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Molecular Simulations of Adsorption and Diffusion in Metal-Organic Frameworks (MOFs)

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DEDICATION

This dissertation is dedicated to my father (Jianhua Xiong) and my mother (Jinhua Liu) for their guidance and support throughout my life. Without their sacrifice, this would not have been possible. This dissertation is also dedicated to my wife (Na Wan) and my sister (Ruijin Xiong) for their love and for always believing in me, encouraging me, and supporting me in achieving my goals. I am also thankful for my daughter, Agnes Joy Xiong, for being the best newborn.

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ABSTRACT

Metal-organic frameworks (MOFs) are a new class of nanoporous materials that have received great interest since they were first synthesized in the late 1990s. Practical applications of MOFs are continuously being discovered as a better understanding of the properties of materials adsorbed within the nanopores of MOFs emerges. One such potential application is as a component of an explosive-sensing system. Another potential application is for hydrogen storage.

This work is focused on tailoring MOFs to adsorb/desorb the explosive, RDX. Classical grand canonical Monte Carlo (GCMC) and molecular dynamic (MD) simulations have been performed to calculate adsorption isotherms and self-diffusivities of RDX in several IRMOFs. Because gathering experimental data on explosive compounds is dangerous, data is limited. Simulation can in part fill the gap of missing information. Through these simulations, many of the key issues associated with MOFs preconcentrating RDX have been resolved. The issues include both theoretical issues associated with the computational generation of properties and practical issues associated with the use of MOFs in explosive-sensing system. Theoretically, we evaluate the method for generating partial charges for MOFs and the impact of this choice on the adsorption isotherm and diffusivity. Practically, we show that the tailoring of an MOF with a polar group like an amine can lead to an adsorbent that (i) concentrates RDX from the bulk by as much as a factor of 3000, (ii) is highly selective for RDX, and (iii) retains sufficient RDX mobility allowing for rapid, real time sensing.

Many of the impediments to the effective explosive detection can be framed as shortcomings in the understanding of molecule surface interactions. A fundamental, molecular-level understanding of the interaction between explosives and functionalized MOFs would provide the necessary guidance that allows the next generation of sensors to be developed. This is one of the main driving forces behind this dissertation.

Another important achievement in this work is the demonstration of a new direction for tailoring MOFs. A new class of tailored MOFs containing porphyrins has been proposed. These tailored MOFs show greater capability for hydrogen storage, which also demonstrated the great functionalization of MOFs and great potential to serve as preconcentrators.

The use of a novel multiscale modeling technique to develop equations of state for inhomogeneous fluids is included as a supplement to this dissertation.

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CHAPTER 1

Introduction

During the last several decades, homeland security and international civilian security have been through a series of acts of terrorism caused by the destructive use of explosives against a range of targets, including civilian populations, military personnel, commercial property, transportation systems, energy infrastructure and cultural symbols[1]. The detection of explosives has been an active area of research against the threat. Up to now, there are two basic detection systems. One is bulk detection systems, which rely on a number of X-ray machines, magnetic resonance imagers and chemical vapor sniffers. These classes of equipment are widely employed in airport security applications[2]. The difficulties associated with these systems are that they are slow, inaccurate and expensive[3].

The other basic detection scheme includes vapor and particle detection systems, which detect the explosives by tracing the quantities of explosive molecules at the molecular level with a variety of analytical techniques. Although these tracing detection systems could avoid some of the difficulties in the bulk detection systems, there are still numerous challenges, both physical and chemical. Most of the challenges come from the physical constraints of explosives such as low vapor pressures and limited sample size[1]. Many common explosives have extremely low vapor pressures at room temperature, especially for those with the highest priority for detection. The vapor pressures of some common explosives[4] are shown in Figure 1.1. Therefore, these tracing detection systems that rely on sampling of air spaces require accumulation of detectable amount of explosive molecules from vapor sampling of a large volume of air. The scheme of these systems can be represented in Figure 1.2. The general process includes some kind of preconcentration and detection. The preconcentration part is completed by a

preconcentrator. Preconcentrators facilitate the detection of explosives. A preconcentrator receives air (including explosive molecules and other components), separates the explosive molecules from air, and then when heated, releases them to a suitable detector. Because of the increased concentration of explosives at the detector, the overall detection threshold and false negatives/positives are significantly reduced. Unfortunately, the current generation of preconcentrators is not able to selectively trap explosive molecules: these preconcentrators separate both explosive and other innocuous molecules[5] from air. A preconcentrator capable of separating explosives from innocuous molecules will be much more efficient, because it will release a larger concentration of explosive molecules to the detector[6]. Such pre-concentrators will constitute a second generation of preconcentrators. We refer to them as Smart Nanoporous Preconcentrators (SNPs).

The development of nanostructured porous materials provides great opportunities for developing SNPs[5]. Traditional nanostructured materials such as zeolites and carbon nanotubes have showed potential promise for gas storage, but they can only be produced in a limited range of structures. Metal-organic frameworks (MOFs) are newly developed porous materials based on metal organic structures, which are considered as a new area for the development of adsorption materials[7]. Yaghi and coworkers[8-10] have first synthesized them and established a connection between MOFs and gas storage. Subsequently a large number of experimental and simulation studies of gas storage applications such as hydrogen and methane storage[11-15] have been reported in a wide variety of MOFs. All studies have shown that MOFs have unprecedented potential for gas storage due to their unique properties such as high porosities and well-defined pore size. More importantly, MOFs offer the possibility of controlling material tailoring parameters.

They can be chosen a combination of the metal connectors and organic linkers leading to control the pore dimension and topology to a high degree of freedom[15]. In other words, MOFs can be tailored to endless number of structures, which makes it possible to synthesize nanomaterials with the desired structures and properties for each specific application. Ni *et al.*[16] have demonstrated an inexpensive process to synthesize many different MOFs with uniform particle sizes that range from 4.5 microns to 0.1 microns through microwave activated precipitation. These are also significant advantages of MOFs over the traditional nanostructured materials. In addition to high storage capacity, MOFs present high selectivity ability. It has been shown by Dybtsev *et al.*[17] that one of MOFs they synthesized selectively adsorbs H₂ and CO₂ over other gases. Moreover, MOFs have high thermal stability, which makes them stable up to several hundreds of Celsius degrees[9]. All of the above properties support the suitability of MOFs for building SNPs. It has also been demonstrated by Ni *et al.*[15] that MOFs are useful as selective preconcentrators.

Unfortunately, it is extremely difficult to perform real explosive experiments using MOFs as the preconcentrator since explosives are dangerous and difficult to be handled; thus, no experimental data are available at this moment. Besides, the experiments need the research progress on the methodologies. In this regard, without a doubt, the computational feasibility of simulating MOFs preconcentrate explosives would be tremendously helpful.

In this work, we study explosive preconcentration in MOFs via molecular simulation. Specifically, we use RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) as the model explosive. RDX is an important energetic material, which releases a large amount

of energy upon bulk decomposition, and it is widely used as rocket propellant and explosive. RDX is often used as a component of the plastic explosive C-4, which was used to make a series of explosive assaults. As mentioned above, the concentration of RDX in air is parts per trillion (parts per billion level under experiment[1]) at ambient conditions, which makes RDX extremely difficult to be detected. The structure of RDX is shown in Figure 1.3.

As the development of computer technology, computer simulation has been a valuable tool in various areas. It has been reported that molecular simulation can predict the results ahead of experiments and obtain good agreements with experimental results[18-20]. In addition, it provides us useful molecular-level insight. Basically, there are two important classes of microscopic molecular simulations: Monte Carlo (MC) and molecular dynamics (MD)[21,22]. They are two different approaches deriving thermodynamics properties with different emphasis. MC simulation is a stochastic approach based on exploring energy surface by randomly probing the geometry of the molecular system. MD is a deterministic approach base on the time evolution of the molecular system providing the actual trajectory of the system. We employ both MC and MD simulations in this work. First we use Grand Canonical Monte Carlo (GCMC) simulation to compute the adsorption isotherms and obtain some other information such as adsorption sites. Then we use MD simulation to explore the trajectory path of RDX inside MOFs and calculate the self-diffusivities. Due to the increased computational speeds, long simulations via MD/MC can be carried out. These two simulations extract the complete set of information that we need to know.

In order to test the ability of MOFs preconcentrate RDX, we evaluate five different MOFs following the concept of tailoring MOFs to adsorb H_2 [23] and CH_4 [15]. These five MOFs have the similar structures, which consist of the same metal connectors (OZn_4) and different organic linkers. The MOFs with the same framework topology are called isorecticular MOFs (IRMOFs). The structures of the unit cells of the five IRMOFs are shown in Figure 1.4. The atom positions are from experimental X-ray diffraction data[24]. IRMOF-1 has the simplest structure, shown in Figure 1.4(a). IRMOF-1 has made of two distinct structural units, the metal cluster and the organic linker. The organic linkers of IRMOF-1 has the form of 1,4-benzenedicarboxylate (BDC). IRMOF-1 also has two different cages reflected by the orientation of BDC link, which makes the cages different pore size and pore volume[24]. In Figure 1.4, the small cages are in the center of the unit cell. The other four structures take IRMOF-1 as the parent structure, either changing the pore chemistry with functionalized organic amine group (NH_2) or expanding the pore size with long link. The former is IRMOF-3, shown in Figure 1.4(b), and the latter is IRMOF-10, shown in Figure 1.4(c). The left two structures are varied from IRMOF-10 with functionalized amine group at two different positions on the benzene rings, denoted as IRMOF-10a and IRMOF-10b in this work, as shown in Figure 1.4(d) and Figure 1.4(e), respectively. The organic linkers for the five IRMOFs are shown in Figure 1.5. The amine groups are disordered over the four sites, as indicated by the dashed circle in Figure 1.5. It should be noted that IRMOF-10a and IRMOF-10b do not have experimental data for the atom positions, but it can be synthesized without doubt[25]. These two structures represent changing both pore size and chemistry based on their parent structure (IRMOF-1). Moreover, there are thousands of functional groups

available to change the pore chemistry of the MOFs. The presence of amine group serves as electrostatic anchors for the RDX in this work. The unit cell length, unit cell mass and free volume for the five IRMOFs are shown in Table 1.1.

Another important achievement of this work is that we evaluate the force field, particularly the charge distribution, for RDX adsorption in MOFs. We compare different quantum mechanical (QM) calculation methods and calculate the charge distributions for RDX and MOFs. This creates a baseline for studying explosives in MOFs theoretically.

In addition to these five IRMOFs evaluated for RDX adsorption, hydrogen storage is also studied in a kind of new MOFs based on porphyrin as the linker. During the past ten years, hydrogen has been considered as the new generation energy source that is renewable and clean. However, the application is still being prevented by the difficulties from the technical challenges such as lack of safe and efficient hydrogen storage technologies. MOFs have considered as the promising materials. Unfortunately, still no materials can meet the goal of U.S. Department of Energy (DOE) Hydrogen Plan (2010) under ambient conditions. In this work, metal porphyrin frameworks (MPFs) are proposed. We evaluate H_2 adsorption in the MPFs via molecular simulation and estimate the ability of adsorption for this new material. MPFs are actually a new class of MOFs. The linker of MPFs consists of porphyrin, which makes the material more functional. The structure of porphyrin linker is shown in Figure 1.6. The porphyrin linker not only has metal inside, but also it can be functionalized to any form, as indicated in dashed circles in Figure 1.6. There are a variety of nanoporous porphyrin-based structures that have been synthesized, see for example [26,27]. The preliminary synthesis work has been

performed[28,29], although MPFs have not yet been well-characterized experimentally. It has been shown that it is a feasible task to build a porphyrin-based framework[30].

In the mean time to study explosive and hydrogen adsorption in nanoporous materials, we have developed a multiscale modeling technique that establishes a connection between the continuum-level of mass, momentum and energy transport balances in the inhomogeneous field and molecular-level simulation. This connection captures the important physics at all scales of description.

The overall focus of this work has been the study of the adsorption and diffusion of explosives in MOFs using molecular simulation and theory. The ultimate goal is to evaluate the ability and selectivity of MOFs to adsorb explosives as preconcentrators and understand how explosives interaction with MOFs. The major accomplishments of this research are constituted from chapter 2 to chapter 4. This work is organized as follows.

In chapter 2, we create a baseline for RDX in MOFs using IRMOF-1 since IRMOF-1 is the typical MOF that has been studied in a large number of literatures and the force field for IRMOF-1 is relatively accurate. In this chapter, many interesting and important phenomena, such as RDX structural changes and the effect of air components on RDX adsorption, have been observed.

In chapter 3, we study the QM methods for calculating the charge distributions using IRMOF-10 since the charge distribution is important as one of force fields in molecular simulation. The effect of charge distributions on RDX adsorption in MOFs has been found. Despite lack of experimental data, relative “best” charge sets have been established.

In chapter 4, the overall examinations on RDX adsorption in five IRMOFs have been made using the force field established in chapter 3. The ability of adsorption enhanced by the functional group has been validated.

In chapter 5, a new class of MOFs named MPFs is proposed in order to show the great functionality of this material. The ability of adsorption is observed via hydrogen storage that is another important application related to MOFs.

In chapter 6, a novel multiscale modeling technique for the connection between the description of continuum-level and molecular-level inhomogeneous fluids has been shown as a supplement to this work.

Appendix 1.A: Table and Figures

Table 1.1. The unit cell length, unit cell mass, free volume for IRMOFs studied in this work.

Structure	Unit cell length (Å)	Unit cell mass (Å)	Free volume (%)*
IRMOF-1	25.832	6156.8	79.8
IRMOF-3	25.7465	6516.8	77.9
IRMOF-10	34.2807	7980.8	87.1
IRMOF-10a	34.2807	8340.8	86.1
IRMOF-10b	34.2807	8340.8	86.3

*Free volume calculations are based on the geometry method in the reference [23].

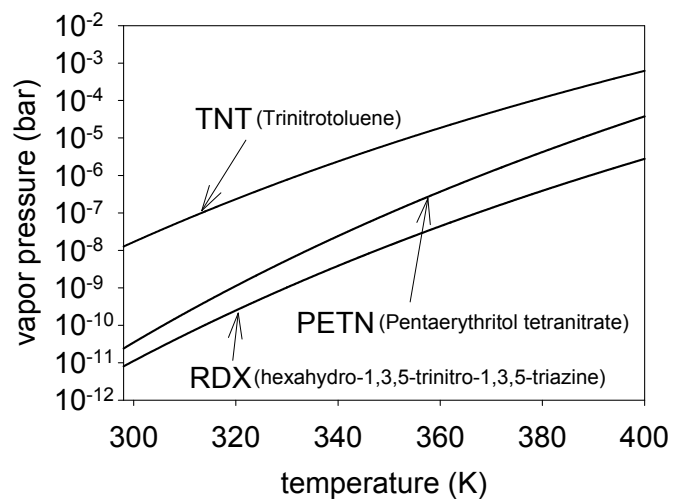


Figure 1.1. The vapor pressure of several common high explosives as a function of temperature[4].

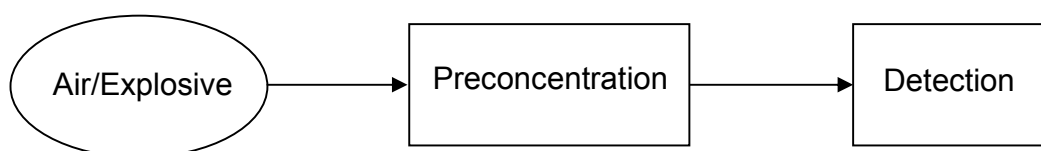


Figure 1.2. Schematic representation of a general trace detection method.

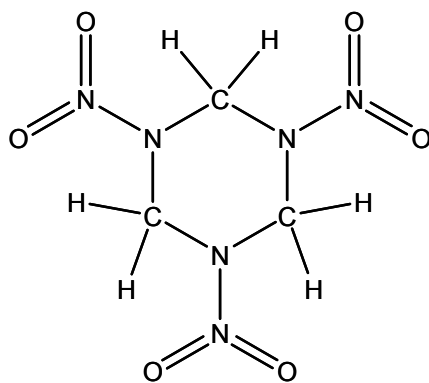


Figure 1.3. The structure of RDX.

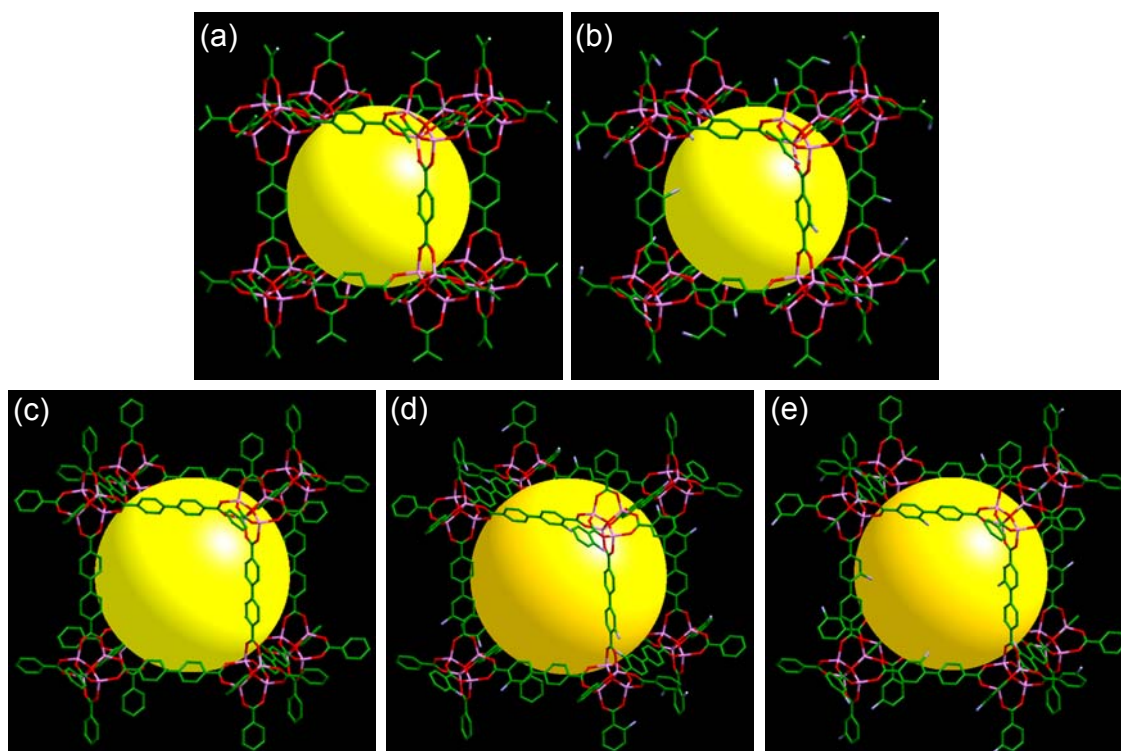


Figure 1.4. The super unit cell structures for the five IRMOFs studied in the work. Hydrogen is not shown. A yellow sphere is included to represent the orientation of benzene rings shows where the small cage located. (Legend: Zn, violet; O, red; C, green; N, blue.). (a) IRMOF-1; (b) IRMOF-3; (c) IRMOF-10; (d) IRMOF-10a; (e) IRMOF-10b.

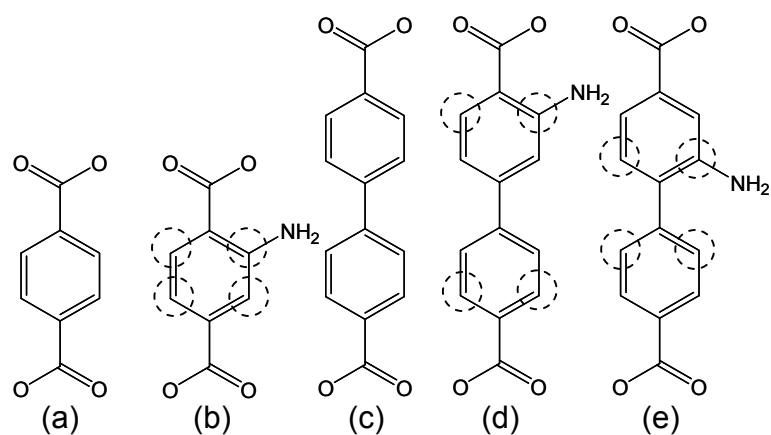


Figure 1.5. Five organic linkers for the structure of (a) IRMOF-1, (b) IRMOF-3, (c) IRMOF-10, (d) IRMOF-10a and (e) IRMOF-10b, respectively. NH_2 group is disordered over four sites, indicated in dotted circles. The unit cells of these five IRMOFs are shown in Figure 1.4.

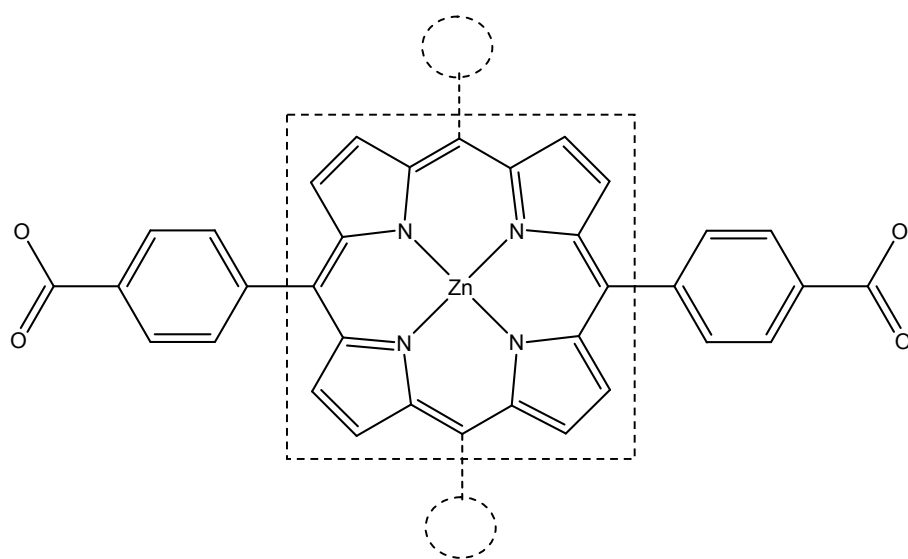


Figure 1.6. The structure for porphyrin-based linker. The porphyrin structure is shown in the dashed square. The metal in the center is not restricted to Zn atom.

CHAPTER 2

Molecular Simulations of Adsorption and Diffusion of RDX in IRMOF-1

This chapter is a slightly revised version of a paper by the same title published in *Molecular Simulation*, 2009 by Ruichang Xiong, Jared T. Fern, David J. Keffer, Miguel Fuentes-Cabrera and Donald M. Nicholson:

R. Xiong, J.T. Fern, D.J. Keffer, M. Fuentes-Cabrera, D.M. Nicholson, *Molecular Simulations of Adsorption and Diffusion of RDX in IRMOF-1*, Mol. Simul. **35** (10), 910 - 919, 2009.

The use of “we” in this part refers to the co-authors and the author of this dissertation. My primary contributions to this paper include (1) building computational models (2) development of the algorithm (3) creating programs to perform both GCMC and MD simulations (4) all of the simulation work (5) all of the figure and table generation and all of the writing.

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Abstract

In order to test the feasibility of using Metal-Organic Frameworks (MOFs) to pre-concentrate explosive molecules for detection, molecular simulations of RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) within IRMOF-1 were performed. Grand Canonical Monte Carlo (GCMC) simulations were used to generate adsorption isotherms for pure RDX, RDX in dry air, and RDX in wet air. In addition to the isotherms, the GCMC simulations provide adsorption energies and density distributions of the adsorbates within the MOF. Molecular Dynamics (MD) simulations calculate diffusivities and provide a detailed understanding of the change in conformation of the RDX molecule upon adsorption. The presence of dry air has little influence on the amount of RDX that adsorbs. The presence of wet air increases the amount of RDX that adsorbs due to favorable interactions between RDX and water. We found a Henry’s law constant of 21.2 mol/kg/bar for both pure RDX and RDX in dry air. The RDX adsorption sites are located (i) in big cages, (ii) near a vertex, and (iii) between benzene rings. The energy of adsorption of RDX at infinite dilution was found to be -9.2 kcal/mol. The distributions of bond lengths, bond angles and torsion angles in RDX are uniformly slightly broader in the gas phase than in the adsorbed phase, but not markedly so. The self-diffusivity of RDX in IRMOF-1 is a strong function of temperature, with an activation energy of 6.0 kcal/mol.

2.1 Introduction

There are many technologies for the detection of explosive molecules[31,32], including mass spectroscopy, ion mobility, surface acoustic wave spectroscopy, Swager-lasing-polymers, and Micro-Electro-Mechanical Systems (MEMs) devices. These detection devices incorporate some level of sampling and preconcentration. Unfortunately, current preconcentrators do not trap explosives specifically.

Metal-Organic Frameworks (MOFs) are a class of nanoporous adsorbents, which hold promise for preconcentration of explosive molecules. MOFs are composed of two distinct structural units, the metal connector and the organic linker, shown in Figure 2.1, which represents the specific example of IRMOF-1. Changing the connector and linker allows creation of MOFs that share similar structures but have pores with different sizes, shapes, and chemical functionalities[15]. That the size, shape, and chemical functionality of the pores can be modified readily has made MOFs a strong candidate for the storage of hydrogen[10,11,33] and methane[15,34]. A similar concept can be applied to tailor the explosive selectivity and storage capabilities of MOFs. Nicholson and co-workers[35] proposed MOFs as preconcentrator materials because of their unique measured and calculated properties[36]. Recently, it has been reported by Ni *et al.* that MOFs have successfully preconcentrated dimethyl methylphosphonate (DMMP)[37]. This demonstrates that MOFs can be quite useful as a selective preconcentrator, however, there are no published reports of the use of MOFs in preconcentrators for explosive compounds.

In this chapter, molecular simulation has been performed to investigate the capability of IRMOF-1[15] as an adsorbent for explosive preconcentration. Specifically,

we study the explosive RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine, CAS # 121-82-4), as shown in Figure 2.2. RDX is an important energetic material, and is widely used as rocket propellant and explosive. For example, RDX is used as a component of the plastic explosive C-4.

Classical force field-based molecular dynamics (MD) has proven to be a valuable tool in the study of RDX [38,39] in the bulk phase. A number of properties of RDX, such as vibrational frequencies and lattice binding energy and dimensions, can be reproduced in satisfactory agreement with experimental data[39].

In this chapter we examine RDX adsorption in IRMOF-1. The structure of IRMOF-1 is shown in Figure 2.1. IRMOF-1 has been studied as a starting point for a number of theoretical investigations on adsorption, for example, the storage of hydrogen[13]. IRMOF-1 contains two types of cages, which we will denote as “big” and “small”. The dimensions of the two types of cages are the same; both are cubic with a length of 12.92 Å[15]. However, the accessible volume in the two types of cages is different due to the orientation of the benzene rings. Big cages with a size of 14.3 Å in diameter consist of benzene rings in which the benzene planes are normal to a vector pointing to the center of the cell and small cages with a size of 10.9 Å in diameter consist of benzene rings in which the benzene planes are oriented toward the center of the cell[24]. The adsorption sites in big and small cages are not equivalent[40]. Figures 2.1(a) and 2.1(b) show a unit cell, containing 8 cages, with a small cage at the center of the image. The space filling image in Figure 2.1(b) gives both an indication of the accessible pore volume as well as a view of the orientation of the benzene rings. All six faces of the small cage open up to big cages and *vice versa*.

In this chapter, classical GCMC simulations are used to investigate the capability of IRMOF-1 to adsorb RDX. We are only interested in room temperature (300 K) and low partial pressure (<1 bar) since these are the typical conditions under which explosives detection occurs. (The purpose of preconcentrators is to concentrate material that may be present only in parts per billion or parts per trillion levels in air. For example, equilibrium vapor pressure of RDX at room temperature is 6 ppt [4].) Classical force field-based MD simulations are used to calculate the self-diffusivity of RDX in IRMOF-1. The GCMC simulations are first performed for pure RDX in order to establish a baseline. Simulations for adsorption of RDX from dry air (N₂ and O₂) and wet air (including H₂O) are also performed to understand the competitive adsorption.

2.2 Interaction Potential

For any classical force field-based molecular simulation, it is essential and important to choose an appropriate interaction potential as an input to the simulation. For the explosive adsorbate molecule, RDX, a number of intramolecular force fields have been proposed. Wallis and Thompson[38] constructed a new potential energy surface for MD simulation to study conformational changes of RDX in isolation and in a dense Xe gas. Chambers and Thompson[41] further refined this potential energy surface. Boyd *et al.* [39] generated an empirical nonreactive force field for RDX.

In this work, we employ a non-reactive, fully flexible, atomistic interaction potential for RDX that takes features from both Wallis and Thompson as well as Boyd *et al.*[38,39]. Essentially, we use all of the features of the potential from Boyd *et al.* except the non-Coulombic contribution to the non-bonded intramolecular and intermolecular

interactions. The non-Coulombic non-bonded interactions are taken from Wallis and Thompson, who used a Lennard-Jones (L-J) form. This allows us to maintain a common form of the dispersive interaction potential with the other species—N₂, O₂ and H₂O—that are also present in the simulation. The RDX intramolecular force field includes bond stretching, angle bending, torsion and non-bonded interactions. The electrostatic interaction is due to a permanent charge distribution, modeled as point charges at each atom center.

The simulations in dry air include molecular nitrogen and oxygen. It has long been known that it is important to include the effect of the quadrupole moment in the adsorption of N₂[42]. Therefore, we used a potential that includes quadrupoles for both N₂ and O₂. We used the three-site Transferable Potentials for Phase Equilibria (TraPPE) force field, which is an optimized potential for vapor-liquid equilibria (VLE) calculations[43,44]. This has also been used by Yang *et al.*[45] who successfully simulated N₂, O₂ and its mixture with CO₂ in Cu-BTC MOF. In this potential, each atom of the molecule is modeled by a L-J site on which a negative point charge is placed. To maintain charge neutrality, a positive point charge is placed at the center of mass (COM) of the molecule. In the published TraPPE force field, bond stretching is neglected. We add bond stretching to N₂ and O₂ with a harmonic potential[46,47].

The simulations of wet air include water. There are many choices for water potential. In this work, we use a three-site model[48]. The most commonly used three-site models are the transferable intermolecular potential with three interaction sites (TIP3P)[49], the simple point-charge (SPC) model[50] and their variants. Greathouse and Allendorf[51] used the flexible SPC model[52] to simulate water interacting with

IRMOF-1. In this work, we employ a flexible 3-site TIP3P potential[53], which also maintains a similar level of description in all adsorbate molecules. The H₂O molecule is modeled by a L-J site on the oxygen and a positive charge placed on each hydrogen atom and negative double charge placed on the oxygen atom to maintain charge neutrality.

There is an understanding that the use of water models parameterized to bulk data in nanoporous systems has a systematic error associated with it. For example, simulations of water in the silicalite zeolites[54] or in Cu-BTC MOF[55], require some empirical adjustment to match experiment. This limitation in potential estimation is addressed later on.

We have several choices for the treatment of the MOF. The first choice involves the mobility of framework atoms. Simulations have been performed comparing the adsorption isotherms of hydrogen in flexible and rigid IRMOF-1. There is a body of work describing the effect of a rigid lattice on the mobility of adsorbates in crystalline nanoporous materials. This work shows that for small adsorbates, the effect of frame rigidity is nominal[56-59]. However, for larger adsorbates, the effect may be significant[60,61].

Studies of MOFs indicate that framework flexibility may be more important in MOFs than in zeolites and other nanoporous materials[62]. Nevertheless, in this work we have assumed a rigid framework, as has been used in other simulations of adsorption in MOFs[13,24,34,55,63-65]. This choice is also motivated by the fact that there are many more framework atoms than adsorbate atoms at low loadings, thus the computational effort is reduced by two or more orders of magnitude by using a rigid framework. In this

case, the coordinates of the framework IRMOF-1 are set at their equilibrium coordinates as determined via experimental x-ray diffraction[15].

There are several potentials that can be used for IRMOF-1, such as universal force field (UFF)[66], DREIDING force field[67], and OPLS force field[68]. Greathouse and Allendorf[51] used the CVFF force field for structurally flexible IRMOF-1 to do MD simulation for H₂O adsorption. Later Greathouse and Allendorf[69] provided a detailed validation for this force field to demonstrate it can predict a number of important properties of MOFs accurately. Tafipolsky *et al.*[70] developed an *ab initio* parameterized MM3 force field, which is a fully bonded but flexible force field that can predict IRMOF-1 structure successfully. Here we employ the MM3 force field from Tafipolsky *et al.*[70], in which the L-J parameters are taken from Allinger *et al.*[71,72], which is the same source for L-J parameters used for RDX. We acknowledge that Tafipolsky *et al.*[70] have indicated that, in their determination of the partial charge of atoms, there is uncertainty on some charges (especially the central oxygen atom). These charges may have a non-negligible impact in the calculation of thermodynamic properties such as adsorption isotherms.

For all intermolecular interactions, the mixture parameters are determined via Lorenz-Berthelot mixing rules[21]. The electrostatic interactions are handled using the spherically truncated charge-neutralized procedure of Wolf *et al.* [73]. The L-J potential and electrostatic potential were truncated at 18 Å. Potential parameters for all the adsorbates and framework can be found in the cited literature and part of them are listed in Appendix 2.B. Due to the relatively long cut-off distance, no long-range corrections are applied for L-J interaction, as has been done previously[65]. Standard periodic

boundary conditions and the minimum image convention are employed in all three dimensions.

2.3 Simulation Methods

Classical equilibrium MD simulations are performed to obtain configurations and diffusivities of RDX adsorbed in nanoporous materials. We integrate the equations of motion using the two-time step r-RESPA algorithm of Tuckerman and co-workers[74]. Intramolecular degrees of freedom were accounted for in the short time loop, with a step size of 0.2 fs. There are 10 short steps per long time step. The temperature is controlled using the Nosé-Hoover thermostat[75,76]. We equilibrate the system for 2 ns. Following equilibration, we simulate an additional 8 ns for data collection. During data production, positions of the center-of-mass of the RDX molecules are saved every 5 ps and used to calculate the self-diffusivity via the Einstein relation. Uncertainties in the self-diffusivity are reported as the standard deviation of the x, y, and z components of the diffusivity.

Also in this work, conventional GCMC simulations are performed to obtain adsorption isotherms, which relate the loading (*i.e.* the weight fraction of adsorbate in the adsorbate/adsorbent system) to the bulk pressure of the adsorbate gas in equilibrium with the adsorbent. The GCMC simulation technique for molecular systems is from Wang *et al.*[77]. We performed GCMC simulation with 4 types of moves: (1) molecular translation based on center-of-mass, (2) molecular rotation based on center of mass, (3) molecular insertion with random position and random orientation, (4) molecular deletion of a molecule in the system. Translation and rotation are accepted or rejected according to Metropolis procedure[78] based on $e^{-\beta\Delta H}$, where ΔH is the change in the total energy

as a result of the move. The acceptance ratio is adjusted to 50% based on the maximum size of position changes or rotational angle changes. The inserted particle is chosen by randomly picking a configuration from the pool where a large number of ideal gas equilibrium configurations at specified temperature are stored.

We will show below, using MD simulation, that there is no significant difference in the distribution of the intramolecular conformations of RDX in bulk gas phase and in the adsorbed phase at the low loadings of interest. Therefore, intramolecular relaxation of the RDX is not sampled in the GCMC simulations, increasing the computational efficiency of the GCMC simulations.

Each of the GCMC moves is attempted with a fixed possibility ratio. The ratio for making a displacement, rotation, insertion and deletion is set to 4:2:3:3 in GCMC simulation. The initial positions is randomly inserted into the accessible volume of the system. The GCMC simulations are allowed to equilibrate with at least 1×10^8 MC steps before the data production with another 1×10^8 MC steps is run to sample the thermodynamic properties of interest. Details of standard GCMC simulation algorithm can be found elsewhere[21,22].

In a GCMC simulation, the temperature, volume and chemical potential are specified. Thus from a single GCMC simulation of the adsorbed phase, one can relate the amount adsorbed to the chemical potential of the adsorbed phase. Since the chemical potential of the adsorbed phase is the same as the bulk phase at equilibrium, this is also the bulk chemical potential. However, in order to generate isotherms in terms of the bulk pressure, we perform a second set of GCMC simulations of the bulk phase at the same set of chemical potentials as used in the adsorbed phase simulations. This allows us to

convert the chemical potential to the more practical bulk pressure. Thus each data point on the isotherm is generated by two simulations, one of the adsorbed phase providing the loading as a function of chemical potential and one of the bulk phase providing the pressure as a function of the same chemical potential. Desbiens *et al.*[79] have also used a similar procedure to generate each point on the isotherm from distinct simulations of the bulk and adsorbed phase. The two molecular simulation programs (MD and GCMC) have been developed in our laboratory. MD is parallelized using MPI.

2.4 Results and Discussion

2.4.1. Pure RDX

We performed simulations of RDX in IRMOF-1 at 300 K across a set of loadings that correspond to bulk pressures ranging from 0 (infinite dilution) to 1 bar. In order to obtain good statistical uncertainties, the simulation box representing the adsorbent varies from $(12 \times 12 \times 12)$ to $(325 \times 325 \times 325)$ unit cells (as pictured in Figure 2.1) with the periodic boundary conditions exerted in all three directions. The size of the system is based on obtaining a simulation with a sufficient number of adsorbate molecules (at least 1000), required to obtain reasonable uncertainties. Unless otherwise mentioned, the uncertainties are smaller than the symbol sizes in the figures presented. The resulting adsorption isotherm is shown in Figure 2.3. The maximum loading studied is less than 3 molecules per 10 cages, half of which are big cages and half of which are small cages. We observe from the simulation that at 300 K virtually all RDX molecules are located in big cages. Thus, even at our highest loading we are below 6 molecules per 10 big cages. In our simulations we do not observe more than one RDX molecule per cage (either

type). We do observe significant non-linear behavior in the adsorption isotherm as we begin to have a substantial fraction of the big cages filled with one RDX.

At low loadings, we observe the linear part of the isotherm, shown as an insert in Figure 2.3. This linear regime is particularly of interest because this corresponds to the very low partial pressures of RDX, where it is present at realistic ppb or ppt levels. The linear regime extends to about 1×10^{-4} bar, which is well above realistic RDX partial pressures. Thus, all practically relevant systems are in the linear regime. At room temperature, the linear regime is defined by a Henry's law constant of 16.3 molecules/cage·bar (21.2 mol/kg/bar) for RDX in IRMOF-1, which is substantially larger than that of hydrogen in IRMOF-1 of 0.3 mol/kg/bar[10], CO₂ in IRMOF-1 of 0.9 mol/kg/bar and CH₄ in IRMOF-1 of 0.4 mol/kg/bar [24].

In Figure 2.4, we plot isodensity surfaces for the center-of-mass of RDX in IRMOF-1 at 300 K and infinite dilution. The volume within these isodensity surfaces is where the highest probability of finding an RDX molecule exists. We will refer to these volumes as adsorption sites. Outside the isodensity surface, a lower RDX density exists. In Figures 2.4(a), (b) and (c) we show the isodensity surfaces with reference to the framework of the entire cage. A small cage is at the center of the image. All density surfaces are centered around vertices. Each vertex is part of 8 cages—4 big and 4 small cages. In Figures 2.4(a), (b) and (c), the four-fold symmetry of the adsorption sites is readily apparent. These four adsorption sites exist exclusively in the big cages. In other words, all adsorption occurs in the big cages. This is also the case for the adsorption of benzene in IRMOF-1[80].

In Figures 2.4(a), (b) and (c), the value of density at which the isodensity surface is plotted is increased from (a) to (c). Thus the adsorption sites become smaller, defining more localized regions of space with the commensurately higher probabilities of finding RDX molecules. We see that there is an internal structure to the adsorption sites. This internal structure is better visualized by examining Figures 2.4(d), (e) and (f), in which we show the same isodensity surfaces with reference to a single vertex. In these latter three figures, the viewpoint is from the center of the big cage. Here we see that the center of the adsorption site is not as favorable as an outer ring. Further increase in the density of the surface shows that there is in fact a three-fold symmetry of sub-sites within the adsorption site. These sub-sites are located between the three benzene rings that extend from the vertex and form the adjacent edges of the big cage. Thus we can characterize the adsorption of an RDX molecule as (i) residing in a big cage, (ii) near a vertex, and (iii) between benzene rings.

The isodensity surfaces are based on RDX center-of-mass positions. For information regarding the orientation of the RDX molecule, we examine snapshots from the simulation. In Figures 2.5 (a) and (b), we show a snapshot of one RDX molecule residing in this adsorption site from the view of the cage and a single vertex. This snapshot was judged to be a typical RDX orientation based on an inspection of a set of snapshots. In this snapshot, we see that there is a strong interaction (Zn-O distance is ~ 2.0 Å) formed between a Zn atom in the vertex and one of the two O atoms of one of the three nitro groups on the RDX molecule. The second O atom of the same nitro group forms a weaker interaction (Zn-O distance is ~ 3.6 Å) with another Zn atom in the same vertex. The other two nitro groups are not interacting closely with the vertex. The

orientation of the RDX plane (as defined by the three N atoms) is mobile within each sub-site, moving from being nearly parallel with one benzene ring to nearly parallel with the other ring. In Figure 2.5(c), we show a particular trajectory where a RDX moves from small cage (position 1) to big cage (position 3). This diffusion event can be characterized as a big cage through small cage to big cage motion. However, the RDX molecule ends up at a different vertex. The diffusion event for benzene in IRMOF-1 is also a big cage through small cage to big cage motion, but the molecule is reported to end up at the same vertex[80].

In Figure 2.6, we show a representative plot of selected structural elements of RDX—the bond distance, bending angles and the torsion—in the ideal gas and in IRMOF-1 at a loading of 0.0625 RDX/cage at 300 K. The solid lines indicate RDX in IRMOF-1 while open symbols represent the bulk gas phase. The RDX molecule undergoes subtle changes in conformation when adsorbed within IRMOF-1 relative to the bulk gas phase at room temperature. In all three plots of Figure 2.6 we observe that the breadth of the distribution functions for bond distance, bending angles and torsion angles for RDX in IRMOF-1 slightly decreases compared to the bulk but the average values remain the same.

The adsorption energy of RDX in IRMOF-1 at room temperature is shown in Figure 2.7. As we can see in Figure 2.7(a), the binding energy is about -9.2 kcal/mol, which is in good agreement with quantum chemistry calculation of -8.8 kcal/mol[81]. The total potential energy in the system increases until 0.2 bar and then changes slightly. We also observe the adsorbate-adsorbate potential energy increases with increasing pressure. This is because of an unfavorable RDX-RDX electrostatic interaction shown in

Figure 2.7(b) and (c), which is likely due to orientations imposed by the framework. The four adsorption sites of RDX have significant attractive electrostatic interactions with the RDX.

In Figure 2.8, we show self-diffusivities of RDX and average travelled distances at different temperatures, which varies from 200 K to 500 K. To determine the self-diffusion coefficient, the mean square displacement (MSD) as shown in Figure 2.9 is examined. The diffusion regime starts at about 4 ns, with a slope of 1 in the double logarithmic plot of the averaged MSD, shown as an insert in Figure 2.9. The self-diffusivity of RDX in IRMOF-1 is a strong function of temperature. An Arrhenian fit of the diffusion coefficient ($D = D_o \exp(-E_a / RT)$) is also shown in Figure 2.8. The activation energy, E_a , for diffusion is 6.0 kcal/mol, which can be compared with activation energy for the diffusion of benzene, methane and ethane in IRMOF-1 of 1.0, 2.0 and 2.3 kcal/mol, respectively[80,82].

In Figure 2.8, we also show the mean distances travelled by the end of the simulation (square root of the final MSD). At 200 K, we do not observe intercage motion, since the average distance travelled is no larger than the cage dimension. At room temperature, we find a self diffusivity for RDX in IRMOF-1 of $(4.55 \pm 0.44) \times 10^{-11}$ m²/s, which is two order of magnitude lower than the diffusion of benzene in IRMOF-1[80].

For the purposes of preconcentrating RDX for sensors, one naturally wonders if this low RDX diffusivity at room temperature precludes IRMOF-1 as a potential adsorbent based strictly on the mobility criterion. Crystals of IRMOF-1 vary from 50 to 150 μm [83]. Thus an order of magnitude estimate of the time RDX would take to

diffuse out of an IRMOF-1 crystal at room temperature is from 55 to 454 seconds, which potentially could lie within an operational timescale.

2.4.2. RDX in Framework with Air

In service as a preconcentrator, the MOF not only adsorbs RDX, but also is struck by other molecules in the air. In our work, we modeled dry air as a mixture of N_2 and O_2 . The bulk pressure of the dry air is atmospheric pressure. In Figure 2.10, we show adsorption isotherms for RDX, N_2 and O_2 as a function of the partial pressure of RDX in the bulk phase. This partial pressure of RDX is defined as the product of the mole fraction of RDX and the total pressure in the bulk simulation. In this series of simulations, the chemical potentials of N_2 and O_2 are held constant, while the chemical potential of RDX is varied. We see in Figure 2.10, that there is very little interaction between the three adsorbents. The amount of N_2 and O_2 is virtually independent of the amount of RDX adsorbed. This is because N_2 and O_2 don't have well-defined adsorption sites[84,85] and are present in fairly small quantities. Furthermore, the RDX adsorption isotherm from this mixture is virtually the same as that of pure RDX, especially in the low pressure limit of practical interest (as seen in the insert). The Henry's law constant for RDX in dry air is the same as that for pure RDX isotherm.

We also simulated adsorption of RDX in the presence of wet air. We acknowledged above that in order to quantitatively reproduce adsorption isotherms of water in MOFs, empirical adjustments are required [54,55]. To avoid this empiricism, we performed a series of grand canonical Monte Carlo simulations of the RDX, N_2 and O_2 in an adsorbent with a fixed number of water molecules. We performed canonical

Monte Carlo simulations of the H_2O , translating and rotating them, but not inserting or deleting them. We limit ourselves to low water content, since IRMOF-1 is known to be unstable at higher water contents (>4 wt%)[51].

In Figure 2.11, we show adsorption isotherms for RDX, N_2 and O_2 at a partial pressure of RDX corresponding to 1 bar as a function of water content in the MOF. We choose a relatively high partial pressure of RDX in order to have a significant amount of RDX present in the system without having to simulate billions of water molecules. The presence of water does not affect the adsorption of N_2 and O_2 . However, the amount of RDX adsorbed increases with increasing water content. In order to explain this result, we can examine the contribution to the potential energy as shown in Figure 2.12. Both water and RDX are competing for adsorption sites near the vertices of the big cage. Therefore as loading increases, we see an unfavorable increase in the RDX-framework contribution to the potential energy. However, we see a more significant favorable decrease in the interactions between RDX and other adsorbates, due to attractive electrostatic interactions between the water and the RDX. Thus, we see RDX and water molecules clustered around the vertices, paying a slight energetic penalty for sharing adsorption sites that is more than compensated for by the enhanced adsorbate-adsorbate interactions.

2.5 Conclusions

MD and GCMC simulations have been performed to understand the adsorptive and diffusive behavior of RDX in IRMOF-1. We generated adsorption isotherms for pure RDX, RDX in dry air, and RDX in wet air. We found a Henry's law constant of 21.2 mol/kg/bar for both pure RDX and RDX in dry air. The presence of water increases the

amount of RDX adsorbed. The RDX adsorption sites are located (i) in big cages, (ii) near a vertex, and (iii) between benzene rings. The energy of adsorption of RDX at infinite dilution was found to be -9.2 kcal/mol. The distributions of bond lengths, bond angles and torsion angles in RDX are uniformly slightly broader in the gas phase than in the adsorbed phase, but not markedly so. The self-diffusivity of RDX in IRMOF-1 is a strong function of temperature, with an activation energy of 6.0 kcal/mol. The path for diffusion can be considered as a motion from the deep adsorption site in a big cage through a small cage to another big cage. This path is similar to that shown for benzene in IRMOF-1, although in that case the destination vertex was the same as the originating vertex, which is not observed for RDX.

2.6 Acknowledgements

The authors gratefully acknowledge the financial support of National Science Foundation (NSF) under grant CMMI-0730207. Work at Oak Ridge National Laboratory (ORNL) was supported by the Center for Nanophase Materials Sciences, sponsored by the Division of Scientific User Facilities, U.S. Department of Energy (USDOE) and used resources of the National Center for Computational Sciences (NCCS), ORNL, supported by the Office of Science, USDOE, as well as resources of the National Institute for Computational Sciences (NICS), ORNL, supported by NSF with agreement number: OCI 07-11134.

Appendix 2.A: Figures

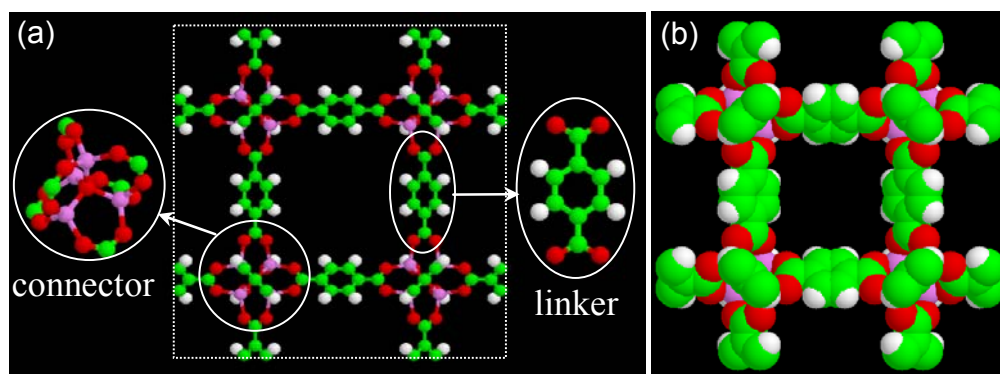


Figure 2.1. (a) IRMOF-1 structure with a small cage in the center; (b) space-filling image of IRMOF-1 (legend: violet-Zn, red-O, green-C, white-H).

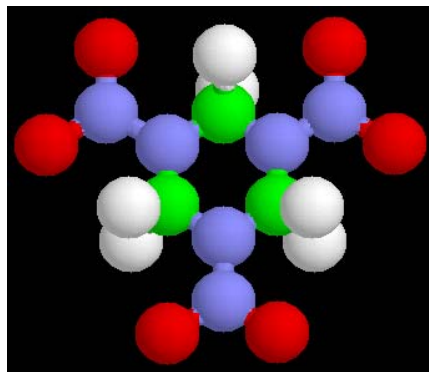


Figure 2.2. RDX structure (legend: blue-N, red-O, green-C, white-H).

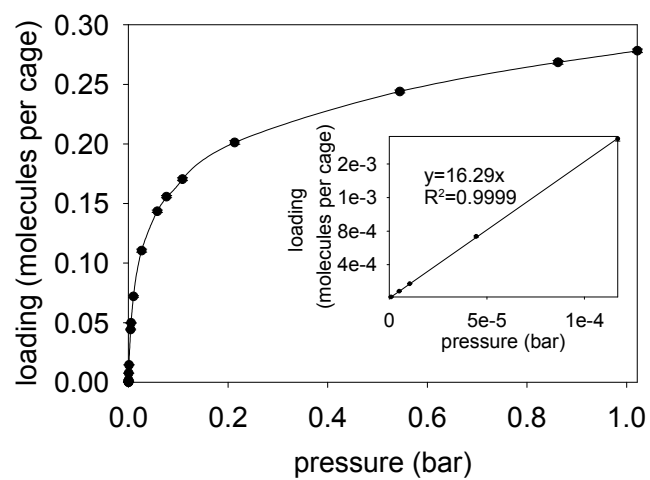


Figure 2.3. Isotherm of RDX in IRMOF-1 from infinite dilution to 1 bar. The inset shows the linear fitting plot of the infinite dilution data.

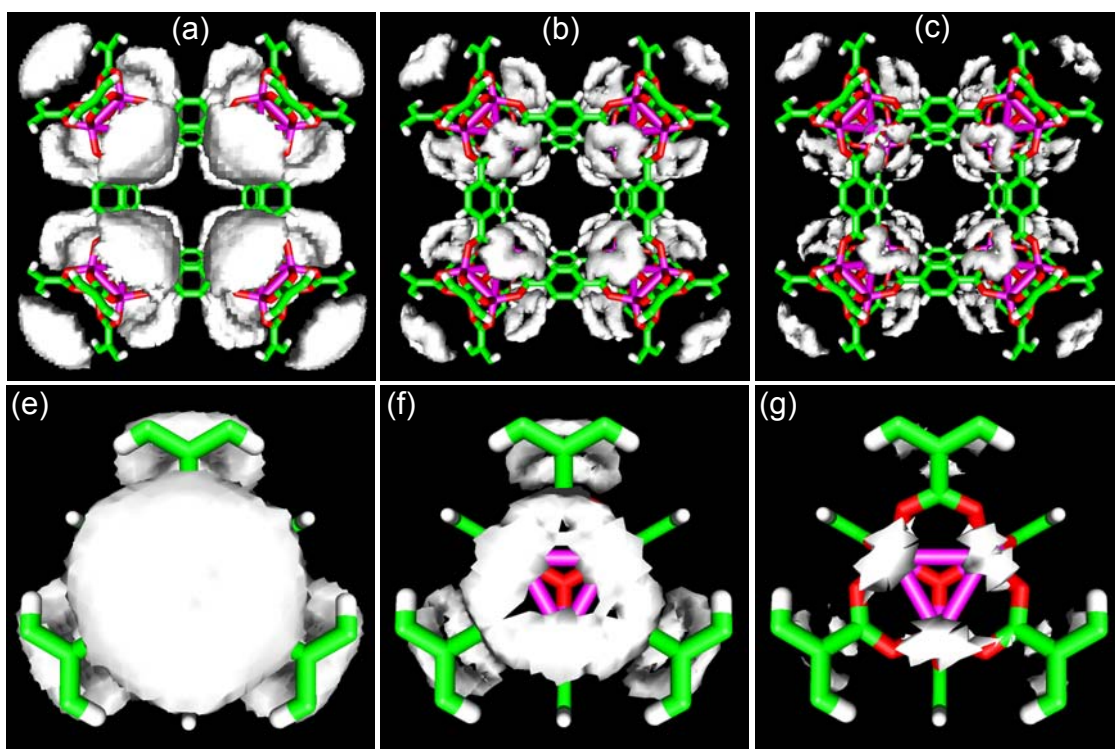


Figure 2.4. Density distribution of RDX in IRMOF-1 with density contour level from low to high (both full cage and vertex view) at 300 K and infinite dilution.

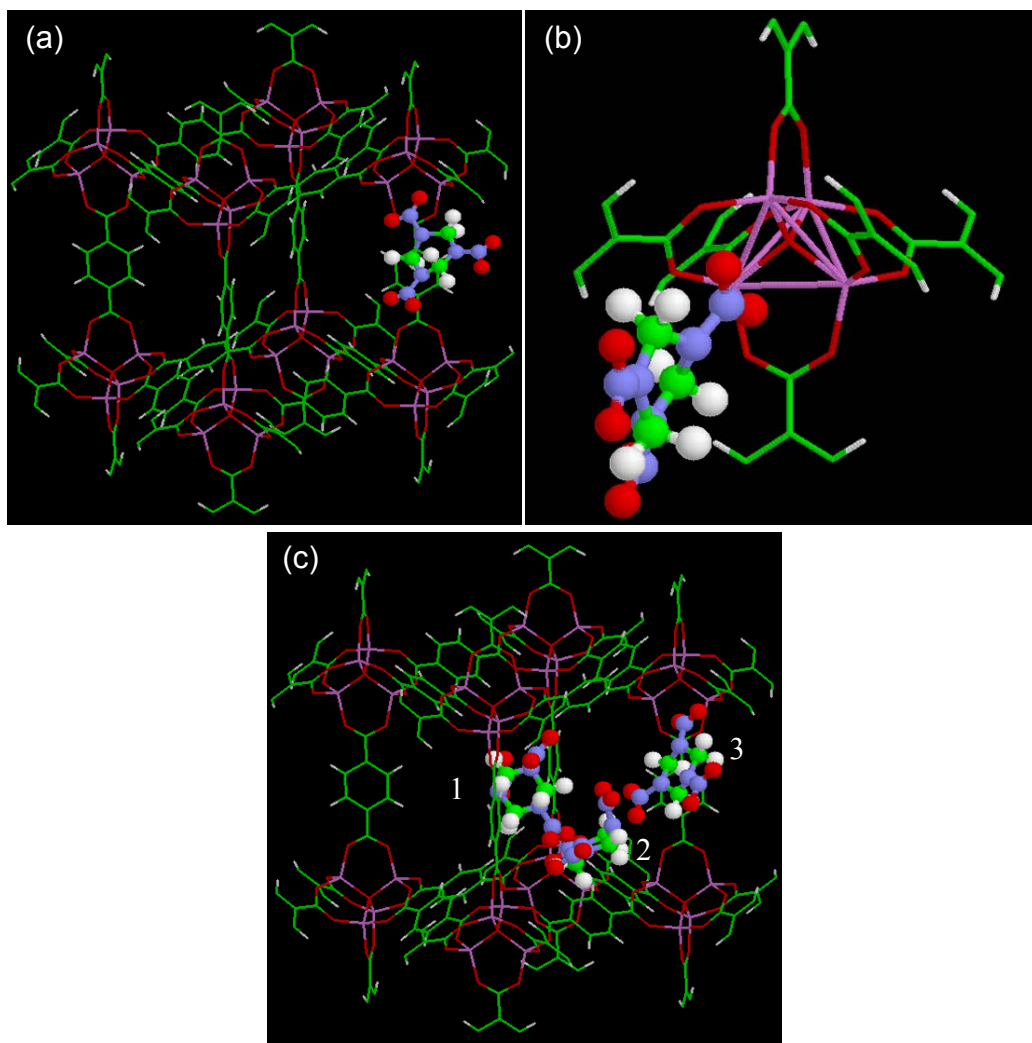


Figure 2.5. Snapshots of RDX configuration in IRMOF-1 (both full cage and vertex view), RDX is currently residing in one of three adsorption sites around the vertex in a big cage (legend: blue-N, red-O, green-C, white-H).

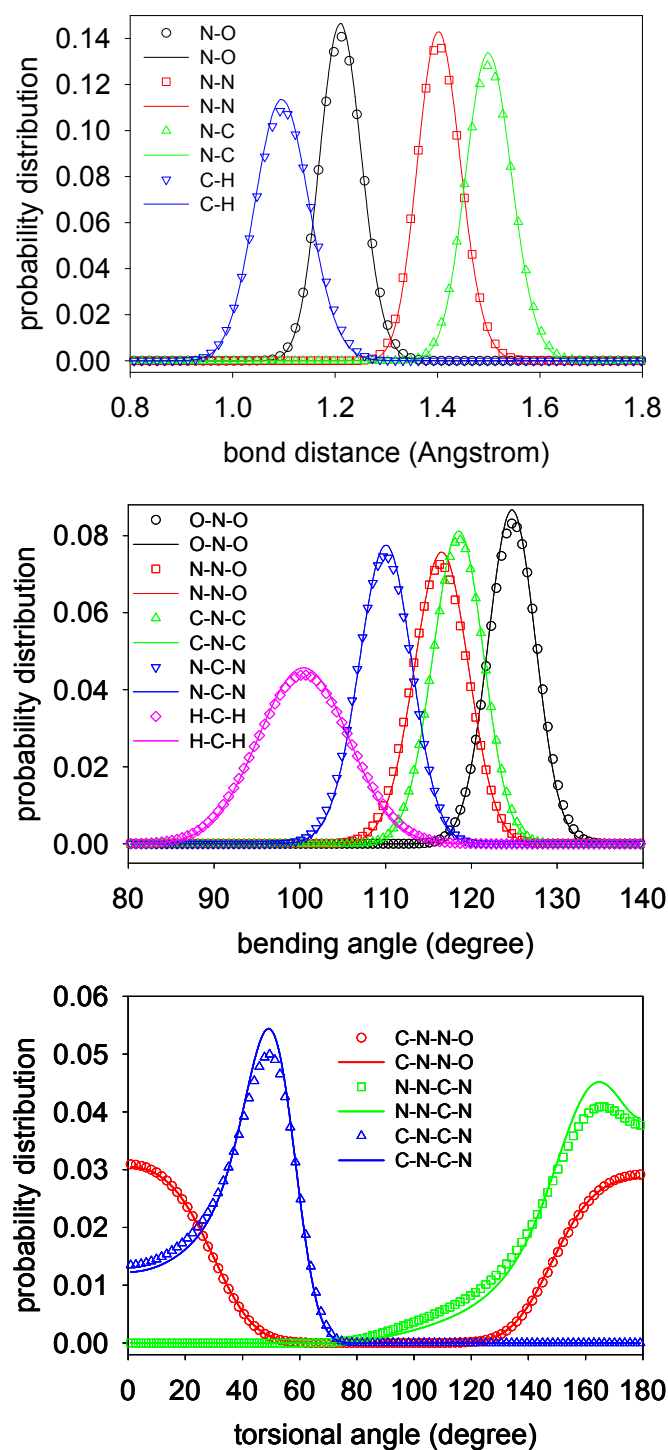


Figure 2.6. Conformational distribution (bond stretching, bond bending and torsion) in bulk and adsorbed phase at 300K. Properties in bulk phase are shown as open symbols and properties in adsorbed phase are shown as solid lines.

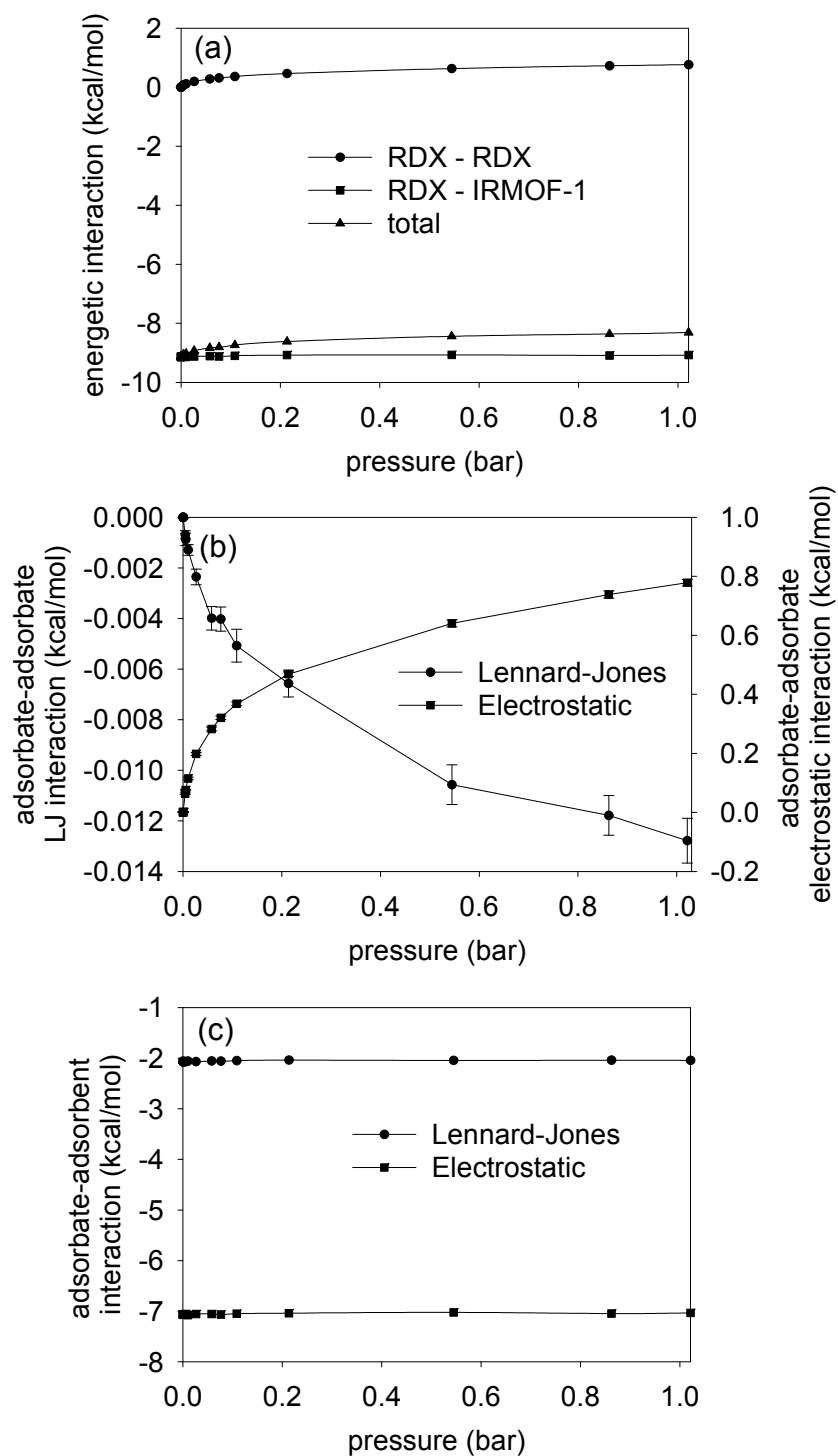


Figure 2.7. Interaction energies of RDX in IRMOF-1 from infinite dilution to 1 bar at 300K. The energies are per mole of RDX.

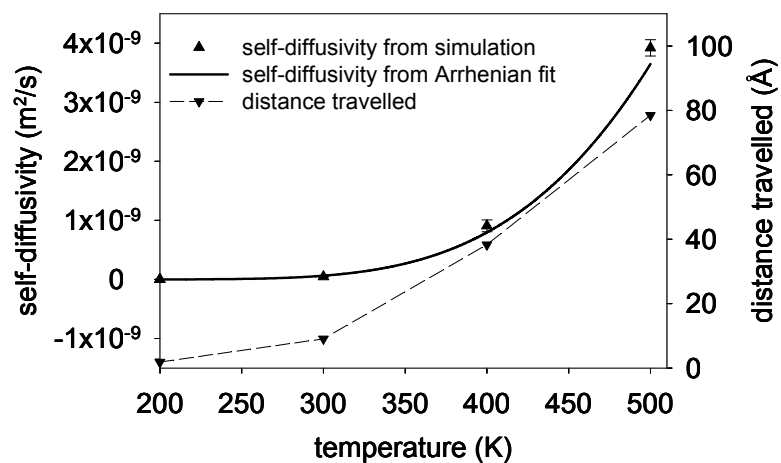


Figure 2.8. Self-diffusivity and Arrhenian fit for RDX in IRMOF-1, as well as average distance travelled at different temperatures from 200 K to 500 K.

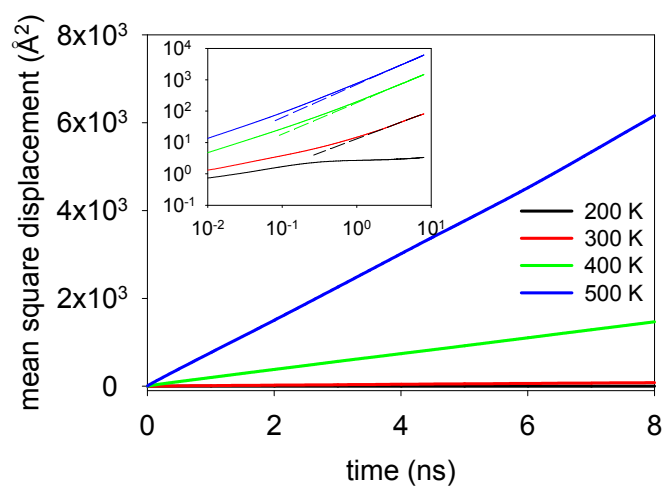


Figure 2.9. Mean square displacement in different temperatures from 200 K to 500 K. The inset shows the log-log plot, giving a slope of 1 (dashed line).

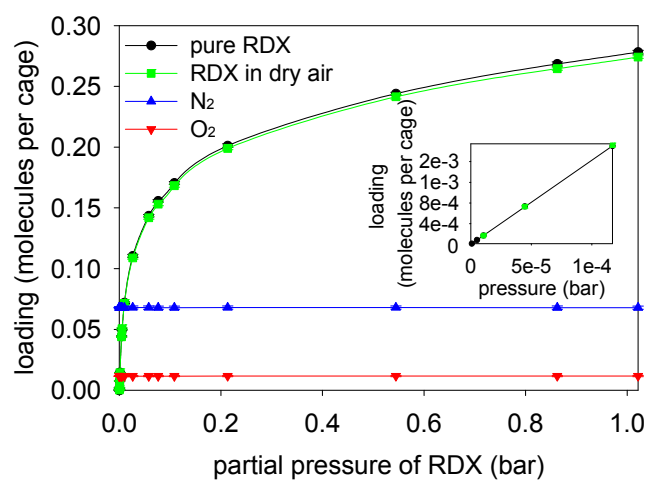


Figure 2.10. Isotherm of RDX mixed with dry air in IRMOF-1 from infinite dilution to 1 bar. The inset shows the linear fitting plot of the infinite dilution data.

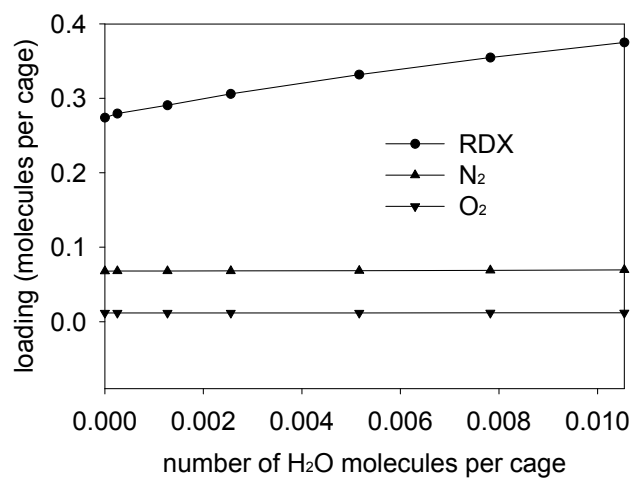


Figure 2.11. The effect of water on RDX adsorption at 300K. The partial pressure for RDX is 1 bar.

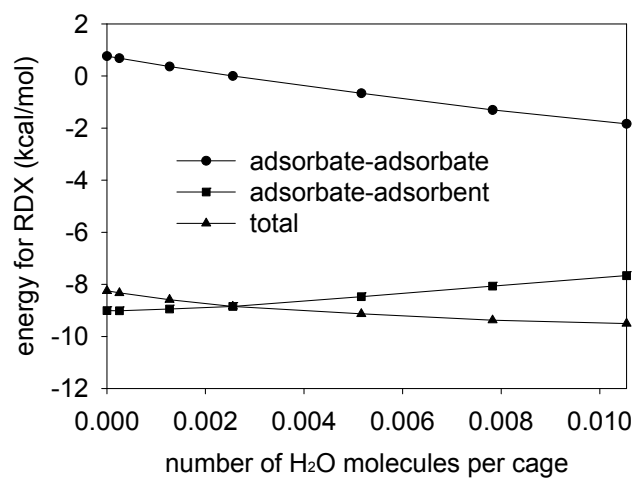


Figure 2.12. The interaction energies for RDX in mixture (RDX and wet air) at 300K.

Appendix 2.B: Supporting Information

The interaction potential parameters for RDX, N₂, O₂, H₂O and IRMOF-1 are listed in Table S-2.1, Table S-2.2, Table S-2.3, and Table S-2.4, respectively. Parameters for bond stretching of RDX in the intramolecular potential can be found in reference [38]. Parameters for bond bending and torsion of RDX in the intramolecular potential can be found in reference [39].

We performed a set of simulations to demonstrate that the bulk phase is an ideal mixture for the entire pressure range studied in this work. This test allows us to use the pressures obtained from the bulk simulation of the pure components (RDX, N₂ and O₂) as partial pressures in the mixture. In Table S-2.5, we calculated the pressure from pure component and mixture simulations for two partial pressures of RDX, 1.0 and 0.86 bar. The partial pressure of each component in the mixture is the same as that in the pure component gas within system error.

Detailed information, including chemical potential, simulation volume and number of molecules, for each simulation of a pure component in bulk and in IRMOF-1 is provided in Table S-2.6.

Detailed information, including simulation volume and number of molecules of each component, for each simulation of the mixture in IRMOF-1 is provided in Table S-2.7.

In Figure S-2.1, we compare the RDX bulk simulations with the ideal gas law. Deviations to the ideal gas law only occur well above any practical RDX pressure.

Appendix 2.C: Tables and Figure in the Supporting Information

Table S-2.1. L-J parameters and charges for RDX [38,39].

Atom	σ (Å)	ε/k_b (K)	q (e)
C	3.64	15.1	0.058
N	3.24	31.2	-0.137
N (nitro)	3.24	31.2	0.272
O	2.94	1.0	-0.267
H	2.89	11.1	0.101

Table S-2.2. Potential parameters for N₂ and O₂.

Atom	σ (Å)	ε/k_b (K)	q (e)
N (in N ₂) [43]	3.31	36.0	-0.482
COM (in N ₂) [43]	0.0	0.0	+0.964
O (in O ₂) [44]	3.02	49.0	-0.113
COM (in O ₂) [44]	0.0	0.0	+0.226
bond	r^0 (Å)	k_s (kcal·mol ⁻¹ ·Å ⁻²)	
N-N [46]	1.09	3185.788	
O-O [47]	1.21	1696.206	

Table S-2.3. Potential parameters for water [49,53].

Atom	σ (Å)	ε/k_b (K)	q (e)
O (in H ₂ O)	3.15	76.6	-0.834
H (in H ₂ O)	0.0	0.0	+0.417
Bond	r^0 (Å)	k_s (kcal·mol ⁻¹ ·Å ⁻²)	
O-H	0.96	1059.162	
Bending angle	θ (deg)	k_θ (kcal·mol ⁻¹ ·deg ⁻²)	
H-O-H	104.5	68.087	

Table S-2.4. The L-J parameters and charges for symmetrically independent atoms on IRMOF-1 [70].

Atom	σ (Å)	ε/k_b (K)	q (e)
O _{cent}	1.62	29.69	-1.44
Zn	2.04	138.89	1.26
O _{carb}	1.62	29.69	-0.67
C _{carb}	1.73	28.18	0.68
C _{ph} (-C _{carb})	1.73	28.18	0.06
C _{ph}	1.73	28.18	-0.16
H	1.44	10.06	0.16

Table S-2.5. Bulk gas pressure comparison for simulation in pure component and mixture.

Specie	group 1		group 2	
	pure	mixture	pure	mixture
N ₂	0.738±0.023	0.767±0.033	0.738±0.023	0.759±0.032
O ₂	0.183±0.006	0.190±0.017	0.183±0.006	0.189±0.016
RDX	1.028±0.028	0.986±0.033	0.868±0.026	0.836±0.030
Total	1.949±0.037	1.943±0.050	1.789±0.036	1.784±0.049

Table S-2.6. Pure component in IRMOF-1.

Molecule type	Specified chemical potential (aJ/molecule)	Simulation volume*		Results		
				bulk		IRMOF-1
		bulk	IRMOF-1	density (mol/liter)	pressure (bar)	number of molecules adsorbed
N ₂	-6.59×10 ⁻²	20×20×20	11×11×11	0.0296±0.0006	0.737±0.015	723±27
O ₂	-7.25×10 ⁻²	32×32×32	20×20×20	0.0073±0.0001	0.183±0.004	743±28
RDX	-7.55×10 ⁻²	18×18×18	12×12×12	0.0377±0.0006	1.021±0.019	3845±21
	-7.65×10 ⁻²	19×19×19	12×12×12	0.0322±0.0005	0.862±0.016	3711±23
	-7.90×10 ⁻²	22×22×22	13×13×13	0.0209±0.0004	0.545±0.010	4288±21
	-8.35×10 ⁻²	31×31×31	14×14×14	0.0084±0.0002	0.213±0.004	4417±33
	-8.65×10 ⁻²	38×38×38	14×14×14	4.3e-3±8.3e-5	0.108±0.002	3741±27
	-8.80×10 ⁻²	43×43×43	15×15×15	3.1e-3±5.8e-5	7.7e-2±1.5e-3	4206±26
	-8.92×10 ⁻²	47×47×47	15×15×15	2.3e-3±4.5e-5	5.8e-2±1.1e-3	3875±29
	-9.25×10 ⁻²	61×61×61	17×17×17	1.1e-3±2.0e-5	2.6e-2±5.1e-4	4340±51
	-9.65×10 ⁻²	84×84×84	19×19×19	4.1e-4±8.0e-6	1.0e-2±2.0e-4	3951±34
	-9.92×10 ⁻²	104×104×104	22×22×22	2.1e-4±4.2e-6	5.3e-3±1.0e-4	4245±34
	-1.00×10 ⁻¹	111×111×111	23×23×23	1.8e-4±3.5e-6	4.4e-3±8.5e-5	4310±44
	-1.06×10 ⁻¹	180×180×180	34×34×34	4.1e-5±8.1e-7	1.0e-3±2.0e-5	4572±41
	-1.09×10 ⁻¹	229×229×229	42×42×42	2.0e-5±3.9e-7	5.0e-4±9.8e-6	4527±43
	-1.15×10 ⁻¹	372×372×372	66×66×66	4.7e-6±9.2e-8	1.2e-4±2.3e-6	4371±64
	-1.19×10 ⁻¹	513×513×513	90×90×90	1.8e-6±3.5e-8	4.5e-5±8.7e-7	4300±53
	-1.25×10 ⁻¹	831×831×831	145×145×145	4.2e-7±8.2e-9	1.0e-5±2.0e-7	4217±44
	-1.28×10 ⁻¹	1058×1058×1058	181×181×181	2.0e-7±4.0e-9	5.1e-6±9.9e-8	3973±45
	-1.35×10 ⁻¹	1858×1858×1858	325×325×325	3.8e-8±7.4e-10	9.4e-7±1.8e-8	4280±55

*Simulation volume is given in terms of number of IRMOF-1 unit cells (as shown in Figure 2.1).

Table S-2.7. RDX, N₂ and O₂ mixture in IRMOF-1.

pressure (bar)	number of framework unit cells**	number of molecules adsorbed			number of molecules adsorbed per cage		
		RDX	N ₂	O ₂	RDX	N ₂	O ₂
1.021±0.019	17×17×17	10772±41	2669±52	460±21	0.274	0.068	0.012
0.862±0.016	17×17×17	10399±50	2672±52	460±21	0.265	0.068	0.012
0.545±0.010	17×17×17	9488±69	2674±51	459±21	0.241	0.068	0.012
0.213±0.004	17×17×17	7820±42	2673±50	458±21	0.199	0.068	0.012
0.108±0.002	17×17×17	6614±47	2669±51	458±21	0.168	0.068	0.012
7.7e-2±1.5e-3	17×17×17	6018±53	2671±50	458±21	0.153	0.068	0.012
5.8e-2±1.1e-3	17×17×17	5576±46	2672±51	458±21	0.142	0.068	0.012
2.6e-2±5.1e-4	18×18×18	5077±48	3174±57	543±23	0.109	0.068	0.012
1.0e-2±2.0e-4	20×20×20	4574±60	4344±65	744±27	0.071	0.068	0.012
5.3e-3±1.0e-4	20×20×20	3237±46	4352±64	744±27	0.051	0.068	0.012
4.4e-3±8.5e-5	20×20×20	2811±31	4349±61	743±27	0.044	0.068	0.012
1.0e-3±2.0e-5	30×30×30	3115±42	14716±117	2507±49	0.014	0.068	0.012
5.0e-4±9.8e-6	35×35×35	2606±58	23267±158	3983±63	0.008	0.068	0.012
1.2e-4±2.3e-6	45×45×45	1397±20	49588±224	8464±91	0.002	0.068	0.012
4.5e-5±8.7e-7	50×50×50	730±28	67998±245	11600±109	0.0007	0.068	0.012
1.0e-5±2.0e-7	55×55×55	229±13	90566±296	15439±119	0.0002	0.068	0.012

**Unit cell is shown in Figure 2.1.

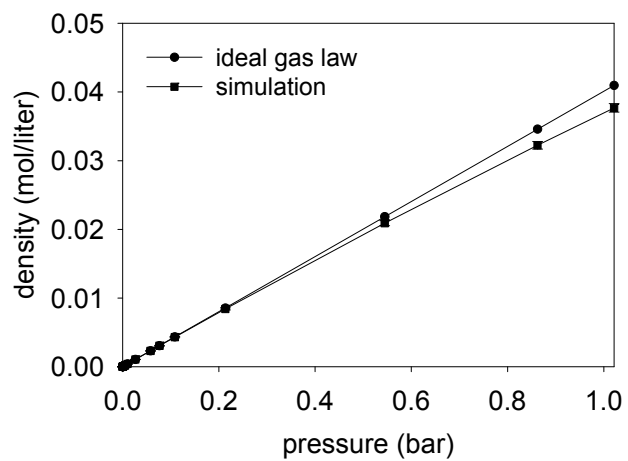


Figure S-2.1. Comparison between the RDX bulk simulations and the ideal gas law.

CHAPTER 3

Effect of Charge Distribution on RDX Adsorption in IRMOF-10

This chapter is a slightly revised version of a paper by the same title published in *Langmuir*, 2010 by Ruichang Xiong, David J. Keffer, Miguel Fuentes-Cabrera, Donald M. Nicholson, Andrea Michalkova, Tetyana Petrova, Jerzy Leszczynski, Khorgolkhuu Odbadrakh, Bryant L. Doss and James P. Lewis.

R. Xiong, D.J. Keffer, M. Fuentes-Cabrera, D.M. Nicholson, A. Michalkova, T. Petrova, J. Leszczynski, K. Odbadrakh, B.L. Doss, J. P. Lewis, Effect of Charge Distribution on RDX Adsorption in IRMOF-10, *Langmuir*, 2010, in press, doi: 10.1021/la9039013.

The use of “we” in this part refers to the co-authors and the author of this dissertation. My primary contributions to this paper include (1) building computational models (2) development of the algorithm (3) creating programs to perform both GCMC and MD simulations (4) all of the simulation work (5) collection and organization of the quantum mechanical calculation data from co-authors (6) all of the table and figure generation and all of the writing

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Abstract

Quantum mechanical (QM) calculations, classical grand canonical Monte Carlo (GCMC) simulations and classical molecular dynamics (MD) simulations are performed to test the effect of charge distribution on hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) adsorption and diffusion in IRMOF-10. Several different methods for mapping QM electron distributions onto atomic point charges are explored, including the electrostatic potential (ESP) method, Mulliken population analysis, Löwdin population analysis and natural bond orbital (NBO) analysis. Classical GCMC and MD simulations of RDX in IRMOF-10 are performed using fifteen combinations of charge sources of RDX and IRMOF-10. As the charge distributions vary, interaction potential energies, the adsorption loading and the self-diffusivities are significantly different. None of the fifteen combinations are able to quantitatively capture the dependence of the energy of adsorption on local configuration of RDX as observed in the QM calculations. We observe changes in the charge distributions of RDX and IRMOF-10 with the introduction of an RDX molecule into the cage. We also observe a large dispersion contribution to the interaction energy from QM calculations that is not reproduced in the classical simulations, indicating that the source of discrepancy may not lie exclusively with the assignment of charges.

3.1 Introduction

The detection of explosive molecules remains a challenge due to the low vapor pressure of explosive compounds, which in a threat situation may be present in the air at only parts per trillion concentrations[4]. To enhance the sensitivity and selectivity of detective sensors, an efficient preconcentration system is crucial for the trace detection process. The role of a preconcentrator is to trap a sufficient quantity of explosive molecules for detection by the sensor element from an extremely low concentration in the local air. To facility continuous operation, the preconcentrator needs to be able to desorb the trapped molecules easily, specifically at room temperature. Therefore, desirable features of a preconcentrator are high sensitivity, selectivity and reversibility[5,86]. Currently no preconcentrators available meet the above requirements. Conventional bulky preconcentrators have slow response times. Recent microfabricated preconcentrators can enhance sensitivity alone, but still are not ideal[5].

However, the fast development of nanotechnology provides an opportunity for developing an ideal preconcentrator. Metal-organic frameworks (MOFs) are a new class of nanoporous materials first synthesized by Yaghi and co-workers[8,9,15] and have been evaluated for many tasks, including their ability to adsorb methane[15,34] and hydrogen[10,11,33]. Due to their unique measured and calculated properties, such as large internal surface area, high thermal stability, high porosity and tailorable pore size and chemistry, MOFs have been recently considered for their potential to preconcentrate explosive compounds[35]. Ni *et al.*[37] have shown that IRMOF-1 is an effective selective preconcentrator when adsorbing dimethyl methylphosphonate (DMMP). In chapter 2, we evaluated the ability of IRMOF-1, an iso-reticular metal organic framework

(IRMOF), to adsorb the highly energetic explosive hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX, CAS # 121-82-4). The structure of RDX is shown in Figure 3.1. In order to understand how the structure of the IRMOF impacts the adsorption isotherm and thus the selectivity, we are in the process of examining RDX adsorption in several IRMOFs.

In this chapter, we report on our evaluation of IRMOF-10. The crystal structure of IRMOF-10 from the X-ray diffraction (XRD) data was given by Eddaoudi *et al.*[15] as shown in Figure 3.2. IRMOF-10 maintains the cubic topology of the framework of the parent structure (IRMOF-1) but substitutes the connecting 1,4-benzenedicarboxylic acid (BDC) linker with a 4,4'-biphenyldicarboxylic acid (4,4'-BPDC). As a consequence, the structure of IRMOF-10 is similar to that of IRMOF-1, but is significantly larger. The unit cell length for IRMOF-1 is 25.832 Å and the unit cell length for IRMOF-10 is 34.2807 Å[3]. Like IRMOF-1, IRMOF-10 consists of two different kinds of alternating cages, denoted as big cage and small cage in chapter 2, which reflects the orientation of the benzene rings as shown in Figure 3.2.

In order to use classical molecular simulations to examine the ability of IRMOF-10 to adsorb RDX, a model of the charge distribution in both IRMOF-10 and RDX is essential as an input to the simulation. There are several reports that evaluate the charge distribution for IRMOF-1, such as the MM3-based force field[70,80] and the CVFF-based force field[51,69]. In each of these cases, the classical distribution of charge is assumed to be point charges located at each atom center. Moreover, the magnitude of the charges is fixed in time. The MM3 force field[70], which is a fully bonded and flexible force field, along with the charge distribution, predicts the IRMOF-1 structure successfully. However, there is less information available for the charge distribution in

IRMOF-10. Babarao and Jiang[63] reported a set of IRMOF-10 atomic charges that are estimated from an electrostatic potential (ESP) using a B3LYP density functional theory (DFT) calculation. ESP is just one of the commonly used methods to estimate atomic charges. Kawakami *et al.*[12] have shown the loadings of CO₂ in a MOF crystal were affected by the charge densities calculated from different density functional methods. Moreover, the inclusion of charges on the framework atoms has been shown to shift the adsorption isotherms but not change the qualitative adsorption behavior for several adsorbate molecules, such as hydrogen[13] and benzene[87]. A recent review[88] points out the atomic charges of IRMOF-1 assigned using quantum mechanical (QM) calculations vary using different charge calculation methods, which may have a significant impact on the outcome of classical force field calculations in examples where electrostatic interactions are important.

In this chapter, we examine the effect of different charge distributions on the binding energies and adsorption isotherms of RDX in IRMOF-10. In each case, we limit ourselves to the same model for charge distributions that were used in IRMOF-1, namely that we place point charges on the atom centers and hold the values of these point charges fixed. We evaluate different charge distributions by comparing the binding energies from the classical potential with those from the QM calculations. Our goal is to determine the best choice of methods which should be used to generate charge distributions yielding the optimal computational results for the IRMOF-10 system. The criteria used for determining the best method could in general include comparing binding energies, adsorption isotherms or self-diffusivities from simulation with experimental data. Unfortunately for the case of RDX, there is no such experimental data available.

Therefore, we use the QM calculations as the standard. (We accept that there is uncertainty associated with this standard.) The QM calculations provide binding energies, but do not provide isotherms or diffusivities. Therefore the criterion used to evaluate the goodness of the various charge distributions will be comparison with binding energies obtained from QM.

This chapter is focused on the electrostatic contribution as the source of greatest uncertainty in the description of the adsorbate-framework interactions in nanoporous materials. We are motivated by findings in the literature, which indicate polar molecules are more difficult to correctly simulate than non-polar molecules. For example, the study of the adsorption of non-polar molecules (such as hydrogen and methane) in MOFs, where the electrostatic are neglected and the Lennard-Jones (L-J) contributions represents 100% of the interaction, experimental isotherms can be reproduced well without adjustment to the interaction parameters[13,14]. Moreover, for methane it has been shown that the isotherm is relatively insensitive to L-J parameters[14]. Furthermore, for polar molecules (like water), experimental adsorption isotherms in nanoporous materials can be reproduced by manipulation of the partial charges of the adsorbent framework[55]. Taken collectively, these findings point to the uncertainty in the charge distribution as a principle source of error.

3.2 Computational Details

3.2.1. Quantum Mechanical Calculations

It is quite common in classical simulations to use interactions that are parameterized by point charges associated with atomic positions. The QM calculations

were found to be useful in defining point charges on MOFs[88]. There is no unique solution for mapping an electron distribution onto point charges which are assigned to atomic centers. Thus, to determine a charge distribution which is most appropriate to IRMOF-10, we evaluate different approaches for assigning charges – the ESP method[89] and three common non-ESP methods including Mulliken population analysis (MPA)[90,91], Löwdin population analysis (LPA)[92] and the natural bond orbital (NBO)[93,94] method. ESP[63,70,95], MPA[95,96], and NBO[13,96] methods were used recently to study the charge population analysis of MOFs.

In the ESP method, atomic charges are fit to the molecular electrostatic potential, which is a rigorously defined QM property. The molecular electrostatic potential is calculated with the atomic wave function basis set. In the three non-ESP methods, atomic charges are determined by partitioning the electron density into atomic contributions. The weaknesses of both ESP and non-ESP methods are well known. It has been shown by Sigfridsson and Ryde[97] that the atomic charges computed by the ESP method strongly depend on how and where the electrostatic potential points are selected. The non-ESP methods are very sensitive to the choice of basis set[98,99]. Although the ESP method has proved to be more accurate in the description of inter-molecular properties, the non-ESP charges remain interesting to show the variation in adsorption and diffusion when different charges are used.

We have used two ESP charge sets in this work. One of the ESP methods has previously been applied to IRMOF-10 by Babarao and Jiang[63]. They have fit the electrostatic potential at grid points located with equal density on different layers around the molecule. In this work, their calculated charges are indicated as ESP-1.

In the second ESP method, the effective atomic charges in the MM3 force field for IRMOF-1 determined by Tafipolsky *et al.*[70] were calculated by fitting to the electrostatic potential at a large number of points on or near the van der Waals surface. We extend this charge distribution to IRMOF-10 since the structure of IRMOF-10 is similar to that of IRMOF-1. For the atoms common to both IRMOF-1 and IRMOF-10 (Zn, O1, O2, C1, C2, C3, and H3: Figure 3.3(a)) we assign the same charges to IRMOF-10 that were generated for IRMOF-1[14]. As was done by Babarao and Jiang[63], the charges of the atoms C4 and H4 are, based on symmetry, set equal to the atoms C3 and H3, respectively. The charge of the remaining atom (C5) is adjusted to satisfy charge neutrality of the unit cell. All ten independent atoms (Zn, O1, O2, C1, C2, C3, C4, C5, H3 and H4) of IRMOF-10 are indicated in Figure 3.3(a). In this work, this set of charges extended from the MM3 force field is also employed. In order to differentiate the previous ESP charge set, we denote it as ESP-2.

For the MPA and NBO analyses, three cluster models are employed in this calculation, which are shown in Figure 3.3. Final charges are the average values of all symmetrical atoms from all three configurations. The MPA and NBO analyses are performed at the DFT level[100,101] as implemented in the Gaussian03 program package[102]. The hybrid Becke's three parameter with Lee-Yang-Parr correlation term (B3LYP) functional[103,104] are used. B3LYP functional is chosen in the first place because it was successfully used in several other theoretical studies of MOFs[70,105-107] and systems containing zinc complexes[108]. The LANL2DZ basis set[109,110], which uses an effective core potential on all metal atoms of IRMOF-10, are applied, since this basis set is generally considered more appropriate for transition metal chemistry.

The LPA analysis are performed using the FIREBALL code[111], which uses atomic orbitals to express electronic wave functions with finite cut-off lengths. The entire unit cell (as shown in Figure 3.2) of IRMOF-10 is used in the LPA analysis with periodic boundary conditions applied. Details of the methodology can be found elsewhere[112,113].

In addition to partial charges for IRMOF-10, we also vary the partial charges for RDX. One of the partial charge distributions for RDX are taken from Boyd *et al.*[39]. The partial charges were calculated for crystalline RDX by fitting to a set of experimentally determined crystal properties. We also calculate charge distributions for ideal gas RDX and RDX in IRMOF-10 from QM calculations using ESP, MPA, NBO and LPA. These ESP charges are obtained at points selected according to the Merz-Singh-Kollman scheme[114,115].

We should note that in this work we have varied the method that generates the charges from the QM electron distribution. The choice of level of theory and basis set also impacts the QM results that are inputs into the charge generation procedure, and therefore indirectly affects the charges as well.

In order to evaluate the charge distributions used in the classical simulations, we compare the binding energy for a given configuration from the classical potential with that from the QM calculations. The QM binding energies are calculated as the relaxed energies (energy calculated after RDX is optimized) of the RDX/IRMOF-10 configurations less the relaxed energies of the isolated RDX molecule and IRMOF-10 cluster model. Dangling bonds of the IRMOF-10 fragments are saturated by hydrogen atoms. The geometry of RDX is fully optimized while the geometry of the IRMOF-10

fragment is kept frozen (the full optimization leads to a slight change of the crystal structure of IRMOF-10, elongation of distances and modification of bond and dihedral angles). The representative cluster models of IRMOF-10 are prepared as cutoffs from the crystal structure of IRMOF-10[15]. Several different initial orientations of an RDX molecule and different sizes of IRMOF-10 fragments are tested in order to estimate the influence of the IRMOF-10 fragment on the binding energies and the intermolecular interactions. Ultimately, we report binding energies for four configurations corresponding to global and local minima in the big and small cages, as shown in Figure 3.4.

The interaction energy calculations are performed using the B3LYP-D functional[116] as implemented in the TURBOMOLE program package[117,118] to include the dispersion correction into the intermolecular interactions because this type of correction is missing in regular B3LYP calculations. B3LYP-D includes a dispersion contribution with an empirical correction ($-C_6/R^6$) to the B3LYP functional. It has been shown that B3LYP-D provides significant improvements comparing B3LYP[119,120]. The B3LYP-D functional was shown to have excellent performance in the study of H/Br exchange in BBr₃ by HSiR₃[121]. In addition, the B3LYP-D method was also shown in an excellent agreement with experimental data for structures and cohesive energies of a representative set of molecular crystals[122] as well as for anisole:ammonia 1:1 molecular complexes[123].

Additional calculations using B3LYP are performed to compare with B3LYP-D so that the discrimination between electrostatic and dispersive interactions in the QM calculations could be analyzed. Moreover, we have calculated the interaction energy using the B97-D functional, which also includes an empirical dispersion function and was

suggested as an accurate QM method for large systems where electrostatic interactions are important[124]. However, B97-D is a reparameterization of the original Becke's hybrid-GGA functional, which includes a change in the exchange-correlation functional[124]; thus it is not just adding the dispersion correction. From comparing B3LYP-D with B97-D, one can understand the whole picture about the electrostatic and dispersion interactions.

The interaction energy (E_{int}) values are corrected by the basis set superposition error (BSSE) using the counterpoise method[125]. The BSSE energy values are denoted as E_{bsse} and the interaction energy values after the BSSE correction are denoted as E_{corr} .

3.2.2. Classical Simulations

We perform GCMC simulations to calculate the adsorption properties and MD simulations to calculate the diffusivities for RDX in IRMOF-10. In chapter 2, we have reported classical simulations (both MD and GCMC simulations) of RDX in IRMOF-1. The simulations in this chapter use the same procedure and potentials except the charge distributions within IRMOF-10 and RDX are varied. We use a rigid structure to model IRMOF-10 in our simulations. The atomic positions of the structure are obtained from published X-ray diffraction data[15]. The RDX potential is fully flexible. RDX molecules interact with each other and with the atoms of the IRMOF-10 framework through a combination of L-J 12-6 potential and Coulombic interactions. The Coulombic interactions are handled by the spherically truncated charge-neutralized procedure of Wolf *et al.*[73]. The RDX-RDX and RDX-IRMOF-10 intermolecular L-J interaction potentials are truncated at 18 Å. Periodic boundary conditions are applied.

In both GCMC and MD simulations, the temperature are at 300 K and average ~ 1000 molecules are maintained in each simulation to obtain good statistics. The GCMC simulations are performed at the ideal gas bulk pressure ($\sim 9.4 \times 10^{-7}$ bar) and consist of a total of at least 3×10^8 trial moves, the last one third of which are used for data production. Four types of trial moves (translation, rotation, insertion and deletion) are involved, the ratios of which are 4:2:3:3, respectively. The MD simulations are performed with the average loading of RDX in IRMOF-10 at 300 K and $\sim 9.4 \times 10^{-7}$ bar. The MD simulations are allowed to equilibrate for 2 ns and subsequently mean square displacement (MSD) data are collected for 20 ns. More detailed information is available in chapter 2.

3.3 Results and Discussion

In this section, we present charges, binding energies, points on the RDX adsorption isotherm and RDX self diffusivities as a function of charge set. To clarify the relative performance of different charge distributions we study fifteen different choices for the charges. The 15 combinations are summarized in Table 3.1. Each set of charges are obtained with a particular method for a particular configuration. For example, the states for RDX include the crystal phase, the ideal gas phase, and the adsorbed phase within IRMOF-10. The states for IRMOF-10 include the case when the pore is empty and the case when the pore contains one RDX molecule (averaged over 4 positions for the adsorbed RDX). We shall further discuss the various choice of methods used to generate charge distributions below. The first five combinations focus on the variation of atomic charges on IRMOF-10 while fixing the atomic charges of RDX from a fit to experimental data. The next ten combinations focus on systematic variation of the atomic charges of

both RDX and IRMOF-10. While there are other possible combinations, the 15 chosen span the interesting parameter space.

In Table 3.2, we show the charge distribution of IRMOF-10 from the MPA, LPA, NBO and ESP applied to the empty cage. For all of the atoms involved in the octahedral zinc carboxylate complex (Zn, O1, O2, and C1 of Figure 3.3(a)) the five sets of charges provide the same sign of the charge for each atom, although the magnitude varies significantly. For the atoms in the Zn carboxylate complex, LPA generally gives the smallest partial charges, while NBO and ESP-1 give the largest partial charges. For the atoms involved in the benzene ring (C2, C3, C4, C5, H3 and H4), the LPA, NBO, ESP-1 and ESP-2 charges are in generally good agreement, with charges that are an order of magnitude smaller than the charges of the atoms in the metal complex. The exception is MPA, which gives significantly larger negative charges to the carbon and larger positive charges to the hydrogen of the benzene rings.

We can understand the differences in charges as a function of the method in part by understanding the approximations that go into the charge-generating procedures. In general, LPA provides the smallest partial charges, which is a consequence of the limited number of atomic orbitals used in LPA. It has been previously found that LPA charges are smaller in magnitude than MPA charges[126-128], which is an observation of the differences between the two methods, rather than a judgment of their relative merits. MPA tends to overestimate the covalent character of a bond (underestimating the bond ionicity and the degree of charge separation between electropositive and electronegative atoms)[129]. Consequently, electropositive atoms like C3 and C4 have larger negative partial charges in MPA than they do, for example, with NBO. At the same time,

electronegative atoms like O1 and O2 have smaller negative charges in MPA than in NBO. The NBO analysis, in contrast, predicts a much more positive charge on electropositive atoms. This explains the difference between the charges on oxygens and carbons when comparing the results of NBO and MPA analyses. This fact also causes the charge on C5 to change sign from positive with MPA to negative with NBO.

In Table 3.3, we show the MPA, LPA and NBO charge sets for IRMOF-10 obtained when one RDX molecule is adsorbed in the cage. These charges are averaged over the four configurations in Figure 3.4. In these configurations, the charges vary by about 2% from one configuration to another. The relative change in average charge on the MOF due to the presence of RDX is 1.9% for MPA, 1.2% for LPA and 7.9% for NBO. The NBO charges of Zn and O1 have a significant change in the presence of RDX. All other changes are relatively small. The differences between the partial charges obtained from MPA, LPA and NBO are due to the same reasons as given above for Table 3.2.

In Table 3.4, we compare the charges calculated for RDX. We include atomic charges from experimental fitting of mechanical properties of crystalline RDX[39]. We also include the DFT calculations for RDX in the ideal gas and RDX adsorbed in IRMOF-10. Even in the ideal gas, there is a great discrepancy between charges from the four methods, MPA, LPA, NBO and ESP. As was the case in IRMOF-10, MPA gives a much larger charge separation to the C and H atoms. The NBO and ESP methods give a large charge separation to the N and O atoms of the nitro group. The ESP method also gives significant charge separation to the C and N of the ring, not seen in any of the other models. A comparison of charges for RDX in the ideal gas and adsorbed phase shows a

relative change in average charge of 33% for MPA, 11% for LPA, 6% for NBO and 158% for ESP.

One method of evaluating the various charge sets is to compare the binding energy from the classical potentials with the QM binding energy for the four configurations shown in Figure 3.4. These four configurations of RDX in IRMOF-10 correspond to a global-minimum QM energy structure (the lowest energy found via QM in this work) with RDX in the small cage (SG=Small, Global; Figure 3.4(a)), a local-minimum energy structure with RDX in the small cage (SL=Small, Local; Figure 3.4(b)), a global-minimum energy structure with RDX in the big cage (BG=Big, Global; Figure 3.4(d)) and a local-minimum energy structure with RDX in the big cage (BL=Big, Local; Figure 3.4(e)). The additional two structures that contain the yellow spheres are included to help visualize the volume where the RDX is located in the small (Figure 3.4(c)) and big cages (Figure 3.4(f)).

The QM binding energies of these four configurations are reported in Table 3.5. The weakest binding is obtained with B3LYP functional whereas the dispersion-corrected B3LYP-D functional leads to much larger bindings. Despite such differences in the energy, the general trend regarding the stability of RDX on different IRMOF-10 fragment remains the same. E_{bsse} is much more pronounced at the B3LYP level, ranging from 3.6 kcal/mol (BG) to 7.8 kcal/mol (SL), which accounts for 47% and 54% of E_{int} , and stems mainly from the contribution of the IRMOF-10 fragment. The most significant finding is that noncovalent (dispersion) interactions appear to be a very important contributor to the total binding energy. This is apparent from the B3LYP and B3LYP-D comparison, which suggests that dispersion interactions involving a single RDX molecule interacting with

the small cage site of IRMOF-10 can sum up from 14 to 15 kcal/mol (about 64%-68% of E_{corr}). The same effect is observed for a configuration with weaker interaction (BG), where the RDX binding energy is -11.8 kcal/mol and the dispersion correction is -7.6 kcal/mol (about 64% of E_{corr}).

Comparison of the energies in Table 3.5 indicates that the dispersion term changes significantly when the RDX is in the small or big cages. The dispersion contribution is much larger than was found for the interaction energies of small strongly H-bonded complexes (about 10-30%)[116]. On the other hand, almost the same trend for the interaction energy and dispersion contribution were found in the study of transition-metal triphenylphosphine complexes at the B3LYP and DFT-D levels of theory[130], where the authors concluded that the dispersion contribution is large and gradually increases with the bulkiness of the ligand. Also in the study of $Mg(OH)_2$, $Ca(OH)_2$ and kaolinite[120], the inter-layer interaction energy increased largely due to the dispersion contribution obtained from comparison of the B3LYP and B3LYP-D results. The dispersion correction for anisole-ammonia 1:1 complex was also revealed to be quite large (about 40%)[123] and in the case of the benzene dimer the inclusion of the dispersion correction was found to be crucial because the bare B3LYP functional does not predict bound complexes, in contrast to the experimental observations[131].

For comparison, the B97-D calculation results of the interaction energies for all studied systems are also shown in Table 3.5. The resulting energy values from this calculation are only slightly larger than those found from the B3LYP-D and also the BSSE values do not change significantly.

The energy analysis of data in Table 3.5 also reveals that the most strongly bound RDX molecules are those bound to the small cage structure. The most energetically favorable orientation of RDX (SG) is such that a C-H group of RDX is located at the midpoint between two oxygen atoms of the ZnO_4 fragment of the small cage. The preferred binding to the big cage fragment (BG) occurs when RDX has an oxygen atom of one nitro group approaching the connector of the big cage fragment. A less stable structure (BL) is found to be the system containing the big cage and RDX oriented towards the cage by one N-O group and one C-H group. The binding energies of above discussed configurations at B3LYP level are close to the values found in *ab initio* study of the adsorption of RDX on IRMOF-1[81]. RDX was revealed to interact more preferably with the 1,4-benzenedicarboxylate site (binding energy value amounts to about -9 kcal/mol) than with the $[\text{Zn}_4\text{O}(\text{CO}_2)_6]$ site of IRMOF-1 (binding energy is about -5 kcal/mol).

In Table 3.6, the binding energies for the 15 different charge sets used in the classical GCMC simulations are reported. In the classical simulation, there are three contributions to the potential energy: intramolecular energy of the RDX (bond stretching, bending, torsion, etc.), intermolecular interactions between RDX and other RDX and intermolecular interactions between RDX and the MOF. The binding energy is the difference in this potential energy between the adsorbed phase and the bulk phase. The intramolecular energy of RDX is the same in the bulk and adsorbed phase and cancels out of the binding energy. There is virtually no RDX-RDX interaction in the bulk phase and no RDX-MOF interaction, so the binding energy is essentially the RDX-RDX and RDX-MOF interactions in the adsorbed phase. Additionally, some key energy differences are

reported. What is immediately apparent is that there is significant variation among the different point-charge sets and that none of them have quantitative agreement with the QM calculations. The differences are manifested in several ways.

First, the magnitudes of the binding energies are significantly different. The classical binding energies range from -0.99 to -16.86 kcal/mol, while the B3LYP binding energies are smaller, ranging from -0.60 to -8.10 kcal/mol, and the B3LYP-D binding energies are larger, ranging from -11.6 to -22.5 kcal/mol. Second, the energy changes between two configurations in the same cage, as captured by the change in binding energies, SG-SL and BG-BL, are different. From the B3LYP analysis there are relatively large changes in binding energy with small changes in configuration for small (-1.40 kcal/mol) and big (-3.60 kcal/mol) cages. From the B3LYP-D analysis, the relative changes in the binding energy, -0.20 (both small and big cage), are much smaller. The classical charge sets result in less sensitivity to small changes in configuration leading to at most energy differences of 0.29 and 0.12 kcal/mol for the small and big cages respectively. Third, the sign of the energy change from one configuration to another within the same cage is universally of the wrong sign for all classical potentials compared to either of the QM results. Fourth and finally, there is significant variation in the difference in binding energy between the big and small cages for the various classical charge sets, ranging from -12.83 to 1.21 kcal/mol. The difference in binding energy between the small and large cages (SG-BG) from the B3LYP calculations is -3.90 kcal/mol while the same difference for B3LYP-D is -10.7 kcal/mol due to the inclusion of the dispersion correction. In general, the LPA charge sets give closer agreement for

this energy difference to the B3LYP results and the NBO and MPA charge sets give closer agreement to the B3LYP-D results.

We next examine the impact of the choice of charge distribution on the adsorption of RDX in contributions to the energy as well as on the one-point adsorption isotherm at a temperature of 300 K and a bulk pressure of $\sim 9.4 \times 10^{-7}$ bar. This low pressure is relevant since we are interested in concentrating RDX from the gas phase in which the vapor pressure is very low. We have previously shown in chapter 2 that for RDX in IRMOF-1, this bulk loading is in the relevant Henry's Law regime of adsorption. In Table 3.7, we present the L-J and electrostatic contributions to the potential energy due to RDX-RDX interactions, RDX-IRMOF-10 interactions and the sum of the both interactions. Considering all but the NBO charge sets (set 6, 8, 10 and 13), the L-J contribution to the RDX-RDX interaction is at least two orders of magnitude smaller than the electrostatic contribution to the RDX-RDX interaction. However, the RDX-RDX electrostatic contribution is at least two orders of magnitude smaller than the RDX-IRMOF-10 electrostatic energy. That the RDX-RDX interactions are small is an indication of the fact that the adsorbate is present in low loadings. For the RDX-IRMOF-10 interactions, the fraction of the total energy that is due to the L-J contribution varies significantly, from 2% (set 5) to 41% (set 9), with an average of 14%. Based on the additional insight provided by the QM calculations above, we observe that the dispersion correction in the QM calculation results in a significant contribution to the total interaction energy, as much as 68%. However, the charge sets with large relative contributions from the L-J interaction have small contributions from the electrostatic interactions and are therefore in poor agreement with the B3LYP-D energies. This poor

agreement demonstrates that the inability of this classical simulation to capture the total interaction energy between RDX and IRMOF-10 could at least in part be due to shortcomings of the L-J potential or its parameters in this application.

We observe a different behavior for the charge sets that employed NBO. In those cases, the large positive charge on the N atom and correspondingly large negative charge on the O atoms of the RDX nitro group resulted in condensation of the RDX within the IRMOF-10 cage. In this case, the RDX-RDX interaction is actually larger than the RDX-IRMOF-10 interaction. At this point in time, it is unclear if this condensation is physical. The system has a low bulk RDX pressure (about 10^{-6} bar) and a temperature of 300 K. There is insufficient experimental evidence to indicate whether condensation should occur within the nanopore at these conditions. Therefore, we cannot rule out the possibility that the NBO charge sets capture a real behavior.

The binding energy has a direct correlation to the amount of RDX that is adsorbed. In Table 3.8, we report the number of molecules of RDX adsorbed per cage. All GCMC simulations that used NBO charge sets resulted in condensation with at least 14 RDX molecules per cage. These NBO GCMC simulations had not completely finished equilibrating (there was a very slight rise in density still occurring, as one would expect due to the low probability of GCMC insertions in high density systems). The lowest adsorption energy for systems that do condense is -20.8 kcal/mol (system 8; NBO RDX and ESP-2 MOF). The highest adsorption energy for systems that do not condense is -18.4 kcal/mol (system 5; RDX from ref. [39] and LPA MOF). Thus we can establish a relatively small range between the two values at which condensation of RDX would likely occur. At the other extreme (system 9; LPA RDX and ESP-2 MOF) has the lowest

binding energy and adsorbs the least amount of RDX (about 7 orders of magnitude less RDX than the condensed systems). For systems with intermediate adsorption energies, the relative amount of RDX adsorbs tracks very closely with the energy of adsorption.

There is also a challenge in reconciling the average total potential energy reported in Table 3.7 with the classical energies of the configurations reported in Table 3.6. The results from group 2, 3, 4, 7 and 9 are consistent with an intuitive understanding that the average energies from a simulation at 300 K have to be higher than the single-point energies reported in Table 3.6. These single-point energies correspond to configurations that were global and local minima in the QM calculations. It is at least qualitatively reasonable that the RDX molecules experience an average potential energy of -8.81, -12.03, -12.00, -5.49 and -4.39 kcal/mol at 300 K when the energy minimum is at -10.51, -13.10, -13.98, -6.97 and -7.50 kcal/mol for the group 2, 3, 4, 7 and 9. However, the energies in Tables 3.6 and 3.7 for other groups require further investigation.

The average total potential energy of an RDX molecule in the GCMC simulation, as reported in Table 3.7, is lower than the energies associated with the configurations in Table 3.6, for the charge sets from group 1, 5, 11, 12, 14 and 15. The only way such a result is possible is if the configurations evaluated in Table 3.6 (which correspond to minima in the QM energy landscape) do not correspond to minima in the classical energy landscapes. We tested this hypothesis by randomly sampling RDX molecules from the GCMC simulations and performing single-point energy calculations. Indeed, our single-point energy calculations show that some configurations from the GCMC simulations provide deeper energies than the QM binding energy.

The difference between the QM and classical energies is not strictly in the depth of the well. From the GCMC simulations, we have generated density distributions, which are shown in Figure 3.5. In Figure 3.5, we have shown density distributions of the RDX center of mass in IRMOF-10 for the first five charge sets. The ESP-1, ESP-2, and LPA charge sets are qualitatively similar, placing the primary adsorption site of RDX in front of the cage vertex in the big cages. The NBO charge set has an adsorption site at the same location as ESP-1, ESP-2 and LPA but has a deeper adsorption site at the vertex of the small cages. This additional adsorption site is presumably due to the very large charges placed on the nitro group by the NBO procedure. The MPA charge set has small adsorption sites at the vertex and deep adsorption sites in front of the benzene rings in the small cages. This difference in MPA is due to the large charge separation on the benzene rings using the MPA procedure.

It is also worth noting that in Table 3.7 the small cage had a deeper binding energy than the big cage for every charge set except sets 12 and 15. However, from the density distributions we observe preferential adsorption in the big cages for many of these charge sets. Of course, the preference of RDX for a big cage is a combination of energetic and entropic effects and cannot completely be explained by differences in 0 K binding energies. However, we do see deeper energetic wells in the big cage using the ESP-1 and ESP-2 charges than are evident in the optimized configurations from the QM calculations, *i.e.* the average energies of adsorption in Table 3.7 are greater in magnitude than the energies of the configurations reported in Table 3.6 that correspond to minima in the QM calculations. Therefore, the conclusion in the comparison of Table 3.6 and Table 3.7 is that the configurations associated with minima in the QM energy landscape do not

necessarily correspond to minima in the classical energy landscape. Therefore, there is no contradiction between the density distributions in Figure 3.5 and the energies in Table 3.6.

In Table 3.8, we also report the self-diffusivity of RDX from independent MD simulations run at the loadings generated from the GCMC simulations and reported in Table 3.8. There is a general correlation between the average energy of adsorption and the self-diffusivity, in which an increase in the magnitude of the energy of adsorption corresponds to a decrease in the self-diffusivity. This relationship is not unexpected since diffusion of RDX in MOFs is an activated process shown in chapter 2, and the activation energy is the difference in energy between the energy peak along the diffusion path (transition state energy) and the site energy. The energy of adsorption reported in Table 3.7 is an average over all energies and thus doesn't necessarily contain the activation energy. However, we do observe this general correlation, likely indicating that the change in charge set has a bigger impact on the adsorption site energy than on the diffusional transition state energy.

When examining the diffusivity as a function of density for a given potential, in general one expects that the diffusivity should decrease as the loading increases, due to steric hindrances. However, we cannot make this correlation between the diffusivities and loadings in Table 3.8, because the potential is different for each case. Thus the depths of the energy wells are different, which impact the activation energy for diffusion more so than does the loading.

3.4 Conclusions

Motivated to understand how RDX is absorbed in IRMOF-10 and how it diffuses within it, we performed classical GCMC and MD simulations of RDX in IRMOF-10. For this purpose force fields were evaluated by comparing binding energies obtained from them with the binding energies obtained from quantum mechanics (QM). We found that the choice of force-field greatly affects the outcome.

We have shown that four different approaches for generating point charges of IRMOF-10 from QM calculations, including the Electrostatic Potential (ESP) method, Mulliken Population Analysis (MPA), Löwdin Population Analysis (LPA) and Natural Bond Order (NBO) analysis, yield significantly different charges. Fifteen combinations are formed by applying different methods for charge calculation to different RDX/IRMOF-10 structures. Comparison of the binding energies for fixed configurations of RDX in IRMOF-10 show great variation between the fifteen combinations, none of which agree particularly well with the binding energy from quantum mechanics. The configurations corresponding to minima in the energy surface from the QM calculations do not necessarily agree with minima in the energy surface using the classical potentials with the various sets of point charges.

We examined whether the discrepancies between the QM and classical distributions might be attributed to the use of charge distributions that do not correspond to the system being simulated. We therefore generated charges from configurations of RDX adsorbed in IRMOF-10. These systems also failed to agree well with binding energies from QM calculations.

For the charge sets studied, the amount of RDX adsorbed tracks with the binding energy, but varies over seven orders of magnitude for the fifteen combinations of charges studied here. The self-diffusivities of RDX in IRMOF-10 for each combination simulated are also significantly different.

Interestingly, the QM calculations show that the dispersion contribution is a significant fraction of the binding energy and is substantially larger than any L-J interaction observed in the classical simulations. Therefore, the inability of the classical simulations to reproduce the QM binding energies may in part be attributed to shortcomings of the L-J potential or its parameters in this application and not just the charge distribution. One could increase the dispersion contribution of the L-J potential to better match the QM energies in this work by increasing the well depth, characterized by ϵ . However, this change would impact all of the other properties to which the parameters were originally fit. Although adsorption isotherms for non-polar molecules like methane in IRMOFs are relatively insensitive to L-J parameters[14], it appears that this may not be the case for polar molecules like RDX.

The adsorption isotherm of polar molecules in IRMOFs is certainly sensitive to partial charges. However, adjusting partial charges to match an experimental isotherm point, may not address the physical issue underlying the discrepancy, if the reason for the discrepancy lies with the dispersion contribution to the interaction energy.

Finally, it is difficult due to the scarcity of experimental data to identify a “best” method for determining charges for polar molecules adsorbed in MOFs. Therefore, additional experimental data are needed (such as points on the isotherm) which could help to resolve key questions, especially that of condensation in the pore.

3.5 Acknowledgements

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Appendix 3.A: Tables and Figures

Table 3.1. Different combinations used to generate sets of charges for the classical GCMC and MD simulations.

run id	RDX state	RDX method	MOF state	MOF method
1	crystal	Ref. [39]	empty	ESP-1
2	crystal	Ref. [39]	empty	ESP-2
3	crystal	Ref. [39]	empty	NBO
4	crystal	Ref. [39]	empty	MPA
5	crystal	Ref. [39]	empty	LPA
6	ideal gas	NBO	empty	ESP-1
7	ideal gas	LPA	empty	ESP-1
8	ideal gas	NBO	empty	ESP-2
9	ideal gas	LPA	empty	ESP-2
10	ideal gas	NBO	empty	NBO
11	ideal gas	MPA	empty	MPA
12	ideal gas	LPA	empty	LPA
13	adsorbate	NBO	w/RDX	NBO
14	adsorbate	MPA	w/RDX	MPA
15	adsorbate	LPA	w/RDX	LPA

Table 3.2. Charge distributions for atoms of IRMOF-10 based on an empty cage.

Atom	MPA	LPA	NBO	ESP-1	ESP-2
Zn	1.083	0.788	1.392	1.420	1.260
O1	-1.170	-0.509	-1.443	-1.680	-1.440
O2	-0.501	-0.255	-0.795	-0.710	-0.670
C1	0.290	0.136	0.868	0.720	0.680
C2	0.232	-0.120	-0.150	0.130	0.060
C3	-0.388	-0.082	-0.113	-0.210	-0.160
C4	-0.433	-0.081	-0.165	-0.210	-0.160
C5	0.371	-0.032	-0.024	0.130	0.000
H3	0.329	0.102	0.202	0.150	0.160
H4	0.283	0.104	0.179	0.150	0.160

Table 3.3. Charge distributions for atoms on IRMOF-10 with one RDX in the cage.

Atom	MPA	LPA	NBO
Zn	1.069	0.795	1.720
O1	-1.173	-0.513	-1.715
O2	-0.507	-0.257	-0.875
C1	0.308	0.139	0.870
C2	0.229	-0.122	-0.165
C3	-0.384	-0.083	-0.115
C4	-0.423	-0.081	-0.170
C5	0.376	-0.031	-0.022
H3	0.323	0.102	0.204
H4	0.276	0.103	0.183

Table 3.4. Charge distributions for atoms on RDX.

Atom	Crystal[39]	Ideal gas				Adsorbate			
		MPA	LPA	NBO	ESP	MPA	LPA	NBO	ESP
C	0.05752	-0.26610	0.05921	-0.04850	-0.21954	-0.33611	0.03754	-0.04978	-0.69571
N	-0.13720	-0.06673	-0.18298	-0.28847	0.06178	-0.04210	-0.19203	-0.32949	0.35054
N (nitro)	0.27157	0.13263	0.17411	0.61897	0.73575	0.20935	0.17835	0.60458	0.66307
O	-0.26724	-0.19964	-0.13056	-0.40409	-0.45281	-0.22327	-0.12318	-0.38769	-0.42941
H	0.10081	0.29974	0.10539	0.26309	0.16382	0.31029	0.11289	0.27566	0.30947

Table 3.5. BSSE corrected interaction energies (kcal/mol) of RDX interacting with IRMOF-10 fragments calculated at the B3LYP, B3LYP-D and B97-D level of theory.

System	SG			SL			BG			BL		
	B3LYP	B97-D	B3LYP-D	B3LYP	B97-D	B3LYP-D	B3LYP	B97-D	B3LYP-D	B3LYP	B97-D	B3LYP-D
E _{int}	-12.6	-27.6	-30.7	-14.5	-27.4	-30.4	-7.8	-16.8	-18.8	-5.1	-16.4	-18.5
E _{bsse}	4.5	4.6	8.2	7.8	4.6	8.1	3.6	4.4	7.0	4.5	4.4	6.9
E _{corr}	-8.1	-23.0	-22.5	-6.7	-22.8	-22.3	-4.2	-12.4	-11.8	-0.6	-12.0	-11.6

Table 3.6. Classical single point energies compared with quantum binding energies.

model	corrected QM interaction energy (kcal/mol)			classical single point energy (kcal/mol)							
	B3LYP	B97-D	B3LYP-D	1	2	3	4	5	6	7	8
BG	-4.20	-12.4	-11.8	-1.70	-2.46	-2.29	-0.99	-5.18	-4.53	-2.74	-4.13
BL	-0.60	-12.0	-11.6	-1.73	-2.50	-2.33	-1.06	-5.27	-4.61	-2.77	-4.21
SG	-8.10	-23.0	-22.5	-7.31	-10.41	-12.96	-13.82	-4.06	-12.27	-6.86	-13.29
SL	-6.70	-22.8	-22.3	-7.39	-10.51	-13.10	-13.98	-4.13	-12.38	-6.97	-13.45
SG-SL	-1.40	-0.20	-0.20	0.08	0.10	0.14	0.16	0.07	0.11	0.11	0.16
BG-BL	-3.60	-0.40	-0.20	0.03	0.04	0.04	0.07	0.09	0.08	0.03	0.08
SG-BG	-3.90	-10.6	-10.7	-5.61	-7.95	-10.67	-12.83	1.12	-7.74	-4.12	-9.16
model	corrected QM interaction energy (kcal/mol)			classical single point energy (kcal/mol)							
	B3LYP	B97-D	B3LYP-D	9	10	11	12	13	14	15	
BG	-4.20	-12.4	-11.8	-2.58	-5.14	-3.79	-3.83	-6.84	-3.43	-3.69	
BL	-0.60	-12.0	-11.6	-2.62	-5.23	-3.83	-3.89	-6.96	-3.47	-3.75	
SG	-8.10	-23.0	-22.5	-7.36	-16.66	-13.92	-2.62	-15.83	-13.86	-2.63	
SL	-6.70	-22.8	-22.3	-7.50	-16.86	-14.21	-2.69	-16.07	-14.09	-2.70	
SG-SL	-1.40	-0.20	-0.20	0.14	0.20	0.29	0.07	0.24	0.23	0.07	
BG-BL	-3.60	-0.40	-0.20	0.04	0.09	0.04	0.06	0.12	0.04	0.06	
SG-BG	-3.90	-10.6	-10.7	-4.78	-11.52	-10.13	1.21	-8.99	-10.43	1.06	

Table 3.7. Potential energies (kcal/mol) from GCMC simulations at 300 K and $\sim 9.4 \times 10^{-7}$ bar.

run id	RDX-RDX		RDX-IRMOF10		total potential (kcal/mol)		total (kcal/mol)
	L-J	electro- static	L-J	electro- static	L-J	electro- static	
1	-9.93e-08	1.20e-05	-1.37	-8.88	-1.37	-8.88	-10.25
2	-3.58e-08	6.86e-06	-1.59	-7.22	-1.59	-7.22	-8.81
3	-1.31e-06	2.58e-04	-1.37	-10.67	-1.37	-10.67	-12.03
4	-2.64e-05	2.38e-03	-0.40	-11.60	-0.40	-11.59	-12.00
5	-3.76e-03	4.87e-01	-0.36	-18.57	-0.36	-18.08	-18.44
6	-1.62	-15.10	-0.53	-5.44	-2.15	-20.55	-22.71
7	-4.49e-08	-3.77e-08	-1.99	-3.49	-1.99	-3.49	-5.49
8	-1.45	-14.00	-0.56	-4.86	-2.01	-18.83	-20.84
9	-2.60e-08	3.83e-08	-1.81	-2.58	-1.81	-2.58	-4.39
10	-1.58	-13.70	-0.30	-7.32	-1.87	-20.98	-22.85
11	-4.24e-02	-3.85e-01	-1.01	-14.87	-1.06	-15.26	-16.31
12	-1.77e-07	-5.14e-08	-1.93	-6.94	-1.93	-6.94	-8.87
13	-1.67	-12.40	0.20	-10.26	-1.47	-22.68	-24.15
14	-2.70e-02	-0.21	-1.34	-13.77	-1.37	-13.97	-15.35
15	-1.93e-07	2.37e-07	-1.96	-6.23	-1.96	-6.23	-8.19

Table 3.8. Adsorption loading and self-diffusivities at 300 K and $\sim 9.4 \times 10^{-7}$ bar.

run id	adsorption loading (molecule/cage)	self-diffusivity (m^2/s)
1	3.41e-05	1.52e-11 $\pm$ 4.37e-12
2	2.67e-05	8.36e-10 $\pm$ 9.65e-11
3	5.02e-04	1.71e-10 $\pm$ 1.33e-11
4	5.48e-03	2.86e-10 $\pm$ 9.09e-12
5	4.92e-01	1.28e-14 $\pm$ 1.84e-15
6	condense (>14)	7.96e-13 $\pm$ 2.23e-13
7	1.20e-06	2.99e-09 $\pm$ 1.86e-10
8	condense (>14)	1.26e-12 $\pm$ 4.27e-13
9	8.37e-07	4.46e-09 $\pm$ 3.76e-11
10	condense (> 14)	1.15e-12 $\pm$ 1.17e-13
11	1.25e-01	1.32e-11 $\pm$ 1.04e-12
12	2.29e-05	1.35e-10 $\pm$ 1.52e-11
13	condense (>14)	1.21e-12 $\pm$ 1.97e-13
14	6.44e-02	2.16e-11 $\pm$ 6.81e-14
15	1.17e-05	2.26e-10 $\pm$ 1.31e-11

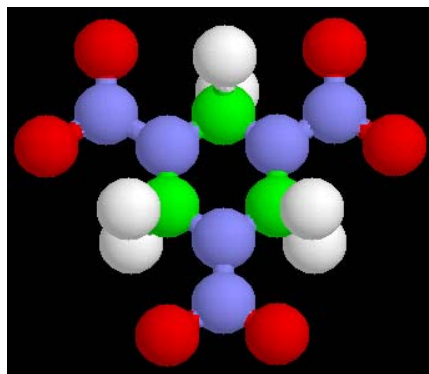


Figure 3.1. RDX structure (legend: N, blue; C, green; O, red; H, white).

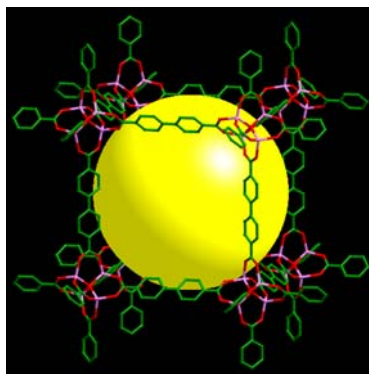


Figure 3.2. IRMOF-10 unit cell structure (legend: Zn, violet; C, green; O, red). All hydrogen atoms are not shown. The yellow sphere is located within the small cage.

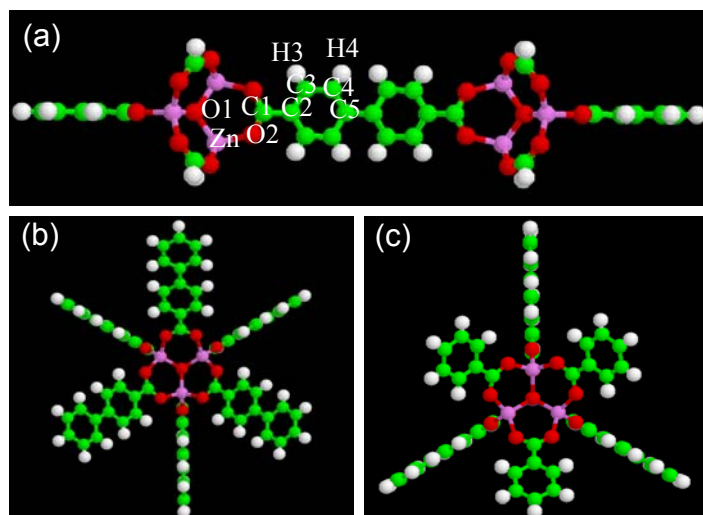


Figure 3.3. Three representative cluster models for calculating charge distribution in IRMOF-10 (legend: Zn, violet; C, green; O, red; H, white).

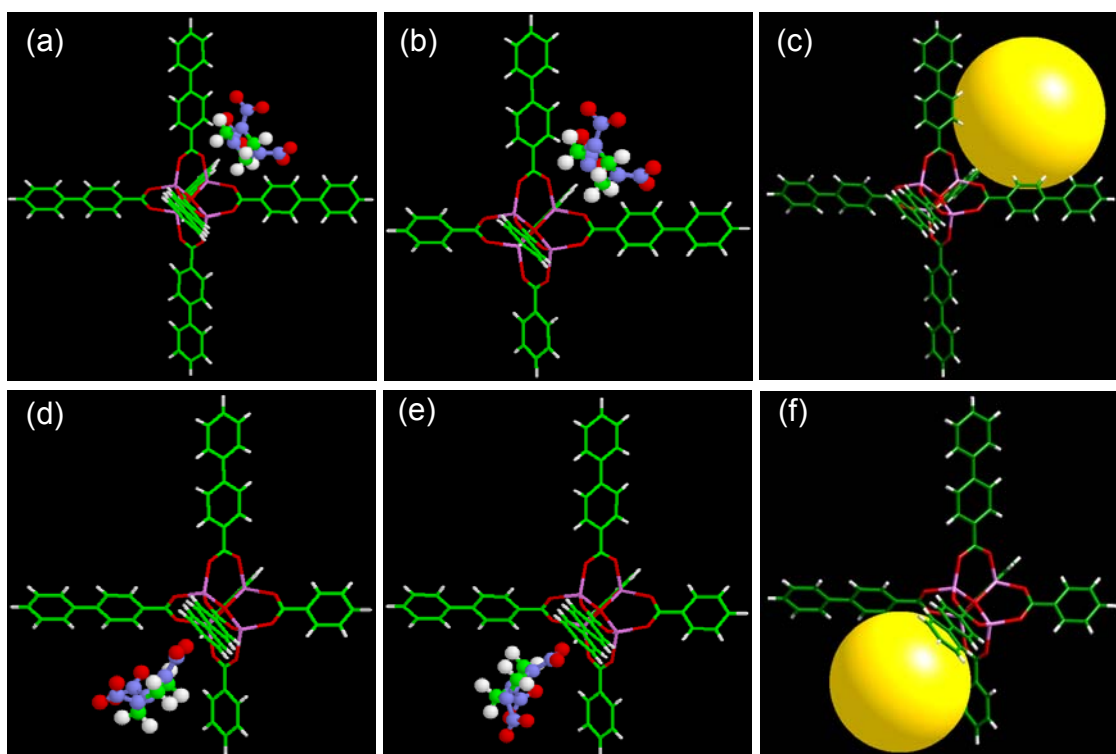


Figure 3.4. Four configurations of RDX in IRMOF-10 for which binding energies were calculated (legend: Zn, violet; N, blue; C, green; O, red; H, white): (a) SG=Small cage, Global minimum; (b) SL=Small cage, Local minimum; (c) a sphere indicating where RDX is located within the small cage; (d) BG=Big cage, Global minimum; (e) BL = Big cage, Local minimum; (f) a sphere indicating where RDX is located within the big cage.

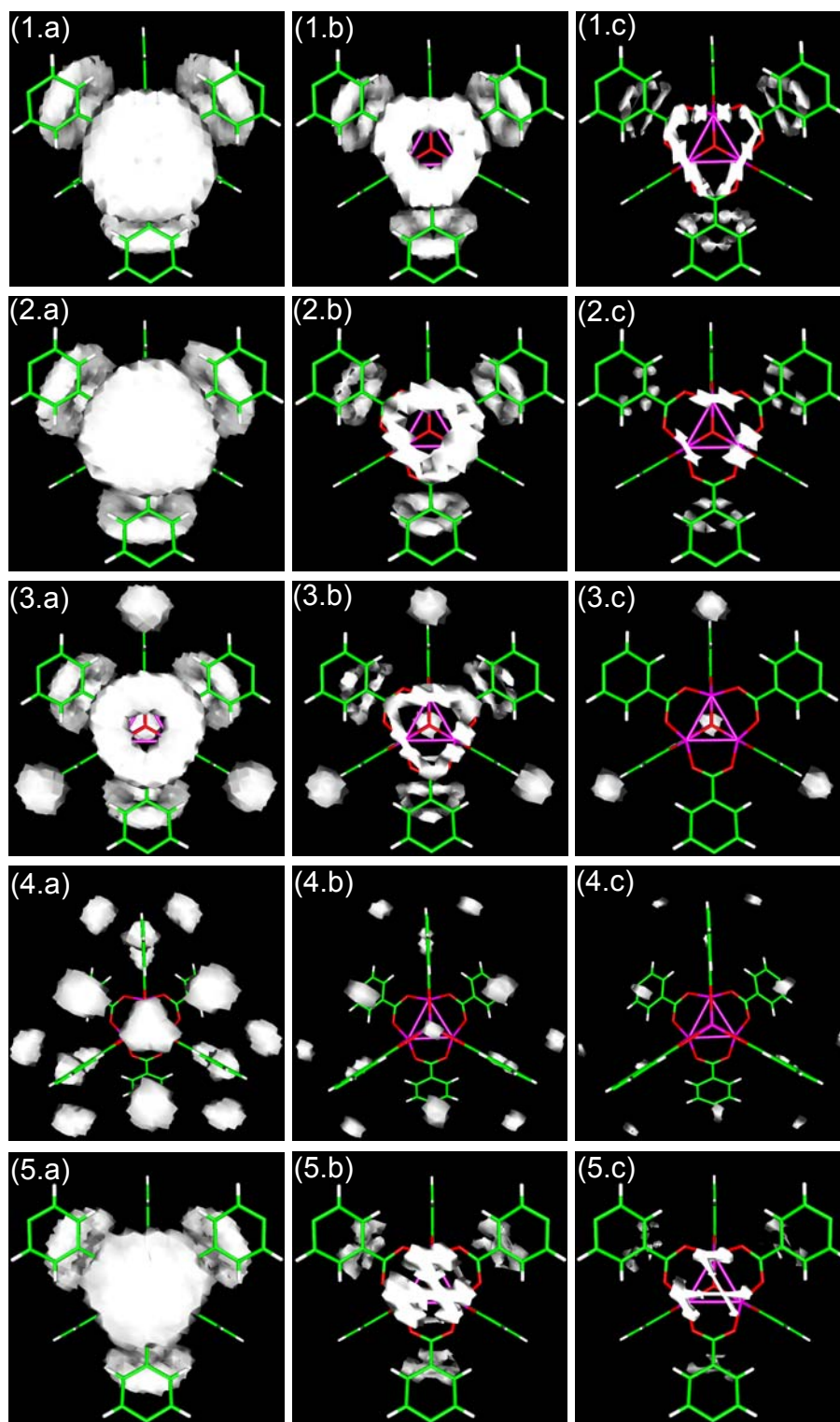


Figure 3.5. The density distributions of RDX in IRMOF-10 for the first five combinations from vertex view at 300 K and infinite dilution. The density contour level is from low to high (legend: Zn, violet; C, green; O, red; H, white).

CHAPTER 4

Evaluation of Functionalized Isorecticular Metal Organic Frameworks (IRMOFs) as Smart Nanoporous Preconcentrators of RDX

Abstract

Classical molecular dynamics (MD) and Grand Canonical Monte Carlo (GCMC) simulations were used to generate self-diffusivities, adsorption isotherms and density distributions for hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) in five isorecticular metal-organic frameworks (IRMOFs), which varied in the cage size and in the presence and location of amine groups. These simulations were performed at room temperature (300 K) and low pressures (up to 1 ppm RDX). The atomic charges required for MD and GCMC simulations were calculated from quantum mechanical (QM) calculations using two different charge generation methods - Löwdin population analysis and natural bond orbital (NBO) analysis. Both charge sets show that the presence of amine groups increases the amount of RDX adsorbed. The cage size and the location of amine groups also affect the loading of RDX. The amount of RDX adsorbed is correlated with the energy of adsorption. The activation energy for diffusion of RDX is not positively correlated with the energy of adsorption. The density distributions identify the location of the adsorption sites of RDX-exclusively in the big cage around the metal complex vertices and between benzene rings. In the absence of amine groups on the framework, one of nitro groups on RDX interacts closely with the metal complex. In the IRMOFs functionalized with amine groups, a second nitro group of the RDX interacts with an amine group, enhancing adsorption. With regard to application as a smart nanoporous preconcentrator, these IRMOFs are found to concentrate RDX up to 3000 times compared to the gas phase, on a volumetric basis. From a simple Langmuir estimation, the selectivity of RDX over butane is up to 5000. The diffusion of RDX is sufficiently high for real time sensor applications. These results indicate IRMOFs can be tailored with functional groups to be highly selective nanoporous preconcentrators.

4.1 Introduction

The detection of explosives has become an important aspect of physical security systems[5,132]. Many explosives such as cyclotrimethylenetrinitramine (RDX) and pentaerythritol (PETN) have extremely low vapor pressures (i.e. the concentration in air is at the parts per trillion level at ambient temperature[4]), which makes their detection very difficult[133]. In order to enhance sensitivity, a detector incorporates a preconcentrator, which is basically a filtering device that concentrates a sufficient quantity of explosives from a large amount of air flow via adsorption and delivers it to the detector via desorption. However, a major challenge still remains in finding an adequate preconcentrator with appropriate adsorptive and transport properties[5].

Metal-organic frameworks (MOFs) are a new class of nanoporous materials that have shown great potential for gas adsorption and separation[15,134] in recent years because they have high thermal stability, large pore volume and surface area, and can be tailored easily. A typical iso-reticular metal-organic framework (IRMOF) is a three-dimensional block structure with periodic cubic unit cell, as shown in Figure 4.1. In a unit cell, there are two distinct cages, denoted as “big” and “small”, distinguished by the orientation of the organic linkers, as indicated in Figure 4.1.

A particularly attractive feature of MOFs is the fact that they can be functionalized by changes in the organic linker. This functionalization affects the adsorptive and diffusive properties of the material. A predictive understanding of the relationship between MOF structure and its corresponding adsorptive and diffusive properties would help match MOFs to a particular application but this understanding does not currently exist. As such experimental or computational techniques are used to

establish these structure/property relationships on a case-by-case basis. The storage of hydrogen[10,13,23] and methane[14,15] in MOFs has generated great interest. For example, Eddaoudi *et al.*[15] synthesized 16 isoreticular MOFs (IRMOFs) by tailoring organic linker based on IRMOF-1 structure. These 16 IRMOFs showed highly different capacities for methane storage. Frost *et al.*[23] predicted hydrogen adsorption isotherms in 10 different IRMOFs and revealed that the adsorption capabilities are strongly correlated with pore volume and surface area.

A similar approach can be taken to identifying MOFs well suited to selectively adsorb explosives as a preconcentrator. In fact, Ni *et al.*[37] demonstrated that MOFs can be quite useful as selective preconcentrators adsorbing dimethyl methylphosphonate (DMMP) on IRMOF-1. Apart from that, there are no published experiments working on preconcentrators for explosives.

Molecular simulation is a useful tool for investigating the structure/property relationships of MOFs, especially for explosive compounds that are more dangerous to study experimentally. Molecular simulations of adsorption in MOFs have shown good agreement with experiments and provided valuable molecular-level insights[13,14,18-20]. In addition, a recent review of MOFs[88] has concluded that molecular simulations can be used to test hypothetical structures for particular applications.

In chapter 2, we investigated the adsorptive and diffusive behavior of an explosive molecule, RDX, in IRMOF-1 via molecular simulation using the MM3 potential for the MOF[70]. RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine, CAS # 121-82-4) is a highly energetic particle often used as modern plastic explosive. The structure of RDX is shown in Figure 4.2. It contains three nitro groups that can interact closely with

metal clusters of IRMOF-1. It was found that RDX adsorbed preferentially near the vertices of the big cages with a Henry's law constant of 21.2 mol/kg/bar at 300 K. The diffusion was activated with an activation energy of 6.0 kcal/mol.

Subsequently, we sought to extend our study from IRMOF-1 to other MOFs. In doing so we discovered that for the vast majority of MOFs, a charge distribution of the MOF is not available. Since RDX is a polar molecule, the electrostatic interactions are important and charge distributions are required. Quantum mechanical (QM) calculation methods are commonly used to define point charges on MOFs, although it has been pointed out that there is a significant variation in the charge distribution of IRMOF-1 using different QM calculation methods, which may significantly impact the classical force field calculations[88]. Therefore, we performed a study on IRMOF-10 in chapter 3, in which point charges associated with atoms were obtained from different QM methods including the electrostatic potential (ESP) method[89], Löwdin populationa (LPA)[92], Mulliken population analysis[90] and natural bond orbital (NBO) analysis[93]. Classical simulation of adsorption and diffusion of RDX in IRMOF-10 using atomic charges from each of these methods led to adsorption isotherms and self diffusivities that varied by as much as *seven orders of magnitude*. None of the choices for atomic charges resulted in a good match to the QM binding energy. Clearly, the choice of atomic charge is important for accurate modeling of the properties of a polar molecule like RDX. Some experimental work would be required to determine, which if any of these charge distributions best reflect reality.

The different choices for atomic charge can be divided according to two types of resulting behavior. The NBO analysis assigned large partial charges to the nitro group of

RDX, which caused RDX to bind more strongly and condense within the pore of IRMOF-10. The other methods, including LPA, predicted a low density phase within the pore. At this time it is not clear whether RDX should condense in a MOF at room temperature.

Our goal now is to establish structure/property relationships for the adsorptive and diffusive behavior of RDX in a variety of MOFs. Given the uncertainty in the atomic charges, we chose to proceed with two charge assignments, LPA and NBO, which in IRMOF-10, yield low-density and condensed phases, respectively. For both assignments, we study how changes in MOF structure affect the amount of RDX adsorbed and the mobility of RDX.

In this chapter, we study RDX in five IRMOFs. These materials have the same framework topology as IRMOF-1, except that they have different functional organic linkers, which are shown in Figure 4.3. Figure 4.3(a) shows IRMOF-1, the base structure. IRMOF-3, which is shown in Figure 4.3(b), is functionalized with an amine group ($-NH_2$) on each phenyl ring in IRMOF-1. Figure 4.3(c) shows IRMOF-10, which replaces the phenyl ring with a biphenyl ring, resulting in a larger cage. In Figure 4.3(d) and Figure 4.3(e), IRMOF-10 is functionalized with an amine group on each biphenyl group. Of these structures, IRMOF-1, IRMOF-3, and IRMOF-10 have been experimentally synthesized[15]. The last two structures assume that the functionalization that leads from IRMOF-1 to IRMOF-3 can also be achieved in IRMOF-10. There are two positions for the amine to be attached in IRMOF-10. We investigated both positions. Experimentally, 1,1'-biphenyl can have an amine attached at either the 2 or 3 position[25]. These final two structures are designated here as IRMOF-10a and IRMOF-10b, where the amine group is

placed on the 2 or 3 position, respectively. In IRMOF-3, the amine group is randomly distributed over four equivalent sites on the phenyl ring[15], which are indicated as dashed circles for each structure in Figure 4.3. We assume the same disorder in the biphenyl group with amine substitution.

These five IRMOFs were chosen for a good reason. In our previous simulation of RDX in IRMOF-1, we observed that the pores in IRMOF-1 are a very tight fit for RDX; thus, we are now motivated to determine if larger pores would enhance adsorption. We also observed in chapter 2, that only one of the nitro groups in RDX participates in strong binding with the Zn in the linker, while the other two nitro groups dangle out into the pore. Therefore, we now seek to add additional binding sites for the other nitro groups. Because the nitro groups are polar, we have added a polar functional group to the MOF structure. Experimentally, it is known that amine groups can be incorporated into MOF structures, as is the case for IRMOF-3. Thus, we have added amine groups to the MOF in order to determine if they act as electrostatic anchors for at least one of the other two nitro groups not interacting with Zn.

This systematic study allows us to perform the following evaluations. We can evaluate the effect of pore size on RDX adsorption in the absence of any amine groups through the comparison of IRMOF-1 and IRMOF-10. The effect of adding an amine group to the framework in small cages can be evaluated through the comparison of IRMOF-1 and IRMOF-3. The effect of adding an amine group to the framework in large cages can be evaluated through the comparison of IRMOF-10 and IRMOF-10a or IRMOF-10b. The effect of placement of the amine group on biphenyl can be evaluated through the comparison of IRMOF-10a or IRMOF-10b.

In this chapter, we use grand canonical Monte Carlo (GCMC) simulation to predict the adsorption of RDX in these five IRMOFs. The proposed application of this fundamental work is to use IRMOFs that can be tailored to selectively adsorb RDX for preconcentration. Since the vapor pressure of RDX is at the ppb or ppt level[1] and it has been demonstrated in chapter 2 that the major parts of air (N_2 and O_2) do not affect RDX adsorption, we limit ourselves to pure RDX adsorption simulation under 1 ppm (parts per million) at ambient temperature (300 K). In addition, we present the self-diffusivities and the activation energy for diffusion of RDX in the five IRMOFs using molecular dynamics (MD) simulation.

4.2 Simulation Details

The five adsorbent IRMOFs studied are shown in Figure 4.3. The framework atoms have been kept rigid during calculations as used in other simulations of adsorption in MOFs[14,55,63]. The atom positions of the frameworks were obtained from published x-ray diffraction data[15]. It should be noted that there is no experimental x-ray diffraction data for IRMOF-10a and IRMOF-10b. Those two structures were formed by adding NH_2 groups to the IRMOF-10 structure. The super unit cell length and mass for each of the IRMOFs used in this work are reported in Table 4.1. It has been shown that IRMOFs are stable to hundreds of degrees Celsius[9] and the effect of the change in linker length and the flexibility in the smaller framework are relatively small[135]. The effect of lattice dynamics on the larger molecules has previously been discussed, and may lower the self-diffusivity from that observed for the rigid framework[80].

The model for RDX is considered fully flexible, including bond stretching, bond bending, bond torsion and non-bonded interactions. The non-bonded interactions are modeled by Lennard-Jones (L-J) potential and Coulombic interactions. The detailed model expressions were given in chapter 2. We adopt a nonreactive force field for crystalline RDX from Boyd *et al.*[39], except for the non-Coulombic nonbonded interactions, which are taken from Wallis and Thompson[38], who used an L-J form. Notably, the model used here does not allow for dissociation of the RDX molecule.

RDX-RDX interactions and RDX-framework interactions are modeled by L-J potential and the Coulombic potential. The L-J potential parameters for both RDX and framework used in this work were reported in chapter 2, except for the L-J parameters for the N and H in the NH₂ group, which are assigned the values for the amine force field[136], as listed in Appendix 4.B. We use the Lorentz-Berthelot mixing rules to calculate the L-J interactions between the different atoms in the system. L-J interactions are truncated at 18 Å with no long-range corrections applied. Conventional periodic boundary conditions are applied during all the calculations. The electrostatic potential is computed using the spherically truncated charge-neutralized procedure of Wolf *et al.*[73].

This model places partial charges centered at each atom of RDX and the MOF. The partial charges were provided in this work by independent QM calculations using either the LPA or NBO method for point charge generation. This process is an approximation and no unique technique is available to determine the atomic charges in a rigorous way. It has also been demonstrated that the change of partial charges substantially varies the adsorption isotherm[12,88]. Nevertheless, Castillo *et al.*[55] demonstrated that experimental isotherms of water in a MOF can be reproduced using

available force fields as a starting point. Similarly it can be applied to RDX. Since there is no experimental data for the adsorption of RDX in IRMOFs, we have to choose a set of partial charges as a starting point. We emphasize the importance of the partial charges in the interaction potential since Düren *et al.*[14] demonstrated that the impact from the choices of L-J parameters is not as sensitive. In chapter 2, the partial charges for RDX atoms were chosen from the force field fitting to crystalline RDX[39] and the partial charges for IRMOF-1 atoms were fit to the electrostatic potential[70]. Charge distributions are not available for all the other IRMOFs.

In this work, in order to generate a consistent set of partial charges for all IRMOFs studied, we performed both LPA and NBO methods to generate charges from QM calculations. These two methods were also applied recently in the charge population analysis in MOFs[96]. We show later in the paper that, at the interested pressure and temperature, the LPA partial charges in this work can reproduce relatively well the previously reported adsorption isotherms and self-diffusivities for IRMOF-1.

The QM calculations were performed using the FIREBALL code[111], which uses atomic orbitals to express electronic wave functions with finite cut-off lengths. The entire unit cell structures from the x-ray diffraction were used to perform QM calculations with periodic boundary conditions applied. Details of the methodology can be found elsewhere[112,113]. QM calculations were also performed for an isolated RDX molecule. The partial charges for RDX and IRMOFs from the LPA and NBO calculations are reported in Appendix 4.B.

Because it still remains unclear whether the use of a cluster-based approach rather than the full periodic structure plays a significant role on the local atomic charges[88], we

computed charge distributions for IRMOFs based on isolated fragments of the MOFs (as compared to full unit cells with periodic boundary conditions), using the NBO analysis in Gaussian03[102]. These partial charge distributions are also reported in Appendix 4.B. We found that there were significant discrepancies in the partial charge distributions between the full cell and fragment calculations. However, not all of the differences can be attributed to the size of the fragment. We applied the same procedure for an isolated RDX molecule; the NBO analyses of FIREBALL and Gaussian03 did not generate the same partial charges, as indicated in Appendix 4.B. The choices of level of theory and basis set also impact the QM results that are inputs into the charge generation procedure, and therefore indirectly affect the charges as well. In the GCMC and MD simulations reported in this work, we exclusively used charges generated from the full unit cells with periodic boundary conditions via FIREBALL.

The adsorption isotherms of RDX in IRMOFs are computed using GCMC simulations at 300 K. Each point on the isotherm consists of two simulation points: a bulk phase simulation of the RDX gas and an adsorbed phase simulation of RDX in the MOF. Each pair of simulations is performed at the same temperature and chemical potential and therefore in thermodynamic equilibrium. The gas phase is an ideal gas since we only considered pure RDX at pressures corresponding to no more than 1 ppm at ambient conditions.

We selected four types of trial moves in the ratio of 4:2:3:3 during GCMC simulation: 1) center-of-mass translation, 2) rigid rotation about the center-of-mass, 3) insertion and 4) deletion. For each simulation the molecule insertions were drawn from a pool of ideal gas configurations. We have previously shown modest changes in RDX

structure upon adsorption into IRMOF-1. Detailed information about GCMC method can be found in chapter 2 and elsewhere[21,22].

We have also performed a series of classical MD simulations in order to obtain information about RDX mobility within the pore that is not available from the GCMC simulations. The MD simulations were performed in the NVT ensemble at densities obtained from the GCMC simulations corresponding to a bulk RDX partial pressure of 1 ppm at ambient conditions. The MD simulations were run across a range of temperatures so that we were able to obtain not only the self-diffusivity but the activation energy for diffusion as well. For all frameworks, we have used 1000 RDX molecules in each MD simulation to yield reliable statistics. Thus the number of cells in each simulation varies since the density varies from one MOF to another.

The diffusion coefficient was determined by the time evolution of the mean square displacement (MSD) of the center of mass (COM) of RDX molecule. According to the Einstein relation[22], the diffusion coefficient is obtained from the MSD curve in the long-time limit where the exponent relating the observation time to MSD is unity. This procedure was successfully applied to benzene[80] and RDX diffusion in IRMOF-1 in chapter 2.

We have used two-time step r-RESPA algorithm[74] to integrate the equations of motion. The short time step is 0.2fs and there are 10 short steps per long time step. To get the linear regime of the MSD curve, we have run 1.5×10^7 long time steps for data production after 6×10^5 long time steps for equilibration. The MSD data were sampled every 2500 long time steps during data production. To obtain the activation energy, the temperature dependence of diffusion coefficient was fit to the Arrhenius expression,

which is seen as an empirical relationship[137]. Additional details of the MD method for RDX in an MOF can be found in chapter 2.

4.3 Results and Discussion

In this section, we present GCMC and MD simulation results for RDX in the five IRMOFs. We first present results for RDX adsorption and diffusion in all IRMOFs using the LPA charges. We then present analogous results using the NBO charges. The key distinction is that the LPA charges predict a low density RDX phase within the IRMOF, while the NBO charges predict a condensed phase. Unless otherwise depicted, the uncertainties are smaller than the symbol sizes in the figures presented.

4.3.1. Adsorption Isotherms and Self-Diffusivities Calculated with Partial Charges from Löwdin Population Analysis (LPA)

In Figure 4.4, we show adsorption isotherms for the five IRMOFs at 300 K and a pressure range from 1.43×10^{-13} bar to 9.36×10^{-7} bar, which is the pressure range of interest since the equilibrium vapor pressure of RDX is 6 ppt at ambient temperature[4]. The adsorption loadings are shown in two different unit bases, one of which is RDX molecule per cage of framework (Figure 4.4(a)) and the other is weight percent of RDX in framework (Figure 4.4(b)). Note that the adsorption loading of IRMOF-1 in this work is in good agreement with the results obtained in chapter 2, which is shown in Figure 4.4(a) even though the partial charges for both RDX and framework are very different (the one in this work is from LPA and the other one in chapter 2 is from ESP calculation[70]). The amount of RDX adsorbed in the MOF is very small, only 1 RDX

molecule per 6000 cages at the highest loading. This low loading is expected based on the LPA charge distribution for IRMOF-10 in chapter 3.

Both Figures 4.4(a) and 4.4(b) show the same RDX adsorption trend, with adsorption as follows: IRMOF-10a > IRMOF-3 > IRMOF-10b > IRMOF-10 > IRMOF-1. To evaluate the effect of pore size on RDX adsorption in the absence of any amine groups, we compare IRMOF-1 (small) and IRMOF-10 (big) and observe that IRMOF-10 adsorbs more RDX on both volumetric and weight basis. To evaluate the effect of the presence of an amine group in small cages, we compare IRMOF-1 (no amine) and IRMOF-3 (amine) and observe that IRMOF-3 adsorbs more RDX, supporting our hypothesis that the polar amine group can act as an electrostatic anchor for a second nitro group of RDX. To evaluate the effect of the presence of an amine group in large cages, we compare IRMOF-10 (no amine) and IRMOF-10a (amine near the vertex) or IRMOF-10b (amine away from vertex). We observe that the amine-containing IRMOFs adsorb more RDX than IRMOF-10, again supporting our hypothesis that the polar amine group can act as an electrostatic anchor for a second nitro group of RDX. To evaluate the effect of the placement of the amine group in large cages, we compare IRMOF-10a and IRMOF-10b, and observe that when the amine group is placed in the 2-position (closer to the vertex), the amount of RDX is more than doubled. This is a consequence of putting the amine in the right geometric position to act as an effective electrostatic anchor for the second nitro group of the RDX molecule. There is more than an order of magnitude difference in the amount of RDX adsorbed when comparing the best adsorbent (IRMOF-10a) and the worst adsorbent (IRMOF-1).

We also notice that almost all the adsorption isotherms are in the linear regime across the pressure range studied except for IRMOF-10a, which presents non-linear behavior at $\sim 8 \times 10^{-7}$ bar. The linear regime can be expressed by the Henry's law constant, shown in Table 4.2, which is substantially larger than observed for H_2 , CO_2 and CH_4 adsorption. The Henry's law constant of IRMOF-1 in this work (16.0 mol/kg/bar) is in good agreement with that in chapter 2 (21.2 mol/kg/bar). IRMOF-10a has the highest Henry's law constant, which is about 10 times larger than that for IRMOF-1. In Table 4.2, we also show how much the framework concentrates RDX from the gas phase, on a volumetric basis. IRMOF-10a concentrates RDX by a factor of 3000.

The binding energies of RDX in the five IRMOFs at 300 K and 9.36×10^{-7} bar are shown in Figure 4.5. In the classical simulation, there are three contributions to the potential energy: intramolecular energy of the RDX (bond stretching, bending, torsion, etc.), intermolecular interactions among RDX molecules and interactions between RDX and the MOF. The binding energy is the difference in this potential energy between the adsorbed phase and the bulk phase. The intramolecular energy of RDX in the bulk phase is virtually the same as that in the adsorbed phase. There is negligible RDX-RDX interaction and no RDX-MOF interaction in the bulk phase since RDX is in the ideal gas regime, so the binding energy is essentially determined by the RDX-RDX and RDX-MOF interactions in the adsorbed phase. In particular, the binding energy is only the RDX-MOF interactions in the adsorbed phase when the loading of RDX is extremely low, as is the case with the LPA charges. The binding energy for RDX in IRMOF-1 is -8.1 kcal/mol, which is in good agreement with the result (-9.2 kcal/mol) in chapter 2 and the quantum chemistry calculation of -8.8 kcal/mol[81].

If adsorption of RDX in IRMOFs is dominated by energetic contributions to the free energy, then we would expect that the amount of RDX adsorbed correlates with the magnitude of the binding energy. This qualitative trend is completely obeyed for the five MOFs studied here. IRMOF-1, which has the least RDX adsorbed, has the smallest binding energy. IRMOF-10a, which has the most RDX adsorbed, has the largest binding energy.

If we can use binding energy as a measure of amount adsorbed, as indicated above, then we can also use binding energies to get an appreciation for the selectivity of the adsorption for different compounds. From an application standpoint, we are interested in adsorbing RDX at a ppt level at a port where alkanes from fuels may be present in the atmosphere at much higher levels. The energy of adsorption of butane in IRMOF-1 is 6.0 kcal/mol[138]. Since butane is not polar, it will not be affected by the presence of the amine to the same degree that RDX is. In IRMOF-10a, RDX has an adsorption energy of 11.1 kcal/mol. Using a simple binary Langmuir adsorption isotherm[139], for a bulk mixture of RDX at 1 ppt and butane at 1 ppm at $T = 300\text{ K}$ and 1 bar, we find a selectivity of RDX over butane of 5000, where we have assumed an 86% free volume calculated based solely on the system geometry[23] and that each vertex of the big cage provides an adsorption site (from density distribution shown later). Complete details of this Langmuir estimate are provided in Appendix 4.B.

In Table 4.3, we provide some additional data for RDX adsorption in the IRMOFs at 300 K and 9.36×10^{-7} bar. We report the number of cages, the number of RDX adsorbed and the distribution of RDX in the small and big cages. Most of RDX molecules reside in big cages of the frameworks. We can see that the highest probability for RDX in the

small cages of the five IRMOFs is still less than 1%. This can be explained by the more favorable energetic interaction energies that RDX experiences in the big cage.

In Figure 4.6, we show isodensity surfaces for the center of mass (COM) of RDX in the five IRMOFs at 300 K and 9.36×10^{-7} bar. The COM positions of RDX are sampled 300 times after equilibrium in GCMC simulation at 300 K and ~ 1 ppm. In each sample there are about 1000 RDX molecules. In the simulation, RDX molecules are adsorbed in a large number of framework unit cells since the loading of RDX is so low. For the purposes of visualization, they are reflected to one unit cell of the framework by the periodic boundary conditions to calculate the probability density. The isodensity plots are shown around a single vertex, of which there are 8 in each cage. The density contour for all IRMOFs has the same value, which is $6.6 \times 10^{-2} \text{ kg/m}^3$. From these isodensity plots, we can see the five IRMOFs have similar adsorption sites, which are all in the big cage and around the vertex. The reason why we see IRMOF-1 has different adsorption sites is because IRMOF-1 adsorbs much less than the other MOFs at the same contour level. If we increase the contour level for those other MOFs, we can see the same shape of the adsorption sites, presenting three-fold symmetry of sub-sites within the adsorption site. This means the outer rings of the adsorption site have more favorable adsorption capability to RDX than the center. The same phenomena have been shown previously for IRMOF-1 using different partial charges in chapter 2.

We have calculated diffusivities using the Einstein Relation. At 200 K for all IRMOFs and at 300 K for IRMOF-3, IRMOF-10a and IRMOF-10b, the RDX molecules do not move between cages during the simulation and thus do not travel a sufficient distance to make it to the linear, infinite time behavior required by the Einstein relation.

Therefore, the slope of log-log plot for MSD versus time is checked to be unity, as shown in Appendix 4.B. In order to calculate the activation energy, we use the self-diffusivities above 400 K, where RDX in all IRMOFs exhibit intercage motion.

In Figure 4.7, we show self-diffusivities for RDX in IRMOFs in an Arrhenius plot. The self-diffusivity is given in a logarithmic scale. The temperature ranges from 400 K to 600 K. We can see that the self-diffusivity of RDX is lowest in IRMOF-3 and highest in IRMOF-10. The activation energies for the five IRMOFs are shown in Figure 4.8. The value for IRMOF-1 is in good agreement with the result in chapter 2.

In Figure 4.9, we show the travelled distance obtained from the square root of the final MSD. At 250 K RDX does not leave the cage. At 300 K, RDX is able to move between cages in the IRMOFs with small activation energies. As temperature increases further, RDX starts to travel between cages in all IRMOFs.

There is a concern that in tailoring an MOF to preferentially adsorb one compound that one could make the binding energy so large that the adsorbate becomes immobile. This concern is valid if the activation energy for diffusion (the difference between the transition state energy and the adsorption site energy) correlates strongly only to the adsorption site energy. If the transition state energy also changes as functionality is introduced then the relationship between binding energy for adsorption and activation energy for diffusion is not a simple one. Therefore, we now explore this relationship.

Although the adsorption energy of RDX in IRMOF-10a is substantially larger than that of RDX in IRMOF-1, the activation energy for diffusion of RDX in IRMOF-10a is lower than that of RDX in IRMOF-1. This implies that there is not a positive

correlation between binding energy and activation energy. Moreover, for a practical application, this means IRMOF-10a not only has a higher adsorption capacity for RDX at equilibrium but also adsorbs/desorbs it more quickly. For cages of a given size, there does appear to be a qualitative relationship between stronger binding and higher activation energies.

We can perform a simple calculation to get an estimate for the timescale involved in loading or unloading RDX in an IRMOF crystal. The maximum production crystal size of IRMOF-1 is $\sim 150\mu\text{m}$ [83]. If we estimate the time for RDX to diffuse out of the framework at 300 K using this crystal size, it would take 428, 4004, 157, 606 and 363 seconds for IRMOF-1, IRMOF-3, IRMOF-10, IRMOF-10a and IRMOF-10b, respectively. For smaller crystals, these times would be reduced.

4.3.2. Adsorption Loading and Self-Diffusivities Calculated with Partial charges from Natural Bond Orbital (NBO) Analysis

In this section, we repeat a portion of the simulations described above using the NBO charge distribution. As a reminder, the NBO charges are much larger on the N and O of the nitro groups of the RDX molecule. Consequently, the binding energies are much higher and the amount of RDX adsorbed is much greater. We report these results for both LPA and NBO since it is not clear, which charges better reflects reality.

In Figure 4.10, we show one-point from the RDX adsorption isotherm for the five IRMOFs at 300 K and 1.43×10^{-13} bar, which is the lowest pressure in the studied pressure range. It is immediately clear that the loadings can be as high as 3 RDX per cage using NBO charges, as compared to a maximum loading of 1 RDX per 4×10^{10} cages at the

same state point using the LPA charges. This increase in amount of material adsorbed by 9 to 11 orders of magnitude is a direct consequence of the binding energies. With the LPA charges, the binding energy ranged from -8 to -11 kcal/mol, while, with the NBO charges, the binding energy ranges from -25 to -33 kcal/mol.

As was the case with LPA, there is a monotonic correspondence between the binding energy and the amount of RDX adsorbed. However, at these high loadings, the binding energies are no longer completely dominated by RDX-IRMOF components. The RDX-RDX component can be significant and in IRMOF-3 is ~6.0% of the total binding energy, as shown in Table 4.4. While this is a small fraction, it is still large enough to make IRMOF-3 adsorb the most RDX. (On the basis of the RDX-IRMOF contribution to the binding energy alone, IRMOF-3 is third.)

We can explore how the changes to structure in the IRMOF impact the amount of RDX when NBO charges are used, as we did when the LPA charges were used. Essentially, this analysis will provide some information as to whether the same qualitative structure/property relationships are observed at high loading as were observed at low loading. To evaluate the effect of pore size on RDX adsorption in the absence of any amine groups, we compare IRMOF-1 (small) and IRMOF-10 (big) and observe that IRMOF-10 adsorbs more RDX on a per cage basis, as was the case at low loadings. To evaluate the effect of the presence of an amine group in small cages, we compare IRMOF-1 (no amine) and IRMOF-3 (amine) and observe that IRMOF-3 adsorbs more RDX, again as was the case in low loadings, although the effect is more pronounced at high loadings. To evaluate the effect of the presence of an amine group in large cages, we compare IRMOF-10 (no amine) and IRMOF-10a (amine near the vertex) or IRMOF-10b

(amine away from vertex). We observe that the amine-containing IRMOFs adsorb more RDX than IRMOF-10, again as was the case at low loadings. To evaluate the effect of the placement of the amine group in large cases, we compare IRMOF-10a and IRMOF-10b, and observe that when the amine group is placed in the 2-position (closer to the vertex), the amount of RDX is slightly reduced, which is in contradiction to what was observed at low loading. However, from the isodensity distributions for IRMOF-10a and IRMOF-10b, as shown in Figure 4.11, we can see clearly that IRMOF-10b has more adsorption sites than IRMOF-10a at the same density contour level, which are located in small cages as indicated in the dotted circle. The effect of the location of amine group in IRMOF-10a and IRMOF-10b is different using the two charge sets, since in NBO, when the cage is full of RDX, an amine group placed away from the vertex can still interact with an RDX nitro group.

There is more than three orders of magnitude difference in the amount of RDX adsorbed when comparing the best adsorbent (IRMOF-3) and the worst adsorbent (IRMOF-1) with the NBO charges. If we quantify the adsorption capability when NBO charges are used on the basis of how much the framework concentrates RDX from the gas phase on a volumetric basis, as we did when LPA charges were used, the best one concentrates RDX by a factor of 4×10^{14} and the worst one by a factor of 4×10^{11} .

In Figure 4.12, we show self-diffusivities for RDX in the IRMOFs in an Arrhenius plot when NBO charges are used. The self-diffusivity is given in a logarithmic scale and the temperature ranges from 400 K to 600 K as was in the LPA case. We can see that the self-diffusivity of RDX in NBO case is two orders magnitude lower than that

in LPA case. This is the consequence of higher binding energy in NBO case, where RDX is more difficult to move between cages.

In Figure 4.13, we show the activation energies for RDX in IRMOFs when NBO charges are used. We see again that there is not a positive correlation between binding energy and activation energy. For example, IRMOF-3 has the highest binding energy in this case, but the activation energy of IRMOF-3 is much lower than that of IRMOF-10, IRMOF-10a and IRMOF-10b. The relative trends in activation energy are different when using the NBO and LPA charge sets. The activation energies for diffusion in the materials with large pores (IRMOF-10, IRMOF-10a and IRMOF-10b) are lower compared to those with small pores (IRMOF-1 and IRMOF-3) in the LPA case, but become higher in the NBO case. We believe that at low loadings (with LPA charges), the molecules diffuse faster in the large pores where there the windows between cages present less of a barrier. However, at high loadings (with NBO charges), this advantage due to the pore structure is lessened or even reversed due to RDX-RDX interactions.

To summarize the comparison, we observed the following RDX adsorption trend with the LPA charges: IRMOF-10a > IRMOF-3 > IRMOF-10b > IRMOF-10 > IRMOF-1; and we observed the following adsorption trend with the NBO charges: IRMOF-3 > IRMOF-10b > IRMOF-10a > IRMOF-10 > IRMOF-1. In both cases, the three IRMOFs with an amine group adsorb more than the two IRMOFs without an amine group. At high loadings, there appears to be a cross-correlation between cage size and amine presence that was not evident at low loadings.

4.4 Conclusions

In this chapter, we used molecular-level simulations to generate a fundamental understanding of the relationship between the structure of a nanoporous material and its ability to serve as a smart nanoporous preconcentrator (SNP) for the explosive molecule RDX.

We performed classical GCMC and MD simulations to investigate the potential of IRMOFs to adsorb and desorb RDX. These IRMOFs were examined by varying cage size and the presence and location of amine groups, which can serve as electrostatic anchors for RDX. The purpose was to show how much the functional groups can increase the adsorption of RDX and affect the selectivity. We applied two different charge generation methods—Löwdin Population Analysis (LPA) and Natural Bond Orbital (NBO) Analysis—to calculate the atomic partial charges for the five IRMOFs. We chose these two methods out of many choices of charge generating techniques to show the lower adsorption phase and higher adsorption phase. In both cases, the conclusion is in a good agreement, which shows the presence of amine groups increase the amount of RDX adsorbed and the cage size and the location of amine groups also affect the loading of RDX.

For the LPA charges, we generated adsorption isotherms, binding energies, density distributions and self-diffusivities for RDX in these IRMOFs. The adsorption isotherms are in the linear regime defined by the Henry's law constants. The IRMOF with larger cage size and the amine group close the vertex, IRMOF-10a, increases the Henry's law constant 10 times when comparing to IRMOF-1. The adsorption isotherms show the loading of RDX increases greatly with amine group. In addition, the positions

of amine group do affect the adsorption loading. The energies of adsorption of RDX at infinite dilution are found to be -8.1, -10.4, -9.3, -11.1 and -10.1 kcal/mol for IRMOF-1, IRMOF-3, IRMOF-10, IRMOF-10a and IRMOF-10b, respectively. The adsorption loading is correlated to the energy of adsorption, which is IRMOF-10a>IRMOF10b>IRMOF-3>IRMOF-10>IRMOF-1. The IRMOF with the largest adsorption loading concentrates RDX up to 3000 times compared to the bulk, on a volumetric basis. The probability density contour shows the adsorption sites of RDX located exclusively in big cages, near a vertex and between benzene rings. One of the nitro groups interact closely with the vertex and the second nitro group interacting with amine groups increases the adsorption. The self-diffusivities of RDX in IRMOFs display an Arrhenius temperature dependence, with activation energies of 6.0, 6.8, 4.6, 5.8 and 5.1 kcal/mol for IRMOF-1, IRMOF-3, IRMOF-10, IRMOF-10a and IRMOF-10b, respectively. The activation energy for diffusion is not strictly positively correlated to the adsorption energy. From a simple Langmuir estimation, the selectivity of RDX over butane at a specific condition is about 5000.

Using the NBO charges, we found that RDX condensed in the pores of the IRMOFs. Simulations using the NBO charges show a much deeper binding energy and consequently orders of magnitude higher adsorption than do comparable simulations using the LPA charges. Despite the fact that the loading was orders of magnitude higher, we found the same general trends for adsorption as a function of cage size and presence of amine for the NBO and LPA charges. The addition of the amine group substantially enhanced adsorption. The effect of the location of amine group in IRMOF-10a and IRMOF-10b is different using the two charge sets, since in NBO, when the cage is full of

RDX an amine group placed away from the vertex can still interact with an RDX nitro group. The adsorption loading is IRMOF-3 > IRMOF-10b > IRMOF-10a > IRMOF-10 > IRMOF-1.

We have shown that tailored IRMOFs can have attractive characteristics for smart nanoporous preconcentrators of explosives, including high concentration factor and high selectivity while maintaining mobility of the RDX within the IRMOF. While the uncertainty in the atomic charges precludes a definitive statement on the quantitative performance of the IRMOFs as smart nanoporous preconcentrators, the trends are independent of charge set and the results span the regime of reasonable expectations.

4.5 Acknowledgements

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Appendix 4.A: Tables and Figures

Table 4.1. Unit cell lengths and masses of the cubic structures of the IRMOFs[15].

Structure	Super unit cell length (Å)	Super unit cell mass (g/mol)
IRMOF-1	25.832	6156.8
IRMOF-3	25.7465	6516.8
IRMOF-10	34.2807	7980.8
IRMOF-10a	34.2807	8340.8
IRMOF-10b	34.2807	8340.8

Table 4.2. The Henry's law constants and concentration factors on a volumetric basis for the IRMOFs studied, using LPA charges.

Structure	Henry's law constant (mol/kg/bar)	RDX concentration factor on a volumetric basis
IRMOF-1	16.0	236
IRMOF-3	100.6	1580
IRMOF-10	32.7	621
IRMOF-10a	148.6	3033
IRMOF-10b	66.9	1336

Table 4.3. The small cage and big cage properties at 300 K and 9.4×10^{-7} bar using the LPA charges. N_1 is the cubic root of the number of the framework unit cells used; N_2 is the total number of RDX molecules adsorbed in N_1^3 of unit cells of the framework; N_3 is the number of RDX molecules adsorbed in the small cages of the framework; N_4 is the number of RDX molecules adsorbed in the big cages of the framework; U_s is the RDX-MOF interaction energy in the small cage; U_b is the RDX-MOF interaction energy in the big cage. The unit of energy is kcal/mol.

Structure	N_1	N_2	N_3	N_4	U_s	U_b
IRMOF-1	221	997 $\pm$ 31	7 $\pm$ 3	990 $\pm$ 31	-3.7 $\pm$ 1.0	-8.1 $\pm$ 0.05
IRMOF-3	118	1001 $\pm$ 32	8 $\pm$ 3	993 $\pm$ 32	-7.8 $\pm$ 0.9	-10.4 $\pm$ 0.06
IRMOF-10	162	1050 $\pm$ 28	3 $\pm$ 2	1047 $\pm$ 27	-1.9 $\pm$ 1.5	-9.4 $\pm$ 0.05
IRMOF-10a	95	1031 $\pm$ 28	2 $\pm$ 1	1028 $\pm$ 28	-4.1 $\pm$ 2.9	-11.1 $\pm$ 0.06
IRMOF-10b	126	1044 $\pm$ 32	4 $\pm$ 2	1040 $\pm$ 32	-4.4 $\pm$ 2.1	-10.1 $\pm$ 0.06

Table 4.4. The adsorption loadings and adsorption energies calculated with NBO charges used for the IRMOFs at 300 K and 1.43×10^{-13} bar.

Structure	Average loading (molecule/cage)	Interaction energy (kcal/mol)		
		RDX-RDX	RDX-MOF	Total
IRMOF-1	$2.8 \times 10^{-3} \pm 1.1 \times 10^{-4}$	$-2.4 \times 10^{-3} \pm 2.6 \times 10^{-3}$	-25.5 ± 0.01	-25.5 ± 0.01
IRMOF-3	3.4 ± 0.04	-2.09 ± 0.08	-31.1 ± 0.17	-33.2 ± 0.13
IRMOF-10	$9.2 \times 10^{-2} \pm 3.7 \times 10^{-3}$	$-8.2 \times 10^{-4} \pm 4.4 \times 10^{-3}$	-27.9 ± 0.09	-27.9 ± 0.09
IRMOF-10a	1.1 ± 0.02	$2.6 \times 10^{-2} \pm 1.9 \times 10^{-2}$	-31.8 ± 0.13	-31.8 ± 0.12
IRMOF-10b	1.8 ± 0.03	0.1 ± 0.02	-32.1 ± 0.07	-32.0 ± 0.08

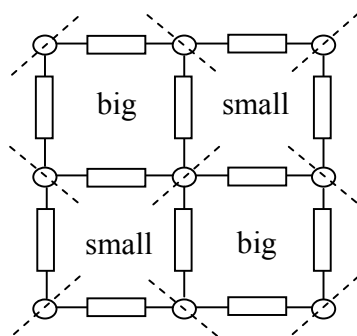


Figure 4.1. Schematic illustration of a typical MOF structure. The spheres indicate the metal connectors and the rectangles represent the organic linkers. Specifically in IRMOF-1, the spheres are Zn_4O and the organic linkers are 1,4-benzenedicarboxylic acid (BDC). The dotted lines represent the orientation of organic linkers. A small cage is the orientation of linkers towards the center of cages, while a big cage has the opposite orientation.

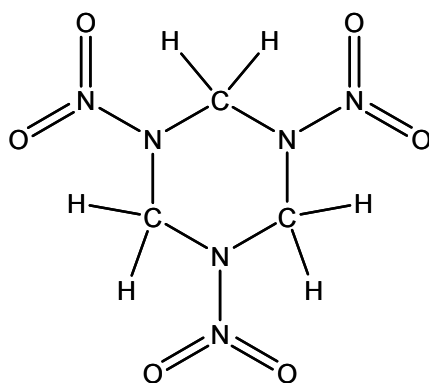


Figure 4.2. The structure of an RDX molecule.

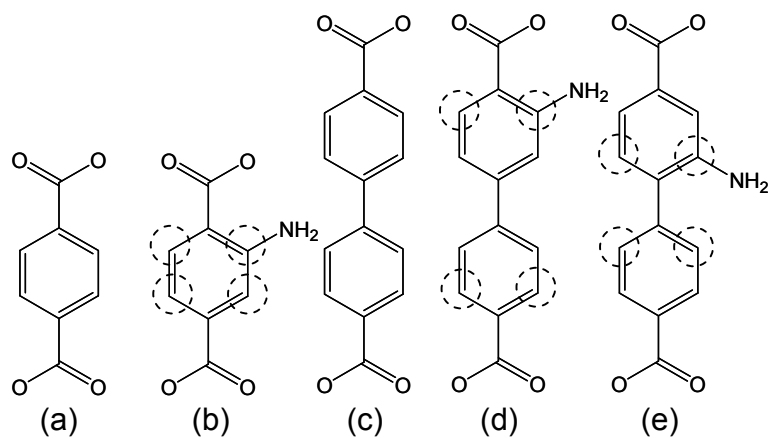


Figure 4.3. Five different IRMOFs have the same metal connectors but with different organic linkers, which represent respectively: (a) IRMOF-1; (b) IRMOF-3; (c) IRMOF-10; (d) IRMOF-10 with amine group at benzene position 2; (e) IRMOF-10 with amine group at benzene position 3. NH_2 group is disordered over four sites, indicated in dotted circles.

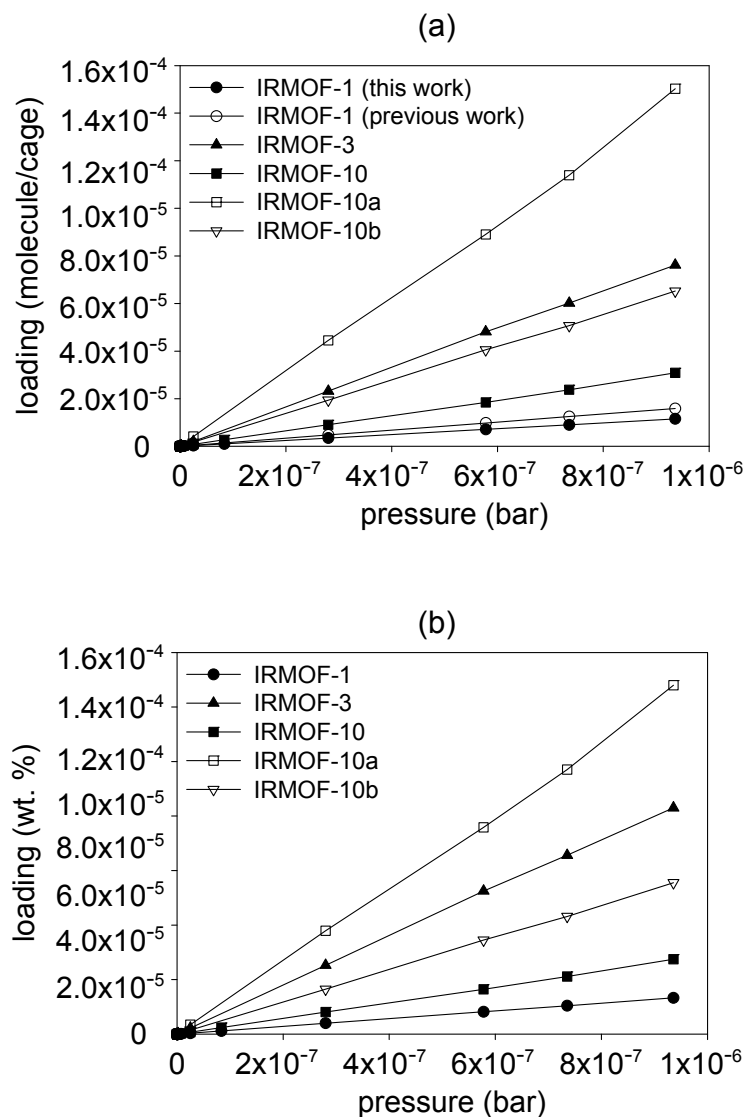


Figure 4.4. The adsorption isotherms for the five IRMOFs studied in this chapter when LPA charges are used. (solid circle: IRMOF-1; open circle: IRMOF-1 in chapter 2; solid upper-triangle: IRMOF-3; solid square: IRMOF-10; open square: IRMOF-10a; open lower-triangle: IRMOF-10b.)

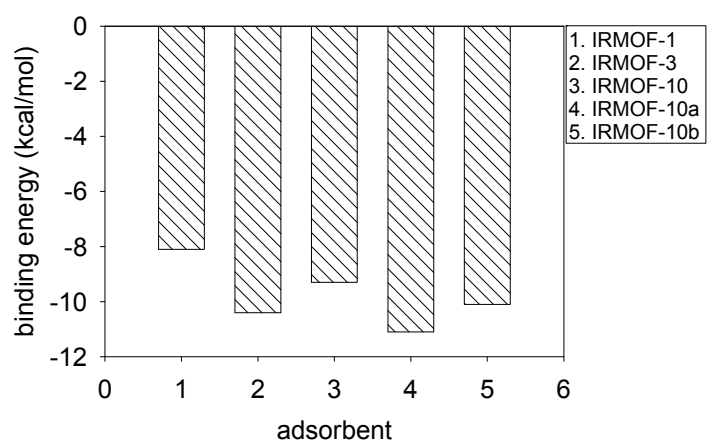


Figure 4.5. The binding energies of RDX in the five IRMOFs studied in this chapter when LPA charges are used.

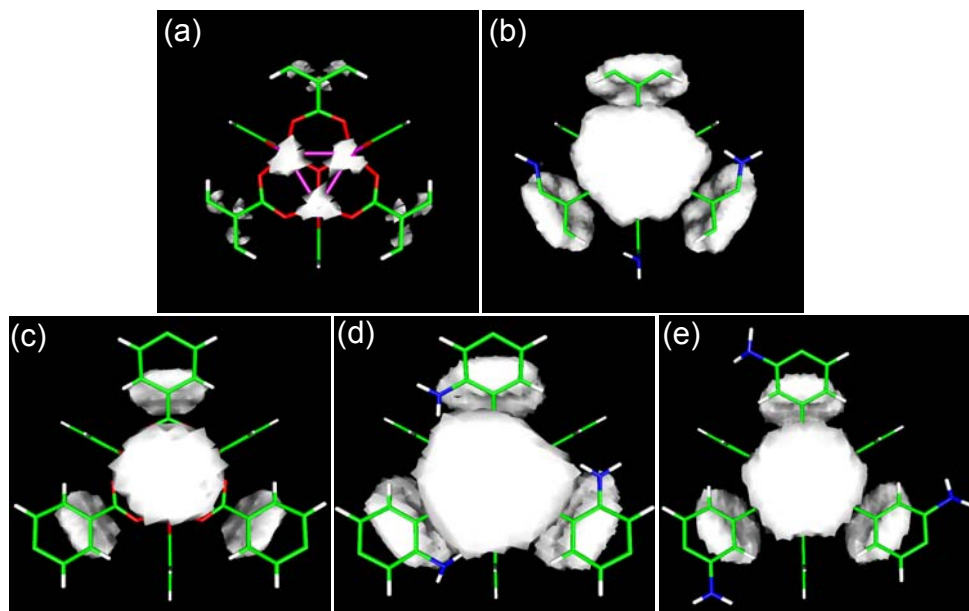


Figure 4.6. Isodensity distributions of RDX in IRMOFs in a single vertex at 300 K and 9.4×10^{-7} bar when LPA charges are used. The viewpoint is from the center of the big cage: (a) IRMOF-1; (b) IRMOF-3; (c) IRMOF-10; (d) IRMOF-10a; (e) IRMOF-10b. The density contour for RDX molecule in all IRMOFs is $6.6 \times 10^{-2} \text{ kg/m}^3$. (Legend: Zn, violet; O, red; C, green; N, blue; H, white.)

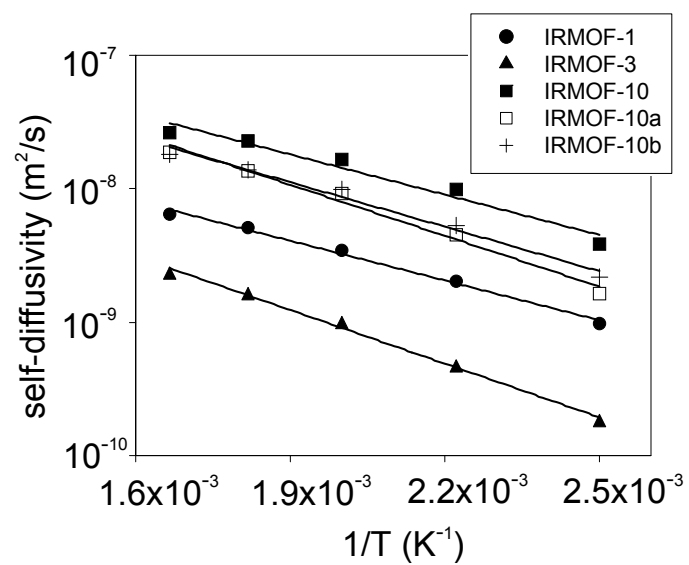


Figure 4.7. Arrhenius plot of RDX self-diffusivities for the IRMOFs when LPA charges are used. The solid line is Arrhenius equation fitting.

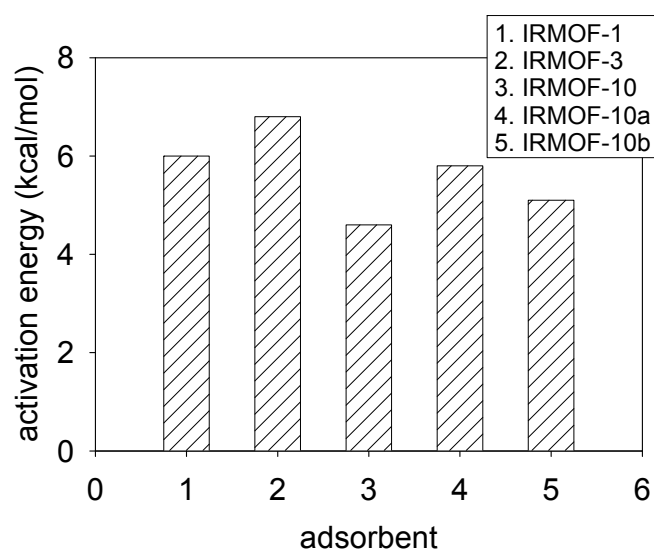


Figure 4.8. The activation energies of RDX in the five IRMOFs studied in this chapter when LPA charges are used.

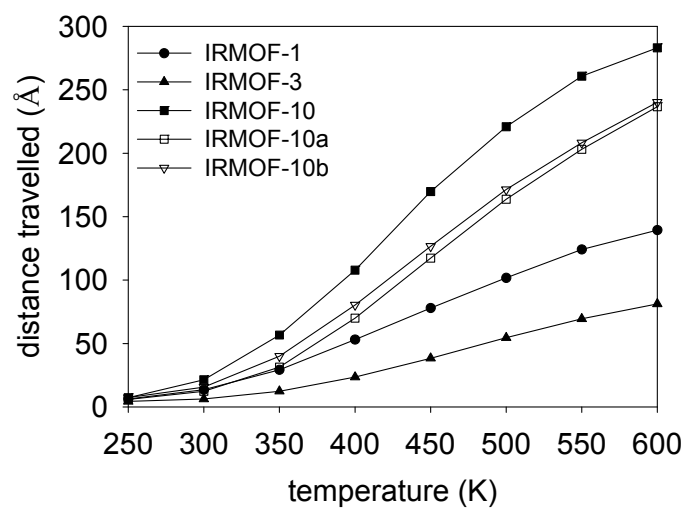


Figure 4.9. Travelled distances for RDX in IRMOFs at temperatures from 250 K to 600 K when LPA charges are used.

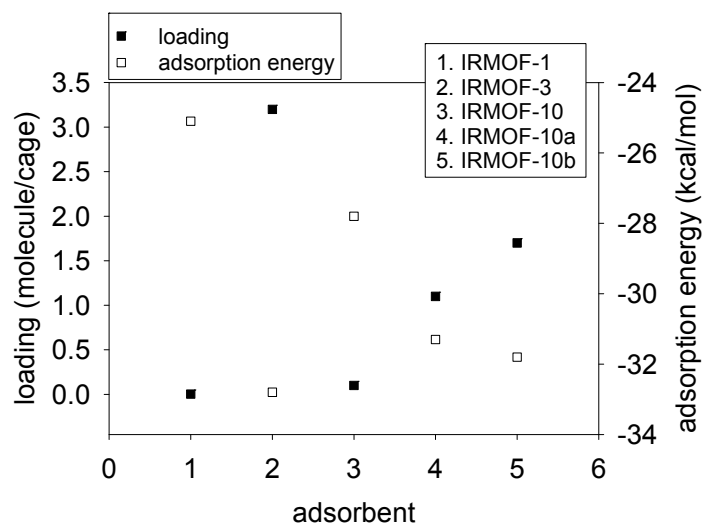


Figure 4.10. One-point adsorption isotherm and energy for RDX in five IRMOFs at 300 K and 1.43×10^{-13} bar when NBO charges are used.

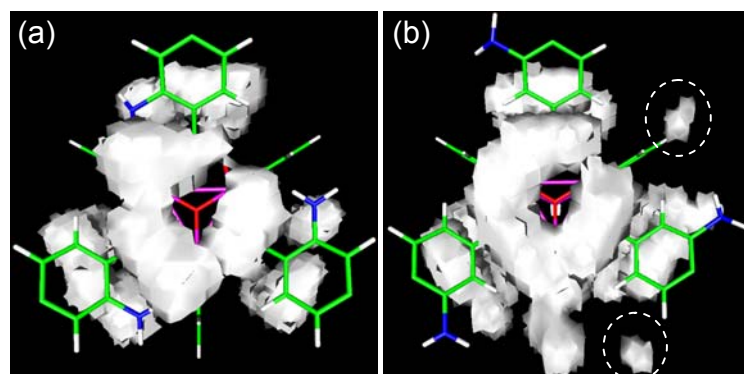


Figure 4.11. Isodensity distributions of RDX in IRMOF-10a and IRMOF-10b in a single vertex at 300 K and 1.43×10^{-13} bar when NBO charges are used. The viewpoint is from the center of the big cage: (a) IRMOF-10a; (b) IRMOF-10b. The density contour is 369 kg/m^3 for RDX molecule. The dotted circles indicate the adsorption sites in the small cage. (Legend: Zn, violet; O, red; C, green; N, blue; H, white.)

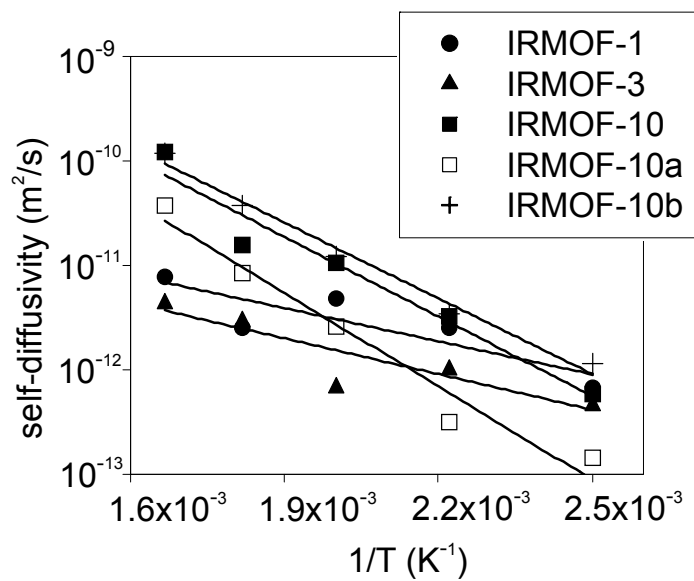


Figure 4.12. Arrhenius plot of RDX self-diffusivities for the IRMOFs when NBO charges are used. The solid line is Arrhenius equation fitting.

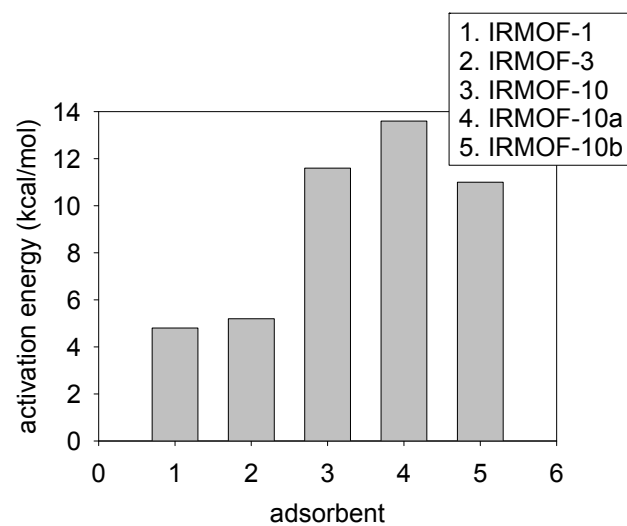


Figure 4.13. The activation energies of RDX in the five IRMOFs studied in this chapter when NBO charges are used.

Appendix 4.B: Supporting Information

The L-J potential parameters for the amine group[136] on the framework are listed in Table S-4.1.

In Table S-4.2, we report the atomic partial charges for the five IRMOFs from LPA calculation in FIREBALL code[111]. The FIREBALL code uses the super unit cells with periodical boundary conditions to calculate the charge distributions. The labeling of symmetrically independent atoms on the frameworks is depicted in Figure S-4.1.

In Table S-4.3, we report the atomic partial charges for the five IRMOFs from NBO calculation in FIREBALL code. The labeling of symmetrically independent atoms on the frameworks is also depicted in Figure SI-2.

In Table S-4.4, we report the atomic partial charges for RDX calculated in FIREBALL and GAUSSIAN03[102]. The structure of RDX is shown in Figure 2 in the manuscript. The atomic positions of RDX are fixed in the ideal gas equilibration during both calculations. There are large discrepancies (the largest difference is about 160%) between LPA and NBO calculations and small differences (the largest difference is about 40%) between NBO calculation in FIREBALL and NBO calculation in GAUSSIAN.

In Table S-4.5 and Table S-4.6, we compare the partial charges for IRMOF-1 and IRMOF-10 calculated in FIREBALL and GAUSSIAN03. We illustrate the difference from FIREBALL and GAUSSIAN by only looking at IRMOF-1 and IRMOF-10. The super unit cells of framework with periodical boundary conditions are employed in the FIREBALL calculation and the fragments of framework employed in the GAUSSIAN calculation are shown in Figure S-4.2. The atomic positions for the framework are fixed

at the experimental X-ray diffraction data during calculations. There are also significant differences between LPA and NBO and between FIREBALL and GAUSSIAN.

In Table S-4.7 to Table S-4.12, we report the data for simulation results with LPA charges such as adsorption loadings, binding energies, self-diffusivities, activation energies and travelled distances that have been reported in the manuscript.

In Table S-4.13 to Table S-4.14, we report the self-diffusivity and activation energy for self-diffusivity for RDX in the IRMOFs using NBO charges.

Below, we describe the Langmuir analysis used to estimate selectivities. The Langmuir adsorption isotherm for pure gas, which gives the amount of gas adsorbed as a function of gas pressure at a fixed temperature, can be expressed by the following equation[139]:

$$\theta(p,T) = \frac{\chi(T)p}{1 + \chi(T)p}, \quad \chi(T) = q(T)e^{\mu^0(T)/kT}$$

where p is pressure, T is temperature, $\theta(p,T)$ is the amount of gas adsorbed as a function of pressure and temperature, k is Boltzmann constant, $\mu^0(T)$ is a standard chemical potential, which is a integration constant, $q(T)$ is the partition function for a single adsorbed molecule.

$$\text{For a monatomic gas, } \mu^0(T) = -kT \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} kT \right], \text{ where } m \text{ is the mass of}$$

gas and h is the Planck's constant, k is Boltzmann constant and T is temperature.

In the harmonic-oscillator approximation, $q(T) = q_x q_y q_z e^{-U_{00}/kT}$, where q_x , q_y , and q_z are one-dimensional harmonic-oscillator partition function. For a monatomic gas,

$q_x = q_y = q_z = \frac{e^{-\Theta/2T}}{1 - e^{-\Theta/T}}$, where $\Theta = h\nu/k$ and ν is the classical frequency, which can be approximated by $\nu = \frac{\bar{v}}{2d}$, where d is the adsorption site diameter and $\bar{v}$ is the mean velocity, $\bar{v} = \sqrt{\frac{8kT}{\pi m}}$. The site diameter is approximated by the site volume of the adsorbent.

Similarly, the binary adsorption isotherm can be expressed by the following equations:

$$\theta_1(p_1, p_2, T) = \frac{\chi_1(T)p_1}{1 + \chi_1(T)p_1 + \chi_2(T)p_2}, \quad \chi_1(T) = q_1(T)e^{\mu_1^0(T)/kT}$$

$$\theta_2(p_1, p_2, T) = \frac{\chi_2(T)p_2}{1 + \chi_1(T)p_1 + \chi_2(T)p_2}, \quad \chi_2(T) = q_2(T)e^{\mu_2^0(T)/kT}$$

The mole fraction of component 1 in the smart nanoporous preconcentrator is

$$X_{SNP}^1 = \frac{\theta_1}{\theta_1 + \theta_2}$$

The mole fraction of component 2 in the smart nanoporous preconcentrator is

$$X_{SNP}^2 = \frac{\theta_2}{\theta_1 + \theta_2}$$

The mole fraction of component 1 in the bulk is (assuming an ideal gas)

$$X_{bulk}^1 = \frac{p_1}{p_1 + p_2}$$

The mole fraction of component 2 in the bulk is (assuming an ideal gas)

$$X_{bulk}^2 = \frac{p_2}{p_1 + p_2}$$

The selectivity is defined by:

$$S = \frac{X_{SNP}^1 / X_{bulk}^1}{X_{SNP}^2 / X_{bulk}^2}$$

Appendix 4.C: Tables and Figures in the Supporting Information

Table S-4.1. The L-J potential parameters for amine group[136].

Atom	σ (Å)	ϵ/k_b (K)
N	1.62	27.68
H	1.18	17.10

Table S-4.2. The partial charges for the symmetrically independent atoms on the five IRMOFs from LPA calculation in FIREBALL. The labeling of the atoms is shown in Figure SI-1. For Figure SI-1(b) and SI-1(c), N is always attached to C₃; For Figure SI-1(e), N is always attached to C₄.

Atom	q (e)				
	IRMOF-1	IRMOF-3	IRMOF-10	IRMOF-10a	IRMOF-10b
Zn	0.751	0.783	0.788	0.778	0.783
O ₁	-0.520	-0.503	-0.509	-0.495	-0.506
O ₂	-0.243	-0.258	-0.255	-0.264	-0.262
C ₁	0.158	0.148	0.136	0.142	0.137
C ₂	-0.094	-0.210	-0.120	0.078	-0.148
C ₃	-0.090	0.087	-0.082	-0.152	-0.125
C ₄	/	-0.113	-0.081	-0.131	0.081
C ₅	/	-0.177	-0.032	-0.048	-0.099
C ₆	/	-0.075	/	-0.098	-0.081
C ₇	/	-0.063	/	-0.077	-0.089
C ₈	/	/	/	-0.082	-0.134
C ₉	/	/	/	-0.190	-0.030
H	0.095	0.110	0.103	0.119	0.122
H(amine)	/	0.246	/	0.239	0.239
N (amine)	/	-0.413	/	-0.417	-0.416

Table S-4.3. The partial charges for the symmetrically independent atoms on the five IRMOFs from NBO calculation in FIREBALL. The labeling of the atoms is also shown in Figure SI-1.

Atom	q (e)				
	IRMOF-1	IRMOF-3	IRMOF-10	IRMOF-10a	IRMOF-10b
Zn	1.172	1.210	1.166	1.144	1.184
O ₁	-0.908	-0.922	-0.872	-0.866	-0.937
O ₂	-0.569	-0.601	-0.590	-0.592	-0.589
C ₁	0.572	0.722	0.632	0.654	0.647
C ₂	-0.066	-0.353	-0.115	-0.300	-0.172
C ₃	-0.309	0.081	-0.270	0.297	-0.292
C ₄	/	-0.343	-0.256	-0.308	0.273
C ₅	/	-0.253	0.052	0.033	-0.102
C ₆	/	-0.107	/	-0.213	-0.182
C ₇	/	-0.146	/	-0.169	-0.193
C ₈	/	/	/	-0.183	-0.172
C ₉	/	/	/	-0.173	0.051
H	0.310	0.168	0.258	0.190	0.162
H(amine)	/	0.526	/	0.483	0.578
N (amine)	/	-0.783	/	-0.937	-0.988

Table S-4.4. Comparison of partial charges for RDX from LPA calculation in FIREBALL, NBO calculation in FIREBALL and NBO calculation in GAUSSIAN03.

atom	LPA (Fireball)	NBO (Fireball)	NBO (Gaussian)
C	0.05921	-0.03672	-0.04850
N	-0.18298	-0.29386	-0.28847
N(nitro)	0.17411	0.44076	0.61897
O	-0.13056	-0.29123	-0.40409
H	0.10539	0.23614	0.26309

Table S-4.5. Comparison of partial charges for IRMOF-1 from LPA calculation in FIREBALL, NBO calculation in FIREBALL and NBO calculation in GAUSSIAN03.

Atom	LPA (Fireball)	NBO (Fireball)	NBO (Gaussian)
Zn	0.751	1.172	1.718
O1	-0.520	-0.908	-1.718
O2	-0.243	-0.569	-0.883
C1	0.158	0.572	0.870
C2	-0.094	-0.066	-0.120
C3	-0.090	-0.309	-0.109
H	0.095	0.310	0.188

Table S-4.6. Comparison of partial charges for IRMOF-10 from LPA calculation in FIREBALL, NBO calculation in FIREBALL and NBO calculation in GAUSSIAN03.

Atom	LPA (Fireball)	NBO (Fireball)	NBO (Gaussian)
Zn	0.788	1.166	1.720
O1	-0.509	-0.872	-1.715
O2	-0.255	-0.590	-0.875
C1	0.136	0.632	0.870
C2	-0.120	-0.115	-0.165
C3	-0.082	-0.270	-0.115
C4	-0.081	-0.256	-0.170
C5	-0.032	0.052	-0.022
H	0.103	0.258	0.194

Table S-4.7. The average loadings for the five IRMOFs at 300 K and pressure range from 1.43×10^{-13} bar to 9.36×10^{-7} bar with partial charges from LPA calculation.

Pressure (bar)	Average loading (molecule/cage)				
	IRMOF-1	IRMOF-3	IRMOF-10	IRMOF-10a	IRMOF-10b
1.43×10^{-13}	1.76×10^{-12}	1.19×10^{-11}	4.65×10^{-12}	2.27×10^{-11}	1.01×10^{-11}
1.79×10^{-11}	2.20×10^{-10}	1.47×10^{-9}	5.80×10^{-10}	2.76×10^{-9}	1.24×10^{-9}
2.24×10^{-9}	2.75×10^{-8}	1.82×10^{-7}	7.20×10^{-8}	3.51×10^{-7}	1.56×10^{-7}
2.50×10^{-8}	3.07×10^{-7}	2.05×10^{-6}	8.00×10^{-7}	4.11×10^{-6}	1.72×10^{-6}
2.80×10^{-7}	3.46×10^{-6}	2.32×10^{-5}	9.07×10^{-6}	4.45×10^{-5}	1.94×10^{-5}
5.78×10^{-7}	7.10×10^{-6}	4.81×10^{-5}	1.85×10^{-5}	8.90×10^{-5}	4.05×10^{-5}
7.36×10^{-7}	9.01×10^{-6}	6.02×10^{-5}	2.38×10^{-5}	1.14×10^{-4}	5.07×10^{-5}
9.36×10^{-7}	1.15×10^{-5}	7.62×10^{-5}	3.09×10^{-5}	1.50×10^{-4}	6.52×10^{-5}

Table S-4.8. The average RDX-framework interaction potential energy including L-J interaction, electrostatic interaction and the total energy for IRMOFs studied using LPA charges. The total energy is essentially binding energy. The unit of energy is kcal/mol.

Structure	L-J interaction	Electrostatic interaction	Binding energy
IRMOF-1	-2.2	-5.9	-8.1
IRMOF-3	-2.3	-8.1	-10.4
IRMOF-10	-1.9	-7.4	-9.3
IRMOF-10a	-2.1	-9.0	-11.1
IRMOF-10b	-2.0	-8.1	-10.1

Table S-4.9. Calculated RDX self-diffusivities (D_{self}) and standard errors (δD_{self}) for the IRMOFs at temperature from 250 K to 600 K using LPA charges.

T (K)	symbol	Self-diffusivity (m^2/s)				
		IRMOF-1	IRMOF-3	IRMOF-10	IRMOF-10a	IRMOF-10b
250	D_{self}	6.73×10^{-12}	2.38×10^{-12}	1.40×10^{-11}	6.94×10^{-12}	9.61×10^{-12}
	δD_{self}	1.08×10^{-12}	1.89×10^{-13}	6.28×10^{-13}	4.03×10^{-13}	9.07×10^{-13}
300	D_{self}	5.25×10^{-11}	5.62×10^{-12}	1.43×10^{-10}	3.71×10^{-11}	6.19×10^{-11}
	δD_{self}	2.41×10^{-12}	9.50×10^{-13}	1.22×10^{-11}	1.33×10^{-11}	1.40×10^{-11}
350	D_{self}	2.88×10^{-10}	4.36×10^{-11}	1.11×10^{-9}	3.13×10^{-10}	5.24×10^{-10}
	δD_{self}	3.01×10^{-12}	1.05×10^{-12}	1.14×10^{-10}	1.65×10^{-11}	6.48×10^{-11}
400	D_{self}	9.81×10^{-10}	1.82×10^{-10}	3.85×10^{-9}	1.63×10^{-9}	2.16×10^{-9}
	δD_{self}	3.24×10^{-11}	1.98×10^{-11}	2.43×10^{-10}	1.03×10^{-10}	2.58×10^{-10}
450	D_{self}	2.02×10^{-9}	4.72×10^{-10}	9.85×10^{-9}	4.55×10^{-9}	5.34×10^{-9}
	δD_{self}	2.10×10^{-10}	7.10×10^{-12}	7.94×10^{-10}	4.95×10^{-10}	6.46×10^{-10}
500	D_{self}	3.44×10^{-9}	9.93×10^{-10}	1.65×10^{-8}	9.27×10^{-9}	9.82×10^{-9}
	δD_{self}	2.95×10^{-10}	6.36×10^{-11}	6.73×10^{-10}	1.91×10^{-10}	5.15×10^{-10}
550	D_{self}	5.09×10^{-9}	1.63×10^{-9}	2.26×10^{-8}	1.36×10^{-8}	1.39×10^{-8}
	δD_{self}	2.19×10^{-10}	1.99×10^{-11}	2.32×10^{-9}	3.05×10^{-10}	1.72×10^{-9}
600	D_{self}	6.44×10^{-9}	2.32×10^{-9}	2.64×10^{-8}	1.87×10^{-8}	1.82×10^{-8}
	δD_{self}	2.81×10^{-10}	1.12×10^{-10}	9.60×10^{-10}	8.45×10^{-10}	1.29×10^{-9}

Table S-4.10. The slope of natural logarithm of MSD versus natural logarithm of time using LPA charges.

T (K)	slope of equation of $\ln(\text{MSD})$ versus $\ln(\text{time})$				
	IRMOF-1	IRMOF-3	IRMOF-10	IRMOF-10a	IRMOF-10b
250	0.42	0.30	0.71	0.49	0.43
300	0.80	0.35	0.91	0.64	0.69
350	1.02	0.79	1.05	0.93	0.98
400	1.05	0.97	0.99	1.00	1.00
450	0.99	0.94	1.04	0.99	0.99
500	1.00	0.99	1.03	1.00	1.00
550	1.02	1.01	1.00	0.99	0.98
600	0.99	0.99	0.97	0.96	0.99

Table S-4.11. The activation energies for the five IRMOFs using LPA charges.

Structure	Activation energy (kcal/mol)
IRMOF-1	6.0
IRMOF-3	6.8
IRMOF-10	4.6
IRMOF-10a	5.8
IRMOF-10b	5.1

Table S-4.12. RDX travelled distances in the IRMOFs calculated by the square root of the final MSD at temperature from 250 K to 600 K using LPA charges.

T (K)	Travelled distance (Å)				
	IRMOF-1	IRMOF-3	IRMOF-10	IRMOF-10a	IRMOF-10b
250	6.3	4.4	7.4	6.0	7.5
300	13.6	6.3	21.4	12.4	15.7
350	29.2	12.4	56.7	31.5	40.0
400	53.2	23.6	107.9	70.0	80.4
450	78.0	38.4	169.7	117.3	126.6
500	101.7	54.6	220.9	163.7	171.4
550	124.1	69.5	260.7	203.0	208.2
600	139.3	81.3	283.0	236.6	240.1

Table S-4.13. Calculated RDX self-diffusivities (D_{self}) and standard errors (δD_{self}) for the IRMOFs at temperature from 400 K to 600 K using NBO charges.

T (K)	symbol	Self-diffusivity (m^2/s)				
		IRMOF-1	IRMOF-3	IRMOF-10	IRMOF-10a	IRMOF-10b
400	D_{self}	6.75×10^{-13}	4.75×10^{-13}	5.82×10^{-13}	1.42×10^{-13}	1.15×10^{-12}
	δD_{self}	2.63×10^{-13}	2.64×10^{-13}	1.59×10^{-13}	1.87×10^{-13}	3.63×10^{-13}
450	D_{self}	2.50×10^{-12}	1.05×10^{-12}	3.22×10^{-12}	3.13×10^{-13}	3.48×10^{-12}
	δD_{self}	1.18×10^{-13}	9.97×10^{-14}	4.20×10^{-13}	2.77×10^{-13}	2.00×10^{-13}
500	D_{self}	4.78×10^{-12}	7.22×10^{-13}	1.05×10^{-11}	2.59×10^{-12}	1.22×10^{-11}
	δD_{self}	3.53×10^{-13}	3.74×10^{-13}	2.11×10^{-12}	1.29×10^{-12}	1.20×10^{-12}
550	D_{self}	2.56×10^{-12}	3.05×10^{-12}	1.56×10^{-11}	8.56×10^{-12}	3.78×10^{-11}
	δD_{self}	1.19×10^{-12}	4.66×10^{-13}	1.67×10^{-12}	2.00×10^{-12}	3.60×10^{-12}
600	D_{self}	7.79×10^{-12}	4.61×10^{-12}	1.20×10^{-10}	3.79×10^{-11}	1.19×10^{-10}
	δD_{self}	3.14×10^{-12}	8.94×10^{-13}	1.08×10^{-10}	8.72×10^{-12}	3.58×10^{-12}

Table S-4.14. The activation energies for the five IRMOFs using NBO charges.

Structure	Activation energy (kcal/mol)
IRMOF-1	4.8
IRMOF-3	5.2
IRMOF-10	11.6
IRMOF-10a	13.6
IRMOF-10b	11.0

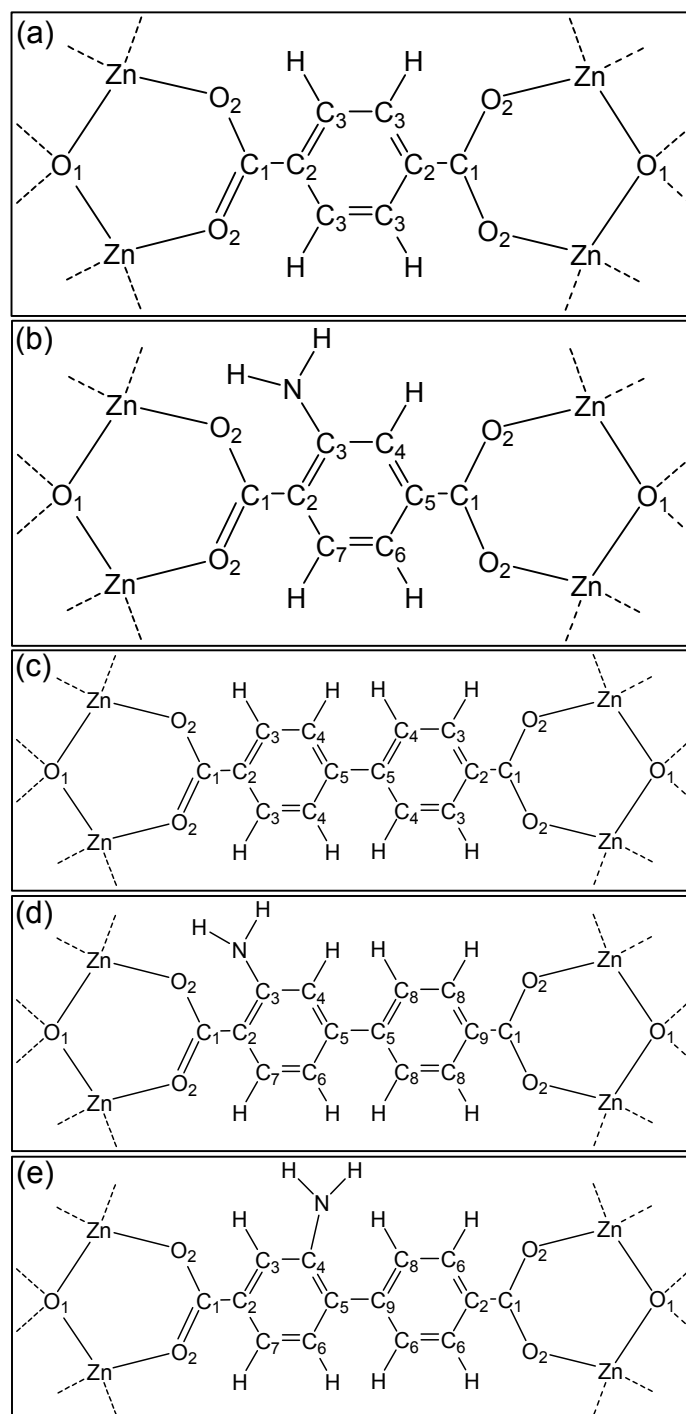


Figure S-4.1. The labeling of symmetrically independent atoms on frameworks as defined in this chapter. For (c),(d) and (e), the atoms with similar point charges are assigned the same names in order to decrease the number of atom names and the point charges of these atoms are averaged together as well.

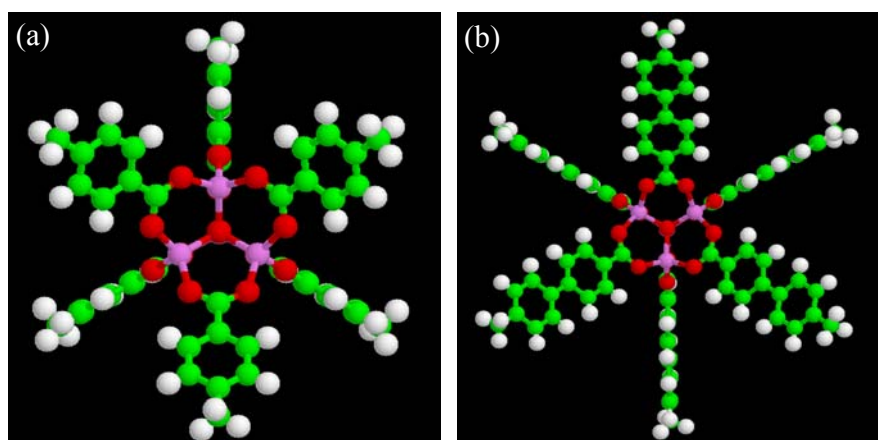


Figure S-4.2. The fragments for IRMOF-1 and IRMOF-10 used to calculate partial charges in GAUSSIAN03: (a) IRMOF-1; (b) IRMOF-10. (Legend: Zn, violet; O, red; C, green; H, white.)

CHAPTER 5

Molecular Simulations of H₂ Adsorption in Metal-Porphyrin Frameworks (MPFs): A Potential New Material Evaluation

Abstract

Path Integral Grand Canonical Monte Carlo (PI-GCMC) simulations using standard force fields were carried out to calculate the adsorption of H_2 in five Metal-Porphyrin Frameworks (MPFs), a new class of Metal Organic Framework (MOF)-type materials. We also calculated the adsorption isotherms of H_2 in IRMOF-1 and IRMOF-10 as a comparison. These simulations were performed at 77 K and room temperature (300 K). All calculations indicated that all MPFs adsorbed a higher weight fraction of H_2 than both IRMOF-1 and IRMOF-10, with one exception (MPF-2). The gravimetric hydrogen capacities were still well short of practical goals. The MPFs provides additional adsorption sites due to the porphyrin. A statistical mechanical lattice model predicted the adsorption well at room temperature. The prediction by this model showed that a weight fraction of hydrogen of 6 wt% adsorbed in pores of the size found in IRMOF-1 at ambient temperature and modest pressures required an energy of adsorption about 17 kJ/mole, which was consistent with other findings.

5.1 Introduction

Hydrogen (H_2) as a pollution-free energy source has been well-recognized as a future energy carrier. The wide utilization of H_2 in vehicles and portable electronics is limited by a safe and efficient storage system. System weight efficiency (weight of stored H_2 /system weight) of 6.0 wt% and volumetric density of 45 kg/m^3 for H_2 storage are first required to meet the goal of U.S. Department of Energy (DOE) Hydrogen Plan (2010) for fuel cell powered vehicles[140]. Note that a change on this target was made in 2009[141]. The targets now are 4.5 wt% and 28 kg/m^3 by 2010, 5.5 wt% and 40 kg/m^3 by 2015 and the ultimate targets are 7.5 wt% and 70 kg/m^3 . Compressed gas, liquefaction, metal hydrides, and physisorption are currently four main technologies for H_2 storage[142]. Each option has strengths and weaknesses in leading to a storage technology that is a viable part of a sustainable H_2 economy. The challenge with physisorption is finding an adsorbent material that can meet the weight fraction and density requirements.

The adsorption of H_2 on various materials has been widely studied for H_2 storage applications. Activated carbon and carbon-based nanomaterials such as carbon nanotubes are well known as candidate materials for H_2 storage, however, their adsorption potentials are limited due to the material properties and synthesis difficulties. During the past decade, metal-organic frameworks (MOFs) have been proposed as promising adsorbents because they have large pore volume and surface areas and can be synthesized in high purity, high crystallinity, potentially large quantities, and at low cost. Most attractively, MOFs can be tailored fairly easily by changing metals and organic ligands, leading to endless variants of structures. Since Yaghi and co-workers first proposed H_2 storage in MOFs[10], a large number of MOF structures have been characterized experimentally

and computationally for their abilities to adsorb H_2 . The enhancement of adsorption compared to typical activated carbon and carbon nanotubes is evident, however, none are currently capable of meeting the DOE targets at room temperature and moderate pressure according to previous works, both experimentally[143-146] and theoretically[18,107,147-149]. Hence, there is still a need to develop highly efficient adsorbents that are specifically designed for H_2 storage.

Porphyrins and their metal complexes have been used as functional building blocks in materials that are of interest for many areas due to their synthetic accessibility and modularity[150,151]. Kosal et al.[152] have demonstrated the feasibility of porphyrin molecules as building blocks for the rational construction of functional porous solids. They built a three-dimensional functional zeolite analogue by assembling a porphyrin building block with a carboxylate cluster. It has also shown in a recent review[29] that porphyrin combined with metalloligand groups may lead to interesting new materials with special properties. Very recently, Eddaoudi and coworkers[153] synthesized a new MOF, rht-MOF, with the largest cage size of 23.287 Å, which represents a new pathway for the hierarchical bottom-up assembly of predetermined highly coordinated supermolecular building blocks. Taken collectively, one could be able to build MOF analogue based on porphyrin building block. These new materials, referred as metal-porphyrin frameworks (MPFs), may have larger pore volume and surface area as well as greater functionalization than regular MOFs due to the joint of porphyrin, which could potentially increase the adsorption ability.

In this chapter, we have evaluated several MPFs for the ability to adsorb H_2 . Specifically we focused on the MPFs that have an isorecticular structure analogous to

IRMOF-1[15], one of MOFs that has been frequently studied. In the MPF, the organic linker in IRMOF-1 is replaced by a functionalized porphyrin. The simplest porphyrin linker is shown in Figure 5.1. The metal in the pore center is specifically indicated as Zn, which is used in this work. The functional groups can be attached anywhere in the porphyrin. They are not necessarily restricted to the metal bound in the porphyrin core, but can also be extended to the porphyrin periphery[29]. The dashed circles in Figure 5.1 indicate where the functional groups are attached in this work. The preliminary synthesis work for these porphyrins has been performed although the MPFs have not yet been well-characterized experimentally. It has been stated that the ideal procedure for identification of most promising structures and compositions to maximize H₂ storage, is to first perform molecular-level simulations, followed by experimental verification of storage capability[154]. That is the philosophy adopted in this work. In addition, many previous works[13,23,65,155] have demonstrated that the good agreement between molecular simulations and experiments can be reached if the force field is valid. Therefore, a combined theoretical and computational study was first performed in order to understand the H₂ storage characteristics of the MPFs.

In order to validate the force field, we performed calculations on IRMOF-1, as a standard for comparison. We also used IRMOF-10 as a comparison since it has a relatively larger cage size that can be compared to the MPF. We then use five different functional groups attached to the porphyrin shown in Figure 5.1 to compare the adsorption ability within the same cage size. The Grand Canonical Monte Carlo (GCMC) simulations are used to calculate H₂ adsorption isotherms of the MPFs and MOFs at 77K

and 300 K. We are only interested in the pressures under 10 bar since it is more realistic in the application fields.

In this chapter, statistical mechanics (SM) modeling was also employed to describe H₂ adsorption. The objective of the SM modeling was to determine whether the GCMC simulation isotherms (which are computationally intensive relative to the SM model) can be predicted or fit with an SM model that requires negligible computational resources.

5.2 Computational Details

5.2.1. Simulation Materials

The crystal structure of IRMOF-1 and IRMOF-10 selected was obtained from crystallographic data of Yaghi and co-workers[15]. Because no crystallographic data were available for the MPFs, we created the structures from two sources. We took the structure of the Zn₄O units that occur at the carboxylate cluster from IRMOF-1. We attached porphyrins with crystal structures determined by x-ray diffraction provided by Zhang and co-workers[28]. Five structure models of MPFs were prepared. In these MPFs, the Zn₄O clusters were located at the vertices, as in the MOF, and they were connected via the functionalized porphyrins to form a three-dimensional nanoporous cubic framework with cubic unit cell dimension (cage size) of 2.5561 nm. One of the structures around the pore space associated with one unit cell is shown in Figure 5.2. Analogous information for the other structures is provided in Appendix 5.B. The five functional groups are shown in Figure 5.3. We refer to these MPFs as MPF-1, MPF-2, MPF-3, MPF-4 and MPF-5, respectively. As a comparison, IRMOF-1 and IRMOF-10 are

also composed of Zn_4O cluster but with 1,4-benzenedicarboxylate (BDC) and 4,4'-biphenyldicarboxylic acid (BPDC) respectively as linkers, forming a three-dimensional network with unit cell dimension of 2.5832 nm and 3.42807 nm, respectively. However, the unit cell of IRMOF-1 and IRMOF-10 contains total 8 cages (4 big cages and 4 small cages reflected by the orientation of the linkage); thus, the cage size dimension for IRMOF-1 and IRMOF-10 is 1.2916 nm and 1.714 nm, respectively. The cage size, unit cell length, unit cell mass and unit cell volume for the MOFs and MPFs studied in this work are shown in Table 5.1. The accessible volume for the MOFs and MPFs was calculated based solely on the system geometry[23], and is shown in Table 5.1.

5.2.2. Simulation Method

The path integral Grand Canonical Monte Carlo (PI-GCMC) simulations[21,22] were employed to perform H_2 adsorption calculations in the MPF and IRMOF-1 since it has been shown to be the most accurate method to calculate H_2 adsorption at both room temperature and low temperature[65]. It is well known that when the molecular mass is small and the temperature is low, quantum effects become non-negligible in the trajectory of molecules. Even at 300 K, quantum effects lead to an overestimation of adsorption by several percent[149]. Therefore we have adopted the path integral formalism in the standard GCMC simulation. The formalism creates an isomorphism between a quantum particle and a classical closed-ring polymer molecule to account for quantum effects. The details for the formalism can be found in the Feynman's theory[156]. Details of the path integral technique can be found in several references[77,157,158].

Four types of moves were involved in the GCMC method: (i) translational moves, (ii) molecule rotation (iii) molecule insertion and (iv) molecule deletion, which were randomly attempted in a ratio of 4:2:3:3. We used 30 beads per molecule in our simulation considering computation efficiency and statistics accuracy. This number has been shown to be sufficient to ensure the convergence of the total energy[13]. The configurations of ring polymers are generated simultaneously using molecular dynamics (MD) simulation to increase the efficiency of energy convergence[77,159]. When the number of beads was set to 1, the classical simulations were reproduced.

For a given choice of chemical potential and temperature, we performed two simulations: one in the bulk phase and one in the adsorbed phase. We generated adsorption isotherms by plotting the fractional loading obtained from the adsorbed phase as a function of the pressure obtained from the bulk phase. We varied the volume of the bulk and number of unit cells of the framework such that the average number of H₂ in the system was sufficiently large to obtain good statistics. In order to compare with experimental isotherms, we converted the absolute adsorption to excess adsorption[13,23,65,155]. The conversion was performed as follows:

$$N^{ex} = N^{abs} - V_g \rho_g \quad (1)$$

In equation (1), N^{ex} is the excess adsorption, N^{abs} is the absolute adsorption calculated from the adsorbed phase, V_g is the pore volume of the adsorbent (thermodynamic definition), calculated as described by Myers and Monson[160], and ρ_g is the bulk gas density calculated from bulk phase. The pore volume is also shown in Table 5.1.

The atomic positions on the framework were kept rigid during the simulations. The non-bonded interactions were modeled by Lennard-Jones (L-J) potential. The L-J parameters for the atoms on the framework were taken from universal force field (UFF) force field[66]. The parameters for H₂ were from the Buch potential[161]. All the L-J cross-interaction parameters were determined by the Lorentz-Berthelot mixing rules. The L-J parameters used in this work are listed in Appendix 5.B.

A spherical cut-off was used in the simulation. The cut-off distance is set to 17 Å and no long-range corrections were used. Standard periodic boundary conditions and the minimum image convention were employed in all three directions. For each state point in this simulation, 2.5 million configurations were used to guarantee equilibrium and next 15 million configurations were tracked to get the desired average ensemble properties.

5.2.3. Statistical Mechanics (SM) Model

From the principles of SM[139,162], we have an expression for the adsorption isotherm relating the fractional occupancy to the bulk gas pressure.

$$\left[\frac{(\beta - 1 + 2\theta)(1 - \theta)}{(\beta + 1 - 2\theta)\theta} \right]^{c/2} \frac{\theta}{1 - \theta} = \rho_b V_s \exp\left(-\frac{U_{00}}{kT}\right) \exp\left(-\frac{cw_x}{2kT}\right) \quad (2)$$

In equation (2), θ is the fractional occupancy, $\beta = \sqrt{1 - 4\theta(1 - \theta)(1 - a)}$, $a = \exp(-\frac{w_x}{kT})$,

c is connectivity constant (i.e. coordination number). w_x is the contribution of adsorbate-adsorbate interaction. U_{00} is defined as the energetic well depth of the adsorbate-adsorbent interaction. V_s is defined as single site volume. The fractional

occupancy is defined as $\theta \equiv N/M$, where N is the number of molecules adsorbed and M is the total number of adsorption sites. For the purposes of the SM model only, we obtained the bulk density (ρ_b) as a function of pressure and temperature from the L-J equation of state, which is a 32-parameter model fit to simulation data[163]. The quasi-chemical approximation is adopted in this model. Detailed derivations are provided in Appendix 5.B.

5.3 Results and Discussion

5.3.1. Force Field Validation

In Figure 5.4, we show simulations of H₂ adsorption in IRMOF-1 at 77 K and 300 K and pressures up to 10 bar to compare against experimental data in the literature. In Figure 5.4(a), we compare our simulation results at 77 K with experimental data of Rowsell *et al.*[11], Panella *et al.*[164] and Wong-Foy *et al.*[165]. The discrepancies from different experimental data can be attributed to several factors such as different sample size and sample purity[164]. As we can see, our simulation results are in reasonable agreement with experimental data except for some slight differences. Our simulations slightly underestimate the amount adsorbed at low pressure compared to the results from Rowsell *et al.*[11], which has also been observed by Garberoglio *et al.*[13]. (They used the Zn potential from the DREIDING force field[67], though it is mistakenly not reported as such, resulting in 0.3 wt% higher adsorption than if the UFF potential had been used[65]. Essentially our simulations are in excellent agreement with their results.) The underestimation at low pressure was also observed by Frost *et al.*[23] using DREIDING

force field. However, our results are in very good agreement with Langmuir fit to experimental data from Panella *et al.*[164] and experimental observations from Wong-Foy *et al.*[165] at low pressure, but overpredict the amount adsorbed at high pressure. The similar phenomena have also been observed by Liu *et al.*[155]. They used both UFF and DREIDING force field in their study of H₂ in a MOF and found both potentials overpredicted the adsorption at high pressure. They attributed this discrepancy to the errors in the solid-fluid potential. In Figure 5.4(b), we only compare our simulation results with experimental data fit from Panella *et al.*[164] at 300 K since the other two did not report data at room temperature. As we can see, our simulation results slightly overpredict adsorption. The largest error at 10 bar is about 0.004 wt% (~10% error to the experiment). The agreement between simulations and experiments is acceptable. Again, the overestimation has also been observed by Liu *et al.*[155] using both UFF and DREIDING force field.

This work does not intend to optimize the force field although one could improve it by adjusting the L-J parameters to fit the experimental data for a specific case. For example, Yang and Zhong[18,107] adjusted the parameters from OPLS-AA force field[68] to better represent the experimental isotherms of H₂ in MOFs. We accept the inability of the simplicity of the model to exactly reproduce the experimental results. However, based on the overall reasonable agreement with experimental data for our simulations, we feel that the force field is basically valid to describe the H₂ interaction with MOF and the adsorption isotherms are reliable as well as the procedure, with its assumptions is reasonable. We can now compare the adsorption isotherms for the MPF and MOF at 77 K and room temperature (300 K).

5.3.2. Low Temperature (77 K)

The adsorption isotherms in terms of excess weight percent H₂ (gravimetric uptake) for IRMOF-1, IRMOF-10 and the five MPFs at 77 K and pressures under 10 bar are shown in Figure 5.5. We first compare IRMOF-1 and IRMOF-10. At low loadings (shown in Figure 5.5(b)), IRMOF-10 slightly adsorbs less than IRMOF-1, but at high loadings (shown in Figure 5.5(a)), IRMOF-10 adsorbs much more than IRMOF-1. This crossing of the isotherms was also observed by Frost *et al.*[23] and the reason is well understood. At low loadings, enthalpic interactions are dominant and small pores increase the interaction while at high loadings the big pore with larger free volume has more space for adsorbate molecules and therefore adsorbs more.

In Figure 5.5(a), we also report the 77 K adsorption isotherms for the 5 MPFs studied here. All of the MPFs except MPF-2 adsorb more hydrogen across the pressure range than do the two MOFs. That the larger MPFs adsorb more hydrogen at higher loading is due to the increased free volume of the MPF. That the larger MPFs also adsorb more hydrogen at lower loadings where energetic contributions are expected to dominate indicates that the porphyrin provides more favorable adsorption sites than those that exist in the IRMOFs. The energies of adsorption at 77 K and the lowest pressure studied (0.01 bar) are respectively for the five MPFs 3.23, 3.57, 3.72, 4.26 and 4.79 kJ/mol. All of these energies of adsorption are greater than those found for IRMOF-1 (3.13 kJ/mol) and IRMOF-10 (2.82 kJ/mol) under the same conditions.

The exception for MPFs adsorbing more hydrogen than the IRMOFs is MPF-2. We attribute this discrepancy to the fact that the functional group on MPF-2, shown in

Figure 5.3(b) contains two bromine atoms. The bromines have a high molecular weight and do not provide strong adsorption sites. So when the comparison of hydrogen adsorption is done on a gravimetric basis as it is in Figure 5.5(a), one observes that high molecular weight atoms in the framework result in a lower amount of hydrogen adsorbed.

We can further understand the exception by looking at the adsorption on a per cage basis as shown in Figure 5.6. Whether at low loadings or at high loadings, we see the same trend that MPF-2 adsorption is larger than IRMOF-1 and IRMOF-10 as well as MPF-1. The difference between MPF-1 and MPF-2 is that MPF-2 has a different functional group which has much more weight due to Br. The increase to the adsorption of H₂ does not compensate for the weight gain. Therefore, there is no contradiction to the reasoning used above to explain the relative amounts of adsorption.

On either a per cage basis or a gravimetric basis, MPF-5 with the functional group shown in Figure 5.3(e) adsorbs the most hydrogen at 77 K. This functional group on MPF-5 has a high surface area to molecular weight ratio, which is advantageous for adsorption.

In Figure 5.7, we report the binding energies in various materials studied in this work at 77 K and under 10 bar. Since the adsorbate-adsorbate interaction is relatively small (the highest contribution at 10 bar is about 10% compared to the total energy), the energy of adsorption is essentially adsorbate-adsorbent interaction energy. We find IRMOF-1 has an adsorption energy of 3.1 kJ/mol, which is in the lower limit of experimental observation of Panella *et al.*[164]. We also observe the adsorption energy is high at low loadings and decreases as the loading increases at 77 K for all materials studied. The initial high adsorption at low loadings is due to the high energy adsorption

sites close to metal-oxide cluster. As the loading increases, the adsorption sites in the larger pore start to be filled. We see IRMOF-1 has a higher adsorption energy than IRMOF-10 within the whole pressure range studied because IRMOF-1 has a smaller pore size. All five MPFs have higher adsorption energies than IRMOF-1 under 0.5 bar although it has much larger pore size than IRMOF-1. This indicates the porphyrin provides additional adsorption sites initially at low loadings. The change in energy of adsorption as a function of loading at 77 K can be substantial. For example, for MPF-5 at 77 K, the energy of adsorption is 4.79 kJ/mol at 0.01 bar and 2.87 kJ/mol at 10.0 bar.

In order to make this point more clear, we further look at the isodensity distribution surfaces of H₂ adsorbed in these materials at 77 K and 1 bar as shown in Figure 5.8. The surfaces are shown in a unit cell of the framework. The contour density level is set to relatively higher so that the deep energy adsorption sites can be seen clearly. In Figure 5.8, the small cages of IRMOF-1 and IRMOF-10 are shown in the center of the plots. We see IRMOF-1 and IRMOF-10 have similar adsorption sites, which are around the metal-oxide cluster in both big and small cage. We observed that IRMOF-1 adsorbs more than IRMOF-10 on a gravimetric basis at this point of the isotherm. Correspondingly the adsorption area for IRMOF-10 is smaller than for IRMOF-1. All five MPFs have the similar adsorption sites, therefore we only show MPF-1 and MPF-5 to make our point. Because of the size of the cage, we show only one vertex of the MPFs. The MPFs provide more adsorption sites around the center of porphyrin, which increases the adsorption. This point can be easily seen by comparing MPF-5 with IRMOF-1. MPF-5 adsorbs about 35% more than IRMOF-1 on a gravimetric basis and more than 500% on the cage basis at 77 K and 10 bar. We also see the functional groups on the porphyrin

provide additional adsorption sites, which increases the adsorption capacity. The point can be also seen clearly when comparing MPF-5 with MPF-1. MPF-5 adsorbs 10% more than MPF-1 on a gravimetric basis and about 70% more on a cage basis at 77 K and 10 bar.

5.3.3. Room Temperature (300 K)

In Figure 5.9, we show the adsorption isotherms of all materials studied in this work calculated at 300 K. The isotherms in terms of gravimetric uptake are shown in Figure 5.9(a). The isotherms in terms of volumetric uptake are shown in Figure 5.9(b). All of them are in the linear regime, which can be defined by Henry's law constants, as shown in Table 5.2. The Henry's law constant for IRMOF-1 from simulation (0.024 mol/kg/bar) is in very good agreement with the Henry's law constant (0.022 mol/kg/bar) from the Langmuir fit to the experimental data of Panella *et al.*[164].

In contrast to the behavior observed at 77 K, all MPFs adsorb more hydrogen than IRMOF-10, which adsorbs more than IRMOF-1, on both gravimetric and cage bases. This is a consequence of the fact that the entropic contribution becomes more dominant as the temperature increases. In other words, larger cages are favored at all pressures at high temperature. Within the same cage size, the energy of adsorption is important. In Figure 5.10, we show the energy of adsorption for all materials at 300 K and pressures up to 10 bar. Clearly, the loading on the cage basis is correlated to the adsorption energy among the five MPFs. MPF-5 has the largest adsorption energy and the highest capacity, followed by MPF-4 and MPF-3. The difference between MPF-2 and MPF-1 is small.

The isotherms on a gravimetric basis show a more complicated trend since the isotherms are weighted by the molecular weight of the framework. Thus we see it is useful to report adsorption isotherms on both the gravimetric and cage basis, since the former is more easily related to experiment and the latter more clearly reveals relationships between the amount adsorbed and other properties of the adsorbent, such as the energy of adsorption.

From Figure 5.10, we observe the energy of adsorption is almost constant at 300 K, in contrast to the observation at 77 K. This indicates that at 300 K, the hydrogen molecules are not bound to preferential adsorption sites but explore much of the cage. This observation is reinforced by the fact that the adsorption energies are much lower at 300 K than they are at 77 K.

We now attempt to determine if the SM model is capable of describing the relative adsorptive capacities of IRMOF-1, as an example. One of the key assumptions in the SM model used here is that there is one type of adsorption site in the system. In other words, all sites have the same adsorption energy. Alternatively, the adsorption energy is constant with loading. Therefore this fundamental tenet of the SM model is violated at 77 K, but it is still valid at 300 K.

There are eight parameters for the SM model that must be specified: 6 parameters that describe the lattice— c (connectivity), l (separation between sites), U_{00} (adsorbate-adsorbent interaction energy), w_x (adsorbate-adsorbate interaction energy at low loading), V_s (site volume), M (number of sites per cage)—and the 2 L-J parameters that describe the adsorbate— σ and ϵ . We set the connectivity, c to 6 and do not vary it and we

use the L-J parameters for σ and ϵ , and do not vary them. The adsorbate-adsorbent well-depth, U_{00} , has also been determined from simulation (-2.13 kJ/mole for IRMOF-1). One can determine w_x by evaluating the L-J potential at site separation, l . Because the loadings are so low at 300 K, the contribution of the adsorbate-adsorbate energy is negligible and the isotherm is insensitive to the value of w_x . The simulation results also show that the adsorbate-adsorbate energy at 10 bar is up to 0.05% of the adsorbate-adsorbent energy. Therefore, there are only two unknowns — V_s , M , which need to be determined. At room temperature the molecules are spread throughout the pore volume[24], thus the number of adsorption sites can be approximated as the maximum number of molecules that the pore volume can hold. We can obtain the number either by dividing the volume of a single H_2 molecule over the pore volume or adsorbing enough molecules into the framework to estimate the maximum number of molecules. The maximum number of molecules is about 1040 calculated using the former method. For the latter method, it turns out to be slightly larger. In this work, we use the former method. Then the site volume can be determined by parameter fit to the simulation results using this SM model. This fit is shown in Figure 5.11. The site volume is $8.12 \text{ \AA}^3$. The site volume is expected to be lower if the maximum number of molecules increases. This indicates that the site volumes accessible to molecules at low loadings are small, indicating highly localized adsorption sites. It should be kept in mind that the SM model assumes a lattice of sites, each with a fixed site volume. The simulation, however, allows a continuous distribution of adsorbates through-out the accessible volume. The discrepancy between continuous and discrete adsorption sites should be responsible for

any discrepancy between the simulations and SM model. We fit the simulation data by adjusting the site volumes.

The SM model is also useful because it allows us to determine the adsorption energy required for a given H₂ capacity. From the SM model, we can predict that IRMOF-1 adsorbs 6 wt% H₂ at 300 K and 1 bar when the adsorption energy is about -17 kJ/mol. The energy (absolute value) is slightly lower when the site volume decreases (or the total adsorption sites increase). This is also consistent with the results from Bhatia and Myers[166]. They found from thermodynamic viewpoint that the binding energy should have about 15 kJ/mol when adsorbing significant amount of H₂ at ambient temperature and modest pressures.

5.4 Conclusions

In this chapter, we performed path integral GCMC simulations with standard force fields and assess their performance in the prediction of adsorption isotherms for H₂ storage in Metal Porphyrin Frameworks (MPFs), a type of potential nanomaterials. We calculated H₂ adsorptions in five MPFs and two IRMOFs (IRMOF-1 and IRMOF-10) at 300 K and 77 K and pressures up to 10 bar. We predict that the adsorption ability of MPFs have significant improvement with the porphyrin introduced. The advantage is not just with their larger pore volume, but also the porphyrin provides additional adsorption sites for H₂, leading to energetic advantage. The functionalization of MPFs also can have a significant impact on hydrogen capacity. At 77 K the best MPF (MPF-5) adsorbs 1.65wt% at 1 bar and 5.81 wt% at 10 bar, which are 68% and 35% larger than IRMOF-1,

respectively. At 300 K, MPF-5 adsorbs 0.007 wt% hydrogen at 1 bar and 0.07 wt% at 10 bar, which are also 48% and 46% larger than IRMOF-1, respectively.

The SM model is also useful to predict H₂ uptake at room temperature. In order to function at low temperature, the SM model would require input to account for the energetic heterogeneity of the pore space within the MOF/MPF. From the SM model, 6 wt% H₂ can be adsorbed in IRMOF-1 at 300 K and 1 bar when the adsorbate-adsorbent interaction energy is about -17 kJ/mol.

5.5 Acknowledgments

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Appendix 5.A Tables and Figures

Table 5.1. Cage size, cage mass, unit cell mass, unit cell length, volume, accessible volume and pore volume for the materials studied in this chapter.

Structure	Cage size (Å)	Cage mass (g/mol)	Unit cell length (Å)	Unit cell mass (g/mol)	Unit cell volume (Å ³)	Accessible volume in a unit cell (Å ³)	Accessible volume in a unit cell (%)	Pore volume in a unit cell (Å ³)	Pore volume in a unit cell (%)
IRMOF-1	12.916	769.6	25.832	6156.8	17237.5	13759.2	79.8	14123.6	81.9
IRMOF-10	17.140	997.6	34.2807	7980.8	40285.5	35106.6	87.1	36196.4	89.8
MPF-1	25.561	2567.8	25.561	2567.8	16700.7	14785.2	88.5	15132.8	90.6
MPF-2	25.561	3514.6	25.561	3514.6	16700.7	14588.1	87.4	14876.1	89.1
MPF-3	25.561	3113.8	25.561	3113.8	16700.7	14303.1	85.6	14775.2	88.5
MPF-4	25.561	3563.8	25.561	3563.8	16700.7	13814.6	82.7	14064.3	84.2
MPF-5	25.561	3899.8	25.561	3899.8	16700.7	13371.7	80.1	13563.3	81.2

Accessible volume is calculated based on geometry method as described by Snurr and co-workers[23] and pore volume is calculated as described by Myers and Monson[160].

Table 5.2. Henry's law constant for the adsorption isotherms at 300 K.

Structure	Henry's law constant (mol/kg/bar)
IRMOF-1	0.024
IRMOF-10	0.032
MPF-1	0.036
MPF-2	0.026
MPF-3	0.039
MPF-4	0.035
MPF-5	0.036

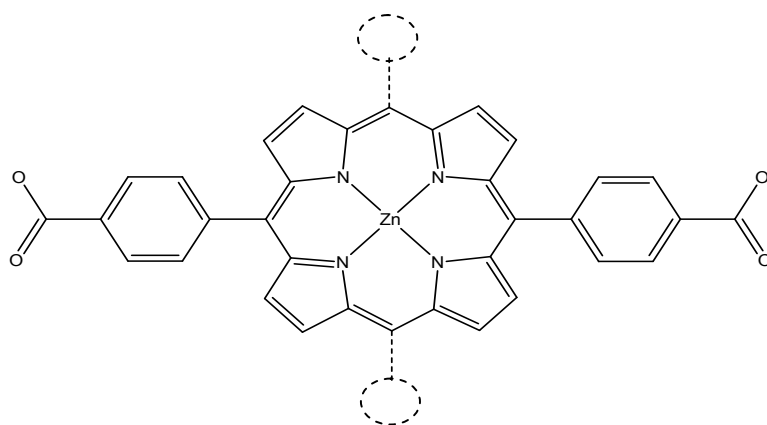


Figure 5.1. Illustration of structure of the porphyrin-based linker. The metal in the pore center is Zn in this chapter, but not limited to Zn. The dashed circles indicate where the functional groups are attached in this chapter, but not limited to these positions.

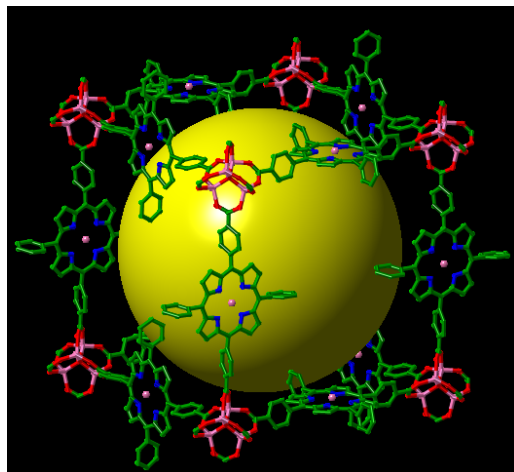


Figure 5.2. Illustration of the pore structure of a MPF (hydrogen atoms are not shown). A yellow sphere indicates the center pore. (Legend: Zn, violet; C, green; N, blue; O, red.)

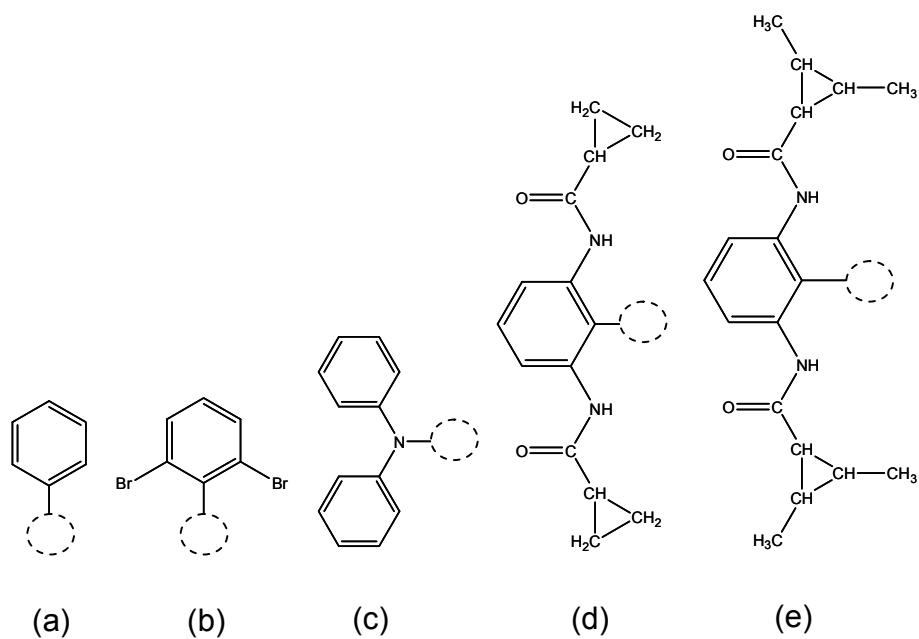


Figure 5.3. Five functional groups on the corresponding five MPFs studied in this chapter: (a) MPF-1; (b) MPF-2; (c) MPF-3; (d) MPF-4; (e) MPF-5. The dashed circles indicate where the functional groups are attached to the porphyrin shown in Figure 5.1. These functional groups are locally optimized to minimal energy when attaching to the porphyrin.

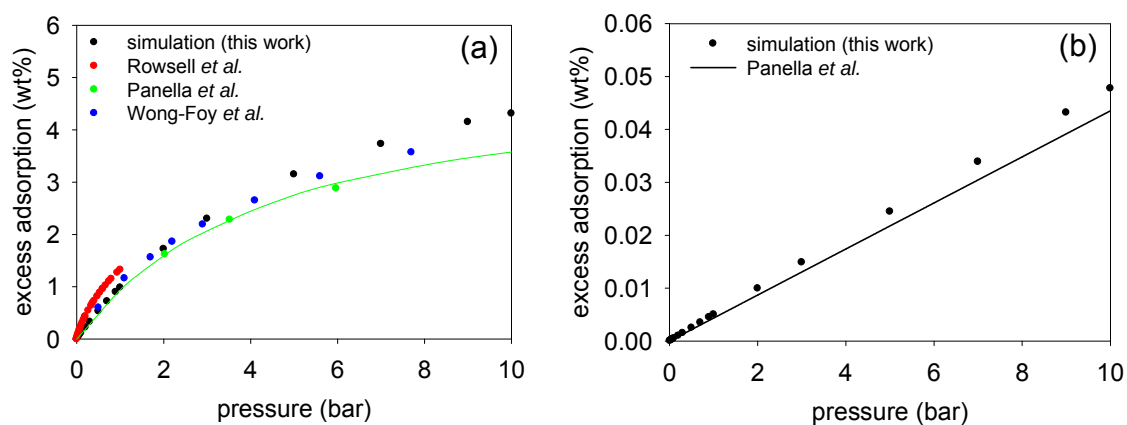


Figure 5.4. Simulated and experimental adsorption isotherms for IRMOF-1 at (a) 77 K; (b) 300 K. The solid line in both plots are Langmuir equation fit to the experimental data by Panella *et al.*[164].

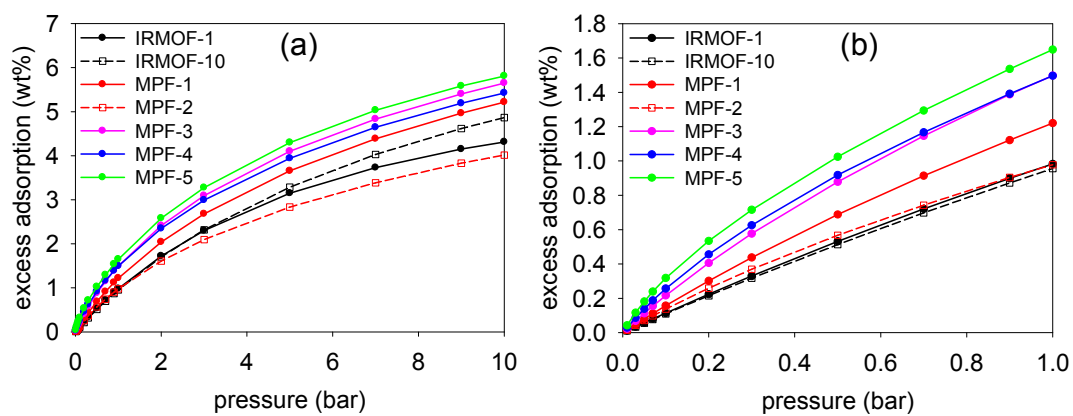


Figure 5.5. Calculated adsorption isotherms in terms of gravimetric uptake at 77 K. (a) whole pressure range under 10 bar; (b) low pressure range under 1 bar.

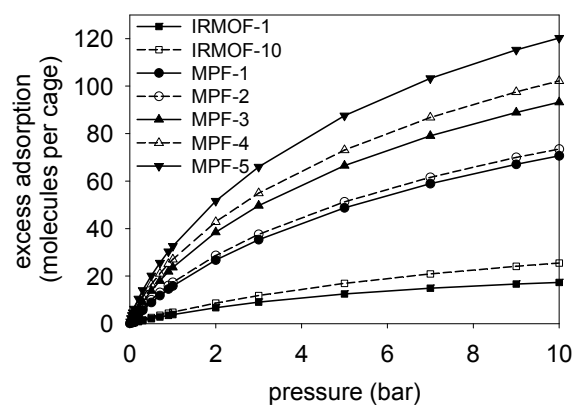


Figure 5.6. Calculated adsorption isotherms in terms of volumetric uptake at 77 K and pressures under 10 bar.

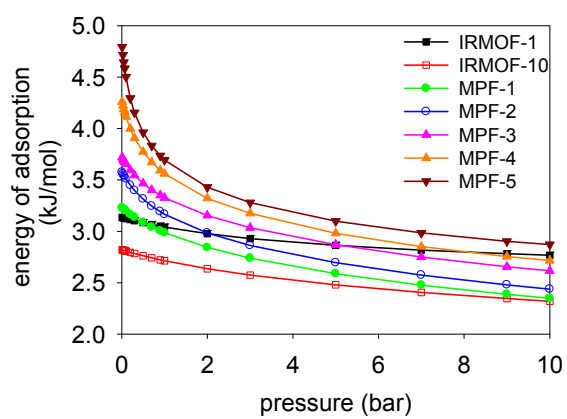


Figure 5.7. Energy of adsorption for H_2 adsorbed in materials studied at 77 K. The unit of energy is kJ/mol.

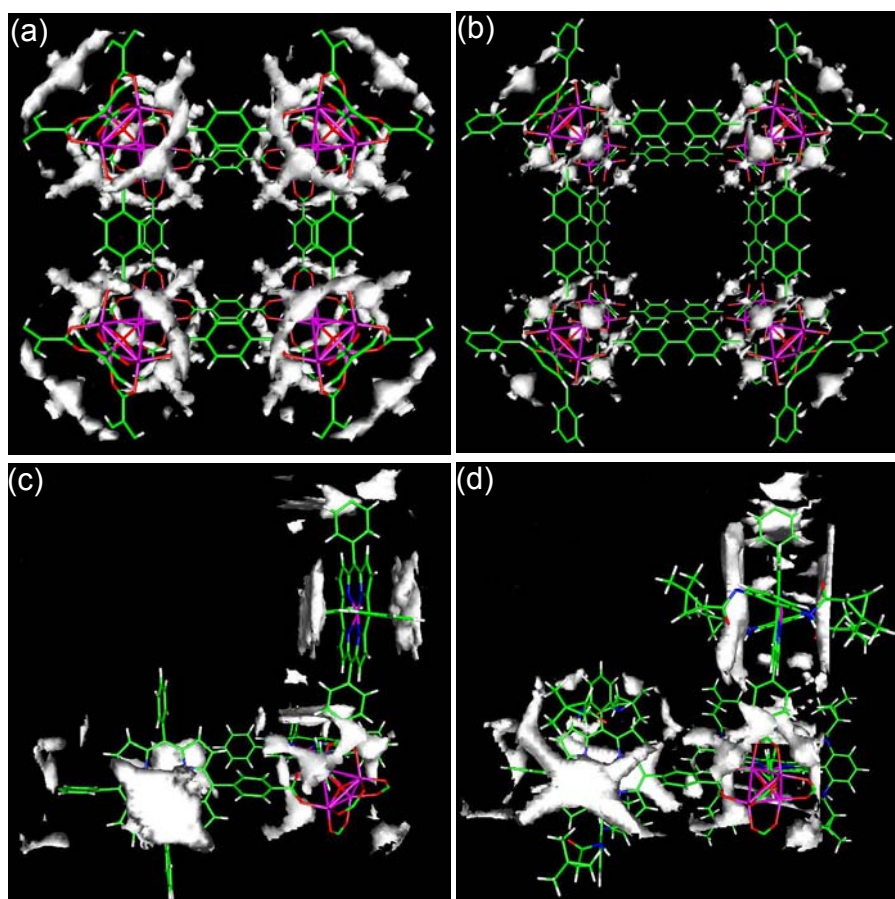


Figure 5.8. Isodensity surfaces (white cloud) at 77 K and 1 bar shown in a unit cell for (a) IRMOF-1; (b) IRMOF-10; (c) MPF-1; (d) MPF-5. The contour density level is about 2×10^{-2} molecule/ $\text{\AA}^3$.

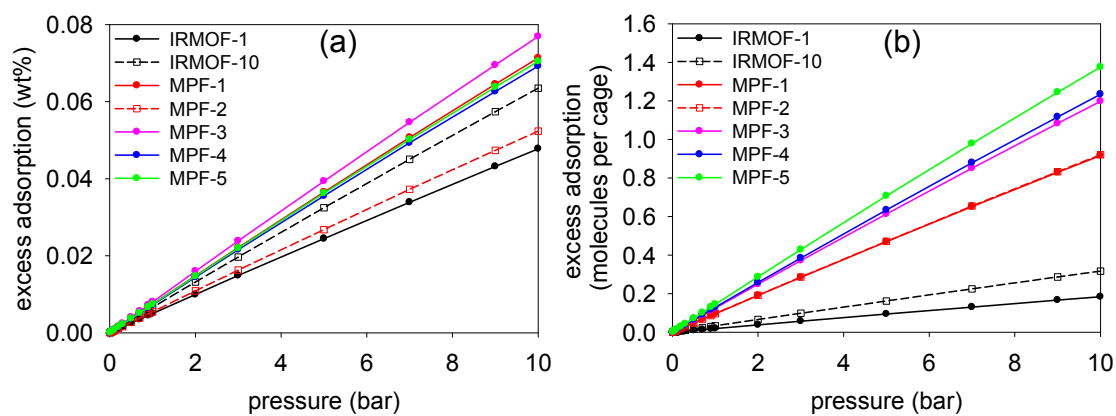


Figure 5.9. Calculated adsorption isotherms of all materials studied in terms of (a) gravimetric uptake and (b) volumetric uptake at 300 K and pressures under 10 bar.

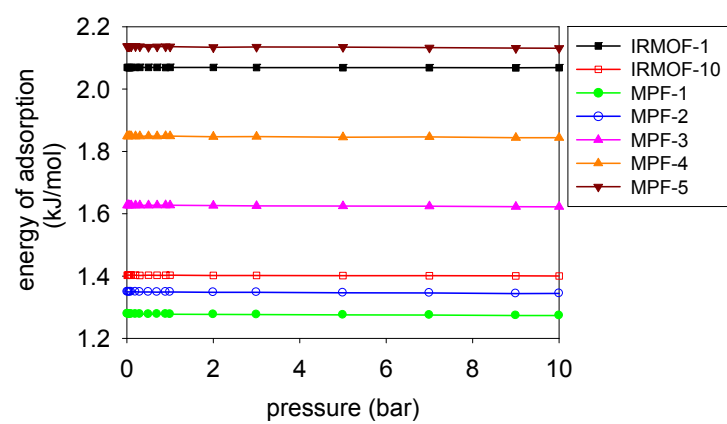


Figure 5.10. Energy of adsorption for H₂ adsorbed in materials studied at 300 K. The unit of energy is kJ/mol.

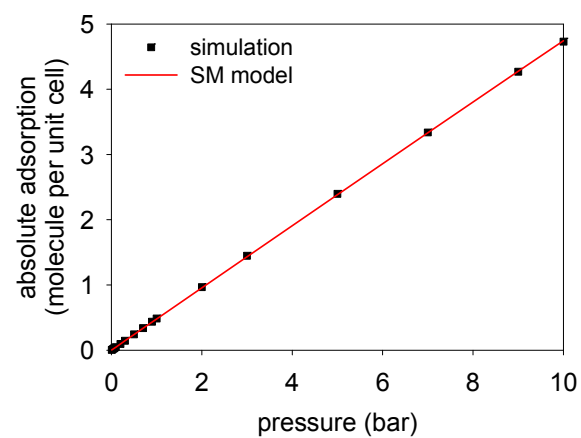


Figure 5.11. SM model fit to the simulation results at 300 K.

Appendix 5.B. Supporting Information

S5.1 Simulation Structures and Force Field Parameters

The illustrations of pore space for the five MPFs are shown in Figure S-5.1. The porphyrin linkers for the corresponding five MPFs are shown in Figure S-5.2. The simulation structure coordinates can be obtained in our website[167].

The Lennard-Jones (L-J) parameters for the force field are listed in Table S-5.1.

S5.2 Statistical Mechanics (SM) Modeling

S5.2.1. Lattice Model

Several SM lattice models of adsorption have been successfully used to describe adsorption in zeolites and other nanoporous materials[168-172]. We use standard statistical mechanics to develop the partition functions for H_2 . From the partition functions, we can directly obtain the desired thermodynamic properties. The nanoporous environment is determined by (i) adsorption site volume, (ii) adsorption site energetic well depth, (iii) lattice connectivity, and (iv) lattice spacing.

Consider an arbitrary lattice with connectivity (in other words, coordination number), c , with sites separated by distance, l . The sites have a well-depth of U_{00} , where this is the potential energy due to adsorbate-adsorbent interactions. The sites have volume, V_s . The four parameters— c , l , U_{00} , and V_s —completely characterize the lattice.

The partition function for the system is composed of 3 factors: (i) the configurational degeneracy $g(N, M)$, (ii) the intrasite partition function $q(T)$, and (iii)

energetic interactions due to neighboring atoms. While the formalism exists to model a nanoporous material with multiple types of sites, each with different site volumes, energetic well depths, and maximum occupancies[168], we limit ourselves to one type of adsorption site. This is an approximation, the validity of which will be tested in this chapter. In this case, where we have one type of site with a maximum occupancy of one adsorbate, the partition function in the canonical ensemble, takes the form:

$$Q(N, M, T) = g(N, M) q(T)^N \exp(-N_{11} \frac{w_x}{kT}) \quad (S1)$$

where N is the number of adsorbates, M is the number of sites, and T is the temperature, N_{11} is the number of neighboring sites each with occupancy one. N_{11} is the only term that contributes to intersite interaction energy, since the other neighbor pairs, namely N_{00} , N_{01} , and N_{10} all contain at least one empty site.

S5.2.1.1. The Adsorbate-Adsorbate Potential Energy

The pure adsorbate is completely characterized by a given potential model. Generally two potential models have been used to describe H₂-H₂ interactions. Vahan V. Simonyan *et al.*[173,174] used the Silvera–Goldman (SG)[172] potential in the molecular simulation of hydrogen storage. The SG model treats each H₂ as a spherical center and includes the effects of three-body interactions via a pairwise correction term. The semiempirical SG potential has been found to be a good model for liquid and solid hydrogen at reasonable pressures[172,175]. However, in most cases, particle-particle interactions between hydrogen molecules are modeled with L-J potential located at the mass-center of the particles[147,176]. In our case, we also use the L-J 12-6 potential

$$U_{LJ}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (S2)$$

In this model, two additional parameters are required : σ , the molecule collision diameter and ε , the well depth of adsorbate-adsorbate interactions. With this potential we specify the adsorbate-adsorbate potential energy due to adsorbates in neighboring sites (an intersite interaction) as this pair potential evaluated at the site separation distance, *i.e.* $w_x = U_{LJ}(l)$. The adsorbate molecule is assumed spherical such that the volume of the adsorbate is given by $V_A = \frac{\pi}{6} \sigma^3$.

S5.2.1.2. The Single-Site Partition Function

We assume that the intramolecular modes of the hydrogen molecules are independent of other adsorbate molecules, allowing us to write the partition function for a single adsorbed molecule, which is given the form[139]:

$$q(T) = q_{site} \exp(-U_{00} / kT) \quad (S3)$$

where U_{00} is the energetic well depth of the adsorbate-adsorbent interaction and q_{site} is a site partition function including translational, rotational, vibrational, electronic and nuclear contributions, $q_{site} = q_{trans} q_{rot} q_{vib} q_{elec} q_{nucl}$. For the translational partition function, we can write[162]

$$q_{trans} = \frac{V_s}{\Lambda^3}, \quad \Lambda = \sqrt{\frac{h}{2\pi mkT}} \quad (S4)$$

where V_s is the volume of single site. For the electronic partition function, we only consider the ground electronic state,

$$q_{elec} = \omega_{el} \exp(D_e / kT) = \exp(D_0 / kT) \exp(\Theta_v / 2T) \quad (S5)$$

where, for ordinary chemically saturated molecules like hydrogen, $\omega_{el} = 1$,

$D_e = D_0 + \frac{1}{2} h\nu$, and $\Theta_v = h\nu / 2k$. The vibrational partition function, it is written as:

$$q_{vib} = \frac{\exp(-\Theta_v / 2T)}{1 - \exp(-\Theta_v / T)} \quad (S6)$$

It is well known that the rotational and nuclear degrees of freedom are coupled in hydrogen, yielding a combined partition function[162]

$$q_{rot,nuc} = \sum_{J \text{ even}} (2J+1) \exp(-\Theta_r J(J+1)/T) + 3 \sum_{J \text{ odd}} (2J+1) \exp(-\Theta_r J(J+1)/T) \quad (S7)$$

where $J = 0, 1, 2, 3, \dots$. In the model above, Θ_v , Θ_r , D_0 are molecular constants which can be found in the literature [139]. For H_2 , we have $\Theta_v = 6215 \text{ K}$, $\Theta_r = 85.3 \text{ K}$, and $D_0 = 103.2 \text{ kcal/mole}$.

Combining these terms with the explicit energy of adsorption yields the single site partition function

$$q(T) = q_{total} \exp(-U_{00} / kT) \quad (S8)$$

where $q_{total} = q_{trans} \cdot q_{elec,vib} \cdot q_{rot,nuc}$

S5.2.1.3. The Configurational Degeneracy

The next objective is to obtain the configurational degeneracy, $g(N, M)$ and the number of neighboring occupied sites, N_{11} , as a function of the known canonical ensemble variables— N , M and T —the 4 parameters that describe the lattice— c , l , U_{00} , and V_s —and the 2 parameters that describe the adsorbate— σ and ε . There is

no analytical solution to this problem except at $N/M = 0.5$. Therefore we must use an approximation.

The first approximation one might use is Langmuir approximation, in which the adsorbate-adsorbate interaction, ε , is set to zero. However, previous work on adsorption in nanoporous materials has shown the importance of adsorbate-adsorbate interactions[170]. The next approximation is the Bragg-Williams approximation, in which the adsorbates are randomly distributed across the lattice and experience a mean field adsorbate-adsorbate interaction[177]. In mean field models of adsorption, there is no clustering of adsorbates. Again, clustering of adsorbates within nanoporous materials can be important [170], therefore we need a more sophisticated model.

The next significantly better approximation but not of unreasonable mathematical complexity is the quasi-chemical approximation[139]. In the quasi-chemical approximation, neighboring pairs are counted independently–double counting some combinations and then reweighted to give the proper total number of states in the configurational degeneracy. This approximation does yield adsorbate clustering in the adsorbent, which is critical to obtaining correct isotherms. In this chapter, we invoke the quasi-chemical approximation. For an adsorbent with one type of site with maximum occupancy of one, it can be shown that the configuration degeneracy is[139]

$$g(N, M) = \left(\frac{M!}{N!(M-N)!} \right)^{1-c} \frac{\left(\frac{cM}{2} \right)!}{N_{00}! \frac{N_{01}}{2}! \frac{N_{10}}{2}! N_{11}!} \quad (\text{S9})$$

where
$$N_{01} = \frac{cM + \sqrt{(cM)^2 - 4(1-a)c^2N(M-N)}}{2(1-a)}, \quad N_{00} = \frac{c}{2}(M-N) - \frac{1}{2}N_{01},$$

$N_{10} = N_{01}$, $N_{11} = \frac{c}{2}N - \frac{1}{2}N_{01}$, and $a = \exp(-\frac{w_x}{kT})$. Therefore the partition function in the canonical ensemble is

$$Q(N, M, T) = \left(\frac{M!}{N!(M-N)!} \right)^{1-c} \frac{\left(\frac{cM}{2} \right)!}{N_{00}! \frac{N_{01}}{2}! \frac{N_{10}}{2}! N_{11}!} q(T)^N \exp(-N_{11} \frac{w_x}{kT}) \quad (\text{S10})$$

S5.2.2. Adsorption Isotherm

All thermodynamic properties can be derived from the partition function. To get the adsorption isotherm, we equate the chemical potential of the adsorbed phase with the chemical potential of the bulk fluid. The chemical potential is given by

$$\frac{\mu}{kT} = - \left(\frac{\partial \ln Q}{\partial N} \right)_{M, T} \quad (\text{S11})$$

For this system, the adsorption isotherm in terms of the fractional occupancy, $\theta \equiv N/M$,

is related to the chemical potential via[139]

$$\left[\frac{(\beta - 1 + 2\theta)(1 - \theta)}{(\beta + 1 - 2\theta)\theta} \right]^{c/2} \frac{\theta}{1 - \theta} = \exp\left(\frac{\mu}{kT}\right) q(T) \exp\left(-\frac{cw_x}{2kT}\right) \quad (\text{S12})$$

where $\beta = \sqrt{1 - 4\theta(1 - \theta)(1 - a)}$.

The adsorbed phase is in equilibrium with the bulk fluid. The pressure of the bulk fluid is related to the chemical potential via an equation of state, and, through the equation of state, it is possible to calculate the pressure of the gas that corresponds to a given chemical potential and *vice versa*[22].

The bulk chemical potential of a pure fluid is given by

$$\frac{\mu_{bulk}}{kT} = -\ln\left(\frac{q'_{total}}{N}\right) \quad (S13)$$

$$\text{where } q'_{total} = q'_{trans} \cdot q_{elec,vib} \cdot q_{rot,nuc} , \quad q'_{trans} = \frac{V_{bulk}}{\Lambda^3} . \quad (S14)$$

Then the chemical potential can be written as

$$\frac{\mu_{bulk}}{kT} = -\ln\left(\frac{1}{\rho_{bulk} \Lambda^3}\right) - \ln(q_{elec,vib}) - \ln(q_{rot,nuc}) \quad (S15)$$

Equating the chemical potential of the bulk phase with the chemical potential of the adsorbed phase yields an expression for the adsorption isotherm relating the fractional occupancy to the bulk pressure.

$$\left[\frac{(\beta - 1 + 2\theta)(1 - \theta)}{(\beta + 1 - 2\theta)\theta} \right]^{c/2} \frac{\theta}{1 - \theta} = \rho_b V_s \exp\left(-\frac{U_{00}}{kT}\right) \exp\left(-\frac{cw_x}{2kT}\right) \quad (S16)$$

For the purposes of the SM model only, we obtain the bulk density, ρ_b , as a function of pressure and temperature from the L-J equation of state, which is a 32-parameter model fit to simulation data[163].

Appendix 5.C. Table and Figures in the Supporting Information

Table S-5.1. L-J parameters used in this chapter, taken from UFF force field.

Atom	ε / k (K)	σ (Å)
O	30.194	3.118
Zn	62.400	2.462
C	52.839	3.431
N	34.722	3.261
H	22.142	2.571
Br	126.310	3.732
H2	34.200	2.960

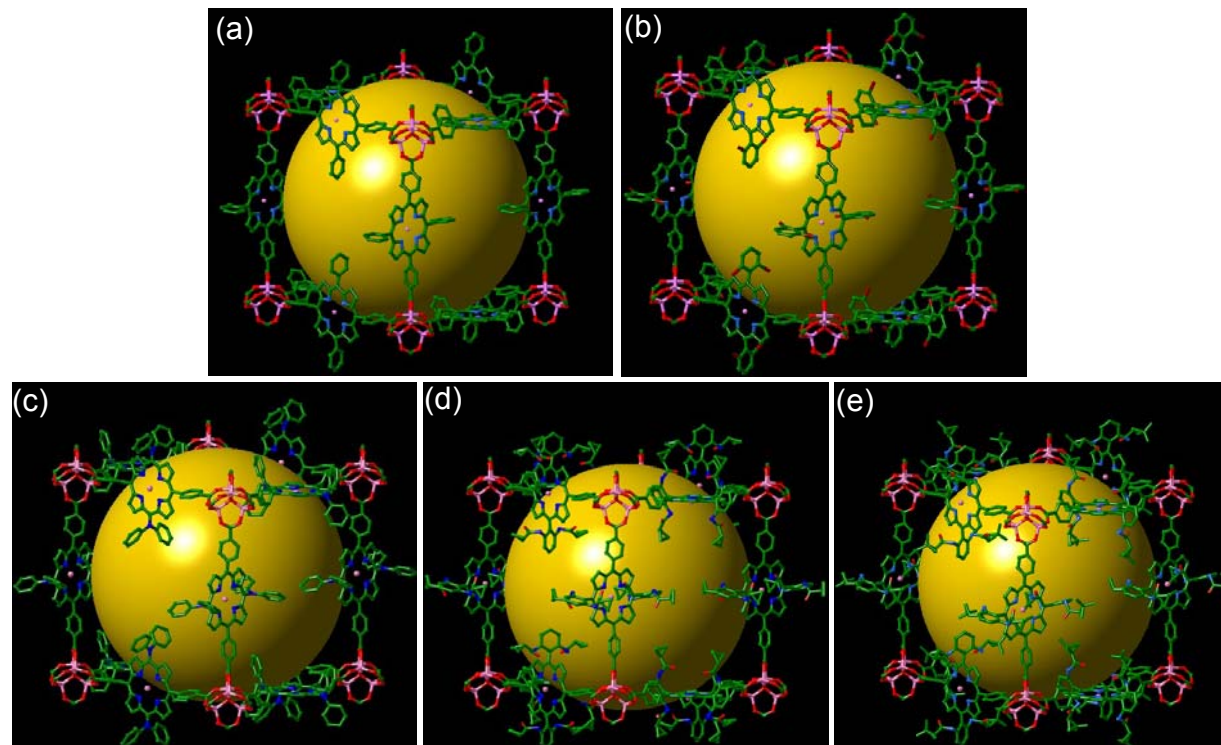


Figure S-5.1. The pore space illustrations for the five MPFs studied in this chapter. (a) MPF-1; (b) MPF-2; (c) MPF-3; (d) MPF-4; (e) MPF-5 (Legend: Zn, violet; O, red; C, green; N, blue; H, white; Br, maroon).

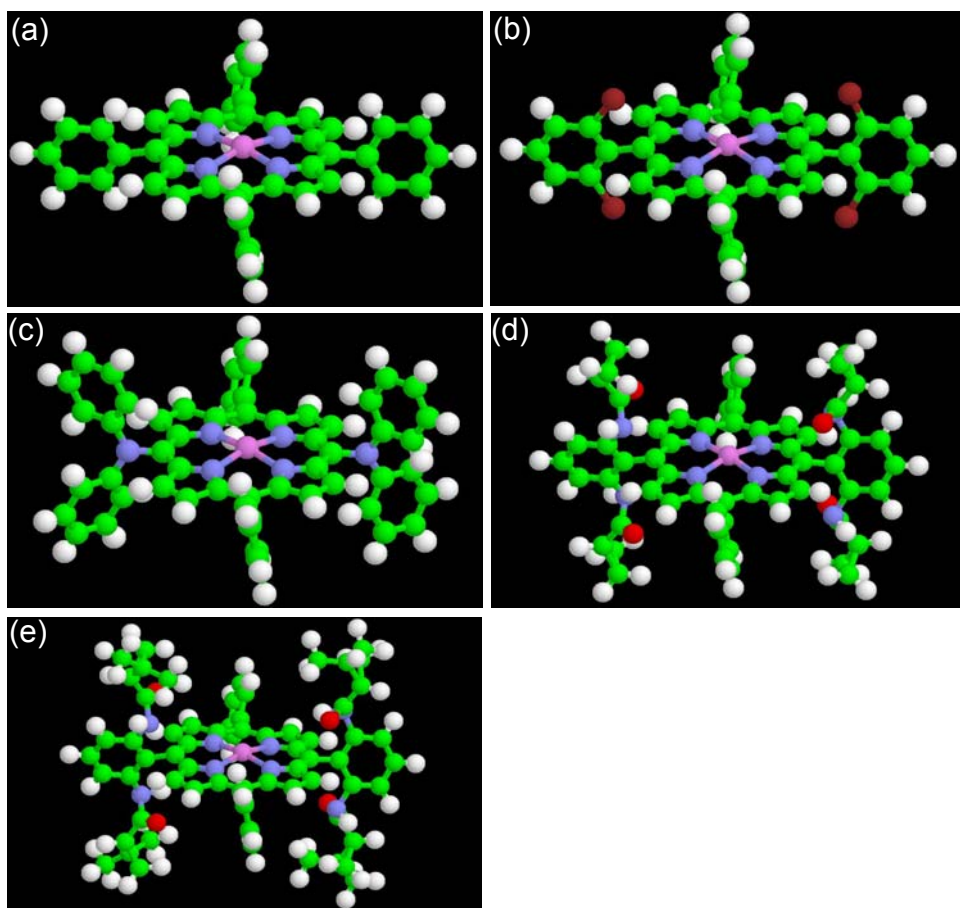


Figure S-5.2. The porphyrin linkers for the five MPFs studied in this chapter.
 (a) Zinc 5,15-diphenyl-10,20-di(4'-carboxyphenyl);
 (b) Zinc 5,15-di(2',6'-dibromophenyl)-10,20-di(4'-carboxyphenyl);
 (c) Zinc 5,15-di(N-diphenylamino)-10,20-di(4'-carboxyphenyl);
 (d) Zinc 5,15-di(2',6'-dicyclopanecarboxamidephenyl)-10,20-di(4'-carboxyphenyl);
 (e) Zinc 5,15-di[2',6'-di(dimethylcyclopanecarboxamidephenyl)]-10,20-di(4'-carboxyphenyl) .

(Legend: Zn, violet; O, red; C, green; N, blue; H; white; Br, maroon).

CHAPTER 6

Self-Consistent Multiscale Modeling in the Presence of Inhomogeneous Fields

This chapter is a slightly revised version of a paper by the same title published in *Multiscale Modeling and Simulation*, 2009 by Ruichang Xiong, Rebecca L. Empting, Ian C. Morris and David J. Keffer:

R. Xiong, R.L. Empting, I.C. Morris, D.J. Keffer, *Self-Consistent Multiscale Modeling in the Presence of Inhomogeneous Fields*, *Multiscale Model. Simul.* **8** (1), 193 - 203, 2009.

The use of “we” in this part refers to the co-authors and the author of this dissertation. My primary contributions to this paper include (1) development of the algorithm (2) creating programs to perform MD simulations (3) all of the simulation work (4) all of the figure generation and all of the writing.

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Abstract

Molecular-dynamics (MD) simulations of a Lennard-Jones (L-J) fluid in an inhomogeneous external field generate steady-state profiles of density and pressure with nanoscopic heterogeneities. The continuum-level of mass, momentum and energy transport balances are only capable of reproducing the MD profiles when the equation of state for pressure as a function of density is extracted directly from the molecular-level of description. We show that the resulting density profile from simulation is consistent with both a molecular-level theoretical prediction from statistical mechanics as well as the solution of the continuum-level set of differential equations describing the conservation of mass and momentum.

6.1 Introduction

The principles of conservation of mass, momentum and energy in classical systems are equally valid at both the continuum and molecular levels. At the continuum level, the density and velocity distributions are given by solutions of partial differential equations (PDEs) describing the mass and momentum balances. It is sufficient for the purposes of this work to limit the investigation to single-component fluids in an isothermal system. Therefore, the relevant continuum equations are a mass balance[178],

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \mathbf{v}) \quad (1.a)$$

where ρ is the mass density, $\mathbf{v}$ is the center-of-mass velocity and t is time, and a momentum balance

$$\rho \frac{\partial \mathbf{v}}{\partial t} = -\rho \mathbf{v} \cdot \nabla (\mathbf{v}) - \nabla p - \nabla \cdot \boldsymbol{\tau} - \rho \nabla \hat{\Phi} \quad (1.b)$$

where p is the hydrostatic pressure, $\boldsymbol{\tau}$ is the extra stress tensor and $\hat{\Phi}$ is an external field. These PDEs require a constitutive equation providing the functional form of the extra stress tensor, $\boldsymbol{\tau}$, e.g. Newton's law of viscosity, as well as a thermodynamic constitutive equation providing the functional form of the pressure, p . e.g. a mechanical equation of state such as the van der Waals equation of state (EOS) or the Lennard-Jones (L-J) EOS (LJEOS)[163]. With a set of boundary conditions, this set of PDEs and constitutive equations can readily be solved.

At the molecular-level, these same principles apply. In a traditional equilibrium molecular dynamics (EMD) simulation, there are no gradients in the system and principles of mass and momentum conservation reduce to the number of particles and

total system momentum being invariant in time. In a non-equilibrium molecular dynamics (NEMD) simulation in the presence of an inhomogeneous, external field, it is possible to generate gradients in the density and velocity profiles. Because of the resolution of MD simulations, these gradients can easily be on the order of nanometers. In this case, the mass and momentum balances of equation (1) are completely valid and should be observed in the simulation. The only issue is that the constitutive equations for both τ and p must now be valid in the presence of nanoscale inhomogeneities.

In general, constitutive equations developed for bulk fluids (both for transport and thermodynamic properties) are not valid in the presence of nanoscale inhomogeneities. Therefore, it is necessary to extract these constitutive equations from the molecular-level models in order to show consistency between the density and velocity profiles obtained through the solution of the continuum-level equations and the profiles directly observed in the simulation.

Molecular-level information in the presence of inhomogeneous fields can be generated in a variety of ways, including molecular density functional theory (DFT), integral equation theory (IET), and molecular simulation—(both Monte Carlo methods and Molecular Dynamics)[179]. In previous multiscale modeling work we have used the Ornstein-Zernike IET to provide molecular information used in continuum-level models[180]. In this work, we choose to generate the molecular-level information from MD simulations.

We perform MD simulations in the presence of an inhomogeneous field to generate time-invariant density profiles with variation on the nanoscale. We directly evaluate the pressure profile in the MD simulations and use it to create a mechanical

equation of state that relates pressure to density for this particular inhomogeneous fluid. When this equation of state is substituted into the continuum-level equations, we find that the macroscopic model reproduces the density profiles from the molecular-level simulation. We also show that neither a bulk mechanical EOS nor local averaging of the bulk EOS reproduces the MD results.

The systems of study include both the ideal gas, for illustrative purposes, and the Lennard Jones fluid. For the ideal gas, it became necessary to develop a new thermostat for the MD systems with inhomogeneous fields. To this end, we developed, applied and validated this thermostat through comparison with statistical mechanical and continuum-level theory.

This chapter demonstrates several important issues associated with multiscale modeling. First, concepts such as the conservation of mass, momentum and energy should be equally applicable at all scales. Failure of equation (1) to describe observed density, momentum or temperature profiles at the molecular-level is due to the use of constitutive equations that are not valid at the nanoscale. Finally, when comparing the continuum and molecular-level systems, all profiles—mass, momentum and temperature—must simultaneously agree between the scales. This may require the development of new simulation nuances, such as a novel thermostat, as was the case in this work.

The remainder of this chapter is organized as follows. In part 6.2, we provide the necessary background to explain and justify the new thermostat. In part 6.3, we present results of the MD simulations. In part 6.4, we provide our conclusions.

6.2 System Formulation

The study of temperature control in molecular dynamics (MD) simulation has received an extensive amount of interest since the early work of Nosé and Hoover[75,181] through more recent analyses and descriptions of families of thermostat formalisms[182-187]. One of the salient features of these thermostats is their application to selective degrees of freedom, allowing for example distinct thermostat of light and heavy particles[183], or exclusive thermostat of the peculiar momentum[186].

In this work, we are interested in thermostating MD simulations in the presence of an arbitrary and potentially anisotropic and spatially inhomogeneous field. The field will generally give rise to inhomogeneous distributions in the density, center-of-mass velocity and temperature. We are interested in performing simulations in an isothermal limit, in which the temperature is constant through-out the simulation volume. For a L-J fluid in which there is exchange of kinetic energy between particles through collisions, a single Nosé-Hoover thermostat will suffice. For an ideal gas, we demonstrate the implementation of a set of Nosé-Hoover thermostats that will provide a spatially uniform temperature distribution. Furthermore, we justify the implementation of the thermostat not only through direct examination of the temperature distribution but also through comparison of the resulting inhomogeneous density distributions with profiles predicted from both statistical mechanics as well as continuum mass and momentum balances evaluated in the isothermal limit.

In order to validate our thermostat, we require standards for comparison. There are various levels of validation that can be checked. First and most obviously, the average temperature of the simulation must be correctly maintained. Second, the spatial

temperature distribution must correspond to the set temperature distribution. These, criteria for a successful thermostat, are however, insufficient to prove the rigor of the procedure.

We require an additional criterion in order to provide evidence that the means by which the uniform profile was obtained did not disturb other results of the simulation. In the absence of any inhomogeneous fields, this additional proof is given by the Hamiltonian-based criterion used by Nosé[188] or the non-Hamiltonian criterion of Tuckerman *et al.*[189,190]. However, the inhomogeneous field will give rise to a density distribution. In this work, we use the density distribution as a criterion for the success of the thermostat by comparing the density distribution from the MD simulations with two standards. For the simulations of the ideal gas, we can compare the density distribution with that predicted by statistical mechanics (SM). The density distribution, $\rho(z)$, of the ideal gas in the presence of an external field is given by the statistical mechanical result

$$\rho(z) = \rho_o \exp\left(\frac{\hat{\Phi}(z)}{k_B T}\right) \quad (2)$$

where ρ_o is a constant, k_B is Boltzmann's constant, T is temperature, $\hat{\Phi}$ is the external potential and z is the spatial dimension.

For both the ideal gas and the L-J fluid, we can validate density distributions from the MD simulations through a multiscale modeling algorithm. Namely, the density distribution that is the solution to the continuum level mass and momentum balances in equation (1) should directly match the profiles from the MD simulations. It is important to understand that, without coupling to an energy balance, equation (1) assumes that the

system is isothermal. Therefore, if the continuum-level system is isothermal then so too must be the molecular-level system.

It is completely sufficient for our purposes to focus on steady-state solutions in which the time derivatives in equation (1) are zero. Furthermore, we will examine an anisotropic external field with variation in the z -direction only. We choose the boundary condition for the velocity to be zero, thus essentially setting the velocity profile to zero and eliminating the convection and dissipation term from equation (1). Consequently, our system of equations becomes,

$$\frac{dp}{dz} = -\rho \frac{d\hat{\Phi}}{dz} \quad (3)$$

We are free to choose any arbitrary form of the external potential. In our examples, we choose the external field to be a time-invariant cosine function with a spatial period equal to the system size in the z -dimension, L , specifically $\hat{\Phi} = A \cos(2\pi z / L)$. This choice is motivated by the fact that we would greatly prefer that the density profile satisfying the continuum equations be periodic. This will allow the corresponding MD simulations to achieve steady state using traditional periodic boundary conditions. (There are no simple boundary conditions that would allow MD simulations to be performed if, for example, the density at one boundary of the box were different than the density at the opposite boundary. In such a case, a technique such as dual-control-volume grand canonical molecular dynamics would be required[191].) In the case of negligible velocity profile, the choice of a periodic external potential is sufficient to generate a periodic density profile.

At the molecular-level, we perform a MD simulation, which is an equilibrium simulation in every respect except that the external field, $\hat{\Phi}$, is present in the z-dimension. We therefore expect that a MD simulation with a correct thermostat will generate the same density profile as that obtained from the continuum description, given that we have a reasonable equation of state for the pressure in the continuum model.

It is worth noting that, in general, the presence of the inhomogeneous field will give rise to variation in density, velocity and temperature. If there is variation in the velocity, then one would call these simulations, “non-equilibrium molecular dynamics” (NEMD) simulations. Based on our specific choice of boundary conditions in the continuum model for this example, we have negligible variation in the velocity and thus our MD simulations are “equilibrium molecular dynamics with an inhomogeneous potential”.

The MD simulations used 10,000 molecules at temperature of 300 K and 150 K respectively and a molecular volume of $100 \text{ \AA}^3/\text{molecule}$. We used the L-J potential[21], truncated at a cut-off of $15 \text{ \AA}$, with $\epsilon/k_B = 93.10 \text{ K}$, $\sigma = 3.446 \text{ \AA}$, and molecular weight 39.948 g/mole . For the ideal gas simulations, we set ϵ to zero. The time step was 10 fs. Equilibration and data collection were performed for 7.5 and 10.0 ns respectively. We used the fifth-order Gear Predictor-Corrector method to integrate the equations of motion[192,193], which has been shown to provide excellent conservation of the Hamiltonian in MD simulations[21].

We present results comparing the molecular and continuum models for two systems: an ideal gas and a L-J fluid. The essential difference between the ideal gas and a

L-J fluid is that the ideal gas lacks any intermolecular interaction. We will see the consequence of intermolecular interactions below.

We examined three sets of thermostats. All of them have the traditional Nosé-Hoover form, with equations of motion given by

$$\frac{dr_{i,\alpha}}{dt} = \frac{p_{i,\alpha}}{m_i} \quad (4.a)$$

$$\frac{dp_{i,\alpha}}{dt} = F_{i,\alpha} - \zeta_{T\alpha} p_{i,\alpha} \quad (4.b)$$

$$\frac{d\zeta_{T\alpha}}{dt} = \frac{\nu_T^2}{f k_B T_{set}} \left(\sum_{j=1}^N \frac{p_{j,\alpha}^2}{m_j} - f k_B T_{set} \right) = \nu_T^2 \left(\frac{T_\alpha(t)}{T_{set}} - 1 \right) \quad (4.c)$$

where $r_{i,\alpha}$, $p_{i,\alpha}$ and $F_{i,\alpha}$ are respectively the position, momentum and force of particle i in dimension α , m_i is the mass of particle i , $\zeta_{T\alpha}$ is the scaled thermostat “momentum”, f is the number of degrees of freedom in the system, ν_T is the frequency controlling the rate of thermostat response, and T_{set} is the set temperature. The force contains both the intermolecular component and the contribution from the external field.

The three thermostats are defined as follows. The first thermostat (TS1) has a single thermostat, based on the total kinetic energy of the system; this is the Nosé-Hoover thermostat. In the second thermostat (TS2), we implement spatially localized thermostats by dividing the simulation volume into N_{bin} spatial bins in the z-dimension. The bins are slabs in shape. In this work, $N_{bin} = 50$. A distinct thermostat is assigned to each spatial bin. Equation (4.c) is written for each bin, where the relevant kinetic energy and degrees of freedom are those belonging to particles located at that instant within the bin. The thermostat still alters momenta through (4.b), with the only extension being that

thermostat variable on the LHS is from the same bin in which the particle is currently located. In TS2, therefore, as particles move from bin to bin, they move from one thermostat to the next. In the third themostatting scheme (TS3), we implement spatially and dimensionally selective thermostats by providing each of the bins used in TS2 with three thermostats, one for each dimension, resulting in a total of $3N_{bin}$ thermostats. Again, equations (4.b) and (4.c) are valid with the only extension being that the kinetic energy and degrees of freedom used in (4.c) correspond to a single dimension.

6.3 Results and Discussion

6.3.1. Ideal Gas Simulations

The purpose of performing ideal gas simulations is strictly to use a simple system, where unambiguous analytical results are available. From our simulations we find that all three thermostats satisfy the most basic criterion, namely that they provide the correct average temperature for the total simulation volume. In Figure 6.1, we present the temperature profiles for the three thermostats of the ideal gas simulations. In Figure 6.1, we see that TS1 does not generate the set temperature profile. The failure of TS1 can be explained as follows. The generation of heat due to the inhomogeneous field is spatially non-uniform. In the absence of any temperature control, this will give rise to hot and cold regions in the simulation volume. The single thermostat in TS1 responds only to the average temperature. Therefore, TS1 stops acting when the average temperature reaches the set point temperature. The average set point temperature can be achieved by adjusting the hot and cold regions so that they average to the set temperature, rather than by eliminating the hot and cold regions altogether.

In both TS2 and TS3, we have spatially selective thermostats. These temperature schemes provide a uniform temperature because the thermostat is based on the local temperature and will act until the local temperature reaches the set point. Based on this evidence alone, one may be inclined to choose TS2 as the optimal thermostat algorithm since it has fewer thermostats. However, validation of the thermostats will provide additional information.

In Figure 6.2, we present the density profiles from the simulations using TS1, TS2 and TS3. We also plot the statistical mechanical solution in equation (2). We also plot the continuum solution in equation (3), where we used the ideal gas law as the equation of state to provide the pressure as a function of density. We see first that, for the case of the ideal gas, the statistical mechanical and continuum solutions are identical. We also observe that only TS3 provides the correct density distribution, despite the fact that both TS2 and TS3 generate correct temperature profiles. TS2 can generate the correct temperature profile but the incorrect density distribution because TS2 reacts to a temperature based on the sum of the x, y and z components of the momentum. The x and y components are unaffected by the external potential. However, if the kinetic energy in the z direction is too high (or too low), the thermostat can reach the set point by lowering (raising) the kinetic energy in all three dimensions. Thus, the z-component of the temperature is still too high (low). Because TS3 has a uniform distribution not only of the sum of the x, y and z components of the temperature, but of each component individually as well, it is capable of generating the correct density profile. At this point, we have established and validated a spatially and dimensionally selective thermostat that correctly generates temperature and density distributions for the ideal gas.

It is worth noting that when an ideal gas is thermostatted with a Nosé-Hoover type thermostat, the velocities cannot change sign since the thermostat scales the velocities by a positive number[194]. The use of multiple thermostats does not solve this pathology; however, the results of these simulations are not likely affected by this pathology.

6.3.2. Lennard-Jones Fluid Simulations

We now perform MD simulations of a fluid with a non-zero intermolecular interaction potential, such as the L-J fluid. We performed this MD simulation using TS1, TS2 and TS3, as was the case for the ideal gas. From ideal gas simulations, we know TS3 absolutely can generate a correct temperature and a correct density profile. As we can see from Figure 6.3, TS1 and TS2 for the L-J fluid can also generate a correct density profile compared to TS3, only the temperature profile from TS1 and TS2 is not quite as good as that from TS3. At this point, we can see that the single thermostat is working relatively well for the L-J fluid, in which the kinetic energy and potential energy are spatially and dimensionally convertible because of the intermolecular interaction. Then we can use any of the thermostats to generate the density profile for L-J fluid; we used TS3. In Figure 6.4, we plot the density profile from the MD simulation of the L-J fluid. We compare this result with the continuum solution, equation (3), only, since the statistical mechanical result of equation (2) applies only to the ideal gas. In order to numerically solve equation (3), we require an accurate equation of state for the pressure. We chose two equations of state. The first choice is the LJEOS [163], which is very accurate in describing the pVT behavior of L-J fluids far from the critical point. The LJEOS, when inserted into equation

(3) does a good job of predicting the density distribution at high temperature, but has a systematic error at low temperature.

The reason for this discrepancy is straightforward. Intermolecular interactions of the type described by the L-J potential are non-negligible on a length scale of 1 nm; in our MD simulations, the potential is truncated at $r_{cut} = 15 \text{ \AA}$. The LJEOS is a bulk equation of state because it is based on simulation data of spatially homogeneous fluids. The use of a bulk EOS in the continuum description is justified only when the length scale associated with the variation of density is much larger than the length scale associated with intermolecular interactions. In other words, when the approximation of evaluating the pressure based on the local density is valid, or $p(z) = p_{bulk}(\rho(z))$, a bulk equation of state is sufficient. However, in the MD simulations the variation in the density is on the order of nanometers, the same scale as the intermolecular interaction potential. Therefore, a bulk EOS is inadequate and therein lies the source of the discrepancy between the MD and continuum results. We did not encounter this problem for the ideal gas or the L-J fluid at high temperature because the ideal gas has no intermolecular interactions and intermolecular interactions have a tiny contribution to the pressure of the L-J fluid at high temperature.

Also shown in Figure 6.4 is excellent agreement between equation (3) when the equation of state extracted directly from the MD simulation (MDEOS) is inserted. The MDEOS was generated as follows. For each bin, the local pressure of the bin was calculated via published procedures[195]. We calculated the normal pressure (the zz element of the pressure tensor), the tangential pressure (the average of the xx and yy elements), and the average pressure (averaged over all three elements). These pressure

profiles are plotted in Figure 6.5. The LJEOS evaluated at the local density as obtained from the MD simulation is also plotted for reference. There is significant difference between the MD pressures and the LJEOS pressure. There are small differences (at least in this system) between the normal and tangential components of the pressure tensor. Figure 6.4, uses the normal component of the pressure tensor. The hydrostatic pressure in equation (1.b) assumed that the diagonal components of the pressure were the same, which is generally not true where there is density variation. (For example at an interface the surface tension is defined by the difference between the normal and tangential components.)

In Figure 6.6, we parametrically plot the pressure from Figure 6.5 versus the density from Figure 6.4. This is a graphical representation of the mechanical equation of state relating pressure to density for this inhomogeneous system. Also on the plot is the LJEOS and what we call a locally averaged LJEOS. We pursued this locally averaged LJEOS to determine if a simple weighting of the bulk LJEOS could approximate the explicit evaluation of the pressure in the MD simulation.

In the locally averaged LJEOS, one can approximate the local pressure in the MD simulation with an average of a bulk EOS evaluated at the local density over the cut-off volume,

$$p(z) \approx \frac{\int_{z-r_{cut}}^{z+r_{cut}} p_{bulk}(\rho(\xi)) d\xi}{2r_{cut}} \quad (5.a)$$

Alternatively, rather than averaging both the ideal and non-ideal contributions to the pressure, one might argue that a better local average is one in which the ideal contribution

is truly local and the non-ideal contribution is due to interactions through-out the cut-off volume, in which case only the non-ideal contributions are spatially averaged over the cut-off volume,

$$p(z) \approx p_{id}(z) + \frac{\int_{z-r_{cut}}^{z+r_{cut}} (p_{bulk}(\rho(\xi)) - p_{id}(\rho(\xi))) d\xi}{2r_{cut}} \quad (5.b)$$

In Figure 6.6, we show that the two locally averaged LJEOS do not provide a good approximation of the MDEOS and are in fact worse than the bulk LJEOS. At this point, we advocate extracting the mechanical equation of state directly from the MD simulation as was done here.

6.4 Conclusions

In this chapter, we have performed a set of MD simulations in the presence of an anisotropic, inhomogeneous field. We performed simulations of an ideal gas in order to develop and validate a thermostat for MD simulations in the presence of an anisotropic, inhomogeneous field. For the ideal gas, a single Nosé-Hoover thermostat is sufficient to generate the correct average temperature, but the spatial temperature distribution is wrong. Through the use of spatially localized thermostats we were able to generate a desired uniform temperature profile. However, the temperature profile is not sufficient to show that one obtains the correct density distribution. Separate spatially localized thermostats must be used to control the kinetic energy in each dimension in order to account for anisotropy in the external field. For the ideal gas, the use of spatially

localized Nosé-Hoover thermostats in each dimension yielded a density distribution that was consistent with both statistical mechanics and a continuum description.

Using this thermostat, we performed MD simulations of a L-J fluid in the anisotropic, inhomogeneous field. We generated density and pressure profiles directly from the MD simulation. From this simulation we extracted a mechanical equation of state relating pressure to density for this specific system with inhomogeneities in the density on the nanoscale. If we insert this equation of state into the continuum-level balances, we find that the solution of these macroscopic equations provides a density distribution that is in complete agreement with that obtained directly from the MD simulations. The use of a bulk equation of state in the continuum-level equations does not in general agree with the MD simulations.

In the development of multiscale modeling techniques, one must insist on capturing the important physics at all scales of description. In this work, we show how the conservation of mass and momentum can be consistently described at both the continuum and molecular levels when certain precautions are taken. First, the assumptions must be the same at both levels. If the continuum-level system is assumed to be isothermal, then the molecular-level system must also be isothermal. In this case, we developed a set of thermostats to generate the isothermal condition in the MD simulation. Second, one must use valid constitutive equations. In this case, we extracted an equation of state applicable to inhomogeneous fluids directly from the MD simulation. These multiscale modeling techniques will lead to transport properties generated by MD simulations in a manner that is completely consistent with continuum level descriptions of mass transport [196].

6.5 Acknowledgments

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Appendix 6.A: Figures

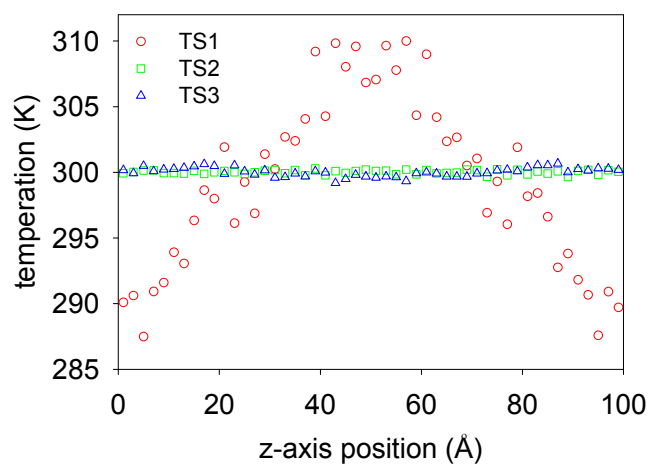


Figure 6.1. Spatial temperature profiles of the ideal gas from MD simulations using three thermostats at 300 K: a single thermostat (TS1), spatially localized thermostats (TS2), and spatially and dimensionally localized thermostats (TS3). Both TS2 and TS3 yield the desired temperature profile.

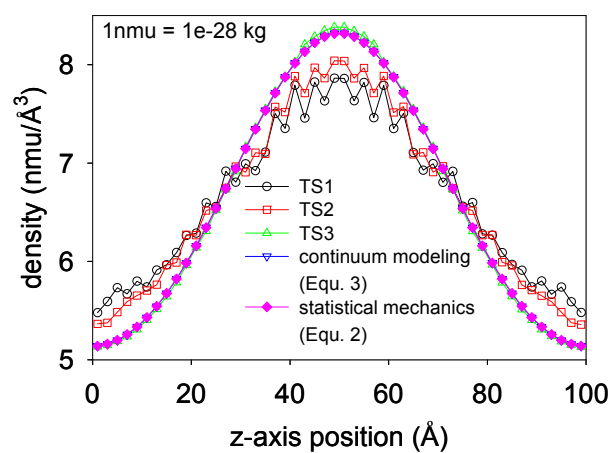


Figure 6.2. Spatial density profiles of the ideal gas from MD simulations using three thermostats at 300 K. Also shown are the profiles from statistical mechanics (equation (2)) and from the continuum description (equation (3)). Only TS3 generates the correct profile.

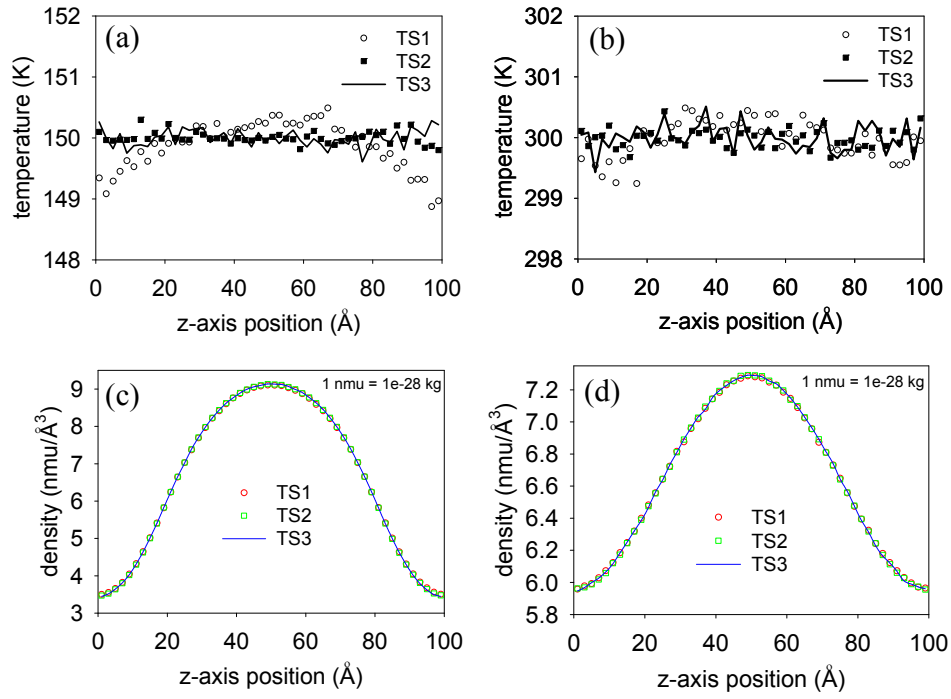


Figure 6.3. Spatial temperature profiles and density profiles of the L-J fluid from MD simulations using three thermostats at 300 K and 150 K: (a) $T = 150\text{K}$; (b) $T = 300\text{ K}$; (c) $T = 150\text{ K}$; (d) $T = 300\text{ K}$.

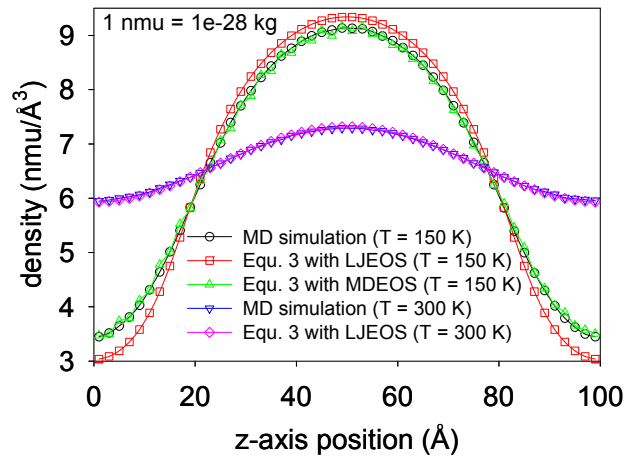


Figure 6.4. Spatial density profiles of the L-J fluid from MD simulations using TS3 at 300 K and 150 K respectively. Also shown are the profiles from the continuum description with a pressure given by the LJEOS and by equation (3), compared with the profile from the continuum description with MDEOS and equation (3).

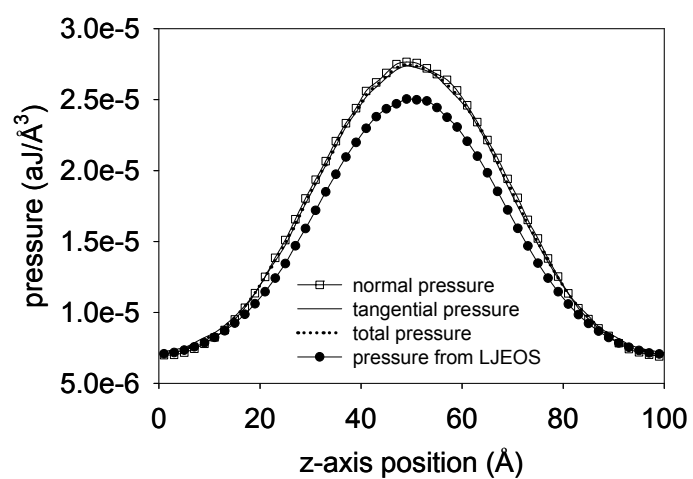


Figure 6.5. Spatial pressure profiles from MD simulation (normal, tangential and total pressure) and L-J Equation of State at 150 K.

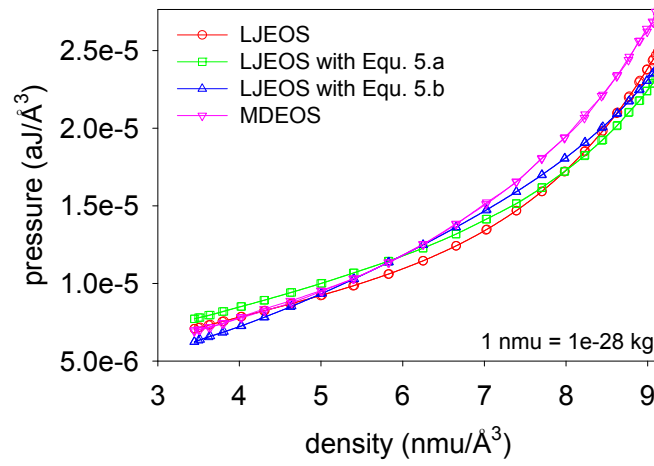


Figure 6.6. Four different equations of state profiles at 150 K: L-J equation of state (LJEOS) , Local average LJEOS with equation (5.a), Local average LJEOS with equation (5.b) and normal pressure calculated from MD simulation (MDEOS).

CHAPTER 7

Conclusions and Future Work

Threatened by explosive assaults, there exists a need to upgrade current explosive detection methods. Metal organic frameworks (MOFs) are a new class of nanoporous materials that have been considered promising in many areas such as hydrogen storage. However, there is no experimental data reported using MOFs to adsorb explosives as the preconcentrator. This is the first time that MOFs are systemically examined to preconcentrate RDX via molecular simulation. A number of technique problems associated with the RDX simulations, especially the impact of charge distribution, have been addressed. In addition, a new class of MOFs using porphyrin-based linkers has also been investigated in this work via hydrogen storage simulations, which is another important application area for MOFs. This work is summarized as follows.

In chapter 2, grand canonical Monte Carlo (GCMC) and molecular dynamics (MD) simulations have been performed to calculate the adsorption isotherms and diffusive coefficient of RDX in IRMOF-1. This is a baseline for further study. In this section, a flexible force field that is fit to crystalline RDX and a modified MM3 force field for IRMOF-1 have been used. A simpler way to increase the efficiency of GCMC methods for non-rigid complex molecules has been taken according to the molecular probability distribution. It has been demonstrated that the probability distributions of RDX molecule properties are virtually no change whether RDX is in bulk system or MOF at the low pressure. A number of important phenomena have been observed. First, RDX exclusively reside in the big cage of IRMOF-1, and the adsorption sites are near the metal cluster and between benzene rings. One of nito groups interacts with Zn atoms in the metal cluster closely. Second, the adsorption energy are found to be -9.2 kcal/mol and the Henry's law constant is 21.2 mol/kg/bar, which is relatively big compared to H₂ and

CH₄. Third, the self-diffusivities of RDX in IRMOF-1 are found to be a strong function of temperature. The activation energy is about 6.0 kcal/mol. Fourth, the major components of air (N₂ and O₂) do not give negative effect on the RDX adsorption and the presence of water increases the amount of RDX adsorbed. Finally, the cage to cage motion for RDX starts from about room temperature. Below room temperature, there is no inter-cage movement.

In chapter 3, a variety of force fields, particularly the charge distributions, have been investigated in IRMOF-10, which are taken as a specific example. Since there are no experimental data available, the only way to validate the force field is to compare the results from simulations and those from quantum mechanical (QM) calculations. The choice of interaction energy calculated by QM, used as a standard, is valid and has been shown to give good agreement with experiments in many other works. A number of electron mapping methods have been used to estimate the point charges required in the simulations. The adsorptions and diffusivities from the simulations with different point charges are significantly different. In addition, the binding energies from the classical potential are also different than those from QM calculations. There are many reasons that results in the differences. One of the reasons is the different QM electron mapping methods. Each method has its advantages and disadvantages. By investigating the density distributions, MPA is found to be the most different and NBO is the second. ESP and LPA have given not only the similar density distributions, but also the similar results for adsorption and diffusivities. Another reason for the differences might lie in the inability of the literature Lennard-Jones (L-J) parameters for polar molecules like RDX to capture the repulsion and dispersion, which can be observed by comparing the dispersive

interaction energy correction in QM calculations with L-J contributions in the classical simulations. From these results, a best method cannot be determined until at least a few points of experimental data are available. However, the possibility can be used to rule out some methods such as MPA. In addition, two types of resulting behavior from using different partial charge distributions have been determined. The NBO analysis assigned large partial charges to the nitro group of RDX, which caused RDX to bind more strongly and condense within the pore of IRMOF-10. The other methods, including LPA, predicted a low density phase within the pore. These findings provide fundamental basis for further study before experimental data have been discovered.

In chapter 4, five IRMOFs have been chosen to show the ability and selectivity to adsorb RDX. In these IRMOFs, some of them are functionalized with amine group and some of them are not. GCMC and MD simulations have been performed to calculate the adsorption isotherms and diffusivities. Partial charges for the atoms on RDX and IRMOFs were calculated by both LPA and NBO mapping methods, which have been identified as two representative methods for low density phase and condensed phase, respectively. Through the comparisons, it is found that the presence of amine groups increases the adsorption greatly when the two different force fields were used. Also it is shown that the location of amine groups on the benzene rings affect the adsorption. The same phenomena found similar to that in IRMOF-1 observed is that RDX resides in big cages, near the vertex and between the benzene rings for all IRMOFs. The presence of amine groups also increases the Henry's law constants and the adsorption energies. The self-diffusivities are strong function of temperature for all IRMOFs. The presence of amine groups does not always increase the activation energy, for some of them it

decreases the activation energy. This fully demonstrates that some of functionalized MOFs desorb more easily while they adsorb more.

Chapter 4 also reveals that IRMOFs could be tailored with functional groups to be highly selective nanoporous preconcentrators. In these IRMOFs studied, they are found to concentrate RDX up to 3000 times from the gas phase, on a volumetric basis. The selectivity of RDX over butane is up to 5000 from a simple Langmuir estimate. The diffusion of RDX is hundreds of seconds, which is sufficiently high for real time sensor applications.

This work was motivated to tailoring MOFs to preconcentrate explosives. The above three chapters constitute most important findings of this work. The next two chapters are supplemental to this work. Chapter 5 shows one potential direction that MOFs can be tailored. The results have been compared using the existing force field for H₂ storage, which has been studied for a long time. Chapter 6 describes a novel multiscale modeling technique connecting the continuum-level and molecular-level description of inhomogeneous fluids.

In chapter 5, hydrogen storage in Metal Porphyrin Frameworks (MPFs) is investigated. GCMC simulations are used to examine the adsorption capability of MPFs. Since hydrogen is a very light gas, the quantum effect is more significant, particularly at low temperatures. Thus, the path integral GCMC methods have been applied. The path integral considers hydrogen as a number of beads connected with harmonic oscillator to counter the quantum effect of hydrogen. The adsorption isotherms for hydrogen in five MPFs and in IRMOF-1 as well as IRMOF-10 have been generated. The structures of the MPFs are similar to IRMOF-1 with the organic linker changed to the linkers based on

porphyrin. It has been demonstrated that the MPF adsorb more hydrogen in weight fraction. At 77 K the best MPF (MPF-5) adsorbs 1.65wt% hydrogen at 1 bar and 5.81 wt% at 10 bar, which are 68% and 35% larger than IRMOF-1, respectively. At 300 K, MPF-5 adsorbs 0.007 wt% hydrogen at 1 bar and 0.07 wt% at 10 bar, which are also 48% and 46% larger than IRMOF-1, respectively. Furthermore, a statistical mechanical model fit to the 300K data indicates that an adsorption energy of 17 kJ/mol is required to adsorb 6 wt% at 1 bar and 300 K. This quantifies the material target for future studies.

In chapter 6, a novel multiscale modeling technique is developed. Continuum-level material and momentum balances are applied to a fluid with nanoscale inhomogeneities in the density. We find that the continuum-level material and momentum balances are satisfied only when a mechanical equation of state relating pressure to density and temperature is extracted from the molecular-level simulations and used in the balances. RDX and hydrogen adsorbed in MOFs are inhomogeneous materials. The material and momentum balances that describe their transport could thus be derived using this method.

In summary, the present work has focused on the molecular simulation of adsorption and diffusion in MOFs. We have applied a whole procedure to calculate adsorption and diffusion of explosive in MOFs. In this development, we have verified the methods to calculate the charge distributions for RDX adsorption in MOFs. We have also demonstrated the functionality of MOFs and its capability in selective explosive preconcentrator. Furthermore, we have proposed a new class of MOFs that have powerful functionality and demonstrated its ability via hydrogen storage. Finally, we have also developed a multiscale modeling technique via MD simulation and continuum-level

modeling. All these significant achievements in the present work are expected to be useful in future developments of explosive and hydrogen adsorption in MOFs.

There are many new interesting avenues of research that can be done in the future. First, the MOFs are assumed rigid in this work in order to increase the computational efficiency. We could allow the framework to be flexible under certain conditions in the future. Second, there are many other explosive molecules like TATP. They have totally different structures and properties. For example, TATP does not have nitro-group in its structure, which might cause different adsorption phenomena. In addition, there are some other molecules in the air, such as kerosene. We have not investigated their effect on the explosive molecule adsorption. Finally, we could also do optimization on the existing force field for each specific case after some points of the experimental data come out. This work will provide more useful information if this kind of investigation is included in the future.

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