two sorbates. Particularly, the C$_2$H$_2$ molecule prefers to align along the X–Cu–Cu–X axis of the copper paddlewheel to allow for favorable H···X$^-$ interactions on each side of the molecule, while the CO$_2$ molecule seems to favor the region between the X$^-$ ions of two adjacent copper paddlewheel units. Both MPMs appear to be more selective toward C$_2$H$_2$ than CO$_2$ because there are a greater number of concurrent interactions about the primary binding site for C$_2$H$_2$.

Herein, we demonstrated how substitution of the halide ion in two isostructural MPMs with the empirical formula [Cu$_2$(adenine)$_4$X$_2$]X$_2$ affects the gas sorption properties in
Table 6.1: Summary of data from key state points for gas sorption in MPM-1-Cl and MPM-1-Br. Experimental values are compared with simulation using various potentials for each sorbate. $Q_{st}^0$ is the $Q_{st}$ value for the lowest reported loading. Units are a kJ mol$^{-1}$, b mmol g$^{-1}$.

<table>
<thead>
<tr>
<th>Model</th>
<th>CO$_2$</th>
<th>Simulation</th>
<th>Exp.</th>
<th>Simulation</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CO$_2$-PHAST*</td>
<td>CO$_2$-PHAST</td>
<td>TraPPE</td>
<td>CO$_2$-PHAST</td>
</tr>
<tr>
<td>MPM-1-Cl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05 atm loading, 273 K</td>
<td>23.76</td>
<td>22.77</td>
<td>24.33</td>
<td>26.22</td>
<td>28.57</td>
</tr>
<tr>
<td>1.0 atm loading, 273 K</td>
<td>3.50</td>
<td>3.63</td>
<td>4.75</td>
<td>5.06</td>
<td>3.86</td>
</tr>
<tr>
<td>0.05 atm loading, 298 K</td>
<td>0.12</td>
<td>0.13</td>
<td>0.17</td>
<td>0.35</td>
<td>0.34</td>
</tr>
<tr>
<td>1.0 atm loading, 298 K</td>
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<td>2.74</td>
<td>3.60</td>
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</tr>
<tr>
<td>MPM-1-Br</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05 atm loading, 273 K</td>
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<td>25.02</td>
<td>25.37</td>
<td>25.40</td>
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</tr>
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<td>1.0 atm loading, 273 K</td>
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<tr>
<td>0.05 atm loading, 298 K</td>
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<td>0.11</td>
<td>0.13</td>
<td>0.20</td>
<td>0.43</td>
</tr>
<tr>
<td>1.0 atm loading, 298 K</td>
<td>1.56</td>
<td>1.52</td>
<td>1.80</td>
<td>2.47</td>
<td>2.82</td>
</tr>
</tbody>
</table>

Table 6.2: Binding energies for gases in MPM-1-Cl and MPM-1-Br as calculated by single-particle simulated annealing using the polarizable models for CO$_2$ and C$_2$H$_2$. The starting temperature for all simulations was 500 K, to ensure free and full exploration of the phase space of the system.

<table>
<thead>
<tr>
<th>Model</th>
<th>Binding energy (kJ/mol)</th>
<th>Steps ($\times 10^6$)</th>
<th>Final Temp. (K)</th>
</tr>
</thead>
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<td>MPM-1-Cl</td>
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<td>2.37</td>
</tr>
<tr>
<td></td>
<td>C$_2$H$_2$</td>
<td>-29.9</td>
<td>2.46</td>
</tr>
<tr>
<td>MPM-1-Br</td>
<td>CO$_2$</td>
<td>-28.2</td>
<td>3.24</td>
</tr>
<tr>
<td></td>
<td>C$_2$H$_2$</td>
<td>-34.7</td>
<td>4.53</td>
</tr>
</tbody>
</table>

the material through molecular simulations. We plan to investigate the CO$_2$ and C$_2$H$_2$ sorption performance in MPM-1-TIFSIX through theoretical studies in future work.
Figure 6.1: (a) Orthographic $a$-axis view, (b) $b$-axis view, and (c) $c$-axis view of the $1 \times 1 \times 2$ supercell of MPM-1-Br used for the simulations in this study. The crystal structure of MPM-1-Cl is very similar. Atom colors are C = cyan; N = blue; H = white; Cu = brown; Br = red.
Figure 6.2: Experimental gas sorption isotherms of (a) C₂H₂ and (b) CO₂ for MPM-1-X (X = Br, circles or Cl, triangles) at two different temperatures (blue = 273 K; red = 298 K) and pressures up to 1 atm. All experimental data were estimated from reference.²¹³

Figure 6.3: Experimental isosteric heats of adsorption (Qₜₜ) for C₂H₂ (circles) and CO₂ (triangles) for MPM-1-X (X = Br, blue or Cl, red). All experimental data were estimated from reference.²¹³
Figure 6.4: Simulated gas sorption isotherms of (a) C\textsubscript{2}H\textsubscript{2} and (b) CO\textsubscript{2} for MPM-1-Cl compared with experiment at two different temperatures (blue = 273 K; red = 298 K) and pressures up to 1 atm. Experiment = pure solid line; C\textsubscript{2}H\textsubscript{2}/CO\textsubscript{2}-PHAST model = solid line with triangles; C\textsubscript{2}H\textsubscript{2}/CO\textsubscript{2}-PHAST* model = solid line with stars; TraPPE model = solid line with circles.

Figure 6.5: Simulated gas sorption isotherms of (a) C\textsubscript{2}H\textsubscript{2} and (b) CO\textsubscript{2} for MPM-1-Br compared with experiment at two different temperatures (blue = 273 K; red = 298 K) and pressures up to 1 atm. Experiment = pure solid line; C\textsubscript{2}H\textsubscript{2}/CO\textsubscript{2}-PHAST model = solid line with triangles; C\textsubscript{2}H\textsubscript{2}/CO\textsubscript{2}-PHAST* model = solid line with stars; TraPPE model = solid line with circles.
Figure 6.6: Simulated isosteric heat of sorption ($Q_{st}$) for (a) C$_2$H$_2$ and (b) CO$_2$ for MPM-1-Cl compared with experiment. Experiment = solid black line; Simulation = solid blue line with symbols (C$_2$H$_2$/CO$_2$-PHAST = triangles; C$_2$H$_2$/CO$_2$-PHAST* = stars; TraPPE model = circles).

Figure 6.7: Simulated isosteric heat of sorption ($Q_{st}$) for (a) C$_2$H$_2$ and (b) CO$_2$ for MPM-1-Br compared with experiment. Experiment = solid black line; Simulation = solid blue line with symbols (C$_2$H$_2$/CO$_2$-PHAST = triangles; C$_2$H$_2$/CO$_2$-PHAST* = stars; TraPPE model = circles).
Figure 6.8: Molecular illustration of the primary binding site for CO$_2$ observed in (a) MPM-1-Cl and (b) MPM-1-Br through simulation, which is nestled between two X (X = Cl, Br) atoms bound to two different [Cu$_2$(adenine)$_4$]$^{4+}$ complexes. Atom colors are C = cyan; N = blue; H = white; Cu = brown; Cl = yellow; Br = red.

Figure 6.9: Molecular illustration of the primary binding site for C$_2$H$_2$ observed in (a) MPM-1-Cl and (b) MPM-1-Br through simulation, which is aligned with the X–Cu–Cu–X (X = Cl, Br) axis of the dinuclear copper paddlewheel complex. Atom colors are C = cyan; N = blue; H = white; Cu = brown; Cl = yellow; Br = red.
Chapter 7

Theoretical study of Ru-tris-bipyridine in USF2 and RWLC-5

7.1 Methods

7.1.1 Atomic Coordinate Determination

Initial X-ray crystallography atomic coordinate files for $[\text{Ru(bpy)}_3]^{2+}$ and the two USF2 cages were supplied by Dr. Randy Larsen, USF.

7.1.2 Parametrization for optimization

Atomic point-charges were calculated for two USF2 cages (labeled 1 (medium) and 2 (large)), and the $[\text{Ru(bipyridine)}_3]^{2+}$ complex using Orca$^{141}$ software (currently free for academic use). Charges for $[\text{Ru(bpy)}_3]^{2+}$ were computed by using Density Functional Theory with PBE0 (25% Hartree-Fock exchange + 75% PBE exchange$^{221}$ + 100% PBE correlation).$^{222}$ All atoms (H,C,N) were represented by the 6-31G* basis sets$^{223}$ except Ru, which was represented using the LANL2DZ basis set and Effective Core Potential,$^{50,224,225}$ for energy calculation. Atomic point charges were then fit using Mulliken population analysis.$^{226}$

The medium USF2 cage charges were computed after first truncating the outer Zn paddleweel carboxyl groups with hydrogen atoms and optimizing these hydrogens with the rest of the system fixed with Orca, using Hartree-Fock$^{227}$ method with 6-31G* basis sets$^{223}$ and LANL2DZ ECP$^{50,224,225}$ for Zn. The CHELPG method was used for charge fitting after the energy calculation converged.
The large USF2 cage charges were computed using the Hatree-Fock\textsuperscript{227} Self-Consistent Field generated energy. Again, the 6-31G* basis sets\textsuperscript{223} were selected for all atoms (H, C, O) except for Zn, which was represented by its LANL2DZ ECP.\textsuperscript{50,224,225} Charges were fit using the CHELPG method. Note, the 6-31G* / LANL2DZ ECP basis set selection has been found useful and widely applicable for accurate simulations of systems involving gas-phase fragments of metal-organic frameworks\textsuperscript{6,7,22,34–36,43,51,68,119} due to the over-polarized nature of 6-31G* basis sets.

Classical simulations were performed to obtain minimum-energy structures of [Ru(bpy)\textsubscript{3}]\textsuperscript{2+} inside cages 1 and 2. A [Ru(bpy)\textsubscript{3}]\textsuperscript{2+} cluster was placed in the center of the respective cage in a canonical ensemble (NVT) Monte Carlo simulation.\textsuperscript{58} The simulation system was a 160Å \times 160Å \times 160Å cube treated without periodic boundary conditions or long-range energy corrections, to evaluate the cage and [Ru(bpy)\textsubscript{3}]\textsuperscript{2+} cluster alone.

To find the minimum-energy structure of [Ru(bpy)\textsubscript{3}]\textsuperscript{2+} inside cages 1 and 2, a [Ru(bpy)\textsubscript{3}]\textsuperscript{2+} molecule was placed in the center of the respective fixed-cage, and \geq 1.7\times10\textsuperscript{6} Monte Carlo moves were performed until the total potential energy was minimized and equilibrated. This was followed by simulated annealing until the molecule did not move significantly [from 298K to 37K (for the medium cage) or 178K (for the large cage)] with an annealing schedule of 0.99999. The total energy was calculated as the sum of repulsion-dispersion, electrostatic, and polarization energies: \( U_{\text{total}} = U_{\text{rd}} + U_{\text{es}} + U_{\text{pol}} \). Methods for calculation of these contributions are provided in former work.\textsuperscript{12,37,119} The atomic-point parameters used for each atom are provided in Table 7.1. Note, the RD sigma and epsilon values were taken from the Universal Force Field.\textsuperscript{52} Polarizability parameters were taken from van Duijnen et al.,\textsuperscript{57} except for Ru, which was calculated by parametrizing the isotropic polarizability of the Ru-bipyridine complex with unknown value for Ru and values from ref. 57 for all other atoms, until a suitable value within 0.001 Å\textsuperscript{3} of the quantum-mechanically (Orca DFT using pbe0, aug-cc-pvtz basis sets and LANL2DZ on Ru) calculated isotropic polarizability was found.
Table 7.1: Atomic point parameters used in Monte Carlo simulations of \([\text{Ru(bpy)}_3]^{2+}\) in USF2 cages 1 and 2.

<table>
<thead>
<tr>
<th></th>
<th>RD sigma (Å)</th>
<th>RD epsilon (K)</th>
<th>Polarizability (Å³)</th>
<th>Charge (e)</th>
</tr>
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<tbody>
<tr>
<td>Ru</td>
<td>2.64</td>
<td>21.18</td>
<td>5.1910</td>
<td>0.893</td>
</tr>
<tr>
<td>Zn</td>
<td>2.46155</td>
<td>62.39923</td>
<td>1.9887</td>
<td>varies</td>
</tr>
<tr>
<td>H</td>
<td>2.571</td>
<td>22.14</td>
<td>0.4138</td>
<td>varies</td>
</tr>
<tr>
<td>C</td>
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<td>varies</td>
</tr>
<tr>
<td>N</td>
<td>3.66</td>
<td>34.72215</td>
<td>0.97157</td>
<td>varies</td>
</tr>
<tr>
<td>O</td>
<td>3.118</td>
<td>30.19</td>
<td>0.8520</td>
<td>varies</td>
</tr>
</tbody>
</table>

A successful optimization of \([\text{Ru(bipyridine)}_3]^{2+}\) in cage 1 was performed using Orca. The HF method was used for computation of the system wavefunction with 3-21G basis sets and LANL2DZ ECPs for Ru and Zn. The cage atoms were constrained during the optimization.

### 7.1.3 TDDFT calculation of \([\text{Ru(bpy)}_3]^{2+}\) excited states

The Ru-bipyridine molecule (alone, or inside of the MOF cage(s)) was used in a Tamm-Dancoff Time-Dependent Density Functional Theory calculation to get information about excited-state energy levels. Orca, QChem and NWChem were used to perform the calculations with different functionals, basis sets, and number of roots (excited states). The results are summarized by the excited state corresponding to the highest oscillator strength in Table 7.4.

### 7.1.4 Solvent occupation determination in USF2 cages

Grand Canonical Monte Carlo simulations were performed using MCMD\textsuperscript{160} without periodic boundary conditions to determine the equilibrium quantity of solvent molecules in cages 1 and 2 with the classically optimized (using repulsion-dispersion and electrostatic potential energy) \([\text{Ru(bpy)}_3]^{2+}\) molecule in the respective cage. Models were made for methanol and ethanol using the CCSDT geometry supplied by the Computational Chemistry Comparison and Benchmark Database (CCCBDB).\textsuperscript{228} As before, repulsion-dispersion parameters were taken from UFF\textsuperscript{52} for each atom. Charge parameters were calculated from DFT pbe0 calculations using the aug-cc-pvtz basis set for all atoms and
the CHELPG charge-fitting method, using Orca. The charges for each model are shown in Table 7.2 (methanol) and Table 7.3 (ethanol). The simulations were run at 298.0 K and 1.0 atm until equilibration, ≥ 1.5 × 10⁵ steps with a correlation time of 500 steps. For cage 1 (medium), the condition for solvent molecules being inside the cage was that their center-of-mass was within 9.01 Å of the origin. For cage 2 (large), it was within 9.33 Å. These distances correspond to the longest distance of carboxyl oxygens to the origin with the cage centered about the origin. For cage 1 (medium), the box size was 25.662 × 17.498 × 25.662 Å³. For cage 2 (large), it was 27.488 × 27.488 × 27.488 Å³. To further evaluate solvent-MOF interactions, the radial distribution \((g(r))\) function was calculated for solvent molecules to observe the distance between Zn metal ions in the MOF and methanol or ethanol. The distances were evaluated and the distribution updated every 500 steps. The results are displayed in Figure 7.10.

### Table 7.2: Positions and charges for the methanol model.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x (Å)</th>
<th>y (Å)</th>
<th>z (Å)</th>
<th>charge (e)</th>
</tr>
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### Table 7.3: Positions and charges for the ethanol model.

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<td>-0.03011</td>
</tr>
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</table>
7.2 Results

7.2.1 Classical Optimization

In cage 1, the Monte Carlo / Simulated annealing classical optimization resulted in a coordination of the terminal hydrogens of $[\text{Ru(bpy)}_3]^{2+}$ to a Zn cluster as shown in Figs. 7.1 and 7.2.

Figure 7.1: Final position of classically-optimized $[\text{Ru(bpy)}_3]^{2+}$ in cage 1 (the medium cage of USF2) The displayed interaction distances are 3.38 and 4.43 Å. Most of the cage is yellow for clarity. Ru = pink; Zn = grey; C = cyan; H = white; N = blue.

7.2.2 Quantum-Mechanical Optimization

The QM-optimized structure of $[\text{Ru(bpy)}_3]^{2+}$ with cage 1 also resulted in a coordination, with increased symmetry, as bond lengths and angles in the molecule were rigid, as shown in Figs. 7.3 and 7.4.

7.2.3 $[\text{Ru(bpy)}_3]^{2+}$ standalone properties

The TDDFT aug-cc-pvtz pbe0 method is compared with b3lyp for the excited-state energies of $[\text{Ru(bpy)}_3]^{2+}$ in Fig. 7.5. Additionally, the molecular orbitals of the complex are displayed in Fig. 7.6, with electron densities in Fig. 7.7.
Figure 7.2: Final position of classically-optimized $[\text{Ru(bpy)}_3]^{2+}$ in cage 1 (the medium cage of USF2, zoomed at a different angle). The displayed interaction distances are 3.38 and 4.43 Å. Most of the cage is yellow for clarity. Ru = pink; Zn = grey; C = cyan; H = white; N = blue.

### 7.2.4 USF2-RuBpy TDDFT calculation

The results for TDDFT excited-state energy calculation are presented in Fig. 7.8.

### 7.2.5 Solvent occupation in cages

Figure 7.9 shows the number of methanol or ethanol molecules occupied in the USF2 cages containing $[\text{Ru(bpy)}_3]^{2+}$ in its classically-optimized position. Figure 7.10 shows the radial distribution function for solvent center-of-masses with Zn atoms in the MOF for the simulations performed in Figure 7.9.
Figure 7.3: Final position of QM-optimized $[\text{Ru(bpy)}_3]^{2+}$ in cage 1 (the medium cage of USF2). The displayed interaction distances are 3.89 and 3.52 Å. Most of the cage is yellow for clarity. Ru = pink; Zn = grey; C = cyan; H = white; N = blue.

Figure 7.4: Final position of QM-optimized $[\text{Ru(bpy)}_3]^{2+}$ in cage 1 (the medium cage of USF2, zoomed at a different angle). The displayed interaction distances are 3.89 and 3.52 Å. Most of the cage is yellow for clarity. Ru = pink; Zn = grey; C = cyan; H = white; N = blue.
Figure 7.5: Comparison of pbe0 and b3lyp methods for excited-state TDDFT energy calculation of Ru-bipyridine. Black = pbe0; Red = b3lyp.

Figure 7.6: Molecular orbitals of Ru-bpy from TDDFT pbe0 aug-cc-pvtz calculation. Blue = negative wavefunction (isovalue = 0.01); Red = positive wavefunction (isovalue = -0.01). Some carbon atoms are visible, colored cyan.
Figure 7.7: Electron density isosurface of Ru-bpy from TDDFT pbe0 aug-cc-pvtz calculation (isovalue = 0.044). C = cyan; H = white; N and Ru are not visible.

Figure 7.8: The TDDFT 6-31G* (LANL2DZ Ru, Zn ECPs) pbe0 excited state energies, compared with experimental\(^\text{229}\) \(\Delta E_1\) value for USF2:Ru-Bpy. Computed with Orca.\(^\text{141}\)
Figure 7.9: Number of solvent molecules in USF2 cages (red = cage 1, medium; green = cage 2, large) at 298 K and 1 atm, shown as a function of Monte Carlo simulation step. Solid = methanol; dashed = ethanol.

Figure 7.10: Radial distribution function of solvent center-of-mass with Zn atoms in USF2 cages. Red = medium cage; Green = large cage. Solid = methanol; dashed = ethanol.
Table 7.4: Summary of TDDFT/TDA singlet excited state energies obtained at highest oscillator strength for different systems (of USF2 MOF). Note: Orca result for oscillator strength is expressed in atomic units. QChem/NWChem unit unknown.

<table>
<thead>
<tr>
<th>#</th>
<th>System</th>
<th>Functional + Basis sets</th>
<th>Software</th>
<th>State</th>
<th>Energy (eV)</th>
<th>Osc. Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>RuBpy, crystal</td>
<td>b3lyp/6-31G*, LANL2DZ ECP Ru</td>
<td>QChem</td>
<td>8</td>
<td>3.0095</td>
<td>0.1097</td>
</tr>
<tr>
<td>2</td>
<td>RuBpy, crystal</td>
<td>b3lyp/6-31G*, LANL2DZ ECP Ru</td>
<td>NWChem</td>
<td>5</td>
<td>3.0492</td>
<td>0.0892</td>
</tr>
<tr>
<td>3</td>
<td>RuBpy, crystal</td>
<td>b3lyp/cc-pVTZ (+PP Ru)</td>
<td>Orca</td>
<td>8</td>
<td>3.3700</td>
<td>0.0862</td>
</tr>
<tr>
<td>4</td>
<td>RuBpy, crystal</td>
<td>b3lyp/6-31G*</td>
<td>Orca</td>
<td>5</td>
<td>3.4001</td>
<td>0.1129</td>
</tr>
<tr>
<td>5</td>
<td>RuBpy, crystal</td>
<td>b3lyp/cc-pVTZ (+PP Ru)</td>
<td>Orca</td>
<td>8</td>
<td>3.4020</td>
<td>0.0705</td>
</tr>
<tr>
<td>6</td>
<td>RuBpy, crystal</td>
<td>b3lyp/cc-pVTZ (+PP Ru)</td>
<td>Orca</td>
<td>5</td>
<td>3.2892</td>
<td>0.0705</td>
</tr>
<tr>
<td>7</td>
<td>RuBpy, crystal</td>
<td>b3lyp/cc-pVTZ (+PP Ru)</td>
<td>Orca</td>
<td>5</td>
<td>3.2892</td>
<td>0.1664</td>
</tr>
<tr>
<td>8</td>
<td>RuBpy, crystal</td>
<td>b3lyp/cc-pVTZ (+PP Ru)</td>
<td>Orca</td>
<td>8</td>
<td>3.0505</td>
<td>0.1305</td>
</tr>
<tr>
<td>9</td>
<td>RuBpy, crystal</td>
<td>b3lyp/6-31G*, LANL2DZ ECP Ru</td>
<td>QChem</td>
<td>3</td>
<td>0.1375</td>
<td>0.0007</td>
</tr>
<tr>
<td>10</td>
<td>RuBpy, crystal</td>
<td>b3lyp/6-31G*, LANL2DZ ECP Ru</td>
<td>QChem</td>
<td>3</td>
<td>0.1412</td>
<td>3.6.62×10⁻⁴</td>
</tr>
<tr>
<td>11</td>
<td>RuBpy, crystal</td>
<td>b3lyp/6-31G*, LANL2DZ ECP Ru</td>
<td>Orca</td>
<td>5</td>
<td>0.1500</td>
<td>0.0030</td>
</tr>
<tr>
<td>12</td>
<td>RuBpy, crystal</td>
<td>pbe0/6-31G*</td>
<td>Orca</td>
<td>8</td>
<td>0.5850</td>
<td>4.1060×10⁻⁶</td>
</tr>
<tr>
<td>13</td>
<td>RuBpy, crystal</td>
<td>b3lyp/3-21G</td>
<td>QChem</td>
<td>5</td>
<td>0.0325</td>
<td>1.623×10⁻⁶</td>
</tr>
<tr>
<td>14</td>
<td>RuBpy, crystal</td>
<td>b3lyp/3-21G</td>
<td>QChem</td>
<td>7</td>
<td>0.2034</td>
<td>8.556×10⁻⁶</td>
</tr>
<tr>
<td>15</td>
<td>RuBpy, crystal</td>
<td>b3lyp/3-21G</td>
<td>Orca</td>
<td>5</td>
<td>0.2034</td>
<td>8.556×10⁻⁶</td>
</tr>
<tr>
<td>16</td>
<td>RuBpy, crystal</td>
<td>b3lyp/3-21G</td>
<td>Orca</td>
<td>5</td>
<td>0.2034</td>
<td>8.556×10⁻⁶</td>
</tr>
</tbody>
</table>

Table 7.5: Summary of TDDFT/TDA singlet excited state energies obtained at highest oscillator strength for different systems (of RWLC-5 MOF). Note: Orca result for oscillator strength is expressed in atomic units. QChem/NWChem unit unknown....
Chapter 8

Single-atom polarizability determination for several metal ions in MOFs

8.1 Introduction

In cases where electronic polarization is treated explicitly in molecular simulation, there exists a need to describe the polarizability of the simulation sites of interest, in order to calculate the energy and force acting on the site due to (re-)arrangement of dipoles in an evolving electric field. After computing dipoles on each site, which comprises the bulk of computational work required, the polarization energy in our code is given by Eqn. A.26.

\[
U_{\text{polar}} = -\frac{1}{2} \sum_i N \left[ (\vec{\mu}_i \cdot \vec{E}) + (\vec{\mu}_i \cdot \vec{E}_{\text{induced}}) \right] \tag{8.1}
\]

Where the Thole-Applequist method\textsuperscript{46,47} is used to compute dipoles (\(\mu_i\)) on each site and \(\vec{E}\) represents the electric field at the site. Before iterative convergence of the shifting dipoles, the initial dipole on atom \(i\) is computed by the simple effect of the electrostatic field on the polarizable sites:

\[
\mu_i = \alpha_i \cdot \vec{E}_{\text{stat}} \tag{8.2}
\]

Where \(\alpha\) is the site polarizability. Since we use models with atomistic resolution (no coarse-graining or dissipative particle dynamics), for simplicity, we treat each site as having an isotropic (scalar) polarizability, although in general the polarizability is a 3×3 tensor.
8.2 Methods

In order to provide reliable parameters for polarizability, we use quantum chemistry software to obtain the isotropic polarizability of a fragment or large molecule containing the atom of interest in an electronic environment similar to the one that will be simulated. Generally, using a software such as Orca\textsuperscript{141} or NWChem,\textsuperscript{48} we obtain the isotropic polarizability of a fragment using Density Functional Theory with the B3LYP or PBE0 functional and cc-pvtz or cc-pvdz basis sets for all atoms (depending on the system).

Using the same level of theory, we then compute partial charges on each atom by fitting the electrostatic surface potential with a scheme such as CHELPG\textsuperscript{143} or RESP. Then we compute the isotropic polarizability in MPMC\textsuperscript{58} of the fragment using the charges obtained previously and polarizabilities known to produce accurate electrodynamics on all atoms except the atom of interest, which has a variable polarizability. The polarizability parameter that produces an isotropic polarizability in best agreement with the quantum software is selected for that atom. Polarizabilities ($\alpha$) for elements of interest in this dissertation are presented in Table 8.1 with reference sources as needed. An example of the fitting procedure data for Eu is shown in Fig. 8.1. An example of input files for MPMC for such a fitting is provided in the below code snippets.

Example MPMC input to compute isotropic polarizability of a molecule:

\begin{verbatim}
ensemble     total_energy
job_name     Eu_cluster
temperature  0.000000000001
numsteps     5
corrtime     1
basis1       100.0 0.0 0.0
basis2       0.0 100.0 0.0
basis3       0.0 0.0 100.0
polarization on
polar_damp_type exponential
polar_damp   2.1304
polar_iterative off
polar_gs_ranked on
polar_palmo on
polar_max_iter 20
polarizability_tensor on
pqr_input input.pqr
\end{verbatim}
Example Orca input for optimizing a EuCl₃ fragment, computing charges via CHELPG and isotropic polarizability:

```plaintext
! BP86 ZORA old-ZORA-TZVP SARC/J opt chelpg allpop printbasis
%basis
NewGTO Eu "SARC-ZORA-TZVP" end
end
%pal
nprocs 8
end
%MaxCore 10000
%elprop dipole true
  polar 1
end
%scf
MaxIter 10000
end
*xyz 0 1
Eu 0 0 0
Cl -2.1252263408870125 -1.2270000000000003 0
Cl 2.125226340887012 -1.2270000000000012 0
Cl 0 2.454 0
*
```

The initial coordinates for the EuCl₃ molecule above were determined by applying the bond-length rules of O’Keeffe and Brese (bond = 2.454 Å) in the trigonal planar geometry.

Example input.pqr file (EuCl₃ molecule with computed charges):

```plaintext
ATOM 1 Eu MOF M 1 -0.014905 -0.019035 0.207404 151.964 1.151788 XXX 4.025757 3.111909
ATOM 2 Cl MOF M 1 -2.174442 -1.235372 -0.067884 35.453 -0.382947 2.40028 114.23084 3.516377
ATOM 3 Cl MOF M 1 2.164380 -1.200764 -0.069110 35.453 -0.382448 2.40028 114.23084 3.516377
ATOM 4 Cl MOF M 1 0.024968 2.455171 -0.070410 35.453 -0.386394 2.40028 114.23084 3.516377
```

Example bash script to run a polarizability search with MPMC:

```bash
#!/bin/bash
base=$(pwd);
mpmc='~/work/d/dfranz/mpmc/build/mpmc'
echo "#Eu_alpha #isotropic_polarizability_A^3" > isotropics.txt # overwrites isotropics.txt
rm -r polar_*
# fine grain search, increments of 0.001 A^3
str=""
for ((i=1; i<1000; i++)); do
  str=$str" "$i / 1000.0 + 4.0 | bc -l); # 4, 4.001, .... 5
done
```

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# coarse grain search, increments of 0.5 \(\text{A}^3\)

```bash
for ((i=0; i<24; i++)); do
  str=$str" "$(echo "($i / 2.0)" | bc -l); # 0.0, 0.5, 1.0, 1.5, ... 12.0
done
```

```bash
for polariz in $str; do
  mkdir polar_$polariz;
  cd polar_$polariz;
  echo "running Eu_alpha = "$polariz;
  cp $base/polar.inp .
  # make PQR
  awk -v polariz="$polariz" '{
    gsub(/XXX/, polariz);
    print;
  }' $base/input.pqr > input.pqr
  # run it.
  mpirun -np 1 $mpmc *inp > runlog;
  # get isotropic
  iso=$(cat runlog | grep "isotropic =" | tail -1 | awk '{print $3'});
  # write isotropic value to master list (iso as function of Eu polar)
  echo $polariz "$iso >> $base/isotropics.txt
  cd .. # out of polar
done
```
Figure 8.1: Fitting procedure for Eu polarizability determination using a fragment from EuCl$_3$. Atom colors in fragment: C = cyan; O = red; N = blue; H = white; Eu = pink.
Table 8.1: List of computed single-atom polarizabilities used in these studies, with reference structure (or literature reference) used. Note, these parameters are suitable for polarization calculations using exponential damping as in the Thole-Applequist model\textsuperscript{46,47} (not linear damping). \textsuperscript{†}Value obtained from Adam Hogan, who used similar methods.

<table>
<thead>
<tr>
<th>Element</th>
<th>Reference molecule/fragment</th>
<th>Single-atom polarizability (Å\textsuperscript{3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>Ref. 57</td>
<td>0.41380</td>
</tr>
<tr>
<td>He</td>
<td>Hogan\textsuperscript{†}</td>
<td>0.204</td>
</tr>
<tr>
<td>B</td>
<td>Hogan\textsuperscript{†}</td>
<td>0.6634</td>
</tr>
<tr>
<td>C</td>
<td>Ref. 57</td>
<td>1.2886</td>
</tr>
<tr>
<td>N</td>
<td>Ref. 57</td>
<td>0.97157</td>
</tr>
<tr>
<td>O</td>
<td>Ref. 57</td>
<td>0.852</td>
</tr>
<tr>
<td>Ne</td>
<td>Ref. 57</td>
<td>0.392</td>
</tr>
<tr>
<td>Mg</td>
<td>Mg\textsuperscript{2+}, gas phase</td>
<td>0.0072</td>
</tr>
<tr>
<td>P</td>
<td>Hogan\textsuperscript{†}</td>
<td>3.35</td>
</tr>
<tr>
<td>Cl</td>
<td>Hogan\textsuperscript{†}</td>
<td>2.40028</td>
</tr>
<tr>
<td>Ar</td>
<td>Hogan\textsuperscript{†}</td>
<td>1.63</td>
</tr>
<tr>
<td>Ca</td>
<td>bnn-1-Ca-beta MOF</td>
<td>3.361</td>
</tr>
<tr>
<td>Mn</td>
<td>MnCl\textsubscript{2}-4H\textsubscript{2}O</td>
<td>2.4875</td>
</tr>
<tr>
<td>Fe</td>
<td>[Fe\textsubscript{3}O(O\textsubscript{2}CH)\textsubscript{6}]\textsuperscript{+},doublet</td>
<td>0.835</td>
</tr>
<tr>
<td>Cu</td>
<td>Ref. 43</td>
<td>2.1963</td>
</tr>
<tr>
<td>Zn</td>
<td>Hogan\textsuperscript{†}</td>
<td>1.9887</td>
</tr>
<tr>
<td>Br</td>
<td>Hogan\textsuperscript{†}</td>
<td>3.493</td>
</tr>
<tr>
<td>Kr</td>
<td>Hogan\textsuperscript{†}</td>
<td>2.465</td>
</tr>
<tr>
<td>Ru</td>
<td>Ru-tris-bipyridine</td>
<td>5.191</td>
</tr>
<tr>
<td>Pd</td>
<td>Hogan\textsuperscript{†}</td>
<td>5.25926</td>
</tr>
<tr>
<td>Xe</td>
<td>Hogan\textsuperscript{†}</td>
<td>4.01</td>
</tr>
<tr>
<td>Eu</td>
<td>EuCl\textsubscript{3}</td>
<td>4.461</td>
</tr>
<tr>
<td>Ho</td>
<td>Ho MOF fragment</td>
<td>4.43760</td>
</tr>
<tr>
<td>Pt</td>
<td>Hogan\textsuperscript{†}</td>
<td>8.56281</td>
</tr>
</tbody>
</table>
Chapter 9

Molecular dynamics studies of the drug molecule Bivalirudin in MMPF-6

9.1 Introduction

Bivalirudin is a direct thrombin inhibitor (DTI) which acts as a blood thinning drug. It is a short, synthetic peptide which has been heavily studied for use with coronary patients. Porphyrin MOFs are of interest as drug carriers, to deliver therapeutic pharmaceuticals for extended release or to specific organs in the body. MMPF-6 is a water-stable Zirconium based porphyrin MOF that is under investigation as a drug carrier due to its low toxicity. It can fit single molecules of Bivalirudin in a single unit cell, in its main pore. The aim of this study was to elucidate key binding interactions of the drug with MMPF-6 to aid experimentalists in design of a MOF analog that could improve drug capture, release, etc.

9.2 Methods

Classical simulations were performed on a 2x2x2 supercell of MMPF-6 with a single Bivalirudin molecule in the main pore, as in figure 9.1 using MCMD.\textsuperscript{160} The MOF atoms were treated as rigid. For bonded interactions (in the drug molecule only), the built-in UFF and UFF4MOF forcefields were used. For non-bonded interactions, the parameters were as follows: (1) UFF Lennard-Jones epsilon and sigma for repulsion-dispersion interactions; (2) partial charges obtained using a RESP fit from the electrostatic surface potential calculated by CP2K\textsuperscript{207} periodic DFT with MOLOPT basis sets on all atoms, DFTD3 pair potential, and the revPBE functional for a 2x2x2 cell of MMPF-6, and
HF/6-31G* calculation of a single Bivalirudin molecule in the gas phase followed by a CHELPG fit using Orca\textsuperscript{141} software.

For the MD simulations, short and long range electrostatic interactions were computed using Ewald summation with $k_{\text{max}} = 2$, interaction cutoff $r_c = 17.143\text{Å}$. The single bivalirudin molecule was placed in the center of a 2x2x2 supercell of MMPF-6 and the system was annealed from a temperature of 298 K to 10 K over 625 picoseconds. Interactions of specific functional groups of the drug with the MOF were computed in the optimized structure.

![Figure 9.1: A single Bivalirudin molecule in a energy-optimized position within the MMPF-6 framework.](image)

### 9.3 Results

The binding energy of the drug to the MOF was found to be -350.66 kJ/mol for a simulation using only the Lennard-Jones potential; -446.07 kJ/mol with inclusion of electrostatics; and -372.63 kJ/mol including electrostatics but excluding drug-drug interactions. (This amounts to the drug-drug interactions comprising -73.44 kJ/mol).

A summary of the functional-group interaction energies is presented in Table 9.1. It can be seen that the strongest observed interaction is that of NH/NH$_2$ in the drug and the ZrOH/ZrOH$_2$ clusters of the MOF. Additionally, the methyl group of Bivalirudin was observed to have a repulsive interaction with the porphyrin center of the MOF.

Figures showing some of the optimized-structure interactions are below, matched with the id # listed in Table 9.1.
Figure 9.2: Interaction (1), two views.
Table 9.1: Summary of interaction energies for Bivalirudin and MMPF-6 in the classically optimized structure.

<table>
<thead>
<tr>
<th>#</th>
<th>Drug functional group(s)</th>
<th>MOF group(s)</th>
<th>Interaction energy (kJ/mol)</th>
<th>Energy per atom (kJ/mol)</th>
<th>% total nonbonded energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NH2 and NH</td>
<td>ZrOH and ZrOH2</td>
<td>-5.686</td>
<td>-0.812</td>
<td>1.53</td>
</tr>
<tr>
<td>2</td>
<td>NH2</td>
<td>Porphyrin ring</td>
<td>-4.756</td>
<td>-0.528</td>
<td>1.28</td>
</tr>
<tr>
<td>3</td>
<td>COOH</td>
<td>Porphyrin carbon</td>
<td>-4.756</td>
<td>-0.528</td>
<td>1.28</td>
</tr>
<tr>
<td>4</td>
<td>Phenyl OH</td>
<td>Open cavity between Zr/porphyrin groups</td>
<td>-3.471</td>
<td>-0.224</td>
<td>0.93</td>
</tr>
<tr>
<td>5</td>
<td>COOH</td>
<td>Porphyrin center</td>
<td>+9.642</td>
<td>+0.964</td>
<td>-2.09</td>
</tr>
<tr>
<td>6</td>
<td>Phenyl</td>
<td>ZrOH and ZrOH2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>COOH</td>
<td>ZrOH and ZrOH2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>H2NCOOH</td>
<td>NH (self drug interaction)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>COOH</td>
<td>COOH (self drug interaction)</td>
<td>-22.743</td>
<td>-2.843</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Figure 9.3: Interaction (2).
Figure 9.4: Interaction (4), three views.
Figure 9.5: Interaction (5).

Figure 9.6: Interaction (7).

Figure 9.7: Interaction (9).
Chapter 10

Studies of gas sorption in Mg and Mn Formate analog MOFs

10.1 Note to Reader

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10.2 Abstract

Simulations of C$_2$H$_2$ sorption were performed in $\alpha$–[Mg$_3$(O$_2$CH)$_6$] and $\alpha$–[Mn$_3$(O$_2$CH)$_6$], two isostructural metal–organic frameworks (MOFs) that consist of a network of M$^{2+}$ ions coordinated to formate linkers. Previous experimental studies revealed that both MOFs display high low-pressure uptake and isosteric heat of adsorption ($Q_{st}$) for C$_2$H$_2$ [Samsonenko, D. G.; *et al. Chem. Asian J.* 2007, 2, 484–488]. Simulations using two recently developed potential energy functions for the sorbate in both MOFs yielded sorption isotherms and $Q_{st}$ values that are in reasonable agreement with the corresponding experimental measurements. Electronic structure calculations revealed that the metal ions are more positively charged in $\alpha$–[Mg$_3$(O$_2$CH)$_6$] than in $\alpha$–[Mn$_3$(O$_2$CH)$_6$], which in turn led to greater partial negative charges on the linker O atoms in the Mg variant. This resulted in the former displaying a higher calculated C$_2$H$_2$ uptake than the latter for all state points considered, which is consistent with what was observed experimentally. While repulsion/dispersion interactions dominated the C$_2$H$_2$ sorption mechanism in $\alpha$–[Mn$_3$(O$_2$CH)$_6$], stationary electrostatic interactions were the main contributor to the total energy for C$_2$H$_2$ sorption in $\alpha$–[Mg$_3$(O$_2$CH)$_6$]; this is ostensibly a consequence of
the different charge environments within the two variants. The simulated C$_2$H$_2$ molecule positions in the pores of both MOFs were found to be in decent agreement with those obtained through X-ray crystallography. Overall, this study demonstrates the accuracy and transferability of two recently established C$_2$H$_2$ potentials and how differences in the C$_2$H$_2$ sorption profiles between two isostructural MOFs can be rationalized by electronic structure calculations and Monte Carlo simulations.

10.3 Introduction

Metal–organic frameworks (MOFs) are a widely studied class of solid crystalline materials with diverse chemical representation and utility. The synthesis of MOFs typically involves the combination of a metal salt and one or more organic ligands (or “linkers”) in solution. The resulting structure consists of a three–dimensional framework that is often porous; such pores can be used to sorb a variety of guest species. Due to the modular nature of MOFs, myriad different structures can be synthesized or envisioned by changing the metal ion or ligand set. Indeed, there are currently over 70,000 different MOF structures reported in the Cambridge Structural Database (CSD). MOFs have been deeply studied since the onset of the field in the early 1990s. They have been shown to be useful for many applications, such as gas storage and separations and catalysis.

The technological industries rely on a steady supply of chemical feedstock that mostly consists of small gas molecules to make manifold products. C$_2$H$_2$ is an example of such a molecule that is used in the synthesis of pharmaceuticals, plastics, and fuels. In general, the production of these raw materials involves a separation or purification process as an essential step in provision. For gases such as C$_2$H$_2$, there are often impurities which are difficult to separate without the use of expensive solvents or high-energy cryogenic distillation. For example, CO$_2$ is a major impurity in the industrial synthesis of C$_2$H$_2$, and thus, the separation of C$_2$H$_2$ from these gas mixtures is desired.

Previous experimental studies have shown that MOFs could be promising candidates for C$_2$H$_2$ sorption and separation. For example, several MOFs that are synthesized
with inorganic “pillars” (e.g., SiF$_6^{2-}$) have been demonstrated to display exceptional uptake, isosteric heat of adsorption ($Q_{st}$), and selectivity for C$_2$H$_2$; such materials belong to a subclass of MOFs called hybrid ultramicroporous materials (HUMs). Most HUMs contain pore widths that are comparable to that of the kinetic diameter of C$_2$H$_2$ (3.30 Å). The combination of small pore sizes and strong electrostatics from inorganic anions permits these materials to exhibit benchmark sorption and separation performance for C$_2$H$_2$.

$\alpha$–[Mg$_3$(O$_2$CH)$_6$] and $\alpha$–[Mn$_3$(O$_2$CH)$_6$] are two of the earliest MOFs that have been investigated for their C$_2$H$_2$ sorption properties. These MOFs are synthesized by mixing formic acid with M(NO$_3$)$_2$ (M = Mg, Mn) in organic solvent. $\alpha$–[Mn$_3$(O$_2$CH)$_6$] was first synthesized in 2004 by Dybtsev et al. and was shown to exhibit high uptake and selectivity for H$_2$ and CO$_2$. Rood et al. synthesized the isostructural Mg variant in 2006 and showed that the material can sorb a variety of small guest molecules. Both MOFs are surprisingly thermally robust and retain their crystallinity after the removal of guest solvent molecules. We note that other metal analogues (e.g., Co, Ni) of these MOFs have also been synthesized.

The structures of $\alpha$–[Mg$_3$(O$_2$CH)$_6$] and $\alpha$–[Mn$_3$(O$_2$CH)$_6$] consist of an extended network wherein each metal ion is coordinated to the surrounding O atoms of the formate linkers in an octahedral fashion. Both MOFs contain very small accessible pores that can be viewed along the crystallographic $b$-axis of the respective structures (Figure 10.1). The windows of the channels in the two MOFs are approximately 4.5 × 5.5 Å based on the van der Waals radii of the atoms. The presence of small pore sizes in these MOFs, combined with their remarkable stability, make these materials very good candidates for applications in gas sorption and separation. For instance, Dybtsev et al. demonstrated that $\alpha$–[Mn$_3$(O$_2$CH)$_6$] can act as a molecular sieve since the MOF can sorb large quantities of H$_2$ and CO$_2$, but not Ar, N$_2$, or CH$_4$. The reason for this is related to the kinetic diameter of these gases. Specifically, H$_2$ and CO$_2$ have smaller kinetic diameters (2.80 and 3.30 Å, respectively) compared to Ar, N$_2$, and CH$_4$ (3.40, 3.64, and 3.80 Å,

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respectively), thus allowing \( \alpha-[\text{Mn}_3(\text{O}_2\text{CH})_6] \) to be selective toward \( \text{H}_2 \) and \( \text{CO}_2 \) based on size exclusion.

Some notable experimental and theoretical studies have provided insights into the gas sorption mechanism in \( \alpha-[\text{Mg}_3(\text{O}_2\text{CH})_6] \). For example, in 2016, our group carried out a joint experimental sorption, inelastic neutron scattering, and computational study of \( \text{H}_2 \) sorption in this MOF. The experimental measurements revealed that the uptake for \( \text{H}_2 \) at 77 K and 1 atm is 0.96 wt\%, which is impressive for a material that exhibits a very low BET surface area (150 m\(^2\) g\(^{-1}\)). In addition, our modeling studies revealed three principal \( \text{H}_2 \) binding sites in \( \alpha-[\text{Mg}_3(\text{O}_2\text{CH})_6] \). We calculated an unusually high rotational barrier for \( \text{H}_2 \) sorbed at the most favorable binding site in the MOF; this barrier height (81.59 meV) is currently the highest of any known neutral MOF. Further insights into the dynamics of \( \text{H}_2 \) sorbed in \( \alpha-[\text{Mg}_3(\text{O}_2\text{CH})_6] \) was obtained through the \(^2\text{H}\) solid-state nuclear magnetic resonance (SSNMR) spectroscopic studies performed by Lucier et al. Their results confirmed that there are three main sorption sites for \( \text{H}_2 \) in the MOF. The same group also carried out \(^{13}\text{C}\) SSNMR and molecular dynamics (MD) simulation studies of \( \text{CO}_2 \) sorbed in \( \alpha-[\text{Mg}_3(\text{O}_2\text{CH})_6] \). The authors observed that there are two \( \text{CO}_2 \) sorption sites located in very similar local environments in the MOF and the motion of these sorbate molecules is restricted at higher temperatures.

In 2007, Samsonenko et al. demonstrated that \( \alpha-[\text{Mg}_3(\text{O}_2\text{CH})_6] \) and \( \alpha-[\text{Mn}_3(\text{O}_2\text{CH})_6] \) display high uptake and \( Q_{st} \) for \( \text{C}_2\text{H}_2 \) through experimental measurements. Notably, the authors showed that, at 298 K and 0.1 atm, both MOFs exhibit gravimetric \( \text{C}_2\text{H}_2 \) uptakes that are over 4 times greater than that for \( \text{CO}_2 \). These results suggest that the two MOFs could have potential at separating \( \text{C}_2\text{H}_2 \) from \( \text{CO}_2 \), which is known to be a difficult task due to the similar physical properties displayed by these gases. For example, both gases are nonpolar, possess the same kinetic diameter of 3.30 Å, and have similar molecular dimensions (\( \text{C}_2\text{H}_2 = 3.3 \times 3.3 \times 5.7 \) Å, \( \text{CO}_2 = 3.2 \times 3.3 \times 5.4 \) Å) and normal boiling points (\( \text{C}_2\text{H}_2 = 189 \) K, \( \text{CO}_2 = 195 \) K). The authors in reference 243 also pinpointed the location of the \( \text{C}_2\text{H}_2 \) sorption sites in both MOFs by collecting a crystal structure of the individual materials with \( \text{C}_2\text{H}_2 \) sorbed in them through single
crystal X-ray diffraction. This work was significant because the authors published the first crystal structures of C$_2$H$_2$ sorbed in porous materials.

Herein, we parametrize and perform grand canonical Monte Carlo (GCMC) simulations of C$_2$H$_2$ sorption in α-[Mg$_3$(O$_2$CH)$_6$] and α-[Mn$_3$(O$_2$CH)$_6$] in order to elucidate important details of the C$_2$H$_2$ sorption mechanism in both MOFs. Even though these MOFs are isostructural, experimental studies revealed that the two MOFs exhibit differences in their C$_2$H$_2$ uptakes and initial C$_2$H$_2$ $Q_{st}$ values$^{243}$ Thus, a major goal of this work is to gain insights into the reason for the difference in the C$_2$H$_2$ sorption properties between two isostructural MOFs that differ by only the metal ion. We will show through electronic structure calculations that both MOFs contain distinct partial charges for the metal ions and O atoms, which in turn leads to different affinities for C$_2$H$_2$ according to our classical simulations.

Furthermore, we utilize two recently developed C$_2$H$_2$ potentials for the simulations in this work.$^{26}$ α-[Mg$_3$(O$_2$CH)$_6$] and α-[Mn$_3$(O$_2$CH)$_6$] appear to be good candidate systems to test the accuracy of these models since they display high experimental C$_2$H$_2$ uptake and $Q_{st}$ and are some of the few sieving materials that exist in the literature.$^{243}$ For both MOFs, we directly compare our theoretical C$_2$H$_2$ sorption isotherms, $Q_{st}$ values, and sorption sites to those obtained experimentally. It will be shown that good agreement with the experimental measurements is obtained for both MOFs, thus generating confidence in our molecular level predictions. We also examine the contributions of each energy component toward C$_2$H$_2$ sorption in both MOFs in order to obtain a better understanding of the C$_2$H$_2$ sorption mechanism in the respective materials.

10.4 Methods

The crystal structures used for parametrizing and simulating in α-[Mg$_3$(O$_2$CH)$_6$] and α-[Mn$_3$(O$_2$CH)$_6$] were taken from references 253 and 252, respectively. Simulations of C$_2$H$_2$ sorption in both MOFs were performed using GCMC methods$^{150}$ within the 2 × 2 × 2 supercell of the respective MOFs. More details of executing the GCMC simulations are provided in the Supporting Information.
Two C$_2$H$_2$ potentials were used for the simulations in this work: an electrostatic (non-polarizable) model known as C$_2$H$_2$-PHAST (PHAST = Potentials with High Accuracy, Speed, and Transferability) and a polarizable model referred to as C$_2$H$_2$-PHAST* (the * denotes the inclusion of explicit polarization). These potentials have been developed previously by our group using a standard sorbate fitting procedure.\textsuperscript{12,40,260,261} We note that simulations using the polarizable C$_2$H$_2$-PHAST* model have produced outstanding results for C$_2$H$_2$ sorption in HUMs recently.\textsuperscript{242,249} The nonpolarizable C$_2$H$_2$-PHAST model was firstly reported earlier this year when it was utilized within a MOF with rht topology.\textsuperscript{26} We note that common force fields such as TraPPE\textsuperscript{?} do not include a model for C$_2$H$_2$. Moreover, with the exception of C$_2$H$_2$-PHAST*, there is no transferable polarizable potential available for C$_2$H$_2$ to the best of our knowledge. This was one of the primary reasons our group sought to develop accurate potentials for C$_2$H$_2$, considering also the industrial importance of the gas.

For simulations using the C$_2$H$_2$-PHAST* model, the total potential energy ($U$) of the MOF–C$_2$H$_2$ system was calculated through the sum of the repulsion/dispersion, stationary electrostatic, and many-body polarization energies. These were calculated using the Lennard-Jones 12–6 potential,\textsuperscript{262} partial charges with Ewald summation,\textsuperscript{59,263} and a Thole-Applequist type model,\textsuperscript{46,47,152,153} respectively. When using the C$_2$H$_2$-PHAST model, only the first two energetic terms were considered. Note, while our group parametrized $\alpha$-[Mg$_3$(O$_2$CH)$_6$] for molecular simulations previously,\textsuperscript{256} the details for obtaining the parameters for both MOFs are nonetheless described below.

The Lennard-Jones parameters ($\epsilon$ and $\sigma$) for all C and H atoms were taken from the Optimized Potentials For Liquid Simulations – All Atom (OPLS-AA) force field, while those for Mg, Mn, and O were taken from the Universal Force Field (UFF).\textsuperscript{7} Utilizing C and H repulsion/dispersion parameters from the OPLS-AA force field has been shown to produce good results for simulations in MOFs in certain cases.\textsuperscript{219,264–266} Scalar point polarizabilities were assigned to the nuclear center of all atoms of $\alpha$-[Mg$_3$(O$_2$CH)$_6$] and $\alpha$-[Mn$_3$(O$_2$CH)$_6$] to model explicit polarization. Such parameters for all C, H, and O atoms were taken from the carefully parametrized set of van Duijnen and Swart.\textsuperscript{57}
polarizability value for Mg\(^{2+}\) was determined in previous work\(^{267}\) and used herein. A description of how the polarizability for Mn\(^{2+}\) was obtained is provided in the Supporting Information. The repulsion/dispersion and polarizability parameters used for all atoms for the simulations in this work are summarized in Table 10.1.

The partial charges for the chemically distinct atoms in both MOFs were determined through periodic fitting of the entire crystal structure using the Vienna \textit{ab initio} Simulation Package (VASP)\(^{268-271}\) with the Projector Augmented Wave (PAW) method\(^{272}\) and Ceperley–Alder (CA) functional.\(^{273}\) A restraining potential was implemented to treat the presence of buried atoms in the structure for both MOFs. The calculations were performed using a charge fitting code that was developed previously.\(^{274,275}\) The calculated partial charges for the chemically distinct M\(^{2+}\) ions in both MOFs are displayed in Table 10.2.

CMC simulations of C\(_2\)H\(_2\) sorption were also performed in \(\alpha-\text{[Mg}_3\text{(O}_2\text{CH)}_6\text{]}\) and \(\alpha-\text{[Mn}_3\text{(O}_2\text{CH)}_6\text{]}\) in order to evaluate the \(Q_{st}\) for C\(_2\)H\(_2\) in the individual MOFs. This method keeps the particle number \((N)\), volume \((V)\), and temperature \((T)\) of the MOF–C\(_2\)H\(_2\) system constant while allowing other thermodynamic quantities to vary. Note, while GCMC methods can be used to calculate the \(Q_{st}\) through fluctuations in \(N\) and \(U\),\(^{66}\) the high affinity that these MOFs have toward C\(_2\)H\(_2\) makes it difficult to obtain sensible \(Q_{st}\) values at low loadings \((< 2 \text{ mmol g}^{-1})\).

The CMC simulations were carried out using the same supercell and potential energy functions as described above with \(N = 1\) and multiples of 4 up until 64. For all loadings considered, the simulations ran for a total of \(5.0 \times 10^6\) Monte Carlo steps to ensure reasonable ensemble averages for \(U\). The theoretical C\(_2\)H\(_2\) \(Q_{st}\) values were estimated by taking the ensemble averaged potential energy and dividing by \(N\). This method to calculate the \(Q_{st}\) appears to be appropriate for the system under the conditions considered.\(^{37,265}\) All Monte Carlo simulations of C\(_2\)H\(_2\) sorption in \(\alpha-\text{[Mg}_3\text{(O}_2\text{CH)}_6\text{]}\) and \(\alpha-\text{[Mn}_3\text{(O}_2\text{CH)}_6\text{]}\) were executed the Massively Parallel Monte Carlo (MPMC) code,\(^{58}\) an open-source code that was developed and maintained by our research group and is currently available for download on GitHub. Note, the simulated results shown herein have also been cross-validated.
using the Monte Carlo - Molecular Dynamics (MCMD) code\textsuperscript{160} with a different random number generator and other Monte Carlo options, e.g., translation trial move distance and dipole convergence iteration minimum.

In order to compute \( \text{C}_2\text{H}_2 \) binding energies from periodic Density Functional Theory, CP2K\textsuperscript{207} was used. All atoms were treated with the native CP2K MOLOPT basis sets and the revPBE XC functional\textsuperscript{276} was used. The MOF atoms were constrained to be rigid as the \( \text{C}_2\text{H}_2 \) followed a truncated gradient path to energy minimization. The binding energy was then computed as the difference between the fully optimized system, and the MOF and \( \text{C}_2\text{H}_2 \) molecule alone.

10.5 Results and Discussion

10.5.1 Isotherms and Isosteric Heats of Adsorption

The simulated \( \text{C}_2\text{H}_2 \) sorption isotherms for the \( \text{C}_2\text{H}_2\)-PHAST and \( \text{C}_2\text{H}_2\)-PHAST\textsuperscript{*} models in \( \alpha-\left[\text{Mg}_3(\text{O}_2\text{CH})_6\right] \) at 275 and 298 K are compared with the corresponding experimental data\textsuperscript{243} in Figure 10.2. The experimental isotherms at both temperatures show a significant sharp increase in \( \text{C}_2\text{H}_2 \) uptake at low loading, followed by a plateau starting at around 0.30 atm. The change in slope in the experimental isotherms under these conditions indicate that the material is near \( \text{C}_2\text{H}_2 \) saturation. At 1 atm, the measured uptakes in \( \alpha-\left[\text{Mg}_3(\text{O}_2\text{CH})_6\right] \) at 275 and 298 K are 3.10 and 2.93 mmol g\textsuperscript{-1}, respectively (Table 10.3). The experimental isotherms also reveal a slight hysteresis in which the desorption curve is mildly higher than that for adsorption. The authors in reference 243 attributed this phenomenon to the slow desorption kinetics of \( \text{C}_2\text{H}_2 \) in the small pores of the MOF, which is a consequence of the material’s high affinity toward the sorbate.

The simulated isotherms for both potentials in \( \alpha-\left[\text{Mg}_3(\text{O}_2\text{CH})_6\right] \) also display a notable sharp increase in \( \text{C}_2\text{H}_2 \) uptake at low pressures. However, such isotherms rise a lot quicker than experiment at pressures less than 0.05 atm for both temperatures. As a result, the simulated uptakes are appreciably greater than those for experiment under these conditions. According to the simulations, the \( \text{C}_2\text{H}_2 \) uptakes start to level off at around 0.1 atm at both temperatures. At higher pressures, the experimental and simulated
isotherms come in closer agreement to each other. This is because both experiment and simulation are approaching $C_2H_2$ saturation in the material under these conditions. The simulated $C_2H_2$ uptakes in $\alpha-\left[Mg_3(O_2CH)_6\right]$ at 275 K/1 atm and 298 K/1 atm are 3.32 and 3.09 mmol g$^{-1}$, respectively (Table 10.3).

The disparity in the experimental and simulated isotherms at low pressures could be due to the fact that it may take some time for the $C_2H_2$ molecules to diffuse into the small channels of the material in experiment at initial loading. This could result in measured low-pressure uptakes that are lower than those predicted through modeling. Here, the simulated uptakes were produced by GCMC methods, which involve the random insertion, deletion, and movement of sorbate molecules in a simulation box containing the host. Thus, the effects of transport and associated kinetic phenomena are not an issue in GCMC simulations. A similar effect was observed for molecular simulations of gas sorption in other porous materials with small pore sizes.\textsuperscript{265,266} The difference between simulated and experimental results could also be explained by pore blockage from solvents, or defects within the actual crystal, as a perfect infinite crystal lattice is assumed in simulations. Minor inadequacies in the potential energy functions for the MOF and/or sorbate models could also lead to the discrepancy. In general, simulations using both models were able to reproduce the overall shape of the experimental isotherms.

Both the nonpolarizable $C_2H_2$-PHAST and polarizable $C_2H_2$-PHAST* models produced comparable isotherms in $\alpha-\left[Mg_3(O_2CH)_6\right]$ at 275 and 298 K. This indicates that the effects of explicit polarization are negligible for $C_2H_2$ sorption in this MOF, as was the case for $H_2$ sorption in the material.\textsuperscript{256} This is likely because there are no exposed metal centers in the MOF. Classical polarization has been shown to be important for the accurate modeling of gas sorption in MOFs with open-metal sites.\textsuperscript{37,103,267–280} In addition, it will be revealed later (in section III.B) that $C_2H_2$ sorption in $\alpha-\left[M_3(O_2CH)_6\right]$ is governed by repulsion/Dispersion and stationary electrostatic interactions.

A comparison of the experimental\textsuperscript{243} and simulated $C_2H_2$ sorption isotherms in $\alpha-\left[Mn_3(O_2CH)_6\right]$ at 275 and 298 K is shown in Figure 10.3. As with the experimental isotherms for $\alpha-\left[Mg_3(O_2CH)_6\right]$, such isotherms for the Mn variant exhibit an abrupt in-
crease in C$_2$H$_2$ uptake at low pressures (< 0.20 atm), followed by slowly increasing and nearly constant uptakes at higher pressures. The experimental isotherms reach atmospheric uptake values of 2.58 and 2.29 mmol g$^{-1}$ at 275 and 298 K, respectively (Table 10.3). These uptake capacities for α-[Mn$_3$(O$_2$CH)$_6$] are lower than those for the Mg variant at the analogous state points. In fact, a direct comparison of the experimental C$_2$H$_2$ sorption isotherms for both MOFs at 275 and 298 K reveals that the uptakes for α-[Mg$_3$(O$_2$CH)$_6$] are higher than those for α-[Mn$_3$(O$_2$CH)$_6$] at all pressures considered.

Simulations using the C$_2$H$_2$-PHAST and C$_2$H$_2$-PHAST* models in α-[Mn$_3$(O$_2$CH)$_6$] produced isotherms that have the same general shape as experiment for both temperatures. The calculated uptakes at low pressures are somewhat higher than those for experiment, whereas they are in closer agreement with experiment as the pressure approaches 1 atm. The simulated uptake for both potentials at 298 K and 1 atm is 2.33 mmol g$^{-1}$, which is in very good agreement with the experimental value for the MOF at this state point (2.29 mmol g$^{-1}$). In general, the simulations captured better agreement with experiment for the sorption isotherms in α-[Mn$_3$(O$_2$CH)$_6$] than in α-[Mg$_3$(O$_2$CH)$_6$]. At 275 K, it can be observed that the experimental isotherm for α-[Mn$_3$(O$_2$CH)$_6$] surpasses those for the C$_2$H$_2$-PHAST and C$_2$H$_2$-PHAST* models at around 0.45 atm. This could possibly be due to slight deformations of the physical crystal under such conditions. As with the Mg analogue, both C$_2$H$_2$ potentials generated isotherms in α-[Mn$_3$(O$_2$CH)$_6$] that are very similar to each other at the two temperatures, suggesting that explicit polarization effects are negligible for C$_2$H$_2$ sorption in this MOF with small pore sizes.

The theoretical C$_2$H$_2$ $Q_{st}$ values for the C$_2$H$_2$-PHAST and C$_2$H$_2$-PHAST* models as produced through CMC simulations in α-[Mg$_3$(O$_2$CH)$_6$] and α-[Mn$_3$(O$_2$CH)$_6$] are shown with the corresponding experimental quantities$^{243}$ in Figures 10.4(a) and 10.4(b), respectively. The experimental $Q_{st}$ values at the lowest loading considered for α-[Mg$_3$(O$_2$CH)$_6$] and α-[Mn$_3$(O$_2$CH)$_6$] are 44.1 and 41.8 kJ mol$^{-1}$, respectively (Table 10.3). These values are comparable to those for Fe-MOF-74 (46 kJ mol$^{-1}$)$^{245}$ and the top-performing HUMs for C$_2$H$_2$ sorption, such as SIFSIX-2-Cu-i (41.9 kJ mol$^{-1}$)$^{246}$ TIFSIX-2-Cu-i (46.3 kJ mol$^{-1}$)$^{242}$ TIFSIX-4-Cu-i (40.8 kJ mol$^{-1}$)$^{250}$ and SIFSIX-14-Cu-i (40 kJ mol$^{-1}$)$^{247}$.
Note, the authors in reference 243 did not include \( Q_{st} \) values below 0.10 molecules/formula unit for both MOFs. This could possibly be due to errors associated with fitting the adsorption data at low pressures.

The experimental \( Q_{st} \) plot for both MOFs show that the \( Q_{st} \) for \( \text{C}_2\text{H}_2 \) decreases with increasing loading, with the Mg variant exhibiting a more rapid decrease. On the other hand, the theoretical \( Q_{st} \) values for the two \( \text{C}_2\text{H}_2 \) potentials in both MOFs are roughly constant for most of the considered loading range. The \( \text{C}_2\text{H}_2 \)-PHAST* model yielded an initial \( Q_{st} \) value of 41.9 kJ mol\(^{-1}\) in \( \alpha-[\text{Mg}_3(\text{O}_2\text{CH})_6] \). Such simulated \( Q_{st} \) values in this MOF slightly decreases with increasing loading beyond 0.2 molecules/formula unit. The \( \text{C}_2\text{H}_2 \)-PHAST model produced \( Q_{st} \) values that are only about 1 kJ mol\(^{-1}\) lower than those for its polarizable counterpoint in \( \alpha-[\text{Mg}_3(\text{O}_2\text{CH})_6] \).

The \( Q_{st} \) values generated by the two models in \( \alpha-[\text{Mn}_3(\text{O}_2\text{CH})_6] \) are noticeably lower than those produced in \( \alpha-[\text{Mg}_3(\text{O}_2\text{CH})_6] \), with initial values of around 34.7 kJ mol\(^{-1}\). This indicates that the MOF–\( \text{C}_2\text{H}_2 \) interactions in \( \alpha-[\text{Mn}_3(\text{O}_2\text{CH})_6] \) are weaker compared to those in the Mg variant. Overall, the simulations confirm the experimental finding that \( \alpha-[\text{Mg}_3(\text{O}_2\text{CH})_6] \) displays higher uptake and \( Q_{st}^0 \) for \( \text{C}_2\text{H}_2 \) than \( \alpha-[\text{Mn}_3(\text{O}_2\text{CH})_6] \). This could be due to differences in the electrostatic parameters for the metal ions in the two analogues. Particularly, the calculated partial positive charges for the Mg\(^{2+}\) ions in \( \alpha-[\text{Mg}_3(\text{O}_2\text{CH})_6] \) are greater than those for the Mn\(^{2+}\) ions in \( \alpha-[\text{Mn}_3(\text{O}_2\text{CH})_6] \) (Table 10.2).

The \( \text{C}_2\text{H}_2 \)-PHAST and \( \text{C}_2\text{H}_2 \)-PHAST* models yield nearly constant \( Q_{st} \) values until about 0.30 molecules/formula unit in \( \alpha-[\text{Mn}_3(\text{O}_2\text{CH})_6] \). Afterward, both models show that the \( Q_{st} \) decreases with increasing loading until the predicted saturation uptake.

Simulations of \( \text{C}_2\text{H}_2 \) sorption in both MOFs resulted in \( Q_{st} \) plots that are not representative of the experimental curves in terms of overall shape. The nearly constant \( Q_{st} \) values produced by simulations in both MOFs suggest homogeneity in the binding sites, with one or more sites having similar energetics. On the other hand, the monotonic decreasing behavior exhibited by the experimental \( Q_{st} \) plots suggest that there are multiple \( \text{C}_2\text{H}_2 \) sorption sites with varying energetics in both MOFs. We believe that the discrepancy in the shapes of the experimental and simulated \( Q_{st} \) plots is due to
the difference in methodology used to extract such values for the individual techniques. Specifically, the experimental C$_2$H$_2$ $Q_{st}$ values for both MOFs were estimated through the Clausius–Clapeyron method,\textsuperscript{281} while the theoretical values were obtained through CMC simulations as described in section II.

The X-ray crystal structure of both MOFs with C$_2$H$_2$ localized in the materials revealed that there are two very similar binding sites as discussed later in section III.C.\textsuperscript{243} According to our simulations, the two C$_2$H$_2$ sorption sites have similar energetics in these materials as shown in the theoretical $Q_{st}$ values. Thus, we believe that the shape of the simulated $Q_{st}$ plots produced herein more closely reflects the C$_2$H$_2$ sorption mechanism in α-[M$_3$(O$_2$CH)$_6$]. It is important to note that, according to the simulations, C$_2$H$_2$ saturation in α-[Mg$_3$(O$_2$CH)$_6$] and α-[Mn$_3$(O$_2$CH)$_6$] is achieved at 8 molecules/unit cell or 0.66 molecules/formula unit. Therefore, our simulations can only calculate the $Q_{st}$ values up until the saturation mark as shown in Figure 10.4. However, the experimental plots for both MOFs display $Q_{st}$ values beyond that loading, which suggests that such quantities are attributed to artifacts of empirical fitting.

10.5.2 Energy Contributions

As described in the Methods section, the total potential energy of the MOF–C$_2$H$_2$ system in this work consists of repulsion/dispersion, stationary electrostatic, and many-body polarization interactions. In order to evaluate the contribution of each energy component toward C$_2$H$_2$ sorption in both MOFs, a decomposition of the total energy per sorbate molecule for simulations in the individual MOFs was undertaken. Table 10.4 presents the averaged percent contributions and absolute energy magnitudes for each energy component from GCMC simulations of C$_2$H$_2$ sorption in both MOFs using the C$_2$H$_2$-PHAST and C$_2$H$_2$-PHAST* models at 298 K/1 atm. Note, similar values for the percent contributions and energy magnitudes were observed for these energetic terms at other state points in the two MOFs using both potentials.

It can be observed that stationary electrostatic interactions are the main contributor to the total energy for C$_2$H$_2$ sorption in α-[Mg$_3$(O$_2$CH)$_6$] according to simulations using
both potentials. For the C$_2$H$_2$-PHAST model in this MOF, the electrostatic energy is slightly greater than that for the repulsion/dispersion energy by about $-2700$ K (or 1.7%). When polarization is included in the simulations (via the C$_2$H$_2$-PHAST* model), the electrostatic contribution in $\alpha$–[Mg$_3$(O$_2$CH)$_6$] increases by about $-6200$ K (or 2.2%), while the contribution from repulsion/dispersion interactions decreases.

Interestingly, C$_2$H$_2$ sorption in $\alpha$–[Mn$_3$(O$_2$CH)$_6$] is dominated by repulsion/dispersion interactions rather than permanent electrostatic interactions according to simulations using both models. Thus, even though $\alpha$–[Mg$_3$(O$_2$CH)$_6$] and $\alpha$–[Mn$_3$(O$_2$CH)$_6$] are isostructural, differing by only the metal ion, the simulations revealed that the two MOFs contain variations in their energy contributions for C$_2$H$_2$ sorption. These differences can be explained by the distinct electrostatic parameters for the two analogues. Specifically, the Mg$^{2+}$ ions in $\alpha$–[Mg$_3$(O$_2$CH)$_6$] are more positively charged than the Mn$^{2+}$ ions in $\alpha$–[Mn$_3$(O$_2$CH)$_6$] according to our periodic charge fitting calculations (Table 10.2). This resulted in more negatively charged O atoms on the formate linkers in the Mg analogue (see Supporting Information, Table S1).

The Mg$^{2+}$ ions are more electropositive than the Mn$^{2+}$ ions on the basis of periodic trends.$^{267}$ In addition, all matching M$^{2+}$–O framework distances in $\alpha$–[Mn$_3$(O$_2$CH)$_6$] are longer than those in $\alpha$–[Mg$_3$(O$_2$CH)$_6$]. The longer M$^{2+}$–O distances in the Mn variant could also explain why the partial positive charges for the Mn$^{2+}$ ions are lower since such ions are farther away from the electronegative O atoms. As reflected by the simulations, the higher partial positive charge for the metal ions in the Mg variant causes electrostatic interactions to increase and play a more dominant role toward C$_2$H$_2$ sorption.

As shown in Table 10.4, the effects of many-body polarization interactions in both MOFs are negligible, with energy percentages of roughly 7% and 5% in $\alpha$–[Mg$_3$(O$_2$CH)$_6$] and $\alpha$–[Mn$_3$(O$_2$CH)$_6$], respectively. This explains why simulations using the C$_2$H$_2$-PHAST* model produced isotherms and $Q_{st}$ values that are very similar to those for the C$_2$H$_2$-PHAST model in both MOFs. Explicit induction contributes slightly more to the C$_2$H$_2$ sorption mechanism in $\alpha$–[Mg$_3$(O$_2$CH)$_6$] than in $\alpha$–[Mn$_3$(O$_2$CH)$_6$]. This might seem counterintuitive given the fact that the polarizability for Mg$^{2+}$ is much lower than
that for Mn$^{2+}$ (Table 10.1). However, the higher calculated partial positive charge for the metal ions in the Mg variant provides a more attractive electrostatic environment for the sorbate molecules, which in turn results in greater induced dipoles.

A comparison of the absolute energy magnitudes between the two MOFs for simulations using the nonpolarizable C$_2$H$_2$-PHAST model revealed that $\alpha$–[Mg$_3$(O$_2$CH)$_6$] exhibits higher magnitudes for all corresponding energy components (Table 10.4). When using the polarizable C$_2$H$_2$-PHAST* model, a similar trend can be observed for the electrostatic and polarization energies, but the magnitude of the repulsion/dispersion energy is greater in $\alpha$–[Mn$_3$(O$_2$CH)$_6$]. Because stationary electrostatic and many-body polarization interactions contribute less to the sorption mechanism in $\alpha$–[Mn$_3$(O$_2$CH)$_6$], this causes the repulsion/dispersion energy to be higher in this variant. It is possible that the stronger dipole interactions (both static and induced) in $\alpha$–[Mg$_3$(O$_2$CH)$_6$] create potential energy wells that are shifted away from the van der Waals minima.

10.5.3 C$_2$H$_2$ Sorption Sites

Single crystal X-ray diffraction measurements of the C$_2$H$_2$ loaded structures of $\alpha$–[Mg$_3$(O$_2$CH)$_6$] and $\alpha$–[Mn$_3$(O$_2$CH)$_6$] revealed the same two distinct sorption sites (denoted sites A and B) in both MOFs (Figure 10.5). These sites alternate within the constrained channels in a 1:1 ratio in the fully loaded structures of these materials. At both sites, each positively charged H atom of the sorbate molecule can interact favorably with a nearby electronegative O atom of a formate linker. Our GCMC simulations captured sorption at both sites in the two MOFs.

Figure 10.6 shows a comparison of the simulated C$_2$H$_2$ molecule positions to those determined experimentally through single crystal X-ray crystallography in both $\alpha$–[Mg$_3$(O$_2$CH)$_6$] and $\alpha$–[Mn$_3$(O$_2$CH)$_6$]. The distribution of the simulated positions was obtained from the Monte Carlo sorption history of post-equilibrated GCMC simulations using the C$_2$H$_2$-PHAST* model in the individual MOFs at 298 K and 1 atm. It can be observed that the simulated positions roughly overlay the two experimental positions in both MOFs. The minor deviations between the experimental and simulated C and H positions could be
attributed to the rigid nature of the C$_2$H$_2$ potential employed for the simulations. Under experimental conditions, it is likely that the confined regions within these MOFs may induce slight changes in the C$_2$H$_2$ bond length and angles relative to the equilibrium values of the classical models. This could explain why the C$_2$H$_2$ molecules in the experimental X-ray crystal structures exhibit shorter C–C bond lengths than the literature value of 1.205 Å for the molecule in the gas phase.$^{282}$ The narrow channels of these materials make these minor alterations more important for localization into the constrained sorption sites than they would be in more spacious systems.

While the modeled C$_2$H$_2$ sorption sites are well-defined in both MOFs, the Mg variant shows a considerably more compact distribution of the sorbate molecule positions within the regions of occupancy for both sorption sites. This finding seems unusual given the fact that both MOFs are isostructural and have nearly identical lattice parameters and pore size dimensions. Nevertheless, we attribute the greater C$_2$H$_2$ mobility in α–[Mn$_3$(O$_2$CH)$_6$] to the weaker binding sites in this analogue. This is ostensibly a consequence of the less favorable electrostatic environment in this variant relative to α–[Mg$_3$(O$_2$CH)$_6$]. It is evident from our simulations that the C$_2$H$_2$ molecules in α–[Mn$_3$(O$_2$CH)$_6$] have more spatial freedom than in α–[Mg$_3$(O$_2$CH)$_6$]. This agrees with the lower C$_2$H$_2$ uptake measured experimentally for α–[Mn$_3$(O$_2$CH)$_6$] given that greater spatial freedom probably corresponds to weaker binding within the material.

As discussed in the previous subsection, the higher partial positive charge of the metal ions in α–[Mg$_3$(O$_2$CH)$_6$] compared to those in α–[Mn$_3$(O$_2$CH)$_6$] results in greater electrostatic interactions between the framework and the C$_2$H$_2$ molecules, which in turn causes the sorbate molecules to lock in more tightly within the pores. Higher partial positive charges for the M$^{2+}$ ions results in greater partial negative charges for the linker O atoms. Since the C$_2$H$_2$ molecules primarily interact with the framework O atoms through their positively charged H atoms, this interaction is enhanced if the O atoms are more negatively charged. These findings are consistent with the observations in the experimental and simulated C$_2$H$_2$ sorption isotherms and $Q_{st}$ values for the two analogues.
Specifically, $\alpha$-[Mg$_3$(O$_2$CH)$_6$] displays higher low loading C$_2$H$_2$ uptakes and $Q_{st}$ values than $\alpha$-[Mn$_3$(O$_2$CH)$_6$] due to greater contributions from electrostatic interactions.

The binding energies computed by periodic DFT are compared to experimental and simulated isosteric heats at initial loading in Table 10.5. General agreement was obtained by comparing both simulated and experimental isosteric heat at initial loading: the magnitude of the interaction energy of C$_2$H$_2$ in $\alpha$-[Mg$_3$(O$_2$CH)$_6$] (-47.3 kJ/mol) was greater than that for $\alpha$-[Mn$_3$(O$_2$CH)$_6$]. (-46.1 kJ/mol).

10.6 Conclusion

GCMC simulations of C$_2$H$_2$ sorption were performed in $\alpha$-[Mg$_3$(O$_2$CH)$_6$] and $\alpha$-[Mn$_3$(O$_2$CH)$_6$], two isostructural MOFs that consist of an extended network of metal ions bonded to formate linkers. Herein, we rationalized the C$_2$H$_2$ sorption mechanism in both MOFs and gained insights into the reason for their distinct C$_2$H$_2$ sorption properties through theoretical studies. Experimental studies revealed that $\alpha$-[Mg$_3$(O$_2$CH)$_6$] exhibits higher C$_2$H$_2$ uptake and initial $Q_{st}$ than $\alpha$-[Mn$_3$(O$_2$CH)$_6$].$^{243}$ This trend was reproduced by our simulations as the theoretical C$_2$H$_2$ sorption isotherms, $Q_{st}$ values, and sorption sites generated in this work are in good agreement with the experimental measurements for both MOFs. These simulations were carried out with two recently developed C$_2$H$_2$ potentials to evaluate their accuracy and transferability for simulations in porous materials.$^{26}$

The distinct C$_2$H$_2$ sorption profiles between the two MOFs can be explained by differences in the calculated partial charges of the M$^{2+}$ ions. According to our electronic structure calculations, the Mg$^{2+}$ ions in $\alpha$-[Mg$_3$(O$_2$CH)$_6$] exhibit a greater partial positive charge than the Mn$^{2+}$ ions in $\alpha$-[Mn$_3$(O$_2$CH)$_6$], which is consistent with trends in electropositivity. As a result, the O atoms of the formate linkers are more negatively charged in the former. This caused the Mg variant to display greater electrostatic interactions with the C$_2$H$_2$ molecules, which in turn led to higher uptake and $Q_{st}$. Our simulations revealed that electrostatic interactions are the main contributor to the total energy for C$_2$H$_2$ sorption in $\alpha$-[Mg$_3$(O$_2$CH)$_6$], followed by repulsion/dispersion interactions. However, this trend is reversed in $\alpha$-[Mn$_3$(O$_2$CH)$_6$], as the repulsion/dispersion contribution
Figure 10.1: Orthographic $b$-axis view of the $2 \times 2 \times 2$ supercell of $\alpha-[M_3(O_2CH)_6]$ (M = Mg, Mn). In (a), the $M^{2+}$ ions are shown in silver color, while in (b), the $M^{2+}$ ions shown in different colors to highlight the chemically distinct $M^{2+}$ ions ($M_1$ = magenta, $M_2$ = lime green, $M_3$ = violet, $M_4$ = blue). Atom colors: C = cyan, H = white, O = red.

Table 10.1: Lennard–Jones $\epsilon$ and $\sigma$ and scalar point polarizability parameters used for the various atoms for the simulations in this work.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$\epsilon$ (K)</th>
<th>$\sigma$ (Å)</th>
<th>$\alpha^\circ$ (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>33.23000</td>
<td>3.50000</td>
<td>1.28860</td>
</tr>
<tr>
<td>H</td>
<td>15.11000</td>
<td>2.42000</td>
<td>0.41380</td>
</tr>
<tr>
<td>O</td>
<td>30.19000</td>
<td>3.11800</td>
<td>0.85200</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>55.85000</td>
<td>2.69100</td>
<td>0.00720</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>6.54620</td>
<td>2.63800</td>
<td>2.48750</td>
</tr>
</tbody>
</table>

is greater in this analogue. The effects of many-body polarization interactions were found to be negligible in both MOFs.

It is next planned to investigate $\alpha-[Mg_3(O_2CH)_6]$ and $\alpha-[Mn_3(O_2CH)_6]$ for their potential utility at separating $C_2H_2$ from $CO_2$ through experimental and theoretical studies. As shown in the previously reported single-component experimental $C_2H_2$ and $CO_2$ sorption isotherms for these materials, both MOFs exhibit much higher uptake for $C_2H_2$ than $CO_2$ at 275 and 298 K and low pressures ($< 0.1$ atm)$^{243}$ This suggests that these MOFs could display high selectivity for $C_2H_2$ over $CO_2$ in a binary mixture under ambient conditions. We also plan to study other metal analogues (e.g., Co, Ni)$^{254,255}$ of these MOFs for their $C_2H_2$ sorption and separation performance.
Table 10.2: Partial charges ($e^-$) for the chemically distinct $M^{2+}$ ions in $\alpha$–[M$_3$(O$_2$CH)$_6$] (M = Mg, Mn) that were used for the simulations in this work. Label of $M^{2+}$ ions correspond to Figure 10.1(b).

<table>
<thead>
<tr>
<th>Atom</th>
<th>$\alpha$–[Mg$_3$(O$_2$CH)$_6$]</th>
<th>$\alpha$–[Mn$_3$(O$_2$CH)$_6$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>1.83260</td>
<td>1.34210</td>
</tr>
<tr>
<td>M2</td>
<td>1.78830</td>
<td>0.98410</td>
</tr>
<tr>
<td>M3</td>
<td>1.72240</td>
<td>0.88000</td>
</tr>
<tr>
<td>M4</td>
<td>1.86400</td>
<td>1.55190</td>
</tr>
</tbody>
</table>

Figure 10.2: Low pressure $C_2H_2$ sorption isotherms in $\alpha$–[Mg$_3$(O$_2$CH)$_6$] at (a) 275 K and (b) 298 K for experiment (adsorption = filled black circles, desorption = open circles) and simulations using the $C_2H_2$-PHAST (green) and $C_2H_2$-PHAST* (red) models. The experimental data was estimated from reference 243.
Figure 10.3: Low pressure C$_2$H$_2$ sorption isotherms in $\alpha$-[M$_3$(O$_2$CH)$_6$] at (a) 275 K and (b) 298 K for experiment (adsorption = filled black circles, desorption = open circles) and simulations using the C$_2$H$_2$-PHAST (green) and C$_2$H$_2$-PHAST* (red) models. The experimental data was estimated from reference 243.

Table 10.3: Summary of experimental and simulated C$_2$H$_2$ sorption data for $\alpha$-[M$_3$(O$_2$CH)$_6$] (M = Mg, Mn). The experimental results were taken from reference 243. The simulated results are shown for the C$_2$H$_2$-PHAST* model.

<table>
<thead>
<tr>
<th></th>
<th>$\alpha$-[Mg$_3$(O$_2$CH)$_6$]</th>
<th>$\alpha$-[Mn$_3$(O$_2$CH)$_6$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp. BET Surface Area (m$^2$ g$^{-1}$)</td>
<td>284</td>
<td>297</td>
</tr>
<tr>
<td>Exp. Pore Volume (cm$^3$ g$^{-1}$)</td>
<td>0.14</td>
<td>0.13</td>
</tr>
<tr>
<td>Exp. Uptake at 275 K/1 atm (mmol g$^{-1}$)</td>
<td>3.10</td>
<td>2.58</td>
</tr>
<tr>
<td>Exp. Uptake at 298 K/1 atm (mmol g$^{-1}$)</td>
<td>2.93</td>
<td>2.29</td>
</tr>
<tr>
<td>Exp. $Q_0^{st}$ (mmol g$^{-1}$)</td>
<td>44.1</td>
<td>41.8</td>
</tr>
<tr>
<td>Sim. Uptake at 275 K/1 atm (mmol g$^{-1}$)</td>
<td>3.32</td>
<td>2.45</td>
</tr>
<tr>
<td>Sim. Uptake at 298 K/1 atm (mmol g$^{-1}$)</td>
<td>3.09</td>
<td>2.33</td>
</tr>
<tr>
<td>Sim. $Q_0^{st}$ (mmol g$^{-1}$)</td>
<td>41.9</td>
<td>34.7</td>
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Figure 10.4: Isosteric heats of adsorption \( (Q_{st}) \) for \( \text{C}_2\text{H}_2 \) plotted as a function of loading in (a) \( \alpha-[\text{Mg}_3(\text{O}_2\text{CH})_6] \) and (b) \( \alpha-[\text{Mn}_3(\text{O}_2\text{CH})_6] \) for experiment (black) and simulations using the \( \text{C}_2\text{H}_2\text{-PHAST} \) (green) and \( \text{C}_2\text{H}_2\text{-PHAST}\* \) (red) models. The blue line represents the \( \text{C}_2\text{H}_2 \) uptake corresponding to \( \text{C}_2\text{H}_2 \) saturation (8 molecules per unit cell). The experimental data was estimated from reference 243.
Table 10.4: Summary of the averaged percent contributions of the total energy and absolute energy magnitudes from GCMC simulations of C$_2$H$_2$ sorption in α–[M$_3$(O$_2$CH)$_6$] (M = Mg, Mn) using the C$_2$H$_2$-PHAST and C$_2$H$_2$-PHAST* potentials at 298 K and 1 atm. $U_{rd}$, $U_{es}$, and $U_{pol}$ represent the repulsion/dispersion, stationary electrostatic, and many-body polarization energy, respectively.

<table>
<thead>
<tr>
<th>Potential</th>
<th>$U$ Contribution</th>
<th>α–[Mg$_3$(O$_2$CH)$_6$]</th>
<th>α–[Mn$_3$(O$_2$CH)$_6$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_2$H$_2$-PHAST</td>
<td>$U_{rd}$ (%)</td>
<td>49.16</td>
<td>56.93</td>
</tr>
<tr>
<td></td>
<td>$U_{es}$ (%)</td>
<td>50.84</td>
<td>43.07</td>
</tr>
<tr>
<td></td>
<td>$U_{pol}$ (%)</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>C$_2$H$_2$-PHAST*</td>
<td>$U_{rd}$ (%)</td>
<td>40.00</td>
<td>52.57</td>
</tr>
<tr>
<td></td>
<td>$U_{es}$ (%)</td>
<td>53.07</td>
<td>42.71</td>
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<tr>
<td></td>
<td>$U_{pol}$ (%)</td>
<td>6.93</td>
<td>4.72</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Potential</th>
<th>$U$ Contribution</th>
<th>α–[Mg$_3$(O$_2$CH)$_6$]</th>
<th>α–[Mn$_3$(O$_2$CH)$_6$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_2$H$_2$-PHAST</td>
<td>$U_{rd}$ (K)</td>
<td>-80183.0</td>
<td>-78651.9</td>
</tr>
<tr>
<td></td>
<td>$U_{es}$ (K)</td>
<td>-82909.3</td>
<td>-59506.5</td>
</tr>
<tr>
<td></td>
<td>$U_{pol}$ (K)</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>C$_2$H$_2$-PHAST*</td>
<td>$U_{rd}$ (K)</td>
<td>-67182.8</td>
<td>-71220.4</td>
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<tr>
<td></td>
<td>$U_{es}$ (K)</td>
<td>-89127.6</td>
<td>-57854.8</td>
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<td></td>
<td>$U_{pol}$ (K)</td>
<td>-11644.7</td>
<td>-6392.7</td>
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Figure 10.5: Molecular illustration of the two C$_2$H$_2$ sorption sites (site A = purple, site B = green) in α–[M$_3$(O$_2$CH)$_6$] (M = Mg, Mn) as determined through the single crystal X-ray diffraction experiments performed in reference 243: (a) a-axis view and (b) b-axis view. Note, in (a) the interaction of the C$_2$H$_2$ center-of-mass with the formate oxygen atoms bound to the metal ions. Atom colors: C = cyan, H = white, O = red, Mg/Mn = silver.
Figure 10.6: Comparison of the simulated C$_2$H$_2$ molecule positions (small spheres) with those determined through X-ray crystallography (CPK representation) in (a) α–[Mg$_3$(O$_2$CH)$_6$] and (b) α–[Mn$_3$(O$_2$CH)$_6$]. The experimental positions were taken from the guest-filled crystal structures published in reference 243. The frameworks have been omitted for clarity. Atom colors: C = orange, H = white (experiment) or gray (simulation).

Table 10.5: Periodic DFT single-molecule C$_2$H$_2$ binding energies obtained from optimization calculations compared with simulated (C$_2$H$_2$-PHAST*) and experimental $Q_{st}$-0 isosteric heats at initial loading.

<table>
<thead>
<tr>
<th>MOF</th>
<th>Periodic DFT optimization energy</th>
<th>$Q_{st}$-0, simulated</th>
<th>$Q_{st}$-0, experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>α–[Mg$_3$(O$_2$CH)$_6$]</td>
<td>-47.3</td>
<td>41.9</td>
<td>44.1</td>
</tr>
<tr>
<td>α–[Mn$_3$(O$_2$CH)$_6$]</td>
<td>-46.1</td>
<td>34.7</td>
<td>41.9</td>
</tr>
</tbody>
</table>
Chapter 11

Conclusions

Synthetic porous materials have a broad range of impact and applicability in science, medicine, and industry. The quantity of different reported structures continues to grow rapidly as new organic compounds are used in different combinations to form crystalline substances. The simulation and theoretical work described in this work is a small sample of the body of work being done in the field. What is clear from this work and others, though, is that existing force fields in common use, such as UFF\textsuperscript{206} have known limitations that fall to capture the complex chemistry introduced by the inorganic/organic hybrid materials described here. A search for a better force field paradigm and improved methods of assigning atomic parameters – especially metals – for modeling is highly desirable.

The main insights from this body of work are that electrodynamic effects (i.e. explicit polarization) become important in systems with high inductivity and complex electronic structures. When polarization is included in simulation, dipoles are computed on polarizable sites and the change in these dipoles’ magnitude and direction concurrently changes the way that guest molecules enter and align into the pores of the material. This is especially true in the case of H\textsubscript{2} in MOFs, where electrostatics play a relatively insignificant role due to the small charge magnitudes on the modelled sites. Polarization makes the difference in discovering a binding site that is observed in experiment through neutron powder diffraction, with very good quantitative agreement.
The massive push in the early 2000s for discovery and synthesis of a material for H₂ sorption that matches the Department of Energy target is revealed to be unrealistic. Though H₂ can be reduced to liquid density due to polarization effects inside of the pores of various MOFs at 77K well above its boiling point of ~20K, the physical/chemical properties of H₂ do not allow for the desired uptake and storage capacities outlined by the DOE. Aspects of H₂ storage and the atomistic interactions of it inside of MOFs are still of high interest for basic science and for separations of deuterium and tritium, for example.

Qualitatively, it is common to observe that the binding site of a given gas or macromolecule in the pores of a MOF corresponds to the alignment of the electropositive parts of the host with the electronegative parts of the guest. Basic coulombic physics can provide that intuition. What polarization adds, however, is a layer of electrodynamic effects that change as the simulation proceeds and as molecules move within the electric field provided by the MOF. This can result in some counterintuitive behavior from simulation. For example, polarization is known to be an exclusively attractive phenomena – the alignment of dipoles produces a negative energy for any configuration of atoms by

$$-\frac{1}{2} \sum_i (\vec{\mu}_i \cdot \vec{E}_i)$$

where $\vec{\mu}_i$ is the dipole and $\vec{E}_i$ is the electric field on atom $i$. One would expect, then, that adding polarization in a GCMC simulation would cause the uptake of the gas to increase with respect to unpolarized control simulations. In some cases, this occurs, as in H₂ in NOTT-112. However, sometimes the addition of polarization causes gas molecules to migrate to an even more preferred geometry within the material (with a lower energy due to polarization) which then excludes one or more secondary binding sites due to van der Waals repulsions, resulting in a net decrease in gas uptake at equilibrium. This is an important insight gleaned for example from the studies of MPM-1-Br/Cl herein. With the assumption that the van der Waals and electrostatic parameters produce a force-field well matched to reality (a large assumption, granted), the addition of polarization intrinsically improves the predictive power of the simulation. In this work, methods have been described to determine the polarizability of atomic sites for classical simulation using high levels of theory in quantum calculations.
References


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Appendix A

Equations used in MPMC and MCMD

A.1 Source Code

The source for MPMC and MCMD is publicly available under the GNU General Public License v3.0 and can be found on github. MCMD: https://github.com/khavernathy/mcmd; MPMC: https://github.com/mpmccode/mpmc.

A.2 Statistical Mechanics

\[ Q = \sum_i e^{-E_i/k_B T} = \int e^{-E(r,p)/k_B T} dr dp \]  
(A.1)

\[ U = k_B T^2 \left( \frac{\partial \ln Q}{\partial T} \right)_V \]  
(A.2)

\[ P = k_B T \left( \frac{\partial \ln Q}{\partial V} \right)_T \]  
(A.3)

\[ H = k_B T^2 \left( \frac{\partial \ln Q}{\partial T} \right)_V + \left( \frac{\partial \ln Q}{\partial V} \right)_T \]  
(A.4)

\[ C_V = \left( \frac{\partial U}{\partial T} \right)_V \]  
(A.5)

\[ A = -k_B T^2 \ln Q \]  
(A.6)

\[ S = k_B T \left( \frac{\partial \ln Q}{\partial T} \right)_V + k_B \ln Q \]  
(A.7)
\[ G = k_B TV \left( \frac{\partial Q}{\partial V} \right)_T - k_B T \ln Q \]  
(A.8)

\[ Z = \frac{PV}{nRT} \]  
(A.9)

### A.3 Force-field Energies

Cut-off terms are implicit below (i.e., interactions with \( r > r_c \) are not counted) and can be found within the code.

#### Lennard-Jones Repulsion-Dispersion

The repulsive and dispersive energies for each pair:

\[ U_{LJ}(r, \sigma_{ij}, \epsilon_{ij}) = \sum_{i}^{N} \sum_{j=i+1}^{N} 4\epsilon_{ij} \left[ \frac{\sigma_{ij}^{12}}{r_{12}^{12}} - \frac{\sigma_{ij}^{6}}{r_{6}^{6}} \right] \]  
(A.10)

The long-range correction for each pair:

\[ U_{lrc}(r_c, \sigma_{ij}, \epsilon_{ij}) = \sum_{i}^{N} \sum_{j=i+1}^{N} \frac{1}{V} \frac{16}{3} \pi \epsilon_{ij} \sigma_{ij}^{3} \left[ \frac{1}{3} r_c^{9} \sigma_{ij}^{3} \frac{1}{3} \sigma_{ij}^{3} \right] \]  
(A.11)

The self-energy for each atom:

\[ U_{self}(\sigma_i, \epsilon_i) = \sum_{i}^{N} \frac{1}{V} \frac{16}{3} \pi \epsilon_i \sigma_i^{3} \left[ \frac{1}{3} r_c^{9} \sigma_i^{3} \frac{1}{3} \sigma_i^{3} \right] \]  
(A.12)

The mass-dependent Feynman-Hibbs correction terms (2nd and 4th order) with \( \mu = \) reduced mass:

\[ U_{FH2}(r, \sigma_{ij}, \epsilon_{ij}, m_i, m_j) = \sum_{i}^{N} \sum_{j=i+1}^{N} \frac{k^2}{24 k_B T (m_i + m_j)} (U'' + \frac{2}{r} U') \]  
(A.13)

\[ U_{FH4}(r, \sigma_{ij}, \epsilon_{ij}, m_i, m_j) = U_{FH2} + \sum_{i}^{N} \sum_{j=i+1}^{N} \frac{\hbar^4}{1152 k_B^2 T^2 \mu^2} \left( \frac{15}{r^3} U' + \frac{4}{r} U'' + U''' \right) \]  
(A.14)

#### Tang-Toennies Repulsion-Dispersion

The repulsive term is a simple exponential:
\[ U_{TT,\text{repul.}} = \sum_{i}^{N} \sum_{j=i+1}^{N} 315.775e^{-b(r-\sigma)} \]  

(A.15)

The attractive (dispersion) term is given with damping functions \( f_n \):

\[ f_n = 1 - e^{-br} \sum_{i=0}^{n} \frac{(br)^i}{i!} \]  

(A.16)

\[ U_{TT,\text{attr.}} = \sum_{i}^{N} \sum_{j=i+1}^{N} \sum_{a=3}^{5} -f_{2a} C_{2a} \]  

(A.17)

The long-range correction for each pair:

\[ U_{TT,\text{lrc.}} = \sum_{i}^{N} \sum_{j=i+1}^{N} -4\pi V \left[ \frac{C_6}{3r_c^3} + \frac{C_8}{5r_c^5} + \frac{C_{10}}{7r_c^7} \right] \]  

(A.18)

The self-energy for each atom:

\[ U_{TT,\text{self}} = \sum_{i}^{N} -4\pi V \left[ \frac{C_6}{3r_c^3} + \frac{C_8}{5r_c^5} + \frac{C_{10}}{7r_c^7} \right] \]  

(A.19)

**Ewald Electrostatics**

Using Ewald \( \alpha = \sqrt{\alpha} \) and a user-defined \( k_{\text{max}} \).

The real-space contribution to energy via pairs is separable by inter- and intra-molecular interactions:

\[ U_{\text{real,intermolec.}}(r) = \sum_{i}^{N} \sum_{j \neq i}^{N} \frac{q_i q_j}{r} \text{erfc}(\alpha r) \]  

(A.20)

\[ U_{\text{real,intramolec.}}(r) = \sum_{i}^{N} \sum_{j \neq i}^{N} \frac{q_i q_j}{r} \text{erf}(\alpha r) \]  

(A.21)

The self-energy from each point-charge:

\[ U_{\text{self}} = -\sum_{i}^{N} \frac{\alpha}{\sqrt{\pi}} q_i q_i \]  

(A.22)

The energy provided in reciprocal space (k-space):
\[ U_{\text{recip}} = \frac{2\pi}{V} \sum_{k \neq 0} e^{-k^2/4\alpha^2} \sum_{i} \left[ q_i \cos(\vec{k} \cdot \vec{r}_i) \right]^2 + \left[ q_i \sin(\vec{k} \cdot \vec{r}_i) \right]^2 \] (A.23)

The mass-dependent Feynman-Hibbs correction terms (2nd and 4th order) with \( \mu = \) reduced mass:

\[ U_{FH2,\text{intermolec.}} = \sum_{i} \sum_{j=i+1}^{N} \frac{\hbar^2}{24k_B T \mu} (U'' + \frac{2}{r} U') \] (A.24)

\[ U_{FH4,\text{intermolec.}} = U_{FH2} + \frac{\hbar^4}{1152 k_B^2 T^2 \mu^2} (\frac{15}{r^3} U' + \frac{4}{r} U'' + U''') \] (A.25)

**Thole-Applequist Polarization**

Here, dipoles \( \mu_i \) on each site \( i \) are computed via the Thole-Applequist iterative scheme with user-defined number of iterations.

\[ U_{\text{polar}} = -\frac{1}{2} \sum_{i} \left[ (\vec{\mu}_i \cdot \vec{E}) + (\vec{\mu}_i \cdot \vec{E}_{\text{induced}}) \right] \] (A.26)

**Bonding Interactions**

The primary justifications for the bonding potentials selected are detailed in Rappe et al.’s UFF. The potential form that allows for flexible treatment of the MOM considers multiple bonding contributions as follows:

For bonds, in place of a simple harmonic approximation, the Morse potential is used between atoms \( i \) and \( j \):

\[ U_{\text{Morse}} = D_{ij} \left[ e^{-\alpha(r-r_{ij})} - 1 \right]^2 \] (A.27)

Likewise for angle-bends, in place of a simple harmonic treatment, a Fourier cosine expansion is used for atoms \( i, j, k \):

\[ U_{\text{Angle}} = K_{ijk} [C_0 + C_1 \cos(\theta) + C_2 \cos(2\theta)] \] (A.28)

And for torsions, a Fourier cosine expansion is also used for atoms \( i, j, k, \) and \( l \):

\[ U_{\text{Dihedral}} = \frac{1}{2} V_{jk} [1 - \cos(n\phi_{ijkl})\cos(n\phi)] \] (A.29)

The details of the parameters included in the bonded potentials are provided in UFF. MCMD has an auto-parameterization feature which takes atomic number (or element name) and structure information only to determine UFF atom-types for the bonding and non-bonding interactions. Computation of the forces for these potentials
(potential gradients as function of each atomic degree of freedom) involved a highly convoluted mathematical expression which is excluded here for brevity. MATLAB was used to compute these gradients, and MCMD calculates them efficiently by recycling redundant components of the math.

A.4 Force-field Mixing Rules

Lennard-Jones Lorentz-Berthelot

\[ \sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j) \quad (A.30) \]
\[ \epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} \quad (A.31) \]

Lennard-Jones Waldman-Hagler

\[ \sigma_{ij} = \left[ \frac{1}{2}(\sigma_i^6 + \sigma_j^6) \right]^{1/6} \quad (A.32) \]
\[ \epsilon_{ij} = \left[ \frac{2\sigma_i^3 \sigma_j^3}{\sigma_i^6 \sigma_j^6} \right] \sqrt{\epsilon_i \epsilon_j} \quad (A.33) \]

Lennard-Jones Halgren

\[ \sigma_{ij} = \frac{\sigma_i^3 + \sigma_j^3}{\sigma_i^3 + \sigma_j^3} \quad (A.34) \]
\[ \epsilon_{ij} = \frac{4\epsilon_i \epsilon_j}{(\sqrt{\epsilon_i} + \sqrt{\epsilon_j})^2} \quad (A.35) \]

Tang-Toennies mixing

\[ \sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j) \quad (A.36) \]
\[ b_{ij} = \frac{2b_i b_j}{b_i + b_j} \quad (A.37) \]
\[ C_6 = \sqrt{C_{6i} C_{6j}} \quad (A.38) \]
\[ C_8 = \sqrt{C_{8i} C_{8j}} \quad (A.39) \]
\[ C_{10} = \frac{49 C_8}{40 C_6} \quad (A.40) \]

A.5 Forces

Cut-off terms are implicit below (i.e. interactions with \( r > r_c \) are not counted) and can be found within the code.
Lennard-Jones Repulsion-Dispersion

\[ \vec{F}_i = \sum_{j \neq i} N \sum_{j \neq i} 24 \vec{r}_{ij} \epsilon_{ij} \left[ \frac{\sigma_{12}^{12}}{\vec{r}_{ij}} - \frac{\sigma_6^{6}}{\vec{r}_{ij}^8} \right] \]  \hspace{1cm} (A.41)

Ewald Electrostatics

Using Ewald \( \alpha = \sqrt{\alpha} \) and a user-defined \( k_{max} \),

\[ \vec{F}_{i,real} = \sum_{j \neq i} N \sum_{j \neq i} - \frac{2q_i q_j \alpha e^{-a^2 r^2}}{r \sqrt{\pi}} - q_i q_j \frac{\text{erfc}(ar)}{r^2} \vec{r}_{ij} \]  \hspace{1cm} (A.42)

\[ \vec{F}_{i,recip} = \sum_{j \neq i} \sum_{k} 4\pi q_i q_j \vec{k} e^{-k^2/\alpha^2} \sin(k \cdot \vec{r}) \]  \hspace{1cm} (A.43)

Thole-Applequist Polarization

Using exponential damping with polarization damping factor \( \beta \) and coulombic cutoff \( r_c \).

The gradients are computed and parsed within the code.

\[ t_1 = e^{-\beta r} \]  \hspace{1cm} (A.44)

\[ t_2 = 1 + e^{-\beta r} + \frac{1}{2} \beta^2 r^2 \]  \hspace{1cm} (A.45)

\[ t_3 = t_2 + \frac{1}{6} \beta^3 r^3 \]  \hspace{1cm} (A.46)

\[ E_t = \left[ \frac{1}{r^2} - \frac{1}{r_c^2} \right] \frac{1}{r} \]  \hspace{1cm} (A.47)

\[ \vec{F}_i = \sum_{j \neq i} N \sum_{j \neq i} - \nabla \left( \frac{1}{2\alpha} (\vec{\mu}_i \cdot \vec{\mu}_j) \right) + \]  \hspace{1cm} (A.48)

\[ \sum_{j \neq i} - \nabla \vec{\mu}_i \cdot (E_t q_i \vec{r}) - \vec{\mu}_j \cdot (E_t q_j \vec{r}) + \]  \hspace{1cm} (A.49)

\[ \sum_{j \neq i} - \nabla \frac{\vec{\mu}_i \cdot \vec{\mu}_j}{r^3} (1 - t_1 t_2) - \frac{3}{r^5} (\vec{\mu}_i \cdot \vec{r})(\vec{\mu}_j \cdot \vec{r})(1 - t_1 t_3) \]  \hspace{1cm} (A.50)
A.6 Statistics

Recursive average:

\[ \langle A_{\text{new}} \rangle = \frac{(N - 1)\langle A_{\text{old}} \rangle + A_N}{N} \]  \hspace{1cm} (A.52)

Recursive standard deviation:

\[ \sigma_{\text{new}} = \sqrt{\sigma_{\text{old}}^2 + \langle A_{\text{old}} \rangle^2 - \langle A_{\text{new}} \rangle^2 + \frac{A_N^2 - \sigma_{\text{old}}^2 - \langle A_{\text{old}} \rangle^2}{N}} \]  \hspace{1cm} (A.53)

A.7 Newtonian Dynamics

Translational force of a molecular is the sum of forces calculated on each of its atoms \( i \):

\[ \vec{F}_{\text{molec.}} = \sum_i \vec{F}_i \]  \hspace{1cm} (A.54)

Acceleration follows Newton’s second law. For constant mass:

\[ \vec{a} = \frac{\vec{F}}{m} \]  \hspace{1cm} (A.55)

Velocity follows by integration, using the Velocity Verlet convention:

\[ \vec{v}(t + \Delta t) = \vec{v}(t) + \frac{1}{2}(\vec{a}(t) + \vec{a}(t - \Delta t))\Delta t \]  \hspace{1cm} (A.56)

Translations follow by integration:

\[ \vec{r}(t + \Delta t) = \vec{r}(t) + \vec{v}(t)\Delta t + \frac{1}{2}\vec{a}(t)\Delta t^2 \]  \hspace{1cm} (A.57)

Torques of atoms \( i \) are computed by atomic forces with respect to molecular center-of-mass:

\[ \vec{\tau}_i = (\vec{r}_i - \vec{r}_{\text{com}}) \times \vec{F}_i \]  \hspace{1cm} (A.58)

Molecular torque is a sum of torques from atoms \( i \):

\[ \vec{\tau}_{\text{molec}} = \sum_i \vec{\tau}_i \]  \hspace{1cm} (A.59)

Angular equations of motion are analogous to translational:
\[ I = \sum_{i} m_i (\vec{r}_i - \vec{r}_{com})^2 \quad (A.60) \]
\[ \vec{\alpha} = \frac{\vec{\tau} I}{I^2} \quad (A.61) \]
\[ \vec{\omega}(t + \Delta t) = \vec{\omega}(t) + \frac{1}{2} (\vec{\omega}(t) + \vec{\omega}(t - \Delta t)) \Delta t \quad (A.62) \]
\[ \vec{\theta}(t + \Delta t) = \vec{\theta}(t) + \vec{\omega}(t) \Delta t + \frac{1}{2} \vec{\alpha}(t) \Delta t^2 \quad (A.63) \]

Rotation of a point \((x, y, z)\) relative to center of mass by angle \(\theta\) in radians, to form new point \((x_n, y_n, z_n)\):

1. In the plane of \(x\):
   \[ \begin{bmatrix} x_n \\ y_n \\ z_n \end{bmatrix} = \begin{bmatrix} x \\ y \cos \theta - z \sin \theta \\ y \sin \theta + z \cos \theta \end{bmatrix} \quad (A.64) \]

2. In the plane of \(y\):
   \[ \begin{bmatrix} x_n \\ y_n \\ z_n \end{bmatrix} = \begin{bmatrix} x \cos \theta \\ y \\ -x \sin \theta + z \cos \theta \end{bmatrix} \quad (A.65) \]

3. In the plane of \(z\):
   \[ \begin{bmatrix} x_n \\ y_n \\ z_n \end{bmatrix} = \begin{bmatrix} x \cos \theta - y \sin \theta \\ x \sin \theta + y \cos \theta \\ z \end{bmatrix} \quad (A.66) \]

A.8 Observables

Kinetic energy of system is the sum of translational and rotational energies:

\[ K = \frac{1}{2} \sum_{i} m_i v_i^2 + I_i \omega_i^2 \quad (A.67) \]

Temperature is given by Kinetic theory of transport in gases, where \(DOF\) is the total degrees of freedom of the simulation sites (atoms):

\[ T = \frac{\sum_{i} m_i v_i^2}{DOF} \quad (A.68) \]

Self diffusivity of a molecule-type with \(N_s\) such molecules is measured via the Einstein relation. This quantity is correct in the limit that \(t \to \infty\). The constant 6 is used here because \(2 \times d\) where \(d = 3\) is the dimensionality of the system (the movement of the
The isosteric heat of sorption $Q_{st}$ is given by potential energy and particle number fluctuations:

$$Q_{st} = -k_B T + \frac{\langle NU \rangle - \langle N \rangle \langle U \rangle}{\langle N^2 \rangle - \langle N \rangle^2}$$  \hspace{1cm} (A.70)

Uptake of a sorbate $s$ in a porous media $p$ (wt\%) is:

$$\text{wt\%} = 100 \times \frac{m_s}{m_s + m_p}$$  \hspace{1cm} (A.71)

Some report this as relative mass (wt\%ME):

$$\text{wt\%ME} = 100 \times \frac{m_s}{m_p}$$  \hspace{1cm} (A.72)

Excess uptake is given by the following, with $M =$ molar mass, $V_f =$ free volume, $f =$ fugacity:

$$N_{\text{excess}} = \frac{M \langle N \rangle - M V_f f}{T m_s}$$  \hspace{1cm} (A.73)

Selectivity of a gas $i$ compared to other gases $j$:

$$S_i = \frac{\langle N_i \rangle}{\sum_{j \neq i} \langle N_j \rangle}$$  \hspace{1cm} (A.74)

### A.9 Monte Carlo Boltzmann Factors

Below, $N_s =$ number of different sorbate types, $V =$ volume; $f =$ fugacity; $T =$ temperature, $N =$ number of sorbate molecules after trial move.

For $\mu VT$ insertion:

$$BF = N_s \exp(-\Delta E/k_B T)V f \frac{1}{TN}$$  \hspace{1cm} (A.75)

For $\mu VT$ deletion:

$$BF = \frac{1}{N_s} \exp(-\Delta E/k_B T)V f \frac{1}{T(N + 1)}$$  \hspace{1cm} (A.76)

For translations, any ensemble except $NVE$:

$$BF = \exp(-\Delta E/k_B T)$$  \hspace{1cm} (A.77)
For $NPT$ volume change:

$$BF = \exp\left[-\frac{\Delta E}{k_B T} + P\Delta V - (N + 1)\ln\left(\frac{V_{\text{new}}}{V_{\text{old}}}\right)k_B T\right]\quad (A.78)$$

For $NVE$ translations, with $E_t$ a user-defined total energy, $E_i$ energy before trial move, and $E_f$ energy after trial move:

$$BF = \frac{(E_t - E_f)^{3N/2}}{(E_t - E_i)^{3N/2}}\quad (A.79)$$
Appendix B

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Simulations of hydrogen, carbon dioxide, and small hydrocarbon sorption in a nitrogen-rich rht-metal–organic framework


**DOI:** 10.1039/C7CP06885A

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About the Author

Douglas M. Franz was born in Seminole, FL and obtained a B.S. in Environmental Science & Policy in 2013 at the University of South Florida. As an undergraduate, he studied nuisance ion removal from water with Prof. Dean Martin using organometallic polymers with an Honors Thesis entitled “Removal of aqueous BPA Model Compound 4-t-butylphenol Using Metalloligs”. His graduate work focused on the development and application of molecular simulation software for porous materials modeling, called Monte Carlo Molecular Dynamics (MCMD) with Prof Brian Space. He has worked in collaboration with several university laboratories in sponsored research programs including that of Prof. Michael Zaworotko at the University of Limerick and Prof. Madhab Das at the Indian Institute of Technology Karagpur. His main scientific interests are next generation force-field development (beyond Lennard–Jones modeling) and more broadly, the application of physical theory to computer programs. He enjoys the use of advanced computer technology in efforts to gain quantitative insight on microscopic phenomena, such as adsorption, selectivity, and diffusion of gases in metalorganic frameworks (MOFs).