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USING STEADY-STATE VIBRATIONAL SPECTROSCOPY TO CHARACTERIZE
THE EFFECT THAT MOLECULAR ENVIRONMENTS HAVE ON THE KINETICS OF
CHEMICAL SYSTEMS

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Chemistry

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ABSTRACT

A goal that unifies all chemists is the desire to understand the intermolecular and intramolecular interactions that occur in a given system. For many chemical systems, we have an understanding of the intramolecular interactions that occur within a molecule, and how these interactions dictate the physical properties of the molecule, such as the dipole moment, color, or the dielectric constant. The intermolecular interactions that occur between molecules and their molecular environment have proven to be more difficult to isolate, due to multiple interactions occurring simultaneously. It is important to understand these interactions between molecules and their molecular environment because such interactions affect nearly every practical chemical system, from biological to industrial applications. Therefore, it is of the upmost importance to understand how the intermolecular interactions can manifest throughout chemical systems.

We are interested in separating the multiple contributions to the intermolecular interactions that arise from the molecular environment. To achieve this goal, I developed theoretical and experimental frameworks for determining kinetic parameters of chemical systems using steady-state vibrational spectroscopy, a tool that has proven very powerful for determining the effects of both intramolecular and intermolecular interactions, therefore, we have chosen to focus on using vibrational spectroscopy in my dissertation. I first demonstrate the equivalency between the kinetic information extracted from IR and Raman spectroscopies by obtaining identical activation energies for the ligand site exchange of Fe(CO)$_3$(η$^4$-norbornadiene) (FeNBD). These experiments rely upon the extraction of kinetic information from steady-state band shapes and demonstrated that either vibrational spectroscopic technique can be used to extract kinetic information from the band shapes of steady-state spectra. In order to do this, I worked with collaborators to extend the theoretical framework for extracting the rate constant from the band shapes of vibrational spectra to include Raman spectroscopy.
The next step towards the goal of separating the multiple contributions to the 
intermolecular interactions is to categorize these contributions as static effects and dynamic 
effects. For the purpose of this work, I define static effects as those that arise from solute-solvent 
interactions that cause changes in the band shape, while dynamic effects are those that arise from 
changes in the dynamics of a system as a result of interaction with the molecular environment. I 
establish a way to separate static effects from dynamic effects by analyzing the solvent effects of 
Fe(CO)$_3$(η$^4$-cyclooctatetraene) using solvent-dependent IR spectroscopy. The dynamic effects 
induced by the solvent environment were analyzed through temperature-dependent Raman 
experiments of FeNBD in a series of linear alkane solvents.

The last part of this dissertation further focused on the consequences of static effects, 
examining the morphology of conducting polymer films used in thin film devices. We used 
Raman spectroscopy to characterize the crystallinity of conducting polymer films with and 
without dopant materials. From this data, we constructed structure-function relationships by 
correlating the morphology of the polymer film to the overall device performance that will aid in 
the rational design of materials used in thin film devices. This part of my dissertation was done 
in collaboration with Prof. Elizabeth von Hauff at The University of Freiburg in Germany.

Future experiments will explore the effects confining environments will have on the 
dynamics of FeNBD. Initial experiments to encapsulated FeNBD into a porous polymer matrix 
were successful, but there are many potential experiments along this line of reasoning that could 
be explored, and are discussed in the final chapter of this dissertation. In its entirety, this 
dissertation will provide the scientific community with a novel approach that combines the ability 
to measure ground state kinetics using steady-state vibrational spectroscopy with a theoretical 
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Chapter 1

Using Vibrational Spectroscopy to Characterize the Effect of Molecular Environments on the Kinetics of Chemical Systems

A goal that unifies all chemists is our desire to understand the intermolecular and intramolecular interactions that occur in a given system and how they control the behavior of these systems. For many chemical systems, we have an understanding of the intramolecular interactions that occur within a molecule, and how these interactions dictate the physical properties of the molecule, such as the dipole moment, color, or the dielectric constant. The intermolecular interactions occur between molecules and their molecular environments, and have proven to be more difficult to isolate due to the multiple dynamically changing interactions occurring simultaneously. The molecular environment is defined as the space immediately surrounding the molecule, such as, solvent molecules, a polymer matrix, or a porous 3-D material. Solvent is the most common molecular environment encountered by chemists since chemical reactions are typically carried out in solution and there have been many techniques developed, theories derived, and models established to explain these intermolecular interactions. However, condensed phase (liquid) systems present numerous complications that prevent a full description of these interactions. For example, a solute could experience one or multiple solvent interactions ranging from interactions with the physical parameters (e.g. viscosity), or with the electrostatic properties (e.g. polarity), or with the specific chemical interactions (e.g. hydrogen bonding) with the solvent.

It is important to understand the implications these intermolecular interactions have for the behavior of chemical systems because such interactions affect nearly every practical chemical system, from biological to industrial applications. For example, during protein folding, the
hydrophobic and hydrophilic interactions of the protein with molecular environment are crucial to
achieve the proper configuration in the folded protein structure. Hence, it is important to
understand which intermolecular interactions are responsible for stabilizing or destabilizing the
folded protein. In another example, the molecular environment has been shown to effect the
catalytic performance by altering the mechanism in which the reaction proceeds. In palladium-
catalyzed cross-coupling reactions, for instance, the polarity of the solvent dictates the
chemoselectivity of the cross-coupling reaction. These two examples illustrate the upmost
importance of understanding how the intermolecular interactions can manifest throughout the
chemical system of interest.

The overall goal of my dissertation project is to develop a universal probe to understand
the intermolecular interactions in various molecular environments, including solvents, surfaces,
and 3-D structures. We currently do not have a single probe that can be used to understand the
intermolecular interactions in solvent, on a surface, and inside of 3-D structures; therefore, it is
hard to accurately compare the impact on the kinetics of chemical systems across different
molecular environments. These three different types of molecular environments are of interest
for their prevalence in the field of catalysis. As mentioned above, the solvent environment can
affect the chemoselectivity of Pd catalysts in cross-coupling reactions. Surfaces are utilized to
catalyze gas phase reactions, with one of the most famous examples being the Haber-Bosch
process for the production of ammonia. 3-D structures, such as zeolites, have been used as
catalysts in biomass conversion. If we can develop a universal probe for all three types of
molecular environments, we can employ this probe to investigate the impacts of the molecular
environment on industrially-relevant catalytic reactions. A universal probe would provide us
with the ability to compare the intermolecular interactions between different molecular
environments and we can apply this knowledge to catalytic chemical systems.
For studying these effects induced by the molecular environment, many time-resolved techniques have been developed to capture these intermolecular interactions in real time. Examples of such techniques include, pump-probe spectroscopies (spanning the UV-Vis, NIR, and vibrational ranges of the electromagnetic spectrum), time-resolved fluorescence, temperature-jump experiments, hole burning experiments, and echo experiments, just to name a few. The development of these techniques has led to many advances in deriving theoretical frameworks to better understand and predict solvent effects.

One major disadvantage of time-resolved techniques is that the very nature of the experiment dictates that the solvent interaction studied is in the excited state. For many chemical systems, with the exception of photo-induced chemical reactions, we are more interested in the interaction between the solute and the solvent in the ground state, since this more accurately represents the state most abundant in a chemical system. Steady-state spectroscopy provides a pathway to quantify solvent effects for chemical systems in the ground state, but theoretical frameworks and experimental protocols are needed to obtain accurate kinetic information from steady-state vibrational spectra. In this dissertation, I will develop and present methods for using steady-state vibrational spectroscopy to accurately quantify the effect that molecular environments have on the ground state kinetics in chemical systems.

The motivating factor for gaining fundamental knowledge about intermolecular interactions in chemical systems is the application of this knowledge for the rational control of molecular behavior. One long-term goal following the work presented in this dissertation is to connect the interactions between molecules in condensed phases to guest molecules inside of three-dimensional structures, such as polymer matrices or metal-organic frameworks, through the development of a universal probe across different molecular environments. Such three-dimensional frameworks are common catalytic environments, and the ability to connect the dynamic behavior of homogenous and heterogeneous systems will aid in further development of
new catalytic materials. If we can utilize steady-state vibrational spectroscopy to probe this interaction, and quantify the nature of the interaction, then we can apply this knowledge to any chemical system and its molecular environment. In the next few sections, I will outline some of the basic principles of vibrational spectroscopy, the information that is present in vibrational spectroscopic features, and how we can obtain kinetic information from steady-state vibrational spectroscopy.

**Steady-State Vibrational Spectroscopy as a Tool for Measuring the Effects Induced by Molecular Environments**

Vibrational spectroscopy has proven to be a very powerful tool for determining the effects of both *intra*molecular and *inter*molecular interactions; therefore, we have chosen to focus on vibrational spectroscopy in my dissertation. In the most fundamental sense, vibrational spectroscopy captures the interaction between light and matter, specifically in the energy range of 100 – 3000 cm$^{-1}$. The result of this interaction is most commonly taken to be an excitation of a molecular vibration from the ground state to the first excited state as shown in Figure 1-1a. By monitoring the light absorbed or scattered by the molecule, we can obtain an infrared (IR) or Raman spectra, respectively. Though both techniques report on vibrational transitions, the mechanisms for these transitions are not the same – nor are the associated spectra. Figure 1-1b shows the IR (blue) and Raman (black) of Fe(CO)$_3$(η$^4$-norbornadiene) (FeNBD) in 2-methylpentane at room temperature. This is an example of a compound with IR and Raman spectra that are very similar. Both spectra show two bands at ~1960 cm$^{-1}$ and 2035 cm$^{-1}$. However, if we consider the IR and Raman spectra for liquid benzene shown in Figure 1-1c, we see an excellent example of a case where the two spectra are completely different. Thus, the IR and Raman spectra span a range of complementarity, expressed by the common rule that IR and
Raman bands for molecules with centers of symmetry (like benzene) are mutually exclusive. While I next briefly explore the underlying causes for these differences between IR and Raman, from a theoretical perspective, several excellent texts are devoted to this topic for when more detailed explanations are desired by the reader.  

![Figure 1-1: (a) Schematic of a vibrational transition. (b) IR and Raman spectra of Fe(CO)₃(η⁴-norbornadiene in 2-methylpentane at room temperature. (c) IR and Raman spectra of liquid benzene at room temperature.](Image)

Theory and Mechanisms of Vibrational Spectroscopy

From a molecular viewpoint, IR and Raman spectroscopies differ in how the molecule interacts with light. For IR, the *permanent* dipole moment of the molecule interacts with infrared light that is passed through the sample. As an example we will consider a molecule of carbon monoxide molecule. The electronegativity difference between carbon and oxygen atoms in a carbon monoxide molecule generates a permanent dipole moment, where the carbon atom has a slight positive charge and the oxygen atom has a slight negative charge that is separated by the bond distance. As the carbon monoxide molecule vibrates, the distance between the carbon and oxygen atoms changes, resulting in an oscillating dipole moment. This change in dipole moment
provides a means for light to interact with the molecule and promote vibrational transitions. The transition dipole moment, \( R_v \), for this process is described by Equation 1-1:

\[
R_v = \int \psi'' \hat{\mu} \psi' d\tau
\]  

(1-1)

where \( \psi'' \) and \( \psi' \) are the wavefunctions of the upper and lower vibrational energy levels involved in the transition, respectively, and \( \hat{\mu} \) is the dipole moment operator expressed as a Taylor series in Equation 1-2 as:

\[
\hat{\mu} = \mu_e + \left( \frac{d\mu}{dx} \right)_e x + \frac{1}{2!} \left( \frac{d^2\mu}{dx^2} \right)_e x^2 + \ldots
\]

(1-2)

where \( e \) is the equilibrium configuration and \( x \) represents the direction of the dipole moment, which also can be in the y or z directions. The higher ordered terms (\( n=2 \) and above) of this expansion are small due to their \( 1/N! \) dependence, therefore we can ignore them.

If we substitute Equation 1-2 into Equation 1-1 to get the a vibrational transition described by Equation 1-3:

\[
R_v = \mu_e \int \psi'' \psi' dx + \left( \frac{d\mu}{dx} \right)_e \int \psi'' x \psi' dx
\]

(1-3)

The first term in Equation 1-3 is zero, because we can pull out \( \mu_e \) as a constant out in front of the integral, leaving the term, \( \int \psi'' \psi' dx \), which must be zero for the case that there is a transition in the vibrational wavefunction (i.e. \( \psi'' \neq \psi' \)). The second term in Equation 1-3 is non-zero when both the \( \left( \frac{d\mu}{dx} \right)_e \) term and the integral are non-zero. The first requirement explains the direct dependence of the intensity of IR absorption upon the magnitude of the dipole moment involved. The second requirement is the same as insisting that the integrand is an even function. If we assume that \( \psi' \) is the vibrational wavefunction of the ground state, then we know that \( \psi' \) will be an even function, as it belongs to the totally symmetric representation. This result imposes the requirement that \( \psi'' \) belongs to the same representation as the component of the dipole moment (in x, y, or z), so that their product is also posses the totally symmetric representation. Finally, it
is worth nothing that, if this transition is the fundamental transition \((v_0 \rightarrow v_1)\), then we also expect it to be the strongest transition present. This result intuitively makes sense if we consider a Boltzmann distribution of particles at room temperature, where the ground vibrational state is the most populated.

Turning to Raman spectroscopy, the molecule interacts with the electric field \((E)\) of the incident light to induce a dipole moment \((P)\) along a direction \(x\), \(y\), or \(z\). The resulting induced dipole moment is proportional to the strength of the electric field and the case in which the dipole moment is induced is, in turn, given by the molecule’s polarizability \((\alpha)\):

\[ P = \alpha E \]  

where \(P\) is the induced dipole moment and \(E\) is the strength of the electric field. Polarizability is a molecular property intrinsic to the molecule, but can be perturbed when the bond distance fluctuates about its equilibrium position in the electric field. Due to the fact that the electric field can induce dipole moments in directions \(x\), \(y\), or \(z\), and the directionally of chemical bonds, it is often easiest to represent the polarizability in Equation 1-4 as a tensor:

\[
\begin{bmatrix}
P_x \\
P_y \\
P_z
\end{bmatrix} =
\begin{bmatrix}
\alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\
\alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\
\alpha_{zx} & \alpha_{zy} & \alpha_{zz}
\end{bmatrix}
\begin{bmatrix}
E_x \\
E_y \\
E_z
\end{bmatrix}
\]  

(1-5)

The oscillation of the polarizability tensor \((\alpha)\) causes an oscillation in the induced dipole moment, which can result in a vibrational transition described by Equation 1-6:

\[ R_v = \int \psi'' \alpha \psi' d\tau \]  

(1-6)

For the integrand of \(\int \psi'' \alpha \psi' dx\) to be non-zero, the symmetry must be the same between \(\psi''\) and \(\alpha\), due to the ground state wavefunction, \(\psi'\), being totally symmetric (even function). Because \(\alpha\) is a tensor, the components of the matrix act like the quadratic terms of a character table, and \(\alpha\) acts like the quadratic functions. Therefore, \(\psi''\) must have matching symmetry for the integrand to be non-zero. The above considerations directly lead to the conclusion that, for
molecules possessing a center of symmetry, the IR and Raman bands will be mutually exclusive. Because \( \beta \) behaves as an odd function (x, y, and z) and \( \alpha \) acts as an even function (quadratic), then they cannot belong to the same representation for groups with a center of symmetry. Referring back to Figure 1-1, we now see why all the IR and Raman bands for benzene (which possesses a center of symmetry) are mutually exclusive, while for FeNBD (without a center of symmetry), the bands are present in both the IR and Raman spectra.

With an understanding of selection rules out of the way, we further consider the applications of them to light-matter interaction and the resulting vibrational spectra. Figure 1-2a presents a cartoon illustration of benzene’s interaction with incident light. There are two competing mechanisms for this interaction, the molecule can either absorb or scatter the incident light. The molecule will absorb the frequencies of light that are resonant with the oscillations of a fluctuating dipole moment in the molecule. Infrared spectroscopy detects the light transmitted and plots it versus the frequency it corresponds to, where a decrease in the percentage of transmitted light indicates an absorption the light by the molecule. When considering the IR spectrum of benzene, a transition occurs at 1479 cm\(^{-1}\), resulting in absorption of light at 1479 cm\(^{-1}\), and a peak in the IR spectrum at 1479 cm\(^{-1}\), as shown in Figure 1-2b.
In contrast to the absorption mechanism of IR spectroscopy, Raman spectroscopy arises from a scattering mechanism, where a molecule absorbs light to generate an extremely short-lived state called the virtual state. Upon returning to the ground state from this virtual state, the system can experience a change in vibrational quantum number. There are three possibilities for this change. If $\Delta \nu = 1$, then the scattered light is at lower energy (longer wavelength) than the incident light, and the inelastic scattering process is called Stokes scattering. If $\Delta \nu = -1$, then the scattered light is at higher energy (shorter wavelength) than the incident light, and the process is
called anti-Stokes scattering. Finally, if $\Delta \nu = 0$, then there is no difference in the energy of the incident and scattered light – a process known as Rayleigh scattering. A Raman spectrum is then generated by counting the number of scattered photons and plotting their total numbers as a function of the change in energy from the incident light, as shown in Figure 1-2c. The most intense scattering comes from Rayleigh scattering followed by Stokes scattering, and then anti-Stokes scattering. Anti-Stokes scattering is not as intense as Stokes scattering because it requires the first excited vibrational state to be populated, and at room temperature the ground vibrational state is often more populated than the first excited vibrational state. Therefore, Stokes scattering is typically presented as the Raman spectrum.

Above, we explored the differences between IR and Raman spectroscopies. While several differences between IR and Raman spectroscopies were found, the information obtained from the appearance of the spectra, such as band position, bandwidth, and overall band shape are the same. Next, I explore the information that can be obtained from the band position, intensity, and bandwidth of vibrational bands.

**Interpreting Vibrational Spectra**

The information most commonly extracted from vibrational spectra is the band position, which is used to identify the energy and modes of the molecular vibrations in a molecule. Different functional groups in organic molecules have characteristic molecular vibrations originating from the frequency of the oscillating dipole moment between atoms. For instance, alkane functional groups (C-H) oscillate with a frequency between 2850 -3000 cm$^{-1}$, therefore bands in this region signify the presence of a C-H group. At the same time, the carbonyl functional groups (C=O) is commonly observed from 1670-1820 cm$^{-1}$ as an intense peak in the vibrational spectrum, but the exact location of this peak varies, depending on if the carbonyl
group is part of a ketone, aldehyde, ester, amide, anhydride, or carboxylic acid functional group. Thus, the exact position of the $\nu$(CO) band provides specific structural information. Many other examples exist of specific chemical information being manifested in vibrational band positions, and analysis of the band position in vibrational spectroscopy is used to aid in the characterization of products or new materials. However, in addition to being diagnostic of internal structure, a shift in the band position of a molecule can be also indicative of the intermolecular interactions with the molecular environment, with larger interactions resulting in larger shifts in band position. In total, the position can be diagnostic of both intramolecular connectivity, as well as the influence of the environment in which a molecule finds itself. It is no wonder then, that this is the principal piece of information often sought in vibrational spectroscopy.

The second most often discussed observable parameter of vibrational bands is the intensity of the bands. In general, the intensity of a vibrational band in linear spectroscopy is proportional to the square of the transition moment integrals in Equations 1-3 and 1-6 for IR and Raman, respectively, to give the probability of that transition occurring as shown in Equation 1-7:

$$\text{IR intensity} \propto \left| \left( \frac{d\mu}{dx} \right)_e \int \psi'' x \psi' dx \right|^2$$

$$\text{Raman intensity} \propto \left| \left( \frac{da}{dQ_k} \right)_e \int \psi'' Q_k \psi' dQ_k \right|^2$$

In Equation 1-7, the Raman intensity is expressed in terms of the normal coordinates of the vibration, $Q_k$, $Q_l$ ... that are associated with molecular vibrational frequencies $\omega_k$, $\omega_l$ ... that are summed over all normal coordinates. From this, we see that the IR intensity is directly related to the square of the change in dipole moment, hence, the larger the change in dipole moment, the greater the intensity of the IR band. Because of this relationship, vibrations with a large change in dipole moment, such as the carbonyl (C=O) function group described above, will have a
greater intensity than a vibration with a smaller change in dipole moment that dictates intensity, such as a C=C functional group. In addition, as it is the square of the change in dipole moment, changes in molecular interactions that alter the change in the dipole moment will result in correspondingly large changes in the absolute intensity of the associated band. For Raman vibrational bands, the intensity is proportional to the square of the change in polarizability tensor. The change in the polarizability tensor is not as straightforward as the change in dipole moment used in IR, but it is also sensitive to the environment local to the molecule participating in the scattering event. In addition to such reasoning concerning the transition dipole moment, it is also worth remembering that the intensity of a band in a linear spectroscopic technique is also directly proportional to the concentration of the species giving rise to that mode. Thus, all things being equal, the intensity of a band can be used to quantify the concentration of molecular species present. In total, the usefulness of intensity of vibrational spectroscopic features is such that it has found wide scale use in the interpretation of changes in molecular environments and concentrations.

The final observable we will consider here is the bandwidth of a vibrational band. The bandwidth is most often reported in terms of the full-width at half-maximum (FWHM) of the vibrational band, and contributions to its value come from two main effects: homogeneous and inhomogeneous broadening. Homogeneous broadening arises from mechanisms that affect all molecules in a sample in the same way, while inhomogeneous broadening arises from mechanisms whose effects differ from molecule to molecule. In some sense, this is a question of timescales, and one must consider the relationship between the intrinsic correlation time of vibrational spectroscopy and that of the broadening mechanism. When the timescale of the effect leading to broadening is much slower than the vibrational correlation times, it is said to be time-averaged, and give rise to homogeneous broadening, while those that are much faster than the correlation time are not averaged, and give rise to inhomogeneous broadening. Examples of
mechanisms that give rise to homogeneous broadening are: the lifetime of the excited vibrational state, the pure dephasing time, and the orientational relaxation effects on the oscillation of the dipole moment or polarizability for IR or Raman spectroscopy, respectively. Inhomogeneous broadening is a consequence of the overlapping static frequency distributions from the oscillation of the dipole moment or polarizability of the chemical system, resulting from the states being in different environments. Common sources of inhomogeneous broadening are differential solvation environments and Doppler effects.

With regard to the shape of spectroscopic features, homogeneous and inhomogeneous broadening give rise to different contributions to the overall band shape. As inhomogeneous broadening results from the presence of multiple populations within the sample, this broadening source results in a Gaussian line shape. Homogenous broadening, on the other hand, gives rise to a Lorentzian band shape. Both homogeneous and inhomogeneous broadening occur simultaneously, and so the observed vibrational band shape of a vibrational spectroscopic feature is neither pure Gaussian nor pure Lorentzian, but rather a convolution of the two – a shape known as a Voigt profile.

From the above considerations, it should be clear that there is much information present in the band shape of vibrational features. One way to view this information, is that the band shape reflects the nature of the molecule itself (homogeneous) and the interaction of the molecule with its environment (inhomogeneous). Another way to think about this is that the band shape contains information about the static (not time averaged) features of the molecule (inhomogeneous) and the dynamic (time averaged) behavior of the molecule (homogeneous). The latter of these is particular interesting, as it implies the possibility of extracting dynamic information from simple steady-state band shapes. In the next section, I will briefly outline the previous efforts to extract such dynamic information, and the theoretical framework that I will employ in continuing this tradition.
Extracting Kinetic Information from Vibrational Spectra

Band shape analysis (BSA) provides an approach for characterizing both intramolecular and intermolecular interactions that results in changes to the band position, bandwidth, or overall band shape. The changes in the overall band shape of vibrational bands that result from a dynamic processes are central to this dissertation. Vibrational spectroscopy can capture dynamics on the picosecond timescale, as governed by the time-energy uncertainty principle as shown in Equation 1-8\(^{20}\)

\[
\Delta E \times \Delta t \geq \frac{h}{2\pi}
\]  

(1-8)

where \(\Delta E\) is the energy difference for a change in the system, \(\Delta t\) is the time the change takes to occur, and \(h\) is Plank’s constant. This principle dictates that the energy separation between two exchanging peaks determines the lifetime of the exchange, therefore, if two exchanging vibrational bands are separated by tens of wavenumbers, the process occurs on the picosecond timescale.

Though the dynamic information is present, it requires careful analysis in order to extract the kinetics of chemical exchange. Thus, we must use theoretical methods to predict the vibrational spectra for a chemical system and match them to the vibrational spectra acquired experimentally. This type of BSA has been developed for NMR spectroscopy for the analysis of chemical exchange in solution using the Bloch equations. \(^{21}\) The Bloch equations can be modified for IR spectra and the analysis parallels that used for chemical exchange in NMR spectra.\(^{20,22-24}\)

The modification of the Bloch equations has been applied to chemical exchange using IR spectroscopy. The initial reports on this phenomenon were given by Weiss and co-workers, who illustrated broadening of IR bands as a result of chemical exchange in three systems.\(^{25,26,27}\) The first system was 1,2-dichloroethane, which has two rotational isomers that can be distinguished
through the CH₂ twisting bands at 1124 cm⁻¹ and 1144 cm⁻¹ (Figure 1-3a). These bands are sensitive to changes in temperature in the neat liquid and to the solvent environment. Analysis of the band shapes yielded the extraction of kinetic and thermodynamic parameters and the most interesting result was the activation energy for the gauche rotamer was raised by 0.318 kcal/mol when in a solution of CS₂. This result reflects the intramolecular interactions of the system in neat liquid and the intermolecular interactions of the solvent environment on the rate of isomerization.

Another system examined by Weiss and coworkers was the enol-keto tautomerization of acetylacetone. They investigated the C=O and C=C stretching frequencies using variable temperature IR spectroscopy (Figure 1-3b) and isotopic substitution of the α-hydrogens for deuterium. These experiments yielded the resolution of several peaks in the IR spectrum, indicating the presence of several tautomeric forms. The kinetics extracted from these spectra concluded that the two enolic forms of acetylacetone interconvert faster than the picosecond.
timescale, therefore, the two enol tautomers cannot be separated with IR spectroscopy. They were able to calculate the activation energy difference between the two enol tautomers to be 1.55 kcal/mol. Thus, this study attempted to investigate intramolecular interactions, but found that the tautomerization was too fast to analyze with IR spectroscopy.

The last system analyzed by Weiss and coworkers was the formation of a charge transfer complex between IBr and acetonitrile. Analysis of the nitrile stretch in the IR as a function of temperature and concentration of IBr resulted in a free and bound nitrile group in solution (Figure 1-3c). The kinetics and thermodynamics of the formation and dissociation of the charge transfer complex were reported. The rate constant for the formation of the charge transfer complex varied from 1.5 -- 6.0x10^{11} s^{-1} depending on the concentration of IBr and the temperature. The rate constant for the dissociation of the charge transfer complex ranged from 4.14x10^{11} s^{-1} through 1.43x10^{12} s^{-1}. This study reported on the intermolecular interactions of acetonitrile with its molecular environment.

The above three studies show the power of using IR spectroscopy to analyze both the intramolecular and intermolecular interactions occurring in chemical systems. They also illustrated the need to acquire temperature-dependent spectra, when trying to extract rates from steady-state band shapes. However, these reports also incited much controversy in the literature regarding the way in which the kinetics were extracted^{22,28,29}. This debate continued until a set of experiments established a rigorous mechanism for the ligand exchange in iron complexes, and developed a theoretical framework for extracting the rate of ligand exchange from IR band shapes.

At the heart of these conclusive experiments were temperature-dependent IR experiments of several tricarbonyl(diene)iron complexes that exhibit dynamic ligand site exchange between the three CO ligands on the complex^{20,24,30,31}. The ligand exchange for tricarbonyl(η^4-norbornadiene)iron (FeNBD) and tricarbonyl(η^4-1,5-cyclooctadiene)iron complexes occurs on the
picosecond timescale, thus, the exchange can be ascribed to the broadening of the CO band as the temperature was decreased in the IR spectrum. At -140 °C, the IR spectrum for both iron complexes displays three carbonyl bands, as expected from their $C_s$ symmetry. As the sample is warmed up to room temperature, the two lower frequency CO bands merge and coalesce together. Figure 1-4 illustrates the changes in band shape of FeNBD resulting from ligand site exchange. For more details about coalescence of their vibrational bands, the reader is referred to Chapter 2, which focuses on comparing IR and Raman spectra for FeNBD. Through these experiments, the authors established that the CO ligand site exchange occurs via a turnstile mechanism that was mapped by isotopically labeling with $^{13}$CO ligands and developed a theoretical framework for extracting the rate of CO ligand site exchange in these iron complexes. Also noted, at the time was that there is “extra” intensity present in dynamically exchanging systems that cannot be explained in the absence of dynamic exchange on the vibrational timescale. A brief account of the theoretical framework developed to calculate vibrational spectra during chemical exchange from the modified Bloch equations will be presented here, but a more detailed derivation can be found in Appendix 2B.

![Figure 1-4: Variable temperature IR experiment for FeNBD in two methyl pentane. The IR spectrum was adopted from reference 23.](image-url)
The main idea behind the theoretical treatment relies on the realization that an IR spectral profile can be expressed as the half-Fourier transformation as

\[
I(\omega) = \text{Re}\{\int_0^{\infty} G(t) e^{-i\omega t} dt\}
\]

where \(G(t)\) is the correlation function, \(\omega\) is the vibrational frequency in wavenumbers, and \(t\) is time. The correlation function can be interpreted as describing how long the oscillating dipole moment persists until the overall motion in the chemical system averages out the oscillation. For this derivation, we are only interested in the fundamental vibrations \((\nu = 0 \rightarrow \nu = 1)\), therefore, the correlation function can be written in terms of the average vibrational frequency,

\[
\omega_{\text{average}}
\]

as

\[
G(t) = \sum_k P_k D_k(0) D_k(t)
\]

where \(P_k\) is the intensity factor, \(D_k(0) = (2\omega_{\text{average}}/\hbar)^{1/2}\), and \(D_k(t) = \langle 1_k | Q_k(t) | 0 \rangle\) is the transition dipole moment. \(Q_k(t)\) is the normal coordinate of the \(k\)th mode and \(1_k\) is the first excited vibrational state. In the absence of chemical exchange, the modified Bloch equation, \(D_k(t)\), obeys the equation of motion for the transition dipole moment as

\[
\frac{dD_k(t)}{dt} = (i\omega_k - \gamma_k - t\sigma_k^2) D_k
\]

where \(\omega_k\) is the vibrational frequency, \(\gamma_k\) accounts for broadening of the Lorentzian component in the spectral profile and consequently, the homogeneous broadening. The \(\sigma_k\) term encompasses the broadening of the Gaussian component that is associated with inhomogeneous broadening. In solving Equation 1-11 and substituting the solution back into Equation 1-10, one obtains a correlation function

\[
G(t) = \sum_k h_k e^{-i(\omega_k - \gamma_k)t - (t^2/\tau^2)} e^{-\sigma_k^2}
\]

where \(h_k\) is the relative peak height. Substituting this new correlation function back into Equation 1-9 yields an IR spectral profile \((I(\omega))\) that is the summation of Voigt line shapes over \(k\).
vibrational modes, where a Voigt line shape is the convolution of a Gaussian component 
\((t^2/2)\sigma_k^2\) and a Lorentzian component \((i\omega_k - \gamma_k)t\). \(^{32}\)

\[
V(h_k, \omega_k, Y_k, \sigma_k) = Re \left\{ h_k \int_0^\infty e^{i(\omega_k - \gamma_k)t - (t^2/2)\sigma_k^2} e^{-i\omega t} dt \right\}
\]  \(\text{(1-13)}\)

Now, we introduce chemical exchange in the Bloch equation for the transition dipole moment 
(Equation 1-11), and it becomes convenient to use the density matrices to describe the chemical exchange. Density matrices describe systems that are in a mixed state, such as a system undergoing a chemical exchange. By introducing chemical exchange into Equation 1-11, we can rewrite the modified Bloch equation in terms of density matrices as \(^{32}\)

\[
\frac{dD}{dt} = -(A + t\Sigma) \cdot D
\]  \(\text{(1-14)}\)

where \(D\) is the column vector with elements \(D_k(t)\), \(\Sigma\) is a diagonal matrix with elements \(\Sigma_{kk} = \sigma_k^{-2}\), \(t\) is time, and \(A\) is given by \(^{32}\)

\[
A_{kl} = \begin{cases} 
-i\omega_k + \gamma_k - K_{kk} & k \neq 1 \\
-K_{kl} & k \neq 1 
\end{cases}
\]  \(\text{(1-15)}\)

where \(K\) is the rate matrix. The rate matrix is equal to \(K = k^\text{ex} \cdot (Z - I)\), where \(k^\text{ex}\) is the exchange rate of the system, \(Z\) is the exchange matrix, and \(I\) is the identity matrix. \(^{32}\)

\[
Z_{kl} = \begin{cases} 
1 - \sum_{m \neq 1} Z_{km} & k \neq 1 \\
R_{kl}^\text{ex} & k \neq 1 
\end{cases}
\]  \(\text{(1-16)}\)

\(R_{kl}^\text{ex}\) is the relative rate of exchange for peaks \(k\) and \(l\), and must be entered for the chemical system of interest. The parameter \(k^\text{ex}\) will be the rate of exchange in the chemical system extracted from the vibrational spectra. From here, the solution to the modified Bloch equation in Equation 1-16 is substituted into the correlation function in Equation 1-10. The new correlation function including the chemical exchange component is substituted into Equation 1-9 to yield a Voigt line shape for the overall IR spectral profile as \(^{32}\)
where $\text{Im}\{-A_k\}$ is the vibrational frequency after exchange, $\text{Re}\{A_k\}$ is the Lorentzian width after exchange, and $\Sigma_k^{-1/2}$ is the Gaussian width after exchange.

This theoretical framework is used in BSA to simulate IR spectra by inputting the parameters of the relative height ($h_k$), band position ($\text{Im}\{-A_k\}$), Gaussian FWHM ($\Sigma_k^{-1/2}$), Lorentzian FWHM ($\text{Re}\{A_k\}$), and the rate of exchange ($k_{\text{ex}}$) into Equation 1-17 to produce a Voigt line shape that best matches experimental spectra. In Chapter 2, our collaborators have extended this theoretical framework to include Raman spectroscopy and wrote a program that simulates both IR and Raman spectra undergoing chemical exchange. This program will be used for our BSA of vibrational spectra undergoing chemical exchange in this dissertation.

**Dissertation Overview**

This dissertation will serve as a contribution to the overarching goal of understanding how various molecular environments impact the kinetics of [*intra*]molecular and [*inter*]molecular interactions in chemical systems. We are interested in separating the [*inter*]molecular interactions caused by the molecular environment from the effects the [*intra*]molecular interactions occurring simultaneously in chemical systems. To achieve this goal, we will develop theoretical and experimental frameworks for determining kinetic parameters of chemical systems using steady-state vibrational spectroscopy.

For this dissertation work, we have chosen to use FeNBD as a model complex for several reasons. First, this complex is known to undergo dynamic exchange on the vibrational timescale, therefore, changes in band shape with temperature will indicate a change in the dynamics of the system. Second, the [*inter*]molecular interactions of this system can be easily
separated by changing the molecular environment. Finally, the complex can be synthetically modified, which would allow for the examination of purely *intramolecular* interactions. The experiments in this dissertation are aimed to fulfill the goal of using steady-state vibrational spectroscopy to understand the effects molecular environments induce on chemical systems.

In Chapter 2, we will test the equivalency between IR and Raman spectroscopy for determining the kinetics of FeNBD and extend the theoretical framework used for BSA for IR spectroscopy to include Raman spectroscopy. This work was performed in collaboration with Prof. Lasse Jensen at The Pennsylvania State University. In Chapter 3, we will investigate untangling of *dynamic* from *static* solvent effects using Fe(CO)_5(η^4^-cyclooctatetraene), which is important for being able to accurately report kinetic information from vibrational spectroscopy. We then direct our attention back to understanding the intermolecular interactions that effect the rate of chemical exchange of FeNBD in a series of linear alkane solvents in Chapter 4. In Chapter 5, we switch our focus to more traditional uses of Raman spectroscopy to characterize the effect the molecular environment has on the crystallinity of conducting polymer thin films, used in transistors and organic photovoltaic cells. The work in this chapter was performed in collaboration with Prof. Elizabeth von Hauff at The University of Freiburg in Germany. The last chapter of this dissertation summarizes the conclusions from each project and explores the idea that different molecular environments can impact the kinetics of FeNBD, such as the void spaces inside of a polymer matrix. In its entirety, this dissertation will provide the scientific community with a novel approach that combines the ability to measure ground state kinetics using steady-state vibrational spectroscopy with a theoretical framework to analyze the effect the molecular environment induces on the ground state kinetics in chemical systems.
References

24. Grevels, F. W. *et al.* The Very Low Barrier of CO Site Exchange in Tricarbonyl(eta 4 -1,5-


Chapter 2

Testing the Equivalency of Kinetic Parameters derived from Steady-State IR and Raman Spectroscopies

Introduction

In Chapter 1, we addressed that the identity of the molecular vibration and the degree of heterogeneity in the molecular environment are determined from the band position and bandwidth, respectively. However, the bandwidth of a steady-state vibrational band is affected by multiple contributions in addition to heterogeneity, including the dynamics of the chemical system. Thus, in principle, analysis of band shapes could lead to extraction of kinetic information in any given system. In most cases, it is difficult to deconvolute all of the contributions to the bandwidth, which has largely prohibited using the band shape of steady-state vibrational spectra to accurately assign kinetic information. However, there are special cases, where the contribution to the bandwidth arising purely from dynamic processes can be isolated and useful dynamic information extracted.

Let us first consider the simplest case, where we have two distinct chemical species (A and B) that undergo exchange (Figure 2-1). At the limit of stopped exchange, A and B give rise to their own spectroscopic features, which can be seen in Figure 2-1a as two peaks. If we then increase the rate at which species A and B exchange (perhaps by increasing the temperature), we observe that the bands move closer together and start to overlap (Figure 2-1b). This overlap in the bands will continue to increase as the rate of exchange is increased until eventually the two bands fully coalesce into one band (Figure 2-1c). The timescale ($\Delta t$) required to observe such effects in steady-state spectroscopy is determined by the energy separating the two exchanging
peaks ($\Delta E$), as described by the time-energy uncertainty principle ($\Delta E \times \Delta t \geq \hbar/2\pi$). Thus, the coalescence of two peaks separated by tens of wavenumbers (as is often the case in a vibrational spectrum) requires a lifetime for exchange to be on the order of picoseconds.\(^1\) Thus, assuming that the spectra shown in Figure 2-1 are vibrational spectra, we can say that the rate of exchange in Figure 2-1a is slower than the picosecond timescale because we were able to resolve both bands from species A and B. Figure 2-1b is representative of an exchange occurring on the picosecond timescale and Figure 2-1c shows the full coalescence of bands A and B when the rate of exchange is faster than the picosecond timescale.

Figure 2-1: Spectroscopic bands associated with two species (A and B) undergoing exchange will broaden and coalesce as the rate of exchange increases (a-c). The rate of exchange can then be extracted from the shape of the resulting band.

Over the last 50 years, there have been several reports using steady-state vibrational spectroscopy to observe picosecond dynamics of chemical systems, including the protonation/deprotonation of acids,\(^5,7\) the transfer of single electrons,\(^8,10\) and the dynamic
coupling to solvation environments.\textsuperscript{10-17} More recently, multiple pump-probe spectroscopic techniques have been developed and used to determine picosecond dynamics in chemical systems.\textsuperscript{13,18-24} However, steady-state spectroscopies still have some advantages over these modern techniques. Steady-state dynamic spectroscopy provides a way to probe the ground state dynamics of a chemical system, while pump-probe spectroscopy requires a perturbation of the chemical system; therefore, only excited state dynamics are accessible. Additionally, the modern pump-probe techniques require both expensive equipment and expert users, which lies beyond the capabilities of many laboratories, such as those present at primarily undergraduate institutions or in developing countries. Finally, the simplicity of linear steady-state spectroscopy promises greater throughput that for the more complex approaches, which would allow for large systematic studies of how changes to a system impact its dynamics.

As there are clear advantages to using steady-state vibrational spectroscopy and this approach should be developed further. One outstanding question is the possible equivalence of dynamic effects in IR versus Raman spectroscopy. It has long been understood that IR and Raman spectroscopies form a complementary pair of spectroscopic techniques – and are often used together to provide a complete picture of the vibrational motion of molecular systems. It would be useful to know if the dynamic information contained in Raman bands is the same as for IR bands, so that the complementary nature of IR and Raman could be exploited in the study of ultrafast ground state chemical dynamics. On one hand, the simple energetic considerations discussed above lead to the conclusion that both spectroscopies should report on the same range of dynamics and the dynamics determined using either IR or Raman spectroscopy should be identical. On the other hand, both spectroscopic techniques arise from different phenomena and differ in the manner vibrational data is collected, therefore, they may report different kinetics (see Chapter I for more detail).
particular, bands which are present in both IR and Raman spectra have no guarantee of equivalent bands shapes. This is an important point, as it is the band shapes that report on chemical dynamics. These potential differences between IR and Raman spectroscopies necessitate a direct test of the equivalency of steady-state IR and Raman spectroscopies.

In this chapter, we provide this test using Fe(CO)$_3(\eta^4$-norbornadiene) (FeNBD). This system has been subject to a number of studies in which it was confirmed that the three carbonyl ligands rotate around the iron center at a rate sufficient to cause dynamic broadening of the carbonyl bands in the IR.$^{1,25,27}$ Fortunately, the same carbonyl bands observed in the IR are also present in the Raman and, thus, this molecule is ideal for a comparison between kinetic analysis acquired from IR and Raman spectroscopies. Below, we detail experiments that demonstrate the equivalency of steady-state IR and Raman for reporting on picosecond dynamics. This result allows for confidence in selecting either IR or Raman spectroscopy as a tool when discussing the kinetics of any particular system.

Experimental

**General Procedures.** Norbornadiene and 2-methylpentane were purchased from Alfa Aesar and hexanes from VWR and were used as received. Iron(0) pentacarbonyl was purchased from Sigma-Aldrich and was filtered through a sterile syringe filter with 0.2 µm cellulose acetate membrane (VWR) before use.

**Spectroscopic Measurements.** Raman spectra were acquired using a Renishaw inVia Raman Microscope equipped with an integral microscope (Leica DM2500 M) and a Linkam LTS420 liquid nitrogen temperature controlled stage. The excitation source was a 647 nm CrystaLaser CL-2000 diode pumped laser (70 mW, model DL647-070). We employed a 1200 l/mm grating, yielding a resolution of 1.9 cm$^{-1}$. The sample cell was home-built by annealing two
glass slides and a cover slip at 873 K for 12 hours then allowed to cool to room temperature. The slides were pre-drilled with holes to hold the liquid samples and allow addition and removal of the sample. A diagram of the cell can be found in the Appendix A. The geometry of the cell allows for the liquid to have maximum contact with the temperature-controlled stage. The temperature of the sample cell was calibrated for the Raman spectrometer with an external thermocouple and the calibration curve can be found in Appendix A. The error in the temperature measurement was determined to be ± 1.8 K. Raman samples were prepared by adding ca. 0.5 mL of 2-methylpentane to ca. 1 mL of FeNBD.

IR spectra were acquired at a resolution of 4 cm\(^{-1}\), using a Perkin Elmer Spectrum 400 FT-IR/FT-NIR with a Specac variable temperature liquid nitrogen cryostat (NaCl exterior windows). A vacuum tight Specac liquid cell with CaF\(_2\) windows was used to hold the samples during acquisition of the variable temperature IR data. Specac reports a ± 2 K sample temperature for their variable temperature cell. IR samples were prepared by diluting the Raman samples with 2-methylpentane.

**Synthesis of Fe(CO)\(_3\)(\(\eta^4\)-norbornadiene) (FeNBD).** Synthesis of FeNBD was adapted from a previously published procedure.\(^{28}\) Under N\(_2\), Fe(CO)\(_5\) (2.9 g, 0.0148 mol) was added dropwise over ten minutes to a flask of norbornadiene (2.7 g, 0.0294 mol) at 80° C and stirred for 18 h. Flash column chromatography with hexanes was used to purify the crude reaction mixture. The second yellow band off the column contained FeNBD. The solvent was removed under vacuum to yield an orange/yellow liquid (0.249 g, 7.25 % yield). Characterization by IR in 2-methylpentane revealed two distinct \nu(CO) bands at 1967 cm\(^{-1}\) and 2035 cm\(^{-1}\), which correspond with previous literature values.\(^1\) The compound could be stored for several weeks in 2-methylpentane under inert atmosphere. Though the compound is mildly air sensitive, it does remain chemically persistent in 2-methylpentane under ambient conditions for several days.
**Computational Details and Fitting Procedure.** Extraction of the rates of chemical exchange was accomplished using the Raman and IR Dynamics program (RAPID).\(^9\) This program is similar to the original VIBEX program\(^{30}\) developed by Schaffner and coworkers, however, it was updated to a modern platform independent programing language (Python) and includes a few corrections to the originally presented theory. A detailed description of this corrected theory is presented in Appendix B. The exchange matrix for FeNBD was taken from Grevels et al. and is given as

$$R^\text{ex} = \begin{pmatrix}
0.962 & 0.028 & 0.010 \\
0.028 & 0.231 & 0.741 \\
0.010 & 0.741 & 0.249 
\end{pmatrix}.$$

The simulated spectra were obtained by entering the peak positions and relative intensities of the raw data into RAPID. Next, the Gaussian and Lorentzian full-width half-max line widths and the rate of exchange were manually adjusted for each peak in the ν(CO) region (1930-2060 cm\(^{-1}\)) until a satisfactory match to the experimental data was achieved. It took several iterations of manipulating the line widths and rate to obtain a reasonable match to the raw data. The input rate of exchange that produced the suitable match provides a rate constant for each spectrum, and this is how the dynamics of exchange are extracted from the spectra. A table of all input parameters that were used to simulate the IR and Raman data (using RAPID) is presented in Appendix A.

**Results and Discussion**

**Vibrational Spectroscopy of FeNBD.** We acquired variable temperature IR spectra of FeNBD in 2-methylpentane. This was done both to ensure that we could reproduce previous temperature-dependent experiments,\(^{30}\) as well as to allow for direct comparison between IR and
Raman spectra. Figure 2-2a shows the two low frequency bands coalesced at 293 K and the resolution of all three $\nu$(CO) bands at 213 K. FeNBD belongs to the $C_s$ point group and these bands are assigned to vibrations with symmetry $A''$, $A'$, and $A'$ (from lowest to highest energy). It should be noted that the IR data is plotted with the Raman convention (energy increases to the right). This behavior of the IR spectra is identical to that reported by Turner et al. and IR spectra from all temperatures acquired are in Appendix A.

With the successful reproduction of previous temperature-dependent experiments, next we acquired variable temperature Raman data of FeNBD in 2-methylpentane, as shown in Figure 2-2b. The symmetries of the vibrations (see Chapter 1) are such that all three carbonyl vibrations are both IR and Raman allowed. At 293 K, the Raman spectrum consists of a broad band at lower frequency and a narrow band at higher frequency. Upon cooling to 209 K, the broad band splits into two bands and all three $\nu$(CO) bands are distinctly observed. This behavior mirrors that of the IR data (Figure 2-2a), and is diagnostic of the CO ligand exchange process. Raman spectra from all temperatures acquired are in the Appendix A. Taken together, this data supports the idea that the variable temperature IR and Raman are reporting on the same dynamics.

Figure 2-2: (a) IR and (b) Raman spectra of FeNBD in 2-methylpentane at three temperatures. In both the IR and Raman spectra, the lower frequency bands are coalesced at 293 K, but split into two bands as the temperature is lowered.
Although the same coalescence is observed in the IR and Raman, there are some differences between these spectra. For instance, at low temperature (where the exchange is slowed) the relative intensities of the two lower frequency bands are equivalent in the Raman, while the intensities of these bands are different in the IR. As the selection rules for IR and Raman differ, this difference is unsurprising. Also, the IR spectra possess a more pronounced shoulder on the higher frequency band. This shoulder is ascribed to the naturally occurring $^{13}$CO isotope.\textsuperscript{30} Finally, we note that at all temperatures, the bands are broader in the Raman than in the IR. Given that the resolution of our Raman instrument is greater than that of the IR, this appears to be a real effect, and is worth considering in more detail.

There are two reasons why one might observe broader bands in the Raman: (1) homogenous broadening and (2) inhomogeneous broadening. When considering homogenous broadening, the contribution to the vibrational line width arising from rotational dephasing is greater for Raman bands than for IR bands.\textsuperscript{2,31-34} Given that the rotational lifetime of the carbonyl groups is very short (the rate of exchange is fast) we might expect significant contributions to the total width from rotational dephasing. When considering inhomogeneous broadening, one must consider that the transition moment for Raman depends on the change in polarizability, while the transition moment for IR depends on the change in dipole moment of the vibration. Thus, the transition moment couples to (and is affected differently by) the local environment of the molecule. The result of this is that the transition moment associated with Raman and IR can be affected differently by changes in environment that give rise to inhomogeneous broadening, and this results in different weighting of local environment effects for IR and Raman spectroscopies, in turn giving rise to observed differences in inhomogeneous broadening. An additional complication for Raman is local heating induced by the focused laser could lead to increased inhomogeneous broadening. As the laser spot intensity has a Gaussian distribution, we would also expect a Gaussian distribution in temperatures. This, in turn, would result in a range of
carbonyl exchange rates, and an increase in the inhomogeneous broadening. We are unable to comment on the relative contribution of these homogenous and inhomogeneous effects, but we do note that these considerations allow for the observed differences in bandwidth between the IR and Raman spectra. However, despite the differences in bandwidths, we find that the width in the IR and Raman display identical temperature dependence (see Appendix A). This last observation seems appropriate, if the underlying dynamics are controlling the shape of these bands (*vide infra*).

Although more differences between Raman and IR bands exist, we choose to highlight these two differences in order to draw attention to the fact that the IR and Raman band *shapes* are not identical. As the shape of the coalesced bands are extremely sensitive to the shape of the bands in the absence of exchange, one cannot simply compare band shapes at a particular temperature in order to determine the equivalency of the effect of exchange on IR and Raman spectra. A more accurate way to compare these two techniques requires analyzing the rate constants extracted from simulating the spectra.

**Extraction of Rate Constants from Simulated IR and Raman Spectra of FeNBD.**

The program used to extract dynamics, Raman and IR Dynamics (RAPID), was developed in-house by Seth M. Morton and Lasse Jensen at the Pennsylvania State University.29 The program is based on an original program, VIBEX, written by Schaffner and coworkers, to simulate chemical exchange in the IR.30 A full presentation of the theory used to write the RAPID can be found in Appendix B. The new program extends the theory of Schaffner and coworkers to include Raman scattering and corrects a few errors encountered in the original presentation. RAPID uses a Voigt line shape, which is a convolution of a Gaussian and Lorentzian line shape, to simulate both IR and Raman spectra. The adjustable parameters available during the fitting process are the rate of exchange, the FWHM of the Gaussian line shape, the FWHM of the Lorentzian line shape, and the relative peak intensities. The specific input parameters used for
each temperature can be found in Appendix A. Exemplars of the fit between simulated and experimental data are shown in Figure 2-3, for both IR and Raman spectroscopies at room and low temperatures. The simulated spectrum (shown as a dashed red line) demonstrates a good agreement with the experimental data. There is a small discrepancy at the base of the bands where simulated data departs from the experimental data as a consequence of the simulated spectra being composed of only three Voigt line shapes. The experimental data could encompass additional bands resulting from isotopes, such as $^{13}$CO mentioned above, or from combination, difference, and overtone bands from the complex or solvent. Difference, combination, and overtone bands result from their low probability of occurring or their violation of vibrational selection rule, $\Delta \nu = \pm 1$, as shown in Figure 2-4. These bands are weak in intensity, therefore, typically they contribute to shoulders or broadening of bands in vibrational spectra. Although there are multiple adjustable parameters, the band shape is quite sensitive to changes in any of them. In fact, after arriving at a good fit to the experimental data, we find that changes to the lifetime of even a few tenths of a picosecond produce fits that are noticeably worse. Thus, Tables 2-1 and 2-2 summarize the temperatures and rate constants ($k^{ex}$) derived from the RAPID program for both IR and Raman. The error associated with the rate constants were determined by the procedure outlined in Appendix A. The ability of a steady-state technique to determine such fast rates with this level of precision is remarkable and speaks to the overall usefulness of this approach.
Figure 2-3: Comparison of experimental (solid black) and simulated (dashed red) data of FeNBD in 2-methylpentane at both room and low (213 K for IR, 209 K for Raman) temperatures.

Figure 2-4: Schematic demonstration of the fundamental (black) vibrational transition, $v_i \rightarrow v_j$. The overtone (blue), combination (red), and difference (green) band are illustrated for two vibrational modes, i and j.
Even though individual simulations are precise, there is a fair amount of spread between the rates determined by IR and Raman measurements for a given temperature, as can be seen by examining Tables 2-1 and 2-2. As we feel quite confident in the reproducibility of the fitting, it is likely that the source of this error stems from determining the temperature. For instance, given the error in temperature determination (± 2 K), two temperatures in Tables 2-1 and 2-2 listed as a single Kelvin apart, could very well be almost 5 Kelvin apart. This is a significant difference and could lead to the observed discrepancies in rates. However, the IR and Raman data display the same trend of increasing rates with temperature (Figure 2-5) and, it seems best to focus on the barrier to rotation that must be controlling these rates, rather than rates at individual temperatures.

Table 2-1: IR rate constants (kex) extracted from simulated data. a Error in temperature is ± 2 K. b Error in the rate constant is ± 0.03 \times 10^{12} \text{s}^{-1}.

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<th>Rate Constant (s^{-1})</th>
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Table 2-2: Raman rate constants (k<sup>a</sup>) extracted from simulated data. <sup>a</sup> Error in temperature is ± 1.8 K. <sup>b</sup> Error in the rate constant is ± 0.02 × 10<sup>12</sup> s<sup>-1</sup>.

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<tr>
<td>209</td>
<td>4.4×10&lt;sup&gt;11&lt;/sup&gt;</td>
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Figure 2-5: Plot of the rate constant for carbonyl exchange (extracted from simulation of IR and Raman spectra) versus temperature, for both IR and Raman spectra. The error in the rate constant is 0.02×10<sup>12</sup> s<sup>-1</sup> for the Raman data and 0.03×10<sup>12</sup> s<sup>-1</sup> for the IR data. The error in the temperature is 1.8 K for the Raman data and 2 K for the IR data.

**Calculation of the Activation Energy of FeNBD.** The activation energy may be extracted from an Arrhenius plot, which we have constructed from both the IR and Raman data (Figure 2-6). The Arrhenius plot yields activation energies of 1.2 ± 0.2 kcal/mol and
1.4 ± 0.1 kcal/mol for the IR and Raman, respectively. These values were obtained from a linear regression analysis performed on IR and Raman data, individually. The error in the activation energy was propagated from the standard error associated with the slope of the linear regression for both techniques. Even with this error, we are reporting activation energies with errors of 0.2 kcal/mol (70 cm\(^{-1}\)). Major sources of error in calculating the activation energy come from the error associated with the rate constant (\(k^{\text{ex}}\) ± 6.25\% error, Tables 2-1 and 2-2) and the temperature measurement from the IR cryostat (> 1.5\%). While this uncertainty could be improved through the use of a more precise cryostat, our results are still precise enough to determine the underlying barrier. Specifically, we find that we may use dynamic Raman and IR to determine changes in barriers of ~70 cm\(^{-1}\). Moreover, it is critical to note that the calculated activation energies agree with each other and with previously reported activation energy within experimental error. Therefore, this result establishes that Raman and IR as complimentary techniques, reporting identical values for the activation energy of a single chemical process.

Figure 2-6: Arrhenius plot for IR (red) and Raman (black) data. The activation energy for exchange of carbonyl ligands in FeNBD can be extracted for IR (1.2 ± 0.2 kcal/mol) and Raman (1.4 ± 0.1 kcal/mol) from the slope of the linear regression.
Conclusions

Using Fe(CO)$_3$(η$^4$-norbornadiene) in 2-methylpentane as a model system, we provided the first direct test of whether steady-state and Raman spectroscopies provide identical determinations of ultrafast chemical exchange. We have also provided a theoretical framework capable of handling dynamic effects in both IR and Raman spectra (Appendix A). Simulation of CO site exchange allowed for extraction of rate constants from temperature-dependent IR and Raman data. An Arrhenius plot, using these rates, yielded activation energies of 1.2 ± 0.2 kcal/mol and 1.4 ± 0.1 kcal/mol for the IR and Raman, respectively. These activation energies are statistically identical and are consistent with previously reported value of ca. 1.5 kcal/mol, therefore, demonstrating the accuracy of Raman measurements as well as the equivalency of steady-state IR and Raman spectroscopies. By coupling together IR and Raman spectroscopies, a complete vibrational picture of the ultrafast dynamics of a chemical system may be achieved using steady-state vibrational spectroscopy.

Following from these results, we are interested in understanding how the molecular environment can impact the kinetics of chemical systems. Porous molecular environments, such as those provided by zeolites, metal-organic frameworks, and cross-linked polymers, may offer environments that confine or restrict kinetics of chemical systems, and we are interested in exploring the effect these confining environments may have on the kinetics of chemical systems. However, first we must develop a way to separate dynamic effects from static effects that will result from changes in the environment. Such static effects are similar (or even equivalent) to the solvatochromism common in vibrational spectroscopy. In the next chapter, we will introduce another model system that exhibits similar spectra as the FeNBD complex presented in this chapter, but without ultrafast dynamics. This new complex allows us to develop a protocol for
separating static solvent effects, such as vibrational solvatochromism from dynamic solvent effects, such as changes in the kinetics of the system induced by the environment.

References


29. RAPID. *https://github.com/jensengroupssu/rapid*. in


Appendix A for Chapter 2

Additional supporting figures and data tables for Chapter 2.

Figure 2A-1: Temperature dependent IR data for Fe(CO)$_3$(η$^4$-norbornadiene) in 2-methylpentane.
Figure 2A-2: Temperature dependent Raman data for Fe(CO)$_3$(η$^4$-norbornadiene) in 2-methylpentane.
Figure 2A-3: Full IR spectrum Fe(CO)$_3$(η$^4$-norbornadiene) in 2-methylpentane at room temperature. The asterisks denote solvent peaks.

Figure 2A-4: Full Raman spectrum for Fe(CO)$_3$(η$^4$-norbornadiene) in 2-methylpentane at room temperature. The asterisks denote solvent peaks.
Table 2A-1: Input parameters for the simulated IR data.

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Table 2A-2: Input parameters for the simulated Raman data.

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Figure 2A-5: Determination of the error in the rate constant. The experimental IR data of FeNBD at 213 K in 2-methylpentane. The only parameter changed between a, b, and c is the rate constant ($k_{\text{exchange}}$). a) The rate constant is too slow. b) The rate constant is correct. c) The rate constant is too fast. (a) and (c) are considered to produce an unsatisfactory match with the experimental data, therefore, the error in the rate constant is determined to be $k_{\text{exchange}} = 0.03 \times 10^{12} \text{ s}^{-1}$. 

\[ k_{\text{exchange}} = 0.45 \times 10^{12} \text{ s}^{-1} \]

\[ k_{\text{exchange}} = 0.48 \times 10^{12} \text{ s}^{-1} \]

\[ k_{\text{exchange}} = 0.51 \times 10^{12} \text{ s}^{-1} \]
Figure 2A-6: Assembly of Raman temperature cell. The cell was composed of three layers that were annealed together at 600 °C for 12 hours. Layers 1 and 2 were scored and a drop of water was used to hold the cells together during the annealing process. The assembly was placed in between two macor plates and a lead weight was placed on top of the plates to ensure the assembly annealed together. Teflon caps were machined to fit inside the holes in layer 1 so the cell could be sealed during the experiment.
Figure 2A-7: Temperature calibration curve for the Raman temperature stage. The error associated with the temperature was calculated from the standard error in the linear regression, which was determined to be ± 1.8 K.

Figure 2A-8: Temperature (K) vs. full width half max (FWHM) of the coalescing band that are centered at 1970 cm\(^{-1}\) for Fe(CO)\(_3\) (\(\eta^4\)-norbornadiene) in 2-methylpentane. The linear regression of the Raman data is \(y = -0.025x + 29.69\) and the IR data is \(y = -0.025x + 26.43\). For the IR data, the points at 283K and 293K were neglected from the linear regression due to their deviation from the rest of the data set. We note that (i) the IR and Raman bands have different FWHM and (ii) these FWHM have the same temperature dependence.
Appendix B for Chapter 2

Appendix contains the theory used to construct the RAPID program. This work was performed and written by our collaborators Seth M. Morton and Lasse Jensen.

In the following we will briefly outline the theory presented by Grevels et al. to describe the dynamic effects on the IR spectra. Here we extend this theory to include Raman scattering as well as correct errors in the original theory. The IR absorption or Raman scattering spectral profile $I(\omega)$ can be written as the half-Fourier transform of the time correlation function $G(t)$ as

$$I(\omega) = \text{Re} \left\{ \int_0^\infty G(t) e^{-i\omega t} dt \right\}$$

(2-1)

where $\omega$ is the vibrational frequency in wavenumbers. For IR absorption, the time correlation function is given by

$$G^{IR}(t) = \sum_{i,f} \rho_i \langle i|\mu(0)|f\rangle \langle f|\mu(t)|i\rangle$$

(2-2)

where $|i\rangle$ and $|f\rangle$ are the initial and final vibrational states, $\rho_i$ is the population of state $|i\rangle$, and $\mu(t)$ is the dipole moment operator of the molecule. A Taylor expansion in terms of vibrational motion can be applied to $\mu(t)$ to give

$$\mu(t) = \mu_0(t) + \sum_k \left( \frac{\partial \mu}{\partial Q_k} \right)_0 Q_k(t) + \cdots$$

(2-3)

where $Q_k$ denotes the normal coordinate of mode $k$ and the subscript 0 indicates that the derivative is about the equilibrium position. Since we are only interested in vibrational motion, the first term in the above expansion can be ignored and Equation 2-2 becomes (assuming uncorrelated vibrational modes)
\[ G^{\text{IR}}(t) = \sum_k \sum_{i,f} \rho_i \left( \frac{\partial \mu}{\partial Q_k} \right)_0^2 \langle i | Q_k(0) | f \rangle \langle f | Q_k(t) | i \rangle \]  

(2-4)

For Raman scattering the time correlation function is given as

\[ G^{\text{Raman}}(t) = \sum_{i,f} \rho_i \langle i | \alpha(0) | f \rangle \langle f | \alpha(t) | i \rangle \]  

(2-5)

where \( \alpha(t) \) is the polarizability operator of the molecule and \( \langle \alpha(t) \rangle \) indicates orientational averaging. As with the IR absorption, by performing a Taylor expansion of the polarizability operator and ignoring the first term we can write the Raman correlation function as

\[ G^{\text{Raman}}(t) = \sum_k \sum_{i,f} \rho_i \left( \frac{\partial \alpha}{\partial Q_k} \right)_0^2 \langle i | Q_k(0) | f \rangle \langle f | Q_k(t) | i \rangle \]  

(2-6)

Since we are only interested in the fundamental vibrational modes of the molecules we can rewrite Equations 2-4 and 2-6 as

\[ G(t) = \sum_k P_k D_k(0) D_k(t) \]  

(2-7)

where we have introduced an average vibrational frequency \( \omega_{\text{average}} \) in

\[ D_k(0) \equiv \left( \frac{2\omega_{\text{average}}}{\hbar} \right)^{-1} \]  

(2-8)

and

\[ D_k(t) = \langle 1_k | Q_k(t) | 0 \rangle \]  

(2-9)

The intensity factor \( P_k \) is

\[ P_k^{\text{IR}} = \rho_0 \left( \frac{\partial \mu}{\partial Q_k} \right)_0^2 \]  

(2-10)

for IR absorption and
for Raman scattering. In the absence of chemical exchange, $D_k(t)$ obeys the modified Bloch equations

$$\frac{dD_k}{dt} = (i\omega_k - \gamma_k - t\sigma_k^2)D_k$$

(2-12)

where $\omega_k$ is the vibrational frequency, $\gamma_k = \frac{1}{2}\Gamma_k^{(L)}$ where $\Gamma_k^{(L)}$ is the full-width at half-max of the Lorentzian broadening due to vibrational relaxation and rotational effects, and

$$\sigma_k = \frac{\Gamma_k^{(G)}}{2\log(2)}$$

where $\Gamma_k^{(G)}$ is the full-width at half-max of the Gaussian contribution to the line shape. This assumes that the perturbations giving rise to the inhomogeneous broadening mainly affects the vibrational frequencies. Note that the corresponding equation in Grevels et al. has an incorrect form for the Gaussian contribution to the line shape. Solving Equation 2-12 gives

$$D_k(t) = D_k(0)e^{(i\omega_k - \gamma_k)t - \frac{t^2}{2}\sigma_k^2}$$

(2-13)

which can be inserted into Equation 2-7 to give the time-correlation function

$$G(t) = \sum_k h_k e^{-i\omega_k t - \frac{\gamma_k t^2}{2} - \frac{t^2}{2}\sigma_k^2}$$

(2-14)

where we have introduced the relative peak height $h_k = P_k(D_k(0))^2$. By framing the equations in terms of the relative height we can unify the expression for both IR absorption and Raman scattering. This results in a spectral profile of

$$I(\omega) = \sum_k V(h_k, \omega_k, \gamma_k, \sigma_k)$$

(2-15)

which is in terms of a Voigt line shape given by
where $i(\nu_k - \gamma_k)t$ and $\frac{t^2}{2}\sigma_k^2$ are the Lorentzian and Gaussian components, respectively.

In the presence of chemical exchange, Equation 2-12 becomes

$$\frac{dD}{dt} = -(A + t\Sigma) \cdot D$$

(2-17)

where $A$ is given by

$$A_{kl} = \begin{cases} -i\nu_k + \gamma_k - K_{kk} & k = l \\ -K_{kl} & k \neq l \end{cases}$$

(2-18)

with $K$ being the rate matrix and $\Sigma$ is a diagonal matrix with elements

$$\Sigma_{kk} = \sigma_k^{-2}.$$  

(2-19)

The rate matrix is defined at the end of this section. The solution of Equation 2-17 can be approximately given by

$$D_i(t) = \sum_k e^{-\lambda_k t - \frac{\Sigma_k t^2}{2}} S_{li} \sum_m S_{km}^{inv} D_m(0)$$

(2-20)

where $S$ and $A$ are the eigenvectors and eigenvalues of $A$, respectively. This assumes that the modified Gaussian widths after exchange can be written as

$$\Sigma'_k = \text{Re}\left\{ [S^{inv} \cdot \Sigma \cdot S]_{kk} \right\}$$

(2-21)

which is identical to neglecting the off-diagonal elements of the matrix $S^{inv} \cdot \Sigma \cdot S$. The modified normal mode frequency after exchange is given by $\text{Im}\{-\Lambda'_k\}$ and the modified Lorentzian width is given by $\text{Re}\{A'_k\}$. We note that the subscripts $k$, $l$, and $m$ run over all exchanging modes.
in the system. Inserting this into Equation 2-7 gives the correlation functions accounting for exchange as

\[ G(t) = \sum_{k} h_k ' e^{-\frac{\Lambda_k t^2}{2}} \]  

(2-22)

where we have defined a modified peak height after exchange as

\[ h_k ' = \sum_{i,m} h_i S_{li} S_{km}^{\text{inv}} \]. The spectral profile is then given by

\[ I(\omega) = \sum_{k} V(h_k, \text{Im}\{-\Lambda_k\}, \text{Re}\{\Lambda_k\}, \Sigma_k^{-\frac{1}{2}}) \]  

(2-23)

Note that the modified peak height in the original code is incorrectly calculated as

\[ h_k ' = \sum_{i,l} h_i S_{lk} \sum_{m} h_m S_{km}^{\text{inv}} \]; while this yields the correct result if all peak heights are 1.0, in general it will give incorrect relative peak heights. Although the equations for the Voigt line shape were derived in terms of a Fourier transform, in practice it is easier to evaluate it using the complex error function \( w \) as

\[ V(h_k, \omega_k, \gamma_k, \sigma_k) = \frac{\text{Re}\left\{ h_k^* w \left(\frac{\omega - \omega_k + i\gamma_k}{\sqrt{2}\sigma_k}\right)\right\}}{\sqrt{2\pi\sigma_k}} \]  

(2-24)

where \( h_k^* \) is the complex conjugate of \( h_k \).

The exchange matrix \( Z \) that describes how the vibrational modes exchange is given by

\[ Z_{kl} = \begin{cases} 1 - \sum_{m \neq l} Z_{km} & k = l \\ R_{kl}^{\text{ex}} & k \neq l \end{cases} \]  

(2-25)

where \( R_{kl}^{\text{ex}} \) is the relative rate of exchange between peaks \( k \) and \( l \), and each row sums to one.

From \( Z \) we can obtain the rate matrix \( K \) that defines the overall rate of exchange between peaks and is given by
\[ K = k^{ex} (Z - I) \quad (2-26) \]

where \( k^{ex} \) is the exchange rate of the system and \( I \) is the identity matrix.
Chapter 3

Separating Dynamic from Static Solvent Effects Using Infrared Spectroscopy

Introduction

We have an interest in extending the approach detailed in Chapter 2 to studies to address our overall goal of understanding the effect intermolecular interactions induce on the dynamics of in chemical systems. These interactions can be studied by examining how changes in the molecular environment impact the observed chemical dynamics, and we would like to use the FeNBD system as a probe of such environmental effects upon dynamics. However, in order to consider the dynamic impacts of the environment changes, we must first consider the static effects the molecular environment has on the band position, intensity, and shape.

Consideration of band position, intensity, and band shape is much more in line with the traditional use of IR spectroscopy to characterize molecules by examining the spectra for the presence of characteristic vibrational bands associated with specific functional groups. Under such analysis, it is merely the energy of the band maximum that is considered, however, additional information can be obtained from the shape of these bands. For instance, changes in bandwidth can be used to track the local environment of a particular functional group, provide information on the structure of biomolecules, heterogeneity of materials, and the effects of confining environments.

Though the analysis of dynamics is focused on changes in the band shape of molecules, the position of the coalescing bands is also important. In particular, the separation in exchanging bands fundamentally controls the rates that can be extracted, via the time-energy uncertainty principle. In addition, the relative intensities of the coalescing bands will also control the
precision of the extracted kinetics, as in the band shape analysis approach presented in Chapters 1 and 2, is the most sensitive when the exchanging bands are of equal intensity. Finally one must know the starting band shapes, in the absence of exchange, in order to extract accurate values for the pre-exponential factor and activation energy components of the rate constant.

All of the above features of vibrational spectra are expected to be dependent upon changes in the molecular environment, with solvatochromism being, perhaps, the most well known example of such a phenomenon. Vibrational solvatochromism refers to a change in band position, intensity, or FWHM of a vibrational band as a function of solvent. This modification to the vibrational spectrum results from an interaction between the solute and solvent, and can usually be tracked as a function of solvent polarity. Thus, we sought a way to isolate static changes to the IR spectra from the dynamic effects. To develop this protocol, we needed two similar compounds, one that experiences chemical exchange on the vibrational timescale and one that is static, but with similar a solvatochromic response. This chapter focuses on the static molecule, Fe(CO)$_3$(η$^4$-cyclooctatetraene), FeCOT.

FeCOT is a complex similar to the dynamic FeNBD, but without known ultrafast dynamics. However, as we will see, FeCOT exhibits vibrational solvatochromism. Interestingly, the solvatochromism of FeCOT gives rise to changes in the band shape (as a function of solvent) that is reminiscent to those observed for FeNBD (as a function of temperature). Figure 3-1a, shows the spectra associated with the temperature dependent dynamic behavior of FeNBD. Because such ground state dynamics are thermally activated, due to the low activation barrier for carbonyl ligand site exchange, temperature-dependent coalescence of bands in the IR is diagnostic of these dynamics. Figure 3-1b shows the solvent dependent band shapes that FeCOT undergoes, which are clearly similar to those seen in Figure 3-1a. In this chapter, we examine the solvent dependent vibrational spectra of FeCOT. We first consider the possibility of the spectral behavior shown in Figure 3-1b could be a result of solvent controlled dynamics instead of
vibrational solvatochromism, and once we have determined the spectral behavior results from static vibrational solvatochromism, we address the nature of these solvatochromic effects. Finally, we use these results for \textbf{FeCOT} to begin to develop a protocol for separating \textit{static} from \textit{dynamic} effects in vibrational spectroscopy.

![Diagram of FeCOT and FeNBD](image)

**Figure 3-1:** Comparison of the band shapes of \textbf{FeNBD} and \textbf{FeCOT} as a function of (a) temperature in 2-methylpentane and (b) solvent at 293 K. The resulting changes in band shapes are similar for both compounds.

\textbf{Experimental}

\textbf{Chemicals.} All solvents were purchased from VWR and used as received. \textit{Fe(CO)}$_3(\eta^4$-norbornadiene) (\textbf{FeNBD}) was purchased from Sigma-Aldrich and used as received.

\textbf{Infrared Measurements.} Perkin Elmer Spectrum 400 FT-IR/FT-NIR with a Pike MIRacle ATR attachment was used to collect room temperature IR spectra with a 4 cm$^{-1}$ resolution. Several solvents were tested using a traditional liquid IR cell to verify that the IR
were not affected by use of the ATR attachment. Variable temperature spectra were acquired with a vacuum tight Specac liquid cell with CaF$_2$ windows and a Specac variable temperature liquid nitrogen cryostat (NaCl exterior windows). Specac reports ± 2 K sample temperature for their variable temperature cell.

**Sample Preparation.** For the alkane and alcohol series of solvents, 20 mM samples were prepared by diluting a 40 mM stock solution (10 mg FeCOT and 1 mL solvent). All other solutions were made by dissolving a small amount of FeCOT in 1mL of solvent, and diluting with solvent until a reasonable IR spectrum was obtained.

**Band Shape Analysis and Statistics.** All data were analyzed in Origin 9.0 or Excel. The band position and FWHM data were acquired using the multiple peak fitting tool in Origin 9.0, and choosing to fit all three bands using the Voigt function. The multiple linear regression analysis was calculated in Excel, following the general statistical protocol for this analysis. The F-ratio is a statistical measure used to assess the quality of fit for any number of parameters and is defined by:

$$F = \frac{\{SS(data) - SS(fit)\} / (p - 1)}{SS(fit) / (N - p)}$$

$$SS(fit) = \sum_i (y_{i}^{\text{obs}} - y_{i}^{\text{fit}})^2$$

$$SS(data) = \sum_i (y_{i}^{\text{obs}} - \bar{y})^2$$

where $y_{i}^{\text{obs}}$ is the experimentally observed band position or FWHM, $y_{i}^{\text{fit}}$ is the calculated band position or FWHM, $\bar{y}$ is the mean of the experimentally observed band position or FWHM, $p$ is the number of fit parameters, and $N$ is the number of data points. The larger the F-ratio, the better the linear regression fit. That is, if the F-ratio increases upon addition of a new parameter to the fit, then the inclusion of the extra parameter improves the overall fit. In contrast, if the F-ratio stays the same or decreases, then the inclusion of the extra variable does not improve the linear
regression. Thus, the F-ratio can be used to aid in judging the relative importance of parameters when performing a multiple linear regression.

Results and Discussion

Solvent-Dependent IR Spectra of FeCOT. The IR spectra of FeCOT were taken in 27 different solvents. For each spectrum, the peak position and FWHM for all three $\nu$(CO) bands were extracted by fitting each band to a Voigt profile in Origin 9.0. All spectra, a table of the extracted values, and details of the extraction of these values, can be found in Appendix. The normalized IR spectra of FeCOT, in the $\nu$(CO) region, for five of these solvents at room temperature are presented in Figure 3-2. As is clear in this figure, we observe a strong dependence of the band position, bandwidth, and the degree of coalescence of the two lower energy bands upon the identity of the solvent.

Figure 3-2: The $\nu$(CO) region of the IR spectra of FeCOT in five solvents at room temperature. The band shape, band position, and degree of coalescence of the $\nu$(CO) bands depend on the identity of the solvent.
Examination of Figure 3-2 shows that the band position decreases in energy as the polarity of the solvent increases. While all three bands show this trend, it is strongest for the middle energy band and weakest for the high energy band. At the same time, as the polarity of the solvent increases, so does the bandwidth. In the case of bandwidth, it is the lowest energy band that displays the strongest dependence on solvent, while the high energy band again has the weakest dependence. The values of the position and width of the bands are quantified and presented for all 27 solvents in Tables 3A-1 and 3A-2 in the Appendix. Finally, the coalescence of the two lower energy bands increases with polarity. This coalescence could be a simple result of the different solvent dependence of the band positions, which would tend to move the two lower energy bands together with increasing polarity, and would result in further apparent (i.e. not dynamic) coalescence. On the other hand, the close relationship of FeCOT to FeNBD demands that we also consider the possibility of solvent controlled dynamic effects, which could result in observed coalescence of these bands. While previous work suggests that dynamics should not be responsible for these effects, due to a high barrier for carbonyl exchange, this can be definitively established through temperature-dependent IR experiments performed in ethyl acetate.

**Temperature-Dependent IR Spectra of FeCOT.** Shown in Figure 3-3a is the temperature dependence of the FeCOT IR spectra in ethyl acetate. Ethyl acetate has a convenient range of temperatures assessable in its liquid state, allowing us to both heat and cool the solvent from room temperature. In addition, the ν(CO) bands in ethyl acetate display an intermediate degree of apparent coalescence. If the observed band shape of FeCOT was a result of ground state dynamics, then these changes in temperature should result in appreciable increases in coalescence or resolution of the lower energy bands as we heat and cool the solution, respectively. Figure 3-3b shows the expected change in band shape if the molecule was
experiencing dynamic exchanges of the carbonyl ligands, similar to that experienced by FeNBD.\textsuperscript{13}

Figure 3-3: (a) Temperature-dependent IR spectra of FeCOT in ethyl acetate. (b) Calculated IR spectra, showing the expected band shapes for FeCOT, if this compound experienced the same dynamic effects as FeNBD.

Figure 3-3a shows that there is very little dependence of the band shape upon the temperature of the system. A similar lack of dependence upon temperature was observed in the other solvents in which we acquired temperature-dependent data. Since the change in the calculated band shape (Figure 3-3b) is much greater than experimentally observed (Figure 3-3a) over the temperature range studied, we can conclude that FeCOT does not undergo carbonyl ligand site exchange on the vibrational timescale. With dynamics excluded as an explanation for the solvent dependence of the IR, we now explore possible static solvent properties responsible for the change in band shape and position observed in Figure 3-2.

\textbf{Consideration of Solvent Properties.} In order to gain an understanding of the observed solvent dependence, we examined the correlations between several solvent properties for both the band position and FWHM. When selecting properties, we consider how a solute molecule might interact with its environment. In particular, it is worth keeping in mind that, while changes in band position are expected to be accompanied by changes in band shape,\textsuperscript{14,15} the converse is not
necessarily true. One could imagine a scenario in which the vibrational lifetime is affected (see Physical Parameters section), but not the average energy of the vibration. This would result in a change in band shape, without a change in band position. Above, we had discussed the observed spectroscopic changes in terms of solvent polarity. This was done due to its familiarity among chemists. However, polarity is a poorly parameterized solvent property and so our subsequent discussions will focus on several other solvent parameters that we classify as physical, electrostatic, or chemical.

**Physical Parameters.** From the available physical parameters (boiling point, density, viscosity, etc.), we chose to focus on the viscosity of the solvent, as it is easiest to understand how changes in viscosity could affect the broadening of our bands. Increases in viscosity means that the solvent environment is undergoing slower changes in its structure near the solute. At the same time, the tumbling of the solute can be slowed by an increase in viscosity. While we believe that these systems lie within the extreme narrowing limit, it is possible that the changes in solvent and solute reorientation times could move the system outside this limit. This, in turn, would result in noticeable changes in bandwidth.

We separate physical from electrostatic or chemical affects using two series of solvents: linear alkanes and linear primary alcohols. Within the linear alkane series, the viscosity of the solvent changes, while the electrostatic (i.e. dielectric constant) and chemical (i.e. hydrogen donor/acceptor strength) properties remain constant. In contrast, as the molecular weight increases within the series of primary alcohols, both the viscosity and the dielectric constant change. The relevant parameters for all of these solvents can be found in Table 3A-1 in the Appendix. The IR spectra of FeCOT shows little change as we move from pentane to hexadecane (Figure 3-4a), but significant changes are observed for the primary alcohol series (Figure 3-4b). From these results, we conclude that while viscosity does not contribute
significantly to the observed solvatochromism, the electrostatic properties of the solvent do. We now turn to the consideration of these electrostatic properties.

**Pure Electrostatic Effects.** The reaction field approach is a common theoretical framework that measures the influence of solvent electrostatic properties on spectral changes by accounting for the solvent dielectric constant ($\varepsilon_0$) and refractive index ($n$) as shown in Equation 3-1.\(^{17-19}\)

$$F(\varepsilon_0, n) = \frac{\varepsilon_0 - 1}{\varepsilon_0 + 2} - \frac{n^2 - 1}{n^2 + 2}$$  \hspace{1cm} (3-1)

The model reduces the solute to a polarizable dipole, and the interaction between the solute and solvent is reduced to the solvent interaction with this dipole in a dielectric continuum. The presence of the solute dipole induces a field within the solvent (the reaction field) that, in turn, affects the electrostatic environment felt by the solute. This electrostatic environment can then change the energy of the changing dipole associated with a molecular vibration. It is also not hard to imagine that the stronger this reaction field, the more heterogeneities in the field are manifested in the band shape of vibrations associated with the solute. Thus, correlations between this reaction field factor and both the band position and the FWHM are expected.

Figure 3-4: IR spectra of FeCOT at room temperature taken in a series of (a) linear $n$-alkanes and (b) primary $n$-alcohols.
Plots of band position and FWHM data for all three carbonyl bands against the reaction field factor, $F(\varepsilon_0, n)$ are shown in Figure 3-5. For all three bands, the FWHM data produces a better correlation with higher $R^2$ values than the band position data, but none of the correlations are particularly strong. This result is unsurprising, as dielectric continuum models for the solvent focus on the link between solvent dielectric constant and the average dipole moment, which inadequately accounts for the polarity of the solvent. Additionally, the failure of the reaction field approach to describe the interactions between FeCOT and the solvent environment suggests that the solvent’s polarity must be accounted for to accurately describe this solute-solvent interaction. Fortunately, there are other models for describing solute-solvent interactions that take into account electrostatic effects, as well as more specific chemical interactions. We consider such a model next.

![Figure 3-5: The band position and FWHM in the $\nu$(CO) region of the IR spectra of FeCOT in all solvents at room temperature versus $F(\varepsilon_0, n)$, for (a) the high energy band, (b) the middle energy band, and (c) the low energy band.](image)

**Electrostatic and Chemical Parameters.** The empirical linear solvation energy relationship is a model that describes solute-solvent interactions in terms of the solvent polarizability ($\pi^*$), hydrogen bond donor strength ($\alpha$), and hydrogen bond acceptor strength ($\beta$), as demonstrated in Equation 3-2.

$$XYZ = XYZ_0 + s\pi^* + a\alpha + b\beta$$ (3-2)
In this equation, XYZ is any experimental observable that displays solvent dependence (ie. band position or band shape), and XYZ₀ is normally interpreted as the value of this observable in vacuum. The coefficients $s$, $a$, and $b$ reflect the sensitivity of the observable to the associated solvent property. The above solvent properties can be classified as either bulk electrostatic ($\pi^*$) or specific chemical interactions ($\alpha$ and $\beta$). The $\pi^*$ scale was derived by Taft and coworkers by correlating the solvatochromic response of seven indicator molecules in 47 solvents, and this scale measures solvents based on their polarity/polarizability properties. In particular, Taft and coworkers investigated the effect of solvent on the $p\rightarrow\pi^*$ or $\pi\rightarrow\pi^*$ electronic transitions using UV-Vis spectroscopy, taking care to isolate solvatochromic effects the specific chemical interaction parameters, such as hydrogen bonding. The values for the specific chemical interactions, $\alpha$ and $\beta$, were derived from the solvatochromic effects on the energy of the longest wavelength absorption peak by carefully selecting appropriate indicator/solvent systems to isolate the hydrogen bonding nature of the solvent. Since FeCOT does not have any hydrogens expected to participate in hydrogen bonding with the solvent, we ignore the $\beta$ term and only consider the $\pi^*$ and $\alpha$ parameters in our correlations.

We start by considering just the non-specific ($\pi^*$) term. As $\pi^*$ accounts for the polarizability of the solvent, this parameter is expected to reflect the strength of the interaction between the solvent and the dipole moment(s) of a solute – such as the dipoles associated with the carbonyl ligands of FeCOT. Figure 3-6 shows the band position and FWHM vs $\pi^*$. The correlation to $\pi^*$ is much stronger than to $F(\varepsilon_0, n)$ – especially when considering band position – with $R^2$ values between 0.59-0.87. This stronger correlation indicates that $\pi^*$ better captures the solvent-FeCOT interaction than $F(\varepsilon_0, n)$. The stronger correlation with $\pi^*$ than the reaction field approach could be attributed to how the parameters are derived, as the $\pi^*$ scale was experimentally derived using solvatochromism and $F(\varepsilon_0, n)$ was theoretically derived from physical reasoning.
Based upon our observations, we feel that an accurate description of the solvent-FeCOT interaction is that of a fluctuating dipole of the carbonyl ligands on FeCOT and the induced and permanent dipoles of the solvent. Such interactions are known to affect the energy of IR bands\textsuperscript{22,23} and this explanation is also consistent with the observation that $\pi^*$ and FWHM are directly related (see General Remarks section below). Stronger interactions between the solvent and the carbonyl ligands should also lead to larger observed effects from any heterogeneity present in the solvent environment. Thus, it is satisfying that we observe a correlation between band position and $\pi^*$ as well as FWHM and $\pi^*$.

Adding in the $\alpha$ term results in even better correlations to the data. Multiple linear regressions to $\alpha$ and $\pi^*$ were conducted on the band position and FWHM data for all three bands in all solvents. Table \textbf{3-1} presents the results of these regressions along with an F-value, which measures how well the proposed model accounts for the changes in band position and FWHM as a function of solvent.\textsuperscript{2} The larger the F-ratio, the better correlation of the model with the observed spectral changes. This value is used to determine if incorporating another parameter into the model increases or decreases the correlation. As the results of multiple linear regressions are

![Figure 3-6: The band position and FWHM in the $\nu$(CO) region of the IR spectra of FeCOT in all solvents at room temperature versus $\pi^*$, for (a) the high energy band, (b) the middle energy band, and (c) the low energy band.](image-url)
difficult to represent in two dimensions, Table 3-1 has more utility than a plot of these correlations.

Table 3-1: Results from the multiple linear regressions using Equation 3-2 for each band. The bolded regression indicates the best fit to the data as judged by the F-ratio. The values for XYZ0, s, and a are reported in wavenumbers.

<table>
<thead>
<tr>
<th>All Solvents</th>
<th>XYZ0</th>
<th>s</th>
<th>a</th>
<th>F</th>
</tr>
</thead>
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<tr>
<td><strong>High energy band</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FWHM</td>
<td>7.1(±0.3)</td>
<td>6.0(±0.6)</td>
<td></td>
<td>31.8</td>
</tr>
<tr>
<td></td>
<td>6.6 (±0.2)</td>
<td>5.9 (±0.2)</td>
<td>1.5 (±0.2)</td>
<td>44.3</td>
</tr>
<tr>
<td>Band Position</td>
<td>2053.1(±0.6)</td>
<td>-6.7(±1.1)</td>
<td></td>
<td>20.4</td>
</tr>
<tr>
<td></td>
<td>2053.1 (±0.2)</td>
<td>-7.0 (±0.1)</td>
<td>0.5 (±0.1)</td>
<td>43.5</td>
</tr>
<tr>
<td><strong>Middle energy band</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FWHM</td>
<td>7.6(±0.6)</td>
<td>11.3(±1.1)</td>
<td></td>
<td>27.4</td>
</tr>
<tr>
<td></td>
<td>7.6(±0.9)</td>
<td>11.9(±0.7)</td>
<td>1.3(±0.6)</td>
<td>28.9</td>
</tr>
<tr>
<td>Band Position</td>
<td>1994.3(±1.0)</td>
<td>-10.2(±2.0)</td>
<td></td>
<td>20.5</td>
</tr>
<tr>
<td></td>
<td>1994.9(±0.5)</td>
<td>-13.0(±0.4)</td>
<td>0.6(±0.3)</td>
<td>20.7</td>
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<tr>
<td><strong>Low energy band</strong></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FWHM</td>
<td>7.9(±0.5)</td>
<td>15.4(±1.3)</td>
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<td>25.9</td>
</tr>
<tr>
<td></td>
<td>8.6(±0.8)</td>
<td>15.8(±0.6)</td>
<td>-1.0(±0.5)</td>
<td>26.4</td>
</tr>
<tr>
<td>Band Position</td>
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<td>-10.1(±1.3)</td>
<td></td>
<td>13.5</td>
</tr>
<tr>
<td></td>
<td>1977.9(±0.9)</td>
<td>-10.1(±0.7)</td>
<td>0.3(±0.6)</td>
<td>16.7</td>
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</tbody>
</table>

An examination of Table 3-1 reveals that, for each band, the highest F-ratio is obtained when including both the $\pi^*$ and $\alpha$ terms into the fit. This result implies that both polarizability and hydrogen bonding parameters are controlling the solvent dependence of FeCOT. For the high energy band, a reasonable increase in the F-ratio is observed when $\alpha$ is included in the linear regression, but the middle and low energy bands show only a slight increase their F-ratios when $\alpha$ is included into the regression. In addition, the magnitude of the coefficient ($s$) is greater than ($a$) for all observables. Taking into consideration both the small changes in the F-ratio when adding $\alpha$, and the small magnitude of $a$, we conclude that the hydrogen bonding interaction between FeCOT and the solvent is a minor contribution. Instead, the interaction between the large dipole
of the carbonyl ligands in FeCOT and the solvent polarizability dominates the solute-solvent interaction. As metal carbonyls are weak hydrogen bonding acceptors, this seems a reasonable result. Thus, we conclude that, while it is important to consider specific chemical interactions, the general electrostatic solute-solvent interactions dominate the observed solvent-dependent IR spectra.

**General Remarks on the Solvent Dependence.** With the above understanding of the origin of the solvent dependence, we sought further insight into the correlation involving the FWHM by decomposing the FWHM into its Gaussian and Lorentzian contributions. These two functions are associated with heterogeneous and homogenous broadening, respectively. Our hope was to determine which of these broadening mechanisms was primarily responsible for the observed solvent dependence, as this might provide additional insight into the solvent-solute interaction. We used a Voigt function, which is a convolution of Gaussian and Lorentzian line shapes, to fit the IR data and extract out the FWHM of the Gaussian and Lorentzian contributions for each band. The overall FWHM for each band was plotted against the FWHM of the Gaussian component and the FHWM of the Lorentzian component to the overall band shape (Figure 3A-3 and 3A-4 in the Appendix). There was little correlation found between the change in FWHM of the overall band shape and the changes in the Gaussian and Lorentzian components of the band shape. We conclude that the observed changes in the FHWM and band position of FeCOT as a function of solvent cannot be reduced to changes in the Gaussian and Lorentzian components of the IR band shape.

Finally, it is worth explicitly addressing the correlation between FWHM and band position. We plotted the FWHM versus band position for all three bands in Figure 3-7, which shows a correlation between the changes in FWHM and band position. This is especially apparent with the middle band, which has an $R^2$ value of 0.89. This correlation demonstrates that the interaction with solvent causes changes in both the band shape and position. As noted earlier,
such correlations are to be expected,\textsuperscript{14,15} however, this relationship is worth emphasizing in this case, as it is the correlation between band position and band shape that gives rise to the apparent coalescence seen in Figure 3-1b.

![Figure 3-7: The band position versus FWHM for (a) the high energy band, (b) the middle energy band, and (c) the low energy ν(CO) bands of FeCOT in all solvents.](image)

**Conclusions**

We find that the solvent-dependent IR spectra of FeCOT display remarkably similar behavior to the temperature-dependent IR spectra FeNBD, which is known to be a result of ultrafast ligand exchange. Despite the similarities in band shape, we find that the solvent dependence of FeCOT is not a result of chemical dynamics. Rather, the observed changes in the FWHM and band position are a result of solvatochromism and can be accounted for using the linear energy solvation model by including the solvent parameters $\pi^*$ (polarizability) and $\alpha$ (hydrogen bond donor strength). Of these parameters, we conclude that the solvent-dependent carbonyl band shapes observed for FeCOT can be mostly attributed to the interaction between the polar carbonyl ligands and the solvent’s polarizability ($\pi^*$), and to a lesser extent to the hydrogen bonding ($\alpha$) interaction between the carbonyl ligands and the solvent. The changes in FWHM and band position are interrelated through the solute-solvent interactions experienced in
this system. It is these interactions, and not any dynamic processes that result in the observed solvatochromism are shown in Figure 3-1b. Thus, the behavior of FeCOT is due entirely to an accidental overlap of the bands, resulting from combined shifts and broadening of the carbonyl bands. This is an effect that is important to keep in mind when attempting to interpret solvent-dependent IR spectra for molecules suspected of picosecond dynamics. There have been reports in the literature from Kubiak and coworkers reporting on the temperature-dependent and solvent-dependent rate of an one-electron transfer between two ruthenium clusters connected by a pyrazine bridge. The dependence was attributed to “solvent friction”, where the rate of electron transfer is controlled by the pre-exponential factor, which, in turn, is dominated by solvent vibrational modes. Therefore, we recommend the utmost care be taken by confirming the dynamics of the chemical system before using vibrational spectroscopy to extract kinetic information from the chemical system.

Additionally, we conclude that FeCOT can be used in future experiments to help separate dynamics (intramolecular) from static (intermolecular) effects in the IR, since our experiments demonstrated that FeCOT is not dynamic on the picosecond timescale. By focusing on how the spectrum of FeCOT changes as a function of solvent, we can use this complex to probe the static effect the molecular environment induces on the carbonyl bands. The static response of this complex will then provide a point of reference when studying the dynamic effects of FeNBD in different molecular environments.

Finally, the results in this chapter suggest that the simplest case for studying the impact of changes in solvent upon dynamics would be to study FeNBD in a series of linear alkanes. Within this series, the FeCOT displayed very little solvatochromic response; therefore, changes in the band shape will result from changes in dynamics and not from solvatochromism. If we assume a similar response for FeNBD, the extraction of dynamics in these solvents should proceed in a relatively facile manner. The next chapter presents a series of experiments aimed to understand
how the kinetics of FeNBD's carbonyl ligand site exchanges are influenced by the solvent environment.

References

13. The IR spectra of FeCOT at room temperature in ethyl acetate was used to calculate the spectra at 70 C and -60 C (Figure 3-3b). We used the RAPID program to fit the room temperature data as if the carbonyl ligands were exchanging. This program allows for the adjustment of the rate of exchange, along with the width of the Gaussian and Lorentzian line shapes. See reference Giordano et al. J. Phys. Chem. A 2013, 117 (10), 2067-2074 for detailed information about the RAPID program. Once we obtained a reasonable fit to the room temperature data, we used the Arrhenius equation to calculate the rate of exchange at 70 C and -60 C. Those rates were entered into the RAPID program to generate the spectra shown in Figure 3-3b.
14. Laird, B. B. & Thompson, W. H. On the connection between Gaussian statistics and


Appendix for Chapter 3

Supplemental Figures and Tables for Chapter 3

Figure 3A-1: Room temperature IR spectra for FeCOT in several common organic solvents.

Figure 3A-2: Variable temperature IR spectra for FeCOT in ethyl acetate.
Table 3A-1: FWHM and band position data for high energy bands and solvent parameters.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>FWHM (cm(^{-1})) ± error (cm(^{-1}))</th>
<th>Band Position (cm(^{-1})) ± error (cm(^{-1}))</th>
<th>ε (\times) (n)</th>
<th>π*</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-dichloroethane</td>
<td>11.205 ± 0.156</td>
<td>2048.687 ± 0.092</td>
<td>0.49269</td>
<td>0.81</td>
<td>0</td>
</tr>
<tr>
<td>acetone</td>
<td>11.109 ± 0.089</td>
<td>2048.216 ± 0.050</td>
<td>0.64853</td>
<td>0.71</td>
<td>0.08</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>10.771 ± 0.183</td>
<td>2049.186 ± 0.095</td>
<td>0.71076</td>
<td>0.75</td>
<td>0.19</td>
</tr>
<tr>
<td>butanol</td>
<td>10.274 ± 0.091</td>
<td>2050.368 ± 0.070</td>
<td>0.60434</td>
<td>0.4</td>
<td>0.79</td>
</tr>
<tr>
<td>carbon tetrachloride</td>
<td>6.342 ± 0.130</td>
<td>2051.710 ± 0.106</td>
<td>0.28</td>
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<td></td>
</tr>
<tr>
<td>chloroform</td>
<td>10.855 ± 0.089</td>
<td>2050.702 ± 0.058</td>
<td>0.58</td>
<td>0.58</td>
<td>0.2</td>
</tr>
<tr>
<td>decane</td>
<td>10.070 ± 0.141</td>
<td>2049.379 ± 0.091</td>
<td>5.18E-04</td>
<td>0.03</td>
<td>0</td>
</tr>
<tr>
<td>decanol</td>
<td>6.363 ± 0.160</td>
<td>2053.528 ± 0.152</td>
<td>0.44203</td>
<td>0.45</td>
<td>0.7</td>
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<tr>
<td>dodecane</td>
<td>13.360 ± 0.174</td>
<td>2043.208 ± 0.093</td>
<td>0.63411</td>
<td>0.54</td>
<td>0.86</td>
</tr>
<tr>
<td>ethanol</td>
<td>6.428 ± 0.122</td>
<td>2053.522 ± 0.121</td>
<td>0.39975</td>
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<td>0</td>
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<tr>
<td>ethyl acetate</td>
<td>11.023 ± 0.146</td>
<td>2049.903 ± 0.108</td>
<td>2.93E-04</td>
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<td>heptane</td>
<td>10.828 ± 0.073</td>
<td>2048.963 ± 0.045</td>
<td>-3.76E-04</td>
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<td>hexadecane</td>
<td>6.424 ± 0.064</td>
<td>2054.173 ± 0.064</td>
<td>-6.39E-04</td>
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<td>hexane</td>
<td>5.577 ± 0.432</td>
<td>2053.350 ± 0.347</td>
<td>0.55313</td>
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<td>isopropanol</td>
<td>10.142 ± 0.109</td>
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<td>0.63411</td>
<td>0.48</td>
<td>0.76</td>
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<td>methanol</td>
<td>9.825 ± 0.070</td>
<td>2050.623 ± 0.047</td>
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<td>methylene chloride</td>
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<td>2048.745 ± 0.074</td>
<td>0.68969</td>
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<td>octane</td>
<td>6.280 ± 0.344</td>
<td>2053.487 ± 0.264</td>
<td>7.11E-04</td>
<td>0.01</td>
<td>0</td>
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<td>6.384 ± 0.157</td>
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<td>10.395 ± 0.109</td>
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<td>0.56409</td>
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<td>11.665 ± 0.108</td>
<td>2046.383 ± 0.061</td>
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<td>6.508 ± 0.295</td>
<td>2052.442 ± 0.256</td>
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<tr>
<td>dimethyl sulfoxide</td>
<td>9.412 ± 0.247</td>
<td>2052.020 ± 0.213</td>
<td>0.65552</td>
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Table 3A-2: FWHM and band position data for low and middle energy bands.

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<tr>
<th>Solvent</th>
<th>Low energy band FWHM (cm(^{-1}))</th>
<th>± error (cm(^{-1}))</th>
<th>Band Position (cm(^{-1}))</th>
<th>± error (cm(^{-1}))</th>
<th>Middle energy peak FWHM (cm(^{-1}))</th>
<th>± error (cm(^{-1}))</th>
<th>Band Position (cm(^{-1}))</th>
<th>± error (cm(^{-1}))</th>
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</thead>
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<td>1,2-dichloroethane</td>
<td>21.1</td>
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<td>0.65</td>
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<td>19.0</td>
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<td>15.85</td>
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<td>1990.67</td>
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<td>1995.54</td>
<td>0.34</td>
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Figure 3A-3: The total FWHM of the high and middle energy bands versus the FWHM of the Gaussian and Lorentzian components. No trends were found.

Figure 3A-4: The total FWHM of the low energy bands vs the FWHM of the Gaussian and Lorentzian components. No trends were found.
Using Vibrational Spectroscopy to Unravel the Influence of Solvent Interactions on the Kinetics of Fe(CO)$_3(\eta^4$-norbornadiene)
theory. \(^6\text{-}^8\) The latter of these was developed specifically to address the solvent frictional effects upon reaction rates in condensed phase reactions. Because these theories of chemical kinetics are integral to interpreting the impact of solvent properties, it is worth considering them in more detail prior to presenting our experimental results.

**Theory of Chemical Kinetics in Condensed Media**

TST was developed by Wigner and Eyring separately in 1938, to describe the flux of reactants being converted into products through an activated process.\(^6\text{-}^7\) This theory can be modeled as a double-welled energy potential, where the energy is dependent upon the “reaction coordinate” (Figure 4-1a). Here, the transition state is the maximum that separates the reaction and product wells, and the reaction coordinate is a reduced coordinate that represents all nuclear motions (intra and intermolecular) that change during the course of reaction. One requirement of TST is that the two wells are separated by a high barrier with respect to \(kT\).\(^9\) Another requirement of TST is that, once the transition state is obtained, the system swiftly proceeds to the minimum of the products well. For simplification, we can think about the forward reaction rate as the rate in which the reactants can escape from a one-dimensional well. From this picture, TST is obtained using two major assumptions, as described next.

The first assumption dictates that the rate-limiting step is the barrier crossing process. This implies that the establishment of thermal equilibrium is fast, within both the reactants’ and products’ wells.\(^9\) As a consequence of this assumption, as soon as a particle reaches the position \((x_\text{A})\) on the reaction coordinate (transition state), it falls into the products well and transfers its energy back to the thermal bath (solvent) before the system has a chance to recross the barrier back to the reactants side. Therefore, a result of the first assumption is that the system is not allowed to recross the barrier back to the reactants potential well, and that the reaction can only
proceed in the forward direction. The second assumption is that the barrier crossing rate is the equilibrium flux across the barrier to the products well. This implies that an equilibrium exists between the reactants and transition state species at the top of the barrier. Thus, due to the ramifications of the first assumption (that the particle cannot recross the barrier), the rate at which the reactants escape from the well is directly related to the population of the transition state at the position $x_A$, represented by $P(x_A)$.

Finally, we note that the rate at which our system explores the reaction coordinate will also fundamentally limit the rate of the reaction. For now, we frame this in terms of the average forward velocity of the reactants. From these assumptions, we can derive the expression for the transition state rate constant ($k_{TST}$):

$$k_{TST} = \int_{-\infty}^{\infty} \langle v_f \rangle P(x_A) dx$$

where $\langle v_f \rangle = \frac{\int_{-\infty}^{\infty} v e^{-\frac{1}{2}\beta m v^2} dv}{\int_{-\infty}^{\infty} e^{-\frac{1}{2}\beta m v^2} dv} = \frac{1}{\sqrt{2\pi\beta m}}$

and $P(x_A) = \frac{e^{-\beta E_A}}{\int_{-\infty}^{\infty} e^{-\beta V(x)} dx}$

where $\beta$ is $kT^{-1}$, $m$ is mass, $E_A = V(x_A)$ the potential at position $x_A$, and $v$ is velocity.

We can, of course, break down Equation 4-1 even more, by providing more physically satisfying expression for each of the terms. For instance, from the Boltzman distribution, we know that $P(x_A)$ (the relative equilibrium population of the transition state) will have an exponential dependence on the energy gap between the transition state and the reactants ($E_A$), as $\exp(-\beta E_A)$. Putting this into Equation 4-1 results in the typical Arrhenius expression for the rate constant shown in Equation 4-2:

$$k_{TST} = \frac{\omega_0}{2\pi} e^{-\beta E_A}$$

where $\omega_0$ is the frequency of oscillation in the reactants well and $E_A$ is the height of the barrier.
In considering Equation 4-2, it is important to realize that the rate of escape from the well is only related to parameters that are determined by the reacting molecules, meaning that the surrounding solvent molecules do not alter the reaction rate of chemical systems within TST. Instead, the solvent is assumed to be merely a bath that couples to the reaction coordinate in a way that establishes and maintains the equilibrium conditions. However, such a treatment does not satisfy the chemist’s intuition. Indeed, from previous studies mentioned above, we know that the reaction rates are altered by the solvent, therefore, we must consider modifications to TST that accounts for the solvent friction on the reaction rate. One such theory was proposed in 1940 by Hans Kramers.\(^8\)

![Diagram](image)

**Figure 4-1**: The potential energy surface versus reaction coordinate used in (a) the intermediate coupling best described by TST and (b) the strong coupling or high friction limit of Kramers theory.

Kramers theory is a modification of TST that directly accounts for coupling of solvent to reaction dynamics, in terms of damping effects on the reaction rate caused by solvent friction. The physical manifestation of solvent friction (\(\gamma\)) is the relaxation of the velocity, where the larger the solvent friction the faster the velocity relaxes.\(^9\) To account for the damping effects caused by solvent friction, Kramers begins with the Langevin equation and adjusted it to account for the
Brownian motion escape from a single well. This resulted in the Kramers equation given in Equation 4-3. 9

\[
\frac{\partial P(x,v,t)}{\partial t} = \frac{1}{m} \frac{dV}{dx} \frac{\partial P}{\partial v} - v \frac{\partial P}{\partial x} + \gamma \left[ \frac{\partial}{\partial v} (vP) + \frac{k_B T}{m} \frac{\partial^2 P}{\partial v^2} \right]
\]  

(4-3)

In Kramers equation, \( P(x,v,t) \) is the joint probability distribution function that the particle position and velocity will be at \( x \) and \( v \), respectively, at time \( t \). 9 The mass of the particle is \( m \) and \( V \) is the potential energy of the particle. Similar to the first assumption made in TST, we assume that the thermal equilibrium deep in the potential well of the reactants is fast compared to barrier crossing, but near the barrier crossing point, dynamics effects can take place allowing the particle to cross and recross the barrier. Invoking the Browning origins of the nature of this theory, an intuitive picture can be arrived at. Essentially, the system explores the reaction surface in a random walk that is both governed by the potential surface and the damping effect of the solvent. However, the nature of the random walks are such that a system at the transition state can cross – and then recross – the barrier. As a consequence of this recrossing, the observed rate will be slowed down, yielding an expression that is proportional to the rate derived from TST, but with a correction factor as shown in Equation 4-4: 9

\[
k = \frac{\omega_r}{\omega_A} k_{TST}
\]

(4-4)

where \( \omega_r = \left( \omega_A^2 + \frac{\gamma^2}{4} \right)^{1/2} - \frac{\gamma}{2} \)

Here, \( \omega_A \) is the frequency at position \( x_A \) on the reaction coordinate and \( \gamma \) is the solvent friction.

We reiterate that Kramers theory is a modification of TST that accounts for strong solvent coupling to the reaction dynamics. Thus, in the limit of low solvent coupling (if we turn off solvent friction) we expect that Kramers theory will restore to the normal TST expression for the rate. By allowing \( \gamma \rightarrow 0 \), we see that \( \omega_r \rightarrow \omega_A \), and \( k \rightarrow k_{TST} \) confirming this anticipated result. This is an important result because it shows that Kramers theory agrees with TST when
the damping effects caused by solvent friction are not dominating the effect on the rate. On the other hand, if we consider what happens when the damping effects from solvent friction are turned on to an extreme \((\gamma \to \infty, \omega_f/\omega_A \to \omega_A/\gamma)\), we find that Equation 4-4 yields an expression for the high friction limit:

\[
k = \frac{\omega_A}{\gamma} k_{TST}
\]

Thus, in the high friction limit, Kramers theory predicts that the rate will be inversely proportional to solvent friction. In other words, the strong coupling of the solvent friction to the reaction coordinate acts to damp the system’s oscillations along reaction coordinate and this will, in turn, slow the observed rate of reaction. This is illustrated in Figure 4-1b, where the particle explores the reaction coordinate by randomly moving about its current position (Brownian motion). This is a result of the fact that, at each position, there are two competing forces: the solvent friction damping progress on the reaction coordinate and the solvent motions that “kicks” the system along the reaction coordinate. The blurriness of the particles in Figure 4-1b is meant to represent the collective result of these effects.

The inverse proportionally of solvent friction on the rate of chemical reactions have been observed experimentally for isomerization reactions of anthracene derivatives by Barbara and coworkers.\(^2\) It is important to note that solvent friction is not an experimental parameter that can be measured, therefore, solvent viscosity \((\eta)\) is often used as a proxy for solvent friction and will be used for the rest of this chapter. Using fluorescence spectroscopy, Barbara and coworkers were able to track the photoinduced cis-to-trans isomerization of an alkene substituted on an anthracene ring through temperature-dependent experiments in a series of linear alkane solvents. They found that as viscosity increased, the rate decreased. In other words, this system possessed a Kramers-like behavior.
The above reaction was an excited-state photo-induced isomerization. However, the majority of chemically relevant processes occur in the ground state, and so it is also important to test the predictions of Kramers theory for ground state reactions. In 2010, Kubarych and coworkers directly tested the validity of Kramers theory to describe solvent effects on ground state dynamics. They were able to separate the rate of isomerization between three rotomers of $\text{Co}_2(\text{CO})_8$ using 2D-IR and found Kramers theory could be used to describe their rate dependence on viscosity. Due to the energetic differences between the three isomeric forms of $\text{Co}_2(\text{CO})_8$, Kubarych and coworkers had to use 2D-IR to track the rate of exchange between isomers. This was one of the first accounts in the literature that used Kramers theory to describe solvent viscosity effects of a system in the ground state. Inspired by this report, we were interested in testing the ability of Kramers theory to describe the effect of solvent viscosity on the dynamics of $\text{FeNBD}$ and to use this as a means to establish the sensitivity of $\text{FeNBD}$ to its environment.

Our $\text{FeNBD}$ system has a few unique advantages as a model system for probing solvent viscosity effects, when compared to the $\text{Co}_2(\text{CO})_8$ system employed by Kubarych and coworkers. The three isomers of $\text{Co}_2(\text{CO})_8$ used by Kubarych and coworkers are energetically different, but give rise to spectral features similar enough that vibrational bands in the IR were convoluted, forcing them to use multidimensional spectroscopy to track each isomer separately. Since the isomers of $\text{FeNBD}$ are isoentergetic, the isomers only produce only three well-resolved bands in the carbonyl region of both vibrational spectra as seen previously in Chapter 2. Therefore, we can use steady-state vibrational spectroscopy to investigate the solvent effects on $\text{FeNBD}$. An additional advantage to using steady-state spectroscopy over multidimensional spectroscopy is the higher throughput of experiments, which will allow for systematic studies of larger breadth to be accomplished in shorter periods of time. Lastly, $\text{FeNBD}$ presents the possibility for being synthetically tuned by exchanging the norbornadiene ligand for other dienes or by functionalizing
the bridgehead of norbornadiene. These future studies will be able to probe the changes in barrier height and how that manifests into dynamics effects caused by solvent friction.

In this chapter, we will investigate the effect solvent viscosity has on the carbonyl ligand site exchange of FeNBD in a series of linear alkane solvents using steady-state vibrational spectroscopy. We hypothesize that the dynamics of FeNBD carbonyl site exchange will exhibit a $\eta^{\alpha}$ dependence, though the value of $\alpha$ may be less than 1. This chapter begins by confirming that the dynamics of FeNBD are sensitive to the solvent viscosity. Then, we quantify this dependence to determine if this interaction is best described by the high friction limit of Kramers theory ($\alpha = 1$) or TST ($\alpha << 1$).

**Experimental**

**General Procedures.** Norbornadiene and 2-methylpentane were purchased from Alfa Aesar and the linear alkanes from VWR and were used as received. Iron(0) pentacarbonyl was purchased from Sigma-Aldrich and was filtered through a sterile syringe filter with 0.2 µm cellulose acetate membrane (VWR) before use.

**Spectroscopic Measurements.** Raman spectra were acquired using a Renishaw inVia Raman Microscope equipped with an integral microscope (Leica DM2500 M) and a Linkam LTS420 liquid nitrogen temperature controlled stage. The excitation source was a 647 nm CrystaLaser CL-2000 diode pumped laser (70 mW, model DL647-070). We employed a 1200 l/mm grating, yielding a resolution of 1.9 cm$^{-1}$. The sample cell was home built by annealing two glass slides and a cover slip at 873 K for 12 hours and then allowing it to cool to room temperature. The slides were pre-drilled with holes to hold the liquid samples and to allow addition and removal of the sample. A diagram of the cell can be found in the Appendix for Chapter 2. The geometry of the cell allows for the liquid to have maximum contact with the
temperature-controlled stage. The temperature of the sample cell was calibrated for the Raman spectrometer with an external thermocouple and the calibration curve can be found in Appendix for Chapter 2. The error in the temperature measurement was determined to be \( \pm 1.8 \) K. Raman samples were prepared by adding 0.1 mL of linear alkane to *ca.* 2 drops of FeNBD.

Perkin Elmer Spectrum 400 FT-IR/FT-NIR with a liquid cell with path length of 0.1 mm was used to collect room temperature IR spectra with a 1 cm\(^{-1}\) resolution. Additionally, IR spectra were taken with a Pike MIRacle ATR attachment to collect room temperature IR spectra with a 4 cm\(^{-1}\) resolution. Variable temperature spectra were acquired with a vacuum tight Specac liquid cell with CaF\(_2\) windows and a Specac variable temperature liquid nitrogen cryostat (NaCl exterior windows). Specac reports a \( \pm 2 \) K sample temperature for their variable temperature cell. All IR solutions were prepared by adding a small amount of liquid FeNBD to 1mL of linear alkane solvent and diluting until a reasonable IR spectrum was obtained.

**Synthesis of Fe(CO)\(_5\)(\(\eta^4\)-norbornadiene) (FeNBD).** Synthesis of FeNBD was adapted from a previously published procedure.\(^{10}\) Under \( N_2 \), Fe(CO)\(_5\) (2.9 g, 0.0148 mol) was added dropwise over ten minutes to a flask of norbornadiene (2.7 g, 0.0294 mol) at 80° C and stirred for 18 h. Flash column chromatography with hexanes was used to purify the crude reaction mixture. The second yellow band off the column contained FeNBD. The solvent was removed under vacuum to yield an orange/yellow liquid (0.249 g, 7.25 % yield). Characterization by IR in 2-methylpentane revealed two distinct \( \nu (CO) \) bands at 1967 cm\(^{-1}\) and 2035 cm\(^{-1}\), which correspond with previous literature values.\(^{11}\) The compound must be stored in an inert atmosphere to avoid decomposition. Though the compound is mildly air sensitive, it does remain chemically persistent in 2-methylpentane under ambient conditions for several days.

**Spectral Analysis and Simulated Data.** All data was analyzed in Origin 9.0. The band position and full-width at half-maximum (FWHM) data was acquired using the multiple peak fitting tool in Origin 9, and all three bands were fit using the Voigt function. Simulated data were
acquired through the use of the Raman and IR Dynamics program (RAPID) described in Chapter 2.

Results and Discussion

To study the effect solvent has on the rate of carbonyl ligand site exchange in FeNBD, we investigated this compound in a variety of common solvents (Figure 4-2). In this series of solvents, the band shape and positions of FeNBD change as a function of solvent. These changes are similar to the behavior we observed with the FeCOT complex in Chapter 3, however, we know that FeNBD is dynamic on the picosecond timescale from experiments performed in Chapter 2. Therefore, the observed changes in band shape most likely stem from both dynamic and static effects. To fully characterize the kinetic parameters governing the rate of exchange in all of these solvents, temperature-dependent studies similar to those performed in Chapter 2 are needed.

Figure 4-2: IR of FeNBD at room temperature in several common solvents.

We chose to begin by focusing on the series of linear alkane solvents for several reasons. First, the linear alkane solvent series is a well characterized solvent series with many previous
reports, such as the reports of Barbara and Kubraych, allowing for similar analyses and comparison to previous literature with our data. Second, the linear alkanes form a solvent series that has minimal changes to electrostatic and chemical interactions, but has significant changes to the solvent viscosity. The solvent viscosity changes from 0.224 cP to 3.032 cP for pentane to hexadecane at room temperature, which is a large enough change to see a change in the rate if solvent viscosity has an impact of the dynamics. Additionally, we showed in Chapter 3 that the linear alkanes did not have much of a solvatochromic response with FeCOT, allowing us to assume that the static effects from the linear alkanes will be minimal for FeNBD and changes in the vibrational spectra result from dynamics. Therefore, this solvent series will allow us to correlate the effect of solvent viscosity on the kinetic parameters of the carbonyl ligand site exchange of FeNBD.

The IR spectra of FeNBD in a series of linear alkanes at room temperature are shown in Figure 4-3. The variation in the band shape and position is much smaller than that found in Figure 4-2. In Chapter 3, the linear alkane solvent series did not greatly impact the band shape of FeCOT; therefore we do not expect static effects to be responsible for the change in band shape for FeNBD observed in Figure 4-3. Instead, the change in band shape of FeNBD in the linear alkane series must arise from changes in dynamic exchange most likely affected by the viscosity changes in this series of solvents.
To confirm that the dynamics of FeNBD are changing as a function of solvent, we did
temperature-dependent experiments on four of the solvents in the series, pentane, octane,
dodecane, and hexadecane, and extracted the rate of exchange using RAPID to fit these spectra.
We then consider the correlation between changes in the extracted kinetic parameters and the
solvent viscosity. In the longer chain alkanes, it is nontrivial to extract a rate of exchange using
RAPID, as the best estimates requires us to input the band positions of non-coalesced bands,
which are then coalesced via exchange. However, for the longest alkanes the solvent freezes
before the carbonyl bands of FeNBD are fully resolved. To address this problem, we first
examined two shorter chain alkanes, pentane and octane, in a variable temperature Raman
experiment and then we used this information to inform the interpretation of the longer chain
alkanes. Figure 4-4 shows the Raman spectra of FeNBD in pentane and octane. Both sets of data
have dynamic behavior similar to that observed in 2-methylpentane (Chapter 2), where there are
fully coalesced lower energy CO bands at room temperature and three carbonyl bands are
resolved at lower temperatures. Simulation of the Raman spectra using the RAPID program (data
in the Appendix) afforded the rate of exchange at each temperature, which allowed us to create an
Arrhenius plot, identical to that of FeNBD in 2-methylpentane experiments in Chapter 2. The
activation energies and pre-exponential factors from the Arrhenius equation are tabulated in Table
4-1. We observe an increase in the activation energy in going from pentane to octane, but we
need to look into the longer alkanes to see if this trend continues.
Figure 4-4: (a) Temperature-dependent Raman of FeNBD in pentane. (b) Arrhenius plot of temperature dependent pentane data. The activation energy ($E_A^{(system)}$) and pre-exponential factor (A) are extracted from the slope and y-intercept of the linear regression, respectively. (c) Temperature-dependent Raman of FeNBD in octane. (d) Arrhenius plot of temperature dependent octane data.

Pentane

Octane

$E_A = 1.50 \pm 0.07 \text{ kcal/mol}$

$A = 1.63 \times 10^{13} \pm 7.5 \times 10^{10} \text{ s}$

$E_A = 1.58 \pm 0.07 \text{ kcal/mol}$

$A = 1.29 \times 10^{13} \pm 5.8 \times 10^{10} \text{ s}$
The longer chain alkanes, dodecane and hexadecane, were not cooled much below room temperature due to freezing points near room temperature. As the systems were heated, the two lower energy carbonyl bands moved closer together and coalesced into a single band, resulting in a carbonyl ligand site exchange slightly faster than the vibrational timescale. Notice in Figure 4-5 that we were not able to resolve all three carbonyl peaks, but we still observed the coalescence of the lower energy bands through the narrowing of that band. To simulate the Raman spectra of the longer chain alkanes in the RAPID program, we used the low temperature parameters from the shorter chain alkane solvents. We justified this choice by considering the very minimal impact that changes in alkane length had upon the spectra of the related compound, FeCOT (Chapter 3). The Arrhenius plots for dodecane and hexadecane are shown in Figure 4-5. From the slope and intercept of the linear regression, we extracted activation energies and pre-exponential factors for these solvents, which are tabulated in Table 4-1.

Table 4-1: Kinetic parameters of FeNBD in pentane, octane, dodecane, hexadecane, and 2-methylpentane. Viscosity data is from reference 13. The 2-methylpentane data is from Chapter 3.

<table>
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<tr>
<th>Solvent</th>
<th>Viscosity at 295 K (cP)</th>
<th>$E_A$(system) (kcal/mol)</th>
<th>$E_A$(solvent) (kcal/mol)</th>
<th>$E_A$(FeNBD) (kcal/mol)</th>
<th>$A$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentane</td>
<td>0.225</td>
<td>1.50 ± 0.07</td>
<td>1.358 ± 0.002</td>
<td>1.35 ± 0.07</td>
<td>$1.63 \times 10^{13} ± 7.5 \times 10^9$</td>
</tr>
<tr>
<td>Octane</td>
<td>0.5151</td>
<td>1.58 ± 0.07</td>
<td>2.13 ± 0.01</td>
<td>1.35 ± 0.07</td>
<td>$1.29 \times 10^{13} ± 5.8 \times 10^9$</td>
</tr>
<tr>
<td>Dodecane</td>
<td>1.378</td>
<td>1.66 ± 0.05</td>
<td>2.92 ± 0.02</td>
<td>1.34 ± 0.07</td>
<td>$1.44 \times 10^{13} ± 3.6 \times 10^9$</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>3.095</td>
<td>1.73 ± 0.04</td>
<td>3.65 ± 0.03</td>
<td>1.33 ± 0.04</td>
<td>$1.73 \times 10^{13} ± 3.3 \times 10^9$</td>
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<td>1.52 ± 0.06</td>
<td>1.23 ± 0.1</td>
<td>$1.1 \times 10^{13}$</td>
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</table>
Before the parameters extracted from Figure 4-4 and 4-5 can be commented on, one final complication must be considered and dealt with: the dependence of viscosity on temperature. Because viscosity itself is an activated process, the activation barrier we have obtained ($E_A$ system) is a combination of intrinsic $E_A$(FeNBD) and $E_A$(solvent). Fleming and Barbara and coworkers derived a way to subtract the $E_A$(solvent) from the observed $E_A$(system) derived from the Arrhenius plot, allowing the extraction of $E_A$(FeNBD), the intrinsic activation energy of the complex.$^{2,12}$ $E_A$(FeNBD) can be calculated using Equation 4-5
\[ E_A(FeNBD) = E_A(\text{system}) - \alpha E_A(\text{solvent}) \]  (4-5)

where \( E_A(FeNBD) \) is the intrinsic \( E_A \) of an isolated compound, \( E_A(\text{system}) \) is \( E_A(FeNBD) \) plus \( E_A(\text{solvent}) \), and \( E_A(\text{solvent}) \) is the \( E_A \) for the solvent to change viscosity at different temperatures. The \( E_A(\text{solvent}) \) can be calculated by plotting the natural log of the viscosity versus \( 1/T \) in a similar fashion to an Arrhenius plot through an empirical relationship that relates temperature and viscosity, \( \eta(T) = \eta_0 \exp\left(\frac{E_A^\eta}{RT}\right) \). In Figure 4-6, is the plot of ln \( \eta \) vs. 1/T for pentane. The viscosity data was obtained from tabulated references. The slope of the plot provides the activation energy of the solvent (\( E_A(\text{solvent}) \)), and its value for the four linear alkane solvents used are reported in Table 4-1, and shown in the Appendix.

![Image](image.png)

Figure 4-6: A plot of ln \( \eta \) versus 1/T for pentane. The viscosity data at different temperatures was used from reference 13. The slope of the linear regression gives the \( E_A(\text{solvent}) \) for pentane.

In Equation 4-5, \( \alpha \) provides information on the barrier crossing process in the system. A value of \( \alpha = 1 \) indicates a barrier crossing process is in the high friction limit, and a deviation of \( \alpha \) from 1 indicates that the barrier crossing process proceeds through more of an intermediate coupling limit. If we assume that the intrinsic activation energy of FeNBD is not changing as a function of solvent, we can plot the observed \( E_A(\text{system}) \) vs \( E_A(\text{solvent}) \) and extract \( \alpha \) from the slope of the linear regression as shown in Figure 4-7. We feel that this is a reasonable assumption.
for two reasons. First, the small solvatochromism experienced by FeNBD and FeCOT indicates that the alkanes interact relatively weakly with the carbonyls, and so it is hard to anticipate a manner in which such a weak interaction would lead to large changes in the activation barrier. Second, Figure 4-7 provides a relatively nice linear fit, which we could not anticipate in the case that solvent was changing the activation barrier of FeNBD significantly. The value of $\alpha = 0.11$, suggests that the barrier crossing is not in the high friction limit of Kramers theory, therefore the rate has only a weak $1/\eta$ dependence.

![Figure 4-7](image.png)

Figure 4-7: The observed $E_A$ (system) versus $E_A$ (solvent) yields a straight line, with the slope of the linear regression corresponding to $\alpha = 0.11$.

If our assumption that the intrinsic $E_A$(FeNBD) remains unchanged is correct, we should obtain a constant $E_A$(FeNBD) in all four solvents studied. Using Equation 4-4 with $\alpha = 0.11$, we obtain $E_A$(FeNBD) for all four solvents to be the same within error, approximately 1.3 kcal/mol (Table 4-1). This result supports our hypothesis that the linear alkane solvents do not interfere with the energetics of FeNBD, thus the change in the observed $E_A$ system arises from the effects of solvent viscosity. It is of interest to comment on the fact that the $E_A$(FeNBD) for linear alkane data and the 2-methylpentane data acquired in Chapter 2 (Table 4-1) are the same within error.
This result also supports the hypothesis that the solvent is neither strongly coupled to the reaction coordinate of FeNBD, nor is it altering the energetics of this complex.

**Conclusions**

We were able to conclude that the changes in the observed $E_A$ system as a function of solvent viscosity arise from the $E_A$ of the solvent contributing to the observed $E_A$ system and not from the solvent influencing the intrinsic energetics of FeNBD. We were able to support this by subtracting out the contribution from the solvent, yielding identical $E_A(\text{FeNBD})$ for all four alkane solvents investigated. This result confirms that the changes in rates for FeNBD are a consequence of solvent viscosity. We then plotted $E_A(\text{system})$ versus $E_A(\text{solvent})$ to extract $\alpha = 0.11$, therefore, an $\eta^{0.11}$ dependence of the rate on solvent viscosity. This small viscosity dependence indicates that the dynamics of FeNBD are not strongly coupled to the reaction coordinate and therefore, not well described by the high friction limit of Kramers theory. However, we do see a dependence of the rate of FeNBD exchange upon $\eta$, which means the coupling to the reaction coordinate must be stronger than the intermediate coupling described in TST.

Future experiments will focus on completing the temperature-dependent linear alkane series in order to further confirm our assignment of FeNBD to the intermediate-to-strong coupling regime of solvent friction. Additionally, we would like to understand the behavior of the preexponential factors (A) extracted in this study, as they vary between solvents in Table 4-1. We anticipate the preexponential factor to be correlated with some type of solvent interaction, but it is unclear at this point which parameter of the solvent will best describe this interaction. In total, this study presented in this chapter is the first step in establishing dynamic vibrational
spectroscopy as a technique to capture the influence of solvent viscosity on the ground state kinetic parameters of FeNBD.

References

Appendix for Chapter 4

Additional figures and data tables to supplement Chapter 4

Figure 4A-1: An Arrhenius type plot to calculate the activation energy for the solvent to change viscosity as the temperature is changed. We plotted $\ln \eta$ vs $1/T$ from the $\eta(T') = \eta_0 \exp\left(\frac{E_A}{RT}\right)$ to extract the activation energy of the solvent. The error in $E_A$ solvent comes from the error in the slope of the linear regression. The viscosity data for all four solvents was obtained from reference 13.
Table 4A-1: Parameters used in simulation of FeNBD in pentane using RAPID.

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<th>Gaussian FWHM (cm(^{-1}))</th>
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Table 4A-2: Parameters used in simulation of FeNBD in octane using RAPID.

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Table 4A-3: Parameters used in simulation of FeNBD in dodecane using RAPID.

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Chapter 5

Traditional Raman Spectroscopy used to Characterize the Morphology of Conducting Polymers in Thin Film Devices

Introduction

The previous chapters of this thesis have focused on the analysis of vibrational spectra, with the ultimate goal of determining kinetic parameters. In this chapter, we turn our attention to a more traditional use of vibrational spectroscopy – the determination of structural parameters. In particular, we examine how polymer morphology can be controlled within polymer-based thin film devices – and how morphological changes of the polymers affect the performance of these devices.

Our interest in thin film devices stems from the desirability of flexible integrated circuits and sensors, which promise light weight, low cost, mechanical flexibility, and ease of fabrication. An ultimate goal of these devices is to make disposable devices, utilizing an approach similar to print on paper. A critical requirement for the development of such thin film devices is to find the “magic recipe” of materials required to produce devices with adequate device performance, while maintaining ease of processing. One component of this recipe requires efficient conducting polymers, which will function to replace metal wires employed in traditional electronics.

In the context of conducting polymers, device performance is often measured in terms of charge mobility, with increased charge mobility being the ultimate goal. Many studies in the literature have shown that the addition of dopants, such as fullerenes, can enhance the charge mobility across the conducting polymer matrix by p-doping the polymer. However, the
underlying mechanism of this enhanced mobility remains unclear. Specifically, it is unknown if the dopants change the polymer matrix through morphological changes, or an electronic interaction - or both.\textsuperscript{3-5} This lack of detailed understanding, with regards to the mechanism of enhancement, precludes the rational development of new materials. Thus, studies are needed that allow for the measurement of the morphological and electronic effects of added dopants, as well as the separation of these modes of action. This chapter describes experiments aimed at providing this analysis.

In this chapter, I detail the use of Raman spectroscopy to examine the morphological impacts of adding dopants to conducting polymers in thin film devices. There have been several reports in the literature using Raman spectroscopy to characterize the changes in crystallinity of conducting polymer materials upon the addition of dopants.\textsuperscript{4-7} Through these reports, three criteria have been developed to characterize the change in polymer morphology when dopants or any other material are added to the polymer matrix. In general, a change in the band position, a change in FWHM, or a change in intensity between Raman bands of the polymer backbone can be used to comment of the degree of crystallinity induced by the dopant as compared to the pristine polymer.\textsuperscript{6} The work presented in this chapter was conducted through a collaboration with Elizabeth von Hauff’s group at the University of Freiburg in Germany, in which we investigated three different conducting polymer/dopant systems. One dopant/polymer system was used to fabricate thin film transistors (TFTs), while the remaining two polymer/dopant systems were used to manufacture two organic photovoltaic (OPV) cells. Here, we briefly outline the systems that we studied.

The TFT project aimed to separate purely electronic interactions from purely morphological changes as a function of dopant and correlate this to overall device performance. This was accomplished by doping with either silica nanoparticles (SiO\textsubscript{2} NPs) or phenyl-C\textsubscript{61}-butyric acid methyl ester (PC\textsubscript{61}BM). The SiO\textsubscript{2} NPs were chosen since they should not strongly
interact with the polymers in the films due to the insulating nature of SiO$_2$. Thus, changes to the charge mobility in the films brought about by the addition of SiO$_2$ NPs can be ascribed to purely morphological changes. The impacts of including SiO$_2$ NPs in TFTs were compared to the impacts of fullerene dopants, which are capable of both inducing morphological changes and undergoing electronic interactions with the conducting polymer.$^4$ We find that, for these systems, the morphological changes contribute a surprising amount to the ultimate device performance.

The first OPV devices I examined were constructed using a bulk-heterojunction motif, in which a conducting electron rich polymer (the donor) was mixed with an electron poor molecular dopant (the acceptor) as shown in Figure 5-1.$^8$ Fullerene derivatives (functionalized with methyl-4-phenylbutyrate) were used as the electron acceptors and were chosen to aid in the phase segregation required for bulk heterojunction OPV cells.$^8$ In these cells, polythiophene was employed as the electron donor. We investigated the impact of the regioregularity of polythiophene derivatives on the overall cell efficiency and the morphological changes that occur upon interaction of the polymer with the fullerene. While the relative effectiveness of the regioregularity of conducting polymers in OPV cells is well studied, the differential interaction of these polymers with dopants, such as PC$_{70}$BM, is not well understood. The goal of this study was to develop a structure-function relationship between the polymer morphology and cell performance upon addition of fullerene acceptors. In this case, we find that the electron interactions between fullerene and the polymer (rather than morphological changes) appear to dominate the performance of the cell.
The second OPV system we examined also focused on OPV cells using the bulk heterojunction approach. This time, we were interested in the effects of using plasmonic gold nanoparticles (Au NPs) as dopant materials to enhance the charge mobility in the conducting polymer. Au NPs are known to greatly enhance the absorption properties of nearby molecules, therefore they may enhance the absorption of the active layer, which is a well-known limitation of current OPV cells. We found that addition of the Au NPs decreased the overall cell performance, but that increasing the protecting layer around the nanoparticle (by changing the length of the passivating ligand on the nanoparticle) mitigated this effect.

The detailed results of these three investigations are presented below. Because this chapter presents the results of three different projects, it is structured differently than the previous chapters. In this chapter, I will highlight my spectroscopic contributions to these projects, but I also include a brief summary of the device architecture and performance to show how polymer morphology can be correlated to device performance. In all cases, I performed Raman spectroscopy of the films and interpreted the results of these spectra in terms of morphological changes to the films, while the von Hauff group characterized the electrical performance of the films. We then worked together to connect changes in device performance to changes in polymer morphology. In addition, to my spectroscopic work, I also traveled to Germany in order to manufacture one set of the OPV cells. Because this collaboration spans three different projects, the results of our collaborative efforts are presented separately, as three vignettes contained
within the results and discussion section. However, I first address experimental methods used for these projects.

**Experimental**

**Raman Measurements.** Spectra were recorded using a Renishaw inVia Microscope equipped with an integral microscope (Leica DM2500 M). The excitation sources were a 532 nm CrystaLaser CL-2000 diode pumped laser (50 mW, model CL532-050-S) and a 647 nm CrystaLaser CL-2000 diode pumped laser (70 mW, DL647-070). For the 532 nm laser line, we employed a 2400 l/mm grating, yielding a resolution of 1.1 cm$^{-1}$/pixel. For the 647 nm laser line, we employed a 1200 l/mm grating, yielding a resolution of 1.7 cm$^{-1}$/pixel. For all samples, the choice of laser line, laser power, laser exposure time, and number of accumulations were dictated by the need to minimize the fluorescence background, while maximizing the desired signal from the polymer.

**Spectral analysis.** All spectra were analyzed using the software package Origin 9.1. Background subtraction and normalization were performed on all spectra to enhance the accuracy of peak fitting. All peak positions and FWHMs were measured by fitting the spectra with a Voigt function using the multiple peak fitting function. The intensities of peaks were acquired by integrating the peaks with the peak analyzer function.

**Synthesis of gold nanoparticle (Au NPs).** The Au NPs were synthesized by Anthony Cirri in Benjamin Lear’s lab at Penn State. The 5 nm Au NPs were prepared using a modified Brust, two phase synthesis, as described by Murray and co-workers.$^{10}$ Tetraoctylammonium bromide (2.18 g) was vigorously stirred in 80 mL of toluene until complete dissolution. An aqueous solution of HAuCl$_4$3H$_2$O (354.5 mg; 30 mL) was added immediately to the solution, and the mixture was stirred at 500 rpm for 15 minutes. Once complete transfer of the gold salt into the
organic layer was observed, the aqueous layer was separated via extraction and discarded. The desired ligand (hexanethiolate or hexadecanethiolate, 0.220 mmol) was added to the remaining solution, and it was again stirred at 500 rpm for 15 minutes. A fresh, aqueous solution of NaBH₄ (380 mg; 25 mL) was prepared and added to the gold salt solution over ca. 10 seconds at room temperature. The reaction immediately turned a wine red color. The reaction was allowed to proceed for one hour. At the conclusion of the synthesis, the aqueous layer was separated, and the newly formed Au NPs were crashed out immediately via the addition of 150 mL of methanol. The final product was collected over a fine-fritted filter and stored in the solid state under ambient conditions until further use.

**Preparation and characterization of thin film transistors.** The thin film transistors were made at the University of Freiburg. For the SiO₂ NP and PC₆₁BM doped films, the gate layer was a silicon substrate with a SiO₂ insulating layer. The source and drain contacts were on a layer of indium tin oxide (ITO) followed by a layer of gold. The TFTs were shipped to The Pennsylvania State University without source and drain contacts for characterization of the polymer morphology by Raman spectroscopy. All experimental details are available in the literature.¹¹

**Preparation and characterization of OPV cells with PTB7:PC₇₀BM:Au NPs.** For this system, I traveled to the University of Freiburg and worked with Sabrina Jütcher from Elizabeth von Hauß’s group to fabricate and characterize these solar cells. All reagents used in the fabrication of OPV cells were used as received. ITO substrates were purchased from Präzisions Glas und Optik GmbH. We also employed nanoparticles passivated by either hexanethiolate or hexadecanethiolate surfactants (see above for synthesis). These surfactants were chosen to vary the effect of distance (or separation) between the polymer and the plasmonic core.

The cell is built in a bottom-up, layer-by-layer approach and the device architecture is illustrated in Figure 5-2a and photo of completed solar cells is in Figure 5-2b. The bottom layer
is a glass substrate with a thin layer of conducting material (ITO in our case). The next layer contains a polymer blend that aids in hole transport and collection at the ITO anode. For our cells, we have chosen poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS). Then, an active layer is added that contains the conducting polymer and any dopants. For this, we used (Poly(4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b’]dithiophene-2,6-diyl) {3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl}) (PTB7) blended with PC_{70}BM, Au NPs, and diiodooctane (additive). The structures of these components of the film are shown in Figure 5-3. The last layer of the solar cell consists of the metal contacts. One is placed on top of the active material, and the other is placed on top of just the ITO layer. For our system, we used calcium contacts that we coated in aluminum to protect them from oxidation.

Figure 5-2: (a) Schematic illustration of OPV cell design used in this study. This figure was adapted from reference 8. (b) Photo of completed solar cells.
The actual manufacture of the layer-by-layer structure was accomplished as follows. The ITO substrates were etched in concentrated HCl from Merck KGaA for 20 minutes, washed with DI water, and then ultrasonicated (Elma, Elmasonic S10H) in isopropanol, then acetone, then DI water, then ethanol for one hour each (all solvents from Carl Roth). The substrates were dried with N₂ and placed in a UV oven (Bioforce Nanosciences, Model: UV.Ozon ProCleaner TM Plus) for 15 minutes to remove any organic substances. Next, the hole transport layer, PEDOT:PSS was spincoated (Laurell Technologies Corporation, Model: WS-650MZ-23NPP) onto the ITO substrates at 3500 rpm for 30 seconds. The PEDOT:PSS (purchased from Clevios) solution was prepared by mixing 5 mL of filtered (0.45 µm) PEDOT:PSS solution with 5 mL of DI water. The substrates were brought into the glovebox and annealed at 180 °C for 10 minutes to evaporate and water remaining in the PEDOT:PSS layer.

Figure 5-3: Structures of conducting polymer, PTB7, and dopants, PC₇₀BM, 5 nm Au NP hexanethiolate, 5 nm Au NP hexadecanethiolate that were used in the active layer.
Next, the active layer solution was prepared in the glovebox. To prepare, 21.1 mg of PTB7 (purchased from 1-Material Inc.), 29.9 mg of PC70BM (phenyl-C70-butyric acid methyl ester, purchased from Solenne), 50 µL of diiodooctane (Alfa Aesar), and 2.2 mL of chlorobenzene (Sigma-Aldrich GmbH) were combined and stirred for 18 h at 40 °C and then passivated for 48 h before use. The PTB7:PC70BM solution was split into 3 vials containing the Au NPs: 1) 0.73 mL of PTB7:PC70BM, 2) 0.73 mL of PTB7:PC70BM and 1.9 mg of Au NPs with hexadecanethiolate ligand, and 3) 0.73 mL of PTB7:PC70BM and 1.6 mg of Au NPs with hexanethiolate ligand. The solutions were stirred until the particles were dissolved. The active layer solutions were spincoated onto the ITO:PEDOT:PSS substrates in the glovebox. Each of the active layer solutions was filtered using a 0.2 µm filter before being used for spincoating. 170 µL of active layer solution was used to spincoat a layer on each substrate using a Specialty Coating Systems Inc, Model: G3P Spincoat at 800 rpm for 30 seconds. The substrates were not annealed.

The last step for solar cell fabrication was to evaporate metal contacts onto the solar cells. A Oerlikon Leybold Vacuum, Model Univex 350 G evaporator in the glovebox was used to evaporate calcium and aluminum contacts onto the solar cells. 30 nm of Ca (Sigma-Aldrich GmbH) were deposited onto the substrates followed by 100 nm of Al (Umicore This Film Products) using a premachined mask for the placement of the contacts.

**Preparation and characterization of OPV cells with P3HT:PC70BM blends.** OPV cells were prepared and characterized by Jasmina Sichert at the University of Freiburg. All experimental details can be found in her Master’s thesis.\(^\text{12}\)
Results and Discussion

The collaboration with Elizabeth von Hauff’s group focused on the effect that dopants have on thin film morphology and device performance spans three separate projects, and I will consider them, in turn, below. Project 1 involved looking into the effect SiO$_2$ NPs had on the properties of TFTs, where we were able to correlate the transistor performance to the morphology of the polymer material. Project 2 investigated the effect of doping two regiospecific polymers to elucidate the impact of molecular order on polymer-dopant interactions and OPV device performance. Acquisition and analysis of Raman spectra was our primary focus, while the device fabrication and characterization were performed at the University of Freiburg. Project 3 also focused on OPV devices, this time aiming to explore the effect of adding plasmonic Au NPs into the active layer of OPV devices. For this project, I went to the University of Freiburg to learn how to assemble and characterize an OPV device. This project was funded through my CarbonEARTH fellowship, a NSF-funded GK-12 grant in the Department of Physics at The Pennsylvania State University. Below, I describe the results of each of these projects, in turn.

**Project 1: Correlating TFT device performance to morphological changes induced by dopants in semiconductor films**

The thin film transistor structure is well suited for low mobility materials, such as polymers and amorphous silicon. The low conductivity of the material determines the ON/OFF behavior of the device. TFTs are a type of field-effect transistor that are fabricated on a substrate, which serves as an insulating layer, followed by an organic semiconductor layer that creates a channel that connects the source and drain contact points, as shown in Figure 5-4. In this type of architecture, charge carriers, either electrons or holes, flow across the channel from the source to the drain. The type of charge carrier is dependent on the material used and how the material
responds to the application of the gate voltage. The electric field applied by the gate, in turn, affects the band energies in the semiconductor and modulates the flow of charge carriers. This flow of charge carriers can be quantified by the field effect mobility ($\mu_{FE}$), which measures the mobility of charge carriers across the channel. As such, much effort has been put into increasing $\mu_{FE}$ of organic semiconductor polymer channels in TFTs.\textsuperscript{1} However, there are still outstanding questions concerning the molecular level origins of the effects of doping upon the field effect mobility. Specifically, the relative rules for electronic versus morphological changes that result from the addition of a dopant to the polymer matrix. The experiments described below were designed to address these questions directly.

![Figure 5-4: Schematic of the architecture of a thin film transistor. Adapted from reference 11.](source)

For this project, the TFT architecture illustrated in Figure 5-4 was used. The semiconductor polymer layer consisted of MDMO-PPV (Figure 5-5), which was blended with SiO\textsubscript{2} NPs or PC\textsubscript{61}BM (Figure 5-5) to observe the effect these dopants have on the field effect mobility of the transistor. PC\textsubscript{61}BM is a common dopant in TFTs, and is known to change the value of $\mu_{FE}$ in these transistors. At the same time, PC\textsubscript{61}BM is known to interact electronically with the polymer and to induce morphological changes in the polymer. It is unknown which of these effects are predominantly responsible for the changes observed in $\mu_{FE}$ when PC\textsubscript{61}BM is added. On the other hand, SiO\textsubscript{2} NPs are a large bandgap insulators, and should undergo only minimal electronic interactions with the polymers. Thus, any changes to the polymer spectra or
electrical performance can be attributed to morphological changes, and the insulating properties of SiO$_2$ NPs allow us to separate the pure morphological changes that are often convolved with the electronic interactions present when the more traditional PC$_{61}$BM dopant is used.

Figure 5-5: Structures for MDMO-PPV conducting polymer and PC$_{61}$BM dopant used in TFTs.

The effects of dopants upon the polymers can be seen by comparing the Raman spectra for three different semiconductor blended materials used to create the channel in the transistor, which were the pristine MDMO-PPV, MDMO-PPV:SiO$_2$ NP, and MDMO-PPV:PC$_{61}$BM. The Raman spectra from each of these semiconductor films are shown in Figure 5-6. Recall that there are three characteristics we can use to diagnose the morphology: shift in band position, change in the FWHM, or a change in intensity between bands characteristic of the polymer backbone. Table 5-1 collects the values of these parameters for the most relevant bands: the out of plane bend of the vinylene CH group at 968 cm$^{-1}$, the symmetric phenyl stretch at 1588 cm$^{-1}$, and the symmetric C=C stretch in the vinylene group at 1625 cm$^{-1}$. We will consider the changes in position, FWHM, and intensity for each of these bands in turn below.
We start by analyzing the information that can be gained from the out-of-plane bend of the vinylene CH group, which is found at 968 cm\(^{-1}\) in the pristine MDMO-PPV film. A previous report in the literature concluded that both red shifts and increases in relative intensity of this band (compared to the symmetric phenyl stretching band at 1588 cm\(^{-1}\)), was a result of increasing planarity of the polymer backbone.\(^4\) In our films, I observed a red shift in the vinylene CH band when SiO\(_2\) NPs were added (963 cm\(^{-1}\)) relative to the pristine polymer (968 cm\(^{-1}\)), and a blue

Figure 5-6: Raman spectra of MDMO-PPV polymer blends. The structure of MDMO-PPV monomer is in the top left corner and the fragments illustrate the symmetric stretch of the phenyl ring at 1588 cm\(^{-1}\) and the out-of-plane bend of the vinylene CH groups at 968 cm\(^{-1}\). The black spectrum is the pristine MDMO-PPV polymer, the red spectrum is the MDMO-PPV and SiO\(_2\) nanoparticle blend, and the blue spectrum is the MDMO-PPV and PC\(_{61}\)BM blend. Both blends contain 60% dopant.

### Table 5-1: Summary of Raman data for pristine polymer and blended polymer TFTs.

<table>
<thead>
<tr>
<th>Semiconductor polymer</th>
<th>Band position (cm(^{-1}))</th>
<th>FWHM (cm(^{-1}))</th>
<th>(I_{968}/I_{1588})</th>
<th>(I_{1588}/I_{1625})</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MDMO-PPV</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>vinylene CH bend</td>
<td>968</td>
<td>0.69</td>
<td></td>
<td></td>
</tr>
<tr>
<td>phenyl stretch</td>
<td>1588</td>
<td>27.6 ± 1.0</td>
<td>0.69</td>
<td>1.32</td>
</tr>
<tr>
<td><strong>MDMO-PPV:SiO(_2)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>vinylene CH bend</td>
<td>963</td>
<td>0.56</td>
<td></td>
<td></td>
</tr>
<tr>
<td>phenyl stretch</td>
<td>1585</td>
<td>20.6 ± 0.5</td>
<td>1.69</td>
<td></td>
</tr>
<tr>
<td><strong>MDMO-PPV:PC(_{61})BM</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>vinylene CH bend</td>
<td>970</td>
<td>19.8 ± 0.8</td>
<td>0.99</td>
<td>5.00</td>
</tr>
<tr>
<td>phenyl stretch</td>
<td>1586</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
shift when PC$_{61}$BM was added (970 cm$^{-1}$). I also observed a decrease in the relative intensity ($I_{968}/I_{1588}$) from 0.68 (MDMO-PPV) to 0.56 (MDMO-PPV:SiO$_2$) to 0.09 (MDMO-PPV:PC$_{61}$BM). Taken together, both behaviors of the spectra support the idea of a decrease in planarity with PC$_{61}$BM is added to the polymer matrix. PC$_{61}$BM is known to intercalate into the side chains of MDMO-PPV, therefore, it is reasonable to think that the intercalation causes a decrease in the planarity of the polymer.$^4$ While the band shift and intensity data from the Raman band at 968 cm$^{-1}$ demonstrates that addition of PC$_{61}$BM decreases the crystallinity of the polymer by decreasing the planarity of the polymer backbone, their behavior is inconclusive with respect to how the addition of SiO$_2$ NPs impact the crystallinity of the polymer. However, there are additional bands present in the Raman spectra that report upon the structure of the MDMO-PPV polymer, which can provide clues to the relative effects of SiO$_2$ NPs and PC$_{61}$BM.

The next band we consider is the symmetric phenyl stretch of MDMO-PPV at 1588 cm$^{-1}$. Reports in the literature attribute an increase in intensity of this band relative to the intensity of the 1625 cm$^{-1}$ band (symmetric C=C stretch in vinylene group) ($I_{1588}/I_{1625}$) to an increase in the conjugation length of the polymer backbone.$^4$ We observed an increase in $I_{1588}/I_{1625}$ when either dopant is added. Specifically, we observe an increase from 1.3 (MDMO-PPV) to 1.7 and 5.0 when SiO$_2$ NPs and PC$_{61}$BM are added respectively. Thus, addition of either dopant results in an increase in the conjugation chain length, though this effect is largest for PC$_{61}$BM.

An increase in conjugation length suggests that one might also expect an increase in the crystallinity of the polymer when dopant is added. Evidence for such an increase in crystallinity is found from analyzing the FWHM of the band at 1588 cm$^{-1}$. We observe a decrease in the FWHMs of this band, from 27.6 ± 1.0 cm$^{-1}$ for the pristine polymer to 20.6 ± 0.5 cm$^{-1}$ when SiO$_2$ NPs are added, and to 19.8 ± 0.8 cm$^{-1}$ when PC$_{61}$BM is added to the polymer matrix. In general, the FWHM of a vibrational band reflects the degree heterogeneity of the environment surrounding the bonds involved in the mode (inhomogeneous broadening), or the dynamics of
this mode (homogeneous broadening). However, in a solid polymer matrix, changes to the width of the band will be dominated by inhomogeneous broadening, and so narrowing of vibrational bands signifies a more homogeneous environment around the polymer. Thus, the narrowing of the band at 1588 cm\(^{-1}\) suggests the polymer film is becoming more crystalline when dopant is added, which agrees with the above results that an increase in conjugation length occurs as dopant is added.

The last piece of evidence we have to consider is the shift in band position of the phenyl stretch at 1588 cm\(^{-1}\). The band position red shifts as dopant is added to the polymer matrix. In the literature, Elizarov and coworkers reported a red shift of the phenyl stretch band for a similar PPV polymer doped with 2,4,7-trinitrofluorenone (TNF). The authors attributed the red shift to a partial electron transfer from the polymer to TNF.\(^5\) We observe that addition of both SiO\(_2\) NPs and PC\(_{61}\)BM result in shifts that are similar to each other and to that reported by Elizarov. Thus, if we were to follow this assignment we would ascribe both the SiO\(_2\) NPs and the PC\(_{61}\)BM to be donating a partial charge to the polymer. However, as we noted above, SiO\(_2\) NPs are not expected to interact electronically with the polymer, as they are both insulating and too large to intercalate the polymer side groups. Therefore, we are forced to ascribe the red shift observed from the addition of SiO\(_2\) NPs to morphological changes, rather than electronic interactions.

The Raman data acquired on these blended polymer samples allow us to conclude that SiO\(_2\) NPs and PC\(_{61}\)BM increase the degree of planarity and conjugation chain length in the thin film of MDMO-PPV, but PC\(_{61}\)BM induces a greater degree of crystallinity. We cannot fully conclude that the effects observed in the Raman spectra for PC\(_{61}\)BM are only a consequence of morphological changes, due to the ability for PC\(_{61}\)BM to intercalate the polymer side groups and participate in a partial charge transfer with the polymer. However, since SiO\(_2\) NPs cannot intercalate the polymer side groups, we can conclude that all observed changes in the Raman spectra resulted because SiO\(_2\) NPs caused an increase in the crystallinity of the polymer through
increases in the planarity and conjugation length in the polymer backbone. The similarity of the results for SiO$_2$ and PC$_{61}$BM (particularly for the 1588 cm$^{-1}$ band) calls into question the relative importance of the charge transfer and morphological effects of PC$_{61}$BM. In order to gain more insight into the ramification of these effects on device performance, we next sought to connect these spectroscopic observations to any changes in device performance.

All device characterization was performed in Elizabeth von Hauff’s group at the University of Freiburg, and the field effect mobility ($\mu_{FE}$) was measured for the TFTs. For this particular TFT, the focus is on measuring the mobility of holes through the channel. The hole mobility was measured for the pristine polymer samples, and various concentrations of dopant blended films. It was found that $\mu_{FE}$ increased from $6.3 \times 10^{-7}$ cm$^2$V$^{-1}$S$^{-1}$ (MDMO-PPV) to $8.3 \times 10^{-6}$ cm$^2$V$^{-1}$S$^{-1}$ (80% SiO$_2$ NPs), and to $1.3 \times 10^{-5}$ cm$^2$V$^{-1}$S$^{-1}$ (80% PC$_{61}$BM). The fact that the SiO$_2$ NPs increased $\mu_{FE}$ by one order of magnitude is unprecedented, and is especially surprising given considering their insulating properties. This result follows nicely from my interpretation of the Raman data, and we conclude that the SiO$_2$ NPs increased the charge carrier mobility through changes in morphology.

In conclusion, we were able to correlate the changes in morphology of the MDMO-PPV semiconductor polymer films that were induced by dopants, SiO$_2$ NPs and PC$_{61}$BM. The blended polymer film’s morphology were analyzed by Raman spectroscopy, and we concluded that the SiO$_2$ NPs induced an increase in the planarity and conjugation length of the polymer backbone of MDMO-PPV. At the same time, the PC$_{61}$BM molecules also induced changes in the Raman spectra that are attributed to a convolution of an increase in the planarity and conjugation length of the polymer backbone and the ability of PC$_{61}$BM to undergo a partial charge transfer with the polymer side groups. The device performance was measured in terms of hole mobility of the blended polymer TFTs, which increased by one order of magnitude when SiO$_2$ NPs are added and two orders of magnitude when PC$_{61}$BM is added. Based upon this, we suggest that the
morphological effects of doping play a significant role in controlling the performance of thin film
devices employing the conducting MDMO-PPV polymer. This is certainly worth further
investigation, and may prove critical in the design of future devices employing this polymer.

**Project 2: Investigating the effect of polymer morphology on OPV cell performance with
two regiospecific polymers**

Organic photovoltaics is a field of research dedicated to fabricating solar cells that have
all the advantages of using conducting polymers, such as flexibility, low cost, and light weight,
but still retain the ability to convert light into electrical energy with reasonable efficiency. Cell
efficiency is defined as the percentage of the incident solar energy that the cell is able to convert
to electrical energy. In 2012, the highest efficiency for an OPV was reported at 11\%, but still
falls short of the 27.8 \% efficiency achieved by silicon-based solar cells.\(^3\) Still, the field of OPV
remains a very active field of research, exploring the effects of device architecture and materials,
as there is a wide range of combinations to investigate.

From previous experiments and literature reports, we know that morphological changes
in the active layer can impact OPV cell performance and efficiencies.\(^8,11,13,14\) To better
understand the structure-function relationship of OPV cells, Jasmina Sichert from Elizabeth von
Haufl’s group dedicated her Master’s thesis to studying the effect the regioregularity of the
conducting polymer has on the morphology and cell efficiency.\(^12\) For this portion of the project,
Jasmina prepared and characterized the OPV cells in Freiburg before sending them to The
Pennsylvania State University for morphological analysis by Raman spectroscopy. The OPV cell
architecture is identical to the design shown in Figure 5-2a. The two regiospecific polymers used
in this study were poly(3-hexylthiophene) regioregular (P3HT-RR) and poly(3-hexylthiophene)
regiorandom (P3HT-RRA) blended with various amounts of PC\(_{70}\)BM. The polymer structures
are shown in Figure 5-7. The main difference between the regiospecific polymer is the arrangement of the hexyl side group, where the regioregular polymer produces a more crystalline polymer film than the regiorandom arrangement. It is known that the regioregular and regiorandom polymers have different mobility values, however, the exact morphological underpinnings for this are not well understood. Furthermore, there are few – if any – studies into the different morphological consequences of adding dopants to either regioregular versus regiorandom polymers. For this project, we measured and analyzed the Raman spectra to understand how the morphology of the P3HT films blended with PC$_{70}$BM correlates to cell performance.

![Poly (3-hexylthiophene) regioregular (P3HT-RR) and Poly (3-hexylthiophene) regiorandom (P3HT-RRA)](image)

Figure 5-7: Structures of conducting polymer used in the active layer of these OPV cells. The blue boxes indicate the C=C symmetric ring stretch and the red box indicates the C—C ring stretch used to characterize the morphology of P3HT.

In order to examine the effects of regioregularity, we prepared and obtained Raman spectra on five samples: pure P3HT-RR, pure P3HT-RRA, and both polymers doped with PC$_{70}$BM in ratios of 1:1 and 1:2 polymer:dopant. In the spectra of all the samples, our focus was on the carbon-carbon stretches in the thiophene ring of the P3HT polymer backbone. The C=C symmetric ring stretching frequency and the C—C ring stretch have been used previously to
characterize the crystallinity of P3HT:PC$_{70}$BM blended films. These stretches in the polymer backbone are indicated on Figure 5-7 by blue and red boxes, respectively. Kim and coworkers established that shifts in C=C band position to lower wavenumbers, narrowing of the FWHM of the C=C band, or increases in the intensity ratio of $I_{C\text{-C}} / I_{C\text{-C}}$, are all reflective of increases in the crystallinity of the P3HT film increases. Using these three characteristics, we can comment on the crystallinity between the P3HT polymer films and how the morphology is affected by adding various amounts of PC$_{70}$BM.

We begin with the series of cells composed of P3HT-RR polymer with increasing amount of PC$_{70}$BM. We observed a slight monotonic blue shift of the C=C band position upon addition of PC$_{70}$BM, indicating that the P3HT-RR becomes less crystalline as more PC$_{70}$BM is added (Figure 5-8 and Table 5-2). However, the very small magnitude of these shifts indicates that the effect of adding PC$_{70}$BM to the polymer morphology is minimal. The FWHM increases when PC$_{70}$BM in introduced into the film (P3HT-RR:PC$_{70}$BM (1:1)) but then slightly decreases when more PC$_{70}$BM is added (P3HT-RR:PC$_{70}$BM (1:2)), indicating less crystallinity upon addition of small amounts of PC$_{70}$BM, followed by increases in crystallinity with increasing PC$_{70}$BM. Regarding the intensity ratio ($I_{C\text{-C}} / I_{C\text{-C}}$), as more PC$_{70}$BM is added, the intensity ratio slightly decreases from 0.22 (P3HT-RR:PC$_{70}$BM) to 0.21 (P3HT-RR:PC$_{70}$BM (1:2)), which again implies that the film is becoming less crystalline. It is important to note that all the changes in position, FWHM, and the intensity ratios for the P3HT-RR series are smaller in magnitude than the Raman spectrometer, therefore, we leading us to conclude that the crystallinity of the P3HT-RR series is becoming slightly more disordered or not changing at all as PC$_{70}$BM is added. However, it is also important to keep in mind that PC$_{70}$BM is capable of intercalating into the side groups of similar polymer structures, allowing close approach to the main polymer chain, where it can undergo a partial charge transfer that will result in the shifts of Raman bands and changes in intensity. Such
effects were reported by Grey and coworkers, and so we have a need, in the future, to deconvolute morphological changes from electronics effects – as was done in Project 1.4

![Raman spectrum of polymer blends P3HT-RR with PC70BM.](image)

**Figure 5-8:** Raman spectrum of polymer blends P3HT-RR with PC70BM.

<table>
<thead>
<tr>
<th>Active layer</th>
<th>Band position C=C (cm⁻¹)</th>
<th>FWHM C=C (cm⁻¹)</th>
<th>Band position C-C (cm⁻¹)</th>
<th>I_C=C/I_C=C</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT-RR</td>
<td>1456.1</td>
<td>30.7</td>
<td>1387.6</td>
<td>0.22</td>
</tr>
<tr>
<td>P3HT-RR:PC70BM (1:1)</td>
<td>1457.6</td>
<td>31.5</td>
<td>1387.4</td>
<td>0.22</td>
</tr>
<tr>
<td>P3HT-RR:PC70BM (1:2)</td>
<td>1457.9</td>
<td>31.0</td>
<td>1387.4</td>
<td>0.21</td>
</tr>
<tr>
<td>P3HT-RRA</td>
<td>1450.4</td>
<td>88.4</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>P3HT-RRA:PC70BM (1:1)</td>
<td>1472.3</td>
<td>40.3</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>P3HT-RRA:PC70BM (1:2)</td>
<td>1471.9</td>
<td>42.2</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 5-2: Raman data for both regiospecificities of P3HT with varying PC70BM concentration.

Moving onto the samples with P3HT-RRA, we found the Raman spectra were hard to acquire, due to a large fluorescence background and high level of noise in the spectra. Several examples in the literature report Raman spectra similar to what we acquired (Figure 5-9) for P3HT-RRA.15 When looking at the Raman spectra in Figure 5-9, the signal to noise ratio is very
low, making it difficult to extract accurate band positions and FWHMs. For all P3HT-RRA samples, the C—C band could not be resolved; therefore, an intensity ratio could not be calculated for this series. For P3HT-RRA, the C=C band is not well resolved and the band position or FWHM cannot be reliably extracted. When PC70BM is added initially, the C=C band position shifts to higher wavenumber indicating less crystalline character in the polymer when PC70BM is added, but the significant decrease in the FWHM as PC70BM is added, suggests that polymer is becoming more crystalline. In total, while we see some changes in the spectra, we cannot quantify the effect PC70BM has on the crystallinity of P3HT-RRA from the Raman data.

![Raman spectrum of polymer blends P3HT-RRA with PC70BM.](image)

Figure 5-9: Raman spectrum of polymer blends P3HT-RRA with PC70BM.

Just as for the TFT films presented in Project 1, it is important to connect changes in film morphology (as determined by Raman spectroscopy) to the performance of devices using these films. Jasmina Sichert in Freiburg, Germany measured the J-V characteristics for all OPV cells. The cells were characterized using typical voltage-current measurement with and without illumination. Figure 5-10 illustrates an ideal J-V curve for a light and dark measurement. From these measurements important cell parameters, such as the fill factor (FF) and the cell efficiency ($\eta$) can be calculated. The FF is defined in Equation 5-1 as:

$$FF = \frac{J_M V_M}{J_{SC} V_{OC}} \times 100$$

(5-1)
where $J_M$ is the current maximum power point, $V_M$ is the voltage maximum power point, $J_{SC}$ is the short-circuit current density, and $V_{OC}$ is the open circuit voltage. In looking at Figure 5-10, $J_{SC}$ is the y-intercept of the light measurement, $V_{OC}$ is the x-intercept of the light measurement, and $J_M$ and $V_M$ are derived from drawing a rectangle in the fourth quadrant of the x-y graph from the origin to the light measurement. The FF accounts for maximum power output for the solar cell, where an ideal FF value is 100%, indicating the maximum power output has been reached. Therefore, the closer the FF is to 100%, the better the solar cell performance, and the better the cell efficiency, due to the FF being proportional to $\eta$ as defined in Equation 5-2 as:

$$\eta = \frac{P_{out}}{P_{in}} = FF \frac{(J_{SC}V_{OC})}{P_{in}}$$  \hspace{1cm} (5-2)

where $P_{in}$ is the power supplied to the cell and $P_{out}$ is the power the cell produces. If the J-V curve is more rectangular, the FF and $\eta$ will be higher due to the decreased resistance in the cell. All of these cell parameters were measured using a typical J-V measurement in an inert atmosphere and the averages are shown in Table 5-3.

Figure 5-10: A typical spectrum from a light and dark current versus voltage (J-V) measurement. The important device parameters are labeled with $J_M$ and $V_M$ being the current and voltage maximum power points, $V_{OC}$ is the open circuit voltage, and $J_{SC}$ is the short circuit current density. From these parameters the fill factor (FF) and the cell efficiency can be calculated. This figure was adapted from reference 8.
We also examined device performance as a function of dopant concentration as shown in Figure 5-11 and is summarized in Table 5-3. It is important to note that the solar cells with no PC<sub>70</sub>BM added only work as a diode and not as a solar cell, therefore, no J-V characteristics are reported for the pristine polymer cells. First, we note that the P3HT-RRA is more responsive to changes in dopant concentration than is the P3HT-RR. Moreover, the regiorandom polymer continues to increase in performance with increased dopant, while the highest cell efficiency measured for the P3HT-RR:PC<sub>70</sub>BM (1:1) solar cell (3.4 %) was obtained for the lower level of doping. The Raman data accompanying the P3HT-RR:PC<sub>70</sub>BM:1:1 solar cell shows its

Table 5-3: Summary of OPV cell parameters, where J<sub>SC</sub> is the short circuit current density, V<sub>OC</sub> is the open-circuit voltage, FF is the fill factor, and η is the cell efficiency.

<table>
<thead>
<tr>
<th>Active layer</th>
<th>J&lt;sub&gt;SC&lt;/sub&gt; (mA/cm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>V&lt;sub&gt;OC&lt;/sub&gt; (V)</th>
<th>FF (%)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT-RR:PC&lt;sub&gt;70&lt;/sub&gt;BM (1:1)</td>
<td>8.90 ± 0.92</td>
<td>0.58 ± 0.00</td>
<td>65.77 ± 1.30</td>
<td>3.40 ± 0.35</td>
</tr>
<tr>
<td>P3HT-RR:PC&lt;sub&gt;70&lt;/sub&gt;BM (1:2)</td>
<td>5.49 ± 1.71</td>
<td>0.59 ± 0.01</td>
<td>60.30 ± 0.57</td>
<td>1.95 ± 0.29</td>
</tr>
<tr>
<td>P3HT-RRA:PC&lt;sub&gt;70&lt;/sub&gt;BM (1:1)</td>
<td>0.38 ± 0.04</td>
<td>0.90 ± 0.00</td>
<td>27.56 ± 0.23</td>
<td>0.09 ± 0.01</td>
</tr>
<tr>
<td>P3HT-RRA:PC&lt;sub&gt;70&lt;/sub&gt;BM (1:2)</td>
<td>0.73 ± 0.11</td>
<td>0.88 ± 0.02</td>
<td>27.94 ± 0.37</td>
<td>0.18 ± 0.02</td>
</tr>
</tbody>
</table>

Figure 5-11: The dark and illuminated J-V characteristics for (a) P3HT-RR:PC<sub>70</sub>BM (1:1) and (b) P3HT-RRA:PC<sub>70</sub>BM (1:1) These graphs were adopted from Jasmina Sichert’s Masters thesis, University of Freiburg, Germany (reference 12).
morphology is the least crystalline for this concentration of PC$_{70}$BM. Interestingly, the performance of the P3HT-RRA is also greatest for the level of PC$_{70}$PB doping (1:2) that was associated with the lowest crystallinity. From this, we conclude that the increase in OPV efficiency is not a result of changes in morphology. Instead it seems likely that the electronic interaction of PC$_{70}$BM with P3HT polymer dominates increases in OPV performance. This is the opposite result as found for the TFT polymer discussed in Project 1, and highlights the importance of understanding the mechanism of doping on a polymer-by-polymer basis.

**Project 3: Examination of the effect plasmonic nanoparticles have on the performance of organic photovoltaic cells**

In Project 2, we saw that the performance of an OPV cell depends on the regioregularity of the polymer. In addition, we found that the degree to which the OPV performance is affected by dopants depends upon the regioregularity. This work was done using traditional fullerene-based materials. However, there are many other possible dopants that could be used to tune the performance of OPV. Owing to their ability to greatly enhance the absorption properties of nearby molecule, Au NPs are of interest to the OPV community for their potential to increase the absorption of the active layer film, which is a well known limitation of current OPV cells. At the same time, there are few studies that focus on the underlying morphological changes that such nanoparticles induce. Here, we describe preliminary investigations into OPV cells incorporating Au NPs. These studies will eventually result in the acquisition of Raman data for these cells. However, the first steps (described below) focus on the generation of the cells for the subsequent Raman studies.

The general cell architecture we used for OPVs with the Au NPs is illustrated in Figure 5-2a. The fabrication procedure for the OPV cells doped with Au NPs can be found in the
experimental section of this chapter. For this project, I went to the University of Freiburg for two weeks and worked with researcher Sabrina Jütcher in Elizabeth von Hauff’s laboratory to fabricate the OPV cells. The goal of my visit was to fabricate a batch of OPV cells with Au NPs blended into the active layer, and test the effect the plasmonic Au NPs would have on OPV cell efficiency. The funding for this part of the project came from my CarbonEARTH fellowship, which had two main objectives: (1) to help establish or enhance an international collaboration and (2) compare and contrast the German and American educational systems. During my visit, I was able to fabricate solar cells with measurable cell efficiencies, and accomplish both of these objectives. Here, I describe the scientific results of this collaboration.

The performances of the OPV cells were evaluated using the same J-V analysis as described for Project 2. Figure 5-12(a) demonstrates representative J-V measurements for each of the three active layers. The light curves for all three active layers are far from ideal, as evidenced by their non-rectangular shape, low FF, and low cell efficiencies. The device performance characteristics are summarized in Table 5-4. These preliminary results show a decrease in FF and $\eta$ when the Au NPs are added to the active layer, regardless of ligand. This was an unexpected result, since our hypothesis was that the Au NPs would increase the cell efficiency. However, it is also of interest to comment that the Au NPs with hexadecanethiolate ligands produced higher cell efficiencies than the hexanethiolate Au NPs. The only difference between these Au NPs is the length of the surfactant. Both of these surfactants are aliphatic and so it seems reasonable to conclude that the decrease in performance is connected to the ability of the Au NPs to electronically communicate with the polymer. However, it is also possible that these different surfactants could be interacting with the polymer differently – and introducing different morphological changes in the film as a consequence. Thus, morphological studies need to be performed in order to assess whether the distribution of the Au NPs is similar in both polymer films and how they affect the morphology of the polymer backbone. Finally, it was
determined after this experiment that the 5 nm Au NPs with hexanethiolate ligands had partially decomposed during the trip to Germany, but the 5 nm Au NPs with hexadecanethiolate ligand remain stable. This result means that the concentration of 5 nm Au NPs with hexanethiolate ligands was significantly less than the reported concentration, which calls for the experiment to be repeated.

Figure 5-12: (a) J-V curves for the most efficient OPV cell with each of the active layers. (b) Bar graph of the all cell efficiencies to show the fluctuation in η between cells with the same active layer.

Table 5-4: Average J-V characteristics of OPV cells with all three active layers.

<table>
<thead>
<tr>
<th>Active layer</th>
<th>$J_{sc}$</th>
<th>$V_{oc}$</th>
<th>$(J_{sc})(V_{oc})$</th>
<th>FF</th>
<th>η</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(mA)</td>
<td>(mV)</td>
<td>(mW)</td>
<td>(%)</td>
<td>(%)</td>
</tr>
<tr>
<td>PTB7:PC$_{70}$BM</td>
<td>2.5 ± 1.0</td>
<td>611.6 ± 31.8</td>
<td>0.9 ± 0.4</td>
<td>59.1 ± 3.3</td>
<td>3.8 ± 0.7</td>
</tr>
<tr>
<td>PTB7:PC$_{70}$BM</td>
<td>3.5 ± 1.9</td>
<td>247.0 ± 38.3</td>
<td>0.3 ± 0.2</td>
<td>38.6 ± 4.2</td>
<td>0.9 ± 0.3</td>
</tr>
<tr>
<td>5 nm Au NP hexanethiolate ligand</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PTB7:PC$_{70}$BM</td>
<td>2.6 ± 2.2</td>
<td>367.0 ± 12.1</td>
<td>0.4 ± 0.4</td>
<td>41.4 ± 0.4</td>
<td>1.33 ± 0.06</td>
</tr>
<tr>
<td>5 nm Au NP hexadecanethiolate ligand</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Overall, it appears from the data that the Au NPs had the opposite effect we were hoping for, but we cannot quantify this effect without fabricating more solar cells for statistical analysis. Figure 5-12(b) shows fluctuations of the cell efficiency between cells with the same active layer. This indicates inconsistencies in OPV cell preparation, which is critical to eliminate before we can quantify the effect Au NPs have on the FF and η. Thus more cells must be made with new preparations of the nanoparticles, in order to ensure that this did not affect the results we obtained. More experiments are currently underway by Xing Fan at the University of Freiburg to optimize several OPV preparation parameters, including Au nanoparticle concentration, spin coating parameters, and preparation of the active layer solution. Once the cell preparation parameters have been optimized, the morphological effects that the Au NPs induce on the active layer needs to be investigated with Raman spectroscopy and TEM. Again, several batches of these cells are needed to statistically quantify of the effect Au NPs have on the FF and cell efficiency in OPV cells.

Conclusion

In this chapter, we explored how Raman spectroscopy can be used to characterize the morphology in thin film devices, including TFTs and OPVs. All three of the projects covered in this chapter were done in collaboration with Elizabeth von Hauß’s laboratory at the University of Freiburg in Germany. For both the TFTs and the OPVs, we were able to correlate the morphological data obtained from the Raman spectra to device performance. For the first project, we demonstrated that incorporating SiO$_2$ NPs into the MDMO-PPV polymer matrix results in a more crystalline film, which causes an increase in the hole mobility across the channel of the transistor by one order of magnitude. In comparing the TFTs with SiO$_2$ NPs to the TFTs with PC$_{61}$BM, we were able to separate the pure morphological effect of SiO$_2$ from the convolution of
morphological and electronic effects induced by PC_{61}BM. The second project explored the effect the regioregularity of the P3HT polymer had on the overall OPV cell performance. We were able to conclude that the changes in cell efficiency induced by doping with PC_{70}BM is most likely due to an electronic interaction between the polymer and PC_{70}BM, and not an increase in the crystallinity of the polymer film, as seen with the TFTs in Project 1. The conflicting results between Projects 1 and 2 require that the morphological changes in each thin film device must be considered individually. The last project involved the fabrication and characterization of OPVs doped with Au NPs to investigate their effect on the overall solar cell efficiency. We were able to successfully fabricate working solar cells, but the inconsistencies between solar cells requires us to obtain more data before we can quantify the effect Au NPs have on the overall OPV cell performance in a statistically meaningful manner.

Overall, Raman spectroscopy is a great tool to gain insight into the changes in crystallinity of conducting polymer films. This chapter has showcased the ability of Raman spectroscopy to correlate morphological changes in the polymer film to thin film device performance. It is important to have a fundamental understanding of how dopants interact with the polymer film and alter the charge mobility properties. By gaining this structure-function knowledge, we can begin to rationally tune the properties of conducting polymer films for their application in TFTs and OPV devices. In the next chapter, we will summarize the projects covered in this dissertation, and outline future experiments using vibrational spectroscopy to probe the effect of molecular environments on chemical dynamics.
References

Chapter 6

Conclusions and Future Directions

The work presented in this dissertation was motivated by the need to understand the impact of molecular environments upon the kinetics of molecules. This need, in turn, is motivated by a diverse range of disciplines, from enzymology to heterogeneous catalysis to electronic materials. The ultimate goal would be to develop a clear, comprehensive, understanding that connects the effects of a diverse set of local environments (from solvents to solid frameworks) have upon kinetics and structures of molecules contained within them. My dissertation represents the initial steps towards developing this cohesive picture of these effects – focusing on developing steady-state vibrational spectroscopy as a tool to quantify the effect the molecular environment has on ground-state chemical dynamics and molecular structure. The steps that I have accomplished in the areas of chemical dynamics and chemical morphology (static) molecular properties are summarized below.

Chemical Dynamics

My work began by establishing the equivalency of IR and Raman spectroscopies for extracting dynamic information from band shape analysis. Simple energetic considerations lead to the conclusion that both spectroscopies should report on the same kinetics, but IR and Raman spectroscopies arise from different phenomena and differ in mechanism of collection. Since no direct test between IR and Raman spectroscopies had been performed, we tested the equivalency of the kinetic information extracted from IR and Raman spectra using Fe(CO)$_3$(η$^4$-norbornadiene) (FeNBD) by calculating the activation energy barrier associated with the carbonyl ligand site
exchange of FeNBD. This work was presented Chapter 2. Additionally, we extended the theoretical framework for extracting kinetic information from vibrational band shapes to include Raman band shapes. We collaborated with Lasse Jensen at The Pennsylvania State University to derive the theoretical framework and developed the RAPID program for extracting rates of chemical processes on the picosecond timescale. Finally, we calculated the activation energies of FeNBD in the IR and Raman data, using the Arrhenius equation, and were found to be the same within experimental error. Therefore, we can conclude that IR and Raman spectroscopies report on the same kinetics. This result is opens the door for the use of either Raman or IR spectroscopy to determine chemical kinetics – in turn allowing for each spectroscopy to be used as the nature of the sample dictates.

Once I established that either IR and Raman spectroscopy can be used to obtain kinetic information, I became interested in understanding how the molecular environment would impact the kinetics of the carbonyl ligand site exchange in FeNBD. I choose to begin with what is perhaps the most common molecular environments employed in chemistry: the solvent environment. Though it is common, the solvent environment is extremely complex. The complexity owes to the dynamic nature of the solvent and, to the potential for multiple types of intermolecular interactions (London dispersion, dipole-dipole, hydrogen bonding, etc). These effects of the solvent environment are manifested in two ways: static solvent effects, such as solvatochromism, and dynamic solvent effects, such as solvent friction. These interactions affect the kinetics of the system through changes to either the activation barrier (static) or the preexponential factor (dynamic). Thus, if we were to use vibrational spectroscopy to quantify the effects of solvent on the rate of carbonyl exchange in FeNBD in a meaningful way, we needed to develop a way to separate static from dynamic effects. Chapter 3 discussed the use of an iron diene compound similar to FeNBD, Fe(CO)$_3$(η$^4$-cyclooctatetraene) (FeCOT), to isolate the static (solvatochromic) effects of the solvent. The key to this approach is that FeCOT does not
undergo carbonyl ligand site exchange on the vibrational timescale, due to its higher activation energy barrier, and so changes to its spectrum that occur when changing solvents can be ascribed solely to solvatochromism. Due to the structural similarities of these two iron compounds, we used FeCOT to follow the static effects induced by different solvent environments. By quantifying the amount of vibrational solvatochromism on the vibrational band shapes of FeCOT, we now have a standard probe of the static effects induced by different molecular environments on the carbonyl bands of FeNBD. The identification of such a standard allows for separation of static and dynamic effects in the molecular environment.

Combining the results from Chapters 2 and 3 together, I then moved toward the ultimate goal of quantifying the effect that the molecular environment has on the rate of carbonyl ligand site exchange in FeNBD. In Chapter 4, we examined the change in activation energy of FeNBD in a series of linear alkane solvents. We were able to use Kramers theory to describe the effect of solvent viscosity on the rate of carbonyl ligand site exchange of FeNBD, which is one of the first systems to use Kramers theory to analyze steady-state vibrational spectra. The results of this chapter also establish iron tricarbonyl systems as sensitive probes of local environment, and open the door for the probing of more complex systems, as will be outlined in the section on future work.

**Chemical Morphology**

The static effects of intramolecular and intermolecular interactions in conducting polymer films were investigated by analyzing the polymer morphology using Raman spectroscopy. Conducting polymer films are a popular material in thin film devices, due to their light weight, low cost, mechanical flexibility, and ease of fabrication. In Chapter 5, we began to develop structure-function relationships between thin film device performance and the morphology of the
conducting polymer films. We analyzed polymer films with and without dopants used in thin film transistors (TFTs) and organic photovoltaic (OPV) cells. All three of the projects covered in the chapter were done in collaboration with Elizabeth von Hauff’s laboratory at the University of Freiburg in Germany. For both the TFTs and the OPVs, we were able to correlate the morphological data obtained from the Raman spectra to device performance. For the first project, we demonstrated that incorporating SiO$_2$ NPs into the MDMO-PPV polymer matrix results in a more crystalline film, which causes an increase in the hole mobility across the channel of the transistor by one order of magnitude. In comparing the TFTs with SiO$_2$ NPs to the TFTs with PC$_{61}$BM, we were able to separate the pure morphological effect of SiO$_2$ from the convolution of morphological and electronic effects induced by PC$_{61}$BM.

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Overall, Raman spectroscopy is a great tool to gain insight into the changes in crystallinity of conducting polymer films. Chapter 5 showcased the ability of Raman spectroscopy to correlate morphological changes in the polymer film to thin film device performance. It is important to have a fundamental understanding of how dopants interact with
the polymer film and alter the charge mobility properties. By gaining this structure-function knowledge, we can begin to rationally tune the properties of conducting polymer films for their application in TFTs and OPV devices.

**Future Work**

*Investigations into Dynamic Effects.* A clear first step, moving forward from the results of my dissertation, would be to examine the impact of a larger range of solvents upon the dynamics of the FeNBD. While the effects of alkane solvents upon chemical dynamics have been well-studies, the impact of a wider range of solvents is relatively unknown. Thus, it is unclear exactly how solvent properties other than viscosity might couple into the solvent frictional effects. A reasonable first hypothesis is that the effects of viscosity are weighted by the strength of the interactions between the solvent and solute, and that this will be described by the empirical linear solvation energy relationship invoked in Chapter 3. Namely,

\[
XYZ = XYZ_0 + a\alpha + b\beta + s\pi^*
\]  

(6-1)

Here, XYZ would be the relative weight given to the viscosity of each solvent. Recall from Chapter 3 that \(\alpha\) is the hydrogen bonding acidity, \(\beta\) is the hydrogen bonding basicity, and \(\pi^*\) is the polarizability of the solvent.

Another environment of interest are confining environments built around solid-state structures, such as polymers, metal-organic frameworks, and zeolites. These environments are of interest due to their potential to physically restrict the dynamics of FeNBD, which should result in a large change in the dynamic exchange, which would be observed in the vibrational spectrum. Once again, temperature-dependent vibrational spectra would allow for separation of the effects of these environments in terms of the preexponential factor and activation energies. Combined with the solvent study above, we would be able to discuss the effects of these confining
environments in terms of a change in activation barrier – or (alternatively) in terms of an \textit{effective} viscosity. Making this connection between “normal” solvent environments and those found in solid materials will provide an empirical way of thinking about the behavior of molecules held within such materials.

To date, I have performed initial investigations into the effects of confining environments, focusing on the on the dynamics of chemical systems encapsulated into porous polymers. Polymers are particularly interesting as their plastic nature allows them to be distorted to a significant degree. These distortions however, will introduce stresses and strains that result in changes to the size or shape of the void spaces (pores) in the polymer matrix. These changes, in turn, are anticipated to result in changes to the dynamics of molecules held within the polymers. By investigating the impact of such distortions of the polymers, we will not only learn how these changes can be exploited to control chemical dynamics, but will (at the same time) develop a probe for understanding how the internal structure of these polymers changes during such distortions. This latter point is a major outstanding question in polymer physics.

As an initial step towards this goal, I incorporated \textbf{FeNBD} into the void spaces of polydimethylsiloxane (PDMS) by swelling the polymer in a toluene solution that contained \textbf{FeNBD}. Figure 6-1 shows the chemical structure of PDMS and the IR spectrum of \textbf{FeNBD} incorporated into PDMS as evidenced by the presence of the carbonyl ligands. There is a clear change in band shape and position of the carbonyl bands of \textbf{FeNBD} when the complex is incorporated into the void spaces of the polymer as compared to in pentane at room temperature. The next step will be to quantify the static and dynamic effects that the polymer matrix has on the carbonyl band shapes, which we should be able to elucidate using \textbf{FeCOT}. Initial attempts to incorporate \textbf{FeCOT} into the polymer’s void spaces by swelling with toluene did not incorporate sufficient amounts of \textbf{FeCOT} into the polymer and the carbonyl bands were too weak to observe. Once a proper concentration of \textbf{FeCOT} is incorporated into PDMS, we can use IR spectroscopy
to quantify the static effects of the polymer matrix on the carbonyl band shapes compared to the band shape in solution. We should be able to use this data to separate static from dynamic effects caused by PDMS on the dynamics of FeNBD. If the PDMS polymer matrix caused dynamic effects on the rate of carbonyl exchange, then the next step would be to see if we could alter the kinetics of FeNBD while inside of the polymer matrix.

An experiment that would be of interest to try would be to stress or strain the polymer while simultaneously taking vibrational spectroscopy. This would have to be done in collaboration with the Materials Research Institute to properly characterize the stress applied to the polymer and would involve the use of their IR microscope. This change in the molecular environment should affect the dynamics of FeNBD molecules in those void spaces, and our goal is to correlate changes in kinetics with changes in the molecular environment. A second experiment to try would be to acquire temperature-dependent Raman spectra to see if the temperature dependence inside the polymer is different from in solution. Determining the effect that the confining molecular environment of PDMS has on the dynamics of FeNBD will
contribute to the overarching goal of understanding intermolecular interactions. From here, the technique for characterizing the static and dynamic effects of the molecular environment using vibrational spectroscopy will have been developed, and this procedure could be applied to any chemical system that has picosecond dynamics in various molecular environments.

Investigations into Static Effects. There is also a number of experiment that can follow the work that was performed on molecular morphology in thin film devices. Chief amongst these is finishing up the project of the impact of doping OPV cells with Au NPs. This is a project that is still active with the von Hauff laboratory, and we have just sent a new batch of Au NPs to her laboratory for device fabrication. Following the successful fabrication of devices, the next step will be to correlate the impact of Au NP doping on cell performance to the morphology of the PTB7 polymer. Fortunately, I have already established the means by which to monitor changes in this film (Chapter 5), and so this analysis should proceed in a fairly facile manner.

In addition to the work on Au NPs, I also feel that is could be interesting to extend the work on the SiO$_2$ NPs by examining their effects on a wider range of films. The result that the morphological impacts of SiO$_2$ NPs were sufficient to increase hole mobility by an order of magnitude is striking. I would be interesting to see the extent to which this observation is general — and if SiO$_2$ NPs can function as a very inexpensive and easy way in which to improve device performance through control of film morphology. However, if this route is to be explored, it will require the continued collaboration with the von Hauff group, who will aid in the identification of polymers, and generation of the relevant devices.

Conclusions

The fundamental knowledge gained from my dissertation contributes to the need to understand the intermolecular and intramolecular interactions that occur in a given system, and
will provide the scientific community with a novel technique for extracting kinetic information from chemical systems in various molecular environments using steady-state vibrational spectroscopy. This technique can be applied to chemical systems that have kinetic processes on the picosecond timescale and that have potential applications in industrial processes or biological applications. This technique will allow scientists to have a better understanding of how the intermolecular interactions can affect the kinetics in the chemical system – an understanding that can only aid in the continuing improvement of humanity’s ability to control our own natural environment.
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