Theoretical description of photo-excited states of 2(5H)-furanone and \( \gamma \)-Valerolactone

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Abstract

The excited states of 2(5H)-furanone and γ-Valerolactone have been investigated from a theoretical point of view to determine the initial relaxation upon photo-excitation. The nature of the excited states were investigated using the multi-configurational method CASSCF along with MS-CASPT2 correction. It was found that the excitation energy for the first intense transition was 1.68 eV higher for γ-Valerolactone compared to 2(5H)-furanone. A similar relaxation path was found for the two molecules, involving breakage of a carbon-oxygen bond, while an additional relaxation path was found for 2(5H)-furanone which involved distortion of the planar ring structure of the molecule.
# Acronyms

<table>
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<td>Hartree-Fock theory</td>
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<td>CASSCF</td>
<td>Complete active space self-consistent field</td>
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<td>FC</td>
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<td>TS</td>
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1 Introduction

Photo-chemical dynamics of large molecules is a difficult study. There are both biological and artificial processes relying on photo-excitation that are essential to human health as well as photo-chemical systems that can be used in technological applications. A very important process for humans is the synthesis of vitamin D which relies on adsorption of UV radiation. Vitamin D is vital to human health and it is thus very important to study the photo-chemical dynamics of the process by which it is synthesised [1]. Another interesting field where the photo-chemical dynamics is important is the development of photo-switches. A photo-switch is a molecule that can change between different thermodynamically stable structures by absorbing light. Photo-switches can be used in a wide variety of applications e.g. to develop new kinds of image detectors [2], and control the release of pharmaceuticals in the body to minimize side effects [3]. The study of photo-chemistry of these large molecular systems imposes some difficulties due to their size when studied with theoretical models, since it would demand a huge amount of computing power. Therefore, very little is known about the dynamics of these photo-chemical processes. One approach is to study smaller structural parts that have a critical role in the photo-chemical dynamics of these larger molecules. This is the approach that will be pursued throughout this bachelor project.

1.1 Background

A group of molecules that serve as light-absorbing parts of larger molecules are five-membered heterocyclic compounds such as furan and lactones. A long term goal is to study these small molecules accurately with theoretical and experimental methods to construct general rules of the dynamics of the photo-chemical processes these molecules undergo upon photo-excitation. Some work has been done regarding this group of molecules (see: ref. [4] and [5]) but there is currently no general understanding about how these systems behave photo-chemically.

The issue of this project is formulated based on the experimental work of Oliver Schalk and co-workers [6] at Stockholm University. They studied a whole range of lactone and furan derivatives with TRPES (Time-resolved photoelectron spectroscopy) including those presented in Figure 1.
Figure 1: Different 5-membered heterocyclic compounds of interest for theoretical examination. 1: 2(5H)-furanone, 2: γ-Valerolactone, 3: 3-Methyl-2(5H)-furanone, 4: α-Angelicalactone, 5: α-Methylene-Butyrolactone.

TRPES is a method which involves a pump-probe experimental setup, where an ultra fast pump-laser pulse “pumps” the system to excited states by promoting electrons to orbitals higher in energy. A probe-laser pulse then ionizes the molecules and the energies of the emitted electrons can be measured. The probe-laser pulse is fired at different stages in the relaxation from the excited states to get information about the paths of relaxation. Relaxation from an excited state is a very quick process so these measurements take place on a nanosecond, picosecond or femtosecond time scale to be able to follow relaxation and study even very short lived excited states [7].

Relevant to this theoretical project is first and foremost the energy of the pump-laser used in the experimental setup, because this determines which states the system will get excited to. In the experiments done by Schalk and co-workers a pump-laser pulse with a wavelength of 200 nm (which corresponds to an energy of 6.2 eV) was used. A wavelength of 200 nm is in the UV range of the electromagnetic spectrum and such a high energy pump-laser pulse is used because it is in this range these molecules absorb. The experiments performed are femtosecond time resolved, since the interest lies in the early relaxation pathways. These TRPES experiments are carried out in the gas phase. More information about the experimental setup can be found in ref. [8].

Among the five molecules presented in Figure 1, two were selected to be investigated in this theoretical project. The first one selected for this purpose was 2(5H)-furanone due to its structural simplicity which will make the calculations much faster than for the other molecules, and is therefore a good starting point to get familiar with the software and the methods
used. The second molecule selected was \( \gamma \)-Valerolactone due to its structural difference compared to the other molecules, i.e. that it does not have a carbon-carbon double bond (which all the other presented molecules have), and a different result would to be expected (which is very interesting indeed to investigate!). It has been shown that the experimental results of 2(5H)-furanone and \( \gamma \)-Valerolactone differ significantly.

1.2 Aim

This project is a theoretical approach to examine photo-excited states and the relaxation paths of 2(5H)-furanone and \( \gamma \)-Valerolactone. The molecules can be seen in Figure 2 where the specific enantiomer of \( \gamma \)-Valerolactone also is specified. The main focus is what the relaxation paths after excitation look like, in terms of geometrical and electronic changes, at a theoretical level to serve as an aid for interpretation of experimental data for these and similar molecules. The TRPES experiments show that \( \gamma \)-Valerolactone has two or three times slower relaxation time compared to 2(5H)-furanone. The reason for the different relaxation times remains an outstanding question and the aim is to suggest answers to why these differences are observed in the experiments. Theoretical calculations are a necessary complement to experiments since the TRPES experimental method only provide information about the energy of the excited states and give no information about the structural changes in the molecule. To be of any help, the calculations therefore need to be performed on the excited electronic states studied in the TRPES experiments in order to be comparable. Since the TRPES experiments are carried out in the gas phase there is no need to take into account solvation effects in the calculation. The nature of the electronic transitions of interest first need to be investigated. The interest lies in the low energy excitations which are expected to be a \( \pi \rightarrow \pi^* \) or a \( n \rightarrow \pi^* \) transition since the energy gap between \( n/\pi \) orbitals and \( \pi^* \) orbitals is much smaller than for transitions involving \( \sigma/\sigma^* \) orbitals. The excitation energy for a transition should be near or lower than the pump-laser pulse at 6.2 eV to be relevant and comparable to the TRPES experimental data. An additional requirement is that the electronic transition is intense enough to be observed experimentally. If a transition is too improbable the intensity of that transition will be low and will not be observed in the experiments to a high extent, hence the primary interest lies in transitions that are both lower in energy than the pump-laser pulse and have a high enough intensity. To find and closely examine complete
relaxation paths is beyond the scope and time frame of this project. Some calculations on the ground state of these molecules has already been done [4] so the focus for this project lies in examine the excited states and suggest relaxation paths in terms of *initial directions* rather than providing complete paths.

Figure 2: Lewis-structures of 2(5H)-furanone and γ-Valerolactone (the specific enantiomer)

## 2 Theoretical concepts

### 2.1 Potential energy surface

A *potential energy surface* (PES) is a plot of the potential energy vs geometry. With a diatomic molecule there is only one geometric parameter that can be altered (the bond length between the two atoms) so the energy vs geometry diagram would simply be a 2-dimensional graph. However, molecules with more than two atoms would yield a more complicated diagram. For example, a water molecule has two changeable parameters (assuming that the two O-H bonds have the same length), the H-O-H angle and the O-H bond length which would yield a 3-dimensional graph, a *surface* of potential energy plotted against the geometrical changes. For even larger molecules (as those of interest in this report) there would be even more parameters that could be altered so that the potential energy will form a *hypersurface*, not possible to draw in 3 dimensional space, when plotted against geometry. Although a hypersurface might seem quite abstract it helps to conceptually think of it as a surface that might have hills and valleys corresponding to maximum and minimum in energy. A minimum energy point on a PES usually is of great interest and can be thought of as a more or less bowl-shaped cavity in the
PES and in the bottom of this cavity there is no tendency for geometrical change since a small change in any direction would lead to an increase in energy. A minimum energy point on a PES corresponds to a relevant chemical structure such as reactant, product or intermediate of chemical reactions.

A point on a PES where there are no tendencies for geometrical change is called a stationary point. A minimum energy point is such a point. Another stationary point of interest is where some directions in changing the geometry is a maximum in energy. When there is a maximum in one direction and a minimum in all other directions the shape of the PES in 3D-space looks like a horse saddle, hence the name (first order) saddle point. A saddle point is therefore a transition state (TS) between stable structures, which is a concept all chemists are familiar with.

2.2 Franck-Condon geometry

Because electronic transitions are very fast compared to geometrical changes, they often occur vertically, i.e. at a given nuclear geometry. Photo-excitation thus occurs at the minimum on the electronic ground state. This geometry is referred to as the Franck-Condon (FC) geometry or FC point. It is unlikely that this is a minimum energy structure on the PES of the other electronic states and the geometry is expected to relax from this FC point. The relaxation usually imposes structural changes in the molecule to minimize the energy and reaching a new geometry that is a minimum energy structure for this excited state. If the molecule relaxes to a minimum energy structure on an excited state, and no further relaxation to a lower electronic state is possible non-radiatively through geometrical changes, the only way to relax further is by emission i.e. radiatively by emitting a photon.

2.3 Conical intersection

A non-radiative relaxation path could be provided by the existence of a conical intersection (CI), a certain geometrical structure of the molecule that has the property that two (or more) electronic states have the same energy, the states are said to be degenerate. One basic (and obvious) requirement when suggesting a relaxation path through a conical intersection is that it is accessible, it needs to be low enough in energy, definitely lower in energy than the initial structure, the Franck-Condon geometry. A picture of a PES diagram with two intersecting electronic states forming a CI can be seen
in Figure 3. Relaxation through a CI is a very fast process compared to emission, hence a molecule is much more likely to relax through a CI if it is nearby geometrically than relaxation by photon emission.

Figure 3: A visual representation of two electronic states that are degenerate at one point forming a conical intersection (the point in the middle). This figure is reused from a blog by Ross H. McKenzie which can be found in ref. [9].
3 Computational methods

The electronic states of a molecule are described in quantum mechanics by the time-independent Schrödinger equation [10]:

\[ \hat{H} \psi = E \psi \] (1)

The Hamiltonian \( \hat{H} \), the energy operator, acts on the wavefunction \( \psi \) to return the energy \( E \) in terms of an eigenvalue (times the wavefunction). The Hamiltonian for an \( n \)-electron atom is:

\[
\hat{H} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{n} \nabla_i^2 - \sum_{i=1}^{n} \frac{Ze^2}{4\pi\varepsilon_0 r_i} + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \frac{e^2}{4\pi\varepsilon_0 r_{ij}} \] (2)

where \( \hbar \) is the reduced Planck’s constant, \( m_e \) and \( e \) are the mass and charge of an electron respectively, \( \varepsilon_0 \) is the permittivity of vacuum, \( r_i \) is the distance from the nucleus to electron \( i \) and \( r_{ij} \) is the distance between electron \( i \) and \( j \). The Greek letter \( \Sigma \) (sigma) is the common summation operator and \( \nabla \) is the notation for the gradient, \( \nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \), for every electron \( i \). [11]

Before continuing, the concept of atomic units should be introduced. The expression in Equation 2 can be greatly simplified by setting \( \hbar, m_e, e \) and \( 4\pi\varepsilon_0 \) numerically equal to 1. The expression then simplifies to the expression in Equation 3.

\[
\hat{H} = -\frac{1}{2} \sum_{i=1}^{n} \nabla_i^2 - \sum_{i=1}^{n} \frac{Z}{r_i} + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \frac{1}{r_{ij}} \] (3)

Equation 1 can be solved exactly for systems with up to two particles, a nucleus and an electron, or a free particle. A two particle system is commonly known as a hydrogen-like atom (H, He\(^{+}\), Li\(^{2+}\) e.t.c.). In the following subsections several approximate methods to solve Equation 1 for larger systems will be introduced. These approximate methods are implemented in the software package OpenMolcas [12] which will be the software used in this bachelor project to perform the calculations.
3.1 Hartree-Fock

One of the most influential and ground-breaking theories in quantum mechanical computing is the Hartree-Fock theory (HF). It is rarely used on its own in modern applications since it is not considered to be accurate enough but has rather provided the foundation for the more advanced methods used today [13]. HF is an \textit{ab initio} (Latin: from the first) method since it does not rely on empirical parameters. HF is an approximate method which deals with this problematic electron-electron repulsion term in a very clever way. Instead of calculating every electron-electron interaction the field an electron experiences is calculated from the average electric field from all the other electrons in the system. First of all, a core Hamiltonian, $\hat{H}^{\text{core}}$, for one electron is constructed by omitting the last sum in Equation 3 and this equation is presented in Equation 4.

$$\hat{H}^{\text{core}}(1) = -\frac{1}{2} \nabla^2_1 - \sum_\alpha \frac{Z_\alpha}{r_{1\alpha}}$$

(4)

The Fock operator $\hat{F}$ can then be constructed as shown in Equation 5 where $\hat{J}$ and $\hat{K}$ are the Coulomb and the exchange operator, respectively and are defined in Equations 6 and 7.

$$\hat{F}(1) = \hat{H}^{\text{core}}(1) + \sum_{j=1}^{n/2} [2\hat{J}_j(1) - \hat{K}_j(1)]$$

(5)

$$\hat{J}_j f(1) = f(1) \int |\phi_j(2)|^2 \frac{1}{r_{12}} dv_2$$

(6)

$$\hat{K}_j f(1) = \phi_i(1) \int \phi_j * (2)f(2) \frac{1}{r_{12}} dv_2$$

(7)

$$\hat{F}(1) \phi_i(1) = \varepsilon_i \phi_i(1)$$

(8)

The HF closed-shell orbital energies $\varepsilon_i$ for every orbital $i$ can be calculated by using Equation 8. However, this equation is impossible to solve without some further theoretical theorems since the Fock-operator $\hat{F}$ depends on the unknown spin-function $\phi_i$. According to the variational theorem the best approximation to the "true" orbital energies are the ones lowest in energy. This makes it possible to solve Equation 8 for the energies and the orbitals.
with an iterative process by first making a guess (called *guess orbitals*) and calculate the energy. The solution is then used as guess orbitals in the next iteration and so on until the energies converge and are unchanged between iterations according to some reasonable criteria. The process of minimizing the energy with this kind of iterative process is called the *Self-consistent field* (SCF) procedure. The name refers to the field an electron feels due to the average charge of all other electrons (this field are the Coulomb and exchange integrals, how these are calculated is not covered in this report). The SCF procedure hence optimizes the orbitals in such a way that the energy is minimized, which yields the best approximate solution to Equation 8. For a more complete description of the HF method there are many books in molecular quantum mechanics reviewing *ab initio* methods, see for example [11] and [13].

### 3.2 Slater-determinants

The wave function used in Hartree-Fock and methods derived from Hartree-Fock is called a *Slater determinant* (usually denoted $D$ or $\Psi$ in equations). The need for a Slater determinant to be used as a wave function arises from the fact that a wave function describing electronic systems need to be anti-symmetric (if two electrons are exchanged the function must change sign) in order to resemble the behaviour of these molecular systems. A Slater determinant consists of a linear combination of *spin functions* (used synonymous with spin orbitals) in such a way that a determinant is formed. A spin function is a one-electron wave function denoted $\psi_n(i)\alpha(i)$ or $\psi_n(i)\beta(i)$ (lower case Greek letter, $\psi$ *psi*, $\alpha$ *alpha* and $\beta$ *beta*) where $\psi_n(i)$ is the spatial part and $\alpha(i)$ or $\beta(i)$ the spin part meaning spin up or spin down, respectively.

$$\Psi_{2n} = \frac{1}{\sqrt{(2n)!}} \begin{vmatrix} \psi_1(1)\alpha(1) & \psi_1(1)\beta(1) & \psi_2(1)\alpha(1) & \psi_2(1)\beta(1) & \cdots & \psi_n(1)\beta(1) \\ \psi_1(2)\alpha(2) & \psi_1(2)\beta(2) & \psi_2(2)\alpha(2) & \psi_2(2)\beta(2) & \cdots & \psi_n(2)\beta(2) \\ \psi_1(3)\alpha(3) & \psi_1(3)\beta(3) & \psi_2(3)\alpha(3) & \psi_2(3)\beta(3) & \cdots & \psi_n(3)\beta(3) \\ \vdots & \vdots & \vdots & \vdots & \cdots & \vdots \\ \psi_1(2n)\alpha(2n) & \psi_1(2n)\beta(2n) & \psi_2(2n)\alpha(2n) & \psi_2(2n)\beta(2n) & \cdots & \psi_n(2n)\beta(2n) \end{vmatrix}$$

A general Slater determinant is shown in Equation 9. Each column in the determinant lists all the electrons with a specific spin in a certain orbital and each row lists a certain electron placed in every orbital. $n$ denotes the
number of spatial orbitals. A Slater determinant is therefore simply a way to arrange all the electrons in all the orbitals such that the anti-symmetry principle is followed. Switching the places of two electrons in two spin orbitals is equivalent to switching rows in the determinant which would change its sign [13].

3.3 Basis sets
A basis set is the set of functions used to define the spin-functions in the Slater-determinant. The spatial part of the spin-functions are defined as linear combinations of Gaussian functions called basis functions. Gaussian functions are used because they have good properties that allow for analytical solutions of integrals and easy implementation in a computer program. Even though the integrals of Gaussian functions have analytical solutions it is still a simplification and an approximation to the true spin-function to represent it as a linear combination of basis functions. The basis sets of most interest in this project are the Atomic Natural Orbital (ANO) basis sets with extended relativistic (RCC) with minimal basis (MB) or Valance double-Zeta plus Polarization (VDZP). The complete labels for the two basis sets used in this project are:

ANO-RCC-MB
ANO-RCC-VDZP

where the latter is larger and gives more accurate results (to a higher computational cost).

3.4 CASSCF
Complete active space self-consistent field (CASSCF) is a multi configurational method which can be used to calculate excited states of molecules. CASSCF differs from HF in that it uses an active space consisting of valence molecular orbitals and some virtual orbitals. All orbitals lower in energy than the active space are doubly occupied (one spin-up and one spin-down electron in each orbital) and all orbitals above the active space in energy are virtual (orbitals containing no electron). Within the active space all possible excitations are considered. Ideally, all orbitals should be included but the reason an active space is used is that it would be way too expensive
in terms of computing power and time to calculate all possible excitations among all orbitals in the molecule. The CASSCF wave function is written as a linear combination of Slater-determinants [14], one for each possible excitation, which would yield an enormous number of mathematical expressions for anything but very small molecules, if excitations among all orbitals were considered [15].

In a CASSCF calculation with the same number of orbitals and electrons in the active space, the number of Slater determinants scales exponentially with an increased number of orbitals in the active space. With an active space of 15 orbitals the calculation starts to demand a significant amount of computing power and for 18 or more orbitals the calculations get unfeasible [16].

Simplifications to reduce the number of Slater determinants can be made by only calculating single and double excitations to singlet states since these are the most relevant ones in most cases (depends on what is being studied obviously). The low energy molecular orbitals are most of the time doubly occupied and only take part in excitations to a very minor extent. This justifies the use of an active space, however, the choice of the active space must include orbitals that are likely to take part in the process of interest, such as excitations involving certain orbitals, or bond breaking involving the bonding and anti-bonding orbitals of that bond. Omitting important orbitals often leads to instabilities and unrealistic results [17]. The orbitals are of course somewhat different since they are optimized in the calculation but if the characteristics of the orbitals (being a $n$, $\pi/\pi^*$ or $\sigma/\sigma^*$) are preserved in the output compared to the input (the guess orbitals) the active space is considered stable. Instabilities in the active space can occur when the orbitals included in the active space are insufficient to describe the process of interest, which causes convergence problems in the CASSCF calculation. OpenMolcas will automatically detect orbitals that cause instabilities and switch those out to orbitals that will make the calculation converge. However, the orbitals that are included in the active space are chosen because they are needed to describe the studied processes. Therefore, it is important that the active space that is chosen is stable.

When trying to minimize the energy for one excited state with CASSCF instabilities in the active space can occur if two or more electronic states are close in energy (e.g. when close to a CI). If the first and second excited states are close in energy, the energy for the second excited state might at some
point during a calculation get lower than the energy for the first excited state. In the next iteration, the state previously regarded as the second excited state is now the first excited state, and vice versa, the two states have "switched places". The states will keep switching places each iteration resulting in a root-flipping problem where no convergence can be reached. Convergence problems are the cause of an unstable active space since OpenMolcas will automatically switch out "problematic" orbitals so that the calculation may converge. To get around this issue one has the possibility to perform a state average calculation where the average energy, for the states included in the state average, is minimized. The number of states to include in the state average is specified with a keyword in the input file for the calculation. The energy for the states in a state average will be slightly higher in order to satisfy the state average constraint but it is a necessary compromise in order to avoid root-flipping. How many states that need to be included in the state average depends on the nature of the states and how the energy changes during e.g. a geometry optimization calculation.

3.5 CASPT2

While CASSCF is a powerful tool for calculating excited states the method lacks dynamic correlation due to the use of an active space. Dynamic correlation would be obtained by including many virtual orbitals in the active space, but this would be too expensive and is contradictory to the purpose of using an active space to reduce the computational cost. One approach is instead to perform a Compete active space second order perturbation theory (CASPT2) correction to the energies to correct for dynamic correlation. There are several kinds of CASPT2 corrections that can be applied to the result of a CASSCF calculation. One way is to treat each state in the state average individually with a single state CASPT2 (SS-CASPT2 or just CASPT2) but this does not take into account interaction between different states. A better correction can be obtained by using a multi state CASPT2 (MS-CASPT2) which takes into account some mixing between the electronic states. MS-CASPT2 gives a realistic view even for a small active space. If the active space is increased, SS-CASPT2 and MS-CASPT2 give more and more similar results. However, it is much cheaper to use MS-CASPT2 than to increase the active space in the CASSCF calculation.
3.6 DFT

The HF derived methods such as CASSCF are considered quite costly in terms of computing power. It could therefore be advantageous to first optimize with a cheaper method before attempting a more accurate but more computationally demanding method like CASSCF. Density functional theory (DFT) is usually the method of choice for larger molecules (such as proteins) due to its low computational cost with reasonable accuracy compared to other methods. It is usually a gain in time and computational effort to first optimize a structure with DFT before computation with CASSCF. One could use CASSCF right away but it would probably take unnecessary long time. The only kind of DFT used in this project is Kohn-Sham DFT (KS-DFT) with the functional B3LYP.

3.7 Geometry optimization, MEP and IRC

Geometrical changes of a molecule (for example changing bond lengths and bond angles) could be thought of as a ball rolling on a surface. If the surface is down hill where a ball is placed it will start to roll downwards when letting go of the grip. A down hill surface corresponds mathematically to a negative gradient. The gradient is a vector that describes the curvature of a surface or hypersurface, a generalisation of the derivative. To be a good analogy for geometrical changes of a molecule in, for example a minimum energy geometry optimization, this particular ball can not have any momentum. The ball is simply placed (and held) on the surface asking the question "would it move if letting go?", if the answer is "yes" the ball is moved slightly in that direction asking again "would it move?" and so on and so forth. When finally the answer is "no" the ball has no tendency to move in any direction, the point on the surface exactly beneath the ball is flat, the gradient is zero and a stationary point has been reached.

To find a minimum energy point on the PES OpenMolcas is instructed to vary the geometry by following the gradient for a state in such a way that the energy for that state is minimized. This provide a quick way to get to the target geometry but might not be a very realistic path but rather like a zigzag across the "true" path a molecule would follow when relaxing from an excited state. It is therefore only the final geometry that is meaningful in a geometry optimization calculation.

In a minimum energy path (MEP) more computational effort is put in
to yield a more realistic path by not only following the gradient but also optimize the structure in all other directions on the PES making sure every MEP geometry stays on the path. A MEP calculation only takes small steps of a fixed “length” as long as the energy gets lower for each new step. When the energy increases the MEP calculation stops, indicating that an energy minimum point has been stepped over. The minimum energy geometry will be somewhere between the two last points in the MEP.

An *intrinsic reaction coordinate* (IRC) is similar to a MEP but the starting geometry is a saddle point instead of the FC point. Instead of following the gradient (since it is zero at a saddle point) the calculation is performed using a *reaction vector* to guide the direction of the path. The reaction vector could be the imaginary vibrational mode found in a first order saddle point. The IRC would then scan across this vibrational mode and calculate two paths from the saddle point in both directions of this vibrational mode. These two paths are then combined to yield a path from one energy minimum structure to another across the saddle point.

Apart from doing a minimum energy geometry optimization, a geometry for a CI could be optimized by specifying a constraint in the calculation to make the energy difference between two states as small as possible (according to some convergence criteria). OpenMolcas will then try to find a direction of geometrical change that lowers the energy difference between the states and pursue that direction until a CI is reached. OpenMolcas will try to find the lowest energy nearby CI with this constraint. If no convergence can be reached it might indicate either that there is no nearby CI or, that the active space and/or state average used in the calculation is not adequate to describe the CI.

## 4 Results and discussion

In the following section the results will be presented along with discussions. All results from calculations presented here are done with the ANO-RCC-VDZP basis set. For more information about the active space and the number of states included in the state average, check the attached description to that particular table or figure. All CASPT2 calculations used settings where IPEA shift was set to 0.0 and IMAGINARY shift was set to 0.1. The units for these values are energies in atomic units (hartree).
4.1 2(5H)-furanone

In the following section the results regarding the molecule 2(5H)-furanone are presented. The results from the calculations are represented both visually in the form of pictures and diagrams as well as tabulated data. These are the digested data which is to help the reader follow the discussions.

4.1.1 Active space

Excitations to the lower energy states are expected to occur from $n$ and $\pi$ orbitals since these are high in energy which makes the energy gap to a low energy unoccupied $\pi^*$ small. A small energy gap means that the excitation energy also will be small. The $n$ and $\pi$ orbitals with corresponding $\pi^*$ are thus included in the active space to be able to describe these excitations.

The orbitals of the active space used in the calculations on 2(5H)-furanone are shown in Figure 4. See numbering of atoms in Figure 5. The active space consists of one $n$ orbital, the lone pair of oxygen O2 in the plane of the ring, and is shown in (a), two orbitals hereafter labelled as $\pi$, which are a mixture between a $n$ orbital of O1 (perpendicular to the plane of the ring), a C4-O2 $\pi$ orbital, shown in (b) and (d), and one C2-C3 $\pi$ shown in (c), with two corresponding mixed C4-O2 and C2-C3 $\pi^*$ orbitals shown in (e) and (f). For some calculations the O1-C4 $\sigma$ and $\sigma^*$ are also included which are shown in (g) and (h). These orbitals were included so that ring-opening where this bond is expected to break [4] is well described. The orbitals are labelled and characterised by visual inspection.
Figure 4: Orbitals used in the active space in the CASSCF calculations of 2(5H)-furanone.
4.1.2 Ground state geometry

The first geometry optimization for the ground state was done at the KS-DFT with functional B3LYP level of theory from a crude drawing of the initial geometry. This DFT optimized geometry then served as the starting point for the ground state optimization at the CASSCF level (first with the ANO-RCC-MB basis set and then expanded to the ANO-RCC-VDZP basis set) and a visual representation of the geometry is presented in Figure 5. In order to have a stable active space a 4, 5 or 6 state average had to be used or the orbitals of interest would not stay in the active space. A 6 state average was chosen as a standard in the calculation of the ground state due to convenience and comparability since some calculations on excited states required a 6 state average.

Figure 5: Minimum energy geometry of the ground state of 2(5H)-furanone. The geometry optimization was performed at the CASSCF level of theory with a 6 state average calculation with the ground state and the first five excited states. All orbitals in Figure 4 were included in the active space.

The values for the relevant bond lengths, angles, dihedral angles and energies are given in Tables 2, 3 and 4 in the first data column of each table. The bond length of the C2-C3 double bond corresponds very well
to a standard sp\(^2\) sp\(^2\) hybridized carbon double bond. The same goes for the C3-C4 bond for a standard sp\(^2\) sp\(^2\) hybridized carbon single bond and the C1-C2 bond for a standard sp\(^3\) sp\(^2\) hybridized carbon single bond. The geometry and the numbering of atoms can be seen in Figure 5.
4.1.3 Search for photo-excited state

This section covers the search for an excitation from the ground state to an excited state that would be likely to occur. An excited state of interest would be a state with an excitation energy near 6.2 eV (corresponding to a photon wavelength of 200 nm) since that is the excitation energy used in the experiments. Also there should be a high oscillator strength between the ground state and the excited state. The oscillator strength is a measure of the probability/intensity of the excitation from the ground state to the specific excited state (analogous to adsorption intensity in spectroscopy). A calculation of 10 excited states was performed at the CASSCF level with MS-CASPT2 correction to energies.

This calculation where the results are presented in Table 1 was done in the initial stages of the project and does not follow the same consistency in the method in terms of the geometry and the active space used. The active space only had orbitals (a) to (f) in Figure 4 included and the geometry was optimized with this active space. At the FC geometry there is no tendency for bond breakage so orbitals (g) and (h) were not needed at this stage. However, these values should be taken with a grain of salt and be used only to identify which states to investigate and not for any applications that requires precision.

Assuming the calculations are reasonable accurate the excitation energy of $S_3$ is 0.62 eV higher than the energy of the exciting photon used in the experiments and it is too high to be overcome. Also, the oscillator strength for $S_1$ is too low to be relevant and the transition would not be intense enough. In Figure 1 it can be seen that the oscillator strength for $S_1$ is almost a thousand times lower than for $S_2$! From this, the conclusion was to further investigate the second excited state $S_2$ since it is the lowest energy transition with a high enough intensity be observed in the TRPES experiments. By looking at the most dominant occupations for $S_2$ in Table 1 and identifying the orbitals in Figure 4 it can be seen that this is a $\pi \to \pi^*$ excitation from orbital (d) to (f) by comparing to the occupations of the ground state (all orbitals doubly occupied). By doing the same for $S_1$ it is seen that it is an excitation from orbital (a) to (f), a $n \to \pi^*$ excitation.
Table 1: Calculation of 10 states at the ground state geometry of 2(5H)-furanone. The character of the state is indicated by the most prominent occupations(s) (electronic configurations) in the active space of the CASSCF calculation. The number "2" indicates that it is a doubly occupied orbital and "u" and "d" indicate spin up and spin down respectively. The oscillator strength is between $S_0$ and the specific excited state. The excitation energy is the MS-CASPT2 corrected energy and is given in terms of electron volt (eV). The orbitals in the active space has the same labels as in Figure 4 and the first row describes the order in which these orbitals are arranged in this particular calculation.

<table>
<thead>
<tr>
<th>state</th>
<th>occupations with highest weight</th>
<th>excitation E (eV)</th>
<th>dipole osc. Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_0$</td>
<td>bdacfe</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>$S_1$</td>
<td>22u2d0</td>
<td>5.02</td>
<td>4.40E-04</td>
</tr>
<tr>
<td>$S_2$</td>
<td>2u22d0</td>
<td>5.66</td>
<td>2.82E-01</td>
</tr>
<tr>
<td>$S_3$</td>
<td>22ud0</td>
<td>6.82</td>
<td>4.38E-01</td>
</tr>
<tr>
<td>$S_4$</td>
<td>22u20d</td>
<td>7.90</td>
<td>5.42E-05</td>
</tr>
<tr>
<td>$S_5$</td>
<td>2u220d, 222u0d</td>
<td>8.40</td>
<td>1.42E-01</td>
</tr>
<tr>
<td>$S_6$</td>
<td>u222d0</td>
<td>9.04</td>
<td>7.62E-02</td>
</tr>
<tr>
<td>$S_7$</td>
<td>22u0d, 2u220d</td>
<td>9.56</td>
<td>2.63E-01</td>
</tr>
<tr>
<td>$S_8$</td>
<td>22ud20</td>
<td>10.47</td>
<td>&lt; 10$^{-5}$</td>
</tr>
<tr>
<td>$S_9$</td>
<td>222020</td>
<td>11.02</td>
<td>1.02E-02</td>
</tr>
</tbody>
</table>
4.1.4 Excited state geometries

After a minimum energy geometry for the ground state had been found and the excited state of interest had been identified it was possible to perform calculations on this excited state. When relaxing the second excited state from the Franck-Condon point the geometry obtained was in fact not a minimum energy structure but rather a saddle point (transition state). A saddle point is a stationary point on the PES but in contrast to a minimum energy structure a saddle point is an energy maximum along one direction. The structure obtained is presented in Figure 6.

Relevant bond lengths, angles, dihedral angles and energies are presented in Tables 2, 3 and 4. It is seen that the bond lengths changing the most are O2-C4 bond and the C2-C3 bond getting significantly longer while the C3-C4 bond gets much shorter. This is very intuitive since electrons are promoted to a mixed $\pi^*$ orbitals that is anti-bonding in the bonds O2-C4 and C2-C3 making the bonds longer while in the other hand the $\pi^*$ happens to be in phase between C3 and C4 making it resemble a double bond between these atoms and thus the bond gets shorter due to this in phase $\pi$ interaction.

It could be found that the geometry in Figure 6 was a saddle point by calculating the vibrational frequencies which showed that one vibrational mode was an imaginary frequency (exactly 1 imaginary frequency = first order saddle point). This imaginary frequency is characterised mainly by the bending of H3 in and out of the plane of the molecular ring. The dihedral angles between O1 C1 C2 H3 and between O1 C4 C3 H4 (see numbering of atoms in Figure 6) are the main geometrical changes characterising this vibrational mode.
Figure 6: Transition state structure found in the relaxation of the second excited state from the Franck-Condon geometry of 2(5H)-furanone. The vibrational mode which is characterised by the change in the dihedral angles between O1 C1 C2 and H3 as well as between O1 C4 C3 and H4, has an imaginary frequency, hence this is a first order saddle point. The geometry optimization calculation was performed with a 6 state average CASSCF with all orbitals in Figure 4 included in the active space.

By manually editing the nuclear coordinate in the xyz-file slightly (by adding 0.05 Å to the z coordinate of H3) it was possible to "push" the molecule into converging to a true minimum energy structure when a new optimization was performed on this distorted structure. The structure obtained from the calculation is presented visually in Figure 7. Values of the relevant bond lengths, bond angles, dihedral angles and energies concerning this structure can be found in data column 3 in Table 2, 3 and 4. The most prominent structural differences in this structure compared to the transition state are the dihedral angles, hydrogen H3 and H4 bending in opposite directions perpendicular to the ring of the molecule. The O2-C4 bond length gets a bit shorter, all other structural changes are small. The energies for the true minimum and the transition state structures are also similar (a bit lower for the true minimum of course).
Figure 7: Optimized minimum energy geometry for the second excited state of 2(5H)-furanone. The initial geometry for this calculation was a manually distorted version of the transition state geometry in Figure 6. The geometry optimization calculation was performed with a 6 state average CASSCF with all orbitals in Figure 4 included in the active space. Note that H3 is bending outwards and H4 is bending inwards relative to the plane of the paper.
4.1.5 MEP and IRC

Figure 8: MS-CASPT2 energy vs the geometry of every point in the MEP. The initial geometry is the Frank-Condon point in the excitation from the ground state. The second excited state is relaxed during the MEP. The energies are expressed relative to the ground state energy. The geometry was optimized at CASSCF at with a 5 state average with the orbitals (a) to (f) in Figure 4 included in the active space, with MS-CASPT2 correction to energies to every point on the path.

A minimum energy path (MEP) calculation was done on the relaxation from the second excited state starting from the Franck-Condon geometry and can be seen in Figure 8. The two last points are very similar to the structure in the previous section (see: Figure 6) and this transition state structure is somewhere between the last two points in the MEP. The MEP calculation shows that there is no energy barrier between the starting point, the FC geometry, and the end point(s), the transition state (the MEP is only calculated as long as the energy decreases, so the fact that it was possible to perform it shows this). This means that the transition state structure in Figure 6 is reachable from the FC point.
Figure 9: Intrinsic reaction coordinate calculation between the two minimum energy structures on each side of the saddle point. The energy is calculated with CASSCF with a 5 state average with the orbitals (a) to (f) in Figure 4 included in the active space. The reaction coordinate used was taken from the imaginary vibrational mode from a vibrational analysis calculation performed on the saddle point geometry.

In Figure 9 is the result from an intrinsic reaction coordinate (IRC) calculation between the two minimum energy structures on each side of the saddle point in Figure 6. One of the minimum structures is identical to the structure found in Figure 7 and the other minimum energy structure is its mirror image. The diagram in Figure 9 confirms that the two minimum energy structures and the corresponding paths have the same energy, which is to be expected from two structures that are mirror images to each other. This relaxation path with a twisted ring as a minimum structure is known as the "ring-puckering" relaxation path [8].
4.1.6 Conical intersections

Information about conical intersections (CI) are presented in this section. All geometries are optimized at the CASSCF level and energies are corrected with MS-CASPT2. Conical intersections are important in the search for non-radiative relaxation paths since the energy is degenerate for two (or more) electronic states at such a geometry and provide a link between these states. When reaching a CI no photon is emitted when relaxing from one electronic state to a lower electronic state since there is no difference in energy at this point, thus providing a non-radiative relaxation path.

Figure 10: Geometry of a conical intersection found between the first and the second excited states of 2(5H)-furanone. The calculation was performed with a 6 state average CASSCF with all orbitals in Figure 4. Note that the double bonds in this figure are not a true representation of the nature of the bonds.

In Figure 10 is shown a conical intersection that could provide a relaxation path from the second excited state. The structure of this conical intersection is an open ring structure and could be of great interest in finding relaxation paths for 2(5H)-furanone involving ring opening reactions, especially since
the minimum energy geometry found in $S_2$ had, in contrast, a closed ring. To see if this CI is reachable a linear interpolation from the FC point to the CI was done. with a total of 15 points (point 0 is the FC point, then 1-13 are intermediate geometries and the last point is the CI). These energies are presented at CASSCF, and MS-CASPT2 level in Figures 11 and 12, respectively.

Figure 11: Linear interpolation from the Franck-Condon geometry to the conical intersection found between the states $S_1$ and $S_2$. CASSCF energies are calculated for each point with a 6 state average with an active space consisting of all the orbitals in Figure 5. Energies from the the 3 higher states were omitted from the diagram.
Figure 12: Linear interpolation from the Franck-Condon geometry to the conical intersection found between the states $S_1$ and $S_2$. First a CASSCF calculation with a 6 state average with an active space consisting of all the orbitals in Figure 5 was performed. Multi state CASPT2 correction to the energies were then calculated for each point. Energies from 3 higher states were omitted from the diagram.

When looking at Figures 11 and 12, it can be seen that the CASSCF and CASPT2 corrected results for the 3 lowest states that are shown are in a reasonable agreement (at least for qualitative purposes). The most important information to extract from these diagrams are that there are no large energy obstacles to overcome when following the plot for $S_2$ which would suggest that the CI is within reach and might provide a relaxation path from $S_2$ to $S_1$. This path (although not optimized) shows an alternative to the ring-puckering relaxation path. Through this CI a relaxation path involving a ring-opening reaction might be possible, since the CI shown in Figure 10 is a ring-opened structure.
4.1.7 Summary of important numerical data

In this section are some tables with the most relevant numerical data about the final structures presented. All values presented here have been calculated with the same method, where a 6 state average CASSCF with all orbitals in Figure 4 included in the active space.

Table 2: Important bond lengths are presented in Ångström. The first column refers to Figure 5 and the second column to Figure 6 and the third to Figure 10. Internuclear distances between atoms where the bond between them has been broken (compared to $S_0$ min.) are written in parenthesis.

<table>
<thead>
<tr>
<th>Bond</th>
<th>$S_0$ min.</th>
<th>$S_2$ TS</th>
<th>$S_2$ min.</th>
<th>$S_2/S_1$ CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2-C4</td>
<td>1.184</td>
<td>1.368</td>
<td>1.324</td>
<td>1.167</td>
</tr>
<tr>
<td>O1-C1</td>
<td>1.410</td>
<td>1.431</td>
<td>1.430</td>
<td>1.389</td>
</tr>
<tr>
<td>O1-C4</td>
<td>1.389</td>
<td>1.368</td>
<td>1.367</td>
<td>(2.526)</td>
</tr>
<tr>
<td>C1-C2</td>
<td>1.501</td>
<td>1.485</td>
<td>1.493</td>
<td>1.500</td>
</tr>
<tr>
<td>C2-C3</td>
<td>1.336</td>
<td>1.486</td>
<td>1.486</td>
<td>1.383</td>
</tr>
<tr>
<td>C3-C4</td>
<td>1.473</td>
<td>1.363</td>
<td>1.366</td>
<td>1.275</td>
</tr>
</tbody>
</table>

Table 3: Comparison of relevant bond angles and dihedral angles between different optimized geometries of 2(5H)-furanone. The angle unit is degree.

<table>
<thead>
<tr>
<th>Bond</th>
<th>$S_0$ min.</th>
<th>$S_2$ TS</th>
<th>$S_2$ min.</th>
<th>$S_2/S_1$ CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1-O1-C4</td>
<td>110.20</td>
<td>108.71</td>
<td>108.42</td>
<td>-</td>
</tr>
<tr>
<td>O1-C1-C2</td>
<td>105.13</td>
<td>105.60</td>
<td>106.24</td>
<td>108.02</td>
</tr>
<tr>
<td>C1-C2-C3</td>
<td>108.85</td>
<td>106.25</td>
<td>105.19</td>
<td>119.79</td>
</tr>
<tr>
<td>C2-C3-C4</td>
<td>108.78</td>
<td>105.79</td>
<td>106.42</td>
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</tr>
<tr>
<td>O1-C4-C3</td>
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<td>113.66</td>
<td>113.50</td>
<td>-</td>
</tr>
<tr>
<td>O1-C4-O2</td>
<td>123.39</td>
<td>111.75</td>
<td>111.94</td>
<td>-</td>
</tr>
<tr>
<td>C3-C4-O2</td>
<td>129.57</td>
<td>134.59</td>
<td>134.55</td>
<td>159.88</td>
</tr>
</tbody>
</table>

<table>
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<tr>
<th>Atoms</th>
<th>$S_0$ min.</th>
<th>$S_2$ TS</th>
<th>$S_2$ min.</th>
<th>$S_2/S_1$ CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1 C1 C2 H3</td>
<td>180.00</td>
<td>-180.00</td>
<td>-151.74</td>
<td>-</td>
</tr>
<tr>
<td>O1 C4 C3 H4</td>
<td>180.00</td>
<td>-180.00</td>
<td>-175.14</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 4: Energies for the final optimized geometries. The data is presented in eV relative to the ground state energy for the geometry optimized at the ground state on the form "CASSCF energy/MS-CASPT2 energy". The calculations for all these structures used a 6 state average CASSCF with an active space containing all orbitals presented in Figure 4.

<table>
<thead>
<tr>
<th></th>
<th>( S_0 ) min.</th>
<th>( S_2 ) TS</th>
<th>( S_2 ) min.</th>
<th>( S_2/S_1 ) CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S_0 )</td>
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<td>1.54/0.93</td>
<td>1.73/1.11</td>
<td>4.00/3.30</td>
</tr>
<tr>
<td>( S_1 )</td>
<td>5.25/5.18</td>
<td>4.24/4.32</td>
<td>4.25/4.34</td>
<td>4.09/4.37</td>
</tr>
<tr>
<td>( S_2 )</td>
<td>7.52/5.88</td>
<td>6.07/4.82</td>
<td>6.03/4.75</td>
<td>4.09/4.56</td>
</tr>
</tbody>
</table>

4.2 \( \gamma \)-Valerolactone

In the following section the results regarding the molecule \( \gamma \)-Valerolactone are presented. The results from the calculations are represented both visually in the form of pictures and diagrams as well as tabulated data. These are the digested data which is to help the reader follow the discussions.

4.2.1 Active space

The choice of the active space was done according to the same principles as with the previous molecule. The orbitals used in the active space when performing CASSCF calculations on \( \gamma \)-Valerolactone are presented in Figure 13. In the figure the orbitals (a) and (c), the \( n \) orbitals, are the orbitals of the oxygen lone pairs in the plane of the ring, the orbitals (b) and (c), are the C-O \( \pi \) (as for the first molecule these orbitals are a mixture of the C4-O2 \( \pi \) and the O1 lone pair perpendicular to the plane of the ring), (e) is the C4-O2 \( \pi^* \) and the orbitals (f) and (g) are the C4-O1 \( \sigma \) and \( \sigma^* \), respectively. The orbitals are labelled and characterized by visual inspection.
When comparing the active space for the two molecules (see: Figure 4 and 13) the orbital (a) in the active space of γ-Valerolactone, showing an O1 n orbital in the plane of the molecular ring, it is seen that this orbital is not included in the active space of 2(5H)-furanone! This orbital had to be included in the active space of γ-Valerolactone for the sake of stability of the active space. However, when the corresponding orbital for 2(5H)-furanone was included in the active space the orbital would not stay in the active space. One possible reason for these deviations in behaviour of the active spaces could be that the C-C π in 2(5H)-furanone offers stability in a way that is lacking in γ-Valerolactone, hence this additional n orbital is needed for stability. It could also be that the size of the active space is simply too small without this orbital which causes instability in the active space.

Figure 13: Orbitals used in the active space in the CASSCF calculations of γ-Valerolactone.
4.2.2 Ground state geometry

A visual representation of the minimum energy optimized geometry for the ground state of $\gamma$-Valerolactone is presented in Figure 14. The first geometry optimization was done at the KS-DFT with functional B3LYP level of theory from a crude drawing of the structure which then in turn was optimized at the CASSCF level with a small basis set (ANO-RCC-MB) and no $\sigma$ orbitals included in the active space. When a stable active space had been found the basis set was expanded to a larger one (ANO-RCC-VDZP) and the active space was expanded to include all the orbitals in Figure 13. In order to have a stable active space a 5 state average had to be used in the CASSCF calculations and this was consistent with the calculations of the excited states as well.

Figure 14: The geometry of the ground state of $\gamma$-Valerolactone. The geometry optimization was performed at the CASSCF level of theory with a 5 state average calculation of the ground state and the first four excited states with all the orbitals in Figure 13 included in the active space.
4.2.3 Search for photo-excited state

This section covers the search for a transition from the ground state to a photo-excited state of γ-Valerolactone that would be likely to occur at the Franck-Condon geometry. A calculation with 10 state average CASSCF was performed with MS-CASPT2 correction to energies and the result is presented in Table 5. The lowest energy state that has a high oscillator strength for the transition is the second excited state $S_2$ which has an excitation energy of 1 eV (!) higher than the pump-laser energy used in the experiments to excite the system. Figure 5 shows that $S_2$ has about a hundred times higher oscillator strength than $S_1$, the transition to $S_2$ is the lowest energy transition with a high enough intensity to be observed experimentally. The state could probably be populated to some extent through non-vertical transitions to lower vibrational states on $S_2$.\(^1\) The excitation $S_0 \rightarrow S_2$ is a $\pi \rightarrow \pi^*$ transition which can be seen by looking at the occupations in Table 5 along with the orbitals in Figure 13.

\(^1\)Further studies should be made to test this assumption, e.g. by calculation Franck-Condon factors. It would be very interesting to investigate but it is beyond the scope of this project.
Table 5: Calculation of 10 states at the ground state geometry of γ-Valerolactone. The character of the state is indicated by the most prominent occupations(s) (electronic configurations) in the active space of the CASSCF calculation. The number "2" indicates that it is a doubly occupied orbital and "u" and "d" indicate spin up and spin down, respectively. The excitation energy is the MS-CASPT2 corrected energy and is given in terms of electron volt (eV). The oscillator strength is between $S_0$ and the specific excited state. The order of the orbitals in the active space is the same as in Figure 13, indicated by the first row.

<table>
<thead>
<tr>
<th>state</th>
<th>occupations with highest weight</th>
<th>excitation E (eV)</th>
<th>dipole osc. Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_0$</td>
<td>22220</td>
<td>0</td>
<td>-</td>
</tr>
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<td>$S_1$</td>
<td>22u2d</td>
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<td>3.78E-03</td>
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<tr>
<td>$S_2$</td>
<td>22ud</td>
<td>7.21</td>
<td>4.26E-01</td>
</tr>
<tr>
<td>$S_3$</td>
<td>u22d</td>
<td>9.08</td>
<td>7.82E-03</td>
</tr>
<tr>
<td>$S_4$</td>
<td>2u2d</td>
<td>9.44</td>
<td>1.71E-01</td>
</tr>
<tr>
<td>$S_5$</td>
<td>22022</td>
<td>13.57</td>
<td>9.01E-04</td>
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<tr>
<td>$S_6$</td>
<td>22ud2</td>
<td>13.93</td>
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<td>u2d22, u22d</td>
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<td>$S_9$</td>
<td>u22d2, u2d22</td>
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</tbody>
</table>

This excitation from $S_0$ to $S_2$ at FC geometry is of the same $\pi \rightarrow \pi^*$ (recall that it is a mixture between a C4-O2 $\pi$ and a O1 $n$ orbital) nature as for 2(5H)-furanone, except for the higher excitation energy mentioned above in this subsection. The reason for this larger energy gap could lie in the shape of the $\pi^*$ orbital (see: Figure 13 (e)), it is different from the orbital excitation happens to in 2(5H)-furanone since this is not a mix between two $\pi^*$ orbitals and does not seem to have any $\pi$-similar looking bonding action between carbons C3 and C4, as in 2(5H)-furanone. Difference in energy of this $\pi^*$ orbital could be an explanation for the very different excitation energies when comparing the two molecules. The excitation energy to $S_2$ at the FC point is 2.45 eV higher for γ-Valerolactone compared to 2(5H)-furanone when comparing the excitation energies in Figures 1 and 5. Calculations performed later with a consistent active space and state average showed a smaller difference however: 1.68 eV (comparing the MS-CASPT2 energies, first column third row in Tables 4 and 8, respectively).
4.2.4 Excited state geometries

When relaxing \( S_2 \) from the Franck-Condon point the structure obtained is an open-ring geometry. The bond between O1 and C4 (see numbering in Figure 14) breaks and the geometry converges to the minimum energy structure found in Figure 15. To allow for a good description of this bond breaking action a 5 state average CASSCF had to be used with all orbitals in Figure 13 included in the active space. Without the \( \sigma/\sigma^* \) orbitals the structure would not converge when trying to find the ring-opened minimum energy structure.

![Figure 15: Optimized minimum energy geometry for the second excited state of \( \gamma \)-Valerolactone. The calculation was performed with a 5 state average CASSCF with all the orbitals in Figure 13 included in the active space.](image)

4.2.5 Conical intersections

A conical intersection between the first and the second excited states could be found when searching from the Franck-Condon point. The geometry obtained
was an open-ring structure which showed large similarities to the minimum energy structure found on $S_2$ described in the previous section. A visual representation of this structure is presented in Figure 16.

![Figure 16: Geometry of conical intersection between first and second excited state of γ-Valerolactone.](image)

4.2.6 Summary of important numerical data

In this section, a selection of numerical data about the optimized structures calculated for γ-Valerolactone are presented in terms of bond lengths, bond angles and energies. When comparing the bond lengths and bond angles in Tables 6 and 7, for the optimized minimum energy structure at $S_2$, and the structure for the conical intersection it is seen that the bond lengths are very similar and bond angles quite similar as well. The energies in Table 8 are also similar for the two structures. This confirms what is visually seen, that the geometries are very similar indeed and that the electronic states $S_1$ and $S_2$ are very close in energy in this region on the PES near the minimum energy structure. Further calculations are needed to investigate whether the minimum energy and the conical intersection structures are accessible energetically from the FC point. However, it can be seen in Figure 8 that these structures are very low in energy compared to the the FC geometry.
Table 6: Comparison of relevant bond lengths between different optimized geometries of \(\gamma\)-Valerolactone. The bond length unit is Ångström. Internuclear distances between atoms where the bond between them has been broken (compared to \(S_0\) min.) are written in parenthesis.

<table>
<thead>
<tr>
<th>bond</th>
<th>(S_0) min.</th>
<th>(S_2) min.</th>
<th>(S_2/S_1) CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>O2-C4</td>
<td>1.187</td>
<td>1.184</td>
<td>1.186</td>
</tr>
<tr>
<td>O1-C1</td>
<td>1.431</td>
<td>1.389</td>
<td>1.389</td>
</tr>
<tr>
<td>O1-C4</td>
<td>1.369</td>
<td>(2.571)</td>
<td>(2.943)</td>
</tr>
<tr>
<td>C1-C5</td>
<td>1.514</td>
<td>1.529</td>
<td>1.528</td>
</tr>
<tr>
<td>C1-C2</td>
<td>1.533</td>
<td>1.529</td>
<td>1.535</td>
</tr>
<tr>
<td>C2-C3</td>
<td>1.524</td>
<td>1.478</td>
<td>1.471</td>
</tr>
<tr>
<td>C3-C4</td>
<td>1.523</td>
<td>1.521</td>
<td>1.523</td>
</tr>
</tbody>
</table>

Table 7: Comparison of relevant bond angles between the final optimized geometries. The bond angle unit is degree.

<table>
<thead>
<tr>
<th>Bonds</th>
<th>Bond angles</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(S_0) min.</td>
</tr>
<tr>
<td>C1-O1-C4</td>
<td>111.64</td>
</tr>
<tr>
<td>O1-C1-C2</td>
<td>105.08</td>
</tr>
<tr>
<td>O1-C1-C5</td>
<td>109.40</td>
</tr>
<tr>
<td>C2-C1-C5</td>
<td>114.79</td>
</tr>
<tr>
<td>C1-C2-C3</td>
<td>103.15</td>
</tr>
<tr>
<td>C2-C3-C4</td>
<td>103.20</td>
</tr>
<tr>
<td>O1-C4-C3</td>
<td>108.96</td>
</tr>
<tr>
<td>O1-C4-O2</td>
<td>123.30</td>
</tr>
<tr>
<td>C4-C5-O6</td>
<td>127.74</td>
</tr>
</tbody>
</table>
Table 8: Energies for the final optimized geometries. The data is presented in eV relative to the ground state energy for the geometry optimized at the ground state on the form ”CASSCF energy/MS-CASPT2 energy”. The calculations were performed with a 5 state average CASSCF with all orbitals in Figure 13 included in the active space.

<table>
<thead>
<tr>
<th></th>
<th>$S_0$ min.</th>
<th>$S_2$ min.</th>
<th>$S_2/S_1$ CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_0$</td>
<td>0.00/0.00</td>
<td>4.22/4.04</td>
<td>4.58/4.78</td>
</tr>
<tr>
<td>$S_1$</td>
<td>5.99/5.84</td>
<td>4.36/4.93</td>
<td>4.68/5.22</td>
</tr>
<tr>
<td>$S_2$</td>
<td>8.85/7.56</td>
<td>4.64/5.06</td>
<td>4.68/5.29</td>
</tr>
</tbody>
</table>
5 Conclusions

When comparing the lower energy excitations for the two molecules it could be seen that the $S_0 \rightarrow S_2$ excitation is the lowest energy transition that is intense enough to be observed experimentally for both molecules. This transition was of similar nature for both molecules, a $\pi \rightarrow \pi^*$ transition from an orbital that is a mixture of the C-O $\pi$ and the lone pair orbital perpendicular to the plane of the ring belonging to the oxygen in the ring, excited to the C-O $\pi^*$. However, in the case of 2(5H)-furanone the C-O $\pi^*$ is mixed with the C-C $\pi^*$. The mixed orbital which the excitation occurs to in 2(5H)-furanone has additional bonding properties since the wave function is in phase, causing constructive interference between two carbon atoms forming something that looks like a $\pi$ bond between these two atoms. This could be the reason for the very large difference in excitation energies (1.68 eV) between the two molecules if this makes the $\pi^*$ much lower in energy for 2(5H)-furanone. Such mixing of $\pi^*$ orbitals is of course impossible for $\gamma$-Valerolactone since there is no C-C $\pi^*$ to mix with. It could be found that 2(5H)-furanone relaxes from the Franck-Condon geometry, after photo-excitation to $S_2$, to a planar transition state geometry on $S_2$ which has two energy minima at either side of this saddle point. The two minimum geometries on $S_2$ for 2(5H)-furanone are mirror images to each other where the main structural difference are the dihedral angles involving two different hydrogen atoms. When at the saddle point, two hydrogen atoms can bend perpendicularly to the plane of the molecular ring in either direction, when relaxed from this transition state, resulting in two mirror image structures with equal energy. Another possible relaxation path for 2(5H)-furanone could be found through a conical intersection with an open ring structure. The conical intersection found is accessible in energy and a path with no energy barrier could be found from the Franck-Condon point to the conical intersection. For the relaxation after the $S_0 \rightarrow S_2$ excitation at the Franck-Condon point for $\gamma$-Valerolactone, an open-ring structure which is a minimum energy geometry at $S_2$ could be obtained. This minimum energy geometry is structurally very similar to a conical intersection found between $S_1$ and $S_2$ which suggests that this should be considered a single path. A possible reason for the different relaxation times, shown experimentally, could be that $\gamma$-Valerolactone has a smaller number of possible relaxation pathways, since the ring-puckering relaxation path might not be possible in $\gamma$-Valerolactone.
6 Acknowledgements

I would like express my honest and sincere thanks to my supervisors Morgane Vacher and Ignacio Fernández Galván for always being available, providing with expert insights and giving helpful guidance and criticism when needed. I thank Oliver Schalk for his reply to my questions about his experimental work. My thanks also goes to the research group of Roland Lindh as whole for their kindly treatment and joyful discussions about apple growing and house renovations.

References


