Ab Initio Characterization of Conical Intersections Related to Chemiluminescence in Methylated 1,2-Dioxetanes

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Abstract

During a chemiluminescent reaction, one of the products is formed in an electronically excited state. The 1,2-dioxetane is probably the smallest known molecule capable of chemiluminescence, and through a thermally activated reaction the molecule dissociates into two formaldehyde molecules, one of which is in the excited state able to emit light. This reaction starts by breaking the peroxide bond, giving rise to a relatively long-lived diradical intermediate structure where four singlet states and four triplet states are near-degenerate. The molecule is said to be “entropically trapped” in this region of the potential energy surface. It has been shown by experiment that systematically substituting the hydrogen atoms on 1,2-dioxetane with methyl groups dramatically increases the chemiluminescence yields. The current hypothesis to explain this trend is the entropic trap mechanism, because the larger number of degrees of freedom lowers the probability of escaping the diradical region. In this thesis, the state-average complete active space self-consistent field method has been used to optimize and topographically characterize seams of conical intersections in the diradical region for the un-, methylated-, and trans-dimethylated 1,2-dioxetane (0Me, 1Me, and 2Me, respectively). This was done in order to investigate whether evidence for the increase in chemiluminescence yield as a result of methylation is visible in the topography of the conical intersections, which would indicate that the entropic trap mechanism alone cannot explain the trend completely. We have found sloped conical intersections for all three molecules, which are known to be beneficial for nonadiabatic transitions from a lower electronic state to an upper electronic state, and are therefore important for chemiluminescence. Further, the region of sloped conical intersections appears to be larger for 2Me compared to 0Me and 1Me, but little or no differences were seen between 0Me and 1Me. In order to confirm if there is a trend in the topography of the conical intersections, we need to extend the present study to tri- and tetramethylated 1,2-dioxetane.
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List of Abbreviations

0Me 1,2-dioxetane
1Me Methylated 1,2-dioxetane
2Me Trans-dimethylated 1,2-Dioxetane
3Me Trimethylated 1,2-dioxetane
4Me Tetramethylated 1,2-dioxetane
acCD Atomic Compact Cholesky Decomposition
ANO-RCC Atomic Natural Orbital Relativistic Correlation Consistent
CASSCF Complete Active Space Self-Consistent Field
CI Conical Intersection
HF Hartree-Fock
MEP Minimum-Energy Path
MO Molecular Orbital
PES Potential Energy Surface
RMSD Root-Mean-Square Deviation
SA-CASSCF State-Average Complete Active Space Self-Consistent Field
TS Transition State Structure
1 Popular Science Summary

Forests, the sea, crime scenes, and rave parties — what do these places have in common? They are all places where you can find things that glow on their own. In some forests you can see swarms of fireflies, glowing yellow in the dark, or fungi glowing in green. A lot of things glow in the sea, for instance algae, jellyfish, and the lure of a deep-sea anglerfish. At crime scenes they look for blood with luminol, and at rave parties everyone wears glow sticks. All of these are examples of chemical reactions that are able to produce light. Not all chemical reactions can produce light, and we call those that can “chemiluminescent reactions”. If they take place inside of living organisms, it is common to call them bioluminescent reactions.

We know today that almost all molecules capable of producing light have a single-bond between two oxygen atoms, O–O, called a peroxide bond. This bond is not very stable, so it tends to break after not too long. When the peroxide bond breaks, interesting things start to happen to the molecule. Molecules exist in different states, and we can think of these states as the floors in a house. Each floor is separated by some height from the adjacent floors. When you move around on the ground floor, imagine that the distance to the first floor varies. There are some very special points in the house where you can be at the ground floor and the first floor at the same time. At these points you need to make a choice: continue on the ground floor or switch to the first floor. If you continue to move on the first floor, eventually the floors will start to separate again — you have now gained some potential energy! To get rid of this extra energy, you could perhaps look for a hole in the floor and jump back down to the ground floor.

This is a picture of what happens in the molecule after the peroxide bond breaks. The states come close in energy, and at some points two states have exactly the same energy. Molecules normally like to be in the lowest-energy state, but when it can choose to be in a higher-energy state at no extra cost, then sometimes the molecule will choose this higher state. The states start to separate in energy once the molecule changes its structure from the crossing point structure, and after a while the molecule jumps back down to the ground state. In the process of jumping down, the excess energy is released in the form of light.

One of the smallest molecules we know that is able to produce light is called 1,2-dioxetane. Researchers more than 30 years ago measured the amount of light that is emitted from different versions of 1,2-dioxetane, and they observed that adding so-called methyl groups, –CH₃, to the molecule steadily increased the amount of light coming out. These methyl groups clearly affect the molecule in a way that makes it a better light producer, but we still do not know exactly what goes on. We call the special points mentioned above “conical intersections”, due to the way they appear when we graphically visualize them. We suspect that the shape of these conical intersections affects the amount of light that comes out of the chemiluminescent reaction. However, no one has yet published research on the shapes of conical intersections for 1,2-dioxetane and methylated versions of 1,2-dioxetane, so we do not know what they look like.
In this project, I have characterized the shape of conical intersections that are thought to be important for the chemiluminescence to occur. I have done this for 1,2-dioxetane with none, one, and two methyl groups, and found that there may be a trend in how the conical intersection shape changes as methyl groups are added to the molecule, and that this change should be beneficial for light production. To be sure that the trend exists, we should also look at the conical intersection shapes for 1,2-dioxetane molecules with three and four methyl groups.

2 Introduction

2.1 Chemiluminescence and Thermal Decomposition of 1,2-Dioxetane

Humans have for a long time been fascinated by living organisms that produce light on their own [1]. Chemical reactions that produce light belong to a special subset of all the reactions taking place on Earth, during which a product molecule is formed in an electronically excited state. This phenomenon is called chemiluminescence, or bioluminescence if taking place inside living organisms, and can be thought of as a reversed photochemical reaction [2]. In a photochemical reaction the absorption of light leads to a chemical reaction, whereas for chemiluminescence a chemical reaction leads to the emission of light.

Luminescent reactions occur frequently in Nature, most often exemplified by the luciferin-luciferase complex in the firefly beetle. Here, luciferase catalyzes the oxidation of D-luciferins to oxyluciferins, some of which are formed in an electronically excited state [3]. The last step of this reaction is the key, where a peroxide bond (O–O) is broken. The peroxide bond is present in almost all known chemiluminescent systems [3], and provides a route from the ground state into electronically excited states.

The 1,2-dioxetane is likely the smallest molecule representative of the firefly system that is capable of chemiluminescence. This four-membered ring exhibits the peroxide bond, and its small size makes it a good candidate for high-level quantum chemical calculations. The 1,2-dioxetane undergoes a thermally activated fragmentation reaction into two formaldehyde molecules. Some of these fragmentation products are formed in the excited state, and then relax to the ground state by emitting light, which is schematically shown in Figure 1.

The chemiluminescence mechanism in 1,2-dioxetane has been studied both experimentally [4] and theoretically [2, 5–9], and today it is understood that the molecule dissociates in a two-step process. The reaction starts with breaking the peroxide bond as the C1C2 bond rotates, which leads to a transition state structure (TS) connecting the reactant with a relatively long-lived diradical intermediate. The activation energy for crossing the barrier has been shown experimentally [4] and theoretically [6] to be approximately 22 kcal/mol. Ballistic behavior of the molecule maintains the C1C2 rotation for some time [6], before dissociation starts by a change in the reaction coordinate to a C1C2 stretch and planarization of the CH2O fragments.

However, some of the fragmentation products are formed in the excited state, which means that crossings to electronically excited states take place during the reaction. A complete picture of what
happens does not exist yet, but one of the key features is how breaking the $O_1O_2$ bond affects the potential energy surface (PES). When the peroxide bond is broken, the bonding and anti-bonding $\sigma$ orbitals are transformed into two p-type lone-pair orbitals, as is typical for homolytic $\sigma$ bond ruptures [10]. Initially (in the reactant geometry) the bonding and anti-bonding orbitals have electron occupations of 2 and 0, respectively, but after the TS, the two electrons distribute into the new lone-pairs with one electron in each. This is the origin of the diradical intermediate species. Due to the two other p-type oxygen lone-pair orbitals perpendicular to the four-membered ring, we now have six electrons in four different p-type lone-pairs on the oxygen atoms. Under the constraints to maintain the diradical character of the electronic configuration, we end up with four possible singlet states and four corresponding triplet states, all of which should be near-degenerate. With eight near-degenerate states, nonadiabatic transitions (internal conversion or intersystem crossing) are expected to occur, both from the ground state to excited states and among the excited states. The breaking of the peroxide bond and formation of a diradical species thus sets the stage for chemiluminescence in 1,2-dioxetane.

It was stated above, without explanation, that the diradical species is relatively long-lived. This is important, as a longer diradical lifetime will increase the probability for nonadiabatic transitions to excited states to occur before the molecule dissociates on the ground state surface. To explain this long diradical lifetime, it is said that 1,2-dioxetane is entropically trapped [2, 3, 5, 6]. The term “entropic trap” is used to describe a special feature of the PES where the molecule is bound in all except for a few degrees of freedom, and is unbound (or very weakly bound) in the remaining degrees of freedom. If the populated vibrational states involve the bound degrees of freedom, then the molecule is entropically trapped [11]. It is not energetically trapped, because one or more reaction paths exist with no or low barriers along which the molecule can escape the trap; it is instead entropically trapped due to the much larger number of degrees of freedom preventing the molecule from escaping. For the 1,2-dioxetane, the path out of the entropic trap is breaking the $C_1C_2$ bond; however, as the populated vibrational modes after reaching the $O_1O_2$ bond-breaking TS is dominated by a $C_1C_2$ rotation, the molecule will tend to stay in this mode for a prolonged duration of time due to ballistic behavior [6]. In this way the molecule
is trapped in the diradical region by two different mechanisms: i) staying in the $C_1C_2$ rotation after the $O_1O_2$ bond has been broken, and ii) nonadiabatic transitions to excited states due to the near-degeneracy of the singlet and triplet diradical states, as explained below.

The mechanism of the entropic trap has been investigated by Vacher et al. [2] by means of ground state and nonadiabatic molecular dynamics simulations of the thermal decomposition of unmethylated 1,2-dioxetane. Ground state dynamics isolates entropic trap effects by neglecting nonadiabatic transitions due to the near-degeneracy. The ground state dynamics show that dissociation on the ground state occurs between 30 fs and 140 fs, and that certain geometrical criteria need to be fulfilled for dissociation to occur under the conditions used. So-called “frustrated dissociations”, or “attempted dissociations”, take place for some of the trajectories, during which the $C_1C_2$ bond length increases as if the molecule dissociates, but then reaches a maximum and decreases until a minimum is reached. We can therefore imagine that the molecule has to “wait” until the molecular geometry allows the dissociation to take place.

By allowing nonadiabatic transitions to excited states during the trajectories, the near-degeneracy effect was included. The results show that dissociation now occurred between 30 fs and 250 fs, significantly delaying the dissociation. The increase in delay is attributed to time spent in excited states because of nonadiabatic transitions from the ground state to excited states. This provides additional means of trapping the molecule in the diradical region. No dissociations on excited state surfaces took place, so any state populated, other than the ground state, delayed the ground state dissociation. This observation agrees with experimental results, which show that the singlet chemiluminescence yield is very low (see next paragraph).

Chemiluminescence in 1,2-dioxetane originates from both the $S_1$ (fluorescence) and $T_1$ (phosphorescence) states. Adam et al. [4] experimentally determined the triplet excitation yield to be approximately 1000 times higher than the singlet excitation yield for 1,2-dioxetane. The higher triplet excitation yield for 1,2-dioxetane has, from theoretical calculations, been attributed to a lower $C_1C_2$ dissociation barrier on the $T_1$ surface compared to on the $S_1$ surface [5].

Interestingly, Adam et al. also observed a steady increase in both triplet and singlet excitation yields by substituting the hydrogen atoms with methyl groups: the triplet and singlet excitation yields increased by a factor of approximately 150 and 800, respectively, going from unmethylated (0Me) to tetra-methylated (4Me) 1,2-dioxetane. The authors explained this trend in the context of a merged reaction mechanism in which the peroxide bond and $C_1C_2$ bond are broken simultaneously; however, the accepted view today is that the thermal decomposition of 0Me is a stepwise process with a diradical intermediate [3]. The validity of their discussion is therefore questionable.

So far, no systematic theoretical study has been undertaken to explain why adding methyl groups to 0Me increases the chemiluminescence yield. However, De Vico et al. [6] claimed that the entropic trap mechanism alone is able to explain the methylation trend. They argued that by increasing the number of degrees of freedom, i.e. increasing the size of the molecule, it will become harder for the molecule to escape the trap. By adding methyl groups to 0Me, we are likely not providing new routes out of the
entropic trap region (the diradical region), since the additional C-H bonds do not affect the diradical character of the molecule. Therefore, the ratio of degrees of freedom that trap the molecule to degrees of freedom that provide an escape route \( R \) increases when adding methyl groups to \( 0 \text{Me} \):

\[
R^{4 \text{Me}} > R^{3 \text{Me}} > R^{2 \text{Me}} > R^{1 \text{Me}} > R^{0 \text{Me}}
\]

The probability of redistributing the vibrational energy into the escape modes becomes lower for each methyl group we add to \( 0 \text{Me} \), which will delay the ground state dissociation, which in turn will lead to a higher number of nonadiabatic transitions to excited states due to the increased diradical lifetime. This is the hypothesis, at least, but it has not yet been tested for 1,2-dioxetanes.

### 2.2 Conical Intersections and Their Importance

Conical intersections (CIs) have become one of the cornerstone concepts in photochemical reactions, and much research has been devoted to how CIs affect chemical dynamics [12]. Briefly, a CI can be understood as an intersection of two PES’s of same spin multiplicity (more details about their definition is given in the Theoretical Methods section). It is well known in photochemistry that CIs are critical to understand nonadiabatic transitions from an upper state to lower state [10]. In these cases the CIs act as “funnels”, guiding the molecule from the excited state to the ground state at the timescale of femtoseconds. A good example of such a process is the ultrafast nonadiabatic relaxation observed when DNA is irradiated by UV light; DNA converts the vast majority of all UV photons that are absorbed by the molecule into heat. This property has been attributed to CIs, which act as funnels, guiding the wave packet from the excited state to the ground state [13]. Indeed, this property is vital to most life forms, as otherwise the organism would experience far too much UV radiation damage to be repaired.

However, it is perhaps less known that certain CIs facilitate transitions from the ground state to an excited state [14–16], i.e. the complete opposite process facilitated by “funnels”. The particular CI topography dictates whether the CI is an effective funnel or “opposite” funnel — or a “dumper” or “pumper”, respectively, as Yarkony [15] explained it. The appropriate topography may either “dump” wave packets from excited states to ground states with high efficiency, or “pump” wave packets from the ground state to the excited state. Wave packet dynamics have shown that the shape of the PES on the excited state at a CI greatly affects the fate of the wave packets [15]. Once the transition has taken place, then the CI topography is crucial for a wave packet’s fate. Malhado et al. [17] have shown that the probability for a nonadiabatic transition does not depend on whether the CI is peaked or sloped (see next section for definition), but what happens after depends on the topography. A proper understanding of CIs is therefore important to understand the mechanism of chemiluminescence, and possibly for explaining the observed trends in increased chemiluminescence yield for methylated 1,2-dioxetanes.
2.3 Aim of Thesis

No systematic theoretical study has yet been published to explain the effect methylation has on the chemiluminescence of 1,2-dioxetanes. The aim for this thesis has been to locate, optimize, and topographically characterize CIs that are relevant to the thermal decomposition reaction for different methylated 1,2-dioxetanes: unmethylated, methylated (1Me), and \textit{trans}-dimethylated (2Me). The goal has been to investigate whether methylation manifests itself in the topography of CIs. The results of these “static” calculations will be interpreted in conjunction with the results from dynamics studies carried out at the Theoretical Chemistry group at Uppsala University [2]. Some questions this study aims to answer: Does adding methyl groups to 0Me affect the CI topographies? If so, can the change in topography help to explain the methylation effect, and provide insight to the fundamental understanding of chemiluminescence? Or, perhaps methylation has no significant effect on the CI topography, and the observed increase in chemiluminescence can be fully attributed to the entropic trap mechanism?

3 Theoretical Methods

3.1 Multi-Configurational Self-Consistent Field

Whenever we are to model a chemical reaction theoretically, we need to ask ourselves what kind of electronic structure method we need. This is important, because the wrong method will fail to describe the system properly, sometimes even at a qualitative level. A wide range of different \textit{ab initio} methods exist to choose from, and they all provide wave functions with different qualities. The simplest useful \textit{ab initio} method for molecules is perhaps the Hartree-Fock (HF) method, in which the wave function is described as a single Slater determinant, which is an antisymmetrized product of spin orbitals. Because only one electron configuration is used to describe the wave function, HF theory is sometimes called a single-configurational method, or a single-reference method.

When dealing with molecules or non-periodic systems, we usually make linear combinations of one-electron wave functions, called basis functions, to describe the molecular orbitals (MOs). The more basis functions we use, the more accurate the MO expansion becomes, but at the cost of being computationally more expensive. Formally we should use an infinite number of basis functions in order to introduce no approximation in our description of the MOs, but this is, of course, impossible in practice. We must therefore resort to a finite set of basis functions, referred to as the basis set. Basis functions could in principle be any square integrable mathematical function, but most often Gaussian functions are used because computing two-electron integrals then becomes very efficient. In HF theory, we minimize the total energy with respect to varying the coefficients used in the MO expansion, and in that way find the best single-configuration wave function.

Naturally, the approximation of using only a single Slater determinant puts restrictions on the HF method’s applicability. For example, it turns out that the instantaneous Coulombic repulsion that each
electron feels due to all other electrons is described only in an average manner. Hence, the so-called
dynamical electron correlation is not accurately described. For example, this shortcoming means that HF
by its formulation is not able to reproduce the weak attractive forces between two argon (Ar) atoms,
because this attractive force is purely due to the correlated movement of their respective electron clouds.
So-called post-HF methods attempt to recover the dynamical electron correlation, examples of which are
Møller-Plesset perturbation theory, configuration interaction, and coupled-cluster theory.

However, it is not the lack of dynamical electron correlation that is the main issue when using
these methods to study chemiluminescence. The use of a single Slater determinant introduces another
shortcoming to the wave function. While the wave function of many molecules in their ground state at
equilibrium geometry can be qualitatively described by a single-configuration HF wave function, this is
not the case in all situations. The 1,2-dioxetane is a prime example. As we have seen in the previous
sections, breaking the peroxide bond in 1,2-dioxetane leads to a near-degeneracy of four singlet states and
four triplet states. For the wave function to even qualitatively describe such a system, we need to take
into account the near-degenerate excited states in addition to the ground state; the wave function needs
to have a multi-reference character. This means that more than one electron configuration contributes
significantly to the description of the system.

To describe the diradical 1,2-dioxetane, we need a wave function that is a linear combination of
configurations, where several configurations have large coefficients; in other words, the wave function is
not dominated by a single configuration. Several methods have been developed that attempt to achieve
this, but the complete active space self-consistent field (CASSCF) method [18, 19] is perhaps the most
popular one. In CASSCF we select a subset of orbitals that we think are involved in the chemical process
we want to study, and allow all possible configurations within this subset of orbitals. These orbitals are
called the active space, and should be a mixture of occupied and virtual orbitals. The wave function is
constructed by making linear combinations of all possible configurations by exciting the electrons from
occupied active space orbitals to virtual active space orbitals, using the HF wave function as a reference.
In other words, we perform a full configuration interaction within the active space. The inactive occupied
orbitals are always doubly occupied, and the inactive virtual orbitals are always unoccupied. We optimize
the configuration expansion coefficients simultaneously as optimizing the MO expansion coefficients. First
we guess the MO coefficients, and minimize the energy by keeping the guess MO coefficients fixed and
varying the configuration coefficients until the energy is stationary (to within a threshold value). We
then vary the MO coefficients (“rotate the orbitals”), and re-optimize the configuration coefficients. This
procedure is repeated until the energy is stationary with respect to both the configuration and MO
coefficients.

The philosophy of CASSCF is to realize that many of the configurations in the full configuration
interaction wave function have very small coefficients; that is, they contribute very little to the wave
function. By selecting the MOs that are the most relevant for the process we want to study, and performing
a full configuration interaction within this subset or MOs, we try to eliminate the irrelevant configurations
from the full configuration interaction wave function. In this way we attempt to capture the important chemistry in our system, but by using far fewer configurations in our wave function. When done correctly, the result is a wave function that is qualitatively correct, but not quantitatively correct.

The energy minimization in CASSCF is done with respect to the ground state energy (in principle the minimization could be done for any state, but we most often want to minimize the energy for the ground state). However, it is possible to do the minimization with respect to the average energy of a pre-selected number of states of the same multiplicity. This is referred to as state-average CASSCF (SA-CASSCF). For example, we can average over the near-degenerate states in the diradical 1,2-dioxetane in order to get a balanced description of the important states.

CASSCF and SA-CASSCF are not so-called “black-box” methods, because specific demands are put on the user in order to get any meaningful results. The active space needs to be properly chosen, and this can in some cases be very difficult. An intuitive rule is that the active space should include the MOs for which the occupation number changes during the reaction under investigation. This makes sense, because if the MO occupation is constant at 2 or 0 for the entire region of the explored PES, then clearly these MOs do not participate in the changes of the molecule. An example could perhaps be the bonding and anti-bonding orbitals for a C-H bond far away from the functional group in an organic molecule. Valence electrons are likely to be the most important, and the MOs around the HOMO-LUMO gap are good candidates for active orbitals. For more information about how to choose the active space, the reader is referred to Veryazov et al. [20], and for more information in general about the multi-configurational self-consistent field method, see Roos et al. [21]

We therefore conclude that to study chemiluminescent reactions, which by nature involve near-degenerate electronic states, we need to use a multi-reference wave function method. The most common method is perhaps the CASSCF method, which has multi-reference capabilities due to the MO coefficients being optimized for each configuration in the wave function. However, this is not a black-box method, because significant chemical insight into the process under investigation is necessary in order to get meaningful results.

### 3.2 Conical Intersection Characterization

When two PES’ become degenerate, and the degeneracy is lifted linearly in two independent dimensions, the point of intersection is referred to as a conical intersection [12]. These two internal degrees of freedom which break the state degeneracies are called the branching space, or branching plane. The remaining $N - 2$ internal degrees of freedom maintain the degeneracy, and are called the intersection space. Conical intersections are not single points, but form a continuous space of $N - 2$ dimensions in which the PES’ are degenerate. The dimension of the intersection space increases rapidly with the size of the molecule, and may contain many local minima.

Recently, analytical SA-CASSCF nonadiabatic coupling vectors were implemented in the Molcas quantum chemistry program [22], allowing CI geometries to be efficiently optimized by means of constrained
optimizations. Nonadiabatic coupling vectors are neglected in the Born-Oppenheimer approximation, but are important in optimization of the CIs (more about this in Section 4.2). In Fdez. Galván et al. [22], the energies of the two crossing states in the immediate vicinity of the intersection point are approximated to first order by knowing three vectors: the gradients of the crossing PES’ and the nonadiabatic coupling. More information about this linear model can be found in the literature [12, 14, 16, 22]. The validity of this model is restricted to the immediate vicinity of the crossing point, and the size of this validity region will be different for each particular CI [22], depending on the curvature of the PES.

The linear model gives the following expression for the state energies (in polar coordinates) [22]:

\[ E^A(r, \theta), E^B(r, \theta) = E^x + \delta_{gh} r \left( \sigma \cos(\theta - \theta_s) \pm \sqrt{1 + \Delta_{gh} \cos 2\theta} \right) \]

where

- \( E^A \) is the energy of the upper surface
- \( E^B \) is the energy of the lower surface
- \( E^x \) is the energy at the intersection point
- \( \delta_{gh} \) is the “pitch” parameter of the CI
- \( \sigma \) is the “relative tilt” parameter of the CI
- \( \Delta_{gh} \) is the “asymmetry” parameter of the CI
- \( \theta_s \) is the “tilt heading” parameter of the CI
- \( \theta \) and \( r \) define the polar coordinates in the branching plane

From this expression, three parameters define the topography of the CI: the asymmetry, relative tilt, and tilt heading. A fourth parameter, the pitch, affects the energy scale of the CI, but not the topography itself (as is clear from the equation). The CI itself is perhaps most easily visualized by plotting the energy as a function of the branching space in Cartesian coordinates. However, we can get all necessary information to characterize the CI by just plotting the gradient of one of the surfaces at fixed \( r \) as a function of the polar angle \( \theta \).

From the combinations of the parameters defining the topography, four categories of CIs can be identified: i) peaked and single-path, ii) peaked and bifurcating, iii) sloped and single-path, and iv) sloped and bifurcating. The CI is classified as “peaked” if the crossing point on the lower surface is a maximum, or equivalently if the crossing point on the upper surface is a minimum. This is quickly seen by checking if the gradient of either curve does not cross the zero-line. If they do cross the zero-line, then the CI is said to be “sloped”. The CI is classified as “single-path” if the gradient plot only has one minimum. If two minima are present, it is called bifurcating. Examples for each of the CI topographies are given in Figure 2, showing both the CI plot and the gradient plot.

Atchity et al. [14] were the first to provide a quantitative description of the topography of PES’ in the immediate vicinity of CIs. They derived an alternative way of classifying CI topographies, and formulated two conditions for whether a CI is peaked/sloped or single-path/bifurcating. These conditions have been
4. Computational details

4.1 Electronic Structure

In this work we want to explore different regions of the PES that require near-degeneracies to be handled in a balanced fashion. In addition, we need to be able to describe bond-breaking. Therefore, all calculations translated into the current notation by Fdez. Galván et al. [22], and are expressed as (assuming $\Delta_{gh} \geq 0$)

$$P = \frac{\sigma^2}{1 - \Delta_{gh}^2} (1 - \Delta_{gh} \cos 2\theta_s) \tag{3}$$

$$B = \left(\frac{\sigma}{2\Delta_{gh}}\right)^{2/3} \left[\left((1 + \Delta_{gh}) \cos^2 \theta_s\right)^{1/3} + \left((1 - \Delta_{gh}) \sin^2 \theta_s\right)^{1/3}\right] \tag{4}$$

If $P < 1$ the CI is peaked, and if $P > 1$ it is sloped. If $B > 1$ the CI is single-path, and if $B < 1$ it is bifurcating.

**Figure 2.** Examples of the four categories of CI topographies, along with the corresponding gradient vs $\theta$ plot. The red traces in the CI plot represent the gradient plots. The CI is peaked if the intersection point is a minimum on the upper surface, otherwise it is sloped. The CI is single-path if only one minimum exists on each surface in the gradient plots; if two minima exist it is bifurcating. The directions of minimum gradient on the upper surface are shown as a blue circle in the gradient plots (see next section for details about their computation).
have been performed with the SA-CASSCF method [18, 19], state-averaged with equal weights over the four lowest singlet states. No symmetry constraints have been imposed on the calculations. The relativistic atomic natural orbital (ANO-RCC) basis set [23] contracted to C,O[4s3p2d1f]/H[3s2p1d] (triple-ζ-with-polarization) was used in all calculations. To be comparable with previous work [5, 6], the following active space of 12 electrons in 10 orbitals was chosen: $\sigma(C_1C_2)$, $\sigma^*(C_1C_2)$, $\sigma(C_1O_1)$, $\sigma^*(C_1O_1)$, $\sigma(C_2O_2)$, $\sigma^*(C_2O_2)$, $\sigma(O_1O_2)$, $\sigma^*(O_1O_2)$, n(O$_1$), and n(O$_2$). The active space orbitals are shown for 0Me in Figure 3. Two-electron integrals were approximated using the atomic compact Cholesky decomposition (acCD) method [24].

The motivation for the above active space is the following. The O$_1$O$_2$ and C$_1$C$_2$ bonds break during the chemiluminescence reaction, so both their bonding and antibonding orbitals should be included in the active space. Further, the lone-pairs originating from the peroxide bond breaking are crucial due to the near-degeneracies that occur. The lone-pairs perpendicular to the four-membered ring also participate in the near-degeneracy, and are therefore also important to get a complete and balanced description of the system. The remaining four orbitals, the bonding and antibonding CO orbitals, are perhaps not needed for the present study, since we do not intend on leaving the diradical region. If we were to model the dissociation, then the CO orbitals might be important, as the nature of the CO bond changes from $\sigma$ character to $\pi$ character, and their occupations may change slightly. The same argument holds for the C$_1$C$_2$ orbitals: since we do not model the dissociation, we could perhaps save computational cost by leaving these orbitals out. However, by changing the active space, our calculations will no longer be directly comparable with previous (and future) work that included the CO and C$_1$C$_2$ orbitals in the active space, and for that reason we decided to include them here.

All calculations have been performed with the Molcas 8 quantum chemistry program suite [25].

4.2 Conical Intersection Optimization

Conical intersections are optimized by doing constrained searches for energy minima. As mentioned in the previous section, the degeneracy of the two intersecting states is maintained in $N - 2$ dimensions, called the intersection space. Minimum-energy CIs correspond to “valleys” in this space [22]. For the remainder of this report, the term “seam” will refer to valleys of minimum-energy CIs. The nonadiabatic coupling vectors are neglected in the Born-Oppenheimer approximation, which is invoked for the majority of quantum chemical calculations. However, this quantity is important in the location of CIs. The nonadiabatic coupling vector is always perpendicular to the polar radius $r$ of the branching space; hence, by having the constraint that we move on the PES in directions perpendicular to the nonadiabatic coupling vector, we are certain that we are either moving directly toward a CI or directly away from a CI. To decide in what direction the optimization should head, we make use of the difference of the gradients of the two surfaces; the direction which lowers the absolute value of the difference gradient leads toward the CI. The magnitude of the difference gradient vector also contains information about “how far” we are from an intersection point, and therefore aids in choosing appropriate step sizes during the optimization.
The finding of a CI and the finding of a local minimum in the seam are performed simultaneously. More details about the procedure can be found in [22]. The projected constrained optimization technique has been used for the constrained optimizations. This method is able to handle an arbitrary number of geometrical and non-geometrical constraints, and is described in detail in De Vico et al. [26].

It is important to find CIs that are relevant to the thermal decomposition. The purely static approach is to compute minimum energy paths (MEPs) in the diradical region, and try to find CIs close in energy and geometry to the MEPs, as has been done in Vacher et al. [2]. A better approach is perhaps to make use of MD simulations of the thermal decomposition reaction, and find CIs close in energy and geometry to a trajectory exploring the diradical region of the PES, in which CIs are known to exist. It is this approach, using a MD trajectory as a reference, that has been used in the present work. Specifically, for 0Me, the unsampled trajectory from Vacher et al. [2] has been used as a reference. For 1Me and 2Me, currently unpublished trajectories from the same research group have been used.

These trajectories have been used in the following way. Conical intersections have been optimized in the $N - 3$-dimensional subspace orthogonal to the velocity vector at a number of points along the trajectory, similar to what was done by De Vico et al. [27]. Two main variants of this approach have been used in the present work: i) using the trajectory geometry as a starting geometry for the CI optimization, and building the orbitals from scratch at this geometry, and ii) using a previously optimized CI geometry and orbitals as starting geometry and orbitals for the “next” CI optimization. These approaches are illustrated in Figure 4. For the latter approach, one could attempt to follow any previously optimized CI. For example, one could first find one seam by starting all CI optimizations from the reference trajectory points. This seam is not guaranteed to be continuous, and one or more discontinuities might be present.
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Figure 4. The three approaches used for finding CI seams in the subspace spanned by those degrees of freedom orthogonal to the velocity at a particular point along the trajectories used. The blue curve represents a trajectory, the pink curves represent a CI seam, and the yellow planes represent the subspace orthogonal to the velocity at each point along the trajectory. For generality, each seam is different. (a) shows an approach where each CI optimization is started at a trajectory geometry, and the orbitals are built from scratch, (b) the previously optimized CI geometry and orbitals were “reused” for the next optimization, and (c) is in principle the same as (b), but a different starting point was used.

Then, one could decide to follow a specific region of the optimized seam, by attempting to “fill in” the missing part of the discontinuous fragments of the seam. Whenever a seam was “followed”, the starting geometry and orbitals always belonged to a seam obtained by starting each CI optimization from the reference trajectory.

The reference velocity vectors, $v$, used in the constraint described above at each point $i$ were calculated from the geometries, $x$, and times $t$ from

$$ v_i = \frac{x_i - x_{i-1}}{t_i - t_{i-1}} $$

(5)

Note that it is the direction of the vector that is needed to invoke the correct constraint; the magnitude is irrelevant. It would therefore be sufficient to just compute the difference coordinate vector, and not divide by the time.

4.3 Conical Intersection Analysis

To analyze whether two different CIs involved crossings of states with the same electronic character, state overlap calculations were performed. In principle, such calculations should evaluate the standard overlap integral of two normalized wave functions $\phi_i$ and $\phi_j$ over all space for all particles, collected in $q$, with the overlap given by $S_{ij}$

$$ S_{ij} = \int_{-\infty}^{\infty} \phi_i^* \phi_j dq $$

(6)

An approximation has been used in the present work: The basis functions used to expand the MOs for one wave function were also used to describe the MOs in the second wave function. This would be no
approximation if the two wave functions belonged to molecules with exactly the same geometry; however, state overlaps have been computed for states in different nuclear geometries. This error is small if the geometrical differences between the molecules are small, which is the case for all computations performed in this work, and the overlap calculations are only used as a qualitative measure.

In addition, the minimum gradient on the upper surface of the CI has been calculated. We do this by taking the derivative of Equation (2) with respect to the polar angle $\theta$ and setting this to zero, thereby finding the direction in which the gradient has a minimum:

$$\frac{\partial E^A}{\partial \theta} = -\sigma \sin(\theta - \theta_s) - \frac{\Delta_{gh} \sin 2\theta}{(1 + \Delta_{gh} \cos 2\theta)^{1/2}} = 0 \quad (7)$$

From here we use trigonometric identities to make sure all arguments of all trigonometric functions involving $\theta$ be $2\theta$

$$[1 - \cos(2\theta) \cos(2\theta_s) - \sin(2\theta) \sin(2\theta_s)] [1 + \Delta_{gh} \cos 2\theta] = \frac{2\Delta_{gh}^2}{\sigma^2} [1 - \cos^2 2\theta] \quad (8)$$

We make the following substitutions to simplify the equation,

$$\alpha = \cos 2\theta_s \quad (9)$$
$$\beta = \sin 2\theta_s \quad (10)$$
$$\gamma = \frac{2\Delta_{gh}^2}{\sigma^2} \quad (11)$$
$$x = \cos 2\theta \quad (12)$$
$$y = \sin 2\theta \Rightarrow y^2 = 1 - x^2 \quad (13)$$

then expand the parentheses and factorize with respect to $y$, square everything to omit $y$, collect the different powers of $x$, and solve the resulting fourth-degree polynomial equation with respect to $x$

$$x^4 (\beta \Delta_{gh}^2 - \gamma^2 - \alpha^2 \Delta_{gh}^2 + 2\alpha \Delta_{gh} \gamma) +$$
$$x^3 (2\alpha \gamma - 2\Delta_{gh} \gamma - 2\alpha \Delta_{gh} + 2\alpha \Delta_{gh}^2 - 2\beta \Delta_{gh}) +$$
$$x^2 (2\gamma^2 - 2\alpha \Delta_{gh} \gamma - 2\gamma - \alpha^2 + 4\alpha \Delta_{gh} + \beta^2 \Delta_{gh}^2 - \beta^2 - \Delta_{gh}^2) +$$
$$x (2\Delta_{gh} \gamma - 2\alpha \gamma + 2\alpha + 2\beta \Delta_{gh} - 2\Delta_{gh}) +$$
$$(\beta^2 - \gamma^2 + 2\gamma - 1) \quad (14)$$

$$= 0$$

This quartic equation can be solved analytically [28], but has in this work been solved numerically. Although this polynomial may have up to four roots, we will have even more solutions that satisfy Equation (7), because we are at two occasions squaring the expression: once to omit the square root in the denominator in Equation (7), and once to get rid of $y$. 

By solving the quartic equation we actually solve for $x = \cos 2\theta$, so we need to rearrange for $\theta$

$$\theta = n\pi \pm \frac{\cos^{-1} x}{2}, n \in \mathbb{Z} \quad (15)$$

By restricting $n$ to only 0, 1, and 2, we make sure to only obtain solutions on the interval $[0, \pm 2\pi]$. Once we have collected all possible solutions to Equation (15), we substitute $\theta$ back into Equation (2) to obtain the minimum energies; dividing by $r$ gives units of a gradient. The solutions we are interested in, i.e. the minima of the upper surface in the gradient plots, can be found by searching for solutions satisfying (to some threshold)

$$\frac{\partial E^A}{\partial \theta} = 0 \quad (16)$$
$$\frac{\partial^2 E^A}{\partial \theta^2} > 0 \quad (17)$$

5 Results

Seams of CIs have been located for 0Me, 1Me, and 2Me. In this section the results will be presented separately for the three molecules.

Energetic and geometrical parameters for the located seams are presented in Figures 7, 9 and 11. These figures show six plots: a) the absolute energy of the CIs, b) the energy difference between each CI with its respective reference point along the trajectory, c) the minimum gradient on the upper surface for each CI, d) the root-mean-square deviation (RMSD) of the CI geometries with their respective trajectory reference (aligned to minimize the RMSD value), e) the C$_1$C$_2$ bond length for each CI structure, and f) the OCC angles for each CI structure. The $x$-axis in each plot is the O$_1$C$_1$C$_2$O$_2$ dihedral angle for each reference trajectory geometry, rather than time. The reason for this is to make easier comparisons to Figure 11a in Vacher et al. [2], which is reproduced in the present report as Figure 5. The O$_1$C$_1$C$_2$O$_2$ evolution during the reference trajectories is given Figure 6. Adding more methyl groups leads to a slower C$_1$C$_2$ rotation, which can be understood in terms of the increased mass of the rotating fragments.
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Figure 5. This figure is reproduced from Vacher et al. [2]. They have done surface hopping molecular dynamics studies of 1,2-dioxetane in the diradical region of the PES. They calculated the total time spent in excited states after a hop from the ground state took place. The time is defined as the time it took from the trajectory did the initial hop until it hopped back down to the ground state, regardless of whether it hopped up to higher excited states in-between. The time spent in excited states was then plotted against the O$_1$C$_1$C$_2$O$_2$ dihedral angle at which the initial hop took place.

Figure 6. The O$_1$C$_1$C$_2$O$_2$ evolution during the reference trajectories. Adding more methyl groups leads to a “slower” exploration of the diradical region, due to the larger mass of the rotating fragments.
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5.1 Unmethylated 1,2-Dioxetane

Conical intersections can be quickly characterized by plotting the $P$ and $B$ values from Equation (3) and Equation (4). These plots are given in Figure 8. We see that most CIs are peaked and bifurcating, some are sloped and single path (all three seams, around 40°), one CI is sloped and bifurcating (teal seam, near 70°), and a few are peaked and single path (blue and red seams, around 50°). The sloped CIs are also identified by the negative minimum slope in Figure 7c).

Seams from three different approaches are presented in the plots (as described in the previous section). The dashed vertical line indicate the position on the red seam that was “followed”. The first thing to notice is the numerous discontinuities in the seams, as seen in Figure 7. All discontinuities for one seam occur at the same positions in every subplot. The red line represents the CI seam obtained by starting each CI optimization from the reference trajectory geometry. Three discontinuities can be found along this seam, most easily seen in subplot (c) The blue line represents the seam by following the first point on the red line; i.e. using the previously optimized CI as the starting point for the next CI. This line has just one discontinuity, most easily seen in subplots (c) and (f). The teal line is the seam located by starting the optimization from an interesting region on the red seam, indicated as a teal vertical and dashed line.

All seams are never more than 2.5 kcal/mol in energy of the reference trajectory, but part of the seams have lower energy than the reference trajectory. The blue and red seams have about the same C$_1$C$_2$ distance, but the teal seam shows a region that differs significantly. We also see regions where the OCC angles are identical and regions where they are different. The smallest value of the minimum gradient is about $-0.2 E_h/a_0$.

A feature seen in Figure 7 is that all three approaches converged to the same seam at low O$_1$C$_1$C$_2$O$_2$ reference dihedral angles, then differed at about 50° to 70°, and then agreed again after this. In subplot (c) we can see that the three approaches are slightly different after 70°. This slight difference in the minimum gradient can be explained by a quite flat PES: for relatively large changes in nuclear displacements, the energy changes very little. This is also indicated by comparing the energies of the seams for each approach in subplot (a): even in the region of quite large differences in C$_1$C$_2$ bond length and OCC angles, the energies of the three seams are almost identical. State overlap calculations indicate that the three seams belong to the same two diabatic states in this region. It also appears that different approaches were able to explore different regions of the same seam. See for example in subplot (c): moving from right to left, the blue line seems to continuously extend the teal seam quite a lot, and state overlap computations confirm that this is indeed the case.
Figure 7. Some energetic and geometric parameters for CI seams for 0Me as a function of the reference O\textsubscript{1}C\textsubscript{1}C\textsubscript{2}O\textsubscript{2} dihedral angle: absolute energy of seam (a), energy difference with trajectory point (b), minimum gradient on the upper CI surface (c), RMSD relative to trajectory point (d), C\textsubscript{1}C\textsubscript{2} bond length (e), and the two OCC angles (f). Three different approaches have been used to locate these seams (see text for details). The legend is only shown in (a) because it is the same for all sub-plots.
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Figure 8. The $P$ and $B$ values [14] for characterizing the topography of the CIs 0Me. The green regions represent sloped (a) and single path (b) CIs, while the red regions represent peaked (a) and bifurcating (b) CIs.

5.2 Methylated 1,2-Dioxetane

Energetic and geometrical parameters for 1Me are presented in Figure 9, while the characterization parameters $P$ and $B$ are given in Figure 10. We see the same sort of discontinuities for 1Me, although they occur at different positions and in different numbers. From Figure 10 we see that all four categories of CIs have been found except sloped and bifurcating. Sloped CIs occur around $40^\circ$ and after $70^\circ$.

For 1Me four approaches were used. The red lines in Figures 9 and 10 are the seam resulting from starting each CI optimization from the trajectory, and six discontinuities can be seen. The middle region of the red seam appears to be oscillating back and forth between the teal and blue/black seams, except for two points which appear to not belong to any of the other seams. The blue seam has only one discontinuity, and was built by following the first point on the red seam. The teal seam starts at around $70^\circ$, and attempted to follow the right-most region of the red seam going left. The black seam attempted to follow the last continuous point of the red seam (just before its first discontinuity) going right, but was only successful for one point, and after this converged to the blue seam. State overlap calculations have confirmed that the teal seam actually is a continuation of the red seam, and that the red points that converged to the blue seam also belong to the blue seam. The slight discrepancy between the blue/red and teal seams around $40^\circ$ is not because they are seams of states of different electronic character; rather, state overlaps show that they converged to different local minima in the same intersection space, likely due to the differences in starting geometry and orbitals. Also for 1Me we get the impression of a flat PES; the energy does not change much between the seams, even when the geometrical changes are quite severe. The smallest value of the minimum gradient is about $-0.2 \, E_h/\alpha_0$. 
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Figure 9. Some energetic and geometric parameters for CI seams for 1Me as a function of the reference $O_1C_1C_2O_2$ dihedral angle: absolute energy of seam (a), energy difference with reference trajectory point (b), minimum gradient on the upper CI surface (c), RMSD relative to reference trajectory point (d), $C_1C_2$ bond length (e), and the two OCC angles (f). Three different approaches have been used to locate these seams (see text for details). The legend in is only shown in (a) because it is the same for all sub-plots.
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5.3 *Trans-*dimethylated 1,2-Dioxetane

Energetic and geometrical parameters for 2Me are given in Figure 11, and CI characterization parameters are given in Figure 12. Yet again we observe discontinuities in the seams, and all four categories of seams are located. Sloped CIs occur around 40° and 50°.

For 2Me, three approaches were used. The red line represents the seam obtained by starting each CI optimization from the reference trajectory. For 2Me, this approach did not lead to discontinuities in the seam. The blue seam was obtained by following the first point on the red seam, and four discontinuities can be seen. The teal seam was obtained by trying to follow the four points disconnected from most of the blue seam, going left and right: going right successfully filled in the missing part, which is also confirmed by state overlap calculations, but going left just converged back to the blue/red seam. We also see that the missing part of the blue seam if filled in by the red seam.

Compared to 0Me and 1Me, the seams show some additional features, despite covering a smaller reference angle range. There is, for example, two different regions along the seams for which the seam energy is lower than the reference trajectory energy. The reason for this is that the 2Me reference trajectory survived in for a longer time in the diradical region of the PES before it dissociated, but the $O_1C_1C_2O_2$ dihedral angle rotated more slowly, perhaps due to the larger mass of the rotating fragments. The minimum gradient in Figure 11c) displays a minimum near 40° of about $-0.3 \, E_h/a_0$. 

![Figure 10](image-url)

**Figure 10.** The $P$ and $B$ values [14] for characterizing the topography of the CIs for 1Me. The green regions represent sloped (a) and single path (b) CIs, while the red regions represent peaked (a) and bifurcating (b) CIs.
Figure 11. Some energetic and geometric parameters for CI seams for 2Me as a function of the reference O1C1C2O2 dihedral angle: absolute energy of seam (a), energy difference with reference trajectory point (b), minimum gradient on the upper CI surface (c), RMSD relative to reference trajectory point (d), C1C2 bond length (e), and the two OCC angles (f). Three different approaches have been used to locate these seams (see text for details). The legend in is only shown in (a) because it is the same for all sub-plots.
6 Discussion

6.1 Discontinuous Seams

From Figures 7, 9 and 11 and the description in the previous section, it is clear that different approaches were able to explore different regions of the same intersection spaces, as indicated by the numerous discontinuities. To explain this behavior we need to consider the PES, and how the optimization methods depend on the PES. One reason for the discontinuities could be that the optimized seams no longer are local minima. If this is the case, then the calculation must converge to either a minimum in a different intersection space, or a different minimum in the same intersection space. (If the discontinuity is between seams that involve different diabatic states, then the seams belong to different intersection spaces.) However, this explanation alone is not sufficient, because we see several examples where one approach is able to fill in the gaps of another approach. Therefore the starting conditions for the optimization decide which local minimum the calculation converges to.

This is logical. The geometry optimization method we are doing cannot cross energy barriers by its own construction; it always lowers the energy. It could be that there is a small barrier that needs to be overcome in order to converge to a minimum on the same seam as the previously optimized CI. It could therefore be that the CI which would form a continuous seam with the previous CI is closer to the starting geometry compared to the minimum to which the calculation converged; however, the barrier prevents the calculation from converging to this point, no matter how small the barrier is. Further, the
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arrival point on the seam during the optimization is arbitrary, since the algorithm tries to simultaneously locate the seam (fulfill the degeneracy constraint) and minimize the potential energy given the current constraints. Therefore, the exact position arrived at on the seam dictates which local minimum on the seam the calculation must converge to, and this arrival point depends on from where on the full PES the optimization was started. This idea is illustrated in Figure 13, where the two black curves represent two different cross sections of the intersection space, and their crossing point with the red vertical line is the arrival point on this seam. A minimum energy path (not computed) from these two arrival points should lead to different minima, since they are on opposite sides of the barrier.

6.2 Relevance to Chemiluminescence

The most significant observation to be made from Figures 7, 9 and 11, is that sloped CIs exist for all three molecules in the vicinity of their reference trajectory, both at low and at higher reference angles. We can also see that the blue seam for 0Me, just before its discontinuity, is rapidly decreasing in the minimum gradient plot, which may indicate that sloped CIs from this seam are also readily accessible from the trajectory, even though our calculations were not able to find them. Sloped CIs are a significant finding, as such CIs have not yet been reported for 1,2-dioxetanes in the literature (to our knowledge). Sloped CIs fit very well into the mechanism of chemiluminescence because once a nonadiabatic transition to the excited state has taken place in the diradical region, the negative gradient on the excited state may guide the molecule away from the CI. Of course, the linear model used to describe the potential energies around the CI is only valid in the immediate vicinity of the CI, so too big statements cannot be made; the actual shape of the excited state PES farther away from the CI would dictate what happens. Since different seams in different regions are sloped, perhaps more than one seam are involved in the nonadiabatic transitions taking place in the entropic trap. The intersection space is large with $N - 2$ dimensions, and it is possible that many other seams in the vicinity of the trajectory exist that could contribute to the population transfer from the ground state to excited states, including seams that are
not local minima in the intersection space.

Vacher et al. [2] performed surface hopping dynamics simulations in the entropic trap region for 1,2-dioxetane [2]. For each hop from the ground state to some excited state, they computed the time it took for this trajectory to hop back down to the ground state from any of the excited states: they computed the total “time spent in excited states”. They then plotted this as a function of the \( \chi_{12} \) dihedral angle at which the initial hop from the ground state took place. If we compare the smallest gradient plot presented in Figure 7 with Figure 5, we see a striking agreement. There is a cluster of trajectories that underwent the initial hop close to 40° \( \chi_{12} \) dihedral angle, and many of these trajectories spent a long time in the excited state. The long time spent in the excited state should imply that some trajectories were able to move away on the excited state PES, as opposed to lingering near the geometry at which it hopped, as they would then likely just hop back down immediately.

It is possible that this behavior is closely related to the sloped CIs located in the present work, since the negative gradient provides a path in which the molecule can move farther away from the CI. The data presented herein seems to fit better with the surface hopping simulations than their reported CI optimizations, because here we have found sloped CIs coinciding with the cluster of hops (Figure 5). The reason for this better agreement may be that a trajectory from Vacher et al. [2] has been used as a reference for the CI optimizations, and the CIs optimized are therefore more relevant for the surface hopping dynamics.

However, we have only used one trajectory as a reference, and this trajectory may not be representative of the real reaction pathway. So to get a more realistic picture of what goes on, several of the ground state trajectories from Vacher et al. [2] should be used as a reference for CI optimizations. It could be that new seams of sloped CIs would be found that also are important for the population transfer from the ground state to excited states.

We can also see a minimum in the RMSD around 40°, coinciding with the minimum in the smallest gradient plot and the cluster of points around this angle in Figure 5. Being geometrically closer to the reference trajectory should be beneficial for the chemiluminescence mechanism, especially if the vibrational mode that is populated involve the nuclear displacements that actually lead from the reference trajectory to the CIs. It is therefore possible that the low RMSD is related to the high number of hops that took place (but not necessarily related to the time spent in the excited state).

Experimentally, the chemiluminescence yield increases dramatically by adding methyl groups to 0Me. Do we see any possible indication in the data for why this is so? Figure 14 shows for each molecule the narrow region of sloped CIs. Molecule 2Me has a smaller minimum gradient compared to 0Me and 1Me by about 0.1 \( E_h/a_0 \). This increase in the slopedness could be a manifestation of the trend in chemiluminescence yield observed experimentally. The steeper gradient could lead to a higher number of molecules capable of evading the intersection point. However, there is no notable difference in the smallest minimum gradient between 0Me and 1Me.

Further, the “well” of sloped CIs is wider for 2Me compared to 0Me and 1Me. This could mean that a
larger “volume” of the intersection space contains sloped CIs for 2Me. The well of 1Me sloped CIs appear to be slightly narrower than 2Me, but slightly wider than 0Me. This also indicates that the minimum gradient on the upper surface of the CI is related to the observed trend. Surface hopping dynamics for 1Me and 2Me have not yet been published, so there is no data to compare with. However, based on the presented data, we could predict that a higher number of trajectories would spend a significant time in excited states for 2Me compared to 1Me and especially compared to 0Me. It is also of interest to characterize the seams of CIs for 3Me and 4Me, which unfortunately was not possible within the time frame of the present work.

Branching space vectors should also be analyzed in detail for the seams, as this will provide information about what kind of nuclear displacements that would actually lead toward the CIs. This information could also be obtained by studying the difference in geometry between each CI and its reference trajectory point. Knowing what nuclear displacements that lead to the CIs on the ground state, and which displacements that lead away from the CIs on the excited state, could help us decide which of the seams are most likely to be important in the chemiluminescence mechanism.

The initial question was whether the effect of methylation manifests itself in the seams of CIs close to the reaction coordinate. A definite answer cannot perhaps be given based on the data presented here, but there is a clear indication of a trend in the minimum gradient plots for the three molecules. With dynamics studies of 3Me and 4Me, and the study of CI seams for 3Me and 4Me, it will be easier to say whether there is a clear connection between the increased chemiluminescence yields and the CI topography.

![Graph](image)

**Figure 14.** A closer look at the narrow region of sloped CIs for 0Me, 1Me, and 2Me. 2Me has a smaller minimum gradient than the other molecules, and the “well” is wider, which fits well with our current understanding of chemiluminescence.
7 Conclusion

Seams of CI’s for 0Me, 1Me, and 2Me have been found. By using molecular dynamics trajectories from the diradical region as references, we have found local minima seams that are relevant to the thermal decomposition reactions taking place during chemiluminescence for these molecules. Different topographies have been found, most significantly sloped CI’s. Such CI’s have not yet been identified for 1,2-dioxetanes, and fit very well with our current understanding of chemiluminescence. The negative gradient on the upper surface of the CI provides a path leading away from the intersection point, which should decrease the probability of an immediate nonadiabatic back-transition to the ground state. It has been shown that sloped CI’s for 2Me have a larger negative slope compared to 0Me and 1Me, and that the region of sloped CI’s appear to grow going from 0Me to 1Me to 2Me. This may be an additional factor in understanding why the chemiluminescence yield increases for 1,2-dioxetane by adding methyl groups, and that this trend is not just an effect of the entropic trap.

However, the results are only indicative, as we can only compare our results directly with dynamics studies of the 0Me molecule. Presently dynamics studies of the remaining methylated 1,2-dioxetanes are being done at the Theoretical Chemistry group at Uppsala University, and it will be of great interest to compare the presented results with the future dynamics results. In addition, due to time constraints, the CI seams for 3Me and 4Me have not yet been optimized, which can provide additional insight when compared to dynamics studies.

Further, the branching space vectors have not been analyzed in the present work. These can provide understanding of the molecular modes that need to be populated in order to reach each of the optimized CI’s, and may help elucidate which seams are more likely to be relevant for the chemiluminescence.

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