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$C_{60}$ purification and $C_{60}$ film characterization

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Rice University, 1994
RICE UNIVERSITY

C$_{60}$ Purification and C$_{60}$ Film Characterization

by

Richard D. Averitt

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C$_{60}$ Purification and C$_{60}$ Film Characterization

Richard D. Averitt

Abstract

A method is described which utilizes the difference in vapor pressure between C$_{60}$ and heavier fullerenes to produce C$_{60}$ powder with a purity of 99.97%. Using the material from this process allows for the growth of high purity polycrystalline C$_{60}$ thin films. These films are characterized using Raman spectroscopy and temperature dependent photoluminescence. The temperature dependence of the photoluminescence spectra indicates that both intermolecular and intramolecular processes are involved in the radiative recombination of the excited states. A model is proposed to describe the temperature dependence of the photoluminescence. A possible interpretation of this model is that there is a barrier to the formation of self trapped excitons.
Acknowledgments

Uhhh, huuh huuh, huhh, there are so many people to thank, where do I begin? Well, my parents support and understanding mean more to me than anything else, so my heart goes out to them.

Then, of course, there are my war buddies who have been with me from the get go. Matt, for reasons too numerous to list, has been a much appreciated companion since day one. Alan, in addition to being an excellent mentor, is a friend whom I was sad and happy to see move on and undoubtedly up.

Dip is a source of inspiration, the consummate thinker, and a great cook besides. Jay’s real world outlook has helped me to understand there is more to life than science, i.e. basketball. Phil, the potato and tuna man, has added a unique and enjoyable dimension to this research group.

Finally, I must thank Dr. Halas. Her perspective has been invaluable to my education.

Peace.
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Chapter 1

Introduction and Outline

1.1 Introduction

Research to elucidate the properties of $C_{60}$, especially in the solid state, remains an active area. This comes as no surprise given the wide variety of applications associated with fullerenes. For example, $C_{60}$ is an optical limiter [1], when doped with alkali metals it becomes superconducting [2], it shows behavior characteristic of a disordered material [3, 4], polymer-$C_{60}$ heterojunctions have been fabricated [5], and $C_{60}$ has been used as a photoresist to create 1 micron linewidths [6]. Despite this active research, there are gaps in our understanding about the fundamental properties of solid $C_{60}$. Much of this ambiguity results from the lack of consistently pure material available to researchers and the inadequate characterization of $C_{60}$ thin films. Thus, although there is a good understanding of solid $C_{60}$ crystalline structure [7, 8, 9], and equilibrium electronic structure [10, 11, 12], those solid state properties most sensitive to the presence of impurities, for example, excited state dynamics, are only beginning to be understood.
1.2 $C_{60}$ Properties

For completeness, a brief account of $C_{60}$ molecular and solid properties is given below.

More detailed discussions can be found in [4, 13].

As is well known, $C_{60}$ consists of 60 carbon atoms at the vertices of a regular truncated icosahedron. This soccer ball geometry is composed of 20 hexagons and 12 pentagons, with the average C-C bond length being 1.44 Å. The sides of adjoining hexagons consist of double bonds, while the pentagonal edges are single bonds. The sixty valence electrons in $\pi$ orbitals of $s^0p$ character are orthogonal to the surface and give $C_{60}$ a closed electron shell [14]. This closed shell structure accounts for the limited reactivity of $C_{60}$. Including the delocalized $\pi$-electrons, the $C_{60}$ molecule has a diameter of 10.18 Å. The HOMO-LUMO ($h_u \cdot t_{1u}$ or $S_0 \cdot S_1$) gap is approximately 1.9 ev, but this transition is symmetry forbidden in the isolated molecule.

In the solid state at room temperature, $C_{60}$ crystallizes in the face-centered cubic structure with a lattice constant of 14.15 Å [7]. The density of this Van der Waals solid is $1.72 \text{ g/cm}^3$. The molecules freely rotate about arbitrary axes of rotation at room temperature thus giving solid $C_{60}$ a degree of rotational disorder. However, at 260 K solid $C_{60}$ undergoes a phase transition to a simple cubic lattice, with a lattice constant
of 14.10 Å[7]. In the 90 - 260 K temperature range, the molecules jump between two energetically favorable configurations. Below 90 K the molecules lock into a static configuration. The changes in the structure of crystalline C₆₀ with temperature are discussed in more detail in Chapter 6.

The electronic structure in the solid state has been the subject of intense investigation. Initial theoretical calculations suggested that solid C₆₀ is a semiconductor with a direct bandgap of 1.5 eV [10]. More recent quasiparticle calculations yield a bandgap of 2.15 eV with approximately 1 eV widths for the HOMO and LUMO derived bands [11]. This is in agreement with joint photoemission and inverse photoemission studies by Lof et al. which yield a bandgap of 2.3 eV [12]. Lof et al. calculate the on-site molecular C₆₀ Coulomb interaction (U) to be ~ 1.6 eV and they suggest this leads to Frenkel type molecular excitons in the 1.5 - 2 eV range [12]. This large Hubbard U is indicative of a strongly correlated system. In strongly correlated systems the ordinary band picture is inappropriate and the solid shows strong molecular character [15, 16]. Several optical studies support this molecular solid interpretation for C₆₀, for example, the similarity between the optical absorption spectrum of solid C₆₀ and C₆₀ solution, and Raman spectroscopy of solid C₆₀ (see Chapter 4). Treating solid C₆₀ as a hybrid semiconductor-molecular solid is not unreasonable and transient and
steady-state photoconductivity experiments as well as a Dember effect study suggest that below 2.3 eV the excited states are of localized excitonic character, while above 2.3 eV free charge carriers can be generated [17, 18]. Finally, it should be noted that the symmetry forbidden HOMO-LUMO transition of the isolated $C_{60}$ molecule is weakly allowed in the solid due to symmetry lowering of vibrational origin. This transition is of extreme importance in the understanding of the energetics of solid $C_{60}$.

1.3 Outline

In order to characterize solid $C_{60}$ (and fullerenes in general) it is necessary to minimize the structural and electronic effects of impurities. In the case of $C_{60}$, the impurities come in two distinct classes; heavier fullerenes such as $C_{70}$, and solvents such as toluene. Both of these dopants can alter the observed behavior of solid $C_{60}$. Chapter 2 presents a method for the solvent free vapor phase purification of $C_{60}$. This high purity $C_{60}$ powder provides the material for the growth of $C_{60}$ thin films, with reasonable control of the impurities. Chapter 3 describes the growth and handling of the $C_{60}$ thin films. In addition, this chapter describes the experimental set up used in both the Raman and photoluminescence studies. Chapter 4 describes the Raman charac-
terization and Chapter 5 details the photoluminescence studies. Finally, Chapter 6 summarizes the important points of this work, and offers directions for the continued study of C_{60} thin films.
Chapter 2

Vapor Phase Purification of \( C_{60} \)

2.1 Introduction

As mentioned in Chapter 1, there has been considerable success in the characterization of \( C_{60} \). However, some investigations have been hindered because of the residual solvent remaining with the fullerenes purified using conventional solvent based chromatographic separation processes [19, 13]. This inadvertent intercalation of solvents sometimes leads to ambiguities in the reported properties of fullerene solids [19, 13, 20, 21]. Vacuum annealing of fullerene powder is currently the most common procedure to outgas residual solvents [19]. However, some impurities, such as partially pyrolyzed solvent and their fullerene reaction products which are formed during the vacuum annealing process and high boiling point solvent impurities, will likely remain in the powdered samples [22]. Thus, it is important to develop useful fullerene purification methods that are either entirely solvent free or capable of removing all remaining traces of solvent during the purification process.
Perhaps the most important area of fullerene research where separation methods are crucially important is in the synthesis of endohedral fullerenes [23]. Gas phase separation and purification would be a viable alternative and would represent a major step towards the purification of species that are either highly reactive, not soluble, or suffer irreversible retention on the stationary phase during conventional chromatography. For example, some of the compounds that have not been successfully isolated by conventional methods and would make good candidates for gas phase separation are the endohedral fullerenes La@C_{60}, and U@C_{28} [23, 24, 25].

The first gas phase separation experiments to demonstrate that fullerenes of varying mass could be partially purified by utilizing the differences in their vapor pressure were performed by Cox et al. [26]. A later experiment by Yeretzian et al. showed the applicability of gas phase methods to partially separate the insoluble fullerenes C_{74} and La@C_{74} [27]. However, both of these experiments were limited in their separation ability because the geometry of the apparatus allowed the fullerenes to effuse with mean free paths that were considerably greater than the length of the temperature gradient. Much higher separation efficiency is obtained when the mean free path is restricted to a small fraction of the temperature gradient. This restriction can be
accomplished either geometrically with baffles or by the use of an inert buffer gas as first suggested by R. N. Compton [28].

This chapter describes a purification method that utilizes the difference in vapor pressure between C_{60} and the higher fullerenes to produce ultrahigh purity C_{60}. Raw fullerene soot or fullerene extract is introduced into one end of a distillation column lined with a series of evenly-spaced baffles with circular perforations. The fullerene starting material is heated under high vacuum to 970 K, while a linear temperature gradient is simultaneously established along the length of the column. As the mixed fullerene vapor traverses to the cooler region of the column by effusion through the perforated baffles, it becomes enriched in the more volatile species. In addition, because of the repeated evaporations and condensations necessary to move down the column, virtually all volatile impurities are removed and pumped away. Depending upon the initial starting composition, the final purity can be quite high. C_{60} purity as high as 99.97% has been obtained.

2.2 Theoretical considerations

If fullerenes are sublimed into the gas phase under high vacuum conditions, their mean free paths can be considerably longer than the distillation apparatus. The
net result is mass transport without any separation or purification of the fullerenes. Figure 2.1a.) depicts this process. The introduction of a buffer gas such as He is one method for restricting the mean free paths of the fullerenes. This method has been successfully employed by Compton et al. and Figure 2.1b.) shows this method. The drawbacks of this diffusional purification process are potential limitations on the achievable purity and the lack of sufficient condensation area for the fullerenes.

Figure 2.1c.) depicts the method described in this work. Baffles are used to geometrically restrict the mean free paths of the fullerenes. By making a few simplifying assumptions, it is relatively easy to develop a useful model to describe this distillation process. Because the perforations in the baffles can be made small compared to the geometrically restricted mean free path of the fullerenes, effusion is the dominant mass transport mechanism in the column. This process is easily understood and modeled using the Knudsen effusion equation [29]. The theoretical rate of effusion through an aperture for each fullerene component (in gm/sec) is

\[
\frac{dW_n}{dt} = p_n A \sqrt{\frac{M_n}{2\pi RT}}
\] (2.1)

where \( p_n \) is the equilibrium vapor pressure of the \( n^{th} \) component in dynes/cm\(^2\), \( T \) is the temperature in degrees Kelvin, \( M_n \) is the molecular weight of the \( n^{th} \) component,
Figure 2.1: a.) mass transport without purification b.) diffusional purification c.) effusional purification using baffles to restrict the mean free paths of the fullerenes
A is the effective aperture area in \(cm^2\), and \(R\) is the gas constant. It is important to note that the effusion equation also describes the maximum theoretical rate of evaporation of a substance into a perfect vacuum.

This process is analogous in many respects to a conventional molecular distillation process [29]. The primary differences between the method described here and molecular distillation is that fullerenes vaporize directly from a solid solution instead of from the liquid and that molecular distillation is usually performed with only one theoretical plate of separation. In this design, one theoretical plate of separation is obtained for each of the baffle plates present in the column. However, the actual degree of separation at each step will depend upon the behavior of the vapor pressure of individual fullerenes in equilibrium with a fullerene solid solution.

Using equation 2.1, a simple model of the molecular distillation column has been devised. The region between two adjacent baffles, for the purpose of simulation, is a cell at a specific temperature. Each cell has a net flux comprised of the \(C_{60}\) and \(C_{70}\) flux into the cell minus the flux exiting at the other end. Assuming the conditions for molecular distillation are valid for each cell, the net flux of \(C_{60}\) and \(C_{70}\) can be calculated using Equation 2.1. This results in a set of \(2N\) differential equations where \(N\) is the number of cells. These equations are readily integrated to yield the mass of
each component in each cell as a function of time. The temperature of each cell is calculated from the value of the temperature gradient at the middle of the cell. The pressure of $C_{60}$ and $C_{70}$ in each cell is determined from data obtained by Mathews et al. [30, 31]. Figure 2.1 is a plot of $C_{60}$ and $C_{70}$ vapor pressure vs. temperature based the Mathews data. These pressures can be corrected to take into account the effect of the solid solution composition if needed, but reasonable agreement between theory and experiment is obtained when the pressures are considered independent of concentration. With this assumption, the amount of separation is determined solely by the difference in the rates of effusion. The determination of the contribution of distillation to the separation process will depend upon separate experiments to measure the partial pressures of fullerenes above solid solutions.

The use of equilibrium vapor pressure data in our simulation is reasonable since calculations show that a steady-state flow condition is quickly achieved. In practice, there are transient periods when establishing the temperature gradient and when cooling down the apparatus. These transient periods have not been included in the simulation, but could be added with minor modifications. In practice they have only a minor effect on the final fullerene mass distribution. This simulation has proven quite adequate for determining the number of baffles required to achieve a particular degree
Vapor Pressure vs. 1000/T

C. K. Mathews et al., Fullerene Science and Technology 1, 101 (1993)

Figure 2.2: Mathews et al. Vapor Pressure Data
of separation and for optimizing the temperature gradient. Since vapor pressure data
are not presently available for fullerenes heavier than $C_{70}$, they are not included in
the simulation. As separation data for higher fullerenes is obtained, it will be possible
to apply parameter estimation techniques to the model to extract vapor pressures as
a function of temperature for higher fullerenes. This would allow a quick method
to determine the enthalpy and entropy of vaporization for a broad range of higher
fullerenes. Appendix A contains the Fortran code for the simulation. The integration
routine is not included as it can be found elsewhere [32].

2.3 Experiment

The apparatus, shown in Figure 2.2, consists of a 100 cm long, 6.35 cm diameter, frac-
tional distillation column made from stainless steel tubing. The system is equipped
with a 60 l/s turbo pump and an ion gauge. At room temperature, the base pres-
sure of the system is $10^{-9}$ torr. The tube end opposing the turbo pump functions as
the loading port. The stainless steel tube is lined with a 4.5 cm diameter removable
quartz tube containing the separation baffles. The baffle configuration consists of 58
stainless steel disks with circular perforations. The baffles are spaced every 0.9 cm
along a quartz supporting rod. The perforations are 0.16 cm diameter holes, with each baffle having about 25% open area for sufficient conductance.

The mass flow down the column is initiated by subliming the starting material at a temperature of 970 K. With the fullerenes now in the vapor phase, a pressure gradient is induced by creating a temperature gradient. A linear gradient is obtained by using a six zone furnace configuration. Figure 2.3 shows a typical temperature gradient. The temperature gradient is monitored with type-K thermocouples evenly spaced along the column. Over the temperature range of 970 K to 620 K the vapor pressures of $C_{60}$ and $C_{70}$ are larger than the operating background pressure of $10^{-6}$ torr. However, at temperatures lower than 670 K the background pressure becomes greater than the sum of the partial pressures. In practice this is not of great concern as long as the actual mean free path is greater than the geometrically restricted mean free path. This is the case as long as the background pressure is less than approximately 1 millitorr.

This baffle configuration satisfies the requirements for molecular distillation over most of the column length. To keep the process effusion-like in nature, the aperture diameter must be smaller than the mean free path of the fullerenes. Otherwise, diffusion and viscous flow become important and Equation 2.1 is no longer valid. In
Figure 2.3: Experimental Apparatus
Figure 2.4: Experimental Temperature Gradient
the higher temperature region, between 820 - 970 degrees Kelvin, the mean free path of the molecules is less than the hole diameters, but this transition region occurs only over the first 5-10 baffles. Beyond this point, the molecular mean free path is greater than the aperture diameters and the baffle spacing, which means that the effective mean free path is the baffle spacing itself. Over this range the mass transport is dominated by effusion.

A typical run consists of loading the molecular distillation unit with 1-2 grams of fullerene source material. The unit is heated to ca. 450 K for approximately 24 hours in order to outgas residual solvents from the starting material (when appropriate). Next, the temperature gradient is established. Once the gradient has equilibrated, the system is run in this steady state configuration for 1 - 3 days. Finally, the system is allowed to cool at which point the pressure is typically $10^{-9}$ torr. The baffles are then removed from the system and the contents are collected from each baffle by scraping.

2.4 Results and Discussion

In order to analyze each molecular distillation trial run, the contents are scraped from the baffles and weighed using a digital scale with 0.1 mg precision. About 1 mg
from each baffle is then dissolved in toluene for analysis. High-performance liquid chromatography (HPLC) is then used to determine the various fullerene percentages present on each baffle. The HPLC system used consists of a reverse phase silica C_{18} column and a Waters 996 photodiode array. The mobile phase is a one to one solution of methanol and toluene. The reverse phase silica C_{18} interacts with components in the mobile phase such that larger molecules move through the column at a reduced rate relative to the smaller molecules. The net result is separation of the different molecules in the mobile phase. The fullerene percentages are determined by integrating the chromatographic peaks at 306 nm, where C_{60} and C_{70} have similar extinction coefficients.

Table 2.4 summarizes the results of three separations using the molecular distillation apparatus. In each case, a different purity starting material was used. For each trial, the temperature gradient was the same (see Fig. 2.3) and the duration was about 48 hours.

The percent yield is defined relative to the total amount collected as opposed to the amount of starting material. The collection losses scale with the number of baffles used and the surface area of the baffles, not with the amount of starting material. Collection losses are primarily due to 5 - 10 milligrams of fullerenes per baffle which are
### Results

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Trial 1</th>
<th>Trial 2</th>
<th>Trial 3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Starting Composition:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>%C₆₀</td>
<td>74.70</td>
<td>95.90</td>
<td>98.00</td>
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<tr>
<td>%C₇₀</td>
<td>19.65</td>
<td>0.97</td>
<td>0.70</td>
</tr>
<tr>
<td>%Other&lt;sup&gt;b&lt;/sup&gt;</td>
<td>5.65</td>
<td>3.13</td>
<td>1.30&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td><strong>Highest Purity C₆₀ Obtained</strong></td>
<td>99.20</td>
<td>99.80</td>
<td>99.97</td>
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<tr>
<td>% Yield at Highest Purity</td>
<td>1</td>
<td>3.8</td>
<td>16.6</td>
</tr>
<tr>
<td>% Yield &gt; 98% C₆₀</td>
<td>2.3</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>(&gt; 99.10%)</td>
<td>(&gt; 99.90%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>% Yield Between 90% - 98% C₆₀</td>
<td>15.8</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

<sup>a</sup> Fullerene purities accurate to ± 0.05%

<sup>b</sup> Includes C₆₀O, C₇₆, C₇₈ and C₈₄

<sup>c</sup> Remaining 1.30% C₆₀O
unretrievable by simple scraping. For this apparatus, the loss of starting material per run is approximately 500 milligrams. This material can be recovered for subsequent reuse by cleaning the baffles with a solvent such as toluene.

In Table 2.4, the composition of the undistilled fullerene material is listed. The starting material for Trial 1 was chromatographically obtained fullerene extract. The starting material for Trial 2 consisted of fullerene powder which the producer certified as being greater than 99% C\textsubscript{60}, while the material for Trial 3 was claimed to be greater than 99.4% C\textsubscript{60}. As Table 2.4 indicates, HPLC analysis yielded results which differed significantly from the producers’ stated purity. As would be expected, Table 2.4 also shows that as the C\textsubscript{60} purity of the starting material is increased, the highest purity C\textsubscript{60} obtained from molecular distillation also increases. In general, the amount of impurities is reduced by a factor of between 25 to 50 per run. However, more importantly, Table 2.4 indicates that starting with higher purity fullerene source material gives a significantly higher yield of ultrahigh purity C\textsubscript{60}. For Trial 2, 100% of the material collected was greater than 99.10 ± 0.05% pure C\textsubscript{60}, and 100% of the material collected from Trial 3 was greater than 99.90 ± 0.05% pure C\textsubscript{60}. As indicated, this method successfully separates C\textsubscript{60} from C\textsubscript{60}O as well as the higher mass fullerenes.
Figures 2.4a and 2.4b show the results for the experiments and simulations for Trials 1 and 2 respectively. As can be seen in Figure 2.4a, the simulation matches up reasonably well with experiment. The curves for $C_{70}$ experiment and simulation are displaced by about 15 degrees Kelvin. This discrepancy may be due to errors in the experimentally measured vapor pressure or result from the effect of distillation from a solid solution. The conductance of the tube between the baffles as well as the neglect of the startup and cool down time will also introduce a shift in the distribution.

The experiment tends to indicate that $C_{70}$ has a higher vapor pressure than that measured by Mathews [30, 31]. The experimental and simulation curves for $C_{60}$ do not match up as well as those for $C_{70}$. The experimental curve appears broader and shifted down to lower temperatures. Again, several sources of error are possible. The agreement between experiment and simulation in Figure 2.4b are much better than for Figure 2.4a. The $C_{70}$ distribution is not displayed in this figure since all of the material collected was greater than $99.10 \pm 0.05\%$ pure $C_{60}$. In this case, there is a ten degree shift between the experimental fullerene distribution and simulation. The vapor pressures used in the simulations were the highest allowable while still staying within the error bounds of the data used [30, 31].
Figure 2.5: Distribution vs. Temperature
The material used in Trials 1 - 3 was chromatographically obtained extract, or commercially purified C₀₀. Though these runs were not performed with solvent free fullerenes, this can easily be done as well. The fullerenes obtained from carbon-arc generation can be directly sublimed from amorphous soot and then purified using this molecular distillation unit yielding truly solvent free fullerenes. It is plausible that a dual stage apparatus could be constructed in which the first stage is essentially a carbon-arc fullerene generator and the second stage consists of a molecular distillation apparatus. Such an apparatus would likely be the separation method of choice in the production of endohedral fullerenes such as La@C₀₀ which require anaerobic handling conditions.

When fullerene material which had been exposed to solvents was distilled, there was a significant amount of carbon residue remaining afterward indicating polymerization of some of the fullerenes. This agrees with observations made by other groups [33]. Material that was distilled a second time sublimed completely leaving no amorphous residue. In addition, preliminary runs with enriched fullerene material that was never exposed to solvents also sublimed completely. This indicates that solvents play a role in the thermally-induced decomposition of fullerenes and that material distilled at least one time is virtually solvent free.
The ultimate limitation to molecular distillation is the difference in vapor pressures of the various fullerenes. However, C_{60} with a purity of 99.97% has been obtained. As implied by our data shown in Table 2.4, this purity should be obtainable by subjecting fullerene extract to three consecutive separation runs in this apparatus. Technological improvements such as a moving temperature gradient applied to a longer column may increase the yield of pure fullerenes and decrease the time of distillation. This method may also prove useful for the separation and purification of heavier fullerenes with suitable modification of the temperature gradient.
Chapter 3

Film Growth and Experimental Apparatus for Optical Studies

3.1 Introduction

The first step in obtaining well characterized C₆₀ thin films is to have well characterized starting material. This is accomplished using the purification method described in the last chapter. Using this material, solvent free C₆₀/C₇₀ thin films ranging from ca. 100% C₆₀ to ca. 100% C₇₀ can be grown. The subsequent handling of these films is important for reasons to be described. Finally, the optical characterization of these films requires the experimental apparatus described here.

3.2 Film Growth and Handling

3.2.1 Film Growth

The vacuum chamber in which films are grown is equipped with a varian 230 l/s ion pump in addition to a 200 l/s turbo pump. The chamber has a base pressure of $10^{-11}$ torr as monitored with an ion gauge. During growth the pressure ranges from $10^{-9}$ to $10^{-8}$ torr.
The substrates typically used are unoriented Al₂O₃. Before loading them into the growth chamber they are degreased in acetone, and then washed in a soap/deionized water solution with subsequent rinsing in deionized water. Once inside the chamber, the substrates are heated to ca. 250° C for several hours to desorb residual species such as H₂O.

For film growth, fullerene powder is loaded into a graphite crucible which is then placed in a tantalum effusion cell. The crucible opening is approximately 10 cm from the substrates. The fullerene powder is resistively heated to between 380° C to 450° C. C₆₀ has a higher sublimation temperature than C₇₀ and therefore using lower growth temperatures results in a higher purity C₆₀ thin film. The typical growth rate as determined from a calibrated quartz crystal microbalance is 5-10 Å/min [34]. During the initial heating of the fullerene powder a shutter is placed between the effusion cell and the substrates in order to eliminate the adsorption of unwanted species on the substrate. In addition to this, the substrate is typically heated to about 120° C to keep any low mass hydrocarbons that may be present from adsorbing onto the substrate.
Finally, it should be noted that for each growth, two films are grown. One film is for optical studies, and the other is destructively analyzed using HPLC so that the fullerene percentages present in the optical quality film can be determined.

3.2.2 Film Handling

The handling of the films upon removal from UHV conditions is very important. Studies have shown that in the presence of light, oxygen readily diffuses into the C\textsubscript{60} films [35]. At first, the molecular oxygen merely diffuses into the interstices. However, after prolonged exposure, the oxygen reacts with the C\textsubscript{60} molecules forming epoxides [35].

In order to minimize the exposure to light and oxygen the films are immediately transferred to a nitrogen glovebox (Vacuum Atmospheres Co. model MO-10-M, < 10ppm O\textsubscript{2}, < 10ppm H\textsubscript{2}O) upon removal from the vacuum system. The glovebox contains a turbo pumped vacuum chamber where the C\textsubscript{60} thin films are kept under 10\textsuperscript{-7} torr.

When the films are ready for optical characterization, the optical sample chamber is loaded into the glovebox. The film is then loaded into the sample chamber and the chamber is closed off with an overpressure of N\textsubscript{2}. Once removed from the glovebox,
the sample is immediately pumped down to less than $10^{-3}$ torr using a sorption pump. At this point the film is ready for optical characterization using the apparatus described in the next section.

3.3 Experimental Setup for Optical Studies

3.3.1 Apparatus

Figure 3.1 shows the experimental apparatus used for the optical studies. The laser used is a Coherent Innova 306 multi-line argon ion laser. The laser line filter has a 1 nm bandwidth centered at 514.53 nm. If other lines are to be used, the high reflector on the laser can be replaced with a prismatic high reflector which allows for resonantly tuning on individual laser transitions. The variable attenuator is for control of the power, and in addition it is used for intensity dependent studies.

The laser beam is steered using Newport DM.5 mirrors with a 1000 W/cm² damage threshold. The beam is focused onto the sample using a 5 cm focal length cylindrical lens. A cylindrical lens is used because for a given incident power it results in a smaller intensity than a biconvex or plano-convex lens due to the larger focusing area. This is important because of the possibility of phototransformation of C_{60}
Figure 3.1: Experimental Apparatus for Optical Studies
under even moderate intensities (i.e. \( \sim 200 \text{ W/cm}^2 \)). Chapter four discusses this phototransformation in more detail.

The cylindrical lens also allows for efficient collection of the Raman scattered light and the photoluminescence because the focus line can be imaged on the monochromator entrance slit. This is accomplished using a 15 cm focal length biconvex lens with a 7 cm diameter. The sample is placed at 3/2f and the monochromator entrance slit at 3f from the lens. This results in a 1.5 times magnification of the imaged area on the sample, but a larger solid angle is collected with the lens closer to the sample. The upper limit on the collectable solid angle (0.3 steradians) is due to the aperture of the radiation shield on the cryostat. The present lens configuration intercepts about 0.1 steradians.

The optical sample chamber used in these studies is a closed system He cryostat (model LTS-22-NGO-C-0.1) from RMC technologies. The cryostat is equipped with a Lakeshore temperature controller (model 320) accurate to within 1 K. This allows for temperature dependent studies from 10 - 300K. The cryostat is pumped out to less than 10^{-3} torr using a sorption pump. There is also an argon attachment so the sample can be maintained under an inert environment when not under vacuum. Finally, the cryostat is equipped with vibration isolation. The sample holder is rigidly
attached to the optic table through bellows on the cryostat, with the cryostat itself being rigidly fastened above the optic table. Vibration isolation is especially important for Raman spectroscopy since the data collection time can be upwards of 2 hours per spectrum.

Again, the collected photons are imaged on the entrance slit of the double monochromator. For Raman studies the entrance slit is 150 \( \mu \text{m} \), the middle slit is 150 \( \mu \text{m} \), and the exit slit is 100 \( \mu \text{m} \). This gives sufficient grating scatter rejection to allow for Raman scans to start as low as 180 cm\(^{-1}\) from the excitation line. The gratings used have 1180 grooves/mm and they are blazed at 500 nm. The monochromators employed have a reciprocal linear dispersion of 3.3 nm/mm and with a 100 \( \mu \text{m} \) slit, this corresponds to a resolution of 2.5 Å\((\sim 8 \text{ cm}^{-1}\) over the range for Raman scans.) For photoluminescence studies the middle slit is removed.

The laser beam is chopped using a mechanical chopper which allows for phase sensitive detection. A peltier cooled Hamamatsu R928 PMT is used for detection. The cooling reduces the dark current of the PMT yielding a SNR of about 15 for the Raman scans. The scans are computer controlled using using an IBM compatible computer and a stepper motor. The data is transferred to the computer using a 12 bit A/D converter.
3.3.2 Monochromator Calibration

The double monochromator consists of two Jarrell-Ash 82-415 single quarter meter monochromators in series with their sine drive shafts connected with a timing belt. For meaningful Raman data it is crucial to have both relative calibration and absolute calibration to within approximately plus or minus 2 cm\(^{-1}\). For the relative calibration the two monochromators were aligned using a Hg lamp. This allowed for relative calibration from 250 nm out to about 800 nm.

For day to day absolute calibration of the double monochromator, Raman scans are performed on CCl\(_4\). This is often used as a standard because of the well defined peaks at 217, 313, and 459 cm\(^{-1}\). Figure 3.2 shows a typical scan on CCl\(_4\) with line assignments. Using these alignment procedures allows for the assignment of Raman modes to within plus or minus 2 cm\(^{-1}\).
Figure 3.2: Raman Spectrum of CCl₄
Chapter 4

Raman Spectroscopy of $C_{60}$ Thin Films

4.1 Introduction

The Raman effect has proved to be an invaluable tool in the characterization of molecules and crystals. In the simplest of terms, the Raman effect is the inelastic scattering of light. The detection of photons inelastically scattered from a sample yields a great wealth of information about the sample, ranging from fundamental vibrations to, in the case of resonance Raman scattering, information about the excited electronic states. Coupled with symmetry arguments based on group theory, Raman spectroscopy is a useful aid in the verification of molecular structure, and the Raman spectrum of $C_{60}$ helped verify its truncated icosahedral structure. Furthermore, solid $C_{60}$ is susceptible to phototransformation, and Raman spectroscopy has proved useful in characterizing this transformation. Before going into the details of the Raman spectra of $C_{60}$, a brief description of the Raman effect follows.
4.2 The Raman Effect

4.2.1 Classical Picture

A classical interpretation of the Raman effect is useful in the sense that it provides a readily understandable physical picture of the process, and in addition, it can yield more quantitative information, such as vibrational selection rules. A more detailed quantum mechanical analysis is required for a full description of the Raman effect, and some aspects of Raman spectroscopy, such as rotational Raman scattering have no quantitative classical description.

Electromagnetic radiation incident upon a medium induces an electric dipole in the medium. In general, the induced dipole moment $\mathbf{P}$, with units of Coulomb-meters, has the form

$$\mathbf{P} = \mathbf{P}^{(1)} + \mathbf{P}^{(2)} + \mathbf{P}^{(3)} + \cdots$$  \hspace{1cm} (4.1)

where

$$\mathbf{P}^{(1)} = \alpha \cdot \mathbf{E}$$  \hspace{1cm} (4.2)

and

$$\mathbf{P}^{(2)} = \beta \cdot \mathbf{EE}$$  \hspace{1cm} (4.3)


\[ P^{(3)} = \gamma : EEE \] (4.4)

In these equations, \( E \) is the electric field in \( V/m \), \( \alpha \) is the polarizability and is a second rank tensor, \( \beta \) is the hyperpolarizability and is a third rank tensor, and \( \gamma \) is the second hyperpolarizability and is a fourth rank tensor. The hyper and second hyperpolarizability become significant only at high field strengths (\( \sim 10^{10} \) \( V/m \)) and they will be neglected in this discussion as they are not important for ordinary Raman scattering. The polarizability can simply be thought of as a measure of the ease with which electrons can be displaced to produce a dipole moment under the influence of an electric field.

The polarizability tensor has nine components and in most cases (e.g. transparent, nonchiral medium) it is real and symmetric thus having only six independent components. A graphical representation of the polarizability tensor is the polarizability ellipsoid. In general the principal axes need not line up with the coordinate frame. However, the coordinate frame can always be rotated such that the coordinate axes coincide with the principal axes of the ellipsoid. In this case there are only three
components $\alpha_{xx}$, $\alpha_{yy}$ and $\alpha_{zz}$ and when these are all equal, the polarizability tensor reduces to a scalar with the polarizability ellipsoid becoming a sphere.

In the general case the polarizability will be a function of the nuclear coordinates. Thus, the effect of nuclear vibrations on the polarizability can be investigated by expanding each component of the polarizability tensor with respect to the normal coordinates $Q_k$ in a Taylor series as shown in 4.5.

$$\alpha_{ij} = (\alpha_{ij})_0 + \sum_k \left( \frac{\partial \alpha_{ij}}{\partial Q_k} \right)_0 Q_k + \cdots \quad (4.5)$$

By examining a simple example, this classical picture reveals a great deal about the physics of the Raman effect. Consider a simple system with a scalar polarizability and one normal coordinate. The harmonic approximation allows us to write this normal coordinate as

$$Q = Q_0 \cos(\omega_k t + \delta_k) \quad (4.6)$$

where $\omega_k$ is the vibrational frequency and $\delta_k$ is a phase factor.

Using 4.5 and 4.6 allows the polarizability to be written as follows:
\[ \alpha = \alpha_0 + \left( \frac{\partial \alpha}{\partial Q} \right)_0 Q_0 \cos(\omega_k t + \delta_k) \] (4.7)

In the presence of a time-varying electric field, \( E = E_0 \cos(\omega_0 t) \), the linear induced dipole moment for this system can be determined by inserting 4.7 and the electric field into 4.2. With a bit of simple manipulation this gives

\[ P^{(1)} = \alpha_0 E_0 \cos(\omega_0 t) + \left( \frac{\partial \alpha}{\partial Q} \right)_0 \frac{Q E_0}{2} \left[ \cos((\omega_0 - \omega_k) t - \delta_k) + \cos((\omega_0 + \omega_k) t + \delta_k) \right] \] (4.8)

This equation for the linear induced dipole moment has three terms. The first term on the right side of 4.8 represents a dipole oscillating at \( \omega_0 \) in phase with the incident radiation. This corresponds to Rayleigh scattering. The last two terms in 4.8 are similar to one another and they correspond to dipoles oscillating at \( \omega_0 - \omega_k \) and \( \omega_0 + \omega_k \) and are known as the Stokes and anti-Stokes Raman scattered radiation, respectively. Two main facts arise from inspection of these last two terms. First, the Raman scattered radiation need not be in phase with the incident radiation. Second, and more importantly, for a vibrational mode to be Raman active, the gradient of the polarizability evaluated at the equilibrium position of the normal coordinate must be nonzero. This illustrates the utility of Raman spectroscopy as an experimental
method with selection rules that are different than for infrared spectroscopy, where infrared activity is determined by variation of the dipole moment with respect to the normal coordinate. For example, a homonuclear diatomic molecule will be Raman active but not infrared active. These two spectroscopies are complementary and in the case of centrosymmetric systems, it can be shown that the vibrationally active modes for Raman and infrared are mutually exclusive.

This simple picture is useful, but other important information can be obtained with a more detailed analysis. For example, based on symmetry arguments, the expected polarization of a vibrational mode can be predicted. This allows for the more precise characterization of the vibrational modes by experimentally measuring the polarization ratio of each Raman peak.

In summary, the classical description of the Raman effect shows that the detected Raman frequencies are simply the beat frequencies between the incident radiation and the molecular vibrational frequency as shown in Figure 4.1. A more complete description of the Raman effect requires a quantum mechanical description.
4.2.2 Quantum Picture

A more complete description of the Raman effect uses time dependent perturbation theory. Essentially, the Raman effect is a two-photon process, or in the terminology of nonlinear optics, spontaneous four-wave mixing. Thus, Raman scattering can be explained in terms of the third order nonlinear susceptibility tensor $\chi^{(3)}(-\omega_b, \omega_o, -\omega_o, \omega_b)$, where $\omega_s = \omega_o - \omega_k$ is the frequency of the scattered radiation.

Figure 4.2 shows the energy level scheme for ordinary Stokes-shifted Raman scattering. A photon excites the system from $|0, 0\rangle$ to the virtual level depicted by the dashed line. The first allowed electronic level $|1, 0\rangle$ lies well above this virtual state in ordinary Raman scattering. This excited virtual state then relaxes to $|0, 1\rangle$ in the ground state manifold. The net result is that the system has gained a quan-
Figure 4.2: Energy level scheme for Raman
turn of vibration and the photon has been Stokes shifted by the energy difference between $|0,0\rangle$ and $|0,1\rangle$. The case of anti-Stokes shifted radiation is nearly the same except now the system must give up a vibrational quantum and since the ground state vibrational manifold of the molecules has a thermal population distribution, anti-Stokes Raman intensities are usually weaker than the Stokes shifted intensities. More complete details of Raman scattering can be found in [36, 37, 38].

4.3 Raman Studies of $C_{60}$

4.3.1 Theory

There are $3n - 6 = 3 \times 60 - 6 = 174$ possible vibrational modes for the $C_{60}$ molecule. However, due to the symmetry of $C_{60}$, there are mode degeneracies thus reducing the number of distinct mode frequencies to 46. $I_h$ is the point group which describes the symmetry properties of the isolated $C_{60}$ molecule and the vibrational mode frequencies are labeled according to their symmetry properties within this icosahedral point group [39]. In Raman, the expected vibrational frequencies are of gerade parity. Specifically, there are two $A_g$ modes and 8 $H_g$ modes for a total of 10 Raman active vibrational modes. There are four infrared active modes ($F_{1u}$) with ungerade parity, thus giving a total of 14 distinct modes which are observable using optical spectroscopic methods.
The other 32 modes are silent, although in principal, all 46 modes are observable with experimental techniques such as neutron inelastic scattering (NIS).

In solid crystalline $C_{60}$ there arises the possibility of additional Raman and IR modes. Symmetry lowering perturbations such as the crystal field associated with the condensed phase can lead to the splitting of degenerate vibrational modes. For example, the $H_g$ vibrational modes are fivefold degenerate and thus splittings may be expected, whereas the $A_g$ modes are nondegenerate and will not split. Silent modes may also be Raman or IR activated due to site symmetry lowering in the condensed phase. In addition, there are other lower energy modes present due to rotational and translational motions. The number of Raman active modes is also a function of temperature since the site symmetry of the crystal changes (fcc to sc) at about 250 K [39]. Based on these symmetry arguments, it is apparent that the experimental Raman spectra of solid $C_{60}$ provides a great deal of information, ranging from the importance of the crystal field in the solid to the phase transition in solid $C_{60}$ [40, 41].
4.3.2 Experiment

Vibrational Mode Assignment

Stanton and Newton were the first to theoretically calculate the vibrational frequencies of the C$_{60}$ molecule [42]. Other more detailed calculations have followed [43]. In addition to these theoretical studies there have been numerous experimental studies to determine the Raman vibrational frequencies [44, 45, 41]. Table 4.3.2 lists the Raman frequencies (in cm$^{-1}$) from selected calculations and experiments. This table also lists the experimentally detected Raman frequencies measured on 2000 Å polycrystalline films grown on unoriented sapphire substrates as described in Chapter 3. Figure 4.3 shows the Raman spectrum of three films with purities of ca. 99% as determined by HPLC. The first scan was taken at room temperature, while the other two scans were taken at approximately 10 K. The numbers in parentheses correspond to H$_{g}$(5) and H$_{g}$(6) as measured by Matus and Kuzmany [41]. These two modes are extremely weak and were not resolved on any of the films studied. The Raman frequencies were repeatable from film to film within about 2 cm$^{-1}$. All Raman spectra were measured with an incident intensity of about 20 W/cm$^2$.
Figure 4.3: Raman Spectra of Polycrystalline C$_{60}$ Thin Films
### Raman Frequencies of C\textsubscript{60} (cm\textsuperscript{-1})

<table>
<thead>
<tr>
<th>Mode</th>
<th>Ref.\textsuperscript{a} [42]</th>
<th>Ref.\textsuperscript{a} [43]</th>
<th>Ref.\textsuperscript{b} [45]</th>
<th>Ref.\textsuperscript{b} [41]</th>
<th>This work</th>
</tr>
</thead>
<tbody>
<tr>
<td>A\textsubscript{g}(1)</td>
<td>610</td>
<td>496</td>
<td>493</td>
<td>492</td>
<td>495</td>
</tr>
<tr>
<td>A\textsubscript{g}(2)</td>
<td>1667</td>
<td>1435</td>
<td>1469</td>
<td>1468</td>
<td>1469</td>
</tr>
<tr>
<td>H\textsubscript{g}(1)</td>
<td>263</td>
<td>265</td>
<td>270</td>
<td>272</td>
<td>268</td>
</tr>
<tr>
<td>H\textsubscript{g}(2)</td>
<td>447</td>
<td>408</td>
<td>431</td>
<td>428</td>
<td>430</td>
</tr>
<tr>
<td>H\textsubscript{g}(3)</td>
<td>771</td>
<td>726</td>
<td>708</td>
<td>709</td>
<td>708</td>
</tr>
<tr>
<td>H\textsubscript{g}(4)</td>
<td>924</td>
<td>786</td>
<td>773</td>
<td>773</td>
<td>773</td>
</tr>
<tr>
<td>H\textsubscript{g}(5)</td>
<td>1261</td>
<td>1149</td>
<td>1099</td>
<td>1080</td>
<td>–</td>
</tr>
<tr>
<td>H\textsubscript{g}(6)</td>
<td>1407</td>
<td>1207</td>
<td>1248</td>
<td>1251</td>
<td>–</td>
</tr>
<tr>
<td>H\textsubscript{g}(7)</td>
<td>1596</td>
<td>1433</td>
<td>1426</td>
<td>1425</td>
<td>1425</td>
</tr>
<tr>
<td>H\textsubscript{g}(8)</td>
<td>1722</td>
<td>1651</td>
<td>1572</td>
<td>1576</td>
<td>1575</td>
</tr>
</tbody>
</table>

\textsuperscript{a} calculated

\textsuperscript{b} experimental

### Impurities

Raman spectroscopy also allows for the detection of impurities. The apparatus used in these experiments (based on the signal to noise ratio) can detect at the level of about \(\sim 5\%\) impurities. In the case of solid C\textsubscript{60} films, the major impurities are C\textsubscript{70} and solvents such as toluene. Figure 4.4 shows three scans, taken at 10 K, on films of 99% pure C\textsubscript{70}, 92% C\textsubscript{60}, and 70% C\textsubscript{60}, respectively. In C\textsubscript{70}, due to its lower symmetry, 53 distinct Raman modes are expected. Figure 4.4a shows 12 distinct vibrational modes. With about 8% C\textsubscript{70} present in the C\textsubscript{60} film, there are no significant changes relative
to the purer films as shown in Figure 4.3, except for the additional line at 748 cm$^{-1}$.

However, for the 70% C$_{60}$ film (Fig. 4.4c) there are now several additional lines due
to the presence of C$_{70}$.

There is also the possibility of detecting the presence of solvent impurities in
C$_{60}$ thin films. This could, in principal, be accomplished by looking for the strong
C-H stretch modes usually found in the 3000 cm$^{-1}$ region for aromatic solvents.

Preliminary experiments, however, revealed no peaks in this range on the films stud-
ied. It is not surprising that such impurities were not detected as the starting material
for the films was purified as described in Chapter 2 and the Raman spectra have a
lower limit of $\sim$ 5 % detectability as described above.

**Photopolymerization**

Initially, there was a dispute about the assignment of the A$_g$ mode at 1469 cm$^{-1}$.

This is often referred to as the pentagonal pinch mode. This mode is the 100%
tangential displacement of the carbon atoms resulting in a shrinking of the pentagons
and an expansion of the hexagons. This mode should be 100% polarized parallel to
the incident radiation. It was observed that this mode shifted to 1458 cm$^{-1}$. Duclos
et al. claimed the 1458 cm$^{-1}$ line was pristine to C$_{60}$ while the 1469 cm$^{-1}$ was due
Figure 4.4: Raman Spectra of $C_{70}$ and $C_{60}/C_{70}$ Thin Films Obtained at 10 K
to oxygen contamination [46]. Subsequent study by Ecklund et al. revealed that the 1469 \(\text{cm}^{-1}\) line was purely polarized as predicted and thus pristine to \(\text{C}_{60}\) while the 1458 \(\text{cm}^{-1}\) line was partially polarized and due to photoinduced polymerization of the \(\text{C}_{60}\) solid [47, 48, 49].

To make sure photopolymerization could be observed, two samples were purposely polymerized. First, a scan was taken at 20 W/cm\(^2\) in order to establish the 1469 \(\text{cm}^{-1}\) line. Then the intensity was increased and the sample irradiated for 20 minutes. The intensity was then decreased back down to 20 W/cm\(^2\) and another Raman scan taken. This process was repeated until it was observed that the 1469 \(\text{cm}^{-1}\) line had in fact down shifted to 1458 \(\text{cm}^{-1}\). Figure 4.5 shows two examples of this down shifting. For Figures 4.5a and b the intensity at which polymerization occurred was 200 W/cm\(^2\) while for Figures 4.5c and d the intensity was 240 W/cm\(^2\).

### 4.4 Discussion

All three scans in Figure 4.3 show 7 or 8 of the 10 Raman active modes expected in the isolated \(\text{C}_{60}\) molecule. The modes below 800 \(\text{cm}^{-1}\) are predominantly radial in nature while those above 800 \(\text{cm}^{-1}\) are of mostly tangential character [42]. The frequencies of the modes which were detected match up well with the other studies as
Figure 4.5: Photoinduced Peak Shift of $A_3(2)$ Line
indicated in Table 4.3.2. The $H_g(5)$ and $H_g(6)$ modes are very weak and do not show up clearly in any of the scans. This is also the case in other studies [45]. In addition, in Figure 4.3c the 1575 cm$^{-1}$ mode is not present. In fact, on these polycrystalline films there was not only sample to sample variation in the Raman spectra (in terms of the number of modes present, not in their frequencies), but there was spot to spot variation on individual samples, indicating film inhomogeneities due possibly to structural defects such as grain boundaries. Other than line narrowing, there is not much difference in the room temperature or 10 K scans. The Raman lines are narrower at 10 K because the librational motion of the C$_{60}$ molecules is quenched thus reducing the homogeneous broadening of the spectral lines. Also, there are no additional modes or mode splittings present. This indicates the molecular nature of the C$_{60}$ solid. It must be kept in mind, however, that the films studied were not single crystals and thus crystal field splitting effects may be extremely small. Additional modes and mode splittings have been observed in single crystals of C$_{60}$ [41]. Such splittings have not been observed with C$_{60}$ thin films. Thus, it is important to grow single crystal thin films in order to more precisely determine the effects of the crystal field (see Chapter 6 for additional discussion).
The effect of C\textsubscript{70} impurities are evident as shown in Figure 4.4. Essentially, with ca. 8\% C\textsubscript{70} additional modes are already present. There is no detectable shift in the mode frequencies of C\textsubscript{60}. It is interesting to note that the ratio of the 495 cm\textsuperscript{-1} to the 1469 cm\textsuperscript{-1} in the high purity C\textsubscript{60} thin films is \(\sim 0.20\) or less while in the film with 30 \% C\textsubscript{70} this ratio has increased to about 0.5. The presence of C70 may affect the intensity of these modes although further investigation will be required. Such variations of Raman intensities or frequencies could be useful in deducing intermolecular interactions. No solvent impurities were detected in any of the Raman scans. However, our Raman apparatus is only capable of detecting impurities at the 5 \% level or greater.

Finally, as can be seen from Figure 4.5, photopolymerization (i.e. the line shift from 1469 cm\textsuperscript{-1} to 1458 cm\textsuperscript{-1}) is detectable with the experimental apparatus used. Figure 4.5a clearly shows the 1469 cm\textsuperscript{-1} line although the \(H_g(7)\) and \(H_g(8)\) modes are not present. Figure 4.5b is the scan taken after irradiation at 200 W/cm\textsuperscript{2} for 20 minutes. An additional peak at 1459 cm\textsuperscript{-1} is now resolved. Figure 4.5c is a scan at a new spot before irradiating at high intensity. There is evidently already some degradation at this spot because of the shoulder at 1458 cm\textsuperscript{-1}. At this spot on the sample the \(H_g(7)\) and \(H_g(8)\) modes are resolved. After irradiating this spot the
1458 cm$^{-1}$ is the strongest and the 1566 cm$^{-1}$ mode overwhelms the 1572 cm$^{-1}$ mode. It should also be noted that in order to discount the potential of photopolymerization due to long exposure times at low intensities (20 W/cm$^2$), Raman scans were taken after several hours of exposure at 20 W/cm$^2$ and no shift of the 1469 cm$^{-1}$ peak was detected.

These photopolymerization studies are especially important because it allows for a reasonable determination for the intensity threshold for photopolymerization. Thus, when photoluminescence (PL) spectra are taken, the intensity used is kept well below this approximate threshold (200 W/cm$^2$) and we can be sure that we are studying the PL of C$_{60}$ and not polymerized C$_{60}$. Chapter 5 presents the PL studies of C$_{60}$ thin films.
Chapter 5

Photoluminescence of C$_{60}$ Thin Films

5.1 Introduction

Photoluminescence (PL) is a common experimental method used in the characterization of inorganic and organic solids and liquids [50]. In molecular solids, the optical properties are associated with the delocalized $\pi$-electrons. Luminescence spectroscopy is a direct probe of the mechanisms associated with radiative recombination from the $\pi^*$ excited states. Energies of excited states, estimates of lifetimes of excited states based on linewidths, and conversion of electronic energy are some of the information available using PL. Temperature dependent luminescence studies increase the information available because changes in the PL spectrum can be related to the known temperature dependent effects in the material. The temperature dependent changes in the PL spectrum are manifested as frequency shifts or, more typically, as changes in the integrated intensity. Photoluminescence is an important method in the understanding of excited electronic states, and in the decay of these excited electronic states.
Several PL studies on C<sub>60</sub> thin films have been published [51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62]. None of these studies have given a consistent interpretation of the photoluminescence of solid C<sub>60</sub>. Due to the lack of pure samples this is not surprising. However, a more complete understanding of the microscopic details of PL in C<sub>60</sub> is essential if we are to thoroughly understand the more complicated dynamics of this system. Before discussing some of these published PL studies of C<sub>60</sub> in the context of the PL work presented here, a brief description of luminescence in molecular systems is presented.

### 5.2 Photoluminescence: Background

All π-electron systems contain an even number of π-electrons since there are two electrons per π-bond. Therefore, the ground state is a singlet state since the electron spins will be paired (the spin multiplicity is 2S + 1 where S is the algebraic sum of the spin quantum numbers). The absorption of a photon with sufficient energy excites an electron to a higher electronic level. The decay of this excited electron back down to the ground state can occur through many different channels. As shown in Fig. 5.1, there is the higher energy fluorescence which is radiative recombination from S<sub>1</sub> to S<sub>0</sub>. Fluorescence lifetimes are typically ~ 10<sup>-9</sup> seconds. Ideally, the fluorescence spectrum
would be the mirror image of the absorption spectrum. This is rarely the case and indicates that other recombination channels are involved. There is the possibility of intersystem crossing, in which a spin flip converts a singlet state $S_1$ to a lower energy triplet state $T_1$. This triplet state can then relax back down to the singlet ground state by the emission of a photon. This radiation is termed phosphorescence. Because a spin flip is involved in going from $T_1$ to $S_0$, triplet lifetimes can be unusually long, ranging from $10^{-6} - 10^{-3}$ seconds. In addition to these radiative channels, there are competing nonradiative channels.

Figure 5.2 gives a more complete picture of the possible recombination channels. The potential energy versus an appropriately chosen configurational coordinate is

![Figure 5.1: Luminescence and Absorption Schematic](image)

Figure 5.1: Luminescence and Absorption Schematic
shown in this schematic for the $S_0$, $S_1$ and $T_1$ vibrational manifolds. For diatomic molecules, the configurational coordinate simply reduces to the internuclear separation. The pump is labeled as $\lambda_{exc}$, while the fluorescence and phosphorescence are labeled with their transition rates $k_f$ and $k_p$, respectively. These transitions are depicted as vertical lines because such transitions take $\sim 10^{-15}$ seconds while complete vibrations take $\sim 10^{-12}$ seconds meaning there is no appreciable change in the molecular structure during the transition. This is the Franck-Condon principle. The nonradiative channels shown as wavy lines are internal conversion ($k_{ic}$) and intersystem crossing ($k_{isc}$). These nonradiative processes compete with the radiative recombination channels. Nonradiative recombination can be explained in terms of the overlap of vibrational wave functions (Franck-Condon factors). However, a complete description of any molecular system is complicated because there are so many competing channels.

In photoluminescence experiments where the incident radiation is pulsed, the excited electrons thermalize to the bottom of the vibrational manifold. The luminescence detected in this case is a probe of the vibrational structure of the ground state. This process is shown in Figure 5.2. However, when the incident radiation is continuous wave, all of the carriers may not thermalize to the bottom of the vibrational
Figure 5.2: Recombination Channels
manifold before radiatively recombining. This is called unrelaxed luminescence. In this case the luminescence detected is a weighted convolution between the vibrational manifolds of the upper and lower states.

In principle, the fluorescent lifetime $\tau_f = 1/k_f$ can be determined from the luminescence spectrum. However, if the luminescence lifetime were experimentally measured, it would deviate from this value because of the competition from other recombination channels. For example, if the fluorescence transition rate is $k_f$ and the total rate of all of the nonradiative channels is $k_{nr} = k_{isc} + k_{ic}$ (assume no phosphorescence), then the observed radiative lifetime will be given by

$$\tau_{ob} = \frac{1}{k_f + k_{nr}}$$

(5.1)

The observed lifetime is shorter than the true radiative lifetime. In this case, knowledge of $\tau_f$ and $\tau_{ob}$ allow for the determination of the overall nonradiative transition rate.

There are obviously many channels for recombination of excited carriers. For a complete understanding of a system these different channels need to be associated with microscopic phenomena. In the present case it is of interest to have some idea of the various possibilities in a solid crystalline (or polycrystalline) environment. In
molecular solids, exciton formation appears to be the rule rather than the exception. There are localized (Frenkel) excitons, free (Wannier) excitons, and charge transfer excitons involving two adjacent molecules. Each of these type of excitons can be either singlet or triplet. Singlet excitons are expected to be much shorter lived than triplet excitons. Exciton diffusion is important in molecular crystals. The excitons can diffuse and radiatively or nonradiatively recombine at an impurity site or at grain boundaries. More complicated processes such as triplet exciton annihilation \((T_1 + T_1 \rightarrow S_1 + S_0)\) can occur. This can lead to phenomena such as delayed fluorescence. Finally, in a molecular solid, many body effects may be of importance. For example, an exciton can distort the lattice around it or the molecule on which it resides leading to effects such as self-trapping. No single experiment can hope to elucidate all of the phenomena associated with such a complex system. However, PL is an important starting point in beginning to understand these effects in polycrystalline \(C_{60}\) thin films.

### 5.3 Results

The PL experiments were done on the same films studied using Raman spectroscopy described in Chapter 4. The PL spectra taken at 10 K were typically obtained after
letting the sample sit at this temperature for 1 - 2 hours. This assured that thermal equilibrium had been achieved before beginning the temperature dependent studies. The temperature was allowed to equilibrate for 20 - 30 minutes at each temperature before beginning a scan. Scans taken sequentially at a given temperature had integrated intensities within 5% of one another indicating that thermal equilibrium is established in the 20 - 30 minutes between scans. At each temperature, the collection optics were adjusted to optimize the signal due to possible thermal changes in the sample holder position. In most cases, there was no significant change upon optimization. The integrated intensity dependence of the photoluminescence between 1W/cm² and 50W/cm² excitation was linear with no new features in the spectra. All scans presented were obtained with 514.53 nm incident photons at ~10 W/cm² unless otherwise indicated. The scans are corrected for the decrease in photomultiplier tube sensitivity with increasing wavelength.

Figure 5.3 shows the photoluminescence spectra at several temperatures as indicated on the plot, for two separate films. The data in Fig. 5.3a is on a film consisting of ca. 99.3% C₆₀, 0.3% C₇₀, and 0.4% C₆₀O. The 0.4% C₆₀O is most likely from surface oxides. These numbers are based on the HPLC analysis of the duplicate film which had more ambient exposure, so the numbers quoted here can be considered as
worst case values. The data in Fig. 5.3b is on a film of similar purity to Fig. 5.3a. Qualitatively, the features are similar for both films. PL spectra on several other high purity C$_{60}$ thin films were performed yielding similar results. Shown in the inset of Figures 5.3a and b are the total integrated intensity of the photoluminescence spectra as a function of temperature. The interesting feature to note is the increase in integrated intensity with temperature up to about 90 K. Above 90 K the integrated intensity again drops off. The lines shown are fits to the data and these fits will be discussed in the next section.

As shown in Figure 5.3, the spectra have distinct features, the most prominent at low temperatures being the 1.69 eV peak. At higher temperatures, this peak dramatically decreases in strength, with the other lower energy features remaining. The PL data of Fig. 5.3a were fitted with three Lorentzians. Figure 5.4a shows the fit obtained with three Lorentzians at 13 K. The three Lorentzians are centered at 1.69 eV, 1.63 eV, and 1.53 eV. The fitting procedure was performed by fitting the 13 K data to find the peak amplitudes, widths, and energies. The other temperatures were then fitted by allowing only the amplitudes to vary. The fits were done in this fashion since the Lorentzians have no explicit temperature dependence and there were no observable peak shifts with increasing temperature in the PL spectra.
Figure 5.3: PL spectra of C$_{60}$ thin films and integrated intensity dependence
Figure 5.4b shows the integrated intensity vs. temperature for each of the three peaks in the photoluminescence as determined from the Lorentzian fits. The 1.69 eV peak shows a dramatic temperature dependence while the other peaks have only a very mild temperature dependence. The following section discusses these results in detail.

5.4 Discussion

In attempting to understand the luminescence spectrum of polycrystalline C\textsubscript{60} thin films, several issues must be addressed. Before addressing the microscopic nature of the radiative decay of the excited states, it is important to know which excited states are involved. In the case of C\textsubscript{60}, radiative recombination is from singlet excitons. This is substantiated by several facts. The S\textsubscript{0} to S\textsubscript{1} transition is about 1.9 eV and the luminescence emission ranges from 1.45 to 1.8 eV. The S\textsubscript{0}-S\textsubscript{1} transition is dipole forbidden, and only weakly allowed in the solid due to symmetry lowering, and it is expected that the quantum yield for fluorescence should be very weak. An exact determination of this fluorescence quantum yield is difficult, but order of magnitude estimates give an efficiency of $\sim 10^{-3} - 10^{-4}$, which is indeed quite small. This
Figure 5.4: a.) Lorentzian fit at 13 K b.) Integrated Intensity vs. Temperature of Lorentzians
estimate was calculated using a experimentally determined absorption coefficient of 3\(\mu\text{m}^{-1}\) at 514.53 nm.

There is also the possibility of \(T_1\)-\(S_0\) radiative recombination. The triplet state energy has been measured in the range from 1.56 to 1.7 eV [63, 64, 65, 66]. The PL spectrum extends above this range indicating the luminescence originates from the singlet manifold and not the triplet manifold. More important are lifetime measurements. PL spectra were obtained at 10K as a function of lockin amplifier modulation frequency. The frequency was varied from 1 Hz to 60000 Hz. No changes in the PL spectra were observed in this frequency range either in terms of integrated intensity or in terms of new spectral features. This corresponds to a lifetime of less than \(\sim 15\mu\text{s}\). Similar results have been reported elsewhere [55]. More exact time resolved PL measurements on solid \(C_{60}\) yielded a photoluminescence lifetime of 1.2 ns at low temperature [60]. The singlet lifetime has also been measured by several groups performing transient absorption on solutions. The measured singlet lifetimes were 0.65 ns [66], 1.2 ns [67], and 1.45 ns [68] which is in good agreement with the PL lifetime measurement. Such a short lifetime favors singlet excitons as triplet excitons would be expected to have a much longer lifetime even in the solid. In solution, this is in fact the case as time resolved triplet state absorption measurements yielded a triplet
state lifetime of 133μs [69]. There are no published triplet state lifetimes on solid C\textsubscript{60}, although measurements in this lab imply it is longer than 1μs [4].

In addition, it has been observed that intersystem crossing (S\textsubscript{1}-T\textsubscript{1}) occurs with almost unit efficiency [68]. Roughly, for every 1000 excited electrons, 1 recombines radiatively from the singlet manifold. The other 999 nonradiatively recombine through internal conversion from S\textsubscript{1} to S\textsubscript{0} or, with higher probability, through intersystem crossing to the triplet manifold with subsequent deactivation to S\textsubscript{0}.

This qualitative explanation of the PL spectrum provides insight into the partitioning of the excited π-electrons but there is still a lack of understanding of the microscopic details. Furthermore, such a simple picture does not give any insight into the unique temperature dependence of the PL spectrum as shown in Fig. 5.4b. Before discussing this temperature dependence, it will be useful to review the temperature dependence of the crystalline structure of solid C\textsubscript{60}.

David et al. have performed high resolution neutron diffraction measurements on solid C\textsubscript{60} from 5 K to 320 K [7]. The results of this study show that above 260 K the C\textsubscript{60} molecules are orientationally disordered and undergo continuous random reordering. The coherence time of this reordering above 260 K is 9 ps as measured by Tycko et al. using NMR [9]. There is a phase transition at 260 K where the crystal
Figure 5.5: Structural schematic for $C_{60} < 260$ K a.) P configuration b.) H configuration

structure becomes simple cubic with a discontinuous jump in the lattice constant from 14.15 to 14.10 Å[7]. In the temperature range from 90 K - 260 K there are two configurations which coexist. There is the $\phi = 98^\circ$ configuration in which the four $C_{60}$ molecules in the unit cell are rotated counterclockwise $98^\circ$ about the <111> directions. This corresponds to an electron rich interpentagon double bond of one molecule centered in an electron deficient pentagon of a nearest neighbor molecule. This is depicted in Fig. 5.5a. This so called P configuration is the optimal van der Waals orientation. The second configuration is just a $60^\circ$ rotation of the P configuration about the <111> axis. The $\phi = 38^\circ$ H configuration corresponds to a double bond centered in an electron deficient hexagon as shown in Fig. 5.5b. The H configuration has slightly higher energy. Between 90 - 260 K there is a ratcheting between the P and H configurations. The site occupancy of the P phase increases from
ca. 63% at 250 K to 83% at 90 K with a corresponding decrease in the site occupancy of the H configuration. This change in site occupancy of the P configuration with temperature as measured by David et al. is shown in Fig. 5.6. Below 90 K there is no longer any hopping between the P and H configurations and the site occupancy remains constant at 83% and 17% for the P and H configurations, respectively. Thus below 90 K there is disorder frozen into the lattice.

A simple three level model allows for the determination of the temperature dependence of the photoluminescence. Figure 5.7 shows a configurational coordinate diagram for the model represented by Equations 5.2 and 5.3.

Figure 5.6: Site occupancy for P configuration. From David et al.
\[
\frac{dN_{FE}}{dt} = a_1 P + k_B N_{STE} - k_F N_{FE}
\]  
(5.2)

\[
\frac{dN_{STE}}{dt} = a_2 P + k_F N_{FE} - k_B N_{STE} - k_R N_{STE} - k_{NR} N_{STE}
\]  
(5.3)

The upper level populations are given by \(N_{FE}\) and \(N_{STE}\). The physical interpretation of these upper levels is discussed below. \(P\) represents the excitation rate from the ground state. The pump energy is greater than both excited state energies such that upon thermalization both \(N_{FE}\) and \(N_{STE}\) are populated. Conservation requires that \(a_1 + a_2 = 1\). The forward and backward rates between \(N_{FE}\) and \(N_{STE}\) are given by \(k_F\) and \(k_B\), respectively. The radiative rate from \(N_{STE}\) is given by \(k_R\) and the nonradiative rate is \(k_{NR}\). Radiative and nonradiative processes from \(N_{FE}\) are neglected. In steady state Equations 5.2 and 5.3 can be set to zero allowing for the determination of the populations \(N_{FE}\) and \(N_{STE}\). The luminescence intensity is proportional to the sum of these populations. If the rates \(k_F\), \(k_B\) and \(k_{NR}\) are assumed to have an exponential temperature dependence while \(k_R\) is temperature dependent, the following equation is obtained for the luminescence intensity:
\[ \eta(T) = \frac{c_0 + c_1 \exp\left(\frac{E_1}{k_BT}\right)}{1 + c_2 \exp\left(\frac{E_2}{k_BT}\right)} \quad (5.4) \]

\( T \) is the temperature and \( k_b = 8.62 \times 10^{-5} \) eV/K is Boltzmann's constant. The photoluminescence integrated intensity vs. temperature shown in Fig. 5.4b was fitted to this functional form. For the fit shown in Fig. 5.4b, the parameters are \( c_0 = 0.86, c_1 = 0.25, c_2 = 2.3 \times 10^5, E_1 = 0.010 \) eV, \( E_2 = 0.172 \) eV. This functional form fits both the low (\( T < 100 \) K) and high (\( T > 100 \) K) temperature regions quite well. The temperature dependent term in the numerator of Eqn. 5.4 is important at low temperatures and will be discussed in the following paragraph. What is immediately obvious, however, is the correlation between Fig. 5.6 and the 1.69 eV peak in Fig. 5.4b in the 90 - 250 K range. This indicates that the site occupancy of the P configuration is possibly related to the emission intensity of the 1.69 eV peak. As the temperature is increased, the site occupancy of the P configuration decreases as does the integrated intensity of the 1.69 eV peak. In the limit where the molecules are reorienting within 9 ps (i.e. \( \sim > \) 260 K), there is no longer any correlation between individual molecules and the 1.69 eV peak is completely quenched. In other words, the 1.69 eV luminescence is enhanced by intermolecular interactions. The radiative recombination may be occurring from an exciton of strong intermolecular character. It is conceivable that this exciton is
delocalized over 5 - 10 molecules, but this seems unlikely since the grain sizes of the polycrystalline C\textsubscript{60} are 60 - 100 Å, which is only 4 - 7 lattice spacings in diameter. In this case the 1.69 eV peak would be quenched due to nonradiative recombination at grain boundaries. Furthermore, as will be discussed in the following paragraph there is also distinct intramolecular character present in the luminescence spectrum. Thus, another possible interpretation for the intermolecular enhancement of the 1.69 eV peak is that in the P configuration, the C\textsubscript{60} molecules are in a polarized environment and this enhances the radiative recombination of what are essentially intramolecular excited states.

In the low temperature region of the PL integrated intensity (below approximately 100 K) the luminescence intensity decreases with decreasing temperature. Matus et al. have reported a similar temperature dependence of the photoluminescence, and they attribute this as an activation barrier to the formation of a self-trapped exciton on a single molecule [56]. Figure 5.7 and Equations 5.2, 5.3 and 5.4 are a simple model of this self trapped exciton phenomenon. \(N_{FE}\) is the population of free excitons and \(N_{STE}\) is the population of self trapped excitons. The agreement between Equation 5.4 and the temperature dependence of the PL integrated intensity (Fig. 5.4b and inset of Fig. 5.3) thus indicates the self trapping of excitons. Furthermore, as shown
Figure 5.7: Configurational diagram for self trapped exciton model
in Figure 5.7, there is a barrier for the formation of self trapped excitons. The temperature dependent term $c_1 \exp\left(\frac{E}{k_B T}\right)$ in Equation 5.4 yields the difference in the minima of the two upper states. The value determined is $\sim 0.010 \text{ eV}$ indicating the levels are nearly degenerate.

Subsequent theoretical analysis by Friedman and Harigaya validated the interpretation of self trapped exciton formation [70, 71]. They termed this self trapped exciton a ring bipolaron because it is localized around the equator of the $C_{60}$ molecule. The configurational coordinate $Q$ Friedman and Harigaya chose was the difference in lengths between the alternating single and double bonds around the equator of the $C_{60}$ molecule. In equilibrium the bond lengths are different, but upon the formation of a self trapped exciton these single and double bond lengths are degenerate and $Q = 0$ as shown in Fig. 5.7. The resultant molecular distortion lowers the symmetry of the molecule resulting in a higher probability for radiative recombination.

The energy of a self trapped exciton should be lower than the energy of a free exciton. Given that for $C_{60}$ this self trapped exciton is intramolecular, it is further expected that the temperature dependence of the integrated intensity due to radiative recombination would be less sensitive to changes in the temperature as compared to intermolecular excitons. Based on this, it is tempting to assign the relatively
temperature independent 1.63 and 1.53 eV peaks in the PL spectra (see Fig. 5.4b) to such intramolecular excitons. However, there is too much spectral broadening and sample to sample variation in the films to make such a definitive assignment. Also, inspection of the temperature dependence of the 1.69 eV peak at temperatures less than $\sim 90$ K indicates that it too shows intramolecular character.

Whether or not the increase in the luminescence integrated intensity from 10 K to 90 K is due to distortion of the $C_{60}$ molecule remains in question. Matus et al. view this change in integrated intensity as a decrease in integrated intensity with decreasing temperature as being due to impurities. Their view is that above 90 K the excitons are efficiently trapped on single molecules where they can radiatively recombine. Below the temperature for self trapping (i.e. $< \sim 90$ K) the excitons are free to move about the crystal and they can radiatively recombine at impurity sites such as $C_{70}$ or $C_{60}O$. This interpretation is based on new features at 1.78 and 1.82 eV appearing in their PL spectra below 90 K. They attribute the 1.78 eV peak to $C_{60}$ impurities and the 1.82 eV peak to $C_{70}$ impurities. The transfer in integrated intensity from the intrinsic luminescence to these impurity peaks accounts for the decrease in intensity below 90 K with decreasing temperature.
The results presented here agree with Matus et al. in terms of the creation of self trapped intramolecular excitons. However, the results presented here bring into question their interpretation of the decrease in luminescence intensity below 90 K as being due to exciton diffusion to impurity sites. First, the temperature dependence of the PL integrated intensity presented here is the same as Matus et al., but there were no additional features at either 1.78 or 1.82 eV in any of the spectra obtained (e.g. see Fig. 5.3a and b.) This indicates that the change in PL intensity in the 10 - 90 K range is intrinsic to solid C₆₀. Secondly, the peak observed at 1.82 eV in their spectra is due to C₇₀, but this does not imply that excitons are diffusing to these C₇₀ impurity sites where they then radiatively recombine. Without knowledge of the temperature dependence of C₇₀ PL, it cannot be ascertained whether the 1.82 eV is due to exciton diffusion, or direct excitation of the C₇₀ impurities. Direct excitation of C₇₀ is certainly a possibility, especially considering the much larger absorption coefficient for C₇₀ than C₆₀ at 514.5 nm (36 μm⁻¹ vs. 3μm⁻¹ as experimentally determined in this lab.)

The combined results of Matus et al. and the work presented here indicate that there is self trapping of excitons on individual C₆₀ molecules. The change in luminescence intensity in the 10 - 90 K is not due to exciton diffusion at impurities, but
rather is intrinsic to C\textsubscript{60} polycrystalline thin films. This is not to say that exciton diffusion does not occur below 90 K, only that the change in PL intensity is not due to impurities. Further study will be required in order to determine if the change in the PL integrated intensity in the 10 - 90 K is due to molecular distortion, or perhaps, nonradiative recombination of untrapped singlet excitons at grain boundaries.

In summary, there is evidence in the temperature dependent luminescence for both intermolecular and intramolecular radiative recombination. There is still ambiguity in some of the features of the luminescence although the temperature dependence and spectral features appear to be due to intrinsic radiative recombination of singlet excitons. At this point, the limiting factor in the PL studies is no longer impurities. A concentration of 0.1\% C\textsubscript{70} roughly corresponds to an impurity every 150 Å. As mentioned earlier, the domain sizes in polycrystalline C\textsubscript{60} thin films are about 60 - 100 Å. Thus the small domain sizes are the limiting factors in understanding the energetics of solid C\textsubscript{60}. Small domains may result in significant inhomogeneous broadening, the complete quenching of features in the PL due to highly delocalized excitons, and the masking of crystal field effects due to short coherence lengths. The next logical step in optical studies of C\textsubscript{60} thin films would be to obtain single crystal C\textsubscript{60} thin films. This will be addressed in the next chapter.
Chapter 6

Future Directions

6.1 Introduction

The study of solid C_{60} has matured dramatically over the past three years. There now exists a foundation upon which future research of C_{60} and other fullerene solids can build. Continued study of C_{60} should provide a better understanding of the properties of this system. This will in turn lead to deeper insight into molecular solids in general. The following two sections offer two different directions for the continued study of solid C_{60}.

6.2 Single Crystal C_{60} Thin Films

The experiments presented in this work were done on polycrystalline C_{60} thin films. As shown in Chapter 5, this lack of structural uniformity clouds the interpretation of the data. Grain boundaries may quench radiative recombination of delocalized excitons, and the effects of the crystal field lose coherence due to the random alignment of domains. The ability to grow C_{60} single crystal thin films would be a great
aid in understanding the dynamics of excited states in this system. Fortunately, a joint effort between this lab and researchers at the University of Houston has yielded C_{60} single crystal thin films [72]. Single crystal thin films of (111) oriented C_{60} were grown epitaxially on single crystal antimony.

It will be worthwhile to repeat the temperature dependent photoluminescence on these thin film C_{60} single crystals. Figure 6.1a shows preliminary photoluminescence data on such a film. The single crystal photoluminescence spectrum shows many more features than the polycrystalline films. In particular, there is much more higher energy structure with well resolved peaks appearing at 1.74 and 1.77 eV. Additional work is required in order to determine if these peaks are due to crystal field effects or delocalized excitons. It will also be important to obtain Raman spectra of these single crystal C_{60} films. Splittings, or lack thereof, of the fivefold degenerate H_{g} modes could yield useful information about the crystal field. In short, PL and Raman spectroscopy on these films will provide further insight into the intramolecular and intermolecular excited states of crystalline C_{60}. 
6.3 Disorder Through Intercalation

The discussion in the previous section does not suggest that noncrystalline C$_{60}$ is not interesting in its own right. With the ability to obtain high purity C$_{60}$ powder, it is now possible to selectively dope C$_{60}$ thin films. Figure 6.1b shows the photoluminescence spectra of a C$_{60}$ polycrystalline thin film which was purposely doped with toluene by cosublimation. The spectrum is very broad and featureless with a maximum at 1.69 eV. This spectrum is indicative of a large distribution of singlet states and indicates a degree of disorder. Doping C$_{60}$ with more or less polar solvents may lead to unique disorder effects. Thus, the C$_{60}$-solvent system is in some sense tunable from ordered to disordered. Harigaya has in fact discussed the presence of impurities in C$_{60}$ leading to site induced disorder [73].

Further work in this direction will of course require reasonable quantification of the amount of impurities present in the film. Current collaboration with researchers at Sam Houston State University will help with the quantification because of their Fourier Transform Infrared spectroscopic capabilities. STM and mass spectroscopy of such films may also help quantify impurity concentration levels. It should also be mentioned that polar solvent intercalation into the C$_{60}$ lattice may have practical ap-
plications. Efficient charge transfer may lead to large third order optical nonlinearities which could have applications in optical signal processing.

6.4 Final Remarks

In addition to the cw measurements presented here, we can additionally perform time resolved optical studies with femtosecond time resolution. Ultrafast carrier relaxation measurements on polycrystalline $C_{60}$ thin films have been reported [4]. With higher purity films and the ability to grow single crystal $C_{60}$ thin films, a great deal can be learned using these ultrafast optical techniques. Of particular importance are transient grating experiments, which will enable the study of exciton dynamics and diffusion in crystalline $C_{60}$. Further discussion of such measurements can be found in Reference [4].

In closing, $C_{60}$ is but one member of the fullerene family. Heavier fullerenes such as $C_{70}$ and $C_{84}$ or endohedral fullerenes such as $La\@C_{60}$ will eventually become more abundant with continued research. It will be most interesting and informative to study the solid phases of these fullerenes. Fullerene research is reaching maturity, and it is up to researchers in this field to make sure that, through continued creativeness, this research remains fruitful.
Figure 6.1: a.) Single Crystal Thin Film $C_{60}$ PL spectrum at 10 K b.) Toluene doped $C_{60}$ Thin Film PL Spectrum at 10K
Appendix A

Simulation Code for Distillation

```
cc Molecular Distillation Simulation Program
cc
cc Results for c60 stored in data file "data60"
cc Results for c70 stored in data file "data70"
cc
cc ****** notes on cell array data and storage ******
cc
cc In order to be compatible with standard ODE solvers,
cc the data array m[n] representing the mass of each component
cc in each cell is stored as
cc m[n] = {m60[0],m70[0],m60[1],m70[1],...,m60[n],m70[n]},
cc where m60 = mass of C60, m70 = mass of C70 and n = the cell
cc number. dmdt is the array of derivatives, dm/dt = net flux
cc in or out of the cells and dm = incremental mass change at
cc each time step. dmdt[] and dm[] have the same form as m[].
cc
cc max # of cells = 100
integer maxcell
parameter(maxcell = 100)
cc
integer ncell,n,iwork(5),iflag,i,neqn
double precision t(maxcell)
double precision m60chk,m70chk,time,tend,tstart,dt
double precision start60,start70,spaze,timeout,relerr,abserr
double precision work(3+6*(2*maxcell))
double precision m60(maxcell),m70(maxcell)
double precision m(2*maxcell)
```
external flux

cc number of "theoretical plates"

write(6,*)'Enter number of plates'
read(5,*)ncell

cc amount of starting material in mgs

write(6,*)'Enter amount of starting material, c60'
read(5,*)start60
write(6,*)'Enter amount of c70'
read(5,*)start70

cc distillation time (seconds)

write(6,*)'Enter final distillation time'
read(5,*)tend

c

write(6,*)'Enter time interval between printings'
read(5,*)dt
tstart = 0.01d0

write(6,*)',
write(6,*)'Number of Plates = ',ncell
write(6,*)'Distillation time = ',tend
write(6,*)'Starting Material, c60 = ',start60,' c70 = ',start70
write(6,*)','

cc The temperature gradient used in simulation (see fig. 5)
cc spaze is the baffle spacing in cm
cc The gradient in in degrees Kelvin
spaze = 0.896d0

do 10 n=ncell,1,-1
   t(n) = (602.61 + 273.15)d0 - 10.287*spaze*(ncell-n)
10  continue

cc  set initial conditions
cc  cells are empty at start:

   do 30 n=1,ncell
      m(2*n-1) = 1.0d-8
      m(2*n)  = 1.0d-8
30  continue

cc  put starting material in the last cell
m(2*ncell-1) = start60
m(2*ncell)  = start70

cc  Integrates:

c  initialization:
   iflag = 1
   relerr = 1d-6
   abserr = 1d-6
   time = tstart
   timeout = time + dt
   nsteps = int(tend-tstart)/dt
   neqn = 2*ncell
cc Start Integrate loop:
cc
do 80 i = 1,nsteps
cc
call rkf45:
crкf45 is the integration package from reference 12
call rkf45(flux,neqn,m,time,timeout,relerr,abserr,
  * iflag,work,iwork,ncell,t)

    if(iflag .eq. 2)then
        time = timeout
        timeout = time + dt
    else
        write(6,70)iflag
        format('Error condition in RKF45; iflag=',i4)
        write(6,*)'On the interval time=',time,'timeout=',timeout
        goto 90
    endif

80  continue

        write(6,*)'Final Integration time = ',timeout
cc come to here if error condition:
90  continue

cc unpack m:
do 110 n = 1,ncell
    m60(n) = m(2*n-1)
    m70(n) = m(2*n)
110 continue

  m60chk = 0.0d0
  m70chk = 0.0d0
cc Place final results in data files

open(12, file='data60')
do 100 n=1, ncell
   write(12,*) m60(n), ', t(n)
m60chk = m60chk + m60(n)
100 continue
close(12)

open(14, file='data70')
do 200 n =1, ncell
   write(14,*) m70(n), ', t(n)
m70chk = m70chk + m70(n)
200 continue
close(14)

write(6,*) ',
write(6,*)' mass check 60 = ', m60chk
write(6,*)' mass check 70 = ', m70chk
stop
end

cc
cc double precision function vp60(t)
cc
calculate pure C60 vapor pressure in mtorr (from ref. 10)
cc
double precision dexp, t

vp60 = 7.5006d0 * dexp(26.96d0 - 22194.0d0/t)
return
end

double precision function vp70(t)
cc
calculate pure C70 vapor pressure in mtorr (from ref. 11)
cc
double precision dexp,t

vp70 = 7.5006d0*dexp(26.856d0 - 23354.0d0/t)

return
end

cc -------------------------------------------------------------
subroutine flux(ncell,t,time,m, dm)
cc
calculate the net mass flow rate from the n to n+1 cell
cc for each species in the cell. the flow is weighted by the
cc mole fraction of that species in the cell.
cc
ccon conductance calculations are based on free molecular flow:
cc pressures are in mtorr,
cc temperature in degrees kelvin,
cc molecular weight in grams/mole,
cc area of aperture(s) between the cells in sq. cm.,
cc flux is returned in mg/sec
cc

integer n, ncell, maxcell
parameter(maxcell=100)
double precision time, mmin, m(2*ncell), dm(2*ncell), t(ncell)
double precision m60(maxcell), m70(maxcell)
double precision flux60(maxcell), flux70(maxcell)
double precision k,a, sqm60, sqm70, k60, k70, dsqrt,
  *   vp60, vp70

cc
cc  unpack m:
do 10 n = 1, ncell
   m60(n) = m(2*n-1)
   m70(n) = m(2*n)
10  continue

k = 5.83307d-2
a = 3.9d0
mmin = 1.0d-2
sqm60 = dsqrt(720.0d0)
sqm70 = dsqrt(840.0d0)
k60 = k*a*sqm60
k70 = k*a*sqm70

do 50 n = ncell, 2, -1
   if (m60(n) .gt. mmin) then
      flux60(n) = k60*(vp60(t(n))/sqrt(t(n)))
   else
      flux60(n) = 0.0d0
   endif

   if (m70(n) .gt. mmin) then
      flux70(n) = k70*(vp70(t(n))/sqrt(t(n)))
   else
      flux70(n) = 0.0d0
   endif
50  continue

cc
cc  combine these fluxes into the net flow
cc  and then put the net flow into dm:
\[ dm(1) = \text{flux60}(2) \]
\[ dm(2) = \text{flux70}(2) \]
\[ \text{do} \ 70 \ n = 2, \ n\text{cell}-1 \]
\[ \hspace{1cm} dm(2*n-1) = \text{flux60}(n+1) - \text{flux60}(n) \]
\[ \hspace{1cm} dm(2*n) \hspace{1cm} = \text{flux70}(n+1) - \text{flux70}(n) \]
\[ 70 \hspace{1cm} \text{continue} \]
\[ dm(2*n\text{cell}-1) = -\text{flux60}(n\text{cell}) \]
\[ dm(2*n\text{cell}) \hspace{1cm} = -\text{flux70}(n\text{cell}) \]

\[ \text{return} \]
\[ \text{end} \]
Bibliography


