## Oh Boi Its my Thesis

by

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#### **Author's Declaration**

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

#### Abstract

This is the abstract.

### Acknowledgements

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### Dedication

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## Chapter 1

## Introduction

In the beginning, there was  $\pi$ :

$$e^{\pi i} + 1 = 0 \tag{1.1}$$

A computer could compute  $\pi$  all day long. In fact, subsets of digits of  $\pi$ 's decimal approximation would make a good source for psuedo-random vectors,  $\mathbf{v}$ .

### 1.1 Motivation

See equation 1.1 on page 1.<sup>1</sup>

### 1.2 Thesis Outline

The credo of the American Association of Amateur Astronomers and Zoologists (AAAAZ) was, for several years, several paragraphs of gibberish, until the dingledorf responsible for the AAAAZ Web site realized his mistake:

<sup>&</sup>lt;sup>1</sup>A famous equation.

## Chapter 2

## Background

### 2.1 Hollow-Core Photonic Crystal Fiber

#### 2.1.1 Conventional TIR Guidance

#### 2.1.2 Photonic Crystal Bandgap

The 1D and 2D views of the structure

A periodic non-magnetic medium will have repeating dielectric constant[?]

$$\varepsilon(\mathbf{r}) = \varepsilon(\mathbf{r} + \mathbf{a}) \tag{2.1}$$

Due to its discrete and invariant translation symmetry, the dielectric constant along the medium can be expanded as a Fourier series

$$\varepsilon(\mathbf{r}) = \sum_{\mathbf{C}} \varepsilon_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}} \tag{2.2}$$

Where G are the reciprocal lattice vectors such that  $G \cdot a = 2\pi n$ . Expressing the electric field also as a Fourier integral

$$E(r) = \iiint d^3k A(k) e^{ik \cdot r}$$
(2.3)

Using the Maxwell equations (2.4) the wave equation can be written in terms of the electric field

$$\begin{cases} \vec{\nabla} \times \vec{H} &= -i\omega\epsilon(\vec{r})\vec{E} \\ \vec{\nabla} \times \vec{E} &= i\omega\mu_0\vec{H} \end{cases}$$
 (2.4)

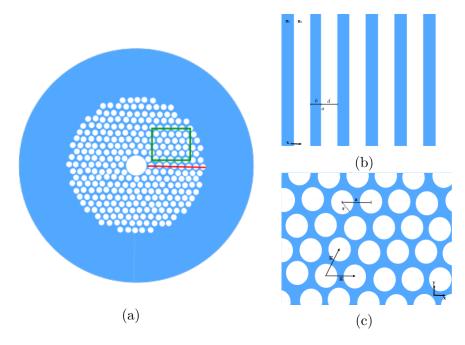


Figure 2.1: (a)cross-section of HCPCF highlighting the PC pattern (b)reduced to 1-dimension (2)in 2-dimensions

$$\nabla \times (\nabla \times \mathbf{E}) - \omega^2 \varepsilon(\mathbf{r}) \mu_0 \mathbf{E} = 0 \tag{2.5}$$

Substituting (2.2) and (2.3) into the above results in the dispersion relation:

$$\mathbf{k} \times (\mathbf{k} \times \mathbf{A}(\mathbf{k})) + \omega^2 \mu_0 \sum_{\mathbf{G}} \varepsilon_{\mathbf{G}} \mathbf{A}(\mathbf{k} - \mathbf{G}) = 0$$
 (2.6)

in where for any vector K the solutions of (2.6) for the coefficient A(K) are grouped with the coefficients A(K-G), decoupling the coefficients of other vectors that cannot be expressed in the form K-G. Disregarding the decoupled vectors, the total electric field can be described as a superposition of normal modes with regard to a chosen vector K:

$$\boldsymbol{E}_{\boldsymbol{k}}(\boldsymbol{r}) = \sum_{\boldsymbol{G}} \boldsymbol{A}(\boldsymbol{K} - \boldsymbol{G}) e^{i(\boldsymbol{k} - \boldsymbol{G}) \cdot \boldsymbol{r}}$$
(2.7)

we can pull out the Bloch theorem for the electric field from (2.7)

$$\boldsymbol{E}_{k}(\boldsymbol{r}+\boldsymbol{a}) = e^{i\boldsymbol{k}\cdot\boldsymbol{a}}\boldsymbol{E}_{k}(\boldsymbol{r}) \tag{2.8}$$

$$u_k(r) = \sum_{G} \varepsilon_G e^{iG \cdot r}$$
 (2.9)

$$\varepsilon_G = \frac{1}{V} \int d^3 r e^{-iG \cdot r} u_k(r)$$
 (2.10)

(Expand) Returning to (2.6), can fix  $\omega$  to find the corresponding K and normal modes os the system. However, in the case of photonic crystals there are ranges of frequencies that have no Ks with real solutions, which implies that waves of these frequencies cannot propagate through the photonic crystal. These non-propagating frequencies are referred to as the photonic band gap.

#### 1D Photonic Bandgap

Returning to the 1D periodic stack pictured in A.1 the periodicity of dielectric constant is described by  $\varepsilon(z) = \varepsilon(z+p)$  where a=b+d, the length of one period. The reciprocal lattice vector will be  $\mathbf{G}_n = n \frac{2\pi}{a} \hat{z}$  and plugging into the Fourier series expansion of  $\varepsilon(z)$  from (2.2)

$$\varepsilon(z) = \sum_{n = -\infty}^{\infty} \varepsilon_n e^{in\frac{2\pi}{a}\hat{z}}$$
 (2.11)

From the reduction to propagation in the z-direction with the electric field oriented in x-direction, (2.6) simplifies

$$K^{2}A(K) + \omega^{2}\mu_{0} \sum_{n=-i\infty}^{\infty} \varepsilon_{n}A(K - n\frac{2\pi}{a}) = 0$$
(2.12)

Expanding the Fourier coefficients to the 1st order and reducing the equations to the dominant coefficients of the form A(K) and  $A(K - \frac{2\pi}{a})$ . |K - g| = K and  $K = \frac{\pi}{a}$  gives a system of equations that can be solved to find the dispersion relation  $\omega(K)$ .

$$\begin{cases}
(K^2 - \omega^2 \mu_0 \varepsilon_{00}) A(K) = \omega^2 \mu_0 \varepsilon_1 A(K - g) \\
\omega^2 \mu_0 \varepsilon_{-1} A(K) = ((K - g)^2 - \omega^2 \mu_0 \varepsilon_{00}) A(K - g)
\end{cases}$$
(2.13)

The equations relating these two modes has a solution at

$$(K^2 - \omega^2 \mu_0 \varepsilon_{00}) ((K - g)^2 - \omega^2 \mu_0 \varepsilon_{00}) - (\omega^2 \mu_0 \varepsilon_1) (\omega^2 \mu_0 \varepsilon_{-1}) = 0$$
(2.14)

noting  $\varepsilon_1 = \varepsilon_{-1}^*$  and  $K \approx 2g$  simplifies the relationship

$$\omega_{\pm}^2 = \frac{K^2}{\mu_0(\varepsilon_{00} \mp |\varepsilon_1|)} \tag{2.15}$$

The dispersion relation has two possible solutions, which specify the top and bottom of the photonic bandgap edges, as illustrated in 2.2 If the solving for the wavevector at a frequency between  $\omega_{\pm}$ , only complex solutions will exist. This means that only evanescent waves, not electromagnetic waves, propagate through the medium while the electromagnetic waves are reflected back; the medium acts as a mirror for the bandgap wavelengths.

This is the phenomena that allows for HCPCF to guide certain frequencies of light - wavelengths in the bandgap are reflected by surrounding Bragg Grating confining them to the core of the fiber, while the rest are allowed to propagate through the grating.

#### 2D Photonic Bandgap

To understand the full picture of light propagation in hollow-core fiber, we need to expand to the 2D case pictured in 2.1c. However, with the electromagnetic waves now propagating in two dimension there is an added layer of complexity with the TE TM wave polarizations and the bandgaps. In addition to controlling the refractive index of the material and the period of the lattice, the lattice structure and hole radius will affect the performance of the

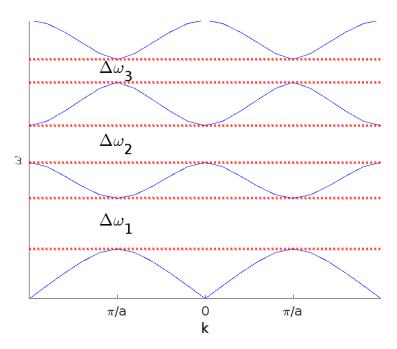


Figure 2.2: Band plot for a 1D photonic crystal with parameters-,-, solved using Finite Difference Time Domain(FDTD) method[4].

photonic crystal, the latter playing a large role in the completeness of the photonic bandgap. In the 2D photonic crystal, the in-plane guided modes will have either magnetic fields in-plane and electric fields perpendicular to the lattice (TE modes) or electric fields in-plane and magnetic fields perpendicular to the lattice (TM modes). As the TE and TM modes are perpendicular to each other they may exhibit wildly different dispersion relations, which means that an optical bandgap is not guaranteed to persist for all polarizations[2]. This is certainly the case for square lattice phonic crystals, but other patterns such as the honeycomb (which is the structure in our HCPCF) do have a bandgap persisting for all all polarizations[3]. This all to say, it is important to consider all polarization effects when making decisions about photonic crystal patterns for two or more dimensions.

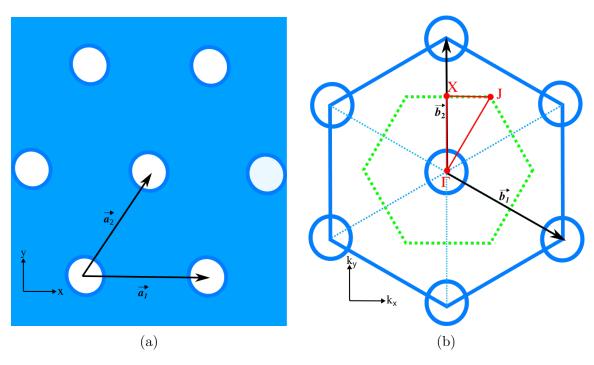


Figure 2.3: (a) primitive lattice vectors and (b) primitive reciprocal lattice vectors with first Brillouin zone (green) and irreducible Brillouin zone (red) depicted for a honeycomb lattice structure.

Considering the lattice structure in 2.3(a), and taking propagation in the xy-plane  $(K_z = 0 \text{ and } z = 0 \text{ for simplicity})$ , the wavevector and position vectors reduce to  $\mathbf{K}_{||} = k_x \hat{x} + k_y \hat{y}$  and  $\mathbf{r}_{||} = x \hat{x} + y \hat{y}$ . The primitive lattice vectors of a honeycomb photonic crystal will be:

$$\mathbf{a}_1 = a\hat{x} \qquad \mathbf{a}_2 = \frac{a}{2}\hat{x} + \frac{a\sqrt{3}}{2}\hat{y} \tag{2.16}$$

and transforming to the momentum-space,  $\mathbf{b} \cdot \mathbf{a} = 2\pi \delta_{ij}$ , as shown in 2.3(b) the primitive reciprocal lattice vectors are

$$\mathbf{b}_1 = \frac{2\pi}{a}\hat{x} - \frac{2\pi}{a\sqrt{3}}\hat{y}$$
  $\mathbf{b}_2 = \frac{4\pi}{a\sqrt{3}}\hat{y}$  (2.17)

Taking these in combination of n, m integer scaling factors, the reciprocal lattice vector is defined  $\mathbf{G}_{||} = n\mathbf{b}_1 + m\mathbf{b}_2$ . The electromagnetic field defined for a two dimensional system

$$\boldsymbol{E}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \sum_{m=-\infty}^{\infty} \sum_{n=-\infty}^{\infty} \boldsymbol{E}_{m,n} e^{i(n\boldsymbol{b}_1 + m\boldsymbol{b}_2)\cdot\boldsymbol{r}}$$
(2.18)

and the correlating Fourier expansion of dielectric function (2.10)

$$\varepsilon_{G_{||}} = \frac{1}{a' \cdot b'} \int dx dy e^{i(G_x x + G_y y)} \boldsymbol{u_k}(x, y)$$
 (2.19)

are substituted into (2.4). Utilizing the lattice symmetry and periodicity, the problem can be restricted to only solve for Bloch modes inside the of the irreducible Brillouin zone. The first Brillouin zone is defined by the perpendicular bisectors to the primitive reciprocal lattice vectors, depicted in green in 2.3(b) and can be further subdivided into the irreducible Brillouin zone shown in red. In order to find the photonic bandgap, solving the dispersion equation just along the irreducible Brillouin zone is sufficient. For a honeycomb lattice, the k-path to follow would be

$$\begin{cases} |\Gamma X| = \frac{2\pi}{a\sqrt{3}}, & k_x = 0, 0 < k_y < \frac{2\pi}{\sqrt{3}a} \\ |XJ| = \frac{2\pi}{3a}, & 0 < k_x < \frac{2\pi}{3a}, k_y = \frac{2\pi}{\sqrt{3}a} \\ |\Gamma J| = \frac{4\pi}{3a}, & 0 < k_x < \frac{2\pi}{3a}, k_y = \sqrt{3}k_x \end{cases}$$
(2.20)

Discretizing 2.18 and 2.19 then picking a few points along the k-path, numerical methods can be used to solve for the optical bandgap. 2.4 shows the resulting TE bandgap for a honeycomb lattice with parameters-,-, using Plane Wave Expansion(PWE)[4].

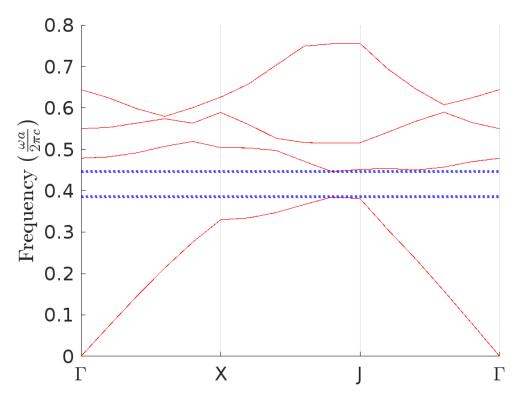


Figure 2.4: Band plot along the irreducible Brillouin zone for a honeycomb lattice with parameters -,-, . Solved for using Plane Wave Expansion(PWE) numerical method[4].

#### 2.1.3 Bandgap Shift

modal magnetic field distributions satisfy:

$$(\nabla_t^2 + k^2 n(\mathbf{r})^2 - \beta) \mathbf{H}(\mathbf{r}) = (\nabla_t \times \mathbf{H}(\mathbf{r})) \times (\nabla_t ln(n(\mathbf{r})^2))$$
(2.21)

gives scaling law for absolute refractive index at fixed contrast "a solution for a transverse scale represented by  $\Lambda$  is replicated in an identical structure with a different  $\Lambda$  if the wavelength is scaled proportionately, to keep  $k\Lambda$  constant"

"We emphasise that the scalar wave equation (and therefore the scaling laws derived from it) is accurate for the smallest index contrasts only. However, for step-index structures the vector term in Eq. (2) only exists at boundaries, so the scalar wave equation accurately represents wave propagation elsewhere. Since bandgaps arise from interference and resonance effects among such generic waves, the scaling laws of Eq. (5) should be at least approximately valid" 1.45 RI contrast[5]

Scaling law for the wave equation for the transverse coordinates  $X=x\Lambda^{-1}$   $Y=y\Lambda^{-1}$  where  $\Lambda$  is a solution to the transverse scale.

$$n(X,Y) = \begin{cases} 1, & n_1 \text{ (high RI)} \\ 0, & n_2 \text{ (low RI)} \end{cases}$$
 (2.22)

normalized scaled wave equation:

$$\nabla_{\perp}^{2} \Psi + (v^{2} n(X, Y) - w^{2}) \Psi = 0$$
(2.23)

With  $\nabla_{\perp} = \partial^2/\partial X^2 + \partial^2/\partial Y^2$  solving for the frequency parameter  $v^2$  and eigenvalue  $w^2$ :

$$v^{2} = \Lambda^{2} k^{2} (n_{1}^{2} - n_{2}^{2})$$

$$w^{2} = \Lambda^{2} (\beta^{2} - k^{2} n_{2}^{2})$$
(2.24)

from the equation above we see that the  $w^2$  is determined by the frequency parameter  $v^2$  and the index distribution function n(X,Y). This implies that  $w^2$  and  $v^2$  are invariant with changes to the parameters  $k, \Lambda, n_1, n_2$ .  $k = \omega/c$   $\beta = k\cos\theta$  longitudinal component of the wavevector. Because the light propagates along the fiber, much of its wavevector is taken up by the longitudinal component.

In the HCPCF case where the glass refractive index is held constant and the air in the fiber is replaced by a new material the equations can be rewritten with  $n1 = n_{glass}$  and  $n_2 = n_{air} = 1$ :

$$v^{2} - w^{2} = \Lambda^{2} (k^{2} n_{glass} - \beta^{2})$$

$$v = k \Lambda n_{glass} \sqrt{n_{air} - \frac{n_{air}}{n_{new}}}$$
(2.25)

The initial index contrast  $N_0 = \frac{n_{air}}{n_{glass}}$  moves to  $N = \frac{n_{new}}{n_{glass}}$  with the change in RI  $n_{air} < n_{new} < n_{glass}$  This leads to the new center bandgap to be governed by the equation:

$$\lambda = \lambda_0 \sqrt{\frac{1 - N^{-2}}{1 - N_0^{-2}}} \tag{2.26}$$

This has been experimentally confirmed to hold for HCPCF [1].

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#### 2.1.4 Mode Distribution

a) For a two-level atom, the coupling constant -g - [Eq. 2.6] scales inversely to this 'effective mode area' [Eq. before 2.1] (in the interaction energy term between atom and the field). mode is like a Gaussian [given by the mode function f(x,y)] the photon interacts

more strongly if the atom is placed in the center of the mode.) effective mode area:

$$A = \frac{\int dx dy |f_k(x, y)|^2}{|f_k(x_a, y_a)|^2}$$
 (2.27)

where  $f_k(x, y)$  is the transverse mode function and  $(x_a, y_a)$  is the position of the atom, is approximately constant in the range of the relevant longitudinal wave numbers coupling constant:

$$g_{\omega} = \sqrt{\frac{\omega}{4\pi\epsilon\hbar cA}} d_{eg} \tag{2.28}$$

- (2.5) dipole interaction Hamiltonian
  - b) Apparently, this coupling constant term tells us parameters such as:
- i) how likely it is for an excitation in the emitter is released into the waveguide mode  $\gamma_{1D}$ , versus free-space  $\gamma_0$ . [3]

$$\gamma_{1D} = 2\pi g_{\omega_A}^2 = \frac{\sigma_A}{2A} \gamma_0 \tag{2.29}$$

"where the second expression directly exhibits the scaling with the transverse extension of the waveguide. It is related to the atomic radiative cross section  $\sigma_A = \frac{3\lambda^2}{2\pi}$ . A natural lower bound on the transverse mode size is at about  $A \sim (\frac{\lambda}{2})^2$ . (lowest-order mode in hollow metallic wave- guide), implying a maximum achievable coupling ratio  $\gamma_{1D}/\gamma_0 \sim 1$ . In the range  $\sigma_A \sim A$ , one has a strong waveguide-atom coupling, which is manifested by the fact that the atom dissipates its energy equally into the waveguide and the free-space "lossy" modes."[1]

ii) optical depth (OD) for a single atom is (about) the ratio of  $(\gamma_{1D})/(\gamma_0)$  or the ratio of the cross-section area of the atom to that of the effective mode-area.

$$OD = \frac{\sigma_A}{\sigma_M} = \frac{\gamma_{1D}}{\gamma_0} \tag{2.30}$$

c) OPTICAL DEPTH CALCULATIONS: Optical depth (OD) tells about how opaque the system is. Transmitted intensity goes by T = exp(-OD). Normally, N emitters might scale linearly to give an optical depth N\*OD. But now (due to its position) each emitter might have its own mode area.

Examples of taking this into account (with maybe slightly different conventions) for atoms are mentioned in these two references[4, 5]:

$$OD_{fiber} = \int_0^L \int_0^r n(\rho, z) OD2\pi \rho d\rho dL$$
 (2.31)

r and L represent the radius and length of the ensemble, which in the case of solution-filled HCPCF is the radius and length of the fiber. This assumes that the particulates outside of the core do not have a significant contribution. If the distribution of molecules is take to be uniform along the fiber length and radius of the core, then the number density will be:

$$n(\rho, z) = \begin{cases} 0, & |z| > L/2\\ (1/L)(1/\rho), & |z| < L/2 \end{cases}$$
 (2.32)

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## Chapter 3

## Liquid-Filled HCPCF

### 3.1 Filling Methods

Fibers were cut to between 6cm and 8cm in length. To ensure consistent coupling and positioning, light was coupled to the core of the fiber by connecting to a solid-core PM780HP fiber via a mechanical splicing chip [2]. We replaced the air in 1550nm HCPCF with deionized water and heavy water by utilizing capillary action. To selectively fill the core of 800nm HCPCF, the photonic crystal cladding was collapsed while leaving the hollow-core open and is similarly filled with liquid using capillary action. We collapsed the cladding by placing the HCPCF opposite of a solid-core fiber in a fusion splicer [3] and adjusting arc current duration and power to melt the cladding structure while remaining distanced enough to prevent fusion with the solid-core fiber.

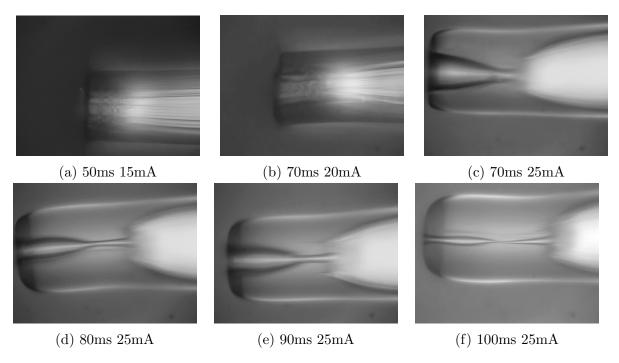


Figure 3.1: Side profile of collapsed cladding 1550HC fiber running the fiber splicer with varying current strength and duration.

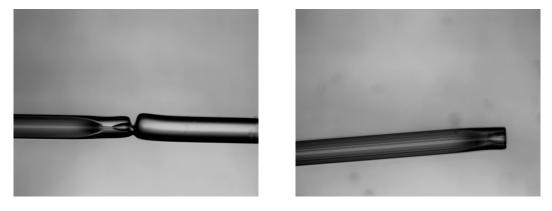


Figure 3.2: Variation between fibers using splicer settings 70ms 25ms

### 3.2 Experimental Set-Up

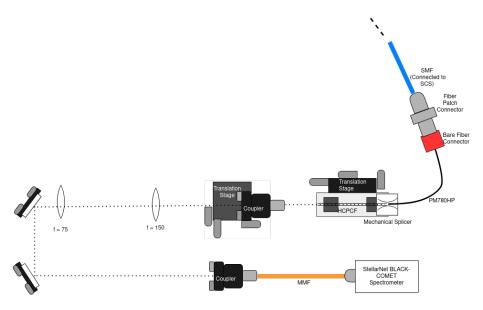


Figure 3.3: Fiber transmission experimental set-up.

### 3.3 $H_2O$ and $D_2O$ Transmission

HCPCF uses a photonic crystal cladding composed of a periodic silica structure that allows light to be guided through a hollow and thus low-refractive index core. In some applications of HCPCF, such as fiber-integrated sensors and on-linear optics, the hollow regions of the fiber are filled with liquids or gasses. Fibers that are fully-filled with water will produce a frequency shift in the bandgap due to refractive index scaling[1]. On the other hand, when the core is selectively filled with water, light will be guided via total-internal reflection. We investigate the transmission spectra of fully-filled and core-filled fibers for deionized water and heavy water.

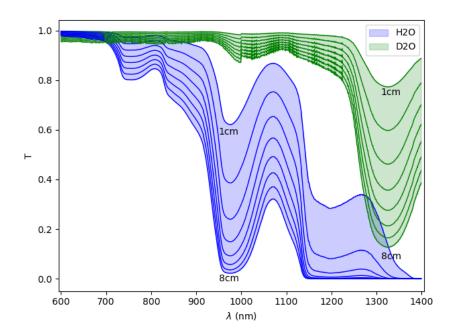


Figure 3.4: The transmission of heavy water(green) and regular water(blue) is shown for slabs of thickness ranging from 1cm to 8cm in increments of 1cm using absorption data recorded by [4].

#### 3.4 Results

The air-filled 800nm HCPCF covers a transmission spectral range of 750nm–950nm. Light exits the fiber with a Gaussian mode shape and has an expected coupling between 75-80% when connected to a solid-core single-mode fiber. A water-filled core retains a Gaussian mode shape and has a 30% reduction in the normalized transmission for wavelengths above 850nm, which is consistent with the absorption spectrum of H2O [4]. We also observe that the coupling efficiency of the fiber drops to 31%. With a heavy water filled core, there are no significant changes in the normalized transmission spectrum, minimal effects to the absorption over this region, and coupling efficiency of up to 67%.

The air-filled 1550nm HCPCF covers a transmission spectral range of 1200nm–1700nm. With a filled core and cladding, the spectral range shifts to transmitting wavelengths between 600nm–1100nm for both heavy water and water, which aligns with the scaling laws prediction. Heavy water achieved a coupling efficiency of 47%, but water only 16%. The existing mode shape is roughly Gaussian but contains noise as some light also leaks from the photonic structure, worse for water than heavy water. The losses seen in water are not entirely explained, but losses and effects from the decrease in refractive index contrast are also present in the D2O-filled fiber. While there is a less than 20% difference in absorption coefficient between the 550nm–830nm for the fiber length, 7.6nm, between 830nm–950nm the absorption coefficient of water increases steeply but stays constant over the same region for heavy water.

### 3.4.1 Selective Filling

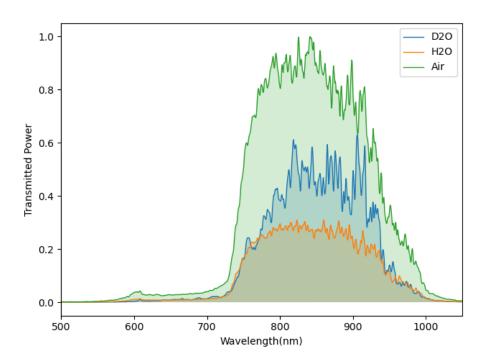


Figure 3.5: Transmission of  $\mathrm{H}_2\mathrm{O}$  and  $\mathrm{D}_2\mathrm{O}$  in (a) selectively-filled 800nm hollow-core fiber.

### 3.4.2 Full-Fiber Filling

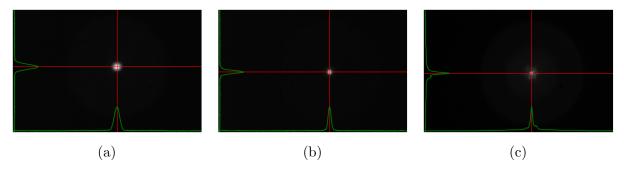


Figure 3.6: Modeshape of 1550 hollow-core fiber filled with (a)air (b)heavy water (c)distilled water. Fiber filled with heavy water maintains a Gaussian profile while the fiber with regular distilled water shows some distortion.

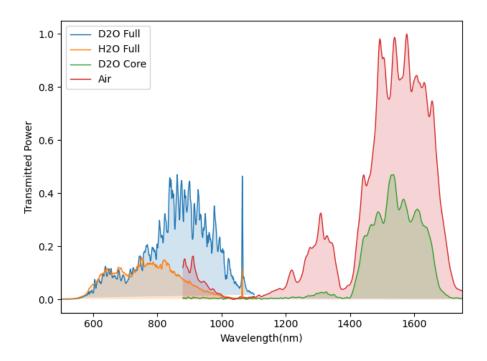


Figure 3.7: Transmission of  $H_2O$  and  $D_2O$  in fully-filed 1550nm hollow-core fiber.

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### 3.5 Carbon Nanotubes

First discovered by S.Iijima and T. Ichihashi in 1993, carbon nanotubes (CNT) are single layers of graphene rolled up into a hollow cylinder near 1 nm in diameter and near 1 nm in length. While graphene is a 2-dimensional material, the dimensions of CNTs allow them to be treated as 1-dimensional materials.

#### 3.5.1 Characterizing Carbon Nanotubes

The main descriptive properties of CNTs are the chiral vector, which is a scaled integer-valued combination of the unit vectors for the honeycomb structure of graphene, written in the form (n, m).

$$C_h = na_1 + ma_2 = (n, m) (3.1)$$

The unit vectors in Cartesian coordinates are

$$a_1 = (\frac{\sqrt{3}}{2}, \frac{1}{2})\sqrt{3}a_{C-C}a_2 = (\frac{\sqrt{3}}{2}, -\frac{1}{2})\sqrt{3}a_{C-C}$$
 (3.2)

and have equal length, where is the length of the carbon bond, which for graphene is 1.421 (Å), and often approximated as 1.44(Å) for CNTs, though there is variation depending on the curvature of the nanotubes[4]. The chiral vector is of high value as it reveals a lot of information about the electronic and optical properties of individual CNTs. The chiral angle, the angle between the unit vectors, gives the direction of the chiral vector and is defined as

$$\theta = \tan^{-1} \left[ \frac{m\sqrt{3}}{m+2n} \right] \tag{3.3}$$

and the diameter of a nanotube as

$$d_t = \frac{a_{CC}\sqrt{3}}{\pi}\sqrt{n^2 + nm + m^2}$$
 (3.4)

Due to the geometry of graphene, CNTs have a six-fold rotational symmetry and the connection points of the lattice, i.e. the way that the graphene is rolled into a tube will produce equivalent CNTs between as , thus the tube geometries are often constrained to the first range. Nanotubes with a chiral angle of are called zigzag tubes and chiral angles of are called armchair tubes due to the pattern made by their circumference as shown in the Figure 2, and are the two configurations in which CNTs are anti chiral, meaning that their structures are indistinguishable from their mirrored image, while all in between-angled nanotubes are chiral, i.e. distinguishable from their mirrored image. The diameter and angle actually vary the electronic band structure of the CNT significantly. CNTs have an additional electron confinement around their circumference[3] and as can be seen from the above definitions, the tube diameter of CNTs is quantized and varies depending on how the graphene honeycomb lattice is cut, will also follow the boundary condition

$$C_h \cdot \kappa = 2\pi q \tag{3.5}$$

where is the cutting line along graphene and q is an integer number. Depending on where graphene energy bands are along the cutting line, the corresponding CNT will become metallic or a semiconductor. In Figure 1, the metallic and semiconducting CNTs are mapped out, and a pattern emerges with CNTs with their chiralities —m-n— being a multiple of 3 emerging as metals. Single CNTs exhibit polarization dependence with the electric field in optical selection rules, i.e. the possible transitions from one quantum state to another [5]. The polarization dependence is only strong in zigzag type nanotubes however. The dipole operator in anti chiral tubes will have a parity of -1 in the horizontal plane dipole operator along the z-axis and a +1 parity for dipole vectors along the x, y plane. For z polarized light there is no electronic band transition, while for light polarized perpendicular to the z axis, the angular momentum quantum number can shift by 1. Thus, CNTs will absorb light with the optical polarization parallel to the axial direction of the tube, but in a bundle or grouping of random-oriented CNTs, there will be no polarization dependence.

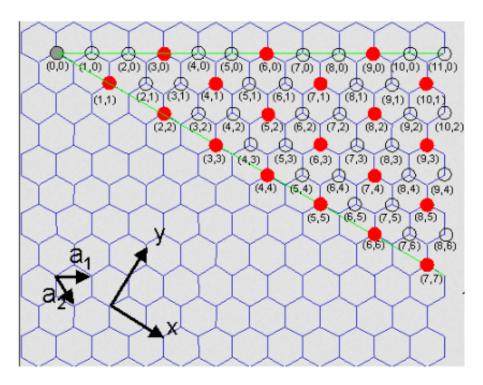


Figure 3.8: REPLACE Chiralities of CNTs with red dots indicating metallic and open dots [1].

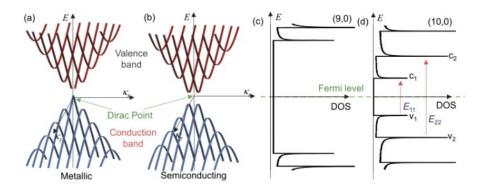


Figure 3.9: REPLACE Bands for (a)(c)Metallic and (b)(d)Semiconducting CNTs and their energy band gaps [3]

In the same year as the emergence of CNTs as a unique material, H. Kataura measured the optical absorption spectra of CNTs of various diameter CNTs performing photothermal deflection spectroscopy, which measures heat produced during relaxation of the electron hole pair generated by the absorbed light [6], an example of the optical absorption spectra are shown in Figure 4. While the absorption spectra across various CNT samples were consistent, the peak positions varied. Using the energy dispersion relations for pi-bands of the graphite [6]

$$E_{2D} = \pm \gamma \sqrt{1 + 4\cos(\frac{\sqrt{3}k_x a}{2})\cos(\frac{k_y}{2}) + 4\cos^2(\frac{k_y}{2})}$$
 (3.6)

where is the overall integration and , are the reciprocal lattice vectors, fulfilling the periodic boundary condition for chiral vectors from Eq. (5), the one-dimensional energy band of CNTs could be calculated. Referring to Figure 3, the spikes in the DOS correspond to the energy levels of the optical transitions. Plotting the Gap energies from this model against the nanotube diameter in Figure 5, referred to commonly as a Kataura plot, shows how the first transition energy of CNTs has a relationship to the diameter by

$$E_{11} = \frac{2\gamma a_{C-C}}{d} \tag{3.7}$$

and the average band gap energies split along semiconductor and metallic chiral values. In short the absorption peak wavelength of a nanotube sample is determined by the mean tube diameter, and the absorption spectral bandwidth will be determined by the tube diameter distribution of the CNT sample.

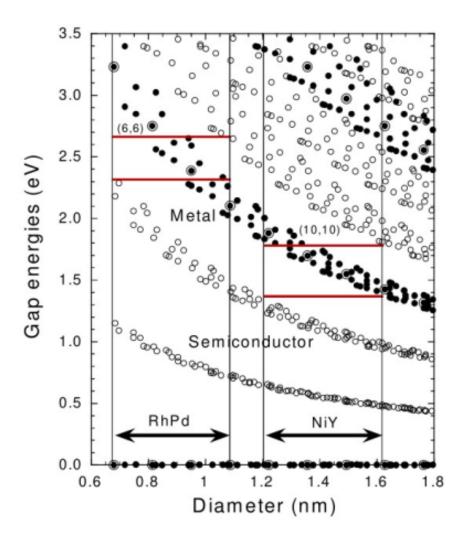


Figure 3.10: Chiralities of CNTs with red dots indicating metallic and open dots Calculated gap energies between mirror-image spikes in density of states for  $\gamma=2.75$  eV. For (solid circles) metallic and (open circles) semiconducting, and (double circles) armchair CNTs. [6].

### 3.5.2 Nonlinear Optical Properties of CNTs

The general relationship between the polarization and electric field of a material is defined [7] as

 $P(t) = \epsilon_0(\chi^{(1)}E(t) + \chi^{(2)}E^2(t) + \chi^{(3)}E^3(t) + \dots)$ (3.8)

where is the linear susceptibility and are the second and third order susceptibility. Due to the inversion symmetry of the CNT's structure, the second-order susceptibility is zero. However, a large third-order nonlinearity in CNTs has been measured [12] and is theorized to be a product of the one dimensional motion of the delocalized  $\pi$ -band electrons at a fixed lattice ion configuration [13]. The third-order nonlinearity is responsible for the saturable absorption of a material as well as the nonlinear Kerr effect. The refractive index as defined in Eq.(9) is composed of the real part of the third-order susceptibility with I defining the optical intensity and as the optical angular frequency, and is the nonlinear refractive index.

$$n = n_0 + n_2 I = n_0 + \frac{3Re[\chi^{(3)}]}{4\epsilon_0 c n_0^2} I$$
(3.9)

The absorption coefficient defined by Eq.() is composed of the imaginary part of the third-order susceptibility and , and are the linear absorption coefficient, the non saturable absorption coefficient, and refractive index respectively.

$$\alpha = \frac{\alpha_0}{1 + \frac{I}{I_S}} + \alpha_{int} \sim \alpha_0 + \alpha_{int} + \frac{3\omega Im[\chi^3]}{2\epsilon_0 c^2 n_0^2} I$$
(3.10)

The saturation intensity, , is the power per unit area it takes in a steady state to reduce the absorption to 1/2 the unbleached (or completely saturated) value and can be written in terms of

$$I_S = \frac{hf}{\sigma\tau} = \frac{E_S}{\tau} \tag{3.11}$$

where  $\sigma$  is the absorption cross section and  $E_S$  is the saturation fluence, which is the fluence (i.e. energy per unit area) it takes to reduce the initial fluence value to  $e^{-1}$  and  $\tau$  is the recovery time of the material.

The saturable absorption, as defined by Eq.(11), is a phenomenon where high intensity light will reduce the absorption of a material, but at weak intensity, the light will be absorbed and cause attenuation. This property of materials with strong third-order susceptibility like CNTs can be used to filter out weaker optical signals in noisy optical pulses, while simultaneously allowing strong pulses to pass through. Saturable absorption is observed in all materials with optical absorption resulting from electron transition

between two energy levels [5], but it is rare to find materials that have a recovery time that has a fast recovery time compared to the pulse duration, which in ultra-fast laser applications is in the few picosecond to femtosecond range. The ultra-fast response time of CNTs is only true however for bundles of CNTs with variations in their diameter due to entanglement between semiconducting and metallic via electrons tunneling and coupling from semiconducting CNTs to metallic CNTs [8].

### 3.5.3 Fluorescence of CNTs

The first Van Hove optical transition (E11) corresponds to the emission frequency and the second Van Hove optical transition (E22) corresponds to the excitation frequency. Equations for first and second van Hoven Transitions optical transition wavelengths as a function of diameter in nanometers and chiral angle are degrees derived in [10], but parameters from [9], which were found by fitting to data of samples of individual SWNT in aqueous sodium dodecyl sulfate (SDS) suspension and are valid for CNT diameters greater than 0.5nm. The parameters differ for each CNT "group", i.e (n-m) mod 3 = 1 is group 1 (n-m) mod 3 = 2 is group 2 (n-m) mod 3 = 0 are metallic CNTs and do not fluoresce.

Though it is unknown what specific effects contribute to the fitted parameters with the particular samples used, [9] found that other aqueous solutions have comparative spectral shifts of less than 2% compared to the equations when compared to other published results. Comparing to an experimental PL map using a different solutio[11], the equation results match quite well (the CNTs present in the left sample are marked in red on the right plot). We can see the expected variation from different solutions, for example CNT (10, 8) has a slightly higher excitation wavelength and slightly lower emission wavelength in SDS than in the NaDDBS/D2O solutions.

Only fully intact and individually dispersed semiconducting CNTs emit fluorescence CNTs coatings or placed on a substrate don't really fluoresce Interactions between CNTs typically cause quenching effects Though certain materials/solvents (varies with each CNT) can increase fluorescence Isolation is one of the largest factors in quantum yield Only in semiconductor-type CNTs

Desired type of CNTs can be targeted and isolated in a single step using modified aqueous two-phase extraction(ATPS). Hydration modulating agents are mixed in to tune the arrangement of surfactants on their surface

Depending on the mixture, selected CNTs turn highly hydrophobic or hydrophilic

Spectral shift due to the change in the local dielectric environment surrounding CNTs created by solvents and adsorbed molecules.[14]

$$(Emission)\lambda_{11} = \left[ \frac{1e7(cm^{-1})}{157.5 + 1066.9d_t} - 771(cm^{-1}) \frac{\cos(3\theta)^{1.374}}{d_t^{2.272}} \right]^{-1}$$
(3.12)

$$(Excitation)\lambda_{22} = \left[ \frac{1e7(cm^{-1})}{145.6 + 575.7d_t} + 1326(cm^{-1}) \frac{\cos(3\theta)^{0.828}}{d_t^{1.809}} \right]^{-1}$$
(3.13)

$$(Emission)\lambda_{11} = \left[ \frac{1e7(cm^{-1})}{157.5 + 1066.9d_t} + 347(cm^{-1}) \frac{\cos(3\theta)^{0.886}}{d_t^{2.129}} \right]^{-1}$$
(3.14)

$$(Excitation)\lambda_{22} = \left[ \frac{1e7(cm^{-1})}{145.6 + 575.7d_t} - 1421(cm^{-1}) \frac{\cos(3\theta)^{1.110}}{d_t^{2.497}} \right]^{-1}$$
(3.15)

Group 1 v. Group 2 Group 1 CNTs have lower Stokes shifts than Group 2 Group 1 have small chiral angles (; 20) Group 2 span full 00 to 300 chiral angle range, but are grouped along chiral number difference (n - m)

Excitation/Emission wavelengths Increase in Stokes shifts with diameter along chiral difference (n - m) lines Noted in red on lower plot, connected by black lines Increase in ex/em wavelengths with diameter

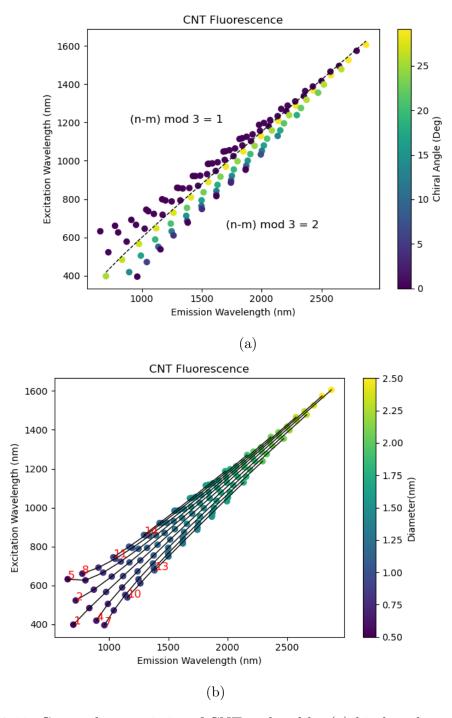


Figure 3.11: Group characteristics of CNTs colored by (a)chiral angle and (b)diameter

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# Chapter 4

## Fluorescence Tests

### 4.1 Bandgap Overlap

Table shows all hollow-core fiber types available from ThorLabs and the central operating wavelengths for air-filled and D2O-filled fibers The "air" range can be used for fibers that are selectively core-filled with D2O The ranges for HC1550 and HC800B are approximated from spectrum measurements and HC2000 and HC1060 are taken from ThorLabs datasheets The D2O central wavelengths are calculated using the band-gap shift equation

HCPCF	$\lambda_{AIR} \text{ (nm)}$	$\lambda_{D_2O}(\mathrm{nm})$	Range (nm)
HC2000	2000	1144	250
HC1550	1550	887	500
HC1060	1060	606	100
HC800B	800	457	200

Table 4.1: Thorlabs fiber bandgap shift.

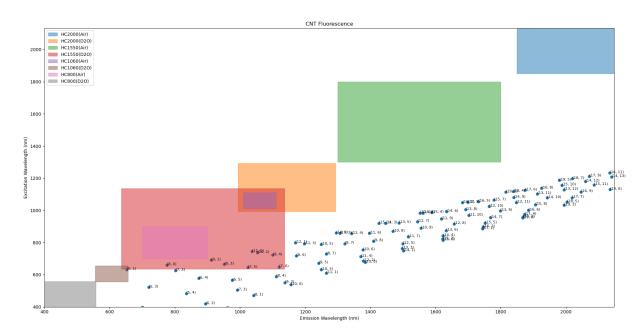


Figure 4.1: Hollow-core fiber bandgap overlayed on CNT emission vs. excitation wavelengths  $\frac{1}{2}$ 

(n,m)	dt	Θ	$\lambda_{11}$	$\lambda_{22}$
	(nm)	(deg)	(nm)	(nm)
(6, 1)	0.52	0.13	652.62	631.79
(7, 2)	0.65	0.21	802.05	625.92
(7, 5)	0.83	0.43	1023.74	645.33
(8, 0)	0.64	0	776.01	660.25
(8, 3)	0.78	0.27	951.61	665.39
(9, 1)	0.76	0.09	912.1	691.29
(10, 2)	0.88	0.16	1053.43	736.68
(11, 0)	0.87	0	1036.93	744.57

Table 4.2: CNTs with emission and excitation transmittable through HC1550 filled with  $\rm D_2O$ .

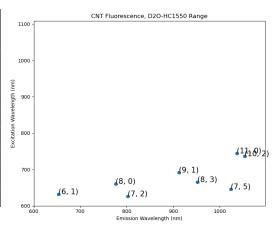


Figure 4.2: 1550 HC CNTs

## 4.2 Indocyanine Green

Due to the difficultly in isolating single-chirality solutions of CNTs, as outlined in in the previous chapter, indocyanine green (ICG) - a fluorescent dye often used in microscopy imaging[8, 9] - was initially used in place of CNTs in the fiber. This particular dye is an organic semiconductor with Homo-Lumo gap calculations estimating a 2eV energy gap, with variations depending on the solvent[1]. The HOMO and LUMO energy levels in organic semiconductors are parallel to the maximum valence and minimum conduction, and the aforementioned energy gap falls within the range of energy bandgaps found in inorganic semiconductors.

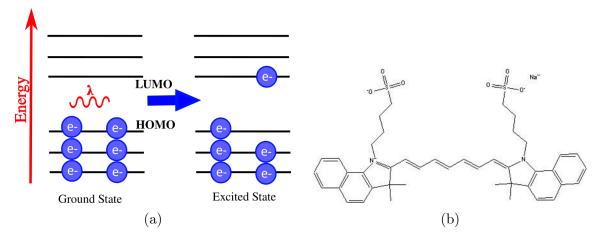


Figure 4.3: (a) Depiction of the Homo-Lumo gap in organic semiconductors and the transition occurring between ground and excited states. (b) The chemical structure of ICG provided by MP Biomedicals.

The following section details the properties of ICG and measurements of the optical properties when confined in HCPCF.

### **Absorption Cross-Section**

Due to the chemical formation of ICG, the absorption of the molecule when dissolved in a solvent is highly concentration-dependent. ICG is made up of monomers, which are a type of molecule that can react with other monomers to form polymer chains. In the case of ICG, its monomers react with each other to form dimers, a chain of two join monomers. With higher concentrations, monomers are closer in proximity and the molecules are more likely shift from monomers to dimers which are less likely to be excited and shift the center absorption wavelength. The concentration of monomer M to dimmers D is governed by the equilibrium reaction

$$M + M \rightleftharpoons D$$
 (4.1)

and law of mass action relation concentration

$$[D] = K_D[M]^2 \tag{4.2}$$

Where  $K_D$  is the dimmerization constant. Written in terms of concentration C and mole fractions,  $[M] = x_M C = (1 - x_D)C$  and  $[D] = \frac{x_D}{2}C$ ., the mole fraction of dimmers can be written in terms of the dimmerization constant and concentration.

$$x_D = 1 + \frac{1}{4K_DC} - \sqrt{\left(1 + \frac{1}{4K_DC}\right)^2 - 1} \tag{4.3}$$

The absorption cross-section model for ICG[4, 6] will be an average of the affects of the of monomers and dimmers, where d  $\sigma_M$  and  $\sigma_D$  are the monomer and dimer absorption cross-sections respectively.

$$\sigma = x_M \sigma_M + x_D \sigma_D = \sigma_M - x_D (\sigma_M - \sigma_D) \tag{4.4}$$

Plugging (4.3) into (4.4), remaining parameters could be found by doing a linear regression fit to absorption cross-section vs. concentration data from literature and the expected absorption cross-section could be calculated for any concentration. For ICG dissolved in H2O, the existing literature has some variation and so the upper/lower bounds and average were taken, while little data was available for ICG dissolved in D2O. The behavior in H2O and D2O are quite similar and are plotted in Fig4.4. At lower concentrations the absorption cross-section is slightly greater for D2O than H2O, with the reverse for high concentrations. The absorption center wavelength also changes with concentration. From the top figure of

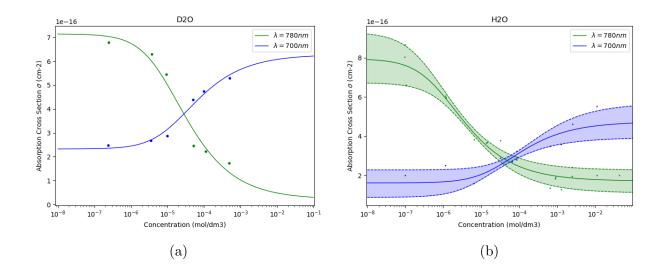


Figure 4.4: Absorption cross-section at peak wavelengths 700 nm(blue) and 780 nm(green) for ICG dissolved in D2O(a) and H2O(b) . Data from (cite) was fitted using a linear regression model.

ICG dissolved in D2O, the low concentrations show an absorption center peak at 778nm. The distribution slowly turns dimeric at concentrations near 38ppm, with a second peak popping up around 695nm. Increasing concentrations will turn the distribution monomeric again, centered at the 695nm absorption peak, reaching a maximum at a concentration near 77ppm and then dimming at increasing concentrations of the solution from here.

$\lambda_{peak} = 780nm$	$K_D$	$\sigma_{M}$	$\sigma_D$
[2]	$6.01x10^5$	$9.29x10^{-16}$	$2.28x10^{-16}$
[3]	$1.03x10^5$	$6.74x10^{-16}$	$1.54x10^{-16}$
[4]	$1.40x10^5$	$6.72x10^{-16}$	$1.11x10^{-16}$
Average	$3.06x10^6$	$7.94x10^{-16}$	$1.72x10^{-16}$

Table 4.3: Absorption Cross Section parameter fitting of ICG dissolved in deionized water. Fitting done with linear regression on  $\sigma$  vs. concentration data measured at  $\lambda = 780nm$  from literature.

$\lambda_{peak} = 700nm$	$K_D$	$\sigma_{M}$	$\sigma_D$
[2]	$3.00x10^3$	$2.29x10^{-16}$	$25.68x10^{-16}$
[4]	$3.06x10^4$	$8.89x10^{-16}$	$3.93x10^{-16}$
Average	$9.31x10^3$	$1.62x10^{-16}$	$4.74x10^{-16}$

Table 4.4: Absorption Cross Section parameter fitting of ICG dissolved in deionized water. Fitting done with linear regression on  $\sigma$  vs. concentration data at  $\lambda = 700nm$  from literature.

$\lambda_{peak}$	$K_D$	$\sigma_{M}$	$\sigma_D$
780nm	$3.22x10^4$	$7.14x10^{-16}$	$2.68x10^{-17}$
700nm	$1.67x10^4$	$2.833x10^{-16}$	$6.28x10^{-16}$

Table 4.5: Absorption Cross Section parameter fitting of ICG dissolved in heavy water. Fitting done with linear regression on  $\sigma$  vs. concentration data at  $\lambda = 700nm$  from literature.

### Photostability

The starting concentration and based on the data previously seen from [?] and [3] indicate that varying the concentration, ICG condition, and solvent will affect the storage life of the ICG solution. A table comparing these variables from [3] is included below.

Data from [7](top right plot) compares two concentrations, 0.4mg/L and 1mg/L ICG in water. Measurements over time indicate that lower concentrations deteriorate at faster rates but will do so linearly based on the initial concentration of ICG. This is corroborated by [?](center right plot) in where the optical density of ICG in water is plotted against different dilutions made from a single stock solution. Initial measurements indicated by the circles. The stock solution was then left out for 4hrs in daylight and then prepared and measured at the same dilutions, indicated by the crosses in the plot.

Light exposure of the solution will also exasperate the degradation process, as seen in the lower right plot from [7]. Fresh ICG solution at a concentration of 1mg/L at room temperature (22C) kept in the dark and room light. The results indicate that light exposure increases the rate of which the % remaining fluorescence reduces with time.

ICG is a "J-aggregate", which is a category of dyes that have a shift in absorption band to larger wavelengths in certain solvents. ICG when mixed into water and other solvents shifts to a center wavelength of 893nm over time and can be accelerated under high heat. For high-concentration ICG solutions J-aggregate solutions are stable. Solutions are typically heat-treated, like done in [5], and can be stored at room temperature for long periods.

### Fluorescence

The fluorescence quantum distribution data from [6] shows that the distribution area decreases as the solution concentration increases. The absorption cross-section data from [6] is shown in the center figure for reference, though the fluorescence and absorption cross-sections were not recorded using the same sample concentrations. The fluorescence peak is around 805nm for concentrations with a 780nm absorption peak and around 810nm for concentrations with a 695nm and absorption peak. The fluorescence peak begins to shift at high concentrations when the absorption cross-section begins to turn dimeric after the shift to the 695nm absorption peak.

The dimerization effects are attributed to: (1) The formation of weakly fluorescent ICG molecular aggregates at high concentrations (2) self-quenching (3) reabsorption of the emitted fluorescence by the ICG molecules due to overlap of the absorption and emission spectra.

The maximum fluorescence intensity in water is investigated in [7] and is achieved with a ICG concentration of 2mg/L, as shown in the bottom plot.

Preparation of J-aggregate ICG from [5]: "The J-aggregates were formed by preparing a 1.5e-3M (1g/L)aqueous solution of ICG-NaI and heating it to 65 °C for a period of 32 h. The solution was then stored at room temperature. The J aggregates formed are very stable. They remain unchanged over several months. Before fluorescence measurements, the samples were diluted to a concentration of  $3e - 5mol/dm^{-}3(27.12mg/L)$ . At this concentration, the J aggregates formed remain stable over about 1 day before they detach to monomers, dimers and small oligomers.."

From [5], plotted on the right is the absorption cross-section and fluorescence quantum distribution of J-aggregate ICG in water. There is no Stokes shift between the emission and absorption peak, but notably the excitation wavelength is at 834nm and the emission peak was measured to be 890nm.

While it is possible to measure the fluorescence of the J-aggregate solution, the quantum yield is very low (roughly 3e-4) and strong light scattering does not lend to accurate measurements.

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## 4.3 Experiment Set-Up

Preparation 1. Stock 1) Using the micropipette, measure 1ml of D2O or H2O into a vial 2) Using the scale, measure 1mg of ICG powder 3) Pour the measured ICG into the 1ml of D2O/H2O 4) Close the vial and shake for 15 seconds to dissolve

2. Dilution 1) Measure 5ml of D2O or H2O into a vial 2) Using the pipette, measure 10ul of the stock solution 3) Output the 10ul of stock solutions into the 100ml of D2O/H2O 4) Close the vial and shake for 15 seconds to dissolve Used within 12 hrs of creation

### 4.4 Results

# Chapter 5

# Future Work

5.1 ECDL

# References

# **APPENDICES**

## Appendix A

# **Bragg Gratings**

## A.1 Derivation of the 1D Propagation Matrix

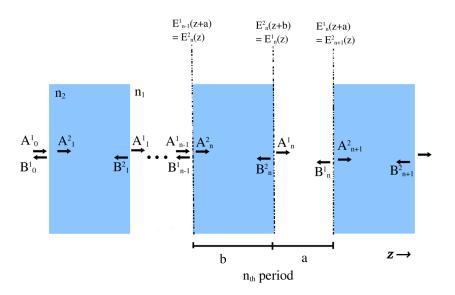


Figure A.1: Schematic of quarter wavelength stack

$$E_n^1(z) = A_n^1 e^{-ik_{z1}(z - (n-1)a)} + B_n^1 e^{ik_{z1}(z - (n-1)a)}; (n-1)a + b < z < na$$

$$E_n^2(z) = A_n^2 e^{-ik_{z2}(z - (n-1)a)} + B_n^2 e^{ik_{z2}(z - (n-1)a)}; (n-1)a < z < (n-1)a + b$$
(A.1)

Where  $k_j = \frac{2\pi}{n_j}$  The boundary conditions:

continuous between the layers:

$$E_n^1(z) = E_n^2(z+b) (A.2)$$

The second condition is that the electric field is smooth, which can be established in the perpendicular magnetic field. i.e. Maxwell's equations for a monochromatic field with freq  $\omega$  and time dependence  $e^-i\omega t$ 

Assuming that the electric field is linearly polarized  $E(z) = \hat{x}E(z)$ , then the magnetic field (via Faraday's law)  $H(z) = \hat{y}H(z)$  gives the corresponding magnetic field for the two layers

$$H_n^1(z) = \frac{1}{\eta_1} [A_n^1 e^{-ik_{z1}(z - (n-1)a)} - B_n^1 e^{ik_{z1}(z - (n-1)a)}]$$

$$H_n^2(z) = \frac{1}{\eta_2} [A_n^2 e^{-ik_{z2}(z - (n-1)a)} - B_n^2 e^{ik_{z2}(z - (n-1)a)}]$$
(A.3)

$$A_n^2(z) = \frac{1}{2} [E_n^2(z) + \eta_2 H_n^2(z)]$$

$$B_n^2(z) = \frac{1}{2} [E_n^2(z) - \eta_2 H_n^2(z)]$$
(A.4)

Where the impedance  $\eta_2 = \frac{\eta_0}{n^2}$ 

Putting these relations into a matrix form we can find a a solution for the transition boundary:

$$\begin{bmatrix}
E_{n-1}^{1}(z+a) \\
H_{n-1}^{1}(z+a)
\end{bmatrix} = \begin{bmatrix}
E_{n}^{2}(z) \\
H_{n}^{2}(z)
\end{bmatrix}$$

$$\begin{bmatrix}
1 & 1 \\
\eta_{1}^{-1} & -\eta_{1}^{-1}
\end{bmatrix} \begin{bmatrix}
A_{n-1}^{1}(z+a) \\
B_{n-1}^{1}(z+a)
\end{bmatrix} = \begin{bmatrix}
1 & 1 \\
\eta_{2}^{-1} & -\eta_{2}^{-1}
\end{bmatrix} \begin{bmatrix}
A_{n}^{2}(z) \\
B_{n}^{2}(z)
\end{bmatrix}$$

$$\begin{bmatrix}
A_{n-1}^{1}(z+a) \\
B_{n-1}^{1}(z+a)
\end{bmatrix} = M_{1\to 2} \begin{bmatrix}
A_{n}^{2}(z) \\
B_{n}^{2}(z)
\end{bmatrix}$$

$$\begin{bmatrix}
A_{n-1}^{1}(z+a) \\
B_{n-1}^{1}(z+a)
\end{bmatrix} = M_{1\to 2} \begin{bmatrix}
A_{n}^{2}(z) \\
B_{n}^{2}(z)
\end{bmatrix}$$
(A.5)

The transition matrix:

$$M_{1\to 2} = \frac{1}{2} \begin{bmatrix} 1 + \frac{k_2}{k_1} & 1 - \frac{k_2}{k_1} \\ 1 - \frac{k_2}{k_1} & 1 + \frac{k_2}{k_1} \end{bmatrix}$$
 (A.6)

The plane wave propagating though the material will acquire a phase:

$$M_{n_2} = \begin{bmatrix} e^{ik_{z2}b} & 0\\ 0 & e^{-ik_{z2}b} \end{bmatrix}$$
 (A.7)

Thus the travel through the n2 material can be summarized by

$$\begin{bmatrix} A_{n-1}^{1}(z+a) \\ B_{n-1}^{1}(z+a) \end{bmatrix} M_{1\to 2} M_{n2} \begin{bmatrix} A_{n}^{2}(z+b) \\ B_{n}^{2}(z+b) \end{bmatrix}$$
(A.8)

For the electric field through the n1 region:

$$M_{1\to 2} = \frac{1}{2} \begin{bmatrix} 1 + \frac{k_1}{k_2} & 1 - \frac{k_1}{k_2} \\ 1 - \frac{k_1}{k_2} & 1 + \frac{k_1}{k_2} \end{bmatrix} M_{n_1} = \begin{bmatrix} e^{ik_{z_1}a} & 0 \\ 0 & e^{-ik_{z_1}a} \end{bmatrix}$$
(A.9)

Becomes one periodic transition matrix:

$$M_p = M_{1\to 2} M_{n2} M_{2\to 1} M_{n1} = \begin{bmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{bmatrix}$$

For an N period block:

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