Infrared Spectroscopy of Adsorbed H$_2$ in an Isostructural Series of Metal-Organic Frameworks

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Michael Friedman

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Executive Summary

In light of current concerns over pollution, climate change, and the dependence on foreign oil, the scientific community is making a considerable effort to create a clean alternative to the petroleum-powered car. The hydrogen fuel cell car is one of those proposed alternatives, and fuel storage is one of the present challenges. While the storage of hydrogen in a stationary environment is straightforward, storing the extremely volatile substance safely and effectively in an automobile proves difficult. The traditional storage systems for hydrogen, which use hundreds of atmospheres of pressure or hundreds of degrees of cooling, are impractical for a normal car.

The U.S. Department of Energy is investigating a new storage method that utilizes a molecular sponge, with pores on the nanometer length scale, to trap hydrogen. These storage systems would safely operate at pressures well below those required for compressed hydrogen tanks and at temperatures well above those required for liquid hydrogen tanks. The ability to both store enough hydrogen and easily release it is the primary goal of research into this storage method.

There is no known material which meets the requirements currently set by the Department of Energy. Because the number of possible hydrogen sponges is exceedingly large, we do not attempt to test as many materials as possible and hope that we stumble upon one that fits our needs. Rather, our research focuses on determining the characteristics of a quality sponge using a small number of samples. In this thesis, we examine the behavior of hydrogen trapped in a material known as MOF-74, prepared using three different metals. Our results help to provide a clearer picture of the interaction between the hydrogen and the framework, so that we may better understand how hydrogen behaves in a molecular sponge.
Chapter 1

Introduction

1.1 Motivation

As consumption of the world’s fossil fuel resources takes an ever-increasing toll on the environment, the drive for clean, alternative fuel has triggered a surge in research into the possibilities of a hydrogen-powered fuel cell car [1, 2]. Hydrogen is an ideal fuel for use in automobiles primarily because, lacking any carbon, the only by-product from its fuel cell reaction is water. A commercial hydrogen-powered car, however, can only be part of the solution to our energy crisis. Lacking any large reserves of molecular hydrogen, as exist with fossil fuels, the hydrogen itself must be produced at a net energy loss [3]. Accordingly, we classify hydrogen as an energy carrier, able to be produced from any primary energy, i.e. energy found in nature, including renewable and nonrenewable sources [1, 4]. The production of carbon free energy carriers, such as hydrogen and electricity, is necessary because, clean primary energy sources, such as solar, hydropower, geothermal, and wind power, are not easily stored or transported and thus do not lend themselves well to automotive use [4].

Hydrogen may be produced from water by electrolysis, which is essentially the fuel cell reaction run in reverse, and by thermolysis, which involves heating the water to over 2000 °C, at which point water decomposes into hydrogen (H₂) and oxygen (O₂). While these reactions involve no pollutants, the most common method of mass
1.1 Motivation

hydrogen production today is a process called “steam reforming,” which reacts fossil fuels with steam to create hydrogen and carbon dioxide [5]. Thus, only when clean primary sources of energy become widely in use will hydrogen power neither require fossil fuels nor contribute to the CO$_2$ content of the atmosphere [3].

We are primarily concerned with hydrogen storage methods in this thesis. Hydrogen’s main competitor as an energy carrier for the model, clean vehicle of the future is the electric battery. How do these two fuel systems compare? Because hydrogen power involves many more inherently inefficient energy conversion steps, the electric battery is by and large more energy efficient, except in certain cases that usually involve a carbon output [6]. However, energy efficiency is only one of many metrics, which include mass, volume, cost, initial greenhouse gas reductions, and refueling times, used to measure the utility of a fuel system [6, 3]. A full comparison is beyond the scope of this thesis, but on the whole, as reported in a paper by Thomas, hydrogen fuel cells outperform batteries for distances greater than 100 miles, primarily as a consequence of the higher costs, the particularly long refueling times, and the large mass and volume associated with high energy capacity batteries [6].

It is useful as well to compare hydrogen power to the current standard, petroleum power. While the available energy density by mass for hydrogen fuel is actually three times greater than that of petroleum, the available energy density by volume at standard temperature and pressure is three orders of magnitude smaller as a result of hydrogen’s gaseous state [7, 4, 8]. A storage system that keeps hydrogen as a liquid would almost overcome this low volumetric energy density, if not for the immense overall weight of the insulation system itself, which at atmospheric pressure would need to keep hydrogen below its boiling point, 20K [9]. Additionally, the monetary and energetic cost of hydrogen liquefaction is prohibitive [4, 9]. A storage system that simply pressurizes hydrogen would also be problematic, not only because of the weight of the system, but also due to the extreme volatility of such an apparatus moving at high speeds. Despite this, early hydrogen fuel cell cars will likely use 5,000-10,000 psi (340-680 atm) compressed hydrogen tanks with a 23,500 psi burst pressure [3]. These storage systems can meet the technical targets set by the U. S. Department of Energy for 2010, but are unlikely to meet future goals [7].
1.2 Metal-Organic Frameworks

For stationary applications, the storage of hydrogen is not an issue; employing many of the same principles used to store natural gas since 1915, underground caverns have been used for decades to safely store pressurized tanks of hydrogen [10]. This practice will likely expand to accommodate energy storage of intermittent sources of energy, such as wind and solar [4]. How would one safely and effectively store hydrogen for use in an automobile? One method currently under investigation utilizes a microporous material, acting as a hydrogen sponge, that will 1) soak up, or adsorb, a significant amount of hydrogen, 2) bind the hydrogen strongly enough that it will not escape into the gas phase at reasonable temperatures and pressures, and 3) hold it loosely enough that only small amounts of energy will be required to release it.

The first restriction concerns the hydrogen uptake for which the U.S. Department of Energy has set a goal of 9% hydrogen by weight for the entire system [3]. The second two restrictions concern the binding energy of the site within the sponge that will hold the hydrogen. Binding energy is the amount of energy it takes to disassemble a system. In our case, this is simply amounts to the removal of the hydrogen from the sponge. There are two basic categories of hydrogen sponges: physisorptive materials, those that weakly bind the entire hydrogen molecule via Van der Waals forces, and chemisorptive materials, those that strongly bind atomic hydrogen via ionic or covalent bonds. For practical use, structures that physisorb hydrogen bind it too weakly, and structures that chemisorb hydrogen bind it too strongly. Ideally, we would like the hydrogen to be bound or released with small changes in temperature and/or pressure around room temperature and atmospheric pressure. A suitable binding energy for hydrogen at atmospheric pressure is approximately 40 kJ/mol, while at 40 atm, 15 kJ/mol has been shown to be ideal [11].

1.2 Metal-Organic Frameworks

A class of structures known collectively as metal-organic frameworks (MOFs) has garnered a great deal of attention for their porous nature and high binding energies [12, 13, 14, 7, 15, 3]. They consist of a repeating structure of metal ions linked together by organic molecules. This structure provides an extraordinary amount of
tunability, i.e. the capability to create new, similar structures by exchanging metal ions or linkers [15]. Since the number of possible metal-organic frameworks is inordinately large, studying them all individually in the hopes of stumbling upon one that meets our criteria would, in all likelihood, be a fruitless endeavor. There is no guarantee a structure ideal for solid-state hydrogen storage in fuel cell cars will ever exist. It is our hope that by extensively examining the behavior of hydrogen in one small set of MOFs we will be able to narrow down the qualities of a “good” physisorbing material and determine to what degree we can adjust any given MOF.

By their nature, the MOFs we have studied have an extraordinarily large affinity for physisorbing hydrogen. This quality, which is so sought-after, is also problematic because it means that any other kind of molecule in the air that can fit through the porous structure will bind itself to the framework, sometimes even more strongly than hydrogen. Since one such species is water, these sponges are highly sensitive to air. The samples, in the form of crystal powders, must be kept either under vacuum or flowing argon at all times to prevent contamination. The other common invader is the solvent in which the MOF is synthesized. Water and solvents can be driven off to different degrees by replacing the solvents and heating, or by simply heating the sample. The effectiveness of these approaches depends on the binding energy of the site and the temperature at which the crystal structure decomposes. The easy destruction of the frameworks, is one of the many difficulties that must be accounted for in hydrogen storage applications.

1.3 The Isostructural Series

In this thesis, we examine one noteworthy framework called MOF-74, a honeycomb-like structure with one of the largest storage capacities yet observed [16, 17]. In fact, the distances between the hydrogen molecules were shown by Liu et. al. to be less than those of solid hydrogen [16]. This framework has four binding sites per metal, and the first to be filled (the primary site) is located directly 2-3Å directly above the metal (see Fig. 1.1) [16]. Consequently, the chosen metal directly affects the binding energy associated with the primary binding site [17]. In order to see the effect of
1.3 The Isostructural Series

Figure 1.1: MOF-74 is a crystal with a trigonal structure and $R\bar{3}$ group symmetry. Metals (pink) are coordinately unsaturated with one open octahedral site.

exchanging metal ions, Zhou et al. recently synthesized five of the isostructural MOF-74 compounds, with magnesium, manganese, cobalt, nickel, and zinc in the open metal sites [17]. To distinguish the members of the series, we will label them $M$-MOF-74 ($M = Mg, Mn, Co, Ni, Zn$). In MOF-74, each metal becomes a divalent cation with coordination number 5, meaning it exists in its $M^{2+}$ state and each metal is bound to five other atoms. In this case, the metal is bonded to five oxygens atoms which are arranged in such a way that the metal is centered at the base of a square pyramid (see Figure 1.1(b)). A site is thus left open for hydrogen to fill and to create an octahedral molecular geometry. The relatively high binding energy of the metal site can be explained by these metals’ preference to have a coordination number of 4 or 6 [17].

Jesse Rowsell in the Oberlin Chemistry Department has synthesized each member of this series as well, and we have data on the zinc, cobalt, and nickel based frameworks. By comparing the data from these MOFs, we can clearly determine the extent to which the species of metal affects the behavior of hydrogen adsorbed in MOF-74. In practice, frameworks which can be produced isostructurally using different metals are few and far between. Thus, this particular structure is exceptional
because we learn not only from its adsorptive properties, but also from the effects that the exchange of metals has on these properties.

Interestingly, the relationship between metal species and isosteric heat of adsorption, a standard characterization of the binding energy, conforms well to the Irving-Williams sequence ($\text{Mn}^{2+} < \text{Fe}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} > \text{Zn}^{2+}$) [17]. This empirical series describes the stability of complexes formed by certain transition metals [18]. In Chapter 4, we will further discuss the Irving Williams sequence and the theory behind it.

1.4 Infrared Spectroscopy

To discover how hydrogen behaves while adsorbed in metal-organic frameworks, we use a technique called Fourier Transform Infrared Spectroscopy (FTIR). Using FTIR, we can probe the interaction that the hydrogen has at each of the MOF’s binding sites. Essentially, we send radiation with a range of frequencies into the sample, and while some of the radiation is absorbed by the sample, the remainder is collected as it escapes. In order for infrared spectroscopy to be an effective technique, the molecule being probed must possess an electric dipole moment to act as an antenna for the incoming infrared radiation. Unfortunately, molecular hydrogen has no permanent dipole moment, only a permanent quadrupole moment (see Figure 1.2). The charge distribution of the host structure, however, with its complicated framework of electrically charged protons and electrons, interacts strongly with the adsorbed hydrogen. This interaction induces a dipole on the hydrogen allowing it to be “infrared active.” We will discuss infrared spectroscopy in more detail in Chapter 3.

Only radiation of specific frequencies, which correspond to the allowed energy transitions for hydrogen, are absorbed by the hydrogen. Upon absorption, these photons cause quantum transitions in the hydrogen, which are associated with dips in the intensity of the radiation received by the detector. Knowing the frequencies of quantum transitions for hydrogen in its gas phase and the measured frequencies for the adsorbed hydrogen, we use their differences to estimate the binding energies of the hydrogen in the host.
1.5 Diatomic Hydrogen and Its Isotopologues

As a diatomic molecule, the motion of hydrogen can be described in terms of vibrational, rotational, and translational motion. We measure transitions in energy levels for these three kinds of motion as well as for combinations of them. Vibrational transitions occur at energies that match the energies of the mid to near infrared, while rotational and translational transitions occur at lower frequencies in the far infrared. Our experimental set-up is designed primarily for the mid to near infrared, thus detecting vibrational, vibrational and rotational (rotovibrational), and vibra-
tional and translational (center-of-mass) transitions. We will further describe the motion of hydrogen in Chapter 2.

It can also be very informative to examine deuterium (chemical symbol D), an isotope of hydrogen consisting of a proton and a neutron. Deuterium is twice as heavy, but is chemically almost identical to hydrogen. If we replace one or both of the hydrogen atoms in H$_2$ with deuterium, we get HD, hydrogen deuteride, and D$_2$, diatomic deuterium, respectively. These compounds behave in a similar way chemically, but their quantum dynamics are different enough so as to be a useful comparison to hydrogen. For example, because the vibrational energy levels are a function of the molecule’s mass, the vibrational frequencies in HD and D$_2$ are reduced by a factor of $\sqrt{\frac{4}{3}}$ and $\sqrt{2}$ respectively from those of H$_2$. Because these molecules appear in different areas of the infrared spectrum, observing their behavior can help us to confirm or to discredit certain features of the data associated with hydrogen. The inherent quantum mechanical differences also help us to verify aspects of the hydrogen data.
Chapter 2

Quantum Mechanics of Motion

2.1 Overview

When we examine the motion of diatomic hydrogen, we are concerned with the mechanics of two protons. The electrons will always remain in their ground state during our experiment and, as their mass is four orders of magnitude smaller than that of the protons’, they do not have an appreciable effect on the mechanics of the molecule. Classically, we would describe a diatomic molecule as having a “dumbbell” shape: two hard spheres attached by a massless spring. This provides our molecular hydrogen with six degrees of freedom. These degrees of freedom can be described in terms of three spatial components (x, y, z) associated with translational motion, two orientation angles (θ, φ) associated with rotational motion about two perpendicular axes, and the separation (ρ) of the two atoms associated with vibrational motion. As we will discuss in Chapter 3, we can detect the spacing of the energy levels for each of these kinds of motion.

In quantum mechanics, we describe the state of a particle in terms of its wavefunction, Ψ, which can be split up into the product of a spatial part and a spin part, ψ and χ. The spatial part describes a position in space, and the spin part describes the z-component of the intrinsic angular momentum, or spin, which for protons can be $+\frac{h}{2}$ (named spin up and labeled $\uparrow$) or $-\frac{h}{2}$ (named spin down and labeled $\downarrow$).
Because these two protons are absolutely indistinguishable from one another, we cannot talk about the state of “Proton 1” or “Proton 2.” Instead, the best we can do is describe the state of the two protons together as a single wavefunction of multiple variables,

$$\Psi = \psi(r_1, r_2)\chi(s_1, s_2),$$

where $r$ is a position in space, and $s$ is a spin state. The state of the molecule is thus described in terms of three spatial coordinates and the basis spin states, $\uparrow\uparrow$, $\downarrow\downarrow$, $\uparrow\downarrow$, $\downarrow\uparrow$. Being indistinguishable fermions, there exists a restriction that the wavefunction of the two protons must be antisymmetric under exchange. In other words,

$$\psi(r_1, r_2)\chi(s_1, s_2) = -\psi(r_2, r_1)\chi(s_2, s_1).$$

This symmetrization requirement can be satisfied in two distinct ways because our wavefunction can be split into spatial and spin parts. If the spatial part of the wavefunction is symmetric (i.e. $\psi(r_1, r_2) = \psi(r_2, r_1)$), the spin part must be antisymmetric. The two proton system allows only one antisymmetric spin configuration,

$$\frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow),$$

which is called the “singlet state.” Molecular hydrogen in this configuration has total
spin zero and is called parahydrogen. Likewise, if the spin parts of the wavefunction are symmetric, then the spatial parts of the wavefunction must be antisymmetric. This configuration results in the triplet state

\[
\begin{pmatrix}
\uparrow \uparrow \\
\frac{1}{\sqrt{2}} (\uparrow \downarrow + \downarrow \uparrow) \\
\downarrow \downarrow
\end{pmatrix}.
\]

Molecular hydrogen in this configuration has total spin one (in units of $\hbar$) and is called orthohydrogen. Because orthohydrogen can be configured in three different ways, and parahydrogen only has one spin configuration, on average we find a 3:1 ortho to para ratio at room temperature. This ratio is one major difference between H\(_2\), D\(_2\), and HD. Because diatomic deuterium consists of two indistinguishable bosons, it has the requirement that its total molecular wavefunction be symmetric under exchange. By a similar argument, using the fact that each deuterium nucleus can exist in three different spin states, D\(_2\) has a 2:1 ortho to para ratio at room temperature, where, in this case, ortho corresponds to the 6 symmetric spin states, and para corresponds to the 3 antisymmetric spin states. Hydrogen deuteride, owing to its distinguishable nuclei, has no symmetrization requirement, and thus is not given the ortho/para designations.

2.2 Vibrational

Every transition that we study in the infrared spectrum of hydrogen involves a vibrational transition. Thus, the behavior of hydrogen as a function of $\rho$, the internuclear separation, is an important system for us to understand, or at least for us to model. Unfortunately, there is no analytic solution for the potential energy of diatomic hydrogen as a function of $\rho$. In the introduction to this chapter, we mentioned modeling the vibrations of H\(_2\) as two masses connected by a spring, and this naturally leads us to the quantum simple harmonic oscillator. It can be shown that plugging the potential energy of a spring from Hooke’s Law into the Schrodinger Equation and solving by either a ladder operators method or power series method (both described
in [19]), results in eigenenergies of this system in the form

\[ E_{\text{vib}} = h v_0 (v + \frac{1}{2}), \]  

(2.4)

for \( v = 0, 1, 2, 3 \), and so forth. From Hooke’s Law, we have

\[ v_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}, \]  

(2.5)

where \( k \) defines the stiffness of our spring, \( \mu \) is the reduced mass. \( \text{H}_2 \), \( \text{HD} \), and \( \text{D}_2 \) are chemically identical, so we assume that their spring constants are equal. Therefore, the vibrational frequencies of these three molecules scales with the reduced mass, \( \mu \), according to Equation 2.5. The fundamental vibrational frequency for \( \text{H}_2 \) is \( v_0 = 4161 \text{ cm}^{-1} \), which corresponds to approximately 0.5 eV. Wavenumbers, cm\(^{-1} \), are the frequency units of choice for infrared spectroscopy, and directly to the energy of light, so we talk about frequencies in cm\(^{-1} \) interchangeably with energy. By Equation 2.4, The energy spacing between any two adjacent vibrational levels is constant at

\[ E_{\text{vib}}(n + 1) - E_{\text{vib}}(n) = h v_0. \]  

(2.6)

Virtually all transitions will begin in the ground state. Even at room temperature, where \( k_b T = 0.025 \text{ eV} \), this energy spacing is 20 times larger, giving a probability of \( e^{-20} \approx 0 \) that a hydrogen molecule will be found in the first vibrationally excited state. As we will see shortly, because a real bond is anharmonic, this potential has limitations, and modification will be necessary to explain the phenomena seen in the infrared spectra.

### 2.2.1 Overtones

Overtones are those transitions for which \( \Delta v \geq 2 \). Assuming the simple harmonic potential, there is zero probability that hydrogen will transition from the \( v = 0 \) state to the \( v = 2 \) state if struck by a photon of energy \( E_{\text{vib}}(2) - E_{\text{vib}}(0) = 2hv_0 \). We do, however, clearly see overtone peaks in our spectra, which indicates that this model
is not well-suited for explaining our observation of the overtone transition. To first order, the simple harmonic potential is still accurate enough for our purposes. To understand the mechanism by which we can see the vibrational overtone, we will need to add anharmonicity to our model. For this we choose the Morse potential, which is described in the next section.

2.2.2 The Morse Potential

We must examine the “anatomy” of the bond between the two hydrogen atoms in order to get a clearer picture of the vibrational potential. If we only consider electrostatic forces, we know that in the limit of large separation, the potential must approach a constant. As we bring the two atoms closer and closer, the electrostatic potential will increase without bound. This situation leads one to modify the simple harmonic approximation to reflect this anharmonicity. Similar in shape to the harmonic oscillator potential, the Morse potential is a commonly used function to describe chemical bonds. This potential is particularly convenient because it has an analytic solution to the Schrodinger equation and like the quantum harmonic oscillator, ladder operator methods can be used to find the eigenenergies and eigenstates. We define it here as

\[ U(\rho) = D_e(1 - e^{-a(\rho - \rho_e)})^2, \tag{2.7} \]

where \( D_e \) is the minimum potential, \( a \) is a constant which depends on \( D_e \) and the force of the bond, and \( \rho_e \) is the equilibrium internuclear distance. If we solve the time-independent Schrodinger equation using this potential we find eigenenergies of the form

\[ E(\nu) = \hbar \nu_0 (v + \frac{1}{2}) - \frac{[\hbar \nu_0 (v + \frac{1}{2})]^2}{4D_e}, \tag{2.8} \]

where

\[ \nu_0 = \frac{a}{2\pi} \sqrt{\frac{2D_e}{\mu}}. \tag{2.9} \]
Figure 2.2: The Morse potential is shown with energy levels and disassociation energy $D_e$ [20]. The parameters were determined by Hugh Churchill by fitting the Morse potential to an $ab\ initio$ potential [21].
Comparing these energies with the energies given by the simple harmonic oscillator model (Eq. 2.4), it is easy to see that they are essentially the same up to a correction term, $\frac{\hbar \omega (v + \frac{1}{2})^2}{4D_e}$, which accounts for the anharmonicity. Because the vibrational quantum number is squared in this term, the correction becomes more important as we increase in vibrational energy levels. That is, the space between the vibrational energy levels decreases with increasing $v$. This model does break down when the energy level spacing becomes negative, but fortunately we are only concerned with $v = 0, 1, \text{ and } 2$, which are well below that breaking point. The anharmonicity in the Morse potential merely allows for the possibility of detecting the overtone, but not with the relatively large intensity with which we detect it. See Chapter 7 for further discussion of the detection of the overtone band.

2.3 Rotational

We assume in our rigid rotor model that hydrogen rotates about its center of mass, and for convenience choose our axes to be the bond axis and two perpendicular axes which intersect at the center of mass. Classically, the rotational kinetic energy associated with a rigid rotor is

$$E_{\text{rot}} = \frac{L^2}{2I}, \quad (2.10)$$

where $L$ is the angular momentum and $I$ is the moment of inertia. In quantum mechanical terms, the eigenvalues of angular momentum operator, $\hat{L}^2$, are simply $\hbar^2 J(J + 1)$, where $J$ is the total angular momentum quantum number. We assume a constant moment of inertia with respect to rotational state, and thus the rotational eigenenergies may be written

$$E_{\text{rot}} = \frac{\hbar^2 J(J + 1)}{2I}, \quad (2.11)$$

or more commonly,

$$E_{\text{rot}} = B_J J(J + 1), \quad (2.12)$$
where $B_v$ is the rotational constant, $\frac{\hbar^2}{2I}$, and is dependent on the vibrational state of the molecule. Higher vibrational states significantly increase the moment of inertia which decreases $B_v$. For the simple harmonic oscillator description of the vibrational mode, the expectation value of the separation between the two hydrogen stays constant when the molecule moves to a vibrationally excited state, though the bond does observably change. The moment of inertia is dependent upon the expectation value of the square of the separation, by

$$I = \mu \langle \rho^2 \rangle,$$  \hfill (2.13)

which does increase in vibrationally excited states. Notice that the rotational constants in H$_2$, HD, and D$_2$ will scale as $1/\mu$. For H$_2$ rotations about the axes that are perpendicular to the bond axis, $B_0 = 7.35$ meV (or 59.3 cm$^{-1}$) and $B_1 = 6.99$ meV (or 56.4 cm$^{-1}$). Rotations about the bond axis are essentially forbidden because the low moment of inertia results in a energy spacing that is too large to be seen in our spectra.

Recall from the opening of this chapter that orthohydrogen has spin 1 and parahydrogen has spin 0. This term is included in the $J$ quantum such that while the rotational ground state for parahydrogen corresponds to $J = 0$, orthohydrogen’s rotation ground state has $J = 1$. Evidently, because of the symmetrization requirement (Eq. 2.2), the spatial wavefunction associated with $J = 0$ must be symmetric under exchange because its spin state is antisymmetric. In fact, all spatial wavefunctions associated with even $J$ quantum numbers are symmetric under exchange and all spatial wavefunctions associated with odd $J$ quantum numbers are antisymmetric under exchange. Thus, orthohydrogen can only occupy states with odd $J$ quantum numbers and parahydrogen can only occupy states with even $J$ quantum numbers.

This provides us with the selection rule, barring any nuclear spin flips, which are highly unlikely for a photon-induced transition, that $\Delta J = 2n$ where $n$ is an integer. Of primary concern to our experiments are transitions for which the rotational quantum does not change and transitions for which $\Delta J = +2$. For reasons which are no longer significant, a widely used notation labels those transitions for which $\Delta J = 0$,
2.3 Rotational

$Q$, and those for which $\Delta J = +2$, $S$. These names are followed by a number in parentheses which indicates the initial rotational state. For example, $S(1)$ indicates a transition from $J = 1$ to $J = 3$.

A transition which changes the $J$ quantum by an odd number does not generally occur on the timescales we consider, especially without an external magnetic field gradient, due to the necessary spin flip associated with ortho-para conversion, which violates the conservation of angular momentum [22]. An interesting consequence of this restriction is that no matter how low the temperature gets, without a catalyst for ortho-para conversion, $3/4$ of the hydrogen will remain “stuck” in their rotationally excited $J = 1$ state. However, the magnetic field produced by the unpaired electrons in the nearby metal ions produces a magnetic field gradient which allows this spin flip, and consequently a faster “relaxation” at low temperatures from the $J = 1$ state to the $J = 0$ state. Depending on the strength of the magnetic gradient in the system, it is possible for spin flips to occur very fast, and in that limit, the population of different energy levels simply follows Boltzmann statistics. Conversion between ortho and para species of hydrogen in Zn-MOF-74 has been well recorded in Brian Burkholder’s Honors thesis [22].

Recall again from the beginning of the chapter that hydrogen deuteride does not have a symmetrization requirement, and thus no ortho/para designation. This means that, from the ground state in HD, the transition with $\Delta J = +1$, the $R$ transition, is allowed.

The Hindered Rotor Model

Recently, Kong et. al. published a paper which described an orientational potential for the hydrogen [23]. This “hindered rotor model” describes a hydrogen molecule as a rotor that is not allowed to freely rotate, but has a higher or lower potential depending on its orientation. By creating a potential model using an expansion of spherical harmonics, they were able to predict energies within 20% of inelastic neutron scattering (INS) data collected at NIST (see Figure 2.4) [16].

We have calculated our own potential model (see Fig. 2.3(b)) for a hindered
(a) Rotational (orientational) potential for the primary binding site found by Kong, et. al. [23].

(b) Our rotational potential for the primary binding site expanded in terms of the spherical harmonics $Y_2^0$ and $Y_2^\pm 1$.

Figure 2.3: Approximation of orientational potential of a hydrogen molecule in MOF-74. In both cases, the z-axis points down the 1-D pores and the highest potential exists when the bond axis points towards the metal ion.

rotor based on the splittings observed in the INS data. Using degenerate perturbation theory on a free rotor with a perturbative potential expanded in terms of the spherical harmonics $Y_2^0$ and $Y_2^\pm 1$, the three $J = 1$ energies were split relative to each other, to within 0.01 eV of the neutron scattering data. However, the energies relative to the ground state were all offset by +2.20 eV from the INS data and we attribute the disagreement to rotational-translational coupling, as described in §2.5. In comparing the theoretical data to the INS data and the infrared spectroscopy data, we obtained similar accuracy (10-20%) to the results published by Kong et. al. [23]. Both our model and the previously published hindered rotor model found the range in orientation potential to be roughly 28 meV and the highest potential occurring when the bond axis is oriented towards the nearby metal. Additionally, we’ve compared the resulting transitions from our model to the infrared spectroscopy data for Zn-MOF-74 found reasonable agreement (see Tab. 2.3).
Table 2.1: We present here the resulting theoretical Q(1), S(0), and S(1) transitions determined by applying our rotational potential, shown in Figure 2.3(b), to our rigid rotor system. We have assumed that the Q(0) transition is 4096 cm\(^{-1}\) and there is a selection rule of \(\Delta m = 0\). These results are consistent with our prediction that the highest energy \(J = 1\) state is not thermally populated. The symbol * denotes a doubly degenerate energy level. We believe that the discrepancies, which are consistent with the level of agreement found by Kong, et. al., are a result of rotational-translational coupling. All values listed are in cm\(^{-1}\). Associated error in the experimental data is ±2 cm\(^{-1}\).

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Figure 2.4: The inelastic neutron scattering spectra of adsorbed H\(_2\) at two different gas loadings are shown [16]. All measurements were performed at 4 K. This data shows rotational transitions from the ground state, \(J=0\), to the three nondegenerate \(J=1\) first excited states. These para-ortho transitions occur at 8.3, 11.1, and 20.9 meV in the 0.8 H\(_2\) per Zn spectrum.
2.4 Translational

Translational motion is movement of the molecule as a whole, which for convenience can be described in terms of the center of mass coordinates, \((x, y, z)\). As with the vibrational modes, we will begin by assuming a harmonic potential, this time with the entire molecule sitting in a three dimensional well. There will be a zero point energy of \(\frac{1}{2}\hbar\omega\) for each degree of freedom. To a first order approximation, we have

\[
E_{\text{trans}} = (n + \frac{3}{2})\hbar\omega,
\]

(2.14)

where \(n\) is the translational quantum number, and \(\hbar\omega\) is the translational energy spacing. Similar to the way that the vibrational frequencies in the 1-dimensional simple harmonic oscillator scale as \(1/\sqrt{\mu}\) in \(\text{H}_2\), \(\text{HD}\), and \(\text{D}_2\), the translational frequencies for the 3-dimensional harmonic oscillator scale as \(1/\sqrt{m}\), where \(m\) is the mass of the whole molecule.

Clearly, in looking at our primary binding site (Fig. 1.1(b)), we see that there is great deal of asymmetry about this local potential minimum. This potential is very complicated, primarily because of our lack of understanding hydrogen-metal interactions. We can make some progress by considering the symmetries of the binding site, and modeling the anharmonicity from empirical evidence.

In our spectra, the bands that correspond to translational transitions are generally much broader than either the rotational or vibrational bands. We believe that this is the result of two effects. First, in the very large number of unit cells, defects and impurities can perturb the potential in a variety of different ways. This leads to a larger continuum of possible energies which broadens the band. The other broadening effect occurs when a phonon, a lattice vibration, is at a close enough frequency to a translational transition that they can couple together. This coupling allows a translationally excited molecule to relax into the ground state in a shorter amount of time than it would otherwise, i.e. by emission of a photon. By the energy-time uncertainty principle,
\[ \Delta E \Delta t \geq \frac{\hbar}{2} \]  

(2.15)

where, in this case, $\Delta t$ is the average time it takes the hydrogen molecule to relax into its ground state [19]. Therefore, if we know the hydrogen will relax into its ground state faster, $\Delta t$ must decrease and $\Delta E$, which is related to the uncertainty in the energy of our transition, must increase. This quantum mechanical effect is called lifetime broadening.

2.5 Rotational-Translational Coupling

The treatment of the rotational eigenenergies at the beginning of this section assumed that the translational energies and rotational energies are different enough that it reasonable to talk about one without the other because they will occur on different time scales. This has been called the “weak-coupling limit,” because as the energies become closer in value, rotational-translational coupling will occur, which causes the molecules center of mass to move as a function of the orientation of the bond axis [24]. In the “weak-coupling limit,” $J$ is called a “good” quantum number because it commutes with the Hamiltonian, assuring that its eigenvalues and eigenenergies will not change over time. We believe that it is the unreliability of the “weak coupling limit” assumption that leads to theoretical values of energy transitions that are larger than those experimentally determined in neutron scattering experiments performed by Liu et. al. [16]. Because rotational-translational coupling jumbles these two types of motion, however, the computation of energies is very difficult.

Mulder et. al. took a different approach, giving the hydrogen an “apparent rotational constant,” which was reduced by as much as 29% from an unperturbed rigid rotor. This did result in lower theoretical transition energies for the rotational levels, as can be seen right from eq. 2.12, which could more accurately approximated the experimental INS data. We do not think that this is a physically reasonable assumption, however, due the large effect such a change would likely have on the vibrational transition. By the relation described in Equations 2.11 and 2.12, a 29%
reduction in $B_v$ results 41% increase in the moment of inertia. The moment of inertia of a quantum rotor is related to the reduced mass and the expectation value of the square of the separation by

$$I = \mu \langle \rho^2 \rangle. \quad (2.16)$$

Since we do not expect the mass of the particles to change, $\langle \rho^2 \rangle$ must increase. We have estimated that the perturbation required to cause such a change is on the order of electron-volts, while we believe that the maximum energy of such a perturbation is an order of magnitude smaller. This precludes the possibility of such a great increase in $\langle \rho^2 \rangle$. 
Chapter 3

Infrared Spectroscopy

To probe the quantum transitions of hydrogen, we use a technique called Fourier Transform Infrared Spectroscopy (FTIR). In FTIR, radiation is sent through a Michelson interferometer and into our sample. The resulting scattered light produces a time-based signal that is Fourier transformed into a frequency-based signal. The absorption of certain frequencies of light by the sample causes a decrease in the amplitude of those frequencies in the collected spectra. A change in the spectra between a sample that is in vacuo and one that is exposed to H\textsubscript{2} provides evidence that hydrogen has been adsorbed in the sample. The specifics of our FTIR setup and data collection will be explained further in Chapter 5.

Not every quantum transition associated with hydrogen necessarily appears in our absorption spectra. This results from a property of the interaction of light with matter. The mere fact that the energy of an incident infrared photon matches the energy splitting of a molecular transition does not guarantee the absorption of that photon. The infrared absorption of gas phase hydrogen, for example, is practically zero for normal conditions. Infrared active molecules, molecules that have a significant probability of absorbing infrared photons, must be able to undergo transitions to states with a different molecular dipole moment [19]. Every transition that gaseous hydrogen can make, whether it be vibrational, rotational, or translational, leaves the electric dipole moment of the molecule at zero. On the other hand, when hydrogen is adsorbed in MOF-74, two mechanisms allow for changes in dipole moment:
the overlap mechanism (§3.1), in which interactions with the framework induce a dipole moment on the hydrogen, and the quadrupole mechanism (§3.2), in which the quadrupole moment of the hydrogen induces a dipole moment on the framework [25].

Classically, the infrared radiation interacts with the hydrogen via resonance with any electric and magnetic moments the hydrogen possesses [26]. In order to determine the probability that a transition will occur, we must calculate matrix elements for the entire electric and magnetic multipole expansion using wave mechanics. The photons that trigger molecular transitions in hydrogen have wavelengths on the order of microns ($10^{-6}$ m), while the internuclear distance of diatomic hydrogen is on the order of angstroms ($10^{-10}$ m). Given the disparity in dimensions, the photon’s electric and magnetic fields are essentially constant over the length of the molecule at any given time. Therefore, we may make the approximation that the dipole moments are dominant in strength, and since the magnetic effects are small compared to electric effects, we are only concerned with the electric dipole moment. Quantum mechanically, given two quantum states $| m \rangle$ and $| n \rangle$, with total molecular state wavefunctions $\psi_m$ and $\psi_n$, the transition moment $\vec{\mu}_{nm} = \langle n | \vec{\mu} | m \rangle$ is given by

$$\vec{\mu}_{nm} = \int \psi_n^* \vec{\mu}^e \psi_m d\tau,$$

(3.1)

where $d\tau$ is a volume element, $\vec{\mu}^e$ is the electric dipole moment operator, and the integral is calculated over all space. The electric dipole moment operator is

$$\vec{\mu}^e = \sum_j q_j \vec{d}_j,$$

(3.2)

which is simply the classical electric dipole moment, where $\vec{d}$ is the displacement vector and the sum is over all charges. For a neutral molecule like hydrogen, this operator is independent of the choice of origin, however, the molecule’s center of mass is generally used [26]. If the eigenenergies of $\psi_m$ and $\psi_n$ are $E_m$ and $E_n$ respectively, then the energy of our transition will be

$$\Delta E_{\text{transition}} = \hbar \omega_0 = E_n - E_m.$$
The transitions that we are concerned about originate in the ground state, so $E_n > E_m$.

As a result of its changing electric field, any incident photon with energy $\hbar \omega$ will create a time dependent perturbation to the Hamiltonian of our system. Using a classical picture of light (i.e. nonrelativistic, nonquantal), it is shown in Griffith’s *Introduction to Quantum Mechanics* [19] that the probability of a transition from state $|m\rangle$ to state $|n\rangle$ is proportional to

$$P_{nm} \propto \frac{|\vec{\mu}_{nm}|^2}{(\omega_0 - \omega)^2}, \quad (3.4)$$

where time dependent perturbation theory is used to first order. This relationship describes a Lorentzian distribution in the transition probability centered around $\omega_0$. This distribution determines the range of frequencies that may cause a transition, and thus what a “pure” absorbance band in our spectra should look like (see Fig. 3.1). Due to the inhomogeneity of the sample, e.g. the presence excess solvent from the synthesis process or defects, our spectral peaks might result from several closely spaced peaks, forming a Gaussian distribution of Lorentzian peaks. In the next two sections, we will discuss the two mechanisms that may lead to the change in the electric dipole moment and allow hydrogen to be infrared active.

### 3.1 Overlap Mechanism

The overlap mechanism is the process by which the framework provides enough of an electric field to induce a significant dipole moment on the adsorbed hydrogen. In general, merely possessing a dipole moment does not guarantee infrared activity because it is a change in $\vec{\mu}$ that is needed for $\mu_{nm}^e$ to be nonzero. Due to the linear geometry of diatomic molecules, however, only hydrogen already possessing a dipole moment will change its dipole moment between the ground and excited states. The magnitude of this induced dipole, $\vec{\mu}_{ind}$, caused by the electric field of the framework, $\vec{E}_{MOF}$, is determined by the polarizability tensor, $\alpha$. The relationship is, simply,
Figure 3.1: The probabilistic nature of quantum mechanics allows for a small range of frequencies to cause a transition between two energy levels [21].

\[ \bar{\mu}_{ind} = \alpha \vec{E}_{MOF} \]  

(3.5)

The 3x3 polarizability tensor can be easily diagonalized by choosing the z-axis to be along the internuclear axis of the hydrogen, and can be written linearly as \((\alpha_\perp, \alpha_\perp, \alpha_\parallel)\). In this configuration, \(\alpha\) is normally broken up [27] into an isotropic part, \(\bar{\alpha}\), where

\[ \bar{\alpha} = \frac{1}{3}(\alpha_\parallel + 2\alpha_\perp), \]  

(3.6)

and an anisotropic part, \(\Delta\alpha\), where

\[ \Delta\alpha = \alpha_\parallel - \alpha_\perp. \]  

(3.7)

The values of both \(\bar{\alpha}\) and \(\Delta\alpha\) are independent of choice of coordinates.

The polarizability of hydrogen has been well-documented in the literature [28],
but the electric field produced by the framework is intractably complex. In the primary site, we predict that the electric field will be dominated by the metal ion in the framework because it is the coordinately unsaturated metal that provides us with the potential well for the primary site. If we could calculate the electric field, and thus the dipole moment of the hydrogen, we could determine selection rules for possible hydrogen transitions between $J$ and $m$ levels, where $m$ is the quantum number describing the z-component of $J$. These restrictions give us information about which transitions are detected as a result of the overlap mechanism. The only selection rule of which we are certain is that the overlap mechanism can only caused Q transitions, in which the rotational state remains unchanged. We conclude this because when hydrogen undergoes a molecular transition, the isotropic polarizability dominates the change in the hydrogen’s dipole moment. A pure isotropic change cannot cause a change in rotational state, so we have a selection rule of $\Delta J=0$ and $\Delta m=0$ for the overlap mechanism.

3.2 Quadrupole Mechanism

The wavelength of the photons in which we are interested, a few microns, is four orders of magnitudes greater than the distance between the hydrogen and the framework, a few angstroms. Consequently, infrared photons will interact with both the hydrogen and the host simultaneously. Thus, if a quantum transition of the hydrogen causes a change in dipole moment not in the hydrogen itself, but in the host framework, the hydrogen molecule will still absorb the photon and shift to a higher energy state. As seen in Figure 1.4, hydrogen has a permanent quadrupole moment, and this lack of spherical symmetry can induce a dipole moment on the host. The strength of the induced dipole is dependent upon the state of the hydrogen, thus making the hydrogen infrared active via the interaction of its quadrupole moment.

The derivation of the hydrogen molecule’s quadrupole moment can be found in the Honors theses of Jesse Hopkins and Hugh Churchill [29, 21], and the important points are summarized here. In gas phase hydrogen, because the net charge (monopole moment) and the dipole moment of hydrogen are both zero, the first nonzero term
in the multipole expansion is the quadrupole moment. This gives hydrogen the property that its quadrupole moment is independent of choice of origin. To simplify the calculation of the quadrupole moment, we may also choose the z-axis to be the internuclear axis. Given these assumptions the quadrupole term reduces from nine terms to [29, 21]

\[ Q_{zz} = \int (3z'^2 - r'^2)\rho(r')d\tau' \]  

(3.8)

where \( \rho(r) \) is the charge distribution of the hydrogen atom.

The numerical value of the quadrupole moment is unimportant to us, but it is useful to determine properties of its symmetry. From this classical picture, we see that the quadrupole moment is directly related to the charge distribution’s deviation from spherical symmetry. If the charge distribution were spherically symmetric (i.e. if the x, y, and z components of the charge distribution were the same), then Eq. 3.8 tells us that \( Q_{zz} = 0 \). Quantum mechanically, we denote this deviation from spherical symmetry as

\[ Q \propto \langle 3z^2 - r^2 \rangle. \]  

(3.9)

This quantity is zero for the case of hydrogen in the spherically symmetric \( J = 0 \) state. The quadrupole mechanism cannot be responsible for a Q(0) transition (where Q now signifies a rotational transition) because the Q(0) transition leaves the quadrupole moment at zero. Changes in rotational state and changes in vibrational state when the hydrogen is rotationally excited, however, will change the hydrogen’s quadrupole moment. That in turn will allow for a change in the framework’s dipole moment via the framework’s polarizability, making the system infrared active. Thus, the Q(1), S(0), and S(1) transitions are allowed. Given this, it is important to note that the S transitions may only result from the quadrupole mechanism, while the Q(1) transition may result from either mechanism. As a result, the relative strengths of the Q and S absorption peaks are affected by the relative strengths of each mechanism. Finally, the complexity of the framework’s polarizability makes the determination of selection rules for the \( m \) quantum numbers intractable.
3.3 Interaction Redshift

One of the quantities that we are most interested in measuring is the binding energy of the material. We are able to measure this by means of the interaction redshift, the decrease in transition frequency of adsorbed hydrogen from gas phase hydrogen. We generally use the pure fundamental vibrational transition, Q(0), for this calculation. The frequency of the Q(0) transition in gas phase H$_2$ comes from the literature, and we experimentally determine the frequency of the adsorbed phase Q(0) transition.

The binding energy is the change in energy between ground state energies of hydrogen in the adsorbed and gas phases. Our goal is to get from a change in transition frequency to this binding energy. A schematic of the following method is shown in Figure 3.2. Let the superscripts $a$ and $g$ refer to adsorbed and gas phases respectively, and let the subscripts 0 and 1 refer to vibrational states. Given a redshift of $\Delta \nu$, we have

$$h\Delta \nu = h(\nu^a - \nu^g) = [(E_1^a - E_0^a) - (E_1^g - E_0^g)]$$  \hspace{1cm} (3.10)
where $E$ is an energy. Rearranging this and setting $E^a - E^g = BE$, the binding energy of a particular vibrational state, we find

$$h\Delta\nu = [BE_1 - BE_0], \quad (3.11)$$

which is simply the change in binding energy. The easiest way to get to a binding energy from here is to divide by the change in binding energy as a fraction of the ground state binding energy, $\frac{BE_1 - BE_0}{BE_0}$. With some algebra we find that

$$BE_0 = \frac{h\Delta\nu}{BE_1 - BE_0} \cdot \frac{BE_1 - BE_0}{BE_0}. \quad (3.12)$$

In other words, to find the binding energy from our experimental data, we must determine the fractional difference between the binding energy of the ground state and the first excited state. This ratio represents the degree to which the vibrational level affects the binding energy, which necessarily must be estimated without knowledge of either binding energy.

We approximate this fractional change by calculating how the general interaction potential changes due to the host from the ground to first excited state. The interaction energy between H$_2$ and MOF-74 can be represented as the sum [31, 32, 29]

$$U = U_{elec} + U_{disp} + U_{rep} \quad (3.13)$$

where $U_{disp}$ and $U_{rep}$ are the attractive and repulsive terms associated with the Van Der Waals potential and $U_{elec}$ includes the Coulombic interaction between the hydrogen’s quadrupole moment and the framework as well as the inductive term resulting from the induced permanent dipole moment of the H$_2$. A detailed derivation of this approximation is given in §3.3.1 and §3.3.2 of Jesse Hopkins’ Honors thesis [29]. The most important factors in the interaction energy are the polarizability and quadrupole moment of hydrogen in its vibrational ground and first excited states, which we approximate as being equal to their gas phase values. The interaction is linear in these two terms, and they scale similarly between the $v = 0$ and $v = 1$ states, so we can approximate the desired ratio of binding energies as
Figure 3.3: This figure comprises literature and our experimental values for transition redshifts and heats of adsorption, which confirm a general linear trend. Included are Zn-MOF-74, Co-MOF-74, Ni-MOF-74, MOF-5, HKUST-1, and ZIF-8 [17, 16, 34, 33]. The slope of the linear least squares fit line is $0.081 \pm 0.008$ kJ/mol/cm$^{-1}$ and the y-intercept is $2.3 \pm 0.7$ kJ/mol.

These fractions are approximately 1.06-1.10, or a 6-10% increase in the vibrationally excited state. In reality, the ratio will be some weighted average with both $\alpha$ and $Q$. If we plot experimental redshift versus literature binding energy, as in Fig. 3.3, we can confirm the validity of this approximation to first order. We would not expect a perfectly linear relationship between redshift and binding energy because for different materials, the various interaction terms in 3.13 may be larger or smaller with respect to one another. Additionally, the attractive and repulsive terms may not be represented equally in the redshift. The linear fit in Fig. 3.3 has a positive y-intercept, which may suggest that the positive repulsive terms in the interaction energy are responsible for more of the redshift than the attractive terms.
Chapter 4

The Isostructural Series

In this section, we detail the structure and synthesis of MOF-74, as well as give one explanation for how the exchange of metal ion might affect the primary site’s binding energy. MOF-74 is an ideal system to examine the interaction between H$_2$ adsorption and metals because the ability to exchange metal species allows us to isolate the variable of metal choice. Additionally, in this particular material, the metal ion provides the primary site to which the hydrogen binds, making the juxtaposition even clearer. No material prior to MOF-74 has provided such a system for comparison [17].

Zhou et. al. first compared the behavior of hydrogen adsorption using different coordinating metal ions, synthesizing MOF-74 with magnesium, manganese, cobalt, nickel, and zinc [17]. We have obtained absorption spectra for MOF-74 samples made with zinc, nickel, and cobalt, though all five in the series have been successfully synthesized by Jesse Rowsell. Two other isostructural metal-organic framework series have been synthesized, but they exhibit some important differences, which we will describe at the end of this chapter.
4.1 Synthesis

Our MOF-74 was synthesized using a solvothermal process modified from literature procedures [30]. Two powders, a metal nitrate, which determines the element at the metal site, and 2,5-dihydroxyterephthalic acid, the organic linker, are dissolved into a mixture of $N,N$-dimethylformamide (DMF), ethanol, and water. This mixture is heated, usually around to $\sim 100^\circ C$, for 24 hours. At this point the crystal is formed in the solution. The solvent is then decanted from the microcrystalline material and replaced with methanol. Here, methanol is known as the activation solvent because it drives off a majority of the solvent mixture, “activating” the binding sites. Next, as much of the solvent as possible must be driven off without destroying the structure. This is one of the most delicate parts of the process. Of primary concern are the remaining DMF and water molecules which will tend to bind strongly to the same sites to which we will eventually want hydrogen to bind. In addition, as we drive off the solvent, the sample cannot be exposed to air, which also contains water. Thus, we slowly heat up the sample to 200-250 $^\circ C$ under flowing nitrogen.

Different MOFs in the series have different temperatures tolerances. Variations in the method of preparing the same structure (e.g. varying composition of the solvent) can also lead to different behavior under high temperature. We can get a sense of where these limits might be by performing a thermogravimetric analysis (TGA). This experiment measures changes in weight as the temperature is increased at a steady rate. It is useful for determining the temperature at which each solvent is driven off, as well as the temperature at which our MOF structure decomposes. These tests are also done under flowing nitrogen in order to simulate conditions used with the sample on which we will eventually experiment.

Our infrared spectroscopy data indicated that we were not removing all of the solvent from our Ni-MOF-74. TGA analysis confirms that the solvent stays in the sample as temperatures close to the decomposition temperature for the framework. The TGA traces of three different preparations of Ni-MOF-74 are presented in Figure 4.1. Unwanted solvent may cause problems in two different ways. First, the solvent molecules may be bound to the same binding sites to which we would like hydrogen
4.2 Structure

The final product is a granular crystalline powder with chemical formula: $M_2(C_8H_2O_6)$. Because our infrared spectroscopy technique, which we will describe in Chapter 5, relies on the powder to scatter light in all directions, the granular nature of the sample is well-suited to our experiment. Powder x-ray diffraction (PXRD) was used to confirm the crystal structure of the Zn-MOF-74 sample, and we compare our results to those found by Zhou for their isostructural series in Figure 4.2. Our results are in good agreement, though there was some evidence that our sample cell was not air-tight.

MOF-74 was first synthesized in 2005 by Rosi, et. al. [15]. Since then, it has also been given the names $M_2$(dhtp), M/DOBDC, and CPO-74-M, where $M$ is the symbol for the metal [17, 34, 30]. The hexagonal pores result from connecting helical rods of composition $[O_2Zn_2](CO_2)_2$ by 2,5-dihydroxyterephthalate (dhtp), which consists of a benzene ring that connects to each rod via two hydroxy groups (see Fig. 4.3) [15]. The framework has a trigonal crystal structure belonging to space group R3 [17]. The 1-dimensional hexagonal pores, of dimensions 10.3 x 5.5 Å, run parallel to the SBUs and allow for the significant sorption of molecules.

Hydrogen is nearly “invisible” to x-ray diffraction techniques as a result of its low electron density. To find out where hydrogen resides in the framework, neutron diffraction must be used. Liu et. al. used neutron diffraction to obtain the locations of four binding sites (see Fig. 4.4 and 1.1) [16]. As mentioned in the introduction, the primary binding site is located near an open metal coordination site. The secondary site is located near a triangle of oxygens, the tertiary site is located near a benzene ring, and the quaternary site is located between two benzene rings closer the center of the hexagonal pores.

to bind. Second, the solvent may block the pores in the framework, preventing adsorbate from entering entire regions of the sample.
Figure 4.1: Thermogravimetric analysis by Jesse Rowsell of three different samples of Ni-MOF-74. All three samples were kept under methanol for ∼7 days. The green trace corresponds to a sample that was washed with H$_2$O a couple times over three days, the blue trace corresponds to a sample with no additional preparation, and the black trace corresponds to a sample that was heated to ∼200°C overnight. Mass loss due to framework decomposition begins at ∼340°C in the green and blue traces, while the decomposition starts at ∼320°C in the black trace, although the framework could be destroyed before these temperatures.
Figure 4.2: Zhou’s isostructural PXRD scans were performed on activated, solvent-free samples. Our diffractometer sample holders were not airtight, leaving adsorbed molecules in our samples during our PXRD scans.

Figure 4.3: MOF-74 with secondary building units (SBUs). (a) and (b) displays helical rod SBUs parallel to the page, and (c) displays SBUs perpendicular to the page connected by the benzene rings of dhtp. Image from Rosi et. al. [15].
4.3 The Irving-Williams Sequence

The Irving-Williams Sequence empirically describes the order of the stabilities in complexes formed by certain bivalent (M$^{2+}$) transition metals. The series,

$$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+},$$  \hspace{1cm} (4.1)

was proposed in 1952 by H. Irving and R. J. P. Williams [18]. Their measure of stability was a stability constant, defined in terms of relative concentrations of separated ligands (binding molecules) and metals, and bound ligand-metal complexes when in a homogenous solution [18]. For any complex ML$_n$ created from a metal M and a ligand L, where n is the maximum coordination number of the metal, we have a dynamic equilibrium of [18]

$$ML_{n-1} + L \rightleftharpoons ML_n.$$

leading to a stability constant defined as

$$K_n = \frac{[ML_n]}{[ML_{n-1}][L]}.$$

This is very similar to the situation of the primary binding site in MOF-74. The metal is bound to five ligands (oxygen atoms), and we would like to know the stability of the
sixth ligand (the hydrogen molecule). Because the hydrogen will always (partially) act as the sixth ligand [17], we will drop the subscript 6 from the stability constant. Irving and Williams hypothesized that, because the stability constant is related to the change in the Gibbs free energy by

\[ \Delta G = -RT \ln K, \]  

(4.4)

where \( R \) is the gas constant and \( T \) is temperature, there ought to be some correlation between the stability constant and the strength of the metal-ligand bonds [18]. The change in enthalpy, \( \Delta H \), is one characterization of the binding energy, which is ultimately what we would like to know. From thermodynamics we know that

\[ \Delta G = \Delta H - T \Delta S, \]  

(4.5)

where \( \Delta S \), the change in entropy, is dominated by the essentially constant entropy of the unadsorbed gaseous hydrogen. Thus, the enthalpy change is related to the stability by

\[ \Delta H = T[\Delta S - R \ln K], \]  

(4.6)

which is referred to as the van ’t Hoff equation. Irving and Williams found that regardless of the ligand, the stability constants seemed to consistently follow the ‘natural’ order of Eq. 4.1 [18]. In the following paragraphs, we will illustrate a possible explanation for this sequence provided by Lancashire [35], in the context of MOF-74.

A couple of competing effects bring about this series. The first is simply a periodic trend corresponding to ionic radii. As one moves across the periodic table from manganese to zinc, we are increasing the effective nuclear charge, so we expect the ionic radius to decrease. A smaller ionic radius brings the potential well created by the coordinatively unsaturated metal closer to the metal, and thus creates stronger electrostatic interaction between the metal and the ligand.

Having said that, Table 4.3 shows that while zinc has a smaller radius than either cobalt or nickel, it also has the smallest isosteric heat of adsorption. This effect can
be explained using crystal field theory. When a transition metal ion is in a crystal, as is the case with MOF-74, the energy levels of the d-orbitals will split around the barycenter, the average energy of the five 3d orbitals. All five metals that can be used to make MOF-74 form octahedral complexes in the framework, in which the 3d-orbitals split into two subsets of energy levels, three below the barycenter (t\text{2g}) and two above the barycenter (e\text{g}) (see Fig. 4.3).

If ∆\text{oct}, the energy difference between the t\text{2g} level and the e\text{g} level, is lower than the extra energy required to put two electrons in the same spatial state, then electrons are found in e\text{g}, when t\text{2g} is only half full. This electron configuration is called “high spin” and is exemplified for manganese in Figure 4.3. The Irving-Williams sequence only holds for high spin octahedral complexes, which happens to be the configuration for all five metals in the isostructural MOF-74 series. In the other possible case, low spin, the magnitude of ∆\text{oct} is large enough that t\text{2g} and e\text{g} are treated as two distinct energy levels, where t\text{2g} is completely filled before any electrons are put into e\text{g}.

Now that we have this foundation, it is easier to understand the behavior of the Irving-Williams sequence. As we move across the periodic table from manganese, the first three electrons are added to the t\text{2g} level (d\text{5} to d\text{8}). The t\text{2g} subset of electrons are of lower energy because they are oriented towards the spaces between the ligands and this positioning minimizes repulsion. The total amount of energy saved by placing electrons in the t\text{2g} subset compared the barycenter is called the crystal field stabilization energy (CFSE). For example, the CFSE is maximized in nickel (d\text{8}) at 3(\frac{2}{3}\Delta\text{oct}). Because crystal field theory is based purely on electrostatics,
4.3 The Irving-Williams Sequence

Figure 4.5: According to crystal field theory, the d-orbitals in an octahedral field split into one triply degenerate lower energy level called $t_{2g}$ and one doubly degenerate higher energy level called $e_g$. This would be the electron configuration for manganese, and moving across the periodic table we fill up the $t_{2g}$ level, then the $e_g$ level with electrons of opposite spin.

The important factor is the charge to radius ratio. As expected, from $d^5$ to $d^8$, we see the ionic radius decrease due to an increase in effective nuclear charge, and thus our charge to radius ratio increases.

The $e_g$ electrons destabilize the structure because they point towards the ligands (see Fig. 4.3), and thus increasing the electrostatic repulsion as well as bringing the total energy back up to the barycenter. So, as we add electrons to the two $e_g$ in copper and zinc, they should increase the radius, lowering the charge to radius ratio, leaving nickel with the highest stability. However, copper ($d^9$) is subject to the Jahn-Teller effect, a distortion in the geometry which removes all degeneracy in the 3d energy levels, leading to an unusually large degree of stability, higher than nickel. A copper form of MOF-74 has not been successfully made, though other metal-organic frameworks, such as HKUST-1, have been synthesized using copper. The only metal left in the series is zinc ($d^{10}$), which is not subject to any distortion effects, and by the argument above has a much lower stability than the others. Therefore, we are left with the Irving-Williams sequence as displayed in Equation 4.1.

As mentioned at the beginning of this chapter, two other groups have studied isostructural metal-organic frameworks using the exchange of metal ions. In one series, $M_3[Co(CN)_6]_2$ ($M = Mn, Fe, Co, Ni, Cu, Zn$), called “Prussian Blue Analogues,”
the open metal ion did not serve as the primary site [36, 17]. This group found that, with the exception of nickel, the enthalpies of adsorption matched the Irving-Williams sequence. They attribute the larger enthalpy associated with their nickel-based sample to a smaller crystal size. In another series, Mn₃[(Mn₄Cl)₃(BTT)₈(CH₃OH)₁₀]₂, the metal being exchanged was an “extra-framework” metal, meaning it was not the metal center of the framework, as is the case with MOF-74 [37, 17]. This group also calculated adsorption enthalpies, though their uncertainty was too high to determine a trend.
Chapter 5

Experimental Procedure and Apparatus

In this chapter, we will give an overview of the spectrometer apparatus used to collect infrared low temperature spectra using Fourier transform infrared spectroscopy (FTIR). In our FTIR setup, radiation is emitted from either a quartz-halogen lamp or a globar source and travels through a Bomem DA3 Michelson Interferometer equipped with a potassium bromide (CaF$_2$) beamsplitter. The radiation then scatters off of our sample and is collected by a liquid nitrogen cooled detector, either a mercury cadmium telluride (MCT) detector or Indium Gallium Arsenide (InGaAs) detector. Except where noted, the experimental data presented in this thesis were collected using the quartz-halogen lamp and the MCT detector.

5.1 The Michelson Interferometer

By using a Michelson interferometer, we are able to send in a large range of frequencies and, through a Fourier transform, obtain information about the degree to which each frequency was absorbed by the sample up to a resolution of 0.5 cm$^{-1}$. The interferometer is positioned between the sample and the radiation source. First, the beamsplitter sends half of the incident beam to the fixed mirror and half to the mov-
able mirror. After reflecting off of their respective mirrors, the two beams recombine. For light of wavelength $\lambda$, the interference will be maximally constructive when the path difference is $n\lambda$, and maximally destructive when the path difference is $(n+\frac{1}{2})\lambda$, where $n$ is an integer. If the path lengths of the two beams are the same, they are said to be at zero path difference (ZPD). At ZPD, all frequencies of light combine constructively. Depending on the phase difference caused by the displacement from ZPD of the moving mirror, different frequencies of light may combine constructively or destructively.

The Fourier transformation is a mathematical tool which converts the signal from a time domain to frequency domain. The speed and maximum displacement of the movable mirror are given as input, and the detector receives a signal in the form of an interferogram, initially in terms of voltage vs. time. The time is related to the mirror displacement by the speed of the mirror, and the voltage is related to the intensity of the light hitting the detector. The Bomem software will perform a Fourier transform of this interferogram, to create a spectra of transmission vs. frequency (see Fig. 5.1).

In principle, when we reference spectra from a sample containing an adsorbate to a spectrum of the pure host, we obtain spectra of just the trapped adsorbate [32]. If the adsorbate changes the host enough, host peaks may shift relative to the reference. This shift may result in an easily recognizable differential peak in the absorption spectrum, i.e. a dip where the peak occurred in the reference next to the newer peak.

### 5.2 DRIFTS

The standard infrared spectroscopy technique involves shining infrared radiation straight through a sample, detecting the output on the other side. Comparing this output to a reference gives the absorption as a function of frequency. Our samples simply scatter too much of the incoming light for this technique to be effective. Instead, we focus and collect the light using ellipsoidal mirrors, each above the sample, relying on the sample to scatter the light out in all directions (see Figure 5.2).
(a) A small segment of the interferograms for Zn-MOF-74 with and without H$_2$ in blue and red respectively.

(b) Transmission spectra for Zn-MOF-74 produced by Fourier transforming the interferograms in (a).

(c) Absorption spectra for Zn-MOF-74 produced taking the absorbance of the red curve with respect to the blue curve in (b). After removing baseline effects seen here, these are our final spectra.

Figure 5.1: A schematic for our data collection.
This technique is called diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Though DRIFTS has been in use for more than 50 years, it has been used very infrequently to investigate adsorbed hydrogen [32].

Using the DRIFTS method, our absorption signal benefits from the scattering of the light. The scattered light has a longer optical path length than it would using a straight transmission method. The increase in time that the light spends bouncing around in the sample increases chance that the weakly absorbing hydrogen will absorb a photon. This effect intensifies our absorption bands.

As mentioned in §1.4, because there is only significant hydrogen adsorption at low temperatures, our H\textsubscript{2} absorption bands only have an observable intensity when the sample is well below room temperature. While room temperature spectra may be collected with relative ease, low temperature data is considerably more difficult due to the large optics required for the DRIFTS technique. A vacuum housing, developed by Phil Korngut and Stephen FitzGerald and constructed by Bill Marton, was custom made for our DRIFTS apparatus, making the collection of low-temperature data
possible. The setup is described by in a paper by FitzGerald, et. al. [32].

The sample mount is placed under a high-pressure dome, allowing pressures up to 100 bars. Inside the dome, the sample is placed in a recess cup which is mounted to a cold finger. As we will describe in the next section, we can be certain of the temperature of the recess cup, however, the temperature of the sample is much harder to determine.

### 5.3 The Thermometer

The temperature of our sample is controlled by a Model 331 Lakeshore cryogenic temperature controller equipped with two DT-670 silicon diode cryogenic temperature sensors. Prior to this year, the temperature sensors have been situated outside
5.3 The Thermometer

Figure 5.4: Relative concentrations of *ortho* and *para* species of hydrogen in MOF-74, where *ortho* and *para* are represented in purple and blue respectively. We assume rapid *ortho-para* conversion such that the relative concentrations are dictated by the Boltzmann distribution. Concentrations of *ortho* and *para* species of hydrogen in gas phase are represented by dashed red and orange lines respectively.

the sample chamber, to the left and right of the beam path and in thermal contact with the cold finger. However, in running cold temperature spectra over the past few years, a few trends indicated that our sample was not as cold as the thermometers were reading.

This warming effect, which very likely originates with the light source, has manifested itself in a few different ways. First, when the thermometer reads below 30K, we notice a reduction in the infrared signal, which we believe to be hydrogen moving away from the illuminated portions of the sample. By its very nature, our signal must come from an illuminated part of the sample, though the unilluminated part may be at a lower energy state, therefore attracting more hydrogen. Second, even when the thermometer read temperatures as low as 15K, there was evidence of significant population of the excited *ortho* $J = 1$ level. From Figure 5.4, we can clearly see that there is only negligible amounts of parahydrogen in at this temperature, but more at higher temperature.

Moreover, we suspect that due to the porous nature of the structure, the sample
5.3 The Thermometer

itself has a very low thermal conductivity. Experiments performed by Huang et. al. determined that below 100K the thermal conductivity of MOF-5, another framework with high porosity, was variable with temperature, increasing to a maximum of \(~0.5 \frac{W}{m\cdot K}\) at 20K, with a room temperature value of \(~0.3 \frac{W}{m\cdot K}\) [38]. For comparison, Thermablok, a nanoporous aerogel used by NASA for thermal insulation in their space shuttle, has a room temperature thermal conductivity of \(~0.01 \frac{W}{m\cdot K}\) [39], while copper, the material used in our cold finger, has a thermal conductivity of over \(10,000 \frac{W}{m\cdot K}\) at 20K. This last value is even greater than values reported for diamond at room temperature (3,320 \(\frac{W}{m\cdot K}\) [40]), the material with the highest known thermal conductivity.

The energy received from the light source focused on a particular spot in combination with the low thermal conductivity of the sample, gives us a situation with a possibly large temperature gradient within the sample itself. If the thermometer reads 30K, then the layer of sample in direct contact with the sample holder may have a temperature close to that value. However, the layer of sample on the top, which is the part that is receiving infrared light and thus the part we care about, may not be at that temperature due to the low thermal conductivity of the sample itself.

In order to determine the temperature more accurately, we placed the thermometer inside the sample chamber, within the sample itself. The primary obstacle presented under this scenario was keeping the sample chamber leak-tight at a wide range of temperatures, while having wires that connected the temperature sensor to the temperature controller. A feedthrough made of small copper tubing was placed through a hole in the bottom of the sample chamber. The silicon diode temperature sensor (\(~1x2x3\) mm) was placed inside the sample chamber with its leads passing through the feedthrough via a Swagelock connection. So that the system was leak-tight, the copper tubing was filled with epoxy (STYCAST© 2850-FT, Catalyst 9). An electrical connector was placed near the sample chamber to make it relatively easy to connect and disconnect the thermometer to the temperature sensor.

To get lower bounds on the temperature of the sample, we cooled the system down with liquid helium with the silicon diode thermometer in the sample cup, so
that it was in good thermal contact with the cold finger and directly in the path of
the light source. The sample was also exposed to \( \sim 160 \) mbar of Helium exchange
gas, though 50 mbar appears to be sufficient. An digital filter that blocks light with
frequencies below \( 0.950 \mu m \) (above \( 10,500 \text{ cm}^{-1} \)) was also used. Our results are
summarized in Table 5.1. This temporary setup demonstrated that the sample it
at the very least several degrees warmer than the thermometers. The low thermal
conductivity of the samples only amplifies this effect.

<table>
<thead>
<tr>
<th>( T_{out} = 29.0 )</th>
<th>Globar</th>
<th>Quartz</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filter</td>
<td>33.5</td>
<td>35.5</td>
</tr>
<tr>
<td>No Filter</td>
<td>34.3</td>
<td>36.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
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<th>Globar</th>
<th>Quartz</th>
</tr>
</thead>
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<td>27.2</td>
</tr>
<tr>
<td>No Filter</td>
<td>26.0</td>
<td>28.0</td>
</tr>
</tbody>
</table>

Table 5.1: Lower bounds on a sample’s temperature (in Kelvin) using our current
experimental setup. The values listed above are the readings of the thermometer
inside the sample chamber (\( T_{in} \)), with the outside thermometer at temperature \( T_{out} \).
Both sensors were in good thermal contact with the cold finger. The globar and the
quartz source were used with and without an optical filter. The sample was exposed
to \( \sim 160 \) mbar of helium exchange gas, and the aperture of the source was 5 mm.
Chapter 6

Results and Analysis

In this chapter, we will present data on $M$-MOF-74 ($M = \text{Zn, Co, Ni}$). We will start by summarizing the results previously found for the zinc compound, before moving on to an analysis of the cobalt and nickel compounds. We will examine the overtones found in all three compounds and the temperature dependence of $\text{H}_2$ in the cobalt-based material.

6.1 Zn-MOF-74

Hopkins has given a full analysis of the Zn-MOF-74 in §6.3 of his Honors Thesis [29]. Here we will summarize the aspects of the Zn-MOF-74 data that provide a useful comparison to our newer data. The frequencies of the $\text{H}_2$ adsorption peaks are given in Table 6.1 and the Q and S Regions of the $\text{H}_2$ spectrum is shown in Figures 6.1 and 6.4 respectively.

6.1.1 Q Region

Q transitions are purely vibrational transitions. At low loadings of $\text{H}_2$, we observe three distinct bands in the Q region. Using parahydrogen as a comparison, two bands were identified with the Q(1) transition and the third with the Q(0) transition. Recall from Figure 2.4 that, when adsorbed in Zn-MOF-74, the $J = 1$ levels are split into
Figure 6.1: The Q Region of Zn-MOF-74 with increasing H$_2$ concentration. Absorbance is given in arbitrary units. Spectra are offset for clarity. Labels indicate assignment as primary (1), secondary (2), and translational (T) bands.
6.1 Zn-MOF-74

<table>
<thead>
<tr>
<th>Site</th>
<th>Q(0)</th>
<th>Q(1)</th>
<th>S(0)</th>
<th>S(1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas [41, 42]</td>
<td>4161.2</td>
<td>4155.3</td>
<td>4497.8</td>
<td>4712.9</td>
</tr>
<tr>
<td>Primary</td>
<td>4096.0</td>
<td>4087.9</td>
<td>4364.3</td>
<td>4586.8</td>
</tr>
<tr>
<td></td>
<td>4092.0</td>
<td>4609.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4181 †</td>
<td>4176 †</td>
<td>4128.0</td>
<td>4143.6</td>
</tr>
<tr>
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<td>4133.7</td>
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<tr>
<td></td>
<td>4136.9</td>
<td>4128.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6.1: Transition frequencies in Zn-MOF-74 as reported by Jesse Hopkins [29]. Frequencies labeled with † correspond to translational sidebands. Ortho-para pairs are listed on the same line. All values listed are in cm$^{-1}$. Associated error is ± 2 cm$^{-1}$.

three (see Fig. 6.2). Our hypothesis is that there exists a $\Delta m = 0$ selection rule, so that there exist as many Q(1) transitions as there are thermally populated levels. The symmetry of the site leads us to believe that the degeneracy is completely broken, and there are three $J$=1 levels. From the neutron scattering data, we know that the energy splitting of these levels are such that only the lowest two $J=1$ levels are thermally populated at 30K, so that we would only observe two Q(1) transitions [16]. Assuming rapid ortho – para conversion, which occurs in MOF-74, the Boltzmann distribution indicates that there only 0.5% of the hydrogen occupy the highest $J=1$ level at 40K (see Fig. 6.3). At higher temperatures, where we expect this level to be thermally populated, the peaks are likely to be too broad to observe.

6.1.2 S Region

The S transitions are combinations of vibrational and rotational transitions, sometimes called rovibrational or rotovibrational transitions, for which $\Delta J = +2$. The initial states for S(0) and S(1) are the same as the initial states for Q(0) and Q(1)
Figure 6.2: Experimental Q transitions for H$_2$ in Zn-MOF-74 found by FTIR, as well as vibrational ground state para-ortho energy differences for Zn-MOF-74 found by neutron scattering [16]. Values are in cm$^{-1}$ and not to scale. The literature rotational constants in vibrational ground and first excited states, $B_0$ and $B_1$, respectively, scale as $1/\mu$, and the literature fundamental vibrational frequency, $v_0$, scales as $1/\sqrt{\mu}$ for HD and D$_2$. We observe only two Q(1) peaks and we believe that this is a result of not thermally populating the highest $J = 1$ state.
6.1 Zn-MOF-74

Figure 6.3: Relative populations of $J = 0$ and $J = 1$ levels in Zn-MOF-74 as a function of temperature assuming rapid ortho-para conversion. Black: $J=0$, Red: lowest energy $J=1$, Blue: middle $J=1$, Green: highest energy $J=1$.

respectively in Figure 6.2, but the final states, $J=2$ and $J=3$, are split into up to 5 and 7 states respectively. Thus, we could theoretically have up to 5 $S(0)$ bands, and, only populating the lowest two $J = 1$ states, up to 14 $S(1)$ bands. In the primary site, we observe only one $S(0)$ band and only 2 $S(1)$ bands, which is consistent with the $\Delta m = 0$ selection rule.

The $S$ Region of $H_2$ in Zn-MOF-74 is presented in Figure 6.4. The redshift of the single $S(0)$ peak is 68.3 cm$^{-1}$ more than the $Q(0)$ redshift. We expect the redshifts of the five possible $S(0)$ peaks to be split, with a barycenter equal to the $Q(0)$ redshift. This additional redshift indicates that we are observing a transition to a $J = 2$ energy that is lower than this barycenter. We also observe two secondary $S(0)$ peaks, with redshifts comparable to the secondary $Q(0)$, though the comparison is more difficult. Experiments run with $para-H_2$ showed two $Q(0)$ peaks, and because the $J = 0$ cannot be split, these must correspond to different environments.

The $S$ bands are all observed to be significantly less intense than the $Q$ peaks. Recall from §3.2 that because the overlap mechanism cannot cause $S$ peaks, this indicates that the quadrupole mechanism is weaker than the overlap mechanism.
Figure 6.4: The S Region of Zn-MOF-74 with increasing H$_2$ concentration. Spectra are magnified by four from Q Region (Fig. 6.1) and offset for clarity. Labels indicate assignment as primary (1) or secondary (2) bands.
6.1 Zn-MOF-74

Figure 6.5: Frequency shift from gas phase of Zn-MOF-74’s Q Fundamental and Q Overtone Region with $D_2$. The red and blue traces correspond to the filling of the primary and secondary sites respectively. No significant changes are seen in the overtone regions where secondary bands are expected. Spectra are offset for clarity.

6.1.3 Overtone Region

Not expecting to be able to observe the vibrational overtones, the Bomem software was only instructed to record the result of the Fourier transform to a maximum of 6000 cm$^{-1}$, high enough to witness the overtones in $D_2$, but not high enough for $H_2$ or HD. Thus, the overtone band was only observed with $D_2$ in Zn-MOF-74. As shown in Figure 6.1.3, an overtone band appears with the primary band, but not with the secondary band. We will discuss this further in §6.2.4.

6.1.4 Error

When analyzing our spectra, we have to be concerned with how accurately we are able to measure the location of any particular peak. We measure the frequencies of light using the position of a moving mirror in our Michelson interferometer. This position is found using a He-Ne laser, whose wavelength is known to great precision. Michelson interferometers have distance resolution on the order of the wavelength of light being used. Our longest wavelength light corresponds to higher than 1000 cm$^{-1}$,
or lower than 10 µm, and the position of mirror moves on the order of centimeters. Thus, the mechanical error is negligible compared to the experimental error.

Using our resolution, we can identify peak locations in our spectra to within ±0.1 cm⁻¹. If we add in variations in sample quality and conditions between runs, we get errors on the order of 1 to 2 cm⁻¹. These two errors are referred to as absolute error. We also have a relative error, on the order of ±0.1 cm⁻¹, which refers to the error in relative peak locations within a given data run. Finally, we may see sloping baselines, which we attempt to remove, improper cancellation of background peaks, and artifacts from the DRIFTS apparatus. These errors are be mentioned when they occur. For most peaks, we are able to quote their values to the tenths digit for our particular sample conditions, but we allow for an uncertainty of ±2 cm⁻¹.

6.2 Co-MOF-74

In this section, we present our data for Co-MOF-74. The transition frequencies for H₂, HD, and D₂ adsorbed in Co-MOF-74 are listed in Tables 6.2 and 6.3. We will again analyze the Q and S regions of the spectrum separately. From our isotherm experiments (see Appendix A), we have found that Co-MOF-74 adsorbs more hydrogen than Zn-MOF-74, which is consistent with isotherms found by Zhou, et. al. [17]. Normally, we report the adsorption of H₂ in terms the number of molecules adsorbed per formula unit. There are two metals in each formula unit, M₂(C₈H₂O₆), but there is only one of each site per metal, so it more convenient in our spectra to report the number of molecules adsorbed per half formula unit, or equivalently per metal.

6.2.1 Q Region

We present the Q Regions of Co-MOF-74 with H₂, HD, and D₂ in Figures 6.6, 6.11, and 6.13 respectively.
Figure 6.6: The Q Region of Co-MOF-74 with increasing H\textsubscript{2} concentration. Labels indicate assignment as primary (1), secondary (2), tertiary (3), and translational (T) bands. Spectra are offset for clarity.
Table 6.2: Transition frequencies in Co-MOF-74. Frequencies labeled with $^t$ correspond to translational sidebands. All values listed are in cm$^{-1}$. Associated error is $\pm$ 2 cm$^{-1}$.

<table>
<thead>
<tr>
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<th>Q(0)</th>
<th>Q(1)</th>
<th>S(0)</th>
<th>S(1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Phase $^{[41, 42]}$</td>
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<td>4155.3</td>
<td>4497.8</td>
<td>4712.9</td>
</tr>
<tr>
<td>Primary</td>
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<td>4040.5</td>
<td>4297.3</td>
<td>4520.4</td>
</tr>
<tr>
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<td>4232.6$^t$</td>
</tr>
<tr>
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<td>4133.4</td>
<td>4124.0</td>
<td>4446.6</td>
<td>4640.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4474.5</td>
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<td></td>
<td></td>
<td></td>
<td>4691.5</td>
</tr>
<tr>
<td>Tertiary</td>
<td>4141.0</td>
<td></td>
<td>4453.9</td>
<td></td>
</tr>
</tbody>
</table>

H$_2$

As we start to fill up the primary site with H$_2$, two distinct bands, at 4047.1 and 4040.5 cm$^{-1}$, appear in the Q region. We also see a very faint band at 4043.5 cm$^{-1}$. As we will discuss in the following paragraph, indicates a Q(0) band at the highest frequency and two Q(1) bands at the lower frequencies, similar to those observed in Zn-MOF-74.

Recall from the discussion of Zn-MOF-74 that given a $\Delta m = 0$ selection rule, the Q(1) band splits into three transition energies as a result of breaking the degeneracy of $m$-levels in the $J = 1$ state, as shown in Figure 6.2. It is likely that this middle band results from a splitting in the Q(1) band as seen in Zn-MOF-74. Since we expect the cobalt ion to have a larger interaction than the zinc ion, we also expect that in Co-MOF-74, there is a larger energy difference between the middle and lowest energy $m$-levels of the $J = 1$ state, compared to this difference in Zn-MOF-74. Thus, in Co-MOF-74, we likely observe a significant absorbance corresponding to the Q(1) transition from the lowest energy $J = 1$ level, and only a small absorbance corresponding to the transition from the middle $J = 1$ level because this level is not
as well thermally populated as in Zn-MOF-74. Another factor that may contribute to this difference is that Co-MOF-74 seems to induce ortho − para conversion faster than Zn-MOF-74. We observe this in the speed with which the intensity of the Q(1) bands and Q(0) peak decreases and the increases respectively. As a result, all of the \(J = 1\) levels of \(\text{H}_2\) may be less populated in Co-MOF-74 as a opposed to Zn-MOF-74.

As the secondary site fills, \(\text{H}_2\) interactions, which do not in general have the same symmetry as the interactions with the host, make the primary bands very difficult to identify. We also observe a definite redshift with the filling of the secondary site (\(\sim 4\) cm\(^{-1}\)), and an additional, larger redshift with the tertiary site (\(\sim 7\) cm\(^{-1}\)), both likely due to \(\text{H}_2 \cdots \text{H}_2\) interactions. This concentration redshift is much greater than the same effect seen in Zn-MOF-74, which had a maximum of \(\sim 2\) cm\(^{-1}\) in the Q Region [29]. This can be explained by the geometry of the binding sites. Not only are we filling the additional third site in Co-MOF-74, but the tertiary site is much closer to the primary site, than the secondary site is to the primary site. The neutron diffraction data indicates that these distances in Zn-MOF-74 are 4.3 and 2.8 Å respectively. \(\text{H}_2 \cdots \text{H}_2\) interactions, and thus concentration redshift, will be greatly increased in Co-MOF-74.

Unlike the pure vibrational region, the translational sidebands appear in a region of spectrum containing several large host peaks. This makes the classification trickier because we must account for the possibility that presence of hydrogen is shifting or splitting peaks associated with the framework. The feature near 4200 cm\(^{-1}\), for example, results from a transition originating in the host shifting to a lower frequency. There is a large translational sideband at 4232 cm\(^{-1}\), along with a smaller unidentifiable band at 4212 cm\(^{-1}\).

We present the absorption spectra of \(\text{H}_2\) in Co-MOF-74 as a function of temperature in Figure 6.7. The temperature shown is the nominal temperature of the thermometer. These spectra were taken while slowly ramping up the temperature recorded at the outside thermometer. As mentioned in §5.3, this nominal temperature is lower than the temperature of our sample, with the discrepancy increasing at lower temperatures. At higher temperatures, the hydrogen is increasingly unlikely to be found in the adsorbed phase, which is reflected in the reduced intensity of the
Figure 6.7: Temperature dependence for the Q region of H$_2$ in Co-MOF-74. Nominal temperatures are based on the average reading of two thermometers, in thermal contact with the cold finger, outside the sample chamber. The initial spectra were taken at low temperatures, and additional spectra were taken as the sample warmed. Spectra are offset for clarity.
Figure 6.8: The S Region of Co-MOF-74 with increasing H₂ concentration. Spectra are magnified by four from Q Region (Fig. 6.6). Labels (1) and (2) indicate assignment of bands to the primary site and secondary site respectively. Spectra are offset for clarity.

absorption bands, as well as in the reduction of the concentration redshift of the primary band.

6.2.2 S Region

As in Zn-MOF-74, the S bands are significantly less intense than the Q bands, indicating a stronger overlap mechanism. There is one primary S(0) peak, which is redshifted from the gas phase by 200 cm⁻¹, which is 86 cm⁻¹ more than the redshift of the Q(0) peak. It is unclear whether this is the same S(0) transition that we observe in Zn-MOF-74, which was redshifted 68 cm⁻¹ more than the redshift of the Q(0) peak. If our hypothesis that there is a \( \Delta m = 0 \) selection rule for Zn-MOF-74
is correct and it applies to Co-MOF-74, then these transitions must be the same.

We do see two distinct S(1) peaks in the primary, which is consistent with the selection rule. We also observe weaker bands corresponding to the primary site in the S(1) region, however, between 4600 and 4640 cm$^{-1}$. The origin of these bands is still unclear. The feature at 4330 cm$^{-1}$ is a differential peak resulting from a host peak that shifted from the reference spectrum.

As in Zn-MOF-74, there are two bands, corresponding to the S(0) transition in the secondary site. They are redshifted by an additional 3 cm$^{-1}$ and 10 cm$^{-1}$ from the two seemingly analogous bands in Zn-MOF-74, with the higher energy transition much stronger than in Zn-MOF-74. The fact that there are two bands in the S(0) is not consistent with the selection rule, unless one is due to different environment. The $\Delta m$ selection are not well understood, so a strong characterization of these peaks is difficult.

When the secondary site is filled, the primary S(0) undergoes a $\sim$8 cm$^{-1}$ concentration redshift, which is roughly the same as seen in Zn-MOF-74, and the primary S(1) bands become much less distinct. Lastly, there appears to be a band associated with the tertiary site in the S(0) region at 4454 cm$^{-1}$.

### 6.2.3 HD and $\text{D}_2$

In the spectra of H$_2$, HD, and $\text{D}_2$, the vibrational transition frequencies approximately scale by $\frac{1}{\sqrt{\mu}}$, where $\mu$ is the reduced mass of the molecule. In Figure 6.9, we show this initial approximation as applied to the redshifts with a solid line and, in the following paragraphs, we discuss how the inclusion of zero-point energy (ZPE) effects improves this approximation, as shown with the dashed line.

We start by making the assumption, described in §3.3, that the redshift, $\Delta \nu$, roughly scales linearly with the ground state binding energy, $B_{E_0}$. Recall from Equations 3.12 and 3.14 that the scaling factor depends upon a weighted average of the change in polarizability and quadrupole moments of hydrogen between the vibrational ground and excited states. Let $\gamma$ be this scaling factor so that
Table 6.3: Transition frequencies for HD and D$_2$ in Co-MOF-74. Frequencies labeled with $^t$ and $^\dagger$ correspond to translational sidebands and vibrational overtones respectively. All values listed are in cm$^{-1}$. Associated error is ± 2 cm$^{-1}$.

<table>
<thead>
<tr>
<th>Site</th>
<th>D$_2$</th>
<th>HD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Phase [43, 42]</td>
<td>2993.5</td>
<td>3632.1</td>
</tr>
<tr>
<td></td>
<td>5868.8$^\dagger$</td>
<td>7088.2$^\dagger$</td>
</tr>
<tr>
<td>Primary</td>
<td>2904.7</td>
<td>3529.7</td>
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<td></td>
<td>5684$^\dagger$</td>
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<td>3696.9$^t$</td>
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<td></td>
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<td>6872$^\dagger$</td>
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<tr>
<td>Secondary</td>
<td>2971.5</td>
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<tr>
<td></td>
<td>2968.4</td>
<td>3600.9</td>
</tr>
<tr>
<td>Tertiary</td>
<td>2976.5</td>
<td>3613.5</td>
</tr>
</tbody>
</table>

Figure 6.9: Redshift comparison for isotopologues of H$_2$ in Co-MOF-74. Solid lines correspond to H$_2$ redshifts scaled by the reduced mass ($1/\sqrt{\mu}$). Spectra are offset for clarity. Dashed lines include zero-point energy effects. A similar comparison is done for Zn-MOF-74 in a paper by FitzGerald, et. al. [33]. This paper uses a scaling factor of 10%, which improves our results by ~1 cm$^{-1}$. 
Figure 6.10: The zero point energies of H$_2$, HD, and D$_2$ scale $1/\sqrt{m}$ where $m$ is the mass of the molecule.

$$h\Delta \nu = \gamma B E_0$$ (6.1)

For H$_2$, we take $\gamma$ to be the slope in Figure 3.3, $\sim$8%. This scaling factor is the value that we expect to directly scale with the square root of the reduced mass. There is some dependence on mass, however, in the binding energy $B E_0$. We assume that in each site, H$_2$, HD, and D$_2$ all occupy an energy well of the same energy depth. The lowest energy at which a particle may exist, the ZPE, depends on the mass, $m$, of the particle (see Fig. 6.10). Recall from §2.4 that the translational transition frequencies scale as $1/\sqrt{m}$, and according to Equation 2.14, the ground state energy, or ZPE, is $3/2$ of the fundamental translational frequency. The binding energy $B E_0$ is then

$$B E_0 = E_{\text{well}} - \frac{3}{2} E_{\text{trans}}$$ (6.2)

where $E_{\text{well}}$ is the height of the energy well, which is constant with $m$, and $E_{\text{trans}} = \hbar \omega_{\text{trans}}$ is the energy of the fundamental translational transition, which scales as
1/\sqrt{m}. We determine $E_{\text{trans}}$ from the translational transition in the $H_2$ spectrum and $BE_0$ using the redshift approximation for $H_2$. Knowing these, we can approximate $E_{\text{well}}$. We now have enough information to go back and predict the more accurate redshifts for HD and $D_2$ presented in Figure 6.9. The improved theoretical redshifts for HD and $D_2$ are then

$$h\Delta \nu = \frac{\gamma}{\sqrt{\mu/\mu_{H_2}}} (E_{\text{well}} - \frac{1}{\sqrt{m/m_{H_2}}} \frac{3}{2} E_{\text{trans}}),$$

which leads to the dashed lines in Figure 6.9.

In the HD spectrum, we see a single primary peak with a shoulder on the lower frequency side (see Fig. 6.11). This is consistent with the two peaks in the $H_2$ spectrum, after the scaling due to the relative masses. The secondary and tertiary peaks also appear in a manner similar to the $H_2$ spectrum, with the secondary site
causing the primary peak to redshift $\sim 2$ cm$^{-1}$ and the tertiary site causing $\sim 4$ cm$^{-1}$ more concentration redshift. The translational band broadens with increasing HD concentration towards higher frequencies, which is again very similar to the H$_2$ spectrum.

Because HD consists of two distinguishable particles, the R branch, for which $\Delta J = +1$, is allowed. Also, since we are significantly populating the J=1 level, the P branch, for which $\Delta J = -1$, is allowed (see Fig. 6.12). Recall from §2.3 that the J=1 levels of H$_2$ in Zn-MOF-74 are split into three nondegenerate levels at 8.3, 11.1, and 20.9 meV according to neutron scattering data (see Fig. 6.2) [16]. To predict transition frequencies for HD in Co-MOF-74 from these values, we must “convert” the energy levels from H$_2$ to HD, which simply means scaling as $1/\mu$ (see §2.3), as well as from Zn-MOF-74 to Co-MOF-74, which is not as straightforward. In one method, we scaled the differences of these values from their theoretical barycenter ($2B_0 = 14.7$ meV) by the ratio of the redshifts in Co-MOF-74 and Zn-MOF-74, 1.75. In the other method, we scaled the perturbation in the orientational potential model (see Fig. 2.3) by this same ratio. These methods lead to a range of energies; 21-51 cm$^{-1}$, 48-74 cm$^{-1}$, and 154-178 cm$^{-1}$ for the R branch transitions to the three J=1 levels respectively. In Figure 6.11, we observe peaks at 35 and 52 cm$^{-1}$ to right of the Q(0) peak as well as reasonably symmetric peaks on the other side. The highest peak’s region occurs near a large translational peak on the right and a large amount of noise on the left. The P branch will differ by the relative small difference in rotational constant between the vibrational states. While these peaks are consistent with our prediction for P and R bands for HD, we will have to perform some additional modeling or perhaps neutron scattering on the Co-MOF-74 sample to be sure of their identity.

In the Q region of D$_2$, we detect only a single primary band (see Fig. 6.13). This could be a few bands, closely spaced as a result of dependence of the energy splittings on the reduced mass of the molecule. We can also resolve the secondary and tertiary sites, which appear analogous to the corresponding regions of the H$_2$ and HD spectra. As the secondary site is filled, the primary peak experiences a concentration redshift of $\sim 2$ cm$^{-1}$. At our highest level of D$_2$ concentration, nominally 3.6 D$_2$/Co, the
Figure 6.12: Selected allowed transitions for the Q fundamental region of HD (not to scale).
Figure 6.13: The Q Region of Co-MOF-74 with increasing D$_2$ concentration. Labels indicate assignment as primary (1), secondary (2), and tertiary (3) bands. Spectra are offset for clarity.
primary peak experiences an additional concentration redshift of $\sim 4$ cm$^{-1}$.

### 6.2.4 Overtone Region

As in Zn-MOF-74, we observe a clear vibrational overtone peak with D$_2$ in Co-MOF-74 (see Fig. 6.2.4). The concentration redshift of the overtone is about double that of the fundamental peak ($13 \pm 2$ cm$^{-1}$). Interestingly, the overtone peak appears to grow much faster than the fundamental, which is not seen in Zn-MOF-74. We are uncertain what is causing this effect. We also observe an overtone peak with HD in Co-MOF-74 (see Fig. 6.2.4). The concentration redshift appears to be about double that of the fundamental, though the weakness and broadness of this band makes a good estimate on the ratio difficult to determine. A distinct vibrational overtone with H$_2$ in Co-MOF-74 was not observed, though we did observe it in Ni-MOF-74 (see Fig. 6.3). We observe all our overtone bands to be broader than the corresponding fundamental transitions.

The mechanism that allows us to see these vibrational overtone peaks appears bizarre. Our models predict overtone intensities much weaker than those that we observe. In addition, we do not observe a secondary overtone band in any of our spectra, even though the secondary bands in the fundamental region are equally intense.

Other groups have observed vibrational overtones in adsorbed D$_2$ with DRIFTS [45], as well in gas phase H$_2$ and D$_2$ with Raman spectroscopy [46, 47]. Though a direct comparison is difficult to make, the relative intensities of the fundamental and overtone bands in the DRIFTS results appear to be of the same order of magnitude as our results. Our best guess is that the molecules at the primary site, regardless of their nuclear makeup, experience some sort of resonance with the metal ion.

### 6.3 Ni-MOF-74

We present the transition frequencies of H$_2$ in Ni-MOF-74 in Table 6.5, and the absorption spectra of the Q and S regions in Figures 6.16 and 6.18 respectively. The
Figure 6.14: Frequency shift from gas phase of Co-MOF-74’s Q Fundamental and Q Overtone Region with D₂. The red, blue, and green traces correspond to the filling of the primary, secondary, and tertiary sites respectively. No significant changes are seen in the overtone regions where secondary and tertiary bands are expected. Spectra are offset for clarity.

Figure 6.15: Frequency shift from gas phase of Co-MOF-74’s Q Fundamental and Q Overtone Region with HD. The red, blue, and green traces correspond to the filling of the primary, secondary, and tertiary sites respectively. No significant changes are seen in the overtone regions where secondary and tertiary bands are expected.
Table 6.4: Transition redshifts for HD and D$_2$ in Co-MOF-74 and H$_2$ in Ni-MOF-74. All values listed are in cm$^{-1}$. Associated error is ± 2 cm$^{-1}$.

<table>
<thead>
<tr>
<th></th>
<th>H$_2$</th>
<th>HD</th>
<th>D$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fund. Redshift</td>
<td>125.3</td>
<td>103.1</td>
<td>89.3</td>
</tr>
<tr>
<td>Overtone Redshift</td>
<td>269.9</td>
<td>216.2</td>
<td>184.8</td>
</tr>
<tr>
<td>Ratio (Over./Fund.)</td>
<td>2.15</td>
<td>2.10</td>
<td>2.07</td>
</tr>
</tbody>
</table>

data from the Ni-MOF-74 sample is of a lower quality than Co-MOF-74, primarily resulting from difficulties in removing the solvent from the synthesis, described in §4.1. A large increase in the overall signal immediately after loading the hydrogen, leading to weak cancellation of the host peaks (see Figure B.4), as well as technical issues with the alignment laser also affected the clarity of the data.

**Q Region**

At low loadings of H$_2$, we observe a broad band in the primary Q region. We believe this to be the combination of four peaks, two of which, at 4035.9 cm$^{-1}$ and 4027.9 cm$^{-1}$ are the result of H$_2$ in the primary site. These are consistent with the Vitillo et. al., who found the primary peaks at 4035 cm$^{-1}$ and 4028 cm$^{-1}$ at low loadings of H$_2$ [34]. Using a fit of four peaks, as shown in Figure 6.17, we extract these two peaks, a very broad band at 4044.9 cm$^{-1}$, three times the width of the two primary peaks, as well as a small peak at 4065.6 cm$^{-1}$. The broader band may result from an alternative primary site in which DMF is present in nearby primary sites, but we cannot do more than speculate at this point. The smaller band appears outside the range presented by Vitillo et. al., but has a width similar to the first two bands and therefore could be from adsorbed H$_2$.

Just as in the zinc and cobalt samples, we observe two distinct secondary Q bands at higher loadings, redshifted by 2-3 cm$^{-1}$ from the analogous transitions in Co-MOF-74. At even higher loadings, we observe a tertiary band in a similar spot.
### Table 6.5: Transition frequencies in Ni-MOF-74

Frequencies labeled with \( t \) correspond to translational sidebands. All values listed are in cm\(^{-1}\). Associated error is ± 2 cm\(^{-1}\).

<table>
<thead>
<tr>
<th>Site</th>
<th>Q(0)</th>
<th>Q(1)</th>
<th>S(0)</th>
<th>S(1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Phase ([41, 43])</td>
<td>4161.2</td>
<td>4155.3</td>
<td>4497.8</td>
<td>4712.9</td>
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<td>4035.9</td>
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<td>4530</td>
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<tr>
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<tr>
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<td>4139.7</td>
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</table>

Figure 6.16: The Q Region of Ni-MOF-74 with increasing H\(_2\) concentration. Labels indicate assignment as primary (1), secondary (2), tertiary (3), and translational (T) bands. Spectra are offset for clarity.
Figure 6.17: Curve fit of the Primary Q band of Ni-MOF-74 at a low loading of H$_2$. Left axis is in arbitrary absorbance units. The two leftmost peaks correspond to H$_2$ adsorbed in the primary site consistent with IR spectra performed by Vitillo, et. al. [34], while the identity of the other two is uncertain. From left to right, the widths of the peaks are 8.6, 8.3, 24.4, and 6.3 cm$^{-1}$. Red: absorption spectra, dashed/purple: peaks fit to the spectra, blue: the resulting curve fit.
Figure 6.18: The S Region of Ni-MOF-74 with increasing H$_2$ concentration. Spectra are magnified by four from the Q region (Fig. 6.16), and offset for clarity. Labels indicate assignment as primary (1) and secondary (2) bands. An asterisk (*) indicates a feature we suspect to have resulted from improper cancellation with a host peak.

as in Co-MOF-74. An additional unidentifiable peak between the two secondary peaks is also observed, like the one seen in Co-MOF-74 at very low temperatures. The lack of a broad peak in the secondary region may be an indication of solvent trapped in the primary sites, or that the broad peak in the primary region is actually a transition of a solvent molecule.

S Region

The improper cancellation of the host peaks in Ni-MOF-74 affected the S region particularly strongly, so we must be especially careful in analyzing these spectra. The feature at 4330 cm$^{-1}$, which appeared clearly as a differential peak in the Co-MOF-74 spectra, no longer cancels as well with the background. The feature at 4540
Figure 6.19: Frequency shift from gas phase of Ni-MOF-74’s Q Fundamental and Q Overtone Region with H₂. The red, blue, and green traces correspond to the filling of the primary, secondary, and tertiary sites respectively. No significant changes are seen in the overtone regions where secondary and tertiary bands are expected.

cm⁻¹ is also highly suspect.

Similar to the other two samples, there are three distinct primary bands in the S region, one S(0) and two S(1) bands. The S(0) is redshifted an additional 82.9 cm⁻¹ from the Q(0) redshift, which is less than in Co-MOF-74, but more than in Zn-MOF-74. This does not follow the usual order, and may indicate a complex splitting of the $J = 2$ level.

**Overtone Region**

The H₂ overtone region is in a region of the spectrum where the frequencies are much higher than we would normally detect. Due to the limitations set by the beamsplitter, the source, and the detectors, this region is very noisy. While we did not have much evidence of a overtone band with H₂ in Co-MOF-74, possibly due to this noise, we do clearly, though weakly, observe it with H₂ in Ni-MOF-74. Similar to the other overtone bands that we observe, there is no evidence of a secondary overtone band.
Chapter 7

Conclusion and Future Work

Our data indicates three distinct binding sites for hydrogen molecules in $M$-MOF-74 ($M = \text{Zn, Co, Ni}$), which is consistent with neutron diffraction data performed on Zn-MOF-74 [16]. At low temperatures, based on the relative redshifts we observe, these sites fill up sequentially according to their binding energy, i.e., the primary site has the highest binding energy, the secondary site is only significantly populated after the primary site is full, and the tertiary site behaves similarly.

When we exchange metal ions, we observe a considerable increase in the redshift corresponding to the primary binding site. The experimental redshifts of the primary site are consistent with hydrogen playing the role of an ligand of the metals in the Irving-Williams sequence (see Tab. 7.1). However, the secondary and tertiary sites do not experience any significant change in redshift (see Fig. 7.1). This result strongly suggests that the metal ion only affects the primary site, which is also

<table>
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<th>Metal</th>
<th>Redshift (cm$^{-1}$)</th>
<th>$Q_{st}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc</td>
<td>66</td>
<td>8.5, 8.8</td>
</tr>
<tr>
<td>Cobalt</td>
<td>115</td>
<td>10.7</td>
</tr>
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<td>Nickel</td>
<td>126</td>
<td>12.9, 13.5</td>
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</tbody>
</table>

Table 7.1: The experimental interaction redshift of the Q(0) transition with just the primary site occupied and literature $Q_{st}$ (Isosteric Heat of Adsorption) for $M$-MOF-74 ($M = \text{Zn, Co, Ni}$) [17, 34, 33].
Figure 7.1: Comparison of the vibrational transition redshifts for H2 in zinc (red), cobalt (blue), nickel (green). Redshifts of the Q(0) peaks can be found in Table 7.1. Labels indicate assignment as primary (1) and secondary (2) bands. Spectra are offset for clarity.

consistent with our explanation of how the Irving-Williams sequence applies to our isostructural series of MOFs. In terms of average binding energy, Ni-MOF-74 is therefore superior, though all three bind equally well at the non-primary sites. Still, an adsorbent with non-uniform binding energies is not an ideal scenario for fuel cell applications because it could lead to unsteady delivery of hydrogen.

We observed an extraordinarily intense absorption band in the overtone region of all three materials. Currently, we do not have a good explanation for the intensity of the overtones. One consequence of our DRIFTS technique is a frequency dependent absorption. Higher frequency photons scatter more often, giving them a higher optical path length and increasing their absorption intensity. Normally, given the relatively small frequency range over which we compare intensities, we ignore this effect. The standard correction for this is called the Kubelka-Munk approximation. Even after this transformation is performed, the overtone peaks are still very
prevalent.

If there exist host transitions close to these overtone transition, another possibility is that the overtones are intensified by a resonance with these transitions, known as a Fermi resonance. It is unlikely that the overtone bands are a result of a Fermi resonance, however, as we observe the intense band in the overtone regions of all three isotopologues of hydrogen, which occur at significantly different frequencies. Only observing the primary overtone, we suspect that there is an unusual interaction between the hydrogen and the metal ion complex, which occurs regardless of the metal and the nuclear composition of the hydrogen molecule.

A major issue that should be worked out is the removal of solvent from the samples. Chavan et. al. successfully synthesized Ni-MOF-74 with a solvent called Tetrahydrofuran (THF) instead of DMF, and Mg-MOF-74 has been prepared in a similar manner [48, 49]. Results by Vitillo et. al. indicate that THF binds to MOF-74 less tightly other solvents, leaving behind only water [34]. Using this procedure would allow us to more easily drive away the solvent without destroying the framework. In order to better confirm the identity and quality of our MOF-74 samples, as well as better characterize any new air-sensitive samples, a new leak-tight sample cell could be built for our x-ray diffractometer.

In order to complete the investigation of the series, low temperature infrared spectroscopy data can be performed on Mg-MOF-74 and Mn-MOF-74. Magnesium and manganese have the advantage of being lighter elements than the one’s studied in this thesis, and thus could potentially hold more hydrogen by weight. Infrared spectroscopy could further confirm that only the primary site is affected by the exchange of metal. Zhou et. al. have determined initial isosteric heats of adsorption for the five samples in their series [17], and our redshift method could also confirm or contradict the placement of the magnesium and manganese samples in this hierarchy. Recently, Bhattacharjee, et. al. synthesized Fe-MOF-74, which could additionally support the validity of applying the Irving Williams sequence [50]. The presence or absence of primary and secondary vibrational overtone bands would also provide a valuable comparison, aiding in the discovery of the mechanism that allows us to observe these typically forbidden bands.
Appendix A

Isotherms

Figure A.1: Gas loading system with which isotherms are performed. Red squares indicate valves.
Figure A.2: Isotherm comparison of Zn-MOF-74 and Co-MOF-74. Our highest adsorption values, with our sample at 77K and atmospheric pressure, were 1.4% H$_2$ by weight for Zn-MOF-74 and 1.9% H$_2$ by weight for Co-MOF-74 (see Fig. A.2). Zhou et. al. found 1.6 wt.% and 1.8 wt.% for Zn-MOF-74 and Co-MOF-74 respectively, at the same conditions [17]. Liu et. al. determined that the maximum storage capacity of Zn-MOF-74 with the first three adsorption sites full was 3.6% H$_2$ by weight [16].
Appendix B

Raw Spectra

Figure B.1: Raw spectra of H₂ in Co-MOF-74. The black spectrum is the reference, and the red, blue, and green spectra correspond to the filling of the primary, secondary, and tertiary bands respectively. Spectra are offset.
Figure B.2: Raw spectra of HD in Co-MOF-74. The black spectrum is the reference, and the red, blue, and green spectra correspond to the filling of the primary, secondary, and tertiary bands respectively. Spectra are offset.
Figure B.3: Raw spectra of D$_2$ in Co-MOF-74. The black spectrum is the reference, and the red, blue, and green spectra correspond to the filling of the primary, secondary, and tertiary bands respectively. Spectra are offset.
Figure B.4: Raw spectra of $\text{H}_2$ in Ni-MOF-74. The black spectrum is the reference, and the red, blue, and green spectra correspond to the filling of the primary, secondary, and tertiary bands respectively. Spectra are offset.
Appendix C

Figure C.1: Full absorption spectra of H₂ in Co-MOF-74. Spectra are offset for clarity.
Bibliography


