MEASURING THE BARRIER TO CHARGE TRANSFER STATE DISSOCIATION IN ORGANIC PHOTOVOLTAIC MATERIALS WITH ULTRAFAST VIBRATIONAL SPECTROSCOPY

A Dissertation in Chemistry

by

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Submitted in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

May 2012
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ABSTRACT

We have developed a technique based on ultrafast vibrational spectroscopy to measure the barrier to charge transfer state dissociation, or alternatively labeled charge separation, in organic photovoltaic materials. Visible pump–infrared probe spectroscopy is used to generate excitons within organic photovoltaic blend films and the photochemical sequence of events that follows is monitored with an infrared probe pulse tuned to a vibrational mode specific to the electron acceptor. A gradient of vibrational frequencies exists in blend films such that the motion of electrons away from sites where electron transfer occurs can be measured. This gradient of vibrational frequencies arises from a gradient of solvent environments present in the blend film. Using two-dimensional infrared spectroscopy and other IR third-order techniques, we characterize the dynamics of the vibrational mode in the ground-state electronic potential and demonstrate that these dynamics do not interfere with the interpretation of the frequency shift observed in the visible pump–infrared probe experiment in terms of electron motion.

We have used this technique to measure the barrier to charge separation at low excitation densities in thin blend films consisting of device-relevant organic photovoltaic materials. For example, we have measured the barrier to charge separation in organic photovoltaic blend films consisting of the π-conjugated polymer RR-P3HT as electron donor blended with either the functionalized fullerene PCBM or soluble perylene diimide derivative BTBP as electron acceptor. We observe barrierless charge separation in the blend with PCBM while we find charge separation is activated in the blend with BTBP. In combination with X-ray scattering measurements performed by our collaborators, we argue that fullerenes are capable of barrierless charge separation in the presence of structural disorder while perylenes may require structural order to effect barrierless charge separation. Lastly, we find that separated charge carriers can be generated without a donor/acceptor heterojunction in films consisting exclusively of PCBM via the dissociation of charge transfer excitons.
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# LIST OF ABBREVIATIONS

## Materials

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tr>
<td>BTBP</td>
<td>( N,N' \text{-bis}(2,5\text{-di-}t\text{ert}\text{-butylphenyl-}p\text{erylene})\text{-3,4,9,10-tetracarboxylic diimide} )</td>
</tr>
<tr>
<td>( \text{C}_{60} )</td>
<td>Buckminsterfullerene</td>
</tr>
<tr>
<td>CN-MEH-PPV</td>
<td>poly[2-methoxy-5-(2'\text{-ethylhexyloxy})\text{-}p\text{-(1-cyanovinylene)}\text{phenylene}]</td>
</tr>
<tr>
<td>MDMO-PPV</td>
<td>poly[2-methoxy-5-(3',7'\text{-dimethyloctyloxy})\text{-}p\text{-phenylene}] vinylene</td>
</tr>
<tr>
<td>ITO</td>
<td>indium tin oxide</td>
</tr>
<tr>
<td>P3HT</td>
<td>poly(3-hexylthiophene)</td>
</tr>
<tr>
<td>PCBM</td>
<td>[6,6\text{-phenyl C}_{61} butyric acid methyl ester]</td>
</tr>
<tr>
<td>( \text{PC}_{71} \text{BM} )</td>
<td>[6,6\text{-phenyl C}_{71} butyric acid methyl ester]</td>
</tr>
<tr>
<td>PCDTBT</td>
<td>poly( [N'\text{-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'\text{-di-2-thienyl-2',1',3'-benzothiadiazole})}] )</td>
</tr>
<tr>
<td>PDI</td>
<td>perylene-3,4,9,10-tetracarboxylic diimide</td>
</tr>
<tr>
<td>PDI-C8</td>
<td>( N,N' \text{-dioctyl-}p\text{erylene-3,4,9,10-tetracarboxylic diimide} )</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>poly(3,4-ethylenedioxythiophene)/poly(styresulfonate)</td>
</tr>
<tr>
<td>PPV</td>
<td>poly(p-phenylene vinylene)</td>
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<td>PS</td>
<td>polystyrene</td>
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## Other

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>BBO</td>
<td>β-barium borate</td>
</tr>
<tr>
<td>CT</td>
<td>charge transfer</td>
</tr>
<tr>
<td>DFG</td>
<td>difference frequency generation</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>FWHM</td>
<td>full width at half maximum</td>
</tr>
<tr>
<td>MCT</td>
<td>mercury cadmium telluride</td>
</tr>
<tr>
<td>OD</td>
<td>optical density</td>
</tr>
<tr>
<td>OPA</td>
<td>optical parametric amplification</td>
</tr>
<tr>
<td>OPV</td>
<td>organic photovoltaic</td>
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<td>RR</td>
<td>regioregular</td>
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<td>regiorandom</td>
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<td>sum frequency generation</td>
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<td>SHG</td>
<td>second harmonic generation</td>
</tr>
<tr>
<td>TRIR</td>
<td>time-resolved infrared</td>
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Chapter 1

Motivation and Background

Global demand for energy is on the rise. In 2008, the U.S. consumed energy at a rate of 3.3 TW.\(^1\) This means that the U.S. consumed energy at a rate one-fifth of the rate of global energy consumption, which amounted to 17 TW in 2008.\(^2\) The global rate of energy consumption is expected to reach 26 TW by 2035.\(^2\) Even though the rate of U.S. energy consumption is expected to only slightly increase between now and 2035, the rate of global energy consumption is expected to accelerate rapidly as emerging economies increase their use of energy.\(^2\) This disproportionate increase is only to be expected as every individual on this planet strives for a better quality of life. This was most eloquently pointed out in a recent presentation by Hans Rosling where he highlighted the benefits of technology (which consumes energy) on individuals and society.\(^3\) Needless to say, technology improves quality of life. As people strive for an improved quality of life, energy consumption will continue to increase.

Hydrocarbons are the world’s primary source of energy. Coal, oil, and natural gas accounted for over 80% of global energy supplies in 2008.\(^4\) U.S. energy consumption of coal, oil, and natural gas in the same year was similarly over 80%.\(^5\) In the U.S., energy consumption can be broken down into two major sources, electricity (40%) and fuel (29%).\(^5\) The other 31% of energy consumption is the non-electrical use of natural gas (17%), industrial use of petroleum (8%) and biomass (2%), and other miscellaneous uses (4%).

The products of the (complete) combustion reaction between a hydrocarbon and oxygen are water and carbon dioxide. Carbon dioxide, a linear triatomic molecule, has \(3N-5\) or 4 normal modes of vibration. Three of these normal modes can absorb radiation, i.e. are transitions allowed by the rules of quantum mechanics, and have transitions energies of 667 cm\(^{-1}\) (a pair of
degenerate bending modes) and 2350 cm\(^{-1}\) (asymmetric stretch mode). These transition energies correspond to the infrared region of the electromagnetic spectrum.

The sun irradiates the earth with a broad spectrum of radiation, including visible light. Considering that a large proportion of the radiation making its way to the earth's surface is absorbed, the earth warms and can re-emit as a blackbody. The infrared spectrum emitted by earth has been measured, for example, using the IRIS (infrared interferometric spectrometer) aboard the Nimbus 4 meteorological satellite.\(^6\) Two general features relevant to the current discussion can be observed in the spectra. First, the spectra can be fit with a blackbody profile to obtain the earth's surface temperature. As one might imagine, this ranges from \(~220\) K in arctic regions to \(~320\) K in arid regions. Second, the \(\text{CO}_2\) bending band at 667 cm\(^{-1}\) is a prominent feature in each of these spectra. Along with other greenhouse gases, \(\text{CO}_2\) absorbs the outgoing thermal energy emitted by the earth helping maintain a proper temperature balance and making life as we know it possible on earth.

It is immediately apparent that increasing the level of \(\text{CO}_2\) concentration in the atmosphere will trap increasingly more heat. Measurements based on ice core data suggest unprecedented levels of carbon dioxide in the earth's atmosphere.\(^7\) The unprecedented levels of carbon dioxide in the atmospheric were attributed primarily to combustion of hydrocarbons. The buildup of greenhouse gases will lead to warmer temperatures that may have severe effects on earth’s climate and ecosystems, including the possibility of longer dry seasons in arid regions, rising & acidified oceans, etc. New technologies in which \(\text{CO}_2\) is not released need to be developed to circumvent these problems and to satisfy the continually increasing global demand for energy.

The sun is the ultimate source of clean, renewable energy. \(170 \times 10^3\) TW of solar energy is incident on the earth.\(^8\) About \(3 \times 10^{24}\) J of solar energy reaches the earth’s surface every year,\(^9\) which is equivalent to \(95 \times 10^3\) TW. Given that we still need light to see, for plants to use in photosynthesis, and to warm the planet to comfortable levels this should come as no problem as
global energy needs are a small fraction of this amount. Plus, the sun is expected to last for another 5 billion years.\textsuperscript{10} The challenge then is to develop the technologies that are able to harness solar energy and convert it into either electrical energy (i.e. electricity) or potential energy (i.e. stored in chemical bonds).\textsuperscript{11}

Semiconducting materials are capable of harnessing solar energy. Materials can be separated by their ability to conduct electrical current into three general groups: metal, semiconductor, and insulator (Figure 1-1A). The ability to conduct electricity in these materials has to do with (1) whether the highest occupied band is partially filled or totally filled with electrons and (2) the energy spacing between the highest occupied band and the lowest unoccupied band. The small gap between bands gives semiconductor their unique properties, namely, lower resistance at higher temperatures (i.e. a negative thermal coefficient of resistivity). Electrons can also be excited to the conduction band by absorption of photons.

On the microscopic level, we can to some extent predict whether a material will be a metal, semiconductor, or insulator based on its position in the periodic table and the essential features of the tight-binding approximation. In their isolated form, electrons within atoms have discrete wavefunctions and energy levels. When atoms are brought together to form a solid, these wavefunctions begin to overlap, mixing the states and causing the energy levels of the isolated atoms to split into levels of higher and lower energy in the solid-state. The proximity of the atoms within the solid determines the spatial overlap of the electronic wavefunctions. The spatial overlap of the electronic wavefunctions, in turn, determines the extent of splitting of the original energy levels into higher and lower energy levels or, in other words, the width of the bands. The number of atoms mixing is another important factor that determines the density, or spacing between levels, within the bands. From this model, for example, we can predict that sodium should be a metal (Figure 1-1B).

Devices based on semiconductors can harness solar energy through the photovoltaic effect. A photovoltaic material converts light into electrical energy. The conversion of light to
electrical energy is brought about by absorption of a photon which leads to an electron and a hole in the material. If the material is placed between two electrodes and the electron and the hole separate and travel in opposite directions, a current and a voltage is generated (Figure 1-2A). This simultaneous generation of photocurrent and photovoltage leads to the desired electrical power. An $J$–$V$ curve of a photovoltaic device highlights the important device parameters (Figure 1-2B). The efficiency of a device, $\eta_e$, is calculated as

$$\eta_e = \frac{J_{SC}V_{OC}FF}{P_{in}}$$

where $J_{sc}$ is the short-circuit current density, $V_{oc}$ is the open-circuit voltage, $FF$ is the device fill factor, and $P_{in}$ is the power irradiating the device. The device $FF$ is calculated as

$$FF = \frac{J_{max}V_{max}}{J_{SC}V_{OC}}$$

where $J_{max}$ and $V_{max}$ represent the current density and voltage whose product gives the maximum attainable power of the device.

The conversion of sunlight into electricity from a single material (for commercial purposes) began with selenium. In wasn’t until 1954 that researchers Gerald Pearson, Daryl Chapin, and Calvin Fuller at Bell labs revealed an optimized silicon solar cell whose efficiency of 6% represented an order of magnitude advancement over the selenium cells of years past. The silicon solar cell poised an ideal match for the space race that ensued as the heavy investments (i.e. satellites) required a power supply that would not require maintenance and would last for long periods of time. Monocrystalline silicon is a very efficient photovoltaic material with devices reported capable of generating up 42 mA/cm$^2$, 0.70 V, with a $FF$ of 0.84 and overall efficiency of 24%. Needless to say, silicon continues to be the dominant photovoltaic material.

There are two parameters that govern the potential utility of a photovoltaic technology – cost and efficiency. In quantitative terms, this is expressed as the cost per peak watt of electricity
generated, i.e. $/\text{W}_{\text{peak}}$. Qualitatively, the cost per watt is directly proportional to costs associated with making a device and indirectly proportional to the device efficiency. The Department of Energy’s goal is $0.33/\text{W}_{\text{peak}}$ (as of 2005).\textsuperscript{16} Although silicon is very efficient, it is very expensive to process requiring nearly $300 / \text{m}^2$.\textsuperscript{11} As such, the price of electricity derived from silicon-based photovoltaic modules is ~10 times higher ($0.35 / \text{kW-hr}$) than that derived from the combustion of fossil fuels ($0.02–0.05 / \text{kW-hr}$).\textsuperscript{11} This places the cost per watt of electricity generated by silicon-based photovoltaic modules at ~$3/\text{W}_{\text{peak}}$. More recent estimates place the cost per peak watt of electricity generated from photovoltaic modules based on crystalline silicon in the range of $1–1.5/\text{W}_{\text{peak}}$.\textsuperscript{17}

Devices based on newer materials, such as CdTe and CIGS (CuInGaSe), have been developed to compete with silicon-based devices. These materials are direct gap semiconductors requiring only small amounts of material to absorb light in the solar spectrum, i.e. thin film (~1-2 μm). Devices based on these materials are dropping in cost and are becoming promising alternatives to silicon. However, these technologies are not without their problems. As the Vice President of Technology at First Solar admits,\textsuperscript{18} “There are two problems with CdTe technology, Cd and Te.” This statement simply points out the low abundance and toxicity of both Cd and Te. But a clever, perhaps necessary, solution to these issues (as immediately followed up with by the VP of Technology at First Solar) is proper enclosure and recycling of the materials. CIGS technology suffers over concerns of the limited supply of indium.\textsuperscript{19} But even if these issues are overcome, costly processing conditions are still necessary to produce the required device efficiencies.

### 1.1 Organic Photovoltaics

Organic photovoltaic (OPV) materials represent a potential alternative that can drive down the cost of photovoltaic devices. The chemical structures of several OPV materials are
displayed in Figure 1-3. OPV materials can be separated into two classes: polymer and molecule. Because of the relatively weak van der Waals forces that hold these materials together in the solid-state, they require less energy to process. Polymers, for example, can be processed at room temperature and atmospheric pressure (i.e. ambient conditions) from solution. Semiconducting polymers combine the ideal mechanical properties of polymers with the electronic properties of semiconductors. Molecular materials need to be processed in vacuum (~10^{-7} torr), but require temperatures substantially lower than those required for inorganic materials because of the weaker forces holding them together in the solid-state. Before continuing a discussion of the solid-state properties of OPV materials, the properties of an individual molecule or polymer chain will be discussed.

An individual molecule or polymer chain consists of multiple atoms held together by σ and π bonds. σ bonds are formed by orbital overlap and sharing of electrons along the axis of the nuclei. π bonds are formed by orbital overlap and sharing of electrons in the same plane as the nuclei, but above and below the axis of the nuclei. σ bonds are typically lower in energy than π bonds and so are harder to break. The σ bonds are primarily responsible for holding the individual molecules together while the π bonds involve interactions between neighboring molecules. The π bonds therefore make up the active portion of the π conjugated material.

OPV materials require extended π-conjugation. According to molecular orbital theory, when two atomic orbitals of the same energy are brought close together, these orbitals mix and two molecular orbitals are formed. These new molecular orbitals are called the π (bonding) molecular orbital and π* (anti-bonding) molecular orbital. An electron that occupies the molecular orbitals is delocalized between both carbon atoms, i.e. it exists on both carbon atoms. Extended conjugation results from the overlap of multiple atomic (p) orbitals (Figure 1-4A). For a series of molecules containing adjacent double bonds, ranging from the limits of ethene to polyacetylene, MO theory predicts that from N atomic orbitals N molecular orbitals will form (Figure 1-4B). Although the energy spacing between MOs is determined by the spatial overlap of
atomic orbitals, the mixing of a greater number of p orbitals, \( N \), results in a larger density of MOs that in turn results in a band of states. The extent of \( \pi \)-conjugation, therefore, is one of the primary determinants of the optical and electronic properties of organic photovoltaic materials.

Although the weak interactions between molecules lowers both the energetic and monetary costs associated with processing the materials, these weak intermolecular interactions have significant implications on the semiconducting properties of the solid. The solid-state structure of a PV material is critical to its device operation. The solid-state structure of the inorganic material silicon, for example, consists of atoms held closely together in a lattice through covalent bonds (strong interactions). As such, inorganic semiconductors exhibit band transport and very efficiently transport charge. On the other hand, in an organic solid the molecules are held in a lattice through intermolecular forces (weak interactions) and so space is less densely occupied. Organic semiconductors exhibit bandlike transport only for highly crystalline materials at low temperature, i.e. pentacene.\(^{21} \) In most cases, however, transport in organic semiconductors is best described by a hopping process.\(^{22} \) In other words, inorganic materials can be semiconductors while organic materials are molecules that can act like semiconductors.

Given these differences, it is not unreasonable to expect that the excited state generated in a solid inorganic semiconductor sample is quite different from that generated in a solid organic semiconductor sample. For example, in an organic semiconductor, absorption of light does not lead directly to charge carriers, but rather to an exciton, a neutral bound electron-hole pair. A picture useful for understanding the difference between organic and inorganic materials comes from studies of molecular crystals.\(^{23} \) In this picture the exciton is characterized according to the relation between the lattice spacing, \( a \), and the mean free path of the carrier, \( a_L \). A Frenkel exciton, the primary excited state of organic materials, is characterized by a small carrier mean free path relative to the lattice spacing \( (a < a_L) \). In other words, the excitation is localized in space to a single lattice site. On the other hand, a large carrier mean free path relative to the lattice spacing \( (a >> a_L) \) is characteristic of Wannier-Mott excitons. Wannier-Mott excitons are
typical of the most highly ordered organic crystals and inorganic materials. In this case, the excitation is thought to be delocalized about many units of the lattice. The intermediate in between the Frenkel and the Wannier-Mott exciton is the charge-transfer (CT) exciton. The CT exciton has a carrier mean free path on the order of a few lattice spacings \((a \approx a_L)\). The terminology exciton generally carries with it the notion of electrical neutrality.\(^{24}\)

Another method of discerning between excitonic and classical semiconductors has emerged recently.\(^{25,26}\) In this model based on hydrogen-like wavefunctions, two factors contribute to the differences between OPVs (and more generally organic semiconductors) and inorganic PVs (classical semiconductors): (1) dielectric constant and (2) Bohr radius. The low dielectric constant of OPVs (due to the low atomic number of the atoms) combined with a small Bohr radius of the charge carrier cause the carrier to sit inside a deep potential well below \(kT\). In contrast, the carrier sits in a shallow well for inorganic PVs. Thus, it might be expected that charge carriers are not readily generated in OPVs solely by thermal energy (i.e. \(kT\)).

A significant reorganization of the molecular bonds is typically associated with exciton formation. A simple way of illustrating this is through the bond alternation brought upon by photoexcitation - the bonds in a PPV-based polymer (chemical structure in Figure 1-3), for example, will change from an initially benzenoid form (low energy) to a quinoid form (high energy) following photoexcitation. The molecular bonds will also reorganize for charge carriers. A polaron, for example, is a charge carrier solvated by reorganization of molecular bonds. In general, the bond lengths and bond angles change in response to the new \(\pi\)-electron density.

This picture of the exciton allows one to grasp why the efficiencies of devices based on OPVs have historically been so low. Devices based on a single material sandwiched between two electrodes do not generate significant amounts of current. Tang, in 1986, found that by layering two materials with different electron affinities and ionization potentials he could produce a device with \(\sim 1\%\) efficiency.\(^{27}\) Tang concluded that the dissociation of excitons at the interface into separate charges, where an electron transfers to the material with high electron affinity (and a
hole to the material with high ionization potential), was responsible for the enhanced efficiency. In other words, excitons generated upon light absorption in the materials are efficiently split at the interface between electron donor and acceptor materials. Unfortunately, the finite lifetime of the exciton combined with a low diffusion coefficient result in a diffusion length \( (L_D = \sqrt{D\tau}) \) that is limited to the order of a few tens of nanometers in both polymeric\textsuperscript{28} and molecular\textsuperscript{29} materials.

To circumvent the issue that the exciton diffusion length is much shorter than the absorption length of a few hundred nanometers, the notion of the bulk heterojunction was introduced in the early ‘90’s, improving upon Tang’s original concept of the interface by distributing it throughout the bulk.\textsuperscript{30,31} In a device based on the bulk-heterojunction concept, the electron donor and acceptor materials are distributed on the nm length scale so that nearly every exciton can reach an interface to undergo charge separation. The caveat is that bicontinuous percolation pathways are necessary for the resulting separated charge carriers to reach the electrodes. Devices based upon this approach in which PPVs or PTs are blended with fullerenes typically result in device efficiencies on the order of several percent.\textsuperscript{32-34} The device with the highest efficiency currently reported in the literature is 7.4\% (based on an alternating donor-acceptor low band gap copolymer blended with PC\textsubscript{71}BM),\textsuperscript{35} although a value of 8.3\% has been reported in the biannual solar cell efficiency tables reported by Green et al.\textsuperscript{36} for a device submitted by Konarka and verified by NREL.

The overall picture that has emerged to explain the cascade of events from photon absorption to charge extraction is as follows.\textsuperscript{37} First, the absorption of a photon results in an exciton. The exciton must then diffuse to an interface between donor and acceptor materials within its lifetime. Once at the interface, or junction, the excited electron on the donor can transfer to the acceptor resulting in a hole on the donor and an electron on the acceptor, i.e. charge separation. These charge carriers must then migrate to their respective electrodes. Finally, the charges must be extracted from the device by the electrodes.
More recently, the dissociation at the interface has been explained in terms of a two-step process. After exciton diffusion to the interface, the exciton at the interface transfers charge from electron donor to acceptor resulting in a charge transfer (CT) state. As a second step, the charge transfer state must overcome its Coulombic attraction to form spatially separated charge carriers (i.e. charge separation). These elementary steps can be visualized as follows:

\[ \text{D}^* - \text{A} \rightarrow \text{D}^{\delta+} - \text{A}^\delta \] (exciton on donor leads to transfer of charge to acceptor, i.e. CT state)

\[ \text{D}^{\delta+} - \text{A}^\delta \rightarrow \text{D}^+ \ldots \text{A}^- \] (CT state dissociates into spatially separated charge carriers)

The forward charge transfer (i.e. formation of CT state) is thought to occur within \( \sim 100 \) fs and has been measured with optical pump–probe techniques. Competing pathways to full charge separation include reformation of the excited state and geminate recombination to the ground state.

CT states existing at the donor/acceptor junction have been observed experimentally with photothermal deflection, photoluminescence and electroluminescence spectroscopy. What these studies have in common is that a new absorption or emission feature appears in the blend films which does not arise from a simple superposition of spectra of the pure materials. Lee et al. used photothermal deflection spectroscopy, an absorption technique capable of measuring transitions with very weak absorption coefficients, to identify a long wavelength absorption feature in films of MDMO-PPV:PCBM that they attributed to a CT state. Tvingstedt et al. found a new low energy electroluminescence feature in several polymer:PCBM blend films that they attributed to the recombination and emission of a CT state. Perhaps the most conclusive evidence for the formation of a CT state comes from photoluminescence experiments on PF10TBT:PCBM blend films where quenching of the donor excited state emission coincides with the formation of a longer-lived emission (\( \sim 4 \) ns; 4x longer than singlet excited state emission).

The CT state is considered to be an important intermediate because it has a lower binding energy than Frenkel excitons in the bulk. Hallermann et al. reported measurements of the CT
state binding energy based on the quenching of the photoluminescence by an applied electric field in MDMO-PPV:PCBM blends as ~0.1 eV while the Frenkel exciton in the polymer is ~0.5 eV.\textsuperscript{43} Muntwiler et al. have used two-photon photoemission spectroscopy to measure the energy of CT states introduced across the pentacene:air interface as ranging from ~0.1 – 0.4 eV.\textsuperscript{44}

At the molecular level, different questions arise. For example, what is the driving force for charge separation? What is the role of an interfacial dipole at the interface? Does excess energy play a role in the electron transfer reaction? Is the electron transfer reaction more sensitive to the free energy difference, $\Delta G$, or the reorganization energy, $\lambda$? Presumably the rate of charge separation greatly exceeds the rate of geminate recombination; otherwise OPV devices would not demonstrate a measurable current at all. Can these rates be measured directly?

In spite of all the pathways in competition with the desired pathways, devices with near unity internal quantum efficiencies have been demonstrated with certain OPV blends.\textsuperscript{45} This begs the question: What makes some material systems better than others? Can we find and control a microscopic parameter that ensures efficient charge separation?

Detailed investigations of the dynamics of excited states in conjugated polymers\textsuperscript{46,47} and polymer:PCBM blends\textsuperscript{48-54} have been carried out with transient absorption spectroscopy. Transient absorption spectroscopy involves exciting the sample with optical pump pulses and detecting changes in the transmittance in the visible and near-IR region of the electromagnetic spectrum. Interpretation of the transient spectra is complicated by the presence of a number of broad, overlapping electronic transitions characteristic of conjugated polymers and polymer:PCBM blends in these regions. This issue is partially circumvented at longer timescales (i.e. $\mu$s) as states such as the singlet and CT states, which have lifetimes on the order of nanoseconds, are no longer present and so there are fewer states present to absorb and overlap (i.e. reduction in complexity by reduction in numbers). Although pump–probe spectroscopic techniques have been used to study the photophysics of OPVs, these techniques are unable to
directly measure the dissociation of CT states into separated charge carriers as these represent electronically similar states that differ only in their spatial location.

1.2 Ultrafast Vibrational Spectroscopy of OPV Materials

Ultrafast vibrational spectroscopy combines the dynamic information obtained in pump–probe spectroscopy with the selectivity of vibrational spectroscopy. By exciting with an optical pump pulse, we generate excited states in the same manner as optical pump–probe techniques. However, we probe the sample with a mid-IR probe pulse that interacts with vibrational modes specific to each material. The sensitivity of the vibrational modes of electron donor and acceptor materials to their environment enables us to observe the dissociation of CT states into separated charge carriers. We have developed a technique based on ultrafast vibrational spectroscopy capable of directly measuring the dissociation of CT states into fully separated charge carriers in OPV materials. A detailed understanding of the microscopic parameters that control the rate of CT state dissociation will enable the rational design of OPV materials for highly efficient devices.

1.3 Thesis Overview

In the present introductory chapter, the motivation and background for the research to be presented in the following chapters has been established. An outline and brief summary of the remaining chapters is presented below.

In Chapter 2 details of the instruments and sample preparation methods used in this work are provided. First, steady-state spectroscopic techniques, including FTIR and UV-Vis spectroscopy, and the characterization technique, surface profilometry, will be discussed. Then, Vis pump–IR probe, 2D IR and other IR third-order techniques, and TRIR spectroscopy will be
discussed. Finally, different methods of sample preparation will be discussed, highlighting the advantages and disadvantages associated with each.

In Chapter 3 we present a proof of principle study using ultrafast Vis pump–IR probe spectroscopy to examine the dynamics of charge separation in an OPV blend film comprised of CN-MEH-PPV and PCBM. These experiments illustrate the general features appearing in the Vis pump–IR probe transient spectra as well as the method which we have developed to measure the rate of CT state dissociation with the system held at several different temperatures.

In Chapter 4 we present experimental evidence highlighting the range of environments in OPV blend films as observed through the carbonyl stretching mode of PCBM. Specifically, the frequency of the carbonyl stretching mode is found to be particularly sensitive to its solvent environment both in solution and in the solid-state. OPV blend films are found to consist of a gradient of solvent environments that result in a gradient of carbonyl stretching frequencies. Thus, the carbonyl stretching frequency of PCBM reports on the spatial proximity of PCBM molecules relative to the electron donor material.

In Chapter 5 we discuss the possible factors that would obscure the interpretation of the frequency shift of a bleach of the carbonyl stretching mode of PCBM resulting from electron transfer in terms of the dissociation of CT states. In particular, we find that spectral diffusion does not occur on the picosecond or longer timescale in OPV blend films consisting of CN-MEH-PPV and PCBM. As such, we are confident that the frequency shift arises from the electron transfer dynamics.

In Chapter 6 we present the first Vis pump–IR probe transient spectra measured in thin OPV blend films at low excitation densities. The measurements are made on two OPV systems of relevance to devices, RR-P3HT:PCBM and RR-P3HT:BTBP, to determine the influence of acceptor structure on the activation energy of CT state dissociation. We find the system with BTBP as electron acceptor to be very weakly activated, while the system with PCBM as electron acceptor to be activationless. We discuss possible reasons for the difference, in particular, the
shape of the acceptor molecules and the necessity of molecular order for the electron transfer reaction.

In Chapter 7 we present Vis pump–IR probe measurements of CT excitons directly excited in films of PCBM. We find that charge carriers can be generated in PCBM in the absence of a donor/acceptor junction. We also find a potentially new spectroscopic marker for CT excitons generated in PCBM.

In the final chapter of this thesis, Chapter 8, the conclusions are presented and recommendations for future direction are discussed.

In the Appendix, the motivation behind studying thin films at low excitations in device-relevant materials is highlighted. The practical aspects required to achieve these new and important experimental conditions are discussed.

1.4 References


(3) Hans Rosling and the magic washing machine.

http://www.ted.com/talks/lang/eng/hans_rosling_and_the_magic_washing_machine.html

Accessed 4/5/12


Figure 1-1. (A) Bands characteristic of three types of solids as grouped by their ability to conduct electrical current: metals, semiconductors, and insulators. (B) Schematic energies of electronic states as a function of internuclear distance, $r$, for atomic sodium with shaded regions corresponding to states occupied by electrons. Internuclear distance expected in the solid is represented by $r_o$. 
Figure 1-2. (A) Basic mechanism of photovoltaic device; simultaneous generation of a photocurrent and photovoltage. (B) $J-V$ curve of a solar cell in the dark and illuminated highlighting the parameters affecting overall device efficiency. The overall device efficiency, $\eta$, is calculated according to eqn. 1.1 and includes the short-circuit current density, $J_{SC}$, open-circuit voltage, $V_{OC}$, and device fill factor, $FF$. The $FF$ is calculated according to eqn. 1.2 and includes $J_{max}$ and $V_{max}$, which represent the current density and voltage whose product gives the maximum attainable power of the device.
Figure 1-3. Chemical structures of the π-conjugated polymers MDMO-PPV, RR-P3HT, and PCDTBT, and molecules PCBM, PC$_{71}$BM, and PDI-R used as organic photovoltaic materials. The author notes that a number of fullerene and PDI derivatives are present in the literature. PDI-R highlights one general example of functionalizing the imide positions (indicated by the R group) to increase solubility.
Figure 1-4. (A) Illustration of extended conjugation via overlap of many p orbitals. (B) Diagram illustrating the formation of molecular orbitals from atomic orbitals. The illustration ranges from the molecule ethene to the polymer polyacetylene.
Chapter 2

Instrument and Methods

This chapter provides general background information and as well as specific details of the steady-state absorption spectroscopy, time-resolved spectroscopy, and sample preparation methods used in the body of this thesis. First, steady-state absorption spectroscopy and associated instruments will be discussed. Next, the instruments used to carry out ultrafast vibrational spectroscopy and time-resolved IR spectroscopy will be described. These instruments are capable of accessing dynamics as short as a few hundred femtoseconds and as long as a few tens of milliseconds as will be described in the text. Last, methods of sample preparation will be discussed, including the advantages and disadvantages associated with each method.

2.1 Absorption Spectroscopy

Absorption of light can occur when the energy of a photon matches the difference between two energy levels in an atom or molecule. The energy levels in an atom or molecule occur at discrete energies that are determined by the rules of quantum mechanics. The result of an absorption event is a transition from a state of lower energy to one of higher energy. Because the energy levels are quantized, transitions also occur at discrete energies. Along with the energy requirement, the transition requires quantum mechanical “permission”. In other words, the transition needs to meet the selection rules described by quantum mechanics.

Omitting nuclear transitions, atomic transitions are purely electronic whereas molecular transitions can include electronic, vibrational, and rotational transitions. Atoms do not have vibrational or rotational transitions because two or more atoms are required to carry out a vibration or rotation. One of the most readily recognized series of electronic transitions are the
Balmer series of emission lines of the H atom. The corresponding experiment in which light is absorbed by atomic H would result in absorption lines at the same energies where light is emitted.\textsuperscript{1} The electronic transition energies observed via emission or absorption of atoms is characteristic of a particular element in the periodic table. Bunsen (a chemist) and Kirchhoff (a physicist) developed the very first atomic emission spectrometer capable of identifying the different elements.\textsuperscript{2} They used their atomic emission spectrometer in 1861 to identify the elements cesium and rubidium, previously unknown.\textsuperscript{3} The atomic absorption or emission spectrum for each element is different because the atomic form of each element has unique electronic states.

Molecular transitions can occur between electronic, vibrational, or rotational states because molecules are a collection of atoms bound together by covalent bonds. Some of the most readily recognized molecular electronic transitions are the $\pi-\pi^*$ transitions of dye molecules (i.e. phthalocyanine-based paints, porphyrin in chlorophyll). Molecular vibrational and rotational transitions are not observable to the naked eye. The energy requirement for vibrational transitions, or molecular vibrational motion, is met by wavelengths in the infrared while microwaves meet the energy requirement for rotational transitions. The transition energies of molecules can be used to gain information on bond strength and molecular structure.

All matter absorbs electromagnetic radiation. Absorption spectroscopy was developed to determine what wavelength and to what extent. Absorption of light by a sample can be measured by determining the sample transmittance, which is calculated according to

$$T = \frac{I}{I_o}$$  \hfill (1)

where $I_o$ is the intensity of light measured before interaction with the sample and $I$ is the intensity of light measured after the light has had a chance to interact with the sample.
A spectrum is obtained by making transmittance measurements at many light frequencies. In order to facilitate comparison of different spectra, the absorbance is often calculated. Absorbance is calculated from the transmittance according to

$$A = -\log T = -\log \frac{I}{I_0}$$

Plotting spectra with absorbance rather than transmittance makes comparing spectra easier for samples at different concentrations. The comparison is made easier because there is a larger difference in absorbance than there is in transmittance for the same series of samples with different concentrations.

The size, shape, and position of a peak in an absorption spectrum contain a wealth of information. The size, or intensity, of an absorption peak contains information on the amount of material present. The amount of a material present is related to the absorbance according to Beer’s law expressed as

$$A = \varepsilon b c$$

where $\varepsilon$ is the molar absorptivity, $b$ is the length of sample, or path length, through which the light travels, and $c$ is the sample concentration. The molar absorptivity is related to the ability of a material to absorb. On a microscopic level, the molar absorptivity is directly proportional to the probability of the transition as well as the cross-sectional area of the absorbing species (reported in cm$^2$). The probability of a transition ranges from 0 to 1 and is determined by the selection rules of quantum mechanics.

The shape of an absorption peak, which can be characterized by the linewidth, contains information about the distribution of environments in which the absorbing species exists. The absolute position of an absorption peak contains information about the specific type of environment. The absolute position also details the type of transition or type of chemical species as well as bond strengths and molecular structure.
Chromophores are regions of molecular structure, or groups of atoms, that absorb light at characteristic wavelengths. Some example chromophores are the C=C, C=O, and benzene/aromatic groups. The C=C group typically absorbs very strongly at 180 nm, while the C=O group, for example, in formaldehyde absorbs weakly at 280 nm. Benzene absorbs around 260 nm. Conjugation tends to lower the energy of these transitions. The C=C and C=O groups are also vibrational chromophores (more commonly referred to as normal modes or group vibrations).

2.1.1 UV-Vis Spectroscopy

A UV-Vis spectrometer is capable of accessing electronic, vibrational, and rotational transitions. However, peaks typically observed in a UV-Vis spectrum are electronic bands broadened by molecular vibrational transitions, rotational transitions, and translations/collisions. Vibrational and rotational transitions can be accessed by a spectrometer with very high resolution or by altering the state of the system, for example, acquiring the spectrum of a gas phase sample. As mentioned previously, atomic electronic transitions such as the Balmer series of the H atom occur in the visible region. Molecular electronic transitions such as \( n-\pi^* \) or \( \pi-\pi^* \) transitions occur in the visible region as well. Quantum mechanics requires that the transition dipole moment generated by interaction with the electrical component of the electromagnetic field must be nonzero in order for an electronic transition to occur. Also, the orbitals of initial and final states have to spatially overlap. For this reason, \( \pi-\pi^* \) transitions are typically particularly strong.

The UV-Vis spectra appearing in this manuscript were acquired with a Beckmann DU-520 UV-Vis Spectrophotometer (Beckman Coulter Inc., Brea, CA). There are two light sources in this instrument. One is a tungsten element, which generates visible light, and the other is a deuterium lamp, which generates UV light. A monochromator spatially separates the light into its component wavelengths with a grating which has 1200 lines/mm. The detector is a silicon
photodiode. The spectrophotometer layout is single beam. The spectrophotometer has a photometric accuracy ± 0.005 and scan between 190 and 1100 nm with an accuracy of ± 1 nm.\textsuperscript{7} The wavelength at which the light sources are switched can be varied, but was fixed at 350 nm for the measurements reported in this manuscript.

Measurements of film thickness were used to calculate film absorptivity in later chapters. Film thickness was determined using a Tencor P10 Surface Profilometer. This is a direct contact instrument in which a 2 µm diameter diamond stylus (60° cone angle) is rastered across a sample to measure step height. A contact force of 0.5 mg was used to determine film thicknesses for the polymer and molecular materials prepared in this manuscript, although higher forces are generally suggested to give more accurate readings (but can only be used for harder materials). Scan speed was set to 10 µm/s at a data sampling rate of 200 Hz which, combined with the scan length, determines the point spacing. Steps in the polymer film were typically introduced by scraping away a portion of the film with an X-Acto knife. Thick glass (i.e. 2-3 mm thick) seemed to give the most accurate measurements. The author posits that thinner glass has the tendency to warp during the measurement making determination of film thickness with thin substrates difficult.

2.1.2 Infrared Spectroscopy

Vibrational transitions are accessed by infrared spectroscopy. In a spirit similar to electronic bands, vibrational bands are broadened in the condensed phase by underlying rotational transitions and molecular translational motion/collisions. The region of the electromagnetic spectrum of importance to the chemist is typically defined by 25 – 2.5 µm (400 – 4000 cm\textsuperscript{-1}) and labeled the mid-infrared region. This region of the electromagnetic spectrum contains the molecular structural information useful to the chemist. The selection rule for vibrational
transitions is the same as for electronic transitions, i.e. there must be a nonzero transition dipole moment generated via interaction with the electrical component of the electromagnetic field.

Molecular vibrational motion can be described, to first approximation, by the harmonic oscillator of classical mechanics (Figure 2-1). The frequency of the vibrational motion, or oscillation, can be approximated as

$$\nu_m = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

(4)

where \(k\) is the force constant of the bond and \(\mu\) is the reduced mass of the oscillator. A quantum mechanical correction to this model which takes into account that only discrete transitions can occur is

$$E = (\nu + \frac{1}{2})\hbar \nu_m$$

(5)

which includes the vibrational quantum number, \(\nu\). Unfortunately, the quantum mechanical harmonic oscillator just presented would not allow for chemical reactions! There is no energy on the potential energy surface of the harmonic oscillator at which the atoms can separate from one another. To circumvent this chemical dilemma, anharmonicity is introduced into the potential energy surface in the form of the Morse potential

$$V(r) = D_e(1-e^{-(r-r_e)})^2$$

(6)

where \(D_e\) is the energy required to dissociate the bond, \(r\) is the internuclear separation, and \(r_e\) is the equilibrium internuclear separation. The harmonic oscillator and Morse potentials are plotted in Figure 2-1 as a function of internuclear separation. The \(|0\rangle, |1\rangle, \text{and} |2\rangle\) vibrational states are also displayed on top of the anharmonic Morse potential.

It is also important to keep in mind that vibrational motion not only consists of stretching motions as depicted in Figure 2-1, but includes bending motions, as well. While stretching motion corresponds to a change in bond length, bending motion corresponds to a change of bond angle.
Dispersive IR Spectroscopy

Dispersive infrared (IR) spectroscopy is the “traditional” infrared absorption spectroscopy. In this technique, a monochromator is used to spatially disperse the light into its component wavelengths. Data is collected at individual wavelengths and the wavelengths are scanned by mechanically moving a grating in the monochromator in a step-by-step fashion. The potential spectral resolution of a dispersive spectrometer is determined by a variety of factors including properties of the grating, such as its size and the number of lines/mm, as well as properties of the monochromator itself, such as the width of the entrance and exit slits.

A diagram of the dispersive IR spectrometer used to collect IR spectra reported in this manuscript is shown in Figure 2-2A. Light output from a ceramic IR element (Oriel Model 6575, Newport Corp., Irvine, CA) is directed toward the sample. The light is mechanically chopped at 50 Hz with an optical chopper (New Focus Model 3501, Newport Corp., Irvine, CA) for lock-in detection. Lock-in detection is accomplished by sequentially measuring the DC response of the detector in the dark and with light. With lock-in detection, only the signal “locked-in” to the frequency of the chopper is amplified. After interaction with the sample, the light is directed toward a monochromator (TRIAX 320, Horiba Jobin-Yvon, Inc., Edison, NJ). The grating in the monochromator has 150 lines/mm and is blazed at 5 μm. Light intensity is detected by a liquid nitrogen cooled mercury cadmium telluride (MCT) detector (FTIR-16-1.00, Infrared Associates Inc., Stuart, FL). The size of the element of the detector is 1 mm x 1 mm. The output of the MCT detector is amplified by a current mode preamplifier (MCT-1000, Infrared Systems Development Corp., Winter Park, FL) before A/D conversion (PCI-6250 M Series Multichannel DAQ device, National Instruments Corp., Austin, TX). The resulting digital signal is processed run-time in LabVIEW (National Instruments, Austin, TX) which also processes the signal for storage. LabVIEW automates the motion of the grating for spectral acquisition, as well.
The instrument is a single-beam design. The spectral resolution, as determined by lowest resolvable peak-to-peak separation, is \(~13\, \text{cm}^{-1}\) with the entrance and exit slit widths set to 0.5 mm (Figure 2-2B) as they were set for the measurements reported in this manuscript.

**FTIR Spectroscopy**

Fourier transform infrared (FTIR) spectroscopy is now almost exclusively used for collecting IR spectra. The light source and detector for FTIR are similar to those used for dispersive IR. However, FTIR spectra are obtained by collecting an interferogram (a time domain signal) with a Michelson interferometer. The advantages of this technique include the throughput (Jacquinot) advantage and the multiplex advantage. The throughput advantage arises because slits are not used in an FTIR spectrometer and so more light that has interacted with the sample is detected. The multiplex advantage is that the entire spectrum is obtained in a single scan via the Fourier transformation of the time-domain interferogram.

FTIR spectra were collected using a Thermo Nicolet 6700 FTIR spectrometer (Thermo Fisher Scientific, Inc., Waltham, MA). An EverGlo™ light source served to generate infrared light. The instrument is equipped with a KBr beamsplitter. Light intensities were detected with a thermoelectrically cooled deuterated triglycine sulfate (DTGS) detector. Adjustable parameters, such as spectral resolution, number of scans, and purging will be reported where necessary.

**2.2 Pump–Probe Spectroscopy**

The shape of the peaks or bands, or the line shape, measured by the absorption techniques discussed above incorporate all of the dynamical processes of the system that occur on a timescale faster than the timescale of the measurement (i.e. a few seconds or longer). Granted, one can obtain information about very slowly evolving systems that change on a timescale longer
than the duration of a measurement.\textsuperscript{8} However, obtaining information on the elementary steps of a chemical reaction requires accessing dynamics that occur on much shorter timescales. The path a particular chemical reaction follows is described by its reaction coordinate. The reaction coordinate of a chemical reaction consists of vibrations and, importantly, vibrations have a period on the order of 10 – 100 fs. For example, the reaction coordinate for the collinear approach of atoms in the hydrogen atom exchange reaction $D + H_2 \rightarrow DH + H$ can be readily visualized to include the stretching motions of $H_2$ and DH.\textsuperscript{9} As will be described below, contemporary laser systems are capable of generating pulses of light on these timescales. For an excellent and concise discussion of the history of pulsed light sources and their application to chemical dynamics, the reader is referred to ref. 10.

The quantity measured in pump–probe spectroscopy is typically the normalized change in transmittance, $\Delta T/T$. There are other ways of representing this quantity, such as the change in absorbance, but we will exclusively use and so discuss the change in transmittance. The normalized change in transmittance is calculated according to

$$\frac{\Delta T}{T} = \frac{T_{\text{pumped}} - T_{\text{not pumped}}}{T_{\text{not pumped}}}$$

where $T_{\text{pumped}}$ is the transmittance measured when the sample interacts with the pump pulse and $T_{\text{not pumped}}$ is the transmittance measured without interaction with the pump pulse. $T_{\text{not pumped}}$ in the denominator is a “normalization factor” which takes into account variations in the transmittance between samples.

The change in transmittance can be readily visualized by considering a simple three level system in which the energy separation between states is much greater than $kT$ (Figure 2-3). In other words, excited states $|1\rangle$ and $|2\rangle$ are assumed to be unoccupied. If the sample were excited from $|0\rangle$ to $|1\rangle$ by a pump pulse, population would be depleted from $|0\rangle$ and added to $|1\rangle$ after the transition. The new population in $|1\rangle$ has the capacity to absorb light. We can measure the extent that the new population absorbs light with the addition of a second pulse that interacts with
the sample called the probe pulse. A probe pulse passing through the sample in resonance with the excited state transition between $|1\rangle$ and $|2\rangle$, for example, would reduce in intensity via absorption. Given that this absorption event (i.e. as in a typical absorption experiment) would not have occurred without the sample interacting with the pump pulse, the new absorption is called photoinduced absorption (or more simply, induced absorption). Recall also that there is less population in $|0\rangle$. Because there are fewer states occupied, there will be fewer photons absorbed by a probe pulse passing through the sample in resonance with the $|0\rangle$ to $|1\rangle$ transition. This will result in an increase of measured light intensity. This is called photobleaching (or bleaching, for short). There is a third interaction possible, stimulated emission from $|1\rangle$ to $|0\rangle$. This process will also increase the measured light intensity.

Just as the horizontal axis in dispersive IR and FTIR (i.e. linear IR) can be obtained in either the frequency- or time-domain, the horizontal axis in pump–probe spectroscopy can be obtained in several ways. The horizontal axis in the pump–probe techniques reported in this manuscript is generated through the use of a monochromator which functions to spatially disperse the light into its component wavelengths which can be detected individually. There are two methods by which the horizontal axis can be generated in the “frequency-domain” using a monochromator. One method of obtaining the spectrum is by physically scanning wavelengths (as discussed for the dispersive IR spectrometer mentioned above). The other method is to obtain the spectrum with an array detector situated at the position of the exit slit of the monochromator. In the latter configuration the instrument is referred to as a spectrograph. The second method has the advantage that the entire spectrum is acquired in a single laser shot, substantially reducing the noise arising from shot-to-shot variations as well as noise introduced by variations in the mechanical motion of the grating in the monochromator. The author notes that the pump–probe spectrum is often denoted as a transient spectrum, highlighting the dynamic nature and brief duration of the entity being studied.
The techniques described below can be differentiated by the temporal nature of the light source (that has implications on the data acquisition hardware), the mechanism by which the temporal signal is determined, and the mechanism by which the spectral signal is determined.

The author recommends a book for the reader interested in exploring a dense source of highly practical, broadly applicable information on pump–probe spectroscopy written by Nikolai Tkachenko.¹¹

2.2.1 Ultrafast Vibrational Spectroscopy

Ultrafast vibrational spectroscopy (i.e. pump–IR probe) is useful for studying molecular structure and dynamics on ultrafast¹² and longer timescales. The lower limit of observable dynamics is limited only by the shortest pulse of light that can be produced. The techniques that will be discussed in the following sections of this chapter include Vis pump–IR probe, broadband IR pump–probe, and 2D IR. These techniques can be differentiated by the different ways in which the sample is pumped into an excited state.

The features shared by the ultrafast vibrational spectroscopic techniques, by virtue of the particular configuration of the instrumentation during the time this body of work was carried out, are: (1) the light source, (2) the method in which spectra are acquired, and (3) the way in which the data is acquired and hardware automated. Following the discussion of these common features will be a discussion of the particulars of each ultrafast vibrational spectroscopy technique.

Light source

Ultrafast vibrational spectroscopy was made possible with the generation of short laser pulses (sub-100 fs) in a self-modelocking Ti³⁺:sapphire laser system.¹³ Ti³⁺:sapphire is an ideal gain medium for ultrafast spectroscopy because it supports an enormous number of longitudinal
modes (~10^4), has a high damage threshold, and high thermal conductivity. These properties of Ti^{3+}:sapphire enable ultrafast (down to a few fs) pulse generation via modelocking. As mentioned previously, the pulse duration sets the lower bound on the ultimate achievable temporal resolution. The generation of ultrafast pulses is accomplished through the design of a laser oscillator. The particular Ti^{3+}:sapphire laser oscillator used in this work is the commercially available Vitesse (Coherent, Inc., Santa Clara, CA). An 80 MHz “train” of ~100 fs, 3 nJ pulses centered about 800 nm (± 10 nm) are typical of this particular laser system. The author notes that output of the Vitesse for our particular configuration has been measured to be ~801 nm (data not shown). At this stage, we have ultrafast pulses of light centered on the fundamental transition of Ti^{3+} in sapphire.

In order to drive nonlinear optics, high peak power densities are required. High peak power densities can be generated by one of two methods, either by reducing the size of the beam or by increasing the pulse energy. We perform the latter with a laser amplifier that amplifies the pulse energy (and thus peak powers) output by the laser oscillator by a factor of 10^6. The output of the Vitesse (with peak power ~30 kW or 3 MW/cm^2) is directed into the commercially available Integra-C (Quantronix Corporation, East Setauket, NY). Before amplification, however, the laser pulse goes through a pulse stretcher (a pair of gratings are used in this particular configuration) that increases the pulse duration by roughly a factor of 10^3. This has the practical advantage of avoiding chirping the pulse during amplification as well as avoiding burning optical materials. Next, the amplification is carried out in two sequential stages. The laser pulse firsts extracts energy from a Ti^{3+}:sapphire crystal situated in a regenerative cavity which is optically pumped by a Nd^{3+}:YVO_4 laser. A two-pass amplification stage follows the regenerative amplification. Again, the laser pulse extracts energy from a Ti^{3+}:sapphire crystal optically pumped by a Nd^{3+}:YVO_4 laser. Finally, the laser pulse is recompressed with another pair of gratings to (roughly) the original pulse duration. This results in pulses on the order of ~2 mJ, 120 fs, 1 kHz @ 808 nm (± 10 nm). The author notes that output of the Integra in our
particular configuration has been measured to be ~807 nm. The peak power at this point (for a 1 cm beam) is roughly 20 GW/cm², a power level capable of driving nonlinear optical processes.

Nonlinear optics vastly expand the wavelength range accessible compared to the output of a Ti³⁺:sapphire laser. Although Ti³⁺:sapphire lasers can be tuned, they can only be tuned over a limited range of wavelengths extending roughly from 700 – 1000 nm. This wavelength range can be further extended to 350 – 500 nm with proper nonlinear optics to generate the second harmonic of the fundamental, i.e. second harmonic generation (SHG). One can perform electronic (i.e. optical) pump–probe spectroscopy in this fashion. Peak powers on the order of a few tens of GW/cm² produced via the laser amplification stage can drive nonlinear optics to carry out difference frequency generation (DFG) and sum frequency generation (SFG) and expand the wavelength range to cover the entire visible through the near-IR and into the mid-IR. Mathematical and conceptual details on nonlinear optical processes such as DFG and SFG can be found in ref. 16.

The generation of either visible or mid-IR light from the output of an amplified Ti³⁺:sapphire laser pulse is accomplished with the commercially available TOPAS package offered by Light Conversion (Lithuania). Two stages of nonlinear optics are required to generate wavelengths in the visible or mid-IR. Both an OPA crystal and a mixer crystal are the essential nonlinear optics extending the tunability of a Ti³⁺:Sapphire laser. First, a signal field (generated via superfluorescence of the BBO crystal) interacting with the fundamental output of a Ti³⁺:sapphire laser, called the pump field, is amplified and an idler field is generated through the nonlinear process of optical parametric amplification/generation in the BBO crystal. The wavelength ranges possible through this interaction are dictated by the conservation of energy and are between 1150 – 1600 nm for the signal field and 1600 – 2600 nm for the idler field.

Second, mixer crystals enable an even greater versatility of wavelengths. For example, the range of 580 – 1200 nm can be generated by second harmonic generation of the signal and the idler fields just mentioned. Higher energy wavelengths centered on the green portion of the
visible spectrum, i.e. 533 – 600 nm, can be generated by sum frequency generation of the idler field with the pump field. To generate mid-IR wavelengths, difference frequency generation in a AgGaS$_2$ crystal between the signal and idler fields can generate wavelengths in the range of 2600 – 11000 nm. Typical bandwidth of the output of the OPAs is the bandwidth of the Ti$^{3+}$:sapphire pulse which is ~200 cm$^{-1}$. Figure 2-4 displays spectra of the pump pulse and SHG of the signal field at 1200 nm resulting in 600 nm (or ~16640 cm$^{-1}$) and SFG of pump and idler fields at 800 nm and 1760 nm resulting in 550 nm (or ~18180 cm$^{-1}$). The bandwidth of all of these pulses of light is ~200 cm$^{-1}$. The mid-IR pulse generated at 5.75 µm, or ~1740 cm$^{-1}$, with DFG between signal and idler fields also has a bandwidth of ~200 cm$^{-1}$ (data not shown).

The pump pulse is mechanically chopped at 500 Hz with an optical chopper (New Focus Model 3501, Newport Corp., Irvine, CA) for lock-in detection. Lock-in detection, or sequential detection, of $T_{pumped}$ and $T_{not\ pumped}$ is particularly useful in the ultrafast pump–probe experiment where the laser light source is subject to a great deal of low frequency drift noise. Noise occurring at frequencies outside of the chopping frequency is largely eliminated, as discussed above for dispersive IR spectroscopy.

The probe beam size typically was measured and set to ~200-300 µm diameter. The pump beam size for the ultrafast vibrational spectroscopy experiments was typically set such that it was ~4/3 the size of the probe beam. The method for measuring and estimating pump and probe beam size will be discussed further below.

It is worthwhile to point out the importance of a stable external environment (in particular, temperature) for this particular light source. Given the large number of optics and long path which the light traverses, the system is highly sensitive to thermal fluctuations. As such, it is necessary to maintain a stable room temperature and to perform daily optical alignment of the laser system to maintain proper power levels and stability.
**Spectral Acquisition**

Spectra are acquired with this system by spatially dispersing the component wavelengths of the laser pulse with a grating in a monochromator having an array detector positioned at the exit slit. A detection system with this particular geometry is sometimes called a spectrograph. As discussed above in the introductory portion of Section 2.2, the advantage of this optical layout is that spectra can be calculated from a single laser shot (i.e. ratio of a single shot of two beams having propagated in different directions) which avoids a substantial amount of noise introduced by calculating a spectrum from the ratio of measurements of two different laser shots. More specifically, the light is directed toward and is dispersed within a monochromator (TRIAX 320 Monochromator, Horiba Jobin-Yvon, Edison, NJ). A 64 element MCT array detector (MCT-9-32x2, Infrared Associates Inc., Stuart, FL) is situated at the focal plane at the exit of the monochromator. The MCT array detector has two rows of 32 elements. Light beams that have interacted with the sample \((I)\) and that have not interacted with the sample \((I_o)\) are directed onto one of the two rows of 32 MCT array detector elements such that a transmittance measurement is calculated at all 32 wavelengths (i.e. a spectrum is calculated) each laser shot. The spectral resolution of this setup is not easily changed (without physically changing optics i.e. the grating), however, there is a large gain in signal-to-noise relative to an optical configuration in which a spectrum is acquired by scanning individual wavelengths. This gain in signal-to-noise arises because spectra are acquired each laser shot, there are no moving parts to obtain the spectrum (i.e. moving parts are subject to mechanical noise), and data averaging is quick (since spectra acquired each laser shot and each measurement corresponds to two laser shots so 1/500 Hz = 2 ms).
Data acquisition and automation

The majority of the hardware is controlled by a high-performance motion controller/driver (XPS-C8, Newport Corp., Irvine, CA). For example, the mechanical delay stages (discussed individually below) are controlled with the XPS-C8 controller. Spectra at different pump–probe time delays are acquired by varying the path length that the pump pulse travels (relative to the probe pulse) with a mechanical delay stage. The upper limit to the dynamics resolvable by the ultrafast pump–probe experiments described in this thesis is determined by the length of the mechanical delay stage.

The way in which the sample is mounted, or the sample geometry, is tailored to the specific experiment. Different substrates are used for different techniques as will be discussed below. For non-cryogenic experiments, the sample is typically mounted on a 3D translation stage. Two dimensions of this stage are controlled by automated, precision motorized actuators (LTA-HL, Newport Corp., Irvine, CA) while the third is controlled manually with a vernier micrometer (SM-13, Newport Corp., Irvine, CA). The non-cryogenic geometry offers simplicity, but the sample is fixed at room temperature and exposed to air during the experiment. Cryogenic experiments, which house the sample under vacuum and enable the researcher to vary the sample temperature over a wide range, are carried out by mounting the sample in an optical cryostat (ST-100, Janis Research Company, Wilmington, MA). Because of space restrictions, this requires the elimination of one automated axis. Thus, for cryogenic experiments, there is 1 manual axis and 1 automated axis (i.e. 2D translation stage).

A multi-channel laser pulse integrator system (IR-6416, Infrared Systems Development Corp., Winter Park, FL) calculates the transmittance at each wavelength and generates a spectrum for each laser shot of the femtosecond pulse. The multi-channel laser pulse integrator is a specialized system that acquires the signal generated by optical elements from a femtosecond laser pulse within the repetition rate of the laser (i.e. 1 ms). The IR-6416 does this by sampling
and holding the 64 signals generated by the 64 array elements via a user defined gate (~2.5 µs), sequentially converting each of these signals from A/D and multiplexing them into FIFO memory (~64 µs), and finally by transferring the data for the computer before the next laser shot fires (1 ms). The user defined gate is set to start when the detector responds (typically a few hundred ns), integrate over the detector response (typically a total of a few µs), and stop integrating when the response has decayed.

The multi-channel laser pulse integrator system is capable of accepting 16 external inputs, as well. The first 8 inputs are integrated according to the gate established for the array inputs. The other 8 inputs are single time measurements 40 µs after the trigger signal. Signals from diagnostic detectors and a chopper output signal are fed into the external channels. The diagnostic detectors are used to optimize the mid-IR laser pulse energy and stability, to optimize alignment throughout the optical bench, as well as to perform run-time statistical analysis (which will be described in the Appendix). The chopper output signal tags the $T_{\text{pumped}}$ and $T_{\text{not pumped}}$ measurements.

LabVIEW code was developed to automate motion of hardware, acquire data, process the data, and store data at the end of experiments. Hardware automated for all techniques includes the monochromator grating and entrance slit width, mechanical delay lines, and sample stage actuators. All data is post-processed in MATLAB (The Mathworks Inc., Natick, MA). Specific routines in both LabVIEW and MATLAB have been developed for each of the techniques that follow.

### 2.2.1.1 Vis Pump–IR Probe

Ultrafast Vis pump–IR probe spectroscopy (technically electronic pump–IR probe) is used to probe the dynamics of a system with a mid-IR probe pulse following excitation with an optical pump pulse. In the context of this thesis, the mid-IR probe pulse will be used specifically
to measure the response of vibrational modes of the materials within the system. However, the author notes that electronic transitions do appear in this spectral window in OPV materials\textsuperscript{19} as will be discussed briefly in Chapter 3. The temporal resolution of the Vis pump–IR probe technique, which sets the limit on the fastest resolvable dynamics, is determined by the widths of the optical pump and mid-IR probe pulses (~200 fs) while the observation time, which sets an upper limit on the measurable dynamics, is determined by the length of the pump–probe delay stage. A 600 mm linear mechanical delay stage (IMS600CCHA, Newport Corp., Irvine, CA) is used to vary the pump–probe time delay setting an upper limit of ~5 ns on the observation time. Pump wavelengths used in the experiments will be reported where necessary.

Pump energy density measurements for Chapters 6 & 7 were made as follows. First, an approximate measure of the beam size was obtained by measuring the beam intensity transmitted through a pinhole according to the equation

\[ I(r) = I_0 \left[1 - \exp\left(-2r^2/w^2\right)\right] \]  

where \( I(r) \) and \( I_0 \) are the intensity measured with the pinhole in place and the total measured intensity, respectively, \( r \) is the radius of the pinhole, and \( w \) is the e\textsuperscript{-2} radius of the beam. Precision, high-energy laser pinholes (04 PHP Series, CVI Melles Griot, Albuquerque, NM) with diameters of 100 and 200 µm were used depending on the beam size to be measured. The beam size was determined with measurements from the array detector for the infrared probe beam, a single element detector for the infrared pump beam, and a photodiode for the visible pump beam.

The visible pump pulse energy was measured with a Coherent pyroelectric sensor (J-10-MB-LE) capable of detecting pulse energies down to 300 nJ over a broad spectral range from 0.19 to 12 µm\textsuperscript{20}. As a brief aside, the detector element (10 mm dia., 78 mm\textsuperscript{2}) is one of the largest commercially available for such a broad spectral response and, importantly, with an RC time constant suitable for a 1 kHz laser system. The large size relative to most small area (i.e. 1 mm\textsuperscript{2}) pyroelectric detectors results in a substantially easier time optimizing the mid-IR pulse energy
and stability and aligning the mid-IR beam. The pump pulse energy density was approximated according to

\[
\text{Energy Density} = \frac{\text{Pulse Energy}}{\text{Beam Diameter}}
\]

(9)

Pump energy density values reported in Chapter 3 were inferred from measurements on later experiments with similar signal sizes.

For a fixed pump beam size, the pump pulse energy can very easily be varied with the use of neutral density filters. We use a neutral density filter wheel (New Focus Model 5215, Newport Corp., Irvine, CA) that has reflective neutral density filters which can vary the optical density (OD) from 0.08 to 3.0. Reflective neutral density filters are used because absorptive neutral density filters significantly affect the path length that the pump pulse travels (and so change the relative pump–probe time delay).

2.2.1.2 IR Pump–IR Probe

IR pump–IR probe comprises both broadband IR pump–probe and 2D IR techniques. Each of these techniques shares in common the distinction that dynamics of vibrational excited states are measured directly through vibrational modes. The utility of each of these techniques will be discussed below, but before that, the optical elements they share in common will be discussed.

A 50 mm linear mechanical delay stage (ILS50CCHA, Newport Corp., Irvine, CA) sets \(~300\) ps to be the mechanical upper limit to the dynamics which can be measured by the IR pump–IR probe experiments. The true upper limit is actually much shorter due to the finite lifetime of vibrational excitations.

Because the pump wavelength is identical to the probe wavelength being detected, both pump and probe photons scattered by the sample can interfere with detected signal if they reach
the detector (either through the monochromator or by other means). Phase cycling is performed in the IR pump–IR probe experiments to reduce the contribution of scattered infrared photons from the measured signal. Scattering sources can include the sample or the chopper, for example. Phase cycling is accomplished by sequentially measuring spectra at $-\lambda/4$ distance and at $+\lambda/4$ distance. The retroreflector mounted on the delay stage for the infrared pump beam is also mounted on a single axis piezo positioner (Thorlabs NF5DP20S, Thorlabs Inc., Newton, NJ), which is controlled by a closed loop piezo controller (Thorlabs BPC203, Thorlabs Inc., Newton, NJ). The single axis piezo positioner varies the distance of the pump delay stage for phase cycling. The summation of the two spectra measured at $-\lambda/4$ distance and at $+\lambda/4$ distance cancels out erroneous signal from randomly scattered photons. Of course, an alternative method to reduce scattered photons is to prepare as smooth a film as possible. This issue will be discussed below for each sample preparation method, i.e. Sections 2.3.1-2.3.3.

*Broadband IR Pump–Probe*

Broadband IR pump–probe spectroscopy is used to measure population relaxation (i.e. determine vibrational lifetimes) as well as measure orientational dynamics. The temporal resolution of the broadband IR pump-probe technique is set by the pump and probe pulse duration (~200 fs) and the observation window limited to ~300 ps as discussed above.

Holographic wire grid polarizers (WP25H Series, Thorlabs Inc., Newton, NJ) are placed in the path of pump and probe beams as close to the sample as possible so as to provide the purest possible linearly polarized light to the sample.\textsuperscript{21} The two polarizers are placed such that the angle of the probe pulse polarization is 45° relative to the pump pulse polarization. Another holographic wire grid polarizer is placed in the path of the probe beam after it has interacted with the sample and is held in an automated rotation stage (NSR1, Newport Corp., Irvine, CA), which is controlled by a stepper motor controller/driver (NSC200, Newport Corp., Irvine, CA). Again,
the polarizer is set in place directly after the sample\textsuperscript{21} so as to minimize deviations of polarization purity through interactions with optics. Measurements of the signal obtained with the polarization component of the probe pulse oriented parallel and perpendicular relative to the pump pulse enables calculation of pure population relaxation and orientational anisotropy, which will be described in Chapter 5. The use of an automated rotation stage to sequentially acquire parallel and perpendicular measurements circumvents substantial noise introduced by low frequency laser drift.

2D IR

2D IR spectroscopy is a multidimensional spectroscopic technique in which the signal is plotted against two energy axes. As with other multidimensional spectroscopic techniques, this technique is a powerful tool capable of measuring molecular structure and dynamics. For example, 2D IR was recently used to measure the timescale for the appearance of cross peaks concentrated aqueous solutions of sodium tetrafluoroborate (NaBF\textsubscript{4}). The appearance of cross peaks indicates coupling between the transition dipole moment of the two vibrational modes and the timescale of its growth was taken to represent the timescale for anion-water hydroxyl hydrogen bond switching.\textsuperscript{22} The measured timescale for this process was 7 ps at 300 K. Also, a technique has been developed based on 2D IR to measure the spatial proximity of vibrational modes over long distances.\textsuperscript{23} The information from 2D IR is not limited to coupling, however. Information on vibrational dynamics through analysis of the dynamic 2D line shape along the diagonal provides information on inhomogeneous broadening, homogeneous broadening, and spectral diffusion. Spectral diffusion was used to determine the solvent structure around the OH stretching mode of deuterated phenol in a mixed solvent consisting of carbon tetrachloride and mesitylene,\textsuperscript{24} for example.
There are two ways to acquire a 2D IR spectrum, either in the frequency or time domain. These methods reflect different ways in which the pump axis is generated. We use an etalon to narrow the bandwidth of the infrared pump (i.e. narrowband IR pump–broadband IR probe) to generate the horizontal axis and use a monochromator to resolve the probe, or vertical axis. The name for this is transient hole burning spectroscopy. Hole burning, in this context, means that the pump pulse spectrum is narrower or equal to the homogeneous linewidth. Transient hole burning is the way in which the first 2D IR spectra were acquired. Generating the horizontal axis in the time domain requires having control of pulse sequences. Shim et al. have recently developed a pulse-shaping technique that makes available a variety of pulse sequences. The interested reader is referred to a very recent and excellent text dedicated to 2D IR.

In all techniques, a narrow distribution of oscillators is populated with a pump pulse, given time to evolve, and the new distribution is detected after some time delay. Transient hole burning is performed with the use of an etalon. The etalon acts to substantially narrow the bandwidth of the pump pulse. The physical basis of an etalon is interference. Specifically, constructive and destructive interference between the different wavelengths of light occurs at the output of the etalon as the light field makes multiple reflections between two highly reflective, nearly parallel mirrors with multiple light fields leaking out. The high reflectivity mirrors are ZnSe substrates with an anti-reflective coating on one surface and a highly reflective dielectric stack coated on the other surface. Picomotor actuators (Newport Model 8301, Newport Corp., Irvine, CA) with high spatial precision, controlled by a picomotor controller & hand terminal (Newport Models 8752 & 8757, Newport Corp., Irvine, CA), enable parallelization of the mirrors. By changing the distance between the mirrors the conditions are changed such that a different wavelength (along with its many orders) passes through. This distance is very short and for the wavelengths in these experiments is on the order tens of micrometers. A few cm$^{-1}$ shift can be introduced by either varying the angles between mirrors by a few hundredths of a degree or by changing the distance between the mirrors a few tens of nanometers. In our case, we vary...
the distance between mirrors with a single axis piezo positioner (Thorlabs NF5DP20S, Thorlabs Inc., Newton, NJ) that is controlled by a closed loop piezo controller (Thorlabs BPC203, Thorlabs Inc., Newton, NJ) and has precision on the order of 10 nm.\textsuperscript{29}

Narrowing the bandwidth of the pump pulse spectrum with an etalon has a significant impact on the temporal profile of the pump pulse. For example, the pulse bandwidth in the "broadband" experiment is \(~200\) cm\(^{-1}\) with a corresponding pulsewidth of \(~200\) fs. The product of these two values results in a time-bandwidth product of \(~1.2\), slightly above the transform-limited value for gaussian-shaped pulses of \(~0.44\).\textsuperscript{30} By physically narrowing the bandwidth of the pump pulse spectrum to \(~5\)–\(~10\) cm\(^{-1}\), the pulse duration becomes \(~1.5\)–\(~3\) ps as determined by the time-bandwidth product for gaussian-shaped pulses (and assuming they are transform-limited). The duration of the pump pulse in the transient hole burning 2D IR experiment therefore sets a lower limit to the pump–probe time delay. Other techniques, such as 2D IR vibrational echo spectroscopy,\textsuperscript{31,32} are capable of accessing faster dynamics and are only limited by the lowest achievable pulse duration (i.e. sub-picosecond).

Although conceptually quite simple, the transient hole burning experiment is subject to a major artifact when purging the system to eliminate water vapor. Significant drift in the absolute frequency of the narrowband IR pump pulse occurs over a period of time. This drift is not unexpected given the sensitivity of the output of the etalon to changes in the distance between the two mirrors. The author finds that variations are significantly pronounced when purging with dry air. Purging with dry air may lead to continuous, but subtle changes in the refractive index between the mirrors of the etalon (which changes the effective distance between the mirrors) as the atmospheric chemical composition is continuously varying (and depends on the purity of the dry air source as well as the steadfastness of the system enclosure). In order to compensate for drift of the narrowband IR pump pulse spectrum during 2D IR experiments, a spectrum of the pump is acquired at a user-defined interval. This is accomplished with an automated, miniature steel linear stage (Newport MFA-CC, Newport Corp., Irvine, CA) controlled by the XPS
controller that interjects the IR probe beam path and directs the narrowband IR pump beam into the monochromator for a measurement of the spectrum. The center of this peak is compared to the center of the peak measured at the beginning of the experiment and from these measurements a correction factor is calculated that is added to the values sent from LabVIEW to the APT controller that controls the etalon mirror spacing.

2.2.2 Time-resolved IR Spectroscopy

Time-resolved infrared (TRIR) spectroscopy is a technique capable of investigating the effect of electronic excited states on molecular vibrational modes on the µs to ms timescale. TRIR is distinguished from ultrafast pump–probe in that only a single laser pulse is present in the experiment and the time axis is generated by an A/D converter. An outline of the setup is illustrated in Figure 2-5. The second harmonic (532 nm) of a solid-state Nd³⁺:YAG laser (Surelite I-50, Continuum, Inc., Santa Clara, CA) serves as the visible pump pulse. The Nd³⁺:YAG laser is operated at 50 Hz and the pulse duration at this wavelength is ~6 ns. The TRIR experiment shares the same components as the dispersive IR setup outlined in section 2.1.2. Specifically, this includes the same IR ceramic element (light source), monochromator, MCT detector, current mode preamplifier, and A/D converter.

The temporal resolution of the TRIR system is determined by the electronics (or A/D converter). A trigger pulse from the Nd³⁺:YAG laser power control unit is used to trigger and initiate analog-to-digital conversion in a multichannel DAQ device (PCI-6250 M Series, National Instruments Corp., Austin, TX) which has 16-bit resolution and samples multiple channels at a rate of 1 MHz. The temporal resolution for this system is 1 µs. The upper limit for these particular experiments is determined by the repetition rate of the laser, i.e. 20 ms.

TRIR spectra are obtained in a fashion similar to the dispersive IR experiment. The grating angle is manually tuned in a step-by-step fashion and the spectral resolution is subject to
all of the constraints mentioned above for the dispersive IR spectrometer. For TRIR experiments, the AC signal (rather than DC) is output to the A/D converter. The AC signal is used because it rejects low frequency noise below the RC time constant of the preamplifier (which is 1.5 Hz for this particular preamplifier) and passes and amplifies the signal generated by the laser (i.e. 50 Hz). For the measurements reported in this thesis, an optical chopper and lock-in detection was not used. In order to account for the electronics noise arising from, for example, the high voltages discharged and used to drive the electrical and electro-optical components in the Nd\textsuperscript{3+:YAG} laser system, \( \Delta T \) measurements were made by first acquiring data with the sample exposed to the laser pulse (i.e. \( T_{\text{pumped}} \)). Measurements were subsequently obtained with the laser pulse blocked (i.e. \( T_{\text{not pumped}} \)). Although not the best configuration (i.e. lock-in detection would be preferred), this allowed for the subtraction of environmental noise associated specifically with the laser power supply. An optical chopper was recently integrated and more properly helps eliminate noise.

### 2.3 Sample Preparation

The films that were prepared for pump–probe spectroscopy will be discussed. A brief discussion of the issues that arise when preparing films for pump–probe spectroscopy will come first. Subsequently the different methods of sample preparation used in this thesis and the advantages and disadvantages associated with each method will be discussed.

The simplest OPV device consists of the active layer (OPV materials) sandwiched between two electrodes (Figure 2-7A). The interested reader is referred to a recent review by Hoppe and Sariciftci\textsuperscript{35} for a discussion of more elaborate device structures. Although ideally a complete device could be studied (this would allow control of voltage across the sample and measurement of current), the work in this thesis only includes pump–probe spectroscopy of the active layer without any electrodes attached (Figure 2-7B).
Given that the probe detects vibrational transitions in the infrared and that the absorption coefficients of these transitions are quite low (ε ~ 10^3 is typical for some of the stronger transitions, i.e. the carbonyl stretching transition), the measured signals are very weak. It is natural to attempt to maximize the thickness in order to obtain the largest signal size. Maximizing the film thickness has important drawbacks as will be discussed in more detail in the Appendix. One issue that arises is that long-drying times are required for thick films that lead to coarse phase separation of materials and a lack of control of film morphology. We will report estimated and measured film thicknesses where necessary, but these are qualitatively determined by the different techniques as discussed below.

The overall quality of the deposited film, or film uniformity, is another factor of concern for Vis pump–IR probe experiments. Raster scanning during the experiment across areas of the film is ideal so as to avoid sample degradation. However, non-uniform films complicate interpretation of a signal obtained by means of raster scanning. Non-uniform films can result from an unlevel surface or inconsistent drying. In the case of inconsistent drying, one region may be exposed to solvent vapor for a long time and become “annealed” while another region is exposed only for a short duration and is “unannealed”. The transient spectrum obtained by rastering will be the average of the two, i.e. information is lost.

Many methods are available to deposit the active layer and have been discussed in a review by Krebs. The deposition methods that are relevant to this thesis include drop casting, spin casting, and spray coating. Below, we will briefly describe each method and the advantages and disadvantages associated with each. It is important to keep in mind the effect that each method of deposition has on active layer morphology (presuming one has control over morphology). In fact, even within a specific deposition method there may be a special ‘recipe’ that gives the best morphology.
2.3.1 Drop casting

Drop casting is the simplest deposition method. No special equipment is required. To drop cast a film, a solution with the active materials is prepared and is dispensed onto a flat substrate. The solution dries leaving a film of the active layer on the substrate.

The advantages of drop casting are that (1) no sample is wasted, (2) thick films can be prepared, and (3) film thickness can be estimated. Although crude because of film non-uniformities as discussed above, the film thickness can be estimated from the amount of active material deposited, the average density of the active materials, and the dimensions of the substrate. Film non-uniformities can be minimized (and generally smoother films can be prepared) by rotating the sample at low rotation cycles (80 rpm) as the solvent is evaporating.

The disadvantage with this method of deposition is that, as discussed above, only annealed films can be prepared. And so there is no control over film morphology. Since films form by slow evaporation of the solvent, this technique produces films that have been solvent annealed.

2.3.2 Spin coating

Spin coating is nearly as simple as drop coating, but requires a spin coater. Spin coating involves dispensing a solution of the active materials on a substrate secured in a spin coater. Subsequently, the substrate is spun at high speeds (>500 rpm) to form a film within a short period of time (i.e. several seconds). We use a single wafer spin processor (WS-400B-6NPP-LITE, Laurell Technologies Corp., North Wales, PA) that has the capacity to spin between 100 – 8000 rpm. Spin coating is the most widely used method of preparing bulk-heterojunction OPV films.

The advantages include the following: (1) ability to generate thin films, (2) ability to control morphology. The disadvantages are as follows: (1) a large portion of sample material wasted, (2) inability to make thick films, and (3) film uniformity can be an issue.
The author has found that solution viscosity and, to a lesser extent, spin speed are the primary factors affecting film thickness. Solution viscosity depends on solution concentration as well as on the material being deposited. The author has found the following reference containing a calibration curve for polystyrene spun at different solution concentrations and spin speeds useful.\textsuperscript{38}

\subsection*{2.3.3 Spray coating}

Finally, spray coating will be discussed. Spray coating was spearheaded as an alternative to spin coating to use less material. Spray coating involves the dispersal of a solution of the active materials through the nozzle of an Iwata Kustom TR series air brush (K9400, Iwata-Media, Inc., Portland, OR). We used nitrogen as a carrier gas.

The advantages of spray coating include: (1) ensuring a homogeneous mixture. Devices based on RR-P3HT and PCBM with efficiencies of up to 3\% have been prepared by spray coating with an airbrush\textsuperscript{39,40} and in a more reproducible fashion with a fixed ultrasonic spray nozzle.\textsuperscript{41} (2) Presumably thick films can be prepared (although effects on morphology are not entirely clear as each additional layer re-dissolves underlying layers). Disadvantages are (1) that the film can come out quite rough and (2) initial wetting of the substrate can be an issue (as the initial droplets have less surface area to interact with the substrate).

\section*{2.4 References}

\begin{enumerate}
\end{enumerate}


(7) Manufacturer specs.


(12) Ultrafast is considered the time range $10^{-9}$ to $10^{-14}$ s; see, for example, ref. 8.


(14) Manufacturer specs.

(15) Manufacturer specs.

TOPAS is an acronym used by Light Conversion which stands for travelling wave optical parametric amplification by superfluorescence.

Superfluorescence meaning fluorescence retaining the properties of a laser pulse.


Manufacturer specs.


The special case where the highly reflective mirrors are parallel is called a Fabry–Pérot interferometer.

Manufacturer spec.


(33) Manufacturer final test report.

(34) Manufacturer spec.


(37) Manufacturer spec.


**Figure 2-1.** Harmonic (dashed) and anharmonic (solid) vibrational potentials. Sold lines overlapping the anharmonic potential indicate quantized vibrational states. 0–1 and 1–2 transitions are indicated with red and blue arrows, respectively.
Figure 2-2. (A) Diagram of dispersive IR spectrometer. (B) FTIR spectrum collected with 0.5 cm⁻¹ resolution (and one level of zero filling) plotted against dispersive IR spectrum collected with exit and entrance slit widths of the monochromator set to 0.5 mm. Spectra have been offset and normalized arbitrarily to highlight differences in spectral resolution.
Figure 2-3. (A) Interaction of a simple three-level system with a pump pulse. (B) Result of absorption. Corresponding possible transitions are discussed in the text.
Figure 2-4. Output of laser amplifier (~12,390 cm\(^{-1}\)) used to pump OPAs and output of OPA used to generate optical pulses of light at either ~16,640 cm\(^{-1}\) via SHG of the signal field or ~18,180 cm\(^{-1}\) via SFG of pump field with idler field. Energies of ~12,390, ~16,640, and ~18,180 cm\(^{-1}\) correspond to wavelengths of ~807, ~600, and ~550 nm, respectively. Spectra were acquired with an Ocean Optics USB2000 fiber optic spectrometer and are normalized to unit height. Scattered light was transmitted to the spectrometer through a QP200-2-UV/Vis µm optical fiber.
Figure 2-5. Simplified diagram of the ultrafast vibrational spectroscopy laser system and associated optical layout.
Figure 2-6. Diagram of the time-resolved IR spectrometer.
Figure 2-7. Diagram of (A) basic OPV device and (B) OPV samples studied in this thesis.
3.1 Introduction

We saw in Chapter 1 that the low cost potential of organic photovoltaics (OPVs) can only be realized with more efficient devices. In an effort to understand the fundamental processes that limit organic photovoltaics and to guide the design of more efficient materials, we have developed Vis pump–IR probe spectroscopy to study the fundamental processes that occur in OPV materials. Toward this end, we present in this chapter Vis pump–IR probe experiments on an OPV blend film consisting of the π-conjugated polymer CN-MEH-PPV and the functionalized fullerene PCBM (Figure 3-1).

The initial elementary steps leading to photocurrent generation in an OPV device are displayed in Figure 3-2. Light absorption by the electron donor results in the formation of an exciton. The exciton then diffuses to the interface between electron donor and acceptor materials. Once at the interface, charge separation occurs in two-steps. First, charge transfer from the electron donor to acceptor material results in a Coulombically bound electron-hole pair at the
interface, i.e. a charge-transfer (CT) state (Step 1). The electron-hole pair in the CT state must overcome their mutual Coulombic attraction to form separated charge carriers, or a CS state (Step 2).

Barbour et al. were the first to use ultrafast vibrational spectroscopy to measure the rate of charge separation in an OPV blend film. The interpretation of the experiment rested on three critical observations/assumptions. First, the carbonyl stretching absorption observed in a blend film comprised of PCBM and CN-MEH-PPV arises solely from PCBM. A gradient of carbonyl stretching frequencies exists in PCBM domains (Figure 3-3A) which correlates with increased interaction of PCBM molecules with the polymer through finer intermixing at different blend-weight ratios (Figure 3-3B). Interaction with the polymer causes those PCBM molecules existing near the interface to have a higher carbonyl stretching frequency. Second, bleaching of the carbonyl stretching mode of PCBM results from the transfer of an electron from the electron donor, CN-MEH-PPV, to the electron acceptor, PCBM (Figure 3-3A). As expected and in accord with the model presented above, the center frequency of the bleach is initially at high frequencies. Finally, resolving the frequency shift of the bleach of the carbonyl stretch of PCBM is a metric of charge separation, i.e. the motion of charge carriers away from the interface (Figure 3-4). The rate at which the bleach center frequency approaches the value of the vibrational frequency of PCBM molecules existing away from the interface is taken as a measure of the rate of CT state dissociation.

The exact mechanism by which a CT state dissociates into separated charge carriers is still debated. Specifically, is excess energy involved in the dissociation reaction? In other words, is the reaction thermally activated? Muntwiler et al. have used two-photon photoemission spectroscopy to identify CT states across the pentacene:air interface, i.e. CT states existing on the surface of pentacene with the image band in vacuum serving as electron acceptor. They observe several CT states ranging in energy from 0.1 – 0.4 eV. They propose that efficient charge separation can only occur through the most energetic, or “hot,” CT states. Vardeny et al.
investigated the role of excess free energy in the charge separation process in MEH-PPV:C60 and RR-P3HT:PCBM blends. They found the efficient generation of fully separated charge carriers, or positive and negative polarons, when exciting these blends either above the band gap of the polymer or below the band gap of the polymer. When exciting the blend below the band gap, CT states were directly excited. Based on the large yield of polarons (and correspondingly long lifetime) observed in the steady-state action spectrum obtained with below-gap excitation, they conjectured that the polarons generated via below-gap excitation did not represent a major contributor to the photocurrent in devices supporting the proposition by Muntwiler et al. However, a recent study by Lee et al. seems to suggest that charge separation does not depend on temperature or excess free energy. These authors found identical internal quantum efficiencies (IQEs) for MDMO-PPV:PCBM and P3HT:PCBM blends excited above as well as below the band gap of the polymer implying the dissociation probability for all of CT states with excess energy is the same as thermalized CT states. Furthermore, they found that the open-circuit voltage, which is logarithmically proportional to the photocurrent under the condition of open-circuit, did not differ for above- or below-gap excitation except at low temperature where very minor differences were observed. They also found that the photocurrent measured at two voltages and at a range of temperatures varied only slightly for above- and below-gap excitation. These observations, again, imply that excess energy is not involved in the generation of separated charge carriers. In an effort to clarify the mechanism of charge separation in OPV materials, we have carried out Vis pump–IR probe experiments to measure the energy required for the dissociation of charge transfer states into separated charge carriers in an OPV blend film consisting of CN-MEH-PPV and PCBM.

First, the materials and methods relevant to this chapter will be presented. The results and discussion will follow, beginning with a discussion of the steady-state spectra of the system under investigation. Next, the reader will be introduced to the ultrafast Vis pump–IR probe data and the methods to analyze this data. Following this demonstration, data collected at different
temperatures will be presented. Finally, we will demonstrate the method which we have developed to calculate the rate of charge separation at each temperature.

### 3.2 Materials and Methods

OPV blend films for the Vis pump–IR probe experiments in this chapter were prepared as follows. Equal masses of the electron donor, CN-MEH-PPV (American Dye Source, Inc., Baie D’Urfe, Quebec, Canada), and electron acceptor, PCBM (Sigma-Aldrich, St. Louis, MO), were added to a vial. Enough chlorobenzene (Sigma-Aldrich, St. Louis, MO) was added to dissolve the materials and make a 20 mg/mL solution. To fully dissolve the materials, the vial containing the OPV materials and solvent was sonicated for ~1 hr at 40 °C. After sonication, 50 drops from this solution were transferred via Pasteur pipette to a 3 mm thick, 1 in. diameter CaF\textsubscript{2} substrate (Red Optronics, Mountain View, CA) in sequential stages; first, 15 drops of solution were transferred via a Pasteur pipette to coat the surface of the substrate, given time to dry, followed by the addition of another 35 drops. The CaF\textsubscript{2} substrates were spun at 80 rpm during the drying process to ensure better quality films. Films prepared in this way had a carbonyl stretching absorbance of ~0.3.

OPV blend films for TRIR experiments were prepared by spray coating. This method was chosen for TRIR experiments because more uniform and smooth films could be prepared. These conditions are needed because the light sources interact with a larger region of the sample in the TRIR experiments. For spray coating, equal masses of CN-MEH-PPV and PCBM were dissolved in chlorobenzene solution with a total concentration of 1 wt\% and sonicated for ~1 hr. The resulting solution was transferred to the air brush via Pasteur pipette and dispensed from the air brush using nitrogen as the carrier gas. The solution was dispensed onto one surface of the substrate in two passes, i.e. one pass comprising the upper half of the substrate surface and the other pass comprising the lower half of the substrate surface. The solution was allowed to dry
(~30 s) following each top and bottom pass. About 60 (top and bottom) passes total yielded a film with a carbonyl stretching absorbance of ~0.2.

For the Vis pump–IR probe experiment, the pump pulse was centered at 550 nm while for the TRIR experiment the pump pulse was centered at 532 nm. The beam diameter for each experiment was on the order of ~500 μm and ~1 cm, respectively. Excitation densities of ~2 mJ/cm² were used to excite the sample in both experiments. The sample was held in an optical cryostat at ~0.1 torr dynamic vacuum at temperatures of 200, 250, 300, and 350 K.

More detailed information on the infrared spectrometers and Vis pump–IR probe techniques is included in Chapter 2.

### 3.3 Results and Discussion

Transient (Vis pump–IR probe) spectra collected in a 1:1 CN-MEH-PPV:PCBM blend film held at 300 K and excited with a 550 nm pump pulse are displayed in Figure 3-5A. All transient spectra have two general features. The first is a broad, negative photoinduced absorption attributed to the photoinduced absorption of polarons and/or excitons generated in the electron donor by the pump pulse. It has been estimated that only ~10% polarons are generated in PPV-based polymers upon direct excitation. Thus, this signal can arise from either the photoinduced absorption of a low-energy polaron transition (with relatively high oscillator strength) or the tail of the photoinduced absorption of a high-energy exciton transition (also with relatively high oscillator strength on resonance, but not expected in this spectral range). The second feature in the transient spectra is a positive going featuring which results from the bleaching of the carbonyl stretching absorption of neutral ground state PCBM. The carbonyl bleach arises from the transfer of charge from polymer to PCBM (i.e. the dissociation of an exciton).
Transient spectra obtained at several pump–probe time delays are shown in Figure 3-5A. At the earliest pump–probe time delays (ps and earlier), the carbonyl bleach is centered at ~1745 cm\(^{-1}\). The bleach is shifted ~5 cm\(^{-1}\) higher relative to the steady-state carbonyl stretching absorption measured in the blend and ~8 cm\(^{-1}\) higher relative to the steady-state carbonyl stretching absorption measured in bulk PCBM. As mentioned in the introduction of this chapter, the appearance of the carbonyl bleach at high frequency initially is expected because electron transfer is highly distance dependent.\(^8\) As such, the transfer of charge must occur at the interface between electron donor and acceptor materials; in other words, excitons generated at the interface upon excitation are dissociated \textit{at the interface} on ultrafast timescales (<100 fs). The presence of charge on PCBM causes the carbonyl stretching frequency of PCBM to change and results in the bleach in the transient spectrum. Transfer of charge occurs preferentially on the high frequency side at early times corresponding to PCBM molecules located near the polymer:PCBM interface. At longer times, the carbonyl bleach feature shifts to lower frequency and broadens.

In order to extract quantitative information on charge separation occurring in this system, a method to fit the transient spectra was developed. In the method, first a 3rd order polynomial is fit to the broad photoinduced absorption offset. Subsequently, a Gaussian line shape is fit to the carbonyl bleach feature. Both of these fits are overlaid on the transient spectra in Figure 3-5A.

The resulting fits to the carbonyl bleach line shape for all transient spectra are displayed in the 2D surface plot in Figure 3-5B. The shift of the carbonyl bleach center frequency toward low frequency at long time delay is reproduced by the fit, as indicated by the dashed line which serves as a guide to the eye. The carbonyl bleach center frequency approaches an asymptotic value which corresponds to the carbonyl stretching frequency of PCBM in the blend (~1740 cm\(^{-1}\)). The shift of the carbonyl bleach toward an asymptotic limit corresponding to the carbonyl stretching frequency of PCBM in the blend is taken to be representative of the dissociation of a CT state existing at the interface into spatially separated charge carriers. The rate of this process
can be calculated by calculating the rate at which the carbonyl bleach frequency approaches its asymptotic limit (as will be described below).

Transient spectra collected at a range of temperatures in a 1:1 CN-MEH-PPV:PCBM blend film are displayed in Figure 3-6A. All datasets show the same general features, i.e. a broad photoinduced absorption and a bleach of the carbonyl stretch of neutral ground state PCBM. Furthermore, all datasets exhibit a high frequency carbonyl bleach feature at the earliest pump–probe time delays which shifts toward lower frequency at longer pump–probe time delays. Interestingly, as the temperature is lowered, the asymptotic center frequency that the bleach approaches becomes progressively lower in value. A dashed line is placed at this asymptotic frequency to illustrate this point. The possible origin of this progression will be described in more detail below. The same fitting routine applied to the transient spectra in Figure 3-5A was applied to the transient spectra displayed in Figure 3-6A; the corresponding Gaussian fit to the carbonyl bleach of each transient spectrum is shown in the 2D surface plots in Figure 3-6B.

The bleach center frequencies obtained from the Gaussian fits are shown in Figure 3-7A. Between 1 and 10 ps the data are nearly identical at all temperatures in which the experiment was carried out. After ~30 ps, the center frequency shifts toward different asymptotic values for different temperatures, becoming progressively lower in frequency for lower temperatures.

Transient (TRIR) spectra of 1:1 CN-MEH-PPV:PCBM films collected 20 µs after excitation by a pump pulse at 532 nm are displayed in Figure 3-7B. The transient spectra show a carbonyl bleach feature whose center frequency is consistent with that measured in the ultrafast experiment at the longest time delay (~5 ns). Thus, it appears that the frequency of the carbonyl bleach nearly approaches its asymptotic limit within a few ns.

We are unsure as to the exact origin of the progression of the asymptotic frequency to lower frequencies at lower temperature. We hypothesize that the charge carriers become trapped in ordered regions of PCBM at low temperature within a few nanoseconds. We expect the films prepared in the manner described in this chapter to be largely solvent annealed. Annealing has
been shown to drive the crystallization of PCBM out of the blend.\textsuperscript{9} Zhu et al. describe that, at least for molecular crystals, crystalline domains rather than domain boundaries may serve as low energy trapping sites.\textsuperscript{10} Crystalline domains are expected to serve as low energy trapping sites because the charge carrier has a lower total energy in crystalline domains. Figure 3-8A displays dispersive IR spectra of 1:1 CN-MEH-PPV:PCBM blend films obtained at 300, 210, and 120 K. The spectra have been normalized to the carbonyl stretching absorption of PCBM. The carbonyl stretching band exhibits a subtle shift to lower frequency with decreasing temperature. The shift is made more pronounced in the difference spectra displayed in Figure 3-8B where the dispersive IR spectrum obtained at 300 K was subtracted from the spectra acquired at 210 and 120 K. A similar effect (i.e. shift of the carbonyl absorption to lower frequency) has been observed in semicrystalline nylon 11 at low temperatures which was attributed to dipolar coupling between polymer segments made possible by increased order.\textsuperscript{11}

In order to calculate the rate of charge separation from the data in Figure 3-6A, a simple kinetic model was developed. First, we calculate the asymptotic frequency from the best fit to the carbonyl bleach frequency shift dynamics with a multi-component function, \( f(\omega) \), expressed in the form:

\[
f(\omega) = \omega_i - (\omega_f - \omega_i) \left[ 1 - a_1 \exp\left(-\frac{t}{\tau_1}\right) - a_2 \exp\left(-\frac{t}{\tau_2}\right) \right. \\
\left. - \left(1 - a_1 - a_2\right) \left(\frac{1}{1 + (t/\tau_3)^n}\right)\right]
\]

\( (1) \)

where \( \omega_i - \omega_f \) is the magnitude of the frequency shift observed for a given temperature. This particular functional form was chosen as it is the simplest that adequately describes the observed kinetics. A biexponential was used to fit the fast time-scales (<100 ps), while a lower power-law form was used to describe the longer, extended kinetics expected for an inhomogeneous distribution of dynamics. Analysis of the ultrafast Vis pump–IR probe data gives asymptotic frequencies of 1738, 1737, 1735, and 1733 cm\(^{-1}\) for measurements at 350, 300, 250, and 200 K. These values for the asymptotic frequencies can be directly compared to those measured for the
carbonyl bleach center frequencies 20 µs after excitation which are 1740, 1738, and 1735 cm\(^{-1}\) at temperatures of 300, 250, and 200 K. All parameters calculated using this analysis scheme are displayed in Table 3-1.

With the asymptotic frequencies, we calculate the average time constant, \(<\tau>\), according to the equation:

\[
<\tau> = \frac{\int t(G(t) - g(\infty))dt}{\int G(t) - g(\infty)dt}
\]

(2)

where \(G(t)\) is the experimental data. Calculating the average time constant takes into account the carbonyl bleach frequency shift for the entire dataset. The asymptotic frequency, \(g(\infty)\), the frequency which each carbonyl bleach frequency approaches at long time delay is the only fit parameter in the calculation. The average time constants calculated for fits overlapping the data in Figure 3-7A are 0.8, 0.8, 0.7, and 0.5 ns for temperatures of 350, 300, 250, and 200 K, respectively. Thus, according to the model presented in the introduction of this chapter, we observe charge separation that is independent or only very weakly dependent on temperature in this material system.

We reserve calculation and discussion of the barrier to CT state dissociation until Chapter 6 where we present measurements obtained from thin OPV blend films at low excitation densities and with device-relevant materials (for more information, see the Appendix).

### 3.4 Conclusion

In conclusion, we have outlined the general features of the transient spectra obtained from blend films consisting of CN-MEH-PPV and PCBM using ultrafast Vis pump–IR probe spectroscopy. We have developed a method to fit the transient spectra in order to extract the spectroscopic observables related to CT state dissociation. We have demonstrated the ability to carry out the Vis pump–IR probe experiment at a range of temperatures between 200 and 350 K.
Lastly, we have demonstrated a simple kinetic model to fit the bleach center frequency in order to determine the average time constant for the decay.

3.5 References


Figure 3-1. Chemical structures of the $\pi$-conjugated polymer, CN-MEH-PPV, and the functionalized fullerene, PCBM.
**Figure 3-2.** Initial elementary steps leading to photocurrent in an OPV device. Light absorption by the electron donor generates an exciton. The exciton then diffuses to the interface between electron donor and acceptor materials (i.e. donor/acceptor junction). Once the exciton reaches the interface, charge transfers from the electron donor to acceptor resulting in a Coulombically bound electron-hole pair at the interface, i.e. a CT state (Step 1). The electron-hole pair must overcome their mutual Coulombic attraction to dissociate into fully separated charge carriers (CS state, Step 2).
Figure 3-3. (A) Comparison of linear IR spectra of polymer blend films with various polymer and PCBM content in the region of the carbonyl stretch. Spectrum labels: PCBM, spectrum of pure PCBM film with no polymer content; 0.03:1 and 1:1, spectra of films with indicated mass ratios of CN-MEH-PPV to PCBM; PPV, spectrum of CN-MEH-PPV film without any PCBM. The spectrum of the 1 ps bleach from the Vis-IR data has been plotted for comparison (black line). (B) SEM image of the morphology of the polymer blend. Reprinted with permission from J. Am. Chem. Soc. 2007, 129, 15884-15894. Copyright 2007 American Chemical Society.
Figure 3-4. Illustration demonstrating the conceptual basis of ultrafast vibrational spectroscopy to measure the rate of CT state dissociation in OPV blend films. [Phys. Chem. Chem. Phys. 2010, 12, 14144-14152] – Reproduced by permission of The Royal Society of Chemistry.
Figure 3-5. (A) Ultrafast Vis pump–IR probe transient spectra of a 1:1 CN-MEH-PPV:PCBM blend film excited at 550 nm at several pump–probe time delays. (B) 2D surface plot of the fit to the bleach of the carbonyl stretching mode of neutral ground state PCBM. Dashed line is a guide to the eye indicating shift of the center frequency of the carbonyl bleach.
**Figure 3-6.** (A) Ultrafast Vis pump–IR probe transient spectra of 1:1 CN-MEH-PPV:PCBM blend film acquired at several temperatures ranging from 200 to 350 K. Vertical dashed line indicates asymptotic center frequency the carbonyl bleach approaches at long pump–probe time delays. (B) Corresponding 2D surface plot of Gaussian fits to carbonyl bleach at all pump–probe time delays.
Figure 3-7. (A) Center frequency of bleach feature plotted against pump–probe time delay obtained from fits to transient spectra measured at 200, 250, 300, and 350 K for a 1:1 CN-MEH-PPV:PCBM blend film. (B) TRIR transient spectra at 20 µs following photoexcitation at 532 nm in a 1:1 CN-MEH-PPV:PCBM blend film at temperatures of 200, 250, and 300 K.
Figure 3-8. (a) Comparison of linear IR spectra of the 1:1 CN-MEH-PPV:PCBM blend collected at 300 and 120 K. (b) Difference linear IR spectra of the polymer blend calculated from the following spectra: 120 – 300 K and 210 – 300 K. The linear IR spectrum (not a difference spectrum) measured at 300 K is displayed for reference. © 2010 IEEE
Table 3-1. Time constants calculated from multi-component fit at different temperatures using eqn. 3.1. The multi-component fit is comprised of two exponentials, $\tau_1$ and $\tau_2$, and a power law, $\tau_3$. Average time constant is calculated from eqn. 3.2.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$\tau_1$/ps (a_1)</th>
<th>$\tau_2$/ps (a_2)</th>
<th>$\tau_3$/ps (1-a_1-a_2)</th>
<th>$\alpha$</th>
<th>$&lt;\tau&gt;/$ns</th>
</tr>
</thead>
<tbody>
<tr>
<td>350 K</td>
<td>0.9 (1.8 cm$^{-1}$)</td>
<td>120 (2.0 cm$^{-1}$)</td>
<td>1600 (3.2 cm$^{-1}$)</td>
<td>1.7</td>
<td>0.8</td>
</tr>
<tr>
<td>300 K</td>
<td>0.85 (1.8 cm$^{-1}$)</td>
<td>160 (2.5 cm$^{-1}$)</td>
<td>1700 (3.7 cm$^{-1}$)</td>
<td>1.65</td>
<td>0.8</td>
</tr>
<tr>
<td>250 K</td>
<td>0.8 (2.5 cm$^{-1}$)</td>
<td>170 (4.1 cm$^{-1}$)</td>
<td>1700 (4.4 cm$^{-1}$)</td>
<td>1.6</td>
<td>0.7</td>
</tr>
<tr>
<td>200 K</td>
<td>0.6 (2.3 cm$^{-1}$)</td>
<td>145 (7.7 cm$^{-1}$)</td>
<td>1700 (3.0 cm$^{-1}$)</td>
<td>1.85</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Chapter 4

Measuring the Barrier to Charge Separation in Organic Photovoltaic Blend Films. II. Origin of Frequency Shift

This chapter has been adapted from the following publication: Pensack, R.D., Banyas, K.M., Asbury, J.B., "Vibrational Solvatochromism in Organic Photovoltaic Materials: Method to Distinguish Molecules at Donor/Acceptor Interfaces" Phys. Chem. Chem. Phys. 2010, 12, 14144–14152, which has been rephrased in the context of this manuscript.

4.1 Introduction

We were able to measure the rate of charge separation in OPV blend films in Chapter 3 by virtue of a gradient of carbonyl stretching frequencies present in PCBM domains. Here, we explore the origin of the shift of the carbonyl stretching frequency of PCBM and, in particular, the role of solvent environment on the carbonyl stretching frequency.

Before exploring the origin of the frequency shift, it will be helpful to briefly discuss morphology in OPV blend films, pointing out the factors affecting morphology. Intimate intermixing and bicontinuous pathways of electron donor and acceptor materials are required for efficient bulk-heterojunction devices. The former is required for harvesting every exciton while the latter is required so that every electron and hole generated through the dissociation of an exciton can reach their respective electrodes. The extent of intermixing and overall morphology depends on a variety of pre- and post-processing conditions, which include but are not limited to blend composition and thermal and solvent treatments. For example, domains of pure PCBM are known to form in films cast from solutions of PPV and PCBM with high weight ratios of PCBM. Furthermore, film morphologies formed via spin casting are not the thermodynamic minimum, but are kinetically trapped. Thus, film morphologies are only metastable and can be driven to
further phase separation with heat\textsuperscript{2} and solvent\textsuperscript{3} treatments. For a further discussion of the variety of parameters that affect film morphology, the reader is referred to a recent review.\textsuperscript{4}

The correlation of the carbonyl stretching frequency of PCBM to blend composition (and morphology)\textsuperscript{5} represents a first step toward understanding the origin of the frequency shift. Obviously the presence of the polymer induces a change in the frequency. What about the polymer, though, is responsible for this frequency shift? One possible mechanism that could give rise to this frequency shift is the presence of a dipole existing at the interface between polymer and PCBM. An interfacial dipole would be present if there were a partial transfer of charge from the polymer, an electron donor, to PCBM, an electron acceptor, at the interface, i.e. a CT state in the dark. The magnitude of such an interfacial dipole can be determined by measuring the vacuum level shift between two organic materials using photoelectron spectroscopy,\textsuperscript{6} which has been measured for OPV systems such as copper phthalocyanine/C\textsubscript{60}\textsuperscript{7} and P3HT/C\textsubscript{60}.\textsuperscript{8} An interfacial dipole would act on a vibrational mode in very much the same way as an applied electric field, i.e. through a Stark shift.\textsuperscript{9,10} To estimate the upper limit to a possible interfacial dipole, we use the value of 4.7 D as reported by Arkhipov et al. for the magnitude of the dipole at the \textit{p-bis[(p-styrl)styryl]benzene/C\textsubscript{60}} interface which represents the transfer of 10\% of an elementary charge over a distance of 1 nm.\textsuperscript{11} A simple electrostatic model was developed to estimate the magnitude of the electric field arising from such an interfacial dipole.\textsuperscript{12} With this model and the parameters mentioned above, it was estimated that the magnitude of the electric field at the interface is \(\sim 10^7\) V m\(^{-1}\). With a Stark tuning rate of 1 cm\(^{-1}\) \(/(10^8\) V m\(^{-1}\)) reported for the carbonyl of acetone and methyl vinyl ketone,\textsuperscript{9} this corresponds to an estimate for the maximum frequency shift for PCBM molecules at the interface of \(\sim 0.2\) cm\(^{-1}\). Thus, it seems that a frequency shift induced by an interfacial dipole would only partially account for the observed 2-3 cm\(^{-1}\) frequency shift.\textsuperscript{5}

Given that the above estimate is an order of magnitude lower than the observed shift, we consider other sources that might affect the frequency of the carbonyl stretch. Solvent induced
changes in the energies of electronic transitions is well-known and has been labeled solvatochromism.\textsuperscript{15} The stabilizing or destabilizing solvation of either ground and/or excited states leads to changes in the electronic transition energies of solute molecules. The equivalent for vibrational transitions of solute molecules, vibrational solvatochromism, was recently explained as a change of the vibrational potential imposed by the local electrostatic potentials that the solvent environment maps onto the solute.\textsuperscript{13} For example, the sum of the local electric fields established by the solvent environment at the solute molecule result in a characteristic total electric field that affects the width of the vibrational potential energy surface of the solute. The width of the vibrational potential affects the strength of the vibration and thus the frequency of the vibrational motion. As such, the frequency of the vibrational motion can be significantly influenced by the solvent environment.

In this chapter, we first revisit the correlation of carbonyl frequency with blend composition (and morphology) and test the generality of this correlation in other OPV blend films consisting of PCBM with different electron donor materials. Second, we measure the carbonyl stretching frequency of PCBM in dilute solutions with several solvents and demonstrate that it is indeed sensitive to solvent environment. We go on to show data that indicate this effect is general to the carbonyl stretching mode (as measured in other molecules containing a carbonyl group). Finally, we use empirical models of solvatochromism to determine the extent of correlation between the observed frequency shift and empirical scales of solvatochromism. We find that the frequency shift correlates well with certain empirical scales of solvatochromism that include nonspecific interactions as well as specific hydrogen bond acceptor interactions (but not hydrogen bond donor interactions). Lastly, we demonstrate that regions of CN-MEH-PPV and PCBM represent distinct solvent environments as measured by the carbonyl stretching frequency of a dilute solute embedded in films of CN-MEH-PPV and PCBM.
4.2 Materials and Methods

Liquid-phase solvents, benzene, carbon tetrachloride, chloroform, 1,2-dichloroethane, dichloromethane, diethyl ether, and hexanes, were purchased from Sigma-Aldrich (St. Louis, MO) and used as received. Molecules containing a carbonyl group, benzophenone, methyl stearate, and PCBM, were also purchased from Sigma-Aldrich (St. Louis, MO) and used as received. The π-conjugated polymers CN-MEH-PPV (American Dye Source, Inc., Baie D’Urfe, Quebec, Canada) and RR-P3HT (Sigma-Aldrich Corp., St. Louis, MO) were purchased and used as received.

Blend films were prepared on ½” diameter NaCl windows (International Crystal Laboratories, Garfield, NJ). Solutions were prepared by dissolving the materials in chlorobenzene, in weight ratios indicated in the text, with the primary component making up ~1 wt% of the solution, followed by sonicating the solution for 1 hour. Except in the special case of the OPV blend sample preparation, where a 2 wt% solution was used for 1:1 and a 1.25 wt% solution was used for 4:1 (PCBM:CN-MEH-PPV). Films were prepared by depositing between 5 and 7 drops on the surface of the ½” diameter window in four successive sessions (total of about 25 drops). The substrate was rotated at 80 rpm during each session to ensure smooth, high quality films. Film thicknesses were estimated to be around 20 µm for films of a single material and between 20 and 40 µm for blend films.

IR spectra of liquid-phase solutions were obtained on a home-built dispersive infrared spectrometer. Solutions of 20 µM concentration were prepared for each solvent. Solutions were transferred to a DLC2 Demountable Liquid Cell (Harrick Scientific Products Inc., Pleasantville, NY) with Leur fittings. Care was taken during the transfer to avoid the introduction of air bubbles into the liquid cell. 500 µm thick PTFE (i.e. Teflon) spacers were used to set the path length. The optical windows were made of CaF₂.
IR spectra of solid-state films were obtained using a Thermo Nicolet 6700 FTIR spectrometer (Thermo Fisher Scientific, Inc., Waltham, MA). The resolution of the instrument was set to 1 cm\(^{-1}\). The spectrometer was continuously purged with nitrogen gas over the course of an experiment. For both background and sample scans, 128 interferograms were averaged and used to calculate a spectrum.

Specific details on the dispersive and FTIR spectrometers used in this study are included in Chapter 2.

4.3 Results and Discussion

The FTIR spectra of films of PCBM, CN-MEH-PPV, and PCBM blended with CN-MEH-PPV at three different weight ratios are shown in Figure 4-1B. The chemical structures of CN-MEH-PPV and PCBM are displayed Figures 4-1A and 4-3A, respectively. We measure a value of 1737 cm\(^{-1}\) for the carbonyl stretching frequency in films of pure PCBM. CN-MEH-PPV exhibits a weak absorption tail in this spectral window. This feature may result from a combination or overtone as there are no fundamental modes between the alkene (~1612 cm\(^{-1}\)) and nitrile (~2212 cm\(^{-1}\)) stretching modes of CN-MEH-PPV and the feature has very low oscillator strength. Given the low dilution of PCBM (0.1:1), we calculate the difference FTIR spectra for PCBM:CN-MEH-PPV blends with weight ratios of 4:1, 1:1, and 0.1:1. The difference spectra were calculated by taking the difference of the two spectra after first normalizing to the CN stretching mode of the polymer at ~2212 cm\(^{-1}\). We see that with the addition of CN-MEH-PPV, the carbonyl stretching mode of PCBM shifts to higher frequency, as observed previously.\(^5\) We measure values of ~1738, 1739, and 1739.5 cm\(^{-1}\) for the carbonyl stretching frequency of PCBM in films of PCBM:CN-MEH-PPV with weight ratios of 4:1, 1:1, and 0.1:1. The carbonyl stretching frequency shifts by ~1, 2, and 2.5 cm\(^{-1}\), respectively, relative to that measured in the
film of pure PCBM. We note that there is a small shift of the CN stretching mode from pure CN-MEH-PPV to 4:1 PCBM:CN-MEH-PPV of ~1.5 cm⁻¹, as well.

The generality of this effect to OPV blend films is investigated by blending PCBM with a different polymer, RR-P3HT, used as electron donor in OPV blend films. The chemical structure of RR-P3HT is given in Figure 4-1A. In Figure 4-1C, we show the spectra measured for pure PCBM and a 1:1 blend of PCBM:RR-P3HT. We measure a shift of ~2.5 cm⁻¹ between pure PCBM and 1:1 blends of PCBM:RR-P3HT. Thus, the shift of the carbonyl stretching frequency of PCBM seems general to OPV systems with different electron donors.

The shift of the carbonyl stretching mode of PCBM to higher frequency results from interaction with the polymer and progression of the shift with blend composition is correlated to film morphology. The addition of a small amount of polymer, which is not expected to significantly affect morphology, alters the carbonyl stretching mode of PCBM such that it absorbs at a frequency ~1 cm⁻¹ higher. Below blends of 50 weight% PCBM, it is anticipated that PCBM intermixes homogeneously with the polymer. Increasing the polymer fraction of the blend, in this case, increases the extent with which polymer interacts with PCBM and causes the carbonyl stretching mode of PCBM to shift to higher frequency. The picture that we adopt given these observations is presented in Figure 4-2. We expect more bulk-like PCBM (which does not interact with the polymer) to contribute more strongly to the absorption in blends with higher PCBM content (i.e. low freq. C=O stretch) while more interfacial PCBM (which does interact with the polymer) contributes to blends with lower PCBM content (i.e. high freq. C=O stretch).

As mentioned in the introduction of this chapter, we expect the contribution of a Stark shift to the shift of the carbonyl stretching frequency to be minimal. Thus, we sought to consider the effect of solvent environment on the carbonyl stretching frequency. We measured the spectra of dilute solutions of PCBM in six solvents ranging from benzene (aromatic, nonpolar) to chloroform (polychlorinated, polar). These spectra are shown in Figure 4-3B in the carbonyl stretching region. The carbonyl absorption band shifts to lower frequency and broadens for more
polar solvents such as chloroform. The magnitude of the frequency shift in this series of solvents is \( \sim 12 \ \text{cm}^{-1} \). Clearly the carbonyl stretching mode of PCBM is sensitive to its solvent environment.

The carbonyl stretching mode of other molecules containing an ester functional group seems to be affected by solvent environment. Figure 4-3C displays spectra of the carbonyl stretching absorption band of methyl stearate, which is about one-third the mass of PCBM. The chemical structure of methyl stearate is displayed in Figure 4-3A. Methyl stearate is generally more soluble than PCBM and so we were able to dissolve methyl stearate in additional solvents such as hexanes, diethyl ether, and acetonitrile. Within this set of solvents, we observe the same general effect on the carbonyl stretching band for methyl stearate as was observed in PCBM. Namely, the carbonyl stretching absorption band shifts to lower frequency and is broadened in more polar solvents. The ability to dissolve methyl stearate in a wider range of solvents is reflected in the magnitude of the frequency shift induced by solvent effects, i.e. \( \sim 22 \ \text{cm}^{-1} \). Furthermore, it appears that the carbonyl stretching absorption band is narrow and absorbs at higher frequencies for the nonpolar aliphatic solvents and broadens and shifts to lower frequency for polychlorinated aliphatics used in the experiments reported here. Values of the carbonyl stretching frequency of PCBM and methyl stearate dissolved in various solvents as determined from the spectra displayed in Figure 4-3 are reported in Table 4-1.

We next show a direct relationship between the observed frequency shift and an empirical scale of solvatochromism, Gutmann’s acceptor number (AN).\(^\text{14}\) Gutmann’s AN was developed to quantitatively describe the accepting properties or, in terms of carbon chemistry, the electrophilicity of a solvent. A solvent’s AN is determined by measuring the \( ^{31}\text{P} \) chemical shift of triethylphosphine oxide in that solvent, i.e.

\[
\begin{align*}
\text{Solvent} & \rightarrow P=O \\
& \text{Triethylphosphine Oxide}
\end{align*}
\]
The AN values for the solvents used in this study are listed in Table 4-1. Note that the limits of the AN scale range from hexane which is arbitrarily defined to have an AN of 0 to the complex \( \text{Et}_3\text{PO} - \text{SbCl}_5 \) in 1,2-dichloroethane which is defined to have an AN of 100. In Figure 4-4, we plot the carbonyl stretching frequencies measured for PCBM and methyl stearate in several solvents against Gutmann’s AN. A clear linear relation is observed between the carbonyl stretching frequency of these molecules in various solvents and Gutmann’s AN. Thus, it is anticipated that the solute-solvent effects occurring between the carbonyl stretching mode of PCBM and methyl stearate and the solvents used in these studies are the same as the solute-solvent effects incorporated into Gutmann’s AN scale.

In an effort to establish further confidence of correlation between the shift observed in the carbonyl stretching frequency in different solvents, we consider other empirical scales of solvatochromism that have been developed, such as the \( E_{\tau}(30) \) scale based on Reichardt’s dye and a multi-parameter scale based on linear-solvation energy relationships (LSER). The \( E_{\tau}(30) \) value for a solvent is determined by measuring the transition energy of a negatively solvatochromic pyridinium \( N \)-phenolate betaine dye in that solvent. Dimensionless \( E_{\tau}^N \) values are normalized values calculated by arbitrarily defining the range of the \( E_{\tau}^N \) scale from 0.000 for tetramethylsilane (nonpolar) and 1.000 for water (polar). The LSER approach is a multi-parameter scale that attempts to take into account separately multiple, orthogonal solvent effects. The full LSER equation is presented below

\[
XYZ = XYZ_0 + s(\pi^* + d\delta) + a\alpha + b\beta + m\delta_H^2
\]

(1)

The \( \pi^* \) value represents a blend of the dipolarity and polarizability of a solvent molecule, i.e. the ability of a solvent to stabilize a charge or a dipole through a nonspecific dielectric effect. Values for \( \pi^* \) range from 0.00 for cyclohexane to 1.00 for dimethyl sulfoxide. \( \delta \) is a correction factor with a value of 0 for aliphatic solvents, 0.5 for polychlorinated solvents, and 1.0 for aromatic solvents. This is typically omitted when considering a single “family” of solvents with similar
characteristics. The value of $\alpha$ is a measure of a solvent’s ability to donate a proton through a hydrogen bonding interaction (or to act as a Lewis acid, i.e. electron acceptor). In a similar spirit, the $\beta$ value is a measure of a solvent’s ability to accept a proton through a hydrogen bonding interaction (or to act as a Lewis base, i.e. electron donor). Values for $\beta$ range from 0.0 for cyclohexane to 1.0 for hexamethylphosphoric triamide. Finally, $\delta_H^2$, the Hildebrand solubility parameter, represents the energy required to form a solvent cavity to accommodate a solute molecule.

In order to quantitatively analyze the extent that the different solvent scales correlate with the carbonyl stretching frequency, we have developed correlation equations. The correlation equations allow us to calculate the carbonyl stretching frequencies expected for methyl stearate in the different solvents using parameters from the different solvent scales and to compare these to the experimentally measured values. We perform the analysis on the carbonyl stretching frequencies of methyl stearate because, as mentioned previously, we were able to dissolve the molecule in a wider range of solvents. We perform the analysis with the following correlation equations

\begin{align*}
\omega_{(C=O)} &= \omega_{(C=O)0} + sAN \quad (2) \\
\omega_{(C=O)} &= \omega_{(C=O)0} + sE_T^N \quad (3) \\
\omega_{(C=O)} &= \omega_{(C=O)0} + s(\pi^* + d\delta) + aa \quad (4)
\end{align*}

We omit the LSER parameters $\beta$ and $\delta_H^2$ from eq. 4 based on the following arguments. First, the $\beta$ value can be omitted because a carbonyl is incapable of acting as a hydrogen bond donor (or as a Lewis acid, i.e. electron acceptor). Second, we omit the $\delta_H^2$ parameter because there is very little change in the size of the solvent cavity (as determined by the size of the solute molecule) between the initial and final states of the vibrational transition. The parameters for each solvent
from each solvent scale used in the ensuing calculations (except for $\delta$, which will be omitted, see below) are listed in Table 4-1.

While the data do not show a good correlation with the $E^N_T$ scale, the data do show good correlation with the AN and LSER scales. In Figure 4-5, we present the carbonyl stretching frequency of benzophenone measured in various solvents plotted against the values expected from calculations using the different models presented above. The correlation with the $E^N_T$ scale from our analysis is $R^2 = 0.55$. This simply reflects that the types of interactions incorporated into Reichardt’s $E^N_T$ scale are not present in the system under study in this work (being either too many or too few). On the other hand, the AN scale and LSER scales do demonstrate good correlation with $R^2$ values of 0.97 and 0.93, respectively. It is expected that the interactions incorporated in these scales are present in the system under study in this work.

Although Gutmann’s AN scale is purportedly a scale of Lewis acidity, implying only specific interactions are included, this may not entirely be the case. Table 4-2 lists the results for $\omega_{(C=O)}$, $s$, $d$, and $a$ from a best fit analysis to the data for each empirical scale of solvatochromism. The coefficients $s$ and $a$ obtained for the LSER scale indicate a substantial proportion of nonspecific $\pi^*$ interactions along with the hydrogen bond acceptor (or Lewis acid) type interactions of $\alpha$. Thus, at least for the solvents under study here, there seems to be a combination of specific and nonspecific interactions occurring.

It is worthwhile to note that the small (~3 cm$^{-1}$) shift of the carbonyl stretching frequency measured in blends of PCBM and CN-MEH-PPV is curiously of the same magnitude as a <6 cm$^{-1}$ shift observed in polymers blends of poly($\epsilon$-caprolactone), a polyester, and polyvinyl chloride (PVC).\textsuperscript{18} In fact, a general trend has been observed for polyesters, polyacetates, and polyacrylates blended with PVC in which the carbonyl band broadens and lowers in frequency.\textsuperscript{19} The consensus reached was that there is some form of specific interaction between the carbonyl of the polyester and a group in PVC. Whether this occurs through a Lewis acid-base interaction involving a weakly acidic methine proton in PVC (Lewis acid) and the carbonyl (Lewis base) or
through a dipole-dipole interaction between the carbon halide bond and the carbonyl is still debated.20

The observation that the carbonyl band broadens and shifts to lower frequency for carbonyl groups in polymer blends with PVC is consistent with the data for PCBM and methyl stearate. Setting 1740 cm^{-1} as an arbitrary mid-point, we observe that the carbonyl stretching band of PCBM and methyl stearate shift to lower frequency and broaden when dissolved in the solvents 1,2-dichlorethane, dichloromethane, and chloroform. The same effect is observed for methyl stearate in acetonitrile. At and above 1740 cm^{-1}, the solvents are benzene, carbon tetrachloride, ether, and hexanes. These solvents range from aromatic to aliphatic, but all are aprotic. It is interesting to speculate that the shift below 1740 cm^{-1} arises from some form of interaction with a weakly acidic proton on the polychlorinated aliphatics (with the exception of carbon tetrachloride, which does not have such a proton). Although requiring a study with more solvents, it is interesting to further speculate that we observe two regimes of solvatochromism within this set of solvents, i.e. nonspecific effects for the range of 1740 – 1750 cm^{-1} and specific + nonspecific effects for the range <1740 cm^{-1}.

Although the above conclusion is speculative, it is worthy of consideration as a great opportunity arises if it is true. If it were possible to blend PCBM with a polymer capable of forming hydrogen bonds with the carbonyl, one may be able to increase the spatial resolution of the ultrafast Vis pump–IR probe experiment measuring the rate of charge separation in OPV materials. Hydrogen bonding interactions are known to significantly weaken the strength of a carbonyl mode and cause a substantial shift of the carbonyl stretching frequency. In fact, a distinct band with a shift on the order of 25 cm^{-1} has been observed for the hydrogen bonded carbonyl stretching mode of poly(methyl methacrylate) in blend films of poly(methyl methacrylate) and poly(4-vinyl phenol).21 Assuming that the interfacial sites in non-hydrogen bonding films have a shift of ~7 cm^{-1}, the spectral resolution between a bleach arising from a CT
state and a bleach arising from a CS state in the Vis pump–IR probe experiment could be increased by at least a factor of three if not more for hydrogen bonded films.

Furthermore, vibrational modes associated with hydrogen bonding are also known to have distinct vibrational frequencies for the “free” and “hydrogen bonded” states. The extent of hydrogen bonding could be quantified by taking a ratio of the amount of “free” vs. “hydrogen bonded” absorption. This would provide a pathway for obtaining further evidence of the extent and nature of interaction between polymer and PCBM.

Lastly, in an effort to differentiate between the solvent environment of PCBM and CN-MEH-PPV, we selected a compound that would act as a dilute solute in blend films with PCBM and CN-MEH-PPV. We chose benzophenone (inset, Figure 4-6A), a molecule containing a ketone functional group, whose carbonyl stretching frequency is lower than that of most carbonyl groups because of its participation in conjugation with two adjacent benzene groups. Since there are no measurable IR active transitions in PCBM or CN-MEH-PPV at the carbonyl transition frequency of benzophenone, we are able to measure the carbonyl stretching frequency of benzophenone as a dilute solute in blend films with PCBM and CN-MEH-PPV.

We have measured the carbonyl stretching frequency of benzophenone as a dilute solute in blend films with CN-MEH-PPV and PCBM. These spectra are displayed in Figure 4-6 for benzophenone:solvent weight ratios of 0.02:1, 0.013:1, 0.01:1 and 0.005:1 in films of both CN-MEH-PPV and PCBM. These weight ratios were chosen to test whether or not benzophenone is indeed dilute, i.e. that there is no observable frequency shift at the lowest measurable solute:solvent ratios. In Figure 4-6A, FTIR difference spectra in the carbonyl stretching region of benzophenone are displayed for benzophenone:CN-MEH-PPV films. The data were again normalized to the polymer CN stretching mode at 2212 cm\(^{-1}\). There is a small bump around 1680 cm\(^{-1}\) arising from incomplete subtraction of a vibrational mode of the polymer (~1683 cm\(^{-1}\)). We measure a value of 1661 cm\(^{-1}\) for the carbonyl stretching frequency of benzophenone as a dilute solute in CN-MEH-PPV blend film and observe that this value does not shift for more dilute
blend ratios. Figure 4-6B shows FTIR spectra of the carbonyl stretching region of benzophenone for a film of PCBM along with blend films of benzophenone:PCBM. In this case, the spectra were normalized to the carbonyl absorption of PCBM at 1737 cm\(^{-1}\). We measure a value of 1659 cm\(^{-1}\) for the carbonyl stretching frequency of benzophenone in films of PCBM. Again there is no observable shift of the carbonyl stretching frequency with further dilution.

With these measurements, we are now in a position to verify quantitatively that CN-MEH-PPV and PCBM represent different solvent environments. In Figure 4-7, we plot the carbonyl stretching frequency of benzophenone in several solvents, as reported by William and Bellamy,\(^{23}\) against Gutmann's AN. Note that we have added data for the solvents pyridine (AN = 14.2) and triethylamine (AN = 1.4) (ANs from ref. 24) to this plot. Once again, the data shows a linear correlation with Gutmann’s AN demonstrating the generality of the solvent effect to the carbonyl group and the applicability of the AN scale as a measure of interactions between the carbonyl group and the solvents used in this study. Figure 4-7 also provides us with a calibration plot that can be used to determine the AN of CN-MEH-PPV and PCBM. Overlaid in Figure 4-7 are the measurements of the carbonyl stretching frequencies of benzophenone as a dilute solute blended with PCBM and CN-MEH-PPV that were discussed previously. From these measurements, we see that CN-MEH-PPV has a lower AN than PCBM. \textit{In other words, we confirm quantitatively through the solvatochromic shift of a vibrational mode of a dilute reporter molecule embedded in solid-state films of CN-MEH-PPV and PCBM that regions of CN-MEH-PPV and PCBM represent distinct solvent environments.}

\subsection*{4.4 Conclusion}

The correlation between carbonyl stretching frequency of PCBM and OPV blend composition (i.e. morphology) is revisited. The data indicate that the stretching frequencies of carbonyl groups are sensitive to their solvent environment. A good correlation exists between the
carbonyl stretching frequency and several empirical scales of solvatochromism, such as Gutmann’s AN scale and LSER. The nature of the interaction giving rise to the solvatochromic shift is discussed in light of the physical manifestations underlying each empirical scale of solvatochromism and studies of vibrational solvatochromism of the carbonyl stretching mode in polymer:polymer blends. By measuring the carbonyl stretching frequency of a dilute solute embedded in films of CN-MEH-PPV and PCBM, we show that CN-MEH-PPV and PCBM represent distinct solvent environments.

4.5 References


Figure 4-1. (A) Chemical structures of π-conjugated polymers CN-MEH-PPV and RR-P3HT. (B) FTIR difference spectra of films of PCBM blended with CN-MEH-PPV at different weight ratios. (C) Comparison of FTIR spectrum of a film of 1:1 PCBM:RR-P3HT blend with a spectrum of a film of PCBM (film thicknesses on the order of tens of μms).
Figure 4-3. (A) Chemical structures of PCBM and methyl stearate. (B) Dispersive IR spectra of the carbonyl stretching absorption of PCBM dissolved in several solvents. (C) Dispersive IR spectra of the carbonyl stretching absorption of methyl stearate dissolved in several solvents. Note that methyl stearate was generally more soluble and so spectra were acquired in a wider range of solvents.
Figure 4-4. Overlay of carbonyl stretching frequencies of PCBM and methyl stearate obtained in several solvents plotted against Gutmann’s AN. ANs for the solvents used in this study were obtained from ref. 14.
<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\tilde{\nu}_{C=O}$ (cm$^{-1}$)</th>
<th>methyl stearate</th>
<th>PCBM</th>
<th>AN</th>
<th>$E_T^N$</th>
<th>$\pi^*$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexanes</td>
<td>1750</td>
<td>–</td>
<td></td>
<td>0.0</td>
<td>0.009</td>
<td>-0.11</td>
<td>0.00</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>1745</td>
<td>–</td>
<td>3.9</td>
<td>0.117</td>
<td>0.24</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>1742</td>
<td>1741</td>
<td>8.2</td>
<td>0.111</td>
<td>0.55</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>1741</td>
<td>1743</td>
<td>8.6</td>
<td>0.052</td>
<td>0.21</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>1736</td>
<td>1737</td>
<td>16.7</td>
<td>0.327</td>
<td>0.73</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>Acetonitrile</td>
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<td>0.460</td>
<td>0.66</td>
<td>0.19</td>
<td></td>
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<tr>
<td>Dichloromethane</td>
<td>1732</td>
<td>1734</td>
<td>20.4</td>
<td>0.309</td>
<td>0.73</td>
<td>0.30</td>
<td></td>
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<tr>
<td>Chloroform</td>
<td>1729</td>
<td>1730</td>
<td>23.1</td>
<td>0.259</td>
<td>0.69</td>
<td>0.44</td>
<td></td>
</tr>
</tbody>
</table>

**Table 4-1.** Measured frequency of the carbonyl stretching mode of methyl stearate and PCBM in various solvents and empirical solvent parameters for these solvents. AN values from ref. 14, Reichardt’s $E_T^N$ values from ref. 15, and LSER parameters, $\pi^*$ and $\alpha$, from ref. 16.
Figure 4-5. Plot of carbonyl stretching frequencies of methyl stearate measured in various solvents against those calculated with three different empirical scales of solvent polarity: (A) Gutmann’s acceptor number, AN; (B) Reichardt’s $E_{r}^{N}$; (C) Kamlet and Taft’s LSER. Parameters obtained from the fits are listed in Table 4-2.
Table 4-2. Parameters calculated from fits to three different empirical scales of solvatochromism.

<table>
<thead>
<tr>
<th>Scale</th>
<th>$\omega_{C=O}$</th>
<th>$s$</th>
<th>$a$</th>
<th>$d$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gutmann’s AN</td>
<td>1748.7</td>
<td>-0.79</td>
<td>n/a</td>
<td>n/a</td>
<td>0.97</td>
</tr>
<tr>
<td>Reichardt’s $E_{T}^N$</td>
<td>1745.9</td>
<td>-34</td>
<td>n/a</td>
<td>n/a</td>
<td>0.55</td>
</tr>
<tr>
<td>LSER</td>
<td>1747.6</td>
<td>-14</td>
<td>-19</td>
<td>0</td>
<td>0.93</td>
</tr>
</tbody>
</table>

n/a: not applicable
Figure 4-6. (A) Difference FTIR spectra in the carbonyl stretching region of benzophenone for films of benzophenone:CN-MEH-PPV at different dilutions. The chemical structure of benzophenone (BP) is displayed in the upper right corner. (B) FTIR spectra in the carbonyl stretching region of benzophenone for films of benzophenone:PCBM at different dilutions. The dashed line is overlaid on the center frequency of the carbonyl stretching mode of benzophenone measured in these films.
Figure 4-7. Plot of benzophenone (BP) carbonyl stretching frequencies measured in several solvents against Gutmann’s AN. Measurements made in dilute solid-state blends of BP with CN-MEH-PPV and PCBM are overlaid in the plot.
Chapter 5

Measuring the Barrier to Charge Separation in Organic Photovoltaic Blend Films. III. Ground-State Vibrational Dynamics of Carbonyl Stretching Mode of PCBM

This chapter represents an adaptation of the following publication: Pensack, R.D., Banyas, K.M., and Asbury, J.B. "Temperature-Independent Vibrational Dynamics in an Organic Photovoltaic Material" *J. Phys. Chem. B* 2010, 114, 12242–12251, which has been rephrased in the context of this manuscript.

5.1 Introduction

In Chapter 3 we were able to determine the rate of charge separation by measuring the dynamic shift of the carbonyl bleach frequency in an OPV blend film consisting of the electron donor CN-MEH-PPV with electron acceptor PCBM following excitation of the electron donor with an electronic pump pulse. In the present chapter, we aim to eliminate factors other than the motion of electrons away from the interface that could cause the observed frequency shift. Other factors that could give rise to the dynamic, time-dependent frequency shift include thermal effects associated with the redistribution of the optical pump energy or dynamic fluctuations of the ground (electronic) state vibrational frequencies, i.e. spectral diffusion.

The vibrational dynamics of the carbonyl stretching mode of PCBM in a blend film comprised of CN-MEH-PPV and PCBM have been measured previously at 300 K. Although the authors did not observe spectral diffusion on the picosecond and longer timescale, they did observe sub-picosecond wobbling-in-cone orientational motion. As orientational motion can potentially cause dynamic fluctuations of the ground-state carbonyl stretching mode, one concern
and motivation for the current chapter is to determine whether or not this is slowed sufficiently at low temperatures such that spectral diffusion is observed on the picosecond timescale.

Here, we study the dynamics of the carbonyl stretching mode of PCBM in an OPV blend film consisting of PCBM and CN-MEH-PPV at several temperatures. Chemical structures of CN-MEH-PPV and PCBM are displayed in Figure 5-1. First, we measure linear infrared spectra in the carbonyl stretching region over the temperature range of 184 to 390 K. Next, we investigate the population relaxation and orientational motion of the carbonyl stretching mode in this blend film at temperatures ranging from 200 to 350 K. We show that the timescale of the sub-picosecond wobbling-in-cone orientational motion does not depend on temperature, but that the cone half angle decreases at lower temperatures. Finally, we establish the absence of spectral diffusion over the same temperature range of 200 to 350 K for the picosecond and longer timescale.

5.2 Materials and Methods

OPV blend films for these experiments were prepared as described in Chapter 3. In brief, equal masses of CN-MEH-PPV and PCBM were used to prepare 20 mg/mL (2 wt%) solutions in chlorobenzene which were then sonicated for ~1 hr at 40 °C. After sonication, 30 drops of solution were transferred to a substrate and given time to dry. Substrates were spun at 80 rpm during the entire drying procedure to ensure smooth films. Substrates for the films prepared for spectroscopy in this chapter were all 1 in. diameter aluminum mirrors (Thorlabs Inc., Newton, NJ).

Detailed information on the IR spectrometer and IR pump–probe techniques is included in Chapter 2. The IR pump pulse in the broadband IR pump–probe experiment has the same characteristics as the probe pulse. For these particular experiments, both pump and probe pulses had a center frequency of 1740 cm\(^{-1}\) and FWHM of 200 cm\(^{-1}\). The IR pump pulse in the 2D IR
(i.e. narrowband IR pump–broadband IR probe) experiments had a FWHM of 7 cm$^{-1}$ after passing through an etalon and the pump axis was scanned in 2 cm$^{-1}$ steps.

The temperature of the sample was controlled through the transfer of nitrogen gas to the sample from a liquid nitrogen dewar (LN-50, Janis Research Company, Wilmington, MA) in combination with a cryogenic temperature controller (LakeShore 331 Temperature Controller, Lake Shore Cryostronics, Inc., Westerville, OH). The temperature of the film was measured with a copper-constantin thermocouple attached to a digital temperature meter (DP116-TC2-GR, Omega Engineering, Inc., Stamford, CT).

A best fit statistical procedure was used for all fitting routines. Error bars were determined by fixing the parameter at a range of values while allowing all other parameters in the equation to vary until the sum of the squares of the residuals increased by 50% relative to the best fit.

5.3 Results and Discussion

Linear IR

Dispersive IR spectra of a 1:1 CN-MEH-PPV:PCBM blend film acquired at temperatures ranging from 184 to 390 K are displayed in Figure 5-2. These spectra have been normalized to the carbonyl stretching band of PCBM. We observe a shift of ~1.5 cm$^{-1}$ to higher frequency and a change in the linewidth of less than 0.3 cm$^{-1}$ for the carbonyl stretching band over the temperature range studied. About one-third of the frequency shift occurs over the temperature range of 300 to 390 K.

The small change in frequency and negligible change in linewidth demonstrate that the carbonyl stretching mode of PCBM in blend films of CN-MEH-PPV and PCBM is relatively insensitive to temperature. This is in contrast to vibrational modes such as the hydroxyl stretch of water$^3$ and the amide I vibration of ceramides$^3$ and proteins$^4$ that are sensitive to temperature.
The sensitivity of these vibrational modes to temperature is a result of stronger interactions with the vibrational modes with the environment in these particular systems.

For example, water consists of a network of hydrogen bonds that rapidly break and reform. The strength of the hydrogen bond is on the order of ~5 kcal/mol (~0.2 eV). The corresponding shallow, broad potential has many closely spaced vibrational levels whose occupation varies with temperature. Because the hydroxyl stretching mode is coupled to these hydrogen bonding interactions, pronounced frequency dependence with temperature is observed.

The absorption frequency of the amide I vibration, which consists primarily of the carbonyl stretching motion, is most strongly influenced by protein secondary structure (i.e. α-helices, β-sheets). It has been suggested that the absorption frequency of the amide I vibration is influenced by the characteristic hydrogen bonding patterns of particular secondary structure and the way in which neighboring amide groups are arranged which impacts transition-dipole coupling. Because the secondary structure of the protein is sensitive to temperature, the amide I frequencies are also sensitive to temperature.

In contrast, the carbonyl stretching mode in PCBM in CN-MEH-PPV:PCBM blend films is expected to interact weakly with its environment. Neither the polymer or PCBM have functional groups capable of hydrogen bonding and the only polar groups present (other than the ester group of PCBM) are the alkoxy and cyano groups of the polymer. Furthermore, PCBM molecules are expected to be far apart given the density is 1.5 g/cm³, which corresponds to 1 molecule/nm³. The average distance between methyl ester groups of PCBM in PCBM clusters is approximately 1 nm, indicating interactions between carbonyl groups are likely weak. The small shift to lower frequency at lower temperature observed in Figure 5-2 is taken to represent enhanced intermolecular order among neighboring carbonyl groups of PCBM molecules. This argument is based on the observation of similar shifts to lower frequency observed in the amide I absorption of semicrystalline nylon with decreased temperature.
Because the linewidth in the linear IR spectrum represents the Fourier transform of the FID which incorporates all dephasing mechanisms, the negligible change in linewidth of the carbonyl stretching band of PCBM with temperature suggests that the vibrational dynamics, i.e. dephasing mechanisms, are insensitive to temperature. The vibrational dynamics of the carbonyl stretching mode of PCBM in an OPV blend film will be explored in the following sections.

**Population (energy) relaxation**

We first investigate the population relaxation, or vibrational lifetime, of the carbonyl stretching mode. The vibrational lifetime of the OD stretch of HOD has been shown to be sensitive to environment, for example, using ultrafast infrared polarization-selective pump–probe spectroscopy.\(^\text{10}\) If the vibrational lifetime were sensitive to environment, a time-dependent frequency shift may be observed.

Figure 5-3A displays broadband IR pump–probe spectra for the carbonyl stretching mode of PCBM in an OPV blend film at 300 K at pump–probe time delays of 0.1 and 10 ps. The pump pulse has the same center frequency as the probe pulse in these experiments which is 1740 cm\(^{-1}\). The transient spectra have been normalized to the bleach feature. The positive going feature at 1740 cm\(^{-1}\) in the 0.1 ps spectrum is caused by bleaching of the ground state 0–1 vibrational transition and stimulated emission from the excited state to ground state (i.e. 1–0 transition). The negative going feature at 1720 cm\(^{-1}\) in the 0.1 ps spectrum is an induced absorption occurring from the first to second excited state (i.e. 1–2 transition). The center frequency and line shape of the bleach feature in the 0.1 ps spectrum (as determined by fitting the spectrum with Gaussian line shapes for both bleach and induced absorption features) are similar to those observed in the linear IR spectra displayed in Figure 5-2. The features in the 10 ps spectrum, however, appear to have shifted to higher frequency.

Broadband IR pump–probe spectra at all pump–probe time delays are displayed in Figure 5-3B as a two-dimensional plot. The vertical axis in Figure 5-3B represents different pump–
probe time delays. The horizontal axis represents the detected probe frequencies. Contours represent normalized change in transmittance values which are displayed at 10% intervals except around zero signal amplitude, where they are 1% intervals. The bleach and induced absorption features progressively shift toward higher frequency with increasing pump–probe time delay as indicated by the dashed lines in Figure 5-3B.

The dynamic frequency shift of the bleach and induced absorption could arise from either frequency-dependent vibrational lifetimes or from an intermediate state that forms during vibrational cooling. To investigate the origin of this dynamic frequency shift, we ran broadband IR pump–probe experiments where we controlled the polarization of pump and probe pulses. In the experiment, the polarization of the pump pulse is fixed while we vary the polarization of the probe relative to the pump polarization. The polarization of the probe was varied so that it was aligned either parallel or perpendicular to the pump polarization. Parallel and perpendicular kinetics traces measured at the center of the bleach feature at 1740 cm\(^{-1}\) are displayed in Figure 5-4 for measurements at 300 K.

The population relaxation can be calculated from the measurements according to

\[
P(t) = \frac{1}{3} (S_\parallel(t) + 2S_\perp(t))
\]

(1)

where \(S_\parallel(t)\) and \(S_\perp(t)\) are kinetics traces measured with the pump polarization oriented parallel and perpendicular to the probe polarization, respectively. The calculation of population relaxation in this fashion removes the influence of orientational motion on the measured signal. The population relaxation is often referred to as the pure population relaxation. The resulting population relaxation kinetics are displayed in Figure 5-4. The population relaxation kinetics are also displayed in a semilog plot in the inset of Figure 5-4. The dotted line in the inset is the decay of a single-exponential function. Clearly, the population relaxation does not decay according to a single-exponential function. The curvature between 5 and 10 ps in the semilog plot of the population relaxation kinetics in the inset of Figure 5-4 indicates that there is a transition in the
population relaxation from a process which has a time constant of a few picoseconds to one which has a much longer time constant. We believe that this transition is associated with the formation of a vibrationally hot intermediate state whose spectral features are present in the 10 ps spectrum in Figure 5-3B. This interpretation will be discussed further below.

In order to extract further information from the population relaxation kinetics, we have developed a model function, \( F_p(t) \), to fit the population relaxation kinetics. The model function is given below

\[
F_p(t) = A \int_{-\infty}^{\infty} \left[ S_{FID}(t+\tau) + C_1(t+\tau) \Theta(t+\tau) \right] G(\tau) d\tau
\]  

(2)

where the amplitude term, \( A \), accounts for the amplitude of the population relaxation kinetics. The Fourier transform of a pseudo-Voigt function, \( S_{FID}(t) \), is used to fit the perturbed free induction decay. A perturbed free induction decay of the signal occurs at negative time delays near the time origin when the pump pulse reaches the sample before the probe pulse. The pseudo-Voigt in our analysis has the functional form

\[
S_{FID}(t) = (1-b) \exp\left(-\frac{t^2}{2\sigma_{FID}^2}\right) + b \exp(-2|t|\sigma_{FID})
\]  

(3)

which includes mixed gaussian/exponential character that share the same width parameter, \( \sigma_{FID} \). The population relaxation is fit with

\[
C_1(t) = (1-a_s-a_{pp}) \exp(-t/\tau_f) + a_s \exp(-t/\tau_s) + a_{pp} \exp(-t/\tau_{pp})
\]  

(4)

which represents the sum of three exponentials with time constants \( \tau_f, \tau_s, \) and \( \tau_{pp} \) and relative amplitudes \( 1-a_s-a_{pp}, a_s, \) and \( a_{pp} \) for the fast, slow, and "photoproduct" components. The function for the perturbed free induction decay and the population relaxation kinetics are alternated in the calculation by the Heaviside step function, \( \Theta(t) \). The model fitting function is convolved with an instrument response function, \( G(t) \), to account for the finite duration of the laser pulses. The instrument response function is given the form
\[ G(t) = \frac{1}{\sigma_{IR} \sqrt{2\pi}} \exp \left( -\frac{t^2}{2\sigma_{IR}^2} \right) \]  

where the width parameter, \( \sigma_{IR} \), is fixed to the duration of pump and probe pulses which is approximately 150 fs.

The curve corresponding to the best fit (from a least-squares fitting procedure) using the model function is overlaid on the population relaxation kinetics in Figure 5-4 in both the main panel and the inset. The measured data and fit curves are indistinguishable. Parameters including lifetimes and amplitudes obtained from the best fit analysis are displayed in Table 5-1. The error limits appearing in Table 5-1 were determined as described in the experimental section. Because the longest time component, \( \tau_{pp} \), is much larger than the vibrational lifetime of the carbonyl stretching mode, the error limits are not precisely determined.

In order to identify the origin of the non single-exponential behavior, we subtracted the exponential with the longest time component, \( \tau_{pp} \), from the population relaxation data. The result is displayed in Figure 5-5 for the measurement at 1740 cm\(^{-1}\) along with measurements at 1751, 1746, and 1735 cm\(^{-1}\). The data have been normalized to the maximum signal that occurs at the time origin. The dotted line in Figure 5-5 is a single-exponential decay with a time constant of 1.7 ps. As can be seen, all datasets overlap. Thus, we do not observe frequency-dependent vibrational dynamics.

The data reveal two components to the population relaxation. Parameters for these two components obtained from the best fit analysis for all frequencies analyzed are displayed in Table 5-1. The first component is sub-picosecond which comprises 40% of the decay and the second component is 1.7 ps which comprises the other 60%. Population relaxation for a vibrational mode with these relative amplitudes and timescales are similar to what has been observed by Tokmakoff and coworkers in the population relaxation of the amide I band of dilute solutions of \( N \)-methylacetamide in D\(_2\)O and DMSO.\(^{11}\) The authors described their observations as follows: the fast component was attributed to the rapid exchange of vibrational energy between amide I
(mostly C=O stretching) and amide II (nearly equal C–N stretching and N–H bending) while the slower component was ascribed to the dissipation of vibrational energy into bath modes. Given the similarity of the ester and amide functional groups, we believe that the same relaxation mechanism occurs in the ester of PCBM in the OPV blend.

Given the above interpretation, we make the following assignments to the spectral features in the 10 ps transient spectrum in Figure 5-3B. The induced absorption is assigned to the 0–1 transition of the carbonyl stretching mode of the vibrationally hot intermediate state. The vibrationally hot intermediate is formed as population is transferred to the C–O stretching mode. The induced absorption feature is shifted to lower frequency (relative to the carbonyl transition) because interaction with the probe field leads to excitation into an overtone transition that is shifted to lower energy through an anharmonic term. To verify this assignment, the population relaxation of the C–O stretching mode should include the first period of a quantum beat corresponding to the coherent exchange of energy between carbonyl and C–O stretching modes (as observed in ref. 11).

Based on the previous assignment, we then assign the bleach feature at 10 ps to the continued bleaching of the original 0–1 carbonyl stretching transition. The population of the original ground state which was excited has not fully recovered because of the formation of the vibrationally hot intermediate state. The bleach feature is shifted to higher frequency because the induced absorption of the vibrationally hot intermediate destructively interferes with the bleach feature of the original ground state. The vibrationally hot intermediate state decays to the thermalized (or original) ground state after the experiment (i.e. >10 ps).

Analyzing the temperature dependence in Table 1, we see that there is weak if not negligible temperature dependence to these data. Population relaxation can still influence the frequency of the carbonyl stretching mode of PCBM. However, they will be affected the same at all temperatures. We will demonstrate below that these dynamics do not result in substantial spectral diffusion, at least after a picosecond and longer.
**Orientational Relaxation**

Orientational relaxation represents another decay channel in vibrational cooling. Orientational motion is characterized by the time-dependent anisotropy, \( r(t) \). We calculate the time-dependent anisotropy according to the following equation

\[
r(t) = 0.4C_2(t) \frac{S_{\parallel}(t) - S_{\perp}(t)}{S_{\parallel}(t) + 2S_{\perp}(t)}
\]

where \( C_2(t) \) is the orientational correlation function and \( S_{\parallel}(t) \) and \( S_{\perp}(t) \) are kinetics measurements at a particular frequency with the pump polarization oriented parallel and perpendicular to the probe polarization, respectively. The time-dependent anisotropy calculated for the carbonyl stretching mode of PCBM measured at 1740 cm\(^{-1}\) is displayed in Figure 5-6 for measurements at temperatures of 350, 300, 250, and 200 K.

We measure anisotropy values of 0.42-0.44 at the time origin which is slightly larger than the value expected for an isotropic distribution of transition dipole moment vectors (i.e. 0.4). This would suggest some degree of molecular ordering, or in other words, that the initial distribution of transition dipole moments interacting with the IR pump pulse is not isotropic. It is also possible that a small nonresonant signal is present in the IR pump–probe signals around the time origin. If this signal were present and larger for parallel polarizations of the pulses, for example, it would give rise to an artificially higher anisotropy value measured.

A model function, \( F_{OR}(t) \), was used to fit the dynamics of orientational relaxation at each temperature. The model function has the following form

\[
F_{OR}(t) = A \int_{-\infty}^{\infty} \left[ S_{FID}(t+\tau) \Theta(-t-\tau) + C_1(t+\tau) \Theta(t+\tau) \right] \left[ 1 + xC_2(|t+\tau|) \right] G(\tau) d\tau
\]

which accounts for population and orientational relaxation simultaneously. We used the results obtained from fitting the pure population relaxation (eqn. 2) as parameters for the perturbed free induction decay, \( S_{FID}(t) \), (eqn. 3) and population relaxation function, \( C_1(t) \), (eqn. 4) that are used
in the present equation (eqn. 7). The parameter $x$ has a value of 0.8 for data collected with parallel pump and probe polarizations or −0.4 for data collected with perpendicular pump and probe polarizations. The orientational correlation function was modeled according to

$$C_2(t) = (Q^2 + (1-Q^2) \exp(-t/\tau_w))[(1-a_{op})\exp(-t/\tau_1)+a_{op}\exp(-t/\tau_2)]$$

which represents the sum of three exponentials with time constants $\tau_w$, $\tau_1$, and $\tau_2$. The orientational correlation function is symmetric about the time origin because orientational motion affects the perturbed free induction decay the same at negative and positive time delays.

The resulting fits for parallel and perpendicular traces measured at 300 K are overlaid on the experimental data in Figure 5-4. The time-dependent anisotropy calculated with this fitting procedure is overlaid on the corresponding anisotropy trace in Figure 5-6. The parameters obtained for each temperature along with error limits are summarized in Table 5-2. Due to the finite vibrational lifetime of the carbonyl stretching mode, we are unable to accurately determine time constants for the two slower orientational components.

The fast and the slow orientational components were assigned to wobbling-in-cone and diffusive orientational motion.$^1$ When orientational motion accesses a range of solvent environments, such as in liquids, orientational motion can lead to spectral diffusion.$^{12}$ Given that wobbling-in-cone orientational motion is complete by a picosecond in this system at 300 K, wobbling-in-cone orientational motion is not expected to give rise to spectral diffusion on the picosecond and longer time scale. We do not expect wobbling-in-cone orientational motion to cause spectral diffusion unless the system was cooled to such a temperature as to slow down the wobbling-in-cone orientational motion.

As can be seen Figure 5-6 and in Table 5-2, wobbling-in-cone orientational motion with time constant $\tau_w$ does not vary with temperature. This observation is consistent with inertial motion of the carbonyl group along with a negligible activation barrier (relative to thermal energy) for the inertial motion.
The relative amplitude, $1 - Q^2$, of the first exponential component in eqn. 8 can be used to characterize the half angle of the cone, $\theta$, in which the carbonyl bonds undergo reorientation. The cone half angle is related to $Q^2$ according to\textsuperscript{13}

$$Q^2 = \left[ \frac{1}{2} \cos(\theta)(1+\cos(\theta)) \right]^2 \tag{9}$$

We calculate values of 34, 30, 28, and 24° for the cone half angle of the carbonyl bond at temperatures of 350, 300, 250, and 200 K, respectively. A smaller cone half angle indicates a decrease in free volume surrounding the PCBM molecules. We expect that the smaller cone half angle (and decreased free volume) is associated with increased density at lower temperatures. To further test this interpretation, the cone half angle should begin to increase at temperatures below 150 K where Kwon et al. found using MD simulations that the sign of the thermal expansion coefficient of C\textsubscript{60} becomes negative.\textsuperscript{14} While the precise mechanism of this contraction was not explicitly stated, the authors noted that the quadrapolar deformation vibrational mode dominated the contraction at low temperatures.

**Spectral Diffusion**

2D IR spectra of the carbonyl stretching mode of PCBM at 1, 3, and 10 ps pump–probe time delays are displayed in Figure 7. Spectra are displayed for temperatures of 350, 300, 250, and 200 K. The 2D IR experiment is performed such that a narrow band of carbonyl stretching vibrations are populated by a pump pulse (horizontal axis), given time to evolve, and their vibrational frequencies are detected (vertical axis) after some pump–probe time delay, $T_w$. The contours represent a 10% change in transmittance which has been normalized to the maximum positive signal in each spectrum.

Two 2D peak shapes are observed in each spectrum. The positive peak shapes corresponds to the 0–1 transitions of the carbonyl stretching mode. The 0–1 transitions appear on the diagonals ($\omega_{\text{probe}} = \omega_{\text{pump}}$). The 0–1 transitions are positive because they correspond to ground
state bleaching and excited state stimulated emission. The negative peak shape is an induced absorption. As explained earlier, we anticipate that this arises from the 1–2 transitions of the carbonyl stretching mode at the earliest timescales. The 1–2 transitions are shifted away from the diagonal along the $\omega_{\text{probe}}$ axis due to vibrational anharmonicity. We calculate a value of 18 cm$^{-1}$ for the vibrational anharmonicity of the carbonyl stretching mode in this system which is similar to what has been measured for the carbonyl stretching mode of methyl acetate in carbon tetrachloride.$^{15}$ The peak shapes change slightly at long time delay in accord with our previous assignment of a vibrationally hot intermediate state.

Diagonally elongated shapes in a 2D IR spectrum are indicative of inhomogeneous broadening. We observe a diagonally elongated shape for both 0–1 and 1–2 transitions of the carbonyl stretching mode in the spectrum at 1 ps pump–probe time delay. The inhomogeneous broadening of the carbonyl stretching mode in this system is due to the wide range of environments in which the carbonyl group exists. We showed in Chapter 4 that a portion of this inhomogeneous broadening can be attributed to vibrational solvatochromism and a small contribution from a vibrational Stark shift in OPV blend films.

We do not observe spectral diffusion on the picosecond and longer timescale at 350, 300, 250, or 200 K. The physical manifestation of spectral diffusion is the population of a narrow band of carbonyl stretching vibrations which, through interactions with the environment, alter their vibrational frequencies and so are detected at a different vibrational frequency after some pump–probe time delay. The dynamic process of spectral diffusion would be apparent in a series of 2D IR spectra if the original diagonally elongated feature were to become circular, i.e. elongated along the anti-diagonal. Spectral diffusion at different rates, for example, has been demonstrated for silica surface-tethered transition metal carbonyl complex as a function of the solvent environment (i.e. no solvent, wet, and bulk solution)$^{16}$ Thus, we do not see spectral diffusion in this system at any temperature measured, which is not unexpected as PCBM is a massive molecule (900 Da) and the system is a glassy solid at these temperatures. The dynamic
linewidths, i.e. the width along the antidiagonal, of the both 0–1 and 1–2 transitions do seem slightly larger at higher temperatures.

The extent of spectral diffusion was determined by calculating the center line slope (CLS)\textsuperscript{17} of the 2D peak shapes as well as the variation in the dynamic linewidth of the 0–1 transition. The first step in calculating the center line of a 2D IR line shape is to take a spectral slice along the $\omega_{\text{probe}}$ axis and determine which point in the spectral slice corresponds to the maximum intensity. The center line is generated by determining the point of maximal intensity for many spectral slices. The slope of this line is a measure of spectral diffusion. For example, the slope of the center line of an inhomogeneously broadened line shape would be unity. For a symmetric line shape which is both inhomogeneously broadened and maximally homogeneously broadened, the center line would be a vertical line with a slope of infinity. The inverse of the CLS is actually a more convenient metric. The inverse of the CLS has a value near unity for an inhomogeneously broadened line shape and the CLS decays to zero for systems that undergo spectral diffusion with increasing pump–probe time delay.\textsuperscript{12}

Not only is the inverse of the CLS a measure of spectral diffusion, but the inverse of the CLS correlates with the frequency–frequency correlation functions (FFCF) of the corresponding vibrational transitions, as well.\textsuperscript{17} This correlation is expressed as the joint probability distribution, $C(t)$, where

$$C(t) = \langle \delta \omega(t) \delta \omega(0) \rangle$$

The FFCF characterizes the fluctuating forces imposed by the bath (i.e. the solvent modes and all other internal vibrational modes) on the system (i.e. the carbonyl stretching mode) and determines the time scale for spectral diffusion.

The inverse of the CLS was calculated from 2D Gaussian line shapes fit to the 0–1 and 1–2 transitions in the 2D IR spectra. Figure 5-8 depicts the variation of the inverse of CLS for the 0–1 transition versus pump–probe time delay for temperatures of 350, 300, 250, and 200 K. The
error bar indicated for the 350 K data set is representative of the error bar for all data sets. The data show that the inverse of the CLS of the carbonyl stretching mode of PCBM does not change between 1 and 10 ps. Small variations in value at different time delays are not significant. Thus, taking the time dependence of inverse of the CLS to reflect the time dependence of the FFCF, this result indicates that thermal fluctuations over the temperature range examined do not give rise to significant fluctuations of the carbonyl stretching frequency of PCBM.

We also evaluated the extent of spectral diffusion in this system by calculating the dynamic linewidths of the 0–1 transition in the 2D IR spectrum. We chose to calculate the dynamic linewidths by determining the linewidth of a spectral slice parallel to the vertical axis. This vertical slice was chosen because spectra along the horizontal axis are complicated by convolution with the pump pulse spectrum (giving line widths wider than the natural line width). Figure 5-9A displays transient vibrational spectra measured at 350 K with the narrowband IR pump pulse centered at 1740 cm\(^{-1}\). Spectra with pump–probe delays of 1, 3, 8, and 10 ps are plotted. The transient spectra at 1 and 3 ps are indistinguishable while the bleaching and induced absorption features are shifted to slightly higher frequency in the transient spectra at 8 and 10 ps. As mentioned previously, we believe that this shift occurs because of excited state relaxation of the carbonyl stretch into a vibrationally hot ground state. The features and dynamics of the transient spectra measured at 300, 250, and 200 K (data not shown) are similar to those measured at 350 K.

We calculate a value of 2 cm\(^{-1}\) for the peak shift observed from 1 to 10 ps. This value matches very closely to that observed in pump–probe experiment in which we excited the sample with a broadband pump pulse. The frequency shifts both originate from the relaxation of the vibrational excited state into a vibrationally hot intermediate state.

The linewidth of the 0–1 and 1–2 vibrational features in the transient spectra were determined by fitting the features with Gaussian line shapes. Dynamic linewidth plotted against pump–probe time delay are displayed in Figure 5-9B for all temperatures. The FWHM of the
linear IR line shape at each temperature is also plotted in each panel as a straight line. If spectral diffusion were to occur, the dynamic linewidth would increase toward the value of the FWHM of the linear IR line shape. These data further confirm that spectral diffusion is not significant on the time scale of these experiments at any temperature reported here.

The variation of the CLS and dynamic linewidth correlates with the temperature dependence of the cone half angle of the wobbling-in-cone orientational motion. We calculated an increase in the cone half angle from 24 to 34°, a decrease of the CLS from near unity to ~0.8, and an increase in the dynamic linewidth from 9 to 11 cm⁻¹ on going from 200 to 350 K. These observations indicate that the dynamic linewidth of the carbonyl stretching mode of PCBM is influenced by the orientational motion. We postulated that spectral diffusion would be observed in this system if the sample were cooled sufficiently to slow the wobbling-in-cone orientational motion into the picosecond time scale. Alternatively, a technique such as 2D IR vibrational echo spectroscopy with sub-ps resolution could be used to study this system to resolve the sub-ps spectral diffusion.

5.4 Conclusion

We have examined the temperature dependence of the linear IR spectra, population relaxation, and orientational motion and tested for spectral diffusion of the carbonyl stretching mode of PCBM in an OPV blend film comprised of CN-MEH-PPV and PCBM. We observed weak temperature dependence to the linear IR spectrum which implies weak temperature dependence to the vibrational dynamics. The vibrational population relaxation is relatively unaffected by changes in temperature. The time constant of the sub-picosecond wobbling-in-cone orientational motion is relatively unaffected by changes in temperature. Changes in the CLS and dynamic linewidth of the 2D IR spectra at different temperatures correlate with changes in the wobbling-in-cone half angle which implies this motion plays a role in homogeneous
broadening. Importantly, we do not observe spectral diffusion in the 2D IR spectra at any temperatures. The data suggest that dynamics of the ground (electronic) state carbonyl stretching mode of PCBM should not conflict with the frequency shift assigned to motion of electrons in PCBM domains in the Vis pump–IR probe experiments.

5.5 References


Figure 5-1. Chemical structures of the $\pi$-conjugated polymer CN-MEH-PPV and functionalized fullerene PCBM.
Figure 5-2. Dispersive IR spectra in the carbonyl stretching region of 1:1 CN-MEH-PPV:PCBM blend film obtained at temperatures ranging from 184 to 390 K. Reprinted with permission from *J. Phys. Chem. B* 2010, **114**, 12242-12251. Copyright 2010 American Chemical Society.
Figure 5-3. (A) Broadband IR pump–probe spectra for the carbonyl stretching mode of PCBM in an OPV blend film at 300 K at pump–probe time delays of 0.1 and 10 ps. (B) Two-dimensional plot of broadband IR pump–probe spectra collected at 300 K. Vertical axis represents pump–probe time delay. Horizontal axis represents probe frequencies. Dashed and dotted lines are added for visualization of shift of the vibrational features toward higher frequency with increasing time delay.
Figure 5-4. Broadband IR pump–probe kinetics at 1740 cm\(^{-1}\) with pump and probe oriented parallel, \(S_\parallel(t)\), and perpendicular, \(S_\perp(t)\), relative to one another. Also, population relaxation at 1740 cm\(^{-1}\) calculated from \(S_\parallel(t)\) and \(S_\perp(t)\). Inset shows population relaxation with maximum value (at the time origin) normalized to 1 and plotted in a semilog fashion. Dotted line is a single exponential with a 1.7 ps time constant. The population relaxation is fit with a model function, \(F_p(t)\), as discussed in the text. Reprinted with permission from \textit{J. Phys. Chem. B} 2010, \textit{114}, 12242-12251. Copyright 2010 American Chemical Society.
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**Table 5-1.** Best fit parameters for population relaxation dynamics, $C_1(t)$, of the carbonyl stretching mode of PCBM. Reprinted with permission from *J. Phys. Chem. B* 2010, 114, 12242-12251. Copyright 2010 American Chemical Society.
Figure 5-5. Population relaxation with longest-time component subtracted for several probe frequencies at 300 K plotted in a semilog fashion. Probe frequencies plotted are 1751, 1746, 170, and 1735 cm$^{-1}$. Dotted line is a single exponential with a 1.7 ps time constant. Reprinted with permission from *J. Phys. Chem. B* 2010, 114, 12242-12251. Copyright 2010 American Chemical Society.
Figure 5-6. Dynamics of the anisotropy of the carbonyl stretching vibration of PCBM at 1740 cm$^{-1}$ at temperatures of 350, 300, 250, and 200 K in 1:1 CN-MEH-PPV:PCBM blend films. Anisotropies were calculated according to eqn. 5.6. Fits to the anisotropy are calculated as described in the text and are overlaid on the experimental data. Reprinted with permission from *J. Phys. Chem. B* 2010, 114, 12242-12251. Copyright 2010 American Chemical Society.
Table 5-2. Best fit parameters for orientational correlation function, $C_2(t)$, of the carbonyl stretching mode of PCBM. Reprinted with permission from *J. Phys. Chem. B* 2010, 114, 12242-12251. Copyright 2010 American Chemical Society.

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Figure 5-7. 2D IR spectra of the carbonyl stretching mode of PCBM in 1:1 CN-MEH-PPV:PCBM blend films collected at temperatures of 350, 300, 250, and 200 K. 2D IR spectra collected at pump–probe time delays of 1, 3, and 10 ps are plotted for each temperature. Center lines are placed on top of the positive-going bleach feature.
Figure 5-8. Inverse of CLS of 2D IR features plotted against pump-probe time delay for measurements at 200, 250, 300, and 350 K. Reprinted with permission from J. Phys. Chem. B 2010, 114, 12242-12251. Copyright 2010 American Chemical Society.
Figure 5-9. (A) Linear IR spectrum and spectral slices obtained from 2D spectrum when the sample at 350 K was excited with a narrowband pump centered at 1740 cm$^{-1}$. Spectra at pump–probe time delays of 1, 3, 8, and 10 ps. (B) Analysis of FWHM of 0–1 bleach feature at each temperature as a function of pump probe time delay. Reprinted with permission from J. Phys. Chem. B 2010, 114, 12242-12251. Copyright 2010 American Chemical Society.
Chapter 6

Measuring the Barrier to Charge Separation in Organic Photovoltaic Blend Films. IV. Influence of Acceptor Structure


6.1 Introduction

As mentioned in Chapter 3, the exact mechanism by which CT states dissociate into separated charge carriers at the donor/acceptor junction in OPV materials is still unclear. One picture is based on Onsager theory (Figure 6-1). Onsager formulated his theory to explain the autoionization (full dissociation) of Coulombically bound electrolytes in solution.\(^1\) Assuming the positive charge (hole) is fixed and that the negative charge (electron) undergoes Brownian motion, the electron has a characteristic thermalization length which depends on properties of the system such as the dielectric constant. There is also a characteristic Coulomb capture radius which is defined as the radius where the attractive potential between positive and negative charges equals thermal energy (i.e. \(kT\)). If the thermalization length is greater than the Coulomb capture radius, the charges are considered fully dissociated. However, if the thermalization length is less than the Coulomb capture radius, there is a finite probability associated with their full dissociation. Within this model, it would be possible for excess energy from light absorption to increase the thermalization length of photogenerated charges, in particular the electron, such that the probability for full dissociation increases. Peumans and Forrest successfully used kinetic
Monte Carlo simulations based on Onsager theory to show that the probability for dissociation increases for a donor/acceptor junction relative to bulk autoionization and that the probability increases for asymmetric electron/hole mobilities (which is proportional to the attempt frequency in their model).\(^2\)

One research direction based on the principles of Onsager theory is led by James Durrant. These researchers have correlated estimates of the free energy difference between the electron donor and acceptor materials with the magnitude of the transient absorption signal of photogenerated polarons (taken to represent the efficiency of charge separation).\(^3\)\(^-\)\(^5,7\) The free energy difference is calculated as \(\Delta G_{CS}^{est} = E_S - (\text{IP}_D - \text{EA}_A)\), where \(E_S\) is the singlet energy of the polymer, \(\text{IP}_D\) the ionization potential of the electron donor, and \(\text{EA}_A\) the electron affinity of the electron acceptor. The difference between ionization potential of the donor and electron affinity of the acceptor is taken as an estimate for the energy of the polaron pair. The free energy difference is thought to be related to the excess free energy available to drive the charge separation reaction. Because the estimate omits the Coulombic attraction between negative and positive polarons, the free energy difference only reflects relative differences between material sets and is not an absolute calculation.

One use of transient absorption spectroscopy to examine the efficiency of charge separation is in a series of polythiophene:PCBM blends.\(^3\)\(^,4\) The observable for charge photogeneration yield in these experiments was the magnitude of a long-time (a few \(\mu\)s) photoinduced absorption measured at the maximum of the near-IR (700 – 1300 nm) which corresponds (primarily) to the absorption of positive polarons in the polymer. In one study, a series of polythiophenes (PTs) were synthesized so as to vary the ionization potential and the corresponding \(\Delta G_{CS}^{est}\) value.\(^3\) The \(\Delta G_{CS}^{est}\) values varied from 0.6 to 0.9 eV. The charge separation efficiency for blends of these PTs with PCBM increased nearly two orders of magnitude with increasing \(\Delta G_{CS}^{est}\) values (i.e. excess free energy). Experiments exclusively on RR-P3HT:PCBM were carried out as well.\(^4\) In this study, they compared unannealed and
annealed RR-P3HT:PCBM polymer blends. Using cyclic voltammetry, they measured an increase in IP of the polymer with annealing (which corresponds to an increase in $\Delta G_{CS}^{\text{est}}$). Furthermore, they measured an increase in the photogenerated carrier yield implying again that excess energy is involved in generating these charges.

On the other hand, a series of perylenediimides (PDIs) blended with RR-P3HT did not exhibit the same variation in charge separation efficiency with $\Delta G_{CS}^{\text{est}}$. In this case, the researchers monitored the photoinduced absorption of the PDI negative polaron in the visible at 700 nm. Using some of the above PTs blended with PDI, the researchers see very little change in charge separation efficiency. This particular PDI had a bulky group substituted on the imide position, presumably to increase solubility. Substituting on the imide position does not affect the optical or electronic properties of the single molecule because there is a node in the HOMO and LUMOs at this position. The researchers synthesized a series of PDI molecules both with different substituents on the imide position as well as the substituents on the perylene core, the latter of which is expected to alter the electron affinity. The charge photogeneration yield in blends of RR-P3HT with these different PDI molecules again showed very little change in charge separation efficiency even with $\Delta G_{CS}^{\text{est}}$ values ranging from 0.4 to 0.7 eV.

Although the above measurements established a correlation between the yield of charge carriers and thermodynamic properties of the materials, they are unable to access the underlying rates that ultimately determine the yield of charge carriers. We have used Vis pump–IR probe spectroscopy to investigate the rate of CT state dissociation in blend films comprised of RR-P3HT blended with either PCBM or a PDI molecule.

In this chapter, we present Vis pump–IR probe experiments on thin OPV blend films consisting of the electron donating polymer RR-P3HT blended with either BTBP (a PDI derivative) or PCBM acting as electron acceptor. Chemical structures of these materials are displayed in Figure 6-2. We use an optical pump pulse to excite RR-P3HT and observe a bleaching of the carbonyl stretching mode of the acceptor molecule in the mid-IR. We measure
the rate that the bleach of the carbonyl stretching mode in each system shifts toward its asymptotic value and take this rate to correspond to the rate of CT state dissociation. We observe that the rate of CT state dissociation depends on temperature for 1:1 RR-P3HT:BTBP blend films, but not 1:1 RR-P3HT:PCBM blend films. From the Vis pump–IR probe data acquired at several temperatures, we determine the activation barrier to CT state dissociation in each system. It appears that the dissociation of CT states in RR-P3HT:BTBP blends is activated, while in RR-P3HT:PCBM blends it is not. With information that neither acceptor phase is particularly crystalline, we attribute this difference to the different shapes of the electron acceptor molecule and discuss this point further.

6.2 Materials and Methods

OPV blend films for these experiments were prepared as follows. The electron donor, RR-P3HT, was purchased (EMD Chemicals Inc., Gibbstown, NJ) and used as received. Electron acceptor materials BTBP and PCBM were purchased (Sigma-Aldrich, St. Louis, MO) and used as received. Equal amounts (by weight) of electron donor and acceptor were added to a vial. An appropriate amount of chlorobenzene (Sigma-Aldrich, St. Louis, MO) was added to make a 50 mg/mL solution. With the exception of PCBM as will be discussed below, films of the individual materials were prepared from a 25 mg/mL solution. The solution was stirred with a Teflon resin-coated magnetic stir bar for ~2 hrs at 65 °C. After stirring, the solution was then transferred with a Pasteur pipette to a 3 mm thick, 1 in. diameter CaF₂ substrate (Red Optronics, Mountain View, CA). After completely covering the CaF₂ substrates with the solution, the substrates were spun at 1000 rpm for 60 seconds. The films were forced dry during the spin coating process with a gentle stream of nitrogen gas coming from ~1/4 in. diameter plastic tube oriented and held in place directly ~1/2 in. above the substrate in order to consistently prepare "unannealed" films (as
assessed via UV-Vis spectroscopy). The author notes that the nitrogen gas most likely kinetically traps the materials before they phase separate through annealing induced by residual solvent.

For films of PCBM, we used either 25 or 70 mg/mL solutions in o-dichlorobenzene (Sigma-Aldrich, St. Louis, MO). These solutions were sonicated for ~1 hr at 40 °C. The solutions were dispensed from a Luer lock syringe (Monoject 8881516135, Covidien, Mansfield, Massachusetts) fit with a 0.2 µm Teflon membrane filter (VWR 28145-495, VWR International, LLC, Radnor, PA). The author notes that the Luer lock and filter combination were used as films of PCBM prepared by this method were smooth and uniform. It is possible that by using this method either the filter prevented undissolved PCBM (which has a finite solubility in these solvents) from creating nucleation sites which made poor films or that a small amount rubber from the Luer lock syringe dissolved in the solution and helped form smooth, uniform films. The small amount of rubber (if any) should have a negligible effect on the measurements reported here.

FTIR spectra were calculated by acquiring 16 interferograms for both the background and sample. Some datasets were acquired in multiples and averaged together to eliminate water lines. Nitrogen gas was used to purge the FTIR instrument. The resolution of the FTIR was set to 1 cm\(^{-1}\) with one level of zero filling. The UV-Vis spectrophotometer was set to have a spectral resolution of 1 nm.

For the Vis pump–IR probe experiment, RR-P3HT:PCBM blend films were excited with the pump pulse centered on 550 nm while for RR-P3HT:BTBP blend films to pump pulse was centered on 600 nm. All experiments were carried out with ~200 µJ/cm\(^2\) incident on the sample. Figure 6-3 displays the excitation density dependence of the induced absorption at 1770 cm\(^{-1}\) that corresponds to primarily polaron absorption in the polymer (discussed in Chapter 3). The nonexponential dynamics indicate biexciton annihilation at high excitation densities. The excitation density of ~200 µJ/cm\(^2\) was chosen because it was the lowest possible providing reasonable signal-to-noise. The sample was held in an optical cryostat under a dynamic vacuum
of ~0.1 torr for the Vis pump–IR probe experiments. Temperature was controlled in the same manner as discussed in the methods section of Chapter 5.

Detailed information on the FTIR spectrometer, UV-Vis spectrometer, and Vis pump–IR probe techniques are included in Chapter 2.

### 6.3 Results and Discussion

FTIR spectra of films of PCBM, RR-P3HT, and a 1:1 RR-P3HT:PCBM blend film are displayed Figure 6-4A. The spectra for the films containing PCBM have been normalized to the carbonyl stretching absorption of PCBM. The spectrum for RR-P3HT was normalized with the same normalization constant as used for the blend. The film was deposited under nearly identical conditions as the blend (but of course, without any PCBM) and so each film should contain similar amounts of RR-P3HT (although we note that this ultimately depends on the solution viscosity which determines film thickness). RR-P3HT does exhibit a weak IR absorption at ~1730 cm\(^{-1}\). As there are no fundamental modes in this region of the IR for RR-P3HT, this weak IR absorption may result from an overtone or combination band.

We measure a ~1-2 cm\(^{-1}\) shift in Figure 6-4A for the carbonyl stretching absorption of PCBM in this OPV blend film whose thickness is on the order of 300 – 500 nm, consistent with our observations in thick films (i.e. > 1 \(\mu\)m). Gearba et al.\(^8\) used ATR-FTIR to acquire FTIR spectra of OPV blend films on the order of 30 – 100 nm thick and observed the same few cm\(^{-1}\) shift. They measured the shift for blend films comprised of PCBM with several different polymers, including RR-P3HT and MEH-PPV. The IR absorption of RR-P3HT does not interfere with the solvatochromic shift as the low frequency absorption would tend to cause the carbonyl stretching mode of PCBM appear to shift to lower frequency.

FTIR spectra of films of BTBP, RR-P3HT, and a 1:1 RR-P3HT:BTBP blend film are displayed in Figure 6-4B. The spectra of films containing BTBP were normalized to the peak at
1667 cm$^{-1}$. There are two sets of peaks in the linear IR spectrum of BTBP at frequencies of 1658, 1667, 1701, and 1708 cm$^{-1}$. The two sets of peaks correspond to the symmetric and asymmetric carbonyl stretching modes of BTBP. The splitting arises in the solid state because there are two inequivalent perylene molecules per unit cell. The carbonyl stretching modes may be shifted to lower frequency relative to 3,3-dimethylglutarimide due to their incorporation into the conjugation network of the perylene core. We see that in the 1:1 RR-P3HT:BTBP blend the peaks associated with carbonyl stretching modes are very slightly shifted to lower frequency. Also, the low frequency peak of the high frequency set of peaks (i.e. 1701 cm$^{-1}$) becomes larger relative to the higher frequency peak (1708 cm$^{-1}$). As can be seen in Figure 6-4B, the linear IR absorption of P3HT does not overlap with either of the carbonyl stretching modes of BTBP.

UV-Vis spectra of films of PCBM, RR-P3HT, and 1:1 RR-P3HT:PCBM blend films are displayed in Figure 6-5A. The spectra are normalized such that the maximum absorbance in the blend film is 1 and the maximum absorbance in the pure material films is 0.5. Overlaid on the spectra is a dashed line indicating the 550 nm excitation wavelength used in the Vis pump–IR probe experiment. According to values reported by Hoppe and Sariciftci for the absorption coefficient of thin films of RR-P3HT and PCBM, RR-P3HT has an absorption coefficient a factor of ten larger than PCBM at 550 nm. Exciting the sample at this pump wavelength ensures that the majority of pump photons are absorbed by the electron donor and that a bleach of the carbonyl stretching mode results from the transfer of an electron from electron donor to acceptor.

Figure 6-5A also highlights the unique UV-Vis absorption of RR-P3HT. Most polymers exhibit a broad, featureless absorption which has been explained as resulting from low-frequency torsional motions that result in a distribution of conjugation lengths. The broadened band has also been attributed to large structural relaxation in the excited state manifold (i.e. a displacement in the harmonic oscillator picture). We observe peaks at 608, 562, and 523 nm with corresponding energies of 2.04, 2.21, and 2.37 eV in the UV-Vis spectrum of RR-P3HT. Assuming an individual polymer chain with a single vibrational mode coupled to the electronic
transition, the peaks correspond to the 0–0, 0–1, and 0–2 vibronic transitions, respectively. We measure 0.16 eV for the energy spacing between 0–1 and 0–2 features. The electronic absorption and photoluminescence of RR-P3HT was recently explained in terms of weakly interacting H aggregates. In dilute solutions, a broad featureless absorption spectrum was observed for P3HT, while the photoluminescence spectrum exhibited fine structure (attributed to coupling of the C=C stretching mode, ~0.18 eV, to the electron transition). By increasing the concentration or changing to a solvent in which the polymer was less soluble, fine structure appeared. The fine structure washed out at higher temperatures. Thus, the fine structure in the UV-Vis spectrum of RR-P3HT is indicative of intermolecular interactions between polymer chains.

Vibronic fine structure also appears in the spectrum of blend films of RR-P3HT:PCBM. These features indicate that there are significant amounts of intermolecular interaction between polymer chains in the blend film with PCBM. These films are very likely “annealed” and have undergone an unknown extent of phase separation. The spectra reported are those acquired after the experiment. These films were annealed by residual hydrocarbons in the cryostat chamber. As will be discussed in the Appendix, films initially prepared exhibit a structureless, lower wavelength (higher energy) absorption feature.

UV-Vis spectra of films of BTBP, RR-P3HT, and 1:1 RR-P3HT:BTBP blend films are displayed in Figure 6-5B. The spectra are normalized such that the maximum absorbance in the blend film is 1 and the maximum absorbance in the pure material films is 0.5. Overlaid on the spectra is a dashed line indicating the 600 nm excitation wavelength used in the Vis pump–IR probe experiment. For thin films of comparable thickness, RR-P3HT absorbs very strongly at this wavelength (relative to BTBP). Assuming a homogeneous blend, P3HT absorbs nearly 5 out of every 6 photons. Although this assumption, the author notes, may not entirely accurate as blend films deposited with PDIs tend to appear rougher because PDIs have a strong tendency to crystallize. However, we presume that the majority of excitations in the Vis pump–IR probe experiment initially reside in the electron donor.
BTBP also exhibits vibronic structure. We measure the most intense peaks at 530 and 493 nm with weaker shoulders at 461 and 430 nm. The corresponding energies are 2.34, 2.52, 2.69, and 2.89 eV. The average energy spacing is ~0.18 eV which again coincides with the energy of the C=C stretching mode. The lowest energy peaks can be assigned to the 0–0 and 0–1 vibronic absorption transitions. We observe that the 0–0 vibronic transition is slightly more intense than the 0–1 vibronic transition for a thin film of BTBP prepared via spin coating from chlorobenzene. For single PDI molecules, the 0–0 vibronic feature is expected to have a much larger intensity than all other vibronic features while reversal of the relative intensities of 0–0 and 0–1 vibronic bands is expected when π-π stacking occurs between PDI molecules, i.e. PDI aggregates. From these observations, we expect BTBP on the molecular scale to exhibit some extent, but incomplete, ordering.

Vis pump–IR probe spectra for RR-P3HT:PCBM blend films collected at 200, 300, and 325 K are displayed in Figure 6-6A. The transient spectra exhibit a small bleach feature and a large induced absorption. We take the bleach feature to represent the transfer of an electron to PCBM and the induced absorption to primarily reflect the induced absorption of polarons/excitons generated in the polymer as discussed in Chapter 3. The dashed lines are placed at the center frequency of the bleach at the longest pump–probe time delay to serve as a guide to the eye. The bleach feature in the transient spectra shifts slightly to lower frequency with increasing pump–probe time delay at all temperatures.

Vis pump–IR probe spectra for RR-P3HT:BTBP blend films collected at 170, 200, 300, and 350 K are displayed in Figure 6-6B. These transient spectra exhibit the same general features as observed in the RR-P3HT:PCBM blend system. Again, the bleach shifts to lower frequency with increasing pump–probe time delay at all temperatures. The magnitude of the shift is much larger in this system than it is in the RR-P3HT:PCBM system. The bleach magnitude in the RR-P3HT:BTBP system is also larger than that observed in the RR-P3HT:PCBM system. The larger magnitude could be occurring for a few reasons. First, the absorption coefficient of the carbonyl
stretching mode in BTBP may be larger than that in PCBM. We have not measured this, but could do so with uniform thin films of BTBP and PCBM. The other possibility is higher yield of charge carriers. Shoae et al., for example, measured a higher yield of charge carriers in polymer:PDI blends versus the same polymer:PCBM blends as assayed by the magnitude of their transient absorption signal at 100 ns time delay.\(^7\)

The induced absorption and bleach features were fit with polynomial and Gaussian functions as described in Chapter 3. The center frequencies obtained from the Gaussian fits to both RR-P3HT:PCBM and RR-P3HT:BTBP data sets are plotted against pump–probe time delay in a semilog plot in Figure 6-7. The vertical axis of Figure 6-7 has been plotted as an arbitrary scale and the data have been vertically offset to highlight differences in kinetics, omitting information on the absolute position of the bleach center frequency in these data sets. In both data sets, the bleach center frequency shifts to lower frequency on ultrafast and longer timescales. In Figure 6-7A, we see that the bleach center frequency in RR-P3HT:PCBM exhibits a slight shift on the picosecond timescale until a few hundred picoseconds when the shift to lower frequency becomes more pronounced. The dynamics of the bleach center frequency in RR-P3HT:BTBP shown in Figure 6-7B exhibit a much larger magnitude shift on the picosecond timescale. This frequency shift slows significantly at lower temperature. We note that there is a slight shift toward higher frequency on the nanosecond timescale in the dynamics measured in RR-P3HT:BTBP.

The dynamic shift of the bleach center frequency was fit according to procedures reported in Chapter 3 in order to obtain time constants for the process. The RR-P3HT:PCBM data was fit with a biexponential function while the RR-P3HT:BTBP data was fit with a function of the following form
\[ f(\omega) = \omega_i - (\omega_f - \omega_i)[1 + a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2) + (1 - a_1 - a_2) \exp(-t/\tau_3)] + (\omega_b - \omega_f)[1 - \exp(-t/\tau_b)] \]  

where \( \tau_b \) represents the timescale for returning to higher frequency \( \omega_b \). The results of the fitting analysis are displayed in Table 6-1. We obtain asymptotic frequencies of 1739, 1740, and 1739 cm\(^{-1}\) for measurements in RR-P3HT:PCBM at 325, 300, and 200 K with corresponding average lifetimes of 2.7, 2.9, and 3.0 ns. In RR-P3HT:BTBP, we obtain asymptotic frequencies of 1709, 1708, 1707, and 1705 cm\(^{-1}\) for measurements at 350, 300, 200, and 170 K with corresponding average lifetimes of 1.1, 1.6, 6.3, and 60 ps.

From the average time constant calculated from the time constants reported above, the rate of CT state dissociation is calculated and the logarithm is plotted against \(1000/T\) in Figure 6-8. The nonlinear progression of the RR-P3HT:BTBP data demonstrate that the data does not follow Arrhenius behavior. We can estimate a barrier to CT state dissociation, however, if we presume that the lower temperature region follows Arrhenius behavior. We estimate a barrier of 0.1 eV for the dissociation of CT states in RR-P3HT:BTBP. In contrast, the RR-P3HT:PCBM system is not dependent on temperature for the temperature range studied. Therefore, we do not expect there to be a significant activation barrier for CT state dissociation in this system. **Thus, we measure fast, activated CT state dissociation in thin blend films of RR-P3HT:BTBP whereas we measure slower, activationless CT state dissociation in thin blend films of RR-P3HT:PCBM.**

Given that PCBM and BTBP have similar electron affinities (as measured with cyclic voltammetry),\(^7,18\) what then sets them apart? What can explain the difference in the CT state dissociation mechanism? What can explain the temperature dependence? Why are fullerene-based materials (such as PCBM) the prototypical electron acceptor in bulk-heterojunction solar cells?
The observation that the bleach frequency in films of RR-P3HT:PCBM is essentially constant until nearly the nanosecond timescale indicates that excess energy is most likely not involved in driving the CT state dissociation in this system. Given that the singlet lifetime in thin films of PCBM is 1 ns, excitons must reach the interface by the nanosecond timescale before decaying to the ground state. Once at the interface, they can dissociate leaving excess energy in the CT state. Kasha observed that molecular excited states rapidly decay to the lowest energy excited state through internal conversion. Thus, any higher lying excited states would rapidly decay to the lowest CT state. Any excess vibrational energy in vibrational modes dissipates very rapidly as well, on the order of ~100 fs. Taking the shift of the bleach center frequency to indicate CT state dissociation, given the long timescale of the shift, and that highly energetic excited states will rapidly decay to the lowest vibrational level of the lowest energy excited state, excess energy would appear to play no role in the RR-P3HT:PCBM system.

Weakly temperature dependent electron transfer has been observed in dye molecules adsorbed onto µm sized AgBr crystals. The researchers measured the rate of electron transfer through fluorescence quenching. They found that the monomer electron transfer was more temperature dependent than aggregates of molecules, specifically J aggregates. Using the Levich-Jortner model of electron transfer to fit their data, they found that J-aggregates had a smaller reorganization energy than the monomer (of a similar dye). They attributed the smaller reorganization energy to the more delocalized wavefunction of the aggregate compared to a single orbital on an isolated molecule.

We argue that the electron wavefunction is significantly more delocalized in a single PCBM molecule than it is in a single BTBP molecule. The methanofullerene, PCBM, was synthesized to retain the properties of C_{60} yet make it more soluble to increase its practical utility in both materials and biological applications. Taking the electronic properties of C_{60} to be preserved in PCBM, C_{60} has a triply degenerate LUMO. One could imagine that the states could mix such that the electron is effectively delocalized about the entire C_{60} molecule. Taking
the calculated radius\textsuperscript{29} of 3.5 Å for C\textsubscript{60} to be similar for C\textsubscript{60} in PCBM, assuming C\textsubscript{60} to be a sphere, and taking the approximate diameter of a carbon atom (1.5 Å) to represent the vertical spread of the electronic wavefunction in C\textsubscript{60}, the resulting differential volume occupied by the electron on C\textsubscript{60} is \sim0.32 \text{ nm}^3. BTBP, on the other hand, is a small, planar molecule whereby the conjugated network consists of a perylene core of 20 carbon atoms. Taking the long-axis and the short-axis of the perylene core to be \sim7.0 Å and \sim4.8 Å, respectively,\textsuperscript{30} and the perpendicular axis to be \sim1.5 Å (appx. diameter of carbon atom), this would give 0.05 nm\textsuperscript{3} as the volume occupied by the electron in the perylene core of BTBP. This value is a factor of six smaller than for C\textsubscript{60}. Thus, the electronic wavefunction is, in effect, automatically more “delocalized” in single molecules of PCBM rather than in single molecules of BTBP.

Imahori et al. investigated the effects of a larger extent of delocalization in 2D vs. 3D acceptors in the intramolecular electron transfer reaction between a porphyrin attached through a spacer of nearly identical length to either of C\textsubscript{60} or quinone.\textsuperscript{31} Because C\textsubscript{60} and quinone have similar reduction potentials (i.e. EA) as measured by cyclic voltammetry, the purpose was to test the effect of the size and shape of each acceptor molecule on the electron transfer reaction. The authors used time-correlated single photon counting (TCSPC) and transient absorption spectroscopy to examine the rate of charge separation and recombination in each system in THF solution. They found an accelerated rate of charge separation and a decelerated rate of charge recombination in the C\textsubscript{60} based dyad (relative to the quinone based dyad) and explained this observation in terms of the lower reorganization of C\textsubscript{60}. For a full discussion of why C\textsubscript{60} is expected to have such a small reorganization, the interested reader is referred to ref. 32.

X-ray diffraction experiments have been carried out and show that the acceptor phase is not highly crystalline in either RR-P3HT:PCBM or RR-P3HT:BTBP.\textsuperscript{33} Molecular packing is known to significantly affect the electronic coupling between molecules.\textsuperscript{34} On the other hand, recent calculations of charge mobility, a macroscopic parameter that depends on the electronic coupling, in films of disordered C\textsubscript{60} differed from crystalline C\textsubscript{60} by only a factor of 2.\textsuperscript{35} With the
information on the crystallinity (or lack thereof) of the acceptor materials in the blend and the previous argument that the electron is delocalized more in PCBM than in BTBP single molecules, we have developed a hypothesis to explain the different dependencies on temperature.

We hypothesize that the different temperature dependencies for the rate of CT state dissociation in the two material systems are due to differences in the ability of electrons to delocalize over several neighboring molecules and the impact of molecular order in the acceptor phase in each system. BTBP would need to have effective packing (i.e. molecular order) in order to have the same extent of delocalization as a single molecule of PCBM. Avilov et al. calculated the electronic coupling between the HOMO–1 of the electron donor tetrathiafulvalene and the LUMO of the electron acceptor tetracyanoquinodimethane as a function of translating the molecules along their long axis. They showed that, as might be expected, the coupling depends sensitively on the translation of the molecules along their long axis. The dependence is not linear because the wavefunctions include bonding as well as anti-bonding components and so there are alternating local minimum and maximum values for the electronic coupling. Thus, it might be expected that molecular order with particular geometries in PDI systems would be necessary to achieve the same extent of electron delocalization in a single PCBM molecule.

Although speculative, the differences in the magnitude of the rate of CT state dissociation in the two material systems may be due to dynamic motions of the system and differences in the requirement of molecular order in the acceptor phase in each system. The idea is that dynamic motions of the PCBM molecules, such as vibrations and librational motion, may be responsible for the observed slow rate of CT state dissociation (i.e. ns vs. ps timescale). Depending on the specifics of the system, such as the location of neighboring molecules and direction of vibrational and librational motions, a vibration could lead to instantaneous moments of high electronic coupling between neighboring molecules while librations could potentially shuttle the electron away from the hole, several concerted librations/vibrations shuttling the electron far enough away
from the hole significantly lowering the rate of charge recombination and promoting full charge separation. These statements will be discussed further below.

For example, C$_{60}$ molecules are separated by a 3.1 Å intercarbon distance.$^{37}$ The distance between C$_{60}$ molecules reduces the electronic coupling between molecular orbitals on neighboring molecules. Vibrational modes stretching and compressing the entire molecule might reduce this distance such that instantaneous moments of high coupling exist. An ellipsoidal deformation, for example, has been discussed in the context of the theoretically predicted negative thermal coefficient below 150 K.$^{38}$ The transition energy for the ellipsoidal deformation is 200 cm$^{-1}$. The corresponding vibrational period is ~200 fs. Green et al.$^{39}$ calculated with density functional techniques that C$_{60}$ anions have Jahn-Teller distorted geometries in which the carbon atoms are no longer equivalent. They suggest that vibrations of the C$_{60}$ molecule may lead to instantaneous moments where the electron wavefunction is localized to some extent. Thus, a vibration could lead to a reduced rate of recombination (as the electron becomes spatially separated from the hole) and a moment of intense coupling with a neighboring molecule.

$^{13}$C NMR data for C$_{60}$ demonstrate that C$_{60}$ undergoes complete orientational motion on the picosecond timescale. Simultaneous and independent reports of $^{13}$C NMR spectra of a C$_{60}$ powder (i.e. solid C$_{60}$) showed a sharp peak without spinning.$^{40,41}$ This observation is quite striking and indicates that orientational motion of the C$_{60}$ molecules at room temperature occurs faster than the timescale of the measurement. It was later found that the free rotation or orientational diffusion in solid C$_{60}$ at 300 K occurs with a timescale of 9 ps as calculated by measuring the $^{13}$C spin-lattice relaxation at different magnetic field strengths.$^{42}$ As the authors in ref. 40 point out, this value is typical of small molecules in solution and is only three times larger than the orientational diffusion of C$_{60}$ in the gas phase! Although a fascinating demonstration of unexpectedly fast orientation motion of C$_{60}$ in the solid state, we expect the full orientational motion of PCBM molecules to be hindered such that only librational motion may be present in films of PCBM.$^{43}$
Recent theoretical efforts have focused on measuring how the structure and structural disorder at the donor/acceptor junction affect the rates of CT state formation and charge recombination. Liu et al. have developed quantum chemical calculations based on the Marcus–Levich–Jortner electron transfer rate to calculate the absolute rates of CT state formation and charge recombination between a conjugated polymer segment (consisting of 6 monomer units) and a single PCBM molecule. They have extended their original idealized version of the structure (based on chemical intuition) by performing MD simulations to determine the most likely structures at the interface. They find a wide distribution of rates for CT state formation and charge recombination, and that the average rate of CT state formation is about three orders of magnitude higher than the average rate of charge recombination. They also found that while the internal reorganization energy significantly affected the rate of charge recombination, it had little to no impact on the rate of CT state formation. While vibrational motions were found to have little to no impact on electron hopping between neighboring PCBM molecules in a similar study (i.e. MD simulations / quantum calculations) of solely PCBM, conformational changes on the nanosecond timescale were found "gate" charge recombination in the polymer:PCBM system when the electron transfer began in conformations where the rate of charge recombination is sufficiently slow.

In the case of BTBP, the molecules are also dynamic, but it would be unexpected for the molecules to be able to rotate freely like C60. Furthermore, it is well known that the anisotropic nature of molecular semiconductors, i.e. strong electronic overlap in only one direction, allow conduction along only one axis. Lemaur et al. calculated the electronic coupling and its effects on the rates of charge recombination and separation between a PDI and phthalocyanine using the semiempirical intermediate neglect of differential overlap method coupled to a single configuration interaction scheme. They found that the rates alternated, sometimes higher for charge recombination, sometimes higher for charge separation, as a function of translation and
rotation. Molecular order in these systems is required for the rate of charge separation to compete with the rate of charge recombination.

In sum, a more delocalized electron wavefunction on PCBM (relative to BTBP) combined with a lack of necessity for molecular order in PCBM may explain the ubiquitous role of fullerene-based materials in OPV bulk-heterojunction devices. Concerted librational and vibrational motion might cause the electron to be far enough away from the electron donor such that the rate of charge recombination is greatly inhibited and the hole begins to migrate into the polymer regions. The combination of these two effects may be responsible for the slow rate of CT state dissociation in these systems, yet provide a high yield of separated carriers as evidenced by the large short-circuit currents in fullerene-based devices.49

6.4 Conclusion

The rate of dissociation of CT states in thin OPV blend films consisting of the \( \pi \)-conjugated polymer RR-P3HT blended with either of PCBM or BTBP is measured at low excitation densities using Vis pump–IR probe spectroscopy. The rates are measured at several temperatures to calculate the activation barrier to CT state dissociation in blend films in which only the electron acceptor was varied. We observe that CT state dissociation in RR-P3HT:BTBP blend films is activated while in RR-P3HT:PCBM blend films the process is activationless. We hypothesize that extended delocalization of the electronic wavefunction in the PCBM molecule and the PCBM phase combined with the lack of necessity for molecular order explain the different dependencies on temperature and that dynamic motions of PCBM molecules serve to slow rate of charge recombination such that long-time CT state dissociation becomes a viable mechanism.
6.5 References


(30) Estimates for perylene core based on C-C bond length of 1.4 Å.


(43) Private communication with Mark Maroncelli.


Figure 6-1. Diagram of attractive potential representative of Onsager theory. Details are included in the text. Reprinted (adapted) with permission from Chem. Rev. 2010, 110, 6736-6767. Copyright 2010 American Chemical Society.
Figure 6-2. Chemical structures of OPV materials studied with Vis pump–IR probe spectroscopy. Electron donor, RR-P3HT, and electron acceptors PCBM and BTBP (a derivative of PDI).
Figure 6-3. Excitation density dependence of the induced absorption at 1770 cm$^{-1}$ for (A) 1:1 RR-P3HT:PCBM and (B) 1:1 RR-P3HT:BTBP. Nonlinear behavior is observed at ultrafast timescales the origin of which is discussed in the text.
Figure 6-4. FTIR spectra of films of individual materials compared to spectrum of blend film. Spectra are normalized such that the maximum carbonyl stretching absorption is 1. The RR-P3HT spectrum normalization is described in the text. FTIR spectra of (A) films of RR-P3HT, PCBM, and 1:1 RR-P3HT:PCBM blend and (B) films of RR-P3HT, BTBP, and 1:1 RR-P3HT:BTBP blend.
Figure 6-5. UV-Vis spectra of films of individual materials compared to blend film. Spectra are normalized such that maximum absorbance of the blend is 1 and of the individual materials is 0.5. UV-Vis spectra of (A) films of RR-P3HT, PCBM, and 1:1 RR-P3HT:PCBM blend and (B) films of RR-P3HT, BTBP, and 1:1 RR-P3HT:BTBP blend. Overlaid on the spectra are dashed lines indicating the excitation, i.e. pump, wavelength used in the Vis pump–IR probe experiment.
Figure 6-6. Vis pump–IR probe spectra at several pump–probe time delays for two OPV blend films: (A) 1:1 RR-P3HT:PCBM at 200, 300, and 325 K, and (B) 1:1 RR-P3HT:BTBP at 170, 200, 300, and 350 K.
Figure 6-7. Bleach peak center frequency obtained from fitting routine described in text plotted against pump–probe time delay for (A) 1:1 RR-P3HT:PCBM at 200, 300, and 325 K and (B) 1:1 RR-P3HT:BTBP at 170, 200, 300, and 350 K. All datasets have been arbitrarily shifted along the vertical axis so as to highlight differences in kinetics. Inset in (A) displays 300 K data in a semilog plot.
Table 6.1. Time constants obtained by fitting the shift of the bleach peak center frequency measured for 1:1 RR-P3HT:PCBM and 1:1 RR-P3HT:BTBP at various temperatures with a multi-exponential function, eqn. 6.1. Average time constant, <τ>, is calculated with eqn. 3.2 as described in Chapter 3.
Figure 6-8. Logarithm of the rate of CT state dissociation plotted against 1000/T for (A) 1:1 RR-P3HT:PCBM and (B) 1:1 RR-P3HT:BTBP blend films.
Chapter 7

Dynamics of Charge Transfer Excitons in PCBM

7.1 Introduction

PCBM, as well as C\textsubscript{60}, largely have the same optical properties in solution as they have in the solid-state.\textsuperscript{1} That the optical properties of the molecule are preserved in the solid-state attests to the weak van der Waals forces that hold the molecules together. However, there is a small red-shift and broadening of UV-Vis absorption features when the molecules are brought together in the solid-state.\textsuperscript{1} These general trends were attributed to arising from intermolecular interactions. Films of C\textsubscript{60} also exhibit a new absorption in the range between 2.3 and 3.0 eV.\textsuperscript{2} Films of PCBM exhibit the same new spectral features in this region.\textsuperscript{3}

These new absorption features have been attributed to charge transfer excitons in thin films of C\textsubscript{60}.\textsuperscript{2} The assignment was made based on observations that, along with the new absorption feature, there is a corresponding luminescence feature in the range between 2.3 and 3.0 eV that appears in the solid-state but not in solution, that the photoluminescence efficiency (i.e. number of luminescent photons divided by number of absorbed photons) decreases indicating additional nonradiative relaxation pathways in this spectral region, and that the new luminescence feature is quenched by an applied electric field (while the luminescence attributable to Frenkel excitons was not). The field acts to dissociate optically generated CT excitons that have a lower binding energy than Frenkel excitons. Furthermore, it was observed that the threshold for photoconductance coincided with the onset of the new absorption feature. On the basis of these observations, the authors assigned the new absorption feature to CT excitons. Later, they estimated the energy of the most significant CT excitons with empirical data and
microelectrostatic calculations and assigned the transition with transition energy 2.43 eV observed in the absorption techniques to be the most significant low energy CT exciton.\textsuperscript{4}

Cook et al.\textsuperscript{3} observed the same absorption and photoluminescence features in thin films of PCBM as those attributed to CT excitons in thin films of $C_{60}$. They demonstrated that these optical absorption and emission signatures disappeared when PCBM is diluted in solid-state blends with polystyrene (PS). Chemical structures of PCBM and PS are displayed in Figure 7-1. They also pointed out that charge carriers have been observed in films of PCBM. For example, transient conductivity was observed for films of PCBM excited by a laser pulse at 500 nm as measured by changes in the microwave absorption.\textsuperscript{5} A response from photodiodes based on PCBM has also been reported at these wavelengths.\textsuperscript{6} These observations and conclusions have important implications as they demonstrate that charge carriers can be generated without the presence of a donor/acceptor junction.

Here, we investigate the dynamics of CT excitons generated in films of PCBM as measured with Vis pump–IR probe spectroscopy. First, we show that, in addition to the loss of the spectral signatures of CT excitons when PCBM is diluted in PS, a solvatochromic shift of the carbonyl stretching mode of PCBM occurs. We then investigate the dynamics of CT excitons in thin films of PCBM using Vis pump–IR probe spectroscopy to investigate the carbonyl stretching mode of PCBM. We examine the excitation density dependence of the mid-IR induced absorption in thin films of PCBM. Then, we show that the line shape and amplitude of the bleach feature attributable to long-lived carriers changes in films of PCBM diluted in blends with PS. Finally, we discuss the special ability of PCBM to generate charge carriers without the presence of a donor/acceptor junction.
7.2 Materials and Methods

Thin films of PCBM and PCBM blended with PS were prepared by spin coating solutions prepared in either o-dichlorobenzene (PCBM) or chlorobenzene (PS:PCBM blends). Total solution concentrations were either 5 or 8 wt%, 8 wt%, and 12 wt% for PCBM, 1:1 PS:PCBM, and 5:1 PS:PCBM, respectively, for films prepared for spin coating. These solutions were transferred to the substrate with a Leur Lock Syringe fitted with a 0.2 µm filter as described in the experimental section of Chapter 6. After waiting ~30 seconds, the substrate was spun at 1000 rpm for ~60 seconds. All thin films had an optical density (OD) at 550 nm of ~0.08 – 0.12 OD. Due to poor film uniformity, these values should be taken only as rough estimates.

Thick films of PCBM and PCBM blended with PS were prepared by drop coating solutions prepared in chlorobenzene. 50 drops of solution were transferred to a CaF$_2$ substrate via a Pasteur pipette either in entirely or in two separate sequences (depending on the solution viscosity) and were rotated at 80 rpm until dry (~2 hrs). Total solution concentrations were 1 wt%, 2 wt%, and 11 wt% for PCBM, 1:1 PS:PCBM, and 10:1 PS:PCBM, respectively.

Information on the UV-Vis spectrometer and Vis pump–IR probe technique is included in Chapter 2. The UV-Vis spectrometer was set to 1 nm spectral resolution for the data reported in this chapter. Outside of the experiments where excitation density are reported, excitation densities in the Vis pump–IR probe experiments were ~1 mJ/cm$^2$. This excitation density corresponds to ~200-250 µJ/cm$^2$ absorbed by each sample, depending on the optical density of the sample and the exact location on the sample. In other words, an attempt was made to keep all samples with the same optical density by varying film thickness and samples were not entirely uniform in thickness, especially for the thicker films. All experiments were carried out with the pump pulse centered at 550 nm. The sample was held in an optical cryostat at room temperature under a dynamic vacuum of ~0.1 torr.
7.3 Results and Discussion

Figure 7-2 displays UV-Vis spectra of thin films of PCBM and PCBM blended with PS in weight ratios of 1:1 and 5:1 PS:PCBM. We observe the same general trend reported by Cook et al. (ref. 3). Specifically, for thin films of PCBM we observe a new absorption feature in the visible region whereas in dilute blend films with PS this absorption feature does not appear. This new absorption feature has been attributed to CT excitons in films of both C₆₀ and PCBM.²⁻⁴

Figure 7-3A displays FTIR spectra of thick films of PCBM and PCBM blended with PS plotted in the carbonyl stretching region. The spectra are normalized to the carbonyl stretching band of PCBM. We observe a slight shift to higher frequency in the when PCBM is blended with PS similar to that observed in blend films with OPV materials (Chapter 4). Specifically, the center of the carbonyl stretching band of PCBM in each sample are measured as 1736.5, 1737.5, and 1740 cm⁻¹ in the thick film of PCBM and the blends consisting of 1:1 and 10:1 PS:PCBM, respectively. The carbonyl stretching frequency measured for PCBM in the 10:1 PS:PCBM blend is very similar to the value 1740.5 cm⁻¹ measured for PCBM dissolved in benzene and reported in Chapter 4. This similarity makes sense as polystyrene consists of repeating units chemically similar to benzene, i.e. phenyl groups. We also point out that there is a very weak feature at ~1773 cm⁻¹ apparent in the blends with large proportion of PS that arises from either a combination or overtone band resulting from the phenyl ring present in PS. Combination or overtone bands present in this spectral region are characteristic of mono-substituted aromatic molecules, such as toluene. Although partially obscured by low signal-to-noise ratio and incomplete subtraction of atmospheric water absorption, the same general solvatochromic shift observed in thick films is observed for thin films of PCBM and 1:1 and 5:1 PS:PCBM blends (Figure 7-3B). The thin films will be the focus of the pump–probe experiments reported in this chapter.
Figure 7-4A displays Vis pump–IR probe spectra for films of PCBM at several pump–probe time delays excited with 1 mJ/cm² incident on the sample and 200 µJ/cm² being absorbed. We observe a broad induced absorption offset in the transient spectra attributable to polarons and/or excitons as discussed in previous chapters. The transient spectra also exhibit bleaching and induced absorptions of vibrational features, i.e. the carbonyl stretch of PCBM. The transient spectra transition from a dispersive line shape at early times to a broad Gaussian-like bleach feature at 1 ns. We observe the same general features in the data with 250 µJ/cm² incident on the sample and 50 µJ/cm² being absorbed (Figure 7-4B).

We measured the excitation density dependence of the broad induced absorption offset observed for thin films of PCBM. Figure 7-5 displays the decay of the induced absorption of PCBM as measured by averaging over several points at the high-frequency end of the transient spectrum (specifically, 1764.5, 1767.0, 1769.5 cm⁻¹) for several excitation densities for short times (Figure 7-5A) and long times in a semilog plot (Figure 7-5B). PCBM does not have any vibrational modes with transitions at these particular transition energies which can be verified by the FTIR spectrum in Figure 7-3. The resulting kinetics traces displayed in Figure 7-5 exhibit a fast component near the time origin that depends on excitation density and a slower component that does not.

Complex, nonexponential dynamics in thin films of C₆₀ following excitation into the first electron excited state (λ_pump = 620 nm) have been observed before with electronic pump–probe spectroscopy.⁷ Dexheimer et al. found that the excited state dynamics in both thermally sublimed and crystalline films of C₆₀ depended on excitation density while the excited state dynamics in solutions of C₆₀ did not. On the basis that these excitation density dependent dynamics did not depend appear in solution, the authors assigned the dynamics to arise from intermolecular interactions. Furthermore, on the basis of the different lattice coherence lengths in thermally sublimed versus crystalline films of C60 (10 nm vs. >150 nm), the authors attributed the
mechanism of the decay to long-range Förster annihilation, with one possible pathway represented as

\[ S_1 + S_1 \rightarrow S_0 + S_n \]

The authors found that the fast timescale dynamics slowed down and eventually disappeared at low excitation densities, which we will discuss further below. Thin films of PCBM prepared by spin casting have been shown to consist of densely and homogeneously distributed nanocrystals and so should be similar to the films of C\textsubscript{60} prepared through thermal sublimation in which the lattice coherence length is short.

The fast dynamics observed in the traces displayed in Figure 7-5A nearly disappear at the lowest excitation density incident on the sample of 250 µJ/cm\textsuperscript{2}. The disappearance at this excitation density is strikingly similar to that reported in ref. 7. It would be tempting to immediately assign the dynamics observed here as arising from the same mechanism of long-range Förster annihilation. However, it is important to keep in mind that the measurements reported in ref. 7 were made on the transient induced absorption resulting from electronic excited state transitions. We point out that the induced absorption plotted in Figure 7-4 could result from excitons and/or polarons. Thus, long-range Förster annihilation of excitons is certainly applicable in this situation, in that the nonlinear dynamics of excitons will ultimately affect the dynamics of polarons, but the situation is complicated in that polarons can be generated on a range of timescales. For example, it was recently shown that annihilation of excitons by charge carriers predominated over either bimolecular charge recombination or triplet–triplet annihilation, at least in polyfluorene blends.

Turning back to the spectra in Figure 7-4, we believe that the bleach feature results from the dissociation of CT excitons into charge carriers. We are confident with this assignment because the bleach feature is still present at 1 ns. PCBM has a very short fluorescence lifetime and so the bleach feature at 1 ns should not arise from a singlet exciton. CT excitons would have
lower activation energy for carrier generation (i.e. 0.2 eV for CT excitons vs. 0.3 eV for Frenkel excitons)\(^2\) and so would more readily generate separated charge carriers.

Further support for this assignment comes from photocurrent measurements of thin films. Lee et al., for example, measured a few hundred µA transient photocurrent at 5 ns for films of C\(_{60}\) excited with a pulse of light at 620 nm and energy density of ~2 mJ/cm\(^2\).\(^{11,12}\) They also saw that the transient photocurrent decreased as they decreased the temperature. Repeated exposure to oxygen reduced the dark current by ~5 orders of magnitude and reduced the lifetime of the photocurrent from ~40 ns to ~2 ns. They found that the transient photocurrent exhibited nonexponential decay at this energy density which became singly exponential at ~100 µJ/cm\(^2\). Taken with the measurements reported above for the nonexponential dynamics of the electronic excited states, the nonexponential decay in these experiments most likely arising from the nonexponential dynamics (i.e. annihilation) of the electronic excited states rather than the photogenerated charge carriers. Kazaoui et al. also found the steady-state dark- and photo-current measured with excitation at 600 nm for a 200 nm thick film to decrease by three orders of magnitude when exposed to oxygen.\(^{13}\) The photoconductivity was nearly restored to its original level by deintercalating the oxygen molecules. Deintercalating the oxygen molecules was accomplished by heating the film at an elevated temperature (i.e. >380 K) under vacuum (~10\(^{-6}\) torr).

These finding with respect to the effects of the incorporation of oxygen into thin films of C\(_{60}\) on the photocurrent yield have important implications on the current study using ultrafast Vis pump–IR probe spectroscopy. The way in which the samples were prepared (in air) and the low vacuum that we were able to pull in these experiments (~10\(^{-1}\) torr) would suggest that a much larger signal can be obtained if more care is taken to eliminate incorporation of oxygen into our thin films. A larger signal would also enable experimentation even lower excitation density, approaching a regime where nonlinear effects are not present.
Although the above considerations are consistent with the bleach arising from charge carriers, the bleach may also result or have contributions from PCBM molecules in which the energy has transferred to the lowest energy triplet state. PCBM in solution has a rather small singlet-triplet splitting of ~9 kcal/mol which brings about strong singlet-triplet coupling.\textsuperscript{14} As such, PCBM in solution undergoes near unity intersystem crossing. Furthermore, the triplet lifetime is on the order of 40 μs in argon-saturated solution. In the solid-state, triplet lifetimes were measured by Cook et al. using transient absorption spectroscopy and determined to be 25 μs for 10:1 PS:PCBM, 13 μs for 1:1 PS:PCBM and <1 μs for PCBM.\textsuperscript{3} The very efficient intersystem crossing explains the short lifetime (and low fluorescence yield) observed for the singlet state.\textsuperscript{15}

Various experiments are possible to rule out the triplet state contributions to the bleach feature. For example, the generation of charge carriers via CT excitons would be suppressed in argon-saturated solution while triplet formation would be favored. The lack of the appearance of a bleach in time-resolved IR experiments (which measure dynamics on timescales greater than 1 μs) would therefore rule out contribution from triplet states. An equivalent experiment in the solid-state would be PCBM diluted in a matrix of PS.

Although efficient intersystem crossing is known to occur in C\textsubscript{60} and PCBM, we expect our films to have an abundance of oxygen which would serve to reduce the lifetime of the triplet states. The vacuum that we pull during the experiment is ~0.1 torr, as reported in the experimental section. And so we expect oxygen to be present intercalated in these samples. The presence of oxygen would tend to decrease the lifetime of the triplet states, although it would probably still be longer than the timescale of the Vis pump–IR probe measurement. For example, the lifetime of the triplet state of C\textsubscript{60} in air-saturated benzene has been reported as ~330 ns.\textsuperscript{14}

Figure 7-6 displays Vis pump–IR probe spectra of thin films of PCBM and PCBM blended with PS at several pump–probe time delays. The transient spectra have been normalized to the bleach feature and the slope has been corrected to make comparison of transient vibrational
features easier. We find from Figure 7-6 that all samples exhibit a bleach feature at 1 ns. We also note that the long-loved bleach feature in the 5:1 PS:PCBM blend is shifted to higher frequency. We attribute this to the different environments in which the PCBM molecules reside in the 5:1 PS:PCBM blend, in accord with the solvatochromic shift observed in the FTIR spectrum in Figure 7-3.

We also observe that the induced absorption at ~1730 cm\(^{-1}\) in the 2 ps transient spectrum has a larger magnitude in the film of PCBM. We have chosen the 2 ps transient spectrum so as to avoid including dynamics attributable to the nonlinear dynamics that occur near the time origin. That the induced absorption has the largest magnitude in films of PCBM suggests the induced absorption may arise an absorption induced by PCBM molecules involved in CT excitons.

Further support for this argument comes from analysis of the kinetics of the induced absorption offset in the different films displayed in Figure 7-7. The dynamics for each film displays a fast component along with a slower component in Figure 7-7A. The relative amplitude of fast components and slow components changes upon dilution of PCBM in PS blend films. We attribute this to the inability of the dilute films to undergo intermolecular annihilation, as has been reported previously for the dynamics observed in films of C\(_{60}\) compared to the dynamics observed in solution.\(^7\)

With the above information in mind, we propose two states to explain the dynamics of the Vis pump–IR probe dynamics as a first, albeit crude, model. First, we assign the bleach at long pump–probe time delays, as discussed above, to charge carriers generated by the dissociation of CT excitons. The lower frequency induced absorption feature at ~1730 cm\(^{-1}\) we assign to the induced absorption feature arising from PCBM molecules involved in CT excitons.

We assign the induced absorption feature at ~1730 cm\(^{-1}\) for the following reasons. First, the induced absorption interferes with the bleach of PCBM at ~1740 cm\(^{-1}\) attributed to charge carriers generated by CT excitons. The transition from a dispersive line shape on early timescales to the Gaussian line shape of the bleach on the nanosecond timescale may result from the decay
of CT excitons to the ground state. This timescale corresponds very closely to the fluorescence lifetime for the CT exciton in PCBM which has been measured as ~1 ns with TCSPC.\textsuperscript{3} Furthermore, PCBM molecules involved in CT excitons would most likely exist in ordered regions of the sample which, as shown in Chapter 5, exhibit a lower frequency carbonyl stretching vibration. In fact, Gearba et al. observed a feature that they attributed to crystalline, ordered PCBM at \textasciitilde1730 \text{cm}^{-1}.\textsuperscript{16} Thus, the above observations imply that the feature induced absorption at \textasciitilde1730 \text{cm}^{-1} most prominent in films of PCBM can be assigned to the absorption induced by PCBM molecules involved in CT excitons.

Taking the bleach present long-time transient spectrum to arise from charge carriers, we have fit the long-time transient spectrum with a polynomial function to approximation the broad induced absorption offset and a Gaussian line shape to approximate the bleach feature. This fitting procedure enables us to extract quantitative information about the charge carriers present in the different blends. Figure 7-8 displays Vis pump–IR probe spectra acquired at 1 ns pump–probe time delay for PCBM and 1:1 and 5:1 PS:PCBM blends. From the fits, we obtain areas of 2.7 x 10\textsuperscript{3}, 1.2 x 10\textsuperscript{3}, and 0.9 x 10\textsuperscript{3}, center frequencies of 1740, 1740.5, and 1746 \text{cm}^{-1}, and widths of 6.5, 7, and 9. It is clear from visual inspection and from the fits that more charge carriers are generated in films of PCBM than in films of the blends. In accord with our interpretations, we find a higher yield of charge carriers for films of PCBM than for films of the 1:1 and 5:1 PS:PCBM blends. \textit{Thus, we believe that we have spectroscopic evidence of separated charge carriers formed in films of PCBM in the absence of a donor/acceptor junction generated through dissociation CT excitons.}

\textbf{7.4 Conclusion}

We observe a solvatochromic shift of the carbonyl stretching mode of PCBM diluted in blends with PS similar to that observed for PCBM dissolved in benzene. We observe a bleach
feature in the Vis pump–IR probe experiment of films of pure PCBM on the nanosecond timescale. We assign the bleach feature in the transient spectrum to charge carriers generated by the excitation and dissociation of CT excitons in PCBM. We also observe an induced absorption of a vibrational feature which we attribute to CT excitons. We have therefore identified two spectroscopic markers indicating that CT excitons are generated in films of PCBM and that charge carriers can be generated by the dissociation of these CT excitons in the absence of a donor/acceptor junction.

7.5 References


Figure 7-1. Chemical structures of polystyrene (PS) and PCBM.
Figure 7-2. UV-Vis absorption spectra of thin films of PCBM, and 1:1 and 5:1 PS:PCBM blend. Spectra are normalized to the first optically allowed transition of PCBM (i.e. 340 nm).
Figure 7-3. FTIR spectra of (A) thick films of PCBM and PS:PCBM blends (1:1 and 10:1) and (B) thin films of PCBM and PS:PCBM blends (1:1 and 5:1). Spectra are normalized to the carbonyl stretching absorption of PCBM.
Figure 7-4. Vis pump–IR probe spectra of thin films of PCBM excited with pump pulse at 550 nm and plotted at several pump–probe time delays. Vis pump–IR probe spectra for excitation energy densities (absorbed) of (A) 200 µJ/cm$^2$ and (B) 50 µJ/cm$^2$. 
Figure 7-5. Excitation density dependence of induced absorption offset for thin film of PCBM excited with a pump pulse of light at 550 nm for two different timescale ranges from (A) -2 to 4 ps and (B) 1 to 1000 ps in a semilog plot. Excitation densities reported in the inset are those incident on the sample. Film had an OD of ~0.08 at 550 nm.
Figure 7-6. Vis pump–IR probe spectra of thin films of PCBM and PS:PCBM blends (1:1 and 5:1) excited with pump pulse at 550 nm and plotted at pump–probe time delays of (A) 1 ns, (B) 10 ps, and (C) 2 ps. Spectra are normalized so as to make differences in transient vibrational features apparent.
Figure 7-7. Excitation density dependence of induced absorption offset for thin PCBM and PS:PCBM blend films excited with a pump pulse of light at 550 nm for two different timescale ranges from (A) -2 to 4 ps and (B) 1 to 1000 ps in a semilog plot. Samples were excited with 1000 μJ/cm² incident on the sample. All thin films had an OD at 550 nm in the range of ~0.08 – 0.12. Due to poor film uniformity, these values should be taken only as rough estimates.
Figure 7-8. Vis pump–IR probe spectra of thin films of PCBM and PS:PCBM blends (1:1 and 5:1) excited with pump pulse at 550 nm and plotted for pump–probe time delay of 1 ns. Spectra have been fit with a polynomial function to approximate the induced absorption offset and a Gaussian line shape to approximate the bleach of the carbonyl stretching transition of PCBM.
Chapter 8
Future Direction and Conclusion

8.1 Future Direction

In the following paragraphs we present and discuss experiments to follow up the work presented in this thesis. First, we discuss experiments necessary to ensure the validity of the model adopted in Chapter 6. Second, we discuss experiments to test the hypotheses presented in Chapter 6. Finally, we discuss progress to be made in the broader context of ultrafast vibrational spectroscopy of OPVs.

First, important follow-up experiments are required to ensure the validity of the model adopted in Chapter 6. These experiments entail a detailed investigation of the nature of the interaction between electron donor materials and the carbonyl stretching modes of BTBP. More information needs to be obtained on the effects on the carbonyl stretching modes of BTBP when incorporated into OPV electron donor materials. Specifically, we observe a slight shift of the carbonyl stretching modes of BTBP to lower frequency that contrasts with the shift to higher frequency observed in blends of PCBM with electron donor materials (see Figure 6-4, for example). The observation of a shift to lower frequency has implications on the interpretation of the dynamic shift of the bleach peak center from high to low frequency as the rate CT state dissociation. However, we point out that the vibrational spectrum of BTBP is complicated by the solid-state effects introduced through aggregation or intermolecular interactions. Intermolecular interactions, for example, cause both the asymmetric and symmetric carbonyl stretching modes to split and appear with two transition energies. Thus, it is unclear at the current time what exactly causes the shift to lower frequency in this system upon blending with the polymer, at least with
the limited dataset presented in this thesis (i.e. FTIR spectra of films of BTBP and 1:1 polymer:BTBP).

The ground (electronic) state dynamics of the carbonyl stretching modes of BTBP need to be investigated as well. Because perylene diimides tend to crystallize, the carbonyl stretching mode in this compound may exhibit a more pronounced temperature dependence (i.e. this contrasts with the carbonyl stretching mode of PCBM which can be considered a dilute local oscillator as discussed in Chapter 5). For example, we observe a large amplitude shift in the center frequency of the bleach feature measured on sub-picosecond timescales in the ultrafast Vis pump–IR probe experiment in the polymer:BTBP system at all temperatures. The large amplitude shift might arise from localized heating generated by the dissipation of the energy absorbed by the electronic pump pulse. The vibrational lifetime can be measured directly, as well, and could be invoked to explain the sub-picosecond shift observed at all temperatures. We might expect the orientational dynamics of BTBP as observed through the carbonyl stretching modes not to exhibit as much variation as that observed in PCBM due to the different geometries of the molecules (as discussed in Chapter 6). However, inertial motion and librations should still cause small changes in the measured anisotropy over the timescale of the experiment (few hundred femtoseconds to few picoseconds). Finally, it is very important to examine for spectral diffusion in the carbonyl stretching modes of the ground (electronic) state of BTBP. We expect similar dynamics as observed recently for dipeptides in a trehalose/D$_2$O glass. In these experiments, Londergan et al. found a very small amplitude, fast component (on the few hundred femtosecond timescale) to the dynamics whereupon the system remained static for the remainder of the experiment (with a timescale of a few picoseconds).

In Chapter 6, we proposed that a larger extent of delocalization (with a corresponding reduction in reorganization energy) in PCBM versus BTBP explained the conclusions drawn from Vis pump–IR Probe spectroscopy that CT state dissociation is weakly activated in RR-P3HT:BTBP and activationless in RR-P3HT:PCBM. This hypothesis is open for further
experimentation. For example, rather than tuning the delocalization (and reorganization energy) of the electron acceptor, why not do the same for the electron donor? As discussed in Chapter 6, RR-P3HT is known to exhibit semicrystalline properties and is expected to have rigid, planar polymer chains exhibiting intermolecular interactions conducive for delocalization. Various ways of reducing this molecular order exist such as preparing films so that they have not been solvent annealed (to be discussed in the Appendix) or by reducing the regioregularity of the polymer, i.e. regiorandom P3HT (RRa-P3HT). For an experiment involving RRa-P3HT:PCBM, for example, we might expect that the CT state dissociation becomes weakly activated as observed in the RR-P3HT:BTBP experiment.

Hallermann et al. recently correlated the steady-state CT state luminescence intensity to device efficiency in blends based on PTs and PPVs with PCBM. Interestingly, they explained their observations in terms of the nature of interaction between the subunits of the polymer chain with the electron acceptor, PCBM. For RR-P3HT, they posited that the rigid, planar nature of the backbone reduces the electronic coupling with PCBM relative to that expected for more disordered polymers such as RRa-P3HT and PPVs where it might be anticipated that the polymer backbone of these polymers can wrap around the fullerene and have very strong coupling. Hallermann et al. also found the steady-state CT state luminescence efficiency to correlate with morphology and short-circuit current in blends based on MDMO-PPV and PCBM. The observations were explained in terms of an increased density of interfaces in fine blends resulting in larger CT emission intensities. These studies point out the difficulties associated with interpreting observables derived from complex systems.

Concerning the second hypothesis presented in Chapter 6, regarding concerted dynamic motions of the acceptor molecule affecting the rates of CT state dissociation and charge recombination, it might be expected that the rate of CT state dissociation is sufficiently slowed when librational motion is hindered. Inhibiting this dynamic motion can be accomplished in one of several ways. The C₆₀ orientational motion is static on the NMR timescale at 77 K, for
example. It might be expected that the rate of CT state dissociation is sufficiently slowed at these low temperatures. Second, bulky functional groups attached to the fullerene molecule without altering its electronic structure would be expected to further hinder rotational motion. Again, the rate of CT state dissociation might be expected to show corresponding changes.

Considering the larger picture of ultrafast vibrational spectroscopy of OPVs, reducing the complexity of the system and/or making spectroscopic measurements on devices would represent perhaps the strongest advancements. Reducing the complexity of the system by carrying out ultrafast vibrational spectroscopy on a bilayer rather than a bulk heterojunction, for example, would significantly reduce complications introduced by the latter on interpretation of the data. Furthermore, exquisite control of molecular order of each layer in a bilayer, i.e. single junction, is possible through thermal evaporation techniques. Making spectroscopic measurements on devices would enable measurements of the dynamics initiated from the thermodynamic conditions expected in actual devices. Furthermore, the ability to control the applied electric field across the sample would aid in the clarifying peak assignments. For example, CT excitons can be selectively quenched with an applied electric field. This experimental handle would facilitate the assignment of transient features to CT excitons as proposed, for example, in Chapter 7.

8.2 Conclusion

In conclusion, we have demonstrated the ability to measure the energetic barrier associated with CT state dissociation in thin films of device-relevant materials at low excitation densities using ultrafast vibrational spectroscopy. We have shown that different solvent environments are responsible for the gradient of carbonyl stretching frequencies observed in OPV blend films. We have demonstrated that the dynamics observed with Vis pump–IR probe spectroscopy will not be obscured by vibrational dynamics that occur in the ground state electronic potential as spectral diffusion does not occur on the picosecond and longer timescale.
Based on an analysis of our Vis pump-IR probe data, we expect fullerene-based devices to exhibit efficient charge separation in the absence of order, while perylene-based devices may require molecular-level order for efficient charge separation. We have also shown that CT excitons are generated in films of PCBM and are able to dissociate into charge carriers when excited directly without the need for a donor/acceptor junction.

8.3 References


Appendix

Expanding the Frontier of Vis Pump–IR Probe Spectroscopy in OPV Research: Thin Films, Low Excitation Densities, and New Materials

Performing Vis pump–IR probe spectroscopy on thin films at low excitation densities requires overcoming several challenges. First we will discuss why we want to study thin films. Then, we will discuss why we want to study films with low excitation density. Finally, we will discuss why we want to study new materials. Last, we will discuss the experimental changes made that make this spectroscopy possible.

A.1 Thin Films, Low Excitation Densities, and New Materials

Thin Films

Although it is natural to be tempted to maximize the signal amplitude in experiments involving vibrational transitions (i.e. $\epsilon \sim 10^3$) by maximizing the path length, many problems arise when applying this principle to OPV blend films. These problems include film surface absorption, inability to tune film morphology, and relevance of measured microscopic parameters to functional devices.

For example, the $\pi$-conjugated polymers used in OPV devices have allowed $\pi-\pi^*$ transitions which tend to absorb very strongly (i.e. $\epsilon \sim 10^5$). The following equation can be used to model the fraction of photons absorbed as a function of depth within a film

$$I(x) = I_0 \exp(-\epsilon x)$$

where $I_0$ represents the incident photon density, $\epsilon$ is the extinction (or absorption) coefficient, and $x$ is a position in the film relative to the front surface of the film. For a 3 $\mu$m thick 1:1 RR-P3HT:PCBM film (and taking $\epsilon \sim 10^4$ for PCBM), from the above equation we observe that
99.995% of the incoming photons are absorbed within the first µm (Figure A-1A). Not only are nearly all of the photons absorbed in the film, but they are nearly all absorbed within the first µm. The probe pulse in the Vis pump–IR probe experiment therefore interacts more with sample that has not been excited by the pump pulse than sample that has been excited by the pump pulse. From the perspective of maximizing the desired signal, more sample actually represents wasted space. A second inspection of Figure A-1A reveals an extreme concentration gradient of photons absorbed exists in the film as well. Because excitons are generated by photon absorption, the excitation density will follow the nonuniform density of photons absorbed by the film. Furthermore, because charge carriers are generated by exciton dissociation, the distribution of charge carrier density within the film will also be nonuniform. The measured microscopic rates from the spectroscopic observables will reflect an average over this entire distribution. A 100 nm thick film with the same properties, on the other hand, absorbs only ~40% of the photons (Figure A-1B). In addition, the distribution of photons within the film is nearly continuous. The latter situation is obviously ideal.

Another problem that arises from studying thick films (i.e. > 1 µm) is the inability to control film morphology. Thick films require long drying times (i.e. minutes and longer) and as such have undergone extensive (if not full) phase separation as the presence of the solvent plasticizes the film permitting the phase separation.

The ability to tune morphology provides an experimental handle capable of studying fundamental as well as practical effects. Many factors, including solvent, materials, concentration and relative concentration, affect the underlying morphology as outlined in a recent review by Hoppe and Sariciftci. Optimizing the morphology through sample deposition conditions significantly impacts device efficiency. Post-processing procedures exist as well, such as solvent and thermal annealing. For example, thermally annealing films of RR-P3HT:PCBM (Figure A-2A) at 150 °C for 30 min. increased device efficiency by over a factor of 5 (the efficiencies were reported as 0.8 and 5% for unannealed and annealed devices illuminated at 80
Various factors have been implicated in affecting the efficiency. Annealed films have undergone some extent of phase separation and the RR-P3HT has undergone some extent of crystallization. The crystallization of RR-P3HT in thin blend films with thermal annealing is clearly observed both with the naked eye (Figure A-2B) and in the UV-Vis absorption spectrum (Figure A-2C).

In terms of Vis pump–IR probe signal, the density of donor/acceptor junctions will have been reduced in thick films which have undergone extensive phase separation. As such, a smaller number of excitons are expected to reach the donor/acceptor junction and result in electron transfer from donor to acceptor. Analytically, the smaller fraction of excitons dissociated at the donor/acceptor junction will lead to a smaller signal size observed for the bleach resulting from electron transfer as observed in the Vis pump–IR probe experiment.

Finally, there is the issue of device relevance. Devices with historic efficiencies typically are prepared with films on the order of 100 – 400 nm as tabulated in a recent review by Dennler et al.\textsuperscript{4}

\textit{Low Excitation Densities}

Again, it is tempting to increase signal levels by increasing excitation densities. However, as discussed in Chapter 7 for PCBM, exciton annihilation mechanisms occur at high excitation densities.

The measurements we reported in Chapter 6 for OPV blends were as low as 250 μJ/cm\textsuperscript{2} at 550 nm. And in Chapter 7, we reported data as low as 50 μJ/cm\textsuperscript{2} (absorbed) at 550 nm for films of PCBM. As for optical pump–probe techniques, Ohkita et al. reported transient absorption measurements on polythiophene:PCBM films with excitation densities below 65 μJ/cm\textsuperscript{2} at 420 and 530 nm.\textsuperscript{5} Marsh et al. recently demonstrated sub-picosecond transient absorption spectroscopy with excitation densities of 6 μJ/cm\textsuperscript{2} at 500 nm\textsuperscript{6} carried out on P3HT:PCBM.
New Materials

It was originally reported that CN-MEH-PPV was the primary absorber at 550 nm in 1:1 CN-MEH-PPV:PCBM blend films.\textsuperscript{7} This film had an optical density of 2.8 at this wavelength and the spectrum was published in a later publication.\textsuperscript{8} Given that nearly all of the pump photons are absorbed by the film (only 0.2% transmitted of photons are transmitted for an OD of 2.8) it is hard distinguish which component really is the primary absorber.

We have recently found that the absorption of PCBM in 1:1 CN-MEH-PPV:PCBM blends is significant. Thin films of PCBM have an absorption coefficient of $\sim 10^4$ cm\textsuperscript{-1} at the wavelength of 550 nm.\textsuperscript{9} As we saw in Chapter 7, this anomalously large absorption coefficient arises from intermolecular interactions between PCBM molecules, i.e. CT excitons. In blend films where the interaction between PCBM molecules is suppressed, we might expect this value to decrease. For C\textsubscript{60} in toluene, for example, the extinction coefficient at 550 nm is $\sim 10^3$ cm\textsuperscript{-1} M\textsuperscript{-1}.\textsuperscript{10} Thus, for blend films the absorption coefficient for PCBM is likely to decrease, but the previous value gives a good lower bound. Figure A-3 displays the absorption coefficients for a thin film of CN-MEH-PPV. CN-MEH-PPV has an absorption coefficient of $\sim 10^3$ cm\textsuperscript{-1} at 550 nm. Thus, PCBM absorbs at least an amount equal to CN-MEH-PPV in CN-MEH-PPV:PCBM blend films.

It is most unusual that PCBM (and C\textsubscript{60}) have such high absorption coefficients in this spectral range. The HOMO to LUMO transition for C\textsubscript{60} molecules is symmetry forbidden.\textsuperscript{11} However, C\textsubscript{60} does absorb quite strongly (i.e. $\varepsilon \sim 10^3$). Wang et al. explain the unexpectedly high oscillator strength as resulting from Herzberg-Teller coupling of vibrational modes with the electronic transitions, which results in a weak transition dipole moment.\textsuperscript{12}

RR-P3HT:PCBM presents an ideal system to move forward with Vis pump–IR probe spectroscopy. Highly efficient devices with efficiencies approaching 5\% have been prepared based on these materials brought together in the bulk heterojunction.\textsuperscript{13,14} Specifically, over 50\%
of the electrons generated in a device in the spectral window where the polymer absorbs are collected at the electrodes (i.e. external quantum efficiency), and nearly 80% of photons are converted to electrons in the active layer (i.e. internal quantum efficiency). Because we are detecting the increased transmittance (i.e. bleach) of a vibrational mode that occurs from electron transfer, we want to maximize the signal by maximizing the number of electrons generated in the film. It is anticipated that bulk-heterojunction films will naturally lead to more electrons given the intimate contact of electron donor and acceptor materials. The observation of a bleach feature in systems other than RR-P3HT:PCBM (i.e. Chapter 6) is promising.

### A.2 Experimental Implementation

In actual practice, a pulsed laser light source is subject to several sources of noise. Unlike conventional light sources, laser light sources are subject to drift over the course of an experiment as the power output and stability of a laser light source is directly associated with the beam alignment within the laser oscillator and amplifier. The alignment can be affected, for example, by the effects of heat (global or local) on the optics that make up the beam path. This is why it is important to maintain the laser within a stable thermal environment. Furthermore, pulsed laser light sources are subject to variable shot-to-shot quality. All of the noise associated with the electro-optical components, mechanical motion of optics, etc. affects this parameter. Even atmospheric contaminants (i.e. dust) can lead to instantaneous moments of bad shots.

In order to detect and average the low signals necessary to push the limits of the Vis pump–IR probe experiment into thin films and low excitation densities, run-time filtering of laser shots (i.e. pulses) is an absolute must. Run-time filtering enables two things. First, signals buried in the noise can actually be detected to set an experiment up. This is not possible without run-time filtering, because the signal-to-noise ratio is too low to even see the signal to set up an experiment. Second, averaging for long periods of time to increase the signal-to-noise will not be
ruined by bad laser shots. The noise introduced by bad laser shots can completely distort the quality of even a well-averaged data set. Also, averaging for long periods of time will not be ruined by the inevitable drift of even the most well-aligned laser light source.

To implement run-time filtering of laser shots, three changes were made. First, code was modified to calculate the standard deviation and variance of signal levels detected for the IR and visible beams of light. It is important to analyze and measure both IR and visible beams because each are subject to different sources of noise as will be discussed below. Comparing each shot to the standard deviation enables bad shots to be filtered out. The variance takes into account data sets in which the laser fluctuated too much over the course of the data set. This is particularly important to essentially halt experiments where extensive averaging is required, but the laser light source has drifted to such an extent that further averaging would negatively impact the quality of the data.

The practical implementation of this approach is relatively straightforward. A liquid nitrogen cooled single element MCT detector (MCT-8-1.0, Infrared Associates Inc., Stuart, FL) detects intensity fluctuations of the IR beam as represented by a portion of the IR pump beam. The response of this MCT detector is sampled in a similar fashion as discussed for the MCT array detector in Chapter 2. A pyroelectric detector (Vector PHF02, Scientech, Inc., Boulder, Co.) detects intensity fluctuations of the electronic pump (the reflection from a ND filter can be used, for example) for statistical analysis. A single measurement at 40 µs is made in the current configuration. A pyroelectric detector is preferred over a silicon photodiode because sampling over the response of a silicon photodiode with a 2.2 µs gate incorporates very little signal and a large amount of electronics noise (Figure A-4). Thus, the pyroelectric detector is more representative of the actual fluctuations arising from the pulsed laser light source and OPA used to generate visible pulses of light.

Detecting and carrying out statistical analysis on the IR light intensity represents a great improvement as the IR light represents the signal being measured. Although statistical analysis
with measurements of the optical pump pulse may seem sufficient as it incorporates noise introduced by the laser system, the optical pump pulse also incorporates noise introduced by the OPA generating these pulses of light. However, the IR light is subject to noise introduced by the laser system as well as the OPA used to generate IR pulses of light. As such, the statistical analysis incorporating both the IR pulses of light and the optical pulses of light includes all of this information so that the run-time filter only lets data through representative of the true signal (i.e. eliminates noise so that you can see low signals).

A recommendation for further improvement on the statistical analysis scheme presented above would be inclusion of the response of the two 32 element strips of the array detector (i.e. IR probe beam) into the statistical analysis scheme. The inclusion could be accomplished, for example, by integrating over each of the two 32 elements for $I$ and $I_o$ measurements and analyzing the statistics of these signals. Along with noise from the laser oscillator, amplifier, and OPA, noise introduced along the different paths travelled by the beams used for $I$ and $I_o$ measurements will be included. Because these signals represent the actual signal being measured, inclusion of the statistical analysis of these signals may lead to even higher quality data.

The statistical analysis scheme discussed above and implemented for the Vis pump–IR probe experiments has not yet been implemented for the IR pump–IR probe and 2D IR experiments. Incorporation of the statistical analysis scheme into the IR pump–probe and 2D IR experiments would greatly increase the quality of these data for the reasons discussed above.

A.3 Conclusion

We can now carry out Vis pump–IR probe spectroscopy on thin films of device-relevant materials at low excitation densities. The ability to study thin films opens up the ability to control the film morphology, an experimental handle that affects microscopic properties of
fundamental importance as well as has the practical implication of highly efficient devices. Pushing the limits to the lowest excitation density instills more confidence that exciton annihilation processes play less of a role complicating the interpretation of the desired dynamics.

A.4 References


Figure A-1. Percentage of photons transmitted as a function of distance through sample for (A) a 3 μm and (B) 100 nm thick film of 1:1 RR-P3HT:PCBM (assuming absorption coefficients for each component of $10^5$ and $10^4$ cm$^{-1}$, respectively).
Figure A-2. (A) Chemical structures of RR-P3HT and PCBM. (B) Photos and corresponding (C) UV-Vis spectra of unannealed and annealed 1:0.8 RR-P3HT:PCBM thin blend films. Annealing conditions were 30 min. at 165 °C.
Figure A-3. (A) Chemical structure of CN-MEH-PPV. (B) UV-Vis absorption spectrum of 115 nm thick film of CN-MEH-PPV.
Figure A-4. Signal of silicon photodiode and pyroelectric detector along with the "sample and hold" gate used to integrate signals plotted against time following firing of laser and initiation of data acquisition sequence.
Ryan D. Pensack earned a bachelor's degree in chemistry from Rutgers University in 2006. Under the direction of Prof. Richard Mendelsohn, he carried out research at Rutgers-Newark using infrared spectroscopy to measure the structural changes that occur in lipid-based systems upon chemical and thermal perturbation. In 2006, he joined the Asbury group at Penn State University. With Prof. Asbury, he developed ultrafast vibrational spectroscopy to study the mechanism of charge separation, i.e. charge-transfer state dissociation, in organic photovoltaic blend films. While at Penn State, he has had the opportunity to present posters and (student) seminars at several conferences including the 63rd OSU International Symposium on Molecular Spectroscopy (2008), the 238th ACS National Meeting (2009), SPIE Optics+Photonics (2009), and the Gordon Conference on Vibrational Spectroscopy (2010). This thesis serves to complete his work as a doctoral candidate at Penn State University.