Optically detected magnetic resonance studies on small $\pi$-conjugated molecules

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Optically detected magnetic resonance studies on small $\pi$-conjugated molecules

by

Brian Leigh Uhlhorn

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Condensed Matter Physics

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DEDICATION

To my mother and father. Their support and patience was critical. They listened to all of my worries and the difficulties that continually presented themselves. They would often remind me why I started this journey and of all the possible directions it could take me. They believed in my abilities, talent, and potential. Without their presence, the darkness would have overwhelmed me.

To the future.

“Ever Forward”
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ACKNOWLEDGEMENTS

Thanks to Christian Kloc at Lucent for providing us with rubrene crystals.

Thanks to Dr. Gary Tuttle and Dr. Wei Lueng for the use of their Olympus microscope and its attached digital camera.

Thanks to Dr. David Johnston, Dr. Lance Miller, and Jullienne Hill for the use of their equipment and help with x-ray diffraction measurements.

This work was performed at Ames Laboratory under Contract No. W-7405-Eng-82 with the U.S. Department of Energy. The United States government has assigned the DOE Report number IS-T 1956 to this thesis.
INTRODUCTION TO \(\pi\)-CONJUGATED MATERIALS

Over the past half-century, the modern world has been more and more influenced by polymers and organic materials. Conventional structural materials such as wood, steel, and ceramics find themselves being replaced by organic materials due to their ease of production, cost, light weight, and high strength. Because of these advantages, it is not surprising that organic materials are being introduced into the world of electronics. In 1977, a study on doped polyacetylene (CH)_x, an organic semiconductor, showed that \(\pi\)-conjugated polymers could be conducting [1]. Organic semiconductors have many properties that make them an attractive alternate to traditional semiconductors such as flexibility, solubility, low cost, and ease of fabrication. There is intense interest in using these materials for applications such as thin film transistors, photovoltaic devices, organic light-emitting devices (OLEDs), and lasers [2-16]. Despite the many advantages, the drawbacks to these materials include long term stability, efficiency, and a lack of a complete explanation of the processes involved. However, some OLEDs have reached the performance level in stability, brightness, and lifetime required by industry for commercialization [17, 18].

A lot of work has gone into developing the understanding of the properties of organic materials, especially in the area of LEDs. The theoretical model of conventional semiconductors is not applicable when dealing with organic materials. Traditional semiconductors are a rigid lattice of atoms and are modeled with conduction and valence bands. Because of the difference in structure, organic molecules use a different scheme involving molecular orbitals which is more applicable than the band structure of tradi-
tional semiconductors. For organic molecules, the band model must be modified or in other cases, abandoned for the molecular orbital model.

1.1 Introduction to $\pi$-Conjugation

Organic materials' ability to conduct basically relies on the $\pi$-conjugation of the molecule. In general, the $\pi$-conjugation delocalizes an electron from the orbitals of only one atom, allowing it to move different locations of a molecule or along the length of a polymer. This $\pi$-conjugation is a result of the hybridization of the atom's orbitals and the bonding scheme between atoms. The conducting particles in organic material can simplistically be thought of moving along the delocalized $\pi$-conjugated bonds but this is not a realistic picture. Typically, this delocalization does not stretch throughout the materials and the conducting excitations hop from molecule to molecule or $\pi$-conjugated section to section. With this mobility of excitations, an organic material can conduct electricity. It was first shown that doped polyacetylene (CH)$_x$ had a conductivity level of 220 $(\Omega \text{cm})^{-1}$ [1]. Then through improvements to the polymerization process which reduced the number of $sp^3$ defects, increasing the delocalization, the conductivity was improved to $>20,000$ $(\Omega \text{cm})^{-1}$ [19]. Other improvements increased the conductivity of the polyacetylene films to $>120,000$ $(\Omega \text{cm})^{-1}$ by improving the alignment of the individual chains [20].

To understand the conductive ability of organic materials, one must start with their orbital hybridization. During the development of valence-bond theory, Linus Pauling introduced the idea of orbital hybridization [21]. The hybridization of molecular orbitals of an atom depend on the energy level of two orbital subshells being close together. The atom makes a small sacrifice in energy to promote an electron from a lower subshell to a higher subshell which is later recovered in the formation of a molecule. A simple example of this is the formation of beryllium hydride (BeH$_2$). In Be, the ground state
Figure 1.1  The hybridization of a) 2s and 2p\textsubscript{x} orbitals in beryllium form b) \textit{sp} hybrid atomic orbitals.

electron configuration is 1s\textsuperscript{2}2s\textsuperscript{2} where all the electrons are paired. To form bonds with the hydrogen atoms, an electron is promoted from the 2s-subshell to the 2p-subshell or for this case, the 2p\textsubscript{x} orbital. These two orbitals, the 2s and the 2p\textsubscript{x}, mix to form two \textit{sp} hybrid atomic orbitals as shown in Figure 1.1. Each hybrid orbital can then share its electrons with one of the hydrogen atoms forming a sigma bond. In BeH\textsubscript{2}, a total of two \(\sigma\)-bonds are formed. The formation of the \(\sigma\)-bonds releases enough energy to account for the promotion of the electron and still have energy left over making the hybridization of the molecular orbitals an energetically favorable process.

A more complex example of orbital hybridization is the carbon atom which form the backbone of all \(\pi\)-conjugated organic molecules. In its ground state, carbon has
Figure 1.2 The hybridization of a) 2s and three 2p orbitals to form b) four $sp^3$ hybrid atomic orbitals. Note that the major lobes are 109.5 degrees from each other.

the electronic configuration of 1s$^2$2s$^2$2p$^2$ and the energy levels of its 2s and 2p orbitals are relatively close. To form one of the possible hybrid orbitals, an electron from the 2s orbital is promoted to a 2p orbital and then the 2s and the three 2p orbitals are combined to give four $sp^3$ orbitals. As shown in Figure 1.2, the $sp^3$ orbitals are arranged around the carbon atom with their major lobes pointing outwards in a tetrahedral fashion. Ethane, CH$_4$ in Figure 1.3 demonstrates the molecule formation that occurs with the four $sp^3$ hybrid orbitals of carbon. Three of the $sp^3$ orbitals on each carbon atom form $\sigma$ bonds with the 1s orbital of three hydrogen atoms. The remaining $sp^3$ orbital of the carbon atom forms a $\sigma$ bond with the other carbon atom.
The carbon atoms of ethane form σ bonds from their sp$^3$ orbitals with the other atoms.

The next orbital hybridization that carbon can form involves combining only two of the three 2p orbitals with the 2s orbital leaving the remaining 2p orbital untouched. The mixing of these orbitals results in three sp$^2$ hybrid orbitals as shown in Figure 1.4. It is important to notice that the remaining 2p orbital has not been hybridized or otherwise affected. An example of a molecule that uses carbon's sp$^2$ orbitals to form is ethylene which is illustrated in Figure 1.5. For each carbon atom, two hydrogen atoms form a σ bond with two of the sp$^2$ orbitals and the third sp$^2$ orbital forms a sigma bond with the sp$^2$ of the other carbon atom. The two unhybridized 2p orbitals of the carbon atoms are still available for bonding and overlap to form a π bond. This type of bond between the two carbon atoms is referred to as a double bond because there are two bonds, the σ bond and the π bond, holding the carbon atoms together. This double bond is stronger and shorter than a single bond because the additional π bond supplements the strength of the σ bond.

The final type of orbital hybridization which can occur for carbon combines only one of the three 2p orbitals with the 2s orbital and results in two sp hybrid orbitals. The shape of the sp orbitals is the same as in beryllium shown in Figure 1.1, but with carbon there are two 2p orbitals which remain unhybridized. How this scheme is used in
Figure 1.4  The hybridization of a) $2s$ and two $2p$ orbitals to form b) $sp^2$ hybrid atomic orbitals.

Figure 1.5  The $sp^2$ orbitals of the carbon atoms in ethylene form a) $\sigma$ bonds with the hydrogen atoms and the remaining $2p$ orbitals form a b) $\pi$ bond.
forming a molecule is illustrated for acetylene in Figure 1.6. A hydrogen atom forms a $\sigma$ bond with one of the $sp$ orbitals for each carbon atom. The remaining $sp$ orbital of the carbon atom forms a $\sigma$ bond with the unbonded $sp$ orbital of the other carbon atom. The remaining unhybridized $2p$ orbitals overlap to form two $\pi$ bonds which supplement the $\sigma$ bond between the carbon atoms. This triple bond is stronger and shorter in length than a double bond because of the additional $\pi$ bond.

A more complex example of $\pi$ bonding, but one of the simplest examples of $\pi$-conjugation, is 1,3-butadiene ($\text{CH}_2\text{CHCHCH}_2$) whose structure is show in Figure 1.7. All of the carbon atoms are $sp^2$ hybridized and the $\sigma$ bonds all lie in the $x$-$y$ plane. The four unhybridized $2p_z$ orbitals of the carbon atoms are free to overlap with each other and form a total of four $\pi$ molecular orbitals into which the four remain electrons from the unhybridized orbitals may fill. These orbitals vary in energy according to how many nodes are present with the highest energy orbital having three nodes while the lowest has none as illustrated in Figure 1.7. The available four electrons then fill the two $\pi$ molecular orbitals with the lowest energy. The node structure of the occupied $\pi$ molecular orbitals also suggest that the two outer carbon-carbon bonds are slightly
stronger and shorter than the interior carbon-carbon bond [22]. The outer carbon-carbon bonds are formed from both the lowest molecular orbital and the next highest while the interior carbon-carbon bond is only form from the lowest molecular orbital. Hence, the bonds between the carbon atoms alternate between double bonds and single bonds which is the original meaning of $\pi$-conjugation. For typical $\pi$-conjugated systems, the delocalization is not so evenly distributed but there is an alternation of bond lengths due to greater overlap between certain pairs of atoms.

Another important example for organic molecules is benzene ($C_6H_6$) shown in Figure 1.8. Again, all the carbons have $sp^2$ hybridization and the sigma bonds form a
Figure 1.8. The structure of a) benzene and b) the nodal structure of the six molecular orbitals formed from the six $2p_z$ atomic orbitals.

Ring in the x–y plane. The unhybridized $2p_z$ orbitals form six $\pi$ molecular orbitals as illustrated in Figure 1.8. The energy level of the $\pi$ molecular orbitals increases with the number of nodes of the orbital so the highest energy orbital has six nodes and the lowest has none. The electrons from the six unhybridized $2p_z$ orbitals fill the lowest three $\pi$ molecular orbitals. The nodal structure of these molecular orbitals suggest that the electrons are delocalized over the entire ring and that the length of the carbon-carbon bonds are all the same. This has been verified experimentally showing that all of the carbon-carbon bonds have a length of 1.39 Å which is between that of typical double bonds (1.34 Å) and single bonds (1.54 Å) [23].

One can extend the idea of delocalization of the $\pi$ electrons further by linking up
π-conjugated molecules to form polymers. The π electrons of each molecule delocalize over neighboring molecules and depending on the quality of the polymer, possibly over the whole chain. This extended electron cloud extends along the polymer until a kink, bend, or defect interrupts the conjugation. The conjugation length of the polymer is the distance between the two nearest defects in the chain. Increasing the conjugation length of a polymer increases the delocalization of the π electrons which will reduce the bandgap of the polymer or lower the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). If enough kinks and bends are present in a polymer, the bandgap will increase, turning it into an insulator [24–27].

1.2 Excitations in π-Conjugated Materials

Due to the differences between π-conjugated materials and traditional inorganic semiconductors, traditional models for the latter cannot accurately explain the excitations in π-conjugated material without modifications. An early model that roughly explained the optical and electric properties of polyacetylene was based on a single electron in a band structure [28]. This model was limited in what it could explain and the authors acknowledged that improvements were needed for it to be practical. Su, Schrieffer, and Heeger [29, 30] invoked solitons in their model as the fundamental excitation in long-chain polyenes. These solitons are a domain wall between two different bond alteration schemes or a topological kink that can move along the polymer [29, 31–35]. They are not true solitons since they cannot pass through one another without affecting the shape of the other [36]. However, these solitons modeled the excitations and charge transfer in polymers with a degenerate ground state, such as trans-polyacetylene, quite well.

When the degeneracy of the ground state is lifted, as in cis-polyacetylene and the majority of π-conjugated polymers, the model based on solitons began to break down.
Without a degenerate ground state, a single isolated soliton is no longer an energetically possible formation [37-39]. On these nondegenerate polymers, pairs of solitons are allowed: bound together in a polaron-like entity [31-34]. In crystals, polarons are the result of the interaction between the electron and the phonon—essentially the electron and the strain field it exerts on the crystal [40]. In a $\pi$-conjugated material, a charged soliton bound to a neutral soliton or a confined kink and anti-kink pair may be considered a polaron and similarly, a confined pair of charged solitons would be a bipolaron [31, 32, 36-39, 41-43]. Injection of charge or the production of charge from photoexcitation results in polarons which can also combine to form bipolarons [32, 43-45]. The formation of doubly charged bipolarons is energetically favorable which is somewhat surprising because of the electrostatic repulsion between similarly charged polarons. However, the energy gained from the relaxation of the lattice compensates for the energy lost to the electrostatic repulsion [32, 43, 44, 46-50].

Another important excitation in $\pi$-conjugated materials is the exciton. These excitations are neutral electron-hole pairs and may exist in either the singlet ($S=0$) or triplet ($S=1$) state [38, 40, 44, 51]. There is a further distinction among excitons in how strongly the electron is bound to the hole. In Frenkel excitons, the electron is bound very tightly to the ion and is very localized [40, 51-54]. In the other type of exciton, a Wannier exciton, the electron and the hole are only loosely bound together which may allow a considerable separation between the two which is sometimes great enough for them to be considered as a pair of polarons [40, 51, 55]. This type of exciton is also referred to as a charge transfer exciton (CTE) [56].

Photoexcitation of $\pi$-conjugated materials will produce polarons, bipolarons, triplet excitons, and singlet excitons [57-62]. Initially, photoexcitation generates an electron-hole pair and depending on the placement of the charges may be either an interchain or an intrachain pair [63, 64]. Intrachain pairs exist on the same conjugation length of the $\pi$-conjugated material [45]. Due to the proximity of the electron and the hole, these are
Frenkel-type singlet and triplet excitons. The singlet excitons decay radiatively or non-radiatively quite quickly, with a lifetime on the order of $10^{-9}$ seconds or less [56, 57, 65]. The triplet excitons decay much more slowly due to the forbidden nature of the transition and have a lifetime on the order of microseconds to milliseconds depending on the material [56, 66]. Interchain pairs exist on different conjugation segments in the π-conjugated material which may or may not be on different chains or molecules [45]. Due to their separation, these loosely bound polaron pairs may further dissociate to produce individual polarons [45, 56, 67]. These separated polarons travel through the material and can form bipolarons or reform back into an exciton [58, 59, 64, 68, 69]. Typically, injection of charge will produce individual polarons which behave in a similar manor either combining into bipolarons or forming excitons which are requisite for electroluminescence [10, 43, 67].

The photoluminescence in π-conjugated materials is attributed mainly to the radiative decay of the singlets, namely prompt fluorescence [64]. In rarer cases, triplets will decay radiatively to the ground state in a process called phosphorescence [70-73]. It is also possible for triplets to recombine with each other, producing an excited singlet which may then radiatively decay. This process is referred to as delayed fluorescence because it occurs after the initial prompt fluorescence [66, 74, 75]. Another slower process proposed by Yan et al. [76, 77] is the dissociation of a singlet into a “spatially indirect exciton” which is also known as a CTE or an interchain polaron pair. This CTE does not dissociate further into separate polarons but recombines back into a singlet after which it can decay radiatively.

In general, the interaction of the singlets with any of the other excitations, such as triplets and polarons, is thought to be detrimental to the fluorescence of the π-conjugated material [78]. Typically, the excitation affects the electric field of the singlet, altering its radiative paths. A summary of the significant decay channels of the excitations in π-conjugated materials is shown in Table 1.1.
Table 1.1 Decay channels and interactions of various excitations in \(\pi\)-conjugated molecules [56, 79–81].

\[
\begin{align*}
S_1^* &\rightarrow S_0 + h\nu + \text{phonons} \\
S_1^* + p_t &\rightarrow S_0 + p_t + \text{phonons} \\
S_1^* + bp &\rightarrow S_0 + bp + \text{phonons} \\
S_1^* + T_1 &\rightarrow S_0 + T_1 + \text{phonons} \\
S_1 + S_1 &\rightarrow S_1^* + S_0 \\
S_1 + S_1 &\rightarrow T_1^* + T_1^* \\
T_1^* &\rightarrow S_0 + h\nu + \text{phonons} \\
T_1 + p &\rightarrow S_0 + p + \text{phonons} \\
T_1 + bp &\rightarrow S_0 + bp + \text{phonons} \\
T_1 + T_1 &\rightarrow S_1^* + S_0 \\
T_1 + T_1 &\rightarrow T_1^* + S_0 \\
T_1 + T_1 &\rightarrow S_0 + S_0 + \text{phonons} \\
p_f^+ + p_f^- &\rightarrow S_1^* \\
p_f^+ + p_f^- &\rightarrow T_1 \\
p_t^+ + p_t^- &\rightarrow S_0 + \text{phonons} \\
p_f^+ + p_f^- &\leftrightarrow bp^{++} \\
p_f^- + p_f^- &\leftrightarrow bp^{--} \\
bp^{++} + p_f^- &\rightarrow p_t^+ \\
bp^{--} + p_f^+ &\rightarrow p_t^-
\end{align*}
\]

where: \(S_0\) and \(S_1^*\) are the ground state and excited state of singlet excitons; \(T_1\) and \(T_1^*\) are the lowest state and excited state of triplet excitons; \(p_f\) and \(p_t\) are free and trapped polarons; \(bp\) is a bipolaron; \(h\nu\) is a photon; phonons participate but are not included in all of the reactions listed above.
2 INTRODUCTION TO PHOTOLUMINESCENCE DETECTED MAGNETIC RESONANCE

The development of photoluminescence (PL) detected magnetic resonance (PLDMR) drew on a number of different areas. The use of microwave photons can be traced to 1934 where Cleeton and Williams used a spectrometer with a range extending into the microwave region to measure the absorption spectrum of ammonia [82]. A technique to measure a magnetic resonance in a solid was introduced by Gorter in 1936 when he attempted to detect a nuclear magnetic resonance by monitoring the temperature of the solid in question [83]. Much later, when technology had advanced enough to provide the required sensitivity and resolution, it became possible to measured the microwave power absorbed as a function of the strength of the magnetic field [84, 85]. This experiment was the beginning of modern day electron spin resonance (ESR). For a more complete treatment of ESR, several thorough monographs have been written on the subject [86, 87]. As ESR techniques improved, the idea of detecting the resonance optically by monitoring effects of the microwaves on the phosphorescence of the triplet states was introduced and provided the basis for PLDMR [88-90].

PLDMR may be described briefly as the optical detection of microwave-induced changes in the PL at the magnetic field for resonance. The general principle of PLDMR relies on the paramagnetic interaction of particles with an applied magnetic field. The substance in question is placed in a microwave cavity and bombarded with microwave photons as well as visible photons. Then as an applied magnetic field is varied, the
microwave photons induce a change in the PL of the sample yielding a resonance which may be detected optically.

2.1 Spin-$\frac{1}{2}$ Resonances

The simplest system that displays a resonance that may be detected by this technique are two weakly bound polarons, a Wannier type exciton. Each polaron has a spin of $\frac{1}{2}$ and therefore may interact with an applied magnetic field. Because the two polarons only interact with each other very weakly, the spin-spin coupling energy is negligible compared with the Zeeman splitting of the energy levels. Hence, the Hamiltonian of this system is:

$$\mathcal{H} = \beta S \cdot g \cdot H$$ (2.1)

where $S$ is the spin of the system, $g$ is the interaction tensor, $\beta$ is the Bohr magneton, and $H$ is the applied magnetic field.

Because of the nature of the electron $\pi$ orbitals, the $g$ tensor may be treated as isotropic and replaced with a constant [47, 87]. Hence, this equation simplifies to:

$$\mathcal{H} = g\beta S \cdot H$$ (2.2)

where $g$ is the gyromagnetic ratio or Landé $g$ factor.

Again, because the two polarons are weakly interacting, each can align itself either with or against the magnetic field. This will produce for different energy levels described by:

$$\mathcal{E} = \frac{1}{2}(\pm g_e \pm g_h)\beta H$$ (2.3)

where $g_e$ and $g_h$ are the $g$ values for the electron polaron and hole polaron, and $H$ is the magnitude of the applied magnetic field. Figure 2.1 shows the energy levels as a function of the applied magnetic field.
Figure 2.1 Energy levels for a weakly bound electron-hole polaron pair in an applied magnetic field.
From spin selection rules, the polaron pairs with anti-parallel spins will recombine more quickly than the pairs with parallel spins.

\[ r_2, r_3 > r_1, r_4 \] \hspace{1cm} (2.4)

This means that under steady state conditions, the population of parallel spin pairs will be greater than that of the anti-parallel spin pairs.

\[ n_2, n_3 < n_1, n_4 \] \hspace{1cm} (2.5)

At resonance, the incident microwave photons will have the appropriate energy to mix the populations which may affect the PL in one of a number of ways. If the PL is from the radiative decay of the anti-parallel polaron pairs \((n_2, n_3)\), the resonance condition will increase their populations and increase the PL. This type of yield mechanism is called a direct radiative PLDMR \([79, 91, 92]\). Another possibility is that these polarons are nonradiatively quenching the excited singlet states. Therefore at resonance, the overall population of polarons will be reduced, decreasing the quenching of the excited singlet states and enhancing the PL. This mechanism does not directly affect the PL and is referred to as indirect non-radiative PLDMR \([79, 91, 92]\). A third possibility is the formation of bipolarons which may be enhanced by the resonance conditions. These bipolarons have longer lifetimes than polarons and are detrimental to the PL. A typical enhancing PLDMR is shown in Figure 2.2.

### 2.2 Spin-1 Resonances

Among the excited states in \(\pi\)-conjugated materials, triplet excitons account for a significant proportion of the excited states and PLDMR has shown itself to be sensitive to the presence of triplets. In the spin-\(\frac{1}{2}\) resonance, the pair of polarons were weakly interacting and the spin-spin coupling could be ignored. Triplet excitons are Frenkel-type excitons where the electron and the hole are tightly bound together so the spin-spin
Figure 2.2 A typical spin $\frac{1}{2}$ PL-enhancing PLDMR spectra. This particular spectrum comes from poly(p-phenylene)-type ladder polymers [80].
coupling energy can no longer be neglected. In this case, the Hamiltonian will be [87]:

$$\mathcal{H} = \mathcal{H}_{\text{Zeeman}} + \mathcal{H}_{s,s} = \beta \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{H} + \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S}$$  \hspace{1cm} (2.6)$$

where $\mathbf{D}$ is the spin-spin coupling tensor and its elements are expressed by [87]:

$$D_{ij} = \frac{(g\beta)^2}{2} \left( \frac{r^2 \delta_{ij} - 3\mu_i \mu_j}{r^5} \right)$$ \hspace{1cm} (2.7)$$

where the average is over the spatial part of the wavefunction, $r$ is the separation of the two spin-carrying particles, and $\mu_i$ is the $x$, $y$, or $z$ component of the separation. This tensor may be diagonalized along the principle axes yielding the diagonal elements [87]:

$$X = \frac{(g\beta)^2}{2} \left( \frac{r^2 - 3x^2}{r^5} \right)$$ \hspace{1cm} (2.8)$$

$$Y = \frac{(g\beta)^2}{2} \left( \frac{r^2 - 3y^2}{r^5} \right)$$ \hspace{1cm} (2.9)$$

$$Z = \frac{(g\beta)^2}{2} \left( \frac{r^2 - 3z^2}{r^5} \right)$$ \hspace{1cm} (2.10)$$

The spin-spin interaction term of the Hamiltonian now simplifies to:

$$\mathcal{H}_{s,s} = \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S} = -(XS_x^2 + YS_y^2 + ZS_z^2)$$ \hspace{1cm} (2.11)$$

Because the spin-spin coupling tensor is traceless, the diagonal elements are related by:

$$X + Y + Z = 0$$ \hspace{1cm} (2.12)$$

This relationship and the equation:

$$S_x^2 + S_y^2 = S^2 - S_z^2$$ \hspace{1cm} (2.13)$$

allows equation (2.11) to be characterized with only two parameters:

$$D = -3\frac{Z}{2} = \frac{3}{4} (g\beta)^2 \left( \frac{r^2 - 3z^2}{r^5} \right)$$ \hspace{1cm} (2.14)$$

$$E = \frac{Y - X}{2} = -\frac{3}{4} (g\beta)^2 \left( \frac{x^2 - y^2}{r^5} \right)$$ \hspace{1cm} (2.15)$$
The parameters, $D$ and $E$ are referred to as the zero field splitting parameters. The Hamiltonian for this spin-spin interaction term now simplifies into:

$$\mathcal{H}_{s.s} = D(S_z^2 - \frac{1}{3}S^2) + E(S_x^2 - S_y^2)$$  \hspace{1cm} (2.16)

The final form of the Hamiltonian for this system is expressed:

$$\mathcal{H} = g\beta \mathbf{S} \cdot \mathbf{H} + D(S_z^2 - \frac{1}{3}S^2) + E(S_x^2 - S_y^2)$$  \hspace{1cm} (2.17)

For arbitrary orientations of the sample in a magnetic field, solving the Hamiltonian (2.17) for the eigenfunctions becomes quite complex. Making the assumption that the magnetic field, $\mathbf{H}$, lies along the axis of the system allows simple closed forms for the energy to be obtained [87].

For $\mathbf{H}$ along $x$:

$$\mathcal{E}_0 = \frac{D}{3} - E$$  \hspace{1cm} (2.18)

$$\mathcal{E}_\pm = -\frac{D - 3E}{6} \pm \left[ (g\beta H)^2 + \frac{(D + E)^2}{4} \right]^{1/2}$$  \hspace{1cm} (2.19)

For $\mathbf{H}$ along $y$:

$$\mathcal{E}_0 = \frac{D}{3} + E$$  \hspace{1cm} (2.20)

$$\mathcal{E}_\pm = -\frac{D + 3E}{6} \pm \left[ (g\beta H)^2 + \frac{(D - E)^2}{4} \right]^{1/2}$$  \hspace{1cm} (2.21)

For $\mathbf{H}$ along $z$:

$$\mathcal{E}_0 = -\frac{2D}{3}$$  \hspace{1cm} (2.22)

$$\mathcal{E}_\pm = \frac{D}{3} \pm [(g\beta H)^2 + E^2]^{1/2}$$  \hspace{1cm} (2.23)

Figure 2.3 shows the above energy levels plotted against magnetic field for their different orientations of the magnetic field. Also in Figure 2.3, the transitions between energy levels are indicated. Transitions A and B are first-order transitions and are called full-field transitions while C is a second-order transition and referred to as a half-field
transition. It is possible to use the positions of the resonances from different orientations of the magnetic field to determine the zero-field splitting parameters of a single crystal. Figure 2.4 shows the PLDMR spectra of 1,5-naphthyridine in a single crystal host of durene [93]. Typically, the full-field resonance spectra of a single crystal would show only two peaks from the full-field transitions, labeled A and B in Figure 2.3. For this case, the naphthyridine may reside at two sites in the crystal which are inequivalent and each configuration will generate two resonances for a total of four.
2.3 Powder Patterns

Obtaining single crystals of all samples is not always possible whereas it is typically easy to find polycrystalline and amorphous samples. In these samples, any resonance detected will be the sum from all possible orientations of the molecules or "crystallites" in the sample and called a "powder pattern." As shown in Figure 2.5, the typical powder pattern has two main characteristics, the first being a resonance at "half-field" from the transition labeled C in Figure 2.3. The second feature is a broad pattern at "full-field" from the transitions labeled A and B in Figure 2.3.

The first step in calculating a powder pattern is finding the resonance condition where the microwaves induce a transition between the energy levels. For a single crystal, these values of the magnetic field are dependent on the orientation of the field and are typically described by a function:

\[ H(n, \phi) \]  

(2.24)
Figure 2.5 A typical half-field (graph on left) and full-field (graph on right) powder pattern PLDMR for LPPP [80]. Note the polaron peak extending off the top of the plot in the full-field graph.
where \( n = \cos \theta \), the cosine of the polar angle and \( \phi \) is the azimuthal angle. As the crystal is rotated, the resonance will shift accordingly. In an amorphous or polycrystalline sample, molecules or "crystallites" will exist with random orientations to each other and the applied magnetic field. The normalized lineshape function \( P(H) \) is determined by the probability that a molecule or crystallite will contribute to a resonance in the region \( H \) to \( H + dH \). Therefore [94, 95]

\[
P(H) = \Omega^{-1} \cdot (dH)^{-1} \int_H^{H+dH} d\Omega
\]

\[
1 = \int_0^\infty P(H) d(H)
\]

where \( \Omega = 4\pi \) and \( d\Omega \) refers to an element of solid angle \( (d\Omega = -dn \cdot d\phi) \). In general, obtaining a closed form for \( P(H) \) is not possible and computer methods must be used to generate a powder pattern. To complicate matters further, equation (2.25) does not take into account the finite width of a resonance and some type of broadening of the line is needed. Compensating for line broadening results in [95–98]:

\[
I(H) = \int_{-\infty}^{\infty} P(H') F(H - H') dH'
\]

where \( P(H) \) in given by equation (2.25) and \( F(H - H') \) is a function that describes the broadening. Shown in Figures 2.6 and 2.7 are computer simulations of powder pattern spectra for varying values of \( D \) and \( E \) which include Gaussian broadening [81].

Typically such an exact powder pattern is not necessary and the location of certain features such as shoulders and singularities are sufficient. The location of these critical points may be determined through the analysis of the resonance condition (2.24) and applying the relation [95, 99]

\[
(\partial H/\partial n)_{n=a, \phi=b} = (\partial H/\partial \phi)_{n=a, \phi=b} = 0
\]

where \((a, b)\) are the coordinates of a critical point. This point may be either a singularity or a shoulder in the powder pattern and its nature may be further determined by the
Figure 2.6 A simulation of a full-field PLDMR spectra for 9.352 GHz microwave photons and zero field splitting parameters of $D = 520 \text{ G}$ and $E = 0 \text{ G}$ [81].

Figure 2.7 A simulation of a half-field PLDMR spectra for 9.352 GHz microwave photons and zero field splitting parameters of $D = 602 \text{ G}$ and $E = 0 \text{ G}$ [81].
observing the sign of $[95, 99]$

$$W = \left[ (\partial^2 H/\partial n \partial \phi)^2 - (\partial^2 H/\partial^2 n)(\partial^2 H/\partial^2 \phi) \right]_{n=a,\phi=b}$$\hspace{1cm} (2.29)

where $(a, b)$ is a singularity if $W > 0$ and a shoulder if $W < 0$.

The following are the critical points for the full-field and half-field powder pattern as functions of $h\nu$ (a microwave photon's energy), $D$, and $E [95, 97, 99, 100]$:

**Full-field resonance:**

shoulders at

$$H = \frac{1}{g\beta} (h\nu \pm \frac{D \pm 3E}{2})$$\hspace{1cm} (2.30)

singularities at

$$H = \frac{1}{g\beta} (h\nu \pm \frac{D \mp 3E}{2})$$\hspace{1cm} (2.31)

steps at

$$H = \frac{1}{g\beta} (h\nu \pm D)$$\hspace{1cm} (2.32)

**Half-field resonance:**

singularity at:

$$H = \sqrt{\left(\frac{h\nu}{2g\beta}\right)^2 + \frac{D^2 + 3E^2}{(g\beta)^2}}$$\hspace{1cm} (2.33)

shoulder at:

$$H = \frac{h\nu}{g\beta} \sqrt{1 - \frac{1}{2} \left(\frac{D - E}{h\nu}\right)^2}$$\hspace{1cm} (2.34)
2.4 Experimental Apparatus

A general schematic of the PLDMR spectrometer used for this research is shown in Figure 2.8. The equipment was originally designed for electron spin resonance (ESR) measurements and then modified and upgraded accordingly to allow flexibility in what measurements are available and to improve the measurements.

For optical excitation of the samples, an argon ion laser with multiline capability was used. The wavelength of the laser was selected according to the optimal absorption of the sample being studied. The laser beam was passed through an external stabilizer to reduce noise and the overall variance of the laser power. For samples that required ultraviolet (UV) excitation, a 200 W mercury vapor lamp was used. The light from this lamp was filtered to remove wavelengths above 450 nm and then through the use of a specially coated reflector, a specific wavelength could be chosen. Typically, the photoexcitation power varied from 5 to 50 mW.

This light was then focused onto the sample sealed inside a fused silica tube as described in section 2.6. This sample is located inside an Oxford Instruments continuous flow cryostat using liquid helium as the cryogen. By regulating the flow of the liquid helium, the temperature could be coarsely controlled down to 10 K. A heating element in the cryostat allowed finer control of the temperature, stabilizing to as low as ± 0.1 K for temperatures below 50 K and to within a couple of degrees for higher temperatures.

The sample holder of the cryostat is located in the center of a high Q, TE microwave cavity which was placed in a magnetic field generated by a computer controlled electromagnet. The magnetic field was monitored and measured with a commercial gaussmeter. The X-band microwaves were generated with a Gunn diode oscillator. The microwaves could be modulated with a pin-switch diode and then were amplified with a solid state linear amplifier up to 1 W of power. Coupling to the microwave cavity was achieved by adjusting the microwave frequency and the iris of the cavity.
Figure 2.8 A schematic diagram of the PLDMR spectrometer.
The PL of the sample was collected with an arrangement of lenses and focused onto a photodetector, either a silicon diode or a photomultiplier tube. Before striking the photodetector, the exciting wavelength was filtered out to increase the signal to noise ratio (S/N). To further increase the S/N, the signal was passed to a lock-in amplifier which was referenced at the microwave chopping frequency. The output from the lock-in amplifier, as well as the overall intensity of the photoluminescence, were monitored and recorded by a computer. The computer also controlled the strength of the magnetic field and recorded the other relevant parameters which are set by the user.

2.5 Similar and Related Techniques

With minor modification to the experimental apparatus similar types of measurements can be made. These include electrically detected magnetic resonance (EDMR), electroluminescence detected magnetic resonance (ELDMR), photocurrent detected magnetic resonance (PCDMR), and frequency-resolved photoluminescence detected magnetic resonance (FR-PLDMR).

EDMR, ELDMR, and PCDMR are all similar in that an electronic circuit is required for the technique. Typically this is done by including the sample in the emitting layer of a light emitting device as shown in Figure 2.9. The base is usually glass which is coated on one side with indium-tin-oxide (ITO). ITO is used because of its transparency and electrical conductivity. On top of the ITO, the sample in question is deposited by an appropriate method such as spin-coating or evaporation. A metal layer is then evaporated onto the top of the device to provide an electrical contact. This device is then placed in the microwave cavity of the PLDMR system and the electrodes are connected to appropriate equipment. For ELDMR, the device is connected to a power supply that allows the device to produce electroluminescence. In this case, a source of photoexcitation is not needed and the electroluminescence is collected by the photodetector and
Figure 2.9 A schematic diagram of a very basic light emitting device.

then passed into the lock-in amplifier. In EDMR, the device is connected to a power supply and the current in the circuit rather than the luminescence is monitored by the lock-in amplifier. Note that not only is the source of photoexcitation not needed but the device need not electroluminesce either. For PCDMR, an external light source is used to photoexcite the device but the photoluminescence is not collected. Instead, the device is connected to the lock-in amplifier which is detecting the photocurrent produced by the device.

In FR-PLDMR, the frequency at which the microwaves are chopped is varied and the strength of the PLDMR is monitored. As the frequency is increased, the process involved in the resonance can no longer respond as fast as required. Hence, the lock-in detected signal will decrease, revealing the lifetime of the process \[101\]. This may be compared to the analysis of an RC circuit. Therefore, the lifetime may be found by fitting the data to a function of the form:

\[
R = \frac{1}{\sqrt{1 + (\tau \omega)^2}}
\]  \hspace{1cm} (2.35)

where \(\tau\) is the lifetime, \(\omega\) is the chopping frequency of the microwaves, and \(R\) is the magnitude of the lock-in detected signal. Typically, the data from the lock-in amplifier
is not given in terms of magnitude but two components referred to as "in-phase" and "quadrature." These are related to the magnitude by the following expressions:

\[ X = R \cos \theta \]  
\[ Y = R \sin \theta \]  
\[ \theta = \arctan \tau \omega \]

where \( X \) is the "in-phase" component, \( Y \) is the "quadrature" component, and \( \theta \) is the phase of the signal from the lock-in amplifier. Figure 2.10 shows a simulation of FR-PLDMR data by using a RC circuit attached to the lock-in amplifier. The derivation of this relation from monomolecular photoexcitation kinetics is more rigorous [102–104] but the result is equivalent to equation (2.35) for a simple RC circuit.
2.6 Sample Preparation

2.6.1 Powder Sample

To produce a powder sample, a small amount of the powder was placed into a fused silica sample tube with an outer diameter of 4.5 mm and an inner diameter of 2.5 mm. These fused silica tubes were previously prepared by sealing one end with a natural gas hand torch. A natural gas hand torch was chosen because the clean flame would not introduce contaminants into the fused silica and would avoid producing soot. With the powder inside the sample tube, the open end was attached to a turbo molecular vacuum pump and then slowly evacuated of air. When the level of the vacuum inside reached less than $10^{-6}$ mbar, the sample tube was sealed which prevented any further degradation of the sample by elements in the air, particularly oxygen.

2.6.2 Solution Sample

A solution sample was made by first preparing a solution of the sample by dissolving a known amount of the powder into toluene or other appropriate solvent. A small amount of the solution was pipetted into a fused silica sample tube and degassed by the following method. The open end of the fused silica tube was attached to the turbo molecular pump and the solution end was placed into liquid nitrogen. With the solution frozen, the remaining air was evacuated from the tube. After closing the valve to the vacuum, the sample was allowed to thaw which would release some of the gas dissolved in the solution. It is necessary to control the rate of thawing or else the dissolved gas would bubble too violently and contaminate the upper portion of the tube which would make sealing it impossible. Once the sample had liquefied, it was refrozen again and the gas evacuated with the pump. This cycle of freezing and thawing was repeated until no more dissolved gases were evident. Then the sample was frozen, evacuated and sealed.
2.6.3 Film Sample

The film samples were made by placing some of the solution in the fused silica sample tube and then slowly evacuating the tube. The solution would slowly evaporate leaving a film on the walls of the sample tube. After the tube was completely evacuated, the tube was then sealed. It is important to note that the quality of the film could be affected by how the temperature of the solution sample was maintained as well as by changing the rate at which the tube was evacuated. Simply allowing the solution to evaporate would decrease the temperature of the solution enough to freeze it. This would negatively impact the quality of the film as the solution would freeze and rethaw during the process. Maintaining the temperature of the solution as it evaporated prevented this freezing process and improved the uniformity and the consistency of the resulting film.
3 STUDIES ON RUBRENE

There has been much interest in rubrene, viz. 5,6,11,12-tetraphenyl tetracene, whose structure is shown in Figure 3.1, as an additive for organic light emitting devices. Studies have shown that using rubrene as a dopant extends the lifetime of devices and improves their efficiency [105-109]. However, the photophysics of rubrene is still far from clear.

In a previous PLDMR study of sublimed rubrene films [111], a negative (PL-quenching) resonance was observed whose shape depended on the conditions under which the sample was formed. A polycrystalline film deposited at room temperature exhibited a negative nearly-Lorentzian resonance lineshape with a full-width at half-maximum \( \Delta H_{1/2} \approx 320 \) G. A film deposited at 77 K exhibited a broad negative triplet exciton powder pattern, suggested to result from randomly oriented crystals. Both resonances were attributed to magnetic resonance induced decorrelation of the spins of geminate pairs of \( 1^3B_u \) triplet excitons, which inhibits their back-fusion to the radiative \( 1^1B_u \):

\[
1^3B_u + 1^3B_u \rightarrow 1^1B_u
\]

(3.1)

In other words, at resonance, one of the spins of the pair is flipped, preventing it from recombining with the other to generate the radiative \( 1^1B_u \). This prevents PL, resulting in the negative, PL-quenching pattern [112].

With the exception of the solution, the rubrene samples studied in this chapter exhibited both quenching and enhancing triplet resonances, but lacked a detectable spin \( \frac{1}{2} \) polaron resonance. These triplet resonances changed over the course of time in both the powder and the film samples. These changes appeared to be correlated with changes
in their morphology or microstructure. In the powder, the relatively narrow quenching pattern weakened after the first measurements leaving the broad enhancing resonance. In the films, the resonance was initially enhancing but became quenching after “aging.” It is suspected that the enhancing resonance results from nongeminate triplet-triplet annihilation to singlets in disordered domains. The quenching resonance is attributed to the mechanism mentioned above, i.e., microwave induced spin decorrelation of geminate triplet pairs in crystalline domains.

3.1 Results

3.1.1 Solution Sample

Solution samples had a very strong PL as previously noted [113] but no detectable resonance was present at either full (g≈2.0) or half field (g≈4.0). It is well known that the efficient fission of the $1^1B_u$ singlet to two $1^3B_u$ triplets is the primary process that competes with the radiative decay of the $1^1B_u$ and therefore is responsible for the relatively low PL yield of ~10% in rubrene films and powders. Since the $1^1B_u$ dissociation is suppressed in dilute rubrene solutions, their PL yield is close to 100% [114-
As the PLDMR of luminescent $\pi$-conjugated molecules is due to intermolecular coupling [79, 111, 117-123], this lack of a resonance is expected due to the separation of the individual rubrene molecules by the solvent.

### 3.1.2 Powder Sample

The solid line in Figure 3.2 shows the PLDMR of a "fresh" powder sample. A broad positive (PL-enhancing) triplet pattern is observed with a shoulder-to-shoulder width of $\Delta H \sim 1050$ G. We note the absence of the PL-enhancing spin $1/2$ polaron resonance, commonly observed in $\pi$-conjugated polymers, in all of the rubrene samples. The relatively narrow PL-quenching resonance at $\sim3380$ G exhibited by the "fresh" powder is striking and reminiscent of the negative PL-quenching resonance displayed in films sublimed by Lesin et al. onto a substrate at $T_s = 300$ K [111]. Its nature and the observation that it disappeared in all subsequent measurements of the "aged" powder, leaving only the broad enhancing pattern, is discussed in section 3.2 below. Later attempts to measure the enhancing pattern with fresh rubrene powder were unsuccessful.

### 3.1.3 Film Sample

Figure 3.3 shows that the fresh rubrene film also displays a broad PL-enhancing triplet resonance but no spin $1/2$ polaron resonance. This triplet resonance has two sets of shoulders, one set at 2850 G and 3900 G and the second at 3000 G and 3700 G. Weak peaks in the enhancing pattern are visible at 3200 G, 3320 G, 3420 G, and 3720 G.

Depending on the quality of the film, the positive (PL-enhancing) pattern lasted up to 2 days. During this period, the morphology of the film changed visibly. Examination with an optical microscope showed that the "fresh" film was semitransparent and uniform as seen in Figure 3.4. Figure 3.5 shows that after "aging" a structure had formed which was inhomogeneous and opaque. This suggests strongly that the film was initially amorphous and recrystallized causing some areas become more opaque depending on the
Figure 3.2 Solid line: 9.45 GHz X-band PLDMR spectrum of “fresh” rubrene powder; dotted line: the spectrum of the “aged” rubrene powder, measured 2 days after the first spectrum.

degree of crystallization. Unfortunately due to the small amount of material in a film, x-ray diffraction of rubrene films returned inconclusive results on this recrystallization process.

The PLDMR of the aged film shows a quenching pattern with a width similar to that of the fresh pattern. Only a single set of shoulders is visible at 2800 G and 3950 G, but the quenching peaks at 3110 G, 3290 G, 3450 G, and 3610 G are prominent.

Figure 3.6 shows the half-field pattern of these triplet excitons, with the characteristic asymmetric lineshape similar to those observed in π-conjugated polymers [79, 117, 118, 120, 121, 124] except that the pattern is quenching rather than enhancing. We note that the lineshapes and amplitudes of the full- and half-field resonances were similar at room temperature and 20 K.

The PL of the aged rubrene film exhibited a linear dependence on the laser power,
Figure 3.3 9.45 GHz X-band PLDMR spectrum of a rubrene film. The spectrum of the "aged" film was measured 3 days after that of the "fresh" film.

Figure 3.4 A magnified image of "fresh" rubrene film where the horizontal dimension is 200 microns.
Figure 3.5 A magnified image of "aged" rubrene film where the horizontal dimension is 200 microns.

Figure 3.6 9.45 GHz X-band half-field PLDMR spectrum of an "aged" rubrene film.
Figure 3.7 The dependence of the total PL intensity of a rubrene film on the power of the exciting Ar$^+$ laser at 488 nm.

$P_{laser}$, as shown in Figure 3.7. This linear dependence suggests that the source of the PL is a monomolecular process. The positive intercept of the fitted line with the ordinate is due to the known background reading of the detector and stray light.

Figure 3.8 shows the PLDMR amplitude in an aged rubrene film excited at $5 \leq P_{laser} \leq 30$ mW. Since the $\Delta I/I$ is independent of $P_{laser}$ within the signal-to-noise ratio of the measurement, it can be inferred that the process producing the resonance is also monomolecular.

The lifetime, $\tau$ of the process responsible for the resonance can be determined from its dependence on the microwave chopping frequency $\nu_c$. As $\nu_c$ increases beyond $1/\tau$, $\Delta I/I$ decreases. As shown in Figure 3.9, the in-phase signal, which is maximal at low $\nu_c$, does not decrease sufficiently to enable a determination of $\tau$. However, the quadrature-signal, which is zero at low $\nu_c$, increases enough at high $\nu_c$ to suggest a lifetime of less than 6 microseconds.
Figure 3.8  The negative (PL-quenching) triplet PLDMR powder pattern excited by 5, 10, 20, 30, and 40 mW Ar\(^{+}\) laser at 488 nm.

![Figure 3.8](image)

Figure 3.9  The dependence of the in-phase and quadrature components of the amplitude of the negative (PL-quenching) triplet resonance in aged rubrene films on the microwave chopping frequency.

![Figure 3.9](image)
3.1.4 Single Crystal Sample

Initially, the PLDMR of a single crystal of rubrene, shown as the solid line in Figure 3.10, displays a broad PL-enhancing triplet resonance without spin $\frac{1}{2}$ polaron resonance which is very similar to the resonance for the fresh rubrene film. It should be noted that this spectrum is suggestive of a polycrystalline sample as opposed to an actual single crystal. As in the aged powder and fresh film, two sets of shoulders are visible in the triplet resonance, the first set at 2850 G and 3900 G and the second at 3000 G and 3750 G; also, weak peaks at 3200 G, 3320 G, and 3410 G are visible in the enhancing pattern.

This enhancing pattern only lasted a couple of hours before a noticeable change occurred. After multiple measurements, the form of the resonance becomes the dashed line as shown in Figure 3.10. A subtle broad enhancing pattern is still visible but a narrower quenching resonance dominates the resonance. Throughout this entire period the amount of PL emitted by the sample decreased until measurements were no longer possible.

The half field pattern of the fresh rubrene crystal shown in Figure 3.11 has the expected asymmetric lineshape except that it is quenching rather than enhancing. As the sample aged, this resonance diminished to the limit of the signal-to-noise of the equipment.

As shown in Figure 3.12, the PL of the aged rubrene crystal displays a linear dependence on the laser power which is similar to the aged rubrene film. This suggests that the source of the PL is a monomolecular process. Further measurements of the aged rubrene crystal resonance were not possible due to its low level of PL.
Figure 3.10  Solid line: 9.45 GHz X-band PLDMR spectrum of a “fresh” rubrene crystal; dotted line: the spectrum of the “aged” rubrene crystal, measured later the same day.

Figure 3.11  The 9.45 GHz X-band half-field PLDMR spectrum of a “fresh” rubrene crystal.
3.2 Discussion and Summary

3.2.1 Powder Sample

As shown in Figure 3.2, the PLDMR of rubrene powder changed irreversibly following laser excitation, as the strong narrow PL-quenching resonance observed initially weakened drastically in subsequent measurements. The state of the powder is unknown. The powder could be in either a mix of polymorphous phases [110] or finely ground crystals.

The initially strong PL-quenching resonance is similar to that exhibited by films sublimed by Lesin et al. onto a substrate at $T_s = 300$ K [111]. That spectrum was attributed to the interchange of the electronic excitation among adjacent molecules. When that interchange proceeds at a rate $\nu \sim [g\beta/h], [g\beta/h]$, where $D$ and $E$ are the zero field-splitting parameters (measured in G) [79, 111, 117, 118, 122, 123], it results
in both averaging of the $D$ and $E$ parameters of the inequivalent molecular sites and merging of pairs of lines into a single line.

The broad positive (PL-enhancing) triplet resonance exhibited by the powder may result from any of the following mechanisms:

(i) Magnetic resonance enhancement of the nonradiative decay of the $1^3B_u$:

$$1^3B_u \rightarrow 1^1A_g + phonons$$

which, by virtue of "ground state recovery" or "ground state repopulation," enhances absorption and hence emission as well [125].

(ii) Magnetic resonance enhancement of the nonradiative decay of the $1^3B_u$, as in process 1, but causing the PLDMR not through ground state recovery, but rather through the diminished nonradiative quenching of the singlet $1^1B_u$ by the triplet $1^3B_u$:

$$1^1B_u + 1^3B_u \rightarrow 3T^* \rightarrow 1^3B_u + phonons$$

where $3T^*$ is a state in the triplet manifold higher than the $1^3B_u$.

(iii) Magnetic resonance enhancement of the recombination of nongeminate pairs of $1^3B_u$ to $1^1B_u$ (Equation (3.1)).

Mechanism (i) is monomolecular, but mechanisms (ii) and (iii) are bimolecular. Further investigation into the laser power dependence of the broad positive triplet PLDMR of rubrene powder will provide more information on whether the process in monomolecular or bimolecular. Unfortunately, later attempts to measure this enhancing powder pattern were unsuccessful due to the unstable nature of the material.

### 3.2.2 Film Sample

Films of rubrene deposited on the walls of the fused silica tubes through evaporation of the toluene solvent changed visibly during 2–3 days. The films went from uniform,
semitransparent apparently amorphous films seen in Figure 3.4. to nonuniform crystallites shown in Figure 3.5. What triggered this change in morphology is unclear, being either laser excitation or recrystallization.

As shown in Figure 3.3, the fresh rubrene films exhibited a positive full-field triplet pattern similar to that of the powder. Typically, this would suggest that the film is amorphous but due to the indeterminate state of the powder no conclusion should be drawn. Fresh films have not been stable or reproducible enough to produce a reliable and meaningful half-field measurement.

A PL-quenching full-field triplet resonance pattern was observed by Lesin et al. [111] which is qualitatively similar to that of the aged films shown in Figure 3.3. However, their triplet X-band (9.5 GHz) PLDMR spectrum exhibited two peaks separated by ~470 G, two shoulders separated by ~660 G, and two steps separated by ~1140 G. In contrast, the PL-quenching spectrum shown in Figure 3.3 contains two “inner” peaks at 3290 and 3450 G, i.e., separated by 160 G, two “outer” peaks at 3110 and 3610 G, i.e., separated by 500 G, and “outer” shoulders at 2800 and 3950 G, i.e., separated by 1150 G. It is suspected that the differences between the spectra may be due to differences between the $D$ and $E$ parameters caused by inequivalent triplet states in inequivalent lattice sites.

Lesin et al. [111] demonstrated a quantitative agreement between the observed resonance and the model mentioned above, which assumes that the mechanism responsible for the resonance is magnetic resonance-induced spin decorrelation of geminate pairs of triplets, which inhibits their back-fusion to the $1^1B_u$ (Equation 3.1). This affects the PL negatively, resulting in the negative, PL-quenching pattern. Since the back fusion of geminate triplet pairs to the $1^1B_u$ is a monomolecular process, the resonance amplitude $\Delta I/I$ should be independent of the exciting laser power $P_{laser}$, as indeed observed by Lesin et al. [111] and verified in Figure 3.8 (see Sec. 3.1 above).
3.2.3 Single Crystal Sample

The single crystals of rubrene were no more stable than the other types of samples making measurements difficult. In addition, the PL of the crystal samples degraded quickly, limiting the measurements that could be obtained. From a visual inspection, no change could be seen as opposed to the film samples which could be seen with the naked eye.

The enhancing triplet powder pattern for a “fresh” crystal is very similar to that of the “fresh” rubrene film suggesting that they shared the same properties initially and share the same mechanisms. The “fresh” crystal had a quenching half-field resonance which implies that the triplets followed a different process than that at full-field or there is more than one triplet present.

For the “aged” rubrene crystal, an entirely different full-field resonance developed. The most notable feature being its low level which hindered any useful measurements of the pattern. The linear dependence of the PL on the laser power suggests that a monomolecular process is responsible for the PL in the “aged” crystal which is consistent with the “aged” films despite the difference of the resonance shape.
4 STUDIES ON TRIS (8-HYDROXYQUINOLINE)

ALUMINUM

Tris (8-hydroxyquinoline) aluminum (Alq₃) has received a lot of attention as the emitting layer in OLEDs. Alq₃, which is shown in Figure 4.1, belongs to a class of chelate compounds consisting of 8-quinolinol groups and a metal ion [126] and more specifically, in a class which have fluorescent properties [127]. Through vapor deposition, Alq₃ may form a smooth, thin film [128, 129] which is necessary for OLEDs. Typically in an OLED, Alq₃ is doped with another organic material which improves the efficiency and allows the color to be tuned [129]. Since it showed potential for commercialization, much effort was placed into further improving the quality of the OLEDs [130, 131]. Despite the research done on its characteristics in devices and how these devices can be optimized, no previous PLDMR studies of Alq₃ have been found in the literature.

From absorption spectra and measurements, the optimal wavelength to excite Alq₃ peaks at 389 nm [132, 133]. To achieve this excitation, the argon-ion laser with visible emission could not be used so a UV lamp with a 353 nm blazing mirror provided the photoexcitation. Because this system set up lacks the stability of the laser, more noise was inherent in the measurement, limiting which measurements could be taken.

Of the Alq₃ samples studied in this chapter, only the powder samples displayed resonances large enough for meaningful interpretation. The powder sample exhibited a weak enhancing spin $\frac{1}{2}$ polaron resonance as well as both quenching and enhancing triplet resonances. As with typical polymers, the polaron resonance is thought to be
enhancing through indirect non-radiative PLDMR. The broad quenching triplet powder pattern at full-field may be the result of magnetic resonance induced spin decorrelation of the geminate triplet pairs. The triplet pattern at half field is enhancing, opposite of the pattern at full field, which suggests that a different process is occurring such as the nongeminate triplet-triplet annihilation to singlets.

4.1 Results

4.1.1 Solution Sample

Very dilute solutions of Alq3 were prepared by the following method. A small amount of Alq3 powder was dissolved into benzene which was well past the saturation point. After the precipitate had settled, a small amount of the solution was siphoned off. This amount of solution was further diluted with more benzene to prevent a saturation point being reached when the solution sample was cooled to the appropriate temperature. Alternate solvents that may allow for more concentrated solutions in future include
chloroform, ethanol, or carbon tetrachloride [133].

Despite the low concentration and the low quantum yield of the fluorescence in solution [133], the photoluminescence available was high enough for a PLDMR measurement. There was no detectable resonance above the noise of the system at either full or half field. A lack of a resonance is expected for solutions in general because of the separation of individual molecules which hinders the intermolecular coupling. Without this coupling, PLDMR in \( \pi \)-conjugated molecules is prevented [79, 111, 117-123].

4.1.2 Powder Sample

Figure 4.2 shows the full-field PLDMR of a powder sample of Alq3. A broad negative (PL-quenching) triplet pattern is observed with a full width at half maximum of about 720 G. No features, such as shoulders or peaks, were apparent in this triplet pattern above the noise. A narrow PL-enhancing resonance occurs at 3380 G which is suggestive of a polaron peak.

The half-field PLDMR of Alq3 powder is shown in Figure 4.3. This triplet pattern has the characteristic asymmetric PL-enhancing lineshape observed in \( \pi \)-conjugated polymers [79, 117, 118, 120, 121, 124].

Because a UV lamp was used instead of a laser, precise power control of the exciting light over a large range was unavailable. For the possible values, shown in Figure 4.4, the PL is roughly linear versus the power of the exciting wavelength which implies that the process responsible for the PL is monomolecular. For a bimolecular process, one would expect the dependence to be supralinear. It is also possible that the PL is leveling off at higher exciting powers which may be due to saturation of the material.

The full-field PLDMR amplitude excited at \( 5 \leq P_{light} \leq 15 \) mW is shown in Figure 4.5. The broad quenching triplet pattern does not significantly reduce within the noise for lower exciting powers. The amplitude the narrow peak, measured from the lowest point of the broad quenching pattern to the top of the peak, increases considerably
Figure 4.2 9.45 GHz X-band full-field PLDMR spectrum of Alq₃ powder.

Figure 4.3 9.45 GHz X-band half-field PLDMR spectrum of Alq₃ powder.
Figure 4.4  The dependence of the total PL intensity of Alq₃ powder on the exciting wavelength power.

for different exciting powers from $0.9 \times 10^{-5}$ to $2.1 \times 10^{-5}$ as the power of the UV lamp increases from 5 mW to 15 mW. The half-field PLDMR amplitude is also affected by the elevation of the exciting power as seen in Figure 4.6, increasing from $4 \times 10^{-5}$ to $5.2 \times 10^{-5}$ over the same range of power from the lamp. These results are plotted in Figure 4.7 to display the amplitude dependence on the power of the lamp. Both the full-field and the half-field resonance show a roughly linear dependence of approximately the same slope. This suggests that the processes involved in the narrow enhancing polaron peak and the enhancing half-field triplet resonance are not monomolecular but bimolecular. The full-field triplet resonance seen in Figure 4.5 does not appear to be affected by the change in lamp power. This lack of dependency suggests that the process involved in the broad quenching pattern is a monomolecular process.

Figure 4.8 shows the temperature dependence of the full-field PLDMR of Alq₃ powder. The broad quenching pattern is largest for 20 K and 50 K and disappearing into the
Figure 4.5  The full-field PLDMR of Alq₃ powder excited by 5, 7, 10, and 15 mW at 353 nm from an UV lamp.

Figure 4.6  The half-field PLDMR of Alq₃ powder excited by 5, 7, 10, and 15 mW at 353 nm from an UV lamp.
Figure 4.7  The dependence of the $\Delta I/I$ amplitude of Alq$_3$ powder on the power of the exciting wavelength. Full-field data is from Figure 4.5 measured from the lowest point of the triplet resonance to the top of the polaron peak. Half-field data is from Figure 4.6.
Figure 4.8  The full-field PLDMR of Alq₃ powder at various temperatures.

noise for lower and higher temperatures. Measuring the amplitude of the narrow spike from the level of the corresponding triplet pattern to the peak shows that the strength of the narrow enhancing spike shows a decrease for an increase of temperature. The half-field response to the temperature, shown in Figure 4.9, is similar to the full-field response in that the greatest PLDMR occurs at 20 K and decreases for lower and higher temperatures. For 125 K and higher, the half-field PLDMR can no longer be detected.

4.1.3 Film Sample

The solution used for the solution sample described early was used in producing the film sample by the solution evaporation method outlined in section 2.6. To the naked eye, the film produced by this method could be seen to be of very low quality. Under an optical microscope, it is apparent that a uniform film is not being produced as shown in Figure 4.10. It appears that material is precipitating out of the solution and small Alq₃
crystals are forming during the evaporation of the solution. By slowing the rate of the solution, the size of these crystals can be increased to long crystalline fingers shown in Figure 4.11.

No PLDMR resonance could be detected at full-field for these Alq₃ “film” samples. However at half-field, a very weak resonance was detected which was barely above the noise level for the measurement as seen in Figure 4.12.

4.2 Discussion and Summary

4.2.1 Film Sample

This points to a weakness of making films in the solution evaporation technique as described in section 2.6. Another technique must be used, such as thermal vacuum evaporation, to provide true films and not just a powder of precipitated crystals. Typically, Alq₃ can form very smooth thin films by vapor deposition [128, 129]. The technique
Figure 4.10 A magnified image of Alq$_3$ “film” made at a moderate evaporation rate where the horizontal dimension is 200 microns. Note that the lighter areas are free of material while dark regions are from the Alq$_3$. 
Figure 4.11 A magnified image of Alq₃ "film" made at a low evaporation rate where the horizontal dimension is 200 microns. Note that the lighter areas are free of material while dark regions are from the Alq₃.
Figure 4.12 9.45 GHz X-band half-field PLDMR spectrum of Alq3 “film.”

of vapor deposition is typically used to produce films on flat substrates rather than inside fused silica tubes that can be inserted into the PLDMR equipment. A small flat substrate may be inserted into the PLDMR equipment but the known method for this loses the ability to seal the sample in a vacuum leaving the sample open to air during the insertion process. This exposure to air and more specifically oxygen is known to be detrimental to Alq3, converting it to a dark, non-emissive polymer [132]. During an actual measurement, this degradation from air will be prevented by the helium gas flowing through the cryostat cavity.

One would expect this “film” of crystals to behave similarly with the powder due to the random orientation of the crystals in the “film” and in the powder. The difference between the powder and this “film” of crystals is the spacing between crystals and the strength of the PLDMR is considerably weaker or nonexistent for the “film.” This situation is similar to the solution which supports the idea that the intermolecular coupling
is required for PLDMR and that the separation between molecules hinders this coupling.

**4.2.2 Powder Sample**

Of the Alq₃ samples studied in this chapter, only the powder samples displayed resonances large enough for meaningful interpretation. The powder sample exhibited a weak enhancing spin \( \frac{1}{2} \) polaron resonance as well as both quenching and enhancing triplet resonances. As with typical polymers, the polaron resonance is thought to be enhancing through indirect non-radiative PLDMR.

The broad quenching triplet powder pattern at full-field may be the result of magnetic resonance induced spin decorrelation of the geminate triplet pairs. The evidence in Figure 4.5 that the resonance amplitude is independent of the exciting power of the UV lamp, suggests that the process involved is monomolecular which supports the back fusion of geminate triplet pairs.

The triplet pattern at half-field is enhancing, opposite of the pattern at full-field, which suggest that a different process is involved. This is further supported by the dependence of the resonance on the power of the lamp. The full-field pattern displays characteristics of a monomolecular process while the data suggests that the half-field pattern is based upon a bimolecular process such as the nongeminate triplet-triplet annihilation to excited singlets.
5 PRELIMINARY INVESTIGATIONS ON 4,4'-BIS (9-CARBAZOLYL) BIPHENYL

4,4'-Bis(9-carbazolyl)biphenyl (CBP), whose structure is shown in Figure 5.1, has drawn increasing attention for use in OLEDs. CBP emits in the blue to violet region with a peak at roughly 400 nm which makes it very attractive as a host material [134, 135] as well as a hole transport layer [136]. With the appropriate dopant, red and green light emitting devices using CBP as the host material have been produced [134, 137]. CBP has also been used as the host material in optically pumped organic semiconducting lasers [16].

In OLEDs, doped CBP produces light by phosphorescence which makes use of both singlets and triplets. This raises the theoretical maximum internal efficiency to 100% [134]. Also, CBP-based devices are the most stable organic light emitting device reported to date [138].

Figure 5.1 The structure of 4,4'-bis(9-carbazolyl)biphenyl (CBP).
CBP has a strong absorption spectra ranging from 250 nm up to 360 nm. In our studies, a UV lamp with a 308 nm blazing mirror provided photoexcitation in this range. A 335 nm cutoff filter was used to remove the exciting wavelength from the signal and help reduce the noise. CBP is also sensitive to light and degrades under exposure. The triplets produced by photoexcitation have been suggested as a cause of the long term degradation [138]. The degradation of the sample and the noise inherent in the UV system severely limited the measurements that could be performed.

CBP powder exhibited a weak enhancing spin $\frac{1}{2}$ polaron resonance which disappeared after the initial measurements. Also present initially and disappearing after time was a subtle broad quenching pattern at full-field. The triplet resonance at half-field was much more stable and allowed more measurements to be taken before becoming undetectable. The half-field triplet pattern has an unusual enhancing shape containing two distinct peaks which suggest that more than one type of triplet is present in CBP.

### 5.1 Results

#### 5.1.1 Powder Sample

The full-field PLDMR of CBP powder is shown in Figure 5.2. A narrow positive PL-enhancing resonance occurs at 3380 G suggestive of a polaron peak. A broad PL-quenching triplet pattern appears but is too obscured by the noise to be measured. After a several measurements, a resonance at full field could no longer be detected.

Figure 5.3 shows the half-field PLDMR of CBP powder which does not have the characteristic asymmetric lineshape common to $\pi$-conjugated molecules. The resonance is PL-enhancing, which is typical, but it contains two peaks and an overall asymmetry. This suggestive of more than one type of triplet in CBP powder.

As mentioned earlier, CBP is sensitive to light and will degrade on exposure. The resonance at full-field disappeared entirely and the resonance at half-field reduce sig-
Figure 5.2 9.45 GHz X-band full-field PLDMR spectrum of CBP powder.

Figure 5.3 9.45 GHz X-band half-field PLDMR spectrum of CBP powder.
nificantly as seen in Figure 5.4. This made comparative measurements difficult and introduced another level of error.

Typically, the peak values of the resonance are plotted against the microwave chopping frequency, yielding the lifetime of the process responsible for the resonance. As seen in Figure 5.5, no detectable change occurred which is not very unexpected for the in-phase signal. Unfortunately, the signal-to-noise ratio of the quadrature signal was too poor to yield the lifetime.

The photoexcitation power dependence of the half-field resonance is shown in Figure 5.6. Despite the level of noise and the limited power levels, it can clearly be seen that the resonance decreases as the power is lowered from 15 mW to 5 mW as well as a sharp drop in the resonance between 15 mW and 19 mW of power. However, the process involved in producing the resonance at half-field is unlikely to be monomolecular because the amplitude of the resonance is not independent of the laser power. Figure 5.7 shows
5.2 Discussion and Summary

5.2.1 Powder Sample

CBP is an important material in upcoming OLEDs due to its stability as a host material \[135, 138\]. Ironically, measurements on this sample are hampered by its sensitivity to UV light and its rapid degradation during measurements. It has been suggested that triplets are causing the degradation of the material \[138\], which can not be avoided with the PLDMR technique. It may be interesting in the future to dope CBP with a phosphor to provide a way to remove the triplets and study this more stable system with PLDMR.
Figure 5.6   The half-field PLDMR of CBP powder excited by 5, 9, 15, and 19 mW at 308 nm from a UV lamp.

Figure 5.7   The dependence of the total PL intensity of CBP powder on the exciting wavelength power.
The broad PL-quenching pattern at full-field that is detected in the “fresh” CBP powder could be due to magnetic resonance induced spin decorrelation of triplet pairs. The half-field resonance is PL-enhancing which suggests that another process is involved in that resonance. The measurements at half-field also contain a dual peak resonance which suggests that there is more than one type of triplet present in CBP. Better data for microwave chopping dependency might show multiple lifetimes which would confirm the existence of multiple triplets. Also, improved data for the photoexcitation power dependence would provide more information about the processes involved.
APPENDIX

SELECTED EXPERIMENTAL PROCEDURES

Liquid Helium System

Filling the Liquid Helium Dewar

1. Remove the transfer tube from the dewar.
   (a) Remove the cryostat insertion end of the transfer tube from the cryostat.
   (b) Plug the cryostat transfer tube entry.
   (c) Place the protective cover over the cryostat insertion end of the transfer tube.
   (d) Loosen the dewar’s transfer tube seal (at the top of the dewar).
   (e) Remove the transfer tube from the dewar. Be aware that parts of the transfer tube will still be extremely cold.
   (f) Close the dewar’s transfer tube valve.
   (g) Plug the dewar’s insertion opening.
   (h) Place the transfer tube in the appropriate holder on the east wall.

2. Close the dewar’s vent valve.

3. Close the lab’s helium recovery line (the valve is located near the clock).

4. Remove the gum-rubber recovery line from the dewar’s vent valve.
5. Bring the dewar to the “low temp” lab (on the first floor behind the elevators).

6. Attach one of the unused gum-rubber tubes to the dewar’s vent valve.

7. Open the helium recovery valve.

8. Open the dewar’s vent valve.

9. The dewar should be filled within a day depending on the “low temp” lab’s schedule.

10. Close the dewar’s vent valve.

11. Close the helium recovery valve.

12. Remove the gum-rubber tube from the dewar’s vent valve.

13. Return the dewar to the lab.

14. Attach the gum-rubber recovery line to the dewar’s vent valve.

15. Open the helium recovery line (the valve is located near the clock).

16. Open the dewar’s vent valve.

17. Insert the transfer tube when desired.

Preparing the Transfer Tube for Insertion

1. Attach the transfer tube’s vacuum flange to the valve on the vacuum manifold.

2. Slowly open the vacuum manifold valve keeping the pressure below $10^{-1}$ mbar.

3. Wait until a vacuum of less than $10^{-4}$ mbar or one hour, whichever is longer.

4. Slowly open the transfer tube vacuum valve keeping the pressure below $10^{-2}$ mbar.
5. Allow the transfer tube to be pumped down overnight which should reduce the pressure to less than $10^{-5}$ mbar.

6. Close the transfer tube vacuum valve.

7. Close the vacuum manifold valve.

8. Detach the transfer tube from the vacuum manifold.

**Insert the Transfer Tube into the Liquid Helium Dewar**

1. Attach the flow control vacuum hose to the suction nozzle of the transfer tube.

2. Make sure protective cover is over the cryostat insertion end of the transfer tube and has formed a seal.

3. Close the dewar’s vent valve.

4. Open the dewar’s transfer tube valve.

5. Insert the transfer tube approximately 20 inches into the dewar.

6. Open the flow control valve two full turns.

7. Turn on the flow control vacuum pump. Note that the flow rate will indicated no flow—this is normal. The pressure should not drop below -0.8 bar.

8. Slowly start lowering the transfer tube into the dewar. The lowering process should take approximately two to three minutes.

9. When the pressure release valve on the dewar begins to hiss, open the dewar’s vent valve and continue to lower the transfer tube into the dewar. Keep an eye on the ball check valve of the room’s recovery line to monitor the speed of the insertion.
10. With tube fully inserted, watch the protective cover and the flow control meters. When helium starts to flow, the flow rate should increase and the pressure will drop.

11. When frost begins to form on the protective cover, fully close the flow control valve.

12. Turn off the flow control vacuum pump.

13. Close dewar’s vent valve.

14. Wait until frost fully evaporates which should take about a half an hour.

15. Remove protective cover from cryostat insertion end of the transfer tube.

16. Insert the cryostat insertion end into the cryostat and seal.

17. Open dewar’s vent valve.

18. Helium system is now prepare to operate.

**Laser System**

**Activating the Laser System**

1. Turn on the Spectra-Physics argon ion laser.

   (a) Open the two water valves marked LASER.

   (b) Turn on the water pump. The switch is on the small box mounted to the top of the magnet power supply console.

   (c) Turn on breaker 18 in the breaker box next to the door. Be careful not to accidentally switch any of the other breakers off—the switch is small and your hand can easily slip off the switch as it snaps on.
(d) On the laser power supply located under the optics bench, check that the three line lights on the laser power supply have lit up indicating that the current is sufficient and stable. Also check that the water light is on and the light labeled hot is not on which means that cooling water subsystem is operating correctly.

(e) Verify that the master control key switch is on. Note that this does not affect the operation of the laser, only the interlock system.

(f) Make sure that the meter function selector is in the 50 amp position.

(g) Check that the mode switch to current mode (the left position).

(h) Verify that the field control is at maximum (fully clockwise).

(i) Set the current control to roughly mid-range or less. Note that if this was set to specific level the last time the laser was on, it does not need to be adjusted.

(j) Switch on the main panel breaker on the laser power supply.

(k) Wait until the ready light comes on (it should take about 30 seconds).

(l) Press the start button.

2. Activate the laser stabilizer located in rack A.

   (a) If the laser stabilizer is not on, turn it on.

      i. Turn on the switch marked POWER.

      ii. Turn on the switch marked TEMP CONTROL.

      iii. Wait 1–2 hours for the internal components to reach a stable temperature.

   (b) Turn on the switch marked HIGH VOLTAGE.

3. Enable the interlock system.

   • The interlock control box is mounted to the optics bench next to the laser.
(a) Turn the key switch to the on position.
(b) Press the start button.
(c) Verify that the shutter is not interfering with the laser beam.

Deactivating the Laser System

1. Disable the interlock system.
   - The interlock control box is mounted to the optics bench next to the laser.
     (a) Turn the key switch to the off position.
     (b) Verify that the shutter has closed.

2. Deactivate the laser stabilizer located in rack A.
   (a) Turn off the switch marked HIGH VOLTAGE.
   (b) (Optional) Turn off the laser stabilizer.
      - Leaving the laser stabilizer on keeps internal components at a stable temperature so it may be reactivated in less time.
      i. Turn off the switch marked TEMP CONTROL.
      ii. Turn off the switch marked POWER.

3. Turn off the Spectra-Physics argon ion laser.
   (a) Switch off the main panel breaker on the laser power supply which is located under the optics bench.
   (b) Turn off breaker 18 in the breaker box next to the door. Be careful not to accidentally switch any of the breakers off.
   (c) Let the water and pump continue to run for about 15 minutes to cool the system down.
(d) Turn off the water pump. The switch is on the small box mounted to the top of the magnet power supply console.

(e) Close the two water valves marked LASER.

Microwave System

Activating the Microwave System

1. Open the two water valves marked ODMR.

2. Make sure the PIN switch is receiving a signal (turn on the lock-in amplifier located in rack A).

3. Verify that the Gunn diode assembly is unbiased.
   - The Gunn diode power supply on top of rack B should have the bias adjust knob turned fully clockwise.

4. Turn on the microwave frequency counter located in rack B.

5. Turn on the Gunn diode power supply.

6. Wait until a frequency reading appears on the microwave frequency counter. If it reads zero, verify that the bias adjust of the Gunn diode power supply is fully clockwise and cycle the power of the Gunn diode power supply.

7. Turn on the microwave switch power supply located on top of rack B.

8. Turn on the linear amplifier power supply located in rack B.
   - This power supply should have been set up before hand to operate at 15 volts in constant voltage mode with a current of roughly 3 amps.
9. Turn on the oscilloscope monitoring the incoming and reflected microwave signal which is in rack B.

10. Turn on the microwave power meter located on the microwave table above the magnet.

11. Wait about an hour for the system to thermally stabilize.

12. Adjust the attenuation dial located in between the Gunn diode and the microwave switch of the microwave setup to the desired level.

Deactivating the Microwave System

1. Adjust the attenuation dial located in between the Gunn diode and the microwave switch of the microwave setup to the maximum attenuation level.

2. Turn off the microwave power meter located on the microwave table above the magnet.

3. Turn off the oscilloscope in rack B.

4. Turn off the linear amplifier power supply located in rack B.

5. Turn off the microwave switch power supply located on top of rack B.

6. Turn the bias adjust of the Gunn diode power supply down to zero (fully clockwise).

7. Turn off the Gunn diode power supply.

8. Turn off the microwave frequency counter located in rack B.
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