



UNIVERSITY OF
CAMBRIDGE

Chemical Engineering and
Biotechnology

Modeling Dark- and Light-Induced Crystal
Structures and Single-Crystal Optical
Absorption Spectra of Ruthenium-Based
Complexes that Undergo SO₂–Linkage
Photoisomerization

Apoorv Jain
Wolfson College

March 2021

This thesis is submitted for the degree of *Doctor of Philosophy*

Declaration

This thesis is the result of my own work and includes nothing which is the outcome of work done in collaboration except as declared in the preface and specified in the text.

It is not substantially the same as any work that has already been submitted before for any degree or other qualification except as declared in the preface and specified in the text.

It does not exceed the prescribed word limit of 65,000 words.

Abstract

A family of coordination complexes of the type $[\text{Ru}(\text{SO}_2)(\text{NH}_3)_4\text{X}]\text{Y}$ exhibit optical-switching capabilities in their single-crystal state. This striking effect is caused by photoisomerization of metastable photoinduced states, which are metastable if kept at suitably low temperatures. This illustrates the possibility of these materials to operate as nanotechnological devices themselves, with the potential for optical actuation, optical-signal processing and nano-optomechanical function. This thesis presents a Plane-Wave (PW) – Density Functional Theory (DFT) based periodic methodology that can effectively model the dark- and light-induced structures, and single-crystal optical absorption spectra of these complexes. Initially, these crystalline materials are modeled via PW-based periodic and Molecular Orbital (MO)-DFT based molecular fragment models, and time-dependent DFT (TDDFT), to calculate their structural and optical properties, which are compared with experimental data. Both the periodic and molecular fragment models simulate these complexes effectively, with small deviations in key bond lengths, successfully replicating experimentally-determined structures. Both models also simulate trends in experimentally-determined optical absorption spectra effectively, with optical absorbance and coverage of the visible region increasing with the formation of the photoinduced geometries. This represents the first study of the optical properties of materials from this family of complexes via DFT-based methods. The PW-DFT study is then expanded to consider more complexes, including both photoswitches and transducers. Periodic models are shown to appreciate the competing chemical and crystallographic forces present in these complexes, namely the possible effects of the *trans*-influence and intermolecular interactions on the simulated optical absorption spectra. Density of states calculations are also showed to appreciate these forces, whilst illustrating the potential for optical tuning capabilities. The periodic models are also used to conduct a study of the photoisomerization process from the dark to the light-induced structures via the Nudged Elastic Band (NEB) method; thereby a ‘cause-and-effect’ relationship between photoisomerization and transduction is suggested to be dependent heavily on the intermolecular forces present. Synthetic work has also been carried out in parallel, resulting in the development of a more sustainable precursor-synthesis route and the synthesis of two new complexes. This thesis demonstrates that PW-TDDFT should be considered as a more than viable method for simulating the optical and electronic properties of this family of single-crystal optical switches whose functionality is based on linkage photoisomerism. It also illustrates the potential for optically tuning these complexes so that they can be developed with desired properties for tailored applications.

Publications

Papers based on this thesis have been published:

Based on Chapter 3:

Jain A. *et al.*

“Modelling dark- and light-induced crystal structures and single-crystal optical absorption spectra of ruthenium-based complexes that undergo SO₂-linkage photoisomerization”

Journal of Chemical Physics. 155, 234111 (2021)

Acknowledgements

I would firstly like to thank my supervisor Jacqui Cole for all the help, support and advice that she has given me over these last four years. Her dedication and incredible work ethic have been a great inspiration to all of us in the group.

To all the other members of the Molecular Engineering group, José Velazquez for all of his synthesis and crystallization wisdom, Leon Devereux for being my DFT soundboard, and to both current and past members: Othman Al Bahri, Callum Court, Juraj Mavracic, Ed Beard, Karim T. Mukaddem, Miao Zhu, Hao Chen, Christopher Ashcroft, Batuham Yildirim and many others, for all the discussions around the lab about work and everything else that made coming in to work that much better.

I would also like to thank Alvaro Vazquez for all his DFT help and continued support particularly on all matters ALCF which were hugely valuable, Michael Sternberg for everything CNM, and to Ulrich Mayer for all of his help with the thesis.

I would like to thank all my friends, even though we have often been physically far apart I have always appreciated the support and love. To my friends here in Cambridge, you have been the best part of this experience and the only reason I was able to stay sane throughout this PhD. Shoutout to 42 Histon.

And finally, to my family. To everyone back home in India and Jaipur, for their constant encouragement and love. To Mrinaalini for being my favorite way to waste time since 1999, and most importantly, to my parents Deepak and Chitra Jain. It will never be possible for me to thank you enough for what you have done for me. All I can say is that this thesis is the result of your hard work as much as mine, I hope you are as proud of it as I am.

Oh, and to Man United, for having their worst run of form from the moment I arrived in England.

Table of Contents

1	Introduction	1
1.1	Overview	1
1.2	Characteristics of [RuSO ₂] Complexes	3
1.2.1	Photoinduced SO ₂ -linkage Isomerization	3
1.2.2	Metastable Photoinduced States	3
1.2.3	Nano-optomechanical Transduction in the Single-crystalline State	4
1.2.4	Photophysical Properties of [RuSO ₂] Complexes	6
1.3	Modelling [RuSO ₂] Complexes and Scope of This Study	10
2	Theoretical Background	13
2.1	Schrödinger's Equation	13
2.2	The Born-Oppenheimer Approximation	13
2.3	The Variational Principle	14
2.4	Density Functional Theory	15
2.4.1	Hohenberg-Kohn Theorems	15
2.4.2	The Kohn-Sham Approach	16
2.4.3	Approximating the Exchange Correlation Energy	18
2.4.4	Linear Combination of Atomic Orbitals and Molecular Systems	19
2.4.5	Extended Systems and Plane-Waves	20
2.5	Time-Dependent Density Functional Theory	21
2.6	The Nudged Elastic Band Method	22
3	Development of Plane-Wave Models	24
3.1	DFT Models and Computational Methodology	25
3.1.1	Optimized DFT Models and Experimental Structure Reproduction	25
3.1.2	Optical Absorption Spectra Calculations via Linear-Response (LR)-TDDFT	38
3.1.3	Provision of Experimental Data	41
3.2	Results	42
3.2.1	Optimized DFT-generated Structural Models	42
3.2.2	TDDFT-generated Optical Absorption Spectral Models	46
3.2.3	LCAO Gaussian Optical Transitions	50
3.3	Discussion	51
3.4	Conclusions	52

4	Optical Tuning Capabilities of Plane Wave-TDDFT Models.....	54
4.1	Modelling Parameters	56
4.1.1	Optimized DFT Models	56
4.1.2	Optical Absorption Spectra Calculations via LR-TDDFT	61
4.1.3	DOS and pDOS Calculations	62
4.2	Provision of Experimental Data	64
4.3	Results and Discussion.....	67
4.3.1	Optimized DFT Models:	67
4.3.2	Optical Absorption Spectra	67
4.3.3	Density of States	72
4.3.4	Potential for Optical Tuning.....	78
4.4	Conclusions.....	79
5	Photoisomerization in Ru-SO₂ Complexes.....	81
5.1	NEB Methodology and Model Parameters.....	83
5.2	Exploring the Ru-SO ₂ Photoisomerization Pathways	85
5.2.1	Pathway I: η^1 -SO ₂ dark-state to η^1 -OSO light-induced configuration	85
5.2.2	Pathway II: η^1 -SO ₂ dark-state to η^2 -(OS)O light-induced configuration	87
5.3	Conclusions.....	88
6	Synthesis of Ru-SO₂ Complexes.....	89
6.1	Modified Synthetic Route to the [Ru(NH ₃) ₄ (SO ₂)Cl]Cl Precursor	90
6.2	Synthesis of New Ru-SO ₂ Complexes.....	91
6.3	Conclusions.....	92
7	Conclusions and Future Work	93
7.1	Conclusions.....	93
7.2	Future Work.....	95
7.2.1	Large-Scale Computational Study	95
7.2.2	Further Nudged Elastic Band Calculations	95
7.2.3	Calculation of Raman Spectra.....	96
7.2.4	Machine Learning Based Prediction of New Complexes	96
	Appendices.....	97
	Appendix 1	97
	Appendix 2:.....	122
	Bibliography	134

1 Introduction

1.1 Overview

Crystalline systems that display solid-state linkage photoisomerization stand to yield new applications in nanophotonics¹ and quantum technology.² Materials that produce molecular crosstalk are of particular interest as they promise potential for optical actuation,³ optical signal processing, and optomechanical function.⁴⁻⁷ One such family of materials is a set of ruthenium-sulfur dioxide coordination complexes that exhibit a rare case of controllable and reversible nano-optical switching and nano-optomechanical transduction in the crystalline state; thus behaving as single-crystal optical actuators.⁸⁻²⁰ Their behavior showcases the possibility for single crystals to operate as nanotechnological devices themselves, potentially overcoming complications that are common in device processing.

Their functional origins stem from optically accessible energy levels of SO₂-linkage photoisomers that can be realized within a crystal lattice and maintained in a relatively persistent metastable state once photoinduced. The photoisomers represent a solid-state binary switch whereby the photoinduced metastable ‘light state’ signifies a 1 and the original ‘dark state’ signifies a 0. The general formula for this series of complexes is **[Ru(SO₂)(NH₃)₄X]Y** (hereafter referred to as [RuSO₂] complexes), where **X** is the ligand in *trans* position with respect to the photoisomerizable SO₂ ligand and **Y** is the counterion. Photocrystallographic studies²¹⁻²⁵ have shown that upon photoisomerization, which is primarily induced by the absorption of broadband light, the SO₂ ligand can occupy one of two metastable photoinduced coordination modes: the O-bound (η^1 -OSO) state and the thermally more stable side-on η^2 -(OS)O state (Figure 1.1). These two photoisomeric configurations may coexist in the light-induced crystal structure in different fractions together with the S-bound dark state (η^1 -SO₂).

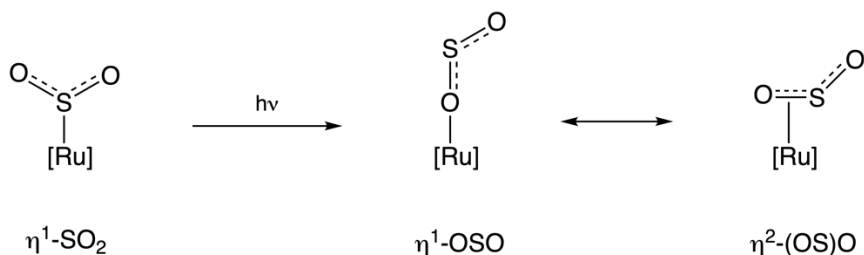


Figure 1.1 Schematic illustration of the coordination modes of the SO_2 ligand in $[\text{Ru}(\text{SO}_2)(\text{NH}_3)_4\text{X}]\text{Y}$ complexes: The $\eta^1\text{-SO}_2$ dark state (left), and the two photoinduced configurations $\eta^1\text{-OSO}$ (center) and $\eta^2\text{-(OS)O}$ (right).

Experimentally, this family of complexes has been studied extensively, whereby new complexes have been characterized mostly via photocrystallography²¹⁻²⁵ and single-crystal optical-absorption spectroscopy,²⁶ which has resulted in highly accurate structural data and optical-absorption spectra for both the dark and light states of these complexes. However, a purely experiment-based materials-discovery pathway is not viable for an extensive large-scale study of the various properties and structural intricacies of these complexes. It is thus desirable to add a computational element to this materials-discovery pathway.

To that end, this thesis presents a Plane-Wave (PW) Density Functional Theory (DFT)-based methodology that is able to model the dark and light-induced structural and electronic properties, as well as to simulate single-crystal optical-absorption spectra of such $[\text{RuSO}_2]$ complexes. The rest of this chapter presents the general chemical background and the properties of these complexes, and it also provides the computational context for this work. Chapter 2 details the theoretical background of the computational methods used in this work. Chapter 3 evaluates the ability of PW-DFT based periodic models to replicate the dark and light-induced structures and simulate the single-crystal optical-absorption spectra of these complexes, with the same calculations conducted via Molecular Orbital (MO)-DFT that allows for an analysis of optical transitions and orbitals involved. Chapter 4 examines the robustness of the PW-based periodic methodology to evaluate a larger variety of complexes, which includes both molecular switches and transducers with various combinations of X/Y , by once again simulating the dark and light-induced single-crystal optical-absorption spectra and by evaluating the density of states. Chapter 5 uses the optimized periodic models to study the photoisomerization mechanism and examine the energy characteristics of the photoisomerization pathways from dark to light-induced states. Chapter 6 presents the synthetic work carried out in parallel to the computational calculations. Specifically, a more

sustainable synthetic route to the precursor for these complexes has been developed, and two new $[\text{RuSO}_2]$ complexes have been synthesized. Chapter 7 summarizes the work in this thesis and proposes future work on the basis of the obtained results.

1.2 Characteristics of $[\text{RuSO}_2]$ Complexes

1.2.1 Photoinduced SO_2 -linkage Isomerization

Photo-linkage isomerization is a photoinduced isomerization process in transition-metal complexes, where photoexcitation of a metal-ligand-charge-transfer (MLCT) band leads to a change in the molecular geometry so that the system subsequently relaxes into a different electronic ground state that is governed by the new, metastable nuclear potential.¹⁸ Upon photoexcitation, certain ligands in transition-metal complexes can exhibit different bonding modes relative to the transition metals and some of these may be metastable.

Photo-linkage isomerization in transition-metal complexes involves ambidentate ligands, *i.e.*, ligands with more than one potential donor atom, such as SO_2 (Figure 1.1). Other common ambidentate ligands include *e.g.* NO , NO_2 , DMSO , or SCN^- . The most extensively studied metal complex that displays such photo-linkage photoisomerization is sodium nitroprusside,¹⁸ albeit that in recent years several Ru-based complexes have become the focus of such studies. This thesis focuses on ruthenium-based sulfur dioxide complexes of the type $[\text{Ru}(\text{SO}_2)(\text{NH}_3)_4\text{X}]\text{Y}$, where **X** is the ligand *trans* to the photoisomerizable SO_2 ligand and **Y** the counterion.

1.2.2 Metastable Photoinduced States

One of the key features of these $[\text{RuSO}_2]$ complexes is their ability to form co-existing long-lasting metastable states, $\eta^1\text{-OSO}$ and $\eta^2\text{-(OSO)O}$, upon photoexcitation. It is important to note that these photoisomers are not ephemeral excited states but rather locally stable with extended lifetimes under certain conditions such as cryogenic trapping,¹⁶ and that they are in effect ground states and must be treated as such. The lifetime and stability of these photoinduced states depends on a number of factors, including the type of ligand and the local crystallographic environment. For instance, the $\eta^2\text{-(OSO)O}$ is the thermally more stable of the two photoinduced complexes and persists to 180-220 K. On the other hand, $\eta^1\text{-OSO}$ decays to the $\eta^2\text{-(OSO)O}$ state at temperatures beyond 120 K.¹⁹

1.2.3 Nano-optomechanical Transduction in the Single-crystalline State

As mentioned above, sodium nitroprusside complexes were one of the earliest set of materials found to display the presence of light-induced metastable isomers as a result of photoisomerization.⁶⁴ Since then, an increasing number of materials that display such properties have been discovered, such as ruthenium nitrosyl complexes. Similarly, ruthenium sulfur-dioxide complexes also had showcased such behavior as well, however Sylvester and Cole⁸ then reported the first example of a ruthenium sulfur-dioxide complex that displayed nano-optomechanical transduction. Since then several complexes of the type $[\text{Ru}(\text{SO}_2)(\text{NH}_3)_4\text{X}]\text{Y}$ that display both optical switching and transduction capabilities have been discovered.

Nano-optomechanical transduction refers to a phenomenon when a small molecular photoswitch induces a large mechanical response in a neighboring molecular constituent via its steric and electronic proximity. This process is usually triggered by the formation of the η^1 -OSO complex, as one of its oxygen atoms protrudes from the cation toward the neighbouring anion. This protruding oxygen atom is naturally present in both photoinduced metastable states and will hereafter be referred to as O_{free} . In certain cases, for example when the counterion Y contains an arene ring such as in *p*-tosylate, the ring rotates about its' molecular axis shifting away to alleviate the resulting strain, as illustrated in Figure 1.2. This arene-ring rotation is metastable, reversible, and reproducible⁸ since the photoisomerization fraction of η^1 -OSO can be controlled by altering temperature and light. For instance, as η^1 -OSO starts to decay, the arene rings will begin to relax back into its their original states.

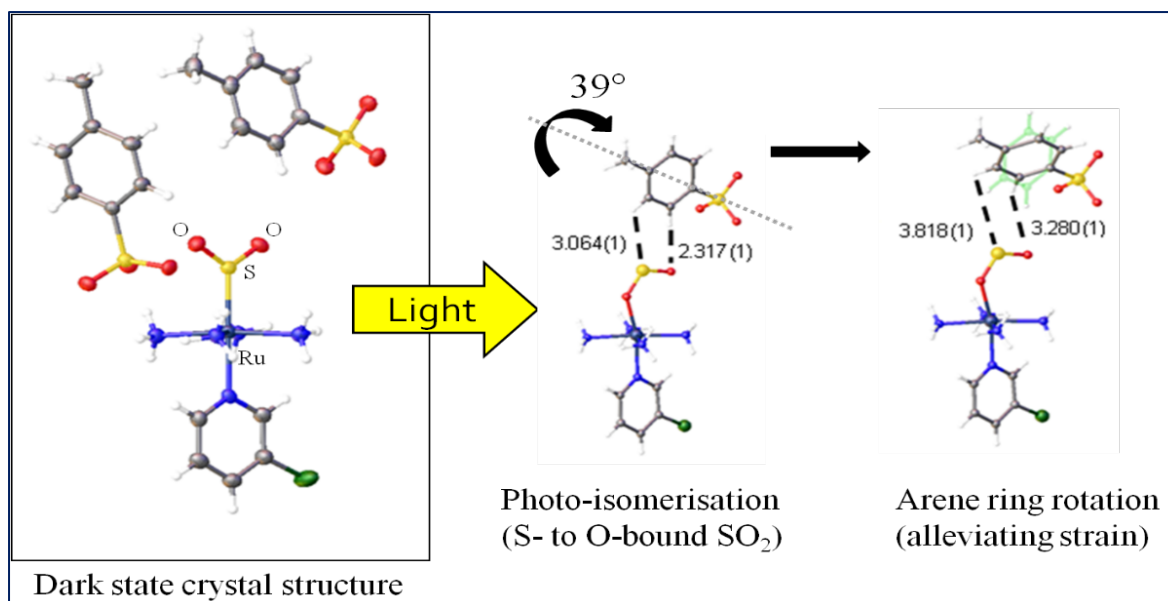


Figure 1.2: Mechanism for crystalline nano-optomechanical transduction from the η^1 -(SO)₂ dark state crystal structure to the η^1 -OSO light-induced structure in [Ru(SO₂)(NH₃)₄(3-chloropyridine)](*p*-tosylate)₂.

This shows the ability of these complexes to act as molecular dials, and in essence as molecular machines. The latter consist of a discrete number of molecular components arranged and designed to carry out specific mechanical movements (linear or rotational) in response to selective external stimuli, which can be chemical or light-based. The majority of recently synthesized artificial molecular machines are based on biological systems and operate in solution.⁵⁶ However, harnessing their mechanical capabilities to produce work remains challenging due to the intrinsic characteristics of operating in a soft medium.⁵⁶ Crystalline systems offer an environment that is a more favorable for controlling molecular motion due to their periodic and well-ordered structure. Yet, molecular machines that operate in the single-crystalline state are affected by crystallographic forces and internal lattice strain, which may limit their performance.⁵⁷

However, using light as a stimulus offers access to photoexcited phenomena that are unattainable via chemical means. As is seen in the subject materials, the structural changes from photoexcitation often leads to the release of strain, which then results in some form of mechanical work.⁵⁶ Devices that use light as a source of energy do not suffer from these issues, and thus possess several unique advantages.⁸ For instance, light intensity and wavelength can be used to control the amount of energy transferred to the system, and energy can be transmitted without the need for complex ‘wiring’. Chief among these advantages is that photo-chemical

processes can exploit a renewable energy source and are ‘clean’, *i.e.*, they do not form waste products.⁸ This family of [RuSO₂] complexes thus represents a class of materials that demonstrate controllable molecular motion in the solid state. They have already been shown to be viable as part of thin films,⁵⁸ which showcases their potential toward device applications.

1.2.4 Photophysical Properties of [RuSO₂] Complexes

Extensive experimental studies have been conducted on complexes of the type [Ru(SO₂)(NH₃)₄X]Y and ultimately, approximately 50 complexes of various combinations of X and Y have been reported. Although applied specifically to the subject materials, there are three main photophysical properties of materials that display photo-linkage isomerization:¹²

1. Geometry of the photoinduced states
2. Photoconversion fraction of isomerisation
3. Thermal stability of photoinduced states

These three photophysical characteristics are governed by three key structural properties:^{12,59,60}

1. The size of the SO₂ photoreaction cavity
2. The nature of the ligand in *trans*-position relative to SO₂
3. The local crystallographic environment

Photoreaction Cavity

The SO₂ photoreaction cavity refers to the free volume surrounding the photoisomerizable ligand. Studying the effects of the photoreaction cavity on the aforementioned photophysical properties is challenging, since the photoreaction cavity itself is affected by the *trans*-ligand and the surrounding crystallographic environment.^{13,19} Sylvester and Cole have studied two complexes of the [Ru(SO₂)(NH₃)₄X](*p*-tosylate)₂ family, *i.e.*, X = isonicotinamide (**1**) and isonicotinic acid (**2**); **1** and **2** exhibit two crystallographically unique but chemically identical ruthenium centers **Ru01** and **Ru02**, respectively. This allowed studying two distinct SO₂ photoreaction cavities whilst minimising the effects of the *trans*-ligand and the crystallographic environment. For both complexes, the **Ru01** dark-state structures had larger photoreaction cavities, quantified using Voronoi Dirichlet polyhedra (VDP), than their **Ru02** counterparts. It was thus predicted that **Ru01** would show larger photoconversion values, which was experimentally verified, and the **Ru01** center showed a photoconversion that was at least 10% higher than that of **Ru02**. For both **1** and **2**, the difference between the individual VDP volumes

of the dark-state oxygen atoms in **Ru01** was much higher than those in **Ru02**, which explains why **Ru01** showed a higher photoconversion. It was also observed that O_{free} in the photoinduced structures isomerized toward the dark-state oxygen with the greater VDP volume. Sylvester and Cole quantified the effects of the size of the photoreaction cavity on the geometry and amount of photoconversion of the photo-excited states via a 'lock-and-key' model,¹² which describes how photoreaction cavities can be used to characterize and identify trends of the ability of these complexes to cause molecular transduction.

Velazquez-Garcia and Cole then took this concept further by using the rationale behind the 'lock-and-key' model to predict the ability of complexes of this family to cause molecular transduction and to predict the corresponding trends in their photophysical properties.⁵⁹ For instance, it was identified that complexes with $X = 3\text{-methylpyridine}$, which contain a large photoreaction cavity, should act as molecular transducers, while complexes with $X = 3\text{-ethylpyridine}$, which contain a smaller photoreaction cavity can be expected to behave as optical switches with large photoconversion fractions.⁵⁹ It was also shown that, in certain cases, the effect of the photoreaction cavity is overridden by one or more other structural properties, such as the crystallographic environment, since in certain complexes (e.g., where $Y = 4\text{-chlorobenzenesulfonate}$), O_{free} in the photo-excited complexes tends to isomerize toward the dark-state oxygen with the smaller photoreaction cavity.⁵⁹ These two studies illustrate the correlated nature of the three structural properties, and that they must be considered simultaneously.

***Trans*-ligand**

The *trans*-ligand imparts electronic and steric effects that influence the photophysical properties and the SO_2 photoreaction cavity. This phenomenon is known as the *trans*-influence. Understanding the Ru- SO_2 and Ru-X bonding mechanisms helps to shed light on the chemical effects imparted by the *trans*-ligand. Figure 1.3 details the bonding mechanisms for the dark state and the two metastable photoinduced states, $\eta^1\text{-OSO}$ and $\eta^2\text{-(OSO)}$. In the dark state, the sulfur atom donates a lone pair of electrons from its filled p_σ -orbital into the empty d_σ -orbital of the ruthenium center whilst the same occurs between the ruthenium center and the *trans*-ligand. There is also π -backbonding from the ruthenium d_π -orbitals into the empty π^* -antibonding orbitals of both the sulfur atom and the *trans*-ligand, which stabilizes both bonds.⁵⁹ With the sulfur and *trans*-ligand competing, the effect of the *trans*-ligand can be gauged by its Lewis basicity and thus its pK_a value. A high pK_a value refers to a strong σ -donor / poor π -acceptor. The *trans*-ligand p_σ -electrons increase the electron density at the ruthenium center,

resulting in a weaker Ru-S bond, which induces a lengthening of the Ru-S bond. A high pK_a value thus means a higher *trans*-influence.

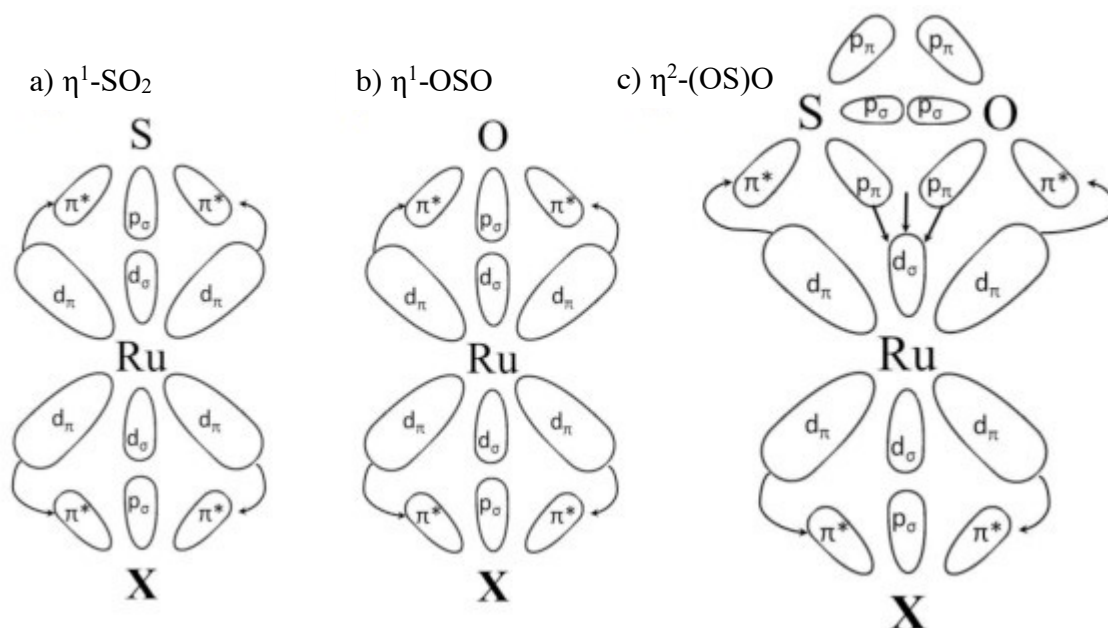


Figure 1.3: Illustration of bonding mechanism for Ru-SO₂ and Ru-X for a) η^1 -SO₂ (dark state), b) η^1 -OSO and c) η^2 -(OS)O²³ with the arrows representing π -backbonding.

The same occurs in η^1 -OSO, albeit that the sulfur atom is replaced by an oxygen atom. The bonding mechanism in η^2 -(OS)O is slightly more complex and follows a mechanism similar to the Dewar, Chatt, and Duncanson model for bonding between alkenes and metal centres,^{1,18,23} with the S-O p_π -orbitals donating electrons into the empty ruthenium d_σ -orbital. Again, this is stabilized by π -backbonding, which follows the same principles as those shown in the ground state and η^1 -OSO. In the case of η^2 -(OS)O, a *trans*-ligand with a high pK_a value results in a weaker and longer S-O bond, whereby stabilization arises from both the Ru-(S,O) σ -bond and π -backbonding.^{59,60}

Kovalevsky et al.¹⁵ were one of the first to observe these effects by varying the *trans*-ligand; however, they also varied the counterions, thus altering the local crystallographic environment. Sylvester et al.¹³ studied the effects of three *trans* ligands, i.e., pyridine (**3**), 3-Cl-pyridine (**4**), and 4-Cl-pyridine (**5**) in the [Ru(SO₂)(NH₃)₄X]Cl₂·H₂O family of complexes. They found that pyridine, which exhibits the highest pK_a value and thus the higher *trans*-influence, showed the highest photoconversion since a higher σ -donating ability lowers the photoisomerization energy barrier (by weakening the Ru-SO₂ bond), leading to increased formation of the metastable geometries. The order of *trans*-influence was found to be **4** < **5** < **3**, which follows

the trend of pK_a values, and was reflected in the η^2 -(OS)O S-O bond lengths and η^2 -(OS)O occupational fractions.¹³ The thermal stability of the η^2 -(OS)O isomers for these three complexes was found to be **4** > **3** > **5**. The long-term stability at 200 K when **X** = 3-Cl-pyridine, showed for the first time that the thermal stability is mainly governed by the Ru-(S,O) σ -bond rather than by the π -backbonding.¹³ The effect of the *trans*-influence on the bond lengths between ruthenium and the SO₂ ligand is particularly noteworthy as it will affect the photoreaction cavity and thus the ability of a complex to act as a molecular motor. These results demonstrate that the *trans*-ligand is of crucial importance for any systematic methodology that aims to model these complexes. However, it is not the only important factor and the intermolecular forces acting on the SO₂ ligand must also be carefully considered.

Crystallographic Environment

The surrounding crystalline environment refers in particular to the nature of the counterions. For a long time, the consensus had been that the counterion fulfils a merely steric role in these complexes, whereby larger counterions lead to increased photoconversion and thermal stability. This was initially challenged by Cole and Sylvester,⁸ who studied the [Ru(SO₂)(NH₃)₄(3-Cl-pyridine)]Y₂ complexes (**6**: Y = *p*-tosylate; **6**: Y = 4-Cl-benzenesulfonate). In both cases, they found that the decay of η^1 -OSO to η^2 -(OS)O led to the rotated arene rings returning to their dark-state positions, which means that the η^1 -OSO geometry is responsible for the molecular transduction. For both **6** and **7**, the O_{free} to H_{aromatic} distance was found to be less than the sum of their van der Waal's radii and this strain results in the rotation of the arene ring.⁸ This distance is shorter in **7** than in **6**, which explains the by approximately 10° larger arene-ring rotation. These results highlight the influence that the counterion can have, since it dictates the intermolecular interactions, which in turn affect the photophysical properties of the complexes (**7** also had a greater photoconversion fraction). For **6**, it was also found that photoconversion levels of > 40%, the strain in the crystal causes it to crack during decay, which indicates higher occupational fractions of η^2 -(OS)O that negatively affect the structural integrity of the system. The same did not occur for **7**, albeit that the decay rate for the η^2 -(OS)O mode of **7** is faster than that of **6**, which indicates that although **6** experienced greater strain, it is in fact thermally more stable than **7**.⁸

Another important study was conducted by Cole et al.,⁹ who looked at [Ru(SO₂)(NH₃)₄X](*p*-tosylate)₂ complexes with the same three *trans*-ligands as those in the study by Sylvester et al.,²¹ i.e., **8** (X = pyridine), **9** (X = 3-Cl-pyridine), and **10** (X = 4-Cl-pyridine). This allows for direct comparison of the effects of changing the counterion from Cl to *p*-tosylate. The results

obtained suggest that upon photoconversion, the closest distance for the η^1 -OSO photoisomer is the $S_{\text{free}} \cdots C_{\text{aromatic}}$, which is less than the sum of van der Waal's radii for S and C, leading to the arene ring to rotate in order to alleviate the strain. However, this was only the case for **9**, whereas in **8** and **10** the interaction was not strong enough to induce rotation. The thermal stability for the η^2 -(OS)O isomer of the three complexes followed the order **10** > **8** > **9**, which is different to that determined by Sylvester et al.¹³ In particular, Cole et al.⁹ showed that the thermal stability of the η^2 -(OS)O isomer increased with increasing SO₂ photoreaction cavity⁹. This was the case for all three complexes here and for complexes **3** and **4** in the study of Sylvester et al.¹³ This was rationalized in terms of the notion that an increased free volume for the photoisomer results in an increased volume for the η^2 -(OS)O geometry to form, which would increase its thermal stability. These studies highlight the influence of the counterion on the thermal stability of such complexes and demonstrate that the counterion does not merely exert its influence via steric effects, but determines the photophysical properties in a more nuanced role by affecting the intermolecular interactions.

1.3 Modelling [RuSO₂] Complexes and Scope of This Study

The simulation of these [RuSO₂] complexes is quite challenging, as they are large (>100 atoms per unit cell), solid, extended, photosensitive crystalline materials that contain heavy elements and long-range electrostatic (LRES) forces. These complexes also exhibit both metal-ligand and metal-centered charge-transfer properties with the largest changes unsurprisingly in the ruthenium coordination environment.⁶⁷ Most importantly, they also exhibit a rare ability to form coexisting long-lasting metastable states upon photoactivation, which are ground states rather than excited states. The ‘dark’ and ‘light’ states of these complexes are distinct ground states that differ in geometry and coordination and must be modeled independently. Both dark- and light-state phenomena are present within a crystal lattice and so this is inherently a crystalline problem. Any effective computational approach will require an appreciation of the periodic nature of these systems and their properties. The success of the models, created by electronic-structure calculations, can be gauged by their ability to accommodate these complications and effectively simulate empirically calculated geometric and optical properties that match experimental results.

The most effective method of obtaining the optical response of bulk solids is by solving the Bethe-Salpeter equation (BSE),^{27,28} which accounts for the electron-hole interaction, on top of the many-body GW method.^{29,30} GW-BSE methods are particularly suited to periodic solids

and excited states as they display more accurate long-range behavior and a better description of core excitations.⁶⁹ This means they are better able to model excitonic and charge-transfer effects, and also allow for absorption spectra calculations to sample more than just the gamma point which is very important for periodic solids. However, GW-BSE methods are computationally intensive, and do not scale well for large systems such as the subject materials. Furthermore, GW-BSE has been shown to struggle in calculating certain ground-state properties as well showing instabilities in its ground-state formalism.⁷⁰ A computationally more feasible method is the quantum mechanics/molecular mechanics (QM/MM) approach.³¹ Here, the system at hand is partitioned into two parts: the QM part, which is treated via *ab initio* methods such as DFT, and the MM part, which models any long-range forces and the like via a force field. QM/MM methods are particularly popular with biomolecular systems though organometallic and solid-state studies have also been conducted.⁷¹ One such study on this family of [RuSO₂] complexes has been conducted by Aono and Sakaki,³² who surveyed the thermal isomerization potential energy surface (PES) and studied the effects of short- and long-range forces on the SO₂ ligand. This study highlights the importance and difficulties associated with accurately defining the two regions, as various approximations have to be made when constructing the QM region, making it difficult to accurately model the LRES forces. Describing the MM region is also not trivial since it requires certain estimations of where and how these forces are localized, which may not always be well understood. This detail required for QM/MM makes conducting optical calculations complicated and often computationally arduous.

More robust ‘black-box’ techniques are thus often preferred, particularly for large complex systems. Thereby, DFT/TDDFT is the ‘go-to’ technique for calculating the optical properties of large complex periodic systems since it is able to provide a more sustainable trade-off between accuracy, simplicity, and computational load.^{27,28} This is despite the well-established shortcomings of TDDFT when dealing with such systems, particularly when high-energy excited states and excitonic character are present (see Section 2.5).^{27,28}

Within the scope of DFT/TDDFT calculations, molecular orbital (MO)-based DFT/TDDFT^{33,34,50} is the typically preferred DFT-based methodology for calculating the optical properties of large extended systems, owing to the large variety of Gaussian basis sets that are available. There are several examples of detailed studies of periodic systems via MO-DFT based methodologies.⁷⁴⁻⁷⁷ A MO-DFT study by Kovalevsky et al.¹⁵ has been conducted on this family

of $[\text{RuSO}_2]$ complexes. However, it did not focus on the optical properties of these crystalline systems; rather, it focused on the evaluation of the various configurations of the SO_2 ligand by studying the surrounding PES.¹⁵ Significantly, these calculations were conducted only on cations of these $[\text{RuSO}_2]$ complexes, where $\mathbf{X} = \text{Cl}$ and H_2O .¹⁵ This study was thus not able to examine these complexes holistically. Extended systems have to be modeled via ‘supercells’ to artificially mimic periodicity and to somewhat consider the effects of periodic phenomena, such as LRES forces. The size of the supercell then becomes a decisive factor in the quality and complexity of these models. When heavy atoms are present, where polarization and diffuse effects are particularly important, extremely detailed basis sets are required to achieve reasonable levels of accuracy, hence further increasing computational load (especially memory requirements). Although MO-DFT does allow for the targeted analysis of certain regions of interest.

In contrast, Plane-Wave (PW)-DFT is a periodic approach that is inherently constructed to treat systems with periodicity, and it is the designated DFT-based methodology when dealing with extended materials.³⁶ It is a viable alternative to MO-DFT for treating periodic phenomena whilst offering the same computational savings. Interestingly, PW-DFT is often overlooked when the prediction of optical properties is required, even though it has widespread use when calculating ground-state properties of large extended systems. Phillips et al.¹⁸ have conducted a PW-DFT study on this family of $[\text{RuSO}_2]$ complexes, whereby they evaluated the PES of the SO_2 ligand and investigated the influence of the crystalline environment on its various configurations. However, this study could not comprehensively examine these $[\text{RuSO}_2]$ complexes since DFT calculations were conducted with constrained geometries and lacked an evaluation of the optical response of these systems. There is thus a need to holistically model these $[\text{RuSO}_2]$ complexes and their electronic, structural, and optical properties.

The work in this thesis attempts to address this need; electronic-structure calculations were conducted on the dark and light-induced structures of these $[\text{RuSO}_2]$ complexes. DFT-based methods were used to calculate structural and electronic properties, to simulate single-crystal optical-absorption spectra, and to study the photoisomerization mechanism. As a result, a novel PW-DFT based periodic methodology has been developed to model these complexes.

2 Theoretical Background

This chapter presents an overview of the theoretical background and methods used in this PhD, in particular the foundational concepts of DFT and related methods.

2.1 Schrödinger's Equation

The Schrödinger equation is the fundamental quantum-mechanical equation and provides the complete description of any system composed of electrons and nuclei, from single atoms to crystals. The solution to this equation allows for the calculation of atomic and molecular properties of the system at hand. The time-independent Schrödinger equation (TISE)^{61,62} is written below (Equation 2.1). The many-electron wave-function of the system is given by ψ , whereas $\hat{H}$ is the Hamiltonian (consisting of the sum of the kinetic and potential energies) and E represents the total energy of the system, which in this case is time-independent.

$$\hat{H}\psi = E\psi \quad (2.1)$$

The non-relativistic Hamiltonian of a many-electron system can then be expressed like so^{61,62} (in atomic units):

$$\hat{H} = -\frac{1}{2} \sum_A \frac{1}{M_A} \nabla_A^2 - \frac{1}{2} \sum_i \nabla_i^2 - \sum_i \sum_A \frac{Z_A}{d_{iA}} + \sum_i \sum_A \frac{Z_A Z_b}{d_{AB}} + \sum_i \sum_{j>i} \frac{1}{d_{ij}} \quad (2.2)$$

Here, A, B represent the nuclei, while i, j denote the electrons of the system, d is the distance between two particles and Z is the charge. The first two terms represent the kinetic energies of the nuclei and electrons respectively, and the next three terms are the Coulomb attraction between the nuclei and electrons, the electrostatic repulsions between the nuclei, and the electrostatic repulsions between the electrons, respectively.^{61,62}

The wave-function, ψ , contains information of all the nuclei and electrons in the system and is a function of $3N$ variables, where N is the total number of particles. The exact solution to Equation 2.1 for many-particle systems is thus extremely complex and so certain simplifications are necessary before an *approximate* solution can be found.

2.2 The Born-Oppenheimer Approximation

One of the most important simplifications is the Born-Oppenheimer approximation, which makes use of the huge difference in masses between the nuclei and electrons. Since the nuclei are so much heavier, they will inevitably move much slower. This implies the velocities of the

nuclei are significantly smaller than those of the electrons, and so it can be assumed that they are in fact stationary, with only the electrons having non-zero velocities.^{61,62} This significantly simplifies Equation 2.2, reducing the nuclei kinetic energy to zero, and the nuclei-nuclei repulsion term simply becomes a constant. Both these terms are thus removed from the Hamiltonian, and this leads to the *electronic* Hamiltonian:

$$\hat{H}_{elec} = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \sum_A \frac{Z_A}{d_{iA}} + \sum_i \sum_{j>i} \frac{1}{d_{ij}} = \hat{T}_e + \hat{V}_{ext} + \hat{V}_{ee} \quad (2.3)$$

The solution of the Schrödinger equation thus becomes:

$$\hat{H}_{elec} \psi_{elec} = E_{elec} \psi_{elec} \quad (2.4)$$

and the total energy term is then given by:

$$E_{tot} = E_{elec} + E_{nuc} \quad (2.5)$$

$$\text{where } E_{nuc} = \sum_i \sum_A \frac{Z_A Z_b}{d_{AB}} \quad (2.6)$$

Since the nuclear coordinates are now fixed, the electronic energy and wave-function only depend on them parametrically. Here onwards the subscript ‘elec’ will be dropped since only the electronic version of the Schrödinger equation is being considered.

2.3 The Variational Principle

The variational principle is another key quantum-chemical theorem that provides a scheme whereby the exact solution to ψ_0 , the exact ground-state wave-function, can be *approximated*. It states that the energy calculated as the expectation value of the Hamiltonian from any normalized trial wave-function, ψ_{trial} , must be greater than or equal to the true energy of the ground-state:

$$\langle \psi_{trial} | \hat{H} | \psi_{trial} \rangle = E_{trial} \geq E_0 = \langle \psi_0 | \hat{H} | \psi_0 \rangle \quad (2.7)$$

where the $E_{trial} = E_0$ when $\psi_{trial} = \psi_0$.^{61,62} It is important to note that the calculated energy is a functional dependent on ψ_{trial} .

The implication of Equation 2.7 is that to find the ground-state properties of a system, E_0 and ψ_0 , the calculated energy needs to be minimized for all *acceptable* trial wave-functions, *i.e.* those that are physically sensible. However, this is a massive and complex undertaking and

often a good approximation of the ground-state is adequate to highly accurately calculate various properties. It is thus crucial to choose an appropriate form of the energy functional that allows for the accurate calculation of the computed ground-state energy from a minimum number of parameters.^{61,62}

2.4 Density Functional Theory

Wave-function-based methods, such as the Hartree-Fock (HF) and post-HF formalisms, aim to solve the TISE for a system with N particles by providing approximations to the many-electron wavefunction. As mentioned previously, this is a $3N$ -dimensional problem. On the other hand, DFT-based methods are based on calculating the electron density of a system, which is solely dependent on the spatial coordinates. For a system with N -particles, this reduces the $3N$ -dimensional problem to simply a 3-dimensional one. DFT is thus able to accurately model large systems for less computational cost. The core theme is that if the ground-state electron density of a system is known, then all other properties of the ground and excited states can be computed. This electron density based formalism is based on the two Hohenberg-Kohn³³ theorems followed by the crucial work of Kohn and Sham.³⁴

2.4.1 Hohenberg-Kohn Theorems

Theorem 1:

For any N -electron system, the external potential $\hat{V}_{ext}(\mathbf{r})$ is a unique functional of the ground-state electron density, $\rho_0(\mathbf{r})$. Since $\hat{V}_{ext}(\mathbf{r})$ is known, the ground-state wavefunction, ψ_0 , can be computed and is also a unique functional of $\rho_0(\mathbf{r})$. Hence, given solely the unique $\rho_0(\mathbf{r})$, all properties of all states of a system can be computed.

This theorem can be proven by using two different external potentials, $\hat{V}_1(\mathbf{r})$ and $\hat{V}_2(\mathbf{r})$, that lead to the same electron density, $\rho(\mathbf{r})$, with each potential associated with a different Hamiltonian and wave-function:³³

$$\begin{aligned} E_1 &= \langle \psi_1 | \hat{H}_1 | \psi_1 \rangle \\ E_2 &= \langle \psi_2 | \hat{H}_2 | \psi_2 \rangle \end{aligned} \tag{2.8}$$

Since ψ_1 is not the ground-state of $\hat{H}_2$ and vice versa:

$$\begin{aligned}
E_2^0 &< \langle \psi_1 | \hat{H}_2 | \psi_1 \rangle = \langle \psi_1 | \hat{H}_1 | \psi_1 \rangle + \langle \psi_1 | \hat{H}_2 - \hat{H}_1 | \psi_1 \rangle \\
&= E_1^0 + \int \rho(\mathbf{r}) [\hat{V}_2(\mathbf{r}) - \hat{V}_1(\mathbf{r})]
\end{aligned} \tag{2.9}$$

and

$$\begin{aligned}
E_1^0 &< \langle \psi_2 | \hat{H}_1 | \psi_2 \rangle = \langle \psi_2 | \hat{H}_2 | \psi_2 \rangle + \langle \psi_2 | \hat{H}_1 - \hat{H}_2 | \psi_2 \rangle \\
&= E_2^0 + \int \rho(\mathbf{r}) [\hat{V}_1(\mathbf{r}) - \hat{V}_2(\mathbf{r})]
\end{aligned} \tag{2.10}$$

The inequalities above have been obtained via the variational principle. Summing Equations 2.9 and 2.10 gives:

$$E_2^0 + E_1^0 < E_1^0 + E_2^0 \tag{2.11}$$

This is clearly contradictory, and so it is not possible for two different external potentials to lead to the same electron density.

Theorem 2:

Any trial density $\tilde{\rho}(\mathbf{r})$, where $\tilde{\rho}(\mathbf{r}) \geq 0$ and $\int \tilde{\rho}(\mathbf{r}) d\mathbf{r} = N$, which is associated with an external potential $\tilde{V}(\mathbf{r})$, can be used variationally to determine the electron density which minimizes the ground-state energy.³³

This theorem presents the variational principle for DFT and can be proven by using the trial wave-function in the variational principle:³³

$$\langle \tilde{\psi} | \hat{H}_1 | \tilde{\psi} \rangle = \int \tilde{\rho}(\mathbf{r}) V(\mathbf{r}) d\mathbf{r} + F[\tilde{\rho}] = E[\tilde{\rho}] \geq E_0[\rho_0] = \langle \psi_0 | \hat{H} | \psi_0 \rangle \tag{2.12}$$

where $F[\tilde{\rho}]$ represents the universal functional of $\tilde{\rho}$:

$$F[\tilde{\rho}] = T[\tilde{\rho}] + V_{ee}[\tilde{\rho}] = \langle \tilde{\psi} | \tilde{T} + \tilde{V}_{ee} | \tilde{\psi} \rangle \tag{2.13}$$

It is important to note that if the exact solution to $F[\tilde{\rho}]$ was known then the exact ground state density and energy could be found, however since that is not possible, approximate functionals are used instead.

2.4.2 The Kohn-Sham Approach

The Hohenberg-Kohn theorems provide the foundations of modern DFT by proving that all properties of a system can be calculated via the electron density, however they do not show *how* this can be done. That has been done by Kohn and Sham.³⁴ They map the system of

interacting electrons onto a fictitious non-interacting system of electrons. This turns the initial N -electron wavefunction into N single-electron functions. These fictitious single-electron orbitals, known as the Kohn-Sham (KS) orbitals, are constructed so that the ground-state energy of the non-interacting fictitious system exactly equals that of the real interacting system.³⁴ The convoluted many-body wavefunction can now be modelled by far simpler single-body equations that still obey the Hohenberg-Kohn theorems. The total energy functional in terms of the KS formalism is then given by:^{34,61,62}

$$E_{DFT}[\rho] = T_s[\rho] + E_{Ae}[\rho] + J[\rho] + E_{xc}[\rho] \quad (2.14)$$

where $T_s[\rho]$ is the kinetic energy of the non-interacting system, $E_{Ae}[\rho]$ is the attractive nuclei-electron Coulomb potential, $J[\rho]$ is the classical Coulomb energy term, and $E_{xc}[\rho]$ is the exchange-correlation energy.^{34,61,62}

It is important to note that the exchange correlation energy, $E_{xc}[\rho]$, is the only unknown term in Equation 2.14, in fact $E_{xc}[\rho]$ is a collection of terms all of which are unknown. It consists of the residual part of the true kinetic energy, $T_c[\rho] = T[\rho] - T_s[\rho]$, the electron-electron Coulomb repulsion term, and an exchange energy contribution.^{61,62} What this also shows however, is that if the form of the $E_{xc}[\rho]$ is known, then DFT yields an *exact* solution for the total energy of the system, and so DFT in the KS formalism is in principle an *exact* method.

The solution to the many-electron wave-function is then given by the iterative solution of the KS equations:

$$\left[-\frac{1}{2} \nabla^2 + v_{eff}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}) \quad (2.15)$$

where $v_{eff}(\mathbf{r})$ is the effective one-particle potential:

$$v_{eff}(\mathbf{r}) = v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r}) \quad (2.16)$$

which includes the nuclei potential, a Hartree-style potential term, and the exchange and correlation potential, which is defined like so:

$$v_{xc}(\mathbf{r}) = \frac{\partial E_{xc}[\rho(\mathbf{r})]}{\partial \rho(\mathbf{r})} \quad (2.17)$$

Initially, a trial charge density is chosen which is then used to calculate the effective potential of a system via Equation 2.16 where an exchange correlation potential is approximated by a chosen exchange correlation functional. This then allows for calculation of the KS orbitals

which are then used to calculate the charge density. This process is then repeated iteratively minimizing the difference between the trial charge density and the calculated charge density until they are *self-consistent*.

If the charge density of a system has been calculated, the Hellman-Feynman theorem⁶² can then be used to determine the force acting on a nuclei located at $\mathbf{R}$:

$$\mathbf{F} = -\left\langle \psi \left| \frac{\delta \hat{H}}{\delta \mathbf{R}} \right| \psi \right\rangle \quad (2.18)$$

where $\hat{H}$ is the electronic Hamiltonian. The force $\mathbf{F}$ refers to the nuclei-nuclei interaction and the nuclei-electron interactions. The calculated interatomic forces at different geometries of a system can then be minimized to calculate the optimized geometric structure.^{61,62} Different strategies for the minimization of the forces can then be employed. It is important to note that the basis set being used will also influence the formalism of calculation of forces.^{61,62}

2.4.3 Approximating the Exchange Correlation Energy

As mentioned, the exchange correlation energy is a collection of all the unknown terms, namely, the residual part of the kinetic energy, the exchange energy and the correlation energy. The correlation energy refers to the electron-electron Coulombic repulsion that occurs as a result of the charge of the electrons. The exchange energy on the other hand, refers to the electron-electron repulsion that occurs as a result of spin, i.e. two electrons of the same spin will repel one another. Both these energies are as a result of the Pauli Exclusion principle, which states that no two identical particles can exist in the same quantum state. For instance, two electrons of same spin cannot occupy the same orbital. This also means that wavefunctions of two spin states must be orthogonal, as they are antisymmetric. This is then reflected in the construction of orbitals in DFT.^{61,62}

The $E_{xc}[\rho]$ is extremely complex and since it is unknown it is approximated via functionals that are based on electron density. The effectiveness of any DFT calculation hinges on the quality of the functional used. There are scores of functionals of many different types, which range in accuracy and computational cost. One of the simplest and earliest functionals is the Local Density Approximation (LDA); where the exchange-correlation energy at any given point $\mathbf{r}$ is assumed to be equal to the exchange-correlation energy of a uniform homogenous gas with the same electron density at point $\mathbf{r}$.^{61,62}

$$E_{xc}^{LDA}[\rho(\mathbf{r})] = \int \rho(\mathbf{r}) \epsilon_{xc}^{hom}[\rho(\mathbf{r})] d\mathbf{r} \quad (2.19)$$

Although an extremely simple approximation it has performed relatively well, especially for solids, however this is thought to be due to the fortunate cancelling of errors in the exchange energy part and LDA unexpectedly struggles heavily for systems with complicated bonding characteristics.^{61,62}

Perhaps the most commonly used set of functionals are known as the Generalized Gradient Approximation (GGA) methods, that take into consideration the gradient of the electron density:

$$E_{xc}^{GGA}[\rho(\mathbf{r})] = \int \rho(\mathbf{r}) F[\rho(\mathbf{r}), \nabla \rho(\mathbf{r})] d\mathbf{r} \quad (2.20)$$

Their popularity stems due to their relatively simplicity, and thus low computational cost, outperforming LDA with far better energetic results.

Even more accurate functionals that take other parameters into account, such as the Laplacian of the electron density or exact exchange energy, also exist. However, naturally the more complex a functional the more computational cost it requires. Higher order functionals are also no guarantee of accuracy particularly for systems that are highly intricate. It is crucial to understand the nature of the problem at hand, and conduct thorough benchmarking before choosing a functional.

2.4.4 Linear Combination of Atomic Orbitals and Molecular Systems

Having considered the exchange-correlation energy, the single-electron $\psi_i(\mathbf{r})$ from the one-electron KS equation (Equation 2.15), also known as the KS molecular orbitals, must now be described. By far and away the most common approach for molecular systems, *i.e.* those without periodic boundary conditions, is the Linear Combination of Atomic Orbital (LCAO) expansion.^{61,62} Here, the KS molecular orbitals are expanded linearly via a set of predefined basis functions, $[\eta_\mu]$:

$$\psi_i(\mathbf{r}) = \sum_{\mu=1}^L c_{\mu i} \eta_\mu \quad (2.21)$$

An exact solution of the KS molecular orbitals would require $L = \infty$, which is not feasible for many-electron systems, hence in reality L is finite. It then becomes crucial to select η_μ such that the exact KS molecular orbitals are approximated as accurately as possible.^{61,62}

2.4.5 Extended Systems and Plane-Waves

When dealing with extended systems, such as bulk crystals, it would seem like an infinite number of single-electron wave-functions (that extend over all space) are required to effectively describe the system. However, Bloch's theorem for infinitely periodic systems offers a solution whereby the single-electron wave-functions can be expressed via plane-waves that are regulated by a periodic function:^{61,62}

$$\psi_i(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u(\mathbf{r}) \quad (2.22)$$

where $\mathbf{k}$ is the wave-vector and $u(\mathbf{r})$ is a function that has the same periodicity as the crystal.

It can then be shown, that the infinite number of wave-functions present in an infinitely periodic system, can be described by a finite number of occupied states at each wave-vector $\mathbf{k}$. This allows $\mathbf{k}$ to lie in the first Brillouin zone, which is uniquely defined by the crystal's lattice vectors.^{61,62} The number of independent $\mathbf{k}$ -points required to adequately describe a crystal will depend on the size of the system at hand.

However, a huge number of plane-waves would be required to model all the electrons in a large system, especially to describe the tightly bound core electrons as the valence wavefunctions oscillate rapidly near the core due to the strong ionic potential. Since most physical properties of solid systems largely depend on the valence electrons rather than the core electrons, an approximation to describe the core region and its effects on the valence electrons can be introduced. This is known as the pseudopotential approximation,^{61,62} where the core electrons are replaced by a weak pseudopotential that acts on a set of pseudo wavefunctions rather than the true valence wavefunctions. This simplifies the problem greatly with these pseudo wavefunctions no longer oscillating in the core region, allowing for large extended systems to be modelled effectively with far fewer plane-waves. These pseudo wave-functions are constructed so that they are identical to the all-electron wavefunction outside of a core cutoff radius, r_c , which is a property of the pseudopotential being used.^{61,62} Two of the most common types of pseudopotentials are norm-conserving (NC) pseudopotentials and ultrasoft (US) pseudopotentials. NC pseudopotentials impose a constraint that the charge density within the

cutoff radius is identical to the charge density of the all-electron wavefunction. Ultrasoft pseudopotentials on the other hand relax this constraint which results in fewer planewaves being required, however more complex calculations such as excited state calculations or the use of hybrid density functionals can mean that the implementation of US pseudopotentials becomes very difficult.^{40,61,62} In more recent times a new formalism for the construction of NC pseudopotentials has been proposed which uses a similar construction methodology as those used for US potentials but still maintains the norm-conserving constraint.⁴⁰ These potentials have been called the Optimized Vanderbilt Norm-Conserving (ONCV) pseudopotentials and have allowed for smaller cutoffs, similar to those seen for US potentials.⁴⁰ These ONCV potentials have thus been used in this work.

2.5 Time-Dependent Density Functional Theory

Time-Dependent Density Functional Theory (TDDFT) is a formalism which allows for the treatment of excited states. It is set up similarly to KS-DFT however, in this case, the aim is to solve the time-dependent version of the Schrödinger equation. The foundational theorem behind modern TDDFT was presented by Runge and Gross⁵⁰ (the analogue to the Hohenberg-Kohn theorems for KS-DFT) who proved that if two potentials differ by a purely time-dependent function, they will produce the same time-dependent electron density. This allowed for a similar Kohn-Sham approach to be applied to then give a time-dependent single-body equation.^{61,62} The work in this thesis has been conducted via the adiabatic linear-response variant of TDDFT, also known as LR-TDDFT.

LR-TDDFT uses perturbation theory to explore excited state characteristics and works particularly well when the perturbing field is weak, as is the case in most spectroscopy methods.^{61,62} The core idea of LR-TDDFT is to compute the excitation frequencies of a system, *i.e.* the frequencies at which the density response of a system has a pole. This is done via the central equation of LR-TDDFT:

$$\chi(\mathbf{r}, \mathbf{r}', \omega) = \chi_{KS}(\mathbf{r}, \mathbf{r}', \omega) + \int d\mathbf{r}_1 \int d\mathbf{r}_2 \chi_{KS}(\mathbf{r}, \mathbf{r}_1, \omega) \left[\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + f_{xc}(\mathbf{r}_1, \mathbf{r}_2, \omega) \right] \chi(\mathbf{r}_2, \mathbf{r}', \omega) \quad (2.23)$$

where χ is the density response of the system, χ_{KS} the density response of the unperturbed non-interacting system, and f_{xc} is the Fourier transform of the exchange-correlation kernel.

The poles of $\chi(\mathbf{r}, \mathbf{r}', \omega)$ are computed by expanding the above equation as products of the occupied and virtual KS orbitals in terms of a matrix eigenvalue problem known as Casida's equations, the solutions of which yield the excitation energies.^{51,52} Like KS-DFT, although LR-TDDFT is an exact method it requires the exact exchange-correlation kernel which is not known. The adiabatic approximation simplifies the problem by assuming the exchange-correlation kernel as local in time, which holds if the time-dependent potential is changed very slowly, *i.e.* adiabatically. This means the exchange correlation kernel is static and becomes frequency independent; $f_{xc}(\mathbf{r}, \mathbf{r}')$, allowing Casida's equations to be set up more easily.^{61,62}

It is important to note that since TDDFT is built upon the wave-functions generated by DFT the two main factors in the effectiveness of how a system is described depend on the ground-state exchange-correlation functional and the TDDFT exchange-correlation kernel. Due to the static nature of $f_{xc}(\mathbf{r}, \mathbf{r}')$ under the adiabatic approximation, TDDFT can struggle with high-energy excited states such as Rydberg states and excitonic effects, since due to the kernel lacking a proper long-range term. However, for low-lying excited states close to the ground-state, TDDFT offers strong performance for low computational cost.^{61,62}

How well DFT/TDDFT is able to model the subject complexes in the framework of the optical selection rules will also influence the quality of the calculated optical spectra. Optical selection rules help determine what transitions, with a focus on the electronic transitions in this case, are allowed and which ones are forbidden. That is, the probability of a transition cannot be zero. The probability of an electronic transition will be dictated by the type of transition occurring, the symmetry of the initial and final wavefunctions, and the nature of the orbitals involved. Naturally, this will vary depending on the chemical nature of the system at hand and its symmetry. For instance, in the case of the subject materials the presence of the ruthenium d-orbitals allows for certain electronic transitions whilst the space group of the crystal also plays a part by influencing which orbitals facilitate a transition.⁷³

2.6 The Nudged Elastic Band Method

The Nudged Elastic Band (NEB) method is a technique to find the saddle points and minimum energy pathway (MEP) between two known endpoints.⁶³ It is often used to explore the PES between two known states of a system, for instance between reactants and products. The reaction pathway between the two known endpoints is described by a set of images (sequences

of atomic positions). The atoms of each image are connected to their equivalent counterparts in the adjacent images by harmonic constraints with a harmonic constant k_s , much like an elastic band. The spring forces and atomic forces are then optimized whilst remaining orthogonal to one another. Since the images are ‘connected’ to one another, the entire pathway minimizes towards the MEP.⁶³

The NEB algorithm therefore seeks to minimize the overall force acting on each atom at image i , which is defined as:⁶³

$$\mathbf{F}_i = \mathbf{F}_\parallel^s + \mathbf{F}_\perp^b \quad (2.24)$$

The overall force acting on each atom in image i is the sum of the spring force which acts parallel to the path, stopping images sliding downwards and keeping them equally spaced, and the atomic forces acting perpendicular to path, which allows the calculation of the MEP closest to the initial guessed pathway.⁶³ This force can be calculated by subtracting the parallel part from the forces calculated via DFT (as mentioned in Section 2.4.2). There are several minimization algorithms that can be used, such as the steepest descent method or the popular Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm. One of the key characteristics of NEB is that the effectiveness of the method depends heavily on the input coordinates, *i.e.* the starting and final images. When these images are representative of the pathway that needs optimizing, then NEB is a powerful method which delivers not only the MEP but the saddle points and energy barriers as well.

3 Development of Plane-Wave Models

This chapter evaluates the ability of using PW-DFT based periodic models to effectively simulate the experimentally determined single-crystal diffraction and optical absorption spectra of these crystalline [RuSO₂] complexes. Calculations were conducted on four structures of two complexes: (i) two variants of the simplest complex in this series where **X** = **Y** = Cl; **1A** only forms the η^2 -(OS)O photoisomer, whereas **1B** forms both η^1 -OSO and η^2 -(OS)O photoisomers; (ii) two variants of the thermally most stable complex in this [RuSO₂] series, where **X** = H₂O and **Y** = *p*-tosylate; **2A** only forms the η^2 -(OS)O photoisomer, whereas **2B** forms both η^1 -OSO and η^2 -(OS)O photoisomers. All four structures behave as photoswitches. Initially, structure relaxation calculations for all dark and light states were conducted in order to reproduce the experimentally-determined crystal-structure geometries. These optimized structures were then used to simulate optical absorption spectra via linear-response TDDFT, to replicate features seen in their experimentally-determined single-crystal absorption spectra. The same series of calculations were also conducted via MO-based DFT. An MO-based analysis of the optical results was also undertaken in order to study the orbitals that are involved in the various electronic transitions. This study thereby showcases the applicability of using a periodic approach in modeling these extremely complex systems and why periodic approaches should be considered as a viable alternative to the use of molecular fragment-based approaches for studying the structural and optical properties of this family of large ruthenium-based crystalline complexes that exhibit single-crystal optical actuation via linkage photoisomerism.

3.1 DFT Models and Computational Methodology

3.1.1 Optimized DFT Models and Experimental Structure Reproduction

PW Models

All PW calculations were conducted using the 6.4 version of the *Quantum Espresso*^{38,39} (QE) suite of codes, as available on the Theta machine at the Argonne Leadership Computing Facility (ALCF), IL, USA. The unit cells of the experimentally-determined crystal structures^{15,16,26} were used to provide the starting geometries for all four structures of these complexes (with 88 atoms in the unit cells for **1A** and **1B**, and 118 atoms for **2A** and **2B**). With few exceptions, the photoconversion levels associated with the SO₂ linkage photoisomerization are not complete; the experimentally-determined crystal structures are therefore modeled with fractional SO₂ atomic occupancies in order to represent the proportionate level by which each SO₂ isomer is present. All calculations in this thesis emulate each SO₂ isomer in its 100% form, for ease of computational demands; the scientific interpretations of their results are partitioned accordingly. So, given that three types of SO₂ isomers have been shown to exist experimentally in [RuSO₂] complexes, there are up to three unit cells to consider per compound in these studies. The unit cells used are illustrated in Figures 3.1 and 3.2 below. Table 3.1 contains the cell parameters for all four complexes. It is important to note that the dark and light states within each complex have different cell parameters. Complexes **1A** and **1B** are orthorhombic crystals with a *Pnma* space group, whereas complexes **2A** and **2B** are triclinic systems with a *P* $\bar{1}$ space group

Table 3.1: PW-DFT simulation parameters for all four structures of the two [RuSO₂] complexes.

	1A		1B			2A		2B		
	η^1 - SO ₂	η^2 - (OS)O	η^1 - SO ₂	η^2 - (OS)O	η^1 - OSO	η^1 - SO ₂	η^2 - (OS)O	η^1 - SO ₂	η^2 - (OS)O	η^1 - OSO
Energy cutoff (Ry)	280	240	240	240	240	280	240	260	240	260
K-mesh size	4x4x4	2x2x2	4x4x4	2x2x2	2x2x2	2x2x2	2x2x2	2x2x2	2x2x2	2x2x2
Number of k-points	27	8	27	8	8	8	8	8	8	8

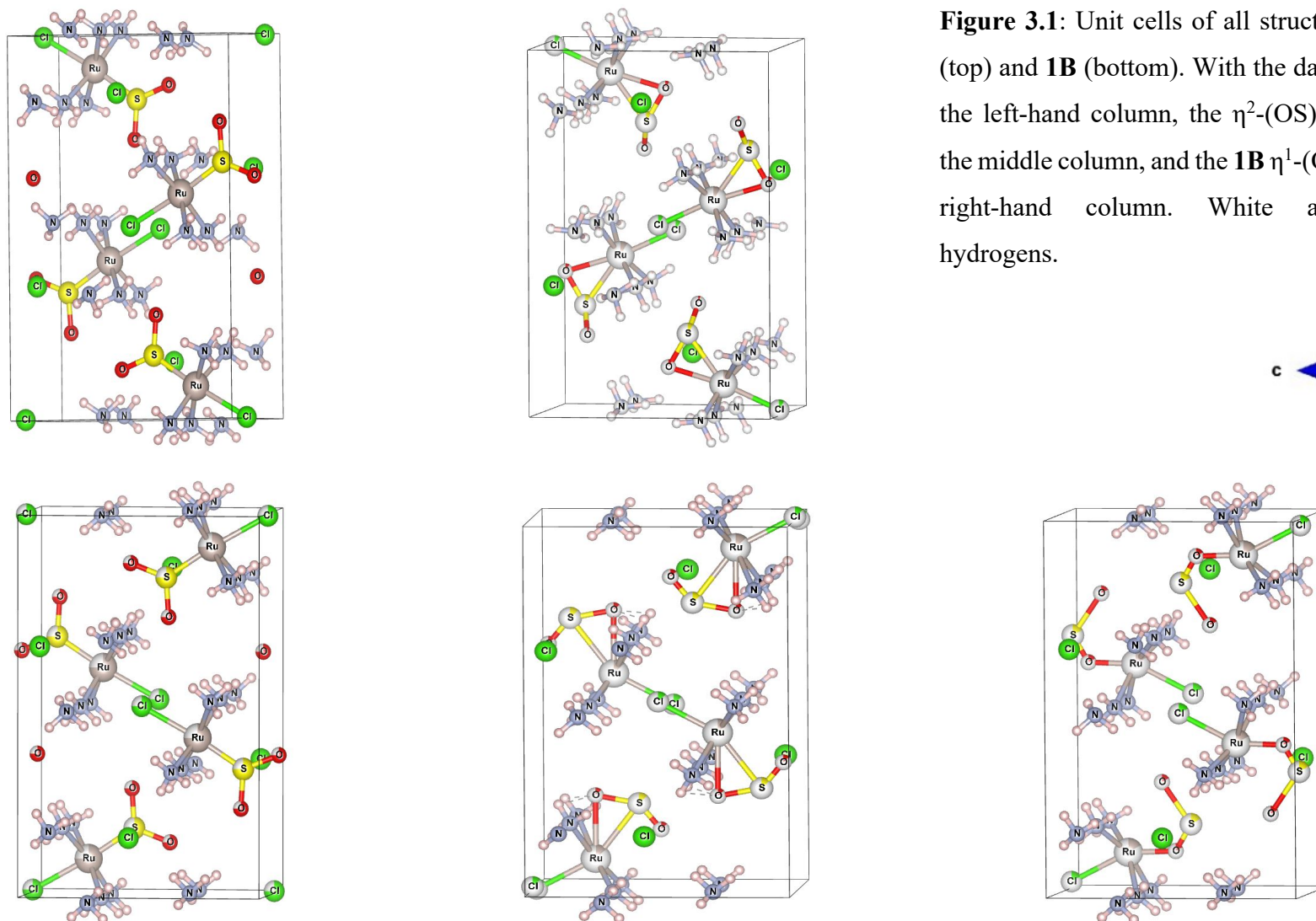


Figure 3.1: Unit cells of all structures of **1A** (top) and **1B** (bottom). With the dark-states in the left-hand column, the η^2 -(OS)O states in the middle column, and the **1B** η^1 -(OS)O in the right-hand column. White atoms are hydrogens.

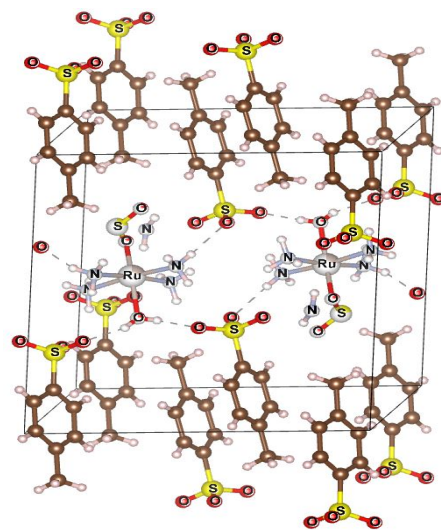
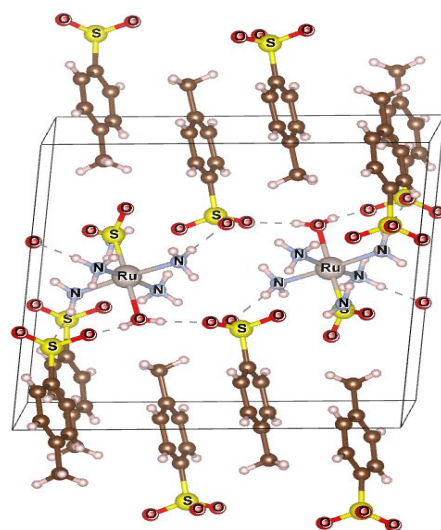
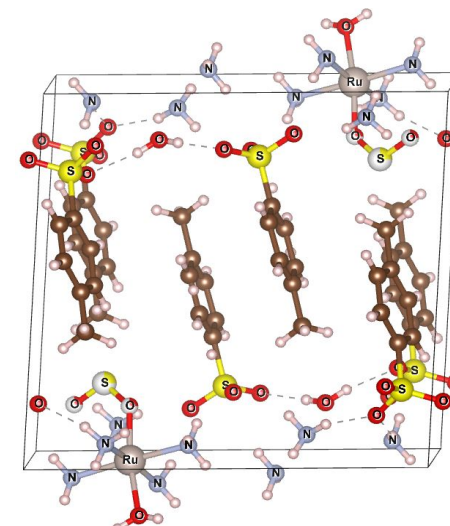
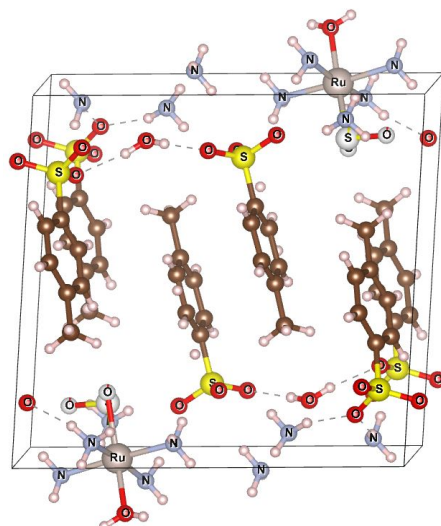
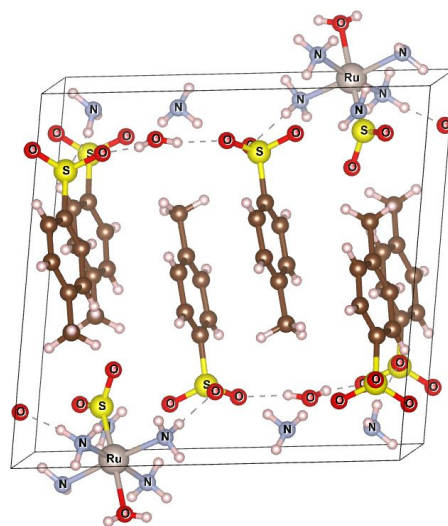
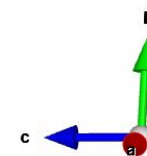


Figure 3.2: Unit cells of all structures of **2A** (top) and **2B** (bottom). With the dark-states in the left-hand column, the η^2 -(OS)O states in the middle column, and the **2B** η^1 -(OS)O in the right-hand column. Brown atoms are carbons and white atoms are hydrogens.



The first task was to determine the ideal functional and pseudopotential choices, which was achieved in an iterative manner. Initially, PW-TDDFT spectra were generated for complex **2A** using both scalar-relativistic norm-conserving (SR-NC) PBE-based ONCV potentials⁴⁰ and Ultrasoft potentials, with PBE as the functional (Figure 3.3). The Ultrasoft potentials required the same energy cutoff (200 Ry) as the ONCV potentials thus not leading to any significant computational savings. The spectra for the ONCV potentials showcased a greater increase in absorbance upon the inclusion of the light-induced spectra, with the overall spectra being broader than that of the Ultrasoft potentials. The SR-NC ONCV potentials were thus the preferred option as they showed slightly better spectral shape. PW-TDDFT spectra using ONCV potentials were then generated for complex **2A** for a series of GGA³⁵ (Figure 3.4) and hybrid functionals (Figure 3.5) with ONCV pseudopotentials. The two hybrid functionals explored were PBE0⁴¹ and HSE⁴², with different exact-exchange fractions and screening parameters tested to reproduce the dark-state spectra for complex **2A**. GGA functionals clearly outperformed their hybrid counterparts. PBEsol⁴³ emerged as the ideal candidate, with its spectra for the light-induced state showing increased absorbance, especially more closely toward the desired energy region of 3.10 – 1.77 eV, with its overall spectra thus more closely resembling experimental spectra as compared to spectra generated via Wu-Cohen and revPBE. The pseudopotential choice was then re-evaluated by comparing ONCV and PBEsol-based SR-NC pseudopotentials, with PBEsol used as the functional (Fig. 3.6). Spectra were generated for the dark and light states of complexes **2A**, **3** and **4**.

This set of complexes encompasses photoswitches and a molecular transducer with both types of metastable geometries. Both potentials showcased increased absorbance with the inclusion of the light-induced spectra, with the overall spectra broadening as well. However, PBEsol spectra were found to be much smoother in shape and less sensitive across all three complexes, showcasing fewer spurious peaks and shoulders, particularly above 5 eV. The overall stability of the spectra generated via PBEsol-based potentials was thus found to be better than that of the spectra generated via ONCV potentials. PBEsol-based SR-NC pseudopotentials with PBEsol as the functional was found to be the ideal pairing for modeling the dark- and light-induced structures of these complexes and simulating their single-crystal optical absorption spectra. This setup was used for all structures of the complexes studied in this thesis along with the Grimme DFT-D2 method,⁴⁴ which was used to account for van der Waals interactions, which are crucially important in these materials.

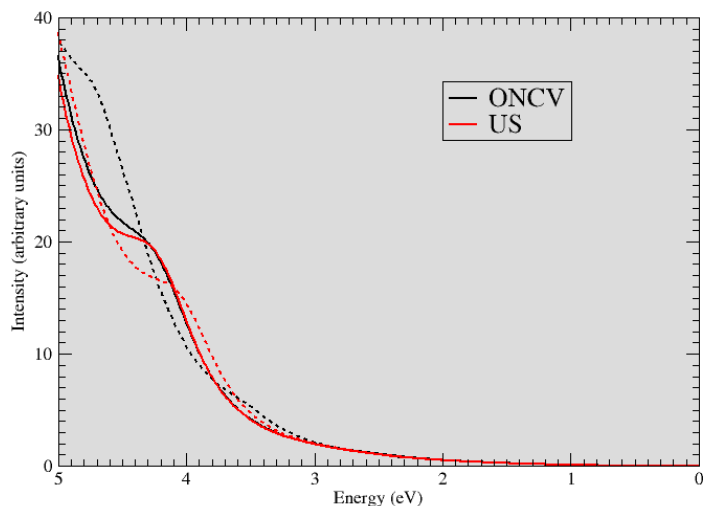


Figure 3.3: PW-TDDFT spectra for complex **2A** with ONCV and Ultrasoft pseudopotentials. The PBE functional has been used with both pseudopotentials. Solid-lines represent the dark-state whereas the dotted lines represent the η^2 -(OS)O light-induced state.

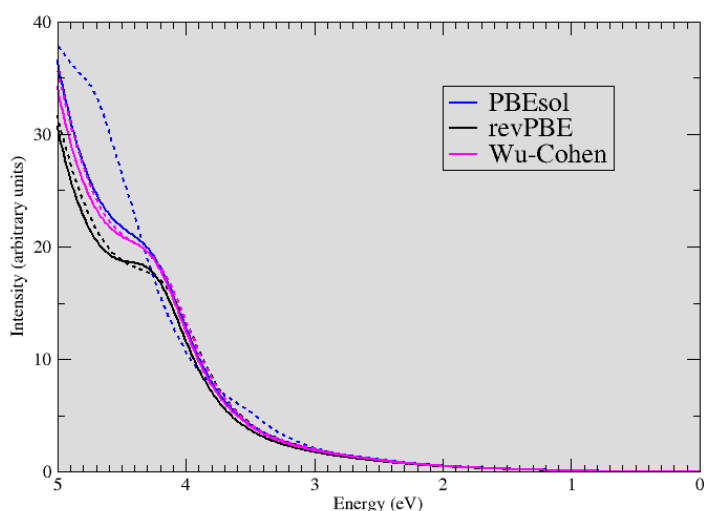


Figure 3.4: PW-TDDFT spectra for complex **2A** with ONCV pseudopotentials for different GGA functionals. Solid-lines represent the dark-state whereas the dotted lines represent the η^2 -(OS)O light-induced state.

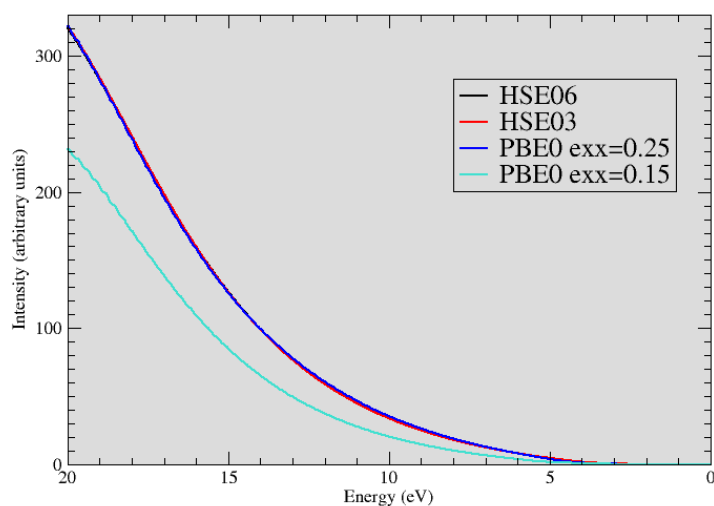


Figure 3.5: PW-TDDFT spectra with ONCV pseudopotentials for **2A** dark-state for functionals with exact exchange: HSE03, HSE06 and PBE0 (for two different exact exchange fractions of 0.25 and 0.15). The initial geometry was optimized using PBE after which the TDDFT optical spectra were calculated using the exact exchange functionals. It is important to note that the TDDFT module in Quantum Espresso only implements exact exchange functionals using orthorhombic unit cells. Consequently, a 118-atom supercell of the **2A** dark state was used with an orthorhombic unit cell, where $a = 20 \text{ \AA}$, $b = 18 \text{ \AA}$, and $c = 14.5 \text{ \AA}$.

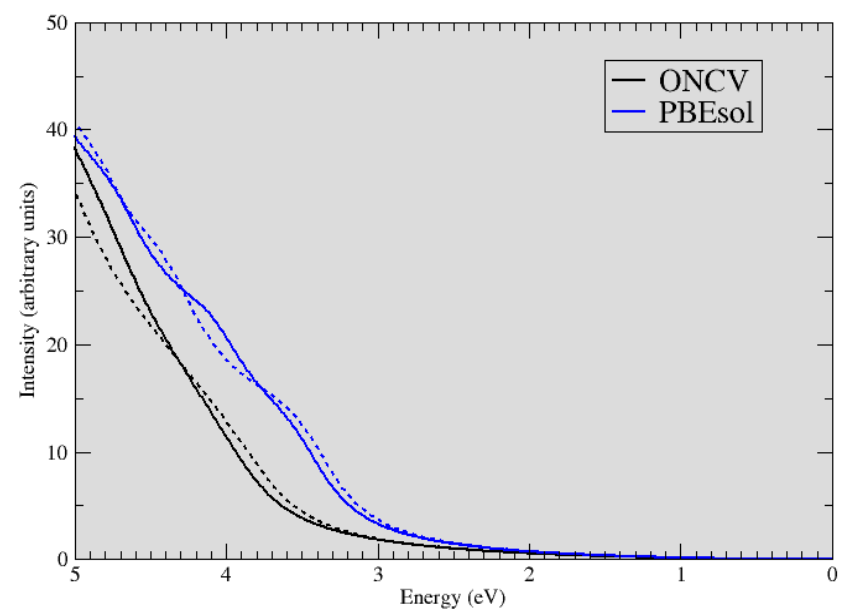
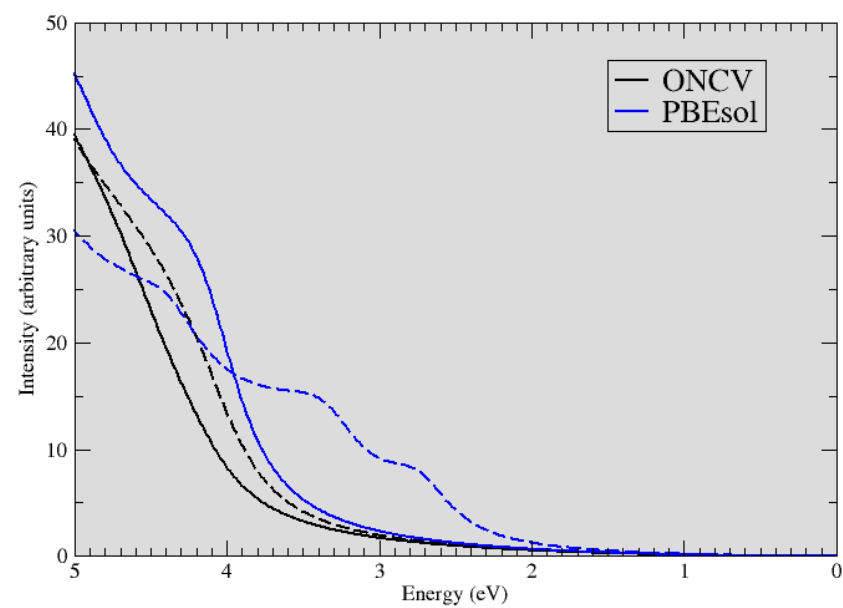
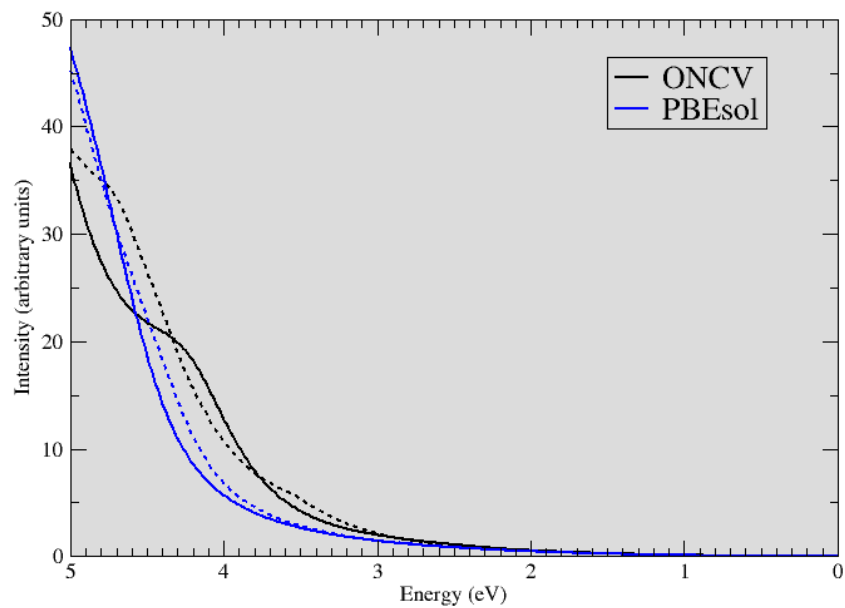


Figure 3.6: PW-TDDFT spectra for complexes **2A**, **3** and **4** with ONCV (black) and PBEsol (blue) pseudopotentials for the PBEsol functional. Solid-lines represent the dark-state whereas the dotted lines represent the η^2 -(OS)O light-induced state and the broken line represents the η^1 -OSO light-induced state.

With the modeling parameters settled, the PW energy cutoff was determined, and Brillouin zone sampling was undertaken for all structures of complexes **1A**, **1B**, **2A** and **2B**. The PW energy cutoff limits the kinetic energy of the PWs, with a larger cutoff resulting in a higher quality basis set but increasing the computation power required. This value needs to converge to a desired tolerance. The ideal PW energy cutoff was chosen by minimizing the total energy-per-atom to a tolerance of 0.00005 eV per atom. A series of energy cutoffs of increasing value were trialed until the total energy-per-atom value of the SCF calculation stabilized and converged to the tolerance specified above. Figures 3.7 and 3.8 detail the energy cutoff values that were trialed for all four structures of the two complexes. In all cases, the charge-density cutoff was four times higher than the energy cutoff. Each system required its own corresponding value, as shown in Table 3.4.

Similarly, the Brillouin zone sampling, i.e., the number and geometry of k-points used, also needs to converge to a desired tolerance. K-point sampling is a particular feature that is necessary when modeling periodic systems. To deal with periodic boundary conditions, Fourier transforms enable calculations to be conducted in reciprocal space, which greatly reduces the computing power required. Every lattice in real space has a corresponding structure in reciprocal space. The larger the real lattice, the smaller its reciprocal counterpart. The k-point sampling refers to the size and shape of reciprocal space that is sampled; the larger the sampling, the better the representation of the system. The number of k-points required is inversely proportional to the unit cell volume (i.e. the size of the system), but it does vary depending on the characteristics of system. The sampling required was determined using the Monkhorst-Pack scheme⁴⁵ and the same energy-per-atom tolerance as the energy cutoff. Different grid sizes were sampled for each structure using the previously determined ideal energy cutoff. The grid sizes sampled are detailed in Tables 3.2 and 3.3. Due to the size and complexity of these systems, with the exception of the dark states of **1A** and **1B**, Monkhorst-Pack grids larger than 8x8x8 were found to be extremely difficult to simulate due to the larger number of k-points (well over a 100 k-points) required. However, it can be seen that for all structures except for the dark states of **1A** and **1B**, there was no change in the total energy-per-atom value within the desired tolerance for Monkhorst-Pack grids larger in size than 2x2x2. Small uniform grids, of 8 to 27 k-points, were found to be optimal in size (Table 3.4). As expected, these large systems require few k-points to be adequately described, which shows that they are not very k-point sensitive.

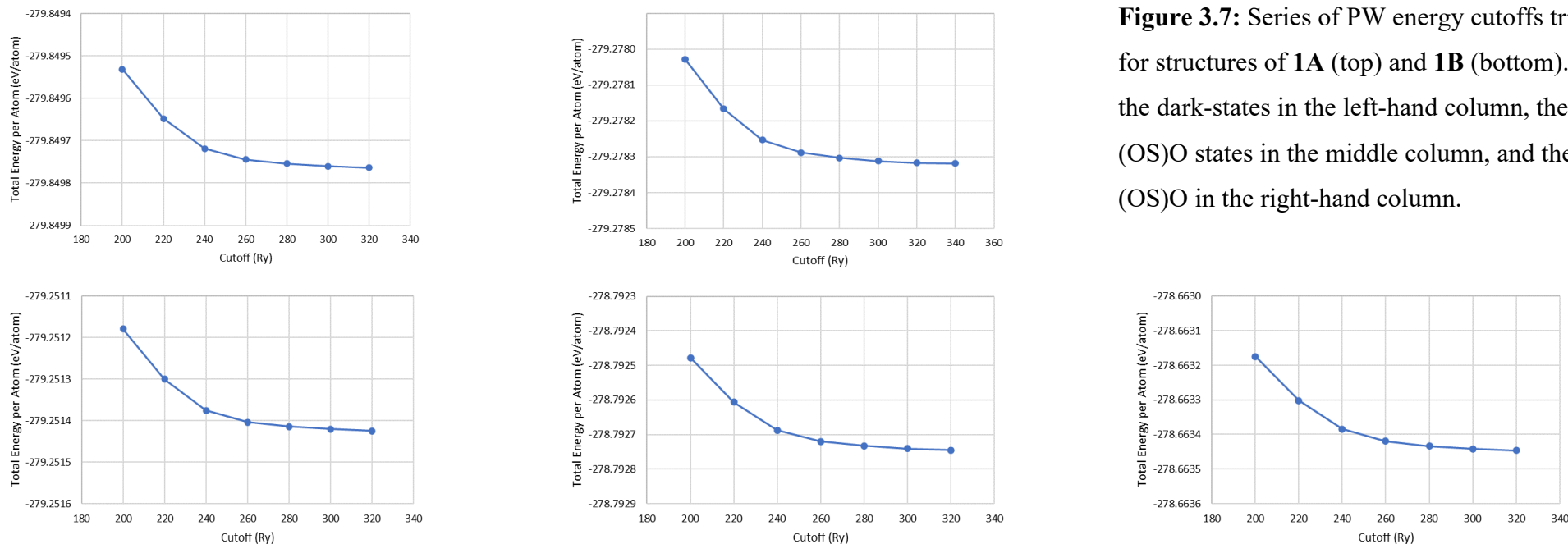


Figure 3.7: Series of PW energy cutoffs trialled for structures of **1A** (top) and **1B** (bottom). With the dark-states in the left-hand column, the η^2 -(OS)O states in the middle column, and the **1B** η^1 -(OS)O in the right-hand column.

Table 3.2: Series of k-meshes trialled for the dark and light-state structures of complexes **1A** and **1B**.

K-mesh Size	Total Energy-per-Atom (eV/atom)				
	1A		1B		
	Dark-State	η^2 -(OS)O	Dark-State	η^2 -(OS)O	η^1 -OSO
1x1x1	-279.8498	-279.2783	-279.2514	-278.7927	-278.6634
2x2x2	-279.8573	-279.2818	-279.2584	-278.7968	-278.6686
4x4x4	-279.8574	-279.2818	-279.2585		-278.6685
8x8x8	-279.8574	-279.2818	-279.2585		-278.6685

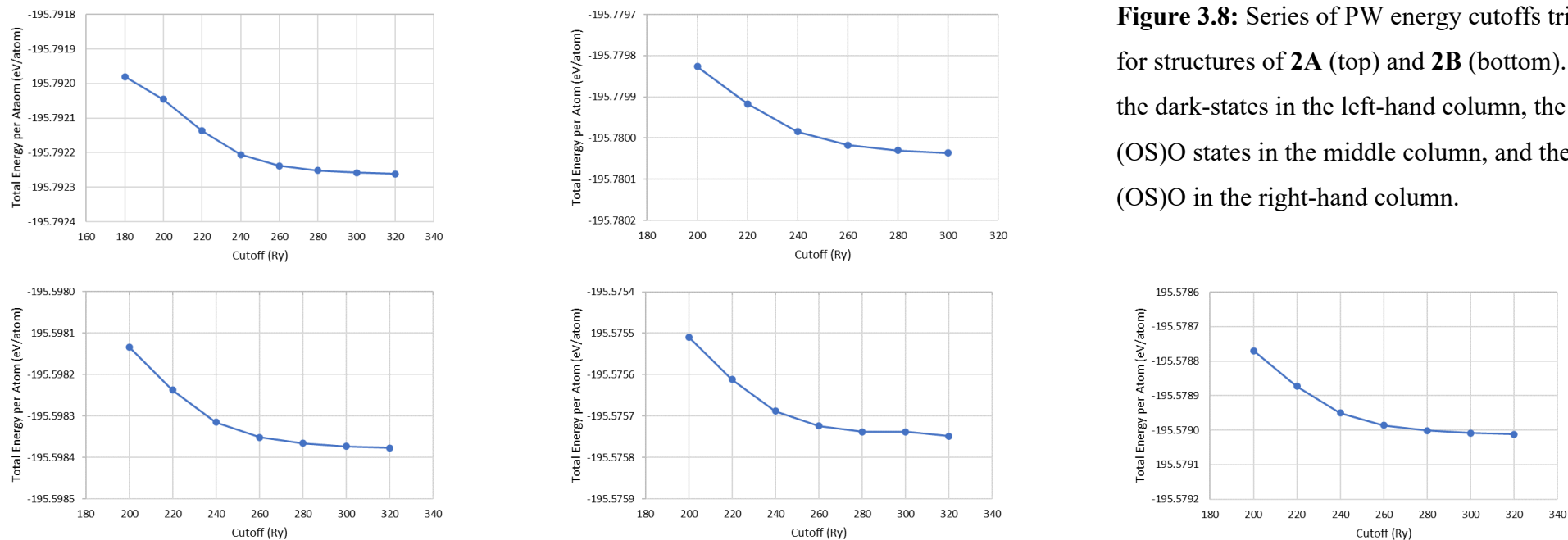


Figure 3.8: Series of PW energy cutoffs trialled for structures of **2A** (top) and **2B** (bottom). With the dark-states in the left-hand column, the η^2 -(OS)O states in the middle column, and the **1B** η^1 -(OS)O in the right-hand column.

Table 3.3: Series of k-meshes trialled for the dark and light-state structures of complexes **2A** and **2B**.

K-mesh Size	Total Energy-per-Atom (eV/atom)				
	2A		2B		
	Dark-State	η^2 -(OS)O	Dark-State	η^2 -(OS)O	η^1 -OSO
1x1x1	-195.7923	-195.7800	-195.5984	-195.5757	-195.5790
2x2x2	-195.7950	-195.7835	-195.6009	-195.5775	-195.5814
4x4x4	-195.7950	-195.7835	-195.6009	-195.5775	-195.5814

Table 3.4: PW-DFT simulation parameters for all four structures of the two [RuSO₂] complexes.

	1A		1B			2A		2B		
	η^1 -SO ₂	η^2 -(OS)O	η^1 -SO ₂	η^2 -(OS)O	η^1 -OSO	η^1 -SO ₂	η^2 -(OS)O	η^1 -SO ₂	η^2 -(OS)O	η^1 -OSO
Energy cutoff (Ry)	280	240	240	240	240	280	240	260	240	260
K-mesh size	4x4x4	2x2x2	4x4x4	2x2x2	2x2x2	2x2x2	2x2x2	2x2x2	2x2x2	2x2x2
Number of k-points	27	8	27	8	8	8	8	8	8	8

With the simulation parameters set, geometry optimizations were conducted on all dark and light states of all four structures of the two complexes. The experimentally-determined crystal structures of the dark and light-induced states were used as the starting geometries. No constraints were placed on any atoms, except for the η^2 -(OS)O isomer of in **1B** where the SO₂-Ru-Cl axis had to be fixed to ensure that the geometry remained in the η^2 -(OS)O configuration (for details, see Section 3.1). The geometry of each structure was considered to have converged when the energy between successive optimization steps was within 10⁻⁴ Ry and the forces were within 10⁻³ Ry/bohr. The unit-cell parameters were fixed to experimental values throughout the simulation (see Table 3.1). Crystal symmetries were also constrained and so the space groups of *Pnma* for the structures of **1A** and **1B**, and *P* $\bar{1}$ for **2A** and **2B** were maintained throughout the calculations.

LCAO Gaussian-DFT Models

All calculations were conducted using the NWChem software⁴⁶ on the Carbon Cluster, the high-performance computing facility at the Center for Nanoscale Materials at the Argonne National Laboratory, IL, USA. The starting geometries used were based on the experimentally-determined dark- and light-induced crystal structures for both types of complexes (for complete geometries see Appendix 1). The experimentally determined unit cell parameters and geometries were expanded to recreate complete molecules that were then used to form complete molecular fragments that appropriately represented the desired structures, as shown in Figures 3.9 and 3.10. These molecular-fragment models were then used to conduct the MO-based DFT and TDDFT calculations. The structures of **1A** and **1B**, where **X** = **Y** = Cl, contained 88 atoms and consisted of four cations and four anions (represented by chlorine atoms), while those of **2A** and **2B**, where **X** = H₂O and **Y** = *p*-tosylate, contained 118 atoms and consisted of two cations and four anions (represented by *p*-toluenesulfonate). The ratio of anions to cations is dependent on the chemical structure of each complex.

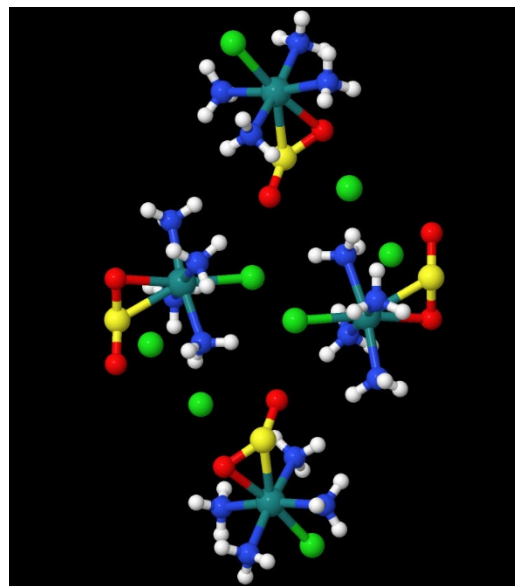
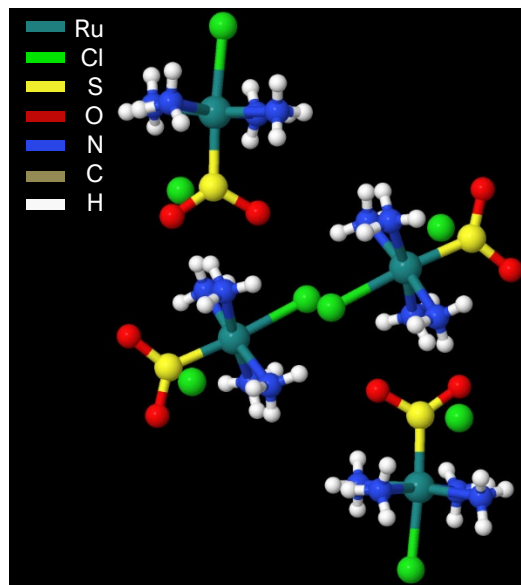
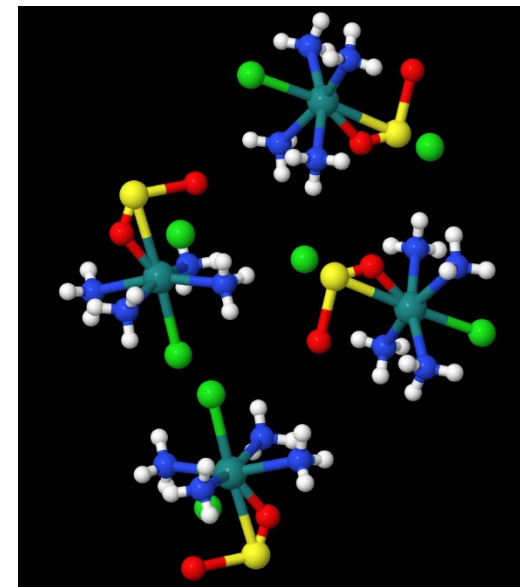
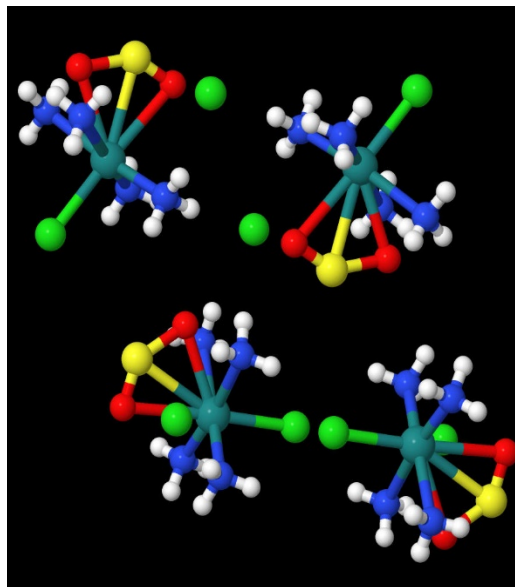
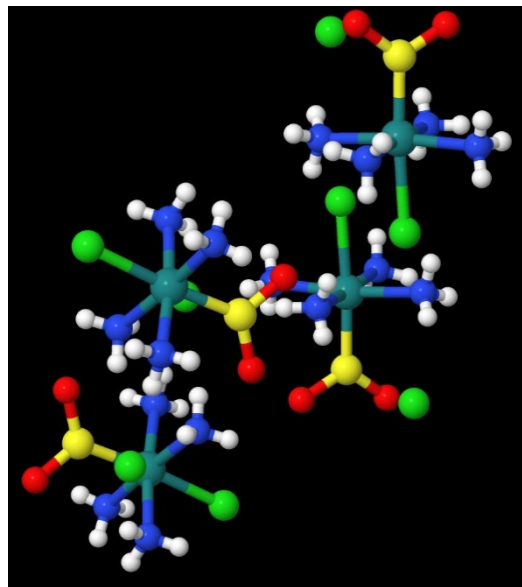


Figure 3.9: Illustrations of the complete fragments used for the starting geometries of the dark and light states of **1A** (top) and **1B** (bottom). With the dark-states in the left-hand column, the η^2 -(OS)O states in the middle column, and the **1B** η^1 -(OS)O in the right-hand column. These fragments were built from the experimentally-determined unit cell parameters and geometries.



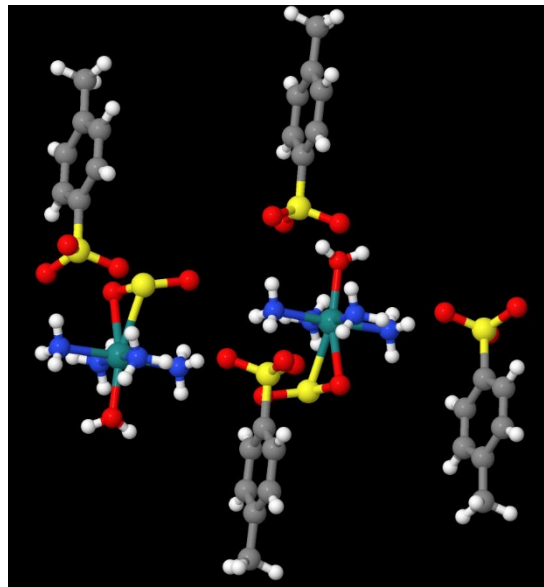
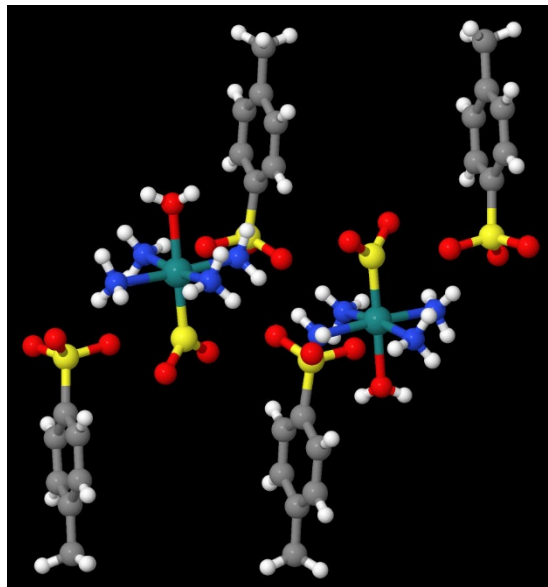
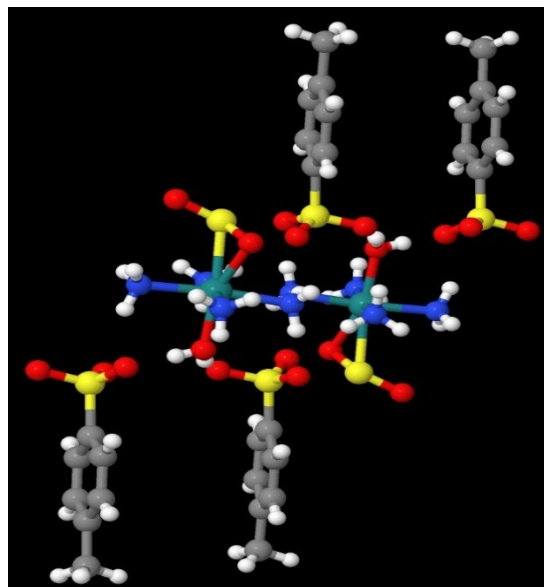
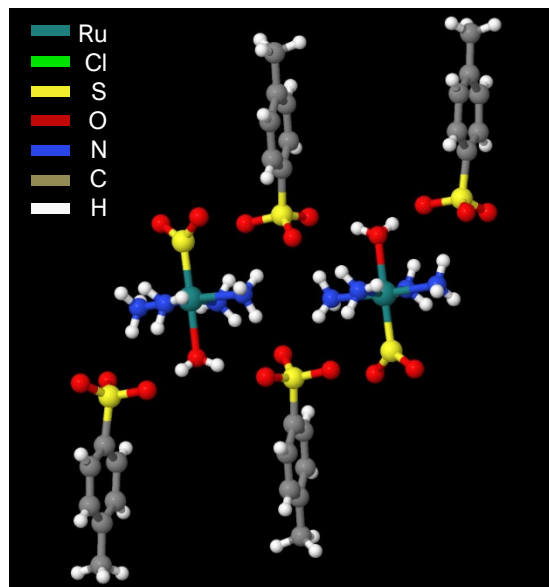
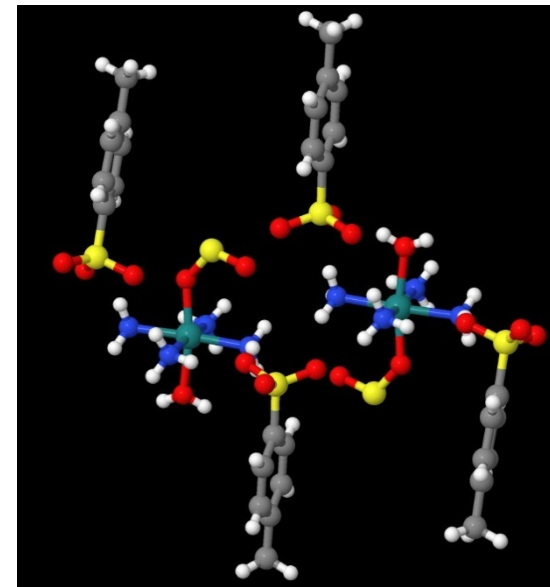


Figure 3.10: Illustrations of the complete fragments used for the starting geometries of the dark and light states of **2A** (top) and **2B** (bottom). With the dark-states in the left-hand column, the η^2 -(OS)O states in the middle column, and the **2B** η^1 -(OS)O in the right-hand column. These fragments were built from the experimentally-determined unit cell parameters and geometries.



The LANLD2Z ECP basis set⁴⁷ was used for ruthenium, while the 6-31G(d,p) set was used for all other atoms except hydrogen, which were modeled using the 3-21G(p) set. This setup was chosen due to the size of the structures, with heavier basis sets resulting in extremely slow geometry optimizations. The lighter basis set for the hydrogen atoms was employed since they have little to no influence on the overall optical properties of these materials.

The next step was to identify the ideal functional. To that end, TDDFT spectra were generated using the experimental geometries of the dark and light states of complex **2A** for four different functionals; CAM-B3LYP,⁷⁹ MPW1K,⁸⁰ PBE0⁴¹ and B3LYP⁴⁸, as shown in Figure 3.11. In all four sets of spectra, it can be seen that absorbance increases with the inclusion of the light-state spectra. As seen from the experimentally determined spectra of these complexes (see Figure 3.11), the region of particular interest for these complexes is the visible region of 400 to 700 nm (3.10 to 1.78 eV). Spectra produced using CAM-B3LYP and MPW1K does not cover the lower end of the visible region, with the dark-state spectra showing absorbance at around 300 nm. As seen from Figure 3.11, the B3LYP functional best produces absorption spectra that includes this desired region, allowing access to almost the entire visible region, and it was found to be the ideal functional choice. The structures of all complexes were thus modeled with the B3LYP functional⁴⁸ with the Grimme-D3 approach⁴⁹ to account for the van der Waals forces.

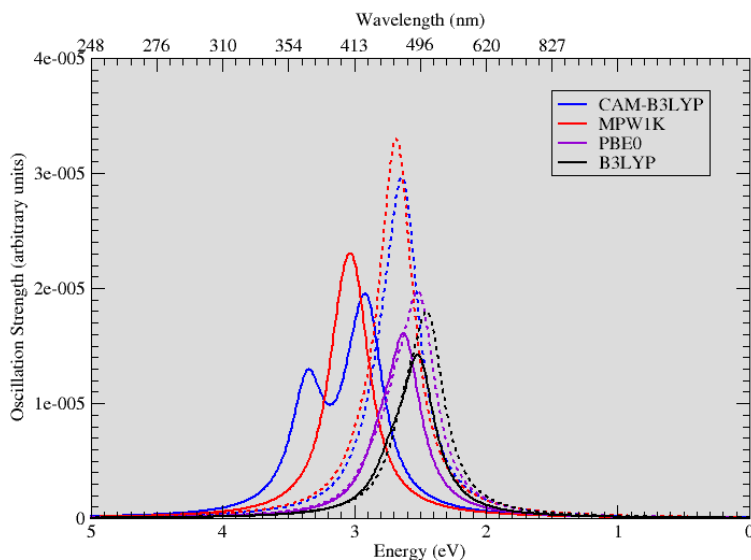


Figure 3.11: Single-crystal optical absorption spectra of Complex **2A** for various functionals, where the solid lines represent the dark-state, and the dotted lines represent the η^2 -(OS)O light-induced state.

Owing to the size and complexity of these structures, geometry optimization was conducted in piecewise steps, with only the final step having all atoms unconstrained. This optimization procedure used the DRIVER module with default convergence parameters for all except for the light-induced states of **2B** where for the final unconstrained optimization the loose convergence parameters were required.⁴¹ Breaking down each structural model into smaller blocks reduced the degrees of freedom making it computationally simpler to optimize. In common with the PW-models, this was the case for all structures of the complexes except for the η^2 -(OS)O conformer in **1B** where the SO₂-Ru-Cl axis was fixed. Symmetry was maintained throughout the structural relaxations.

3.1.2 Optical Absorption Spectra Calculations via Linear-Response (LR)-TDDFT

PW Models

The optimized geometries were then used to conduct TDDFT⁵⁰ calculations in order to determine the optical absorption spectra via the *turbo_tddft* QE module.^{51,52} This module uses the Liouville-Lanczos approach⁵³ to TDDFT, which allows for the calculation of absorption spectra for a wide frequency range without computing any empty states, i.e. only occupied states are considered. This greatly reduces the computational effort required to calculate absorption spectra, which allows for the spectra for large systems, such as the subject materials, to be calculated with relative ease. However, it does mean that electronic transitions from occupied to virtual states cannot be analyzed via the Liouville-Lanczos approach⁵³. Furthermore, *turbo_tddft*^{51,52} can only sample the gamma point for periodic systems. This is particularly difficult for bulk systems since they typically require a large Brillouin zone sampling to effectively simulate the optical response. This is usually the case for materials with high-energy excited states or charge-transfer states. To somewhat circumvent this issue, a supercell approach (much like that used for MO-based DFT) is often employed for large bulk materials. However, we found that the performance of TDDFT in the periodic setup outperformed the supercell approach and it was computationally less intensive.

Using the Liouville-Lanczos algorithm⁵³, Lanczos coefficients are computed which are then used to calculate the absorption coefficients at various frequencies. The parameter *itermax* controls the number of Lanczos coefficients calculated. The larger the value of *itermax*, the better the quality of the spectrum generated, eventually leading to a converged spectrum. This

still remains a computationally expensive calculation and for large systems such as these Ru-based complexes, a huge number of Lanczos coefficients is required to effectively calculate absorption spectra. However, since the Lanczos coefficients are calculated from a tridiagonal matrix computed as part of the LL algorithm⁵³, they can be extrapolated^{51,52}. This renders the overall procedure to calculate absorption spectra via *turbo_tddft*^{51,52} far less computationally intensive. The calculation is therefore conducted in two stages; firstly, a large number of Lanczos coefficients are calculated via the Liouville-Lanczos algorithm⁵³, after which an extrapolation scheme is used to then determine a far larger number of Lanczos coefficients at a negligible computational cost^{51,52}. This allows for the convergence of the absorption spectra to be attained far more quickly. In the case of these Ru-complexes, 2000 Lanczos coefficients were initially calculated via the Liouville-Lanczos algorithm⁵³ as this was the largest number of *itermax* that was computationally accessible for the subject materials. Within the *turbo_tddft*^{51,52} module, the bi-constant extrapolation scheme was then used to determine a far larger number of Lanczos coefficients which were then used to ultimately generate the spectra. The ideal overall *itermax* was thus determined to be 30000, since this produced smooth spectra, especially in the lower energy region (below 10 eV), which is particularly relevant for these complexes. As shown in Figure 3.12 below, the spectra generated for *itermax*=20000 still showed some oscillations which were then smoothed out for *itermax*=30000. The PW-TDDFT spectra generated for complexes **1A**, **1B**, **2A**, and **2B** required 30000 Lanczos coefficients extrapolated from 2000 coefficients calculated using the Liouville-Lanczos algorithm⁵³ as implemented in *turbo_tddft*^{51,52}.

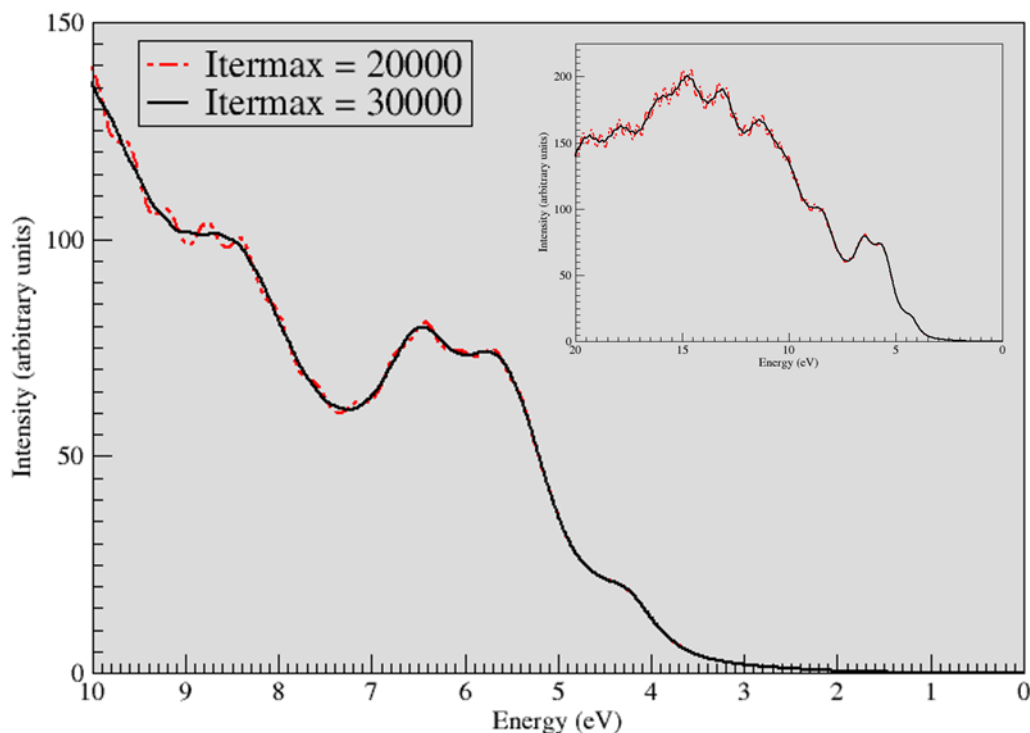


Figure 3.12: PW-TDDFT generated absorption spectra for the dark-state for **2A** for *itermax* values of 20000 and 30000. Spectra including a higher energy region is inset.

A Lorentzian broadening value of 0.3 eV was used for all TDDFT-generated spectra throughout this work. Broadening is used to ‘smooth’ out calculated results, whether they be absorption spectra or density of states. If too large a value is used some features may be smeared out and if too small a value is used it may introduce some spurious features. In the case of TDDFT-generated absorption spectra for the subject materials a large broadening value is not required since the spectra does not contain many specific features, particularly in the low energy region which is the main region of interest for these materials. Hence a value of 0.3 eV ensured any small perturbations were removed when used in conjunction with choice of *itermax* (see Figure 3.12 above).

It is important to note that spin-polarization is not implemented in the *turbo_tddft*^{51,52} module. Certain materials showcase high levels of spin asymmetry and so spin-polarization refers to the degree to which the spin is aligned with a specified direction.⁸⁰ Materials where spin-polarization is present display magnetic properties, and the degree of spin-polarization affects the electronic and physical characteristics of these materials. In the case of the subject materials, spin-polarization is not a particular feature as they do not display magnetic or other

spin-related phenomena. These can be considered as closed-shell systems, and so spin-polarization was not implemented in the calculations of these materials.

LCAO Gaussian-DFT Models

As with PW-DFT, the optimized geometry of each structure was used as the starting point to calculate the singlet excited states and thus the optical absorption spectra of each complex via TDDFT. The Random Phase Approximation⁵³ was used throughout, with 30 states calculated for **1A** and **1B**, and 20 states calculated for **2A** and **2B**. These calculations also gave access to the optical transitions involved. As mentioned above, these complexes do not display magnetic or spin-related characteristics and can be considered as closed-shell systems. This means that triplet states are not required as part of their optical calculations, and so only singlet states were used in the optical calculations of these complexes. A Lorentzian broadening value of 0.3 eV was used.

3.1.3 Provision of Experimental Data

Dark- and light-induced crystal structures for both subject complexes were determined using photocrystallographic data, which had been collected at a N₂-based temperature using visible light. The temperatures and wavelengths varied according to: 90(1) K, $\lambda = 488$ nm for **1A**;¹⁴ 100(2) K, $\lambda = 505$ nm for **1B**;²⁶ 90(1) K, $\lambda = 488$ nm for **2A**;¹⁴ 13(2) K, broad-band white light for **2B**.¹⁶ Single-crystal optical absorption spectra for **1** and **2** were acquired by Cole et al.,²⁶ and Cole et al.,³⁷ using a custom-built experimental setup.²⁶

3.2 Results

3.2.1 Optimized DFT-generated Structural Models

Before evaluating the DFT-optimized structures, it is important to assess the robustness of these models. Empirical studies have shown that the η^1 -OSO geometry is energetically the least stable with the η^1 -SO₂ configuration naturally being the most stable. In general, this is observed for both techniques for all four structures of the two complexes except for the periodic model of **1B**, where calculations suggest that η^1 -OSO is the least stable conformer. Otherwise, for the periodic models: η^2 -(OS)O in **1A** is 2.62 eV above the η^1 -SO₂ and η^1 -OSO in **1B** is 4.81 eV less stable than the η^1 -SO₂ isomer. Similarly, the η^2 -(OS)O configurations in both **2A** and **2B** are 1.37 eV higher than their corresponding dark-state η^1 -SO₂ isomers, with η^1 -OSO in **2B** being the least stable structure, 2.20 eV above the η^1 -SO₂ state. For the fragment models: In **1A** and **1B**, η^2 -(OS)O is 1.14 and 1.57 eV above that of the η^1 -SO₂ state, respectively, while η^1 -OSO in **1B** is 1.66 eV above that of the η^1 -SO₂ state. Likewise, in **2A** η^2 -(OS)O is 0.33 eV above that of η^1 -SO₂, whereas in **2B** it is 0.47 eV. η^1 -OSO in **2B** is 0.87 eV above its dark-state η^1 -SO₂ configuration and again the least stable of the three structures.

As mentioned previously, the periodic models of **1B** did not display the expected trends. The modeled η^2 -(OS)O configuration is far less stable than that of the dark-state η^1 -SO₂ configuration, with its energy calculated to be even lower than that of the η^1 -OSO isomer. This can be explained by the fact that the η^2 -(OS)O isomer in **1B** is the only structure in which atomic constraints were required to successfully conduct geometry optimization. These constraints were necessary since unconstrained structural relaxation via both PW and MO methods resulted in the η^2 -(OS)O geometry transitioning to the η^1 -OSO state. Naturally, this meant that the η^2 -(OS)O state could not be minimized to the same extent as the η^1 -SO₂ or η^1 -OSO structures. Consequently, periodic models did not produce the expected stability trends, although the molecular fragment models did. This difference is due to the nature of the two techniques. Owing to the periodic nature of the PW method, any changes in one region of a system naturally affect the entire system since the forces propagate throughout the structure. In contrast, MO-based DFT treats a system as one of finite molecules, where forces in one part of a system remain largely localized to that region; thus, in this case, the effects of fixing the Ru-SO₂-Cl axis had less of an impact. This is also presumably why the energy differences between the dark and light states are larger for the periodic models; for instance, the η^1 -OSO conformer in complex **1B** is 4.81 eV above that of the dark-state η^1 -SO₂ isomer, whereas for the fragment

models, it is 1.57 eV above that of the dark state. It is important to note, however, that PW self-consistent field calculations on the experimental geometries of complex **1B** (conducted before structural relaxation) did produce the expected trends.

Tables 3.5 and 3.6 present selected bond lengths of the optimized geometries from all four structures of the two complexes. It is important to note that since hydrogen atoms are notoriously difficult to identify via X-ray crystallography, an idealized model was used to estimate their positions. This meant that one would expect that bonds that involve hydrogen to show the largest changes, which was indeed the case. The focus of this analysis is thus on the non-hydrogen bonds.

In general, both the periodic and molecular fragment models show small deviations from the experimental geometries. It can also be seen from both sets of models, that the smallest changes are observed for the dark-state structures, whereas calculations on the light-induced η^2 -(OS)O and η^1 -OSO states show larger deviations from their experimental geometries. This can be explained by considering the way that DFT models the light states. Both η^2 -(OS)O and η^1 -OSO are modeled assuming 100% photoconversion, which stands in contrast to experiment, where they coexist in various photoconversion fractions along with the residual dark-state η^1 -SO₂ configuration. This alters the surrounding environment and the LRES forces that are at play. It is thus not surprising that larger changes manifest where the SO₂ atoms are concerned, as this region is particularly influenced by crystal forces. This also explains why DFT struggles with the η^2 -(OS)O structure in **2**. Clearly, the crystalline environment that surrounds SO₂ in the experimental structure is crucial in keeping this geometry stable.

Table 3.5: Key bond lengths for structures of complex **1**.

Structure 1A							Structure 1B								
	η^1 -SO ₂			η^2 -(OS)O			η^1 -SO ₂			η^2 -(OS)O*			η^1 -OSO		
	Exp	PW	LCAO	Exp	PW	LCAO	Exp	PW	LCAO	Exp	PW	LCAO	Exp	PW	LCAO
Ru-S	2.0797(12)	2.07471	2.21132	2.323(16)	2.30202	2.46271	2.0702(17)	2.07460	2.21684	2.564(8)	2.56388	2.56388			
			2.22677			2.48203			2.15836						
			2.21132			2.46271			2.21711						
			2.22677			2.48203			2.18194						
Ru-O ₁				2.19(3)	2.11928	2.16454				2.369(14)	2.36794	2.36794	1.75(4)	1.93690	2.15558
						2.16731									2.01493
						2.16454									2.13299
						2.16731									2.01493
Ru-Cl _{trans}	2.4069(12)	2.39090	2.43521	2.322(11)	2.35273	2.39897	2.416(2)	2.39383	2.47146	2.367(18)	2.36776	2.36776	2.369(14)	2.33211	2.47767
			2.47630			2.40467			2.42480						2.39849
			2.43521			2.39897			2.46669						2.46575
			2.47630			2.40467			2.40745						2.39365
S-O ₁	1.451(3)	1.46969	1.48886	1.46(3)	1.54228	1.54583	1.441(4)	1.46857	1.48113	1.544(15)	1.54388	1.54388	1.14(4)	1.52881	1.52966
			1.48780			1.55709			1.49742						1.52667
			1.48886			1.54583			1.48044						1.51924
			1.48780			1.55709			1.48336						1.53341
S-O ₂	1.426(4)	1.46625	1.47594	1.41(6)	1.47803	1.51251	1.450(3)	1.46643	1.49554	1.23(5)	1.23256	1.23256	1.87(3)	1.47938	1.48489
			1.48878			1.48034			1.49326						1.50356
			1.47594			1.51251			1.48680						1.49042
			1.48878			1.48034			1.47917						1.49855

*Structural relaxation for η^2 -(OS)O was conducted by fixing the SO₂-Ru-Cl_{trans} axis, hence the PW and LCAO key bond lengths are the same as experimental values.

Table 3.6: Key bond lengths for structures of complex **2**.

	Structure 2A						Structure 2B								
	η^1 -SO ₂			η^2 -(OS)O			η^1 -SO ₂			η^2 -(OS)O			η^1 -OSO		
	Exp	PW	LCAO	Exp	PW	LCAO	Exp	PW	LCAO	Exp	PW	LCAO	Exp	PW	LCAO
Ru-S	2.0892(5)	2.07406	2.17699	2.36552	2.31940	2.47012	2.0863(8)	2.07464	2.20640	2.481(14)	2.32302	2.41901			
												2.43795			
Ru-O ₁				2.084(16)	2.08215	2.14970				2.307(8)	2.09280	2.15956	1.923(11)	1.92660	2.01445
												2.14142			2.13828
Ru-O _X	2.12825	2.11554	2.12861	2.034(15)	2.03567	2.06286	2.1312(15)	2.11531	2.26940	2.086(2)	2.04286	2.08925	2.086(2)	2.04198	2.10448
												2.08543			2.18044
S-O ₁	1.4368(16)	1.46117	1.47631	1.487(17)	1.54273	1.55687	1.4451(14)	1.46143	1.47788	1.49(4)	1.53973	1.54856	1.514(10)	1.52573	1.49142
												1.51091			1.46631
S-O ₂	1.4415(15)	1.46199	1.47300	1.436(17)	1.47872	1.49162	1.4431(14)	1.46206	1.47674	1.57(6)	1.47667	1.56092	1.426(15)	1.47863	1.52748
												1.48708			1.50947

3.2.2 TDDFT-generated Optical Absorption Spectral Models

Figures 3.13 (top, left) and (top, right) show the experimental optical absorption spectra for **1B** and **2A**, respectively, which have been published^{26,37} but are reproduced here for easy reference. Although the presence or absence of the η^1 -SO₂ isomer has noticeable effects, the general shape and characteristics of the spectra remain largely unchanged. There are some characteristics that are common to both experimental spectra, and in essence all experimental spectra of these complexes. Firstly, the transition from dark to light sees the absorption spectra broaden, to encompass effectively the entire visible region (400-700 nm; 3.1-1.77 eV). The effect of light irradiation, and hence the formation of the metastable states, is thus to raise the optical absorbance throughout the visible region, with the 500-700 nm region rising most significantly. It can thus be inferred that the major influence of the photoisomer formation lies in the lower region (red) of the spectrum. It is also important to note that the experimental spectra for these complexes do not contain specific peaks. Rather, the comparison between experiment and computation will center on how well the TDDFT-generated spectra reproduce the abovementioned spectral trends. The focus of this computational study is on the shape and coverage of the TDDFT-generated optical absorption spectra, particularly the differences between the spectra of the dark and light-induced structures.

It is also important to briefly discuss the importance of oscillation strength, and its importance in this analysis. Oscillation strength quantifies the probability of absorption or emission of radiation in any electronic transitions between energy levels of an atom. In the case of absorption spectra, the values of oscillation strength indicate the energies where there is the highest probability of absorption of a photon. This will then indicate the nature of the optical characteristics of a molecule, and the type of radiation it absorbs. In the case of the subject materials, experimentally-determined absorption spectra have shown that absorbance is particularly high in the visible region. One of the aims of the TDDFT-generated spectra will therefore also be to reproduce this characteristic, with a focus on generating spectra that illustrates absorbance in the visible region.

Before the comparison between experiment and computation can be conducted, it is important to recognize that the experimental spectra for the light-induced structures is a combination of the optical response of any photoisomers that have been formed *and* any residual dark-state not having undergone photoisomerization. Hence, the light-induced experimental spectra of a

complex must be compared to a *convolution* of the TDDFT-generated spectra of the dark-state and all photoinduced states of that same complex.

Figure 3.13 (middle panel) shows that the periodic-model spectra replicate these features relatively well. For all four structures of the two complexes, the optical absorbance increases from dark upon light induction, while the spectra become broader. Although not always in the desired region (400-700 nm or; 3.10 to 1.77 eV), the spectra of the light-induced states are red-shifted as compared to those of their corresponding dark states, corroborating the experimental results that the photoinduced states are more influential in the lower-energy region of the spectrum when compared to the dark state. Spectra generated from the molecular-fragment models (Figure 3, bottom panel) also show much of the same trends, albeit that the transitions are slightly narrower when compared to the periodic-model spectra. This is likely to be due to the finite nature of MO methods and the fact that these molecular-fragment models do not fully account for the periodicity of these complexes. As mentioned previously, the presence of light-induced states should broaden the spectra with contributions from the η^2 -(OS)O and η^1 -OSO states expected to be red-shifted when compared to their dark states, as seen for **1B** and **2B**. However, this is not the case for the molecular-fragment models of **1A** and **2A** where the inclusion of the light-induced state does not increase the optical absorbance. For both complexes, the η^2 -(OS)O spectral contribution lies within the spectra of the η^1 -SO₂ state, with the spectrum of the total photoinduced structure not broadening upon photoinduction, as seen in the periodic-model spectra for **1A** and **2A**. The spectra generated via PW-TDDFT have effectively reproduced the features seen in the experimentally-determined optical absorption spectra that were specified previously. It is also worth mentioning that although both computational methods have spectra that do not fully lie in the desired energy range, they all fall well within 1 eV of the desired energy range. This is significant, because optical absorption spectra for complicated materials are often manipulated via scissor functions or scaling factors to achieve desired results. This shows that these PW-based periodic models can be used to effectively simulate optical properties of this family of Ru-based crystalline complexes for linkage photoisomerization studies.

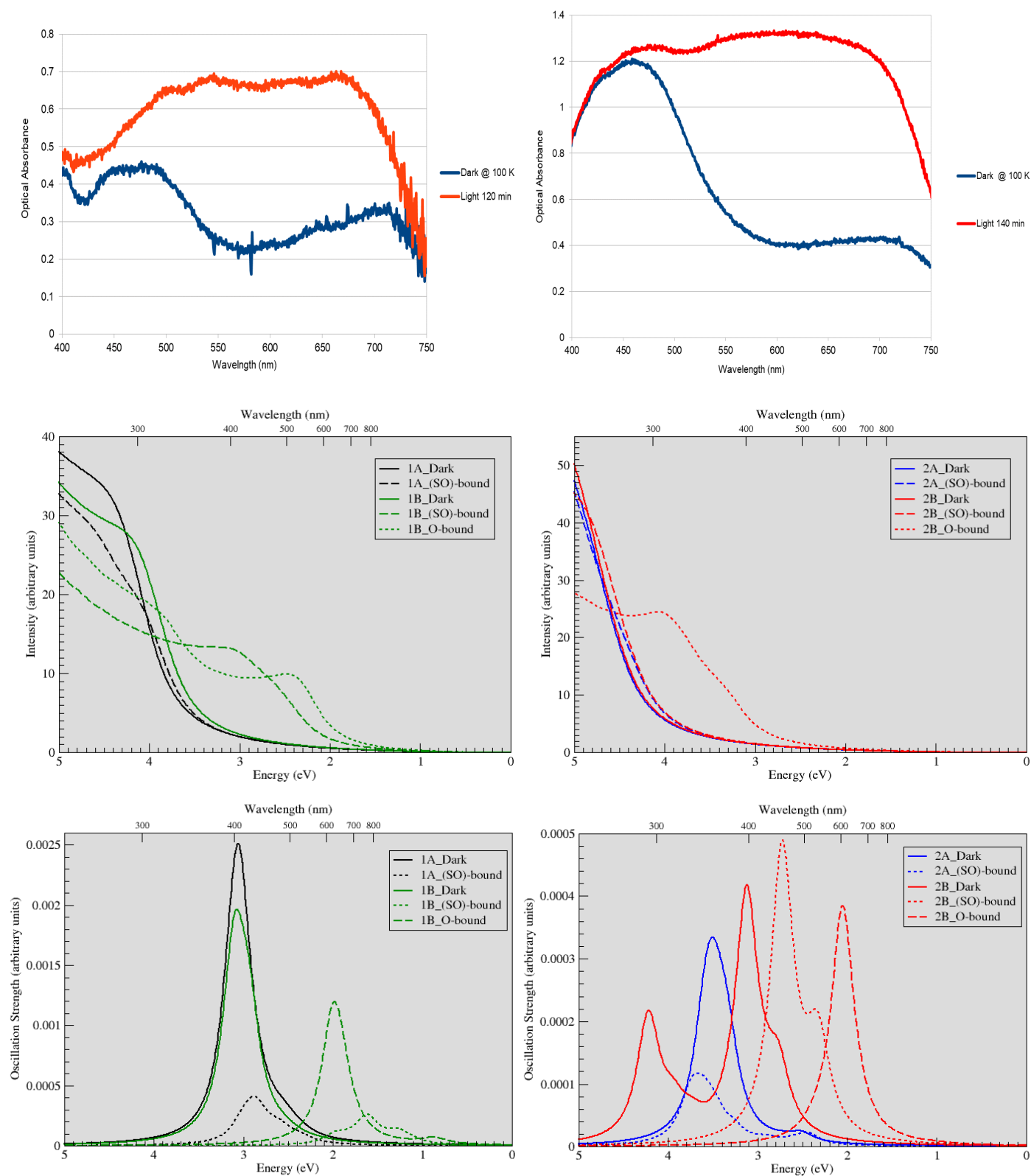


Figure 3.13: Single-crystal optical absorption spectra for the dark- and light-induced states of (left) **1** and (right) **2**, from: (top) experimentally-determined spectra;^{26,55} (middle) periodic models; (bottom) molecular-fragment models. A Lorentzian broadening term of 0.3 eV was used for both periodic and molecular fragment spectra. The experimentally-determined single-crystal optical absorption spectra for **1** and **2** have been reproduced with permission from Cole et al²⁶ and Cole et al⁵⁵, respectively.

However, some shortcomings of DFT are harder to overcome. As mentioned previously, DFT is well known to struggle when accounting for metal-based charge transfer and high-energy states.^{61,62} To this end, there are several instances of ‘gaps’ in the TDDFT-generated spectra that indicate missing features. By comparison, experimental spectra show how the optical absorbance of the light-induced structures is more or less equal across the visible region, with the spectral features rising to a plateau shape. Nevertheless, spectra generated via periodic models have showcased good coverage of the visible region (within 1 eV), with the absorption spectra broadening upon the inclusion of the light-state spectra. In contrast, spectra for the molecular-fragment models display marginally sharper peaks whose widths are insufficiently broad. This is not entirely surprising since periodic approaches can be more effective than MO-based methods at accessing high-energy states of a system.⁵⁶ This can be somewhat compensated for by the use of appropriate molecular fragments that closely represent the extended system. However, in the case of the subject materials, this is unfeasible since these are large and intricate complexes. An extremely large molecular fragment would be needed, which would severely increase computational load. This then limits the appreciation of the LRES forces and intermolecular interactions that are inherent in these crystalline complexes, which likely contributed to the issues seen in the spectra that were calculated via the molecular-fragment models.

The shape of optical absorption spectra generated via the molecular-fragment models is also affected, to some extent, by the choice of the *nroots* parameter. *Nroots* refers to the number of excited-state roots that are calculated. A larger number of roots allows better access to a greater number of features that are present in the optical absorption spectrum of a system, particularly towards the higher-energy parts of the spectrum. This does not mean that high-energy states will suddenly become accessible, since these failings are characteristic of the TDDFT method; yet, medium-energy states or relatively low-lying metal-based charge-transfer transitions may be revealed. For instance, the peak at 2.1 eV in the LCAO-Gaussian-generated spectrum of **2B** was not determined for a *nroots* value of 10; yet, it became accessible when a value of 20 was selected. The minimum value of the *nroots* parameter that is required to access such states is characteristic of each complex, since it will depend on its chemical nature (ligand **X**; counterion **Y**). The choice of the *nroots* parameter is easily deduced when experimental data are available for comparison, but it becomes difficult to validate when this is not the case. Thus, MO-based optical property calculations can be somewhat arbitrary. If sufficient experimental data are available for a large set of complexes,

then the *nroots* value can become a ‘tunable’ parameter; however, this is usually an exhaustive endeavor.

The PW-based periodic models developed in this chapter have shown to be robust and are an effective approach for modeling the optical properties of the subject complexes particularly when limited experimental data are present. This can allow for both PW and MO based approaches to be potentially used collectively to model these Ru-based crystalline materials. For instance, if experimentally-obtained optical absorption spectra are only available for a small set of complexes, their periodic DFT-model spectra can be used as a baseline to which ‘new’ predicted spectra can be compared and characterized. Once a sufficiently large dataset of experimental spectra become available, PW and MO methods can be used in tandem to study these complexes more effectively. PW methods could be used in extensive large-scale studies for screening purposes after which spectra could be studied further with MO methods.

3.2.3 LCAO Gaussian Optical Transitions

An invaluable feature of MO-based TDDFT calculations is that they provide relatively easy access to the optical transitions and excited-states information of a complex. Since the subject complexes are large, complicated crystal structures with many heavy atoms, the distinguishability of their various transitions and understanding their effects is not straightforward. However, comparisons between the complexes in their dark- and light-induced states can still be very insightful. The focus here has been on the ‘major’ transitions, i.e., those that we define as contributing at least 10% toward a photoinduced state.

Looking at the dark-state η^1 -SO₂ configuration of **1A**, there are only two instances where there are significant contributions from other atoms: the large peak just above 3 eV also has contributions from the Cl_{counterion} p-orbitals and to a lesser extent the photoactive sulfur s-orbitals. As expected, the unfilled ruthenium d-orbitals provide the dominating contributions to the spectra with no counterion contributions in the visible region. This is also the case for the dark-state η^1 -SO₂ configurations of **1B**, **2A** and **2B**. The simulated spectra for these complexes show that any contributions from the non-ruthenium atoms, particularly counterions, occur at the higher-energy end of the spectra, with the visible region dominated by the contributions from the unfilled ruthenium d-orbitals, as expected.

The story is not as straightforward for the light-induced spectra, as they show greater contributions from the non-ruthenium atoms, particularly the counterions. This is the case for both complexes with the exception of the photoinduced structures of **1B** where the spectra for both the η^2 -(OS)O and η^1 -OSO configurations are almost exclusively dominated by the unfilled ruthenium d-orbitals. In contrast, the spectrum for the η^2 -(OS)O structure of **1A**, although mostly dominated by ruthenium d-orbital based transitions, does show counterion contributions from the chloride ions. The spectra for photoinduced structures of **2A** and **2B** show yet greater contributions from the counterions as compared to **1A** and **1B**, with the light-induced states in **2B** even displaying counterion contributions in the visible region. This is surprising, since the visible region of the spectrum should be dominated by Ru-based transitions. Furthermore, as is known from its optical nature, *p*-tosylate should not be displaying transitions in the visible region. These contributions were present for the structures in **2**, since the *p*-tosylate counterions are substantially larger and more influential than the chloride ions of **1**. The optical switching capabilities of **1** and **2** clearly indicate that there are intricate crystallographic forces at play and a proper understanding of these highly influential LRES forces is a necessity to effectively model the optical characteristics of this family of materials.

3.3 Discussion

It can be seen that both periodic and molecular-fragment methodologies have performed relatively well in modeling the optical properties of these large periodic structures, and have, especially for periodic methods, managed to replicate a lot of the features of the experimental optical absorption spectra despite the innate methodological limitations of TDDFT. It is important to try and understand what allowed TDDFT to succeed.

Firstly, the structures of the subject complexes are not sensitive to a large sampling of the *k*-space. In general, the use of a dense *k*-point mesh allows for a more detailed analysis of optical properties, resulting in more features and characteristics of the optical response of the periodic system to be calculated. Techniques such as GW/BSE have this capability whereas PW-TDDFT is limited to only sampling the gamma point. Although the use of more *k*-points in a TDDFT model does not correct for its inherent limitations, it does allow for higher-quality spectra to be produced. Optical studies of periodic systems via PW-TDDFT are generally conducted using suitable supercells in order to circumvent this problem; yet, this is not viable for such large systems as the subject complexes. The use of supercells was not necessary when

modeling the subject complexes since they are not k-space sensitive. Fortunately, sampling the gamma point still allowed for adequate calculation of the optical response of these complexes, producing spectra that effectively reproduced the characteristics seen in the experimentally-generated optical absorption spectra. PW-TDDFT would not have been an appropriate choice had these complexes been more sensitive to sampling of the k-space. Access to high-quality experimental data also allowed for careful validation of these computational results.

Secondly, the most significant feature of these complexes is that they form long-lasting metastable photoinduced states. TDDFT particularly struggles with excitonic effects and high-energy excited states, such as Rydberg states, due to the lack of a long-range term in standard exchange-correlation functionals. Metastable states can be low-lying excited states or, as in the subject case, ground states given that they have a distinct chemical structure and bonding compared to that of their dark-state configuration. This makes the subject complexes far more accessible to TDDFT-based methods, and this is why PW-TDDFT was selected to model these systems.

On a related point, TDDFT is often overlooked for optical studies due to the assumption that it will inherently fail for large periodic systems. However, the limitations of TDDFT, where high-energy states, metal-based charge transfer, or excitonic effects prevail, do not manifest themselves in the same way for every system. The mere presence of one or more of these electronic characteristics does not render TDDFT totally unusable; one simply has to be wary of what features can be successfully simulated. The performance of TDDFT will vary depending on the nature of the electronic states of the system at hand. Evaluating the attributes of these electronic states as a first step thus becomes crucial.

3.4 Conclusions

Plane-Wave (PW) and Molecular-Orbital (MO)-based DFT approaches have been used to develop periodic and molecular-fragment models respectively, to study the structural and optical properties of a family of ruthenium-based photosensitive crystal complexes. These materials have a rare ability to form long-lasting metastable states upon photoexcitation and exhibit optical photo-switching capabilities. These models represent the first study of the optical properties of this class of materials. Initially, structure relaxation calculations were conducted for all four structures of the two complexes, using experimentally-determined

crystal structures as starting geometries. The DFT-optimized geometries were then used to calculate optical absorption spectra via Linear Response-TDDFT. MO-DFT also allowed for the analysis of the optical transitions involved, with a specific focus on the contributions of different atoms and orbitals toward the features in the optical absorption spectra.

Both periodic and molecular-fragment models replicated the experimentally-determined structural parameters well, by showing small deviations between calculated and experimentally-determined bond lengths. Periodic models also effectively simulated the features from the experimentally-determined single crystal optical absorption spectra, whereby light-induced states show better coverage over the desired visible region of the spectra. MO-based methods allow for easier access to optical transitions and excited-state properties, and they reveal greater contributions for the counterions to the light-state spectra than that of the dark states of the subject complexes. With more experimental data, this analysis could be even more fruitful, allowing for a detailed analysis of specific regions of interest. Periodic models are more robust, given that the quality of molecular-fragment-based spectra depends on the number of states considered, which is difficult to assess for systems with limited experimental data for comparison. Nonetheless, there are great merits to using the two TDDFT methods together. In general, both periodic and molecular-fragment models have been able to effectively model the structural and optical properties of two complexes from this family of large ruthenium-based crystalline materials. This represents the first holistic PW-DFT based study of these materials with periodic models proving a level of computational savings similar to that offered by molecular-fragment models. Periodic models should thus be considered a more than viable alternative to conduct optical studies of complexes from this family of materials. For investigations into linkage photoisomerization processes, this study has also illustrated the possibility of using PW-TDDFT to effectively model large crystalline complexes, something that has hitherto been considered highly unlikely, *if* the excited states and electronic properties can be considered by the kernel chosen. It is thus crucial to initially try to understand the nature of the photoinduced states of the system at hand to determine the appropriate methodology that offers both accuracy and computational feasibility.

4 Optical Tuning Capabilities of Plane Wave-TDDFT Models

This chapter examines the robustness of the PW-based periodic models that were developed in Chapter 3. The previous chapter examined the effectiveness of this methodology to simulate the dark- and light-induced structures and optical absorption spectra of complexes from this family of ruthenium-based nano-optomechanical single crystals. As mentioned in Chapter 1, the characteristics of these materials are affected by competing chemical and crystallographic effects. This chapter focuses on assessing the ability of these models to simulate these effects, as assessed by modelling a larger range of complexes. This includes both molecular transducers and photoswitches with both types of metastable geometries.

Calculations have been conducted for seven structures of five complexes: the four types of structures of the two complexes that were examined previously; **1A** (which forms the η^2 -(OS)O photoisomer) and **1B** (which forms both η^1 -OSO and η^2 -(OS)O) where **X** = **Y** = Cl, and **2A** (which forms the η^2 -(OS)O photoisomer) and **2B** (which forms both η^1 -OSO and η^2 -(OS)O) where **X** = H₂O and **Y** = *p*-tosylate; a transducer where **X** = 3-bromopyridine and **Y** = *p*-tosylate which forms the η^1 -OSO photoisomer (**3**); a photoswitch where **X** = 4-bromopyridine and **Y** = *p*-tosylate which forms η^2 -(OS)O (**4**); another transducer where **X** = 3-methylpyridine and **Y** = *p*-tosylate which forms both η^1 -OSO and η^2 -(OS)O (**5**). This set of complexes contains two different counterions and distinct *trans*-ligands for the same counterion as well. These differences permit an in-depth examination of chemical effects, such as the *trans*-influence, and crystallographic effects on the nature of these complexes; for instance, the substitutional effects of using 3-bromopyridine versus 4-bromopyridine, and the different counterions as well. The three new complexes are also larger than those modelled previously and contain heavier atoms, which showcases the capability of the periodic models to handle larger more computationally intensive crystalline materials. This set of complexes is representative of materials in this series of ruthenium-based nano-optomechanical crystalline materials.

As stated, this chapter assesses the depth and breadth of the previously developed PW-based periodic models to simulate these large photosensitive crystalline materials and their metastable states, with a particular focus on the appreciation of the chemical and crystallographic features

that are inherent to these complexes. To that end, periodic models have been constructed via the same methodology shown in Chapter 3. Initially, structural relaxation calculations were conducted using the experimentally-determined crystallographic geometries. The DFT-optimized geometries were then used to conduct LR-TDDFT calculations and predict single-crystal optical absorption spectra, which showcase the differences in optical properties that manifest as a result of the different chemical and crystallographic features of these complexes. These optical property calculations have been supplemented with density of states (DOS) and partial density of states (pDOS) calculations in order to further investigate the electronic properties of these materials, with the pDOS showcasing the atomic and orbital contributions towards the DOS with a focus on the occupied states. This investigation shows that these periodic models are able to appreciate the chemical and crystallographic effects that are associated with altering the *trans*-ligand or counterion. This illustrates the possibility for a ‘dial-a-molecule’ or ‘materials-by-design’ approach where the properties of a complex could be ‘tuned’ as desired, particularly the optical properties. Such ‘optical tuning’ has not been undertaken for these complexes and would open up a huge set of possibilities for predicting new complexes in this family of materials with targeted properties.

4.1 Modelling Parameters

4.1.1 Optimized DFT Models

All calculations were conducted using the 6.4 version of the *Quantum Espresso* (QE) suite of codes^{38,39} that are available on the Theta machine at the Argonne Leadership Computing Facility (ALCF), IL, USA. The experimentally-determined crystal structures^{14,16,26} were used as the initial geometries for all complexes (with 88 atoms in the unit cells for **1A** and **1B**, 118 atoms for **2A** and **2B**, 134 atoms for **3** and **4**, and 140 atoms for **5**). The unit cells used for complexes **3** and **4** (Figure 4.1), and **5** (Figure 4.2) are shown below. Table 4.1 contains the unit cell parameters for complexes **3**, **4** and **5**. As with complexes **1** and **2**, it is important to note that the dark and light states within each complex have different cell parameters. Complexes **3**, **4** and **5** are all triclinic systems and of the $P\bar{1}$ space group.

Table 4.1: Experimentally-determined unit-cell parameters for the dark and light-induced states for complexes **3**, **4**, and **5**. The axes lengths are in Ångstroms, whereas the angles are in degrees.

	a	b	c	α	β	γ
3 Dark-State	8.3651	12.5370	13.2877	99.389	98.458	90.652
3 Light-State	8.4239	12.3569	13.8050	104.113	98.789	90.270
4 Dark-State	8.2544	12.1811	14.1063	92.247	97.270	93.706
4 Light-State	8.9040	11.2120	14.3550	92.062	93.206	93.908
5 Dark-State	8.3891(1)	12.5019(2)	13.1614(2)	99.481(1)	98.613(1)	90.270(1)
5 Light-States	8.4845(2)	12.4241(3)	13.3243(4)	101.456(1)	98.732(1)	91.001(1)

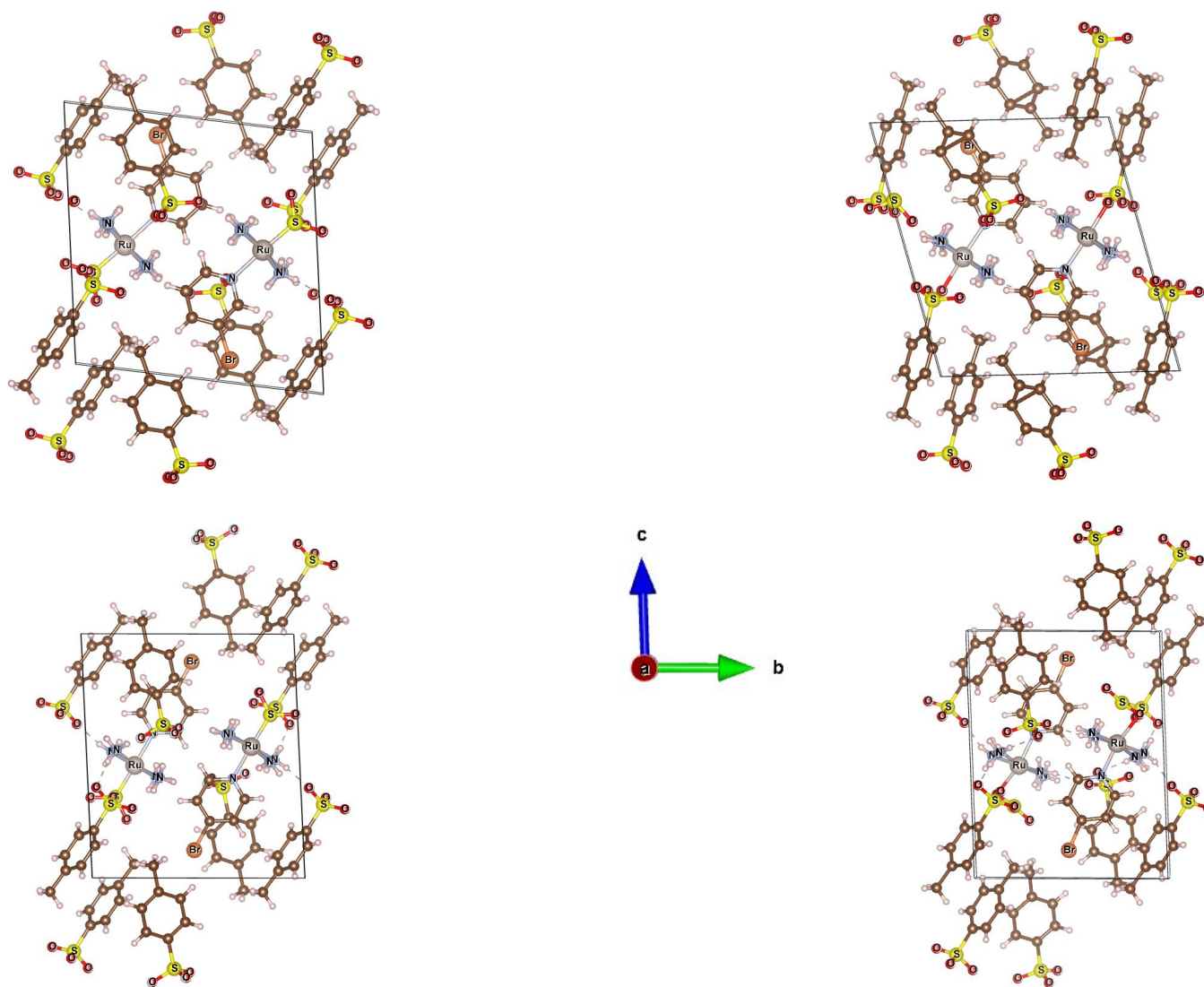


Figure 4.1: Unit cells of complexes **3** (top) and **4** (bottom), with dark-states on the left and the light-states on the right; η^1 -(OS)O for complex **3** and η^2 -(OS)O for complex **4**. Brown atoms are carbons, and white atoms are hydrogens.

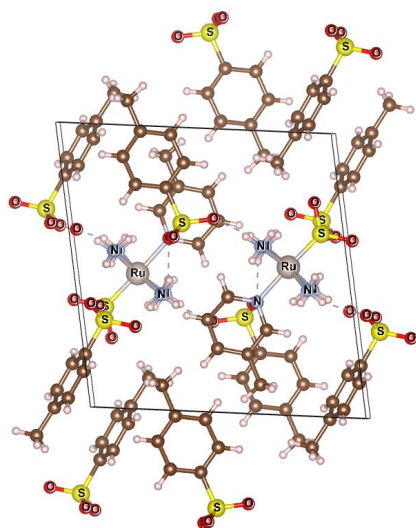
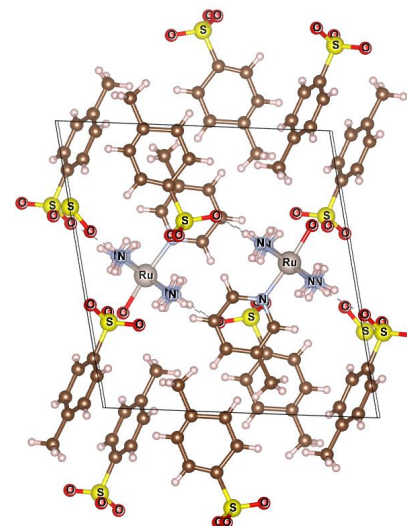
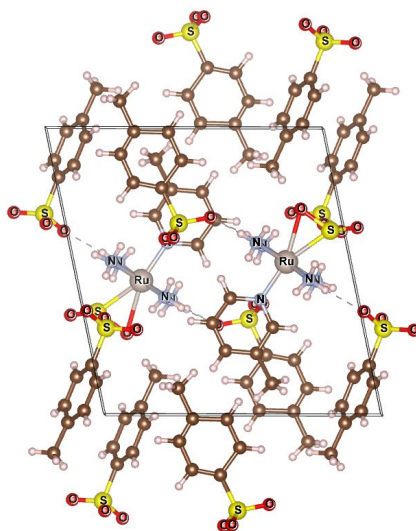
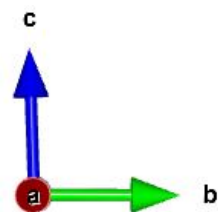


Figure 4.2: Unit cells of the dark (top left), η^2 -(OS)O (bottom left) and η^1 -(OS)O (bottom right) states of complex **5**. Brown atoms are carbons, and white atoms are hydrogens.



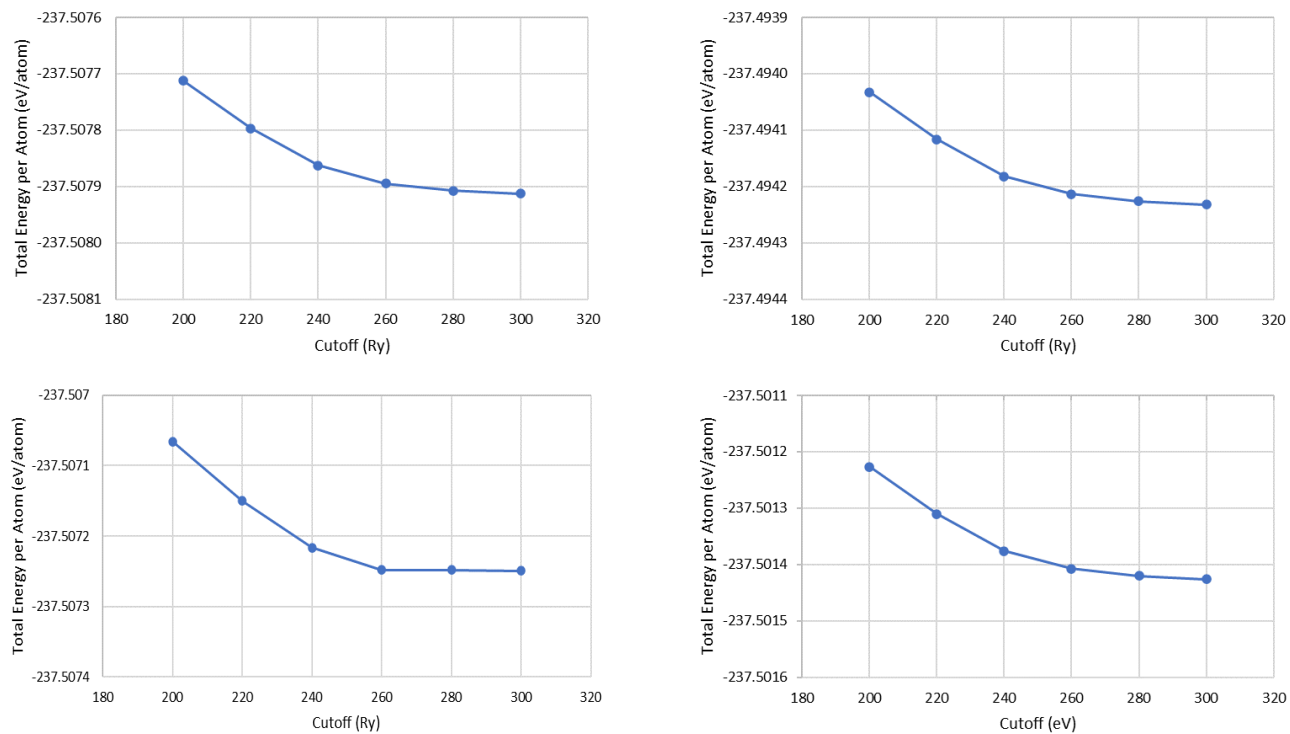


Figure 4.3: Series of PW energy cutoffs trialled for structures of complex **3**; Dark-State (top left) and η^1 -(OS)O (top middle), and complex **4**; Dark-State (bottom left) and η^2 -(OS)O (bottom middle).

Table 4.2: Series of k-meshes trialled for the dark and light-state structures of complexes **3** and **4**.

K-mesh Size	Total-Energy-per-Atom (eV/atom)			
	3		4	
	Dark-State	η^2 -(OS)O	Dark-State	η^1 -OSO
1x1x1	-237.5079	-237.4942	-237.5072	-237.5014
2x2x2	-237.5101	-237.4951	-237.5090	-237.5017
4x4x4	-237.5101	-237.4951	-237.5090	-237.5017

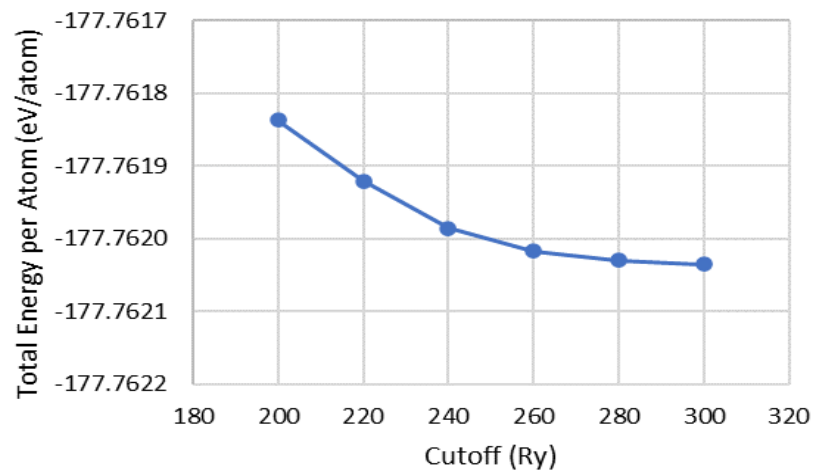


Figure 4.4: Series of PW energy cutoffs trialled for structures of complex **5**; Dark-State (top), η^2 -(OS)O (bottom left) and η^1 -(OS)O (bottom right).

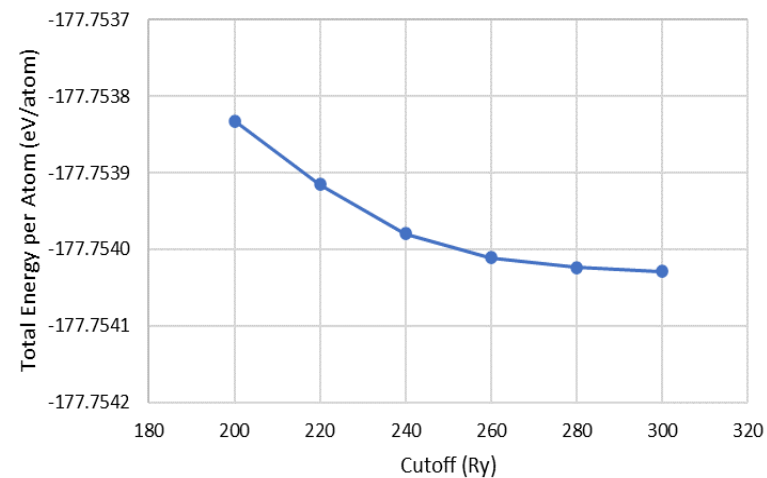
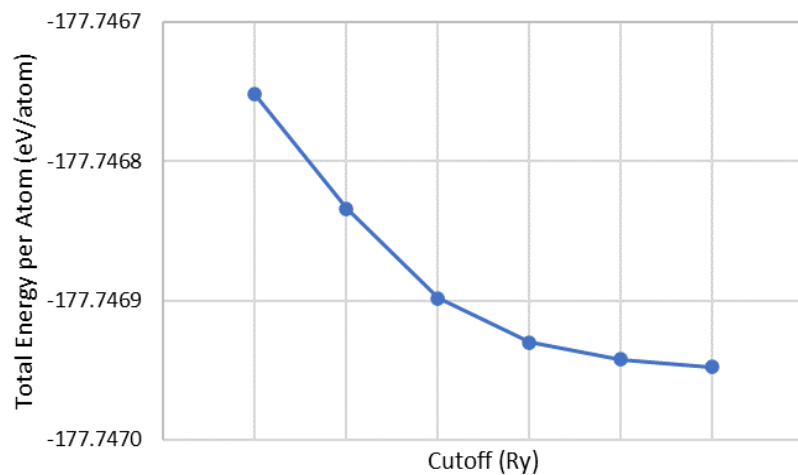


Table 4.3: Series of k-meshes trialed for the dark and light-state structures of complex **5**.

K-mesh Size	Total Energy-per-Atom (eV/atom)		
	Dark-State	η^2 -(OS)O	η^1 -OSO
1x1x1	-177.7620	-177.7469	-177.7540
2x2x2	-177.7639	-177.7482	-177.7549
4x4x4	-177.7639	-177.7482	-177.7549

As described in Section 3.1.1, from the analysis conducted using different functionals and pseudopotentials, the same functional and pseudopotential pairing was used to model complexes **3**, **4** and **5** as that used for the periodic models of the structures of **1** and **2**. The GGA functional for solids, PBEsol, was used along with PBEsol-based scalar relativistic-norm conserving (SR-NC) pseudopotentials. The Grimme DFT-D2 method was also used to account for van der Waals interactions. The ideal PW energy cutoffs (see Table 4.4 for complexes **3**, **4** and **5**) were chosen by minimizing the total energy to a tolerance of 0.00005 eV per atom, with the charge-density cutoff being four times larger than that of the corresponding energy cutoff. A series of energy cutoffs of increasing value were trialled until the total energy-per-atom value converged to within the tolerance specified above. Figures 4.3 and 4.4 detail the energy cutoffs trialled for complexes **3** and **4**, and **5** respectively. The sampling of the Brillouin zone was conducted via the Monkhorst-Pack scheme, with the ideal k-mesh for each complex chosen by minimizing to the same tolerance as the energy cutoff. The grid sizes sampled are detailed in Tables 4.2 and 4.3. As seen with complexes **1A**, **1B**, **2A** and **2B**, small uniform grids with 8 to 27 k-points were found to be the optimum sizes (see Table 4.1 for complexes **3**, **4** and **5**), once again emphasizing that these structural models require few k-points and are not k-sensitive. Parameters for complexes **1A**, **1B**, **2A** and **2B** are the same as those used stated in Chapter 3.

These optimized parameters were then used to conduct geometry optimization on all dark and light-induced states for complexes **3**, **4** and **5**, with the experimentally-determined crystal structures used as the initial geometries. No constraints were placed on any atoms for these complexes. The geometry optimization was considered to be converged when the energy between successive optimization steps was within 10^{-4} Ry and the forces were within 10^{-3} Ry/bohr. The unit cell parameters were fixed to their experimental values and the crystal symmetry was constrained, meaning that the space groups of $P\bar{1}$ was maintained for all structures of complexes **3**, **4** and **5**.

4.1.2 Optical Absorption Spectra Calculations via LR-TDDFT

TDDFT calculations to simulate optical absorption spectra were conducted using the optimized geometries via the *turbo_tddft* QE module^{51,52} (which utilizes the Liouville-Lanczos approach). Only the gamma point was sampled, using a periodic set-up. As detailed from the TDDFT calculations conducted for the periodic models of complexes **1** and **2**, 2000 Lanczos iterations

were initially calculated via the Liouville-Lanczos algorithm⁵³ as this was the largest value of *itermax* that was computationally accessible for these complexes. The bi-constant extrapolation scheme was then used within the *turbo_tddft* module to determine a much larger value of *itermax*. An overall *itermax* value of 30000, as with complexes **1** and **2**, was used to generate the absorption spectra. A Lorentzian broadening value of 0.3 eV was used.

4.1.3 DOS and pDOS Calculations

The optimized tetrahedron method was used for the DOS calculations whereas it is not available for pDOS calculations. The DOS and pDOS calculations were also conducted using larger k-meshes, as is customary (as shown in Table 4.5 below).

The optimized geometries of the periodic models of complexes **1**, **2**, **3**, **4** and **5** were then used to calculate their DOS and pDOS. Initially SCF calculations were conducted using the ideal k-mesh size for each complex (see Table 4.4). Using the wavefunctions generated from the SCF calculations, non-SCF calculations were then conducted using larger k-meshes as is customary. A larger sampling of k-points is required to form the density of states as a denser grid of k-points leads to a better representation of how the state energies differ throughout the Brillouin zone. As mentioned previously, the subject materials investigated in this work are not particularly sensitive to the sampling of the k-space due to the size of these complexes. This is further illustrated by the denser k-meshes used to calculate the DOS. Figure 4.5 presents the DOS for the dark and light states of complexes **2A**, **3**, **4** and **5** calculated with a k-mesh of the same size as the SCF calculation, and a denser k-mesh. The fermi levels of the various structures can be found in Table 4.8. Although there are slight changes in the intensities, which is to be expected, increasing the k-mesh does not in fact lead to the presence of states at any new energy levels. The increase in the k-mesh effectively provides a clearer presentation of the DOS. This once again illustrates that these complexes are not particularly sensitive to sampling of the k-space. K-meshes denser than those shown in Figure 4.5 required the calculation of well over 200 k-points which for systems of this size was too computationally intensive. The k-meshes used for the DOS and pDOS calculations are detailed in Table 4.5.

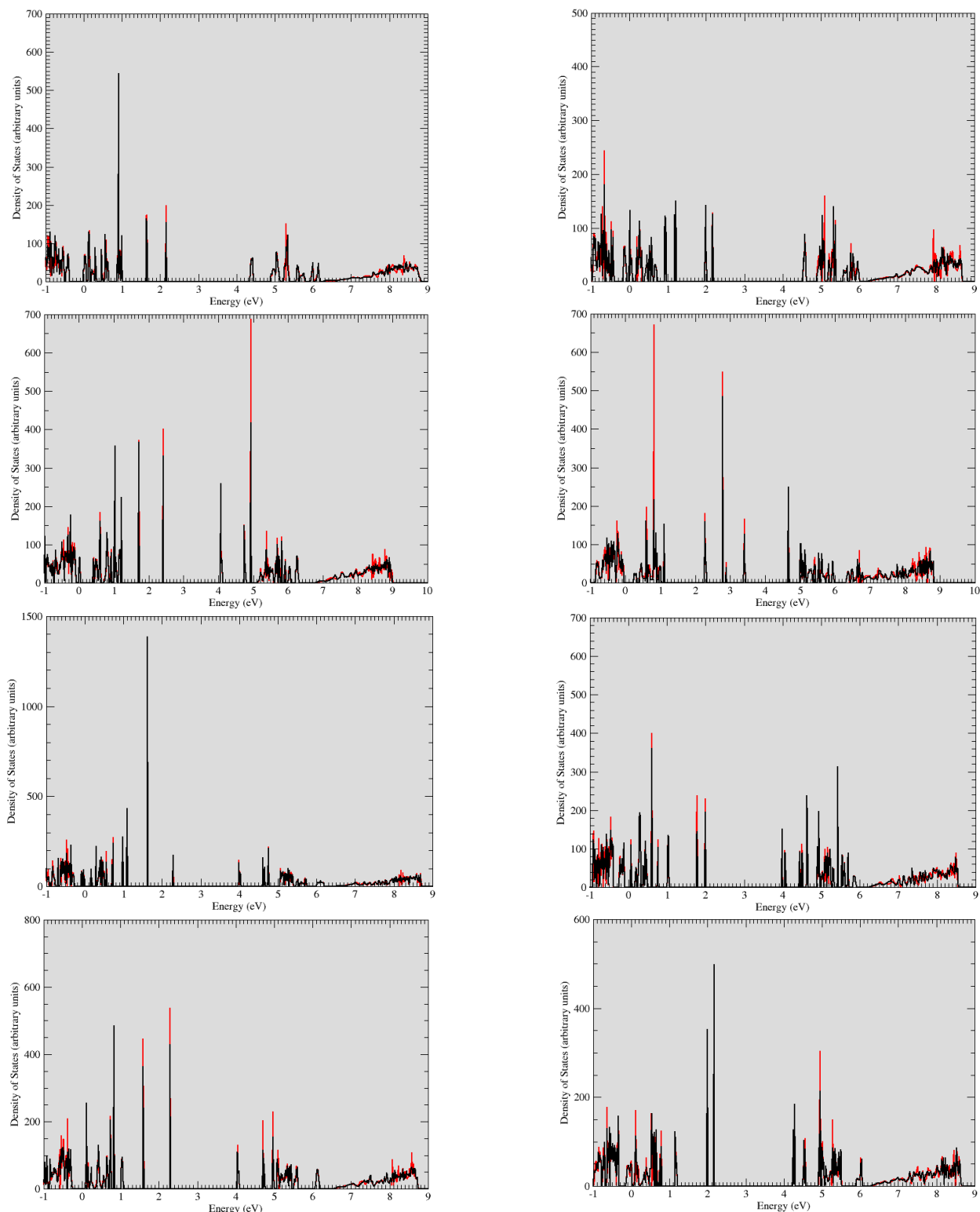


Figure 4.5: Density of states of complexes **2A**, **3**, **4** and **5** for two different Monkhorst-Pack k-meshes; red represents a grid of 2x2x2 whereas black represents 4x4x4. The left-hand column represents the dark-states, with the light-induced states in the right-hand column. First row: **2A**, second row: **3**, third row: **4**, fourth row: **5**, with the O-bound state of **5** in the bottom right.

As part of the DOS calculations a number of conduction bands also have to be included. In the case of the subject complexes, 20% more conduction bands were used for the DOS and pDOS calculations. Due to the size of these complexes this that meant a very large number of bands were considered overall for these calculations. It is also important to note that the optimized tetrahedron method was used to calculate the DOS. This inherently calculates an appropriate broadening value; so, for the DOS calculations it was not necessary to explicitly provide a broadening term. However, the optimized tetrahedron method is not available for the calculation of pDOS and so a Gaussian broadening value of 0.3 eV was used.

4.2 Provision of Experimental Data

Dark- and light-induced crystal structures for all subject complexes were determined using photocrystallographic data, which had been collected at a N₂-based temperature using visible light. The temperatures and wavelengths varied according to: 90(1) K, $\lambda = 488$ nm for **1A**;¹⁴ 100(2) K, $\lambda = 505$ nm for **1B**;²⁶ 90(1) K, $\lambda = 488$ nm for **2A**;¹⁴ 13(2) K, broad-band white light for **2B**;¹⁶ 100(2) K, , $\lambda = 505$ nm for **3**, **4** and **5**. Single-crystal optical absorption spectra for **1** and **2** were acquired by Cole et al.,²⁶ and Cole et al.,³⁷ using a custom-built experimental setup.²⁶

Table 4.4: PW-DFT simulation parameters for all complexes **3**, **4** and **5**.

	Complex 3		Complex 4		Complex 5		
	Dark-State	η^1 -OSO	Dark-State	η^2 -(OS)O	Dark-State	η^2 -(OS)O	η^1 -OSO
Cutoff (Ry)	240	240	220	240	240	240	240
K-mesh	2x2x2	2x2x2	2x2x2	2x2x2	2x2x2	2x2x2	2x2x2
K-points	8	8	8	8	8	8	8

Table 4.5: K-mesh details for DOS and pDOS calculations for all complexes. Important to note that k-points were generated via the tetrahedron method for DOS, unlike for pDOS.

Complex	K-mesh details		
	Dark-State	η^2 -(OS)O	η^1 -OSO
1A	8x8x8 = 125 k-points	4x4x4 = 27 k-points	
1B	8x8x8 = 125 k-points	4x4x4 = 27 k-points	4x4x4 = 27 k-points
2A	4x4x4 = 36 k-points	4x4x4 = 36 k-points	
2B	4x4x4 = 36 k-points	4x4x4 = 36 k-points	4x4x4 = 36 k-points
3	4x4x4 = 36 k-points		4x4x4 = 36 k-points
4	4x4x4 = 36 k-points	4x4x4 = 36 k-points	
5	4x4x4 = 36 k-points	4x4x4 = 36 k-points	4x4x4 = 36 k-points

Table 4.6: Key bond parameters for both dark and light-induced states for complexes **3**, **4** and **5**. All bond lengths are in Ångstroms.

	Complex 3				Complex 4				Complex 5					
	Dark-State		η^1 -OSO		Dark-State		η^2 -(OS)O		Dark-State		η^2 -(OS)O		η^1 -OSO	
	Exp	PW	Exp	PW	Exp	PW	Exp	PW	Exp	PW	Exp	PW	Exp	PW
Ru-N _{pyr}	2.1221	2.0870	2.0629	1.9984	2.1253	2.0834	2.1122	2.0268	2.1209	2.0891	2.0631	2.0177	2.0631	2.0074
Ru-S	2.1177	2.1034			2.1179	2.1096	2.3995	2.3551	2.1036	2.1036	2.4368	2.3571		
Ru-O ₁			2.0545	1.9845			2.1545	2.3551			2.4853	2.1291	1.9833	1.9748
S-O ₁	1.4282	1.4635	1.3422	1.5105	1.4280	1.4599	1.4194	1.5363	1.4478	1.4652	1.6328	1.5304	1.5101	1.5096
S-O ₂	1.4467	1.4615	1.4256	1.4668	1.4320	1.4638	1.3906	1.4727	1.4478	1.4619	1.4782	1.4743	1.4668	1.4716

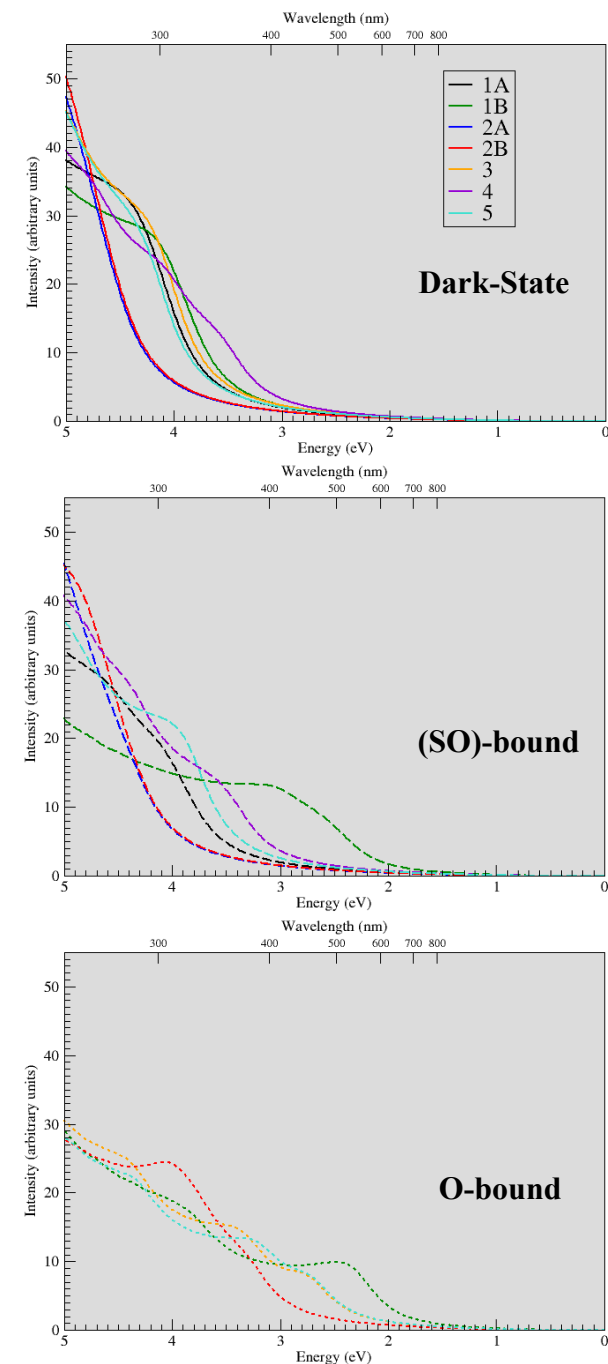
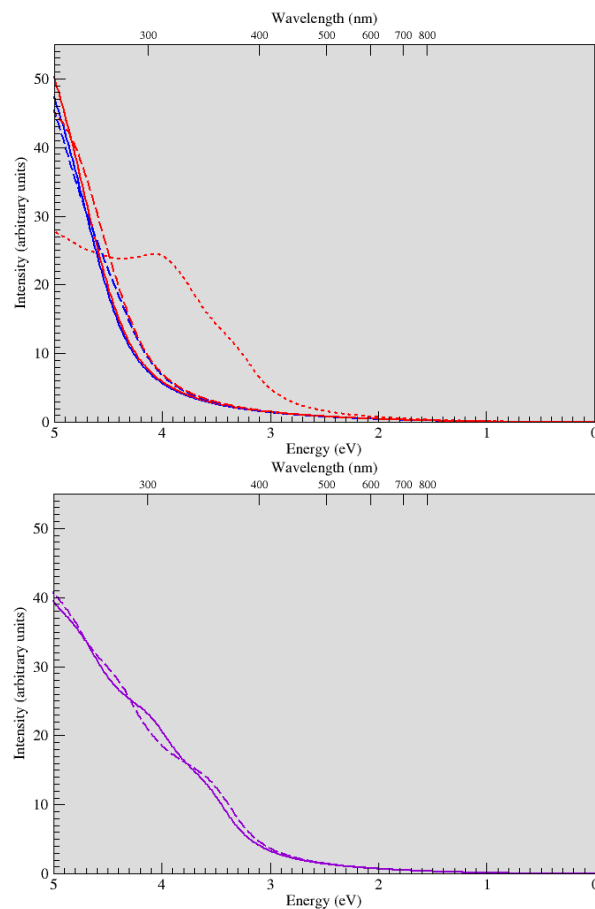
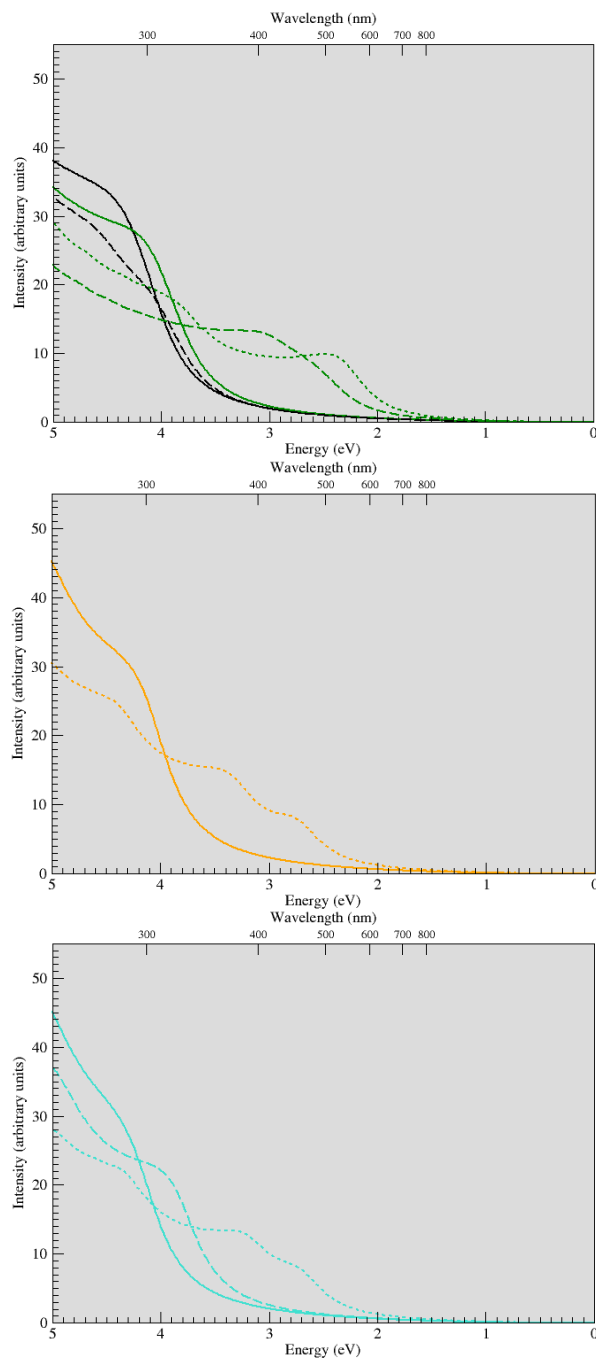


Figure 4.6: Optical absorption spectra for complexes **1A** and **1B** (top left), **2A** and **2B** (top middle), **3** (middle left), **4** (middle) and **5** (bottom left) are shown in the left-hand and middle columns. Solid lines represent the dark-state, dashed lines the (SO)-bound states, and dotted lines the O-bound. The right-hand column compares the three conformers; for all complexes.

4.3 Results and Discussion

4.3.1 Optimized DFT Models:

It is important to first examine the energy values and key geometric parameters for complexes **3**, **4**, and **5** before evaluating their optical and electronic properties. Since the same periodic models that were constructed in Chapter 3 for complexes **1A**, **1B**, **2A** and **2B** have been used in this study as well, the key parameter values and structural parameters for these complexes can thus be found in Table 3.4 in Chapter 3. Energy differences between the dark- and light-induced states from complexes **3**, **4**, and **5** are as expected, with η^1 -SO₂ being the most energetically stable and η^1 -OSO being the least energetically stable: η^1 -OSO in **3** is 2.00 eV above η^1 -SO₂, η^2 -(OS)O in **4** is 0.98 eV above η^1 -SO₂, and in **5** η^2 -(OS)O and η^1 -OSO are 1.25 and 2.20 eV above η^1 -SO₂.

The key structural parameters for complexes **3**, **4**, and **5** are presented in Table 4.6. As mentioned previously, an idealized model was used to estimate the positions of the hydrogen atoms and so the largest changes in bond lengths were expectedly seen in the hydrogen bonds; hence, the focus of this analysis is on the non-hydrogen bonds. Again, as expected, larger changes were seen in the light-induced states, particularly the SO₂ ligand, since DFT models the η^2 -(OS)O and η^1 -OSO structures assuming 100% photoconversion, unlike in experiment. However, the key difference here, as compared to complexes **1A**, **1B**, **2A** and **2B**, is the presence of the transducers **3** and **5**. Both of these transducers showed larger changes in their light-induced states in the C-C bond lengths of both the cation and anion, than seen in the corresponding light-induced states from the photoswitches. This is unsurprising since molecular transduction results in a significant geometric alteration, rotation of the arene ring. Furthermore, given that the light-induced states are modelled at 100% photoconversion, there are substantial changes in the crystal forces which have resulted in deviations to these bond lengths. However, in general, the DFT structural parameters show small deviations from experiment and illustrate the effectiveness of these periodic models.

4.3.2 Optical Absorption Spectra

Figure 4.6 shows the optical absorption spectra of the dark- and light-induced states for all seven sets of structures in the left-hand and middle columns. The right-hand column compares the spectra for each conformer across the five complexes. As seen from the experimental

spectra for **1B** and **2A** (Figure 3.13, Chapter 3), the transition from dark to light broadens the absorption spectra to cover the entire visible region of 400-700 nm (3.1 to 1.78 eV), with the lower energy (red) region seeing the most significant rise in optical absorbance. This is seen for all seven structures of the five complexes with the periodic model generated spectra broadening with the presence of η^2 -(OS)O and η^1 -OSO and the spectra of the light-induced states red-shifted, compared to their corresponding dark states. Besides **1A** and **2A**, the spectra for all other complexes overlap with the desired visible region (400 to 700 nm). This shows the applicability of using such periodic models for a large variety of complexes in this series of SO₂-linkage photoisomers.

It is now pertinent to examine the differences between the spectra of the various photoisomers and complexes. However, before this discussion can take place, there is an important point that needs to be considered. The optical absorption spectrum of a material is a highly nuanced characteristic that is chiefly dependent on the atomic and molecular structure of the material. The absorption frequencies are also influenced by the intermolecular interactions present in the material, and in the case of solids, the crystal structures as well. Coming to the subject materials, these crystal complexes are highly intricate materials with competing chemical and crystallographic forces. Although these effects are difficult to untangle, the periodic models do provide valuable insights on the differences between the generated spectra by focusing on the structural properties identified in Chapter 1, namely the *trans*-influence and the intermolecular interactions.

Using this approach, the dark-state spectra (Figure 4.6 top right) can now be examined, with an initial focus on the *trans*-influence. As stated in Chapter 1, ligands with high pK_a are good σ -donors and poor π -acceptors. This results in a stronger *trans*-influence which increases the electron density around the Ru²⁺ ion and weakens the Ru-S σ -bond *trans* to this ligand. For the complexes where Y = *p*-tosylate, **2A** and **2B** have the shortest and thus the strongest Ru-S bonds (Table 3.6, Chapter 3), when compared to the other complexes, since H₂O has a high *trans*-influence. Furthermore, complexes with X/Y = H₂O/*p*-tosylate are also known to be the most stable in this family of materials. These characteristics may explain why the dark-state spectra for **2A** and **2B** happen to be the most blue-shifted. The effect of the *trans*-influence can also be seen in complexes **3** and **4**, where the Ru-S bond distance for **3** is shorter than that of **4**, which follows their pK_a values for Lewis basicity (2.91 and 3.96, respectively). Once again, the effect of the *trans*-influence can be attributed as a possible reason for the dark-state

spectrum for **4** to be red-shifted in comparison. However, many more complexes with varying *trans*-ligands and thus different pK_a values need to be modelled to understand the effect of the *trans*-influence on the optical spectra of these complexes. Examining the effects *trans*-ligands that are structurally similar, such as 3-bromopyridine and 4-bromopyridine that differ only by the coordination position of the bromine atom, would be particularly interesting.

However chemical effects, such as the *trans*-influence, do not always account for all observations. Intermolecular interactions and the crystallographic environment also play a huge role in the bond strengths and overall structure of these complexes. For instance, looking at the intermolecular interactions between the SO₂ ligand and an aromatic hydrogen for the dark states of complexes **3** and **4**, the closest O $\cdots$ H_{aromatic} distances are 2.2627 Å and 2.4295 Å, respectively. Weak intermolecular interactions between the oxygen atoms of SO₂-ligand and aromatic hydrogens, have been known to help stabilize these complexes.⁵⁹ Such intermolecular interactions may also contribute to the dark-state optical absorption spectra of **4** to be red-shifted in comparison. The Ru-S and Ru-N_{pyr} distances for dark-state of **5**, in comparison with those of **3** and **4**, also seem to suggest that crystallographic effects influence optical properties. Although the *trans*-ligand of **5** (3-methylpyridine) has the highest pK_a amongst the pyridine-based ligands in this study; the Ru-S distance in **5** is shorter than that of **4** and its Ru-N_{pyr} is longer than those of **3** and **4**. This could be why the periodic model dark-state absorption spectra for **5** is blue-shifted as compared to the spectra of **3** and **4**. The effect of crystallographic forces is also visible for **1A** and **1B**, where the *trans*-ligand for both complexes is the same. The origin of the distinct crystallographic forces present in **1A** and **1B** are due to the differences in light sources used, and the temperatures at which the photocrystallographic studies were conducted, 488 nm and 90 K, and 505 nm and 100 K for **1A** and **1B** respectively.^{14,26} The effect of these differences is visible in the Ru-Cl_{trans} and Ru-S distances (Table 3.5, Chapter 3), which are both longer in **1B** than **1A**. Since the chemical effects in the structure of **1A** and **1B** are identical, due to both having the same X/Y combination, it stands to reason that the differences in their dark-state spectra are likely due to the differences in the crystallographic environment. Like with **1A** and **1B**, the conditions of the photocrystallographic studies conducted on **2A** and **2B** were different: 488 nm light at 90 K¹⁴, and broad-band white light at 13 K,¹⁶ respectively. Yet the dark-state periodic model spectra for both are effectively identical. This can once again likely be attributed to the particularly stable nature of H₂O as a ligand, as seen by the very similar structural parameters for both

(Table 3.5, Chapter 3). The complexes with H₂O as the *trans*-ligand are far more robust than others in this family of materials, as evidenced by their high thermal stability.^{14,16}

A similar type of analysis can also be conducted for the η^2 -(OS)O and η^1 -OSO spectra. Firstly, it is important to note that the spectra for all seven structures of both light-induced states are red-shifted as compared to their corresponding dark states, with η^1 -OSO even more red-shifted than η^2 -(OS)O. It is particularly interesting to look at the Ru-X bond lengths, which become shorter and thus stronger going from dark state to η^2 -(OS)O to η^1 -OSO. This indicates that the Ru-(SO₂ ligand) bond becomes progressively weaker as a result of the changing crystal environment due to SO₂ photoisomerization. This has also been observed experimentally, with η^1 -OSO being the least thermally stable and the dark-state naturally being the most thermally stable. The significant weakening of the Ru-(SO₂ ligand) bond caused by photoisomerization could be the chief reason behind the spectra of the light-induced states being red-shifted (to the lower energy or red region) as compared to those of the dark-state, with η^1 -OSO spectra even more red-shifted than those of η^2 -(OS)O.

From the η^2 -(OS)O bonding mechanism discussed in Section 1.2.4, it is known that a higher pK_a, and thus a greater *trans*-influence, results in a stronger Ru-N_{pyr} σ -bond which weakens the *trans* Ru-(S,O) σ -bond. This effect of the *trans*-ligand manifests in a shorter S-O_{bound} distance. As seen in experiment, the DFT-optimized η^2 -(OS)O geometries of **2A** and **2B** have the longest S-O_{bound} distances indicating that their Ru-(S,O) bonds are stronger than those of **4** and **5**. Looking at the various η^2 -(OS)O geometries, where Y = *p*-tosylate (Figure 4.6: middle right), the **2A** and **2B** η^2 -(OS)O spectra are the most blue-shifted. The effect of the *trans*-influence and the stability of the H₂O ligand are once again the likely reasons for this behavior. The S-O_{bound} distances for **4** and **5** (Table 4.6) correspond to their pK_s values for Lewis basicity (3.96 and 5.68, respectively) with the **4** having a longer S-O_{bound} distance. Based purely off the *trans*-influence, the η^2 -(OS)O spectra for **5** could be expected to be the most red-shifted owing to the weakest Ru-(S,O) σ -bond; yet this is not the case. Once again, intermolecular interactions may offer an explanation. Looking at the η^2 -(OS)O geometry of **4**, the closest interaction between the SO₂ ligand and a hydrogen atom in an aromatic counterion, O_{free}...H_{aromatic}, is 2.4459 Å, whereas for **5** it is 2.2450 Å. As mentioned earlier, weak intermolecular interactions help stabilize a structure and could be why the periodic model-absorption spectrum for the η^2 -(OS)O structure of **5** is blue-shifted, compared to that of the η^2 -(OS)O structure of **4**. This shows the ability of these PW-DFT based periodic models to appreciate the competing

chemical *and* crystallographic effects. As for **1A** and **1B**, where the counterion is the same, the crystallographic effects are likely to be the dominant factor affecting the periodic model spectra. The η^2 -(OS)O geometry in **1B** is unique and different to the five other η^2 -(OS)O structures in this study. With longer, and thus weaker, Ru-S and Ru-O_{bound} distances, the η^2 -(OS)O geometry of **1B** is less stable than the other η^2 -(OS)O structures. In fact, it is important to remember that η^2 -(OS)O of **1B** is the only structure for which the structural relaxation was done with geometric constraints (the S-Ru-Cl_{trans} axis was kept fixed) owing to the geometry trying to transition to η^1 -OSO if left unconstrained. This less stable η^2 -(OS)O geometry with weaker Ru-(SO) bonds, could be why the optical spectra of η^2 -(OS)O for **1B** is red-shifted as compared to that of **1A**. It is quite clear that the crystallographic forces and intermolecular interactions do play a role in influencing the optical properties of these complexes; however the nature of this influence needs to be investigated further by conducting a large-scale study that includes complexes with various types of counterions.

The η^1 -OSO structures (Figure 4.6 bottom right) represent the most nuanced geometries of these complexes, particularly when transduction is involved. It is quite difficult to untangle the chemical and crystallographic effects here, especially since, in the cases of **3** and **5**, there are significant geometric alterations due to the arene rotation. Once photoisomerization and the formation of η^1 -OSO have occurred, the intermolecular interactions before and after arene rotation also significantly change. It is instead noteworthy to examine the optical absorption spectra profiles of the various η^1 -OSO structures. The complexes that form η^1 -OSO structures, particularly those that exhibit molecular transduction, are the most photosensitive complexes in this family of materials. This is reflected in the periodic model optical spectra as well, since complexes that form η^1 -OSO have spectral profiles that are broader than those that exclusively form η^2 -(OS)O upon photoexcitation. The periodic model-optical spectra of the two transducers **3** and **5**, also resemble the experimental spectral profiles more closely by displaying greater coverage across the visible, but most importantly they more closely resemble the shape of the experimental spectra (Figure 3.13, Chapter 3).

4.3.3 Density of States

Table 4.7: Band gaps of all seven structures of the five complexes, calculated from the HOMO-LUMO differences. The η^2 -(OS)O band gap for **1B** is not representative of a complex since it was structurally optimized using constraints.

	Band gap (eV)		
	η^1 -SO ₂	η^2 -(OS)O	η^1 -OSO
1A	1.94	1.97	
1B	1.95		0.41
2A	2.19	2.35	
2B	2.17	2.36	0.78
3	1.64		0.56
4	1.67	1.87	
5	1.73	2.06	0.51

Table 4.8: Fermi level of all seven structures of the five complexes, calculated from the HOMO-LUMO differences.

	Band gap (eV)		
	η^1 -SO ₂	η^2 -(OS)O	η^1 -OSO
1A	3.74	4.03	
1B	3.68	2.30	3.64
2A	3.27	3.37	
2B	3.30	3.52	3.21
3	3.24		3.17
4	3.14	3.04	
5	3.17	3.21	2.95

DFT also allows for the study of the electronic properties of these materials via the total and partial DOS. Figure 4.7 contains the total DOS for the dark and light-induced states of all seven structures of the five complexes. The band gaps for each structure are shown in Table 4.4 with the corresponding Fermi levels stated in Table 4.8. It can be seen that the presence of η^2 -(OS)O increases the band gap, whereas η^1 -OSO decreases it. Interestingly, the largest band gaps for the dark and light-induced states are seen in the two H₂O/*p*-tosylate complexes (**2A** and **2B**) which are the most stable complexes in this family of materials. The band gaps for the dark state and its corresponding η^2 -(OS)O geometry are relatively similar, though as stated the η^2 -(OS)O structures have a slightly larger band gap, whereas the band gaps for the η^1 -OSO geometries are significantly smaller. A look at the structure of the SO₂ ligand may shed some light on this characteristic. As stated, the Ru-N_{pyr} distance decreases going from dark state to η^2 -(OS)O to η^1 -OSO, with this bond being stronger for the light-induced states. This leads to an increase in electron density towards the Ru²⁺ ion. However, in η^2 -(OS)O, this results in a weaker and thus longer Ru-(SO₂) σ -bond. Thus, this lack of σ -orbital interaction with the Ru

d_{σ} -orbitals could result in the band gap opening up. In contrast, the η^1 -OSO structure sees the electron density surrounding the Ru^{2+} ion increased even further since its Ru-N_{pyr} bond is shorter than that of η^2 -(OS)O. This coupled with the $\text{Ru-O}_{\text{bound}}$ σ -bond offering greater interaction with the Ru d_{σ} -orbitals may then reduce the overall band gap. It is important to note that crystallographic forces may also play a part. This does however require further investigation. An analysis of the atomic orbitals along with band-structure calculations, should also allow for improved understanding of the electronic properties of these complexes.

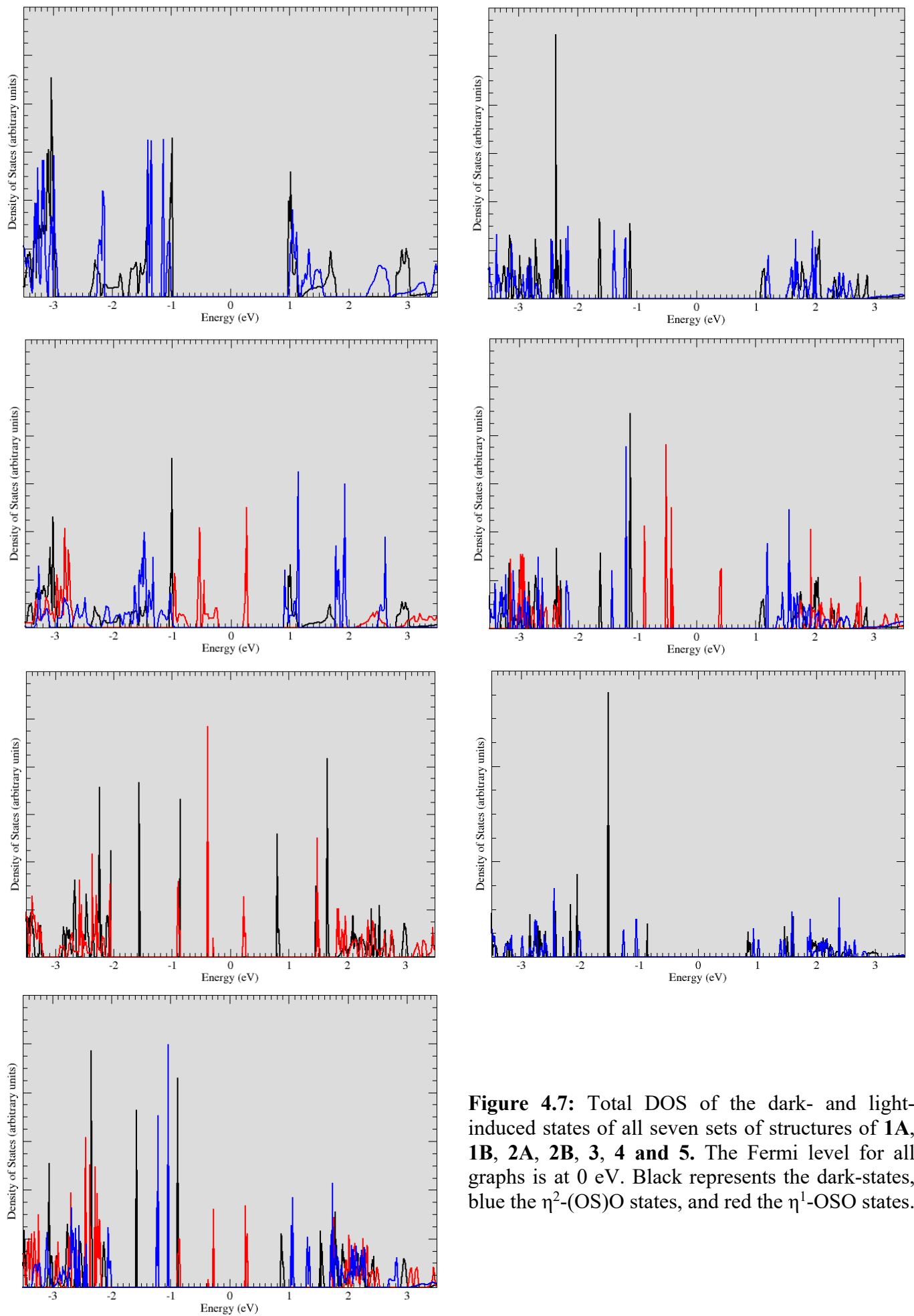


Figure 4.7: Total DOS of the dark- and light-induced states of all seven sets of structures of **1A**, **1B**, **2A**, **2B**, **3**, **4** and **5**. The Fermi level for all graphs is at 0 eV. Black represents the dark-states, blue the η^2 -(OS)O states, and red the η^1 -OSO states.

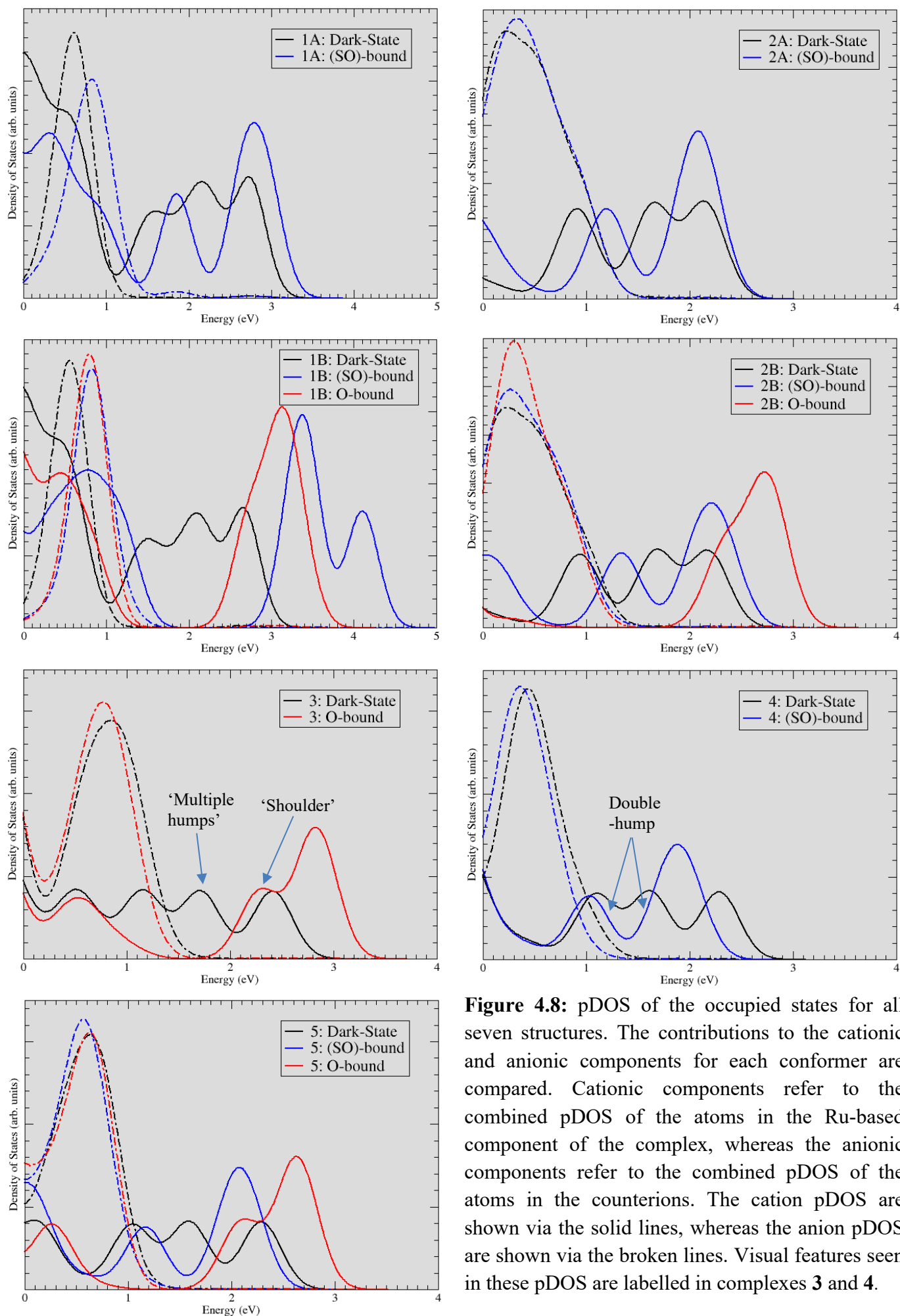


Figure 4.8: pDOS of the occupied states for all seven structures. The contributions to the cationic and anionic components for each conformer are compared. Cationic components refer to the combined pDOS of the atoms in the Ru-based component of the complex, whereas the anionic components refer to the combined pDOS of the atoms in the counterions. The cation pDOS are shown via the solid lines, whereas the anion pDOS are shown via the broken lines. Visual features seen in these pDOS are labelled in complexes **3** and **4**.

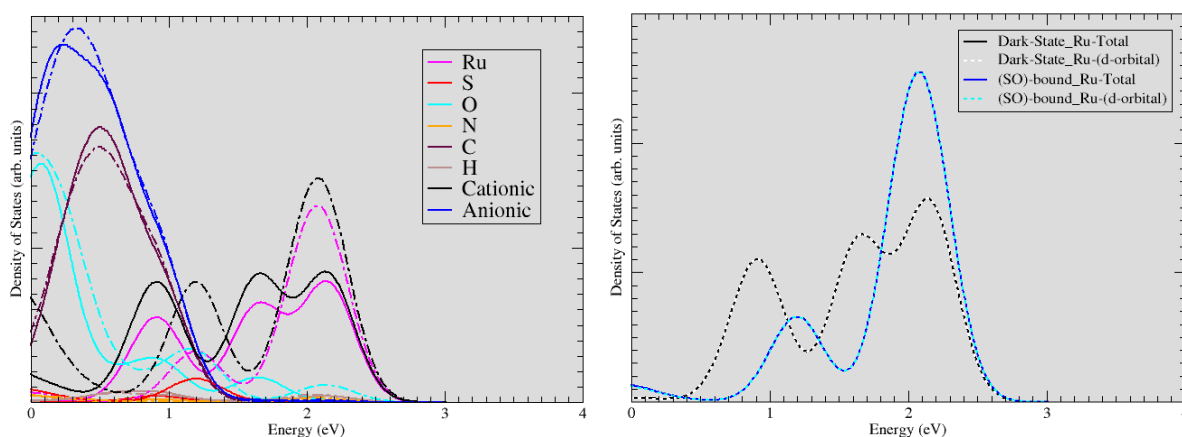


Figure 4.9: pDOS of the occupied states of complex **2A**. The atomic contributions to the total cationic and anionic components pDOS (left) are shown, where the solid lines represent the Dark-State and the broken lines the (SO)-bound state. The d-orbital contributions to the ruthenium pDOS (right) are also shown; where the dark coloured solid lines are the total ruthenium pDOS and the light-coloured dotted lines represent the ruthenium d-orbital pDOS.

Figure 4.8 contains the pDOS for the occupied states of all seven structures of the five complexes, with a focus on the contributions to the cationic and anionic components of each structure. This analysis is focused on the occupied states of the subject materials as we are particularly interested in the change in the valence states upon photoisomerization. This allows for the examination of differences between the Dark, (SO)-bound and O-bound conformers. The cationic contributions refer to the combined pDOS of all atoms in the Ru-based component of the complex, whereas the anionic contributions refer to the combined pDOS of all the atoms in the counterions. The pDOS provides further details about the electronic nature of these structures by calculating the contributions of the various atoms and orbitals towards the DOS. It is important to note that the pDOS was calculated by using the occupied orbitals only. Before comparing the pDOS of the different complexes, it is important to briefly discuss the atomic and orbital contributions to the overall pDOS. Figure 4.9 illustrates the atomic contributions to the pDOS of the cationic and anionic components (left) and the ruthenium orbital contributions (right) for the dark- and light-induced states of complex **2A**. From Figure 4.9 it is clear that ruthenium provides the largest contribution towards the cationic pDOS, with its d-orbitals being overwhelmingly the most influential. This is as expected, since the empty Ru d-orbitals are the most prominent factor in determining its chemical and optical properties. Encouragingly, this is seen across all dark- and light-induced structures for all five complexes. Looking at Figure 4.3, the cation pDOS of all seven structures also overlaps quite well with the

desired energy region (1.78 to 3.1 eV). The shape of the cation dark and light-induced pDOS is also noteworthy. The cation-dark pDOS has a ‘multiple humps’ feature that resembles a wave with the ‘peak’ at the higher energy end the tallest (as labelled for the pDOS of complex **3** in Figure 4.8). For complexes where **Y** = *p*-tosylate, the pDOS is much flatter as compared to those for **Y** = Cl. This indicates the possibility of discerning the effects of the counterion on the cation pDOS. The pDOS of the light-induced states have very different shapes, with the η^2 -(OS)O pDOS being a ‘double hump’ feature and η^1 -OSO having a ‘shoulder’ starting halfway down the peak (as labelled for the pDOS of complexes **3** and **4** in Figure 4.3). These features are present for all complexes, except for the η^2 -(OS)O of **1B** where geometry optimization was conducted by constraining the S-Ru-N_{pyr} axis. The η^1 -OSO pDOS for Ru is also at a higher energy than that of η^2 -(OS)O. The sulfur and oxygen atoms also have a small influence on the cationic-pDOS, as seen from Figure 4.9, with their contribution rising slightly when transitioning from dark to light. The other atoms have next to no contribution to the cationic-pDOS (Figure 4.4) themselves, which perhaps suggests that the chemical effects of the non-Ru atoms directly or indirectly affect the Ru center and are reflected in its pDOS. This makes it the key feature of the cationic-pDOS. In contrast, the anion-pDOS shows very little change when going from dark to light with the major contributions coming from the oxygen and carbon atoms (Figure 4.4).

As discussed in Section 2.4.3, the approximation to the exchange-correlation energy, namely the choice of functional, greatly impacts the manner in which the electronic characteristics of these materials are interpreted. These DOS and pDOS calculations also provide an avenue for the investigation of how the calculations of band gaps and absorption spectra are affected by the parameters chosen in these periodic models, namely the functional choice. To better gauge how well these periodic models represent the occupied and unoccupied orbitals of the subject materials, further studies for the different conformers for complexes from this family of materials with various combinations of **X** and **Y** can be conducted. This would allow for a more complete examination of how absorption spectra and band gaps vary with respect to the changes in the chemical nature of these materials and shed light on the success and failings of these periodic models. To that extent, an analysis of the atomic orbitals along with band-structure calculations, could also be conducted. These periodic models have laid the foundations for such large-scale analysis of the optical and electronic properties of the subject materials to be conducted.

4.3.4 Potential for Optical Tuning

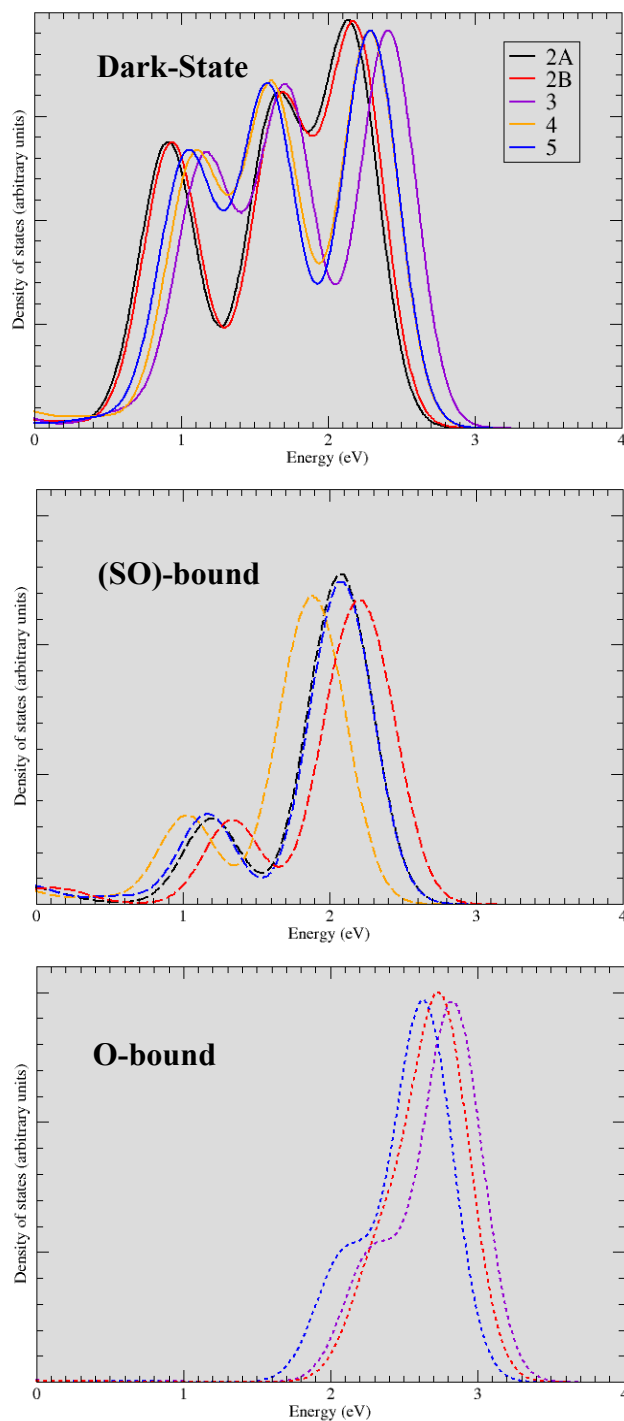


Figure 4.10: Ru pDOS (occupied states only) for complexes with $Y = p$ -tosylate. The solid line represents the dark states (top), the dashed lines the η^2 -(OS)O states (middle) and the dotted lines the η^1 -OSO states (bottom).

Periodic models have been used to calculate the electronic and optical properties of these complexes. It is clear that these are extremely intricate systems and to differentiate the various phenomena is difficult. However, these calculations show that there is a possibility to optimize the functionality of these complexes with the aim being to create complexes with targeted properties. Figure 4.10 showcases the Ru-pDOS for the complexes where $\mathbf{Y} = p$ -tosylate. The dark and light-induced states are distinct and easily identifiable. The pDOS calculations could also be used to probe the difference between complexes where the *trans*-ligand remains the same and the counterion is altered. This would allow for a deeper understanding of the different chemical and crystallographic phenomena at play, and potentially provide an avenue to ‘tune’ the properties of a complex, as desired. The optical absorption and DOS calculations can also be used in a similar vein. Since it has been shown that η^2 -(OS)O closes the band gap, whereas η^1 -OSO opens it, this could be used to try to create a complex with tailored band gap and electronic properties. The optical property calculations allow for a robust method to analyze the competing chemical and crystallographic effects in these materials. Most significantly, this PW-based approach has the potential to be scaled up for a large extensive study of these complexes, something that is not feasible via experiments alone.

4.4 Conclusions

This chapter has examined the robustness of the periodic models developed in Chapter 3 to effectively model a larger range of complexes. Chapter 3 demonstrated that the structural properties and single-crystal optical absorption spectra of these complexes could be treated effectively via PW-DFT. This chapter has modelled a larger set of complexes with various combinations of $\mathbf{X}/\mathbf{Y}$. This set includes both photoswitches and transducers and aims to determine if the periodic models can appreciate the competing chemical and crystallographic forces present in these complexes. Structural relaxation calculations were conducted for seven structures of five different complexes using experimentally-determined crystal structures as starting geometries. The DFT-optimized structures once again showed small deviations from experiments for all five different complexes, with the two transducers unsurprisingly showing marginally larger differences than the photoswitches.

These DFT-optimized geometries were then used to simulate the single-crystal optical absorption spectra, via Linear Response-Time Depending Density Functional Theory, for the dark- and light-induced states as well as their total and partial density of states (DOS). The

differences between the generated dark- and light-induced optical spectra were rationalized in terms of the competing chemical and crystallographic forces, particularly the *trans*-influence and the intermolecular interactions between the SO₂ ligand and the counterion hydrogens. Of note was the fact that the light-induced spectra were red-shifted as compared to those of the dark state, with the η^1 -OSO spectra further red-shifted than those of η^2 -(OS)O. The spectra for the transducers also displayed the broadest spectra, and most closely resembled the shape of experimentally-determined optical spectra. The effect of the stability of H₂O as a *trans*-ligand was also seen with its spectra the most blue-shifted. The total DOS and calculated band gaps then showed that the η^2 -(OS)O geometry ‘opens’ the band gap whereas the η^1 -OSO geometry ‘closes’ it. This was once again discussed within the context of the competing chemical and crystallographic forces. Interestingly, once again, the stable nature of H₂O ligand was on display since its dark- and light-induced structures had the largest band gaps amongst all structures. The partial-DOS (pDOS) of the occupied states showed that the major atomic contributions to the cationic component of the pDOS is ruthenium, as expected, and that the d-orbitals are solely contributing to the ruthenium-pDOS, which is again expected.

This study has conducted three avenues of analysis; structures, optical spectra and DOS, which allow for the modelling of the structural, optical and electronic properties of these ruthenium SO₂-based complexes. They showcase the possibility of optical tuning, where the functionality of these complexes could be altered to produce complexes with targeted properties. For instance, the band gap of these models could be altered or pDOS could be used to rationalize the differences between dark- and light-induced structures of complexes with different *trans*-ligands or counterions. This study has demonstrated the ability of these PW-based periodic models to examine the nuances associated with the competing chemical and crystallographic forces present and provides a framework for a large-scale study of these complexes to better understand these effects and characteristics.

5 Photoisomerization in Ru-SO₂ Complexes

This chapter examines the photoisomerization process in these ruthenium-based single crystals. A deeper accurate understanding of the mechanism behind the SO₂-linkage photoisomerization that occurs in these complexes would allow for better control of the photoisomerization step, potentially improving photoconversion levels and even allowing for the targeted formation of a desired photoisomer. Although the thermal isomerization and decay of the light-induced photoisomers of these complexes have been well-studied,⁸⁻²⁶ the photoisomerization process has seen little attention. One of the benefits of these DFT-based models is that they allow for complex phenomena that are notoriously difficult to observe experimentally to be studied computationally. The formation of the photoisomers is too fast to observe by current experiments. Moreover, computational methods can provide an energy dimension, as well as a structural projection, while current experiments can only afford the latter.

The calculations in this study have been conducted via the Nudged Elastic Band (NEB) method, which calculates the minimum energy pathway (MEP) between two geometries. DFT-based NEB studies have been conducted on related materials; see for instance, a study of the photoisomerization mechanism of ruthenium-based complexes that undergo NO-linkage photoisomerization.^{64,65} However, these materials were treated as isolated ions, whilst ignoring counterions, *i.e.* only the cationic component was studied via NEB. Furthermore, NO-linkage photoisomers are photoswitches and do not have the complexity of materials that produce molecular cross-talk and exhibit complex intermolecular interactions. In contrast, the subject materials are much larger crystal structures that contain complex intermolecular interactions and exhibit transduction. The photoisomerization process in Ru-SO₂ transducers is much more intricate, since it involves a change in the SO₂ geometry *and* the rotation of an arene ring in the counterion. The NEB calculations have to be able to appreciate both phenomena.

NEB simulations have not been conducted on such large extended materials, particularly those that undergo linkage photoisomerization and exhibit transduction in the solid state. To that end, PW-based NEB calculations have been conducted for complex **5**, as defined in Chapter 4: a transducer where **X** = 3-methylpyridine and **Y** = *p*-tosylate. Two photoisomerization pathways have been explored: (i) S-bound η^1 -SO₂ (dark-state) to O-bound η^1 -OSO (light-induced configuration), which is pathway **I**; (ii) η^1 -SO₂ (dark-state) to side-bound η^2 -(OS)O (light-induced configuration) which is pathway **II**. The mechanisms, showing the evolution of the

dark-state to the light-induced photoisomers, for both photoisomerization pathways have been simulated, along with the activation energies and overall energy profiles of the MEPs. Potential transition states have also been predicted. These calculations indicate an Ru-(SO) bound structure-based mechanism for the photoisomerization for pathway **I**, whilst maintaining an appreciation of the transduction, clearly showing the rotation of the arene ring. It is important to note that the calculated mechanism does *not* go through the η^2 -(OS)O geometry, but through a transitive Ru-(SO) bound structure instead. These calculations also provide a framework for more extensive PW-NEB studies of the photoisomerization mechanism as more experimental data on the photoisomerization step is obtained, particularly allowing for the comparison of different transducers and the manner in which they exhibit transduction.

5.1 NEB Methodology and Model Parameters

NEB calculations were conducted using the *neb.x* Quantum Espresso (QE) module^{38,39} as available on the Theta machine at the Argonne Leadership Computing Facility (ALCF), IL, USA. The optimized PW-DFT models developed in Chapters 3 and 4 were used in this study as well. However, one of the complications in conducting NEB for these complexes is that the dark and light-induced states have slightly different unit cell parameters. The effect of photoisomerization and the formation of light-induced structures and the resulting crystallographic forces, means the unit cell parameters of the photoexcited crystal are not the same as those of the dark state. Yet, variable cell NEB is not implemented in QE, *i.e.* the unit cell parameters for all geometries calculated via NEB must be the same. Complex **5** was thus chosen since it is the only complex studied throughout this thesis which has its residual dark-state characterized, *i.e.* the remaining dark-state that did not undergo photoisomerization. More importantly however, complex **5** was chosen for this study since it sees very small changes to its unit-cell upon photoexcitation, unlike many other complexes from this family of materials.

However, its geometry is still influenced by the crystallographic forces present in the crystal structure upon photostimulation. The importance of these forces has already been seen, with larger geometric changes being seen in the PW-models of the light-induced states. Modelling the residual dark-state with the light-state unit cell parameters will not yield a true representation of the dark-state. Hence, to somewhat incorporate the effects of the dark-state, the dark and light-induced unit cell parameters were averaged (Table 5.1). It is important to note that the difference between the two sets of unit cell parameters is very small. Although it may seem like this would adversely affect the light-induced geometries, this is not the case since the light-induced states already undergo artificially larger changes in DFT as it assumes 100% photoconversion. The effect of using the ‘average’ cell parameters is thus negligible in terms of changes to bond lengths and angles. This is illustrated in Table 5.2, which contains the key bond parameters for the residual dark and light-induced states, where the changes to bond lengths are less than 0.1%. The residual dark-state, and the light-induced states were optimized via the same procedure that was used for all geometries in Chapters 4 and 5.

Table 5.1: Experimentally-determined unit-cell parameters for the dark and light-induced states, along with the new averaged cell parameters used in NEB. The axes lengths are in Ångstroms, whereas the angles are in degrees.

	Dark	Light-Induced	NEB
a	8.3891(1)	8.4845(2)	8.4368
b	12.5019(2)	12.4241(3)	12.4630
c	13.1614(2)	13.3243(4)	13.2429
α	99.481(1)	101.456(1)	100.469
β	98.613(1)	98.732(1)	98.673
γ	90.270(1)	91.001(1)	90.136

Table 5.2: Key structural parameters of the DFT-optimized dark and light-induced structures of complex **5**. Original refers to the DFT-optimized structural parameters using experimentally-determined unit-cell parameters, whereas NEB refers to the DFT-optimized structural parameters using the new averaged cell parameters. The dark-state values are also provided as a reference. All distances are in Ångstroms and all angles are in degrees.

	Dark-state	Residual dark-state		η^2 -(OS)O		η^1 -OSO	
		Original	NEB	Original	NEB	Original	NEB
Ru-S	2.1036	2.1026	2.1042	2.3571	2.3572		
Ru-N _{pyr}	2.0891	2.0886	2.0891	2.0177	2.0171	2.0074	2.0067
Ru-O ₁				2.1291	2.1261	1.9748	1.9738
S-O ₁	1.4652	1.4655	1.4657	1.5304	1.5315	1.5096	1.5092
S-O ₂	1.4619	1.4619	1.4625	1.4743	1.4748	1.4716	1.4713
N _{pyr} -Ru-S	178.2	177.6	177.9	157.0	157.2		
N _{pyr} -Ru -O ₁				163.5	163.2	176.4	176.1

The remaining NEB parameters were then chosen. The NEB MEP is divided into a number of images; geometries calculated by NEB that fall along the optimized energy pathway between the initial and final states. The residual dark state was the initial state, *i.e.* the first image, and the light-induced structures were the final image: η^1 -OSO for pathway **I**, and η^2 -(OS)O for pathway **II**. The more images that are used, the more detailed a mechanism is tractable, but this will require more computational load. For pathways **I** and **II**, six and five images were used respectively. This includes the fixed initial and final states, so that the mechanism itself is expressed via remaining images or geometries. This number of images was ideal, as a smaller number did not elucidate the mechanism with enough detail whereas a larger number would have made NEB non-viable due to the size of these complexes. The Broyden optimization algorithm was used throughout. The *minimum_image* tag was also used. This generates a periodic replica of any atom that moves beyond the borders of the unit cell, thus reducing the possibilities of an unwanted pathway. The default *neb.x* convergence parameters were used otherwise.^{38,39}

5.2 Exploring the Ru-SO₂ Photoisomerization Pathways

As mentioned, the photoisomerization pathways for **I** and **II** are split into 6 and 5 images respectively, with the first image being the residual dark state, and the final image being the photoisomer in both cases. The energy profiles for both pathways are shown in Figure 5.1. As expected, the activation energy for **I** is higher than that of **II**, 3.91 eV vs 1.62 eV, respectively. The transition states for both pathways are also clearly visible: image 4 for **I** and **II**.

5.2.1 Pathway I: η^1 -SO₂ dark-state to η^1 -OSO light-induced configuration

Visualizing the NEB-generated MEP for **I** illustrates the photoisomerization mechanism. Initially the, Ru $\cdots$ O₁ distance begins to decrease as the oxygen atom transitions from the η^1 -SO₂ position towards something more akin to the η^2 -(OS)O position. Pathway **I** indicates that the photoisomerization process from the dark state to η^1 -OSO configuration proceeds via a Ru-(SO) bound geometry-based mechanism. This is illustrated by the key bond parameters in Table 5.2, where the Ru $\cdots$ O₁ distance starts to decrease whilst the Ru-S distance increases. As mentioned, this process does not ‘pass through’ the η^2 -(OS)O state itself, but rather through a transitive Ru-(SO) bound structure (image 4), as shown by the geometric parameters of the transition state and other images.

The second half of the energy profile for Pathway **I** is particularly interesting. Image 5 shows that photoisomerization from the dark-state to the formation of the η^1 -OSO geometry has occurred. Upon further visual inspection of the MEP, it can be seen that arene ring rotation effectively occurs only in the final image, *i.e.* after the SO₂ ligand has assumed the η^1 -OSO geometry. This is further corroborated by looking at the intermolecular interactions, in particular at the closest O_{free} $\cdots$ H_{aromatic} distance, as displayed in Table 5.3 below, where O_{free} refers to the unbound oxygen of the SO₂ photoisomer. Image 5 has the shortest O_{free} $\cdots$ H_{aromatic} distance of just 2.3121 Å. The NEB-generated pathway seems to indicate that photoisomerization and transduction do not occur simultaneously. Rather, transduction only seems to occur once the η^1 -OSO geometry has more or less fully formed, and the O_{free} $\cdots$ H_{aromatic} distance is small enough to cause the arene ring to rotate and alleviate the resulting strain.

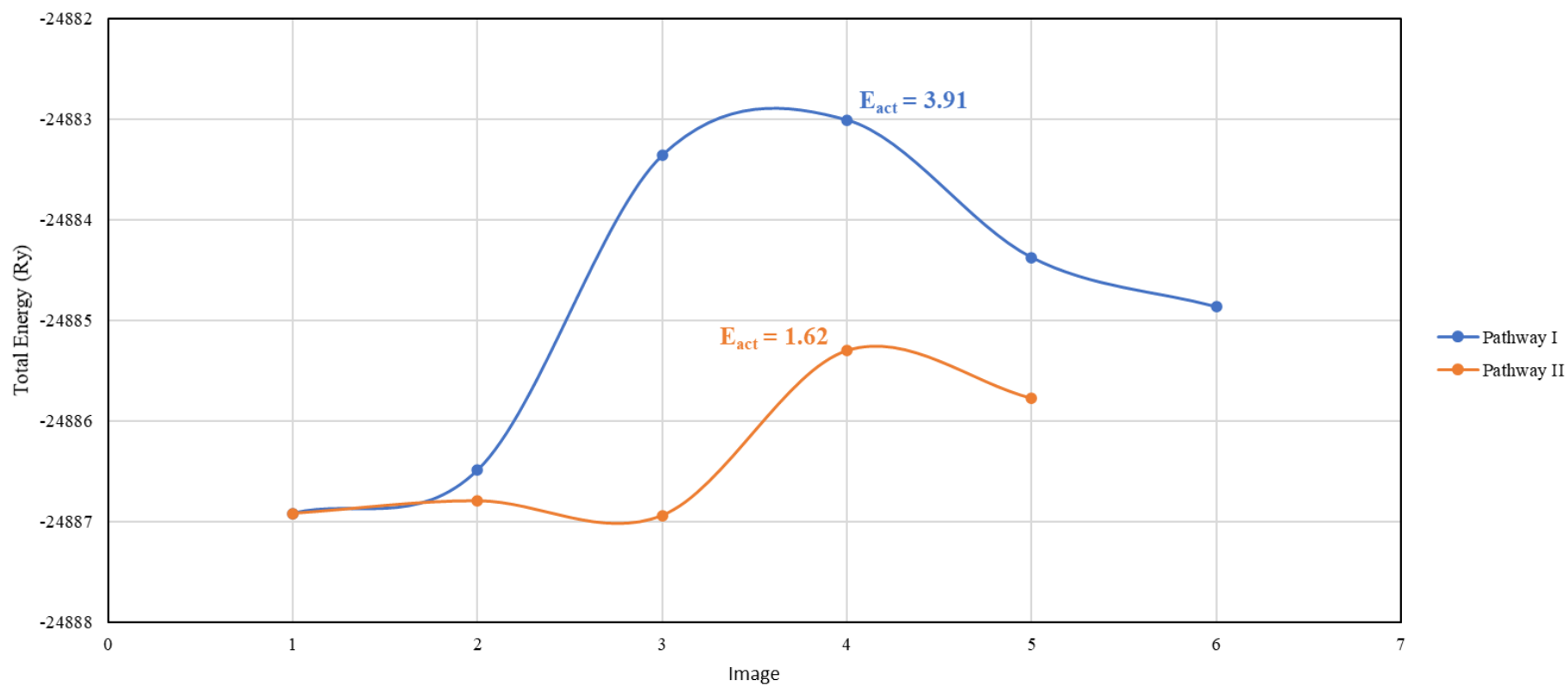


Figure 5.1: Energy profiles for the two photoisomerization pathways along with their activation energies. Pathway **I** (shown in blue): η^1 -SO₂ dark-state to η^1 -OSO light-induced configuration. Pathway **II** (shown in orange): η^1 -SO₂ dark-state to η^2 -(OS)O light-induced configuration.

Table 5.3: The $O_{\text{free}} \cdots H_{\text{aromatic}}$ distance for all images for both pathways. All distances are in Ångstroms. It is important to note that image 1 is the residual dark-state and the final image is η^1 -OSO and η^2 -(OS)O for pathway **I** and pathway **II**, respectively.

Image	Pathway I	Pathway II
1	2.2478	2.2478
2	2.3499	2.3493
3	2.3456	2.2847
4	2.3885	2.3308
5	2.3121	2.3091
6	2.3843	

5.2.2 Pathway **II**: η^1 -SO₂ dark-state to η^2 -(OS)O light-induced configuration

Pathway **II** has a slightly different energy profile to that of **I**. Firstly, it can be seen that there is a local maxima at image 2 which then leads to a local minima at image 3. The energy between this local maxima and minima is very small. It likely occurs due to the fact that the starting geometry here is the dark-residual state, rather than the 100% dark-state. The residual state geometry portrays small changes in geometric parameters relative to the 100% dark-state species (Table 5.2) as a result of its experimentally-determined form co-existing within the photo-induced state crystal structure alongside both the η^1 -OSO and η^2 -(OS)O light-state structures. The profile seen in the first three images appears to represent a readjustment of the dark-state geometry as it navigates these effects. The difference between the starting residual state geometry (image 1) and that of image 3 is extremely small, just 0.0002 eV/atom, which shows that this readjustment in structure was minute. This is also shown in the minute differences in bond lengths (less than 0.05%) between the two structures. Such a feature is not seen in Pathway **I**, due to the dominating effects towards the MEP of the SO₂ ligand transitioning from the η^1 -SO₂ dark-state to η^1 -OSO light-state structure. Pathway **II** then proceeds with the transition state at image 4, indicating the formation of an (SO)-bound state. It can also be seen, like with pathway **I**, any changes in the geometries or positions of the counterions occur after photoisomerization has occurred, with the transition from image 5 to 6 including an adjustment of the positions of the counterions to their η^2 -(OS)O positions.

5.3 Conclusions

These Ru-based crystal complexes undergo SO₂-linkage photoisomerization and in certain cases also exhibit molecular transduction. The mechanism and processes behind photoisomer formation have not been studied experimentally since they are extremely difficult to do so. It is thus desirable to use computational methods to try and understand this phenomenon and to provide some indication of the mechanism behind this process. This study examines the photoisomer formation step for one of the complexes in this family of materials, where **X** = 3-methylpyridine and **Y** = *p*-tosylate. The Nudged Elastic Band (NEB) method in the Plane Wave (PW) density functional theory (DFT) ansatz has been used to study two photoisomerization pathways: **(I)**: η^1 -(SO)₂ dark-state to η^1 -OSO light-induced configuration; and **(II)** η^1 -(SO)₂ dark-state to η^2 -(OS)O light-induced state.

The NEB-generated pathway **I** indicates an Ru-(SO) bound structure based mechanism, which was thought to likely be the case but has not been observed experimentally. It has also shown the importance of the intermolecular interactions towards causing transduction and indicates a cause-and-effect relationship between photoisomerization and transduction. The two do not occur simultaneously. Once photoisomerization has occurred and the η^1 -OSO geometry is well formed, if the O_{free}...H_{aromatic} distance is small enough to result in substantial steric repulsion, whereupon the arene ring will rotate to alleviate this strain. This study provides a strong framework for more extensive NEB-based studies of the photoisomerization process in the future. In particular, different transducers could be studied to explore the different characteristics of transduction that are specific to a complex; such as the degree of arene ring rotation. NEB also has the capability of including greater experimental information into the initial pathway. Any structural data that can be obtained during the photoisomerization process can be included in the potential pathway, which would then be optimized via NEB.

6 Synthesis of Ru-SO₂ Complexes

This chapter details experimental work that was carried out in parallel to the computational work that was discussed previously. A modified, more sustainable method to synthesize the precursor to these complexes; [Ru(NH₃)₄(SO₂)Cl]Cl, has been developed. This revised synthesis route removes the need to use an SO₂ gas cylinder; instead, the gas is ‘internally-generated’ and then immediately consumed. Two new Ru-SO₂ complexes have also been synthesized: (i) **X** = 3-propylpyridine and **Y** = Cl₂·H₂O; and (ii) **X** = 4-pyridinecarboxaldehyde and **Y** = *p*-tosylate, with their synthesis routes presented herein.

6.1 Modified Synthetic Route to the $[\text{Ru}(\text{NH}_3)_4(\text{SO}_2)\text{Cl}]\text{Cl}$ Precursor

All Ru-SO₂ complexes in this family of materials are synthesized from the precursor $[\text{Ru}(\text{NH}_3)_4(\text{SO}_2)\text{Cl}]\text{Cl}$ using ligand and counterion exchange reactions. The conventional procedure for the synthesis of the precursor is reported elsewhere.^{59,60} Part of the synthesis route requires slowly sparging SO₂ gas through solution to maintain acidic conditions and prevent side reactions.⁶⁶ This is usually done via an SO₂ gas cylinder, which is hazardous and unsustainable. An alternative method for the generation of SO₂ was thus developed, with the experimental setup shown in Figure 6.1.

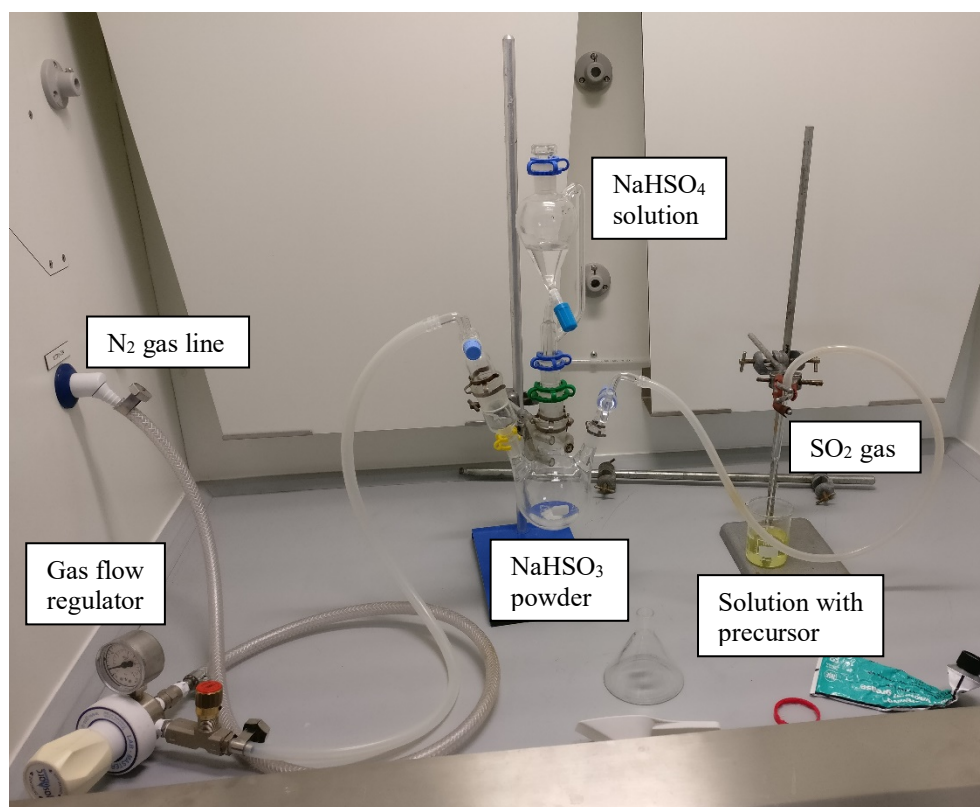
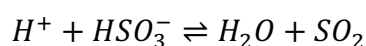
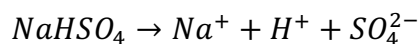


Figure 6.1: Experimental setup of the modified precursor synthesis route along with the ‘internally-generated’ SO₂ method.

An aqueous solution of NaHSO₄ (28% /w) is added dropwise to powdered NaHSO₃ which results in the formation of gaseous SO₂, as illustrated by the chemical reactions shown below.



Sodium bisulfate dissociates in water to form the acidic sulfate ion, which then reacts with the sulfite ions from the sodium bisulfite leading to the generation of gaseous SO₂. The gas is generated in a reaction flask, then bubbled through the solution by being pushed through by N₂ gas. It is important to note that before dissolution of the precursor, the generation of SO₂ is

confirmed by decolourizing a 0.025 M aqueous solution of KMnO_4 . This method of generating SO_2 is far less hazardous and much more sustainable than using a gas cylinder, with the final waste products of the SO_2 gas generation solely some sodium salts dissolved in water. The rest of the precursor method is used unchanged. A full method summary of the synthesis route to $[\text{Ru}(\text{NH}_3)_4(\text{SO}_2)\text{Cl}]\text{Cl}$ is given below.

$[\text{Ru}(\text{NH}_3)_4(\text{SO}_2)\text{Cl}]\text{Cl}$. In a dropping funnel, 70 g of $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ is dissolved in 250 mL of H_2O (28% /w) and added dropwise into a reaction flask with 50 g of NaHSO_3 . A small flow of N_2 (g) is passed through the reaction flask. A 10 mL 0.025 M solution of KMnO_4 is decolourised to confirm the generation of SO_2 (g). $[\text{Ru}(\text{NH}_3)_4(\text{SO}_2)\text{Cl}]\text{Cl}$ (1 g) was then added to a solution of NaHSO_3 (40 ml, 0.3 M) and heated to 75°C for 1h under continuous SO_2 (g) sparging. The resulting solution was then allowed to slowly cool to room temperature for 1 h whilst SO_2 (g) sparging was maintained. The precipitating $[\text{Ru}(\text{NH}_3)(\text{HSO}_3)_2]$ was then collected via vacuum filtration and added to an 80 ml solution of H_2O and HCl (50:50 /v). The solution was heated to boiling point and maintained for 15 min before being filtered whilst hot and left to cool overnight in the absence of light. The resulting needle-like deep-red crystals of $[\text{Ru}(\text{NH}_3)_4(\text{SO}_2)\text{Cl}]\text{Cl}$ were then collected via vacuum filtration and washed with methanol then dried at 60°C for 1 h.

6.2 Synthesis of New Ru-SO₂ Complexes

The synthesis route of new Ru-SO₂ complexes from this family of materials is from $[\text{Ru}(\text{NH}_3)_4(\text{SO}_2)\text{Cl}]\text{Cl}$, which is usually dissolved in water, and involves the substitution of the *trans*-ligand or counterion or both. These complexes crystallize from solution in acidic conditions; however, the speed of precipitation must be controlled to afford good crystal growth. If the solution is too acidic, they will crystallise too quickly, often forming a powder. This is why a 1M sodium carbonate solution is sometimes used instead of water as it acts as a buffer, keeping the solution from becoming overly acidic. A second solvent is sometimes also added to increase the solubility of the target *trans*-ligand or counterion and slow down precipitation.

Two new Ru-SO₂ complexes have been synthesized: (i) **X** = 3-propylpyridine and **Y** = $\text{Cl}_2 \cdot \text{H}_2\text{O}$; and (ii) **X** = 4-pyridinecarboxaldehyde and **Y** = *p*-tosylate. 3-Propylpyridine represents another addition to the **X** = 3-alkylpyridine series, being the longest 3-alkylpyridine

used as a *trans*-ligand to date. 3-Propylpyridine is not easily soluble in H₂O and thus required the use of a second solvent: methanol. 4-Pyridinecarboxaldehyde required the use of stronger acid due to its high pK_a value and will offer a direct comparison against the previously complex with **X** = 3-pyridinecarboxaldehyde for the same counterion. The dark-state structures of both new Ru-SO₂ complexes have been confirmed via crystallography as carried out by another researcher, whilst work on characterizing their light-induced structures via photocrystallography is ongoing. Synthesis routes for both new complexes are given below:

[Ru(NH₃)₄(SO₂)(3-propylpyridine)][Cl₂·H₂O]. [Ru(NH₃)₄(SO₂)Cl]Cl (5 mg or 16 μmol) is dissolved in an aqueous solution of Na₂CO₃ (1M, 300 μmol), after which a solution of 3-propylpyridine (5 μL) in methanol (300 μL) was added, which induced a colour change to yellow. Subsequently, HCl (32%, 168 μL) was added dropwise to the solution which induced a colour change to light orange. This resulted in the formation of red crystals within 2-4 h which were then isolated by filtration.

[Ru(NH₃)(SO₂)(4-pyridinecarboxaldehyde)][*p*-toluenesulfonate₂]. [Ru(NH₃)(SO₂)Cl]Cl (5 mg or 16 μmol) and 4-pyridinecarboxaldehyde (5 μL) were dissolved in a solution of H₂O and methanol (50:50 v/v, 700 μmol), giving a red solution. Subsequently, tosylic acid (4M, 400 μL) was added dropwise to the solution which was then stored at 5 °C. This resulted in the formation of red needle-like crystals within 2-4 h which were then isolated by filtration and washed with methanol.

6.3 Conclusions

This chapter details the experimental work carried out in parallel with computational calculations. An updated, more robust, and sustainable method to synthesize the precursor to these Ru-SO₂ complexes; [Ru(NH₃)₄(SO₂)Cl]Cl, has been presented, which removes the need of using a gas cylinder by ‘internally-generating’ SO₂ gas that is then immediately consumed. Two new Ru-SO₂ complexes: (i) **X** = 3-propylpyridine and **Y** = Cl₂·H₂O; and (ii) **X** = 4-pyridinecarboxaldehyde and **Y** = *p*-tosylate, have also been synthesized with their dark-states having been confirmed via crystallography. With the formation of PW-DFT models discussed previously, there is now the potential to synergize the experimental and computational aspects of the work to allow for a more systematic materials discovery pathway for this family of Ru-SO₂ complexes.

7 Conclusions and Future Work

7.1 Conclusions

The dark- and light-induced structures and single-crystal optical absorption spectra for a $[\text{Ru}(\text{SO}_2)(\text{NH}_3)_4\text{X}]\text{Y}$ family of ruthenium-SO₂ based complexes that form metastable long-lasting photoexcited structures and exhibit optical switching and nano-optomechanical transduction in the single-crystal state, have been modelled and simulated via density functional theory (DFT) based methods.

Initially two types of models were developed; Plane-Wave (PW)-DFT based periodic models, and Molecular Orbital (MO)-DFT based molecular fragment models. These calculations were conducted for the dark- and light-induced structures on two variants of two different complexes: **1A** and **1B** where $\text{X} = \text{Y} = \text{Cl}$; and **2A** and **2B** where $\text{X} = \text{H}_2\text{O}$, $\text{Y} = p\text{-tosylate}$. Structure relaxation calculations were conducted followed by the generation of single-crystal optical absorption spectra. Both periodic and molecular fragment models showed small deviations from experimental structures, although DFT did show slightly larger changes for the light-induced states which was expected since it models them at 100% photoconversion which is not the case in experiment. The optimized structures were then used to simulate the optical spectra via linear-response time-dependent density functional theory (LR-TDDFT) with periodic methods again effectively simulating the spectral features of experimental spectra and showing good coverage of the visible region. This showed that the periodic models are a viable alternative to molecular fragment models when it comes to simulating the optical properties for these complexes.

The periodic models were then used to conduct calculations for a larger set of complexes with different combinations of X/Y to examine the robustness of the models and determine if they can appreciate the competing chemical and crystallographic forces inherent in these complexes. This set included both photoswitches and transducers: **1A**, **1B**, **2A**, **2B** and three new complexes where $\text{Y} = p\text{-tosylate}$ and $\text{X} = 3\text{-bromopyridine}$ (**3**); 4-bromopyridine (**4**); and 3-methylpyridine (**5**), with **3** and **5** being transducers. As done for **1A**, **1B**, **2A**, **2B**, initially structure relaxation calculations were conducted after which single-crystal optical absorption spectra were generated. As seen previously, the DFT-optimized structures showed small deviations from experimental geometries. The generated optical spectra for the light-

induced structures were red-shifted as compared to their dark-state counterparts likely due to the competing chemical and crystallographic forces; namely *trans*-influence, and intermolecular interactions between the SO₂-ligand and counterion hydrogens. Density of states (DOS) were also calculated which revealed that the presence of the η^2 -(OS)O light-induced configuration ‘opens’ the bandgap, whereas the η^1 -OSO photoisomer ‘closes’ the bandgap. Partial density of states (p-DOS) then revealed the atomic and orbital contributions to the DOS, showing that the ruthenium and its d-orbitals were overwhelmingly responsible for the contributions to the pDOS of the cationic components. These calculations also showcased the potential for tuning of the optical and electronic properties of a complex.

The optimized periodic models were also used to conduct a study on the photoisomerization process via the Nudged Elastic Band (NEB) method since the formation of photoisomers occurs too quickly to study effectively. PW-NEB was conducted for complex **5** with two photoisomerization pathways studied: η^1 -SO₂ dark-state to η^1 -OSO light-induced configuration (**I**); and η^1 -SO₂ dark-state to η^2 -(OS)O light-induced configuration (**II**). The NEB generated minimum energy pathway (MEP) for **I** showed a Ru-(SO) bound geometry based mechanism and also indicated a cause-and-effect relationship between photoisomerization and transduction; whereby once the isomerization of SO₂ is complete, and the intermolecular interactions between the free unbound oxygen and the aromatic hydrogens are at their strongest, then transduction may occur. MEP **II** on the other hand does not generate those close interactions and thus does not result in transduction.

Experimental work on these [Ru(SO₂)(NH₃)₄X]Y complexes was also conducted in parallel with the computational calculations. A modified more sustainable and safer synthesis route to the precursor to this family of complexes; [Ru(SO₂)(NH₃)₄Cl]Cl, was developed that eliminated the need for an SO₂ gas cylinder, instead ‘internally-generating’ the SO₂ gas which is then immediately consumed. Two new complexes to this series of materials were also synthesized: (i) X = 3-propylpyridine and Y = Cl₂·H₂O, and (ii) X = 4-pyridinecarboxaldehyde and Y = *p*-tosylate.

And so, a novel PW-DFT based periodic methodology has been developed for this series of Ru-[SO₂] based complexes that has effectively been able to model the structural properties of these materials whilst also simulating their single-crystal optical absorption spectra. A solely experimental-based materials discovery pathway for these complexes is not viable and these

periodic models now offer a computational complement to this pathway, showcasing the potential for a more systematic materials discovery pathway to help develop new complexes with targeted properties. This methodology offers a complement to the experimental work on these materials allowing for the development of a more streamlined and systematic materials discovery pathway.

7.2 Future Work

The results from this thesis provide the opportunity for future work to be conducted on these $[\text{Ru}(\text{SO}_2)(\text{NH}_3)_4\text{X}]\text{Y}$ family of materials, particularly opening up avenues for more computational work on the dark- and light-induced photoisomers of these materials.

7.2.1 Large-Scale Computational Study

Chapters 3 and 4 have shown that the developed PW-methodology is applicable for both photoswitches and transducers from this family of materials, with the ability to investigate the structural, optical and electronic properties of these systems. However, certain trends such as the effect of the *trans*-influence or intermolecular interactions on the optical properties of the photoisomers still require further investigation. This is why a large-scale study of these complexes would be the logical next step, as it would magnify these trends and allow for deeper analysis of the effects of the competing chemical and crystallographic forces. This would involve conducting PW-DFT based calculations on a much larger set of complexes with several combinations of X/Y . Such a study would also allow for the investigation of ‘series’ within this family of complexes; for instance, the effect of increasing the size of the alkyl group of complexes all with $\text{X} = 3\text{-alkylpyridine}$ where the counterion is kept fixed. This would require large computational resources, however, the results from this thesis have provided a strong foundational framework for such a large-scale study to be carried out.

7.2.2 Further Nudged Elastic Band Calculations

The use of NEB to study the photoisomerization process illustrated the further functionality possible with optimized periodic models. In particular, as experimental methods improve and further data on these complexes comes in, NEB can emerge as a powerful tool to investigate the photoswitching and transduction capabilities of these complexes. As stated in Chapter 5, photoisomerization is complicated to study empirically since the formation of photoisomers

occurs too quickly to be properly characterized via current experimental methods. However, the growth of the photoisomers, once they have been formed, can be studied. Snapshots of this process can be taken, which could then act as intermediate images in an NEB pathway.

In addition, NEB could also be used to study the photoisomerization mechanism and how it may be affected depending on the *trans*-ligand and counterions present. It is known that different combinations of **X/Y** can produce differences in the transduction capabilities of a complex, for instance the degree of arene rotation. NEB could then be used to examine whether there are any differences or nuances within the photoisomerization and following transduction process. NEB also provides the energetics associated with these processes, and how these may vary depending on the *trans*-ligand or counterion.

7.2.3 Calculation of Raman Spectra

Raman spectra has been calculated on some of the complexes²⁶ from this family of materials, and is another avenue of analysis that could be conducted via these periodic models. However, the calculation of Raman spectra for large periodic systems is not straightforward. At the moment, Quantum Espresso does not compute the Raman coefficients and such for GGA functionals, this capability is restricted to LDA and can only be conducted at the gamma point. However, finite differences can still be used along with calculations from DFT to then calculate Raman spectra. This would allow for further investigation of the capabilities of these PW-DFT models.

7.2.4 Machine Learning Based Prediction of New Complexes

Once a large-scale study of these complexes where a much larger dataset has been constructed with many combinations of **X/Y**, new complexes could then be predicted computationally via machine learning methods. A machine learning algorithm could be used to identify the ideal *trans*-ligand and counterion combinations that deliver specific properties (based on the DFT and TDDFT models). Such a materials discovery pathway offers a more systematic approach to selecting new *trans*-ligands and counterions to sample. This could then be combined with experimental work where the predicted complexes are synthesized and characterized, with their properties then compared with those predicted via DFT. This information could then be fed back into the machine learning environment thus improving the predictive model.

Appendices

Appendix 1

DFT optimized geometries for all complexes are given. Initially MO and PW geometries for complexes **1** and **2**, followed by PW geometries of **3**, **4** and **5**.

MO-DFT optimised geometries are presented below. All coordinates are in Ångstroms.

1A Dark state:

N	0.96149063	-8.03823046	0.64621570
H	0.25929102	-8.27674748	1.35413632
H	0.94142803	-8.74086694	-0.10038563
N	-1.48658404	-6.65695618	-0.60848354
H	-1.86051739	-7.29758686	0.09729597
H	-1.61026666	-7.08663024	-1.52995408
H	-3.78775165	-1.23222258	-2.76786055
H	-2.87366814	4.82420875	0.94882025
H	-4.72149582	-0.89189880	-1.44155119
H	-3.25838160	6.36295881	0.52311072
H	-3.06545768	1.34806144	-3.78928720
H	-1.87732968	8.10077928	-1.09929192
Cl	-1.11004387	7.32184740	2.36180313
O	-3.99876989	3.30089990	-1.32705743
Ru	0.58743489	-6.11900910	-0.33276253
Cl	-2.40725417	-3.60695197	0.18030557
S	0.06777606	-5.33094954	1.63933771
N	2.67295896	-5.56662296	-0.25555660
H	3.03801361	-5.17636491	0.62114020
O	0.70519267	-4.19935716	2.35727131
O	-0.78340346	-6.20781526	2.47444451
Ru	-2.39100600	0.55508547	-1.21060746
Ru	-0.58743489	6.11900910	0.33276253
Ru	2.39100600	-0.55508547	1.21060746
Cl	-0.63638126	-0.92131502	-2.09241597
Cl	0.63638126	0.92131502	2.09241597
Cl	-3.09737780	2.74607730	1.81243484
Cl	2.40725417	3.60695197	-0.18030557
Cl	3.09737780	-2.74607730	-1.81243484
S	-4.02777018	1.93979294	-0.72972532
S	-0.06777606	5.33094954	-1.63933771
S	4.02777018	-1.93979294	0.72972532
N	-3.76039086	-1.04615226	-1.76246589
N	-0.21060330	4.42529490	1.56963676
N	2.35577273	0.32072409	-0.75712968
N	-2.67295896	5.56662296	0.25555660
N	3.76039086	1.04615226	1.76246589
N	0.21060330	-4.42529490	-1.56963676
N	-2.35577273	-0.32072409	0.75712968
H	-3.41476785	-1.91004309	-1.31472846
H	-1.03767846	3.83818330	1.75984373
H	2.35655581	1.35255055	-0.74069996
H	-3.03801361	5.17636491	-0.62114020
H	3.41476785	1.91004309	1.31472846

H	1.03767846	-3.83818330	-1.75984373
H	-2.35655581	-1.35255055	0.74069996
H	0.08723404	4.77727409	2.48448462
H	1.52951862	0.00555688	-1.28266114
H	-0.08723404	-4.77727409	-2.48448462
H	-1.52951862	-0.00555688	1.28266114
H	0.54822416	3.82640806	1.20536279
H	3.15555470	0.01175729	-1.31930359
H	-0.54822416	-3.82640806	-1.20536279
H	-3.15555470	-0.01175729	1.31930359
N	-2.25360138	1.47844621	-3.18083188
N	0.92238305	-1.92456016	0.54488371
N	2.25360138	-1.47844621	3.18083188
N	-0.92238305	1.92456016	-0.54488371
H	-2.09372299	2.48905381	-3.10730680
H	0.68469390	-2.66134512	1.21247591
H	2.09372299	-2.48905381	3.10730680
H	-0.68469390	2.66134512	-1.21247591
H	2.05659194	5.79433981	0.54608458
H	1.30201498	-2.36568753	-0.30121021
H	-2.05659194	-5.79433981	-0.54608458
H	-1.30201498	2.36568753	0.30121021
H	-1.44132420	1.05960382	-3.64622528
H	0.05483172	-1.47114687	0.25230785
H	1.44132420	-1.05960382	3.64622528
H	-0.05483172	1.47114687	-0.25230785
O	-5.34940324	1.42824198	-0.31497951
O	-0.70519267	4.19935716	-2.35727131
O	5.34940324	-1.42824198	0.31497951
O	0.78340346	6.20781526	-2.47444451
Cl	1.11004387	-7.32184740	-2.36180313
O	3.99876989	-3.30089990	1.32705743
H	2.87366814	-4.82420875	-0.94882025
H	3.25838160	-6.36295881	-0.52311072
H	1.87732968	-8.10077928	1.09929192
H	3.78775165	1.23222258	2.76786055
H	4.72149582	0.89189880	1.44155119
H	3.06545768	-1.34806144	3.78928720
N	1.48658404	6.65695618	0.60848354
N	-0.96149063	8.03823046	-0.64621570
H	1.86051739	7.29758686	-0.09729597
H	-0.25929102	8.27674748	-1.35413632
H	1.61026666	7.08663024	1.52995408
H	-0.94142803	8.74086694	0.10038563

1A η^2 -(OS)O:

N	0.88409194	-6.10387901	2.12577828
H	0.44253085	-6.99306442	2.37813040
H	0.34973355	-5.32411152	2.56422864
N	-1.28035327	-5.60950007	0.31456361
H	-1.74082809	-6.50352081	0.51126758
H	-1.45160212	-4.98857940	1.12257695
H	-3.03583527	-0.53695585	-2.84789203
H	-3.49357882	5.68232882	0.51885994
H	-4.51130358	-1.21117267	-2.49710748
H	-2.90787637	7.00697423	1.35233723
H	-4.82949575	0.96268641	-1.11259012
H	-1.81955466	6.10380724	-2.54031749
Cl	-2.30784317	-4.27842098	-2.64232831
Ru	0.78093588	-5.93324235	-0.04742844
Cl	0.42102804	-8.30343089	0.04037733
S	1.82383951	-3.77840544	0.53047000
O	0.83204923	-3.85569064	-0.65272883
N	2.85554153	-6.48861129	-0.47182797
H	3.19228147	-7.13252505	0.24873248

Cl	-0.82335778	-3.46146126	2.82080369
Cl	2.30784317	4.27842098	2.64232831
Cl	0.82335778	3.46146126	-2.82080369
Ru	-2.97086967	-0.82924954	-0.18619947
Ru	-0.78093588	5.93324235	0.04742844
Ru	2.97086967	0.82924954	0.18619947
Cl	-1.32360840	0.61431990	-1.18307384
Cl	-0.42102804	8.30343089	-0.04037733
Cl	1.32360840	-0.61431990	1.18307384
S	-4.36623860	-2.85326967	0.15549426
S	-1.82383951	3.77840544	-0.53047000
S	4.36623860	2.85326967	-0.15549426
O	-4.58485559	-1.59238672	1.04257708
O	-0.83204923	3.85569064	0.65272883
O	4.58485559	1.59238672	-1.04257708
O	-3.25948242	3.69138938	-0.06245113
O	3.68514655	3.97773280	-0.83601006
O	3.25948242	-3.69138938	0.06245113
O	-3.68514655	-3.97773280	0.83601006
N	-3.51465750	-1.23026279	-2.26387398
N	-0.39644238	6.04268109	2.15339774
N	1.44824247	2.28350397	0.20662933
N	-2.85554153	6.48861129	0.47182797
N	3.51465750	1.23026279	2.26387398
N	0.39644238	-6.04268109	-2.15339774
N	-1.44824247	-2.28350397	-0.20662933
H	-0.22015733	7.01141974	2.43624000
H	0.54527812	1.81583072	0.31662779
H	0.22015733	-7.01141974	-2.43624000
H	-0.54527812	-1.81583072	-0.31662779
H	0.44627830	5.48157502	2.39417515
H	1.37809166	2.81399125	-0.67601868
H	-0.44627830	-5.48157502	-2.39417515
H	-1.37809166	-2.81399125	0.67601868
H	-3.16275610	-2.16569193	-2.54566254
H	-1.15942794	5.66678727	2.72191841
H	1.54079542	2.95503570	0.98383973
H	-3.19228147	7.13252505	-0.24873248
H	3.16275610	2.16569193	2.54566254
H	1.15942794	-5.66678727	-2.72191841
H	-1.54079542	-2.95503570	-0.98383973
N	-4.36845318	0.84916710	-0.20585760
N	2.16532133	0.42688101	-1.76234224
N	4.36845318	-0.84916710	0.20585760
N	-2.16532133	-0.42688101	1.76234224
H	-3.94166555	1.76256736	0.00262937
H	1.26620793	-0.06018953	-1.67993159
H	3.94166555	-1.76256736	-0.00262937
H	-1.26620793	0.06018953	1.67993159
H	-5.10239966	0.66085077	0.48365671
H	2.78163693	-0.12639152	-2.36192631
H	5.10239966	-0.66085077	-0.48365671
H	-2.78163693	0.12639152	2.36192631
H	1.77857635	5.19822599	0.48965304
H	1.96637096	1.30901722	-2.26313380
H	-1.77857635	-5.19822599	-0.48965304
H	-1.96637096	-1.30901722	2.26313380
H	3.49357882	-5.68232882	-0.51885994
H	2.90787637	-7.00697423	-1.35233723
H	1.81955466	-6.10380724	2.54031749
H	3.03583527	0.53695585	2.84789203
H	4.51130358	1.21117267	2.49710748
H	4.82949575	-0.96268641	1.11259012
N	1.28035327	5.60950007	-0.31456361
N	-0.88409194	6.10387901	-2.12577828
H	1.74082809	6.50352081	-0.51126758

H	-0.44253085	6.99306442	-2.37813040
H	1.45160212	4.98857940	-1.12257695
H	-0.34973355	5.32411152	-2.56422864

1B Dark state:

H	-1.16628583	-0.83260226	-2.60322176
H	-4.76152534	-0.06287059	-3.81667187
O	-5.17947596	2.06261285	-1.08922926
Cl	0.70992369	1.84207434	-2.43160943
N	-0.93045650	4.73738183	-1.11203522
H	-0.31600068	4.18525116	-1.72494873
H	-1.83658465	4.24939121	-1.09115158
Ru	-0.30647936	-4.15038276	1.49191101
Ru	3.64818845	-0.19002208	-1.13602840
Ru	-3.56548845	-0.66040374	-1.39989023
Cl	-2.72930372	-3.85395509	1.87941471
Cl	-3.39886138	-3.00036430	-2.16236467
Cl	-3.71806397	1.35487751	1.69048181
Cl	2.14879776	-5.54894803	-0.87324524
S	1.88816613	-4.40684554	1.31270224
S	1.50261766	-0.40232596	-1.03623331
S	-3.82856164	1.48512814	-0.90688841
O	2.53088174	-5.38446911	2.22094665
O	0.81661848	-1.35419543	-1.96661948
O	-2.68334303	2.40668316	-1.13002738
O	0.67623800	-0.12357702	0.17588409
N	-0.22645652	-4.84505895	3.55199649
N	3.55931981	0.25498402	-3.25075501
N	-2.16269995	-0.95775176	0.16298627
N	3.83488797	-2.31386618	-1.55966162
N	-1.96545650	-0.20987069	-2.77400840
N	-0.72729634	-6.15223651	0.80561689
H	4.47996751	0.59576296	-3.54371037
H	-2.18988907	-1.92801431	0.49264804
H	-1.69729012	-6.18027174	0.47541202
H	0.49319776	-5.56319525	3.68743793
H	3.32022022	-0.54647686	-3.84055756
H	-1.19609832	-0.69580244	-0.05179338
H	3.23523540	-2.66640442	-2.31150473
H	-1.57851609	0.74062403	-2.69968554
H	-0.62833850	-6.87818105	1.52038322
H	-0.03525625	-4.10631039	4.23502151
H	2.84908179	0.97916007	-3.42644371
H	-2.45949284	-0.35659165	0.94803443
H	3.60109237	-2.88364894	-0.73508297
H	-2.22667464	-0.36200150	-3.75210320
H	-0.09902606	-6.41229216	0.03380027
N	-0.01663561	-2.12508415	2.20740079
N	-5.01989417	-1.30460836	0.06554383
N	-5.09740036	-0.46526179	-2.93724893
N	-0.42139427	2.65037147	0.81395248
N	-0.51374257	-3.60821424	-0.57336964
H	0.64390094	-2.04979309	2.98681024
H	-5.99433341	-1.33776375	-0.24418216
H	-5.87170500	0.12822931	-2.62198069
H	-0.37431113	2.29129533	-0.14571372
H	-0.12441755	-2.70512691	-0.86622478
H	3.03701502	2.45067625	-1.28005868
H	-4.97838626	-0.68535585	0.88724237
H	0.00580324	-4.28871174	-1.14174833
H	0.32996118	-1.46494198	1.49781479
H	-4.76103805	-2.25188696	0.36561976
H	-5.44732307	-1.40465395	-3.15074752
H	-1.34304034	2.38527421	1.18526311
H	-1.49042952	-3.61590388	-0.90422871

Cl	6.06479243	-0.10019055	-1.31384264
O	2.69978710	-3.19003888	1.00079851
H	-1.14652770	-5.22780397	3.79142928
H	4.81079400	-2.50251662	-1.80793791
H	-0.91681199	-1.76555904	2.54156771
H	3.59313637	-1.45304889	1.26298947
H	-1.08426681	7.13242964	1.72815409
H	-1.07639366	5.64827329	-1.55284480
Cl	-2.51736655	4.94294680	1.62091999
Ru	-0.21992743	4.75800821	0.92565551
S	1.87810493	4.94845374	0.35744986
O	2.70376304	5.85626968	1.19082977
O	2.47430869	4.54072712	-0.93337614
N	-0.24289788	6.93867843	1.17416042
H	0.58269632	7.29830335	1.66385852
H	-0.32664814	7.46647643	0.30150641
Cl	2.43682754	2.10854382	2.38835132
N	0.32879723	4.55899243	2.99715979
H	-0.52444669	4.41203079	3.54545200
H	0.83554165	5.35440438	3.39512452
H	0.95065080	3.73726041	3.09901014
N	3.66187679	1.88925009	-0.69027225
N	3.90797238	-0.52328488	0.96686814
H	3.36459510	2.07433310	0.28315512
H	3.42016268	0.18294984	1.54347808
H	0.32093215	2.16784702	1.34194748
H	4.61177103	2.25874998	-0.79476243
H	4.91043338	-0.44874701	1.16500099

1B η^2 -(OS)O:

H	-2.42528307	-1.92444772	-2.70762363
H	-5.67047671	-0.58063910	-2.02141786
Cl	-3.14182881	4.39068162	0.59633839
Cl	0.25794369	1.33329181	-1.89800758
N	-1.43617837	4.29167357	-2.08412412
H	-0.83278679	3.45670349	-2.15686158
H	-2.39216160	3.92958481	-2.00142951
Ru	0.57237329	-5.09735412	0.58545234
Ru	3.96861337	0.95382108	-0.00155029
Ru	-3.48649199	-1.19962552	-0.34752667
Cl	1.02194697	-3.08403684	1.87369994
Cl	-3.74919367	-3.61107177	-0.64030397
Cl	-2.57098705	0.72935784	3.07377554
Cl	-0.21755389	-6.94379096	-2.82931771
S	0.83956804	-7.52685430	-0.18888286
S	1.97117014	-0.37522845	0.90250012
S	-3.75368673	1.22987465	0.42680849
O	-0.41871013	-7.24658462	0.66067034
O	2.98028405	-1.19674774	0.07162657
O	-2.49540856	0.94960498	-0.42274468
O	1.81535351	-6.92588945	-0.64263106
O	1.80430128	0.78098398	1.29560456
O	-4.72947223	0.62890981	0.88055670
N	-1.31396860	-5.01868750	1.64812437
N	3.84715793	0.31175793	-2.05729996
N	-1.49965306	-1.31384384	0.46140777
N	5.53397873	-0.45721436	0.63382201
N	-2.67052060	-0.99845242	-2.34452146
N	-0.43001499	-4.27594525	-1.12970954
H	4.53108419	0.84429262	-2.60406401
H	-1.06367596	-2.22301264	0.63761145
H	0.01890222	-3.43390891	-1.50109459
H	-2.08656117	-4.77268839	1.01496722
H	4.02598726	-0.68474151	-2.20397021
H	-0.86515883	-0.78030558	-0.14433484

H	5.45141559	-1.37616628	0.19203274
H	-1.82185690	-0.41427570	-2.31555888
H	-1.42411986	-4.04558795	-0.99607879
H	-1.56829041	-5.91350806	2.07313602
H	2.90607499	0.50754532	-2.42418131
H	-1.49825284	-0.80479471	1.36037932
H	5.60427286	-0.61985263	1.64215215
H	-3.28189667	-0.56253352	-3.04101558
H	-0.40958693	-5.00878456	-1.87152272
N	1.59438063	-5.96957044	2.33661449
N	-4.13076783	-1.68201401	1.70628191
N	-5.53548090	-1.10362437	-1.15141303
N	-0.10158274	3.60201583	0.58197172
N	2.45966361	-4.53122668	-0.51327362
H	1.69332456	-5.18331045	2.98919064
H	-5.13895212	-1.60686872	1.86156948
H	-6.21189365	-0.72991324	-0.47939519
H	0.00431899	2.86003137	-0.12109162
H	3.31754823	-5.01279224	-0.23438555
H	1.89223149	2.35647900	-1.13154569
H	-3.67428355	-1.06566892	2.40549618
H	2.35139721	-4.70023887	-1.51742601
H	1.04258052	-6.70153532	2.79383259
H	-3.87607896	-2.65423489	1.89438719
H	-5.79055686	-2.07962301	-1.34125345
H	-0.70598245	3.19628099	1.30585279
H	2.59746133	-3.52885603	-0.34985802
H	-1.26874968	-4.30044171	2.37775560
H	6.41004656	-0.02049483	0.32759560
H	2.53187664	-6.35383116	2.18482752
H	3.86633581	1.45467119	2.82690803
H	-3.44321807	6.51735485	-0.68585829
H	-1.36816392	4.78337385	-2.97969945
Ru	-1.08818104	5.33647122	-0.19493653
S	0.90926217	6.66552072	-1.09898694
O	-0.09985171	7.48704002	-0.26811339
O	1.07613104	5.50930829	-1.49209138
N	-2.52334360	6.89517020	-0.93596456
H	-2.40156728	7.78871442	-0.45329600
H	-2.52309201	7.10050344	-1.93857707
Cl	2.72452660	4.91478147	1.39964814
N	-0.78114706	6.03117660	1.83750993
H	-1.41187909	5.51741465	2.46058693
H	-0.95240264	7.03094747	1.96913966
H	0.19004653	5.84977796	2.12639191
N	2.81060607	2.58780429	-0.73436267
N	4.16481471	1.92088494	1.96575597
H	2.70973967	3.33869533	-0.03352549
H	3.65971625	2.82389983	1.93018907
H	0.82216687	3.79436412	0.99691104
H	3.37119575	3.01620983	-1.47686717
H	5.15028914	2.18017351	2.07414544
Cl	5.82443027	2.39010704	-0.61365809

1B η^1 -OSO:

H	-3.67552273	0.80519652	-1.65948100
H	-5.81764338	-0.84830883	-2.25895679
Cl	-0.02688960	0.82301529	-0.81556375
N	-2.15282565	3.45359329	-0.72911075
H	-1.63684935	2.70851180	-1.21265162
H	-2.49327083	3.03584332	0.14724792
Ru	0.57426791	-4.54281439	0.55452248
Ru	3.89658971	0.78948077	0.31534300
Ru	-3.90769315	-1.61565055	-0.44489937
Cl	-1.73297707	-4.96998428	1.35012455

Cl	5.77475757	0.39422672	-1.12305781
Cl	-2.79391235	-3.18766948	-1.98378390
Cl	-2.66868552	1.57792482	2.12417801
Cl	2.58660355	-3.54384256	-2.88546327
S	3.47054232	-4.78303568	-0.95556865
S	1.23181076	0.49249814	2.17815780
S	-4.95167753	1.18685379	1.07138091
O	2.63404980	-4.08244475	0.11649664
O	2.37655038	1.27418227	1.53842556
O	-4.91082565	-0.32478008	0.92514634
O	3.00058853	-6.17059105	-1.19792165
O	1.36845284	-0.98799459	1.95421784
O	-4.78173337	1.89525661	-0.22886861
N	1.04403062	-6.54318732	1.25575458
N	2.85029692	-0.74618642	-0.76629149
N	-2.27285598	-1.47432998	0.95095407
N	4.64728230	-0.80258170	1.59909096
N	-3.10134983	-0.04242468	-1.67813713
N	0.04189301	-5.32923642	-1.39286420
H	3.34955611	-0.98018307	-1.63138594
H	-1.84551300	-2.38427529	1.15760754
H	-0.95308856	-5.12502321	-1.54784797
H	1.61934959	-7.00471429	0.54355913
H	2.72486448	-1.63377270	-0.26900783
H	-1.54672537	-0.82111058	0.63798107
H	5.45691804	-1.20158645	1.11147157
H	-3.01186137	-0.38333720	-2.63988144
H	0.17732064	-6.33798905	-1.49222101
H	1.55243928	-6.61391640	2.14186464
H	1.90926174	-0.41730319	-1.02622649
H	-2.61936790	-1.07498406	1.82754982
H	3.94370930	-1.53815008	1.71467360
H	-2.14988673	0.23031901	-1.39102782
H	0.57041677	-4.89651054	-2.15930909
N	0.95046889	-3.76569308	2.53817795
N	-4.61762520	-3.28328970	0.73725950
N	-5.58650999	-1.74562916	-1.82323132
N	0.02339272	3.71555148	1.14619765
N	0.17060513	-2.66216796	-0.40597098
H	1.80287681	-4.12805395	2.97516925
H	-5.29020058	-3.88232471	0.25098603
H	-6.45189961	-2.09793068	-1.40531924
H	0.02427206	2.77250637	0.73916455
H	0.32006023	-1.81513378	0.14687943
H	2.16696175	2.05004040	-1.28632436
H	-5.04766189	-2.99235464	1.62043035
H	0.80457786	-2.59607637	-1.21035351
H	1.01940778	-2.74270701	2.54474162
H	-3.81033122	-3.88633840	0.95604522
H	-5.30831241	-2.39570134	-2.56794600
H	-0.53173138	3.68256365	2.00668037
H	-0.77489729	-2.61947804	-0.80789867
H	0.16692027	-7.06140003	1.37234096
H	4.95350526	-0.52586273	2.53549795
H	0.15312756	-4.03307649	3.12462573
H	5.25897185	2.19549811	2.26434294
H	-2.38060696	7.09106811	-1.06501800
H	-2.99332308	3.67581382	-1.26775507
Ru	-0.84292467	5.08365529	-0.24103896
Cl	-2.41310309	5.82848590	1.40496440
S	1.46347360	5.20213542	-2.51480845
O	0.55234867	4.44050374	-1.54469510
O	1.09184345	6.64502872	-2.67482524
N	-1.76379594	6.49150922	-1.62316272
H	-1.05598399	7.06604927	-2.09112174
H	-2.33514645	6.06452198	-2.35680042

Cl	3.18696934	4.98526655	0.78941573
N	0.46415113	6.67955842	0.39002035
H	0.06191850	7.11434239	1.22593005
H	0.61692821	7.40964492	-0.31096891
H	1.39911629	6.30553489	0.63208091
N	3.14092654	2.26043785	-1.03207187
N	5.03097513	2.35612160	1.27963406
H	3.14258429	3.20289226	-0.60448571
H	4.52974125	3.26339553	1.23643448
H	1.00005418	3.95983691	1.36238009
H	3.70937792	2.28580382	-1.88315603
H	5.91596340	2.46236714	0.77383441

2A Dark state:

O	-2.99116938	-7.77843914	-1.06679443
S	-1.80962509	-7.27487073	-0.33933206
O	-1.10792834	-6.15822981	-1.11533326
H	-3.54854398	-3.73355039	-2.03827116
H	-2.43820960	-4.87771337	-1.53103360
C	-0.59389932	-8.59006522	-0.23529796
C	0.31402053	-10.66306101	-1.05091984
H	0.25282605	-11.51850327	-1.72567040
C	-0.67721870	-9.68075012	-1.09991591
H	-1.51248264	-9.75493957	-1.79425599
C	1.44183324	-9.46159020	0.70863098
C	1.38627274	-10.56966585	-0.15181140
C	2.43581765	-11.65500949	-0.08711704
H	2.11993544	-12.46671817	0.58761859
H	3.39355038	-11.26912509	0.28920696
H	2.61306480	-12.10195608	-1.07552774
C	-5.35447046	4.71478877	-0.72781172
H	-6.39766583	2.96967550	-1.46462686
C	-6.42291828	5.68554038	-1.17314890
H	-6.75483334	5.47289206	-2.19989270
H	-7.30974945	5.61772789	-0.52360106
H	-6.06459073	6.72329077	-1.13900760
H	-2.26547851	9.37345531	-1.41925800
Ru	-2.28812624	-2.86966409	0.26042170
S	-4.13350370	-1.72995302	0.44736390
S	2.14233762	-1.73060471	-0.62498032
O	-4.68767914	-0.99682994	-0.70802431
O	-4.96148180	-1.79945153	1.66365533
O	-0.48212085	-3.99214088	0.16372224
H	-0.63279234	-4.90454774	-0.24796233
H	0.17833942	-3.53088377	-0.42016402
O	2.79528139	-0.65621283	-1.42588786
O	1.52295829	-1.18659219	0.63695917
O	1.13121733	-2.52314432	-1.41355012
O	-2.06044738	-6.82647015	1.06798404
N	-1.16227263	-1.69947437	1.64835608
H	-0.20706680	-1.55139327	1.28140959
H	-1.05586904	-2.14693529	2.56220356
H	-1.60518882	-0.77942469	1.79318378
N	-1.62778534	-1.59765484	-1.34647872
H	-1.63076928	-0.60083493	-1.07048367
H	-2.21878387	-1.65941387	-2.17923528
H	-0.66255786	-1.83626999	-1.61755142
N	-3.16592180	-4.20966516	-1.21676474
H	-3.91801595	-4.80274956	-0.85088608
N	-2.81271519	-4.22437484	1.85839037
H	-3.76976248	-4.10972357	2.20501659
H	-2.19719019	-4.10298879	2.66732289
H	-2.67524744	-5.21155896	1.55992313
C	3.40543353	-2.89913545	-0.12872889
C	3.22770756	-4.26083942	-0.37134605

H	2.34608489	-4.61728566	-0.89898544
C	4.20500670	-5.15967734	0.06230489
H	4.06647214	-6.22496931	-0.12718333
C	5.50644034	-3.33536970	0.95220164
C	4.54300308	-2.42215342	0.53022371
H	4.67721105	-1.35534835	0.70349869
C	0.45970603	-8.47226731	0.67350514
H	0.50054982	-7.61991813	1.35016943
Ru	2.28812624	2.86966409	-0.26042170
S	4.13350370	1.72995302	-0.44736390
S	-2.14233762	1.73060471	0.62498032
O	4.68767914	0.99682994	0.70802431
O	4.96148180	1.79945153	-1.66365533
O	0.48212085	3.99214088	-0.16372224
H	0.63279234	4.90454774	0.24796233
H	-0.17833942	3.53088377	0.42016402
O	-2.79528139	0.65621283	1.42588786
O	-1.52295829	1.18659219	-0.63695917
O	-1.13121733	2.52314432	1.41355012
O	2.06044738	6.82647015	-1.06798404
N	1.16227263	1.69947437	-1.64835608
H	0.20706680	1.55139327	-1.28140959
H	1.05586904	2.14693529	-2.56220356
H	1.60518882	0.77942469	-1.79318378
N	1.62778534	1.59765484	1.34647872
H	1.63076928	0.60083493	1.07048367
H	2.21878387	1.65941387	2.17923528
H	0.66255786	1.83626999	1.61755142
N	3.16592180	4.20966516	1.21676474
H	3.91801595	4.80274956	0.85088608
N	2.81271519	4.22437484	-1.85839037
H	3.76976248	4.10972357	-2.20501659
H	2.19719019	4.10298879	-2.66732289
H	2.67524744	5.21155896	-1.55992313
C	-3.40543353	2.89913545	0.12872889
C	-3.22770756	4.26083942	0.37134605
H	-2.34608489	4.61728566	0.89898544
C	-4.20500670	5.15967734	-0.06230489
H	-4.06647214	6.22496931	0.12718333
C	-5.50644034	3.33536970	-0.95220164
C	-4.54300308	2.42215342	-0.53022371
H	-4.67721105	1.35534835	-0.70349869
C	-0.45970603	8.47226731	-0.67350514
H	-0.50054982	7.61991813	-1.35016943
C	5.35447046	-4.71478877	0.72781172
H	6.39766583	-2.96967550	1.46462686
C	6.42291828	-5.68554038	1.17314890
H	6.75483334	-5.47289206	2.19989270
H	7.30974945	-5.61772789	0.52360106
H	6.06459073	-6.72329077	1.13900760
H	2.26547851	-9.37345531	1.41925800
C	-1.44183324	9.46159020	-0.70863098
C	-1.38627274	10.56966585	0.15181140
C	-2.43581765	11.65500949	0.08711704
H	-2.11993544	12.46671817	-0.58761859
H	-3.39355038	11.26912509	-0.28920696
H	-2.61306480	12.10195608	1.07552774
S	1.80962509	7.27487073	0.33933206
O	1.10792834	6.15822981	1.11533326
H	3.54854398	3.73355039	2.03827116
H	2.43820960	4.87771337	1.53103360
C	0.59389932	8.59006522	0.23529796
C	-0.31402053	10.66306101	1.05091984
H	-0.25282605	11.51850327	1.72567040
C	0.67721870	9.68075012	1.09991591
H	1.51248264	9.75493957	1.79425599

O	2.99116938	7.77843914	1.06679443
---	------------	------------	------------

2A η^2 -(OS)O:

C	2.15886646	7.64052854	-1.61795677
H	0.72041099	8.15014281	-3.14543554
C	3.35077976	7.66085115	-2.54695710
H	3.14845618	8.24948566	-3.45216493
H	4.23579452	8.08954893	-2.05503669
H	3.61692063	6.64154525	-2.87132694
C	4.81574703	4.66856808	-0.36393239
H	4.94757764	5.56903444	-0.96464266
O	-2.34886759	-0.39994920	-0.39224035
S	-1.46368762	7.41829768	1.22710489
O	-1.54918540	8.65134239	2.01736829
O	-2.65073284	7.15100151	0.33162695
O	-1.15062135	6.18358461	2.06066299
O	1.43353270	2.05827778	-1.23785665
C	-0.05534873	7.52666551	0.10319331
C	1.22503376	7.27689178	0.60320155
H	1.35651669	7.02342980	1.65401313
C	2.31977536	7.33898550	-0.25622431
H	3.31662156	7.14057756	0.13801923
C	0.86540481	7.89808720	-2.09346056
C	-0.24161394	7.84647064	-1.24137996
H	-1.24378205	8.05639146	-1.61276281
C	3.63882567	3.93084540	-0.49143827
H	2.85437030	4.24386411	-1.17801094
Ru	-2.46412064	3.28542834	-0.06652210
S	-4.54775128	1.96201706	0.02586739
O	-4.18628737	2.77891425	-1.24923351
O	-5.57250795	2.59901513	0.90280983
O	-0.69402848	4.19699822	0.47311848
H	-0.79700847	4.95955746	1.14244290
H	0.05742092	3.59804085	0.74751644
N	-2.53615970	4.93377309	-1.42953973
H	-2.58818861	5.83048097	-0.90654643
H	-3.33976643	4.86397104	-2.05922449
H	-1.67801275	4.96492979	-1.98672678
N	-3.46557297	4.54097328	1.39561711
H	-2.91923848	4.65326695	2.25569864
H	-4.40187426	4.19304474	1.63499071
H	-3.55790134	5.50555382	1.04414358
N	-1.87106352	1.78009957	1.39145239
H	-2.06079288	0.83230381	1.03153887
N	-1.45279759	2.08827562	-1.52625442
H	-0.42563823	2.19701461	-1.52100055
H	-1.79949104	2.29232037	-2.46704647
H	-1.64925149	1.09182204	-1.34865312
S	-1.96673129	-1.82365033	-0.13329355
O	-1.02923264	-2.33507186	-1.20431492
C	-3.48091345	-2.77252680	-0.27094020
C	-5.64123828	-3.10811535	-1.27694688
H	-6.41955116	-2.78409254	-1.96902854
C	-4.47399368	-2.35392685	-1.15861358
H	-4.33545954	-1.44363021	-1.73947603
H	0.85081705	-1.84534352	-1.52436944
H	2.31705161	-1.87078024	-2.30780460
C	-5.83339273	-4.27171873	-0.51616404
C	-7.11846370	-5.05947992	-0.61487241
H	-7.83384958	-4.73702704	0.15848363
H	-6.94424478	-6.13519970	-0.47153832
H	-7.60338658	-4.91947197	-1.59045245
C	5.83339273	4.27171873	0.51616404
C	7.11846370	5.05947992	0.61487241
H	7.83384958	4.73702704	-0.15848363

H	6.94424478	6.13519970	0.47153832
H	7.60338658	4.91947197	1.59045245
S	1.96673129	1.82365033	0.13329355
O	1.02923264	2.33507186	1.20431492
C	3.48091345	2.77252680	0.27094020
C	5.64123828	3.10811535	1.27694688
H	6.41955116	2.78409254	1.96902854
C	4.47399368	2.35392685	1.15861358
H	4.33545954	1.44363021	1.73947603
H	-0.85081705	1.84534352	1.52436944
H	-2.31705161	1.87078024	2.30780460
S	1.46368762	-7.41829768	-1.22710489
O	1.54918540	-8.65134239	-2.01736829
O	2.65073284	-7.15100151	-0.33162695
O	1.15062135	-6.18358461	-2.06066299
O	-1.43353270	-2.05827778	1.23785665
C	0.05534873	-7.52666551	-0.10319331
C	-1.22503376	-7.27689178	-0.60320155
H	-1.35651669	-7.02342980	-1.65401313
C	-2.31977536	-7.33898550	0.25622431
H	-3.31662156	-7.14057756	-0.13801923
C	-0.86540481	-7.89808720	2.09346056
C	0.24161394	-7.84647064	1.24137996
H	1.24378205	-8.05639146	1.61276281
C	-3.63882567	-3.93084540	0.49143827
H	-2.85437030	-4.24386411	1.17801094
Ru	2.46412064	-3.28542834	0.06652210
S	4.54775128	-1.96201706	-0.02586739
O	4.18628737	-2.77891425	1.24923351
O	5.57250795	-2.59901513	-0.90280983
O	0.69402848	-4.19699822	-0.47311848
H	0.79700847	-4.95955746	-1.14244290
H	-0.05742092	-3.59804085	-0.74751644
N	2.53615970	-4.93377309	1.42953973
H	2.58818861	-5.83048097	0.90654643
H	3.33976643	-4.86397104	2.05922449
H	1.67801275	-4.96492979	1.98672678
N	3.46557297	-4.54097328	-1.39561711
H	2.91923848	-4.65326695	-2.25569864
H	4.40187426	-4.19304474	-1.63499071
H	3.55790134	-5.50555382	-1.04414358
N	1.87106352	-1.78009957	-1.39145239
H	2.06079288	-0.83230381	-1.03153887
N	1.45279759	-2.08827562	1.52625442
H	0.42563823	-2.19701461	1.52100055
H	1.79949104	-2.29232037	2.46704647
H	1.64925149	-1.09182204	1.34865312
O	2.34886759	0.39994920	0.39224035
C	-2.15886646	-7.64052854	1.61795677
H	-0.72041099	-8.15014281	3.14543554
C	-3.35077976	-7.66085115	2.54695710
H	-3.14845618	-8.24948566	3.45216493
H	-4.23579452	-8.08954893	2.05503669
H	-3.61692063	-6.64154525	2.87132694
C	-4.81574703	-4.66856808	0.36393239
H	-4.94757764	-5.56903444	0.96464266

2B Dark state:

O	-4.34603667	-0.44121391	-1.76877682
H	-5.08835244	4.45023594	-2.68536309
C	-4.52434534	2.57377236	-1.79028812
H	-4.86623972	1.96367656	-2.62515138
H	-0.77641586	2.89441731	-3.00077466
H	-1.72759422	3.53204669	-1.82450050
N	-2.53257740	-3.05284510	-0.55067442

H	-2.66555035	-4.01985853	-0.87667632
H	-3.38308997	-2.74247419	-0.07059223
H	-2.47057542	-2.46148954	-1.38539709
N	0.12207218	-1.61539981	-0.71117398
H	0.50353205	-2.09135974	-1.53388344
H	-0.59236020	-0.94531681	-1.02738911
H	0.87781893	-1.07321532	-0.27437682
O	-1.48578088	-1.15983031	1.80598925
H	-1.70831378	-1.29617742	2.74212222
H	-2.32715867	-0.80478868	1.36767985
S	-3.51614436	0.22476693	-0.75245627
O	-3.66668923	-0.33135464	0.64336682
C	-3.94419433	1.96378149	-0.67916424
C	-3.50366684	2.72406664	0.40927226
H	-3.05913936	2.23709819	1.27559212
C	-3.62331374	4.10985200	0.36811296
H	-3.24409322	4.70160941	1.19993049
C	-4.17647972	4.75651990	-0.75173831
C	-4.63901303	3.96827687	-1.81567126
C	-4.22841465	6.26409269	-0.79457065
H	-4.80609499	6.66497975	0.05175421
H	-3.21077440	6.67446734	-0.71772392
H	-4.68698423	6.62947321	-1.72343397
Ru	0.74384156	2.99521456	-0.69646472
S	-0.18595116	4.67639305	0.38857839
O	-0.87616158	5.70792667	-0.41370788
O	-0.71871195	4.41924991	1.74165098
N	1.70094113	4.31810981	-2.17783076
H	1.09744477	4.53073828	-2.97735136
H	2.57288694	3.93736687	-2.55763419
H	1.93502182	5.24121409	-1.75871343
N	-1.00610409	2.82619572	-2.00541338
H	-1.43997315	1.90022432	-1.85757943
S	2.16188991	6.99167081	0.45343331
O	1.53127403	5.71787478	1.10035191
O	3.45569555	7.25096756	1.09850188
O	2.15266187	6.85187377	-1.02952084
C	1.03547630	8.32246609	0.86472762
C	1.19832290	8.99578764	2.07507250
H	2.03368104	8.74579371	2.72795061
C	0.28640270	9.99499578	2.42181360
H	0.41011592	10.52610396	3.36673260
C	-0.78109698	10.32698187	1.57585371
C	-0.91071474	9.63684773	0.35972207
H	-1.73284661	9.88636718	-0.31379349
C	-0.01132475	8.63706119	-0.00354362
H	-0.11744337	8.09630646	-0.93965350
C	-1.77325879	11.40472262	1.94732631
H	-1.54507785	11.84630159	2.92666282
H	-2.79705260	11.00237138	1.98959237
H	-1.77413052	12.21612431	1.20345951
O	-2.03867392	0.26035080	-1.11612886
O	2.03867392	-0.26035080	1.11612886
Ru	-0.74384156	-2.99521456	0.69646472
S	0.18595116	-4.67639305	-0.38857839
O	0.87616158	-5.70792667	0.41370788
O	0.71871195	-4.41924991	-1.74165098
N	-1.70094113	-4.31810981	2.17783076
H	-1.09744477	-4.53073828	2.97735136
H	-2.57288694	-3.93736687	2.55763419
H	-1.93502182	-5.24121409	1.75871343
N	1.00610409	-2.82619572	2.00541338
H	1.43997315	-1.90022432	1.85757943
S	-2.16188991	-6.99167081	-0.45343331
O	-1.53127403	-5.71787478	-1.10035191
O	-3.45569555	-7.25096756	-1.09850188

O	-2.15266187	-6.85187377	1.02952084
C	-1.03547630	-8.32246609	-0.86472762
C	-1.19832290	-8.99578764	-2.07507250
H	-2.03368104	-8.74579371	-2.72795061
C	-0.28640270	-9.99499578	-2.42181360
H	-0.41011592	-10.52610396	-3.36673260
C	0.78109698	-10.32698187	-1.57585371
C	0.91071474	-9.63684773	-0.35972207
H	1.73284661	-9.88636718	0.31379349
C	0.01132475	-8.63706119	0.00354362
H	0.11744337	-8.09630646	0.93965350
C	1.77325879	-11.40472262	-1.94732631
H	1.54507785	-11.84630159	-2.92666282
H	2.79705260	-11.00237138	-1.98959237
H	1.77413052	-12.21612431	-1.20345951
N	2.53257740	3.05284510	0.55067442
H	2.66555035	4.01985853	0.87667632
H	3.38308997	2.74247419	0.07059223
H	2.47057542	2.46148954	1.38539709
N	-0.12207218	1.61539981	0.71117398
H	-0.50353205	2.09135974	1.53388344
H	0.59236020	0.94531681	1.02738911
H	-0.87781893	1.07321532	0.27437682
O	1.48578088	1.15983031	-1.80598925
H	1.70831378	1.29617742	-2.74212222
H	2.32715867	0.80478868	-1.36767985
S	3.51614436	-0.22476693	0.75245627
O	3.66668923	0.33135464	-0.64336682
C	3.94419433	-1.96378149	0.67916424
C	3.50366684	-2.72406664	-0.40927226
H	3.05913936	-2.23709819	-1.27559212
C	3.62331374	-4.10985200	-0.36811296
H	3.24409322	-4.70160941	-1.19993049
C	4.17647972	-4.75651990	0.75173831
C	4.63901303	-3.96827687	1.81567126
C	4.22841465	-6.26409269	0.79457065
H	4.80609499	-6.66497975	-0.05175421
H	3.21077440	-6.67446734	0.71772392
H	4.68698423	-6.62947321	1.72343397
H	0.77641586	-2.89441731	3.00077466
H	1.72759422	-3.53204669	1.82450050
O	4.34603667	0.44121391	1.76877682
H	5.08835244	-4.45023594	2.68536309
C	4.52434534	-2.57377236	1.79028812
H	4.86623972	-1.96367656	2.62515138

2B η^2 -(OS)O:

O	-1.69849734	0.46501540	-3.08261875
C	-5.79968979	1.89249743	-2.75535997
H	-6.36809738	2.00955798	-3.67967793
C	-4.49970456	1.38035799	-2.81150974
H	-4.04286016	1.09903598	-3.75917938
H	0.15658780	2.71633712	-0.69496046
H	1.80204212	2.46345667	-0.68059324
H	1.22394698	4.01939388	-0.51484419
S	2.19648900	7.16047156	-0.42829527
O	2.04171092	5.64233700	-0.31647297
O	2.33805057	7.72275092	0.94544812
O	3.18292040	7.57498859	-1.44144247
C	0.57521215	7.68854197	-1.03299425
C	-0.17298160	8.62550996	-0.32400282
C	-1.42686838	9.01545662	-0.80907713
C	-1.94327038	8.47974631	-1.99513574
C	-1.16930822	7.53582702	-2.69219254
H	-1.55534734	7.10377437	-3.61747816

C	0.08167787	7.14221485	-2.22240481
H	0.67562401	6.41161895	-2.77046296
C	-3.28648999	8.91542721	-2.53555944
H	-3.89941698	8.05066567	-2.83159353
H	-3.16718904	9.54883615	-3.42905454
H	-3.85266379	9.49412219	-1.79239587
O	2.73482285	-0.82826092	-1.36992718
H	1.56420191	-7.02174845	-3.30609095
H	3.97631904	-7.15022975	-2.70618000
S	3.58773479	0.01399845	-0.52156909
O	3.64262611	1.46830379	-0.87560674
C	5.25884251	-0.63336771	-0.60791582
C	5.43850602	-2.01541737	-0.71031949
H	4.57022289	-2.66915553	-0.78074438
C	6.73337118	-2.52955239	-0.75009334
H	6.87900567	-3.60768625	-0.84050905
C	7.85384423	-1.68399644	-0.69363177
C	9.25103394	-2.25980550	-0.72037265
H	9.52044637	-2.68658014	0.25908056
H	9.99911676	-1.49315760	-0.96419945
H	9.33784450	-3.06719831	-1.46204548
N	-2.47001958	-3.45330404	-1.03161704
H	-1.91975331	-4.27229937	-1.39369311
H	-3.36126535	-3.44315509	-1.53460658
H	-1.98610019	-2.59604144	-1.32793712
H	-4.48135003	-5.41272172	-0.18966872
N	-1.81981101	-1.65188027	1.56565661
H	-1.64997089	-1.15557994	0.67520241
H	-2.29982893	-0.97568792	2.16944170
O	-4.26781321	-1.96790626	0.37516918
H	-5.04149752	-2.22251096	-0.15781973
H	-3.70084048	-1.36244344	-0.20918105
S	-2.11184324	0.52488136	-1.67671987
O	-2.31173102	-0.83958623	-1.02521771
C	-3.77004834	1.24062137	-1.63214818
C	-4.32336679	1.60921852	-0.40217648
H	-3.72925578	1.52474710	0.50712475
C	-5.62248957	2.11754138	-0.36277646
H	-6.05069191	2.42303827	0.59450735
C	-6.38045156	2.27011159	-1.53652778
C	-7.76492319	2.87500189	-1.49119331
H	-8.39474794	2.50547425	-2.31242947
H	-8.27423753	2.65236540	-0.54257754
H	-7.71521276	3.97148952	-1.58524724
Ru	0.96035442	2.73717222	1.82220562
N	1.35319938	4.81753112	2.17122729
H	1.69979283	5.24989685	1.27440498
H	0.49982359	5.33951812	2.39476260
N	1.04051146	3.02913476	-0.27026841
H	-0.07568813	0.69739663	0.50899421
H	0.23065246	9.04094132	0.59814893
H	-2.01067264	9.75228936	-0.25368135
S	-1.24654945	2.68591999	2.84382781
O	-1.06298653	3.32260007	1.44702709
O	-1.86218227	1.31572223	2.86981033
O	-1.28638576	1.37077860	-0.76209387
Ru	-2.85636843	-3.48087970	1.04510867
N	-3.73012478	-5.40469621	0.50635055
H	-4.07938156	-5.91976248	1.31960274
H	-2.96326100	-6.00937369	0.11487174
N	-3.75110594	-3.35127596	3.04282534
H	-0.90804625	-1.86965168	1.98506048
S	-0.80908333	-6.74197720	-1.70581054
O	-0.89780048	-5.25180523	-1.89994033
O	-1.12640316	-7.53713819	-2.90654247
O	-1.62005021	-7.12426793	-0.47490645

C	0.91037581	-7.01968257	-1.25295460
C	1.87334274	-7.05472795	-2.26246093
C	3.22339205	-7.12703161	-1.91676552
C	3.62980344	-7.16103154	-0.57402304
C	2.64094997	-7.14531981	0.42081865
H	2.93592466	-7.19078047	1.47103880
C	1.28610512	-7.07192222	0.09052844
H	0.51800769	-7.06832619	0.86225976
C	5.09567597	-7.18113539	-0.20618101
H	5.46639991	-6.15949750	-0.02304806
H	5.27449412	-7.76209666	0.71002025
H	5.70802953	-7.61404188	-1.00933643
S	-0.52697753	-4.38672488	1.16285393
O	-1.64204460	-4.80402741	2.17486085
O	0.41091505	-3.39320876	1.74633258
N	1.53710638	2.34488827	3.92038407
H	1.29615346	3.08704147	4.58260316
H	2.56029233	2.29335604	3.85893005
H	1.20481462	1.46093867	4.31562607
H	2.04652134	5.06127855	2.88456506
N	0.53469532	0.68261432	1.34209341
H	0.00925658	0.21237585	2.07975258
H	1.38609336	0.13327871	1.13413106
O	3.02922081	2.35223302	1.72628618
H	3.44000057	2.81965881	0.96782879
H	3.17885159	1.34885325	1.47662193
O	3.20447146	-0.07306747	0.97538105
C	7.64217439	-0.30123632	-0.60495938
H	8.49936497	0.37344583	-0.58178767
C	6.35098191	0.23107791	-0.55998302
H	6.18660355	1.30647427	-0.51552247
H	-4.12204371	-2.41884648	3.24652123
H	-4.50933047	-4.02017509	3.20264712
H	-3.01537047	-3.56703697	3.72235453

2B η^1 -OSO:

O	-1.59810470	0.72673750	-3.01920313
C	-5.60054197	2.38203233	-2.81168725
H	-6.02841439	2.76582564	-3.73937651
C	-4.29628218	1.87967510	-2.81768179
H	-3.70106878	1.86098018	-3.72924531
H	0.32965045	2.77718947	-0.76079111
H	1.95849803	2.47237101	-0.69607516
H	1.42311668	4.04060084	-0.54066790
S	2.40030293	7.19377962	-0.38718010
O	2.21859255	5.68214154	-0.28284272
O	2.55138011	7.75884351	0.98416928
O	3.39047190	7.59851585	-1.40219715
C	0.78115833	7.73582504	-0.99007435
C	-0.07603659	8.46237801	-0.16690377
C	-1.34702305	8.81664438	-0.63504776
C	-1.77491954	8.44889920	-1.91645843
C	-0.88851971	7.72409072	-2.73194484
H	-1.19942529	7.43601334	-3.73825621
C	0.38063546	7.36989559	-2.27950252
H	1.06461332	6.81329386	-2.91921019
C	-3.15499604	8.80934784	-2.41872239
H	-3.65764135	9.51710180	-1.74464338
H	-3.79401013	7.91541154	-2.50162805
H	-3.11076267	9.26854716	-3.41776146
O	2.72805943	-0.96910193	-1.27464357
H	1.74023723	-5.18754117	-1.59347409
H	3.99632704	-6.08334833	-1.03976526
S	3.57162435	-0.07415402	-0.46725260
O	3.59924365	1.36307834	-0.88031244

C	5.25806124	-0.69091947	-0.56383104
C	5.50025548	-1.92786964	-1.15742338
H	4.66868196	-2.49117859	-1.57690991
C	6.81064186	-2.41159876	-1.21896078
H	7.00233452	-3.37644618	-1.69146913
C	7.88087926	-1.67495895	-0.69630716
C	9.30086310	-2.18556865	-0.78054370
H	9.79124876	-2.16859027	0.20449493
H	9.90601489	-1.55995316	-1.45508126
H	9.33743548	-3.21606205	-1.15921515
N	-2.91547864	-3.24228808	-1.21426499
H	-2.15500673	-3.87988672	-1.49267432
H	-3.71608415	-3.45970792	-1.81514046
H	-2.60373593	-2.28731702	-1.45322839
H	-4.81013862	-5.39121620	-0.57818008
N	-2.28646164	-1.66943458	1.49779154
H	-2.06818056	-1.11891454	0.64700817
H	-2.74206926	-1.01944058	2.14654464
O	-4.97232030	-1.95817956	0.40026839
H	-5.74130663	-2.22797122	-0.13129234
H	-4.51303795	-1.26395731	-0.12174338
S	-2.05977301	0.72634839	-1.62727713
O	-2.22605958	-0.65156069	-1.01276775
C	-3.74604072	1.38697038	-1.63528592
C	-4.49265853	1.39517174	-0.45369627
H	-4.04663009	1.02897991	0.46985604
C	-5.79333321	1.90197604	-0.45996437
H	-6.37003776	1.92111739	0.46753602
C	-6.36797872	2.40581882	-1.63846756
C	-7.76179383	2.99033613	-1.64028502
H	-8.32084426	2.69406272	-2.53948214
H	-8.33731463	2.67018519	-0.76049618
H	-7.72568901	4.09120452	-1.62844115
Ru	1.04711169	2.73218087	1.78933006
N	1.57291208	4.77861846	2.19003835
H	1.87726995	5.24396360	1.29858207
H	0.78588654	5.33885281	2.53097657
N	1.20494649	3.05925871	-0.30137790
H	-0.03293526	0.69194394	0.47441143
H	0.26230360	8.75285267	0.82674935
H	-2.01397708	9.39411192	0.00869785
S	-2.22585792	2.66610889	2.04004537
O	-2.18898190	1.26884796	2.58914831
O	-0.85936790	3.29383837	1.77383408
O	-1.30187688	1.59932909	-0.67030137
Ru	-3.36064516	-3.44724801	0.87849584
N	-4.19941923	-5.39399496	0.24425561
H	-4.70347761	-5.92036444	0.96356164
H	-3.37606175	-5.97530813	-0.01669100
N	-3.90505822	-3.72517793	3.00006021
H	-1.38158117	-1.92535059	1.89848213
S	-0.88058523	-6.40119772	-1.61043367
O	-0.75566025	-4.91660475	-1.34623549
O	-1.18217993	-6.73487515	-3.01478956
O	-1.83110172	-7.01055385	-0.60025008
C	0.74506329	-7.05689872	-1.19023644
C	1.86295539	-6.22453359	-1.28403652
C	3.12427564	-6.73609207	-0.97177883
C	3.28876689	-8.07096541	-0.57401603
C	2.14869389	-8.88560406	-0.48852877
H	2.25519552	-9.92581613	-0.17508476
C	0.88069384	-8.38872000	-0.79461949
H	-0.00229376	-9.02110165	-0.71389235
C	4.66247801	-8.62722606	-0.27711552
H	5.34421172	-7.84536787	0.08629951
H	4.62143122	-9.42348177	0.47982324

H	5.11426831	-9.06030114	-1.18404734
S	-0.26694183	-4.53006594	0.89631702
O	0.18277544	-3.13986048	0.75535273
O	-1.71378887	-4.67141975	1.32553833
N	1.09899608	2.27728319	3.93224757
H	0.79630625	3.04711386	4.53556926
H	2.07881154	2.07689950	4.15898080
H	0.54566552	1.45624833	4.19149129
H	2.34152303	4.91541625	2.85329752
N	0.51527935	0.68459390	1.34626340
H	-0.09383268	0.26554890	2.05107881
H	1.34241536	0.08270017	1.20810949
O	3.11104879	2.28868561	1.84535430
H	3.57021900	2.77235646	1.12939773
H	3.24087575	1.29842931	1.58072915
O	3.21229632	-0.12939497	1.03186905
C	7.60852470	-0.42843256	-0.10648457
H	8.43102245	0.16514002	0.29672111
C	6.30843982	0.06709695	-0.03938232
H	6.10936254	1.04304035	0.40103405
H	-3.75962431	-2.88229408	3.56387922
H	-4.87525796	-4.01195590	3.15459000
H	-3.30472122	-4.45560974	3.39642969

PW-DFT optimized geometries are presented below.

Experimental unit cell parameters were used for all structures of the five complexes.^{15,16,26} The geometries of the PW structures are given in crystal coordinates.

1A Dark state:

Ru	0.085601342	0.750000000	0.779324490
Cl	0.003602596	0.750000000	0.006700257
Cl	0.149378399	0.250000000	0.565158153
S	0.166197808	0.750000000	0.590385193
N	0.174388450	0.957468390	0.869909511
H	0.232077577	0.904743580	0.927362812
H	0.135161895	0.038420915	0.940308617
H	0.201137930	0.045720072	0.792528804
N	0.987742538	0.952862986	0.707716621
H	0.938765795	0.904544078	0.632643926
H	0.022448031	0.063923592	0.660771125
H	0.949972177	1.003934256	0.794684659
O	0.271926604	0.750000000	0.597689643
O	0.128536639	0.750000000	0.442235928
Ru	0.414398658	0.250000000	0.279324490
Ru	0.914398658	0.250000000	0.220675510
Ru	0.585601342	0.750000000	0.720675510
Cl	0.496397404	0.250000000	0.506700257
Cl	0.996397404	0.250000000	0.993299743
Cl	0.503602596	0.750000000	0.493299743
Cl	0.350621601	0.750000000	0.065158153
Cl	0.850621601	0.750000000	0.434841847
Cl	0.649378399	0.250000000	0.934841847
S	0.333802192	0.250000000	0.090385193
S	0.833802192	0.250000000	0.409614807
S	0.666197808	0.750000000	0.909614807
N	0.325611550	0.042531610	0.369909511
N	0.825611550	0.457468390	0.130090489
N	0.674388450	0.542531610	0.630090489
N	0.825611550	0.042531610	0.130090489
N	0.674388450	0.957468390	0.630090489
N	0.174388450	0.542531610	0.869909511
N	0.325611550	0.457468390	0.369909511
H	0.267922423	0.095256420	0.427362812

H	0.767922423	0.404743580	0.072637188
H	0.732077577	0.595256420	0.572637188
H	0.767922423	0.095256420	0.072637188
H	0.732077577	0.904743580	0.572637188
H	0.232077577	0.595256420	0.927362812
H	0.267922423	0.404743580	0.427362812
H	0.364838105	0.961579085	0.440308617
H	0.864838105	0.538420915	0.059691383
H	0.635161895	0.461579085	0.559691383
H	0.864838105	0.961579085	0.059691383
H	0.635161895	0.038420915	0.559691383
H	0.135161895	0.461579085	0.940308617
H	0.364838105	0.538420915	0.440308617
H	0.298862070	0.954279928	0.292528804
H	0.798862070	0.545720072	0.207471196
H	0.701137930	0.454279928	0.707471196
H	0.798862070	0.954279928	0.207471196
H	0.701137930	0.045720072	0.707471196
H	0.201137930	0.454279928	0.792528804
H	0.298862070	0.545720072	0.292528804
N	0.512257462	0.047137014	0.207716621
N	0.012257462	0.452862986	0.292283379
N	0.487742538	0.547137014	0.792283379
N	0.012257462	0.047137014	0.292283379
N	0.487742538	0.952862986	0.792283379
N	0.987742538	0.547137014	0.707716621
N	0.512257462	0.452862986	0.207716621
H	0.561234205	0.095455922	0.132643926
H	0.061234205	0.404544078	0.367356074
H	0.438765795	0.595455922	0.867356074
H	0.061234205	0.095455922	0.367356074
H	0.438765795	0.904544078	0.867356074
H	0.938765795	0.595455922	0.632643926
H	0.561234205	0.404544078	0.132643926
H	0.477551969	0.936076408	0.160771125
H	0.977551969	0.563923592	0.339228875
H	0.522448031	0.436076408	0.839228875
H	0.977551969	0.936076408	0.339228875
H	0.522448031	0.063923592	0.839228875
H	0.022448031	0.436076408	0.660771125
H	0.477551969	0.563923592	0.160771125
H	0.550027823	-0.003934256	0.294684659
H	0.050027823	0.503934256	0.205315341
H	0.449972177	0.496065744	0.705315341
H	0.050027823	-0.003934256	0.205315341
H	0.449972177	1.003934256	0.705315341
H	0.949972177	0.496065744	0.794684659
H	0.550027823	0.503934256	0.294684659
O	0.228073396	0.250000000	0.097689643
O	0.728073396	0.250000000	0.402310357
O	0.771926604	0.750000000	0.902310357
O	0.371463361	0.250000000	0.942235928
O	0.871463361	0.250000000	0.557764072
O	0.628536639	0.750000000	0.057764072

1A η^2 -(OS)O:

Cl	0.150418279	0.237292446	0.550650569
Ru	0.082639358	0.754090639	0.769556822
Cl	0.009894599	0.752086509	1.000615982
S	0.212412901	0.781807154	0.614538164
O	0.115992789	0.719337785	0.546509851
O	0.286562543	0.636789927	0.627500967
N	0.162951437	0.973554094	0.867166902
H	0.117801730	0.038581077	0.940227196
H	0.183083658	0.069857283	0.790831951

H	0.223388994	0.928092401	0.922838022
N	0.991022373	0.964791976	0.694781254
H	0.958628917	1.031423372	0.780492654
H	0.938005203	0.915521881	0.625508890
H	0.030663243	0.061749729	0.637488511
Cl	0.349581721	0.762707554	0.050650569
Cl	0.849581721	0.762707554	0.449349431
Cl	0.650418279	0.237292446	0.949349431
Ru	0.417360642	0.245909361	0.269556822
Ru	0.917360642	0.245909361	0.230443178
Ru	0.582639358	0.754090639	0.730443178
Cl	0.490105401	0.247913491	0.500615982
Cl	0.990105401	0.247913491	-0.000615982
Cl	0.509894599	0.752086509	0.499384018
S	0.287587099	0.218192846	0.114538164
S	0.787587099	0.218192846	0.385461836
S	0.712412901	0.781807154	0.885461836
O	0.384007211	0.280662215	0.046509851
O	0.884007211	0.280662215	0.453490149
O	0.615992789	0.719337785	0.953490149
O	0.213437457	0.363210073	0.127500967
O	0.713437457	0.363210073	0.372499033
O	0.786562543	0.636789927	0.872499033
N	0.337048563	0.026445906	0.367166902
N	0.835295197	0.467466709	0.149358523
N	0.664704803	0.532533291	0.649358523
N	0.837048563	0.026445906	0.132833098
N	0.662951437	0.973554094	0.632833098
N	0.164704803	0.532533291	0.850641477
N	0.335295197	0.467466709	0.350641477
H	0.382198270	0.961418923	0.440227196
H	0.875704523	0.543347280	0.077030040
H	0.624295477	0.456652720	0.577030040
H	0.882198270	0.961418923	0.059772804
H	0.617801730	0.038581077	0.559772804
H	0.124295477	0.456652720	0.922969960
H	0.375704523	0.543347280	0.422969960
H	0.316916342	0.930142717	0.290831951
H	0.813538317	0.551560339	0.233399410
H	0.686461683	0.448439661	0.733399410
H	0.816916342	0.930142717	0.209168049
H	0.683083658	0.069857283	0.709168049
H	0.186461683	0.448439661	0.766600590
H	0.313538317	0.551560339	0.266600590
H	0.276611006	0.071907599	0.422838022
H	0.774528397	0.425905111	0.093437080
H	0.725471603	0.574094889	0.593437080
H	0.776611006	0.071907599	0.077161978
H	0.723388994	0.928092401	0.577161978
H	0.225471603	0.574094889	0.906562920
H	0.274528397	0.425905111	0.406562920
N	0.508977627	0.035208024	0.194781254
N	0.016668280	0.448394232	0.294611844
N	0.483331720	0.551605768	0.794611844
N	0.008977627	0.035208024	0.305218746
N	0.491022373	0.964791976	0.805218746
N	0.983331720	0.551605768	0.705388156
N	0.516668280	0.448394232	0.205388156
H	0.541371083	-0.031423372	0.280492654
H	0.058000477	0.490732538	0.207946322
H	0.441999523	0.509267462	0.707946322
H	0.041371083	-0.031423372	0.219507346
H	0.458628917	1.031423372	0.719507346
H	0.941999523	0.509267462	0.792053678
H	0.558000477	0.490732538	0.292053678
H	0.561994797	0.084478119	0.125508890

H	0.062644208	0.400327586	0.374985290
H	0.437355792	0.599672414	0.874985290
H	0.061994797	0.084478119	0.374491110
H	0.438005203	0.915521881	0.874491110
H	0.937355792	0.599672414	0.625014710
H	0.562644208	0.400327586	0.125014710
H	0.469336757	0.938250271	0.137488511
H	0.980263357	0.559683102	0.337017183
H	0.519736643	0.440316898	0.837017183
H	0.969336757	0.938250271	0.362511489
H	0.530663243	0.061749729	0.862511489
H	0.019736643	0.440316898	0.662982817
H	0.480263357	0.559683102	0.162982817

1B Dark state:

Ru	0.085836983	0.250000000	0.221722208
Cl	0.003333346	0.250000000	0.993364449
Cl	0.851143252	0.250000000	0.564926908
S	0.165017439	0.250000000	0.412886903
O	0.270925770	0.250000000	0.409802285
O	0.124688778	0.250000000	0.560101829
N	0.173526252	0.045077704	0.129414202
H	0.132743587	0.965875920	0.060163253
H	0.230572775	0.096520726	0.069777498
H	0.201181579	-0.042648293	0.205675134
N	0.988248582	0.049901892	0.293704822
H	0.939858877	0.097870973	0.370007333
H	0.022579761	0.939035067	0.339332062
H	0.949751690	0.001821949	0.206303294
Ru	0.414163017	0.750000000	0.721722208
Ru	0.914163017	0.750000000	0.778277792
Ru	0.585836983	0.250000000	0.278277792
Cl	0.496666654	0.750000000	0.493364449
Cl	0.996666654	0.750000000	0.006635551
Cl	0.503333346	0.250000000	0.506635551
Cl	0.648856748	0.750000000	0.064926908
Cl	0.148856748	0.750000000	0.435073092
Cl	0.351143252	0.250000000	0.935073092
S	0.334982561	0.750000000	0.912886903
S	0.834982561	0.750000000	0.587113097
S	0.665017439	0.250000000	0.087113097
O	0.229074230	0.750000000	0.909802285
O	0.729074230	0.750000000	0.590197715
O	0.770925770	0.250000000	0.090197715
O	0.375311222	0.750000000	0.060101829
O	0.875311222	0.750000000	0.439898171
O	0.624688778	0.250000000	0.939898171
N	0.326473748	0.954922296	0.629414202
N	0.826473748	0.545077704	0.870585798
N	0.673526252	0.454922296	0.370585798
N	0.826473748	0.954922296	0.870585798
N	0.673526252	0.045077704	0.370585798
N	0.173526252	0.454922296	0.129414202
N	0.326473748	0.545077704	0.629414202
H	0.367256413	0.034124080	0.560163253
H	0.867256413	0.465875920	0.939836747
H	0.632743587	0.534124080	0.439836747
H	0.867256413	0.034124080	0.939836747
H	0.632743587	0.965875920	0.439836747
H	0.132743587	0.534124080	0.060163253
H	0.367256413	0.465875920	0.560163253
H	0.269427225	0.903479274	0.569777498
H	0.769427225	0.596520726	0.930222502
H	0.730572775	0.403479274	0.430222502
H	0.769427225	0.903479274	0.930222502

H	0.730572775	0.096520726	0.430222502
H	0.230572775	0.403479274	0.069777498
H	0.269427225	0.596520726	0.569777498
H	0.298818421	1.042648293	0.705675134
H	0.798818421	0.457351707	0.794324866
H	0.701181579	0.542648293	0.294324866
H	0.798818421	1.042648293	0.794324866
H	0.701181579	-0.042648293	0.294324866
H	0.201181579	0.542648293	0.205675134
H	0.298818421	0.457351707	0.705675134
N	0.511751418	0.950098108	0.793704822
N	0.011751418	0.549901892	0.706295178
N	0.488248582	0.450098108	0.206295178
N	0.011751418	0.950098108	0.706295178
N	0.488248582	0.049901892	0.206295178
N	0.988248582	0.450098108	0.293704822
N	0.511751418	0.549901892	0.793704822
H	0.560141123	0.902129027	0.870007333
H	0.060141123	0.597870973	0.629992667
H	0.439858877	0.402129027	0.129992667
H	0.060141123	0.902129027	0.629992667
H	0.439858877	0.097870973	0.129992667
H	0.939858877	0.402129027	0.370007333
H	0.560141123	0.597870973	0.870007333
H	0.477420239	0.060964933	0.839332062
H	0.977420239	0.439035067	0.660667938
H	0.522579761	0.560964933	0.160667938
H	0.977420239	0.060964933	0.660667938
H	0.522579761	0.939035067	0.160667938
H	0.022579761	0.560964933	0.339332062
H	0.477420239	0.439035067	0.839332062
H	0.550248310	0.998178051	0.706303294
H	0.050248310	0.501821949	0.793696706
H	0.449751690	0.498178051	0.293696706
H	0.050248310	0.998178051	0.793696706
H	0.449751690	0.001821949	0.293696706
H	0.949751690	0.498178051	0.206303294
H	0.550248310	0.501821949	0.706303294

1B η^2 -(OS)O:

Ru	0.067500000	0.250000000	0.213800000
Cl	0.984600000	0.250000000	0.989000000
Cl	0.843705508	0.250000000	0.596726057
S	0.216800000	0.250000000	0.378100000
O	0.238300000	0.250000000	0.213600000
O	0.147000000	0.250000000	0.461000000
N	0.140712308	0.034729110	0.106364819
H	0.095656649	0.965661335	0.036739627
H	0.199120202	0.082956384	0.049133793
H	0.165392460	-0.060910424	0.179457496
N	0.983554580	0.043756556	0.312117908
H	0.935652732	0.093385322	0.388385603
H	0.026269154	0.944829852	0.360015166
H	0.943874120	-0.022159439	0.233937076
Ru	0.432500000	0.750000000	0.713800000
Ru	0.932500000	0.750000000	0.786200000
Ru	0.567500000	0.250000000	0.286200000
Cl	0.515400000	0.750000000	0.489000000
Cl	0.015400000	0.750000000	0.011000000
Cl	0.484600000	0.250000000	0.511000000
Cl	0.656294492	0.750000000	0.096726057
Cl	0.156294492	0.750000000	0.403273943
Cl	0.343705508	0.250000000	0.903273943
S	0.283200000	0.750000000	0.878100000
S	0.783200000	0.750000000	0.621900000

S	0.716800000	0.250000000	0.121900000
O	0.261700000	0.750000000	0.713600000
O	0.761700000	0.750000000	0.786400000
O	0.738300000	0.250000000	0.286400000
O	0.353000000	0.750000000	0.961000000
O	0.853000000	0.750000000	0.539000000
O	0.647000000	0.250000000	0.039000000
N	0.359287692	0.965270890	0.606364819
N	0.859287692	0.534729110	0.893635181
N	0.640712308	0.465270890	0.393635181
N	0.859287692	0.965270890	0.893635181
N	0.640712308	0.034729110	0.393635181
N	0.140712308	0.465270890	0.106364819
N	0.359287692	0.534729110	0.606364819
H	0.404343351	0.034338665	0.536739627
H	0.904343351	0.465661335	0.963260373
H	0.595656649	0.534338665	0.463260373
H	0.904343351	0.034338665	0.963260373
H	0.595656649	0.965661335	0.463260373
H	0.095656649	0.534338665	0.036739627
H	0.404343351	0.465661335	0.536739627
H	0.300879798	0.917043616	0.549133793
H	0.800879798	0.582956384	0.950866207
H	0.699120202	0.417043616	0.450866207
H	0.800879798	0.917043616	0.950866207
H	0.699120202	0.082956384	0.450866207
H	0.199120202	0.417043616	0.049133793
H	0.300879798	0.582956384	0.549133793
H	0.334607540	1.060910424	0.679457496
H	0.834607540	0.439089576	0.820542504
H	0.665392460	0.560910424	0.320542504
H	0.834607540	1.060910424	0.820542504
H	0.665392460	-0.060910424	0.320542504
H	0.165392460	0.560910424	0.179457496
H	0.334607540	0.439089576	0.679457496
N	0.516445420	0.956243444	0.812117908
N	0.016445420	0.543756556	0.687882092
N	0.483554580	0.456243444	0.187882092
N	0.016445420	0.956243444	0.687882092
N	0.483554580	0.043756556	0.187882092
N	0.983554580	0.456243444	0.312117908
N	0.516445420	0.543756556	0.812117908
H	0.564347268	0.906614678	0.888385603
H	0.064347268	0.593385322	0.611614397
H	0.435652732	0.406614678	0.111614397
H	0.064347268	0.906614678	0.611614397
H	0.435652732	0.093385322	0.111614397
H	0.935652732	0.406614678	0.388385603
H	0.564347268	0.593385322	0.888385603
H	0.473730846	0.055170148	0.860015166
H	0.973730846	0.444829852	0.639984834
H	0.526269154	0.555170148	0.139984834
H	0.973730846	0.055170148	0.639984834
H	0.526269154	0.944829852	0.139984834
H	0.026269154	0.555170148	0.360015166
H	0.473730846	0.444829852	0.860015166
H	0.556125880	1.022159439	0.733937076
H	0.056125880	0.477840561	0.766062924
H	0.443874120	0.522159439	0.266062924
H	0.056125880	1.022159439	0.766062924
H	0.443874120	-0.022159439	0.266062924
H	0.943874120	0.522159439	0.233937076
H	0.556125880	0.477840561	0.733937076

1B η^1 -OSO:

Ru	0.060987740	0.250000000	0.219857925
Cl	0.000799199	0.250000000	-0.016626977
Cl	0.844232250	0.250000000	0.558756323
S	0.213333186	0.250000000	0.475643013
O	0.110247659	0.250000000	0.416684180
O	0.288859383	0.250000000	0.362155007
N	0.157688322	0.046339320	0.154569806
H	0.123248115	0.962075404	0.081093589
H	0.218836228	0.097756294	0.105499050
H	0.178111070	-0.034603388	0.241091100
N	0.963428808	0.046677899	0.286638655
H	0.913882776	0.096444882	0.360695541
H	-0.000159686	0.941213125	0.335943374
H	0.927353566	-0.006270143	0.198852361
Ru	0.439012260	0.750000000	0.719857925
Ru	0.939012260	0.750000000	0.780142075
Ru	0.560987740	0.250000000	0.280142075
Cl	0.499200801	0.750000000	0.483373023
Cl	0.999200801	0.750000000	1.016626977
Cl	0.500799199	0.250000000	0.516626977
Cl	0.655767750	0.750000000	0.058756323
Cl	0.155767750	0.750000000	0.441243677
Cl	0.344232250	0.250000000	0.941243677
S	0.286666814	0.750000000	0.975643013
S	0.786666814	0.750000000	0.524356987
S	0.713333186	0.250000000	0.024356987
O	0.389752341	0.750000000	0.916684180
O	0.889752341	0.750000000	0.583315820
O	0.610247659	0.250000000	0.083315820
O	0.211140617	0.750000000	0.862155007
O	0.711140617	0.750000000	0.637844993
O	0.788859383	0.250000000	0.137844993
N	0.342311678	0.953660680	0.654569806
N	0.842311678	0.546339320	0.845430194
N	0.657688322	0.453660680	0.345430194
N	0.842311678	0.953660680	0.845430194
N	0.657688322	0.046339320	0.345430194
N	0.157688322	0.453660680	0.154569806
N	0.342311678	0.546339320	0.654569806
H	0.376751885	0.037924596	0.581093589
H	0.876751885	0.462075404	0.918906411
H	0.623248115	0.537924596	0.418906411
H	0.876751885	0.037924596	0.918906411
H	0.623248115	0.962075404	0.418906411
H	0.123248115	0.537924596	0.081093589
H	0.376751885	0.462075404	0.581093589
H	0.281163772	0.902243706	0.605499050
H	0.781163772	0.597756294	0.894500950
H	0.718836228	0.402243706	0.394500950
H	0.781163772	0.902243706	0.894500950
H	0.718836228	0.097756294	0.394500950
H	0.218836228	0.402243706	0.105499050
H	0.281163772	0.597756294	0.605499050
H	0.321888930	1.034603388	0.741091100
H	0.821888930	0.465396612	0.758908900
H	0.678111070	0.534603388	0.258908900
H	0.821888930	1.034603388	0.758908900
H	0.678111070	-0.034603388	0.258908900
H	0.178111070	0.534603388	0.241091100
H	0.321888930	0.465396612	0.741091100
N	0.536571192	0.953322101	0.786638655
N	0.036571192	0.546677899	0.713361345
N	0.463428808	0.453322101	0.213361345
N	0.036571192	0.953322101	0.713361345
N	0.463428808	0.046677899	0.213361345
N	0.963428808	0.453322101	0.286638655

N	0.536571192	0.546677899	0.786638655
H	0.586117224	0.903555118	0.860695541
H	0.086117224	0.596444882	0.639304459
H	0.413882776	0.403555118	0.139304459
H	0.086117224	0.903555118	0.639304459
H	0.413882776	0.096444882	0.139304459
H	0.913882776	0.403555118	0.360695541
H	0.586117224	0.596444882	0.860695541
H	0.500159686	0.058786875	0.835943374
H	1.000159686	0.441213125	0.664056626
H	0.499840314	0.558786875	0.164056626
H	1.000159686	0.058786875	0.664056626
H	0.499840314	0.941213125	0.164056626
H	-0.000159686	0.558786875	0.335943374
H	0.500159686	0.441213125	0.835943374
H	0.572646434	1.006270143	0.698852361
H	0.072646434	0.493729857	0.801147639
H	0.427353566	0.506270143	0.301147639
H	0.072646434	1.006270143	0.801147639
H	0.427353566	-0.006270143	0.301147639
H	0.927353566	0.506270143	0.198852361
H	0.572646434	0.493729857	0.698852361

2A Dark state:

Ru	0.311520259	0.493345034	0.244760284
Ru	0.688479741	0.506654966	0.755239716
S	0.398764052	0.356007574	0.199426719
S	0.601235948	0.643992426	0.800573281
O	0.299526660	0.252796208	0.230464511
O	0.700473340	0.747203792	0.769535489
O	0.561322347	0.354510846	0.131597505
O	0.438677653	0.645489154	0.868402495
O	0.232946895	0.636812124	0.288879482
O	0.767053105	0.363187876	0.711120518
H	0.113505045	0.649241328	0.247516581
H	0.886494955	0.350758672	0.752483419
H	0.198424008	0.642163146	0.359872187
H	0.801575992	0.357836854	0.640127813
N	0.599705699	0.569337358	0.319344238
N	0.400294301	0.430662642	0.680655762
H	0.577755719	0.617366811	0.379711304
H	0.422244281	0.382633189	0.620288696
H	0.697391418	0.614298463	0.274263613
H	0.302608582	0.385701537	0.725736387
H	0.671670195	0.513601355	0.344641522
H	0.328329805	0.486398645	0.655358478
N	0.201806533	0.434900225	0.376951311
N	0.798193467	0.565099775	0.623048689
H	0.296960835	0.394076050	0.410909305
H	0.703039165	0.605923950	0.589090695
H	0.056453640	0.385684339	0.365228382
H	0.943546360	0.614315661	0.634771618
H	0.184891296	0.495481187	0.426658142
H	0.815108704	0.504518813	0.573341858
N	0.009894726	0.439238175	0.177819341
N	0.990105274	0.560761825	0.822180659
H	0.907602748	0.389302093	0.216985609
H	0.092397252	0.610697907	0.783014391
H	0.014181521	0.400292561	0.109226699
H	0.985818479	0.599707439	0.890773301
H	0.944930919	0.502109941	0.166948680
H	0.055069081	0.497890059	0.833051320
N	0.406439080	0.562078369	0.114080773
N	0.593560920	0.437921631	0.885919227
H	0.354204732	0.507266583	0.054326152

H	0.645795268	0.492733417	0.945673848
H	0.564051040	0.586501861	0.112222470
H	0.435948960	0.413498139	0.887777530
H	0.344058725	0.626162709	0.103029798
H	0.655941275	0.373837291	0.896970202
S	0.320804370	0.677663643	0.552873372
S	0.679195630	0.322336357	0.447126628
O	0.271101534	0.624638365	0.643421999
O	0.728898466	0.375361635	0.356578001
O	0.522521376	0.670138613	0.518668312
O	0.477478624	0.329861387	0.481331688
O	0.150986254	0.637873877	0.474814249
O	0.849013746	0.362126123	0.525185751
C	0.328198527	0.812522004	0.581261383
C	0.671801473	0.187477996	0.418738617
C	0.144490978	0.846170148	0.573650090
C	0.855509022	0.153829852	0.426349910
H	-0.000078417	0.789984890	0.546400679
H	1.000078417	0.210015110	0.453599321
C	0.148790921	0.951566477	0.600376544
C	0.851209079	0.048433523	0.399623456
H	0.005540358	0.978443381	0.594431034
H	0.994459642	0.021556619	0.405568966
C	0.333797619	0.024437144	0.634457856
C	0.666202381	0.975562856	0.365542144
C	0.515123170	0.988372466	0.641251416
C	0.484876830	0.011627534	0.358748584
H	0.660350085	0.044436225	0.667823844
H	0.339649915	0.955563775	0.332176156
C	0.514124556	0.883036506	0.615284359
C	0.485875444	0.116963494	0.384715641
H	0.655387276	0.854860913	0.622575464
H	0.344612724	0.145139087	0.377424536
C	0.335722906	0.137687590	0.662263685
C	0.664277094	0.862312410	0.337736315
H	0.486353975	0.182331535	0.697226552
H	0.513646025	0.817668465	0.302773448
H	0.215829735	0.143518675	0.714066490
H	0.784170265	0.856481325	0.285933510
H	0.303874545	0.176813227	0.596073226
H	0.696125455	0.823186773	0.403926774
S	0.963506843	0.702101501	0.082783515
S	0.036493157	0.297898499	0.917216485
O	0.833037821	0.637131448	1.000025192
O	0.166962179	0.362868552	-0.000025192
O	0.185166934	0.722775348	0.071187430
O	0.814833066	0.277224652	0.928812570
O	0.910689875	0.652749444	0.177248477
O	0.089310125	0.347250556	0.822751523
C	0.896687488	0.824912299	0.093960740
C	0.103312512	0.175087701	0.906039260
C	0.044386565	0.914136528	0.135610334
C	0.955613435	0.085863472	0.864389666
H	0.201594528	0.907724266	0.155443194
H	0.798405472	0.092275734	0.844556806
C	0.989492636	0.010191747	0.150196615
C	0.010507364	0.989808253	0.849803385
H	0.104401862	0.080772746	0.181875567
H	0.895598138	0.919227254	0.818124433
C	0.788070824	0.018520300	0.124369787
C	0.211929176	0.981479700	0.875630213
C	0.643862143	0.927998373	0.081877491
C	0.356137857	0.072001627	0.918122509
H	0.486442796	0.933110356	0.060435316
H	0.513557204	0.066889644	0.939564684
C	0.696337627	0.831270019	0.065772072

C	0.303662373	0.168729981	0.934227928
H	0.582880632	0.762157730	0.030318281
H	0.417119368	0.237842270	0.969681719
C	0.731125907	0.122331322	0.140548194
C	0.268874093	0.877668678	0.859451806
H	0.764941195	0.168988361	0.076342583
H	0.235058805	0.831011639	0.923657417
H	0.820195336	0.169747682	0.205758043
H	0.179804664	0.830252318	0.794241957
H	0.565487428	0.112360093	0.151193682
H	0.434512572	0.887639907	0.848806318

2A η^2 -(OS)O:

S	0.269760279	0.671962037	0.541366817
S	0.730239721	0.328037963	0.458633183
S	0.962411222	0.700300855	0.085647970
S	0.037588778	0.299699145	0.914352030
O	0.208622960	0.616547118	0.628471221
O	0.791377040	0.383452882	0.371528779
O	0.467750924	0.657299755	0.507565950
O	0.532249076	0.342700245	0.492434050
O	0.101159895	0.640762923	0.461489269
O	0.898840105	0.359237077	0.538510731
O	0.818445758	0.632568597	1.009132714
O	0.181554242	0.367431403	-0.009132714
O	0.180226211	0.718893385	0.064854635
O	0.819773789	0.281106615	0.935145365
O	0.928491985	0.656194907	0.182812032
O	0.071508015	0.343805093	0.817187968
C	0.295315707	0.808187774	0.574172000
C	0.704684293	0.191812226	0.425828000
C	0.115009984	0.844759530	0.583531282
C	0.884990016	0.155240470	0.416468718
H	-0.037339144	0.790185875	0.569927712
H	1.037339144	0.209814125	0.430072288
C	0.131605033	0.951042911	0.611480207
C	0.868394967	0.048957089	0.388519793
H	-0.009128910	0.979820726	0.619379963
H	1.009128910	0.020179274	0.380620037
C	0.325612626	0.022151725	0.630485198
C	0.674387374	0.977848275	0.369514802
C	0.503298618	0.983346266	0.620474367
C	0.496701382	0.016653734	0.379525633
H	0.655822189	0.038133553	0.634021907
H	0.344177811	0.961866447	0.365978093
C	0.489942431	0.877140556	0.592477631
C	0.510057569	0.122859444	0.407522369
H	0.628924262	0.847035270	0.586087952
H	0.371075738	0.152964730	0.413912048
C	0.341294219	0.136698619	0.658610617
C	0.658705781	0.863301381	0.341389383
H	0.490519246	0.175126199	0.699380851
H	0.509480754	0.824873801	0.300619149
H	0.214876706	0.147693346	0.704152167
H	0.785123294	0.852306654	0.295847833
H	0.331445700	0.178769994	0.592205535
H	0.668554300	0.821230006	0.407794465
C	0.895710235	0.823271605	0.097768835
C	0.104289765	0.176728395	0.902231165
C	0.041232148	0.911323027	0.143426857
C	0.958767852	0.088676973	0.856573143
H	0.197677216	0.904598319	0.165978547
H	0.802322784	0.095401681	0.834021453
C	-0.015561627	0.006648015	0.159833184
C	1.015561627	0.993351985	0.840166816

H	0.095859314	0.075693678	0.197124654
H	0.904140686	0.924306322	0.802875346
C	0.783954731	0.015792779	0.130882385
C	0.216045269	0.984207221	0.869117615
C	0.641557299	0.926561657	0.084918214
C	0.358442701	0.073438343	0.915081786
H	0.484216859	0.931998716	0.062008599
H	0.515783141	0.068001284	0.937991401
C	0.695741249	0.830314934	0.068057707
C	0.304258751	0.169685066	0.931942293
H	0.583006895	0.761321405	0.032149985
H	0.416993105	0.238678595	0.967850015
C	0.726821850	0.119378638	0.148571104
C	0.273178150	0.880621362	0.851428896
H	0.780684689	0.170600747	0.090131083
H	0.219315311	0.829399253	0.909868917
H	0.799749953	0.160666291	0.219737723
H	0.200250047	0.839333709	0.780262277
H	0.557934898	0.109247607	0.148840816
H	0.442065102	0.890752393	0.851159184
Ru	0.319240608	0.488688513	0.243053426
Ru	0.680759392	0.511311487	0.756946574
S	0.289404581	0.310990913	0.198301715
S	0.710595419	0.689009087	0.801698285
O	0.501811830	0.387248379	0.191825786
O	0.498188170	0.612751621	0.808174214
O	0.277484924	0.245592974	0.281928809
O	0.722515076	0.754407026	0.718071191
O	0.234800438	0.622617148	0.291359942
O	0.765199562	0.377382852	0.708640058
H	0.186037025	0.628644963	0.360758705
H	0.813962975	0.371355037	0.639241295
H	0.127813251	0.643200318	0.247168047
H	0.872186749	0.356799682	0.752831953
N	0.608844649	0.561989074	0.316001667
N	0.391155351	0.438010926	0.683998333
H	0.587614969	0.609569110	0.376443661
H	0.412385031	0.390430890	0.623556339
H	0.679431018	0.504753314	0.339782961
H	0.320568982	0.495246686	0.660217039
H	0.707820104	0.607156966	0.272220815
H	0.292179896	0.392843034	0.727779185
N	0.245307300	0.438417618	0.381552961
N	0.754692700	0.561582382	0.618447039
H	0.315867000	0.495764384	0.436461438
H	0.684133000	0.504235616	0.563538562
H	0.087532605	0.423362046	0.388745216
H	0.912467395	0.576637954	0.611254784
H	0.295571020	0.371534929	0.394547116
H	0.704428980	0.628465071	0.605452884
N	0.004531288	0.441620370	0.181055598
N	0.995468712	0.558379630	0.818944402
H	0.947632095	0.507586589	0.172608295
H	0.052367905	0.492413411	0.827391705
H	-0.006853566	0.400799088	0.112747211
H	1.006853566	0.599200912	0.887252789
H	0.906530023	0.396230921	0.224943643
H	0.093469977	0.603769079	0.775056357
N	0.397333909	0.554215788	0.110502142
N	0.602666091	0.445784212	0.889497858
H	0.336004532	0.618445683	0.099093835
H	0.663995468	0.381554317	0.900906165
H	0.554620261	0.576836949	0.105186936
H	0.445379739	0.423163051	0.894813064
H	0.337847222	0.496829672	0.053470669
H	0.662152778	0.503170328	0.946529331

2B Dark state:

Ru	0.309484291	0.993448434	0.244500403
Ru	0.690515709	0.006551566	0.755499597
S	0.396915831	0.855922032	0.199486836
S	0.603084169	0.144077968	0.800513164
O	0.297789580	0.752770112	0.230814727
O	0.702210420	0.247229888	0.769185273
O	0.560278159	0.854354454	0.131763348
O	0.439721841	0.145645546	0.868236652
N	0.597423861	0.069143342	0.318928848
N	0.402576139	0.930856658	0.681071152
H	0.669056970	0.013394637	0.344763585
H	0.330943030	0.986605363	0.655236415
H	0.576012257	0.117828640	0.378998309
H	0.423987743	0.882171360	0.621001691
H	0.695273886	0.113364494	0.273251182
H	0.304726114	0.886635506	0.726748818
N	0.200231841	0.935058545	0.377182784
N	0.799768159	0.064941455	0.622817216
H	0.055140782	0.885776915	0.365349441
H	0.944859218	0.114223085	0.634650559
H	0.182969596	0.995141509	0.427437853
H	0.817030404	0.004858491	0.572562147
H	0.296192471	0.894152996	0.410609414
H	0.703807529	0.105847004	0.589390586
N	0.007792238	0.939652957	0.177440444
N	0.992207762	0.060347043	0.822559556
H	0.013530576	0.901356802	0.108637839
H	0.986469424	0.098643198	0.891362161
H	0.941637232	1.002303367	0.166830100
H	0.058362768	-0.002303367	0.833169900
H	0.905796216	0.889053964	0.216323212
H	0.094203784	0.110946036	0.783676788
N	0.404326704	0.061322452	0.113007825
N	0.595673296	0.938677548	0.886992175
H	0.561980777	0.085654437	0.111114185
H	0.438019223	0.914345563	0.888885815
H	0.341591168	0.125196536	0.101137646
H	0.658408832	0.874803464	0.898862354
H	0.352521881	0.005914614	0.053686457
H	0.647478119	0.994085386	0.946313543
O	0.233051156	0.137535662	0.288612386
O	0.766948844	0.862464338	0.711387614
H	0.198889552	0.142653470	0.359846535
H	0.801110448	0.857346530	0.640153465
H	0.112774023	0.149748584	0.247596062
H	0.887225977	0.850251416	0.752403938
S	0.962075820	0.201437711	0.082704188
S	0.037924180	0.798562289	0.917295812
O	0.831386111	0.136118072	1.000318808
O	0.168613889	0.863881928	-0.000318808
O	0.183662954	0.222070700	0.070411691
O	0.816337046	0.777929300	0.929588309
O	0.910046373	0.152356082	0.177588608
O	0.089953627	0.847643918	0.822411392
C	0.894591678	0.324181337	0.093626786
C	0.105408322	0.675818663	0.906373214
C	0.694136770	0.330609840	0.065405421
C	0.305863230	0.669390160	0.934594579
H	0.581008871	0.261633778	0.029825767
H	0.418991129	0.738366222	0.970174233
C	0.641287733	0.427328049	0.081604066
C	0.358712267	0.572671951	0.918395934
H	0.483732578	0.432609118	0.060261073

H	0.516267422	0.567390882	0.939738927
C	0.785370753	0.517718566	0.123994815
C	0.214629247	0.482281434	0.876005185
C	0.987232923	0.509452910	0.149616277
C	0.012767077	0.490547090	0.850383723
H	0.102263497	0.580048845	0.180916596
H	0.897736503	0.419951155	0.819083404
C	0.042242321	0.413312026	0.135133360
C	0.957757679	0.586687974	0.864866640
H	0.199443599	0.406528426	0.154783134
H	0.800556401	0.593471574	0.845216866
C	0.727516561	0.621407183	0.140118412
C	0.272483439	0.378592817	0.859881588
H	0.810625479	0.667147726	0.207476282
H	0.189374521	0.332852274	0.792523718
H	0.560448786	0.611152918	0.147456029
H	0.439551214	0.388847082	0.852543971
H	0.768093799	0.669516501	0.077134947
H	0.231906201	0.330483499	0.922865053
S	0.678629856	0.822574092	0.447162633
S	0.321370144	0.177425908	0.552837367
O	0.729219979	0.875582593	0.356407429
O	0.270780021	0.124417407	0.643592571
O	0.848315193	0.861864873	0.525215792
O	0.151684807	0.138135127	0.474784208
O	0.476844864	0.830747267	0.481333276
O	0.523155136	0.169252733	0.518666724
C	0.670299721	0.687609008	0.418947202
C	0.329700279	0.312390992	0.581052798
C	0.854027663	0.653595395	0.426184520
C	0.145972337	0.346404605	0.573815480
H	0.998855884	0.709582360	0.453175759
H	0.001144116	0.290417640	0.546824241
C	0.849121521	0.548166617	0.399266071
C	0.150878479	0.451833383	0.600733929
H	0.992324514	0.520915484	0.404549161
H	0.007675486	0.479084516	0.595450839
C	0.663611840	0.475692510	0.365529829
C	0.336388160	0.524307490	0.634470171
C	0.482310769	0.512117682	0.359105617
C	0.517689231	0.487882318	0.640894383
H	0.336797313	0.456242228	0.332801431
H	0.663202687	0.543757772	0.667198569
C	0.483971385	0.617515098	0.385203462
C	0.516028615	0.382484902	0.614796538
H	0.342837832	0.646089065	0.378348350
H	0.657162168	0.353910935	0.621651650
C	0.661068712	0.362351515	0.337640885
C	0.338931288	0.637648485	0.662359115
H	0.780120225	0.356339415	0.285107033
H	0.219879775	0.643660585	0.714892967
H	0.509907814	0.317977043	0.303183861
H	0.490092186	0.682022957	0.696816139
H	0.694126190	0.323271413	0.403904060
H	0.305873810	0.676728587	0.596095940

2B η^2 -(OS)O:

Ru	0.339687771	0.987447397	0.251681957
Ru	0.660312229	0.012552603	0.748318043
N	0.650111256	0.066439536	0.315772493
N	0.349888744	0.933560464	0.684227507
H	0.729500612	0.020208849	0.355746243
H	0.270499388	0.979791151	0.644253757
H	0.635022266	0.126243286	0.362217775
H	0.364977734	0.873756714	0.637782225

H	0.740757324	0.100824898	0.262972651
H	0.259242676	0.899175102	0.737027349
N	0.288788427	0.953194559	0.396734407
N	0.711211573	0.046805441	0.603265593
H	0.131561562	0.932284782	0.406280563
H	0.868438438	0.067715218	0.593719437
H	0.359641165	0.018713249	0.443248098
H	0.640358835	0.981286751	0.556751902
H	0.354993714	0.893293758	0.419471029
H	0.645006286	0.106706242	0.580528971
N	0.018233492	0.943169166	0.203242254
N	0.981766508	0.056830834	0.796757746
H	0.989692577	0.891329499	0.142086623
H	0.010307423	0.108670501	0.857913377
H	0.959356450	1.006550325	0.183243424
H	0.040643550	-0.006550325	0.816756576
H	0.934630961	0.905616121	0.256527788
H	0.065369039	0.094383879	0.743472212
N	0.379272810	0.031564579	0.105977760
N	0.620727190	0.968435421	0.894022240
H	0.535375575	0.051315940	0.096111760
H	0.464624425	0.948684060	0.903888240
H	0.321669403	0.095469691	0.088106132
H	0.678330597	0.904530309	0.911893868
H	0.301630390	0.968232423	0.057835352
H	0.698369610	0.031767577	0.942164648
O	0.311600416	0.136938341	0.278822007
O	0.688399584	0.863061659	0.721177993
H	0.231919804	0.146434445	0.335482173
H	0.768080196	0.853565555	0.664517827
H	0.260686373	0.172351283	0.219736771
H	0.739313627	0.827648717	0.780263229
S	0.975810061	0.199199590	0.083554396
S	0.024189939	0.800800410	0.916445604
O	0.934181166	0.165779071	0.979355949
O	0.065818834	0.834220929	0.020644051
O	0.200903492	0.221106686	0.121962507
O	0.799096508	0.778893314	0.878037493
O	0.845267278	0.122168414	0.142930758
O	0.154732722	0.877831586	0.857069242
C	0.907497971	0.320402624	0.098861055
C	0.092502029	0.679597376	0.901138945
C	0.702632379	0.324578306	0.067868905
C	0.297367621	0.675421694	0.932131095
H	0.586689010	0.255063570	0.032119546
H	0.413310990	0.744936430	0.967880454
C	0.648263888	0.419488739	0.081450809
C	0.351736112	0.580511261	0.918549191
H	0.487201877	0.422676308	0.058011745
H	0.512798123	0.577323692	0.941988255
C	0.794711840	0.510853960	0.124241081
C	0.205288160	0.489146040	0.875758919
C	-0.000237362	0.504615640	0.154058782
C	1.000237362	0.495384360	0.845941218
H	0.116199092	0.575579628	0.186953292
H	0.883800908	0.424420372	0.813046708
C	0.056696711	0.410235596	0.141997012
C	0.943303289	0.589764404	0.858002988
H	0.216597835	0.405350563	0.165112085
H	0.783402165	0.594649437	0.834887915
C	0.735676264	0.612795477	0.137887403
C	0.264323736	0.387204523	0.862112597
H	0.770667999	0.642202183	0.215845309
H	0.229332001	0.357797817	0.784154691
H	0.568064091	0.603720750	0.114326346
H	0.431935909	0.396279250	0.885673654

H	0.826540064	0.674622952	0.095328263
H	0.173459936	0.325377048	0.904671737
S	0.750548515	0.823226062	0.479445241
S	0.249451485	0.176773938	0.520554759
O	0.841888813	0.894834302	0.405947644
O	0.158111187	0.105165698	0.594052356
O	0.890779041	0.840370827	0.573191000
O	0.109220959	0.159629173	0.426809000
O	0.538100380	0.829802916	0.494161132
O	0.461899620	0.170197084	0.505838868
C	0.727371421	0.692273372	0.434728210
C	0.272628579	0.307726628	0.565271790
C	0.908112169	0.656553594	0.434157713
C	0.091887831	0.343446406	0.565842287
H	0.061529445	0.709098981	0.461428164
H	0.938470555	0.290901019	0.538571836
C	0.889936796	0.553099235	0.399984531
C	0.110063204	0.446900765	0.600015469
H	0.030361942	0.524027700	0.400069066
H	0.969638058	0.475972300	0.599930934
C	0.694068558	0.484155037	0.366572336
C	0.305931442	0.515844963	0.633427664
C	0.515580919	0.522328600	0.367286137
C	0.484419081	0.477671400	0.632713863
H	0.361477336	0.469383654	0.341532687
H	0.638522664	0.530616346	0.658467313
C	0.530692794	0.625653597	0.400908238
C	0.469307206	0.374346403	0.599091762
H	0.391264431	0.655155092	0.401866552
H	0.608735569	0.344844908	0.598133448
C	0.675349354	0.372234735	0.332401758
C	0.324650646	0.627765265	0.667598242
H	0.828077670	0.361217427	0.317672390
H	0.171922330	0.638782573	0.682327610
H	0.565517712	0.348921338	0.264344835
H	0.434482288	0.651078662	0.735655165
H	0.614283788	0.317122151	0.388173911
H	0.385716212	0.682877849	0.611826089
S	0.510529410	0.861178292	0.210589674
S	0.489470590	0.138821708	0.789410326
O	0.279036369	0.823502033	0.227449977
O	0.720963631	0.176497967	0.772550023
O	0.550966004	0.858361333	0.106990180
O	0.449033996	0.141638667	0.893009820

2B η^1 -OSO:

Ru	0.326977234	0.995838456	0.256563047
Ru	0.673022766	0.004161544	0.743436953
N	0.643439525	0.063081814	0.311331288
N	0.356560475	0.936918186	0.688668712
H	0.712021087	0.008296057	0.344506267
H	0.287978913	0.991703943	0.655493733
H	0.652608510	0.122391972	0.363607144
H	0.347391490	0.877608028	0.636392856
H	0.732010434	0.096048221	0.257444120
H	0.267989566	0.903951779	0.742555880
N	0.273778720	0.957341967	0.401075899
N	0.726221280	0.042658033	0.598924101
H	0.116719504	0.935365184	0.409793306
H	0.883280496	0.064634816	0.590206694
H	0.344063057	0.021148527	0.449495333
H	0.655936943	0.978851473	0.550504667
H	0.339625211	0.896588505	0.421612914
H	0.660374789	0.103411495	0.578387086
N	0.007295656	0.940557319	0.204568966

N	0.992704344	0.059442681	0.795431034
H	0.985212666	0.888164286	0.144253619
H	0.014787334	0.111835714	0.855746381
H	0.943483158	1.001130171	0.180863546
H	0.056516842	-0.001130171	0.819136454
H	0.920281696	0.903272979	0.256958488
H	0.079718304	0.096727021	0.743041512
N	0.380570412	0.034672173	0.111588948
N	0.619429588	0.965327827	0.888411052
H	0.537703729	0.053553786	0.103491419
H	0.462296271	0.946446214	0.896508581
H	0.325014489	0.098231990	0.090236267
H	0.674985511	0.901768010	0.909763733
H	0.306109671	0.971554249	0.062949753
H	0.693890329	0.028445751	0.937050247
O	0.286027261	0.142783939	0.283516159
O	0.713972739	0.857216061	0.716483841
H	0.208735041	0.153015036	0.340215075
H	0.791264959	0.846984964	0.659784925
H	0.243599981	0.178826985	0.223900831
H	0.756400019	0.821173015	0.776099169
S	0.971107976	0.200898848	0.078341647
S	0.028892024	0.799101152	0.921658353
O	0.928598506	0.173316795	0.972649934
O	0.071401494	0.826683205	0.027350066
O	0.195611492	0.221640693	0.116702592
O	0.804388508	0.778359307	0.883297408
O	0.839589482	0.121292280	0.134666716
O	0.160410518	0.878707720	0.865333284
C	0.903644526	0.321332220	0.098497728
C	0.096355474	0.678667780	0.901502272
C	0.696036487	0.324550666	0.074154047
C	0.303963513	0.675449334	0.925845953
H	0.575378171	0.253513233	0.045143894
H	0.424621829	0.746486767	0.954856106
C	0.643875206	0.419997689	0.087006609
C	0.356124794	0.580002311	0.912993391
H	0.481112982	0.422757066	0.067728836
H	0.518887018	0.577242934	0.932271164
C	0.794840111	0.512324819	0.124191877
C	0.205159889	0.487675181	0.875808123
C	0.002229091	0.506921149	0.148062508
C	0.997770909	0.493078851	0.851937492
H	0.122309069	0.578723716	0.176237952
H	0.877690931	0.421276284	0.823762048
C	0.057449055	0.412199122	0.135524546
C	0.942550945	0.587800878	0.864475454
H	0.219240305	0.407857264	0.153751210
H	0.780759695	0.592142736	0.846248790
C	0.735456654	0.613782287	0.139462621
C	0.264543346	0.386217713	0.860537379
H	0.751031550	0.636374200	0.218897395
H	0.248968450	0.363625800	0.781102605
H	0.571547548	0.605690742	0.108629459
H	0.428452452	0.394309258	0.891370541
H	0.836467221	0.679283441	0.104566442
H	0.163532779	0.320716559	0.895433558
S	0.735225946	0.816592890	0.467832328
S	0.264774054	0.183407110	0.532167672
O	0.810741488	0.885062887	0.388851915
O	0.189258512	0.114937113	0.611148085
O	0.890565679	0.838599160	0.556571592
O	0.109434321	0.161400840	0.443428408
O	0.526091688	0.821834586	0.488813610
O	0.473908312	0.178165414	0.511186390
C	0.714463179	0.684865220	0.425982504

C	0.285536821	0.315134780	0.574017496
C	0.897139432	0.650437618	0.427940098
C	0.102860568	0.349562382	0.572059902
H	0.048724499	0.704512829	0.455520965
H	0.951275501	0.295487171	0.544479035
C	0.883025241	0.546673437	0.396277503
C	0.116974759	0.453326563	0.603722497
H	0.025087971	0.518671332	0.398587395
H	0.974912029	0.481328668	0.601412605
C	0.689095398	0.476103725	0.362846825
C	0.310904602	0.523896275	0.637153175
C	0.508507589	0.513017006	0.360695803
C	0.491492411	0.486982994	0.639304197
H	0.356053626	0.458706168	0.334579178
H	0.643946374	0.541293832	0.665420822
C	0.519603500	0.616646217	0.392012763
C	0.480396500	0.383353783	0.607987237
H	0.378599214	0.645195918	0.391372449
H	0.621400786	0.354804082	0.608627551
C	0.674132537	0.363696032	0.332177111
C	0.325867463	0.636303968	0.667822889
H	0.827501795	0.353106170	0.317969399
H	0.172498205	0.646893830	0.682030601
H	0.563713125	0.337499085	0.264796869
H	0.436286875	0.662500915	0.735203131
H	0.615338659	0.310439329	0.389644665
H	0.384661341	0.689560671	0.610355335
S	0.466919994	0.794926820	0.171694495
S	0.533080006	0.205073180	0.828305505
O	0.571832149	0.856446894	0.094558529
O	0.428167851	0.143553106	0.905441471
O	0.366099039	0.856047896	0.239526608
O	0.633900961	0.143952104	0.760473392

3: Dark state

Ru	0.762820169	0.782410006	0.526107074
Ru	0.237179831	0.217589994	0.473892926
Br	0.638979141	0.629636657	0.088345576
Br	0.361020859	0.370363343	0.911654424
S	0.795817257	0.916014818	0.646437722
S	0.204182743	0.083985182	0.353562278
S	0.710674413	0.086946158	0.313629992
S	0.289325587	0.913053842	0.686370008
N	0.587983095	0.700179651	0.589539609
N	0.412016905	0.299820349	0.410460391
H	0.501520209	0.665343295	0.528495578
H	0.498479791	0.334656705	0.471504422
H	0.527866841	0.752221239	0.637888134
H	0.472133159	0.247778761	0.362111866
H	0.636262805	0.640039570	0.628274746
H	0.363737195	0.359960430	0.371725254
N	0.953746203	0.693151718	0.591042321
N	0.046253797	0.306848282	0.408957679
H	0.044044683	0.740109128	0.640674670
H	0.955955317	0.259890872	0.359325330
H	0.008852534	0.654904907	0.530750436
H	0.991147466	0.345095093	0.469249564
H	0.913122486	0.634700292	0.628881890
H	0.086877514	0.365299708	0.371118110
N	0.563331873	0.856055853	0.449825048
N	0.436668127	0.143944147	0.550174952
H	0.491154958	0.798108551	0.398691923
H	0.508845042	0.201891449	0.601308077
H	0.587845035	0.919224317	0.412788320

H	0.412154965	0.080775683	0.587211680
H	0.492202505	0.887028849	0.504510168
H	0.507797495	0.112971151	0.495489832
N	0.935863308	0.846313732	0.449015915
N	0.064136692	0.153686268	0.550984085
H	0.985332969	0.783404973	0.404825378
H	0.014667031	0.216595027	0.595174622
H	0.029737727	0.883705948	0.503427235
H	0.970262273	0.116294052	0.496572765
H	0.895643956	0.904141220	0.404808662
H	0.104356044	0.095858780	0.595191338
N	0.727019806	0.654113538	0.402538901
N	0.272980194	0.345886462	0.597461099
O	0.832563884	0.908583283	0.756159033
O	0.167436116	0.091416717	0.243840967
C	0.702627726	0.675007478	0.305565133
C	0.297372274	0.324992522	0.694434867
H	0.704210938	0.759903825	0.295870098
H	0.295789062	0.240096175	0.704129902
O	0.777619452	0.026301849	0.625041133
O	0.222380548	0.973698151	0.374958867
C	0.726564765	0.550579071	0.417866131
C	0.273435235	0.449420929	0.582133869
H	0.746664878	0.537847718	0.498160543
H	0.253335122	0.462152282	0.501839457
C	0.611379749	0.875526203	0.995042939
C	0.388620251	0.124473797	0.004957061
C	0.669844274	0.006287385	0.189609901
C	0.330155726	0.993712615	0.810390099
C	0.520761679	0.951228417	0.156692823
C	0.479238321	0.048771583	0.843307177
H	0.426933706	0.959586389	0.206516083
H	0.573066294	0.040413611	0.793483917
C	0.493275336	0.885984665	0.059851001
C	0.506724664	0.114015335	0.940148999
H	0.377123274	0.841599847	0.034616573
H	0.622876726	0.158400153	0.965383427
C	0.701932800	0.464300350	0.336492363
C	0.298067200	0.535699650	0.663507637
H	0.703819343	0.381073730	0.351548266
H	0.296180657	0.618926270	0.648451734
C	0.759353860	0.933337822	0.029242625
C	0.240646140	0.066662178	0.970757375
H	0.851628661	0.927185815	0.978193824
H	0.148371339	0.072814185	0.021806176
C	0.675689799	0.592118905	0.220901627
C	0.324310201	0.407881095	0.779098373
C	0.790161350	0.997884433	0.126114633
C	0.209838650	0.002115567	0.873885367
H	0.907499077	0.040433415	0.153543880
H	0.092500923	0.959566585	0.846456120
S	0.783156750	0.408170182	0.655941909
S	0.216843250	0.591829818	0.344058091
O	0.919048992	0.368541478	0.603044117
O	0.080951008	0.631458522	0.396955883
O	0.734908656	0.199634953	0.299854699
O	0.265091344	0.800365047	0.700145301
O	0.568317254	0.070904293	0.363842620
O	0.431682746	0.929095707	0.636157380
O	0.627010591	0.356943366	0.604163560
O	0.372989409	0.643056634	0.395836440
O	0.858638003	0.044430572	0.365929594
O	0.141361997	0.955569428	0.634070406
O	0.779567730	0.527405326	0.674870594
O	0.220432270	0.472594674	0.325129406
C	0.818680242	0.366730366	0.778759488

C	0.181319758	0.633269634	0.221240512
C	0.675343520	0.484592794	0.235506140
C	0.324656480	0.515407206	0.764493860
H	0.654762926	0.418443144	0.169778261
H	0.345237074	0.581556856	0.830221739
C	0.838289966	0.256667920	0.782930833
C	0.161710034	0.743332080	0.217069167
H	0.829139633	0.196743196	0.712292133
H	0.170860367	0.803256804	0.287707867
C	0.858537344	0.406010031	0.964308737
C	0.141462656	0.593989969	0.035691263
H	0.867860913	0.465268187	0.035334684
H	0.132139087	0.534731813	0.964665316
C	0.869167040	0.222583164	0.878301185
C	0.130832960	0.777416836	0.121698815
H	0.885441908	0.136356923	0.880553659
H	0.114558092	0.863643077	0.119446341
C	0.828006509	0.441666094	0.869343259
C	0.171993491	0.558333906	0.130656741
H	0.812963861	0.527479115	0.865279749
H	0.187036139	0.472520885	0.134720251
C	0.917278871	0.261130666	0.073767102
C	0.082721129	0.738869334	0.926232898
H	0.921665668	0.330155438	0.137274268
H	0.078334332	0.669844562	0.862725732
H	0.035020510	0.222070223	0.082746103
H	0.964979490	0.777929777	0.917253897
H	0.826368256	0.200945579	0.084535789
H	0.173631744	0.799054421	0.915464211
C	0.582552457	0.802672778	0.892528133
C	0.417447543	0.197327222	0.107471867
H	0.453079741	0.781457143	0.867454102
H	0.546920259	0.218542857	0.132545898
H	0.649073880	0.727141765	0.895763253
H	0.350926120	0.272858235	0.104236747
H	0.627684159	0.841326182	0.832850900
H	0.372315841	0.158673818	0.167149100
C	0.880820941	0.296879742	0.970755817
C	0.119179059	0.703120258	0.029244183

3: η^1 -OSO

Ru	0.236879017	0.227890034	0.464802568
Ru	0.763120983	0.772109966	0.535197432
Br	0.381189488	0.360581099	0.893125712
Br	0.618810512	0.639418901	0.106874288
S	0.708116355	0.057798559	0.303304670
S	0.291883645	0.942201441	0.696695330
N	0.417286309	0.306567309	0.411002164
N	0.582713691	0.693432691	0.588997836
H	0.504472563	0.341543035	0.472400418
H	0.495527437	0.658456965	0.527599582
H	0.373778779	0.367868239	0.375854158
H	0.626221221	0.632131761	0.624145842
H	0.473700273	0.249118983	0.361760153
H	0.526299727	0.750881017	0.638239847
N	0.047617813	0.316457253	0.405550046
N	0.952382187	0.683542747	0.594449954
H	0.958464175	0.262874574	0.357956758
H	0.041535825	0.737125426	0.642043242
H	0.086352543	0.372297200	0.368235568
H	0.913647457	0.627702800	0.631764432
H	0.992991062	0.359737504	0.464649939
H	0.007008938	0.640262496	0.535350061
N	0.427454851	0.141155849	0.525596065

N	0.572545149	0.858844151	0.474403935
H	0.513186533	0.196920151	0.574069890
H	0.486813467	0.803079849	0.425930110
H	0.485660520	0.098779652	0.467715202
H	0.514339480	0.901220348	0.532284798
H	0.396930210	0.083285994	0.562882609
H	0.603069790	0.916714006	0.437117391
N	0.059839008	0.152014013	0.521298840
N	0.940160992	0.847985987	0.478701160
H	-0.009305432	0.213496909	0.557017370
H	1.009305432	0.786503091	0.442982630
H	0.102244123	0.103836015	0.570455905
H	0.897755877	0.896163985	0.429544095
H	0.981393249	0.100359717	0.463047330
H	0.018606751	0.899640283	0.536952670
N	0.272323621	0.350608180	0.591574308
N	0.727676379	0.649391820	0.408425692
C	0.299324711	0.325231234	0.682367789
C	0.700675289	0.674768766	0.317632211
H	0.294857156	0.236636995	0.681487054
H	0.705142844	0.763363005	0.318512946
C	0.276096716	0.459777476	0.589701245
C	0.723903284	0.540222524	0.410298755
H	0.253301884	0.476318472	0.514538671
H	0.746698116	0.523681528	0.485461329
C	0.632701737	0.881231815	0.964868315
C	0.367298263	0.118768185	0.035131685
C	0.675955201	0.990653515	0.171723428
C	0.324044799	0.009346485	0.828276572
C	0.536323227	0.925619145	0.127046589
C	0.463676773	0.074380855	0.872953411
H	0.444280876	0.917807173	0.173197076
H	0.555719124	0.082192827	0.826802924
C	0.515604113	0.871745786	0.024317975
C	0.484395887	0.128254214	0.975682025
H	0.404430132	0.822114396	0.989151052
H	0.595569868	0.177885604	0.010848948
C	0.307397572	0.545382332	0.677264132
C	0.692602428	0.454617668	0.322735868
H	0.307731828	0.632351548	0.671898715
H	0.692268172	0.367648452	0.328101285
C	0.771984719	0.948385469	0.011300194
C	0.228015281	0.051614531	0.988699806
H	0.863723005	0.958674330	0.965475813
H	0.136276995	0.041325670	0.034524187
C	0.334398467	0.407369165	0.772176438
C	0.665601533	0.592630835	0.227823562
C	0.794196270	1.002906197	0.113608018
C	0.205803730	-0.002906197	0.886391982
H	0.902764583	0.055365850	0.149132087
H	0.097235417	0.944634150	0.850867913
S	0.785050388	0.411734770	0.653098349
S	0.214949612	0.588265230	0.346901651
O	0.912605695	0.372141715	0.593143052
O	0.087394305	0.627858285	0.406856948
O	0.743472401	0.176470199	0.311617725
O	0.256527599	0.823529801	0.688382275
O	0.559314196	0.037366187	0.340786387
O	0.440685804	0.962633813	0.659213613
O	0.628137578	0.354385055	0.608563523
O	0.371862422	0.645614945	0.391436477
O	0.846605874	0.003317737	0.347866815
O	0.153394126	0.996682263	0.652133185
O	0.774490082	0.534369896	0.676531924
O	0.225509918	0.465630104	0.323468076
C	0.843327269	0.378296055	0.771536418

C	0.156672731	0.621703945	0.228463582
C	0.338435020	0.519831925	0.771244126
C	0.661564980	0.480168075	0.228755874
H	0.365252687	0.585125727	0.841610185
H	0.634747313	0.414874273	0.158389815
C	0.936583257	0.286136240	0.776743010
C	0.063416743	0.713863760	0.223256990
H	0.976450163	0.236375167	0.708613171
H	0.023549837	0.763624833	0.291386829
C	0.838819847	0.415054654	0.950793562
C	0.161180153	0.584945346	0.049206438
H	0.803308297	0.467575667	1.019480119
H	0.196691703	0.532424333	-0.019480119
C	0.979001530	0.258242383	0.868957321
C	0.020998470	0.741757617	0.131042679
H	1.053835158	0.186646638	0.872938861
H	-0.053835158	0.813353362	0.127061139
C	0.794603084	0.443309810	0.858936477
C	0.205396916	0.556690190	0.141063523
H	0.723902978	0.516500702	0.854673515
H	0.276097022	0.483499298	0.145326485
C	0.974390463	0.291636107	0.056420290
C	0.025609537	0.708363893	0.943579710
H	0.996907257	0.366818966	0.119842102
H	0.003092743	0.633181034	0.880157898
H	0.082478052	0.241711005	0.056637728
H	0.917521948	0.758288995	0.943362272
H	0.876691585	0.240610876	0.071191154
H	0.123308415	0.759389124	0.928808846
C	0.610241386	0.821644532	0.854957223
C	0.389758614	0.178355468	0.145042777
H	0.482162725	0.799957751	0.824621172
H	0.517837275	0.200042249	0.175378828
H	0.676995167	0.743808093	0.842667742
H	0.323004833	0.256191907	0.157332258
H	0.655318151	0.873326280	0.809331348
H	0.344681849	0.126673720	0.190668652
C	0.929981079	0.321849186	0.957211943
C	0.070018921	0.678150814	0.042788057
S	0.195212918	0.984248074	0.309674558
S	0.804787082	0.015751926	0.690325442
O	0.199586856	0.110375025	0.335913379
O	0.800413144	0.889624975	0.664086621
O	0.227509925	0.934049170	0.396266482
O	0.772490075	0.065950830	0.603733518

4: Dark state

Ru	0.204355063	0.232319752	0.463320167
Ru	0.795644937	0.767680248	0.536679833
S	0.156754796	0.143056125	0.330411155
S	0.843245204	0.856943875	0.669588845
N	0.249197213	0.318156865	0.595724452
N	0.750802787	0.681843135	0.404275548
N	0.395812387	0.132222106	0.513143807
N	0.604187613	0.867777894	0.486856193
H	0.355213185	0.065509640	0.549284851
H	0.644786815	0.934490360	0.450715149
H	0.489802532	0.176909228	0.556075376
H	0.510197468	0.823090772	0.443924624
H	0.448891589	0.105431273	0.454624475
H	0.551108411	0.894568727	0.545375525
N	0.020914227	0.341566455	0.425255711
N	0.979085773	0.658433545	0.574744289
H	0.060483061	0.413473574	0.396348802

H	0.939516939	0.586526426	0.603651198
H	0.969393716	0.366343056	0.485287019
H	0.030606284	0.633656944	0.514712981
H	0.929282231	0.300258517	0.377706465
H	0.070717769	0.699741483	0.622293535
N	0.397428256	0.335017483	0.421394268
N	0.602571744	0.664982517	0.578605732
H	0.479101392	0.358041056	0.481598772
H	0.520898608	0.641958944	0.518401228
H	0.367770137	0.407722862	0.390400528
H	0.632229863	0.592277138	0.609599472
H	0.458692659	0.289143201	0.376295251
H	0.541307341	0.710856799	0.623704749
N	0.021049001	0.137375292	0.522409150
N	0.978950999	0.862624708	0.477590850
H	0.067470705	0.082638979	0.570879859
H	0.932529295	0.917361021	0.429120141
H	0.940629658	0.092708553	0.470404198
H	0.059370342	0.907291447	0.529595802
H	0.945885048	0.186240599	0.556244321
O	0.054114952	0.813759401	0.443755679
O	0.157385282	0.193001900	0.238042001
O	0.842614718	0.806998100	0.761957999
C	0.275424717	0.263122517	0.676760403
C	0.724575283	0.736877483	0.323239597
H	0.271316949	0.173193772	0.668526809
H	0.728683051	0.826806228	0.331473191
O	0.120761549	0.023547450	0.324131614
O	0.879238451	0.976452550	0.675868386
C	0.252466779	0.428874896	0.602427634
C	0.747533221	0.571125104	0.397572366
H	0.230531503	0.470286050	0.535008108
H	0.769468497	0.529713950	0.464991892
C	0.309174337	0.430611750	0.772161992
C	0.690825663	0.569388250	0.227838008
C	0.281190895	0.488661703	0.689360075
C	0.718809105	0.511338297	0.310639925
H	0.281646445	0.578507245	0.691630539
H	0.718353555	0.421492755	0.308369461
C	0.306331607	0.316054787	0.766631224
C	0.693668393	0.683945213	0.233368776
H	0.328383063	0.267462912	0.829903053
H	0.671616937	0.732537088	0.170096947
Br	0.353162307	0.506670989	0.892446509
Br	0.646837693	0.493329011	0.107553491
S	0.686729111	0.102500595	0.312632953
S	0.313270889	0.897499405	0.687367047
C	0.654890907	0.022270212	0.203460291
C	0.345109093	0.977729788	0.796539709
C	0.611656950	0.887132233	0.035507101
C	0.388343050	0.112867767	0.964492899
C	0.775086173	0.026464142	0.142115453
C	0.224913827	0.973535858	0.857884547
H	0.884885839	0.082455372	0.160246318
H	0.115114161	0.917544628	0.839753682
C	0.512762607	0.952522471	0.181685848
C	0.487237393	0.047477529	0.818314152
H	0.417816923	0.952187711	0.229320388
H	0.582183077	0.047812289	0.770679612
C	0.492450352	0.885377231	0.098175629
C	0.507549648	0.114622769	0.901824371
H	0.380628968	0.830927175	0.081104947
H	0.619371032	0.169072825	0.918895053
O	0.763618645	0.028882853	0.384236777
O	0.236381355	0.971117147	0.615763223
C	0.751791310	0.959253637	0.058485961

C	0.248208690	0.040746363	0.941514039
H	0.843737678	0.963229620	0.008835964
H	0.156262322	0.036770380	0.991164036
O	0.524742454	0.130796275	0.334321406
O	0.475257546	0.869203725	0.665678594
O	0.796474925	0.197936390	0.298257236
O	0.203525075	0.802063610	0.701742764
C	0.589983796	0.812929446	0.947044233
C	0.410016204	0.187070554	0.052955767
H	0.460001331	0.800822463	0.916751269
H	0.539998669	0.199177537	0.083248731
H	0.632730073	0.730763419	0.963641519
H	0.367269927	0.269236581	0.036358481
H	0.660085892	0.845242049	0.891475866
H	0.339914108	0.154757951	0.108524134
S	0.246404480	0.636564893	0.376373719
S	0.753595520	0.363435107	0.623626281
C	0.191074802	0.660394983	0.253691950
C	0.808925198	0.339605017	0.746308050
C	0.139801772	0.762962198	0.226876746
C	0.860198228	0.237037802	0.773123254
H	0.141576650	0.830501508	0.280575984
H	0.858423350	0.169498492	0.719424016
C	0.190472562	0.574120453	0.185357531
C	0.809527438	0.425879547	0.814642469
H	0.231233301	0.494129901	0.207212794
H	0.768766699	0.505870099	0.792787206
C	0.086042053	0.693610932	0.060631852
C	0.913957947	0.306389068	0.939368148
C	0.137881655	0.591196579	0.089668046
C	0.862118345	0.408803421	0.910331954
H	0.136498291	0.523704476	0.035795708
H	0.863501709	0.476295524	0.964204292
C	0.087327747	0.778609015	0.130746090
C	0.912672253	0.221390985	0.869253910
H	0.045321691	0.858779842	0.110054083
H	0.954678309	0.141220158	0.889945917
O	0.276967817	0.744982011	0.427045571
O	0.723032183	0.255017989	0.572954429
O	0.391256819	0.571796614	0.383656555
O	0.608743181	0.428203386	0.616343445
O	0.103922415	0.573287826	0.406186443
O	0.896077585	0.426712174	0.593813557
C	0.034723148	0.712228057	0.957217240
C	0.965276852	0.287771943	0.042782760
H	-0.058535370	0.772946367	0.947541891
H	1.058535370	0.227053633	0.052458109
H	0.986148012	0.635095973	0.917281740
H	0.013851988	0.364904027	0.082718260
H	0.139898596	0.743965204	0.922437329
H	0.860101404	0.256034796	0.077562671

4: η^2 -(OS)O

Ru	0.227019068	0.242486557	0.456892929
Ru	0.772980932	0.757513443	0.543107071
N	0.246242499	0.326994203	0.584646594
N	0.753757501	0.673005797	0.415353406
N	0.371964795	0.111671928	0.498425103
N	0.628035205	0.888328072	0.501574897
H	0.319372734	0.047254295	0.537839083
H	0.680627266	0.952745705	0.462160917
H	0.470241431	0.146587803	0.534457463
H	0.529758569	0.853412197	0.465542537
H	0.406761819	0.070372506	0.439101594

H	0.593238181	0.929627494	0.560898406
N	0.066391810	0.365992983	0.416842914
N	0.933608190	0.634007017	0.583157086
H	0.108696956	0.450138699	0.401014866
H	0.891303044	0.549861301	0.598985134
H	-0.006578629	0.376511815	0.469522998
H	1.006578629	0.623488185	0.530477002
H	0.001659596	0.329784889	0.359396441
H	0.998340404	0.670215111	0.640603559
N	0.432873374	0.348431709	0.440468882
N	0.567126626	0.651568291	0.559531118
H	0.483646491	0.371557984	0.505805192
H	0.516353509	0.628442016	0.494194808
H	0.418444485	0.426446522	0.405917326
H	0.581555515	0.573553478	0.594082674
H	0.506058493	0.296435642	0.406251342
H	0.493941507	0.703564358	0.593748658
N	0.038408330	0.149902062	0.508938594
N	0.961591670	0.850097938	0.491061406
H	0.069189177	0.085036039	0.553863397
H	0.930810823	0.914963961	0.446136603
H	0.966847156	0.110098408	0.455371452
H	0.033152844	0.889901592	0.544628548
H	0.975601841	0.209268559	0.544214554
H	0.024398159	0.790731441	0.455785446
C	0.249049999	0.260722886	0.661759896
C	0.750950001	0.739277114	0.338240104
H	0.248438544	0.163553371	0.650973236
H	0.751561456	0.836446629	0.349026764
C	0.249835725	0.447575458	0.596552791
C	0.750164275	0.552424542	0.403447209
H	0.247644592	0.498955996	0.533078574
H	0.752355408	0.501044004	0.466921426
C	0.255321554	0.435216505	0.762382943
C	0.744678446	0.564783495	0.237617057
C	0.254501782	0.505216573	0.684039288
C	0.745498218	0.494783427	0.315960712
H	0.254471700	0.603080371	0.690047268
H	0.745528300	0.396919629	0.309952732
C	0.252537053	0.311108305	0.751523976
C	0.747462947	0.688891695	0.248476024
H	0.255657551	0.252830918	0.810941452
H	0.744342449	0.747169082	0.189058548
Br	0.263534687	0.507877755	0.883287969
Br	0.736465313	0.492122245	0.116712031
S	0.724307924	0.116683262	0.322604049
S	0.275692076	0.88316738	0.677395951
C	0.673525410	0.030557502	0.218092351
C	0.326474590	0.969442498	0.781907649
C	0.592944767	0.893521642	0.053178125
C	0.407055233	0.106478358	0.946821875
C	0.762359361	0.042215197	0.141347886
C	0.237640639	0.957784803	0.858652114
H	0.860736190	0.106709220	0.146008085
H	0.139263810	0.893290780	0.853991915
C	0.545126431	0.951104826	0.213559617
C	0.454873569	0.048895174	0.786440383
H	0.474602595	0.943079026	0.273464906
H	0.525397405	0.056920974	0.726535094
C	0.505988703	0.883168136	0.131348552
C	0.494011297	0.116831864	0.868651448
H	0.404234061	0.821948079	0.127648301
H	0.595765939	0.178051921	0.872351699
O	0.805765467	0.034230127	0.383454064
O	0.194234533	0.965769873	0.616545936
C	0.721342729	0.974022967	0.059727973

C	0.278657271	0.025977033	0.940272027
H	0.788529957	0.985101454	-0.001440716
H	0.211470043	0.014898546	1.001440716
O	0.581954277	0.146618776	0.360975402
O	0.418045723	0.853381224	0.639024598
O	0.821215121	0.219808001	0.298772808
O	0.178784879	0.780191999	0.701227192
C	0.549279858	0.823001700	0.964123008
C	0.450720142	0.176998300	0.035876992
H	0.445017026	0.765823213	0.969914022
H	0.554982974	0.234176787	0.030085978
H	0.639403894	0.765677024	0.944476907
H	0.360596106	0.234322976	0.055523093
H	0.530246190	0.883472668	0.906217315
H	0.469753810	0.116527332	0.093782685
S	0.272089676	0.682415460	0.379125159
S	0.727910324	0.317584540	0.620874841
C	0.203632947	0.697906071	0.262197337
C	0.796367053	0.302093929	0.737802663
C	0.154274951	0.808177235	0.236226079
C	0.845725049	0.191822765	0.763773921
H	0.167912242	0.885579066	0.285491869
H	0.832087758	0.114420934	0.714508131
C	0.188163069	0.598689786	0.199771239
C	0.811836931	0.401310214	0.800228761
H	0.225634169	0.512098597	0.220743864
H	0.774365831	0.487901403	0.779256136
C	0.069698753	0.720230036	0.082817199
C	0.930301247	0.279769964	0.917182801
C	0.121978043	0.610905935	0.110701625
C	0.878021957	0.389094065	0.889298375
H	0.108186223	0.532754326	0.062058207
H	0.891813777	0.467245674	0.937941793
C	0.087397656	0.818177120	0.146883399
C	0.912602344	0.181822880	0.853116601
H	0.045977079	0.903917501	0.126794089
H	0.954022921	0.096082499	0.873205911
O	0.336106591	0.800548631	0.413032458
O	0.663893409	0.199451369	0.586967542
O	0.382488246	0.590248340	0.378977696
O	0.617511754	0.409751660	0.621022304
O	0.136599385	0.641736915	0.428250750
O	0.863400615	0.358263085	0.571749250
C	0.994231347	0.730646144	0.987847007
C	0.005768653	0.269353856	0.012152993
H	0.961993837	0.822427966	0.976875853
H	0.038006163	0.177572034	0.023124147
H	0.890535872	0.670401275	0.978922238
H	0.109464128	0.329598725	0.021077762
H	0.066528111	0.704917154	0.931528659
H	0.933471889	0.295082846	0.068471341
S	0.254445192	0.223178503	0.294932361
S	0.745554808	0.776821497	0.705067639
O	0.166655489	0.121634680	0.342162986
O	0.833344511	0.878365320	0.657837014
O	0.161591766	0.298421557	0.236442360
O	0.838408234	0.701578443	0.763557640

5: Dark state

Ru	0.761540563	0.782442785	0.524785977
Ru	0.238459437	0.217557215	0.475214023
S	0.796198431	0.913649362	0.649208286
S	0.203801569	0.086350638	0.350791714
O	0.837487726	0.902175294	0.758984378

O	0.162512274	0.097824706	0.241015622
O	0.775328205	0.025839936	0.632625267
O	0.224671795	0.974160064	0.367374733
N	0.933686775	0.845924860	0.447141846
N	0.066313225	0.154075140	0.552858154
H	0.027758508	0.882523431	0.502110954
H	0.972241492	0.117476569	0.497889046
H	0.893753590	0.904492799	0.403021132
H	0.106246410	0.095507201	0.596978868
H	0.981876699	0.782466583	0.401980697
H	0.018123301	0.217533417	0.598019303
N	0.561969792	0.858114874	0.449623114
N	0.438030208	0.141885126	0.550376886
H	0.491458363	0.888948822	0.505186437
H	0.508541637	0.111051178	0.494813563
H	0.489912257	0.800498097	0.397701107
H	0.510087743	0.199501903	0.602298893
H	0.585760603	0.921514656	0.412354944
H	0.414239397	0.078485344	0.587645056
N	0.587137515	0.699910298	0.587812464
N	0.412862485	0.300089702	0.412187536
H	0.526364610	0.752316209	0.636137495
H	0.473635390	0.247683791	0.363862505
H	0.635361657	0.639731272	0.627314480
H	0.364638343	0.360268728	0.372685520
H	0.501646828	0.664843056	0.525822308
H	0.498353172	0.335156944	0.474177692
N	0.953131553	0.691507640	0.588300237
N	0.046868447	0.308492360	0.411699763
H	0.913350169	0.632456082	0.625953046
H	0.086649831	0.367543918	0.374046954
H	0.042965962	0.737994543	0.638949258
H	0.957034038	0.262005457	0.361050742
H	0.007446730	0.653889638	0.526753320
H	0.992553270	0.346110362	0.473246680
N	0.723405849	0.655367823	0.398231558
N	0.276594151	0.344632177	0.601768442
C	0.723053086	0.551303725	0.413205967
C	0.276946914	0.448696275	0.586794033
H	0.746190712	0.537946154	0.494131465
H	0.253809288	0.462053846	0.505868535
C	0.694340631	0.465703237	0.330513429
C	0.305659369	0.534296763	0.669486571
H	0.697053979	0.382000326	0.345063414
H	0.302946021	0.617999674	0.654936586
C	0.662622540	0.488089869	0.229297371
C	0.337377460	0.511910131	0.770702629
H	0.638711110	0.421713425	0.162878035
H	0.361288890	0.578286575	0.837121965
C	0.661429736	0.595656687	0.212559986
C	0.338570264	0.404343313	0.787440014
C	0.694589255	0.676379628	0.300338194
C	0.305410745	0.323620372	0.699661806
H	0.697052214	0.762084001	0.292095312
H	0.302947786	0.237915999	0.707904688
C	0.624119507	0.625774189	0.106303364
C	0.375880493	0.374225811	0.893696636
H	0.615351850	0.553184020	0.045449335
H	0.384648150	0.446815980	0.954550665
H	0.717170981	0.682151188	0.092538566
H	0.282829019	0.317848812	0.907461434
H	0.508456285	0.667737295	0.097714814
H	0.491543715	0.332262705	0.902285186
S	0.217001116	0.591000185	0.340571696
S	0.782998884	0.408999815	0.659428304
O	0.078574072	0.632236709	0.390221661

O	0.921425928	0.367763291	0.609778339
O	0.370838546	0.643568001	0.393942916
O	0.629161454	0.356431999	0.606057084
O	0.221524082	0.471566252	0.324092799
O	0.778475918	0.528433748	0.675907201
C	0.186708671	0.629182535	0.214745056
C	0.813291329	0.370817465	0.785254944
C	0.180633072	0.551838945	0.124879408
C	0.819366928	0.448161055	0.875120592
H	0.194724417	0.466250253	0.131744531
H	0.805275583	0.533749747	0.868255469
C	0.153283074	0.584852814	0.027479801
C	0.846716926	0.415147186	0.972520199
H	0.144256096	0.524027107	0.956660495
H	0.855743904	0.475972893	0.043339505
C	0.131190161	0.693860835	0.017929884
C	0.868809839	0.306139165	0.982070116
C	0.139883848	0.770459217	0.109856070
C	0.860116152	0.229540783	0.890143930
H	0.123901715	0.856536777	0.105111179
H	0.876098285	0.143463223	0.894888821
C	0.167396615	0.739027777	0.207512003
C	0.832603385	0.260972223	0.792487997
H	0.173825768	0.800772565	0.277569676
H	0.826174232	0.199227435	0.722430324
C	0.097405816	0.727367714	0.912728548
C	0.902594184	0.272632286	0.087271452
H	0.093572456	0.656990303	0.849751410
H	0.906427544	0.343009697	0.150248590
H	0.189054221	0.786235211	0.901188579
H	0.810945779	0.213764789	0.098811421
H	0.980526287	0.767512588	0.901730904
H	0.019473713	0.232487412	0.098269096
S	0.286685532	0.913525928	0.688441367
S	0.713314468	0.086474072	0.311558633
O	0.263294765	0.801417675	0.704781988
O	0.736705235	0.198582325	0.295218012
O	0.428977512	0.928004271	0.638017500
O	0.571022488	0.071995729	0.361982500
O	0.139004836	0.955015383	0.634151157
O	0.860995164	0.044984617	0.365848843
C	0.326029450	-0.002534993	0.812489766
C	0.673970550	1.002534993	0.187510234
C	0.203100635	0.011730657	0.874058823
C	0.796899365	0.988269343	0.125941177
H	0.085363776	0.970592629	0.845773412
H	0.914636224	0.029407371	0.154226588
C	0.231464085	0.080649882	0.969913202
C	0.768535915	0.919350118	0.030086798
H	0.136635015	0.092212204	0.019241573
H	0.863364985	0.907787796	0.980758427
C	0.380062698	0.136448781	0.005105558
C	0.619937302	0.863551219	0.994894442
C	0.501678093	0.119049981	0.942643628
C	0.498321907	0.880950019	0.057356372
H	0.618908697	0.161130210	0.969231774
H	0.381091303	0.838869790	0.030768226
C	0.476351569	0.050072532	0.846780107
C	0.523648431	0.949927468	0.153219893
H	0.572145358	0.037166083	0.798396091
H	0.427854642	0.962833917	0.201603909
C	0.406872204	0.215331256	0.105248256
C	0.593127796	0.784668744	0.894751744
H	0.315430063	0.203468280	0.154653504
H	0.684569937	0.796531720	0.845346496
H	0.399159395	0.299508604	0.089269691

H	0.600840605	0.700491396	0.910730309
H	0.527492298	0.207686136	0.149798067
H	0.472507702	0.792313864	0.850201933

5: Residual dark state

Ru	0.231403845	0.218363254	0.473281563
Ru	0.768596155	0.781636746	0.526718437
S	0.192150546	0.085290783	0.345865821
S	0.807849454	0.914709217	0.654134179
O	0.152954279	0.096343915	0.237530720
O	0.847045721	0.903656085	0.762469280
O	0.209231961	0.971859415	0.359183780
O	0.790768039	0.028140585	0.640816220
N	0.060825766	0.154774883	0.549094901
N	0.939174234	0.845225117	0.450905099
H	0.967453595	0.114789261	0.494456739
H	0.032546405	0.885210739	0.505543261
H	0.012677803	0.219398344	0.594180205
H	0.987322197	0.780601656	0.405819795
H	0.102670149	0.098454560	0.593144758
H	0.897329851	0.901545440	0.406855242
N	0.426952795	0.140336499	0.543537218
N	0.573047205	0.859663501	0.456462782
H	0.492995184	0.107529243	0.486451811
H	0.507004816	0.892470757	0.513548189
H	0.400048962	0.077934885	0.579641533
H	0.599951038	0.922065115	0.420358467
H	0.502488259	0.198496036	0.595463552
H	0.497511741	0.801503935	0.404536448
N	0.405858517	0.300709205	0.412837225
N	0.594141483	0.699290795	0.587162775
H	0.462674550	0.246112253	0.363412501
H	0.537325450	0.753887747	0.636587499
H	0.492816120	0.335977274	0.474670503
H	0.507183880	0.664022726	0.525329497
H	0.359791573	0.361429356	0.375489306
H	0.640208427	0.638570644	0.624510694
N	0.045371425	0.311332455	0.414650110
N	0.954628575	0.688667545	0.585349890
H	0.086587029	0.369678134	0.378011664
H	0.913412971	0.630321866	0.621988336
H	0.994064276	0.350662381	0.476832592
H	0.005935724	0.649337619	0.523167408
H	0.953850779	0.263800022	0.364187646
H	0.046149221	0.736199978	0.635812354
N	0.276634713	0.346422291	0.603308680
N	0.723365287	0.653577709	0.396691320
C	0.278801273	0.452292641	0.593600764
C	0.721198727	0.547707359	0.406399236
H	0.251566784	0.466941308	0.514595367
H	0.748433216	0.533058692	0.485404633
C	0.314218106	0.537967479	0.679224320
C	0.685781894	0.462032521	0.320775680
H	0.311414819	0.623208366	0.669062422
H	0.688585181	0.376791634	0.330937578
C	0.352545960	0.513457962	0.777378117
C	0.647454040	0.486542038	0.222621883
H	0.381833353	0.579813286	0.845865440
H	0.618166647	0.420186714	0.154134560
C	0.353655552	0.403875047	0.788439357
C	0.646344448	0.596124953	0.211560643
C	0.311198162	0.323487514	0.698418945
C	0.688801838	0.676512486	0.301581055
H	0.205386799	0.454111836	0.135800101

H	0.794613201	0.545888164	0.864199899
C	0.162695350	0.567984430	0.030798247
C	0.837304650	0.432015570	0.969201753
H	0.153971425	0.503738117	0.960629278
H	0.846028575	0.496261883	0.039370722
C	0.147070180	0.757830253	0.111480639
C	0.852929820	0.242169747	0.888519361
H	0.128992665	0.843770057	0.106103000
H	0.871007335	0.156229943	0.893897000
C	0.174996638	0.730945403	0.208986792
C	0.825003362	0.269054597	0.791013208
H	0.179692801	0.795923191	0.278305399
H	0.820307199	0.204076809	0.721694601
C	0.138238747	0.676693106	0.020519747
C	0.861761253	0.323306894	0.979480253
C	0.100226762	0.705326550	0.915643542
C	0.899773238	0.294673450	0.084356458
H	0.074399913	0.631027988	0.853908166
H	0.925600087	0.368972012	0.146091834
H	0.199213945	0.753271324	0.897219313
H	0.800786055	0.246728676	0.102780687
H	0.995690007	0.756800673	0.911278713
H	0.004309993	0.243199327	0.088721287
S	0.292364694	0.916328592	0.688735244
S	0.707635306	0.083671408	0.311264756
O	0.253094626	0.804487930	0.700850398
O	0.746905374	0.195512070	0.299149602
O	0.438380583	0.924087461	0.642613778
O	0.561619417	0.075912539	0.357386222
O	0.155258832	0.963922066	0.633551796
O	0.844741168	0.036077934	0.366448204
C	0.333814371	0.000465858	0.814704392
C	0.666185629	0.999534142	0.185295608
C	0.212605205	0.013689443	0.875906715
C	0.787394795	0.986310557	0.124093285
H	0.095363864	0.971620575	0.846057094
H	0.904636136	0.028379425	0.153942906
C	0.242791833	0.081714769	0.973928210
C	0.757208167	0.918285231	0.026071790
H	0.149721325	0.092005735	0.023311070
H	0.850278675	0.907994265	0.976688930
C	0.391853685	0.137329629	0.011959399
C	0.608146315	0.862670371	0.988040601
C	0.511616098	0.121000578	0.949770191
C	0.488383902	0.878999422	0.050229809
H	0.629213271	0.162650085	0.978529221
H	0.370786729	0.837349915	0.021470779
C	0.484053368	0.053129086	0.851476010
C	0.515946632	0.946870914	0.148523990
H	0.578267548	0.040700133	0.803203594
H	0.421732452	0.959299867	0.196796406
C	0.420107197	0.214486566	0.115346825
C	0.579892803	0.785513434	0.884653175
H	0.337594621	0.193772914	0.165846949
H	0.662405379	0.806227086	0.834153051
H	0.399167427	0.299822355	0.105772827
H	0.600832573	0.700177645	0.894227173
H	0.543800289	0.213009666	0.154974270
H	0.456199711	0.786990334	0.845025730

5: η^2 -(OS)O

Ru	0.223542749	0.226594537	0.466550578
Ru	0.776457251	0.773405463	0.533449422
S	0.148683443	0.052546715	0.359911757

S	0.851316557	0.947453285	0.640088243
O	0.189687993	0.146161649	0.307564470
O	0.810312007	0.853838351	0.692435530
O	0.268223593	0.968031080	0.362567889
O	0.731776407	0.031968920	0.637432111
N	0.045587292	0.168186370	0.544378694
N	0.954412708	0.831813630	0.455621306
H	0.949144268	0.127332718	0.493906963
H	0.050855732	0.872667282	0.506093037
H	0.002182675	0.235787604	0.589089513
H	0.997817325	0.764212396	0.410910487
H	0.092273321	0.114262390	0.589626531
H	0.907726679	0.885737610	0.410373469
N	0.415926955	0.138956053	0.525939177
N	0.584073045	0.861043947	0.474060823
H	0.471913316	0.102160152	0.465033097
H	0.528086684	0.897839848	0.534966903
H	0.378651278	0.078994523	0.562063031
H	0.621348722	0.921005477	0.437936969
H	0.499723398	0.191906287	0.576982977
H	0.500276602	0.808093713	0.423017023
N	0.404328398	0.307045505	0.413256350
N	0.595671602	0.692954495	0.586743650
H	0.456701744	0.246673938	0.365561677
H	0.543298256	0.753326062	0.634438323
H	0.491077729	0.340564869	0.475551329
H	0.508922271	0.659435131	0.524448671
H	0.362382936	0.367417361	0.374064437
H	0.637617064	0.632582639	0.625935563
N	0.042698039	0.325177296	0.414422141
N	0.957301961	0.674822704	0.585577859
H	0.084306830	0.381791507	0.376077409
H	0.915693170	0.618208493	0.623922591
H	0.991974108	0.365100795	0.476316956
H	0.008025892	0.634899205	0.523683044
H	0.954535663	0.273289806	0.364920411
H	0.045464337	0.726710194	0.635079589
N	0.276734500	0.339086369	0.600137373
N	0.723265500	0.660913631	0.399862627
C	0.282962109	0.446864905	0.594623989
C	0.717037891	0.553135095	0.405376011
H	0.254590750	0.465647478	0.517316250
H	0.745409250	0.534352522	0.482683750
C	0.323813837	0.529181438	0.682229311
C	0.676186163	0.470818562	0.317770689
H	0.324775720	0.615110103	0.674194736
H	0.675224280	0.384889897	0.325805264
C	0.362064761	0.500889993	0.778741835
C	0.637935239	0.499110007	0.221258165
H	0.395173802	0.564373717	0.849077551
H	0.604826198	0.435626283	0.150922449
C	0.358001607	0.390093403	0.785508004
C	0.641998393	0.609906597	0.214491996
C	0.312459943	0.312187937	0.694000304
C	0.687540057	0.687812063	0.305999696
H	0.305832646	0.224373500	0.695238295
H	0.694167354	0.775626500	0.304761705
C	0.405506506	0.354220962	0.885894658
C	0.594493494	0.645779038	0.114105342
H	0.390315854	0.420179095	0.951972368
H	0.609684146	0.579820905	0.048027632
H	0.532863673	0.334424974	0.894934270
H	0.467136327	0.665575026	0.105065730
H	0.336446584	0.279669689	0.889740170
H	0.663553416	0.720330311	0.110259830
S	0.223781215	0.587675848	0.337559068

S	0.776218785	0.412324152	0.662440932
O	0.078785374	0.623902748	0.380174088
O	0.921214626	0.376097252	0.619825912
O	0.369266883	0.648149617	0.396958008
O	0.630733117	0.351850383	0.603041992
O	0.233745098	0.467379964	0.321536455
O	0.766254902	0.532620036	0.678463545
C	0.202921836	0.620107024	0.212056977
C	0.797078164	0.379892976	0.787943023
C	0.192808662	0.537386676	0.123437301
C	0.807191338	0.462613324	0.876562699
H	0.202553666	0.451842215	0.131752147
H	0.797446334	0.548157785	0.868247853
C	0.166055391	0.564963155	0.025766255
C	0.833944609	0.435036845	0.974233745
H	0.154023091	0.500013788	0.955897204
H	0.845976909	0.499986212	0.044102796
C	0.163531157	0.756205213	0.105754815
C	0.836468843	0.243794787	0.894245185
H	0.152408204	0.842446625	0.099505002
H	0.847591796	0.157553375	0.900494998
C	0.191641785	0.730303835	0.203678518
C	0.808358215	0.269696165	0.796321482
H	0.204063433	0.795887614	0.273167825
H	0.795936567	0.204112386	0.726832175
C	0.147103026	0.674021990	0.015061289
C	0.852896974	0.325978010	0.984938711
C	0.104895862	0.701584649	0.909997608
C	0.895104138	0.298415351	0.090002392
H	0.102918060	0.628193067	0.847846712
H	0.897081940	0.371806933	0.152153288
H	0.187931635	0.764556287	0.896058245
H	0.812068365	0.235443713	0.103941755
H	0.985264820	0.735586874	0.901260727
H	0.014735180	0.264413126	0.098739273
S	0.298678327	0.924540475	0.690265612
S	0.701321673	0.075459525	0.309734388
O	0.190806514	0.833770849	0.696800480
O	0.809193486	0.166229151	0.303199520
O	0.454451942	0.889864544	0.665211330
O	0.545548058	0.110135456	0.334788670
O	0.224673955	0.995003582	0.620375040
O	0.775326045	0.004996418	0.379624960
C	0.335036398	0.007306143	0.817157815
C	0.664963602	0.992693857	0.182842185
C	0.210965110	0.021217340	0.875947355
C	0.789034890	0.978782660	0.124052645
H	0.094569666	0.979179443	0.843252793
H	0.905430334	0.020820557	0.156747207
C	0.238802548	0.086486153	0.975363692
C	0.761197452	0.913513847	0.024636308
H	0.142436391	0.097364534	0.022161873
H	0.857563609	0.902635466	0.977838127
C	0.389687720	0.137631187	0.017656286
C	0.610312280	0.862368813	0.982343714
C	0.511894306	0.121328926	0.957345636
C	0.488105694	0.878671074	0.042654364
H	0.630258194	0.160138549	0.989484587
H	0.369741806	0.839861451	0.010515413
C	0.486036791	0.057147853	0.857420984
C	0.513963209	0.942852147	0.142579016
H	0.581432451	0.044088979	0.810017066
H	0.418567549	0.955911021	0.189982934
C	0.418600044	0.208982734	0.124023060
C	0.581399956	0.791017266	0.875976940
H	0.348178001	0.178807656	0.176745759

H	0.651821999	0.821192344	0.823254241
H	0.384791357	0.294118313	0.121186776
H	0.615208643	0.705881687	0.878813224
H	0.545684569	0.212246689	0.158503039
H	0.454315431	0.787753311	0.841496961

5: η^1 -OSO

Ru	0.228433759	0.235599912	0.475466491
Ru	0.771566241	0.764400088	0.524533509
S	0.183283398	1.006037057	0.306696052
S	0.816716602	-0.006037057	0.693303948
O	0.177883822	0.128890609	0.342421691
O	0.822116178	0.871109391	0.657578309
O	0.241362123	0.945097702	0.387975872
O	0.758637877	0.054902298	0.612024128
N	0.052649833	0.161261167	0.538543247
N	0.947350167	0.838738833	0.461456753
H	0.967403230	0.116439801	0.480648919
H	0.032596770	0.883560199	0.519351081
H	-0.006971766	0.221737560	0.580872529
H	1.006971766	0.778262440	0.419127471
H	0.096851418	0.107538988	0.584601425
H	0.903148582	0.892461012	0.415398575
N	0.411379119	0.139706042	0.532950243
N	0.588620881	0.860293958	0.467049757
H	0.470653523	0.103905494	0.473412272
H	0.529346477	0.896094506	0.526587728
H	0.371650808	0.077068222	0.564456815
H	0.628349192	0.922931778	0.435543185
H	0.496635696	0.188175308	0.587187113
H	0.503364304	0.811824692	0.412812887
N	0.410951037	0.311409772	0.417876551
N	0.589048963	0.688590228	0.582123449
H	0.463149170	0.251913896	0.369849231
H	0.536850830	0.748086104	0.630150769
H	0.498612176	0.344346417	0.479965173
H	0.501387824	0.655653583	0.520034827
H	0.371357859	0.372023156	0.378308702
H	0.628642141	0.627976844	0.621691298
N	0.044944630	0.329807135	0.417336699
N	0.955055370	0.670192865	0.582663301
H	0.085600715	0.385991392	0.378157235
H	0.914399285	0.614008608	0.621842765
H	0.993050514	0.370589757	0.478381946
H	0.006949486	0.629410243	0.521618054
H	0.955426537	0.279256949	0.367987688
H	0.044573463	0.720743051	0.632012312
N	0.275836602	0.351594892	0.605839948
N	0.724163398	0.648405108	0.394160052
C	0.282687309	0.459523491	0.601078816
C	0.717312691	0.540476509	0.398921184
H	0.256156699	0.477811191	0.523419718
H	0.743843301	0.522188809	0.476580282
C	0.321706243	0.541775407	0.689011856
C	0.678293757	0.458224593	0.310988144
H	0.322058913	0.628063855	0.681861510
H	0.677941087	0.371936145	0.318138490
C	0.358764488	0.512767921	0.785424570
C	0.641235512	0.487232079	0.214575430
H	0.390776795	0.576093210	0.856090065
H	0.609223205	0.423906790	0.143909935
C	0.354585496	0.401789452	0.791795539
C	0.645414504	0.598210548	0.208204461
C	0.309295665	0.324703277	0.699862506

C	0.690704335	0.675296723	0.300137494	C	0.636343109	0.868512327	0.972451745
H	0.301599609	0.236760675	0.700305383	C	0.487231414	0.124920242	0.968224716
H	0.698400391	0.763239325	0.299694617	C	0.512768586	0.875079758	0.031775284
C	0.402647260	0.364547287	0.891680409	H	0.600995819	0.170656772	1.001193049
C	0.597352740	0.635452713	0.108319591	H	0.399004181	0.829343228	-0.001193049
H	0.400788233	0.432530136	0.958586770	C	0.468911526	0.060457386	0.868428642
H	0.599211767	0.567469864	0.041413230	C	0.531088474	0.939542614	0.131571358
H	0.525678866	0.335887629	0.896165110	H	0.566385146	0.055108281	0.822749100
H	0.474321134	0.664112371	0.103834890	H	0.433614854	0.944891719	0.177250900
H	0.324718643	0.295384818	0.898674363	C	0.383446258	0.203354127	0.133691571
H	0.675281357	0.704615182	0.101325637	C	0.616553742	0.796645873	0.866308429
S	0.223402423	0.586083668	0.332365842	H	0.301388593	0.176595012	0.181652399
S	0.776597577	0.413916332	0.667634158	H	0.698611407	0.823404988	0.818347601
O	0.085753693	0.626099751	0.381415318	H	0.358508270	0.289528141	0.129116130
O	0.914246307	0.373900249	0.618584682	H	0.641491730	0.710471859	0.870883870
O	0.374319405	0.644596120	0.384798624	H	0.506646744	0.203372681	0.174718763
O	0.625680595	0.355403880	0.615201376	H	0.493353256	0.796627319	0.825281237
O	0.231159101	0.465550742	0.316451125				
O	0.768840899	0.534449258	0.683548875				
C	0.189545239	0.616648795	0.205718315				
C	0.810454761	0.383351205	0.794281685				
C	0.198499283	0.536970997	0.117187561				
C	0.801500717	0.463029003	0.882812439				
H	0.226729484	0.453195793	0.125159363				
H	0.773270516	0.546804207	0.874840637				
C	0.165996258	0.564541117	0.019612199				
C	0.834003742	0.435458883	0.980387801				
H	0.166354730	0.501229926	0.949628678				
H	0.833645270	0.498770074	0.050371322				
C	0.120262694	0.750268900	0.099090614				
C	0.879737306	0.249731100	0.900909386				
H	0.086939114	0.833705073	0.092376789				
H	0.913060886	0.166294927	0.907623211				
C	0.150699143	0.723556649	0.196608989				
C	0.849300857	0.276443351	0.803391011				
H	0.143557129	0.784760186	0.266888655				
H	0.856442871	0.215239814	0.733111345				
C	0.125948459	0.670915169	0.008641312				
C	0.874051541	0.329084831	0.991358688				
C	0.085237192	0.698593929	0.903434869				
C	0.914762808	0.301406071	0.096565131				
H	0.063324029	0.623856210	0.841946930				
H	0.936675971	0.376143790	0.158053070				
H	0.181069618	0.749266819	0.884797716				
H	0.818930382	0.250733181	0.115202284				
H	0.976894495	0.746485667	0.898907377				
H	0.023105505	0.253514333	0.101092623				
S	0.295925774	0.920361308	0.697556207				
S	0.704074226	0.079638692	0.302443793				
O	0.235386653	0.811300184	0.705116926				
O	0.764613347	0.188699816	0.294883074				
O	0.452450944	0.919023040	0.662956702				
O	0.547549056	0.080976960	0.337043298				
O	0.177621611	0.977665819	0.636577390				
O	0.822378389	0.022334181	0.363422610				
C	0.325224224	0.000733545	0.826358793				
C	0.674775776	0.999266455	0.173641207				
C	0.201063149	0.004368820	0.884887341				
C	0.798936851	0.995631180	0.115112659				
H	0.089860650	0.955496477	0.852069324				
H	0.910139350	0.044503523	0.147930676				
C	0.220859850	0.069510106	0.984369686				
C	0.779140150	0.930489894	0.015630314				
H	0.123862028	0.072336839	0.030547320				
H	0.876137972	0.927663161	0.969452680				
C	0.363656891	0.131487673	0.027548255				

Appendix 2: NEB Pathway Geometries

The geometries of every image for both PW-NEB pathways: **I** and **II**, are presented below. All geometries are in Åndstroms.

Pathway I:

140

Ru	1.0307734251	1.5645014229	6.1124343982
Ru	-1.0307734251	-1.5645014229	-6.1124343982
S	1.0042338695	0.2089053155	4.5061094020
S	-1.0042338695	-0.2089053155	-4.5061094020
O	0.9022785985	0.5977100399	3.0968849028
O	-0.9022785985	-0.5977100399	-3.0968849028
O	1.1406199994	-1.2309204069	4.7179211839
O	-1.1406199994	1.2309204069	-4.7179211839
N	1.4399889531	3.0039414115	-5.7695763328
N	-1.4399889531	-3.0039414115	5.7695763328
H	-1.2324308840	0.2414234330	6.3842225055
H	1.2324308840	-0.2414234330	-6.3842225055
H	0.9322972843	3.6833138579	-5.1804470099
H	-0.9322972843	-3.6833138579	5.1804470099
H	1.7011145737	2.1707577806	-5.2143930889
H	-1.7011145737	-2.1707577806	5.2143930889
N	4.5600742237	2.8700120828	-5.8003857256
N	-4.5600742237	-2.8700120828	5.8003857256
H	-5.1720472816	0.1854968036	6.3464254310
H	5.1720472816	-0.1854968036	-6.3464254310
H	-3.3733420059	3.4687961695	-5.1294192792
H	3.3733420059	-3.4687961695	5.1294192792
H	4.2885810117	1.9914478881	-5.3327263579
H	-4.2885810117	-1.9914478881	5.3327263579
N	2.6066474605	2.7493124602	5.3148789272
N	-2.6066474605	-2.7493124602	-5.3148789272
H	3.2127934616	2.2108744186	4.6829291055
H	-3.2127934616	-2.2108744186	-4.6829291055
H	3.2041326780	3.0375633328	6.1123929755
H	-3.2041326780	-3.0375633328	-6.1123929755
H	2.2716031051	3.5943767496	4.8222951567
H	-2.2716031051	-3.5943767496	-4.8222951567
N	-0.4564132381	2.8483172375	5.3134990122
N	0.4564132381	-2.8483172375	-5.3134990122
H	-0.0520724352	3.6690817604	4.8306025620
H	0.0520724352	-3.6690817604	-4.8306025620
H	-1.0310634340	3.1813482889	6.1075422658
H	1.0310634340	-3.1813482889	-6.1075422658
H	-1.1151867081	2.3823274037	4.6675271171
H	1.1151867081	-2.3823274037	-4.6675271171
N	3.0880853750	5.2861170622	-5.1109158138
N	-3.0880853750	-5.2861170622	5.1109158138
C	3.1067777390	6.6246118140	-5.2714119904
C	-3.1067777390	-6.6246118140	5.2714119904
H	3.0677473581	6.9935619677	-6.3009422011
H	-3.0677473581	-6.9935619677	6.3009422011
C	3.3126576352	-4.9729105849	-4.1877851185
C	-3.3126576352	4.9729105849	4.1877851185
H	3.3050475416	-3.8897163027	-4.3458796425
H	-3.3050475416	3.8897163027	4.3458796425
C	3.3842003995	-5.5055967367	-2.9021573841
C	-3.3842003995	5.5055967367	2.9021573841
H	3.4443203150	-4.8419470701	-2.0322309361
H	-3.4443203150	4.8419470701	2.0322309361

C	3.2405207458	5.5707476566	-2.7200736189
C	-3.2405207458	-5.5707476566	2.7200736189
C	3.1427273574	4.7811028390	-3.8665732252
C	-3.1427273574	-4.7811028390	3.8665732252
H	3.1158669036	3.6894785406	-3.7904198444
H	-3.1158669036	-3.6894785406	3.7904198444
C	3.3556190562	4.9337685024	-1.3698829895
C	-3.3556190562	-4.9337685024	1.3698829895
H	3.2753298801	5.6916152555	-0.5738387511
H	-3.2753298801	-5.6916152555	0.5738387511
H	4.3290248110	4.4197445975	-1.2659169399
H	-4.3290248110	-4.4197445975	1.2659169399
H	2.5734226743	4.1700017965	-1.2153683871
H	-2.5734226743	-4.1700017965	1.2153683871
S	1.2031016948	-5.9233441507	4.3814886999
S	-1.2031016948	5.9233441507	-4.3814886999
O	-0.0637572731	-5.5175220399	5.0082682656
O	0.0637572731	5.5175220399	-5.0082682656
O	2.3805220426	-5.3800523252	5.0731113295
O	-2.3805220426	5.3800523252	-5.0731113295
O	1.1475552157	5.0813705394	4.1744756821
O	-1.1475552157	-5.0813705394	-4.1744756821
C	1.2050597826	-5.1658731568	2.7683094749
C	-1.2050597826	5.1658731568	-2.7683094749
C	1.3461039035	-5.9186194666	1.6041664895
C	-1.3461039035	5.9186194666	-1.6041664895
H	1.3196607209	5.4571403058	1.6724642550
H	-1.3196607209	-5.4571403058	-1.6724642550
C	1.3089819905	-5.2731843039	0.3637352810
C	-1.3089819905	5.2731843039	-0.3637352810
H	1.3804314400	-5.8639833084	-0.5549966361
H	-1.3804314400	5.8639833084	0.5549966361
C	1.0095975166	-3.1497804438	1.4525758126
C	-1.0095975166	3.1497804438	-1.4525758126
H	0.8726436216	-2.0629314167	1.4131161584
H	-0.8726436216	2.0629314167	-1.4131161584
C	1.0466527546	-3.7763835407	2.6950476920
C	-1.0466527546	3.7763835407	-2.6950476920
H	0.9481796401	-3.1737806822	3.6038905912
H	-0.9481796401	3.1737806822	-3.6038905912
C	1.1282786146	-3.8885328395	0.2617083523
C	-1.1282786146	3.8885328395	-0.2617083523
C	1.0407021362	-3.2222968421	-1.0798370712
C	-1.0407021362	3.2222968421	1.0798370712
H	1.1254112717	-3.9555992246	-1.8974603306
H	-1.1254112717	3.9555992246	1.8974603306
H	1.8281424127	-2.4601676115	-1.2280167590
H	-1.8281424127	2.4601676115	1.2280167590
H	0.0791825484	-2.6927101259	-1.2017909255
H	-0.0791825484	2.6927101259	1.2017909255
S	3.0590109882	-0.3040914291	-4.0222734935
S	-3.0590109882	0.3040914291	4.0222734935
O	2.8252133241	-1.7432783001	-3.8439107828
O	-2.8252133241	1.7432783001	3.8439107828
O	4.3536840870	-0.0066881158	-4.6602903590
O	-4.3536840870	0.0066881158	4.6602903590
O	1.9294162659	0.3558438575	-4.7055637870
O	-1.9294162659	-0.3558438575	4.7055637870
C	3.1384478889	0.4361840134	-2.4133312281
C	-3.1384478889	-0.4361840134	2.4133312281
C	1.9827047293	0.4593127215	-1.6259551195
C	-1.9827047293	-0.4593127215	1.6259551195
H	1.0551167539	0.0123609986	-2.0011288060
H	-1.0551167539	-0.0123609986	2.0011288060
C	2.0242040110	1.0852276119	-0.3822409719
C	-2.0242040110	-1.0852276119	0.3822409719

H	1.1298030437	1.1062305254	0.2496401679
H	-1.1298030437	-1.1062305254	-0.2496401679
C	3.1969111225	1.6971866985	0.0851897478
C	-3.1969111225	-1.6971866985	-0.0851897478
C	-4.0934301855	1.6361316900	-0.7147417761
C	4.0934301855	-1.6361316900	0.7147417761
H	-3.1665667888	2.0997866866	-0.3642558944
H	3.1665667888	-2.0997866866	0.3642558944
C	4.3277556465	1.0082863804	-1.9579806565
C	-4.3277556465	-1.0082863804	1.9579806565
H	-3.2086820266	0.9647761481	-2.5786933585
H	3.2086820266	-0.9647761481	2.5786933585
C	3.2155076494	2.4334255534	1.3886838877
C	-3.2155076494	-2.4334255534	-1.3886838877
H	2.3640195198	2.1394709361	2.0228318506
H	-2.3640195198	-2.1394709361	-2.0228318506
H	3.1480376517	3.5241538269	1.2120422373
H	-3.1480376517	-3.5241538269	-1.2120422373
H	-4.2863442548	2.2470467509	1.9452269528
H	4.2863442548	-2.2470467509	-1.9452269528

140

Ru	0.9592289556	1.5194958310	6.1437627998
Ru	-0.9592289556	-1.5194958310	-6.1437627998
S	0.9814479750	0.1668303543	4.5441605699
S	-0.9814479750	-0.1668303543	-4.5441605699
O	0.7693525847	0.6638265357	3.1908422487
O	-0.7693525847	-0.6638265357	-3.1908422487
O	1.3844793121	-1.2369130399	4.6415242546
O	-1.3844793121	1.2369130399	-4.6415242546
N	1.3002524355	3.0657124110	-5.7523972310
N	-1.3002524355	-3.0657124110	5.7523972310
H	-1.3855839929	0.2995030516	6.4162377056
H	1.3855839929	-0.2995030516	-6.4162377056
H	0.8295885946	3.8031823036	-5.1992338289
H	-0.8295885946	-3.8031823036	5.1992338289
H	1.5620323977	2.2594019347	-5.1666928573
H	-1.5620323977	-2.2594019347	5.1666928573
N	4.5629587007	2.8156118388	-5.8843502302
N	-4.5629587007	-2.8156118388	5.8843502302
H	-5.1365291797	0.3917957794	6.2483255313
H	5.1365291797	-0.3917957794	-6.2483255313
H	-3.5128187800	3.3542426642	-5.0922579250
H	3.5128187800	-3.3542426642	5.0922579250
H	4.4757298837	1.8416493059	-5.5679628796
H	-4.4757298837	-1.8416493059	5.5679628796
N	2.5363436601	2.7187332622	5.3547470589
N	-2.5363436601	-2.7187332622	-5.3547470589
H	3.1279540951	2.1479559075	4.7297227448
H	-3.1279540951	-2.1479559075	-4.7297227448
H	3.1382558223	3.0197068334	6.1436120492
H	-3.1382558223	-3.0197068334	-6.1436120492
H	2.2037988463	3.5594156017	4.8515419717
H	-2.2037988463	-3.5594156017	-4.8515419717
N	-0.4728685787	2.8503855809	5.3411856196
N	0.4728685787	-2.8503855809	-5.3411856196
H	-0.0398293517	3.6560808720	4.8550632537
H	0.0398293517	-3.6560808720	-4.8550632537
H	-1.0571688853	3.2112199429	6.1143276104
H	1.0571688853	-3.2112199429	-6.1143276104
H	-1.1187294485	2.3848280792	4.6755371332
H	1.1187294485	-2.3848280792	-4.6755371332
N	3.0675362862	5.2256825327	-5.1019939205
N	-3.0675362862	-5.2256825327	5.1019939205
C	3.0986815417	6.5619287472	-5.2582067286

C	-3.0986815417	-6.5619287472	5.2582067286
H	3.0371309253	6.9334666374	-6.2854695043
H	-3.0371309253	-6.9334666374	6.2854695043
C	3.3436592450	-5.0464882437	-4.1715952831
C	-3.3436592450	5.0464882437	4.1715952831
H	3.3340001452	-3.9637716026	-4.3270358881
H	-3.3340001452	3.9637716026	4.3270358881
C	3.4561796545	-5.5921983550	-2.8949797788
C	-3.4561796545	5.5921983550	2.8949797788
H	3.5539404329	-4.9384935806	-2.0226278065
H	-3.5539404329	4.9384935806	2.0226278065
C	3.3049136781	5.4825212345	-2.7225313358
C	-3.3049136781	-5.4825212345	2.7225313358
C	3.1496483614	4.7028247553	-3.8669805590
C	-3.1496483614	-4.7028247553	3.8669805590
H	3.0970052777	3.6098418801	-3.7995822870
H	-3.0970052777	-3.6098418801	3.7995822870
C	3.4849914558	4.8291165270	-1.3913057149
C	-3.4849914558	-4.8291165270	1.3913057149
H	3.3249500001	5.5512641981	-0.5757873357
H	-3.3249500001	-5.5512641981	0.5757873357
H	4.5129415848	4.4314654679	-1.3011401079
H	-4.5129415848	-4.4314654679	1.3011401079
H	2.7994619586	3.9752373537	-1.2601765513
H	-2.7994619586	-3.9752373537	1.2601765513
S	1.2205328057	-6.0126877373	4.3492963833
S	-1.2205328057	6.0126877373	-4.3492963833
O	-0.0432220465	-5.5914935923	4.9755092303
O	0.0432220465	5.5914935923	-4.9755092303
O	2.4031826908	-5.5007780217	5.0511688851
O	-2.4031826908	5.5007780217	-5.0511688851
O	1.1320385238	4.9928680409	4.1236536485
O	-1.1320385238	-4.9928680409	-4.1236536485
C	1.2351315071	-5.2550473293	2.7368173822
C	-1.2351315071	5.2550473293	-2.7368173822
C	1.4136063136	-6.0196537820	1.5852778415
C	-1.4136063136	6.0196537820	-1.5852778415
H	1.4160609978	5.3613411635	1.6755779269
H	-1.4160609978	-5.3613411635	-1.6755779269
C	1.3660590632	-5.3975496403	0.3345767784
C	-1.3660590632	5.3975496403	-0.3345767784
H	1.4619635861	-6.0004996171	-0.5737674894
H	-1.4619635861	6.0004996171	0.5737674894
C	0.9874165108	-3.2685664252	1.3868821456
C	-0.9874165108	3.2685664252	-1.3868821456
H	0.8057430363	-2.1899400110	1.3209578772
H	-0.8057430363	2.1899400110	-1.3209578772
C	1.0374899940	-3.8718626146	2.6412116929
C	-1.0374899940	3.8718626146	-2.6412116929
H	0.9167508241	-3.2598073366	3.5409947103
H	-0.9167508241	3.2598073366	-3.5409947103
C	1.1342537734	-4.0224970040	0.2090792894
C	-1.1342537734	4.0224970040	-0.2090792894
C	1.0132396451	-3.3837717399	-1.1422471072
C	-1.0132396451	3.3837717399	1.1422471072
H	1.0157989237	-4.1397116546	-1.9438340277
H	-1.0157989237	4.1397116546	1.9438340277
H	1.8316915195	-2.6703116296	-1.3525111107
H	-1.8316915195	2.6703116296	1.3525111107
H	0.0766142257	-2.8050542090	-1.2276910191
H	-0.0766142257	2.8050542090	1.2276910191
S	3.0962561366	-0.3578982826	-3.9526559972
S	-3.0962561366	0.3578982826	3.9526559972
O	2.4837008644	-1.6735120073	-3.7406094674
O	-2.4837008644	1.6735120073	3.7406094674
O	4.4982674386	-0.4435416447	-4.4021249219

O	-4.4982674386	0.4435416447	4.4021249219
O	2.2976949825	0.5069692891	-4.8431661612
O	-2.2976949825	-0.5069692891	4.8431661612
C	3.1338860152	0.4234325332	-2.3609502938
C	-3.1338860152	-0.4234325332	2.3609502938
C	1.9720419633	0.3999524481	-1.5820360425
C	-1.9720419633	-0.3999524481	1.5820360425
H	1.0737828805	-0.0994069148	-1.9618285360
H	-1.0737828805	0.0994069148	1.9618285360
C	1.9830986353	1.0098075706	-0.3298315871
C	-1.9830986353	-1.0098075706	0.3298315871
H	1.0852064721	0.9850581924	0.2984299804
H	-1.0852064721	-0.9850581924	-0.2984299804
C	3.1366532546	1.6412901362	0.1613744278
C	-3.1366532546	-1.6412901362	-0.1613744278
C	-4.1480570841	1.6338201704	-0.6340614523
C	4.1480570841	-1.6338201704	0.6340614523
H	-3.2341475404	2.1060827813	-0.2581361567
H	3.2341475404	-2.1060827813	0.2581361567
C	4.2988782692	1.0325525738	-1.8919094106
C	-4.2988782692	-1.0325525738	1.8919094106
H	-3.2303772080	1.0152247738	-2.5042268600
H	3.2303772080	-1.0152247738	2.5042268600
C	3.1278858825	2.3240805053	1.4946825285
C	-3.1278858825	-2.3240805053	-1.4946825285
H	2.3436199788	1.9104558141	2.1485265395
H	-2.3436199788	-1.9104558141	-2.1485265395
H	2.9260233602	3.4059188365	1.3737383570
H	-2.9260233602	-3.4059188365	-1.3737383570
H	-4.3357521733	2.2220599610	2.0045747531
H	4.3357521733	-2.2220599610	-2.0045747531

140

Ru	0.9323832001	1.5819007987	6.0367645280
Ru	-0.9323832001	-1.5819007987	-6.0367645280
S	0.6128392038	-0.3056636990	4.6615432657
S	-0.6128392038	0.3056636990	-4.6615432657
O	0.9800525430	1.0288135118	4.0030917997
O	-0.9800525430	-1.0288135118	-4.0030917997
O	1.6775005198	-1.3201351949	4.6165527604
O	-1.6775005198	1.3201351949	-4.6165527604
N	1.2854839475	3.1211829661	-5.8035440255
N	-1.2854839475	-3.1211829661	5.8035440255
H	-1.4292359396	0.3415011442	6.4040014194
H	1.4292359396	-0.3415011442	-6.4040014194
H	0.8364767576	3.8547922088	-5.2262028658
H	-0.8364767576	-3.8547922088	5.2262028658
H	1.5884645504	2.3200415956	-5.2270449884
H	-1.5884645504	-2.3200415956	5.2270449884
N	4.5567277621	2.6808438996	-6.0371848438
N	-4.5567277621	-2.6808438996	6.0371848438
H	-5.1765145277	0.4443762940	6.1031460338
H	5.1765145277	-0.4443762940	-6.1031460338
H	-3.9225032485	3.2262861448	-5.2026149832
H	3.9225032485	-3.2262861448	5.2026149832
H	4.9708755879	1.8609919133	-5.5734228316
H	-4.9708755879	-1.8609919133	5.5734228316
N	2.5467660130	2.7700470663	5.3481087016
N	-2.5467660130	-2.7700470663	-5.3481087016
H	3.1119236177	2.1623092724	4.7269107685
H	-3.1119236177	-2.1623092724	-4.7269107685
H	3.1464285049	3.0438057170	6.1489924621
H	-3.1464285049	-3.0438057170	-6.1489924621
H	2.2389490729	3.6165272795	4.8376618812
H	-2.2389490729	-3.6165272795	-4.8376618812

N	-0.4860673827	2.9105412424	5.3379182969
N	0.4860673827	-2.9105412424	-5.3379182969
H	-0.0683215776	3.7200098181	4.8411126226
H	0.0683215776	-3.7200098181	-4.8411126226
H	-1.0699926272	3.2446822831	6.1237536564
H	1.0699926272	-3.2446822831	-6.1237536564
H	-1.1152028283	2.4014290704	4.6801507074
H	1.1152028283	-2.4014290704	-4.6801507074
N	3.0676373227	5.1585439234	-5.1404709551
N	-3.0676373227	-5.1585439234	5.1404709551
C	3.0982642529	6.5084576116	-5.2867651702
C	-3.0982642529	-6.5084576116	5.2867651702
H	3.0376973008	6.8959891625	-6.3064535569
H	-3.0376973008	-6.8959891625	6.3064535569
C	3.3415658748	-5.0958647847	-4.2039022450
C	-3.3415658748	5.0958647847	4.2039022450
H	3.3321967764	-4.0131276915	-4.3688429912
H	-3.3321967764	4.0131276915	4.3688429912
C	3.4524414656	-5.6274895153	-2.9215343113
C	-3.4524414656	5.6274895153	2.9215343113
H	3.5475899361	-4.9701871704	-2.0508656407
H	-3.5475899361	4.9701871704	2.0508656407
C	3.3019410564	5.4481939919	-2.7516281818
C	-3.3019410564	-5.4481939919	2.7516281818
C	3.1499642771	4.6549690285	-3.8909729460
C	-3.1499642771	-4.6549690285	3.8909729460
H	3.0972136321	3.5641080807	-3.8000062534
H	-3.0972136321	-3.5641080807	3.8000062534
C	3.4824494054	4.8100900991	-1.4120784682
C	-3.4824494054	-4.8100900991	1.4120784682
H	3.3210287944	5.5430640025	-0.6056635339
H	-3.3210287944	-5.5430640025	0.6056635339
H	4.5113463561	4.4171806534	-1.3145604996
H	-4.5113463561	-4.4171806534	1.3145604996
H	2.7978739897	3.9581315677	-1.2684379991
H	-2.7978739897	-3.9581315677	1.2684379991
S	1.2070625885	-6.0402199001	4.3456584572
S	-1.2070625885	6.0402199001	-4.3456584572
O	-0.0517443303	-5.6051896835	4.9755319080
O	0.0517443303	5.6051896835	-4.9755319080
O	2.3970553203	-5.5759328743	5.0582624768
O	-2.3970553203	5.5759328743	-5.0582624768
O	1.0824963850	4.9677002195	4.0904295900
O	-1.0824963850	-4.9677002195	-4.0904295900
C	1.2327213196	-5.2646579879	2.7404681280
C	-1.2327213196	5.2646579879	-2.7404681280
C	1.4115801658	-6.0254222311	1.5862581788
C	-1.4115801658	6.0254222311	-1.5862581788
H	1.4107543009	5.3551724619	1.6743804890
H	-1.4107543009	-5.3551724619	-1.6743804890
C	1.3669705458	-5.4015461051	0.3367869716
C	-1.3669705458	5.4015461051	-0.3367869716
H	1.4631495492	-6.0026741159	-0.5726944469
H	-1.4631495492	6.0026741159	0.5726944469
C	0.9904620418	-3.2762863300	1.3945577801
C	-0.9904620418	3.2762863300	-1.3945577801
H	0.8102031879	-2.1976083783	1.3260307387
H	-0.8102031879	2.1976083783	-1.3260307387
C	1.0395768536	-3.8808920478	2.6487552715
C	-1.0395768536	3.8808920478	-2.6487552715
H	0.9304981954	-3.2725170488	3.5525865854
H	-0.9304981954	3.2725170488	-3.5525865854
C	1.1358828054	-4.0264774752	0.2145327874
C	-1.1358828054	4.0264774752	-0.2145327874
C	1.0136984834	-3.3861408921	-1.1362450854
C	-1.0136984834	3.3861408921	1.1362450854

H	1.0157332826	-4.1409710197	-1.9388567562
H	-1.0157332826	4.1409710197	1.9388567562
H	1.8304321838	-2.6709748903	-1.3473429717
H	-1.8304321838	2.6709748903	1.3473429717
H	0.0734125985	-2.8126878003	-1.2192055222
H	-0.0734125985	2.8126878003	1.2192055222
S	3.1048341621	-0.3582506661	-3.9614334782
S	-3.1048341621	0.3582506661	3.9614334782
O	2.3667119570	-1.6123180078	-3.7547022889
O	-2.3667119570	1.6123180078	3.7547022889
O	4.5098800616	-0.5747126105	-4.3203225949
O	-4.5098800616	0.5747126105	4.3203225949
O	2.4334392673	0.5616354126	-4.8948883950
O	-2.4334392673	-0.5616354126	4.8948883950
C	3.1257817934	0.4286628292	-2.3694643547
C	-3.1257817934	-0.4286628292	2.3694643547
C	1.9658692722	0.4051883087	-1.5896929772
C	-1.9658692722	-0.4051883087	1.5896929772
H	1.0757649494	-0.1095594429	-1.9676670463
H	-1.0757649494	0.1095594429	1.9676670463
C	1.9747911905	1.0124239914	-0.3360314125
C	-1.9747911905	-1.0124239914	0.3360314125
H	1.0732919113	0.9916713848	0.2873232971
H	-1.0732919113	-0.9916713848	-0.2873232971
C	3.1284191150	1.6397465053	0.1594355513
C	-3.1284191150	-1.6397465053	-0.1594355513
C	-4.1564029598	1.6342536887	-0.6371725470
C	4.1564029598	-1.6342536887	0.6371725470
H	-3.2424138096	2.1055542855	-0.2594454506
H	3.2424138096	-2.1055542855	0.2594454506
C	4.2895305600	1.0379642714	-1.8973210791
C	-4.2895305600	-1.0379642714	1.8973210791
H	-3.2444742297	1.0216010849	-2.5178223326
H	3.2444742297	-1.0216010849	2.5178223326
C	3.1213853435	2.3172627857	1.4953884824
C	-3.1213853435	-2.3172627857	-1.4953884824
H	2.3491348033	1.9010335837	2.1624660957
H	-2.3491348033	-1.9010335837	-2.1624660957
H	2.9168998054	3.3990567287	1.3776503333
H	-2.9168998054	-3.3990567287	-1.3776503333
H	-4.3400744191	2.2160440446	2.0007934720
H	4.3400744191	-2.2160440446	-2.0007934720

140

Ru	0.9863641277	1.6621502266	6.0555941484
Ru	-0.9863641277	-1.6621502266	-6.0555941484
S	0.6203004736	-0.2349948446	4.7137645980
S	-0.6203004736	0.2349948446	-4.7137645980
O	1.0007605034	1.0611098356	3.9960622041
O	-1.0007605034	-1.0611098356	-3.9960622041
O	1.6705177245	-1.2714529851	4.6284915681
O	-1.6705177245	1.2714529851	-4.6284915681
N	1.3012989783	3.1423820485	-5.7934820319
N	-1.3012989783	-3.1423820485	5.7934820319
H	-1.4124589123	0.3644342492	6.4091787773
H	1.4124589123	-0.3644342492	-6.4091787773
H	0.8429461108	3.8710121341	-5.2161190281
H	-0.8429461108	-3.8710121341	5.2161190281
H	1.5822654343	2.3328926105	-5.2164804025
H	-1.5822654343	-2.3328926105	5.2164804025
N	4.7115443810	2.8286593480	-5.9631762145
N	-4.7115443810	-2.8286593480	5.9631762145
H	-5.4350457160	0.0589852423	5.9774400589
H	5.4350457160	-0.0589852423	-5.9774400589
H	-4.5082852688	2.4005966979	-5.4960514231

H	4.5082852688	-2.4005966979	5.4960514231
H	5.4462554597	2.4176200588	-5.3652638280
H	-5.4462554597	-2.4176200588	5.3652638280
N	2.5632630719	2.8013562478	5.3422789460
N	-2.5632630719	-2.8013562478	-5.3422789460
H	3.1146524096	2.1676221042	4.7339673843
H	-3.1146524096	-2.1676221042	-4.7339673843
H	3.1592562174	3.0525225925	6.1517619752
H	-3.1592562174	-3.0525225925	-6.1517619752
H	2.2545433899	3.6411881501	4.8258993918
H	-2.2545433899	-3.6411881501	-4.8258993918
N	-0.4904819982	2.8988144553	5.3361612099
N	0.4904819982	-2.8988144553	-5.3361612099
H	-0.0744252162	3.7097731141	4.8377484941
H	0.0744252162	-3.7097731141	-4.8377484941
H	-1.0744369035	3.2312730112	6.1234765924
H	1.0744369035	-3.2312730112	-6.1234765924
H	-1.1160270150	2.3846767751	4.6783433294
H	1.1160270150	-2.3846767751	-4.6783433294
N	3.0773968403	5.1774010564	-5.1313055321
N	-3.0773968403	-5.1774010564	5.1313055321
C	3.0984210274	6.5215469200	-5.2836517468
C	-3.0984210274	-6.5215469200	5.2836517468
H	3.0365932212	6.9019051673	-6.3064095542
H	-3.0365932212	-6.9019051673	6.3064095542
C	3.3408892630	-5.0871561139	-4.2008023968
C	-3.3408892630	5.0871561139	4.2008023968
H	3.3318310151	-4.0064777517	-4.3682475192
H	-3.3318310151	4.0064777517	4.3682475192
C	3.4521301189	-5.6259325620	-2.9222232343
C	-3.4521301189	5.6259325620	2.9222232343
H	3.5480421579	-4.9711254795	-2.0508442617
H	-3.5480421579	4.9711254795	2.0508442617
C	3.3026057202	5.4490832864	-2.7530604127
C	-3.3026057202	-5.4490832864	2.7530604127
C	3.1584828140	4.6577292965	-3.8924573169
C	-3.1584828140	-4.6577292965	3.8924573169
H	3.1146420771	3.5671609361	-3.8101034159
H	-3.1146420771	-3.5671609361	3.8101034159
C	3.4822607420	4.8095982973	-1.4141668296
C	-3.4822607420	-4.8095982973	1.4141668296
H	3.3204773767	5.5427196584	-0.6081810899
H	-3.3204773767	-5.5427196584	0.6081810899
H	4.5112130832	4.4166714829	-1.3172655090
H	-4.5112130832	-4.4166714829	1.3172655090
H	2.7974893754	3.9574404536	-1.2708722707
H	-2.7974893754	-3.9574404536	1.2708722707
S	1.2027321403	-6.0492248523	4.3476035107
S	-1.2027321403	6.0492248523	-4.3476035107
O	-0.0550878969	-5.6066714054	4.9775288937
O	0.0550878969	5.6066714054	-4.9775288937
O	2.3939230149	-5.6029023740	5.0611712047
O	-2.3939230149	5.6029023740	-5.0611712047
O	1.0624237299	4.9586548338	4.0844945332
O	-1.0624237299	-4.9586548338	-4.0844945332
C	1.2317842898	-5.2665337921	2.7438563357
C	-1.2317842898	5.2665337921	-2.7438563357
C	1.4105661041	-6.0256826779	1.5884692060
C	-1.4105661041	6.0256826779	-1.5884692060
H	1.4087561216	5.3547394173	1.6759089856
H	-1.4087561216	-5.3547394173	-1.6759089856
C	1.3667954642	-5.4018278863	0.3389417134
C	-1.3667954642	5.4018278863	-0.3389417134
H	1.4627414678	-6.0030587139	-0.5704835399
H	-1.4627414678	6.0030587139	0.5704835399
C	0.9919468297	-3.2771360141	1.3971265507

C	-0.9919468297	3.2771360141	-1.3971265507
H	0.8121772347	-2.1983784772	1.3284699247
H	-0.8121772347	2.1983784772	-1.3284699247
C	1.0413260439	-3.8820916130	2.6513831143
C	-1.0413260439	3.8820916130	-2.6513831143
H	0.9317454424	-3.2729112574	3.5544989804
H	-0.9317454424	3.2729112574	-3.5544989804
C	1.1361638040	-4.0268564599	0.2166707617
C	-1.1361638040	4.0268564599	-0.2166707617
C	1.0136661710	-3.3864885006	-1.1342959495
C	-1.0136661710	3.3864885006	1.1342959495
H	1.0155416241	-4.1414747129	-1.9368014485
H	-1.0155416241	4.1414747129	1.9368014485
H	1.8305943863	-2.6714753565	-1.3452161790
H	-1.8305943863	2.6714753565	1.3452161790
H	0.0733443067	-2.8131089699	-1.2176889939
H	-0.0733443067	2.8131089699	1.2176889939
S	3.1123947205	-0.3535313440	-3.9617463843
S	-3.1123947205	0.3535313440	3.9617463843
O	2.3508458826	-1.5946146343	-3.7639015306
O	-2.3508458826	1.5946146343	3.7639015306
O	4.5132344749	-0.5863018765	-4.3059131989
O	-4.5132344749	0.5863018765	4.3059131989
O	2.4572337846	0.5803023135	-4.9035838427
O	-2.4572337846	-0.5803023135	4.9035838427
C	3.1237789859	0.4322502548	-2.3712170764
C	-3.1237789859	-0.4322502548	2.3712170764
C	1.9640434799	0.4079158386	-1.5918942002
C	-1.9640434799	-0.4079158386	1.5918942002
H	1.0742051776	-0.1073159680	-1.9697733124
H	-1.0742051776	0.1073159680	1.9697733124
C	1.9743464942	1.0136247209	-0.3376379376
C	-1.9743464942	-1.0136247209	0.3376379376
H	1.0733866920	0.9927919776	0.2862516594
H	-1.0733866920	-0.9927919776	-0.2862516594
C	3.1287141865	1.6398477258	0.1573850228
C	-3.1287141865	-1.6398477258	-0.1573850228
C	-4.1560379386	1.6340509721	-0.6391491786
C	4.1560379386	-1.6340509721	0.6391491786
H	-3.2416599374	2.1043795237	-0.2615417554
H	3.2416599374	-2.1043795237	0.2615417554
C	4.2888352739	1.0388607956	-1.8992218733
C	-4.2888352739	-1.0388607956	1.8992218733
H	-3.2455072035	1.0200391710	-2.5200633929
H	3.2455072035	-1.0200391710	2.5200633929
C	3.1225965704	2.3170380901	1.4931323921
C	-3.1225965704	-2.3170380901	-1.4931323921
H	2.3515748277	1.9003992253	2.1609570602
H	-2.3515748277	-1.9003992253	-2.1609570602
H	2.9175928074	3.3986368621	1.3753983675
H	-2.9175928074	-3.3986368621	-1.3753983675
H	-4.3384465855	2.2162193748	1.9974823962
H	4.3384465855	-2.2162193748	-1.9974823962

140

Ru	0.9936467008	1.7342236914	6.1169421990
Ru	-0.9936467008	-1.7342236914	-6.1169421990
S	0.8151710939	-0.5865392195	3.9334806332
S	-0.8151710939	0.5865392195	-3.9334806332
O	0.7213682996	0.8429749646	4.3873970287
O	-0.7213682996	-0.8429749646	-4.3873970287
O	1.5268929199	-1.4898971642	4.8489493100
O	-1.5268929199	1.4898971642	-4.8489493100
N	1.3564473102	3.1360496179	-5.8424986846
N	-1.3564473102	-3.1360496179	5.8424986846

H	-1.3234945371	0.3486446774	6.3309012649
H	1.3234945371	-0.3486446774	-6.3309012649
H	0.8470096983	3.8346437782	-5.2707727781
H	-0.8470096983	-3.8346437782	5.2707727781
H	1.6297875535	2.3316686534	-5.2578512805
H	-1.6297875535	-2.3316686534	5.2578512805
N	4.4531961206	2.7757381958	-6.0156967569
N	-4.4531961206	-2.7757381958	6.0156967569
H	-5.4830348739	-0.0252914619	6.0263952060
H	5.4830348739	0.0252914619	-6.0263952060
H	-4.4979785351	2.0051300813	-5.5754195898
H	4.4979785351	-2.0051300813	5.5754195898
H	5.2018971303	3.0298556076	-5.3596573990
H	-5.2018971303	-3.0298556076	5.3596573990
N	2.5990525029	2.8311326323	5.3509614750
N	-2.5990525029	-2.8311326323	-5.3509614750
H	3.1506971170	2.1977732235	4.7472399239
H	-3.1506971170	-2.1977732235	-4.7472399239
H	3.2087309167	3.0993287263	6.1443098504
H	-3.2087309167	-3.0993287263	-6.1443098504
H	2.3015918038	3.6732877026	4.8315359170
H	-2.3015918038	-3.6732877026	-4.8315359170
N	-0.4896269524	2.9955129966	5.3531069291
N	0.4896269524	-2.9955129966	-5.3531069291
H	-0.0945715905	3.8016081509	4.8401205638
H	0.0945715905	-3.8016081509	-4.8401205638
H	-1.0843126406	3.3277180662	6.1280946881
H	1.0843126406	-3.3277180662	-6.1280946881
H	-1.1049309494	2.4616241359	4.7107352453
H	1.1049309494	-2.4616241359	-4.7107352453
N	3.0915445760	5.2511330454	-5.0981563954
N	-3.0915445760	-5.2511330454	5.0981563954
C	3.1110466617	6.5972877020	-5.2324841586
C	-3.1110466617	-6.5972877020	5.2324841586
H	3.0462047327	6.9728617619	-6.2573032056
H	-3.0462047327	-6.9728617619	6.2573032056
C	3.3503386788	-5.0250114665	-4.1399709625
C	-3.3503386788	5.0250114665	4.1399709625
H	3.3371227096	-3.9423772665	-4.2926456252
H	-3.3371227096	3.9423772665	4.2926456252
C	3.4563945327	-5.5842617821	-2.8676054597
C	-3.4563945327	5.5842617821	2.8676054597
H	3.5486975504	-4.9418755542	-1.9871181969
H	-3.5486975504	4.9418755542	1.9871181969
C	3.3076063059	5.4877050760	-2.7150036299
C	-3.3076063059	-5.4877050760	2.7150036299
C	3.1714146614	4.7146449292	-3.8647656782
C	-3.1714146614	-4.7146449292	3.8647656782
H	3.1421184254	3.6208220961	-3.8129903905
H	-3.1421184254	-3.6208220961	3.8129903905
C	3.4858508704	4.8258039317	-1.3868123244
C	-3.4858508704	-4.8258039317	1.3868123244
H	3.3268752475	5.5443787999	-0.5677489962
H	-3.3268752475	-5.5443787999	0.5677489962
H	4.5128089865	4.4262898267	-1.2969683663
H	-4.5128089865	-4.4262898267	1.2969683663
H	2.7969313585	3.9741494300	-1.2603813721
H	-2.7969313585	-3.9741494300	1.2603813721
S	1.2106919822	-6.0216398589	4.3342389127
S	-1.2106919822	6.0216398589	-4.3342389127
O	-0.0571233021	-5.6029062999	4.9517686287
O	0.0571233021	5.6029062999	-4.9517686287
O	2.3877492121	-5.5179566868	5.0425801451
O	-2.3877492121	5.5179566868	-5.0425801451
O	1.1205884059	4.9879034402	4.0873740377
O	-1.1205884059	-4.9879034402	-4.0873740377

C	1.2319727780	-5.2629288463	2.7241696801			
C	-1.2319727780	5.2629288463	-2.7241696801			
C	1.4154882777	-6.0231956659	1.5721006797			
C	-1.4154882777	6.0231956659	-1.5721006797			
H	1.4196587889	5.3583920033	1.6634526124			
H	-1.4196587889	-5.3583920033	-1.6634526124			
C	1.3689968127	-5.3986836463	0.3230895660			
C	-1.3689968127	5.3986836463	-0.3230895660			
H	1.4683437556	-5.9981931274	-0.5868124671			
H	-1.4683437556	5.9981931274	0.5868124671			
C	0.9838113841	-3.2735426811	1.3805859878			
C	-0.9838113841	3.2735426811	-1.3805859878			
H	0.7975845170	-2.1951524744	1.3120636942			
H	-0.7975845170	2.1951524744	-1.3120636942			
C	1.0296765909	-3.8827077164	2.6310865245			
C	-1.0296765909	3.8827077164	-2.6310865245			
H	0.9053891395	-3.2951978107	3.5448918895			
H	-0.9053891395	3.2951978107	-3.5448918895			
C	1.1361743411	-4.0240191364	0.2017335322			
C	-1.1361743411	4.0240191364	-0.2017335322			
C	1.0139904646	-3.3832595838	-1.1482432982			
C	-1.0139904646	3.3832595838	1.1482432982			
H	1.0167908810	-4.1373646704	-1.9511206431			
H	-1.0167908810	4.1373646704	1.9511206431			
H	1.8308921593	-2.6682480738	-1.3589135466			
H	-1.8308921593	2.6682480738	1.3589135466			
H	0.0722822803	-2.8112787059	-1.2265582640			
H	-0.0722822803	2.8112787059	1.2265582640			
S	3.1295603728	-0.3493370953	-3.9430728369			
S	-3.1295603728	0.3493370953	3.9430728369			
O	2.4256446208	-1.6207564746	-3.7548396748			
O	-2.4256446208	1.6207564746	3.7548396748			
O	4.5413070193	-0.5079321413	-4.3098072206			
O	-4.5413070193	0.5079321413	4.3098072206			
O	2.4180319262	0.5696129499	-4.8579432112			
O	-2.4180319262	-0.5696129499	4.8579432112			
C	3.1344537749	0.4265876221	-2.3479390285			
C	-3.1344537749	-0.4265876221	2.3479390285			
C	1.9751049867	0.3959765911	-1.5694528185			
C	-1.9751049867	-0.3959765911	1.5694528185			
H	1.0892954270	-0.1248598081	-1.9459430241			
H	-1.0892954270	0.1248598081	1.9459430241			
C	1.9763634411	1.0077188367	-0.3187903946			
C	-1.9763634411	-1.0077188367	0.3187903946			
H	1.0712337083	0.9860273678	0.2992029691			
H	-1.0712337083	-0.9860273678	-0.2992029691			
C	3.1248405390	1.6423441365	0.1779723129			
C	-3.1248405390	-1.6423441365	-0.1779723129			
C	4.1576153331	1.6422847176	-0.6141477259			
C	-4.1576153331	-1.6422847176	0.6141477259			
H	3.2456760268	2.1185227568	-0.2388126101			
H	-3.2456760268	-2.1185227568	0.2388126101			
C	4.2900570645	1.0449291216	-1.8716496478			
C	-4.2900570645	-1.0449291216	1.8716496478			
H	3.2420921566	1.0337342599	-2.4875009554			
H	-3.2420921566	-1.0337342599	2.4875009554			
C	3.1140683451	2.3224117053	1.5114077698			
C	-3.1140683451	-2.3224117053	-1.5114077698			
H	2.3344008201	1.9102424268	2.1719051332			
H	-2.3344008201	-1.9102424268	-2.1719051332			
H	2.9138857724	3.4041906882	1.3923872044			
H	-2.9138857724	-3.4041906882	-1.3923872044			
H	4.3510410210	2.2180768653	2.0228528551			
H	-4.3510410210	-2.2180768653	-2.0228528551			
Ru	0.9403833888	1.7778668611	6.1203889004			
Ru	-0.9403833888	-1.7778668611	-6.1203889004			
S	0.9346215085	-0.6296694328	3.9458994534			
S	-0.9346215085	0.6296694328	-3.9458994534			
O	0.7940017226	0.7984991278	4.4130046578			
O	-0.7940017226	-0.7984991278	-4.4130046578			
O	1.2865601021	-1.6098721384	4.9851263237			
O	-1.2865601021	1.6098721384	-4.9851263237			
N	1.3245747847	3.1428383152	-5.9138019057			
N	-1.3245747847	-3.1428383152	5.9138019057			
H	-1.2780026860	0.3102798554	6.2135000380			
H	1.2780026860	-0.3102798554	-6.2135000380			
H	0.7371674153	3.8009913475	-5.3726558506			
H	-0.7371674153	-3.8009913475	5.3726558506			
H	1.6117826128	2.3548602310	-5.3132390271			
H	-1.6117826128	-2.3548602310	5.3132390271			
N	4.3895367770	2.8689844051	-5.9844925376			
N	-4.3895367770	-2.8689844051	5.9844925376			
H	-5.4100136080	0.1488030357	6.1170903313			
H	5.4100136080	-0.1488030357	-6.1170903313			
H	-4.4329715014	2.0086968535	-5.5716831062			
H	4.4329715014	-2.0086968535	5.5716831062			
H	4.9883743108	3.3325796268	-5.2864558144			
H	-4.9883743108	-3.3325796268	5.2864558144			
N	2.5997662460	2.8503698155	5.3663199969			
N	-2.5997662460	-2.8503698155	-5.3663199969			
H	3.1448431960	2.2319499855	4.7482584355			
H	-3.1448431960	-2.2319499855	-4.7482584355			
H	3.2140389479	3.0965441676	6.1634438360			
H	-3.2140389479	-3.0965441676	-6.1634438360			
H	2.3347812365	3.7094806897	4.8548133887			
H	-2.3347812365	-3.7094806897	-4.8548133887			
N	-0.5165762192	3.0962629208	5.3497282903			
N	0.5165762192	-3.0962629208	-5.3497282903			
H	-0.0978657008	3.8987854626	4.8493858234			
H	0.0978657008	-3.8987854626	-4.8493858234			
H	-1.0970164315	3.4420315485	6.1300496433			
H	1.0970164315	-3.4420315485	-6.1300496433			
H	-1.1544844804	2.5964060125	4.7064730402			
H	1.1544844804	-2.5964060125	-4.7064730402			
N	3.0623836752	5.3175882225	-5.0774986200			
N	-3.0623836752	-5.3175882225	5.0774986200			
C	3.1028839505	6.6696792734	-5.1651928952			
C	-3.1028839505	-6.6696792734	5.1651928952			
H	3.0203960198	7.0833488823	-6.1746321490			
H	-3.0203960198	-7.0833488823	6.1746321490			
C	3.3859527131	-4.9844814071	-4.0483916152			
C	-3.3859527131	4.9844814071	4.0483916152			
H	3.3843563457	-3.8949981677	-4.1590517474			
H	-3.3843563457	3.8949981677	4.1590517474			
C	3.5223756632	-5.5797521616	-2.7949867768			
C	-3.5223756632	5.5797521616	2.7949867768			
H	3.6459673329	-4.9667809970	-1.8959984451			
H	-3.6459673329	4.9667809970	1.8959984451			
C	3.3588075777	5.4890722896	-2.6847326510			
C	-3.3588075777	-5.4890722896	2.6847326510			
C	3.1710066218	4.7547379218	-3.8547076774			
C	-3.1710066218	-4.7547379218	3.8547076774			
H	3.1255794251	3.6613331510	-3.8240558709			
H	-3.1255794251	-3.6613331510	3.8240558709			
C	3.5737235796	4.7854690551	-1.3816289262			
C	-3.5737235796	-4.7854690551	1.3816289262			
H	3.4009282459	5.4665736441	-0.5322280128			
H	-3.4009282459	-5.4665736441	0.5322280128			
H	4.6172850181	4.4250580849	-1.3141989140			

H	-4.6172850181	-4.4250580849	1.3141989140
H	2.9179774954	3.9051278163	-1.2787528201
H	-2.9179774954	-3.9051278163	1.2787528201
S	1.2670141829	-5.9623462773	4.2935047490
S	-1.2670141829	5.9623462773	-4.2935047490
O	-0.0110396527	-5.5853898338	4.9151746619
O	0.0110396527	5.5853898338	-4.9151746619
O	2.4286493451	-5.3741390702	4.9666791263
O	-2.4286493451	5.3741390702	-4.9666791263
O	1.2451651672	5.0427151352	4.1049539155
O	-1.2451651672	-5.0427151352	-4.1049539155
C	1.2380570461	-5.2653927880	2.6551726662
C	-1.2380570461	5.2653927880	-2.6551726662
C	1.4927752031	-6.0459153785	1.5287317148
C	-1.4927752031	6.0459153785	-1.5287317148
H	1.5751126613	5.3520766104	1.6533896714
H	-1.5751126613	-5.3520766104	-1.6533896714
C	1.4161630497	-5.4655129051	0.2595475043
C	-1.4161630497	5.4655129051	-0.2595475043
H	1.5684448859	-6.0838844612	-0.6309258457
H	-1.5684448859	6.0838844612	0.6309258457
C	0.8595774971	-3.3431090859	1.2473124778
C	-0.8595774971	3.3431090859	-1.2473124778
H	0.5832876059	-2.2879201642	1.1404656749
H	-0.5832876059	2.2879201642	-1.1404656749
C	0.9282289462	-3.9093629706	2.5168262686
C	-0.9282289462	3.9093629706	-2.5168262686
H	0.7296823104	-3.3130357782	3.4122706728
H	-0.7296823104	3.3130357782	-3.4122706728
C	1.0918849629	-4.1135909713	0.0951019469
C	-1.0918849629	4.1135909713	-0.0951019469
C	0.9556295485	-3.5097601305	-1.2708151442
C	-0.9556295485	3.5097601305	1.2708151442
H	0.9032783265	-4.2859438326	-2.0509201988
H	-0.9032783265	4.2859438326	2.0509201988
H	1.7985224640	-2.8385969333	-1.5227610751
H	-1.7985224640	2.8385969333	1.5227610751
H	0.0393187612	-2.8970512518	-1.3357825533
H	-0.0393187612	2.8970512518	1.3357825533
S	3.1111310154	-0.2563787085	-3.8837301453
S	-3.1111310154	0.2563787085	3.8837301453
O	2.6139718871	-1.6319774933	-3.7583221940
O	-2.6139718871	1.6319774933	3.7583221940
O	4.5046649804	-0.1807390192	-4.3457536379
O	-4.5046649804	0.1807390192	4.3457536379
O	2.2058309477	0.6007770199	-4.6761241851
O	-2.2058309477	-0.6007770199	4.6761241851
C	3.0956836700	0.4283801772	-2.2373292620
C	-3.0956836700	-0.4283801772	2.2373292620
C	1.9276541495	0.3291307298	-1.4742910782
C	-1.9276541495	-0.3291307298	1.4742910782
H	1.0588299138	-0.1961028755	-1.8850421247
H	-1.0588299138	0.1961028755	1.8850421247
C	1.8874434082	0.8980037537	-0.2034325431
C	-1.8874434082	-0.8980037537	0.2034325431
H	0.9751944673	0.8215954826	0.4001755574
H	-0.9751944673	-0.8215954826	-0.4001755574
C	3.0001023310	1.5647274368	0.3336443785
C	-3.0001023310	-1.5647274368	-0.3336443785
C	-4.2709186942	1.6281309334	-0.4385671115
C	4.2709186942	-1.6281309334	0.4385671115
H	-3.3816171203	2.1199146557	-0.0297985511
H	3.3816171203	-2.1199146557	0.0297985511
C	4.2194262510	1.0685338553	-1.7144215158
C	-4.2194262510	-1.0685338553	1.7144215158
H	-3.3025777071	1.1154894839	-2.3134454395

H	3.3025777071	-1.1154894839	2.3134454395
C	2.9380679356	2.2066441244	1.6862271924
C	-2.9380679356	-2.2066441244	-1.6862271924
H	2.1657538671	1.7449009894	2.3226461593
H	-2.1657538671	-1.7449009894	-2.3226461593
H	2.6896257144	3.2815743401	1.5986696634
H	-2.6896257144	-3.2815743401	-1.5986696634
H	-4.5308592435	2.1331803860	2.2110215609
H	4.5308592435	-2.1331803860	-2.2110215609

Pathway II:

140

Ru	1.0307734251	1.5645014229	6.1124343982
Ru	-1.0307734251	-1.5645014229	-6.1124343982
S	1.0042338695	0.2089053155	4.5061094020
S	-1.0042338695	-0.2089053155	-4.5061094020
O	0.9022785985	0.5977100399	3.0968849028
O	-0.9022785985	-0.5977100399	-3.0968849028
O	1.1406199994	-1.2309204069	4.7179211839
O	-1.1406199994	1.2309204069	-4.7179211839
N	1.4399889531	3.0039414115	-5.7695763328
N	-1.4399889531	-3.0039414115	5.7695763328
H	-1.2324308840	0.2414234330	6.3842225055
H	1.2324308840	-0.2414234330	-6.3842225055
H	0.9322972843	3.6833138579	-5.1804470099
H	-0.9322972843	-3.6833138579	5.1804470099
H	1.7011145737	2.1707577806	-5.2143930889
H	-1.7011145737	-2.1707577806	5.2143930889
N	4.5600742237	2.8700120828	-5.8003857256
N	-4.5600742237	-2.8700120828	5.8003857256
H	-5.1720472816	0.1854968036	6.3464254310
H	5.1720472816	-0.1854968036	-6.3464254310
H	-3.3733420059	3.4687961695	-5.1294192792
H	3.3733420059	-3.4687961695	5.1294192792
H	4.2885810117	1.9914478881	-5.3327263579
H	-4.2885810117	-1.9914478881	5.3327263579
N	2.6066474605	2.7493124602	5.3148789272
N	-2.6066474605	-2.7493124602	-5.3148789272
H	3.2127934616	2.2108744186	4.6829291055
H	-3.2127934616	-2.2108744186	-4.6829291055
H	3.2041326780	3.0375633328	6.1123929755
H	-3.2041326780	-3.0375633328	-6.1123929755
H	2.2716031051	3.5943767496	4.8222951567
H	-2.2716031051	-3.5943767496	-4.8222951567
N	-0.4564132381	2.8483172375	5.3134990122
N	0.4564132381	-2.8483172375	-5.3134990122
H	-0.0520724352	3.6690817604	4.8306025620
H	0.0520724352	-3.6690817604	-4.8306025620
H	-1.0310634340	3.1813482889	6.1075422658
H	1.0310634340	-3.1813482889	-6.1075422658
H	-1.1151867081	2.3823274037	4.6675271171
H	1.1151867081	-2.3823274037	-4.6675271171
N	3.0880853750	5.2861170622	-5.1109158138
N	-3.0880853750	-5.2861170622	5.1109158138
C	3.1067777390	6.6246118140	-5.2714119904
C	-3.1067777390	-6.6246118140	5.2714119904
H	3.0677473581	6.9935619677	-6.3009422011
H	-3.0677473581	-6.9935619677	6.3009422011
C	3.3126576352	-4.9729105849	-4.1877851185
C	-3.3126576352	4.9729105849	4.1877851185
H	3.3050475416	-3.8897163027	-4.3458796425
H	-3.3050475416	3.8897163027	4.3458796425
C	3.3842003995	-5.5055967367	-2.9021573841

C	-3.3842003995	5.5055967367	2.9021573841
H	3.4443203150	-4.8419470701	-2.0322309361
H	-3.4443203150	4.8419470701	2.0322309361
C	3.2405207458	5.5707476566	-2.7200736189
C	-3.2405207458	-5.5707476566	2.7200736189
C	3.1427273574	4.7811028390	-3.8665732252
C	-3.1427273574	-4.7811028390	3.8665732252
H	3.1158669036	3.6894785406	-3.7904198444
H	-3.1158669036	-3.6894785406	3.7904198444
C	3.3556190562	4.9337685024	-1.3698829895
C	-3.3556190562	-4.9337685024	1.3698829895
H	3.2753298801	5.6916152555	-0.5738387511
H	-3.2753298801	-5.6916152555	0.5738387511
H	4.3290248110	4.4197445975	-1.2659169399
H	-4.3290248110	-4.4197445975	1.2659169399
H	2.5734226743	4.1700017965	-1.2153683871
H	-2.5734226743	-4.1700017965	1.2153683871
S	1.2031016948	-5.9233441507	4.3814886999
S	-1.2031016948	5.9233441507	-4.3814886999
O	-0.0637572731	-5.5175220399	5.0082682656
O	0.0637572731	5.5175220399	-5.0082682656
O	2.3805220426	-5.3800523252	5.0731113295
O	-2.3805220426	5.3800523252	-5.0731113295
O	1.1475552157	5.0813705394	4.1744756821
O	-1.1475552157	-5.0813705394	-4.1744756821
C	1.2050597826	-5.1658731568	2.7683094749
C	-1.2050597826	5.1658731568	-2.7683094749
C	1.3461039035	-5.9186194666	1.6041664895
C	-1.3461039035	5.9186194666	-1.6041664895
H	1.3196607209	5.4571403058	1.6724642550
H	-1.3196607209	-5.4571403058	-1.6724642550
C	1.3089819905	-5.2731843039	0.3637352810
C	-1.3089819905	5.2731843039	-0.3637352810
H	1.3804314400	-5.8639833084	-0.5549966361
H	-1.3804314400	5.8639833084	0.5549966361
C	1.0095975166	-3.1497804438	1.4525758126
C	-1.0095975166	3.1497804438	-1.4525758126
H	0.8726436216	-2.0629314167	1.4131161584
H	-0.8726436216	2.0629314167	-1.4131161584
C	1.0466527546	-3.7763835407	2.6950476920
C	-1.0466527546	3.7763835407	-2.6950476920
H	0.9481796401	-3.1737806822	3.6038905912
H	-0.9481796401	3.1737806822	-3.6038905912
C	1.1282786146	-3.8885328395	0.2617083523
C	-1.1282786146	3.8885328395	-0.2617083523
C	1.0407021362	-3.2222968421	1.0798370712
C	-1.0407021362	3.2222968421	-1.0798370712
H	1.1254112717	-3.9555992246	1.8974603306
H	-1.1254112717	3.9555992246	-1.8974603306
H	1.8281424127	-2.4601676115	-1.2280167590
H	-1.8281424127	2.4601676115	1.2280167590
H	0.0791825484	-2.6927101259	-1.2017909255
H	-0.0791825484	2.6927101259	1.2017909255
S	3.0590109882	-0.3040914291	-4.0222734935
S	-3.0590109882	0.3040914291	4.0222734935
O	2.8252133241	-1.7432783001	-3.8439107828
O	-2.8252133241	1.7432783001	3.8439107828
O	4.3536840870	-0.0066881158	-4.6602903590
O	-4.3536840870	0.0066881158	4.6602903590
O	1.9294162659	0.3558438575	-4.7055637870
O	-1.9294162659	-0.3558438575	4.7055637870
C	3.1384478889	0.4361840134	-2.4133312281
C	-3.1384478889	-0.4361840134	2.4133312281
C	1.9827047293	0.4593127215	-1.6259551195
C	-1.9827047293	-0.4593127215	1.6259551195
H	1.0551167539	0.0123609986	-2.0011288060

H	-1.0551167539	-0.0123609986	2.0011288060
C	2.0242040110	1.0852276119	-0.3822409719
C	-2.0242040110	-1.0852276119	0.3822409719
H	1.1298030437	1.1062305254	0.2496401679
H	-1.1298030437	-1.1062305254	-0.2496401679
C	3.1969111225	1.6971866985	0.0851897478
C	-3.1969111225	-1.6971866985	-0.0851897478
C	-4.0934301855	1.6361316900	-0.7147417761
C	4.0934301855	-1.6361316900	0.7147417761
H	-3.1665667888	2.0997866866	-0.3642558944
H	3.1665667888	-2.0997866866	0.3642558944
C	4.3277556465	1.0082863804	-1.9579806565
C	-4.3277556465	-1.0082863804	1.9579806565
H	-3.2086820266	0.9647761481	-2.5786933585
H	3.2086820266	-0.9647761481	2.5786933585
C	3.2155076494	2.4334255534	1.3886838877
C	-3.2155076494	-2.4334255534	-1.3886838877
H	2.3640195198	2.1394709361	2.0228318506
H	-2.3640195198	-2.1394709361	-2.0228318506
H	3.1480376517	3.5241538269	1.2120422373
H	-3.1480376517	-3.5241538269	-1.2120422373
H	-4.2863442548	2.2470467509	1.9452269528
H	4.2863442548	-2.2470467509	-1.9452269528

140

Ru	0.9270340354	1.4885900541	6.1253719775
Ru	-0.9270340354	-1.4885900541	-6.1253719775
S	0.8727169629	0.2174502414	4.4513887317
S	-0.8727169629	-0.2174502414	-4.4513887317
O	0.7568509628	0.6877600957	3.0694729935
O	-0.7568509628	-0.6877600957	-3.0694729935
O	1.0846896351	-1.2264801689	4.5767989922
O	-1.0846896351	1.2264801689	-4.5767989922
N	1.3098404133	2.9733077586	-5.7528100970
N	-1.3098404133	-2.9733077586	5.7528100970
H	-1.3550205871	0.1992208616	6.4015807162
H	1.3550205871	-0.1992208616	-6.4015807162
H	0.8053717629	3.6766274218	-5.1890916221
H	-0.8053717629	-3.6766274218	5.1890916221
H	1.5616402866	2.1621900719	-5.1643212747
H	-1.5616402866	-2.1621900719	5.1643212747
N	4.4116433081	2.6537217813	-5.8911689500
N	-4.4116433081	-2.6537217813	5.8911689500
H	-5.2170552482	0.2129135008	6.3268953110
H	5.2170552482	-0.2129135008	-6.3268953110
H	-3.6604376916	2.9879089324	-4.9934240230
H	3.6604376916	-2.9879089324	4.9934240230
H	4.1051751915	1.6811412540	-5.7495861653
H	-4.1051751915	-1.6811412540	5.7495861653
N	2.5231116407	2.6392881334	5.3288091596
N	-2.5231116407	-2.6392881334	-5.3288091596
H	3.1214651494	2.0614969343	4.7210421815
H	-3.1214651494	-2.0614969343	-4.7210421815
H	3.1217267959	2.9499167666	6.1176877374
H	-3.1217267959	-2.9499167666	-6.1176877374
H	2.1946098762	3.4749972441	4.8168013622
H	-2.1946098762	-3.4749972441	-4.8168013622
N	-0.5196381816	2.8399931074	5.3922179090
N	0.5196381816	-2.8399931074	-5.3922179090
H	-0.0887668967	3.6670874778	4.9439965664
H	0.0887668967	-3.6670874778	-4.9439965664
H	-1.0931432300	3.1536093677	6.1966016822
H	1.0931432300	-3.1536093677	-6.1966016822
H	-1.1743004619	2.4104894028	4.7138310238
H	1.1743004619	-2.4104894028	-4.7138310238

N	3.0883912234	5.1540949426	-5.0563292371
N	-3.0883912234	-5.1540949426	5.0563292371
C	3.1380268755	6.4925773355	-5.1983069804
C	-3.1380268755	-6.4925773355	5.1983069804
H	3.0345428103	6.8770825353	-6.2167623512
H	-3.0345428103	-6.8770825353	6.2167623512
C	3.4628441250	-5.1220168226	-4.1135299749
C	-3.4628441250	5.1220168226	4.1135299749
H	3.4625504390	-4.0374840800	-4.2604780025
H	-3.4625504390	4.0374840800	4.2604780025
C	3.6449635652	-5.6747900051	-2.8502965350
C	-3.6449635652	5.6747900051	2.8502965350
H	3.8151085628	-5.0302541131	-1.9809988784
H	-3.8151085628	5.0302541131	1.9809988784
C	3.4695568891	5.3986255657	-2.6867684665
C	-3.4695568891	-5.3986255657	2.6867684665
C	3.2249337934	4.6289953581	-3.8242347281
C	-3.2249337934	-4.6289953581	3.8242347281
H	3.1383399913	3.5394879306	-3.7444717493
H	-3.1383399913	-3.5394879306	3.7444717493
C	3.7209318115	4.7484146057	-1.3679660239
C	-3.7209318115	-4.7484146057	1.3679660239
H	3.3645652851	5.3810368965	-0.5382758646
H	-3.3645652851	-5.3810368965	0.5382758646
H	4.8077435510	4.6004385351	-1.2293705105
H	-4.8077435510	-4.6004385351	1.2293705105
H	3.2495159515	3.7559235409	-1.3025748013
H	-3.2495159515	-3.7559235409	1.3025748013
S	1.2537883487	-6.0207942507	4.4500484533
S	-1.2537883487	6.0207942507	-4.4500484533
O	-0.0401516922	-5.5533805230	4.9721061629
O	0.0401516922	5.5533805230	-4.9721061629
O	2.3972157116	-5.4652845615	5.1762357699
O	-2.3972157116	5.4652845615	-5.1762357699
O	1.1600318018	4.9738584107	4.3142794868
O	-1.1600318018	-4.9738584107	-4.3142794868
C	1.3586107032	-5.3661728588	2.8031073482
C	-1.3586107032	5.3661728588	-2.8031073482
C	1.4415151134	-6.2041649909	1.6935435942
C	-1.4415151134	6.2041649909	-1.6935435942
H	1.3497768550	5.1749776853	1.8417404946
H	-1.3497768550	-5.1749776853	-1.8417404946
C	1.4208046089	-5.6448383146	0.4127483332
C	-1.4208046089	5.6448383146	-0.4127483332
H	1.4493108478	-6.2978545734	-0.4646442767
H	-1.4493108478	6.2978545734	0.4646442767
C	1.2609852535	-3.4386912888	1.3609655989
C	-1.2609852535	3.4386912888	-1.3609655989
H	1.1809282744	-2.3525352969	1.2443966999
H	-1.1809282744	2.3525352969	-1.2443966999
C	1.2926253868	-3.9779426477	2.6428663193
C	-1.2926253868	3.9779426477	-2.6428663193
H	1.2399008419	-3.3156703428	3.5133679059
H	-1.2399008419	3.3156703428	-3.5133679059
C	1.3057397825	-4.2620399322	0.2227813498
C	-1.3057397825	4.2620399322	-0.2227813498
C	1.2123884588	-3.6770931398	-1.1526701330
C	-1.2123884588	3.6770931398	1.1526701330
H	1.1721364365	-4.4645094714	-1.9215213028
H	-1.1721364365	4.4645094714	1.9215213028
H	2.0674601358	-3.0177409569	-1.3905167816
H	-2.0674601358	3.0177409569	1.3905167816
H	0.3095291006	-3.0499024745	-1.2556253346
H	-0.3095291006	3.0499024745	1.2556253346
S	3.0383142815	-0.3694130005	-3.8954921361
S	-3.0383142815	0.3694130005	3.8954921361
O	2.6429697498	-1.7666441500	-3.6861713216
O	-2.6429697498	1.7666441500	3.6861713216
O	4.3765891527	-0.2301629406	-4.5010769232
O	-4.3765891527	0.2301629406	4.5010769232
O	2.0162280725	0.3880807937	-4.6496324543
O	-2.0162280725	-0.3880807937	4.6496324543
C	3.1285783259	0.4009175432	-2.2945145498
C	-3.1285783259	-0.4009175432	2.2945145498
C	1.9620584328	0.4964380698	-1.5242401274
C	-1.9620584328	-0.4964380698	1.5242401274
H	1.0189858695	0.0883246749	-1.9046334839
H	-1.0189858695	-0.0883246749	1.9046334839
C	2.0158678556	1.1276077690	-0.2838292549
C	-2.0158678556	-1.1276077690	0.2838292549
H	1.1140631325	1.1993518427	0.3348868134
H	-1.1140631325	-1.1993518427	-0.3348868134
C	3.2148807809	1.6719969512	0.2038120551
C	-3.2148807809	-1.6719969512	-0.2038120551
C	-4.0675040173	1.5350283897	-0.5724671644
C	4.0675040173	-1.5350283897	0.5724671644
H	-3.1217616563	1.9318177558	-0.1918367814
H	3.1217616563	-1.9318177558	0.1918367814
C	4.3385006875	0.9064101021	-1.8169981864
C	-4.3385006875	-0.9064101021	1.8169981864
H	-3.1894862985	0.7988347767	-2.4172548770
H	3.1894862985	-0.7988347767	2.4172548770
C	3.2446147641	2.4153790804	1.5035446527
C	-3.2446147641	-2.4153790804	-1.5035446527
H	2.5416717767	1.9724646159	2.2284377997
H	-2.5416717767	-1.9724646159	-2.2284377997
H	2.9322149254	3.4667040293	1.3486847759
H	-2.9322149254	-3.4667040293	-1.3486847759
H	-4.1822836064	2.4230999079	1.9461469023
H	4.1822836064	-2.4230999079	-1.9461469023
140			
Ru	0.9704999970	1.5193623213	6.1028177903
Ru	-0.9704999970	-1.5193623213	-6.1028177903
S	0.9018912581	0.2403602827	4.4352003829
S	-0.9018912581	-0.2403602827	-4.4352003829
O	0.7576450702	0.7167171481	3.0567564831
O	-0.7576450702	-0.7167171481	-3.0567564831
O	1.0842746041	-1.2060430906	4.5520708008
O	-1.0842746041	1.2060430906	-4.5520708008
N	1.3676651055	2.9819991495	-5.7740930696
N	-1.3676651055	-2.9819991495	5.7740930696
H	-1.2992170253	0.2075472207	6.3820768559
H	1.2992170253	-0.2075472207	-6.3820768559
H	0.8591799650	3.6767878794	-5.2036300854
H	-0.8591799650	-3.6767878794	5.2036300854
H	1.6235578492	2.1660940410	-5.1926826989
H	-1.6235578492	-2.1660940410	5.1926826989
N	4.5013219558	2.7706794889	-5.8717717160
N	-4.5013219558	-2.7706794889	5.8717717160
H	-5.3896404634	0.9285535309	7.6435602393
H	5.3896404634	-0.9285535309	-7.6435602393
H	-3.2695539786	2.4959549941	-6.6144299958
H	3.2695539786	-2.4959549941	6.6144299958
H	4.2135179048	1.9103438691	-5.3803795859
H	-4.2135179048	-1.9103438691	5.3803795859
N	2.5598895632	2.6821529274	5.3037229519
N	-2.5598895632	-2.6821529274	-5.3037229519
H	3.1571686401	2.1207891147	4.6825414635
H	-3.1571686401	-2.1207891147	-4.6825414635
H	3.1610837601	2.9779584069	6.0959727187

H	-3.1610837601	-2.9779584069	-6.0959727187
H	2.2324991560	3.5260724681	4.8046290783
H	-2.2324991560	-3.5260724681	-4.8046290783
N	-0.5019224302	2.8448604569	5.3580315362
N	0.5019224302	-2.8448604569	-5.3580315362
H	-0.0845765693	3.6732754473	4.9012482962
H	0.0845765693	-3.6732754473	-4.9012482962
H	-1.0725543488	3.1598270712	6.1631207655
H	1.0725543488	-3.1598270712	-6.1631207655
H	-1.1610328245	2.4057910629	4.6917476069
H	1.1610328245	-2.4057910629	-4.6917476069
N	3.1025145290	5.1945429226	-5.0833502064
N	-3.1025145290	-5.1945429226	5.0833502064
C	3.1294733451	6.5343215364	-5.2231223779
C	-3.1294733451	-6.5343215364	5.2231223779
H	3.0340849722	6.9186168326	-6.2429306775
H	-3.0340849722	-6.9186168326	6.2429306775
C	3.4194594318	-5.0802062218	-4.1336112832
C	-3.4194594318	5.0802062218	4.1336112832
H	3.4078850809	-3.9951693853	-4.2771933366
H	-3.4078850809	3.9951693853	4.2771933366
C	3.5786072096	-5.6333557544	-2.8661167790
C	-3.5786072096	5.6333557544	2.8661167790
H	3.7103941077	-4.9865001224	-1.9919200080
H	-3.7103941077	4.9865001224	1.9919200080
C	3.4297066891	5.4396806342	-2.7056048994
C	-3.4297066891	-5.4396806342	2.7056048994
C	3.2329443814	4.6682539705	-3.8517071535
C	-3.2329443814	-4.6682539705	3.8517071535
H	3.1887824166	3.5762284331	-3.7831405121
H	-3.1887824166	-3.5762284331	3.7831405121
C	3.6535657823	4.7880616645	-1.3803186299
C	-3.6535657823	-4.7880616645	1.3803186299
H	3.3659447199	5.4628589993	-0.5573725445
H	-3.3659447199	-5.4628589993	0.5573725445
H	4.7254825380	4.5435136094	-1.2557953131
H	-4.7254825380	-4.5435136094	1.2557953131
H	3.0953573130	3.8427877473	-1.2883240312
H	-3.0953573130	-3.8427877473	1.2883240312
S	1.2430234780	-5.9614428946	4.4367436046
S	-1.2430234780	5.9614428946	-4.4367436046
O	-0.0520799474	-5.5268908836	4.9819525062
O	0.0520799474	5.5268908836	-4.9819525062
O	2.3851168920	-5.3842274065	5.1554318087
O	-2.3851168920	5.3842274065	-5.1554318087
O	1.1846658339	5.0358902070	4.2957136274
O	-1.1846658339	-5.0358902070	-4.2957136274
C	1.3216125956	-5.2880449077	2.7945470787
C	-1.3216125956	5.2880449077	-2.7945470787
C	1.4211964043	-6.1107325565	1.6748192465
C	-1.4211964043	6.1107325565	-1.6748192465
H	1.3464819456	5.2673203074	1.8080670591
H	-1.3464819456	-5.2673203074	-1.8080670591
C	1.3999922437	-5.5348444288	0.4010323720
C	-1.3999922437	5.5348444288	-0.4010323720
H	1.4403980852	-6.1769280474	-0.4841113361
H	-1.4403980852	6.1769280474	0.4841113361
C	1.2037574079	-3.3434140228	1.3752476444
C	-1.2037574079	3.3434140228	-1.3752476444
H	1.1063945638	-2.2568954938	1.2727221940
H	-1.1063945638	2.2568954938	-1.2727221940
C	1.2328255965	-3.8990041103	2.6502930968
C	-1.2328255965	3.8990041103	-2.6502930968
H	1.1644137405	-3.2459388595	3.5263459772
H	-1.1644137405	3.2459388595	-3.5263459772
C	1.2688675846	-4.1514417259	0.2269158735
C	-1.2688675846	4.1514417259	-0.2269158735
C	1.1701848138	-3.5516612850	-1.1428221640
C	-1.1701848138	3.5516612850	1.1428221640
H	1.1627022899	-4.3304578237	-1.9215566950
H	-1.1627022899	4.3304578237	1.9215566950
H	2.0050465463	-2.8617629735	-1.3656967273
H	-2.0050465463	2.8617629735	1.3656967273
H	0.2477807066	-2.9534902951	-1.2480372853
H	-0.2477807066	2.9534902951	1.2480372853
S	3.0469459601	-0.3235882923	-3.9193094033
S	-3.0469459601	0.3235882923	3.9193094033
O	2.7436008974	-1.7494408043	-3.7452184065
O	-2.7436008974	1.7494408043	3.7452184065
O	4.3671917079	-0.0853184012	-4.5333725641
O	-4.3671917079	0.0853184012	4.5333725641
O	1.9662190746	0.3854635169	-4.6351633250
O	-1.9662190746	-0.3854635169	4.6351633250
C	3.1243586646	0.4183850819	-2.3052583449
C	-3.1243586646	-0.4183850819	2.3052583449
C	1.9599400907	0.4904856323	-1.5307340921
C	-1.9599400907	-0.4904856323	1.5307340921
H	1.0211433110	0.0735339277	-1.9121835316
H	-1.0211433110	-0.0735339277	1.9121835316
C	2.0087780631	1.1182790048	-0.2879109608
C	-2.0087780631	-1.1182790048	0.2879109608
H	1.1083693766	1.1744923080	0.3343965718
H	-1.1083693766	-1.1744923080	-0.3343965718
C	3.1995670667	1.6837601631	0.1950709868
C	-3.1995670667	-1.6837601631	-0.1950709868
C	-4.0832629049	1.5679701931	-0.5857194737
C	4.0832629049	-1.5679701931	0.5857194737
H	-3.1428259152	1.9849069075	-0.2137278124
H	3.1428259152	-1.9849069075	0.2137278124
C	4.3281440675	0.9420128387	-1.8304600275
C	-4.3281440675	-0.9420128387	1.8304600275
H	-3.2020950532	0.8599510442	-2.4377296500
H	3.2020950532	-0.8599510442	2.4377296500
C	3.2236052694	2.4323372587	1.4917829835
C	-3.2236052694	-2.4323372587	-1.4917829835
H	2.4658777733	2.0398957050	2.1894039992
H	-2.4658777733	-2.0398957050	-2.1894039992
H	2.9888617585	3.5008561046	1.3190009182
H	-2.9888617585	-3.5008561046	-1.3190009182
H	-4.2225571479	2.3801192934	1.9736960823
H	4.2225571479	-2.3801192934	-1.9736960823
140			
Ru	0.9218694198	1.5626880850	6.0826232497
Ru	-0.9218694198	-1.5626880850	-6.0826232497
S	0.5996254739	-0.3453981667	4.7252087240
S	-0.5996254739	0.3453981667	-4.7252087240
O	0.9885175936	0.9666627849	4.0413197784
O	-0.9885175936	-0.9666627849	-4.0413197784
O	1.6772843727	-1.3594949503	4.8094129963
O	-1.6772843727	1.3594949503	-4.8094129963
N	1.2941223835	3.0493053637	-5.7487888185
N	-1.2941223835	-3.0493053637	5.7487888185
H	-1.4268840864	0.2990666791	6.4472585734
H	1.4268840864	-0.2990666791	-6.4472585734
H	0.8502679258	3.7580135014	-5.1421652656
H	-0.8502679258	-3.7580135014	5.1421652656
H	1.5995461564	2.2254284451	-5.2055174804
H	-1.5995461564	-2.2254284451	5.2055174804
N	4.4464741339	2.7710157562	-5.9659850302
N	-4.4464741339	-2.7710157562	5.9659850302

H	-5.0597038782	0.7683085215	6.7804384499	H	1.4102520425	-6.0359608006	-0.5217123949
H	5.0597038782	-0.7683085215	-6.7804384499	H	-1.4102520425	6.0359608006	0.5217123949
H	-3.9671990511	1.8786956144	-6.4873847878	C	1.1440959012	-3.2889441191	1.4581905002
H	3.9671990511	-1.8786956144	6.4873847878	C	-1.1440959012	3.2889441191	-1.4581905002
H	4.3621467119	2.5237877141	-4.9738953980	H	1.0337971952	-2.2007794223	1.3949223929
H	-4.3621467119	-2.5237877141	4.9738953980	H	-1.0337971952	2.2007794223	-1.3949223929
N	2.4941320353	2.7480559043	5.3595949350	C	1.1880484511	-3.8960179047	2.7087440851
N	-2.4941320353	-2.7480559043	-5.3595949350	C	-1.1880484511	3.8960179047	-2.7087440851
H	3.0675797703	2.1213284691	4.7634375904	H	1.1353830766	-3.2885679860	3.6187043970
H	-3.0675797703	-2.1213284691	-4.7634375904	H	-1.1353830766	3.2885679860	-3.6187043970
H	3.0913558957	3.0614514742	6.1458963677	C	1.2164736297	-4.0460956365	0.2760103836
H	-3.0913558957	-3.0614514742	-6.1458963677	C	-1.2164736297	4.0460956365	-0.2760103836
H	2.1678877840	3.5721879596	4.8272462840	C	1.1088566443	-3.3906595669	-1.0672016025
H	-2.1678877840	-3.5721879596	-4.8272462840	C	-1.1088566443	3.3906595669	1.0672016025
N	-0.5393794301	2.8726003239	5.3561170045	H	1.0488070580	-4.1359885057	-1.8757887137
N	0.5393794301	-2.8726003239	-5.3561170045	H	-1.0488070580	4.1359885057	1.8757887137
H	-0.1241643761	3.6927053623	4.8812018226	H	1.9654736202	-2.7278298572	-1.2903659351
H	0.1241643761	-3.6927053623	-4.8812018226	H	-1.9654736202	2.7278298572	1.2903659351
H	-1.1271341169	3.1946626853	6.1441203128	H	0.2073434923	-2.7556265348	-1.1227293028
H	1.1271341169	-3.1946626853	-6.1441203128	H	-0.2073434923	2.7556265348	1.1227293028
H	-1.1696832886	2.3927021994	4.6818829985	S	3.1468054731	-0.4326039154	-3.9813562610
H	1.1696832886	-2.3927021994	-4.6818829985	S	-3.1468054731	0.4326039154	3.9813562610
N	3.0437459878	5.1233774154	-5.1001127355	O	2.4880333546	-1.7195253106	-3.7143324758
N	-3.0437459878	-5.1233774154	5.1001127355	O	-2.4880333546	1.7195253106	3.7143324758
C	3.0577261522	6.4696725526	-5.2612529864	O	4.5384533520	-0.5659690031	-4.4013425501
C	-3.0577261522	-6.4696725526	5.2612529864	O	-4.5384533520	0.5659690031	4.4013425501
H	2.9699263680	6.8424373249	-6.2837755189	O	2.3762252369	0.4292462359	-4.9016088932
H	-2.9699263680	-6.8424373249	6.2837755189	O	-2.3762252369	-0.4292462359	4.9016088932
C	3.3193340061	-5.1219614989	-4.1915263564	C	3.1782918334	0.4018358597	-2.4145460590
C	-3.3193340061	5.1219614989	4.1915263564	C	-3.1782918334	-0.4018358597	2.4145460590
H	3.2919198251	-4.0418923469	-4.3674786778	C	2.0180579668	0.4450362342	-1.6353618045
H	-3.2919198251	4.0418923469	4.3674786778	C	-2.0180579668	-0.4450362342	1.6353618045
C	3.4688469998	-5.6396397776	-2.9085867402	H	1.1061181752	-0.0402600331	-1.9997184874
C	-3.4688469998	5.6396397776	2.9085867402	H	-1.1061181752	0.0402600331	1.9997184874
H	3.5797199798	-4.9725067306	-2.0474642574	C	2.0498996295	1.0881136094	-0.4000057108
H	-3.5797199798	4.9725067306	2.0474642574	C	-2.0498996295	-1.0881136094	0.4000057108
C	3.3343080121	5.4375783652	-2.7234065291	H	1.1465813768	1.1261229040	0.2194866819
C	-3.3343080121	-5.4375783652	2.7234065291	H	-1.1465813768	-1.1261229040	-0.2194866819
C	3.1560025828	4.6306136836	-3.8489982103	C	3.2273021592	1.6835373920	0.0789970797
C	-3.1560025828	-4.6306136836	3.8489982103	C	-3.2273021592	-1.6835373920	-0.0789970797
H	3.1034432537	3.5428259645	-3.7398077325	C	-4.0605990180	1.6116880644	-0.7165526015
H	-3.1034432537	-3.5428259645	3.7398077325	C	4.0605990180	-1.6116880644	0.7165526015
C	3.5626394984	4.8262520151	-1.3787073061	H	-3.1338967891	2.0666536420	-0.3554801889
C	-3.5626394984	-4.8262520151	1.3787073061	H	3.1338967891	-2.0666536420	0.3554801889
H	3.3127259144	5.5422888139	-0.5787865462	C	4.3625823560	0.9814529337	-1.9592920146
H	-3.3127259144	-5.5422888139	0.5787865462	C	-4.3625823560	-0.9814529337	1.9592920146
H	4.6287493474	4.5519382761	-1.2637474816	H	-3.1763500359	0.9169404129	-2.5837246256
H	-4.6287493474	-4.5519382761	1.2637474816	H	3.1763500359	-0.9169404129	2.5837246256
H	2.9749847114	3.9051432949	-1.2394777935	C	3.2496127508	2.4170333464	1.3849589664
H	-2.9749847114	-3.9051432949	1.2394777935	C	-3.2496127508	-2.4170333464	-1.3849589664
S	1.2305124704	-6.0317812083	4.4050826473	H	2.4835949141	2.0399681391	2.0821405819
S	-1.2305124704	6.0317812083	-4.4050826473	H	-2.4835949141	-2.0399681391	-2.0821405819
O	-0.0387951126	-5.5741682542	4.9922058752	H	3.0528000751	3.4940191114	1.2176292954
O	0.0387951126	5.5741682542	-4.9922058752	H	-3.0528000751	-3.4940191114	-1.2176292954
O	2.4040218279	-5.5396845499	5.1286716708	H	-4.2037416517	2.3325070077	1.8784169242
O	-2.4040218279	5.5396845499	-5.1286716708	H	4.2037416517	-2.3325070077	-1.8784169242
O	1.1068129289	4.9732986785	4.1830581602				
O	-1.1068129289	-4.9732986785	-4.1830581602	140			
C	1.2937519772	-5.2883477674	2.7929864381	Ru	0.9231119469	1.6903549113	6.0033438505
C	-1.2937519772	5.2883477674	-2.7929864381	Ru	-0.9231119469	-1.6903549113	-6.0033438505
C	1.3974939836	-6.0612082480	1.6388583836	S	0.5338574465	-0.1967431300	4.6455927230
C	-1.3974939836	6.0612082480	-1.6388583836	S	-0.5338574465	0.1967431300	-4.6455927230
H	1.3323229813	5.3128036558	1.7260754409	O	0.9785166666	1.0994570649	3.9617837715
H	-1.3323229813	-5.3128036558	-1.7260754409	O	-0.9785166666	-1.0994570649	-3.9617837715
C	1.3661595970	-5.4329954302	0.3905047430	O	1.5517926259	-1.2631386622	4.6862286394
C	-1.3661595970	5.4329954302	-0.3905047430	O	-1.5517926259	1.2631386622	-4.6862286394

N	1.2613665973	3.2091722603	-5.8431054849	O	1.2655078882	5.0542130147	4.1614484087
N	-1.2613665973	-3.2091722603	5.8431054849	O	-1.2655078882	-5.0542130147	-4.1614484087
H	-1.4510549274	0.4105809616	6.3787859739	C	1.3343107453	-5.2371081465	2.7294941618
H	1.4510549274	-0.4105809616	-6.3787859739	C	-1.3343107453	5.2371081465	-2.7294941618
H	0.8023113777	3.9420440230	-5.2711737844	C	1.4391508858	-6.0484192776	1.6016176707
H	-0.8023113777	-3.9420440230	5.2711737844	C	-1.4391508858	6.0484192776	-1.6016176707
H	1.5731003791	2.4189098259	-5.2555654159	H	1.3795944425	5.3301926983	1.7286371694
H	-1.5731003791	-2.4189098259	5.2555654159	H	-1.3795944425	-5.3301926983	-1.7286371694
N	4.4455289131	2.8731733140	-6.0861626139	C	1.4062758091	-5.4669129179	0.3317273453
N	-4.4455289131	-2.8731733140	6.0861626139	C	-1.4062758091	5.4669129179	-0.3317273453
H	-5.3852836727	0.1409519144	5.9941091049	H	1.4564120923	-6.1017845671	-0.5585454007
H	5.3852836727	-0.1409519144	-5.9941091049	H	-1.4564120923	6.1017845671	0.5585454007
H	-4.3748580069	2.0370742810	-5.6163771830	C	1.1898976736	-3.2870144807	1.3256165954
H	4.3748580069	-2.0370742810	5.6163771830	C	-1.1898976736	3.2870144807	-1.3256165954
H	5.0452296179	3.3921304101	-5.4300201426	H	1.0909241136	-2.2007630441	1.2218885846
H	-5.0452296179	-3.3921304101	5.4300201426	H	-1.0909241136	2.2007630441	-1.2218885846
N	2.5585221865	2.8130454176	5.3084250960	C	1.2372101776	-3.8469312159	2.5993294093
N	-2.5585221865	-2.8130454176	-5.3084250960	C	-1.2372101776	3.8469312159	-2.5993294093
H	3.1028504180	2.1800926108	4.6960170979	H	1.1938908730	-3.2022694441	3.4847703430
H	-3.1028504180	-2.1800926108	-4.6960170979	H	-1.1938908730	3.2022694441	-3.4847703430
H	3.1650536650	3.0639595287	6.1087170614	C	1.2507201534	-4.0852734810	0.1705409925
H	-3.1650536650	-3.0639595287	-6.1087170614	C	-1.2507201534	4.0852734810	-0.1705409925
H	2.2764468148	3.6684932506	4.8004999403	C	1.1139407037	-3.4819779620	-1.1947016038
H	-2.2764468148	-3.6684932506	-4.8004999403	C	-1.1139407037	3.4819779620	1.1947016038
N	-0.5305935339	3.0444109179	5.3119312158	H	1.2417954861	-4.2412018621	-1.9823824263
N	0.5305935339	-3.0444109179	-5.3119312158	H	-1.2417954861	4.2412018621	1.9823824263
H	-0.1116086289	3.8505970616	4.8186582340	H	1.8399376175	-2.6694907936	-1.3792516641
H	0.1116086289	-3.8505970616	-4.8186582340	H	-1.8399376175	2.6694907936	1.3792516641
H	-1.1011263831	3.3779828817	6.1046722798	H	0.1135831444	-3.0311655629	-1.3241582861
H	1.1011263831	-3.3779828817	-6.1046722798	H	-0.1135831444	3.0311655629	1.3241582861
H	-1.1569123000	2.5244134364	4.6707956483	S	3.1396840687	-0.1881796240	-3.9661476749
H	1.1569123000	-2.5244134364	-4.6707956483	S	-3.1396840687	0.1881796240	3.9661476749
N	3.0813557569	5.1788316612	-5.1522789681	O	2.2242472934	-1.3264876922	-3.8593326465
N	-3.0813557569	-5.1788316612	5.1522789681	O	-2.2242472934	1.3264876922	3.8593326465
C	3.1281366189	6.5302834147	-5.2496568330	O	4.5153691926	-0.5642756741	-4.2918292795
C	-3.1281366189	-6.5302834147	5.2496568330	O	-4.5153691926	0.5642756741	4.2918292795
H	3.0385024640	6.9502045915	-6.2551651918	O	2.6412999759	0.8639534112	-4.8811057557
H	-3.0385024640	-6.9502045915	6.2551651918	O	-2.6412999759	-0.8639534112	4.8811057557
C	3.4278184998	-5.1224361179	-4.1375868831	C	3.1881054766	0.5292068000	-2.3429611073
C	-3.4278184998	5.1224361179	4.1375868831	C	-3.1881054766	-0.5292068000	2.3429611073
H	3.4404548868	-4.0357386168	-4.2641202445	C	2.0178938651	0.5674110177	-1.5784418703
H	-3.4404548868	4.0357386168	4.2641202445	C	-2.0178938651	-0.5674110177	1.5784418703
C	3.5652190148	-5.7090586938	-2.8817104367	H	1.0977253351	0.1357017900	-1.9865515788
C	-3.5652190148	5.7090586938	2.8817104367	H	-1.0977253351	-0.1357017900	1.9865515788
H	3.6993601716	-5.0926300179	-1.9870477117	C	2.0508022970	1.1345320995	-0.3068405445
H	-3.6993601716	5.0926300179	1.9870477117	C	-2.0508022970	-1.1345320995	0.3068405445
C	3.3922746129	5.3609710623	-2.7666511018	H	1.1396058727	1.1651964725	0.3010491930
C	-3.3922746129	-5.3609710623	2.7666511018	H	-1.1396058727	-1.1651964725	-0.3010491930
C	3.1999501104	4.6158922429	-3.9309902917	C	3.2406635173	1.6572465973	0.2235678556
C	-3.1999501104	-4.6158922429	3.9309902917	C	-3.2406635173	-1.6572465973	-0.2235678556
H	3.1532580910	3.5223527791	-3.8913650755	C	-4.0385647753	1.5912057175	-0.5589158891
H	-3.1532580910	-3.5223527791	3.8913650755	C	4.0385647753	-1.5912057175	0.5589158891
C	3.5961802916	4.6708596558	-1.4576662592	H	-3.1026749131	1.9853413122	-0.1540715857
C	-3.5961802916	-4.6708596558	1.4576662592	H	3.1026749131	-1.9853413122	0.1540715857
H	3.3217111605	5.3324929972	-0.6194801333	C	4.3840224155	1.0403933557	-1.8383970791
H	-3.3217111605	-5.3324929972	0.6194801333	C	-4.3840224155	-1.0403933557	1.8383970791
H	4.6615768143	4.3969800156	-1.3363181020	H	-3.1475849957	0.9889406777	-2.4532606436
H	-4.6615768143	-4.3969800156	1.3363181020	H	3.1475849957	-0.9889406777	2.4532606436
H	3.0143525894	3.7379062773	-1.3911222418	C	3.2657793314	2.2953691686	1.5780563565
H	-3.0143525894	-3.7379062773	1.3911222418	C	-3.2657793314	-2.2953691686	-1.5780563565
S	1.2658743097	-5.9545265247	4.3543370442	H	2.5812248142	1.7937877507	2.2815699406
S	-1.2658743097	5.9545265247	-4.3543370442	H	-2.5812248142	-1.7937877507	-2.2815699406
O	-0.0585972174	-5.6124694842	4.8994726678	H	2.9543760919	3.3558151127	1.5115363436
O	0.0585972174	5.6124694842	-4.8994726678	H	-2.9543760919	-3.3558151127	-1.5115363436
O	2.3680306991	-5.3557697844	5.1122157394	H	-4.1577419536	2.2674624113	2.0125173114
O	-2.3680306991	5.3557697844	-5.1122157394	H	4.1577419536	-2.2674624113	-2.0125173114

Bibliography

- [1] Liu, T.; Pagliano, F.; van Veldhoven, R.; Pogoretskiy, V.; Jiao, Y.; Fiore, A. Integrated nano-optomechanical displacement sensor with ultrawide optical bandwidth. *Nat. Commun.* 2020, 11, 2407.
- [2] Bochmann, J.; Vainsencher, A.; Awschalom, D. D.; Cleland, A. N. Nanomechanical coupling between microwave and optical photons. *Nat. Phys.* 2013, 9, 712-716.
- [3] Abendroth, J. M.; Bushuyev, O. S.; Weiss, P. S.; Barrett, C. J. Controlling motion at the nanoscale: rise of the molecular machines. *ACS Nano* 2015, 9, 7746-7768.
- [4] Tong, F.; Xu, W.; Guo, T.; Lui, B. F.; Hayward, R. C.; Palffy-Muhoray, P.; Al-Kaysi, R. O.; Bardeen, C. J. Photomechanical molecular crystals and nanowire assemblies based on the [2+2] photodimerization of a phenylbutadiene derivative. *J. Mater. Chem. C* 2020, 8, 5036–5044.
- [5] Al-Kaysi, R. O.; Tong, F.; Al-Haidar, M.; Zhu, L.; Bardeen, C. J. Highly branched photomechanical crystals. *Chem. Commun.* 2017, 53, 2622–2625.
- [6] Naumov, P.; Karothu, D. P.; Ahmed, E.; Catalano, L.; Commins, P.; Halabi, J. M.; Al-Handawi, M. B.; Li, L. The Rise of the Dynamic Crystals. *J. Am. Chem. Soc.* 2020, 142, 13256-13272.
- [7] Naumov, P.; Chizhik, S.; Panda, M. K.; Nath, N. K.; Boldyreva, E. Mechanically Responsive Molecular Crystals. *Chem. Rev.* 2015, 115, 12440-12490.
- [8] Sylvester, S. O.; Cole, J. M. Solar-Powered Nanomechanical Transduction from Crystalline Molecular Rotors. *Adv. Mater.* 2013, 25, 3324-3328.
- [9] Sylvester, S. O.; Cole, J. M.; Waddell, P. G.; Nowell, H.; Wilson, C. SO₂ Phototriggered Crystalline Nanomechanical Transduction of Aromatic Rotors in Tosylates: Rationalization via Photocrystallography of [Ru(NH₃)₄SO₂X]tosylate₂ (X = pyridine, 3-Cl-pyridine, 4-Cl-pyridine). *J. Phys. Chem. C* 2014, 118, 16003-16010.

- [10] Cole, J. M.; Gosztola, D. J.; Velazquez-Garcia, J. d. J.; Wang, S. G.; Chen, Y.-S. Rapid build up of nanooptomechanical transduction in single crystals of a ruthenium-based SO₂ linkage photoisomer. *Chem. Commun.* 2021, 57, 1320-1323.
- [11] Cole, J. M.; Velazquez-Garcia, J. J.; Gosztola, D. J.; Wang, S.-Y. G.; Chen, Y.-S. Light-Induced Macroscopic Peeling of Single-Crystal Driven by Photoisomeric Nano-Optical Switching. *Chem. Mater.* 2019, 31, 4927-4935.
- [12] Sylvester, S. O.; Cole, J. M. Quantifying Crystallographically Independent Optical Switching Dynamics in Ru SO₂ Photoisomers via Lock-and-Key Crystalline Environment. *J. Phys. Chem. Lett.* 2013, 4, 3221e3226.
- [13] Sylvester, S. O.; Cole, J. M.; Waddell, P. G. Photoconversion Bonding Mechanism in Ruthenium Sulfur Dioxide Linkage Photoisomers Revealed by in Situ Diffraction. *J. Am. Chem. Soc.* 2012, 134, 11860-11863.
- [14] Kovalevsky, A. Yu.; Bagley, K. A.; Coppens, P. The First Photocrystallographic Evidence for Light-Induced Metastable Linkage Isomers of Ruthenium Sulfur Dioxide Complexes. *J. Am. Chem. Soc.* 2002, 124, 9241-9248.
- [15] Kovalevsky, A. Yu.; Bagley, K. A.; Cole, J. M.; Coppens, P. Light-Induced Metastable Linkage Isomers of Ruthenium Sulfur Dioxide Complexes. *Inorg. Chem.* 2003, 42, 140-147.
- [16] Bowes, K. F.; Cole, J. M.; Husheer, S. L. G.; Raithby, P. R.; Savarese, T.; Sparkes, H. A.; Warren, J. E. Photocrystallographic structure determination of a new geometric isomer of [Ru(NH₃)₄(H₂O)(η 1-OSO)][MeC₆H₄SO₃]₂. *Chem. Commun.* 2006, 2448-2450.
- [17] Phillips, A. E.; Cole, J. M.; d'Almeida, T.; Low, K. S. Ru–OSO Coordination Photogenerated at 100 K in Tetraammineaqua(sulfur dioxide)ruthenium(II) ($\pm$)-Camphorsulfonate. *Inorg. Chem.* 2012, 51, 1204-1206.
- [18] Phillips, A. E.; Cole, J. M.; d'Almeida, T.; Low, K. S. Effects of the reaction cavity on metastable optical excitation in ruthenium-sulfur dioxide complexes. *Phys. Rev. B* 2010, 82, 155118.
- [19] Mukaddem, K. T.; Cole, J. M.; Beyer, K. A.; Sylvester, S. O. Local Atomic Structure in Photoisomerized Ruthenium Sulfur Dioxide Complexes Revealed by Pair Distribution Function Analysis. *J. Phys. Chem. C* 2020, 124, 10094-10104.

- [20] Phillips, A. E.; Cole, J. M.; Low, K. S.; Cibin, G. L2,3-edge x-ray absorption near-edge spectroscopy analysis of photoisomerism in solid ruthenium–sulfur dioxide complexes. *J. Phys. Cond. Matt.* 2013, 25, 085505.
- [21] Coppens, P.; Fomitchev, D. V.; Carducci, M. D.; Culp, K. Crystallography of molecular excited states. Transition-metal nitrosyl complexes and the study of transient species. *J. Chem. Soc., Dalton Trans.* 1998, 6, 865-872.
- [22] Cole, J. M. Single-crystal X-ray diffraction studies of photo-induced molecular species. *Chem. Soc. Rev.* 2004, 33, 501-513.
- [23] Cole, J. M., Photocrystallography. *Acta Crystallogr., Sect. A: Found. Crystallogr.* 2008, 64, 259-271.
- [24] Cole, J. M. A new form of analytical chemistry: distinguishing the molecular structure of photo-induced states from ground-states. *Analyst* 2011, 136, 448-455.
- [25] Cole, J. M., Applications of photocrystallography: a future perspective. *Z. Kristallogr.* 2008, 223, 363-369.
- [26] Cole, J. M.; Gosztola, D. J.; Velazquez-Garcia, J. d. J.; Chen, Y-S. Systems Approach of Photoisomerization Metrology for Single-Crystal Optical Actuators: A Case Study of [Ru(SO₂)(NH₃)₄Cl]Cl. *J. Phys. Chem. C* 2020, 124, 51, 28230–28243.
- [27] González, L.; Escudero, D.; Serrano-Andrés L. Progress and Challenges in the Calculation of Excited States. *ChemPhysChem* 2012, 13, 28–51.
- [28] Loos, P.; Scemama, A.; Jacquemin D. The Quest for Highly Accurate Excitation Energies: A Computational Perspective. *J. Phys. Chem. Lett.* 2020, 11, 2374–2383.
- [29] Strinati, G. Application of the Green's Functions Method to the Study of the Optical Properties of Semiconductors. *Riv. Nuovo Cimento* 1988, 11, 1– 86.
- [30] Hedin, L. New Method for Calculating the One-Particle Green's Function with Application to the Electron-Gas Problem. *Phys. Rev.* 1965, 139, A796.
- [31] Warshel, A.; Levitt, M. Theoretical studies of enzymic reactions: Dielectric, electrostatic and steric stabilization of the carbonium ion in the reaction of lysozyme. *J. Mol. Biol.* 1976, 103, 227– 249.

- [32] Aono S; Sakaki, S. QM/MM Approach to Isomerization of Ruthenium(II) Sulfur Dioxide Complex in Crystal; Comparison with Solution and Gas Phases. *J. Phys. Chem. C* 2018, 122, 36, 20701–20716.
- [33] Hohenberg P.; Kohn, W. *Phys. Rev.* 1964, 136, B864.
- [34] Kohn, W.; Sham, L. *J. Phys. Rev.* 1965, 140, A1133.
- [35] Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*, International Series of Monographs on Chemistry (Oxford University Press, USA, 1994).
- [36] Pickett, W. E.; *Comput. Phys. Rep.* 1989, 9, 115.
- [37] Cole, J. M.; Gosztola, D. J.; Sylvester, S. O. Low-energy optical switching of SO₂ linkage isomerisation in single crystals of a ruthenium-based coordination complex, *RSC Adv.* (submitted).
- [38] Giannozzi, P.; Baroni, S.; Bonini N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; *et al.* Quantum ESPRESSO: a modular and open-source software project for quantum simulations of materials. *J. Phys. Condens. Matter.* 2009, 21, p. 395502.
- [39] Giannozzi, P.; Andreussi, O.; Brumme, T.; Bunau, O.; Buongiorno N. M.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Cococcioni, M.; Colonna, N.; Carnimeo, I.; Corso, A. D.; Gironcoli, S. d.; *et al.* Advanced capabilities for materials modelling with Quantum ESPRESSO. *J. Phys. Condens. Matter.* 2017, 29, p. 46.
- [40] Hamann, D. *Phys. Rev.* 2013, B 88, 085117.
- [41] Adamo, C.; Barone, V. Toward reliable density functional methods without adjustable parameters: The PBE0 model. *J. Chem. Phys.* 1999, 110, 6158.
- [42] Heyd, J; Scuseria, G. E.; Ernzerhof, M. *J. Chem. Phys.* 2003, 118, 8207.
- [43] Perdew, J. P.; Ruzsinszky, A.; Csonka, G. I.; Vydrov, O. A.; Scuseria, G.E.; Constantin, L. A.; Zhou, X.; Burke, K. *Phys. Rev. Lett.* 2008, 100, 136406.
- [44] Grimme, S. *J. Comp. Chem.* 2006, 27, 1787.
- [45] Monkhorst, H. J.; Pack, J. D. *Phys. Rev.* 1976, B 13, 5188.
- [46] Aprà, E. *et al.* NWChem: Past, present, and future. *J. Chem. Phys.* 2020, 152, 184102.

- [47] Hay, P. J.; Wadt, W. R. J. Chem. Phys. 1985, 82, 299.
- [48] Becke, A. D. Density-functional thermochemistry. V. Systematic optimization of exchange-correlation functionals. J. Chem. Phys. 1997, 107, 8554.
- [49] Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. J. Chem. Phys. 2010, 132, 154104
- [50] Runge, E.; Gross, E. K. Phys. Rev. Lett. 1984, 52, 997.
- [51] Malcioğlu O. S.; Gebauer, R.; Rocca, D.; Baroni, S. turboTDDFT – A code for the simulation of molecular spectra using the Liouville–Lanczos approach to time-dependent density-functional perturbation theory. Comput. Phys. Commun. 2011, 182, 1744-1754.
- [52] Ge, X.; Binnie, S. J.; Rocca, D.; Gebauer, R. turboTDDFT 2.0—hybrid functionals and new algorithms within time-dependent density-functional perturbation theory. Comput. Phys. Commun. 2014, 185, 2080-2089.
- [53] *Fundamentals of Time-Dependent Density Functional Theory*, Lecture Notes in Physics, edited by M. Marques, N. Maitra, F. Nogueira, E. Gross, and A. Rubio (Springer, Berlin, Heidelberg, 2012), Vol. 837.
- [54] Jornet-Somoza, J.; Lebedeva, I. : J. Chem. Theory Comput. 2019, 15, 3743–3754.
- [55] Lian, C.; Guan, M.; Hu, S.; Zhang, J.; Meng, S. Adv. Theory Simul. 2018, 1: 1800055.
- [56] Lancia, F., Ryabchun, A. & Katsonis, N. Nat Rev Chem 2019, 3, 536–551.
- [57] Aprahamian, I. ACS Cent. Sci. 2020, 6, 347–358.
- [58] Cole, J. M.; Yeung, K. Y. M.; Pace, G.; Sylvester, S. O.; Mersch, D.; Friend, R. H. CrysEngComm, 2015, 17, 5026.
- [59] Velazquez-Garcia, J. (2017). Solid-State Photo-Linkage Isomers of Ruthenium Sulfur-Dioxide Complexes: Synthesis, Characterisation and Property Prediction. University of Cambridge.
- [60] Sven, S. O. (2013). Solid-State Photo-Linkage Isomerisation in Ruthenium Sulfur-Dioxide Single Crystals: Synthesis and Photocrystallography. University of Cambridge.
- [61] Koch, W., & Holthausen, M. C. (2001). *A Chemist's Guide to Density Functional Theory*. Wiley-VCH.

- [62] Dronskowski, R. (2005). *Computational Chemistry of Solid State Materials*. Wiley-VCH.
- [63] Herbol, H. C.; Stevenson, J.; Clancy, P. J. *Chem. Theory Comput.* 2017, 13, 3250–3259.
- [64] Garcia, J. S.; Alary, Boggio-Pasqua, M.; F.; Dixon I. M.; Malfant, I.; Heully J. *Inorg. Chem.* 2015, 54, 8310–8318.
- [65] Garcia, J. S.; Talotta, F.; Alary, F.; Dixon I. M.; Heully J.; Boggio-Pasqua, M. *Molecules*, 2017, 22, 1667.
- [66] Vogt, L. H.; Katz, J. L.; Wiberley, S. E. *Inorg. Chem.* 1956, 4, 1157-1163.
- [67] Cole, J.; Gosztola, D.; Sylvester, S.; Wang, S.; Chen, Y. (2021). Assigning Optical Absorption Transitions with Light-Induced Crystal Structures: Case Study of a Single-Crystal Nanooptomechanical Transducer. *Journal of Physical Chemistry C*, 125 (28), 15711-15723.
- [69] Holze, C.; Pausch, A.; Klopper, W. (2021). The GW/BSE Method in Magnetic Fields. *Front Chem.* 9: 746162.
- [70] Loos, P.; Scemama, A.; Duchemin I.; Jacquemin D.; Blase, X. Pros and Cons of the Bethe-Salpeter Formalism for Ground-State Energies. *J. Phys. Chem. Lett.* 2020, 11, 9, 3536–3545.
- [71] Senn, H. M.; Thiel, W. (2009). QM/MM Methods for Biomolecular Methods. *Angew. Chem. Int. Ed.* 48, 1198-1229.
- [72] Bagayoko, D. (2014). Understanding density functional theory (DFT) and completing it in practice. *AIP Advances* 4. 127104.
- [73] Hotta, S. (2020). Optical Transition and Selection Rules. In: *Mathematical Physical Chemistry*. Springer, Singapore.
- [74] Towler, M. D.; Zupan, A.; Causá, M. (1996) *Comput. Phys. Commun.* 98. 181-205.
- [75] Brugnoli, L.; Urata, S.; Pedone, (2022). H₂O₂ adsorption and dissociation on various CeO₂ (111) surface models: first principles study. *J. Phys.: Condens. Matter.* 34. 164006.
- [76] Mali, D.; Kumar, K.; Jangid, P. K.; Arora, G.; Ahuja, B. L. (2021). Electronic structure of tantalum dichalcogenide using Compton scattering technique and density functional theory. *Radiat. Phys. Chem.* 182. 109379-1–109379-8.

- [77] Jangid, P. K.; Arora, G.; Mali, D.; Joshi, P. K.; Kumar, K.; Ahuja, B. L. (2020) *J. Phys.: Conf. Ser.* 1504. 012017.
- [78] Yanai, T.; Tew, D. P.; Handy, N. C. (2004). A new hybrid exchange–correlation functional using the Coulomb-attenuating method (CAM-B3LYP). *Chem. Phys. Lett.* 393. 51-57.
- [79] Lynch, B. J.; Fast, P. L.; Harris, M.; Truhlar D. G. (2000). Adiabatic Connection for Kinetics. *J. Phys. Chem. A* 2000, 104, 21, 4811–4815.
- [80] Ray, S. C. (2020). 1 – The fundamental aspects of Spintronics. In: *Magnetism and Spintronics in Carbon and Carbon Nanostructured Materials*. Elsevier, Amsterdam.