Magnetic resonance spectroscopy of fullerenes and [pi]-conjugated polymers

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Magnetic resonance spectroscopy of fullerenes and π-conjugated polymers

Lane, Paul Andrew, Ph.D.
Iowa State University, 1994
Magnetic resonance spectroscopy of fullerenes and $\pi$-conjugated polymers

by

Paul Andrew Lane

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Physics and Astronomy
Major: Condensed Matter Physics

Approved:
Signature was redacted for privacy.

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For the Major Department
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For the Graduate College

Iowa State University
Ames, Iowa
1994
DEDICATION

To my mother and father, for everything.
To my brothers Steve and Mark, for helping me to keep everything in perspective.
To the gang from Macalester, especially Eric, Joe, Robert, Dave, Chris, Scott, and Patty, for your years of friendship and your various couches.
To my friends from Iowa State, especially Steve, Ben, Susan, Lars, Dan, Leif, Kurt and Tony, for reminding me that there's more to life than the lab.
To the folks from St. Thomas Aquinas, especially Fathers Jon, Dan, and Ev.
And to Ralph. I owe you more than words could ever say.
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CHAPTER 1. INTRODUCTION TO PHOTOLUMINESCENCE DETECTED MAGNETIC RESONANCE (PLDMR)

1.1 Description of PLDMR

Since its introduction in 1967-68, Optically Detected Magnetic Resonance (ODMR) has proven to be a highly sensitive method for detection of paramagnetic excited states in a wide variety of materials. Originally used to monitor changes in photoluminescence due to magnetic resonance (PLDMR), ODMR has been extended to include detection of changes in photoinduced absorption (PADMR) and electroluminescence (ELDMR) as well as related changes in conductivity (CDMR) and photoconductivity (PCDMR). All forms of non-zero-field magnetic resonance rely upon the paramagnetic interaction of particles with an applied magnetic field. For a particle with non-zero spin placed in a magnetic field, the interaction can be described by the following Hamiltonian:

\[ H = \vec{S} \cdot \vec{g} \cdot \vec{H} \]  

where \( \vec{S} \) is the spin of the particle, \( \vec{g} \) is a tensor defining the interaction of the particle with the field, and \( \vec{H} \) is the applied magnetic field.

Electron \( \pi \) orbitals in organic molecules are locked in fixed directions relative to the molecular frame by the electric field of the chemical bonds and are not free to precess or become oriented in an imposed magnetic field. The electronic orbital motion becomes decoupled from the spin in a process called "quenching." As a result, the orbital angular momentum is effectively quenched and organic molecules have nearly isotropic \( g \) factors, very close to the free electron value of 2.0023. Thus, the \( g \) tensor can be replaced by a constant and the Hamil-
Ionian reduces to:

\[ H = g \vec{S} \cdot \vec{H} \]  

Consider a non-interacting or weakly bound spin-1/2 electron-hole pair. For this case, the spin-spin coupling energy will be usually be negligible compared to the Zeeman splitting of the energy levels. The spin of each particle can align against or along the magnetic field, resulting in four possible energy levels. When this system is placed in a magnetic field, the energy levels are:

\[ E = \frac{1}{2}(\pm g_e \pm g_h) \beta H_0 \]

where: \( g_e \) and \( g_h \) are the electron polaron and hole polaron g values
\( \beta \) is the Bohr magneton
\( H_0 \) is the magnitude of the applied magnetic field.

The energy levels as a function of the applied field intensity are shown in Figure 1.

As states with antiparallel spins can decay radiatively, whereas those with parallel spins will decay nonradiatively, the recombination of pairs with anti-parallel spins will be faster than pairs with parallel spins. This results in a greater population of pairs with parallel spins than anti-parallel spins \((n_2, n_3 < n_1, n_4)\). The application of a microwave field at resonance such that:

\[ h\nu = g_e \beta H \quad \text{or} \quad h\nu = g_h \beta H \]
will mix the state populations such that $n_1 = n_3$ or $n_2 = n_4$. Initially, there is a rapid increase in $n_2$ and $n_3$ which is accompanied by an increase in the PL. This is referred to as a PL enhancing resonance.

Figure 2 shows a time-resolved PLDMR experiment performed on a doped ZnS crystal. The application of microwaves causes an initial spike upwards in the PL. The PL decays to a new steady state level at a rate limited by the spin lattice relaxation rate $1/T_1$ of the system. The new steady state PL is more intense than the original PL as populations no longer build up in
the nonradiative levels. When the microwaves are removed, the PL decays to its original steady state level at a rate governed by the radiative recombination lifetime $1/t_R$.

Some processes yield a quenching PLDMR. For example, a spin-dependent nonradiative channel which is enhanced at the expense of the PL. Another case would involve a population of geminate electron-hole pairs. These pairs of particles are created with anti-parallel spins and can quickly decay to radiative singlet excitons. If one of the spins is flipped as a consequence of magnetic resonance, the pair is converted to a parallel spin configuration. The pair will no longer be able to decay to a radiatively and a negative PLDMR will be detected.

Often the PL of semiconductors will be due to various channels with different spin dependence. Thus, PLDMR may serve as a technique permitting one to separate and identify these separate channels. It is possible to isolate these components by either measuring the spectral dependence of the various PLDMR resonances or the PLDMR of selected bands of the PL. In this work, comparing the PLDMR of the phosphorescence and fluorescence of C_{70} glasses was particularly revealing.

1.2 Detection of triplet excitons

Much attention has been devoted to the detection and analysis of triplet excitons detected in fullerenes and conjugated polymers. PLDMR has proven to be an especially sensitive technique to detect and characterize these triplet excitons. A brief review of the theory behind detection of triplet excitons follows. A more comprehensive treatment can be found in references 6-9. The spin Hamiltonian for a pair of interacting, spin-1/2 particles in a magnetic field is:

$$H = H_z + H_{ss} + H_{hfs}$$  \hspace{1cm} (5)
where $H_Z$ is the paramagnetic Zeeman interaction of the spins with the applied magnetic field, $H_{S-S}$ is the spin-spin dipole interaction, and $H_{hfs}$ is the hyperfine interaction between the electronic and nuclear dipole moments.

All samples studied in this work were disordered. Due to fast exciton diffusion, no hyperfine structure should be detected, as the exciton should sample all possible hyperfine environments in a relatively short interval. Since the resonances detected are quite broad (> 200 G),
the effects of hyperfine splitting have been largely neglected as the primary effect of hyperfine splitting will be to broaden the detected resonances.

The dipole interaction for an ensemble of magnetic moments is as follows:

$$H_{DD} = \sum_{i<j} \frac{\vec{\mu}_i \cdot \vec{\mu}_j}{r_{ij}^3} - \frac{3}{r_{ij}^5} (\vec{r}_{ij} \cdot \vec{\mu}_i) (\vec{r}_{ij} \cdot \vec{\mu}_j)$$  \hspace{1cm} (6)

where $\vec{r}_{ij}$ is the displacement vector between any pair of moments and $\vec{\mu}_j$ is the magnetic moment of any dipole. The magnetic moment of a particle $\vec{\mu} = g\beta \vec{S}$, where $\vec{S}$ is the spin vector for the particle. Thus, for a pair of particles the spin-spin Hamiltonian can be written

$$H_{s-s} = (g\beta)^2 \left[ \frac{\vec{S} \cdot \vec{S}}{r^3} - \frac{3}{r^5} (\vec{r} \cdot \vec{S}) (\vec{r} \cdot \vec{S}) \right]$$  \hspace{1cm} (7)

The spin-spin Hamiltonian can rewritten in terms of the components of the total spin angular momentum $\vec{S}$ to:

$$H_{s-s} = \frac{(g\beta)^2}{r^5} \left[ \begin{array}{c} (r^2 - 3x^2)S_x^2 + (r^2 - 3y^2)S_y^2 + (r^2 - 3z^2)S_z^2 \\ -3xy(S_yS_x + S_xS_y) - 3yz(S_yS_z + S_zS_y) - 3zx(S_zS_x + S_xS_z) \end{array} \right]$$  \hspace{1cm} (8)

or:

$$H = \vec{S} \cdot \vec{D} \cdot \vec{S}$$

where

$$D = \begin{bmatrix} r^2 - 3x^2 & -3xy & -3zx \\ -3xy & r^2 - 3y^2 & -3yz \\ -3zx & -3yz & r^2 - 3z^2 \end{bmatrix}$$  \hspace{1cm} (9)
Because D is not singular, it can be diagonalized. This basis determines the principle axes of the triplet. In this system, the Hamiltonian reduces to

\[ H_{S^{-}} = -\frac{\hbar}{2} \beta \left[ \left( \frac{r^2 - 3x^2}{r^4} \right) S_x^2 - \left( \frac{r^2 - 3y^2}{r^4} \right) S_y^2 - \left( \frac{r^2 - 3z^2}{r^4} \right) S_z^2 \right] \]

\[ = -XS_x^2 -YS_y^2 -ZS_z^2 \]

\[ = D \left[ S_z^2 - \frac{1}{3} S(S+1) \right] + E \left( S_x^2 - S_y^2 \right) \]

(10)

As \( X + Y + Z = 0 \), the triplet can be characterized by only two, independent parameters.

\[ D = -\frac{3Z}{2} = \frac{3}{4} g^2 \beta \left( \frac{r^2 - 3z^2}{r^4} \right) \]

(11)

\[ E = \frac{Y - X}{2} = -\frac{3}{4} g^2 \beta \left( \frac{x^2 - y^2}{r^4} \right) \]

(12)

The zero field splitting of energy levels in a triplet exciton is shown in Fig. 3. Each zero-field energy level is associated with a principal axis. When all three axes are inequivalent, they are assigned such that \( D \geq 3E \). Thus, the z axis is associated with the principal axis of the sublevel split furthest from the other two. The splitting between the two remaining triplet sublevels equal 2E. When two levels are degenerate, which implies their axes are equivalent, the third direction is taken as the z axis and \( E = 0 \).

D and E are called the zero-field (zfs) splitting parameters and characterize the triplet exciton. Using the convention stated above, \( E \) is largely a measure of the departure from axial symmetry. An upper bound on the spatial extent of the exciton can be calculated from D.
For example, the triplet exciton detected on isolated C_{60} molecules is characterized by D = 120G and E = 7G. For this case, \( r_{jjg} \approx 6.3 \, \text{Å}, \) which implies a nearly axially symmetric triplet exciton delocalized over the entire fullerene molecule. The spin Hamiltonian is thus written:

\[
H_{s,s} = g \beta \cdot H_0 + D(S_z^2 - \frac{1}{3}) + E(S_x^2 - S_y^2)
\]

The eigenvalues of the spin Hamiltonian will depend upon both the magnitude of the applied field \( H_0 \), and its direction relative to the principal axes of the molecule. Hence, the orientation of the molecule relative to \( H_0 \) will determine the energies of the triplet sub-levels. Figure 4 shows a diagram of energy vs. applied field intensity for the applied field aligned along the three principal axes for a triplet exciton with three distinct axes. The sublevel with its axis parallel to the applied field is unaffected by the field and becomes the \( m_s=0 \) sublevel. The other two sublevels are mixed, with one split upwards \( (m_s=+1) \) and the other split downwards.
Figure 4. Energies of triplet levels for magnetic field $\mathbf{H}$ aligned with each of the three principal axes.
\( m_s = -1 \) in energy as the applied field intensity increases. A and B mark the two full-field microwave-induced transitions (\( |{-1}\rangle \rightarrow |0\rangle \) and \( |0\rangle \rightarrow |1\rangle \)) and C marks the half-field transition (\( |{-1}\rangle \rightarrow |+1\rangle \)).

The magnetic resonance signals will be detected at different points, depending upon the orientation of the triplet relative to the magnetic field. If a single crystal sample is used, the zero field splitting parameters can be determined by measuring the positions of the resonance transitions at different orientations of the crystal relative to the applied magnetic field.

Figure 5 shows the PLDMR of naphthalene in a single crystal of durene.\(^{12}\) The naphthalene molecule can reside at two inequivalent sites in the crystal. As a consequence, four resonances were detected; two for each orientation (\( H||x \) and \( H||z \)) and two for each full-field transition (\( |{-1}\rangle \rightarrow |0\rangle \) and \( |0\rangle \rightarrow |1\rangle \)).

In order to detect a PLDMR, the populations of the different sublevels must be unequal. The magnitude of the departure from equality is generally referred to as the spin polarization of the system and is defined below:

\[
\mathcal{P}_y \equiv \frac{n_i - n_j}{n_i + n_j}
\]

where \( n_i \) and \( n_j \) are the populations of levels \( i \) and \( j \).

Even in the absence of zero-field splitting, the energies of the different triplet sub-levels will be different in a magnetic field. The spin polarization of a system in thermal equilibrium with the lattice will follow Boltzmann statistics, \( \mathcal{P}_{ij} = e^{\Delta E / kT} \), such that:

\[
\begin{align*}
n_i &= n_0 e^{-(E_i - E_0) / kT} , \\
n_0 &= n_{-1} e^{-(E_0 - E_{-1}) / kT} \\
\end{align*}
\]
A spin will be subjected to a constantly fluctuating magnetic field arising from its environment. This field at a particular electron will contain a component at the Larmor frequency which will be able to induce transitions between the levels. The efficiency of the spin-lattice coupling is determined by the spin-lattice relaxation time ($T_1$), which characterizes the rate at which departure of the spin polarization from Boltzmann statistics decays to thermal equilibrium. An alternate phrasing is that $T_1$ is the parameter which characterizes the rate at which the bulk magnetization approaches its thermal equilibrium value when the magnetic field is switched on.

Figure 5. PLDMR Spectra of napthalene in a single crystal of durene.
This decay should be exponential.\textsuperscript{7} Thus, $T_1$ is defined by the relationship:

$$p_{10}(t) = [-p_{10}(0) - p_{10}(\infty)] \neq \exp(-t/T_1)$$

where $p_{10}(\infty)$ is the thermalized spin polarization.

Spin polarization can also result from generation and recombination. Triplet excitons in $\pi$-conjugated systems are generated by decay of singlet excitons via intersystem crossing due to spin-orbit coupling. The efficiency of intersystem crossing is usually different for each of the triplet sublevel states. As a consequence, there is an inherent spin polarization by generation. Even if the generation of triplets is homogenous by sublevel, spin polarization can still be achieved as the sublevel recombination rates are different. Generally, recombination is fastest from the $m_s = 0$ sublevel, resulting in $n_1, n_{-1} > n_0$. The PLDMR signal detected for this spin polarization will be symmetric about $g = 2$.

All samples studied in this work were amorphous or polycrystalline. Thus, any detected resonance is the sum of contributions from all possible orientations of $H_0$ relative to the triplet axes. The resulting resonance is therefore analogous to an ESR “powder pattern.” For a randomly oriented sample, the detected resonance is an average over all orientations. Powder patterns are calculated by first finding the resonance condition, which are the values of $H$ where absorption of microwaves occur and averaging over all possible orientations.

The transition field $H(n,\phi)$ is a function of the cosine of the polar angle ($n = \cos \theta$) and the azimuthal angle $\phi$. To simplify the analysis, $E$ is assumed to be zero, so that the transition field is independent of $\phi$. In a randomly-oriented sample, the number of molecules oriented such that the resonance field $H$ lies between $\theta$ and $d\theta$ is proportional to $\sin \theta \ d\theta$. The intensity of the absorption in the field range $H$ to $H + dH$ is
\[ dl = \sum_{\theta} A(H,n) \frac{dn}{dH} dH \]  

(18)

where the relationship \( H = H(n) \) has been inverted to \( n = n(H) \) and \( A(H,n(H)) \) is the transition probability. For cases where \( E \neq 0 \), the analysis is more complicated (see Atherton\(^7\) for more detail), but tractable. In general, the following critical points are found in a full-field powder pattern:

shoulders at

\[ H = \left( hv \pm D / 2 \pm 3E / 2 \right) / g\beta \]  

(19a)

singularities at

\[ H = \left( hv \pm D / 2 \mp 3E / 2 \right) / g\beta \]  

(19b)

and steps at

\[ H = (hv \pm D) / g\beta \]  

(19c)

Two of the most important powder patterns are those of an axially symmetric (\( E=0 \)) triplet exciton with singularities at \( H = (hv \pm D / 2) / g\beta \) and steps at \( H = (hv \pm D) / g\beta \) and an \( E=D/3 \) triplet exciton for which the inner singularities merge to a form a singularity at \( H = hv / g\beta \) and the shoulders and steps merge at \( H = (hv \pm D) / g\beta \).

The half-field powder pattern is much narrower than the full-field powder pattern as it is dependent on \( D \) and \( E \) in the second order (first order perturbation terms vanishing). The half-field resonance will have the following critical points:

a singularity at

\[ H = \sqrt{\left( \frac{hv}{2g\beta} \right)^2 - \frac{D^2 + 3E^2}{g^2\beta^2}} \]  

(20a)
and a shoulder at \( H = \frac{h\nu}{2g\beta} \left[ 1 - \frac{1}{2} \left( \frac{D-E}{h\nu} \right)^2 \right] \) 

Shown in Figures 6 and 7 are simulations\(^{13}\) of full-field triplet powder patterns for excitons with zfs \( D = 520 \text{G} \) and \( E = 0 \) and \( D = 520 \text{G} \) and \( E = D/3 \) with the DC magnetic field perpendicular to that generated by the microwave field. A simulated half-field triplet powder pattern for a triplet with zfs \( D = 602 \text{G} \) and \( E = 0 \) is shown in Figure 8.

![SIMULATED PLDMR Powder Pattern](image.png)

**Figure 6.** Simulation of a full-field triplet powder pattern for \( D = 520 \text{G} \) and \( E = 0 \text{G} \).
Figure 7. Simulation of a full-field powder pattern for $D = 520\, \text{G}$ and $E = D/3$.

Figure 8. Simulation of a half-field triplet powder pattern for $D = 602\, \text{G}$ and $E = 0\, \text{G}$. 

\begin{align*}
\text{SIMULATED PLDMR} \\
\text{Powder Pattern} \\
D=520\, \text{G}, \ E=D/3 \\
hv = 9.352 \, \text{GHz} \\
H_1 \perp H_0
\end{align*}

\begin{align*}
\text{SIMULATED HALF FIELD} \\
\text{POWDER PATTERN PLDMR} \\
H_1 \perp H_0 \\
D=602\, \text{G}, \ E=0
\end{align*}
1.3 Description of Experimental Apparatus

There are several possible experimental methods to perform PLDMR experiments. It is not necessary to apply an external magnetic field to detect a magnetic resonance signature. At zero field, the resonance occurs at the frequency which is equal to the energy splitting due to spin-spin interactions ($\Delta E_{S,S} = \hbar \nu$). The sample is placed in a microwave cavity and the microwave frequency is swept through a resonance condition. Zero-field ODMR requires the use of a microwave sweep oscillator capable of generating microwaves over an octave of frequencies and a cavity continuously tunable over a wide frequency range.

This technique frees one from the need to generate a magnetic field and the complication of analyzing powder patterns due to random orientation of triplets with respect to the applied field. However, it does not permit the study of paramagnetic species with no energy splitting in zero-field. The use of single crystal samples permits the precise determination of the zero-field splitting (zfs) parameters. When single crystals are not available, analysis of powder pattern spectra enables one to extract the desired parameters. All PLDMR spectra reported here were taken with an applied DC magnetic field.

A PLDMR spectrum is generally detected with a photodiode appropriate to the wavelength range of interest or a photomultiplier tube (PMT). Changes in the total PL are typically monitored. Where one wavelength range is of interest, optical filters or a monochromator can be used to limit the PL band. This is of particular interest for materials possessing both fluorescence and phosphorescence. One can also measure the spectral dependence of the PLDMR. The microwave frequency and magnetic field are set to the peak of the resonance of interest. The spectral dependence of the change $\Delta I$ in the PL is measured by dispersing the PL with a monochromator which is swept and locking in on changes in the PL spectrum due to chopping the microwaves. All PLDMR spectra reported here were detected with a silicon photodiode driving a solid state transconductance amplifier with a gain of $\sim 10^6$ volts per amp.
PLDMR spectra are dimensionless, given in terms of the difference in PL due to the resonance condition divided by the total PL (ΔI/I). The intensity relative to the total PL is quite small, typically in the range from 1 part in 10⁶ to several parts in 10³. The most common PLDMR scheme uses lock-in detection. The microwaves are amplitude modulated by a diode switch while the magnetic field slowly scans the region of interest. The detector output is fed to the input of a lockin amplifier and the signal referenced to the amplitude modulation frequency. The period of the modulation frequency should be long compared with the spin-lattice relaxation time (T₁) or the lifetime of the species of interest. Otherwise, the spin polarization is artificially limited by too rapid modulation of the microwaves.

Lockin amplification is a powerful technique. It permits the detection of signals with quite a quite high S/N ratio which would otherwise be undetectable. However, one cannot determine the sign of the resonance (enhancing or quenching) nor can one directly measure T₁ or radiative lifetimes. In time-resolved PLDMR measurements, the detector is connected to a boxcar integrator or digitizing oscilloscope, permitting one to resolve the time-dependence of the signal. All spectra reported in this thesis were detected using lockin amplification. Time-resolved PLDMR measurements remain to be undertaken in future work.

A schematic of the PLDMR spectrometers used in this study is given in Figure 9. X-Band microwaves were generated between 9.30 and 9.35 GHz by a Gunn diode oscillator with an output power of <100 mW. The signal amplitude is controlled by calibrated attenuators and modulated by a pin-switch diode. Microwaves were further amplified by either a travelling wave tube amplifier (TWTA) or solid state linear amplifier up to 1400 mW. Coupling to a high-Q microwave cavity was performed by adjustment of the microwave frequency and a coupling screw mounted on the cavity inlet.

The sample is photoexcited by either a visible or ultraviolet source. The visible excitation source is an argon ion (Ar+) laser. The wavelength could be adjusted between 457.9 and 514.5
nm. Total power used was \(<50\) mW to avoid sample heating. An external stabilizer was used to reduce noise and minimize slow fluctuations in the laser intensity. The ultraviolet excitation source is a high pressure Mercury or Mercury-Xenon lamp. The IR output of the lamp is eliminated with a low-pass filter and a specified wavelength range between 250 and 450 nm can be selected with either a dichroic mirror or filter. A lens corrected for spherical aberration is used to gather the light. The optics can be adjusted to switch between visible and UV excitation and to focus the luminescence on either the input slit of a monochromator or a silicon photodiode. The exciting light was filtered out to reduce noise in the PLDMR signal.

Samples were inserted into an Oxford Instruments continuous flow liquid helium cryostat and spectra were measured at temperatures ranging between 5K and 300K. The cryostat was centered in a TE microwave cavity and manufactured from quartz so as to not absorb microwaves. Coarse temperature control was achieved by regulation of liquid helium flow. The use of a temperature controller with a fine heating element permitted measurements to be taken with temperatures stable to within 0.1 K.

The apparatus described above was also used with minimal modifications to measure PL spectra. PL from the sample was dispersed through either a one-quarter or one meter monochromator and detected with a PMT. The laser intensity was amplitude modulated by the laser stabilizer and lockin detected. The spectral response of the detector/monochromator system was determined using a glow bar. The glow bar luminescence is that of a black body source at a known temperature and can be used to calibrate the system. The calibration curve was then applied to correct the detected spectra.

The entire experimental apparatus is computer controlled, with all data acquisition performed by the computer. The magnetic field strength and monochromator position are computer controlled, with the user setting temperature, microwave power, photoexcitation intensity, detector and lockin gain.
Figure 9. A schematic diagram of the PLDMR spectrometer.
1.4 Sample Preparation

All liquid samples studied consisted of the material of interest dissolved in a solution of 90% toluene and 10% polystyrene by weight. Polystyrene was added to solutions as a glassing agent so that when frozen, the sample formed a transparent glass. All dissolved gases, particularly oxygen, were removed by multiple freeze-thaw cycles. The sample was pipetted into a quartz tube sealed at one end. The end with the solution was immersed in liquid nitrogen and the open end pumped to vacuum by a turbo molecular vacuum pump. After a sufficiently low pressure was reached, the sample was closed off to the pump and permitted to thaw slowly. Dissolved gases bubbled out of the sample and were pumped from the tube. The cycle was repeated as many times as necessary until no more dissolved gases are evident. The sample was then frozen, pumped, and sealed by an oxyacetylene torch. Care must be taken not to leave an organic deposit on the upper portion of the quartz tube or the contamination will make it impossible to seal the tube.

For preparation of film samples, the material (polymer or fullerene) was dissolved in toluene, pipetted into a quartz tube, and degassed as above. The sample is then slowly evacuated to leave a deposit on the bottom of the tube. The sample was then pumped to a pressure of less than $10^{-5}$ Torr. To more quickly drive out the remaining solvent, the sample would be heated. Some polymer samples were spin cast in an inert atmosphere and the free standing film was sealed in an evacuated quartz tube.
CHAPTER 2. AN INTRODUCTION TO PHOTOEXCITATIONS OF 
\( \pi \)-CONJUGATED POLYMERS AND BUCKMINSTERFULLERENE

During the past 17 years, a remarkable new class of organic polymers with the ability to conduct electrical current has been developed. Polyacetylene \((\text{CH})_x\) was the first of the \( \pi \)-conjugated polymers, named for the dimerization of \( \pi \)-bonds along the backbone of the polymer chain. \( \pi \)-Conjugated polymers are promising new materials which combine unique mechanical properties such as flexibility and solubility with the electronic properties of semiconductors. Potential applications in non-linear optical devices and light-emitting diodes have stimulated interest in the radiative decay processes of these materials.

The theoretical picture of elementary excitations in \( \pi \)-conjugated polymers is very different from that of conventional semiconductors. In a traditional three-dimensional semiconductor such as silicon, the four-fold coordination of each atom to its neighbor through covalent bonds leads to a rigid structure. However, the less rigid two-fold coordinated \( \pi \)-conjugated polymers are more susceptible to structural deformations. Solitons, which are domain walls between two energetically equivalent ground states, are seen in some \( \pi \)-conjugated polymers. Electrons and holes are replaced by positive and negative polarons, named for the polarization of the medium due to distortions of atoms from their equilibrium positions. Excitons (bound electron-hole pairs) are also accompanied by a distortion of the bonds along the polymer chain and are termed self-trapped or polaronic excitons.

It is generally accepted that photoluminescence from \( \pi \)-conjugated polymers is largely due to radiative decay of singlet excitons. The lowest-lying triplet states are primarily nonradiative. Recent experimental results, some of which are described in this work, provide evidence for a scenario in which charged excitations (polarons and bipolarons) and triplet excitons quench the
photoluminescence. Furthermore, these PL-quenching photoexcitations appear to be stabilized by defects which break the conjugation such as bends and twists of the polymer chain.

Buckminsterfullerene (C_{60}) is a unique material which has captured the interest of both laymen and scientists alike. Much attention has been paid to the photophysics of fullerenes. As the bonding of carbon atoms in both \( \pi \)-conjugated polymers and fullerenes is similar, the development of a comprehensive theory of photoexcitations in \( \pi \)-conjugated polymers has proven especially fortuitous for researchers investigating the photophysics of this novel material. Polarons and polaronic excitons have been both predicted and observed in fullerenes. With a few modifications, the theory developed for \( \pi \)-conjugated polymers has been successfully applied to fullerenes.

2.1 Introduction to Photoexcitations in \( \pi \)-Conjugated Polymers

Carbon has six electrons in the atomic configuration \( 1s^2 2s^2 2p^2 \) in the ground state, two of which are valence electrons available for bonding. Very close in energy is the \( 1s^2 2s 2p^3 \) state, which has four valence electrons and is the state of carbon from which most compounds are formed.\(^1\) Methane, CH\(_4\), is a compound in which the 2s and 2p orbitals are completely hybridized (sp\(^3\) hybridization). There are four \( n=2 \) orbitals and each bonds to a hydrogen atom. The bonds are highly oriented in a tetrahedral configuration at 109.5° to each other.

In most conjugated polymers and fullerenes, three electrons from each carbon atom are in sp\(^2\) orbitals. The prototypical example of an sp\(^2\) hybridized molecule is ethylene, C\(_2\)H\(_4\), shown in Figure 10. Each carbon atom is bonded to two hydrogen atoms and the other carbon atom.

The three sp\(^2\) hybridized orbitals of each carbon atom (\( \uparrow \downarrow \)) are at an angle of 120° relative to each other and define the x-y plane. The p\(_z\) orbitals lie perpendicular to the plane of the molecule. The orbitals of each carbon atom are then:
Each of the $sp^2$ hybridized orbitals forms a $\sigma$ bond with a hydrogen atom or the other carbon atom. These bonds are highly directional and the electrons are localized. The structure of ethylene is determined by the five $\sigma$ bonds lying directly between the atoms. The two $p_z$ orbitals form what is called a $\pi$ bond between the two carbon atoms. This $\pi$ bond is weaker and
more delocalized than the $\sigma$ bond. The greatest stability of this arrangement occurs when the atomic orbitals are parallel and the orbital overlap is maximized.\(^2\) Thus, it is able to form only when both CH$_2$ structures are coplanar and both $p_z$ orbitals of the same phase.

The $\pi$ bond will form a molecular $\pi$ orbital. There are three types of $\pi$ orbitals: bonding, non-bonding, and antibonding. Antibonding orbitals destabilize molecules, tending to force them apart, while non-bonding orbitals neither stabilize nor weaken the bonding between atoms. All the $\pi$ electrons of a molecule in its ground state will be in either bonding or non-bonding orbitals. Photoexcitation of an ethylene molecule will excite an electron from a bonding $\pi$ orbital to an antibonding $\pi^*$ orbital. While $\sigma$ bonds are of interest, the gap between $\sigma$ and $\sigma^*$ orbitals is much greater than that between $\pi$ and $\pi^*$ orbitals. Thus, the excited state properties of ethylene will be determined by $\pi$, not $\sigma$ electrons. The level schemes, showing the highest occupied (HOMO) and lowest unoccupied (LUMO) $\sigma$ orbital only are shown in Figure 11.

The third possible hybridization scheme is $sp$, seen in some $\pi$-conjugated polymers. The prototypical molecule with $sp$ hybridization is acetylene, C$_2$H$_2$. The two $sp$ orbitals form $\sigma$-bonds with a hydrogen atom and the other carbon atom, defining the $x$ axis of the molecule. The remaining four orbitals, two $p_y$ and two $p_z$, combine with the $\sigma$-bond to form a carbon-carbon triple bond (C≡C). This consists of a cylindrical sheath of charge from the $\pi$-orbitals about the $\sigma$-bond and is shown in Figure 12. A C≡C bond is more rigid than a C=C bond and less susceptible to structural deformations such as rotations about the axis of the bond.

The simplest $\pi$-conjugated hydrocarbon is buta-1,3-diene (C$_4$H$_6$). Its two isomers are shown in Figure 13. In ethylene, all six atoms are coplanar and rotation about the carbon-carbon bond requires a great deal of energy. The rotation barrier for the central carbon-carbon bond is relatively low for butadiene. As a consequence, conformational defects such as twists and bends along carbon chain can break the $\pi$-conjugation.
Figure 11. Occupation of energy levels for (a) the ground and (b) excited state configurations.

Figure 12. Diagram of an acetylene molecule with the carbon-carbon triple bond shown.
Figure 13. Representations for (a) transoid or s-trans and (b) cisoid or s-cis buta-1,3-diene.

The original meaning of $\pi$-conjugation as sequences of alternating single and double bonds is dated, though the terminology still persists. However, the chemistry of $\pi$-conjugated unsaturated molecules is considerably more complicated than that of the individual structural units. Overlap of the $p_2$ orbitals between adjacent molecules along the backbone of polymers accounts for the extraordinary properties of these systems. For most $\pi$-conjugated systems, the overlap between molecules is not evenly distributed. Rather, there is an alternation of bond lengths due to the greater overlap between some pairs of neighbors than others.

An outstanding exception to this rule for $\pi$-conjugated systems is benzene ($C_6H_6$), shown in Figure 14. Like ethylene, the orbitals are $sp^2$ hybridized, with each carbon atom forming $\sigma$ bonds with two neighboring carbon atoms and one hydrogen atom. Each carbon atom also has one $p_2$ orbital, lying above and below the plane of the molecule. There are two equivalent and hence, energetically degenerate bonding configurations (Figure 15). Rather than three pairs of single bonds and double bonds, all six carbon-carbon bonds are equivalent and have a length between that of a conventional double bond and a single bond. A delocalized electron cloud
Figure 14. Representation of benzene molecule with $p_z$ orbitals shown.

Figure 15. (a) and (b) The two equivalent configurations of benzene and (c) the normal representation of the delocalized $\pi$-orbitals.
cloud forms above and below the benzene ring (Figure 16). Aromatic rings can incorporate a heteroatom, such as sulfur (thiophene), oxygen (furan), or nitrogen (pyrrolle).

Serious investigations into conjugated polymers were spurred by the discovery in 1977 that polyacetylene could be chemically doped to a conductivity of up to 1000 S/cm at room temperature. Improvements in polymerisation methods raised this value to 145,000 S/cm. The two isomers of polyacetylene, (CH)$_x$, are shown in Figure 17.
Figure 17. The two isomers of polyacetylene and the two possible alternation states.

The order parameter \( \phi_n \) is defined such that \( \phi_n = +1 \) on the top segments and \( \phi_n = -1 \) on bottom segments. Trans-polyacetylene has the unique property that there is no preferred sense of bond alternation. Thus, the ground state is twofold degenerate. Adjacent neighbors in the cis structure differ in the relative position of their third nearest neighbor, lifting the degeneracy. The energy levels as a function of the alternation parameter are diagrammed in Figure 18.

Work on photoexcited \((\text{CH})_x\) was stimulated in large part by the prediction of soliton formation.\(^6\)\(^7\) Figure 19 diagrams a soliton lying between the two sense of alternation. From electron-hole symmetry considerations, a soliton has one quantum state, of \( p_z \) non-bonding character, that lies at mid-gap. This orbital can accommodate 0, 1, or 2 electrons with the interesting consequence that a neutral soliton is a spin-1/2 excitation and a charged solitons are
Figure 18. The total energy of (a) trans- and (b) cis-polyacetylene vs. $\phi_n$.

Figure 19. (a) A schematic diagram of a soliton on a segment of trans-(CH)$_x$, (b) the order parameter $\phi_n$, and (c) the occupation of the energy levels for neutral and charged solitons.
spinless. The energy levels are shown in Figure 19c with the occupation states of neutral, positive, and negative solitons represented by the spin states of the electrons.

The ground state of nearly all π-conjugated polymers is not degenerate. Solitons are not stable on these polymers, as an extended segment of the higher energy alternation state is energetically unfavorable. The dominant charged photoexcitations in these polymers are polarons (Figure 20). Polarons have the same spin-charge relationship as electrons and holes, being spin-1/2 with a charge of ±e. Due to distortion of the bond lengths around the charge, the lowest conduction band level and the highest valence band level split off from the band edges into the gap. In molecular chemistry terms, the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) intrude into the gap. All π-conjugated polymers studied in this work have a non-degenerate ground state.

Figure 20. (a) Schematic diagram of a polaron on a segment of cis-(CH)ₙ, (b) the order parameter $\phi_n$, and (c) the occupation for positively- and negatively-charged polarons.
Figure 21. Schematic diagram and occupation of energy levels of doubly-charged bipolarons.

It is energetically favorable for two like-charged polarons to form a doubly charged, spinless bipolaron. The energy cost of electrostatic repulsion is more than balanced by the gain due to lattice relaxation. The energy diagrams of bipolarons are shown above (Figure 21).

Neutral photoexcitations play a dominant role in radiative decay processes for $\pi$-conjugated polymers. As for charged particles, a neutral bound pair of charged particles will be accompanied by a distortion of the polymer chain. Thus, neutral photoexcitations are self trapped or polaronic excitons. It is generally agreed that the decay of singlet excitons is responsible for photoluminescence in conjugated polymers. Singlet excitons decay will decay radiatively within about 600 ps of their formation. Only recently has phosphorescence been observed in $\pi$-conjugated polymers. Excitation of poly(p-phenylenevinylene) at 518 nm yields only very weak phosphorescence at 826 nm, indicating that the primary decay path for triplet excitons is nonradiative.

$\pi$-Conjugated polymers are attracting intense attention as a new class of optoelectronic materials. The initial report of electroluminescence from PPV films and the rapid advances that followed have stimulated extensive studies of the radiative and nonradiative decay processes of the excited states of these materials. Therefore, models that determine what
physical processes limit the luminescence from conjugated polymers are of great interest. Results described in this work have profound implications for the efficiency of radiative decay processes in these materials.

Polarons and bipolarons are generally recognized to be nonradiative PL-quenching centers. It has also been recently suggested that triplet excitons are also PL quenching species. These models explain the fact that PLDMR spectra have been found to be PL-enhancing, while photoinduced absorption-detected magnetic resonance (PADMR) spectra are PA-quenching. Photoexcitation creates polarons, bipolarons, and triplet excitons in addition to radiative singlets. The magnetic resonance condition will enhance the decay of these excitations to the ground state. If these photoexcitations quench the PL, then their removal will increase the total PL, resulting in an enhancing PLDMR spectrum. Furthermore, as the photoinduced absorption is due to transitions among excited state levels, removing these states will reduce the PA, resulting in a quenching PADMR spectrum.

As it is widely agreed that geminate singlet excitons are the dominant photoexcitations, a complete model of π-conjugated polymer photophysics must account for the relatively low (τ < 0.2) quantum yield. Recently, Yan et al. have argued that bound polaron pairs residing on separate chains, so-called spatially indirect excitons, are the primary photoexcitations of conjugated polymers. If singlet excitons decay with a yield close to unity, this would imply that spatially indirect excitons are formed with a yield of up to 0.9 (1 - τ). Furthermore, their studies on oxidized PPV show that excitonic emission is quenched at carbonyl (C=O) defect sites. These results will be discussed in light of the PLDMR of fullerene-doped π-conjugated polymers.

A wide variety of conjugated polymers have been synthesized (see ref. 18). Three polymers are studied in this work (Figure 22). Of the three, PPV has been by far the most widely studied as it is the most promising candidate for electroluminescent devices. Polythiophene was
Figure 22. Diagrams of unsubstituted and substituted \( \pi \)-conjugated polymers.
the first conjugated polymer to be studied by PLDMR. Finally, poly(p-phenyleneacetylene) (PPA) has not been widely studied. This material has a higher yield and band gap than PPV and may serve as the basis for future applications. A novel block copolymer made from \( \pi \)-conjugated PPV trimers and non-conjugated ethylene segments is also studied.

Polymer chains are bound to one another by weak Van der Waals forces or occasional cross links. The strength of these interactions determines their solubility in weakly polar compounds and their mechanical flexibility. While the unsubstituted polymers are insoluble and brittle, addition of side groups to the aromatic rings separates chains and weakens interchain interactions. As a result, the substituted materials are easily soluble and flexible.

The extremely fast photoinduced charge transfer from 2-methoxy, 5-(2'-ethyl)hexoxy PPV (MEH-PPV) to \( \text{C}_60 \) has stirred widespread attention due to its potential implication for the photochemistry of various organic and biological systems.\(^{19-21}\) Studies of \( \text{C}_60 \)-doped polymers have included photoluminescence (PL), \(^{19,21}\) photoinduced absorption,\(^{19,21}\) photoconductivity\(^{20-21}\) light-induced ESR (LESR),\(^{19}\) and device applications.\(^{22}\) Doping not only quenches the PL, but the lifetime of the emission decreases from \( \sim 500 \) ps to \( \sim 60 \) ps.\(^{19,21,23}\) This behavior is consistent with very fast charge transfer to \( \text{C}_60 \) as well as nonradiative quenching of the singlet excitons by the positive polarons injected onto the chain by \( \text{C}_60 \). While the PC was dramatically enhanced by doping P3HT with \( \text{C}_60 \), only modest enhancement of the PC was seen for \( \text{C}_{70} \) doping.\(^{20}\)

### 2.2 The Photophysics of Buckminsterfullerenes

The discovery of fullerenes has spurred intense research into the properties of these novel allotropes of carbon. The synthesis of buckminsterfullerene, or \( \text{C}_{60} \), was reported in 1985 as the result of experiments aimed at understanding the mechanism by which long-chain carbon...
molecules are formed in interstellar space and circumstellar shells.\textsuperscript{24} Time-of-flight mass spectra of carbon clusters showed a sharp peak at 60 carbon atoms as well as a less intense peak at 70 carbon atoms. A schematic diagram of the apparatus used to generate carbon clusters is shown in Figure 23. A laser beam vaporized carbon from a rotating graphite disk in 10 atm. helium. While the discovery of $C_{60}$ drew widespread interest, the technique produced only microscopic quantities of the new material. Cluster chemists ran many sophisticated experiments, but none achieved the goal of synthesizing visible quantities of $C_{60}$. After learning of the Krätschmer-Huffman results, Kroto and Smalley realized the stumbling block to high yields was the high helium pressure. At lower pressures, this technique efficiently generates $C_{60}$.

In 1983, physicists Wolfgang Krätschmer and Donald Huffman and their students evaporated a graphite rod by resistive heating in a helium atmosphere. The Krätschmer-Huffman apparatus is shown in Figure 24. At certain pressures of helium, the dust strongly absorbed wavelengths in the far ultraviolet, creating a double-humped spectrum. It was dubbed their "camel" sample, but its significance was not understood.\textsuperscript{25} After reading of the discovery of $C_{60}$, they considered the possibility that a hollow soccerball molecule might explain their results. By 1989, they became convinced of this hypothesis and began rigorous tests to confirm it. Ultimately, the rule of organic chemistry that like dissolves like led them to attempt to dissolve their sample in an aromatic solvent. When the carbon soot was mixed with benzene, the solution turned red and history was made.\textsuperscript{26}

$C_{60}$ is the third known pure crystal form of carbon, in addition to graphite and diamond. The $C_{60}$ molecule, or "buckyball," is shown in Figure 25a. $C_{60}$ takes the form of a truncated icosahedron with a calculated diameter of 7.1 Å. Two carbon-carbon bond distances were found, corresponding to nominally single and double carbon-carbon bonds. The average lengths in the optimized structure are 1.40 and 1.45 Å. Thus, like the conjugated polymers discussed in section 2.1, fullerenes are a dimerized, $\pi$-conjugated system. $C_{70}$, diagrammed in
Figure 23. Laser vaporization apparatus used to first produce fullerenes. At much lower helium pressures, this apparatus efficiently generates fullerenes.

Figure 24. Apparatus first used to efficiently generate C₆₀. Carbon is resistively heated in a helium atmosphere.
Figure 25. Diagrams of (a) $C_{60}$ and (b) $C_{70}$ molecules.

Figure 25b, has been readily produced and studied. The stability of both $C_{60}$ and $C_{70}$ relative to other carbon clusters can be understood if the molecule takes the form of geodesic dome. Hence, this new class of molecules was named after the inventor of the geodesic dome, Buckminster Fuller. The Swiss mathematician Euler proved that all such structures are composed of a number of hexagons and exactly twelve pentagons. The spherically symmetric $C_{60}$ molecule has 20 hexagons, while $C_{70}$ has 25, producing a structure reminiscent of a rugby ball.

The carbon dust prepared by the Kratschmer-Huffman method produces a mixture of roughly 75% $C_{60}$ and 23% $C_{70}$, as well as larger fullerenes. More recently, pure films of larger fullerenes such as $C_{76}$ and $C_{84}$ have been produced and investigation of their properties
has begun.\textsuperscript{28}

At 300K, solid $C_{60}$ molecules condense into an fcc lattice bound by weak van der Waals. X-Ray diffraction studies have determined the lattice constant to be $14.1569 \pm 0.0001 \text{ Å}$. The fullerene molecules freely rotate, the rotational correlation time of 9-12 ps is faster than any other known solid state rotor.\textsuperscript{30} As the temperature is lowered, the rotational motion abruptly changes. At 249K, the crystal undergoes an orientational ordering transition to a simple cubic structure with a four atom basis.\textsuperscript{31} The first-order transition is accompanied by a change in the nature of the rotational motion to hopping between inequivalent orientations. Finally, at $\sim$85K, the molecular hopping motion freezes and a transition to an orientational glass phase occurs.\textsuperscript{32,33}

Carbon atoms in fullerene molecules are $sp^2$ hybridized, with three electrons bound to neighbors on the sphere of the molecule and one $p_z$ orbital. Thus, there are a total of sixty carbon $\pi$ electrons, which determine the electronic properties of $C_{60}$. Figure 26 shows the electronic structure of $C_{60}$, as determined by Hückel 3D molecular orbital calculations. The HOMO-LUMO bandgap is 1.897 eV for the isolated molecule and 1.54 eV for the crystal.\textsuperscript{34-35}

The Su-Schrieffer-Heeger Hamiltonian originally developed to describe photoexcitations in $\pi$-conjugated polymers has been directly applied to photoexcitations of fullerenes by several groups. Upon addition of one or two charges to a $C_{60}$ molecule, electron-phonon coupling results in the formation of an unusual excitation, a string polaron or bipolaron. Bond lengths are altered along a loop circling the equator of the $C_{60}$ molecule (Figure 27) and the energy levels intrude into the energy gap.\textsuperscript{36-37} Calculations of bond lengths in neutral and charged $C_{70}$ have also been conducted and are diagrammed in Figure 28.\textsuperscript{37} Neutral photoexcitations have also been successfully modeled in the context of the SSH model.\textsuperscript{38} The lowest energy spin-triplet state of $C_{60}$ is predicted to be stable against decay due to a large Coulomb binding. This would possibly explain the lack of observable phosphorescence in $C_{60}$. 
Figure 26. The calculated energy levels of a single C\textsubscript{60} molecule. The labelling on the left axis indicates the parity of the state. Arrows indicate occupation.
Figure 27. The string polaron and bipolaron on a $C_{60}$ molecule. The heavy curve indicates the path in which dimerization is suppressed for the string polaron and bipolaron. (a) is the front of the molecule while (b) is the back.

Figure 28. Bond lengths of $C_{70}$ for (a) undoped, (b) polaron, and (c) bipolaron.
Studies of the photophysical properties of C_{60} include optical absorption,\textsuperscript{39-43} photoluminescence (PL),\textsuperscript{40,43-54} light-induced ESR (LESR),\textsuperscript{42,55-62} optically detected magnetic resonance (ODMR),\textsuperscript{63-69} and other techniques.\textsuperscript{70-73} Upon excitation, a free singlet exciton is formed which self-localizes to a polaronic singlet within 15 ps.\textsuperscript{21,26} The low PL yield (\(\sim 7 \times 10^{-4}\))\textsuperscript{53,63} is a consequence of the fast intersystem crossing to the triplet state at a rate of \(\sim 10^9\) Hz,\textsuperscript{49,54} and the long radiative lifetime of the singlet exciton (1.2 \(\mu\)s).\textsuperscript{47}

Fluorescence spectra of different samples have varied widely.\textsuperscript{40,43-54} Emerging evidence indicates that the vibrational structure is dominated by several, independent pairs of false origins\textsuperscript{48,74} due to fluorescence from bulk emission or sites due to defects and impurities.

Detection of an intense triplet powder pattern LESR by Wasielewski et al.\textsuperscript{60} spurred much interest in the lowest triplet state. Its energy level was determined to be \(\sim 1.6\) eV by a variety of techniques.\textsuperscript{39-44,66,71-73} PLDMR\textsuperscript{63-64} measurements revealed a second triplet exciton in films, the zero field splitting (zfs) parameters of which indicated that it is comparable in size to a pentagonal or hexagonal face of the molecule. Its presence in films, but not glasses, indicated that it is likely pinned to sites distorted by intermolecular coupling. In addition to triplet excitons, narrow polaron resonances were also observed by PLDMR\textsuperscript{40-41} and photoinduced absorption detected magnetic resonance (PADMR).\textsuperscript{51,73}

Several recent magnetic resonance studies\textsuperscript{55,66,68} have reported the existence of a second triplet state in C_{60} glasses with varying zfs parameters. There is general agreement that the first triplet state is axially symmetric and delocalized over the entire molecule. However, there is little agreement on the zfs parameters of the second triplet. Angerhofer et al.\textsuperscript{66} raise the possibility of residual fullerene clusters, while Bennati et al.\textsuperscript{55} suggested that the reduced value of \(|D_z|\) could be interpreted by pseudo-rotation due to a dynamic Jahn-Teller effect between close-lying states. In an LESR study of C_{70} glasses, Levanon et al.\textsuperscript{76} described the coexistence of two triplets, with identical zfs parameters, but varying relaxation rates.
While initial interest focused upon C\textsubscript{60}, there has been increasing interest in C\textsubscript{70}. The latter molecule has D\textsubscript{5h} symmetry and the structure of a prolate spheroid with long axis 7.80 Å and diameter 6.94 Å. Studies of the excited state properties of C\textsubscript{70} have included photoluminescence (PL),\textsuperscript{39,46,50-53,77} triplet state dynamics,\textsuperscript{69,73,76} LERS,\textsuperscript{59-60,78-79} and ODMR.\textsuperscript{65-66,80} The PL studies revealed two distinct emission bands: The 650-720 nm band was attributed to radiative decay of photoexcited singlets of lifetime $\tau_s$~560 ps.\textsuperscript{51,73,75,81} A phosphorescence band at 800-1000 nm was also observed and assigned to decay of triplets via intersystem crossing.\textsuperscript{39,46,51-53} LERS studies have detected a delocalized triplet exciton with zfs parameters $|D_I| = 56 G$ (52x10\textsuperscript{-4} cm\textsuperscript{-1}) and $|E_I| = 7.4 G$ (6.9x10\textsuperscript{-4} cm\textsuperscript{-1}).\textsuperscript{59-60,75-76} Reports of its lifetime $\tau_T$ have ranged from 41.7 ms to 51 ms.\textsuperscript{59-60,69,73,76} Fraelich and Weisman\textsuperscript{46} measured the effects of oxygen-induced quenching, self-quenching and triplet-triplet annihilation on $\tau_T$. When these effects are excluded, they report a lifetime of 2.2 ms at 295K; Wasielewski et al.\textsuperscript{36} reported $\tau_T$~51 ms at 9K. The PLDMR measurements reported in this work are consistent with these results.

Photochemistry of C\textsubscript{60} has also received considerable attention (for a review of fullerene chemistry, see ref. 82). Both photopolymerization\textsuperscript{83-86} and photooxidation\textsuperscript{87-91} occur upon irradiation of C\textsubscript{60}. These processes are more efficient when the sample is irradiated with ultraviolet, rather than visible light, suggesting that they are initiated by excitation of electrons beyond the energy gap. Yet Eklund et al.\textsuperscript{83-85} argue that the reaction proceeds via the lowest excited triplet state. There is also disagreement as to whether the resulting material is an epoxide (C=O\textsuperscript{88,90}) or a carbonyl (C=O).\textsuperscript{91} Thomann et al.\textsuperscript{89} detected a triplet exciton in photooxidized C\textsubscript{60} with $|D_I| = 31 G$, which would imply delocalization greater than one molecule. This resonance matches that found in this work in films photopolymerized in vacuum, and is indeed assigned to a triplet exciton delocalized across several molecules.
CHAPTER 3. THE PHOTOLUMINESCENCE-DETECTED MAGNETIC RESONANCE OF C\textsubscript{60} AND C\textsubscript{70} FILMS AND GLASSES

The major part of this chapter describes and contrasts the X-Band PLDMR of C\textsubscript{60} and C\textsubscript{70} in toluene/polystyrene glasses (C\textsubscript{60}:T/PS and C\textsubscript{70}:T/PS) and films. A triplet exciton delocalized over the entire molecule is detected in both glasses. However, the PLDMR of C\textsubscript{70}:T/PS sharply differs from that of C\textsubscript{60}:T/PS, giving insight into the triplet state dynamics and relative populations of the levels. In addition to the delocalized triplet, the PLDMR of C\textsubscript{60} films reveals (ii) a narrow, PL-enhancing resonance attributed to charged, spin-1/2 polarons, (iii) a second triplet exciton localized on a pentagonal or hexagonal face and apparently pinned to sites distorted by intermolecular coupling. The behavior of C\textsubscript{70} films is similar, but with noticeably different lineshapes and temperature dependence. The half-field resonance due to the $\Delta m_s = 2$ transition between the spin sublevels of the triplets is detected in films, but not glasses. These resonances are assigned to fusion of triplets into singlets. This process is not possible for isolated fullerenes, explaining its presence in films and its absence in glasses.

The effect of photopolymerization and photooxidation on the PLDMR are also described and discussed. Both procedures quench the localized triplet exciton. The PLDMR of photopolymerized films, however, also reveals the existence of a triplet exciton delocalized across several molecules, possibly similar to that detected by zero-field PLDMR of a C\textsubscript{60} single crystal\cite{81}, and LESR of oxidized films.\cite{102} Thus, there are three distinct triplet excitonic states in fullerene films that are sufficiently long-lived to be observed by PLDMR.
3.1 Experimental results

3.1.1 Fullerene Glasses

The PL spectrum of C\textsubscript{60}·T/PS glass displayed in Figure 29a is relatively unstructured, with weak features at 1.58, 1.62, 1.68, 1.76 and 1.84 eV. Detailed studies of the fluorescence of C\textsubscript{60}, including the apparently dominant role of X-traps, are described elsewhere (see Chapter 2). The fluorescence of C\textsubscript{70} (Figure 29b) peaks at 1.86, 1.79 and 1.72 eV, apparently due to a 70 meV vibronic progression. The phosphorescence band of C\textsubscript{70} (Figure 29c) is much sharper and more intense with strong peaks visible at 1.533, 1.490, 1.455, 1.394, and 1.346 eV and weaker peaks at 1.31, 1.25 and 1.21 eV.

Figure 30 shows the total PLDMR of C\textsubscript{60}·T/PS and of the fluorescence and phosphorescence of C\textsubscript{70}·T/PS glasses at 20K. The powder pattern of C\textsubscript{60}·T/PS at 10K is symmetric with two peaks split by ~120G and two shoulders separated by ~230G. This pattern is characteristic of a nearly axially symmetric triplet exciton delocalized over the entire molecule, with D = 122G and E = 9G. The PLDMR of the fluorescence and phosphorescence of C\textsubscript{70}·T/PS differ sharply from one another. The fluorescence PLDMR of C\textsubscript{70}·T/PS is ~200G wide with a central peak at g = 2. The PLDMR is assigned to a triplet exciton with zfs parameters D = 100 G and E = D/3. The phosphorescence PLDMR of C\textsubscript{70}·T/PS is roughly ten times more intense than the fluorescence PLDMR and consequently dominates the total PL-detected magnetic resonance. Its lineshape is asymmetric and is sharply affected by both temperature and the microwave chopping frequency \( v_C \) (see below). We assign this resonance to a triplet exciton delocalized over the C\textsubscript{70} molecule with zfs parameters D = 62G and E = 7G. The linewidth of \(^3\text{C}_{70}\) is narrower than that of \(^3\text{C}_{60}\), consistent with the larger dimensions of the C\textsubscript{70} molecule. No half-field resonances due to the \( \Delta m_s = 2 \) transitions between triplet sublevels are detected.

The PLDMR of C\textsubscript{60}·T/PS at increasing temperatures is shown in Figure 31. As T increases, an inner pair of shoulders split by 50G develops and the powder pattern narrows. This
Figure 29. Spectra of the (a) photoluminescence of C_{60}:T/PS and of the (b) fluorescence and (c) phosphorescence of C_{70}:PS.
Figure 30. PLDMR spectra of the (a) photoluminescence of C$_{60}$:T/PS and of the (b) fluorescence and (c) phosphorescence of C$_{70}$:T/PS.
Figure 31. PLDMR spectra of ~1 mg/ml C₆₀: T/PS between 5K and 50K.
inner pair of shoulders has been interpreted by Wei and Vardeny as evidence for a second, thermally activated triplet exciton. Zero-field PADMR and pulsed ESR measurements of C60 glasses support this assessment, though the origin of the second triplet remains unclear.

The temperature dependence of the PLDMR of a C70:T/PS glass at a concentration of 0.125 mg C70 per ml Toluene differs sharply (Figure 32). Depending upon T and vC, one of two asymmetric powder patterns is seen. The first type consists of two PL-enhancing peaks split by ~120G; the low-field peak is much more intense than the high-field peak. The second type consists of a low-field enhancing peak and a high-field quenching resonance, split by ~90G. At 5K, the powder pattern is of the first type. However, as the temperature increases, a quenching resonance emerges and the high-field PL-enhancing peak vanishes. The intensity of the powder pattern rapidly drops with increasing temperature, disappearing above 80K.

Figure 33 shows the variation of the PLDMR lineshape of 0.125 mg/ml C70:T/PS at 20K as vC is varied from 10.6 to 164 Hz. At lower frequencies, the powder pattern is of the first type. As vC is increased, the high-field enhancing peak diminishes and a quenching resonance emerges. There is a sharp increase in the integrated PLDMR intensity below 40 Hz. This is consistent with a triplet lifetime τT ~ 25 ms at 20K. The effects of increasing T and vC are thus qualitatively similar.

Angerhofer et al. suggested that residual clusters may play a significant role in the excited state properties of fullerenes in solution. Figure 34 displays the PLDMR at 20K of C70:T/PS samples with concentrations of 0.125, 0.25 and 2 mg/ml as well as a sample with ~1% C70 in polystyrene (vC=500 Hz). The PL was most intense in the polystyrene glass and decreased in the T/PS glasses with increasing C70 concentration. The PLDMR of the most concentrated sample clearly shows the effects of coupling between C70 molecules.

While the effects on PLDMR lineshape due to concentration dependence appear to be limited, there appears to be a significant variation in the excited state dynamics. Figures 35 and 36
Figure 32. PLDMR spectra of 0.125 mg/ml C$_{70}$:T/PS between 5K and 40K for $v_c=26$ Hz.
Figure 33. PLDMR Spectra of 0.125 mg/ml C_{70}:T/PS at 20K for ν_c between 10 and 164 Hz
Figure 34. PLDMR Spectra of ~1% C70 in PS and C70:T/PS at concentrations of 0.125, 0.25, and 2 mg/ml with T = 20K and \( v_c = 502 \) Hz.
Figure 35. PLDMR spectra of the phosphorescence at 850 ± 35 nm of 0.25 mg/ml C$_{70}$-T/PS between 5K and 40K for $\nu_c = 26$ Hz.
Figure 36. PLDMR spectra of the phosphorescence band (850 ± 35 nm) of 0.25 mg/ml C\textsubscript{70}:TIPS at 20K for \(v_e\) between 10 and 502 Hz.
display the temperature and chopping frequency dependence of the phosphorescence PLDMR of a 1/4 mg/ml C^giT/PS sample. As observed for the 0.125 mg/ml sample, the PLDMR intensity decreases as the chopping frequency increases and rapidly decreases with increasing temperature. However, the quenching resonance is much weaker and a completely anti-symmetric lineshape is never observed. Furthermore, at 5K, the PLDMR lineshape is nearly symmetric. Comparison of the variation of the total PLDMR and that of the phosphorescence band confirmed that changes in the total PLDMR are dominated by the phosphorescence band.

A 0.125 mg/ml C^giT/PS sample used for PLDMR measurements was studied after storage for three months in an evacuated quartz tube. The total PLDMR, shown in Figure 37, is remarkably different from that originally observed. The fluorescence PLDMR is much more intense than the phosphorescence PLDMR. This could be due to the formation of fullerene clusters and/or photochemical reaction of C^qi with PS. An attempt to redissolve the sample by ultrasonic vibration enhanced the phosphorescence of the sample at the expense of the fluorescence. Additionally, the fluorescence PLDMR was sharply diminished. Rather than the asymmetric powder pattern characteristic of the freshly prepared C^giT/PS, a narrow, enhancing resonance was observed. It should be noted that no such ageing effects have been observed in C^gi glasses, even in samples similarly stored for three years.

3.1.2 Fullerene Films

Figures 38 and 39 show the full-field PLDMR spectra of C^gi films at 20K with 800 mW and C^gi at 16K with 1400 mW of microwave power. The respective PL spectra are shown in the insets and the lower half of each figure displays the localized triplet exciton pattern on a magnified scale. As for numerous π-conjugated polymers, a sharp narrow resonance is observed at g = 2, attributed to charged, spin-1/2 polarons (see below). The delocalized triplet pattern of C^gi is narrower than that of C^gi due to the larger molecule and consequent greater
Figure 37. PLDMR spectra of the (a) PL, (b) fluorescence and (c) phosphorescence of an aged 0.125 mg/ml C$_{70}$T/PS sample at 20K for $v_c = 26$ Hz and (d) of a redissolved sample.
Figure 38. Full-field triplet PLDMR spectrum of C$_{60}$ Film at 20K.
Figure 39. Full-field triplet PLDMR psectgrum of C\textsubscript{70} Film at 20K.
delocalization of the triplet. This triplet also displays shoulders separated by 37, 90, and 235 G. However, while the values of D in the films and glasses are similar, the patterns are strikingly different, reflecting a distribution of the zfs values due to inequivalent sites arising from intermolecular coupling. The spectra also exhibit a broad (~650G wide) pattern due to a localized triplet exciton (see below). In C_{60} films, the integrated intensity of the broad localized triplet pattern is comparable to that of the narrow delocalized triplet exciton. In C_{70} films, the broad (localized) pattern is relatively much weaker.

Figures 40 and 41 display the full-field (\Delta m_s = 1) PLDMR of C_{60} and C_{70} films between 16 and 300K. The temperature dependence of the triplet PLDMR of C_{60} and C_{70} films differ considerably. The rapid decrease in the intensity of the delocalized exciton PLDMR in C_{60} is not surprising, in view of the rapidly increasing rotational motion of the molecule, to the point where no powder pattern could be detected in C_{60} above 150K. In contrast, the intensity of the delocalized triplet in C_{70} is only weakly temperature dependent and it can be detected at 295K, probably due to the slower rotational dynamics. In both fullerenes, the intensity of the broad (localized triplet) pattern decays less rapidly with increasing T than the narrow (delocalized triplet) pattern.

The broad (localized triplet exciton) pattern is much more prominent in the half-field PLDMR of C_{60} and C_{70} films, displayed at various temperatures in Figures 42 and 43. This is expected, since the \Delta m_s = 2 transition probability scales roughly as (D/hv)^2 [ref 111]. As with the full-field patterns, the narrow (delocalized triplet exciton) pattern decays more rapidly with increasing temperature. There is an intriguing rise in the intensity of the half-field spectra of C_{70} between 10K and 20K, followed by a gradual decline at higher T.

The narrow (delocalized triplet) pattern was saturated with photoexcitation intensity over 8 mW (Figure 44). Its amplitude relative to the broad (localized triplet) pattern decreased sharply in C_{60} and moderately in C_{70}. This excitation power corresponds to the absorption of roughly
Figure 40. Full-field PLDMR spectrum of C\textsubscript{60} film between 16K and 96K.
Figure 41. Full-field triplet PLDMR of C$_{70}$ film between 16K and 300K.
Figure 42. Half-field triplet PLDMR spectrum of C\textsubscript{60} film between 8K and 50K.
Figure 43. Half-field triplet PLDMR spectrum of C\textsubscript{70} film between 10K and 120K.
Figure 44. Photoexcitation saturation of the half-field PLDMR of C$_{60}$ and C$_{70}$. 
10^3 photons per molecule per second and is therefore consistent with the measured triplet lifetimes.\textsuperscript{94,112} However, the localized triplet powder pattern was not saturated, possibly due to either a shorter lifetime or multiple sites on a single fullerene for these triplets. These effects were also observed in the full-field powder patterns, though not quite as striking.

The full-field PLDMR of C\textsubscript{60} films has a narrow, \textasciitilde{5.3}G wide resonance at \( g = 2.0017 \) and of C\textsubscript{70} films a \textasciitilde{3.5}G wide resonance at \( g = 2.0029 \). The resonance could be fit to the sum of two Gaussians and is assigned to enhanced recombination of charged polarons. The narrow resonance of C\textsubscript{60} as fit to the sum of two Gaussians between 16K and 48K with 800 mW of microwaves is shown in Figure 45. While there is a sharp decrease in the intensity of the signal between 16K and 48K, no broadening of the resonance is discernible. The narrow resonance of C\textsubscript{60} at 48K with 50, 160, and 800 mW of microwaves is shown in Figure 46. Remarkably, there is no detectable saturation of the resonance at available levels of microwave power. The narrow resonance of C\textsubscript{70} at 20K with 28 mW and 1400 mW is shown in Figure 47. As for C\textsubscript{60}, this resonance does not saturate even at high microwave power.

3.1.3 Photopolymerized and Photooxidized Fullerene Films

Figures 48 and 49 show the full-field PLDMR of photopolymerized and photooxidized C\textsubscript{60} and C\textsubscript{70} films, resp. Several features are worth noting. The first is the strong quenching of the broad (localized triplet exciton) pattern by UV irradiation. The intensity of the narrow (delocalized triplet exciton) pattern in both films is enhanced by photopolymerization and moderately reduced by photooxidation. The half-field powder patterns are similarly affected. There are also intriguing effects on the lineshape of the delocalized triplet exciton resonance in both fullerenes which are discussed in section 4.4 below. The powder pattern of UV-irradiated C\textsubscript{70} is unstructured, most likely due to a greater distribution of zfs parameters.

The presence of a pair of shoulders separated by 37G in the powder pattern of photopoly-
Figure 45. The narrow polaron resonance of C\textsubscript{60} between 16K and 48K.
Figure 46. Microwave power dependence of C₆₀ narrow resonance at 48K.
Figure 47. The narrow polaron resonance of C\textsubscript{70} at 16K.
Figure 48. The full-field PLDMR of pristine, photopolymerized, and photooxidized C₆₀ film.
Figure 49. The full-field PLDMR of pristine, photopolymerized, and photooxidized C$_{70}$ Film.
Figure 50. Temperature dependence of narrow shoulders in photopolymerized C\textsubscript{60}. 
merized C\textsubscript{60} (Figure 48b) is particularly striking. The temperature dependence of this narrow pattern (Figure 50), sharply differs from either previously observed exciton. The 37G splitting matches a faintly observed pattern in pristine C\textsubscript{60} films below 20K as well as C\textsubscript{70} films (Figures 38 and 39). These shoulders may indicate the presence of a third triplet exciton, a state delocalized across several molecules and described in other studies\textsuperscript{81,102}. While no corresponding resonance is seen in the half-field powder pattern, it could easily be masked by the much more intense resonance of the triplet exciton delocalized over one molecule.

An intriguing phenomenon was observed while preparing photopolymerized and photo-oxidized samples. The sample to be photopolymerized was sealed in vacuum while that to be photooxidized was left in air. When the samples were irradiated with the focused, IR-filtered output of a 100W Mercury lamp, a purple fluorescence was observed. After one hour of illumination, the PL of the oxidized sample was completely quenched while the protected sample continued to fluoresce. This phenomenon should be studied in the future.

3.2 Discussion

3.2.1 The PLDMR of fullerene glasses

In order to interpret the results on the fullerene glasses, one must examine the nature of the processes which may be responsible for the magnetic resonance signals. We suggest that the fluorescence PLDMR seen in both C\textsubscript{60}:T/PS and C\textsubscript{70}:T/PS is due to enhanced non-radiative decay of triplets to the ground state, so-called "ground state recovery.\textsuperscript{113} The enhanced non-radiative decay increases the ground state population, resulting in enhanced absorption from the ground state, and hence greater fluorescence. Thus, a positive PLDMR is seen in the fluorescence band. The positive (negative) phosphorescence PLDMR can only be due to enhanced (quenched) radiative decay of excited triplets to the ground state.

The lineshape of the phosphorescence PLDMR of C\textsubscript{70}:T/PS is intriguing. As isolated mol-
ecules exclude triplet-triplet fusion, the resonance must be due to direct decay to the ground state. In previous PLDMR studies of π-conjugated polymers and C_{60}, an enhancing triplet resonance symmetric about g = 2 was invariably observed. As decay from the m_s = 0 triplet sublevel to the ground state is generally more rapid than from m_s = +1 or -1, symmetric patterns entail that the population n_0 of the m_s = 0 sublevel be less than either that of n_{-1} or n_{+1}, and that n_{+1} - n_0 = n_{-1} - n_0. However, the PLDMR of C_{70} glasses is indicative of far different triplet state sublevel populations and dynamics.

The nature of the PLDMR is determined by the spin-lattice relaxation rate 1/T_1, the radiative triplet decay rate 1/\tau_R, and the total decay rate 1/\tau_T. At very low temperatures, 1/T_1 is slower than the triplet decay rate, resulting in an unthermalized spin population with n_0 depopulated relative to the other sublevels, as described in the forgoing paragraph. However, as the temperature increases 1/T_1 probably increases rapidly due to spin-phonon coupling and becomes greater than 1/\tau_T. This results in a Boltzmann distribution of triplet spin population; n_{+1}/n_0 = e^{4\beta / k T}, and n_{+1}/n_0 = e^{4\beta / k T} is established. Hence, n_{+1} < n_0 < n_{-1}, so that at the higher field for resonance, n_{+1} is enhanced at the expense of n_0 to give a quenching resonance, and at the lower field for resonance, n_0 is enhanced at the expense of n_{-1}, to give an enhancing resonance. The overall triplet pattern is consequently roughly antisymmetric. As the thermalized spin polarization now rapidly increases with temperature, the PLDMR weakens with increasing T. At 20K, the PLDMR intensity doubles as the chopping frequency becomes comparable to the triplet lifetime or 1/T_1 (Figure 33). The changes in intensity and lineshape occur at 10 < v_c < 40 Hz, yielding a triplet lifetime of ~25 ms at 10K, comparable to the value reported by Wasieliewski et al.

Further evidence for these distinct spin polarization-induced processes is seen in the decay of the integrated PLDMR intensity as the temperature increases. The integrated intensity of the PLDMR of C_{60}:T/PS decays exponentially with increasing temperature, but that of C_{70} decays as the sum of two exponentials (Figure 51). This crossover is matched by changes in the
Figure 51. Temperature-dependence of the integrated PLDMR of C\textsubscript{60}:T/PS and C\textsubscript{70}:T/PS lineshape. The lineshape changes from an asymmetric pattern with two enhancing peaks at low T to a totally antisymmetric pattern with nearly equally intense enhancing and quenching components at higher T.

Hence, two physical processes must be responsible for spin polarization in C\textsubscript{70}. The low temperature behavior is dominated by the long triplet lifetime $\tau_T$ and even longer $T_1$, while the high temperature behavior is governed by spin lattice relaxation. To estimate the overall triplet lifetime $\tau_T$, note that the PLDMR intensity doubles as the chopping frequency becomes comparable to $1/\tau_T$. The greatest changes in intensity and lineshape occur for $10<v_C<40$ Hz (Figure 32), yielding $\tau_T=25$ ms at 10K, consistent with the previously reported values of 50 ms at 5K and 2.2 ms at 295K.\textsuperscript{73,94} A dip in the PLDMR intensity at $\sim80$ Hz was observed in both
0.125 and 0.25 mg/ml \( C_{70} \) T/PS samples. The origin of this phenomenon is unclear.

Intriguing effects on the PLDMR lineshape have been observed for varied concentrations as well as ageing effects. The phosphorescence and PLDMR intensity are quenched by increasing concentration, presumably due to increased coupling between fullerenes at higher concentrations. Samples with a concentration of 0.125 and 0.25 mg/ml showed similar variation in the PLDMR intensity due to changes in \( T \) and \( \gamma_C \), but differing lineshape variations. This effect is attributed to host-guest coupling. The PLDMR of the aged sample can be explained as due to clustering over time. However, the attempt to redissolve the sample with ultrasonic vibration resulted in an enhancement of the phosphorescence and quenching of the fluorescence. This is consistent with breaking up fullerene clusters which have developed over time. However, the resulting PLDMR lineshape is unlike any observed previously in \( C_{60} \) or \( C_{70} \). This is perhaps due to a chemical interaction between fullerenes and the host T/PS glass.

### 3.2.2 The polaron resonance in films

A narrow enhancing PLDMR resonance is detected at \( g = 2.0017 \) in \( C_{60} \) and \( g = 2.0029 \) in \( C_{70} \) films, but not in the glasses. These have been fit to the sum of two Gaussians and are attributed to enhanced recombination of positively- and negatively-charged polarons. Isolated excited molecules quickly decay to an excitonic state, and thus no polarons should be detectable in the glasses. However, coupling between molecules in a film apparently enables the charges to separate, dramatically increasing their lifetimes. The narrow polaron resonance is more intense in \( C_{70} \) than in \( C_{60} \), probably due to longer lifetimes resulting in a greater spin polarization.

The narrow polaron resonances are strikingly reminiscent of those observed in \( \pi \)-conjugated polymers.\(^{105-6}\) However, the lineshapes are far narrower than those observed in any \( \pi \)-conjugated polymer investigated to date (see Chapter 4). The delocalization of the polaron along a belt about the fullerene molecule could explain the narrowness of the polaron reso-
Another hypothesis which might explain the narrowness of the polaron resonance is the relative lack of disorder present in fullerene films. The narrow polaron resonance of a conjugated polymer with an apparent greater density of structural defects (PPA) was significantly broader than that of more ordered PPV films. The PLDMR is quenched at relatively low laser excitations powers (~ 5 mW), consistent with lifetimes on the order of milliseconds. However, no microwave saturation of the resonance lineshape or intensity was observed.

There are three possible mechanisms which explain their presence: (i) fusion of polarons to singlet excitons which decay radiatively. However, theoretical studies of C_{60} predict that the polaron energy levels are deep in the gap, so that the recombination of two charged polarons does not generate sufficient energy to form a singlet exciton. Experimental evidence for this model is found in a photoconductivity study by J. Mort et al., who detected a weak absorption band at 1.5 eV. (ii) Nonradiative polaron recombination. As polarons are probably non-radiative singlet quenching centers, their enhanced removal at the field for resonance by recombination enhances the radiative decay rate of the singlets. This second scenario is consistent with the reported quenching of the fluorescence of C_{70} by long-range intermolecular electron transfer by Williams and Verhoeven. (iii) Ground state recovery, as discussed above for triplets. We thus conclude that the narrow enhancing PLDMR seen is due to the removal of charged polarons which may quench the PL and/or increase the ground state population.

3.2.3 The triplet exciton resonances

The half-field powder pattern detected in fullerene films is clearly due to the Δm_s = 2 transition of two distinct triplet excitons. The intensity of the narrow (delocalized triplet), higher-field resonance decreases much more rapidly with increasing T than that of the broad (localized triplet), lower-field resonance. Unlike the broad resonance mentioned above, the narrow resonance saturates at relatively low laser intensities. The ZFS parameters of the narrow resonance are also much smaller than the broad resonance. These factors unambiguously assign the
narrow resonance to the delocalized triplet and the broad resonance to the localized triplet.

The clear detection of half-field resonances in the films, in contrast to their absence from the glasses, bears examination. Their absence from the glasses implies that the radiative transition probabilities from the \( m_s = +1 \) and \( m_s = -1 \) sublevels of isolated molecules are roughly equal. Transitions between two similarly radiative levels will not enhance one channel at the cost of another. Thus, no half-field PLDMR is seen in fullerene glasses. Enhancement of triplet-triplet fusion to singlets is a well known mechanism in molecular crystals such as anthracene,\(^{112-13}\) which may explain the presence of this resonance in films and its absence in glasses. Previous work on the half-field PLDMR of \( \pi \)-conjugated polymers demonstrated that its spectral dependence is similar to the PL, as this mechanism should entail.

The lineshape of the delocalized triplet exciton power patterns of films were distorted due to intermolecular coupling. The PLDMR lineshape of \( ^3\text{C}_{60}:\text{T/PS} \) at 5K closely resembles the calculated triplet powder of an axially symmetric (\( E_l = 0 \)) triplet exciton, whereas the PLDMR lineshape of a \( \text{C}_{60} \) film showed far less structure. The pyramidal lineshape of the PLDMR of \( \text{C}_{70} \) films differs from normal triplet patterns. This could be explained by a broad distribution of the zfs parameters, perhaps due to the reduced symmetry of the \( \text{C}_{70} \) molecule as well as the different crystal structure. These factors result in a number of inequivalent sites on the molecule.

3.2.4 The PLDMR of photopolymerized and photooxidized films

Several features of the PLDMR spectra of the photopolymerized and photooxidized fullerene films are noteworthy:

(i) The broad (localized triplet) powder pattern is quenched by both processes. The ~600G wide pattern, absent from the glasses, was previously attributed to a localized triplet exciton, believed to reside at sites distorted by intermolecular coupling, probably between adjacent molecules.\(^{27}\) Both photooxidation and photopolymerization affect these sites by creating bonds
which eliminate the \( \pi \)-wavefunction in the intermolecular region. Therefore, it is not surprising that this exciton is quenched by UV exposure.

(ii) The intensity of both the narrow polaron resonance and the narrow (delocalized triplet) powder pattern is enhanced by photopolymerization. This is possibly due to increased coupling between molecules, which might enhance exciton mobility and charge separation. The reason behind the enhanced triplet resonance is less clear. Perhaps greater exciton mobility leads to a higher probability for triplets to meet and fuse.

(iii) Most interesting is a new pair of shoulders separated by 37G which develop in the PLDMR of photopolymerized \( C_{60} \). These shoulders show a sharply different temperature dependence than the other features, ruling out association with those triplets. The narrow width suggests the presence of a third triplet delocalized over several molecules and stabilized by photopolymerization. A triplet exciton delocalized over two \( C_{60} \) molecules has actually been detected elsewhere.\(^{81-102} \) It is thus apparent that there are three, distinct triplet excitons in fullerene films and crystals: an exciton delocalized over several molecules, another delocalized over a single molecule (\( ^2C_{60} \) and \( ^3C_{70} \)), and a third localized on a hexagon or pentagon, apparently adjacent to a neighboring molecule.

3.3 Summary

The PLDMR of \( C_{60} \) and \( C_{70} \) films and glasses has been described and discussed. The PLDMR lineshape of \( C_{70} \) T/PS strikingly differs from that of \( C_{60} \) T/PS due to much longer triplet lifetimes. Surprisingly, two triplet excitons have been detected in glasses of both fullerenes. The PLDMR of films indicates that the delocalized triplet is distorted by intermolecular interactions and shows a half-field resonance tentatively attributed to triplet-triplet fusion. In addition, a weak broad pattern is assigned to a triplet exciton localized on a pentagon or hexagon face adjacent to a neighboring molecule. A narrow enhancing line at \( g = 2.0017 \) in \( C_{60} \) and
g = 2.0029 in C_{70} is observed, which results from recombination of relatively long-lived charged polarons. The effects of UV exposure in vacuum (photopolymerization) and open to atmosphere (photooxidation) on the PLDMR have been examined. Photopolymerization enhances the intensity of the delocalized triplet, whereas both processes quench the localized triplet. Results on photopolymerized C_{60} also reveal the presence of a third triplet exciton apparently delocalized over several molecules.
CHAPTER 4. THE PHOTOLUMINESCENCE-DETECTED MAGNETIC RESONANCE OF π-CONJUGATED POLYMERS

A number of π-conjugated polymer systems are studied in this work. The PL and PLDMR of fullerene-doped poly(dihexoxy)p-phenylenevinylene (DHO-PPV), poly(3dodecyl)thiophene (P3DT), and poly(dibutoxy)p-phenyleneacetylene (DBO-PPA) are described in Section 4.1. The PLDMR of unsubstituted PPV is compared and contrasted with that of cyano-substituted PPV in Section 4.2. The PLDMR of the novel block copolymer composed of trimer precursors of DMO-PPV linked with nonconjugated segments is described in Section 4.3. The results are discussed and summarized in Section 4.4.

Previous PLDMR studies of these and similar polymers all exhibited three distinct features: (i) A narrow PL-enhancing polaron resonance, attributed to magnetic resonance enhancement of generation of the lowest 1B_u singlet exciton by polaron fusion. (ii) Broad full- (at g = 2) and (iii) half-field (at g = 4) triplet exciton powder patterns, due to Δm_s = 1 and Δm_s = 2 transitions among the triplet sublevels. These have been attributed to magnetic resonance enhancement of singlet exciton generation via triplet-triplet fusion.

The PL and PLDMR spectra of the PPAs indicated that these materials are considerably more disordered than the poly(3-alkylthiophenes) (P3ATs), which were less ordered than the PPVs. The results of this work lead to a reexamination of the dynamics of the polarons and 1B_u singlet excitons. As polarons are generally recognized to be nonradiative 1B_u quenching sites, it is suggested that the narrow polaron resonance is due to magnetic resonance enhancement of nonradiative low-energy polaron recombination. This eliminates their contribution to such 1B_u quenching processes. In addition, the results are also consistent with suggestions that fission of photogenerated 1B_u singlet excitons to polarons and intersystem crossing to the low-lying
triplet excitons is induced by structural defects. Since the electroluminescence (EL) of the corresponding light-emitting diodes is clearly due to the fusion of polarons to \(^1\text{B}_u\) excitons, which yield an EL spectrum similar to the PL, the revised scenario then implies that the energy levels of the polarons are distributed over a significant range.

4.1 PL and PLDMR of Fullerene-doped \(\pi\)-Conjugated Polymers

The PLDMR of several fullerene-doped \(\pi\)-conjugated polymers is described and discussed. The following polymers were studied: 2,5-dihexoxy poly(p-phenylenevinylene) (DHO-PPV), poly(3-dodecylthiophene) (P3DT), and 2,5-dibutoxy poly(p-phenylene acetylene) (DBO-PPA). DHO-PPV was doped with both \(C_{60}\) and \(C_{70}\) in order to compare the differences in doping with these fullerenes. Both the polymer and fullerene were dissolved in toluene. \(C_{60}\):DHO-PPV and \(C_{60}\):P3DT samples were prepared by spin-casting the solution onto a glass slide. The film was then peeled off the slide and sealed in an evacuated quartz tube. \(C_{70}\):DHO-PPV and \(C_{60}\):P3DT samples were prepared by degassing the solution in a quartz tube and then evaporating the film onto the inner surface of the tube before sealing in the evacuated tube.

The PL spectra of \(C_{60}\) and \(C_{70}\)-doped DHO-PPV, P3DT, and DBO-PPA at 0, 1, and 10 mol\% are shown in Figures 52 through 55, resp. The PL quantum yield \(\eta\) vs the fullerene concentration are shown as well. The spectra are independent of the dopant content, but \(\eta\) sharply decreases with content, as previously observed. It is noteworthy that \(C_{60}\) quenches the emission more efficiently than \(C_{70}\), probably due to a higher doping efficiency.

The polaron resonances of \(C_{60}\):DHO-PPV, \(C_{70}\):DHO-PPV, \(C_{60}\):P3DT, and \(C_{60}\):DBO-PPA at 20K and with 40 mW of microwave power is shown in Figures 56 through 59. The weakness of the resonance in undoped DHO-PPV, where \(\Delta I/I = 6 \times 10^{-6}\), is striking. Equally striking is the observation that in the lightly doped 0.1 mol\% \(C_{60}\):DHO-PPV, \(\Delta I/I = 1.9 \times 10^{-4}\), about 30 times more intense. At higher doping levels, it decreases with \(C_{60}\) content, to \(4 \times 10^{-5}\)
Figure 52. Uncorrected PL Spectra of PPV at 295K doped with 0, 0.1, 1 and 10 mol% C_{60}. 

Figure 53. Uncorrected PL Spectra of PPV at 295K doped with 0, 0.1, and 1.0 mol% C_{70}. 
Figure 54. Uncorrected PL Spectra of P3DT at 295K doped with 0, 0.1, 1 and 10 mol% C$_{60}$.

Figure 55. Uncorrected PL Spectra of PPA at 295K doped with 0, 0.1, and 1.0 mol% C$_{70}$. 
Figure 56. The narrow resonance of C₆₀-doped DHO-PPV at various doping levels.
Figure 57. The narrow resonance of C$_{70}$-doped DHO-PPV at various doping levels.
Figure 58. The narrow resonance of C$_{60}$-doped P3DT at various doping levels.
Figure 59. Narrow resonance of C\textsubscript{60}-doped DBO-PPA at various doping levels.
However, the intensity of this resonance increases at higher doping, to $-3.5 \times 10^{-4}$ at 1.0 mol%. The lineshape of the narrow resonance appears to be largely unaffected by doping. In C$_{60}$:P3DT and C$_{60}$:DBO-PPA, the polaron resonance is initially strong ($\Delta I/I \sim 3.6 \times 10^{-4}$ and $\sim 1.2 \times 10^{-4}$, resp.) and moderately intensifies with initial (0.1 mol%) doping. Increased doping quenches the resonance, similar to C$_{60}$:DHO-PPV. The lineshapes of P3DT and DBO-PPA are visibly altered by doping. The linewidth of the polaron resonance of DBO-PPA narrows upon doping, from $\sim 16$G in the undoped material to $< 9$G at all levels of doping. The asymmetry of the polaron resonance of P3DT is notably reduced by doping.

The triplet PLDMR of C$_{60}$:DHO-PPV, C$_{70}$:DHO-PPV, C$_{60}$:P3DT, and C$_{60}$:DBO-PPA at 20K and 800 mW of microwave power is shown in Figures 60-63. Most striking is the contrast between the PLDMR of undoped and fullerene-doped DHO-PPV. There is no detectable triplet resonance in undoped DHO-PPV. However, upon 0.1 mol% doping by either C$_{60}$ or C$_{70}$, a triplet exciton similar to that previously seen in previously studied DHO-PPV samples develops. This resonance is quenched by a factor of 30 as C$_{60}$ doping increases from 0.1 mol% to 1 mol%, becoming nearly unobservable at 10 mol% doping. However, sharply different behavior is seen for C$_{70}$ doping (Figure 61). The resonance is enhanced from $-2.5 \times 10^{-5}$ at 0.1 mol% to $-3.4 \times 10^{-5}$ at 1.0 mol%. These differences are attributed to differences in doping efficiency. Similar changes in the half-field resonance of the triplets are seen (Figures 64-65).

The triplet powder pattern (Figure 62) of undoped P3DT is structured and is rapidly quenched by doping, becoming unobservable above 1 mol%. Most intriguing is the complete absence of structure in the triplet powder pattern at 0.5 mol% doping. The structure of the triplet resonance of 0.5 mol% C$_{60}$:P3DT at 20K is strikingly similar to that seen at 295K in undoped polythiophene. The $\sim 1$ kG wide resonance seen in undoped PPA (Figure 63) is barely discernable at all doping levels. As no corresponding half-field resonance was detected,
Figure 60. Full-field triplet powder pattern of C_{60}-doped DHO-PPV at various doping levels.
Figure 61. Full-field triplet powder pattern of C\textsubscript{70}-doped DHO-PPV at various doping levels.
Figure 62. Full-field triplet powder pattern of C\textsubscript{60}-doped P3DT
Figure 63. Full-field triplet powder pattern of C\textsubscript{60}-doped DBO-PPA.
Half-field PLDMR of C60:PPV

T=20K  0.1 mol%  

0  1x10^{-5}  2x10^{-5}  3x10^{-5}  4x10^{-5}  

1.0 mol%  

0  2x10^{-7}  4x10^{-7}  6x10^{-7}  

10 mol%  

0  4x10^{-7}  8x10^{-7}  

Magnetic Field (kG)  

1.62  1.63  1.64  1.65  1.66  1.67  

Figure 64. Half-field triplet powder pattern of C_{60}-doped DHO-PPV.
Figure 65. Half-field triplet powder pattern of C$_{70}$-doped DHO-PPV.
the ~200G wide resonance is apparently the base of the polaron resonance, broadened by the high microwave powers used to detect triplets.

The dependence of the polaron resonance on temperature was examined for all three polymers at 1% mol. C₆₀. While the polaron resonance intensity of P3DT and DBO-PPA declines with increasing temperature (Figures 66-67), that of DHO-PPV displays a different temperature dependence (Figure 68). The narrow resonance is quite weak at 5K (ΔI/I = 6 × 10⁻⁹) and increases to ~1.8 × 10⁻⁴ at 20K before decreasing to ~1.2 × 10⁻⁴ at 80K. C₆₀-doped DBO-PPA was examined for the effects of microwave saturation (Figure 69). Below saturation, the PLDMR intensity should increase as the square root of the microwave power.

The experimentally measured integrated and peak intensities are compared with those expected for a nonsaturated resonance. The scaled values were calculated by the following formula:

\[ I_{\text{calculated}}(800 \text{ mW}) = I_{\text{measured}}(X \text{ mW}) \times \sqrt{\frac{800}{X}} \]

If the resonance is not saturated, the calculated resonance intensity should equal the measured intensity at 800 mW. The integrated intensity only modestly departs from square-root dependence (about 13% below that expected from the measurement performed at 40 mW), but the peak intensity substantially departs from this dependence (roughly one-third below that expected in the absence of saturation). Thus, the resonance saturates as the microwave power increases above 40 mW.

4.2 The PLDMR of PPV and Cyano-substituted PPV

Recently, fabrication of bilayer electroluminescent devices with efficiencies of up to 4% has been reported. This motivated both ELDMR studies of these devices as well as PLMDR of
Figure 66. T-dependence of 1% C_60:DH0-PPV narrow resonance.

Figure 67. T-dependence of 1% C_60:P3DT narrow resonance.
Figure 68. T-dependence of 1\% C_{60}:DBO-PPA narrow resonance.

Figure 69. Narrow resonance of 1\% C_{60}:PPA with 10 to 800 mW of \textit{\textmu}waves.
the polymers. The PLDMR of unsubstituted PPV is contrasted with that of cyano-substituted PPV (CN-PPV). No triplet exciton is observed in the unsubstituted material, only a narrow ~21G wide resonance. However, a ~7G wide narrow resonance as well as an ~800G wide triplet powder pattern are detected in CN-PPV. As both polymers are insoluble, samples were prepared by spin-casting a polymer precursor onto a quartz substrate before polymerization. The substrate was cut and sealed in an evacuated quartz tube for these measurements.

The narrow resonance of unsubstituted PPV between 10K and 295K is shown in Figures 70-71. The resonance is relatively broad and only modestly quenched by increasing temperature. No triplet exciton resonance was observed at either full-field or half-field. The PLDMR intensity varies only between ~4.7 x 10^{-4} at 20K and ~3 x 10^{-4} at 200K before sharply dropping to ~2.6 x 10^{-5} at 295K. The resonance narrows as T increases, from a half-width of 24G at 10K to 16G at 300K. The narrowing of the polaron resonance as well as the sharp decline of the PLDMR intensity above 200K is consistent with a thermally activated process.

The narrow resonance of CN-PPV, fit to the sum of two Gaussians between 10 and 40K is shown in Figure 72 and between 80 and 300K in Figure 73. The resonance intensity steadily decreases with increasing temperature, from ΔI/I = 1.6 x 10^{-4} at 10K to ΔI/I = 8 x 10^{-6} at 300K. Furthermore, the half-width of the resonance is only ~7 G at 10K, narrower than any previously observed in conjugated polymers. The resonance broadens at higher T, up to a half-width of ~10G at 295K. Thermally activated hopping of polarons trapped at CN sites should broaden the resonance, as conjugation defects result in a significantly broader resonance.

Most notable is the detection of a triplet exciton powder pattern in the cyano-substituted PPV, shown in Figure 74. As the polaron resonance is quite narrow, the location of inner shoulders of the powder pattern was not obscured. This permitted determination of the zfs parameters of this triplet; |D| = 460G, |E| = 110G.
Figure 70. Narrow resonance of PPV between 10K and 80K.
Figure 71. Narrow resonance of PPV between 120K and 300K.
Figure 72. Narrow resonance of CN-PPV between 10K and 40K.
Figure 73. Narrow resonance of CN-PPV between 80K and 300K.
Figure 74. Full-field triplet powder pattern of CN-PPV at 20K and 800 mW of μwaves.

4.3 The PLDMR of π-Conjugated Block Copolymers

The PLDMR of a novel conjugated material, a soft-block copolymer consisting of 2,5-dimethoxy PPV trimers linked by nonconjugated polyethylene segments is described. While no PLDMR has been observed in polymer trimers, the block copolymer exhibits both a ~25G wide narrow resonance as well as a ~1 kG wide, structureless triplet powder pattern. The juncture between the conjugated and nonconjugated segments breaks the conjugation. This site stabilizes both polarons and triplet excitons. All results presented in this study are consistent with a picture where polarons and triplet excitons serve to quench the photoluminescence and
are stabilized by either conjugation defects or heteroatoms interacting with the \( \pi \)-band.

The narrow resonance of a 2,5-dimethoxy PPV soft-block copolymer film (BCP-PPV) is shown in Figure 75. The resonance is quite broad, roughly ~25G, and does not vary in linewidth between 10K and 80K. Furthermore, only modest changes in intensity are seen, with resonance intensity \( \Delta I/I = 1.2 \times 10^{-5} \) between 10K and 40K and declining to \( \sim 1 \times 10^{-5} \) at 80K. Further studies are obviously warranted, though the initial results are similar to that of high-quality PPV films studied in Section 4.2. The triplet powder pattern at 20K, shown in Figure 76, is ~900G wide. The powder pattern appears to be more structured than that detected in PPV. Samples of soft-block copolymers with varied conjugated segments are underway.

4.4 Discussion and Summary

Advances made in the preparation of PPV must be considered. The samples used in this study show both a higher PL quantum yield and improved solubility with respect to PPV samples previously studied.\(^5\) It appears that a weak PLDMR in PPV is associated with a high degree of order and a low density of defects. This is consistent with a picture which suggested that polarons and triplet excitons are generated at defect sites and serve as non-radiative (PL-quenching) centers which compete with PL emission.\(^4\)

The following model is proposed. Charged polarons and triplet excitons quench the PL and are stabilized by conformational defects. These conformational defects are introduced by doping by fullerenes, which results in longer lifetimes and higher populations of these PL-quenching excitations. The PLDMR detected in all studies of conjugated polymers is due to enhanced decay of these excitations to the ground state. The PLDMR of doped PPV is much stronger than the undoped as the polaron and triplet exciton populations are much higher. This model has profound implications for applications of conjugated polymers.

Two mechanisms are at work in the quenching of the PLDMR as photoinduced doping in-
Figure 75. Narrow resonance of PPV Block Copolymer between 10K and 80K.
creases. The triplet PLDMR of DHO-PPV and P3DT are strongly quenched by 1 mol% C₆₀ doping for P3DT and 0.1 mol% doping for DBO-PPA. Charge transfer from the polymer chain to C₆₀ competes with formation of triplet excitons. Singlet excitons which might have converted to triplets via intersystem crossing instead dissociate to p⁺ and C₆₀⁻. The rapid decrease in the PL lifetime is consistent with charge transfer on a picosecond time scale.

The narrow polaron resonance is only modestly quenched in PPV at 1 mol% doping by C₆₀, but is sharply quenched at 10 mol% doping. While this is also due to photoinduced doping, a different physical mechanism is at work. At higher doping levels, there should be a significant charge imbalance in the doped system with negative charge residing on C₆₀ and an excess of positive polarons residing on the polymer. This charge imbalance results in
conditions favorable for formation of PL-quenching, positively-charged bipolarons. As the formation of bipolarons is a spin-dependent process, this process can be detected by PLDMR. Previous work on the electroluminescence- and conductivity-detected magnetic resonance of PPV light emitting diodes\(^1\) indicated the lineshape of the PL-quenching bipolarons matches that of the PL-enhancing fusion of polarons to singlet excitons. Thus, rather than detecting a separate quenching resonance, the PLDMR intensity is quenched at high doping levels. The PLDMR is intense at low doping levels as non-radiative PL-quenching polarons are being removed from the system. The PLDMR is detected at higher C\(_{60}\) concentrations, but is reduced in intensity relative to lower doping concentrations since polarons on the polymer chains are fusing to long-lived PL-quenching bipolarons.

This scenario also explains the effects on the PL and PLDMR of DHO-PPV by C\(_{70}\). The PL is quenched and the PLDMR enhanced upon initial doping by C\(_{70}\) due to conformational defects created by doping. However, the PLDMR is not enhanced by increased doping. We have interpreted the quenching of the PLDMR as due to photoinduced charge transfer from the polymer chain to C\(_{60}\). The absence of any quenching by C\(_{70}\) doping leads to the conclusion that C\(_{70}\) is an inefficient dopant of \(\pi\)-conjugated polymers. This conclusion is consistent with photoconductivity measurements performed by Yoshino et al.\(^{10}\) which indicated that a strong increase in PC is seen in C\(_{60}\)-P3AT, but not C\(_{70}\)-P3AT.

The nature of the PLDMR in undoped DBO-PPA and P3DT is quite different from that of undoped DHO-PPV. The narrow PLDMR of DBO-PPA is much stronger and broader than that of DHO-PPV. Previous PLDMR of DBO-PPA\(^{11}\) indicated that this is a disordered material, as shown by its relatively unstructured PL and photoinduced absorption (PA) as well as its large Stokes shift. Additionally, the triplet resonance is broader than that of PPV and completely unstructured. It is not surprising that the polaron resonance of DBO-PPA is only modestly enhanced by 0.1 mol\% C\(_{60}\) doping. However, the triplet exciton resonance is completely
quenched and the polaron resonance is visibly narrowed at only 0.1 mol% doping. This suggests that photoinduced charge transfer from DBO-PPA onto C₆₀ is rapid and efficient.

The triplet PLDMR of undoped P3DT is strong, but structured, which seems to contradict the assertion that a strong PLDMR is associated with disorder. However, contrary to original suggestions that the sulfur heteroatom would not significantly interact with the π-system, this heteroatom could serve as a trapping site for polarons and triplet excitons, resulting in a strong PLDMR. The results comparing the PLDMR of unsubstituted and cyano-substituted PPV used for the fabrication of light-emitting diodes support this assessment. No triplet powder pattern could be detected in the PLDMR of unsubstituted PPV and the polaron resonance was quite broad. The polaron resonance of CN-PPV was much sharper and a triplet powder pattern more structured than that previously seen in PPV was clearly detected.

However, the effects of increased disorder are clearly seen in the triplet PLDMR of 0.5 mol% C₆₀-doped P3DT. The PLDMR intensity is moderately quenched from ΔI/I = 1.5 × 10⁻⁵ for undoped to ~7 × 10⁻⁶ at 0.5 mol% C₆₀. Most striking is the nearly complete loss of structure in doped P3DT. The lineshape detected is virtually identical to that detected in undoped P3HT at 300K. The low temperature pattern of P3AT was previously suspected to result from triplets localized on thiophene rings. As the temperature increases, the mobility of the triplets rapidly increases, resulting in a more disordered powder pattern due to conformational defects.

The studies presented in this work require a reexamination of the narrow resonance lineshape. In materials where conformational defects which break the π-conjugation of the system stabilize polarons, the narrow resonance is broad (15 to 25G) and both weakens and narrows with increasing temperature. These materials would include PPV, PPA, and the soft-block copolymer of PPV. In materials where a heteroatom interacts with the system, such as CN-PPV and P3DT, the triplet powder pattern is structured. The narrow resonance of CN-PPV is
The narrow resonance of P3DT was asymmetric with broad and narrow components originally attributed to breaking of charge conjugation symmetry. This study suggests an alternative explanation. The narrow component of the polaron resonance of P3DT is due to polarons trapped at heteroatoms and the broad component is due to conformational defects.

The following conclusions are reached: (i) Polarons & triplet excitons quench the PL and are stabilized by conformational defects and traps due to heteroatoms. (ii) Enhancement of the PLDMR of DHO-PPV by doping with 0.1 mol% C₆₀ or C₇₀ is due to higher populations of charged polarons and triplet excitons stabilized by conformational defects introduced by doping-induced defects. A PL-enhancing PLDMR is detected due to removal of PL-quenching resonances (and possibly ground state recovery). (iii) The triplet PLDMR is quenched at higher doping concentrations due to charge transfer which competes with formation of triplets. (iv) The polarons resonance is quenched at high (>1 mol%) doping levels due to fusion of polarons to both ground state and bp⁺⁺. (v) A structured triplet powder pattern is due to excitons trapped by heteroatoms. (vi) A broad (>15G) polaron resonance at low T is due to polarons stabilized by conjugation defects while a narrow polaron resonance. This resonance narrows as T increases is due to greater delocalization of charged excitations. (vii) A narrow polarons resonance (<10G) at low T is due to polarons trapped by heteroatoms. This resonance broadens as T increases due to effects of disorder on the formerly trapped excitations.
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ACKNOWLEDGEMENTS

I would like to thank the following individuals for their assistance:

Joseph Shinar, for many years of advice and encouragement.
Leland Swanson and Jonathan Partee for assistance and instruction.
Larry Jones, John Engel, and Tom Barton for preparation and purification of C\textsubscript{60}.
Ye-Wei Ding, Tom Barton, Katsumi Yoshino, Fred Wudl, Neil Greenham, Donal Bradley,
and Frank Karasz for preparation of \(\pi\)-conjugated polymer samples studied in this work.
Xing Wei and Valy Vardeny for useful discussions on both fullerene and \(\pi\)-conjugated polymer photophysics.
P. Canfield, S. Zollner, R. Höek and S. Katt for useful discussions.