PHOTONIC CRYSTALS WITH ACTIVE ORGANIC MATERIALS

by

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*We also certify that written approval has been obtained for any proprietary material contained therein.
Dedicated to my wife, Fang(Dawn), my parents, and my daughter, Iris, who was born in the same day of my defense.
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The concept of photonic crystals, which involves periodically arranged dielectrics that form a new type of material having novel photonic properties, was first proposed about two decades ago. Since then, a number of applications in photonic technology have been explored. Specifically, organic and hybrid photonic crystals are promising because of the unique advantages of the organic materials.

A one-dimensional (1D) photonic crystal (multilayer) has high reflectance across a certain wavelength range. We report on studies of 1D multilayer polymer films that were fabricated using spin-coating, free film stacking, and co-extrusion techniques. For example, a stack fabricated by placing a laser dye-doped gain medium between two multilayer reflecting polymer films forms a micro-resonator laser or distributed Bragg laser. The resulting laser system is made entirely of plastic and is only several tens of micrometers in thickness.

When the gain, a dye-doped medium, comprises one type of a two-type multilayer film, it results a laser exhibiting distributed feedback. At the edge of the photonic band, the group
velocity becomes small and the density of photon states becomes high, which leads to laser emission. Such distributed feedback lasers were fabricated using the co-extrusion technique.

The refractive indices and the photonic lattice determine the photonic band gap, which can be tuned by changing these parameters. Materials with Kerr nonlinearity exhibit a change in refractive index depending on the incident intensity of the light. To demonstrate such switching, electrochemical etching techniques on silicon wafers were used to form two-dimensional (2D) photonic crystals. By incorporating the nonlinear organic material into the 2D structure, we have made all-optical switches. The reflection of a beam from the 2D photonic crystal can be controlled by another beam because it induces a refractive index change in the active material by altering the reflection band. A mid-IR pump-probe experiment was used to observe the Kerr switching effect.

In addition to these photonic crystal topics, nonlinear optical measurements for determining the nonlinear optical response (hyper-Rayleigh scattering and Z-scan) in organic materials are also discussed.
CHAPTER 1

INTRODUCTION TO NONLINEAR OPTICS AND PHOTONIC CRYSTALS

1.1 BRIEF INTRODUCTION TO NONLINEAR OPTICS

Optical phenomena are common in our daily life; most of them are related to linear optics (e.g. such as refraction, reflection, imaging, scattering, fluorescence, etc.). In the linear regime, the optical properties (dielectric constant, magnetic susceptibility, refractive index, etc.) of the media are independent on the external field. In the classical picture, the optical properties of the media are able to be explained by the motion or vibration of the electrons [1]. The external field is very small compared to the internal field (atomic) of the material (Table 1-1), which is on the order of $10^{11}$ V/m. However, the weak external field can still
affect the motion of the electrons, which are bound by Coulomb potential. Figure 1-1 (a) shows that the dipole moments of individual molecules are randomly oriented. In an exaggerated schematic, Figure 1-1(b), shows how the projection of the molecular dipole moment reorients when an electric field is applied. This effect can be generalized to an induced dipole moment as well. The induced dipole moment, which arises from the displacement of electrons, contributes to the propagating electromagnetic field as described by Maxwell’s equations. The reaction of the electrons (or the medium) is described as the optical response.

The atomic potential has a complex form (Figure 1-1(c)). The motion of the electron can be modeled as a harmonic oscillator if the amplitude of the displacement is small. The driving force on the electrons due to the external field is treated as a perturbation. In this case, the electron’s response to the external field is linear. The optical response of materials only depends on the electronic structure of the material.

Nonlinear optical phenomena refer to consequences of the changes of the optical properties of the media by an external field, which is usually the result of an intense optical illumination (or electromagnetic wave). Classically, this means that the induced motion of the electrons is not linearly proportional to the external driving field. As shown in Figure 1-1 (c), the electrons will enter into the nonlinear region if the driving force is large. In this case, higher-order perturbations should be considered. The size of the linear region varies by material. The material response that is attributed to the nonlinear motion is called the nonlinear optical response, which depends largely on the strength of the external field. For example, the second order nonlinear response, which is related to the second harmonic generation, is quadratically proportional to the applied field.
To be able to observe the nonlinear optical effects, one needs an intense light source that can generate a strong electrical field that is close in magnitude to the atomic field. Usually, a pulsed laser is able to produce such a strong electrical field during a short time interval. The first nonlinear optical phenomenon to be discovered - second harmonic generation (SHG) in a quartz crystal – was observed by Franken et al. in 1961 [2]. The discovery occurred shortly after the first ruby laser was made in 1960 by Maiman [3].

<table>
<thead>
<tr>
<th>Light source</th>
<th>Intensity (W/cm²)</th>
<th>Electric field strength (V/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Unfocused</td>
</tr>
<tr>
<td>Full moon</td>
<td>$10^{-7}$</td>
<td>$10^{-1}$</td>
</tr>
<tr>
<td>Candle</td>
<td>$10^{-7}$</td>
<td>$10^{-1}$</td>
</tr>
<tr>
<td>Sunlight</td>
<td>0.1</td>
<td>$10^{4}$</td>
</tr>
<tr>
<td>Hg-lamp</td>
<td>0.01</td>
<td>$10^{4}$</td>
</tr>
<tr>
<td>Pulsed Nd: YAG</td>
<td>$10^{8}$</td>
<td>$10^{7}$</td>
</tr>
<tr>
<td>Femtosecond laser pulsed, CPA</td>
<td>$10^{10}$</td>
<td>$10^{8}$</td>
</tr>
<tr>
<td>Atom</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

### 1.1.1 NONLINEAR SUSCEPTIBILITY

#### 1.1.1.1 BULK MATERIAL

The nonlinear response of the bulk material is described by the nonlinear electric susceptibility. The interaction between electromagnetic waves and media can be considered as the polarization density and relaxation of the permanent or induced dipole moment $\mathbf{p}$ in
the media. Assume that the external field inside the media is \( E \). The polarization density \( P \) inside the media is usually written as the sum of a power series:

\[
P_i = \chi_{ij} E_j + \chi_{ijk} E_j E_k + \chi_{ijkl} E_j E_k E_l + \ldots
\]  

(1.1)

where \( E_i (i = x, y, z) \) denote the Cartesian components of the electrical field. The first term \( \chi_{ij} \), known as the linear susceptibility, determines the linear optical properties of the medium. In an isotropic medium, the second order tensor, \( \chi_{ij} \), becomes a scalar \( \chi \) times the unit matrix. Then we have the expression for the dielectric constant:

\[
\varepsilon = n^2 = 1 + \chi
\]  

(1.2)

In a non-isotropic medium, the dielectric constant \( \varepsilon \) or refractive index \( n \) is a second order tensor. The birefringence arises from a non-isotropic dielectric constant.

![Figure 1-1](image)

Figure 1-1 Classical picture of the interaction between electrons and electromagnetic wave. (a) No external field. (b) External field polarizes the medium and creates an induced dipole moment. (c) Atomic potential plotted against the distance between electron and nuclei.
The high-order terms in Eq. (1.1) represent the nonlinear response of the medium. The third order tensor, $\chi_{ijk}$, is the second order nonlinearity, and the fourth order tensor, $\chi_{ijkl}$, represents the third order nonlinearity. It should be noted that all of these nonlinear coefficients are functions of frequencies of the external fields. For this reason, even the lowest order of nonlinear response yields a complicated mathematical expression. In some studies in this thesis, we were interested in the optical Kerr effect, which is described by the real part of the third-order nonlinearity depending only on a single frequency. This is related to the electric Kerr effect or DC Kerr effect. Both effects lead to a change in refractive index of the medium from an applied electric field. The two-photon absorption (TPA) arises from its imaginary part.

It is known that the second-order nonlinearity vanishes in centrosymmetric media [4] and the third-order nonlinearity usually does not. Generally, the third-order nonlinearity is much more complicated than the second-order nonlinearity because of additional frequency combinations. Here we are not interested in the frequency dependence (dispersion) of $\chi(3)$, but, rather, how it affects the linear susceptibility. The third-order nonlinear polarization can be written as:

$$P^{(3)} = \chi^{(3)}(-\omega_1, \omega_2, \omega_3, \omega_4)E_1E_2E_3E_4$$

(1.3)

Particularly, for the degenerate case, this becomes:

$$P^{(3)} = \chi^{(3)}(-\omega; \omega, \omega, -\omega)|E|^2 E$$

(1.4)

and for the pump-probe case, it becomes:

$$P^{(3)} = \chi^{(3)}(-\omega_{pr}; \omega_{pr}, \omega_{pu}, -\omega_{pu})|E_{pu}|^2 E_{pr}$$

(1.5)
Plugging this additional polarization in linear Eq. (1.1), ignoring the second order effect and considering only the real parts, we find:

\[ n(x, y, z) = n_0(x, y, z) + n_2(x, y, z)I(x, y, z) \]  

(1.6)
yielding an intensity-dependent refractive index.

**1.1.1.2 MOLECULAR NONLINEARITY**

The bulk material often refers to material in solid state, such as crystal, powder, or film. Its nonlinear susceptibility is the summation of the contribution from the nonlinearity of the molecular response of its component atoms or molecules. The nonlinearity of the molecules is usually called hyperpolarizability and is described in a similar manner as is the bulk material but with different notation. In general, we relate the bulk nonlinear coefficients to the molecular nonlinear coefficients \( \alpha \), \( \beta \), and \( \gamma \) as the following:

\[ \chi^{(3)} \leftrightarrow \alpha \]  

(1.7)
\[ \chi^{(2)} \leftrightarrow \beta \]  

(1.8)
\[ \chi^{(3)} \leftrightarrow \gamma \]  

(1.9)
respectively.

**1.1.2 SELF-PHASE AND CROSS-PHASE MODULATION**

As just described, third-order optical nonlinearity can produce an intensity-dependent change of the refractive index, which determines the phase of the beam as it propagates through the
material. Note that four frequencies (three incoming and one outgoing) are involved in Eq. (1.3). These frequencies can come from either the same beam or different beams. In fact, if two fields propagate in the same medium, they can affect each other’s phases; this is known as cross-phase modulation. If the two fields have the same frequency and propagation direction (i.e. from the same beam), similar effect happens and is called self-phase modulation. Both self-phase and cross-phase modulations are related to the optical Kerr nonlinearity of the medium. The optical properties of the medium can be controlled by changing the intensity of the beam, which offers the possibility of controlling one beam of light with another.

1.1.3 NONLINEAR ORGANIC MATERIAL

In organic materials, the optical Kerr effect is mainly determined by four mechanisms - electronic, orientation, electrostrictive, and thermal - each of which is characterized by different response times. The orientation contribution comes from the molecules’ rotation with a typical response time in the range of 1 ps ($10^{-12}$ second) depending on the size of the molecule and its permanent dipole moment. The electrostrictive response arises from the collective motion of the molecules or phonons with a response time around 10 ns. The thermal contribution is a heating effect and responds in a microsecond or longer. The electronic contribution originates from the distortion of the electron cloud with a characteristic time of about 1 fs ($10^{-15}$ second).

The ultrafast response of the electronic nonlinearity has attracted a great deal of attention. The nonlinear susceptibilities that relate to this are determined by the electronic structure of
the atom or molecule. The electrons and photons have a large interaction cross section near resonance that leads to a large nonlinear optical response. Organic dyes have a rich spectrum in the visible range, which makes it possible to obtain large nonlinear effects in these molecules near their resonance frequencies. In addition, organic materials often possess large quantum mechanical transition moments that lead to a large nonlinear optical response.

1.1.3 MEASUREMENT OF NONLINEARITY

Usually, nonlinear responses are very small compared to the linear response of the medium (refractive index and absorption). With the help of the laser, however, a number of methods have been developed to measure the nonlinearity of the organic molecules, such as electric-field-induced second harmonic (EFISH) [5-7], Maker fringes [8] in poled polymer film (doped with nonlinear molecules) [9], hyper-Rayleigh scattering (HRS) [10-12], Z-scan[13], etc.

1.1.3.1 HYPER RAYLEIGH SCATTERING

When light passes through the media (e.g., air or water), the interaction between the molecules and the photons causes the photons to scatter all the directions. The scattered photons have the same frequency/energy as do the incoming photons. This is known as the Rayleigh scattering. According to scattering theory, the intensity of the scattered light is inversely proportional to the fourth power of the wavelength.
As previously mentioned, the elements of the $\chi^{(2)}$ tensor vanish in media that has inversion symmetry. That is, in isotropic media, second-harmonic generation is not allowed. Dye solutions are made with chromophores and organic solvents, which usually have negligible nonlinear responses. In a completely dissolved solution, the solution is isotropic and should not exhibit any second-harmonic generation because of the symmetry. It is true that there is no coherent second-harmonic generation from the isotropic solution. However, correlated orientation fluctuations of non-centrosymmetric molecules can lead to small amounts of incoherent second harmonic generation [14]. This phenomenon is known as the hyper-Rayleigh scattering (HRS). The HRS signal can be seen emerging in any direction (Figure 1-2) with a complicated description of the angular distribution. The efficiency of generating harmonic waves in HRS is very low, which requires that one to focus a very intense beam in order to observe it.

![Figure 1-2](image)

**Figure 1-2** Hyper Rayleigh scattering. Second harmonic light is generated in an isotropic solution.

It is possible to determine the nonlinearity of the molecules by studying the HRS signal [15]. One should be aware that the HRS signal comes from the sum of the random fluctuation of the molecules. Thus, the detected signal is the average of the fluctuation. The first-order of
the sum of fluctuation is always zero as is required for maintaining the isotropic phase. Only the even orders of fluctuation exhibit non-zero contributions. Therefore, the HRS produces the components of $\beta^2$.

1.1.3.2 Z-SCAN

The simplest way to explore the power dependence of the refractive index change or absorption change due to the third-order optical Kerr effect is to change the intensity of the beam on the sample, which is usually a thin and transparent film, and measure the response. In a Z-scan (Figure 1-3) measurement, the laser beam with a Gaussian profile is focused by a lens. This creates intensity variation in the laser beam along the Z-direction, where the highest intensity occurs at the focal point. In the laser-illuminated film, the local refractive index is determined by the illumination level at that position. Because the intensity of laser beam has a Gaussian distribution at the XY-plane, the inhomogeneously illuminated thin film acts as a passive lens. The effective focal length of this lens depends on the intensity, which depends on the sample location on Z-axis. If the Kerr coefficient of the medium is positive, the passive lens is a positive lens and vice versa. The thin film lens will affect the propagation of the Gaussian beam depending on the position of the film. While the film is translated along the Z-axis, the beam size in the far field changes accordingly as a consequence of the induced lensing. By studying how the beam spot changes by measuring the amount of light that passes through a fixed aperture, one can extract the Kerr coefficient of the medium. This measurement is called closed aperture Z-scan. To measure the two-photon or multi-photon absorption, the aperture is removed, and the intensity is measured in
the far field while the sample is translated along Z-axis. In fact, the closed aperture Z-scan signal comprises both the contribution from the Kerr nonlinearity and multi-photon absorption. More details will follow in Chapter 8.

![Figure 1-3 Schematic of Z-scan measurement.](image)

1.2 INTRODUCTION TO PHOTONIC CRYSTALS

1.2.1 PHOTONIC CRYSTALS IN GENERAL

Before being proposed as photonic crystals, periodic dielectrics had already been used to make novel optical devices. For example, highly-reflective dielectric mirrors (Bragg reflectors) are made of multiple quarter-wave stacks. Rayleigh (1842-1919) first studied Bragg reflectors in the 19th century. However, the concept of photonic crystals was first proposed more than 100 years later by Eli Yablonovitch [16, 17] and Sajeev John [18] as a description of the optical interactions inside of a periodic medium as analogous to that observed due to periodicity in material crystals. In the late 1980s, they published their theoretical studies on periodic photonic structures independently. Since their pioneering work...
in this field, photonic crystals have been deeply and broadly studied, and many new phenomena have been discovered.

The photonic band gap in photonic crystals was derived from studies of electromagnetic waves in periodic media. The idea of band gap originates from solid-state physics. Scholars have devised a number of analogies for the difference between conventional crystals and photonic crystals, which has been helpful for understanding and applying photonic crystals. Normal crystals have a periodic structure at the atomic level, which creates periodic Coulomb potentials for electrons with the same modulation. In photonic crystals, the dielectrics are periodically arranged and the propagation of photons is largely affected by the structure. The periodicity in photonic crystals is on the order of the electromagnetic wavelength. Because of their similar structures, photonic crystals and conventional crystals share a number of similar features as a result of the wave nature of quantum mechanical electrons in relationship to light waves. For example, the photonic band gap and the electronic band gap in normal crystals can be connected. Photonic crystals can be either one, two or three dimensional (Figure 1-4).

In normal crystals, such as silicon, there are valence and conduction bands due to the Pauli exclusion principle for electrons as fermions. Electrons are bounded or localized if they are in a valence band. Electrons are free to move inside the crystal if they overcome the band gap and jump to the conduct band. Because the photons are bosons, all bands in the photonic crystals’ band structure are conduction bands. This means that the coupled photon modes can travel through the media as long as they fall on the dispersion lines. Between these conduction bands, there are stop bands at frequencies without dispersion lines, inside which photons cannot propagate.
Figure 1-4 Example of 1D, 2D and 3D photonic crystals. All of the photonic crystals shown above have two different dielectric media.

For the photonic crystals that have complete photonic band gaps, the intersection of the photonic band gaps at all directions and polarizations is not empty. A complete band gap yields an optical insulator, with which we are able to trap the photons. The face-centered cubic (FCC) lattice was the first photonic structure predicted to have a complete photonic band gap [17, 19].

At the band edge, some novel phenomena may arise because of the low group velocity of the light (photon localization) and anomalous dispersion behavior. This low group velocity can provide the necessary feedback to induce laser action if a gain medium is associated with a photonic crystal. A distributed feedback laser (DFB) has the gain medium distributed periodically to form an emissive photonic crystal [20, 21]. The photonic crystal acts as both the resonator and gain medium compared to the conventional laser, where the resonator and gain medium are two parts. The lasing in a perfect DFB laser will occur at the band edge. In
contrast, a distributed Bragg reflector (DBR) laser consists of a gain medium sandwiched between two distributed Bragg reflectors, which define the optical cavity. Microscopic multilayer semiconductor structures called VCSELs (vertical cavity surface emitted laser) are an example [22]. One of the advantages of photonic crystal lasers is that they are compact, efficient, and easy to align (almost no need to).

Unlike electrons, photons are massless. This intrinsic property makes Maxwell’s equations work for any length and energy scale. Theories and experiments related to the photonic crystals based upon Maxwell’s equations are similar for both at the radar scale (cm or meter) and at the optical scale (μm). In addition to those previously mentioned, there are some other important characteristics of photonic crystals that warrant discussion [23].

1. **Existence of photonic band gap (PBG).** In the common linear and uniform medium, the dispersion of the wave vector and frequency is a continuous curve which is actually a straight line in the perfect vacuum. In photonic crystals, the periodicity creates the so-called Brillouin zone in the k-space. Recall that, in solid state physics, the energy levels of electrons break at the boundary of the Brillouin zone; this also occurs in photonic crystals. The photonic band gap is created by discontinuities of the dispersion curve at the edge of the Brillouin zone: one band bends down and another bends up. Optical modes inside the photonic band gap are not allowed to exist/propagate inside the photonic crystal. If photons of this energy are incident on the photonic crystal, they are totally reflected. This has led to the concept of a photonic crystal an optical insulator. It should be noted that the band gap varies with direction of the propagation vector \( \mathbf{k} \). If the photonic crystal is an optical insulator in all directions and there is a frequency window where all the band gaps overlap, it is then called complete optical insulator. Obviously, this happens only in the 3D photonic crystals.
Yablonsvitch argued that there will be no spontaneous emission if this window covers the entire spontaneous emission spectrum [16].

2. **Existence of defect or local mode**  As previously described, photons inside the photonic band gap cannot propagate inside the photonic crystal. A perfectly periodic structure creates perfect band gaps. In some applications, allowing the existence of single or multi-modes inside the band gap is necessary. By introducing defects to the photonic crystal structure, the band structure can be changed. For example, inserting a thick layer into a multilayer system (1D photonic crystal) creates defect modes [24-26]. This is useful if the defect media have a certain optical gain because doing so enables lasing from the defect mode. In this manner, we have successfully demonstrated the first roll-to-roll polymer DBR laser [27]. Details are presented in Chapter 3 of this thesis.

3. **Group velocity and anomalous group velocity dispersion**. Near the band gap in the k-space, the dispersion curve bends toward the k axis (Figure 1-5, at M or K point). The group velocity is determined from the dispersion curve to be $v_g = \frac{\partial \omega}{\partial k}$. As the curve bends down more, the group velocity becomes smaller and smaller. The dispersion or band structure is determined by the photonic crystal structure and the dielectric constants. Therefore, it is possible to control the speed of the light by properly designing the photonic crystal structure [28]. Many interesting phenomena in photonic crystals are attributed to the slow light near or inside the gap. At the edge of the band gap, the group velocity may even become negative [29]. This creates a new type of material called negative refractive index material or left-handed material. In these materials, the energy flow direction (Poynting vector $\mathbf{S}$) is opposite to the $\mathbf{k}$ vector direction. In conventional electromagnetic waves, $\mathbf{S}$ and $\mathbf{k}$ vectors are usually in the same direction.
Figure 1-5 Typical band structure of a 2D photonic crystal. Dashed lines are “dispersion curves” in a medium that has the average dielectric constant of the periodic structure.

The zero group velocity at the band edges means that the electric field is very strong: the density of photon states is very high and the photons are localized. This enhances the nonlinear optical effect, which usually requires high-intensity light to create observable nonlinear effects. One example is that the strengthened electric field in photonic crystals can dramatically increase the efficiency of the second-harmonic generation and other nonlinear optical process [30-32]. The slow-light effect has also been shown to induce lasing in 2D photonic crystals [33].

4. **Remarkable polarization dependence.** Although we can make analogies between photons and electrons, their mathematical descriptions differ. The electromagnetic wave is a vector wave in contrast to the Schrödinger wave, which is a scalar wave. Unlike the probability wave, the electro-magnetic wave has polarizations (TE and TM) that describe the
direction of the electric field $E$. Thus, the propagation of light in a photonic crystal is polarization dependent; this results in differing band gaps for the TE and TM waves. This is the principle behind a photonic crystal polarizer [34].

5. **Existence of a singular point in the band structure.** In photonic bands, singular points exist; this leads to the concept of gap soliton or confinement [35]. Snell’s law of refraction does not generally apply when the incident light is at the band singularity.

Most of the photonic crystals are artificially made, although some exist in nature and give color to butterfly wings, for example. In the microwave range, researchers have built photonic crystals with various lattice structures. In the optical wavelength range, it is more difficult to directly manipulate the material due to the short length scale. Several approaches have been developed to make photonic crystals in this spectral region. In the 1960s, polystyrene particles (diameter $\approx 100$ nm) as colloids in water were used to produce colorful light. The resulting suspension was, in fact, a form of 3D photonic crystals with a close-packed structure.

Silicon, which has good optical properties in the near IR region as well as a number of micro-fabrication techniques for silicon chips, is a good material to use when constructing 2D photonic crystals in the near IR region. Etching long, straight, and uniform pores in a silicon substrate was first reported by Lehmann in the 1990s [36]. The macro-porous silicon technique is now a standard method used to fabricate 2D photonic crystals on a thin silicon wafer. Many photonic devices that have been built on such chips have been proposed for a range of applications in optical communication, switching, and computing [37-39].
1.2.2 NONLINEAR PHOTONIC CRYSTALS

Whereas the linear optical properties of the photonic crystals have received considerable attention, the more complicated nonlinear optical response in photonic crystals has not been thoroughly studied. Nonlinear photonic crystals are made from nonlinear optical materials. Prior to the discovery of the concept of photonic crystals in the 1980s, research had already been carried out on various kinds of periodic structures. Bloembergen studied the second-order nonlinearity in periodic structures in the early 1970s [40]. Following this, quasi-phase matching in various materials under periodic conditions was investigated [41-44]. In the late 1970s, Winful et al. discussed the possibility of producing bi-stable periodic nonlinear optical devices that could serve as the basis for optical memory [45, 46].

One of the key factors for generating efficient second-harmonic wave is the phase matching between the fundamental and harmonic waves. If the phases are not matched, the energy transfer between the waves would change sign after certain distance of propagation and the net energy transfer would be zero. The coherent length between the fundamental and harmonic waves plays an important role in determining the conversion efficiency. Normal crystals usually are birefringent, which means that the light travels inside the crystals at different speed depending on its polarization and direction. Usually, the refractive indices can be described by a refractive index ellipsoid [1]. The fundamental and harmonic waves are phase-matched by choosing an appropriate angle at which point the two waves are travelling at the same speed. Because of the dispersion inside the crystal, the coherent length limits the distance that the two waves can stay phase-matched. As a consequence of this, there is a fundamental limit on the conversion efficiency. As would be expected, the nonlinear response also depends on the nonlinear coefficients.
Another conventional way to generate efficient harmonic waves is quasi-phase matching. In quasi-phase matching, the sign of the nonlinear coefficient is changed periodically on the scale of the coherent length by properly arranging the nonlinear material. For example, alternating the orientation of organic molecules in layered material can create this kind of structure. The energy transfer from the fundamental wave to the harmonic wave will always be positive whenever these waves are in-phase or out-of-phase, which results in high nonlinear conversion efficiency.

A new way to phase-match the fundamental and harmonic waves is to change their speed without changing the angle. As mentioned above, a photonic crystal can exhibit anomalous dispersion behavior (negative group velocity) on either side of the photonic band gap, which gives a way to compensate for the dispersion inside the material as a result of phase matching. Both theoretical work [47, 48] and experimental work [49-51] have consistently supported this phenomenon. It should be pointed out that, although both quasi-phase matching and anomalous dispersion phase matching are realized in periodic structures, they arise from different mechanisms.

### 1.2.3 ONE-DIMENSIONAL NONLINEAR PHOTONIC CRYSTALS

A 1D photonic crystal is the simplest type and can be constructed, for example, from a multilayered film that alternates between two different materials for each layer. It is well known that 1D photonic crystals have high reflectance bands that corresponds to their photonic band gap. Including a nonlinear material into the 1D photonic crystal can produce an optical limiter [52] by having an intensity-dependent reflection band. This type of optical
protection gear works as a passive optical limiter, which differs from the conventional absorptive optical attenuator. The reflection band of the limiter is changed by the intensity of the incident light. It is possible to design a photonic crystal carefully such that the reflectance decreases if the intensity increases. The transmitted light could then be kept under a certain level. In this way, one would not lose the track of the intense laser beam by wearing the optical limiter. However, it is also known that the 1D photonic crystal band gap shifts when the incident light is off-axis. Thus, higher dimensional photonic crystals are more desireable for real-world applications.

### 1.2.4 DISORDERED ONE-DIMENSIONAL PHOTONIC CRYSTALS

Disorder in the crystal lattice changes the coherence conditions, which, in turn, increases the scattering rate of the waves. Anderson predicted that, in metals, electrons may be localized if the degree of disorder reaches a certain level [53]. Similarly, wave localization has also been observed in disordered photonic crystals. The photonic band gap prohibits the propagation of photons inside the photonic crystal. Thus, it is interesting to study the localization behavior near or inside the photonic band gap. The transmittance of the light wave inside the band gap decays exponentially so that photons become highly localized. Outside the band gap, photons can travel freely inside the crystal. According to localization theory, introducing disorder (e.g., dislocation of the lattice or variation in the dielectric constants) into the photonic crystal will localize photons outside the band gap. Inside the band gap, instead of enhancing the localization, the disorder actually delocalizes the photons.
1.2.5 FUNCTIONALIZED PHOTONIC CRYSTALS WITH ORGANIC MATERIAL

Photonic crystals are novel materials that have many interesting properties. However, the application of pure photonic crystals is still limited. We know that, by doping silicon crystals, function can be imparted to semiconductors as evinced in semiconductor technology. Using a similar idea, we can add functionalizing materials to photonic crystal structures to functionalize the crystals and thereby lead to the development of photonic crystal devices. For example, by adding Kerr materials to the photonic crystal, one can make the photonic bands shift as the intensity of the light changes. The corresponding transmission or reflection bands would have the same shifts. Thus, one beam of light can control another (transmitted or reflected), which can ultimately produce an all-optical switch. All-optical switches are the essential parts in optical communication or computing.

1.2.6 SIMULATION METHODS FOR PHOTONIC CRYSTALS

The essential equations for calculation of electromagnetic waves in a photonic crystal system are Maxwell’s equations (in SI units):

\[ \nabla \cdot D = \rho_f \]  \hspace{1cm} (1.10)

\[ \nabla \cdot B = 0 \]  \hspace{1cm} (1.11)

\[ \nabla \times E = -\frac{\partial B}{\partial t} \]  \hspace{1cm} (1.12)
\[ \nabla \times H = J_f + \frac{\partial D}{\partial t} \]  

(1.13)

where \( D \) is the electric displacement, \( B \) is the magnetic field, \( E \) is the electric field, \( H \) the magnetizing field, \( \rho_f \) is the free charge density, and \( J_f \) is the free current density. Applying the constitutive equations, \( D = \varepsilon_0 \varepsilon(r) E \) and \( B = \mu_0 \mu(r) H \), to Maxwell’s equations and assuming that there is no free charge and current, we have[54]

\[ \nabla \times \left( \frac{1}{\varepsilon(r)} \nabla \times H \right) + \frac{\mu(r)}{c^2} \frac{\partial^2 H}{\partial t^2} = 0 \]  

(1.14)

where \( c = 1/\sqrt{\varepsilon_0 \mu_0} \) is the speed of light in vacuum. Eq. (1.14) shows that the \( H \) field is a transverse wave. Similar equation exists for the electric field \( E \).

It is possible to solve these equations analytically for simple systems that depend on the boundary conditions. For more complicated systems, symmetries, approximations and numerical methods can be employed to solve for the electric and magnetic fields. Here, I will discuss three commonly used computation methods as well as the advantages and disadvantages of each.

### 1.2.6.1 FREQUENCY DOMAIN (PLANE WAVE EXPANSION)

Writing the left side of equation (1.14) as a sum of the Fourier series in time,

\[ \nabla \times \left( \frac{1}{\varepsilon(r)} \nabla \times \sum \omega H_\omega e^{-i\omega t} \right) + \frac{\mu(r)}{c^2} \frac{\partial^2}{\partial t^2} \sum \omega H_\omega e^{-i\omega t} = 0 \]  

(1.15)

we then have equations for each frequency component,
\[ \nabla \times \left( \frac{1}{\varepsilon(r)} \nabla \times H_\omega \right) - \frac{\omega^2 \mu(r)}{c^2} H_\omega = 0 \]  

(1.16)

If we assume that \( \varepsilon(r) \) and \( \mu(r) \) are uniform, a plane wave solution to Eq. (1.16) can be used, \( H_\omega = H_0 e^{ikr} \). In this case, a simple dispersion relation arises from the relationship between the wave vector \( k \) and \( \omega \), which can be written as

\[ k^2 = \frac{\omega^2 \varepsilon \mu}{c^2} \]  

(1.17)

An important conclusion to note from Eq. (1.16) is that the frequency components are independent. Thus, we can simulate individual behaviors for each frequency in order to obtain the full spectrum of the system by superposition.

According to Bloch’s theorem, we can write the \( H \) field as the following summation,

\[ H_\omega (r) = \sum_k u_k(r)e^{ikr} \]  

(1.18)

Plugging this into Eq. (1.16), we have

\[ \left[ (ik + \nabla) \times \left( \frac{1}{\varepsilon(r)} (ik + \nabla) \times u_k \right) \right] - \frac{\omega^2 \mu(r)}{c^2} u_k = 0 \]  

(1.19)

This is actually an eigen equation of \( u_k \). Thus, for any value of \( k \) that is of interest, by dividing the system into small grids, we can numerically solve the eigenfunction above to find the eigenvalue \( \frac{\omega^2 \mu(r)}{c^2} \) and eigenvector \( u_k \). The field can then be computed by using (1.18). This method is less useful in a medium of finite size or an imperfect periodic dielectric distribution.
1.2.6.2 TRANSFER MATRIX METHOD IN A 1D OPTICAL SYSTEM

Transfer matrix methods are useful when the system can be broken into a sequence of subsystems that interact only with its adjacent neighbor subsystems. Linear 1D photonic crystals can be described well using this method [55].

Consider a multilayered system that is divided into many subsystems like the one depicted in Figure 1-6 (a). Each of these subsystems contains only one type of material. Let \( t_m \) be the thickness of the \( m^{th} \) layer, and \( n_m \) be the refractive index of \( m^{th} \) layer, where \( m \) is an integer (Figure 1-6 (b)). As mentioned above, we can have a plane wave solution to the Maxwell equations in each subsystems regardless of the boundary conditions. Let \( E_F \) be the amplitude of the right-traveling electric wave, and \( E_B \) the amplitude of the left-traveling electric wave. We define the following:

![Diagram of a 1D multilayer system](image)

**Figure 1-6** (a) A 1D multilayer system divided into small sub-systems. (b) The electric field inside the layers and interfaces.
\( E_{F,m-1} \): right-traveling wave at the left side of the interface of \((m-1)\) and \(m\)th layer

\( E_{B,m-1} \): left-traveling wave at the left side of the interface of \((m-1)\) and \(m\)th layer

\( E'_{F,m} \): right-traveling wave at the right side of the interface of \((m-1)\) and \(m\)th layer

\( E'_{B,m} \): left-traveling wave at the right side of the interface of \((m-1)\) and \(m\)th layer

\( E_{F,m} \): right-traveling wave at the left side of the interface of \(m\) and \((m+1)\)th layer

\( E_{B,m} \): left-traveling wave at the left side of the interface of \(m\) and \((m+1)\)th layer

\( E'_{F,m+1} \): right-traveling wave at the right side of the interface of \(m\) and \((m+1)\) th layer

\( E'_{B,m-1} \): left-traveling wave at the right side of the interface of \(m\) and \((m+1)\) th layer

A column vector \((E_F, E_B)^T\) provides a complete description of the electric field inside the layers. Applying the boundary conditions at each interface and propagating throughout the medium, finding the relationships between the fields defined above using matrix arithmetic is relatively straightforward [55].

\[
\begin{pmatrix}
E_{F,m-1} \\
E_{B,m-1}
\end{pmatrix} =
\begin{pmatrix}
1 & 1 \\
n_{m-1} & -n_{m-1}
\end{pmatrix}^{-1}
\begin{pmatrix}
1 & 1 \\
n_m & -n_m
\end{pmatrix}
\begin{pmatrix}
E'_{F,m} \\
E'_{B,m}
\end{pmatrix}
\]

\( (1.20) \)

\[
\begin{pmatrix}
E'_{F,m} \\
E'_{B,m}
\end{pmatrix} =
\begin{pmatrix}
e^{i\kappa_x l_m} & 0 \\
0 & e^{-i\kappa_x l_m}
\end{pmatrix}
\begin{pmatrix}
E_{F,m} \\
E_{B,m}
\end{pmatrix}
\]

\( (1.21) \)
\[
\begin{pmatrix}
E_{F,m} \\
E_{B,m}
\end{pmatrix} = \begin{pmatrix}
n_m & -n_m \\
n_{m+1} & -n_{m+1}
\end{pmatrix}^{-1} \begin{pmatrix}
1 & 1 \\
n_{m+1} & -n_{m+1}
\end{pmatrix} \begin{pmatrix}
E'_{F,m+1} \\
E'_{B,m+1}
\end{pmatrix}
\] (1.22)

After performing the same analysis on all of the layers, we have

\[
\begin{pmatrix}
E_{F,0} \\
E_{B,0}
\end{pmatrix} = \begin{pmatrix}
n_0 & -n_0 \\
n_s & -n_s
\end{pmatrix}^{-1} M \begin{pmatrix}
1 & 1 \\
n_s & -n_s
\end{pmatrix} \begin{pmatrix}
E'_{F,s} \\
E'_{B,s}
\end{pmatrix}
\] (1.23)

where \( n_0 \) is the refractive index of the incident medium, \( n_s \) is the refractive index of the substrate, and

\[
M = \prod_{m} \begin{pmatrix}
n_m & -n_m \\
0 & e^{-ik_m v_m} \\
n_m & -n_m
\end{pmatrix}^{-1} \begin{pmatrix}
1 & 1 \\
0 & e^{-ik_m v_m}
\end{pmatrix} \begin{pmatrix}
1 & 1 \\
n_m & -n_m
\end{pmatrix}
\] (1.24)

Thus, the propagation of the wave through the multilayered dielectric system can be described as a 2×2 matrix \( M \). Using the matrix method, one can compute the transmittance and reflectance spectra of a 1D system as well as the intensity distribution in each layer [56].

The transfer matrix method is a powerful tool for a variety of periodic systems. For an arbitrary 1D system, Pendry has shown how to calculate the localization length related to the transmittance and reflectance of the system [57].

1.2.6.3 FINITE DIFFERENCE TIME DOMAIN (FDTD)

One of the constraints of the plane wave expansion method is that the material needs to be static. Some of the phenomena, especially in nonlinear optics, are, instead, dynamic. When the material has a nonlinear response, the dielectric constant of the material depends on the

42
strength of the local electric field. Therefore, the above methods for solving the steady eigen problems do not work in these situations.

![Example of FDTD calculation](image.png)

Figure 1-7 An example of FDTD calculation. (a), (b), and (c) shows the electric field at various time points.

As can be observed in Figure 1-7, the most straightforward way to solve for the field distribution using the Maxwell’s equations is to calculate temporal evolution of the electric and magnetic field by adding very small time increments, \( \Delta t \), in each step. By far, the most common technique for time-domain calculation is the finite difference time domain method (FDTD). Because the fields \( E \) and \( H \) are related through time derivatives (Eq. (1.12), (1.13)), the time grids for these two fields differ by \( \Delta t/2 \) in the calculation. In another words, \( E(t) \), \( E(t+\Delta t) \), \( H(t-\Delta t/2) \) and \( H(t+\Delta t/2) \) are calculated during the actual simulation. Figure 1-7 shows an example of the FDTD calculation.

The field employed in FDTD calculation can be any shape, although it is common to use a short pulse (Gaussian shape) to compute transmission and reflection spectra. It is known that the Fourier transform of a Gaussian function is also a Gaussian function.
\[ E(t) = e^{-t^2/\tau^2} E_0 e^{-i\omega t} = \frac{1}{\sqrt{2\pi}} \sum_{\omega} E_0 \tau^2 \exp \left( -\frac{(\omega - \omega_0)^2}{4/\tau^2} \right) e^{-i\omega t} \]  

(1.25)

Figure 1-8 Spectrum of a short pulse. (a) Electric field of a short pulse that has a Gaussian temporal profile. (b) Spectrum of the same pulse.

One advantage of using the FDTD method for spectral calculations is that it can compute the response of a linear system at many frequencies with a single computation. As shown in Figure 1-8, a short pulse contains a certain band width of frequency components. The calculation is done by sending a short pulse into the photonic structure and then placing a “detector” (plane or point) at points of interest for observing the resulting fields \( E(t) \) and \( H(t) \). By comparing the Fourier transforms of the resulting fields to those of the original fields, one can determine the flux spectrum of the system.

Using the same method, FDTD and other time-domain methods can be used to solve frequency eigenvalues. The eigen-frequencies are identified by considering the peaks in the spectral response. To obtain the desired precision, the calculation must be divided into a grid of discrete points, both spatially and temporally. The size of the calculation is determined by the size of system and the time duration of the simulation. Thus, this calculation requires a
large amount of floating computation and memory. However, with the powerful computers that are available today, this ab-initio calculation can be done for photonic systems of reasonably large sizes.

The disadvantages of FDTD calculation are: (1) it requires a long time to resolve a sharp peak in the spectrum because of the uncertainty associated with Fourier transformation; (2) it also requires a long time to build up the steady state if one is interested in the steady state behavior of the system; (3) to best describe a system that has arbitrarily shaped dielectrics, a high-precision calculation is required. In this case, all dimensions (space and time) need to be divided into a super-fine grid, which results in very large size of computation which increases by 4\textsuperscript{th} power of the system size.

1.3 SUMMARY AND THESIS OUTLINE

Nonlinear optics has become an important field of study as a consequence of the invention of the laser. In fact, a number of applications for nonlinear optics have been developed. Organic materials are especially promising because of the large nonlinear response due to their electronic structure and rich spectrum. In addition, organic materials have flexibility in both their structure and function, which increase their potential for use in a broad range of applications.

Photonic crystals are periodically arranged dielectrics; their periodicity is similar to the wavelength of light. Because there is no scaling factor in the Maxwell’s equations, a photonic crystal can be any size and composed of material so long as the periodicity is consistent with
the wavelength. Many novel optical phenomena have been found in such structures. One important feature is that the photons slow down near the edge of the bands; this produces a high density of states and strong fields, which enhance nonlinear optical phenomena.

Photonic crystals can be functionalized with active materials. For example, an all-optical switch can be realized by incorporating an optical Kerr medium into a photonic crystal. We have studied such devices made with 2D porous silicon and nonlinear organic molecules, and the results are reported herein. Photonic crystal can also be used in making linear devices. 1D photonic crystals exhibit very high reflectance in their band gap. One can make a high-Q cavity using such photonic crystals to enable compact laser systems (DFB and DBR laser).

In the following chapters, I will cover the topics listed below, both theoretically and experimentally:

Chapter 2 - Fabrication of 1D Organic Photonic Crystals

Chapter 3 - Enhanced Emission in 1D Organic Photonic Crystals

Chapter 4 - Mode Delocalization in 1D Photonic Crystals

Chapter 5 - 2D Photonic Crystals Made of Porous Silicon

Chapter 6 - Dynamic Photonic Band Gap Tuning

Chapter 7 - Improvement of Kleinman Disallowed Hyper-Rayleigh Scattering

Chapter 8 - Z-Scan Experiment for Measuring the Nonlinear Refractive Index
1.4 REFERENCES


CHAPTER 2

FABRICATION OF 1D ORGANIC PHOTONIC CRYSTALS

2.1 INTRODUCTION TO 1D PHOTONIC CRYSTALS

As the name indicates, one-dimensional photonic crystals exhibit periodicity in just one dimension, and are homogeneous in the other two dimensions. In the case herein considered, the 1D photonic crystal has a layered structure comprising a multilayer film. The most common application for multilayer films is highly reflective dielectric mirrors that are used in optics labs. Because of their high refractive indices and high optical-damage thresholds, inorganic materials are employed to make most of these mirrors via vacuum thin-film deposition methods.
An important property of 1D photonic crystals is their high reflectance in the photonic band gap. The high reflectance in the band gap is, in fact, the result of coherent reflections at each layer interface. The shape of the reflection band is determined by the difference of the refractive indices and optical thicknesses of the layers. For example, in quarter wave stacking, which is also called Bragg reflection, the peak reflectance $R$, resonance wavelength $\lambda_c$ and band width can be written analytically as [1]:

$$R = \left(\frac{1-(n_2/n_1)^N}{1+(n_2/n_1)^N}\right)^2$$  \hspace{1cm} (2.1)

$$\lambda_c / 4 = n_1 t_1 = n_2 t_2$$  \hspace{1cm} (2.2)

$$\Delta \lambda \approx \frac{2|n_2-n_1|}{n_2+n_1} \frac{2}{\pi} \lambda_c$$  \hspace{1cm} (2.3)

where $n_1, n_2, t_1$ and $t_2$ are the refractive indices and thicknesses of the two materials. The quantity $N$ is the total number of periods. For multilayer films of arbitrary thicknesses, Eq. (2.2) is no longer satisfied. Although it is almost impossible to write down the exact analytical expressions, the center of the reflection band can still be estimated as $2(n_1 t_1 + n_2 t_2)$. Eq. (2.1) and (2.3) can still be used to calculate the approximation of $R$ and $\Delta \lambda$. The whole spectrum can be calculated numerically using the transfer matrix method. The theory of light propagation in the arbitrary stacking periodic structure (arbitrary stacking) is discussed thoroughly in literature [1].

Generally speaking, the ratio $(n_1/n_2)$ of the two refractive indices determines the width of the band; the larger the ratio is, the higher the reflectance and the wider the stop band. The
optical thicknesses of the layers determine the location of the band. The peak reflectance is determined by both the ratio and the layer thickness.

The multilayer film can be functionalized by adding functional materials. For example, after adding third-order nonlinear materials, a 1D photonic crystal can be used as an optical limiter [2] and an all-optical gate [3, 4]. Some researchers have attempted to make compact, mirrorless organic lasers by doping a laser dye in polymers [5].

As we know, photonic crystals have a periodic structure at the same scale as the wavelength of light. For optical photonic crystals, this scale is sub-micron (i.e., between the atomic and macroscopic scales). Unlike the formation of normal crystals, the different materials in sub-micron length range do not spontaneously self-assemble to form bulk photonic structures because of the absence of natural forces in this range. For this reason, it is difficult to find photonic crystals in nature. However, because living cells in creatures are similar in size, many naturally made photonic crystal structures have developed, such as butterfly wings and peacock tails. However, most of the photonic crystals have been created artificially. In the last century, thin-film deposition techniques, such as physical vapor deposition (e-beam, ion-beam, sputter coating), chemical-vapor deposition and molecular beam epitaxy [6], were developed and adapted for making inorganic multilayered film.

Although it is difficult to manipulate organic materials at the sub-micron scale, there are various ways to make organic photonic crystals. Some researchers have used dielectric colloids or suspensions of spherical nanometer-scale particles [7-10], block polymer self-assembly [11, 12] and holographic lithography [13] to fabricate high-dimensional photonic crystals. Spin coating [14] is a common method for fabricating thin film of organic materials.
To make multilayer structures, multilayer spin coating [5, 15-17], co-extrusion [18, 19] and free-standing film stacking techniques have been successfully developed. In this chapter, I will mainly introduce these three techniques, which were used to make 1D polymeric photonic crystals for our projects.

2.2 FILM CHARACTERIZATION

2.2.1 FILM THICKNESS MEASUREMENTS

Two methods were used to directly measure the thickness of the polymer films. The first one used a surface profiler (Sloan Dektak II-D) to measure the step change from the film to substrate. As illustrated in Figure 2-1 (a), the stylus is sensitive to the force applied on the tip. The sample translated linearly during the measurement. The second method used an atomic force microscope (AFM) to measure the cross section of the film. A smooth cross section of the multilayered film is required to complete this measurement. Epoxy was cast on the film to hold the sample in which the multilayered film was embedded [20]. A sharp razor blade was then used to cut the epoxy and film. The non-contacting (tapping, AC) mode was used to measure the cross section (Figure 2-1 (b)). The phase shift of the cantilever’ oscillation of is correlated with specific material properties that affect the tip/sample interaction. Thus, we can differentiate different materials, such as PMMA and PS, by looking at the phase shifting signal.
2.2.2 OPTICAL MEASUREMENTS

To characterize the spectra behavior of the multilayered sample, optical methods such as transmission and reflection measurements at normal or oblique angles are used. A spectrophotometer (CARY 500 by Varian) was used to determine the optical properties. To avoid variations across the film, a small pin hole (1mm) was used as a mask to locate a specific position of interest. To reduce noise from the spectrophotometer light sources, two arms were used in data collection. One of the arms was used as a reference that monitored fluctuations in the light sources.
2.3 FABRICATION OF 1D PHOTONIC CRYSTAL

Due to their mechanical and physical properties, organic materials cannot be fabricated using the same techniques that are used for inorganic materials; other techniques are needed.

2.3.1 MULTILAYER SPIN COATING TECHNIQUE

2.3.1.1 INTRODUCTION TO SPIN COATING

As previously mentioned, spin coating [14] is a powerful method for creating thin and uniform films; it is routinely used in the electronics industry. The substrate is vacuum-mounted on a spinner. Before spinning, the solution is drop cast onto the substrate. Usually, the solution is spread all over most of the substrate in order to create uniform film. The spin speed is usually in the range of one thousand to several thousand rpm (round per minute); the duration of the rotation can be a few seconds to several minutes. The spinning process creates a uniform solution layer on top of the substrate. The thickness of the solution layer depends on the spinning speed, spinning time, and the viscosity and evaporation rate of the solution. With other conditions fixed, the thickness of the solution layer is usually inversely proportional to the spin speed [21]. The relationship between thickness and spinning time is more complicated. After a sufficient spinning time, the thickness becomes constant.

After the thin, uniform solution layer has been created on the substrate, the sample is put into an oven to evaporate the solvent. The baking temperature and duration depend on the solvent used. Usually, a period of 15 minutes or more is required for baking to ensure the
quality of the film. After the solvent is evaporated, the remaining material forms a solid and flat layer. The thickness of the solid film is determined by the thickness and concentration of the solution layer. Figure 2-2 shows a linear relationship between the PMMA film thickness and the concentration of the polymer solution.

![Figure 2-2 Typical trend of solid film thickness versus concentration in spin coating. The spin speed was 1500 rpm and duration was 40 seconds.](image)

### 2.3.1.2 MULTILAYER SPIN COATING

Given the geometry of the multi-layered film, one might consider sequential deposition to produce such a film. Using the spin coating technique, one can spin a new layer on top of an existing layer. So as not to damage the existing layers, the solvent that is chosen should not dissolve the existing layer, which is considered to be a solid substrate for the new layer. Therefore, to create an alternating structure of two different polymers, the two solvents used should only dissolve the two polymers in each respectively layer.
Kimura et al. first fabricated multilayered polymer films with polystyrene (PS) in Toluene and polyvinyl alcohol (PVA) in water [15]. Alvarez et al. successfully made a multilayered structure, which had 10 pairs of layers, with polyvinyl carbazole (PVK) in Toluene and PVA in water [17]. Because the polymer layer is porous, the solvents could theoretically penetrate the thin layer and dissolve the layer underneath it. Komikado et al. successfully minimized this effect by carefully choosing high molecular weight solvents for make these polymer solutions [16]. They used PVK in chlorobenzene and cellulose acetate (CA) in diacetone alcohol for the fabrication.

The fabrication process is straightforward and not time-consuming. However, the porous polymer film allows the solvent or solution to penetrate the ultra thin layers, which dissolves and eventually changes the thickness of the formed layer. Also, the film thicknesses from each spin coating process are close but not identical; this ultimately produces considerable variation in layer thickness. Because there are such strict requirements for the polymer and solvents, the multilayer spin coating technique has not been widely used for the creation of 1D polymeric photonic crystals.

### 2.3.2 FREE-STANDING FILM STACKING

As mentioned above, the multilayer spin coating technique was successfully developed for fabricating multilayer polymer film. To avoid its disadvantages, I have successfully developed the free standing film stacking technique.
The original polymer film stacking technique was used by G. Khanarian et al. to fabricate alternative structures of polymer films in the study of quasi-phase matching in poled polymers [22]. To make free-standing film, a sacrificial layer is first created on a substrate first. Depending on the material in the sacrificial layer, various methods can be used to create the films. After the sacrificial layer is created, the polymer layer is spin coated on top of it. Then the whole system is baked in an oven, and the whole thin film is cut into squares. The sample is then soaked in a solvent that dissolves only the sacrificial layer; the polymer squares will then float off the substrate and become free-standing films as shown in Figure 2-3.

As with the multilayer spin coating method, the potential incompatibility of the polymers and solvents in each of the respective layers must be taken into consideration. However,
because the sacrificial layer is not used to build up photonic crystals, there is no strict optical requirement on the material; even an inorganic material can be used as the sacrificial layer [22]. Another advantage of this stacking method is that, because each layer is cut from a single or small number of large uniform layers, the thicknesses of the polymer layers are always the same. Because no organic solvent is used during the stacking, the thickness of each individual layer remains unchanged.

The single film thickness reported by Khanarian was about 1.5 μm. For applications that require photonic crystals whose primary photonic band gap is in the visible range, much thinner films (100 nm) are needed, which makes this method somewhat limited. Furthermore, layering these ultra thin films by hand remains a challenge. Thus, the disadvantage of this method is that it requires substantial labor and patience to create a good stack.

2.3.2.1 MATERIAL AND PROCESS

In this experiment, PVK (n=1.683) was mixed with the plasticizer BBP (Butyl Benzyl Phthalate, n=1.535) to produce the high refractive index material. The polymer poly methyl methacrylate (PMMA, n=1.492) was chosen as the low refractive index material. All materials are transparent in the visible and near infrared regions. Although PVK is a photoconductive material that is used to make photorefractive materials [23], it has low optical loss in the visible range (12 dB/cm) [24]. PVK also has a high refractive index, which is desirable for making 1D photonic crystals. However, our work showed that it was difficult to manipulate pure PVK films because they are brittle reflecting its high glass transition temperature T_g, which is around 423 K [25]. To enhance the mechanical properties
by lowering $T_g$, we added a certain amount of plasticizer into the polymer film. PMMA has very good optical properties (optical loss 32 dB/m [26]) and is a promising candidate for making organic optical fiber [26, 27]. Moreover, it has very good mechanical properties, which increases the yield of the little squares in the free standing film floating process. This also makes it easier to manipulate the polymer film at the sub-micron level.

As mentioned in the previous section, PVA is a polymer that dissolves in water but does not dissolve in most organic solvents. PVA was chosen as the sacrificial layer.

Table 2-1 Physical properties of the solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Melting point (°C)</th>
<th>Boiling point (°C)</th>
<th>Vapor pressure at 20°C (mmHg/Torr)</th>
<th>Viscosity at 20°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>-95</td>
<td>110.6</td>
<td>23.2</td>
<td>0.59</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>-47</td>
<td>155</td>
<td>2</td>
<td>2.54</td>
</tr>
<tr>
<td>PGMEA</td>
<td>-87</td>
<td>146</td>
<td>3.8</td>
<td>1.1 (at 15°C)</td>
</tr>
<tr>
<td>GBL</td>
<td>-45</td>
<td>205</td>
<td>1.5 (4.0 at 60°C)</td>
<td>1.7 (at 25°C)</td>
</tr>
<tr>
<td>Water</td>
<td>0</td>
<td>100</td>
<td>19</td>
<td>0.89 (at 21°C)</td>
</tr>
</tbody>
</table>

Solution preparation: The solvent for PMMA was a mixture of PGMEA (propylene glycol methyl ether acetate, 65% vol) and GBL($\gamma$-butyrolactone, 35% vol). One reason for choosing these is their high boiling points, a helpful characteristic when attempting to produce high-quality film via the spin-coating method. The boiling points of PGMEA and GBL are 146 °C and 204 °C respectively. The concentration of the polymer solution was 2%-5% (wt%, for example, 150 mg PMMA in 5 ml of solvent mixture makes a 3% solution.). Because we began this project with the aim of making distributed feedback lasers (discussed
in more depth in the next chapter), 0.86% of Rhodamine 6G (wt% to PMMA) was added into the solution.

The solvent for the PVK and BBP mixture is also a mixture, which has 80% of Toluene and 20% cyclohexanone (by volume). The polymer concentration used for spin coating was 1.0% - 1.5% (wt%, for example, 60 mg PVK and BBP were added to 5 ml of the mixture to make the 1.5% solution).

The PVA solution was made by adding PVA into warm de-ionized water (DI-water). A sonicator was used to aid in dissolving the polymer. Depending on the degree of hydrolyzation of the PVA, the dissolving process took anywhere from a few hours to a few days. The concentration used in the experiment ranged from 2% - 3% (wt%).

**Film square (7×7 mm²) preparation:** The thin films were made using the spin coating method; the substrates were 4-inch silicon wafers. After the wafers were cleaned using the RCA-1 procedure, the whole surface was spread with the PVA water solution. The wafer was rotated at 1500 rpm for 40 seconds. It was then put into the oven, which was set at 75°C for soft baking. One hour of baking was enough to evaporate all of the water in the film. Two wafers covered with thin PVA layers were prepared for later coating with PMMA and PVK films. The solvents for the PMMA and PVK solutions were specifically chosen because they would not dissolve PVA. Using the surface profiler (Dektak-IIID), the thickness of the PVA film was measured as 93 nm.

One of the PVA layers was coated with the PMMA layer. The spin speed applied in spin coating was 1500 rpm and the duration was 40 seconds. After being baked at 80°C for several hours, the solid film was cut into 7 mm × 7 mm squares with a razor blade (a sharp
The film thickness was measured with the profiler Dektak. After the film was cut into small squares, the substrate was placed in warm DI-water (40 – 60 °C) after which the water container was placed on a hot plate. The thin PVA film between the PMMA film and the substrate was dissolved by the water. Without the PVA film, the small squares were detached from the substrate and eventually floated to the surface of the water. Although the density of the polymer was slightly greater than the water, the motion of the water helped the film reach the surface, and the polymer squares were kept on the top of the water because of the surface tension of the water. It turned out that it was better to keep the water container on a hot stage because of the water circulation inside the tank helps helped to force the little squares to the surface.

The PVK:BBP layer was coated on top of another PVA wafer. The spinning speed and time were the same as those for spin coating the PMMA layer. The film was baked at a temperature of 70 °C because the boiling point of Toluene is lower than that of PGMEA and GBL (Table 2.1). The procedure for producing little squares of PVK:BBP film was the same as the procedure described above for PMMA.

After being successfully med, the high quality polymer squares were transferred with a clean glass slide to Petri dishes filled with DI-water for storage. Because of surface tension, the little-film stays on the surface of the water even though the density of the polymer film may be larger than the water.

**Film-square stacking:** To avoid breaking other films in the storage dish, the to-be-stacked films were transferred to a special dish that had more water which is favorable for the film stacking. A clean glass slide was used as the substrate upon which the films were
stacked. The glass slide was carefully put underneath a square which was floating on the water surface at an angle of about 30 degrees (Figure 2-4). Lifting the glass slide slowly, the right side of the film was anchored on the slide first. Then, the entire glass slide was lifted out of the water, and the film stayed on top of the glass slide.

For the baking phase, the slide was placed in the oven and baked for at least 15 minutes to evaporate the water between the top 2 layers. Soft baking at 60 °C was chosen for this step of the fabrication process because hard baking (i.e., high-temperature baking) would likely have resulted in air bubbles between the layers.

![Figure 2-4 Free standing film stacking. (a) A piece of glass was put beneath the floating polymer square at an angle of about 30 degrees. (b) The glass was lifted close to the square and the film was attached to the glass; the glass slide was then removed from the water.](image)

After the film stack dried, cleaning was sometimes necessary to remove dust from the film or substrate. A gentle breeze of dry nitrogen can be used for this purpose.

After the film and substrate had been dried and cleaned, the stacking process was repeated with another type of polymer film. Of course, arbitrary order of the films can be
realized easily. We stacked PMMA and PVK:BBP alternatively to create 1D photonic crystals.

2.3.2.2 RESULT AND DISCUSSION

The refractive index of the PVK:BBP layer was determined by both the polymer and the plasticizer. Assume that the density of the film that was affected by the plasticizer is limited. The refractive index of the mixture, \( n_{\text{avg}} \), can be estimated from the percentage of the compounds (\( \alpha_1 \) and \( \alpha_2 \) for PVK and BBP respectively) in the mixture using a simple model [28, 29]

\[
n_{\text{avg}} = n_1 \alpha_1 + n_2 \alpha_2
\]

where \( n_1 \) and \( n_2 \) are the refractive indices of compounds 1 and 2. In this case, \( n_1 = 1.683 \) and \( n_2 = 1.535 \). The mixture had 4 parts of PVK and 1 part of BBP; therefore \( n_{\text{avg}} = 1.653 \).

The thicknesses of the PMMA film and the PVK film as measured by Dektak were 82 nm and 90 nm, respectively. These values can be fed into the transfer matrix calculation to predict the center of the reflection band as being 543 nm with a bandwidth of 52 nm. The band structure can also be calculated by with the transfer matrix method.

The films were nicely cut using a razor blade or sharp needle for precision. All of the results presented throughout this work were derived from samples created through this method. It is worth mentioning that laser cutting does not work well with polymer films. When attempting to cut the film with a focused femtosecond pulsed laser (CPA-2010), the edge of the film was burned, which caused the film to be misshapen, thereby degrading its...
uniformity. The irregular shape of the edge makes it easier to generate bubbles inside the water in the floating step. The focused beam also etches the wafer substrate and makes it not reusable.

![Figure 2-5 Pictures of the sample taken from two different angles and that exhibit different colors. Picture (a) was taken at normal incidence whereas picture (b) was taken at an incident angle of about 30 degrees.](image)

Figure 2-5 Pictures of the sample taken from two different angles and that exhibit different colors. Picture (a) was taken at normal incidence whereas picture (b) was taken at an incident angle of about 30 degrees.

![Figure 2-6 (a) Transmittance curve of the multilayered film made with PVK:BBP (4:1) (95 nm) and PMMA (86 nm). The lowest (2.8%) transmittance occurs at 564 nm. The peak at 533 nm is the absorption peak of R6G. (b) Comparison of the experimental and theoretical data, which had no consideration of the optical losses. Circles represent experiment data and the solid line was calculated using the transfer matrix method.](image)

Figure 2-6 (a) Transmittance curve of the multilayered film made with PVK:BBP (4:1) (95 nm) and PMMA (86 nm). The lowest (2.8%) transmittance occurs at 564 nm. The peak at 533 nm is the absorption peak of R6G. (b) Comparison of the experimental and theoretical data, which had no consideration of the optical losses. Circles represent experiment data and the solid line was calculated using the transfer matrix method.
The sample shown in Figure 2-5 had a total of 26 pairs of the polymer films. The color of the film is a result of its reflection band, which shifts with incident angle. Figure 2-5 (a) was taken at the normal angle (where the yellowish green color can be seen). This can be verified quantitatively in its transmittance curve shown in Figure 2-6. Figure 2-5 (b) was taken at 30 degrees to the normal angle (where the purple color can be seen).

The transmittance curves of the stacked sample are shown in Figure 2-6 (a). The PMMA films were doped with R6G for a target concentration of 0.86%. However, the absorption peak of R6G (533 nm) as seen on the curve indicates a lower dye concentration. From the curve of the sample which has 26 pairs, the absorption due to dye was estimated to be around 0.38 – 0.47. Using the extinction coefficient of R6G in PMMA and the total thickness of PMMA films (i.e., 26×82 nm=2.1 μm), we calculated the dye concentration inside the PMMA film to be 0.65% -0.8%. The decrease in the dye concentration happened in the stacking process, as part of which all of the films were stored in a DI-water filled petri dish. Even though the films floated on top of the water, the dye in the PMMA films films may have diffused into the water despite the fact that the solubility of the dye in the water was very low. This complication can be avoided by using a saturated water solution to fill the petri dish.

Theoretical simulation using the transfer matrix method was used to verify the experimental data (Figure 2-6 (b),Table 2-2). Figure 2-6 (b) compares the experimental data to the theoretical calculations. The theoretical and experimental results are in agreement from 530 nm to the near infrared; likewise, the reflection band matches the theoretical counterpart very well. The transmittance at the peak is 2.8% in the experimental version whereas the theoretical model gives 2.1%. The difference may be attributed to the layer thickness
variation introduced by an imperfect stack. Dust, water, or air may be trapped between the layers. It is also possible that intermediate layers between the two different films were created during the fabrication process. Any impurities that may have been introduced into the 1D stacked system would result in a lowered peak reflectance (higher transmittance). The disagreement at wavelengths shorter than 500 nm is due to the absorption of the polymer and the Rayleigh scattering inside the system.

### Table 2-2 Summary of samples made with the stacking method

<table>
<thead>
<tr>
<th>Film thickness (nm)</th>
<th>Final pairs</th>
<th>Peak of the transmittance curve</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Position (nm)</td>
</tr>
<tr>
<td>PMMA (n=1.49)</td>
<td>PVK:BBP (n=1.653)</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td></td>
<td>566</td>
</tr>
<tr>
<td></td>
<td></td>
<td>787</td>
</tr>
<tr>
<td></td>
<td></td>
<td>776</td>
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</table>

### 2.3.2.3 CONCLUSION

The free standing film stacking method was successfully used to fabricate 1D polymer multilayered polymer films. Because all of the layers of the same material are derived come from the same, thin, uniform, film, they have the same thickness, which helps to create more uniform layer distribution. The multilayered structure can be verified by examining the transmittance curve, for which the experimental results was found to have a good agreement with theoretical simulations. Because of its good mechanical properties, thin PMMA film was easy to produce. However, because the PVK:BBP film was brittle, the yield of good
PVK:BBP films was low. For this reason, the largest number of stacked pairs did not exceed 26. Finding a material that has better mechanical properties will be helpful for fabricating a multilayered film with a greater number of layers.

2.2.3 LAYER MULTIPLYING CO-EXTRUSION METHOD

2.3.3.1 INTRODUCTION

Melt extrusion is a high-volume manufacturing process that is used to produce plastic sheets. Following extrusion in the melt, polymer flow is spread out by the exit die, stretched into a thin film, and cooled to room temperature (Figure 2-7). The thickness of the film can be easily controlled by changing the extrusion speed, as well as the ratio of spreading and stretching. The extrusion method can produce uniform polymer films with thicknesses of less than 0.5 mm.

The co-extrusion process was developed to fabricate films when more than one layer is desired. Two or more different polymers are melted and brought together using a multi-exit die. The polymers are not blended; rather, they are layered in a liquid state. After they have cooled, the layered structure persists and forms a solid-state multilayered film.

There are certain requirements for the materials that are used in the co-extrusion process. First, the polymer must be thermally stable. Second, the liquid flow needs to be of a certain viscosity in order to be stretched. Third, the polymers’ viscosities should be similar at the co-extrusion temperature.
2.3.3.2 CO-EXTRUSION PROCESS

To make photonic crystals, two materials that have differences in their indices of refraction should be chosen for co-extrusion. A typical pair is PS ($n=1.59$) and PMMA.

![Co-extrusion Process Diagram](image)

Figure 2-7 The co-extrusion process. (a) Feedblock and layer-multiplying dies. Multilayered fluid is forms inside the multipliers. (b) A schematic drawing of the entire co-extrusion process. Different polymers (PS and PMMA) are in extruders A and B. Cascaded multipliers can be used to make hundreds or thousands of polymer layers. At the end of the last multiplier, there is an extruder that supplies the skin layer (low density polyethylene) for the protection of the multilayer.

Two different polymers were in two different extruders. After being melted, they were brought together by a feed block, which has two rectangular exits. Because the two polymers had different melting temperatures, the temperature of extruder (A), which fed PS, was set at 225°C whereas the temperature of extruder (B), which fed PMMA, was set at 235°C. These temperatures were chosen to ensure that the viscosities of the polymers would match when
entering the feed block. The temperatures of the surface layer feed block and multipliers were maintained at 230 °C, and the exit die was kept at 220 °C. Because we sought to maintain uniform thickness among the polymers, the volumetric flow rates of the two extruders were both kept at 3.0 cm³/min. The volumetric flow rate of the surface layer extruder was 54 cm³/min.

As shown in Figure 2-7, the melt stream flowed through a series of cascaded layer-multipliers after the two polymer melts had been stacked. The layer multipliers were used to sequentially double the number of layers. At the entrance of a multiplier, the melt stream was split vertically into two halves; next, there were two parallel blocks (top and bottom) at the exit of multiplier. After the split, one half was forced downward and spread horizontally at the bottom exit and the other half was spread horizontally at the top exit. In this way, the number of layers doubled. Therefore, if there are \( n \) multipliers, we will have \( 2^{n+1} \) layers after the melt stream has left the exit die.

2.3.3.3 RESULTS

For different applications of the multilayer films, 128-layer (64 bi-layer) and 32-layer (16 bi-layer) films were produced through layer multiplication co-extrusion. Figure 2-8 is an AFM phase image that shows a typical cross section of a 128-layer film. The layered structure can be clearly seen. As expected, the layers were not perfectly uniform with a certain amount of fluctuation in the layer thicknesses. Temperature gradients, uneven split ratios in the dies, unstable forces and diffusion (Brownian motion) at the interfaces of the two fluids can create such fluctuations in the thickness of each layer [18].
Figure 2-8 A typical cross section of the multilayered film was taken using AFM. The film shown has a total of 128 layers in total.

Even though there were fluctuations in layer thickness, a good reflection band was obtained as shown in Figure 2-9. The lowest transmission was 3.2%, which corresponded to a high reflectance of 96.8%. The film thickness could be changed by evenly stretching the film after it was made. As a result, the reflection band shifted accordingly.

Figure 2-9 Typical transmission curve a 128-layer film made via co-extrusion.
2.4 CONCLUSION

Three methods for producing multilayer polymer films have been presented: a multilayer spin coating technique, a free-standing film stacking method, and layer multiplying co-extrusion. The advantages and disadvantages of each method have been discussed. For example, the multilayer spin-coating technique has certain limitations related to the solvents and materials. Although its processing time is advantageous (i.e., it can create multilayered film structures in a few hours), it is difficult to eliminate the penetration of the solvent during the spin coating, which dissolves the previously deposited layers. This limits the quality and size of the 1D system. In contrast, the free standing film stacking method creates a perfect stack of the polymer film. However, to create a system that is large enough, the polymers must have good mechanical properties. Another disadvantage is that this method is time-consuming. As a time-saving alternative, the layer multiplying co-extrusion produces multilayered film very quickly. The film that is generated through this process can be stretched to tune the reflection band. This feature was particularly useful for our micro-cavity laser project because we required different reflection bands for different active gain media. However, the diffusion and uneven flow of the polymer melts create intrinsic randomness in the thickness of individual layers.

2.5 REFERENCES


CHAPTER 3

ENHANCED EMISSION IN 1D ORGANIC CRYSTALS

3.1 INTRODUCTION

Laser is an acronym for Light Amplification by Stimulated Emission of Radiation. Since the first discovery in the last century by Maiman[1], lasers have become indispensable tools in a variety of applications such as spectroscopy, communications, information technology, and medicine. Indeed, CD and DVD players, printers, and communication systems have made lasers part of our daily lives. New materials and fabrication schemes have opened many doors for applications at various wavelengths and will continue to do so. In addition, new concepts for low-cost production, new properties, and easy systems integration will promise yet more applications for lasers.
Organic materials have been used in lasers as dye-doped liquid and solid-state lasers for decades. These lasers are wavelength tunable because of the wide gain spectrum of the dye. Dye lasers were also widely used in the early days of ultrashort pulsed lasers. New interest in studying polymer lasers is mainly aimed at their potential for low-cost production, easy integration, and flexible design. Much of this recent research has been related to polymer semiconductor lasers[2], but new schemes for dye-doped polymer lasers have also been investigated because progress in polymer synthesis and processing allows for morphological control of a material’s structure over multiple length scales from nano to macroscopic structures. These advances have led to the development of increasingly complex polymeric devices.

Polymer-containing lasers attract significant attention because of the broad tailorability and potential processing advantages of polymers [3]. A major reason for the widespread interest in lasers that comprise either polymeric gain media, polymeric resonators, or a combination thereof, is the relative processing ease of polymeric materials vis-à-vis inorganic semiconductors [2]. The possibility of fabricating all-polymer lasers through plastic fabrication processes is particularly attractive [4, 5]. However, because polymer resonators involve periodic microstructures, the vast majority of organic lasers reported in the literature require comparably complex fabrication processes; for example embossing,[6] (nano)imprinting [7], conventional or soft lithography [8, 9], or repetitive spin coating [10-12].

Recently, a distributed Bragg reflector (DBR) laser made with commercial multilayer film reflectors was reported [13]. Distributed Feedback (DFB) lasers created via repetitive spin coating was also reported [12]. The DFB laser, in particular, is characterized by discrete
distribution of the gain medium in the multilayer structure. The multilayer film functions as both the resonator and gain medium. Through careful design and process optimization, we have made DBR and DFB lasers with outstanding performance capabilities. In this chapter, I will discuss these two types of lasers, which were fabricated by multilayer polymer co-extrusion.

3.2 DISTRIBUTED BRAGG-REFLECTOR LASER

3.2.1 MATERIALS AND FABRICATION

The DBR lasers consist of a compression-molded dye-doped polymer gain medium and photonic crystal resonators (Figure 3-1). Only organic materials (polymers or chromophores) were used for this experiment. DBR lasers were assembled by sandwiching two DBR mirrors (with reflection bands matched to the emission maxima of the gain medium) and the gain medium between two glass slides; a minute amount of silicon oil was applied to all interfaces as an index-matching fluid in order to avoid air bubbles between the films. The DBR lasers have very compact structure which requires no optical alignment on the resonator to achieve lasing because the total thickness of it is typically less than 50 μm whereas the dimension of the pumping area is larger than 100 μm.
Gain media were prepared by incorporating the fluorescent organic dyes Rhodamine 6G perchlorate (R6G) (with molecular weight, MW=546 g/mole) and 1,4-bis-(α-cyano-4-methoxystyryl)-2,5-dimethoxy-benzene [14] (C1-RG, whose chemical structure is shown as an inset in Figure 3-2 (a)) (with molecular weight, MW=452 g/mole) into glassy amorphous host polymers and compression-molded thin films whose thicknesses varied between 10 and 137 μm. The absorption and emission spectra of C1-RG and R6G are shown in Figure 3-2. C1-RG is highly soluble in PMMA [15] and C1-RG/PMMA blends (1.6 x 10^{-3} to 5.3 x 10^{-2} M) display strong green fluorescence and a large Stokes shift with absorption (λ_a) and emission (λ_e) maxima of ~430 and ~501 nm (Figure 3-2 (a)). The R6G/PMMA blends (3.3 x 10^{-4} to 1.0 x 10^{-2} M) display a smaller Stokes shift (λ_a=532 nm; λ_e=565 nm) (Figure 3-2 (b)) than do the C1-RG/PMMA blends and were also more photochemically stable. R6G dissolved in PMMA/PVDF (poly(vinylidene fluoride-co-hexafluoropropylene)) blends were also prepared as gain media. The results of the study indicated that the fluorescence of the
monolithic film was enhanced in the PMMA/PVDF blend. Furthermore, the optimized ratio between PMMA and PVDF is about 30:70.

The resonators were fabricated via a layer-multiplying co-extrusion process [16], and consisted of 128 alternating layers of poly(methyl methacrylate) (PMMA) and polystyrene (PS). The difference in the refractive indices $n$ of PS ($n=1.585\pm0.002$) and PMMA ($n=1.489\pm0.002$) caused the multilayer films to display a sharp reflection band. The centers of the resonators’ reflection bands were matched (Figure 3-2) with the emission spectra of two series of gain media by controlling the thicknesses of the polymer layers during the extrusion process; moreover, the properties were fine-tuned by reducing the film thickness through subsequent biaxial stretching. In the optical end-pumped laser system, the pump light should be able to excite the active medium without significant loss (reflection, scattering, etc). For this reason, the layers thicknesses of the layers in the multilayer film were designed so that the high-energy edge of the reflection band coincided with the emission maximum of the laser dye. For R6G lasers, the layer thicknesses of the reflectors were approximately $92\pm21$ nm which yielded a band center at 565 nm. In the case of C1-RG lasers the layer thicknesses of the reflectors were approximately $84\pm19$ nm, which resulted in a band center at 510 nm. To minimize the fluctuation on the layer thickness, a 50:50 feed-block was employed and each individual layer has approximately the same thickness.

The DBR mirrors comprising 128 alternating PS and PMMA layers (i.e., 64 each) had a 22% standard deviation of layer thickness and a film thickness of about 10-12 μm as determined by direct measurement of AFM images of the film cross section. This non-uniformity resulted in the appearance of relatively intense and irregular side peaks as can be seen in Figure 3-2 (a) and (b).
Figure 3-2 (a) Reflection band (green), absorption (black), and emission (red) of C1-RG (inset shows molecular structure) (b) Reflection band (green), absorption (black) and emission (red) of R6G.

3.2.2 EXPERIMENTAL METHOD

Figure 3-3 shows the schematic layout of the optical setup for characterizing lasers. The surface-emitting lasers were pumped at oblique incidence with a tunable optical parametric oscillator (OPO), which was pumped by a frequency-tripled Nd:YAG laser (λ=355 nm, pulse length 7 ns, frequency 10 Hz, p-polarized). Lasers comprising R6G and C1-RG gain media were pumped at 530 nm and 430 nm, respectively. A rotatable half-wave plate together with a linear polarizer was used to control the power of the incident beam in a continuous manner. The pump beam, which was focused by a lens with 7.5 cm focal length, was incident at an angle of 10° from normal; this allowed the pump light to fully penetrate the DBR reflectors by avoiding the reflection band. A knife-edge technique was used to measure the spot size of the focused pump beam. An objective lens was employed to collect the emission in the normal direction. Color filters (XC12 for blocking 430 nm, OC11 or OC12 for blocking 532
nm) were used to block the scattered pump light. An ICCD camera attached to a monochromator was used to measure the emitted spectrum (both monolithic film and laser devices) and calibrated photodiodes (PD) were employed to measure the input and output power.

Refractive indices of the polymers were measured at 633 nm with a Metricon 2010™ prism coupler.

![Schematic layout of plastic laser measurement setup.](image)

**Figure 3-3 Schematic layout of plastic laser measurement setup.**

### 3.2.3 RESULTS

Intense laser emission was observed from all devices as can be seen from the picture shown in Figure 3-4. Note the high quality emission mode. The minimum threshold fluence observed in the C1-RG samples was 435 \( \mu \text{J/cm}^2 \) in a laser that had a 135 \( \mu \text{m} \) thick gain layer comprising the dye in a concentration of \( 1.6 \times 10^{-3} \) M, In the case of the R6G lasers, the minimum threshold fluence was 90 \( \mu \text{J/cm}^2 \) in a device that had a 40-\( \mu \text{m} \)-thick gain layer at \( 5.4 \times 10^{-3} \) M. The laser output in C1-RG samples decayed over several hours of service.
Interestingly, the output of the R6G samples was stable over long periods of time, which bodes well for the potential technological application of these devices.

Figure 3-4 Picture of lasing behavior of DBR laser. Bright emission from R6G DBR laser. The saturated bright spot on the screen (yellowish green) is the lasing emission and the fainter green spot to the right is the residue of the pump light.

Typical emission spectra - both below and above the threshold for DBR laser samples - are shown in Figure 3-5. Multimode emission was observed with the number of modes and spacing, of course, depending on the film thickness. Emission near the band center was as expected. The spectral width (full width half maximum) of a single lasing mode was about 0.4 nm, which was near the instrumental resolution. The emission spectra of the photoluminescent dyes that had been employed were rather broad with distinct phonon modes as can be observed in Figure 3-2. In contrast, the emission spectra of the DBR devices that had been pumped below the lasing threshold were more complex and included contributions that arose from the reflection of the multilayer film as well as periodic oscillations as shown in Figure 3-5 (black curve). The oscillations are due to interference effects associated with DBR cavity reflection and were indicative of the cavity modes.
We also characterized the energy conversion efficiency of the lasers studied. A typical plot of output power in the forward direction versus input power is shown in Figure 3-6. The slope efficiency for this sample was 14.3%. The highest efficiency observed for C1RG lasers was 14.3% in a device having a 120-μm thick PMMA gain layer doped with $1.3 \times 10^{-2}$ M dye. The highest efficiency that we observed was 19.3% for an R6G sample having a 40-μm thick PMMA core layer doped with $5.4 \times 10^{-3}$ M dye. All of the measurements for the different DBR samples have been listed in Table 3-1 and Table 3-2.

The beam size at the focal point was measured using the knife-edge technique. We determined that different beam sizes correlated with different pumping wavelengths. For the 430-nm pump light, the spot size was measured to be $\pi \times 113 \times 65$ μm$^2$. For the 532-nm pump light, the spot size was measured to be $\pi \times 217 \times 102$ μm$^2$.

![Figure 3-5 Emission spectrum of an R6G sample pumped below threshold (black curve) and above threshold (red). Transmission curve of the whole sample is shown as the green curve.](image-url)
Figure 3-6 Slope efficiency (14.3%) of a C1-RG laser with a 120-μm-thick gain layer at 1.3×10⁻² M in PMMA.

Table 3-1 Energy conversion efficiency samples with R6G as the gain medium. The quantities are: L=gain medium thickness; Abs=absorption of the sample at the pump wavelength; \( \lambda_0 \)=center emission wavelength; \( \frac{P_{\text{out}}}{P_{\text{in}}} \)=Efficiency referenced to the incident power; \( \frac{P_{\text{out}}}{P_{\text{in}}(\text{absorbed})} \)=Efficiency referenced to the absorbed power.

(a) R6G in PMMA:PVDF blend

<table>
<thead>
<tr>
<th>Sample</th>
<th>L(μm)</th>
<th>Dye concentration wt%</th>
<th>Absorption</th>
<th>( \lambda_0 )(nm)</th>
<th>Threshold (μW)</th>
<th>( \frac{P_{\text{out}}}{P_{\text{in}}} )</th>
<th>Efficiency(%)</th>
</tr>
</thead>
<tbody>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( \frac{P_{\text{out}}}{P_{\text{in}}(\text{absorbed})} )</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>10</td>
<td>0.13</td>
<td>0.33</td>
<td>556</td>
<td>4.93(1.38)</td>
<td>0.49(0.03)</td>
<td>1.2 (0.06)</td>
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<tr>
<td>B</td>
<td>10</td>
<td>0.13</td>
<td>0.28</td>
<td>575</td>
<td>3.63 (0.84)</td>
<td>1.16(0.42)</td>
<td>3.0 (1.11)</td>
</tr>
<tr>
<td>C</td>
<td>15</td>
<td>0.13</td>
<td>0.43</td>
<td>560</td>
<td>2.73(0.18)</td>
<td>2.66(0.6)</td>
<td>5.3 (1.2)</td>
</tr>
<tr>
<td>D</td>
<td>15</td>
<td>0.03</td>
<td>0.12</td>
<td>562</td>
<td>5.3 (1.8)</td>
<td>0.72 (0.3)</td>
<td>3.77(1.57)</td>
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<td>20</td>
<td>0.13</td>
<td>0.66</td>
<td>566</td>
<td>1.96(0.65)</td>
<td>3.9(0.44)</td>
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<tr>
<td>F</td>
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<td>22</td>
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<td>0.66</td>
<td>570</td>
<td>1.67 (0.22)</td>
<td>3.37(0.22)</td>
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(b) R6G in PMMA

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<th>Sample</th>
<th>L(µm)</th>
<th>Dye concentration wt%</th>
<th>Absorption</th>
<th>λ₀(nm)</th>
<th>Threshold (µW)</th>
<th>Efficiency(%)</th>
<th>P_{out}/P_{in}</th>
<th>P_{out}/P_{in} (absorbed)</th>
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<td>555</td>
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<td>557</td>
<td>209(21)</td>
<td>0.55(0.1)</td>
<td>0.55(0.1)</td>
<td></td>
</tr>
</tbody>
</table>

Table 3-2. Efficiency of various samples with C1-RG as the gain medium.

<table>
<thead>
<tr>
<th>Sample</th>
<th>L (µm)</th>
<th>Dye concentration wt%</th>
<th>Absorption</th>
<th>λ₀ (nm)</th>
<th>Threshold (µW)</th>
<th>Efficiency (%)</th>
<th>P_{out}/Pin</th>
<th>P_{out}/P_{in} (absorbed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>19</td>
<td>0.06</td>
<td>0.07</td>
<td>517</td>
<td>5.6(1.0)</td>
<td>0.38(0.3)</td>
<td>2.5(2.0)</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>20</td>
<td>0.5</td>
<td>0.42</td>
<td>508</td>
<td>3.0(1.2)</td>
<td>4.3(1.0)</td>
<td>6.9(1.6)</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>35</td>
<td>0.06</td>
<td>0.09</td>
<td>509</td>
<td>5.15(1.0)</td>
<td>0.71(0.46)</td>
<td>3.8(2.5)</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>40</td>
<td>0.5</td>
<td>1.21</td>
<td>511</td>
<td>2.0(0.7)</td>
<td>6.5(4.0)</td>
<td>6.9(4.2)</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>40</td>
<td>2.0</td>
<td>~4</td>
<td>525</td>
<td>2.9(0.7)</td>
<td>4.9(0.9)</td>
<td>4.9(0.9)</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>85</td>
<td>0.5</td>
<td>2.53</td>
<td>515</td>
<td>2.6(0.9)</td>
<td>6.1(2.2)</td>
<td>6.1(2.2)</td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>85</td>
<td>0.06</td>
<td>0.36</td>
<td>516-520</td>
<td>2.65(0.9)</td>
<td>5.1(3.5)</td>
<td>9.1(6.2)</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>120</td>
<td>0.5</td>
<td>3.7</td>
<td>512</td>
<td>3.6(2.1)</td>
<td>10.4(3.4)</td>
<td>10.4(3.4)</td>
<td></td>
</tr>
<tr>
<td>S1</td>
<td>128</td>
<td>0.06</td>
<td>0.59</td>
<td>510</td>
<td>3.0(1.0)</td>
<td>4.0(1.4)</td>
<td>5.4(1.9)</td>
<td></td>
</tr>
<tr>
<td>S2</td>
<td>127</td>
<td>0.06</td>
<td>0.61</td>
<td>510</td>
<td>2.7(0.7)</td>
<td>4.4 (1.6)</td>
<td>5.8(2.1)</td>
<td></td>
</tr>
<tr>
<td>S3</td>
<td>137</td>
<td>0.06</td>
<td>0.67</td>
<td>509</td>
<td>2.4(0.26)</td>
<td>5.3(1.76)</td>
<td>6.7(2.2)</td>
<td></td>
</tr>
</tbody>
</table>
3.2.4 FOUR LEVEL MODEL

The dye lasers that have been investigated here can be quantitatively described by a four-level end-pumped laser model including re-absorption and scattering of the laser output, as well as non-uniform pumping in an absorbing gain medium. For steady-state lasing, the threshold gain, $g_{th}$, can be expressed by: [17]

$$g_{th} = -\frac{1}{2l} \ln(r_1 r_2) + a$$

(3.1)

where $l$ is the length of the gain medium, $r_1$, $r_2$ are the reflectivities of the two mirrors and $a$ is the general loss at the lasing wavelength (that arises from absorption, collision, scattering, etc) in the cavity. This expression reflects that a device with a thinner gain medium should have a higher threshold gain, which, in turn, requires higher pump intensity. Further, the required minimum population inversion $\Delta N_{th}$ is determined by $g_{th}$ and the stimulated emission cross section $\sigma(\omega)$. In a four-level system, the population inversion is proportional to the pumping density:

$$\Delta N_{th} = g_{th} / \sigma(\omega)$$

(3.2)
Considering the case in which the pumping is nonuniform (i.e., when the absorption is sufficiently high so that the pump intensity attenuates over the thickness of the active core), the threshold power, $P_{th}$, can then be expressed as:

$$P_{th}(1 - e^{-\alpha l}) \approx \hbar \omega N_{th} \Gamma_{e'g'}$$

(3.3)

where $\alpha$ is the absorption coefficient at the pump wavelength, and $V$ is the volume of the gain medium, which, in the low attenuation limit, equals the product of the spot area $S$ and the length of the gain medium $l$. $\Gamma_{e'g'}$ is the transition rate from $e'$ to $g'$ (i.e., the lasing transitions from the LUMO to the HOMO level). On the left-hand side of Eq. (3.3), the average pump density was used. Therefore, with Eqs. (3.1)-(3.3), we can express the pump threshold $P_{th}$ by,

$$P_{th} \approx \frac{K(- \ln(r_1 r_2) + 2(\alpha l) \alpha / \alpha)}{1 - e^{-\alpha l}}$$

(3.4)

In Eq. (3.4), $K$ is a constant determined only by the type of molecule and the focusing of the pump beam.

The lasing thresholds as a function of thickness for R6G films that have a gain medium doped at $5.4 \times 10^{-3}$ M are shown in Figure 3-8. The relatively large uncertainties are a result of sample-to-sample variations as well as variations across the sample surface of the DBR films, which are, in turn, due to variations in the layer thicknesses across the sample surface as noted above. For each sample, results were averaged over several spots on the surface. Despite the uncertainties, it is obvious from Figure 3-8 that R6G lasers comprising a gain medium doped with $5.4 \times 10^{-3}$ M dye exhibit a threshold minimum when the core thickness is about 25 $\mu$m. This corresponds to an optical density (OD) of about 1.1. For lasers
containing either R6G or C1-RG doped gain media of various dye concentrations, the minimum threshold was observed to be in the 1.1-1.4 OD range, which indicated that this was a generally favorable design criterion.

Figure 3-8 Threshold trend observed in R6G samples. Data points were fitted by a four-level lasing model (Eq. (3.4)). The solid curve is the fitting curve.

The trend of the data shown in Figure 3-8 is fully consistent with Eq. (3.4). The observed trends can be explained physically in the following way. In thin gain media layers, the dye molecules were efficiently excited throughout. However, the overall gain was small because most of the pump light had not been absorbed by dye molecules whereas the loss due to the reflectors was fixed. As a result, a high pump threshold was observed for the thin gain layer samples. However, for lasers with thicker gain layers, the pump light penetration was limited by absorption, which implies an effective gain thickness smaller than the physical thickness,
and, consequently, nonuniform pumping. In addition, re-absorption of the laser output by the dye molecules in lasers with thicker gain layers reduces the output. Both of these effects tended to increase the threshold in the lasers with thicker gain layers.

Eq. (3.4) further implies that, for a specific dye concentration, there is an optimum absorption at which the device exhibits a minimum lasing threshold. The optimized absorption is determined by the output coupling and the ratio of loss to pump efficiency, described by $a/\alpha$. For example, in the system that we studied, the typical value of $r_1r_2$ would be around 0.9 and $a/\alpha \approx 0.005$ - if only the absorption loss from the dye molecule itself is considered. Then the optimized absorption would be 1.13 OD. It should be noted that Eq. (3.4) implies that the optimized absorption increases when the $r_1r_2$ increases or $a/\alpha$ decreases. If the dye concentration in the polymer film is increased, $a/\alpha$ will become smaller because the scattering and collision losses from the polymer host do not change. As a result, the optimized absorption is greater for higher concentration film. We plotted Eq. (3.4) with $K$ adjusted to fit the data and the other parameters estimated from transmission data; theory and data were in reasonable agreement.

### 3.2.5 POLARIZATION OF THE LASER OUTPUT

The polarization of the output was measured by putting an additional polarizer (analyzer) before the detector. The data taken from a 33μm sample are shown in Figure 3-9. The pump light was set to s-polarization (vertical). The power conversion efficiency was 1.2% for ss configuration, for which the analyzer was set to s-polarization, and 1.1% for sp configuration,
for which the analyzer was set to p-polarization (horizontal). The depolarization ratio can be calculated, based on the measurement results, as:

$$ r = \frac{I_\parallel - I_\perp}{I_\parallel + 2I_\perp} = 0.038 $$

We can conclude from the data that the lasing output of the DBR lasers was completely unpolarized. In fact, at normal direction, the s and p polarization (TM and TE) are degenerate. The chances of having stimulated emission at different polarizations are the same. The polarization of the lasing output should be determined only by the device and not by the pump light. Similar results were found for p-polarized pump.

Figure 3-9 Output of the DBR laser for different polarizations. Solid square: the pump and output have the same polarization. Open circle: the pump and output have different polarization.
3.2.6 LIFETIME OF THE C1-RG LASER

The C1-RG lasers degraded after several tens of minutes of pumping. The consecutive power dependence measurements at the same spot on the same sample are shown in Figure 3-10 (a). The time duration for each measurement was 6 minutes. The red lines in Figure 3-10 (a) are the linear fit for data points above threshold. The slope of the line determines the power conversion efficiency of the system. Figure 3-10 (b) shows the trend of efficiency change over time. The sample had power conversion efficiency of about 3.8% for the first time measurement. The efficiency dropped to 1.2% after an hour of measurement.

The data points were fitted with the exponential decay model. The life time (1/e) as determined from the fitting parameters for this sample was around 35 minutes.

Figure 3-10 C1-RG DBR laser output against time. (a) Power dependence curves. Data points with different colors were taken at different time. Red lines are the fittings to the data points. (b) Lasing efficiency determined from (a) versus illumination time. Data points were fitted to an exponential decay model.
Not only did the lasing efficiency change after prolong time of exposure to the pump light, but the threshold of lasing also changed. The relationship between the threshold and efficiency is shown in Figure 3-11. The data points were extracted from the power dependence measurement by extrapolating the linear fit on the X-axis. The data was fitted with $y = 1/x$ model. It shows that, when the photo bleaching process was occurring inside the sample, the threshold increased and the efficiency decreased. In fact, photo bleaching degrades the dye, which contributes to the gain; this causes a decrease of the overall gain of the cavity. The products that resulted from the decomposition introduced additional loss inside cavity. That is, what is changing over time in Eq. (3.4) is the pump absorption of the film $\alpha$ and loss $a$. During the photobleaching process, the ratio $a/\alpha$ increased; as a direct consequence of this, the lasing threshold increased.

![Figure 3-11 Relationship between the threshold and efficiency. The fitting model is $y=1/x$.](image)

Figure 3-11 Relationship between the threshold and efficiency. The fitting model is $y=1/x$. 

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3.3 DISTRIBUTED FEEDBACK LASER (DFB)

3.3.1 MATERIALS AND FABRICATION

Unlike the DBR laser, as part of which the gain medium was sandwiched by two polymer mirrors that constituted the laser cavity, a distributed feedback (DFB) laser is, typically, defined as a laser for which the gain medium is an integral part of the cavity. The lasers that have been fabricated for this study have the schematic structure shown in Figure 3-12. They are optically pumped surface-emitting lasers.

The optical feedback of the laser is achieved by optical interference in the periodic structure that contains the gain medium. This periodic structure forms a one-dimensional photonic crystal. In this case, emission is not permitted within the reflection band, also known as the photonic crystal band gap. However, near the band edge of the photonic crystal, the group velocity of photons approaches zero equivalent to an enhanced density of photon states that leads to enhanced gain and thereby provides the necessary optical feedback [18]. Low thresholds can be obtained when the band edge coincides with the gain medium emission peak. A DFB laser fabricated through spin coating (layer-by-layer) has been reported [12]. Here, I will demonstrate lasing from a DFB structure that was fabricated using a single roll-to-roll multilayer processing technique. The output power, emission spectrum, slope efficiency and threshold for various designs are described.
In the case of DFB lasers, more careful consideration of the dye is required. The emitting species, such as fluorescent dyes or quantum dots, are doped directly into the multilayered photonic crystal and are subjected to the melt-extrusion process. For example, at the temperatures involved in the co-extrusion process, small molecules can easily diffuse throughout the multilayered film. This hinders control over the placement of emitting species within layers of a specific type. Several strategies for minimizing or preventing this diffusion are available. One approach is covalent attachment of small molecules to larger species that are less prone to diffusion is one approach. In this scheme, fluorescent chromophores can be covalently attached to polymers as part of the chain backbone or as pendant groups, bound to the surface of a nano-particle or even trapped within the core of a core-shell nanoparticle. In addition, one can exploit non-bonding interactions to attempt to limit diffusion by selecting polymers for which the chromophore has a strong affinity for one of the host layers, but a strong aversion to the other.
DFB film lasers with alternating layers of SAN25 (a styrene acrylonitrile – random copolymer, 25 mol% acrylonitrile, \( n=1.56 \)) and THV 220G (fluoroelastomer – terpolymer of vinylidene fluoride, hexafluoropropylene, and trifluoroethylene, \( n=1.37 \)) were fabricated using a continuous co-extrusion process. The laser dye was put into the high refractive index material (i.e. SAN25).

We found that films with a minimum of 128 layers were required to provide sufficient optical feedback for lasing. More layers can be made, but in our experimental setup, the layer uniformity in layer thickness degraded as the number of layers increases, with a concomitant decrease in laser performance. For better quality and uniformity of the multilayered film, we fabricated 64-layer film using the co-extrusion method. The film was approximately 5 \( \mu \)m thick with each layer having a thickness of approximately 85 nm. Thus, instead of using single-run, 128-layer samples, the 128-layer DFB lasers were created by stacking two 64-layer films. The stacked films were selected based on reflection band similarity. Stacked films lasers exhibited better energy-conversion efficiency and lower thresholds because of their improved distributed feedback.

### 3.3.2 EXPERIMENTAL

The experiment setup for characterizing DFB lasers was the same as the previously described setup for the DBR lasers.
3.3.3 RESULTS

Figure 3-13 Lasing-DFB laser pumped by a 530 nm pulse generated from a YAG-triplet-operated OPO. The right small spot on the screen was the residue of pump.

DFB lasers with R6G dye were pumped at a wavelength of 532 nm, which is the absorption peak of the R6G dye. The image in Figure 3-13 shows lasing from a DFB laser, which emits a greenish-yellow color (about 560 nm). The actual lasing wavelengths of the DFB lasers are determined by the band structure of the photonic crystal.

Figure 3-14 shows the emission and transmission spectra of a 2×64-layer DFB laser. As is clearly visible, the sample had a very narrow emission at 557 nm when it was pumped at a high pumping level. The pumping threshold for this sample was about 5 mJ/cm² as measured by observing at its emission spectrum. The lasing efficiency measured for this sample was 1.7% (see Figure 3-15) as measured by the slope of curve above the lasing threshold. This is a relatively low efficiency, but it can be improved by stacking a few more thin films.
All multilayer-film-based lasers exhibit pump-angle-dependent output because the reflection band shape and location varies with the angle of incidence. The absorbance
spectrum blue shifts with increasing pump angle. Lasing occurs where the transmission window at normal incidence and the spontaneous emission peak area overlap. Strong lasing occurred near 15 and 55 degrees, which corresponds to high effective absorption of pump energy as the reflection band of the multilayer film shifted across pump wavelength with incident angle. We have found that DFB lasers show better conversion efficiency range from 40 to 60 degrees. This is consistent with the fact that p-polarized beam transmission increases with increasing incident angles.

In a DFB laser, emission should occur at the band edge due to the enhanced density of photon states and the concomitant low group velocity. Our DFB lasers emitted either at the band edge or somewhere inside the band gap. As mentioned in earlier, the co-extruded 1D multilayer film had certain non-uniformities in the layer thicknesses. This would lead to bad photonic crystal bands and would have caused the lasing to occur in unpredictable wavelengths. Especially if there is defect layer in the 1D structure, defect modes exists and causes modes leakage inside the band gap [19]. Such defect-like structures can act to produce emission within the nominal gap[10]. An exaggerated example would be the DBR laser for which the centered gain medium was so thick that it could not accurately be considered a DFB laser.

3.4 CONCLUSION

In summary, all-polymer surface emitting micro-resonator dye lasers with distributed Bragg reflectors have been discussed. These lasers were produced entirely by melt-processes that
lend themselves to high-throughput roll-to-roll production methods. The resulting lasers can be mass produced for spectroscopy, remote sensing, data-storage, and display applications.

Low-threshold, high-efficiency lasers with well-defined spatial and temporal modes were observed. Threshold measurements for lasers of various thicknesses and dye concentrations were consistent with a simple four-level lasing model that included inhomogeneous end-pumping and re-absorption.

Full characterization of the lasing behavior was carried out. The output of the DBR laser was completely unpolarized. The DBR laser made with C1-RG dyes showed photo-bleaching over repeated pump pulses. The lifetime of this type of laser was around 45 minutes under 50 μW of illumination.

All-polymer surface emitting DFB lasers were also discussed. These lasers were fabricated by stacking 64-layer films that had been made by the roll-to-roll co-extrusion method. Gain materials were added into the polymer layers that had higher refractive index. Intense lasing output was observed from a 2×64-layer DFB laser. The power conversion efficiency was about 1.7% on one side of the laser.

3.5 REFERENCES


CHAPTER 4

MODE (DE)LOCALIZATION IN 1D

PHOTONIC CRYSTALS

4.1 INTRODUCTION

Anderson localization is a concept related to the physics of solids that deals with, for example, a transition from metal phase to insulator phase due to multiple scattering of electronic wave functions from random disorder in an otherwise periodic potential, which is a result of interference of locally scattered waves [1]. The analogous, photon localization in disordered photonic crystals has also received considerable theoretical attention during the last decade [2-4]. Early microwave measurements demonstrated photon localization in a disordered system [5, 6]. A number of experiments on photon localization have been carried out on 2 or 3 dimensional systems [5-10]. Both weak localization [7, 11] and strong photon
localization [9] have been observed in coherent backscattering experiments. Localization in random media has been applied to in the study of random lasers [12, 13].

In one dimension (1D), Anderson localization has been studied in electrons, matter waves [14], photons [8], and acoustic waves [15]. As discussed in the previous chapters, in a perfectly periodic dielectric material in a 1D photonic crystal, a reflection band appears as a photonic band gap. Within the band gap, light is localized as coherent reflection attenuates the light penetrating the structure [3, 7]. Defects in a photonic crystal structure lead to localized defect modes within the band gap [16]. In contrast, theory and simulations have predicted that a loss of coherent reflection in disordered structures that results in delocalization of the optical mode as it penetrates the photonic crystal structure [17, 18].

In the previous chapter, the all-polymer surface-emitting distributed Bragg reflector lasers that had been fabricated using a roll-to-roll compatible melt process [19] were discussed. When attempting to perfect the structure, it is worthwhile to study a disordered system. In addition to the fundamental interest, such reflectors have the potential to find practical application in low cost-photonic devices.

In this chapter, I will discuss Anderson localization in the case of a 1D disordered photonic lattice by studying the phase delay that is associated with the longitudinal mode separation in a polymer distributed Bragg reflector laser [19]. We have confirmed that, indeed, the optical mode in the Bragg mirrors becomes delocalized within the band gap in the presence of disorder, and we were able to quantify the corresponding delocalization. Through transfer matrix theory and simulations, we were able to study this delocalized mode and its connection to Anderson localization outside the band gap in keeping with Pendry’s analysis [4].
4.2 ONE-DIMENSIONAL TRANSFER MATRIX

THEORY

4.2.1 GENERAL TRANSFER MATRIX THEORY

The basic philosophy behind the transfer matrix method assumes that the 1D system can be divided into thin sub-systems whose properties can be independently studied independently. For example, the 1D electron system has only nearest neighbor interaction can be studied by the transfer matrix method. For our application of the theorem, we used this method to study the optical behavior of the multilayered system.

Considering the system in Figure 4-1, the left-to-right propagating wave and right-to-left propagating wave have different coefficients, which are related to the properties of the system, for determining the amplitudes of reflected and transmitted waves. The actual waves on each side of the system are the superposition of the waves in two cases. Writing down the amplitudes of the waves as a vector compromising left-going and right-going waves,

\[
\begin{pmatrix}
a \\
R_L^+ a + T_L^- b
\end{pmatrix}
\]  

We want the amplitude vector at the right side of the system to be calculated from Eq. (4.1) by multiplying a 2×2 matrix \(X_L\).

\[
\begin{pmatrix}
T_L^+ a + R_L^- b \\
b
\end{pmatrix}
= X_L \begin{pmatrix}
a \\
R_L^+ a + T_L^- b
\end{pmatrix}
\]  (4.2)
The elements of $X_L$ can be determined by setting $a$ and $b$ to different values. For example, by setting $(a, b) = (0,1)$ and $(1,0)$ four equations, which would be sufficient for determining the elements of $X_L$, will result. The expression for $X_L$ is

$$X_L = \begin{pmatrix} T_{L}^{++} - R_{L}^{-+} R_{L}^{+-} / T_{L}^{--} & R_{L}^{--} / T_{L}^{--} \\ -R_{L}^{+-} / T_{L}^{--} & 1 / T_{L}^{--} \end{pmatrix}$$

(4.3)

![Figure 4-1 Definition of the T and R in the transfer matrix method](image)

Obviously, the system has time-reversal symmetry. Thus, $X_L$ should also have such symmetry. Taking the complex conjugation of the waves and performing an analysis similar to that described above, Pendry showed $X_L$ can be rewritten as:

$$X_L = \begin{pmatrix} 1 / T_{L}^{--} & R_{L}^{++} / T_{L}^{--} \\ R_{L}^{--} / T_{L}^{--} & 1 / T_{L}^{--} \end{pmatrix}$$

(4.4)
Now, a large system is considered to be divided into many small sub-systems (i.e., thin layers) (Figure 4-2). Each thin layer has its own properties of reflection and transmission that can be described by a similar matrix as Eq. (4.3). For example, the transfer matrix for the $n$th layer can be written as:

$$X_n = \begin{pmatrix}
\frac{1}{t_n^{-}} & r_n^{+} / t_n^{-} \\
r_n^{-} / t_n^{+} & 1 / t_n^{-}
\end{pmatrix}$$

(4.5)

Evidently, we can apply the transfer matrices of all of the thin layers to obtain the matrix of the whole system,

$$X_L = X_N X_{N-1} \ldots X_1 = \prod_n X_n$$

(4.6)

Of course, we can also calculate the waves on the left side from those on the right side. It can be done by simply inversing all of the matrices, which basically involves rearranging the terms in Eq. (4.2).

Figure 4-2 Dividing the large system into many sub-systems, which are easier to study.

### 4.2.2 TRANSFER MATRIX METHOD IN 1D OPTICAL SYSTEM

For a perfect quarter wave stack, it is possible to calculate the transmittance and reflectance of the system analytically [23]. However, if the system is not a regular stack, it is hard to find
an exact analytical solution for it. The major concern here is the variations in thickness of
each layer. It is possible to use the transfer matrix method to numerically calculate the
transmittance and reflectance.

In this study, we were interested in the waves that are normal to the layers in a 1D optical
system. The formula of the transfer matrix has been given in Chapter 1, section (1.2.6.2).
Consider the example of a beam incident in a multilayer film from the left. At the right end
of the system, there is a right-traveling wave, which is treated as the transmitted output. We
define $M_i$ as the product of the matrices of $(i+1)$th layer to the right-most layer.

$$
M_i = \left( \prod_{j=i+1}^{N} X_j \right) D(n_s) = \begin{pmatrix}
M_{i,11} & M_{i,12} \\
M_{i,21} & M_{i,22}
\end{pmatrix}
$$

(4.7)

where $n_s$ is the refractive index of the substrate and $X_j$ is the matrix for $j$th layer.

$$
X_j = D(n_j)P(k_j, t_j)D(n_j)^{-1}
$$

(4.8)

The quantity $D(n) = \begin{pmatrix} 1 & 1 \\ n & -n \end{pmatrix}$ is the dielectric matrix and
$P(k_j, x_j) = \begin{pmatrix} e^{ik_j x_j} & 0 \\ 0 & e^{-ik_j x_j} \end{pmatrix}$ is the
 propagator matrix. Here, $x_j, k_j$ are the thickness of the $j$th layer and the corresponding wave
vector, respectively. Therefore, the electric field inside the $i$th layer would be

$$
\begin{pmatrix}
EF_i \\
EB_i
\end{pmatrix} = D(n_i)^{-1} M_i \begin{pmatrix}
EF_s \\
0
\end{pmatrix}
$$

(4.9)

where $EF_s$ is the field inside the substrate layer. The intensity inside the thin layer can be
easily determined from the forward and backward electric fields. The phase factors of the E-
fields are canceled in the expression of intensity by time averaging:
Putting (4.9) into (4.10), we have

\[ I_i = \frac{n_i}{4} \left( |M_i^{11}|^2 + |M_i^{21}|^2 / n_i^2 \right) EF_s^2 \]  

(4.11)

Knowing each element of the transfer matrix the whole system, the reflectance \((R = |EB_0|^2 / |EF_0|^2)\) and transmittance \((T = n_i |EF_1|^2 / n_0 |EF_0|^2)\) of a 1D system can be easily computed. The phase difference between the reflected and incident wave \(\Delta \varphi = \text{angle}(EB_0 / EF_0)\) can also be determined from the transfer-matrix elements.

\[ \Delta \varphi = \text{angle} \left( \frac{M_0^{11} - M_0^{21} / n_0}{M_0^{11} + M_0^{21} / n_0} \right) \]  

(4.12)

### 4.2.3 TRANSFER MATRIX WITH ENSEMBLE AVERAGE

It is interesting to study disordered periodic systems using the general transfer matrix method. In most circumstances, Anderson localization will occur because of the presence of disorder outside the photonic band gap. Pendry has reviewed the relationship of the localization length to the transmittance,

\[ l_{\text{loc}} = -L / \ln T \]  

(4.13)

and shown that Anderson localization leads to localized modes in a 1D system that has disorders [4]. Here, \(L\) is the size of the system and \(T\) is the transmittance, which can be measured or calculated using the transfer matrix method for any chosen realization of a random system.
Disorder is realized differently in different systems. To understand the effect of the degree of disorder, it is necessary to study the ensemble average of the transfer matrices of many systems. As we know, two values ($n_1$ and $n_2$) of refractive indices appear in the structure of 1D photonic crystals. To simplify the problem without losing generality, we assume that both the incident medium and the substrate have a refractive index of $n_2$. Therefore, the transfer matrix for the whole system becomes:

$$X = D(n_2)^{-1} M_0 = D(n_2)^{-1} \left( \prod_{j=1}^{N} X_j \right) D(n_2)$$  \hspace{1cm} (4.14)

$$= \prod_{x=0}^{N/2-1} D(n_2)^{-1} D(n_x) P(k_1, x_{2x}) D(n_x)^{-1} D(n_2) P(k_2, x_{2x+1})$$

Pendry demonstrated how to relate the average of the inverse transmittance to a $3 \times 3$ matrix $<X^{(2s)}>$, which is the average of the symmetric direct product of the transfer matrix $X$ with itself. One of the components of the product of $N$ such average transfer matrices is the average inverse transmittance for a stack of $N$ bi-layers. For a sufficiently large $N$, all components of this product are dominated by the eigenvalue of this matrix with the largest absolute value as well as by its eigenvector. As a consequence, a definition of the localization length can be taken to be

$$l_{loc} = P/t$$

where $P$ is the (average) period of the system or average bi-layer thickness $P = \langle n_1 x_1 + n_2 x_2 \rangle = 2n \bar{x}$ and $t = \ln \left( \lambda_{max}^{(2)} \right)$ where $\lambda_{max}^{(2)}$ is the eigenvalue of $<X^{(2s)}>$. For which $t$ has the largest real part. Therefore, the problem becomes to find out $t$, which is always a finite number.

We have calculated the $3 \times 3$ matrix $\left<X^{(2s)}\right>$ (see Appendix) assuming that the layer thicknesses have a Gaussian distribution about a mean; that is, the thickness $x$ has a mean and variance given by $\langle x \rangle = \bar{x}$ and $\langle (x-\bar{x})^2 \rangle = \sigma^2$, respectively. The averaging of the
matrices in this study requires the averaging the products of propagators through a layer. Assuming a Gaussian distribution assumption, the relevant average for calculating the propagator matrix is

\[ \left\langle e^{i2knx} \right\rangle = e^{i2kn\bar{x}} \left\langle e^{i2kn(x-\bar{x})} \right\rangle = e^{i2kn\bar{x}} e^{-2(\sigma kn)^2} \]  

(4.15)

The resultant eigenvalue equation for \( y_{max}^{(2)} \) is rather complicated and was calculated using Mathmatica®. A simplified equation that can be understood physically was obtained by substituting \( y_{max}^{(2)} = e^t \) and expanding in small \( t \), which was anticipated to be realized provided only that the difference in indices between the layers was not unexpectedly large. The result can be summarized by

\[ \left( 1 + \frac{1}{6} \left( p^2 - \kappa^2 \right) \right) t^3 + s \left( 2 - \frac{1}{2} \kappa^2 \right) t^2 + t \left( p^2 - \kappa^2 \right) - \kappa^2 s = 0 \]  

(4.16)

with the parameters \( \kappa \), \( p \) and \( s \) defined as follows. Let \( a = (n_1 - n_2) / (n_1 + n_2) \) be the fractional difference between the indices of refraction of the two layers, \( \lambda = 2\pi / k \) be the wavelength of light in the vacuum, and \( n = (n_1 + n_2) / 2 \) be the average of the refractive indices. The function

\[ p^2 = \sin^2 (2kn\bar{x}) + \frac{1}{2} \left( \frac{a^2}{1-a^2} \right)^2 \left( 1 - \cos (4akn\bar{x}) \right) \]  

(4.17)

describes deviation from the coherent addition of the light reflected by successive bi-layers of a perfect dielectric mirror with the average spacing. The function

\[ \kappa^2 = \frac{4a^2}{1-a^2} \left( \sin^2 (kn\bar{x}) \cos (2akn\bar{x}) + \sin^2 (akn\bar{x}) \right) \]  

(4.18)
describes the fraction of incident light that is reflected by a given bi-layer: approximately it is the fraction of the light intensity that would be reflected by a single bi-layer in an index matching medium. The greater the quantity index mismatch \(a\) is, the larger \(\kappa^2\) is. It is related to the localization length of the perfect photonic crystal. The quantity 
\[
s = 1 - \exp\left(-2(k\sigma n)^2\right) + O\left(a^2\right)
\]
is a measure of the effect of randomness. Eq. (4.16) is expected to give good approximation to the logarithms for all eigenvalues of this matrix, provided that the logarithms of the eigenvalues that are being calculated are small and (at least for our system) that \(sa^2\) is also small.

To understand Eq. (4.16), it is instructive to examine three cases of interest for the solution of this equation. In the region near the “center of the band gap”, we have \(p^2 << 1\), \(\kappa^2 << 1\) and \(p^2 - \kappa^2 < 0\), and the localization behavior can be deduced to be:

\[
t \sim \left[\frac{\kappa^2 - p^2}{1 + \frac{1}{6}(p^2 - \kappa^2)}\right]^{1/2} + s \left[-\frac{1 - \frac{1}{4}(\kappa^2)}{1 + \frac{1}{6}(p^2 - \kappa^2)} + \frac{\kappa^2}{2(p^2 - \kappa^2)}\right] + O\left(s^2\right) \tag{4.19}
\]

Here the first term can be obtained by ignoring randomness (e.g. the \(t^2\) and \(t^0\) terms) in Eq. (4.16). It is simply the (approximate, expanded in small \(a^2\)) localization length inside the band gap of the uniform system \((s=0)\). The second term gives the modifications due to randomness; this equation is a good approximation only if this second term is small in comparison to the first one. The negative \(O(s)\) term in this equation, which comes from the \(t^2\) term in Eq. (4.16) describes an increase in the localization length near its center because the random dielectric mirror no-longer has the ideal period to reflect (localize) the light, the positive \(O(s)\) term, which comes from the \(t^0\) term in Eq. (4.16) is a decrease in the
localization length (or decrease in this prior increase) due to increased scattering from the randomness in the stack.

In the “far from the band gap” limit $p^2 >> \kappa^2 > 0$, only the $t^3, t^0$ terms matter at first order for the relevant solution and, at the lowest order, the light is localized primarily by random scattering from ranges of layers that still scatter coherently with each other. With the first order correction, the solution for $t$ can be written as

$$t \sim \frac{\kappa^2}{p^2 - \kappa^2} s - \frac{2p^2 - \kappa^2 - \frac{1}{3} \kappa^2 (p^2 - \kappa^2)^2}{(p^2 - \kappa^2)^3} s^3 + O(s^5) \quad (4.20)$$

In order for Eq. (4.20) to be a good approximation, we need for the terms that we had ignored in Eq. (4.16) to be much smaller than the $t^1$ or $t^0$ term. The requirements can be written explicitly as the following:

$$\left(1 + \frac{1}{6} (p^2 - \kappa^2) \right) \left( \frac{s \kappa^2}{p^2 - \kappa^2} \right)^3 \ll s \kappa^2 \quad (4.21)$$

and

$$\left(2 - \frac{1}{3} \kappa^2 \right) \frac{s \left( s \kappa^2 \right)^2}{\left( p^2 - \kappa^2 \right)^2} \ll s \kappa^2 \quad (4.22)$$

which are obviously true under the condition $p^2 >> \kappa^2 > 0$.

The solution of $t$ under this limit can be understood as the ratio of weak scattering from each cell, given by the $t^0$ term, $s \kappa^2$, divided by the rate at which the scattering from successive bi-layers becomes incoherent. In this region, only this eigenvalue of the transfer matrix is given accurately by the solution to this equation; the other two (complex)
eigenvalues are typically of order unity. The first-order correction in Eq. (4.20) describes an increase in the localization length. The magnitude of this term depends largely on $p^2$ and $\kappa^2$. The dependence on $\kappa^2$ can be understood by the fact that the disorder effect weakens as the index mismatch, $a$, becomes larger, which produces a larger $\kappa^2$.

Finally, in the rather narrow range of wavelengths for which neither Eq. (4.19) nor Eq. (4.20) remains valid, we are so close to the edge of the band gap that only a full solution of the cubic would result in correct answers. The solutions can be calculated numerically using Matlab.

![Figure 4-3](image)

**Figure 4-3** The inverse of localization length for a “perfect” (solid) and “real” (dashed) disordered multilayer polymer film by calculating the largest eigenvalue of the average transfer matrix. $P$ is the average bi-layer thickness. The refractive indices used in the calculation are 1.49 and 1.585. In our real system, $4\bar{x} \sim 370 \text{ nm}$

The inverse localization length (i.e. $t/2$) of a perfect and real film as calculated from Eq. (4.16) is given in Figure 4-3, for which we used $\sigma = 0.22\bar{x}$ during the calculation. The degree of randomness was actually determined from the statistics on the multilayer film cross
section shown in Figure 4-4. The black curve represents the perfect structure and the red curve represents the “real” system randomness. This figure clearly depicts both the increased localization outside the gap and the delocalization inside the gap. Note that, outside the band gap, significant enhanced localization is observed only over a limited region near the band edges.

### 4.2.4 SIMULATION WITH A REAL RANDOM SYSTEM

The thicknesses of the layers that comprised the polymer Bragg mirrors were measured using atomic force microscopy (AFM) of the cross section; a typical cross section is shown in Figure 4-4(a). Although the multilayer film was characterized by considerable thickness fluctuations in thickness (Figure 4-4 (b)), it exhibited a clear reflection band as shown in Figure 4-5 and Figure 4-6. These fluctuations occurred as a result of the co-extrusion process, during which layer multiplication is used to make a the large number of layers [24]. The viscosities of the two melted polymer fluids were well matched by controlling their temperatures. However, remaining rheological differences, edge effects during melt spreading in the layer-multiplication dies, and path-length differences in the dies created fluctuations in the layer thickness [25].

The materials that were used for making the multilayer film were all transparent. Therefore, the photons could travel into the structure even in a high reflectance region. Light penetration into dielectric mirrors has been previously described [20, 21]. The penetration depth is related to the phase dispersion and to the reflection delay. The former relationship can be written as [22]
Figure 4-4  (a) Atomic force micrograph (AFM) of the cross section of the multilayer polymer film. (b) Statistics on the layer thicknesses. The layer thickness variation was 22%.

\[
L_p = \frac{1}{2k} \lambda \frac{d}{d\lambda} \Delta \varphi = \frac{\lambda^2}{4\pi n} \frac{\partial \Delta \varphi}{\partial \lambda}
\]  \hspace{1cm} (4.23)

where \(\Delta \varphi\) is the phase difference between the reflected and incident wave. The latter relationship is rather complicated because, in a periodic structure, the phase shift of the reflected wave is based on the superposition of the waves reflected from all of the interfaces. However, the delay can be determined by using a complex transfer matrix calculation [23]. Calculations were carried out both by assuming a perfectly periodic structure as well as by using the actual layer thicknesses as determined from the image in Figure 4-4 (a).
Figure 4-5 Transmission spectrum of “real” film (dashed) and “ideal” film (solid)

Figure 4-5 depicts the transmission spectrum as calculated for the perfect and “real” films. For the “real” film calculation, the layer thicknesses used for the calculation were extracted from the cross section of the film. Figure 4-6 (a) and (b) depict the penetration lengths that were calculated using Eq. (4.23) and the reflectance spectra for a perfect film and the actual film. It can be observed that the penetration length in the mid-band-gap region for the perfect film is less than 1 μm whereas, for the “real” film, it is between 3 and 4 μm. It should be noted here that, outside the band gap where the reflection is weak, Eq. (4.23) is invalid simply because the phase of the reflected wave is not the only factor that determines the penetration.

As can be clearly seen, the light penetration inside the band gap is related to the localization behavior in that region. Although the direct relationship between them is still
unknown, we found that a large penetration depth corresponded to a large localization length and vice versa.

Figure 4-6 Effective penetration length (dashed curves) of (a) perfect film and (b) real film calculated with the transfer matrix method. Solid curves represent the reflection spectrum.

Figure 4-7 Intensity distribution in a “perfect” 128-layer film.
Figure 4-8 Intensity distribution in a “real” 128-layer film

We can also examine the intensity distribution throughout the layers in order to verify the analysis based on the phase of the reflected wave. Again, let’s assume that there is a uniform light beam incident from the left. Using Eq. (4.11), it is easy to calculate the intensity distribution inside the films. Figure 4-7 depicts the results of our numerical transfer matrix calculations on a perfect film, and Figure 4-8 depicts a specific realization of a disordered film. In Figure 4-7, intense bands near the band edge can be easily seen reflecting the enhanced density of photonic states at the band edge. In Figure 4-8, the large intensity regions (red spots) are seen to be more localized, which reflects Anderson localization induced by the disorder on the layer thicknesses. The appearance of the localized fields outside the gap is consistent with the results depicted in Figure 4-3 except that, in Figure 4-3, average values of many systems are given.

Figure 4-9 depicts the intensity distribution across the film for the two wavelengths $\lambda_1, \lambda_2$, which are outside the band gap as denoted in Figure 4-8. It is more clearly verified in this plot because photon localization is enhanced in the presence of disorder, which appears as
narrowed peaks in the figure. The width of the intensity peak is directly related to the localization length of a system from its definition. The narrowed peak means that the localization has been strengthened and the localization length has become shorter. Thus, this calculation confirmed that there is weak Anderson localization outside the photonic band gap with the disorder presence in the photonic structure.

![Graph showing intensity against position outside the band gap](image)

**Figure 4-9** Intensity against the position outside the band gap. Solid curves: perfect structure; dashed curves: real film with disorder; Wavelength $\lambda_2$ and $\lambda_1$ have the same value as those denoted in Figure 4-8.

As we saw in the results from the phase calculation, mode delocalization occurs inside the reflection band. Figure 4-10 shows the intensity distributions across the perfect and real film at wavelength $\lambda_2$ as denoted in Figure 4-8. The intensity inside the perfect film has a perfect exponential decay whereas the decay is non-exponential in the disordered real system. The intensity inside the structure is directly related to the transitivity of the right side sub-system. Thus, using the formula (4.13) given by Pendry, we can easily notice from the plot that the localization length of the real system is longer than that of the perfect system. In the
real film, the mode penetrates further and, thus, is less localized, which is also consistent with the conclusions drawn from Figure 4-3. The phase delay calculated from the laser modes includes the phase accumulated over. There is also a non-exponential section beyond layer 60 in the real film system. In finite systems, the effects from disorder dominate if the system is small. Thus, for the sub-system that includes layers 60 to 128, the modes are more delocalized. As a consequence of this, the intensity distribution has a large decay constant. The disorder effects become less dominating when the system size increases. It eventually should behave in the same manner as has been shown Figure 4-3 if the system is infinite.

Figure 4-10 Exponential decay (perfect film, solid line) non-exponential decay(real film, dashed curve) behavior of the intensity inside the band gap ($\lambda_3$ Figure 4-8).
4.3 EXPERIMENT AND RESULTS

Here, the localization length or penetration length of the multilayer film is determined from the optical resonance of the films. By placing a gain medium inside the resonator, which actually creates a DBR laser, we can study its optical properties by measuring the emission spectra.

The lasers were produced from two 128-layer (i.e. 64 bi-layers) co-extruded polymer films and polymer core layers containing laser dyes sandwiched between the Bragg reflectors. The schematic can be found in Figure 3-1. The polymers that were used to make multilayer Bragg mirrors were poly(methyl methacrylate) (PMMA, $n=1.49$) and polystyrene (PS, $n=1.585$). The core layer consisted of Rhodamine 6G dye doped into a 30/70 blend of PMMA and poly(vinylidenefluoride-co-hexafluoropropylene) (PVDF, $n=1.4$) with a refractive index of 1.43. The core films were fabricated in various thicknesses with a dye (Rhodamine 6G) concentration of $5.4 \times 10^{-3}$M.

![Figure 4-11 Evenly spaced lasing modes in DBR lasers. Dashed curve is the transmission spectrum of the micro-resonator (laser).](image)
The output longitudinal modes from the samples were carefully recorded using an image intensified CCD spectrometer; an example has been provided in Figure 4-11. The optical setup and pump laser were described as in the previous chapter. The measurement configurations were kept the same for every sample. The red curve in Figure 4-11 is the transmission spectrum of a DBR laser. Regardless of the absorption of the dye molecule in the structure, the spectrum for the real film in Figure 4-5 agrees only qualitatively with the measured transmission spectrum in Figure 4-11 due to variations in the layer thicknesses across the surface of the film and our inability to measure the thickness at the exact spot where the lasing experiments were conducted. It should be noted that the cross section depicted in Figure 4-4 is not the actual laser mirror area but, rather, merely taken from the same film.

When lasing occurs, standing waves are formed inside the cavity. In other words, the cavity modes are enhanced by the gain medium. The FWHM of each peak (mode) is determined by the Q factor of the cavity. The FWHM measured as narrow as 0.4 nm, which was the limit of our instrument. For various core thicknesses, we observed different mode spacing, which was determined by the round trip time as related to the length of the cavity ($L_{\text{eff}}$).

$$\lambda_0^2 / \Delta \lambda = 2n_{\text{eff}}L_{\text{eff}}$$ \hfill (4.24)

The effective cavity length comprises the optical length (thickness) of the core layer, but also includes the penetration of the mode into the reflective Bragg structures.

$$L_{\text{eff}} = L_{\text{core}} + 2L_p$$ \hfill (4.25)
where $L_p$ is the penetration length. Figure 4-12 is a plot of the inverse of the mode spacing versus core thickness. Using Eq. (4.24) and (4.25), we found that the average $L_p$ was $4.8 \pm 0.3 \mu m$ with $n_{eff} = 1.39 \pm 0.04$ in reasonable agreement with the core refractive index of 1.43 especially considering that the core layer contribution to the effective index varies with core thickness as well. Because the thickness of the 128-layer film was approximately 10.8 \mu m, significant penetration of the mode into each Bragg mirror was apparent.

![Figure 4-12](image.png)

**Figure 4-12** The relationship between core-layer thickness and the reciprocal of the mode spacing. The solid line is the linear fitting.

In the transfer matrix simulation with the real film, we showed that the penetration depth of the modes in the gap region was around 3 to 4 \mu m. When comparing this to the experimental results, we found reasonable agreement in terms of the variation across the surface of the films.
4.4 CONCLUSION

In summary, we have found - both experimentally and theoretically - that the disorder that is introduced into the periodic structures causes the penetration depth to increase well inside the band gap of the corresponding perfect mirror. We have noted that the penetration into the layers within the reflection band as deduced from the phase delay reflected in the longitudinal mode spacing has, qualitatively, the same trend as photon delocalization/localization as determined by the energy distribution derived from two types of transfer matrix calculations.

We were able to observe agreement between transfer matrix theory and the experiment for disorder-induced delocalization within the band gap by studying the phase delay of the reflected wave. We were also able to quantify the disorder-induced localization outside the band gap by studying the transmission spectrum of the Bragg mirrors, and to theoretically identify three parameters that control the localization in such reflectors.

Our observations of delocalization using longitudinal modes in a laser, which we have related to Anderson localization in disordered 1D photonic crystals, opens a new experimental path for the study and measure of Anderson localization in disordered media. The internal photoluminescence and amplified luminescence is a way of injecting photons into the structure and examining localization. The disorder decreases the coherent reflections well inside the band gap of the perfect mirror, but it localizes light close to the band edge. The enlargement of the effective penetration depth as calculated by phase dispersion is the result of photon delocalization inside the band gap when disorder is introduced into the 1D
system. Our theoretical treatment has also revealed the parameters that characterize a somewhat random photonic crystal.

4.5 REFERENCES


CHAPTER 5

2D PHOTONIC CRYSTAL MADE WITH POROUS SILICON

5.1 INTRODUCTION TO 2D PHOTONIC CRYSTAL

In the previous chapters, I discussed the interesting phenomena in 1D organic photonic crystals. In this and the following chapters, I will discuss functionalized 2D photonic crystals based on macro-porous silicon.

Two-dimensional photonic crystals are periodical in two dimensions and homogeneous in the third dimension. They are usually made with long dielectric rods in air or long air holes in a dielectric background. Although there is no periodic structure in the third dimension, the size in this dimension \( h \) matters when we study the 2D photonic crystals. It is called a photonic crystal slab if \( h \) is of the order of the wavelength or the lattice constant \( a \) of the 2D
structure, where confinement in the third dimension arises from guided waves. Such structure requires 3D analysis. In our study, the size of the third dimension (>100 μm) was much larger than the lattice constant \((h>>a)\). Here, an analysis based on plane waves is suitable.

The 2D photonic crystals are important in the fundamental research or applications. Compare to 3D photonic crystals, a low-dimension photonic system is much easier to fabricate and very useful for verifying theoretical models. The application of 2D photonic crystals has been proposed in many areas, such as making photonic crystal fibers[1-4], gratings [5], edge-emitting lasers [6-9], etc.

### 5.2 PHOTONIC BAND STRUCTURE OF THE TRIANGULAR LATTICE

A typical 2D photonic crystal lattice structure is depicted in Figure 5-1(a). The basis of the Bravais lattice can be written as:

\[
\begin{align*}
\mathbf{a}_1 &= a(i\sqrt{3}/2 + j/2) \\
\mathbf{a}_2 &= a(i\sqrt{3}/2 - j/2)
\end{align*}
\]  

where \(a\) is the lattice constant and \(i, j\) are the unit vectors in the x and y directions.

Borrowing the notation from solid-states physics, we name \(\frac{2\pi}{a}(0,0)\), \(\frac{2\pi}{a}\left(\frac{1}{2}, 0\right)\) and \(\frac{2\pi}{a}\left(\frac{1}{2}, \frac{\sqrt{3}}{6}\right)\) as the \(\Gamma\), M, and K points, respectively, in the reciprocal lattice (Figure 5-1(b)).
Two-dimensional photonic crystals are characterized by periodicity in a 2D plane, for which we can apply Bloch’s theorem. According to Bloch’s theorem, the wave functions have the same periodicity as the lattice grid. Their eigenvalues as determined by $k$ can be calculated through a reduced $k$, which forms the first Brillouin zone.

The eigenmodes for the 2D photonic crystals are polarization dependent. Usually, they are classified into the TE or TM modes. In the TE mode, which is also called the E-polarized mode, the $E$ field is parallel to the dielectric cylinders (the third dimension). While for TM modes, the $H$ field is parallel to the dielectric cylinders.

Figure 5-1 (a) Triangular photonic lattice. $a_1$ and $a_2$ denote the basis of the lattice space. (b) First Brillouin zone of the triangle lattice where $b_1$ and $b_2$ denote the reciprocal vector.
5.2.1 BAND STRUCTURE (BLOCH STATES) CALCULATION

WITH MPB PACKAGE

The photonic band structure was calculated with the MPB software package (MIT Photonic Bands, the Joannopoulos Research Group, Department of Physics, Massachusetts Institute of Technology). The MPB package computes the frequency eigenmodes for a given wave vector. It performs a frequency-domain calculation using a plan wave decomposition (solving Eq. (1.16)), which is suitable for calculating the band structure and eigenmodes.

The energy contour map provides a wealth of information on how the waves interact with the photonic crystals from the long wavelength limit down wavelengths on the order of the lattice constant. The calculation of a triangular lattice is shown in Figure 5-1 as an example. The background material was silicon ($\varepsilon$=12) and diameters of the air holes were $0.6a$. Other essential parameters that were fed into MPB were, \textit{resolution}=32, \textit{num-bands}=8. MPB accepts $\vec{k}$ vectors in the basis of $\vec{b}_1$ and $\vec{b}_2$. In order to plot the contour map correctly, we must convert these vectors to the normal basis ($k_x, k_y$). The conversion is as follows:

Consider an arbitrary $\vec{k}$ ($k_1, k_2$) in ($\vec{b}_1, \vec{b}_2$) basis,

$$\vec{k} = \left( \begin{array}{c} \vec{b}_1 \\ \vec{b}_2 \end{array} \right) \left( \begin{array}{c} k_1 \\ k_2 \end{array} \right)$$

(5.3)

We know the expressions for ($b_1$, $b_2$) in the normal basis,

$$\left( \begin{array}{c} \vec{b}_1 \\ \vec{b}_2 \end{array} \right) = \left( \begin{array}{c} \vec{x} \\ \vec{y} \end{array} \right) \frac{1}{2} \left( \begin{array}{cc} 1 & 1 \\ \sqrt{3} & -\sqrt{3} \end{array} \right)$$

(5.4)

Putting Eq. (5.4) into Eq. (5.3), we have
\[
\vec{k} = (\tilde{x} \quad \tilde{y})\frac{1}{2} \begin{pmatrix} 1 & 1 \\ \sqrt{3} & -\sqrt{3} \end{pmatrix} \begin{pmatrix} k_1 \\ k_2 \end{pmatrix} = (\tilde{x} \quad \tilde{y})\frac{1}{2} \begin{pmatrix} (k_1 + k_2) \\ \sqrt{3}(k_1 - k_2) \end{pmatrix}
\] (5.5)

A triangular hole lattice on the silicon wafer was calculated using the MPB package. The geometry of the lattice is similar to the lattice in Figure 5-1(a) with the hole and background material inverted. The radius of the holes is 0.3\(a\), where \(a\) is the distance between the centers of the holes. MPB solves the energy eigenmode for each given \(k\) point. The region in \(k\)-space for calculation is \([0, 2/3](k_1) \times [0, 2/3](k_2)\), which covers both the M and K points. Notice that the triangle lattice has C6 symmetry. Thus, we need only calculate 1/6 of the \(k\)-space and then apply symmetry to generate the whole contour map. Figure 5-2 (a) shows the result of the energy contour calculation in the first Brillouin zone. From the plot, one can see that at the adjacent region of the \(\Gamma\) point, optical waves behave as they do in the free space, where circles are seen as the energy-contour plots. This occurs because the wavelength in this region is much larger than the lattice constant and the system becomes isotropic at the 2D plane. In another words, the wave in this region sees a nearly uniform structure as it propagates. As the wavelength shortens toward the edge of the Brillouin zone, optical waves interact strongly with the discrete dielectrics, an interaction that distorts the circles in the contour plot. At the M point, there is a saddle region that leads to a wide band gap. This can be seen more clearly in Figure 5-2 (b). Note that the vertical axis is the ratio of the lattice constant to the wavelength. It is also equivalent to a frequency axis whose unit is \(2\pi c/a\). In the \(\Gamma M\) direction, there is a band gap extending from 0.18 to 0.27. Changing the incident direction of the light toward the \(\Gamma K\) direction, we can see that the band gap becomes narrower and shifts toward higher frequency or shorter wavelengths. The second and third bands have an intersection point at the K point.
Figure 5-2 The TE band structure of the triangular lattice, $r=0.3a$. (a) Energy contour plot in the first Brillouin zone. The M point is a saddle point. (b) The first 4 photonic bands of the triangular lattice. The first band gap appears between 0.18 and 0.27 in the ΓM direction.

The lower energy side of the band gap, which is near the edge of the Brillouin zone, is usually called “dielectric band” because the electric field is concentrated in the high refractive index region. The higher energy side of the band gap is called “air band” because the field is concentrated in the lower refractive index region. For example, the distribution of fields at $M_1$ and $M_2$ is very different even though they have the same wave vector. For higher bands, similar distribution of fields can also be found, but the difference between the dielectric band and the air band becomes less distinct because the wavelength is shorter than the lattice constant.

The structure of the TM bands of the triangular lattice is different from that of the TE bands. As shown in Figure 5-3, the first and second band of the TM waves (dashed black and red) always intersect at the K point. As the ratio between the air hole radius and lattice constant increases,
constant increases, a gap between the second and third TM bands appears. In addition, the primary band gap of the TE modes widens. Eventually, with a large enough dielectric contrast, these two band gaps can overlap where the light is forbidden to propagate regardless of its polarization and direction. The band structure for $a/r=0.45$ is shown in Figure 5-3.

![Band structure diagram](image)

Figure 5-3 Illustration of an all-photonic band gap in a 2D triangular lattice of porous silicon. $r=0.45a$. The solid curves are the TE bands and dashed curves are the TM curves. Frequencies from 0.40 to 0.43 (shaded) are all forbidden in the lattice regardless of their direction and polarization.

### 5.2.2 REFLECTION BAND MEASUREMENT BY FTIR

The FTIR (Fourier Transformed Infrared spectroscopy) is a common technique used to measure spectra in the infrared region. It is a fast and precise measurement of a spectrum using a broad band light source. By varying the time delay, which corresponds to varying phase delays at different wavelengths, one can obtain the temporal response in one scan. The Fourier transform of the temporal response yields the entire spectrum.
The schematic of the setup for measuring the porous silicon sample is actually a microscope that interfaces to an FTIR spectrometer (Figure 5-4(a)). In contrast to a conventional optical microscope, the objective lens is replaced by a curved reflective mirror, which has no dispersion effect on the broad band infrared light. A rectangular aperture inside the microscope selects the region of interest in the sample image.

Figure 5-4(b) is a typical FTIR measurement result of a porous silicon sample with a lattice constant of 2 μm and pore radius of 0.6 μm. The data shown is taken in the TM direction using TE-polarized light. A reflection band from 6.8 μm to 10.4 μm that corresponds to the primary band gap \( (a/\lambda = 0.18 - 0.27) \) of the 2D photonic crystal can be clearly seen.

![Figure 5-4 FTIR measurement of a porous silicon sample. (a) Schematic drawing of the FTIR microscope. (b) Typical results of the reflection spectrum of a 2D porous silicon. The measurement scheme is shown in the insert. The directions of incident and polarization were TM and TE respectively. The primary reflection band for this sample was from 6.7 μm to 10.4 μm.](image-url)
5.3 FABRICATION OF POROUS SILICON

Electrochemical etching that was used to fabricate the porous silicon membrane has two main steps. The first step is photolithography (patternning), and the second is infrared-light-assisted electrical-acid etching. Details of the fabrication process can be found in [10, 11].

5.3.1 MATERIAL

Silicon is a semiconductor that is characterized by an indirect band gap of 1.1 eV, which corresponds to a band edge at a wavelength of about 1.1 μm. Thus, silicon absorbs photons that have energy more than 1.1 eV (i.e., wavelength shorter than 1.1 μm) while transmitting photons that have energy less than 1.1 eV so that silicon is transparent in the infrared region. Silicon also has a high dielectric constant, $\varepsilon \approx 12$ ($n \approx 3.46$). Good optical properties in the infrared region make silicon a good candidate for making photonic crystals in the near- and mid- infrared region.

Many advanced techniques for fabricating photonic devices on silicon wafers have been developed because of their enormous success in the silicon industry. Electrochemical etching is one of them. This technique requires that the material be conductive, which is true for lightly doped silicon. In our case, n-type silicon wafers (doped with phosphorus at $10^{15}$ cm$^{-3}$ concentration) were chosen as the substrate for growing 2D periodic pores.
5.3.2 PHOTO PATTERNING (STANDARD LITHOGRAPHY)

Prior to undergoing electrochemical etching, the silicon wafer was patterned by standard photolithography. A layer of positive photoresist was spin coated on top of the wafer. Masked with a predesigned pattern (triangle lattice), the wafer was exposed to ultra violet (UV) light for a specific amount of time in order to selectively change the solubility of the photoresist. The part of the photoresist that had been exposed to the UV light became soluble in the photoresist developer. After being treated by the photoresist developer, the wafer was coated with a patterned photoresist.

After the pattern was developed, alkaline (NaOH or KOH are often used) etching of silicon was performed on the silicon wafer. Hillock-shaped pores were developed (Figure 5-5) in the unprotected silicon region. The photolithography process was stopped after the all of the hillock-shaped pores had been developed.

In our project, patterns with a triangular lattice and a lattice constant of 2 \( \mu m \) were used. The size of the pores was around 1.2 \( \mu m \).

![Figure 5-5 The first step of alkaline etching of silicon which creates a tip at the pores.](image-url)
5.3.3 ELECTROCHEMICAL ETCHING

After the first etching step, the wafer was imparted with a desired pattern. The second step of the etching process was electrochemical etching, which continued the etching along the direction of the hillock-shaped tip and, finally, formed long, straight pores on the wafer. A schematic drawing of the electrochemical etching setup is shown in Figure 5-6 (a). The top of the wafer was covered by aqueous acid HF, which was connected to a negative electrode; the bottom of the wafer had an electrode that was connected to the positive bias. A steady current between the wafer and the acid solution was driven through the circuit by applying a bias between the negative and positive electrodes. The wafer was illuminated with a uniform infrared light that helped to generate electron-hole pairs inside the wafer.

The generated charges (holes) were collected at the end of the pore tips because of the geometry of the pores. The dissolution process was favored in high-density regions of positive charges (i.e., holes). Thus, the tips of the pores were much easier to be dissolved by the acid than were the walls. It is important that all generated holes should be consumed in the etching reaction at the pore tips; otherwise the remaining holes will penetrate the walls between the pores. The maximum flow of current in the electrolyte limited the etching speed. Furthermore, the charge transfer speed depended on the ion concentration (pH value), temperature, and diffusion coefficients.

By carefully controlling the illumination, and current density, one can etch deep, straight and uniform pores (Figure 5-6(b)). Lehmann [10] has demonstrated that all pore tips can be in a steady-state condition of maximum mass transfer related to the current density. Thus, it is the photo-generation of holes not the applied bias that determines the current. This is
helpful in controlling the etching process. The depth of the holes is determined by the etching time and current. Typically, samples of 100 μm to 200 μm straight deep holes can be easily produced (Figure 5-8 (b)).

Figure 5-6 Electrical chemical etching. (a) Schematic setup. (b) Sample with long pores (pores were filled with dyes.).

5.4 INFILTRATION OF ORGANIC MATERIALS

Porous silicon can be considered to be a new type of artificial optical material that has a specially designed photonic band structure. Such a structure only exhibits a linear response to incident light. One can use this new type of material to make linear optical components, such as Bragg reflectors, photonic crystal fibers, etc.

To expand the application of these materials, functional materials can be added to the photonic crystals. Nonlinear optical materials, in which the index of refraction depends on the beam intensity, can produce structures of importance in optical communication, signal
processing and computing [12, 13]. This Kerr nonlinearity of the material can help realize all-optical switching.

In our project, we infiltrated nonlinear optical materials into the porous silicon to make a photonic crystal device.

### 5.4.1 ORGANIC MOLECULES

There are two requirements for the organic molecules that were used to make optical switches. First, the dye should have good thermal stability and be melt processable as is necessary for the infiltration process. Second, the dye should have large Kerr nonlinearity.

Organic dyes can have substantial third-order resonant nonlinearity, especially at their resonance [14]. Three dyes (1,4-bis-(α-cyano-4-methoxystyryl)benzene (C1-YB), Cruciform and ethylhexyl indole Squaraine) were selected for the project. Figure 5-7 shows their chemical structures.

### 5.4.2 THE MELT-INFILTRATION PROCESS

To infiltrate pores with the material, the material should be in a liquid state using melt infiltration. In this project, the material was heated above its melting temperature and cooled down after filling all the pores.

First, the organic material was placed on top of the porous silicon. Next, the whole sample was heated slowly above the melting temperature of the organic material on a hot
stage. The melted material was drawn into the pores by capillary action. Both the organic materials and the silicon are hydrophilic; therefore the interfaces were wetted as can be seen from the SEM micrographs (Figure 5-6 (b), Figure 5-8). After a few minutes of flow at the elevated temperature, the sample was cooled down to room temperature slowly.

Figure 5-7 Chemical structure of (a) C1-YB, (b) Cruciform, (c) EHO-ISQ (Squaraine)
Figure 5-8 SEM picture of infiltrated sample. The cross section view shows that the pores are filled with organic dye.

AFM (Atomic Force Microscopy) and fluorescence microscopy were conducted to verify the infiltration of the organic materials. Figure 5-9 shows a comparison between the empty sample and the infiltrated sample. As seen from the AFM images, most of the pores were successfully infiltrated with the organic materials.

After the sample being cooled down to room temperature, it was cleaved with a diamond cutter to expose the regions of best infiltration in the middle of the wafer. The well-defined edge of the sample can be easily seen in the SEM images. The cutting was usually along the ΓK direction. Therefore, the light coupled at the normal direction of the interface was in the ΓM direction.
Figure 5-9 AFM topography of (a) the empty porous silicon and (b) the sample after infiltration. (c) is the profile at the cross-section that is marked with dashed line in (b).

5.4.3 FTIR MEASUREMENTS

Another way to confirm that the pores have been filled with the dye is to look at the reflectance behavior of the infiltrated sample. The refractive indices of the organic material are usually around 1.5. Thus, after infiltration, the contrast of the refractive indices of the photonic lattice changed roughly from 3.46:1 to 3.46:1.5. The photonic band structure and the reflection behavior changed as a consequence of the contrast change. FTIR measurements were carried out to verify the changes. Figure 5-10 shows the comparison between the reflection behavior of the infiltrated and empty samples. The polarization and direction of the incident light were TE and TM, respectively. Calculation of the photonic band structure shows that the air band was most affected. The ratio $a/\lambda$ at $M_2$ should have changed from 0.29 to 0.25, which corresponds to wavelength from 6.7 to 8.0 μm. The measurement indicated a short wavelength band edge of 7.3 μm.
The difference between the theory and experiment suggests that there might be air bubbles that were trapped inside the pores or that the refractive index of the dye was less than 1.5 in the region near the reflection band.

5.5 CONCLUSION

Photonic crystals in 2D systems have been described. Such 2D photonic crystals are relatively easy to fabricate with good tailorability of the photonic band structure. A triangular lattice in silicon can be constructed to exhibit a complete band gap; in this gap, light at any direction and with any polarization is unable to propagate inside the photonic crystal.

Electrochemical etching is a powerful method that has been developed over the past few decades and can now be used to create 2D photonic crystals on silicon wafers; this makes it possible to fabricate photonic devices on a chip. Hybrid organic photonic crystals were fabricated by infiltrating organic molecules into the pores of macro-porous silicon. Using material with large Kerr nonlinearities, one can make optical switches and other all-optical devices. To verify the success of the electrochemical etching, infiltrated samples were studied using SEM, AFM, and FTIR techniques. All of these techniques indicated that most of the pores had been successfully filled with target materials.
Figure 5-10 Comparison of the reflection behavior of the infiltrated and empty porous silicon. The solid curve represents the empty porous silicon, and the dashed curve represents the infiltrated sample. The direction and polarization of the light were \( \Gamma M \) and \( TE \), respectively.

### 5.6 REFERENCES


CHAPTER 6

DYNAMIC PHOTONIC BAND GAP

TUNING

6.1 INTRODUCTION TO OPTICAL SWITCHING

In many applications, the ability to control the flow of the light is necessary or desirable. Such functions always require optical switches. Optical logic devices, which are a kind of optical switch, are key elements for optical computing systems. Some features of these devices that are worthy of mention include size, switching time, and sensitivity.

A mirror or a beam-blocker may be the first examples of optical switches that come to mind. A more complicated and widely used optical-switching scheme is electro-optical switching. Applications that use electro-optical switching include liquid crystal displays, projectors, and optical communication devices. The interactions between the material and electric fields are the key to these devices. For example, in liquid crystal displays, an electric
field is used to control the alignment of molecules, which are usually in the nematic phase. The switching speed in a common display is typically a few milliseconds.

Higher speed switches would open up new applications. The speed of electro-optic switches are limited by the electronic (circuit) responses. The inductance and capacitance of the circuit are the major factors that limit the response speed to just below a nanosecond.

All-optical switches offer a potential alternative for high speed switching devices. All-optical switches do not have electrical circuits that are limited by circuit response, which exists in the electro-optical switches. There is general consensus among researchers that all-optical switches will be the fastest elements for future computing technology. In most cases, an all-optical switch has two parts: a resonant structure and active material. In all-optical switching, an important factor that is worthy of consideration is the photon-medium interaction, which essentially affects how fast the material can respond to a change in the external field or the control signal. Fortunately, the nonlinear optical response is very fast [1] because it arises from electron motion. Hypothetically, all-optical devices will have two advantages over traditional electronic devices: ultrafast switching and lower power loss.

In the past, a great deal of research focused on optical switching in optical fibers [2, 3]. However, photonic crystals provide a novel way of controlling the propagation of light [4] with greater tailorability. Silicon photonic crystals could enable the integration of many switches on one chip, a concept that poses numerous opportunities for the future of optical communications [5]. Research on tunable photonic crystals made by infiltrating liquid crystals into porous photonic structures has been reported [6-9]. Unfortunately, the molecular reorientation process used in those experiments has a relatively slow response time - in the
nanosecond range. Leonard and van Driel et al. studied empty 2D silicon photonic crystals using a femtosecond laser to induce a nonlinear response from the silicon [10, 11]. A fast response was observed at a relatively low pumping level at which the contribution from free carrier generation is suppressed.

In this chapter, I will discuss a method for making an optical switching device using an infiltrated 2D silicon photonic crystal that requires lower pumping power. Organic material with a large Kerr nonlinearity was incorporated into the photonic crystal structure and worked as the active material. A mid-IR pump-probe experiment was used to detect the optical switching effect.

6.2 PHOTONIC CRYSTAL BASED OPTICAL SWITCHING DEVICES

As discussed in the previous chapter, 2D photonic crystals have a photonic band gap that is determined by the refractive indices that comprise the periodic structure. Without changing the lattice grid arrangement, the band structure of a 2D photonic crystal changes if the refractive indices of the materials change. This can be verified by looking at the reflection band shifts after infiltration of the organic molecules. The previous chapter also discussed how the “air band” is affected to a greater extent when the low-refractive-index material undergoes index changes because of the field distribution.
6.2.1 PHOTONIC BAND STRUCTURE

Figure 6-1 (a) shows the TE-band structures of a triangular lattice \((r/a=0.3)\) for different pore dielectric constants \((\varepsilon_{\text{pore}})\). The dielectric constants used for the calculation were 1.00 (dashed curve), 2.25 \((n=1.5)\), 2.26, 2.27 and 2.28 (solid curves). As shown in the figure, both the high- and low-energy sides of the first band gap shifts down as the \(\varepsilon_{\text{pore}}\) increases. It can be clearly seen that the edge of the “air band” changes much more than the “dielectric band” does when the \(\varepsilon_{\text{pore}}\) changes from 1.0 to 2.25.

![Figure 6-1 (a) First and second bands of a triangular lattice with \(r/a=0.3\). Dielectric constants 1.00 (dashed curves), 2.25, 2.26, 2.27 and 2.28 (solid curves) were used for the pore. (b) Close-up of the region marked with a green box in (a).](image)

To quantitatively study the shift, we can define the sensitivity of the shifting of the second band at M point as \(\Delta(a/\lambda)/\Delta\varepsilon\). The sensitivity can be determined by numerically calculating the derivative. In Figure 6-1 (b), which is a close-up of the second band at the M point, four calculations with different dielectric constants \((\varepsilon_{\text{pore}}=2.25, 2.26, 2.27, 2.28)\) are
shown. From the calculation, we found that $\Delta(a/\lambda)/\Delta \varepsilon = -0.018$ for the TE modes and $(r/a=0.3)$. The minus sign signifies that the gap becomes smaller as the dielectric constant increases. The primary band gaps of the configurations are all located between $8.1 \mu m$ and $11 \mu m$, if the lattice constant $a=2 \mu m$.

Figure 6-2 Band structure for the TM modes, $r/a=0.3$, $\varepsilon_{pore}=2.25$. In the $\Gamma M$ direction, the first gap appears between the first and second bands. The second gap appears between the fourth and fifth bands.

Figure 6-2 shows the band structure of TM modes. There are two band gaps in the $\Gamma M$ direction. One appears between the first and second bands ($11.3 \mu m$, $9.8 \mu m$ for $a=2 \mu m$) and the other appears between the fourth and fifth bands ($5.4 \mu m$, $4.87 \mu m$ for $a=2 \mu m$). Using the same definition and method above, we can also numerically calculate the sensitivity of the band edge shift as $\varepsilon_{pore}$ varies. For the second band at M point, we found that
\[ \Delta(a/\lambda)/\Delta\varepsilon = -0.004 \], and for the fifth band at M point, we found that \[ \Delta(a/\lambda)/\Delta\varepsilon = -0.008 \].

From the results of the numerical calculations, we found that the TE waves are the best for detecting the change of \( \varepsilon_{\text{pore}} \). The probe light is in the \( \Gamma M \) direction. Unfortunately, the probe wavelength must be near the primary band gap, which is not favorable for the nonlinear response of the molecule (see the following section) because of the mismatch between the photonic crystals and the materials’ resonances. Because it has the same lattice constant, the second gap of the TM mode lies close to the near infrared region, where the nonlinear response of the material would be favored.

Similar calculations can be done on the sensitivity of the band-edge shift in relation to the change of the dielectric constant of the background material (silicon, \( \varepsilon=12 \)). The results are:

**TE mode:** \( \Delta(a/\lambda)/\Delta\varepsilon = -0.006 \) (2\(^{\text{nd}}\) band)

**TM mode:** \( \Delta(a/\lambda)/\Delta\varepsilon = -0.008 \) (2\(^{\text{nd}}\) band), \( \Delta(a/\lambda)/\Delta\varepsilon = -0.019 \) (5\(^{\text{th}}\) band)

### 6.2.2 OPTICAL SWITCHING

Each photonic band gap corresponds to a highly reflective spectral region. If the band gap changes, the reflectivity and transmissivity spectra change accordingly. I have just discussed how the edge of the bands shift when there is a change in the dielectric constants of the materials that constitute the photonic crystal. The reflection of the light near the edge of the band gap will change dramatically because of the shift of the edge. Thus, if we can control
the refractive index of the material, we can control the amount of light being reflected at the edge of the reflection spectrum.

The goal of an all-optical switching device is to manipulate the light that passes through it. In our experimental scheme, we looked at the reflected light from a 2D photonic crystal. By design, we wanted the reflected light to be turned on/off by another beam of light, which would control the reflection band of the photonic crystal by dynamically changing the refractive index of the nonlinear material in the pores.

The dynamic band-tuning effect can be probed by having a second (probe) beam incident at the same region as the control (pump) beam illumination. The desired effect the on the probe beam is a change of intensity of the reflected light. In the ideal case, which is shown in Figure 6-3, we can calculate the signal sensitivity based on a few reasonable assumptions. Assume that the reflectance changes from 1 to 0 or 0 to 1 at the band edge. Therefore, approximately half of the light is reflected back from the sample for the configuration in Figure 6-3. Let’s also assume that the refractive index of the dye is 1.5 (\( n_{\text{dye}}=1.5 \) (\( \varepsilon=2.25 \))) and the lattice constant is 2 \( \mu \text{m} \).

In nonlinear optics, the refractive index can be a function of the external field if a third-order nonlinearity is present. The response of the third order nonlinearity (optical Kerr effect) is very fast. The change of refractive index \( \Delta n \) is linearly proportional to the intensity of the light,

\[
\Delta n = n_2 I
\]  

(6.1)
where $n_2$ is the nonlinear refractive index. The refractive index is the square root of the dielectric constant $n = \sqrt{\varepsilon}$; it is easy to relate the change of the refractive index to the change of the dielectric constant.

In this experiment, we fabricated 2D photonic crystals, which had a triangular lattice, on silicon substrates as discussed in the previous chapter. Nonlinear optical materials were melted and infiltrated into the pores. The active material (nonlinear optical material) changes its dielectric constant under high-intensity illumination when the change is proportional to the Kerr coefficient and the illumination intensity. The change of $\varepsilon_{\text{pore}}$ that can result in a change of the reflectivity of the photonic crystal is of interest. To calculate the ideal signal response in this experiment, I will assume that there is a 0.01 change on the dielectric constant of the active material.

![Figure 6-3 Band tuning illustration. Red and green lines are the reflection bands before and after tuning.](image)

The quantity we were interested is how much the band edge shifts:
\[
\frac{\Delta(a/\lambda)}{\lambda^2} = -a\Delta\lambda/\lambda^2
\]  
(6.2)

With a small change of the dielectric constant, \(\Delta\varepsilon_{\text{pore}} = 0.01\)

\[
\Delta\lambda = -\frac{\lambda^2}{a} \frac{\Delta(a/\lambda)}{\Delta\varepsilon} \Delta\varepsilon_{\text{pore}} = 6 \text{nm}
\]  
(6.3)

According to the uncertainty principle, an ultrafast light pulse has a much larger band width than does a CW or nanosecond laser. Usually, the temporal profile of a short pulse is very complicated. Fortunately, it can be approximated in its ideal form as a Gaussian distribution. It is known that the frequency bandwidth is inversely proportional to its time duration (i.e., width of the temporal profile). Its spectral width is, thus, proportional to the center wavelength. The laser that was used in this experiment had a temporal width of 100 fs and a spectral width of about 10 nm at 800 nm. Therefore, for the probe light at 8 \(\mu\)m, the spectral width is calculated to be around 100 nm, which corresponds to a frequency bandwidth of \(\sigma_{\omega} = 2.2 \times 10^3\) GHz.

Assume that the center of the spectrum of the probe light is at the edge of the reflection band (Figure 6-3). Let \(\lambda_0\) be the center of the spectrum, \(2\sqrt{\ln 2}\sigma = 100\) nm be the FWHM (full width half maximum), \(\lambda_t\) be the band edge after the refractive index is changed by the external field and \(\Delta r\) be the change of reflectivity from band to band gap (\(\Delta r_{\text{max}} = 1\)). Then

\[
S = \frac{\Delta I}{I} \approx \frac{(1 + \exp(-((\lambda_t - \lambda_0)^2 / \sigma^2))) \Delta\lambda\Delta r}{\sigma\sqrt{\pi}}
\]  
(6.4)

Thus, the maximum response, \(S_{\text{max}}\) is approximately 16% if there is a 0.01 change in the dielectric constant of the active material inside the pores. It should be pointed out that \(S_{\text{max}}\) is approximately linear to the change of \(\varepsilon_{\text{pore}}\) for small \(\varepsilon_{\text{pore}}\). Therefore, the change on the reflected light should be linearly proportional to the intensity of the pump light.
6.2.3 NONLINEAR MATERIAL

Organic materials can have a large nonlinear response because of the large collection of electrons and the rich optical spectrum. For the same reason, it is difficult to accurately calculate the nonlinear response of molecules. The Lorentz model (2-level or 3-level) is commonly used to model the dispersion. We developed and tested several molecules in order to find the most suitable molecules for optical switching; measurements at specific wavelengths along with the Lorentz model were used to estimate the nonlinear response at other wavelengths.

6.2.3.1 THE LORENTZ MODEL

The nonlinear response of a molecule can be approximated using perturbation theory in which the external electromagnetic field is treated as the perturbation. In general, the complete expression for the dispersion of the nonlinear susceptibility $\chi^{(n)}$ is complicated. However, near a specific resonant frequency, the response due to the nearby resonance dominates the value of $\chi^{(n)}$; therefore, the two-level Lorentz model can adequately approximate the dispersion. When the frequencies are far from the resonance, this model usually overestimates the nonlinear response. In our system, we were interested in the dispersion property of the Kerr response, which is the real part $(\chi^{(3)}(-\omega_4;\omega_1,\omega_2,-\omega_3))$. In the experiment, there were two frequencies of light (pump and probe). Thus, we can write $\chi^{(3)}$ as:
\[ \chi^{(3)}(-\omega_1, \omega_1, -\omega_2, \omega_2) \propto \left( D(\omega_1 - \omega_2) + D(\omega_1 + \omega_2) + D(-\omega_2 + \omega_1) \right) D(\omega_1)D(\omega_1)D(-\omega_2)D(\omega_2) \]  

(6.5)

where, \( D(\omega) = \frac{1}{\omega_0^2 - \omega^2 - i\Gamma \omega} \), \( \omega_0 \) is the resonant frequency and \( \Gamma \) is the damping coefficient.

Both \( \omega_0 \) and \( \Gamma \) can be determined from the linear absorption spectrum. The Z-scan experiments were used to determined the degenerate nonlinear susceptibility \( \chi^{(3)}(-\omega;\omega,\omega,-\omega) \) (related to \( n_2 \)). In this case, Eq. (6.5) becomes,

\[ \chi^{(3)}(-\omega, \omega, -\omega, \omega) \propto (D(0) + D(2\omega) + D(0)) |D(\omega)|^2 D(\omega)^2 \]  

(6.6)

At resonance \( \omega_0 = 2\omega \), the real part of the denominator of \( D(2\omega) \) vanishes; only the imaginary part remains. Therefore, the Kerr effect at the resonance is close to zero and the two photon absorption reaches its maximum. We will see in the following calculations that the dispersion of the Kerr nonlinearity actually has both a peak and a valley on both sides of the resonant frequency. In the off-resonance region, both \( \omega_1 \) and \( \omega_2 \) are small compared to \( \omega_0 \) and the damping effect \( i\Gamma \omega \) is then becomes negligible. Therefore, the imaginary part of \( \chi^{(3)} \) given by Eq. (6.5) is almost zero, and the real part of the \( \chi^{(3)} \) is inversely proportional to \( \omega_0^6 \), which is constant for a particular molecule.

### 6.2.3.2 C1-YB

Figure 6-4 (a) shows the linear absorption spectrum of the C1-YB dye. The Lorentz absorption model can be used to fit the absorption peak. From the fitting, we can extract the resonant frequency and the damping coefficient. For C1-YB, we have \( \omega_0 = 3.16 \) eV (~ 380 nm) and \( \Gamma = 0.33 \) eV.
Plugging the parameters from the fitting into the nonlinear Lorentz model, the degenerate $\chi^{(3)}$ (Figure 6-4(b)) and the non-degenerate $\chi^{(3)}$ (Figure 6-5) can be calculated. The measured absorption peak of C1-YB was around 390 nm; therefore, the nonlinear resonance was expected to appear at the twice of the absorption peak (~780 nm) for the degenerate situation. In fact, open aperture Z-scan measurements of C1-YB near this wavelength showed that it had a large two-photon absorption coefficient.

**Figure 6-4** (a) Linear absorption of C1-YB dye. The solid curve is the fitting with Lorentz model. (b) The calculated real part of the degenerate $\chi^{(3)}$ for C1-YB dye.
Figure 6-5 Dispersion behavior of the real part of $\chi^{(3)}$ for C1-YB dye. The black curve shows the dispersion of the fixed probe wavelength (7.8 µm). Blue, red, and green curves show fixed pump light wavelengths for 1.25, 1.44 and 1.80 µm respectively.

Figure 6-5 shows the dispersion behavior of Re($\chi^{(3)}$) calculated with the Lorentz model using the parameters given by the fitting of the linear absorption curve. Both fixed pump and fixed probe wavelengths (used in the pump probe experiment) were used in the calculations. The peaks of the curves were different and all appeared in the visible range. However, in the near infrared region (off resonance), all of the peaks are nearly equal. Because the molecule has a wide absorption peak, the resonant peak was also wide.

### 6.2.3.3 SQUARAINE

Figure 6-6 shows the linear absorption spectrum of the Squaraine dye. The Lorentz absorption model was used to fit the absorption peak. The fit parameters gave us $\omega_0=1.88$ eV, $\Gamma=0.036$ eV.
The degenerate (Figure 6-6 (b)) and non-degenerate (Figure 6-7) $\text{Re}(\chi^{(3)})$ were calculated by plugging these numbers into the nonlinear Lorentz model. The nonlinear resonance of the Squaraine dye appears at around $1.3\mu$m for the degenerate situation. From the curve, we can see that $\text{Re}(\chi^{(3)})$ changes sign at the nonlinear resonance.

The important information we want to get from the calculation is the ratio between the degenerate nonlinear response and the non-degenerate nonlinear response. In order to determine the absolute value of the molecules at any wavelength, nonlinear measurements were carried out to scale the curves. The Z-scan measurement gave $-2.7 \times 10^{-2}$ cm$^2$/GW at $1\mu$m. Using this number, we can estimate the off-resonance response of the non-degenerate $\chi^{(3)}$ to be at the order of $10^{-2}$ cm$^2$/GW. That is to say, to induce a change of 0.01 on the refractive index, we need a beam intensity of 1 GW/cm$^2$.

**Figure 6-6 (a)** Linear absorption of Squaraine dye. The solid curve is the fitting with Lorentz model. **(b)** Calculated real part of degenerate $\chi^{(3)}$ for Squaraine dye.
Figure 6-7 The real part of non-degenerate $\chi^{(3)}$ for Squaraine dye. The black curve shows the dispersion of the fixed probe wavelength (7.8 µm). Blue, red, and green curves show the fixed pump light wavelength for 1.25, 1.44, and 1.8 µm respectively.

When comparing Figure 6-5 and Figure 6-7, we can see that Re($\chi^{(3)}$) of the Squaraine dye has a much narrower resonance peak. According to both the theoretical calculation and the experimental measurements, a narrower peak implies a higher absolute peak value. In the off-resonance region, the Re ($\chi^{(3)}$) of the four different calculations differ considerably. The nonlinear coefficient Re($\chi^{(3)}$(7.8 µm;7.8 µm, ω, -ω)), which is related to the pump-probe measurement, appears to be the smallest.
6.3 INFRARED PUMP-PROBE EXPERIMENTS

6.3.1 THE PUMP-PROBE EXPERIMENT

The pump-probe experiment has been widely used to determine the dynamics of a system [12-14]. In a pump-probe experiment, a beam of pump light (photon) excites the material into an intermediate state first; next, a beam of probe light is directed to the same spot in order to detect the change induced by the pump light. In our project, we employed the pump-probe technique to measure the optical switching effect in a 2D photonic crystal. In our experiment, the pump light was near infrared light and the probe light was middle infrared light.

A Ti:Sapphire regenerative amplifier (Quantronix Integra) laser was used as the original light source. It generates 800 nm, 100 fs laser pulses at a 1 kHz repetition rate. For the experiment, each pulse had energy of around 2.4 $\mu$J. The output was halved; each half pumped a passive laser, TOPAS (travelling optical parametric amplifier system). One of the TOPAS units (UV-VIS TOPAS) was used for producing the pump light and another one (MID-IR) was used for producing the probe light. The different output ranges of the two TOPAS provide the ability to choose different combinations of pump and probe lights. UV-VIS TOPAS has a tuning range of 260 nm to 2600 nm. MID-IR TOPAS has a tuning range of 1100 nm to 12000 nm.

The pump and probe beams have the same pulse repetition rate as the Ti:Sapphire regenerative amplifier. A chopper was used to modulate the pump beam. The modulation frequency was exactly half of the laser repetition rate; that is, the chopper blade blocked every other pulse. The reflected probe light was directed into an HgCdTe (MCT) detector.
Germanium windows were used to block the scattered pump light. As shown in Figure 6-8, two lock-in amplifiers, operating at different frequencies, were used to analyze the signal. Lockin-1 locked at the repetition rate of the laser pulse \( f \) (i.e., 1 kHz). Lockin-2 was synchronized to the chopper, which locked at the half frequency of the laser repetition rate (i.e., 500 Hz). Therefore, lockin-1 yielded the average of the signal over time, and lockin-2 acquired the signal that corresponded to the pump-induced effect (i.e., the change of the reflectivity).

![Figure 6-8 Schematic of signal detection in the pump-probe experiment](image)

Using the same laser system and setup, the temporal response of the setup (the time resolution in the phenomena that has been observed) was checked by observing the sum frequency generation (SFG, second-order nonlinearity) in a BBO crystal. The SFG in the BBO crystal can be considered as an immediate process. Figure 6-9 gives the SFG signal versus the time delay between the pump and probe arm. Thus, from the data, we can conclude that this setup can resolve 0.2 ps.
Two different pump-probe schemes were used to measure the optical response of the samples: the parallel pump-probe and the orthogonal pump-probe.

![Graph showing sum frequency generation](image)

**Figure 6-9** Sum frequency generation from the BBO crystal using the same laser system that represented the temporal resolution of the setup.

### 6.3.2 PARALLEL PUMP-PROBE

The experiment layout for parallel pump-probe scheme is shown in Figure 6-10. Because the pump and probe lights are invisible, a collinear He-Ne laser (red, 632 nm) was added (not shown in the layout map) to help align the optics. Two polarizers and a half-wave plate in the pump arm were used to adjust the power of the pump beam continuously without changing the optical delay or the alignment of the pump light. The CM1 and CM2 mirrors formed a telescope, which was used to fine tune the focus and the delay of the pump beam. In the probe arm, a delay line was constructed with two mirrors mounted on a linear translational stage. This was used to change the temporal overlap of the pump and probe lights. A
removable polarization switch, consisting of two orthogonal mirrors, was placed in the probe arm as well. The pump and probe beam were brought together by a parabolic mirror PM1.

Figure 6-10 Edge pump-probe experiment layout. Two TOPAS were pumped by Quantronix Integra (not shown). The red line represents the trace of the pump light. The blue line represents the trace of the probe light. A chopper, two polarizers, and a half wave plate were put in the pump arm. Optical delay line was put in the probe arm.

Figure 6-11 Edge pump-probe scheme. The xyz reference frame is the lab frame.
Figure 6-11 shows the scheme of the pump-probe overlap on the sample. Both of the pump probe beams were incident on the edge of the silicon wafer. The sample was tilted slightly so that the reflected probe light was slightly lower than the incident probe beam. Therefore, a mirror could be used to redirect the reflection into a detector.

The sample holder is shown in Figure 6-12. The sample was mounted on the holder using double-sided tape. The direction of the pores and the ΓM direction (incident direction of the probe light) of the sample were in the horizontal plane. The direction of the pores was along the Y axis in the lab reference frame. The sample holder had freedoms of rotation, tilting and translation, which were very helpful for aligning the samples and locating the area we were interested in.

![Sample holder and stage for the 2D photonic crystals.](image)

Figure 6-12 Sample holder and stage for the 2D photonic crystals.

### 6.3.2.1 EXPERIMENT RESULTS

Before running the mid-IR pump-probe experiment, the zero time delay between the pump and probe was determined by looking at SFG of the near IR outputs of the two TOPAS using
a BBO crystal (1 mm thick). Light of 1300 nm wavelength light was always used because the sum frequency was 650 nm which is visible.

Pump-probe measurements of empty samples and functionalized samples (with C1-YB, Cruciform and Squaraine) were performed. Two polarizations (vertically polarized and horizontally polarized) of probe light were used to effectively couple to the various bands. Different polarizations of the pump light were also tried but no difference was observed. In our 2D photonic crystal, the H-polarized light was the TM wave and the V-polarized light was the TE wave. Thus, V-polarized light was used if the probe was at the primary band gap and H-polarized light was used to probe the higher band. Because the refractive index of the active material was smaller than the background material (silicon), the probe light was chosen to be at the edge of the air band (upper band) in order to maximize the response.

---

**Figure 6-13** Pump-probe signals from (a)empty sample with pump intensity of 90GW, (b)functionalized sample (C1-YB)
To estimate the intensity of the pump light, we needed to know the spot size of the pump right on the sample. The easiest way to visualize and estimate the size was to burn the silicon with high pump intensity and then to measure the size of the burned spot under microscope. The results showed that the beam spot was around 50 μm in the Y direction and 100 μm in the Z direction. Knife-edge measurements that were conducted later confirmed the size of the beam.

Figure 6-13 (a) shows the pump-probe response of the empty sample pumped at 90 GW/cm². The curve shows exponential decay of the signal against the delay. The characterization time of the pump-probe signal was about 40 ps.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Probe (μm)</th>
<th>λ (μm)</th>
<th>Power (GW/cm²)</th>
<th>ΔR (%)</th>
<th>τ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1-YB</td>
<td>7.7</td>
<td>1.8</td>
<td>96</td>
<td>0.65</td>
<td>~18</td>
</tr>
<tr>
<td>infiltrated</td>
<td>7.8</td>
<td>1.8</td>
<td>24</td>
<td>0.7</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>7.8</td>
<td>1.44</td>
<td>48</td>
<td>2.8</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>7.8</td>
<td>1.44</td>
<td>24</td>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>Cruciform</td>
<td>7.8</td>
<td>1.44</td>
<td>24</td>
<td>No signal</td>
<td></td>
</tr>
<tr>
<td>infiltrated</td>
<td>7.8</td>
<td>1.8</td>
<td>20</td>
<td>No signal</td>
<td></td>
</tr>
<tr>
<td>Empty</td>
<td>7.0</td>
<td>1.44</td>
<td>90</td>
<td>3.5</td>
<td>&gt;20</td>
</tr>
<tr>
<td></td>
<td>7.0</td>
<td>1.44</td>
<td>72</td>
<td>0.9</td>
<td>40</td>
</tr>
</tbody>
</table>
At a lower pumping level (~25 GW/cm²), we were able to observe a signal (black curve) from the infiltrated samples as shown in Figure 6-13 (b). The response time on this sample was measured to be about 0.5 ps. At a high pumping level (~48GW/cm²), the life time of the signal is increased. There might be two or more contributions to the signal at this pumping level: one from the C1-YB and the other from silicon background. The contribution from the silicon was mainly from the free carrier generation. The signal due to this was long lived because the life time of the generated free carriers was long.

Other wavelengths and pump powers were tried on the empty and infiltrated samples. All of them had similar results. Table 6-1 lists the results for all of the samples that were measured.

### 6.3.3 ORTHOGONAL PUMP-PROBE

In orthogonal pump-probe experiments, the probe light has the same travel path as was seen in the parallel pump-probe experiment. The difference between the two pump-probe experiments is the way in which the pump and probe lights overlaps. In this experiment, they intersected orthogonally on the sample (Figure 6-14). Figure 6-15 shows a close-up view of the pump probe scheme.

The pump light was focused by a lens L1, whose focal point was behind the sample. Thus, the size of pump beam spot on the sample was much larger than of the probe beam, which was focused into a small spot by the parabolic mirror. This helped to ensure spatial overlap of the pump and probe. The size of the pump beam on the sample was measured by the knife-
edge technique. The size was 0.85 mm (1/e) at the Z direction and 0.41 mm (1/e) at the X direction.

Figure 6-14 Orthogonal pump-probe layer out. The red and blue lines represent the pump and probe traces respectively.

Figure 6-15 Orthogonal pump-probe scheme. Both the pump and probe light propagate on the horizontal plane.
6.3.3.1 EXPERIMENT RESULTS

The results of the experiment on the sample that had been infiltrated with Squaraine are shown in Figure 6-16. The sample was pumped by 1.58 μm light with various pumping powers. The wavelength of the probe light was 7.8 μm and polarization was TE. At all pumping levels, the sample exhibited long-lived pump probe effects. Figure 6-16 (b) plots the peak response of the sample against the pumping power. The points fit into a parabolic model very well. Tan et al. have discussed the contribution from the free carrier generation in silicon [11]. This part of the signal is quadratically proportional to the pumping power according to the Drude model. The lifetime of the pump-probe signal shown in Figure 6-16 (a) is over 100 ps. This is also an indication that the signal observed was attributed to the background material, silicon.

Figure 6-16 Results of orthogonal pump-probe measurement on the sample infiltrated with Squaraines. (a)Temporal response at different pumping powers. (b) Peak pump-probe response against the pumping power. The parabola model fits to the data points very well.
6.4 DISCUSSION AND FUTURE WORK

6.4.1 CONCLUSIONS AND DISCUSSION OF CURRENT WORK

We have made all-optical switches by infiltrating organic active material into 2D silicon photonic crystals. Mid-IR pump-probe experiments were conducted on these functionalized photonic devices. Different wavelengths of the probe light were used to detect the band tuning effect for different sample and polarizations. In the all of the samples and schemes of the experiments, long-lived (>20 ps) pump-probe signals were seen at high levels of pumping.

Silicon has a small value of Kerr nonlinearity at the order of $10^{-6}$ cm$^2$/GW. Dinu et al. reported a value of $n_2 = 4.5 \times 10^{-6}$ cm$^2$/GW at 1540 nm [15] measured by the Z-scan technique. Although the non-degenerate $\chi^{(3)}$ is different from the degenerate $\chi^{(3)}$, they usually have close values. We can then use $10^{-6}$ cm$^2$/GW as the non-degenerate $\chi^{(3)}$ to estimate the pump probe signal response as a result of this contribution. At a pumping level of 50 GW/cm$^2$, $\Delta R$ is around 0.1% or less.

The experiment that was conducted in orthogonal pump-probe scheme showed that the peak response was quadratically proportional to the pumping power. This can be explained by the free electron generation model that has been proposed by Tan and van Driel [11].

The free charge carriers are created in the silicon through two photon absorption. The TPA coefficient of silicon has been reported to be around 0.8 cm/GW [15] with a nearly flat dispersion curve from 1.27 $\mu$m to 1.54 $\mu$m. The density of the free carriers was estimated to be around $10^{17}$ cm$^{-3}$ at a 50 GW/cm$^2$ illumination level. Using the formula given by Tan [11], the corresponding change of refractive was estimated to be around $-3 \times 10^{-4}$. It should be note
that the change of refractive index is proportional to $\lambda^2$. Therefore, we estimate the pump-probe response, $\Delta R$, from this contribution to be around 2%, which is 1 or 2 orders larger than the contribution due to the Kerr nonlinearity at this pumping level. This rough estimation is in accord with the current data taken on samples having both empty and infiltrated pores.

The sample that had been infiltrated with C1-YB showed a fast response (life-time ~500 fs) at a low pump level and a slow (10 ps) response at high pump level. We suspect that the fast response might come from the response of the dye when it was pumped at a relatively low intensity. Recall that the contribution from the free carrier generation is quadratically proportional to the pumping power. So, at a 25 GW/cm² pumping level, the $\Delta R$ attributed to the free carrier generation should be around 0.5%. As the Figure 6-13 shows, 1% of the change was observed at this pumping level. It is possible that a small portion of the contribution came from other mechanisms, including the Kerr nonlinearity of the dye. When the pumping level was increased, the signal portion due to the free carrier generation became dominant as it was proportional to the square of the pumping power. This can be confirmed by the life time of the pump-probe signal.

We calculated the $\chi^{(3)}$ response of the organic molecules using a 2-level Lorentz model. The model predicts that the real part of the off-resonance response approaches a non-zero value in the long wavelength region. It is known that this model usually overestimates the off-resonance value. Although we suspect that there was some contribution from the dye in the sample that had been infiltrated with C1-YB, from all of the experiment data, there was no strong evidence of a band tuning effect that would have been due to the optical Kerr effect of the organic molecules.
6.4.2 OUTLOOK FOR THE FUTURE WORK

All-optical switching is a relatively new and promising way of controlling the flow of light. It is most useful if a low switching power can be attained. The key issue in optical switching is how to change the refractive index of the material rapidly using an ultrafast laser pulse.

Our samples were made with silicon, which is not transparent in the visible range. In other words, the linear resonance occurs in the visible region whereas the nonlinear resonance occurs in the infrared region. As discussed above, silicon has certain level of two-photon absorption in the near infrared region; it generates free carriers, which contribute most of the pump-probe signal. To avoid the background signal from silicon, it is important to keep the incident intensity lower than 10 GW/cm². This would require a good nonlinear active material with a large nonlinear response at this pumping level.

Organic materials have large nonlinearity close to their resonance regions. As we can see from the calculation and the Z-scan measurement, both C1-YB and Squaraine have detectable peak response ($\Delta n > 0.01$) at a low pumping intensity (1 GW/cm²) if the light is near resonance.

The Lorentz model predicts that the peak response of $\text{Re}(\chi^{(3)})$ appears at the adjacent of the molecule resonance, which is approximately twice the linear absorption peak. In the non-degenerate case, the resonance condition becomes $\omega_{pu} + \omega_{pr} = \omega_0$. Thus, one has to choose a wavelength close to the absorption peak of the dye if the probe wavelength is in the mid-IR region. However, visible light cannot be used because the silicon is strongly absorbent in that wavelength region.
Therefore, improvement could be achieved if the pump and probe are kept in the near infrared region, which can be easily tuned to match the resonance conditions. In consequence, the pore periodicity needs to be scaled down to a few hundred nanometers. For example, if we want to tune the first TE band gap and scale it down to 1.5 μm, the lattice constant $a$ should be 369 nm. If we want to tune the bandgap between 4th and 5th TM band and scale it down to 1.2 μm, the lattice constant should be 625 nm.

The ratio $r/a$ remains 0.3 in both cases. However, it would be better to have a large $r/a$ ratio for three reasons. First, the photonic band gap becomes larger with larger $r/a$. The sensitivity of the band edge is also increased. Second, the whole gap shifts towards the shorter wavelength side, which thereby improves the nonlinear response of the organic materials. Third, the background signal attributed to the silicon decreases because less space is occupied by the silicon.

Moving the probe wavelength into the near-IR region can favor the signal response. However, since the pump and probe wavelengths are very close, care should be taken to ensure that the pump light does not leak into the detector.
6.4.3 OBLIQUE BACKSCATTERING EXPERIMENT

With the sample dimension ($a=2\ \mu m$) unchanged, a completely new pump-probe scheme might be possible. The experiment scheme is shown in Figure 6-18. The idea in this experiment design is to use a short wavelength to measure the angular-dependent backscattering signal that relates to the band structure of the 2D photonic structure. The backscattering angle should be carefully chosen to ensure that there is no diffraction.

Experiments in which the band structure was measured at oblique angle, were previously reported [16, 17]. When a light is illuminates a 2D structure at an oblique angle, most of the light is reflected in the specular direction. Some of the light is coupled into the photonic crystal. If the in-plane wave-vector $k_\parallel$ is near resonance of the 2D photonic band gap, strong reflection will be observed. This would generate changes in the specular reflected light or the backscattering light. The amplitude of $k_\parallel$ is dependent on the incident angle. Thus, we can

Figure 6-18 Schematic drawings for oblique backscattering experiment on 2D photonic crystals. (a) Experiment scheme for linear band structure measurement. (b) Pump-probe scheme for band tuning measurement.
continuously change it by rotating the sample along ΓK direction if we are interested in the band structure in the ΓM direction. Pacradouni and Astratov have studied the spectrum of the specular reflection [16, 17]. However, in that experiment, because there is a strong background signal from the specular reflection, the signal-to-noise ratio was not optimized. We propose an experiment that looks at the backscattering signal which comes only from the band structure interaction and should exhibit a better signal-to-noise ratio.

A nonlinear optical experiment can also be done under this scheme. An additional pump light should be added to produce a pump-probe experiment (Figure 6-18 (b)). The advantage of doing the pump-probe experiment in this way would be that we could use near-infrared light as the pump and probe lights, which could maximize the Kerr effect from the molecules while still using the current samples.

The preliminary measurements in this study have been derived from experiments for which only one beam was used. To avoid the diffraction signal, the wavelengths used ranged from 3.5 μm to 5 μm. Although interesting data were collected from the experiment, it did not really follow our theoretical prediction. There may be an unknown source that contributes to the backscattering signal. Figure 6-19 shows a typical measurement of the oblique backscattering experiment. More measurements would help to produce a better understanding of this data.
Figure 6-19 Typical oblique backscattering signal from a 2D photonic crystal sample.

6.5 REFERENCES


CHAPTER 7

IMPROVEMENT OF KLEINMAN

DISALLOWED HYPER-RAYLEIGH

SCATTERING

7.1 INTRODUCTION

Second-order nonlinear optics in organic materials have been studied for decades with considerable effort aimed at measuring the first molecular hyperpolarizability $\beta$ of chromophores that comprises bulk organic material [1-3]. Such measurements have been critical to the development of the understanding of the physical mechanisms that contribute to the nonlinear optical response as well as to the optimization of materials. Because of the requirements for noncentrosymmetry for measuring $\chi^{(2)}$ of bulk material, most work has focused on understanding and designing dipolar molecules. Electric-field-induced second-
harmonic generation (EFISHG) has been a favored technique for such molecules because the technique measures the figure of merit for the vector component of $\beta$ [4]. In this case, most chromophores fit the scheme of donor-acceptor substituted linear conjugated molecules where the 1D nature of the molecule implies that Kleinman symmetry (full index permutation symmetry) applies, and the hyperpolarizability is dominated by the vector component.

Recent interest, however, has also focused on other schemes for producing non-centrosymmetric media [5]. These schemes couple with other aspects of the hyperpolarizability tensor. This coupling is best understood by using group theory to extract the rotationally invariant figures of merit as appropriate for the oriented gas models of the bulk nonlinear optical response. In the most general case, the $\beta^2$ tensor can be decomposed into seven irreducible representations [6, 7]. In second harmonic generation, four rotationally invariant tensors contribute, namely, two that transform as a first rank tensor (vector and pseudovector), one as a second-rank pseudotensor, and one as a third-rank tensor (often named the octopolar component). The vector and octopolar components appear whether or not Kleinman symmetry applies whereas the pseudovector and second rank pseudotensor components require that Kleinman symmetry be broken. All of these components can be exploited in media of the appropriate symmetry. For example, coupling to the octopolar part has been seriously studied [3, 8, 9].

Hyper-Rayleigh Scattering (HRS), a powerful technique for extracting the first-order hyperpolarizability $\beta$ tensor, is capable of extracting all of the figures of merit appropriate for exploitation of the rotationally invariant components [2, 3, 10-12]. It can be used to measure both polar and non-polar materials as well as charged materials and is, therefore, widely
applicable. Although the technique has been known for some time, it has recently undergone intense development in order to measure charged dipolar materials and octopolar materials. Because these applications couple to Kleinman symmetric components, scattering at 90° is adequate to extract the relevant figures of merit [11, 12]. In this cases when the Kleinman symmetry holds, HRS couples to two observables in the $\beta$ tensor: the vector component and the octopolar component.

We have been investigating the possibility of axially aligned chiral media for second order nonlinear optics [5, 13]. In this case, the nonlinear optical response couples to the Kleinman nonsymmetric second-rank pseudotensor figure of merit related to the hyperpolarizability. The lack of Kleinman symmetry implies that the constituent chromophores exhibit charge delocalization in two or three dimensions [5].

To measure the molecular response that is relevant for the axially aligned chiral media, a more general form of HRS is required namely, Kleinman-disallowed HRS (KD-HRS), which has been previously described in detail [3, 10]. Since HRS involves incoherent second harmonic scattering from fluctuations, the scattering tensor is quadratic in the hyperpolarizability, which when decomposed into its rotationally invariant form leads to 6 invariant tensor components. Figures of merit for these 6 components are measured by KD-HRS. We have reported on KD-HRS carried out at a 45° scattering angle using elliptically polarized input and scattered light. The tensor invariant figures of merit were obtained, in our case, by varying the polarization of the incident beam using a rotating quarter wave plate [3, 10]. Recently, Lemailet et al. reported on a data analysis based on discrete measurements (non-Fourier transform) that varied both the input and analyzing polarization states as well as the scattering angle.[14]
It is well-known that multiphoton excited fluorescence can appear along with second harmonic light in HRS. Three approaches to separating these contributions have been reported: spectral separation [15], temporal separation in the Fourier domain [16], and temporal separation [17]. None of these approaches is completely effective. In spectral separation, it is not always possible to find spectral regions of interest where fluorescence is negligible. In the time domain, fluorescence and HRS do not always appear on separable time scales.

The variation of the polarization state has been affected by using a motor-rotated quarter-wave plate. This works well, but, when requiring a highly tunable source is required to carry out dispersion measurements, or when finding wavelengths for which fluorescence is negligible, the use of rotating wave plates or compensators becomes cumbersome and expensive. In addition, the results are very sensitive to the alignment and precise retardation of the wave plate.

In this chapter, I will discuss improvements to the KD-HRS technique. Two hardware improvements – i.e., a method to electrically vary the polarization state and a method to temporally separate the second-harmonic signal from multi-photon excited fluorescence, will be presented in the discussion. The new method has been successfully applied to measurements for a series of nonlinear optical chromophores. A comparison between the new and previous techniques will also be provided.
7.2 KLEINMAN DISALLOWED HYPER-RAYLEIGH SCATTERING

7.2.1 THEORY OF EXPERIMENT WITH ARBITRARY PHASE

To understand KD-HRS, let’s consider two optical fields, $E_1$ and $E_2$, with frequencies $\omega_1$ and $\omega_2$, that propagate in an isotropic solution of nonlinear optical chromophores. The nonlinear optical interaction incoherently generates at the sum frequency, for example,

$$I_{\mathcal{L}}^{\text{opt}} = G N B_{LKLMN}^{2} (\omega_3; \omega_1, \omega_2) E_{J}^{\text{opt}} E_{K}^{\text{opt}} (E_{M}^{\text{opt}})^* (E_{N}^{\text{opt}})^*$$

(7.1)

where $G$ includes experimental factors including local field factors and geometry (the exact form is unimportant because it will be eliminated by appropriate referencing), $N$ is the number density of the nonlinear molecules in the solution, and $B^2$ the square of the molecular hyperpolarizability averaged over all spatial orientations that we wish to measure.

The quantity $B^2$ tensor can be analyzed by decomposing $\beta^2$ into components that are irreducible under 3D rotation [18, 19]. This decomposition defines the maximum number of observable contributions to $B^2$. Thus, it becomes possible to write $B^2$ as a sum of rotationally invariant tensors $\Delta_{LKLMN}$ with scalar coefficients $\beta^2$ that are the rotational invariants of the hyperpolarizability tensor $\beta^2$:

$$B_{LKLMN}^2 \equiv \langle \beta_{LKL} \beta_{LKM}^* \rangle = \sum_{\mathcal{L}} \Delta_{\mathcal{L}} (\mathcal{L})_{LKLMN} \beta^2 (\mathcal{L})$$

(7.2)

The scalar coefficients $\beta^2 (\mathcal{L})$ are quantities for each of the processes associated with the tensors, $\Delta_{\mathcal{L}}$. The square root of these scalar coefficients will be the figures of merit that we wish to extract. Note that the sign of the response is not available using this technique. The
index \( \mathcal{L} \) can be 1ss, 1mm, 1sm+, 1sm-, 2mm, or 3ss, which denote the tensor rank and the
permutation symmetries (s: symmetric; m: mixed symmetry). The full decomposition in
terms of the \( \Delta \) have been given elsewhere.[3, 10]

The general scheme of KD-HRS as has been previously described is given in Figure 7-1. The incoming light is elliptically polarized using a polarizer and wave plate and then is
scattered from the sample. The scattered light at 45° is passed through an elliptical
polarization analyzer and is then filtered and detected. For the incoming light, the scattering
Jones matrix can be written as

\[
M = R(-\gamma_i)M_{\text{waveplate}}R(\gamma_i)R(-\alpha_i)M_{\text{polarizer}}R(\alpha_i)
\]  

(7.3)

where \( \gamma_i \) is the angle between the fast axis of the incident wave plate and the Y axis (vertical)
and \( \alpha_i \) is the angle between the polarization direction and the Y axis. Without losing
generality, we write the Jones matrices of the wave plate, polarizer and rotation as,

\[
M_{\text{waveplate}} = \begin{bmatrix} 1 & 0 \\ 0 & t \end{bmatrix}, \quad M_{\text{polarizer}} = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}, \quad R(\alpha) = \begin{bmatrix} \cos(\alpha) & \sin(\alpha) \\ -\sin(\alpha) & \cos(\alpha) \end{bmatrix}
\]

(7.4)

where \( t = e^{ir} \) is the phase factor between fast and slow axes of the wave plate and \( r \) is the
retardation. Therefore, the polarization configuration of the incoming laser light is,

\[
\hat{e}_i = \cos(\gamma_i - \alpha_i)(\hat{x}\sin \gamma_i + \hat{y}\cos \gamma_i) + t_i \sin(\gamma_i - \alpha_i)(-\hat{x}\cos \gamma_i + \hat{y}\sin \gamma_i)
\]

(7.5)
Calculated with the same method, the output polarization is given by:

\[
\hat{e}_o = \cos(\gamma_o - \alpha_o)((\hat{x}\cos \theta + \hat{z}\sin \theta) \sin \gamma_o + \hat{y}\cos \gamma_o) \\
+ t_o \sin(\gamma_o - \alpha_o)(-(\hat{x}\cos \theta + \hat{z}\sin \theta) \cos \gamma_o + \hat{y}\sin \gamma_o)
\]  

(7.6)

where \( \gamma_o \) is the angle between the fast axis of the output wave plate and the Y axis (vertical) and \( \alpha_o \) is the angle between the direction of the polarizer and Y axis.

As we will see later, the KD-HRS measurement involves changing the polarization of the incoming and outgoing beams. For alignment purposes, the polarization configuration of the incoming beam is varied continuously for one data scan. Usually, the polarizer is fixed in horizontal direction (\( \alpha_i = \pi / 2 \)), which is the same as the output of the lasers. The only factor that we can change is the configuration of the wave plate, which actually has two variables: the fast axis direction \( \gamma_i \) and the retardation between the fast and slow axis \( t_i \). The
conditions on polarization components $e_i$, $e_o$ and the scattering angle for obtaining the best fits have been carefully analyzed for the case in which the elliptical polarizers that comprise the linear polarizers and wave plates are used [3, 10]. In the configuration discussed in reference [3, 10], both the input and output wave plates are $\frac{1}{4}\lambda$ waveplates ($t_i = t_o = i$) and the scattering angle $\theta$ is 45°. During the experiment, the orientation of the quarter-wave plate at the incoming light beam ($\gamma_i$) was continuously changed from 0 to 360 degrees. It has been found that the six invariant figures of merit can be extracted by fitting the Fourier components of scattered light when varying the input polarization. However, because no more than four components of $\beta^2$ can be determined in one data scan, two scans with different output polarization settings are needed. It was shown that the optimum values for the output polarization settings are $(\alpha_o)_1 = 57.8^\circ$, $(\gamma_o)_1 = 75.25^\circ$ and $(\alpha_o)_2 = (\gamma_o)_2 = -30.4^\circ$.

### 7.2.2 KD-HRS USING LIQUID CRYSTAL RETARDER

To obtain a system that is more easily aligned, tuned and varied over a broad wavelength range, we have replaced the input $\frac{1}{4}\lambda$ waveplate with an electrically controlled liquid crystal retarder. In this case, we fixed the orientation of the waveplate in the incoming beam path but varied the its retardation $t_i$. In the new experiment setup, we choose $\alpha_i = \pi / 2$, $t_i = \pi / 4$, and $\theta = 45^\circ$. By introducing new variables to simplify the calculation, we can rewrite $e_i$ and $e_o$ as the follows:

$$
\hat{e}_o = a\hat{z} + b[\cos \kappa(\hat{x} \cos \phi + y \sin \phi) + i \sin \kappa(-x \sin \phi + y \cos \phi)]
$$

(7.7)

$$
\hat{e}_i = \frac{1}{2}[(1 + \cos r)\hat{x} - (1 - \cos r)y + i \sin r(x - y)]
$$

(7.8)
where $a$, $b$, $\kappa, \phi$ are new variables for simplifying the expressions. The six contractions of the rotationally invariant tensors and the electric field are: [10]

$$\Delta_{1ss} = c_{1ss} \frac{1}{9} [AA^* + 4BB^* + 4 \text{Re}(BA^*C)]$$

$$\Delta_{1mm} = c_{1mm} \frac{4}{9} [AA^* + BB^* - 2 \text{Re}(BA^*C)]$$

$$\Delta_{1ms+} = c_{1ms+} \frac{4}{9} [AA^* - 2BB^* + \text{Re}(BA^*C)]$$

$$\Delta_{1sm-} = c_{1sm-} \frac{-4i}{3} \text{Im}(BA^*C)$$

$$\Delta_{2mm} = \frac{4}{9} c_{2mm} [AA^* + 2BB^* - 2 \text{Re}(BA^*C)] + \frac{2}{3} \tilde{c}_{2ss} [1 - CC^*]$$

$$\Delta_{3ss} = \frac{1}{3} c_{3ss} [1 + 2CC^*] + \frac{1}{9} \tilde{c}_{3ss} [AA^* + 4BB^* + 4 \text{Re}(BA^*C)]$$
\[ A = e_i e_o = \cos^2 \frac{r}{2} e^{ir} + \sin^2 \frac{r}{2} e^{i(r-\pi)} = e^{ir} \left( \cos^2 \frac{r}{2} - \sin^2 \frac{r}{2} \right) = e^{ir} \cos r \] (7.15)

\[ B = e_i e_o^* = \left( \cos \frac{r}{2} e^{ir/2}, \sin \frac{r}{2} e^{i(r-\pi)/2} \right) \left( \begin{array}{c}
\cos \kappa \cos \phi + i \sin \kappa \sin \phi \\
\cos \kappa \sin \phi - i \sin \kappa \cos \phi
\end{array} \right) \] 

\[ = \frac{b}{2} \left( 1 + \cos r + i \sin r, 1 - \cos r - i \sin r \right) \left( \begin{array}{c}
\cos \kappa \cos \phi + i \sin \kappa \sin \phi \\
\cos \kappa \sin \phi - i \sin \kappa \cos \phi
\end{array} \right) \] 

\[ = \frac{b}{2} \left( (1 + \cos r) \cos \kappa \cos \phi - \sin r \sin \kappa \sin \phi + (1 - \cos r) \cos \kappa \sin \phi - \sin r \sin \kappa \cos \phi \\
+ i((1 + \cos r) \sin \kappa \sin \phi + \sin r \cos \kappa \cos \phi - (1 - \cos r) \sin \kappa \cos \phi - \sin r \cos \kappa \sin \phi) \right) \] (7.16)

\[ C = e_i e_o = \frac{b}{2} \left( 1 + \cos r + i \sin r, -\cos r - i \sin r \right) \left( \begin{array}{c}
\cos \kappa \cos \phi + i \sin \kappa \sin \phi \\
\cos \kappa \sin \phi - i \sin \kappa \cos \phi
\end{array} \right) \] 

\[ = \frac{b}{2} \left( (1 + \cos r) \cos \kappa \cos \phi + \sin r \sin \kappa \sin \phi + (1 - \cos r) \cos \kappa \sin \phi + \sin r \sin \kappa \cos \phi \right) \\
+ i((-1 + \cos r) \sin \kappa \sin \phi + \sin r \cos \kappa \cos \phi + (1 - \cos r) \sin \kappa \cos \phi - \sin r \cos \kappa \sin \phi) \] (7.17)

Therefore, the intensity at the detector can be rewritten as the sum of the trigonometric functions of the retardance.

\[ I^{2\omega} = \sum \Delta \beta \beta = \sum_n \left( \sum \Delta A \beta \sin nr + \sum \Delta B \beta \cos nr \right) \] (7.18)

That is, the \( \beta \) components are generalized into the Fourier components of retardance. It should be noted that only \( \cos r \), \( \cos 2r \), \( \sin r \) and \( \sin 2r \) are present in Eq. (7.18). There are five coefficients \( q_n (A_n \beta \beta \text{ or } B_n \beta \beta) \) that can be determined from the Fourier analysis of the data.

### 7.2.3 DATA ANALYSIS METHOD

As we mentioned earlier, \( \beta^2 \) has six quantities that need to be determined whereas one set of data just yields only five Fourier components. Therefore, at least two experiments need to be conducted with different settings for the scattered light polarization analyzer are needed to
extract all $\beta^2$ components. Assuming the noise is Gaussian, we used an unweighted least square fit to determine the $\beta^2$ components from these two experimental runs,

$$\chi^2 = \sum_n (q_n - A_{n,\varepsilon} \beta^2_{n,\varepsilon})^2 + \sum_n (q_n' - A_{n,\varepsilon} \beta^2_{n,\varepsilon})^2$$  \hspace{1cm} (7.19)

$$0 = \frac{\partial \chi^2}{\partial \beta_j^2} = 2M_{ij} \beta^2_i + 2M'_{ij} \beta^2_j - 2q_n A_{n,j} - 2q_n' A'_{n,j}$$ \hspace{1cm} (7.20)

$$(M_{ij} + M'_{ij}) \beta^2_j = q_n A_{nj} + q_n' A'_{nj}$$ \hspace{1cm} (7.21)

where $M$ and $M'$ are the scattering matrices for two different configurations. We numerically searched for the configurations that would yield the smallest statistical error as determined from the eigenvalues of the covariance matrix $(M + M')^{-1}$. The criterion for this is to maximize the smallest eigenvalue of the matrix. Two very good configurations, \{$\kappa = \frac{\pi}{8}$, $\phi = \frac{\pi}{8}$\} and \{$\kappa = \frac{\pi}{2}$, $\phi = \frac{\pi}{8}$\} were found. The corresponding configuration of the wave plate and polarizer are (\(\alpha_o = 20.8^\circ\), \(\gamma_o = 15.9^\circ\)) and (\(\alpha_o = 73.1^\circ\), \(\gamma_o = 60.0^\circ\)), respectively.

### 7.2.4 CONTRIBUTIONS FROM EACH ROTATION-INVARIANT COMPONENT

The contributions in the detected signal from each $\beta^2$ component are plotted in Figure 7-2 and Figure 7-3. Figure 7-2 shows the results for the configuration of $\alpha_o = 20.8^\circ$, $\gamma_o = 15.9^\circ$. In this configuration, the contribution due to the 3ss component has small variation indicating that it is more related to the zero order Fourier component. The 1mm and 2mm components have similar contributions. The 1sm- component has negative contribution at region [0, 90]
and [180, 270] and is centro-symmetric. The magnitude of this contribution is usually 5 times smaller than that of other components.

Figure 7-2 Theoretical polar plots of the indicated rotational invariants $\Delta_L$. The curves show how the scattered light intensity changes as the retardance changes if only one $\beta$ component is present. The output polarization settings are $\alpha = 20.8^\circ$, $\gamma = 15.9^\circ$.

Figure 7-3 shows the results for configuration of $\alpha = 73.1^\circ$, $\gamma = 60.0^\circ$. In this configuration, contributions from 2mm and 3ss components are both dominated by the zero order term. The behavior of the 1sm- contribution is nearly the same as it was in the previous configuration.
Figure 7-3 Theoretical polar plots of the indicated rotational invariants $\Delta L$. The curves show how the scattered light intensity changes as the retardance changes if only one $\beta^3$ component is present. The output polarization settings are $\alpha_o = 73.1^\circ$, $\gamma_o = 60.0^\circ$.

7.3 EXPERIMENT

In general, the detected light contains contributions from multi-photon excited fluorescence as well as the second-harmonic generation. An example is shown in Figure 7-4. The SHG and multi-photon fluorescence can be clearly seen clearly. The SHG signal has very fast response time and its wavelength changes as the pump wavelength changes. The temporal
response of the fluorescence signal depends on the lifetime of the states and can be very long (nanosecond). The shape of the fluorescence spectrum does not change as the pump wavelength changes.

Because of the different mechanisms behind these two signals, they can be separated in either the time or the spectral domains. Hubbard et al. have reported techniques based on spectral separation [15]. However, to measure the nonlinearity at the region that is close the resonance of the molecule, the SHG is overlapped in the spectrum with the multi-photon induced fluorescence. Olbrechts et al. have developed a technique for temporal separation in the Fourier domain using synchronous detection [16, 20]. Using high frequency demodulation of detected sidebands, the system is able to minimize fluorescence signal. Nordmann and Van Hulst[17] introduced a time-correlated single photon counting (TCSPC) technique [21] to separate the processes temporally. This technique is a widely used technique in fluorescence lifetime measurements. TCSPC is a highly sensitive photon counting technique that yields a high signal to noise ratio with an ultrafast Ti:Sapphire laser system. We have applied their technique to a commercially available TCSPC system and carefully analyzed the signal separation. We have implemented this for 90° and 45° scattering experiments, which are conventional HRS and KD-HRS respectively. The photon counting nature of the technique also leads to excellent sensitivity.
Figure 7-4 The emission spectrum of Di-8 contains SHG and two photon fluorescence.

7.3.1 SETUP

The TCSPC-KD-HRS setup shown in Figure 7-5 is very similar to the standard KD-HRS[10] except in its signal detection; TCSPC-KD-HRS measures the arrival-time distribution of single photons rather than the scattering intensity directly. In this setup, the TCSPC module consists of a fast multi-time-channel chip, TimeHarp200 (from PicoQuant, Inc.), a photon counting photomultiplier tube (PMA185 from PicoQuant, Inc.), and an avalanche photodiode. A fast photodiode was used to trigger the counting device. In principle, the TCSPC operates when the laser output triggers the START input of the TCSPC module, and the arrival of a single photon at the photomultiplier tube stops the timer at the STOP input. A histogram of single photon arrival times is thus produced. Detection running under this scheme requires the STOP pulse to always be correlated with a single photon event. To ensure that only a
single photon event is detected, the photon count rate must be far below one photon per laser pulse. Typically, single photon events below the 10% level are required. In practice, then, the single photon event is used to START the timer, and a laser pulse under a fixed delay is used to STOP it in order to minimize dead time. The delay is adjusted with lengths of cable in order to capture the signal events in an appropriate time window.

Figure 7-5 TCSPC-KD-HRS setup: The components are denoted as, BS: beam splitter; LCR: Liquid Crystal Retarder; D2040: LCR controller (Meadowlark); F: color and 400 nm narrow-band filter; QW: quarter-wave plate; P: polarizer; PD: fast-speed Si photo diode PMA185: single photon detector (PicoQuant Corp.); TH200: photon counting board TimeHarp200 (PicoQuant Corp.).

The laser source is a self mode-locked Ti:Sapphire laser of our own design. The Ti:Sapphire crystal has a length of 9 mm. The round trip of the cavity is 6.6 m, which means that the mode-locked repetition rate would be 45 MHz. The low repetition rate is good for lifetime measurements because it provides a 22 ns time window. The center wavelength of the output is 800±5 nm. The pulse duration is 120 fs as measured with the SHG
autocorrelation method. The typical average power output is 500 mW at the pumping level of 6.6 W from an Argon ion laser.

Before the detector, a BG39 and a 400-nm notch filter were used to block the fundamental light (pump) and pick up the SHG signal. The detector was sealed very carefully because we were detecting the single photon event. Any scattered photon from the space would have a chance to be detected as a fake signal if the detector was not isolated appropriately.

### 7.3.2 MATERIALS

The materials used in this study are shown in Figure 7-6. They are disperse red 1 (DR1) $N$-Ethyl-$N$-(2-hydroxyethyl)-4-(4-nitrophenylazo)aniline, which was purchased from Sigma-Aldrich, Malachite Green (MG) 4-[(4-dimethylaminophenyl)-phenyl-methyl]-$N,N$-dimethyl-aniline from Sigma-Aldrich, and di-8-ANEPPS (4-(2-[6-(Dioctylamino)-2-naphthalenyl]ethenyl)-1-(3-sulfopropyl)pyridinium inner salt) from Invitrogen. All of the molecules were dissolved in organic solvents, and the solutions were filtered with 0.22 μm filter. DR1 and MG were dissolved in chloroform; Di-8-ANEPPS was dissolved in DMSO.

DR1 was chosen because of the large body of literature on it and its ability to calibrate the system. It is a one dimensional molecule and some components of $\beta^2$ vanish from the theoretical prediction. Di-8-ANEPPS was chosen because of its strong two-photon fluorescence to test the TCSPC technique for separating fluorescence from the HRS signal. This dye has been extensively studied and has been used as a potentiometric biological imaging dye[22]. Electron delocalization in this dye is essentially one-dimensional. MG is a planar dye, and its 2D nature is appropriate for multi-polar media. Rhodamine-6G, which
was purchased from Sigma-Aldrich, was used as a fluorescence source for calibrating and aligning the TCSPC setup.

![Chemical structures](image)

**Figure 7-6** Chemical structure for (a) Disperse Red 1, (b) Di-8-ANEPPS, (c) Malachite Green

### 7.3.3 RESULTS AND COMPARISON TO THE PREVIOUS MEASUREMENT TECHNIQUE

Figure 7-7 shows histograms for various samples. Figure 7-7 (a) shows the histogram of a typical fluorescent photon, from the fluorescent dye Rhodamine 6G, which shows a sharp rise and a slow decay line. The fluorescent lifetime of Rhodamine 6G is measured to be about 4ns, which is consistent with other studies [23].
Figure 7-7 Histograms from the TCSPC measurements. (a) The typical fluorescence time-domain spectrum of a fluorescent dye (Rhodamine 6G). The solid line is the fit of the fluorescence tail. (b) The time-domain spectrum of Malachite Green and Disperse Red 1. (c) The time-domain spectrum of Di-8-ANEPPS, which has a strong fluorescence tail. The solid line is the fit of the fluorescence tail.

Figure 7-7 (b) depicts a histogram of a typical SHG signals, generated by DR1 and MG, which show sharp peaks with no apparent tails; this indicates only small portion of long-lived fluorescence. The SHG intensity is calculated by integrating the SHG peak over the indicated time window $<T_L, T_R>$ (36.4 ps $\times 50 = 0.82$ ns wide), where $T_L$ is the set at the start position of signal peak and $T_R$ is set at the end position of the signal peak, then subtracting the background part in the window yields the total counts of pure signal, $I(2\omega)$. 

$\tau = 3.84$ ns
By fitting the SHG peak to a Gaussian function, the histogram pulse was found to have a FWHM of 450 ps, which yields the time resolution of the system limited mostly by the photomultiplier tube jitter. Figure 7-7 (c) shows the histogram of the sample, Di-8-ANEPPS, which exhibits both strong SHG and multi-photon induced fluorescence. The time ranges that are appropriate for each contribution to the signal are clearly visible. The peak (between $<T_L, T_R>$) contains contributions from both fluorescence and SHG. The SHG signal was calculated by subtracting the fluorescence, which can be estimated from the long tail, from the whole peak.

Both the pure SHG signal and the uncorrected signal were quadratic in the incident power, which verified that the signal was a composite of SHG and two-photon excited fluorescence. The integration was carried out at each setting of the retarder in order to generate the data scans as shown in Figure 7-8 (DR1), Figure 7-9 (Di-8-ANEPPS) and Figure 7-10 (MG). The retardation of the LCR changed was continuously with changes in the voltage that was applied to the liquid crystal cell. Each measurement scanned from zero to one wave of retardation. The scans were fit using the Fourier analysis and error minimization technique described the experiment theory section.

It should be noted that the DR1 and Di-8-ANEPPS are both 1D molecules. Measurement results from these two molecules were similar.
Figure 7-8 Polar data plots and fits for KD-HRS measurements of DR1 at different output configurations, (a) $\alpha = 20.8^\circ \gamma = 15.9^\circ$ (b) $\alpha = 73.1^\circ \gamma = 60.0^\circ$.

Figure 7-9 Polar data plots and fits for KD-HRS measurements of Di-8 at different output configurations, (a) $\alpha = 20.8^\circ \gamma = 15.9^\circ$ (b) $\alpha = 73.1^\circ \gamma = 60.0^\circ$. 
We also measured the same molecules using the old method, which employs a rotating quarter-wave plate (RQW) in the incoming beam path. The comparison between the two is presented in Table 7-1. In the table, all of the values are in arbitrary units that have been normalized to the 1ss component as measured by RQW method.

The results in Table 7-1 indicate that the LCR method yields results that generally agree with the RQW results. As expected, and as previously seen, DR1 and di-8ANEPPS have Kleinman disallowed components (1mm and 2mm) that are considerably smaller than the Kleinman allowed components. Since 1D molecules are Kleinman symmetric, these two molecules are primarily albeit not entirely one dimensional. Indeed, the relative magnitude of the Kleinman-disallowed components to the Kleinman-allowed components can be considered to be a measure of the degree to which the molecules are one dimensional.
The uncertainties that are listed in Table 7-1 reflect those determined solely from the fitting in the data analysis. It is clear that the LCR technique yields better precision in the fit than the RQW technique. This might be understood by comparing the polar plots of the six allowed components of $\beta^2$ as determined in the LCR experiment shown in Figure 6 to those given in previous studies [3, 10] for the RQW. The LCR components are less symmetric than the RQW components and, therefore, would be more sensitive to broken symmetries in the data.

In developing the LCR technique, we examined the sensitivity of the various fits determining the tensor components to experimental variations in order to assess the reproducibility of this technique. We found that the 1mm and 2mm components are quite sensitive to the orientation of the fast axis of the quarter-wave plate in the old method. This is indicated in Table 7-1 with the numbers that correspond to the deviation in parentheses assuming a one-degree reproducibility in setting the fast axis direction of the quarter-wave plate, and an accuracy of 10 nm retardation in the LCR due to thermal and other effects. Table 7-2 and Table 7-3 list the sensitivity of each $\beta^2$ component in terms of the change of the retardance or the orientation of the wave plate. The following definitions were used,

$$D_L = \Delta (\beta_{L} / \beta_{1ss}) / \Delta \gamma$$  \hspace{1cm} (7.22)

$$DL_L = \Delta (\beta_{L} / \beta_{1ss}) / \Delta r$$  \hspace{1cm} (7.23)

where $L$ can be 1mm, 1sm-, 1sm+, 2mm or 3ss. For Table 7-2, $\Delta \gamma = 1^\circ$ was assumed and for Table 7-2, $\Delta r = 10nm$ was assumed.
Table 7-1 Rotational invariant figures of merit for the hyperpolarizability, $\beta$. RQW: data measured with a rotating quarter-wave plate. LCR: data measured with a liquid crystal retarder. The numbers in the table are in arbitrary unit. Results for (a) disperse red 1 (DR1), Di-8-ANEPPS (Di-8), and Malachite green (MG). All the data in the table of each molecule is normalized to the 1ss component value as measured by the RQW method.

<table>
<thead>
<tr>
<th></th>
<th>1ss</th>
<th>1mm</th>
<th>1sm+</th>
<th>1sm-</th>
<th>2mm</th>
<th>3ss</th>
</tr>
</thead>
<tbody>
<tr>
<td>DR1</td>
<td>RQW</td>
<td>1.00±0.01</td>
<td>0.20±0.03</td>
<td>-0.02±0.01</td>
<td>-0.03±0.02</td>
<td>0.17±0.03</td>
</tr>
<tr>
<td></td>
<td>LCR</td>
<td>0.986±0.007</td>
<td>0.16±0.01</td>
<td>0.034±0.007</td>
<td>-0.007±0.01</td>
<td>0.13±0.01</td>
</tr>
<tr>
<td>Di-8</td>
<td>RQW</td>
<td>1.00±0.01</td>
<td>0.17±0.03</td>
<td>0.05±0.01</td>
<td>-0.05±0.01</td>
<td>0.16±0.03</td>
</tr>
<tr>
<td></td>
<td>LCR</td>
<td>1.034±0.004</td>
<td>0.14±0.01</td>
<td>0.087±0.006</td>
<td>0.00±0.01</td>
<td>0.14±0.01</td>
</tr>
<tr>
<td>MG</td>
<td>RQW</td>
<td>1.00±0.09</td>
<td>1.4±0.2</td>
<td>0.43±0.09</td>
<td>0.04±0.09</td>
<td>0.8±0.1</td>
</tr>
<tr>
<td></td>
<td>LCR</td>
<td>0.74±0.04</td>
<td>1.17±0.09</td>
<td>0.39±0.04</td>
<td>0.04±0.09</td>
<td>0.74±0.09</td>
</tr>
</tbody>
</table>

In earlier work, we found that it is necessary to adjust the quarter wave plate fast axis very carefully by comparing results for 1D molecules for 90° and 45° scattering. For the LCR technique, we found that only the 1sm- and the 1sm+ components were generally more sensitive to small errors in retardance than were the other components. This is an important reason to use this technique because those two components arising from the interference between the other two vector components are of little practical interest. Based on the arguments above as well as the higher precision in the fit, we conclude that the LCR technique is both more accurate and more precise than the RQW technique.
Table 7-2 Sensitivity of the measurement to the change of retardation in the RQW method.

<table>
<thead>
<tr>
<th>Dye</th>
<th>$D_{1mm}$</th>
<th>$D_{1sm^+}$</th>
<th>$D_{1sm^-}$</th>
<th>$D_{2mm}$</th>
<th>$D_{3ss}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DR1</td>
<td>-0.081</td>
<td>0.037</td>
<td>0.00071</td>
<td>0.070</td>
<td>-0.040</td>
</tr>
<tr>
<td>Di-8</td>
<td>-0.074</td>
<td>0.034</td>
<td>0.0027</td>
<td>0.065</td>
<td>-0.037</td>
</tr>
<tr>
<td>MG</td>
<td>0.16</td>
<td>-0.00027</td>
<td>0.012</td>
<td>-0.019</td>
<td>0.075</td>
</tr>
</tbody>
</table>

Table 7-3 Sensitivity of the measurement to the change of retardation in the LCR method.

<table>
<thead>
<tr>
<th>Dye</th>
<th>$DL_{1mm}$</th>
<th>$DL_{1sm^+}$</th>
<th>$DL_{1sm^-}$</th>
<th>$DL_{2mm}$</th>
<th>$DL_{3ss}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DR1</td>
<td>0.017</td>
<td>-0.0086</td>
<td>-0.081</td>
<td>-0.013</td>
<td>0.0056</td>
</tr>
<tr>
<td>Di-8</td>
<td>0.016</td>
<td>-0.0084</td>
<td>-0.093</td>
<td>-0.014</td>
<td>0.0054</td>
</tr>
<tr>
<td>MG</td>
<td>-0.025</td>
<td>0.0097</td>
<td>-0.17</td>
<td>-0.0014</td>
<td>0.012</td>
</tr>
</tbody>
</table>

7.3.4 LIMITATIONS

Although our TCSPC-KD-HRS setup is designed to separate the signal that has a different temporal behavior, there is still a limit on the detector side. For the molecules that have fast fluorescence, such as crystal violet (CV) [24], our current setup is not able to measure it precisely even with the help of color filters.

We also examined the reliability of separating the second-harmonic signal from the multi-photon excited fluorescence signal. In order to examine this issue, we used a two filter technique. First, we collected TCSPC data for the signal that was obtained with a narrow band centered at the second-harmonic wavelength. This significantly reduces the broadband
fluorescence contribution, while passing the second-harmonic generation. Next, we used a filter that cut the second harmonic signal while passing the fluorescence signal (either a notch filter displaced from the second harmonic, or a long pass filter). As shown in experiments on CV in DMSO solution as depicted in Figure 7-11 (a), we found that the light transmitted through the two filters is similar in magnitude and that both occur within the instrumental time resolution. This indicates a fast lifetime fluorescent decay. This is confirmed by the scattered spectrum in Figure 7-11 (b), which indicates a broad fluorescent emission and no evidence of second harmonic. Thus, using the time-resolved technique in this case could result in at least orders of magnitude overestimation.

![Graph](image)

**Figure 7-11 (a)** Time-resolved hyper-Rayleigh scattering signal for CV pumped at 790 nm using two notch filters, one at the second harmonic wavelength and one spectrally displaced. (b) Spectrum of scattering light of CV in acetone that confirms significant fluorescence when pumped with a nanosecond pulse at 780 nm.

In addition, we find that the displaced filter contains a significant prompt contribution, which indicates that there is some short time fluorescent contribution for both DR1 and MG. The fluorescence for di-8-ANEPPS was effectively filtered in the time domain as described above. For DR1 and MG, we found that the second harmonic could be reliably separated from the second harmonic signal by a combination of spectral and temporal filtering.
However, when we tried to measure CV at this wavelength, we were unable to separate the two due to a large prompt fluorescence signal even when a notch filter was in place.

Therefore, a spectrum of scattered light (as measured, in this case, with the ICCD spectrometer) coupled with careful spectral and temporal filtering is necessary to obtain the most reliable results. Further, even with these precautions, it is not always possible to perform such measurements at a particular wavelength because of the presence of prompt fluorescence. In this case, analysis of the spectrum of the scattered light is necessary to find appropriate wavelengths for measurement. Thus, a tunable laser source for a TCSPC-KD-HRS experiment may also be necessary.

### 7.4 CONCLUSIONS

We have made two improvements in our previously described hyper-Rayleigh scattering technique: (a) the use of time-correlated single photon counting to separate multi-photon excited fluorescence from second-harmonic generation, and (b) the use of an electrically controlled LCR to vary the input polarization. Three measurements of different molecules have been shown and compared to the measurement done with the previous technique (RQW). The new method (LCR) has been shown to have improved (day to day) reproducibility as well as the accuracy of KD-HRS measurement. Because the absolute retardance of the LCR is independent of the wavelength of the light, the new method is also more convenient for use in systems with a broadly tunable laser source. The quarter-wave plate always has a limited working wavelength range.
We found that TCSPC can effectively separate second-harmonic scattering from fluorescence. However, great care must be used to determine that the signal is purely second-harmonic since prompt fluorescence can also occur. A combination of spectral measurement or filtering, including the simple two-filter method described here, coupled with an appropriate spectral and temporal are necessary for accurate results. We note that these cautions and techniques should also be applied when using temporal filtering in the Fourier domain [16, 20]. We also note that our analysis of the accuracy and reproducibility of the HRS experiments that have been presented relate only to the issues addressed here. Other factors (such as other misalignments) can limit the accuracy as well as the overall accuracy of the reference standard being used, which is usually never reported as being better than 15%.

7.5 REFERENCES


CHAPTER 8

Z-SCAN EXPERIMENT FOR MEASURING

THE NONLINEAR REFRACTIVE INDEX

8.1 INTRODUCTION

The third-order optical nonlinear susceptibility is small; for this reason, interest in these effects emerged only after the invention of the laser. One of the most common phenomena related to the third-order nonlinearity is the optical Kerr effect, which describes the change of refractive index that is induced by intense illumination. Another type of Kerr effect, the electro-optical Kerr effect, is widely found in liquid that has a larger dipole moment per molecule [1]. In this chapter, I will discuss the optical Kerr effects in various organic solvents and the experiment to measure them.
In the past few decades, theories on optical Kerr effect and experiments to measure the relevant nonlinear optical coefficient, $n_2$, have been developed and conducted. Several mechanisms [2], such as photorefractive, thermal, saturated atomic absorption, electrostriction, molecular reorientation, and electronic polarization, can lead to such intensity-dependent refractive index changes. It is well known that self-focusing, self-defocusing, and filament forming are related to the Kerr nonlinearity as well as a number of schemes for optical switching. Each mechanism that causes the Kerr effect behaves differently. Shen [3] pointed out that the thermal effect is proportional to the cube of pulse width. The typical relaxation time for rotation of the molecule is $10^{-10}$ s, which eliminates the possibility of a short-pulse orientational response. The thermal-induced Kerr effect (thermal lensing) has been studied for a long time as well [4, 5]. The thermal effect is caused by the accumulation of the heat absorbed by the material. This is an instantaneous response, but it relaxes slowly. The thermal response depends on the energy of the laser pulse. Precise measurements of the electronic polarization contribution to $\chi^{(3)}$ are helpful for determining the nonlinearity of the media and for verifying the theoretical models.

There are several ways to measure the Kerr nonlinearity. Maker [6] used an elliptically polarized laser beam to measure the intensity dependent changes in refractive index. A giant pulsed ruby laser, which has a pulse duration of 40 ns, was used to produce the 16 mJ laser pulse. With the help of the ultrafast laser, McMorrow [7] and Righini [8] developed pump-probe technique to study the dynamics of Kerr nonlinearity. Similarly, other techniques have been developed [9-11].

The Z-scan technique, which was first systematically studied in 1989 by M. Sheik-Bahae et al. [12, 13], is a method to measure both the real and imaginary parts the third order
nonlinearity. One advantage of this method is that only one laser beam is employed during the measurement. When a Gaussian beam travels through a Kerr medium, self-focusing or self-defocusing occurs because of a non-uniform change of the phase front. The effect that is induced inside the medium from the intense beam changes its intensity distribution in the far field. For a Gaussian beam that passes through a thin medium, a Gaussian decomposition [14] can be used to analyze the beam pattern and the induced phase distortion theoretically. The Z-scan experiment has been adapted to a number of configurations. For example, Zhao et al changed the Gaussian beam to a top-hat [15] beam in order to improve the Z-scan technique. They demonstrated that a wide variety of laser sources, which may not necessarily have a good Gaussian profile, can be used in the Z-scan experiment.

There have been a number of \( n_2 \) measurements on pure solvents using different methods and laser systems; most of these are not in good agreement with each other (see Table 8-1). In this chapter, I will report the \( n_2 \) values of various organic solvents measured by the Z-scan technique using a femto-second laser at 1300 nm. The third order nonlinearity that was measured by this method arises from the electronic response of the molecule.

**8.2 EFFECTIVE \( \chi^{(3)} \) RESPONSES OF THE MATERIAL**

In the pure transparent solvent, thermal, electrostriction, molecular reorientation, and electronic polarization are responsible for the optical Kerr effect. The change of refractive index is the sum of those effects [16].
\[
\Delta n = n_z^e <E^2(t)> + \frac{n_z^0}{\tau_0} \int_{-\infty}^{t} <E^2(t)> e^{-(t-\tau)/\tau_0} d\tau
\]

(8.1)

where \( n_z^e \) is the electronic contribution and \( n_z^0 \) is related to the first order correction of the orientation of the molecules. The reorientation contribution is essentially caused by the presence of the dipole moment and the asymmetric shape of the molecule. As we know, a dipole undergoes a torque under an electric field if it is not parallel to the field that is causing the molecular dipole moment to align along the external electrical field. Under laser illumination, the molecules will respond to the field and tend to align along the polarization direction instead of being randomly aligned. The typical response time for molecule reorientation is about \( 10^{-12} \) s. As we can see from Eq. (8.1), the final contribution from molecular re-orientation depends on the duration of the laser pulse; the longer the pulse, the bigger the response is. The thermal contribution is mainly determined by the energy of each laser pulse and the size of the focus region. The temperature increase at the focal point is also determined by the heat capacity and dissipation rate.

The electronic polarization contribution to \( n_z \) is usually the smallest and the fastest. It is small because it is the third order correction to the linear susceptibility. Compared to the mass of the molecule, the mass of the electron is very small. The distortion of the electronic cloud can happen in \( 10^{-15} \) s or even faster. Because the optical pulse has an oscillation period ranging from 1 fs to a few fs, the nonlinear response from electronic polarization is always treated as an instantaneous effect that follows the temporal shape of the laser pulse.
Therefore, in order to minimize other contributions while measuring the electronic contribution of $n_2$, a short laser pulse that has high instantaneous power but low energy per pulse is needed. In our experiment, the pulse duration of the laser was about 200 fs.

### 8.3 Z-SCAN EXPERIMENT

A schematic drawing of the Z-scan experiment is shown in Figure 8-1. There are two basic types of Z-scan; closed-aperture Z-scan (for measuring $n_2$) and open-aperture Z-scan (for measuring multi-photon absorption). In a closed aperture Z-scan experiment, the TEM$_{00}$ laser mode, which has a Gaussian distribution of intensity in the XY plane, propagates along the Z-direction and is focused by a positive lens. In the far field, a round aperture is centered on the Z-axis to block part of the beam. A detector behind the aperture is used to collect the light that passes through the aperture. The sample is placed near the focus of the beam at normal incidence. During the scan, the sample is moved continuously along the z-axis passing through the focal point of the beam.

![Figure 8-1 Schematic drawing of closed-aperture (with the aperture) and open-aperture (without the aperture) Z-scans.](image-url)
In the absence of nonlinear absorption, the refractive index \( n \) of Kerr media is linear in light intensity:

\[
n = n_0 + n_2 I \tag{8.2}
\]

where \( I \) is the light intensity. The Kerr coefficient \( n_2 \) can either be negative or positive, which corresponds to self-defocusing and self-focusing, respectively. The phase change of the optical wave inside the medium is proportional to the refractive index. For a laser beam that has a non-uniform intensity distribution on its phase front, the phase change is not uniform across the whole beam. As a consequence of this, different portions of the beam have different phase delays even if the medium has a uniform thickness. In the Z-scan experiment, the intensity profile of the beam has a Gaussian distribution:

\[
I(r, z) = I_0 \frac{w_0^2}{w(z)} e^{-\frac{2r^2}{w(z)^2}} \tag{8.3}
\]

where \( r = \sqrt{x^2 + y^2} \) is the distance of the point to the center of the beam. Let \( L \) be the thickness of the sample \( \alpha \), which is the linear absorption coefficient. The effective length related to the phase change is given by:

\[
L_{\text{eff}} = \frac{1 - e^{-\alpha L}}{\alpha} \tag{8.4}
\]

In addition to the phase change due to the linear refractive index, there is another phase term that is caused by the light intensity,

\[
\Delta \varphi(r, z) = \frac{\Delta \varphi_0}{w(z)^2} e^{-\frac{2r^2}{w(z)^2}} \tag{8.5}
\]
for which the $\Delta \varphi_0$ is defined as

$$\Delta \varphi_0 = \frac{2\pi}{\lambda} <\Delta n(t) > L_{\text{eff}}$$  \hspace{1cm} (8.6)$$

where $\lambda$ is the wavelength. In the steady state, the Kerr effect can be attributed to various origins, including the electronic contribution, molecular reorientation, and the thermal effect. In this case, $n_2$ of a medium can be written as the sum of those contributions. If we extend the concept of $n_2$ at a steady state to a pulsed state, we can define the time-averaged index change as:

$$< \Delta n(t) > = \frac{\int_{-\infty}^{\infty} \Delta n(t) I_0(t) dt}{\int_{-\infty}^{\infty} I_0(t) dt}$$  \hspace{1cm} (8.7)$$

For each type of Kerr effect, $\Delta n(t)$ will have a different form. In our study, we were mainly interested in the electronic contribution, which has the form, $\Delta n(t) = I_0(t) n_2$. Putting this into Eq. (8.7), we have

$$< \Delta n(t) > = \frac{1}{\sqrt{2}} I_0 n_2$$  \hspace{1cm} (8.8)$$

The additional phase change is not uniform along the cross section of the sample. In a laser beam, the index change in the flat sample takes the form of a lens whose effective focal length is determined by the nonlinear response. If the sample has a positive $n_2$, it acts as a positive lens under illumination. If the sample is placed before (left side) the original focal point, the actual focal point of the beam will shift left. As a result of this, the beam diameter at the far field becomes larger, and the amount of light that can pass through a fixed size of aperture decreases. If the sample is put after (right side) the original focal point, the diverging
beam after the focal point will be further focused. Therefore, the beam diameter at the far field becomes smaller and the amount of light that passes through the aperture increases. A similar analysis can be done with negative $n_2$. The result is the detected light after the aperture increases if the sample is put before the focal point and decreases if the sample is put after the focal point.

With some reasonable approximations (thin sample, small phase distortion, etc), one can derive the normalized transmittance of the closed-aperture z-scan,

$$T = 1 - \frac{4\Delta \varphi_0 \xi}{(\xi^2 + 1)(\xi^2 + 9)}$$  \hspace{1cm} (8.9)

with $\xi = z / z_0$. If the sample moves along the propagation direction of the beam, the transmittance versus distance curve will show a valley-peak for positive $n_2$ or peak-valley for negative $n_2$. The distance between the valley and peak is proportional to the Rayleigh range $z_0$. From Eq. (8.9), the difference between the valley and peak is proportional to the phase distortion $\Delta \varphi_0$.

$$\Delta T_{p-v} = 0.406(1 - S)^{0.25} |\Delta \varphi_0|$$  \hspace{1cm} (8.10)

where $S$ is the ratio between the light that goes into the detector and the total light.

### 8.3.1 EXPERIMENTAL LAYOUT

The light source that was employed for this experiment was a TOPAS (travelling optical parametric amplifier system) pumped by Clark-MXR CPA 2010, which outputs 1 mJ pulses with 1 kHz repetition rate. The center wavelength of CPA laser was 794 nm. The pulse width
of 1300 nm output from the TOPAS was around 200fs, which was determined by measuring
the second harmonic generation from an intensity autocorrelation. The laser beam was
focused along the Z-axis by a lens (focal length, $f=10\text{cm}$). The ultra-fast pulse has two
advantages in the $n_2$ measurement: (1) a high instantaneous power that allowed us to
measure small $n_2$, (2) a low pulse energy and short pulse duration that allowed us to rule out
the thermal and molecule reorientation effects. Therefore, in our experiment, the electronic
polarization is the major contribution to $\chi^{(3)}$ or $n_2$.

![Figure 8-2 The schematic layout for the Z-scan experiment](image)

### 8.3.2 BEAM CHARACTERIZATION

The beam cross-section profile was determined by using the knife-edge technique (Figure 8-3)
[17, 18]. A razor blade was used to block part of the Gaussian beam. The remaining
transmitted beam was collected by the detector behind a lens. To measure the beam cross-
section along the X-direction, one only needs to translate the blade across the beam in the X-
direction as the integration in the Y-direction is constant.
Figure 8-3 Schematic drawing of knife-edge measurement

Figure 8-4 shows the typical measurements of the beam size in X- and Y-directions. The data points were fit with the error function \( \text{erfc}(x) = 1 - \int_{-\infty}^{x} e^{-\frac{x'^2}{2}} \, dx' \). We see that the fits are almost perfect, which indicates that the laser beam was very close to TEM\(_{00}\) mode. Because the beam was focused and we wanted to find the spot size at the focal point, we had to measure the beam sizes at different locations in the Z-direction.

![Graphs showing intensity vs. position in X and Y directions](image)

**Figure 8-4 Knife-edge measurement of beam size at (a) X-direction (horizontal) (b) Y-direction (vertical). Data points were fitted with error function (erfc).**
We know that Gaussian beam propagation must obey the Helmholtz equation. The beam spot size depends on the focal length of the lens. Figure 8-5 shows the beam sizes for different Z-positions. The fitting model that was used is:

$$w(z) = w_0 \sqrt{1 + \left( \frac{M^2 \lambda(z - z_0)}{\pi w_0^2} \right)^2} \quad (8.11)$$

where $M^2$ describes how close the beam is to a Gaussian shape (a perfect Gaussian beam has $M^2 = 1$), and $w_0$ is the beam waist. From the fit, we found that $M^2_x = 1.2$, $w_{0x} = 46.3 \pm 0.9 \mu m$, $M^2_y = 1.06$ and $w_{0y} = 38.5 \pm 0.8 \mu m$. The value of $M^2$ confirms that the laser beam is very close to a Gaussian beam. It should be pointed out that the $w_0$ given here is the size at 1/e^2.

To calculate the intensity at the center of the beam, there will be an additional factor of 2.

![Figure 8-5 Beam sizes at different Z positions. Data points were fitted with the Gaussian beam propagation function. (a) X-direction (horizontal), (b) Y-direction (vertical).](image)
8.3.3 MATERIALS AND SAMPLE PREPARATION

In the experiment, five solvents (i.e., cyclohexane, acetone, chloroform, toluene, and water) were measured. All of the solvents are absorbent in the UV region and are transparent at 1300 nm ($\alpha \approx 0$). For example, water has an absorption peak at of 6.5 eV. The measuring wavelength (1300 nm) is also far from the region where nonlinear absorption might occur.

With the exception of water, the solvents were measured in a 1-mm-thick quartz cuvette. At 1300nm, the $n_2$ of water is very close to the quartz ($\sim 0.95 \times 10^{-20} \text{ m}^2/\text{W}$). In order to differentiate the two contributions, a 2-mm-thick quartz cell was used for the water measurement. Because the materials have different $n_2$s, two different power levels were used in order to get a good signal-to-noise ratio. The peak powers at the focus were calculated to be about 70 GW/cm$^2$ and 199 GW/cm$^2$.

8.3.4 RESULTS OF MEASUREMENTS OF THE NONLINEAR REFRACTIVE INDEX

The Z-scan curves are shown in Figure 8-6. All of the data were good fits to Eq. (8.9). It should be noted that, in Figure 8-6 (b), the signal from the 2-mm quartz cell was slightly distorted because the two walls of the quartz cell were separated by 2 mm and both of them had contributions.

Table 8-1 lists both our measurement results and the results published elsewhere. In most cases, the discrepancies arise from the fact that the measurements were carried out at
different wavelengths. For chloroform and toluene, we found our results in good agreement with the results reported by Brzozowski [19].

Figure 8-6 Z-scan curves. (a) Solvents measured in 1-mm-thick quartz cell. The peak irradiance of the laser was 70 GW/cm$^2$. (b) Water measured in a 2-mm-thick quartz cell with a peak power 199 GW/cm$^2$. 
Table 8-1 Table of the $n_2$s of different solvents from different studies

<table>
<thead>
<tr>
<th>Material</th>
<th>Wavelength (nm)</th>
<th>Pulse width</th>
<th>$n_2$ $10^{-16}$ cm$^2$/W</th>
<th>Method</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI-water</td>
<td>1300</td>
<td>200 fs</td>
<td>0.82</td>
<td>Z-scan</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>1064</td>
<td>30 ps</td>
<td>2.7</td>
<td>Critical power</td>
<td>[20]</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>1300</td>
<td>200 fs</td>
<td>1.43</td>
<td>Z-scan</td>
<td>This work</td>
</tr>
<tr>
<td>acetone</td>
<td>1300</td>
<td>200 fs</td>
<td>1.85</td>
<td>Z-scan</td>
<td>This work</td>
</tr>
<tr>
<td>chloroform</td>
<td>1300</td>
<td>200 fs</td>
<td>2.89</td>
<td>Z-scan</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>1300</td>
<td>1.2 ps</td>
<td>~4.5</td>
<td>Z-scan</td>
<td>[19]</td>
</tr>
<tr>
<td>toluene</td>
<td>1300</td>
<td>200 fs</td>
<td>4.66</td>
<td>Z-scan</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>1300</td>
<td>1.2 ps</td>
<td>~4.5</td>
<td>Z-scan</td>
<td>[19]</td>
</tr>
<tr>
<td></td>
<td>1064</td>
<td>40 ns</td>
<td>0.37</td>
<td>Birefringence</td>
<td>[21]</td>
</tr>
<tr>
<td>quartz</td>
<td>1300</td>
<td>200 fs</td>
<td>0.95</td>
<td>Z-scan</td>
<td>This work</td>
</tr>
<tr>
<td>Fused silica</td>
<td>800</td>
<td>160 fs</td>
<td>3.2</td>
<td>Critical power</td>
<td>[22]</td>
</tr>
</tbody>
</table>

For the $n_2$ of the water, we can explain the difference between our results and the results reported by Smith [20], which was measured by a 30 ps laser. Table 8-2 lists the dipole moments of the solvents. Water molecules have relatively large dipole moment, $6.2 \times 10^{-30}$ Cm. Also, the water has a short relaxation time because of small moment of inertial from the data reported by Righini [8]. Thus, there will be considerable contributions will result from molecular re-orientation in water if it is measured with a long pulse.
From the beam size measurement, we know that the Z positions, for which the beam spot has minimum size in the X- and Y-directions, were not exactly the same; in the X- and Y-direction, the laser beam may have different focal points. In another words, the laser we used in measuring $n_2$ has an elliptical profile at its focal point. Considering these system issues, we claim that the intensity at the focus was over estimated and thus the $n_2$ in our measurements was slightly smaller than the real value.

All of our $n_2$ data were consistent with a critical power measurement that used the same laser system [23].

**Table 8-2 Dipole moment of molecules**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Structure</th>
<th>Dipole moment ($10^{-30}$ Cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexane</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Toluene</td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td>Chloroform</td>
<td></td>
<td>3.8</td>
</tr>
<tr>
<td>Water</td>
<td></td>
<td>6.2</td>
</tr>
<tr>
<td>Acetone</td>
<td></td>
<td>9.0</td>
</tr>
</tbody>
</table>

(table adapted from literature [24])
8.5 REFERENCES


APPENDIX A

DIRECT PRODUCT OF THE TRANSFER MATRIX†

The transfer matrix for the 1D optical system can be expressed as,

\[
X_L = \prod_{x=0}^{N/2} D(n_x) P(k_1, x_{2x}) D(n_x)^{-1} D(n_{x+1}) P(k_2, x_{2x+1}) = \prod_{x=0}^{N/2} X = \bar{X}^{N/2} \tag{A.1}
\]

where \( \bar{X} \) is the average of matrices of all the slices.

\[
\bar{X} = D(n_2)^{-1} D(n_1) P(k_1) D(n_1)^{-1} D(n_2) P(k_2) \tag{A.2}
\]

The function D and P have the same definition as in Chapter 4. It’s known that for any matrices if

† With the help of Professor Rolfe Petschek.
\[ C = AB \]  \hspace{1cm} (A.3)

then,

\[ C \otimes C = (AB) \otimes (AB) = (A \otimes A)(B \otimes B) \]  \hspace{1cm} (A.4)

Therefore, the direct product of \( X_L \) is

\[
X_L^{(2)} = X_L \otimes X_L = \left( D(n_2)^{-1} D(n_1) P(k_1, x_1) D(n_1)^{-1} D(n_2) P(k_2, x_2) \right) \\
\otimes \left( D(n_2)^{-1} D(n_1) P(k_1, x_1) D(n_1)^{-1} D(n_2) P(k_2, x_2) \right) \\
= \left[ D(n_2)^{-1} D(n_1) \otimes D(n_2)^{-1} D(n_1) \right] \left[ P(k_1, x_1) \otimes P(k_1, x_1) \right] \\
\left[ D(n_2)^{-1} D(n_2) \otimes D(n_2)^{-1} D(n_2) \right] \left[ P(k_2, x_2) \otimes P(k_2, x_2) \right]  \hspace{1cm} (A.5)
\]

Pendry (Adv. Phys. 43(4), 461-542 (1994)) argued that only the symmetric part of the direct product of \( X_L \) matters for the 1D localization behavior. Because transferring each of the matrices into the basis in which the symmetric and antisymmetric parts of the matrix are separate, we have,

\[
X_{Sl}^{(2)} = \text{Sym} \left\{ \left[ D(n_2)^{-1} D(n_1) \otimes D(n_2)^{-1} D(n_1) \right] \left[ P(k_1, x_1) \otimes P(k_1, x_1) \right] \\
\left[ D(n_2)^{-1} D(n_2) \otimes D(n_2)^{-1} D(n_2) \right] \left[ P(k_2, x_2) \otimes P(k_2, x_2) \right] \right\} \\
= \text{Sym} \left\{ \left[ D(n_2)^{-1} D(n_1) \otimes D(n_2)^{-1} D(n_1) \right] \right\} \text{Sym} \left\{ \left[ P(k_1, x_1) \otimes P(k_1, x_1) \right] \right\} \\
\text{Sym} \left\{ \left[ D(n_2)^{-1} D(n_2) \otimes D(n_2)^{-1} D(n_2) \right] \right\} \text{Sym} \left\{ \left[ P(k_2, x_2) \otimes P(k_2, x_2) \right] \right\}  \hspace{1cm} (A.6)
\]

Pendry also gave the general expression for the symmetric part of the direct product of any \( 2 \times 2 \) matrix \( X_L \) (Eq. (3.27) in his paper).

\[
\left[ X_{lM}^{(M)} \right]_{ij} = \sum_{p=0}^{\min\{i,j\}} \frac{i!}{(i-p)! p!} \frac{(M-i)!}{(M-i-j+p)!(j-p)!} \\
\times \left[ X_L^{(1)} \right]_{22}^{p} \left[ X_L^{(1)} \right]_{21}^{i-p} \left[ X_L^{(1)} \right]_{j2}^{j-p} \left[ X_L^{(1)} \right]_{11}^{M-i-j+p}  \hspace{1cm} (A.7)
\]
The \( D \) matrices are taken to be fixed. Only the \( P \) matrix is assumed to be random. It’s useful to write down the average of the \( P \) matrix.

\[
\langle e^{i k n x} \rangle = e^{i k n \bar{x}} \langle e^{i k n (x-x')} \rangle = e^{i k n \bar{x}} e^{-\sigma k n^2/2}
\] (A.8)

\[
\langle e^{i 2 k n x} \rangle = e^{i 2 k n \bar{x}} \langle e^{i 2 k n (x-x')} \rangle = e^{i 2 k n \bar{x}} e^{-(2\sigma k n)^2/2}
\] (A.9)

\[
\bar{P}(n_k, x_i) = e^{-\frac{1}{2}(n_k^2 \alpha_i)} \begin{pmatrix} e^{i n_k x_i} & 0 \\ 0 & e^{-i n_k x_i} \end{pmatrix}
\] (A.10)

For \( P \) the matrix, we can directly calculate the symmetric part of the direct product.

\[
S_{mn}\{P(n_k, x_i) \otimes P(n_k, x_i)\} = e^{-(n_k^2 \alpha_i)} \begin{pmatrix} e^{i 2 n_k x_i} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{-i 2 n_k x_i} \end{pmatrix}
\] (A.11)

With the help of Mathematica®, we calculated each of the elements of \( X_{SL}^{(2)} \). As an example, \( X_{SL}^{(2)} \) has the expression as,

\[
\left[ X_{SL}^{(2)} \right]_{ij} = \frac{1}{16(1-a^2)} \left( 2a^2 e^{2i(1+a) k n x} + (e^{4i k n} + a^4 e^{4i a k n x}) (1-s) \right)
\] (A.12)

In fact, we need to find the eigenvalues of \( X_{SL}^{(2)} \). The characteristic function for the eigenvalues \( y^{(2)} \) is given by

\[
\left| X_{x}^{(2)} - y^{(2)} I \right| = 0
\] (A.13)

where \( I \) is the identity matrix. Notice that in our particular system, we have two small quantities

\[
a = \frac{n_1 - n_2}{n_1 + n_2}
\] (A.14)
\[ s = 1 - e^{-2\sigma k^2\sigma^2} \]  

(A.15)  

and is it useful to define the average index  

\[ n = (n_1 + n_2) / 2 \]  

(A.16)  

where \( n_1 \) and \( n_2 \) are refractive indices. In our study, they very close numbers. Thus, we can use approximations \( n \approx n_1 \approx n_2 \) if necessary for simplifying the expressions. Expanding Eq. (A.13) gives a third order polynomial equation for \( y^{(2)} \).  

\[ c_0 + c_1 y^{(2)} + c_2 \left( y^{(2)} \right)^2 + c_3 \left( y^{(2)} \right)^3 = 0 \]  

(A.17)  

where we find,  

\[ c_0 = -(1-s)^4 \]  

(A.18)  

\[ c_1 = (1-s)^2 (3-2r_1 + 8r_2(1-s) + s(-2+s+4r_3s)) \]  

(A.19)  

\[ c_2 = (-3-8r_2(1-s) + 2r_1(1-s)^2 - 2s(-2+s+2r_3s) \]  

(A.20)  

\[ c_3 = 1 \]  

(A.21)  

\[ r_1 = 2\sin^2(2knx) + \frac{a^4}{(1-a^2)^2}(1-\cos(4aknx)) \]  

(A.22)  

\[ r_2 = \frac{2a^2}{(1-a^2)^2} \left( \sin^2(knx)\cos(2aknx) + \sin^2(aknx) \right) \]  

(A.23)  

\[ r_3 = \frac{a^2}{(1-a^2)^2} \]  

(A.24)  

Notice that \( r_2 \) and \( r_3 \) are both small quantities. We argued that the localization length is related to the eigenvalue which has the largest real part. We also defined \( t = \ln \left( y^{(2)}_{\text{max}} \right) / 2 \), where \( y^{(2)}_{\text{max}} \) is the eigenvalue of \( \langle X^{(2s)} \rangle \) for which \( t \) has the largest real part. Therefore, we
can expand Eq. (A.17) into power series of $t$ by keeping the first 4 terms and first order of $s$ term,

$$
\frac{2}{3}(12 + r_1 - 4r_2)t^3 + 8(2 - r_2)st^2 + 4(r_1 - 4r_2)t - 16r_2s = 0 
$$

(A.25)

Or

$$
\left(1 + \frac{1}{12}(r_1 - 4r_2)\right)t^3 + (2 - r_2)st^2 + \frac{1}{2}(r_1 - 4r_2)t - 2r_2s = 0
$$

(A.26)

By introducing two variables that are directly related to $r_1$ and $r_2$,

$$
p^2 = r_1 / 2
$$

(A.27)

$$
\kappa^2 = 2r_2
$$

(A.28)

we can rewrite Eq. (A.26) as

$$
\left(1 + \frac{1}{6}(p^2 - \kappa^2)\right)t^3 + s(2 - \frac{1}{2}\kappa^2)t^2 + t\left(p^2 - \kappa^2\right) - \kappa^2 s = 0
$$

(A.29)

which is Eq. (4.16).


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