Platinum(II) and phosphorous MM3 force field parameterization for chromophore absorption spectra at room temperature

Jonas Sjöqvist

Platinum(II) and phosphorous MM3 force field parameterization for chromophore absorption spectra at room temperature

Jonas Sjöqvist

Adviser: Mathieu Linares
IFM, Linköpings Universitet

Patrick Norman
IFM, Linköpings Universitet

Examiner: Patrick Norman
IFM, Linköpings Universitet

Linköping, 2 June, 2009
**Title**
Platinum(II) and phosphorous MM3 force field parameterization for chromophore absorption spectra at room temperature

**Abstract**
The absorption properties of the Pt1 chromophore at room temperature have been studied. Stretch, bend and torsion parameters for Pt(II), P, C (type 1, 2 and 4) and H have been parameterized for use in the MM3 force field. Parameters were fitted to energies computed at the B3LYP level of theory. The parameterized model was used to perform molecular dynamics simulations at room temperature. This was done for several environments and for time periods of up to 200 ps. Absorption properties were computed for snapshots from the dynamics, from which average absorption spectra were created. A conformational broadening of around 40 nm was found in the theoretical spectra, which is in good agreement with experiments. Due to a lack of solvent-solute interactions and the use of a less extensive basis set, a systematic blue shift of 40 nm is evident in the computed spectra.

**Keywords**
MM3, force field, molecular dynamics, linear absorption, platinum, phosphorous
Abstract

The absorption properties of the Pt1 chromophore at room temperature have been studied. Stretch, bend and torsion parameters for Pt(II), P, C (type 1, 2 and 4) and H have been parameterized for use in the MM3 force field. Parameters were fitted to energies computed at the B3LYP level of theory. The parameterized model was used to perform molecular dynamics simulations at room temperature. This was done for several environments and for time periods of up to 200 ps. Absorption properties were computed for snapshots from the dynamics, from which average absorption spectra were created. A conformational broadening of around 40 nm was found in the theoretical spectra, which is in good agreement with experiments. Due to a lack of solvent-solute interactions and the use of a less extensive basis set, a systematic blue shift of 40 nm is evident in the computed spectra.
Acknowledgements

I would like to thank my supervisors, Patrick Norman and Mathieu Linares, for the many hours spent helping me. Thanks should also go to the rest of the computational physics group, along with everyone else I have met at IFM, for being such nice people.
Contents

1 Introduction ......................................................... 1
  1.1 Background ..................................................... 1
  1.2 Goals ........................................................... 1
  1.3 Outline of the report .......................................... 2

2 MM3 force field .................................................... 5
  2.1 Force fields .................................................... 5
    2.1.1 Bond stretching .......................................... 6
    2.1.2 Angle bending ............................................ 6
    2.1.3 Torsion .................................................... 6
    2.1.4 van der Waals interaction .............................. 7
    2.1.5 Electrostatic interaction .............................. 7
  2.2 MM3 force field ................................................ 8
    2.2.1 Bond stretching .......................................... 8
    2.2.2 Angle bending ............................................ 9
    2.2.3 Torsion .................................................... 9
    2.2.4 van der Waals interaction .............................. 9
    2.2.5 Electrostatic interaction .............................. 9
    2.2.6 Out-of-plane bending .................................. 10
    2.2.7 Stretch-bend interaction ............................. 11
    2.2.8 Torsion-stretch interaction ......................... 11
    2.2.9 Bend-bend interaction ............................... 11

3 Parameterization of ethane ..................................... 13
  3.1 Stretch parameters ......................................... 13
  3.2 Bend parameters ........................................... 15
  3.3 Torsion parameters .......................................... 17

4 Parameterization of the Pt1 chromophore .................. 19
  4.1 Introduction .................................................. 19
  4.2 Stretch parameters .......................................... 21
  4.3 Bend parameters ............................................ 24
  4.4 Torsion parameters ......................................... 26
    4.4.1 384–60–1–3 ............................................. 27
    4.4.2 384–60–1–1 ............................................. 28
4.4.3 5–1–60–1 .................................................. 28
4.4.4 1–1–60–1 .................................................. 29
4.4.5 5–1–1–60 .................................................. 29
4.4.6 1–1–1–60 .................................................. 29
4.4.7 Results .................................................. 30
4.5 Validation .................................................. 32

5 Molecular dynamics ........................................ 35
  5.1 Numerical methods ..................................... 35
  5.2 Ensembles .............................................. 37

6 Chromophore absorption spectra ......................... 39
  6.1 One-photon absorption ................................. 39
  6.2 Test cases .............................................. 40
  6.3 Pt1-G0 dynamic in vacuum ............................ 42
  6.4 Comparison to experimental data .................... 45
  6.5 Pt1-G5 dynamic in vacuum ............................ 47
  6.6 Pt1-G5 dynamic in solvent ............................ 49

7 Summary and conclusions ................................ 53

Bibliography .................................................. 55
Chapter 1

Introduction

1.1 Background

This thesis is a small part of a larger project, which is funded by the Swedish Defence Research Agency, FOI, and is a collaboration of many groups in several countries [1, 2, 3, 4]. This project aims to create materials capable of protecting sensors from high-intensity light. Examples of sensors that could need this kind of protection are night vision goggles or just the human eye. The problem lies in the fact that when light of an intensity high enough to damage the sensor is detected, the damage is already done. By the time the light has been detected, and some sort of mechanical shield lowered to protect the sensor, enough light has already reached the sensor to cause damage. What is needed is a material that can be placed in front of the sensor, transparent for normal conditions, but capable of high absorbance for high-intensity light. That way, there is enough time to lower the shield and protect the sensor. This thesis aims to study the absorption properties of one chromophore, the part of a molecule responsible for the absorption of light, using computational methods. These will then be compared to experimental results.

1.2 Goals

The thesis focuses on the Pt1 chromophore, seen in Figure 1.1 and how it absorbs light. The ultimate goal of the project is to compute absorption spectra for the Pt1 chromophore at room temperature. This needs to be done for several different environments, both for the chromophore in its original form and with appended dendrimers. At any temperature above absolute zero, the atoms in a molecule have some amount of kinetic energy, meaning they are constantly vibrating, twisting and bending. This means that at any given moment, a Pt1 chromophore at room temperature could be at in any one of a large number of possible structures. These structures have slightly different properties and absorb light of slightly different wavelengths. Therefore, the absorption properties need to be computed for as
Introduction

Figure 1.1. The Pt1 chromophore.

many as possible of these structures and an average created in order to get the room temperature absorption spectrum.

To find all these possible structures, molecular dynamics are used. In order to do this, the molecule is described using a force field. In force fields, the potential energy of the molecules is approximated as only depending on the positions of the atoms. Simple expressions are used to describe the energy changes from, among other things, stretching of bonds and bending of the angles between atoms. All these simple expressions added together gives the total potential energy of the system. Using this, the forces acting on the atoms can easily be obtained. From this, the evolution of the system in time can be computed using Newton’s equations and numerical integration.

The force field used, MM3 [5], is not, however, capable of fully describing the Pt1 chromophore. The expressions used to describe the interactions between different types of atoms use parameters, fitted to data obtained using quantum mechanical methods or from experiments. Several such parameters needed for the Pt1 chromophore are missing, mostly involving the platinum and phosphorous atoms, and must therefore be determined.

1.3 Outline of the report

The project can be divided into two major parts: The parameterization of the Pt1 chromophore in the MM3 force field and the use of these parameters in molecular dynamics simulations to compute room temperature absorption spectra for the chromophore. The parameterization is covered in Chapters 2, 3, and 4. Chapter 2 gives a short overview of the theory behind force fields and a more thorough
1.3 Outline of the report

explanation of the MM3 force field. Chapter 3 explains the process of parameterization using the ethane molecule as an example. Chapter 4 applies this process to the Pt1 chromophore, obtaining the parameters needed to describe the molecule in the MM3 force field.

The second part consists of Chapters 5 and 6. Chapter 5 gives an introduction to the theory behind molecular dynamics, covering methods of numerical integration and statistical ensembles. In Chapter 6, molecular dynamics are used to compute average absorption spectra at room temperature for the Pt1 chromophore in a vacuum and the Pt1 chromophore with dendrimer coating, both in a vacuum and in a solvent. Finally, Chapter 7 summarizes the project and the conclusions drawn.
Chapter 2

MM3 force field

2.1 Force fields

*Ab initio* quantum chemistry calculations are usually quite resource demanding. The computational power and time needed to carry out a structure optimization of a molecule larger than at most a few hundred atoms quickly becomes challenging, and a dynamic evolution is out of reach for all but the smallest of systems. To get around this problem some form of approximation is needed. One such approximation is given by force fields, by which electrons are assumed at an ideal position around the nuclei, and the energy of the system depends only on the position of the atoms, their type and the bonds between them. This is built upon the idea that similar structures in different molecules will behave in the same way, or at least similarly enough to be approximated as behaving in the same way. This is called the transferability principle. For example, the C–C bond in ethane is very similar to the C–C bonds in propane. The two bond distances are almost the same and contraction or stretching of the bonds produce similar changes in energy. In a force field, this kind of distortion would be represented by one analytical function, giving the energy of only one specific bond. Bonds of the same kind use the same parameters and thus behave in the same way. In addition to bond stretching, force fields usually contain at least four more kinds of terms: angle bending, torsion, van der Waals interactions and electrostatic interactions. The total energy of the system becomes a sum of all these terms:

\[ E = E_s + E_\theta + E_\omega + E_{vdw} + E_{el}. \] (2.1)

where \( E_s, E_\theta, \) etc. are the summed interactions of the respective type.

While the C–C bonds in ethane and propane are very similar, the C–C bond in acetylene is very different. It has a much shorter bond distance and gives much larger energy differences for distortions from the equilibrium. This shows that having just one type for each atom is usually not enough. Where the line is drawn depends on the specific force field. Accuracy is weighed against generality. A lot of different types for a lot of different structures may give good results, but it
also requires a lot more work in finding parameters for all needed combinations of types.

2.1.1 Bond stretching

When stretching or contracting a bond from the equilibrium distance, as shown in Figure 2.1, the energy increases. In the bond stretch energy term, this change in energy is approximated by a simple analytical function, which is usually just a harmonic oscillator around the equilibrium point. In that case, the parts specific to the two atoms involved are condensed down into two parameters: the equilibrium distance, which the atoms strive to return to, and the force constant, which gives the force with which they do this.

![Figure 2.1. Stretching and contraction of a bond.](image)

2.1.2 Angle bending

The bend term involves three atoms bonded together. It works in much the same way as the stretch term. The two atoms bonded to the central atom form an angle. When this angle is distorted, as in Figure 2.2, the energy of the system rises. As with the stretch term, the bend term is usually approximated with a harmonic oscillator, giving two parameters for the combination of three atoms: an equilibrium angle and a force constant.

![Figure 2.2. Bending of three atoms bonded together.](image)

2.1.3 Torsion

The torsion term deals with four atoms bonded one after the other. The torsion term concerns twisting around the central two atoms, as shown in Figure 2.3. The torsional angle is measured between the two atoms on opposite sides of the
structure while looking through the middle two atoms, measured from $-180^\circ$ to $180^\circ$. As an example, the torsional angles between two hydrogens on opposite sides of an ethane molecule in the staggered conformation are $-60^\circ$, $60^\circ$ and $180^\circ$. Twisting ethane around the central C–C bond produces a change in energy which rises until a maximum is reached for the eclipsed conformation. This kind of energy can also be approximated by a simple function, which is usually a Fourier series. The number of terms from this expansion that are included depends on the specific force field.

Figure 2.3. Twisting around a central bond.

2.1.4 van der Waals interaction

The van der Waals interaction is the first of the non-bonded interactions. These are usually only computed for atoms within a certain distance of each other. They are also not computed for atoms directly bonded to each other or bonded to a common neighbour. This is because their contribution is already contained in the bond stretching and angle bending terms.

The van der Waals energy is such that when the two atoms are close together it is strongly repulsive. The energy becomes lower as the atoms are separated, leading to a minimum when they are a few Å apart. After this, the energy rises again, though slowly and tending to the value in the separation limit. This gives rise to a weak attractive force. In force fields the van der Waals energy term is usually given by one attractive and one repulsive term. It can be shown that the attractive term is proportional to $R^{-6}$. Less can be said about the repulsive term, but it should tend to zero as $R$ tends to infinity, and do this faster than the $R^{-6}$ term. Common forms for the repulsive terms is to have them be $R^{-12}$ or exponential terms. The distance for the minimum along with force constants in front of the attractive and repulsive terms give the parameters that can be fitted to known data.

2.1.5 Electrostatic interaction

The second non-bonded term is the electrostatic term, which is a result of unevenly distributed charges. This can be expressed in several ways. One of these is to assign to each atom a charge. Computing the energy is then simply a matter of using
the Coulomb potential,

\[ E = \frac{Q_1 Q_2}{4\pi\varepsilon_0 r}, \]  

(2.2)

where \( Q_1 \) and \( Q_2 \) are the charges of the two atoms, \( r \) is the distance between them and \( \varepsilon_0 \) is the electric constant. Using water as an example, this would mean assigning a partial positive charge to the hydrogens and a negative one to the oxygen. Another way is to assign a dipole moment to every bond in the molecule. In the case of water, this would mean assigning one dipole moment, pointing in the direction of the hydrogens, to each O–H bond. The energy term for this representation becomes a bit more complex. One example of this approach is given by the MM3 force field for which the electrostatic term is described in Section 2.2.5.

2.2 MM3 force field

The MM3 force field, where MM stands for Molecular Mechanics, was developed by Norman L. Allinger, Young H. Yuh and Jenn-Huei Lii in 1989 [5]. It is the third force field bearing the molecular mechanics name, following the initial MM force field in 1976 [6] and the MM2 force field in 1977 [7].

In the MM3 force field, the energy of a system is given by nine terms: Bond stretching, angle bending, torsion, van der Waals interactions, electrostatic interactions, out-of-plane bending, stretch-bend interactions, torsion-stretch interactions and torsion-bend interactions. The last three are called cross terms. These exist to handle situations where changing one term affects another. One example of this can be seen in water molecules. Bending the H–O–H bond inwards will cause the two hydrogens to come closer together. Their repulsion will then cause the O–H bonds to become elongated. If there were only separate stretch and bend terms, this could not be modeled, but a cross term containing both the angle and the bond length makes it possible.

One thing to note about the MM3 force field, as well as the implementation in the Tinker package [8], is that it uses the energy unit mdyn·Å for many parameters. Since energies are most often given in either atomic units or kcal/mol, conversions are required, and the relevant conversion factors are:

\[ 1 \text{E}_h = 4.3597 \text{ mdyn} \cdot \text{Å} \]  

(2.3)

\[ 1 \text{kcal/mol} = 6.948 \cdot 10^{-3} \text{ mdyn} \cdot \text{Å} \]  

(2.4)

In the following sections the energy terms in the MM3 force field are detailed. All terms are taken from MM3(2000) [9] as implemented in the Tinker package.

2.2.1 Bond stretching

The bond stretching energy is given by

\[ E_s = 143.88 \frac{k_s}{2} (l - l_0)^2 [1 - 2.55(l - l_0) + (7/12)2.55(l - l_0)^2], \]  

(2.5)
2.2 MM3 force field

where \( k_s \) is the force constant, \( l \) is the bond length and \( l_0 \) is the equilibrium bond length. \( k_s \) is given in mdyn/Å, \( l \) and \( l_0 \) are given in Å and \( E_s \) is given in kcal/mol. The constant 143.88 converts from mdyn/Å to kcal/mol.

As evident, in addition to the quadratic term the energy is also dependant on a cubic and quartic term. These, however, are very small for the distortions usually seen in bonds.

### 2.2.2 Angle bending

The angle bending energy is given by

\[
E_\theta = 0.043828 \frac{k_\theta}{2} (\theta - \theta_0)^2 [1 - 0.014(\theta - \theta_0) + 5.6 \cdot 10^{-5}(\theta - \theta_0)^2 - 7.0 \cdot 10^{-7}(\theta - \theta_0)^3 + 9.0 \cdot 10^{-10}(\theta - \theta_0)^4] 
\]  

where \( k_\theta \) is the force constant, \( \theta \) is the bond angle and \( \theta_0 \) is the equilibrium bond angle. For reasons unknown, the force constant is given in the unit mdyn-Å/rad\(^2\) while the angles \( \theta \) and \( \theta_0 \) are given in degrees. The actual energy, \( E_\theta \), is given in kcal/mol. The constant 0.043828 converts from mdyn-Å·degrees\(^2\)/rad\(^2\) to kcal/mol.

### 2.2.3 Torsion

The torsional energy, in kcal/mol, is given by

\[
E_\omega = \frac{V_1}{2} (1 + \cos \omega) + \frac{V_2}{2} (1 - \cos 2\omega) + \frac{V_3}{2} (1 + \cos 3\omega) 
\]  

where \( V_1, V_2 \) and \( V_3 \) are force constants given in kcal/mol and \( \omega \) is the torsional angle, given in degrees.

### 2.2.4 van der Waals interaction

In MM3, the repulsive part of the van der Waals interaction is modeled with an exponential function according to

\[
E_{vdw} = \epsilon (-2.25(r_v/r)^6 + 1.82 \cdot 10^5 \exp[-12.00(r/r_v)]),
\]  

where \( r \) is the distance between the two atoms, \( r_v \) is the atomic distance for which the energy is at a minimum (both in Å), and \( \epsilon \) is an energy scale factor which has the unit of kcal/mol.

### 2.2.5 Electrostatic interaction

In MM3, to each bond is assigned a dipole moment and the electrostatic energy comes from the interaction of these. The energy term is given by

\[
E_{el} = 14.39418^\mu \mu^\prime (\cos \chi - 3 \cos \alpha \cos \beta) \frac{\mu^\prime \rho}{Dr^4},
\]  

where \( \mu^\prime \) is the dipole moment, \( \chi \) is the angle between the bond and the dipole, \( \alpha \) and \( \beta \) are the angles between the dipole and the bond, \( \rho \) is the charge density, and \( r \) is the distance between the atoms.
where $\mu$ and $\mu'$ are the two dipole moments, $r$ is the distance between them, $D$ is a dielectric constant (set to 1.5 as standard) and the angles $\chi$, $\alpha$ and $\beta$ are defined as in Figure 2.4. The dipole moments are given in Debye, $r$ in Å and $E_{el}$ in kcal/mol. The constant 14.39418 converts from erg/molecule to kcal/mol.

**Figure 2.4.** Definition of angles for the interaction between two dipoles.

### 2.2.6 Out-of-plane bending

For three atoms bonded to a central, $sp^2$-hybridized atom, bending the central atom out of the plane, forming a pyramid, causes a rise in energy. This is hard to handle with only the angle bending term since distortions out of the plane only gives rise to small distortions in the individual three-atom angles. To get around this, the extra out-of-plane term is added, which depends on the angle $\chi$ which is defined in Figure 2.5. This energy term is

$$E_{oop} = 0.04382836 \frac{k_{oop}}{2} \chi^2 (1 - 0.014\chi + 5.6 \cdot 10^{-5}\chi^2 - 7.0 \cdot 10^{-7}\chi^3 + 2.2 \cdot 10^{-8}\chi^4),$$

where $k_{oop}$ is the force constant, given in mdyn·Å/rad², and $\chi$ is the angle detailed above, given in degrees. The constant 0.04382836 converts to kcal/mol from mdyn·Å·degrees²/rad².
2.2 MM3 force field

2.2.7 Stretch-bend interaction

Stretch-bend interaction occurs when one or two bonds are distorted at the same time as the angle formed between the two bonds. The stretch-bend energy term has the form

\[ E_{s\theta} = 2.51118 K_{s\theta} [(l - l_0) + (l' - l'_0)](\theta - \theta_0), \]  

(2.11)

where \( l \) and \( l' \) are the lengths of the two bonds, \( l_0 \) and \( l'_0 \) are equilibrium lengths, \( \theta \) is the angle between the two bonds, \( \theta_0 \) is an equilibrium angle and \( K_{s\theta} \) is the force constant. Lengths are given in Å, angles in degrees, \( K_{s\theta} \) in mdyn/rad and \( E_{s\theta} \) in kcal/mol. The constant 2.51118 converts mdyn·Å·degrees/rad to kcal/mol.

2.2.8 Torsion-stretch interaction

Torsion-stretch interactions are needed because when a molecule is twisted around a bond, this will affect the bond length. For example, ethane in the staggered conformation will have a shorter C–C bond length than in the eclipsed conformation. The energy term is given by

\[ E_{\omega s} = -11.995 \frac{K_{\omega s}}{2} (l - l_0)(1 + \cos(3\omega)), \]  

(2.12)

where \( l \) is the bond length, \( l_0 \) is the equilibrium bond distance, \( \omega \) is the torsional angle and \( K_{\omega s} \) is a force constant. \( E_{\omega s} \) is given in kcal/mol, lengths are given in Å and angles in degrees. For unexplained reasons, the force constant has the unit 11.995 · mdyn and 11.995 squared gives the conversion factor needed to convert from mdyn·Å to kcal/mol (but why one part of this conversion is contained within the force constant is a mystery).

2.2.9 Bend-bend interaction

Bend-bend interactions occur when two bond angles are centered around the same atom. The energy term, in kcal/mol, has the form

\[ E_{\theta\theta'} = -0.043828 \frac{K_{\theta\theta'}}{2} (\theta - \theta_0)(\theta' - \theta'_0), \]  

(2.13)

where \( \theta \) and \( \theta' \) are the two angles, \( \theta_0 \) and \( \theta'_0 \) are the equilibrium values and \( K_{\theta\theta'} \) is the force constant. Angles are given in degrees and the force constant is given in mdyn/rad^2. The constant 0.043828 converts from mdyn·Å·degrees^2/rad^2 to kcal/mol.
MM3 force field
Chapter 3

Parameterization of ethane

To illustrate the method used for obtaining MM3 parameters, ethane will be used as an example. One stretch parameter, one bend parameter and one torsional parameter will be studied and the process of parameterization will be explained. The four atoms involved in the three parameters are marked in Figure 3.1. Since all parameters needed to describe ethane in the MM3 force field are already available, the fitted parameters can be compared to the already existing values to validate the method. All energy calculations and structure optimizations were carried out in Gaussian 03 [10] using the B3LYP hybrid functional [11] with the 6-31G* [12, 13] basis set.

3.1 Stretch parameters

Ethane contains two carbon atoms and six hydrogen atoms. The $sp^3$ hybridized carbons have atom type 1 in the MM3 force field and hydrogen bonded to carbon has type 5 [5]. For this example, the bond between the two $C_{sp^3}$ atoms (C1 and C2 in Figure 3.1) will be parameterized. That is, the 1–1 bond. The first step is to optimize the structure of the molecule. The optimized distance between the two atoms provides the starting point for the $l_0$ value. Using the optimized molecule as a starting point, the bond distance is varied by $-0.2$ to $+0.2$ Å with a step of $0.025$ Å. This produces 17 structures, for which the energy is calculated. The

![Figure 3.1. Structure of ethane with labeled atoms.](image-url)
changes in energy for the points are not just made up of contributions from the stretching and contraction of the bond, but also from other sources such as non-bonded interactions and cross-terms. The contribution from these can be found by setting the force parameter of the bond to zero and computing the energy of the structures using the MM3 force field. Subtracting these extra contributions from the B3LYP values leaves only the effect of the bond stretching.

Variations from the equilibrium will typically be quite small, therefore it is most important to accurately model the area closest to the equilibrium point. For this reason, the first fitting of a second degree polynomial is done only for the five-point stencil of the equilibrium point. That is, the equilibrium point and the two nearest neighbours on either side. The second derivative in this point can be approximated by:

\[ f''(x) \approx \frac{-f(x + 2h) + 16f(x + h) - 30f(x) + 16f(x - h) - f(x - 2h)}{12h^2}, \quad (3.1) \]

where, in this example, \( h = 0.025 \ \text{Å} \). This gives an initial value for \( k_s \).

At this point, values for both the \( l_0 \) and \( k_s \) parameters have been obtained. These values are, however, not guaranteed to be optimal. The \( l_0 \) value and the equilibrium bond distance are two separate things. Having \( l_0 \) as a certain value means that the bond will strive to retain that position. It does not, however, mean that the bond will have this distance in the optimized structure of a molecule. Optimizing a molecule means finding the lowest possible total energy for the molecule. This will usually mean some bonds, angles and other components will be distorted from their preferred position in order for some other bond or angle not to be distorted so much from its preferred position. The result becomes a compromise, with no component being at its minimum, but the total energy being the lowest. In this example, the C–C bond distance is mostly affected by the non-bonded interaction between the hydrogens on opposite sides of the molecule. These, in turn, are affected by the H–C–H and H–C–C angles. Thus, it is very hard to completely separate one parameter from all the others, even in such a small molecule.

The preliminary parameters can be used in Tinker \[8\] to compute the energies of the 17 geometries. These can then be plotted together with the energies computed using B3LYP, both with their lowest energies put to zero. If the parameterization is perfect, these should be identical. As can be seen in the left panel of Figure 3.2, this is not the case. At this point, some manual tweaking of the parameters is required. The first step is to change \( l_0 \) until the minimum of the curve computed in tinker is the same as the minimum of the quantum mechanical one. When this has been accomplished, \( k_s \) can be changed to adjust the curvature. This part is a bit more subjective, but usually, more effort should go into making sure the points closest to the equilibrium correspond than the ones farther away. After manual tweaking of the parameters the plot becomes the one in the right panel of Figure 3.2. The resulting parameters can be found in Table 3.1, where they can be compared to values that already exist in the MM3 force field \[5\]. As can be seen, they are not identical. This is mainly due to two reasons. First, the MM3 parameters were fitted to experimental data, not computed values. Second, the
3.2 Bend parameters

MM3 parameters were meant to be general. For that reason they were fitted not just to one molecule, but to several containing the same kind of bond.

![Figure 3.2.](image)

**Figure 3.2.** Energy differences from stretching and contraction of the C–C bond in ethane, computed using B3LYP and MM3. Preliminary MM3 parameters to the left and manually adjusted parameters to the right.

<table>
<thead>
<tr>
<th>bond type</th>
<th>atoms</th>
<th>$l_0$ (Å)</th>
<th>$k_s$ (mdyn/Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameterized</td>
<td>1–1</td>
<td>C1–C2</td>
<td>1.521</td>
</tr>
</tbody>
</table>

### 3.2 Bend parameters

There are two kinds of angles in ethane: the angle formed by two hydrogens and the carbon they are both connected to as well as the angle formed by the two carbons and one hydrogen. For this example the C–C–H bond will be studied (C1–C2–H2 in Figure 3.1). The procedure is much the same as for the bending parameters, though made more complicated by the more complex connections between parameters in the molecule. This can be immediately seen when varying the C–C–H angle. The problem arises from the fact that there is no way of changing the C–C–H angle without also changing the H–C–H angle in some way. This is illustrated in Figure 3.3.

For these parameterizations the relevant angle is distorted from its optimal value by −5 degrees to +5 degrees with a step of 1 degree, producing 11 points for which the energy is computed using B3LYP. When the C–C–H angle is at its maximum distortion of 5 degrees, the H–C–H angle is distorted from its optimum by 2.6 degrees. This is large enough to be relevant on its own, but then there is also the fact that there are two of these H–C–H bonds that are being distorted. Thus, the energies computed for each of the 11 points are very much a combination
of several different distortions. This does not, however, need to be a problem. If all involved parameters except the main one are known, as is the case in this example, the problem can easily be solved. There are more forces at work than just the stretch, bend and torsional parameters, such as the non-bonded interactions. These have to be removed before any fitting can be done, same as for the stretch parameter in Section 3.1. To do this, $k_\theta$ is set to zero and the MM3 force field is used to compute the energies for the 11 points. These energies should, if all other parameters are correct, be from all other contributing sources except the C–C–H bending. Subtracting these from the B3LYP energies results in only the contribution from the C–C–H bending. A second order curve is fitted to these energies. This is done using the polyfit command in Matlab [14], which fits a polynomial to the points using the method of least squares. The second derivative of the curve, that is the second-degree term multiplied by two, gives a preliminary value for the $k_\theta$ parameter. Again, the energy unit of choice for the parameter is mdyn·Å, while the displacement from equilibrium is given in radians, meaning the unit of $k_\theta$ is mdyn·Å/rad². A preliminary value for $\theta_0$ is also given by the C–C–H angle in the optimized structure.

As for the stretch parameters, some manual adjustment is needed to better fit the preliminary parameters to the quantum mechanical data. The energy is calculated using the parameters, compared to the B3LYP energies and then the parameters are adjusted to get a better fit. The process is repeated until a satisfactory agreement is reached. The energy from the preliminary parameters along with the B3LYP energies are plotted in the left panel of Figure 3.4 while the energy calculated with the adjusted parameters can be seen in the right panel. As can be seen, the difference between the equilibrium angle and $\theta_0$ is quite large, showing that just using the equilibrium value is too rough an approximation. The resulting parameters are also presented, along with the already existing values in the MM3 force field, in Table 3.2. Same as for the stretch parameters, they do not quite agree.
3.3 Torsion parameters

For ethane, there is only one kind of torsional angle, H–C–C–H (H1–C1–C2–H2 in Figure 3.1). There are, however, nine of them. Each of the three hydrogens on one side of the C–C bond can meet one of the three hydrogens on the other side, giving a total of nine torsional angles. Twisting the molecule around the C–C bond affects all of these, giving nine separate torsional contributions. Looking at the structure of the molecule, however, shows that these must all be the same. Turning one of the methyl groups 120° produces the exact same molecule, meaning all terms except $V_3$ must be zero. Furthermore, since

$$
\frac{V_3}{2} \left[ 1 + \cos(3\omega) \right] = \frac{V_3}{2} \left[ 1 + \cos(3(\omega + 120°)) \right] = \frac{V_3}{2} \left[ 1 + \cos(3(\omega + 240°)) \right]
$$

all nine contributions must be the same.

The fitting of the parameter is carried out in a manner similar to the procedure used for the stretch and bend parameters. The energy is computed using B3LYP for a number of points and a curve is fitted to it. These points are spread out at 7.5° intervals for a full revolution around the bond in question, giving 48 energies. A set of parameters $V_1$, $V_2$ and $V_3$ are fitted to the energies using the least squares method. The unit of these terms is kcal/mol. It is important to remember that in this case there are nine torsional angles distorted and the result should thus be divided by nine. Note that this is done without removing contributions other than the torsional bending, as was done for previous parameters. This is not because

**Table 3.2.** Bend parameters for ethane. $\theta_0$ in degrees and $k_\theta$ in mdyn·Å/rad².

<table>
<thead>
<tr>
<th>Parameterized</th>
<th>bond type</th>
<th>atoms</th>
<th>$\theta_0$</th>
<th>$k_\theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MM3 [5]</td>
<td>1–1–5</td>
<td>C1–C2–H2</td>
<td>110.4</td>
<td>0.637</td>
</tr>
<tr>
<td></td>
<td>1–1–5</td>
<td>–</td>
<td>110.7</td>
<td>0.590</td>
</tr>
</tbody>
</table>

**Figure 3.4.** Energy differences from bending of a C–C–H bond in ethane, computed using B3LYP and MM3. Preliminary MM3 parameters to the left and manually adjusted parameters to the right.
these contributions are insignificant but because any error introduced by them is easily corrected in the next step. In fact, if one wishes, this step can be skipped entirely and a suitable guess of the \( V_3 \) parameter can be used instead. The next step consists of computing the energy for the points in Tinker, comparing them with the B3LYP energy and them making adjustments to the \( V_3 \) parameter. This is repeated until they correspond as well as possible. Since there is only one degree of freedom, \( V_3 \), this is easily done. For torsional angles involving more than just this term things become a bit more complicated. In that case, the energies of the contributions from sources other than the torsional angle should be computed in Tinker and then subtracted from the B3LYP energies. Fitting to these energies will then produce preliminary \( V \)-parameters which can then be manually modified to give a better fit.

The energy computed using the preliminary parameter can be seen in the left panel of Figure 3.5 and the energy computed using the manually corrected parameters can be seen in the right panel, both along with the B3LYP energies. The final parameters are compared to the existing MM3 parameters in Table 3.3.

**Figure 3.5.** Energy differences from twisting around the C–C bond in ethane, computed using B3LYP and MM3. Preliminary MM3 parameters to the left and manually adjusted parameters to the right.

<table>
<thead>
<tr>
<th>bond type</th>
<th>atoms</th>
<th>( V_1 )</th>
<th>( V_2 )</th>
<th>( V_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameterized</td>
<td>5–1–1–5</td>
<td>H1–C1–C2–H2</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>MM3</td>
<td>5–1–1–5</td>
<td>–</td>
<td>0.000</td>
<td>0.000</td>
</tr>
</tbody>
</table>

**Table 3.3.** Torsion parameters for ethane. \( V_1 \), \( V_2 \) and \( V_3 \) in kcal/mol.
Chapter 4

Parameterization of the Pt1 chromophore

4.1 Introduction

The dynamic behaviour of the Pt1 chromophore is to be studied, both alone and as part of a larger molecule, where it has been dendrimer coated. Even alone,
the molecule consists of 131 atoms, making it too large to comfortably use \textit{ab initio} methods. Thus, the MM3 force field will be used. However, several of the parameters needed to describe the molecule are not available and a type has not even been defined for the platinum atom. These missing parameters need to be obtained before the MM3 force field can be used. The missing parameters are listed in Table \ref{table:MissingParameters} with atom numbering corresponding to the labels in Figure \ref{fig:Pt1Structure}. In these parameters, platinum has been given the type 384.

\begin{table}[h]
\centering
\caption{The missing parameters needed to describe the Pt1 chromophore in the MM3 force field. Atom types used are 1 (C_{sp^3}), 2 (C_{sp^2}), 4 (C_{sp^1}), 5 (H), 60 (P) and 384 (Pt). The atoms column gives an example of the bond, angle or torsional angle in question using the labeled atoms from Figure \ref{fig:Pt1Structure}.}
\begin{tabular}{ll}
\hline
\textbf{Stretch parameters} & \\
\hline
\textbf{Bond type} & \textbf{Atoms} \\
1–60 & C1–P1 \\
384–4 & Pt–C5 \\
384–60 & Pt–P1 \\
\hline
\textbf{Bend parameters} & \\
\hline
\textbf{Angle type} & \textbf{Atoms} \\
4–2–2 & C6–C7–C8 \\
1–1–60 & C2–C1–P1 \\
5–1–60 & H1–C1–P1 \\
1–60–1 & C1–P1–C4 \\
4–384–4 & C5–Pt–C9 \\
384–4–4 & Pt–C5–C6 \\
60–384–4 & P1–Pt–C5 \\
60–384–60 & P1–Pt–P2 \\
384–60–1 & Pt–P1–C1 \\
\hline
\textbf{Torsion parameters} & \\
\hline
\textbf{Torsional type} & \textbf{Atoms} \\
1–1–60–1 & C2–C1–P1–C4 \\
1–1–1–60 & C3–C2–C1–P1 \\
5–1–1–60 & H2–C2–C1–P1 \\
5–1–60–1 & H1–C1–P1–C4 \\
384–4–4–2 & Pt–C5–C6–C7 \\
384–60–1–1 & Pt–P1–C1–C2 \\
384–60–1–5 & Pt–P1–C1–H1 \\
4–384–4–4 & C9–Pt–C5–C6 \\
60–384–4–4 & P1–Pt–C5–C6 \\
4–384–60–1 & C5–Pt–P1–C1 \\
60–384–60–1 & P2–Pt–P1–C1 \\
\hline
\end{tabular}
\end{table}

Also, when comparing the molecule optimized using B3LYP to the molecule
4.2 Stretch parameters

optimized using the MM3 force field, as described in Section 4.5, the C\textsubscript{sp\textsuperscript{1}}–C\textsubscript{sp\textsuperscript{2}} bonds connecting the phenyl rings were found to be very different in the two structures. This suggested that the 2–4 parameter needed to be reparameterized. Upon further study of the B3LYP optimized structure, it was also found that the C\textsubscript{sp\textsuperscript{2}}–C\textsubscript{sp\textsuperscript{2}} bonds in the phenyl rings varied depending on the position of the bond in the ring, as shown in Figure 4.2. To better model this, a new kind of C\textsubscript{sp\textsuperscript{2}} type, with number 385, was introduced. The atoms converted to this type are marked with C’ in Figure 4.2. The carbon at the end falls somewhere between the two types, but it is closer to the type 2 carbons, so it was allowed to stay that way. Thus, an additional three stretch parameters needed to be parameterized, listed in Table 4.2. All other extra parameters required due to the introduction of the 385 type were taken from the corresponding parameters for the 2 type.

Figure 4.2. The C–C bond distances in the phenyl rings of the B3LYP optimized structure vary. Carbon atoms marked with C are of type 2 and those marked with C’ are of type 385.

Table 4.2. Stretch parameters that need to be reparameterized to better correspond to the structure of the Pt1 chromophore. The type 385 is an additional kind of C\textsubscript{sp\textsuperscript{2}} atom.

<table>
<thead>
<tr>
<th>Bond type</th>
<th>Atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>385–4</td>
<td>C\textsubscript{6}–C\textsubscript{7}</td>
</tr>
<tr>
<td>2–2</td>
<td>C\textsubscript{8}–C\textsubscript{10}</td>
</tr>
<tr>
<td>385–2</td>
<td>C\textsubscript{7}–C\textsubscript{8}</td>
</tr>
</tbody>
</table>

The first step in the parameterization is optimization of the molecule. This was carried out using the B3LYP hybrid functional and using the 6-31G* [12, 13] basis set for carbon, the 6-31G [12] basis set for hydrogen and the sdd effective core potential [15, 16] for P and Pt. All energy scans done for the Pt1 chromophore also use these basis sets. They are also used for the optimization and energy calculations for the additional molecules in Sections 4.4.1 and 4.4.2. For the molecules in Sections 4.4.3 to 4.4.6 the 6-31G* basis set was used for all atoms.

4.2 Stretch parameters

All of the initial three stretch parameters were parameterized in the manner described in Section 3.1. The bond distances were varied and second derivatives were obtained from the energies, providing preliminary parameters. These were
then manually fitted to better correspond to the B3LYP energies. The energies computed using MM3 from the preliminary parameters can be seen in the upper part of Figure 4.3, plotted against the B3LYP energies. The lower part shows the same thing, but with the manually adjusted parameters. The resulting parameters can be found in Table 4.3.

**Figure 4.3.** Energy differences from stretching and contraction of bonds, computed using B3LYP and MM3. Preliminary MM3 parameters in the upper row and manually adjusted parameters in the lower.

**Table 4.3.** Stretch parameters. \( l_0 \) is given in Å and \( k_s \) in mdyn/Å. Atom numbering from Figure 4.1.

<table>
<thead>
<tr>
<th>bond type</th>
<th>atoms</th>
<th>( l_0 )</th>
<th>( k_s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1–60</td>
<td>C1–P1</td>
<td>1.850</td>
<td>2.689</td>
</tr>
<tr>
<td>384–4</td>
<td>Pt–C5</td>
<td>2.019</td>
<td>2.563</td>
</tr>
<tr>
<td>384–60</td>
<td>Pt–P1</td>
<td>2.330</td>
<td>1.790</td>
</tr>
</tbody>
</table>

Of the three extra C–C parameters, the 385–4 parameter can be easily obtained by the same procedure as before. For the 385–2 parameter, however, things are not as easy. This is because it is not possible to change only one such bond without also distorting other bond lengths and angles. To get around this, all four 385–2 bonds in one of the phenyl rings closest to the platinum atom were varied at the same time. By varying them by the same amount all angles and other bond lengths are maintained. This gives four times the energy contribution of distorting one 385–2 bond. Due to their similarity, the force constant from the 385–2 parameter was also used for the 2–2 parameter, along with an \( l_0 \) value taken from the optimized bond distance. In the upper part of Figure 4.4, the MM3 energies computed using preliminary parameters are plotted against the B3LYP
4.2 Stretch parameters

energies. The lower part shows the same thing but with MM3 energies computed using the manually adjusted parameters. The final parameters can be found in table 4.4.

![Graphs showing energy differences from stretching and contraction of bonds, computed using B3LYP and MM3. Preliminary MM3 parameters in the upper row and manually adjusted parameters in the lower.]

Figure 4.4. Energy differences from stretching and contraction of bonds, computed using B3LYP and MM3. Preliminary MM3 parameters in the upper row and manually adjusted parameters in the lower.

<table>
<thead>
<tr>
<th>bond type</th>
<th>atoms</th>
<th>$l_0$ (Å)</th>
<th>$k_s$ (mdyn/Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>385–4</td>
<td>C6–C7</td>
<td>1.426</td>
<td>6.025</td>
</tr>
<tr>
<td>2–2</td>
<td>C8–C10</td>
<td>1.388</td>
<td>7.759</td>
</tr>
<tr>
<td>385–2</td>
<td>C7–C8</td>
<td>1.406</td>
<td>7.759</td>
</tr>
</tbody>
</table>

Table 4.4. Additional stretch parameters. $l_0$ is given in Å and $k_s$ in mdyn/Å. Atom numbering from Figure 4.1.
4.3 Bend parameters

The procedure for obtaining the bend parameters follows that detailed in Section 3.2, with some variations for specific cases.

As explained in Section 3.2, bending one angle usually means bending other angles at the same time. This presents a problem if parameters are missing for one or more of the affected angles. Then it becomes impossible to separate which energy contribution comes from which unknown angle. Of the nine parameters needed, two suffer from this problem: the 1–60–1 angle and the 384–60–1 angle.

In this case, the chosen solution to this problem was to first fit curves directly to the B3LYP energies, without removal of the other contributions. This provides a rough approximation of the force constant. These can then be used in the ordinary procedure. One is set to zero and the energies of the corresponding scan are computed. This gives an approximation of the energies from other contributing terms, which can then be subtracted from the B3LYP energies, giving the contribution from the relevant term. Preliminary parameters can then be fitted to the curves. At the end, manual fitting is carried out with both of the angles at the same time, since altering the parameters of one changes the energies of both.

It should be noted that the 4–2–2 angle also cannot be altered without changing two angles at the same time. However, they are the same kind of angle and the distortion is the same in both, only in opposite direction from the equilibrium, so the problem is easily solved by a simple division by two for the force parameter.

For three of the parameters, 4–384–4, 384–4–4 and 60–384–60, the angles are very close to 180°. This causes problems with Gaussian 03 when performing scans of the angles. This is due to the fact that the structures in the input files are given in Z-matrix form. In these, angles are defined from 0 to 180 degrees. When performing a energy scan of an angle close to 180°, the results from the points above 180° will become unpredictable and should not be relied upon. Therefore, when performing the manual fit of the parameters, more care was taken to better fit the curve to the points corresponding to angles below 180°. In addition to this, because of the symmetry of the molecule, all three equilibrium angles were set to exactly 180 degrees. For the same reason, the equilibrium value of the 60–384–4 parameter is set to exactly 90 degrees.

Plots showing the energies of the angle scan, computed using the preliminary parameters, along with the B3LYP energies are shown in the Figure 4.5. Corresponding plots, computed using the manually adjusted parameters, can be seen in Figure 4.6. The resulting parameters can be seen in Table 4.3.
4.3 Bend parameters

Figure 4.5. Energy differences from bending of angles computed using B3LYP and MM3, using preliminary parameters.

Figure 4.6. Energy differences from bending of angles computed using B3LYP and MM3, using manually adjusted parameters.
26 Parameterization of the Pt1 chromophore

Table 4.5. Bend parameters. $\theta_0$ is given in degrees and $k_\theta$ in mdywn-Å/rad$^2$. Atom numbering from Figure 4.1.

<table>
<thead>
<tr>
<th>angle type</th>
<th>atoms</th>
<th>$\theta_0$</th>
<th>$k_\theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4–2–2</td>
<td>C6–C7–C8</td>
<td>121.1</td>
<td>0.70</td>
</tr>
<tr>
<td>1–1–60</td>
<td>C2–C1–P1</td>
<td>114.8</td>
<td>0.70</td>
</tr>
<tr>
<td>5–1–60</td>
<td>H1–C1–P1</td>
<td>105.2</td>
<td>0.47</td>
</tr>
<tr>
<td>1–60–1</td>
<td>C1–P1–C4</td>
<td>105.2</td>
<td>0.98</td>
</tr>
<tr>
<td>4–384–4</td>
<td>C5–Pt–C9</td>
<td>180.0</td>
<td>0.82</td>
</tr>
<tr>
<td>384–4–4</td>
<td>Pt–C5–C6</td>
<td>180.0</td>
<td>0.35</td>
</tr>
<tr>
<td>60–384–4</td>
<td>P1–Pt–C5</td>
<td>90.0</td>
<td>0.80</td>
</tr>
<tr>
<td>60–384–60</td>
<td>P1–Pt–P2</td>
<td>180.0</td>
<td>0.56</td>
</tr>
<tr>
<td>384–60–1</td>
<td>Pt–P1–C1</td>
<td>116.0</td>
<td>0.31</td>
</tr>
</tbody>
</table>

4.4 Torsion parameters

Of the 11 missing torsion parameters, four can immediately be given due to symmetry. Looking at the optimized structure in Figure 4.1, it can be seen that for the torsional angles given in Table 4.6, at least three of the atoms included are linear or very close to linear. For these structures of four atoms, twisting them any amount around the central bond produces a structure identical to the initial one. Thus, there can be no rotational barriers and all $V$ terms must be zero.

Table 4.6. Torsion parameters with at least three linear atoms. Atom numbering from Figure 4.1.

<table>
<thead>
<tr>
<th>dihedral type</th>
<th>atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>384–4–4–2</td>
<td>Pt–C5–C6–C7</td>
</tr>
<tr>
<td>4–384–4–4</td>
<td>C9–Pt–C5–C6</td>
</tr>
<tr>
<td>60–384–4–4</td>
<td>P1–Pt–C5–C6</td>
</tr>
<tr>
<td>60–384–60–1</td>
<td>P2–Pt–P1–C1</td>
</tr>
</tbody>
</table>

In addition to these, one more parameter can be given due to symmetry, though for not quite as obvious reasons. The parameter in question is the 4–384–60–1 parameter (C5–Pt–P1–C1 in Figure 4.1). Twisting around the Pt–P1 bond will affect six of these torsional angles, each of the two $C_{sp^2}$ meeting the three $C_{sp^3}$. Looking through the Pt–P1 bond, the two $C_{sp^2}$ atoms are offset from each other by 180° and the three $C_{sp^3}$ atoms are spaced with 120°. The structure, with $C_2$ symmetry on one side and $C_3$ symmetry on the other, indicates that there can only be $V_2$ and $V_3$ terms. The $V_2$ part of the energy from one of the $C_{sp^2}$ atoms meeting the three $C_{sp^3}$ atoms is given by:
The same is of course true for the second $C_{sp^2}$ atom, meaning the total energy contribution from the $V_2$ part of twisting around the Pt–P1 bond is simply the constant $3V_2$.

Going from the other direction, the $V_3$ part of the energy from one of the $C_{sp^3}$ atoms meeting the two $C_{sp^2}$ atoms is given by:

\[
E = \frac{V_3}{2}[1 + \cos(3\omega)] + \frac{V_3}{2}[1 + \cos(3(\omega + 180^\circ))] = V_3 + \frac{V_3}{2}[\cos(3\omega) - \cos(3\omega)] = V_3
\]

Since there are three of these, the total energy contribution from the $V_3$ part is just the constant $3V_3$. Thus, the total torsional energy from twisting around the Pt–P1 bond is just $3V_2 + 3V_3$, which is constant. This means that rotation around the bond can be done without any change in energy, regardless of the values $V_2$ and $V_3$ values. For this reason, all $V$ terms for the 4–384–60–1 parameter are set to zero. This does not, however, mean that $V$ terms can be set to zero for all 4–384–60–1 torsional angles, just those that occur with this specific symmetry.

A problem arises when attempting to parameterize the remaining six torsion angles. The problem lies in the fact that in the Pt1 chromophore, they are all entangled. If one wishes to scan the 1–1–60–1 (C2–C1–P1–C4) angle, the molecule would be twisted around the C1–P1 bond, turning the butyl group. However, this also distorts torsion angles of type 5–1–60–1 (H1–C1–P1–C4), 384–60–1–1 (Pt–P1–C1–C2) and 384–60–1–5 (Pt–P1–C1–H1), all of which are unknown. The same goes for the 1–1–1–60 (C3–C2–C1–P1) and 5–1–1–60 (H2–C2–C1–P1) angles, which both require twisting around the C2–C1 bond. The only way around this is to use other molecules which isolate the relevant torsion angle. For this reason, different molecules were used for each of the six remaining parameters, described in the following sections. The actual parameterization was done using the method described in Section 3.3.

### 4.4.1 384–60–1–5

For the 384–60–1–5 parameter, a smaller version of the Pt1 chromophore was used. This molecule replaced the butyl groups attached to the phosphorus atoms with methyl groups, creating the molecule shown in Figure 4.7. A scan was then performed by turning one of the methyl groups.
4.4.2 384–60–1–1

The scan for the 384–60–1–1 parameter used a modified version of the one used for the 384–60–1–5 parameter. One methyl group was replaced by a tert-butyl group as shown in Figure 4.8, which was then turned during the scan.

4.4.3 5–1–60–1

Trimethylphosphine, as shown in Figure 4.9, was used for the 5–1–60–1 parameter. For the scan, one of the methyl groups was turned.

---

**Figure 4.7.** The molecule used to scan the 384–60–1–5 parameter. The atoms forming one of the distorted torsional angles are labeled.

**Figure 4.8.** The molecule used to scan the 384–60–1–1 parameter. The atoms forming one of the distorted torsional angles are labeled.

**Figure 4.9.** Trimethylphosphine was used to scan the 5–1–60–1 parameter. The atoms forming one of the distorted torsional angles are labeled.
4.4 Torsion parameters

4.4.4 1–1–60–1

The molecule used for the 1–1–60–1 parameter is created by replacing one of the methyl groups in trimethylphosphine with a \textit{tert}-butyl group, creating the molecule shown in Figure 4.10. The \textit{tert}-butyl group was then turned for the scan.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure410}
\caption{The molecule used to scan the 1–1–60–1 parameter. The atoms forming one of the distorted torsional angles are labeled.}
\end{figure}

4.4.5 5–1–1–60

For the 5–1–1–60 parameter a molecule with three PH\textsubscript{2} groups and one methyl group attached to a central carbon atom, as shown in Figure 4.11, was used. For the scan, the methyl group was turned.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure411}
\caption{The molecule used to scan the 5–1–1–60 parameter. The atoms forming one of the distorted torsional angles are labeled.}
\end{figure}

4.4.6 1–1–1–60

A molecule similar to the one used for the 5–1–1–60 parameter was used for the 1–1–1–60 parameter. Instead of a methyl group it had a \textit{tert}-butyl group, which was turned for the scan.
Figure 4.12. The molecule used to scan the 1–1–1–60 parameter. The atoms forming one of the distorted torsional angles are labeled.

4.4.7 Results

The B3LYP energies are compared to energies computed using MM3 with preliminary parameters in Figure 4.13 and with the manually adjusted parameters in Figure 4.14. The resulting parameters can be found in Table 4.7.

Table 4.7. Torsion parameters. $V_1$, $V_2$ and $V_3$ given in kcal/mol. Atom numbering from Figure 4.1.

<table>
<thead>
<tr>
<th>dihedral type</th>
<th>atoms</th>
<th>$V_1$</th>
<th>$V_2$</th>
<th>$V_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1–1–60–1</td>
<td>C2–C1–P1–C4</td>
<td>0.000</td>
<td>0.000</td>
<td>0.712</td>
</tr>
<tr>
<td>1–1–1–60</td>
<td>C3–C2–C1–P1</td>
<td>0.000</td>
<td>0.000</td>
<td>0.600</td>
</tr>
<tr>
<td>5–1–1–60</td>
<td>H2–C2–C1–P1</td>
<td>0.000</td>
<td>0.000</td>
<td>0.400</td>
</tr>
<tr>
<td>5–1–60–1</td>
<td>H1–C1–P1–C4</td>
<td>0.000</td>
<td>0.000</td>
<td>0.386</td>
</tr>
<tr>
<td>384–4–4–2</td>
<td>Pt–C5–C6–C7</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>384–60–1–1</td>
<td>Pt–P1–C1–C2</td>
<td>0.000</td>
<td>0.000</td>
<td>1.400</td>
</tr>
<tr>
<td>384–60–1–5</td>
<td>Pt–P1–C1–H1</td>
<td>0.000</td>
<td>0.000</td>
<td>-0.330</td>
</tr>
<tr>
<td>4–384–4–4</td>
<td>C9–Pt–C5–C6</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>60–384–60–1</td>
<td>P1–Pt–C5–C6</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>4–384–60–1</td>
<td>C5–Pt–P1–C1</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>60–384–60–1</td>
<td>P2–Pt–P1–C1</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
</tbody>
</table>
Figure 4.13. Energy differences from twisting of torsional angles computed using B3LYP and MM3, using preliminary parameters.

Figure 4.14. Energy differences from twisting of torsional angles computed using B3LYP and MM3, using manually adjusted parameters.
4.5 Validation

The fitting of parameters makes sure that the individual terms of the energy fit well, or at least as well as possible, with the B3LYP energies. The real test, however, is to investigate the entire molecule. Before parameterization began, the Pt1 chromophore was optimized using B3LYP. This gave a structure for which the molecule was in a local energy minimum. If the parameterization has been carried out correctly, optimization in the MM3 force field should yield the same structure, or at least something close to it.

The first test of this kind was done without the parameters in Table 4.2. The energy for the B3LYP optimized structure was computed using the MM3 force field. Then, starting from this optimized structure, another optimization was run, this time using the MM3 force field. The energy of the resulting structure was then compared to the energy from the B3LYP structure. In this initial test the difference in energy was found to be large, over 50 kcal/mol. Study of individual contributions to the energy showed that the majority of this difference in energy came from stretching of the C–C bonds in and near the phenyl rings. To remedy this an extra type of atom was introduced and three C–C bond stretch parameters reparameterized, as described in Sections 4.1 and 4.2.

With the new parameters, the process was repeated. The MM3 energy was computed for the B3LYP optimized structure and then compared to the energy computed for the MM3 optimized structure. The difference in energy was found to be just over 10 kcal/mol. A much smaller difference than the previous attempt. Study of the different energy term contributions showed that the difference in energy came from many small distortions, not a few large ones, as in the previous case. The changes in structure between the two optimizations can be seen in Figure 4.15, with the B3LYP optimized structure at the top and the MM3 optimized structure on the bottom. The main difference between the two is that the two phenyl rings closest to the platinum have turned 90 degrees. Since all torsional parameters controlling the rotation of the phenyl rings are zero, meaning they give no change in energy when turned, the reason for this change must come from the non-bonded interactions. The difference in energy between having the the rings turned and not turned is so small that it only takes a little difference in the non-bonded interactions to cause one structure to have lower energy than the other.
Figure 4.15. Structure optimized Pt1 chromophore. Upper structure optimized using B3LYP and lower structure optimized using MM3.
Parameterization of the Pt1 chromophore
Chapter 5

Molecular dynamics

5.1 Numerical methods

When described by a force field, the potential energy of an entire system is available in a simple form dependent on $3N$ variables, corresponding to the Cartesian coordinates of the $N$ atoms in the system. To find the evolution in time of the system is now only a matter of using classical mechanics. If the position of the atoms as a function of time is given by $r(t)$, a Taylor expansion around the current time $t = 0$, gives

$$r(t) = r(0) + \frac{\partial r}{\partial t} \Delta t + \frac{1}{2} \frac{\partial^2 r}{\partial t^2} (\Delta t)^2 + \frac{1}{6} \frac{\partial^3 r}{\partial t^3} (\Delta t)^3 + \ldots,$$

and a time step of $\Delta t$ gives a series of positions:

$$r_{i+1} = r_i + \frac{\partial r}{\partial t} \Delta t + \frac{1}{2} \frac{\partial^2 r}{\partial t^2} (\Delta t)^2 + \frac{1}{6} \frac{\partial^3 r}{\partial t^3} (\Delta t)^3 + \ldots$$

This also works backwards, with the previous step given by replacing $\Delta t$ with $-\Delta t$:

$$r_{i-1} = r_i - v_i \Delta t + \frac{1}{2} a_i (\Delta t)^2 - \frac{1}{6} b_i (\Delta t)^3 + O(\Delta t^4).$$

Adding (5.2) and (5.3) together results in the velocity and hyperacceleration terms canceling and the remaining terms can be written as

$$r_{i+1} = (2r_i - r_{i-1}) + a_i (\Delta t)^2 + O(\Delta t^4).$$

This is good since it only depends on the coordinates of the current and previous step as well as the acceleration. The acceleration can easily be obtained from Newton’s second equation, $F = ma$:
where $E$ is the potential energy from the force field. This method of numerical integration is called the Verlet algorithm \cite{17}, which has an error term of the order $\Delta t^4$.

Often, it is important to know the velocities in addition to the positions and accelerations. The easiest way of obtaining them is to just use the mean value theorem,

$$v_i = \frac{r_{i+1} - r_{i-1}}{2\Delta t} + O(\Delta t^2).$$

The disadvantage of this approach is the error term of the order $\Delta t^2$. A better expression can be obtained with the velocity Verlet algorithm. In this algorithm the position is given by the first three terms in the Taylor expansion in (5.2),

$$r_{i+1} = r_i - v_i \Delta t + \frac{1}{2} a_i (\Delta t)^2 + O(\Delta t^3),$$

eliminating the need to save the previous position, but also introducing a larger error of the order $\Delta t^3$. The velocity term can be derived from differentiation of the position term with respect to $t$:

$$\frac{dr_{i+1}}{dt} = \frac{dr_i}{dt} + \frac{dv_i}{dt} \Delta t + \frac{1}{2} \frac{da_i}{dt} (\Delta t)^2 + O(\Delta t^3),
$$

$$v_{i+1} = v_i + a_i \Delta t + \frac{1}{2} b_i (\Delta t)^2 + O(\Delta t^3).$$

For this to useful $b_i$ must be expressed in known quantities. To do this, the expression is differentiated once more:

$$\frac{dv_{i+1}}{dt} = \frac{dv_i}{dt} + \frac{da_i}{dt} \Delta t + \frac{1}{2} \frac{db_i}{dt} (\Delta t)^2 + O(\Delta t^3),
$$

$$a_{i+1} = a_i + b_i \Delta t + O(\Delta t^2),$$

which can be rewritten as

$$b_i \Delta t = a_{i+1} - a_i + O(\Delta t^2).$$

Inserting this into (5.8) gives the expression for the velocity,

$$v_{i+1} = v_i + \frac{1}{2} (a_i + a_{i+1}) \Delta t + O(\Delta t^3).$$

Thus, the procedure for the Verlet velocity algorithm is to first calculate the next position with (5.7), then the acceleration of the next position using (5.5) and finally the velocity using (5.11). Both the position and velocity will have an error term of the order $\Delta t^3$.  

$$a_i = -\frac{1}{m_i} \frac{d^2 E}{dx_i^2}, \quad (5.5)$$
5.2 Ensembles

An alternative to the Verlet algorithm is Beeman’s algorithm [18], which has the form

\[ r_{i+1} = r_i + v_i \Delta t + \frac{2}{3} a_i (\Delta t)^2 - \frac{1}{6} a_{i-1} (\Delta t)^2 + O(\Delta t^4) \]  
(5.12)

\[ v_{i+1} = v_i + \frac{1}{3} a_{i+1} \Delta t + \frac{5}{6} a_i \Delta t - \frac{1}{6} a_{i-1} \Delta t + O(\Delta t^3). \]  
(5.13)

This algorithm also has a position error of the order \( \Delta t^4 \), as the Verlet algorithm, and a velocity error of the order \( \Delta t^3 \), as the velocity Verlet algorithm.

The Tinker package [8] has implementations of the velocity Verlet algorithm as well as a modified version of Beeman’s algorithm [19], which is what will be used for all molecular dynamics simulations in Chapter 6, of the form:

\[ r_{i+1} = r_i + v_i \Delta t + \left[ 5a_i - a_{i-1} \right] \frac{(\Delta t)^2}{8} \]  
(5.14)

\[ v_{i+1} = v_i + \left[ 3a_{i+1} + 6a_i - a_{i-1} \right] \frac{\Delta t}{8}. \]  
(5.15)

5.2 Ensembles

When computing the time evolution of a system its ensemble must be considered. That is, all possible states in which the system can be found. The simplest ensemble to use when computing the dynamic behaviour of a system is the microcanonical ensemble. This ensemble is also called the \( NVE \) ensemble, since all possible states have the same number of particles (\( N \)), the same volume (\( V \)) and the same total energy (\( E \)). To use this in a simulation one needs only to start a numerical method, such as velocity Verlet or Beeman’s algorithm, with a set of starting positions and velocities. The potential and kinetic energy will fluctuate, but the total energy will remain as constant as the error in the numerical method will allow. While the evolution of this kind of system is easy to compute, it is also not very realistic. Most often, the dynamic behaviour is examined for systems with constant temperature, not constant total energy. Since the temperature is directly proportional to the average kinetic energy, which is allowed to fluctuate, the temperature will also fluctuate.

The canonical ensemble, also called the \( NVT \) ensemble, is similar to the microcanonical ensemble but instead of having constant total energy it has constant temperature, meaning constant kinetic energy. One way to imagine this is to have the system surrounded by a heat bath, containing an infinite supply of the desired temperature. This means that if the temperature is too low in the system, energy flows into it, and if the temperature is too high, energy flows out. While this may be a simple concept in theory, implementing it in a computer simulation is a bit more tricky. This is usually done with the aid of a thermostat, which scales the velocities, and thus the kinetic energy, of the atoms in the system. One such scaler is the Berendsen thermostat [20], for which all velocities are multiplied with a factor
\[ \lambda = \sqrt{1 + \frac{\Delta t}{\tau} \left( \frac{T_0}{T} - 1 \right)} \] (5.16)

in each time step. In (5.16), \( \Delta t \) is the time step, \( T_0 \) is the desired temperature, \( T \) is the current temperature and \( \tau \) is a coupling parameter that determines the rate of heat transfer. All dynamics simulations in Chapter 6 use this thermostat.

Other ensembles, also used in molecular dynamics, are the isothermal-isobaric ensemble (\( NPT \)), which keeps number of particles, pressure and temperature constant, and the isoenthalpic-isobaric ensemble (\( NPH \)), which keeps the number of particles, pressure and enthalpy constant.
Chapter 6

Chromophore absorption spectra

6.1 One-photon absorption

One-photon absorption, OPA, occurs when a single photon is absorbed by an atom or a molecule, exciting it from a state of lower energy to one of higher energy. When studying the absorption spectrum for an atom or molecule, one studies the probability of absorption occurring for the wavelengths of light within a specific spectrum. An electromagnetic wave can be seen as consisting of an electric field component and a magnetic field component. When the electric field, \( \mathbf{E} \), interacts with the molecule, which is made up of a number of charged particles and thus has a dipole moment \( \mathbf{\mu} \), the energy of the interaction is given by \( E = -\mathbf{\mu} \cdot \mathbf{E} \). If the Schrödinger equation has been solved for the system without the electric field, the change it induces can be added in the form of a perturbation in time-dependent perturbation theory. That way, going through some approximations and simplifications, it is possible to calculate the probability of a transition occurring from one state, \( \Psi \), to another \( \Psi' \). When the energy of the photons the electromagnetic wave consists of have an energy that is different from the energy difference between the two states \( \Psi \) and \( \Psi' \), this probability is found to be low. Also, the probability of absorption is found to be proportional to the square of the transition dipole moment, given by

\[
M_\alpha = \langle \Psi | \hat{\mu}_\alpha | \Psi' \rangle, \quad (6.1)
\]

where \( \hat{\mu}_\alpha \) is the electric dipole operator along a molecular axis \( \alpha \). The probability of absorption can also be expressed in the dimensionless property oscillator strength, \( f \), which depends on the transition moment and the energy of the absorbed photon, \( E_{\text{phot}} \). It has the form

\[
f = \frac{2}{3} E_\gamma \sum_{\alpha=x,y,z} |M_\alpha|^2, \quad (6.2)
\]
where $E_\gamma$ and $M$ are given in atomic units.

Thus, to build an absorption spectrum for a molecule, the energy of the excited states are needed along with the corresponding oscillator strengths. This shows which absorptions are possible and how probable these are. To compute these properties, the Dalton program \cite{21} was used, which is capable of obtaining them analytically.

### 6.2 Test cases

Though all previous discussion in this report has been about the Pt1 chromophore, this is not the only molecule of this kind that is of interest to us. What is of real interest is the Pt1 chromophore with the addition of dendrimers to the two phenyl rings at the end of the molecule. Dendrimers are branched structures made up of repeated segments, dividing out from a single source. For each branching, the number of end points increases according to $b^n$, where $b$ is the number of branches in each segment and $n$ is the number of generations. For the end points, the pattern is stopped by terminating the dendrimers with a different atom or molecule. The dendrimer used in this case has the form given in Figure 6.1 which doubles the number of end points for each generation. The full molecule that is of interest has five generations and is denoted Pt1-G5, where G5 stands for the number of generations of the dendrimer. Pt1-G0 is simply the Pt1 chromophore discussed previously. The reason the dendrimers are added is to increase solubility and to protect the chromophore.

![Figure 6.1](image)

**Figure 6.1.** One generation of the dendrimer. It is attached to the molecule or a previous generation at point X. The points marked Y can either be the next generation or an atom or molecule that terminates the dendrimer.

The reason that the Pt1-G0 molecule was used for all energy calculations and fittings was that the computational cost of doing these for the Pt1-G5 molecule would have been prohibitively large. The number of atoms grows quickly with the number of generations, meaning that while the Pt1-G0 molecule has 131 atoms the full Pt1-G5 molecule has 1067. In the MM3 force field, structure optimizations and dynamic simulations can easily be carried out for molecules this large, but when computing the excitation energies and oscillator strengths, they are much too large. Because of this, all one-photon absorption calculations were carried out on smaller molecules.

A study was carried out to determine the effect of different variables on the OPA results. This was done to see how large an effect the different approximations would
6.2 Test cases

have and if these were acceptable. Three variables were studied, the first of which was the use of the MM3 force field. Second, the addition of the dendrimers. And third, the basis set used for the carbon atoms. This was done by first computing the OPA spectrum for the B3LYP optimized structure of the Pt1-G0 molecule, using the 6-31G \cite{12} basis set for carbon atoms. This was repeated for the Pt1-G1 molecule, the Pt1-G0 molecule optimized with the MM3 force field as well as another for the B3LYP optimized Pt1-G0, but with the aug-cc-pVDZ \cite{22} basis set used for carbon. In addition, one more structure was tested, the MM3 optimized structure, but with the two phenyl rings closest to the platinum rotated so that phenyls came closer to being planar and the molecule better resembled the B3LYP optimized structure. The results can be found in Table 6.1.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Geometry( ^a )</th>
<th>Basis set</th>
<th>( \lambda )</th>
<th>( f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt1</td>
<td>A</td>
<td>6-31G</td>
<td>310</td>
<td>3.75</td>
</tr>
<tr>
<td>Pt1</td>
<td>A</td>
<td>aug-cc-pVDZ</td>
<td>329</td>
<td>3.64</td>
</tr>
<tr>
<td>Pt-G1</td>
<td>A</td>
<td>6-31G</td>
<td>315</td>
<td>3.74</td>
</tr>
<tr>
<td>Pt1</td>
<td>B</td>
<td>6-31G</td>
<td>316</td>
<td>1.96</td>
</tr>
<tr>
<td>Pt1</td>
<td>C</td>
<td>6-31G</td>
<td>304</td>
<td>3.69</td>
</tr>
</tbody>
</table>

\( ^a \) A: Pt1 part is B3LYP optimized. B: MM3 optimized. C: MM3 optimized with forced planarity of phenyl ligands.

From this data, it would appear that using the 6-31G basis set for the carbon atoms brings about a blue shift of around 20 nm. Using the MM3 optimized structure gives a small red shift of about 5 nm, but using the geometry with twisted phenyl rings instead gives a blue shift of about 5 nm. The main difference due to the turning of the phenyl rings seems to lie in the oscillator strength, which is much lower for the non-planar conformation. This might appear to be a problem with the MM3 representation, but as will be shown when studying the dynamic evolution of the molecule, the phenyl rings rotate very easily. The difference in energy between the two conformations is very small and at higher temperatures, the rings will be turning quite freely. Thus, it is of little importance that the optimized structures vary between MM3 and B3LYP, since the absorption spectra that will be studied will be obtained by creating an average of the absorption spectra of many of the possible structures at room temperature.

For the addition of the first generation dendrimer, a small red shift of 5 nm is seen. More worrying, however, is the fact that an extra excited state appears. For all previous OPA results, the first excited state was also the one with the highest oscillator strength. This is not the case for the Pt1-G1 molecule. Instead, an extra excited state appears with a shorter wavelength. For this reason, all snapshots taken from the dynamic evolution of the entire Pt1-G5 molecule were truncated down to Pt1-G1, not Pt1-G0.
6.3 Pt1-G0 dynamic in vacuum

The first dynamic to be run was for the Pt1-G0 molecule in a vacuum. Starting from the MM3 optimized structure, the dynamic ran for a period of 50 ps, with an integration step of 1 fs. The current structure was saved every 5 fs, giving a total of 10000 snapshot structures. This was done in the canonical ensemble with a temperature of 300 K, to simulate the system at room temperature. The resulting time evolution showed mostly minor changes to the structure and with no major deformations. Except for some slight bending of the butyls, the only interesting changes in the molecule concerned the orientation of the phenyl rings. Since the rotational barrier is so low, the phenyl rings are allowed to rotate quite freely. This is most evident in the two rings farthest from the platinum, which, due to their distance from the other parts of the molecule, are not affected much by steric hindrance from the butyl groups. Because of this lack of outside interference, they are allowed to rotate with close to constant angular velocity. This can be seen in Figure 6.2 where the angle of the two phenyl rings are plotted for the time of the dynamic.

![Figure 6.2](image.png)

**Figure 6.2.** The rotation of the phenyl rings farthest from the platinum.

This is of interest, since, as explained in the previous section, the rotation of the phenyl rings is of large importance to the oscillator strength. If the rings rotate with fixed periods, this might give some insight into what the average structure of the molecule over time will be. This is not the case, however. Though the periods of the two plots in Figure 6.2 may appear the same, they are not. While the plot on the left has a period time of close to 1.2 ps, the one on the right is closer to 1 ps. This is most likely due to the random assignment of energy at the start of the dynamic. One ring rotates with a certain angular velocity simply as a result of the energy it was assigned at the start and the fact that there is nothing to interfere with it. The rotation of the phenyl rings with constant angular velocity appears to be a quite unrealistic scenario. This will be shown in later dynamics, involving dendrimers attached to the phenyl rings and a solvent surrounding the molecule,
both interfering with the rotation of the phenyls. This interference can be seen in this dynamic too, for the phenyl rings closest to the platinum. The angles of these two phenyls are plotted in Figure 6.3. There are sections of constant angular velocity, but interruptions cause the rotation to stop, reverse and for the periods to change.

![Figure 6.3. The rotation of the phenyl rings closest to the platinum.](image)

At room temperature, the molecule can be found in a large number of structures with varying probability. For an absorption spectrum at room temperature, this needs to be reflected. To do this, a selection of structures from the dynamic is used and the absorption spectrum is built from an average of their OPA. For this dynamic, first 100 and then an additional 100 structures were selected from the 10000 saved snapshots. The first 100 were taken at 0.5 ps intervals, starting from \( t = 0.5 \) ps. The second batch of 100 were also taken at 0.5 ps intervals, but starting from \( t = 0.25 \) ps, giving a total interval of 0.25 ps. For all these, the energies and oscillator strengths of the ten lowest excited states were computed. This was done using CAMB3LYP [23] and with the sdd-DZ [15, 16] basis set for Pt and P and the 6-31G basis set for O, C and H. This results in ten excitation energies with corresponding oscillator strengths for each of the structures. All these are plotted in Figure 6.4 with energies converted to wavelengths. The upper plot contains the first set of 100 samples and the lower plot contains both sets of 100 samples, for a total of 200. This plot gives a general sense of the fact that there is one set of excited states around 300 to 330 nm that have high oscillator strengths and another with lower oscillator strengths around 250 to 300 nm.

To better visualize this, a Lorentzian function is placed around each excited state. The Lorentzian has the form

\[
L(x) = I \frac{\Gamma^2}{(x - x_0)^2 + \Gamma^2},
\]

where \( I \) is the height of the peak, which in this case is the oscillator strength, \( x_0 \) is the location of the peak, which is the wavelength for the excited state and \( \Gamma \) is a
scale parameter, which is the distance from the peak for which the amplitude has dropped to half. The Lorentzian used in this case has a quite low $\Gamma$ of 0.01 eV, which translates to about 3 nm. The Lorentzians for all excited states are added together and then an average is obtained by dividing by the number of snapshots used. This gives something that, for a large number of snapshots, approaches the absorption spectrum for the molecule at 300 K. The resulting spectrum for 100 snapshots can be seen in the upper part of Figure 6.5 and for 200 snapshots in the lower part. These show a large peak around 310 nm. The figure also contains separate plots for just the contribution from the first excited state and just for the nine others, showing clearly that the large peak is due to the first excited state. There are several other, smaller, peaks, but it is hard to determine if these are a genuine result of the absorption of the molecule at room temperature or just an
6.4 Comparison to experimental data

Effect of an insufficient sample for the average. As is evident when going from 100 to 200 snapshots, peaks disappear and the curve becomes more smooth. A larger sample would give a more definitive answer.

![Graph showing average absorption spectra for the Pt1-G0 molecule in vacuum made from 100 snapshots (upper) and 200 snapshots (lower). The total absorption from the first ten excited states has been plotted. Also plotted are the contributions of just the first excited states, which gives a large peak, along with the contributions from the nine others, which gives a smaller peak.]

Figure 6.5. Average absorption spectra for the Pt1-G0 molecule in vacuum made from 100 snapshots (upper) and 200 snapshots (lower). The total absorption from the first ten excited states has been plotted. Also plotted are the contributions of just the first excited states, which gives a large peak, along with the contributions from the nine others, which gives a smaller peak.

6.4 Comparison to experimental data

To see if the obtained theoretical spectrum is good, it is compared to experimental data. There exist experimentally obtained absorption spectra for the Pt1 chromophore with dendrimers from generation 0 to 4 [24]. These can be seen in Figure
In these, it can be seen that for generations 1 to 4, the spectra are almost identical, only differing vertically. These differences are likely not results of actual differences in absorbance between the molecules, but due to the process used to obtain the spectra. For this method, very small amounts of the molecule is used, with a molarity of just 10 µM. Such low concentrations are hard to measure, and the differences in the spectra are likely due to variations from the desired concentration. The Pt1-G0 spectrum, however, shows a clear difference compared to the other four. It is blueshifted by about 5 nm compared to them, which fits very nicely with the results found in Section 6.2. The fact that adding more than one generation of the dendrimer seems to have no effect is good, since that means that when computing the OPA for the dynamics involving the Pt1-G5 molecule, it can be truncated to Pt1-G1 without affecting the results too much.

While not perfect, the calculated Pt1-G0 spectrum matches quite well with the experimental one, at least as far as general appearance goes. One larger peak with a tail for shorter wavelengths. For the experimental spectra, there are three clear peaks. The large one around 355 nm, a smaller one near 300 nm and a third, even smaller, around 270 nm. Looking at the computed spectrum, at least the two larger of these peaks are clearly visible. The third could be visible too, but it is impossible to tell for sure without a larger sample for the spectral averaging. While the general appearance of the computed and experimental spectra are the same, the computed spectrum is blueshifted by about 40 nm. As shown in Section 6.2, a large part of this shift comes from the use of a smaller basis set for the carbon atoms. Some might also come from the structural differences due to the use of the MM3 force field. In addition, the experimental values were obtained for the molecule in a solvent, which can cause both blue shifts [25] and red shifts [26]. This could be an explanation for the remaining difference of 20 nm between the computed and the experimental spectra.

![Figure 6.6. Experimental spectra for Pt1 chromophore with dendrimers of generation 0 to 4.](image)
6.5 Pt1-G5 dynamic in vacuum

To see how the addition of dendrimers would affect the structure of the Pt1 chromophore another dynamic simulation was run, this time using the full Pt1-G5 molecule. This was again done in a vacuum, using the canonical ensemble at 300 K. It was still done with a time integration step of 1 fs, but for a longer time, 200 ps, and with a longer interval between saved frames, 50 fs, giving a total of 4000 saved frames. The reason for the longer dynamic was that the molecule started in an unoptimized structure, as shown in Figure 6.7, and the extra time was given so that the molecule could settle into a more stable conformation. What happened during the dynamic was that the dendrimers were attracted to the central butyl groups, causing them to bend in over the molecule. In this position they were attracted to each other, causing further bending inwards over the molecule, resulting in a structure that can be seen in Figure 6.8. As expected, the rotation of the outer phenyl rings was a lot less structured compared to the first dynamic. The rotation seems to start and stop at different speeds and directions without any discernable pattern.

For the snapshots used to create the average absorption spectrum, only states after the molecule had taken the form seen in Figure 6.8 were used, meaning they were selected from the last 50 ps of the dynamic. 20 of the structures in the last 50 ps were selected to be used for creation of an absorption spectrum. Before the OPA parameters of the snapshots were calculated, the dendrimers in the snapshots were truncated to the first generation, creating Pt1-G1 molecules. As discussed in Section 6.3 even 200 snapshots is on the lower side of what is needed to create a good average, and 20 is much too low. However, due to the resources needed to calculate the OPA spectra of the molecule, even when it has been truncated down to Pt1-G1, no more could be examined within the scope of this project. For a further study, many more samples should be included.

Lorentzians were placed around the excited states in the same manner described in Section 6.3, resulting in the average absorption spectrum in Figure 6.9. While it is clear that the lower number of samples has given a much more jagged and uncertain result, the general appearance of the spectrum in Figure 6.9 is still there.
Figure 6.8. Structure for the later part of the Pt1-G5 dynamic in a vacuum. The dendrimers have bent inwards, over the central chromophore.

A larger peak, in the region over 300 nm with a longer tail for shorter wavelengths. What is impossible to see, however, is the blue shift seen when adding dendrimers to the molecule, shown in the test cases in Section 6.2 and the experimental data in Figure 6.6.

Figure 6.9. Average absorption spectrum for the Pt1-G5 molecule, truncated to Pt1-G1, in vacuum made from 20 snapshots. The total absorption from the first ten excited states has been plotted. Also plotted are the contributions of just the first excited states and just the contributions from the nine others.
6.6 Pt1-G5 dynamic in solvent

Having a single molecule in vacuum is perhaps not the most realistic scenario, and for that reason a final dynamic was run. Experiments conducted on the Pt1-G5 molecule were done at an approximate molarity of 30 mM in a solution of tetrahydrofuran (THF). This molarity is equivalent to each molecule taking up a volume of about 55000 Å³, which is roughly what a cube with side 40 Å can contain. The best way to replicate the experimental conditions would be to examine a large system, containing several Pt1-G5 molecules surrounded by THF molecules. This would make it possible to see how the molecules move and orient themselves in relation to each other. Sadly, the computer time needed to accomplish this, even when using the MM3 force field, is out of reach for this project. As a compromise, one Pt1-G5 molecule was studied, placed inside a box with periodic boundary conditions and filled with THF molecules. This way, the molecule feels the presence of itself on all sides, acting as other molecules. The box needed to comfortably contain the molecule without it coming to close to the edge, and thus itself, has the dimensions 75 Å by 35 Å by 35 Å. This translates to a molarity of about 18 mM, which is lower than what has been used in experiments. This is to be expected however, since the molecules in the experiments are not contained to boxes and are not all oriented in the same way, but are free to orient themselves in more space efficient ways. This box was filled with THF molecules, each taking up a volume of about 135 Å³, which corresponds to a molarity of about 12 M. The Pt1-G5 molecule was then placed in the box, removing any overlapping THF molecules. The starting position can be seen in Figure 6.10. For this system, a dynamic of 200 ps was run, with an integration step of 1 fs and frames saved every 50 fs, giving a total of 4000 snapshots. This was done in the canonical ensemble at a temperature of 300 K.

![Figure 6.10. Starting position for the Pt1-G5 molecule in a solvent of THF molecules.](image)
The immediately obvious change from previous dynamic simulation is that there is a lot less movement. This is in part due to the solvent, which slows down larger movements, and in part due to the periodic boundary conditions, meaning there can be no major changes to the structure of the molecule, such as the one seen in Section 6.5 since that would require the molecule to bend into the adjacent box and coming too close to itself. What does happen is that the molecule stays in a conformation that is close to the one it started in, turning slightly to reorient itself due to the attraction of the dendrimers to the ones in the nearby boxes. An example of this is shown in Figure 6.11 where the dendrimers have placed themselves in a diagonal position in the box. The rotation of the phenyl rings is again seemingly random.

![Structure](image)

**Figure 6.11.** Structure for the Pt1-G5 molecule in a solvent of THF molecules from the later part of the dynamic.

To get an absorption spectrum for this Pt1-G5 molecule in this kind of environment, the OPA of a number of snapshots from the dynamic were computed. However, same as for the previous dynamic, due to constraints on time and available computer power, only 20 snapshots were used. For these, all THF molecules were removed and the Pt1-G5 molecule was truncated to Pt1-G1. For these structures, the OPA was computed, Lorentzians were placed around the excited states and an average absorption spectrum was created in the same way as in Section 6.3. The result can be seen in Figure 6.12. The spectrum once again contains the same general appearance, with a larger peak in the region over 300 nm and a tail for shorter wavelengths. However, due to the low number of snapshots used, little else can be said with certainty.
Figure 6.12. Average absorption spectrum for the Pt1-G5 molecule in THF solvent, truncated to Pt1-G1, made from 20 snapshots. The total absorption from the first ten excited states has been plotted. Also plotted are the contributions from the first excited state and the summed contributions from the nine others.
Chapter 7

Summary and conclusions

The parameters needed to describe the Pt1 chromophore in the MM3 force field have been obtained. These parameters have been shown to perform well when comparing the energies for distortions of individual bonds, angles and torsional angles, computed using MM3 and B3LYP. In addition, structure optimizations carried out with MM3 and B3LYP have have yielded very similar structures with energies within a few kcal/mol of each other. This indicates that the parameterization was a success and that the parameters can be used to describe the behaviour of the Pt1 chromophore.

Using these parameters, three dynamics of lengths up to 200 ps were run for the Pt1 chromophore, simulating its behaviour at room temperature. For each of the three dynamics, one for the Pt1 chromophore in vacuum, one for the Pt1-G5 molecule in vacuum and one for the Pt1-G5 molecule in a solvent, an average absorption spectrum was created using structures selected from the dynamic. The number of structures used was, due to constraints on the computer resources available, not high enough to give definitive answers. However, as far as the low number of sample points allowed, the obtained spectra showed a good agreement with experimental data. Further study of a larger number of samples points is needed for better results. Dynamics for larger systems, allowing for interactions between several chromophores, would also be of interest.
Bibliography


