EXAMINING ELECTRON TRANSFER AND CHARGE TRANSPORT
IN ORGANIC PHOTOVOLTAIC MATERIALS

A Thesis in
Chemistry
by
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ABSTRACT

Energy consumption is extremely high and costly in the world today. The use of fossil fuels is climbing at a rapid rate; and with the demand so high, costs could skyrocket. Also, the use of more fossil fuels is leading to worldwide issues such as global warming. A change to more renewable energy resources is needed to eliminate emissions and potentially lower the cost of energy. Several options are available for substituting or even replacing fossil fuels. The most promising renewable resource is solar energy. Solar radiation hits the Earth around the clock and will not become depleted in the seeable future.

Current inorganic solar technology has been used for decades, but the cost of production is too high to replace current energy sources. A new and cheaper technology is emerging that has the potential to become cheaper than fossil fuels in terms of the amount of energy produced. This technology is known as organic photovoltaics (OPVs). These materials use electron donating polymers in conjunction with electron accepting materials (such as fullerenes). Current efficiencies of OPVs are drastically low in order to become implemented into energy collection methods. Improvement on solar energy harnessing and conversion to electrical energy is currently being examined to make these materials efficient enough to succeed in making solar energy a feasible substitute for an energy source.

Current issues of OPVs include charge carrier separation, degradation, charge carrier mobility and extraction. This study will focus on examining charge separation and mobility in OPV materials. Studies utilizing two-dimensional infrared (2D IR) spectroscopy were used to examine the local structure of PCBM molecules within the OPV bulk heterojunction (BHJ). In conjunction with SEM and FTIR studies, it was found that
the fullerene molecules tend to cluster together into roughly spherical domains surrounded by a layer of polymer. The addition of the polymer perturbs the fullerene molecules which allows for the measure of electron transfer from the polymer to the PCBM domains using Vis-IR spectroscopy. Vis-IR studies give a measure of the charge transfer process and allow for a kinetic study of charge transfer from optically mobile charge carriers. In conjunction with these kinetic studies, CELIV experiments began to measure electrically mobile charge carriers. All together, these experiments allow for the understanding of rates of the charge transfer process as a function of morphology of the OPV samples.
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<tr>
<td>2D IR</td>
<td>Two-Dimensional Infrared</td>
</tr>
<tr>
<td>A/D</td>
<td>Analog to Digital</td>
</tr>
<tr>
<td>BHJ</td>
<td>Bulk Heterojunction</td>
</tr>
<tr>
<td>CaF₂</td>
<td>Calcium Fluoride</td>
</tr>
<tr>
<td>CELIV</td>
<td>Charge carrier Extraction using Linearly Increasing Voltage</td>
</tr>
<tr>
<td>CN-MEH-PPV</td>
<td>Poly[2-Methoxy-5-(2'-ethylhexyloxy)-1,4-(1-cyanovinylene)phenylene]</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon Dioxide</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared</td>
</tr>
<tr>
<td>FTO</td>
<td>Fluorine doped Tin Oxide</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
</tr>
<tr>
<td>H₂O</td>
<td>Water</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>MDMO-PPV</td>
<td>Poly[2-methoxy-5-(3’,7’-dimethyloctyloxy)-1,4-phenylenevinylene]</td>
</tr>
<tr>
<td>Nd³⁺-YAG</td>
<td>Neodymium³⁺ Yttrium Aluminum Garnet</td>
</tr>
<tr>
<td>OPA</td>
<td>Optical Parametric Amplifier</td>
</tr>
<tr>
<td>OPV</td>
<td>Organic Photovoltaic</td>
</tr>
<tr>
<td>PCBDM</td>
<td>{6}-1-(3-(methoxycarbonyl)propyl)-{5}-1-phenyl-[6,6]-C61</td>
</tr>
<tr>
<td>PV</td>
<td>Photovoltaic</td>
</tr>
<tr>
<td>RR-P3DT</td>
<td>Regio-Regular poly(3-decyl-thiophene-2,5-diyl)</td>
</tr>
<tr>
<td>RR-P3HT</td>
<td>Regio-Regular poly(3-hexyl-thiophene-2,5-diyl)</td>
</tr>
<tr>
<td>RRa-P3DT</td>
<td>Regio-Random poly(3-decyl-thiophene-2,5-diyl)</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>TCSPC</td>
<td>Time Correlated Single Photon Counting</td>
</tr>
<tr>
<td>Vis-IR</td>
<td>Visible pump – Infrared probe</td>
</tr>
</tbody>
</table>
In loving memory of

Gene L. and Gladys R. Bush
Chapter 1

INTRODUCTION

1.1 Energy Market and Global Warming

In today’s world, energy is becoming very dependent on fossil fuels, which is a resource that will eventually run out.\textsuperscript{1,2} A change to a renewable energy resource is necessary in order to ultimately allow the world to have a source of clean energy.\textsuperscript{1} Current estimates show that petroleum could only last up to 50 years;\textsuperscript{3,4} natural gas supplies could also run dry within 25 - 75 years.\textsuperscript{1,3} By implementing renewable energy sources, such as wind, hydroelectric, and/or solar, we can get away from our dependency on fossil fuels. Current renewable technologies are being implemented at a slow rate and currently cannot match the energy output of fossil fuels.\textsuperscript{1,5,6}

Another worldwide issue coming to light is global warming. It is believed that the increase in green house gas (such as CO$_2$) emissions is a major contributor to warming of the planet.\textsuperscript{1,4,7} These emissions are a direct result of burning fossil fuels. There has been a steady rise in CO$_2$ emissions since the start of the industrial revolution, and increasing emissions since the early to mid 1800’s.\textsuperscript{3,4} If emissions continue to increase, it is possible that the planet could warm to an unstable level and unforeseen consequences could occur.\textsuperscript{7} Given that fossil fuels are a direct source of energy, if we wish to cut back on emissions, then we must find an alternative source of energy that will, at a minimum, equal the energy output of fossil fuels.
Solar energy seems to be one of the best solutions to solving the energy issue currently at hand.\textsuperscript{1, 4, 8} If the solar radiation hitting the earth everyday could be harnessed and converted into electrical energy, the demand for fossil fuels should decrease dramatically. Current inorganic (silicon) based photovoltaics (PVs) are not cheap enough to replace current fossil fuels.\textsuperscript{9} A newer breed of PVs is currently emerging and show promise of cheaper solar energy per watt of electrical energy generated. Organic photovoltaics (OPVs) have shown improved efficiencies based on a bulk heterojunction (BHJ) solar cell.\textsuperscript{10−13} Recent efficiencies of OPV devices have reached up to five percent; and with the cost of materials, these devices show promise to be the front runner for capturing solar energy and converting it into electricity at a cheaper cost of production than current solar technologies.\textsuperscript{8, 13−15}

1.2 History of Organic Photovoltaic Devices

Initial observations on PV devices using organic materials occurred in 1959, when a current was run through a single crystal of anthracene placed between electrodes and illuminated.\textsuperscript{10−11} It was not until the late 1980’s that developments in the field of OPVs began to take off.\textsuperscript{8, 10−11} During this time, it was found that OPVs do not operate in a similar fashion to the inorganic counterparts. Within traditional PVs, charge carriers are generated within the bulk of the material, whereas with OPVs, these carriers are strongly bound to each other, typically called an exciton.\textsuperscript{16} These bound charges can only separate at an interface between electron and hole transporting materials. This was known as a heterojunction device, where two materials were layered and sandwiched between electrodes.\textsuperscript{11} Early efficiencies (~1%) of these OPVs were very low, which lead to the
development of the bulk heterojunction in the early 1990’s.\textsuperscript{8,11} In this concept, both the donating and accepting materials were combined together in a single layer and sandwiched between electrodes. Efficiencies were improved, but continued to be lower than expected. Recent efficiencies have been reported up to 5.8\%.\textsuperscript{11}

1.3 Current Limitations of OPVs

One major contributor to low efficiencies is charge carrier separation.\textsuperscript{15} In order for OPVs to operate properly, the charge carriers must be separated efficiently and quickly. Unlike inorganic devices, there is a large potential barrier that the exciton must surpass before the charges can separate.\textsuperscript{12,17} The barrier at interfaces between the donor and acceptor is low enough for the charges to effectively separate. After excitation, the exciton has a limited amount of time before it relaxes back to the ground state. During this time, the exciton must diffuse through the polymer layer to an interface with the electron accepting material. For this to occur before relaxation, the polymer layer must be thin enough (5 – 10 nm).\textsuperscript{18–19}

Another major issue holding back OPVs is charge carrier mobility.\textsuperscript{20} For PVs to work efficiently, charges must be extracted quickly. In other words, for efficient charge carrier extraction in thick OPV solar cells, the mobility of the charge carriers must be high for the charge carriers to traverse the BHJ region. The thicknesses of the films are generally determined by the absorption of the incident photons, and vary for different polymers. For thicker devices, the charges must have a higher mobility to traverse the BHJ to the electrodes.
Degradation of the materials is another problem that occurs in these devices. Many polymers with vinylene bonds will rapidly degrade in the presence of oxygen and light. Since these devices use light to operate, oxygen must be kept clear of the polymer layer. Encapsulation of the solar cells has shown promise to prevent degradation from oxygen, but there are other factors that contribute to degrading of the device. Electrodes can prove to be major sites of degradation during production of the cells. Metal electrodes can degrade the polymer at contact sites. Water is a major contributor to degradation as well in the polymer layer.

Charge recombination is another concern for OPV devices. Charges can recombine readily after charge separation. If the charge mobility is low, holes and electrons can recombine soon after separation. Recombination of the electron and hole that come from the same exciton is known as geminate recombination. Charges can also recombine if the charge carriers do not have a direct path to their respective electrode.

The last major issue with OPVs is charge trapping. After the exciton dissociates into electron and hole, the charge carriers may become trapped enroute to an electrode. If charges become trapped, they can no longer reach an electrode, and the device will not work efficiently. A major trapping site of charge carriers is photo-degraded areas of the polymer. Trapping of charge carriers will also decrease the overall charge mobility due to restricting some charges from moving.

1.4 Charge Transfer Dynamics

My contribution to the study of OPVs is looking at ultrafast charge transfer dynamics. These dynamics occur on the picosecond (ps) timescale. Vis-IR spectroscopy
can be used as a way to watch electrons transfer from donor to acceptor. As electrons are transferred from the electron donor to electron acceptor, we see a vibrational signature (called a bleach) grow in the Vis-IR data that is representative of a change in the neutral ground state of the electron acceptor. That is, as electrons transfer, the bleach that grows in is proportional to the concentration of electrons that are transferred. Over the course of hundreds of fs to a few ns, we can watch the change in the bleach and model it precisely to measure dynamics of the electron transfer in OPV thin films.

In combination with Vis-IR spectroscopy, 2D-IR studies were completed to show the local environments that the PCBM molecules reside. Using this method, in conjunction with linear FTIR studies and SEM studies (both in collaboration with Maureen Hegadorn), we can compare the morphology of the films to how electrons are transferred across the interface between PCBM and the polymer. The shifting of the bleach in the Vis-IR spectra, representing the carbonyl stretch in PCBM, is understood by this comparison of techniques. Other studies involve studying the temperature dependence of the carbonyl vibrational mode of PCBM as well as anisotropy spectra to study the vibrational relaxation dynamics of the PCBM molecules in the OPV thin film mixtures. These studies were all done in conjunction with each other to support the interpretations of the Vis-IR data.
Chapter 2

Experimental Techniques

2.1 2D-IR and Vis-IR Spectroscopies

These experiments used an ultrafast Ti:sapphire laser producing 800 nm light that was used to pump two optical parametric amplifiers (OPA). One OPA generated mid-infrared pulses at 5.8 μm at 1 kHz with 6 μJ/pulse and 100 fs duration. The IR pulses were split into two beams for the pump and probe pulses. The IR probe and pump pulses were characterized to be 200 and 250 μm in diameter with energies of 0.1 μJ and 3 μJ at the sample, respectively. The pump beam was passed through a Fabry-Perot interferometer (etalon) to create a continuously adjustable pump spectrum with a full width at half maximum of ~5 cm⁻¹ that was stabilized to within ±1 cm⁻¹. Occasionally during a 2D IR experiment, a mechanically controlled translation stage moves a mirror to block the probe beam and direct the pump beam into the spectrograph to measure the frequency of the beam and correct for any spectral drift from the etalon. Polarization resolved IR pump–probe studies were carried out by collecting the probe beam with parallel and perpendicular polarizations relative to the pump beam. An optical rotator is used to hold and rotate the polarizer each scan to the respective polarization. The probe beam is separated into probe and reference beams which are directed into a 64-element dual mercury cadmium telluride array detector. The detector is used to capture 32 simultaneous frequencies of each beam through a spectrograph while facilitating single shot normalization. The second OPA was
used to produce the optical excitation pulse that is continuously tunable throughout the visible spectrum with 100 fs pulse duration. This beam is passed through a quadruple pass 0.6 m translation stage that is used to control the time delay of the visible pump pulse out to 5 ns. The visible pump pulses were characterized to be 250 µm in diameter with pulse energy of 1.0 µJ at the sample. The excitation beam used for the Vis-IR experiments was 550 nm light. Automated raster scanning was feasible on the OPV samples via mounting them on a stage movable in orthogonal directions. This was done to ensure that a fresh sample area was examined for each data point collected. The samples were deposited on both CaF$_2$ windows and silver mirrors. Linear FTIR spectra for OPV samples on each substrate were identical in comparison. Upon excitation of the OPV material deposited on the silver mirror with visible light, a change in the refractive index of the material is induced. This change in refractive index alters the surface reflection of the sample. This transformation in reflectivity creates problems in the Vis-IR experiment, and samples are deposited on CaF$_2$ windows to avoid these complications. The optical density of the OPV sample at 550 nm is ~2 and around 1% of the pump photons transmit through the CaF$_2$ window. Therefore a nonresonant signal is not observed in the Vis-IR experiment. This is not the case in the 2D IR experiments. Nonresonant signals are present in samples deposited on CaF$_2$ windows, therefore OPV samples are deposited on silver mirrors for these experiments. The silver mirror reflects the IR beams so that the beams do not encounter window materials in the overlap region. This routine also aids in the examination of OPV cells that require one metallic electrode. The entire beam path and sample area were encompassed by a dry air purged enclosure to remove ambient H$_2$O and CO$_2$. All experiments were conducted at room temperature. A schematic of the ultrafast
laser system, where the 2D IR and Vis-IR experiments are completed, can be seen in figure 1.

![Figure 1: Schematic of ultrafast laser setup used for 2D IR and Vis-IR spectroscopies.](image)

### 2.2 CELIV

The CELIV (Charge carrier Extraction by Linearly Increasing Voltage) technique measures charge carriers that are electrically mobile, or measures charges that are forced to move towards their respective electrode with a voltage ramp bias. The OPV samples were excited with 532 nm pulsed light from a Nd$^{3+}$-YAG laser customized to operate at a repetition rate of 50 Hz. The pulse energy was ~1 mJ with a spot size of 2 cm$^2$ at the sample. Measurements were made by sampling 1000 scans with and without light by measuring current through the sample cell with a 350 MHz oscilloscope. The saw-tooth voltage ramp was applied with a homemade wave generator; generating a six-volt ramp, with a one volt negative bias, over a 450 µs timeframe. The delay between light pulses and onset of the saw-tooth voltage bias was set by a Digital Delay Generator that was externally triggered off the Nd$^{3+}$-YAG laser pulses. Time delays from 1 µs to 18 ms were
used to measure charge carrier extraction with this setup. The lower limit of the time scale is constrained by the speed of the A/D board, while the upper limit is limited by the timing between laser pulses. All experiments were conducted at room temperature. The setup is schematically shown in Figure 2.

**Figure 2:** Schematic of CELIV experimental setup.

### 2.3 Sample Preparation

OPV samples for 2D IR and Vis-IR were prepared by spin casting solutions of polymer and fullerene mixtures onto CaF$_2$ windows and silver mirrors, respectively. Solutions were composed of various polymers with fullerene derivative PCBM (American Dye Source). Polymers included CN-MEH-PPV (H.W. Sands), RR-P3DT (American Dye Source), RRA-P3DT (American Dye Source), MEH-PPV (Sigma Aldrich), MDMO-PPV (Sigma Aldrich), RR-P3HT (Rieke Metals). Structures of the materials can be found in Figure 3. These solutions had various compositions depending on polymer. Generally a 1:1 by weight ratio of polymer to PCBM was used for experimentation. For RR-P3DT and RR-P3HT samples, a 2:1 and 4:1 (polymer to PCBM) mass ratio was used respectively. For samples prepared with MDMO-PPV, a 1:4 mass ratio was used. These ratios were used to compliment work that is currently being done with OPVs.$^{12-13,24}$
Solutions were prepared by dissolving the solids in chlorobenzene (Sigma Aldrich) or toluene (Sigma Aldrich) depending on the solubility of the polymer (PCBM is soluble in both). Solutions were made to a 1.0% mass ratio of solute; for example, the 1:1 mixtures would be composed of 0.50% PCBM and 0.50% polymer. Solutions were then deposited on the appropriate substrate and spun at a rate of 80 RPM until the solvent fully evaporated away. Film thicknesses were generally on the order of five to ten microns. All films were then tested using FTIR to see the strength of the carbonyl (C=O) stretching mode of the PCBM molecule.

Samples prepared for CELIV were depositing in a similar fashion. The substrate for these samples was FTO (Fluorine doped Tin Oxide) coated glass. FTO coated glass is used as a transparent electrode. Samples were spun at a rate of 15 RPM to ensure uniformity of the film. Samples thicknesses were on the order of one micron. FTIR studies could not be conducted on these samples because IR light is absorbed by the glass and FTO layer. Samples were then coated with a 50 nm thick layer of aluminum via electron beam deposition. This metal layer acts as the second electrode to complete the circuit of the solar cell. A diagram of the cell can be seen in figure 4.

Figure 3: Structures of materials used to make OPV samples.
Figure 4: Side and top view of a sample OPV cell used for CELIV studies. A portion of FTO coated glass was not coated for use as an electrode.
Chapter 3

Examining Local Environments and Morphology

3.1 2D IR Studies of CN-MEH-PPV:PCBM Mixtures

Initial studies on the BHJ devices were to probe the local structure of the materials. The 2D IR technique is sensitive to the molecular order of materials by probing their native vibrational modes. Studies on the OPV mixtures were conducted on the carbonyl stretching mode (C=O) of PCBM. Inspection of the inhomogeneously broadened line shapes can provide information that is not available with linear IR. Figure 5A shows 2D IR spectra of the C=O stretch at two $T_w$ delay times, where $T_w$ refers to the time delay between the pump and probe pulses.

![Figure 5](image.png)

Figure 5: A) 2D IR spectra of carbonyl stretch of PCBM measured at 1,3 and 10 ps. B) One dimensional slices of the 2D IR spectra along the pump frequency axis at probe frequency of 1740 cm$^{-1}$. The linear FTIR is shown for comparison.

These spectra contain two frequency axes, where the vertical axis, $\omega_p$, corresponds to the probe beam that is dispersed onto spectrograph. The horizontal axis, $\omega_{pr}$, corresponds to the frequency of the pump pulse where the spectrum was recorded for the probe. The
diagonals of the spectra represent where the pump and probe frequencies are equal and are represented by the dashed lines. The ground to first excited state (0 – 1) transition occurs on the diagonals, and the 1 – 2 transition is seen offset from the diagonal on the probe axis due to vibrational anharmonicity. These vibrational transitions are diagramed in figure 6 for clarity. The vibrational anharmonicity of these samples is given by the differences in the peaks of each transition and is ~18 cm\(^{-1}\) for this sample.

![Figure 6: Pictorial view of the vibrational transitions seen in 2D IR spectra. The transitions shown are ground to first excited (red) state and first to second excited (blue) states.](image)

One-dimensional (1D) slices of the 2D IR plots are shown in Figure 5B to show the time dependence of the line shapes. The 1D slices are taken from the probe frequency axis equal to 1740 cm\(^{-1}\) along the pump axis and plotted as a function of their absorbance. The slices are taken from each of the 2D IR spectra shown corresponding to their respective time delay and compared with a linear FTIR spectrum of the sample. The 1D horizontal slices were fit with a Gaussian function to yield 6.9, 6.5 and 7.0 cm\(^{-1}\) full width half-maximum for the 1, 3 and 10 ps spectra, respectively. A comparison of these slices can be made with the linear IR of the carbonyl stretch which has a FWHM of 16.7 cm\(^{-1}\). Since the linear spectrum gives an equilibrium distribution of all environments that the PCBM molecules reside within, then it is possible that the distribution could be a result of spectral diffusion of the PCBM molecules. Spectral diffusion is defined as the changing of a
vibrational mode over time due to the diffusion of a molecule through multiple environments. It was found that spectral diffusion does not occur on the 10 ps timescale since the 1D time slices from the 2D spectra do not broaden with increasing time delay. Additional experiments have been completed to verify this result, and will be presented in the following sections.

3.2 Measuring Orientational Dynamics of the Carbonyl Mode

Studies were completed on the 1:1 OPV mixture of CN-MEH-PPV and PCBM to examine the movement of PCBM molecules within the OPV thin films. Dispersive IR pump probe experiments were done by measuring the probe beam parallel and perpendicular to the pump beam to collect vibrational relaxation and orientational dynamics. Figure 7 shows kinetic traces of the carbonyl stretch at 1740 cm\(^{-1}\) at parallel and perpendicular polarizations of the probe beam (\(S_{\text{par}}\) and \(S_{\text{perp}}\), respectively).

\[
P(t_w) = \frac{1}{3} \left[ S_{\text{par}}(t_w) + 2S_{\text{perp}}(t_w) \right].
\]

(1)

where \(t_w\) is the time delay between pump and probe beams. This method was borrowed from others currently doing similar studies.\(^{25}\) These dynamics can also be seen in figure 7.

![Figure 7](image-url)
with the polarization resolved data. Closer inspection of the population kinetics data shows a multi-exponential decay, or in other words, decays with fast and slow time scales. Fitting the population decay trace, it was found that time constants of 0.4 and 2.0 ps fit best, of which each contribute 36 and 64% of the data, respectively. These times can be used to help confirm the time that the vibrations of the carbonyl stretching mode last in the excited state. In other words, these times show relaxation times of the excited state of the C=O stretching mode of PCBM.

Also from the polarization resolved data, anisotropy could be calculated. The anisotropy, \( r(t_w) \), is given by

\[
\begin{align*}
    r(t_w) &= \frac{S_{\text{par}}(t_w) - S_{\text{perp}}(t_w)}{S_{\text{par}}(t_w) + 2S_{\text{perp}}(t_w)},
\end{align*}
\]  

(2)

Again, \( S_{\text{par}} \) and \( S_{\text{perp}} \) are the signals of the polarizations of the probe been seen is figure 7. The anisotropy decay can bee seen in figure 8.

![Figure 8: Anisotropy decay measured at 1740 cm\(^{-1}\) indicating orientational motion of the carbonyl bond of PCBM molecules. Shown in red is the fit function for the anisotropy.](image)

From the orientational anisotropy data, it can be seen that orientational relaxation occurs on two timescales, a fast and slow component. It should also be noted, that the maximum value of the anisotropy (at \( t_w=0 \)) is 0.34, below the ideal of 0.40. Since the anisotropy maximum occurs below this ideal value, it is indicative that the carbonyl orientational motion occurs of multiple timescales. This decrease from the ideal value is due to competition between the excitation and the orientational relaxation. The data was fit with a
multiexponential function to yield a fast component or the orientational relaxation
dynamics of 110 fs and a slower factor of 22 ps. The fast portion of the orientational
kinetics was assigned to be related to wobbling in the cone motion. This motion does
not occur over the entire fullerene molecule, but only the butyric methyl ester group
attached to the C_{60}. In other words, this group could be considered a tether attached to ball
that is free to move in its environment and can process about the attachment point in the
shape of a cone. The cone angle was approximated by fitting an orientational correlation
function to the anisotropy data and found to be 29°. The slower, 22 ps motion was
assigned to be rotational motion of the PCBM molecules. Orientational dynamical studies
of C_{60} in solid matrices revealed that the molecules undergo motion on the 10 ps timescale.
It is believed that the PCBM molecules rotate slower due to the butyric methyl ester
group constraining the molecule in place.

3.3 FTIR Study of Carbonyl Shift

In collaboration with Maureen Hegadorn, a study was done to see how the
vibrational frequency of the carbonyl stretch of PCBM varies in different mixtures with
CN-MEH-PPV. Figure 9 shows a comparison of various compositions of the OPV blend.

![Figure 9: Comparison of FTIR spectra of various compositions of the OPV mixture. These spectra show the frequency shift as a function of PPV content.](image-url)
The linear IR spectrum labeled PCBM shows the carbonyl stretching frequency at 1735 cm\(^{-1}\). With the addition of a small amount of polymer (0.03:1 mass ratio), there is a frequency shift to 1738 cm\(^{-1}\). Just the addition of a minute amount of polymer greatly shifts the frequency of the carbonyl stretch of PCBM. The 1:1 mass ratio mixture gives a signature frequency at 1740 cm\(^{-1}\). A linear spectrum of pure CN-MEH-PPV (labeled PPV) at this frequency is also shown to demonstrate that the carbonyl shift is not a direct result of vibrational signatures from the polymer. This shift towards higher frequency seen in the linear spectra will help to explain a phenomenon seen in Vis-IR studies to be discussed in the next chapter. The addition of polymer perturbs the carbonyl stretch of PCBM molecules near the interface between polymer and PCBM domains. This perturbation is a direct result from the addition of polymer, as seen in the linear spectra in figure 9.

### 3.4 Morphology Studies Using SEM

In collaboration with Maureen Hegadorn, a study was conducted to examine the morphology of the OPV thin films. Several films were investigated to see how the morphology of the OPV films change as a function of weight ratios of the components, PCBM and CN-MEH-PPV. Variations in morphology can have a major effect on the charge transfer dynamics within OPV devices. Comparison of the morphology with charge transfer dynamics (using Vis-IR studies) will give information about which morphology is ideal. Figure 10 compares two SEM micrographs of a 1:0.3 mixture (figure 10A) and 1:1 mixture (figure 10B) of CN-MEH-PPV: PCBM. From these two micrographs, it can be seen that spherical domains of PCBM (light color) form surrounded by a layer of polymer (dark color). The difference between the two is that
the film with more PCBM has larger domains. Domain sizes were determined to be 15 – 20 nm for the 1:0.3 mixture and up to 50 nm in the 1:1 mixture. Although the size of the domains grows slightly with the addition of more PCBM, it can be seen that the spacing between the PCBM domains decreases.

Figure 10: SEM images of A) 1:0.3 weight ratio of CN-MEH-PPV:PCBM and B) 1:1 weight ratio. The comparison is made to show that as the weight ratio of PCBM increases, the domain size of PCBM increases. PCBM domains are seen as the light colored areas. This work was done in collaboration with Maureen Hegadorn.
Chapter 4

Charge Transfer Dynamics Using Vis-IR Spectroscopy

4.1 Vis-IR on OPV Thin Films

Information about the environments of the fullerene domains that are mainly involved in charge transfer can be observed with Vis-IR spectroscopy. Initial studies of the OPV mixtures were done with an ultrafast 400 nm optical pulse. There is an excited state of the polymer that results in a broad absorption in the mid-IR region. This absorption gives rise to a time dependent offset in the Vis-IR data seen in figure 11A.

Figure 11: A) Vis-IR time slices of 0 to 1 ns excited state transition of C=O stretch of PCBM in 1:1 OPV mixture. B) 2D IR spectrum of all PCBM molecules in a similar sample. The dotted vertical line represents the equilibrium peak of 1740 cm⁻¹. The dashed line represents the center frequency of bleach in the Vis-IR spectra as a function of time.
Also seen in figure 11A is a bleach resulting from the change in the neutral ground state of the PCBM molecules. This change is an increased transmission of the 0 to 1 transition of the carbonyl stretch. It can be seen overlaid with the broad absorption. The horizontal dotted line in the 2 ps spectrum shows the bleach explicitly.

Looking closer at the bleach in the Vis-IR spectra, it can be seen that over time there is a shift from \(~1747\) cm\(^{-1}\) at early times towards \(1740\) cm\(^{-1}\) (the equilibrium center frequency). Comparison of the bleach with a 2D IR (shown in figure 11B), it is believed that not all PCBM molecules take part in charge transfer because the bleach is localized to higher frequencies. Dotted and dashed vertical lines were added to the spectra to show the center frequency and the bleach center frequencies, respectively. Since initial charge transfer occurs at early times, PCBM molecules near the interface will accept the electrons. As shown from earlier studies discussed (Chapter 3), the addition of polymer perturbed the carbonyl mode of PCBM molecules closer to the interface shifting the linear FTIR spectrum of the OPV blend towards higher frequency.

Initial Vis-IR studies were completed using an optical pump of 400 nm, but it was found that a large absorption, \(~33\)% of the pump photons was coming from PCBM molecules. This is found by considering the number of photons absorbed by the polymer and PCBM molecules. At an excitation wavelength of 400 nm the total optical absorption of the OPV films is \(~4\) and the PCBM component of the absorption is \(~1\). If the film is divided into 1000 layers approximately 3 nm thick (for a 3 \(\mu\)m thick film), then it can be assumed that the flux of photons is equal throughout each layer the optical pulses pass. The transmission of the light can be calculated through each layer and the number of photons absorbed is found. Using 550 nm excitation pulses reduces the percentage of
photons absorbed by PCBM molecules from 33% (400 nm) to 10%. Since PCBM molecules were being excited, it may not provide an accurate account of charge transfer. To primarily excite the polymer, it was found via UV-Vis experiments (collaboration with Maureen Hegadorn) that PCBM absorbs at a local minimum at 550 nm, whereas the polymer absorbs light on a rising edge. Vis-IR experiments were repeated on the 1:1 OPV mixture on CN-MEH-PPV and PCBM using 550 nm optical pump pulses. Figure 12A shows a few select time slices from the Vis-IR experiments. The spectra appear to be similar to the experiments with an optical pump of 400 nm, but excitation of the PCBM molecules has been minimized with the 550 nm pump pulses. Overlaid on the data are fit functions that will be explained in the next section. Figure 12B shows a 2D surface plot of the bleach. This plot was created from the fit functions of the bleach in each time slice and will also be explained in the following section.

**Figure 12:** A) Comparison of Vis-IR time slices of 1:1 OPV mixture. The data is overlaid with 3rd order polynomial fit (baseline) and bleach fit (baseline and Gaussian line shapes). B) 2D surface plot of the carbonyl bleach spectrum versus time delay.

### 4.2 Fitting, Extracting and Characterizing the Bleach

The bleach data from the Vis-IR spectra were modeled using a least squares fitting routine. The broad absorption offset was modeled using a 3rd order polynomial, while the
bleach was modeled with a Gaussian line shape. A single Gaussian and polynomial was fit for each time slice from the Vis-IR data. The fitting procedure started with the 50 fs time slice due to the fact that no bleach was available to fit before this time point. The sum of the polynomial and Gaussian functions are shown overlaid on the data in figure 12A. The line below the bleach in this figure is the fit function of the broad absorption only. Figure 12B shows the Gaussian fit functions for each time slice as a function of time. The dashed line shows the peak, or center frequency, of the Gaussian line shape. This is used as a guide to see how the bleach shifts as a function of time. Also shown in figure 12B is a dotted line that shows the equilibrium center frequency of 1740 cm\(^{-1}\).

The charge transfer dynamics were obtained by integrating the carbonyl bleach to obtain their area at each delay time in the experiment. Since the bleach was characterized by the Gaussian line shapes, the integration over the Gaussian line shapes for each time point was completed to yield what is seen in figure 13A.

![Figure 13](image)

**Figure 13**: A) Bleach area versus corresponding time delay plotted on a logarithmic scale. The three distinct features are labeled as detailed in the writing. B) Kinetic model of charge transfer in OPV samples. The three processes described in A) are shown here.

The bleach area versus time plot is shown on a logarithmic scale for viewing purposes and a best fit for the data is shown in red. There are three distinct regions illustrated on the
curve corresponding to three processes assigned to charge transfer: 1) fast charge transfer, 2) charge recombination and 3) excitation diffusion. These three processes are illustrated in figure 13B (a simplistic version of a kinetic model of the charge transfer process).

Process 1 (the fast rise of the bleach area) corresponds to initial charge transfer from excitations that form in areas of the polymer that are near interfaces with a PCBM domain. The process occurs on the approximately 100 fs to one ps time scales. This bleach area peaks around five ps and then decays on the tens of ps time scale. Since the bleach area is proportional to the concentration of electrons transferred to PCBM, this process corresponds to charge recombination (or back electron transfer) from the PCBM domains to the polymer (process 2). The second rise in the bleach area occurs between 100 ps and a few ns and is assigned to be from charge transfer that occurs after excitations diffuse through the bulk polymer layer to an interface with PCBM. SEM images reveal that polymer layers between PCBM domains can reach up to tens of nm in thickness. Since excitations do not only occur at interfaces, those in the bulk must diffuse through the polymer. Also, the probability that an excitation can transfer an electron to PCBM domains is very distance dependent. Therefore, excitations forming in the bulk regions of the polymer must diffuse to an interface before charge transfer can occur (process 3).

### 4.3 Modeling Charge Transfer Dynamics

It was stated previously that the bleach area is proportional to the concentration of electrons that transfer from the polymer to the fullerene domains. Figure 8A shows the bleach area versus time plotted on a logarithmic scale. The three processes labeled are
assigned to 1) fast charge transfer, 2) charge recombination and 3) exciton diffusion and charge transfer. The processes are detailed in pictorial form in figure 13B. A detailed kinetic model was developed to model these processes and is composed of three coupled differential equations.

\[
\frac{dN_e(t)}{dt} = k_f N^*_\text{INT}(t) - k_b N_e(t) \tag{3}
\]

\[
\frac{dN^*_\text{INT}(t)}{dt} = k_d N^*_\text{BULK}(t) - (k_f + k_r) N^*_\text{INT}(t) \tag{4}
\]

\[
\frac{dN^*_\text{BULK}(t)}{dt} = -(k_d + k_r) N^*_\text{BULK}(t) \tag{5}
\]

Referring to figure 8B, the terms \(N_e(t), N^*_\text{INT}(t)\) and \(N^*_\text{BULK}(t)\) represent the density of electrons transferred to PCBM domains, the density of excitations in the interfacial polymer (PPV\(_\text{INT}\)) and the density of excitations in the bulk polymer (PPV\(_\text{BULK}\)), respectively. The rate constants \(k_f, k_b, k_d\) and \(k_r\) refer to the rates of forward charge transfer to PCBM, back charge transfer to PPV, diffusion of excitations to the interfaces and the relaxation of excitations within the polymer, respectively. It is assumed that the relaxation of excitations is the same at the interfaces as in the bulk polymer.

Breaking apart these equations to further understand them, the density of electrons transferred to PCBM, \(N_e(t)\), is determined by the rate of forward charge transfer from the polymer to PCBM, \(k_f N^*_\text{INT}(t)\), and the rate at which charges recombine, \(k_b N_e(t)\). The density of excitations at the interfaces between polymer and PCBM, \(N^*_\text{INT}(t)\), is controlled by the rates of forward charge transfer, \(k_f N^*_\text{INT}(t)\), diffusion of excitations towards the interfaces, \(k_d N^*_\text{BULK}(t)\), and relaxation of the excitations (or the excitations that relax before reaching an interface), \(k_r N^*_\text{INT}(t)\). The density of excitations in the bulk of the polymer, \(N^*_\text{BULK}(t)\), is
determined by the rates of diffusion of excitations toward the interfaces, $k_d N_{BLK}^*(t)$, and relaxation of the excitations, $k_r N_{BULK}^*(t)$. It was assumed that forward charge transfer rate is fast in comparison to the rate of diffusion of excitations. Therefore a term for excitations diffusing away from the interfaces has not been included since the charges will separate once reaching an interface. The solutions to the set the coupled differential equations above are:

\begin{equation}
N_e(t) = C_1 \exp[-k_b t] - C_2 \left( \exp[-(k_f + k_r) t] - \exp[-k_b t] \right) - C_3 \left( (k_d - k_f) \exp[-k_b t] + (k_f - k_b + k_r) \exp[-(k_d + k_r) t] + (k_b - k_d - k_r) \exp[-(k_f + k_r) t] \right) \tag{6}
\end{equation}

\begin{equation}
N_{INT}^*(t) = C_2 \exp[-(k_f + k_r) t] - C_3 \left( \frac{k_d}{k_f - k_d} \right) \left( \exp[-(k_f + k_r) t] - \exp[-(k_d + k_r) t] \right) \tag{7}
\end{equation}

\begin{equation}
N_{BLK}^*(t) = C_3 \exp[-(k_d + k_r) t] \tag{8}
\end{equation}

For modeling purposes, equation 6 represents the density of electrons that have transferred from the polymer to the PCBM domains. Therefore, this equation will be the discussed further on modeling charge transfer dynamics in OPV thin film mixtures.

Many dynamic processes in these types of systems are not best described by a single exponential process.\textsuperscript{34} In order to describe the dynamics best for the OPV samples, bi-exponential functions were used to replace the single exponentials from equation 6. These functions included in the model are for the forward transfer, recombination and relaxation processes in equation 6. The substitutions are as follows:

\begin{equation}
\exp[-k_f t] = a \exp[-k_{f1} t] + (1 - a) \exp[-k_{f2} t] \tag{9}
\end{equation}

\begin{equation}
\exp[-k_b t] = b \exp[-k_{b1} t] + (1 - b) \exp[-k_{b2} t] \tag{10}
\end{equation}

\begin{equation}
\exp[-k_r t] = c \exp[-k_{r1} t] + (1 - c) \exp[-k_{r2} t] \tag{11}
\end{equation}
The diffusion of excitations through the polymer layer will not include a bi-exponential function because it is assumed that the diffusion process occurs on one time scale.

Substituting these equations equation 6 and reorganizing the terms to make the equation simpler yields

$$N_c(t) = A(B(\beta(t) - \phi(t)) + (1 - B)[(k_d - C_f)\beta(t) + (C_f - C_b + C_r)\delta(t) + (C_b - k_d - C_r)\phi(t)]]}$$  \hfill (12)

Equation 12 will be the serve as the model of the bleach area kinetics, where the bi-exponentials are as follows:

$$\beta(t) = b\exp[-k_b t] + (1 - b)\exp[-k_b t] \hfill (13)$$

$$\delta(t) = c\exp[-(k_d + k_r) t] + (1 - c)\exp[-(k_d + k_r) t] \hfill (14)$$

$$\phi(t) = ac\exp[-(k_f^1 + k_r) t] + (1 - a)c\exp[-(k_f^2 + k_r) t] +$$

$$a(1 - c)\exp[-(k_f^1 + k_r) t] + (1 - a)(1 - c)\exp[-(k_f^2 + k_r) t] \hfill (15)$$

Since bi-exponential functions are being used to describe the processes of charge transfer, a series of ratios for the rate constants were used as prefactors.

$$C_f = ak_f^1 + (1 - a)k_f^2 \hfill (16)$$

$$C_b = bk_b^1 + (1 - b)k_b^2 \hfill (17)$$

$$C_r = ck_r^1 + (1 - c)k_r^2 \hfill (18)$$

As for the constants, $C_1$, $C_2$ and $C_3$, in Equation 6, the latter two have been replaced by $A$ and $B$, respectively and $C_f$ was set equal to zero due to the time ordering of the visible and IR pulses. $A$ now represents the overall amplitude of the fit function and $B$ is used to separate the amplitude between the first and second terms in equations 12. The first term describes forward and back transfer from excitations that form near an interface, and the second term describes charge transfer from excitations that diffuse to an interface.
In order to make the fitting procedure simpler, the excitation relaxation times of CN-MEH-PPV were determined by the photoluminescence decay measured with a time-correlated single photon counting (TCSPC) instrument. The decay traces were measured at 525 nm and at 50 nm intervals from 550 to 750 nm. The traces were integrated over time to produce the population dynamics of excitations of the CN-MEH-PPV that are displayed in figure 14.

The excitation dependence of CN-MEH-PPV was examined by exciting the polymer film at both 400 nm (black) and 460 nm (red). The polymer is only dependent on the wavelength of excitation on timescales faster than 300 ps. Since excitation transport takes longer than this time, the photo-luminescence decay was used to measure the relaxation time of the excited state of the polymer. A bi-exponential curve best fit curve (yellow) is overlaid on the photo-luminescence decays in figure 14. This data gives parameters $k_{r1}$, $k_{r2}$ and $c$ from equations 11, 15 and 18, which are used to fit the bleach area kinetics.

Recall figure 13A, where the bleach area kinetics were shown. Also shown in this figure is the best fit curve (from equation 12). All the parameters (aside form the relaxation times) were fit using a least squares fitting procedure. The forward transfer (or process 1 of figure 13A) was fit using parameters $k_{f1}$, $k_{f2}$ and $a$. Process 2 (back electron
transfer) was fit between 5 and 100 ps. This time frame gave fitting parameters $k_{b1}$ and $b$.

There is a slower component to the back charge transfer that does not occur on within the time domain of the instrument. Since the charge recombination was broken into a bi-exponential, the longer time parameter, $k_{b2}$, was set equal to zero. The results of the least-squares fitting procedure are provided in Table 1.

<table>
<thead>
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<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{f1}$</td>
<td>(1/0.09 ps)</td>
<td>$k_{r1}$</td>
<td>(1/0.93 ns)</td>
</tr>
<tr>
<td>$k_{f2}$</td>
<td>(1/0.90 ps)</td>
<td>$k_{r2}$</td>
<td>(1/3.10 ns)</td>
</tr>
<tr>
<td>$k_{b1}$</td>
<td>(1/42 ps)</td>
<td>$k_{d}$</td>
<td>(1/2.50 ns)</td>
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<tr>
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<tr>
<td>$b$</td>
<td>0.12</td>
<td>$B$</td>
<td>0.96</td>
</tr>
</tbody>
</table>

Table 1: Values of the given parameters for fitting the bleach area versus time.
5.1 Bleach Shift versus Time

In section 4.2, figure 12B shows that the bleach of the carbonyl vibrational mode of PCBM shifts as a function of time. From discussions in chapter 3 about the 2D IR spectra and anisotropy data, it is believed that this shift is due to diffusion of electrons through the PCBM domains. Also in chapter 3, it was shown that PCBM forms roughly spherical domains and with the addition of polymer, the vibrational frequency of the $\text{C}=\text{O}$ stretch changes. When electrons are transferred into the PCBM domains, interfacial PCBM molecules accept the electron. As discussed earlier, addition of the polymer shifts the carbonyl mode frequency to 1740 cm$^{-1}$. Since the bleach at early times is shifted to higher frequency, these modes were assigned to the interfacial PCBM molecules. As time progresses, electrons can diffuse throughout the PCBM domains sampling different environments of PCBM. This sampling of various environments is what is assigned to the shifting bleach. Before this could be concluded, there are a few other possibilities to why the bleach shifts that must be addressed.
5.2 Temperature Dependent FTIR Studies

Given the high energy density of the visible excitation pulses, it is possible that heating effects are shifting the bleach to higher frequency. Figure 15 shows linear IR spectra of the carbonyl mode of PCBM in the 1:1 OPV mixture with CN-MEH-PPV.

These spectra were collected at a series of temperatures from 393 K to 313 K in decrements of 20 K. Also collected were spectra at room temperature before and after the experiment, which were identical. The sample was heated first to allow any annealing effects take place throughout the entire series. Also shown in the diagram are the 1 ps and 3 ns time slices of the Vis-IR data for comparison. Over the series of temperature dependent studies (temperature range of 97 K), the linear spectra show less than a 0.5 cm\(^{-1}\) shift in center frequency as well as little to no change in the width of the peaks.

These temperature studies were conducted over a large range to see how the carbonyl mode of PCBM reacted to heat. The excitation pulses contribute an estimated temperature change of 9 K to the sample area it interacts with, assuming no heat is transferred to the substrate or surrounding OPV mixture blend. This estimate was based on the specific heat and density of most polymers being \(\sim 1\) Jg\(^{-1}\)K\(^{-1}\) and \(\sim 1\) gcm\(^{-3}\), respectively;
and the specific heat and density of crystalline C\textsubscript{60} are 0.8 Jg\textsuperscript{-1}K\textsuperscript{-1} and 1.6 gcm\textsuperscript{-3}, respectively. \textsuperscript{38} It was assumed that PCBM has the same specific heat and density as C\textsubscript{60}. The specific heat and density of the OPV mixture was estimated by taking the overall average of the properties of the two materials. It was found that the specific heat and density for the OPV mixture are 0.9 Jg\textsuperscript{-1}K\textsuperscript{-1} and 1.3 gcm\textsuperscript{-3}, respectively. The temperature change of 9 K was estimated using these values and that the spot size was 250 µm, the film thickness is ~3 µm and a excitation pulse has an energy of 1 µJ.

Recall figure 15 with the temperature dependent studies; over a 97 K temperature change, the carbonyl modes shifts no more than 0.5 cm\textsuperscript{-1}. From the Vis-IR slices shown, there is a 4 cm\textsuperscript{-1} shift of the bleach. Also, there is a large change in the width of the bleach from 11.5 cm\textsuperscript{-1} to 16.5 cm\textsuperscript{-1} FWHM between the 1 ps and 3 ns spectra, respectively. In the temperature study on the OPV mixture, there is a negligible change in width of the carbonyl mode. From this data, it is believed that the shift in frequency of the bleach is not due to temperature change of the sample upon excitation.

5.3 Diffusion of Molecules and Orientational Dynamics

In the liquid and gaseous states, atoms and molecules can move around freely. In solids though, atoms and molecules move on a much slower time scale. But, it is not uncommon in amorphous solids for molecules to move around. It is possible that in the OPV samples the migration of PCBM molecules in the domains could result in the bleach shifting seen in figure 12B. The validity of this statement can be tested by determining whether the carbonyl frequency of PCBM is sensitive to the structure of the local environment. The spectral diffusion of the carbonyl stretch can be compared with the
corresponding orientational relaxation dynamics. If motion of the PCBM molecules throughout their domains was present, then when electrons are transferred to PCBM molecules, the change in bleach could be due to PCBM molecules moving to different environments. It was stated previously that the carbonyl mode is affected by the polymer and closer to the core of the PCBM domains, a frequency of 1740 cm$^{-1}$ is expected. If an electron is transferred to an interfacial PCBM molecule and that molecule can diffuse through the domain towards the center portion of the domain, the frequency of the carbonyl mode of that PCBM molecule will shift accordingly.

Recall from Chapter 3 that no spectral diffusion is present in the OPV samples. The only motion occurring on the 10 ps time scale is wobbling-in-the-cone motion of the butyric methyl ester group of PCBM and rotational motion of the PCBM molecules. If spectral diffusion was present, it could be concluded that this is the source of the bleach shifting from high to low frequency. The only motion present should have no effect on the carbonyl mode of PCBM because the molecule resides in one spot and does not move through the domain. Given that there is no spectral diffusion present, the orientational motion is not a result of spectral diffusion and will not have a frequency dependence on the bleach spectra.

5.4 Diffusion of Electrons through PCBM Domains

The connection between the frequency of the carbonyl vibrational stretching mode of PCBM and the radial position of the molecules in the PCBM domains indicates that the time dependent shift of the bleach frequency must result from the diffusion of electrons from the interfaces to the centers of the domains. The distribution of carbonyl frequencies
that appear in the bleach at a given time delay is therefore related to the average radial
distribution of electrons at that time. As electrons move toward the centers of the domains,
their average radial distribution changes, which causes the carbonyl bleach to approach the
equilibrium spectrum which has a center at 1740 cm$^{-1}$. After electrons are transferred to the
PCBM domains, they can either stay in place or diffuse throughout the PCBM domain.
Since there is a shift in the bleach over time (figure 12B), the electrons must be moving
through the PCBM domains. As electrons migrate towards the center of these domains, the
carbonyl mode of PCBM molecules near these mobile electrons will be affected and this is
seen as the shifting bleach.
Chapter 6

Measuring Electrically Mobile Charge Carriers

6.1 Measuring Charge Carriers Electrically

Up to this point, only optically excited charge carriers have been examined. Solar cells are circuits, and in order to get a good measure of their ability to operate properly, one must quantify the charge carriers movement electrically. Measuring charge carriers electrically will give a good comparison to the studies completed already, as well as gain additional information. The technique for measuring electrically mobile charge carriers is called Charge carrier Extraction using Linearly Increasing Voltage (CELIV). These experiments facilitated the comparison of charge transfer dynamics of electrically mobile charge carries to optically excited charge carriers.

6.2 Initial CELIV Experiments

To this point only preliminary data has been collected using the CELIV technique. Initial samples were introduced into the circuit via alligator clips and mounted in line with the 532 nm Nd\textsuperscript{3+} YAG beam. Each sample was run through scans measuring light and dark currents over the circuit. Time delays were used to offset the voltage ramp from the light pulses hitting the sample. An example of a few sets of time slices can be seen in figure 16. An unusual result was found when running these experiments. Normally, these solar cells act as capacitors and should give a square wave capacitive
current. The traces seen in figure 16 do not show this, but rather fast rising curve, followed by a slow curved decay. It is believed that the curve is due to conductance of the samples. All materials were bought commercially and it was reported that P3DT contained catalyst contamination. These metal atoms could allow for some conductivity of the sample to push ions through the circuit.

To measure the mobility of the charge carriers, difference spectra were taken for each time slice. This means, that the data from the light current were subtracted by the dark currents. An example of this can be seen in figure 17. These difference spectra show the amount of charge carriers extracted after light hit the sample. Note there are a decreasing number of charge carriers extracted at longer time delays. This is due to the fast mobility of the carriers being extracted. Also, there is a second rise that appears in these spectra. It is believed that the second rise is from measuring both charge carriers, electrons

**Figure 16:** CELIV time slices of light and dark currents at various time points. It should be noted that a capacitive current is not seen; this is explained further in the text.
and holes. Currently, it is unclear whether electrons or holes are extracted faster, therefore each peak has not been assigned to a specific charge carrier.

Figure 17: Difference spectra of light and dark currents for CELIV time slices of mixtures of 2:1 weight ratio of P3DT:PCBM.
Chapter 7

Concluding Remarks

The results from the 2D IR and Vis-IR spectroscopy experiments were used to study charge separation and charge mobility within OPV samples of CN-MEH-PPV with PCBM. The studies were completed by studying the carbonyl (C=O) stretching mode of PCBM. Analysis of the vibrational line shapes allowed for the extraction of the bleach, which is directly related to the concentration of electrons that transferred from the polymer to the PCBM domains. In conjunction with other experiments, it was found that interfacial PCBM molecules show a high frequency shift from the equilibrium frequency. As time progresses, a shift towards the asymptotic limit of 1740 cm\(^{-1}\) was seen. This shift was due to electrons diffusing through the PCBM domains, sampling multiple environments of the PCBM molecules.

The correlation between the frequency of a carbonyl mode and the radial position of its host fullerene molecule within the PCBM domains provides a means to observe the movement of electrons within individual domains through the spectral evolution of the carbonyl bleach. These studies reveal that organic solar cells with dramatically higher mobility and thus efficiency might be developed if the geometries of the interpenetrating networks of electron donating and accepting materials can be controlled to eliminate interfacial boundaries along the charge migration pathways. It was also demonstrated that the application of ultrafast infrared spectroscopy to study organic PV materials at the
molecular level is useful to provide insight into the fundamental dynamics that determine the efficiency of organic solar cells.
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