A FOURIER TRANSFORM - INFRARED SPECTROSCOPY STUDY OF HYDROGEN INTERACTION WITH METAL-ORGANIC-FRAMEWORKS

BY DANIEL A. MAYER

A thesis submitted to the
Graduate School—New Brunswick
Rutgers, The State University of New Jersey
in partial fulfillment of the requirements
for the degree of
Master of Science
Graduate Program in Physics

Written under the direction of
Professor Dr. Yves J. Chabal

and approved by

New Brunswick, New Jersey
October, 2007
ABSTRACT OF THE THESIS

A Fourier Transform - Infrared Spectroscopy Study of Hydrogen Interaction with Metal-Organic-Frameworks

by Daniel A. Mayer

Thesis Director: Professor Dr. Yves J. Chabal

In the following the interaction of hydrogen with Metal-Organic-Frameworks investigated by Fourier-Transform Infrared (FT-IR) Spectroscopy is presented.

The study was performed using two different compounds: \((\text{Zn}(BDC)(TED)_{0.5})\cdot 2\text{DMF}\cdot 0.2\cdot \text{H}_2\text{O}\) and the very similar \(\text{Ni}(\text{NDC})(TED)\), whose exact structure was not characterized yet.

The removal of the solvent N,N-dimethylformide (DMF) was shown during the initial activation procedure. In addition, the decrease of an adsorbed water mode between 2000 and 4000 cm\(^{-1}\) could be confirmed while the benzene ring structure of the organic linkers (1610-1550 cm\(^{-1}\) and 1420-1335 cm\(^{-1}\)) stayed intact.

Furthermore the MOFs were exposed to high-pressure hydrogen (300-1000 psi) while performing in-situ FT-IR measurements. For the Zn-MOF new modes in the range from 4000 to 4300 cm\(^{-1}\) were observed and are believed to represent modes related to adsorption sites of hydrogen inside the MOF. After decreasing the pressure, these modes disappear slowly. No such results could be found for the Ni-MOF.

While the MOFs were exposed to high-pressure hydrogen a very intensive feature around 3400 cm\(^{-1}\) was observed. This mode was growing over time without any saturation and
was identified as water inside the MOF whose origin was determined to be the hydrogen gas.

An additional feature extending from 2900 to 3200 cm$^{-1}$ was associated with the destruction of C-H bonds. This development might be attributed to destructive effects of the water adsorption on the MOF or due to contaminations.

When considering MOF materials for storage application it has to be noted that the adsorption properties for water can interfere with other properties of the material.
Acknowledgements

My thanks go to Dr. Jean-Francois Veyan and Dr. Silvie Rangan whose knowledge and skills were very helpful and from whom I learned a lot.

Further I would like to thank professor Dr. Yves J. Chabal for his guidance and advice as well as professor Dr. Jing Li of the Chemistry Department at Rutgers University for preparing and providing the used Metal-Organic-Framework samples.

Adina A. Luican, Stefan P. Schäfer and Steffen Kahle for very useful discussions.
Dedication

I dedicate this work to my parents whom I thank for everything they did for me and their continuous support.
# Table of Contents

Abstract ................................................................. ii
Acknowledgements ....................................................... iv
Dedication ................................................................. v
List of Figures ........................................................... ix

1. Motivation and Introduction ........................................ 1
   1.1. Hydrogen as the Fuel of the Future ............................ 1
   1.2. Hydrogen Storage ................................................ 3

2. Introduction to Metal-Organic-Frameworks ......................... 7

3. Vibrational Spectroscopy .......................................... 10
   3.1. Rotations and Vibrations ....................................... 10
      3.1.1. Vibrations .................................................. 10
      3.1.2. Rotations .................................................. 13
      3.1.3. Coupling of Vibrations with Rotations .................... 16
   3.2. Fourier Transform-Infrared Spectroscopy ..................... 16
      3.2.1. The Michelson Interferometer .............................. 17
   3.3. Spectroscopy of High-Pressure Hydrogen ...................... 19
   3.4. Absorbance ..................................................... 22

4. Experimental Setup ................................................. 23
   4.1. High Temperature High Pressure (HTHP) Cell .................. 24
      4.1.1. Connections to the HTHP Cell ............................. 25
   4.2. Water Evaporator ................................................. 28
4.3. Pumping Station .............................................. 29
  4.3.1. Turbomolecular Pump .................................... 29
  4.3.2. Bakeout .................................................. 31
  4.3.3. Adsorption Pump ......................................... 32
  4.3.4. Ionisation Gauge ......................................... 32
4.4. The Nexus 670 FT-IR Spectrometer and its Components ............ 33
  4.4.1. Beampath .................................................. 33
  4.4.2. IR-Lightsource ........................................... 34
  4.4.3. IR-Detector .............................................. 34

5. Sample Composition and Preparation .................................... 37
  5.1. Metal-Organic-Framework Compounds .......................... 37
    5.1.1. Zn (BDC) (TED) ...................................... 37
    5.1.2. Ni (NDC) (TED) ...................................... 39
  5.2. Sample Preparation .......................................... 40
  5.3. Absorption of Self-Pressed KBr Pellets ........................ 41
  5.4. Determination of the Sample Amount ............................ 42

6. Experimental Results ............................................... 45
  6.1. Sample-Activation ........................................... 45
    6.1.1. Spectrum of N,N-dimethylformide (DMF) ................. 45
    6.1.2. Removal of the Solvent ................................ 48
    6.1.3. Stability of the MOFs .................................. 50
    6.1.4. Water removal ......................................... 51
    6.1.5. Experimental Difficulties ............................... 54
  6.2. Hydrogen-MOF Interaction ..................................... 55
    6.2.1. The Spectrum of Hydrogen ................................ 55
    6.2.2. Hydrogen-MOF Interaction ............................... 56
    Hydrogen - Zn-MOF Interaction ................................ 57
    Removal of the Hydrogen From the Zn-MOF ....................... 59
List of Figures

1.1. Chart of the consumption of petroleum by End-Use Sector in 2006 . . . 2
1.2. Illustration of Hydrogen as the exchange energy-form with its different
types of production mechanisms and uses. . . . . . . . . . . . . . . . . . 3
1.3. Comparison of different hydrogen storage techniques . . . . . . . . . 4
2.1. Single crystal x-ray structures for IRMOFs with different linkers. . . . 8
2.2. SEM images of MOF-5 crystals . . . . . . . . . . . . . . . . . . . . . . . 9
3.1. The Morse potential and its energy levels . . . . . . . . . . . . . . . . . 12
3.2. Example for harmonics of higher order in the spectrum of CO measured
with low spectral resolution. . . . . . . . . . . . . . . . . . . . . . . . . . . 13
3.3. High-resolution spectrum of $CO_2$ . . . . . . . . . . . . . . . . . . . . 15
3.4. Energy levels of the rotation of a rigid rotator. . . . . . . . . . . . . . 15
3.5. Intensity distribution of a rotation spectrum obeying the optical transi-
tion rule $\Delta J = \pm 1$. . . . . . . . . . . . . . . . . . . . . . . . . . . . . 17
3.6. Structure of the rotational-vibrational energy levels and allowed transi-
tions between them. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 17
3.7. Sketch of the beam through a Michelson Interferometer . . . . . . . . 18
3.8. Illustration of the interferogram and its corresponding spectrum which
can be transformed in each other using the Fourier Transformation. . . . 20
3.9. Illustration of a collision induced dipole. . . . . . . . . . . . . . . . . . 20
3.10. Temperature dependence of the spectral hydrogen features . . . . . . . 21
4.1. Photograph of the HTHP cell. The main components are labeled. . . . 23
4.2. Photograph of the HTHP cell inside the spectrometer. . . . . . . . . . 24
4.3. Photograph of the sampleholder which is placed inside the HTHP cell. 24
4.4. Schematic representation of the experimental setup. . . . . . . . . . . 26
4.5. Illustration of the basic internal principle of a regulator. 27
4.6. Schematic view of the self-built water evaporator 28
4.7. Sketch of the rotor-stator principle used in a turbo molecular pump. 30
4.8. Schematic view of a turbo molecular pump. 30
4.9. Illustration of the infrared beam inside the spectrometer. 33
4.10. Example of a single beam as it is recorded when measuring an empty, evacuated \(7 \cdot 10^{-6}\) torr chamber. 35

5.1. Secondary Building unit, organic linker and resulting structure of the Zn-based MOF 38
5.2. Chemical structure of N,N-dimethylformide (DMF). 39
5.3. Chemical structure of 2,6-Naphthalenedicarboxylic acid (NDC). 40
5.4. Schematic view of the used samples. 41
5.5. Photograph of an empty KBr pellet 41
5.6. Illustration of the loss in beam intensity due to the self-pressed KBr-pellets. 42
5.7. Absorption of the MOF samples 43
5.8. Photograph of a Ni-MOF based sample 43
5.9. Photograph of a Zn-MOF based sample 43
6.1. Spectrum of liquid DMF on KBr recorded in air. 46
6.2. Low-frequency region of the spectrum of liquid DMF on KBr recorded in air. 47
6.3. Spectra of DMF and a DMF-water mixture. 47
6.4. Spectrum showing the removal of DMF from the NDC-sample during activation 49
6.5. Spectrum showing the removal of DMF from the BDC-sample during activation 50
6.6. Spectrum of Zn (BDC) (TED) before and after the activation 51
6.7. Spectrum of Ni (NDC) (TED) before and after the activation 51
6.8. Spectra taken 10, 20, 30 and 50 minutes after the start of the baking process of the Zn-MOF. The removal of the O-H-water feature between 2000 and 4000 cm\(^{-1}\) is visible.

6.9. Spectra taken 10, 20, 30 and 50 minutes after the start of the baking process of the Ni-MOF. The removal of the O-H-water feature between 2000 and 4000 cm\(^{-1}\) is visible.

6.10. O-H stretch region before and after the activation process.

6.11. Shift of the O-H peak during the cool-down.

6.12. Oscillations appearing in the single beam for an empty cell.

6.13. The spectrum of high pressure hydrogen for different pressures.


6.15. Hydrogen spectrum with Ni-MOF.

6.16. Hydrogen interaction with Zn-MOF after subtraction of the pure \(H_2\) spectrum.

6.17. Spectra of the removal of the hydrogen modes using the Zn-MOF.

6.18. Hydrogen interaction with Ni-MOF after subtraction of the pure \(H_2\) spectrum.


6.20. Spectra taken during a long time hydrogen exposure using the Ni-MOF.

6.21. Plot of the integrated area of the O-H stretch feature over time using the Ni-MOF.

6.22. Spectra of the \(CO_2\) mode taken during a long time hydrogen exposure using the Ni-MOF.

6.23. Plot of the integrated area of the \(CO_2\) mode over time using the Ni-MOF.

6.24. Spectra of the destruction feature in the C-H region taken during a long time hydrogen exposure using the Ni-MOF.

6.25. Plot of the integrated area of the destruction feature in the C-H region over time during long-time hydrogen exposure using the Ni-MOF.

6.26. Spectra showing the decrease of the O-H mode.
6.27. The secondary building unit of Zn (BDC) (TED) with complete ligands. 70
6.28. Development of the CO$_2$ mode during exposure of a KBr-pellet to high-pressure hydrogen. 70
6.29. Spectral-development during the introduction of water vapor into the HTHP cell using the Zn-MOF. 73
6.30. The O-H feature as recorded for introduced water vapor in comparison to the one appearing for hydrogen exposure. 74
6.31. Water content in high-pressure hydrogen gas 75
Chapter 1
Motivation and Introduction

The steadily growing energy consumption of the world’s population in combination with our limited resources of fossil fuels lead to increased research efforts in alternative energy sources during the last few years.

With the greenhouse effect and global warming in mind, new technologies should have zero or near zero emissions but at the same time provide comparable efficiencies and reliabilities as traditional fossil fuels like petroleum. Hydrogen is a promising candidate to address these problems in short- and mid-term applications in hydrogen powered fuel cells as well as combustion engines.

1.1 Hydrogen as the Fuel of the Future

The consumption of fossil fuels is steadily increasing and at the same time earth’s reserves are shrinking and will be depleted in the next 100 years if the current trend will continue. By far the largest amount of petroleum is being used in the transportation sector as figure 1.1 illustrates. Nearly 68 % of this fossil resource is used in the United States for powering cars, trucks and trains.[1]

Not only will this resource in the near future not be available in the needed quantities anymore, but the combustion process also produces large amounts of $CO_2$, one among the greenhouse gases which are a major factor for the global warming process. The emissions of $CO_2$ from oil contributes 42% to the worlds total $CO_2$ emissions[1].

Taking all this into account it is necessary to find an alternative energy source which can
be used as a substitute for fossil fuels. At the same time the new technology should address the problem of the greenhouse gas emissions and minimize these as far as possible.

The main focus of the current hydrogen research is on the transportation sector due to its large consumption mentioned above. Also other fossil fuel-powered application as off-grid power generators can be exchanged as soon as technologies get available.[2]

In general the hydrogen technology is more comparable to a battery which has to be refilled rather than a new form of primary energy. Hydrogen itself can not be an energy source which will substitute renewable energies, nuclear power etc. In contrast these will be used to produce the hydrogen which then can be utilized especially in mobile applications. The advantage is, that we can use electricity and therefore all current and future sources of electricity to produce hydrogen, which then can universally be used (see figure 1.2).

In order to make hydrogen usable in the transportation sector there are several problems to be solved. The U.S. Department of Energy (DOE) founded a program to address
these problems and to support targeted basic and applied research[2]. The following section will focus on the different hydrogen storage technologies available and under development.

1.2 Hydrogen Storage

The use of hydrogen as fuel for either fuel cells or combustion engines requires the storage of hydrogen on board a car for example. It is desirable to achieve a storage capacity which allows driving 300 miles per fuel filling as ordinary cars do today. At the same time safety, performance, weight and cost requirements have to be fulfilled.[2]

Therefore the Department of Energy (DOE) set well defined targets which should be achieved in order to make the new technology ready for deployment. The next milestone is set for the year 2010 where the systems should achieve $2 \frac{\text{kWh}}{\text{kg}}$ (i.e. 6 wt%), $1.5 \frac{\text{kWh}}{\text{l}}$ (i.e. 45 g $\text{H}_2$), and $4 \text{ per kWh}$. Another milestone exists for 2015 with higher
limits which can be found detailed in the DOE’s plan.[2]

Figure 1.3: Overview of different storage techniques currently under investigation and their efficiencies relative to the DOE’s targets for the next years.

The DOE-Program is supporting research for most of the promising techniques of which none is currently meeting the set requirements. Some of these materials will be discussed in the following. Figure 1.3 puts different storage mechanisms in relation and also shows the DOE’s goals for the next years. Currently investigated techniques include the more traditional high-pressure and cryogenic storage as well as novel approaches which include the storage in solids and the adsorption on high surface area materials.

When storing hydrogen as a compressed gas, high storage densities but a poor volumetric uptake is achieved. The secure tank containing the high-pressure gas is very heavy, has to be in cylindrical shape for stability reasons and is a high security risk in case of an accident. Even though it looks promising on chart 1.3 most of the research on this technique has been done and the desired performance can not be achieved.
Liquid hydrogen is another candidate which looks promising in the presented graph. But as the compressed storage method it is close to its limit. Liquid hydrogen (at 20.15 K) requires a well isolated tank. But even modern ones still cannot prevent the hydrogen from evaporating slowly when heat reaches the interior. This so called "boil-off" could lead to an empty tank within days and the leaking gas represents a high security risk especially when a vehicle is parked inside a closed building.

Metal hydrides, like sodium alanate for example, which is also investigated in our group [3], are the third possible storage technique presented. The storage is achieved by a reversible chemical reaction of the material with the hydrogen gas. These materials are getting close to the early DOE targets but are still under investigation.

Metal-Organic-Frameworks (MOFs) are high-surface area ($\approx 4500 \text{m}^2 \text{g}^{-1}$ for MOF-177 [4]) materials. Other examples of this material-class are various types of carbon nanotubes for examples. Hydrogen can be stored by physisorption inside the porous lattice structure of the MOFs. High-pressure (1100 psi) measurements at low temperatures (77 K) using MOF-177 showed hydrogen uptakes of up to 7.5 wt% [5]. This example of an exceptional uptake shows the relevance of MOFs for the development of storage materials. Even though many different MOFs were synthesized and characterized using various techniques, only few studies about the identification of possible binding-sites were performed. These studies could reveal valuable information on how to optimize the structure for increased storage capacity.

Fourier Transform-Infrared (FT-IR) Spectroscopy is a powerful tool to determine vibrational energies of bonds which are present inside the investigated sample. These energies allow conclusions about the position of adsorbed species. Comparison with theoretical calculations can further improve the identification of favored binding sites. While FT-IR was used more often to characterize a certain compound ([6, 7, 8, 9]), only very few FT-IR studies ([10] for example) on the interaction of MOFs with hydrogen
are known in literature.

The combined knowledge of the application of Van der Waals Density Functionals in the group of professor Langreth, the experience in synthesis of different MOF compounds by professor Jing Li in combination with the expertise on FT-IR available in the group of professor Yves J. Chabal lead to a joint approach to optimize Metal-Organic-Frameworks for hydrogen storage applications at Rutgers - The State University of New Jersey.
Chapter 2

Introduction to Metal-Organic-Frameworks

The name "Metal-Organic-Frameworks" (MOF) refers to coordination frameworks which consist of metal atoms at the framework's intersections and organic ligands which are often called "linkers". The name MOF was given to this class of materials by Omar Yaghi who was one of the first chemists working with these organic structures. The linker molecules are long chain organic molecules which are connecting the metal atoms to form a lattice structure. By choosing the linker and metal atoms carefully one can obtain porous structures which are called Microporous Metal-Organic-Frameworks (MMOF). For the scope of this thesis the phrase MOF is always referring to the sub-class of MMOFs. Omar Yaghi introduced a numbering scheme for MOF materials which makes references much easier as the chemical formulas can be very complex.[11]

MOF-2 was created in 1998 and in 2004 MOF-177 was synthesized for the first time. This shows that we are dealing with a very young but rapidly developing area at the same time. All MOFs have a one-pot synthesis in common which is performed using an organic solvent. This solvent is later still present in the framework's pores but can easily be removed by heating the material to according temperatures while pumping. The framework has to be designed in such a way that it remains stable and keeps its porous structure after the solvent molecules have been removed.[11]

After this removal has been successfully accomplished the resulting structure has extremely high surface area of up to $4500 \, \text{m}^2/\text{g}$ for the MOF-177 for example.[4]. These large surface areas exceed even those of active carbon, which had one of the largest known surface areas before. While having this large surface area MOFs have only a
Figure 2.1: Single crystal x-ray structures of IRMOF-n (n through 7, 8, 10, 12, 14, and 16), labeled respectively. Color scheme is as follows: Zn (blue polyhedra), O (red spheres), C (black spheres), Br (green spheres in 2), amino-groups (blue spheres in 3). The large yellow spheres represent the largest van der Waals spheres that would fit in the cavities without touching the frameworks. All hydrogen atoms have been omitted. (figure adapted from [12])

very low density of 0.5 - 1.5 $\text{g cm}^{-3}$ and therefore offer good starting conditions for high gravimetric uptakes of hydrogen.

One of the most studied MOF materials is the MOF-5 which can be easily produced using ZnO, an UV pigment and terephthalic acid which is an intermediate of the production of polyethylene terephthalate (PETP) that is being produced in enormous amounts for the production of PETP plastic bottles. This shows that a cheap mass production of MOF materials is in general possible.[11]

The mentioned elements of the MOF are not necessarily fixed to one special combination. Mohamed Eddaoudi et al. [12] showed that the pore size of a MOF-5 can be adjusted if the linker molecules are exchanged. One can think of the MOF as being built using a construction kit which allows many combinations that have to satisfy some border conditions. Exchanging the terephalat anions by benzocyclobutandicarboxylat one obtains smaller pores (IRMOF-6) while the substitution by naphtalindicarboxylat or pyrendicarboxylat results in larger pores (IRMOF-8 and IRMOF-14). Figure 2.1 illustrates different possible sizes using different linker molecules and shows the largest
van der Waals sphere which would fit in the porous structure. This variability of the pores makes MOFs suitable for gas storage applications as the structure can be adjusted to select only gas molecules of a certain size.[12]

Besides controlling the pore sizes it is also possible to change the dimensions of the MOF crystals themselves. As figure 2.2 shows, using MOF-5 as an example, the growth of ordered bigger crystals (Figure 2.2(a)) is possible as well as smaller crystals, which results in a rougher structure (Figure 2.2(b)).

The high uptake of 7.5 wt% [5], mentioned in the introduction section, is only achieved for temperatures of 77K at a pressure of 1100 psi. Measurements of the gravimetric uptake performed at room temperature and moderate pressures of 300 psi achieved less than 0.4 wt% for MIL-101 [13]. However, using a techniques called "Spillover", which uses a platinum catalyst, combined with carbon bridges, which were originally introduced to enhance the storage capabilities of carbon nanotubes[14], a gravimetric uptake of 4 wt% at room temperature and 1450 psi was achieved.[15] This recent development shows that further enhancement of MOFs can be achieved.
Chapter 3
Vibrational Spectroscopy

Vibrational Spectroscopy refers to a collection of techniques which allow the study of the inner degrees of freedom of molecules. By exciting these degrees of freedom one can gather information about the inner structure of the molecule and its bonding.

3.1 Rotations and Vibrations

In this section the rotations and the vibrations of diatomic molecules and the influences on their optical spectra will be discussed.

3.1.1 Vibrations

The inner degrees of freedom mentioned before are referring to the oscillations of the atoms inside a molecule around their equilibrium distances. The energy of these oscillations is in the region of infrared light which continues the visible spectrum on the low energy edge.

To derive a suitable model to describe vibrations we first assume a diatomic molecule whose atoms are connected by a harmonic oscillator system with a force constant $k$. Solving the problem for the resulting quadratic potential (equation 3.1) quantum-mechanically yields its energy eigenvalues (equation 3.2). The index $e$ will in the following refer to the equilibrium.

\[
V = \frac{V}{2} (R - R_e)^2 \\
E_{vib} = \hbar \omega \left( \nu + \frac{1}{2} \right) \quad \nu = 0, 1, 2, \ldots
\]
The quantum number $\nu$ refers to the energy levels of the possible vibrational states. In spectroscopy it is common to measure vibrational energies in the unit cm$^{-1}$, which can be easily obtained by evaluation $E_{\nu \nu} \approx \frac{hc}{\nu}$.[16]

The ground state according to this assumption has an energy $E_0 = \frac{\hbar \nu}{2}$ and states of higher quantum number are equally spaced by an energy $\Delta E = E_{\nu+1} - E_{\nu} = \hbar \nu e$. Given the selection rule $\Delta \nu = \pm 1$ for allowed optical transitions one would expect the resulting vibrational spectrum to only consist of one line. In order to observe this spectrum, the molecule must have a permanent dipole moment, which especially homonuclear diatomic molecules do not have and are therefore not, or only extremely weakly, due to multipole transitions, observable in optical spectra.[16]

The harmonic potential which has been discussed up to now has to be refined to better approximate the physical reality. If the interatomic distance $R$ decreases from the equilibrium $R_e$ repulsive forces between the atoms have to be represented by a steep increase in potential for the region $R < R_e$. On the other hand, when separating the atoms, i.e. for $R > R_e$, the molecule dissociates if the distance is large enough. The potential therefore has to have horizontal tangent in this region. The empirically derived Morse potential (equation 3.3) agrees well with experimental results.

$$V_{\text{Morse}} = D_e \left( 1 - e^{-\alpha (R - R_e)} \right)^2 \quad (3.3)$$

Important quantities in this relation are the dissociation energy $D_e$ and $\alpha := \left( \frac{m_r}{2D_e} \right)^{\frac{1}{2}} \omega_e$ which is characteristic to the molecule and contains the reduced mass $m_r$ and the harmonic oscillation frequency $\omega_e$. Figure 3.1 shows a sketch of the Morse compared to the harmonic potential and also illustrates the change in energy levels which shall be discussed further.[16]
Solving Schrödinger’s equation for the anharmonic oscillator one obtains the approximated energy levels and oscillation frequencies shown in figure 3.1 as

\[
E_\nu = \hbar \omega_e \left( \nu + \frac{1}{2} \right) - \chi_e \hbar \omega_e \left( \nu + \frac{1}{2} \right)^2
\]

\[
= \hbar \omega_e \left( \nu + \frac{1}{2} \right) \left( 1 - \chi_e \left( \nu + \frac{1}{2} \right) \right)
\]  \hspace{1cm} (3.4)

\[
\omega_e = \omega_e \left( 1 - \chi_e \left( \nu + \frac{1}{2} \right) \right)
\]  \hspace{1cm} (3.5)

with \( \omega_e = 2\pi \nu_e \). Knowing the anharmonicity constant \( \chi_e = \frac{\hbar \omega_e}{4D_e} > 0 \) one can see from equation 3.4 that the Morse potential causes the energy levels to shift down compared to the harmonic oscillator. There is only a finite number of allowed energy levels as for a certain quantum number the energy exceeds the dissociation energy \( D_e \) and the following states form a continuum for the dissociated molecule.[16]

The selection rule mentioned above changes for the anharmonic oscillator to \( \Delta \nu = \pm 1, \pm 2, \pm, \ldots \) and results in "harmonics" which are decreasing in intensity with increasing order (figure 3.2).
Vibrational spectroscopy is usually performed as absorption spectroscopy because at room temperature most molecules are in their ground state and spontaneous emissions are very rare. The occupation of vibrational energy levels is given by the Boltzmann distribution. Room temperature corresponds to an energy of $kT_{room} = 200 \text{ cm}^{-1}$ and thus the occupation of energy states above 1000 cm$^{-1}$, which are very common for the investigated compounds, is very low. Therefore mainly transitions originating from the ground state are visible in the spectra.

![Figure 3.2](image.png)

Figure 3.2: Example for harmonics of higher order in the spectrum of CO measured with low spectral resolution. Taken from [16]

### 3.1.2 Rotations

The discussion so far explains the appearance and the position of the lines which can be observed in an infrared absorption spectrum at low resolution (compare figure 3.2). However, high-resolution spectra as the one in figure 3.3 show a substructure of the line which cannot be explained by vibrations alone. Taking also rotations by the molecule of interest into account will enable us to understand also this phenomenon.

Assuming a diatomic molecule as a rigid rotor, i.e. with a fixed interatomic distance $R$, one can calculate the expected energy states of this system quantum mechanically. The calculation follow the ones well known in literature (compare [16]) and yield the
The following result.

\[ E_{\text{rot}} = \frac{\hbar^2}{2\Theta} J(J+1) \quad J = 0, 1, 2, \ldots \]  

(3.6)

with \( \Theta = m_r R^2 \) and \( m_r \) being the reduced mass

For spectroscopic purposes this energy is usually rewritten to units of \( \text{cm}^{-1} \)

\[ F(J) = \frac{E_{\text{rot}}}{\hbar c} = BJ(J+1) \]  

(3.7)

The new introduced quantity \( B \) is called the rotational constant, carries units of \( \text{cm}^{-1} \) and is given by

\[ B = \frac{\hbar}{8\pi^2 e^2 \Theta} \]  

(3.8)

The corresponding quantisation rule for the angular momentum \( |L| = \sqrt{J(J+1)} \cdot \hbar \) and \( L_z = M\hbar \) leads to a \( 2J+1 \) - fold degeneracy of the quantum states which will be important for analysis of the line intensities. Figure 3.4 shows the different rotational energy levels for each quantum number \( J \). One can easily see that the distance between two consecutive levels is increasing with \( J \). As a photon, which causes a transition to a higher state, carries a spin of 1, conservation of momentum tells us that the angular momentum of the rotation can only change by one unit, i.e. \( \Delta J = \pm 1 \). This relation can also be systematically derived from the symmetry of the wavefunctions using time-dependent perturbation theory. Using this selection rule and the relation for the energy states 3.7 the following condition has to be obeyed for a valid optical transition

\[ h\nu = E_{J+1} - E_J \]  

(3.9)

\[ \Rightarrow \quad \tilde{\nu}_{J\rightarrow J+1} = 2B(J+1) \]  

(3.10)

This relation determines the distance between two spectral lines and it turns out that each transition has an energy of \( 2B \) more than the one with the next lower quantum number. Therefore the observed lines are equally spaced from each other.[16]
The intensity of the observed lines depends on several factors. Firstly, each state has a different degeneracy as this increases with larger quantum number $J$ according to $(2J + 1)$. From that we would conclude that higher quantum numbers will have more and more intensity. But a transition $J \rightarrow J + 1$ can only be triggered from an already occupied state with quantum number $J$. Thus the thermal occupation of the states is important. As already discussed in the previous chapter the thermal energy distribution is given by Boltzmann and follows the relation $e^{-\frac{ Bhc \cdot J(J+1)}{kT}}$ which is decaying for large $J$ assuming the other parameters are constant.

Combining the occupation probability due to degeneracy of the energy levels and the thermal distribution of the occupied states one can write the total occupation probability as

$$ \frac{N_J}{N_0} = (2J + 1) \cdot e^{-\frac{ Bhc \cdot J(J+1)}{kT}} \quad (3.11) $$

This relation completely describes the intensity distribution as shown in the spectrum 3.5. For small $J$ the intensity increases with $J$ but for larger quantum states the exponential decay of the thermal occupation dominates and causes a decrease of intensities.
3.1.3 Coupling of Vibrations with Rotations

Having discussed vibrations and rotations separately it is now possible to understand the whole vibrational-rotational spectrum as one sees it in high-resolution spectroscopy. The fine structure which is observed in the lines of the vibrational spectrum corresponds to a rotational transition which occurs simultaneously. Without coupling between the two processes one can write the resulting energy levels simply as the sum of the already derived ones in the previous chapters.

\[ E(\nu, J) = E_{\text{vib}}(\nu) + E_{\text{rot}}(J) = \hbar \omega \left( \nu + \frac{1}{2} \right) + Bhc \cdot J(J + 1) \quad (3.12) \]

In addition to the allowed transitions \( \Delta J = \pm 1 \) and \( \Delta \nu = \pm 1 \), which have already been mentioned, a pure rotational transition with \( \Delta J = \pm 1 \) and \( \Delta \nu = 0 \) is also allowed. Figure 3.6 illustrates the allowed transitions. On can see the vibrational levels at \( \frac{1}{2} \hbar \nu_0 \) and \( \frac{3}{2} \hbar \nu_0 \), the resulting levels when taking rotations into account and the allowed transitions between them. In the resulting spectrum the transitions \( J' - J'' = -1 \) are forming the P-branch whereas the R-branch is formed by transitions yielding \( J' - J'' = +1 \). The Q-branch \( J' = J'' = 0 \) is in general not allowed because a sudden change in bond length due to a vibrational transition causes the rotational energy to change also.

The taken spectrum of \( CO_2 \) presented in figure 3.3 shows exactly the derived structure and can therefore be explained by this model.

3.2 Fourier Transform-Infrared Spectroscopy

Fourier Transform-Infrared (FT-IR) Spectroscopy is one of several possible techniques which is used to study vibrational modes. One major improvement compared to the previously frequently used grating techniques, is FT-IR’s multiplex-advantage which allows the analysis of all available wavelengths at the same time instead of using only monochromatic radiation.

To gather information about the intensity \( I \) of a single wavenumber \( I(\nu = \frac{1}{\lambda}) \) a detector
is used to measure interference patterns which are being produced as the infrared beam is passed through an interferometer. The interference process and how the spectral distribution is obtained from that will be discussed in the following section.

3.2.1 The Michelson Interferometer

A Michelson Interferometer consists of two mirrors and a beam splitter which are arranged as shown in figure 3.7. An incoming parallel beam from a source S is equally divided by the beam splitter. The fraction which is transmitted hits the fixed mirror, gets reflected and is partially reflected at the beam splitter towards the detector D. The other half of the beam gets reflected at the beam splitter, travels towards a movable mirror and gets partially transmitted through the beam splitter to also reach the detector D.

Depending on the position of the movable mirror the two beams travel a differently long distance before they reach the detector where they interfere. Therefore the type of interference, i.e. constructive or destructive, of certain frequencies is given by the position of the movable mirror.
Assuming we have an ideal beam splitter the waves coming from the two mirrors respectively have the same amplitudes $E_0$ and the sum at the detector for the total wave $E_t$ therefore yields

$$E_t = E_0 \cdot (\sin(\omega t - \alpha_1) + \sin(\omega t - \alpha_2))$$

$$= (\cos(\alpha_1) + \cos(\alpha_2)) \cdot E_0 \cdot \sin(\omega t) - (\sin(\alpha_1) + \sin(\alpha_2)) \cdot E_0 \cdot \cos(\omega t)$$

Squaring this relation and using the identity $A \cdot \cos(\phi) = E_0 \cdot (\cos(\alpha_1) + \cos(\alpha_2))$ one obtains

$$A^2 = 2E_0^2 + 2E_0^2 \cdot \cos(\alpha_1 - \alpha_2)$$

$$= 2E_0^2 \cdot (1 + \cos(\delta))$$

And since the intensity is proportional to the square of the amplitude

$$\Rightarrow I(\delta) = 2I_0 (1 + \cos(\delta))$$

To obtain an interferogram as in figure 3.8(a) the movable mirror is scanned and the phase difference $\delta$ can therefore be written as $\delta = 2\pi x/\lambda = 2\pi x\nu$ where $x$ is the position of the mirror. Because the light-source does not emit monochromatic radiation the spectral distribution $S(\nu)$ has to be taken into account. Using equation 3.15 this leads
to the following dependence for the intensity

\[ I(x) = \int_0^\infty 2S(\nu) d\nu + \int_0^\infty 2S(\nu) \cos(2\pi x \nu) d\nu \]  \hspace{1cm} (3.16)

Evaluating this equation for a zero path difference gives

\[ I(0) = 4 \int_0^\infty S(\nu) d\nu \]  \hspace{1cm} (3.17)

Together with equation 3.16 this leads to

\[ J(x) = I(x) - \frac{1}{2} I(0) = 2 \int_0^\infty S(\nu) \cos(2\pi x \nu) d\nu \]  \hspace{1cm} (3.18)

\[ = \int_{-\infty}^{\infty} S(\nu) \cos(2\pi x \nu) d\nu \]  \hspace{1cm} (3.19)

\[ \Rightarrow S(\nu) = \int_{-\infty}^{\infty} J(x) \cos(2\pi x \nu) dx \]  \hspace{1cm} (3.20)

Equations 3.19 and 3.20 show that \( J(x) \) and \( S(\nu) \) can be converted to each other using a Fourier Transformation. As we are measuring an interferogram \( J(x) \) (figure 3.8(a)) one can obtain the spectral distribution \( S(\nu) \) (figure 3.8(b)), which is often referred to as "single beam", by performing a Fourier Transformation on the data.

In a real spectrometer the intensity measured by the detector is stored as discrete data points which are averaged over a position \( x + \delta x \) of the mirror. To transform these values one can use the discrete Fourier Transformation which is executed using the Fast Fourier Transform algorithm in modern spectrometers / spectrometer software.

### 3.3 Spectroscopy of High-Pressure Hydrogen

As mentioned in section 3.1.1 FT-IR measurement are only sensitive to molecules which carry a permanent dipole moment. Hydrogen, a homonuclear diatomic molecule, has in a dilute gas a symmetric charge distribution and therefore no dipole moment (compare figure 3.9(a)).
(a) Interferogram $J(x)$ as it is recorded by the detector.

(b) Resulting spectrum obtained by performing a Fourier Transformation on the interferogram of figure 3.8(a).

Figure 3.8: Illustration of the interferogram and its corresponding spectrum which can be transformed in each other using the Fourier Transformation.

(a) Hydrogen, a homonuclear diatomic molecule with symmetric charge distribution

(b) Induced dipole which can be caused by collisions for example.

Figure 3.9: Illustration of a collision induced dipole in comparison to the symmetric charge distribution of a homonuclear diatomic molecule.

However, in high-pressure gases the molecules are involved in many collision which cause the symmetric charge distribution to be perturbed. This leads to a period of broken symmetry and a resulting electromagnetic dipole moment as illustrated in figure 3.9(b). While this dipole is present, the infrared radiation can excite transitions which can be seen in the spectrum primarily around $3500-5000 \text{ cm}^{-1}$ as presented in figure 3.10 for various temperatures. The reason for the breadth of the feature especially at 300 K can be explained by Heisenberg’s uncertainty principle. As the relaxation time after
a collision is very short, i.e. the dipole of the molecule only exists for a short period of time, the frequency of the according vibrational transition cannot be measured precisely. Lowering the temperature results in slower moving atoms which leads to longer collisions and therefore more distinct peaks.[18]

![Temperature dependence of the spectral hydrogen features. Picture adapted from [19]](image)

Due to induction effects the rotation selection rules are the same as for Raman scattering namely $\Delta J = 0, \pm 2$. This corresponds to the notation used in figure 3.10 where $Q = \Delta J = 0$, $S = \Delta J = -2$ and $O = \Delta J = +2$ with $J$ corresponding to the rotational quantum number of the initial state.[18].

The presence of two maxima in the Q branch as visible in figure 3.10 has been explained in 1968 by Van Kranendonk in terms of an intercollisional interference effect whose theoretical details are beyond the scope of this work. However, it should be mentioned that this splitting gets more intense with increasing pressure and is the only pressure/density dependent feature of the hydrogen spectrum.[18]
3.4 Absorbance

For interpreting IR-spectra, the introduction of the quantity "Absorbance" or "Optical Density" is very useful. Its definition is presented in equation 3.21 where $I_0$ refers to the intensity before the light passes through the sample while $I$ refers to it after.

$$A = \log_{10} \left( \frac{I_0}{I} \right)$$  (3.21)

The absorbance is therefore a measure for the fraction of the light which gets absorbed by the sample. The definition is especially useful because the absorbance is proportional to the concentration $c$ and extinction coefficient $\alpha$ of the sample. This can be derived from Beer’s law, where $l$ refers to the length of the path traveled through the sample.

$$I = I_0 e^{-\alpha c l}$$  (3.22)

$$\Rightarrow \ln \left( \frac{I_0}{I} \right) = \alpha \cdot c \cdot l$$  (3.23)

Transition from $\ln$ to $\log_{10}$ and the introduction of a new constant $\alpha'$ yields the term for the absorbance.

$$\Rightarrow \log_{10} \left( \frac{I_0}{I} \right) = \alpha' \cdot c \cdot l = A$$  (3.24)
Chapter 4
Experimental Setup

The experiments which have been performed require the variation of the sample temperature as well as the possibility to use hydrogen at preferably high pressures. For this purpose we are using an industrial built High Temperature High Pressure (HTHP) cell which is described in more detail in section 4.1. Various connections were made to the cell. These include a pumping station (section 4.3), high-pressure gas and a Fourier-Transform Infrared Spectrometer which is described in section 3.2.

Figure 4.1: Photograph of the HTHP cell. The main components are labeled.
4.1 High Temperature High Pressure (HTHP) Cell

The HTHP cell has been produced by the British company "Specac Limited" and is available under the product number P/N 5850. According to the specifications [21] the cell can sustain pressures up to 1000 psi and maintain a vacuum of 0.1 torr. Lower pressures can be achieved by constantly pumping the cell.

Figure 4.2: Photograph of the HTHP cell inside the spectrometer. The purge-tubing which connects the cell’s windows with the spectrometer can be seen. For clarity all connections were omitted.

Figure 4.3: Photograph of the sample-holder which is placed inside the HTHP cell. The circular opening holds the sample discs and is positioned in the optical axis when the sampleholder is inside the cell. The connections which are visible on the left border carry the signal for the temperature controller.

For the investigation of the sample using Fourier Transform Infrared (FT-IR) Spectroscopy the cell is placed in the sample compartment of a spectrometer which is illustrated in figure 4.2. In our case a Thermo Nicolet Nexus 670 spectrometer was used which is described in section 4.4. To allow the analysis using the infrared beam the cell has two zinc selenide (ZnSe) windows on the sides which are aligned in the optical axis of the spectrometer. These windows are mainly transparent for electromagnetic waves in the infrared region and can sustain the high pressures inside the cell.

The cell’s body is manufactured out of 316 stainless steel and can be heated together
with the window assembly from ambient temperature up to 200°C. A maximum temperature of 800°C can be reached for the sample-holder (figure 4.3) inside the cell. The temperature of both can be set independently by an electronic control-system which determines the temperatures through K-type NiCr/NiAl thermocouples. The accuracy in temperature is 0.2% for the sample and 1% for the body including the windows [21].

To cool the system down faster and to avoid exposure of the electronics-, plastics- and the outside heatshield parts to high temperatures, the cell is continuously cooled by a water pumping/chilling system. The cooling system needs to have a water flow between 0.75 and 1 liters/minute and to avoid damage to the cell care was taken that it did not exceed a water temperature of 25°C.

The sample holder which is shown in figure 4.3 can support a disc having a diameter of approximately 13 mm centered in the optical axis. The sample can be analyzed in transmission mode.

As the sample compartment can not be closed when the cell is in position, the windows of the cell are connected to the spectrometer using a tube on each side (see figure 4.2). These tubes are being purged with either nitrogen or dry air which helps minimizing unwanted influences of ambient water for example and protecting the windows and other sensitive parts of the setup.

4.1.1 Connections to the HTHP Cell

The HTHP cell has several connection ports and configuration options. The setup which has been designed and built for these experiments (figure 4.4) uses one port on the top (1) which is connected to a high-pressure (6000 psi), high-purity (99.9997%) hydrogen cylinder for the introduction of gaseous hydrogen. In addition to a valve placed directly on the hydrogen cylinder a regulator is attached to the bottle followed by another valve.

The regulator is used to control the pressure inside the cell. A normal valve would only
allow a direct connection between the hydrogen cylinder and the cell which would lead to the same equilibrium pressure in the whole system. In order to adjust the pressure the regulator uses a spring as an additional force on the low-pressure side (figure 4.5). Equation 4.1, in which the "A"-terms refer to the effective area of the parts marked in figure 4.5, quantifies this relationship.

\[ (P_2 \cdot A_{diaphragm}) + F_{diaphragm} + F_{bias-spring} + (P_1 \cdot A_{poppet}) = F_{range-spring} \]  

(4.1)

An additional regulator is attached to one of the side connectors (3) with the high
Figure 4.5: Illustration of the basic internal principle of a regulator. P1 is the high pressure and P2 the low pressure side.

A pressure side directed towards the cell and the low pressure side connected to another valve and then to an exhaust to the environment. This device can be used to release the pressurized gas from the cell in a secure and controlled way. The remaining pressure inside the cell is approximately the surrounding room pressure. In addition, the attached gauge is used to measure the pressure inside the cell. The gauge only has a very low precision of $\approx \pm 100$ psi.

To obtain a clean environment with as little residual gases as possible a pumping station is connected to the cell using the second top connector (2). This system and its parts is described thoroughly in section 4.3.

The last remaining port (4) is connected to a security burst disc which will prevent the cell from over-pressurization. A membrane / burst disc ruptures if the pressure inside the cell exceeds the safe upper limits of approximately 1000 psi.

All connections were done with 1/4 inch stainless steel tubing and swagelok connectors.

Two HTHP cells were used for two different experiments in the laboratory. Both were sharing all the connections to the hydrogen and the pump but could be separated using valves on all lines.
4.2 Water Evaporator

For some parts of the performed experiments it was necessary to introduce water vapor into the HTHP cell. Figure 4.6 shows an illustration of the designed and self-built water evaporation system.

A stainless steel nipple was connected to a swagelock cross which allowed the connection of all necessary tubing. The top port was connected to the pumping station, more precisely to the sorption pump between valves (V4) and (V5) in figure 4.4. One of the side connectors was connected to a nitrogen purge-line which could be used to clear remaining water out of the tubing and also to allow the creation of nitrogen/water mixtures. The remaining port went directly to the cell (connected after valve (V2) in sketch 4.4). The connections in this case were done with a combination of stainless...
steel tubing and flexible tubes. All connected lines can be closed using ball-valves which allows individual settings and configurations.

4.3 Pumping Station

The pumping station which is attached to connector (2) of the HTHP cell (figure 4.4) is used to create a clean environment in the cell after it has been opened to change the sample. This is important for the conducted experiments in order to achieve spectra which can be analyzed with as little unwanted features as possible. Besides the remaining hydrocarbons, carbon dioxide and especially water are residua which are not desirable.

Pumping, as mentioned earlier, is also an irreplaceable tool for the sample preparation where solvent molecules have to be removed from the MOF material which is described in section 6.1.2 and for the removal of adsorbed hydrogen molecules as shown in section 6.3.2.

The pumping system consists out of a turbomolecular pump, a rotary vane roughening pump as its backing pump and a cryogenic sorption pump.

4.3.1 Turbomolecular Pump

The used turbomolecular pump (in the following called shortly ”turbo pump”) is of the model ”TSF 12” and has been produced by ”Pfeiffer-Balzer”. Turbo pumps are molecular drag pumps which remove gas molecules from the pumped vessel by transferring momentum to them.

In a turbo pump the momentum transfer is realized by turbine like rotors which are alternated with stators in a cylindrical setup (figure 4.7). The pumped molecules collide with the rotors and due to the angle of the rotor’s blades the resulting momentum is directed towards the exhaust of the pump. The blades of the intermediate stator layers
are tilted in an opposite angle so that the molecules are held back and get compressed in this area (figure 4.8). The volume of the different stages is decreasing as a compression by a factor of ten is achieved in each step.[22, 23]

Due to very high rotation speeds ($10^4$ rpm) the demands on the bearings are very high. In recent models magnetic or ceramic bearings are being used which are maintenance-free and don’t require to be oiled. This is a great advantage because oil can travel from the pump into the evacuated vessel if pumps are stopped or fail which causes contamination with hydrocarbons inside the pumped compartment. The used bearings as well as the used DC motor can get hot very easily if high loads of gasses are being pumped. That is why most turbo pumps are being cooled by a water cooling system.
The used cell in this project does have a very small volume (80 ml) and hence a turbo pump without a water but air-cooling system is used.[22]

The turbo pump works in molecular flow conditions where \( \frac{\text{size of pumping stage}}{\text{mean free path}} < 1 \), i.e. the distance a molecule travels between collisions is large compared to the volume of the stage. At environmental pressure the mean free path of air is approximately 70 nm which requires final stages of a size below any possible design at the moment. For this reason a rotary vane pump is connected to the exhaust of the turbo pump to roughen the vacuum and reduce the pressure into the working region of the turbo pump. Before turning the pumps off, a valve (V9 in figure 4.4) has to be closed to prevent the already mentioned backstream of oil from the backing pump.

Using this kind of setup pressures of \( 6 \cdot 10^{-7} \text{ torr} \) could be achieved in our system after using the technique of bakeout (see section 4.3.2). The pressure measurement is performed using an ionisation gauge which is described in section 4.3.4.

### 4.3.2 Bakeout

To gain very low pressures and for this experiment especially to get rid of water vapors which can influence the taken spectra considerably it is necessary to accelerate the pumping process and therefore the outgassing and desorption of residua.

Baking the cell itself and the sample through the sampleholder to above 100° C was used to achieve this accelerated outgassing process. Baking was also used in the sample preparation process which is described in section 6.1.2 and 6.3.2. The pumping station which has been built using stainless steel UHV components could be baked to higher temperatures using heating strips at a voltage of approximately 70 V. These higher temperatures significantly accelerate the desorption of molecules (for example carbon monoxide) and improve the achievable pressures by one order of magnitude in the used setup.
4.3.3 Adsorption Pump

A running turbomolecular pump can not be exposed to room pressures for pumping because the high density of the molecules would cause damage to the blades. In order to maintain a clean environment in the pumping station however, it is favorable to keep the turbo pump running at all times.

Thus an adsorption pump was introduced to roughen the vacuum in the cell down to $\approx 10^{-4}$ torr. During the roughening process the pumping line of the turbomolecular pump is disconnected from the system. After a rough vacuum has been created, one can switch back to the running turbopump.

Sorption pumps consist of a vessel which is filled with zeolite, a high surface area ($\approx 1 \cdot \frac{m^2}{mg}$) alumino-silicate. This vessel is cooled from the outside using liquid nitrogen and causes all incoming particles to be adsorbed on the zeolite material. Baking the pump regenerates its pumping capabilities almost completely.[22]

4.3.4 Ionisation Gauge

The pressure inside the pumping station can be determined using an ionisation gauge. For our HV to UHV application a Bayard - Alpert gauge (BAG) is used.

This type of gauge has the design of an inverted triode with a thin wire as the collector in the middle which is surrounded by a metal grid. Further outside of this grid a hot tungsten filament is producing electrons which can positively ionize the present gas molecules. The collector is grounded whereas the grid is at a potential of +180V and the filament at +30V. Thus the ionized gas molecules are accelerated by the grid and can be detected using the collector by measuring the resulting current. The current is approximately linearly dependent on the pressure inside the system.[22]

Because of the position of the gauge inside the pumping station the measured pressure does not directly represent the pressure inside the cell. The precise difference in
pressure could not be determined but it was estimated that the resulting pressure inside the cell is not more than two orders of magnitude higher than inside the pumping station. The pressures mentioned in the following chapters are always referring to the pressure actually measured inside of the pumping station.

4.4 The Nexus 670 FT-IR Spectrometer and its Components

4.4.1 Beampath

![Illustration of the path traveled by the infrared beam inside of the spectrometer in the used setup. Besides the interferometer (see section 3.2.1) the positions of the detector, light-source and aperture are shown. The HTHP cell was placed in the sample compartment which is shown in the lower center.]

Figure 4.9: Illustration of the path traveled by the infrared beam inside of the spectrometer in the used setup. Besides the interferometer (see section 3.2.1) the positions of the detector, light-source and aperture are shown. The HTHP cell was placed in the sample compartment which is shown in the lower center.

Figure 4.9 shows a computer rendered image of the used spectrometer. The red line represents the infrared beam inside the system. It originates at the right side at the light-source and passes a variable aperture before it enters the Michelson interferometer already described in section 3.2.1. A KBr (potassium bromide) beam splitter was used in our setup. After passing the interferometer the radiation crosses through the sample
compartment and is measured by the detector.

To avoid chromatic and spherical aberration as well as other lens defects only mirrors are being used to focus and guide the light.[24] The whole spectrometer is closed and purged using nitrogen or dry-air to avoid damage to the sensitive parts such as the KBr windows for example. KBr is a material which is transparent in the infrared region and is therefore widely used as window material.

4.4.2 IR-Lightsource

The most common infrared light-source is a SiC (silicon carbide) stick which is heated electronically up to 2400 K and is commonly called a "globar". It turns out that the temperature T and therefore the overall intensity, which goes with $T^4$, is more important for the overall signal than the position of the maximum of the radiation. It is therefore favorable to use a lightsource which is as hot as possible.[24] The exact technology which is used in the light-sources for the used spectrometer is not publicly available but is most likely based on the globar principle. The intensity, wavelength dependence and range of the available infrared beam is a combined result of the light-source, the detector and other influences in the beam’s path such as apertures and gas molecules. Figure 4.10 shows the single beam intensity distribution of the used spectrometer.

The diameter of the beam can be set using an aperture which is located between the lightsource and the interferometer as seen in figure 4.9. This is necessary because the detector has only a limited detection range and cannot register too small signals and saturates on too high ones. Therefore setting the initial intensity of the beam using the aperture increases the range of possible samples which can be investigated, i.e. with small and large absorption of IR-radiation.

4.4.3 IR-Detector

For the detection of infrared radiation in spectroscopy applications semiconductor based photo-detectors are the instrument of choice. They can be selected according to the
required wavenumber regions, detections speed, cooling possibilities and several other parameters.[16]

The photoconductive, semiconductor-based HgCdTe (mercury - cadmium - telluried (MCT)) detector offers very high sensitivities at high detection speeds. In this detector type an incoming photon gives energy to an electron in the valence band so that it can overcome the bandgap and reach the conduction band. As the detector is biased at a constant voltage this results in a change in current which can be detected.[24]

Because of its high sensitivity this detector is suitable for low signal intensities and therefore ideal for our experiment. The MCT/A type was selected because it has higher efficiencies than the MCT/B for the cost of reduced detection region down to 750 cm$^{-1}$ instead of 450 cm$^{-1}$ for the MCT/B. In the high wavenumbers reasonable intensities could be obtain till 5500 cm$^{-1}$.

Due to variations in spectrometer- and detector-temperature as well as fluctuations in the lightsource, it was necessary to perform a baseline correction for most of the
spectra. The baseline correction adjusts the zero-point to remove shifts, background-signals and changes caused by the factors mentioned before.
5.1 Metal-Organic-Framework Compounds

The Metal-Organic-Framework compounds which have been used in this work were produced by the group of professor Dr. Jing Li of the Chemistry Department of Rutgers University. Dr. Li is an expert in the field of Metal-Organic-Frameworks and is conducting present research on new materials of this class.

5.1.1 Zn (BDC) (TED)

One of the available MOFs is based on Zn-metal-centers which are connected by benzene-1,4-dicarboxylic acid (BDC) as linker to form a two dimensional mesh. BDC is more commonly known as terephthalic acid and consists of one benzene ring which has a (COOH)-group connected to the 1,4 atoms. This adds to a chemical formula of $C_6H_4(COOH)_2$ whose structure is shown in figure 5.1(a).[25]

The third dimension is added by connecting these meshes using 1,4-diazabicyclo [2.2.2] octane (DABCO) also called triethylenediamine (TED). The chemical structure of TED is shown in figure 5.1(b).[25]

The synthesis is, as for many MOFs, performed in N,N-dimethylmethanamide (N,N-dimethylformamide, DMF) an organic solvent whose chemical composition is shown in figure 5.2.[25]

After the synthesis and a drying process at moderate temperatures the resulting structure, determined by X-ray diffraction (XRD), turns out to be the one in figure 5.1(d).
(a) Chemical structure of BDC = benzene-1,4-dicarboxylic acid which is better known as terephthalic acid.

(b) Chemical structure of TED = 1,4-diazabicyclo (2.2.2) octane which is better known as triethylenediamine or DABCO.

(c) $\text{Zn}_4(\text{COO})_4(\text{TED})_2$ Secondary building unit[25]

(d) Crystal structure of $(\text{Zn}(\text{BDC})(\text{TED})_{0.5}) \cdot 2\text{DMF} \cdot 0.2 \cdot \text{H}_2\text{O}$ [25]

Figure 5.1: For all structures the following color scheme was used: Zn: green, O: red, N: blue, C:gray. Hydrogen as well as the solvent molecules were omitted for clarity.

which corresponds to a chemical formula of $(\text{Zn}(\text{BDC})(\text{TED})_{0.5}) \cdot 2\text{DMF} \cdot 0.2 \cdot \text{H}_2\text{O}$ (short Zn(BDC)(TED) in the following). In the shown structure especially the BDC-linker are bent which is attributed to the solvent guest molecules inside the material. After removal of the solvent the structure relaxes to a tetragonal P4/ncc structure which has been determined by Li et al. [26].

The pore size was determined to be $7.5\text{Å} \times 7.5\text{Å}$ and $4.8\text{Å} \times 3.2\text{Å}$ calculated between the carbon atoms of the BDC linkers and taking the van der Waals radius into account.
The volume accessible by a solvent turned out to be 61.3% and the Brunauer-Emmett-Teller surface area was estimated to be $1794 \text{ m}^2 \text{ g}^{-1}$. [25]

Figure 5.1(c) shows the paddle-wheel Secondary Building Unit (SBU) of Zn(BDC) (TED). The SBU is a concept being used for both characterization and prediction of complex structures such as MOFs. It describes the topology of the metal centers and is a useful tool to predict the layout and structure of the whole material from the orientation of the carbon atoms in the SBU for example.[6].

Hydrogen sorption isotherms were recorded by Li et al. and show a $H_2$ uptake of approximately 2.1 wt% at 1 atm and 77 K.[25, 27]

5.1.2 Ni (NDC) (TED)

The second material which was used during the majority of the experiments is very similar to the Zn(BDC)(TED) material. The only difference is the pore size of the two dimensional mesh formed by the BDC and the metal center. In this compound the BDC linker is exchanged by 2,6-Naphthalenedicarboxylic acid (NDC) which consists of two benzene rings as shown in figure 5.3. The longer chain of NDC leads to higher pore sizes for this material.

This MOF has only been developed at the beginning of this work and no complete characterization could be performed by Li et al. up to now. But due to the similarities between the two materials the structure is believed to be also tetragonal and therefore
Figure 5.3: Chemical structure of 2,6-Naphthalenedicarboxylic acid (NDC). The grey atoms represent carbon while the red ones stand for oxygen atoms. Hydrogen was omitted for clarity.

analogous to the one shown in figure 5.1(d). In this case the SBU is identical to the one in structure 5.1(c).

It was shown by Li et al. that the hydrogen sorption capabilities of Ni(NDC)(TED) at 77 K are less than for Zn(BDC)(TED).[26]

5.2 Sample Preparation

After the production and the drying process the Metal-Organic-Framework material is available in powder form. To analyze the MOF, it has to be supported by a solid with special properties. It is important that this material is highly transparent to infrared light so that it does not interfere with the actual measurements and does not absorb too much intensity of the infrared beam. The commonly used KBr (potassium bromide), which is transparent in the region of 400-5000 cm\(^{-1}\), was chosen.

Care has to be taken when KBr is used in combination with water as it is hygroscopic and it can be etched by water [24]. As our sample will be heated during the experiments, temperatures close to the melting point of 730 °C [28] were avoided.

As mentioned in section 4.1 the sample holder is designed for discs of 13 mm diameter. Mono-crystalline, polished pellets of this size are commercially available. The MOF material has to be fixed on the supporting KBr which is not very easily to achieve on a mono-crystalline disc because KBr is a very fragile material. KBr is also available in
5.3 Absorption of Self-Pressed KBr Pellets

Preliminary measurements showed that the infrared radiation is heavily scattered and absorbed by the MOF material. Therefore, other influences which are reducing the infrared intensity should be avoided. A homemade KBr pellet is not as highly ordered as a single crystalline one and it can be expected that scattering will occur more heavily on displacements and other lattice defects. To check the loss due to the pellet the single beam with and without a sample was recorded using the same spectrometer settings. Using the integrated areas under the graphs in the range from 4000 to 2000 cm\(^{-1}\), which is interesting for our experiments, we can calculate the loss.

\[
\text{Area}_{\text{without}} - \text{Area}_{\text{with}} = 76300 - 67900 = 8400
\]

\[
\Rightarrow \text{Loss due to KBr pellet:} \frac{8400}{76300} = 11\%
\]

Figure 5.6 shows the two single beams and illustrates the area of loss. The signal quality is still good enough to perform the experiments with these pellets.
5.4 Determination of the Sample Amount

For the preparation of the samples the following procedure was used. About 200 mg of KBr powder were pressed at a pressure corresponding to 1.5 metric tons to form a supporting disc of the desired diameter. Picture 5.5 shows such a homemade KBr pellet. The disc was removed from the press and the MOF material was added on the surface of the KBr pellet. The whole composition is then pressed again up to a pressure corresponding to 6.5 metric tons. This second pressing procedure fixes the MOF on the KBr pellet.

To analyze just the MOF material itself it is common in the literature [9, 7] to mix the MOF with KBr. For the investigation of the interaction of hydrogen with the MOF it is however important, that surrounding hydrogen gas can reach the MOF crystals. Therefore the sample was only put on the surface of the KBr pellet.

To determine a suitable sample amount, the absorption due to the MOF itself was investigated. The strong vibration modes of the linker molecules cause very high absorption especially in the low frequency region between 600 and 1700 cm$^{-1}$. In addition,
the newly-prepared MOF contains water molecules, which cause a strong feature in the O-H stretching region between 3000 and 3500 cm\(^{-1}\). Both phenomena can be seen in the red spectrum of figure 5.7 in which the absorption is so high, that no signal is detected for certain wavenumbers. While the water can be partly removed during the activation process (compare section 6.1.4) the MOF structure is expected to stay intact and the absorption will therefore not improve.

Figure 5.7: Comparison of a singlebeam signal for 5 mg and 9 mg of Zn-MOF. The strong absorption in the low frequency as well as in the O-H stretching region especially for the 9 mg sample can be seen.

Figure 5.8: Photograph of one sample holding 3.5 mg of the Ni-based MOF material supported by 200 mg KBr.

Figure 5.9: Photograph of one sample holding 3.7 mg of the Zn-based MOF material supported by 200 mg KBr.
The systematic analysis showed that samples with less or equal to 5 mg of MOF on a 200 mg KBr pellet have a sufficient transmission to resolve all features also in the low-frequency region (black spectrum in figure 5.7). In addition, care has to be taken that the material is not accumulated in the center of the pellet but is as equally distributed as possible to form a thin layer. Because of the large diameter of the infrared beam especially for large apertures a complete coverage of the sample is not necessary.

Figure 5.8 and 5.9 show pictures taken from one sample of each compound respectively. In case of the green Ni-MOF the presence of the sample is obvious while for the white Zn-MOF only a loss in transparency (compare figure 5.5) reveals its presence.
Chapter 6
Experimental Results

First the sample activation and preparation for the measurements is described as well as the removal of the solvent. The second part describes the interaction of hydrogen with the Metal-Organic-Framework and shows the determined modes. The third section deals with interaction of water with the Metal-Organic-Frameworks and discusses problems which can arise when the hydrogen gas contains a high concentration of water.

6.1 Sample-Activation

Before any hydrogen-related experiment can be performed using the MOF-materials they have to be activated, i.e. the solvent and other guest molecules have to be removed from the porous structure.

The activation can be achieved when the sample is heated to a temperature of 150 °C while pumping. Our setup using the HTHP cell allowed this process to be done while in-situ FT-IR spectroscopy was performed to monitor the changes in the sample. Each sample was prepared as described in section 5 and was therefore available on a KBr disc. This disc was placed together with the sample holder inside the cell which then was evacuated using a turbomolecular pump. The sample-holder was heated to 150°C and the cell’s body to 110°C.

6.1.1 Spectrum of N,N-dimethylformide (DMF)

In order to be able to assign modes in the IR spectra to DMF, a spectrum of the liquid phase of DMF was taken. For this purpose a KBr pellet, intended as support for the liquid, was pressed out of 200 mg KBr powder. To remove adsorbed water from the
pellet it was baked at 120°C while the cell was heated to 110°C for one hour. Afterwards the pellet was removed from the HTHP cell and a drop of DMF was placed on the pellet using a glass dropper. To avoid contamination, the sample was placed back in the cell as fast as possible and a spectrum of the liquid DMF on the KBr pellet was taken in air. The resulting spectrum is shown in figure 6.1.

The spectrum 6.1 shows several features in the low frequency region between 600-1800 cm\(^{-1}\) which are presented in higher resolution in figure 6.2. Around 2800 cm\(^{-1}\) additional modes related to C-H stretches are visible. Table 6.1 summarizes the features and their associated vibrations which have been calculated by Sharma et al. [29] using Density Functional Theory calculations.

Measurements and calculations done by Sharma et al. have been performed for pure DMF as well as a DMF-water mixture. Because figure 6.1 shows an adsorbed water feature (3200-3700 cm\(^{-1}\)) it is likely that the observed DMF-spectrum is influenced by water. This makes also the DMF-water mixture results of Sharma et al. very interesting and they are therefore listed in table 6.1. Taking the C-N asymmetric stretch mode
Figure 6.2: Low-frequency region of the spectrum of liquid DMF on KBr recorded in air. A plain KBr pellet was used as reference.

Figure 6.3: Spectra of DMF (a) and a DMF-water mixture (b). Note the reversed wavenumber axis. Figure adapted from [29]

as an example, spectrum 6.2 clearly shows the undisturbed DMF mode at 1504 cm\(^{-1}\) as well as a weak feature at 1497 cm\(^{-1}\) which has been associated with the DMF-water mixture in [29]. The same is true for the C=O stretch at 1678 cm\(^{-1}\) and 1655 cm\(^{-1}\) for pure DMF and water + DMF respectively. Also the O=C-N-C torsion shows a double feature around 659 cm\(^{-1}\) of which one is slightly shifted upwards as shown in [29] for the water mixture.

The water concentration in the used DMF appears to be low as all the features associated with the interaction of DMF with water are weak compared to the pure DMF
<table>
<thead>
<tr>
<th>Band / [cm$^{-1}$]</th>
<th>Assigned Mode</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMF pure</td>
<td>DMF + water</td>
<td>ref. [29]</td>
</tr>
<tr>
<td>659</td>
<td>O=C=NC tor</td>
<td>(s)</td>
</tr>
<tr>
<td>865</td>
<td>NCH$_3$ sym st</td>
<td>(w)</td>
</tr>
<tr>
<td>1015</td>
<td>$C_n$H def</td>
<td>(w)</td>
</tr>
<tr>
<td>1063</td>
<td>$C_m$H def</td>
<td>(w)</td>
</tr>
<tr>
<td>1093</td>
<td>$NC_n$H def</td>
<td>(vs)</td>
</tr>
<tr>
<td>1150</td>
<td>$C_m$H def</td>
<td>(w)</td>
</tr>
<tr>
<td>1256</td>
<td>NCH$_3$ st</td>
<td>(s)</td>
</tr>
<tr>
<td>1388</td>
<td>CN st</td>
<td>(vs)</td>
</tr>
<tr>
<td>1408</td>
<td>NCH$_3$ st</td>
<td>(w)</td>
</tr>
<tr>
<td>1438</td>
<td>NCH$_3$ def</td>
<td>(w)</td>
</tr>
<tr>
<td>1492</td>
<td>NCH$_3$ def</td>
<td>(w)</td>
</tr>
<tr>
<td>1504</td>
<td>CN asym st</td>
<td>(w)</td>
</tr>
<tr>
<td>1678</td>
<td>C=O st</td>
<td>(vs)</td>
</tr>
<tr>
<td>2780</td>
<td>CH st (formyl)</td>
<td>(w)</td>
</tr>
<tr>
<td>2861</td>
<td>CH st (cis-methyl)</td>
<td>(s)</td>
</tr>
<tr>
<td>2931</td>
<td>CH st (cis-methyl)</td>
<td>(s)</td>
</tr>
<tr>
<td>2994</td>
<td>CH st (cis-methyl)</td>
<td>(w)</td>
</tr>
<tr>
<td>3428</td>
<td>OH st</td>
<td>(w)</td>
</tr>
</tbody>
</table>

Table 6.1: Table of modes found in pure DMF and in DMF-water mixtures. The wavenumbers and assignments are taken from [29]. The listed intensities are according to our measurements. The following abbreviations were used: (vs) = very strong, (s) = strong, (w) = weak.

modes. For a mixture of higher concentration as used in [29] the pure DMF spectrum is significantly more disturbed as visible for example around 1105 cm$^{-1}$ in figure 6.3. There are multiple ways how the water could have entered the system. As KBr is hydrophilic it is possible that some water from the atmospheric air adsorbed on it while putting the DMF droplet. As the DMF was stored in a bottle under normal environmental conditions, water from the air could have entered the DMF. The hydrolysis of the DMF solvent is a known phenomenon described by Burrows et al.[30]

6.1.2 Removal of the Solvent

The selected temperature of 150°C is very close to the boiling point of the used solvent (DMF), 426 ± 1K ($≈$ 152.9°C) [31]. Therefore baking allows efficient outgassing
Figure 6.4: FT-IR spectra taken during the initial activation process of the Ni-MOF. Shown are selected spectra after 10, 20, 30 and 60 minutes as well as 8:25 hours of baking. These spectra are referenced to one taken at the beginning of the baking process. In addition, the spectrum of DMF (black) is presented. The removal of the DMF modes in the area is clearly visible.

Figures 6.4 and 6.5 present the low frequency region between 900-1800 cm\(^{-1}\) during the baking process. The colored spectra indicate the time dependence of the removal of the DMF solvent. These spectra are referenced to the newly prepared sample and therefore the changes during the baking process can be seen. The modes of DMF, as described in section 6.1.1, are clearly removed for both MOFs. Figure 6.4 contains the spectrum of DMF (black) for better comparison of the modes. The removal saturates after 1-2 hours and only few changes could be observed in later spectra.

Adsorbed water is also expected to be removed not only from the sample but also from the cell’s walls as its boiling point of 100°C is below both temperatures used. It is important however, that the MOF-structure stays intact during this process. Thermo-gravimetric analysis (TGA) performed on the Zn-MOF by independent groups \[25, 27\] shows that while a weight loss accounted to the solvent- and water-removal occurs in the 100-200°C region, the decomposition temperature is above 300°C. The sample was
Figure 6.5: FT-IR spectra taken during the initial activation process of the Zn-MOF. Shown are selected spectra after 10, 20, and 70 minutes as well as 11:10 hours of baking. These spectra are referenced to one taken at the beginning of the baking process. The removal of the DMF modes in the area are clearly visible.

characterized after baking it at $150^\circ$C and it did not show any signs of destruction which led to the chosen baking temperature of $150^\circ$C [25].

6.1.3 Stability of the MOFs

The infrared spectrum also contains information about the structure of the MOF and can give indications for a decomposition of the material. Figure 6.6 compares the spectra of Zn(BDC)(TED) before (red) and after (black) the initial activation. The strong characteristics of the symmetric (1610-1550 cm$^{-1}$) and asymmetric (1420-1335 cm$^{-1}$) vibrations of the BDC linker are clearly visible. [7]

During the baking process the symmetric mode undergoes some changes around 1668 cm$^{-1}$ which can be associated with the solvent removal and therefore the C=O stretch mode of DMF which has been discussed in the previous section. The overall shape of the structures stays intact and we can conclude that the BDC is not damaged during the baking process and the structure is not significantly disturbed. This is in agreement with the results of Huang et al. for the similar MOF-5 material [9].
For the Ni(NDC)(TED) MOF the result is similar. Figure 6.7 shows the spectra before (red) and after (black) of the activation process. The removal of the strong 1668 cm\(^{-1}\) mode of DMF is also visible for this compound. The vibrational modes of the benzene rings don’t change significantly and one can conclude that also this structure stays intact during the activation process.

### 6.1.4 Water removal

Water as guest molecule inside the MOF or simply on the surface can limit and perturb the interaction of hydrogen with the MOF. The activation procedure performed exposes the water to temperatures above its boiling point and one expects a fast removal.

For both MOFs we see a clear removal of the mode of adsorbed water between 2000 and 4000 cm\(^{-1}\) as shown in the spectra 6.8 and 6.9. The time dependency of the process is for both in the same order (several tens of minutes) but the Ni-MOF shows in total a faster removal. After 50 minutes both materials reach the saturation of the removal, i.e. also after several hours of further baking no significant additional amount of water is removed. This is visible in spectra taken after a longer time of baking. Compared to the DMF modes the water features decrease faster.
Figure 6.8: Spectra taken 10, 20, 30 and 50 minutes after the start of the baking process of the Zn-MOF. The removal of the O-H-water feature between 2000 and 4000 cm$^{-1}$ is visible.

Figure 6.9: Spectra taken 10, 20, 30 and 50 minutes after the start of the baking process of the Ni-MOF. The removal of the O-H-water feature between 2000 and 4000 cm$^{-1}$ is visible.

Figure 6.10: The O-H stretch region before and after the initial baking process.

Figure 6.11: Shift of the O-H peak during the cool-down. The mode at 3300 - 3400 cm$^{-1}$ gets removed and a new one at 3100 - 3150 cm$^{-1}$ grows.

It should be mentioned that in case of the Zn-MOF after cooling down the spectrum referenced to an empty cell still shows a mode in the O-H region (compare figure 6.10). This mode is red-shifted by 330 cm$^{-1}$ and also has a different shape. It is interesting that this feature is slowly created during the cool-down after the baking was turned off. This process is shown in figure 6.11. The resulting feature after the cool-down is already visible as a small shoulder on the red spectrum in figure 6.10.
No further experiments were performed to investigate this behavior directly but it is possible that water on the surface of the pellet or the MOF diffuses inside the material and gets adsorbed. The water sorption properties of MOFs are well known as shown and predicted by [9, 32]. Because this feature could not be removed using our baking temperature of 150°C and it is located in the O-H region, it might also be strongly bound (or framework) water as mentioned by Huang et al. [9].
6.1.5 Experimental Difficulties

The HTHP cell which was used for the majority of the experiments has a construction failure which favors the creation of wave-like features in the taken spectra. These sine-like structures can be seen in figure 6.12 directly on the single beam. A likely reason for these features is interference due to thin films inside the cell. The problem could not be solved completely but it turned out that the structures disappear almost completely as soon as a sample is in place which causes some scattering of the infrared beam. Commercially polished KBr pellets in contrast, did not improve the situation and left spectra with the wave. The second HTHP cell, used for a different experiment, was available for some measurements which needed an empty cell as reference. For all remaining experiments requiring an empty cell a KBr pellet was put in place.

Figure 6.12: Oscillations appearing in the single beam for an empty cell.

In addition, none of the two available HTHP cells was able to maintain a pressure of several hundred to 1000 psi without significant losses over more than a few hours. This could be due to design problems of the HTHP cell. But in addition it is important that hydrogen as the lightest atom, is able to diffuse through stainless steel and thus the pressure in the cell can decrease.
6.2 Hydrogen-MOF Interaction

The long-time goal of our group’s work with Metal-Organic-Framework is the identification of possible binding-sites of adsorbed hydrogen. When a hydrogen molecule enters the MOF at least one new mode due to the H$_2$-MOF-interaction is expected to appear in the FT-IR spectrum. In order to increase the presumably weak interaction between hydrogen and the investigated sample, high-pressure (300-1000 psi) hydrogen was used.

6.2.1 The Spectrum of Hydrogen

To get information on how the pure hydrogen spectrum appears in the used infrared setup, at first spectra with no sample were recorded. For this purpose a KBr pellet was placed in the sample holder and the cell was filled with the desired pressure of hydrogen gas.

![Figure 6.13: The spectrum of high pressure hydrogen for different pressures from 300 to 900 psi. Labeled are the main features including the Q and S branch.](image)

Figure 6.13 shows spectra of hydrogen taken at different pressures. The area indicated contains the most significant feature which can be seen in the wavenumber range detectable in our setup between 600 and 5500 cm$^{-1}$ and it is located in the range of
3900-5200 cm\(^{-1}\). The spectral features are getting more intense with increasing pressure and also the Q-branch splitting mentioned in section 3.3 gets larger as predicted. In addition, the mode related to the \(S_1(J=0)\) transition is better resolved due to the overall higher intensity.

From this experiment we can conclude that our setup allows us seeing the high-pressure spectrum of hydrogen which forms the base for the planned study. The features with and without a KBr pellet inside the cell are strong, easy to measure and distinguishable.

Using the MCT detector, due to low signal intensity, it was not possible anymore to distinguish the hydrogen spectrum for pressures below 300 psi. The induced dipoles at this pressure are not strong enough to be detected. A limitation of the used detector is its cut-off in the low-frequency region. Close to 600 cm\(^{-1}\) and below no reliable data can be determined. The reason for this is the rapid change in sensitivity in this area. If a signal varies only slightly the detector’s response amplifies this change thus resulting in very high peaks in the absorbance spectrum which do not correspond to actual vibrations of the material. Therefore the far-infrared spectrum of hydrogen, which is located between 300 and 1200 cm\(^{-1}\) [19] could not be seen.

### 6.2.2 Hydrogen-MOF Interaction

After proving that hydrogen can be seen in the system, the interaction of hydrogen with the Metal-Organic-Framework was studied. For this, a sample of the MOF was placed inside the cell and it was activated as described in section 6.1.

After the sample cooled down, the pressure was typically in the order of \(5-10 \cdot 10^{-7}\) torr. At this point a spectrum of the sample was taken and used as a reference for the following measurements. The cell was disconnected from the pump and hydrogen gas of the desired pressure was immediately introduced into the cell. Figure 6.14 and 6.15 show hydrogen spectra for different pressures while the Zn- and Ni-MOFs were in place. Because the signal to noise ratio between 3900 and 5200 cm\(^{-1}\) decreased compared to
Figure 6.14: Spectra of hydrogen at different pressures while the Zn-MOF was inside the cell. One can see the undisturbed hydrogen modes as well as a sharp feature around 4076 cm$^{-1}$.

Figure 6.15: Spectra of hydrogen at different pressures while the Ni-MOF was inside the cell. One can see the undisturbed hydrogen modes. No special feature is directly visible.

an empty cell, usually several spectra for one pressure setting were taken. This has the advantage that statistical noise can be reduced when the average of the available spectra is calculated. Because the investigated features might be very weak, a high signal to noise ratio is desirable.

Hydrogen - Zn-MOF Interaction

Comparing figure 6.14 with the pure hydrogen spectrum in figure 6.13 one can conclude that the pure hydrogen spectrum is still visible. This is expected as the infrared beam passes through the hydrogen inside the cell and outside the MOF. The amount of hydrogen which is interacting with the sample is very small compared to the total amount of molecules inside the whole cell.

Even though all spectra shown in the two figures were averaged over 1000 individual measurements one can see the already mentioned decrease of the signal to noise ratio especially for the lower pressure spectra. To be able to resolve small features more easily, as many spectra as available were averaged for each pressure.

Besides the undisturbed hydrogen spectra a clear additional mode at 4076 cm$^{-1}$ as
Figure 6.16: Hydrogen interaction with Zn-MOF. The spectrum of pure $H_2$ gas of the specific pressure was subtracted from the spectra taken with the MOF.

well as further disturbance of the hydrogen’s Q branch is visible in graph 6.14. To investigate this further, the pure hydrogen spectrum was subtracted from the one taken with the MOF for all pressures. Figure 6.16 shows the subtraction results for the Zn-MOF.

Now the peak at 4076 cm$^{-1}$ is clearly visible as well as additional structures towards higher wavenumbers which are labeled in figure 6.16. Compared to the noise, which is visible at the left edge of the figure, these features are more distinct. The two shoulders at 4090 and 4178 cm$^{-1}$ can be associated with overtones of the CO and the CC modes of the framework [10].

All other labeled peaks are pressure dependent and growing with increasing pressure. The difference for hydrogen at 700 and 900 psi is less significant compared to the increase between the lower pressures. Because the pressure gauge used for the high pressure measurements has a large uncertainty ($\approx \pm 100$ psi) the smaller growth could be attributed to an error in the pressure measurement rather than to a saturation of the interaction signal. The free hydrogen vibration frequency, which cannot be seen using FT-IR techniques, was theoretically determined to be 4246 cm$^{-1}$ by the group
of Professor David Langreth at Rutgers University [33]. For adsorption sites inside the MOF a shift is expected. As all peaks are pressure dependent and appear in the region where we expect new modes for hydrogen-MOF interaction, it is possible that they represent binding sites inside the material. A clear statement about the nature of these cannot be made with the current knowledge. Van der Waals Density Functional Theory calculations done by Langreth et al. in collaboration with our group aim at the identification of possible binding sites and their energies for the investigated material. Once these results are available one can proceed more profoundly with the identification or falsification of the peaks.

It should be mentioned that Brodiga et al. [10] performed FT-IR measurements on MOF-5, a very similar compound. In MOF-5 connections in all directions are formed by BDC instead of the one TED linker used in our material. Brodiga et al. used low temperatures (15 K) and low hydrogen pressures (maximum of 0.087 psi) for their spectroscopic investigation. Several features appeared in the same region as the ones described above but none at exactly the same location. A direct comparison of the two materials especially under these different experimental conditions might not be possible but feature in the same region make the association of the shown peaks with hydrogen-MOF interaction likely.

**Removal of the Hydrogen From the Zn-MOF**

After the hydrogen was in contact with the MOF for the duration of the first part of the experiment also the removal is very interesting for storage applications.

High-pressure hydrogen can not be introduced in the pump directly as it would damage the pumping system. The pressure was therefore first released to the environment which just left hydrogen at room pressure inside the cell. From this time on spectra were recorded continuously to follow the pumping process. After the release to the environment the turbopump, which was off before, was turned on in order to remove the hydrogen from the cell. The turbo pump takes approximately 5 minutes to reach
its maximum speed. After approximately half an hour of pumping the pressure is in the low $10^{-6}$ torr range and decreases only very slowly.

Figure 6.17 shows the beginning of the pumping process where the spectra were referenced to the spectrum taken after the hydrogen was released to the environment. In this way the negative high-pressure hydrogen feature is not covering the smaller feature in this area, which were already presented in figure 6.16. The interaction of 900 psi hydrogen is shown for comparison.

![Figure 6.17: Spectra taken during the pumping process after the exposure of the Zn-MOF to 900 psi of hydrogen. After 16 minutes all hydrogen modes are completely removed. The thick black spectrum shows the 900 psi hydrogen spectrum in comparison.](image)

In the first spectra directly after the pump was started no change in the region between 3950 - 4350 cm$^{-1}$ was visible. However, after 6 minutes of pumping the hydrogen modes are getting removed. The removal continues until it saturates at the level shown for 16 minutes of pumping.

This leads to the conclusion that the labeled modes are related to adsorbed species inside or on the sample. Room pressure hydrogen, as it is present after the release to the environment, keeps the hydrogen inside the MOF and only after the pressure
was reduced through pumping, the modes disappear. During the pumping process the overall absorbance changed, which could be seen in the single beam spectra. Because the black hydrogen spectrum and the ones for the removal were referenced to different spectra, the absorbance cannot be compared directly.

**Hydrogen - Ni-MOF Interaction**

An identical experiment was conducted using the other available MOF species. The spectra of the hydrogen area were already shown in figure 6.15. After subtraction of the pure hydrogen modes one obtains the spectrum presented in figure 6.18.

![Figure 6.18: Hydrogen interaction with Ni-MOF. The spectrum of pure $H_2$ gas of the specific pressure was subtracted from the spectra taken with the MOF.](image)

Even the highly averaged spectrum for 900 psi of hydrogen still has a very high noise level and spectral features are very hard to distinguish. The high noise level also made a baseline correction very difficult. The baseline correction is very important for the subtraction of the pure hydrogen spectrum as the spectra should have the same shape, which is determined by the baseline.

The subtraction $S$ is performed by varying a prefactor $k$ in front of one of the spectra
(A,B): $S = A - k \cdot B$. When the baseline is not exact enough and the noise level is so high it is not possible to see when exactly the hydrogen spectrum is removed. If $k$ is chosen too high, one can even add the negative of the hydrogen spectrum and create artificial peaks by that. In figure 6.18 the Q-branch and the $S_1$ mode are labeled. One can see that the only visible features are exactly in this area and cannot be clearly distinguished from new peaks related to hydrogen-MOF interaction.

**Removal of the Hydrogen From the Ni-MOF**

For the Ni-MOF a removal procedure analogous to section 6.2.2 was used. No significant change could be seen in the spectra for the hydrogen region.

![Figure 6.19: Spectra taken for the same hydrogen pressure after the sample was in contact with the high-pressure gas for several hours. First signs of a time dependence of the O-H stretch feature are visible.](image)

The problems in the hydrogen investigation using the Ni-MOF could be due to problems with the MOF crystals themselves. Due to poor crystal quality [26], no complete characterization of this MOF could be performed. It is possible that the poor quality of this sample made hydrogen measurements very hard up to now. It is as well possible that the interaction with the Ni-MOF is significantly weaker than with the Zn-MOF and therefore no modes could be seen up to now.
During the measurements for the high-pressure spectra and the interaction with the MOF, hydrogen was inside the HTHP cell for a longer period of time. Figure 6.19 shows three spectra for the same pressure of hydrogen. These spectra were taken with a time difference of several hours as indicated and one can see that a feature in the O-H stretch region between 2800 and 3800 cm$^{-1}$ is present and shows little time dependence. This phenomenon lead to the following experiments which deal with the development of this significant band.
6.3 Water-MOF Interaction

To analyze the time dependence of the O-H stretch feature several long-time measurements were performed. For these, a MOF sample was placed in the cell. New samples were activated before usage while already used samples were baked at a temperature of 120°C just to remove adsorbed water. After the sample reached room temperature one spectrum of the sample without hydrogen interaction was taken which was used as a reference for the analysis of all interactions with the hydrogen. Unless stated otherwise the Ni-based MOF was used in this part of the experiment.

The cell was disconnected from the pump and hydrogen of either 500 or 700 psi was introduced into it. To be able to follow the development of the IR modes over time, spectra were taken in a loop over a period of up to 14 days. Not each spectrum will be presented here but rather a collection of interesting features and selected spectra to illustrate them as clearly as possible.

Due to the instability in pressure mentioned in section 6.1.5, in early experiments the cell was re-pressurized to the desired pressure. Because this resulted in very high fluctuations in the hydrogen pressure and unreliable spectrographic data it was decided to keep the valve to the hydrogen bottle open at all times. This assures a constant pressure during the whole experiment.

6.3.1 Observations During Long-Time Hydrogen Exposure

Several modes in the recorded region between 600 and 5500 cm\(^{-1}\) showed a time dependent behavior. Besides the O-H stretch feature (2400 - 3700 cm\(^{-1}\)), which has already been mentioned in section 6.2.2, also the CO\(_2\) (2300 - 2400 cm\(^{-1}\)) and C-H modes (2850 - 3100 cm\(^{-1}\)) are of special interest. They are all presented in figure 6.20 and each of the features will be discussed separately in the following sections.
The O-H Stretch Feature

The O-H stretch feature presented in figure 6.20 for the Ni-MOF extends over a very wide range of wavenumbers which is an indication for an adsorbed phase containing O-H bonds [34]. Adsorbed species usually have a feature which is heavily broadened by interactions with surrounding atoms in contrast to the sharp modes of gas phase transitions. The major peak covers 3000 - 3800 cm\(^{-1}\) but its tail extends further till 2400 cm\(^{-1}\). The exact end of the feature is not defined sharply.

Between 2850 - 3100 cm\(^{-1}\), the region of the C-H modes, a negative feature, which will be discussed in the next section 6.3.1, superimposes the O-H feature. A negative feature represents a loss of modes, i.e. bonds are destructed and we will therefore refer to it as destruction feature in the following. To make a quantitative analysis of the growth of the whole O-H region this feature was removed from the spectrum.

This removal was done by first isolating this destruction feature using a baseline along
Figure 6.21: The plots show the integrated area of the O-H feature over time. For both measurements the Ni-MOF was used and an apparent linear, non-saturating behavior can be assumed.

the right edge of the O-H mode. The resulting spectra are shown in figure 6.24. Having these available it is now possible to subtract them from the whole spectrum which results in an O-H peak without any destruction feature. This makes the analysis of the pure O-H peak possible. Calculating the integrated area between the beginning of $CO_2$, i.e. 3380 cm$^{-1}$, and 3700 cm$^{-1}$ lead to the time development shown in figure 6.21 for 700 psi measurements.

Figure 6.21 contains information about the development of the O-H stretch modes for two measurement using the same Ni-MOF sample at 700 psi. The increase goes linear with time for both cases but the slope is different. A saturation of the growth was not visible in both experiments.

**Increase of the $CO_2$ Mode**

During the long-time hydrogen exposure not only the O-H stretch feature was growing but also the $CO_2$ branches at 2361 and 2335 cm$^{-1}$ showed a change over time as can be seen for selected spectra in figure 6.22. Fluctuations in the $CO_2$ intensities are expected
due to changes in the air of the environment and the gas (gaseous nitrogen or dry air) used to purge the spectrometer.

Figure 6.22: Spectra of the development of the CO\textsubscript{2} modes during long-time hydrogen exposure using the Ni-MOF. A clear change over time is visible.

Figure 6.23: Plot of the integrated area of the CO\textsubscript{2} mode over time during long-time hydrogen exposure using the Ni-MOF. Besides minor fluctuations an overall increase over a long time can be seen.

The fluctuations were analyzed in more detail by calculating the integrated area under both peaks. Plot 6.23 shows the time-dependence of the CO\textsubscript{2} lines. Besides some (expected) fluctuations the overall trend is a steady increase. Plot 6.23 corresponds to some selected spectra of those presented in figure 6.22

**Destruction in the C-H Bond Region**

The C-H destruction feature whose removal was discussed in section 6.3.1 is shown in figure 6.24. Also here a time-dependence is clearly visible. Analogous to the CO\textsubscript{2} in the previous section the integrated area of the peak is presented in plot 6.25 for the same measurements which were used in the section describing the O-H mode (6.3.1).

The behavior of the two series of data points are identical to those described in section 6.3.1 where both follow a linear increase with time but the second measurement has a slightly lower slope. This can be attributed to the imprecise control of the pressure inside the cell. An analog gauge with a very rough scale was used for this purpose. In
addition to the rough scale two different used gauges showed a discrepancy of almost 100 psi which makes also the read value subject to error. The gap in the black plot is due to experimental difficulties which made the spectra in this time-block not usable for analysis. Both graphs show a different starting point. The emphasize during the experiment was the long-time development and the starting point was therefore not recorded precisely. Because of the long duration of the experiment it was not repeated.

The spectra were fitted linearly to illustrate the increase. The slope of the linear fits was compared to the O-H stretch mode presented in figure 6.21. When normalizing the peak areas it turns out that the growing rate for both structures is in the same order of magnitude.

### 6.3.2 Removal of the Hydrogen

After the long-time exposure the hydrogen had to be removed from the cell. This step was done analogous to the process described in 6.2.2 for the hydrogen measurements. After the turbo pump was running at full speed, the sample was heated to 120°C and the cell’s body to 110°C to support the desorption. Figure 6.26 shows the removal of the O-H mode for the Ni-MOF. The spectra are referenced to the MOF right after the
activation, before any hydrogen experiment was performed with it. After approximately 80 minutes the O-H mode was almost completely removed. Further baking still showed an additional decrease of the feature but it is orders of magnitude smaller.

Figure 6.26: Spectra showing the decrease of the O-H mode while pumping the cell and baking the sample.

It should be mentioned that during all baking processes, i.e. during the initial solvent removal as well as after the hydrogen exposure, some modes in the C-H stretching region undergo changes. Because this process is superimposed by the removal of the O-H mode the trend is hard to determine but appears to be a reconstruction of the C-H bonds. No further investigation was done on this so far.

6.3.3 Analysis and Results

In summary, the previous sections describe the growth of two features (CO$_2$ and O-H stretches) as well as a destruction in the organic region. One possible conclusion is that a chemical reaction takes place and produces CO$_2$ and H$_2$O while deconstructing the organic compounds of the MOF. Carbon and oxygen are both available in the MOF structure whereas the cell is filled with hydrogen which completes the list of necessary elements.
Figure 6.27 shows that the oxygen atoms (red) are bound directly to the metal centers of the framework. A removal would therefore cause the framework to collapse as the linker molecules are not attached anymore. In addition the growth and destruction processes described before are continuing over several days without any signs of saturation or slow-down. This behavior is very untypical for chemical reactions and therefore other possibilities for the presented phenomena were investigated and will be presented in the following sections.

Figure 6.27: The secondary building unit of Zn (BDC) (TED) with the complete ligands shown. Coloring scheme: Zn: green, O: red, N: blue, C: gray. Hydrogen as well as the solvent molecules were omitted for clarity.

Figure 6.28: Development of the CO$_2$ mode during exposure of a KBr-pellet to high-pressure hydrogen.

**Analysis of the CO$_2$ modes**

Firstly the CO$_2$ feature will be discussed. To check whether its growth is only related to the high-pressure hydrogen or to interaction / reaction with the MOF the experiment was repeated by simply putting a KBr pellet inside the cell. Figure 6.28 shows the development of the carbon dioxide modes during the first 12 hours of hydrogen contact. A clear increase over time is observable. Comparison with the work done by S. Kahle [35] using the same HTHP cell in our laboratory showed the same behavior with KBr and silicon (silicon dioxide surface) samples containing single walled carbon nanotubes.
The release of pressure and the pumping described in sections 6.2.2 and 6.3.2 showed a complete removal of the $CO_2$ modes while pumping down. We therefore conclude that the $CO_2$ is in the cell and not outside in the system of the spectrometer.

The presence of the feature when using plain KBr or silicone samples lead to the conclusion that the effect is sample independent. In addition, figure 6.22 shows that the increase starts at zero and does not show a quick increase in the beginning which could be related to the introduction of $CO_2$ with the hydrogen gas. Because the cell is opened frequently when changing the sample, air reaches the inside walls and different compounds can stick to them. High-pressure hydrogen gas is characterized by very fast moving hydrogen molecules which can sputter these compounds off the walls of the cell and bring them back into the gas-phase. This would lead to an increase as measured and presented before. Because other obvious possibilities have been ruled out, we assume that this is the mechanism which is happening.

**Analysis of the O-H Stretch Modes**

Figure 6.27 shows the secondary building unit of Zn (BDC) (TED) and illustrates that the oxygen atoms (red) can be accessed by the surrounding hydrogen gas. One possible and for hydrogen storage applications favorable behavior, which would explain the appearance of an O-H stretch mode, is physisorbed water at the oxygen sites. The resulting order could resemble two hydrogen atoms bonded to one oxygen and therefore show a mode in the described region. The easy release when the surrounding pressure is decreased also supports the hypothesis of a storage mechanism.

However, hydrogen is expected to penetrate the large (diameter $\geq 3$ Å) hollow structure of the MOF very easily and therefore the slow growth of the feature makes an adsorption process of hydrogen unlikely. In addition, the destruction of the C-H modes cannot be explained by it.
The O-H stretch region is very commonly associated with adsorbed water and its vibrations for MOFs as well as other materials [8, 34, 36]. Therefore the observed mode could also correspond to water in contact with the MOF material. The interaction of water with the MOF was investigated further and is described in the next section.

6.3.4 Exposure to Water Vapor

To determine the effects of water on the MOF, gaseous water was introduced directly in the cell. For this purpose the evaporator, which has been described in section 4.2, was used. One sample was placed inside the cell and activated (compare section 6.1). Before any vapor introduction took place, the sample cooled down to room temperature and the HTHP cell was pumped down to $5 \cdot 10^{-7}$ torr. At this point a reference spectrum was taken.

To introduce vapor, the pumping line was separated from the cell. At the evaporator (compare figure 4.6) the nitrogen line (V3) and the line towards the cell (V4) were closed. After valve (V2) towards the pump has been opened the sorption pump was used to remove the gas above the stainless steel vessel and in the tubing. The connection to the water reservoir (V1) was opened after one minute of pumping and the pressure above the water was therefore reduced due to the pumping process. The reduction of the pressure above the water causes more molecules to go into the gas phase to reestablish the vapor pressure above the surface. After a total of five minutes the pumping line (V2) was closed and the created vapor was introduced into the evacuated cell by opening valve (V4). The water reservoir was continuously connected to the HTHP cell.

During the introduction of the water vapor spectra were taken constantly. Each was averaged over 200 single measurements. Thus it is possible to see the development over time which can be compared to the features seen when introducing hydrogen gas. Figure 6.29 shows the interesting area of the spectrum as an overview. The separate parts will be analyzed in the following. Spectra taken after more than 10 minutes showed such big absorption in the area between 3000 and 3800 cm$^{-1}$, that the signal got down
Figure 6.29: Spectral-development during the introduction of water vapor into the HTHP cell using the Zn-MOF.

to zero in these areas. These spectra are therefore omitted in the graph.

For the Ni-MOF sample a similar experiment was performed. In this case the evaporator was closed a few seconds after the water vapor was introduced inside the cell.

Figure 6.30 compares a spectrum taken directly after the introduction of the water vapor to the ones growing during hydrogen introduction. The similarity of the O-H features is clearly noticeable.

The collection of peaks between 3600 and 3900 cm\(^{-1}\) in the water vapor spectrum correspond to the gas-phase water vibrations of the vapor filling the cell. The destruction feature in the organic C-H region between 2800 and 3100 cm\(^{-1}\) is visible as well as an increase in the CO\(_2\) modes.

When the valve to the evaporator is closed, as done for the Ni-MOF, the O-H stretching mode does not change over time. However, opening the valve leads to a very fast increase which can be see in spectrum 6.29.
Before the water vapor was introduced into the system, the tubing and the volume above the water was pumped down using the sorption pump. This pumping process only reaches a pressure of estimated $10^{-4}$ torr and many molecules contained in the air are left and being mixed with the evaporated water. This is the reason why $CO_2$ is visible in the water vapor spectrum even when no high-pressure gas is present, which was assumed for the conclusion in section 6.3.3.

The results of the water vapor measurement allow the conclusion that the O-H stretch feature is attributed to water molecules inside the MOF. It also shows, that the feature grows, when the supply of water is kept open, i.e. a decrease in pressure due to adsorption of some gas molecules causes more water to evaporate.

Possible sources for water during the hydrogen exposure include water adsorbed at the cell’s walls as well as the hydrogen gas itself. Water penetrating the system from the outside is unlikely because of the high pressure inside of the cell. A sputtering effect on the walls due to the impact of hydrogen atoms as it is described in section 6.3.3 for $CO_2$ is also possible. However, the O-H feature occurs immediately with very
fast growth rate in the beginning. This suggests that the initial water amount get introduced directly with the hydrogen gas. The following section describes the analysis of the hydrogen gas for water content.

6.3.5 Water in the Hydrogen Gas

Because the used hydrogen does not have 100% purity there exists the possibility for water contamination and this is investigated in the following.

![Graph of the integrated area of the water-peaks in the infrared spectrum in dependence of the hydrogen pressure. More than one water-peak was analyzed for clarity.](image)

To analyze a possible water content in the hydrogen gas the integrated area of gas-phase water peaks for a series of high-pressure hydrogen spectra was determined. The hydrogen spectra were taken only with a KBr pellet in place and could be measured in a total time of 3 hours and 20 minutes. Except normal, statistical fluctuations of the humidity in the laboratory no other significant changes of the environmental water should have occurred in this time frame.

In order to quantify the water content using the FT-IR spectrum, the area of gas-phase water features between 3776-3718 cm\(^{-1}\), 3860-3845 cm\(^{-1}\) and 3696-3662 cm\(^{-1}\)
were integrated and are presented in figure 6.31 in dependence of the gas pressure.

It turns out that all three features are increasing with pressure. Using the ideal gas equation one sees that the amount of particles \( n \) increases proportionally with the pressure \( p \). The trend of an increase is also true considering the partial pressure of water inside the hydrogen gas. This leads to the conclusion that a significant water content is present in the hydrogen gas.

According to the specifications given by "Gas Technology and Services (GTS, Inc.)", the company providing our hydrogen cylinder, up to 2.5 ppm of water can be contained in the gas. To compare the water amount in the hydrogen with the pure, introduced water vapor, the partial pressure of water as well as the molecular densities per unit volume were calculated and are presented in the following two sections.

6.3.6 Conclusions

It was shown that the introduction of water vapor produces a feature identical to the one increasing slowly when the MOF is exposed to hydrogen. In addition, a water content in the hydrogen gas could be measured. The slower rate measured for the hydrogen exposure compared to the water vapor can be explained by the different water contents in both as calculated in the appendix A.2 and A.1. The mechanism which is believed to take place is the adsorption of the water contained in the hydrogen gas, on the sample. When hydrogen is introduced into the cell, it contains water molecules. These are getting adsorbed on or in the sample and cause the original appearance of the O-H stretch feature. When more water inside the cell gets adsorbed on the sample, the concentration of water decreases. The open connection to the bottle allows water from this reservoir to diffuse back into the cell. This leads to the slow increase of the feature.

The effect does not occur in the same magnitude when pure KBr or silicon with nanotubes [35] is exposed to hydrogen over a long-time and is therefore believed to be
The C-H destruction feature grows at a comparable rate as the O-H water feature and could therefore be related to it. Greathouse et al. simulated the interaction of water with MOF-5 by molecular dynamics [32]. Their results showed, that water can reduce the pore sizes (at low concentrations of 2.3% water content) and even can deconstruct the framework partly or completely (at 3.9 - 9.5%). They claim that a water oxygen atom can replace the oxygen of one of the ligands at the metal center. In addition, hydrogen bonding of water atoms can occur. It is possible that the decrease of the modes in the organic C-H region is attributed to such substitutions inside the material and that the MOF structure is partly destroyed. As FT-IR is a sensitive techniques this does not mean that the framework gets completely destroyed. The water concentrations in the MOF, calculated in the appendix A.3, show that no high water concentrations is present right away. The growing feature is an indication for a hydrophilic sample and therefore water is accumulated. Thus the concentration might reach regions were significant deconstruction takes place. It should be mentioned that C-H modes are visible in most spectra due to contamination introduced during the sample preparation. Therefore it is possible that these contaminations get removed by the introduced water. For a final conclusion further investigation has to be done.

In any event our data shows that water gets adsorbed and accumulated inside the sample. This should be taken into account for the development of production-ready MOFs especially as the Department of Energy assumes only a purity of 99.99% of hydrogen, which therefore contains big amounts of water, for all applications [2].
Chapter 7
Summary

The interaction of hydrogen with Metal-Organic-Framework was investigated using Fourier Transform - Infrared (FT-IR) Spectroscopy. Two different MOF compounds were used for the experiments: Zn(BDC)(TED)$_{0.5}$ and Ni(NDC)(TED)$_{0.5}$.

At first the activation, i.e. the removal of the solvent N$_2$N-dimethylformide (DMF) from the MOF structure, was investigated. The activation was performed by heating the sample to 150$^\circ$C for at least twelve hours. The comparison of the spectra taken during the baking process with the one of pure DMF clearly showed the removal of the DMF modes for both MOFs [29]. At the same time the mode corresponding to adsorbed water between 2000 and 4000 cm$^{-1}$ got removed while the benzene ring structure (1610-1550 cm$^{-1}$ and 1420-1335 cm$^{-1}$) stayed intact [9]. Therefore it was concluded that the solvent and water could get removed without damaging the MOF-structure.

For the investigation of hydrogen-MOF interaction, the MOF was exposed to high-pressure hydrogen (300-1000 psi) inside a special high-pressure cell which allowed in-situ FT-IR measurements. For the Zn-based MOF several new, pressure-dependent modes in the region from 4000 to 4300 cm$^{-1}$ could be seen. The features appear in the region were modes for adsorbed hydrogen are expected [10]. An identification of specific binding sites could not be performed yet because the necessary theoretical calculations are still in progress. When reducing the pressure a decrease of the hydrogen modes could be observed.

No hydrogen interaction could be determined for the Ni-based MOF, probably due to weak interaction or poor crystal quality [26].
During the hydrogen experiments the $CO_2$ modes were increasing constantly. Most likely this is due to $CO_2$ molecules sputtered off the walls of the cell by the high-pressure hydrogen and it is therefore a sample independent effect.

In addition, a very intensive feature around 3400 cm$^{-1}$ was growing without any detectable saturation. This feature, which is located in the O-H stretching region of the spectrum, was identified as water inside the MOF. It was concluded that the water is contained in the used hydrogen gas and that additional water molecules can diffuse from the bottle into the system. These act as supply for the constant growth.

Superimposed to this structure a negative feature in the region of C-H modes (2800 - 3200 cm$^{-1}$) was observed. This feature is increasing over time, indicating the destruction of C-H bonds. While this destruction could be a possible deconstruction related to the water uptake [32], also contaminations on the sample could be the reason. In any event the adsorption of water in the MOF has to be considered for future storage applications of the MOF because it might interfere with other properties of the it.

7.1 Project Outlook

To further confirm the origin of the adsorbed water feature it is planned to remove the water from the hydrogen gas. For this purpose a commercial hydrogen purifier has already been ordered. This purifier works at room temperature using molecular sieves. This material has a very high surface area and it is commonly used for adsorption of water and also other contamination. When big parts of the water got removed from the hydrogen gas, one should see a significant decrease in the growth rate of especially the O-H feature. In general the quality of the measurements will be improved if as little contaminations as possible are inside the system.

The hydrogen interaction will be further analyzed in cooperation with the theoretical physics group of professor David Langreth. As soon as Van der Waals Density
Functional Theory results on the whole system are available the experimental work will focus on finding evidence for these modes and their intensities.

This project is done in collaboration with the groups of professors Li and Langreth and will continue for at least the next three years as part of the DOE’s program for hydrogen storage.
References


[26] Professor Jing Li. Email and personal conversation about unpublished results of the characterisation of metal-organic-frameworks. Group of professor Jing Li, Rutgers University, Chemistry department, 2007.


Appendix A

Supplementary Calculations

A.1 Vapor Pressure and Molecule Density of Water

In order to determine the amount of water present in the HTHP cell during the water vapor experiment the vapour pressure and the density of the water molecules was calculated.

The temperature dependence of the water vapour pressure of is traditionally calculated using the empirical Goff-Gratch equation A.1 [37]. Through analysis of more recent data the Arden Buck equation, which is based on the Clausius-Clapeyron relation, has been suggested in 1996. For the assumed average laboratory temperature of $T = 24 \, ^\circ C \approx 297 \, K$ this newer equation gave inside the error of temperature measurement the same results for the vapor pressure as the older Goff-Gratch formula.

$$
\log_{10}(P_{\text{vapor}}) = -7.90298 \cdot \left( \frac{T_{st}}{T} - 1 \right) + 5.02808 \log_{10} \left( \frac{T_{st}}{T} \right)
- 1.3816 \cdot 10^{-7} \cdot \left( 10^{11.344 \cdot \left(1 - \frac{T}{T_{st}} \right)} - 1 \right)
+ 8.1382 \cdot 10^{-3} \cdot \left( 10^{-3.49149 \cdot \left( \frac{T}{T_{st}} - 1 \right)} - 1 \right) + \log_{10}(P_{st}) \quad (A.1)
$$

In formula A.1 the term $T_{st}$ refers to the steam point temperature $T_{st} = 373K$ and $P_{st}$ to the assumed steam point pressure of $P_{st} = 101.3kPa$. The remaining parameter $T$ refers to the room temperature in Kelvin. Table A.1 contains the calculated vapor pressures for some temperatures which were apparent in the laboratory. It can be deduced that the vapor pressure stayed within the same order of magnitude. For the following calculations an average temperature of $T = 24^\circ C$ is assumed as we want to calculate primarily the order of the searched terms.
<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Goff-Gratch [kPa]</th>
<th>Arden Buck [kPa]</th>
<th>Number of particles [mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>2.64</td>
<td>2.64</td>
<td>1.08</td>
</tr>
<tr>
<td>23</td>
<td>2.80</td>
<td>2.81</td>
<td>1.14</td>
</tr>
<tr>
<td>24</td>
<td>2.98</td>
<td>2.98</td>
<td>1.21</td>
</tr>
<tr>
<td>25</td>
<td>3.17</td>
<td>3.17</td>
<td>1.28</td>
</tr>
<tr>
<td>26</td>
<td>3.36</td>
<td>3.36</td>
<td>1.35</td>
</tr>
</tbody>
</table>

Table A.1: Calculated vapor pressures of water using both, the Goff-Gratch and the Arden Buck equation. The forth column contains the resulting number of particles in a unit volume of $m^3$ according to the ideal gas law.

Using the ideal gas equation A.2 we calculate the density of water molecules per unit volume. The resulting values are also listed in table A.1.

\[ p \cdot V = n \cdot R \cdot T \quad \text{(A.2)} \]
\[ \Rightarrow \frac{n}{V} = \frac{p}{R \cdot T} \quad \text{(A.3)} \]

### A.2 Water in High-Pressure Hydrogen Gas

According to the information given by the supplier of the used hydrogen cylinder, the water contamination has a concentration of 2.5 ppm (parts per million). According to Dalton’s law the sum of all partial pressures of all components present in a gas mixture gives the total pressure of the gas [38]. Equation A.4 applies Dalton’s law to the current problem. Our gas mixture contains besides hydrogen, water and a mixture of other gases, denoted ”others”.

\[ P_{\text{total}} = \sum_i P_i = P_{H_2} + P_{H_2O} + P_{\text{others}} \quad \text{(A.4)} \]

The overall pressure $P_{\text{total}}$ is known, as it is set during the experiment. Using the knowledge of the water concentration we can calculate the partial pressure given by the
gaseous $H_2O$.

$$P_{H_2O} = P_{\text{total}} \cdot \frac{2.5}{10^6} \quad (A.5)$$

Having the partial pressure available it is possible to estimate the number of water molecules in a unit volume. For simplicity we assume the ideal gas law (equation A.2) and use an average laboratory temperature $T = 24^\circ C \approx 297 \text{ K}$.

<table>
<thead>
<tr>
<th>Pressure [psi]</th>
<th>Pressure $[10^8 \text{ Pa}]$</th>
<th>Partial pressure of $H_2O$ $[10^{-3} \text{ psi}]$</th>
<th>Number of particles $[10^{-3} \text{ mol}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>3.45</td>
<td>1.25</td>
<td>3.49</td>
</tr>
<tr>
<td>700</td>
<td>4.83</td>
<td>1.75</td>
<td>4.89</td>
</tr>
<tr>
<td>900</td>
<td>6.21</td>
<td>2.25</td>
<td>6.29</td>
</tr>
</tbody>
</table>

Table A.2: Calculated partial pressures of the water content in the used hydrogen gas and the corresponding number of particles in a unit volume of one cubic meter.

During the experiments pressures of 500 psi, 700 psi and 900 psi were used and table A.2 lists the corresponding partial pressures for water and the number of molecules per cubic meter for each of them.

### A.3 Water Inside the Metal-Organic-Framework

MOFs have a density between 0.2 and $1 \frac{\text{g}}{\text{cm}^3}$. Assuming a sample of 3 mg and an average density of $0.6 \frac{\text{g}}{\text{cm}^3}$ the MOF occupies a volume of $5 \cdot 10^{-3} \text{cm}^3$.

Using the molecule densities calculated in sections A.1 and A.2 the ratio of water to MOF can be estimated.

$$\text{Water-vapor} : 3 \cdot 10^{-3} \text{wt}\% \quad (A.6)$$

$$\text{Water in 700 psi hydrogen gas} : 5 \cdot 10^{-8} \text{wt}\% \quad (A.7)$$