Characteristics of $H_2$ sorption onto Metal-Organic-Frameworks

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Abstract: The interaction energy between molecular hydrogen and the Metal Organic Framework 5 crystal was measured. Also, the $H_2$ loading of the MOF-5 crystal was measured at temperatures of 78K and 298K and pressures ranging from 0.2 bar to 160 bar. Results from this experiment show that in addition to the expected 1.2kcal/mol binding site, there are additional sites near the corners of the MOF-5 crystal with binding up to 1.8kcal/mol. The information is expected to aid in the production of Hydrogen fuel storage devices that will meet the U.S. Department of Energy’s goal of 10.8% Hydrogen storage by weight by 2015. (DoE, 32)

Introduction

To achieve its goals of building a Hydrogen based economy, the U.S. department of energy set a goal for Hydrogen fuel cells to be able to store enough fuel, within specific weight and volume constraints, to transport a vehicle 300 miles without refueling. This amounts to 10.8% Hydrogen storage by weight for automotive use by 2015. (DoE, 32) Current methods of storing hydrogen cannot meet this goal safely due to the dangers of high pressure hydrogen storage and the difficulty of storing liquid $H_2$. There are two general solutions to this problem, one is to extract $H_2$ from some other fuel on-board the vehicle. This presents problems because of the complexities involved with converting the fuel into $H_2$. The other solution is to use the fact that only free, gaseous $H_2$ count as far as the pressure of a storage tank is concerned. The idea is then to trap some of the $H_2$ by sorption into a structure.

It has been known for awhile that materials such as zeolites and metal organic frameworks are able to absorb small molecules, such as $H_2$. Primarily this has been attributed to their crystal structure which consists of regular large vacant areas that allow smaller molecules to pass through them. (Rosi, 1127) This property, as opposed to a more typical crystal where the atoms take up most of the free space, presents a very large surface area of the framework to the smaller molecules. The large amount of surface accessible to the smaller molecules exposes a large number of binding sites on the framework compared to a typical crystal which only presents its outside surface area.

In this experiment, a framework called Metal Organic Framework 5 (MOF-5) was studied. MOF-5 is a cubic crystal with a side length of about 12.8 Angstroms.
The MOF-5 Crystal

Its make up consists of \( Zn_4O(BDC)_3 \) where BDC is 1,4-benzene dicarboxlate. (Rosi, 1127) In the past, research was completed on MOF-5 by measuring the amount of \( H_2 \) the MOF-5 would adsorb at various temperatures and pressures. This past research has indicated that MOF-5 has favorable Hydrogen sorption characteristics of up to 4.5% loading by mass. (Rosi, 1128) However, improvement is still necessary to fulfill the DoE’s goal. Therefore, the goal of this project was to study MOF-5 and how it interacts with the Hydrogen molecule by creating and calibrating a computer model of the MOF-5+\( H_2 \) interaction. The model would then be used to investigate properties of the interaction such as the location, number, and energies of various binding sites, as well as to predict \( H_2 \) loading versus temperature and \( H_2 \) pressure. It is hoped that the knowledge gained by the study of the MOF-5+\( H_2 \) interaction will serve as a guide for how to modify the MOF-5 framework so as to increase its usability for Hydrogen storage.

Theory

The calculations and methods used in this experiment focused on classical (not quantum) models of the molecules because accurate calculations involving quantum theory require a very large basis set of wave-functions to accurately describe the many weak electron-electron interactions involved with MOF-5+\( H_2 \) interactions. Working with such a large basis set would require too much computational time to be feasible. To speed calculations, empirical potentials, most notably the Lennard-Jones 6-12 potential and the Coulomb potential with point charges were used. The potentials were adjusted to fit past measured values as well as fit a relatively small set of single point quantum mechanically correct energy computations carried out by Eric Ganz’s team at the University of Minnesota, Solid-State Physics.

The basic theory used is from thermal physics and describes the behavior of an ideal gas in a grand canonical ensemble. The system is MOF-5 and \( H_2 \) which is placed in thermal and diffusive contact with a reservoir of \( H_2 \), treated as an ideal gas at constant temperature and pressure. However, the chemical potential must be modified from that of an ideal gas to take into account the varying amount of binding of the \( H_2 \) to the MOF-5. This binding term was expressed in terms of an electrostatic quadrupole potential and a Lennard-Jones 6-12 potential. By using these two potentials, the calculation was reduced considerably from that of a true quantum calculation since all possible electron orbitals no longer have to be considered, instead, a point charge can be assigned to each atom position and a LJ 6-12 potential fitted to approximate the quantum model of the electron cloud surrounding the atoms.

The Coulomb potential energy of a hydrogen molecule is given by:

\[
U_c = \sum_{i=0}^{n} \sum_{j=0}^{2} \frac{-q_i q_j}{4\pi \epsilon_o r_{ij}}
\]  

(1)

where \( i \) is the sum over all the “nearby” atoms of the MOF-5 (and \( H_2 \)’s) and \( j \) is the sum over the three point charges that represent the \( H_2 \). Three charges are needed to describe the \( H_2 \) because the \( H_2 \) molecule
the separation of the two atoms. The parameters $R_{ij}$ gives the radius of the minimum in the potential and $D_{ij}$ is a scaling parameter for the strength of the interaction. Both parameters must be fit to the system for each atom-atom interaction. It is clear this potential falls off much quicker than the Coulomb potential does. However, it is still expected to be an important term in the binding energy of the $H_2$ to the MOF-5.

To make sure the approximation to an ideal gas, is valid, the quantum concentration of $H_2$, $n_q = \langle m k_B T / (2 \pi \hbar^2) \rangle^{3/2}$, was calculated and compared to the expected maximum concentration of 20 $H_2$’s within the MOF-5. For $T = 300 K$, $n_q = 2.810^{30} m^{-1}$. This was compared to 20 $H_2$ molecules inside a volume of $(15 \text{ Angstroms})^3$. This yielded a concentration of $n = 5.910^{27} m^{-1}$. So, $n/n_q << 1$ and thus the ideal gas approximation applies. The numbers used to find $n$ were chosen because it is known from previous work that the MOF-5 saturates at about 17 $H_2$’s per unit, and that a unit cell is about 15 Angstroms per side. (Rosi, 1128)

Equilibrium is reached when the differential of the Gibbs free energy is zero, at constant pressure and temperature this means the total chemical potential must be zero. (Kittle, 266) Therefore, equilibrium is reached when the chemical potential of the $H_2$ in the reservoir is equal to that of the $H_2$ in contact with the MOF-5. The chemical potential for this system consists of that for an ideal gas in addition to that from the sorption of the $H_2$ onto the MOF-5. The chemical potential is $\mu = \frac{P}{n} \ln \left( \frac{P}{k_B T n_q} \right) - \sum (U_c + U_v)$ where $P$ is pressure, $n$ is $H_2$ concentration, $T$ is absolute temperature, and the sum is the sum over all pairs of atoms in the MOF-5 framework and in all present $H_2$’s. Setting $\mu = 0$ predicts $n$ should increase with increasing pressure and decrease with increasing temperature in equilibrium. The dependence on the sum term is unknown since that term also depends on the number of $H_2$’s present.

The above result gives a way to calculate if equilibrium has been reached given we know $\sum_{H_2} U_c$ and $\sum_{H_2} U_v$. Unfortunately, both are functions of the positions of the locations of every $H$ atom within the framework. With the 400+ atoms that make up a MOF-5 cubic cell and the 20 $H_2$’s expected to occupy the cube, it becomes clear that an analytical solution to the above task of minimization of the Gibbs free energy with respect to the positions of the $H$ atoms is very unlikely to exist. The method that will be used is to use perform numerical minimization by a Monte-Carlo based algorithm to minimize the Gibbs free energy. In this method, $H_2$ molecules are randomly added (to a random location) or removed from the framework. If the total energy after the change is less than the energy before the change, then the change is accepted. Otherwise, the change is reverted. After many iterations, energy starts to converge to a minimum value, and the changed states become representative of an ensemble of acceptable states. An estimate of the uncertainty can be made by finding the typical value by which the quantity of interest changes between the various states in the ensemble.

**Apparatus**

An application produced by Accelrys Inc. called Cerius2 will be used to perform the required calculations. It is expected this application is of a better design and more optimized than could be written on site. Also, Cerius2 is well accepted by the chemical modeling community. The Cerius2 application provides the three major components required to complete the required calculations. These components are a method of inputting the atom positions and electrostatic potential as previously computed with quantum mechanics. The necessary approximations to calculate the interaction energy at any fixed point. This is provided by the Cerius2 Open Force Field module with Universal Force Field 1.02. It provides both Coulomb and Lennard-Jones 6-12 interaction energies for a given configuration. Also, both potentials are capable of calibration.
The Coulomb potential allows scaling, and the LJ 6-12 potential provides a means to adjust the effective radius, \( R \), and interaction energy \( D \) for each possible atom-atom interaction. Lastly, there is a tool to perform Monte-Carlo simulation called Sorption. This tool adds and removes, at random, \( H_2 \) molecules from the MOF-5 crystal. The total energy of the system is calculated from the force fields both prior and after the modification. If the total energy decreases with the change, the change is accepted, otherwise the change is thrown out.

**Experimental Technique**

The approach to completing this experiment followed a multiple step approach. The steps broadly break down into calibration, initial test run, analysis of the initial run and formulation of an approach for the rest of the experiment, final data runs, and the final analysis.

**Creating the Model**

To perform a computer simulation requires a model that represents the physical system. To create this model, Eric Ganz’s team had already calculated the positions of the atoms in the MOF-5 molecule. The positions were calculated by performing a Density Functional Theory (DFT) quantum mechanical calculations to minimize the internal energy of the MOF-5 framework. All that was left was to transfer the atomic positions calculated by Ganz’s team into Cerius2.

This was overall a relatively straightforward process involving importing the basic atomic structure, setting up the periodicity of the crystal, and adding the charges to the atoms. However, with all things that should be straightforward, there were complications. The first was that the oxygens atoms in the Gaussian model were imported as hydrogen atoms. This was relatively easy to fix by just changing the atom types of the affected atoms in Cerius2. The second problem was the conditions for repeating the crystal in Gaussian were incompatible with Cerius2. Therefore, the unit cell MOF-5 molecule had to be expanded to a larger cubic cell. This process was performed by hand by making copies the unit molecule and manually performing the necessary translations. A cubic structure consisting of 4 unit cells was then selected as the new “unit” cell for use in Cerius2. This has the implication that the per unit cell calculations Cerius2 performs will really be per four unit cells, and must be taken into account during analysis. The final problem was Gaussian has multiple methods of mapping the electrostatic potential generated by the calculated wave-function into point charges assigned to atomic centers. Which one to choose became a calibration issue.

For calibration purposes, subsets of the MOF-5 molecule were also imported from Gaussian into Cerius2. These subsets are simpler molecules than the MOF-5, and are expected to be reasonably good models to use for interactions near a certain area on the MOF-5 molecule. However, their relative simplicity over the MOF-5 allows their binding energies to Hydrogen at multiple distances to be easily calculated using quantum methods. Similar calculations were then performed in Cerius2 and the results were used to tune the model parameters so the binding energies closely matched the quantum calculations.

**Calibration**

After the geometries of the models had been imported into Cerius2, the empirical model describing the interaction between atom used in Cerius2 had to be calibrated. As stated earlier, the calibration reference used was the quantum mechanical MP2 calculations performed by Eric Ganz’s team. The method used in calibration was heavily influenced by the data available from the MP2 calculations. Most of this data was for non-periodic molecules that were subsets of the MOF-5. The other available data was for the hydrogen-hydrogen interaction and a charge calculation for MOF-5.

One assumption that was made in the calibration of the models was that once an acceptable method of using the MP2 calculations to determine what charge to assign to each atom was found, that the electrostatic potential produced by that mapping of charge would adequately match the real potential produced by the molecule. Therefore, most of the charge calibration occurred on the quantum side of the calculation. The final charges used were from a ChelpG calculation which works by fitting the atomic point charges to the calculated electrostatic potential derived from the wave-function of the molecule. These final ChelpG charges were then used for the calibration of the model for all molecules used.
Given that the charge assignment was handled almost entirely from the MP2 calculations (and thus from first principles), the only free parameters of model calibration left were the Lennard-Jones 6-12 Van-der-Walls interaction parameters. Cerius2 allows two parameters to specify this interaction, $R_o$ to describe the distance from the center of the atom to the minimum of the potential and $D_o$ to describe the strength of the interaction. A separate $R_o$ and $D_o$ were provided for each atom type from the Universal Force Field 1.02. To calculate the interaction between two separate atoms, Cerius2 uses a sixth-power averaging method. However, these calculated values can be overridden and explicit values given for a specific atom-atom interaction.

The first interaction to be calibrated was the Hydrogen-Hydrogen interaction. This actually involved two steps. The first step was to match the charges calculated by ChelpG to the hydrogen molecule. Normally, this would be automatic, however, with only two points to work with, the quadrapole nature of the charge separation within the molecule could not be accounted for. To remedy this, a dummy atom was placed at the center of the hydrogen molecule. To insure there was no Van-der-Walls contribution from this atom, it was bonded to both hydrogens. With these three points, the charge assignment proceeded normally. The second step was to calibrate the $H_2$ to $H_2$ Van-der-Walls interaction. To do this, two hydrogen molecules were placed perpendicular to each-other as shown.

The total interaction energy was then calculated using both MP2 and Cerius2 at multiple separations ranging from 1 to 4 Angstroms. The above plot shows the final $H_2+H_2$ calibration as well as the MP2 5Z calculation of the interaction. The minimum of the calibrated curve 4.2 meV binding versus the MP2 calculated value of 4.0 meV. As can be seen, the final $H_2$ calibration is within 5% of the MP2 value. Since this is well within the 10% accuracy of the MP2 calculation, it was deemed good enough.

The next interaction to be calibrated was the Benzene + $H_2$ interaction. This was a first attempt to
calibrate how the Hydrogen interacts near the center of the Benzene ring that is part of the MOF-5 molecule. This site was considered important during calibration since prior experiment had shown this to be a significant binding site. (Rosi, 1128) The graph below compares the binding energy calculated in Cerius2 versus that calculated using MP2. Note that there are two MP2 results shown, one for an incomplete basis set (DZ), and the minimum point calculated using the basis set limit. The MP2 DZ results show the general trend of the potential versus distance, but the magnitude of the values are wrong. The MP2 basis set limit calculation gives the best value calculated. It is assumed the basis set limit calculation is accurate to approximately 10% in the energy and distance of the minimum. This uncertainty is shown on the plot.

The resulting calibrated potential curve from Cerius2 is shown both with (OFF total) and without (OFF VdW) the Coulomb component. Notice the Coulomb component accounts for about 25% of the interaction. This calibration results in a binding energy that is 6% from the MP2 basis set value. One catch was that it was found for this calibration to be good, the default values for Hydrogen needed to be used. This meant to satisfy both the $H_2 + H_2$ interaction and this interaction, the $H_2 + H_2$ interaction parameter needed to be set explicitly, while the default values were left for the general calculations.

Later, it was determined by Eric Ganz’s team that BDC-$2H_2 + H_2$ would be a better model for the MOF-$5 + H_2$ interaction near the center of the Benzene ring because the additional atoms cause a charge dispersion over the ring. The Cerius2 and MP2 results were compared in the same was as for the Benzene+$H_2$ calibration.
Another item to note is that to save calculation time, Cerius2 ignores interactions over distances longer than a preset distance. In this case the default was 8 Angstroms. This value had to be increased to prevent false minima from appearing in the calculated potential energy sweep. It was found these false minima were a result of the interactions between the $H_2$ and the atoms at the far edges of the BDC-$2H_2$ turning off to soon, thus lowering the effective total energy of the system. To remedy this situation, the cutoff distance was increased to 25.7 Angstroms. After this was resolved, the final calibration yielded a binding energy of 5.0 meV at 3.2 Angstroms compared to the MP2 basis set limit calculation of 5.5 meV at 2.9 Angstroms. Therefore the calibration is acceptable since the Cerius2 potential matches the MP2 basis set limit result within 10%.

The final calibration parameters used for the remainder of the calculations were:
Charges used for $H_2$ calibration (atomic units)

Charges used for MOF5 calibration (atomic units)

Relevant Van-der-Walls parameters:

<table>
<thead>
<tr>
<th>Atom Type</th>
<th>$R_o$ (Angstroms)</th>
<th>$D_o$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_{gas} + H_{gas}$</td>
<td>3.10</td>
<td>.017</td>
</tr>
<tr>
<td>H</td>
<td>2.98</td>
<td>.044</td>
</tr>
<tr>
<td>C</td>
<td>3.85</td>
<td>.105</td>
</tr>
<tr>
<td>O</td>
<td>3.50</td>
<td>.060</td>
</tr>
<tr>
<td>Zn</td>
<td>2.76</td>
<td>.124</td>
</tr>
</tbody>
</table>

Notice: the parameters for H, C, O, and Zn are the default values as part of the Universal Force Field 1.02 (Rappe).

**Initial Runs**

Now that there was a calibrated model inside the computer to work with initial simulations could be performed. The purpose of this step was to determine if the model appeared to be operating correctly and to help show what kind of interesting information could be gleaned from the calculations. To do this, it was desirable to run a fast calculation so the results would be ready for analysis quickly. Also, since there was experimental data available for 78K and 298K, those temperatures were chosen for the simulation so a comparison to the experimental values could be made. The simulations were to run for 100,000 iterations, and at about 10 pressures per temperature. The pressures used ranged from 1kPa to 64000kPa. The idea was to cover the entire range of pressures covered in the experiment as well as hopefully saturate the MOF-5 with $H_2$ at 298K.

One problem that was discovered right away was the increased cutoff distance determined above did not fit within a unit cell. As part of an optimization used to calculate the total energy of a periodic structure,
Cerius2 requires the cutoff distance to be less than half the minimum unit cell dimension. (Accelrys, Sorption) To accommodate this, the current unit cell (comprising of 4 primitive unit cells) had to be doubled in length in each dimension. This means now the unit cell consists of 32 \((4 \times 2^3)\) primitive unit cells. This is why the loading numbers reported for the simulations refer to the number of \(H_2\) atoms per 32 unit cells.

**Analysis of Initial Runs**

The results of the preliminary run proved very interesting. The first piece of information that was determined was that the simulations did not converge in 100,000 iterations. This can be seen from the loading versus time plots. The plot shown for a pressure of 60kPa and a temperature of 78K, however it is representative of most of the points in this respect.

![Loading vs Monte-Carlo Steps](image)

The most interesting piece of information gained from this run was there must be a better binding site than the one near the center of the Benzene ring with a higher binding energy. This was illustrated by the energy distribution plot. If the Benzene site were the best binding site, the energy distribution should fall off sharply for energies greater than the 1.1 kcal/mol binding energy of the Benzene site. The energy distribution plot shows there is a second peak somewhere around 1.7 kcal/mol.
To investigate this, a canonical ensemble (fixed loading) Monte-Carlo simulation was run for 100,000 iterations with only one $H_2$ in the system. It was run at 298K to promote the $H_2$ not getting stuck in any potential well for too long. The result of this simulation were then a random sampling of many sites within the MOF-5 framework. The positions as well as the binding energies of each site were recorded. After the simulation, the locations of the sites with bindings greater than 1.7kcal/mol were plotted in the same space with the MOF-5 framework. What was determined was that the new better binding site was near the Zinc cluster, at the corners of the MOF-5 framework.

To determine the best location for the $H_2$ within this site, a model of the MOF-5 corner area was constructed and a $H_2$ placed near the best indicated site from the Monte-Carlo simulation. The geometry of the system was then minimized given the constraint that both the MOF-5 and the $H_2$ were to be treated as rigid bodies so the Universal Force Field calculation could not upset the MP2 calculated geometries. What was found was a binding site of energy 1.8 kcal/mol and is located about 3.5 Angstroms from the center oxygen of the zinc cluster. This is almost 60% stronger binding that what was found for the location at the center of the Benzene ring.
Location of 1.8 kcal/mol binding site is 3.5 Angstroms from center O

This result still needs to be verified with a MP2 calculation. This is especially true since there was no data to calibrate the Zinc+Hydrogen and Oxygen+Hydrogen Van-der-Walls parameters, so default values were used. This work will be carried out by Eric Ganz’s team over the summer of 2004.

The Plan

Now that some preliminary data was available to guide the project, a plan was compiled as how to best complete the project. The problems encountered with the preliminary data gathered basically boiled down to two things. The first was that the simulation had not yet converged for all temperature/pressure points. To solve this, it was decided to increase the number of iterations by a factor of ten from 100,000 to 1 million. This would ensure there would be a large ensemble of converged configurations to sample for each data point.

The second problem was that there was no way to distinguish the $H_2$ loading reported that was due to the gas phase from the $H_2$ loading that had actually adsorbed onto the MOF-5 framework. This would be solved by running an additional simulation at each pressure/temperature point. The difference between the first simulation and the additional one would be the additional simulation would not have any framework atoms present in the unit cell. Also, the unit cell volume would be decreased to take into account the volume of the original unit cell occupied by the MOF-5. The result was a simulation that measured only the gas phase at that specific pressure and temperature. This result could then be subtracted from the total loading result to obtain the loading attributable to the MOF-5.

Final Runs

As per the new plan, Monte-Carlo simulations were run at 78K and 298K for 1 million iterations. At 78K pressures from 1 kPa to 400 kPa were explored, while at 298K pressures from 100kPa to 2000kPa were explored. These pressures were chosen because they greatly overlap data available from past experimental work. Also, for each pressure, temperature point a Monte-Carlo simulation was run with an empty unit cell (without the MOF-5). The volume of the empty unit cell was calculated by subtracting the volume used by the MOF-5 molecule from the total volume of the original unit cell. This was done by calculating the volume filled by the (overlapping) spheres described by the equilibrium Van-der-Walls radius of all the atoms in the MOF-5. It was assumed this volume would not be accessible to the Hydrogen due to the strong repulsive portion of the LJ 6-12 potential. These calculations took about 3 days to complete.

Final Analysis

The results of the final calculation are as follows:
Hydrogen loading per 32 unit cells with gas phase subtracted

In general, the results look as expected. The loading increases with pressure up to a point, and then begins to level off. This is especially apparent in the 78K case. Also, it was noted that the all of calculations had converged by about 300,000 iterations, with the low loading calculations converging quickest. The errors on the points were calculated by averaging the specific values of loading and energy respectively that were obtained from iterations 300,000 to 1,000,000 of the simulation. The tiny uncertainty that resulted is the standard deviation of the respective data points relative to that average. Note that this uncertainty does not include the error induced by uncertainties in the calibration, with is assumed to be on the order of ±25%.

When these results are compared to the experimental data, some discrepancies of about a factor of two arise. As can be seen on the graphs however, this factor of two is in different directions at 78K and 298K. The 298K data appears to be linear for pressures less than 2000kPa (20 bar), like the experimental data, however the slope of the simulation data in this region is 21 vs 60 ($H_2/32$ unit cells/bar) for the experimental data. It appears the simulated interaction at 298K is weaker than in the real system. A different pattern can be seen at 78K. The experimental data shows a saturation of the MOF-5 with 17.2 $H_2$’s per unit cell. The simulation shows a saturation of about 35. This discrepancy is expected to be caused by an anomalous Hydrogen-Hydrogen interaction which is allowing the Hydrogen to somehow stack up on the MOF-5. This is further supported by the fact that while the experimental data shows saturation by 20kPa, the simulation does not start to saturate until 100kPa. Of particular interest is the loading at 20kPa in the simulation is about 54% of the experimental value. This is comparable to the disagreement between simulation and experiment at 298K.

Unexpected, but promising results

In addition to the expected results detailed above, more information was extracted from the simulation. Unknown at the beginning of the project was the ability of the simulations to produce energy distributions specifying the number of hydrogens, on average, had a certain energy over the course of the simulation. (Actually from steps 300,000 to 1,000,000 of the simulation to ensure the system had converged.) This data revels a wealth of information about the behavior of the system.
Mass distribution within framework. Left is at 78K, Right is at 298K

One thing that can be inferred from the above data is there are two main groups of binding sites. One with energies of about 1.8 kcal/mol and another with energies of 1.1 kcal/mol. This is shown by the two peaks of the low pressure 78K plot. Previously, the 1.1 kcal/mol site was identified as the center of the Benzene ring, and the 1.8 kcal/mol site identified as the Zinc cluster site. Also, the gradual decrease in $H_2$'s at energies below the 1.1 kcal/mol peak show there are many similar sites near this location. Presumably they are rotations or displacements farther away from the Benzene ring from the equilibrium position. This is showing that as sites fill up, the Hydrogen left is forced to take “weaker” binding sites.

Another thing that can be inferred from the above data is that the number of sites with a higher binding energy of about 1.8 kcal/mol is very limited compared to the sites with an energy of around 1.1 kcal/mol. This is seen most clearly in the high pressure 78K plot which shows the number of $H_2$ in this region remains constant, while the number of $H_2$ in the 1.1 kcal/mol region increases with pressure. By integrating to find the percentage of the area under the curve that falls between 1.65 kcal/mol and 2 kcal/mol, and multiplying by the number of $H_2$ per unit cell for a given pressure, it was found there are approximately 3 $H_2$ per unit cell that occupy the Zinc cluster site. This result was expected because the Zinc cluster site exhibits three-fold symmetry and geometrically, the site is so deep and narrow that only one Hydrogen molecule would fit before its Van-der-Walls repulsion would exclude other Hydrogen from the site. An important consequence of this is that while the Zinc cluster site exhibits stronger binding energy, most of the binding will occur at other sites due to the few available sites near the cluster.

An interesting feature of the 78K plot is also how the curves broaden on the greater binding energy side of both peaks by about a tenth of a kcal/mol as pressure is doubled. This corresponds very closely to the calculated Hydrogen-Hydrogen interaction binding value. It is expected this represents the Hydrogens beginning to interact with each other as the pressure is increased. This may be part of why the calculated loading saturation values calculated at 78K were larger than the experimental values.

However, I think the most revealing piece of information in the energy density plots is from the 298K
plots. When plotting the mass density of the $H_2$ within the MOF-5 crystal at 298K it appears the Hydrogen contains a significant gas phase when compared to 78K where the $H_2$ is mostly stuck to the MOF-5. This, along with the relative flat topped nature of the curve indicates the Hydrogen is equally likely to take any of the available energy states. Making the assumption of a constant number of Hydrogens, means the Boltzmann factor and Partition function should describe the probability a state is chosen.

$$P_i = \frac{e^{E_i/kT}}{Z}$$  \hspace{1cm} (3) \\
$$Z = \sum_i e^{E_i/kT}$$  \hspace{1cm} (4)

An equal probability for each state occurs if $T$ is large compared to all $E_i$’s, so the $P_i$ goes to $1/Z$. Notice the energy distribution is a histogram, and is thus reporting all $H_2$’s with an energy that falls between the limits of the current point. Therefore, a value $N_i$ given in the energy distribution for a given energy represents $N_i$ states of an energy of approximately $E_i$. Therefore the probability becomes:

$$P_i = \frac{N_i e^{E_i/kT}}{Z}$$  \hspace{1cm} (5)

Since the sum of all the probabilities of all the states must be equal to 1, $Z$ can be calculated by normalization to be carried out later. This gives a method of calculating the density of states, $N_i$, given the energy distribution at 298K in known.

To improve the method, we know the Boltzmann factor is also present at 298K, this can be handled by dividing by the Boltzmann factor for 298K. Therefore:

$$N_i = \frac{P_i e^{E_i/kT}}{Z}$$  \hspace{1cm} (6)

where $P_i$ is the probability of an energy state $E_i$ at a $T$ of 298K.

Now the energy distribution can be calculated for any $T$ since the density of states is known. Below is the results of this calculation for 120K. The input for the $P_i$ was the energy density at 298K and 1600 kPa. Notice how closely this matches the energy distribution the simulation produced at 78K. I would like to admit there is a slight problem here since this should work if the temperatures match. In general, I have found the temperature given to the for this calculation has to be about 40K warmer than the simulation temperature to give a similar plot. The reason for this discrepancy is let unknown. I will also verify the similarities between this predicted and calculated Energy densities at 100K, 150K, and 200K. A more careful analysis needs to be carried out to eliminate noise from the density of states information and determine relative errors. I plan to carry this analysis out over the Summer of 2004.
Conclusion

When I first started this project, I was a little worried that because only computer simulation was involved, instead of a physical experiment, that I was going to have a hard time gathering data that would be able to shed light on a physical system. From the results obtained so far, I can see this worry was completely unjustified. In fact, this project was very successful with respect of its goal to create and use computer models to determine characteristics of the MOF-5 Hydrogen sorption. Not only were the original goals of predicting the number of $H_2$’s that adsorbed onto the MOF-5 and determining and classifying likely binding sites met, but additional information was also obtained from the models. This new information basically stems from being able to calculate the density of states of the MOF-5 $H_2$ interaction. Being a unexpected result, it has not been fully analyzed yet, however, it is expected this will allow fewer calculations to be necessary to predict the properties of new, improved MOF like materials. This should further speed the development of these new materials by allowing preliminary testing before the material is even synthesized.

To that end, this project only represents a very small part of what can be done with these methods and I expect there is a nearly endless amount of future study to be done on this topic.

References