

**Computational Modeling of Spectral Properties of Nickel Dithiolenes**

Rui Wang

**Fairport High School**  
Fairport, NY

Advisor: Kenneth Marshall

**Laboratory for Laser Energetics**  
University of Rochester  
Rochester, NY

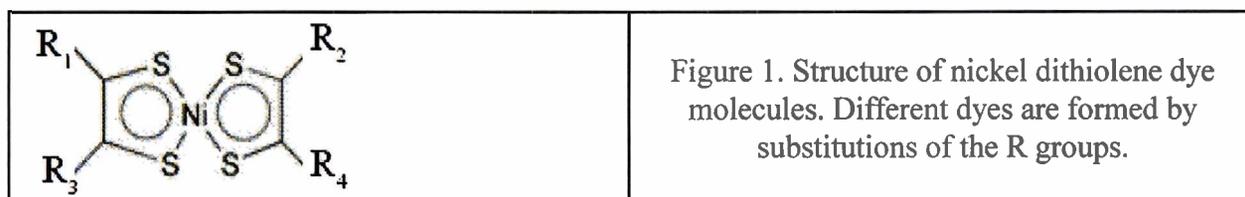
November 2006

## Abstract

Nickel dithiolene dyes, noted for their intense long-wavelength electronic transitions, have been notoriously difficult molecules to model. This study has investigated the use of time-dependent density functional theory (TDDFT) to model these dyes. The absorption spectra of an extensive set of near-infrared nickel dithiolene dyes have been evaluated for the first time using TDDFT. Bulk solvent effects have also been accounted for. Excellent agreement between theoretical and experimental maximum absorption wavelengths has demonstrated the high accuracy of TDDFT. Successful prediction of the physical properties of proposed nickel dithiolene dyes leads to informed selection of candidates for future synthesis, significantly reducing the time and cost of materials development. Calculations for new nickel dithiolene dyes predict that the addition of sulfur atoms to the side chains will increase the maximum absorption wavelength by up to 160 nm. These results can aid in the further development of nickel dithiolene dyes in applications including near-infrared lasers, telecommunications, and sensor protection.

## 1. Introduction

Nickel dithiolenes were first synthesized in the 1960s and were noted for their intense absorption over a broad range of near-infrared (IR) wavelengths. These organometallic dyes contain a zerovalent planar core with dithiolene rings surrounding a nickel atom (Figure 1).



Nickel dithiolene dyes have characteristics that can be useful in an array of applications. Their intense long wavelength absorption is a result of the low-energy  $\pi$ - $\pi^*$  transition between

the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO)<sup>1</sup>. In addition, this class of dyes exhibits an auxochromic shift (shift in absorption spectra) depending on the R groups attached<sup>2</sup>. This property makes nickel dithiolenes useful as near-IR dyes for optical applications. The zerovalent nature of the dithiolene core imparts relatively high solubility in nonpolar solvents, including liquid crystal hosts, and makes these dyes useful for near-IR liquid crystal device applications<sup>3</sup>. Some metal dithiolenes have an inherent liquid crystal phase<sup>4</sup> and thus can be dissolved in a liquid crystal host in relatively large quantities without changing the characteristics of the host fluid.

Transition-metal dithiolenes are of interest for many applications. First, the inherent solubility and stability of these materials lead to their use in photodetectors<sup>5</sup>, which are used by the fiber-optic telecommunications market as components that detect laser light in fiber-optic systems and transform that light into electrical current. The primary wavelengths of interest for this application are 1300 nm and 1550 nm. They can be used for both long-haul transport and telecommunications receiver systems carrying high-speed voice and data/Internet traffic<sup>5</sup>. Second, nickel dithiolene dyes are used in Q-switching saturable absorbers to produce short intense pulses for IR lasers because of their high thermal and optical stability.<sup>2</sup> A dye with an absorption maximum near the laser wavelength will absorb the laser radiation and the electrons of the dye molecules will be boosted into the excited state as the energy level in the lasing medium increases. When the dye is optically “saturated” (most of the dye molecules are in the excited state) the dye no longer absorbs the laser radiation and a short, intense laser pulse is released. These lasers generally operate at wavelengths between 950 and 1100 nm. Third, because nickel dithiolenes absorb in the near-IR range, they are of interest for IR sensor protection for the military. For this application, the electronic absorption band is tunable from

around 600 nm to 1600 nm by changing either the dye structure (through synthesis), or the helical pitch length of the dye (if it is chiral).<sup>3</sup> The Air Force is currently investigating the application of transition metal dithiolenes absorbing in the 700-900 nm region as part of a liquid crystal electro-optical device for night vision and avionics applications.<sup>3</sup>

The synthesis of nickel dithiolenes is a multi-step, low-yield process and is thus costly and time-consuming. Conventional trial-and-error synthesis approaches result in the need to synthesize a large number of compounds to establish physical properties trends. As has been previously demonstrated in the pharmaceutical industry, computational chemistry can be used to predict the most promising materials for synthesis, thus resulting in substantial savings in time, resources, and cost.

Although computational methods are well established for organic compounds, very little work has been done in modeling the electron interactions in transition metal organometallic molecules. The most recent attempt at computing the structures and properties of nickel dithiolenes was performed by C. Lauterbach and J. Fabian.<sup>6</sup> Because of computational limitations and data availability, only a few nickel dithiolenes were modeled using an older method known as single configuration interaction (CIS).<sup>7</sup> More recently, D. Jacquemin et al.<sup>8, 9, 10</sup> predicted the optical properties of other classes of organic dyes such as indigo and nitro-diphenylamine derivatives using a newer method known as time dependent density functional theory (TDDFT)<sup>11</sup>. Their methodology produced relatively high computational accuracy for absorption spectra calculations. Thus, TDDFT seems a promising solution to the computational difficulties of nickel dithiolenes, which are also optical dyes.

In this study, the computational approach of TDDFT has been applied for the first time to predict the absorption spectra of nickel dithiolenes. The maximum absorption

wavelengths have been accurately predicted for a large number of nickel dithiolene dyes and four new dyes have been proposed that extend the maximum absorption wavelength further into the IR. This improved computational method can lead to advances not only in near-IR devices, but also in applications of optical dyes across the electromagnetic spectrum.

## 2. Previous Research

There are three common methods for excited state computation: (1) semiempirical and Zerner's Intermediate Neglect of Differential Overlap (ZINDO);<sup>12</sup> (2) Hartree-Fock and single configuration interaction (CIS);<sup>7</sup> and (3) density functional theory (DFT) and time-dependent density functional theory (TDDFT).<sup>11</sup>

The first calculations of nickel dithiolene properties used the early semiempirical quantum chemical models.<sup>13, 14</sup> These models save computational time by using experimental data to fit the calculation according to known parameters. Using approximations, this method decreases the computational time but at the cost of accuracy. ZINDO is one type of semiempirical algorithm for studying excited state and spectroscopic properties of molecules. This method is limited in accuracy, as all semiempirical models are, by the degree of similarity between the molecule being studied and known molecules from which parameters are taken.

In the Hartree-Fock method, all nuclei are assumed motionless with respect to the electrons, electron orbitals are expressed as one-electron functions centered on each atom, and the multi-electron calculation of the model is assumed to be given by the sum of all single-electron calculations of the molecule.<sup>15</sup> Relativistic effects and electron correlation effects (electron-electron interactions) are mostly neglected. The Hartree-Fock method becomes decreasingly accurate with increasing molecular size.<sup>15</sup> This method is used for approximating the ground state energy of a molecular system. Post-Hartree-Fock methods have been developed

to improve on the Hartree-Fock method by approximating the electron correlation of a system.<sup>16</sup> This gives more accurate results but at a greater computational cost. The single configuration interaction (CIS) is one example of a post-Hartree-Fock method limited to single excitations. This method is expanded from the Hartree-Fock calculations to incorporate electronic excitation and changing shell levels. However, known results using this method indicate that its accuracy is not high for larger molecules.<sup>15, 17</sup>

Previous work done on modeling nickel dithiolene dyes by Lauterbach and Fabian utilized the CIS method for excited-state absorption spectra calculations.<sup>6</sup> Their study calculated the structure, electron distribution, electron bonding, and spectral properties of transition-metal molecules including nickel dithiolenes. Other transition metal compounds investigated included metal diiminolenes, dioxylenes, and diselenolenes utilizing nickel, palladium, and platinum as the central metal. Lauterbach and Fabian performed all calculations in the gas phase and thus omitted all effects associated with the solvents that host the dyes during experimental measurements of the absorption spectrum. Their analysis of the structure focused mostly on the effect of substitutions for the nickel and sulfur atoms in Figure 1.

More recently, density functional theory has emerged as a useful computational method for ground state properties. Unlike the Hartree-Fock method, DFT uses the electron density as the foundation of its calculations instead of the many-electron wavefunction.<sup>16</sup> The main advantage is that the wavefunction, a complex function in multi-dimensional space that takes into account individual electrons, is replaced by a density function in three spatial dimensions, which greatly lowers the computational cost. DFT has been extended to time-dependent density functional theory (TDDFT), which models the evolution of the system in time in response to an external disturbance, as described below. Jacquemin used TDDFT extensively to model the absorption

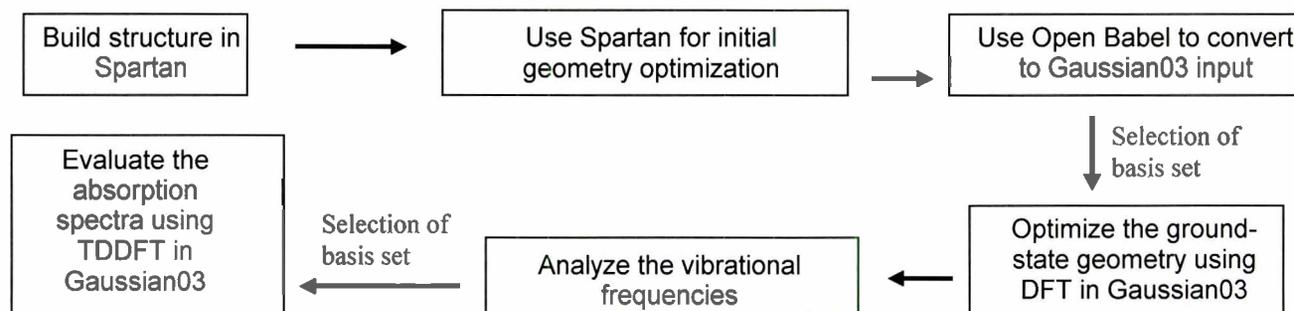
spectra of other optical dyes including indigo and anthraquinones-based dyes,<sup>8, 9, 10</sup> and consistently demonstrated the high accuracy of TDDFT for these dyes. DFT and TDDFT were selected for this study for their improved accuracy over other methods and comparable computational cost.

### 3. Methodology

This study used the Gaussian03 program<sup>18</sup> by Gaussian Inc. to carry out the quantum chemical calculations using DFT and TDDFT. Gaussian03 predicts the energies, molecular structures, vibrational frequencies, and excited-state transitions of molecular systems along with other physical properties derived from these calculations.<sup>18</sup>

The methodology shown in Figure 2 was developed for this study. First, the atoms, bonds,

Figure 2. An overview of the methodology developed.



and arrangement of each molecule are entered into a molecular modeling program, Spartan (Wavefunction Inc.), which is used to roughly approximate the initial geometry and output the Cartesian coordinates of each atom.<sup>19</sup> Spartan checks the bond lengths and angles with known molecules but does not optimize the geometry using energy minimization. Using OpenBabel, the coordinates are converted into a format that can be read by Gaussian03, which rigorously optimizes the ground state geometry through energy minimization, using DFT and a carefully selected basis set. Figure 3 shows the electron density map of the nickel dithiolene core in the

ground state calculated by Gaussian03.

Basis sets play an important role in these calculations. The electron density function of the given molecule is calculated using a linear combination of spatially dependent elementary functions contained in the basis sets. The potential function is calculated as the sum of the external potential (interactions with ions), the Hartree potential (classical electron-electron interactions), and the “exchange-correlation” potential (complex many-body effects that have to be approximated).<sup>20</sup> The basic concept of DFT is to vary the coefficients in the basis functions

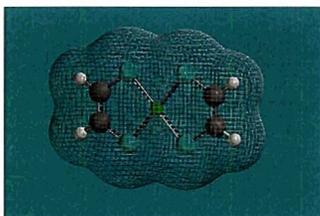


Figure 3. The ground-state electron density of the nickel dithiolene core (R=H).

and the coordinates of all the ions until a

stationary point with minimum energy is

found. The geometry at the point of the

energy minimum is given as the optimized

geometry. The choice of basis sets is important because enough functions are needed to give sufficient accuracy, yet too many or inappropriate functions may cause convergence problems that result in the program failing to find the lowest-energy minimum.

The vibrational spectrum is then analyzed to check the computed geometry, since the accuracy of the absorption spectra depends on the accuracy of the structure. The substantial computational time for the larger molecules leads to the omission of this step unless an anomaly in the absorption maximum warrants investigation of the vibrational frequencies.

Finally, the transition energy to the excited state is calculated using TDDFT. TDDFT disturbs the ground state density calculated by DFT by applying an impulse potential. This impulse potential contains all frequencies so that the frequency-dependent time evolution of the electron density allows the absorption spectrum and the wavelength of maximum absorption to be calculated.<sup>20</sup>

Since all reported experimental maximum absorption wavelengths of nickel dithiolene dyes were measured in solution, solvent effects are taken into account for both DFT and TDDFT calculations. The potential function is adjusted for the presence of solvents using the polarizable continuum model (PCM).<sup>21</sup> The PCM divides the calculation into a solute part (the nickel dithiolene molecule) and a solvent part (the surrounding solvent molecules), which is characterized by its dielectric constant, radius and other macro-scale properties.

#### **4. Optimization Of Basis Sets**

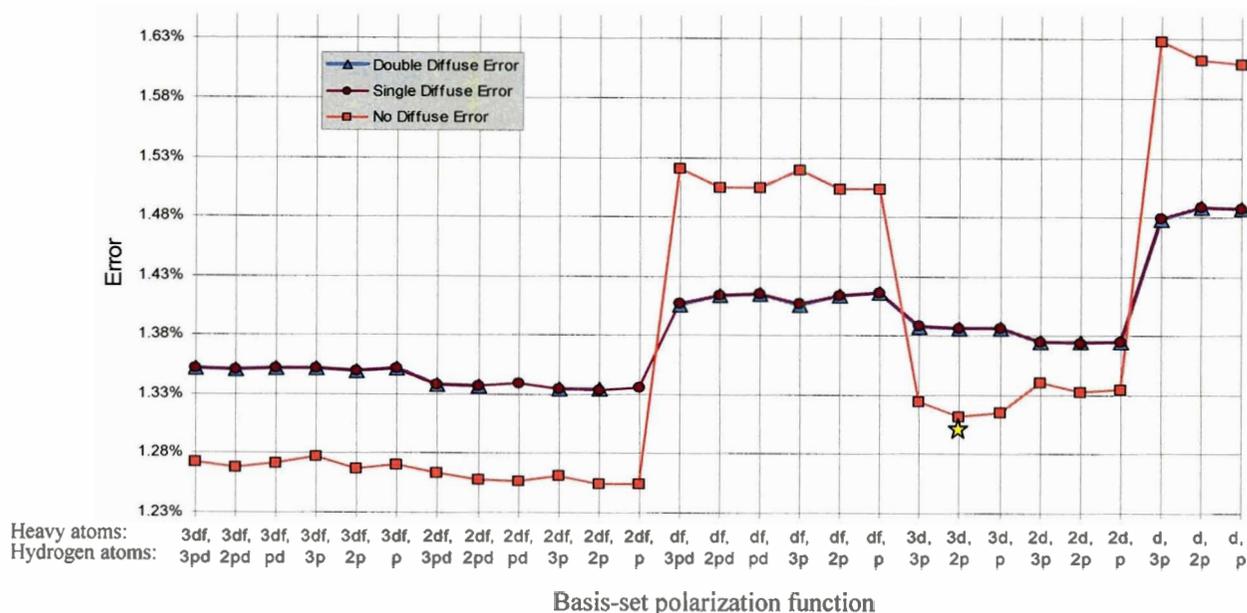
##### **4.1 Basis Sets For Energy Minimization**

To evaluate the density function using Gaussian03, the exchange-correlation portion of the potential function was approximated using the hybrid functional PBE1PBE (25% electron-exchange and 75% electron-correlation).<sup>22</sup> This was done for both DFT and TDDFT calculations.

It was important to choose an appropriate basis set. A large number of basis sets are commonly used, which are clarified with standard notation. For instance, in 6-311++G(d, p), '6-311' indicates 11 functions (6+3+1+1) for the s-orbital and 5 functions (3+1+1) for the p-orbital in large atoms, and 5 functions (3+1+1) for the s-orbital in hydrogen, while G denotes this as a Gaussian basis set. The notation '++' indicates the addition of "double diffuse" functions (designed to model more accurately electrons farther from the nucleus of an atom) for all atoms; single diffuse, '+', treats only nonhydrogen atoms. The notation '(d, p)' indicates the addition of "polarization" functions (describing more orbitals, in this case one function for the d-orbital in larger atoms and one function for the p-orbital in hydrogen).<sup>23</sup> Eighty-one Gaussian basis sets, with combinations of polarization and diffuse functions supplementing the basic 6-311G set, were systematically analyzed with the nickel dithiolene core (R = H in Figure 1). The polarization functions, which aid in the modeling of bonding interactions, ranged from (d, p) to

(3df, 3pd). Each polarization function variation was evaluated with double diffuse, single diffuse, and no diffuse functions. The core structure was chosen for this study because it is the part of the overall nickel dithiolene molecule that affects the absorption spectra the most.<sup>24</sup> Because no extensive R groups are attached, the computational time was relatively short (~30 minutes). If a basis set failed to converge on the nickel dithiolene core, it was avoided for calculations of structures with R groups attached. This problem was sometimes encountered for relatively large basis sets. For each optimized geometry derived from a specific basis set, measurements were taken and compared with experimental values<sup>25</sup> for the bond lengths of Ni-S, S-C, and C-C, and for the bond angles of S-Ni-S, Ni-S-C, and S-C-C of the nickel core. The error is reported in Figure 4 as a percentage error averaged over all measurements for each basis set. The errors for all basis sets are graphed with groups of double, single, and no diffuse functions. Larger basis sets generally require greater computational time because more polarization functions are used. The results in Figure 4 are arranged from the most extended to the least extended basis sets so that the trade-off between accuracy and computational time can be assessed. Because the

Figure 4. Mean absolute error of selected bond lengths and angles using various basis sets, which are labeled by polarization and diffuse functions. (Double and single diffuse errors overlap.) The star indicates the chosen basis set.



difference in accuracy between double and single diffuse functions is minimal, it was determined that adding double diffuse functions is not necessary. The underlying assumption for this choice was that hydrogen does not play a significant role in the modeling of these compounds. The line graphs for the basis sets with diffuse functions follow a general trend upward in percent error as smaller basis sets are used. In Figure 4, the polarization functions for the heavy atoms seem to affect the error more than the polarization functions for hydrogen atoms. This observation is also true for basis sets without diffuse functions, though more fluctuation occurs.

Recognizing that even with the fluctuations shown on the graph, the difference between the highest point and the lowest point on the entire graph is only an error of 0.38%, the goal was to find the least time-consuming basis set with a reasonably small error. The focus is on the right side of the graph with relatively small basis sets since convergence problems sometimes arise with the larger basis sets and the addition of more polarization functions does not seem to produce better results. Therefore, the basis set 6-311G(3d, 2p) (star on the graph) was chosen for the geometry optimization since it produced a local minimum in error for a reasonable computational time. In the previous study by Lauterbach and Fabian,<sup>6</sup> though the list of molecules investigated was more extensive than in previous studies, the experimental absorption maximum value cited was for the nickel dithiolene with H as each of the four R groups. This compound thus provides the only useful error comparison between this study and theirs. Table 1 compares the structural data from this study and data obtained by Lauterbach and Fabian along with the experimental data. The average error obtained by Lauterbach and Fabian, 1.77%, is higher than the 1.31% error obtained here.

Table 1. Comparison between theoretical and experimental bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ]			
Bond lengths:	Experimental <sup>[a]</sup>	This work <sup>[b]</sup>	Lauterbach and Fabian <sup>[c]</sup>
Ni(1)-S(1)	2.100	2.123	2.178
S(1)-C(1)	1.687	1.685	1.705
C(1)-C(2)	1.353	1.372	1.374
Bond angles:			
S(1)-Ni(1)-S(2)	88.5	92.5	92.1
Ni(1)-S(1)-C(1)	107.8	103.5	102.9
S(2)-C(2)-C(1)	117.9	120.2	121.1
Average % Error		1.31%	1.77%
[a] Ref. 25 — [b] Calculated using 6-311G(3d, 2p) — [c] Ref. 6 Calculated using 6-311+G*			

The choice of basis set in these calculations was verified by computing the vibrational frequencies using the chosen basis set, 6-311G(3d, 2p). Using DFT, Gaussian03 computes force constants and the resulting vibrational frequencies of the molecule, along with the intensities at those frequencies.<sup>18</sup> The major frequencies, (799  $\text{cm}^{-1}$  and 1132  $\text{cm}^{-1}$  for C=S bonds; 1399  $\text{cm}^{-1}$  for the C=C bond; and around 3175  $\text{cm}^{-1}$  for C-H bonds) all agreed with experimental data,<sup>26</sup> confirming the accuracy of both the molecular structure and the computed absorption spectra.

When the procedure developed for the nickel dithiolene core was applied to larger nickel dithiolene dye molecules using DFT, the basis set 6-311G(3d, 2p) was found to produce convergence errors and the computational time increased dramatically. The basis sets may have been too restricting, and often no stationary energy minimum could be found within computational limits. Several smaller basis sets were then tested, and 6-311G(d, p) was found to satisfactorily produce the geometry optimization.

#### 4.2 Basis Sets For Time-Dependent Absorption Wavelength Calculations

The next step is the excited state, time-dependent calculations. Figure 5 shows the electron density shift in the nickel dithiolene core when the molecule transitions from the ground state (HOMO) to the excited state (LUMO). The blue area indicates the most electron-rich region, while the red area indicates the electron-deficient region. The electron density shifts from

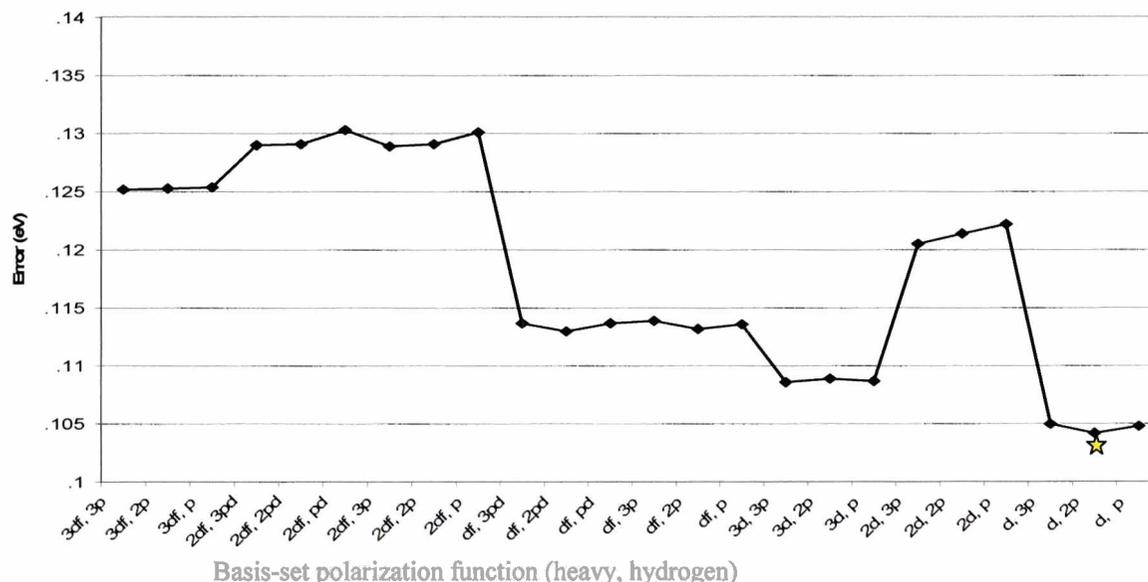
Figure 5. Electron density maps of the electronic transition modeled by TDDFT for the nickel core (Figure 1). Blue indicates high electron density.



the center of the molecule to the four sulfur ligands during this energy transition.

A new basis set was needed, as the TDDFT calculations differ from the geometry calculations. First, TDDFT calculations were performed using basis sets without diffuse functions, but the errors in the resulting absorption spectra were not acceptable and the focus turned to basis sets with single-diffuse functions. Therefore, a systematic test was run in which all the single-diffuse basis sets were used to calculate the absorption spectra of the core, holding the optimized structure constant (Figure 6). The graph again demonstrates that the polarization functions for heavy atoms are more important in determining the errors in the calculation. From the global minimum of this graph, the 6-311+G(d, 2p) basis set was chosen for the TDDFT calculations of all the remaining nickel dithiolene dyes under investigation.

Figure 6. Error in the absorption-maximum photon energy of the nickel dithiolene core using different single diffuse (+) basis sets for the excited state calculations. The ground-state geometry was optimized using the 6-311G(3d, 2p) basis set.



## 5. Determination of Maximum Absorption Wavelengths

The main purpose of this study was to investigate the accuracy of TDDFT in predicting the maximum absorption wavelengths  $\lambda_{\max}$  of various nickel dithiolene dyes. The computed  $\lambda_{\max}$  for all investigated nickel dithiolene dyes are reported in Table 2 along with experimental data. The graph in Figure 7(a) provides a comparison of the theoretical  $\lambda_{\max}$  with experimental results. The electron energy transition responsible for producing these maximum absorption wavelengths was between the ground state and the first excited state (see Figure 5), which confirms both experimental and previous computational findings.<sup>25, 27</sup> Only systems with solvents that are parameterized in Gaussian03 were selected so that a fair comparison could be performed. The computational time for each molecule on eight processors running on a 1.6 GHz Itanium II SGI Altix supercomputer ranged from hours to days, depending on the complexity of the structure and the properties of the solvent.

As a measure of accuracy, the maximum absorption wavelength calculated for the nickel dithiolene core in this study was compared with that of a previous study.<sup>6</sup> The absorption wavelength is 678.92 nm, an error of 0.10 eV (all errors are compared in eV for consistency and convention) from the experimental value of 720 nm.<sup>2</sup> This result is a substantial improvement from the previous result of 623 nm determined with the CIS method<sup>6</sup> (an error of 0.27 eV).

Since TDDFT is to be used as a predictive tool for determining the maximum absorption wavelength of optical dyes, the data collected in this study was statistically treated to provide a more direct prediction of experimental values. It is clear from Figure 7(a) that the raw wavelengths calculated here consistently underestimate the experimental values. Such data are usually subjected to statistical treatment<sup>10</sup> using simple linear regression. The data plotted in Figure 7(a) were fit with the equation:  $\lambda_{\max, \text{exp.}} = 64.84 + 1.0021 \lambda_{\max, \text{raw theory}}$ , with a Pearson

R-Groups		Solvent	Theory (raw) $\lambda_{\max}$ (nm)	Theory (treated) $\lambda_{\max}$ (nm)	Experiment $\lambda_{\max}$ (nm)	Ref.
R1, R4	R2, R3					
H	H	Hexane	678.9*	745.7*	720	2
Methyl	Methyl	Chloroform	704.3	771.2	774	2
Methyl	Methyl	Dichloromethane	702.7	769.6	770	28
Butylthio	Butylthio	Acetone	893.4	961.0	1002	4
Butylthio	Butylthio	Chloroform	900.7	968.3	1004	2
Phenyl	Phenyl	Chloroform	809.9	877.2	866	2
2-Naphthyl	2-Naphthyl	Chloroform	852.2	919.7	905	2
H	Phenyl	Dichloromethane	774.8	841.9	810	28
Ethyl	Ethyl	Dichloromethane	680.2	747.0	770	28
Phenyl	Methyl	Dichloromethane	731.7	798.7	795	28
Phenyl	Ethyl	Dichloromethane	719.0	786.0	795	28
Phenyl	Phenyl	Dichloromethane	811.9	878.4	865	28
4-octylphenyl	H	Dichloromethane	776.3	843.5	865	28
4-octylphenyl	H	Hexane	764.8	832.0	850	2
4-bromophenyl	4-bromophenyl	Dichloromethane	830.9	898.2	870	28
4-methylphenyl	4-methylphenyl	Dichloromethane	854.1	921.6	900	28
Pentylthio	Pentylthio	Acetone	905.2	972.9	1002	4
2-thienyl	2-thienyl	Chloroform	957.4	1025.3	982	2

\*This geometry was calculated using 6-311G(3d, 2p). The geometry for all other structures was calculated using 6-311G(d,p).

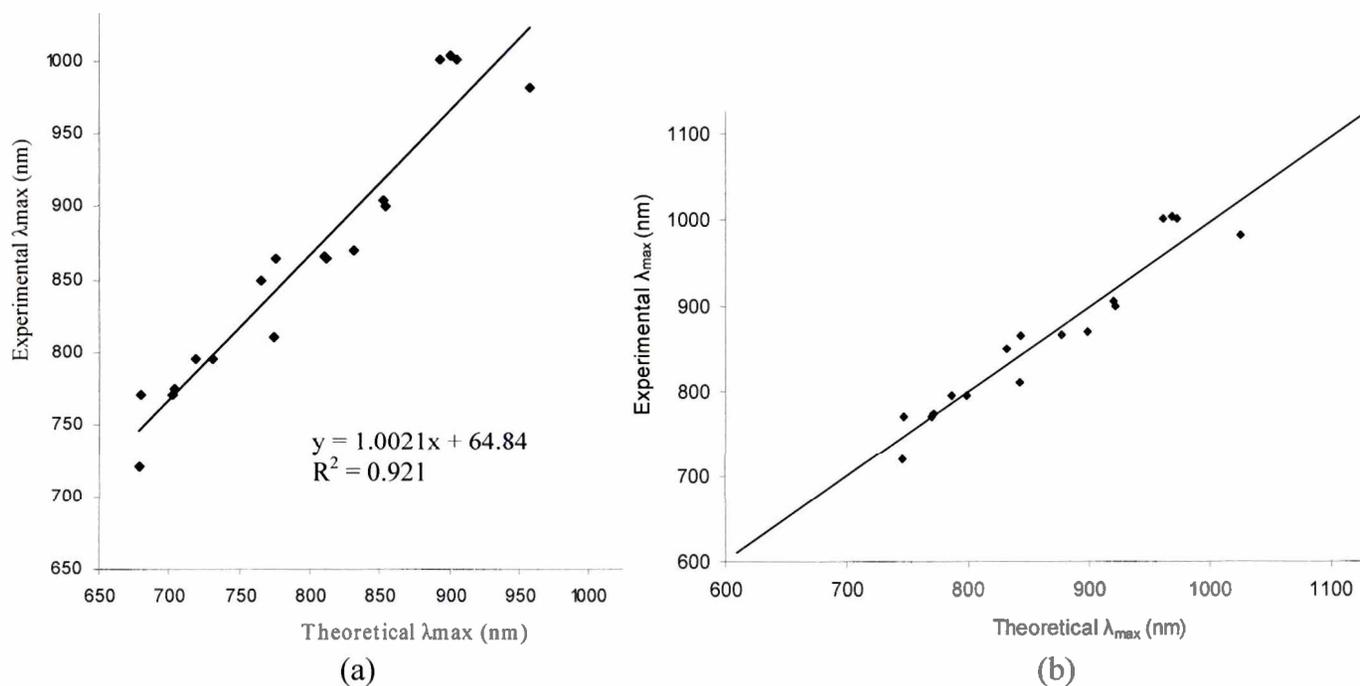


Figure 7.

(a) Comparison between the raw theoretical  $\lambda_{\max}$  and the experimental  $\lambda_{\max}$ . The line shows linear regression.

(b) Comparison between the statistically treated theoretical  $\lambda_{\max}$  and the experimental  $\lambda_{\max}$ . The line indicates  $\lambda_{\max, \text{theory}} = \lambda_{\max, \text{exp}}$ .

correlation coefficient  $R^2$  of 0.921. All the raw values were then adjusted using this equation, giving the treated theoretical wavelengths of Figure 7(b), which can then be used to improve the theoretical predictions.

These predictions of the maximum absorption wavelength of the nickel dithiolene core are the most accurate to date. For the entire group of nickel dithiolene dyes investigated, the mean unsigned error is 0.033 eV. This translates to an absolute difference of 20.8 nm between experimental values and treated theoretical values on average. These errors are much smaller than previously reported errors; even studies using TDDFT typically report errors ranging from 0.2 to 0.4 eV for transition-metal molecules.<sup>29, 30</sup>

The trends among various nickel dithiolene dyes are correctly modeled. The structures with terminal groups containing sulfur or phenyl rings are found to have longer-wavelength absorption maxima. The solvatochromatic effects (solvent effects on the  $\lambda_{\text{max}}$ ) are also reasonably predicted. For the structure  $R_1R_4 = 4\text{-octylphenyl}$  and  $R_2R_3 = \text{H}$ , the experimental values show a hypsochromic shift (blue shift) of 15 nm, when the solvent changes from dichloromethane to hexane, while the theoretical values give a shift of 11.5 nm. Similarly, the solvatochromatic effects on the nickel dithiolene dye with  $R = \text{methyl}$  and the dye with  $R = \text{butylthio}$  are modeled accurately. These further demonstrate the validity of TDDFT for the quantitative evaluation of the maximum absorption wavelength of various nickel dithiolene dyes.

With the accuracy of the methodology validated, several new nickel dithiolene dyes were designed and modeled using DFT and TDDFT in an attempt to extend the measured absorption wavelength into the IR. Since sulfur seems to effect a bathochromic shift (red shift) when included as part of the R groups, and sulfur-containing structures have traditionally been more soluble than phenyl-containing structures<sup>31</sup> (which also effect a bathochromic shift), the new

dyes were designed with sulfur added to the R groups. The results shown in Table 3 confirm this hypothesis in each of three groups, with significant red shifts in the maximum absorption wavelength of up to 160 nm. It is anticipated that this work will allow more nickel dithiolene dyes to be synthesized with maximum absorption wavelengths further into the infrared region.

R <sub>1</sub> R <sub>4</sub>	R <sub>2</sub> R <sub>3</sub>	Solvent	Predicted $\lambda_{\max}$ (nm)	Exp. $\lambda_{\max}$ (nm)
4-phenyl-Br	4-phenyl-Br	DiChloroMethane	895.2	870
<b>SBr</b>	<b>SBr</b>	DiChloroMethane	<b>975.2</b>	-
<b>SF</b>	<b>SF</b>	DiChloroMethane	<b>971.6</b>	-
Methyl	Methyl	Chloroform	772.0	774
<b>S-methyl</b>	<b>S-methyl</b>	Acetone	<b>845.8</b>	-
H	H	Hexane	745.7	720
<b>SH</b>	<b>SH</b>	Hexane	<b>907.5</b>	-

## 6. Discussion/Conclusions

The absorption spectra of an extensive set of nickel dithiolene dyes have been studied using TDDFT to compute excited state energies, with bulk solvent effects taken into account. A hybrid functional and two basis set combinations, 6-311G(d, p) for the ground state geometry and 6-311+G(d, 2p) for the excited state energies, were used in this study. Close agreement between the theoretical and experimental  $\lambda_{\max}$  has been achieved for 18 known dyes, with a mean absolute error limited to 0.033 eV. A methodology has been used for nickel dithiolene dyes that can be adapted to future studies of these and other optical dyes.

This study provides a significant step forward in advancing the science of computational chemistry in organometallics, especially shown by the low error in this study as compared with those currently reported in the literature. Four new nickel dithiolene molecules have been designed and modeled, with findings that indicate that adding sulfur to the R groups will increase the  $\lambda_{\max}$  by up to 160 nm. Future work will seek to extend the  $\lambda_{\max}$  further into the infrared region, by making additional modifications to the terminal R groups. The success of this method

will greatly assist the development and synthesis of new transition metal dithiolenes and will aid in the use of nickel dithiolenes as near-IR dyes in applications such as telecommunications, sensor protection, and liquid crystal devices in laser systems.

### Acknowledgements

I would like to thank my advisor Mr. Kenneth Marshall for his guidance and support in my research, as well as Dr. R Stephen Craxton for not only providing the opportunity to work at the University of Rochester's Laboratory for Laser Energetics but also helping me during the final stage of my project. In addition, I would like to thank Anthony Noto for mentoring me on the applications and limitations of the Gaussian03 program.

### References

1. Mueller-Westerhoff, U. T.; Vance, B. Dithiolenes and Related Species. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, 1987; Vol. 2, pp 595-631.
2. Mueller-Westerhoff, U. T.; Vance, B.; Yoon, D. I. *Tetrahedron* 1991, *47*, 909-932.
3. Marshall, K. L.; Schudel, B.; Lipka, I. A. *Proc. SPIE* 2003, *5213*, 201-212.
4. Marshall, K. L.; Klehn, B.; Watson, B.; Griffin, D. W. *Proc. SPIE* 2003, *5188*, 48-60.
5. Caironi, M.; Natali, D.; Sampietro, M.; Ward, M.; Meacham, A. P.; Devillanova, F. A.; Arca, M.; Denotti, C. *Proc. SPIE* 2004, *5464*, 165-175.
6. Lauterbach, C.; Fabian, J. *Eur. J. Inorg. Chem.* 1999, *11*, 1995-2004.
7. Stanton, J. F.; Gauss, J.; Ishikawa, N.; Head-Gordon, M. *J. Chem. Phys.* 1995, *103*, 4160-4174.
8. Jacquemin, D.; Preat, J.; Wathelet, V.; Perpète, E. A. *J. Chem. Phys.* 2006, *124*, 074104.
9. Jacquemin, D.; Preat, J.; Charlot, M.; Wathelet, V.; André, J.; Perpète, E. A. *J. Chem. Phys.* 2004, *121*(4), 1736-1743.

10. Perpète, E. A.; Wathélet, V.; Preat, J.; Lambert, C.; Jacquemin, D. *J. Chem. Theory Comput.* 2006, 2, 434-440.
11. Runge, E.; Gross, E. K. U. *Phys. Rev. Lett.* 1984, 52, 997-1000.
12. M.C. Zerner, ZINDO, A Semiempirical Quantum Chemistry Program, Quantum Theory Project, University of Florida, Gainesville, FL, 1996.
13. Schrauzer, G. N.; Mayweg, V. P. *J. Am. Chem. Soc.* 1965, 87, 3585-3592.
14. Schrauzer, G. N. *Acc. Chem. Res.* 1969, 2, 72-80.
15. Corsello, S. *Student Research Reports, 1998 Summer Research Program for High School Juniors at the University of Rochester's Laboratory for Laser Energetics*, 1998.
16. Hehre, W. J. *Ab Initio Molecular Orbital Theory* 1986 (Wiley, New York).
17. Jacquemin, D., private communication, 2006.
18. Frisch, M.J. et al., Gaussian03, Gaussian, Inc., Pittsburgh, PA, 2004.
19. SPARTAN '04, Wavefunction, Inc., 18401 Von Karman Ave., #370, Irvine, CA 92715, 2003.
20. Marques, M. A. L.; Gross, E. K. U. *Annu. Rev. Phys. Chem.* 2004, 55, 427-455.
21. Amovilli, C.; Barone, V.; Cammi, R.; Cancès, E.; Cossi, M.; Mennucci, B.; Pomelli, C. S.; Tomasi, J. *Adv. Quantum Chem.* 1998, 32, 227.
22. J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* 1996, 77, 3865.
23. Ahlrichs, R.; Taylor, P. R. *J. Chem. Phys.* 1981, 78, 315-324.
24. Eisenberg, R. *Prog. Inorg. Chem.* 1970, 12, 295-369.
25. Herman, Z. S.; Kirchner, R. F.; Loew, G. H.; Mueller-Westerhoff, U. T.; Nazzari, A.; Zerner, M. *Inorg. Chem.* 1982, 21, 46-56.
26. Schlapfer, C. W.; Nakamoto, K. *Inorg. Chem.* 1975, 14, 1338-1344.
27. Hill, C. A. S.; Charlton, A.; Underhill, A. E.; Malik, K. M. A.; Hursthouse, M. B.; Karaulov, A. I.; Oliver, S. N.; Kershaw, S. V. *J. Chem. Soc. Dalton Trans.* 1995, 4, 587-594.
28. Winter, C. S.; Oliver, S. N.; Manning, R. J.; Rush, J. D.; Hill, C. A. S.; Underhill, A. E. *J. Mater. Chem.* 1992, 2, 443-447.

29. Petit, L.; Makdivi, P.; Adamo, C. *J. Chem. Theory Comput.* 2005, *1*, 953-962.
30. Adamo, C.; Barone, V. *Theor. Chem. Acc.* 2000, *105*, 169-172.
31. Marshall, K. L., Painter, G. Lotito, K., Noto, A.G., Chang, P., *Mol. Cryst. Liq. Cryst.* 2006, *454*, 47[449] – 79 [481].