Theoretical Photochemistry

*Halogenated Arenes, Phytochromobilin, Ru(II)polypyridyl complexes and 6-4 photoadducts*

ANDERS BORG
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Abstract

This thesis presents Quantum Chemical calculations on the Photochemistry of Halogenated benzenes, Phytochromobilin, Ruthenium Polypyridyl complexes and 6-4 photoadducts in DNA. The work is focused on improving the understanding of a number of experimentally observed photochemical processes in these systems. New results regarding the mechanism of photodissociation of halogenated arenes, photointerconversion of phytochromobilin are presented, as well as of the photoprocesses of Ruthenium Polypyridyl complexes and new mechanistic insights in the repair of 6-4 photoadducts in DNA.

Keywords: Quantum Chemistry, Halogenated Arenes, Phytochromobilin, Phytochrome, Ruthenium, 6-4 photoadducts, Photochemistry

Anders Borg, Department of Physical and Analytical Chemistry, Quantum Chemistry, Box 518, Uppsala University, SE-75120 Uppsala, Sweden

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List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.


IV  The mechanism for Photodissociation of Chlorobenzene - Beyond the pseudo diatomic model, O. A. Borg, D. Karlsson, M. Isomäki-Krondahl, J. Davidsson and S. Lunell *Submitted to Chem. Phys. Lett.*


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1. Introduction

When I started my Ph.D. studies in December 2003, I had a vague idea about the differences between a physicist and a chemist. Chemistry, I had been told, is Physics on an electron-volt scale. Interestingly, I have during the course of this work become more and more aware that inside the heads of people in the field, Chemistry is not a subset of Physics. They rather find Chemistry and Physics to be two different approaches to the same problems within the area of molecular science. It is two different ways of thinking. While a physicist likes formulas, wave functions and electron densities, a chemist likes orbitals and free energies.

It soon became apparent to me that linking those two different ways of thinking for any molecular system, is in itself a subject interesting enough for building a thesis upon. The fine thread connecting physicists and chemists is followed in this thesis. I have therefore tried to write this thesis, not with aim of necessarily copying formulas from Szabo and Ostlund,1 or Yang and Parr,2 and thereby show that Chemistry is a subset of Physics. Rather I try to outline the theory of the systems presented in an intuitive and pragmatic, as in Chemistry, but hopefully still correct and abstract, as in Physics, way.
2. Predissociation of Halogenated Arenes

In this chapter, the core of the thesis is presented, theoretical modelling of photodissociation processes in halogenated arenes. The chapter starts with a motivation of why this kind of processes are relevant to study (Section 2.1). Since Quantum Chemistry of excited states sometimes needs some extra care compared to ground state Quantum Chemistry, Section 2.2 couples the photochemical description of these system to the methods used. The actual results, the mechanism of pre-dissociation of halogenated arenes, are thereafter presented in Section 2.3.

2.1 Background

It was first found by Ichimura et al.,3–5 that photodecomposition of the X-Ph bond is an important depopulation process of electronically excited states in halogenated arenes. The photodecompositions of these systems was studied by Bersohn and co-workers,6–8 by means of photofragment translational spectroscopy. Those investigations gave information about which products were formed, but they did not say much about the dissociation mechanism. With the incentive of exploring the mechanism, time resolution was obtained by Zewail9 on iodobenzene, and later refinements were made by Davidsson,10–12 Reilly13 and He.14 With time resolution down to hundreds of femtoseconds, it will in the future be possible to follow, and even control, the reactions on the same timescale as they appear. The high quantum yield of dissociation of the halogen provides a possibility to ultimately control the formation of the phenyl radical. In doing that, a detailed understanding of the reaction mechanism is needed, and the details of the reactions for long remained uncertain. Clearly, the interpretations of the experiments are far from straightforward. Several computational studies have therefore been done to elucidate the mechanism. It was in 2000 suggested for chlorobenzene by Sobolewski and Domcke,15 that the dissociation mechanism is described by a bound singlet to repulsive singlet, \( \pi\pi^* \rightarrow \pi\sigma^* \), mechanism mediated by the three lowest vibrational modes of this molecule, C-Cl stretch, Cl out-of-plane bending and Cl+ring skewing. This was a very important step in the right direction, but that study did not fit into the explanations given so far. This was so since several effects of suggested importance were not
investigated. The calculations reported there only contained three electronic states, $S_0, \pi \pi^*, \pi \sigma^*$. In addition, Zewail suggested that the dissociation might involve states of other multiplicities than singlets as well. Several different spatial characters of the repulsive state other than $\pi \sigma^*$ have also been suggested since the days of Bersohn. In a series of papers, the number of states within reach of the wavelength used in most experiments (250-270 nm) grew from 2 to 8, four bound states and four repulsive. The first paper of this thesis (Paper I, 2004) presents a one-dimensional model, with the energy as a function of the C-Br distance. An illustrative example is the para-bromo-fluorobenzene, displayed in Figure 2.1.

![Figure 2.1: One-dimensional PES along C-Br of para-bromo-fluorobenzene.](image)

The one-dimensional model is in Paper I proven to give a good notion of which states need to be investigated for describing the dissociation, but also clearly demonstrates that more nuclear dimensions are needed for quantification of this process. A barrier for dissociation, in the one-dimensional case, approximated as the difference in energy between bound-repulsive crossing point and pulse energy, can not be accurately captured in a
one-dimensional picture such as the one in Figure 2.1. In order to identify the most important parameters in the dissociation mechanism, the model is refined in the three following papers of the thesis (Paper II 2005, Paper III 2006, Paper IV 2007) and now we are actually able to say what is necessary for quantifying these reactions.

2.2 Photochemistry of Halogenated Arenes and it’s Coupling to Methodology

A molecule is a mixture of electrons and nuclei. The wave function of the total molecule is not necessarily always separable in one nuclear and one electronic part. The concept of chemical structures, however, is based upon the separation of atomic nuclear and electronic movements. It is easier to speak about Chemistry in that way, since we are used to this formalism from ground state Chemistry. We usually do not stop at this stage of simplification however, sometimes it is convenient to imply that the different electrons in a molecule can be distinguished, and we speak about core electrons and valence electrons or even sometimes, π electrons, forming e.g. the second bond in a double bond. In many cases, we do not need to deeper reflect on what these concepts really mean. The separability of motions is usually a very good approximation, and the discussions of orbitals are often used to confirm what is already known.

In excited state Chemistry the validity of the separability of motions needs to be tested in each case, and a deeper understanding of what an orbital is, can actually be very helpful in carrying out calculations. We start here with the separability problem. It is known that the energetical separations between the electronically excited states are smaller than the separation between the ground state and first excited state. It can even be so that several excited states are near-degenerate, or even crossing each other when the nuclear configuration is changed. To understand why and how states interact in halogenated benzenes, we were helped by investigating the orbital structure of the states. In Subsections 2.2.1 and 2.2.2, the relevant orbitals of these systems are introduced. These chemically active orbitals are then coupled to the description of the relevant electronic states.

2.2.1 The Orbital Classification

Solving the electronic Schrödinger equation of a molecule of any relevance for Chemistry is a problem including at least three bodies, and therefore no analytical solutions to a relevant quantum chemical problem exist. Instead, a solution is guessed and thereafter iteratively improved until the wave function or some property of it is not changed. In this thesis, orbitals are used to build either a wave function or an electron density. Orbitals are not observables, and
are here regarded as a computational aid. One type of orbitals, that is often used, is the Natural Spin Orbitals\textsuperscript{22} whose eigenvalues can be interpreted as electron occupation numbers in terms of a fraction of, or the whole of electrons. The origin of these orbitals is the $N \times N$ one-electron reduced density matrix, which can be obtained from any $N$-electron wave function;

$$\gamma(r_1 | r'_1) = N \int \Psi^*(r'_1, r_2...r_N)\Psi(r_1, r_2...r_N)dr_2...dr_N$$ (2.1)

where the wave function (for one spin) is integrated over all sets of electronic coordinates except for two sets, $r_1, r'_1$. The (matrix)element, $\gamma(r_1 | r'_1)$, has in the general case no apparent interpretation. The matrix is therefore diagonalized, and the eigenvalues are, in analogy to the Born Interpretation\textsuperscript{23} seen as an occupation numbers. One conceptual complication here is that the occupation can indeed be a fraction of an electron. This is throughout the thesis chosen to be seen as a consequence of that the one-orbital-per-electron picture is not perfect. The advantage of these orbitals is that they might be intuitive since $|\gamma|^2$ is a probability density with some kind of chemical interpretation.

Having established which kind of orbitals we want to use, we can return to the classification of the orbitals in type and symmetry. Of the molecular orbitals used here, the $\sigma$ orbital is most important. A $\sigma$ orbital does not change phases (+,-) when rotated along the line connecting the atoms it is located around. A $\sigma^*$ orbital has a nodal plane orthogonal to the line connecting the atoms, i.e. it is non- or antibonding. Typically, a bonding orbital forming a single bond in between two atom is $\sigma$, and an antibonding is $\sigma^*$. HOMO-4 in Figure 2.2 is bonding in between the bromine and the closest carbon. LUMO+2 is antibonding with respect to those atoms.

In Figure 2.2, the frontier orbitals of 1-Br-3,5-diFPh are displayed, below the horizontal line are the occupied ones and above the unoccupied ones. This molecule has two mirror planes, one in the molecular plane, and one orthogonal to the molecular plane (Figure 2.3). In this thesis, the symmetries used used are $C_{2v}$ and $C_5$. A $C_{2v}$ symmetric molecule has two mirror planes, and the phases of the orbitals can change in four different ways with respect to these planes. The phase can be the same on both sides of both planes (denoted $a_1$), different on both sides of both planes (denoted $a_2$) and different with respect to one plane but not to the other ($b_1$ or $b_2$). In $C_5$, only $a_1$ (denoted $a'$) and $b_1$ or $b_2$ (denoted $a''$) exist. The most important thing for the following explanations is that orbitals with different symmetries are orthogonal. The $\sigma$ orbitals (HOMO-4, HOMO-2, LUMO+2) possess $a_1$ (in $C_{2v}$) symmetry, which is $a'$ in $C_5$. $\pi$ orbitals, such as LUMO, change phases upon reflection in at least one of the symmetry planes. These orbitals are of $a''$ symmetry in a $C_5$ symmetric molecule and either $b_1$, $b_2$ or $a_2$ in $C_{2v}$. We have throughout chosen the orientation such that $\pi$ orbitals are $b_1$ or $a_2$ symmetric. An alternative would have been $b_2$ and $a_2$. A $n$ orbital is in Paper I a non-bonding $Br – 3p$ orbital of either $b_1$ or $b_2$ symmetry.
Figure 2.2: Frontier orbitals of 1-Br-3,5-diFPh.

2.2.2 The Multiconfigurational Nature of the Wave function

No Quantum Chemistry thesis is complete if the combination of names Hartree and Fock\(^ {24} \) (HF) is not mentioned. The wave function of a restricted Hartree-Fock wave function, which is represented by a Slater determinant,\(^ {25} \) has a diagonal one-electron reduced density matrix with integer occupation numbers.\(^ {26} \) This makes the interpretation of the orbitals straightforward, but unfortunately Hartree-Fock is a mean-field theory\(^ {1} \) and is as such bad for describing bond-breaking and formation, as well as excited states. As a
consequence, bond breaking in excited states is not adequately modelled using this theory.

The **Complete Active Space, CASSCF** method employs several Slater-determinants representing several different types of Hartree-Fock like configurations. In this thesis, one of the molecular model systems used has been 1-Bromo-3,5-difluorobenzene. In that molecule, as seen in Figure 2.2, the two energetically highest occupied molecular orbitals are of $\pi$ type. These are formed from linear combination of out-of-plane oriented carbon $2p_z$ and bromine $3p_z$ atomic orbitals. The two lowest unoccupied orbitals are the corresponding $\pi^*$ orbitals. This is true in the Hartree-Fock approximation. (Even though the orbitals in Figure 2.2 are calculated at the CASSCF level.) Henceforth denote this HF reference wave function $|\Psi\rangle_{HF}$, and use it as a zeroth order approximation to improve upon. The first excited singlet state, which is obtained by a $\pi \rightarrow \pi^*$ excitation, can be approximated by moving one $\pi$ electron to a $\pi^*$ orbital, *i.e.* HOMO-1→LUMO, and the resulting state can be denoted $|\Psi_{H-1\rightarrow L}\rangle$. An even better description of the first excited state is obtained by a linear combination of several configurations, and this can be referred to as if the state is *multiconfigurational* in nature. To a first approximation, write our initial guess of the first excited state as:

$$
|\Psi_{S_1}\rangle = c_1|\Psi_{H-1\rightarrow L}\rangle + c_2|\Psi_{H\rightarrow L+1}\rangle \cdot (|c_1|^2 + |c_2|^2 = 1).
$$

So far, this would be referred to as a **Configuration Interaction** (CI) wave function, and not a multiconfigurational one. Multiconfigurational methods require that the orbitals of the configurations are optimized as well. The first step in a multiconfigurational calculation is however, as in CI, obtaining the coefficients $c_i$ by diagonalizing the Hamiltonian matrix in the basis $\{|\Psi_{H-1\rightarrow L}\rangle, |\Psi_{H\rightarrow L+1}\rangle\}$. The lowest eigenvalue will correspond to the first excited state, $\pi\pi^*$, and the second to a higher state of $\pi\pi^*$ type. In between
these two there might in the real world exist more states that are not described in this basis. It is to be aware that we have here constrained the calculation to a subspace consisting of two $\pi\pi^*$ states. In CASSCF, all possible configurations originating from all possible excited determinants within a pre-defined orbital subspace are included. For our particular wave function here, the active space is $H − 1, H, L, L + 1$ and a CASSCF description would also include the excitations $H \rightarrow L, H − 1 \rightarrow L + 1...$ et cetera.

In the orbital optimization step, which is step number two, the virtual orbitals are optimized as if they were occupied. In one sense, this means that all configurations are made comparable to a Hartree-Fock type configuration. In the super-CI\textsuperscript{27} approach this orbital optimization is done by forming the one-electron reduced density matrix from the CI-configuration above $|\Psi_{S_1}\rangle$. This new Slater determinant $|\Psi_{dens}\rangle$, built up from natural orbitals of the $|\Psi_{S_1}\rangle$, is used for building up a CI-singles configuration,

$$|\Psi_{\text{super-CI}}\rangle = \sum_i \sum_j c_{ij} |\Psi_{\text{dens},\text{occ}_i\rightarrow\text{virt}_j}\rangle.$$  

(2.3)

The one-electron reduced density matrix is formed from $|\Psi_{\text{super-CI}}\rangle$, a new $|\Psi_{\text{super-CI}}\rangle$ is formed and this is repeated until changes between two consecutive steps are small. After this, the CI-step is repeated and new $c_1, c_2$ coefficients are calculated. These two steps are repeated until the changes between two steps are small.

The description of the excited state can be improved by extending the active space, but the principle for obtaining the CASSCF wave function remains the same even with more configurations included.

**Drawbacks with the CASSCF Description**

One formal objection against using CASSCF for describing Chemistry is that it lacks, or at least is deficient in dynamical electron correlation. Dynamical electron correlation is described as the instantaneous interaction between two electrons, which of course is a dubious definition since this effect can not be measured, or even distinguished from non-dynamical correlation. More pragmatically, CASSCF is usually bad for describing weak intermolecular interaction such as van der Waals forces. A much more serious complication, important for this work, is that systems are usually underbound at the CASSCF level. If a virtual orbital, say a C-Br $\sigma^*$, is optimized as if it would be occupied, the energy of this orbital will be too low and a configuration with this antibonding orbital occupied too low in energy. The corresponding coefficient in the CI expansion will be too large. That is, the system will be underbound. This has severe effects on the study of weakly bound covalent systems such as halogenated benzenes, since the halogen will be too easily dissociated. Note here that methods such as CIS will most probably overbind systems instead, since virtual HF-orbitals in reality describes negatively ionized states, and the separations between the virtual orbitals are too high.\textsuperscript{28}
Time-Dependent DFT will have a behaviour dependent on the functional chosen, and in a pre-study it was seen that the excited states are even wrongly ordered for these systems.

A rigourous and accurate method of adding dynamical-correlation to a CASSCF wave function is to form the one electron reduced density matrix (again!), of the converged CASSCF wave function, and build a CI-wave function from this, usually with single and double excitations. This adds dynamical correlation to the CASSCF wave function in the same way as ordinary CI adds dynamical correlation to the HF-wave function, by interactions between configurations. This is appealing since this method provides a systematic way of improving the description of the wave function. In addition, the resulting states will be orthogonal as they should. In this thesis however, the focus has not been to press as many numbers of accuracy as possible out of a particular calculation. Rather, an iterative approach with a constant discussions with experimentalists have been used, and the results were directly compared to experiments. It was therefore sufficiently accurate to estimate the effect of the double and single excitations by means of perturbation theory, as is made in Complete Active Space Perturbation Theory of second order (CASPT2). Further improvements were obtained in the multistate version of that method, Multi-State (MS) CASPT2, which provides orthogonalization of the states. The Hamiltonian, energy and wave function of the system, is described as the zeroth order (in this case the CASSCF ones) entities \( \hat{H}_0, \Psi_0, E_0 \), plus some perturbation:

\[
\hat{H} = \hat{H}_0 + \lambda \hat{H}_1, \tag{2.4}
\]

\[
|\Psi\rangle = |\Psi_0\rangle + \lambda |\Psi_1\rangle, \tag{2.5}
\]

\[
E = E_0 + \lambda E_1, \tag{2.6}
\]

from which is obtained:

\[
\hat{H}|\Psi\rangle = E|\Psi\rangle \tag{2.8}
\]

\[
(\hat{H}_0 + \lambda \hat{H}_1) (|\Psi_0\rangle + \lambda |\Psi_1\rangle) = (E_0 + \lambda E_1) (|\Psi_0\rangle + \lambda |\Psi_1\rangle). \tag{2.9}
\]

If this expression is arranged with respect to the power of \( \lambda \), an expression relating the zeroth and first order wave functions is obtained:

\[
(\hat{H}_0 - E_0|\Psi_1\rangle) |\Psi_1\rangle = (E_1 - \hat{H}_1) |\Psi_0\rangle. \tag{2.10}
\]

In CASPT2 theory, the Hamiltonian is defined in such a way that only singly and doubly excited configurations need to be included in the basis for the first order wave function, that is,

\[
|\Psi_1\rangle = \sum_{\text{doubly,singly}} c_l |\Psi_{\text{excited}}\rangle. \tag{2.11}
\]
Multiplication from left with the same expansion as in Equation 2.11 in Equation 2.10, gives the following expression for the coefficients:

\[ C = -V (F - E_0 S)^{-1}, \]  

(2.12)

where \( C \) is the coefficient matrix, \( V \) is the interaction between the zeroth order matrix and the excited configurations, \( F \) a Fock matrix, defined in analogy with the corresponding matrix in Hartree-Fock theory but with configurations, and \( S \) is a overlap matrix between configurations. CASPT2, as always is the case with perturbation theory, should be used for cases where the coefficients \( C \) are small. If the numerator in Equation 2.12 is small, it means that the reference state is only weakly interacting with the “correcting” state, and the choice of not including the “correcting” state in the preceding CASSCF calculation was sensible, and some computational resources were saved. In other cases, the configuration should be included in the CASSCF step. A large denominator is obtained if the difference of the terms are large. This, in turn, is obtained if the \( S \)-terms are small, which is the case if the perturbing states are close to orthogonal. The eigenstates of the Hamiltonian should be orthogonal, but this is not automatically included in conventional CASSCF. If the CASSCF is a good description of the real state, the overlap is small. In this project on halogenated benzenes, the perturbation coefficients as an indication of the quality of the active space was used. An active space is a set of orbitals, usually frontier orbitals, among which all possible configurations are created in the CASSCF step. Especially the \( \pi \) system is sensitive to the choice of configurations, since those orbitals are often near-degenerate and their relative importance in forming configurations is more or less the same. Including all \( \pi \) orbitals might be computationally too expensive, and therefore the perturbation coefficients were examined to see if a particular configuration could be excluded.

### 2.3 The Mechanism

With a slightly more profound understanding of the difficulties in describing the Chemistry of these molecules, we turn to the actual dissociation mechanism. As an aid in reading the upcoming text, Figure 2.1 is useful.

Initial excitation of these molecules with one photon at about 270 nm, reaches the lowest \( 1\pi\pi^* \) state. To immediately reach a repulsive state, two-photon absorption is required. That process is also interesting, but if selective dissociation is aimed for, cases with more than one decay channel should be avoided. Another important fact that defines the initial conditions is that the triplet character of the \( 1\pi\pi^* \) state is negligible (calculations originally performed by T. Österman, unpublished).
It is not obvious at all why the $^1\pi\pi^*$ state should be depopulated through dissociation of X-Ph. For understanding exactly how and why the halogen leaves the ring, a number of effects have been investigated:

1. The Franck-Condon active mode was identified. (Subsection 2.3.1)
2. The excited electron is transferred from $\pi^*$ to X-Ph $\sigma^*$ (Subsection 2.3.2)
3. We can also suspect a break-down of the adiabatic approximation, since electronic states are near degenerate in excited states. (Subsection 2.3.3)
4. Spin-orbit coupling? What is the effect of the halogens being quite heavy? (Subsection 2.3.4)

These effects will be explained and their relative importance presented in the following subsections.

### 2.3.1 Vibrational Excitation and Internal Vibrational Relaxation

Every electronic state has a number of associated nuclear vibrational states, and the higher vibrational state initially excited, the more energy is available for the dissociation. Within the energy span of the photons used for the experiments presented in Paper I, III and IV, ($\sim$4.5-5.0 eV) four bound different excited states are within reach, three triplets and one singlet, all of $\pi\pi^*$ character. In Paper I, the orbital structure of a typical halogenated benzene is presented. Since a ring-located $\pi \rightarrow \pi^*$ excitation is taking place, the bond lengths of the ring will change upon excitation. The ring will remain planar since only secondary bonding is affected, but the ring will become wider upon excitation. This means that the minima on the $^1\pi\pi^*$ PES will correspond to another geometry than the $S_0$ minima, and that this relocation of the minima is only in a subspace of this ring-breathing. Therefore the ring will end up in an excited ring-breathing vibrational state. Translated into formulas, the transition dipole moment of the system is given by:

$$\mu = \langle \Psi_i | e \hat{r} | \Psi_f \rangle,$$

which, if nuclear and electronic motions are separable becomes:

$$\mu = \langle \Psi_{i,nuc}^{\text{nuc}} | \Psi_{f,nuc}^{\text{nuc}} \rangle \langle \Psi_{i,e}^{\text{e}} | e \hat{r} | \Psi_{f,e}^{\text{e}} \rangle.$$  \hspace{1cm} (2.14)

Here, $\langle \Psi_{i,nuc}^{\text{nuc}} | \Psi_{f,nuc}^{\text{nuc}} \rangle$ is the overlap of the nuclear wave functions. This overlap will be unity for all vibrational modes that are not changed, and less than unity for those who are. In our case, the ring geometry is expanded, and therefore a vibrational mode affected by this expansion will be the one that gives a value lower than one, and the mode will correspond to the excited mode, the Franck-Condon active mode. For a dissociation to take place, the energy of the excited ring-breathing mode needs to be transferred to the vibrational modes responsible for the actual dissociation (Figure 2.4), i.e. X-Ph stretch (d) (Paper I), X out-of-plane bending (α) (Paper II, III) and X in-plane bending (β) (Paper IV). This transfer, usually referred to as
Internal Vibrational Relaxation, IVR, is not instantaneous. In Paper III, where Quantum Dynamics simulations of the dissociation are performed, IVR is neglected. Ring breathing is not addressed at all. Even so, almost quantitative agreement with experiments is obtained. IVR is therefore fast, down to a picosecond time scale, in bromated benzenes.

2.3.2 Electron Rearrangements and Symmetry Restrictions

The following Subsection is more or less an attempt to clarify the conclusions drawn in Paper I. To begin with, as already stated in Section 2.2.1, an orbital is a one-electron function and has an absolute value and a phase. If a molecule has a plane of reflection, any orbital of that molecule will have the same shape on both sides of this plane, but the phase of a particular orbital might be the same or different on the respective sides. The orbitals are classified with respect to their phase change under symmetry transformations. The wavefunction of a particular state is classified in an analogous way as the orbitals. With two mirror planes, as Cl-Ph, the molecule is $C_2v$ symmetric, and the symmetries are $A_1$, $B_1$, $B_2$ and $A_2$. If an electronic state has a particular symmetry, each determinant in the CASSCF expansion has this symmetry. To obtain the symmetry of a given determinant, the product of the orbitals must have the same symmetry as the determinant. Consider a state vector from Equation 2.2, and with the symmetries of the orbitals taken from Figure 2.2:

$$|\Psi_{H\rightarrow L+1}\rangle = |b_1(e^-)a_2(e^-)\rangle,$$

and define the symmetry operators $\sigma$ (reflection in the molecular plane) and $\sigma'$ (reflection orthogonal to the molecular plane), which have $C_{2v}$ symmetric
orbitals as eigenvectors, and corresponding eigenvalues 1 or -1 depending on the phase of the orbital. If the phase is different on each side of the symmetry plane, the eigenvalue is -1, otherwise it is 1:

$$\sigma |b_1(e^-)a_2(e^-)\rangle = (-1)(-1)|b_1(e^-)a_2(e^-)\rangle = |b_1(e^-)a_2(e^-)\rangle,$$  \hspace{1cm} (2.16)

$$\sigma' |b_1(e^-)a_2(e^-)\rangle = (1)(-1)|b_1(e^-)a_2(e^-)\rangle = -|b_1(e^-)a_2(e^-)\rangle.$$  \hspace{1cm} (2.17)

Reflection in the molecular plane ($\sigma$) of both $a_2$ and $b_1$ gives -1 and -1 since the phases are different on each side of this plane. With respect to the other plane however ($\sigma'$), only $a_2$ has different phases on different sides. Clearly, this state vector does not transform as $A_1$, since it has a negative phase on one side of the molecular plane. It is not $B_1$ either, since $B_1$ was defined as positive on both sides of the $\sigma'$ plane, and not $A_2$ since $A_2$ changes sign with respect to both planes. So the state possesses $B_2$ symmetry.

Now imagine that the repulsive $\pi\sigma^*$ state is formed by moving the electron in the $a_2$ orbital to the antibonding CBr $\sigma^*$ orbital. Since this orbital has rotational symmetry, it has $a_1$ symmetry, and the state is $B_1$ symmetric (it is a product of a $a_1$ and a $b_1$ orbital). The bound and repulsive states are said to be uncoupled since $\langle B_1|\hat{H}|B_2\rangle = \varepsilon_{B_2} \langle B_1|B_2\rangle = 0$, and a system in one of the states moving with retained symmetry will not change from one state to another. Ultimately, the symmetry of the orbitals determines if two states interact or not.

### 2.3.3 Coupling of PES, Non-Adiabatic Parametrization

In the two state problem described above with a bound $B_2$ and repulsive $B_1$ state, the states were orthogonal and thereby non-interacting. No matter how slowly the system would be moving, the probability of changing from the bound to the repulsive state is zero. The dissociation of the halogen is therefore not allowed. In Paper II, the dissociation via a repulsive state with the same symmetry as the bound state was investigated. The $n\sigma^*$ states, which are the third (triplet) and fourth (singlet) lowest repulsive states, have like $^1\pi\pi^*$ $B_2$ symmetry. The molecule used there is 1-Bromo-3,5-difluorobenzene, which is $C_{2v}$ symmetric. In Paper III, a $C_s$ symmetric molecule is used instead, 1-Bromo-3-fluorobenzene. By doing this geometrical alteration, out-of-plane bending of the bromine, the lowest singlet dissociation channel (via $^1\pi\sigma^*$) is enabled in this molecule. Paper IV takes this a step further and couples the bound repulsive state to the lowest repulsive singlet in a $C_{2v}$ symmetric molecule. This can be obtained by breaking the symmetry of the molecule completely to $C_1$, and the easiest way of doing this is by changing the nuclear coordinates corresponding to the three lowest normal modes, C-Cl stretch ($d$), Cl out-of-plane ($\alpha$) and Cl in-plane bending ($\beta$) (Figure 2.4).

One might ask why we have to demolish the molecule down to $C_1$ symmetry just for dissociating it via the lowest repulsive state. To understand this it is helpful to recollect the adiabatic approximation. Two types of terms are
neglected in the adiabatic approximation, the vector type:

$$\langle \Psi_i | \nabla_n | \Psi_j \rangle,$$

and the scalar type:

$$\langle \Psi_j | \nabla^2_n | \Psi_i \rangle.$$  \hspace{1cm} (2.19)

When \( i = j \), these terms might be large or not, but they do not induce any transfer between electronic states. When \( i \neq j \), they arise\(^{34}\) as off-diagonal terms in the electronic Hamiltonian matrix. If the Hamiltonian matrix is:

$$H = \begin{pmatrix} H_{11} & \lambda \\ \lambda & H_{22} \end{pmatrix}$$  \hspace{1cm} (2.20)

the eigenvalues are:

$$E_1 = H_{11} - \lambda$$  \hspace{1cm} (2.21)

$$E_2 = H_{22} + \lambda$$  \hspace{1cm} (2.22)

and in other words the minimum separation of two surfaces in an adiabatic calculation is more or less the same as \( 2\lambda \). The larger this separation is, the larger is the probability of the system to transfer from the bound to the repulsive state instead of continuing moving on the bound state PES. If the off-diagonal terms (in the \( C_{2v} \) case: \( \langle B_1 | \hat{H} | B_2 \rangle \)) is zero, no transition will take place.

Having established how the reaction can be made allowed, the next step is to find out how fast it is. It was done for a molecule possessing \( C_s \) symmetry in Paper III. As mentioned above, the lowest repulsive state can be reached by changing only two internal coordinates of this molecule. A dynamical simulation for this system needs to include non-adiabatic effects. This is readily done by a quantum mechanical description of the nuclei, with a potential energy operator as the matrix in Equation 2.20. A kinetic energy operator \( T \) was created by transforming the ring+bromine system into a three-body system. The kinetic energy operator might be a problem or not to construct, but one major problem with quantum dynamics simulations is that the number of data points for the \( V \)-operator grows with the power of the dimension of the geometrical subspace. Another problem is to find a non-adiabatic representation of \( V \). In Paper III, the coupling elements \( \lambda \) are estimated from adiabatic calculations, and thereby parameterized non-adiabtic PES, with \( 2\lambda \) being just the separation of the electronic states. This paramerization is absolutely necessary, the vector coupling elements are singular in the electronically degenerate case. This can be implied by calculating the vector coupling elements in the adiabatic representation. Start by considering the electronic Schrödinger equation:\(^{35}\)

$$\hat{H}_e | \pi \pi^* \rangle = V_{\pi \pi^*} | \pi \pi^* \rangle.$$  \hspace{1cm} (2.23)
Here we assume that there are indeed strictly electronic states, that is that electronic and nuclear motion is separable. The gradient of this with respect to the nuclei is:

\[
\nabla_n (\hat{H}_e|\pi\pi^*\rangle) = \nabla_n (V_{\pi\pi^*}|\pi\pi^*\rangle) = \nabla_n V_{\pi\pi^*}|\pi\pi^*\rangle + V_{\pi\pi^*}\nabla_n |\pi\pi^*\rangle. \tag{2.24}
\]

Then multiply from left with \langle \pi\sigma^*|, and use the fact that \hat{H}_e is hermitian and \langle \pi\sigma^*|\hat{H}_e = \langle \pi\sigma^*|V_{\pi\sigma^*}:

\[
\langle \pi\sigma^*|\nabla_n \hat{H}_e|\pi\pi^*\rangle + \langle \pi\sigma^*|\hat{H}_e \nabla_n |\pi\pi^*\rangle = V_{\pi\pi^*}\langle \pi\sigma^*|\nabla_n |\pi\pi^*\rangle + \nabla_n V_{\pi\pi^*}\langle \pi\sigma^*|\hat{1}|\pi\pi^*\rangle \tag{2.26}
\]

\[
\langle \pi\sigma^*|\nabla_n \hat{H}_e|\pi\pi^*\rangle + \langle \pi\sigma^*|V_{\pi\sigma^*}\nabla_n |\pi\pi^*\rangle = V_{\pi\pi^*}\langle \pi\sigma^*|\nabla_n |\pi\pi^*\rangle \tag{2.27}
\]

\[
\frac{\langle \pi\sigma^*|\nabla_n \hat{H}_e|\pi\pi^*\rangle}{V_{\pi\pi^*} - V_{\pi\sigma^*}} = \langle \pi\sigma^*|\nabla_n |\pi\pi^*\rangle. \tag{2.28}
\]

The left hand numerator has the dimension force, and represents a force driving the system from the bound to the repulsive state, represented by the changes of the electronic Hamiltonian with respect to the nuclear movements. It is large if the curvature of the PES is large. The denominator is the separation of the surfaces. In Paper III, the separation of the surfaces is small in some parts of the avoided crossing region, from 0.0 to about 0.2 eV (Figure 2.5, right at E=4.8 eV, d=2.15 Å). It is from this expression clear that the gradient coupling is not only large, it is singular in the crossing region if the adiabatic approximation is used. In Paper III, the PES in the critical regions, close to the \(\pi\pi^*/\pi\sigma^*\) crossing is diabatizised. The avoided crossing region of the molecule used, 1-Br-3-FPh is displayed in Figure 2.5 in both the non-adiabatic and adiabatic case. The left, diabatic surface, is obtained by least-square fit of the right surface towards Quantum Chemically calculated values, a method inspired by the work of by Domcke and co-workers.\(^{36}\)

2.3.4 The Effect of Spin-Orbit Coupling

It has for long been claimed that spin-orbit coupling is important for the photodissociation of these molecules\(^{6}-^{9}\) Spin-orbit coupling is the interaction between spin and angular momenta for an electron,\(^{33}\) and if this interaction is strong enough, the spin direction can even be flipped. Spin-orbit coupling is therefore a measure of a probability of an electron to change its spin, and this will in a time-independent adiabatic calculation be manifested as a mixing of states of different multiplicities.

If a singlet and a triplet state is having the same spatial electronic arrangement, the triplet will have a lower energy. This is ultimately a
consequence of that the electron is uniquely defined by its spin and angular momenta, and if both spatial distribution and spin of two electrons are the same, as in a triplet, the electrons have to be slightly differently distributed in space, and thereby the Coulomb interaction is lowered and also the total energy. This model is originating from Hartree-Fock Theory, and the interaction is called exchange interaction, but is generally applicable, all triplets are lower in energy than the corresponding singlet. The effect is referred to as a fermi hole. Mixing in triplet character in a singlet will lower the energy of the “singlet”, and mixing-in triplet character in a transition state but not in the corresponding reactant, will lower the activation energy. The large number of near degenerate singlet and triplet states in these molecules.

Figure 2.5: Diabatic to adibatic transformation performed in Paper III.
motivates why spin-orbit coupling was explicitly addressed in Paper II and IV. First, at the initial excitation, three bound $\pi\pi^*$ states are lower than the first singlet bound state. The magnitudes of the transition dipole moments, $\langle S_0 | e \hat{r} | 1/3 \pi\pi^* \rangle$, of the first 24 transitions from $S_0$ were investigated by Tomas Österman. That study showed that the transitions to the triplet states are by a factor of at least one million weaker than transitions to singlets. In Paper II and IV, it is demonstrated that as long as the halogen is bound, the mixing of singlets and triplets is insignificant. After the X-Ph bond is broken, the states become mixtures of singlets and triplets. In Figure 2.6, the fraction of singlet upon C-Br elongation in 1-Br-3,5-difluorbenzene when bent 42° out of the molecular plane is displayed. Clearly, the singlet-triplet mixture after bond-rupture is 50-50%, and this is so since the bromine is mediating spin-orbit coupling.

\[ \text{Figure 2.6: Fraction of singlet upon C-Br elongation in 1-Br-3,5-difluorbenzene when bent 42° out of the molecular plane.} \]

The derivation of spin-orbit coupling effects has its origin in inclusion of relativistic effects in the electronic Hamiltonian. Linearization and transformation of the resulting Hamiltonian results in a Hamiltonian containing a spin-dependent term decaying as $r^{-3}$ from the nuclei, and proportional to $z^4$, of the nuclear charge. For spin-orbit effects, and thereby mixing of singlet and triplet states, to be of any significance, an unpaired electron needs to be close to a heavy atom. In the $\pi\pi^*$ electronic configuration, the unpaired electrons are too far away from the heavy halogen. In the repulsive states, an unpaired electron resides on the halogen, and a 90-10% mixing is obtained for the chlorine (Paper IV), and 50-50% for the bromine. In practice, the barrier for a predissociation can thereby be captured in a purely spin-independent
calculation, but such a calculation can not describe the dissociative state accurately.

2.3.5 Some Final Words about Halogenated Benzenes

It is clear that several other decay mechanisms than the ones described here are conceivable, maybe excitation at other wavelengths increases the significance of “hot-molecule” mechanisms, maybe radiative mechanisms are important for other bound excited states. Might be, but apart from a deeper understanding from an academic point of view of these processes, one of the goals is to carry through highly sophisticated control of chemical reactions, and in that case only one or a few number of radical formation processes are needed.

In that sense, the Papers I through IV is a large step in the right direction.
3. Photointerconversion of Phytochromobilin

3.1 Introduction

The third chapter of this thesis concerns a process of biological relevance, but still the subject is Photochemistry. Plants regulate growth and development in response to light in their environment through the action of several sensory photoreceptors in the form of light-absorbing proteins. Of these, phytochromes are the most thoroughly studied. The holoprotein Phytochrome has been observed to exist in two thermostable forms: the inactive red-light absorbing form called Pr ($\lambda_{\text{max}} = 660$ nm) and the active far-red-light absorbing form referred to as Pfr ($\lambda_{\text{max}} = 730$ nm). Light absorption by Pr triggers the phototransformation to Pfr, a process which proceeds by a number of metastable intermediates and activates different signal transduction pathways. The chromophore of phytochrome, which is the focus of our study, phytochromobilin (PΦB, Figure 3.1), is a linear methine-bridged tetrapyrrole that forms a thioether linkage to a cysteine residue of the apoprotein. The most studied plant-phytochrome Pfr conformation is the one displayed in Figure 3.1.

Kinetics of the Pr $\rightarrow$ Pfr phototransformation of the protein has been thoroughly studied, and the structure of the chromophore binding domain of a Pr bacteriophytochrome is also known. No X-ray structures on plant phytochrome exists however, and in addition, the transformation of the chromophore has not been well characterized. For the chromophore structure in plants, the most abundant view has been that PΦB adopts a Z configuration around the C15=C16 bond (C15-Z) in Pr and a C15-E configuration in Pfr, and that the photoactivation thus proceeds via a Z $\rightarrow$ E isomerization of the chromophore around the C15=C16 bond (Figure 3.1). It is this photoisomerization process that was investigated in Papers V and VI, for a chromophore carrying a net charge of +1 in Paper V, and a chromophore deprotonated on ring B or C in Paper VI.

The conformation used in Papers V and VI was first proposed by Rüdiger and co-workers in 1983 on the basis of $^1$H NMR spectra of phytochrome chromopeptide fragments, and has been confirmed in subsequent resonance Raman (RR) studies. It was also chosen to include rotation around the C14-C15 bond in our studies since RR vibrational spectra of phytochrome also show that the configuration of PΦB is different with respect to the
C14-C15 bond in Pr (C15-syn) and Pfr (C15-anti).\textsuperscript{45,46,48} In Paper V, it was found that a stepwise $Z \rightarrow E$, syn $\rightarrow$ anti mechanism is more probable than a concerted $Z$,syn $\rightarrow$ E,anti mechanism. As a consequence of this, it was proposed that the photochemical event comprises a $Z \rightarrow E$ isomerization only, and that the subsequent syn $\rightarrow$ anti isomerization proceeds thermally. The RR-based assignment of a C15-syn chromophore configuration in Pr is not unambiguous,\textsuperscript{47,49} and any assignment with respect to single bonds is not definite.

As a response to a referee comment on Paper V, we started to investigate what effect detachment of the nitrogen bond protons has. Indeed, both RR\textsuperscript{47,50–52} and Fourier transform infrared (FTIR)\textsuperscript{53,54} spectroscopic studies have shown that PФB is protonated in Pr, as was assumed when conducting the calculations underlying Paper V, but RR spectra recorded by Mizutani \textit{et al.}\textsuperscript{50,51} suggest that a proton transfer from the BC dipyrrolic moiety to the surrounding protein takes place during the phototransformation, and that PФB...
therefore is neutral in Pfr. The story does not end there, several groups\textsuperscript{47,52–54} suggest that the chromophore is protonated not only in Pr and Pfr, but also in each intermediate state connecting these. Therefore in Paper VI, the influence of \( \Phi_B \) protonation state (protonated or neutral) on the C15-Z C15-E photoisomerization was investigated through the computation of \( n_B/n_C \Phi_B \) (deprotonated on ring B or C) excited-state potential energy surfaces.

The shortcoming of Paper VI was that only B or C ring deprotonation was assessed. The resonance structures displayed in Figure 3.1 suggest that these are plausible choices for sites of deprotonation. Without being sure about the structure of the Pr state, or being able to describe what governs the acidity of the moieties, this choice is somewhat arbitrary however, and therefore a thorough investigation of the acidity of the phytochrome was conducted and presented in Paper VII and VIII.

3.2 Computational Aspects

Phytochromobilin is a large molecule for performing highly accurate calculations, it contains 45 atoms in its protonated form. In Paper VII, some calculations at the CASSCF level are presented, with geometry optimizations using four electrons in four orbitals. This is a formally feasible active space, since it corresponds to the \( \pi \) system around C13-C14-C15, and the excitations of interest should therefore be captured in those calculations. The problem is that already this calculation is very large, at least when using somewhat accurate basis sets, and still most of the electronic structure is treated at the Hartree-Fock level of theory. Through a benchmark presented in Paper VII, it is found that geometry optimization at the CIS levels together with single point energy calculations at the time-dependent DFT level is accurate enough for capturing the relevant features of the processes investigated. This was assumed in Paper V and VI, mainly since qualitative properties were searched for, the presence or absence of a non-radiative decay channel. The excitation is one-electron in character, and this can be at least semi-quantitatively described on the level of theory chosen. Why the method might not give really quantitative results and why benchmark of the methods for the \( pK_a \) study was necessary, is explained in Section 3.2.1.

3.2.1 When does Time Dependent Density Functional Theory Work?

Density functional theory describes the molecular properties as a functional of the electron density.\textsuperscript{55} As much as possible of the Hamiltonian is exactly described at a classical level, and quantum mechanical effects are included as an exchange-correlation “correction”. It is a ground-state theory, in the sense that it was originally shown\textsuperscript{55} that the ground state energy is a one-to-one
mapping of the ground state electronic structure. The theory can be extended to find properties of excited states by calculating the linear response of the one electron reduced density matrix to an external electric field. The poles of the mean dynamic polarizability are the same as vertical excitation energies.

Apply an external potential field \( E = (0, 0, E_z \cos(\omega t)) \) to a molecule and Taylor expand the dipole moment:

\[
\mu(\omega) = \mu_0 + \frac{\partial \mu}{\partial E_z} E. \tag{3.1}
\]

The mean dynamic polarizability is

\[
\langle \frac{\partial \mu}{\partial E} \rangle = \frac{1}{3} \left( \frac{\partial \mu}{\partial E_x} + \frac{\partial \mu}{\partial E_y} + \frac{\partial \mu}{\partial E_z} \right), \tag{3.2}
\]

which can be proven to be equal to

\[
\langle \frac{\partial \mu}{\partial E} \rangle = \sum_I \frac{\frac{2}{3} \omega_0 |\langle \Psi_I | \mu_0 | \Psi_0 \rangle|^2}{\omega_0^2 - \omega^2}, \tag{3.3}
\]

where \( \frac{2}{3} \omega_0 |\langle \Psi_I | \mu_0 | \Psi_0 \rangle|^2 \) is the oscillator strength for the transition from the ground state to \( I \). The poles are located at \( \omega_0 = \omega \) and this, translated to energy, is \( \omega_0 = \omega = E_v/\hbar \). Qualitatively, the dynamic polarizability is the change of the electronic structure with respect to an external field, and when this change is infinite, a structure that is completely different, orthogonal, is obtained. Then two criteria of an excited state is achieved, it is an electronic state with higher energy than the ground state that is orthogonal to the ground state. Typically, low-lying, locally excited states are well described by TD-DFT.

Problems in describing excited states can arise since exchange interaction between electrons is, in DFT, often local, it does not arise from integration over all space. Head-Gordon and coworkers have claimed that the absence of an exact exchange functional is responsible for the inadequate treatment of charge transfer states by TD-DFT. In this study, TD-DFT is adequate since it is a local, one-electron process, \( \pi \rightarrow \pi^* \), to the lowest excited state that is calculated. Actually, low-lying excited states are often well described by TD-DFT. In Hartree-Fock theory, the virtual orbitals are indeed virtual, while in DFT they are usually optimized as if they were occupied. This is best illustrated by looking at the canonical Kohn-Sham orbital equations, which are given by:

\[
[h(r) + v_{eff}] |\psi_i\rangle = \varepsilon_i |\psi_i\rangle, \tag{3.4}
\]

\[
v_{eff}(r) = \int \frac{\rho(r')}{|r - r'|} d\mathbf{r'} + v_{xc}(r), \tag{3.5}
\]

\[
\rho(r) = \sum_{i=1}^{N} \sum_{\alpha, \beta} \langle \psi_i(r, s) | \psi_i(r, s) \rangle. \tag{3.6}
\]
From this we calculate the orbital energy:

\[ \varepsilon_i = \langle \psi_i | h(r) + \int \frac{\rho(r)}{|r-r'|} d\mathbf{r}' + v_{xc}(r) | \psi_i \rangle \]  

\[ = \langle \psi_i | h(r) | \psi_i \rangle + \langle \psi_i | \int \frac{\rho(r)}{|r-r'|} d\mathbf{r}' | \psi_i \rangle + \langle \psi_i | v_{xc}(r) | \psi_i \rangle. \]  

(3.7)

(3.8)

The Coulomb interaction with a virtual orbital is zero. What remains is:

\[ \varepsilon_i = \langle \psi_i | h(r) | \psi_i \rangle + \langle \psi_i | v_{xc}(r) | \psi_i \rangle. \]  

(3.9)

The orbital energy is dependent on the exchange interaction term. It is zero in Hartree-Fock, and typically something negative in DFT. In other words, DFT virtual orbital energies are lower than HF-dittos, and excitation energies are thereby lower. The energies are therefore sometimes more accurate in TD-DFT than CIS.

3.3 To be or not to be a non-Radiative Decay Channel

The Z→E isomerization requires rotation around a C=C double bond. At a physiological temperature in the ground state, this is normally energetically not an accessible reaction pathway. By absorbing a photon, the positively charged PΦB can undergo a low energetic rotation around C15=C16 in S_1. This is since HOMO is bonding between C15=C16 and antibonding between C13-C14, while the opposite is true for LUMO. The system decays back to the S_0 state while rotating, since S_1 and S_0 are crossing. In Figure 3.2, S_0 and S_1 of the postively charged PΦB^+ as well as B and C deprotonated (nB PΦB, nc PΦB) phytochromobilin are displayed.

All three S_0 surfaces display a large barrier for the C15,Z→C15,E isomerization, and a small one for single bond rotation. From the right-hand side S_1 surfaces it can be seen that the protonation state affects the shape of the S_1 surface. For the top one, corresponding to PΦB^+, a decay channel down to S_0 is located around an C15 dihedral angle of 90°, and C14 dihedral of 0 or 180°. A nice interpretation is that if the structure suggested by Rüdiger and co-workers is correct, the Pr→Pfr isomerization can proceed by means of light induced C15 double bond rotation.

3.3.1 The Effect of Deprotonation

Even so, one might get worried by the fact that the reaction is stopped if the molecule is deprotonated. The photoactivation channel is clearly dependent on the protonation state of the molecule. Paper V and VI studies the isomerization of the commonly adopted conformation proposed for plant phytochromobilin, C4,Z,C5,anti,C9,Z,C10,syn,C14,Z,C15,anti (ZaZsZa). In
bacteriophytochrome, a ZsZsZa\textsuperscript{42,43} conformation is adopted. Resonant Raman spectra has suggested a ZaEaZs conformation of Pr and ZaEaEa of Pfr\textsuperscript{46,48} Apart from meeting the requirement of investigating the acidity of all plausible biologically important conformations, a complete mapping of ALL possible conformations and ALL possible deprotonations will make it possible to rationalize which factors determines the acidity of PΦB, and thereby which factors might be inhibiting the phototransformation. All four rings contain protons that could be abstracted. In total this gives:

\[ 2 (\text{states}) \times 4 (\text{rings}) \times 2^3 (Z \rightarrow E) \times 2^3 (\text{syn} \rightarrow \text{anti}) = 512 \text{ pK}_a \text{ values!} \] \hspace{1cm}(3.10)  

From this quite large amount of data, it is possible to isolate some effects determining the pK\textsubscript{a} value of the structure, and exclude others. i) The effect of initial charge distribution. Ring D is inherently 7 pK\textsubscript{a} units less acidic than rings A, B and C. This is because of that the positive charge in PΦB\textsuperscript{+} is

---

**Figure 3.2:** The PES calculated for phytochromobilin. Top: PΦB\textsuperscript{+}, middle: n\textsubscript{B}PΦB, bottom: n\textsubscript{C}PΦB. S\textsubscript{0} to the left and S\textsubscript{1} to the right.
distributed as (25%, 33%, 33%, 8%) on (A, B, C and D) and the more positive the ring is, the more prone it is to lose a proton. A and D can be claimed to be less positive than B and C since the carbonyl groups are electron withdrawing. 

**ii) The effect of different conformations.** This effect is negligible unless internal hydrogen bonds between a nitrogen and a hydrogen attached to a nitrogen are formed. These bonds are formed in the Zs conformation, and the effect is illustrated in Figure 3.3.

![Figure 3.3: Periodic change of $\Delta pK_a$ upon formation of Zs conformation. Note that the effect of hydrogen bonding is additive.](image)

Creation of one hydrogen bond, as in ZsZaZa, lowers the $pK_a$ with $\sim 4$ units of a ring involved in the bonding. Two bonds as in ZsZsZa doubles this effect. 

**iii) The effect of excitation.** A small decrease in $pK_a$ is obtained upon excitation for rings B and C, and an increase for A and D. This is originating from a slight electron rearrangement from the ring A and D to B and C upon excitation. This effect is typically smaller than 2 $pK_a$ units.

**iv) The effect of intermolecular hydrogen bonds.** In Paper VIII, water and alanine are hydrogen bonded to $\Phi B$, and essentially the same effect is obtained as in intramolecular hydrogen bonds. Hydrogen bonding stabilizes the deprotonated species and increases the acidity.

If the average acidity over all conformations is compared for the rings, rings B and C are most acidic followed by A and then D. B and C have more conformations with strong intramolecular hydrogen bonds than A since...
they have two nearest neighbours. D is not very likely to be deprotonated. We can state that the choice of deprotonating B or C in Paper VI was sensible, since these species are stabilized in the ZaZsZa conformation. More importantly, however, we can predict which ring is most likely deprotonated in any suggested conformation. For the recently suggested bacteriophytochrome, for example, the effect of A-ring deprotonation should absolutely be further investigated since the Pr conformation is ZsZsZa.
4. Ruthenium Centered Photoactive Polypyridyl Complexes

4.1 Motivation and Background

Ruthenium centered polypyridyl complexes have a very appealing Chemistry, it is Chemistry where ligand field theory meets Photochemistry.

The Ruthenium(II)polypyridyl complexes used here are six-coordinated (Figure 4.1) Ruthenium centered complexes with excited state properties that have lead to a wide range of applications in Photochemistry and photocatalysis. Two properties of interest for this work are mentioned here. The lowest (and most intense) transitions to excited states lie in the sunlight region of the electromagnetic spectrum. Secondly, they have long-enough excited state lifetimes to initiate electron transfer to neighbouring molecules, enhancing the possibility to use these complexes as antennas in photo-active systems. With these two properties, these molecules can be used in dye-sensitized solar cells, and donor-photosensitizer-acceptor triads in artificial photosynthesis. The lowermost, most intense peaks, in a Ru(II)polypyridyl UV-vis spectrum correspond to singlet ground state (S$_0$) to singlet metal-to-ligand charge transfer (1MLCT) transitions, i.e., the highest occupied orbitals are mainly of Ruthenium 4d-character, and the lowest unoccupied ones are pyrimidine $\pi^*$ orbitals. So called $d \rightarrow d$ transitions, transitions from one Ruthenium d orbital to another, are not allowed in a free Ruthenium atom ($\Delta l = 0$), and are typically weakly allowed in perturbed systems, as when the ligands do not have perfectly octahedral coordination.

Ruthenium belongs to the 2$^{nd}$ transition metal series, and therefore readily mediates spin-orbit coupling, and the system is transferred to a state that is mainly triplet in character, $^3$MLCT. This process has thoroughly been described for [Ru(bpy)$_3$]$^{2+}$. The stability of the $^3$MLCT state is crucial for the capability of these complexes to induce further reactions, since the excitation energy is carried by the electron transferred to the pyrimidine $\pi^*$-orbital. The $^3$MLCT state is depopulated through both radiative and non-radiative pathways, but the major deactivation channel at room temperature arguably proceeds over an adiabatic transition state from the $^3$MLCT state to a metal centered, $^3$MC, state. The high symmetry of these molecules therefore suggests that the interaction between the states might be dependent on the ability of the system to undergo symmetry distortion,
tf 3MLCT and 3MC would belong to different irreducible representations. The 3MC state thereafter relaxes to the S0 state. This deactivation, taking place internally in the complex, therefore implies a loss of excited state energy, and large research efforts are made towards avoiding this process.

4.2 Methodological Concerns

The models used consisted of full Ruthenium+ligands systems. All calculations in this study were conducted using density functional theory with the B3LYP functional.76,77 B3LYP is known to perform well for several metal-centered complexes.78 Several theoretical studies of Ru-centered complexes exist, with different methodologies chosen, ranging from semi-empirical,79–81 to gradient-corrected DFT,82 and hybrid-functional methods such as PBE083–85 and B3LYP.85–91 The advantage of using a hybrid density functional is the inclusion of the non-local Hartree-Fock exchange in such functionals.

The standard, time-independent, DFT method was chosen. The problem with the Time-dependent DFT scheme for CT states58 can be avoided by constraining the calculation to triplet multiplicity, and run "ground-state" calculations instead.

The basis set dependencies of energies and geometries were thoroughly studied. It was thereby found that double-ζ plus polarization (DZP) quality or better is necessary for obtaining reliable results, but also that d-polarization on second-row atoms is essential when describing these systems. LANL2DZ92 geometries were found to differ considerably from the geometries presented in this work. Several stationary points occur at the LANLDZ level that are indeed artefacts, and larger basis sets should be used. This is in fact a result in itself, since most studies performed so far used B3LYP/LANL2DZ or lower level of theory.

Mulliken spin density analysis was used for establishing the nature of the electronic state, a 3MLCT state associated with a unity net spin on Ruthenium, while a net spin of 2 on Ruthenium classified the state as 3MC. In some cases, a barrier between two 3MC states could be found, and transition state optimizations were conducted. Ligand-field theory was used to explain the elongations of the Ru-N bonds in the 3MLCT→3MC transition.

4.3 A Thermodynamical versus Kinetical Explanation

One approach for designing Ru centered complexes with long lived 3MLCT states, which was used by Abrahamsson et al. in a recent report,93 was based upon the idea of making the 3MC state thermodynamically less accessible from the 3MLCT state. A perfect octahedral environment is well known to
split the frontier d-orbitals in a transition metal into two energy levels, the lower ($t_{2g}$) consisting of $d_{xy}$, $d_{yz}$ and $d_{xz}$, and the upper ($e_{g}$) of $d_{x^2-y^2}$ and $d_{z^2}$. In an octahedral environment, Ru$^{2+}$ has the ground state electronic configuration [Kr]4d$^6$, with the $t_{2g}$ orbitals occupied, and the $e_g$ orbitals unoccupied. In the approach used in the abovementioned work, it was assumed that the $^3$MC state can be made less accessible by strong ligand field splitting rising from (nearly) perfect octahedral ligand coordination of the central Ruthenium ion, i.e. the coordination increases the energy of the $^3$MC state by pushing the $e_g$ orbitals energetically upwards. This provided a natural start for us. It is clear that the virtual Ru-d orbitals might be pushed upwards, but this is different from pushing the state upwards. Optimizing the $^3$MLCT and $^3$MC geometries and comparing their energetics is a way of testing the hypothesis of a thermodynamically controlled reaction. This optimization for several $^3$MLCT and $^3$MC states was made for the complexes displayed in Figure 4.1.

Figure 4.1: The four Ru centered antenna complexes investigated in Paper IX.
The tpy ligand in itself, used in \([\text{Ru(tpy)}_2]^{2+}\), has been claimed to have the disadvantage that it is structurally far from allowing octahedral coordination of Ru\(^{2+}\), and that therefore the lifetime of the \(^3\text{MLCT}\) state of this complex only 0.25 ns at room temperature.\(^9^4\) Improved ligand coordination is obtained in \(\text{cis-[Ru(bpy)}_2\text{py}_2]^{2+}\) and \([\text{Ru(pmp)}_2]^{2+}\). Finally, a lifetime of 3 \(\mu\)s for a \([\text{Ru(tpy)}_2]^{2+}\)-related complex, \([\text{Ru(bqp)}_2]^{2+}\), was obtained by Abrahamsson and co-workers.\(^9^3\) If the reaction is thermodynamically controlled, \(^3\text{MLCT}\) should be much more stable than \(^3\text{MC}\) in this molecule. If this is the case, it can be found by means of Quantum Chemistry. In Figure 4.2 the stationary points for on the first triplet surface for the “supermolecule” with (\(\tau = 3 \mu s\)) with two bqp ligands is displayed together with the other three complexes investigated. The thermodynamics of this molecule display the same pattern as the other three, the \(^3\text{MC}\) state is lower in energy than the \(^3\text{MLCT}\) state.

It is seen in Figure 4.2 that the two \(^3\text{MC}\) states are less stable than the \(^3\text{MLCT}\) states by 1.6 and 2.2 kcal/mol. The reaction is therefore not thermodynamically controlled. It is therefore in Paper IX suggested that the reaction in kinetically controlled. The rigidity that this molecule provides makes symmetry breaking difficult, and therefore the lifetime of this molecule is long. It was in this work it was found that \(^3\text{MLCT}\) of \([\text{Ru(tpy)}_2]^{2+}\) (in \(\sim C_2\) symmetry) has an electronic structure belonging essentially to the irreducible representation \(A\), and \(^3\text{MC}\) close to \(B\). The transition \(^3\text{MLCT} \rightarrow ^3\text{MC}\) is allowed, \(i.e.\) a minimal requirement for coupling the electronic states is that the overall symmetry is reduced to \(C_1\). An analysis of the stability of the \(^3\text{MLCT}\) state should take into account the ability of the structure to undergo symmetry breakage, or better said structural distortion. Computationally, we are out of business at this stage. Explicit transition state optimization for the \(^3\text{MLCT} \rightarrow ^3\text{MC}\) transition state is probably not possible with DFT. A large amount of near degenerate MLCT and MC states exists for this molecule (this is one of the reasons why it is used as sunlight absorber) and this creates some computational problems. One would need to use a highly correlated multistate method without deficiencies for CT states to find the transition states.

### 4.4 What Still can be Concluded

Apart from the negative result from this study, that the \(^3\text{MLCT} \rightarrow ^3\text{MC}\) transition is not thermodynamically controlled, some positive conclusions of major importance can be drawn on the basis of this study. i) The geometrical alterations during \(^3\text{MLCT} \rightarrow ^3\text{MC}\) transition are determined by the singly occupied Ru d-orbital (of the \(e_g\) type). Two axial bonds are changed if \(d_{z^2}\) is occupied, and four coplanar ones if it is \(d_{x^2−y^2}\). ii) Octahedral coordination of the Ru-center, leading to destabilization of the \(^3\text{MC}\) state, is not the only important factor for the photostability. Complexes with significantly different lifetime display more or less the same thermodynamical pattern,
Figure 4.2: The stationary points on the lowest triplet surface of [Ru(bqp)_2]^{2+}.

$^3$MC being somewhat less stable than $^3$MLCT. iii) When comparing the pmp family with the bq family, both showing very good coordination, we can assume that single bonds in the ligands should be avoided since they lead to a bigger flexibility of the structure, possibly inducing an easier access to the deactivation pathway. iv) On the computational side, at least double-$\zeta$ polarization basis is needed for accurate description of the triplet state. By investigating electronic structures by means of the spin population at the Ruthenium center, we see that a coupling between experiments and
calculations at this level of theory can be made. Experimental ($S_0$) structures are well reproduced (bond lengths within 2% around Ru) using B3LYP/6-31G(d,p) (C,N,H) SDD (Ru). In Paper IX, a reliable level of theory for these calculations is presented and, in addition, shown that it is worthwhile going beyond the ligand-field splitting orbital model to obtain quantitative measurements on the relative stability, and thus find geometrical features defining the $^3\text{MLCT}$ and the different $^3\text{MC}$ states. This, in turn, provides further insight needed for the understanding of the photostability of these complexes.
5. Repair of 6-4 Photoadducts in DNA

The last paper of this thesis is about repair of a photoinduced damage of DNA, resulting from far-UV absorbition of π-electrons in pyrimidines.95, 96 This study was originally intended as a pre-study to the formation process of 6-4 photoadducts, which is believed to proceed via a $S_0 \rightarrow S_1 \rightarrow T_1 \rightarrow S_0$ mechanism, where the first arrow is an absorption the second one is an intersystem crossing, and the third one is a non-radiative decay channel. The number of calculations soon became tremendously large however, and the project only got to the point of saying something about breaking two of the bonds in the repair process.

5.1 Introduction

UV-radiation is known to cause structural alterations of nucleic acids, which may inhibit the enzymes responsible for DNA transcription and replication and thereby ultimately induce apoptosis or skin cancer.97–100 Of these, DNA damages the cyclobutane pyrimidine dimers (CPDs) are the most common (80-90%),101 while the ones studied here, the pyrimidine (6-4) pyrimidone photoproducts (6-4 photoproducts),96, 101 correspond to 10-20% of the observed damages. Both these lesions are formed from two adjacent pyrimidine (Pyr) nucleobases of the same DNA strand upon absorption of far-UV radiation (200-300 nm). Through a 2+2 addition of C5=C6 and C4=(O/N)4 two \(\pi\)-bonds are transformed to two \(\sigma\) bonds, creating a four-membered ring,96, 101 as seen in Figure 5.1.

Figure 5.1: Formation of 6-4 photoproducts.
Since CPDs are the most common lesions, and therefore a plausible starting point for investigations, the formation and repair of CPDs have been studied extensively by means of both experimental techniques and theoretical computations.\textsuperscript{95,96,101–113} For these lesions, the enzymatic repair mechanism is well characterized, and it contains an electron transfer system that is indirectly assessed in Paper X for 6-4 photoadducts. This repair system is provided by electron-transferring DNA photolyases,\textsuperscript{95,96,101,102,104} whose activity is induced by a light-harvesting cofactor [either methenyltetrahydrofolate (MTFH) or 8-hydroxy-5-deazariboflavin (8-HDF)] and a catalytic cofactor [always the deprotonated FADH form of 1,5-dihydroflavin adenine dinucleotide (FADH\textsubscript{2})]. The photoenzymic repair process is initiated by absorption of near-UV and visible light (300-500 nm), followed by excitation-energy transfer to the catalytic cofactor. The CPD is then split in a redox-process. In which direction the electron is transferred for long remained a subject of much controversy.\textsuperscript{104,114,115} Today, it has been established that the photoenzymic repair is accomplished through the formation of a CPD radical anion, which readily fragments into a closed-shell monomeric Pyr [\textit{i.e.}, the parent thymine (T) or cytosine (C)] and an open-shell monomeric Pyr radical anion (\textit{i.e.}, the parent T or C in a reduced form).\textsuperscript{96,101} Finally, the excess electron of the reduced Pyr is transferred back to the catalytic cofactor, which restores the resting state of the enzyme. A 6-4 photoadduct can not be repaired as readily as the CPD. The formation of 6-4 photoadducts proceeds via the cyclic oxetane/azetidine intermediates resulting from the cycloaddition of the C5=C6 and C4’=O/NH bonds of two excited Pyrs,\textsuperscript{96,101} and thereafter the thermodynamically more stable\textsuperscript{116} 6-4 photoproducts are formed through proton or hydrogen-atom transfer from N3’ to the O/N heteroatom of the oxetane/azetidine, which is linked to the breakage of the C4’-O/NH bond.\textsuperscript{96,102} This hydrogen/proton transfer process needs to be reversed as a first step and the cyclic intermediate (Figure 5.2) has to be reformed for a splitting in analogy with the CPD repair mechanism to take place.

The focus of this study is a mechanism proceeding like this, which is mediated by DNA photolyases recognizing and repairing 6-4 photoproducts in many organisms.\textsuperscript{117–121} The mechanistic action of these enzymes, which are not as well-characterized as the CPD photolyases, is still the subject of much research.\textsuperscript{119,122,123} The mechanism proceeding through the initial regeneration of the oxetane/azetidine intermediates has been suggested,\textsuperscript{119,124} and is indirectly supported by the similarity between CPD and 6-4 photolyases in terms of structure and binding of cofactors.\textsuperscript{125} A plausible mechanism for the photoenzymic repair of 6-4 photoproducts is as follows. First, the enzyme recognizes and binds to the DNA and flips the lesion into a cavity of the enzyme.\textsuperscript{118,126} Two histidines are then involved in the regeneration of the cyclic intermediate. One is responsible for making C4’ more prone to nucleophilic attack by adding a proton to N3’, the other removes a proton from the C5 OH/NH\textsubscript{2} group. Thereby, a nucleophilic attack of O/NH on
C4’ is enabled, resulting in the formation of the cyclic oxetane/azetidine.\textsuperscript{127} Thereafter, the light-harvesting cofactor then absorbs light and the excitation energy is transferred to the catalytic cofactor.\textsuperscript{101,118} As for CPD, both anionic and cationic reaction mechanisms are conceivable also for the photoenzymic repair of this type of DNA lesion.

5.1.1 Methodology
Several quantum chemical studies have been made on CPD lesions repair.\textsuperscript{107–111} 6-4 lesions have also been the subject of theoretical computations.\textsuperscript{116,128,129} Given the lack of high-level computational data, it was motivated to explore both anionic and cationic reaction mechanisms for the regeneration of native Pyrs from oxetane and azetidine by means of DFT calculations. To date, the original paper by Becke on the role of exact exchange interaction leading to the famous B3LYP functional,\textsuperscript{130} has more that 20000 citations. The use of B3LYP in Quantum Chemistry on first and second row atoms is therefore not so inventive, but hardly controversial neither. Kcal/mol accuracy was needed and therefore this was the method of our choice. As noted above, the photoenzymic repair is likely to proceed via these cyclic structures. Since both reduction\textsuperscript{120,131} and oxidation\textsuperscript{132,133} facilitate cycloreversion, a comparison between the two mechanisms in terms
of calculated energetics was made in order to deduce whether either is more favorable from the point of view of its intrinsic (i.e., neglecting the influence of the surrounding enzyme) chemical features. For this purpose, the calculated energetics of a non-catalyzed (i.e., non-radical) cycloreversion reaction was used as reference.

5.1.2 Results
It was found that the ET processes of the two mechanisms have markedly different reaction energies. Reductive ET from the catalytic cofactor of the enzyme (FADH\(^{-}\)) to the lesions initiating an anionic mechanism is a favorable process with an appreciable driving force. Oxidative ET in the opposite direction initiating a cationic mechanism is impossible by the resulting species (FADH\(^{2-}\) and T+T oxetane/T+C azetidine radical cation) lying significantly higher in energy than the corresponding species produced by the reductive ET. This is also the core point of the entire project. Oxidation of the lesion requires much more thermal energy than reduction, and no matter what happens after that point, reduction is most likely what is taking place. From a more academic point of view, it is shown that the formation of open-shell forms of the 6-4 lesions via both reduction and oxidation has a catalyzing effect on their propensity to fragment into monomeric Pyrs, with energy barriers for favoured pathways reduced to a few kcal/mol. Interestingly, the formation process and its reversal is forbidden for the closed shell neutral species according to the so-called Woodward-Hoffman rules,\(^{134}\) which basically say that the 2+2 addition is symmetry forbidden. Symmetry is here broken by oxidation or reduction. Another interesting result is that the sequence of intermonomeric bond cleavages depends on whether the lesion is reduced or oxidized, schematically displayed in Figure 5.3. Anionic T+T oxetane can only fragment along a pathway involving first C5-O4′ then C6-C4′ bond cleavage(CO-CC), whereas fragmentation of the cation proceeds CC-CO. Anionic T+C azetidine, in turn, can fragment both CN-CC (first C5-N4′ then C6-C4′) and CC-CN, but the cation only CC-CN. For the anionic radicals, the calculations tells that the bonds are being cleaved by different mechanisms along the oxetane CO-CC (heterolytic and homolytic, respectively) and azetidine CN-CC (homolytic and heterolytic, respectively) pathways. The results are rationalize by the following: The unpaired electron in the oxidized species ends up at C5′ since the C5=C6 secondary bond corresponds to HOMO. The positive “hole” created is easily relocated to the closest bond, which is CC. In the reduced species the unpaired electron ends up at C4 (carbonyl carbon), and this is closest to the CO/N bond.
Mechanism 1:

Mechanism 2:

Fragmentation of anionic T=O oxetane  $X = O$:
Fragmentation of anionic T=C azetidine  $X = NH$

*Figure 5.3:* Electron rearrangements accompanying the anionic and cationic repair mechanisms.
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7. Summary in Swedish

Teoretisk Fotokemi - det möjligas konst!

Om man lyser på en molekyl kan en mängd olika saker hända, den kan börja lysa, den kan gå sönder, den kan ändra form. Det första kallar man fosforescens eller fluorescens, det andra kallar man fotodissociation och det tredje är i många fall fotoisomerisering. Vad som faktiskt händer, när det händer och hur fort det händer är inte så självklart, och det är det man vill mäta eller räkna ut inom fotokemi.

Fosforescens och fluorescens är två sätt för molekylen att göra sig av med överskottsenergin som i allmänhet inte är kopplade till någon geometrisk förändring av molekylen, ljus sänds ut genom att enbart den elektroniska strukturen ändras. Molekylens energi kan göra sig av med överskottsenergin även utan att sända ut elektromagnetisk strålning, då antingen genom en så kallad icke radiativ kanal (Publikation V-VIII) eller genom dissociation (Publikation I-IV).

Publikationerna I-IV handlar väsentligen om hur en halogenerad bensen går sönder om man lyser på den. Man väljer halogenerad bensen eftersom man då kan vara något säkrare på att det är halogenen som lossnar och inget annat, man väljer att ha sönder den eftersom man vill använda produkten som byggnadsmaterial för att bygga en annan molekyl, och man väljer att lyssa på den för att man idag kan välja ljuspulser som är så korta att de är på samma tidsskalj som en molekylvibration.


Publikation IX handlar om fotokemin hos runtiumpolypyridylkomplex. Dessa komplex absorberar ljus i nästan hela det synliga spektrumet, och är därför lämpliga att använda till att absorbera solljus i solceller och artificiell fotosyntes. Vi visade här med beräkningar att en tidigare teori om
att koordination av ligander runt ruteniumjonerna bestämmer det exciterade tillståndet livslängd, inte stämmer.

Publikation X handlar om reparation av 6-4 fotoaddukter i DNA. Dessa skador uppstår i DNA som en följd av att DNA kan absorbera UV-ljus. Ett flertal olika skador och reparationsmekanismer existerar, och vi studerade en som medieras av att en elektron tas bort eller tillförs till skadan. Troligtvis sker detta i naturen genom att en elektron tillförs.

Teoretiska studier av fotokemiska processer kräver att man beräknar potentialytor, det vill säga att man måste veta hur systemets energi varierar med de geometriska förändringarna man vill studera. Detta gör man med hjälp av kvantkemisk programvara och en stor portion kemisk intuition. Kvantkemi, och kanske särskilt kvantkemi för exciterade tillstånd, är därför inte enbart ett teoretiskt ämne utan handlar till stor del om att man ska känna sitt system och känna att det man gör är rätt. Den här avhandlingen presenterar ett smakprov från det stora smörgåsbord av processer relaterade till ljusabsorption som kan studeras med denna teoribildning. En teoribildning som har sin hemvist mitt emellan kemi och fysik.
8. Bibliography


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