Terms and Conditions of Use of Digitised Theses from Trinity College Library Dublin

Copyright statement

All material supplied by Trinity College Library is protected by copyright (under the Copyright and Related Rights Act, 2000 as amended) and other relevant Intellectual Property Rights. By accessing and using a Digitised Thesis from Trinity College Library you acknowledge that all Intellectual Property Rights in any Works supplied are the sole and exclusive property of the copyright and/or other IPR holder. Specific copyright holders may not be explicitly identified. Use of materials from other sources within a thesis should not be construed as a claim over them.

A non-exclusive, non-transferable licence is hereby granted to those using or reproducing, in whole or in part, the material for valid purposes, providing the copyright owners are acknowledged using the normal conventions. Where specific permission to use material is required, this is identified and such permission must be sought from the copyright holder or agency cited.

Liability statement

By using a Digitised Thesis, I accept that Trinity College Dublin bears no legal responsibility for the accuracy, legality or comprehensiveness of materials contained within the thesis, and that Trinity College Dublin accepts no liability for indirect, consequential, or incidental, damages or losses arising from use of the thesis for whatever reason. Information located in a thesis may be subject to specific use constraints, details of which may not be explicitly described. It is the responsibility of potential and actual users to be aware of such constraints and to abide by them. By making use of material from a digitised thesis, you accept these copyright and disclaimer provisions. Where it is brought to the attention of Trinity College Library that there may be a breach of copyright or other restraint, it is the policy to withdraw or take down access to a thesis while the issue is being resolved.

Access Agreement

By using a Digitised Thesis from Trinity College Library you are bound by the following Terms & Conditions. Please read them carefully.

I have read and I understand the following statement: All material supplied via a Digitised Thesis from Trinity College Library is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of a thesis is not permitted, except that material may be duplicated by you for your research use or for educational purposes in electronic or print form providing the copyright owners are acknowledged using the normal conventions. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone. This copy has been supplied on the understanding that it is copyright material and that no quotation from the thesis may be published without proper acknowledgement.
Polymeric Waveguides for use as Solid State Laser Materials

by

Kevin P. Kretsch

A thesis submitted to the University of Dublin, Trinity College, for the degree of
Doctor of Philosophy.

Department of Physics,
University of Dublin,
Trinity College.

November 1999
DECLARATION

This thesis is submitted to the University of Dublin, Trinity College as an exercise for the degree of Ph.D. The work contained within this volume is entirely my own, except where otherwise acknowledged. This thesis has not been submitted to any University as part of another degree. I agree that this work may be freely lent or copied by the library of Trinity College, Dublin.

Kevin P. Kretsch
DEDICATION

To my Mother and Father

For Everything.
SUMMARY

The work presented is intended to identify promising candidate materials for use as solid state lasers utilising planar optical waveguides, and to gain an insight into the physical processes that may be controlled through materials selection, and device preparation and design.

Characteristics of planar optical waveguides are reviewed, along with fabrication and testing procedures, and an overview of photophysical processes in organic materials is given. The effect of the environment of a molecule on the emission processes is investigated.

Fluorescent conjugated polymers are found to exhibit prohibitively large propagation losses in thin films, generally unsuitable for optical waveguide applications. Poly(styrene) films doped with oligo phenylene vinylene model compounds are found to have excellent propagation losses.

A material's potential for use in a solid state laser device is tested through solution lasing measurements, optical gain characterisation in thin films, and pump beam induced distributed feedback measurements in thin films. The model compounds are found to exhibit single pass optical gains of $g \approx 20 \text{ cm}^{-1}$, and exhibit distributed feedback laser action at $\mu\text{J}$ pulse energies.
PUBLICATIONS

  "Distributed Feedback Lasing in oligo Phenylene Vinylene doped Polymeric Waveguides: Guided Mode Thresholds"

  "Distributed Feedback Laser Action from Polymeric Waveguides doped with oligo Phenylene Vinylene Model Compounds"

  "Amplified Spontaneous Emission and Optical Gain Spectra from Stilbenoid and PPV Model Compounds"

  "Effective Stimulated Emission and Excited State Absorption Measurements in Phenylene-Vinylene Oligomer (1,4-Bis-(alpha-cyanostyryl)-2,5-dimethoxybenzene)"

  "Laser Emission from Solutions of PPV-Derivatives and Stilbenoid model Compounds"
*Synth. Met.*, Accepted for publication.
"Optical Gain Spectra from Doped Polymeric Waveguides"

"Luminiscent Quantum Yields and Vibrational Spectroscopy"
# Table of Contents

Declaration  
Dedication  
Summary  
Publications  
Table of contents  
Acknowledgements

## Chapter 1  Introduction

1.1 Historical Perspective  
1.2 Solid State Organic Lasers - Overview  
1.2.1 Material Requirements  
1.3 Thesis Outline

## Chapter 2  Introduction to Planar Waveguides

2.1 Introduction  
2.2 Electromagnetic theory of Dielectric Waveguides  
2.2.1 EM Theory of the Asymmetric Slab Waveguide  
2.2.2 Modes of an Asymmetric Slab Waveguide  
2.3 Experimental Considerations

## Chapter 3  Optical Process in Organic Materials

3.1 Introduction  
3.2 Transitions between two Electronic Levels  
3.2.1 The Franck-Condon Principle  
3.3 Optical Properties of a Broadened Two Level System  
3.3.1 Gain Analysis of two Broadened Energy Levels

vii
Chapter 4  Environmental Effects on Emission Processes  39
4.1 Introduction  39
4.2 Raman Spectroscopy and Fluorescence Quantum Yield  40
  4.2.1 Experiment  42
  4.2.2 Results  42
4.3 Spontaneous Emission in a Dielectric Slab  44
  4.3.1 Theoretical Treatment  45
  4.3.2 Overview of Results  48
  4.3.3 Effect on the Stimulated Emission Cross Section  50
  4.3.4 Implications for Waveguide Devices  52
4.4 Conclusions  53

Chapter 5  Fluorescent Materials and Characterisation  55
5.1 Introduction  55
  5.1.1 Materials  56
5.2 Solution Lasing Measurements  58
  5.2.1 Lasing properties of the compounds  59
5.3 Thin Film Preparation and Characterisation  61
  5.3.1 Spin Coating of Thin Films  62
  5.3.2 Prism-Film Coupling  63
  5.3.3 Thin Film Results  67
5.4 Conclusions  70

Chapter 6  Amplified Spontaneous Emission in a Planar Waveguide  73
6.1 Introduction  73
6.2 Single Pass Fluorescence Amplification  76
  6.2.1 Wavelength Dependent Optical Gain  78
6.3 Experiment  81
  6.3.1 Sample Preparation  82
6.4 Results and Discussion  83
Chapter 7  Distributed Feedback Lasing 92

7.1  Introduction 92

7.2  Coupled Wave Theory of Distributed Feedback Lasers 93
  7.2.1  Coupled Wave Solutions 95
  7.2.2  Optically Induced Gratings 98
  7.2.3  Application to Planar Waveguides 101

7.3  Experiment 102
  7.3.1  Sample Preparation 104

7.4  Results and Discussion 104
  7.4.1  DFB Laser Tuning Range 104
  7.4.2  Simultaneous Multi-Wavelegth Lasing 106
  7.4.3  Lasing Thresholds of Waveguide Modes 110

7.5  Conclusions 113

Chapter 8  General Conclusions 115
ACKNOWLEDGEMENTS

Firstly, I must thank my supervisor Prof. Werner Blau for the opportunity to do this work, and for his constant support, advice, and patience. The largely uninhibited freedom given to me to make my own path through this work has earned my eternal gratitude.

To those with whom much of this work was done in collaboration:

Prof. Jean-Michel Nunzi, Dr. Celine Fiorini, Dr. Vincent Dumarcher, Licinio Rocha and all at the CEA Saclay, France, for their help, patience, and advice during the distributed feedback measurements, presented in chapter 7.

Prof. Dr. Hans-Heinrich Hörhold, of the Institute for Organic Chemistry and Macromolecular Chemistry, Friedrich-Schiller University, Jena, Germany, for synthesis of the materials used in this thesis.

Prof. Fryad Henari, formerly of TCD and now at University of Bahrain, for the fruitful collaboration with measurements of the Jena samples, presented in chapter 5, and much support and friendship.

Dr. Hugh Byrne, Dublin Institute of Technology, for a most enjoyable collaboration on the Raman spectroscopy presented in chapter 4, and for all his advice and friendship.

Colin Belton and Stephen Lipson, for their assistance with sample fabrication and characterisation, chapters 5, 6, and 7. Without their (last minute) assistance, this thesis would not have been submitted on time. Also to Mr. Moussa Dembele, for his assistance with waveguide characterisation in chapter 5, (though some results are not presented here).
My thanks to all in Group Bu, past and present, for all their help, support, and friendship. To give everyone the attention they deserve here would simply take too long. However, I will single out the following people for special mention: Dr. Andy Davey, Dr. Dave Gray, and Dr. Karl Cazzini, three good friends from whom I have learned more than everyone else put together. Anna Drury and Stephanie Maier, whose patience and assistance in the chemistry lab deserves a very big, shiny medal. Jean-Edouard Communal, Colin Belton, Stephen Lipson, and Margaret Brennan, four good friends I have spent a lot of time with, enjoyed every minute, and whom I have no doubt will make damn fine scientists in their own right.

Many thanks to all the staff of the TCD Physics Department, particularly to Tom Burke, James Egan, John Kelly, Jeanette Cummins, Michelle Duffy, and Liz Gray.

To the gang "back home": John, Shane and Sinead, Darren, Paul and Jennifer, Mick, Niall, and Gearoid, and also to Rich and Shelley, Clare, and all my friends around the world.

And finally to my Family: my mother and father, Noah and Geraldine, my brothers Conor and Barry, and the rest of the family at home and abroad. Thank you so much for everything.
Chapter 1 Introduction

1.1 Historical Perspective

In 1972 Ulrich and Weber\textsuperscript{1} demonstrated low loss dielectric optical waveguides deposited from solution. While not the first paper demonstrating optical waveguides in organic materials, Ulrich and Weber's paper demonstrated fluorescence amplification in polymeric waveguides doped with the laser dye Rhodamine 6G, preceding all-organic solid state waveguide lasers.

The appearance of conjugated polymers in optical research started in 1990, when Burroughs \textit{et al.}\textsuperscript{2} demonstrated efficient electrically pumped light emission from a polymer film, though Partridge\textsuperscript{3} had also demonstrated this some seven years earlier. In 1991 Zhou \textit{et al.}\textsuperscript{4} proposed that conjugated polymers offered increased nonlinear optical susceptibilities, theoretically in excess of any other material class, spawning an active field of research. While efficient photoluminescence is not a necessary requirement for electroluminescent or nonlinear optical polymers, it was a prominent feature of many of the novel polymeric materials. It was not long before the emissive properties prompted much interest in their own right and the possibility of using these materials for laser generation, optically or electrically pumped, prompted active consideration.
Chapter 1: Introduction

1.2 Solid State Organic Lasers - Overview

Recent has work has produced solid state polymeric devices that exhibit stimulated emission\(^5,6\) and laser action\(^7,8\). These devices often utilise waveguide geometries\(^9,10\) making high optical power densities readily achievable and thus ideal for compact laser sources and optical amplification. The devices can be divided into two categories: systems where the active layer of the device is composed entirely of the active polymer material\(^11,12\) and solid guest-host systems where the emissive molecule or polymer is suspended in an organic host material\(^13,14\). The active layers in both cases are often polymerised or dried from a solution which helps to ensure the molecular distribution in the solid is highly homogeneous, an important factor for narrow-linewidth oscillators.

Solid state lasers based on thin films require some resonant structures to provide optical feedback for laser action, and to induce wavelength selection in the laser emission. Current research focuses on two specific device structures, with a long term view toward an electrically pumped polymer diode laser. First, distributed feedback lasers\(^15,16\) (DFBs) where optical feedback is produced by backward scattering from a periodic modulation of the properties of the film, e.g. refractive index, thickness. Secondly, there are microcavity devices\(^17,18\) where the spontaneous and stimulated emission properties can be modified by 'sandwiching' the emitting film between two reflecting surfaces.

Microcavities are generally limited to very thin films, typically < 100 nm, which is advantageous for electroluminescent devices. However, as the emission is to be directed vertically out of the device, perpendicular to the plane of the film, this leaves a very small gain region for amplification of light, even if the microcavity forms a resonant cavity for laser action. In contrast, waveguides offer much longer propagation lengths for optical gain or feedback, limited only by the scattering and absorption losses of the material. The drawback is that waveguides are restricted to thicker films, generally > 300 nm thickness, which is a disadvantage for electrically pumped devices as it is much more difficult to transport charge through the film.
1.2.1 *Material Requirements*

If organic light emitting materials are to find success in commercial devices, there are a number of properties that are important. Firstly, and most obvious, is the ability to emit light, characterised by the fluorescence quantum yield, now approaching values close to one for some materials, and covering a broad range of the visible spectrum. Secondly, for use as a laser medium or optical amplifier, efficient stimulated emission is required, with stimulated emission cross-sections of the order $\sigma_{s.e.} \approx 10^{-17} - 10^{-15} \text{ cm}^2$. The laser emission must also be tuneable, over a range of at least 30 nm, if polymeric devices are to achieve any commercial viability.

In addition, the materials must be of high optical quality, exhibiting low scattering and absorption losses. They must be reasonably robust, and capable of operating at temperatures in excess of 60°C. In addition, devices must be capable of working lifetimes on the order of 10,000 hrs. Most important of all, they must be cheap to produce and easy to process.

1.3 *Thesis Outline*

This work will study a variety of fluorescent species in a planar waveguide geometry. Both polymers and low molecular weight materials will be characterised in waveguide structures under a variety of conditions to determine their potential for use as solid state laser materials and gain an insight into important parameters for design of emissive waveguide devices.

In chapter 2 a theoretical description of planar waveguides will be introduced. Chapter 3 will introduce the photophysics of organic materials and the relevant molecular processes. Chapter 4 will detail the effect of the environment on the properties of an emitting molecule. This will include a study using Raman spectroscopy to examine the effect of non-radiative decay rate on the fluorescence
Chapter 1: Introduction

quantum yield. The second section of chapter 4 reviews the results of two recent papers concerning the effect of the electromagnetic environment on spontaneous emission. In particular, this deals with emission in the presence of an optical waveguide structure. Using the results from these papers, the effect of the waveguide structure on stimulated emission will be examined.

Chapter 5 will introduce the fluorescent materials to be studied, and give an overview of thin-film fabrication and characterisation. In addition, solution lasing properties of the materials are presented. Chapter 6 involves a study of amplified spontaneous emission (ASE) in planar waveguides. Using an explicitly wavelength dependent description of optical gain, optical gain spectra are determined. It will be shown how meaningful comparisons can be made between different materials, and a figure of merit based on the optical gain experiment is presented. Finally, in chapter 7, distributed feedback lasing in planar waveguides is detailed. Tuning ranges, lasing thresholds and the effect of waveguide modes on these properties is examined. The results from chapter 7 will be compared to the solution lasing results of chapter 5 and the optical gain spectra of chapter 6.
References

Chapter 2 Introduction to Dielectric Waveguides

2.1 Introduction

In this chapter the basic concept of an optical waveguide is introduced, along with a quantitative analysis of the propagation of electromagnetic radiation in such structures. The details regarding the fabrication and characterisation of optical waveguides and devices, and the effect of guided modes on light emission processes, will be left to later chapters. During this discussion the reader can assume that only monochromatic plane electromagnetic waves are discussed.

In general, a dielectric waveguide may be described as a structure that is used to confine electromagnetic fields and enhance or control radiation propagation in some preferred direction. The most familiar type of optical waveguide in common use (e.g. modern telecommunications systems) is the optical fibre, normally of a circular cross-section. Only the planar (or slab) optical waveguide will be discussed theoretically as it is the structure of most relevance to this work. Many of the ideas pertaining to this structure may be extended to other, two-dimensional structures.

The simplest optical dielectric waveguide consists of a thin planar film deposited on a dielectric substrate, and covered by a dielectric cladding layer. This is illustrated in fig. 2.1. Cladding and substrate layers will be assumed semi-infinite in extent. The linear refractive indices of the film (guiding layer), cladding, and substrate are denoted by \( n_f \), \( n_c \), and \( n_s \) respectively.
Chapter 2: Introduction to dielectric waveguides

Fig. 2.1: Schematic representation of a planar waveguide.

Note that often the cladding is simply air, in which case $n_c = 1$. It is a necessary condition for waveguiding that $n_f > n_c, n_e$. Both the substrate and the cladding may be made of the same materials in which case $n_s = n_c$ and the guide is described as being symmetric. In general the refractive index difference between the guiding region and the cladding or substrate region is between $10^{-1}$ and $10^{-4}$, the former regarded as a large difference, and the latter a small difference.

The manner in which light is confined to the guiding region of the waveguide may be described using geometrical optics as propagation through total internal reflection at the film/substrate and film/cladding interfaces. Fig. 2.2 shows the ray diagram representation of a planar waveguide. The properties of a planar waveguide are determined entirely by the refractive indices of the three layers and by the thickness of the guiding layer, $d$.

For a waveguide structure only discrete modes of propagation are permitted. In addition, there are orthogonal propagation modes, labelled TE and TM, which involve propagation of light of orthogonal polarisations. For TE modes the electric
field component is oriented parallel to the plane of the film, and perpendicular for
the TM modes. Each orthogonal set of modes have their own propagation
conditions and TE and TM modes cannot be thought of simply as different
polarisations of the same mode.

In describing the properties of planar waveguides, there are necessarily two
interfaces to consider: film/substrate and film/cladding. In the geometrical optics
formalism, propagation of a waveguide mode is subject to the condition that the
path length from one side of the waveguide to the other must be an integer multiple
of wavelengths, often referred to as a resonance condition. This condition is all that
is necessary to bring about discrete modes of propagation, as only a finite number of
angles, $\theta$, in fig. 2.2 can supply the necessary path length. The Fresnel conditions
for reflection at a dielectric boundary include polarisation dependence of the
reflection coefficients, and thus produce the orthogonal (TE and TM) modes of
propagation supported by a waveguide structure.

### 2.2 Electromagnetic Theory of Dielectric Waveguides

The geometrical discussion will be omitted in favour of the more rigorous
electromagnetic theory approach. For further discussions, the reader is referred to
Yariv\(^1\), and Tamir\(^2\). The discussion will be kept as general as possible. While many
of the same results are obtained with both methods, the latter approach can also tell
us about the field profiles in the waveguide structure, and will help to avert later
confusion in other matters.

Consider a waveguide of arbitrary crossection, such as that depicted in fig. 2.3. The
$z$-direction is chosen as the axis of the waveguide, and the propagation direction of
an optical wave having a temporal variation of the form $e^{i\omega t}$. The $x$-direction is
chosen to be perpendicular to the plane of the film. The $y$-direction is parallel to the
plane of the film (into the plane of the page), perpendicular to the $x$- and $z$-
directions.
Maxwell's equations in the absence of polarisation charges for a dielectric medium may be written as:

\[ \nabla \times \vec{H} = i \omega \varepsilon_0 n^2 \vec{E} \] \hspace{1cm} [2.1]

\[ \nabla \times \vec{E} = i \omega \mu_0 \vec{H} \] \hspace{1cm} [2.2]

where \( n \) is the refractive index distribution within the dielectric structure. The structure is homogeneous in the \( z \)-direction, therefore the refractive index is a function of \( x \) and \( y \) only:

\[ \frac{\partial n}{\partial z}(x,y) = 0 \] \hspace{1cm} [2.3]

solutions to [2.1] and [2.2] are of the form:

\[ \vec{E} = E(x,y) \exp\left[(\omega t - \beta z)\right] \] \hspace{1cm} [2.4]

\[ \vec{H} = H(x,y) \exp\left[(\omega t - \beta z)\right] \] \hspace{1cm} [2.5]

where \( \beta \) is the propagation constant, which may be determined from Maxwell's equations for isotropic dielectric media:

\[ \nabla \times \vec{E} = -\mu_0 \frac{\partial \vec{H}}{\partial t} \quad \nabla \times \vec{H} = \varepsilon_0 \frac{\partial \vec{E}}{\partial t} \] \hspace{1cm} [2.6]
Substituting [2.4] into [2.6] gives the expression

$$\left(\nabla_i^2 + [k^2 n^2(x,y) - \beta^2]E(x,y) = 0\right)$$

[2.7]

where \(E(x,y)\) is called the mode function and \(\nabla_i^2 = \nabla^2 - \frac{\partial^2}{\partial z^2}\) is the transverse Laplacian operator. This governs the transverse nature of the field. Equation [2.7] must be solved subject to the boundary condition that the tangential components of the field \(E(x,y)\) must be matched at each interface, and also that the field amplitudes must be zero at infinity. In order to satisfy the boundary conditions, the propagation constant \(\beta\) must be the same at all points along the interfaces of the homogeneous media which make up the dielectric structure. The solution for the allowed propagation modes of the waveguide involves finding the eigenvalues of [2.7] subject to the conditions on the tangential field components and the field amplitudes at infinity.

Given an arbitrary refractive index profile, \(n(x,y)\), there are in general an infinite number of solutions for \(\beta^2\), corresponding to an infinite number of allowed modes. However, it is found that in order for there to be no net flow of energy in the transverse direction, the modes must propagate confined but freely near the core region of the guide. Physically this means that the field amplitudes must decay exponentially outside the central guiding region, resulting in the condition:

$$\beta^2 = k_0^2 n^2(\infty)$$

[2.8]

where \(n(\infty)\) is the refractive index at infinity, and \(k_0\) the free space wavenumber. Since it is required that \(E^2(\infty) = 0\), continuity requires that \(E(x,y)\) attains a maximum value at some point on the \(xy\)-plane, assuming that \(E(x,y)\) is a smooth piece-wise continuous function of space. For a maximum, eqn. [2.7] requires that \(\nabla^2(x,y)E(x,y) < 0\), which constrains the propagation constant \(\beta\) of a confined guided mode to the condition:

$$k^2 n^2(x,y) - \beta^2 > 0$$

[2.9]
with \[ \beta^2 < k^2 n^2(x, y) \] \[2.10\]

In particular, if \( n_f \) is the maximum value of the refractive index profile, then the following condition must always apply:

\[ \beta^2 < k^2 n_j^2 \] \[2.11\]

Within the region where \[2.10\] is satisfied, the solutions of the wave equation \[2.7\] are oscillatory, and these must be matched to the exponential solutions at the boundaries of the dielectric interfaces. Therefore not all the solutions satisfying \[2.11\] and \[2.8\] can be considered as eigenvalues of confined guided modes.

### 2.2.1 EM Theory of the Asymmetric Slab Waveguide

The cladding, guiding region and substrate have refractive indices \( n_c \neq n_f \neq n_s \). By convention, for an asymmetric waveguide, the substrate is of higher index than the cladding, i.e. \( n_s > n_c \). Both substrate and cladding are assumed semi-infinite in the \( x \)-direction. The co-ordinate system is chosen so that the field is propagating along the \( z \)-direction in the \( xy \)-plane, as before. Again, the structure has \( \partial n/\partial z = 0 \), and a refractive index profile given by:

\[
n(x, y) = \begin{cases} 
  n_c & 0 < x \\
  n_f & -d < x < 0 \\
  n_s & x < -d 
\end{cases} \quad [2.12]
\]

with \( n_f > n_s > n_c \)

As there is no \( y \)-dependence on the refractive index, insertion of \( \partial/\partial y = 0 \) into eqn. [2.7] yields:
Here, the quantity $E(x,y)$ is the Cartesian component of the mode function $E(x,y)$ of eqn. [2.7]. With the assumption that $n_f > n_s > n_c$, consider now the solutions of eqns. [2.13] as a function of the propagation constant $\beta$ for a fixed frequency $\omega$, in a qualitative manner:

$$\beta > k_0 n_f$$

If $\beta > k_0 n_f$ then eqns. [2.13] imply that

$$\frac{\partial^2 E}{\partial x^2} > 0$$

everywhere and $E(x)$ is exponential in the three regions of the waveguide. Since the fields must be matched at the interfaces, the resulting field distribution is shown in fig. 2.4a. The field profile is therefore not physically achievable and hence does not represent a real wave. Next consider:

$$k_0 n_s < \beta < k_0 n_f$$

Eqn. [2.13] implies a sinusoidal solution in the film region since

$$\frac{1}{E} \left( \frac{\partial^2 E}{\partial x^2} \right) < 0,$$

but is exponential in the cladding and substrate regions. This allows us to have a solution $E(x)$ satisfying the boundary conditions with exponentially decaying fields in the cladding and substrate. These solutions correspond to the guided modes of the guided structure. Hence they can only exist if $n_f > n_c$, $n_s$ is satisfied. Now consider:

$$k_0 n_c < \beta < k_0 n_s$$

(cf Fig. 2.4d)
Figs. 2.4: Top: the different regimes (a), (b), (c), (d), (e) of the propagation constant, $\beta$, of the waveguide shown in fig. 2.3. Middle: the field distributions corresponding to different values of $\beta$. Bottom: the propagation triangles corresponding to the different propagation regimes. Note that $n_1$, $n_2$, and $n_3$, correspond to $n_0$, $n_0$, and $n_s$ in the above discussion. (adapted from ref.(1))

Now eqns. 2.13 give exponential fields in the cladding and sinusoidal fields in the film and substrate. These are referred to as the substrate (radiation) modes. The final case to consider is:
Chapter 2: Introduction to dielectric waveguides

0 < β < \( k_0 n_c \)  

(cf Fig. 2.4e)

The solutions to eqns. \([2.13]\) become sinusoidal in all three regions of the structure. These are the radiation modes of the structure. There are no guided modes supported by the structure and the radiation modes are equivalent to propagation of plane waves through the three layers.

While the solutions of \([2.13]\) in the regimes illustrated in Figs. 2.4d,e are for continuous \( \beta \) (subject to the boundary conditions), the solutions for the eigenvalues \( \beta \) in the regime \( n_fk_0 < \beta < n_fk_0 \) are discrete, and the number of guided modes increases from zero with increasing film thickness, \( d \).

Finally we will consider the propagation triangles at the bottom of fig. 2.4. These triangles correspond directly to the geometrical optics point of view, i.e. that of a plane wave propagating at some angle \( \theta \) to the \( z \)-axis and undergoing total internal reflection at the interfaces. This is directly related to eqn. 2.13 b. On the assumption that \( E \propto \sin(\alpha + \alpha)\exp(-i\beta z) \), one obtains:

\[
\beta^2 + h^2 = k^2 n_f^2 \tag{2.14}
\]

The propagation is considered as a plane of wave of constant propagation constant, \( k_f \), for all cases in fig. 2.4. As \( \beta \) decreases, \( \theta \) increases until \( \beta = k_n \) and total internal reflection ceases at the film/substrate interface. The condition for exponential decay into the cladding is identified by writing \( \beta = k_f \cos \theta \), with the geometrical optics condition for the onset of total internal reflection.

### 2.2.2 Modes of an Asymmetric Slab Waveguide

We can now solve eqn. \([2.7]\) for the waveguide shown in fig. 2.3. The derivation is applied only to those modes which satisfy the condition:
Since there is no $y$ variation, $\frac{\partial}{\partial y} = 0$, and eqn. [2.7] becomes:

\[
\left[ \frac{\partial^2}{\partial x^2} + (k_0 n_j^2 - \beta^2) \right] E = 0 \quad j = c, f, s \tag{2.15}
\]

i.e. the subscript $j$ refers to the different regions of the waveguide structure. The structure supports a finite number of propagation modes with field components $E_y$, $H_x$, and $H_z$. These are the transverse electric (TE) modes. The structure may (simultaneously) support a finite number of modes with field components $H_y$, $E_x$, and $E_z$. These are the transverse magnetic (TM) modes. In practice, the TE modes correspond to light having been launched into the structure with field component $E_y$ oriented parallel to the plane of incidence, while TM modes have $H_y$ oriented normal to the incidence plane. First, propagation of the TE modes is examined. The field component of the TE modes can be written:

\[
E_y(x, z, d) = \tilde{\varepsilon}_y(x) \exp i(\alpha d - \beta z) \tag{2.16}
\]

and the mode function $\tilde{\varepsilon}_y(x)$ is taken as

\[
\tilde{\varepsilon}_y(x) = \begin{cases} 
C \exp(-qx) & 0 < x \\
C \left( \cos(hx) - \frac{q}{h} \sin(hx) \right) & -d \leq x \leq 0 \\
C \left( \cos(hd) - \frac{q}{h} \sin(hd) \right) \exp p(x + d) & x < -d
\end{cases} \tag{2.17}
\]

for $n_c < n_s$
Chapter 2: Introduction to dielectric waveguides

i.e. exponential solutions in the cladding and the substrate regions, while an oscillatory solution for the film region. Substitution of [2.17] into [2.15] yields the following relations:

\[
h = \left( n_-^2 k_0^2 - \beta^2 \right)^{\frac{1}{2}}
\]
\[
q = \left( \beta^2 - n_+^2 k_0^2 \right)^{\frac{1}{2}}
\]
\[
p = \left( \beta^2 - n_+^2 k_0^2 \right)^{\frac{1}{2}}
\]
\[
k = \frac{\omega}{c}
\]

[2.18]

The choice of the coefficients in [2.17] is such as to make \(\partial \tilde{E}_y / \partial x\) continuous at \(x = 0\) and \(x = -d\). Through the imposition of continuity on \(\partial \tilde{E}_y / \partial x\) at \(x = -d\), eqn.[2.17] leads to the so-called TE mode condition,

\[
hsin(hd) - q \cos(hd) = p \left[ \cos(hd) + \frac{q}{h} \sin(hd) \right]
\]

or

\[
\tan(hd) = \frac{p + q}{h \left( 1 - \frac{pq}{h^2} \right)}
\]

[2.19]

The propagation of all TE modes must satisfy [2.19]. Eqn. [2.19] in conjunction with eqns. [2.18] is used to obtain the eigenvalues of \(\beta\) for the confined TE modes. Using such a calculation, the general properties of TE (and TM) modes are shown for a poly(styrene) in fig.(2.5). It is clear that that \(\beta/k_0\) for each guided mode approaches \(n_f\) as the film thickness increases. In addition, at the birth of each mode, at the so-called cut-off thickness, \(\beta/k_0\) approaches \(n_s\).
The derivation of the guided TM modes follows a similar approach. The TM modal field components are $H_y$, $E_x$, and $E_z$, where:

$$H_y(x, z, d) = \mathcal{H}_y(x) \exp(i \omega t - \beta z)$$

$$E_x(x, z, d) = \frac{i}{\omega \varepsilon} \frac{\partial H_y}{\partial z} = \frac{\beta}{\omega \varepsilon} \mathcal{H}_y(x) \exp(i \omega t - i \beta z)$$

$$E_z(x, z, d) = -\frac{i}{\omega \varepsilon} \frac{\partial H_y}{\partial x}$$

This time the mode function $\mathcal{H}_y(x)$ is taken to have the form:

$$\mathcal{H}_y(x) = \begin{cases} 
\frac{h}{q} C \exp(-qx) & 0 < x \\
\left[ \frac{h}{q} \cos(hx) - \sin(hx) \right] & -d \leq x \leq 0 \\
C \left[ \frac{h}{q} \cos(hd) - \sin(hd) \right] \exp p(x + d) & x < -d 
\end{cases}$$

[2.21]
2.3 Experimental Considerations

In the preceding sections it has been shown that for monochromatic radiation a waveguide structure will support propagation of some number of discrete orthogonal guided modes, except in the trivial cases that no modes are supported, or only one mode (TE\textsubscript{0}) is supported. This will allow a characterisation of film thickness and refractive index of a waveguide by determining the waveguide modes and their propagation constants at some wavelength, \( \lambda \), as described in chapter 5.

Fluorescent light emission in a waveguide structure and its propagation will form the bulk of the results presented in this thesis. It has been shown above that at a fixed wavelength, a finite number of guided modes of (necessarily) different values of \( \beta \) are supported. If we remove the restriction on wavelength then guided modes of the same value of \( \beta \) can guide, provided they are of different wavelengths. In general there will be a continuum of guided modes present, limited by the spectral bandwidth of the (continuous) fluorescence spectrum and the transparency of the material. In addition, this is subject to the guided mode cut-off conditions: as the wavelength increases the normalised film thickness drops and a situation is possible where guided modes are not supported in some portion of the fluorescence band. Wavelengths close to the cut-off condition may display increased propagation losses.

In a homogenous infinite dielectric medium, the only electromagnetic modes present will be (an infinite set of) plane waves, isotropically distributed throughout space. In the vicinity of a waveguide structure, the situation will be very different. As spontaneous emission from an emitting dipole can be affected by the surrounding electromagnetic environment, we can expect a waveguide structure to have some influence on fluorescent emission, and also on stimulated emission. This will be further discussed in chapter 4 and has important implications on the devices discussed in later chapters.
References

Chapter 3 Optical Processes Organic Materials

3.1 Introduction

Organic dyes have found widespread use as laser materials since the first demonstration of dye laser action in 1966. Optical properties of the materials under study here can be described using the same formalisms applied to organic dyes. A broad definition of organic dyes, as compounds containing an extended system of conjugated bonds and demonstrating a strong absorption band somewhere between the near infra-red and ultra violet. This includes most conjugated polymers and their model compounds. These compounds are too complex to derive their absorption and emission from quantum mechanics and non-radiative processes are even more complex. But a relatively simple formalism can be applied which greatly eases the problems of modelling the properties of these materials.

In dilute systems (solution or solid guest/host materials) the photophysics of these materials can be described first by considering the processes between two electronic energy bands. These energy bands are broadened by a continuum of vibrational and rotational states and the spectral properties associated with these bands are correspondingly broad, in contrast to the sharp optical features associated with atomic transitions. Once these processes are understood we can then proceed to a more general discussion involving a larger number of electronic energy bands and thus begin to understand all the associated optical features of a molecule. For a more complete description of the physics of dye lasers, which will form the bulk of this chapter, the reader is referred to Shank, Peterson et al., and Svelto.
Chapter 3: Optical processes...

It should be noted that for condensed systems, i.e. where the molecules are in very close proximity and can interact with each other, the model described in the next two sections may not adequately explain all the optical properties. In particular, conjugated polymers, which may also have a weakly semiconducting nature, display inter- and intra-chain excitations, which are of importance under some conditions. Some of these excitations are relevant only when the material is electrically excited and are not relevant to this work. Other excitations which are not explicitly described below, are generally weak and/or cannot be easily identified from other excited state processes.

3.2 Transitions between two Electronic Levels

Optical processes in organic materials can be described using a model involving two electronic levels. The electronic states are vibrationally broadened into bands, typically 50 nm (0.2 eV) FWHM. The vibrational levels are separated by ~0.05 eV (1000K) and are themselves broadened by rotational sublevels of ~10^-3 eV (100K) separation.

Fig. 3.1, known as a configurational coordinate diagram, allows us to represent both the electronic and vibrational states on the same diagram. It is assumed that molecular vibrations are restricted to simple harmonic oscillation. The potential energies of the states are represented by harmonic oscillator parabolas, which become anharmonic at large vibrational energies. The vibrational levels are represented in fig. 3.1 by horizontal lines. The configurational coordinate (x-axis) represents the mean distance of the electronic molecular orbital from some reference axis of the molecule, usually defined by the nuclear positions of the molecule in its ground state. The two levels in fig. 3.1 are not labelled and can represent any two electronic levels for which an optical transition can occur.

A change in electronic state also entails a change in the molecular orbital, including geometry, and therefore a net change in the configurational coordinate. The two energy levels depicted in fig. 3.1 not only have different energies but also have
different configurational coordinates associated with the lowest points of their respective parabolas.

Figure 3.1: Configurational coordinate diagram of two vibrationally broadened electronic energy levels.

3.2.1 The Franck-Condon Principle

To investigate the transitions we can use the Franck-Condon principle. This applies well to many different materials and the reader is referred to ref. 6 for a good description (though applied to vibronically broadened inorganic systems). It is assumed that any transition between electronic states occurs fast enough that there is no change in configurational coordinate immediately before or after the transition. Transitions are thus represented as vertical lines on the diagram. For a molecule in the lowest (zero) vibrational level the most probable value of configurational coordinate is at the base of the parabola. However, for excited vibrational states, the
vibrational states, the most probable value is at the edge of a parabola. The most likely transition will be from the base of the ground state parabola to a vibrational level which 'terminates' at the edge of the excited state parabola, i.e. vertically above the base of the ground state parabola along line AB. Other transitions are also available, though less favoured, giving rise to a broad absorption band.

A molecule in an upper vibrational state will quickly decay nonradiatively to a lower vibrational state, along the line BC, with creation of phonons. This is known as 'thermalisation' or Franck-Condon relaxation. The molecule can then reach the ground state by emission of a photon, of energy $h\nu_2$, along the line CD. This is generally known as luminescence, the distinction between fluorescence and phosphorescence is described later. A broad luminescence band is present for the same reason as the absorption band. This also explains why the absorption and emission bands are approximate mirror-images. Finally the molecule relaxes via thermalisation to a lower lying vibrational state, along line DA.

It is clear from fig. 3.1 that there is a greater energy difference between the lines AB and CD, i.e. absorbed photons are of a higher energy, resulting in a red-shift of the emission spectrum relative to the absorption. The difference in energy (or wavelength) between the emission and absorption is known as the Stokes' shift. If the lowest vibrational level of the two electronic states are sufficiently close in configurational coordinate, then for a transition between these levels, no emission of phonons is required before luminescence. Transitions of this energy, $h\nu_0$, are known as zero-phonon transitions and will be present at the same frequencies in absorption and emission. As will be described below, this can also give rise to emission at higher energies than the absorption transition when the pump energy approaches $h\nu_0$. If however, the configurational coordinate offset is large enough, the zero-phonon line will be very weak or not present at all.

Organic dyes are in general homogeneously broadened. By this we mean that the mechanisms responsible for broadening of the electronic levels are the same for all the molecules. All the excited molecules in a system are under the influence of the same local environment and are equally likely to emit at a particular wavelength.
Chapter 3: Optical processes...

This important feature is responsible for the efficiency of dye lasers: consider a frequency selective element (such as a prism or grating) inserted into a laser cavity, allowing oscillation only at one frequency. All molecules in the system have an equal chance to contribute to the laser output, with little appreciable loss in the output power of the laser when compared to the output of a broadband, non-frequency selective cavity, under identical pump conditions.

3.3 Optical Properties of a Broadened Two Level System

Following excitation of a system of molecules, the vibronic sublevels of the electronic states will very quickly achieve a thermal equilibrium (via thermalisation). The states will be distributed in energy, $\varepsilon$, according to a distribution function, $\eta_i(\varepsilon_i)$. The electronic level populations are given by:

$$N_i = \int \eta_i(\varepsilon_i) d\varepsilon \quad i = 0, 1$$  [3.1]

with $N_1$ and $N_0$ representing the populations of the upper and lower electronic states, respectively. Under conditions of rapid thermalisation the states will be populated according to a Boltzmann distribution:

$$\eta_i(\varepsilon_i) = C_i g_i(\varepsilon_i) \exp\left(\frac{-\varepsilon_i}{kT}\right)$$  [3.2]

where $g_i(\varepsilon_i)$ are the level degeneracies, $C_i$ is a normalising factor, and $i = 0, 1$ refer to the ground and excited states respectively. At room temperature the lowest vibronic sublevel of (almost) all of the electronic levels are populated. A good approximation to the actual case is that most transitions occur from the lowest vibronic level of any electronic state. In figure 3.1, the absorbative and emissive transitions are represented in this manner.

Taking the case of absorption, there are a range of photon energies, $h\nu_1$, which are possible due to the vibronic levels of the upper electronic state, but also due to the
small population of excited vibronic levels of the ground state. Fig. 3.2 shows
typical absorption and emission of an organic dye. Evident is a well defined peak in
the absorption. The short wavelength (high frequency) side of this absorption band
is relatively long, extending more than 200 nm below the main peak. In contrast,
the long wavelength side of the absorption decreases more quickly and no
absorption is evident more than 100 nm from the main peak. The long wavelength
side of the absorption can be (loosely) attributed to absorption from the higher
vibration levels of the ground state, while the short wavelength features are
dominated by absorption to the higher vibronic levels of the excited state.

![Absorption and Emission Spectra](attachment:image.png)

*Fig. 3.2: Absorption and emission spectra typical of organic molecules.*

A similar argument applies to the radiative transition provided the emission lifetime
is longer than the characteristic thermalisation time. For most organic emitters,
radiative lifetimes are typically in the range 100 ps - 10 ns, and the thermalisation
time is generally very short (~ picoseconds). In the broadened two-level system
presented here it is also possible to observe anti-Stokes or upconversion
fluorescence, i.e. fluorescence at a shorter wavelength than the exciting radiation.
This comes about from the rapid thermalisation of the bands and is noticeable as the
pump frequency decreases toward $\nu_0$, into the region of spectral overlap between
the absorption and fluorescence.

Luminescent emission from a molecule (or atom) is classified as spontaneous
emission. The rate of spontaneous emission from the upper excited state will be
Chapter 3: Optical processes...

proportional to the number of molecules in the excited state, \( N_1 \), and therefore so will the rate of change of the excited state population due to spontaneous emission:

\[
\frac{dN_1}{dt}_{sp} = -AN_1 \tag{3.3}
\]

where \( A \) is the Einstein coefficient for spontaneous emission: \( A = 1/\tau_f = k_f \) where \( \tau_f \) is the fluorescence lifetime and \( k_f \) is the fluorescence decay rate.

There is another emission process to look at, known as stimulated emission. Consider a molecule in the excited vibrational level with photons of energy \( h\nu_2 \) incident on the material. (Fig. 3.3 illustrates both spontaneous and stimulated emission processes.) Because the incident photons are of the same energy as an allowed radiative transition of the molecule, there is a finite probability that an incident photon can force the molecule to undergo radiative relaxation to the ground state. The emitted photon is identical in every respect to the incident photon, in contrast to spontaneous emission, where the emitted photon has no definite relationship in phase or direction to any other photon within the material. In a similar manner to spontaneous emission we can characterise stimulated emission with a rate equation:

\[
\frac{dN_1}{dt}_{st} = -W_{10}N_1 \tag{3.4}
\]

where \((dN_1/dt)_st\) is the rate at which the radiative transition occurs by stimulated emission and the stimulated emission probability \( W_{10} = B_{10}u_v \), where \( B_{10} \) is the Einstein coefficient for stimulated emission and \( u_v \) is the spectral energy density of radiation at frequency \( v \).
Chapter 3: Optical processes...

Fig. 3.3: Schematic representations of a) spontaneous emission and b) emission stimulated by an incident photon.

Similarly, for absorption it can also be written:

\[
\frac{dN_0}{dt} = -W_{01} N_0 \tag{3.5}
\]

with \( N_0 \) the number of molecules in the ground state. Eqns. [3.3]-[3.5] have assumed that each process occurs independently of the others, which of course is not the case and rate equations are generally expressed including many of the above terms. Also of note is that in the case of a two discrete energy levels, as in atomic systems, the Einstein coefficients \( B_{10} \) and \( B_{01} \) are equal.

### 3.3.1 Gain Analysis of two Broadened Energy Levels

The net absorption coefficient for a system of two discrete levels is given by:

\[
\alpha_v = \frac{hv_n}{c} \left( B_{01} N_0 - B_{10} N_1 \right) \tag{3.6}
\]

where \( v \) is radiation frequency, \( n \) is the refractive index, and \( B_{01} \) and \( B_{10} \) are the Einstein coefficients for absorption and stimulated emission respectively. In systems with discrete energy levels, laser action can only take place when there is a population inversion, \( N_1 > N_0 \). This is usually accomplished by using additional
energy levels, as in the case of three level (e.g. Ruby, Cr\textsuperscript{3+}:Al\textsubscript{2}O\textsubscript{3}) and four level (e.g. Nd:YAG) systems. In a broadened two level system, the width of levels themselves can provide the necessary conditions for achieving optical gain.

The absorption coefficient can be expressed in terms of gain coefficient at a frequency, \( \nu \), for a system of broadened levels:

\[
\alpha(\nu) = [N_1 \sigma_e(\nu) - N_0 \sigma_a(\nu)]
\]

such that positive values of \( \alpha(\nu) \) correspond to a gain and negative values describe absorption (or other losses). The absorption and stimulated emission cross-sections are defined in terms of the Einstein coefficients:

\[
\sigma_e(\nu) = (\hbar \nu / c) B_{10}(\nu)
\]

(3.8a)

\[
\sigma_a(\nu) = (\hbar \nu / c) B_{01}(\nu)
\]

(3.8b)

and the frequency dependant cross-sections are defined in terms of the electron distribution functions (eqn. [3.2]):

\[
\sigma_e(\nu) = \int \sigma_e(\varepsilon_1, \nu) \eta(\varepsilon_1) d\varepsilon_1
\]

(3.9a)

\[
\sigma_a(\nu) = \int \sigma_a(\varepsilon_0, \nu) \eta(\varepsilon_0) d\varepsilon_0
\]

(3.9b)

From eqn. [3.7] the condition for amplification, \( \alpha(\nu) > 0 \), becomes:

\[
\frac{N_1}{N_0} > \frac{\sigma_a(\nu)}{\sigma_e(\nu)}
\]

(3.10)

Note that if \( \sigma_a = \sigma_e \), then \( N_1 > N_0 \) for net gain to occur, i.e. a population inversion is required. However, eqns. [3.7] and [3.10] do not explicitly include the vibrational states, which have a strong effect on the threshold condition. To determine the ratio
Chapter 3: Optical processes...

of the absorption and emission cross-sections, it is assumed that $C_1 = C_0$ in eqn. [3.2]. Equating the absorption and emission transitions gives:

$$\sigma_\epsilon(\epsilon_1, \nu)g_1(\epsilon_1) = \sigma_\epsilon(\epsilon_0, \nu)g_0(\epsilon_0) \quad [3.11]$$

where

$$\epsilon_1 = \epsilon_0 + h(\nu - \nu_0) \quad [3.12]$$

and energy $h\nu_0$, corresponds to the zero-phonon energy, described above. Using eqns. [3.2], [3.11], [3.12], [3.8], and [3.9], one obtains:

$$\frac{\sigma_\epsilon(\nu)}{\sigma_\epsilon(\nu)} = \exp\left[-\frac{h(\nu_0 - \nu)}{kT}\right] \quad [3.13]$$

Now with eqn. [3.10] it can be seen that the requirement for optical gain in a system of two vibronically broadened levels is:

$$\frac{N_1}{N_0} > \exp\left[-\frac{h(\nu_0 - \nu)}{kT}\right] \quad [3.14]$$

The condition for optical gain is now achieved for $\nu < \nu_0$, even when there is no net population inversion, $N_1 > N_0$, between the ground and excited states. In a two or three level atomic system this is never possible and a population inversion is always required. In the case where $\nu = \nu_0$, gain can only be achieved with a population inversion.

By equating absorption and emission of photons, we can determine the optical gain under conditions of optical pumping with pump intensity $I_p$, at frequency $\nu_p$:

$$N_0\sigma_\epsilon(\nu_p)I_p = N_1\left[\frac{1}{\tau} + \sigma_\epsilon(\nu_p)I_p\right] \quad [3.15]$$
Chapter 3: Optical processes...

where $t_f$ is the fluorescence (spontaneous emission) lifetime. Defining the total number of molecules as $N = N_0 + N_1$, solving for $N_1$ reveals:

$$\frac{N_1}{N} = \frac{1}{\left\{1/\sigma_a(v_p)I_p\right\} + 1 + \exp\left[h(v_0 - v_p)/kT\right]} \quad [3.16]$$

and thus $v_p > v_0$ to obtain a large population in level, limited by the width of the absorption band. To examine the effect of the width of the vibronic bands on the gain condition, a substitution of eqn. [3.7] into eqn. [3.16] yields an expression for the gain at frequency $v$:

$$\alpha(v) = \sigma_e(v)N \times \left(\frac{1 + \exp[-h(v_0 - v)/kT]}{\left\{1/\sigma_a(v_p)\tau_fI_p\right\} + 1 + \exp[h(v_0 - v_p)/kT] - \exp[-h(v_0 - v)/kT]}\right) \quad [3.17]$$

Under the assumption of infinite pumping, eqn. [3.17] requires that:

$$\exp[h(v - v_p)/kT] < 1 \quad [3.18]$$

and as a result, a net gain is not possible for upconverted fluorescence ($v > v_p$). The width of the broadened levels also has an effect on the gain. In the case of very narrow bands, $h\Delta v \ll kT$ the system reduces to the equivalent of a two-level system, as expected. Conversely, in the case of a very wide band with $h(np-n0) \ll kT$, eqn. [3.17] reduces to:

$$\alpha(v) = \sigma_e(v)N \quad [3.19]$$

which is the limiting gain for a totally inverted system. However, $\sigma_e(v)$ decreases as the width of the bands $\Delta v$ increases. In addition, the spontaneous emission lifetime is also linked to the width of the bands. Consequently, as $\tau_f$ becomes shorter eqn. [3.17] requires $I_p$ to increase in order to achieve gain.
3.4 A Five Level System

A two level Franck-Condon scheme, as described above, is an oversimplification of the true picture, which shall be treated as an electronic system containing five levels. This scheme is described in fig. 3.4. There are two systems of electronic states, characterised by their spin. Singlet states, denoted $S_n$, and triplet states, denoted $T_n$.

![Diagram](image)

*Fig. 3.4: Schematic representation of a five level system typical of organic molecules.*

The lowest state of the molecule, the ground state, is normally a singlet, denoted $S_0$. Absorption occurs to the next highest state $S_1$ with an absorption cross section $\sigma_a$. This gives the absorption coefficient, $\alpha$, under conditions of low pump intensity, from eqn. [3.7]:

$$\alpha_\nu (\nu) = \sigma_\nu (\nu) N_0$$

where $N_0$ is the number density of absorbing species. Typical absorption cross-sections for the $S_0$-$S_1$ transition in organics are of the order $\sigma_a = 10^{-16}$ cm$^2$, which gives absorption coefficients in the solid state of $10^3$-$10^5$ cm$^{-1}$. These are large values and consequently organic materials are very strongly absorbing.
Chapter 3: Optical processes...

From $S_1$ the relaxation process of prime consideration is radiative decay, via spontaneous emission, to $S_0$ with a typical characteristic decay rate $k_f \sim 10^9 \text{s}^{-1}$. The emission occurs to the variety of vibrational levels of the ground state, giving rise to the broad emission band as described above. Light emission in general is referred to as luminescence, but when there is no change in spin between the upper and lower levels, the emission is specifically referred to as fluorescence. Non-radiative decay to $S_0$ (with emission of phonons to the surroundings) competes with the radiative decay mechanism, characterised by a decay rate $k_n$, of similar magnitude to the radiative decay rate. This process is often referred to as internal conversion.

The fluorescence quantum yield, $\phi_f$, defined as the ratio of emitted photons per number of absorbed photons, can be described in terms of the decay rates of the system:

$$\phi_f = \frac{k_f}{\sum k}$$

where $\sum k$ is the sum over all decay rates, radiative and non-radiative. There are three pathways for a molecule to leave the $S_1$ state (neglecting $S_1$-$S_2$ absorption, described below): $k_f$, $k_n$ and $k_{\text{ISC}}$, the inter-system crossing rate from $S_1$ to $T_1$, (also described below). As $k_{\text{ISC}} \ll k_f, k_n$, it can be simply written:

$$\phi_f = \frac{k_f}{k_f + k_n}$$

It should be noted that the fluorescence quantum yield applies to the integrated (total) emission, not to a particular wavelength. The quantum yield can also be defined in an wavelength dependant manner according to $^{7,3}$:

$$\phi_f = \int_{\lambda_c}^{\lambda_u} E_f(\lambda) d\lambda$$

[3.23]
where $E_f(\lambda_i)$ is known as the fluorescence quantum distribution, or lineshape function. The integration is performed from $\lambda_a$ to $\lambda_b$, the upper and lower limits of the fluorescent spectrum. This explicitly describes the variation of emission efficiency across the spectrum and is similar in profile to a fluorescence spectrum, but normalised such that the area under the spectrum is numerically equal to fluorescence quantum yield. In the case where there is no reabsorption of the fluorescence by $S_0$ states then $E_f(\lambda_i)$ is identical in shape to the fluorescence spectrum.

Eqns. [3.22] and [3.23] imply that there is a different radiative lifetime associated with each wavelength in the emission spectrum. This is in fact a natural consequence of the vibronically broadened levels. The radiative transition takes place from the lowest vibrational level of $S_1$ to some vibrational level of $S_0$. But the transition probabilities to the vibronic sub-levels of $S_0$ are not equal, the highest probability occurring for those downward transitions terminating at the edge of the vibronic envelope, in accordance with the Franck-Condon principle. The further from the edge of the vibronic envelope the downward transition terminates, the smaller the corresponding transition probability. As the transition probabilities are different for different wavelengths, and assuming internal conversion occurs after thermalisation, $k_f$ is therefore wavelength dependent. Usually only one value of $k_f$ is given, which is the fluorescence decay rate for the collection of emitting states as in eqn. [3.21]. This fundamental point is often missed and there have been publications presenting wavelength dependant $k_f$ as solely due to emission from different chemical species or due to some phonon coupling mechanism.

Upon absorption of a photon, an electric dipole is formed along some portion of the molecule, oriented parallel to the polarisation of the exciting radiation. Light emitted from the molecule will be of polarisation parallel to the dipole and preferentially of direction in the plane perpendicular to the dipole. In solutions, the molecules are free to rotate and consequently the molecular dipoles quickly achieve a random distribution. The characteristic dipole reorientation time in this case is typically in the sub-picosecond regime. As a result, emission from solutions will in general display no net polarisation, as the fluorescence lifetime is much longer than
Chapter 3: Optical processes...

the reorientation time. However, when a molecule is a solid host, molecular reorientation is largely prohibited. The molecular dipole reorientation will now occur on a timescale longer than 10 ns. Emission polarisation in this case is predominantly parallel to the pump polarisation. This is an important point for later chapters, where emission from thin solid films is discussed.

There are two additional pathways for a molecule to leave the $S_1$ state for consideration. Absorption from $S_1$ to higher lying singlet states $S_n$, $n > 1$, may occur. The lifetime of these higher excited states is very short, $\tau_{Sn} \sim 10^{-12}$ s, so the state population is consequently very low and there is little change in the $S_1$ population. The $S_2$ states are thus assumed to have a negligible effect and are not considered further. It should be noted however that the absorption cross-section $\sigma_{ex,s}$ for these transitions can be of the same order of magnitude as the ground state absorption and this process can be of importance, particularly where short duration, high intensity pump pulses are concerned. This allows a population of $S_1$ to build to such levels that the absorption coefficient for $S_1$-$S_2$ becomes important and this process can contribute to quenching of laser action when the pump pulse is shorter than the radiative lifetime of $S_1$.

From $S_1$ non-radiative decay to the lowest lying triplet state, $T_1$, is possible. This is known as the intersystem crossing, with a characteristic rate $k_{ic} \approx 10^5$ - $10^7$ s$^{-1}$. $T_1$ typically has a long life time, $\tau_{T1} \sim 10^{-3}$ - $10^{-7}$ s. Excited triplet-triplet absorption, cross-section $\sigma_T$ takes place to higher lying triplet states. The $T_1$-$T_2$ transition is of primary importance as the triplet-triplet absorption cross section is generally of similar size to the $S_0$-$S_1$ cross-section. This absorption can become observable$^9$, particularly when the input pump pulse for $S_0$-$S_1$ is longer than about $2\tau_T$, allowing an appreciable $T_1$ population to build up. Triplet-triplet absorption is the primary mechanism for quenching of laser action in organic materials when the duration of the pump pulse is longer than a few tens of nanoseconds. $T_2$ is short lived, with a lifetime similar to $S_2$, and is also neglected from further consideration. $T_1$ decays to $S_0$, with a decay rate $k_{T1} = 1/\tau_{T1}$, usually non-radiatively. If radiative emission...
occurs to a ground state of different spin, as the case would be here, it is termed phosphorescence.

### 3.5 Spontaneous Emission as a Stimulated Emission Process

A semi-classical approach to spontaneous emission from a discrete two-level system does not produce predictions that match with experimental results (cf. Ref. 4). In particular, the time dependence of the upper state population (and hence $\tau_f$) is incorrectly expressed as a hyperbolic tangent. Also, the time dependence is a function of the initial population of the upper state. However, these problems are correctly treated by quantum electrodynamic calculations. Quantum electrodynamics will not be treated in any detail here, but the results are important to note.

Dealing with an electromagnetic field in a blackbody cavity, quantum electrodynamics treats the field in a quantised manner, and not in a classical manner. Classically, the electric, $E$, and magnetic, $H$, field components can become zero (when $T = 0$). The quantum approach does not permit this and the values of $E_2$ and $H_2$ will attain a nonzero value even at $T = 0$. This limiting value is known as the zero-point field. The zero-point field fluctuations are responsible for spontaneous emission. Consequently, spontaneous emission can be viewed as a special case of stimulated emission; i.e. the emission is stimulated by the zero-point field fluctuations. It can be shown (ref. 3) that the stimulated emission cross section, $\sigma_e$, and the fluorescence lifetime, $\tau_f$, are linked by:

$$\sigma_e(\lambda) = \frac{\lambda^4 E_F(\lambda)}{8\pi n^2(\lambda)c_0\tau_f}$$  \[3.24\]

where $E_F(\lambda)$ is the fluorescence quantum distribution, $n(\lambda)$ is the refractive index at wavelength $\lambda$. 

36
In chapter 4, the effect of sample geometry on the zero-point field fluctuations, and hence on the spontaneous emission rate will be examined. This is of particular importance in waveguide structures, where the electromagnetic fields are strongly modified by the modes of the structure.
References


2 C. V. Shank, Rev. of Modern Physics, 47 (3), 649 (1975).


Chapter 4 Environmental Effects on Emission Processes

4.1 Introduction

In previous chapters, optical waveguide structures and optical processes in organic materials have been examined. However, the effect of the environment on an emitting molecule has so far been omitted. Of particular importance is the effect on the spontaneous emission rate (and hence on the fluorescence quantum yield), and the stimulated emission cross section of an emitting molecule due to the nature of its surroundings. Here it will be assumed that emitting molecules do not interact with each other, but interact with either the surrounding host molecules or the surrounding electromagnetic environment.

In this chapter it will be shown how, in the absence of other effects, Raman spectroscopy can be used as a tool to predict suitable solvents (or solid host materials) to maximise the fluorescence quantum yield of a molecule. Next, two previously published works will be examined to determine the effect of the electromagnetic environment on spontaneous emission rates when an emitting molecule is placed within an optical waveguide. Following a brief discussion of the theoretical treatment, a qualitative report of the results, as they apply to the waveguide structures studied here, will be presented. Using the results of these papers, the effect on the stimulated emission cross-section will be derived and finally implications for waveguide devices utilising stimulated emission will be discussed.
4.2 Raman Spectroscopy and Fluorescence Quantum Yield

Photoluminescent yields as high as 90% can now be obtained in conjugated polymers. However, much of this efficiency is lost in the solid state. Aggregation effects can often account for much of the differences but changes in the electronic states of the polymer, associated with the aggregation, are not always observed. This advocates a more complete investigation of factors that control the luminescent yield of molecular materials.

Previous studies of dyes in solution have illustrated that solvatochromic effects resulting from dipole interactions, rotary effects and conformational changes can effect the fluorescence quantum yield. Solvatochromism is manifested as changes in the electronic transitions of a molecule due to interactions with the solvent molecules. By interaction with lone electron pairs, solvents can form van der Waals interactions, or more commonly, hydrogen bonds of varying stability with the emission molecules. This is dependent on the chemical nature of the solvent, e.g. polarity, acidity, etc., and of the emitting species. The result is a shift in the energies of the electronic transitions dependent on the nature of the solvent employed. These shifts can be predicted to some degree but corresponding changes in the fluorescence quantum yield are more difficult to quantify.

Here, two simple dye species are studied to illustrate that a major contribution to the fluorescence quantum yield is the inhibition of non-radiative processes in local environments whose vibrational structure does not correlate with that of the dye moiety. Relative yields are measured in a range of organic solvents and it is shown that the variations with solvent are not solvatochromic in origin, but rather are determined by the overlap between the vibrational spectra of the chromophore and the solvent, as measured using Raman Spectroscopy.

Non-radiative decay through internal conversion is one of the principle competing processes to radiative decay in molecules and in order to undergo this process, the local environment of the molecule must be capable of absorbing the vibrational
quanta. The fluorescence quantum yield can be expressed in terms of the radiative and non-radiative relaxation decay rates (cf. chapter 3):

$$\phi_f = \frac{k_f}{k_f + k_n}$$  \[4.1\]

where $k_f$ and $k_n$ are the fluorescence and non-radiative decay rates respectively. In the absence of solvatochromic effects, the fluorescence decay rate can be assumed to be constant and only changes in the non-radiative decay will affect $\phi_f$. If the host environment is inhibited from absorbing a phonon emitted by the fluorescent species, then $k_n$ will consequently drop and $\phi_f$ will increase.

![Raman Spectra](image-url)

*Fig. 4.1: Raman Spectra of dioxane (top), terphenyl (middle) and benzene (bottom).*

Here we study two simple fluorescent molecules, terphenyl and anthracene. For example, fig. 4.1 compares the Raman spectrum of terphenyl with those of solvents benzene and dioxane. For comparison, there is a strong overlap between the double bond (~1600 cm$^{-1}$) vibrations of the terphenyl and those of the benzene, whereas there is no such feature in the dioxane spectrum.
Terphenyl has a higher fluorescence quantum yield when in dioxane solutions, indicating that the lack of corresponding vibrational features of the solvent play an important role. Phonon emission from the chromophore will, naturally, occur at energies corresponding to features in the Raman spectra. With no corresponding vibrational state in the environment capable of accepting the phonon, its emission must consequently be suppressed, slowing the rate of internal conversion. It is proposed that the overlap of the vibrational spectra is a gauge of the efficiency of the internal conversion process, and therefore of the luminescent efficiency.

4.2.1 Experiment

Solvents employed for the study were cyclohexane, hexane, toluene, benzene, methanol, ethanol and dioxane. The solvents were chosen to have similar (small) polarities, hence reducing solvatochromic effects, but availability and solubility are also factors to consider. A range of solutions of both dyes were prepared to constant concentration, 6.25 mg/l in the case of anthracene and 1.6 mg/l in the case of terphenyl. In both cases accuracies in concentrations are ~5%. UV/Visible spectra were measured using a Shimadzu UV-2101PC absorption spectrometer. Luminescence was measured using a Perkin Elmer LS50B fluorimeter. In all cases excitation wavelengths for fluorescence measurements were at the first absorption maximum and all other parameters were kept equal. Raman spectra were recorded using an Instruments S.A. Labram 1B spectroscopic microscope operating at 632.8 nm. Raman spectra for the solvents were taken keeping conditions constant such that a semi-quantitative comparison could be made. For all solvents the overlap across the entire spectrum (200 - 3500 cm\(^{-1}\)) was calculated.

4.2.2 Results

In both the anthracene and terphenyl solutions, weak solvatochromic shifts in the absorption and emission spectra are observed. The positioning of the spectral maxima, plotted against the Onsager polarisation function\(^3\) of the solvent, is well behaved, and for anthracene is well documented\(^4\). While the absorption coefficients
are, within the accuracy of the measurement, constant over the range of solvents, there are dramatic variations in the luminescent output of both chromophores. These variations do not correlate with solvatochromatic parameters.

In figure 4.2 is plotted the integrated luminescence output versus the overlap of the vibrational spectra for terphenyl. There is a clear correlation between the two parameters, illustrating that the highest luminescent output occurs in solvents which have the weakest vibrational coupling to the dye moiety. A similar correlation is observed for anthracene in the range of solvents, as shown in fig. 4.3.

![Graph showing integrated luminescence output versus sum of vibrational overlaps for terphenyl.](image)

**Fig. 4.2**: Plot of the integrated luminescence versus the summed overlap of Raman Spectra for Terphenyl in a range of solvents.

The correlation demonstrates that efficient light emission in molecules is achievable by inhibiting vibrational coupling to the local environment. In the fabrication of films in solid matrices materials which have little or no vibrational correlation with the luminescent chromophore should be employed. This study highlights the importance of vibrational coupling to the local environment in determining the luminescent efficiency of a material. It furthermore illustrates how Raman spectroscopy can be employed to make predictions of the relative fluorescence yields of a material in different solvents or solid hosts.
The observations also give pointers for the design of conjugated polymers for luminescence applications. In such materials coherent vibrational coupling can occur along the backbone of the polymer, transferring the excitation from an emissive segment of the polymer chain to a non-emissive segment. A move towards more complex backbone structures may further enhance the emission efficiency, with the remaining challenge being to control the interchain vibrational coupling in solids. It is intended that this study will be carried out using the same dye moieties in non-conjugated polymer matrices, and the conclusions will be employed in the design of novel luminescent materials.

4.3 Spontaneous Emission in a Dielectric Slab

When dealing with fluorescent species within a planar waveguide, questions arise concerning the effect of the waveguide modes on the emission processes. Widespread assumptions are that only fluorescence emitted at discrete angles can couple to a waveguide mode, and that all other emission is radiated out of the guide. Polarisation of the guided fluorescence is assumed imposed by the mode structure of the waveguide and both spontaneous and stimulated emission processes are assumed unchanged relative to the values of bulk materials.
Here the results of two previously published papers concerning these questions will be examined: Zakowicz and Bledowski\textsuperscript{6}, and Urbach and Rikken\textsuperscript{7}, which use a quantum electrodynamic treatment of the problem. The papers are at time of writing practically unknown to most working in the field of organic light emitting devices, to date only cited in publications related to this thesis. The results of these two papers are relevant to practically all planar light emitting devices, whether optically or electrically pumped.

Both papers describe the spontaneous emission rate as a function of physical parameters of the planar structure for emitting dipoles oriented parallel and perpendicular to the plane of the waveguide. As quantum electrodynamics is beyond the scope of this thesis the reader is referred to these papers for the full, quantitative treatment. Strangely, Urbach and Rikken do not even cite Zakowicz and Bledowski, apparently unfamiliar with the work. Further more, both cite an earlier paper\textsuperscript{8}, and correct the same error in calculating the effect of guided modes.

4.3.1 Theoretical Treatment

The starting point is to describe the full set of electromagnetic modes within the structure. For the planar dielectric film these modes are well known, consisting of radiation modes pertaining to plane waves, and guided modes of either polarisation, evanescent in both cladding and substrate layers. This is described in some detail in chapter 2. For reasons of consistency, the co-ordinate system as described in chapter 2 will be used for this discussion, i.e. $z$-axis defines the propagation direction through a planar waveguide, $x$-axis is perpendicular to the plane of the film. When approaching these two papers, be warned that the co-ordinate systems used differ from that described here, the main difference being a simple transposition of the $x$- and $z$-axes.

Excitations are assumed localised, so that any change in spontaneous emission is due only to changes in the electromagnetic modes of the structure. This requirement on localisation is satisfied when organic molecules or rare-earth
species are present. Thus many of the results can be directly applied to the polymeric waveguides under study here. Once the full set of electromagnetic modes are described, a field quantisation procedure is applied, allowing a quantum mechanical treatment of the interaction of the emitting dipoles with the modes of the electromagnetic field.

The spontaneous emission rate can be expressed in terms of the zero-point fluctuations of the electromagnetic field at the position of the emitting dipole (cf. chapter 3). Zero-point field fluctuations are dependent on the field strengths of the available electromagnetic modes, which are themselves dependent on the configuration and electromagnetic properties of the surrounding media. Spontaneous emission can occur into any electromagnetic mode of frequency \( \omega_0 \), or of wave vector \( k_0 \) in a vacuum. The spontaneous emission rate of an emitter at position \( \mathbf{r} \) whose dipole moment is oriented parallel to the \( j \) axis is given by:

\[
\frac{1}{\tau} = \frac{2\pi e^2}{\hbar c} |D_{12}|^2 \mathcal{F}'(x)
\]

where \( D_{12} \) is the dipole matrix element of the transition, and \( \mathcal{F}(x) \) is the contribution of all modes of wavenumber \( k_0 \) to the \( j \)th component of the zero-point field fluctuations, as depicted in fig. 4.4. In practice, \( \mathcal{F}(x) \) describes the zero-point field fluctuations experienced by an emitting dipole oriented along the \( j \)-axis.

![Co-ordinate axes and emitting dipole orientations](image_url)

*Fig. 4.4: Co-ordinate axes and emitting dipole orientations in the quantum electrodynamic treatment of spontaneous emission considered here.*
Since the electric field of a guided mode vanishes at the birth of the guided mode (i.e. at the cut-off condition) and increases as \( k_0 \) increases, the total sum of the electric fields over the guided modes changes continuously with \( k_0 \). It is found that the zero-point field fluctuations will therefore also depend continuously on \( k_0 \). In addition, the zero-point field fluctuations will also depend on other physical parameters (such as refractive index and film thickness) in some manner related to the dependence of waveguide modes with the same parameters. Immediately, we can expect the zero-point field fluctuations, and hence the spontaneous emission rate, to increase as the number of waveguide modes increases. In a planar waveguide, the \( j = z \)- and \( j = y \)- components of \( \mathcal{F}(x) \) are, naturally, identical.

In a homogeneous dielectric of refractive index \( n_1 \), it is found that:

\[
\mathcal{F} = \mathcal{F}' = \mathcal{F} = n_1 \mathcal{F}_{\text{free}}
\]  

where \( \mathcal{F}_{\text{free}} \) denotes the vacuum field fluctuations in free space. This is in full agreement with a treatment of spontaneous emission in solutions based on Fermi's golden rule described by Lamouche et al.\(^{10} \) with experimental verification, and briefly mentioned in chapter 3. For an atom at position \( x \) relative to the centre of the waveguide layer, having a dipole moment parallel to the \( j \)-th coordinate axis the spontaneous emission rate relative to free space is:

\[
\mathcal{F}' = \mathcal{F}'(x)/\mathcal{F}_{\text{free}}
\]  

such that \( \mathcal{F}' = 1 \) in free space and \( \mathcal{F}' = n_1 \) in a bulk material of refractive index \( n_1 \). For a randomly oriented atom the relative transition rate is found using the mean of the \( j \)-th components:

\[
\mathcal{F} = \frac{1}{3} \left[ \mathcal{F}'(x) + \mathcal{F}'(x) + \mathcal{F}'(x) \right]/\mathcal{F}_{\text{free}}
\]  

[4.5]
Finally, the mean relative spontaneous emission rate of the total film relative to free space is found from the average of eqn. [4.4] over the thickness of the film.

4.3.2 Overview of Results

Urbach and Rikken calculate $\mathcal{F}(x)$ for two structures of relevance to this work. First is that of a symmetric waveguide, with $n_s = n_c = 1$, with different values of $n_f$, and for two different thicknesses. Second is the case of a poly(styrene) waveguide doped with a Eu$^{3-}$ complex, deposited on a quartz substrate. The emission rate is experimentally measured as a function of film thickness and compared to calculated values of the mean relative spontaneous emission rate.

For the symmetric waveguides, calculation of $\mathcal{F}(x)$, relating to a dipole oriented parallel to the plane of the film (TE oriented), shows a similar profile to the electric field profile through the layer structure of the guide, summed over all the waveguide modes. There are a number, $m$, peaks in $\mathcal{F}(x)$ within the waveguide layer, where $m$ is the number of supported TE modes. $\mathcal{F}(x)$ becomes exponential in the cladding and substrate half-spaces, corresponding to positions of the emitting dipoles outside of the guided region. In general, the average value of the guided mode contribution to $\mathcal{F}(x)$ approaches the bulk value as the refractive index (and hence the number of guided modes) increases.

The radiation mode contribution to $\mathcal{F}(x)$ is suppressed, lower than even the free space value, $\mathcal{F}_{\text{free}}$. The bulk value is of course $n_f \mathcal{F}_{\text{free}}$ so emission from such an oriented dipole is quite strongly suppressed indeed, the strength of the suppression increasing with refractive index. As with the guided mode contribution, the exact value is a (roughly) sinusoidal function of position within the guiding layer.

$\mathcal{F}(x)$, corresponding to emitting dipoles oriented perpendicular to the plane of the film (TM), show somewhat similar properties to the case of $\mathcal{F}(x)$. However, there are now $m-1$ peaks in the profile of $\mathcal{F}'(x)$, where $m$ is the number of supported TM modes. Interestingly, when only one TM mode is supported ($m=1$), both the
radiation and guided mode components of $F'(x)$ are strongly suppressed relative to $F_{\text{free}}$ (as $m-1 = 0$). Variations in $F'(x)$ across the thickness of the guide layer are less pronounced than in the case of $F(x)$. $F'(x)$ approaches zero within the guiding layer as the dipole position approaches the layer boundary.

For Eu$^{3+}$:poly(styrene) waveguides, the measured and calculated emission rates show good agreement. As the film thickness increases, the emission rate increases from a value of approximately $1 \times 10^{-3} \, s^{-1}$ for a 100 nm thick film, toward the bulk value of $1.53 \times 10^{-3} \, s^{-1}$. At thicknesses larger than 1 \, $\mu$m the measured and computed rates are almost equal to the bulk value.

Zakowicz and Bledowski's results are largely consistent with those reported by Urbach and Rikken, but are treated somewhat differently. They compute the angular emission distribution and the excitation intensities for each guided mode for different positions of the emitting dipole within the waveguide structure. Consistent with Urbach and Rikken, TM polarised emission into radiation modes of the structure, is suppressed when the emitting dipole is within the guiding layer. It is found that dipoles oriented perpendicular to the plane of the film can only couple to TM polarised modes and, as expected, show a cylindrical emission distribution within the plane of the film. However, Zakowicz and Bledowski state that dipoles parallel to the plane of the film can couple to both TE and TM modes. Here the TE emission is maximum in the x-y plane (i.e. perpendicular to the emission polarisation) while TM emission is maximum in the x-z plane (parallel to the emission polarisation). For organic molecules, emission is predominately polarised parallel to the dipole axis and the coupling of TE oriented dipoles to the TM guided modes will be omitted from further consideration. Further more, as the dipole reorientation time in solids is very long, under conditions of transverse pumping only TE oriented dipoles need be considered.

The polar characteristics of the emission distributions of light emitted out of the slab, associated with radiation modes are complicated. They display a lobed structure, revealing reflection and transmission properties of the slab well known for thin-films and coatings. These effects, interpreted in the classical picture by
means of interference between the direct and reflected waves, propagating together in a given direction. In the quantum interpretation this is attributed to spatial modulation of photon emission probability caused by the standing wave pattern of the individual modes. Thus the emitting dipole in a given position couples differently to various modes, forming the lobed angular radiation pattern, similar to that observed in microcavity devices.

For spontaneous emission emitted in the plane of the film, one deals with a discrete distribution of a set of waveguided modes, rather than an emission being a continuous function of the polar emission angle. For a dipole within the plane of the guiding layer, the position of the dipole determines which guided modes are excited. Emitting dipoles at the centre of the guide will only couple to the 'symmetric' modes, having a field maximum near the centre of the guide. In general, the excitation of modes through emission shows an oscillatory behaviour, with more oscillations occurring for dipoles closer to the centre of the guide. Total excitation decay rates (as a function of position within the guide layers) derived by Zakowicz and Bledowski are identical to those derived by Urbach and Rikken.

### 4.3.3 Effect on the Stimulated Emission Cross Section

As discussed in chapter 3, the stimulated emission cross-section and the fluorescence (spontaneous emission) lifetime are linked by:

\[
\sigma_{s.e.}(\lambda) = \frac{\lambda^4 E_{F}(\lambda)}{8\pi n^2(\lambda)c_0\tau_f}
\]  

[4.6]

In the weak-coupling regime, the interaction between the emitting dipoles and the electromagnetic fields is weak, and no effect is seen on the energies of the electronic states. As a result, the shape of \( E_F(\lambda) \) will not change, only the values, as defined by eqns. [3.22] and [3.23] relating fluorescence quantum yield, \( \phi_f \), to \( E_F(\lambda) \) and \( \tau_f \). In addition, the interaction of the electromagnetic fields can be assumed to have no effect on the dipole matrix element in eqn. [4.2]. The stimulated emission
cross section can therefore affected through changes in the spontaneous emission lifetime described in eqn. [4.6].

To explore this fully, the stimulated emission cross section is expressed in terms of the emission rate using eqn. [4.6]:

\[ \sigma_{s.e.}(\lambda) = C_1 \left[ E_f(\lambda) k_f \right] \]  \[4.7\]

with

\[ C_1 = \frac{\lambda^4}{8\pi m^2(\lambda)c_0} \quad \text{and} \quad k_f = \frac{1}{\tau_f} \]

As described above, in the weak-coupling approximation, the shape of \( E_f(\lambda) \) is not altered, only the values change through changes in \( \tau_f \). Hence \( E_f(\lambda) \propto \phi_f \) and therefore:

\[ E_f(\lambda) \propto \frac{k_f}{k_f + k_n} \]  \[4.8\]

and with eqn. [4.7] one immediately obtains:

\[ \sigma_{s.e.}(\lambda) = C \left\{ \frac{k_f^2}{k_f + k_n} \right\} \]  \[4.9\]

which can be re-expressed as:

\[ \sigma_{s.e.}(\lambda) = C \left\{ \frac{k_f^2}{k_n + k_f} \right\} \]  \[4.10\]

where \( C \) is a constant of proportionality which includes \( C_1 \) from eqn. [4.7]. With \( k_f = 1/\tau_f \) eqn [4.2] then implies:
### 4.3.4 Implications for Waveguide Devices

Above it has been shown that the stimulated emission cross section is strongly dependent on the zero-point field fluctuations, and hence on the thickness of the waveguide and the position of the emitting dipole within the waveguide structure. As emission into radiation modes is suppressed, optical waveguides have a significant advantage for use as laser materials, the stimulated emission predominantly occurring into guided modes. Neglecting losses through excited state absorption and scattering, the primary loss mechanism competing against laser action will be amplified spontaneous emission (ASE) into waveguide modes.

In the case of distributed feedback (DFB) laser action in waveguides, as described in chapter 7, laser action at a wavelength $\lambda$, is limited to a single guided mode satisfying the Bragg condition. ASE is not restricted in this manner and other guided modes will compete for excited states with the lasing mode. In general, there will always be some overlap of the guided mode field distributions irrespective of the mode order, but competition for excited states will be strongest where modal field maxima coincide. For modes with symmetric field profiles, this is at the centre of the waveguide, and one will expect, for example, TE$_0$ to always compete to some extent with TE$_2$. In addition, high order modes (symmetric or anti-symmetric) display a significant field overlap toward the waveguide/cladding and waveguide/substrate boundaries. Guided modes close to the cut-off condition (eqn. [2.23]) will act as a "photon drain", increasing propagation losses dramatically.

Effects due to the mode confinement are naturally included in the above QED treatment. For a single mode guide, as film thickness increases zero-point field fluctuations have a quadratic dependence on the zero-point field fluctuations.

\[ \sigma_{\text{se}}(\lambda) \propto C \left[ \frac{\mathcal{F}'(x)^2}{k_n} + \mathcal{F}'(x) \right] \]  

[4.11]
fluctuations increase and the stimulated emission cross section also increases. A decrease in the lasing threshold can therefore be expected as the excited state population necessary to achieve the threshold gain decreases. In addition, as the film thickness increases further, thresholds for DFB lasing will increase as higher order guided modes, competing for excited states, are introduced to the structure.

4.4 Conclusions

The importance of the non-radiative decay rate, \( k_n \), on fluorescence quantum yield has been examined using Raman spectroscopy. Quite clearly, a careful choice must be made when solvents or perhaps solid host materials are chosen for fluorescent materials. Provided solvatochromism can be accounted for, Raman spectroscopy could prove to be an invaluable tool in predicting the emissive properties of a molecule in an arbitrary chemical system. At time of writing, this study is being extended to solid materials, it will be interesting to see if the potential use of this technique applies as well to solids as it does to solutions. As if to highlight the point, note that the stimulated emission cross-section dependence on zero-point field fluctuations, eqn [4.11] also includes a factor of \( 1/k_n \).

The results of Urbach and Rikken, and Zakowicz and Bledowski, indicate that waveguide devices have a fundamental advantage for use as light emitting devices over vertically emitting devices, such as microcavities. Extending Urbach and Rikken's analysis to stimulated emission shows that if spontaneous emission is changed by a small amount the change in stimulated emission cross-section will be much greater and on this analysis alone, microcavities look like a poor choice. Of course, this oversimplifies the problem. But waveguides may have their disadvantages too; mode competition for excited states may severely limit DFB laser performance.
Chapter 4: Environmental Effects...

References


Chapter 5 Fluorescent Materials and Characterisation

5.1 Introduction

Conjugated polymers have attracted much recent interest for use in diodes, light emitting diodes, and electroluminescent displays. Many conjugated polymers exhibit high photoluminescence quantum yields in solution and solid films. Laser action in solutions has been observed for many of these materials. Accurate characterisation of the properties of new molecular materials is naturally an important part of any device fabrication process. Of particular importance for solid state optical devices is the ability to accurately produce high quality thin films at low cost. Solid films are routinely made from these materials but many important parameters are rarely, if ever reported. Propagation losses of waveguiding films are an important example.

In the following sections, the basic characteristics of the materials will be presented. Solution lasing measurements will be presented (though not all of the materials were available for these measurements). This is followed by a description of the spin coating process for thin film deposition, and the prism coupling technique for determination of film thickness, refractive index and waveguide propagation loss. Materials to be used in later chapters will be selected on the basis of the characteristics presented here.
5.1.1 Materials

The materials under study here were produced by Hans-Heinrich Hörhold and co-workers at the Friedrich-Schiller University, Institute for Organic and Macromolecular Chemistry, Jena, Germany. The chemical structures are shown in fig. 5.1 and optical properties in dioxane solution are listed in table 5.1. Synthesis of the materials is reported in refs. 8, 9, and 10. The polymeric materials are based on poly(phenylene vinylene) structures (PPV), which have been under study for many years. The compound G33 is a model compound for cyano-PPV\textsuperscript{11}, and SP35 and SP48 are model compounds for phenylamino-PPV\textsuperscript{11}.

Solvatochromic shifts between dioxane and other common aromatic solvents are generally less than 10 nm. In addition, fluorescence quantum yields listed for dioxane solutions generally display little change for other solvents. The main exception here is G33; $\phi_f \approx 0.70$ in toluene and ortho-xylene solutions. In addition, the polymeric materials display higher fluorescence quantum yields in solid form, and in general values of $0.50 < \phi_f < 0.90$ are achievable, though this is generally difficult to quantify exactly for thin films or powders.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absorption $\lambda_{\text{max}}$ (nm)</th>
<th>Emission $\lambda_{\text{max}}$ (nm)</th>
<th>Quantum Yield, $\phi_f$</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP19</td>
<td>442</td>
<td>494</td>
<td>0.65</td>
<td>Polymer, $\phi_f$ high in solid film</td>
</tr>
<tr>
<td>AT63</td>
<td>412</td>
<td>510</td>
<td>0.50</td>
<td>Polymer, $\phi_f$ high in solid film</td>
</tr>
<tr>
<td>HT73</td>
<td>488</td>
<td>488</td>
<td>0.25</td>
<td>Copolymer</td>
</tr>
<tr>
<td>Ro177</td>
<td>452</td>
<td>515,530</td>
<td>0.69</td>
<td>Copolymer</td>
</tr>
<tr>
<td>DPOP-PPV</td>
<td>365</td>
<td>530</td>
<td>0.06</td>
<td>Polymer, $\phi_f \approx 0.6$ in solid film</td>
</tr>
<tr>
<td>SP48</td>
<td>385</td>
<td>429,456</td>
<td>0.98</td>
<td>Model Compound</td>
</tr>
<tr>
<td>SP35</td>
<td>407</td>
<td>457,485</td>
<td>0.94</td>
<td>Model Compound</td>
</tr>
<tr>
<td>G33</td>
<td>419</td>
<td>510</td>
<td>0.31</td>
<td>Model Compound, $\phi_f \sim 65%$ in poly(styrene) films</td>
</tr>
</tbody>
</table>

Table 5.1: Optical properties of the Jena materials in dioxane solution (Courtesy of H.-H. Hörhold)
Fig. 5.1: Chemical Structures of the materials under study.
(Courtesy of H.-H. Hörhold)
Fluorescence excitation and emission spectra were obtained using a Perkin Elmer LS50 fluorimeter with dioxane as a solvent, and photoluminescence quantum yields were determined from corrected spectra against quinine sulfate in 0.1 M H$_2$SO$_4$ as a standard ($\phi_{pl}=55\%$).

In general, the compounds are soluble in common aromatic organic solvents. Solubility is not as high as many common polymeric materials, such as poly(styrene) and poly(methyl methacrylate) which are capable of concentrations in excess of 100 g/l. In general, the Jena polymers display good solubilities up to 5 g/l with gelation causing problems close to 10 g/l. If thin film deposition is attempted by spin coating, the low concentrations will limit film thicknesses to 200 - 300 nm. Many fluorescent conjugated polymers have been reported with large refractive indices, McGehee et al.\textsuperscript{12} reporting $n = 1.76$ for BuEH-PPV films. While the small film thicknesses may not limit waveguiding properties (due to large $n$) in practice only single mode waveguides may be possible and confinement of the modes may be weak.

5.2 Solution Lasing Measurements

The experimental setup is schematically shown in fig. 5.2. The pump laser was a PRA high power N$_2$ laser, wavelength 337 nm, pulse width of 0.5 ns and repetition rate of 2 Hz. The pump beam is focused onto the cell by means of a cylindrical lens. Emission from the cell is diffracted by the grating. The grating is positioned such that the angle between the incident light from the cuvette and grating is $87^\circ$. The cuvette is tilted $7^\circ$ with respect to the oscillator beam to avoid regenerative feedback by reflection from the cuvette faces. Wavelength tuning is achieved by rotating the end mirror with respect to the grating. The input and output pulse energies were measured using calibrated pyroelectric detectors.
5.2.1 Lasing properties of the compounds

The lasing properties of the compounds were examined using a coumarin laser dye (C485 from Exciton Inc.) for comparison. Fig. 5.3 shows the normalized tuning range; all compounds were tested at same input energy. The lasing action spectra cover a wide range, from 442 to 613 nm. The lasing wavelength maxima, tuning range, efficiencies and thresholds of all samples are listed in table 5.2. The ratio of the lasing output to the spontaneous emission was in the range 3-6 for all samples, the spontaneous emission was measured by blocking the high reflector preventing feedback to the system. The conversion efficiencies and threshold energies of all compounds are listed in table 5.2.

Table 5.2: Solution lasing properties of Jena compounds.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tuning Range (nm)</th>
<th>Lasing max. (nm)</th>
<th>Lasing Eff. (%)</th>
<th>Threshold (µJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP48</td>
<td>442 - 459</td>
<td>541</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>SP35</td>
<td>473 - 492</td>
<td>483</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>SP19</td>
<td>521 - 538</td>
<td>532</td>
<td>0.8</td>
<td>15</td>
</tr>
<tr>
<td>AT63</td>
<td>523 - 557</td>
<td>543</td>
<td>0.6</td>
<td>25</td>
</tr>
<tr>
<td>HT73</td>
<td>589 - 613</td>
<td>602</td>
<td>0.7</td>
<td>16</td>
</tr>
<tr>
<td>C485</td>
<td>510 - 556</td>
<td>530</td>
<td>2</td>
<td>7</td>
</tr>
</tbody>
</table>
Fig. 5.3: Toluene solution lasing tuning range of the studied compounds under 337nm excitation, 0.5 ns pump pulse width.

Fig. 5.4 shows the output lasing energy of the samples as a function of the input energy. The plots show the conversion efficiency of sample SP35 is high, ~ 4%, in agreement with high quantum yield of the sample. Sample SP48 also has a high quantum yield, but the efficiency is lower at ~ 2%. The efficiencies of the model compounds compare favorably to that of the coumarin dye, though tuning ranges are somewhat reduced. However, all of the polymeric samples tested displayed reduced slope efficiencies and increased thresholds. Holzer et al.\textsuperscript{6,13} have studied a range of fluorescent polymers and found that the excited singlet absorption spectrum generally follows the fluorescence spectrum quite closely, resulting in poor lasing performance. This is in contrast with common organic laser dyes, and also model compounds of polymers, the excited singlet spectra are broadened and red shifted from the fluorescence maxima. This is no doubt a significant contribution to the poor performance of the polymeric samples. In addition, scattering due to aggregation or gellation, and problems with chemical purity may also contribute to the low efficiencies.
5.3 Thin Film Preparation and Characterisation

In chapter 2 the properties of thin film planar waveguides were examined. Here the fabrication and characterisation of planar waveguides will be discussed. In order to produce waveguides to predetermined specifications, accurate characterisation of both the fabrication process and the properties of the films produced are necessary. This includes spin-rate vs. thickness dependence of polymer solutions, optical dispersion of the materials, and optical propagation losses of waveguiding samples.

Spin coating from solution, a well-established technique for producing high quality organic films, will be introduced. This is followed by a discussion of the prism-film coupling technique, which allows an accurate, simultaneous determination of both refractive index and film thickness. In addition, propagation losses in the waveguides can be determined from a similar experimental setup.
5.3.1 Spin Coating of Thin Films

Spin coating is well established as a cost effective technique for production of thin films. It involves deposition from liquid solutions by evaporation of the solvent on a rotating substrate, usually followed by subsequent heat treatment at a slightly elevated temperature. Early descriptions of the technique by Emslie et al.\textsuperscript{14} and Acirivos et al.\textsuperscript{15}, using hydrodynamics describe the general usefulness of the technique for producing uniform films of a desired thickness. Umeda\textsuperscript{16} gives an excellent description of the technique and associated problems.

In general, the thickness of a film produced by spin coating is related to the viscosity, and hence concentration, of the solution, by the spin rate (revolutions per minute), and by the surface properties of the substrate. The film thickness, d, displays a power law dependence on both spin rate and concentration, given by:

\[ d = C(rpm)^a (conc.)^b \]  \hspace{1cm} [5.1]

where \( C \) is constant of proportionality, \( rpm \) is the spin-rate in revolutions per minute and \( conc. \) is the concentration of the solution. In general, the power law coefficients, \( a \) and \( b \), are both solvent and polymer dependent. At constant concentration, eqn. [5.1] can be simply re-written as:

\[ d = C(rpm)^a \]  \hspace{1cm} [5.2]

and the constant \( C \) includes the now invariant term \( (conc.)^b \). In addition to solvent and polymer dependence, polymer molecular weight also play a role. Umeda\textsuperscript{16} measured these parameters for many polymers/solvent combinations. However, unless identical batches of solution can be prepared, these coefficients should be determined for each prepared solution. The shelf life for solutions is limited by solvent evaporation, with small changes in concentration often leading to substantial deviations in film thickness, particularly at low spin rates.
Successful solvents for spin coating have boiling points in the range 110-130°C. Due to the high rotation rates during coating, evaporation of the solvent occurs quickly; typically 90% of the solvent evaporating from the deposited layer after the first ten seconds of spinning. Spinning is continued for a total of 30-90 seconds to ensure uniform deposition. The wet films are then baked at elevated temperatures (50-80°C) for periods of a few hours to ensure complete removal of the solvent. Typical solvents for use with most common polymers include cyclohexanone, cyclopentanone, isobutyl acetate, xylanes, and many high boiling point chlorinated solvents. Considerations in choosing a solvent are primarily dominated by solubility. For common optically transparent polymers, such as poly(methyl methacrylate) and poly(styrene), concentrations higher than 100 g/l are readily achievable.

5.3.2 Prism-Film Coupling

The prism coupler provides a fast, accurate and reliable method of determining the refractive index and thickness of thin dielectric films\(^\text{17,18}\). The technique involves the distributed coupling of evanescent optical fields to the modes of an optical waveguide. The theoretical evaluation of this technique is reminiscent of the tunnelling of electrons through a potential barrier, and indeed has been referred to as optical tunnelling. An in depth discussion based on ray optics and electromagnetic theory of dielectric waveguides is given by Ulrich et al\(^\text{19}\).

A schematic of the prism coupler is shown in fig. 5.5. In this arrangement the coupling between the prism and the film takes place along the entire width of the optical beam. The coupling occurs through the interaction of the evanescent field of the wave in the prism and the wave in the film. The coupling is strongest if the components of the wave vectors parallel to the gap are equal for the prism wave and the film wave. If they are not, the net coupling is zero. The parallel component is given by \(k_n \sin \theta_p\). As discussed in chapter 2, thin dielectric films can support a number of guided modes, which propagate in the z-direction, each with a different
phase velocity $v_p$. Optical energy can be transferred from the prism to the thin film, and back again, when

$$\beta = \frac{\omega}{v_p} = k \sin \theta_p$$  \[5.3\]

i.e. when the direction of the incident field is equal to the direction of one of the allowed waveguide modes. Such a method allows one to selectively excite a particular mode of the waveguide.

If both the thickness and the refractive index are to be measured, then the simplest and most accurate (as far as $n$ is concerned) method is to determine the effective indices of the guided modes using a prism coupler. The effective mode indices $N_m$ and the propagation constant $\beta_m$ are inter-related through:

$$\beta_m = k N_m = k n_f \sin \theta_m$$  \[5.4\]

where the subscript $m$ refers to the $m^{th}$ order guided mode. The importance of $N_m$ lies in the fact that it allows the film index and/or thickness to be determined through the modal conditions given by eqns. [2.18] and [2.19]. For a single mode waveguide either the thickness or the refractive index must be known in order to calculate the other. If there are two modes present, then both the index and thickness may be determined from the two effective indices $N_m$. When more than two modes are observed, then the technique becomes self-consistent. The coupling
angle which excites each mode is obtained by measuring the angle of incidence on the prism entrance face for which the $m^{th}$ mode is excited. The effective index of the $m^{th}$ mode is given by

$$N_m = n_p \sin[A + \sin^{-1}(\sin \theta_m / n_p)]$$  \[5.5\]

where $n_p$ is the refractive index of the prism, $A$ is the prism angle between the incident face and the prism, and $\theta_m$ is the mode excitation angle measured normal to the incident face of the prism. In addition, the refractive indices of the substrate and cladding layers must be accurately known. A computational routine for the PC by Umeda was used for evaluating the linear refractive indices and thickness of the guiding layer, based on the above method.

Measurements were carried out spanning the wavelength range 458 - 633 nm. The material dispersion curves can then be calculated using a form of the Sellmeier equation:

$$n^2 = 1 + A + A \frac{\lambda_0^2}{\lambda^2}$$  \[5.6\]

where $\lambda$ is the wavelength, and $\lambda_0$ corresponds to a resonance in classical dispersion theory. Once the dispersion curves are calculated, one can calculate the guided mode properties of a material at any wavelength over the measurement interval by use of the transcendental mode equations.

Propagation losses for guided modes can be conveniently estimated during prism coupling experiments. When a guided mode is excited, some of the coupled energy is not coupled out of the film through the prism but continues propagating through the film. Monitoring the intensity of the guided light as a function of propagation distance allows the losses to be characterised according to:

$$\alpha(cm^{-1}) = \ln(I/I_0)$$  \[5.7a\]

or

$$\alpha(dB \ cm^{-1}) = 10 \log_{10}(I/I_0)$$  \[5.7b\]
where $\alpha$ is the propagation loss, $l$ is the propagation length in centimetres. For reference, a loss of 50% over 1 cm gives $\alpha = 0.69 \text{ cm}^{-1} = 3 \text{ dB cm}^{-1}$. A 1mm core optical fibre was used for these measurements coupled to PIN photodiode. This is illustrated schematically in fig. 5.6. The fibre is mounted as close to the film as possible, without making contact, and is scanned across the film using a translation stage with it's axis parallel to the film plane. Typically the coupling beam is chopped and the scattered light detected with a lock-in amplifier.

This is not the most accurate method of determining propagation loss, other techniques are preferable. With this setup, losses higher than 9 dB cm$^{-1}$ ($\sim$ 4% transmission) and losses lower than $\sim$ 3 dB cm$^{-1}$ have poor signal to noise ratios are difficult to quantify. But, losses higher than 9 dB cm$^{-1}$ (implying $\sim$ 4% transmission over 1 cm path length) are generally unacceptable, so this limit poses few problems.
5.3.3 Thin Film Results

For guest/host systems, poly(styrene) was chosen as the host material. It was found that the fluorescent compounds retained their high fluorescence yields and displayed small shifts in absorption and emission. Ortho-xylene solutions were used for the poly(styrene) films (doped and undoped) and toluene was used for the neat films of fluorescent polymers. Where possible, all solutions are filtered, 0.3 µm pore size, prior to spinning. For doped poly(styrene) films, this is not possible once the poly(styrene) is added due to the high viscosities. In this case solutions are filtered prior to addition of the poly(styrene). If necessary, the solutions are heated to ~ 60° C to ensure complete dissolution of the solutes and also serves to prevent aggregation or gellation of the fluorescent polymers.

For the neat polymeric films from samples AT63, HT73, and SP19, no waveguide measurements were possible, due to strong propagation losses > 9 dB cm\(^{-1}\). The films were found to be highly scattering, clearly visible under appropriate lighting conditions as an enhanced fluorescence emission out of the plane of the film when compared to highly fluorescent films of low propagation loss. Poly(styrene) films doped with these materials at concentrations of 1 - 2 wt. % also displayed propagation high losses, in excess of 6 dB cm\(^{-1}\). Table 5.3 lists the propagation losses for waveguides for different materials.

The problem of scattering losses in neat conjugated polymer films is not generally recognised as a widespread problem, as electroluminescent properties of the materials are generally studied more intensively than the optical properties. In the case of electroluminescent devices, scattering centres in the film are advantageous as light preferentially emitted into the plane of the film (cf. chapter 4) is scattered out, increasing the measured efficiency of the device. For waveguide based devices scattering of this magnitude may severely inhibit device performance. The evidence presented here and elsewhere\(^{24}\) suggests that this problem is common to most conjugated polymers.
Table 5.3: Propagation losses of the materials tested. Number greater than 10 dB cm\(^{-1}\) indicate where losses are too high to measure.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Propagation Loss (dB cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Polystyrene host</td>
</tr>
<tr>
<td>SP19</td>
<td>6</td>
</tr>
<tr>
<td>AT63</td>
<td>~ 9</td>
</tr>
<tr>
<td>HT73</td>
<td>&gt; 10</td>
</tr>
<tr>
<td>Ro177</td>
<td>&gt; 10</td>
</tr>
<tr>
<td>DPOP-PPV</td>
<td>&lt; 2.5</td>
</tr>
<tr>
<td>SP48</td>
<td>&lt; 2.5</td>
</tr>
<tr>
<td>SP35</td>
<td>&lt; 2.5</td>
</tr>
<tr>
<td>G33</td>
<td>&lt; 2.5</td>
</tr>
</tbody>
</table>

Fig. 5.7 shows typical spin rate vs. thickness curves for spin cast films of (neat) poly(styrene) from 100 g/l and 75 g/l ortho-xylene. The power law dependence of eqn.[5.2] is clear and is well behaved for all measured poly(styrene) samples, doped or undoped. Material dispersion curves are also well behaved, as shown in fig. 5.8 for doped and undoped poly(styrene) films.

Doping the poly(styrene) films in general increases the refractive index, as expected with the absorption resonance of the materials closer to the spectral range of the measurement. The exception here are the SP19/poly(styrene) films, which show slightly decreased refractive indices relative to undoped films. This is most likely due to free volume affects, the SP19 chains affect the arrangement of the polymer chains in the material, decreasing the density with a resultant decrease in refractive index. The SP19/PS films also exhibited higher thicknesses than 'neat' poly(styrene) films, consistent with an increase in free volume.
Chapter 5: Fluorescent Materials...

*Fig. 5.7: Semilog plot of spin rate vs thickness for poly(styrene) films spin cast from ortho-xylene solution. Dark circles - 100 g/l solution, light circles - 75 g/l solution.*

*Fig. 5.8: Material Dispersion curves for doped poly(styrene) waveguides containing 1.3 wt. % dopants. ● - poly(styrene) no dopant, ○ - SP35/PS, ▼ - G33/PS, ▽ - SP19/PS.*
To estimate measurement accuracies, film thicknesses were measured using a Dektak 3ST profilometer. Prism coupled and profilometry values agreed to within 0.05 μm. To examine the batch-to-batch variation of the film parameters, films were spun from different poly(styrene) solutions prepared to similar concentrations, using identical spin conditions and baking times. A mean error of $\Delta n = \pm 4 \times 10^{-4}$ was determined for refractive index measurements and a mean thickness error of $\Delta t = \pm 0.1 \mu m$, acceptable tolerances for most applications.

### 5.4 Conclusions

Laser action in solutions of PPV-derivative polymers and model compounds across the visible spectrum has been demonstrated. The efficiencies and the threshold energy for the polymeric compounds do not compare favourably to the properties of the coumarin dye used for comparison. This is attributed to excited singlet state absorption. In addition, all but one of the polymers tested proved satisfactory for use in waveguide devices, with propagation loss due to scattering the primary concern.

The polymer model compounds tested in solution lasing experiments exhibit properties comparable to the coumarin dye used for comparison. In addition, when used as dopants in poly(styrene) films, waveguide fabrication and optical properties are not compromised. Using the film fabrication and material dispersion data, in conjunction with eqn. [2.23] for guided mode cut-off thickness, allows accurate fabrication of waveguides with a required number of guided modes.
References

Chapter 5: Fluorescent Materials...


24 W. Blau *et al.*, Trinity College Dublin, *unpublished results*. In addition to the materials presented here, polymer films produced from a wide range of materials have been tested by Blau *et al.*, the majority of which exhibit significant scattering.
Chapter 6 Amplified Spontaneous Emission in a Planar Waveguide

6.1 Introduction

There have been many publications reporting stimulated emission processes in organic waveguides. In general, the bulk of the reports concern amplified spontaneous emission (ASE). This is a purely random process relying on chance interactions of spontaneously emitted (fluorescent) photons with excited states lying along the optical path. The fluorescent photons stimulate emission from the excited states, producing a net amplification of photons whose energies lie within the gain band of the material. By measuring the change in the intensity of the fluorescent emission as the pump conditions are changed we can determine if stimulated emission is occurring. It is also possible to deduce the gain spectrum of a material, allowing us to predict a material’s use for laser applications.

ASE does not require a population inversion to be observed, only that a sufficient number of excited states exist along some propagation direction, such that

\[ \exp(gl) > 1 \]  

[6.1]

where \( g \) is the optical gain per unit length and \( l \) is the optical path length through the region containing the excited states. Provided optical losses (e.g. scattering and absorption) are sufficiently low, and the optical path is sufficiently long, fluorescence amplification and spectral narrowing may be observed for arbitrarily small pump intensities.
Here a model of amplified spontaneous emission (ASE) that explicitly includes wavelength dependant optical gain will be presented. This model is used to produce optical gain spectra for two of the model compounds previously mentioned (SP35 and G33) under study. It will be show how it may be possible to use the optical gain spectrum to predict a material's potential for use as a laser medium. Finally, a figure of merit is presented which will allow semi-quantitative comparisons between different materials for use as solid state laser materials when under optically pumped conditions.

The measurement of optical gain presented involves the measurement of fluorescent emission, amplified via stimulated emission, as it passes through the excited volume of a sample, as depicted in fig. 6.1. This technique is similar to the method used by Shaklee and Leheny\(^5\) in semiconductor crystals, and by Sorek \textit{et. al.}\(^3\) in organic doped glass waveguides. The pump laser is incident on the sample in the form a thin stripe of variable length. The sample fluorescence is emitted isotropically within the plane of the film, and some photons will travel along the length of the pumped region. It is these photons that can stimulate further photons to be emitted with the same propagation vector, resulting in an amplification of light travelling along the pumped stripe and a resultant increase in the output emission intensity.

![Fig. 6.1: Schematic diagram of pumping geometry for observation of amplified spontaneous emission in a waveguide geometry.](image-url)
6.2 Single Pass Fluorescence Amplification

What is now commonly referred to as ASE theory usually starts with a one-dimensional approximation\(^5\)\(^3\) describing the rate of change of fluorescence intensity with length of the pumped region:

\[
\frac{dI}{dz} = AP_0 + gI
\]  \hspace{1cm} [6.2]

where \(I\) is the fluorescence intensity propagating along the z-axis, \(g = g' - \alpha\) is the net optical gain, \(\alpha\) accounts for all loss mechanisms, and \(AP_0\) describes spontaneous emission proportional to pump intensity, \(P_0\). The solution of this equation with respect to pump length is:

\[
I = \frac{AP_0}{g} \left\{ \exp(gl) - 1 \right\}
\]  \hspace{1cm} [6.3]

where \(l\) is the length of the pumped strip. This is the standard equation for the change in output intensity with pump length and can in fact be applied to all values of \(g\). When \(g\) is negative, then the equation describes losses, due to absorption or scattering. Positive values of \(g\), as is the case here, describe amplification.

A more general approach will also be described, which affords a more complete picture of what is actually happening inside the waveguide. With reference to fig. 6.1, consider a segment on the pumped strip of length \(dz\), at position \(z = l\). The spontaneous emission (i.e. fluorescence) generated by this segment is given by:

\[
I_{(z=l)} = AP_0 dz
\]  \hspace{1cm} [6.4]
and spontaneous emission is proportional to pump intensity, \( P_0 \), as before. A portion of the emission travels along the z-axis toward the edge of the waveguide, \( z = 0 \), and is absorbed or amplified, according to the normal Beer-Lambert law:

\[
I_{(z=0)} = AP_0 \exp(gz)dz
\]  

[6.5]

i.e. an exponential decrease or increase in the emission intensity as the light from the segment travels through the pumped region. The total light output from the entire length of the pumped strip is naturally a sum of contributions from each segment. So, we integrate to get the total intensity, \( I \):

\[
I = \sum_z I(z) = \int_0^z AP_0 \exp(gz)dz
\]  

[6.6]

the solution of which is identically equal to eqn. [6.3]. Aside from giving a 'clearer mental picture' of the process, when a non-intensity dependent process is involved (such as scattering losses) we can substitute any z-dependant intensity profile for \( P_0 \). This lifts the restriction on keeping \( P_0 \) constant across the pump length, an implicit assumption in equation [6.2], although we will not concern ourselves further with this.

Fig. 6.2 shows the effect of different gain values, \( g \), on the output intensity, \( I \). Plotted on fig. 6.2 are intensity vs. pump length curves for five different gain values; \( g = \pm 2 \text{ cm}^{-1} \), \( g = \pm 0.69 \text{ cm}^{-1} \) and \( g = 0 \text{ cm}^{-1} \) (i.e. no loss or gain). Note that values of \( 0.69 \text{ cm}^{-1} = 3 \text{ dB cm}^{-1} \Rightarrow I/I_0 = 50\% \). While the gain values used to model the curves in fig. 6.2 are quite small, the effect of gain on the output intensity is clear. For \( g = 0 \text{ cm}^{-1} \) the intensity is simply proportional to the pump length. For negative gain values (i.e. an energy loss from the system), a sublinear increase is seen resulting in a saturation of the output for large values of \( gl \).

Positive gain values naturally lead to an exponential increase in intensity with pump length. In practice there is also an output saturation effect seen for longer pump length.
lengths due to gain saturation. Photons travelling along the pumped strip, while inducing stimulated emission, are also removing excited states from the optical path. Thus photons emitted further from the edge of waveguide (larger values of $z$) have less excited states per unit length available for amplification. The total output intensity will reach some maximum value determined by the gain coefficient of the material, $g$, and the density of excited states in the material. These propagation effects will not be explicitly considered when modelling ASE processes but are worth keeping in mind.

![Graph](image)

**Fig. 6.2: Output Intensity, $I$, vs. pump length, $l$, for different values of gain, $g$.**

The curves are calculated using eqn. [6.3].

It should also be noted that we are dealing with a system under short pulse excitation. The pump pulse is of much shorter duration than the characteristic radiative lifetime (for spontaneous emission) of the materials. The pump pulse, as detailed below, is of 35 ps duration and is assumed short enough that spontaneous emission is not significant over this timescale. For most organic emitters, with spontaneous emission times on the order of nanoseconds, this assumption is valid. Further more, stimulated emission is assumed to occur on a correspondingly short timescale (approx. $2l/c \sim 50 \text{ ps}$) and spontaneous emission does not strongly deplete the excited states in competition with stimulated emission. Under conditions of longer pump pulse duration, the time dependence of these processes must be explicitly considered.
6.2.1 Wavelength Dependent Optical Gain

To explicitly include wavelength dependence of the fluorescence amplification, we first start by expressing fluorescence quantum yield, $\phi_f$, in a wavelength dependant manner as:

$$\phi_f = \int_{\lambda_a}^{\lambda_b} E_f(\lambda) d\lambda$$  \[6.7\]

where $E_f(\lambda)$ is the fluorescence quantum distribution, $\lambda_a$ and $\lambda_b$ are the limits of the fluorescence spectrum (cf. Chapter 3). When considering equations [6.2] and [6.3], it is apparent that if $AP_0$ is to describe spontaneous emission proportional to pump intensity, $A$ must be proportional to the fluorescence quantum yield, $\phi_f$. If we express $AP_0$ directly proportional to $\phi_f$ as:

$$AP_0 = C\phi_f P_0$$  \[6.8a\]

where $C$ is a constant of proportionality, we can also write

$$A(\lambda)P_0 = C(\lambda).E_f(\lambda).P_0$$  \[6.8b\]

where $A(\lambda)P_0$ describes the fluorescence intensity at wavelength $\lambda$, proportional to pump intensity $P_0$, and $C(\lambda)$ is a wavelength dependent expression of the constant, $C$. The fluorescence lineshape of the material will be identical to the shape of $E_f(\lambda)$ if we neglect re-absorption of the fluorescence.

By substitution of equations [6.8] into equation [6.3] we can now write an equation describing amplified spontaneous emission which explicitly includes wavelength dependence;
Chapter 6: Amplified Spontaneous Emission...

\[
I(\lambda) = \frac{C(\lambda)E_0(\lambda)P_0}{g(\lambda)} \left\{ \exp(g(\lambda)I) - 1 \right\}
\]  

[6.9]

where \( g(\lambda) \) is the net gain per unit length at wavelength \( \lambda \). The general form of this equation is identical to that of eqn. [6.3]. However, not all wavelengths are amplified to the same extent, i.e. \( g(\lambda) \) is not constant.

In general, the gain spectrum of a material will be of a smaller bandwidth to that of the fluorescence spectrum. As stimulated emission occurs only a band of wavelengths within the fluorescence is amplified. This produces a narrowing of the fluorescence output as some wavelengths are amplified to a greater extent than others. In addition, as stimulated emission removes excited states from the pumped region, this also induces a reduction in the emission efficiency of wavelengths not being amplified. This leads to an earlier saturation of the output intensity than the analysis based on linear propagation losses would suggest.

Equation [6.9] implies that spectral narrowing is influenced by the low pump intensity fluorescence spectrum, proportional to \( E_0(\lambda) \) unless there is significant overlap between absorption and emission spectra. It is quite clear that \( E_0(\lambda) \) is not constant under conditions where stimulated emission is significant, increasing for strongly amplified wavelengths and decreasing for others, in accordance with the contribution of each wavelength to the total output intensity. In the case mentioned above of fluorescence saturation via stimulated emission, \( E_0(\lambda) \) decreases for wavelengths not involved in amplification.

Similarly, if one considers the number of emitted photons detected per pump photon absorbed, the \( C(\lambda) \) term in eqn. [6.9] must also include a term accounting for the geometric distribution of the emitted photons, assumed isotropic within the plane of the film. But the distribution of emitted photons is not constant due to the anisotropic nature of stimulated emission. As fluorescence amplification becomes observable, a greater proportion of photons are emitted parallel to the axis of the pumped region, reducing the number of excited states available for isotropic
spontaneous emission, which changes the distribution described by $C(\lambda)$. This produces a further increase in the apparent emission efficiency for the range of amplified wavelengths, i.e. parallel to the direction of the pumped strip, but a decrease in efficiency at all wavelengths in all other emission directions. The changes in $C(\lambda)$ can account for the decrease in emission efficiency seen by Gelinck et al. when detecting at $45^\circ$ to the plane of the film, as also suggested by McGehee et al.2.

The quantum electrodynamic approach to spontaneous emission in a dielectric slab, due to Urbach and Rikken7 and Zakowicz and Bledowski8, demonstrates that the spontaneous emission rate in a dielectric slab is modified by the presence of waveguide modes, by film thickness, and by the position (relative to the x-axis) of an emitting molecule within the waveguide structure (cf. chapter 4). As a result, assumptions to the effect that emission is isotropic from a fluorescent waveguide are not be valid. In addition, $C(\lambda)$ will change strongly across the fluorescence spectrum at wavelengths close to waveguide mode cut-off conditions, as emission processes into waveguides are severely modified.

For the ASE study presented here, thickness dependence is not considered and values for $\phi$, and $C(\lambda)$ are not explicitly considered. Never the less, the use of bulk values for $E_0(\lambda)$, and hence for $\phi$, should be treated with care for any emissive dielectric thin film. This maybe of particular importance for electroluminescent devices, necessarily of small thickness, and may be an important consideration in the design and optimisation of optically emissive thin-film devices.

For our purposes, we note the linear dependence of output intensity on $E_0(\lambda)$ and $C(\lambda)$ and assume for large (absolute) values of $g(\lambda)$ that the exponential term in equation [6.9] will dominate over changes in $E_0(\lambda)$ or $C(\lambda)$. No sudden changes in $C(\lambda)$ due to waveguide cut-off conditions are expected across the fluorescence region, possible with careful choice of film thickness. No further consideration is given to changes in $E_0(\lambda)$ and $C(\lambda)$, as general features in the optical gain spectra will not be affected.
To obtain an optical gain spectrum from a sample, we measure emission spectra from the sample as a function of pump length. For each wavelength in the spectra we apply a nonlinear least squares fitting routine (Gauss-Newton method), written using the MATLAB modelling package, adjusting $g(\lambda)$ and $A_0$ to obtain the best fit to equation [6.9].

### 6.3 Experiment

Figure 6.3 shows the experimental setup. The sample is pumped using a frequency tripled beam from a Nd:YAG laser, producing 0.9 μJ pulses of 35 ps duration at 355 nm. The fundamental and second harmonic beams from the laser head pass through a 1mm aperture, AP1, acting as a diffractive spatial filter to smooth the beam profile. The beam then passes through the harmonic generation crystal, THG, (KD*P, type II). Apertures AP2 and AP3 are used for alignment purposes. Filters, F, remove residual fundamental and second harmonic radiation. Two Glan-Taylor polarisers, P, are used after the filters, the first selecting vertical polarisation and the second for adjusting the pump power.

![Experimental setup for optical gain determination](image)

*Fig. 6.3: Experimental setup for optical gain determination.*
Chapter 6: Amplified Spontaneous Emission...

The 355 nm beam is expanded with lens LI. The beam intensity profile at aperture AP3 is a far field diffraction pattern from AP1, approximately following a Bessel function (type 1). The diameter of AP3 is set to only pass the central maximum of the diffraction pattern. The beam is then focused onto the sample with cylindrical lens, CL1, producing a thin pumped stripe 30 mm long by 0.1 mm wide. The pump beam is aligned so that the centre of the beam and the edge of the sample are coincident. The pump length is adjusted by means of the shutter mounted on a translation stage. Maximum pulse intensity incident on the sample is $8.7 \times 10^7$ W cm$^{-2}$, corresponding to pulse energy densities of $2.9 \times 10^{-5}$ J cm$^{-2}$. Because of the wide intensity profile of the beam, the central 4mm of the beam can be assumed of constant intensity. The maximum pump length used for the calculations was 3 mm.

The guided fluorescence is coupled out of the waveguide and collimated using a 20x microscope objective (MO) (approximately f/3). The light is coupled into a monochromator (MC) (f/4.5) and detected with a peltier cooled CCD spectrometer. We note that fluorescence intensity continued to increase for pump lengths in excess of 9 mm, despite the drop in pump intensity (due to the beam profile, discussed above) and available excited states (depleted via stimulated emission of photons emitted at shorter pump lengths). This suggests that ground state re-absorption and scattering losses can be neglected for the short pump lengths used, across most of the fluorescence band.

6.3.1 Sample Preparation

The samples are produced by spin coating from a 75 g/l poly(styrene) solution in ortho-xylene doped with 1.5 g/l of the model compounds SP35 and G33 (cf chapter 3). The substrates used were silicon wafers with a 1.5 µm thick thermal oxide overlayer, cleaved along the <100> plane after the polymer film was deposited. Refractive index and film thickness were measured using mode-line spectroscopy with a prism film coupler. Waveguide propagation losses are estimated at $\lambda = 632.8$ nm to be between 2.2 dB cm$^{-1}$ and 3.0 dB cm$^{-1}$, and no higher than 4 dB cm$^{-1}$ at $\lambda = 514.5$ nm, measured during prism coupling experiments.
The thickness of the polymer films were chosen to support two guided modes, \( \text{TE}_0 \) and \( \text{TM}_0 \), at the fluorescence maximum of the samples. This results in a desired thickness of 0.45 \( \mu \text{m} \) for G33 doped films (\( \lambda_{\text{max}} = 510 \text{ nm} \)) and 0.4 \( \mu \text{m} \) for SP35 doped films (\( \lambda_{\text{max}} = 490 \text{ nm} \)). All films were fabricated to within 10% of the required thickness. Optical measurements and sample preparation were performed in air at room temperature.

### 6.4 Results and Discussion

Figs. 6.4a,b illustrate the evolution of the fluorescence spectra as the pump length, \( l \), is changed, for SP35 and G33 doped waveguides respectively. Clearly evident is the growth of a well defined peak in the fluorescent emission as a relatively narrow band of wavelengths are amplified. Each graph displays spectra obtained at three different pump lengths: \( l = 0.2 \text{ cm}, 0.1 \text{ cm}, \) and 0.025 cm for plots 1, 2, and 3 respectively.

Figs. 6.4: Evolution of the output fluorescence spectra as pump length is increased.

\( a) \) SP35 doped waveguide \( b) \) G33 doped waveguide
Fig. 6.5 shows the optical gain spectra obtained for the doped poly(styrene) waveguides at the maximum incident pump intensity of $8.7 \times 10^5$ W cm$^{-2}$, determined by fitting to eqn. [6.9]. Results obtained from these spectra are included.

![Optical gain spectra](image)

**Fig. 6.5:** Optical gain spectra produced using a nonlinear least squares fit to eqn. [6.9] at incident pump power of $8.7 \times 10^5$ W cm$^{-2}$. Solid circles are for SP35 doped waveguides, open circles are for G33 doped waveguides.

![Length dependence](image)

**Fig. 6.6:** Length dependence of the amplified fluorescence at the maximum gain wavelength for SP35 and G33 doped waveguides. The solid line is a least-squares fit using eqn. [6.9]. SP35 samples yield a net gain $g = 19.8$ cm$^{-1}$ at $\lambda = 488$ nm, G33 samples yield $g = 15.5$ cm$^{-1}$ at $\lambda = 510$nm.

Chapter 6: Amplified Spontaneous Emission...
Chapter 6: Amplified Spontaneous Emission

in table 6.1 below. Fig. 6.6 shows typical length dependences of the amplified fluorescence at the gain maxima for both samples. SP35 and G33 doped samples exhibit a single well defined peak in g(λ), at λ = 487 nm and 510 nm respectively, with G33 also exhibiting a weak shoulder near 520 nm. The maximum net gains obtained are g = 19.8 cm⁻¹ for SP35 and g = 15.5 cm⁻¹ for G33. Full width at half maximum for the gain spectra are 12 nm and 15 nm respectively. Minimum full width at half maximum for the narrowed fluorescence spectra approached 8 nm for SP35 doped samples and 12 nm for G33 doped samples.

Table 6.1: Optical properties of SP35 and G33 doped poly(styrene) waveguides. F is the figure of merit described below.

<table>
<thead>
<tr>
<th></th>
<th>SP35</th>
<th>G33</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption λ_max (nm)</td>
<td>390</td>
<td>410</td>
</tr>
<tr>
<td>Fluorescence λ_max (nm)</td>
<td>470, 490</td>
<td>505</td>
</tr>
<tr>
<td>Fluorescence Yield, φ_f</td>
<td>0.85</td>
<td>0.65</td>
</tr>
<tr>
<td>Gain λ_max (nm)</td>
<td>487</td>
<td>510</td>
</tr>
<tr>
<td>G_max (cm⁻¹)</td>
<td>19.8</td>
<td>15.5</td>
</tr>
<tr>
<td>G(λ) FWHM (nm)</td>
<td>12</td>
<td>15</td>
</tr>
<tr>
<td>F (nm cm J⁻¹)</td>
<td>4.2×10⁸</td>
<td>4.1×10⁸</td>
</tr>
</tbody>
</table>

On either side of the gain peak, there are regions exhibiting negative values of g(λ). As excited state absorption is normally red-shifted from the fluorescence maximum in organic materials, we assume excited singlet absorption to be principally responsible for the long wavelength negative values of g(λ). The short duration (35 ps) pump pulse allows us to neglect triplet-triplet absorption, which was reported by Henari et al. for G33 with a characteristic lifetime for T₁ of 11 ms. Similar spectral features are present in femtosecond pump-probe measurements on ladder type poly(para-phenylene) (LPPP)¹²,¹³, in picosecond Kerr ellipsometry measurements on poly(aryleneethynylene) derivatives¹⁴, and in nanosecond ASE measurements on GaInN/GaN¹⁵. The short wavelength negative g(λ) values are attributed primarily to fluorescence output saturation via stimulated emission, as discussed above.
By estimating the density of dopant molecules in the poly(styrene) matrix we can set a lower limit on the value of the effective stimulated emission cross-section, 

\[ \sigma_{S.E.,eff} = \sigma_{S.E.} - \sigma_{abs} \]

by using the relation (eqn. [3.19]):

\[ g = N_{chr} \sigma_{S.E.,eff} \tag{6.10} \]

where \( g \) is the net optical gain and \( N_{chr} \) is the chromophore number density. This assumes that all dopant molecules are excited by the pump pulse and that stimulated emission dominates over spontaneous emission for all wavelengths. \( N_{chr} \) is estimated to be approximately \( 10^{18} \text{ cm}^{-3} \) for SP35 and G33 in the poly(styrene) waveguides, which implies a minimum value for \( \sigma_{S.E.,eff} = 2 \times 10^{-17} \text{ cm}^2 \), in good agreement with the value reported by Henari et al. of \( \sigma_{S.E.,eff} = 5.5 \times 10^{-17} \text{ cm}^2 (\lambda = 514.5 \text{ nm}) \) for G33 in toluene solution.

### 6.4.1 Comparison with recent Publications

When comparing results from various publications, it is apparent that some are carried out by monitoring the total (integrated) fluorescence intensity, some monitor a single wavelength, and some, as in this case, monitor the entire fluorescence spectrum. We must now examine eqns. [6.3] and [6.9] and relate the integrated gain coefficient, \( g \) from eqn. [6.3], to the spectral gain coefficient, \( g(\lambda) \) from [6.9]. We start by relating the total fluorescence intensity, \( I \) in eqn. [6.3], to the integrated intensity of the fluorescence spectrum, \( I(\lambda) \):

\[ I = \int_{\lambda_0}^{\lambda_0} I(\lambda) d\lambda = \lim_{\lambda \to \infty} \sum \lambda I(\lambda) \tag{6.11} \]

and as \( I \propto \exp(g/\lambda) \), we can also write:

\[ I \propto \sum \lambda \exp(g(\lambda) I) \tag{6.12} \]
For $g(\lambda)/<<1$ then the sum in equation [6.12] is close in value to the maximum value of $g(\lambda)$, i.e. $\exp(20) + \exp(20) \approx \exp(20)$. Assuming that optical gain spectra exhibit a reasonably well defined peak, then the net gain, $g$, for the integrated intensity (eqn. [6.3]) is very close to the maximum value of $g(\lambda)$. With this in mind, we are in a position to compare similar single-pass fluorescence amplification experiments, irrespective of whether the amplification is measured at a single wavelength, across the fluorescence spectrum, or for the total fluorescence intensity.

To enable a comparison between different materials for use in laser devices a figure of merit may find use. This figure of merit must account for experimental conditions and must also include properties that will be advantageous for development for commercial devices. If organic materials are to be successful as solid-state laser materials, tuneability must be considered. Therefore, in comparing candidate materials, we must favour not only large net gains, but large gain bandwidths, which we characterise by the full width at half maximum of the gain spectrum and denote as $f$. We therefore arrive at a simple figure of merit, $F$, of the form:

$$F = \frac{g_{\text{max}} \cdot f}{P_{\text{abs}}}$$  \[6.13\]

where $P_{\text{abs}}$ is the absorbed pump pulse energy density to produce $g_{\text{max}}$, the maximum value of $g(\lambda)$. We choose pulse energy density [J cm$^{-2}$] in lieu of pump intensity [W cm$^{-2}$] to enable comparisons of measurements using different pump pulse widths. This assumes that the pump pulse duration is shorter than the fluorescence lifetime of the sample, so that re-population of the excited states does not inflate the gain values. This will be valid for sub-nanosecond pulse widths as long as the emission lifetimes are of the order of nanoseconds, typical for most fluorescent organic emitters (cf. Chapter 3).

Estimating approximately 20% of the incident pump pulse is absorbed by the waveguides studied, including reflection from the Si substrate, suggests $P_{\text{abs}} =$
Chapter 6: Amplified Spontaneous Emission...

$5.6 \times 10^{-7}$ J cm$^{-2}$. This implies values of $F = 4.2 \times 10^8$ nm cm J$^{-1}$ and $F = 4.1 \times 10^8$ nm cm J$^{-1}$ for SP35 and G33 doped films respectively. These values are included in Table 6.1 above.

Lasing measurements of SP35 solutions indicate that SP35 is at comparable to coumarin dyes in slope efficiency and output (chapter 6 and ref. 16). The lasing tuning range in solution and the limits of positive $g(\lambda)$ determined here are similar. As the optical properties of the SP35 toluene solution and SP35 doped poly(styrene) sample are similar, we can reasonably link the ASE characteristics, and hence the value of $F$, to lasing performance. This suggests that a material test using this optical gain measurement with a figure of merit $F > 10^8$ nm cm J$^{-1}$ may be reasonably expected have some use as a solid-state laser medium.

It is instructive to compare the figure of merit of our polymer waveguides with those obtained from other optical gain studies. We estimate a figure of merit for ladder type poly(para-phenylene), LPPP$^{4,12,17}$, to be $F = 8.3 \times 10^7$ nm cm J$^{-1}$. For BuEH-PPV$^2$ we estimate $F = 3.3 \times 10^8$ nm cm J$^{-1}$, despite the enormous optical losses$^{18}$. For GaInN/GaN double heterostructures$^{15}$ we estimate $F = 4.7 \times 10^7$ nm cm J$^{-1}$, and for AlGaN/GaN DHs$^{19}$ $F = 2.7 \times 10^7$ nm cm J$^{-1}$. These figure of merit values are included in table 6.2. These figures indicate that G33 and SP35 doped poly(styrene) waveguides may be suitable candidates for optically pumped laser media, and are at least comparable in performance to other organic materials.

6.5 Conclusions

An explicitly wavelength dependent analysis of amplified spontaneous emission has been presented. Maximum optical gains of $g(\lambda) = 19.8$ cm$^{-1}$ and $g(\lambda) = 15.5$ cm$^{-1}$ were determined for SP35 and G33 doped poly(styrene) waveguides respectively. A method of comparing different fluorescence amplification experiments has been described and a figure of merit for this purpose presented. The figure of merit indicates that organic materials can outperform traditional semiconductors under optically pumped conditions.
It is worth noting that the SP35 and G33 doped waveguides are dilute guest/host systems and waveguide propagation losses are much lower here than for the ‘neat’ polymeric systems, which in general have propagation losses in excess of 10 dB cm\(^{-1}\). While the absolute gains reported for the other organic materials are often higher than those for our waveguides, the increased propagation losses of the other materials may lower the figure of merit values substantially.

Table 6.2: Comparison of materials reported in recent publications using the figure of merit, $F$, described in this report.

<table>
<thead>
<tr>
<th>Material</th>
<th>Figure of Merit, $F$ (nm cm J(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP35/PS</td>
<td>(4.2 \times 10^8)</td>
<td>-</td>
</tr>
<tr>
<td>G33/PS</td>
<td>(4.1 \times 10^8)</td>
<td>-</td>
</tr>
<tr>
<td>BuEH-PPV</td>
<td>(3.3 \times 10^8)</td>
<td>2</td>
</tr>
<tr>
<td>LPPP</td>
<td>(8.3 \times 10^7)</td>
<td>4,12</td>
</tr>
<tr>
<td>GaInN/GaN</td>
<td>(4.7 \times 10^7)</td>
<td>15</td>
</tr>
<tr>
<td>AlGaN/GaN</td>
<td>(2.7 \times 10^7)</td>
<td>19</td>
</tr>
</tbody>
</table>
References:


17. For LPPP we use \( g = 50 \text{ cm}^{-1} \) at \( 22\text{kW/cm}^2 \) @ 10 Hz, 6 ns pulse width from ref. 4, \( f \approx 20 \text{ nm} \) from figure 2 of ref. 12. We estimate 90% of the pump pulse is absorbed using typical absorption spectra for LPPPs. The gain bandwidth may be an over estimate.
Chapter 6: Amplified Spontaneous Emission...

18 Ref. 2 reports linear optical losses of 44 cm$^{-1}$ for BuEH-PPV waveguides, suggesting 99% losses over 1mm path length.

Chapter 7 Distributed Feedback Lasing

7.1 Introduction

Laser oscillation can be obtained by using a periodic structure within the gain medium, rather than using external mirrors as in conventional lasers. In these systems optical feedback is provided by Bragg scattering from a spatially periodic modulation of the properties of the gain material. This is known as distributed feedback. The period of the modulation is equal to half the oscillation wavelength. As laser oscillation can only occur at wavelengths satisfying the Bragg condition, the feedback is strongly frequency selective.

Kogelnik and Shank first demonstrated the distributed feedback (DFB) dye laser in a dye doped gelatin film with a photobleached grating. High order distributed feedback, where the modulation period is a multiple of half the wavelength, in dye solutions via a pump beam induced grating was demonstrated by Bjorkholm and Shank in 1972. More recently, distributed feedback lasing has been reported by McGehee et al. in BuEH-PPV waveguides deposited on a corrugated substrate. Nunzi et al. have also demonstrated DFB laser action using an identical setup to that described below. Kogelnik and Shank’s theoretical treatment of DFB lasers using coupled wave theory showed that optical feedback can be obtained from a pump beam induced spatial modulation of both gain and refractive index. An interesting discussion based on Kogelnik and Shanks' theory is also given by Yariv.
In this chapter second-order pump beam induced distributed feedback laser action is demonstrated in doped poly(styrene) waveguides. Using an experimental setup which allows the grating period to be easily changed, tuning ranges for the samples are determined and compared to the solution lasing results of chapter 5, and the optical gain spectra of chapter 7. Only a single waveguide mode can satisfy the Bragg condition for any one wavelength. This allows simultaneous lasing of many wavelengths with multi-mode devices, subject to the width of the gain spectrum. The dependence of the modal lasing thresholds on film thickness is examined. Finally implications for the design of commercial devices, whether optically or electrically pumped, will be discussed.

### 7.2 Coupled Wave Theory of Distributed Feedback Lasers

In this discussion the same coordinate systems used in the other chapters will be employed, i.e. propagation direction is along the z-axis. A bulk periodic medium is therefore described with a complex dielectric constant, given by:

\[
\begin{align*}
k^2 &= \omega^2 \mu \varepsilon = \omega^2 \mu (\varepsilon_r + i\varepsilon_i) = k_0^2 n^2(z) \left[ 1 + i \frac{2\alpha(z)}{k_0 n} \right] \\
\end{align*}
\]

where \(k_0\) is the propagation constant in a vacuum, \(\alpha \ll k_0\) is the gain constant, and \(\varepsilon_r\) and \(\varepsilon_i\) are the real and imaginary components of the dielectric constant, \(\varepsilon\). The refractive index and gain coefficient are expressed as a function of propagation direction, \(z\), usually taking a cosine variation:

\[
\begin{align*}
n(z) &= n + n_1 \cos(2\beta_0 z) \\
\alpha(z) &= \alpha + \alpha_1 \cos(2\beta_0 z) \\
\end{align*}
\]

where \(n_1\) and \(\alpha_1\) are the amplitudes of the modulation about the average values \(n\) and \(\alpha\). At the Bragg condition, assuming that the laser oscillates close to the Bragg frequency, i.e. \(\omega \approx \omega_0\):
which implies a spatial period \( \pi/\beta \) equal to half the wavelength of light in the medium, i.e. \( \lambda/2n \) (and hence the \( \cos(2\beta_0 z) \) term in eqn. [8.3]). It is assumed that perturbations in the refractive index and gain coefficient are small, i.e.:

\[
\alpha << \beta_0 = \frac{2n}{\lambda} \\
n_1 << n \\
\alpha_1 << \beta_0
\]  

[7.5]

From eqns. [7.2] and [7.3], \( k^2(z) \) can be expressed as:

\[
k^2(z) = \beta^2 + i2\beta\alpha + 4\beta\kappa \cos(2\beta_0 z) \]  

[7.6]

where \( \beta = k_0 n \) is the propagation constant of the unperturbed medium and \( \kappa \), known as the coupling constant for reasons described below, is defined as:

\[
\kappa = \frac{n_1}{\lambda} + i\frac{\alpha_1}{2}
\]  

[7.7]

Writing the scalar wave equation as \( \nabla^2 E + k^2(z)E = 0 \) and using eqn. [7.6] one obtains:

\[
\frac{d^2 E}{dz^2} + \left[ \beta^2 + i2\beta\alpha + 4\beta\kappa \cos(2\beta_0 z) \right] E = 0
\]  

[7.8]

In principle a periodic perturbation generates an infinite set of diffraction orders but only two significant waves are in phase synchronisation, corresponding to two counter-propagating waves, \( \exp(\pm i\beta z) \). In fact, the field \( E(z) \) cannot be described by a single field but is well approximated by a linear superposition of the two waves:

\[
E(z) = R(z)\exp(i\beta_0 z) + S(z)\exp(-i\beta_0 z)
\]  

[7.9]
It is now clear from eqn. [7.8] that the coupling coefficient, $k$, describes the frequency selective coupling between the two counter-propagating waves, which introduces the feedback necessary for laser action. From eqn. [7.7] it is also evident that coupling between the two waves can be due modulations of the refractive index and/or the gain coefficient.

The second derivatives $\partial^2 R/\partial z^2$ and $\partial^2 S/\partial z^2$ are assumed to be small due to eqns. [7.5]. In organic materials, $\alpha$ is generally less than $10^2$ cm$^{-1}$, very much less than $\beta \approx 10^5$ cm$^{-1}$ near the visible spectrum, and $n_1 \approx 10^{-4}$, these assumptions are certainly valid. With these assumptions, eqn. [7.9] is inserted into the scalar wave equation. Comparing terms with equal exponents obtains a pair of coupled wave equations of the form:

$$
\begin{align*}
R' - (\alpha - i\delta)R &= -i\kappa S \\
S' + (\alpha - i\delta)S &= i\kappa R
\end{align*}
$$

where $\delta$ is a normalised frequency parameter defined by:

$$
\delta = (\beta^2 - \beta_0^2)/2\beta = \beta - \beta_0 = m(\omega - \omega_0)/c
$$

$\delta$ is a measure of the departure of the oscillation frequency $\omega$ from the Bragg frequency $\omega_0$. At the Bragg condition $\delta = 0$.

### 7.2.1 Coupled Wave Solutions

In a self oscillating device there are no incoming waves and the internal waves, $R$ and $S$, start with zero amplitude at the device boundaries, growing exponentially through the medium, as in fig. 7.1. Considering a device of length $L$, extending from $z = -\frac{1}{2}L$ to $z = +\frac{1}{2}L$, the boundary condition is simply:

$$
R(-\frac{1}{2}L) = S(\frac{1}{2}L) = 0
$$
Kogelnik and Shank\textsuperscript{5} show that the general solution to the coupled wave equations [7.10] is of the form:

\[
R = r_0 \exp(j\gamma z) + r_2 \exp(-j\gamma z) \\
S = s_0 \exp(j\gamma z) + s_2 \exp(-j\gamma z)
\]

with the complex propagation constant \(\gamma\) obeying the dispersion relation:

\[
\gamma^2 = \kappa^2 + (\alpha - i\delta)^2
\]

The assumed symmetry of the device gives symmetric \([E(-z) = E(z)]\) and anti-symmetric \([E(-z) = -E(z)]\) field solutions. This implies that the coefficients \(r_1\) and \(s_1\) are given by:

\[
\begin{align*}
r_1 &= \pm s_2 \\
r_2 &= \pm s_1
\end{align*}
\]

In addition, the boundary conditions of eqn. [7.12] also imply that:
Chapter 7: Distributed Feedback Lasing

\[ r_1 = s_2 = -e^{\mu} \]
\[ r_2 = s_1 \] \[ \text{[7.16]} \]

From these results, the longitudinal field distribution of the modes of DFB structure is given by:

\[ R = \sinh \gamma (z + \frac{1}{2} L) \]
\[ S = \pm \sinh \gamma (z - \frac{1}{2} L) \] \[ \text{[7.17]} \]

There are now a discrete set of longitudinal modes which correspond to eigenvalues of \( \gamma \) for a structure of given length, \( L \), and coupling constant, \( \kappa \). It is found that in the cases of a pure gain (\( n_i = 0 \)) or a pure index (\( \alpha_i = 0 \)) grating, that the modes of the structure are analogous to the longitudinal modes of a conventional two-mirror laser cavity. The mode frequency spacing is approximately \( c/2nL \), the same as the two-mirror cavity. For the devices under consideration here, \( n = 1.6 \), \( L = 2 \text{ mm} \), this is of the order \( 10^{10} \text{ Hz} \), implying a mode separation in the visible region of the order of 0.1 nm.

In general, periodic structures are dispersive and display stop bands of frequencies where propagation is forbidden. This property is now widely used for a variety of applications in such devices as microcavities and photonic crystals. The same is also true of the Bragg gratings considered here, which are often treated as one-dimensional photonic crystals.

For a pure index modulation, \( \alpha = 0 \) and the dispersion relation of eqn. [7.14] yields imaginary values of \( \gamma \) when \( \delta^2 > \kappa^2 \) and real values of \( \gamma \) when \( \delta^2 < \kappa^2 \). In this case there is a stop band centred at the Bragg frequency, \( \omega_0 \), of width \( 2\kappa = 2\pi n_1/\lambda \) (eqn. [7.3]). For an index modulation of \( n_i = 10^{-4} \) and \( \lambda = 500 \text{ nm} \), the stop band width is \( \Delta\omega/c = 10^3 \text{ m}^{-1} \), corresponding to a forbidden wavelength gap of about 0.1 nm. There is no resonance within the stop band and the modes are symmetrically distributed about the Bragg wavelength \( \omega_0 \).
7.2.2 Optically Induced Gratings

The above discussion have described distributed feedback lasing from a cosine modulation of the materials refractive index and/or gain. It will now be shown how any periodic modulation, not necessarily of a (simple) cosine longitudinal profile, can be treated in the same manner. In the experiment described below, the spatial modulation of the material properties is due an interference pattern produced by overlapping pump beams. The modulation period, $\Lambda$, is given by:

$$\Lambda = \frac{\lambda_p}{2\sin \theta}$$  \hspace{1cm} [7.18]

where $\lambda_p$ is the wavelength of the pump beams, and $\theta$ is the angle of incidence, as illustrated in fig. 7.2. This modulation will have a cosine$^2$ intensity profile along the z-axis, the interference pattern being cosine in the electric field.

Assuming the change in gain coefficient and refractive index follow a simple intensity dependence, the material modulation functions, $n(z)$ and $\alpha(z)$ will have a similar profile given by:

$$n(z) = n_0 + 2n_1 \cos^2(\varphi z)$$
$$\alpha(z) = \alpha_0 + 2\alpha_1 \cos^2(\varphi z)$$  \hspace{1cm} [7.19]

where $n_0$ and $\alpha_0$ are the unperturbed refractive index and gain coefficients, $2n_1$ and $2\alpha_1$ are the ‘peak-to-peak’ modulations, equal to twice the modulation amplitude.
The modulation period is $\Lambda = \pi/\beta = \sigma/2\pi$. To enable a comparison with Kogelnik and Shank's theoretical treatment outlined above, eqns. [7.19] are re-expressed in terms of a modulation oscillating about the average values of $n$ and $\alpha$. Taking only the refractive index case:

$$n(z) = n_{\text{avg}} + n_1 f(z)$$  [7.20]

where $n_{\text{avg}}$ is the average value of the refractive index in the modulated medium and $f(z)$ is a periodic function with a $\cos^2$ profile, but oscillating between $-1$ and $+1$. This suggests the following:

$$n(z) = n_{\text{avg}} + n_1 \left\{ 2\cos^2(\sigma z) - 1 \right\}$$  [7.21]

and now $f(z)$ has the required profile and upper and lower limits. Noting that $2\cos^2(\Lambda) = 1 + \cos(2\Lambda)$ eqn. [7.21] can be re-expressed in a similar manner to the theoretical treatment given above, i.e. the same form as eqn. [7.3]:

$$n(z) = n_{\text{avg}} + n_1 \cos(2\sigma z)$$  [7.22]  

$$\alpha(z) = \alpha_{\text{avg}} + \alpha_1 \cos(2\sigma z)$$

including the similar equation for the gain modulation. It is now seen that the cosine$^2$ modulations expressed in eqns. [7.19] are equivalent a cosine modulation with half the period (twice the spatial frequency) and a full amplitude of half the modulation depth.

In general any periodic modulation, $F(z)$, can be expressed as a Fourier series of cosine and/or sine terms:

$$F(z) = a_0 + \sum_{m=1}^{\infty} \left( a_m \cos \frac{m\pi}{\Lambda} z + b_m \sin \frac{m\pi}{\Lambda} z \right)$$  [7.23]
where \( a_0, a_m, \) and \( b_m \) are the Euler coefficients. Each high order term produces a harmonic of the modulation spatial frequency for which Bragg reflection can be considered. Indeed, the functions expressed in eqn. [7.22] are in fact the Fourier expansions of the cosine\(^2\) functions of eqn. [7.19]. A comparison with eqn. [7.23] shows that only a single harmonic term is present, that of \( m = 2 \).

Most real periodic perturbations of a medium can be described as even \([F(z) = F(-z)]\) or odd \([F(z) = -F(-z)]\) functions of \( z \), and one need only consider the corresponding Fourier cosine or sine series of the modulations, respectively. For example, the cosine series for even periodic functions is simply:

\[
F(z) = a_0 + \sum_{m=1}^{\infty} a_m \cos \frac{m\pi}{\Lambda} z
\]  

[7.24]

In general, the effective modulation amplitude for the \( m^{th} \) order diffraction terms are reduced by a factor of approximately \( a_m/a_1 \). The coupling constant, \( \kappa \), is therefore modified by the same factor, assuming that the index and gain modulations are described by the same function.

The modulation period, \( \Lambda \), can be expressed in terms of the Bragg condition, the lasing wavelength, \( \lambda_L \), and the diffraction order, \( m \), as:

\[
\Lambda = \frac{m\lambda_L}{2n} = \frac{m\pi}{\beta} = \frac{\lambda_p}{2\sin \theta}
\]  

[7.24]

and therefore:

\[
\lambda_L = \frac{n\lambda_p}{m\sin \theta}
\]  

[7.25]

\( \lambda_p \) is the wavelength of the pump beams producing the grating, \( \theta \) is the angle of incidence of the pump beams (cf. fig. 7.2), and \( n \) is the refractive index of the material. Note that in some cases the grating period required for first order diffraction is not achievable at some pump wavelength where eqn. [7.25] would require \( \sin \theta > 1 \). In addition, even if \( \lambda_p \) was such that a grating for first order
diffraction could be optically induced, first order diffraction is not possible from a cosine$^2$ modulation profile as there is no corresponding (m = 1) Fourier component.

7.2.3 Application to Planar Waveguides

It is clear from the above arguments that the Bragg condition is related to the propagation constant. However, when waveguide modes (chapter 2) are introduced into the medium, propagation at frequency \( \omega \) is only allowed at discrete values of the propagation constant. Quite clearly then, only one waveguide mode can satisfy the Bragg condition at frequency \( \omega \).

As discussed in chapter 2, light propagating in the waveguide is due to the fluorescence of the material. There are in principle an infinite number of frequencies for which propagation is allowed, limited only by the range of transparency of the material, and the emission bandwidth. The situation now exists that any number of waveguide modes can satisfy the Bragg condition provided the oscillations occur at different wavelengths. The number of waveguide modes for which lasing can occur is thus limited only by the spectral width of the gain region and the number of guided modes supported by the film.

As described in chapter 2, the effective mode index \( N_{\text{eff}} \) of the waveguide modes is related to the propagation constant by the relation:

\[
\beta_j = kN_{\text{eff},j} = \frac{2\pi N_{\text{eff},j}}{\lambda} \quad [7.26]
\]

where \( j = 0, 1, 2, 3 \ldots \) are the guided mode orders (using \( j \) to avoid confusion with the diffraction order, \( m \)). With the period of the modulation \( \Lambda = m\pi/\beta \) at the Bragg condition, with \( m \) the diffraction order, the lasing wavelength for the \( j^{th} \) order guided mode is given by:
Chapter 7: Distributed Feedback Lasing

\[ \lambda_{L,j} = \frac{N_{\text{eff},j} \lambda_p}{m \sin \theta} \]  

[7.27]

7.3 Experiment

Fig. 7.3 shows the experimental set-up. The pump source is a frequency tripled Nd\textsuperscript{3}:YAG laser delivering 33 picoseconds pulses at \( \lambda_p = 355 \) nm, at 5 Hz repetition rate. A cylindrical lens is used before the beam splitter in order to enable efficient pumping over a narrow stripe on the sample. The spot size of the beam on the film is \( 2 \times 10^{-5} \) cm\(^2\) resulting in a maximum pump intensity of \( 4 \times 10^8 \) W cm\(^2\).

The filters, F, remove residual 1064 nm and 532 nm beams. The polarisation is selected vertical by the polariser P. The pump beam is split by two edge-to-edge prisms, P\(_{1,2}\). The two resulting beams are directed to the film by co-rotating mirrors M\(_1\) and M\(_2\).

The beam intensity is adjusted by a combination of calibrated neutral density filters, ND, after the prisms P\(_{1,2}\), and by adjusting the 1064 nm beam power. The 355 nm pulse energies are measured before the polariser P, using a calibrated fibre-bundle coupled bolometric detector. In making threshold measurements, often the 355 nm
pulse energy is too low to be detected with the bolometric detector. With neutral density filters placed after the prisms, the beam intensity can be increased before the prisms, to a level that can be measured, while keeping the energy at the sample approximately constant. Placing the ND filters after the prisms, where the beam is divided reduces nonlinear transmission effects in the filters.

Fig. 7.4: Schematic diagram of the co-rotating mirror assembly, allowing control of the angle of incidence, $\theta$, of the pump beams at the sample.

Fig. 7.4 shows the sample pumping geometry in more detail. By adjusting the position of the prisms and the mirrors, the two beams can be combined on the sample for a large range of angles, $\theta$. As stated above, for second order diffraction, $m = 2$, corresponding to angles near $\theta = 35^\circ$ for emission at $\lambda_L = 500 \text{ nm}$, with $n = 1.6$. The light emitted from the sample is collected by a $f = 50 \text{ mm}$ lens and focused onto an optical fiber bundle (core diameter = 0.6 mm) coupled to a CCD spectrometer with 0.15 nm resolution. Once laser action is obtained, the emission spectra are monitored as $\theta$ is changed.
7.3.1 Sample Preparation

The samples are produced by spin coating from ortho-xylene solutions onto silicon wafers as described in earlier chapters, producing poly(styrene) optical waveguides doped with 1.3 wt. % of the model compounds. Waveguide characterisation was determined using prism coupling experiments detailed in chapter 5. Waveguide propagation losses for the samples are less than 2.5 dB cm$^{-1}$ at $\lambda = 632.8$ nm and less than 3.5 dB cm$^{-1}$ at $\lambda = 514.5$ nm. A range of film thicknesses were prepared to allow comparison of films with different numbers of guided modes.

7.4 Results and Discussion

7.4.1 DFB Laser Tuning Range

Figs. 7.5 a,b show the tuning curves obtained for SP35 and G33 doped poly(styrene) as the angle of incidence, $\theta$, of the pump beams on the sample is changed. Clearly evident are strong laser emission peaks, typically of FWHM = 0.6 nm for all samples. A prominent broad spectral background, FWHM $\approx$ 10 nm, is also present, due to amplified spontaneous emission. Figs. 7.6 a-c contour plots showing the laser emission spectra as a function of angle of incidence for multi mode waveguides. Table 7.1 includes the characteristics obtained from these measurements. For comparison solution lasing results (chapter 5) and optical gain results (chapter 6) are also included in this table 7.1. As the molecular reorientation time is much longer than the timescale for stimulated emission only TE polarised emission can occur for transversely pumped films. TM mode emission was observed.

The samples exhibit a laser emission maximum, at $\lambda_{\text{max}} = 483$ nm for SP48/PS films, $\lambda_{\text{max}} = 483$ nm for SP35/PS, and $\lambda_{\text{max}} = 523$ nm for G33/PS, in excellent agreement with solution lasing $\lambda_{\text{max}}$. (G33 was not available for the solution lasing
SP48/PS films, 472 - 505 nm for SP35/PS films, and 510 - 535 nm for G33/PS films. The SP35/PS and SP48/PS waveguide tuning ranges are in excellent agreement with the toluene solution tuning ranges. The positive limits of the optical gain spectra also show excellent agreement for SP35 doped samples.

![Graph](image)

**Figs. 7.5:** Tuning curves for SP35/PS (a) and G33/PS (b) waveguides demonstrating tuning of the laser emission as the angle of incidence, $\theta$, of the pump beams on the samples is changed.

The DFB lasing maximum of the G33/PS samples displays a redshift of $\sim 13$ nm relative to the optical gain maximum of chapter 6, as indicated in table 7.1. This is accompanied by a similar redshift of the DFB tuning range (and ASE background) relative to the positive limits of the optical gain spectrum. While there is some
relative to the positive limits of the optical gain spectrum. While there is some evidence for a weak shoulder in the optical gain spectrum, at approximately 520 - 525 nm, there is no obvious reason why the DFB devices should exhibit such a redshift. At time of writing, a reasonable explanation for this is unknown, though chemical impurity is suspected.

### Table 7.1: Optical properties and lasing characteristics of the model compounds under study in solid poly(styrene) films. Solution lasing measurements from chapter 5. Optical gain measurements from chapter 6.

<table>
<thead>
<tr>
<th></th>
<th>SP48/3</th>
<th>SP35</th>
<th>G33</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption $\lambda_{\text{max}}$ (nm)</td>
<td>386</td>
<td>390</td>
<td>410</td>
</tr>
<tr>
<td>Fluorescence $\lambda_{\text{max}}$ (nm)</td>
<td>430, 455</td>
<td>460, 485</td>
<td>505</td>
</tr>
<tr>
<td>Fluorescence Yield, $\phi_f$</td>
<td>0.90</td>
<td>0.85</td>
<td>0.65</td>
</tr>
<tr>
<td>DFB Lasing $\lambda_{\text{max}}$ (nm)</td>
<td>452</td>
<td>483</td>
<td>523</td>
</tr>
<tr>
<td>Mean threshold, $TE_0$ (J)</td>
<td>$3 \times 10^{-6}$</td>
<td>$2 \times 10^{-6}$</td>
<td>$3 \times 10^{-5}$</td>
</tr>
<tr>
<td>DFB Tuning Range (nm)</td>
<td>440 - 462</td>
<td>472 - 505</td>
<td>510 - 540</td>
</tr>
<tr>
<td>Solution Lasing $\lambda_{\text{max}}$ (nm)</td>
<td>451</td>
<td>483</td>
<td>-</td>
</tr>
<tr>
<td>Solution Tuning Range (nm)</td>
<td>442 - 459</td>
<td>473 - 492</td>
<td>-</td>
</tr>
<tr>
<td>Optical Gain $\lambda_{\text{max}}$ (nm)</td>
<td>-</td>
<td>487</td>
<td>510</td>
</tr>
<tr>
<td>Gain Spectral Range (nm)</td>
<td>-</td>
<td>477 - 501</td>
<td>503 - 530</td>
</tr>
</tbody>
</table>

### 7.4.2 Simultaneous Multi-wavelength Lasing

Figs. 7.6 a-c demonstrate the ability of multi-mode waveguides to exhibit laser action at several wavelengths simultaneously. The diagonal lines indicate the progression of the individual waveguide modes across the gain region as the angle of incidence, $\theta$, is changed. However, the angle of incidence is not known directly, only the relative mirror positions. But, there are two methods available to determine $\theta$. 
Chapter 7: Distributed Feedback Lasing

Fig. 7.6 a: Contour plot of DFB laser emission spectra for SP48/PS waveguide.  
Film thickness is 1.16 μm

Fig. 7.6 b: Contour plot of DFB laser emission spectra for G33/PS waveguide.  
Film thickness is 1.15 μm
The first method simply assigns the bulk refractive index of the film, $n_b$, to the TE$_0$ mode \textit{in lieu} of an effective mode index. For thick films, the effective mode index, $N_{\text{eff}}$, for the TE$_0$ mode approaches the film index, as described in chapter 2. The angle of incidence can then be calculated from eqn [7.27] for each of the lasing wavelengths of TE$_0$ using the material dispersion parameters determined by prism coupling with eqn. [5.6]. The angle of incidence can then be extrapolated to mirror positions where TE$_0$ is not lasing. This method was used to calculate the angles of incidence in figs. 7.6.

The second method the material dispersion parameters to calculate the effective mode indices through the transcendental mode equation, eqn. [2.19], for the lasing wavelengths of all of the guided modes. The effective indices can now be used directly in conjunction with eqn [7.27] to calculate $\theta$. Both methods were applied to the SP35 tuning curves of fig. 7.6c. The angles of incidence determined using the bulk index approximation vs. the values determined from calculation of the
effective mode indices are plotted in fig. 7.7. There is an excellent agreement between the two sets of values, with the slope of the graph very close to one.

![Graph showing the angle of incidence of pump beams, \( \theta \), determined from bulk index approximation vs. \( \theta \) determined from effective mode indices.](image)

**Fig 7.7:** Angle of incidence of pump beams, \( \theta \), determined from bulk index approximation vs. \( \theta \) determined from effective mode indices.

Of note in figs. 7.6 are the relative strengths of the lasing modes compared to the stimulated emission background. In fig. 7.6a, SP48/PS device, intensity contours of the stimulated emission background are very prominent, 'surrounding' the lasing peaks. G33/PS devices show very strong lasing peaks with little stimulated emission background evident, and SP35/PS films midway between the extreme two cases. It is likely that this is due to differences in the extent of homogeneous broadening for the three active materials. As discussed in chapter 3, in systems which are homogeneously broadened the excited states are equally likely to emit at any given frequency. This allows frequency selective laser action with little loss in output power compared to a non-frequency selective laser device.

The apparent range of homogeneous broadening exhibited by these compounds suggest that differences in this regard are due to properties of the emitting species themselves, rather than local effects in the poly(styrene) matrix. Indeed, the strong homogeneous broadening of G33 may provide a useful tool for comparison of host materials, allowing a study of the effect of host molecules on broadening processes.
7.4.2 Lasing Thresholds of Waveguide Modes

To measure the mode thresholds, angle of incidence of the pump beams was adjusted so that the required guided mode lases at the maximum of the (background) stimulated emission peak. The pulse energies are then reduced to the point where the lasing peak is equal in intensity to the stimulated emission peak. The evolution of the lasing peak as the pulse energy is increased, is illustrated in fig. 7.8. Efficiencies of the DFB devices could not be measured as the output pulse energies are below the detection limit of the detectors.

Mean lasing thresholds for the \( \text{TE}_0 \) guided mode are included in table 5.1. Pump pulse energies at threshold for \( \text{TE}_0 \) were below \( 10^{-5} \) J for all samples, corresponding to pulse energy densities of \( < 5 \times 10^{-3} \) J cm\(^{-2} \). However, the average pulse energy densities for the \( \text{TE}_0 \) mode thresholds are two orders of magnitude higher than the maximum pulse energies used in the optical gain experiments (0.9 \( \mu \)J). It is unfortunate that pulse energy dependence of the optical gains measured in chapter 6 could not be examined, but it would appear that there is a significant loss mechanism present.

![Fig. 7.8: Evolution of laser emission peak as pulse energy is increased from threshold. Pulse energies above are 2 \( \mu \)J (threshold), 5 \( \mu \)J, 11 \( \mu \)J, and 13 \( \mu \)J.]

As discussed in chapter 4, guided modes may be expected to compete for excited states. As DFB structures restrict laser action to single modes at discrete wavelengths, other guided modes will rapidly deplete available excited states.
through amplified spontaneous emission, and the lasing threshold will increase as a result. In order to investigate the effects of mode competition, lasing thresholds were measured as a function of film thickness for SP35 doped poly(styrene) waveguides. Fig. 7.9 displays the results of this study.

At the maximum film thickness of 1.41 µm, thresholds for all guided modes are high. In this case the effective mode indices of TE$_0$ and TE$_1$ are close enough in value that TE$_1$ still lases at the edge of the stimulated emission band when TE$_0$ is at the stimulated emission maximum, and the two modes are thus competing for laser action. This mode competition is of course due to the width of the stimulated emission band, while all guided modes at all other wavelengths are involved in amplified spontaneous emission.

![Mode Cutoff Condition](image)

**Fig. 7.8:** Lasing thresholds for TE guided modes as a function of film thickness.
- • - TE$_0$, △ - TE$_1$, ■ - TE$_2$, ⟨ - TE$_3$. Dotted lines - Cut-off thickness for modes indicated on top axis.
Chapter 7: Distributed Feedback Lasing

At 1.28 μm film thickness the TE₃ guided mode is no longer lasing. Waveguide modelling using a commercial software package¹ indicates that TE₃ has not yet reached cut-off condition (indicated on fig. 7.9 by vertical dotted lines) but is evanescent through the 1.5 μm dioxide overlayer on the silicon substrate.

The absorption by the silicon wafer results in a large propagation loss for TE₃. TE₀ is not expected to compete with TE₃ for excited states as the TE₀ modal field is at a maximum close to the centre of the waveguide, while TE₃ is at a minimum. The maxima of the TE₁ field are also coincident with field minima of TE₃ for this film thickness. Indeed both TE₀ and TE₁ display reduced thresholds here. TE₂ does have a strong overlap of a field maximum with TE₃ close to the polymer/air interface. So, the increased threshold for TE₂ may be interpreted due to competition with the leaky TE₃ mode.

As the film thickness decreases and the number of supported modes also decreases, the situation becomes less complicated and the TE₀ mode threshold is approximately constant. As the film thickness decreases TE₂ approaches cut-off and it's modal field strength is diminishing more rapidly than that of TE₀, so competition between these symmetric mode becomes small.

At 0.84 μm film thickness, TE₁ is just past cut-off condition and may exist as a (very) leaky mode. This may be responsible for the increased thresholds of both TE₀ and TE₁, as energy coupling between modes is now a high loss process. Below this thickness, field symmetry reduces competition between TE₁ and TE₀ modes. TE₀ is no longer in significant competition for excited states with any other guided mode. However, rather than the lasing threshold for TE₀ decreasing further, it appears to remain approximately constant, at least to the cut-off condition for TE₁. This is to be expected as the stimulate emission cross-sections of all modes are decreasing as the film thickness decreases, in accordance with the quantum electrodynamic discussion of chapter 4. Below 0.5 μm thickness, the lasing threshold for TE₀ are therefore expected to increase, if this increase has not already begun.
7.5 Conclusions

Distributed feedback lasing has been demonstrated in poly(styrene) waveguides doped with phenylene vinylene model compounds. Tuning ranges and laser emission maxima are in excellent agreement with the solution lasing measurements (chapter 5), and in the case of SP35 doped films, good agreement is also found with the positive limits of the optical gain spectrum (chapter 6).

Simultaneous lasing at multiple wavelengths was observed, due to guided modes with different wavelengths to satisfy the Bragg condition at fixed propagation constant. Lasing thresholds of the guided modes were examined and can be explained in terms of competition of guided modes for excited states. For these devices, quantum electrodynamic effects on spontaneous emission rates are expected to be of significance for thinner films.
References:

10. BPM_CAD, Waveguide Optics Modelling Software, Optiwave Corporation.
Chapter 8  
General Conclusions

The work presented studied the optical properties of a variety of fluorescent polymers and model compounds, with a number of aims:

1) To identify promising candidates for organic solid state lasers,
2) To identify general problems associated with the materials that may inhibit laser action in the solid state,
3) To develop a further understanding of the processes important to laser action in solid organic materials,
4) To gain an insight into the connection between these fundamental physical processes and device geometries and performance.

In chapter 4 it was shown that both the fluorescence quantum yield and the stimulated emission cross-section are dependent on the non-radiative decay rate. The use of Raman spectroscopy may allow selection of solvents or host materials, or provide an aid to molecular engineering, so as to minimise the non-radiative decay and hence maximise the spontaneous emission rate, and fluorescence quantum yield. In addition, the spontaneous emission rate and stimulated emission cross-section are dependent on the properties of a waveguide structure through changes in the zero-point field fluctuations.

In chapter 5 solution lasing measurements were presented, indicating that fluorescent polymeric molecules exhibit higher lasing thresholds and reduced efficiencies compared to standard laser dyes. Planar waveguides fabricated from the fluorescent polymers generally exhibit high propagation losses, in excess of 6 dB cm⁻¹, even when used as dopants in poly(styrene) films. This is believed to be due to scattering centres in the film, presumably a result of polymer chain...
aggregation. Low molecular weight model compounds used as dopants in poly(styrene) had no adverse affect on waveguide propagation losses.

In chapter 6 an explicitly wavelength dependent model of amplified spontaneous emission in planar waveguides was presented. Optical gain spectra were measured for SP35 and G33 doped poly(styrene) waveguides, displaying peak optical gains of $g = 19.8 \text{ cm}^{-1}$ and $g = 15.5 \text{ cm}^{-1}$ respectively. It was shown how a semi-quantitative comparison of materials for use in solid state lasers was possible using this experiment and a figure of merit based on the optical gain experiment was presented. The results suggest that organic materials can exceed traditional semiconductor materials under optically pumped conditions.

In chapter 7 distributed feedback laser action was demonstrated in poly(styrene) films doped with model compounds SP35, SP48, and G33, using an optically induced grating. Lasing thresholds are low, typically of the order 1 $\mu$J. Lasing tuning ranges are in excellent agreement with the tuning ranges determined with the solution lasing measurements of chapter 5, and with the positive limits of the optical gain spectra from chapter 6. Lasing was demonstrated simultaneously at multiple wavelengths attributed to the waveguide modes supported by the films. Thresholds for lasing were found to be dependent on the film thickness, showing evidence for mode competition for excited states, in a manner consistent with the discussion of chapter 4.

Optical waveguides have some fundamental advantages for use as laser materials, notably the increased emission rates in the plane of the film coupling to waveguide modes, and a suppression of emission into radiation modes. However, it is found that guided mode competition for excited states is the principle cause of high thresholds in distributed feedback lasers. The implication is that if DFB devices are to prove useful, single mode waveguides may be the preferable option, despite the inherent loss in stimulated emission cross-section at lower film thicknesses.

For fabrication of polymeric waveguides for use as nonlinear optical devices, the importance of low waveguide losses on device performance is accepted as a
primary consideration. If organic light emitting devices utilising a waveguide geometry are to find any commercial use, the same strict standards on optical quality must also apply. If the materials discussed above were of higher optical quality, the figures of merit may be improved by at least a factor of two or more. For electrically driven devices, this would result in a decrease in the turn on voltage by a similar factor.