Bachelor Project

Chemistry

Metal-organic complexes for
Time-Resolved Faraday Rotation Analysis

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Date: 5th July 2017

Abstract

We study the excited states of three metal-organic complexes: porphine platinum (PtP), a platinum cyanine (PtCY) and *fac*-tris(2-phenylpyridyl)iridium(III) (Irppy$_3$) to use in the Time-Resolved Faraday Rotation (TRFR) experiment. This technique can be used to find potential new materials for opto-electronic devices. The Frank-Condon factors for the lowest singlet $\rightarrow$ triplet excitations are calculated using unrestricted density functional theory. The focus here lies on the 0-0 line since a transition to the lowest vibronic state involves the least amount of energy loss. The excitation energies and oscillator strengths are calculated with spin-orbit coupling in a perturbative way to see whether the triplet excitation is possible. Unfortunately Irppy$_3$ does not seem to be a suitable candidate since its geometry changes too much. However, we observed promising Franck-Condon factors in PtP and PtCY that tell us that the research into metal-organic complexes for the TRFR experiment should be continued by for example using heavier metal centres.

Introduction

Research into opto-electronic devices has been largely focussed on inorganic crystals [1]. However, organic molecules are also suitable candidates because of their low costs, ease of processing and chemical tunability [2]. It is believed that organic molecules will also have applications in the field of spintronics [3], where a net electron spin is created. Controlling and probing triplet spin states is important in both opto-electronics and spintronics [2]. In optical polarization a net electron spin is created by absorption of circularly polarized light [4]. It seems a good method to control and probe triplet spin states. In materials with strong spin orbit coupling (SOC) spin-up and spin-down electrons couple to left- or right polarized light due to optical selection rules that rely on SOC [5]. These correlations between spin and optical polarization can be analysed with the Time-Resolved Faraday Rotation (TRFR) technique [2].

The aim of this research is to find suitable candidates to analyse with the TRFR experiment. In this pump-probe technique the optical rotation angle (polarization rotation) of a probe pulse is measured upon transmission trough a sample. This angle is a measure for the spin polarization induced by the pump pulse. Spin precession is reflected by the oscillation of the polarization rotation as a function of the time difference between pump and probe [2].

Candidate complexes are researched by calculating the Franck-Condon factors of the singlet $\rightarrow$ triplet excitation. A suitable candidate for the TRFR experiment will be a molecule with a strong 0-0 line, meaning a strong transition from the lowest vibrational state of the ground state to the lowest vibrational state of the first triplet excited state. A large 0-0 line is caused by a minimal change in geometry upon excitation. In a 0-0 transition there is no Stokes shift, meaning there is no energy loss in absorption and emission [4]. This will give the most efficient materials for opto-electronic devices. Also, a minimal change in geometry decreases the chance of undesirable photochemical processes upon excitation.

Metal-organic complexes containing a heavy metal centre typically have large SOC. Therefore in this research we will look at several of these complexes. Phosphorescent iridium(III) complexes have shown promising activities in organic light-emitting diodes (OLEDs) [6]. Smith *et al.* found large SOC in *fac*-tris(2-phenylpyridyl)iridium(III), referred to as Irppy$_3$. This means it is potent in singlet $\rightarrow$ triplet excitations, and interesting to investigate.

As mentioned before, a minimal change in geometry upon excitation is of importance. Unsubstituted porphine platinum (PtP) has a rigid structure. Therefore it is expected that it will undergo a minimal change in geometry upon excitation. Diaconu *et al.* found interesting photoluminescence activity in the zero-phonon region [5], which makes it interesting to investigate in this research.

Cyanine dyes have shown to have relatively small stokes shifts [7]. This is an important feature of a possible candidate for TRFR. Therefore we will investigate a metal complex of platinum with two cyanine dye ligands, PtCY. These three

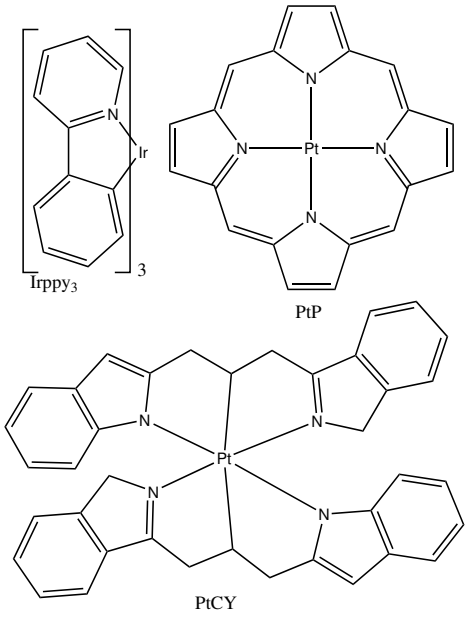

Figure 1: Irppy, PtP and PtCY

complexes are shown in figure 1.

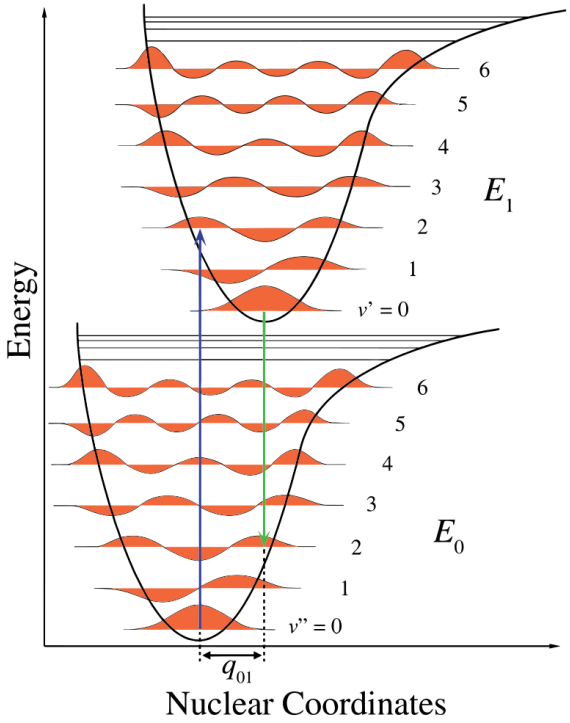

Figure 2: Franck-Condon Principle

Theory

In this section, three theories are discussed that are used in this research. These theories are: the Franck-Condon principle which is used to calculate Franck-Condon factors, the Hartree-Fock approach which is similar to the more complicated Density Functional theory used to calculate geometry optimizations and Spin-Orbit coupling which is used to calculate excitation energies.

Franck-Condon Principle

The Franck-Condon principle [8] [9] states that an electronic transition occurs within a stationary nuclear framework. That means that nuclei preserve their dynamical state during an electronic transition, hence the nuclear wavefunction stands unaffected when a transition occurs. Therefore, a transition from the lowest vibrational state of the lowest electronic state goes to the most similar vibrational state of the upper electronic state, undergoing the least change in dynamical state of the nuclei [10]. A visual representation of the Franck-Condon principle is shown in figure 2.

In a molecule, the electric dipole moment operator is given as:

$$\mu = -e\sum r_i + e\sum Z_I R_I = \mu_e + \mu_N \quad (1)$$

Where r_i and $-e$ are respectively the locations and charges of the electrons, and R_I and Z_I the locations and charges of the nuclei.
The vibronic state $|\varepsilon\nu\rangle$ of a molecule is described by $\Psi_e(\mathbf{r};\mathbf{R})\Psi_\nu(\mathbf{R})$ within the Born-Oppenheimer approximation. $\mathbf{r}$ denotes the collective electronic coordinates and $\mathbf{R}$ the collective nuclear coordinates. The electric dipole transition moment is therefore:

$$\langle \varepsilon\prime\nu\prime|\boldsymbol{\mu}|\varepsilon\nu\rangle = \int \boldsymbol{\Psi}^*_{e\prime}(\boldsymbol{r};\boldsymbol{R})\boldsymbol{\Psi}^*_{\nu\prime} \quad (2)$$
$$(\boldsymbol{R})(\boldsymbol{\mu}_e + \boldsymbol{\mu}_N)\Psi_\varepsilon(\boldsymbol{r};\boldsymbol{R})\Psi_\nu(\boldsymbol{R})d\tau_e d\tau_N =$$
$$\int \boldsymbol{\Psi}^*_{\nu\prime}(\boldsymbol{R})\left(\int \boldsymbol{\Psi}^*_{e\prime}(\boldsymbol{r};\boldsymbol{R})\boldsymbol{\mu}_e\boldsymbol{\Psi}_\varepsilon(\boldsymbol{r};\boldsymbol{R})d\tau_e\right)$$
$$\Psi_\nu(\boldsymbol{R})d\tau_N$$
$$+\int \boldsymbol{\Psi}^*_{\nu\prime}(\boldsymbol{R})\boldsymbol{\mu}_N\left(\int \boldsymbol{\Psi}^*_{e\prime}(\boldsymbol{r};\boldsymbol{R})\boldsymbol{\Psi}_\varepsilon(\boldsymbol{r};\boldsymbol{R})d\tau_e\right)$$
$$\Psi_\nu\nu(\boldsymbol{R})d\tau_N$$

For each selected value of **R** are the electronic states orthogonal to one another. Consequently, the integral over the electronic coordinates in the final term is zero. The remaining integral over the electronic coordinates is the electric dipole transition moment for nuclear coordinates **R**. As long as the locations of the nuclei are not largely displaced from equilibrium the transition moment is independent of these locations. So the integral is approximated to $\boldsymbol{\mu}_{\varepsilon\prime\varepsilon}$:

$$\langle \varepsilon\prime\nu\prime|\boldsymbol{\mu}|\varepsilon\nu\rangle = \boldsymbol{\mu}_{\varepsilon\prime\varepsilon}\int \boldsymbol{\Psi}^*_{\nu\prime}(\boldsymbol{R})\Psi_\nu(\boldsymbol{R})d\tau_N = \boldsymbol{\mu}_{\varepsilon\prime\varepsilon}S(\nu\prime,\nu) \quad (3)$$

Here $S(\nu\prime,\nu)$ is the overlap integral between the vibronic states. The larger the overlap, the larger the electric dipole transition moment. For most transitions a significant overlap is found for multiple vibrational states $\nu\prime$, so in the electronic spectrum, a series of vibrational transitions is observed. The intensities of the corresponding lines are proportional to the square of the overlap integral, called the **Franck-Condon factors**, $|S(\nu\prime,\nu)|^2$ [10].

Hartree Fock

In the Hartree-Fock approach, each electron is thought to move in a potential due to the average of the potential caused by the other electrons and the nuclei. We will derive the Hartree-Fock equations by looking at a trial Slater-determinant Φ_0:

$$\Phi_0(1...n) = \frac{1}{\sqrt{n!}}|\Psi_1(x_1)\Psi_2(x_2)...\Psi_i(x_i)...\Psi_n(x_n)| \quad (4)$$

We want to determine the spinorbitals that make $\Phi_0(1,...,n)$ the approximation for the exact ground state wavefunction $\Psi_0(1,...,n)$ with a minimal energy expectation value:

$$E = \frac{\langle\Phi_0|H|\Phi_0\rangle}{\langle\Phi_0|\Phi_0\rangle} \quad (5)$$

with respect to any variation in Φ_0.
We require:

$$\delta E = \delta\langle\Phi_0|H|\Phi_0\rangle = \langle\delta\Phi_0|H|\Phi_0\rangle + \langle\Phi_0|H|\delta\Phi_0\rangle = 0 \text{ and } \langle\delta\Phi_0|\Phi_0\rangle + \langle\Phi_0|\delta\Phi_0\rangle = 0 \quad (6)$$

This gives us two conditions:

$$\langle\Phi_0|H|\delta\Phi_0\rangle = 0 \quad \langle\Phi_0|\delta\Phi_0\rangle = 0 \quad (7)$$

The complete orthonormal set of spinorbitals in the Slater-determinant are divided in a subset of unoccupied spinorbitals $\Psi_a,\Psi_b,...,\Psi_h$ and a subset of occupied spinorbitals $\Psi_i,\Psi_j,...,\Psi_n$.
Φ_0 is built from Ψ_i, thus variations in Φ_0 can be written as variations in Ψ_i. Only variations that involve change in the spatial part of one of the spinorbitals are considered:

$$\delta\Phi_0 = \frac{1}{\sqrt{N!}}\sum_i|\Psi_1(x_1)\Psi_2(x_2)...\delta\Psi_i(x_i)...\Psi_n(x_n)| \quad (8)$$

Where

$$\delta\Psi_i = \sum_j \Psi_j c_i^j + \sum_a \Psi_a c_i^a \quad (9)$$

Equation 7 leads to the demand that:

$$\langle\Psi_k|\delta\Psi_i\rangle = 0 \quad (10)$$

for all occupied spinorbitals Ψ_k and thus $\delta\Phi_i$ must be a linear combinations of the unoccupied spinorbitals:

$$\delta\Psi_i = \sum_a \Psi_a c_i^a \quad (11)$$

in such a way that $\delta\Phi_0$ is a linear combination of Slater-determinants, each having one occupied spinorbital replaced by an unoccupied spinorbital. Such Slater-determinants are denoted as:

$$\Phi_i^a = \frac{1}{\sqrt{N!}}|\Psi_1(x_1)\Psi_2(x_2)...\Psi_a(x_i)...\Psi_n(x_n)| \quad (12)$$

Therefore,

$$\delta\Phi_0 = \sum_i\sum_a \Phi_i^a c_i^a \quad (13)$$

$$\text{and } \langle\Phi_0|\delta\Phi_0\rangle = \sum_i\sum_a \langle\Phi_0|\Phi_i^a\rangle c_i^a = 0 \quad (14)$$

Equations 13 and 7 give:

$$\langle\Phi_0|H|\Phi_0\rangle = \sum_i\sum_a \langle\Phi_0|H|\Phi_i^a\rangle c_i^a = 0 \quad (15)$$

Which has to hold for all c_i^a so $\langle \Phi_0|H|\Phi_i^a\rangle = 0$ for all i and a. According to Brillouin's theorem, we choose the spinorbitals so that the Hamilton matrix elements between Φ_0 and all singly substituted determinants Φ_i^a vanish. We then find:

$$\langle \Phi_0|H|\Phi_i^a\rangle = \langle \Psi_i(x_1)|F(x_1)|\Psi_a(x_1)\rangle = 0 \quad (16)$$

Where the one-electron operator $F(x_1)$, the Fock operator is given by:

$$F(x_1) = T(x_1)+V^{ext}(x_1)+G(x_1) = h(x_1)+G(x_1) \quad (17)$$

and $G(x_1)$ is given by:

$$G(x_1) = \sum_j^{occ} \langle \Psi_j(x_2)|\frac{(1-P_{12})}{r_{12}}|\Psi_j(x_2)\rangle \quad (18)$$

Equation 16 implies that $F\Psi_i$ must be orthogonal to all unoccupied spinorbitals Ψ_a. Thus, they can be expanded as a linear combination of all occupied spinorbitals:

$$F\Psi_i = \sum_j^{occ} \Psi_j \varepsilon_{ji} \text{ for } i = 1...n \quad (19)$$

The matrix ε is chosen to be a diagonal matrix since a unitary transformation amongst the Ψ_i does not change the Slater-determinant Φ_0. The same is done for the unoccupied spinorbitals which leads to:

$$F\Psi_i = \varepsilon_i\Psi_i \text{ for } i = 1..n \quad (20)$$

Equation 20 gives the canonical Hartree-Fock equations.
The Hartree-Fock approach starts by choosing approximate starting spinorbitals. Solving the Hartree-Fock equations gives a set of improved spinorbitals which are used again to calculate a new Fock-operator. This ultimately leads to a cycle without significant change, and a set of Molecular Orbitals are given.
In Unrestricted Hartree-Fock the occupied orbitals do not have to be doubly occupied, so that the orbital parts fo the spinorbitals with β spin can be different from those with α spin. [11]
Density Functional theory (DFT) uses this Hartree-Fock approach. In this research the hybrid functional B3LYP is used. The implementation is described by Stephens *et al* [12].

Spin-Orbit Coupling

According to the spin selection rule $\Delta S = 0$, a singlet $\rightarrow$ triplet excitation is spin-forbidden. This is true as long as the electronic wave function is separated in a spin and orbital magnetic moment. However, when this separation is broken down by the so-called spin orbit coupling the singlet $\rightarrow$ transition is allowed [13]. The orbital magnetic moment is given by:

$$\boldsymbol{m} = \gamma_e \boldsymbol{l} \quad (21)$$

Where $\boldsymbol{l}$ is the orbital angular momentum and γ_e the magnetogyric ratio $-\frac{e}{2m_e}$.
And the spin magnetic moment is given by:

$$\boldsymbol{m} = g_e\gamma_e\boldsymbol{s} \quad (22)$$

Where $\boldsymbol{s}$ is the spin angular momentum and g_e the g-factor of the electron.
The spin-orbit coupling hamiltonian is:

$$H_{so} = -\frac{e}{2m_e^2rc^2}\frac{d\varphi}{dr}\boldsymbol{l}\cdot\boldsymbol{s} = \xi(r)\boldsymbol{l}\cdot\boldsymbol{s} \quad (23)$$

The state of the electron is defined as $|nlm_lm_s\rangle$, where n is the principal quantum number, l the orbital angular momentum quantum number, m_l the magnetic quantum number, and m_s the electron spin quantum number. The spin-orbit matrix element $\langle nlm_lm_s|H_{so}|nlm_lm_s\rangle$ governs the effect of the spin-orbit coupling on the state of the electron. At an angular momentum, l, of zero, the matrix element vanishes. For all states $l \geq 1$, $\boldsymbol{l}\cdot\boldsymbol{s}\,|nlm_lm_s\rangle$ is proportional to $\hbar^2$. Thus, we write the radial average of the state $|nlm_lm_s\rangle$ in the following way:

$$hc\zeta_{nl} = \langle nlm_lm_s|\xi(r)|nlm_lm_s\rangle\,\hbar^2 \quad (24)$$

Where ζ is the spin-orbit coupling constant.
The radial wavefunction $R_{nl}(r)$ is independent of m_l and gives the radial dependence of the state. Thus, $zeta$ is a wavenumber and $hc\zeta$ an energy. For an hydrogenic atom, the potential arising from the nucleus of charge Ze is Coulombic and $\varphi = Ze/4\pi\varepsilon_0 r$. Therefore:

$$\xi(r) = -\frac{e}{2m_e^2rc^2den}\frac{d}{dr}\left(\frac{Ze}{4\pi\varepsilon_0 r}\right) = \frac{Ze^2}{8\pi\varepsilon_0 m_e^2 r^3 c^2} \quad (25)$$

The expectation value of r^{-3} is given as:

$$\langle nlm_l m_s|r^{-3}|nlm_l m_s\rangle = \frac{Z^3}{n^3 a_0^3 l(l+\frac{1}{2})(l+1)} \tag{26}$$

From equation 24, 25 and 26 the spin-orbit coupling constant is:

$$\begin{aligned}\zeta_{nl} &= \frac{\frac{Z^4 e^2 \hbar^2}{hc}}{8\pi\varepsilon_0 m_e^2 c^2 n^3 a_0^3 l(l+\frac{1}{2})(l+1)} \\ &= \frac{\alpha^2 R_\infty Z^4}{n^3 l(l+\frac{1}{2})(l+1)}\end{aligned} \tag{27}$$

Where R_∞ is the Rydberg constant and $\alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c}$, the fine-structure constant.
The SOC constant ζ_{nl} is proportional to Z^4, thus SOC effects are much larger in heavy atoms than in light atoms. So in heavy elements, as Platinum and Iridium SOC is of dominating importance [10].
To calculate the SOC, perturbation theory is used to limit the computational costs. In perturbation theory, the Hamiltonian is split in a zeroth order term and a small perturbation of strength $\lambda(0 \leq \lambda \leq 1)$. For the zeroth order Hamiltonian we can find all exact solutions.

$$\hat{H} = \hat{H}_0 + \lambda\hat{H}_1 \tag{28}$$

The eigenvalues and eigenfunctions of H obey the Schrödinger equation:

$$\hat{H}\Psi_i = E_i\Psi_i \tag{29}$$

and are expanded as:

$$\Psi_i = \Psi_i^{(0)} + \lambda\Psi_i^{(1)} + \lambda^2\Psi_i^{(2)} + \lambda^3\Psi_i^{(3)} + ... \tag{30}$$

$$E_i = E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \lambda^3 E_i^{(3)} + ... \tag{31}$$

Here it is assumed that the i-th exact solution of the zeroth order Schrödinger equation are the zeroth order wavefunction $\Psi_i^{(0)}$ and energy $E_i^{(0)}$. Equation 30 and 31 are inserted in the Schrödinger equation, demanded that the equation holds for $0 \leq \lambda \leq 1$. All terms with the same power of λ up to the second order are collected:

$$(\hat{H}_0 - E_i^{(0)})\Psi_i^{(1)} = (E_i^{(1)} - \hat{H}_1)\Psi_i^{(0)} \tag{32}$$

$$(\hat{H}_0 - E_i^{(0)})\Psi_i^{(2)} = (E_i^{(1)} - \hat{H}_1)\Psi_i^{(1)} + E_i^{(2)}\Psi_i^{(0)}$$

The eigenfunctions of $\hat{H}_0$ form a complete orthogonal set, thus:

$$\Psi_i^{(1)} = \sum_j{}' \Psi_j^{(0)} c_{ji}^{(1)} \tag{33}$$

Where $j = i$ is excluded, indicated by the prime. This give us:

$$\begin{aligned}E_i^{(1)} &= \langle\Psi_i^{(0)}|\hat{H}_1|\Psi_i^{(0)}\rangle \\ E_i^{(2)} &= \langle\Psi_i^{(0)}|\hat{H}_1|\Psi_i^{(1)}\rangle\end{aligned} \tag{34}$$

Thus, the coefficients, $c_{ji}^{(1)}$ are equal to:

$$c_{ji}^{(1)} = \frac{\langle\Psi_j^{(0)}|\hat{H}_1|\Psi_i^{(0)}\rangle}{E_j^{(0)} - E_i^{(0)}} \tag{35}$$

From equations 35 and 34 we can conclude that for the first order corrected wavefunction and the second order corrected energy we only need the zeroth order solutions and their matrix elements of $\hat{H}_1$.
This theory of perturbation is implemented as described by Wang and Ziegler [14].

Methods

In order to calculate Franck-Condon factors one needs harmonic frequencies of two states, thus to calculate the Franck-Condon factors of the singlet $\rightarrow$ triplet transition of the complexes first the ground state geometry had to be optimized. Then the harmonic frequencies of the ground state had to be calculated and the lowest triplet excited state had to be optimized. After the harmonic frequencies of the triplet state had been calculated the Franck-Condon factors could be calculated. All these calculations were performed with the Amsterdam Density Functinal 2017 (ADF) [15] using the B3LYP functional [12]. For Platinum and Iridium a TZP basis set [16] was used and for hydrogen, carbon and nitrogen a DZP basis set [16]. The harmonic frequencies were calculated numerically. Scalar relativistic effects were taken into account using the ZORA method [14]. The Franck-Condon factors were calculated with the FCF programme of ADF

[17]. The triplet excited frequencies were calculated using unrestricted density functional theory.

To determine the probabilities of triplet transitions the 50 lowest singlet → singlet and 50 lowest singlet → triplet excitation energies were calculated.
The ZORA/TZP basis set was used for the excitation energies with spin-orbit coupling by perturbation theory with the SOPERT programme of ADF [14] where time dependent density functional theory (TDDFT) [18] was used.

The B3LYP functional was chosen because of its widespread use and good performance [19]. Due to computational costs the DZP basis set was chosen for H, C and N, further improvement of the calculations may be possible with the use of a TZP basis set for all atoms. The ground state geometry optimizations and harmonic frequencies calculations were performed on the Peregrine Falcon cluster at the University of Groningen. The cluster is composed of nodes of Intel Xeon E5 2680v3 CPUs with 128 GB memory. The rest of the calculations were performed on the Nieuwpoort cluster at the University of Groningen.

Results and discussion

PtP

As mentioned in the introduction, a suitable molecule for the TRFR experiment has a strong 0-0 line and a high transition probability. The optimised geometries of the ground state and the excited state are shown in figures 3 and 4. For PtP we found a minimal geometry change from the ground state to the excited state.

We have calculated the Franck-Condon factors of the excitation from the singlet ground state to the first triplet excited state of PtP. The resulting spectrum is shown in figure 5. There is a strong 0-0 line of an intensity of 0.2539. The sum of the found Franck-Condon factors is 0.984. Thus, for this molecule the first condition is met.

The triplet excitation energies are calculated both with unrestricted DFT and TDDFT. These values can be found in table 1. The energies correspond reasonably well.

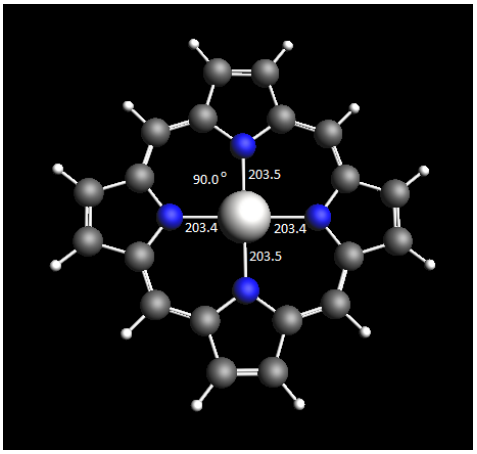

Figure 3: Singlet ground state of PtP with bond lengths in pm. All four angles surrounding platinum are 90.0°.

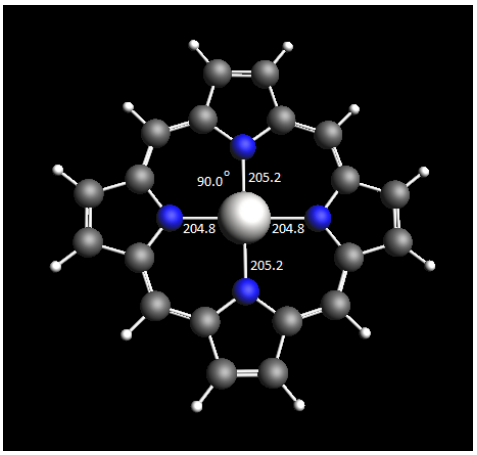

Figure 4: Triplet excited state of PtP with bond lengths in pm. All four angles surrounding platinum are 90.0°.

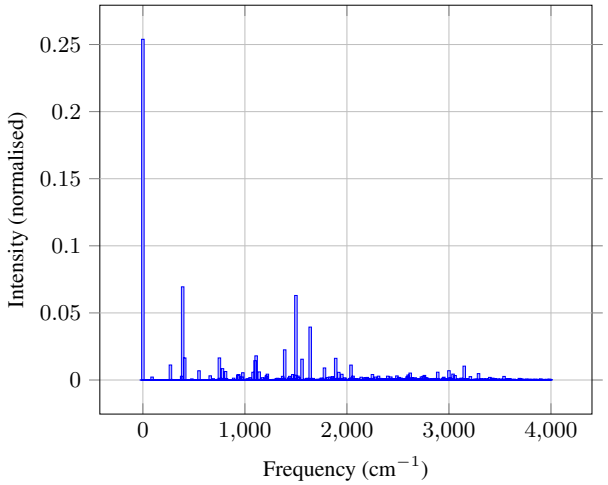

Figure 5: Franck-Condon factors PtP

UDFT (eV)	TDDFT (eV)
2.0173	2.0439

Table 1: Lowest triplet excitation energy of PtP calculated by UDFT and TDDFT

The excitation to the first triplet excited state is from two degenerate molecular orbitals comprised of $2P_y$ and $2P_z$ orbitals of both nitrogen and carbon to a molecular orbital which also comprises of $2P_y$ and $2P_z$ orbitals and a little bit Pt $5D_{xz}$. More details can be found in table 2. It shows that the

	Occupied MO 118a	Occupied MO 119a	Unoccupied MO 120a	Unoccupied MO 121a
C* $2P_z$	44.38%	72.55%	57.64%	57.59%
C $2P_y$	13.74%	17.16%	14.66%	14.69%
N $2P_z$	17.18%		9.58%	9.62 %
N $2P_y$	5.32%			
Pt			1.70% $5D_{xz}$	1.36% $5D_{z^2}$

Table 2: Orbitals involved in excitation of PtP. *This is the sum of all contributions from different carbon atoms. The same accounts for the other C and N orbitals.

metal is not very involved in the excitation. It is basically the ligand that gets excited.
The 200 lowest excitation energies and their oscillator strengths of PtP were calculated with spin-orbit coupling. The 25 lowest are plotted in figure 6. The first excited state unfortunately has an oscillator strength of only $0.626 \cdot 10^{-9}$. However, the lowest two spin-orbit coupling states are both a mix of the first and second non relativistic triplet excited states. The third SOC state is purely made of the first non-relativistic triplet excited state. Thus, it seems that the Franck-Condon factors we calculated are not from the SOC excited state with the lowest energy, but with the third lowest energy. This state has a significant oscillator strength of $0.609 \cdot 10^{-5}$. A combination of these results and the Franck-Condon factors means that a transition from the singlet ground state to the lowest vibronic state of a SOC triplet excited state is possible. However, this triplet excited state is not the lowest state and therefore the complex will most likely quickly relax to the lower excited states and the signal will die out very quickly.

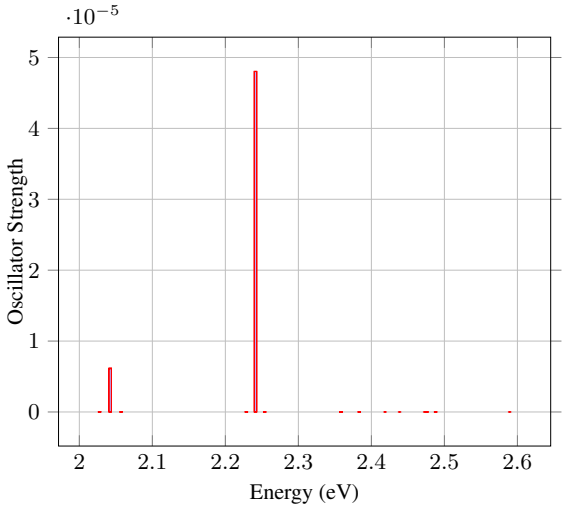

Figure 6: Excitation spectrum PtP

PtCY

For PtCY, the geometries of the ground state and the excited state can be found in figures 7 and 8. The bond lengths are in table 3. Again for this molecule the geometry change is not very large.

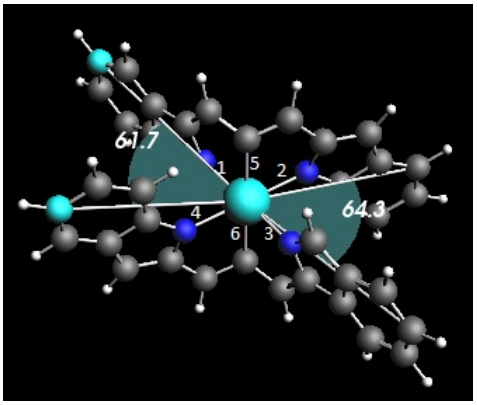

Figure 7: Singlet ground state of PtP. The bond lengths corresponding to the numbers 1-6 can be found in table 3.

Bond	PtCY S_0 (pm)	PtCY T_1 (pm)
1: Pt-N	206.0	205.6
2: Pt-N	208.3	207.8
3: Pt-N	206.0	205.6
4: Pt-N	208.4	207.7
5: Pt-C	213.1	211.7
6: Pt-C	213.0	211.7

Table 3: Selected bond lengths (in pm) of the optimised molecular geometries of the ground state and first triplet excited state ot PtCY

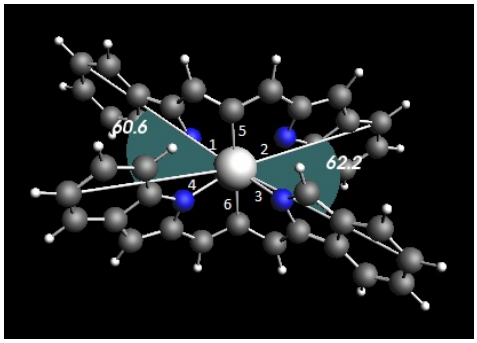

Figure 8: Triplet excited state of PtCY. The bond lengths corresponding to the numbers 1-6 can be found in table 3.

The spectrum of Franck-Condon factors of PtCY can be found in figure 9. Unfortunately the 0-0 line only has an intensity of $7.9 \cdot 10^{-3}$. However, a clear trend can be seen that after approximately $100cm^{-1}$ the intensity quickly decreases. The sum of the found Franck-Condon factors is 0.426, so not all factors are found. This is due to a low number of quanta used in the calculation. However, a higher number of quanta would make it too computationally expensive.

The excitation energies of PtCY calculated

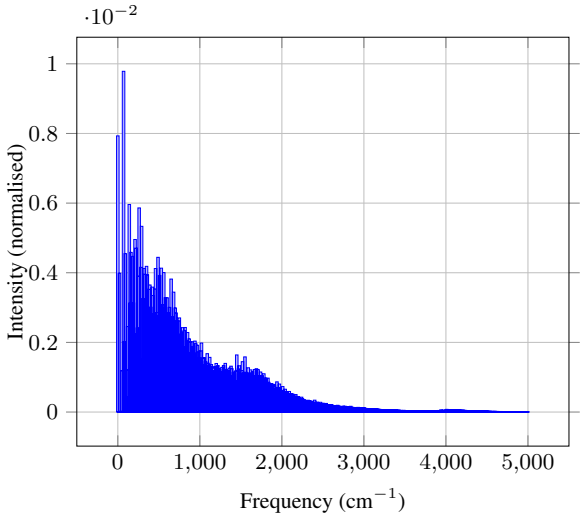

Figure 9: Franck-Condon factors PtCY

by unrestricted DFT and TDDFT can be found in table 4. Again, these values correspond reasonably well.

UDFT (eV)	TDDFT (eV)
1.2948	1.2150

Table 4: Lowest triplet excitation energy of PtCY calculated by UDFT and TDDFT

	Occupied MO 178a	Occupied MO 179a	Unoccupied MO 180a	Unoccupied MO 181a
C* $2P_x$	9.35%	3.44%	12.35%	13.19%
C $2P_y$	56.24%	64.29%	50.28%	46.48%
C $2P_z$	9.35%	7.36%	2.27%	2.67%
N $2P_x$			2.79%	3.35%
N $2P_y$			3.62%	2.89%

Table 5: Orbitals involved in excitation of PtCY. *This is the sum of all contributions from different carbon atoms. The same accounts for the other C and N orbitals.

As in PtP, the excitation to the first triplet excited state is from two degenerate molecular orbitals. These are made of $2P_x$, $2P_y$ and $2P_z$ orbitals from carbon. The excitation goes to two degenerate MO orbitals which are made of $2P_x$ and $2P_y$ orbitals of carbon and nitrogen and $2P_z$ of carbon. More details are in table 5.

Also for this molecule the first 200 excitation energies and corresponding oscillator strengths were calculated with spin-orbit coupling. The lowest 25 are plotted in figure 10. The three lowest SOC excited states are degenerate, see table 6. Unfortunately, the oscillator strengths are again rather low. These three states are completely made of the lowest non-relativistic triplet state, so it seems that for PtCY the Franck-Condon factors are indeed calculated for the SOC excited state with the lowest energy. A combination of these results and the Franck-Condon factors means that a transition from the singlet ground state to the lowest vibronic state of the lowest triplet excited state is possible. However, both the 0-0 line and the oscillator strength of this state is rather low. Therefore it will be difficult to excite a significant amount of complexes to this state.

State	Energy (eV)	Oscillator Strength
1	1.21447	$4.95 \cdot 10^{-6}$
2	1.21447	$2.81 \cdot 10^{-6}$
3	1.21451	$9.80 \cdot 10^{-6}$

Table 6: Energies and oscillator strengths of the lowest SOC excitations of PtCY

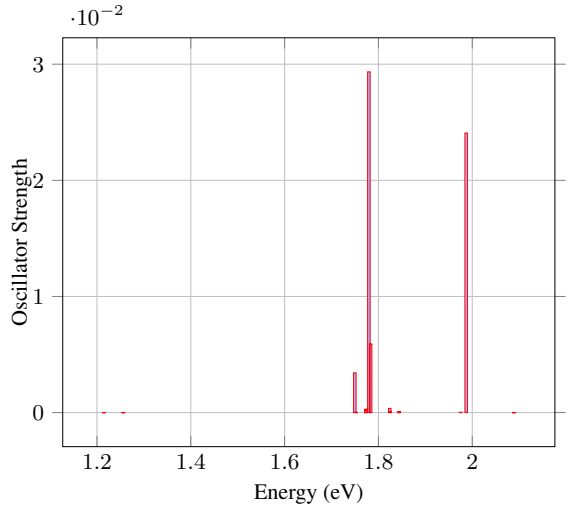

Figure 10: Excitation spectrum PtCY

$Irppy_3$

Figure 11 and 12 show the optimised geometries of the ground state and first triplet excited state of $Irppy_3$. The bond lengths are given in table 7. As can be seen in the table and figures, $Irppy_3$ changes more in geometry upon excitation than PtP and PtCY.

Bond	$Irppy_3$ S_0 (pm)	$Irppy_3$ T_1 (pm)
1: Ir-N	208.1	206.5
2: Ir-N	206.3	208.0
3: Ir-N	220.2	231.1
4: Ir-C	209.4	206.1
5: Ir-C	201.5	198.6
6: Ir-C	211.0	211.0

Table 7: Selected bond lengths (in pm) of the optimised molecular geometries of the ground state and first triplet excited state ot $Irppy_3$

The Franck-Condon factors of $Irppy_3$ are found in figure 13. Unfortunately, no significant intensities were found between 0 and 10000 cm^{-1}. This is most likely due to a too large change in geometry upon excitation, as can be observed in table

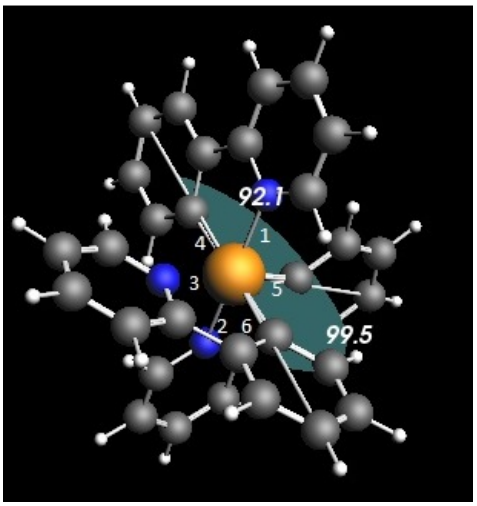

Figure 11: Singlet ground state of PtP. The bond lengths corresponding to the numbers 1-6 can be found in table 3.

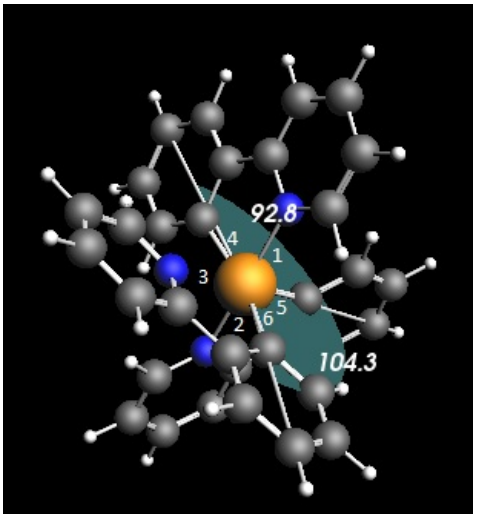

Figure 12: Triplet excited state of PtCY. The bond lengths corresponding to the numbers 1-6 can be found in table 3.

7. The ligands probably have too much freedom to change their angles, which causes a large geometry change.

The energy of the triplet excitation of $Irppy_3$ is also calculated with UDFT and TDDFT, see table 8. For this complex too, the values correspond reasonably well.

UDFT (eV)	TDDFT (eV)
2.4013	2.5565

Table 8: Lowest triplet excitation energy of $Irppy_3$ calculated by UDFT and TDDFT

As with the previous complexes, the 200 low-

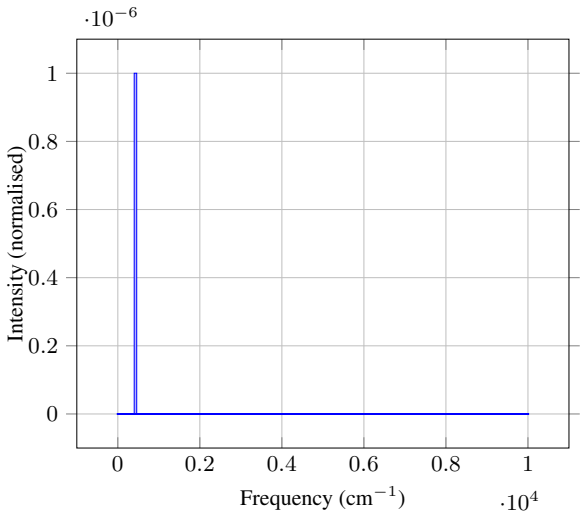

Figure 13: Franck-Condon factors Irppy$_3$

est spin-orbit coupling excitations have been calculated for Irppy$_3$. The first 25 are plotted in figure 14. The lowest state has an oscillator strength of $0.379 \cdot 10^{-4}$. This first SOC state is a mix of several non-relativistic triplet states, but for 82% it is the first non-relativistic triplet state. This is an excitation from one molecular orbital to two degenerate molecular orbitals. Table 9 shows what these orbitals are composed of. This shows that this excitation is a charge transfer from the metal to the ligand. This starts a relatively large disruption in the ligand, which causes the earlier found geometric change. Therefore no Franck-Condon factors can be found for this excitation.

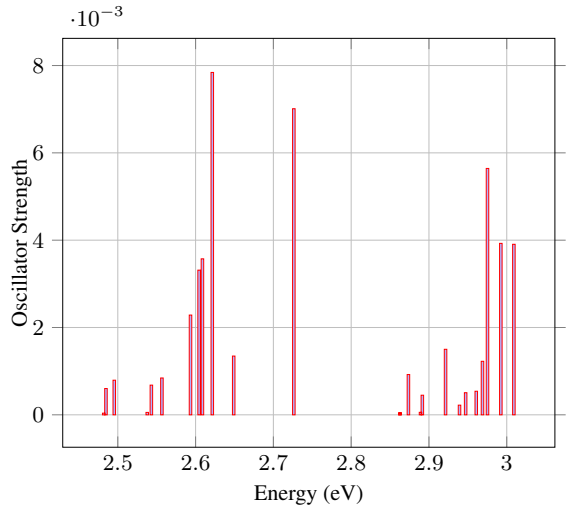

Figure 14: Excitation spectrum Irppy3

	Occupied MO 160a	Unoccupied MO 161a	Unoccupied MO 162a
C*	14.73%	9.88%	13.74%
2P$_x$			
C 2P$_y$	11.09%	24.63%	32.87%
C 2P$_z$	14.76%	18.78%	18.62%
N 2P$_x$		2.18%	4.67%
N 2P$_y$		8.45%	7.52%
N 2P$_z$		3.40%	5.23%
Ir	13.63%		1.48%
3D$_{xy}$			
Ir	21.03%		
3D$_{yz}$			
Ir	1.94%		
3D$_{xz}$			
Ir	3.16%		1.58%
3D$_{x^2-y^2}$			

Table 9: Orbitals involved in excitation of Irppy$_3$. *This is the sum of all contributions from different carbon atoms. The same accounts for the other C and N orbitals.

Conclusions and further research

We have searched for suitable metal-organic complexes for the TRFR-experiment by calculating the Franck-Condon factors and spin-orbit coupling excitations of PtP, PtCY and Irppy3. It showed that Irppy$_3$ is not a good candidate because the excitation is a charge transfer from the metal to the ligand which causes such a large geometrical change that no 0-0 transition is possible. PtP shows promising Franck-Condon factors, but unfortunately it seemed that they do not belong to the lowest spin-orbit coupling excited state. An excitation to the calculated state will relax to the lowest excited state and the signal will die. Therefore, the Franck-Condon factors of this lowest SOC state should be calculated. For PtCY, the Franck-Condon factors are promising, but the 0-0 line could probably be strengthened by connecting the two ligands so that they are more constrained. This should cause a smaller change in geometry and thus a stronger 0-0 line. The oscillator strength for the lowest excited state is promising, but this could probably be increased by increasing the SOC. This can be done by using a heavier metal, for example lead or bismuth, but also lanthanides such as samarium and

europium should be investigated.

To conclude, the search for suitable materials for organic opto-electronic devices has given encouraging results and it seems that research into the use of metal-organic complexes should be continued.

Acknowledgements

I would like to thank my project supervisor dr. R.W.A. Havenith for his enthusiastic help in this project.

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