

**Mechanistic Investigation of Photochemistry and
Chemiluminescence using Multi-configurational
Quantum Chemistry**



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To my parents

Declaration

I hereby declare that except where specific reference is made to the work of others, the contents of this dissertation are original and have not been submitted in whole or in part for consideration for any other degree or qualification in this, or any other Institute. This dissertation is my own work and contains nothing which is the outcome of work done in collaboration with others, except as specified in the text and Acknowledgements.

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Abstract

The mechanistic description of excited state reactions involves unique challenges. Unlike ground state chemistry, where transition states control reactions, excited state molecular transformations are largely governed by crossings of potential energy surfaces called "conical intersections". Commonly used quantum chemical methods like Hartree-Fock and DFT, which work well for ground states are not suitable for describing conical intersections and regions of potential energy surfaces around them. We have used multiconfigurational quantum chemical approaches like CASSCF and its extensions to investigate three important chemical reactions, all of which involve excited electronic states. Multiconfigurational approaches are technically challenging and require adept chemical intuition for their correct application.

Ortho-nitrotoluene (oNT), on photoexcitation undergoes excited state intramolecular hydrogen transfer (ESIHT) as well as dissociation to various photo products. The ESIHT process is representative of the primary step in the deprotection of *ortho*-nitrobenzyl (oNB) derivatives that are widely used as photo-labile caged compounds. In the literature, an experimental study on oNT has reported two distinctly different time scales (1 and 1500 ps) for the ESIHT reaction. Our study explains the reason for these lifetimes and provides a detailed mechanistic picture of the photodecay. The photodissociation of oNT is also of major interest because it is a prototype for high-energy materials. Using 1-nitropropene as a model system for oNT, we have studied the photodissociation and proposed an unexplored excited singlet pathway for the formation of NO, which rationalizes its observed bimodal translational energy distribution. We have also investigated the origin of chemiluminescence in the NO + O₃ gas phase reaction. We found that the chemiluminescence is due to emission

from the NO₂ vibronic states associated with the ground and first excited electronic states, which are populated in the nascent NO₂ produced in the reaction. An analysis of the product energy distribution indicates that the major fraction of the reaction energy channeled into the vibrational modes of NO₂, sufficient to populate the vibronic states of NO₂. Besides obtaining new mechanistic insights on reactions involving electronically excited states, we have also developed a method to find a crossing point between three states when these states have two different spin multiplicities. Taken together, our studies demonstrate that multiconfigurational quantum-chemical methods provide fundamental insights on complex excited state processes that are not obtainable by experiment or other theoretical methods.

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Chapter 1

Introduction

The knowledge of reaction mechanism provides an in-depth understanding of a chemical reaction. It allows one to predict and control the outcome of reactions, which is of both fundamental and applied interest. For instance, an advancement like artificial photosynthesis [2–4] which mimics natural photosynthesis to capture and store light energy in chemical bonds is only possible by understanding the photosynthesis mechanism at a molecular level. Understanding the reaction mechanisms also offers a way to avoid the undesirable reactions like DNA photodamage [5, 6] by altering reaction conditions.

Chemical reactions may involve only the ground electronic state or both the ground and multiple excited electronic states, and depending on this, their mechanisms are broadly different. Ground state reactions are driven by thermal energy whereas excited state reactions are often initiated by light and are called photochemical reactions. Experimental investigation of photochemical reactions began in the late 1950's, after the invention of laser technology. The flash-photolysis technique was developed at that time by the 1967 Noble laureates, Eigen, Porter, and Norrish to study chemical reactions on the microsecond timescale [7]. A more advanced technique, femtosecond spectroscopy which uses laser pulses in the femtosecond ($1 \text{ fs} = 10^{-15}$) timescale was developed in the 1990's. The Nobel Prize in chemistry was awarded to Ahmed H. Zewail in 1999 *"for his studies of the transition states of chemical*

reactions using femtosecond spectroscopy". It would not be an exaggeration to say that the invention of femtosecond laser brought about a revolution in experimental photochemistry and consequently accelerated the advancement of photochemical theories.

The theoretical description of a reaction, whether on ground or excited states, hinges on the knowledge of the relevant potential energy surfaces. While ground state reactivity is mainly governed by the transition state geometry, excited state reactions are controlled by crossings of two PESs. The topological features associated with crossings of two states of the same spin multiplicity is known as a conical intersection (CI). These CIs along with singlet-triplet crossings play a major role in excited state chemistry [8–11].

Within the Born-Oppenheimer approximation proposed by Max Born and J. Robert Oppenheimer in 1927, the total wavefunction can be separated into the electronic and nuclear part [12]. Due to this separation, the electronic energy can be obtained by solving the electronic Schrödinger equation while keeping the nuclear coordinates fixed. By calculating this electronic energy at different nuclear positions, the potential energy surface for the reaction can be obtained.

Various energy or electron transfer processes cause the decay of electronically excited molecules. Some prominent ones are fluorescence, phosphorescence, photo-product formation and nonradiative decay via CIs or singlet-triplet crossing points. All these processes are shown schematically in Fig 1.1. Another type of process involving multiple electronic states is chemiluminescence. In this case, a thermally activated reaction emits light. A knowledge of the ground and excited state PESs is essential to identify and understand the mechanism of such processes.

With the currently available theoretical methods, obtaining the ground state PES is relatively straightforward. However, the exploration of the excited state PESs involves unique theoretical challenges due to the presence of surface crossing regions. The first is the breakdown of the Born-Oppenheimer approximation, which is due to the rapid change in the nature of the electronic states along nuclear degrees of freedom in regions around the surface

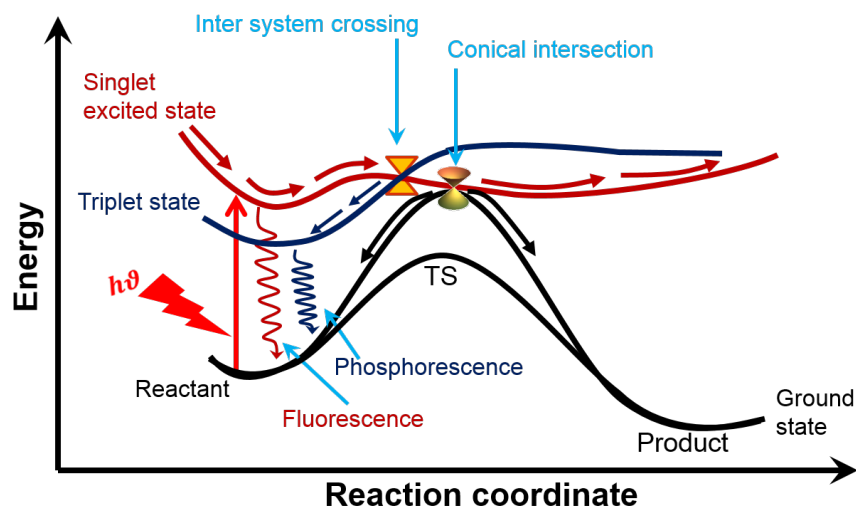


Figure 1.1: Schematic representation of molecular transformations on the ground and the excited states

crossing. This makes the nuclear dynamics particularly challenging. The second challenge is that the electronic wavefunction of the system at CIs and the regions of PESs around them cannot be described by commonly used single-reference methods such as Hartree-Fock [13], DFT [14, 15], MP2 [16], and CCSD [17, 18]. Therefore, multi-reference electronic structure methods along with non-Born-Oppenheimer dynamics approaches are needed to investigate most excited state molecular processes. Moreover, the application of multi-reference methods is not as straightforward as single-reference methods and often involve significant human intervention with adept chemical intuition for their correct application.

In this thesis, different chemical reactions which involve multiple electronic states have been explored using multi-reference methods. The complete active space self-consistent field method (CASSCF) along with second order perturbative inclusion of dynamical electron correlation has been used. All feasible photophysical and photochemical pathways starting from the lowest optically bright electronic state have been characterised for the photo-induced chemical reactions. We optimized stationary points on the relevant electronic states and the minimum energy crossing points (MECPs) between the electronic states involving same spin multiplicity as well as different spin multiplicities. By considering the energetics and

geometrical parameters of critical points (stationary points and MECPs), the barriers to access them and the spin-orbit coupling (SOC) values at the optimized singlet-triplet crossing points, the relative importance of multiple photo-decay pathways have been estimated. Regarding chemiluminescence, the reaction's minimum energy path (MEP) calculations on the ground state and relaxed potential energy scans on the electronic excited state have been performed. Based on the computed paths, the mechanism for the formation of ground and excited state products in the chemiluminescent reaction have been proposed. Besides exploring excited state chemistry, we also developed a method for finding a crossing point between three electronic states having two different spin multiplicities using gradient and derivative coupling vectors.

1.1 Outline of the thesis

In *Chapter 2*, the details of the electronic structure methods that have been used in this study are given. First, a brief description of single-reference methods and their limitations in describing the electronic wavefunction is given, followed by the formalism of multi-reference methods and their advantages over single-reference methods are discussed. We also mention the challenges involved in using multi-reference methods. The crucial part in using multi-reference method is choosing active space which consists of the orbitals (active orbitals) and electrons (active electrons) that are mostly involved in chemical process of our interest. Thus, few strategies that are helpful in selecting an appropriate active space are given.

Chapter 3 discusses the mechanism of oNT photo-tautomerization on both the singlet and triplet excited states. This excited state tautomerization involves an excited state intramolecular hydrogen transfer (ESIHT) process from the methyl group to the oxygen of the nitro group and produces the *aci*-nitro tautomers of oNT on the ground state as the photo-products. We obtained all possible pathways corresponding to the photo-decay and photo-tautomerization of oNT starting from its lowest optically bright state. The molecule

from this bright state relaxes to the lowest triplet state in a barrierless way. On the T_1 state, the molecule undergoes intramolecular hydrogen transfer process to form the more stable tautomerized products. The hydrogen transferred products on the T_1 state relax to the ground state to give the ground state *aci*-nitro products. On the singlet pathway, in contrast to the triplet, the ground state tautomer is formed from the S_1 -oNT through a geometrically distant and energetically higher S_1/S_0 CI. Our results which consider the relative propensity to access different MECPs and the magnitude of spin-orbit coupling at singlet-triplet MECPs, suggest that a significant fraction of the isomerization yield is due to the triplet channel. Interestingly, the triplet pathway appears to also be reduce the overall yield of the photo-tautomerization in oNT.

Chapter 4 deals with the photo-dissociation mechanism of nitropropene (NP), which serves as the simplest model system for studying photo-dissociation in nitrobenzene (NB) and oNT. The major products in the photo-dissociation of NB and oNT have been identified to be NO_2 and NO radicals. Experimentally, a bimodal translational energy distribution was observed for the formation of NO and this indicates the presence of two different NO formation channels in the excited state decomposition process of NB and oNT. We investigated the photo-decomposition mechanism for both the *trans* and *cis* isomers of NP and proposed an unexplored excited singlet pathway for the formation of NO. We also identified a triplet pathway and two ground state pathways for the NO formation. Among the two ground state pathways, one involves a roaming transition state where the molecule reaches the region of dissociation limit and the other involves a normal transition state. Our results suggest that the experimentally observed fast and slow NO formation channels can be attributed to the above mentioned excited state singlet and triplet paths, and the ground state path which involves a roaming mediated isomerization, respectively.

The mechanism of the chemiluminescent reaction between NO and O_3 to produce nitrogen dioxide and oxygen is presented in *Chapter 5*. In this reaction, oxygen is produced in the ground state, while NO_2 formed in both its ground ($\tilde{X}^2A_1$) and first excited ($\tilde{A}^2B_2$)

electronic states, and the process of relaxation of the excited NO_2 leads to chemiluminescence. The MEP calculation results indicate that there is no direct path for the formation of excited NO_2 in the reaction. Our study suggests that the chemiluminescence in the reaction is due to the emission from NO_2 vibronic states associated with the $\tilde{X}^2\text{A}_1$ and $\tilde{A}^2\text{B}_2$ electronic states, which are populated in the nascent NO_2 produced in the reaction. The vibronic coupling between the $\tilde{X}^2\text{A}_1$ and $\tilde{A}^2\text{B}_2$ states is due to a CI between them, which is geometrically and energetically close to the $\tilde{A}^2\text{B}_2$ minimum energy geometry. Further, the energy of the CI is lower than the energy of the reactants, $\text{NO} + \text{O}_3$, and therefore thermodynamically accessible following the reaction. An analysis of the product energy distribution indicates that the major fraction of the reaction energy is channelled into the vibrational modes of NO_2 , sufficient to populate the vibronic states of NO_2 around the $\tilde{X}/\tilde{A}$ CI. These vibronic states show dipole allowed emission in a frequency range that is consistent with the observed broad chemiluminescence spectrum.

In *Chapter 6*, a method for finding a crossing point between three electronic states of two different spin multiplicities or spatial symmetries has been discussed. Our strategy here, is to start with a two state CI point, say $E_1 = E_2$, and minimize the energy difference, $E_3 - 1/2(E_1 + E_2)$ while ensuring that the $E_1 = E_2$ degeneracy is maintained. We applied this method successfully on the oNT molecule and a three state crossing point was obtained on the PES.

Chapter 2

Theoretical Methods

Energy plays a central role in predicting or explaining chemical phenomena. *Ab initio* methods for modeling chemical phenomena involve solving the time independent Schrödinger equation,

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

where $\hat{H}$ is the molecular Hamiltonian and E is the energy of the system. This equation does not have an exact solution for systems with two or more electrons. Therefore, approximations are needed to solve the equation. The Hartree-Fock (HF) wavefunction is a starting point for most methods for solving this equation [13]. The HF wavefunction is an anti-symmetrized product of single electron spin orbitals and is written as a so called *Slater determinant*. In this form of the wavefunction the electron repulsion is treated in an average manner. For most closed shell molecules near their equilibrium geometry, the HF method will give a qualitatively correct description of the system. However, there are several chemically relevant systems where a single Slater determinant does not give a satisfactory description. The hydrogen molecule at bond lengths close to dissociation is an example of such a system. This is discussed in greater detail below.

Consider H_2 in a minimal basis of two atomic $1s$ orbitals, $1s_a$ and $1s_b$, located on each atom. These two AOs ($1s_a$ and $1s_b$) lead to two MOs (ϕ_1 and ϕ_2) as shown in Figure 2.1.

Considering α and β as spin eigenfunctions, the HF ground state wavefunction for the hydrogen molecule with these MOs is,

$$\psi = |\phi_1 \bar{\phi}_1| = \phi_1(1)\alpha(1)\phi_1(2)\beta(2) - \phi_1(2)\alpha(2)\phi_1(1)\beta(1) \quad (2.2)$$

$$= \phi_1(1)\phi_1(2)[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

$$= [1s_a(1) + 1s_b(1)][1s_a(2) + 1s_b(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad (2.3)$$

$$= [1s_a(1)1s_a(2) + 1s_b(1)1s_b(2) + 1s_b(1)1s_a(2) + 1s_a(1)1s_b(2)]$$

$$[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad (2.4)$$

The first two terms in the spatial part of the wavefunction in Eq. 2.4 are referred to as ionic terms and the remaining terms are referred to as covalent terms. At the restricted HF (RHF) level, the hydrogen wavefunction, ψ is 50% ionic and 50% covalent at all bond lengths of hydrogen. But, at the dissociation limit of hydrogen molecule, H_2 must separate into individual hydrogen atoms where the wavefunction must have 100% covalent character. Therefore, H_2 dissociation cannot be correctly described at the RHF level.

The HF method also fails to describe the system in regions near a conical intersection and this occurs frequently for excited states. To overcome these drawbacks, post-HF methods were developed. Among them, the multi-reference methods like complete active space self consistent field (CASSCF) [19–21] and multi-reference configuration interaction [22, 23] have been found to be successful in describing the CI regions of PES and bond-breaking situations.

In the full configuration interaction (CI) method, the reference configuration coefficient (C_0) gives an indication about the multi-reference character of the system. The results obtained from a single reference wave function are considered qualitatively correct if C_0 is 0.95 or more [24]. But, the cost of a full CI calculation increases rapidly as the system size increases, which makes using full CI impractical. For many years quantum chemists have used c_0 , the reference configuration coefficient when the wave function is approximated as a

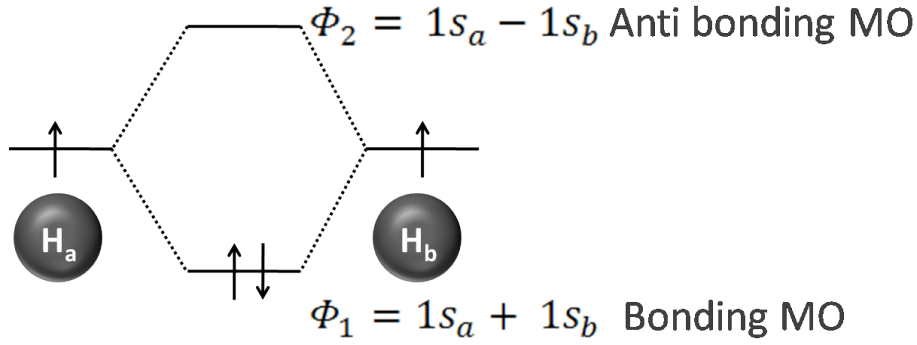


Figure 2.1: Molecular orbital diagram of H₂

truncated CI having only singles and doubles configuration interaction (CISD). Since the molecular orbitals in this case are strongly biased towards the single-reference wave function, it is not uncommon for a multi-reference system to yield c_0 which is 0.95 or larger. Thus, the c_0 is of limited utility. Currently T1 [24] which is related to the t_1 amplitudes of the CCSD wave function is widely recognized as a diagnostic tool for multi-reference character. The permissible values of T1 is 0.02 (0.03 for open shell systems) for single-reference systems. If the value of T1 exceeds this, the system needs to be treated with multi-reference methods.

2.1 Multi-reference methods

In any multi-configurational self consistent field (MCSCF) method, one writes the wavefunction $|0\rangle$, as a linear combination of configuration state functions (CSFs), $|\Phi_i\rangle$ which are spin adapted linear combination of Slater determinants

$$|0\rangle \equiv \sum_{i=1}^n C_{0_i} |\Phi_i\rangle \quad (2.5)$$

Solving the HF equation with k basis functions results in $2k$ spin orbitals. These $2k$ spin orbitals and N electrons generate $\binom{2k}{N}$ determinants. ϕ_j are the molecular spin orbitals that appear in the CSFs $|\Phi_i\rangle$ and are written as a linear combination of atomic orbitals χ_k (basis

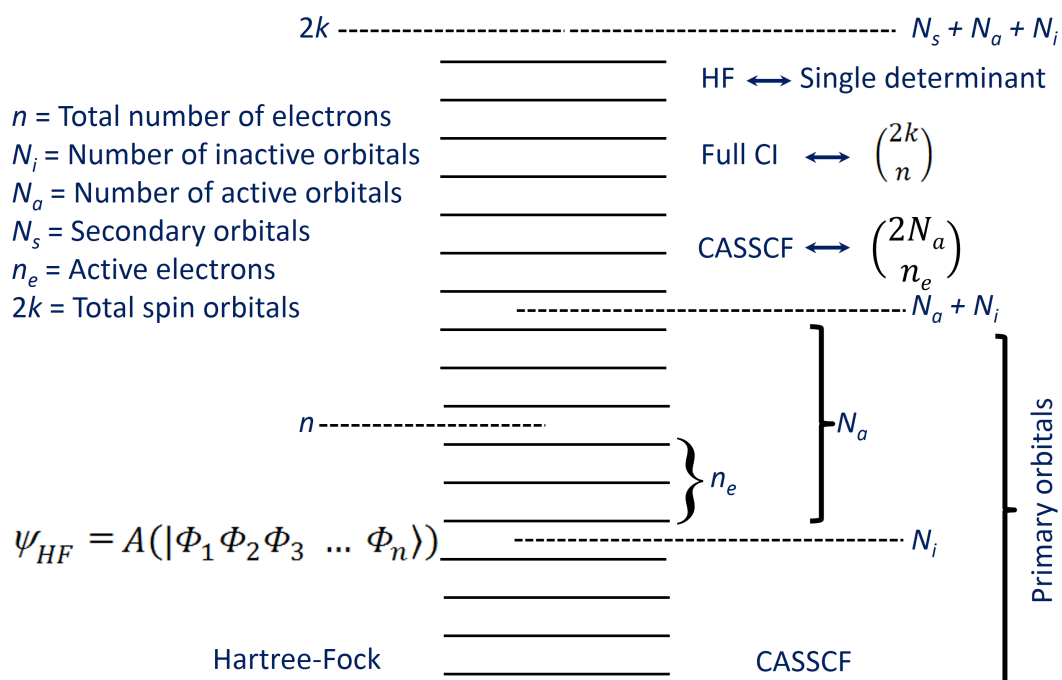
functions).

$$\phi_j \equiv \sum_{k=1}^m c_{jk} |\chi_k\rangle \quad (2.6)$$

In the HF method, the single Slater determinant wavefunction, formed from the N lowest molecular spin orbitals, is variationally optimized with respect to the molecular orbital coefficients c_{jk} . The full CI wavefunction is a linear combination of all $\binom{2k}{N}$ CSFs and is variationally optimized with respect to the determinantal coefficients. The form of the MCSCF wavefunction is given in Eq.(3) where only important CSFs will be included and this wavefunction is optimized with respect to both determinantal coefficients C_{0i} and molecular orbital coefficients c_{jk} .

The CASSCF [19–21] method is the most commonly used type of MCSCF methods in which the important CSFs will be included in a systematic way. The molecular orbitals in CASSCF method are divided into primary and secondary orbitals. The CSFs are constructed using the primary orbitals while the secondary orbitals are only used to improve the primary orbitals. These primary orbitals are again subdivided into active and inactive orbitals. The CASSCF wavefunction can be written as a linear combination of all possible CSFs generated by keeping the inactive orbitals doubly occupied and distributing the remaining electrons (active electrons) within the active orbitals. These different types of orbitals involved in the CASSCF method are schematically shown in Figure 2.2.

The CASSCF method is not as easy to use as single-reference methods and requires a certain amount of human intervention for it to work correctly. The tricky part of the method involves selecting an appropriate active space (active orbitals and active electrons) which can be guided to some extent by chemical intuition. The active space of n_e electrons and N_i orbitals is usually denoted as $\text{cas}(n_e\text{-in-}N_a)$. In principle, all the orbitals and electrons can be included in the active space, which essentially means a so called full CI (configuration interaction) treatment. However, a full CI calculation even for a small size molecule is computationally expensive, and thus a limited number of orbitals need to be selected. The formula given in Eq. 2.7 can be used to obtain the total number of CSFs, N_{CSFs} for a system



2.2 Active space selection

The following strategies are helpful while choosing the active space for a CASSCF calculation.

1. If affordable, include all the valence orbitals and the corresponding electrons in the active space. E.g., the full valence active space for NO_2 is cas(17-in-12).
2. All π/π^* orbitals for unsaturated molecules if possible, or include few highest π and few lowest π^* orbitals.
3. The σ/σ^* orbitals corresponding to the bonds that are formed or broken in the process of the reaction.
4. Based on the analysis of orbital occupation numbers (eigenvalues of 1-D reduced density matrix), active space can be chosen. One could start a CASSCF calculation with a large active space. If the occupation number of the particular orbital is higher than a certain threshold (say 1.98), then it can be considered to be an inactive orbital and if it is less than 0.02, it can be considered to be a secondary orbital. After reducing the active space, CASPT2 or MRCI energies can be calculated with both initial and reduced active spaces. If the energy difference is within a few milli-Hartree, it can be concluded that the reduced CAS space is good enough to describe the system. The effect due to the small occupation number orbitals is recovered by the dynamical correlation included in CASPT2 or MRCI.
5. First, compute the vertical energies for few electronic excited states with accurate single-reference methods like EOM-CCSD. Identify the orbitals involved in the electronic transitions by analysing the nature of the calculated excited state and include them in the active space.

2.3 Linear interpolation in internal coordinates method to estimate barriers along the reaction path

The accessibility of an optimized MECP from any other point (usually either Franck-Condon geometry or one of the excited state stationary points) on the PES depends on the relative energy of MECP with respect to the other point and also the barrier along the path connecting the two points. The MEP towards the MECP gives the barrier. However, obtaining the MEP can be computationally expensive. The linear interpolation in internal coordinates (LIIC) is a practical way to estimate barriers along the paths. In this method, intermediate geometries between two ends of the path are obtained by linear interpolation, and single point energies are calculated at these geometries. The LIIC path gives an upper bound to the barrier for the decay path. The formula used for interpolation is,

$$q_p = q_i + p\left(\frac{q_f - q_i}{n + 1}\right) \quad (2.8)$$

which gives the p^{th} interpolated structure. Here, n is the number of intermediate geometries between initial point q_i and final point q_f .

Chapter 3

Photo-isomerization Mechanism of *o*-Nitrotolunene, a Model for Photo-labile Caged Compounds

Photo-removable protecting groups are used in organic chemistry for chemoselective synthesis [25] and in biology as photoactivable molecular probes [26, 27]. Such molecular probes, referred to as caged compounds, can be activated with spatio-temporal control by irradiating with light, allowing one to study kinetic processes in tissues. *Ortho*-nitrobenzyl (oNB), and related groups such as *ortho*-nitrophenylethyl and *ortho*-nitrobenzyloxycarbonyl are commonly used photo-removable protecting groups [27]. The primary step in photo deprotection involving such groups is the excited state intra-molecular hydrogen transfer (ESIHT) in the oNB moiety from the benzylic carbon to the oxygen atom of the adjacent nitro group (Figure 3.1). The hydrogen transfer leads to tautomerization and subsequent release of the protecting group resulting in the molecule being available in its active form [27]. This ESIHT reaction in oNB and related moieties has been the subject of several experimental and theoretical studies, [28–50] but the precise mechanistic roles of the multiple close lying excited states of different spin multiplicities remains unknown.

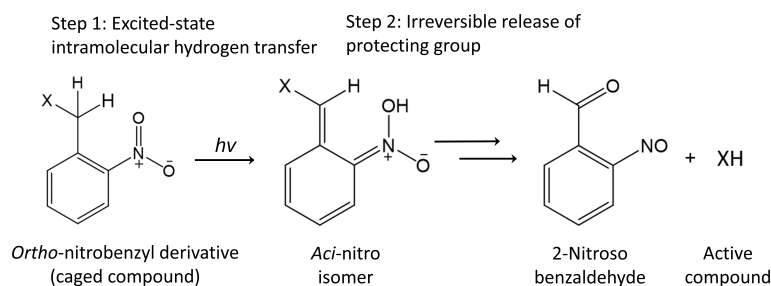


Figure 3.1: Photo de-protection of *ortho*-nitrobenzyl derivatives.

The simplest oNB molecule demonstrating photo-induced tautomerization is *ortho*-nitrotoluene (oNT) and it therefore serves as a model to study the photochemistry of such caged compounds [31, 32, 39, 48, 50]. Recent time-resolved spectroscopic studies of oNT by Gilch and co-workers have shown that photo-tautomerization occurs on two distinctly different timescales, 1-10 ps and 1500 ps, with a quantum yield of 0.08 [39, 50]. The two timescales have been attributed to the singlet and triplet channels respectively. The existence of the triplet channel has been proposed based on the close similarity of oNT to nitrobenzene which has a $\sim 80\%$ triplet yield [51, 52]. The *aci*-nitro formation time scale (1500 ps) is longer than the decay of triplet (430 ps). The decay has been assigned based on comparable lifetimes of several nitrobenzene derivatives [51, 53], while the delayed product formation has been attributed to the formation of a bi-radical intermediate on the triplet state. Direct spectroscopic evidence of the bi-radical was not available and its formation was suggested based on the similarity of the photo-tautomerization reaction to that in *ortho*-nitrobenzaldehyde where such a bi-radical was observed [54]. A description of the deactivation pathways from accurate quantum chemical calculations can assist in reliable assignment of the time-resolved spectral data.

Šolomek et al. have explored the ESIHT reaction in oNT in the context of understanding the variation in quantum yields of uncaging of different oNB caged compounds [48]. Using electronic structure calculations and by studying a series of oNB derivatives, they showed that the excited-state barriers decrease when the exothermicity of the photoreaction increases, thereby demonstrating the applicability of the Bell–Evans–Polanyi principle for

photochemical reactions. Further, they proposed that for the different oNB compounds, the barrier for hydrogen transfer on the excited state determines the branching between the singlet and triplet channels, which affects the yield. They suggested that in oNT, an impenetrable barrier on the S_1 state causes most of the S_1 population to transfer to the T_1 state. However, in their study, the singlet-triplet and triplet-triplet minimum energy crossing points (MECPs) were not optimized, and as shown in the present paper, a knowledge of these MECPs provides a different mechanistic picture of the singlet-triplet branching in oNT.

The role of the singlet versus triplet pathways for ESIHT has also been investigated in *ortho*-nitrobenzylacetate, a molecule related to oNT, by Mewes and Dreuw [47]. Using relaxed scans of the potential energy surfaces along the ESIHT coordinate at the riCC2 level of theory, these authors found intersections of the S_1 and T_1 surfaces with the ground state at similar O–H distances. They proposed that majority of the excited molecules undergo singlet ESIHT, while only a minority of excited state molecules undergo intersystem crossing (ISC) and triplet ESIHT, although the latter process is more efficient. A knowledge of the S_1 –ground and S_1 –triplet MECPs would have provided valuable information on the ESIHT mechanism, but these were not optimized in the above study presumably because of computational bottlenecks in the case of this relatively large molecule.

In this chapter, we present a detailed mechanistic picture of the oNT photo-tautomerization, the simplest oNB compound. The goal is to explain the various spectroscopic observations on this molecule and get general mechanistic insights on oNB photo-isomerization. Using multi-reference electronic structure calculations, we have explored all the photophysical and photochemical processes occurring after photoexcitation of oNT to its lowest optically bright electronic state. We have optimized the excited state minima and MECPs, and plotted these in the space of the significantly changing coordinates involved in the tautomerization. Based on geometrical proximity of these critical points, barriers for accessing them and values of spin–orbit coupling (SOC), we have estimated the relative likelihood of different energy transfer pathways.

The outline of the chapter is as follows. Section 3.1 describes our computational methods. Results and discussion are in four subsections of section 3.2. In the first subsection, the structures of the various oNT isomers on the ground state are presented and the absorption spectrum is assigned. In the second, excited state stationary geometries and crossing points are described. In the third, the accessibility of the various relevant critical points is examined while in the final subsection the mechanism of oNT photo-tautomerization is presented. Summarizing remarks are presented in section 3.3.

3.1 Computational Methods

All ground state stationary points were obtained with the MP2 [16] method and the cc-pVDZ basis set. For vertical excitation energies, the EOM-CCSD [55] and state-specific (SS) CASPT2 [56] methods along with the cc-pVDZ basis set were used. The five state-averaged CASSCF [19–21] wave functions for the singlet ($S_0 - S_4$) and triplet ($S_0, T_1 - T_4$) manifolds separately were used as the reference for SS-CASPT2. A level shift of 0.3 a.u was used to avoid intruder state problems in SS-CASPT2 and no IPEA shift was applied. Gaussian 09 [57] was used for the EOM-CCSD calculations and Molpro 2012 [58, 59] for all other calculations.

Two-state-averaged CASSCF was used for finding most of the minimum energy crossing points (MECPs) between electronic states. State-specific CASSCF was used for finding stationary points on the excited states. The CIs among the higher singlet states, S_4/S_3 , S_3/S_2 and S_2/S_1 required using five ($S_0 - S_4$), four ($S_0 - S_3$) and three SA-CASSCF ($S_0 - S_2$) respectively to ensure convergence of the CASSCF calculation. Similarly, two SA-CASSCF (S_0, S_1) was needed to obtain the transition state on the S_1 state. SOC values were computed at CASSCF level by using the Breit–Pauli Hamiltonian. The active space used in CASSCF and CASPT2 calculations consisted of 16 electrons in 13 orbitals, denoted as (16,13). Active orbitals were two π/π^* orbital pairs from the benzene moiety, two π orbitals

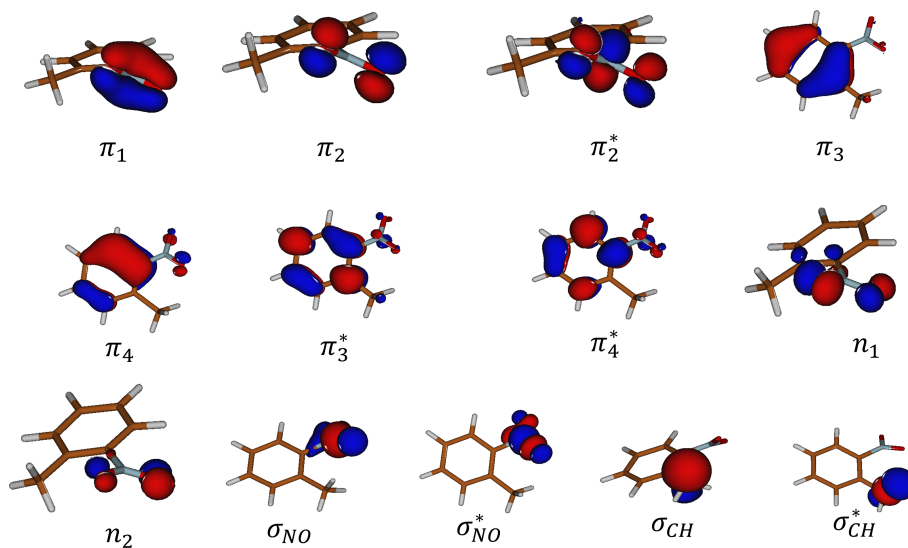


Figure 3.2: Orbitals involved in the (16,13) active space used in CASSCF and CASPT2 calculations.

and one π^* orbital of the NO_2 group, two lone pairs from two oxygen atoms of NO_2 group, and the σ/σ^* orbital pairs of the C–H and the N–O bonds (the bonds involved in hydrogen transfer). The active orbitals have been shown in Figure 3.2. In the case of SOC calculations and CI optimizations of higher singlets, where more than two states were required in the state-averaged CASSCF, reduced active spaces of (14,11) and (12,9) respectively were used so that the calculations were computationally reasonable. The C–H σ/σ^* orbitals were excluded for both calculations and additionally the N–O σ/σ^* orbitals were excluded for the CI optimization. The Hessian cannot be computed analytically for excited states in Molpro. This makes finding the transition state on the S_1 state with the large (16,13) active space impractical. Since, for this geometry, the C–H and the N–O bonds are stretched whereby the σ/σ^* orbitals are essential the active space was reduced to (12,11) by removing one of the lone pairs of oxygen and the lowest π -orbital of the NO_2 group.

Potential energy curves along linearly interpolated internal coordinate (LIIC) paths were calculated using the SS-CASPT2 method. A five state-averaged ($S_0 - S_4$) CASSCF reference wave function and the (12,9) active space described above was used to obtain the path from the S_4 state to the S_1 state. For all other LIIC paths, a four state-averaged (S_0, S_1, T_1, T_2)

CASSCF reference wave function and the (16,13) active space described above was used. The standard 6-31G(d,p) basis set was used for all calculations described in this and the preceding paragraph.

3.2 Results and Discussion

3.2.1 Geometry of oNT isomers and absorption spectrum

The lowest energy structure of oNT is shown in Figure 3.3, part(a). In the minimum energy geometry, the nitrogen atom of the nitro group is in the plane of the ring; the atoms in the NO₂ group and the carbon atom to which this group is attached are also in a single plane, which is tilted with respect to the plane of the ring with a dihedral angle $\delta(\text{C}^1\text{C}^2\text{N}^{11}\text{O}^{12})=147^\circ$. The optimized geometry is in agreement with the structure obtained from gas phase electron diffraction experiments where the NO₂ tilt is 142° [60]. The ground state structures of the different *aci*-nitroforms of the molecule, i.e. the tautomerization products where the hydrogen has transferred to the oxygen of the NO₂ group, have also been optimized. One non-planar minimum energy structure, the *anti*-Z conformer and two planar minimum energy structures, *syn*-Z and *syn*-E conformers have been obtained which are shown in Figure 3.3, parts 1(b), 1(c) and 1(d) respectively. In the non-planar structure, the OH and methylene groups are out of the plane spanned by the rest of the atoms. This reduces steric strain. The minimum for an expected fourth product which might have been called the *anti*-E isomer was not found by either MP2 or CASSCF methods. These results are consistent with previous DFT based structure optimizations [31, 39]. The transition state between the oNT and *aci*-nitro *anti*-Z structure, as well as the transition states for interconversion between other isomers have been optimized and the relative energies of the minima and transition states are shown in Figure 3.4. There exist two different transition states for the interconversion between *syn*-Z and *syn*-E isomers. One involves the rotation about the C²–N¹¹ double bond referred as TS_{3-rot} and the other involves the hydrogen transfer from O¹³ to O¹², referred as TS_{3-ht}. Based on

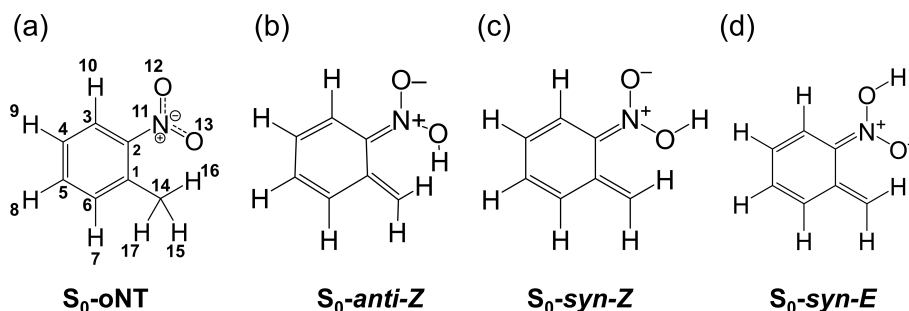


Figure 3.3: Molecular Structures of oNT (a) and its *aci*-nitro isomers (b, c and d) in the ground state. The atom numbering in (a) is used throughout the text.

energetics, the interconversion is likely to proceed preferentially through TS₃-ht. The greater stability of oNT with respect to the *aci*-nitro tautomers can be attributed to the loss of cyclic delocalization in the latter (Scheme 3.1). There is a relatively large barrier (2.17 eV) for oNT to *anti*-Z isomer conversion on the ground state, while the barrier for the reverse process (0.22 eV) is small.

The vertical excitation energies and oscillator strengths of the lowest excited states of oNT are presented in Table 3.1 and the orbitals characterizing the transitions are shown in Figure 3.5. The CASPT2 values are in good agreement with the EOM-CCSD values, which reaffirm that the selected active space for the former method is appropriate for the current study. The energies of the states are very close to those of nitrobenzene (Table 3.2). This is consistent with the similar absorption spectrum of oNT [39, 61] and nitrobenzene [62, 63], and is expected because the additional methyl substitution in oNT does not significantly alter the electronic structure of the frontier orbitals.

Based on the calculated vertical excitation energies and oscillator strengths, the weak intensity bands of the oNT absorption spectrum [39] between 3.3 and 4.4 eV can be assigned to $n\pi^*$ and $\pi\pi^*$ transitions with low oscillator strengths. The lowest intense band, which is around 4.9 eV can be assigned to the S_4 state with large oscillator strength, consistent with previous assignments for oNT as well as nitrobenzene [39, 64]. The S_4 state of oNT has charge transfer character and involves a transition from the π orbital localized on the benzene ring (π_4 in Figure 3.5) to the π^* orbital localized on the nitro group (π_2^* in Figure 3.5). The

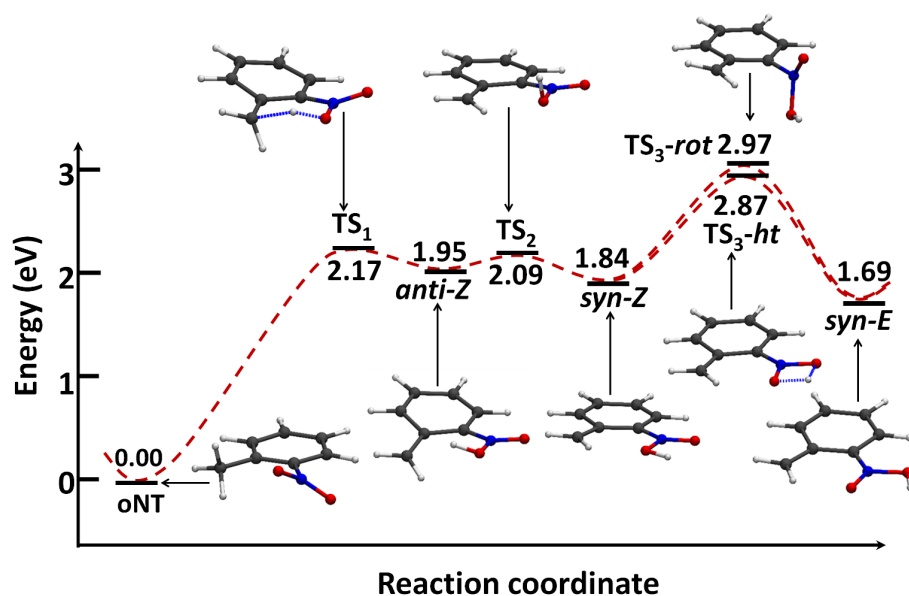


Figure 3.4: Relative energies of oNT isomers on the ground state and barriers for their interconversion at the MP2/cc-pVDZ level of theory. The interconversion paths are shown schematically with dashed lines.

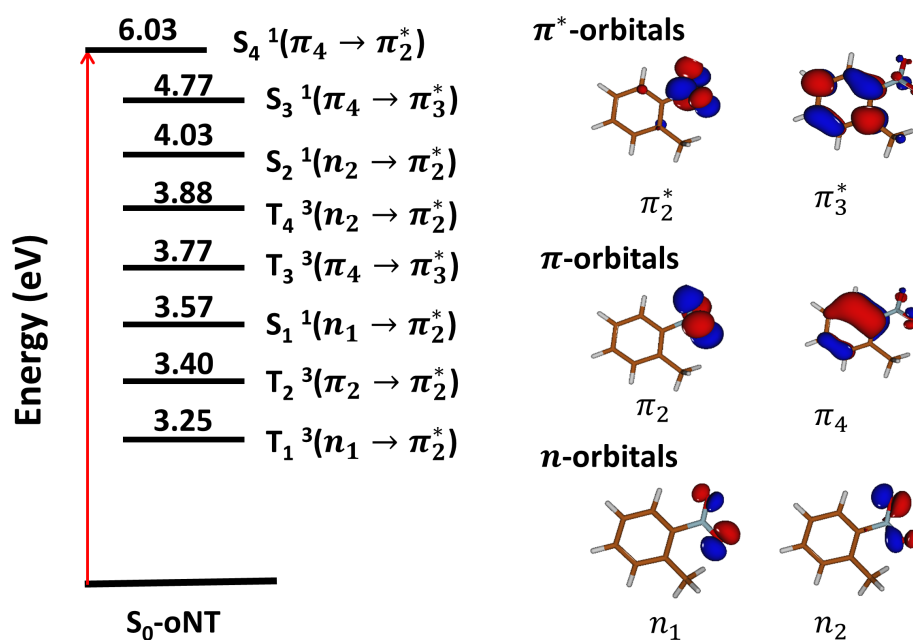


Figure 3.5: CASPT2/cc-pVDZ vertical excitation energies of the lowest few electronic excited states of oNT and the orbitals characterizing these states.

Table 3.1: Vertical excitation energies (ΔE) and oscillator strengths (f) for four lowest singlet and triplet excited states of oNT.

State	Nature	SS-CASPT2/cc-pVDZ		EOM-CCSD/cc-pVDZ		Exp (eV) ^b
		ΔE (eV)	f^a	ΔE (eV)	f	
T ₁	³ $n_1\pi_2^*$	3.25	—	3.39	—	
T ₂	³ $\pi_2\pi_2^*$	3.40	—	3.56	—	
S ₁	¹ $n_1\pi_2^*$	3.57	0.003	4.06	0.006	3.7
T ₃	³ $\pi_4\pi_3^*$	3.77	—	3.94	—	
T ₄	³ $n_2\pi_2^*$	3.88	—	4.23	—	
S ₂	¹ $n_2\pi_2^*$	4.03	0.000	4.54	0.000	
S ₃	¹ $\pi_4\pi_3^*$	4.77	0.010	4.93	0.013	4.1
S ₄	¹ $\pi_4\pi_2^*$	6.03	0.034	5.99	0.147	4.9

^aOscillator strength values computed at CASSCF method.^bExperimental data is for nitroethylene from Reference [39]**Table 3.2:** Comparison of vertical excitation energies (ΔE) between *ortho*-nitrotoluene and nitrobenzene at the EOM-CCSD/cc-pVDZ level of theory.

State	Nature	<i>Ortho</i> -nitrotoluene		Nitrobenzene	
		ΔE (eV)	f^a	ΔE (eV)	f
T ₁	³ $n\pi^*$	3.39	—	3.35	—
T ₂	³ $\pi\pi^*$	3.56	—	3.73	—
S ₁	¹ $n\pi^*$	4.06	0.0064	4.07	0.0000
T ₃	³ $\pi\pi^*$	3.94	—	3.76	—
T ₄	³ $n\pi^*$	4.23	—	4.64	—
S ₂	¹ $n\pi^*$	4.54	0.0002	4.54	0.0001
S ₃	¹ $\pi\pi^*$	4.93	0.0128	4.96	0.058
S ₄	¹ $\pi\pi^*$	5.99	0.1474	5.91	0.2177

lowest intense band of nitrobenzene has been analogously assigned to a $\pi\pi^*$ charge transfer transition by several authors [63, 65, 66]. Note that there is a fairly large difference (about 1.1 eV) between our calculated vertical excitation energy and the experimental peak maximum for this state. The experimental number is from a spectrum obtained in tetrahydrofuran (THF) [39]. On the basis of a study of peak shifts of nitrobenzene in different solvents [63], we can estimate that a solvent with the polarity of THF can possibly decrease the absorption frequency with respect to the gas phase by about 0.3 eV, suggesting that the gas phase absorption peak might be around 5.2 eV. The discrepancy between theory and experiment still remains. The EOM-CCSD/cc-pVDZ value of vertical excitation energy of the $\pi\pi^*$ charge transfer state in the related molecule nitrobenzene is about 6.0 eV [65], which is nearly the same as oNT. In the case of nitrobenzene, a detailed analysis of several electronic structure methods for calculating vertical excitation energy of this and some other states has shown a relatively large variation in energy values across methods, illustrating the challenges in describing the electronic structure of this molecule [65].

3.2.2 Excited state stationary points and crossings

On photoexcitation to the S_4 state, the molecule is expected to relax to the lowest singlet excited state as per Kasha's rule [67], following which the two triplet states ($^3n\pi^*$ and $^3\pi\pi^*$) lower in energy than S_1 can be expected to be important for the photo decay. We optimized the excited state minima on the four lowest singlet and two lowest triplet states starting from the Franck-Condon (FC) geometry. On the S_1 and T_1 states where ESIHT might be expected, we additionally optimized the *aci*-nitro products, *syn-Z* and *syn-E* isomers starting from the corresponding ground state geometries. The optimization starting with the *anti-Z* ground state geometry led to the *syn-Z* structure on both the excited states, suggesting that the *anti-Z* isomer, which is the least stable configuration on the ground state, may be nonexistent in the excited states. We also optimized the transition state geometries on the S_1 and T_1 states for the hydrogen transfer leading to the formation of the *syn-Z* isomer. These are denoted

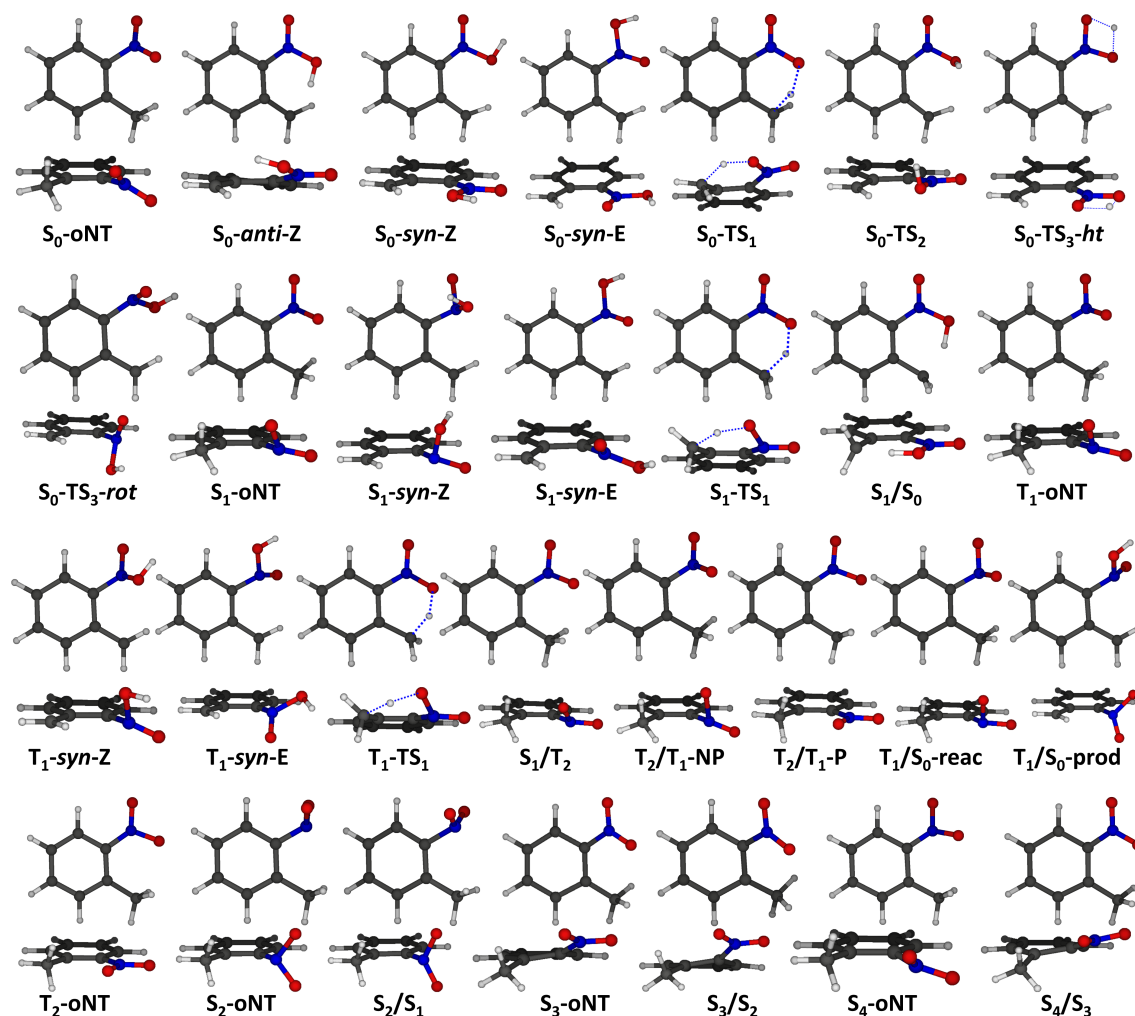


Figure 3.6: Structures of all the optimized critical points (stationary points and minimum energy crossing points) involved in the photo-tautomerization of oNT. Front and side view are given for clarity.

as S_1 -TS₁ and T₁-TS₁ respectively. All optimized geometries are shown in Figure 3.6, and their energies and structural parameters are presented in Table 3.3. Interestingly, on the T₁ state, the *aci*-nitro tautomers are found to be more stable than the reactant, unlike the S₁ or the ground state.

We optimized the CIs and singlet-triplet surface crossings between the four lowest singlet and two lowest triplet states. The searches for MECPs were started from two different geometries: one, the FC geometry and two, the minimum energy geometry of the higher energy state associated with the crossing. The optimized CIs S₄/S₃, S₃/S₂, S₂/S₁ and T₂/T₁,

and the minimum energy intersystem crossing geometries S_1/T_2 , S_1/T_1 and T_1/S_0 -Reac were obtained. The geometries of the MECPs were independent of the starting geometry except in the case of T_2/T_1 where starting from the FC geometry gave a non-planar CI (T_2/T_1 -NP), while starting from the T_2 minimum energy geometry (which is planar) gave a planar CI (T_2/T_1 -P).

We could not optimize the CI between S_1 and S_0 by starting from the FC or S_1 minimum geometries. Considering that the S_1 state has $n\pi^*$ nature, where there is a hole located on the n orbital of oxygen at the FC geometry, this state can be anticipated to be stabilized as the hydrogen (carrying an electron) moves towards the oxygen atom. This movement away from the FC geometry would destabilize the ground state of oNT and can lead to a CI. So, we started the CI optimization at the transition state geometry between oNT and S_0 -*anti-Z* isomer on the ground state where the hydrogen is partially transferred to the oxygen atom, and successfully obtained the S_1/S_0 CI. The T_1 has the same spatial character as S_1 and therefore a similar procedure was used to find another MECP between T_1 and S_0 , namely T_1/S_0 -Prod.

The SOC values for the singlet-triplet MECPs were calculated to evaluate their importance in molecular deactivation through intersystem crossing (ISC) (Table 3.4). Because of the relatively small magnitude of SOC at S_1/T_1 , the intersystem crossing from S_1 directly to T_1 is unlikely to be efficient. Moreover, this crossing involves a large geometrical distortion ($N^{11}-O^{13} = 1.68$) making it unlikely to be accessed. So, we did not consider the S_1/T_1 any further in the decay pathways. The low SOC for S_1/T_1 is consistent with El-Sayed's rule according to which the intersystem crossing between states having the same character is not efficient [68].

The S_1 and T_1 states have $n\pi^*$ nature implying a decrease of the π -bond order of the NO_2 group with respect to the ground state and a change in hybridization of nitrogen from sp^2 to sp^3 . The hydrogen transfer is driven by the interaction of the electron-carrying hydrogen with the hole on the n orbital of oxygen, as alluded to earlier. Consequently, the

Table 3.3: Geometrical parameters and relative energies of critical points (minima, transition state and MECPs) on the oNT potential energy surfaces.

Structure	C ² N ¹¹ O ¹² O ¹³ (deg)	O ¹³ N ¹¹ O ¹² (deg)	C ¹⁴ -H ¹⁶ (Å)	O ¹³ -H ¹⁶ (Å)	N ¹¹ -O ¹³ (Å)	N ¹¹ -O ¹² (Å)	C ² -N ¹¹ (Å)	Energy (eV) ^a
Minima								
FC	178.6	125.4	1.1	2.62	1.24	1.23	1.48	0.0
S ₀ - <i>anti</i> -z	177.2	114.7	2.02	0.99	1.40	1.22	1.38	1.95
S ₀ - <i>syn</i> -Z	179.0	114.4	3.72	0.97	1.41	1.23	1.32	1.84
S ₀ - <i>syn</i> -E	179.9	114.7	4.68	0.97	1.43	1.22	1.32	1.69
S ₁ -oNT	140.7	109.7	1.11	2.62	1.46	1.23	1.42	2.85
S ₁ - <i>syn</i> -Z	115.7	101.7	3.93	0.98	1.44	1.39	1.44	4.18
S ₁ - <i>syn</i> -E	168.5	117.0	4.69	0.97	1.45	1.22	1.39	4.38
S ₂ -oNT	118.8	108.8	1.08	3.49	1.36	1.36	1.45	4.41
S ₃ -oNT	179.3	123.8	1.08	2.64	1.21	1.21	1.41	4.68
S ₄ -oNT	159.3	106.7	1.08	2.62	1.30	1.28	1.30	5.33
T ₁ -oNT	139.1	111.5	1.11	2.69	1.35	1.29	1.43	2.69
T ₁ - <i>syn</i> -Z	139.3	116.3	3.88	0.97	1.47	1.22	1.43	2.29
T ₁ - <i>syn</i> -E	143.4	116.7	4.64	0.97	1.45	1.23	1.43	2.28
T ₂ -oNT	179.6	108.1	1.08	2.53	1.33	1.24	1.39	2.95
Transition states								
S ₀ -TS ₁	173.6	118.8	1.50	1.13	1.32	1.24	1.40	2.17
S ₀ -TS ₂	178.2	115.9	2.90	0.98	1.43	1.22	1.38	2.09
S ₀ -TS ₃ -rot	152.3	118.1	3.47	0.98	1.42	1.23	1.46	2.97
S ₀ -TS ₃ -ht	180	104.4	4.03	1.26	1.31	1.32	1.34	2.87
T ₁ -TS ₁	147.0	113.8	1.47	1.25	1.48	1.22	1.41	3.29
S ₁ -TS ₁	149.8	112.9	1.31	1.26	1.45	1.22	1.41	3.34
Minimum energy crossing points								
S ₄ /S ₃	178.4	119.8	1.09	2.58	1.26	1.22	1.38	5.18
S ₃ /S ₂	178.8	123.7	1.09	2.69	1.21	1.21	1.42	4.87
S ₂ /S ₁	124.7	128.7	1.08	3.26	1.32	1.32	1.49	3.87
S ₁ /S ₀	179.9	115.6	1.61	1.06	1.39	1.21	1.40	3.23
S ₁ /T ₂ (³ ππ*)	141.3	105.7	1.11	2.53	1.45	1.23	1.41	2.89
S ₁ /T ₁ (³ nπ*)	179.4	111.6	1.1	2.41	1.68	1.20	1.40	3.18
T ₂ /T ₁ -NP	131.1	115.1	1.11	2.85	1.58	1.20	1.42	2.90
T ₂ /T ₁ -P	179.8	105.5	1.11	2.52	1.33	1.24	1.38	2.79
T ₁ /S ₀ -Reac	119.2	94.5	1.11	2.76	1.38	1.31	1.44	2.71
T ₁ /S ₀ -Prod	138.2	116.7	4.53	0.95	1.46	1.23	1.44	2.35

Table 3.4: Spin-orbit coupling values evaluated at the CASSCF/6-31G(d,p) level of theory at different singlet-triplet MECPs and their role in the photo-decay.

Crossing point	Spin-orbit coupling (cm ⁻¹)	Major role in decay
S ₁ /T ₂ (¹ n ₁ π ₂ [*] / ³ π ₂ π ₂ [*])	30.97	Yes
S ₁ /T ₁ (¹ n ₁ π ₂ [*] / ³ n ₁ π ₂ [*])	0.48	No
T ₁ /S ₀ -Reac	20.64	Yes
T ₁ /S ₀ -Prod	6.12	Yes (Slower ISC expected)

most significant geometrical parameters for oNT deactivation are N¹¹–O¹³ bond elongation, hydrogen transfer coordinate (C¹⁴–H¹⁶ distance) and pyramidalization ($\delta(\text{C}^2\text{N}^{11}\text{O}^{12}\text{O}^{13})$). The values of these parameters are presented in Table 3.3. These structures have certain similarities to the corresponding structures of nitrobenzene [65, 69, 70], but the presence of the methyl group in oNT which breaks the C_{2v} symmetry of the molecule and provides a possibility for hydrogen transfer to oxygen, leads to major differences. For instance, the minimum energy geometry on the S₁ state of oNT (denoted as S₁-oNT) has a large difference between the N¹¹–O¹² and N¹¹–O¹³ bond lengths, and the NO₂ group is significantly out of the plane of the aromatic ring and pyramidalized as compared to nitrobenzene. Similarly the optimized S₁/S₀ CI has a major distortion along the C¹⁴–H¹⁶ hydrogen transfer coordinate, but this coordinate obviously does not exist in nitrobenzene. Moreover, the *n*π* triplet state (T₁) plays an important role in oNT deactivation as discussed below unlike in nitrobenzene [65, 70].

Accessibility of MECPs

The results in the previous subsections suggest that oNT in a higher excited state (S₄, S₃ or S₂) can relax to the minimum energy geometry on the lowest singlet excited state through a series of CIs, the last of which is S₂/S₁. The corresponding LIIC path is barrierless (Figure 3.7). A similar pathway has been suggested for nitrobenzene [65]. This pathway and subsequent ones for deactivation, which are discussed below, are shown schematically in Figure 3.8.

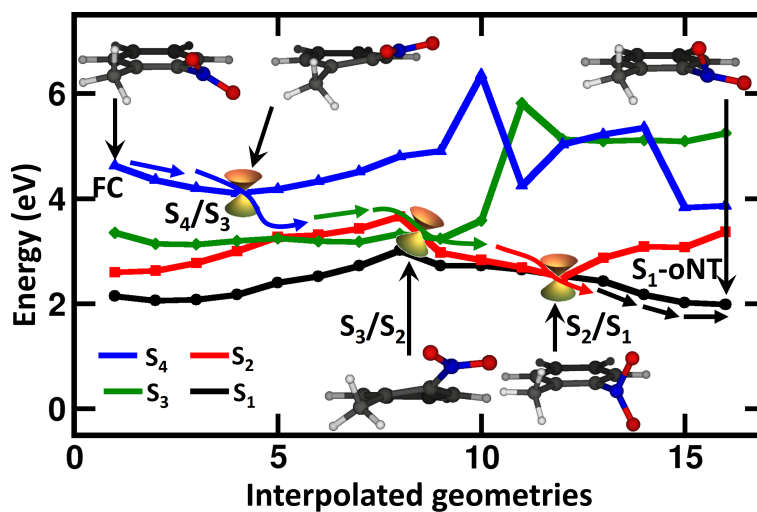


Figure 3.7: LIIC plots showing the deactivation of the S_4 state starting at the FC geometry, going through the S_4/S_3 , S_3/S_2 , S_2/S_1 optimized CIs, and ending at the S_1 minimum energy geometry (S_1 -oNT). The deactivation path is barrierless and marked with arrows. All energies are calculated at CASPT2/6-31G(d,p) level of theory.

From S_1 -oNT there are three branches, two singlet branches, one through S_1/S_0 and another through S_1 -TS₁, and a triplet branch through S_1/T_2 . Of the three critical points involved in the branching, the S_1/T_2 is geometrically closer to S_1 -oNT than S_1/S_0 and S_1 -TS₁ (Figure 3.9 and Table 3.3). Furthermore, S_1/T_2 is lower in energy than S_1/S_0 and S_1 -TS₁. Thus S_1/T_2 is likely to be more easily accessed than the latter points that lead to singlet deactivation. Note that the LIIC path from S_2/S_1 to S_1/S_0 (Figure 3.10) shows a barrier which is greater than the energy of S_2/S_1 and thus access to the S_1/S_0 directly is unlikely. Instead, the path through the S_1 minimum has a smaller barrier (Figure 3.11), and the energy of the highest point on this path is in fact lower than the energy of the S_2/S_1 CI. The path on the triplet branch from S_1 -oNT to S_1/T_2 is virtually barrierless (Figure 3.12, parts (a) and (b)).

From S_1/T_2 the molecule reaches the T_2 state after which it can access CIs, T_2/T_1 -NP and T_2/T_1 -P through which it relaxes to T_1 -oNT, the equilibrium geometry on the T_1 state (Figure 3.12, parts (a) and (b) respectively). The former CI is geometrically closer while the latter is slightly more energetically favorable (Figure 3.13 and Table 3.3). From T_1 -oNT, there are two branches: One, to the T_1/S_0 -Reac MECP leading to the ground state oNT

3.14).



reduce the overall yield of oNT photoisomerization.

Hydrogen transfer can occur on the T_1 state. The T_1 and S_0 LIIC curves from T_1 -oNT to the T_1 *aci*-nitro isomer along with the singly occupied valence molecular orbitals (SOMOs) at a few points on the path are shown in Figure 3.15. The triplet state at the reactant minimum (T_1 -oNT) is characterized by SOMOs n_1 and π_2^* . The n_1 is a non-bonding oxygen orbital while the π_2^* is delocalized on the nitro group of the molecule. There is a hole located on the n_1 orbital of oxygen with respect to the ground state, which favors the hydrogen atom transfer from C^{14} to O^{13} . This is consistent with a lower barrier for transfer on the excited state than that on the ground state (0.598 eV on T_1 versus 2.17 eV on S_0). During the process, the n_1 SOMO on the oxygen combines with the s orbital of hydrogen to give a O^{13} -H σ

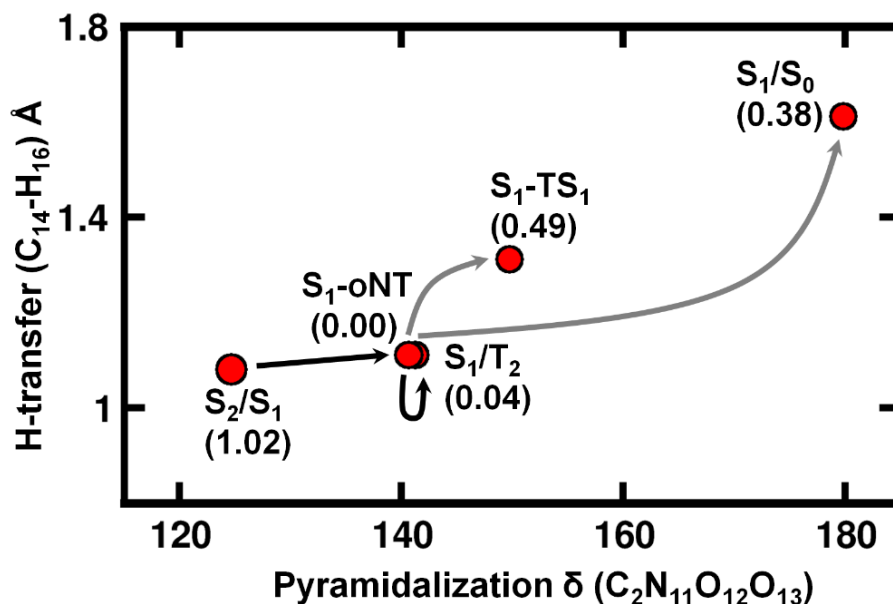


Figure 3.9: Critical points involved in the singlet-triplet branching represented in the space of two significantly changing geometrical coordinates, pyramidalization and hydrogen transfer. Relative energies (eV) computed at the CASPT2/6-31G(d,p) level of theory are given in parenthesis. Black and grey arrows schematically represent the major and minor paths respectively.

orbital, while the C^{14} -H σ bond breaks leaving a SOMO at C^{14} which is primarily of p-orbital nature. In the hydrogen transferred species (T_1 -*syn-Z*) the SOMOs are located at two distinct parts of the molecule, one on the nitro group and the other on the methylene group. This bi-radical is more stable than the T_1 -oNT presumably because of the decreased repulsion between the valence electrons occupying spatially distant SOMOs. The path for the decay of the intermediate to the ground state *aci*-nitro product is through the T_1/S_0 -Prod MECP, which has a small barrier for access.

3.2.3 Photo-decay mechanism

Our calculations, in combination with the femtosecond spectroscopy experiments of Gilch and coworkers [39] provide a detailed mechanistic picture of the photo-decay of oNT. Light of 258 nm used in the experiment excites oNT to the S_4 state and from this state the molecule relaxes to the lowest singlet excited state via a series of CIs. Relaxation can be expected to

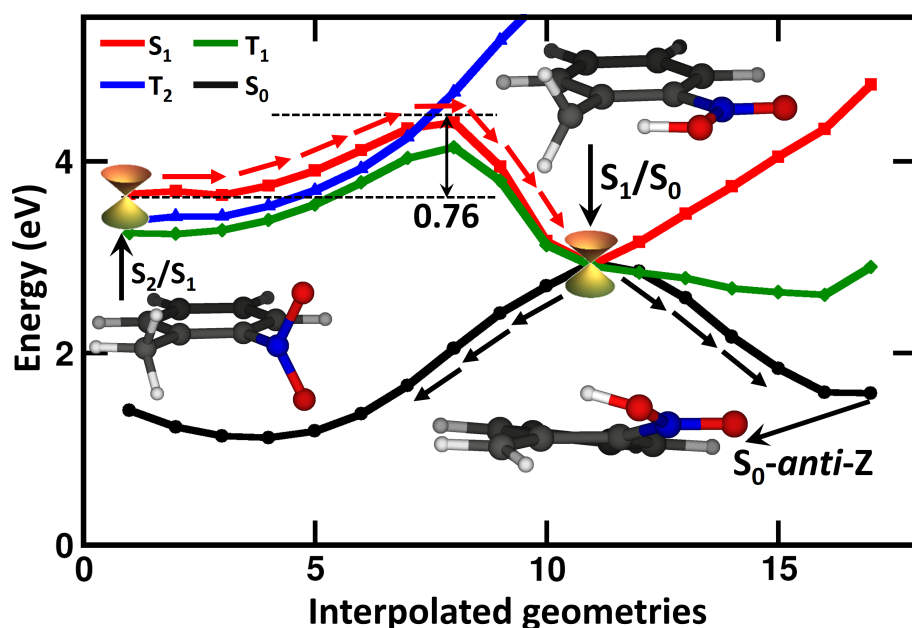


Figure 3.10: LIIC plots showing the deactivation through the singlet pathway starting at S_2/S_1 CI, going through the S_1/S_0 CI, and ending at the S_0 -anti-Z product. The deactivation path is marked with arrows. All energies are calculated at CASPT2/6-31G(d,p) level of theory.

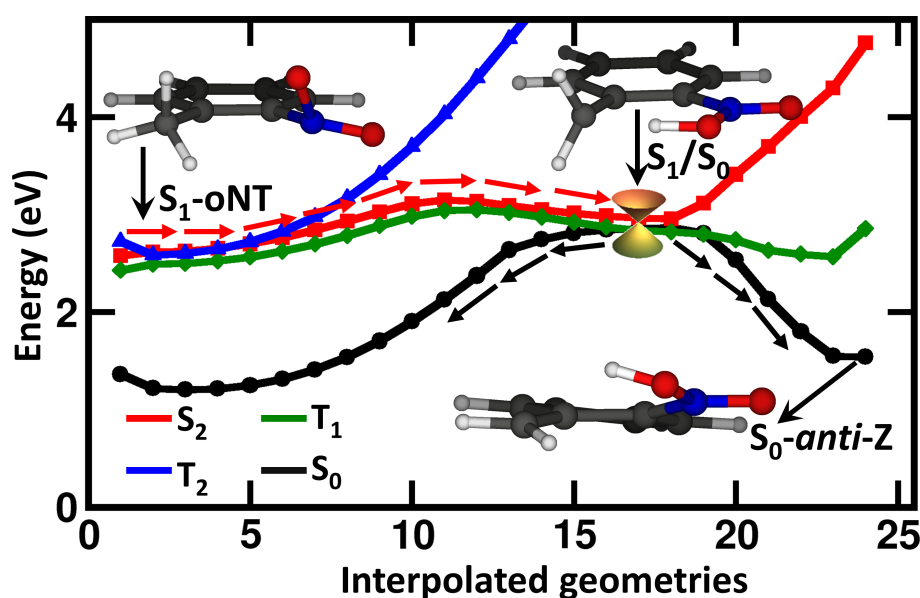


Figure 3.11: LIIC plots showing the deactivation through the singlet pathway starting at the S_1 minimum energy geometry (S_1 -oNT), going through S_1/S_0 optimized CIs and ending at the S_0 -anti-Z product. The deactivation path is marked with arrows. All energies are calculated at CASPT2/6-31G(d,p) level of theory.

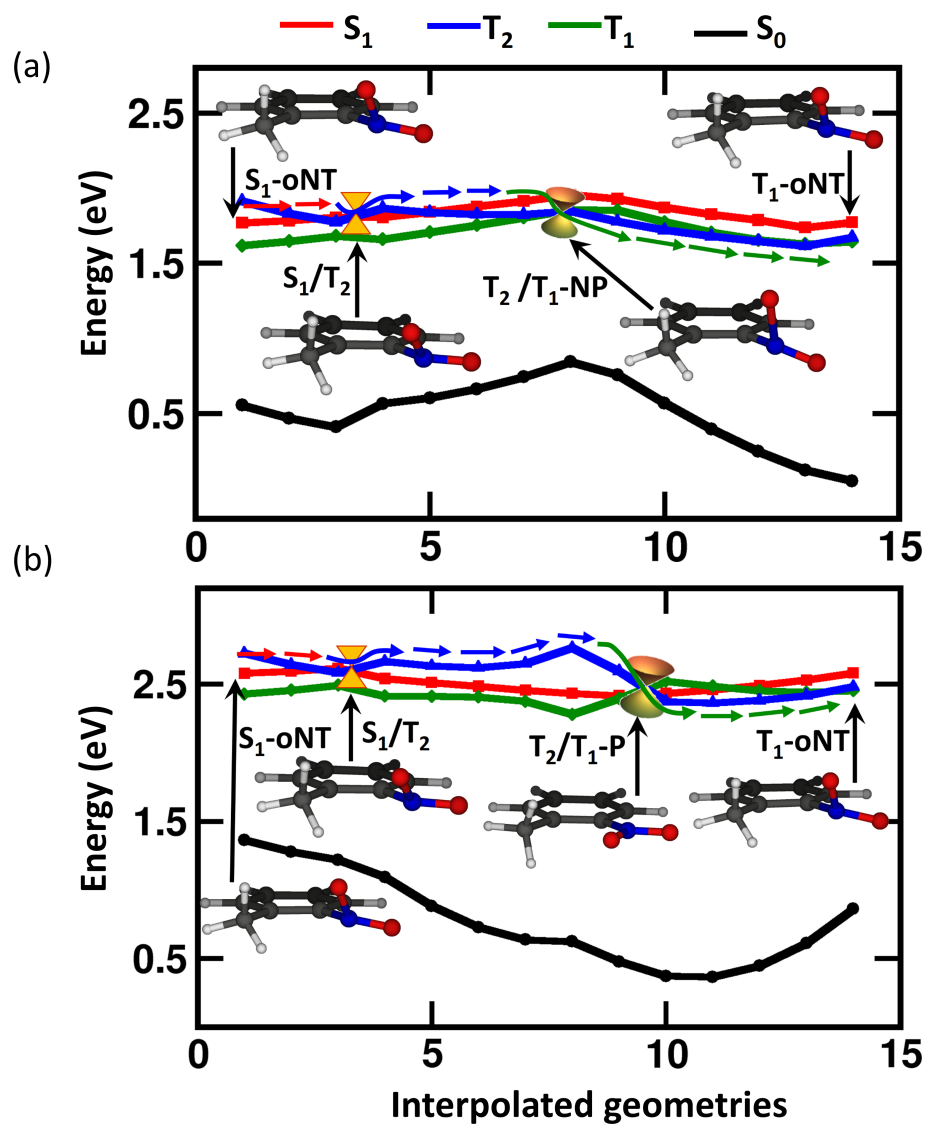


Figure 3.12: LIIC plots showing the deactivation through the triplet pathway starting at the S_1 minimum energy geometry (S_1 -oNT) and ending at the T_1 minimum energy geometry (T_1 -oNT). There are two paths marked with arrows and shown in (a) and (b). Both paths go through the S_1/T_2 MECP and then bifurcate. One goes through a non-planar T_2/T_1 -NP MECP (a), and the other through a planar T_2/T_1 -P MECP (b). All energies are calculated at CASPT2/6-31G(d,p) level of theory.

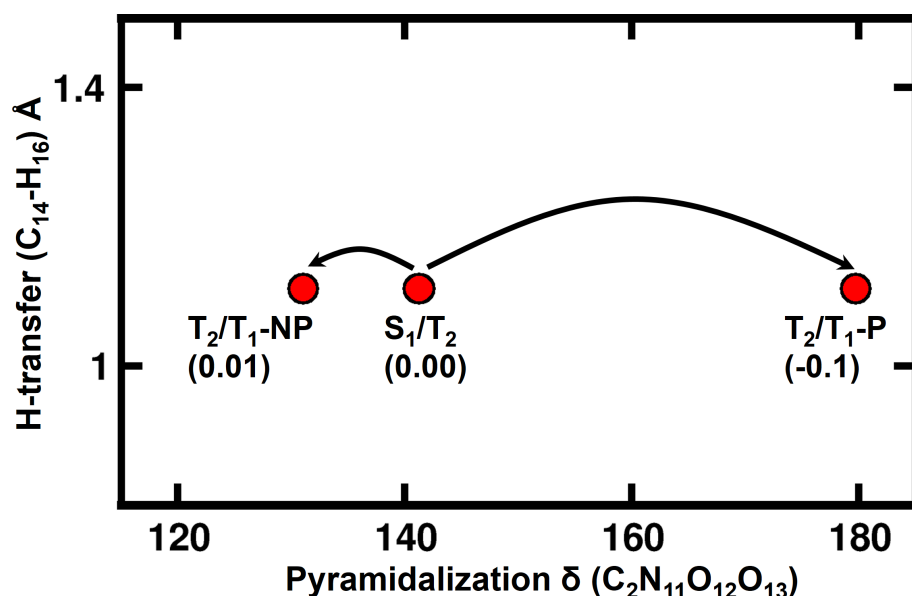


Figure 3.13: Critical points involved in the decay pathway from the T_2 to the T_1 state via T_2/T_1 -NP and T_2/T_1 -P represented in the space of the significantly changing geometrical coordinates, pyramidalization and hydrogen transfer. Relative energies (eV) calculated at CASPT2/6-31G(d,p) level of theory are given in parenthesis.

be ultrafast due to the barrierless deactivation pathway and the existence of CIs, S_4/S_3 , S_3/S_2 and S_2/S_1 , close to the minimum energy configurations on S_4 , S_3 and S_2 states respectively (Figures 3.7 and 3.6). This corresponds to the ~ 100 fs decay process that has been observed [39].

From the S_1 minimum configuration, the oNT can evolve either towards the S_1/T_2 MECP, S_1/S_0 CI or S_1 -TS₁. The S_1/T_2 MECP is structurally and energetically very close to the S_1 minimum unlike S_1/S_0 and S_1 -TS₁, and given the large SOC at the S_1/T_2 MECP, the triplet path can be expected to have a higher branching ratio than the singlet paths. Fluorescence from the S_1 minimum is unlikely to be significant given the low S_1 - S_0 oscillator strength (0.0002 using CASSCF) at the S_1 minimum energy geometry. The decay of the S_1 state through ISC is likely to correspond to the observed ~ 1 ps process [39]. The two singlet paths involve accessing the S_1/S_0 CI and the S_1 -TS₁, both of which have comparable barriers, much greater than the barrier to access S_1/T_2 . Excess energy from the electronic excitation may allow these singlet processes to occur although with a smaller branching ratio than the

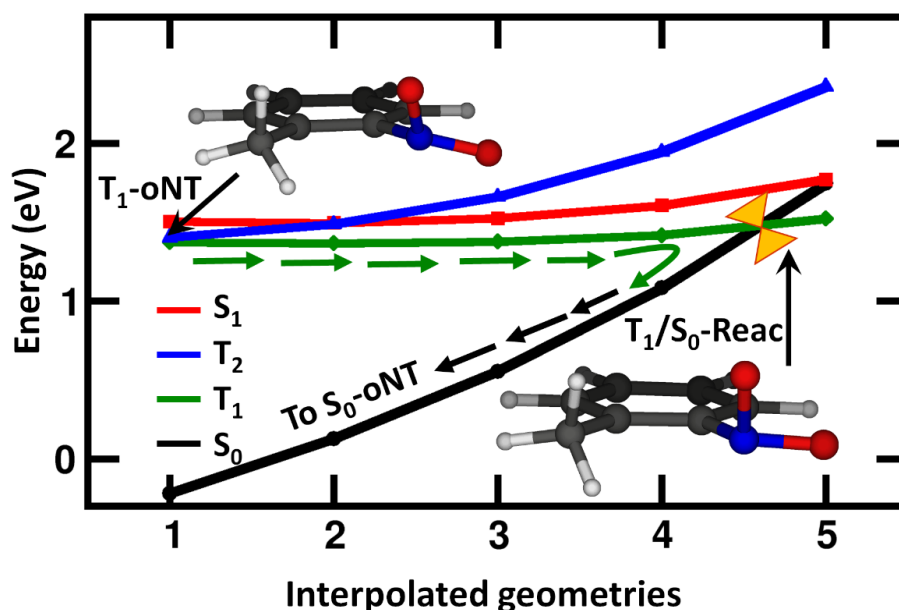


Figure 3.14: LIIC plots showing the deactivation of the lowest triplet state starting at the T_1 minimum energy geometry (T_1 -oNT) and going to the T_1/S_0 -Reac MECP. This path leads to regeneration of the ground state oNT and thereby a reduction of the photoisomerization yield. The deactivation path is nearly barrierless and marked with arrows. All energies are calculated at CASPT2/6-31G(d,p) level of theory.

triplet processes. The S_1/S_0 CI can be expected to give the *anti-Z aci*-nitro product based on its close geometrical proximity to this product. The S_1 -*syn-Z* isomer can also be formed through S_1 - TS_1 and is expected to relax to the ground state *aci*-nitro products via the S_1/S_0 CI. Both these processes may correspond to the ~ 10 ps timescale observed in the experiment and is larger than the decay of S_1 through the triplet channel. The alternative assignment of the ~ 10 ps timescale to vibrational relaxation as suggested by Gilch and coworkers [39] is also possible, but cannot be established by the present calculations.

On the triplet path, from S_1/T_2 the molecule can decay to the lowest triplet state via either T_2/T_1 -NP or T_2/T_1 -P. From both T_2/T_1 -NP and T_2/T_1 -P, the molecule can relax to T_1 -oNT, the reactant-like local minimum on the T_1 state (Figure 3.12). Close to the T_1 -oNT, lies the slightly higher energy T_1/S_0 -Reac MECP with significant SOC through which the molecule can relax to ground state oNT (Figure 3.14). This path reduces the yield of the *aci*-nitro isomer in the oNT photo-tautomerization. On the T_1 state, the *aci*-nitro isomers *syn-Z* and

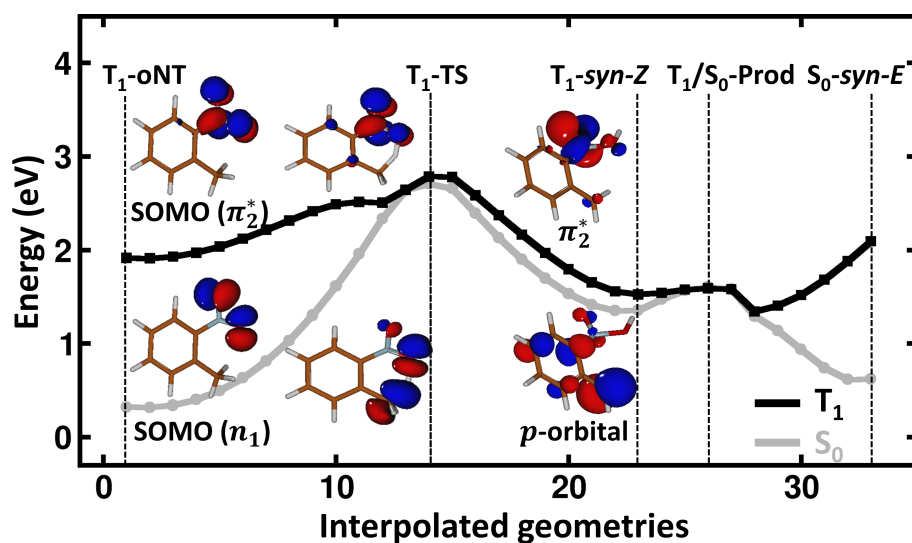


Figure 3.15: LIIC plots showing the hydrogen transfer on the lowest triplet state starting at the T_1 minimum energy geometry (T_1 -oNT), going through a transition state to form the intermediate T_1 -*syn-Z* *aci*-nitro isomer, and eventually forming the S_0 -*syn-E* product through the T_1/S_0 -Prod MECP. The singly occupied molecular orbitals (SOMO) which characterize the triplet states are shown along the path. All energies are calculated at CASPT2/6-31G(d,p) level of theory.

syn-E are more stable than the reactant (Figure 3.15 and 3.16). Intramolecular vibrational energy redistribution and vibrational cooling can temporarily trap the molecule in the T_1 -oNT local minimum and thermal equilibration can drive the *aci*-nitro product formation. A similar process on the triplet state has been suggested in the case of *ortho*-nitrobenzylacetate [47]. Consequently, a significant fraction of the molecules on the T_1 state end up as the *aci*-nitro isomers. From here, the molecule reaches the ground state *aci*-nitro isomers through the T_1/S_0 -Prod MECP, which is energetically higher than the T_1 *aci*-nitro isomers (Figure 3.15) and where the SOC value has a modest value of 6.12 cm⁻¹. Therefore, a time lag is expected between the formation of the *aci*-nitro isomers on the triplet state and their decay, and can be assigned to the observed 430 ps and 1500 ps decay lifetimes [39]. This insightful assignment was made by Gilch and coworkers who suggested that a bi-radical intermediate, which we identify as the *aci*-nitro isomers on the triplet state, is present.

The *aci*-nitro product that is produced through the singlet channel is expected to be primarily of the *anti-Z* *aci*-nitro form. The *anti-Z* and *syn-Z* isomers can interconvert (about

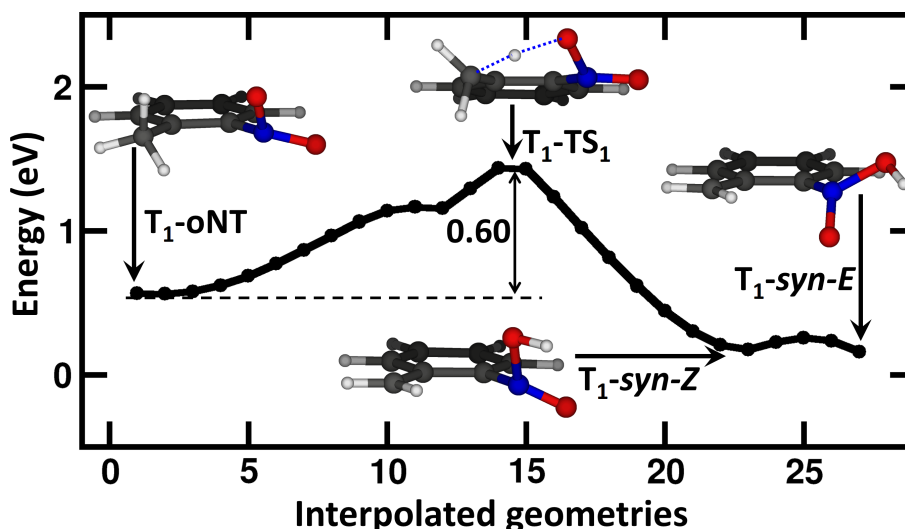


Figure 3.16: LIIC plot showing the hydrogen transfer on the lowest triplet state starting at the T_1 minimum energy geometry (T_1 -oNT) going through a transition state to form the T_1 -syn-Z and T_1 -syn-E *aci*-nitro isomers. All energies are calculated at CASPT2/6-31G(d,p) level of theory.

0.1 eV barrier) and both of these can back tautomerize to the more stable oNT on the ground state by crossing a barrier of about 0.2 eV. This back tautomerization has been attributed to be the cause of the discrepancy [39] in measured yields across different studies [39, 32]. Unlike the singlet channel, the *aci*-nitro product formed through the triplet channel can be of both *Z* and *E* forms. The ground state *E* product is more stable than the *Z* products and is kinetically trapped with a 1.2 eV barrier. This appears to be the dominant contributor to the net yield after considering the loss of *Z* product by back tautomerization.

The role of solvent in the photo-tautomerization of oNT has not been considered in the present study. Based on the literature, it appears that the solvent, as long as it is aprotic, may not significantly affect the excitation dynamics: Gilch and coworkers have shown the transient absorption behavior of oNT to be very similar in two different aprotic solvents, tetrahydrofuran and acetonitrile [39]. Mewes and Dreuw, based on calculations with and without solvent on *ortho*-nitrobenzylacetate, a related molecule, have shown that the ESIHT in this molecule is independent of solvent [47], although in another molecule namely *ortho*-nitrophenylacetate they found the solvent's influence to be significant [71]. A protic solvent,

which would induce protonation of oNT can be expected to interfere with the ESIHT and requires further experimental and theoretical investigation.

3.3 Summarizing Remarks

Multiple pathways for photo-tautomerization and energetic deactivation of oNT, a model system for nitrobenzyl type photo-protecting groups, have been studied (Figure 3.8). The MECPs between excited states have been optimized using the CASSCF method and potential energy curves obtained using the CASPT2 method. Considerations like relative energies of MECPs and extent of geometrical distortion to access them, barriers along the path, and SOC value at singlet-triplet MECPs have been used to suggest the relative importance of different paths. A greater yield of the photo-tautomerization product through the triplet channel compared to the singlet channel is proposed. This is due to the presence of the S_1/T_2 MECP with large SOC near the S_1 minimum, which is the point of bifurcation of the singlet and triplet channels. Efficient intersystem crossing through S_1/T_2 brings oNT to the T_2 state after which it reaches T_1 via two optimal T_2/T_1 CIs. On the long lived lowest triplet state, T_1 -oNT converts to the lower energy T_1 *syn-Z* and *syn-E aci*-nitro isomers by equilibration before forming the ground state *aci*-nitro isomers. In contrast, formation of *aci*-nitro isomers through the singlet pathway requires accessing the S_1/S_0 CI and S_1 -TS₁ geometries, which are relatively distant from the S_1 minimum. Moreover, the S_1/S_0 CI and S_1 -TS₁ have higher energy than the S_1/T_2 MECP.

Šolomek et al. have suggested that most of the S_1 state population is transferred to the T_1 state in oNT because of the high barrier for ESIHT on the S_1 state, based on their comparative analysis of four different oNB derivatives [48]. However, the molecule because of the initial photoexcitation, is expected to possess excess energy whereby the effective barrier to access S_1 -TS₁ and S_1/S_0 CI can be expected to be lower than the simple energy difference between these points and the S_1 reactant minimum. The effective barrier will actually depend on

the rate of energy redistribution along coordinates orthogonal to the reaction coordinate as the wavepacket with excess energy evolves. Our study provides an alternative explanation for the greater contribution of the triplet path to the yield in oNT even if it turns out that there is no effective barrier on the S_1 state: The triplet path is favored because accessing the S_1/T_2 MECP from the S_1 minimum energy geometry is structurally and energetically more favorable than accessing the S_1/S_0 CI or S_1-TS_1 . The S_1/T_2 MECP is geometrically close and energetically similar to the S_1 reactant minimum, and the SOC between the two states is large, implying large ISC. Studies on other oNB derivatives, where MECs are calculated, as well as dynamical calculations can provide a general understanding of singlet-triplet branching in oNB compounds.

The photo-isomerization yield of oNT is small. Moreover, the yield of the most stable *aci*-nitro product, namely the *syn-E* isomer, which is kinetically trapped and insulated from reactant regeneration, is a fraction of the total *aci*-nitro yield [39]. The primary mechanism for quenching of the excitation energy and total yield reduction appears to be reactant regeneration through the T_1/S_0 -Reac MECP on the triplet pathway. Interestingly, at the same time, the triplet pathway appears to be the dominant contributor to the formation of the most stable *syn-E* isomer. This is in contrast with the *Z aci*-nitro isomers formed through both singlet and triplet channels, which can undergo reactant regeneration on the ground state by crossing a small barrier.

The present study assists in interpreting the oNT photodecay experiments of Gilch and coworkers [39]. Our calculations are largely consistent with the assignment of lifetimes of the different processes by these authors. The different lifetimes of the singlet decay (1 ps) and product formation via the singlet channel (10 ps) may be due to decay of S_1 through ISC and delayed product formation through the higher energy S_1/S_0 CI and S_1-TS_1 . This interpretation is different from that proposed in the experimental paper for the 10 ps lifetime, and non-adiabatic dynamics calculations may resolve the discrepancy. The triplet bi-radical intermediate proposed in the experimental paper is confirmed and characterized

to be the *syn-Z* and *syn-E aci*-nitro isomers on the triplet state. In general, the results of this study which suggest a significant role of the triplet pathway in the photochemistry of oNT, emphasize the need to include such high-spin electronic states in ab initio studies of molecular photophysics and photochemistry. The study also highlights the importance of characterizing MECs between excited states to understand the mechanism of photochemical reactions.

Chapter 4

Photodissociation and Photoisomerization Mechanism of 1-Nitropropene, a Model for Nitro-aromatic High Energy Materials

Several nitro-containing compounds such as TNT (2,4,6-trinitrotoluene), RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) and HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocane) are high energetic materials (HEMs) in which the nitro group acts as the explosophore [72]. These HEMs are composed of relatively weak X-NO₂ (X = C, N, O) bonds which makes them thermally unstable, and have various applications such as military explosives, propellants and fuels. The decomposition processes in HEMs to produce various products along with the large amount of energy have been suggested to be triggered by the generation of a “hot spot”, a small region in the crystal, where the energy provided by the external stimulus (like impact, shock, friction and heat) is localized [73]. The formation of this hotspot has been shown to be associated with the electronic excited states and therefore multiple electronic states are expected to be involved in the decomposition process of HEMs [74–78]. The topology of

ground and excited state potential energy surfaces (PESs) of HEMs are hence essential to unveil the decomposition mechanism.

The thermal decomposition mechanism of HEMs have been studied extensively [79–84]. However, the experimental elucidation of the initial steps of decomposition on electronic excited states is quite challenging due to the ultrafast [85, 86] and highly exothermic nature of photodissociation. The large number of atoms in HEMs further creates a computational bottleneck in exploring the photochemical processes theoretically. In this regard, nitromethane (NM), a simple model system has been studied extensively [87–99]. Recently, in a study by Isegawa et al. [100], the photodissociation mechanism of NM on four lowest singlet states has been thoroughly investigated using theoretical methods. Due to the complexities involved in theoretically exploring the excited state potential energy surfaces, no other nitro-containing system has been studied at detailed atomic and electronic level.

NM because of its simplicity has some shortcomings in modelling the behavior of HEMs. Other nitro-containing molecules like nitrobenzene (NB) [64, 101–106] and *ortho*-nitrotoluene (oNT) [64, 103, 61, 107, 108] have also been explored, but not at the level of depth as NM. Several techniques such as resonance-enhanced multiphoton ionization, laser induced fluorescence [106], vacuum ultraviolet photo ionization [105], multimass ion imaging [64] and state selected direct current slice imaging [103] has been used to detect the photo-products. In a study by Ni and coworkers, the photodissociation dynamics of NB (at 193, 248 and 266 nm) and oNT (at 193 and 248 nm) have been investigated by both experimental and theoretical methods [64]. Using multimass ion imaging techniques, photo-product yields and their translational energy distributions have been determined. Though NO₂ was found to be the major photo-product, a significant fraction of NO with a branching ratio of $\sim 0.3 - 0.4$ was also reported. Interestingly, a bimodal distribution in the translational energy of NO product channel was seen and the higher energy component in the distribution was found to become smaller with increase in the photodissociation wavelength. This bimodal translation energy distribution indicates the presence of two different mechanisms for the

NO formation. In later work by Suits and coworkers on NB, consistent results for NB were obtained. The slow and fast product formation channels were proposed to be the roaming mediated isomerization from NB to its nitrite isomer followed by NO elimination in the ground state and isomerization involving the lowest triplet state, respectively [103]. Roaming reactions [109, 110] have been identified recently as a new class of reactions involved in the dissociation by demonstrating it in the several molecular systems such as formaldehyde [111, 112], NO₃ [113, 114] and nitromethane [99]. In roaming reactions, the molecule first forms near-dissociative radical fragments by a simple bond rupture. These radicals then roam about each other in a region of the PES which is flat before recombining to form closed-shell products. The triplet path mechanism for the formation of NO was further extensively investigated by Giussani and Worth using high level theoretical calculations [115].

The precise roles of the excited states, particularly the singlet excited states, in the photo-dissociation of NB and oNT is not well understood. High-level quantum chemical calculations are lacking, which is probably due to the computational difficulties involved in dealing with these relatively large molecules. Thus, the smaller molecules that are qualitatively similar in nature with the nitro aromatic compounds would be useful to understand their photodecomposition mechanisms. A smaller molecule having the essential molecular components of NB and oNT is 1-nitropropene(NP) and can be considered a model system to understand the photophysical and photochemical processes in NB and oNT. As shown in figure 4.1, the two possible geometrical isomers of NP namely, *trans*-NP and *cis*-NP represents the NB and the oNT molecules respectively. The *cis*-NP has already been applied as a model system to discern the thermal decomposition mechanism of 2,4,6-trinitrotoluene (TNT) [116, 117].

In the present study, the photophysical and photochemical processes of NP, the simplest model system for nitro-aromatic HEMs, have been studied in detail using multi-reference electronic structure methods. Our aim here is to provide a global mechanistic picture for the non-radiative decay processes in NP from its lowest optically bright electronic state

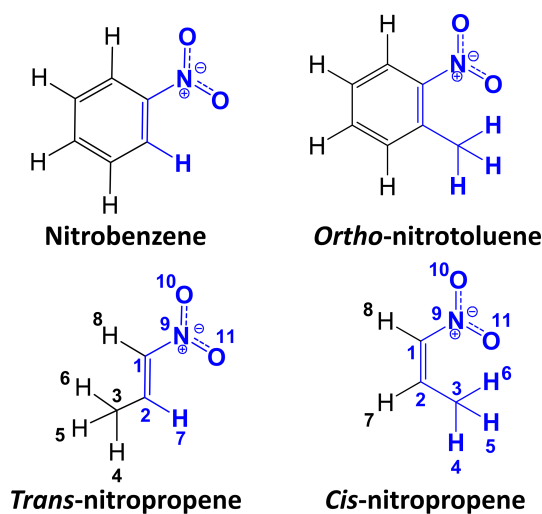


Figure 4.1: Structures of trans and cis isomers of 1-nitropropene as model systems for NB and oNT respectively. The blue color for the atoms has been used to show the similarity between the nitro aromatic molecule and the model system. The assigned atomic numbering has been used throughout the text

by exploring all the possible photodecay pathways in *trans* and *cis* isomers of NP. The photodissociation mechanism in both the isomers of NP might be expected to be similar. However in the case of *cis*-NP, due to the presence of methyl group adjacent to the NO₂ group, an additional excited state process, excited state intramolecular hydrogen transfer (ESIHT) from methyl to the oxygen of NO₂ group might compete with the photodissociation. Based on the experimentally observed major photo-products in the photochemical processes of nitro-compounds, multi photo-processes that are shown in Figure 4.2 have been explored in this study . We have optimized the minimum energy crossing points (MECPs) involving same spin multiplicity as well as multiple spin multiplicity electronic states, and the stationary points on all the relevant electronic states. The geometrical and energetic considerations, the barriers to access the critical points (minima, transition states and MECPs) and the spin-orbit coupling (SOC) values have been used to evaluate the importance of multiple photodecay pathways.

The rest of the chapter is organized as follows. The computational details are given in section 4.1. Results and discussion are presented in three subsection of section 4.2. The first

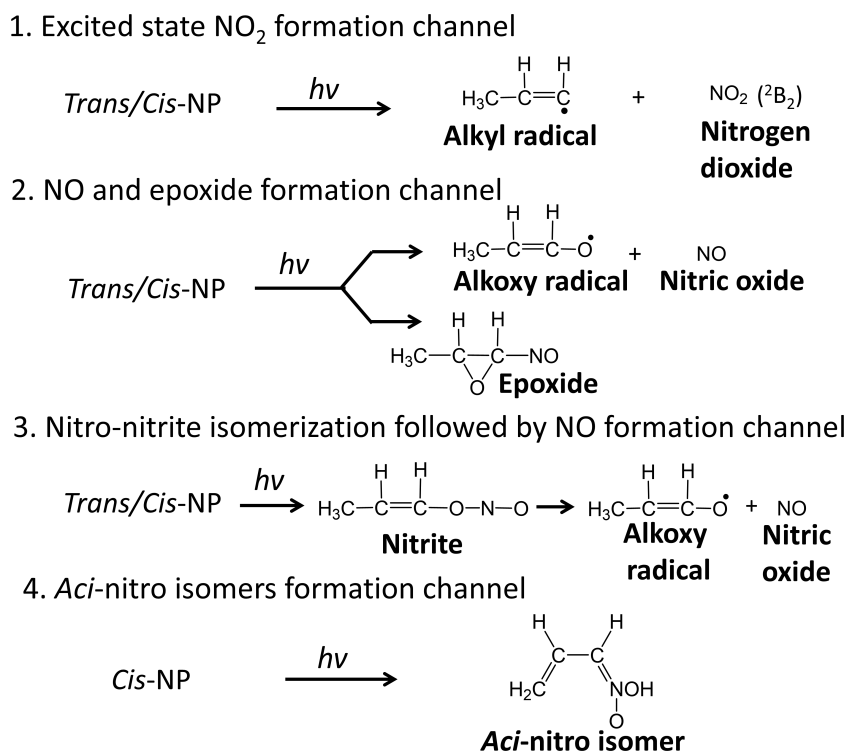


Figure 4.2: Various photochemical processes in *trans* and *cis* isomers of NP explored in this study

subsection deals with the ground state geometry and the vertical excitation energies. The optimized stationary points and the MECPs are described in the second subsection. In the final subsection, all the possible photodecay pathways in *trans* and *cis* isomers of NP are discussed. Summarizing remarks are presented in the section 4.3.

4.1 Computational Details

All the stationary points on the multiple potential energy surfaces and the minimum energy crossing points between electronic states were obtained with the CASSCF [19–21] method and the 6-31G(d,p) basis set. The vertical excitation energies were computed at the EOM-CCSD [55] and the state-specific CASPT2 (SS-CASPT2) [56] methods along with the cc-pVDZ basis set. The Franck-Condon geometry used for the vertical excitation calculations was obtained at MP2 [16] method along with the 6-31G(d,p) basis set. Five states ($S_0 - S_5$

for singlet and S_0 , $T_1 - T_4$ for triplet) with equal weights were considered in the reference CASSCF wavefunction of SS-CASPT2 used to calculate the vertical energies. In all the SS-CASPT2 calculations, a level shift of 0.3 a. u was used for avoiding the intruder state problem and no IPEA shift was applied. Molpro 2012 [58, 59] was used for all the CASSCF and SS-CASPT2 calculations and Gaussian 09 [57] for EOM-CCSD calculations.

The stationary points on the S_1 state and most of the MECPs were obtained using two-state averaged (SA) CASSCF wavefunction. State-specific CASSCF was used for obtaining the stationary points on the S_0 and T_1 states. Due to the convergence issues, five ($S_0 - S_4$), four ($S_0 - S_3$) and three ($S_0 - S_2$) states were necessary to include in the SA-CASSCF to optimize S_4/S_3 , S_3/S_2 and S_2/S_1 crossings respectively. For the similar reason, 3SA-CASSCF was needed to find the S_1/S_0 and T_1/S_0 MECPs, which are involved in the formation of dissociative products from *trans*-NP. SOC values were computed at 4SA-CASSCF (S_0 , S_1 , T_1 and T_2) level by using the Breit-Pauli Hamiltonian. The active space of 14 electrons in 11 orbitals, denoted as (14,11) was used for the hydrogen transfer process in *cis*-NP. The active orbitals were, π/π^* pair of C^1-C^2 (See Figure 4.1 for atomic numbering) bond, two π orbitals, one π^* orbital and two lone pair orbitals of NO_2 group, and the σ/σ^* orbital pairs of C^3-H^6 and N^9-O^{11} bonds. For the dissociation process, bigger active space of (16,13) was necessary for the correct description of all the dissociation pathways explored. In the (16,13) active space, two more σ/σ^* pairs of C^1-N^9 and N^9-O^{10} bonds were added to the above mentioned (14,11) active space by excluding the σ/σ^* orbital pairs of C^3-H^6 . The smaller active space of (9,7) was used in the CI optimizations involving higher singlet excited states.

The barriers along the proposed paths were estimated using linearly interpolated in internal coordinates (LIIC). The hydrogen transfer process and the path from the S_4 state to the S_1 state were obtained by calculating the SS-CASPT2 energies along the LIIC paths. A 4SA-CASSCF (S_0 , S_1 , T_1 and T_2) for the hydrogen transfer and 5SA-CASSCF (S_0-S_4) for the deactivation path from S_4 to S_1 state were used as the reference wavefunction for the corresponding SS-CASPT2 calculations. The SS-CASPT2 calculations with bigger active

space of (16,13) were computationally unreasonable. Thus, the following approach was used to get an estimation of the barrier along the dissociation pathways. First, 4SA-CASSCF (S_0 , S_1 , T_1 and T_2) potential energy curves along the LIIC paths were obtained. The energies at the highest energy points of these CASSCF potential energy curves were reevaluated at the SS-CASPT2 level of theory. These SS-CASPT2 energy values then used to calculate the barrier for the photodissociation pathways.

4.2 Results and Discussion

4.2.1 Franck-Condon geometry and vertical energies

Among the two possible geometrical isomers of NP, the *trans* isomer is found to be lower in energy than the *cis* isomer by 0.1 eV. At the minimum energy configuration, the *trans*-NP belongs to the C_s point group and the *cis*-NP belongs to the C_1 point group. In the case of *cis*-NP, the planar NO_2 group is slightly tilted by 16° ($\delta(\text{C}^2\text{C}^1\text{N}^9\text{O}^{11})$) with respect to the plane formed by C^1 , C^2 , and C^3 atoms. It is interesting here to note that the optimized geometries of NB and oNT also show similar geometrical differences as *trans* and *cis* isomers of NP by acquiring C_{2v} and C_1 symmetries respectively [70, 118]. Apart from the above mentioned dihedral angle ($\delta(\text{C}^2\text{C}^1\text{N}^9\text{O}^{11})$) and the dihedral angle, $\delta(\text{C}^3\text{C}^2\text{C}^1\text{N}^9)$ that differentiates the *trans* and *cis* isomers, all the remaining geometrical parameters of the optimized ground state geometry are similar for both *trans* and *cis* isomers of NP.

The optimized geometries obtained at MP2/6-31G(d,p) level of theory were employed to calculate the vertical excitation energies and oscillator strengths of *trans* and *cis* isomers of NP. To the best of our knowledge, the experimental absorption spectra of NP (both *trans* and *cis*) or its theoretical assignment does not exist in the literature. Thus, the assigned absorption peaks in NP are compared with the absorption spectra of the qualitatively similar molecule, nitroethylene for which the experimental and theoretical data on absorption spectra is available [119, 120]. The additional methyl group in NP as compared to the nitroethylene

Table 4.1: Vertical excitation energies (ΔE) and oscillator strengths (f) for four lowest singlet and triplet excited states of *trans*-NP and *cis*-NP

State	Nature	<i>Trans</i> -NP			<i>Cis</i> -NP			Exp (eV) ^b
		ΔE (eV) CASPT2/ aug-ccpVDZ	ΔE (eV) EOM-CCSD/ aug-ccpVDZ	f^a	ΔE (eV) CASPT2/ aug-ccpVDZ	ΔE (eV) EOM-CCSD/ aug-ccpVDZ	f^a	
T ₁	³ $n_1\pi_2^*$	3.288	3.742	—	3.220	3.665	—	
T ₂	³ $\pi_2\pi_2^*$	3.395	3.496	—	3.386	3.474	—	
S ₁	¹ $n_1\pi_2^*$	3.564	4.076	0.000	3.511	4.047	0.002	4.20
T ₃	³ $n_2\pi_2^*$	3.786	4.226	—	3.753	4.182	—	
S ₃	¹ $n_2\pi_2^*$	4.054	4.512	0.001	3.992	4.480	0.001	
T ₄	³ $\pi_3\pi_2^*$	4.079	4.122	—	4.086	4.168	—	
S ₃	¹ $\pi_2\pi_2^*$	5.678	6.020	0.108	5.865	6.183	0.079	5.12
S ₄	¹ $\pi_3\pi_2^*$	6.680	6.431	0.384	6.421	6.315	0.344	6.12

^aOscillator strength values computed at EOMCCSD/aug-ccpVDZ level of theory^bExperimental data is for nitroethylene from Reference [119]

does not affect the nature of the frontier orbitals and therefore similar absorption spectra for NP as nitroethylene can be expected. At the FC geometry, the energies for four low-lying singlet and triplet excited states, and the oscillator strengths between ground and singlet excited states have been computed and compiled in Table 4.1. The orbitals involved in the electronic transitions associated with the electronic excited states are shown in Figure 4.3, part (a) for *trans*-NP and in Figure 4.3, part(b) for *cis*-NP. As anticipated, the excited states of NP isomers are close to each other and are also matching with the absorption spectral bands of nitroethylene.

On the basis of the calculated vertical excitation energies and the oscillator strengths, the two lowest singlet excited states of *trans* and *cis* isomers of NP are optically dark and have $n\pi^*$ character. These two dark states involve the respective transitions from the n_1 and n_2 orbitals to the same final π_2^* orbital. Both the initial (n_1 and n_2 in Figure 4.3) and final orbitals (π_2^* in Figure 4.3) of these transitions are mostly localized on the NO₂ group of the molecule. The next two singlet excited states, S₃ and S₄, of *trans*-NP and *cis*-NP are of $\pi\pi^*$ type. The S₃ state has been characterized by the electronic transition from π to π^* orbital localized on the NO₂ group (π_2 and π_2^* in Figure 4.3), while the S₄ state, a charge transfer

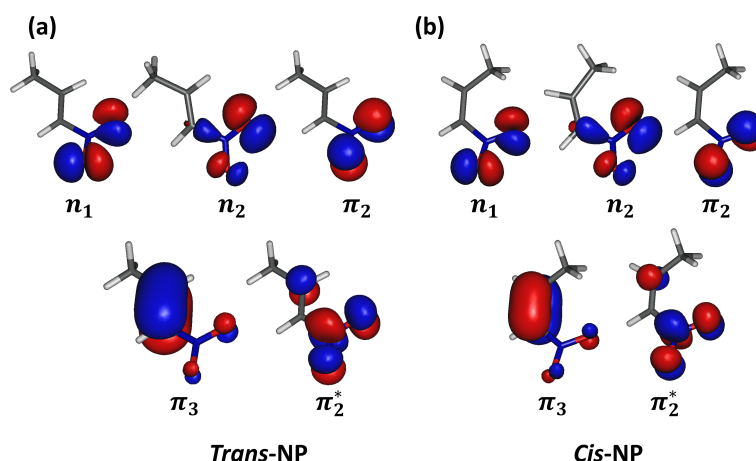


Figure 4.3: Molecular orbitals characterizing the lowest few electronic excited states of (a) *trans*-NP and (b) *cis*-NP.

state, has been characterized by the electronic transition from the π orbital localized along the C¹–C² bond (π_3 in Figure 4.3) to the π^* orbital localized on the NO₂ group (π_2^* in Figure 4.3). Among the four singlet excited states of NP, the charge transfer state has the largest oscillator strength with the ground state. Consequently, the S₄ state is expected to populate initially upon exposing the molecule to ultraviolet (UV) radiation. Regarding the triplet states, the two lowest states which have $\pi\pi^*$ and $n\pi^*$ characters respectively are found to be lower in energy than the S₁ state. The orbitals correspond to the transitions of the T₁ and T₂ states are localized on the NO₂ group. Another $n\pi^*$ triplet state (T₃) which also originates from the electronic transition between the localized orbitals of the NO₂ group lies between S₂ and S₁ states and the T₄ state that corresponds to the charge transfer singlet excited state exist between S₃ and S₂ states.

4.2.2 Stationary points and minimum energy crossing points

As mentioned in the previous subsection, the photophysics and photochemistry of the *trans* and *cis* isomers of NP starts from the S₄ state of the FC region. According to Kasha's rule, the molecule relaxes very quickly to the lowest singlet excited state after which it undergoes either photodissociation or photoisomerization (including ESIHT in *cis*-NP) to

form various photo-products. The two lowest triplet states ($^3n_1\pi_2^*$ and $^3\pi_2\pi_2^*$) which appear energetically between S_0 and S_1 states are likely to play a role in the formation of photo-products and have been considered. Several stationary points on the S_1 , T_1 and S_0 states, and the MECPs between four low-lying singlet and two low-lying triplet states have been optimized. The inspection of all the optimized critical points leads us to conclude that a large number of geometrical parameters are involved in the photodecay process, which also can be expected from the rich photochemistry of NP to produce numerous photo-products. These important geometrical parameters and the energies of critical points for *trans*-NP and *cis*-NP have been tabulated in Table 4.2 and Table 4.3 respectively, and the optimized structures of them are shown in Figure 4.4. The potential energy profiles of NP involving all the optimized stationary points and the MECPs along with their energies relative to the ground state geometry have depicted in Figure 4.5 (for *trans*-NP) and Figure 4.6 (for *cis*-NP). The horizontal axis in Figure 4.5 and 4.6 represents the different reaction coordinates for different photo-deactivation channels, from the origin (S_0 -NP) to both right and left ends of the profile. The critical points of *trans*-NP and *cis*-NP are now described.

A. Critical points of *trans*-NP

Besides the global minima, three more isomers of NP have been optimized on the ground state. Among them, two are planar at which the C^1 atom is bonded to one of the oxygen atoms of NO_2 group (O^{10} or O^{11}) denoted as S_0 -nitrite-*cis* and S_0 -nitrite-*trans*, and one is non-planar isomer with epoxide bond (between O^{10} , C_1 and C_2) referred as S_0 -ep. The nitrite isomers are similar in energy with the NP, whereas the epoxide isomer lies around 0.36 eV above the remaining isomers (Figure 4.5). The products in the dissociation limit associated with the NO_2 and NO formation channels have been optimized with the interfragment distance of 10 Å. Two different transition states (TSs) have been found for the nitro-nitrite isomerization on the ground state. One (S_0 -TS) corresponds to the isomerization path that involves the formation of an oxaziridine ring, a three membered ring of N^9 , O^{11} and C^1 atoms, and the

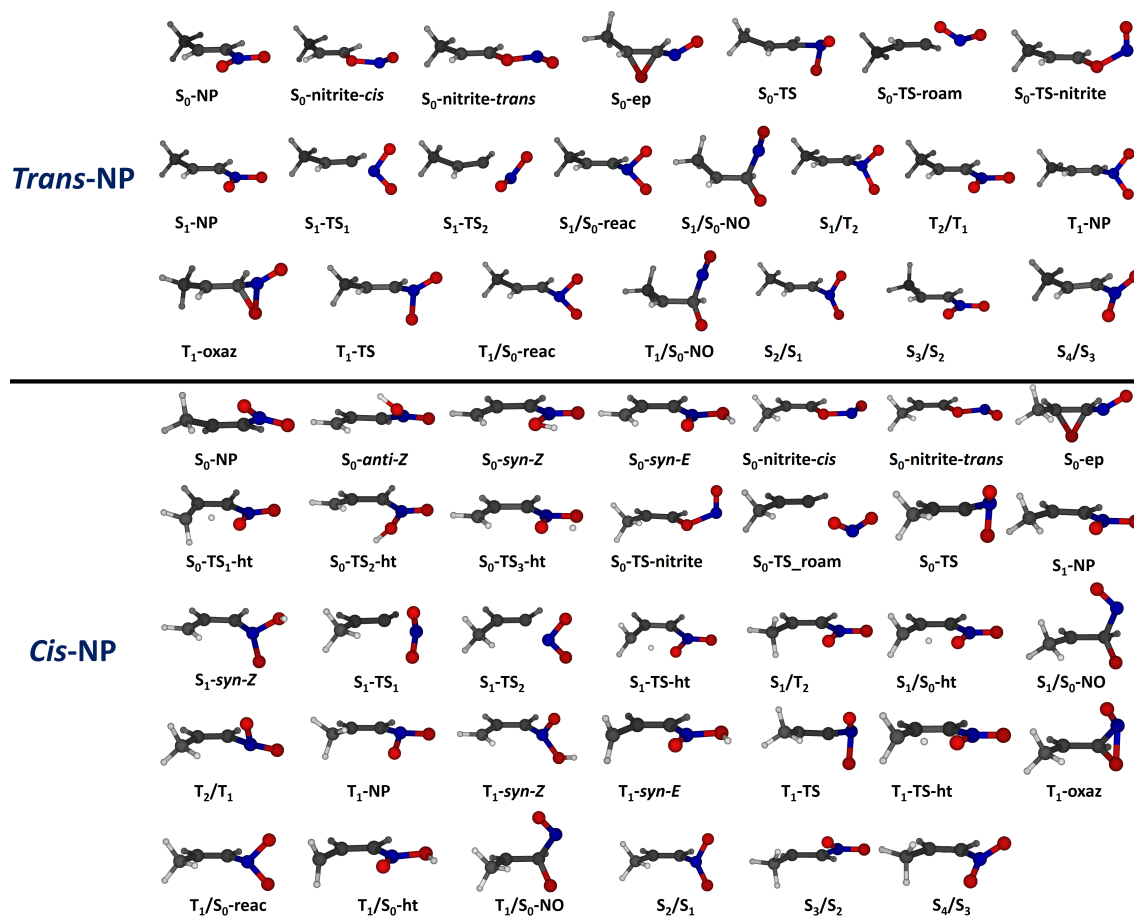


Figure 4.4: Structures of all the optimized critical points (stationary points and minimum energy crossing points) involved in the photochemistry of *trans* and *cis* isomers of NP

other (S_0 -TS-roam) corresponds to the roaming mediated isomerization which entails the partial dissociation of C^1-N^9 bond that extends till 3.4 Å, followed by the reaction between NO_2 and alkyl radicals. The roaming TS is around 0.1 eV lower in energy than the energy of the completely separated radical fragments (NO_2 and alkyl radicals) and is around 0.30 eV higher in energy than the S_0 -TS (Figure 4.5). The IRC results demonstrated that the S_0 -TS and S_0 -TS-roam leads to the formation of the *trans* and *cis* isomers of nitrite respectively. We also have optimized the transition state for the interconversion between *cis* and *trans* isomers of nitrite on the ground state which is referred as S_0 -TS-nitrite. These results are consistent with the nitro-nitrite isomerization mechanism in NB molecule proposed recently based on the DFT calculations [103].

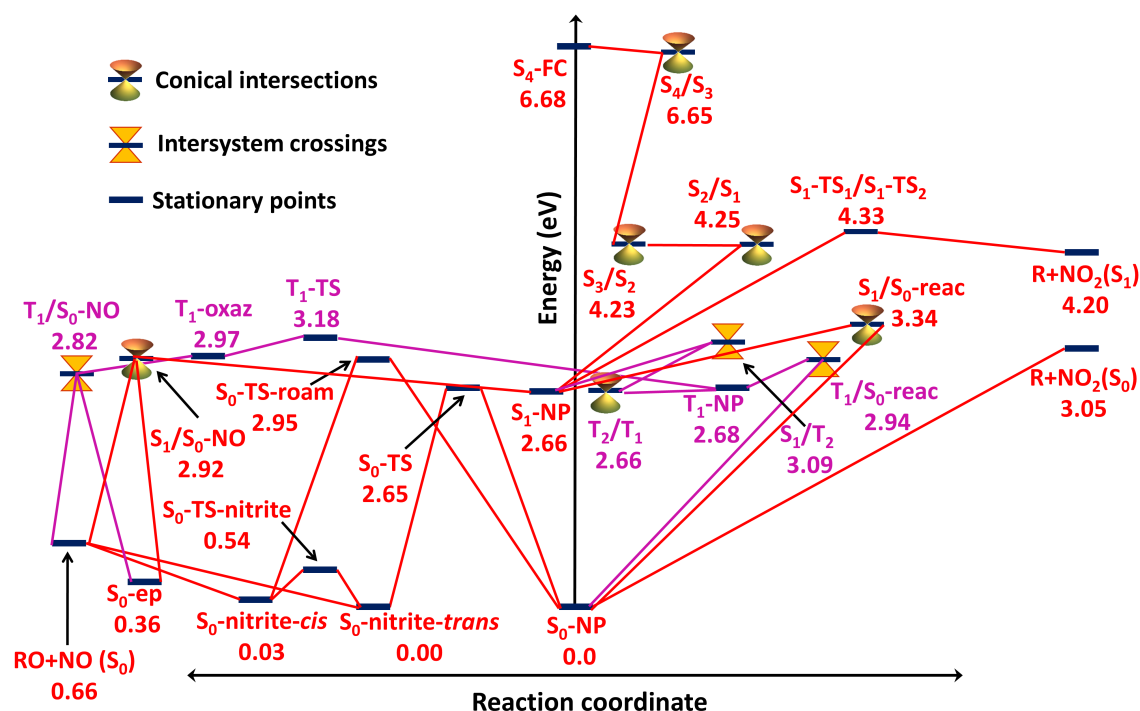


Figure 4.5: Potential energy profile of *trans*-NP starting from the FC region of the S_4 state (S_4 -FC) to various photo-products calculated at CASPT2//CASSCF/6-31G(d,p) level of theory. The red colored lines are used to indicate the singlet decay paths and the purple colored lines are used to indicate the decay channels involving triplet states

The minimum energy geometries of NP have also obtained on the lowest singlet and triplet excited states starting from the FC geometry. Regarding the TS geometries on these excited states, two different TSs on the S_1 state, S_1 -TS₁ and S_1 -TS₂, which have nearly the same energy and are associated with the C¹–N⁹ bond fission with the elongation of 2 Å, and one TS on the T_1 state, T_1 -TS related to the S_0 -TS have been optimized. No roaming TS has been found to be possible on these excited states. In the process of the molecular dissociation on the S_1 state along C¹–N⁹ bond via S_1 -TS₁ or S_1 -TS₂, the O¹⁰–N⁹–O¹¹ angle changes from 126° (at FC geometry) to 103° or 106° respectively (Table 4.2). This angle at S_1 -TS₁/ S_1 -TS₂ is similar to that of the NO₂ optimized geometry on the 2B_2 state which is 101° [121]. Therefore, the molecule on the S_1 state can be expected to form NO₂ on the 2B_2 state through S_1 -TS₁ or S_1 -TS₂. The IRC path starting from the T_1 -TS leads to an oxaziridine intermediate (T_1 -oxaz) on the T_1 state, unlike the S_0 state.

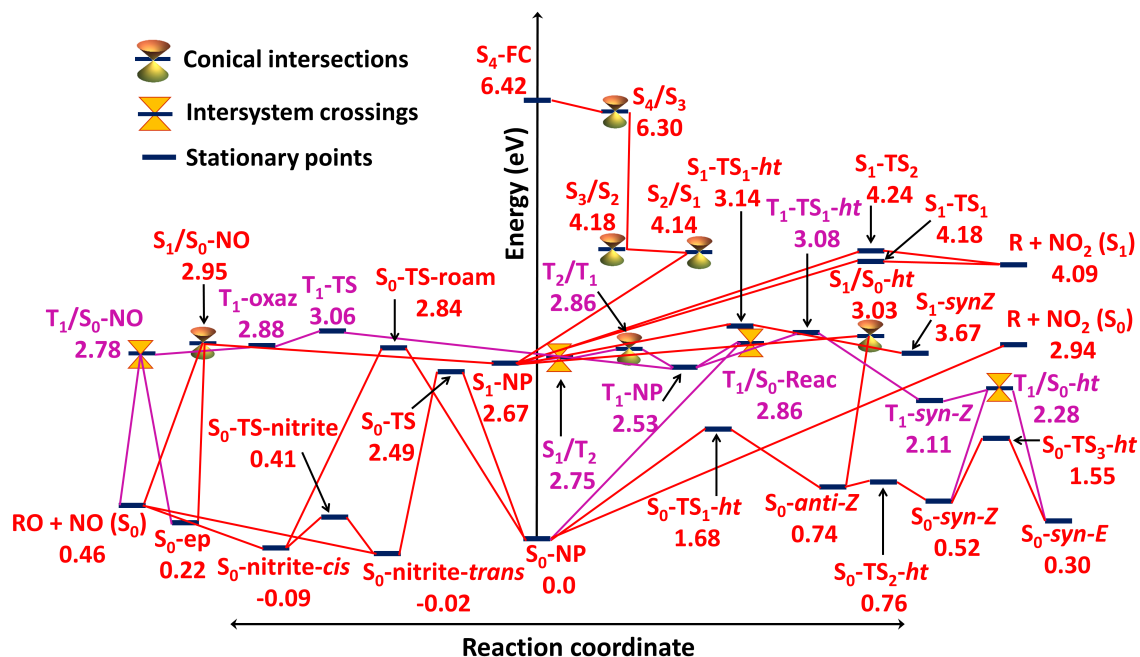


Figure 4.6: Potential energy profile of *cis*-NP starting from the FC region of the S_4 state (S_4 -FC) to various photo-products calculated at CASPT2//CASSCF/6-31G(d,p) level of theory. The red colored lines are used to indicate the singlet decay paths and the purple colored lines are used to indicate the decay channels involving triplet states

The CIs S_3/S_2 , S_2/S_1 , S_1/S_0 -reac and T_2/T_1 , and the singlet – triplet crossing geometries, S_1/T_2 and T_1/S_0 -reac have been optimized by using S_0 -NP as the starting geometry. To determine the fate of the oxaziridine intermediate on the T_1 state to which the molecule relaxes from the T_1 -NP through T_1 -TS, we obtained another MECP between T_1 and S_0 states referred as T_1/S_0 -NO starting from the T_1 -oxaz. Since the S_1 state has the same electronic nature as the T_1 state, similar strategy has been used to locate an additional CI between S_1 and S_0 states, namely S_1/S_0 -NO. This S_1/S_0 -NO MECP has not been recognized before in any nitro compounds. The optimized T_1/S_0 -NO and S_1/S_0 -NO geometries have been characterized by the opening of the three membered oxaziridine ring along the N^9-O^{11} bond. We could not find a CI between S_4 and S_3 states inspite of using different initial structures for the CI optimization. In a recent MRCI study on the photochemistry of nitroethylene molecule, the NO_2 torsion around C–N bond has shown to be affecting the energy of the excited states [120]. Motivating from this study, the rigid CASPT2 potential energy scans for

Table 4.2: The relative energies and the key geometrical parameters of the optimized critical points on the PESs of *trans*-NP

Structure	C ¹ -N ⁹ (Å)	C ¹ N ⁹ O ¹⁰ O ¹¹ (deg)	C ¹ -O ¹¹ (Å)	C ¹ N ⁹ O ¹¹ (deg)	N ⁹ -O ¹¹ (Å)	O ¹⁰ N ⁹ O ¹¹ (deg)	C ¹ O ¹¹ N ⁹ O ¹⁰ (deg)	O ¹¹ N ⁹ C ¹ C ² (deg)	Energy (eV)
S ₀ -NP	1.486	180.0	2.345	119.0	1.231	125.6	180.0	0.0	0.000
S ₀ -nitrite- <i>cis</i>	2.446	-0.4	1.401	30.7	1.471	115.4	-0.7	-12.4	0.027
S ₀ -nitrite- <i>trans</i>	2.339	0.0	1.399	34.5	1.479	110.1	180.0	2.2	0.002
S ₀ -ep	1.504	-26.2	1.427	32.6	2.442	136.7	-49.9	67.6	0.361
S ₀ -TS	1.690	100.7	1.802	71.9	1.341	121.1	140.6	97.8	2.647
S ₀ -TS-roam	3.403	-80.1	3.502	84.6	1.212	133.5	80.1	-33.1	2.954
S ₀ -TS-nitrite	2.416	33.9	1.389	33.2	1.599	110.3	82.8	58.7	0.536
S ₁ -NP	1.376	-180.0	2.409	129.7	1.285	107.1	-180.0	-0.0	2.662
S ₁ -TS ₁	2.020	-119.7	2.769	113.9	1.245	102.9	-113.9	125.3	4.329
S ₁ -TS ₂	2.035	-114.2	2.763	106.1	2.763	103.5	-119.0	-121.5	4.329
S ₁ /T ₂	1.464	-128.1	2.394	111.9	1.425	106.2	-132.8	108.5	3.086
S ₁ /S ₀ -reac	1.427	119.5	2.362	115.6	1.363	91.5	119.5	-127.6	3.336
S ₁ /S ₀ -NO	1.621	-31.9	1.397	34.3	2.395	133.7	-60.7	121.5	2.924
T ₂ /T ₁	1.395	-179.3	2.392	119.8	1.369	111.8	-179.4	-179.5	2.659
T ₁ -NP	1.469	-128.6	2.362	114.6	1.336	107.3	128.6	-119.1	2.683
T ₁ -TS	1.446	-99.5	1.847	78.4	1.475	123.3	-124.2	95.6	3.177
T ₁ -oxaz	1.453	-69.2	1.457	56.7	1.605	120.5	-116.5	110.4	2.973
T ₁ /S ₀ -reac	1.470	-117.9	2.363	113.3	1.358	94.8	-117.9	126.7	2.942
T ₁ /S ₀ -NO	1.604	-27.4	1.392	33.1	2.424	134.9	-51.9	116.4	2.821
R + NO ₂ (S ₀)	10.00	120.6	9.897	81.7	1.212	133.5	137.4	-115.3	3.054
RO + NO (S ₀)	10.06	-5.3	1.240	7.1	10.00	67.1	-41.4	122.5	0.659
R + NO ₂ (S ₁)	10.02	-137.4	11.01	138.1	1.276	101.3	-88.4	148.5	4.200
S ₂ /S ₁	1.481	-122.4	2.219	115.9	1.321	128.3	-122.4	111.6	4.251
S ₃ /S ₂	1.331	-179.2	2.295	122.8	1.284	114.3	-179.8	178.6	4.228
S ₄ /S ₃	1.486	180.0	2.345	119.0	1.231	125.6	180.0	40.0	6.648

lowest five singlet states along the NO₂ torsion have been performed (Figure 4.7, part(a)) starting from the FC geometry. Upon NO₂ torsion, we have found two crossings between S₄ and S₃ states at $\delta(\text{C}^2\text{C}^1\text{N}^9\text{O}^{11}) = 40^\circ$ (denoted as S₄/S₃-40) and at $\delta(\text{C}^2\text{C}^1\text{N}^9\text{O}^{11}) = 70^\circ$ (denoted as S₄/S₃-70) among which the S₄/S₃-40 is lower in energy than the S₄/S₃-70. It is also worth to mention here that the NO₂ torsional mode in NP shows negligible effect on the energy of the singlet states below S₃ state.

B. Critical points of *cis*-NP

All the stationary points and the MECs (except S₁/S₀-reac) which obtained in the case of *trans*-NP are also optimized on the PESs of *cis*-NP. Most of these optimized structures have similar geometrical and energetic features as the critical points of *trans*-NP. The S₁/T₂ crossing of has been found to be located very close to the S₁-NP on the *cis*-NP PES whereas

Table 4.3: The relative energies and the key geometrical parameters of the optimized critical points on the PESs of *cis*-NP

Structure	C ¹ -N ⁹ (Å)	C ¹ N ⁹ O ¹⁰ O ¹¹ (deg)	C ¹ -O ¹¹ (Å)	C ¹ N ⁹ O ¹¹ (deg)	N ⁹ -O ¹¹ (Å)	O ¹⁰ N ⁹ O ¹¹ (deg)	C ³ -H ⁶ (Å)	C ¹ O ¹¹ N ⁹ O ¹⁰ (deg)	O ¹¹ N ⁹ C ¹ C ² (deg)	Energy (eV)
S ₀ -NP	1.483	179.5	2.346	119.3	1.23	125.4	1.080	179.4	-16.2	0.000
S ₀ - <i>anti</i> -Z	1.313	179.8	2.363	118.0	1.44	114.0	2.490	179.8	-5.2	0.735
S ₀ - <i>syn</i> -Z	1.303	-180.0	2.320	116.8	1.420	114.6	3.835	180.0	0.3	0.517
S ₀ - <i>syn</i> -E	1.304	-179.9	2.283	115.9	1.430	115.9	4.799	180.0	-0.151	0.300
S ₀ -nitrite- <i>cis</i>	2.450	0.1	1.400	30.7	1.477	115.5	1.082	0.216	3.6	-0.091
S ₀ -nitrite- <i>trans</i>	2.340	0.0	1.399	34.5	1.480	110.1	1.082	180.0	1.8	-0.119
S ₀ -ep	1.505	-26.6	1.425	32.3	2.448	134.5	1.081	-51.5	68.2	0.219
S ₀ -TS ₁ -ht	1.373	175.0	2.328	118.8	1.332	118.6	1.445	175.1	5.6	1.681
S ₀ -TS ₂ -ht	1.313	179.7	2.360	117.4	1.448	114.4	2.589	179.8	3.9	0.755
S ₀ -TS ₃ -ht	1.289	180.0	2.345	130.1	1.298	103.0	4.137	180.0	0.0	1.500
S ₀ -TS	1.696	101.3	1.810	72.2	1.339	121.1	1.082	141.0	97.6	2.489
S ₀ -TS-roam	3.471	80.4	3.653	88.8	1.212	133.5	1.083	77.4	-37.6	2.839
S ₀ -TS-nitrite	2.416	34.0	1.389	33.2	1.596	110.3	1.083	83.4	52.0	0.411
S ₁ -NP	1.378	179.4	2.425	132.6	1.270	107.8	1.079	179.3	-1.8	2.671
S ₁ - <i>syn</i> -Z	1.400	114.9	2.270	110.0	1.371	105.7	4.456	109.1	-147.4	3.667
S ₁ -TS ₁	2.015	-116.4	2.755	108.0	1.356	102.6	1.081	-120.5	-60.4	4.179
S ₁ -TS ₂	2.023	112.2	2.720	104.4	1.383	103.2	1.082	118.5	-123.0	4.239
S ₁ -TS-ht	1.367	-180.0	2.434	118.9	1.458	114.3	1.321	180.0	-0.0	3.140
S ₁ /T ₂	1.381	180.0	2.429	123.0	1.384	109.0	1.085	180.0	0.0	2.750
S ₁ /S ₀ -ht	1.382	180.0	2.392	121.0	1.367	116.1	1.672	-179.8	0.345	3.027
S ₁ /S ₀ -NO	1.635	31.3	1.391	34.8	2.374	132.6	1.084	58.9	122.7	2.950
T ₂ /T ₁	1.450	134.0	2.371	107.7	1.486	116.1	1.080	139.8	-59.2	2.863
T ₁ -NP	1.450	-139.5	2.404	119.9	1.327	109.4	1.081	-137.7	40.2	2.533
T ₁ - <i>syn</i> -Z	1.427	-135.4	2.351	108.7	1.466	116.5	4.605	-140.4	120.2	2.105
T ₁ - <i>syn</i> -E	1.366	179.6	2.327	112.4	1.434	118.1	4.823	179.7	179.6	2.298
T ₁ -TS	1.441	102.3	1.847	79.0	1.462	123.8	1.081	127.1	96.7	3.064
T ₁ -TS-ht	1.368	180.0	2.423	119.2	1.441	114.4	1.285	180.0	-0.0	3.082
T ₁ -oxaz	1.461	66.7	1.442	55.6	1.617	119.6	1.082	-66.7	110.4	2.877
T ₁ /S ₀ -reac	1.471	117.6	2.362	113.2	1.358	94.7	1.082	-117.6	-126.9	2.858
T ₁ /S ₀ -ht	1.366	179.6	2.327	112.4	1.434	118.2	4.825	179.7	179.2	2.281
T ₁ /S ₀ -NO	1.599	36.6	1.403	35.5	2.354	129.2	1.082	72.0	50.7	2.784
R + NO ₂ (S ₀)	10.00	-120.2	10.02	87.5	1.212	133.5	1.084	-132.2	-68.5	2.942
RO + NO (S ₀)	10.04	6.9	1.240	6.8	9.589	52.9	1.081	-131.1	117.2	0.464
R + NO ₂ (S ₁)	10.00	-119.8	10.48	108.8	1.276	101.3	1.084	-127.8	-43.2	4.087
S ₂ /S ₁	1.481	120.6	2.220	104.7	1.321	128.2	1.082	122.6	-111.6	4.148
S ₃ /S ₂	1.339	-179.8	2.318	123.6	1.291	114.9	1.083	-179.8	0.5	4.183
S ₄ /S ₃	1.483	179.5	2.346	119.3	1.23	125.4	1.080	179.4	40	6.299

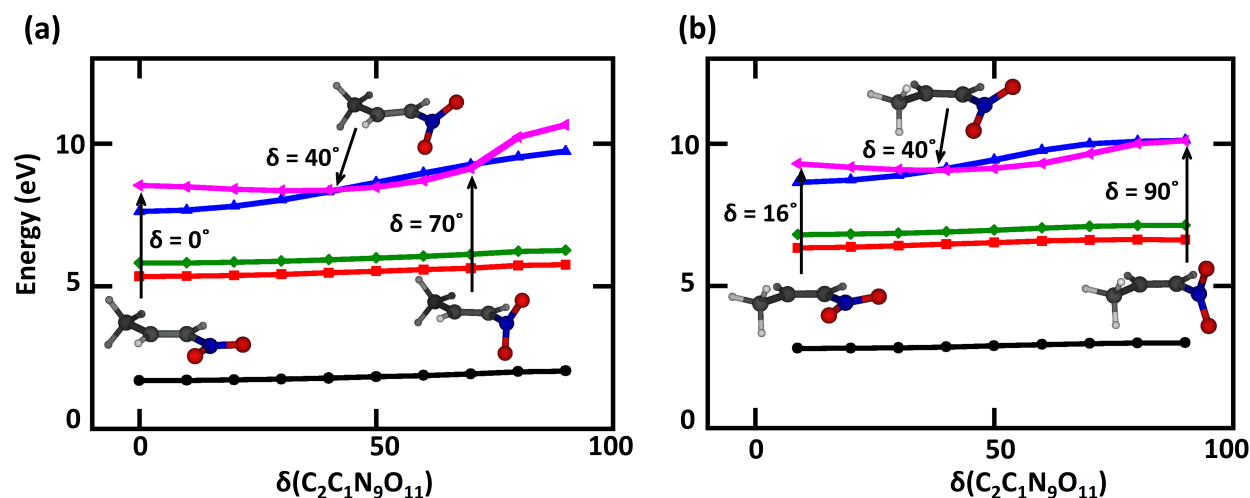


Figure 4.7: The rigid CASPT2 potential energy scans of (a) *trans*-NP and (b) *cis*-NP along the NO₂ torsion over C¹–N⁹ bond

the corresponding crossing of *trans*-NP has distinct structural and energetic parameters compared to its minimum energy structure on the S₁ state (Figure 4.5 and 4.6). We also have seen dissimilarity between the potential energy curves of *trans* (Figure 4.7, part(a)) and *cis* (Figure 4.7, part(b)) isomers of NP along the NO₂ torsion, which results the second crossing between S₄ and S₃ states occurs at two different NO₂ torsional angles for *trans*-NP ($\delta(\text{C}^2\text{C}^1\text{N}^9\text{O}^{11}) = 70^\circ$) and *cis*-NP ($\delta(\text{C}^2\text{C}^1\text{N}^9\text{O}^{11}) = 90^\circ$). As pointed out earlier, the presence of methyl group adjacent to the NO₂ group creates an additional decay channel in *cis*-NP which involves ESIHT from methyl to the nitro group to form the *aci*-nitro isomers on the ground state. Three *aci*-nitro isomers, one nonplanar (S₀-*anti*-Z) and two planar (S₀-*syn*-Z and S₀-*syn*-E), have been optimized on the ground state. At the non-planar *aci*-nitro isomer, the H⁶ atom and the methylene group move out of the plane formed by the rest of the atoms to reduce the steric strain between them. We obtained the transition state, S₀-TS₁-ht for the tautomerization from S₀-NP to S₀-*anti*-Z *aci*-nitro isomer as well as the transition states, S₀-TS₂-ht and S₀-TS₃-ht for the interconversion between the other *aci*-nitro isomers. The S₀-TS₂-ht corresponds to the conversion from S₀-*anti*-Z to S₀-*syn*-Z conformer and the S₀-TS₃-ht corresponds to the conversion from S₀-*syn*-Z to S₀-*syn*-E conformer. The hydrogen transfer process has also explored on the T₁ and S₁ states by identifying the stationary points,

T_1 -*syn*-Z, T_1 -*syn*-E, S_1 -*syn*-Z, T_1 -TS₁-ht and S_1 -TS₁-ht starting from the corresponding ground state optimized structures. The *aci*-nitro isomers have been found to be more stable than the reactant on the T_1 state whereas in the case of S_0 or S_1 state, the reactant is more stable than the hydrogen transferred products (Figure 4.6 and Table 4.3). It is also noted that the CASPT2 energy of the S_1 -*syn*-Z is higher than that of the S_1 -TS₁-ht, while at the CASSCF level the energy of the S_1 -*syn*-Z is lower than that of the S_1 -TS₁-ht by 0.5 eV. The unphysical situation at CASPT2 level arises because the CASPT2 energies have been evaluated at the CASSCF optimized geometries.

The CI between S_1 and S_0 states of *cis*-NP was not found by using the S_0 -NP as the initial geometry for the CI optimization. The $n\pi^*$ nature of the S_1 state at the FC geometry implies there is a hole situated on the n_1 orbital of the oxygen atom due to which the S_1 state gets stabilized by the movement of hydrogen atom with an electron towards the oxygen atom. This hydrogen transfer at the same time, destabilizes the ground state by deviating the NP geometry from its minimum energy configuration (FC geometry) and can lead to a CI between S_1 and S_0 states. Thus, the CI optimization search was initiated with the S_0 -TS₁-ht geometry at which the hydrogen atom is partially transferred to the oxygen atom and obtained the CI between S_1 and S_0 states, S_1/S_0 -ht. The T_1/S_0 -ht was also optimized using similar approach because the T_1 state has the same electronic character as the S_1 state. The stabilization effect of the hydrogen atom movement on the states having $n\pi^*$ character also reflected in the reduction of the barriers for the hydrogen transfer process on S_1 (0.47 eV) and T_1 (0.55 eV) states as compared to the corresponding barrier on the ground state (1.68 eV).

We computed the SOC at the optimized singlet–triplet MECPs for *trans* and *cis* isomers of NP to determine the efficiency of the molecular deactivation via intersystem crossing (Table 4.4). The S_1/T_2 MECP of NP (both *trans* and *cis* conformers) shows relatively large SOC value compared to that evaluated at singlet–triplet crossings in organic molecules such as ethylene (9.15 cm⁻¹), pyrrole (11.65 cm⁻¹), toluene (4.54 cm⁻¹) and benzene (6.23

Table 4.4: Spin-orbit coupling values evaluated at the CASSCF/6-31G(d,p) level of theory for different singlet–triplet MECPs

Conformer	Crossing point	Spin-orbit coupling (cm^{-1})
<i>Trans</i> -NP	S_1/T_2	32.22
	$T_1/S_0\text{-reac}$	9.11
	$T_1/S_0\text{-NO}$	9.23
	S_1/T_2	37.64
<i>Cis</i> -NP	$T_1/S_0\text{-reac}$	7.31
	$T_1/S_0\text{-NO}$	2.60
	$T_1/S_0\text{-ht}$	0.35

cm^{-1}), and therefore the higher triplet quantum yield in NP can be expected. Interestingly, similar high SOC values were also reported for S_1/T_2 crossing in NB and oNT molecular systems which explain the experimentally determined high triplet quantum yield in these nitro-aromatic compounds [115, 118]. This consistency reinforces the validity of the NP which has salient structural features of the nitro-aromatic compounds providing the accurate reflection of the NB by *trans*-NP and oNT by *cis*-NP.

4.2.3 Photodecay pathways

Upon the photo-excitation to the S_4 state, the molecule (*trans*-NP and *cis*-NP) decays non-radiatively to the S_1 state through S_4/S_3 , S_3/S_2 and S_2/S_1 CIs. The computed decay pathways for both *trans*-NP (Figure 4.8, part (a)) and *cis*-NP (Figure 4.8, part (b)), starting from $S_4\text{-FC}$ to the $S_1\text{-NP}$, are found to be barrierless. This barrierless path suggests that the molecule deactivates from the S_4 state to the lowest singlet excited state within ultrafast timescale. Several energy transfer processes are available from the S_1 state for *trans* and *cis* isomers of NP which can be seen from Figure 4.5 and 4.6, respectively. These processes include internal conversion, either via $S_1/S_0\text{-NO}$ (for both isomers) or $S_1/S_0\text{-reac}$ in the case of *trans*-NP and $S_1/S_0\text{-ht}$ in the case of *cis*-NP, intersystem crossing via S_1/T_2 , and the dissociation on the S_1 state either via $S_1\text{-TS}_1$ or $S_1\text{-TS}_2$. The *cis*-NP has additional channel on the S_1 state which

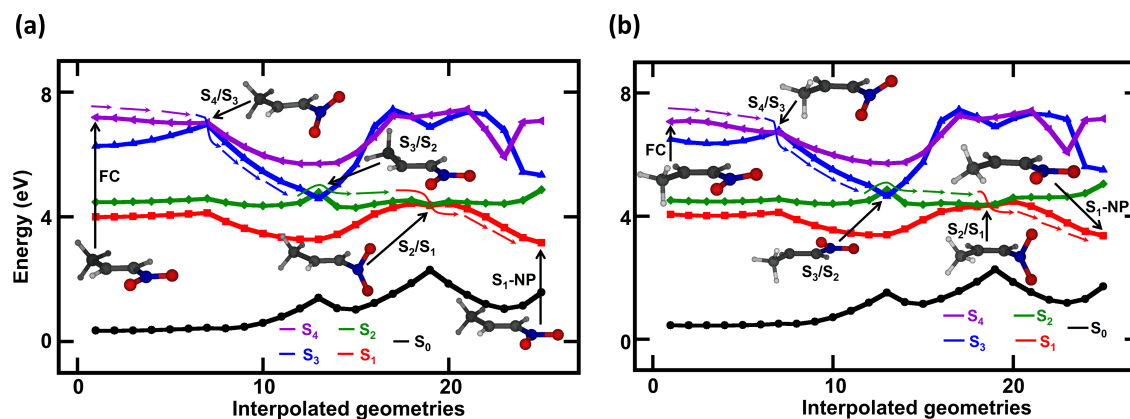


Figure 4.8: LIIC plots showing the deactivation of the S₄ state starting at the FC geometry, going through the S₄/S₃, S₃/S₂, and S₂/S₁ CIs and ending at the S₁ minimum energy geometry (S₁-NP) for (a) *trans*-NP and (b) *cis*-NP. The deactivation path is barrierless and marked with arrows. All energies are calculated at the CASPT2/6-31G(d,p) level of theory.

proceeds through the S₁-TS₁-ht to form the S₁-*syn*-Z. Figures 4.9–4.15 show the LIIC plots for the molecular deactivation from the S₁ state along both the singlet and triplet manifolds which have are to estimate the barriers for the corresponding processes.

Among all the possible energy transfer processes, energetically and geometrically, the most favorable path from the S₁-NP is the intersystem crossing to the T₂ state through S₁/T₂ MECP (Figure 4.5 and 4.6, Table 4.2 and 4.3). Furthermore, the S₁/T₂ shows large SOC value (Table 4.4) which allows the efficient intersystem crossing. Though the S₁/T₂ and S₁/S₀-NO have comparable energies, the path towards the S₁/S₀-NO exhibits significant barrier (Figure 4.9 and 4.10) unlike the path towards the S₁/T₂ (Figure 4.12). This makes the S₁ to T₂ conversion more favorable and higher triplet quantum yield similar to NB and oNT is expected. Another dominant pathway on the S₁ state is the nonradiative transition through S₁/S₀-reac for *trans*-NP and through S₁/S₀-ht for *cis*-NP which have relatively small barriers (Figure 4.11). The path involving S₁/S₀-reac regenerates the *trans*-NP with excess internal energy which subsequently give various ground state products, as will be discussed later. The path involving S₁/S₀-ht forms S₀-*anti*-Z, which either converts into the more stable *aci*-nitro isomer, S₀-*syn*-E or back tautomerizes to *cis*-NP (Figure 4.6). There also exist adiabatic pathways on the S₁ state which go over either S₁-TS₁ or S₁-TS₂ (both the TSs

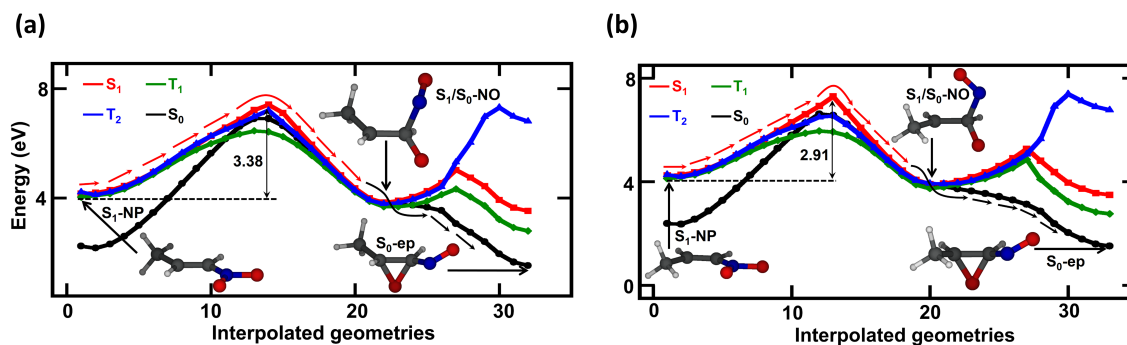


Figure 4.9: LIIC plots showing the deactivation of the S_1 state starting at the S_1 -NP, going through the S_1/S_0 -NO CI and ending at the epoxide configuration, S_0 -ep for (a) *trans*-NP and (b) *cis*-NP. The deactivation path is marked with arrows. The path has been calculated at the CASSCF/6-31G(d,p) level of theory. The barriers are computed at CASPT2/6-31G(d,p) level of theory

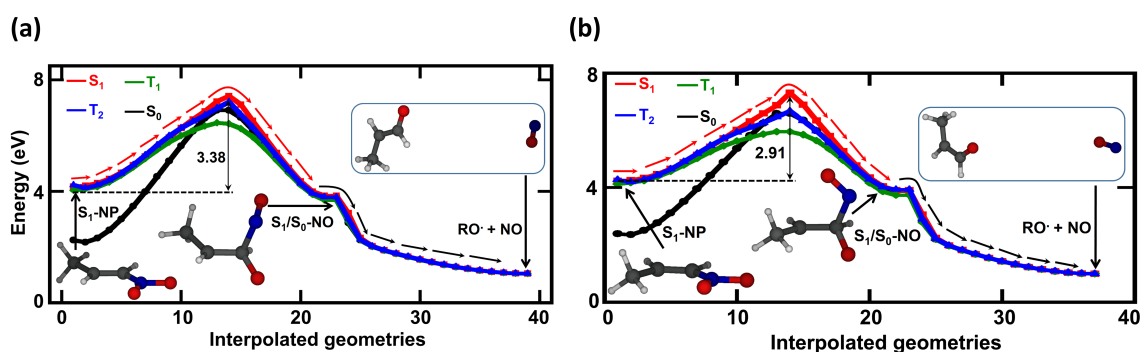


Figure 4.10: LIIC plots showing the deactivation of the S_1 state starting at the S_1 -NP, going through the S_1/S_0 -NO CI and ending at the NO and RO ($R=CH_3-CH-CH$) for (a) *trans*-NP and (b) *cis*-NP. The deactivation path is marked with arrows. The path has been calculated at the CASSCF/6-31G(d,p) level of theory. The barriers are computed at CASPT2/6-31G(d,p) level of theory.

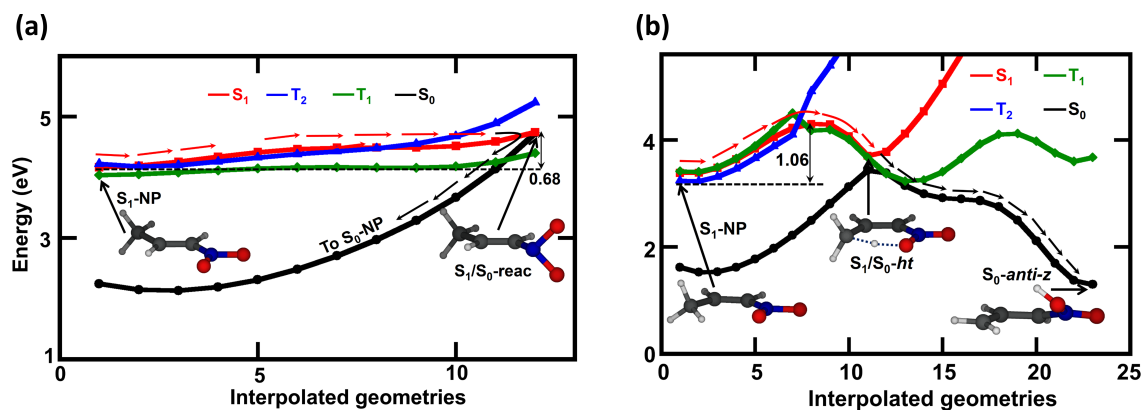


Figure 4.11: LIIC plot for (a) *trans*-NP showing the deactivation of the S_1 state starting at the S_1 -NP, going through the S_1/S_0 -reac which leads to the regeneration of ground state *trans*-NP calculated at CASSCF/6-31G(d,p) level of theory. LIIC plot for (b) *cis*-NP showing the deactivation of the S_1 state starting at the S_1 -NP, going through the S_1/S_0 -ht and ending at the S_0 -anti-Z calculated at CASPT2/6-31G(d,p) level of theory. The deactivation path is marked with arrows. The barriers are computed at CASPT2/6-31G(d,p) level of theory

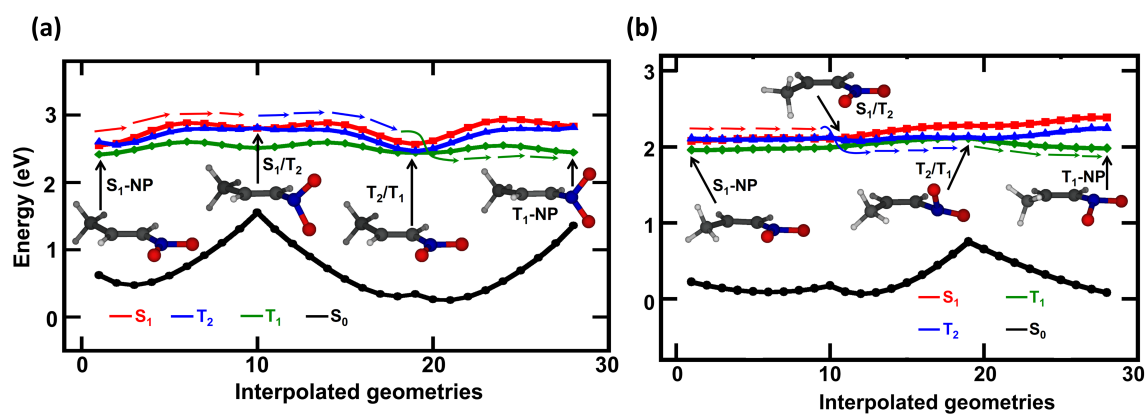


Figure 4.12: LIIC plots showing the deactivation of the S_1 state starting at the S_1 -NP, going through the S_1/T_2 CI and ending at the minimum energy configuration on the T_1 state, T_1 -NP for (a) *trans*-NP and (b) *cis*-NP. The deactivation path is marked with arrows. All energies are calculated at the CASSCF/6-31G(d,p) level of theory.

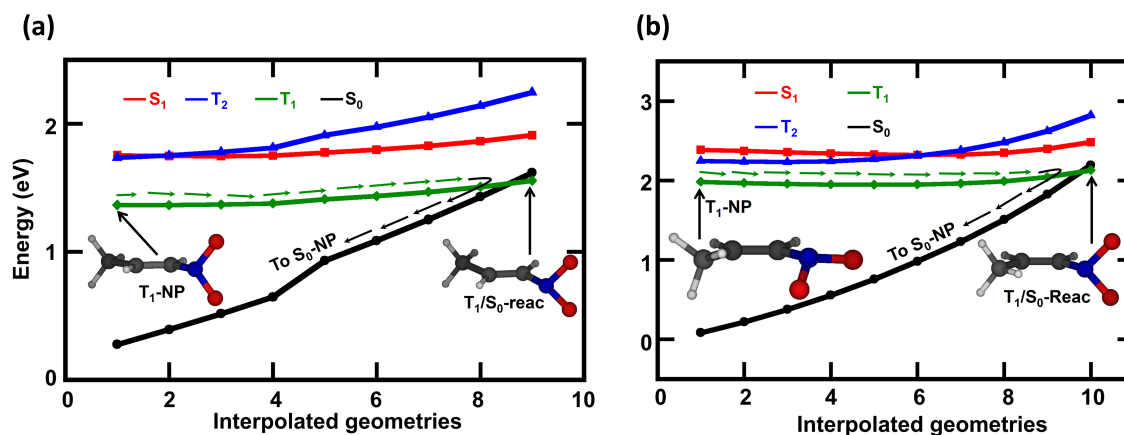


Figure 4.13: LIIC plots showing the deactivation of the T₁ state starting at the T₁-NP, going through the T₁/S₀-reac CI which leads to the regeneration of ground state NP for (a) *trans*-NP and (b) *cis*-NP. The deactivation path is marked with arrows. All energies are calculated at the CASSCF/6-31G(d,p) level of theory

have approximately similar energies) with a barrier of 1.7 eV for *trans*-NP and 1.6 eV for *cis*-NP to produce directly NO₂ (²B₂) and CH₃–CH–CH. A similar adiabatic pathway has been proposed for the formation of NO₂ (²B₂) in the case of NM. The most important pathways from the S₁-NP hence are the intersystem crossing via S₁/T₂ MECP and the internal conversion via S₁/S₀ (S₁/S₀-reac for *trans*-NP and S₁/S₀-ht for *cis*-NP). Though the path towards the S₁/S₀-NO involves a significant barrier, the importance of the path cannot be ignored completely. This is because the LIIC between S₁-NP and S₁/S₀-NO, which has been used to estimate the barrier, results in unphysical geometries at which the oxygen atom, O¹¹ is not bonded with any other atoms. These unphysical geometries are very high in energy so the paths involving them show huge barriers. An accurate estimation of the barrier along this path is necessary to know the accessibility of the S₁/S₀-NO MECP from S₁-NP.

On the T₂ state from S₁/T₂ MECP, the molecule easily accesses the T₂/T₁ crossing and relaxes to the minimum energy configuration on the T₁ state, T₁-NP (Figure 4.12). The corresponding path for the *trans*-NP is barrierless whereas the T₂/T₁ crossing of *cis*-NP lies energetically 0.11 eV higher than the S₁/T₂ (Figure 4.5 and 4.6). At T₁-NP, there are two branches: One, towards to the T₁/S₀-reac through which the molecule relaxes to the ground state reactant and two, towards to the formation of T₁-oxaz by crossing a barrier at T₁-TS.

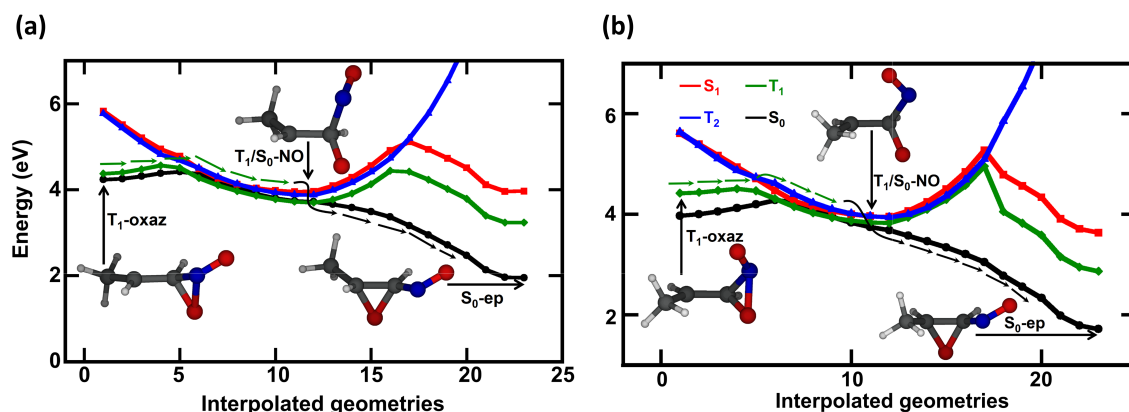


Figure 4.14: LIIC plots showing the deactivation of the T_1 state starting at the T_1 -oxaz, going through the T_1/S_0 -NO CI and ending at the ground state epoxide configuration, S_0 -ep for (a) *trans*-NP and (b) *cis*-NP. The deactivation path is marked with arrows. All energies are calculated at the CASSCF/6-31G(d,p) level of theory.

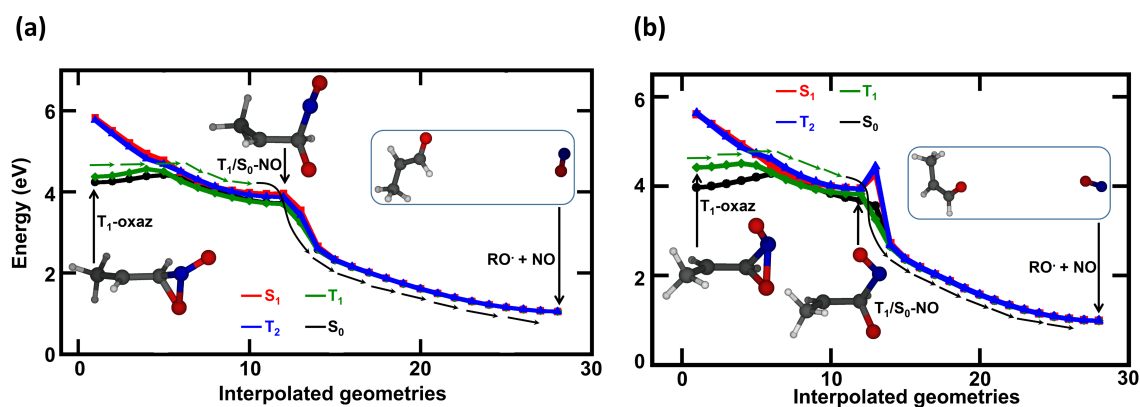


Figure 4.15: LIIC plots showing the deactivation of the T_1 state starting at the T_1 -oxaz, going through the T_1/S_0 -NO CI and ending at the NO CH_3 -CH-CHO for (a) *trans*-NP and (b) *cis*-NP. The deactivation path is marked with arrows. All energies are calculated at the CASSCF/6-31G(d,p) level of theory.

An additional path is possible for the *cis* isomer from T_1 -NP, which proceeds through the T_1 -TS₁-ht and gives a more stable isomer on the T_1 state, T_1 -*syn*-Z. The hydrogen transferred product, T_1 -*syn*-Z relaxes to the S_0 -*syn*-Z or S_0 -*syn*-E via T_1/S_0 -ht crossing. The barriers for the hydrogen transfer process on the T_1 state and for the T_1 -oxaz formation path are nearly same. Thus, both the paths on the T_1 state are equally probable. After reaching to the T_1 -oxaz, the molecule decays to the ground state by accessing the T_1/S_0 -NO which has moderate SOC value and energetically lower than the T_1 -oxaz (Figure 4.14 and 4.15). Subsequently, the molecule from the T_1/S_0 -NO can form either ground state epoxide isomer, S_0 -ep (Figure 4.14) or ground state dissociative products, NO and $\text{CH}_3\text{-CH-CHO}$, (Figure 4.15) in a barrierless way. Since the S_1/S_0 -NO CI is geometrically similar to T_1/S_0 -NO MECP (Table 4.2 and 4.3, and Figure 4.4), the path involving S_1/S_0 -NO also produces the ground state epoxide (Figure 4.9) and the dissociative products (Figure 4.10).

The photoexcited molecule that decays non-radiatively back to the ground state reactant (Figure 4.13 and 4.11, part(a)) acquires large amount of excess energy. The NP (*cis* and *trans*) with this excess internal energy on the ground state either isomerizes into nitrite isomer (via S_0 -TS or S_0 -TS-roam) followed by the dissociation into NO and $\text{CH}_3\text{-CH-CHO}$, or directly dissociates into NO_2 and $\text{CH}_3\text{-CH-CH}$. In Figure 4.16, the roaming pathway for the nitro-nitrite isomerization for *cis*-NP is presented to show one of the characteristic feature of the roaming path, a long range of flat region along the path. For the *cis*-NP, hydrogen transfer channel is also possible to proceed with the excess internal energy. In fact, the hydrogen transfer process is more favorable among all the possible paths on the ground state (Figure 4.6). On the S_1 and T_1 states of *cis*-NP also, the hydrogen transfer process competes with the other energy transfer processes. Consequently, the reduction in the yield of dissociative products (NO_2 , NO and O) in *cis*-NP as compared to the *trans*-NP can be expected.

Experimentally, two different paths have been suggested for the formation of NO in the photodissociation of NB and oNT based on the observed bimodal distribution of translational energy of NO [103]. The nitro-nitrite isomerization, which is the primary step in the

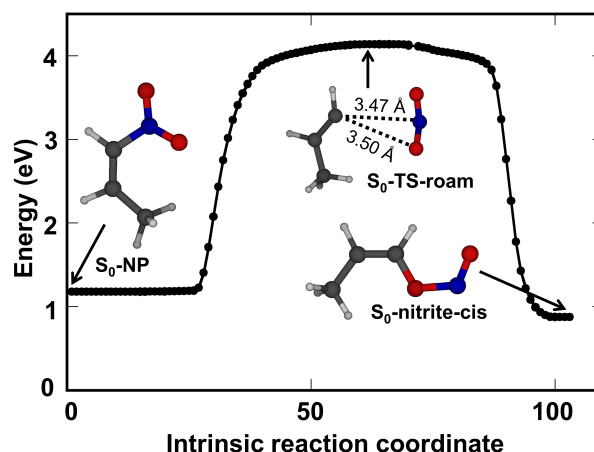


Figure 4.16: The IRC path for the nitro-nitrite isomerization in *cis*-NP involving the roaming transition state, S_0 -TS-roam calculated at CASSCF/6-31G(d,p) level of theory.

formation of NO, in NB has been explored using DFT calculations and a roaming type saddle point, as well as a conventional TS, has been obtained. In the same study, the branching ratio calculations have shown that the thermal dissociation of NB involving roaming-mediated isomerization channel is dominant over the dissociation channel involving the conventional TS. This roaming path has been attributed to the channel which forms NO with low kinetic energy and the triplet dissociation path was suggested to be the channel to form the NO with high kinetic energy. More recently, the triplet dissociation pathway in NB involving T_1 - S_0 crossing has been explored using multi-reference methods [115]. The reported triplet mechanism in NB is slightly different from the mechanism proposed for NP in the present study. In the case of NP, the molecule on the T_1 state first converts to T_1 -oxaz intermediate which further relaxes to the ground state via T_1/S_0 -NO MECP whereas, such intermediate has not been found to be involved in the path for NB. We also have found an alternative NO formation channel for NP, which starts from S_1 -NP and proceeds through the S_1/S_0 -NO CI to form NO in the ground state. This additional singlet path also produces the NO with high kinetic energy.

4.3 Summarizing Remarks

We explored various pathways for photophysical and photochemical processes in *trans* (Figure 4.5) and *cis* (Figure 4.6) isomers of NP, which are simplest model systems of NB and oNT respectively, starting from their lowest bright state, S_4 . The CASSCF//CASPT2 approach has been used for this purpose. Several critical points (MECPs and stationary points) on the relevant electronic states have been optimized. The relative energies and geometrical proximity information of the critical points, barriers involved along the paths and SOC values at the optimized singlet–triplet crossings have been used to estimate the accessibility of multiple paths.

Our study suggests that both the *trans* and *cis* isomers have similar photo-decay pathways except in the case of *cis*-NP, the hydrogen transfer channel competes with the dissociation processes and reduces the yield of NO and NO₂ yield in photodissociation. The molecule from the S_4 state cascades down immediately to the S_1 state through a series of CIs without any barrier. On the S_1 state, four different energy transfer channels are possible for both the *trans* and *cis* isomers of NP: 1) Adiabatic pathways involving either S_1 -TS₁ or S_1 -TS₂ to give NO₂ (2B_2), 2) intersystem crossing via S_1/T_2 , 3) Internal conversion via S_1/S_0 (S_1/S_0 -reac in *trans*-NP and S_1/S_0 -ht in *cis*-NP), and 4) Internal conversion through S_1/S_0 -NO. Among the four processes, intersystem crossing path has been found to be dominant and a greater triplet quantum yield has been proposed. The T_2/T_1 MECP allows the molecule to decay to the T_1 -NP from T_2 state. From T_1 -NP, the molecule either relaxes to the ground state reactant via T_1/S_0 -reac or converts to T_1 -oxaz after which it relaxes to the ground state through T_1/S_0 -NO CI. The regenerated ground state molecules with excess internal energy can undergo nitro-nitrite isomerization followed by the dissociation into NO and CH₃–CH–CHO. Two different mechanisms have been found to be possible for the nitro-nitrite isomerization on the ground state: one, path involving the roaming TS, S_0 -TS-roam and two, path involving conventional TS, S_0 -TS. Another possibility on the ground state is the direct dissociation of the molecule into NO₂ and CH₃–CH–CH.

Ni and coworkers found that the photodissociation of NB and oNT produces NO with two different translational energies [103]. By exploring the ground state profile of NB, the roaming path has been attributed to the formation of NO with low kinetic energy and the triplet path has been suggested to be the channel that produce NO with high kinetic energy. In the later work by Gussani and Worth, the dissociation of NB on the triplet state has been investigated by obtaining the T_1-S_0 MECPs [115]. In the present study, four different NO formation channels have been found to be possible for NP: two ground state (one via roaming TS and the other via conventional TS) channels, one triplet channel and one singlet channel involving S_1 state. The singlet NO formation channel was not recognized before in any nitro compounds. Dynamical calculations on the photodissociation of NP would give much more insights by providing the branching ratio between the proposed four different NO formation channels.

Chapter 5

Mechanism of the Chemiluminescent Reaction between Nitric Oxide and Ozone

Chemiluminescence is the emission of light as a consequence of a chemical reaction. This process brings to mind fireflies and glow sticks where the mechanism of light emission is entirely different from the commonly observed emission of radiation from a hot body. Moreover, chemiluminescence stands out from most other chemical reactions because it involves both ground and excited molecular electronic states, yet is a thermally activated reaction rather than a photo-induced one. There has been significant interest recently in exploring the mechanism of chemiluminescence, with several theoretical studies exploring the reaction in models representing firefly dioxetanone [122–132]. In those systems, which are four-membered-ring peroxides there exists a conical intersection between the ground and excited states near the transition state. On accessing this conical intersection, the molecule gets populated in both ground and excited states, and the excited state product gives light while decaying to the ground state. However, no other class of chemiluminescent reactions,

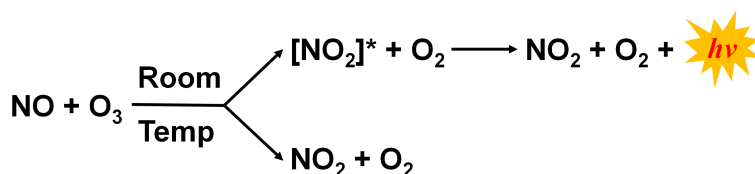


Figure 5.1: Reaction of nitric oxide with ozone.

particularly non-enzymatic reactions, has been examined in depth and the general principles of the mechanism of chemiluminescent reactions are yet to be established.

In the gas phase, perhaps the most well-known and widely applied chemiluminescent reaction is that of nitric oxide with ozone to produce nitrogen dioxide and oxygen (Scheme 5.1). This reaction is routinely used commercially for quantitative determination of NO_x (NO and NO₂) in gas mixtures. It also plays a crucial role in the atmospheric ozone budget [133–135]. In this reaction, it is thought that oxygen is produced in the ground electronic state, while NO₂ is formed in both the ground and excited electronic states (with majority fraction in the ground state), and the process of relaxation of excited NO₂ leads to chemiluminescence [136–143]. The molecular details of this reaction are yet largely unknown. Being a gas phase process and because of the relatively small size of the reacting molecules, one might expect that accurate quantum mechanical methods can be easily applied to describe this reaction. However, because of multiple challenges discussed below, this has not been the case. In the present work, we have sought to obtain a detailed and fundamental understanding of the mechanism of the reaction in Figure 5.1 — in particular the process of chemiluminescence — with the help of high-level quantum chemical calculations.

A detailed study of any reaction mechanism requires a knowledge of potential energy surfaces (PES) and nuclear dynamics going from reactant to product. Although the NO + O₃ chemiluminescent reaction has been known for long, such fundamental aspects have barely been explored due to several theoretical challenges specific to this reaction: (1) There is coupling between nuclear and electronic motion, and consequent breakdown of the Born-Oppenheimer approximation due to the presence of energetically close electronic states typical of chemiluminescent reactions. This requires a treatment of the nuclear dynamics with

the inclusion of non-adiabatic effects. (2) In bond stretching situations (when a bond is broken and another formed) and sometimes in regions where states are very close energetically, the electronic wave function of the system cannot be described by commonly used single-reference electronic structure methods. (3) Three of the molecules involved in the reaction are open shell systems — NO and NO₂ are doublets, and O₂ is a triplet. The fourth molecule O₃ is known to have multi-reference character even in the ground state [144]. So closed shell single reference methods with a Hartree-Fock reference function or density functional theory methods which are relatively easy to apply are not suitable. (4) Unlike the firefly-type chemiluminescent systems which involve intra-molecular reactions, the present system has two molecules as reactants and two others as products. This makes it especially difficult to correlate the state character between reactant and product electronic states, and understand changes in electronic structure as the reaction proceeds. In essence, a proper description of this system requires the use of multi-reference electronic structure methods to obtain the PES, and careful analysis of the state characters to obtain reaction pathways.

The current knowledge about this system is now summarized. Chemiluminescence from NO + O₃ mixtures was observed in the visible region of the electromagnetic spectrum as early as 1911, [142] but these were later attributed to the reaction of NO with atomic oxygen [141]. Chemiluminescence for the reaction in Figure 5.1 was first reported in the red and infrared regions of the electromagnetic spectrum (590-1085 nm) by Greaves and Garvin [138], and a more extended intensity distribution (600-3000 nm) was presented by Clough and Thrush [1]. There have been only a handful of studies on understanding the mechanism of this reaction. The ground state reaction mechanism has been explored using single-reference methods like unrestricted Hartree-Fock theory (UHF) [145], unrestricted Møller-Plesset second-order perturbation theory (UMP2) [145, 146], density functional theory (DFT) [146] and the coupled cluster singles and doubles method (CCSD) [147]. Nonetheless, as explained earlier, single-reference methods are inadequate. Redpath et. al., using minimal state correlation diagrams have proposed two different mechanisms for the reaction [140]: (a) the end-atom

approach — NO abstracts the terminal oxygen atom of ozone, and (b) the middle-atom approach NO approaches O₃ in the plane which bisects the O₃ bond angle and abstracts the central oxygen atom of ozone. The first pathway is energetically favourable, while only the second can explain the absence of excited O₂ in the products, rendering the discussion inconclusive given the complexity of the NO + O₃ system and the available experimental results. A recent experimental study by Savarino et al. suggests that the end-atom approach has a higher probability than the middle-atom approach, with probability of the latter pathway being (8±5) % [148]. In summary, the present understanding of the reaction exists only in pieces and leaves a lot to be desired.

In this chapter we have used multi-reference electronic structure methods to investigate the molecular details of the NO + O₃ reaction. Our goal is to explore the thermally relevant minimum energy paths, reproduce the activation energy barrier, and to explain the broad-chemiluminescence associated with the NO + O₃ reaction. We have restricted ourselves to studying the end-atom approach which is the experimentally suggested major reaction pathway [148]. The mechanism of chemiluminescence in this reaction is found to be distinct from the cycloperoxide systems that have been studied previously [122–132].

5.1 Computational details

The complete active space self-consistent field (CASSCF) [19–21] method, perhaps the most widely applied multi-reference electronic-structure method, has been used to explore the ground and excited state PES of the reaction. Dynamical electron correlation has been accounted for perturbatively. No symmetry constraints have been imposed.

The key to the successful application of the CASSCF method for reactions is the proper selection of the active space (active electrons and orbitals) that describes the system along the whole reaction path. The ideal active space in our case would consist of 19 electrons in 15 orbitals denoted as (19-in-15). This comprises of nitric oxide's σ/σ^* orbitals (2-in-2)

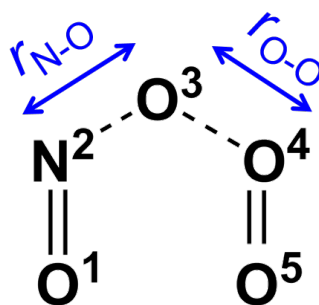


Figure 5.2: Schematic representation of the NO + O₃ system showing the atom numbering and the important reaction coordinates namely the $r_{\text{N-O}}$ and $r_{\text{O-O}}$ bond lengths.

plus two sets of π/π^* orbitals (5-in-4), and ozone's two sets of σ/σ^* orbitals (4-in-4), three π orbitals formed from three p -orbitals (4-in-3) plus the two lone pairs on the terminal oxygen atoms (4-in-2). In terms of atomic orbitals, the 15 orbitals can be thought of as all the valence p orbitals of nitrogen and oxygen. However, exploring reaction pathways with this large active space is computationally untenable and we have used a more reasonable active space for our calculations by excluding the σ/σ^* orbitals of O¹–N² and O⁴–O⁵ bonds from the space (refer Figure 5.2 for atom numbering and definitions of $r_{\text{N-O}}$ and $r_{\text{O-O}}$). This is not expected to lead to any significant loss of accuracy because during the reaction, the O³–O⁴ bond dissociates and the N²–O³ bond is formed, whereas the O¹–N², O⁴–O⁵ bonds are not affected significantly. Representative calculations presented in Tables 5.1 and 5.2 bear this out. The active space that we have finally used for all calculations consists of 15 electrons in 11 orbitals, (15-in-11) and the corresponding active orbitals are shown in Figure 5.3. The active space used for calculations on NO₂ consists of 17 electrons in 12 orbitals where all the valence orbitals have been included. The 6-311++G(2df, 2pd) basis set has been used. This relatively large basis set is necessary to correctly describe the decomposition process in O₃ [149–151]. All calculations have been performed using the MOLPRO-2012 suite of programs [58].

We have taken four electronic states with equal weights in the CASSCF state-averaged (4SA-CASSCF) wave function describing the reaction. The state averaging helps in providing

Table 5.1: Comparison of optimized geometrical parameters with the bigger active space, CAS(19-in-15) and reduced active space, CAS(15-in-11) at 4SA-CASSCF/6-311++G(2df,2pd) level of theory using $r_{\text{N-O}}=3.5$ Å as the constraint for the reactant and $r_{\text{O-O}}=3.5$ Å as the constraint for the product.

CAS(19-in-15)		CAS(15-in-11)	
Reactant			
O ¹ –N ²	1.17 Å	O ¹ –N ²	1.14 Å
O ³ –O ⁴	1.29 Å	O ³ –O ⁴	1.32 Å
O ⁴ –O ⁵	1.29 Å	O ⁴ –O ⁵	1.22 Å
O ³ –O ⁴ –O ⁵	117.2°	O ³ –O ⁴ –O ⁵	116.2°
Product			
O ¹ –N ²	1.20 Å	O ¹ –N ²	1.16 Å
N ² –O ³	1.20 Å	N ² –O ³	1.20 Å
O ⁴ –O ⁵	1.21 Å	O ⁴ –O ⁵	1.18 Å
O ¹ –N ² –O ³	129.4°	O ¹ –N ² –O ³	134.4°
ΔE = E _{prod} - E _{react} (kcal/mol)			
-37.3		-37.2	

Table 5.2: Occupation numbers for the orbitals those have removed from the bigger active space at the reactant and product optimized geometry with CAS(19-in15) active space

Reactant		Product	
σ of O ¹ -N ²	1.97	σ of O ⁴ -O ⁵	1.96
σ^* of O ¹ -N ²	0.03	σ^* of O ⁴ -O ⁵	0.04
σ of O ⁴ -O ⁵	1.95	σ of O ¹ -N ²	1.98
σ^* of O ⁴ -O ⁵	0.05	σ^* of O ¹ -N ²	0.02

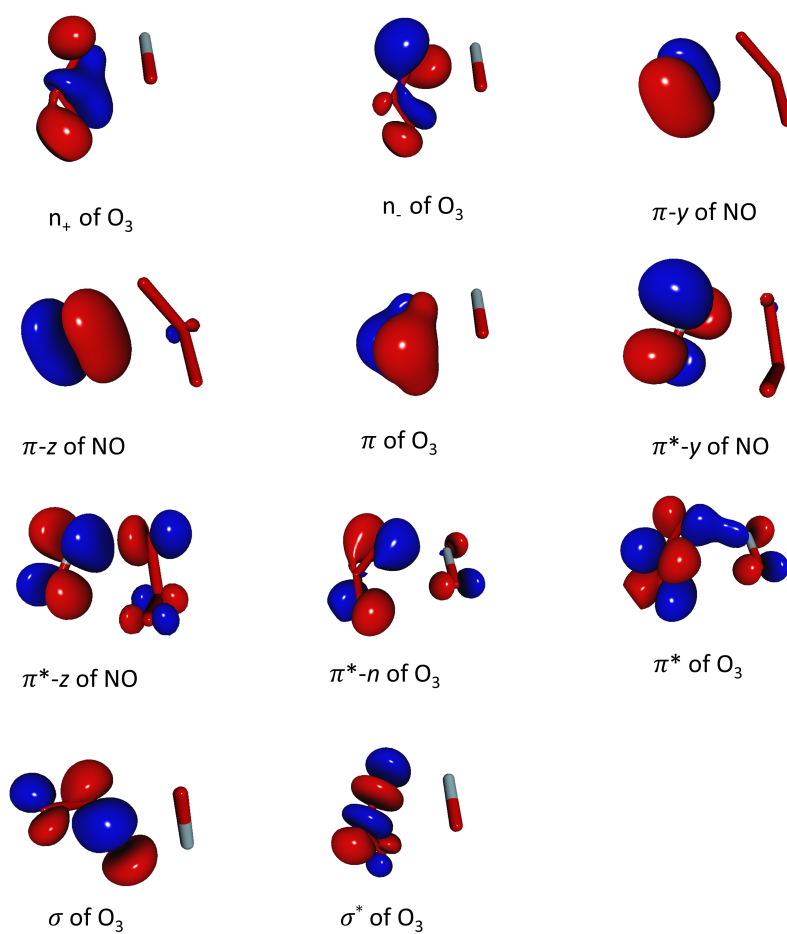


Figure 5.3: Orbitals comprising the active space, CAS(15-in-11) used for the CASSCF and MS-CASPT2 calculations on the NO + O₃ system.

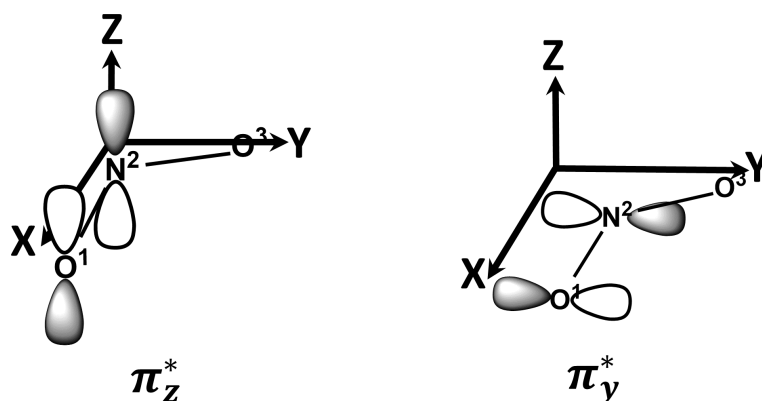


Figure 5.4: Schematic representation of the degenerate HOMOs (π_z^* and π_y^* respectively) of nitric oxide showing their relative orientation

a balanced description of the states included in the wave function and also helps with convergence of the CASSCF. The nature of the four states and the rationale for them being a good choice is provided below. On the reactant side (the composite system of NO and O₃), the ground state is doubly degenerate corresponding to the double degeneracy of the NO ground state — a consequence of either π_y^* or π_z^* being the singly occupied HOMO (Figures 5.4 and 5.5). On the product side (the composite system of NO₂ and O₂), the ground state is non degenerate. The first excited product state is doubly degenerate due to the degeneracy of the oxygen singlet [152]. The second excited product state corresponds to the non-degenerate oxygen singlet. As the reaction proceeds, the electronic states change to become those of the product and these are shown in the state correlation diagram (SCD) in Figure 5.5. The SCD is constructed by connecting the reactant and product states having the same character based on analysis of their wave functions. One of the doubly degenerate ground states of the reactant correlates with the ground state of the product. The second doubly degenerate ground state does not correlate with any of these four lowest product states and likely correlates with a higher energy NO₂ excitation. While going from reactants to products, this state will cross the two states corresponding to the oxygen excitations in the product. The four states that are included in the state-averaged wave function are the two degenerate ground states of the reactant (one of which has the same character as the ground state of the products) and the

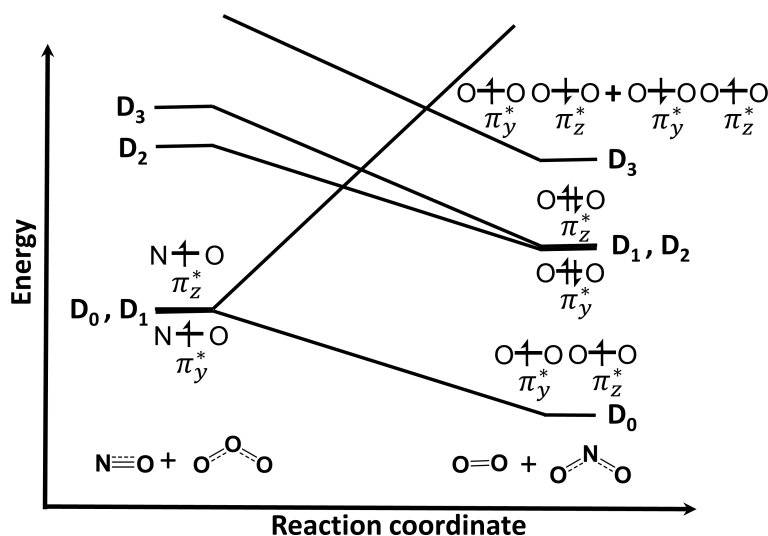


Figure 5.5: State correlation diagram (SCD) between lowest few reactant and product electronic states. The doubly degenerate ground state of the reactant is due to the degeneracy in NO. For the product, D₀ corresponds to the ground state of NO₂ and O₂ while the higher states (D₁, D₂ and D₃) correspond to the ground state of NO₂ and singlet excited states of O₂. The HOMOs of NO on the reactant side and O₂ on the product side, which characterize the states, are shown

two degenerate lowest energy excited states of the products. For the calculations of only NO₂ a 2SA-CASSCF wave function with the ground and first excited state has been used.

The minimum energy path (MEP) of the reaction was obtained using the method of Sun and Ruedenberg to follow the intrinsic reaction coordinate (IRC) [153, 154] as implemented in MOLPRO-2012 [58]. The reactant and product geometries taken for energy calculations were the two end points of the MEP calculations. To account for dynamical correlation, single point energies on the corresponding CASSCF optimized geometries were computed with multi-state complete active space second-order perturbation method (abbreviated as MS-CASPT2) [56]. Given the impracticality of geometry optimization using CASPT2, this CASPT2//CASSCF approach has been the method of choice for several mechanistic studies of chemical reactions [127, 130, 155–160]. In the MS-CASPT2 method, an imaginary level shift of 0.3 a.u. has been used to avoid the intruder state problem [161]. No IPEA correction has been applied.

The disposal of reaction energy into the products vibrational and translational modes has been predicted using sudden vector projection (SVP) model developed and successfully applied to various molecular reactions by Hua Guo and co-workers [162–171]. This model involves the projection of the product vibrational/translational vectors on to the reaction coordinate vector. The fraction of the reaction energy dissipated into the particular mode of the product is proportional to the overlap between that particular mode and the reaction coordinate mode vectors. The reaction coordinate vector corresponds to the imaginary frequency mode at the first order saddle point geometry and the vibrational normal modes of the product (obtained by performing forward IRC from the transition state) corresponds to the product vibrational vectors. Note that all the mentioned normal mode vectors must be mass weighted and normalized before evaluating projections.

5.2 Results and Discussion

5.2.1 Pathways from reactant to product

In the well studied chemiluminescent system dioxetanone, the ground and excited state products are produced through two different paths [123, 127, 128]. For the NO + O₃ reaction, there is consensus in the literature that the emissive species is NO₂ [136–143]. There are however contrasting views about whether the ground ($\tilde{X}^2A_1$) and first excited ($\tilde{A}^2B_2$) electronic states of NO₂ are formed through the same or different electronic channels in the reaction [139, 1, 172–174]. We have investigated the lowest two PESs of the NO + O₃ reaction starting from the side of the reactants in an attempt to resolve this issue. The ground state of the reactant, when NO and O₃ molecules are far apart, is doubly degenerate corresponding to an electron occupying either the π_y^* or π_z^* orbital of NO (Figure 5.4). These two orbitals are oriented perpendicular to each other and interact differently with the HOMO of O₃ as the NO and O₃ molecules approach each other (Figure 5.6). We will refer to the electronic state of the reaction complex characterized by the interaction of the singly occupied

π_z^* orbital of NO with the HOMO of O₃ as the π_z^* state, and the complementary state as the π_y^* state. As one would expect, the double degeneracy breaks as the reactants approach giving two energetically distinct states. We have performed relaxed scans using 4SA-CASSCF on both these states by following their respective characters while constraining $r_{\text{N-O}}$ in steps starting from large values corresponding to the reactant going to small values corresponding to the product (Figure 5.7). The main difference in the wave functions along the two paths is in one of the orbitals, which is either π_y^* or π_z^* , in the respective leading determinants. In the case of the π_z^* scan the energy increases up to $r_{\text{N-O}}=2.12$ Å and then begins to decrease till $r_{\text{N-O}} = 2.06$ Å (black line in Figure 5.7). For $r_{\text{N-O}} < 2.06$ Å, say $r_{\text{N-O}} = 2.04$ Å, constrained optimization leads to a very different geometry compared to the starting geometry, with the O³–O⁴ bond breaking giving well separated NO₂ and O₂. We initiated a transition state (TS) optimization from the highest point on the relaxed scan curve corresponding to $r_{\text{N-O}}=2.12$ Å which led to a converged TS geometry.

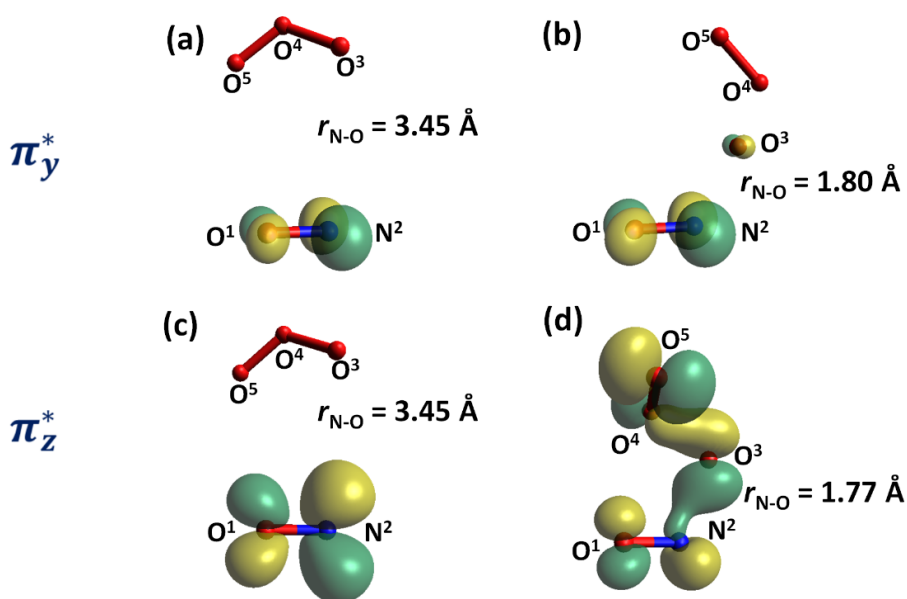


Figure 5.6: Orbitals characterizing the π_y^* and π_z^* electronic states in the reactant (a and c) and product (b and d) regions. In the reactant region these are the π_y^* and π_z^* orbitals of NO which are oriented perpendicular to each other. In the product region, the O₃-NO complex has different structures in the two states to maximize the orbital overlap leading to bond formation. There is lateral π -type overlap in the π_y^* state and head-on σ -type overlap in the π_z^* state.

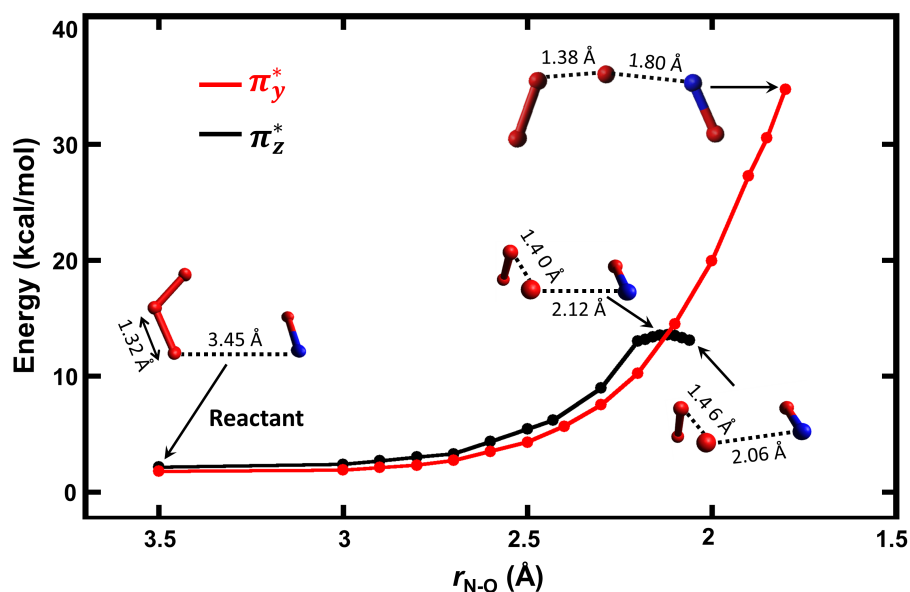


Figure 5.7: Relaxed potential energy surface scans on the π_z^* (black curve) and π_y^* (red curve) states along the $r_{\text{N-O}}$ for the reaction between NO and O₃ calculated at 4SA-CASSCF level of theory.

The geometrical parameters of the optimized TS is presented in Table 5.3 and the structure is shown in Figure 5.8, part (a). The reported geometry from a CCSD calculation [147] (Figure 5.8 and Table 5.4) is presented alongside for comparison. There are significant differences in the optimized structure between the two methods, particularly in the $r_{\text{N-O}}$ distance and ($\text{O}^1\text{N}^2\text{O}^3\text{O}^4$) dihedral angle. Given that the NO + O₃ system is known to have multireference character, this difference can be presumably attributed to an inadequate description of the non-dynamical electronic correlation in CCSD, which is a single reference method.

The MEP connecting the reactants to the products was calculated on the π_z^* state. Interestingly, the geometry of the reactant O₃ obtained along the MEP is not precisely symmetric (Table 5.3). This is an artefact of the exclusion of the σ/σ^* orbitals of O⁴–O⁵ from the active space. The asymmetry in geometry is not significant enough to make a difference in the overall description of the reaction path. A similar situation exists in the optimized product geometry for NO₂ due to the exclusion of the σ/σ^* orbitals of O¹–N² (penultimate column of Table 5.3. The 15-in-11 active space used here attempts to balance accuracy of description and computational feasibility, and using larger active spaces would

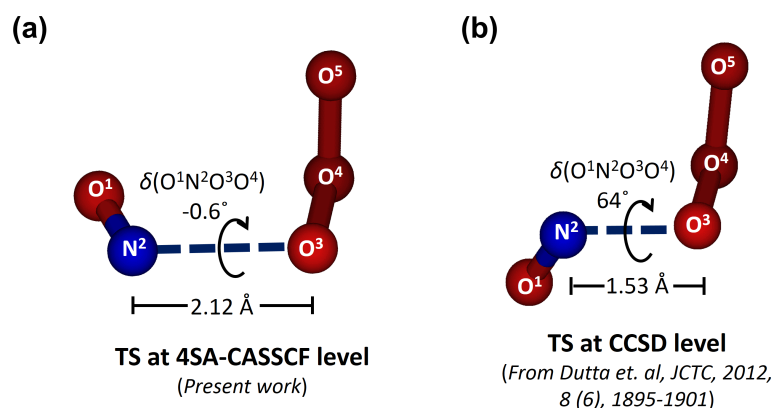


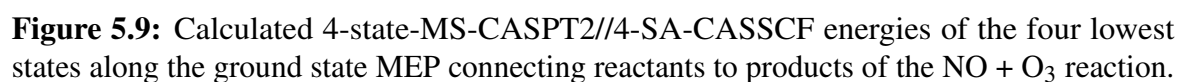
Figure 5.8: Comparison between the transition state geometries obtained at 4SA-CASSCF and CCSD level of theory. The geometrical parameters that differ significantly between the two structures are shown .

Table 5.3: Relative energies and key geometrical parameters of relevant stationary points on the potential energy surface of the NO + O₃ reaction.

		Reactant	Transition state	Product (NO ₂ in $\tilde{X}^2A_1$)	Product(NO ₂ in $\tilde{A}^2B_2$)
Relative energies kcal/mol	4-state-MS-CASPT2//4-SA-CASSCF	0.0	3.3	-58.9	-24.4 Å
Bond lengths (Å)	O ¹ -N ²	1.14	1.13	1.16	1.26
	N ² -O ³	3.45	2.12	1.20	1.27
	O ³ -O ⁴	1.32	1.40	3.30	3.30
	O ⁴ -O ⁵	1.22	1.24	1.18	1.18
Bond angles (deg)	O ¹ -N ² -O ³	93.0	107.9	134.4	101.6
	N ² -O ³ -O ⁴	112.4	100.2	92.1	106.7
	O ³ -O ⁴ -O ⁵	116.2	112.8	126.5	96.8

Table 5.4: Comparison of geometrical parameters between the transition state at 4SA-CASSCF and CCSD methods.

Internal coordinates	Transition state (4SA-CASSCF)	Transition state (CCSD) ^a
O ¹ -N ²	1.13 Å	1.15 Å
N ² -O ³	2.12 Å	1.53 Å
O ³ -O ⁴	1.40 Å	1.43 Å
O ⁴ -O ⁵	1.24 Å	1.29 Å
O ¹ -N ² -O ³	107.9°	110.5°
N ² -O ³ -O ⁴	100.2°	104.4°
O ³ -O ⁴ -O ⁵	112.8°	109.6°
O ¹ -N ² -O ³ -O ⁴	-0.6°	64.0°
N ² -O ³ -O ⁴ -O ⁵	87.2°	94.3°



The π_y^* relaxed scan curve (red line in Figure 5.7) was obtained up to $r_{\text{N-O}} = 1.8 \text{ \AA}$. For smaller $r_{\text{N-O}}$, for example $r_{\text{N-O}} = 1.7 \text{ \AA}$, the constrained optimization leads to the breaking of $\text{O}^3\text{--O}^4$ bond. We analysed the electronic states on the constrained optimization path and the π_y^* -character state was found to increase in energy and cross another electronic state. The $\text{O}^3\text{--O}^4$ bond breaking takes place on this latter lower energy state. At larger $\text{O}^3\text{--O}^4$ distances, the π_y^* state crosses other electronic states and corresponds to a much higher excited state.

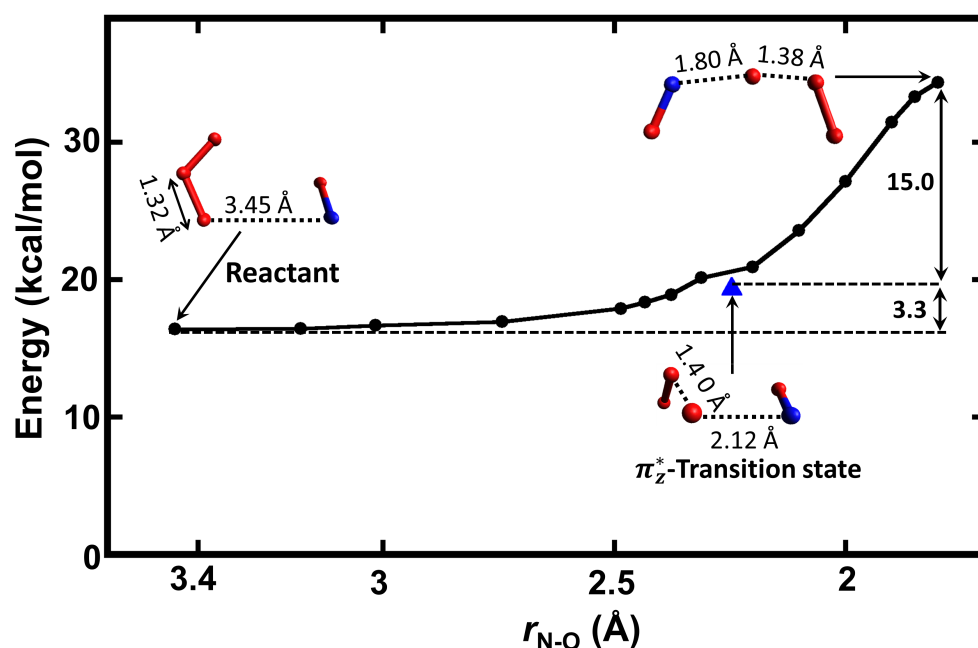


Figure 5.10: Calculated 4-state-MS-CASPT2//4SA-CASSCF energy of the π_y^* state along the relaxed scan path of NO + O₃ reaction with $r_{\text{N-O}}$ as constraint starting from the reactants. The geometry and energy of the optimized transition state on the π_z^* state marked with a blue triangle.

This is consistent with the state correlation diagram in Figure 5.5. At geometries where the π_y^* state becomes the fourth adiabatic excited state, it is no longer included in the lowest four states of SA-CASSCF calculation. From the nature of the π_y^* molecular orbital at $r_{\text{N-O}} = 1.8 \text{ \AA}$ (Figure 5.6, part(b)), the π_y^* state appears to correlate with a B_1 symmetry orbital of NO₂, which characterizes a higher excited state of NO₂ [177, 178]. Energies at the 4-state-MS-CASPT2 level of theory were calculated at the points on the relaxed scan curve up to $r_{\text{N-O}} = 1.8 \text{ \AA}$ (Figure 5.10). The energy on this path is much higher than the barrier on the ground state, and it is therefore unlikely that this path would be thermally accessed with any significant probability.

Since we were unable to find a path for NO₂ formation in the $\tilde{A}^2B_2$ state starting from the reactants, we attempted to find such a path starting from the product side, i.e., from the optimized NO₂ – O₂ complex where NO₂ is in the $\tilde{A}^2B_2$ state, O₂ in the ground state and $r_{\text{O-O}} = 3.3 \text{ \AA}$ (last column of Table 5.3). A relaxed scan with $r_{\text{O-O}}$ as constraint was

performed. Points on the curve were obtained till $r_{\text{O-O}} = 3 \text{ \AA}$. However, for a smaller $r_{\text{O-O}}$, say $r_{\text{O-O}} = 2.9 \text{ \AA}$, the optimization of the other coordinates invariably led to the $\tilde{X}^2A_1$ product geometry. Therefore all commonly used approaches to find a path for the formation of NO₂ in the $\tilde{A}^2B_2$ state from NO + O₃ proved elusive. It is well established that the $\tilde{X}^2A_1$ and $\tilde{A}^2B_2$ states are strongly vibronically coupled [179–189]. In fact the $\tilde{X}/\tilde{A}$ conical intersection (CI) is geometrically and energetically close to the $\tilde{A}^2B_2$ state minimum and because of the complex topologies around a CI, it is possible that there is no minimum energy adiabatic path on the PES to access the $\tilde{A}^2B_2$ minimum, which is not influenced by the $\tilde{X}^2A_1$ state. In other words it is possible that in this case the only way to access the $\tilde{A}^2B_2$ state is through its vibronic manifold, which is of $\tilde{X} - \tilde{A}$ mixed character.

5.2.2 Energy distribution in the products

We explore the possibility of formation of vibronically excited NO₂ in the NO + O₃ reaction. The calculated energy of the reaction (58.9 kcal/mol) is greater than the energy of the first electronically excited state NO₂ (34.5 kcal/mol) implying it is possible for the $\tilde{A}^2B_2$ NO₂ to be formed in the course of the reaction depending on how the released energy is partitioned. It would require crossed molecular beam experiments and full quantum dynamical calculations to accurately quantify this partitioning. Such experiments on this system have not been reported. Full quantum calculations appear computationally impracticable since both dynamical and non-dynamical electron correlation have to be treated to get accurate PES and couplings, and in our experience, a calculation of energy at a single point at the 4-state-MS-CASPT2 level with 15-in-11 active space and 6-311++G(2df, 2pd) basis set with parallelization over 4 processors takes several days indicating the enormous computation cost of simulating the quantum dynamics. We thus resort to more approximate methods, which can provide an estimate of the energy distribution.

The SVP method has been demonstrated as a promising way of estimating energy disposal in reactions in the various product modes. It gives comparable results to experiment and more

accurate theoretical methods for a variety of systems [162–171]. The SVP model is based on the premise that the timescale of the collisions that lead to reaction or product internal conversion is shorter than the timescale of intramolecular vibrational energy distribution. The extent of overlap of the reaction coordinate at the transition state with the various product modes is proportional to the amount of energy disposed in those modes following the reaction. We have applied the SVP approach to the present reaction.

The SVP analysis showing the largest contributions to the energy distribution in the products of the NO + O₃ reaction is presented in Figure 5.11 and the full distribution is presented in Table 5.5. The reaction coordinate and all the product modes are shown in Figure 5.12. A geometry on the MEP corresponding to NO₂ and O₂ being sufficiently far away from each other for their interaction to be negligible ($r_{\text{O-O}}=3.30$ Å) is used to represent the products in the SVP analysis. It turns out that the three vibrational normal modes of NO₂ constitute 75 % of the projection (sum of squares of overlaps) of the reaction coordinate at the transition state. This suggests that the majority of the energy of the reaction flows into the vibrational modes of NO₂, particularly in the symmetric stretch vibration. While for most reactions, products are formed in vibrationally excited states of the ground electronic state and they cool primarily by collisions, NO₂ has a rather unique electronic structure, which is discussed in the next subsection, whereby vibrational cooling can also take place through radiative relaxation to give chemiluminescent emission.

5.2.3 Origin of the chemiluminescent emission

The energy of the equilibrium geometry on the $\tilde{A}^2B_2$ state of NO₂ is calculated to be 1.29 eV higher than the ground state equilibrium geometry at the 2-state-MS-CASPT2//2SA-CASSCF level of theory (Table 5.6), consistent with previous calculations using other methods [188–190]. We must clarify that in the previous subsection the energy of the reaction product in the first excited state, which would be expected to be the same as the energy of NO₂ in the $\tilde{A}^2B_2$ state, was stated as 34.5 kcal/mol (1.50 eV). This energy difference is because that

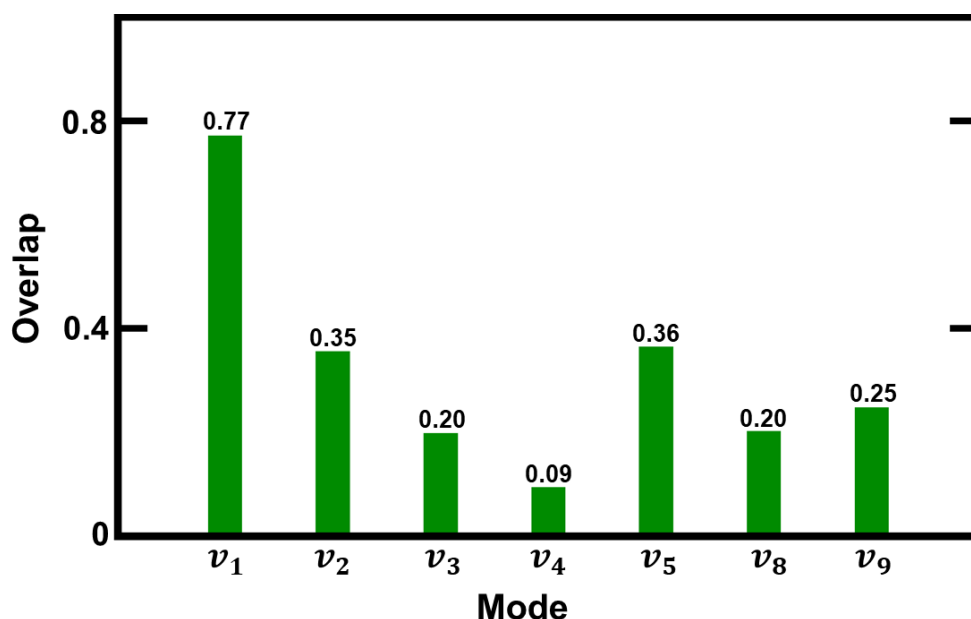


Figure 5.11: Projections of the product modes onto the reaction coordinate vector at the transition state. ν_1 , ν_2 , and ν_3 correspond to symmetric stretch, bend and asymmetric stretch of NO₂. ν_4 corresponds to the O₂ stretch and, ν_5 , ν_8 , and ν_9 correspond to intermolecular motion.

Table 5.5: Projections of product modes onto the reaction coordinate. The significant overlap values are shown in bold

Mode	Description	Frequency (cm ⁻¹)	Overlap with reaction coordinate
ν_1	NO ₂ symmetric stretch	1365	0.7689
ν_2	NO ₂ bending	779	0.3541
ν_3	NO ₂ asymmetric stretch	1865	0.1957
ν_4	O ₂ stretch	1767	0.0918
ν_5	Intermolecular motion	225	0.3624
ν_6	Intermolecular motion	109	0.0075
ν_7	Intermolecular motion	52	0.0416
ν_8	Intermolecular motion	32	0.1998
ν_9	Intermolecular motion	23	0.2459
ν_{10}	Translational	0	0.0004
ν_{11}	Translational	0	0.0305
ν_{12}	Translational	0	0.0352
ν_{13}	Rotational	0	0.0150
ν_{14}	Rotational	0	0.0218
ν_{15}	Rotational	0	0.0057

Table 5.6: Geometrical parameters and the relative energies of some NO₂ geometries at the 2-state-MS-CASPT2//2SA-CASSCF level of theory

Geometry	Bond length (Å)	Bond angle (deg)	Energy (eV)
NO ₂ ($\tilde{X}^2A_1$ min)	1.21	133.7	0.0
NO ₂ ($\tilde{A}^2B_2$ min)	1.27	101.5	1.29
NO ₂ ($\tilde{X}^2A_1/\tilde{A}^2B_2$ CI)	1.26	107.2	1.33

calculation was of NO₂ + O₂ and used a smaller number of active orbitals for NO₂. The ground state PES intersects the $\tilde{A}^2B_2$ PES close to its minimum energy geometry. The CI is present for NO₂ in C_{2v} symmetry and different pairs of values of NO distance and ONO bond angle. The degeneracy breaks when the C_{2v} symmetry is broken. The $\tilde{X}/\tilde{A}$ CI and the $\tilde{A}^2B_2$ minimum are very similar geometrically and energetically (Table 5.6) and this leads to strong vibronic effects between the $\tilde{X}^2A_1$ and $\tilde{A}^2B_2$ states.

The nascent NO₂ from the reaction can be expected to be, based on the energy partitioning analysis above, highly vibrationally excited and be formed in the $\tilde{X} - \tilde{A}$ vibronic states. Delon, Jost and co-workers have through a series of studies of NO₂ in a supersonic jet, systematically characterized the nature of the vibronic states of this molecule [184–187]. They have explained the laser induced dispersed fluorescence spectrum (LIDFS) in terms of the emission from the states near the $\tilde{X}-\tilde{A}$ conical intersection by considering strong vibronic coupling between the dense set of high vibrational levels of the $\tilde{X}^2A_1$ state and the sparser isoenergetic vibrational levels of the $\tilde{A}^2B_2$ state. The overall symmetry of the emitting vibronic states studied by them is B_2 which are a combination of b_2 (asymmetric stretch) vibrational levels of the $\tilde{X}^2A_1$ state and the a_1 (symmetric stretch and bend) vibrational levels of the $\tilde{A}^2B_2$ state. They considered only the B_2 vibronic states because these are the only ones to which absorption is allowed [187, 191]. Further, they showed that the vibronic states below and around 2 eV are well described as a linear combination of one dominant vibrational level of $\tilde{A}^2B_2$ and a few highly excited vibrational levels of the $\tilde{X}^2A_1$. Following

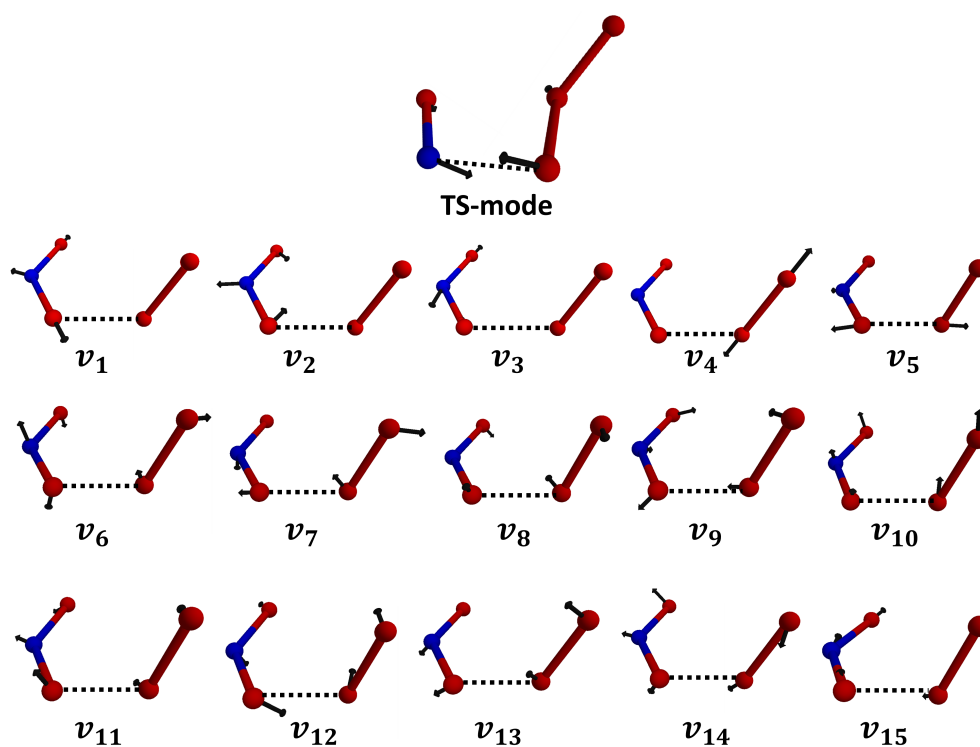


Figure 5.12: Projections of the product modes onto the reaction coordinate vector at the transition state. v_1 , v_2 , and v_3 correspond to symmetric stretch, bend and asymmetric stretch of NO₂. v_4 corresponds to the O₂ stretch and, v_5 , v_8 , and v_9 correspond to intermolecular motion.

the notation of Delon et. al. [187], such vibronic states can be written as,

$$|B_2(\text{vibronic})\rangle \propto |\tilde{A}^2B_2; v_1, v_2, v_3(\text{even})\rangle + \sum C_{v_i} |\tilde{X}^2A_1; v'_1, v'_2, v'_3(\text{odd})\rangle$$

where v_1, v_2, v_3 (v'_1, v'_2, v'_3) are the number of quanta in the symmetric stretch, bending and asymmetric stretch normal modes respectively of the ground (excited) state. The asymmetric stretch is a basis for the b_2 irreducible representation of the C_{2v} point group. The even number of quanta v'_3 in $\tilde{A}^2B_2$ and the odd number of quanta v_3 in $\tilde{X}^2A_1$ ensures B_2 symmetry of the vibronic state.

We hypothesize that the chemiluminescence is due to formation of NO₂ molecules in $\tilde{X}^2A_1 - \tilde{A}^2B_2$ vibronic states which subsequently emit light. The emission process is much like that in the LIDFS, except that in the case of chemiluminescence the vibronic states are populated in the course of a chemical reaction after thermally crossing a barrier rather than by absorption of light. A product NO₂ formed in the $\tilde{X}^2A_1$ state with odd (even) v_3 will be of B_2 (A_1) vibronic symmetry and can mix with a $\tilde{A}^2B_2$ state with even (odd) v'_3 . The uniqueness of NO₂ is in the vibronic mixing of the ground and first excited electronic states, due to which vibrational hot molecules are actually in the mixed $\tilde{X}^2A_1 - \tilde{A}^2B_2$ vibronic states, from which emission to lower vibrational states is significant. This can be contrasted with typical vibrationally hot molecules where excitation is to the vibrational levels of the ground electronic state. If such a hot molecule is produced in a chemical reaction, it mostly relaxes through collisions because vibrational emission is subject to the selection rule $\Delta v_i = \pm 1$ and is slow because of the small Einstein A coefficient, which determines the rate of spontaneous emission. This is because the A coefficient is proportional to the cube of the energy difference between the two states: Emission to the immediately lower vibrational state is of relatively small frequency corresponding to a small rate compared to an electronic or vibronic transition which is of relatively higher frequency. Moreover, A is proportional to the transition dipole moment which is generally much smaller in a vibrational transition than in an electronic transition [192].

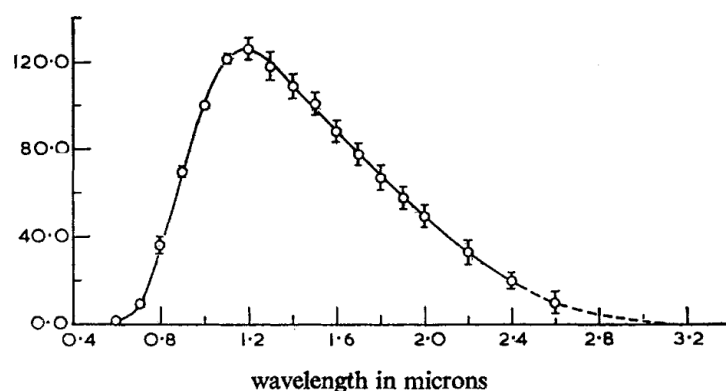


Figure 5.13: Chemiluminescence emission spectra (Figure taken from [1] : Clough, P. N.; Thrush, B. A. Mechanism of chemiluminescent reaction between nitric oxide and ozone. *Trans. Faraday. Soc.* 1967, 63, 915-925). The peak of the spectrum is at approximately 1.2 microns corresponding to an energy of ~ 1.03 eV.

The energies of the proposed emissive states with energy close to the $\tilde{X}^2A_1/\tilde{A}^2B_2$ CI with energy 1.33 eV are consistent with the NO + O₃ emission spectrum (Figure 5.13) which corresponds to energies from 0.4 to 2.0 eV with a peak near 1.1 eV. The quantum yield of the excited NO₂, which leads to chemiluminescence, is estimated to be $\sim 0.12 - 0.18$ [174]. The reduction in yield of chemiluminescence can be due to competing collision induced relaxation pathways in NO₂ and the distribution of reaction energy in degrees of freedom other than the NO₂ modes.

5.3 Summarizing Remarks

The chemiluminescent reaction of NO + O₃ to give NO₂ + O₂ has been studied using the 4-state-MS-CASPT2//4SA-CASSCF method. The MEP of the reaction has been obtained. The TS barrier is found to be 3.3 kcal/mol in good agreement with experiment. The reactant ground electronic state is doubly degenerate and splits into two paths as the reactants approach. The barrier on the higher path is much greater than the TS barrier on the MEP and is thermally inaccessible. The reaction is highly exothermic and the majority of the reaction energy is disposed in the vibrational modes of NO₂. This molecule has an energetically accessible CI between the ground ($\tilde{X}^2A_1$) and first excited ($\tilde{A}^2B_2$) electronic states, and these two

states are strongly vibronically coupled. The excess energy in the nascent NO₂ populates its vibronic states. The typical $\Delta v_i = \pm 1$ vibrational selection does not apply to these states and emission to the lower states is allowed, which explains the broad chemiluminescence. The mechanism of chemiluminescence in the NO + O₃ reaction is very different from that in cycloperoxides, the only type of chemiluminescent system explored in depth until now, and the results provide fundamental new insights on the phenomenon of chemiluminescence.

Chapter 6

A new Method for Locating a Three-state Crossing of Potential Energy Surfaces

Non-radiative transitions between electronic states, through processes like internal conversion or inter system crossing, usually occur in regions of the potential energy landscape where two surfaces cross [193, 194]. For a long time, surface crossings were considered to be too rare to occur in the regions of reaction MEP and their importance in photophysical and photochemical processes was not appreciated. However, it is now well established that the CIs are quite common and wide-spread. To quote a recent study: “In the last two decades, it became clear that state crossings play a central role for internal conversion” [195]. While the impact of two-state crossings on excited state processes is well established, the role of surface crossings involving more than two states is still not well understood. In a study by Matsika, the importance of three-state CIs has been explored in the pyrimidine base, uracil, and the purine base, adenine [196]. It was concluded based on energetics, that in the case of adenine a three-state CI probably plays an important role in radiationless decay.

The most successful methods for locating two-state MECP on the PESs are based on either the Lagrange multiplier method [197] or the gradient projection method [198]. The Lagrange multiplier method involves the minimization of the upper electronic state subject to constraints

on the energy gap between the two electronic states. Keal et al. have tested these methods on a set of well known CIs in small molecules and their study suggest that the methods using the Lagrange multiplier are most efficient in terms of optimization cycles and CPU time, but the gradient projection methods are also competitive [199]. However, the former method involves calculating the Lagrange Hessian, which is not positive definite and cannot be computed using efficient updating methods such as Broyden-Fletcher-Goldfarb-Shanno (BFGS) scheme. This makes it harder to incorporate it in an existing optimization module [199–201]. In contrast, the gradient projection method does not involve computing the Hessian and saves considerable computational cost while optimizing the two-state crossings. It may be this advantage of the gradient projection method, which has led to it being implemented in popular electronic structure packages such as Gaussian [57], MOLPRO [58] and MOLCAS [202]. Implementation of the Lagrange multiplier method can be found in the COLOMBUS suite of programs [203]. The Lagrange multiplier method has been extended by Matsika and Yarkony to optimize three-state CIs [204]. There appears to be no implementation of method in standard quantum chemistry packages. Moreover there is no report on using the gradient projection method to locate a three-state crossing.

In our study of the ESIHT process in oNT which has been discussed in *Chapter 3*, it is found that the lowest triplet state, T_1 was very close in energy (about 1 kcal/mol) to the optimized S_1/S_0 CI. This suggested that a three-state crossing involving S_1 , T_1 and S_0 states might exist and if energetically accessible, plays an important role in the photophysics and photochemistry of oNT. We have developed a method to locate such a three-state crossing which is described in this chapter.

The method uses the gradient projection approach. It can be used to locate an intersection of three electronic states with two different spin multiplicities, where two states are of one spin multiplicity and the third state is of different spin multiplicity. It can also be used to locate a crossing of three states with two different spatial symmetries. Such types of three-state crossings will be referred to as 2+1 crossings in the rest of the discussion. The

starting geometry for locating a 2+1 crossing is a two-state CI. The idea is to minimize the energy gap between doubly degenerate states and the third state, while requiring that the two-state degeneracy is maintained. The theoretical description of the method is given in the next section followed by the application of the method on oNT to find a 2S+1T crossing. Summarizing remarks are presented in the final section.

6.1 Description of the Method

The theoretical framework is provided first followed by the actual procedure.

6.1.1 Theoretical Formulation

Before going into discussing 2+1 crossings, some background on two-state crossing is helpful. A two-state crossing between two PESs $E_i(\mathbf{R})$ and $E_j(\mathbf{R})$ is a geometry $\mathbf{R}$ where $E_i(\mathbf{R}) = E_j(\mathbf{R})$. To derive the conditions for a two-state CI, let us start with the assumption that we already have all the eigenfunctions of the Hamiltonian $\hat{H}(\mathbf{r}; \mathbf{R})$, where $\mathbf{r}$ denotes the electronic degrees of freedom, except the eigenfunctions, $\Psi_i(\mathbf{r}; \mathbf{R})$ and $\Psi_j(\mathbf{r}; \mathbf{R})$ corresponding to the two adiabatic states which are crossing. Further, we have two real diabatic functions, $\Phi_1(\mathbf{r}; \mathbf{R})$ and $\Phi_2(\mathbf{r}; \mathbf{R})$ which satisfy $\langle \frac{\partial}{\partial \mathbf{R}} \Phi_1 | \Phi_2 \rangle = 0$ and span the same space as $\Psi_i(\mathbf{r}; \mathbf{R})$ and $\Psi_j(\mathbf{r}; \mathbf{R})$. Suppose the matrix elements of the Hamiltonian in this diabatic basis are denoted as $H_{st} = \langle \Phi_s | \hat{H} | \Phi_t \rangle$; $s, t = 1, 2$, the eigenvalues of the Hamiltonian can be obtained by solving secular equation,

$$\begin{vmatrix} H_{11}(\mathbf{R}) - E(\mathbf{R}) & H_{12}(\mathbf{R}) \\ H_{21}(\mathbf{R}) & H_{22}(\mathbf{R}) - E(\mathbf{R}) \end{vmatrix} = 0 \quad (6.1)$$

The expression for the two eigenvalues are,

$$E_1 = \frac{1}{2}(H_{11}(\mathbf{R}) + H_{22}(\mathbf{R})) + \sqrt{[(H_{11}(\mathbf{R}) - H_{22}(\mathbf{R}))^2 + 4H_{12}(\mathbf{R})^2]} \quad (6.2a)$$

$$E_2 = \frac{1}{2}(H_{11}(\mathbf{R}) + H_{22}(\mathbf{R})) - \sqrt{[(H_{11}(\mathbf{R}) - H_{22}(\mathbf{R}))^2 + 4H_{12}(\mathbf{R})^2]} \quad (6.2b)$$

For E_1 and E_2 to be equal, two conditions,

$$H_{11}(\mathbf{R}) - H_{22}(\mathbf{R}) = 0 \quad (6.3a)$$

$$H_{12}(\mathbf{R}) = 0 \quad (6.3b)$$

must be satisfied simultaneously. For a diatomic molecule with a single internal degree of freedom, this is not possible for states of same symmetry and is called non-crossing rule [205]. For states with different spatial symmetry or different spin multiplicity, $H_{12}(\mathbf{R})$ is zero at all $\mathbf{R}$ and a crossing is possible. The non-crossing rule is not a consideration for polyatomics, since they have multiple internal coordinates, and thus multiple variables.

The Taylor expansion of the above two conditions (6.3a and 6.3b) up to first order at a geometry $\mathbf{R}_0$ is,

$$H_{11}(\mathbf{R}) - H_{22}(\mathbf{R}) = H_{11}^0(\mathbf{R}_0) - H_{22}^0(\mathbf{R}_0) + \mathbf{a}^\dagger d\mathbf{R} = 0 \quad (6.4a)$$

$$H_{12}(\mathbf{R}) = H_{12}^0(\mathbf{R}_0) + \mathbf{b}^\dagger d\mathbf{R} = 0 \quad (6.4b)$$

where

$$\mathbf{a} = \left(\frac{\partial(H_{11}^0(\mathbf{R}_0) - H_{22}^0(\mathbf{R}_0))}{\partial \mathbf{R}} \right)_{\mathbf{R}=\mathbf{R}_0} \quad (6.5)$$

$$\mathbf{b} = \left(\frac{\partial H_{12}^0(\mathbf{R}_0)}{\partial \mathbf{R}} \right)_{\mathbf{R}=\mathbf{R}_0} \quad (6.6)$$

$$d\mathbf{R} = \mathbf{R} - \mathbf{R}_0 \quad (6.7)$$

If $\mathbf{R}_0$ is the geometry at which two states cross, then Eq. 6.3a and 6.3b are satisfied at $\mathbf{R}_0$ whereby Eq. 6.4a and 6.4b reduce to,

$$\mathbf{a}^\dagger d\mathbf{R} = \mathbf{0} \quad (6.8)$$

$$\mathbf{b}^\dagger d\mathbf{R} = \mathbf{0} \quad (6.9)$$

It is clear from Eq. 6.8 and 6.9 that if the geometry is distorted in orthogonal directions to the vector space spanned by $\mathbf{a}$ and $\mathbf{b}$, the degeneracy is maintained. This $N-2$ dimension space (here, N is the number of molecular degrees of freedom) is called the intersection space, while the two-dimensional space spanned by $\mathbf{a}$ and $\mathbf{b}$ where the degeneracy is lifted is called the branching space.

So far, the formalism has been developed in a diabatic basis. We now show that the branching space vectors in an adiabatic basis, say $\mathbf{X}_1$ and $\mathbf{X}_2$, span the same two-dimensional space as the vectors $\mathbf{a}$ and $\mathbf{b}$. The transformation of the branching space vectors from diabatic basis to adiabatic basis can be shown using the fact that the diabatic and adiabatic functions are related by a unitary matrix as below.

$$\begin{pmatrix} \Phi_1(\mathbf{r}; \mathbf{R}) \\ \Phi_2(\mathbf{r}; \mathbf{R}) \end{pmatrix} = \begin{pmatrix} \cos \theta & \sin \theta \\ -\sin \theta & \cos \theta \end{pmatrix} \begin{pmatrix} \Psi_1(\mathbf{r}; \mathbf{R}) \\ \Psi_2(\mathbf{r}; \mathbf{R}) \end{pmatrix} \quad (6.10)$$

The expanded form of vector $\mathbf{b}$ is,

$$\frac{\partial H_{12}(\mathbf{R})}{\partial \mathbf{R}} = \frac{\partial \langle \Phi_1 | \hat{H} | \Phi_2 \rangle}{\partial \mathbf{R}} \quad (6.11)$$

$$= \left\langle \frac{\partial \Phi_1}{\partial \mathbf{R}} | \hat{H} | \Phi_2 \right\rangle + \langle \Phi_1 | \frac{\partial \hat{H}}{\partial \mathbf{R}} | \Phi_2 \rangle + \langle \Phi_1 | \hat{H} | \frac{\partial \Phi_2}{\partial \mathbf{R}} \rangle \quad (6.12)$$

The diabatic functions are now written in terms of their adiabatic counterparts

$$\Phi_1(\mathbf{r}; \mathbf{R}) = \cos \theta \Psi_1 + \sin \theta \Psi_2 \quad (6.13)$$

$$\Phi_2(\mathbf{r}; \mathbf{R}) = -\sin \theta \Psi_1 + \cos \theta \Psi_2 \quad (6.14)$$

in Eq. 6.12 and each of the three terms of the expression are evaluated individually. First term becomes,

$$\langle \frac{\partial \Phi_1}{\partial \mathbf{R}} | \hat{H} | \Phi_2 \rangle = \langle \frac{\partial}{\partial \mathbf{R}} (\cos \theta \Psi_1 + \sin \theta \Psi_2) | \hat{H} | -\sin \theta \Psi_1 + \cos \theta \Psi_2 \rangle \quad (6.15)$$

$$= (E_2 - E_1) \sin \theta \cos \theta \langle \frac{\partial}{\partial \mathbf{R}} \Phi_1 | \Phi_1 \rangle = 0 \quad (6.16)$$

The above simplification uses the diabatic condition, $\langle \frac{\partial}{\partial \mathbf{R}} \Phi_1 | \Phi_2 \rangle = 0$ and the assumption that Φ_1 and Φ_2 are real which implies $\langle \frac{\partial}{\partial \mathbf{R}} \Phi_1 | \Phi_1 \rangle = 0$. The third term in 6.12 is symmetrically related to the first term and is also zero. The second can be simplified as,

$$\langle \Phi_1 | \frac{\partial \hat{H}}{\partial \mathbf{R}} | \Phi_2 \rangle = \langle \cos \theta \Psi_1 + \sin \theta \Psi_2 | \frac{\partial \hat{H}}{\partial \mathbf{R}} | -\sin \theta \Psi_1 + \cos \theta \Psi_2 \rangle \quad (6.17)$$

$$\begin{aligned} &= \cos \theta \sin \theta (\langle \Psi_2 | \frac{\partial \hat{H}}{\partial \mathbf{R}} | \Psi_2 \rangle - \langle \Psi_1 | \frac{\partial \hat{H}}{\partial \mathbf{R}} | \Psi_1 \rangle) \\ &\quad + \cos^2 \theta \langle \Psi_1 | \frac{\partial \hat{H}}{\partial \mathbf{R}} | \Psi_2 \rangle - \sin^2 \theta \langle \Psi_2 | \frac{\partial \hat{H}}{\partial \mathbf{R}} | \Psi_1 \rangle \end{aligned} \quad (6.18)$$

Using the Hellman-Feynman theorem, Eq. 6.18 can be written as,

$$\begin{aligned} \langle \Phi_1 | \frac{\partial \hat{H}}{\partial \mathbf{R}} | \Phi_2 \rangle &= \cos \theta \sin \theta \left(-\frac{\partial}{\partial \mathbf{R}} \langle \Psi_1 | \hat{H} | \Psi_1 \rangle + \frac{\partial}{\partial \mathbf{R}} \langle \Psi_2 | \hat{H} | \Psi_2 \rangle \right) \\ &\quad + \cos^2 \theta \langle \Psi_1 | \frac{\partial \hat{H}}{\partial \mathbf{R}} | \Psi_2 \rangle - \sin^2 \theta \langle \Psi_2 | \frac{\partial \hat{H}}{\partial \mathbf{R}} | \Psi_1 \rangle \end{aligned} \quad (6.19)$$

$$= \cos \theta \sin \theta \frac{\partial}{\partial \mathbf{R}} (E_1 - E_2) + (\cos^2 \theta - \sin^2 \theta) \langle \Psi_2 | \frac{\partial \hat{H}}{\partial \mathbf{R}} | \Psi_1 \rangle \quad (6.20)$$

$$= \frac{\sin 2\theta}{2} \frac{\partial}{\partial \mathbf{R}} (E_1 - E_2) + \cos 2\theta \langle \Psi_2 | \frac{\partial \hat{H}}{\partial \mathbf{R}} | \Psi_1 \rangle \quad (6.21)$$

The expression for $\frac{\partial H_{12}(\mathbf{R})}{\partial \mathbf{R}} = \mathbf{b}$ in Eq. 6.12, in terms of the adiabatic functions, has the above form.

One now notices that " $\mathbf{b}$ " is a linear combination of two vectors. Denoting

$$\mathbf{X}_1 = \frac{\partial}{\partial \mathbf{R}}(E_1 - E_2) \quad (6.22)$$

$$\mathbf{X}_2 = \langle \Psi_2 | \frac{\partial \hat{H}}{\partial \mathbf{R}} | \Psi_1 \rangle \quad (6.23)$$

one can write

$$2\mathbf{b} = \sin 2\theta \frac{\partial}{\partial \mathbf{R}}(E_1 - E_2) + 2 \cos 2\theta \langle \Psi_2 | \frac{\partial \hat{H}}{\partial \mathbf{R}} | \Psi_1 \rangle \quad (6.24)$$

$$2\mathbf{b} = \sin 2\theta \mathbf{X}_1 + 2 \cos 2\theta \mathbf{X}_2 \quad (6.25)$$

The vectors $\mathbf{X}_1$ and $\mathbf{X}_2$ referred to as gradient difference and derivative couplings vectors, respectively.

Now, let's do a similar procedure for the vector $\mathbf{a}$. The expanded form of vector $\mathbf{a}$ is,

$$\frac{\partial}{\partial \mathbf{R}}(H_{11}(\mathbf{R}) - H_{22}(\mathbf{R})) = \frac{\partial}{\partial \mathbf{R}}H_{11}(\mathbf{R}) - \frac{\partial}{\partial \mathbf{R}}H_{22}(\mathbf{R}) \quad (6.26)$$

Consider the first term in the above expression.

$$\frac{\partial}{\partial \mathbf{R}}H_{11}(\mathbf{R}) = \frac{\partial \langle \Phi_1 | \hat{H} | \Phi_1 \rangle}{\partial \mathbf{R}} \quad (6.27)$$

$$= \langle \frac{\partial \Phi_1}{\partial \mathbf{R}} | \hat{H} | \Phi_1 \rangle + \langle \Phi_1 | \frac{\partial \hat{H}}{\partial \mathbf{R}} | \Phi_1 \rangle + \langle \Phi_1 | \hat{H} | \frac{\partial \Phi_1}{\partial \mathbf{R}} \rangle \quad (6.28)$$

The diabatic functions are now written in terms of their adiabatic counterparts in first term of Eq. 6.28,

$$\langle \frac{\partial \Phi_1}{\partial \mathbf{R}} | \hat{H} | \Phi_1 \rangle = \langle \frac{\partial}{\partial \mathbf{R}} (\cos \theta \Psi_1 + \sin \theta \Psi_2) | \hat{H} | (\cos \theta \Psi_1 + \sin \theta \Psi_2) \rangle \quad (6.29)$$

$$= (E_1 \cos^2 \theta + E_2 \sin^2 \theta) \langle \frac{\partial \Phi_1}{\partial \mathbf{R}} | \Phi_1 \rangle = 0 \quad (6.30)$$

The above simplification uses the assumption that Φ_1 and Φ_2 are real which implies $\langle \frac{\partial}{\partial \mathbf{R}} \Phi_1 | \Phi_1 \rangle = 0$. The third term in 6.28 is symmetrically related to the first term and is also zero. This simplifies $\frac{\partial}{\partial \mathbf{R}} H_{11}(\mathbf{R})$ to,

$$\frac{\partial}{\partial \mathbf{R}} H_{11}(\mathbf{R}) = \langle \Phi_1 | \frac{\partial \hat{H}}{\partial \mathbf{R}} | \Phi_1 \rangle \quad (6.31)$$

$$= \cos^2 \theta \frac{\partial}{\partial \mathbf{R}} E_1 + \sin^2 \theta \frac{\partial}{\partial \mathbf{R}} E_2 - 2 \cos \theta \sin \theta \langle \Psi_2 | \frac{\partial \hat{H}}{\partial \mathbf{R}} | \Psi_1 \rangle \quad (6.32)$$

After doing the similar manipulations to $\frac{\partial}{\partial \mathbf{R}} H_{22}(\mathbf{R})$ (second term in Eq. 6.26) it reduces to,

$$\frac{\partial}{\partial \mathbf{R}} H_{22}(\mathbf{R}) = \langle \Phi_2 | \frac{\partial \hat{H}}{\partial \mathbf{R}} | \Phi_2 \rangle \quad (6.33)$$

$$= \cos^2 \theta \frac{\partial}{\partial \mathbf{R}} E_2 + \sin^2 \theta \frac{\partial}{\partial \mathbf{R}} E_1 + 2 \cos \theta \sin \theta \langle \Psi_2 | \frac{\partial \hat{H}}{\partial \mathbf{R}} | \Psi_1 \rangle \quad (6.34)$$

The expression for $\frac{\partial}{\partial \mathbf{R}} (H_{11}(\mathbf{R}) - H_{22}(\mathbf{R})) = \mathbf{a}$ in Eq. 6.12, in terms of the adiabatic functions, has the form shown below.

$$\mathbf{a} = \langle \Phi_1 | \frac{\partial \hat{H}}{\partial \mathbf{R}} | \Phi_1 \rangle - \langle \Phi_2 | \frac{\partial \hat{H}}{\partial \mathbf{R}} | \Phi_2 \rangle \quad (6.35)$$

$$\mathbf{a} = (\cos^2 \theta - \sin^2 \theta) \frac{\partial}{\partial \mathbf{R}} (E_1 - E_2) - 2 \langle \Psi_2 | \frac{\partial \hat{H}}{\partial \mathbf{R}} | \Psi_1 \rangle \quad (6.36)$$

$$\mathbf{a} = \cos 2\theta \frac{\partial}{\partial \mathbf{R}} (E_1 - E_2) - 2 \sin 2\theta \langle \Psi_2 | \frac{\partial \hat{H}}{\partial \mathbf{R}} | \Psi_1 \rangle \quad (6.37)$$

$$\mathbf{a} = \cos 2\theta \mathbf{X}_1 - 2 \sin 2\theta \mathbf{X}_2 \quad (6.38)$$

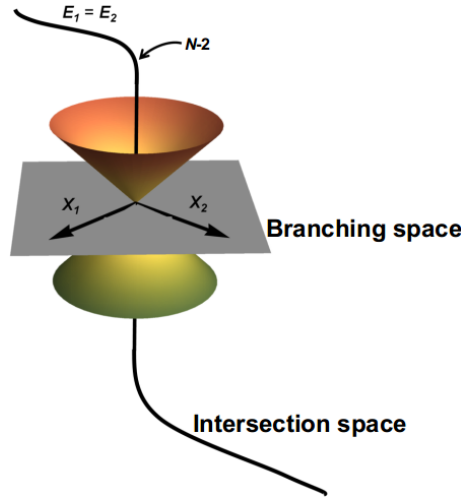


Figure 6.1: Schematic representation of the two-state CI. The black curve is a hyper line with $N-2$ dimension and represents the intersection space, and the branching space consists of $\mathbf{X}_1$ and $\mathbf{X}_2$ vectors

In conclusion, the vectors in diabatic basis ($\mathbf{a}$, $\mathbf{b}$) are related to the vectors in adiabatic basis ($\mathbf{X}_1$, $\mathbf{X}_2$) by an unitary matrix as given below.

$$\begin{pmatrix} \mathbf{a} \\ 2\mathbf{b} \end{pmatrix} = \begin{pmatrix} \cos 2\theta & -\sin 2\theta \\ \sin 2\theta & \cos 2\theta \end{pmatrix} \begin{pmatrix} \mathbf{X}_1 \\ 2\mathbf{X}_2 \end{pmatrix}$$

It is thus clear that the two-dimensional branching space (spanned by $\mathbf{a}$ and $\mathbf{b}$) in the diabatic representation is same as that (spanned by $\mathbf{X}_1$ and $\mathbf{X}_2$) in the adiabatic representation.

The topological features of a two-state CI with branching and intersection spaces is shown in Figure 6.1. It is worth noting that if the two states have different spin multiplicity or different spatial symmetry, Eq. 6.23 automatically goes to zero at all geometries. This increases the dimensionality of the intersection space for such crossings to $N-1$.

The conditions for a three-state crossing can be derived using a similar approach as that used for a two-state crossing. $\Psi_i(\mathbf{r}; \mathbf{R})$, $\Psi_j(\mathbf{r}; \mathbf{R})$ and $\Psi_k(\mathbf{r}; \mathbf{R})$ are considered to be the unknown adiabatic wavefunctions of the three electronic states which become degenerate at the three-state crossing. These adiabatic functions can be written as a linear combination of

three real orthonormal diabatic wavefunctions $\Phi_1(\mathbf{r}; \mathbf{R})$, $\Phi_2(\mathbf{r}; \mathbf{R})$ and $\Phi_3(\mathbf{r}; \mathbf{R})$.

$$\Psi_m(\mathbf{r}; \mathbf{R}) = c_{m1}\Phi_1(\mathbf{r}; \mathbf{R}) + c_{m2}\Phi_2(\mathbf{r}; \mathbf{R}) + c_{m3}\Phi_3(\mathbf{r}; \mathbf{R}) \quad m = i, j, k \quad (6.39)$$

The corresponding eigenvalues of the Hamiltonian can be obtained by solving 3×3 secular equation,

$$\begin{vmatrix} H_{11}(\mathbf{R}) - E(\mathbf{R}) & H_{12}(\mathbf{R}) & H_{13}(\mathbf{R}) \\ H_{21}(\mathbf{R}) & H_{22}(\mathbf{R}) - E(\mathbf{R}) & H_{23}(\mathbf{R}) \\ H_{31}(\mathbf{R}) & H_{32}(\mathbf{R}) & H_{33}(\mathbf{R}) - E(\mathbf{R}) \end{vmatrix} = 0 \quad (6.40)$$

The three eigenvalues of $\hat{H}(\mathbf{r}; \mathbf{R})$ will be degenerate if the five conditions given below are satisfied.

$$H_{11}(\mathbf{R}) - H_{22}(\mathbf{R}) = H_{22}(\mathbf{R}) - H_{33}(\mathbf{R}) = 0 \quad (6.41a)$$

$$H_{12}(\mathbf{R}) = H_{13}(\mathbf{R}) = H_{23}(\mathbf{R}) = 0 \quad (6.41b)$$

The Taylor expansion of the above five conditions and the subsequent manipulations that were discussed previously in the case of two-state CI, one can show that the five branching space vectors in which the three-state degeneracy is lifted are,

$$\mathbf{a} = \frac{\partial(H_{12})}{\partial \mathbf{R}} \quad (6.42a)$$

$$\mathbf{b} = \frac{\partial(H_{13})}{\partial \mathbf{R}} \quad (6.42b)$$

$$\mathbf{b} = \frac{\partial(H_{23})}{\partial \mathbf{R}} \quad (6.42c)$$

$$\mathbf{c} = \frac{\partial(H_{11} - H_{22})}{\partial \mathbf{R}} \quad (6.42d)$$

$$\mathbf{d} = \frac{\partial(H_{22} - H_{33})}{\partial \mathbf{R}} \quad (6.42e)$$

The transformation of the branching space vectors, 6.44 from diabatic basis to adiabatic basis can be shown using the fact that the diabatic and adiabatic functions are related by an unitary matrix as below.

$$\begin{pmatrix} \Phi_1 \\ \Phi_2 \\ \Phi_3 \end{pmatrix} = \begin{pmatrix} c\beta c\gamma(a) & -c\beta s\gamma(b) & s\beta(c) \\ c\alpha s\gamma + s\alpha s\beta c\gamma(d) & c\alpha c\gamma - s\alpha s\beta s\gamma(e) & -s\alpha c\beta(f) \\ s\alpha s\gamma - c\alpha s\beta c\gamma(g) & s\alpha c\gamma + c\alpha s\beta s\gamma(h) & c\alpha c\beta(i) \end{pmatrix} \begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \Psi_3 \end{pmatrix} \quad (6.43)$$

Here, c refers $\cos$ and s refers $\sin$. Alphabets $(a, b, c, d, e, f, g, h, i)$ in parenthesis are just notations for corresponding matrix elements. By using the above relation between diabatic and adiabatic functions, one can find a rotation matrix which transforms the branching space vectors of three-state conical intersection from diabatic to adiabatic. The five branching space vectors in adiabatic representation are,

$$\mathbf{X}_1 = \frac{\partial(E_i - E_j)}{\partial \mathbf{R}} \quad (6.44a)$$

$$\mathbf{X}_2 = \frac{\partial(E_j - E_k)}{\partial \mathbf{R}} \quad (6.44b)$$

$$\mathbf{X}_3 = \langle \Psi_i | \frac{\partial \hat{H}}{\partial \mathbf{R}} | \Psi_j \rangle \quad (6.44c)$$

$$\mathbf{X}_4 = \langle \Psi_j | \frac{\partial \hat{H}}{\partial \mathbf{R}} | \Psi_k \rangle \quad (6.44d)$$

$$\mathbf{X}_5 = \langle \Psi_i | \frac{\partial \hat{H}}{\partial \mathbf{R}} | \Psi_k \rangle \quad (6.44e)$$

the vectors in diabatic basis ($\mathbf{a}, \mathbf{b}, \mathbf{c}, \mathbf{d}, \mathbf{e}$) are related to the vectors in adiabatic basis ($\mathbf{X}_1, \mathbf{X}_2, \mathbf{X}_3, \mathbf{X}_4, \mathbf{X}_5$) by an unitary matrix, $\mathbf{U}$ which is given below.

$$\mathbf{U} = \begin{pmatrix} ae + bd & af + cd & bf + ce & c\beta c\gamma(c\alpha s\alpha + s\alpha s\beta c\gamma) & s\alpha s\beta c\beta \\ ah + bg & ai + cg & bi + ch & c\beta c\gamma(s\alpha s\gamma - c\alpha s\beta c\gamma) & -c\alpha c\beta s\beta \\ dh + eg & di + fg & ei + fh & (c\alpha s\gamma + s\alpha s\beta s\gamma)(s\alpha s\gamma - c\alpha s\beta c\gamma) & -s\alpha c\alpha c^2\beta \\ 2(ab - de) & 2(bc - df) & 2(ac - fe) & c^2\beta c^2\gamma + (c\alpha s\gamma + s\alpha s\beta c\gamma)^2 & c^2\beta - c^2\alpha - s^2\alpha s^2\beta \\ 2(de - gh) & 2(df - gi) & 2(fe - hi) & (c\alpha s\gamma + s\alpha s\beta c\gamma)^2 - (s\alpha s\gamma - c\alpha s\beta c\gamma)^2 & c^2\alpha c^2\beta - s^2\alpha c^2\beta \end{pmatrix}$$

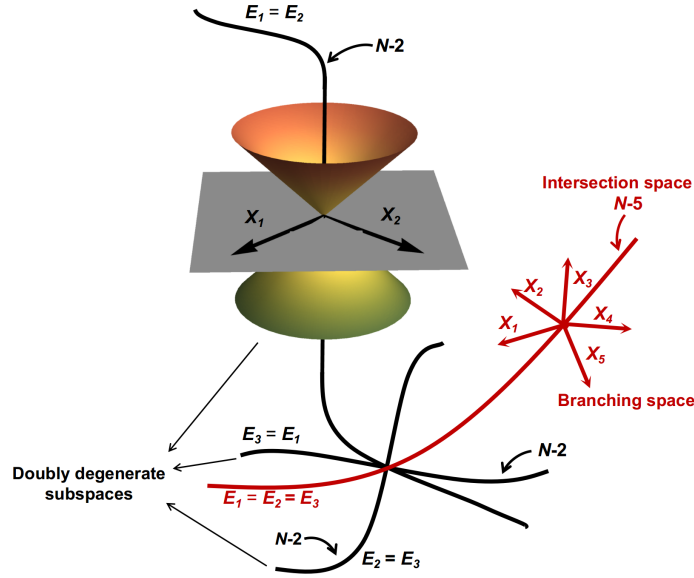


Figure 6.2: Schematic representation of the three-state crossing seam is shown in red. Higher dimensional seams where only double degeneracy exists are shown in black.

In the case of three-state crossing, the branching space has three subspaces where only one of the three states becomes non-degenerate with respect to the other two. Doubly degeneracy is maintained in these subspaces. The schematic representation of the three-state crossing along with the doubly degenerate subspaces within the branching space of three-state crossing is depicted in Figure 6.2. The black and red curves in the figure represent the three-state crossing and two-state crossing subspaces, respectively.

6.1.2 Procedure for Locating a 2+1 Crossing point

For a 2+1 crossing, where one of the states (say $\Psi_k(\mathbf{r}; \mathbf{R})$) has a different spin multiplicity or different spatial symmetry than the other two states. With this consideration, the two coupling elements ($\langle \Psi_j | \Psi_k \rangle$ and $\langle \Psi_i | \Psi_k \rangle$) of the 3×3 Hamiltonian matrix in adiabatic basis become zero at all geometries. As a result, the corresponding derivative coupling elements go to zero and the branching space in which the three-state degeneracy is broken, reduces to a three-dimensional space and the intersection space increases to $N-3$ dimensions. the three

branching space vectors, along which the 2+1 crossing degeneracy is lifted are,

$$\mathbf{X}_1 = \frac{\partial(E_i - E_j)}{\partial \mathbf{R}} \quad (6.45a)$$

$$\mathbf{X}_2 = \frac{\partial(E_j - E_k)}{\partial \mathbf{R}} \quad (6.45b)$$

$$\mathbf{X}_3 = \langle \Psi_i | \frac{\partial \hat{H}}{\partial \mathbf{R}} | \Psi_j \rangle \quad (6.45c)$$

As stated earlier, our strategy to find a 2+1 crossing is as follows; start with an optimized two-state CI, $E_i = E_j$ and minimize the energy gap $0.5(E_i + E_j) - E_k$, while preserving the two state degeneracy ($E_i - E_j = 0$). To minimize the energy gap between the doubly degenerate ($E_i = E_j$) state and the third state (E_k), we define the gradient vector $\mathbf{G}$,

$$\mathbf{G} = -\frac{\partial}{\partial \mathbf{R}}(0.5(E_i + E_j) - E_k) \quad (6.46)$$

To preserve the degeneracy between states i and j , we must project out the branching space vectors Eq. 6.45a and Eq. 6.45c from $\mathbf{G}$. After projecting them out, we obtain a new gradient vector, $\mathbf{G}'$, which will lead to a 2+1 crossing point on the seam,

$$\mathbf{G}' = \mathbf{G} - d_1 \mathbf{X}_1 - d_2 \mathbf{X}_3 \quad (6.47)$$

here, $d_1 = \mathbf{X}_1^\dagger \mathbf{G}$ and $d_2 = \mathbf{X}_3^\dagger \mathbf{G}$.

6.2 Application to *o*-Nitrotoluene

The photo-chemistry of oNT has been extensively discussed in *Chapter 3*. The oNT molecule can be considered as a model system for oNB derivatives (which are mostly used as photo-labile caged compounds) as well as a prototype for nitro-aromatic HEMs. As discussed in the introduction of the current chapter, in the course of our investigation of the ESIHT process in oNT (*Chapter 3*), we found the PES regions where the two lowest singlet states, S_0 , S_1

and triplet state, T_1 have very similar energies. The method to locate a 2+1 crossing point described in the previous section has been used to find the 2S+1T (S_0 , S_1 and T_1) crossing point in oNT, thereby confirming the existence of a three-state crossing region on the PESs of oNT. This three-state crossing may provide a more efficient relaxation pathway by causing a complex branching from S_1 to T_1 and S_0 states, which has yet to be investigated.

The CASSCF method implemented in MOLPRO[58] has been used to evaluate adiabatic coupling and gradient vectors analytically. The Pople basis set, 6-31G(d,p) was used for all calculations. The employed active space consists of 16 electrons in 13 orbitals denoted as cas(16-in13). The starting point was the S_0/S_1 CI which was optimized using a three state-averaged CASSCF wavefunction composed of two lowest singlets and the lowest triplet.

Table 6.1: Energy gap between the degenerate and the third state, and, the energy gap between two lowest singlet states along the gradient $\mathbf{G}'$ coordinate

Step size	$\Delta E_{1,2,3}(\text{kcal/mol})$	$\Delta E_{1,2}(\text{kcal/mol})$
0.01	-0.809	0.098
0.03	-0.731	0.064
0.06	-0.642	0.131
0.09	-0.573	0.093
0.11	-0.487	0.021
0.13	-0.407	0.046
0.15	-0.332	0.103
0.17	-0.262	0.191
0.19	-0.196	0.191

The geometry of the S_1/S_0 CI has been displaced along the gradient vector $\mathbf{G}'$, and gradient and derivative coupling vectors are recalculated after every step to obtain a new $\mathbf{G}'$. The change in the two-state energy gap, $\Delta E_{S_0,S_1} = E_{S_0} - E_{S_1}$ and the energy gap between the

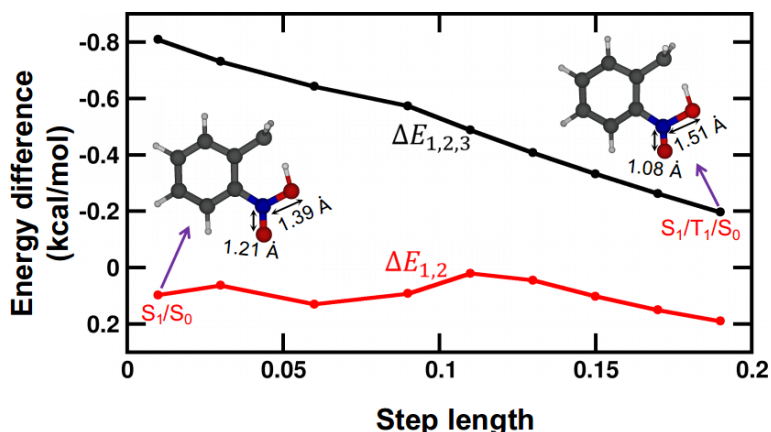


Figure 6.3: Change in the energy gap between the degenerate (S_1 and S_0) and the third state (T_1), and, the energy gap between two lowest singlet states along the gradient $\mathbf{G}'$ coordinate

degenerate states (S_0 and S_1) and the third state (T_1), defined as, $\Delta E_{S_0,S_1,T_1} = E_{T_1} - \frac{1}{2}(E_{S_0} + E_{S_1})$ along $\mathbf{G}'$ coordinate are presented in Table 6.1, and shown graphically in Figure 6.3. From Table 6.1 and Figure 6.3, it is clear that the energy gap $\Delta E_{S_0,S_1,T_1}$ is reducing without significantly affecting the two state degeneracy, $\Delta E_{S_0,S_1}$. The geometrical parameters of oNT that change significantly from the two-state CI to the 2S+1T crossing were found to be the N-O bond distances of the NO_2 group as shown in Figure 6.3.

6.3 Summarizing Remarks

We have described a method for locating a crossing point of three states having two different spin multiplicities or different spatial symmetries by using a two-state CI as the initial structure. The gradient projection approach has been used to obtain the vector along which the energy gap between the two states of the crossing and the third state decreases, while maintaining the existing degeneracy. Using this method, a three-state crossing point ($S_1/S_0/T_1$) on the PES of oNT was found. The three-state crossing region found in this study may create additional pathways for the ESIHT process in oNT. To rigorously evaluate the importance of a three-state crossing region on the photochemistry of oNT, one has to obtain the lowest energy crossing point on the seam. This lowest energy crossing point on the

PES can be obtained by simultaneously minimizing the energy gap in the branching space (through which one can reach a crossing point on the seam) and the energy of any state (or average energy of all states involved at crossing) in the complementary intersection space.

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List of Publications

1. M. Gudem and A. Hazra, *Intersystem Crossing Drives Photoisomerization in o-Nitrotoluene, a Model for Photolabile Caged Compounds.*, J. Phys. Chem. A. **122**, 21 (2018)., Chapter 3
2. M. Gudem and A. Hazra, *Ab initio Study of Photodissociation and Photoisomerization Mechanism in 1-Nitropropene, a Model for Nitro-aromatic High Energy Materials .*, (Manuscript under preperation), Chapter 4
3. M. Gudem and A. Hazra, *Mechanism of the Chemiluminescent Reaction between Nitric Oxide and Ozone.*, J. Phys. Chem. A. Accepted (DOI: 10.1021/acs.jpca.8b08812), Chapter 5
4. S. R. Malwal, M. Gudem, A. Hazra and H. Chakrapani, *Benzosultines as Sulfur Dioxide (SO₂) Donors.*, Org. Lett. **15**, 5 (2013).
5. D. P. Chauhan, S. J. Verma, M. Gudem, N. Panigrahi, K. Singh, A. Hazra and P. Talukdar, *Intramolecular cascade rearrangements of enynamine derived ketenimines: access to acyclic and cyclic amidines*, Org, Biomol. Chem. **15**, 4822 (2017).

