Infrared Spectroscopy of Trapped Gases in Metal-Organic Frameworks

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Contents

List of Figures

List of Tables

Executive Summary

1 Introduction

1.1 Motivation .................................................. 1
1.2 MOF-74 ..................................................... 3
1.3 Infrared Spectroscopy ...................................... 5
1.4 Carbon dioxide ............................................. 5
1.5 Methane .................................................... 7

2 Quantum mechanics of motion

2.1 Overview .................................................. 9
2.2 Vibrations .................................................. 10
2.3 Rotations .................................................. 12
2.4 Librations and Translations ............................... 13
2.5 Selection rules ........................................... 14
2.6 Fermi resonance .......................................... 15
2.7 Methane .................................................. 16

3 Infrared spectroscopy ........................................ 17

3.1 Absorption of radiation ................................. 17
3.2 Interaction frequency shift ............................. 19
CONTENTS

4 Mg-MOF-74 and the isostructural series 23
  4.1 Synthesis ........................................... 24
  4.2 Structure .......................................... 26
  4.3 Gas-adsorption properties ............................ 27

5 Experimental apparatus and procedure 31
  5.1 The Michelson interferometer .......................... 31
  5.2 DRIFTS ............................................ 32
  5.3 The sample compartments .............................. 34
  5.4 Data collection and manipulation ....................... 37

6 Results and Analysis 39
  6.1 Overview ............................................. 39
  6.2 Asymmetric Stretch of CO\textsubscript{2} ...................... 42
    6.2.1 Blueshift in Mg-MOF-74 .......................... 43
    6.2.2 Band Identification ............................... 47
    6.2.3 Low-temperature peak .............................. 51
    6.2.4 Isotopologue peak ................................ 56
  6.3 High-frequency region .................................. 56
  6.4 Concentration-dependent frequency shifts ............... 57
  6.5 Librations and translations ........................... 57
  6.6 Methane in Mg-MOF-74 ................................ 58

7 Conclusion ............................................ 61

References .............................................. 63
List of Figures

1.1 The MOF-74 structure, from neutron diffraction data taken by Wu et al. ................................................................. 4

2.1 The three normal modes of the CO2 molecule .................................................. 11

4.1 Thermogravimetric analysis of three Ni-MOF-74 samples ............................ 25
4.2 MOF-74 structure with secondary building units in blue ............................ 26
4.3 Image of MOF-74 with bound CO2 and CH4 in their primary sites, from neutron diffraction experiments .............................. 27
4.4 Adsorption isotherms of CO2 in three MOF-74 species .............................. 29

5.1 Schematic of radiation propagation through DRIFTS optics within a sample compartment .................................................. 33
5.2 Schematic of liquid helium cryostat used in variable temperature DRIFTS 34
5.3 Photograph of room-temperature sample holder and compartment in spectrometer .............................................................................. 36

6.1 Full absorbance spectra of CO2 in Mg-MOF-74 ................................. 40
6.2 Infrared spectra of gas-phase carbon dioxide. ........................................ 41
6.3 Asymmetric stretch (ν3) region of adsorbed CO2 in Mg-MOF-74 .......... 43
6.4 Absorbance spectra of ν3 transition of CO2 in the isostructural series .... 45
6.5 Temperature dependence of ν3 peaks of CO2 in Mg-MOF-74 .............. 49
6.6 Temperature dependence of peak intensities ........................................ 53
6.7 Concentration dependence of ν3 peak of 13C18O2 in Mg-MOF-74 .......... 54
6.8 Combination vibrational peaks of CO2 in Mg-MOF-74 ............................ 55
6.9 Gas-phase and adsorbed-phase CH4 in Mg-MOF-74: ν3 transition ......... 58
## List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>Isosteric Heats of CH₄ and CO₂ in MOF-74</td>
<td>28</td>
</tr>
<tr>
<td>6.1</td>
<td>CO₂ ν₃ peaks in Mg-MOF-74</td>
<td>312</td>
</tr>
<tr>
<td>6.2</td>
<td>CO₂ ν₃ peaks in M-MOF-74</td>
<td>346</td>
</tr>
<tr>
<td>6.3</td>
<td>CO₂ ν₃ right shoulder in M-MOF-74 series</td>
<td>51</td>
</tr>
<tr>
<td>6.4</td>
<td>Frequencies of ν₃ peaks of $^{13}$C$^{16}$O₂ in Mg-MOF-74</td>
<td>56</td>
</tr>
<tr>
<td>6.5</td>
<td>Frequencies of combination vibrational transitions of CO₂ in Mg-MOF-74</td>
<td>57</td>
</tr>
</tbody>
</table>
Executive Summary

There are a range of environmental and industrial applications to capturing carbon dioxide from gas mixtures. Currently, materials being used in these applications bind carbon dioxide too strongly, such that they require large amounts of energy to be regenerated to that they can be reused. Highly porous materials called metal-organic frameworks could serve much more effectively as much better carbon-capturing materials, as they suck up large amounts of carbon dioxide gas at pressures and temperatures that are nearly ideal for carbon capture applications. Moreover, they require much less energy than current materials to release the carbon dioxide and be regenerated. Additionally, many different structures can be created fairly easily, so scientists are on the hunt for the ideal carbon-capturing metal-organic-framework. In this thesis we study Mg-MOF-74, a particularly promising metal-organic framework material for separating carbon dioxide from gas mixtures. We use infrared spectroscopy to probe the interactions between the Mg-MOF-74 framework and both carbon dioxide and methane. By shining infrared radiation on Mg-MOF-74 with bound gases and looking at which frequencies of radiation are absorbed by the bound gases, we can learn about the binding nature of the framework. This in turn helps us to better understand properties are preferable in metal-organic frameworks, and will aid chemists in fabricating new structures that are ideal for carbon-capture and other applications.
0. EXECUTIVE SUMMARY
1

Introduction

1.1 Motivation

As global temperatures have been rising over the past century, so have atmospheric concentrations of greenhouse gases. A large and growing body of evidence links these two phenomena and attributes the increased greenhouse gas levels to human activity, specifically to the burning of fossil fuels \( \text{3} \). Carbon dioxide, the primary greenhouse gas emitted in fuel combustion, is at its highest atmospheric concentration in 650,000 years and continues to rise \( \text{3} \). Among the effects of the planet’s changing climate are destruction of ecosystems and increased flooding of coastal regions \( \text{4} \). In order to combat these changes and to ensure that the earth will continue to support life in the future, humans must reduce greenhouse gas emissions.

In response to this global climate crisis, there has been much effort devoted to developing alternative energy technologies. Emissions reduction requires a multipronged approach, ultimately involving a switch away from fossil fuels, although realistically a complete switch to clean energy sources will take years. In the mean time, methods to mitigate the harmful effects of fossil fuel combustion are needed. In particular, technologies for carbon capture and storage (CCS) are being developed to reduce CO\(_2\)-emissions.

CCS consists of separating CO\(_2\) from exhaust gas streams, compressing it, and injecting it into geologic structures in the earth. Of the multiple steps in the CCS process, separating CO\(_2\) from exhaust gases, also called flue gases, is the most costly \( \text{5} \). Current technologies involve scrubbing with amines, in which CO\(_2\) in a flue gas
1. INTRODUCTION

mixture reacts with an aqueous amine solution. CO₂-rich solution is then removed from the solvent via heating, and in principle the amines are regenerated [1].

Amine-scrubbing is the best-understood CO₂-separation method and has been in practice for over 60 years [6]. The process, however, uses significant amounts of energy to remove CO₂ and regenerate the solvents. It is also both costly and harmful, as trace flue gases can degrade the amine solvents, and amines are corrosive [4]. Therefore, there has been a push to develop alternative methods for separating CO₂ from gas mixtures. Recently, a different class of material is receiving attention for CCS applications. Metal-organic frameworks (MOFs) are extremely porous structures with record-breaking surface areas and high affinities for binding gases to their surfaces [4, 7, 8, 9, 10, 11, 12]. They have the highest known storage densities for carbon dioxide, methane, cryogenic diatomic hydrogen [4]. Their structure and adsorption properties will be discussed further in § 1.2.

MOFs are promising candidates for use in CO₂ separation and capture technologies, as they have been shown to selectively bind CO₂ over other gases including nitrogen and methane (cite). Since metal-organic frameworks can be easily modified, a variety of different structures have been fabricated. This thesis focuses in particular on a framework with the name MOF-74. This MOF is especially promising for CCS applications because it has a particularly high selectivity for binding carbon dioxide over other gases. MOF-74 has an especially high CO₂-affinity at low pressures and ambient temperatures, which makes it one of the best MOFs fabricated thus far for separating CO₂ from gas mixtures, because typical CO₂-concentrations in flue gases are low, at 4-12 percent volume [13].

In addition to CCS, there is interest in employing MOFs in the processing of natural gas prior to combustion, to remove carbon dioxide from methane streams. Natural gas with methane as its main component also contains CO₂ and other impurities that reduce the energy content of the gas and can lead to corrosion of pipelines [14]. Thus an important step in natural gas processing is the removal of CO₂. Cryogenic distillation is commonly used for this step, in which the gas mixture is cooled to freeze out CO₂ and other impurities. However, separation methods that run at or near ambient temperatures are often preferable to cryogenic distillation as they are less costly, more energy efficient, and easier to control [14]. Selective adsorption of carbon dioxide onto
porous materials is one such promising gas-separation method. In the past, aluminosilicate materials called zeolites have been used as the adsorbents, although MOFs have received attention in recent years as a family of materials with promise for use in gas separation because of their CO$_2$-uptakes and because they can be regenerated under milder conditions than most zeolites [14].

Metal-organic frameworks also show promise as hydrogen-storage hosts, although current MOFs in existence bind H$_2$ too weakly to be viable hosts at ambient temperatures and pressures. Still, much research is being done into the hydrogen-storage properties of MOFs [8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20]. The Oberlin College Honors theses of Jesse Hopkins, Brian Burkholder, and Michael Friedman report on infrared spectroscopy of hydrogen in a range of MOFs [21, 22, 23], and their results can help direct the search for MOFs that are practical for hydrogen storage applications.

There is still much to be learned about metal-organic framework structures and the nature of the binding mechanism of CO$_2$ and other gases to their surfaces. The work presented in this thesis has two overarching goals. The first is to probe through infrared spectroscopy the nature of the interactions between adsorbed gases and the particular MOFs we study. Specifically, we focus on CO$_2$ in Mg-MOF-74 because of the promise of that particular MOF in CCS applications and in separating CO$_2$ from natural gas streams.

The second goal is to gain a better understanding the electronic environments within MOFs in general so that theoretical models can more accurately predict the properties of these structures. We aim to use the adsorbed molecules as probes to measure the electric field at locations within MOFs. This information can be used to calibrate theoretical models so that they better predict the structures and compositions of new MOFs. Reliable models would give chemists direction in fabricating MOFs with ideal adsorption capacities for a variety of applications ranging from CCS and gas separation to hydrogen storage.

1.2 MOF-74

Metal-organic frameworks, which typically exist in crystalline powder form, consist of metal-oxide clusters linked together by organic bridging ligands to form a threedimensional repeating structures. Solvent molecules are evacuated from the MOF pores
leaving open surfaces for gas molecules to bind to. The binding of gas molecules to the framework surfaces is termed adsorption. As noted in the previous section, MOFs have high gas-storage capacities and potential applications to gas separation and hydrogen-storage for fuel cells.

![The MOF-74 structure, from neutron diffraction data taken by Wu et al.](image)

In this thesis we focus on a particular metal-organic framework structure termed MOF-74, which has one of the largest gas-uptake capacities yet observed. MOF-74 consists of metal oxide clusters bound by organic linkers to form a honeycomb-like structure with infinite hexagonal channels into which gases can diffuse. Figure 1.1 shows the framework structure. We refer to the coordination metals occupying the corners of the hexagons as open or exposed metal ions because when the framework is activated and solvent molecules are removed, each metal, which is in a $2^+$ oxidation state, is bound to five ligands and has one binding site open.

The first MOF-74 sample created contained zinc as the metal ion, although in subsequent years a range of MOF-74 species have been fabricated with different coordination metals including magnesium, manganese, cobalt, and nickel (CITE. have any others been created?). We refer to individual members of the isostructural series by
the name $M$-MOF-74, where $M$ represents whichever metal is substituted into the framework.

The MOF-74 species with the highest CO$_2$-affinity is Mg-MOF-74, for reasons that are not yet fully understood but which we will discuss in Chapter 4. In this thesis we focus the bulk of our study on CO$_2$ in Mg-MOF-74. We compare the CO$_2$-adsorption properties of Mg-MOF-74 to those of three other MOFs in the isostructural series, namely Mn-, Co-, and Zn-MOF-74. We also compare CO$_2$ to CH$_4$ adsorbed to Mg-MOF-74, as gas separation applications of Mg-MOF-74 would include selectively binding CO$_2$ over CH$_4$ in natural gas streams.

1.3 Infrared Spectroscopy

To probe the interactions between the adsorbed gas and the MOF host we use Fourier transform infrared spectroscopy (FTIR). In our setup, infrared radiation strikes a sample of MOF-74 loaded with CO$_2$. Some of the radiation is absorbed, causing parts of the MOF and the trapped gas molecules to transition to higher energy levels. A detector collects radiation that is not absorbed, and our software generates a spectrum of intensity versus frequency.

Traditionally, frequencies are measured in wavenumbers ($\nu/c$) which have units of cm$^{-1}$. We study the frequencies at which trapped CO$_2$ absorbs radiation and how they differ from the frequencies at which gas-phase CO$_2$ absorbs. We look at trends in peak shapes and relative intensities as we change the sample temperature and as we increase the CO$_2$ concentration.

1.4 Carbon dioxide

In this thesis we focus on the quantum transitions of the adsorbed carbon dioxide molecule. CO$_2$ is a linear triatomic molecule composed of a carbon atom double-bonded to two oxygens, one on each side. To describe its motion, we use coordinates that represent the translations of its center of mass, its internal vibrations, and rotations about its principle axes. We can further break up the molecule’s vibrations into normal modes. CO$_2$ gas has three vibrational modes.
1. INTRODUCTION

Because adsorbed CO$_2$ is subject to the laws of quantum mechanics, it can translate, vibrate, and rotate only with discrete energies. A CO$_2$ molecule can absorb radiation and transition into an excited state with higher energy; however it can only absorb photons at particular frequencies corresponding to the energy difference between the initial and final states.

In this thesis we are primarily concerned with vibrational transitions of adsorbed CO$_2$ because they occur in an energy range that matches the mid- to near-infrared energy range of our radiation source. At room temperature, virtually all of the molecules are in their vibrational ground state, so in our spectra we see transitions from the ground state to the first or second vibrationally excited state.

When CO$_2$ transitions to its first vibrationally excited state, its change in energy corresponds to the frequency of an infrared photon. As we will discuss in Chapter 3, experimentalists can determine the energy spacing between the molecular vibrational levels via measuring these photon frequencies. We call the three frequencies associated with the transitions to the first excited states of CO$_2$’s three vibrational modes $\nu_1$, $\nu_2$, and $\nu_3$. $\nu_1$ corresponds to excitation of the first mode, which is a symmetric stretch, $\nu_2$ corresponds to a transition of the second mode, which is a bending of the molecule, and $\nu_3$ corresponds to excitation of the third mode, which is an asymmetric stretch. In Chapter 2 we will discuss these modes and their transition frequencies in more detail. In gas phase CO$_2$, these transitions occur at 1388 cm$^{-1}$ ($\nu_1$), 667 cm$^{-1}$ ($\nu_2$), and 2349 cm$^{-1}$ ($\nu_3$) [24].

Rotational and translational transitions of adsorbed CO$_2$ correspond to microwave frequencies, which are outside of our spectral range. We can, however, see rotational and translational sidebands near our vibrational peaks in our spectra, in which molecules undergo a vibrational and rotational, or a vibrational and translational, transition upon absorbing a photon. We can also see combinations of two or more vibrational transitions. In Chapter 3 will describe how only the transitions of certain modes are infrared active and appear in our spectra.

When a CO$_2$ molecule is trapped in an enclosure, such as when it is adsorbed to a MOF, its motion is constrained. It cannot translate freely. Furthermore, the CO$_2$ may not be able to freely rotate. In this case it becomes relevant to consider librational motion of the molecule. A libration can be thought of as a rotational vibration, in which
1.5 Methane

the molecule is constrained to rotate only over a small angle. Librational energy levels of trapped CO$_2$ are quantized as well, and we will discuss them further in Chapter 2.

Roughly 99% of naturally abundant carbon dioxide is $^{12}$C$^{16}$O$_2$ and 1% is $^{13}$C$^{16}$O$_2$. The energy spacings between the levels of these two carbon dioxide isotopologues differ from one another. As we will see in Chapter 2, the difference in spacing leads to a different transition frequency for each isotopologue. Other isotopologues, with $^{18}$O substituting one or both of the $^{16}$O nuclei, exist as trace percentages of natural CO$_2$, but their infrared peaks are too small to be visible in our spectra.

1.5 Methane

Geometrically, methane (CH$_4$) is described as a spherical top. The carbon is located at the center and is covalently bonded to four hydrogens in a tetrahedral orientation. Methane’s motion is more difficult to describe than that of CO$_2$. CH$_4$ has fifteen degrees of freedom, which we split into three coordinates for translations, three for rotations about the three principle axes, and nine coordinates to describe vibrations. Degeneracy reduces these to four vibrational modes. Of these modes, only two of them are infrared active, and only one of those has energy spacings that correspond to the infrared region we probe. This mode is a triply degenerate asymmetric stretching mode, which occurs at 3019 cm$^{-1}$ \( \text{[24]} \). Methane has no permanent dipole or quadrupole moment, so it interacts with MOFs via dispersion forces primarily. Thus, it binds to MOF-74 much more weakly than carbon dioxide does.
1. INTRODUCTION
2

Quantum mechanics of motion

2.1 Overview

In describing the motion of the CO₂ molecule, for our purposes we may ignore electronic motion, as the electrons remain in their ground states throughout our experiments. Thus we model the molecule as three nuclei bound together.

A three-particle system typically has nine degrees of freedom. We can describe the motion of the CO₂ molecule by assigning three spacial coordinates to each nucleus. For our purposes, however, it is most convenient to work with a different set of coordinates. We assign three coordinates \((x, y, z)\) to represent the motion of the center of mass of the molecule. We then treat the molecule as a rigid rotor and assign two orientation angles \((\theta, \phi)\) to describe rotations about the molecule’s principle axes. The remaining four coordinates represent vibrational motion of the molecule.

As mentioned in §1.1, carbon dioxide’s vibrational and rotational energies are quantized. When it is bound to a metal-organic framework, its translational energies are quantized as well. A CO₂ molecule can transition into an excited state with higher energy via absorption of photons at frequencies corresponding to the energy difference between the molecule’s initial and final states. We discuss absorption of radiation further in §3.1.

We can treat rotations, vibrations, and translations separately because their transitions have dissimilar energies. For CO₂, rotational energy spacings correspond to frequencies on the order of 1 cm⁻¹ and vibrational spacings are on in the thousands of cm⁻¹ range, where cm⁻¹ are the traditional units for infrared frequencies. In gas
2. QUANTUM MECHANICS OF MOTION

phase, the translational energies are not quantized, although when bound to a MOF, CO\textsubscript{2} translational energies become quantized and have spacings on the order of 100 cm\textsuperscript{-1} \cite{13}.

2.2 Vibrations

In this work we are primarily concerned with vibrational transitions of adsorbed CO\textsubscript{2}. At room temperature, virtually all of the molecules are in their vibrational ground state, so in our spectra we see transitions from the ground state to the first or second vibrationally excited state.

As a first approximation, we treat the CO\textsubscript{2} molecule as a system of coupled oscillators. Classically, we can solve the coupled-oscillator problem of three masses connected by two springs and find the normal vibrational modes of the molecule and its equations of motion. The resulting modes are a symmetric stretch, in which the center of mass remains fixed and the connecting springs expand and contract together; an antisymmetric stretch, in which one spring contracts while the other expands; and two bending modes, which, for a symmetric molecule such as CO\textsubscript{2}, are degenerate.

Thus our four remaining coordinates are sufficient to describe the molecular vibrations. We use dimensionless variables \((q_1, q_2, q_3)\) to describe vibrational motion of the CO\textsubscript{2} molecule along the three normal modes. Figure 2.1 shows a schematic of the vibrational modes of CO\textsubscript{2}. These normal modes can be modeled as quantum mechanical harmonic oscillators, for which exact solutions to the Schrödinger equation exist.

Plugging the effective potential energy of each mode into the Schrödinger equation, and solving via either the power series method or the ladder operator method, as detailed in Chapter 3 of Griffiths’ Introduction to Quantum Mechanics, we can find the eigenenergies \(E_i\) associated with each vibrational mode \(25\),

\[
E_i = h\nu_i \left( v_i + \frac{1}{2} \right),
\]

where, \(v_i\) is the quantum number of the vibrational mode \(i\), and \(i\) takes on the values of 1, 2, and 3, for the symmetric stretching, doubly-degenerate bending, and asymmetric stretching modes, respectively. From Hooke’s Law we have

\[
\nu_i = \frac{1}{2\pi} \sqrt{\frac{k_i}{m_i}},
\]
2.2 Vibrations

where $k_i$ is the effective spring constant and $m_i$ is the effective mass of the oscillator describing the mode $i$.

The energy spacings between levels are given by

$$\Delta E_i = h\nu_i.$$  

(2.3)

We can make a more accurate approximation of the vibrational energies of the CO$_2$ molecule by considering anharmonicity in the vibrations. In general, we can approximate the energy levels of a slightly anharmonic oscillator polyatomic molecule using perturbation theory. However, we can no longer consider the modes separately because the anharmonicity couples them such that they are no longer truly normal modes. Using the notation from Buckingham [26], we express the anharmonic perturbing Hamiltonian $\hat{H}_a$ for a polyatomic molecule as

$$\hat{H}_a = \sum_{i,j,k} V_{ijk} q_i q_j q_k + \sum_{i,j,k,l} V_{ijkl} q_i q_j q_k q_l + \ldots,$$  

(2.4)

where $V_{ijk}$ and $V_{ijkl}$ are anharmonic constants specific to the molecule being modeled and the $q_i$ terms represent motion along the normal modes of the harmonic approximation.

Including these anharmonic terms allows us to reach a better approximation for the energy spacings of the CO$_2$ vibrational levels. The spacings are no longer all the same, as they were in the harmonic approximation. In addition to affecting the energy

Figure 2.1: The three normal modes of the CO$_2$ molecule -
2. QUANTUM MECHANICS OF MOTION

Spacings such that the energy difference between the first and second levels is slightly different from the energy difference between the second and third levels, anharmonicity also allows for overtone transitions to occur, in which the vibrational quantum number $v_i$ of a particular mode changes by two upon transition.

The energy differences between the vibrational ground state of the CO$_2$ molecule and each mode’s first excited state have been determined experimentally and calculated theoretically (27). When CO$_2$ transitions to the first excited level of the asymmetric stretch while remaining in the ground levels for the other two modes, the energy change,

$$\Delta E_3 = E_{(0,0,1)} - E_{(0,0,0)},$$  \hspace{1cm} (2.5)

where $E_{(0,0,0)}$ is the total vibrational energy in the ground state and $E_{(0,0,1)}$ is the vibrational energy in the state in which one quantum of the asymmetric stretch mode is excited, is equivalent to the energy of an infrared photon of frequency $\nu_3$.

Thus in infrared spectrometry the energy difference $\Delta E_3$ is traditionally expressed as a fundamental transition frequency $\nu_3$.

Experimentally, the fundamental frequencies—$\nu_1$, $\nu_2$, and $\nu_3$—of the three modes of the free CO$_2$ molecule have been found to be 1388.3, 667.3, and 2349.3, respectively (24).

2.3 Rotations

To describe the rotational motion of the carbon dioxide molecule, we consider CO$_2$ to be a linear rigid rotor that rotates about two principle axes perpendicular to the nuclear axis with energy

$$E_{\text{rotor}} = \frac{\hbar^2 J(J + 1)}{2I} = \hbar c B_e J(J + 1)$$  \hspace{1cm} (2.6)

where $J$ is the rotational (angular momentum) quantum number and $B_e = \hbar/(8\pi^2 c I)$ is the rotational constant of CO$_2$, and $I$ is the molecule’s moment of inertia.

In reality the rotational constant $B$ depends on the vibrational state of the molecule, as anharmonicity causes the average bond length of the molecule, and hence $I$ to be slightly larger in the excited vibrational states.
For rotations of CO\textsubscript{2} about the two axes perpendicular to its bond axis, the rotational constant \( B_e = 0.39\text{cm}^{-1} \). In gas-phase CO\textsubscript{2}, infrared spectra show rotational sidebands in which the molecule undergoes a transition to a different vibrational level and a different rotational level. In fact, as we will discuss in \S2.5 gas phase CO\textsubscript{2} is quantum mechanically forbidden from transitioning to the first excited asymmetric vibrational level alone and must simultaneously transition to a different rotational level.

When a carbon dioxide molecule is bound to a metal-organic framework, it is constrained such that it cannot rotate freely. For adsorbed CO\textsubscript{2}, therefore, rotational sidebands do not appear in our spectra. (In \S2.5 we will describe how interaction with the MOF allows for transitions in which only the vibrational quantum number of the CO\textsubscript{2} molecules changes).

\section*{2.4 Librations and Translations}

In the gas phase, carbon dioxide is unbound and can translate at any energy. When bound to a MOF, however, its translations become quantized. Similarly, when bound to a metal-organic framework structure, a CO\textsubscript{2} molecule is unable to rotate, yet it may be able to librate. A libration can be thought of as an angular vibration, in which the molecule is constrained to rotate only over a small angle. A mean libration angle of CO\textsubscript{2} trapped in channels of a crystal framework has been reported at \( 28^0 \) \textsuperscript{(29)}.

When CO\textsubscript{2} is bound to a MOF, five intermolecular modes are expected. These modes comprise constrained three-dimensional translations of the center of mass and two constrained rotations (librations).

By treating the potential well in which the molecule’s center of mass sits as that of a three-dimensional harmonic oscillator, we arrive at approximate translational eigenenergies of

\[ E_{\text{trans}} = h\nu_1 \left( n_1 + \frac{1}{2} \right) + h\nu_2 \left( n_2 + \frac{1}{2} \right) + h\nu_3 \left( n_3 + \frac{1}{2} \right) \]

where \( n \) is the translational quantum number, \( \nu_1, \nu_2, \) and \( \nu_3 \) now represent translational frequencies in each of the three normal directions.

Broad translational bands have been observed in spectra of adsorbed molecular hydrogen in metal organic frameworks, \textsuperscript{(21) [23]}, the breadth of which are attributed
to a range of slightly different potentials experienced by molecules bound in different unit cells and to lifetime broadening \( [23] \).

Wu et al. report that these intermolecular transitions in \( \text{CO}_2 \) bound to \( \text{Mg-MOF-74} \) lie in the 30-60 cm\(^{-1}\) range \( [30] \). Dietzel et al. reports a translational transition peak in their infrared spectra of \( \text{CO}_2 \) in \( \text{Ni-MOF-74} \) at \( \sim 70 \) cm\(^{-1}\) \( [13] \). However, we were unable to identify any of the five intermolecular transitions in our infrared spectra, for reasons that we discuss in Chapter 6.

### 2.5 Selection rules

In gas phase, the overall symmetrization requirement of the wavefunction describing \( \text{CO}_2 \) prohibits the molecule from undergoing pure rotational transitions in which the change in the angular momentum quantum number \( \Delta J \) is odd. Furthermore, the pure fundamental antisymmetric vibrational transitions are prohibited. Here we give an informal theoretical explanation for these selection rules. For a more detailed treatment, see Chapter 4 of Herzberg’s *Molecular Spectra and Molecular Structure* Volume 2. \( [31] \).

The \( ^{16}\text{O} \) atoms in \( ^{16}\text{O}_2 \) are identical bosons. Therefore, when the molecule undergoes a rotation and the oxygens are exchanged, the overall wavefunction describing the \( \text{CO}_2 \) molecule must be unchanged in sign \( [25] \).

\[
\Psi = \psi_e \psi_v \psi_r \psi_n, \tag{2.8}
\]

where \( \psi_e \), \( \psi_v \), \( \psi_r \), and \( \psi_n \) represent the electronic, vibrational, rotational, and nuclear components of the overall wavefunction \( \Psi \), respectively.

As mentioned previously in § 2.1, the electronic wavefunction does not change with the molecular transitions we are studying, so we may disregard it in this treatment. Similarly, the wavefunction describing the nuclei of the constituent atoms remains unchanged under exchange of the oxygens \( [32] \). Thus we focus on the rovibrational wavefunction \( \Psi_{rv} \)

\[
\Psi_{rv} = \psi_v \psi_r \tag{2.9}
\]

and require that it be symmetric under interchange of the oxygens.

When the oxygens are exchanged, the sign of rotational wavefunction changes according to \( (-1)^J \).
When considering vibrations, we will focus on the fundamental asymmetric stretch transition, in which the symmetric and bending modes remain in their ground levels. We find that in the molecule’s ground state \( (v_1 = v_2 = v_3 = 0) \), the vibrational wavefunction keeps the same sign upon exchange of the oxygen nuclei. Thus, in this vibrational state, rotational states with odd values of \( J \) do not exist.

On the contrary, when \( \text{CO}_2 \) is in the first excited state of the asymmetric stretch \( (v_1 = v_2 = 0, v_3 = 1) \), the vibrational wavefunction \( \psi_v \) is antisymmetric under exchange of the oxygen atoms. In this vibrational state, rotational states with even values of \( J \) do not exist.

Therefore, when the \( \text{CO}_2 \) makes a fundamental asymmetric vibrational transition \((\nu_3)\), \( \Delta J \) cannot be zero. In other words, the pure \( \nu_3 \) \( \text{CO}_2 \) transition is quantum-mechanically forbidden. In gas phase spectra, we see an envelope of rotational sidebands at higher and lower frequencies than the pure \( \nu_3 \) transition, but we see no pure vibrational band in the center at \( 2349 \text{ cm}^{-1} \). The combination rotation and vibration transitions that lead to the sidebands are called rovibrational transitions. Furthermore, conservation of angular momentum further restricts the allowed transitions so that \( \Delta J = \pm 1 \).

This restriction that upon the fundamental asymmetric vibrational transition \( \Delta J \neq 0 \) is absolute for free \( \text{CO}_2 \). However, when \( \text{CO}_2 \) is bound to a MOF, the wavefunction describing the system can be written to include host framework terms. When a bound \( \text{CO}_2 \) molecule undergoes a vibrational \( \nu_3 \) transition, a simultaneous transition can occur in the MOF that balances the sign of the total wavefunction describing the system. These MOF-transitions may be associated with only tiny energies changes, such that they have negligible effects on energy spacings of the transitions.

In the adsorbed phase, \( J \) is no longer a good quantum number. A particular \( \text{CO}_2 \) state could be expressed as a linear combination of \( J \) levels, but since the coefficients would span large range of \( J \) values, it becomes meaningless to talk about rovibrational selection rules in bound \( \text{CO}_2 \).

### 2.6 Fermi resonance

When two different transitions have similar energies, such as the fundamental \( \nu_1 \) transition and the \( 2\nu_2 \) overtone transition in \( \text{CO}_2 \), the two modes can become coupled and
lead to an effect called Fermi resonance. A Fermi resonance can be thought of as an accidental degeneracy. The Fermi resonance in CO$_2$ can be thought of as as a splitting of the $\nu_1$ transition into two transitions, one of higher energy and one of lower energy. Realistically, it is more accurate to describe both transitions as linear combinations of the $\nu_1$ and $2\nu_2$ transitions.

2.7 Methane

Methane (CH$_4$), has a tetrahedral geometry, with the carbon at the center, in which the moments of inertia $I_a$, $I_b$, and $I_c$ about the three principle axes are all equal. A molecule with this geometry is termed a spherical top because it consists of five atoms which, although constrained, can move independently, its motion is more difficult to describe than that of CO$_2$. CH$_4$ has fifteen degrees of freedom, which we split into three coordinates for translations, three for rotations about the three principle axes, and nine coordinates to describe vibrations. However, its spherical top symmetry leads to vibrational degeneracies that reduce these nine coordinates or degrees of freedom to just four different vibrational modes $\nu_1$, $\nu_2$, $\nu_3$, and $\nu_4$. Experimentally, the fundamental frequencies associated with the modes are $\nu_1 = 2917$ cm$^{-1}$, $\nu_2 = 1534$ cm$^{-1}$, $\nu_3 = 3019$ cm$^{-1}$, and $\nu_4 = 1306$ cm$^{-1}$. Of these transitions, only the $\nu_3 = 3019$ cm$^{-1}$ transition is both infrared active and has energy spacings that correspond to the infrared region we probe. This mode is a triply degenerate asymmetric stretching. When we study spectra of adsorbed CH$_4$, we focus on the molecule’s $\nu_3$ transition.

Because methane has no permanent dipole or quadrupole moment, it interacts with metal-organic frameworks via dispersion forces primarily. Thus, it binds to MOF-74 much more weakly than carbon dioxide does, and its infrared spectra show weaker bands.
3

Infrared spectroscopy

Infrared spectroscopy involves shining radiation on a sample and measuring the frequencies at which the radiation is absorbed by molecules in the sample. Those frequencies correspond to quantum transitions in the molecules. The infrared spectrum thus provides information on the energy spacings between quantum vibrational, rotational, and translational states of the molecules being studied. In this chapter we discuss how molecules interact with infrared radiation, and we discuss how interaction of carbon dioxide with a metal-organic framework affects the frequencies of radiation that the molecule absorbs.

3.1 Absorption of radiation

Using time-dependent perturbation theory, we can approximate the interaction of the electric field of an infrared photon with a molecule and find the transition probability of the molecule absorbing the photon’s energy and entering an excited state. When charges interact with a photon, we can write the perturbing Hamiltonian as

\[ \hat{H}' = \int \vec{E}_{ph} \sum_i q_i dr_i. \]  \hspace{1cm} (3.1)

The electric field \( \vec{E}_{ph} \) of a photon is given by

\[ \vec{E}_{ph} = \vec{E}_o e^{i(\vec{k} \cdot \vec{r} - \omega t)} , \]  \hspace{1cm} (3.2)

where \( \vec{E}_o \) is the amplitude of the traveling wave, \( \vec{k} \) is the wavevector of the photon with \( k = 2\pi/\lambda \) with \( \lambda \) being the photon’s wavelength, \( \vec{r} \) describes a position in space,
\section{Infrared Spectroscopy}

$\omega$ is the photon’s angular frequency, and $t$ denotes time passed. In the limit that the wavelength of the infrared radiation is much larger than the radius of the molecule, we can approximate the spacial part of the electric field as constant. The perturbing Hamiltonian is then approximated as

$$\hat{H}' \approx \vec{E}_0 \sum_i q_ir_i$$

$$\approx \vec{E}_0 \mu. \quad (3.3)$$

Such an approximation is called the dipole approximation because the perturbing Hamiltonian is taken to be a constant times the dipole moment $\mu$ of the molecule. This is a reasonable approximation for our purposes as the length of a CO$_2$ molecule is roughly 3 Å and the wavelength of a typical infrared ray is four orders of magnitude larger at $\sim$ 3 microns.

Under the dipole approximation, for a molecule to absorb a photon, it must have a dipole moment. More specifically, it must have a nonzero matrix element of the dipole moment operator $\hat{\mu}$ between the initial and final states (see Griffiths’ \textit{Introduction to Quantum Mechanics} § 9.1-9.2 for a derivation \cite{25}). This can be thought of as a change in the dipole moment upon transition from the initial to the final state. All of the transitions with which we are concerned in this thesis have nonzero dipole moment matrix elements and are thus infrared active. As is shown in Griffiths \cite{25}, the probability of a molecule interacting with the electric field of the infrared photon and undergoing a transition from a state $|\psi_a\rangle$ to $|\psi_b\rangle$, to first order, is proportional to

$$P_{a \rightarrow b} \propto \frac{|\langle \psi_a | \hat{\mu} | \psi_b \rangle|^2}{(\omega_0 - \omega)^2}, \quad (3.4)$$

where $\omega$ is the frequency of the incident radiation and $\hbar \omega_0$ is energy difference between the initial and final states. As conservation of energy requires, this probability is virtually zero unless $\omega \approx \omega_0$.

Thus a particular transition in a molecule will correspond to a narrow range of infrared frequencies, which produce an absorption band in an infrared spectrum. The maximum of the band, with frequency proportional to the energy difference between $|\psi_a\rangle$ and $|\psi_b\rangle$, is traditionally termed the peak of the band.
3.2 Interaction frequency shift

In CO$_2$, the fundamental asymmetric stretch transition $\nu_3$, that is, the transition from the ground vibrational state to the first excited state of the asymmetric stretch mode, is infrared active, as it corresponds to a dipole moment change. The fundamental symmetric stretch transition $\nu_1$ does not correspond to a dipole moment change and is thus infrared inactive. As mentioned in §2.2, anharmonicity in CO$_2$ vibrations allows for transitions from the ground vibrational level of a particular mode to its second excited level. These transitions are called overtones.

3.2 Interaction frequency shift

The following analysis relies heavily on the Buckingham’s work on solvent effects in vibrational spectroscopy [20]. In his seminal paper he employs perturbation theory to approximate the energy levels of diatomic and polyatomic molecules interacting with solvents as a function of the interaction potential energy, $U$, and its derivatives with respect to the normal coordinates of vibration.

As discussed in §2.2, the vibrations of a polyatomic molecule can be approximated as a system of harmonic oscillators with each oscillator corresponding to a normal mode. A better approximation for vibrational motion involves incorporating anharmonicity into the vibrational potential-energy terms. Using perturbation theory we can approximate the energy eigenvalues of each vibrational mode. We treat the anharmonic Hamiltonian $\hat{H}_a$ as a perturbation to the harmonic Hamiltonian $\hat{H}_o$, for which exact solutions exist. When a polyatomic molecule interacts with a solvent, such as when it is adsorbed to a metal-organic framework, its vibrational energy levels are perturbed further by the interaction between the molecule and the framework. We thus express a new perturbing Hamiltonian $\hat{H}'$ in terms of the interaction potential energy $U$:

$$\hat{H}' = \hat{H}_0 + U(q_1, q_2, ..., q_n; \tau) - U_e,$$  \hspace{1cm} (3.5)

where $q_i$ are the normal coordinates of vibration of the free molecule, $\tau$ represents all the positions and orientations of the atoms composing the solvent environment surrounding the molecule. $\tau$ depends on the molecule’s center of mass and orientation relative to the solvent molecules, and $U_e$ is the interaction potential energy in the molecule’s equilibrium position. $U_e$ is an expression of the binding energy of adsorption.
3. INFRARED SPECTROSCOPY

After expanding $U$ as a Taylor series about the equilibrium position of the molecule with respect to vibrations, that is at $q_1 = q_2 = \ldots = q_n = 0$, Buckingham performs first and second order perturbation theory to find the energy eigenvalues of the adsorbed molecule:

$$
W_{v_1,v_2,\ldots,v_n}(\tau) = W_v(\tau)
= W_v^{(0)} + U_e - \sum_i \beta_i \frac{(U_i')^2}{\hbar \nu_i} + \sum_i (\nu_i + \frac{1}{2}) \beta_i [U''_{ii} - 12 \sum_j \beta_j \frac{U_j'}{h \nu_j} V_{ij}] + \ldots,
$$

where $W_v$ is the energy of a particular vibrational state of the molecule interacting with solvent, $W_v^{(0)}$ is the energy of the corresponding state in the isolated molecule, the $v_i$ terms represent energy quantum numbers of the vibrational modes $i$, $\beta_i = h/(8\pi^2 c \nu_i)$, $U'_i = (\partial U/\partial q_i)_e$ is the partial derivative of the interaction potential energy with respect to the normal coordinate $q_i$ evaluated at the equilibrium position of that mode in the unperturbed molecule, i.e., at $q_i = 0$. At this stage $U''_i$ is still a function of $\tau$. We use the convention that $\nu_i$ represents the harmonic oscillator frequency in wavenumbers, which the traditional measure of infrared radiation frequencies and is the reciprocal of wavelength.

The fundamental frequency $\nu_i$, that is, the frequency of the adsorbed molecule’s transition to the first excited level of vibrational mode $i$ while remaining at the ground levels for all other modes is given by:

$$
\nu_i(\tau) = \frac{[W_{0,0,\ldots,0,0\ldots}(\tau) - W_0(\tau)]}{\hbar c}
= \nu_i^{(0)} + \frac{\beta_i}{\hbar c} \left\{ U''_{ii} - 12 \sum_j \frac{\beta_j}{h \nu_j} U_j' V_{ij} \right\} + \ldots,
$$

where the $V_{ij}$ terms are anharmonic constants for the CO₂, which have been calculated theoretically and can be found in a paper by Suzuki (27).

The observed absorption frequencies $\tilde{\nu}_i = \langle \nu_i(\tau) \rangle_0$ are calculated by taking an average of $\nu_i(\tau)$ over all $\tau$, that is, an average over all the discrete orientational and center-of-mass-translational quantum states.

The frequency shift, $\Delta \nu_i = \tilde{\nu}_i - \nu_i^{(0)}$, of the observed band upon the molecule’s interaction with a solvent is thus
3.2 Interaction frequency shift

\[ \Delta \nu_i = \frac{\beta_i}{\hbar c} \left\{ \langle U''_{ii} \rangle_0 - 12 \sum_j \frac{\beta_j}{\hbar c \nu_j} \langle U'_j \rangle_0 V_{ij} \right\} + \ldots \]  

(3.8)

where \( \langle U''_{ii} \rangle_0 \) and \( \langle U''_{ii} \rangle_0 \) are the average values for all \( \tau \) of \( U'_i \) and \( U''_i \) in the ground vibrational state. For a linear, triatomic, symmetric molecule such as carbon dioxide, the expression in (3.8) becomes simplified. In CO\(_2\) the subscripts \( i \) take on the values 1, 2, and 3, where, as before, 1 represents the symmetric stretching mode, 2 the doubly-degenerate bend, and 3 the asymmetric stretch. Symmetry requires that \( \langle U'_2 \rangle_0 = \langle U'_3 \rangle_0 = 0 \), which results in approximate frequency shifts of

\[ \Delta \nu_1 = \frac{1}{8\pi^2 c^2 \nu_1} \left\{ \langle U''_{11} \rangle_0 - \frac{3}{2\pi^2 c^2 \nu_1^3} \langle U'_1 \rangle_0 V_{111} \right\} \],

\[ \Delta \nu_2 = \frac{1}{8\pi^2 c^2 \nu_2} \left\{ \langle U''_{22} \rangle_0 - \frac{3}{2\pi^2 c^2 \nu_2^3} \langle U'_1 \rangle_0 V_{221} \right\} \],

(3.9)

\[ \Delta \nu_3 = \frac{1}{8\pi^2 c^2 \nu_3} \left\{ \langle U''_{33} \rangle_0 - \frac{3}{2\pi^2 c^2 \nu_3^3} \langle U'_1 \rangle_0 V_{331} \right\} \].

From here we will focus on \( \Delta \nu_3 \) and discuss its sign qualitatively. We see that the \( U'_1 \) influences the frequency shift of the asymmetric stretch transition through the anharmonic constant \( V_{311} \), which was calculated by Suzuki and found to have a negative sign (27).

We can assume that \( \langle U''_{33} \rangle_0 \) is small compared to \( 3/(2\pi^2 c^2 \nu_3^2) \langle U'_1 \rangle_0 V_{331} \) and can be ignored (33). This allows us to place the dependence of the frequency shift on the sign of \( \langle U'_1 \rangle_0 \). If \( \langle U'_1 \rangle_0 \) is positive, \( \Delta \nu_3 \) is likely to be positive; the solvent interaction causes a blueshift. If \( \langle U'_1 \rangle_0 \) is negative, there will likely be a redshift.

If the interaction potential energy increases as the molecule expands via the symmetric stretch and decreases as it contracts, then \( \langle U'_1 \rangle_0 \) will be positive in that region. We can think of \(-\langle U'_1 \rangle_0\) as a measure of the force on the CO\(_2\) molecule due to the interaction with the solvent as it expands or contracts. A positive value of \( \langle U'_1 \rangle_0 \) is in simpler terms a repulsive force on the CO\(_2\) from the solvent.

To be clear, this repulsion does not push the molecule away from the solvent but rather causes it to contract, as \( \langle U'_1 \rangle_0 \) is a function of the symmetric vibrational mode, not of translations.

The cause for such a repulsive force remains to be discussed. There has been speculation on the particular conditions likely to result in a blueshift for CO\(_2\) interacting...
with a metal ion, as occurs when CO$_2$ is adsorbed to MOF-74: Gregoire et al. claim that a blueshift is more likely to result from an end-on-configuration, in which the CO$_2$ molecule interacts with the solvent mainly via one of its oxygens, such that symmetric and antisymmetric vibrations bring the oxygen closer to the solvent. As we will discuss further in Chapter 4, CO$_2$ binds to MOF-74 surfaces in such a configuration, making a blueshift in $\nu_3$ a reasonable possibility.

To summarize, the asymmetric-stretch fundamental frequency of CO$_2$ interacting with a solvent may blueshift if the net force on the molecule from the solvent pushes it into a slightly contracted configuration compared to its length in gas phase. If instead the solvent forces the molecule to expand slightly with respect to its gas-phase length, the $\nu_3$ frequency shift is more likely to be to the red.
Mg-MOF-74 and the isostructural series

In this chapter we examine Mg-MOF-74 and other members of the MOF-74 isostructural series. We detail the synthesis, structure, and gas adsorption properties of the different MOF-74 species, and we provide a justification for the comparatively high CO₂ affinity of the magnesium compound.

Metal-organic frameworks (MOFs) are characterized by highly porous structures consisting of metal-oxide clusters joined by organic linkers usually containing aromatic rings. They exhibit high surface areas and high affinity for binding gases to their surfaces. In recent years there have been a number of review articles published on MOFs and their gas adsorption capacities.

MOF-74 is a particularly interesting metal-organic framework for study because it contains unsaturated coordination metal sites where adsorbates can interact strongly. The structure of the framework surrounding these open metal sites will be described further in §4.2. MOF-74 has been shown to have a particularly high initial gas uptake compared to other metal-organic frameworks. The high gas-affinity of this compound at low-equilibrium-pressure can be attributed to strong interactions between the adsorbate and the metal ion. Characterizing this interaction is important, as MOFs fabricated in the future are likely to contain these highly adsorptive exposed metal sites.

MOF-74 was first synthesized in 2005 by Rosi et al. with zinc as the coordinating metal ion. Other names for the compound include $M_2$(dhtp), $M$/DOBDC, and
4. MG-MOF-74 AND THE ISOSTRUCTURAL SERIES

CPO-74-M where M denotes the coordination metal \(^{18, 19, 36}\).

Hydrogen-storage properties of the MOF-74 isostructural series have been studied, first by Zhou et al., in compounds synthesized with magnesium, manganese, cobalt, nickel, and zinc. FitzGerald et al. expanded on the work, reporting absorption spectra for \(\text{H}_2\) in the same five members of the series \(^{57}\).

The CO\(_2\)-adsorption behavior in the MOF-74 series has been characterized more recently by Caskey et al. \(^{39}\) and other groups, and CH\(_4\)-adsorption properties in \(M\)-MOF-74 for \(M=\text{Mg, Mn, Co, Ni, and Zn}\) have been measured by Wu et al. \(^{11}\) In this chapter we report binding energies of CO\(_2\) in \(M\)-MOF-74 for \(M=\text{Mg, Co, and Ni}\) as well as CH\(_4\) binding energies in all five members of the series.

4.1 Synthesis

The MOF-74 species studied were synthesized by Dr. Jesse Rowsell of the Oberlin Chemistry and Biochemistry Department using a solvothermal process described in Michael Friedman’s Honors thesis \(^{23}\) and modified from literature procedures \(^{36}\). Either water or methanol was used as the activation solvent, and the samples were heated to 200-250\(^\circ\)C in flowing nitrogen to drive off solvent molecules, activating the gas-binding sites.

Each MOF sample must be heated above a particular temperature to drive off the solvent, yet not above a temperature at which the structure decomposes. Thermogravimetric analysis (TGA) is used to determine the temperature range for each MOF species for which the solvent has been driven off yet the structure remains intact. Figure 4.1 shows the TGA traces of the samples of Ni-MOF-74 each prepared under different conditions by Dr. Jesse Rowsell of the Oberlin College Department of Chemistry and Biochemistry. The sample heated to 200\(^\circ\)C overnight lost mass due to framework decomposition at a lower temperature (320\(^\circ\)C) than samples that did not receive this additional preparation, which degraded at 340\(^\circ\)C. TGA gives rough boundaries on the temperature range to which the sample can be safely heated, although the framework may be destroyed below the temperature at which mass loss occurs.

Activated MOF-74 is extremely air-sensitive and must be stored in inert gas. Our samples were stored in an argon-filled glove box. MOF-74 contaminated with air
Figure 4.1: Thermogravimetric analysis of three Ni-MOF-74 samples - All three samples were kept under methanol for ~7d. The green trace represents a sample that was washed with H$_2$O several times over three days, the black trace represents a sample that was heated to 200°C overnight, and the blue trace represents a sample with no additional preparation. Sample preparation and TGA were conducted by Dr. J. Rowsell. Mass loss from framework decomposition begins at 340°C in the green and blue traces and at 320°C in the black trace, although the framework may be destroyed at lower temperatures, before mass loss occurs.
molecules or with remaining solvent may adsorb less of the desired gas as the con-
taminating molecules may both fill the adsorbate binding sites and block framework
holes, preventing adsorbate from reaching regions of the sample.

4.2 Structure

M-MOF-74 has chemical formula $M_2(C_8H_2O_8)$ \(^{16}\) where $M$ represents the coordi-
nation metal. The framework assumes a honeycomb structure with parallel hexag-
onal channels, which result from helical $M$-O-C rods composed of $[O_2M_2](CO_2)_2$,
termed secondary building units (SBUs), and are connected to one another by the
hydroxy groups of 2-5-dihydroxyterephthalate (dhtp), as is shown in Figure 4.2. The
6-coordinated $M^{2+}$ center is thus bound to five oxygens: three from carboxyl groups
and two from hydroxy groups that each connect to the benzene ring of a dhtp. The
remaining coordination site is bound to a solvent molecule, which is removed upon ac-
tivation of the material, allowing adsorbates to bind. The crystal structure is trigonal
and belongs to space group R$3$ (17 in Michael’s thesis). The pores are large enough for
gas molecules to access and they allow for significant gas adsorption.

![MOF-74 structure with secondary building units in blue](image)

Figure 4.2: MOF-74 structure with secondary building units in blue - Image
courtesy of Rosi et al. \(^{11}\)

Mg-MOF-74 has an estimated surface area of 1495 m\(^2\)/g \(^{36}\), which allows for
significant gas-adsorption per weight. Other members of the series have lower surface areas per mass, which can be attributed in part to their higher formula unit mass, as they contain heavier metals. Estimated surface areas are 1080 m²/g (76), 1070 m²/g (15), and 816 m²/g (30) for Co, Ni, and Zn compounds, respectively.

The MOF-74 samples used in our experiments are in granular crystalline powder form, which is well suited to our particular infrared spectroscopy technique, as will be described further in Chapter 5. Powder X-ray diffraction (PXRD) scans match literature results for the five members of the isostructural series (19), which confirms their crystal structure. Figure (number) shows our scans compared side-by-side with scans published by Zhou et al. (19).

4.3 Gas-adsorption properties

Neutron diffraction experiments conducted by Wu et al. for CO₂ in Mg-MOF-74 indicate that the primary binding site for CO₂ is next to the Mg²⁺ coordination ion (30). Similar neutron experiments for CH₄ in the MOF-74 isostructural series show that CH₄ occupies the same primary binding site (1). Figure 4.3a shows a MOF-74 pore filled with CO₂ occupying the primary sites and Fig. 4.3b shows a pore filled with CH₄ in its primary sites.

Caskey et al. report an initial isosteric heat of adsorption (Q₂₅), which is a measure of binding energy, of 47 kJ/mol for CO₂ in Mg-MOF-74, and they report 41 and
4. MG-MOF-74 AND THE ISOSTRUCTURAL SERIES

37 kJ/mol for CO₂ in Co-MOF-74 and Ni-MOF-74, respectively (cite caskey et al). There exists a range of published values for Qₚₚₚ in Mg-MOF-74, ranging from 39 to 73 kJ/mol [13, 35, 38, 29]. The variation may be due to large errors in the measurement techniques or to differences in quality of the samples investigated.

The initial Qₚₚₚ values for CH₄ and CO₂ in the isostructural series are given in Table 4.1 [4]. Clearly, MOF-74 has a significantly higher CO₂ affinity than CH₄ affinity.

Table 4.1: Isosteric Heats of CH₄ and CO₂ in MOF-74

<table>
<thead>
<tr>
<th>MOF compound</th>
<th>CH₄ initial Qₚₚ (kJ/mol)*</th>
<th>CO₂ initial Qₚₚ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-MOF-74</td>
<td>18.5</td>
<td>47</td>
</tr>
<tr>
<td>Mn-MOF-74</td>
<td>19.1</td>
<td>-</td>
</tr>
<tr>
<td>Co-MOF-74</td>
<td>19.6</td>
<td>41</td>
</tr>
<tr>
<td>Ni-MOF-74</td>
<td>20.2</td>
<td>37</td>
</tr>
<tr>
<td>Zn-MOF-74</td>
<td>18.3</td>
<td>-</td>
</tr>
</tbody>
</table>

Fig. 4 shows adsorption isotherms of CO₂ in Mg-, Co-, and Zn-MOF-74 conducted at room temperature. The curves match data published by Caskey et al. [35], except that our Zn-MOF-74 sample shows an even higher uptake than that in [35]. That our isotherms yield as high or higher CO₂ uptakes and that the shapes of our isotherm curves match those from the literature indicate that the materials used in our infrared spectroscopy measurements are relatively pure and uncontaminated.

Practically, isotherm measurements require a much larger volume of powder sample than infrared spectroscopic measurements require. Thus we did not conduct a Mn-MOF-74 CO₂ isotherm for lack of a sufficient quantity of sample.

Clearly, Mg-MOF-74 has a higher uptake of CO₂ than the other members of the series, even at atmospheric pressure. In Mg-MOF-74, the Mg-O bonds in the framework have high ionic character compared to those of other M-MOF-74 species [36], which we attribute to the comparatively small ionic radius of magnesium. We speculate that more polar bond results in a stronger electric field that the CO₂ molecule feels, causing the CO₂ to interact more strongly at the metal site in Mg-MOF-74 than in the other series members.
4.3 Gas-adsorption properties

Figure 4.4: Adsorption isotherms of CO$_2$ in three MOF-74 species - The circles, triangles, and squares represent Mg-, Co-, and Zn-MOF-74 isotherms, respectively. Lines are drawn between points to aid in viewing. The curves match isotherm data published by Caskey et al. [36].
4. MG-MOF-74 AND THE ISOSTRUCTURAL SERIES

Because CH$_4$ lacks permanent dipole and quadrupole moments it interacts with the MOF primarily via dispersion forces rather than electrostatic forces. Thus the increased electric field in the magnesium compound leads to only a minor increase CH$_4$-affinity. Thus, other factors dominate and Ni-MOF-74 is reported to have the highest CH$_4$-affinity of the members of the series [1].
Experimental apparatus and procedure

This chapter contains an overview of the experimental setup for conducting variable temperature, Fourier transform infrared spectroscopy. The spectrometer consists of a modified Bomem DA3 Michelson interferometer with a globar infrared source and a calcium fluoride (CaF$_2$) beam splitter. The spectrometer contains two sample compartments, one of which is used for taking room-temperature spectra, and the other of which is equipped with a custom-made vacuum chamber and cryostat for low temperature experiments. A mercury cadmium telluride (MCT) detector, cooled with liquid nitrogen, collects infrared signal, and Bomem software performs the Fourier transform to produce infrared spectra, which are saved to a computer.

5.1 The Michelson interferometer

Fourier transform infrared spectroscopy (FTIR) relies on the use of a Michelson interferometer to create a time-varying source of infrared radiation. The time-domain interferogram is converted via a Fourier transform to the frequency-domain, such that the degree to which each frequency is absorbed by the sample can be measured, up to a specified resolution.

In our spectrometer, a polychromatic infrared beam is split, sent down two paths, one to a fixed mirror and one to a movable mirror, and then recombined to create a time-varying interference pattern. For a particular wavelength $\lambda$, fully constructive
5. EXPERIMENTAL APPARATUS AND PROCEDURE

interference occurs when the path difference between the two beams, $\Delta x$, is equal to $m\lambda$ for integer values of $m$, and fully destructive interference occurs when $\Delta x = (m + \frac{1}{2})\lambda$.

Output from the detector shows intensity as a function of time. Time is related to $\Delta x$ using the mirror speed, and an interferogram of intensity versus path difference is produced. An example interferogram is shown in Fig. ???. When $\Delta x = 0$, the beams are at zero path difference (ZPD), and all wavelengths interfere constructively, producing a sharp peak in the interferogram. For nonzero values of $\Delta x$, different wavelengths combine constructively and destructively. The Bomem software performs a Fourier transform on the interferogram, producing a spectrum of intensity versus frequency.

In our spectrometer, an HeNe laser with a precisely known wavelength determines the distance traveled by the mirror. A white light source is used to determine the location of ZPD so that all scans of the mirror through a complete cycle have same starting point.

The frequency-resolution of the spectrum depends on the distance covered by the movable mirror. The resolution, measured in cm$^{-1}$, is the reciprocal of the maximum distance traveled by the mirror. The maximum resolution achievable with this apparatus is 0.04 cm$^{-1}$. High-resolution spectra are more susceptible to noise and to drift in sample and spectrometer conditions than low-resolution spectra are, because they take longer to obtain. Unless otherwise noted, all spectra in this thesis were taken at 1 cm$^{-1}$ resolution.

5.2 DRIFTS

The typical infrared spectroscopic method used to probe interactions between an adsorbate and a host is transmission spectroscopy, in which infrared radiation passes through the sample and is detected. Absorption signal manifests as dips in detected intensity at particular frequencies.

As granular powders, MOFs scatter too much incident radiation for this method to be effective. If a thin film of MOF sample were fabricated, such that scattering would be minimal, the path length of radiation in the sample would be so small that the absorption signal from CH$_4$ and other molecules with only small induced dipoles would be too weak to analyze.
5.2 DRIFTS

Therefore, we use a method called diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), which takes advantage of the high level of scattering from the powder MOF to increase the path length through which infrared radiation interacts with the sample, thus enhancing the absorption signal.

MOF samples in forms other than powder can be prepared but preparation is much more difficult than for powders. Pressing pure-MOF pellets is very difficult; thus MOF powders are diluted with KBr powder before pressing. Single-crystal MOFs in existence are too small for IR spectroscopy, and free-standing thin films cannot be made. Air-sensitivity of the materials complicates the sample preparation process, making it most practical to produce MOF samples in powder form. Thus DRIFTS is a practical IR spectroscopy method for MOFs.

![Figure 5.1: Schematic of radiation propagation through DRIFTS optics within a sample compartment](image)

Figure 5.1 shows a schematic of the DRIFTS optics. Radiation enters the chamber and is focused onto the sample by a series of mirrors. It scatters multiple times off of the irregularly shaped powder grains, which results in a long path length in which the radiation interacts with the sample and an increased probability of absorption.
Radiation that is not absorbed is reemitted at a random angle, then reflected and focused by an ellipsoid mirror, and sent into the detector.

This setup is ideal for probing weakly infrared active adsorbates. DRIFTS is less ideal for systems that have high infrared activity. For example, because the antisymmetric stretch mode of adsorbed carbon-dioxide is strongly active in the infrared, our DRIFTS method can lead to signal saturation at high concentrations of adsorbed CO₂, in which all of the radiation at that frequency is absorbed. In the event of CO₂ signal saturation, we study the absorption peak due to $^{13}$C$^{16}$O₂, a naturally occurring isotopologue of $^{12}$C$^{16}$O₂, which occupies 1% of the carbon dioxide in our system and thus produces a smaller adsorbed-phase signal than $^{12}$C$^{16}$O₂.

### 5.3 The sample compartments

![Diagram of DRIFTS cryostat setup](image)

Figure 5.2: Schematic of liquid helium cryostat used in variable temperature DRIFTS - Symbols: (a) gas line, (b) vertical alignment stage, (c) vacuum line, (d) DRIFTS optical mount, (e) ellipsoidal mirror, (f) high-pressure sapphire dome, (g) copper sample holder, (h) CaF₂ window, (i) copper cold finger, (j) radiation shield, and (k) cryostat vacuum shell, (image courtesy of Y. E. Strangas).
5.3 The sample compartments

The two sample compartments are equipped with DRIFTs optics and a sample mount. The right compartment contains a cryostat for cooling the sample with liquid nitrogen or liquid helium. Figure 5.2 shows a schematic. The sample is enclosed in a dome with sapphire windows, transparent between 1600 and 15000 cm\(^{-1}\), and is sealed with an indium o-ring, which unlike rubber o-rings maintains its seal down to our base temperature of 10K and below. Surrounding the sample mount is a vacuum chamber with a CaF\(_2\) windows through which radiation enters, travels through the DRIFTS optics, and exits. Cooling occurs via a modified Janis Research Company ST-300T cold finger that transports liquid cryogens. At the base of the cold-finger is a heating element with a maximum temperature of 200 °C. A Model 331 Lakeshore cryogenic temperature controller with DT-670 silicon diode cryogenic temperature sensors sets and measures the sample temperature. We regulate the systems temperature by setting to the first sensor, which is situated at the base of the cold finger, next to the heating element. The other sensor is placed directly beside the sample dome and gives a more accurate reading of the sample temperature. Further description of the cryogenic apparatus and low-temperature procedure can be found in a paper by FitzGerald et al. (10).

The left sample compartment is configured for room-temperature experiments. Figure 5.3, a photograph of the room-temperature apparatus. The sample fills a recess cup, which is screwed into a removable copper stand. A zinc selenide (ZnSe) dome, sealed to the copper stand with a rubber o-ring, encloses the sample and allows pressures over 100 bar to be applied. The stand is screwed to an aluminum bracket, which holds the sample in place within the DRIFTS optics in the sample compartment.

Adsorbates are let into the sample via a gas line. The number of moles of gas introduced to the sample is calculated using the Ideal Gas Law, with knowledge of the volume and pressure of the gas introduced. By measuring the resulting pressure and comparing it to the expected equilibrium pressure if no adsorption were to occur, we calculate the number of moles of gas adsorbed. By measuring the mass of MOF sample in the system before loading it, we determine the number of gas molecules adsorbed per sample formula unit.
5. EXPERIMENTAL APPARATUS AND PROCEDURE

Figure 5.3: Photograph of room-temperature sample holder and compartment in spectrometer - Symbols: (a) aluminum sample bracket, (b) High pressure ZnSe dome, (c) copper sample holder, (d) gas valve, (e) high-pressure gas line, (f) ellipsoid mirrors, and (g) vertical alignment adjust.
5.4 Data collection and manipulation

Each spectrum taken is an average of multiple scans. By averaging 50 or 100 scans, we reduce random noise in our spectra. Raw spectra of the MOF sample with adsorbate are referenced to pure-MOF spectra to obtain absorbance spectra showing peaks due to adsorbate molecules. If a reference spectrum has intensity $I_o(\omega)$ and a spectrum with adsorbate has intensity $I(\omega)$, an absorbance spectrum showing absorbance $A(\omega)$ is found by calculating

$$A(\omega) = -\log \frac{I(\omega)}{I_o(\omega)}.$$  \hfill (5.1)

In general we are more interested in relative absorbance than absolute absorbance because a variety of factors that change from experiment to experiment affect the measured absorbance magnitude, such as the quantity of sample and the optical alignment. In principle, absorbance spectra show only peaks due to adsorbate molecules. In practice, interactions between the adsorbate and the host can cause shifts in the host peaks, leading to differential peaks in the absorbance spectrum where a shifted host peak is divided by the reference host peak. Differential peaks are easily recognizable and can be disregarded. We apply a piecewise linear baseline correction and a fourfold interpolation to each absorbance file.

Carbon dioxide and methane are infrared-active in the gas phase as well as the adsorbed phase; thus gas-phase peaks appear in our CO$_2$ and CH$_4$ spectra. In general gas peaks are significantly sharper than adsorbed features making it straightforward in practice to distinguish one from the other. Nonetheless, spectra displayed in this thesis at pressures above 100 mbar have gas phase signal removed through the following procedure: Raw spectra are taken of CO$_2$ or CH$_4$ in a sample of CaF$_2$, which adsorbs no gas and scatters infrared radiation. Spectra of CaF$_2$ with gas-phase CO$_2$ or CH$_4$ are referenced to spectra of CaF$_2$ at vacuum to create absorbances showing only gas-phase peaks. These spectra are subtracted from absorbances of CO$_2$ or CH$_4$ in the MOF host at comparable equilibrium pressures to create absorbance spectra that in principle show adsorbed-phase peaks alone. In practice, some gas phase peaks remain after subtraction, but they are easily recognized and ignored.
6

Results and analysis

In this chapter we present and analyze spectroscopic data of carbon dioxide adsorbed to Mg-MOF-74. We compare spectra of CO$_2$ in Mg-MOF-74 to spectra of CO$_2$ in Mn-, Co-, and Zn-MOF-74 and discuss relative peak shifts in among the species. Finally, we present spectra of methane adsorbed to Mg-MOF-74 and comment on differences in adsorption capacity for CH$_4$ versus CO$_2$.

6.1 Overview

Figure 6.1 displays two absorbance spectra of CO$_2$ bound to Mg-MOF-74 at concentrations of 0.21 and 0.50 CO$_2$ per open Mg site. For MOF-74 we typically measure concentration in adsorbed molecules per open metal site, which is equivalent to adsorbed molecules per half-formula unit and is what Liu et al. used in their neutron diffraction investigations (L7).

There are two principle regions of the spectra in which peaks appear. The lower frequency region (2200-2500 cm$^{-1}$) has bands that we associate with the adsorbed-phase $\nu_3$ transition of CO$_2$. A higher frequency region (3500-3800 cm$^{-1}$) contains bands due to adsorbed-phase combination-mode transitions consisting of the the fundamental symmetric stretch transition plus the fundamental asymmetric stretch transition ($\nu_1 + \nu_3$) and the overtone of bending mode transition plus the fundamental asymmetric stretch ($2\nu_2 + \nu_3$). The two combination-mode transitions are altered by the Fermi resonance of the $\nu_1$ fundamental and $2\nu_2$ overtone transitions. While keeping in mind that in reality the two frequencies in the 3500-3800 cm$^{-1}$ region result from a linear
Figure 6.1: Full absorbance spectra of CO$_2$ in Mg-MOF-74 - The red trace corresponds to a concentration of 0.21 CO$_2$ per open Mg site; the blue trace corresponds to 0.50 CO$_2$ per Mg site. Dashed lines indicate Q(0) gas phase values of the $\nu_3$ transition (2349 cm$^{-1}$) and the $\nu_1 + \nu_3$ and $2\nu_2 + \nu_3$ Fermi resonance combination transitions (3613 cm$^{-1}$ and 3715 cm$^{-1}$). Spectra have gas-phase peaks subtracted off and are offset for clarity.
combination of the two transitions, we will refer to the dashed line in the figure at 3613 cm$^{-1}$ as the $2\nu_2 + \nu_3$ transition and the line at 3715 as the $\nu_1 + \nu_3$ transition for ease in referring to the peaks independently.

![Figure 6.2: Infrared spectra of gas-phase carbon dioxide.](image)

**Figure 6.2: Infrared spectra of gas-phase carbon dioxide.** - From bottom to top, spectra were taken at pressures of 5.8, 27, 81, 167, 423, and 940 mbar, all at 0.5 cm$^{-1}$. Inset are zoomed-in plots of the two regions where rovibrational bands appear. The left inset plot shows the rotational sidebands of the $\nu_3$ vibrational transition. The central Q-frequency, which is quantum-mechanically forbidden, is marked by the dashed line. The right inset plot shows the rotational sidebands of the $2\nu_2 + \nu_3$ and $\nu_1 + \nu_3$ combination transitions with Q-frequencies marked by dashed lines. (should I mention how we needed to go to 0.1 to resolve the peaks?)

In Fig. 6.2 we show infrared spectra of gas-phase CO$_2$ at a variety of concentrations. Rovibrational peaks in the 2200-2500 cm$^{-1}$ and the 3500-3800 cm$^{-1}$ regions are visible. Inset are zoomed-in plots of the two regions where bands appear. The left inset plot shows rotational sidebands surrounding the central $\nu_3$ transition frequency, which, as
6. RESULTS AND ANALYSIS

discussed in § 2.5 is quantum-mechanically forbidden. The right inset plot shows rotational sidebands of the \(2\nu_2 + \nu_3\) and \(\nu_1 + \nu_3\) combination transitions with Q-frequencies marked by dashed lines. The gas-phase rovibrational bands are very sharp and are unresolved in our 0.5 \(\text{cm}^{-1}\) resolution spectra, and even at 0.1 \(\text{cm}^{-1}\) resolution, the bands were still not fully resolved.

In the adsorbed-CO\(_2\) spectra, we do not see rotational side bands, which is consistent with neutron-diffraction data, indicating that the bound molecule cannot rotate freely \([30]\). Instead a single or a few peaks appear that are due to pure vibrational transitions in the CO\(_2\) molecule. Recall from § 2.5 that the restriction in free CO\(_2\) prohibiting transitions in which only the vibrational quantum number of the CO\(_2\) changes is lifted in the adsorbed phase. An infrared photon can cause simultaneous transitions in the molecule and in the host framework that balance the sign of the wavefunction describing the system.

In the following section we examine the asymmetric stretch (\(\nu_3\)) peaks of adsorbed CO\(_2\) in Mg-MOF-74 and compare them to equivalent peaks of CO\(_2\) in other members of the MOF-74 isostructural series.

6.2 Asymmetric Stretch of CO\(_2\)

In this section we focus on the \(\nu_3\) transition of adsorbed CO\(_2\) in Mg-MOF-74 as compared to Mn-, Co-, and Zn-MOF-74. We identify the adsorbed-phase bands and discuss their shifts with temperature and concentration.

Figure 6.3 displays the \(\nu_3\) region of spectra of adsorbed CO\(_2\) in Mg-MOF-74 at low equilibrium pressures, all below 3 mbar. All peaks that appear are given in Table 6.1 and are labeled either 1, 2, or 3.

<table>
<thead>
<tr>
<th>Isotopologue</th>
<th>Gas Phase</th>
<th>Peak 1</th>
<th>Peak 2</th>
<th>Peak 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{12}\text{C}^{16}\text{O}_2)</td>
<td>2349</td>
<td>2352.5</td>
<td>2340.5</td>
<td>2367.5</td>
</tr>
<tr>
<td>(^{13}\text{C}^{16}\text{O}_2)</td>
<td>2283.5</td>
<td>2286</td>
<td>2257</td>
<td>–</td>
</tr>
</tbody>
</table>

The smaller peaks numbered 1 and 2 are due to the \(\nu_3\) transition in the \(^{13}\text{C}^{16}\text{O}_2\) isotopologue, which occupies 1% of naturally occurring CO\(_2\). In § 6.2.4 we will analyze
Figure 6.3: Asymmetric stretch ($\nu_3$) region of adsorbed CO$_2$ in Mg-MOF-74 - Spectra were taken at 1 cm$^{-1}$ resolution at ambient temperature and decreasing equilibrium pressure. From top to bottom, spectra were taken at 2.6 mbar, 0.9 mbar, 0.2 mbar, and base pressure ($\leq$0.1 mbar), all of which correspond to concentrations of adsorbed CO$_2$ of less than 0.2 CO$_2$/Mg. The dashed line marks the gas-phase $\nu_3$ frequency. The smaller peaks numbered 1 and 2 are due to the $^{13}$C$^{16}$O$_2$ transition; the larger peaks numbered 1, 2, and 3 are due to $^{12}$C$^{16}$O$_2$. 
these peaks further and justify their designation as belonging to $^{13}\text{C}^{16}\text{O}_2$.

Focusing on the main $^{12}\text{C}^{16}\text{O}_2$ peaks in the 2300-2400 cm$^{-1}$ region, we have labeled the peaks 1, 2, and 3 for clarity. Peak 1 refers to the central, highest intensity absorption peak of trapped CO$_2$. Peak 2 is the left shoulder redshifted from peak 1 by 12 cm$^{-1}$. Peak 3 is the right shoulder blueshifted from the main peak by 15 cm$^{-1}$. In §6.2.2 we will discuss the origins of peaks 2 and 3 as contrasted with peak 1.

### 6.2.1 Blueshift in Mg-MOF-74

Here we discuss the frequency shift upon adsorption of the $\nu_3$ transition of carbon dioxide, focusing on the central, highest intensity band, which we have termed peak 1. The peak corresponds to the CO$_2$ adsorbed to the primary binding site in Mg-MOF-74, which neutron diffraction data confirms is next to the open metal site. This primary site peak is blueshifted from the gas phase $\nu_3$ transition by approximately 4 cm$^{-1}$, although the shift depends on concentration of adsorbed CO$_2$, as we will discuss in §6.4.

Figure 6.4 shows spectra of adsorbed CO$_2$ in four members of the MOF-74 isostructural series. From top to bottom, the traces correspond to CO$_2$ in the magnesium, manganese, cobalt, and zinc compounds. The Mg-MOF-74 spectrum was taken at base pressure; all loaded CO$_2$ was adsorbed. The Mn-MOF-74 spectrum was taken at an equilibrium pressure of 48 mbar, and the Co- and Zn-MOF-74 spectra were taken at equilibrium pressures of 58 and 77 mbar respectively. All spectra were taken at 1-cm$^{-1}$ resolution.

The higher CO$_2$ signal in the Mg-MOF-74 sample at lower equilibrium pressure as compared to the Mn-, Co-, and Zn-MOF-74 samples is a result of the higher CO$_2$ binding energy of the Mg compound with respect to the other compounds. At equivalent pressures, there is a higher concentration of adsorbed CO$_2$ in the Mg sample than in the other samples.

The spectra CO$_2$ in the four compounds have similar features. Each clearly has a central, highest intensity peak shaped like the Mg-MOF-74 trace’s peak 1 and a right shoulder shaped like what we termed peak 2. The principle difference among the spectra are the frequency shifts of the adsorbed peaks relative to the gas-phase frequency. As is shown in Table 6.2, the frequency of the main, highest intensity peak...
Figure 6.4: Absorbance spectra of $\nu_3$ transition of CO$_2$ in the isostructural series - From top to bottom, the traces correspond to CO$_2$ in the magnesium, manganese, cobalt, and zinc compounds. The dashed line at 2349 cm$^{-1}$ marks the gas phase CO$_2$ asymmetric stretch transition frequency. The Mg-MOF-74 spectrum was taken at base pressure; all loaded CO$_2$ was adsorbed. The Mn spectrum was taken at an equilibrium pressure of 48 mbar, and the Co and Zn spectra were taken at equilibrium pressures of 58 and 77 mbar respectively, all of which correspond to concentrations of less than 0.2 CO$_2$/Mg. All spectra were taken at 1-cm$^{-1}$ resolution and are offset for clarity.
6. RESULTS AND ANALYSIS

is redshifted with respect to the gas-phase asymmetric stretch transition in the Mn-, Co-, and Zn-MOF-74 materials, whereas it is blueshifted in Mg-MOF-74.

Table 6.2: Frequencies of CO$_2$ $\nu_3$ peaks in M-MOF-74—Values are given to the nearest cm$^{-1}$

<table>
<thead>
<tr>
<th>M</th>
<th>Frequency</th>
<th>Shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>(gas phase)</td>
<td>2349</td>
<td>-</td>
</tr>
<tr>
<td>Mg</td>
<td>2353</td>
<td>4</td>
</tr>
<tr>
<td>Mn</td>
<td>2343</td>
<td>-6</td>
</tr>
<tr>
<td>Co</td>
<td>2341</td>
<td>-8</td>
</tr>
<tr>
<td>Zn</td>
<td>2340</td>
<td>-9</td>
</tr>
</tbody>
</table>

The precise mechanism behind the blueshift in Mg-MOF-74 is as of yet unknown. Theoretical calculations reported by Wu et al. predict a redshift in the $\nu_3$ transition of CO$_2$ upon adsorption to Mg-MOF-74. In the as of yet unpublished paper by FitzGerald et al. on MOF-74 binding sites for molecular hydrogen, the vibrational frequency redshift for adsorbed H$_2$ is found to correlate with binding energy. Adsorbed CO$_2$ clearly bucks this trend, as Mg-MOF-74 is the most strongly binding species for carbon dioxide. However, the vibrational peaks due to hydrogen in the Mg-MOF-74 primary site are less redshifted than the trend would suggest. This discrepancy is consistent with that observed in our adsorbed CO$_2$ spectra. FitzGerald et al. speculate that the inconsistency could be a reflection of magnesium’s smaller cationic size relative to the other metals in the series (37).

Many literature sources have reported a blueshift of the CO$_2$ asymmetric-stretch transition frequency upon interaction with adsorbents (34, 41, 42). In particular, Valenzano et al. have published IR data on adsorbed CO$_2$ in Mg-MOF-74 and report the same 4 cm$^{-1}$ blueshift we see (43). Although they report that the blueshift agrees with computational calculations, they offer no physical explanation for it. Zhou et al., in studies of CO$_2$ adsorbed to metal ions attribute their observed blueshift in the $\nu_3$ transition to the electrostatic character of the interaction (41). They offer no further explanation however. In a paper on IR spectroscopy of Fe$^+$(CO$_2$)$_n$ clusters, Gregoire and Duncan attribute a blueshift in the $\nu_3$ frequency to increased repulsion from the metal as the oxygen vibrates against it (42). In another paper on metal-CO$_2$ clusters,
Gregoire et al. attribute observed blueshift to increased repulsion on the inside potential wall due to the metal ion (34).

As follows from the interaction frequency shift analysis in §3.2, increased repulsion on the vibrational potential walls corresponds to a positive value of $\langle U_s \rangle_r$, which can lead to a blueshift. Therefore, it seems likely that Gregoire’s explanation for blueshift applies to the $\nu_3$ transition of CO$_2$ adsorbed to Mg-MOF-74. The redshifts in the other three compounds suggest that the repulsive interaction between CO$_2$ and the other metals is less.

### 6.2.2 Band Identification

The spectra of CO$_2$ in the four compounds have similar features. Each clearly has a central, highest intensity peak and a right shoulder shaped like peaks 1 and 2 in the Mg-MOF-74 spectra. We call the central peak in each MOF-74 species peak 1 and we attribute it to CO$_2$ in its primary binding site and preferred orientation in the framework, bound end-on next to the exposed metal, as shown in neutron diffraction data (33). We attribute the right shoulder feature in each MOF, which we call peak 2 for all MOFs in the series, to CO$_2$ in a particular location or configuration with respect to the framework.

Dietzel et al. and Valenzano et al. display spectra of the $\nu_3$ bands of adsorbed CO$_2$ in Ni-MOF-74 and Mg-MOF-74 respectively. Both sets of spectra show the same shoulder band that we have called peak 2 (13, 43). Dietzel et al. attribute peaks 1 and 2 to CO$_2$ occupying the primary binding site by the exposed metal.

In the following paragraphs we will justify the conclusion that peak 2 arises from CO$_2$ in the primary site, just like peak 1. We will further speculate on possible origins for the 12 cm$^{-1}$ difference between the frequencies of the two peaks.

We begin by considering a range of possible explanations for the origin of peak 2 and rule out explanations that are incompatible with our results, while keeping in mind that there may exist other explanations that we have not considered. Possible origins of peak 2 are as follows: it could arise from CO$_2$ occupying secondary sites in the framework; it could arise from CO$_2$ in the same primary site that leads to peak 1 but in a slightly different orientational configuration; it could be due to CO$_2$-CO$_2$ interactions; it could arise from librational or translational sidebands.
6. RESULTS AND ANALYSIS

Even though none of the CO$_2$ concentrations reported are above one adsorbed CO$_2$ molecule per primary site, it is possible that bands due to less-energetically-favorable secondary sites could appear in our spectra. At ambient temperatures, at which the majority of our spectra were taken, entropic effects become important and allow for less energetically favorable sites to begin to fill before all primary sites are completely occupied. Therefore, we cannot use a low-concentration argument to rule out a secondary site as the cause of peaks 2 and 3.

We rely on the results found by FitzGerald et al. to conclude that peak 2 does not arise from carbon dioxide occupying a secondary site in a different location in the framework cell (37). In spectroscopic studies of molecular hydrogen in the MOF-74 series, the frequency of the peaks due to hydrogen in the primary binding site shift upon substitution of coordination metal, whereas the secondary site peaks remain essentially fixed. Neutron studies indicate that the primary binding site for H$_2$ in MOF-74 is next to the exposed metal whereas secondary sites are farther away from the metal (19). FitzGerald et al. conclude that the proximity of the primary site to the metal explains the dependence of the measured frequency shift on the metal’s identity, whereas secondary sites are far enough away from the metal such that the vibrational frequency shifts are virtually unaffected by the identity of the metal.

In spectra of CO$_2$ in the MOF-74 series, as shown in Fig. 6.4, peaks 1 and 2 shift the same amount upon metal substitution. Table 6.3 gives the shift of peak 2 relative to peak 1, which is consistently -12 cm$^{-1}$ across the series, indicating that the two peaks must be due to carbon dioxide with the same center of mass location relative to the MOF with respect to the metal. In particular they are both due to CO$_2$ occupying the primary, open metal site, as their frequency shifts depend on the identity of the coordination metal.

Spectra taken at a range of temperatures aid us in narrowing down the possible origins of peak 2. Figure 6.5 displays temperature dependent spectra of the $\nu_3$ CO$_2$ peaks in Mg-MOF-74. At low concentration (0.025 ± 0.005 CO$_2$ molecules per open metal site), peak 2 appears as a discrete band at 2341 cm$^{-1}$. As the system cools, the peak shrinks, and it disappears below the noise level at roughly 100K. Peak 1, at 2353 cm$^{-1}$, sharpens with cooling. At 65K a distinct right shoulder appears at 2355 cm$^{-1}$. We discuss the origin of this right shoulder peak in the following section.
6.2 Asymmetric Stretch of CO$_2$

Figure 6.5: Temperature dependence of $\nu_3$ peaks of CO$_2$ in Mg-MOF-74 - Spectra were taken at 0.5 cm$^{-1}$ resolution as the system cooled at a concentration of 0.025 ± 0.005 CO$_2$ per open metal site. From top to bottom, traces correspond to spectra taken at 303K, 251K, 222K, 193K, 163K, 133K, 104K, 75K, 65K, 54K, 44K, and 34K. The dashed line represents the gas phase $\nu_3$ transition; the solid lines mark the central frequencies of the adsorbed CO$_2$ peaks.
If peak 2 were due to interactions among CO₂ molecules in adjacent sites perturbing the potential energy well of CO₂ in the primary site, then molecules would have to migrate to sites farther away from one another at low temperatures for peak 2 to disappear upon cooling. On the timescale of our experiments, however, we observe that the molecules are frozen into their sites below 200K and do not migrate. Thus, CO₂–CO₂ interactions cannot explain the difference between the origins of peak 2 and peak 1. In §6.4, we discuss features in our spectra that can be attributed to CO₂–CO₂ interactions.

The shrinking of peak 2 with decreasing temperature suggests that peak 2 corresponds to a configuration of the molecule in the framework that is less energetically favorable than that which causes peak 1. The transitions corresponding to peak 2 may arise from molecules at a slightly different angle with respect to the metal, or molecules at a slightly different center-of-mass position. The potential well for bound CO₂ may have two local minima at slightly different energies, corresponding to two different orientations or positions with respect to the metal. Vibrational transitions while the molecule is in one configuration may differ from transitions in which the molecule is in the other configuration.

A slightly different possible explanation does not require the existence of a potential well with two local minima. Wu et al. report that their neutron diffraction measurements indicate that CO₂ bound to Mg-MOF-74 can occupy a range of angular orientations with respect to the metal[30]. At high temperatures they report that the orientational disorder increases. In other words, the CO₂ populates more excited librational levels. It is possible that peaks 1 and 2, correspond to two transitions, one in which the molecule remains in a librational ground state and one in which it remains in a librational excited state. This phenomenon would be analogous to vibrational transitions of ortho and para hydrogen (22).

In hydrogen there exist peaks corresponding to ΔJ = 0 vibrational transitions in which the initial state has J=1 (ortho hydrogen) and ΔJ = 0 transitions in which the initial state has J=0 (para hydrogen). The energy spacings between these two transitions differ slightly from one another, such that there is a six cm⁻¹ difference between the peaks.

It is plausible that a similar phenomenon may be leading to the 12 cm⁻¹ difference between the frequencies of peaks 1 and 2. If at room temperature, bound CO₂ occupies...
two different librational states, one of lower energy than the other, then pure vibrational transitions in which the molecule remains in its ground librational state may differ from transitions in which it remains in the second, excited librational state by 12 cm\(^{-1}\). The temperature dependent data would allow us to assign peak 2 to the librational excited state. As the temperature decreases, that excited state becomes depopulated, and peak 2 disappears.

Knowledge of librational energy spacings would aid in classifying peak 2 with more certainty.

### Table 6.3: Frequencies in cm\(^{-1}\) of CO\(_2\) \(\nu_3\) peaks in M-MOF-74

<table>
<thead>
<tr>
<th>(M)</th>
<th>Peak 2</th>
<th>Shift from peak 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>2341</td>
<td>12</td>
</tr>
<tr>
<td>Mn</td>
<td>2331</td>
<td>12</td>
</tr>
<tr>
<td>Co</td>
<td>2329</td>
<td>12</td>
</tr>
<tr>
<td>Zn</td>
<td>2328</td>
<td>12</td>
</tr>
</tbody>
</table>

Analysis similar to that used for identifying the origin of peak 2 may be applied to the right shoulder band that we have named peak 3. However, present data is insufficient as the temperature-dependent spectra and spectra taken of CO\(_2\) in the other MOF-74 species are at concentrations that are too low for peak 3 to be visible. The characterization of peak 3 will be left as a topic for future work.

#### 6.2.3 Low-temperature peak

Figure 6.5 shows that as the temperature decreases, a band at 2355 cm\(^{-1}\) becomes resolved as separate from the 2353 band we have called peak 1. Curve fits suggest that both overlapping peaks exist even at high temperatures and sharpen upon cooling, such that the doublet is visible. However, the sharpening effect alone is not enough to explain the appearance of the doublet band. The 2355 cm\(^{-1}\) band grows significantly with decreasing temperature, while the 2353 cm\(^{-1}\) band decreases in intensity. Just as with peak 2, the 2355 cm\(^{-1}\) band, which we will call peak 1a, likely arises from a slightly different configuration of CO\(_2\) in its primary site. We conclude that the configuration leading to peak 1a is slightly more energetically favorable than the configuration leading to peak 1. The energy difference between the two configurations \(\Delta E\) is only significant at temperatures for which the value of \(k_B T\) is comparable to \(\Delta E\), with \(k_B\) being the
Boltzmann constant and $T$ the temperature in K. At higher temperatures, entropic effects dominate and the configuration producing peak 1a is not preferred over that producing peak 1.

Comparing the intensities of the two peaks, that is, the areas under the curves, at a range of temperatures allows us to extract a rough measurement for $\Delta E$ between the configurations. We fit the bands to Lorentzian functions and find the areas $A_1$ and $A_{1a}$ underneath them. The ratio of these intensities is proportional to the ratio of the populations $P_1$ and $P_{1a}$ of the two configurations,

$$\frac{A_1}{A_{1a}} \propto \frac{P_1}{P_{1a}}. \quad (6.1)$$

Thus we can relate the ratio of areas to the energy difference $\Delta E$ via the Boltzmann factor,

$$\frac{A_1}{A_2} \propto e^{-\Delta E/k_B T} \quad (6.2)$$

Applying the natural logarithm to both sides of the equation yields

$$\ln \left( \frac{A_1}{A_2} \right) \propto \frac{\Delta E}{k_B T} \left( \frac{1}{T} \right) \quad (6.3)$$

Thus, by plotting the natural log of the ratio of the areas under the curves against the reciprocal of temperature, we can extract $\Delta E$. Figure 6.6 shows such a plot, called an Arrhenius Law plot, for the intensities of peaks 1 and 1a. The spectra from which the areas were calculated were taken at a concentration of $0.1 \pm 0.05$ CO$_2$/Mg at temperatures ranging from 30 to 100 K. Using such a low concentration allowed for the peaks to be narrow enough that they were distinguishable from one another. In (a), the blue trace that increases with temperature marks the intensity $A_1$ of peak 1. The red trace represents the intensity $A_{1a}$ of peak 1a.

The slope of the linear fit in (b) gives a difference in binding energy between the two configurations of $80 \pm 10$K, or $0.7 \pm 0.1$ kJ/mol.

We were unable to apply this Arrhenius Law analysis to find the energy difference between the configuration leading to peak 1 and that leading to peak 2 because the shape of the features in the $\nu_3$ region complicated curve-fitting. The region in which peaks 1, 2, and 3 appear likely contains other broader, overlapping bands. Fitting to
Figure 6.6: Temperature dependence of peak intensities - Intensities of bands at 2353 and 2355 cm⁻¹ plotted against temperature are given in (a). The blue trace that increases with temperature plots the intensity $A_1$ of the 2353 band (peak 1); the red trace represents the intensity $A_{1a}$ of the 2355 band (peak 1a). The intensities were calculated via fitting the overlapping bands to Lorentzian curves. In (b) is an Arrhenius Law plot based on the same peak intensities $A_1$ and $A_{1a}$ over the temperature range 50-90K. The slope of the linear fit in (b) gives a difference in binding energy between the two configurations of $80 \pm 10$K, or $0.7 \pm 0.1$ kJ/mol.
Figure 6.7: Concentration dependence of ν₃ peak of $^{13}$C$^{18}$O₂ in Mg-MOF-74. From bottom to top, spectra correspond to concentrations of 0.21, 0.35, 0.50, 0.63, 0.73, 0.84, and 1.0 CO₂ per open Mg site. The dashed line represents the gas phase ν₃ transition frequency for $^{13}$C$^{18}$O₂. Adsorbed phase frequencies and shifts are given in Table 6.4. Spectra are offset for clarity and gas-phase peaks are subtracted off.
Figure 6.8: Combination vibrational peaks of CO$_2$ in Mg-MOF-74 - Shown in (a) are the spectra with increasing concentration. Dashed lines represent gas-phase frequencies. From bottom to top, concentrations are 0.21, 0.35, 0.50, 0.63, 0.73, 0.84, and 1.0 CO$_2$ per open Mg site. In (b) the same spectra are divided by their associated CO$_2$ concentrations. Spectra are offset for clarity and gas-phase peaks are subtracted off.
three curves produced poor fits, yet fitting to more than four curves required more free parameters than we could justify.

6.2.4 Isotopologue peak

Bands due to the \( \nu_3 \) transition in the \( ^{13}\text{C}^{16}\text{O}_2 \) isotopologue appear near the gas phase \( ^{13}\text{C}^{16}\text{O}_2 \) frequency. Peak frequencies are given in Table \[6.1\]. At high CO\(_2\) concentrations the peaks due to the more abundant \( ^{12}\text{C}^{16}\text{O}_2 \) saturate and we can analyze the features of high-concentration spectra by studying the \( ^{13}\text{C}^{16}\text{O}_2 \) peaks.

As the concentration increases, the isotopologue’s peaks 1 and 2 increase in intensity before leveling off, suggesting saturation of the primary site to which they correspond. With increased concentration, the intensity of peak 2 may increase slightly relative to the peak 1 intensity. However, the increase is too small to lie outside of the associated uncertainty in the measured intensities.

\textbf{Table 6.4: Frequencies in cm}^{-1} \textit{of} \( \nu_3 \) \textit{peaks of} \( ^{13}\text{C}^{16}\text{O}_2 \) \textit{in Mg-MOF-74 at two characteristic CO}_2 \textit{concentrations} - Frequency shifts at increased concentrations are due to CO\(_2\)-CO\(_2\) interactions.\n
<table>
<thead>
<tr>
<th>CO(_2) Concentration</th>
<th>Peak 1</th>
<th>Peak 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.21 CO(_2)/Mg</td>
<td>2286.2</td>
<td>2274.6</td>
</tr>
<tr>
<td>1.0 CO(_2)/Mg</td>
<td>2284.8</td>
<td>2273.9</td>
</tr>
</tbody>
</table>

6.3 High-frequency region

In the high frequency region of 3500-3800 cm\(^{-1}\), two large peaks appear at 3597 cm\(^{-1}\) and 3706 cm\(^{-1}\) that grow with increasing CO\(_2\) concentration, as displayed in Fig. \[6.8\]. We attribute these peaks to the doublet transition due to the Fermi resonance of the combination \( \nu_1 + \nu_3 \) and \( 2\nu_2 + \nu_3 \) transitions, where \( 2\nu_2 \) is the overtone transition of the bending mode, which occurs at nearly the same energy as the \( \nu_1 \) transition. In the gas phase CO\(_2\) spectrum, we see two envelopes of peaks corresponding to this vibrational doublet in combination with rotational transitions. The gas-phase, pure-vibrational frequencies have been found to be 3613 cm\(^{-1}\) and 3715 cm\(^{-1}\) \( [24] \). Table \[6.5\] shows the peak frequencies and the shifts from their respective gas phase values. Both peaks are redshifted from their gas-phase values. Further work should include studying the
6.4 Concentration-dependent frequency shifts

As the concentration of CO₂ is increased, the adsorbed-CO₂ bands redshift by approximately 1 cm⁻¹. This shift-with-filling phenomenon was observed in H₂ data and was attributed to interactions among adsorbed CO₂ molecules in nearby sites.

As the concentration approaches 1 adsorbed molecule per metal site, the CO₂ molecules are packed closely together, such that their quadrupole moments interact, changing the potential well that each molecule experiences and thus changing their transition frequencies slightly.

6.5 Librations and translations

As mentioned in Chapter 2, bound CO₂ may undergo intermolecular transitions, in which it transitions to higher energy translational or librational levels. We do not see sidebands corresponding to these transitions clearly in our spectra, however, as the
predicted frequency-range in which they occur is in the same as a region in which there are many intense MOF bands. Additionally, the peaks may be smeared out due to slightly different conditions experienced by molecules in different unit cells.

### 6.6 Methane in Mg-MOF-74

![Graph showing frequency range and absorbance](image)

**Figure 6.9: Gas-phase and adsorbed-phase CH$_4$ in Mg-MOF-74: $\nu_3$ transition**  
- From top to bottom, spectra correspond to 150K, 200K, and 300K and concentrations all less than 0.3 CH$_4$ per Mg. Sharp bands are gas-phase rovibrational transitions. The broad band at 3001 cm$^{-1}$ corresponds to the $\nu_3$ transition of adsorbed-phase CH$_4$.

For the sake of comparison, we show spectra of the $\nu_3$ transition of CH$_4$ adsorbed to Mg-MOF-74. Figure 6.9 shows spectra taken, from top to bottom, at 150K, 200K, and 300K and concentrations all less than 0.3 CH$_4$ per Mg. Sharp bands are gas-phase rovibrational transitions. The broad band at 3001 cm$^{-1}$ corresponds to the $\nu_3$
transition of adsorbed-phase CH$_4$. The band is much weaker and broader and does not appear at temperatures above 150K. We attribute the broadening to greater rotational freedom of the adsorbed CH$_4$ molecule with compared to adsorbed CO$_2$. A redshift of -16 cm$^{-1}$ is observed from the gas-phase transition frequency of 3017, which suggests that the mechanism inducing the blueshift in the CO$_2$ has a weaker effect on CH$_4$. Future work should include further characterization of the adsorbed methane infrared spectrum in the MOF-74 series.
6. RESULTS AND ANALYSIS
Conclusion

Our data show a primary binding site for CO$_2$ in Mg-MOF-74 that leads to blueshifted frequencies of the asymmetric stretch fundamental transition. The blueshift is unique to Mg-MOF-74, and does not appear in Zn-, Co-, or Mn-MOF-74 spectra. More study must be done to develop a more rigorous theoretical explanation for the origin of the blueshift. For the time being we can state only that it appears likely that the shift is caused by an increased repulsion between the CO$_2$ and the magnesium ion with which it interacts strongly. Combination-mode transitions are redshifted with respect to gas-phase frequencies.

Adsorbed CO$_2$ in its primary site has several different configurations that lead to other smaller peaks in the adsorbed CO$_2$ spectra. CO$_2$–CO$_2$ interactions cause a slight shift in the observed frequencies.

Adsorbed methane in its primary site results in a broad band at 3001 cm$^{-1}$, which suggests more rotational freedom than bound carbon dioxide. The methane peak is redshifted with respect to the gas-phase transition frequency, from which we conclude that the mechanism producing the blueshift in the CO$_2$ transition does not produce a dominating effect on methane.

Suggestions for further work are given throughout Chapter 6. Investigation of CO$_2$ CH$_4$ more fully in the other members of the isostructural MOF-74 series would help confirm trends and explain features observed in this thesis.
7. CONCLUSION
References


REFERENCES


