First-Principles Study of Emission Spectra of Fluorescent Dyes in the Gas Phase

by

Margarita Gladkikh

A thesis submitted in conformity with the requirements for the degree of Master of Science
Department of Chemistry
University of Toronto

© Copyright by Margarita Gladkikh 2017
Abstract

Isotope effects were found experimentally in four fluorescent dyes: cresyl violet, darrow red, oxazine 4 and oxazine 170. To understand the underlying mechanism responsible for these effects, we searched for a first-principles approach to describe the electronic structure of these dye molecules. We found that TD-DFT methods using TPSS and B3LYP functionals with the 6-31G* basis set performed well in describing emission spectra of these dyes. This provided us with a solid base for further investigation of the isotope effect in these compounds.
Acknowledgements

I would like to acknowledge my supervisor Prof Artur Izmaylov for his contribution to this thesis. I would also like to thank Dr Jayashree Nagesh for all the work she did on cresyl violet and for the discussions that we had on the topics related to this project. She was always friendly, patient, encouraging and kind, which I really appreciated. I’d like to thank my colleagues Sarah, Rami and Loïc for all their great help. I’d also like to thank Hava for her friendship both in and outside of the office.

My family and friends have been really supportive throughout this project and for that I am grateful. This thesis would not have been possible without my many friends here and in Vancouver, as well as my parents Valeri and Neonila, and my sister Maria, who I love very much.
# Contents

Acknowledgements iii

Table of Contents iv

List of Tables v

List of Figures vi

1 Introduction 1

2 Theory 3
  2.1 Born-Oppenheimer Representation ........................................ 3
  2.2 Franck-Condon Principle ...................................................... 8
  2.3 Comparing Theoretical and Experimental Energies ..................... 10
  2.4 Radiative and Nonradiative Transitions ................................ 13
  2.5 Intersystem Crossing and Spin-Orbit Coupling ................................................................. 15
  2.6 Normal Modes .................................................................. 16

3 Methods 19
  3.1 Electronic Structure: Density Functionals and Basis Sets .................. 19
  3.2 Time-Independent vs. Time-Dependent Methods for Obtaining Emission Spectra .... 22

4 Results 24
  4.1 Electronic Structure: Density Functionals and Basis Sets .................. 24
  4.2 Emission Spectra of Four Oxazine Dyes ........................................ 24

5 Conclusion 32

Bibliography 33
# List of Tables

1.1 Fluorescence quantum yields, $\Phi_{rel}$, and lifetime ratios, $\frac{\tau_D}{\tau_H}$, of four oxazine dyes. *The experimentalists from the Jockusch group responsible for generating this data were unable to obtain a quantum yield for deuterated darrow red. 

3.1 Temperatures of vibrational energy redistribution in four oxazine dyes.

4.1 A comparison of functionals and basis sets for cresyl violet. The third column, $\bar{E}$, was calculated from Equation 2.21, using $E'_{e,i}(R_e)$ and $E_{e,i}(R_e)$ obtained from the Gaussian program for the respective functional and basis set combinations.

4.2 A comparison of functionals and basis sets for darrow red. The basis set for all the entries was chosen to be $6-31G^*$. 

4.3 A comparison of functionals and basis sets for oxazine 4. The basis set for all the entries was chosen to be $6-31G^*$. 

4.4 A comparison of functionals and basis sets for oxazine 170. The basis set for all the entries was chosen to be $6-31G^*$. 

1

22

25

25

25

26
List of Figures

1.1 Molecular structures of four oxazine dyes. .............................................. 1

2.1 Appearance of emission spectra. ............................................................... 14
2.2 Two competing processes in the emission of energy. ................................. 15
2.3 Pathways available for emission. .............................................................. 16

3.1 Excitation, thermal relaxation and emission processes in a dye molecule. ...... 20

4.1 Emission spectra with different methods for cresyl violet. In the legend, TI denotes
time-independent, TD denotes time-dependent, 0K denotes emission spectra that were
performed at $T = 0K$, 315K denotes emission spectra that were performed at $T = 315K$,
and exp denotes the experimental spectrum of cresyl violet from Figure 1.1. .......... 28
4.2 Emission spectra with different methods for deuterated cresyl violet. The same color
scheme is used here as in Figure 4.1. .......................................................... 28
4.3 Emission spectra with different methods for darrow red. The same color scheme is used
here as in Figure 4.1. .................................................................................. 29
4.4 Emission spectra with different methods for deuterated darrow red. The same color
scheme is used here as in Figure 4.1. .......................................................... 29
4.5 Emission spectra with different methods for oxazine 4. The same color scheme is used
here as in Figure 4.1. .................................................................................. 30
4.6 Emission spectra with different methods for deuterated oxazine 4. The same color scheme
is used here as in Figure 4.1. ...................................................................... 30
4.7 Emission spectra with different methods for oxazine 170. The same color scheme is used
here as in Figure 4.1. .................................................................................. 31
4.8 Emission spectra with different methods for deuterated oxazine 170. The same color
scheme is used here as in Figure 4.1. .......................................................... 31
Chapter 1

Introduction

It has been found recently \cite{1} that the deuteration of a series of standard oxazine dyes (Figure 1.1) increases the lifetimes of their excited states (Table 1.1) and the brightness of the fluorescence they emit. We aim to obtain a microscopic picture of the isotope effect in this series from first principles.

![Cresyl violet](image1.png)

![Darrow red](image2.png)

![Oxazine 4](image3.png)

![Oxazine 170](image4.png)

Figure 1.1: Molecular structures of four oxazine dyes.

Our work is organized as follows. Chapter 2 provides background information on topics relevant

<table>
<thead>
<tr>
<th>Dye</th>
<th>$\frac{\tau_D}{\tau_H}$</th>
<th>$\Phi_{rel}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cresyl violet</td>
<td>1.19 ± 0.06</td>
<td>1.42</td>
</tr>
<tr>
<td>Darrow red</td>
<td>1.12 ± 0.04</td>
<td>N/A*</td>
</tr>
<tr>
<td>Oxazine 4</td>
<td>1.10 ± 0.03</td>
<td>1.41</td>
</tr>
<tr>
<td>Oxazine 170</td>
<td>1.17 ± 0.03</td>
<td>1.43</td>
</tr>
</tbody>
</table>

Table 1.1: Fluorescence quantum yields, $\Phi_{rel}$, and lifetime ratios, $\frac{\tau_D}{\tau_H}$, of four oxazine dyes. *The experimentalists from the Jockusch group responsible for generating this data were unable to obtain a quantum yield for deuterated darrow red.
Chapter 1. Introduction

to this thesis. Chapter 3 features a discussion of the computational methods used and the approach we took to calculating emission spectra. Due to limited time, we did not model the quantum yields and lifetime ratios for the four dyes. Chapter 4 presents all of the emission spectra generated, as well as a discussion on our findings. We found electronic structure methods that provided excellent agreement with experimental emission spectra. We hope that these methods will allow us to quantitatively model the isotope effect in future. Finally, Chapter 5 closes this thesis, and provides future directions we will take to complete this project, such as the further exploration of processes which compete with fluorescence in the hydrogen forms of these dyes, and investigate the behaviour of the quantum yields and lifetime ratios in Table 1.1.
Chapter 2

Theory

2.1 Born-Oppenheimer Representation

To establish some notation, we will introduce the Born-Oppenheimer representation. The overall molecular Hamiltonian is

\[ H_{\text{mol}} = T_N + T_e + V_{eN} + V_{NN} + V_{ee} \]  

(2.1)

where \( T_e \) and \( T_N \) are the kinetic energies of the electrons and nuclei, and \( V_{eN}, V_{ee} \) and \( V_{NN} \) are the electron-nuclear attractive, electron-electron repulsive and nuclear-nuclear repulsive Coulombic potential energies, respectively. Explicitly, \( T_e, T_N, V_{eN}, V_{ee} \) and \( V_{NN} \) can be described by the equations below, in atomic units:

\[
T_N = \sum_A^N \frac{p_A^2}{2m_A} \\
T_e = \sum_a^n \frac{p_a^2}{2} \\
V_{eN} = -\sum_A^N \sum_a^n \frac{Z_A}{|R_A - r_a|} \\
V_{ee} = \sum_a^n \sum_{b<a}^n \frac{1}{|r_a - r_b|} \\
V_{NN} = \sum_A^N \sum_{B<A}^N \frac{Z_A Z_B}{|R_A - R_B|}
\]

(2.2)  

(2.3)  

(2.4)  

(2.5)  

(2.6)

where \( A \) corresponds to the index of the \( N \) nuclei, \( a \) corresponds to the index of the \( n \) electrons, and \( R_A = (X_A, Y_A, Z_A) \) and \( r_a = (x_a, y_a, z_a) \) are nuclear and electronic coordinates. \(^2\)

The molecular wavefunction is given by \( \Psi(\mathbf{r}, \mathbf{R}) \), where \( \mathbf{r} \) and \( \mathbf{R} \) represent the collective elec-
tronic and nuclear coordinates:

\[ \mathbf{r} = (r_1, r_2, ..., r_n) \]
\[ \mathbf{R} = (R_1, R_2, ..., R_N). \]

As a result, the molecular time-independent Schrödinger equation is [2]

\[ H_{\text{mol}} \Psi(\mathbf{r}, \mathbf{R}) = E \Psi(\mathbf{r}, \mathbf{R}). \] (2.7)

The molecular Hamiltonian given above is general, and can be used to solve for any chemical or physical property in our system of interest. \( \Psi(\mathbf{r}, \mathbf{R}) \) takes on the form

\[ \Psi(\mathbf{r}, \mathbf{R}) = \sum_{i} \phi_i(\mathbf{r}; \mathbf{R}) \chi_i(\mathbf{R}), \] (2.8)

which is termed the Born-Huang expansion and is exact, since the basis set of electronic wavefunctions, \( \phi_i \), is complete and \( \chi_i \) is not fixed. Each term in the basis set is comprised of a product of \( \phi_i \) and a nuclear wavefunction, \( \chi_i \). [3] Unfortunately, for large systems, solving the molecular Schrödinger equation using the Born-Huang expansion can be computationally expensive. [2] Hence, we introduce the Born-Oppenheimer approximation, which is applicable to most chemical problems and in which the molecular wavefunction is separated into a single product of the electronic and nuclear components: [3]

\[ \Psi(\mathbf{r}, \mathbf{R}) = \phi(\mathbf{r}; \mathbf{R}) \chi(\mathbf{R}). \] (2.9)

The justification for the Born-Oppenheimer approximation is presented in the following derivation. Let us designate an electronic Hamiltonian, \( H_e \), to be

\[ H_e = T_e + V_{eN} + V_{ee} + V_{NN}, \] (2.10)

whose eigenfunction is the electronic wavefunction. Thus, the molecular Schrödinger equation, using the Born-Huang expansion, is now

\[ (H_e + T_N) \sum_i \phi_i(\mathbf{r}; \mathbf{R}) \chi_i(\mathbf{R}) = E \sum_i \phi_i(\mathbf{r}; \mathbf{R}) \chi_i(\mathbf{R}). \] (2.11)
Now, if we integrate out the electronic coordinates,

\[
\sum_i \int dr \phi^*_i(r; R)(H_e + T_N)\phi_i(r; R)
= \sum_i \sum_A \frac{1}{2m_A} \sum_i \int dr \phi^*_i(r; R) \frac{\partial^2}{\partial R^2_A} \phi_i(r; R) \chi_i(R)
= E_{c,j}(R)\chi_j(R) - \sum_A \frac{1}{2m_A} \sum_i \int dr \phi^*_i(r; R) \frac{\partial^2}{\partial R^2_A} \chi_i(R)
= \sum_A \frac{1}{2m_A} \sum_i \int dr \phi^*_i(r; R) \frac{\partial^2}{\partial R^2_A} \chi_i(R)
= E_{c,i}(R) + T_N \chi_i(R).
\] (2.12)

Under the Born-Oppenheimer approximation, the integral terms present in the above derivation are considered to be negligible. In this case, the final solution to the above would equate to the simple and compact

\[
(E_{c,i}(R) + T_N)\chi_i(R) = E_i(R).
\] (2.13)

Suppose we want to find under which conditions the integral terms in Equation 2.12 are negligible. We first make the following designations:

\[
\begin{align*}
F_{ji} &= \int dr \phi^*_j(r; R) \frac{\partial}{\partial R} \phi_i(r; R) \\
&= \langle \phi_j | \frac{\partial}{\partial R} \phi_i \rangle \\
G_{ji} &= \int dr \phi^*_j(r; R) \frac{\partial^2}{\partial R^2} \phi_i(r; R) \\
&= \langle \phi_j | \frac{\partial^2}{\partial R^2} \phi_i \rangle.
\end{align*}
\]

Now, to derive an alternative expression for \(F_{ji}\) in terms of energies,

\[
\frac{\partial}{\partial R} \langle \phi_j | H_e | \phi_i \rangle = \langle \phi_j | H_e | \frac{\partial}{\partial R} \phi_i \rangle + \langle \phi_j | \frac{\partial}{\partial R} | H_e | \phi_i \rangle + \langle \phi_j | \frac{\partial H_e}{\partial R} | \phi_i \rangle
= E_{c,i}(R) \langle \phi_j | \phi_i \rangle + E_{c,j}(R) \langle \phi_j | G_{ji} \phi_i \rangle + \langle \phi_j | F_{ji} \phi_i \rangle.
\]
If
\[ \frac{\partial}{\partial R_A} \langle \phi_j | \phi_i \rangle = \langle \phi_j | \frac{\partial \phi_i}{\partial R_A} \rangle + \langle \phi_j | \frac{\partial \phi_i}{\partial R_A} \rangle, \]
then after a rearrangement,
\[ \frac{\partial}{\partial R_A} \langle \phi_j | H_e | \phi_i \rangle = E_{e,i}(R) \left( \frac{\partial}{\partial R_A} \langle \phi_j | \phi_i \rangle - \langle \phi_j | \frac{\partial \phi_i}{\partial R_A} \rangle \right) + E_{e,j}(R) \langle \phi_j | \frac{\partial \phi_i}{\partial R_A} \rangle + \langle \phi_j | \frac{\partial H_e}{\partial R_A} | \phi_i \rangle = (E_{e,i}(R) - E_{e,j}(R))F_{ji} + \langle \phi_j | \frac{\partial H_e}{\partial R_A} | \phi_i \rangle. \]  
(2.14)

where \( \langle \phi_i | \phi_i \rangle \) is a constant so its derivative is 0. If \( j \neq i \), then
\[ \frac{\partial}{\partial R_A} \langle \phi_j | H_e | \phi_i \rangle = \frac{\partial}{\partial R_A} (E_{e,i}(R) \langle \phi_j | \phi_i \rangle) = 0. \]

Inserting this result into Equation 2.14 produces
\[ 0 = (E_{e,i}(R) - E_{e,j}(R))F_{ji} + \langle \phi_j | \frac{\partial H_e}{\partial R_A} | \phi_i \rangle \]
and with a simple rearrangement, we obtain the nonadiabatic derivative coupling term, \( F_{ji} \):
\[ F_{ji} = \frac{\langle \phi_j | \frac{\partial H_e}{\partial R_A} | \phi_i \rangle}{E_{e,j}(R) - E_{e,i}(R)}. \]  
(2.15)

In Equation 2.15, if \( E_{e,j} >> E_{e,i} \) (or vice versa), \( F_{ji} \approx 0 \). This suggests that when the electronic states, \( i \) and \( j \), are well-separated, the coupling between them is negligible and the Born-Oppenheimer approximation holds, enabling us to separate the molecular wavefunction into nuclear and electronic degrees of freedom. In contrast, if \( E_{e,j} \to E_{e,i} \), \( F_{ji} \to \infty \). This suggests that if the electronic energy eigenvalues are nearly equal, a small change in the nuclear coordinates produces a large change in the electronic wavefunctions. In this event, the Born-Oppenheimer approximation breaks down and \( F_{ji} \) can no longer be ignored. [4]
Next, we derive an expression for $G_{ji}$, once again differentiating with respect to $R_A$:

$$\frac{\partial}{\partial R_A} \left( \frac{\partial}{\partial R_A} \langle \phi_j | H_e | \phi_i \rangle \right) = \frac{\partial}{\partial R_A} \left( (E_{e,i}(R) - E_{e,j}(R))F_{ji} + \langle \phi_j | \frac{\partial H_e}{\partial R_A} | \phi_i \rangle \right)$$

$$= F_{ji} \frac{\partial}{\partial R_A} (E_{e,i}(R) - E_{e,j}(R))$$

$$+ (E_{e,i}(R) - E_{e,j}(R)) \left( \frac{\partial \phi_j}{\partial R_A} | \frac{\partial \phi_i}{\partial R_A} \right)$$

$$+ (E_{e,i}(R) - E_{e,j}(R)) \langle \phi_j | \frac{\partial^2 \phi_i}{\partial R_A^2} \rangle$$

$$+ \frac{\partial}{\partial R_A} \left( \phi_j | \frac{\partial H_e}{\partial R_A} | \phi_i \right).$$

Recalling that $G_{ji} = \langle \phi_j | \frac{\partial^2 \phi_k}{\partial R_A^2} \rangle$ and $(E_{e,j}(R) - E_{e,i}(R))F_{ji} = \langle \phi_j | \frac{\partial H_e}{\partial R_A} | \phi_i \rangle$, we make the appropriate substitutions:

$$\frac{\partial}{\partial R_A} \left( \frac{\partial}{\partial R_A} \langle \phi_j | H_e | \phi_i \rangle \right) = F_{ji} \frac{\partial}{\partial R_A} (E_{e,i}(R) - E_{e,j}(R))$$

$$+ (E_{e,i}(R) - E_{e,j}(R)) \left( \frac{\partial \phi_j}{\partial R_A} | \frac{\partial \phi_i}{\partial R_A} \right)$$

$$+ (E_{e,i}(R) - E_{e,j}(R))G_{ji}$$

$$+ \frac{\partial}{\partial R_A} \left( (E_{e,j}(R) - E_{e,i}(R))F_{ji} \right).$$

We use a resolution of identity to simplify the second term in the above:

$$\langle \frac{\partial \phi_j}{\partial R_A} | \frac{\partial \phi_i}{\partial R_A} \rangle = \sum_k \langle \frac{\partial \phi_j}{\partial R_A} | \phi_k \rangle \langle \phi_k | \frac{\partial \phi_i}{\partial R_A} \rangle$$

and given that

$$\frac{\partial}{\partial R_A} \langle \phi_j | \phi_k \rangle = \langle \frac{\partial \phi_j}{\partial R_A} | \phi_k \rangle + \langle \phi_j | \frac{\partial \phi_k}{\partial R_A} \rangle$$

$$0 = \langle \frac{\partial \phi_j}{\partial R_A} | \phi_k \rangle + \langle \phi_j | \frac{\partial \phi_k}{\partial R_A} \rangle,$$

the resolution of identity is therefore

$$\langle \frac{\partial \phi_j}{\partial R_A} | \frac{\partial \phi_i}{\partial R_A} \rangle = - \sum_k \langle \phi_j | \frac{\partial \phi_k}{\partial R_A} \rangle \langle \phi_k | \frac{\partial \phi_i}{\partial R_A} \rangle$$

$$= - \sum_k F_{jk} F_{ki}.$$
The overall expression for $G_{ji}$ is now
\[
\frac{\partial}{\partial R_A} \left( \frac{\partial}{\partial R_A} \langle \phi_j | H_e | \phi_i \rangle \right) = F_{ji} \frac{\partial}{\partial R_A} (E_{e,i}(R) - E_{e,j}(R)) \\
+ (E_{c,i}(R) - E_{c,j}(R)) \left( - \sum_k F_{jk} F_{ki} \right) \\
+ (E_{c,i}(R) - E_{c,j}(R)) G_{ji} \\
+ \frac{\partial}{\partial R_A} [(E_{c,j}(R) - E_{c,i}(R)) F_{ji}].
\]

From before, we know that $\frac{\partial}{\partial R_A} \langle \phi_j | H_e | \phi_i \rangle = 0$ since $j \neq i$,
\[
0 = 2F_{ji} \frac{\partial}{\partial R_A} (E_{e,i}(R) - E_{e,j}(R)) + (E_{c,i}(R) - E_{c,j}(R)) \left( - \sum_k F_{jk} F_{ki} \right) \\
+ (E_{c,i}(R) - E_{c,j}(R)) G_{ji} + \frac{\partial}{\partial R_A} (E_{c,j}(R) - E_{c,i}(R)) F_{ji} \\
+ (E_{c,j}(R) - E_{c,i}(R)) \left( \frac{\partial F_{ji}}{\partial R_A} \right)
\]
\[
G_{ji} = \sum_k F_{jk} F_{ki} + \frac{\partial F_{ji}}{\partial R_A},
\]
which is the nonadiabatic scalar coupling term. If the electronic states, $i$ and $j$, are well-separated, the nonadiabatic derivative coupling term ($F_{ji}$) will be negligible, resulting in a negligible $G_{ji}$ under these conditions.

### 2.2 Franck-Condon Principle

The Born-Oppenheimer approximation is used not only to establish the mathematical equations and variables we will use throughout later chapters of this thesis, but also to introduce the concept of electronic energy surfaces. Each electronic energy surface is described by $E_{e,i}(R)$, and supports a series of vibrational energy levels. To describe the electronic transitions between these surfaces, we will be using the Franck-Condon principle. This principle describes the vertical transitions of the system between surfaces during absorption or emission events.

The Franck-Condon principle is a rule that describes the excitation of a system from the ground vibrational state on the ground electronic state, to an excited vibrational state on an excited electronic state of our system of interest. The Franck-Condon principle is based on the idea that the nuclear masses in a molecule are considerably larger than the masses of the electrons, and as a result, the nuclear framework can be considered stationary during an electronic transition. This is because the time required for a nuclear vibration is considerably longer than that of an electronic excitation.\[5\]

Mathematically, the vertical excitation of the system can be formulated using the following
procedure. We evaluate the transition dipole moment between the ground and excited states (in this thesis we will focus on transitions to the first excited state only, for simplicity), which are represented by $|\phi_0 \chi_i\rangle$ and $|\phi_1 \chi'_j\rangle$ according to the Born-Oppenheimer approximation, respectively, where $\phi_0$ and $\phi_1$ are the ground and first excited electronic wavefunctions and $\chi_i$ and $\chi'_j$ are the vibrational wavefunctions.

In a molecule, the dipole moment operator is given by the following expression:

$$
\mu = \sum a z_a r_a + \sum A Z_A R_A
= \mu_e + \mu_N, \tag{2.16}
$$

where $z_a$ and $Z_A$ are the charges of the electrons and nuclei, respectively, and $r_a$ and $R_A$ are their coordinates. [5, 6]

The transition dipole moment is given by [5]

$$
\langle \phi_0 \chi_i | \mu | \phi_1 \chi'_j \rangle = \langle \phi_0 \chi_i | \mu_e + \mu_N | \phi_1 \chi'_j \rangle
= \langle \phi_0 \chi_i | \mu_e | \phi_1 \chi'_j \rangle + \langle \chi_i | \mu_N | \chi'_j \rangle \langle \phi_0 | \phi_1 \rangle. \tag{2.17}
$$

Since the ground and first excited states are orthogonal, $\langle \phi_0 | \phi_1 \rangle = 0$, the second term in Equation 2.17 is zero.

The electronic transition dipole moment can be defined as

$$
M_{01}(R) = \langle \phi_0 | \mu_e | \phi_1 \rangle, \tag{2.18}
$$

which can be expanded in a Taylor series about a convenient $R$, $R_e$:

$$
M_{01}(R) = M_{01}(R_e) + \sum_A \frac{\partial M_{01}(R)}{\partial R_A} \bigg|_{R_e} (R - R_e) + \frac{1}{2} \sum_A \sum_B \frac{\partial^2 M_{01}(R)}{\partial R_A \partial R_B} \bigg|_{R_e} (R - R_e)^2 + \ldots. \tag{2.19}
$$

It is assumed that the $R$ dependence of the electronic transition dipole is weak because it originates only from the electronic functions. Thus, we truncate the Taylor expansion at $M_{01}(R_e)$, a much simpler version of $M_{01}(R)$. [6, 7] For convenience, we will choose the $R_e$ value to equal the minimum of the first excited electronic state energy. Now, the electronic dipole moment, and the overall transition dipole moment become

$$
\langle \phi_0 \chi_i | \mu | \phi_1 \chi'_j \rangle \approx M_{01}(R_e) \langle \chi_i | \chi'_j \rangle. \tag{2.20}
$$
2.3 Comparing Theoretical and Experimental Energies

Now that we have given a detailed analysis of the Born-Oppenheimer approximation and the Franck-Condon principle, we would like to turn our attention to the determination of the emission energy, or the energy from the minimum of the excited electronic state to a point directly below on the ground electronic state. To compute the emission energy using the Gaussian program, we must choose the best method and basis set. To accomplish this, we would need to compare the experimentally obtained emission energy to the theoretically obtained one via Gaussian, and the method and basis set which yield the theoretical values closest to experimental ones can be considered the best for the purposes of our study. Unfortunately, in our method and basis set search, we quickly encounter a problem. Experimental emission spectra yield bands consisting of multiple peaks. In electronic structure theory, however, the simplest quantity to evaluate is a vertical electronic energy difference. How, then, can we compare the broad bands from experimental spectra to the single value representing the electronic transition in theory? To address this question, we turn to a paper written by Davidson and Jarzęcki. [8]

Davidson and Jarzęcki developed a procedure of estimating the vertical electronic excitation energy from ab initio calculations and experimental absorption spectra. We modified their equations to accommodate emission spectra. Following Davidson and Jarzęcki’s procedure, below is the average energy of an emission event, using ab initio calculations:

\[ \bar{E} = E_{e,1}(R_e) - E_{e,0}(R_e), \]  

where \( \bar{E} \) is the difference between the excited and ground electronic states at the equilibrium geometry of the latter state. \( \bar{E} \) can also be obtained from the experimental emission spectrum using the following expression:

\[ \bar{E} = \frac{\sum_i I_{0'\rightarrow i}}{\sum_i \Delta E_{0'\rightarrow i}}, \]  

where \( I_{0'\rightarrow i} \) is the intensity of the electronic transition and \( \Delta E_{0'\rightarrow i} \) is the energy separation between the ground, 0′, and excited, i, vibrational levels belonging to different electronic states. Below is the derivation of Equation 2.22.

The intensity \( I_{0'\rightarrow i} \) of the emission process is defined by the expression below:

\[ I_{0'\rightarrow i} = N_{0'} h c \nu_{0'\rightarrow i} \kappa_{0'\rightarrow i}, \]  

where \( N_{0'} \) is the number of molecules on the ground vibrational level of the excited electronic state, \( h c \nu_{0'\rightarrow i} \) is the energy of individual light quanta, \( \nu_{0'\rightarrow i} \) is the wavenumber of each quantum, and \( \kappa_{0'\rightarrow i} \) is the Einstein probability of transition emission, denoting the fraction of molecules which participate.
in the emission process taking them from the ground vibrational level on the excited electronic state
to various vibrational levels on the ground electronic state. Furthermore, $\kappa_{0'\rightarrow i}$ is proportional to the
matrix element of an electronic transition:

$$\kappa_{0'\rightarrow i} = \frac{64\pi^3 \nu_{0'\rightarrow i}^3}{3\hbar} |\langle \chi'_0 | M_{10} | \chi_i \rangle|^2. \quad (2.24)$$

Thus, disregarding some constants, $I_{0'\rightarrow i}$ can be rewritten as

$$I_{0'\rightarrow i} \approx \nu_{0'\rightarrow i}^4 |\langle \chi'_0 | M_{10} | \chi_i \rangle|^2. \quad (2.25)$$

Equation 2.25 can be rearranged to obtain the intensity weighted average energy of the emission
process, which is

$$\frac{I_{0'\rightarrow i}}{\Delta E_{0'\rightarrow i}^4} \approx |\langle \chi'_0 | M_{10} | \chi_i \rangle|^2. \quad (2.26)$$

If there are transitions to multiple vibrational states on the ground electronic state, the sum of the
intensity weighted average energies produces

$$\sum_i I_{0'\rightarrow i} = \sum_i \langle \chi'_0 | M_{10} | \chi_i \rangle \langle \chi_i | M_{10} | \chi'_0 \rangle$$

$$\approx M_{10}(R_e)^2 \sum_i \langle \chi'_0 | \chi_i \rangle \langle \chi_i | \chi'_0 \rangle$$

$$= M_{10}(R_e)^2 \langle \chi'_0 | \chi'_0 \rangle$$

$$= M_{10}(R_e)^2. \quad (2.27)$$

We can use Equation 2.26 to obtain an expression for the third power of energy by rearranging it:

$$\frac{I_{0'\rightarrow i}}{\Delta E_{0'\rightarrow i}^3} = \langle \chi'_0 | M_{10} | \chi_i \rangle \Delta E_{0'\rightarrow i} \langle \chi_i | M_{10} | \chi'_0 \rangle. \quad (2.28)$$
As a result, the sum of the intensity weighted average energies produces

\[
\sum_i \frac{I_{\alpha'\rightarrow i}}{\Delta E_{\alpha'\rightarrow i}} = \sum_i \langle \chi_0' | M_{10} | \chi_i \rangle \Delta E_{\alpha'\rightarrow i} \langle \chi_i | M_{10} | \chi_0' \rangle
\]

\[
= \sum_i \langle \chi_0' | M_{10} | \chi_i \rangle (E_{\alpha'} - E_i) \langle \chi_i | M_{10} | \chi_0' \rangle
\]

\[
= \sum_i \langle \chi_0' | M_{10} | \chi_i \rangle \langle \chi_i | M_{10} | \chi_0' \rangle \langle \chi_0' | H' | \chi_0' \rangle
\]

\[
- \sum_i \langle \chi_0' | M_{10} | \chi_i \rangle \langle \chi_i | H M_{10} | \chi_0' \rangle
\]

\[
= M_{10}(R_e)^2 \sum_i \langle \chi_0' | M_{10} | \chi_i \rangle \langle \chi_i | \chi_0' \rangle \langle \chi_0' | H' | \chi_0' \rangle
\]

\[
- \sum_i \langle \chi_0' | M_{10} | \chi_i \rangle \langle \chi_i | H M_{10} | \chi_0' \rangle
\]

\[
= M_{10}(R_e)^2 \langle \chi_0' | H' | \chi_0' \rangle - \langle \chi_0' | M_{10} H M_{10} | \chi_0' \rangle.
\] (2.29)

where \( H' = T_N + E_{e,1} \) is the excited state Hamiltonian, and \( H = T_N + E_{e,0} \) is the ground state Hamiltonian. Putting it all together,

\[
\sum_i \frac{I_{\alpha'\rightarrow i}}{\Delta E_{\alpha'\rightarrow i}} = M_{10}(R_e)^2 \frac{\langle \chi_0' | H' | \chi_0' \rangle - \langle \chi_0' | M_{10} H M_{10} | \chi_0' \rangle}{M_{10}(R_e)^2}
\]

\[
= M_{10}(R_e)^2 \langle \chi_0' | H' | \chi_0' \rangle - M_{10}(R_e)^2 \sum_i \sum_k \langle \chi_0' | M_{10} | \chi_k \rangle \langle \chi_k | H | \chi_i \rangle \langle \chi_i | M_{10} | \chi_0' \rangle
\]

\[
= \frac{M_{10}(R_e)^2}{M_{10}(R_e)^2}
\]

\[
= \frac{M_{10}(R_e)^2}{M_{10}(R_e)^2}
\]

\[
= \frac{M_{10}(R_e)^2}{M_{10}(R_e)^2}
\]

\[
= \langle \chi_0' | H' | \chi_0' \rangle - \langle \chi_0' | H | \chi_0' \rangle
\]

\[
= \langle \chi_0' | T_N + E_{e,1}(R) | \chi_0' \rangle - \langle \chi_0' | T_N + E_{e,0}(R) | \chi_0' \rangle
\]

\[
= \langle \chi_0' | T_N | \chi_0' \rangle + \langle \chi_0' | E_{e,1}(R) | \chi_0' \rangle - \langle \chi_0' | T_N | \chi_0' \rangle - \langle \chi_0' | E_{e,0}(R) | \chi_0' \rangle
\]

\[
= \langle \chi_0' | E_{e,1}(R) | \chi_0' \rangle - \langle \chi_0' | E_{e,0}(R) | \chi_0' \rangle.
\] (2.30)

To a first approximation, the result of Equation 2.30 becomes

\[
\sum_i \frac{I_{\alpha'\rightarrow i}}{\Delta E_{\alpha'\rightarrow i}} = E_{e,1}(R_e) - E_{e,0}(R_e).
\] (2.31)

The left-hand side in Equation 2.31 can be generated using broad experimental bands from emission...
spectra discretized appropriately, and the right-hand side contains a single value corresponding to the vertical transition in an emission event that can be easily calculated in theory.

2.4 Radiative and Nonradiative Transitions

Up to this point, we have been constructing the theoretical and mathematical foundations we need to understand and discuss the phenomena of absorption and emission in the general case. We would like to now present a few radiative and non-radiative pathways which compete with fluorescence, to rationalize why the replacement of a hydrogen atom with deuterium affects the fluorescence properties of our four oxazine dyes.

Upon photoexcitation, the excited state of a molecule can be deactivated by either radiative or nonradiative channels. If the excited molecule exists in a high-energy singlet state, for instance, it will transition to the lowest-energy excited singlet or triplet state, after which it will fluoresce or release energy via a radiationless transition. Internal conversion is nonradiative, and occurs between states of the same spin multiplicity. In contrast, intersystem crossing while also nonradiative occurs between states of different spin multiplicity. Both internal conversion and intersystem crossing are a means to bring a highly excited molecule to the lowest-energy excited state, before the molecule releases energy in the form of fluorescence or a radiationless transition via a conical intersection and arrives at the ground electronic state. [9]

We will first discuss the appearance of emission spectra to analyze possible radiative decay pathways which can deactivate an excited molecule, after which we will differentiate radiative and nonradiative transitions before delving into internal conversion and intersystem crossing. On the following page, we present two example spectra that can appear differently depending on the orientation of the electronic energy levels.

The rightmost diagrams in Figure 2.1 show two electronic energy surfaces, $S_0$ and $S_1$, which arise from the Born-Oppenheimer approximation, and the horizontal lines, $\chi_1$, $\chi_2$, etc., represent the vibrational energy levels. If the excited electronic energy surface, $S_1$, is directly above the ground electronic energy surface, $S_0$, the largest peak that will be found in the corresponding emission spectrum will be the 0-0 transition. The system will reside in the ground vibrational state, $\chi'_0$, on $S_1$, and will emit energy enabling it to relax to the ground vibrational state, $\chi_0$, on $S_0$.

The 0-0 transition is the most intense due to the greatest overlap, $S(\chi_i, \chi'_j)$, occurring between the two ground vibrational levels. If, however, the excited electronic energy surface is greatly horizontally displaced relative to the ground, the 0-0 transition will be small because the overlap between the two ground vibrational levels will be small. Better overlaps will occur between $\chi'_0$, and other vibrational levels on $S_0$, such as $\chi_2$ in this example. As a result, other peaks in the emission spectrum will be more intense than the 0-0 transition, such as the 0-2 peak here.
In the figure below (Figure 2.2), are depicted two competing phenomena in the hydrogen species: fluorescence, which is shown in red, and the dispersion of energy through heat via a conical intersection, shown in blue.

The importance of the conical intersection in this competition depends on the horizontal displacement of the excited electronic energy surface relative to the ground electronic energy surface. From the rightmost diagram in Figure 2.2, evidently \( S_1 \) is quite significantly horizontally displaced relative to \( S_0 \). As a result, \( S_0 \) and \( S_1 \) overlap, which forms a point termed a conical intersection where the two states intersect. If the conical intersection is sufficiently low in energy, which is caused by a large horizontal displacement, the radiationless transition pathway will then compete with fluorescence. This would result in electronic energy transforming to heat, rather than light, as the system undergoes a transition to the ground electronic energy surface. The left diagram features a very minimal horizontal displacement of \( S_1 \) relative to \( S_0 \). As a result, the conical intersection is not observed in this example because the point at which these two states meet is too high in energy. Thus, in this event the conical intersection will not play a major role in the release of energy by the electron and the system will primarily release its energy through fluorescence.
2.5 Intersystem Crossing and Spin-Orbit Coupling

Besides fluorescence and $S_1 \rightarrow S_0$ nonradiative transitions, there exist other means of deactivating the excited state energy. Intersystem crossing is a nonradiative transition that occurs between states of different multiplicity. It is a phenomenon which has been observed in a variety of systems— in the presence of heavy atoms, triplet oxygen, in transition metal complexes and in organic compounds. [10]

In chromophores, fluorescence can compete with radiationless transitions or intersystem crossing. Radiationless decay occurs from the first excited singlet state, $S_1$, to the ground electronic state, $S_0$. In intersystem crossing, $S_1$ is converted to a triplet state, $T_n$. The reaction rate coefficient of intersystem crossing has an inverse dependence on the energy gap between the singlet and triplet states. [9]

In summary, evidently several pathways are available for emission (Figure 2.3). One such pathway proceeds by first, internal conversion, during which the spin state is conserved, followed by a quenching of the lowest-energy excited state by either radiative (fluorescent) or nonradiative (via a conical intersection) decay. The second pathway proceeds by first, intersystem crossing, during which the spin state changes from singlet to triplet, followed by a quenching of the lowest-energy excited state by either radiative (phosphorescent) or nonradiative (via a conical intersection) decay.
2.6 Normal Modes

In polyatomic molecules, vibrations are complex (relative to diatomics). Normal modes are especially useful here because they greatly simplify the vibrational Hamiltonian in the harmonic approximation.

The vibrational Hamiltonian for an \( N \)-atom molecule is given by the following:

\[
H_{\text{vib}} = -\frac{1}{2} \sum_{i=1}^{N} \frac{1}{m_i} \frac{\partial^2}{\partial R_i^2} + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{\partial^2 V}{\partial R_i \partial R_j} (R_i - R_{i,e})(R_j - R_{j,e}) + V(R_{eq}),
\]

(2.32)

where \( m_i \) are the nuclear masses, \( R_i = (X_i, Y_i, Z_i) \) are the nuclear coordinates, and \( R_{eq} = (R_{1,e}, R_{2,e}, ..., R_{i,e}) \) is the equilibrium position. To remove the mixed derivatives in the second term in Equation 2.32, we implement a mass-weighted transformation:

\[
q_i = \sqrt{m_i} (R_i - R_{i,e}),
\]

(2.33)

where \( q_i \) represents the displacement of each atom from its equilibrium position during a vibration. The
potential energy can then be written as

\[ \Delta V = V(q_1, q_2, ..., q_N) - V(0, 0, ..., 0) \]

\[ = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left( \frac{\partial^2 V}{\partial q_i \partial q_j} \right) q_i q_j + \cdots \]

\[ = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} f_{ij} q_i q_j + \cdots, \]

(2.34)

a Taylor expansion of \( V \) about the equilibrium nuclear geometry. The derivative in the first-order term equates to 0 at the minimum of the potential energy surface of a polyatomic molecule, resulting in only quadratic terms or higher in Equation 2.34. [11]

If we consider only small displacements about the minimum of the potential energy surface, terms beyond the second-order, or anharmonic terms, will be negligible. Furthermore, the second derivative cross terms in Equation 2.34 will greatly complicate the process of obtaining a solution for the Schrödinger equation of a polyatomic molecule, but using a unitary transformation from \( q \) to a new set of coordinates \((Q_i)\), we can eliminate them. This new set of coordinates is called normal coordinates, [11] or normal modes: [12]

\[ \Delta V = \frac{1}{2} \sum_{i=1}^{N_{\text{vib}}} \Omega_i^2 Q_i^2, \]

(2.35)

where \( N_{\text{vib}} \) is the number of vibrational degrees of freedom.

The vibrational Hamiltonian in terms of normal coordinates is given by the following:

\[ H_{\text{vib}} = \sum_{i=1}^{N_{\text{vib}}} H_{\text{vib},i} \]

\[ = \sum_{i=1}^{N_{\text{vib}}} \left( -\frac{1}{2} \frac{\partial^2}{\partial Q_i^2} + \frac{1}{2} \Omega_i^2 Q_i^2 \right). \]

(2.36)

The corresponding eigenfunction will be [11]

\[ \eta_i(Q_1, Q_2, ..., Q_{N_{\text{vib}}}) = \eta_1(Q_1)\eta_2(Q_2)\cdots\eta_{N_{\text{vib}}}(Q_{N_{\text{vib}}}). \]

(2.37)

Earlier, we had written the overall transition dipole moment in Equation 2.20. Since the method we are implementing in the Gaussian program relies on the harmonic approximation detailed in the equations above, we resort to writing the multidimensional wavefunctions \( \chi_i \) and \( \chi_j \) in Equation 2.20 in the form of Equation 2.37— a product of one-dimensional wavefunctions, each dependent on a normal coordinate.

If we rewrite \( M_{01}(R) \) in Equation 2.19 using normal coordinates about \( Q_0 \), the equilibrium geometry of the final state, we can truncate this Taylor expansion to the zeroth-order term, according
to the Franck-Condon principle. This corresponds to the Franck-Condon (FC) approximation in our method in the Gaussian program. The FC approximation yields relatively accurate results for electronic transitions which are fully allowed ($|M_{01}(Q_0)| \gg 0$). [13]

To account for the changes in the transition dipole dependence on the nuclear coordinates, we can use the Herzberg-Teller (HT) approximation instead, which involves conserving only the linear term in the Taylor expansion while discarding all others. The last approximation, which we chose for our calculations, is the Franck-Condon Herzberg-Teller (FCHT) approximation, which includes both the zeroth- and first-order terms. [13]
Chapter 3

Methods

3.1 Electronic Structure: Density Functionals and Basis Sets

For our electronic structure method, we chose the time-dependent density functional theory (TD-DFT) because it provides a good combination of affordable computational cost and accuracy. [14] We tested many functionals by comparing $\bar{E}_{th}$ calculated by them with $\bar{E}_{exp}$ and found that the Tao-Perdew-Staroverov-Scuseria (TPSS) [15] density functional provides the best agreement between theoretical and experimental $\bar{E}$ for most of the systems (however, Becke-3-Parameter (Exchange)-Lee-Yang-Parr (B3LYP) [16]–[17] was used for darrow red because TPSS experienced convergence issues in this case). We also used the popular basis set 6–31G*, since other basis sets such as the polarized valence triple zeta correlation consistent basis set cc-pVTZ, [18] and 6–311G*+ [19] did not yield much difference in the vertical excitation energy but were somewhat more computationally expensive.

Estimating the Temperature of the Vibrational Relaxation Process

We are interested in evaluating the vibrational temperature of an excited molecule as the initial energy is redistributed among the vibrational degrees of freedom on an excited electronic state. To accomplish this, we first present an illustration of the process of emission in a dye molecule. In our diagram, $S_0$ and $S_1$ correspond to ground and excited electronic energy surfaces, with each surface containing vibrational energy levels, represented by the symbols $\chi_i$ and $\chi'_j$. Both electronic energy surfaces are built according to the Born-Oppenheimer approximation described earlier in this thesis.

In Figure 3.1, the labels $E_{0,elec}$ and $E_{1,elec}$ refer to the ground and excited electronic state energy minima, respectively. They are determined by a geometry optimization in Gaussian, and are calculated relative to electrons and nuclei separated at an infinite distance. As a result, the energy minima for many molecular systems, including our dye molecules of interest, are very large and negative, hence the ground and excited electronic states in Figure 3.1 lie below the $R$-axis. The labels $ZPE_0$ and $ZPE_1$
Figure 3.1: Excitation, thermal relaxation and emission processes in a dye molecule.

refer to the ground and excited zero-point energies, respectively. The zero-point energy is defined as the energy of the system at $T = 0K$, which is the ground vibrational state on any electronic state of a molecule.

In Figure 3.1, the system initially resides on the ground vibrational state of the ground electronic state. If the molecule is at $T = 0K$, the system will be found on the ground vibrational state on the ground electronic state. Otherwise, the system can have contributions from an excited vibrational state on the ground electronic state if the molecule is at nonzero temperature.

If light energy is delivered to the molecule, the system will then transition from the ground to the excited electronic state, as shown by the upward arrow labeled $\Delta E_{\text{exc}}$. This excitation of the system will occur directly vertically upwards, as dictated by the Franck-Condon principle. The system will reach a point on the excited electronic state which is directly above its starting position on the ground electronic state, and this point is labelled $E_{\text{FCpoint}}$, the Franck-Condon point.

Next, the system experiences a vibrational energy redistribution from the non-stationary distribution at the Franck-Condon point to the Boltzmann distribution on the excited electronic state, as illustrated by the purple arrows. This redistribution process is driven by anharmonic couplings between normal modes. Originally, upon excitation, the energy delivered to the system via light was restricted to only a few modes, but due to couplings between modes this energy eventually dissipated among all
the modes.

Suppose we label this vibrational energy redistribution process by \( f(T) \). Let \( f(T) \) be some function, which depends on the temperature of the vibrational relaxation process, \( T \). We can now formulate an equation for \( f(T) \) to find the root \( T \):

\[
E_{0,tot} + \Delta E_{exc} = f(T) + ZPE_1 + E_{1,elec}. \quad (3.1)
\]

To compute the energies in Equation 3.1, we begin with the following equations. We calculate the internal energy of an Avogadro’s number of molecules which occupy the ground state:

\[
E_{0,tot} = E_{trans} + E_{rot} + E_{vib} + E_{0,elec}
\]

\[
= \frac{3}{2} RT_{exp} + RT_{exp} + \left[ \sum_i R\theta_i^2 + \sum_i \frac{R\theta_i}{e^{\theta_i/T_{exp}} - 1} \right] + E_{0,elec}. \quad (3.2)
\]

\( E_{trans} \) and \( E_{rot} \) are the translational and rotational energies of the molecule, respectively. \( E_{0,elec} \) is the ground state energy minimum. \( E_{vib} \) is the vibrational energy of the molecule and is comprised of two parts: the first term is the zero-point energy \((ZPE_0)\), consisting of a summation which contains the vibrational temperature, \( \theta_i \); the second term is the energy of each vibrational energy level. The experiments used to observe the fluorescence in cresyl violet, darrow red, oxazine 4 and oxazine 170 were conducted at 315K, which is the value of \( T_{exp} \) in Equation 3.2. We can now calculate \( E_{0,tot} \), the energy of an electron in a dye molecule residing on some vibrational energy level on the ground electronic state. We also obtain \( \Delta E_{exc} \), the excitation energy of the electron by finding the difference between the sum of \( E_{0,elec} \) and \( ZPE_0 \), and the Franck-Condon point, \( E_{FCpoint} \). Lastly, the value of \( ZPE_1 \) can be calculated using the same equation as for \( ZPE_0 \), and the value of \( E_{1,elec} \) can be found in the log file from the excited state geometry optimization in Gaussian. After rearranging Equation 3.1 and inserting the energy values we calculated, we can conclude that

\[
f(T) = E_{0,tot} + \Delta E_{exc} + ZPE_1 - E_{1,elec} = \text{constant.} \quad (3.3)
\]

Now, we want to determine an expression for \( f(T) \) with respect to \( T \). To transition to the excited electronic state from the ground electronic state, an energy of \( \Delta E_{exc} \) must be delivered to the system. Thus, the following is true:

\[
E_{0,tot} + \Delta E_{exc} = E_{1,tot} \quad (3.4)
\]

Note that the left-hand side of Equation 3.4 is identical to the left-hand side of Equation 3.1. The right-hand side of \( E_{1,tot} \) is structured the same way as \( E_{1,tot} \):

\[
E_{1,tot} = E_{trans} + E_{rot} + ZPE_1 + \sum_i \frac{R\theta_i}{e^{\theta_i/T_{exp}} - 1} + E_{1,elec} \quad (3.5)
\]
### Table 3.1: Temperatures of vibrational energy redistribution in four oxazine dyes.

<table>
<thead>
<tr>
<th>Dye</th>
<th>$T_H(K)$</th>
<th>$T_D(K)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cresyl violet</td>
<td>378.0</td>
<td>376.5</td>
</tr>
<tr>
<td>Darrow red</td>
<td>344.2</td>
<td>342.8</td>
</tr>
<tr>
<td>Oxazine 4</td>
<td>338.8</td>
<td>337.9</td>
</tr>
<tr>
<td>Oxazine 170</td>
<td>338.7</td>
<td>338.0</td>
</tr>
</tbody>
</table>

If we compare the right-hand side of Equation 3.4, defined in Equation 3.5, to the left-hand side of Equation 3.1, we observe that the components $ZPE_1$ and $E_{1,elec}$ are common to both equations. This means that the expression for $f(T)$ consists of the other three components of $E_{1,tot}$, which are

$$f(T) = E_{trans} + E_{rot} + \sum_i \frac{R\theta_i}{e^\frac{R\theta_i}{T} - 1}$$

$$= \frac{3}{2}RT + RT + \sum_i \frac{R\theta_i}{e^\frac{R\theta_i}{T} - 1}. \quad (3.6)$$

Now we solve $f(T) = 0$ to get the temperature of the equilibrium Boltzmann distribution on the excited electronic state (Table 3.1). The temperatures for the hydrogen ($T_H$) and deuterium ($T_D$) species of the dyes are different because the vibrational frequencies and masses of the hydrogen and deuterium forms of these dyes are different. We also observe that the substitution of a hydrogen atom for deuterium does not significantly change the vibrational temperature according to Table 3.1, which means that not many vibrational frequencies are affected by deuteration.

#### 3.2 Time-Independent vs. Time-Dependent Methods for Obtaining Emission Spectra

Emission spectra can be obtained via either time-independent or time-dependent approaches. The time-independent, or sum-over-states, method generates an emission spectrum as a collection of all transitions occurring from the initial to the final vibrational levels, while considering each level as independent of all others. Unfortunately, the time-independent approach is very cost-intensive for the types of molecules we are interested in. This prompted us to seek other methods of spectrum calculation, such as the time-dependent method. [20]

The time-independent method can be mathematically formulated below:

$$I = \frac{2N_A \omega^4}{3\epsilon_0 c^3} \sum_i \sum_j p_i |\langle \chi'_j | M_{10} | \chi_i \rangle|^2 \delta \left( E_i - E'_j - \omega \right), \quad (3.7)$$

where $I$ is the transition intensity for one-photon emission, $N_A$ is Avogadro’s number of molecules, $\epsilon_0$ is the permittivity of free space, $c$ is the speed of light, $\omega$ is the angular frequency, $p_i$ is the Boltzmann
population, and $\delta$ is the Dirac delta function. The indices $i$ and $j$ enumerate the initial and final vibrational states with energies $E_i$ and $E_j$, respectively. \[20\]

Conversely, the time-dependent method can be derived by substituting the Dirac delta function with its integral representation,

$$\delta(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} dt.$$ \hfill (3.8)

The full derivation of the time-dependent approach is given in Bloino’s paper, [20] which we will not provide here except for the final result:

$$I = \frac{2N_A\omega^4}{3\epsilon_0 c^3 Z} \int_{-\infty}^{\infty} dt \text{Tr} (\gamma(t)) e^{-i(\omega_{ij} - \omega)t},$$ \hfill (3.9)

where $\omega_{ij}$ is the frequency of the energy gap separating the ground vibrational levels on the excited and ground electronic states. Equation 3.9 is the Fourier transform of the autocorrelation function $\gamma(t)$,

$$\gamma(t) = M_{10}e^{-\left(\frac{i}{\hbar} - it\right)M'_{10}}e^{-it\hbar}.$$ \hfill (3.10)

where $\hbar$ is the Boltzmann constant and $T$ is the temperature. In Equation 3.9, $Z$ is the Boltzmann population of all the vibrational levels on the excited electronic state:

$$Z = \prod_{i=1}^{N_v} \left(2\sinh\left(\frac{\omega_i}{2k_BT}\right)\right)^{-1},$$ \hfill (3.11)

where $\omega_i$ are vibrational frequencies of the excited electronic state. \[20\]
Chapter 4

Results

4.1 Electronic Structure: Density Functionals and Basis Sets

To choose the best functional and basis set, we screened a range of functionals and basis sets for each dye.

The density functional/basis set combination LC-wPBE/6–31G* (as well as LSDA/6–31G* and TPSS/6–31G* for darrow red) terminated early due to errors, and further attempts to finish these calculations will be performed in the future. Since choosing larger basis sets did not have an appreciable effect on $\bar{E}$, we used only the basis set 6–31G* for future screening procedures. On the following page are the screens for darrow red, oxazine 4, and oxazine 170.

We found that the functional/basis set combination that produced the closest $\bar{E}$ relative to its experimental equivalent from Equation 2.22 was TPSS/6–31G*. Despite our best efforts, we could not successfully optimize the excited state of darrow red, thus we settled on the B3LYP/6–31G* combination for it instead.

4.2 Emission Spectra of Four Oxazine Dyes

After selecting a functional and basis set for each dye, we generated vibronically-resolved electronic emission spectra in the Gaussian program. We found that the peak progressions and intensities of the theoretical spectra produced by Gaussian matched well with the experimental spectra we were given by the Jockusch group. We also noted that the time-independent spectra were less broadened while the time-dependent spectra were more broadened. The time-independent spectra were originally generated as stick spectra, and then artificially broadened. In comparison, the time-dependent spectra relied on the autocorrelation function (Equation 3.10) for broadening, which decayed rapidly due to a large number of nuclear degrees of freedom.
### Table 4.1: A comparison of functionals and basis sets for cresyl violet. The third column, $\bar{E}$, was calculated from Equation 2.21, using $E_{e,i}'(R_e)$ and $E_{e,i}(R_e)$ obtained from the Gaussian program for the respective functional and basis set combinations.

| Functional | Basis Set | $\bar{E}_{th}$ | $|\bar{E}_{th} - E_{ex}|$ |
|------------|-----------|-----------------|--------------------------|
| B3LYP      | 6 – 31G*  | 2.43            | 0.28                     |
| CAM-B3LYP  | 6 – 31G*  | 2.65            | 0.49                     |
| LC-wPBE    | 6 – 31G*  | N/A             | N/A                      |
| LSDA       | 6 – 31G*  | 2.13            | 0.03                     |
| PBE        | 6 – 31G*  | 2.05            | 0.10                     |
| PBEh       | 6 – 31G*  | 2.53            | 0.37                     |
| TPSS       | 6 – 31G*  | 2.11            | 0.04                     |
| B3LYP      | cc-pVTZ   | 2.44            | 0.29                     |
| TPSS       | cc-pVTZ   | 2.13            | 0.02                     |
| TPSSh      | cc-pVTZ   | 2.33            | 0.18                     |
| B3LYP      | 6 – 311G*+| 2.42            | 0.27                     |

### Table 4.2: A comparison of functionals and basis sets for darrow red. The basis set for all the entries was chosen to be 6 – 31G*.

| Functional | $\bar{E}_{th}$ | $|\bar{E}_{th} - E_{ex}|$ |
|------------|-----------------|--------------------------|
| B3LYP      | 2.42            | 0.23                     |
| CAM-B3LYP  | 2.61            | 0.43                     |
| LC-wPBE    | N/A             | N/A                      |
| LSDA       | N/A             | N/A                      |
| PBE        | 1.83            | 0.35                     |
| PBEh       | 2.50            | 0.36                     |
| TPSS       | N/A             | N/A                      |

### Table 4.3: A comparison of functionals and basis sets for oxazine 4. The basis set for all the entries was chosen to be 6 – 31G*.

| Functional | $\bar{E}_{th}$ | $|\bar{E}_{th} - E_{ex}|$ |
|------------|-----------------|--------------------------|
| B3LYP      | 2.51            | 0.39                     |
| CAM-B3LYP  | 2.71            | 0.59                     |
| LC-wPBE    | N/A             | N/A                      |
| LSDA       | 2.18            | 0.06                     |
| PBE        | 2.10            | 0.02                     |
| PBEh       | 2.64            | 0.52                     |
| TPSS       | 2.15            | 0.03                     |
Chapter 4. Results

| Functional   | $\tilde{E}_{th}$ | $|\tilde{E}_{th} - \tilde{E}_{ex}|$ |
|--------------|------------------|-------------------------------|
| B3LYP        | 2.39             | 0.33                          |
| CAM-B3LYP    | 2.56             | 0.50                          |
| LC-wPBE      | N/A              | N/A                           |
| LSDA         | 2.14             | 0.09                          |
| PBE          | 2.08             | 0.02                          |
| PBEh         | 2.64             | 0.41                          |
| TPSS         | 2.13             | 0.07                          |

Table 4.4: A comparison of functionals and basis sets for oxazine 170. The basis set for all the entries was chosen to be $6-31G^*$.  

The emission spectra at $T = 0K$ enabled us to observe the vibronic transitions which were participating in the emission process. At $T = 0K$, the rightmost peak in the emission spectrum corresponds to the 0-0 transition. According to Figures 4.1 – 4.8, in each $T = 0K$ curve the 0-0 transition was found to be the most intense. The intensity of the 0-0 peak is a result of the excited electronic state being minimally horizontally displaced relative to the ground electronic state. Thus, the best vibrational overlap occurs between the ground vibrational state on each electronic state (as illustrated in Figure 2.1).  

We used the spectra in Figures 4.1 – 4.8 to qualitatively determine which process was likely competing with fluorescence. As we noted before, phosphorescence occurred on too long of a timescale to be observed so we know we will not see evidence of its competition with fluorescence here. This leaves us with two non-radiative options: the $S_1 \rightarrow S_0$ transition or the $S_1 \rightarrow T_n$ transition. We came to the conclusion that the $S_1 \rightarrow S_0$ transitions were not likely to play a major role in the reduction of fluorescence in the deuterium species. The 0-0 peak in these plots is the most intense, a phenomenon which occurs when the excited electronic state is directly above the ground electronic state. However, if this is the case, the conical intersection involved in this transition would then be very high in energy. Consequently, it would be improbable in this event for the system to proceed via the radiationless channel, rather than the fluorescence channel as it relaxes to the ground state. We can conclude, then, that the most likely pathway competing with fluorescence would be an excitation, first, to the $S_1$ state, followed by a transfer to a $T_n$ state via intersystem crossing. We have yet to verify our hypothesis, however, which would be the basis for future work on this project.  

Lastly, we found that there were no significant differences between the spectra of the hydrogen forms of the dyes versus their deuterated counterparts. The only exception in the spectra we have included appears in cresyl violet (Figure 4.1) versus deuterated cresyl violet (Figure 4.2). These two spectra feature noticeable differences. Otherwise, the lack of differences between the deuterated and non-deuterated spectra suggests to us that we must look for an explanation for the effect of isotopic substitution in these dyes elsewhere, such as in terms of the singlet-triplet channel. We also observed that the deuterated and non-deuterated experimental spectra of the dyes were indistinguishable so we
were not expecting differences in the theoretical spectra we generated in Gaussian.
Figure 4.1: Emission spectra with different methods for cresyl violet. In the legend, TI denotes time-independent, TD denotes time-dependent, 0K denotes emission spectra that were performed at $T = 0K$, 315K denotes emission spectra that were performed at $T = 315K$, and exp denotes the experimental spectrum of cresyl violet from Figure 1.1.

Figure 4.2: Emission spectra with different methods for deuterated cresyl violet. The same color scheme is used here as in Figure 4.1.
Figure 4.3: Emission spectra with different methods for darrow red. The same color scheme is used here as in Figure 4.1.

Figure 4.4: Emission spectra with different methods for deuterated darrow red. The same color scheme is used here as in Figure 4.1.
Figure 4.5: Emission spectra with different methods for oxazine 4. The same color scheme is used here as in Figure 4.1.

Figure 4.6: Emission spectra with different methods for deuterated oxazine 4. The same color scheme is used here as in Figure 4.1.
Figure 4.7: Emission spectra with different methods for oxazine 170. The same color scheme is used here as in Figure 4.1.

Figure 4.8: Emission spectra with different methods for deuterated oxazine 170. The same color scheme is used here as in Figure 4.1.
Chapter 5

Conclusion

In this thesis, we sought to investigate the effect of exchanging an acidic proton for a deuterium atom in the dyes cresyl violet, darrow red, oxazine 4 and oxazine 170. As of now, the full explanation has not been obtained yet. The first objective of our work was to find an electronic structure method in order to build a microscopic picture of this isotope effect. The second objective was to reproduce the experimental emission spectra with their vibrational structures and to analyze the features of these spectra.

To accomplish these tasks, we tested a number of functionals and basis sets, and found that TPSS/6−31G* worked well to provide an accurate microscopic picture (B3LYP/6−31G* was chosen for darrow red). Furthermore, we were able to reproduce time-independent and time-dependent emission spectra which were comparable with the experimental spectra of the oxazine chromophores.

Future directions of this project would include verifying that the process which competes with fluorescence is the intersystem crossing pathway \( S_1 \rightarrow T_n \), and finishing our calculations for the quantum yield and lifetime ratios of the four dyes.
Bibliography


