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Modelling UV/Vis Spectroscopy using Density Functional Theory

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Abstract

UV/Vis spectroscopy is a key analytical tool to establish information about how molecules interact with light. Naturally this can provide interesting insight into how molecules can be used as dyes and catalysts for example. This work examines the results of UV/Vis spectroscopy with Density Functional Theory (DFT) to understand processes at a finer level. A key focus is the vibrational structure of UV/Vis spectra and how these can be recreated using DFT.

The systems examined are broad but tied together by the presence of planar aromatic structures, which have strong UV/Vis spectra due to being highly conjugated. They can be split into three different types of system; the first were diimide based complexes with uses in molecular machines, the second were smaller polycyclic aromatic hydrocarbons and the final type of system are gold-based complexes with central aromatic platforms.

The computed spectra were compared to experimental results to further enhance the understanding of the experimental spectra and confirm the validity of the computational approach.

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Abbreviations

CCSD Coupled Cluster Singles Doubles.

CI Configuration Interaction.

DFT Density Functional Theory.

DIB Diffuse Interstellar Band.

ECP Effective Core Potential.

HF Hartree-Fock.

HOMO Highest Occupied Molecular Orbital.

IR Infrared.

LUMO Lowest Unoccupied Molecular Orbital.

MOM Maximum Overlap Method.

MRI Magnetic Resonance Imaging.

NBO Natural Bond Order.

NDI Naphthalene Diimide.

NMR Nuclear Magnetic Resonance.

OLED Organic Light Emitting Diode.

OPLS Optimised Potential for Liquid Simulations.

PAH Polyaromatic Hydrocarbon.

PCM Polarisable Continuum Model.

PDI Perylene Diimide.

PES Potential Energy Surface.

SCF Self-Consistent Field.

TDA Tamm-Dancoff Approximation.

TDDFT Time-Dependent Density Functional Theory.

TDM Transition Dipole Moment.

XRD X-Ray Diffraction.

Chapter 1

Introduction

This chapter will cover the motivations behind the research undertaken, including a broad overview of the scientific context and will highlight links between the research themes.

Briefly, there are three main research themes in terms of chemical environments and their relevance including molecular machines, polyaromatic hydrocarbons and transition metal complexes. A common technique underlying all chapters is UV/Vis spectroscopy, it was used to investigate all of the different types of molecules, both computationally and experimentally. It will be discussed first in some depth.

1.1 UV/Vis Spectroscopy

Spectroscopy is the study of the interactions of molecules and how they interact with electromagnetic radiation, or light, and it is often the first tool in analysing the properties of molecules. Formally light is only the visible part of the electromagnetic spectrum, but here it is being used more broadly for the entire wavelength range of electromagnetic radiation. The wavelength of light determines exactly which properties of a molecule are being examined.

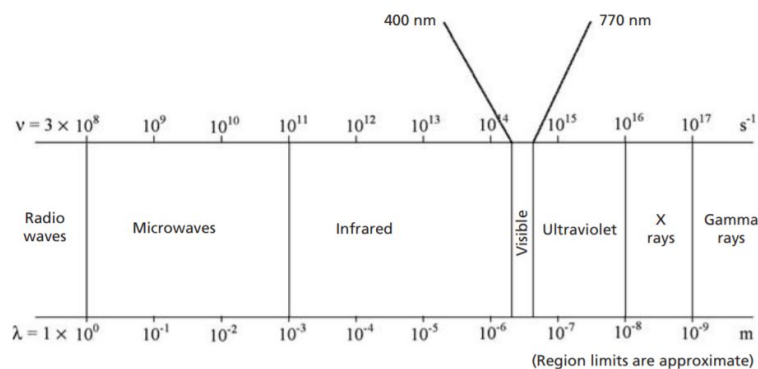


Figure 1: The complete electromagnetic spectrum, taken from D. W. Ball, Spectroscopy, 2007, 21, 1-4.¹

Figure 1¹ shows that there is a wide range of types of light that molecules can interact with. In reality, visible light makes up a tiny proportion of the electromagnetic spectrum and all types of electromagnetic radiation can be used in spectroscopy.²

For example, low energy radio waves are used in Nuclear Magnetic Resonance (NMR) spectroscopy, which gives access to details of the electronic structure of a molecule and its individual functional groups as well as a wealth of information about the chemical environment of a nucleus in a molecule, dynamics and reaction state. When it is used in medical physics, this is more commonly known as Magnetic Resonance Imaging (MRI). Infrared (IR) spectroscopy uses infrared radiation to identify molecular fragments based on the vibrations of bonds. At the high energy end of the spectrum, x-rays are used to detect photons with wavelengths in the $10^{-8} - 10^{-9}$ m portion of the electromagnetic spectrum to aid understanding of the chemical and elemental properties of an object. This technique is familiar in a medical setting where it is used to study the deficiencies of human tissues (different tissues absorb different amount of radiation). In a chemical setting, x-rays are used for x-ray photoelectron spectroscopy. These are only examples of spectroscopic and crystallography techniques that use some of

the electromagnetic spectrum outside of visible light range, but as science and spectroscopy progresses we continue to develop analytical tools with light as a driving force.

Most relevant to the work undertaken, UV/Vis spectroscopy uses ultraviolet and visible light to probe the electronic transitions of molecular systems. It is an essential experimental tool to investigate the properties of materials and molecules, including but not limited to their reactivity and colour. This is a reasonably easy and relatively inexpensive analytical technique, which provides great insight into the electronic structure of molecules. It is mainly performed in solution, although both solid state and gas-phase UV/Vis spectroscopy are also used.

UV/Vis spectroscopy requires a reasonably simple setup as shown in Figure 2, with a light source, monochromator, sample holder and detector making up the vast majority of the components. Depending on the experiment being run (absorption or emission), the final stages (i.e. detection) will have to be changed slightly, although this does not significantly complicate the measurements.

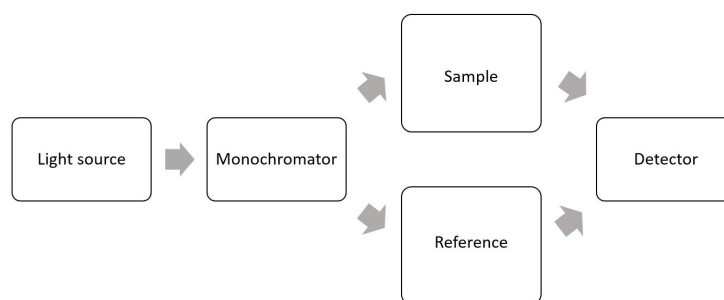


Figure 2: Schematic diagram of a UV/Vis spectrometer

Although UV/Vis spectroscopy is a tool to investigate properties like reactivity, it is directly measuring the electronic transitions of molecules. In general, the most easily accessible and measurable transition is the Highest Occupied Molecular Orbital (HOMO) $\rightarrow$ Lowest Unoccupied Molecular Orbital (LUMO) transition,

which is also usually the transition with the lowest energy.

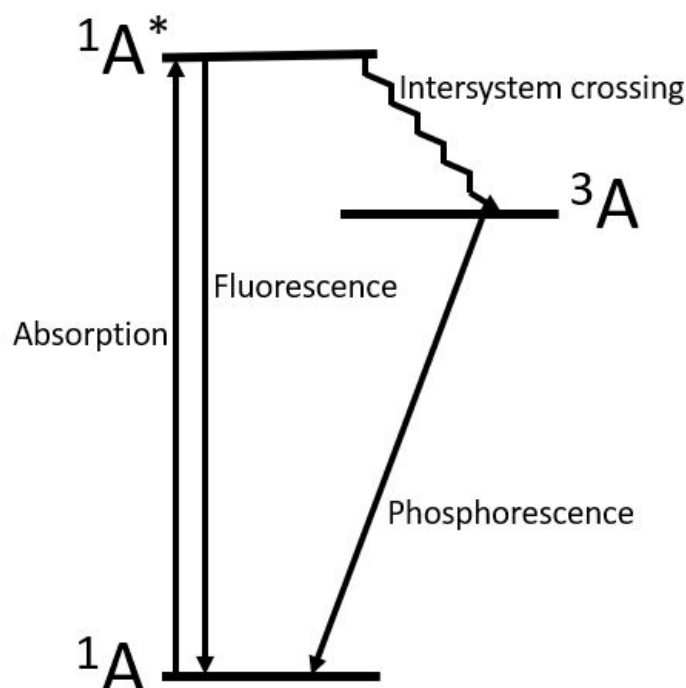


Figure 3: Jablonski diagram showing the excitation of a molecule to its singlet excited state ($1A^*$) and relaxing to the ground ($1A$) both directly from the singlet state and via a triplet state ($3A$).

While UV/Vis spectroscopy is relatively straightforward to measure, there are many complex processes that can occur within the electronic structure of a molecule following an electronic excitation. These can be captured by a Jablonski diagram. Figure 3 illustrates a Jablonski diagram showing the excitation of a molecule to its singlet excited state ($1A^*$) followed by intersystem crossing to the triplet state ($3A$) that relaxes to the ground state ($1A$) by the process known as phosphorescence.

Both absorption spectroscopy and emission spectroscopy can be performed, which give slightly different information about the molecule of interest. In absorption spectroscopy the absorption of light is measured as the molecule is excited from the ground state up into excited states to give an indication of the position of

several electronic levels relative to the ground state energy. In contrast, emission spectroscopy measures the emitted light from a previously excited molecule, so it studies the transition from an excited state to a lower energy state, usually the ground state. Emission spectroscopy is related to luminescence, and from the time scale of the emission we get an indication whether this emission is fluorescence (a transition between two states of the same symmetry) or phosphorescence (a transition between states of different symmetry). Phosphorescence has a longer timescale because it involves an intersystem crossing step, which is the slowest step in emission. Both fluorescence and phosphorescence, along with the intersystem crossing step, are represented in Figure 3.

One of the limitations of UV/Vis spectroscopy is that while all molecules have a vast number of excited states, not all of them can be accessed by this technique. This can be because the excitations are outside the energy range scanned by the spectrometer, the excitations are forbidden by selection rules so do not occur readily enough to be captured by experiment or potentially outside factors affecting the spectrum.

One of the selection rules most relevant to this work is the Laporte selection rule, which states that in a centrosymmetric environment, transitions between like atomic orbitals (s - s , p - p , d - d or f - f transitions) are forbidden. Transition metal complexes often have d - d transitions, which are formally forbidden. The Laporte rule applies to electric dipole transitions. The transition dipole moment (TDM) is a vector, its direction identifies the polarisation of the transition which determines how the chemical system interacts with an electromagnetic wave of a given polarization. The square of the magnitude of the TDM gives the strength of this interaction driven by the distribution of charge within the system. For a single charged particle, a TDM is the product of a particles charge and the off-diagonal matrix elements of the position operator. For a transition where a

charge particle changes state the TDM is defined as

$$\overrightarrow{TDM} = q \int \psi_b^*(\vec{r}) \vec{r} \psi_a(\vec{r}) d^3 \vec{r} \quad (1)$$

from $|\psi_a\rangle$ to $|\psi_b\rangle$, where q is the particle's charge, $\vec{r}$ is its position and the integral is taken over all space. For a species to be spectroscopically active, it has to have a non-zero TDM.³ This means that for a molecule with a ground singlet state, the transition from the ground state into a triplet state is spin forbidden. It will have a very small TDM and as a consequence the associated spectral band for the transition will be very weak, giving rise to the rate limiting intersystem crossing step.

Another important selection rule is the spin selection rule. The wavefunction of a single electron is the product of a space-dependent wave function and spin wave function. Spin is directional, and transitions in which direction of the spin changes are forbidden. Formally, only states with the same total spin quantum number are spin-allowed. Although these selection rules can be broken through spin-orbit or vibronic coupling, forbidden transitions will have a much lower intensity. In general, brightly coloured compounds, for example transition metal complexes, will produce good UV/Vis spectra, although some colourless compounds are also interesting to look at with UV/Vis spectroscopy.

Electronic energy levels are split further into vibrational energy levels, so it is often possible to observe vibrational structure in UV/Vis spectroscopy. vibrationally resolved spectra with well defined bands are typically seen at low temperature. Higher temperatures broaden all peaks in the spectrum and specific vibrational structure is lost in these broader bands. In vibrational spectroscopy, transitions are observed between different vibrational states. For a vibrational transition to be allowed, the symmetry of the excited state wave function must

be the same as the symmetry of the transition moment operator.

Three different classes of molecular system will be covered in the context of UV/Vis spectroscopy including molecular machines, polyaromatic hydrocarbons and transition metal complexes which are introduced in the next sections.

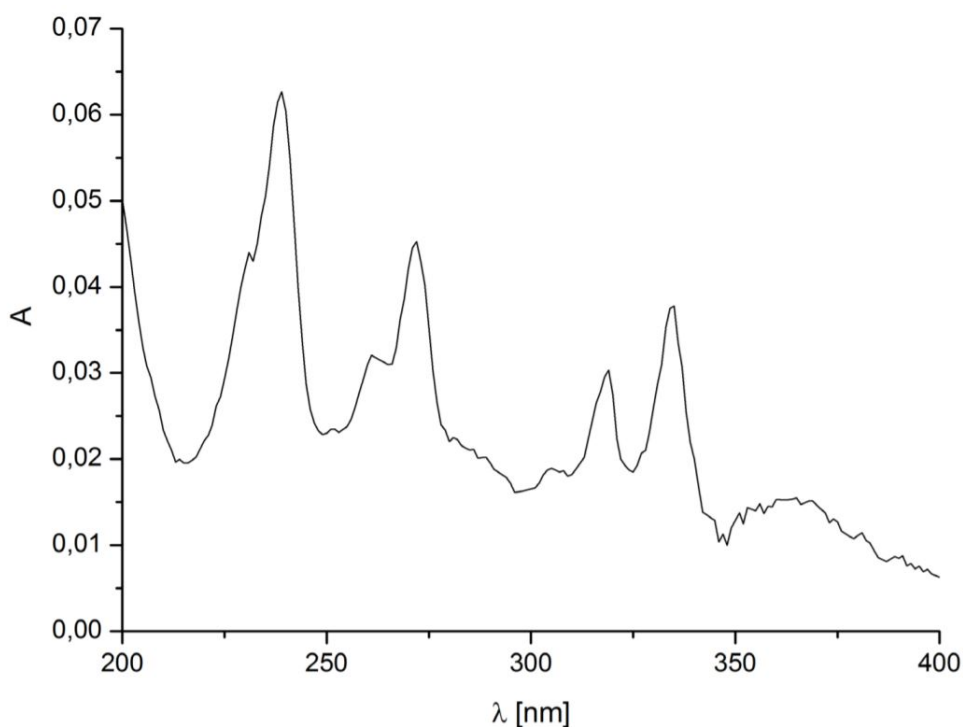


Figure 4: UV/Vis spectrum of pyrene to illustrate vibrational structure.⁴

An example of a spectrum with vibrational structure is shown in Figure 4.⁴ This example is pyrene, and it shows three distinct bands, which are split further into vibrational states. The electronic transitions are sufficiently far apart (about 50 nm) to reveal a clear distinction between electronic transitions and vibrational structure but this is not the case in all examples, which stresses the importance of being able to use computational methods as a way to identify the elements of the spectrum. Vibrational structure is most easily explained using the idea of vertical transitions, and overlap of electronic and vibrational levels.

1.2 Molecular Machines

In 2016, the Nobel Prize for Chemistry was awarded to Jean-Pierre Sauvage, Sir J. Fraser Stoddart and Bernard L. Feringa for "the design and synthesis of molecular machines".⁵ This award represents an acknowledgement from the scientific community of the up and coming area of molecular machines. Molecular machines are characterised by several subunits of a single molecule, where the fragments are held together by mechanical bonds. On the application of an external force, for example a magnetic field, the molecule can be manipulated. We find examples of molecular machines in nature quite readily, and the vast area of proteins can be seen as the study of molecular machines given that proteins are examples of natural molecular machines. The synthesis of molecular machines is a far more complex process, which has only made advances more recently.⁶

Mechanical bonds are less easy to define than other chemical bonds. Although the distinction between the two is not always clear, in general covalent chemical bonds involve the sharing of electron pairs, and ionic bonds are formed with the exchange of electrons to form charged particles. Even hydrogen bonds are reasonably easily understood on a basic level by considering the interaction of electron pairs and hydrogen atoms. Mechanical bonds however exist where two fragments are threaded together and the separation of them would force the breaking of covalent bonds. They do not necessarily involve the movement or behaviour of electrons.⁷ The example easiest to understand is a catenane, which demonstrates the idea of mechanical bonds perfectly. A catenane, shown in the schematic diagram below, is a set of two or more interlinking rings, like the Olympic rings, on a molecular level.⁸

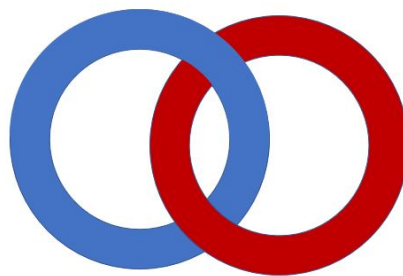


Figure 5: Schematic diagram of a catenane molecule

Strictly speaking a catenane is not a molecular machine, because it does not fulfil the machine aspect in that it does not perform a useful task by mechanical work.⁹ It does however have a clear mechanical bond, and some molecular machines are built on catenanes.¹⁰

Rotaxanes are a more adaptable example of a structure on which molecular machines are based. They are rings held on rods by stoppers¹¹ and, depending on the adjustments made, can be used as a single molecule motor or switch.

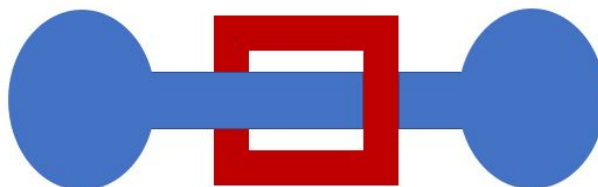


Figure 6: Schematic diagram of a rotaxane molecule

Motors and switches have particular definitions within the molecular machines field, and they do bear good resemblance to their macroscopic counterparts. Understanding how molecules stack and the stacking of aromatic molecules has strong links to DNA studies, although the importance of this is broader than that. The work here uses a handcuff style molecule to trap a stoppered prisoner molecule and to hold two perylene diimide (PDI) platforms in close proximity. This allows the stacking of this aromatic dye to be studied in a controlled way.

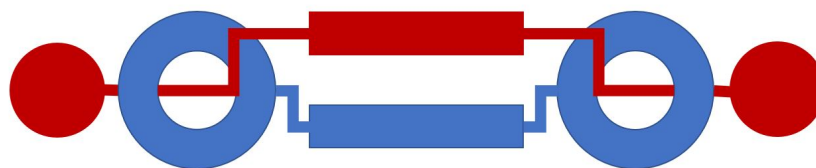


Figure 7: Schematic diagram of the perylene diimide based 'handcuff' molecule, which will be revisited in Chapter 3.

Our main focus is investigation of the UV/Vis of the platforms, and the impact that stacking of platforms has on their chemistry and electronic transitions.

1.3 Polyaromatic Hydrocarbons

Polyaromatic Hydrocarbons (PAHs) are molecules made up of several fused aromatic rings and are similar to the PDI platforms of the handcuff molecules. PAHs are of scientific interest much more broadly, specifically in astrochemical and astrophysical context. It has been suggested that there is a link between interstellar PAHs and the formation of life in the universe, and whilst this may be a little sensational, the need to more fully understand exactly this connection is clear.¹²

Formally, a PAH contains only carbon and hydrogen atoms but in some cases they are discussed more broadly to include also substituted molecules.¹³ They readily form ions, both positive by deprotonation, and negative by allowing additional electrons in the aromatic system. Despite the fact that PAHs are limited in their chemistry in the laboratory, they are surprisingly active chemically in space, and the understanding of PAH chemistry might provide insight into several astrochemical processes.

In space, PAHs are formed in the collapse of old 'dying' stars. The molecules

formed in these stars depend mainly on the C:O ratio, with PAHs being formed when the proportion of carbon is high. Usually oxygen starts off making up a significantly higher proportion and as nucleosynthesis in the core of the star occurs, the proportion of carbon increases. When the proportion of carbon is sufficiently high, carbon containing molecules, often HCN and C₂H₂ are formed and from these building blocks, PAHs are produced. They can subsequently break down into smaller PAHs and fragments in the atmosphere, reversing the chemical balance. Interestingly the clustering of PAHs to eventually make fullerenes is also observed, and fullerenes are widely investigated at the moment.¹⁴

IR spectroscopy has been previously used to identify PAHs in space, although despite them having very strong UV/Vis spectra when measured in the laboratory, they have not yet been detected this way in space. In fact, even the use of IR has been severely limited, rather than the PAHs being observed directly, the depletion of C₂H₂ starting material has instead been observed.¹⁴

Diffuse Interstellar Bands (DIBs) are a class of absorption bands which arise in the interstellar region.¹⁵ DIBs are a particular research interest for many astrophysical chemists, because they are an unsolved mystery, being heavily disputed spectral bands which are caused by absorption of the interstellar medium. In total, more than 500 bands are defined under diffuse interstellar bands ranging from near IR to near UV.¹⁶ It is clear that the understanding of PAH chemistry will help understand these diffuse bands, because although the hydrocarbons have not been positively identified as definitely being part of the DIBs, there is a vast range of PAHs that could contribute. Even if it is not a PAH directly, there has also been studies showing that fullerenes contribute to DIBs¹⁷ and fullerenes could be built from PAHs.

Both the PAH and molecular machines work involved organic molecules, with a

focus on planar aromatic systems. The inclusion of metals in the systems can significantly complicate the spectroscopy.

1.4 Transition Metal Complexes

Transition metal complexes are ubiquitous in nature and almost all commercial industries, from dyes^{18,19} to catalysts.²⁰ In a very basic description, a transition metal complex consists of a central metal atom surrounded by several ligands. The ligands are usually organic based and the number of ligands can range in general between 2 and 8. There is a loose set of rules which dictate the behaviour of complexes which partly explains the way they dominate several industries, because the properties are well understood and can be manipulated.

In catalysis, the flexible number of bonds and reversible nature of the reactions are essential properties required to speed up rates of reaction. Catalysis has always been and will continue to be a huge chemical industry, particularly with the drive for more ethical and sustainable chemical practices. Perhaps, the only catalyst the public will be familiar with is a catalytic converter in cars, and even this is an example of a transition metal based catalyst, given historically catalytic converters are platinum and palladium based.²¹ In dyes, the interaction between the molecules and light dictates the colour of the dye. In general, transition metal complexes have strong electronic transitions because of the transfer bands between metal to ligand and vice versa, although transition metal based dyes can only be used in certain contexts, because of the toxicity of heavy metals but they are still a common chemical commodity because of their effectiveness.

In this work, the transition metal complexes are being used to investigate the potential for organic light emitting diodes, so their interaction with light and lu-

minescence must be understood in depth. The luminescence of transition metal complexes is interesting because there exists a vast range of transitions that can be accessed using spectroscopic techniques. Subtle changes can result in forbidden transitions being present in the spectra, and many transition metal complexes both fluoresce and phosphoresce. This requires a good understanding of the difference between fluorescence and phosphorescence, and factors affecting the intersystem crossing.

Figure 3 illustrates the idea of intersystem crossing, and that is the primary difference between fluorescence and phosphorescence. While fluorescence is the emission from a energy level of the same symmetry to the ground state, phosphorescence is the emission from an energy level of a different symmetry. As mentioned earlier, phosphorescence has a longer timescale associated with it, because the intersystem crossing step is slow. This is because of the spin flip step is formally forbidden. This is an observable response, where fluorescence commonly lasts up to 10 ns but can be much shorter,²² phosphorescence can in some cases last years, but typically lasts in the order of seconds.

Chapter 2

Computational Methods

Computational chemistry is used extensively when examining transition metal complexes, so there is a wealth of knowledge and literature to draw on, regardless of the intended use of the complex itself. These studies can range from very small systems²³ to reasonably large ones.^{24,25}

There are several computational methods available when calculating UV/Vis spectroscopy. The balance of accuracy and computational cost is often the most important factor when choosing a method, although this balance will vary based on both the type of calculation and the size of the system. For very large systems, methods which are based on more classical models are used, although these approaches were not used in this work and therefore will not be discussed further. Quantum chemical methods can be split up into wavefunction based methods and density functional theory (DFT). Only limited wavefunction based methods will be discussed, primarily Hartree-Fock as a starting point for introducing more advanced methods.

2.1 Schrödinger Equation

The behaviour of the electrons dictates the chemical properties of molecules and all chemistry is based on the movement of electrons, including UV/Vis spectroscopy. At the beginning of the twentieth century, experimental evidence suggested that electrons were wave-like in nature. For example, electrons were found to give diffraction patterns when passed through a double slit in a similar way to light waves. Therefore, it was reasonable to assume that a wave equation could explain the behaviour of electrons. Schrödinger was the first person to write down such a wave equation, known as the Schrödinger equation.²⁶

The time-independent Schrödinger equation can be written as

$$\hat{H} |\Psi\rangle = E |\Psi\rangle \quad (2)$$

where E is the energy of the chemical system, Ψ is the wavefunction of the system, and $\hat{H}$ is the Hamiltonian operator. Here, we are assuming a non-relativistic Hamiltonian operator. A molecule has both kinetic and potential energy, therefore the Hamiltonian can be split up into kinetic and potential operators using the Born-Oppenheimer approximation.²⁷ This is the assumption that the nuclear and electronic motion can be uncoupled because of the different timescales on which they move. Solving the Schrödinger equation (2), we can generate a Potential Energy Surface (PES) where nuclear coordinates are the parameters for electronic energy. For a system of N electrons and M nuclei, the Hamiltonian looks like

$$\hat{H} = \hat{T}_n + \hat{T}_e + \hat{V}_{ne} + \hat{V}_{ee} + \hat{V}_{nn} \quad (3)$$

Where $\hat{T}_n$ and $\hat{T}_e$ are kinetic (translational) energy operators for the nuclei and electrons respectively, and $\hat{V}_{nn}$, $\hat{V}_{ne}$ and $\hat{V}_{ee}$ are the potential energy operators for

the interactions between nuclei, nuclei and electrons, and between electrons. In the Born-Oppenheimer approximation, the nuclei are fixed so $\hat{T}_n$ is zero and $\hat{V}_{nn}$ is a constant. The Hamiltonian operator can be written more explicitly as (4).

$$\hat{H} = \sum_A^M \frac{-\hbar^2}{2m_A} \nabla_A^2 + \sum_i^N \frac{-\hbar^2}{2m_e} \nabla_i^2 + \sum_i^N \sum_A^M \frac{-e^2 Z_A}{r_{iA}} + \sum_{i>j}^N \frac{e^2}{r_{ij}} + \sum_{A>B}^M \frac{e^2 Z_A Z_B}{r_{AB}} \quad (4)$$

$\hbar$ is Planck's constant, e is the charge of an electron, m_e is the mass of an electron, m_A is the mass of the nucleus, Z_A and Z_B are nuclear charges, r_{ij} is the interelectron distance, r_{iA} is the distance between the nucleus and the electron and r_{AB} is the distance between nuclei.

The interactions between charges (potential energy operators, $\hat{V}$) are some of the more complex terms, and the most problematic term is $\hat{V}_{ee}$ which is the potential energy between electrons. This term describes the repulsion between the electrons in the system and although it accounts for a reasonably small amount of the overall energy, it does need to be taken into consideration, and this is where most wavefunction methods differ. This term can be thought of in two parts; exchange and correlation. Exchange is the portion of the interaction which accounts for the Pauli Principle,²⁸ so ensures that the wavefunction is anti-symmetric. Correlation relates the position of the electrons to the repulsion, so in some ways is a more complex term to deal with. These are treated in different ways by different methods.

2.2 Wavefunction Based Methods

Wavefunction based methods involve solving the Schrödinger equation directly for electrons, but they are varied in their complexity and therefore their computa-

tional cost. It would be remiss to discuss wavefunction based methods, or indeed computational chemistry generally, without discussing Hartree-Fock (HF).^{29,30} Based on a theory by Hartree, it is the most simple computational method in its treatment of electrons and therefore is often used as an initial step, or for very qualitative results. Compared to other computational methods, particularly other wavefunction based methods, HF is computationally cheap.

In the HF method, we express the wavefunction as a product of one electron orbitals ($\chi_1(\mathbf{x}_1)$), and ensure the wavefunction is anti-symmetric so the electrons satisfy the Pauli Principle. This means that because the wavefunction is anti-symmetric, the exchange energy is treated exactly.

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \dots) = \chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2)\chi_3(\mathbf{x}_3)\dots \quad (5)$$

$$\chi_1(\mathbf{x}_1) = \phi_1(\mathbf{r}_1)\sigma(s) \quad (6)$$

where $\phi_1(\mathbf{r}_1)$ is a spatial orbital and $\sigma(s)$ is a spin orbital. In order for this to satisfy the Pauli principle, the wavefunction must be antisymmetrised which can be done by rewriting Equation (5) as the Slater determinant rather than the simple Hartree product.

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \dots) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \dots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \dots & \chi_N(\mathbf{x}_2) \\ \dots & \dots & \dots & \dots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \dots & \chi_N(\mathbf{x}_N) \end{vmatrix} \quad (7)$$

This then gives the Fock equation by reformulating the electronic Hamiltonian;

$$\hat{f}_i \chi_i = \epsilon_i \chi_i \quad (8)$$

where ϵ_i is the orbital energy and $\hat{f}$ is the Fock operator.

$$\hat{f}_i = -\frac{1}{2}\nabla_i^2 - \sum_A^M \frac{Z_A}{r_{iA}} + V_{HF}(i) \quad (9)$$

$$V_{HF}(\mathbf{i}_1) = \sum_j^N [\hat{J}_j(\mathbf{x}_i) - \hat{K}_j(\mathbf{x}_i)] \quad (10)$$

The Hartree-Fock potential V_{HF} is made up of the Coulomb operator $\hat{J}$ and the exchange operator $\hat{K}$.

$$\hat{J}_j(\mathbf{x}_1) = \int |\chi_j(\mathbf{x}_2)|^2 \frac{1}{r_{12}} d\mathbf{x}_2 \quad (11)$$

$$\hat{K}_j(\mathbf{x}_1)\chi_i(\mathbf{x}_1) = \int \chi_j^*(\mathbf{x}_2) \frac{1}{r_{12}} \chi_i(\mathbf{x}_2) d\mathbf{x}_2 \chi_j(\mathbf{x}_1) \quad (12)$$

The labels i and j can correspond to the same electron but this can produce a self-interaction energy. This is exactly cancelled out by the exchange term so is not an issue for HF calculations, but need to be allowed for in DFT.

In the HF method the electrons ‘see’ the average potential created by the other electrons and this is the fundamental assumption in HF theory. A consequence of this is that electrons of the opposite spin are too close to each other and the corresponding energy is too high. The HF energy is given from the energy of the Slater determinant.

Hartree-Fock is a Self-Consistent Field (SCF) method which is an iterative process, that involves selecting an approximate Hamiltonian, solving the Schrödinger Equation (2) to obtain a more accurate set of orbitals, and then solving the Schrödinger Equation again with these new orbitals until the results converge to the lowest energy.

HF method takes quite a simplistic approach to electron interaction, which is why in some ways it is seen as a starting point for other more complex calculations.

Although it can sound like a very poor technique, the majority of the electron interaction is the exchange portion, so this can give reasonable results. However, we do see some major problems with strongly correlated systems and HF method generally does not predict chemical properties to a good enough level of accuracy that allows us to compare to experimental results, and as such we need to look for an alternative.

These alternative wavefunction based methods include Configuration Interaction (CI) and coupled cluster methods. These methods solve the Schrödinger equation more accurately compared to HF theory by inclusion of correlation energy. Coupled cluster is a far more accurate wavefunction based method, although naturally this comes at a steeper computational cost. While HF doesn't make any attempt to calculate electron correlation and instead treats them as an average field, CCSD (Coupled Cluster Singles Doubles) makes a correction to this using the cluster operator. This relates the HF wavefunction to the exact wavefunction (within the basis set approximation, so full CI).

$$\Psi = e^T \Psi_{HF} \quad (13)$$

Where Ψ is the exact wavefunction, Ψ_{HF} is the Hartree Fock wavefunction and T is the cluster operator.

$$T = T_1 + T_2 + T_3 + \dots + T_n \quad (14)$$

T_i is an operator which generates determinants with i excitations from the reference. CCSD is restricted to single and double excitations, so $T = T_1 + T_2$. Although it is not as commonly used due to the computational expense, the addition of triple excitations leads to a high level of accuracy, which in most cases is seen as the closest calculated value to the true value from a single reference state, however it is not practical for most systems because they are too large.

2.3 Basis Functions

The initial guess for the spatial part of molecular orbitals, $\psi_i(\mathbf{r})$ is calculated by a linear combination of L basis functions η_μ

$$\psi_i(\mathbf{r}) = \sum_{\mu=1}^L c_{\mu i} \eta_\mu(\mathbf{r}) \quad (15)$$

where $c_{\mu i}$ is the expansion coefficient. This expression can be combined with the Fock equation to give

$$\sum_{\mu=1}^L c_{\mu i} \int \eta_\mu^*(\mathbf{r}) \hat{f}(\mathbf{r}) \eta_\nu^*(\mathbf{r}) d\mathbf{r} = \epsilon_i \sum_{\mu=1}^L c_{\mu i} \int \eta_\mu(\mathbf{r}) \eta_\nu^*(\mathbf{r}) d\mathbf{r} \quad (16)$$

This can also be written as

$$\mathbf{F}\mathbf{C} = \epsilon\mathbf{S}\mathbf{C} \quad (17)$$

where ϵ is a diagonal matrix of the orbital energies ϵ_i , $\mathbf{F}$ is the integral matrix on the left, $\mathbf{S}$ is the overlap matrix on the right and $\mathbf{C}$ is the matrix containing the $L \times L$ expansion coefficients. This is known as the Roothaan-Hall equation. A transformation of basis to an orthogonal basis needs to be performed to make the overlap matrix $\mathbf{S}$ become a unit matrix. Since $\mathbf{F}$ depends on its own solution (through the orbitals), the process must be done iteratively.

The choice of the functional form of the basis functions is important, and a key criterion in the efficiency of the calculations. The most accurate basis sets will be based on Slater type functions, because this corresponds to the known form of the molecular orbitals of the hydrogen atom. However the Slater type functions are harder to handle mathematically than other options, so it is more common to use Gaussian basis functions. These functions are more convenient to use math-

ematically but do not describe the form of the molecular orbitals as accurately. Therefore the most common basis sets are built using a sum of Gaussian functions. These are the ones we will discuss at length.

We often discuss the size of the basis set based on the number of functions which represent each orbital. For example a ‘double zeta’ basis set uses two functions to describe each orbital; a ‘triple zeta’ basis set uses three functions and so on. These functions can either be a single Gaussian function, or a function made up of several contracted Gaussian functions in order to get a closer fit to the actual behaviour of the orbital. Core electrons and valence electrons are often treated differently, with a greater number of basis functions used for valence orbitals. Triple zeta basis sets are usually the standard choice for most calculations, since they provide a high level of accuracy without being prohibitively expensive. We can also add additional functions, e.g. diffuse or polarisation functions.

Polarisation functions add an additional function onto each atom with one higher quantum number than the valence orbital of the atom, so adds p functions onto a hydrogen atom. They allow more flexibility to the calculation, but with increased computational cost, which is particularly important for the geometry optimization of certain molecules, such as phosphates and ammonia.

Diffuse functions allow electrons to occupy space at a larger distance from the atom, which is particularly important for highly excited electronic states and anions, because these tend to have quite diffuse molecular orbitals. Again, additional functions come at an additional computational cost.

In general, most calculations are run using an all-electron basis set, which is a basis set which describes all of the electrons explicitly. One of the most common types of basis set that are used in modern computational chemistry are the Pople

basis sets, developed by the group of John Pople.³¹ The notation of the Pople basis sets are X-YZG, where the core orbital is described by a basis function that is a contraction of X Gaussian functions. Y and Z represent the 2 valence basis functions, made up of Y and Z number of Gaussians respectively. Pople basis sets are examples of split valence basis sets. Additional functions are indicated using * for polarisation functions and + for diffuse functions. The letters d and p can also be used. One of the most popular Pople basis sets is 6-31G*, which has these a basis function made up of 6 Gaussians to describe the core electrons, and 2 basis functions made up of 3 and 1 Gaussians to describe the valence orbitals. It has additional polarisation functions on heavy atoms. The other most common all-electron basis sets are the Dunning basis sets,³² which have a different notation. They are in general named cc-pVXZ where X is the number of functions. The addition of ‘aug’ to the start of the basis set name indicates an augmented basis set. The Dunning basis sets are examples of correlation consistent basis sets, which is what the ‘cc’ in the name stands for.

In some ways all-electron basis sets are a natural choice for all calculations, but there are two problems with using them for certain systems, including transition metal complexes. The first is simply the computational cost, atoms like transition metals are big enough that they can significantly increase the cost of the calculation in themselves, but also complexes tend to be reasonably large in general. This means that to get a meaningful answer we may have to wait weeks. A more scientifically relevant although potentially less impactful issue with all-electron basis sets is that they do not take relativistic effects into account. Obviously this will be more or less relevant depending on the complex, and more specifically the metal, being studied but nevertheless is something to consider.

An alternative to all-electron basis sets is basis sets with effective core potentials (ECPs). In the ECP basis set, the innermost electrons are replaced by a potential

that models the effect of these electrons on the valence electrons. This reduces the cost of the calculation since few basis functions are required, but also more accurately describes relativistic effects because the potentials are based on either experimental measurements or the Dirac equation.

Some examples of these basis sets that will be discussed later include LANL2DZ³³ and SRSC. LANL2DZ³³ is a double zeta basis with an ECP, developed by the Los Alamos National Laboratory. It has a large core ECP and therefore is a relatively small basis set. It was developed in 1985 and is used extensively. SRSC stands for Stuttgart Relative Small Core, and is a small core ECP. This means that it is a comparatively large basis set because it only has a small amount of electrons confined to the ‘core’ part of the ECP.

2.4 Density Functional Theory

In contrast to the higher cost of methods such as CCSD, Density Functional Theory (DFT) is a very popular computational method because it provides a compromise between high computational cost and scientific accuracy. This is because in place of the wavefunction in the Schrödinger equation, the electron density of the system is used. This in principle reduces the calculation from having $3N$ variables in the wavefunction of a system, where N is the number of electrons, to only 3, because the density of the same system is a function of only 3 variables. This represents a vast reduction in complexity which can provide a foundation for reducing the computational cost of the method.³⁴ The electron density is given by

$$\rho(\mathbf{r}) = \sum_i^N |\psi_i(\mathbf{r})|^2 \quad (18)$$

where $\rho(\mathbf{r})$ is the electron density, $\psi_i(\mathbf{r})$ is the molecular orbitals. The integral of the electron density gives the number of electrons in the system. An additional advantage of DFT is that the electron density is an observable property.

The use of DFT in chemistry is primarily based on the work of Hohenberg and Kohn,³⁵ which proved that the electron density of a system can be related to the Hamiltonian, and from there can be used to find the energy of the system. DFT as a concept was already in use in other fields, such as solid state physics, prior to the theorems put forward by Hohenberg and Kohn³⁵ but its initial use in chemistry was limited by the large errors observed.

In 1964, Hohenberg and Kohn proved two essential theorems which underpin the widespread use of DFT in chemistry today. The first is an existence theorem, which proves by reductio ad absurdum that the external potential is a unique functional of the electron density. This means that each electron density will solve the Schrödinger equation uniquely and therefore produce one answer for the energy. This forms the mathematical basis to why we are able to use DFT in computational chemistry. Unfortunately it does not provide an answer as to how we are able to use it. Hohenberg-Kohn's second theorem proves that the density follows a variational principle, so the electron density that minimises the energy is the exact electron density.³⁵ This underpins the use of DFT because it gives us a way to iteratively calculate and improve the energy calculation, in an analogous way to the SCF process in HF theory.

2.4.1 Kohn-Sham DFT

Most DFT calculations used in computational chemistry are Kohn-Sham DFT.³⁶ This is an approach that makes DFT useable for more complex systems by ap-

proximating to the real system to non-interacting electrons, with each electron experiencing an external potential. This gives us a way to calculate the electron density, because while the work of Hohenberg and Kohn prove its theoretical use for molecules, they do not offer much insight into a practical solution. The aim of Kohn-Sham DFT is to find an external potential where the electron density of the reference system is equivalent to the electron density of the real system.

In 1965, Kohn and Sham extended the fundamental theorems of Hohenburg and Kohn from HF to DFT, in order to make it workable for computational chemistry. They derived the Kohn Sham equations, based on the variational principle of DFT and they show that the electron density of the real system (ρ_s) and reference system (ρ_0) are equal and the electron density can be expressed as

$$\rho_0 = \rho_s = \sum_i^N |\psi_i^{KS}(1)|^2 \quad (19)$$

where ψ_i^{KS} are the Kohn Sham orbitals and N is the number of occupied orbitals, which is the number of electrons for closed shell systems. KS-DFT attempts to minimise the energy of the individual orbitals and the Kohn Sham energy is exact in theory, assuming an exact exchange correlation functional.

2.4.2 Exchange Correlation Functionals

A key decision when using DFT is selecting an appropriate exchange-correlation (XC) functional. As mentioned earlier, the exchange-correlation functional describes how the inter-electron interaction is treated. These tend to be based on parameters fitted using experimental data, so can have more or less relevance to the system being studied depending on the similarity of the system studied and the systems used to build the functional. Given that HF treats exchange exactly, some functionals build some HF theory into them so that the exchange is

more accurately represented. These are known as hybrid functionals, and make up some of the more common functionals in use today. A general expression for hybrid functionals is given in Equation (20) below.

$$E_{xc}^{hybrid}[\rho] = E_c^{DFT}[\rho] + (1 - a)E_x^{DFT}[\rho] + aE_x^{HF}[\rho] \quad (20)$$

B97-1 is a hybrid functional, which works well for geometry optimizations and energy calculations, and has been included in some TDDFT calculations, with mixed success. The first version of this functional was developed by Becke in 1997,³⁷ then re-optimised in 1998.³⁸ This particular functional was developed using transition metal complexes, which indicates it is a sensible choice for work with complexes.

Pure DFT functionals fail in some specific contexts, one of which is predicting charge transfer processes when the electrons are excited from an occupied orbital to an unoccupied orbital that is spatially separated from the occupied orbital. The origin of this failure is the approximate exchange used in functionals, and these transitions require a high proportion of HF exchange to be described accurately. CAM-B3LYP³⁹ is a long-range corrected functional, based on the popular B3LYP⁴⁰ functional. B3LYP is expressed as

$$E_{xc}^{B3LYP} = (1 - a)E_x^{LSDA} + aE_x^{HF} + b\Delta E_x^B + (1 - c)E_c^{LSDA} + cE_c^{LYP} \quad (21)$$

where a , b and c are free parameters optimised to 0.20, 0.72 and 0.81.

Despite B3LYP^{41,42} being a hybrid functional with 20% HF, this is insufficient to accurately describe charge transfer behaviour so the long range corrected functional should describe charge transfer transitions better than B3LYP alone.

CAM-B3LYP corrects for long range behaviour by preserving the functional (in this case B3LYP) at short range, but increasing the HF exchange at long range. It combines the two behaviours at medium range. Functionals which correct for this behaviour in this way are known as ‘Coulomb-attenuated’ functionals, hence the prefix CAM or Coulomb attenuated method. The partitioning of this behaviour is described with Equation (22).

$$\frac{1}{r_{12}} = \frac{1 - [\alpha + \beta \text{erf}(\mu r_{12})]}{r_{12}} + \frac{\alpha + \beta \text{erf}(\mu r_{12})}{r_{12}} \quad (22)$$

where erf is the error function, the first term is a short range term and the second term is the long range correction term. α controls the HF exchange contribution across the whole range and β controls the DFT counterpart. The parameter μ controls the mixing of these terms at medium separation. These parameters were evaluated by comparing to experimental values and the optimum values were found to use $\alpha = 0.19$, $\alpha + \beta = 0.65$ and $\mu = 0.33$.

2.4.3 DFT-D

Dispersion interactions aren’t usually accounted for in DFT calculations, but can be a significant factor for many systems. Proteins and other biological systems, some metal complexes and rare gas dimers are all examples where dispersion interactions are important for their reactivity or stability. Dispersion interactions, also known as London dispersion forces, are long range attractive forces between molecules or atoms that are not chemically bonded. They occur because of instantaneous dipoles, which in turn induce dipoles on the other system. They are a subset of van der Waals interactions, which include interactions between permanent multipoles. In 1930, London showed that the dispersion interaction energy

between two particles (A and B) can be approximated by

$$E_{disp} = -\frac{3}{2} \frac{I_A I_B}{I_A + I_B} \frac{\alpha_A \alpha_B}{R^6} \quad (23)$$

where R is the intermolecular distance, α_A and α_B are the dipole polarizabilities and I_A and I_B are the ionization potentials. Equation (23) is actually just the leading term in London's expansion, but it is this term that is most significant.⁴³

DFT-D, or density functional theory with dispersion, is a semi-empirical correction to DFT, which involves the separate calculation of dispersion interactions in the system and adding this correction to the calculated DFT energies. Although it had been used in select cases previously, Grimme systematically employed and tested this as a method in 2006 and it was at this point that he referred to it as DFT-D.⁴⁴ The total energy of a system with DFT-D is the sum of the total energy computed with DFT and the dispersion energy correction

$$E_{DFT-D} = E_{DFT} + E_{disp} \quad (24)$$

where E_{disp} is given by

$$E_{disp} = -s_6 \sum_{i=1}^{N_{at}} \sum_{j=i+1}^{N_{at}} \frac{C_6^{ij}}{R_{ij}^6} f_{dmp}(R_{ij}) \quad (25)$$

where N_{at} is the number of atoms in the system, C_6^{ij} is the dispersion coefficient for each atom pair ij , s_6 is a scaling factor that depends on the functional used for the DFT calculation and R_{ij} is the interatomic distance. To prevent singularities at very low R , a damping function (f_{dmp}) is used. The original proposed damping function took the form

$$f_{dmp}(R_{ij}) = \frac{1}{1 + e^{-d(R_{ij}/R_r - 1)}} \quad (26)$$

where R_r is the sum of the atomic van der Waals radii.

Since this initial work, this correction has been improved following work by Chai and Head-Gordon on their dispersion-corrected functional ω B97X-D.⁴⁵ Some of the improvements implemented in this functional were subsequently adopted by Grimme. This improvement removes the global scaling factor which depends on the functional (s_6) and add both the next term in the dispersion series (with a $\frac{1}{R^8}$ dependence) and the option for three body interactions. This improvement is known as DFT-D3.⁴⁶ This means that the E_{disp} can now be expressed as

$$E_{disp} = E^{(2)} + E^{(3)} \quad (27)$$

where $E^{(2)}$ is the two-body interaction, similar to the previous DFT-D equation (Equation (25)) and $E^{(3)}$ is the optional three-body interaction.

A major difficulty with DFT-D methods is that the empirical correction is determined before the DFT calculation, and therefore it makes little difference what chemical environment a particular atom is in, so the use of it outside of the training set must be considered. Adjustment of the dispersion parameters according to the chemical environment is crucial for valid dispersion corrected calculations and while DFT-D3 makes some effort to correct for this, it is still an issue and errors reported for dispersion dominated interactions can be from 0.1 to 0.9 kcal/mol.

2.4.4 Time-Dependent DFT

Within DFT, electronic excitations are usually calculated using linear response time dependent DFT, which determines the linear time-dependent response of the time-independent ground-state electron density to an external electric field.

Runge-Gross Theorem

Like with the discussion of time-independent DFT earlier in the chapter, TDDFT is most easily understood if we first consider the fundamental theory behind it. Although there was some time dependent work published pre 1984, it was in this year that Gross and Runge decided to emulate the work of Hohenburg, Kohn and Sham in a time dependent system, which lead to the Runge-Gross theorem.⁴⁷ Much like Hohenburg and Kohn's work, it is primarily an existence theorem. It proves the time dependent electron density can be used in place of the wavefunction and there is a one to one mapping between the time-dependent external potential and its time-dependent density. Much like the Hohenberg-Kohn theorems, this does not present a workable method for TDDFT.

Casida Equations

The formalism that is most widely used is linear response TDDFT, as mentioned above, and an outline of this method is presented here. Linear response TDDFT can be used if the external perturbation does not completely destroy the ground state structure of the system, so that the variation of the system will depend only on the ground state wavefunction.⁴⁸

Casida presented a formalism of linear response TDDFT which is implemented in many wavefunction codes today. Essentially the exact excitation energies are given by extremes of the density-density response, which diverges if the system is perturbed at an exact frequency, matching an eigenmode of the system. The Casida equations take the form;

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \Omega \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} \quad (28)$$

where matrix elements A and B are defined as

$$A_{ia\sigma,i'a'\sigma'}(\Omega) = \delta_{ii'}\delta_{aa'}\omega_{a'i'\sigma'} + K_{ia\sigma,i'a'\sigma'}(\Omega) \quad (29)$$

$$B_{ia\sigma,i'a'\sigma'}(\Omega) = K_{ia\sigma,i'a'\sigma'}(\Omega) \quad (30)$$

and in principle equation (28) gives exact Ω_n assuming exact Kohn-Sham ground state and frequency XC kernel are used to solve the equation, and since this equation depends on the frequencies based on the XC kernel, this must be done by an iterative process. In practice, some approximations must be done for all of these requirements.

A further approximation is the Tamm-Dancoff Approximation (TDA)⁴⁹ which reduces the computational time and usually gives reasonable excitation energies, although the validity of the approximation has been discussed in some cases. TDA corresponds to where B (Equation (32)) is assumed to be zero.

However the alternative form of the Casida equation is computationally simpler and is often therefore used. We start from

$$\mathbf{CZ} = \Omega^2 \mathbf{Z} \quad (31)$$

where, assuming that the Kohn-Sham orbitals are real, we can see

$$\mathbf{C} = (\mathbf{A} - \mathbf{B})^{1/2}(\mathbf{A} + \mathbf{B})(\mathbf{A} - \mathbf{B})^{1/2} \quad (32)$$

$$\mathbf{Z} = (\mathbf{A} - \mathbf{B})^{1/2}(\mathbf{X} - \mathbf{Y}) \quad (33)$$

and therefore

$$\sum_{i'a'\sigma'} [\delta_{ii'}\delta_{aa'}\delta_{\sigma\sigma'}\omega_{a'i'\sigma'}^2 + 2\sqrt{\omega_{ai\sigma}\omega_{a'i'\sigma'}}] Z_{i'a'\sigma'} = \Omega^2 Z_{ia\sigma} \quad (34)$$

This version of the equation (Equation (34)) is the least computationally demanding and therefore the one most used in most codes. Assuming the orbitals are real, an expression for the oscillator strengths can also be derived, which is an essential .

$$f_n = \frac{2}{3} \sum_{i=1}^3 |x_i^T (\mathbf{A} - \mathbf{B})^{1/2} Z_n|^2 \quad (35)$$

2.4.5 Maximum Overlap Method

As discussed above, TDDFT uses the ground state orbitals in an electric field to calculate excited state properties. While these methods are incredibly useful and flexible, the orbitals are not optimised to fully describe the excited state of interest.

The Maximum Overlap Method (MOM) is an algorithm which finds the solution to excited state problems using the overlap of wavefunctions.⁵⁰ Rather than optimising to the lowest energy using the aufbau principle (which would remove the excited state aspect), it instead preserves the overlap of successive solutions and finds the nearest minimum energy wavefunction that has the orbital occupancies that correspond to a desired excited state. The solution can be treated in the same way to a ground state calculation, which again offers a saving in computational cost, particularly in terms of the calculation of derivatives. The use of MOM does require an accurate initial set of molecular orbitals and also involves preliminary work to identify the orbitals and therefore excited states in question, but it still offers a cost cutting alternative to TDDFT. If the previously calculated virtual orbitals are low quality then the calculation may collapse to a lower energy state than the one desired.

The MOM has some very specific benefits and uses compared to linear response TDDFT. TDDFT with standard hybrid exchange-correlation functionals is inaccurate for charge-transfer states and Rydberg transitions, and the flexibility of MOM allows specific high energy states to be targeted. In terms of computational cost, MOM is the same as the ground-state method and memory requirements do not scale with number of states. A limitation of MOM is that states with multi-reference characteristics will not be well characterised with MOM because it is a single determinant method.

2.5 Solvent Models

In general, computational spectra are calculated in the gas phase, and ideally compared to gas phase data. However, there are some cases where gas phase data is inappropriate or unavailable and the inclusion of a solvent can make a significant difference in the spectra and it is therefore useful to include it in some way. Broadly there are two types of solvent model; explicit models and implicit models.

Explicit solvent models are relatively easy to explain but difficult to use. Like the name implies, they explicitly include all solvent molecules that are being modelled. This can be at an equal or somewhat lower level of theory than the studied system itself but given that enough solvent molecules need to be included to act in a bulk way, this vastly increases the cost of calculation and is therefore unviable in lots of cases. There are specific examples where an explicit model will be the most appropriate option, for example if interactions with solvent molecules play a part in the reactivity or studied properties.

An alternative is an implicit model. Rather than including each solvent molecule

individually, the solvent is modelled in a bulk way. This decreases the cost of solvent inclusion massively and makes it a more useful tool. An example of an implicit model is the Polarizable Continuum Model (PCM).⁵¹ One of the first developed implicit models use a spherical cavity for the molecule which is polarised by the dipole moment of the molecule, and is known as the Kirkwood-Onsager model.⁵² This model depends on the cavity radius, determined to a degree by the size of the molecule, and the solvent's dielectric constant. While this represented a real step towards reality in solvent models, it obviously has its limitations particularly when the molecule is significantly non-spherical.⁵³

PCM offers a solution to this by instead constructing a cavity based on atom centred spheres. This also improves on the Kirkwood-Onsager model by using the exact electron density of the solute rather than a multipole expansion.

Sometimes a combination of both implicit and explicit solvent models will be used. This is analogous to a QM/MM approach and a particularly obvious example of this is in proteins where the solvent molecules make hydrogen bonds (or other significant specific interactions) with the binding site but the whole protein needs to feel the effect of a bulk solvent.

2.6 Computing IR Spectra

Before considering both electronic and vibrational transitions as a combination, it is useful to establish a fundamental foundation of vibrational spectra individually and how these are calculated computationally. Infrared (IR) spectroscopy was discussed briefly in the introduction but it is a useful and flexible analytical tool to identify and understand structures. From a computational chemist's perspective, the use of the experiment and the computational method go hand in hand and therefore the importance of a robust method for calculating IR spectroscopy

is also important.

Basic vibrational information can be found very easily, using the quantum harmonic oscillator model, which is an extension of the classical harmonic oscillator model. The classical harmonic oscillator describes how kinetic and potential energy are converted as the system vibrates and the total energy of the system stays constant. The same principle can be used for molecules because the potential energy curve can be approximated to a harmonic potential close to the stationary points which indicate a stable structure, and the bonds can be approximated as springs.

The harmonic oscillator is easiest to understand by considering the behaviour of a diatomic molecule. We know that a diatomic molecule has the lowest energy at its optimum bond length, or stationary point. If the two atoms in the molecule are forced closer together then the energy increases sharply and the atoms naturally repel each other back to its lowest energy state. If the atoms are pulled further apart, the energy also increases up until a limit when the two atoms will dissociate. The mathematical basis for this model is, in concise terms, the simplification of the Taylor series expansion of the full vibrational potential energy curve.

$$V(r) = V(r_0) + \left. \frac{dV(r)}{dr} \right|_{r_0} (r - r_0) + \frac{1}{2!} \left. \frac{d^2V(r)}{dr^2} \right|_{r_0} (r - r_0)^2 + \dots + \frac{1}{n!} \left. \frac{d^n V(r)}{dr^n} \right|_{r_0} (r - r_0)^n \quad (36)$$

The harmonic approximation reduces this expression to Equation (37) below;

$$V(r) = V(r_0) + \left. \frac{dV(r)}{dr} \right|_{r_0} (r - r_0) + \frac{1}{2!} \left. \frac{d^2V(r)}{dr^2} \right|_{r_0} (r - r_0)^2 \quad (37)$$

When we are at an equilibrium structure, $V(r_0)$ is constant and $\left. \frac{d^2V(r)}{dr^2} \right|_{r_0}$ is equal to zero. Therefore, the potential energy curve becomes

$$\frac{1}{2!} \left. \frac{d^2V(r)}{dr^2} \right|_{r_0} (r - r_0)^2 \quad (38)$$

The energy contact $V(r_0)$ is zero and the displacement $r = r - r_0$ so we get

$$V(r) = \frac{1}{2}kr^2 \quad (39)$$

where $k = \frac{d^2V(r)}{dr^2}$.

Following the evaluation of the harmonic potential, the nuclear Schrödinger equation can be solved with the Born-Oppenheimer approximation by

$$\left[-\frac{1}{2\mu} \frac{\partial^2}{\partial r^2} + \frac{1}{2}kr^2 \right] \psi(r) = E\psi(r) \quad (40)$$

For polyatomic molecules, a multi-dimensional analogue of Equation (40) is used;

$$\left[-\sum_i^{3N} \frac{1}{2m_i} \frac{\partial^2}{\partial r_i^2} + \frac{1}{2}(r - r_{eq})\mathbf{H}(r - r_{eq}) \right] \psi(r) = E\psi(r) \quad (41)$$

where r is the matrix of atomic coordinates, r_{eq} is the coordinates of the equilibrium structure and $\mathbf{H}$ is the Hessian matrix. Equation (40) can be solved by first mass-weighting the Hessian and transforming this mass-weighted Hessian through diagonalisation. This gives a matrix which describes the molecular vibrations, or normal modes, of the system and a diagonal matrix of the square root of the force constant corresponding to each normal mode.

Given that vibrational frequencies are often overestimated by computational methods in a reasonably uniform way, it is common to scale these harmonic modes. This both accounts for the neglect of anharmonicity in the calculation of the vibrational modes and the errors in the method used to calculate the frequencies. Scaling factors have been determined for a variety of computational methods based on comparison to experimental results, and the scaling factor for a B3LYP calculation with a moderate sized basis set (6-31G(d)) is approximately 0.96.⁵⁴ Scaling in this way gives results which fit more closely to experiment.

2.7 Vibrationally Resolved UV/Vis Spectra

A major focus of this work has been the calculation of vibrationally resolved UV/Vis spectra.⁵⁵ Experimentally vibrational structure is more commonly observed at low temperature. In order to calculate vibrationally resolved spectra, there needs to be some understanding of the fundamental scientific concepts which underpin the transitions. In a very basic description, electronic energy levels can be split further into vibrational energy levels and the overlap of these dictates the vibrational structure of the spectra.

2.7.1 Franck-Condon Principle

The Franck-Condon Principle is a rule which uses the Born-Oppenheimer approximation to rationalise the strengths of vibronic transitions. It states that the nuclear configuration does not change when an electronic transition occurs, so they are vertical transitions. The excited molecule then relaxes by vibration.^{56,57}

The relative intensities of vibronic transitions can be calculated using the prob-

ability of a vibrational transition and the overlap of the wavefunctions by

$$P_{i \rightarrow f} = |\langle \psi_{final}^* | \boldsymbol{\mu} | \psi_{initial} \rangle|^2 = \left| \int \psi_{final}^* \boldsymbol{\mu} \psi_{initial} d\tau \right|^2 \quad (42)$$

where $\boldsymbol{\mu}$ is the transition dipole operator.

Using the Born-Oppenheimer approximation, the total wavefunction is therefore

$$\psi_{total}^*(Q, q) = |\psi_{nuc}(Q)\rangle |\psi_{el}(Q; q)\rangle \quad (43)$$

From above, the electronic and nuclear components can be separated to Equation (44)

$$\begin{aligned} \langle \psi_{total,f}^* | \boldsymbol{\mu} | \psi_{total,i} \rangle &= \langle \psi_{nuc,f}^* | \langle \psi_{el,f}^* | \boldsymbol{\mu} | \psi_{el,i} \rangle | \psi_{nuc,i} \rangle \\ &= \langle \psi_{nuc,f}^* | \psi_{nuc,i} \rangle \langle \psi_{el,f}^* | \boldsymbol{\mu} | \psi_{el,i} \rangle \end{aligned} \quad (44)$$

Given that $\langle \psi_{nuc,f}^* | \psi_{nuc,i} \rangle$ is the nuclear overlap, if this is zero then the transition will not be observed.

This allows the calculation of intensities, analogous to the absorbance in experimental spectra. The Franck-Condon Principle relies on the Condon approximation, which assumes that the electronic transition occurs at a time scale short enough to be calculated at a fixed nuclear position. Calculation of the Franck-Condon factors has been attempted in several ways, which broadly can be split into two groups; one set involves storing the overlap integrals in a two-dimensional array⁵⁸ and the other is based on the binary state tree method.⁵⁹

The code FCclasses, developed by Fabrizio Santoro in Pisa,⁶⁰ was used to calculate vibrationally resolved spectra by incorporating Franck-Condon effects, using

the binary state tree method developed by Gruner and Brumer⁵⁹ to calculate Franck-Condon factors. FCclasses is an example of a type of code which uses the Franck-Condon principle to calculate overlaps between vibrational levels in two different energy states.⁶¹ It uses the vibrations of both energy states along with the energy difference between the two. FCclasses requires a very specific step of inputs and information - 4 input files need to be supplied, one of which is an input file which details the parameters for the calculation, two are vector inputs which detail the vibrational information of both the ground and excited state which includes the geometrical coordinates, normal modes in cartesian coordinates and the frequencies. The final information required is the transition dipole information, which for a Franck-Condon calculation is the transition dipole moment at the ground state geometry, the transition dipole moment at the excited state geometry and the transition dipole derivatives.

2.7.2 Methodology and Vibrationally Resolved Spectra in Practice

While the fundamental concepts of the work have been discussed, the actual implementation of the FCclasses code in combination with other computational codes, in this case Q-CHEM, can be broken down into six basic steps which will be briefly outlined in this subsection.

1. Geometry optimization

As with many computational jobs, some form of optimization or equilibration of the system needs to be done. This is the process of finding stationary points, in this case minima, by an iterative process. This is an essential part of the process when it comes to vibrationally resolved spectra even more than non-resolved spectra because frequency calculations need to be performed at a stationary point.

2. TDDFT calculation

Time dependent density functional theory (TDDFT) has been discussed as a way to calculate UV/Vis spectra without vibrational structure. This is the first step of the spectrum building. This gives a stick spectrum of bands which is the skeleton of the spectrum itself, including both the energy and the oscillator strength of the transitions. It also details to which excited states each band corresponds. This is important information when it comes to selecting appropriate excited states for the excited state calculations.

3. Ground state frequency calculations

This is the frequency calculations of the ground state structure, comparable to an IR calculation. The only major difficulty with this step can be imaginary frequencies, which indicates a saddle point rather than a stationary point or minimum. Chemically, a saddle point represents a transition state rather than a stable state of the molecule. If an imaginary frequency is found, the coordinates are slightly adjusted in the direction of the frequency and the structure re-optimised. This is all run in Q-Chem, using an adapted code so the frequencies and dipole moments, along with other variables, are printed at the bottom of the file to read into the FCclasses program.

4. Excited state frequency calculations

The excited state frequency calculations are very similar to the ground state calculations in lots of ways. First the excited state geometry has to be optimised, either using MOM (Maximum Overlap Method) or TDDFT, depending on the system. In general, the excited state geometry is very close to the ground state, and certainly given that we assume the transitions are vertical, as discussed, we expect the allowed transitions to be very close in geometry.

The frequency calculation for the excited state is then performed, much the same as the ground state calculation. Again, there is a risk of imaginary frequencies, in which case the excited state is simply re-optimised.

5. Franck Condon calculations

FCclasses was used to calculate Franck-Condon effects, and it directly prints an output file ready to plot. Q-Chem was adapted to print a readable file at the end of its output, which aided the preparation of input files. Certain parameters can be chosen in the calculation, as discussed above. There is also an inbuilt temperature control in FCclasses which primarily determines the broadening of the bands.

6. Plotting a spectrum

FCclasses prints a ready to plot output file so the plotting of the spectrum itself is a reasonably trivial process.

Chapter 3

Characterisation of Rylene Diimides using ‘Handcuff’ Molecules

3.1 Background

As described in the introduction, molecular machines are a widely discussed and active area of research. Their potential uses are vast and they are generally heralded in popular science as a lifesaver for electronics⁶² and drug delivery.⁶³ In the systems studied here, mechanical (rather than covalent) bonds have been used to control the aggregation of dye molecules. As a result, controlled subunits of dyes have UV/Vis spectra that warrant investigation by computational methods.

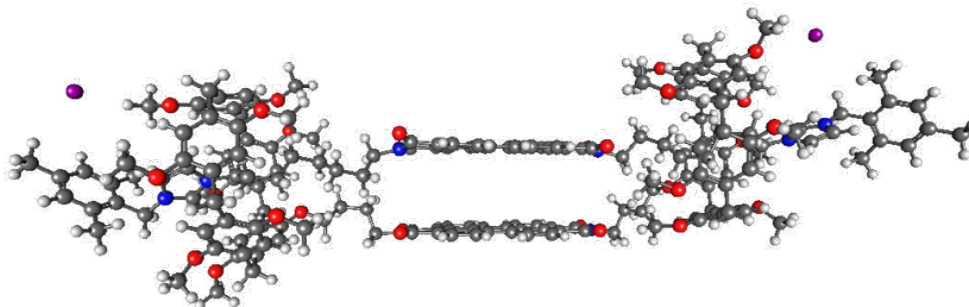
Rylene diimides are an important family of molecules that are used in dyes because of their strong visible absorption and high stability. They have also been used as organic semiconductors.⁶⁴ Their primarily planar structure aids stacking, although the control of the aggregation can make them challenging to study. It is also possible to use mechanical bonds to lock two platforms into place parallel to one another, and the resulting UV/Vis spectra will be a combination of both

platforms and their interactions.

Previous investigations into the synthesis of discrete dimers has previously focussed on covalent coupling at the imide position, and this has been performed for perylene diimides^{65–67} (PDIs) and less commonly for naphthalene diimides^{68–71} (NDIs) and terrylene diimides.⁷² However this leads to quite rigid structures with restricted positions and orientations. Other alternatives are hydrogen-bonded systems and metal coordination, which allow for more flexibility in the dimer geometry.



(a) Schematic of PDI based handcuff dimer molecule.



(b) Atomic structure of PDI based handcuff dimer molecule.

Figure 8: Comparison of schematic and atomic structure of PDI dimer molecule to clearly show the way the platforms are locked into the dimer geometry.

Figure 8 illustrates how the PDI fragments are held in place with mechanical bonds and compares the schematic representation used in the introduction to a more accurate atomic structure representation of the molecule. In Figure 8b, the PDI platforms can be identified in the centre between the large 'handcuff' like rings. The iodine counterions which counteract the handcuffs structures which

have a charge are also evident.

The synthesis of these dimer molecules was performed by the group of Prof. Neil Champness⁷³ and involves high temperature and reaction under dinitrogen. The full synthesis is shown below.

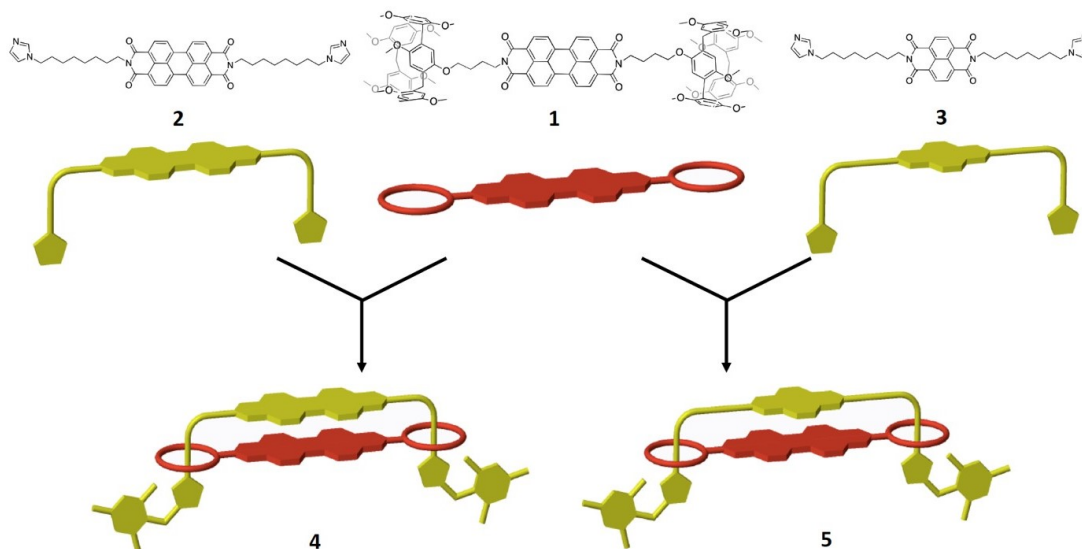


Figure 9: PDI (**1,2**) or NDI (**3**), containing components that are used to synthesise handcuff rotaxanes. Note the simple design of each component, either a bis-pillar[5]arene or bis-imidazole functionalized aromatic core. Handcuff formation is readily achieved through the formation of pseudo-rotaxanes between imidazole and pillar[5]arene moieties followed by stoppering through reaction of the imidazole groups and benzyl-iodides.

Reaction of the bis-pillar[5]arene, **1**, with either bis-imidazole functionalized species, **2** or **3**, gives rise to pseudo-rotaxanes in which each imidazole group sits within a pillar[5]arene host. Subsequent reaction with a bulky aryl iodide, 2-(iodomethyl)-1,3,5-trimethylbenzene, at -15°C leads to alkylation of the available imidazole nitrogen and stoppering of the rotaxane to form a handcuff structure. Whereas combination of **1** with the PDI-containing species **2** leads to the formation of a PDI-PDI dimer, **4**, reaction of **1** with the NDI-containing rod **3** affords an NDI-PDI handcuff dimer, **5**. Formation of the handcuff structure is confirmed through a strong upfield shift of the ^1H NMR for both protons associated with the imida-

zole and the alkyl chain linking the imidazole to the PDI/NDI core. Such shifts are consistent with the formation of a rotaxanes between the pillar[5]arene and the imidazole arms.

Following the synthesis, the systems were characterised with a range of spectroscopic techniques, including EPR and UV/Vis spectroscopy. Alongside this, molecular dynamics simulations were performed which confirmed the geometry and behaviour of the dimer complexes. These were performed using the OPLS force field, optimised for liquid simulations. Further details of this simulation are given in the reference.⁷³ However, in this work we focus on the UV/Vis spectroscopy of these systems.

3.2 Computational Details

3.2.1 Details of DFT Calculations

Transition energies and oscillator strengths were computed with TDDFT with the CAM-B3LYP XC functional³⁹ and 6-311+G* basis set for the neutral, mono-reduced and di-reduced PDI and NDI species. Calculations were performed for a single molecule with the polarized continuum model (PCM) with a dielectric constant of 78.39 to describe the solvent and focus on the low energy region of the spectrum. Vibrational resolved spectra have been computed using the FCclasses code based upon Franck-Condon factors. The spectra were simulated at 100K using the in built temperature feature in FCclasses, but we find in initial studies that the computed spectra to be relatively insensitive to the temperature. As a consequence, higher temperature studies would add additional computational cost for no improvement in the calculated spectrum. Harmonic vibrational frequencies have been computed using the B3LYP functional and 6-31G* basis

set. The vibrational frequencies for the excited states were determined using the maximum overlap method. The spectra for PDI—PDI and PDI—NDI dimers were computed using TDDFT with the CAM-B3LYP functional and 6-31+G* basis set with the PCM solvent model. The structure for the PDI—PDI dimer was adapted from the molecular dynamics simulation, while a model PDI—NDI dimer was used with the two molecules placed 6 Å apart. Computed spectra were generated by convoluting Gaussian functions with a full-width at half maximum of 0.1 eV.

3.2.2 Monomer and Dimer Models

The size of the full handcuff system (Figure 8b) means that it is not practical to use the full system to simulate the UV/Vis spectra. However, the low energy transitions occur between orbitals localised on the PDI or NDI unit. As a consequence, calculations were performed for monomer and dimer models, the structure of the cropped PDI monomer is shown in Figure 10 and the analogous model for the dimer in Figure 11.

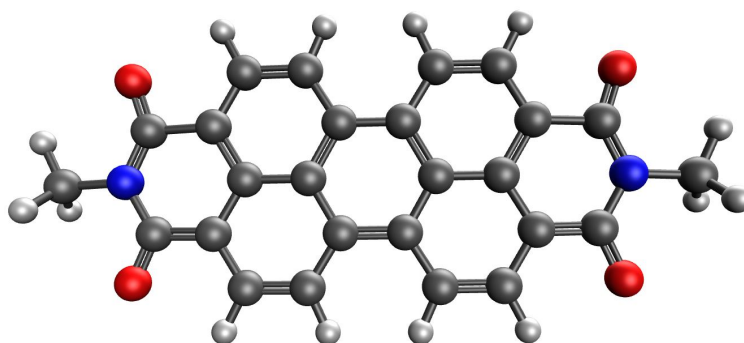


Figure 10: Atomic structure of the cropped PDI monomer.

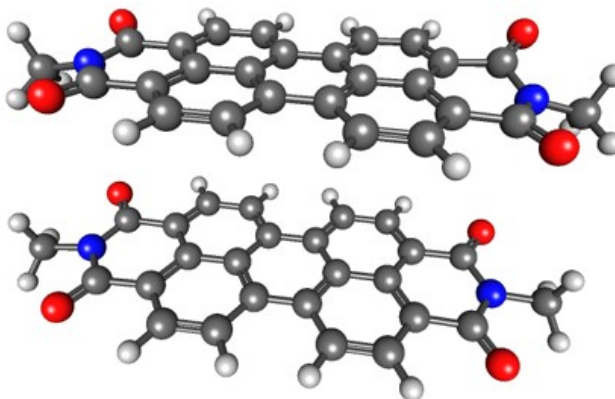


Figure 11: Atomic structure of the cropped PDI-PDI dimer.

In the full system, the dimer is held together by the mechanical bond, which is removed in the cropped structure. A consequence of this is that the optimisation of the structure using DFT leads to a structure that does not resemble the structure of the full system because the platforms move much further apart since they are no longer constrained by the mechanical bond. Therefore the geometry of the dimer is taken from the molecular dynamics simulation.

3.3 Results and Discussion

3.3.1 Computed Spectra for PDI and NDI monomers

Initially we consider calculations for the monomer PDI and NDI species to serve as a foundation to understand the more complex dimers. The computed transitions are shown in Table 1 and computed spectra shown in Figure 12. The figures illustrate the electronic transitions associated with the observed bands in the computed spectra for the monomers. For the neutral species one intense band is observed which arises from a transition from the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO). These transitions lie at 493 nm and 343 nm in PDI and NDI, respectively.

For the mono-reduced species bands are observed at longer wavelength. These transitions arise from the excitation of the unpaired electron to higher lying unoccupied orbitals. For NDI two of these bands are observed at 682 and 519 nm, while for PDI only the lower energy of these bands can be distinguished clearly. The most intense transition is analogous to the HOMO to LUMO transition in the neutral species, although the band is shifted to lower energy. The lowest energy state for the di-reduced species is found to be a singlet state. For PDI the spectrum has one intense band at 568.0 nm that is associated with the (new) HOMO to LUMO transition.

Charge State	PDI	NDI
0	493 (1.01)	343 (0.48)
-1	819 (0.37)	682 (0.08)
	690 (0.08)	519 (0.22)
	658 (0.71)	434 (0.34)
-2	568 (1.76)	575 (0.23)
	561 (0.29)	431 (0.81)

Table 1: Computed transition energies (in nm) for neutral, mono-reduced and di-reduced PDI and NDI. Oscillator strengths are given in parenthesis. Only transitions with non-zero oscillator strength are shown.

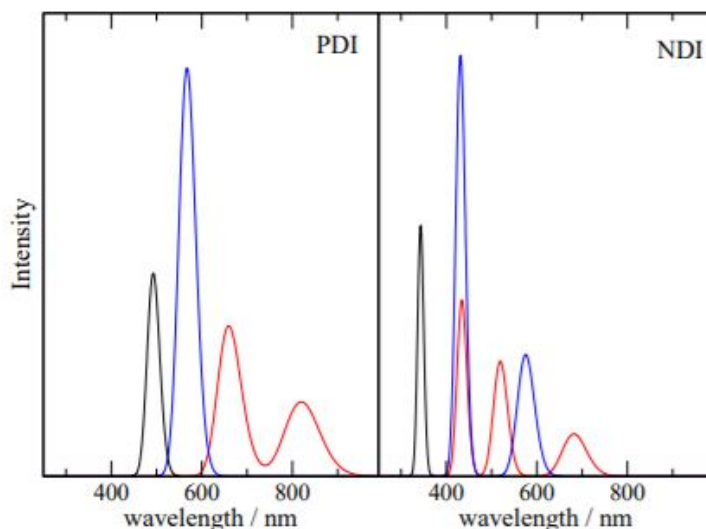


Figure 12: Computed spectra for PDI and NDI. Black line: neutral, red line: mono-reduced and blue line: di-reduced.

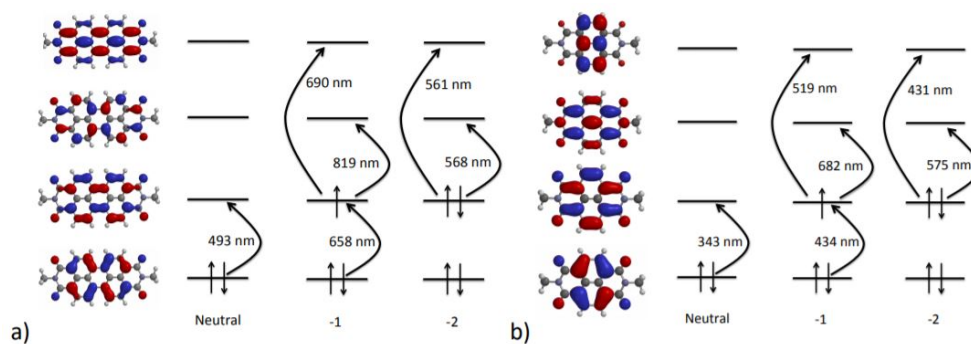
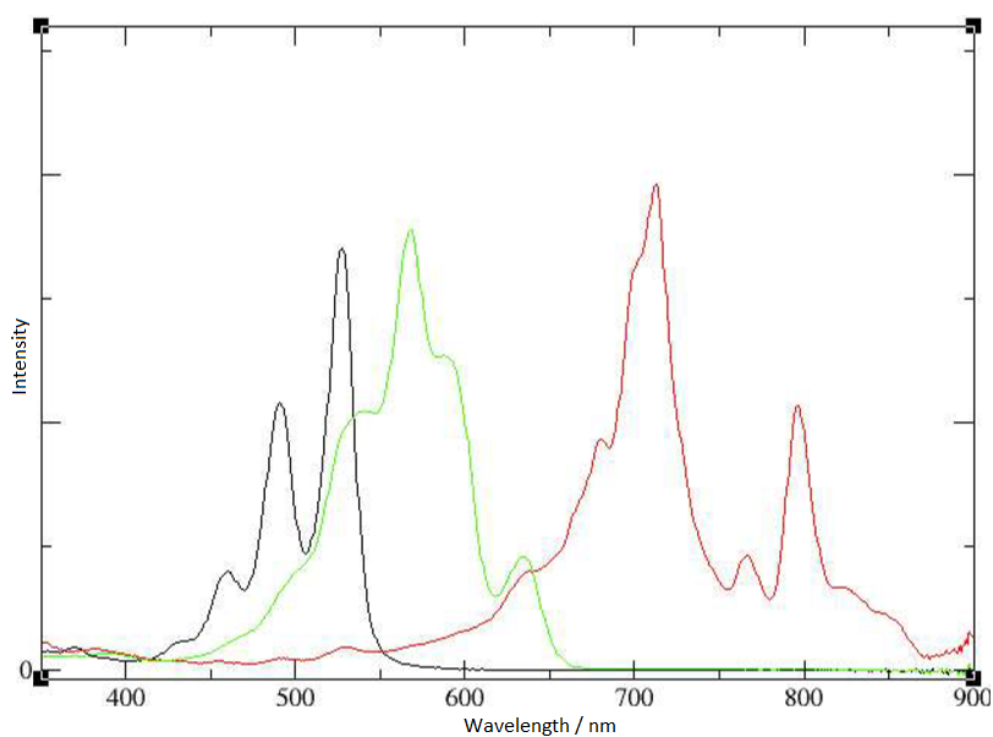


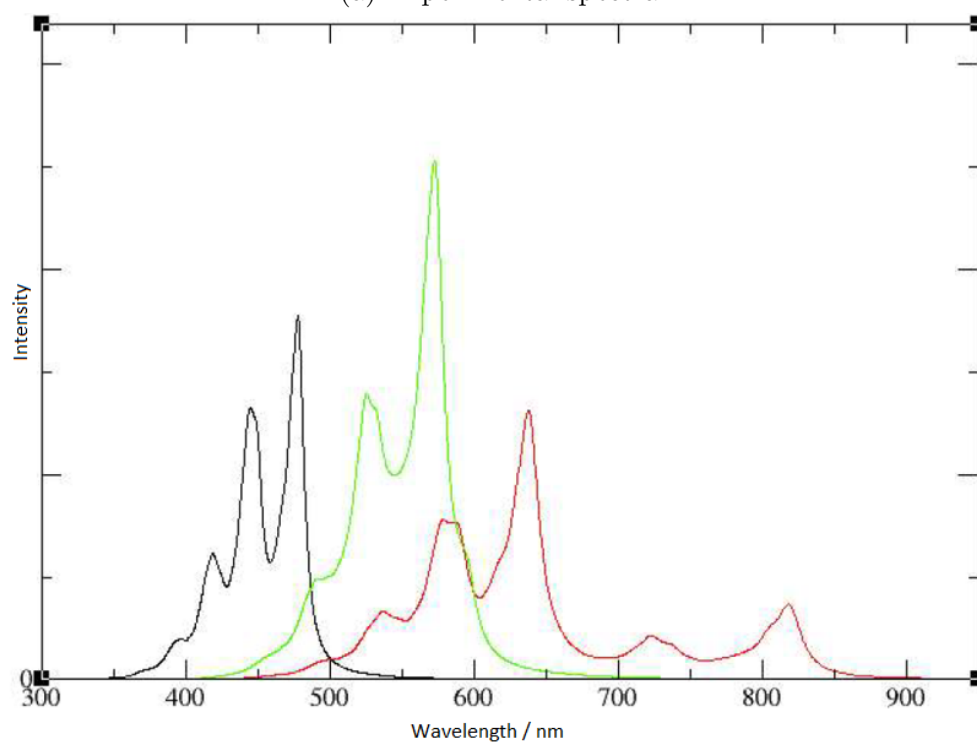
Figure 13: Electronic transitions associated with the observed bands a) in PDI and b) NDI.

3.3.2 PDI Monomer Results

To validate the computational procedure used, the calculated spectra for the neutral, singly charged and doubly charged species were compared to experimental results. A feature of the experimental spectrum is that vibrational structure can be distinguished clearly. In order to provide a more detailed comparison with experiment, the calculated spectra have been extended to include vibrational structure. The resulting experimental and computational spectra are shown in Figure 14.



(a) Experimental spectra



(b) Computational spectra

Figure 14: Comparison of experimental and computational results for all of the charged states of the PDI monomer. Neutral molecule is in black, mono-reduced molecule is in red, di-reduced is in green.

The spectrum for the neutral PDI monomer is dominated by a single band corresponding to the HOMO to LUMO transition. This band splits into four vibrationally resolved peaks, which increase in intensity as wavelength increases and there is excellent agreement between the calculated and experimental spectra. This vibrationally resolved band can be explored further by examining and assigning specific vibrational modes to the different peaks. This is presented in Figure 15 and Table 2 below. In this analysis, only the major contributions to the vibrational structure are identified. All of these bands correspond to excitation from the vibrational ground state of the initial S_0 state to excited vibrational levels (except 0-0 transition) of the excited state (S_1)

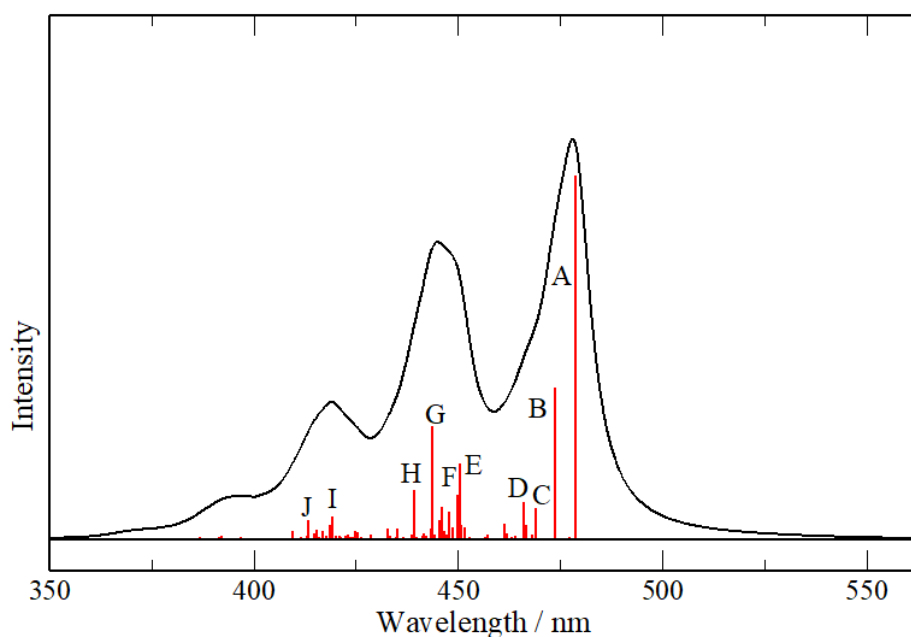


Figure 15: Vibrational structure of neutral monomer PDI spectrum.

The most intense band corresponds to the 0-0 transition and the key vibrational modes that lead to the observed vibrational structure are illustrated in Figure 16. A common feature of these vibrational modes is that they correspond to in-plane distortions of the molecule. If the molecule has approximate C_{2v} symmetry, then these modes can be seen to have A_1 symmetry which is consistent with them being vibronically allowed.

Band	Wavelength / nm	Assignment
A	478.7	0-0
B	473.7	ν_{14}
C	468.8	$2 \nu_{14}$
D	465.9	ν_{38}
E	450.4	ν_{86}
F	449.9	ν_{90}
G	443.6	ν_{114}
H	439.3	$\nu_{14} + \nu_{114}$
I	419.1	$\nu_{86} + \nu_{114}$
J	413.2	$2 \nu_{114}$

Table 2: Assignment of vibrational modes in the neutral PDI monomer spectrum.

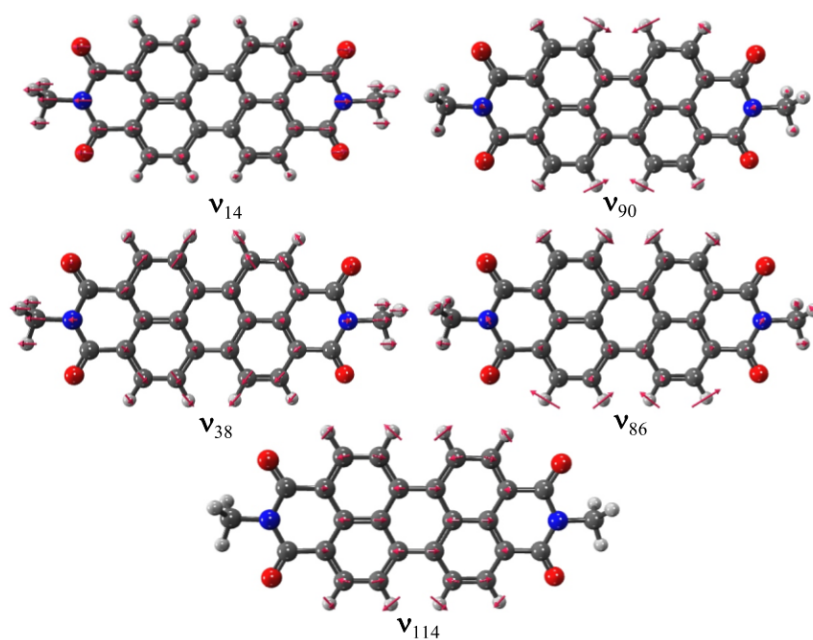


Figure 16: Vibrational modes of the neutral PDI monomer that lead to the observed vibrational fine structure.

The addition of another electron to the molecule to form the mono-reduced species changes the previously assigned LUMO to a singly occupied orbital and this leads to a more complex UV/Vis spectrum. There are two bands; the first is weaker and arises from the excitation of the unpaired electron into a higher energy orbital and the second stronger band arises from excitation from the highest doubly occupied orbital into the singly occupied orbital. Both bands have vibrational structure; the low energy band ($\text{HOMO} \rightarrow \text{LUMO}$) is split into two different peaks while the higher energy band ($\text{HOMO} \rightarrow \text{LUMO}+1$) resolves into four different peaks. Again there is good agreement between the calculated and experimental data. Assignment of the vibrational structure is shown in Figure 17 and Table 3 with the active vibrational modes illustrated in Figures 18 and 19. Similar to the neutral species, these modes are totally symmetric.

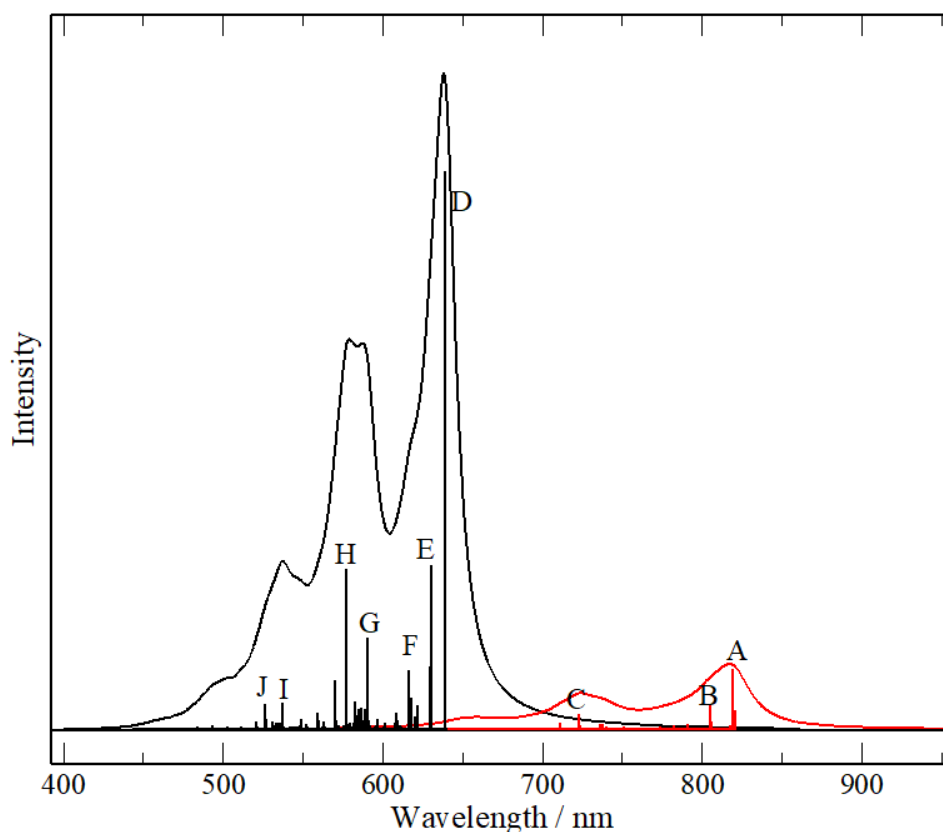


Figure 17: Vibrational structure of mono-reduced PDI monomer spectrum.

Band	Wavelength / nm	Assignment
HOMO $\rightarrow$ LUMO		
A	819.1	0-0
B	804.8	ν_{14}
C	722.4	ν_{113}
HOMO $\rightarrow$ LUMO+1		
D	638.9	0-0
E	630.1	ν_{14}
F	616.3	ν_{38}
G	590.3	ν_{85}
H	577.2	ν_{116}
I	537.3	$\nu_{85} + \nu_{116}$
J	526.4	$2 \nu_{116}$

Table 3: Assignment of vibrational modes in the mono-reduced PDI monomer spectrum.

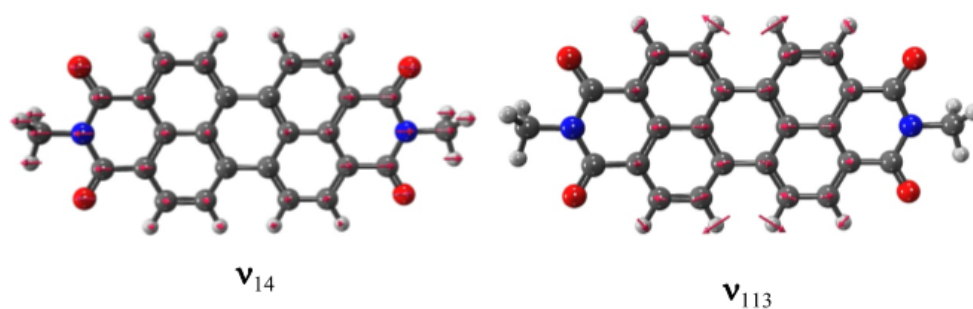


Figure 18: Vibrational modes of the mono-reduced PDI molecule that lead to the observed vibrational fine structure in the low energy band (HOMO $\rightarrow$ LUMO transition).

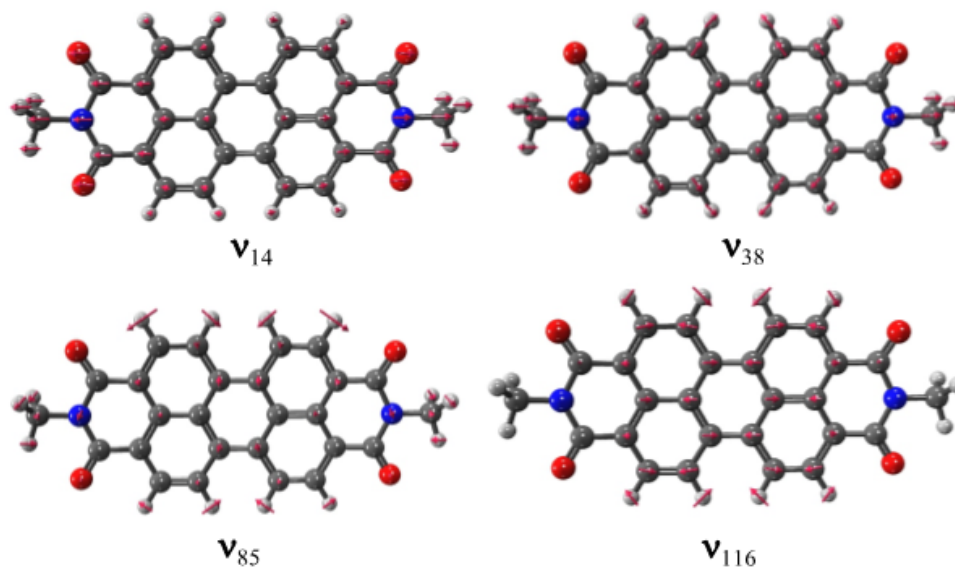


Figure 19: Vibrational modes of the mono-reduced PDI molecule that lead to the observed vibrational fine structure in the higher energy band (HOMO $\rightarrow$ LUMO+1 transition).

Finally, in the di-reduced molecule, two electrons are added to the neutral dimer, and again the spectrum is more complex than the neutral molecule. There are two bands in the spectrum, both exciting from the HOMO into both the LUMO (strong transition) and into the LUMO+1 (weak transition). The vibrational structure has been calculated for the strong HOMO $\rightarrow$ LUMO transition. The calculated vibrational structure is shown in Figure 20 with the assignment of the vibrational structure given in Table 4 with the relevant vibrational modes illustrated in Figure 21.

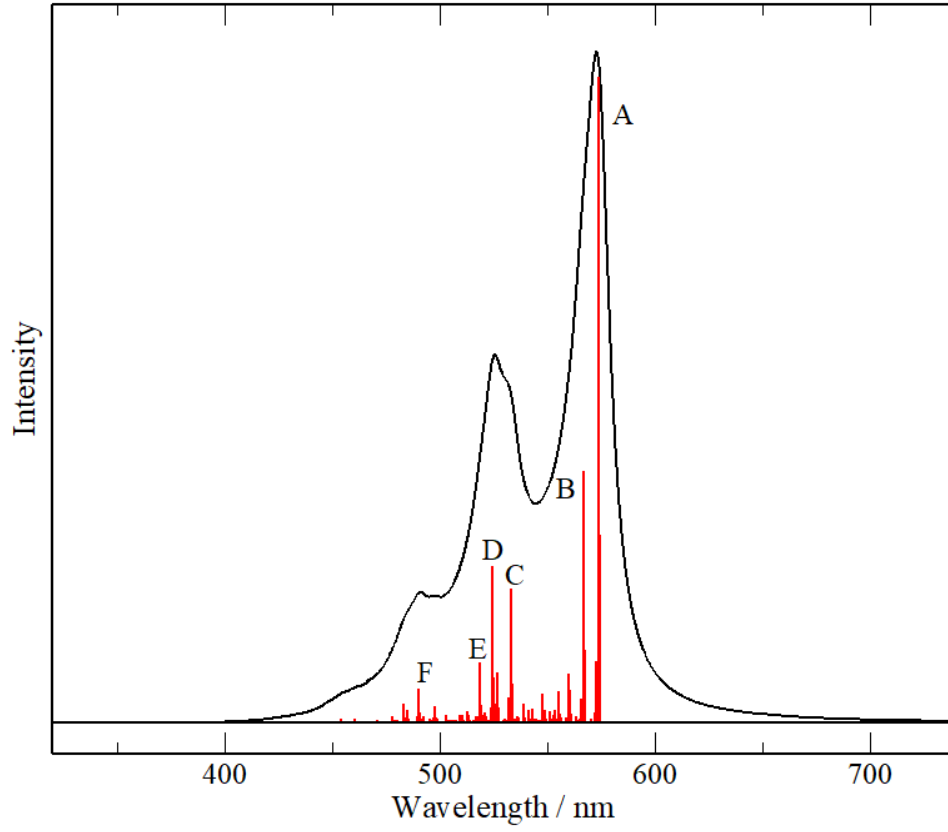


Figure 20: Vibrational structure of di-reduced PDI monomer spectrum.

Band	Wavelength / nm	Assignment
A	478.7	0-0
B	473.7	ν_{14}
C	468.8	$2 \nu_{14}$
D	465.9	ν_{38}
E	450.4	ν_{86}
F	449.9	ν_{90}

Table 4: Assignment of vibrational modes in the di-reduced PDI monomer spectrum.

The calculated spectrum predicts the most intense band to arise from the 0-0 transition which is consistent with the neutral and mono-reduced species. Two distinct higher energy bands are also predicted by the calculations and these can also be distinguished in the experimental spectrum. However, the experimental spectrum also shows bands at a greater wavelength than the most intense (0-0) band. Exploratory calculations at higher temperatures do lead to transitions that appear at lower energies than the 0-0 band, which correspond to excitations from vibrationally excited levels in the ground electronic state. However, these do not have the intensity to reproduce the bands observed in experiment. The disagreement between experiment and calculation for these bands may arise from other factors such as the complex solvent environment of the experiment.

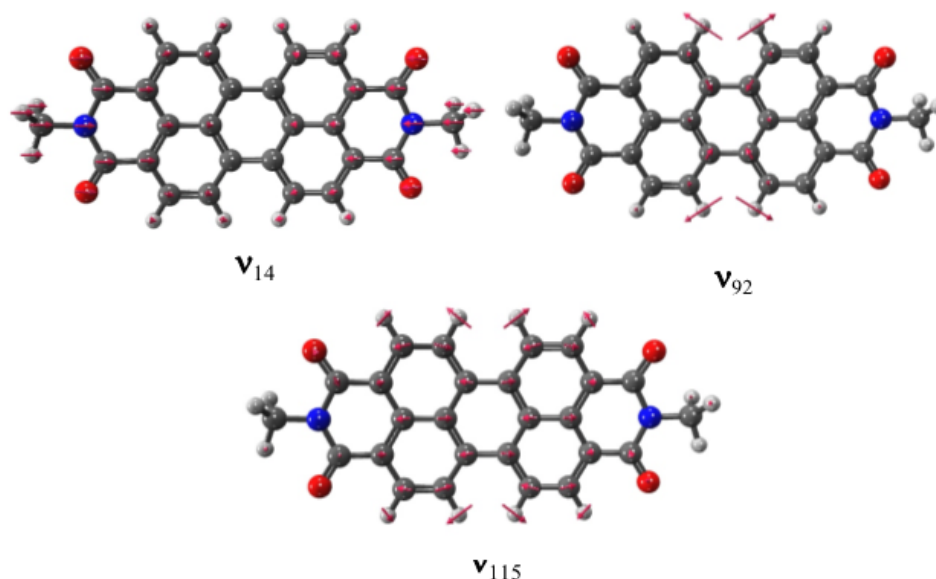


Figure 21: Vibrational modes of the di-reduced PDI molecule that lead to the observed vibrational structure.

A common feature for the different charge states that emerges is that the vibrational structure arises from in-plane totally symmetric vibrations. This feature will remain for the more complex dimer species since the vibrational modes will not change greatly with the presence of a second molecule.

3.3.3 PDI-PDI Dimer Results

The first dimer studied was the symmetrical PDI-PDI dimer. The structure was taken from a molecular simulation, performed using OPLS with additional DFT derived parameters. We now discuss the calculated spectra for the different charge states.

Neutral Dimer

The calculations predict a single peak at 529 nm in agreement with experiment. The additional detail in the experimental spectrum arises from vibrational structure, which has not been calculated for the dimer species. There are two transitions related to the calculated band but both are between the HOMO and LUMO of each platform respectively, and shows no mixing between the platforms. The platforms are symmetrical so the molecular orbitals are identical but based on the two platforms. For clarity, Figure 22 represents the two orbitals at separate energies, however they are degenerate and we therefore see a single band in the spectrum. The energy of the transition is comparable to that of the PDI monomer.

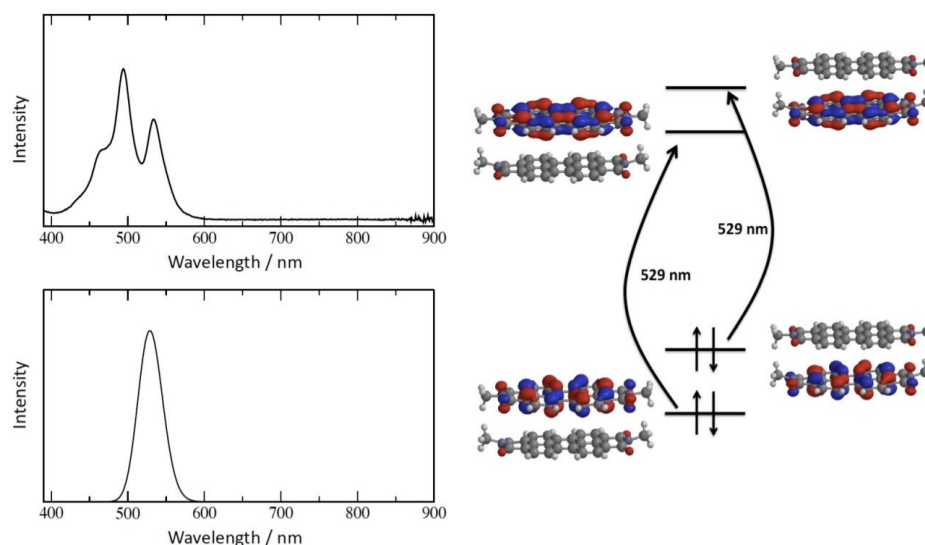


Figure 22: Experimental (upper panel) and computed (lower panel) spectra for the neutral PDI-PDI dimer with the orbitals associated with the electronic transitions.

Singly Charged Dimer

The mono-reduced species is no longer symmetric which leads to more bands being observed in the spectrum. The UV/Vis spectrum of the singly charged system resembles a combination of the UV/Vis spectra of neutral and mono-reduced monomers. The calculations show that the lower energy bands at 795 nm and 651 nm are associated with the PDI molecule that has been reduced while the band at 502 nm corresponds to the HOMO to LUMO on the neutral PDI molecule, and this is illustrated in Figure 23. Again, the energy of the transition is comparable to the neutral and mono-reduced monomer.

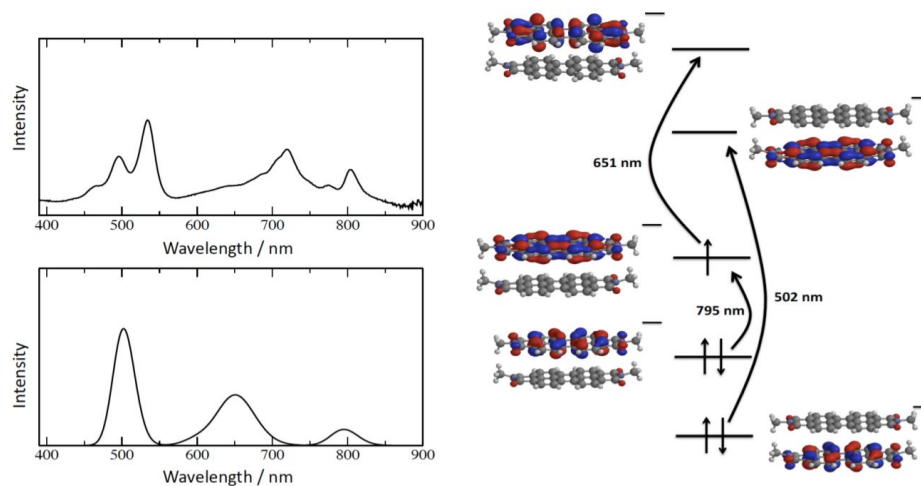


Figure 23: Experimental (upper panel) and computed (lower panel) spectra for the mono-reduced $[4]^-$, PDI^- -PDI dimer, with the orbitals associated with the electronic transitions. The negative charge is localized on the upper PDI molecule.

Doubly Charged Dimer

There are two possibilities for the di-reduced dimer species, either a singlet state or a triplet state. The calculations find the triplet state where there is an unpaired electron on each PDI molecule to have a lower energy than the closed shell singlet state where both additional electrons are on the same PDI molecule.

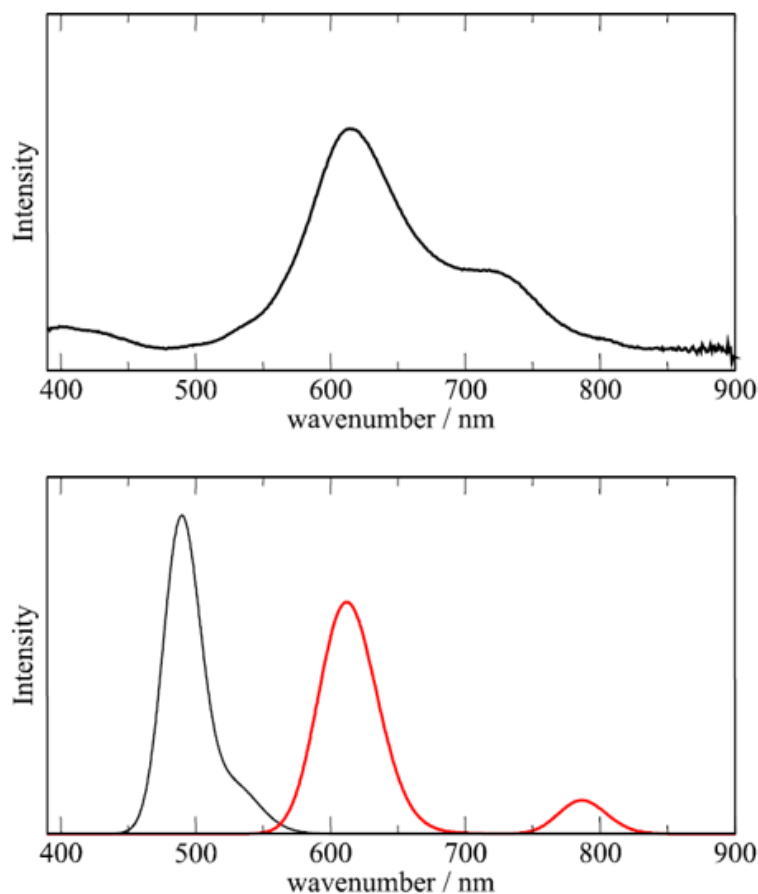


Figure 24: Comparison of the two possible states of the doubly charged PDI-PDI dimer with the singlet state in black and the triplet state in red, which more closely resembles the experimental spectrum.

The formation of the triplet state is consistent with the UV/Vis spectra which are closer to experiment for the triplet state (Figure 24). The band at longer wavelength arises from excitation of electrons in lower energy orbitals to the singly occupied orbital, while the band at 612 nm corresponds to excitation of the unpaired electron. We note that this band is shifted in energy compared with the mono-reduced species.

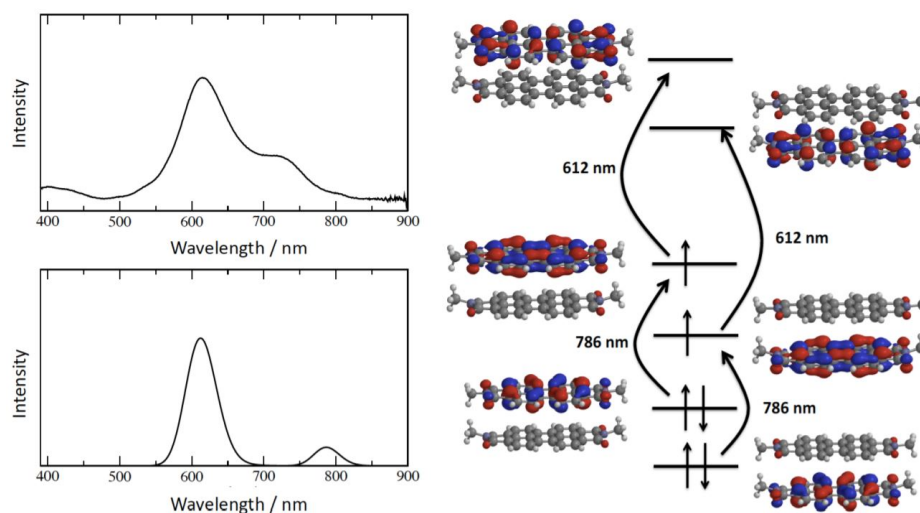


Figure 25: Experimental (upper panel) and computed (lower panel) spectra for the di-reduced PDI^- - PDI^- dimer, with the orbitals associated with the electronic transitions.

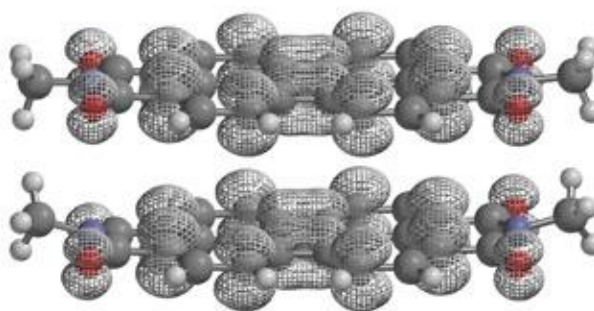


Figure 26: The triplet state for di-reduced dimer exhibits spin density spread across both PDI species.

The spin density shown in Figure 26 confirms that the spin density is spread across both platforms, which supports the conclusion that there is an unpaired electron on each platform.

Quadruply Charged Dimer

For the quadruply reduced species, where two electrons have been added to each PDI molecule, the experiment shows a spectrum that is similar to the di-reduced monomer spectrum and the calculations predict an intense band at 494 nm with

a much weaker band at 526 nm. These bands arise from transitions from the HOMO to the first and second unoccupied orbitals of the PDI molecules. The spectra arise from bands that are localised on a single PDI molecule that are only slightly charged by the presence of the second PDI molecule. The wavelengths of these bands are slightly lower than the equivalent monomer bands.

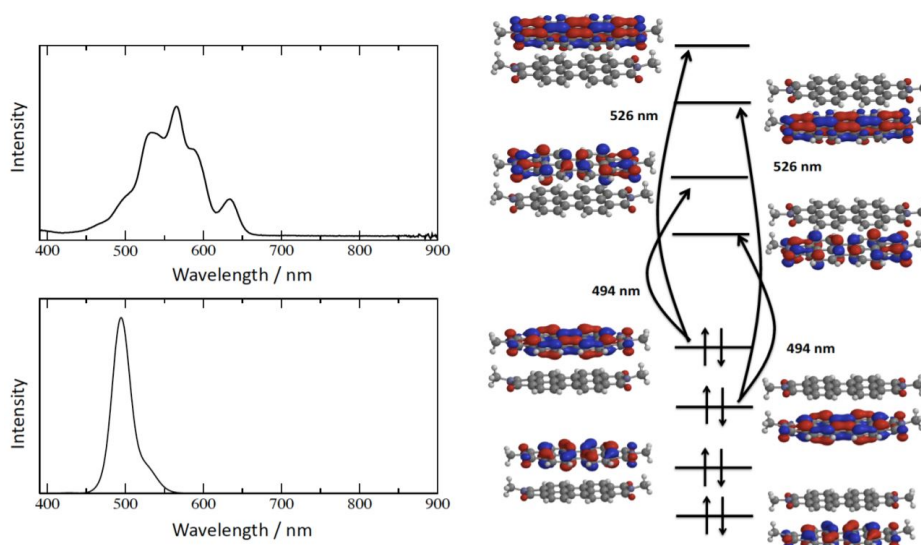


Figure 27: Experimental (upper panel) and computed (lower panel) spectra for PDI^{2-} - PDI^{2-} dimer, with the orbitals associated with the electronic transitions.

3.3.4 PDI-NDI Dimer Results

The second dimer studied was the non-symmetrical NDI-PDI dimer. Again the starting structure was adapted from a molecular simulation, performed using Optimised Potential for Liquid Simulations (OPLS) with additional DFT derived parameters and the neutral, di-reduced and quadruply reduced species were studied.

Neutral Dimer

For the neutral species two bands are predicted which arise from the HOMO to LUMO transitions on PDI (492 nm) and NDI (343 nm). In the experimental spectrum, the characteristic vibrational spectra of PDI (Figure 14) can be seen

in the band around 492 nm. The bands of both the NDI and PDI platforms has a very similar energy to that of the associated monomer.

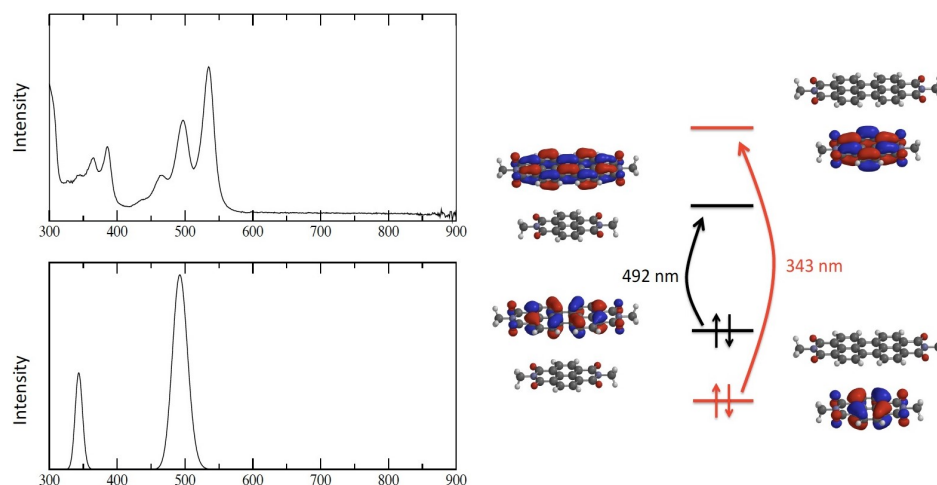


Figure 28: Experimental (upper panel) and computed (lower panel) spectra for the neutral PDI-NDI dimer, with the orbitals associated with the electronic transitions. Orbitals and transitions associated with NDI shown in red.

Singly Charged Dimer

In the mono-reduced species the lowest energy electron configuration has the additional electron on PDI.

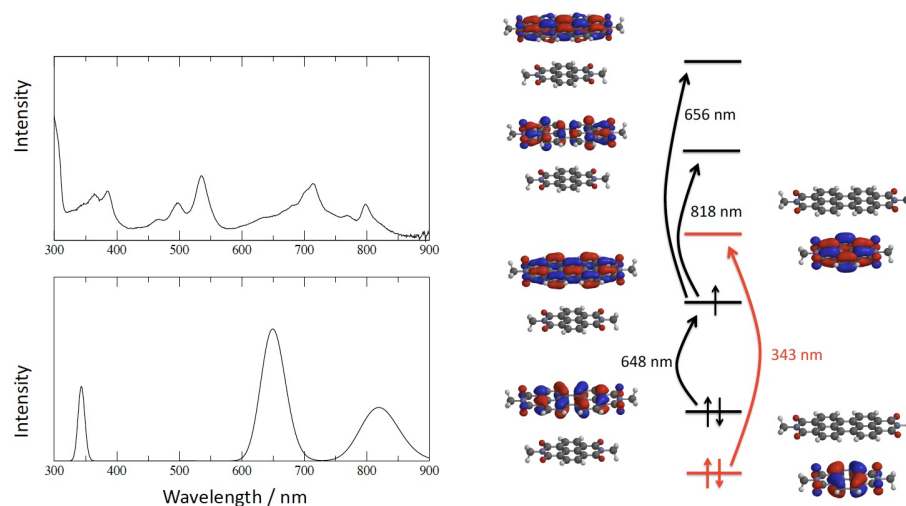


Figure 29: Experimental (upper panel) and computed (lower panel) spectra for the mono-reduced PDI-NDI dimer, with the orbitals associated with the electronic transitions. Orbitals and transitions associated with NDI shown in red.

The resulting spectrum, shown in Figure 29 has a band a 343 nm associated with

neutral NDI and bands at higher wavelength arising from the mono-reduced PDI. The experimental spectrum also has a band about 500 nm which is characteristic of neutral PDI and may indicate that not all of the PDI-NDI dimers have been reduced.

Doubly Charged Dimer

The di-reduced species has an unpaired electron on each molecule and is a triplet state. The computed spectrum, given in Figure 30, shows the bands associated with the mono-reduced state of each molecule and the intense bands predicted by the calculations are observed in the experimental spectrum.

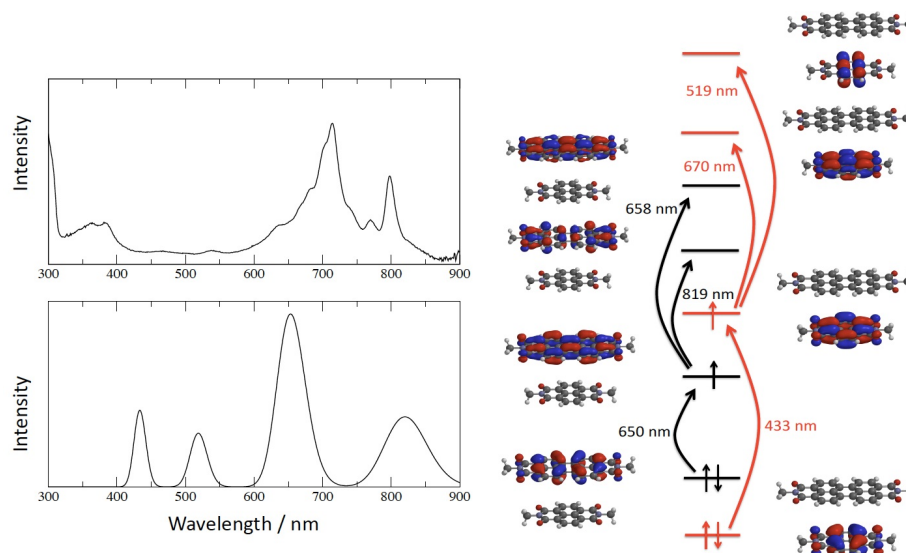


Figure 30: Experimental (upper panel) and computed (lower panel) spectra for the di-reduced PDI^- - NDI^- dimer, with the orbitals associated with the electronic transitions. Orbitals and transitions associated with NDI shown in red.

Quadruply Charged Dimer

The calculated spectrum for the PDI^{2-} - NDI^{2-} dimer is shown in Figure 31 and has a band at 570 nm arising from the HOMO to LUMO transition on PDI and bands at 400 nm and 522 nm arising from transition from the HOMO of NDI. These bands can also be clearly distinguished in the experimental spectrum.

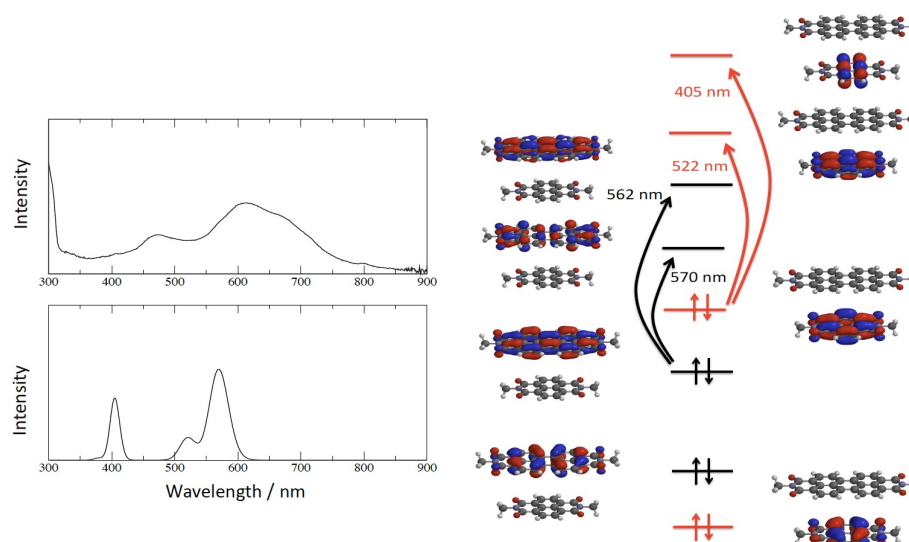


Figure 31: Experimental (upper panel) and computed (lower panel) spectra for the di-reduced PDI^{2-} - NDI^{2-} dimer, with the orbitals associated with the electronic transitions. Orbitals and transitions associated with NDI shown in red.

3.4 Conclusions

The experimental work conducted by the group of Neil Champness offered a useful and important foundation for building an interesting computational study. The UV/Vis spectra could not be examined at such close detail by experiment alone and it is this reason that experiment and computation must work together to understand the molecular systems in greater depth.

The monomer results show well-resolved spectra which can be compared to experimental results and vibrational modes involved in vibrational structure have been identified. These identified modes were all in-plane vibrations and were consistent across all charged states, due to the molecular geometry not changing greatly when charge is added. The electronic transitions were identified for the dimer spectra. The observed spectral bands arise from transitions between orbitals localised on the same PDI or NDI molecule, and for the di-reduced species a single charge is present on each molecule. Given that the vibrations were con-

sistent in the monomer states, it is not unreasonable to hypothesise that the vibrational structure in the dimer spectra are also due to similar in-plane vibrations.

Chapter 4

Vibrationally Resolved Spectra of Polyaromatic Hydrocarbons

4.1 Background

Diffuse interstellar bands (DIBs) are absorption bands caused by absorption of light in the interstellar medium. The origin of the DIBs remain difficult to identify despite being discovered almost a century ago. Over the course of time, hundreds of DIBs have been observed and lots of work has been done to investigate their origin.⁷⁴

The bulk of previous work has focussed on the infrared (IR) spectroscopy of the molecules to compare to the diffuse interstellar bands, and other astrochemical features. Both experimental and theoretical methods have been used to examine the diffuse interstellar bands from an IR perspective and the scope of the literature is extensive. Much of these previous theoretical studies have used DFT and a mix of systems have been studied ranging in size, substituents and charge states.^{75,76} A common strategy is to compare calculated spectra with the features observed in the DIBs in order to identify a unique molecular source. Unfortunately, despite the scope of the previous work, the identification of the source

of the diffuse interstellar bands remains an ongoing and unsolved problem. One challenge for this work is the inherent inaccuracies in calculated IR spectra.

Links have been made between the diffuse interstellar bands and the UV/Vis absorption spectra of small PAHs, which confirms that while the IR work is certainly relevant because the DIBs span from near-IR to near-UV, their UV/Vis spectroscopy is also relevant. For example, it was hypothesised that a pyrene-like molecule could be responsible for the 4,430-Å band based on laboratory experiment⁷⁷ which confirms that the bands cannot be understood by examination of IR spectra alone. A link has also been made between charged PAH molecules, including naphthalene, and the unidentified astrochemical features.⁷⁸

There is some previous computational work about UV/Vis spectroscopy as well, including a database which has calculated excitation energies for a range of PAHs,⁷⁹ which provides a first step to interpreting the experimental data.

In this chapter, a high resolution computational study of the UV/Vis spectra for some prototypical PAH molecules is presented.

4.2 Computational Details

The structure of the molecules were optimised with 6-31G* basis set and B3LYP exchange correlation functional using Q-Chem. The excited state energies were computed using TDDFT, with the same basis set and CAM-B3LYP exchange-correlation functional. Vibrational resolved spectra were computed using the FCclasses code based upon Franck-Condon factors. The spectra were simulated at several temperatures using the in built temperature feature in FCclasses, which is discussed in the results. Harmonic vibrational frequencies have been computed

using the B3LYP functional and 6-31G* basis set. The vibrational frequencies for the excited states were determined using the maximum overlap method. A FWHM of 0.025 nm was used to generate the computational spectrum.

4.3 Results and Discussion

The results are broken down into results sections for each polyaromatic hydrocarbon studied, namely pyrene, naphthalene, and coronene.

4.3.1 Pyrene

Pyrene is a relatively small PAH and given the potential links to astrochemistry, it is an ideal system to examine. The vibrational structure present in the UV/Vis spectrum of pyrene was seen earlier in Figure 4. Pyrene itself is shown in Figure 32 below, which shows the structure after geometry optimisation.

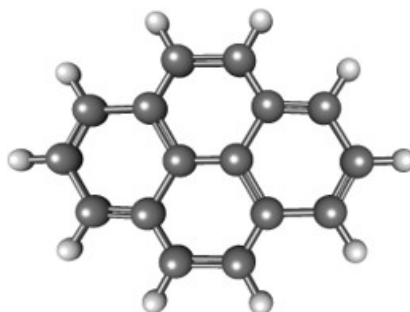


Figure 32: Atomic structure of pyrene molecule.

Pyrene is a planar fully conjugated system, made up of only carbon and hydrogen, and is a prototypical PAH. Pyrene was chosen as a starting point as it has a reasonably well resolved UV/Vis spectrum with vibrational structure, which is a good point for comparison with computational results and it is not too large for the computational analysis. From an astrochemical perspective which is perhaps the most relevant, pyrene will be one of the smallest PAHs present in space and therefore is a natural starting point for these studies.

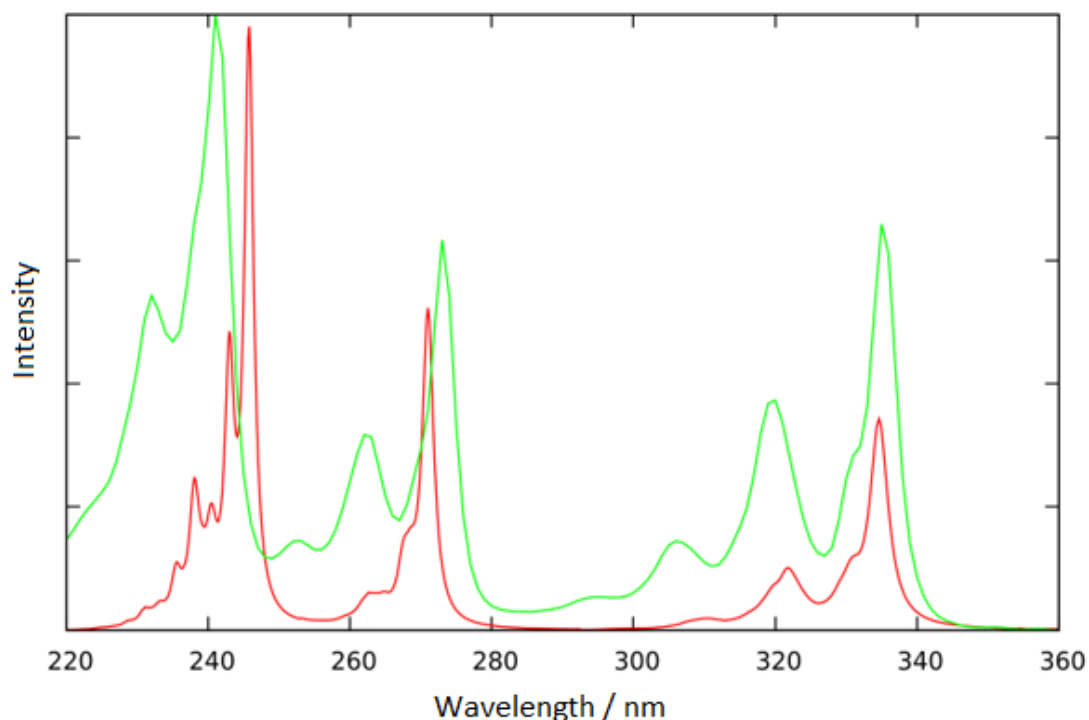


Figure 33: Comparison of experimental and computational spectrum of pyrene, with the experimental spectrum in green and the computational spectrum in red.

The experimental spectrum for pyrene is shown in Figure 33 and consists of three separate bands, and vibrational structure is evident in each of these bands. The figure also shows the computational results have been slightly shifted such that the lowest energy band aligns with the equivalent band in the experimental spectrum. This band (centred around 330 nm) is the one for which the calculations most accurately reproduce the vibrational structure of the experimental spectrum. The most intense band lies at highest wavelength, with a noticeable shoulder, then a further two peaks with the correct spacing. There is an additional peak in the experimental spectrum which has a low intensity and this band is not observed in the computational spectrum. The agreement between experiment and theory for the next band (centred around 270 nm) is not quite as good but again the initial peak with shoulder is reproduced and the first vibrational peak is also clear, but the spacing is less consistent with the experimental spectrum. The final band (centred around 240 nm) appears to have more resolved structure in

the computational spectrum than the experimental spectrum. This could be as a result of the temperature settings of FCclasses, because while the computational spectrum was run at 100 K the experiment was run at 298 K. The lowest energy transition is again an intense peak with a shoulder in the experimental spectrum while the computed spectrum shows more distinct and sharp peaks. The final peak seen on the experimental spectrum is a lower intensity peak with a shoulder and again more structure is observed in the computational spectrum. It is likely that if the broadening of the peaks was increased for this final band that it would more closely resemble the experimental spectrum.

A key advantage of the computational studies is the opportunity to examine the transitions associated with the spectral bands. As pyrene is highly conjugated with no substituents, the low energy transtions are expected to be between π and π^* molecular orbitals.

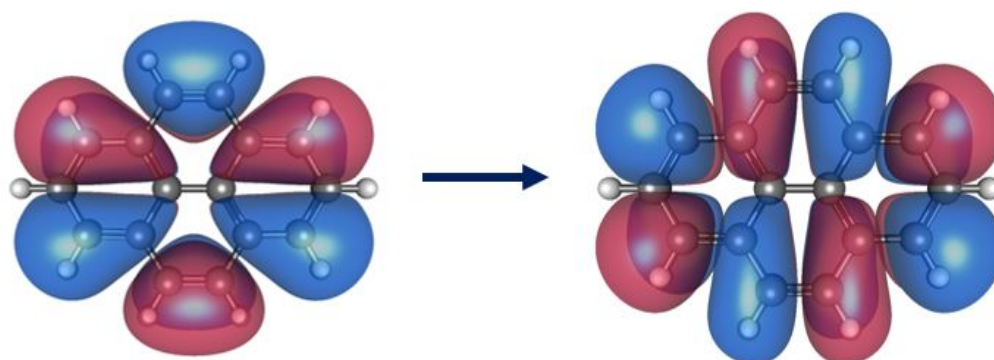


Figure 34: The molecular orbitals associated with the electronic transition of pyrene for the band centred at 330 nm.

This first transition arises from the HOMO to the LUMO transition, shown in Figure 34. Although the molecular orbitals have been visualised from a ‘top down’ perspective, there is a node in the plane of the molecule, which is consistent with the behaviour of the orbitals as π type orbitals.

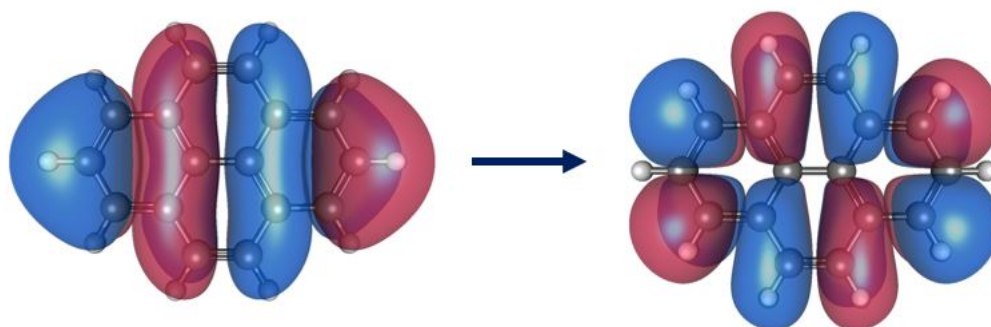


Figure 35: The molecular orbitals associated with the electronic transition of pyrene for the band centred at 270 nm.

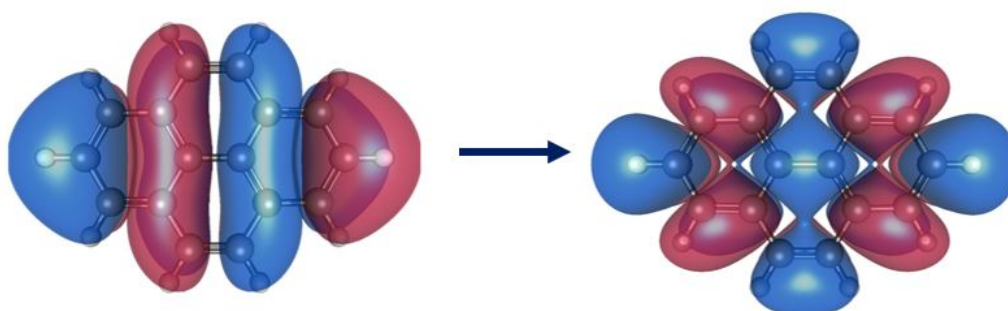


Figure 36: The molecular orbitals associated with the electronic transition of pyrene for the band centred at 240 nm

The second band arise from the HOMO-1 to the LUMO energy level, and these orbitals are shown in Figure 35. The final transition seen in the spectrum is from the HOMO-1 to the LUMO+1 energy level. All of these molecular orbitals are π type orbitals, without any noticeable causes for concern. The vibrational structure can then be examined in more depth and vibrational modes assigned for the vibrational structure.

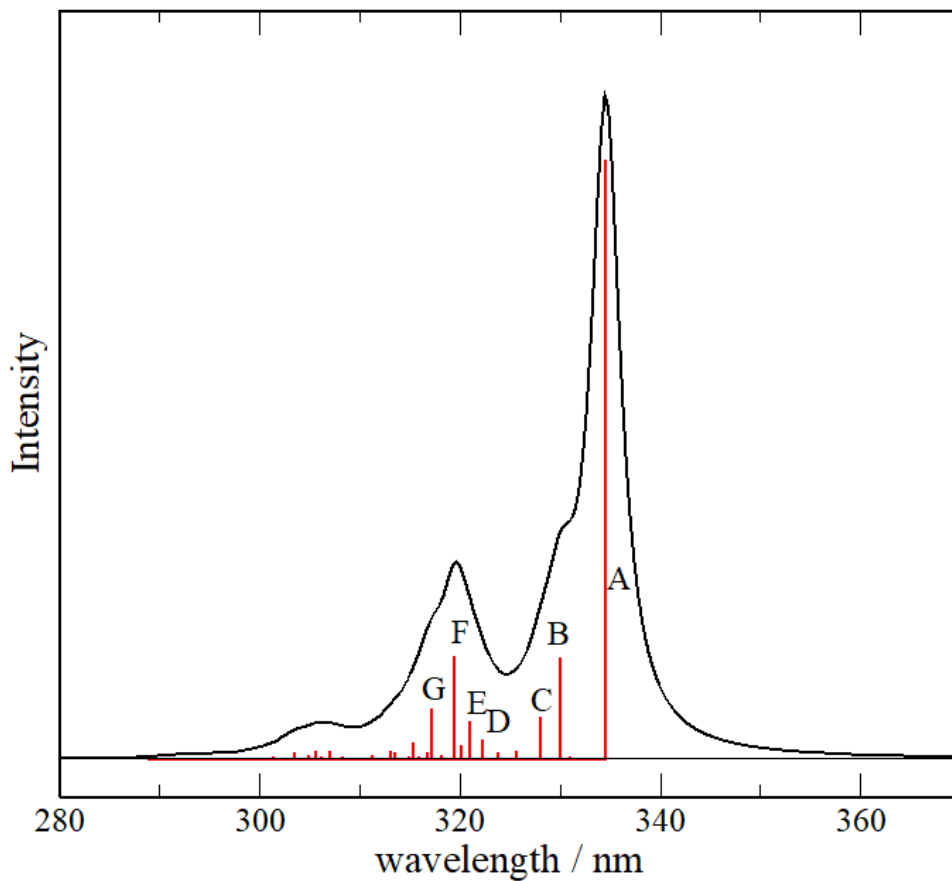


Figure 37: Vibrationally resolved computed spectrum of the band of pyrene centred around 320 nm in black with vibrational stick spectrum in red.

Band	Wavelength / nm	Assignment
A	334.5	0-0
B	330.0	ν_7
C	328.0	ν_{17}
D	322.2	ν_{40}
E	320.9	ν_{46}
F	319.4	ν_{51}
G	317.1	ν_{62}

Table 5: Assignment of vibrational modes in the band of the pyrene spectrum centred around 330 nm.

The calculated vibrationally resolved band for the low energy transition is shown in Figure 37 with the assignment of the dominant contributions to the bands given in Table 5. Although this band appears to be three different peaks, when the vibrations are studied we can see that each of these peaks are made up of multiple vibrations. The most intense band arises from the 0-0 transition while the shoulder can be assigned to 1 quanta in the ν_7 mode of the excited final state and the distinct band to 1 quanta in the ν_{51} mode. The vibrational modes are illustrated in Figure 38. There is a strong parallel with the study of the PDI and NDI discussed in the previous chapter. The active vibrational modes again have totally symmetric symmetry which is expected for excitations the 0th level of the ground electronic state. These modes are all in plane vibrations.

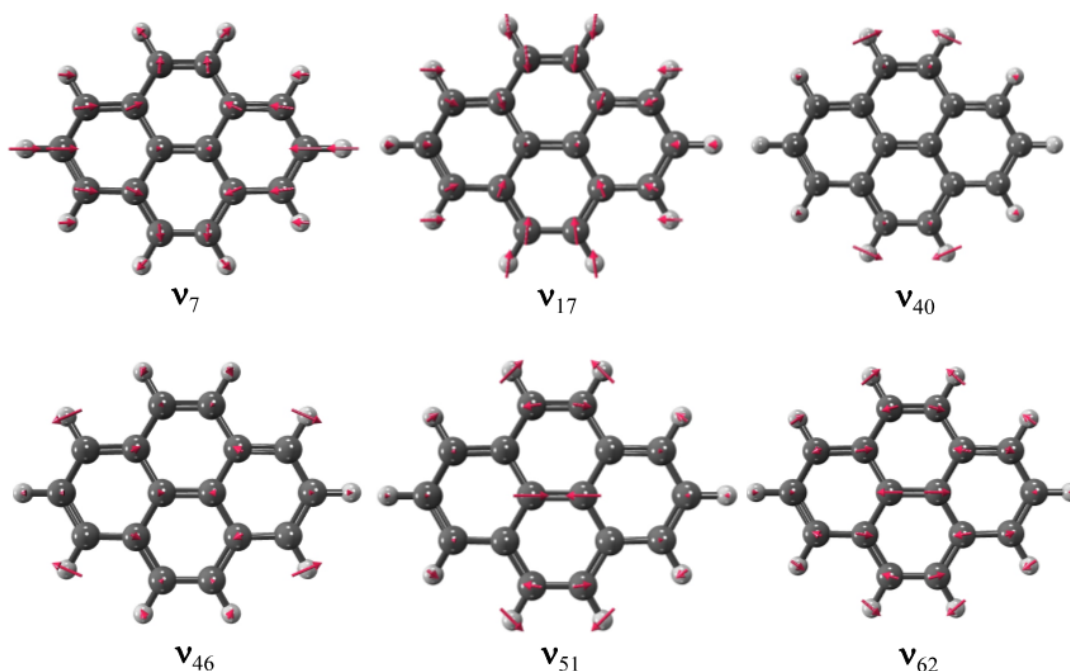


Figure 38: Vibrations of pyrene associated with band centred around 320 nm.

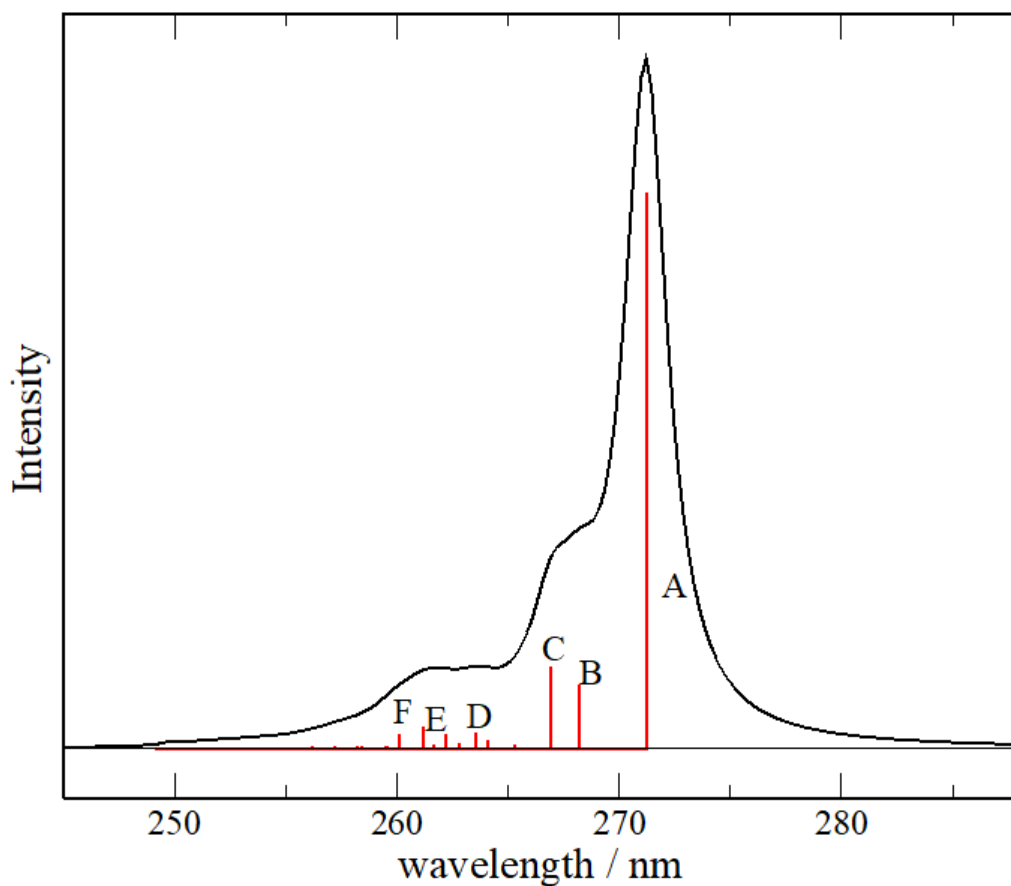


Figure 39: Vibrationally resolved computed spectrum of the band of pyrene centred around 270 nm in black with vibrational stick spectrum in red.

Band	Wavelength / nm	Assignment
A	271.2	0-0
B	268.2	ν_7
C	267.0	ν_{16}
D	263.6	ν_{37}
E	261.2	ν_{51}
F	260.1	ν_{58}

Table 6: Assignment of vibrational modes in the band of the pyrene spectrum centred around 270 nm.

A corresponding analysis is presented for the bands centred at 270 nm and 240 nm in Figures 39 and 41, and Tables 6 and 7. The relevant vibrational modes are depicted in Figures 40 and 42. In these spectra, several vibrational modes can contribute to the same feature. However, the conclusions drawn from the 330 nm band also apply to these higher energy bands with the in-plane symmetric vibrations leading to the vibrational structure.

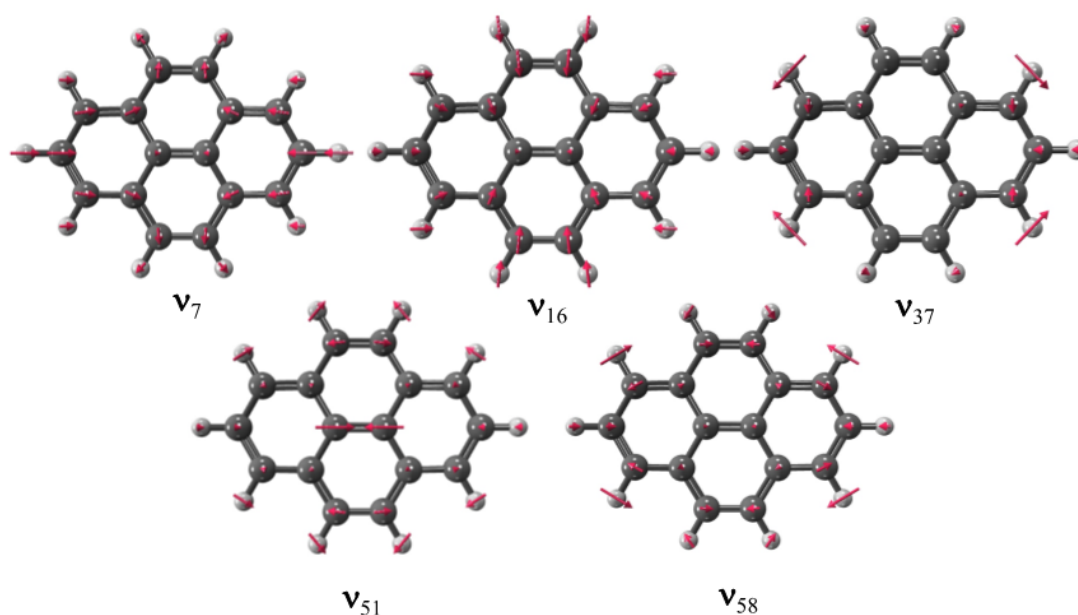


Figure 40: Vibrations of pyrene associated with band centred around 270 nm.

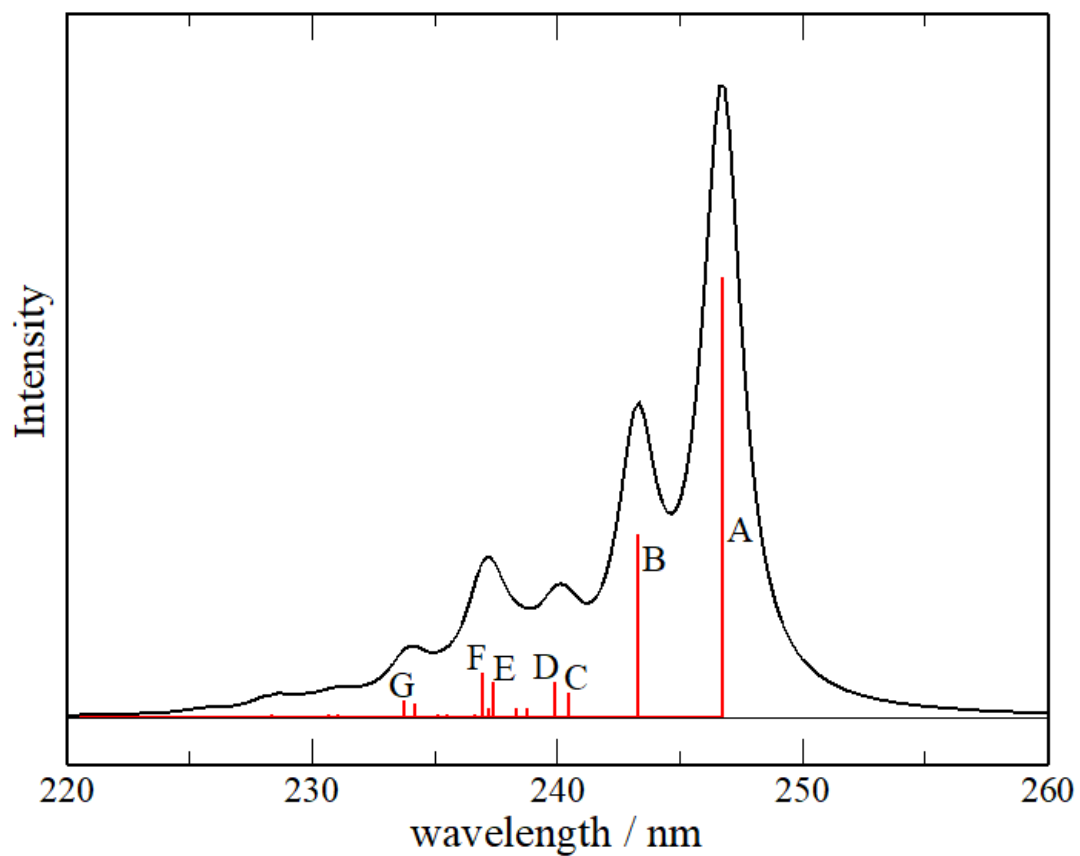


Figure 41: Vibrationally resolved computed spectrum of the band of pyrene centred around 240 nm in black with vibrational stick spectrum in red.

Band	Wavelength / nm	Assignment
A	246.7	0-0
B	243.3	ν_{16}
C	240.5	ν_{37}
D	239.9	$2\nu_{16}$
E	237.4	ν_{59}
F	236.4	ν_{62}
G	233.8	$\nu_{16} + \nu_{62}$

Table 7: Assignment of vibrational modes in the band of the pyrene spectrum centred around 240 nm.

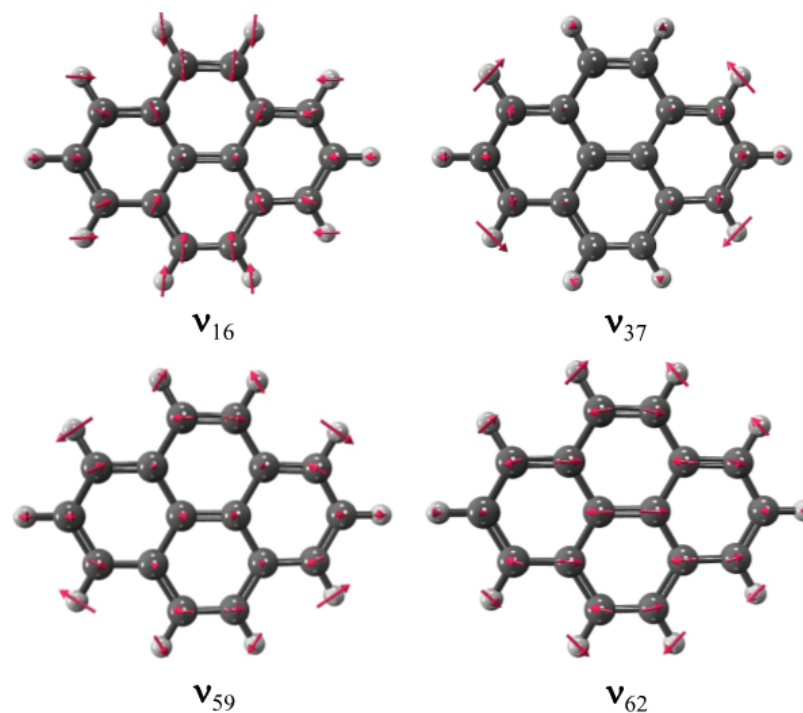


Figure 42: Vibrations of pyrene associated with band centred around 240 nm.

4.3.2 Naphthalene

Naphthalene is the smallest system studied here but is also of astrochemical interest. The structure of naphthalene is shown in 43. Naphthalene has a well resolved UV/Vis spectrum with vibrational structure, which provides a good test for the calculations.

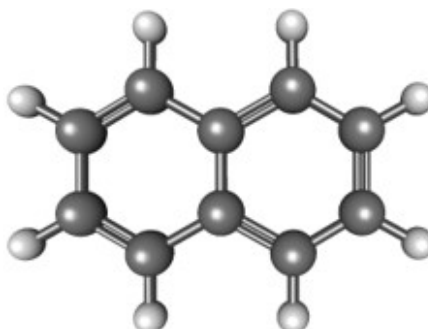


Figure 43: Atomic structure of naphthalene molecule.

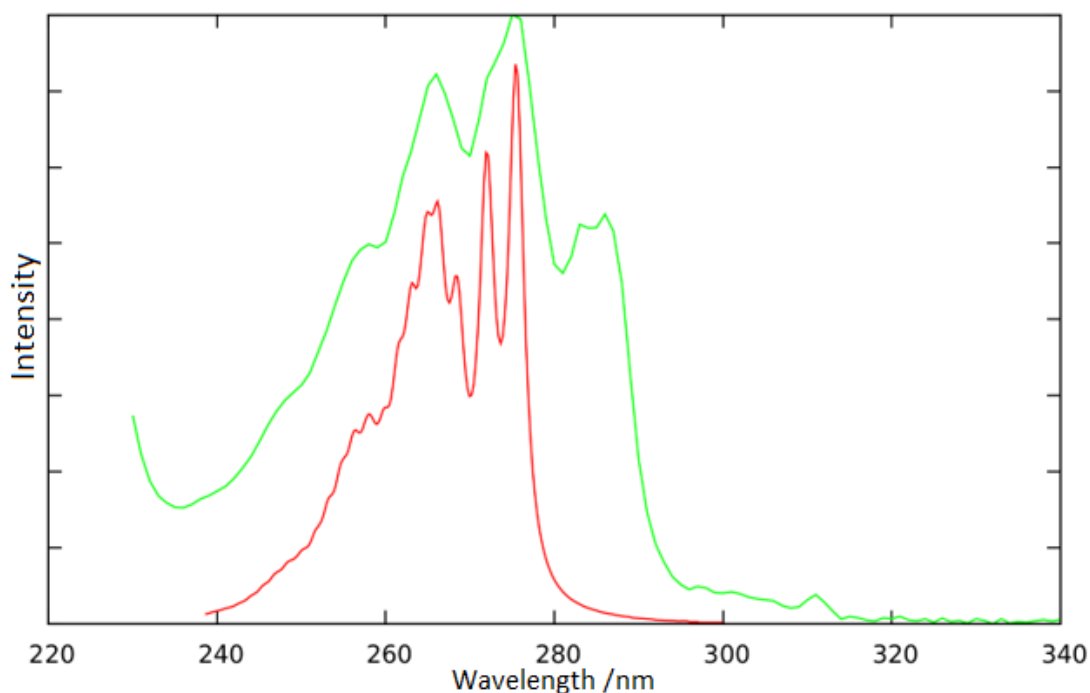


Figure 44: Comparison of experimental and computational spectrum of naphthalene, with the experimental spectrum in green and the computational spectrum in red.

Figure 44 shows two spectra; experimental and computational vibrationally resolved UV/Vis spectra for the lowest energy ($\text{HOMO} \rightarrow \text{LUMO}$) transition, which corresponds to a π to π^* excitation. There is some vibrational structure evident, but examining the experimental spectrum without the computational results can make assignment of the bands and vibrational structure challenging. To facilitate the comparison, the computed spectrum is shifted by 0.2 eV to align with the experimental spectrum to the lowest energy band.

Despite the fact that one low energy band appears to be missing, this is discussed in more detail below, we can still see many corresponding features in the spectrum. The lowest energy band in the computed spectrum is shown to have two contributions and this corresponds to a peak with a shoulder in the experimental spectrum, which again appears to be due to the lower temperature giving artificially sharp peaks in the computed spectrum.

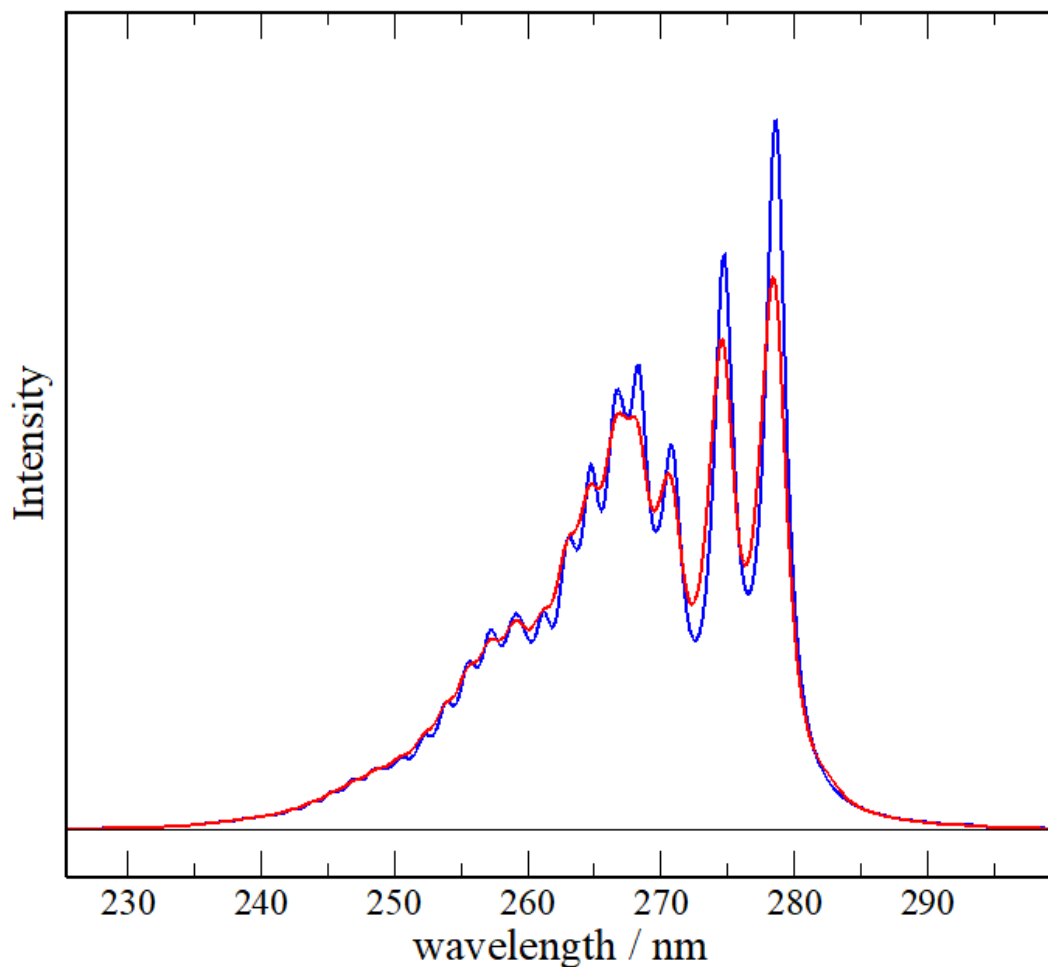


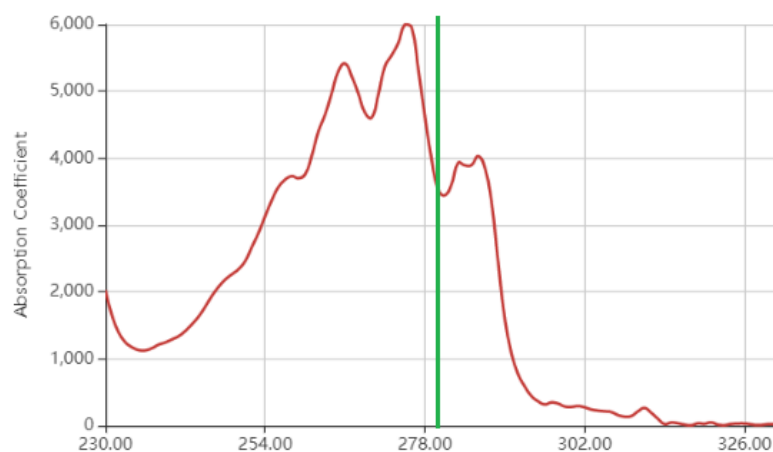
Figure 45: Comparison of low and high temperature spectra, blue trace is run at 20 K and red trace is at 1000 K.

The most striking disagreement between the experiment and computed spectra is the band at 290 nm which is absent in the calculated spectrum. Examining the spectra and specifically this missing lower energy band, it was hypothesised that it could be due to the temperature of the system and this band was an excitation from a vibrationally excited ground state, which wouldn't be occupied at low temperature. Figure 45 shows the comparison of low and high temperature spectra. At the higher temperature there is some broadening of the bands, but the low energy band is still not observed.

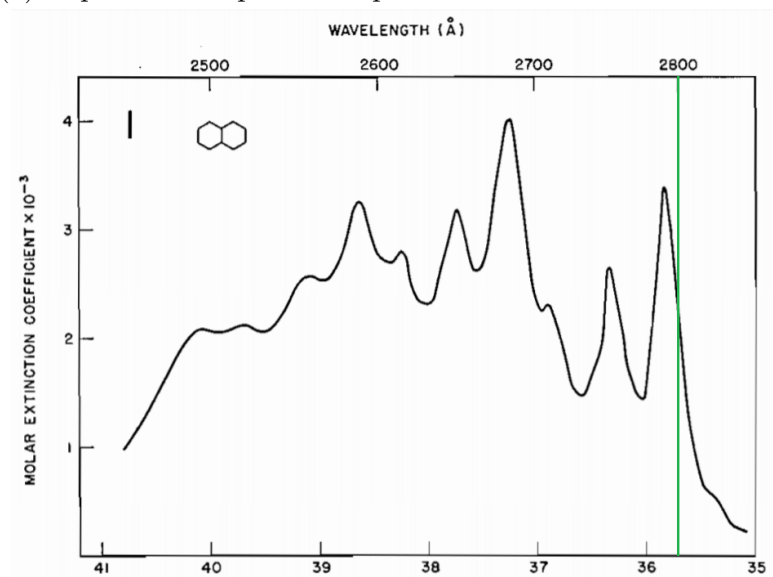
Returning to literature, further experimental spectra for naphthalene were found and a comparison of these are in Figure 46. This made the problem with the miss-

ing experimental band clearer, it appeared to only be visible in this experimental spectrum used initially for comparison, which is the oldest experiment and in more recent measurements this band is not observed. We see that the bands reproduced by calculation are common to both experimental spectra, although they have slightly different levels of broadening. It makes for an interesting observation as a computational chemist, as experiment is often upheld as the benchmark for calculations to compare to and aim for but in this case the experiment appeared to lead to some misleading conclusions and information.

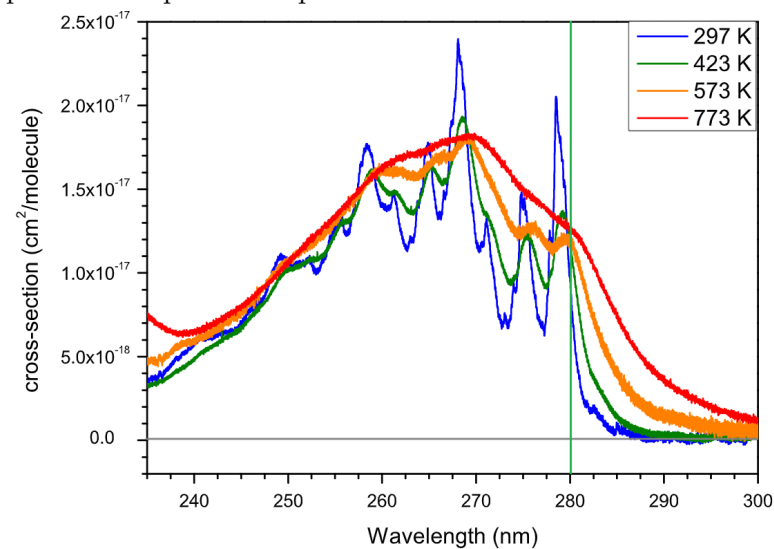
Some experimental information investigating the effect of temperature on this spectrum were also examined and we see very similar results; general broadening of the peaks and evening out of the peak intensities of the two bands above 270 nm. It is important to note that although the general trends of the changing spectrum are similar, the temperatures are not comparable and we do not see the broadening that the experimental spectrum captures, even at 1000 K. This is due to additional effects that will affect the experimental spectrum, such as the increased occupation of different rotational levels and variations in the molecular structure.



(a) Experimental spectra adapted from PhotochemCADTM.⁸⁰



(b) Experimental spectra adapted from Canadian Journal of Chemistry.⁸¹



(c) Experimental spectra adapted from Journal of Quantitative Spectroscopy and Radiative Transfer.⁸²

Figure 46: Different experimental spectra found in literature for naphthalene, green vertical line at 280 nm is shown for comparison.

Subsequently, a full vibrational analysis of naphthalene was therefore conducted. The first figure (Figure 47) shows the full computed spectrum with both high energy and low energy bands, the vibrational analysis of these were separated and presented after the full spectrum (Tables 8 and 9 and Figures 48 and 50). Figures 49 and 51 show the vibrations relevant to these spectra.

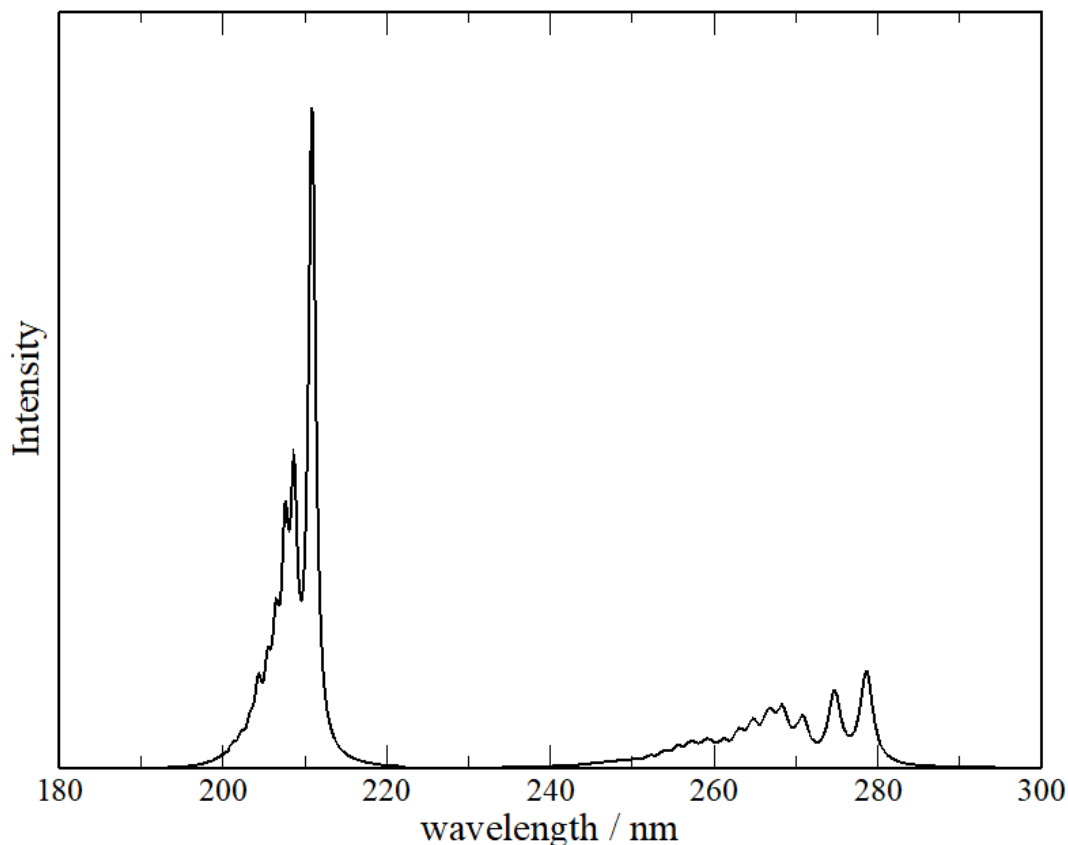


Figure 47: Total calculated spectrum of naphthalene.

The full spectrum includes a low and high energy band, the higher energy band centred around 208 nm has a significantly higher intensity. This reproduces the behaviour seen in experiment although the experimental results are often presented as two separate spectra. Exploring the two separately allows for more detailed comparison to experiment, particularly of the lower energy lower intensity band which is overshadowed in the full spectrum.

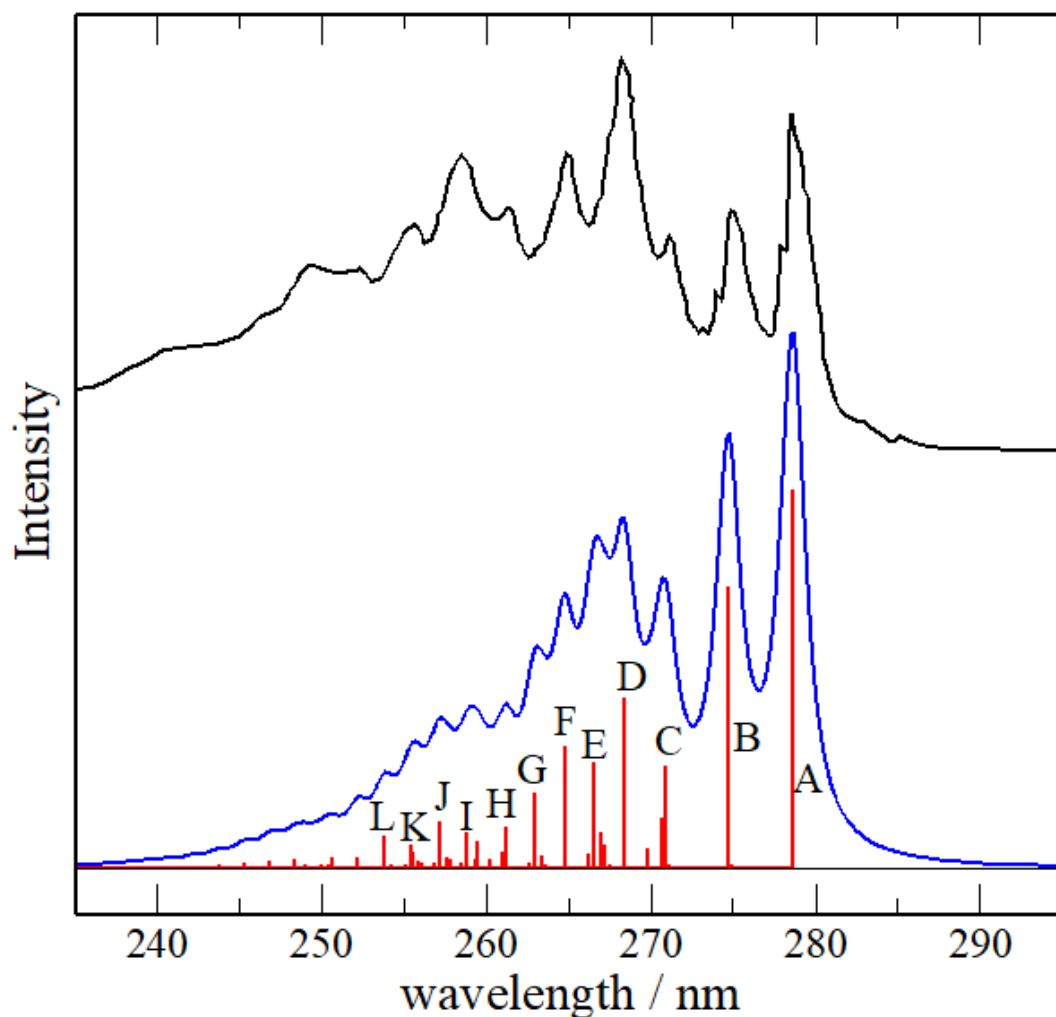


Figure 48: Calculated vibrationally resolved low energy band of naphthalene, computed spectrum in blue with vibrational stick spectrum in red, shifted to match experimental spectrum in black above.

The agreement between calculated and experimental spectra is good, although some minor features in the experimental spectrum haven't been reproduced in the calculation. In particular the higher energy side of the band provides a less accurate description of the experiment.

The calculations predict the most intense peak to correspond to the 0-0 vibrational transition of the molecule, but we actually see in the experiment that the most intense peak is the one which corresponds to band D (ν_{33}). There are also noticeable minor peaks associated with the A peak and B peak, at a slightly

higher energy. Without further investigation, any hypotheses about these features are speculative, but these could be due to isotope effects or different temperatures.

Band	Wavelength / nm	Assignment
A	278.6	0-0
B	274.7	ν_8
C	270.9	$2\nu_8$
D	268.4	ν_{33}
E	266.5	ν_{40}
F	264.7	$\nu_8 + \nu_{33}$
G	263.0	$\nu_8 + \nu_{85}$
H	261.2	$2\nu_8 + \nu_{33}$
I	258.8	$2\nu_{33}$
J	257.1	$\nu_{33} + \nu_{40}$
K	255.5	$\nu_8 + 2\nu_{33}$
L	253.8	$\nu_8 + \nu_{33} + \nu_{40}$

Table 8: Assignment of vibrational modes in the low energy band of the naphthalene spectrum.

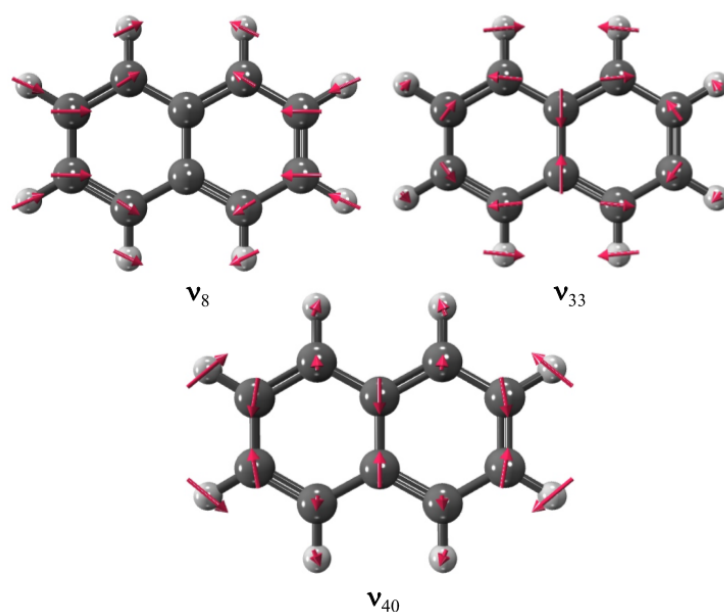


Figure 49: Vibrations of naphthalene associated with low energy band.

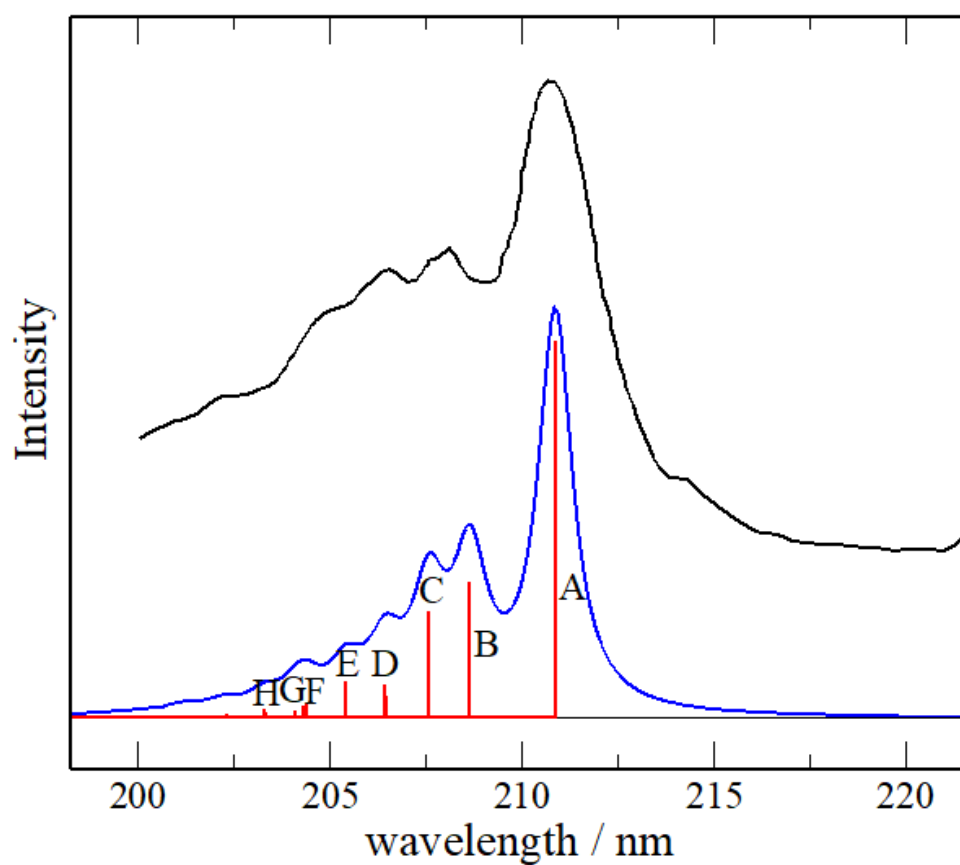


Figure 50: Calculated vibrationally resolved high energy band of naphthalene, computed spectrum in blue with vibrational stick spectrum in red, shifted by 0.2 eV to match experimental spectrum in black above.

Band	Wavelength / nm	Assignment
A	210.9	0-0
B	208.7	ν_6
C	207.6	$2\nu_{12}$
D	206.4	ν_{24}
E	205.4	$\nu_6 + \nu_{12}$
F	204.4	$2\nu_{12}$
G	204.3	$\nu_6 + \nu_{24}$
H	203.3	$2\nu_{12} + \nu_{24}$

Table 9: Assignment of vibrational modes in the high energy band of the naphthalene spectrum.

The features of this high energy band are also well reproduced compared to the experimental spectrum. Interestingly there is a minor band at slightly lower energy than the 0-0 band, at approximately 214 nm. This is not reproduced in the computational spectrum but this may be due to the lower temperature at which this was calculated. Given that this transition has a lower energy than the 0-0 band, it is possible that is due to a transition from a vibrationally excited electronic ground state to the vibrational ground electronic excited state.

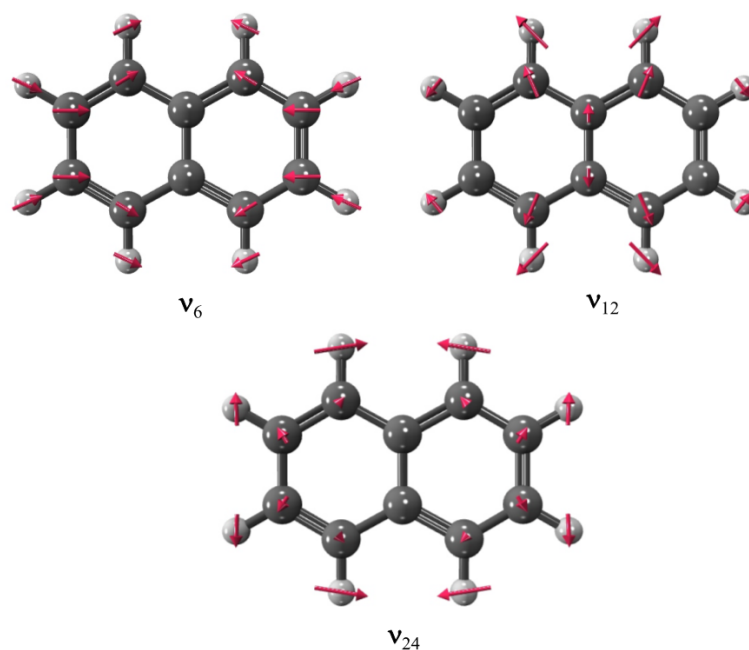


Figure 51: Vibrations of naphthalene associated with high energy band.

4.3.3 Coronene

The final PAH studied here was coronene, although this is by no means the full scope of the possible molecules that could be studied. The optimised geometry of coronene is pictured in Figure 52. Coronene is significantly larger than the two other hydrocarbons studied in this work. The size of coronene makes the calculation of the spectra considerably more computationally demanding.

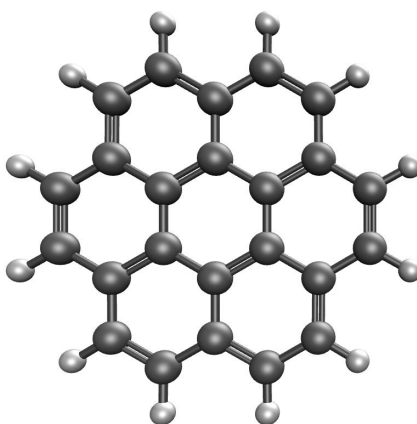


Figure 52: Atomic structure of coronene molecule.

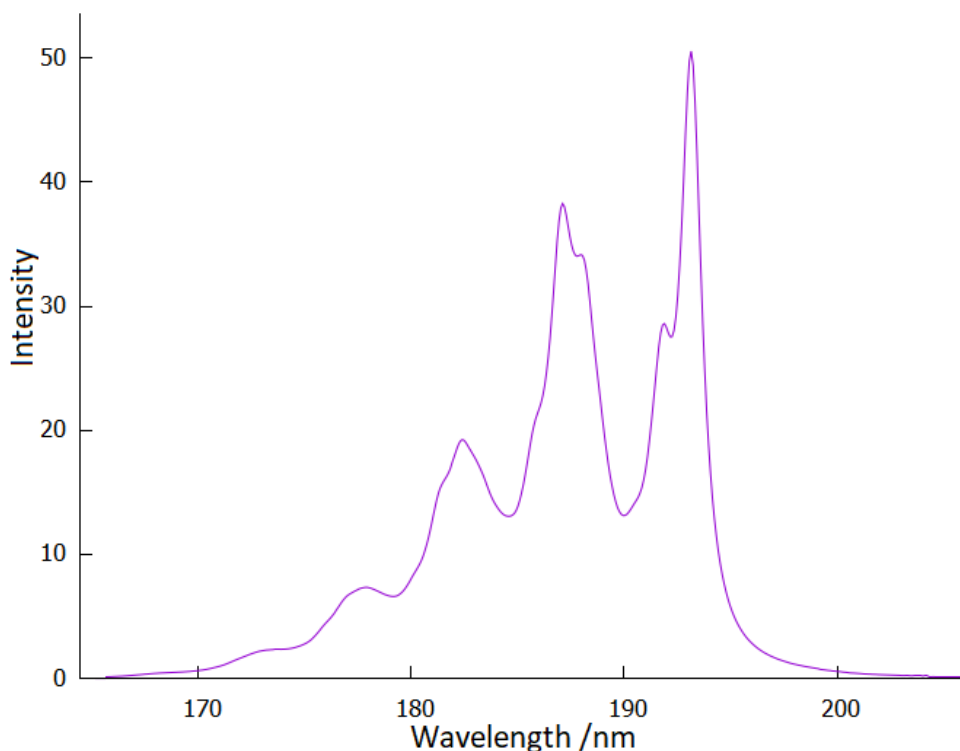


Figure 53: Computational spectrum of coronene.

The calculated spectrum of coronene is in Figure 53. We can see that this again has clear vibrational structure, with a familiar pattern that seems common among all of the vibrationally resolved spectra where the lower energy transitions have higher intensities. There is a strong, sharp peak at approximately 192 nm which corresponds to the 0-0 band, and there are four distinct peaks of higher energy. A detailed comparison with experiment has not been performed for coronene since the available spectra^{83,84} are relatively old data from 1942 which are not sufficiently well resolved.

4.4 Conclusions

The results presented show that DFT and TDDFT calculations provide a framework for simulating the vibrationally resolved UV/Vis spectra of PAHs. Both pyrene and naphthalene calculated spectra match well with the experimental re-

sults. The vibrational assignments for both naphthalene and pyrene have been discussed. This is a concise method to begin exploration into UV/Vis spectroscopy as a method to understand DIBs rather than the more traditional IR studies, backed by the previous experimental work.

The potential scope of this is vast given the number of PAHs that could potentially be examined. However naturally the size of the molecules make a significant difference to the size of the calculation and therefore limit the use with larger structures. While coronene was studied in brief, extending the molecules much past this size needs to be considered in depth with reference to computational cost. However, the DFT and TDDFT methods used here can be applied to study larger systems in contrast to, for example, coupled cluster wavefunction based approaches. A potentially more scientifically significant avenue for future research is broadening the molecules to start to consider different charged states, particularly given the links made in experiment to these charged molecules and diffuse interstellar bands. Some experimental studies have also linked hydrocarbons which contain heteroatoms with the diffuse interstellar bands, as well as non-planar hydrocarbons. Both of these would also offer an interesting avenue for further investigation.

Chapter 5

Investigation of Electronic Transitions of Gold Diphosphine Complexes

5.1 Background

Transition metal complexes were discussed broadly in the introduction. In this work we consider the spectroscopy of gold based complexes as a part of a collaboration with the experimental group of Prof Tunik at the University of St. Petersburg. A range of gold complexes were synthesised by the Tunik group that required further computational investigation, particularly with a focus on their photophysical properties. To put these complexes into a broader chemical context, the Tunik group works primarily on developing molecules within the context of organic light emitting diodes, or OLEDs. Historically, OLEDs are often iridium or platinum complexes, but there is scope to use a variety of different metal atoms. Interestingly, OLED development is related to PAHs because much of the history and development of OLEDs came from the luminescence of anthracene and related PAH compounds.

The complexes studied contain two gold atoms, which are bonded to two different ligands. The first is an alkyne which breaks to form a covalently bonded alkene ligand, and the second is a phosphine ligand, which is formally neutral and so donates the lone pair. The phosphine ligands are both bonded to a single aromatic centre, which is what links the two gold atoms together. These ligands mean the gold atoms are in a +1 oxidation state, and with investigation it was determined that the complexes had a singlet ground state. This will be discussed in more detail later.

The reaction scheme for all of these complexes is outlined in Figure 54, with some indication of the numbering of the complexes below.

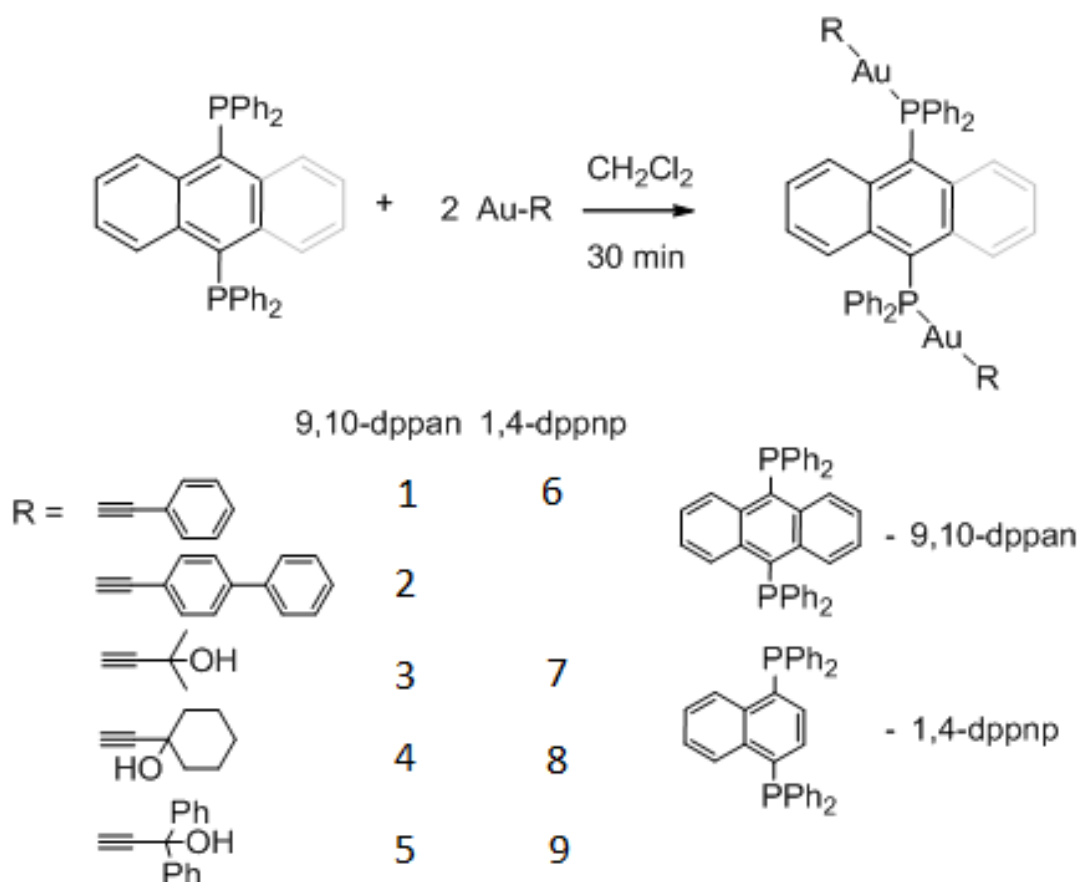


Figure 54: Reaction scheme for synthesis of gold phosphine complexes, outlining the numbering system used in the following chapter.

The complexes exhibited unusual luminescence properties, which was the motivation to investigate them further with computational methods. Although it is usually metal atoms which are responsible for unusual spectroscopic behaviour, it is important to note that these molecules contain either a naphthalene or anthracene fragment. Interestingly, the presence of naphthalene or anthracene seems to determine the type of luminescence the molecule exhibits, and it was of interest to understand how this change influences the photophysical properties.

Experimentally the complexes were characterised in both solution and solid state, although the computational results are in the gas phase. The synthesis of the complexes is reasonably simple and finishes within an hour. This means that an extensive set of complexes has been synthesised, which gives the scope to investigate a range of differently structured factors.

5.2 Computational Details

Since charge-transfer bands could play a significant role in the UV/Vis spectroscopy of these complexes, the spectra were calculated with the CAM-B3LYP functional, due to the long range correction that is built into the functional,³⁹ which was discussed in more depth in Chapter 2.

The photophysical data was obtained experimentally by the Tunik group for all complexes 1-5, 6-9 and 10-13. Both the structures were optimised and the absorption spectra have been calculated computationally using CAM-B3LYP/SRSC for all complexes. The SRSC basis set corresponds to the Stuttgart Relativistic small core basis set for the gold atoms and the 6-311G* basis set for all other atoms.

5.3 Results and Discussion

5.3.1 Geometry Optimization Results

One of the first steps in a computational study is a geometry optimization, but for this work this also gave us a useful opportunity to compare the geometry calculated with the crystal structure determined experimentally. This allows the theoretical method used in terms of exchange-correlation functional and, to some extent, basis set to be assessed. Figures 55 to 58 below show a comparison between x ray diffraction (XRD) results and computational results.

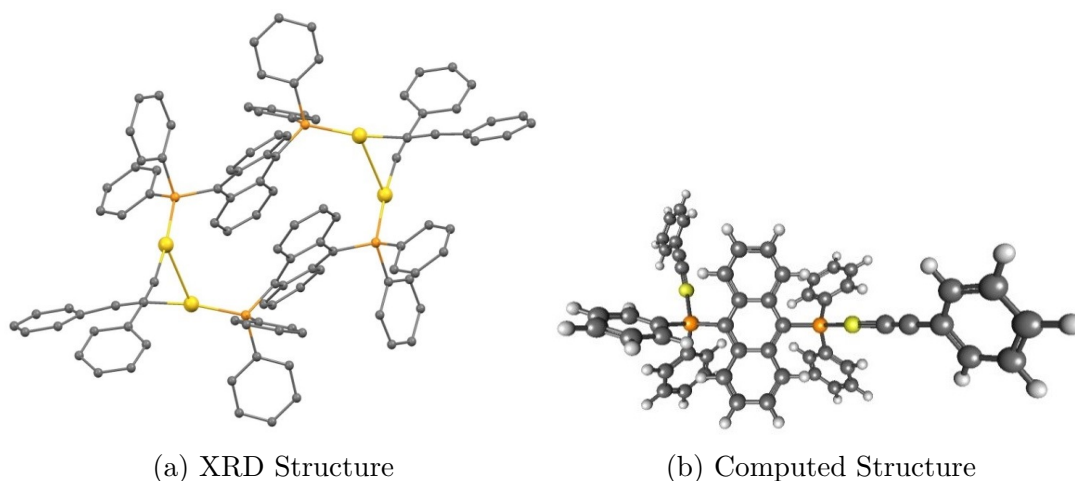


Figure 55: Comparison of experimental x-ray diffraction and theoretical atomic structures for complex 1.

The XRD structure determined for complex 1 is clearly a dimeric complex. This is not mirrored in the computational results, simply because the calculations considered a single molecule. Obviously this could be confirmed by optimization of the dimer but the experimental results were performed in solution, where the dimerization is unlikely to be preserved.

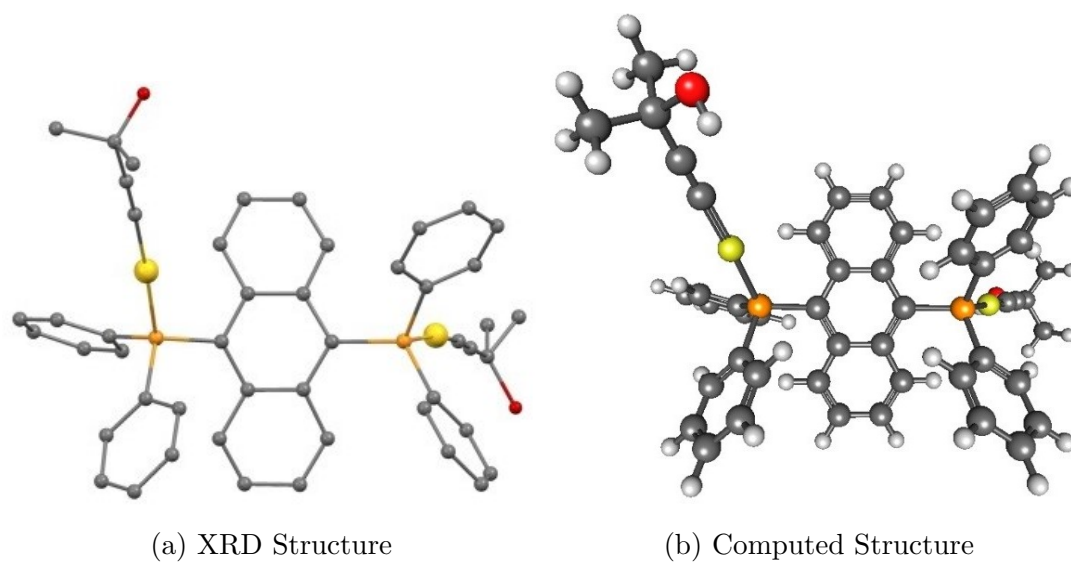


Figure 56: Comparison of experimental x-ray diffraction and theoretical atomic structures for complex 3.

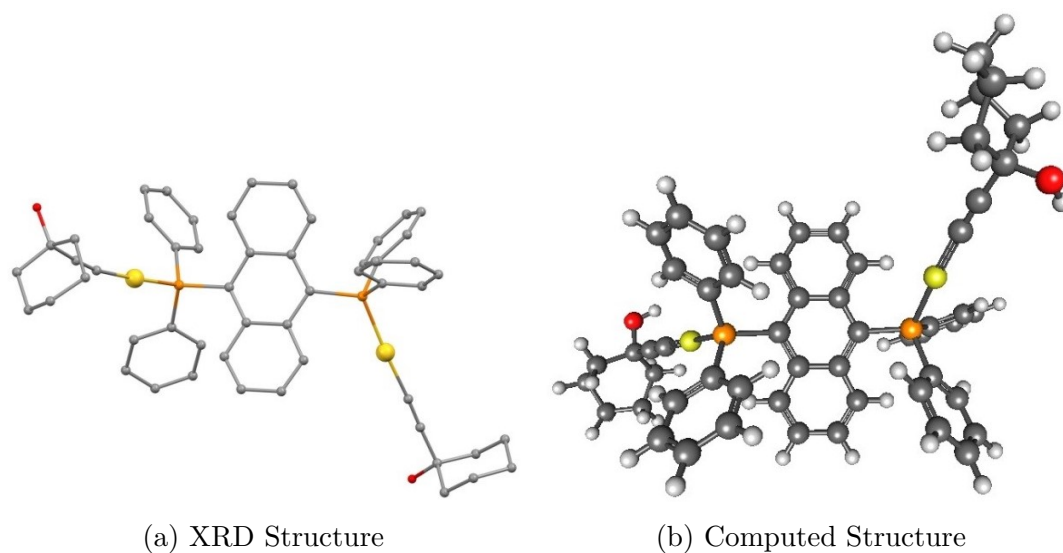


Figure 57: Comparison of experimental x-ray diffraction and theoretical atomic structures for complex 4.

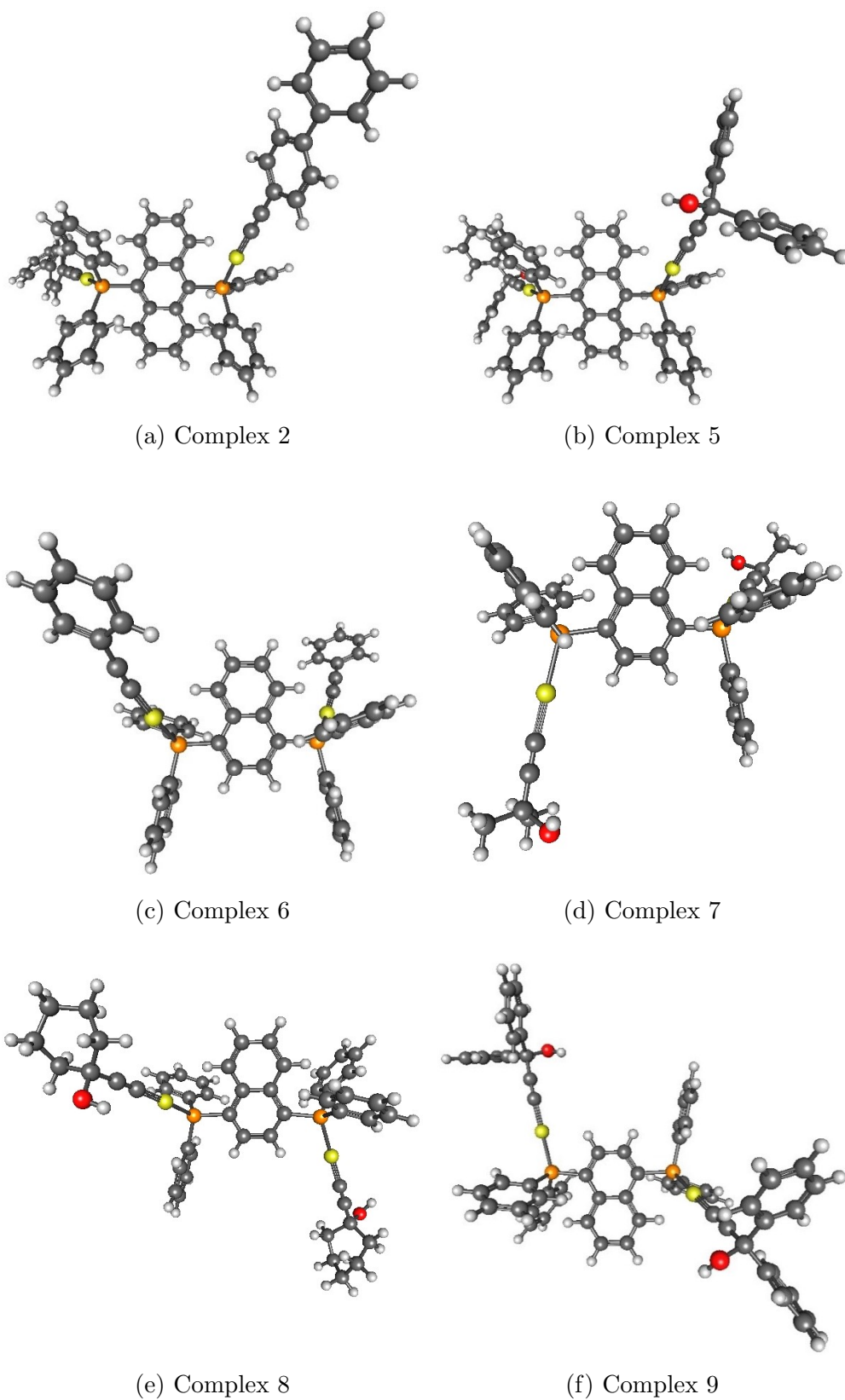


Figure 58: Computational atomic structures for complexes 2, 5, 6, 7, 8 and 9. All of these molecules have no XRD structures for comparison.

Examining the complexes by eye, the computational and XRD results look similar. There is a curvature of the naphthalene/anthracene centre in the DFT results which is not observed in the XRD.

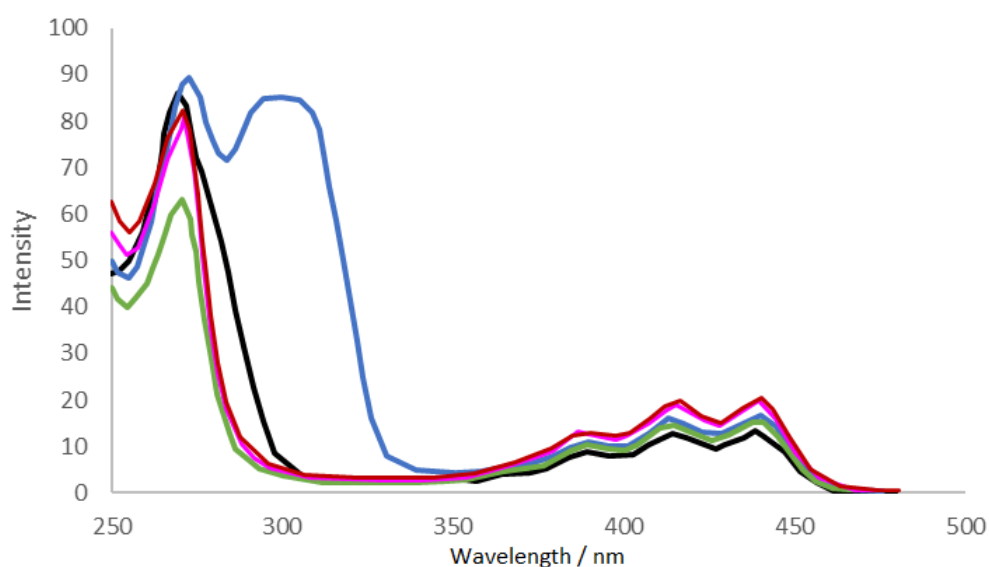
For some of the complexes, XRD is not available, presumably due to problems with crystallisation of the compounds. Therefore in these cases the DFT results represent our best prediction for solid state structure. The agreement for the complexes for which both DFT and XRD results are available is therefore reassuring for these cases with no crystallographic data as well.

There are some notable differences between the results, but none that would significantly impact the UV/Vis spectra. The experimental and computed geometries of **3** are optical isomers of each other but it would offer little benefit to attempt to change this in the computed results as it shouldn't change the UV/Vis spectrum. More significantly, **9** seems to be a slightly different geometry. This shouldn't have a significant impact because the difference between the two is simple rotation of single bonds, which would all be sampled at room temperature. However it may have a small impact on the UV/Vis spectra because they are formally different energies, despite being a small change in geometry.

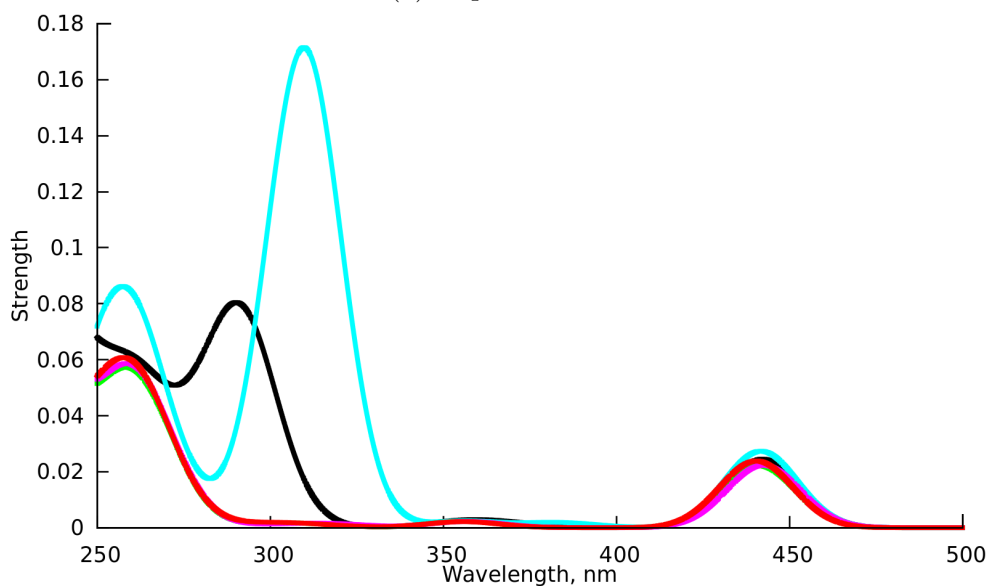
Because of the size of the systems, vibrational frequency calculations were not performed. Therefore it is not guaranteed that the stationary points found represent minima, however the agreement with experimental results was enough to continue. If the geometry optimization results needed to be quantified further, either comparative RMSD with the experimental results or vibrational analysis could be done. Given that the geometry results themselves were a starting point rather than a focus, this was not pursued.

5.3.2 Absorption Results

Although emission is the primary concern when it comes to the development of potential complexes for OLEDs, absorption was the first photochemical aspect studied.



(a) Experimental



(b) Theoretical

Figure 59: Comparison of experimental and theoretical spectra of gold complexes 1-5, with experimental above and computed below. Black is complex 1, blue is complex 2, green is complex 3, pink is complex 4 and red is complex 5.

At first inspection of Figure 59, the experimental and theoretical results for 1-5 do not seem to agree. However when comparing the peaks directly we can see a reasonable agreement. The calculated positions are consistently lower than the experimental positions, which implies a systematic difference between the two, this could be a solvent effect or associated with the exchange-correlation functional. We can therefore shift the theoretical spectra by 0.4 eV to more closely resemble the measured experimental spectra.

This shifted spectrum bears a closer resemblance to the experimental spectrum, although the vibronically resolved peak around 415 nm seems a little high. We have also lost the end of the peak that is lower than the experimental range of the spectrum, but can be seen on the experimental and initial theoretical spectrum.

Complex(es)	Experimental position (nm)	Calculated position (nm)
1-5	270	237
1	Shoulder (280)	266
2	305	282
1-5	370 (?)	325
1-5	385	387
1-5	415	387
1-5	445	387

Table 10: Table to compare experimental and computational peak positions of complexes 1-5. Computational peak positions are before shifting.

Another important aspect of consideration is the transitions that these peaks in the UV/Vis spectra represent.

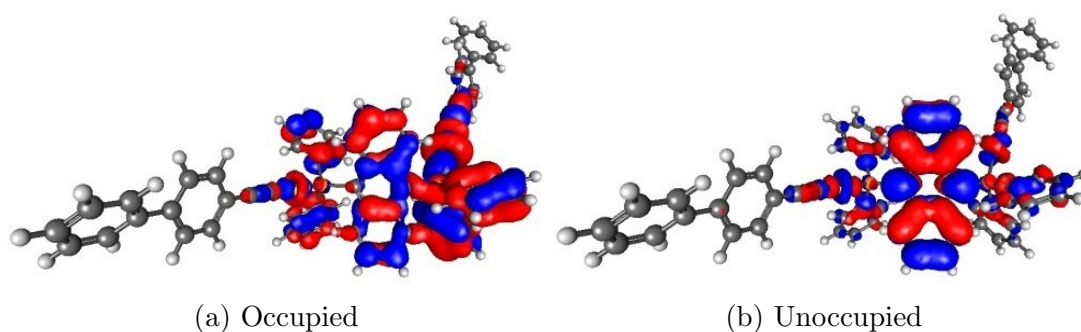


Figure 60: Molecular orbitals associated with the electronic transition of complex 1-5 for the band centred around 237 nm.

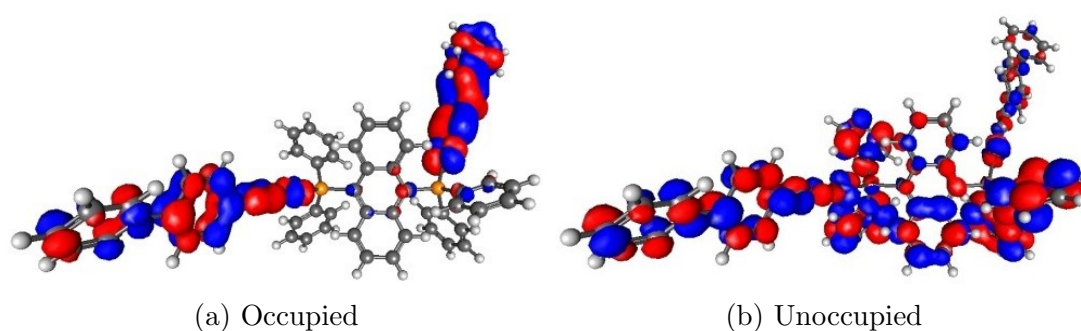


Figure 61: Molecular orbitals associated with the electronic transition of complex 2 for the band centred around 283 nm.

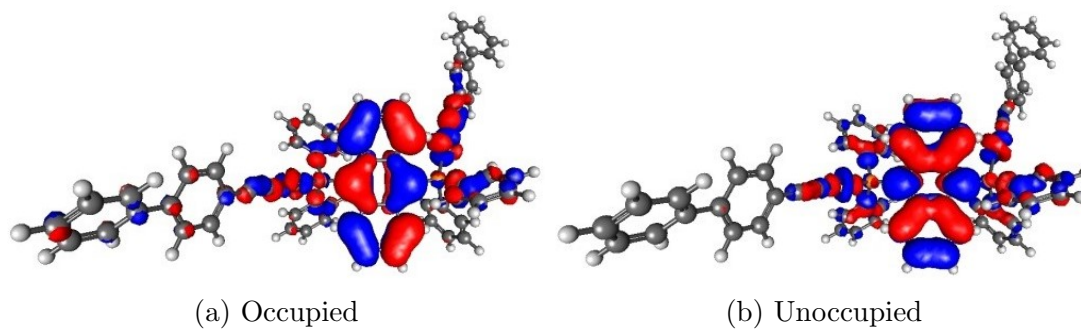


Figure 62: Molecular orbitals associated with the electronic transition of complex 1-5 for the band centred around 387 nm.

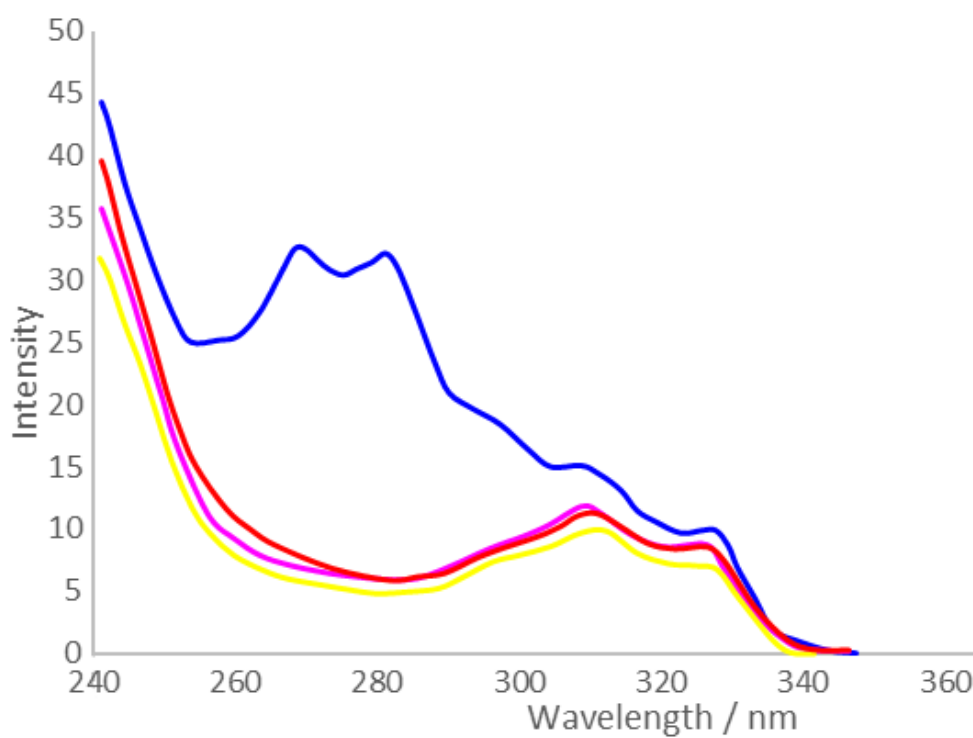
When examining the molecular orbitals, we see that the peaks that feature in all of the spectra (237 and 387) are based on the anthracene centre. This is as we would expect because it is the only part of the molecules that remains constant when the ligands are changed.

The transition that is only seen in 2 (282) is electron transfer from the conjugated ring systems to the rest of the molecule. The presence of this transition in 2 alone can be rationalised by comparing the ligands that are being used. Complex 2 has an extended conjugated system so we see a significant peak that deviates from the spectra of the others. Complex 1 has a single conjugated ring, which explains the slight deviation from the spectra of the other complexes (a shoulder in the experimental spectra), but it is not as prominent as the peak in 2.

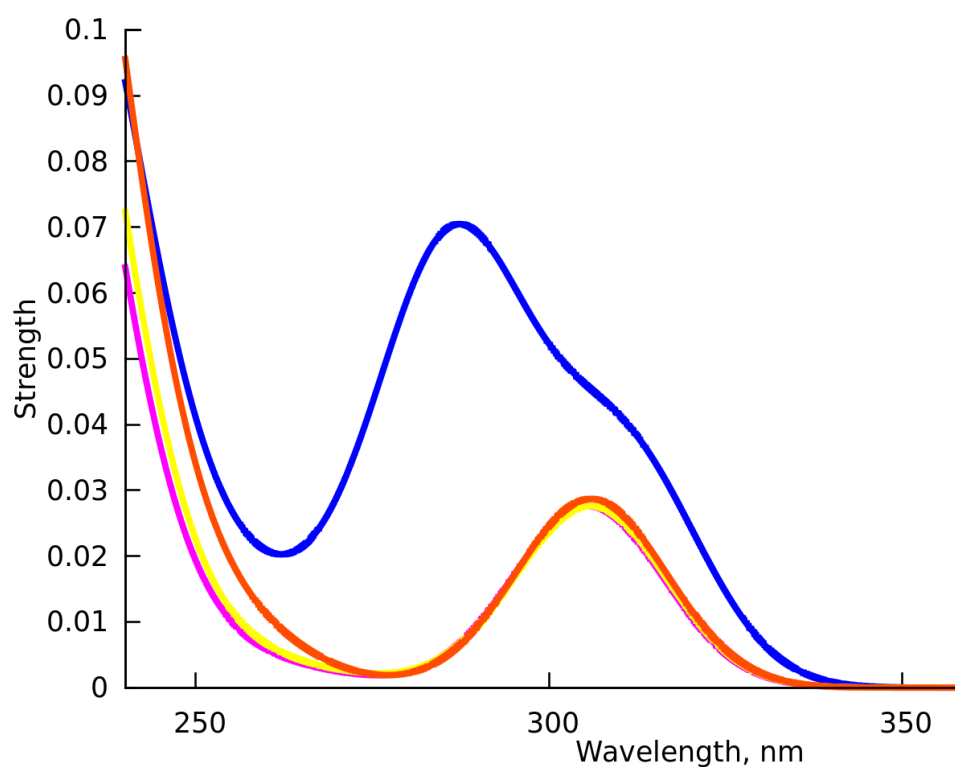
We believe that the set of three peaks centred around 415 nm for the anthracene based complexes are a result of vibrational structure being seen in the electronic spectrum. Given that the spacing between the vibrationally resolved peaks is consistent across the different complexes, we would expect that again these corresponded to vibrational modes which are localised on the anthracene centre.

The spacing between the vibrationally resolved peaks has been calculated to be 1408, 1746, 1367 cm^{-1} . We would therefore expect the vibrations to be in a similar order. We cannot quantitatively assign the peaks to vibrations, but we do see vibrational modes that are localised to the anthracene centre around 1000 cm^{-1} (903, 971, 1028, 1063 etc.). This supports the idea that these peaks correspond to vibronic structure.

We can now look at systems 6-9 and again we find some similarities when comparing experimental and computational results. Again we shifted the computed spectra by 0.4 eV, to improve agreement with the experimental spectra. This supports the idea that the shift is due to a systematic difference between the experimental and computed spectra, like solvent effects.



(a) Experimental



(b) Theoretical

Figure 63: Comparison of experimental and theoretical spectra of gold complexes 6-9, with experimental above and computed below. Blue spectra is complex 6, pink spectra is complex 7, yellow spectra is complex 8 and red spectra is complex 9.

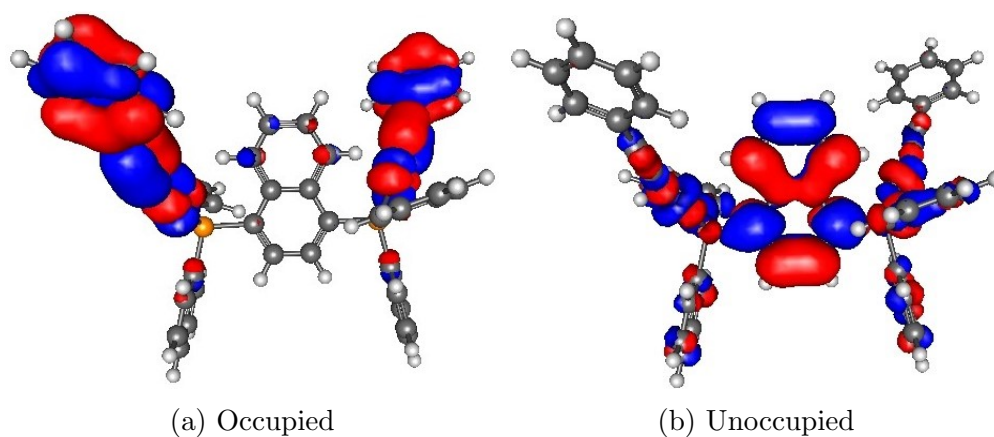


Figure 64: Molecular orbitals associated with the electronic transition of complex 6 for the band centred around 283 nm.

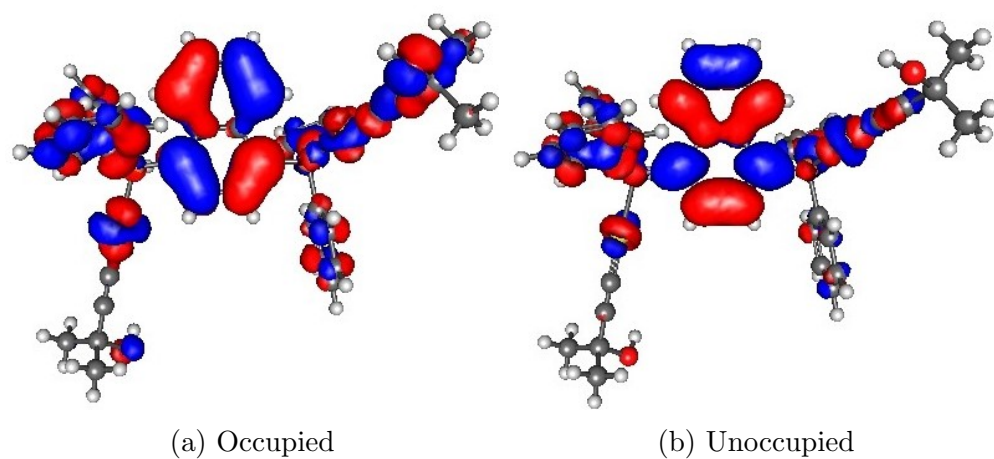


Figure 65: Molecular orbitals associated with the electronic transition of complex 7 for the band centred around 278 nm.

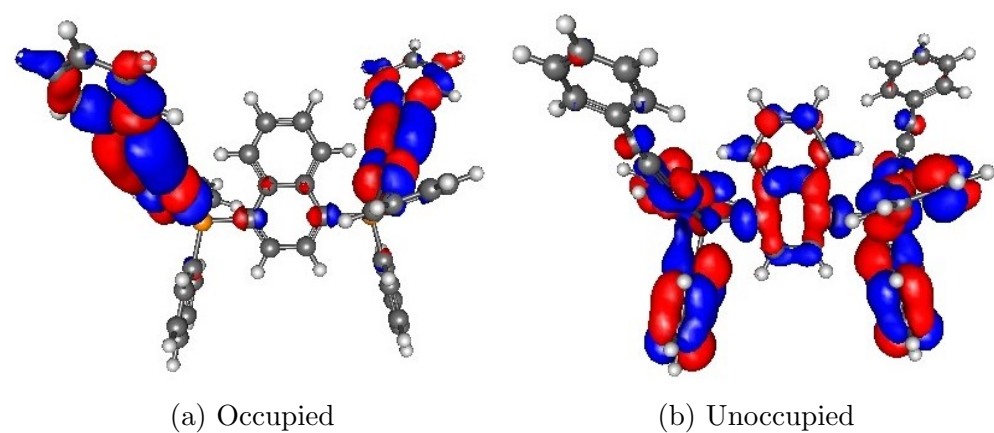


Figure 66: Molecular orbitals associated with the electronic transition of complex 6 for the band centred around 217 nm.

It is interesting to note that the conclusions made with the complexes 1-5 are less clear cut in the 6-9 complexes if we consider complex 6 alone. The peak that appears in the spectrum of complex 6 only (217 nm) is a transition which starts at an orbital localised on the ligand. This is as expected because it is the unique section to the specific complex.

However if we examine the band that appears consistent across all of the complexes using complex 6 as an example, this appears to look very similar to the transition at 217 nm, also having the occupied orbital localised on the ligand. This is difficult to rationalise because it isn't possible that this could be consistent across all of the molecules, despite the band being present for all of them. Therefore complex 8 was also used to investigate the transitions, and see that in this case, both orbitals are localised across the molecule, including the central naphthalene. This is as we expect given that it is a transition which occurs in all of the complexes.

5.3.3 Investigating Emission

Since the calculations are able to describe the main features in the absorbance spectra the emission was also studied. Experimentally, it was determined that the naphthalene based structures emitted via fluorescence and anthracene based complexes via phosphorescence. This is curious because the difference in backbone is reasonably minor, and as a bare molecule they actually exhibit the opposite types of emission.^{85,86} It was postulated that the primary source of investigation should be the gold atoms, because of the heavy atom effect, despite the atoms in the two types of complex seeming to be in similar environments. The heavy atom effect is the concept that the presence of a heavy atom, like gold, will enhance the rate of a spin forbidden process, like the intersystem crossing step in phosphoresence.⁸⁷

A first step in this study was to explore the emission energies from the S_1 and T_1 states of the complexes in order to see how these compared with the observed emission energies. The triplet emission energies have been determined using DFT and TDDFT, while the S_1 emission energy is only determined using TDDFT.

	1	2	3	4	5
Triplet (DFT)	0.055	0.056	0.055	0.055	0.549
Triplet (HF/TDDFT)	0.078	0.083	0.078	0.080	0.084
Singlet (HF/TDDFT)	0.105	0.111	0.122	0.124	0.126
Experimental	0.094	0.096	0.096	0.095	0.095

Table 11: Comparison of emission energies (eV) from various states and computational methods with experiment. Computational energy closest to experimental energy highlighted in blue.

	6	7	8	9
Triplet (DFT)	0.097	0.098	0.097	0.098
Triplet (HF/TDDFT)	0.115	0.116	0.118	0.123
Singlet (HF/TDDFT)	0.131	0.141	0.148	0.145
Experimental	0.130	0.130	0.130	0.130

Table 12: Comparison of emission energies (eV) from various states and computational methods with experiment. Computational energy closest to experimental energy highlighted in blue.

The results are shown in Tables 11 and 12 and the computational result closest to the experimental number has been highlighted in blue. The results show some significant variation between the triplet emission energies determined using DFT and TDDFT. For complexes 1-5 the experimental emission energies lie between the calculated singlet and triplet emission energies, making it difficult to make definitive conclusions from this analysis.

From existing studies, we know that the metal orbitals play a key role in inter-system crossing. This is often associated with the heavy atom effect, which was discussed earlier, but is essentially the idea that the presence of a heavy atom, in this case the gold atoms, can enhance the intersystem crossing and therefore improve the chances of phosphorescence.⁸⁸ However, given both types of complex contain the same heavy atoms, more analysis in terms of the metal atoms need to be undertaken.

Some previous studies⁸⁹ have examined the metal orbitals qualitatively to assess their relevance in luminescence, and so this was attempted for these complexes. The HOMO and LUMO of each complex was examined, as these are the orbitals that correspond to the transition we are interested in. While we can see this is a charge transfer transition from ligand to metal, and we can see similarities in the MO shape, it isn't immediately clear if the orbital shape is responsible for the difference in emission. Qualitatively, it looks as though the metal based orbitals on complexes 7-10 more closely resemble traditional d orbitals, which is a promising sign. However the MO coefficients seem to show a more mixed picture. MO coefficients should give an indication of the 'amount' of the orbital based on each atom, and therefore how much that atom is contributing to the orbital.

Natural Bond Order (NBO) analysis was used instead to assess the part that the gold atoms play. NBO analysis gives a quantitative picture of the amount of electrons based on each atom, much like the comparison of MO coefficients, and therefore gives a more robust way to compare the different complexes,⁹⁰ given the fact that the type, number and position of the heavy atom was consistent across both types of complex. The results are presented in Table 13 below.

Complex	Ground	Excited
1	157.347	157.319
2	157.338	157.326
3	157.354	157.281
4	157.350	157.350
5	157.350	157.308
6	157.362	157.338
7	157.371	157.368
8	157.361	157.360
9	157.349	157.357

Table 13: NBO analysis results of complexes 1-5 and 6-9, comparing the number of electrons based on the gold atoms.

These results offer the most promising answer for rationalising the emission differences, because we do see some patterns between the two different types of complex. The most promising indicator between the NBO analysis and the luminescence behaviour is simply that the amount of electrons based on the gold atoms is higher for complexes 6-9 compared to 1-5. Remembering that 1 and 6 are comparable in terms of ligand, we can see a difference of approximately 2%

of an electron in the ground state and 1% in the excited state. 2 does not have an equivalent. The difference between 3 and 7 is again approximately 2% in the ground state and 9% in the excited state. The difference between 4 and 8 is 1% in both ground and excited states, and it is interesting to note that the difference between ground and excited states in both cases is minimal, in contrast to the other complexes. 5 and 9 do not follow the trend as 5 has a higher electron count than 9 by 0.1% of an electron in the ground state. The general pattern is followed in the excited state where 9 has a higher electron count by 5% of an electron.

This is not the only way in which these NBO results differ for 5 and 9 compared to the other results. For all other complexes, both naphthalene centre and anthracene centre, the ground state has more electrons based on the gold atoms than the excited state. Complex 9 does not behave like this and instead we see that the excited state has a higher number of gold based electrons.

There were other effects briefly considered but none that offered a more useful or clear picture of the reasons behind the difference. These included the differences in geometry, which was quantified using Kabsch RMSD. There was not a significant pattern between the type of emission and either the difference in geometry between ground and excited states or, perhaps more relevant, between the singlet and triplet excited states. It is this geometry change which would impact inter-system crossing and therefore the emission type. This is as expected because the spectra are measured in solution so some tumbling and geometry changes would be expected, as well as the movement of thermal energy generally. Solvent effects were considered but haven't been taken into account because there is no reason to expect that they would have a significant difference based on the different type of complex.

5.3.4 Additional Complexes

As the work progressed, additional complexes were synthesised and characterised in a similar way to the initial set, and these were then studied as well, primarily from an absorption perspective. First the complexes were optimised, unfortunately with no crystallography data to compare with. The optimised structures are shown below, in Figure 67.

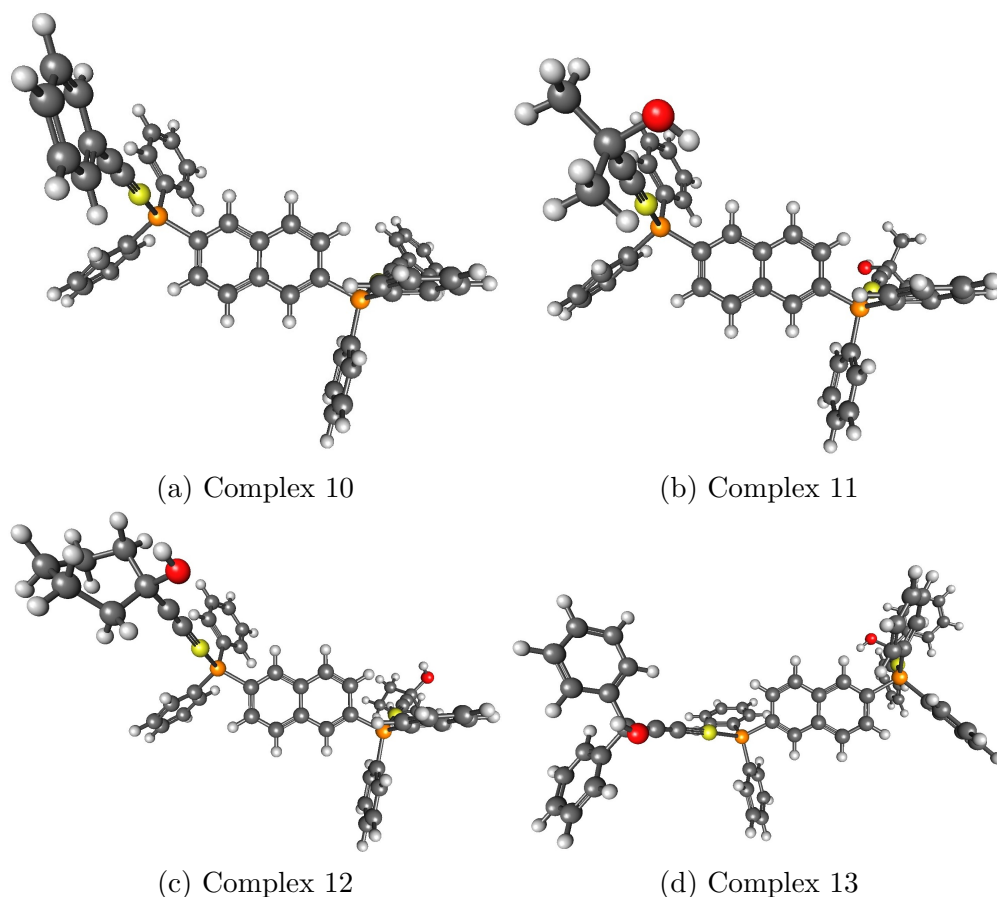
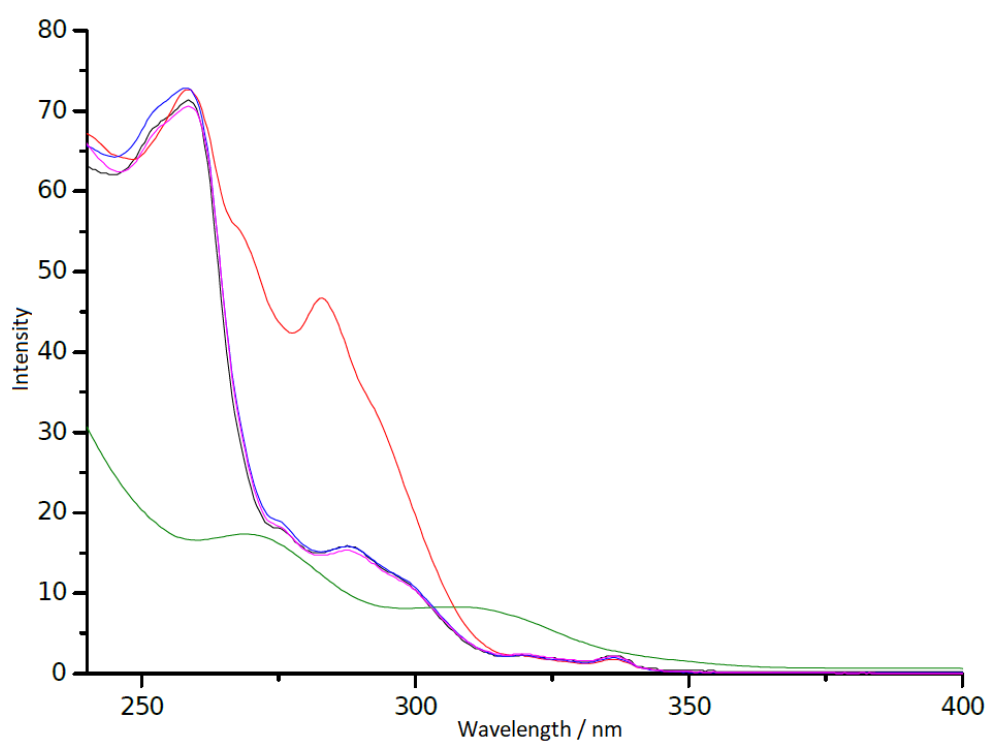
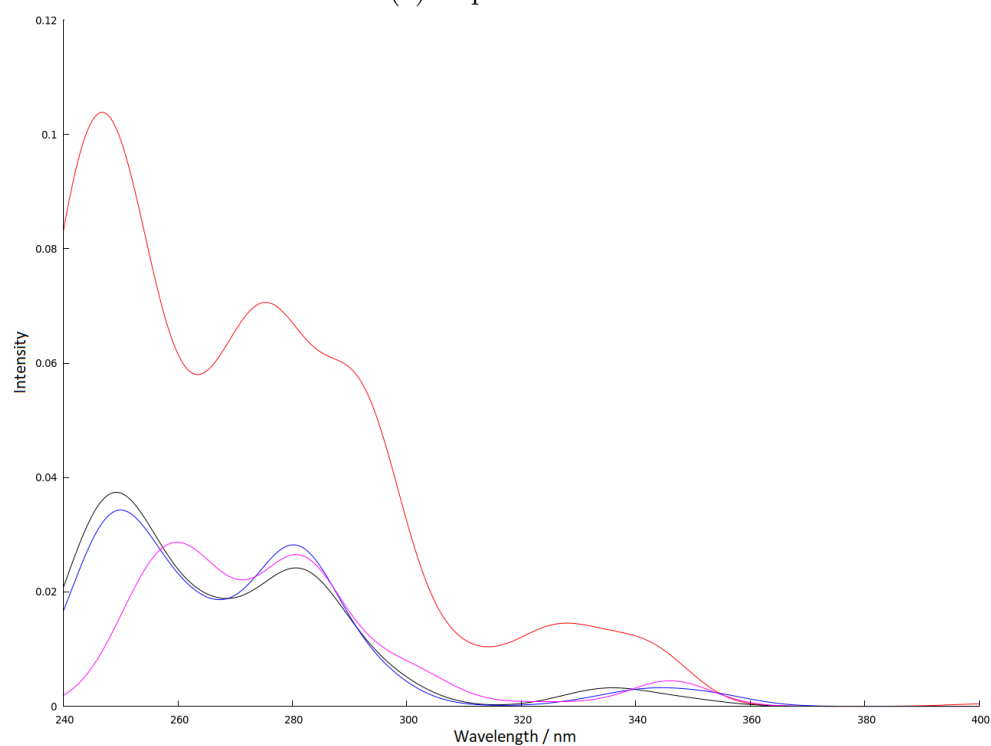


Figure 67: Computational atomic structures for complexes 10-13.

The primary difference between these new complexes and the complexes previously studied is the relative positions of the ligands. Whereas the previous structures had the two gold complexes across from each other in 1,4 positions on the same ring structure, these new structures are further from each other, in 2,6 positions on different rings.



(a) Experimental



(b) Theoretical

Figure 68: Comparison of experimental and theoretical absorption spectra of gold complexes 10-13, with experimental above and computed below. Green is the 2,6-dppnp fragment (experiment), red is complex 10, black is complex 11, blue is complex 12 and pink is complex 13.

The absorption spectra were computed using the same procedure. Again there is good agreement between the calculated results and experimental data. We can see a common peak around 250 nm and another around 280 nm. It is somewhat difficult to assign these bands exactly because there is a debate to be had about whether the bands match directly. It is interesting and important to note that the structure of the spectrum of complex 10 is most significantly different from the others in both the theoretical and experimental sets of data. Some of these differences are common between both the experimental and computational results. Both spectra of complex 10 have a peak with a shoulder and an additional high wavelength peak which the spectra of the other complexes do not have.

5.4 Conclusions and Future Work

This chapter is only a glimpse into the work that can be done computationally in this area, and within the scope of this project alone there were still several complexes, computational methods and hypotheses that could be investigated. One of the most significant conclusions to be drawn here is the confirmation of the link between the gold atoms and the luminescence behaviour. While this conclusion draws on both scientific intuition and fundamental concepts, it is important to consider and confirm these ideas. This conclusion could not have come about without the foundations of the absorption results to build on. In a broader chemical context, this work demonstrates the use of computational chemistry for metal based systems and science, while potentially highlighting some stumbling blocks.

It seems a natural extension to the work in previous chapters to try to push the vibrationally resolved aspect of this work to include these systems, but this may result in a significant increase in computational difficulty and time with a limited

gain in knowledge. Vibrational analysis was conducted on the core aromatic system in order to confirm experimental conclusions about vibronic structure, but to fully resolve the spectra vibrationally would require a full vibrational analysis including metal atoms, which would be an incredibly large calculation and therefore have a high cost, which would not necessarily contribute to the conclusion to justify this cost.

Chapter 6

Final Remarks

This is a short summary of conclusions and potential avenues for future work that can be drawn from all chapters, individual conclusions have been discussed in the relevant chapters.

6.1 Overall Conclusions

The most interesting conclusion that can be drawn is the use of both Q-Chem and FCclasses to model vibrational structure in UV/Vis spectra, which extends the use of UV/Vis spectroscopy models. This gives more insight into the exact vibrations and behaviours of the molecule studied, and has the potential to be implemented in other systems. As mentioned, more specific conclusions can be found in the relevant chapters, but broadly the computational spectra capture the shape of the experimental spectra in cases where they have been compared. Specific vibrations for different bands have been identified for several of these vibrationally resolved spectra.

Not all of the systems studied were modelled using vibrational structure. This work still pushed the modelling of UV/Vis spectroscopy, particularly the use of

transition metals in complex systems. Emission and luminescence were touched on briefly in order to hypothesise about differences between similar systems but this makes up a small portion of the work.

6.2 Future Work

Given that much of the work was built on collaboration with experimental groups, the work which could be pushed forward independently most readily is the PAH based chemistry. There is some scope to extend the studies which were conducted in collaboration with experimental groups, and the method could in principle be extended further to include other UV/Vis active molecules with vibrationally resolved spectra, although the size of the system would need to be taken into account. It would be good to extend the vibrationally resolved models to more complex systems, potentially including more inorganic systems and metals.

Formally polyaromatic hydrocarbons are limited to combinations of carbon and hydrogen, but heteroatoms could be included to extend the information. Specifically, it seems that the charged states of the PAHs have been linked with the diffuse interstellar bands.

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