Mechanistic photodissociation of small molecules explored by electronic structure calculation and dynamics simulation

Qiu Fang

Department of Theoretical Chemistry and Biology
School of Biotechnology
Royal Institute of Technology
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Abstract

In this thesis, the combined electronic structure calculations and dynamics simulations have been performed to explore mechanistic photodissociation of phosgene, oxalyl chloride, benzoic acid, and the NO$_2$-H$_2$O complex.

The potential energy surfaces for Cl$_2$CO dissociation into CO + Cl + Cl in the $S_0$ and $S_1$ electronic states have been determined by the CASSCF, CCSD, and EOM-CCSD calculations, which are followed by direct ab initio molecular dynamics simulations to explore its photodissociation dynamics at 230 nm. It was found that the C-O stretching mode is initially excited upon irradiation and the excess internal energies are transferred to the C-Cl symmetric stretching mode within 200 fs. On average, the first and the second C-Cl bonds break completely within subsequent 60 and 100 fs, respectively. Electronic structure and dynamics calculations have provided strong evidence that the photo-initiated dissociation of Cl$_2$CO at 230 nm or shorter wavelengths is an ultrafast, adiabatic, and concerted three-body process.

Photoexcitation in UV region leads to the (CICO)$_2$ molecule in the $S_1$ state. Since the C-C bond fission has a high barrier on the $S_1$ pathway and the internal energies are redistributed among all vibrational modes, the $S_1$ direct dissociation was predicted to occur with little possibility. Internal conversion (IC) to the ground state is a possible pathway for the excited (CICO)$_2$ molecule to deactivate. But there is little possibility for the subsequent reactions to take place in the $S_0$ state. From the combined electronic structure calculation and dynamics simulation, we come into conclusion that the $S_1\rightarrow T_1$ intersystem crossing and followed by four-body dissociation to 2Cl($^2P$) and 2CO($^1\Sigma$) is the dominant pathway for photodissociation of (CICO)$_2$ in UV region, while the three-body dissociation is a minor channel with little possibility for the two-body dissociation. More importantly, the four-body dissociation of (CICO)$_2$ in the $T_1$ state is an ultrafast and synchronous concerted process.

The potential energy profiles for the alpha C-OH bond cleavage of benzoic acid in the low-lying electronic states have been determined by the combined CASSCF and CASPT2 calculations, which show that the photo-induced cleavage of the C-O alpha bond is of wavelength-dependent character. Finally, we report a quantitative understanding on how to generate hydroxyl radical from NO$_2$ and H$_2$O in troposphere upon photo-excitation at 410 nm by using multiconfigurational perturbation theory and density functional theory. The conical intersections were found to dominate the non-adiabatic relaxation processes after NO$_2$ irradiated at ~410 nm light source in troposphere and further control the generation of OH radical by means of hydrogen abstraction, which is in good agreement with two-component fluorescence observed by experimentally.
Acknowledgements

First of all, I am very grateful to my supervisor-Prof. Yi Luo for his guidance in the process of my study in Department of Theoretical Chemistry and Biology, Royal Institute of Technology. It was him that leads me into the field of theoretical chemistry. It was his help and encouragement that I can complete my thesis’ work. I greatly appreciate everything he taught me and really enjoy my stay in Stockholm. The four-year study in Stockholm is one of the most colorful seasons in my life, which will be kept in my mind forever.

I must thank Dr. Yajun Liu and Xuebo Chen in Beijing Normal University for their help on how to use advanced electronic structure methods and how to solve problems in mechanistic photochemistry. Finally I would like to express my gratitude to all friends and colleagues in Royal Institute of Technology and Beijing Normal University, whoever gave me help in study and in life.

I’m indebted to my parents for their continuous support, encouragement, and unselfish love.
Preface

The work presented in this thesis has been carried out at the Department of Theoretical Chemistry and Biology, School of Biotechnology, Royal Institute of Technology, Stockholm, Sweden.

List of papers included in the thesis

(1) Photodissociation of Phosgene: Theoretical Evidence for the Ultrafast and Synchronous Concerted Three-Body Process
Qiu Fang, Feng Zhang, Lin Shen, Wei-Hai Fang, and Yi Luo
Journal of Chemical Physics, 2009, 131, 164306.

(2) The Conical Intersection Dominates the Generation of Tropospheric Hydroxyl Radicals from NO₂ and H₂O
Qiu Fang, Juan Han, Jieling Jiang, Xuebo Chen, and Wei-Hai Fang

(3) Wavelength-Dependent Photodissociation of Benzoic Acid Monomer in α C-O Fission
Qiu Fang and Ya-Jun Liu

(4) Synchronous Concerted Four-Body Photodissociation of Oxalyl Chloride Explored by ab initio based Molecular Dynamics Simulations
Qiu Fang and Yi Luo
Manuscript
List of papers not included in the thesis

(5) Photoisomerization Mechanism of 4-Methylpyridine Explored by Electronic Structure Calculations and Nonadiabatic Dynamics Simulations
Jun Cao, Qiu Fang, and Wei-Hai Fang,

(6) Exploring Concerted Effects of Base Pairing and Stacking on the Excited-State Nature of DNA Oligonucleotides by DFT and TD-DFT Studies
Yue-Jie Ai, Gang-Long Cui, Qiu Fang, Wei-Hai Fang, and Yi Luo

Comments on My Contribution to the Papers Included

I have carried out most of calculations for all four papers, I, II, III, and IV, and had major responsibility for the writing of the papers.
## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>CCSD</td>
<td>Coupled-cluster method with single and double excitations</td>
</tr>
<tr>
<td>CASSCF</td>
<td>Complete active space self-consistent field</td>
</tr>
<tr>
<td>CIS</td>
<td>Configuration interaction with single excitation</td>
</tr>
<tr>
<td>CASPT2</td>
<td>Multiconfiguration second-order perturbation theory</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>EOM-CCSD</td>
<td>The equation-of-motion coupled-cluster method with single and double excitations</td>
</tr>
<tr>
<td>IC</td>
<td>Internal conversion</td>
</tr>
<tr>
<td>ISC</td>
<td>Intersystem crossing</td>
</tr>
<tr>
<td>MO</td>
<td>Molecular orbital</td>
</tr>
<tr>
<td>MP2</td>
<td>Second-order perturbation theory</td>
</tr>
<tr>
<td>MR-CI</td>
<td>Multireference configuration interaction</td>
</tr>
<tr>
<td>PES</td>
<td>Potential energy surface</td>
</tr>
<tr>
<td>TS</td>
<td>Transition state</td>
</tr>
<tr>
<td>ZPE</td>
<td>Zero-point energy</td>
</tr>
<tr>
<td>VR</td>
<td>Vibrational relaxation</td>
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Chapter 1

Research background

Photochemical reactions have long been regarded as basic and very important areas of physical chemistry, the results of which are relevant to atmospheric chemistry, biological systems, functional material, and many other processes. It has been realized in the 19th century that photochemical reactions occurred in the atmosphere and that these led to oxidation of pollutants and the formation of acidity in rainwater. The near-ultraviolet photochemistry of ozone has been a central theme in atmospheric chemistry, since the first photochemical theory proposed by Chapman in 1930 for stratospheric ozone formation. The photochemistry of nitrogen oxides (NOx) is of great contemporary interest and a radical catalytic cycle involving NOx was identified as one of the key ingredients of photochemical ozone production in urban areas. Ultraviolet light absorbed by DNA sometimes initiates damaging photochemical reactions and results in mutagenic photoproducts. This vulnerability is compensated for in all organisms by enzymatic repair of photo-damaged DNA. Equally important safeguards are associated with the intrinsic photophysical properties of nucleic acids. Understanding how the spatial organization of the bases controls the relaxation of excess electronic energy in the double helix and in alternative structures is currently one of the most exciting challenges in the field.

Photo-induced cis–trans isomerization of N=N or C=C double bond is a ubiquitous photochemical process and represents one of the simplest pathways for converting light energy into mechanical motion on a molecular level, which forms a fundamental step in optical memories, opto-electronic switching, molecular motors, and light-driven molecular shuttle.

Thermochemical reactions have been extensively investigated experimentally and theoretically, which lead to deep understanding of the nature of thermal reactions. In comparison, photochemical reactions have received less attention of theoretical and experimental chemists. Photochemical reactions start from one excited electronic state, but final products are in the ground state, namely, photo-induced reactions are non-adiabatic in most cases. Photochemical reactions have many pathways that are accessible in energy and several transient intermediates might be involved in the photochemical processes, which are not easy to measure experimentally. Importantly, photo-physical processes are probably in competition with photochemical reactions. Besides radiation transition, photochemical and photophysical processes include generally excited-state vibrational relaxation (VR), internal conversion (IC), intersystem crossing (ISC), and direct reactions along excited- or ground-state pathways, which are summarized in Scheme 1-1. It is evident that photochemical processes are much more complicated than thermochemical reactions and are difficult to treat theoretically. Even for some of classically
photochemical reactions, our understanding is far from complete. A lot of basic concepts and fundamental theories are required to be set up in order to better understand dynamics and mechanistic photochemistry of a polyatomic molecule.

A detailed understanding of the photo-reaction mechanism for any system has to be based on theoretical calculations and spectroscopic measurements. Recent advances in femtosecond laser and ultrafast electron diffraction techniques have led to unprecedented progress in the level of our understanding of photochemical processes for a polyatomic molecule. Meanwhile, the last twenty years have been seen a great leap forward in the ability to carry out accurate electronic structure calculations for photochemical reactions, due to enhanced computational power and significant methodological advances. 

Experimental data can be well reproduced for molecular reaction in the ground state and, in some case, deviations in the experimentally inferred structural parameters and thermochemical properties were corrected by high-level electronic structure calculations. However, theoretical characterization of photochemical reactions requires a knowledge of excited-state potential energy surfaces (see scheme 1-1) and the related dynamics information. What kind of photoproducts can be formed is determined by branching ratio of competing channels on each state and by the relative rates of adiabatic and non-adiabatic processes. In comparison with thermochemical reaction in the ground state, molecular photochemical reactions, which always involve electronically excited states, are difficult to treat theoretically. In general case, electronic structure methods based on single-reference configuration are not suitable for optimizing stationary structures on excited-state pathways. Configuration interaction with single excitation (CIS) can be used to trace excited-state pathways, but results from the CIS calculations are only qualitatively reliable. The multi-reference configuration interaction (MR-CI) and multi-configuration second-order perturbation theory (CASPT2) can reproduce experimental data well, but the calculations to date have
mainly been performed for very small molecules.

The photochemical reactions and photophysical processes (VR, IC and ISC) can be treated by quantum mechanics by solving Schrödinger equation for nuclear motion on the full-dimensional potential energy surfaces (PES). However, this can be done at most for five-atom molecules. Various semiclassical approaches have been developed for describing mechanistic photodissociation of a polyatomic molecule. However, these semiclassical methods require a very large amount of information about potential energy surfaces, which are hard or even impossible to obtain from first principles for a medium-size polyatomic molecule. Ab-initio-based adiabatic and non-adiabatic molecular dynamics simulations only involve structures and properties of several critical points of the potential energy surfaces and can be performed by a combination of electronic structure calculations with molecular dynamics simulations (on the fly), which are realistically feasible for study of photochemical processes of a large polyatomic molecule.

In the present thesis, electronic structure calculations have been performed by using different electronic correlation methods, including density functional theory (DFT), the second-order perturbation theory (MP2), the complete active space self-consistent field (CASSCF), the coupled-cluster method with single and double excitations (CCSD), multiconfiguration second-order perturbation theory (CASPT2), and multireference configuration interaction (MR-CI). Ab-initio-based molecular dynamics simulations have been carried out at the CASSCF level for the excited singlet state and at the DFT and MP2 levels for the ground state or the lowest triplet state. The systems studied here are phosgene (Cl₂CO), oxalyl chloride ((ClCO)₂), benzoic acid(C₆H₅COOH), and the NO₂-H₂O complex. More attentions were paid to mechanisms of the photo-induced multiple body dissociation for Cl₂CO and (ClCO)₂.

The coming chapter 2 introduces the detail for electronic structure calculations and ab-initio-based molecular dynamics simulations. Chapter 3 is concerned with synchronous concerted four-body photodissociation of oxalyl chloride and chapter 4 is devoted to photo-induced three-body dissociations of (ClCO)₂. In chapter 5 we report the combined CASSCF and CASPT2 calculations of wavelength-dependent photo-induced cleavage of the C-O alpha bond. Finally, in chapter 6 we explored how to generate hydroxyl radical from NO₂ and H₂O in troposphere upon photo-excitation in ultraviolet region by the the combined CASSCF and CASPT2 calculations.
Chapter 2
Ab initio molecular dynamics

Electronic structure theory has emerged as an important tool for solving a wide range of chemical, physical, medical, and material problems. Currently, electronic structure methods are routinely used to optimize molecular structures, to calculate reaction energies, to explain spectroscopic measurements and so on. In this chapter, we will pay more attentions to electronic structure methods for description of electronically excited states, with the Hartree-Fock approximation as start point and followed by the complete active space self-consistent field (CASSCF) and other methods.

2.1 The Hartree-Fock approximation

The Hartree-Fock (HF) approximation\textsuperscript{19,20} is central to wave function-based electronic structure theory. The HF method serves not only as a useful approximation in its own right, but also constitutes an important starting point for almost all ab initio methods. Thus, we give a brief description on the HF approximation firstly.

The HF approximation is equivalent to the molecular orbital approximation, in which the electronic wave function is approximated by a single Slater determinant,

$$\Psi = \frac{1}{{\sqrt {N!} }} \begin{vmatrix} \chi_i(x_1), \chi_j(x_1), \cdots, \chi_k(x_1) \\ \chi_i(x_2), \chi_j(x_2), \cdots, \chi_k(x_2) \\ \vdots \\ \chi_i(x_N), \chi_j(x_N), \cdots, \chi_k(x_N) \end{vmatrix}$$

(1)

\(\frac{1}{{\sqrt {N!} }}\) is a normalization factor. This Slater determinant is for the system with \(N\) electrons distributed in \(N\) spin orbitals \((\chi_i, \chi_j, \cdots, \chi_k)\). If the coordinates of two electrons are interchanged in the determinant, which corresponds to interchanging two rows, the determinant changes its sign. If two electrons occupy the same spin orbital, which results in the two same columns in the determinant, the determinant becomes zero. The Slater determinant satisfies the requirement of anti-symmetry principle. For the \(N\)-electrons in the ground state, its wave function can be represented as

$$\left| \Psi_0 \right> = \chi_i \chi_j \cdots \chi_a \chi_b \cdots \chi_N$$

(2)

If spin orbitals meet orthogonalization, the energy of the system is of form,

$$E_0 = \frac{\langle \Psi_0 | \hat{H} | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle} = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle$$

(3)

The variation principle states that the best wave function of functional form (2) is the one that gives the lowest possible energy, namely, the energy is optimized with respect to variation of the spin orbitals in the determinant. Thus we are interested in
finding a set of spin orbitals such that the single determinant formed from these spin orbitals is the best possible approximation to the ground state of the N-electron system. By using the rules of calculation for matrix elements and electronic Hamiltonian operator,

$$\hat{H}_c = \sum_i \hat{h}_i + \sum_i \sum_{j \neq i} \frac{1}{r_{ij}}, \quad \hat{h}_i = -\frac{1}{2} \nabla_i - \sum_{\lambda} \frac{Z_{\lambda}}{r_{i\lambda}}$$

(4)
equation (3) becomes,

$$E_0 = \langle \Psi_0 | \sum_i \hat{h} + \sum_i \sum_{j \neq i} \frac{1}{r_{ij}} | \Psi_0 \rangle$$

$$= \sum_i \langle \chi_i | h_i | \chi_i \rangle + \frac{1}{2} \sum_i \sum_{j \neq i} \left( \langle \chi_i \chi_j | \chi_i \chi_j \rangle - \langle \chi_i \chi_j | \chi_j \chi_i \rangle \right)$$

(5)

We have to minimize the energy of $E_0$ subject to the constraint that the trial wave function remains normalized. Lagrange’s method of undetermined multipliers is used,

$$L = E_0 - \sum_{i=1}^{N} \sum_{j=1}^{N} \varepsilon_{ij} \left( \langle \chi_i | h_j | \chi_j \rangle - \delta_{ij} \right)$$

$$= \sum_{i=1}^{N} \langle \chi_i | h_i | \chi_i \rangle + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left( \langle \chi_i \chi_j | \chi_i \chi_j \rangle - \langle \chi_i \chi_j | \chi_j \chi_i \rangle \right)$$

$$- \sum_{i=1}^{N} \sum_{j=1}^{N} \varepsilon_{ij} \left( \langle \chi_i | \chi_j \rangle - \delta_{ij} \right)$$

(6)

Let us set the first variation in $L$ equals to zero,

$$\partial L = \partial E_0 - \sum_{i=1}^{N} \sum_{j=1}^{N} \varepsilon_{ij} \delta \langle \chi_i | \chi_j \rangle = 0$$

(7)

After some transformation and simplifications, then we can use the definitions of the coulomb and exchange operators,

$$\hat{K}_j (1) \chi_i (1) = \left[ \int \chi_j^* (2) r_{12}^{-1} \chi_i (2) d\mathbf{x}_2 \right] \chi_j (1)$$

(8)

$$\hat{J}_j (1) \chi_i (1) = \left[ \int \chi_j^* (2) r_{12}^{-1} \chi_j (2) d\mathbf{x}_2 \right] \chi_i (1)$$

(9)

to write the first variation in the form,

$$dL = \sum_{i=1}^{N} \int \partial \chi_i^* (1) \left[ \hat{h}_i (1) \chi_i (1) + \sum_j \hat{J}_j (1) \chi_i (1) - \sum_j \hat{K}_j (1) \chi_i (1) - \sum_j \varepsilon_{ij} \chi_i (1) \right] d\mathbf{x}_i = 0$$

(10)

Since the $\partial \chi_i^* (1)$ is arbitrary, the quantity in the above square bracket must be zero for all $i$.

$$\hat{h}_i (1) \chi_i (1) + \sum_j \hat{J}_j (1) \chi_i (1) - \sum_j \hat{K}_j (1) \chi_i (1) - \sum_j \varepsilon_{ij} \chi_i (1) = 0$$

(11)

Let us define the Fock operator as,

$$\hat{F} (1) = \hat{h}_i (1) + \sum_j \hat{J}_j (1) - \sum_j \hat{K}_j (1)$$

(12)

Using the invariance of the coulomb and exchange operators to a unitary transformation of the spin orbitals, finally, we derive the standard Hartree-Fock equation,

$$\hat{F} \chi_a = \varepsilon_a \chi_a$$

(13)
The solution to the standard Hartree-Fock equation gives the canonical spin orbitals.

2.2 Multi-configurational self-consistent field (MCSCF) method

The HF calculations are remarkably successful in many cases. But the HF method has a lot of limitations. When two configurations are near degenerate, the single-configuration SCF description gives qualitatively wrong conclusion. A well-known example is dissociation behavior of the ground-state H₂ molecule. The restricted HF calculations predict that the H₂ molecule in the ground state dissociates into H⁻ and H⁺, while the correct dissociation products are two equivalent H atoms. The electron-electron repulsion is treated only on an average sense, rather than in a dynamical fashion in the HF method discussed above, which is the main reason why the HF calculation results in a considerable error in energy and other quantities. The error in the HF calculated energy is called the correlation energy, defined as the difference between the exact non-relativistic energy and the HF calculated values.

\[ \Delta E = E_{\text{exact}} - E_{\text{SCF}} \]  

(14)

Different configuration interaction (CI) methods have been developed on the basis of the SCF wave function, which is conceptually simplest way to obtain correlation energy. The full CI wave function can be represented as a linear combination of ground-state and excited configurations,

\[ |\Phi\rangle = \sum_{s} c_{s} |\Psi_{s}\rangle = c_{0} |\Psi_{0}\rangle + \sum_{ar} c_{ar}^{r} |\Psi_{ar}^{r}\rangle + \sum_{ab} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + \sum_{a=bc} c_{a=bc}^{rst} |\Psi_{a=bc}^{rst}\rangle + \sum_{a=bc=cd} c_{a=bc=cd}^{rstu} |\Psi_{a=bc=cd}^{rstu}\rangle + \cdots \]  

(15)

The restrictions on the summation indices insure that a given excited configuration is included in the sum only once, where the indices of \( a, b, c, d, \cdots \) are designed as occupied spin orbitals, while the \( r, s, t, u, \cdots \) are unoccupied spin orbitals. It is more convenient to rewrite the equation (15) as,

\[ |\Phi\rangle = c_{0} |\Psi_{0}\rangle + \sum_{S} c_{S} |S\rangle + \sum_{D} c_{D} |D\rangle + \sum_{T} c_{T} |T\rangle + \cdots \]  

(16)

where \(|S\rangle\), \(|D\rangle\) and \(|T\rangle\) represent terms involving single, double, and triple excitations with respect to \(|\Psi_{0}\rangle\) respectively.

For a given trial function of (16), in principle, we can construct the generalized eigenvalue equation of configuration interaction,

\[ F \mathbf{c} = S \mathbf{c} \mathbf{E} \]  

(17)

The coefficient of a configuration and the correlation energy can be determined by using the linear variation method. The lowest eigenvalue is the upper bound of the ground-state energy. The higher eigenvalues are the upper bounds of the corresponding excited states. However, the full CI calculation is computationally intractable as basis functions and electrons are added and can be performed only for very small molecule with use of small basis set.
Multi-configurational self-consistent field (MCSCF) is a method in quantum chemistry used to generate qualitatively correct reference states of molecules in cases where the Hartree–Fock method is not adequate (e.g., for molecular ground states which are quasi-degenerate with low lying excited states or in bond breaking situations). As pointed out before, the Hartree–Fock approximation only involves one determinant, but the molecular orbitals are varied. However, the molecular orbitals are not varied but the expansion of the wave function in CI method. The MCSCF method makes use of advantages of Hartree–Fock approximation and configuration interaction method and uses a linear combination of configuration state functions (CSF) or configuration determinants to approximate the exact electronic wavefunction of an atom or molecule. In the MCSCF theory, the set of coefficients of both the CSFs or determinants and the basis functions in the molecular orbitals are varied to obtain the total electronic wavefunction with the lowest possible energy. With the same number of configuration state functions, the MCSCF calculations can provide more accurate results than the CI calculations.

The MCSCF wave function can be written as a linear combination of CSFs whose expansion coefficients are optimized simultaneously with spin orbitals in line with the variation principle. The MCSCF variation calculation of the method is similar to that for derivation of the HF equation. The Fock equation of the MCSCF method can be written in the form of

\[ \mathbf{F}_c\{\{c_i\}, \{c_{ik}\}\} \mathbf{c}_i = \varepsilon_i \mathbf{S} \mathbf{c}_i + \sum_{j \neq i} \varepsilon_j \mathbf{S} \mathbf{c}_j \]  

(18)

where \( c_i \) is the coefficient of a configuration, \( c_{ik} \) is the co-efficient of a spin orbital, and the \( \varepsilon_i \) is the matrix of the spin orbital co-efficient. The \( \mathbf{S} \) is the overlap matrix of spin orbitals,

\[ S_{pq} = \langle \chi_p | \chi_q \rangle \]  

(19)

\( \varepsilon_{ij} \) is defined by the undetermined multipliers of Lagrange’s method, which satisfies,

\[ \varepsilon_{ij} = \varepsilon_j^* \]  

(20)

The overlap matrix is diagonalizable,

\( \mathbf{c}^* \mathbf{S} \mathbf{c}_j = \delta_{ij} \)  

(21)

Then the Fock equation (18) can be changed into,

\[ \mathbf{F}_c \mathbf{c}_j = \varepsilon_i \mathbf{S} \mathbf{c}_i + \sum_{j \neq i} \varepsilon_j \mathbf{S} \mathbf{c}_j = \varepsilon_i \mathbf{S} \mathbf{c}_i + \sum_{j \neq i} \mathbf{S} \mathbf{c}_j \mathbf{c}^* \mathbf{F}_c \mathbf{c}_i \]

\[ = \varepsilon_i \mathbf{S} \mathbf{c}_i + \sum_{j \neq i} [ \mathbf{S} \mathbf{c}_j (\mathbf{F}_c \mathbf{c}_j)^* + \mathbf{F}_c \mathbf{c}_j (\mathbf{S} \mathbf{c}_j)^* ] \mathbf{c}_i \]  

(22)

The second term in the square bracket of the above equation is defined as,

\[ \mathbf{R}_j = \sum_{j \neq i} [ \mathbf{S} \mathbf{c}_j (\mathbf{F}_c \mathbf{c}_j)^* + \mathbf{F}_c \mathbf{c}_j (\mathbf{S} \mathbf{c}_j)^* ] \]

(23)

then, the equation (18) becomes,

\[ (\mathbf{F}_c - \mathbf{R}_j) \mathbf{c}_j = \varepsilon_i \mathbf{S} \mathbf{c}_i \]  

(24)

In practice, the simultaneous optimization of orbital and configuration coefficients is a nonlinear problem, which restricts the expansion length of the MCSCF wave functions. The most difficult question encountered in the MCSCF calculation is how to select the configuration space. A general selection scheme is the partitioning of orbital space into some subspaces, which are characterized by some restrictions on the occupation numbers of the configurations in the MCSCF wave
functions. A particularly important MCSCF approach is the complete active space SCF method (CASSCF), where the linear combination of CSFs includes all that arise from a particular number of electrons in a particular number of orbitals. In the CASSCF wave functions, the total orbital space is partitioned into core orbitals, active orbitals, and empty orbitals. The core orbitals are doubly occupied in all CSFs, while the empty orbitals are unoccupied in all CSFs. There are no restrictions of occupations for the active orbitals. The CASSCF method is not a black-box method and is not easily used for non-specialists.

It should be pointed out that the configuration space within the framework of the CASSCF method is relatively small. Generally speaking, it is impossible to recover the dynamics correlation energy by the CASSCF calculations. As a result, the CASSCF calculation is difficult to meet the high-accuracy requirement. However, the CASSCF wave functions are unique for giving a flexible framework for treatment of the static correlation from nearly degenerate electronic configurations. For the treatment of dynamical correlation, additional calculations have to be carried out on the basis of the CASSCF wave functions, such as multi-reference configuration interaction theory (MR-CI) and multi-configurational perturbation theory (CASPT2).

2.3 Ab initio molecular dynamics methods

Classical trajectory calculations, which are based on empirical data or on electronic structure calculations, are well established as a powerful tool for exploring reaction dynamics, which can provide more information on the dynamics than conventional transition state theory and reaction path Hamiltonian method. The classical trajectory method is especially interesting because it is readily applicable to large systems for which a full quantum dynamical treatment is likely to remain prohibitively expensive in near future. Traditionally, the trajectory calculation requires accurate global potential energy surface. Subsequently, Newton’s equation of motion,

$$\mathbf{m}\ddot{\mathbf{x}} = -\frac{dV(\mathbf{x})}{d\mathbf{x}}$$

is solved to determine a trajectory. Here $V(\mathbf{x})$ is the potential energy of the system and $\mathbf{m}$ is a 3N-dimensional diagonal matrix of the N-atom system,

$$\mathbf{m} = \text{diag}(m_1, m_1, m_1, m_2, m_2, m_2, \cdots m_N, m_N, m_N)$$

The bottleneck in the traditional trajectory calculation is the construction of the potential energy surface. Because of advances in computer techniques and improvements in electronic structure theory, now it has become possible to calculate classical trajectories directly from ab initio calculations without first fitting a global potential energy surface. The basic idea underlying ab initio molecular dynamics (AIMD) is to calculate forces acting on nuclei by using electronic structure theory, which is performed “on-the-fly” when trajectories are generated. The AIMD simulations on molecular systems with up to thousands of atoms are nowadays feasible, due to highly efficient electronic structure methods. A number of systems
have been studied with the gradient-based direct molecular dynamics method.

Conventional molecular dynamics simulation is based on two fundamental approximations: The first is the Born–Oppenheimer (BO) or adiabatic approximation where the static electronic structure is straightforwardly solved at a set of fixed nuclear positions determined in each molecular dynamics step. The second approximation is treatment of the atomic motion with classical equation of motion, Eq. (25). The time-dependence of the electronic structure is a consequence of nuclear motion, and not intrinsic as in quantum dynamics. The BO dynamics has become popular recently, since more efficient electronic structure codes in conjunction with sufficient computer power are available currently. Classical trajectories can be calculated on a local second-order approximation surface, which is constructed by using the analytical first and second derivatives computed directly by the electronic structure method.\textsuperscript{46-53}

\[
V(x) = E^0 + G^0(x - x^0) + \frac{1}{2}(x - x^0)^T H^0(x - x^0)
\]

(27)

where \( E^0 \) is the potential energy, \( G^0 \) the energy gradients, and \( H^0 \) the Hessian at \( x^0 \). This can be considered as the Hessian-based direct molecular dynamics method. In combination of equations of (3) and (1) we obtain

\[
m_i \frac{d^2x_i}{dt^2} = -\frac{dV(x)}{dx_i} = -G_i^0 - \sum_j H_{ij}^0(x - x_j^0)
\]

(28)

Since potential energy surface is expanded to the second-order approximation, the equation (28) is only valid in a small region around the \( x^0 \) geometry and the integration can be performed to the boundary of this region. A correct step can be taken to go beyond the local second-order approximation by fitting a higher-order surface. The energies, gradients, and Hessians are calculated at the beginning and at the end of each propagation step of trajectory, which is followed by the fifth-order polynomial fit,

\[
V(x) = E^a(\Delta x_\perp) y_1(\mu) + g^a(\Delta x_\perp) y_2(\mu) + h^a(\Delta x_\perp) y_3(\mu) + E^b(\Delta x_\perp) y_4(\mu) + g^b(\Delta x_\perp) y_5(\mu) + h^b(\Delta x_\perp) y_6(\mu)
\]

(29)

where

\[
y_1(\mu) = 1 - 10\mu^3 + 15\mu^4 - 6\mu^5
\]

(30)

\[
y_2(\mu) = s(\mu - 6\mu^3 + 8\mu^4 - 3\mu^5)
\]

(31)

\[
y_3(\mu) = s^2/2(\mu^2 - 3\mu^3 + 3\mu^4 - \mu^5)
\]

(32)

\[
y_4(\mu) = 10\mu^3 - 15\mu^4 + 6\mu^5
\]

(33)

\[
y_5(\mu) = s(-4\mu^3 + 7\mu^4 - \mu^5)
\]

(34)

\[
y_6(\mu) = s^2/2(\mu^2 - 2\mu^4 + \mu^5)
\]

(35)

\[
s = |x^2 - x^1|
\]

(36)

\[
\mu = \Delta x_\parallel / s
\]

(37)
As shown in Scheme 2-1, a quadratic approximation to the surface at the beginning of a predictor step \((x^1)\) is used to obtain \(x^2\). The energies, gradients, and Hessians at \(x^1\) and \(x^2\) are fitted by a fifth-order polynomial. A correction step is then taken on this fitted surface. The procedure is repeated for the next step, starting with the quadratic approximation to the surface at \(x^2\). To carry out the fit, the Cartesian coordinates are rotated so that one component is parallel to the predictor step, \(x_\parallel\) and the others are perpendicular to the step, \(x_\perp\).

Let \(H\) be the eigenvectors of the mass-weighted Hessian and \(h\) the corresponding eigenvalues,

\[
H' (m^{-\frac{1}{2}}HM^{-\frac{1}{2}}) H = h_i \delta_j
\]  

(38)

After the coordinates are transformed to the eigenvector space of the mass-weighted Hessian,

\[
q_i = H' m^{\frac{1}{2}} (x - x^0)
\]

(39)

the equations of motion become

\[
\frac{dp_i}{dt} = -g_i - h_i q_i
\]

(40)

where \(p_i\) is the conjugate momentum of \(q_i\) and

\[
g_i = H' m^{-\frac{1}{2}} G
\]

(41)

The solutions to equation (40) is readily obtained, which is dependent on the \(h_i\) eigenvalue,

\(h_i > 0\),

\[
q_i(t) = -a_i \left[ 1 - \cos(\omega_i t) \right] + b_i \sin(\omega_i t)
\]

(42)

\[
p_i(t) = \omega_i \left[ -a_i \sin(\omega_i t) + b_i \cos(\omega_i t) \right]
\]

(43)

\(h_i = 0\),

\[
q_i(t) = -\frac{1}{2} g_i t^2 + p_i(0)t
\]

(44)
\[ p_i(t) = p_i(0) - g_i t \]  
\[ h_i < 0, \]
\[ q_i(t) = -a_i \left[ 1 - \cosh(\omega_i t) \right] + b_i \sinh(\omega_i t) \]  
\[ p_i(t) = \omega_i \left[ -a_i \sinh(\omega_i t) + b_i \cosh(\omega_i t) \right] \]

where \( a_i = g_i / h_i \), \( b_i = p_i(0) / |\omega_i| \), and \( \omega_i^2 = |h_i| \). Finally, the Cartesian coordinates and velocities can be obtained by reverse transformation,
\[ x = x^0 + m^{-1/2} \mathbf{H} \mathbf{q} \]  
\[ \frac{dx}{dt} = m^{-1/2} \mathbf{H} \mathbf{q} \]

The molecular dynamics method discussed above is founded on the assumption that motion of the nuclei is governed by one adiabatic potential energy surface. However, electronic transition is often involved in photochemical and photophysical processes. When a transition between electronic states occurs, the forces experienced by the nuclei change drastically. The non-adiabatic effects can be crucial for describing some dynamical processes in photochemistry. The treatment of non-adiabatic effects in molecular dynamics has a long history with development of classical, semiclassical, and quantum mechanical approaches.\(^{54-61}\) Initially restricted to a single adiabatic state within the BO approximation, molecular dynamics has recently been extended to the nonadiabatic regime, providing an important tool for the study of photophysical and photochemical processes. One of the most commonly used nonadiabatic molecular dynamics schemes is Tully’s fewest switches trajectory surface hopping.\(^{61}\) Early in 1990, Tully has proposed a surface-hopping method for performance of molecular dynamics simulations that involve electronic transitions. The nuclei are treated classically by solving the Newton’s equation (1), while the electrons are treated quantum-mechanically by solving the time-dependent electronic Schrödinger equation. The total Hamiltonian describing both electronic and atomic motion can be written as
\[ H = T_R + H_0(r, R) \]  

where \( H_0(r, R) \) is the electronic Hamiltonian for fixed atomic positions and \( T_R \) is kinetic energy operator of the atomic motion. After selecting a set of orthonormal basis functions \{\( \phi_i \)\}, which depend parameterically on atomic positions \( R \), the \( H_0(r, R) \) matrix elements can be written as,
\[ V_{ij} = \langle \phi_i(r, R) | H_0(r, R) | \phi_j(r, R) \rangle \]  
then the nonadiabatic coupling vector is defined as,
\[ d_{ij}(r, R) = \langle \phi_i(r, R) | \nabla_R | \phi_j(r, R) \rangle \]

The gradient of \( \nabla_R \) is defined with respect to the atomic coordinate \( R \). Since atomic
positions are a function of time \( t \), the electronic Hamiltonian \( H_e(\mathbf{r}, \mathbf{R}) \) is a time-dependent operator. The wave function of \( \Psi(\mathbf{r}, \mathbf{R}, t) \) is defined to describe electronic state at time \( t \), which is expanded in terms of the electronic basis functions,

\[
\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_i c_i(\mathbf{R}, t) \varphi_i(\mathbf{r}, \mathbf{R}),
\]

where \( c_i \) are the time-dependent complex-valued expansion coefficients. Substituting equation (53) into the time dependent electronic Schrödinger equation,

\[
i \hbar \frac{\partial \Psi}{\partial t} = H_e \Psi
\]

multiplying from the left by \( \varphi_k(\mathbf{r}, \mathbf{R}) \), and then integrating over \( \mathbf{r} \) give

\[
i \hbar \frac{dc_k}{dt} = \sum_j c_j \left\{ V_{kj} - i \hbar \left\langle \varphi_k \left| \frac{\partial \varphi_j}{\partial t} \right. \right\rangle \right\}.
\]

Using the chain rule,

\[
\left\langle \varphi_k \left| \frac{\partial \varphi_j}{\partial t} \right. \right\rangle = \left\langle \varphi_k \left| \frac{\partial \varphi_j}{\partial \mathbf{R}} \right. \right\rangle = \frac{\partial \varphi_k}{\partial \mathbf{R}} \cdot \mathbf{d}_{kj}
\]

Equation (55) becomes,

\[
i \hbar \dot{c}_k = \sum_j c_j \left( V_{kj} - i \hbar \dot{\mathbf{R}} \cdot \mathbf{d}_{kj} \right)
\]

where \( \dot{\mathbf{R}} \) is the nuclear velocity vector, \( \mathbf{d}_{kj} \) is the non-adiabatic coupling vector between the electronic states \( j \) and \( k \), and \( c_k \) is the expansion coefficient of the electronic state \( k \) in the total wave function.

The fewest-switches surface-hopping algorithm was developed by Tully\textsuperscript{61}, which assumes that the nuclear dynamics of the system may be approximately described by an ensemble of non-interacting trajectories and each trajectory moves on a single potential energy surface at all times, interrupted only by the possibility of sudden switches from one state to another that occurs in infinitesimal time. A surface switch from the occupied electronic state \( k \) to some target electronic state \( j \) occurs with a probability. In the fewest-switches surface-hopping algorithm, the number of hopping events within one time step \( \Delta t \) is minimized. The hopping probability between states \( k \) and \( j \) is (in adiabatic representation)

\[
P_{k \rightarrow j} = \max \left[ 0, 0.2 \Re(c_k^* c_j) \dot{\mathbf{R}} \cdot \mathbf{d}_{kj} |c_k|^2 \Delta t \right]
\]

The expansion coefficients of \( c_k \) in the total wave function can be obtained by solving the time-dependent electronic Schrödinger equation (29). At each integration time step, a decision is made whether to switch electronic states, according to probabilistic fewest switches algorithm. If a switch occurs, the component of velocity in the direction of the nonadiabatic coupling vector is adjusted to conserve energy. The hopping probability \( P_{k \rightarrow j} \) from the current state \( k \) to \( j \) is calculated with equation (58). If \( P_{k \rightarrow j} \) is negative, it is set to be zero. A uniform random number \( \zeta(0 < \zeta < 1) \) was generated and used to determine whether a hopping will be invoked. If \( P_{k \rightarrow j} > \zeta \), hopping will occur. If \( P_{k \rightarrow j} < \zeta \), no hopping occur and the system will
remain in the current state.

The choice of sudden state switches is made only for simplicity. Although real state switches can occur over extended regions of coupling, the fewest switches algorithm is a good approximation in most cases. One single trajectory makes a sudden switch of states, but for a large number of trajectories entering a broad region of coupling, some trajectories will switch early, others later, and the net result will be a gradual flow of flux from one state to the other. This is the reason why the sudden switch procedure may be quite acceptable even in cases where transitions are not localized.

Finally, it should be pointed out that there are some fundamental limitations that result from the basic assumptions of the molecular dynamics method. Quantum mechanical behavior is neglected and a single potential energy surface governs the motion. Quantum effects such as tunneling, interference and level quantization can be significant, particularly in low-energy processes involving hydrogen atom motion. Quantum dynamics methods can treat both electronic and nuclear wavefunctions exactly. However, the applicability of these methods is hampered by their high computational costs, which limit the number of accessible nuclear degrees of freedom. Various alternative schemes have been proposed to describe the dynamics of the nuclear wavefunction, such as ab initio multiple spawning methods,\textsuperscript{62} decoherence and momentum rescaling in the surface hopping algorithm,\textsuperscript{63} and a singularity free surface hopping expansion method for the multistate wave functions.\textsuperscript{64} It is feasible to design a theory in which trajectories evolve on an effective potential that changes smoothly from that of the initial state to that of the final state during a finite time interval, which is currently under development. Truhler and co-workers present a modification of trajectory surface-hopping algorithm,\textsuperscript{65} which improves the self-consistency of the fewest-switches algorithm by incorporating quantum uncertainty into the hopping times of classically forbidden hops. This uncertainty allows an electronic transition that is classically forbidden at some geometry to occur by hopping at a nearby classically allowed geometry if an allowed hopping point is reachable within the Heisenberg interval of time uncertainty. The non-relativistic quantum dynamics of nuclei and electrons has been developed within the framework of quantum hydrodynamics, which is solved by using the adiabatic representation of the electronic states. An on-the-fly trajectory-based nonadiabatic molecular dynamics algorithm is derived, which is able to capture nuclear quantum effects that are missing in the traditional trajectory surface hopping approach based on the independent trajectory approximation. The use of correlated trajectories produces quantum dynamics, which is in principle exact and computationally very efficient.\textsuperscript{66}
Chapter 3

Photodissociation of Oxalyl Chloride

3.1 Many-body photodissociation of carbonyl compounds

Carbonyl compounds play an important role in the development of our understanding of photochemistry of a polyatomic molecule. Photo-dissociation of carbonyl compounds has served as the basis for developing new experimental techniques for direct observation of transient intermediate and for discovering new mechanisms of photochemical reactions. The photochemistry of aldehydes and ketones has been the subject of numerous experimental investigations over many decades. Also, there are several theoretical studies that focused on photodissociation of aliphatic, aromatic, and unsaturated carbonyl compounds. The alpha-dicarbonyls have attracted the attention of researchers from diverse scientific disciplines such as water quality chemistry, food chemistry, and medical research. As a representative system, oxalyl chloride, \((\text{ClCO})_2\), had been characterized as an excellent source of chlorine atoms for kinetic studies, since it has a relatively large absorption cross section at 193 nm with a quantum yield of Cl atoms \(\sim 2.00\). UV-irradiation of \((\text{ClCO})_2\) in the Xe matrix led to formation of CO and \(\text{Cl}_2\text{CO}\). The same products were observed in the thermal decomposition of \((\text{ClCO})_2\), suggesting a concerted decomposition pathway,

\[
(\text{ClCO})_2 \rightarrow \text{CO} + \text{Cl}_2\text{CO} \tag{1}
\]

The photodissociation dynamics of \((\text{ClCO})_2\) near 235 nm was investigated with a photofragment imaging technique. It was suggested that the photodissociation proceeds via an impulsive three-body mechanism yielding Cl, CO, and ClCO radicals. The formed ClCO radical undergoes subsequent dissociation to yield CO and Cl. The overall dissociation process can be summarized as,

\[
(\text{ClCO})_2 + \text{hv} \rightarrow \text{Cl} + \text{CO} + \text{ClCO} \rightarrow 2\text{Cl} + 2\text{CO} \tag{2}
\]

The same mechanism was suggested for the \((\text{ClCO})_2\) photodissociation at 193 nm using photofragment translational spectroscopy with intense tunable vacuum-UV probe. The further evidence for this comes from photolysis of oxalyl chloride at 248 nm with a step-scan time-resolved Fourier transform spectrometer under nearly collisionless conditions.

Time-resolved and rotationally resolved emission from CO are observed upon photolysis of \((\text{ClCO})_2\) at 193 nm. A four-body dissociation mechanism was proposed for photolysis of \((\text{ClCO})_2\) at 193 nm,

\[
(\text{ClCO})_2 + \text{hv} \rightarrow \text{Cl} + \text{CO} + \text{Cl} + \text{CO} \tag{3}
\]

which produces one pair of translationally rapid and internally excited CO and one pair of translationally rapid Cl. Kong and co-workers have studied photodissociation processes of \((\text{ClCO})_2\) at 193 and 248 nm, and they proposed a
different mechanism that a two-body dissociation takes place firstly via breaking the central C-C bond at both 193 and 248 nm, followed by the CICO dissociation into CO + Cl,

\[(\text{CICO})_2 + \text{hv} \rightarrow \text{CICO} + \text{CICO} \rightarrow \text{Cl} + \text{CO} + \text{Cl} + \text{CO} \quad (4)\]

Although a lot of experimental investigations have been dedicated to photolysis of \((\text{CICO})_2\), there is not a general conclusion regarding the photodissociation mechanism up to now. Oxalyl chloride had been the subject of extensive \textit{ab initio} investigations over the past many years,\textsuperscript{114-122} but all \textit{ab initio} calculations focused on conformational behavior of \((\text{CICO})_2\) in the ground state, such as molecular structures, fundamental frequencies, and internal rotation around the center C-C bond. As far as we know, there is no report on \textit{ab initio} calculation and dynamics simulation of photo-induced \((\text{CICO})_2\) dissociation processes. In the present work, we have carried out complete active space self-consistent field (CASSCF) and multi-reference configuration interaction (MR-CI) studies on potential energy surfaces of the \((\text{CICO})_2\) dissociation in different electronic states, which provide a fundamental description on the reactivity of oxalyl chloride in electronically excited states.

The study of photo-induced multiple body dissociation is of fundamental interest in the field of reaction dynamics. Dynamic information of two-body decay can be obtained through straightforward experiments. However, the acquisition of dynamic information for photo-initiated three-body processes has proven to be a challenge for theoreticians and experimentalists alike, due to the inherent difficulties in predicting behavior of excited molecules and in directly observing multiple dissociation products.\textsuperscript{123} There is a history of controversy over whether the photo-initiated three-body dissociation proceeds in a stepwise or a concerted fashion for the well-known systems, such as CH\textsubscript{3}COCH\textsubscript{3},\textsuperscript{45,48} SOCl\textsubscript{2},\textsuperscript{46,48,124} Cl\textsubscript{2}CO,\textsuperscript{45} CH\textsubscript{2}XCH\textsubscript{2}Y (X,Y=Br,Cl),\textsuperscript{46,48} and C\textsubscript{3}N\textsubscript{3}H\textsubscript{3} (sym-Triazine).\textsuperscript{46,48} The mechanistic controversy stems from the challenges of characterizing dissociation of a polyatomic system at a molecular level.

\begin{center}
\textbf{Scheme 3-1 Many-body dissociations}
\end{center}

Experimentally, it has been observed that UV-irradiation of \((\text{CICO})_2\) can lead to formation of four fragments (2Cl + 2CO). However, two-, three-, and four-body
dissociation mechanisms have been proposed for the observed products in different experiments.\textsuperscript{107,110-113} The key issue is a time scale of the C-C and C-Cl bond scissions. As shown in Scheme 3-1, if the two C-Cl bond scissions occur within a rotational period after the C-C bond fission, photo-initiated dissociation of (CICO)\textsubscript{2} into 2Cl and 2CO is a synchronous concerted four-body process. Reversely, the CICO radicals formed by the C-C bond fission have a lifetime much longer than their rotational period, and the photo-initiated dissociation is a sequential two-body process. When the CICO radical has a lifetime comparable to its rotational period, the photo-initiated dissociation is considered as asynchronous concerted process. In this way, we can classify the photo-induced dissociation as sequential, asynchronous, synchronous concerted three- or four-body process. To our knowledge, no reports have appeared to date for other systems dissociating to four fragments following absorption of a single UV photon, and four-body dissociation processes have never been investigated from the viewpoint of theory. In the present work, \textit{ab initio} molecular dynamics simulations have been conducted to determine dissociation processes upon irradiation of (CICO)\textsubscript{2} in the wavelength range of 248 -193 nm. Three- and four-body dissociations were predicted to be synchronous concerted processes, which is dependent on the initial internal energies and their distribution in different vibrational modes. The present study provides a real-time quantitative description on photo-induced dissociation of oxalyl chloride.

3.2 Details of computations

A combined CASSCF and CCSD(T) method has been used to calculate potential energy surfaces for the (CICO)\textsubscript{2} dissociation in the low-lying electronic singlet states. For comparison, the stationary points (minima and transition states) on the ground and lowest triplet states are fully optimized with the MP2 analytical energy gradient techniques. All calculations have been performed with the cc-pVDZ basis set in the present study. The choice of active space for the CASSCF computations requires some comments. To describe equilibrium structures of oxalyl chloride in the low-lying electronic states, the $\pi$ and $\pi^*$ orbitals of the two C=O groups and the non-bonding orbitals located at the two O atoms should be included in the active space, that is eight electrons in six orbital. For investigating the bond fission processes, which involve a breakage of C-C or C-Cl sigma bond, the C-C or C-Cl $\sigma$ and $\sigma^*$ orbitals are chosen as the active orbitals. This leads to an active space with ten electrons in eight orbital, referred to as CAS(10,8) hereafter. The multi-reference configuration interaction (MR-CI) approach is a very efficient algorithm for treating dynamic correlation. Single-point energies of the stationary points were calculated with the MR-CI approach on the CAS(10,8) optimized structures. All \textit{ab initio} calculations described here had been carried out with the Gaussian 03 and Molpro 02 program packages.\textsuperscript{125,126}

\textit{Ab initio} molecular dynamics calculations that are based on the Born-Oppenheimer approximation have been performed with the second order Hessian-based integration method.\textsuperscript{16} A local quadratic surface is constructed from the analytic
first and second derivatives of the energies calculated at the CAS(10,8) level. The local second-order surface is a good approximation to the true surface only in a small region around the expansion point and the calculated trajectory is not allowed to leave this region. An improved method with the fifth-order polynomial fitted surface was developed by Millam and co-workers,\textsuperscript{48} which is used in the present dynamical calculations. The initial conditions for the dynamics simulations were chosen to simulate the photolysis of oxalyl chloride in the wavelength range of 248 - 193 nm.

### 3.3 Structures and their relative energies

Geometric and electronic structures are fundamental and important properties of a molecule. However, there remains a general lack of information on the structures and properties of oxalyl chloride in the excited states, although oxalyl chloride had been studied with different experimental and \textit{ab initio} methods in the past four decades. Before discussing the photo-induced multiple body dissociation, we pay attention to structures and relative energies of (CICO)\textsubscript{2} in the low-lying electronic states.

![Figure 3-1](image-url)  
**Figure 3-1** Geometric structures of oxalyl chloride in the low-lying electronic states, along with some key bond parameters (bond length in angstrom and bond angle in degree) from the CCSD(T)/cc-pVDZ calculations (The S\textsubscript{3} structure was optimized at the CAS(10,8)/cc-pVDZ level).

Both experiment and theory agree in predicting that the trans conformation with C\textsubscript{2h} symmetry is the most stable for (CICO)\textsubscript{2} in the ground state (S\textsubscript{0}). The gauche conformer was experimentally deduced to be the second stable isomer in 1973,\textsuperscript{113} which was reproduced recently by high-level \textit{ab initio} calculations.\textsuperscript{50} The energy difference between the two conformers was determined to be less than 1.0 kcal mol\textsuperscript{-1} and the potential energy surface along the O=C-C=O torsional mode is very flat.\textsuperscript{50} The CAS(10,8) and CCSD calculations with the cc-pVDZ basis predicted the C-C bond length to be 1.537 and 1.556 Å for (CICO)\textsubscript{2} in the ground state. In comparison, the CAS(10,8)/cc-pVDZ optimized C-C bond distance is in good agreement with the experimental value of 1.534 Å.\textsuperscript{113} It is evident that the C-C bond is a normal single
bond in the ground state of (ClCO)₂. This is quite different from that for a molecule with the C=C-C=C backbone, such as CH₂=CH-CH=CH₂, where the middle C=C bond is partially of double bond character. In addition to the inductive effects of oxygen atoms that weaken the conjugation interaction of the two carbonyl groups, effect of the steric repulsion between Cl and O atoms is also responsible for the C-C single bond character in the ground state of (ClCO)₂. This can be seen from a comparison with the (HCO)₂ structure where the conjugation interaction of the two carbonyl groups makes the C-C bond less than 1.5 Å. The optimized (ClCO)₂ structures are shown in Figure 1, along with the selected bond parameters.

There are two carbonyl groups in the molecule of oxalyl chloride, which can give rise to the two equivalent n→π* excitations from viewpoint of localized valence bond theory. Upon electronic excitation, the conjugated interaction exists in the two C=O groups, the two new excited states are formed, which can be considered as a linear combination of the two localized 1nπ*(C=O) states. The lower-energy excited singlet and triplet states are denoted as the S₁ and T₁ states, while the excited singlet and triplet states with higher energies are referred to as the S₂ and T₂ states. The CCSD(T) optimized structures for the S₁, T₁, S₂, and T₂ states are schematically shown in Figure 3-1. One electron excitation from n orbital to the π* orbital weakens to a large extent the C-O π bond. However, the C-C bond length is decreased in going from S₀ to S₁ or S₂ and is of partial double-bond character for (ClCO)₂ in the S₁ and S₂ states. It is well known that the n→π* electron excitation results in a pyramidal S₁ equilibrium structure for aliphatic carbonyl compound, such as H₂CO and CH₃COCH₃. However, the equilibrium structure of (ClCO)₂ in the S₁ and S₂ state possesses C₃v symmetry with all atoms in the molecular plane. The planar structure becomes more stable than the pyramidal one, due to the conjugation interaction in the S₁ and S₂ equilibrium structures of (ClCO)₂. Similar situations occur for the T₁ and T₂ equilibrium structures. One high-energy excited singlet state for (ClCO)₂ was optimized at the CAS(10,8) level and was confirmed to be minima by frequency calculations, which is labeled as the S₃ state hereafter. The S₁ equilibrium structure was predicted to be planar with C₂h symmetry. Natural orbital analysis shows that the S₃ state comes from one-electron excitation of π*(O=C-C=O) → π*(O=C-C=O). The S₃ state is the 1ππ* state, which is of a biradical character with the O=C=C=O backbone from viewpoint of valence bond theory.

The relative energies of the S₁, T₁, S₂, and T₂ states were calculated at the CCSD(T) level of theory with the aug-cc-pVDZ basis set, which are 79.1, 70.3, 101.1, and 94.7 kcal-mol⁻¹, respectively. The vapor-phase absorption spectrum of oxalyl chloride in the 300–418 nm region has been re-examined at high resolution. Singlet–singlet A₁Σg ← X₁Σg and singlet–triplet A¹Σg ← X¹Σg electronic transitions of the trans-conformer have been measured and their band origins were assigned to be 27190.9 (77.7 kcal-mol⁻¹) and 24373.4 cm⁻¹ (69.7 kcal-mol⁻¹), respectively. In comparison with the band origins measured experimentally for the S₁←S₀ (A¹Σg ← X¹Σg) and T₁←S₀ (A¹Σg ← X¹Σg) transitions, the CCSD(T)/aug-cc-pVDZ calculations provide a reasonable description on the relative energies of the excited electronic states. Since the S₁(1ππ*) state is only optimized at the CAS(10,8)/cc-pVDZ level, its relative energy is determined to 146.5 kcal-mol⁻¹ by the MR-Cl/aug-cc-pVDZ single-point calculation on the basis of the CAS(10,8)/cc-pVDZ optimized structures for the S₀ and S₃ states.
The transition states in the product side. Once the Cl dissociation and the C-C dissociation along the T1 pathway was predicted to be 12.6 kcal-mol$^{-1}$ by the CCSD(T) calculations. The CICO($^2A'$) radical can dissociate into CO($^1\Sigma$) and Cl($^3P$), which has a barrier of 2.1 and 3.2 kcal-mol$^{-1}$ at the CAS(10,8) and CCSD levels, respectively. The transition state of the C-C bond fission on the S1 state is optimized with the CCSD(T) method. The optimized structure, denoted by S1-TS1, hereafter, is shown in Figure 3-2. Qualitatively, the C-C bond fission on the S1 state leads to formation of CICO($^2A''$) + ClCO($^2A'$). Since the excited CICO($^2A''$) fragment is unstable with respect to the C-Cl separation and it decomposes into CO($^1\Sigma$) and Cl($^3P$) very easily, S1-TS1 connects the fragments of CICO($^2A'$) + CO($^1\Sigma$) + Cl($^3P$) in the product side. Once the (CICO)$_2$ molecules have sufficient internal energies to overcome the barrier of $\sim$40.0 kcal-mol$^{-1}$ on the S1 pathway, the C-C bond fission is accompanied with the C-Cl dissociation and the (CICO)$_2$ dissociation is a four-body process. Also, the formed ClCO($^2A'$) radical can decompose into CO($^1\Sigma$) + Cl($^3P$), due to a small barrier on the ground-state pathway. Once the C-C bond is broken, the subsequent C-Cl bond cleavages take place very...
early. Upon photoexcitation of (CICO)$_2$ at 193 nm, the (CICO)$_2$ dissociation could be a four-body process.

**Figure 3-3 (a) Schematically potential energy surfaces for the C-C and C-Cl dissociations of oxalyl chloride in the $S_0$, $S_1$, and $T_1$ electronic states.**

**Figure 3-3 (b) Schematically potential energy profiles for the C-C dissociation of oxalyl chloride in the $S_0$, $S_1$, and $T_1$ electronic states and subsequent process.**
Figure 3-3 (c) Schematically potential energy profiles for the C-Cl dissociation of oxalyl chloride in the $S_0$, $S_1$, and $T_1$ electronic states and subsequent process.

The ground-state CICOCO radical and Cl($^2P$) can correlate adiabatically with (CICO)$_2$ in the $S_0$, $S_1$, and $T_1$ states, as shown in Figure 3-3 (c). The dissociation of (CICO)$_2$ to the CICOCO and Cl in the ground state is endothermic by $\sim 77.6$ kcal-mol$^{-1}$ without any barrier above the endothermicity at the CAS(10,8) and CCSD levels of theory. A non-planar transition state on the $T_1$ pathway is found by the CAS(10,8) and CCSD calculations, referred to as $T_1$-TS$_2$ hereafter. The C-Cl distance in $T_1$-TS$_2$ is 2.109 Å, much longer than the C-Cl bond length of 1.740 Å in the trans-$T_1$ minimum. A similar transition state was determined on the $S_1$ pathway, referred to as $S_1$-TS$_2$ hereafter. The C-Cl bond cleavage has a barrier of 10.6 kcal-mol$^{-1}$ on the $T_1$ pathway and 17.4 kcal-mol$^{-1}$ on the $S_1$ pathway at the CCSD(T)/aug-cc-pVDZ level with the vibrational zero-point energy correction. It is evident that the C-Cl bond cleavage proceeds more easily than the C-C bond fission along the $S_1$ and $T_1$ pathways. After the C-Cl bond cleavage, the formed CICOCO radical in the ground state can decompose into CICO($^2A'$) and CO($^1\Sigma$), but it is not easy. The CICOCO radical is optimized at the CAS(9,7) level, which shows that the radical is non-planar with the O=C=O dihedral angle of 97.7°. The CICOCO dissociation into CICO($^2A'$) and CO($^1\Sigma$) has a barrier of 15.4 kcal-mol$^{-1}$ at the CAS(9,7) level with the zero-point energy correction.

The concerted pathway of (CICO)$_2$ to CO and Cl$_2$CO has been proposed for the thermal decomposition of (CICO)$_2$ which involves 1,2-Cl migration. The same products were observed in UV-irradiation of (CICO)$_2$ in the Xe matrix. The transition state of the 1,2-Cl migration in the ground state, referred to as TS$_{Cl-12}(S_0)$, was optimized with the B3LYP, MP2, and CCSD methods. The obtained structure reveals that the 1,2-Cl migration is accompanied with an intramolecular rotation, which is nearly free for (CICO)$_2$ in the ground state. The further evidence for this comes from direct ab initio molecular dynamics calculations. The activation barriers were
predicted to be 37.8 and 38.7, and 32.8 kcal-mol\(^{-1}\) at the B3LYP, MP2, and CCSD levels, respectively. The potential energy profile for the 1,2-Cl migration in the ground state was plotted in Figure 3-4, together with the CCSD/cc-pVDZ relative energies. The 1,2-Cl migration is a favorable pathway in energy for \((\text{ClCO})_2\) in the ground state, as compared with the C-C or C-Cl dissociation that is endothermic by about 80 kcal-mol\(^{-1}\).

![Potential Energy Profile](image)

**Figure 3-4** Schematically potential energy profiles for the 1,2-Cl migration in the \(S_0\) state, along with the relative energies of the stationary structures.

### 3.5 Ab initio dynamics simulation

The features of potential energy surface, such as well depths and barrier heights, can provide a qualitative understanding of a chemical reaction. In most cases, however, a reaction mechanism is controlled by the reaction dynamics rather than simply the PES shape. Therefore, it is very helpful to study reaction dynamics for determining atomic-level mechanism of a reaction. We carried out direct *ab initio* molecular dynamics simulations on dissociation processes upon photoexcitation of \((\text{ClCO})_2\). The trajectories were integrated with a Hessian-based algorithm and Hessian matrix was updated at each step. To overcome the CASSCF convergence problem, the state-averaged CAS(10,8)/cc-pVDZ calculations were performed for determining energies, energy gradients, and Hessian matrix of \((\text{ClCO})_2\) in the \(S_1\) state.

### 3.5.1 The dynamics simulation for the \(S_1\) dissociation

Firstly, forty trajectories were calculated starting from the FC geometry on the \(S_1\) state with the initial kinetic energy of \(0 – 45\) kcal-mol\(^{-1}\), which corresponds to vertical excitation of \((\text{ClCO})_2\) at 248 nm or longer wave length. The C-C, C-O, and
C-Cl distances are plotted in Figure 3-5 as a function of time for one representative trajectory with the initial kinetic energy of 45 kcal·mol$^{-1}$.

![Graphs of C-C, C-O, and C-Cl distances](image)

**Figure 3-5** The C-C, C-O, and C-Cl distances are plotted as a function of time for one representative trajectory starting from the FC geometry with the initial kinetic energy of 45 kcal·mol$^{-1}$.

The bond parameters oscillate in their equilibrium positions and the initial energies in the C=O and C-C stretching modes were statistically distributed in twelve vibrational modes during ~1200 fs of the trajectory integration. The C-C and C-Cl cleavages were not observed to occur on condition that trajectories start from the $S_1$ FC geometry with the initial kinetic energy less than 45 kcal·mol$^{-1}$. It should be pointed out that only a few kcal·mol$^{-1}$ of the initial kinetic energies were converted
into potential energy in the trajectory propagation and the initial kinetic energy has a little influence on the C-C and C-Cl dissociations.

Figure 3-6 The C-C, C-O, and C-Cl distances are plotted as a function of time for one trajectory starting from the C-C distance at 1.26 Å and all other bond parameters at the S₀ equilibrium values.

In order to explore the effect of the initial condition on the S₁ dissociation of (CICO)₂, we consider some extreme cases. In the first extreme case, a structure, in which the C-C distance is 1.26 Å and all other bond parameters are the S₀ equilibrium values, was used as the initial structure for the trajectory calculation, which corresponds to the initial energy of ~40 kcal·mol⁻¹ distributed on the C-C stretching mode. As can be seen from Figure 3-6, all vibrational modes are located in low-energy vibrational states, and all parameters oscillate around their equilibrium positions. The C-C bond cleavage was not observed even with the initial potential energy of 40 kcal·mol⁻¹ distributed on the C-C stretching mode.
Figure 3-7 The C-C, C-O, and C-Cl distances are plotted as a function of time for one trajectory starting from the $S_1$-TS$_1$ geometry.

Time evolution of the C-C, C-Cl, and C-O distances are plotted in Figures 3-7 and 3-8 for other two special cases, where the trajectories start from the transition-state structures of the C-C and C-Cl bond cleavages on the $S_1$ state, respectively. The first observation is that the C-C bond cleavage occurs within 200 fs, once the trajectory propagates from the $S_1$-TS$_1$ geometry (see Figure 7). It was also found that the two C-Cl bonds were cleaved in the same period with the C-C bond fission. Therefore, once sufficient internal energies were distributed in the C-C stretching mode, the (ClCO)$_2$ dissociation proceeds to give 2CO($^1\Sigma$) and 2Cl($^2P$) as the products in a synchronous concerted fashion.

But the situation is quite different for the C-Cl bond fission in the $S_1$ state. Although the initial C-Cl bond was found to break immediately, no subsequent C-C or C-Cl bond fission was observed by the dynamics simulation, as shown in Figure 3-8. If the C-Cl bond is broken firstly, the dissociation of (ClCO)$_2$ is only a two-body process, leading to formation of Cl and CICOCO radicals in the ground state, which is consistent with existence of a considerable barrier on the pathway from CICOCO to
CICO + CO. From the combined electronic structure calculations and dynamics simulations, it can be concluded that the direct S\(_1\) dissociation (two-, three-, and four-body) occurs with little possibility upon photo-excitation at 248 nm and even at 193 nm.

**Figure 3-8** The C-C, C-O, and C-Cl distances are plotted as a function of time for one trajectory starting from the S\(_1\)-TS\(_2\) geometry.

### 3.5.2 The dynamics simulation for the T\(_1\) dissociation

Since there is little possibility for the dissociation along the S\(_1\) pathways, we pay more attentions to the T\(_1\) processes in the following. It should be pointed out that electronic structure calculations for the trajectory propagation in the T\(_1\) state were
carried out at the unrestricted MP2 level, which is different from the CASSCF calculation for the $S_1$ trajectories. The CASSCF calculation is time consuming in comparison with the MP2 calculation, but the MP2 calculation is more efficient for treating electronic correlation. Totally, 500 trajectories were integrated starting from the $T_1$ state with the initial energy in the range of 10-45 kcal·mol$^{-1}$, but 48 trajectories failed, due to the problems in the SCF convergence. Among the 452 trajectories, 286 trajectories (~65%) lead to four-body dissociation, 67 trajectories (15%) lead to three-body dissociation, 85 unreactive trajectories (~20%) stay in the FC region, 3 trajectories lead to the C-C bond fission (two-body) and 2 trajectories lead to one C-Cl bond fission (two-body).

![Graphs](image)

**Figure 3-9** The C-C, C-O, and C-Cl distances are plotted as a function of time for one of the representative trajectories with the initial C-C bond length of 1.45 Å and other bond parameters at their $S_0$ equilibrium geometry.

The C-C, C-Cl, and C-O distances are plotted in Figure 3-9 as function of time for one of the representative trajectories for the four-body dissociation along the $T_1$ pathway. In the first period of about 900 fs, the C-C and C-Cl bonds oscillate about their $T_1$ equilibrium values and the C-C and C-Cl stretching modes lie in vibrational
ground or lower excited states. But the two C-O stretching modes are in highly vibrational levels and the initial potential energies are mainly distributed in the C1-O3 stretching vibration in the first period. After passing through this “transition-period” of about 900 fs, the vibrational energies are transferred from the C-O stretching to the C-C and C-Cl modes and the C-C and C-Cl bond fissions take place nearly in the same time.

Figure 3-10 The C-C, C-O, and C-Cl distances are plotted as a function of time for one of the representative trajectories with the initial C-C bond length of 1.47 Å and other bond parameters at their S0 equilibrium geometry.

Upon analyzing time evolution of structures and energies for the 286 trajectories that leads to four-body dissociation in the T1 state, it is found that the time of the C-C bond fission is in the range of 300 - 1000 fs and the averaged time constant is 452 fs for the C-C bond fission. It is obvious that the C-C bond cleavage along the T1 pathway is an ultrafast process upon photoexcitation at 248 nm or shorter wave lengths. On average, the first and the second C-Cl bonds break completely in about 50 and 70 fs after the C-C bond complete cleavage, which clearly shows the bond
fissions to be a synchronous concerted process. Therefore, the four-body dissociation of (ClCO)₂ in the T₁ state is an ultrafast and synchronous concerted process.

Figure 3-11 The C-C, C-O, and C-Cl distances are plotted as a function of time for one of the representative trajectories with the initial C-C bond length of 1.43 Å and other bond parameters at their S₀ equilibrium geometry.

The dynamics simulations reveal that the three-body dissociation is a possible pathway for the (ClCO)₂ dissociation in the T₁ state. The C-C, C-Cl, and C-O distances are plotted in Figure 3-10 as a function of time for one of the representative trajectories for the three-body dissociation. The total energy given for this three-body process is the same as that for dynamics simulation for the four-body dissociation shown in Figure 3-9, but the initial potential energies of 4.0 kcal·mol⁻¹ are changed into the initial kinetic energies. In the first period of about 500 fs, the C-C and C-Cl bonds oscillate around their equilibrium values, the C-O stretching vibrations are in their vibrational excited states. After the transition period of ~500 fs, one C-Cl bond exhibits a tendency toward breaking firstly. Then the C-C and one C-Cl bonds were broken in a concerted way, but the other C-Cl stretching mode is still in its vibrational
ground state. Meanwhile, one C-O stretching vibration relaxes to the ground state and the other C-O stretching vibration is still in its excited state. Also, the three-body dissociation of (CICO)₂ in the T₁ state is an ultrafast and synchronous concerted process.

**Figure 3-12** The C-C, C-O, and C-Cl distances are plotted as a function of time for one of the representative trajectories with the initial bond parameters at their S₀ equilibrium geometry.

The two-body dissociation of (CICO)₂ was observed to take place in the T₁ state, although the possibility is relatively small. As shown in Figure 3-11, only the C-C bond fission was observed by the dynamics simulation, in spite of more initial potential energies distributed in the C-C stretching mode in comparison with the case shown in Figure 3-9. In a transition period of about 200 fs, the C-C and C-Cl bonds oscillate around their equilibrium values, the C-O stretching vibrations are in their vibrational excited states. After the transition period, the C-C bond was observed to break immediately, but the two C-Cl stretching modes are in their low-energy vibrational excited states. It should be pointed out that one C-O stretching mode is in high-energy excited vibrational state, while the other C-O stretching vibration is nearly in its ground state. The initial internal energies are localized in the C-C
stretching mode, but most of them are transferred to the C-O stretching mode in about 200 fs, which is the main reason why only the C-C two-body dissociation was observed even with large quantity of the initial internal energy distributed in the C-C stretching mode.

Figure 3-12 gives one example for the C-Cl two-body dissociation along the T\textsubscript{1} pathway. After one C-Cl bond fission, the left internal energies distributed in the C-C, and one C-O stretching modes. As a result, the C-C stretching mode does not have sufficient energies to overcome a barrier of about 15 kcal-mol\textsuperscript{-1} on the decomposition pathway of \text{CICO} \rightarrow \text{CICO}(^2\text{A}') + \text{CO}(^1\Sigma\text{)}. Thus the C-Cl two-body dissociation becomes dominant pathway under this condition. Once the system decays to the T\textsubscript{1} state, the four-body dissociation of (CICO)\textsubscript{2} is the dominant pathway, leading to 2 Cl(^2P) and 2 CO(^1\Sigma\text{)} in the ground state; The three-body dissociation is a minor channel with little possibility for the two-body dissociation.

### 3.5.3 The dynamics simulation for the S\textsubscript{0} processes

Before the end of this chapter, we explore the possibility of (CICO)\textsubscript{2} dissociation in the ground state. As pointed out before, the CASSCF calculation is more time consuming in comparison with the MP2 and B3LYP calculations, which are reliable for studying a molecule in the ground state. In addition, the MP2 and B3LYP methods are more effective for treating electronic correlation than the CASSCF method. In principle, electronic structure calculations for dynamics simulation of ground-state processes should be performed with the MP2 or B3LYP method. However, the (CICO)\textsubscript{2} dissociation in the S\textsubscript{0} state leads to formation of radical products. In this case, both the restricted and unrestricted MP2 (B3LYP) methods can not give a consistent description on the whole dissociation processes. For example, the restricted MP2 (B3LYP) is suitable for structural region around equilibrium geometry, but is not suitable for the dissociation limit of \text{CICO}(^2\text{A}') + \text{CICO}(^2\text{A}') or \text{CICO} + \text{Cl}(^2\text{P}); In principle, the unrestricted MP2 (B3LYP) method can give a right description on asymptotic behavior of \text{CICO} \rightarrow \text{CICO}(^2\text{A}') + \text{ClCO}(^2\text{A}') or (CICO)\textsubscript{2} \rightarrow \text{CICO} + \text{Cl}(^2\text{P}). But trajectories always stay around the equilibrium position, if the unrestricted MP2 (B3LYP) method was used for electronic structure calculation. In comparison, the CASSCF method is suitable for both stable structure and its radical products, which is employed in the dynamics simulation of the (CICO)\textsubscript{2} dissociation in the ground state.

Totally, thirty-five trajectories were calculated starting from the S\textsubscript{0} state with the initial energy in the range of 50-100 kcal-mol\textsuperscript{-1}. Firstly, eighteen different structures, in which the C-C distance is decreased from 1.54 Å (the equilibrium C-C bond length of the S\textsubscript{0} state) to 1.18 Å with the other bond parameters at the S\textsubscript{0} equilibrium geometry, were used for trajectory calculations. It was found that seventeen trajectories stay in the region of the S\textsubscript{0} equilibrium geometry. The C-C, C-O, and C-Cl distances are plotted in Figure 3-13 as a function of time for one representative trajectory with the initial bond parameters at their S\textsubscript{0} equilibrium geometry, except for the C-C distance at 1.50 Å. It can be seen from Figure 3-13 that all stretching vibrations are in their low-energy excited states. Finally, the excess internal energies are statistically distributed on all vibrational modes.

When the C-C distance is decreased to 1.20 Å in the initial structure, which corresponds to the initial energy of ~95 kcal-mol\textsuperscript{-1} distributed on the C-C stretching
mode, the C-C bond cleavage was observed within a half of the C-C stretching vibrational period. As shown in Figure 3-14, the two C-Cl bond cleavages take place nearly in the same period as the C-C bond cleavage. Once a large quantities of the internal energies (~100 kcal-mol$^{-1}$) are initially distributed on the C-C stretching mode, the (CICO)$_2$ dissociation in the ground state is an ultrafast and synchronous concerted four-body process, leading to formation of 2 Cl($^2P$) and 2 CO($^1\Sigma$). It should be pointed out that the initially formed CO($^1\Sigma$) molecules are in different vibrational states.

![Graphs showing C-C, C-O, and C-Cl distances over time](image)

**Figure 3-13** The C-C, C-O, and C-Cl distances are plotted as a function of time for one of the representative $S_0$ trajectories with the initial bond parameters at their $S_0$ equilibrium geometry, except for the C-C distance at 1.50 Å.
Seventeen trajectories were calculated with the initial energies of ~100 kcal·mol\(^{-1}\) distributed in the C-C and C-Cl stretching modes. Most of them went back to the reactant region (14 out of 17 trajectories), oscillating in the S\(_0\) equilibrium position. Time evolution of the bond parameters are similar to those shown in Figure 3-13. Two trajectories left the reactant region, one leading to two-body dissociation by the C-C bond cleavage and the other giving rise to three-body dissociation by fissions of the C-C bond and one C-Cl bond. In some cases (3 trajectories out of 16), the CICO(\(^{2}A'\)) radical is formed by the C-C bond cleavage as an intermediate. However, the intermediate was predicted to have a lifetime less than 70 fs in the present case. Actually, the C-C and C-Cl bond cleavages occur in a synchronous concerted way.

**Figure 3-14** The C-C, C-O, and C-Cl distances are plotted as a function of time for one of the representative S\(_0\) trajectories with the initial bond parameters at their S\(_0\) equilibrium geometry, except for the C-C distance at 1.18 Å.
3.6 Mechanistic photodissociation of (CICO)₂

Photoexcitation in the ultraviolet region leads to the (CICO)₂ molecule in the S₁ state. From the S₁ state, the (CICO)₂ molecule can deactivate via three nonradiative channels: internal conversion (IC) to the ground state, intersystem crossing (ISC) to the T₁ state, and the direct dissociations along the S₁ pathways. The C-C bond fission has a barrier of about 40 kcal-mol⁻¹ on the S₁ pathway, which shows that the S₁ fission of the C-C bond takes place with little possibility, which is supported by ab initio dynamics simulations. There is a barrier of 17.4 kcal-mol⁻¹ for the C-Cl bond fission on the S₁ pathway, which is lower than that for the S₁ C-C bond cleavage. The S₁ C-Cl bond fission is accessible in energy upon photoexcitation of (CICO)₂ by ultraviolet light. However, the ab initio MD simulations reveal that the S₁ C-Cl bond fission occurs only in extreme cases. The reason for this comes from fast redistribution of the internal energies among all vibrational modes. The combined electronic structure calculation and MD simulation reveals that the S₁ direct dissociation occurs with little possibility.

Internal conversion (IC) to the ground state is a possible pathway for the excited (CICO)₂ molecule to deactivate. The (CICO)₂ molecule is left with sufficient internal energies to overcome barriers on the S₀ pathways to products, once relaxing to the ground state. However, the internal energies are fast redistributed into all vibrational modes. The C-C and C-Cl stretching modes do not have enough energy to reach their dissociation limits, since a high enthermic character exists for the C-C and C-Cl bond fissions. The products of CO and Cl₂CO were observed in UV-irradiation of (CICO)₂ in the Xe matrix. The concerted pathway from (CICO)₂ to CO + Cl₂CO involves 1,2-Cl migration and a large structural deformation. Before formation of CO + Cl₂CO, internal energies are distributed into all vibrational modes. The 1,2-Cl migration in the ground state takes place with little possibility, although the barrier on the concerted pathway is relatively small (~38 kcal-mol⁻¹).

The optimized Sᵢ/T₁ intersection structure is given in Figure 3-2. A comparison with the S₁ equilibrium structure shown in Figure 3-1 indicates that the S₁/T₁ intersection point is close to the S₁ minimum in structure, except for one C-O bond distance that is 1.559 Å in the S₁/T₁ structure and 1.242 Å in the S₁ structure. Since the initial n→π* excitation is localized in one C-O stretching mode, many trajectories starting from the S₁ FC structure propagate into the S₁/T₁ region within a half of the C-O stretching vibration. The spin-orbit coupling matrix element was calculated to be 47 cm⁻¹ at the S₁/T₁ intersection structure, which reveals that the spin-orbit interaction between the S₁ and T₁ states is strong in the vicinity of the S₁/T₁ intersection structure. All these indicate that the ISC from S₁ to T₁ takes place with high efficiency.

As pointed out before, the C-C bond fission on the T₁ state has a barrier of 12.6 kcal-mol⁻¹, which is a little higher than that for the T₁ C-Cl bond cleavage. Among the 452 trajectories for the T₁ state, the four-body dissociation is a dominant pathway with ~65 percent (286 trajectories), where the C-C bond fission takes place prior to the two C-Cl bond cleavages. The three-body dissociation on the T₁ state is a minor channel with 15% percent. Among sixty-seven trajectories leading to CICO(²A') + CO(¹Σ⁺) + Cl(²P), only half of them (32 trajectories) give rise to the products through the mechanism of (CICO)₂ → CICOCO + Cl(²P) → CICO(²A') + CO(¹Σ⁺) + Cl(²P). The C-C bond fission followed by one C-Cl bond cleavage was observed in the other 35 trajectories. It is evident that intramolecular energy transfer controls the selectivity.
of the C-C and C-Cl bond fissions. From the combined electronic structure calculation and dynamics simulation, we come into conclusion that the $S_1 \rightarrow T_1$ ISC and followed by four-body dissociation to $2\text{Cl}(^2P)$ and $2\text{CO}(^1\Sigma)$ is the dominant pathway for photodissociation of $(\text{ClCO})_2$ in UV region, while the three-body dissociation is a minor channel with little possibility for the two-body dissociation. More importantly, the four-body dissociation of $(\text{ClCO})_2$ in the $T_1$ state is an ultrafast and synchronous concerted process.
Chapter 4

Photodissociation of phosgene

Since phosgene (Cl₂CO) is an excellent model molecule for studying three-body dissociation dynamics, its photodissociation has received considerable attention in the past decades. We have performed direct ab initio trajectory calculations to explore the dynamics of the photo-induced Cl₂CO dissociation. The dissociation is predicted to be an ultrafast and synchronous concerted three-body process, which is summarized in this chapter (for details see the paper 1).

![Potential Energy Surfaces](image)

**Figure 4-1.** One- and two-dimensional potential energy surfaces of the ground and excited states for Cl₂CO, along with the stationary structures (bond length in angstrom, bond angles in degree, and $\beta$ : the Cl-C-O-Cl dihedral angle) and their relative energies (kcal mol$^{-1}$, the red numbers). Reprinted with permission from American Institute of Physics.

4.1 Structures and relative energies

Geometric and electronic structures of Cl₂CO have been investigated with different ab initio methods,$^{130}$ such as CCSD, MP2, CASSCF, and DFT. It was found that double-$\zeta$ is suitable basis set for electronic structure calculations of the Cl₂CO molecule.$^{129}$ Thus, the cc-pVDZ basis set is employed for studying the structure and relative energy. The optimized structures and calculated relative energies are shown in Figure 4-1 along with the CCSD/cc-pVDZ bond parameters, which are close to experimental values. The equation-of-motion CCSD calculations (EOM-CCSD) reveal that the first excited singlet state ($S_1$) of Cl₂CO originates from the $n\rightarrow\pi^*$ excitation localized on the C=O group. The further evidence for this comes from changes in bond parameters from $S_0$ to $S_1$. The O-C bond is increased from 1.182 Å in
S₀ to 1.311 Å in S₁, while the Cl-C-O-Cl dihedral angle is decreased from 180° in the S₀ structure to 130° in the S₁ structure. Thus, the S₁ state is assigned as \(^1\text{no}\pi^*\text{(C=O)}\) hereafter.

The relative energies for the stationary structures calculated at the CAS(10,8) and EOM-CCSD(CCSD) levels are listed in Table 4-1, along with the experimental values where available. The S₁ equilibrium geometry has its relative energy of 99.0 kcal·mol\(^{-1}\) at the EOM-CCSD/cc-pVDZ level with the vibrational zero-point energy correction, while the vertical excitation from S₀ to S₁ is 128.6 kcal·mol\(^{-1}\) at the same level of theory. As compared with the experimental findings of the maximum absorption at 232 nm and the S₀→S₁ band origin of 32730 cm\(^{-1}\) (93.4 kcal·mol\(^{-1}\)),\(^{130,131}\) the present EOM-CCSD calculations overestimate the relative energy of the S₁ state by ~ 5.0 kcal·mol\(^{-1}\).

### Table 4-1 The relative energies (kcal·mol\(^{-1}\)) for the stationary structures

<table>
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<th>CAS(10,8) cc-pVDZ</th>
<th>CAS(10,8) cc-pVTZ</th>
<th>EOM-CCSD(^a) cc-pVDZ</th>
<th>EOM-CCSD(^a) cc-pVTZ</th>
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<td>99.0</td>
<td>101.2</td>
<td>93.4(^b)</td>
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<td>134.4</td>
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<td>129.4</td>
<td>123.2(^c)</td>
</tr>
<tr>
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<td>110.3</td>
<td>105.1</td>
<td>109.3</td>
<td>-</td>
</tr>
<tr>
<td>CICO((^2)A') + Cl((^2)P)</td>
<td>67.4</td>
<td>68.9</td>
<td>70.1</td>
<td>71.9</td>
<td>74.6(^d)</td>
</tr>
<tr>
<td>TS(CICO→CO+Cl)+Cl</td>
<td>67.9</td>
<td>71.1</td>
<td>70.9</td>
<td>74.5</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^a\): The relative energies in ground state calculated at the CCSD level; \(^b\): Band origin (32730 cm\(^{-1}\)) from Refs. 130 and 131; \(^c\): The absorption maximum at 232 nm from Ref. 116; \(^d\): The dissociation energy calculated from heats of formation at 0K in Ref. 117.

### 4.2. The C-Cl bond dissociation

The Cl₂CO in the S₀ and S₁ states can correlate adiabatically with the CICO(\(^2\)A') radical and Cl(\(^2\)P) in the ground state, due to three-fold degenerate of Cl(\(^2\)P). The one and two-dimensional potential energy surfaces of the C-Cl bond cleavages in the S₀ and S₁ states are shown in Figure 4-1 along with the relative energies of the stationary points. The first C-Cl bond cleavage in the ground state is endothermic by 70.1 kcal·mol\(^{-1}\) (D₀) at the CCSD/cc-pVDZ level. A transition state is found on the S₁ pathway to CICO(\(^2\)A') and Cl(\(^2\)P) by the EOM-CCSD calculation. The first C-Cl bond fission has a barrier of 6.1 kcal·mol\(^{-1}\) on the S₁ pathway. When the first C-Cl bond is dissociated with the C-Cl distance of 2.078 Å at the TS₁ structure, the second C-Cl bond is elongated by 0.013 Å in the TS₁ structure, as compared with that in the S₁ structure. This shows that the first C-Cl bond cleavage has a considerable influence on the second C-Cl bond dissociation.

The CCSD calculations with the cc-pVDZ and cc-pVTZ basis sets indicate that
the ClCO(\(^2A'\)) dissociation into CO(\(^\Sigma^+\)) and Cl(\(^2P\)) is exothermic by 4.5 and 3.1 kcal·mol\(^{-1}\) (\(D_0\)), respectively. The barrier to the dissociation is predicted to be 0.8 and 2.6 kcal·mol\(^{-1}\) by the CCSD/cc-pVDZ and CCSD/cc-pVTZ calculations, respectively. The present calculations reveal that the ClCO(\(^2A'\)) radical decomposes into CO(\(^\Sigma^+\)) + Cl(\(^2P\)) very easily. However, the dissociation was inferred to be endothermic by 2600 ± 1200 cm\(^{-1}\) (4.0 – 10.9 kcal·mol\(^{-1}\)) in the previous studies,\(^{117,132}\) and the ClCO(\(^2A'\)) radical exhibits a well with a depth of 5850 cm\(^{-1}\) (16.7 kcal·mol\(^{-1}\)).\(^{131,133-135}\) The present electronic structure calculations give us a reason to expect that the second C-Cl dissociation of Cl\(_2\)CO takes place very easily, once the first C-Cl is broken, a concerted three-body process occurs. The further evidence for this comes from ab initio molecular dynamics, which is discussed below.

![Figure 4-2](image)

**Figure 4-2** The C-O and C-Cl distances plotted as a function of time for a representative trajectory with the initial kinetic energy set to zero. The initial part is enlarged in the upper inset. Reprinted with permission from American Institute of Physics.
4.3 Ab initio dynamics simulations

Firstly, fifty trajectories were calculated starting from the Franck-Condon geometry in the $S_1$ state, which corresponds to the internal energy of 23.5 kcal-mol$^{-1}$ above the barrier top of the C-Cl bond cleavage on the $S_1$ pathway. Meanwhile, the initial kinetic energy is set to zero for all trajectories. Different step sizes, which are changed from 0.01 to 0.15 (amu)$^{1/2}$-bohr, were used to propagate trajectories. All fifty trajectories were found to be reactive and propagate into the product region within 450 fs. The calculated trajectories show that the first C-Cl bond breaks completely in the time range of 110 – 420 fs with an average value of 260 fs (the average of the time difference), while it takes 230 – 460 fs for the second C-Cl bond to break fully with an average value of 298 fs. On average, the second C-Cl bond breaks completely at 40 fs after the cleavage of the first C-Cl bond, but the two C-Cl bonds begin to break (C-Cl distance ≥ 2.0 Å) at the same time. The $S_1$ dissociation is a three-body process, leading to CO($^1\Sigma^+$) + Cl($^2P$) + Cl($^2P$) in the ground state. The C-O and C-Cl distances are plotted in Figure 4-2 as a function of time for a representative of the reactive trajectories. After photo-excitation to the $S_1$ FC point, the initial potential energies are mainly distributed in the C-O stretching mode. As a result, the C-O bond oscillates around its $S_1$ equilibrium value at the initial stage. After a few vibrational periods (~150 fs), the C-O bond distance is suddenly decreased and the C-O stretching mode returns to its vibration ground state. At the same time, the internal energies are transferred to the C-Cl symmetric stretching mode and the two C-Cl bonds begin to break simultaneously. The first C-Cl bond breaks completely at 205 fs, while it takes another 30 fs for the second C-Cl bond to break fully.

Secondly, one hundred trajectories were initiated at the $S_1$ FC geometry and the initial kinetic energy is set to 1 – 15 kcal-mol$^{-1}$ with the step-size fixed at 0.05 (amu)$^{1/2}$-bohr. A few kcal-mol$^{-1}$ of the initial kinetic energies were found to convert into potential energies in the trajectory propagation. The initial kinetic energies have a noticeable influence on the C-Cl bond dissociation. On average, the first C-Cl bond fully breaks with a time constant of 114 fs, while the time constant is about 160 fs for the second C-Cl bond to fully break. Increasing the initial kinetic energies results in the time scale of the C-Cl bond fission shortened by about 140 fs, but the time difference between the two C-Cl bond cleavages is nearly unchanged with increase of the initial kinetic energies for the reactive trajectories. The C-O and C-Cl distances are plotted in Figure 4-3 as a function of time for the reactive trajectory with the initial kinetic energy of 5.0 kcal-mol$^{-1}$. It has been found that the initial energies distributed in the C-O stretching mode are transferred to the C-Cl symmetric stretching mode within one vibrational period and the two C-Cl begin to break at the same time of ~30 fs. Then the two C-Cl distances are monotonically increased with the time of trajectory propagation. The first and second C-Cl bonds break completely at a time of ~100 and ~140 fs, respectively.

For the photo-induced three-body decay of Cl$_2$CO, the synchronous and asynchronous concerted mechanism, as well as a stepwise mechanism, have been suggested to be responsible for formation of three-body products of CO and 2Cl($^2P$) in the previous studies.\textsuperscript{117,132,134,136,137} From the time constants for the two C-Cl bond cleavages calculated in the present work, we come into conclusion that the photo-initiated dissociation of Cl$_2$CO is the synchronous concerted three-body process and the sequential dissociation can be ruled out.

It has been pointed out before that the $S_1$ C-Cl bond cleavage yields the
ClCO($^2A'$) fragment with a barrier of 6.1 kcal/mol and the further decomposition of ClCO($^2A'$) is exothermic with a barrier in the range of 0.8 – 2.6 kcal-mol\(^{-1}\). Once the molecule of is populated in the \(S_1\) state by photo-excitation at 230 nm, the molecule has sufficient internal energies to overcome the barrier on the pathways of the two C-Cl bond cleavages. The feature of the calculated potential energy surface is in good agreement with the concerted mechanism of the Cl\(_2\)CO dissociation into CO($^1\Sigma$) and 2Cl($^2P$).

Figure 4-3 The C-O and C-Cl distances plotted as a function of time for a representative trajectory with the initial kinetic energy set to 5.0 kcal-mol\(^{-1}\). Reprinted with permission from American Institute of Physics.

The atomic Cl fragments were experimentally observed both in the ground ($^2P_{3/2}$) and the spin-orbit excited states ($^2P_{1/2}$).\(^{117,137}\) The energy difference of the two spin-orbit states, Cl($^2P_{3/2}$) and Cl($^2P_{1/2}$), is about 0.1 eV. In particular, the energy splitting is less than 100 cm\(^{-1}\) between the two spin-orbit states in the region of the reactant and transition state (C-Cl distance < 3.0 Å).\(^{138,139}\) It is reasonable to expect that the spin-orbit interaction has little influence on the mechanism of the Cl\(_2\)CO
photodissociation.

The present ab initio molecular dynamics simulations predict that the symmetric C-Cl stretching mode is initially excited and the two C-Cl bond begin to break in a concerted fashion. But, they have different time constants for fully breaking of the first and the second C-Cl bonds. One reason for this comes from the fact that the transition state has asymmetric structure for the first C-Cl bond cleavage on the S1 surface. A very small barrier on the pathway of the second C-Cl bond cleavage is another reason that is responsible for its delayed breaking. As a consequence, the two Cl atoms produced by photodissociation of Cl2CO have different velocity and energy distributions. It also reveals that the first Cl fragment is released in a fast process with a time constant less than 260 fs, which is close to the experimentally inferred lifetime of 210 fs for the Cl2CO molecule. However, the second Cl fragment was predicted to be released within a rotational period of the CICO(2A') radical, which is shorter than the time constant inferred experimentally.

The competing fragmentation channels for Cl2CO, Cl2SO, and FCICO at 235 nm have been suggested to take place either directly on the excited state or after internal conversion on the ground state potential energy surface. Especially, the photo-initiated three-body decay of Cl2CO has been inferred to involve both the ground and first excited singlet states. The present electronic structure calculations show that the S1 state exhibits clear 1noπ*CO character in the FC region. In the transition-state (TS) region of the first C-Cl bond fission, however, both the (n'1π*1) and (σ'1σ*1) configurations makes important contributions to the S1 wave function. When the trajectory passes through the TS region, the (σ'1σ*1) configuration becomes main contribution to the S1 wave function. It has been pointed out before that the first C-Cl bond cleavage along the S1 pathway is an ultrafast process upon photo-excitation of Cl2CO at 230 nm, internal conversion to the ground state and intersystem crossing to the lowest triplet state are not in competition with the S1 direct C-Cl bond dissociation. The present electronic structure calculation and dynamics simulation indicate that the concerted three-body decay of Cl2CO is an adiabatic and ultrafast process, which does not support non–adiabatic process proposed in the previous experimental studies.

4.4 Conclusion.

The potential energy surfaces of Cl2CO dissociation to CO + 2Cl(2P) in the S0 and S1 states have been determined with high-level electronic structure methods. The Cl2CO molecules in the S1 state by photo-excitation have sufficient internal energies to overcome the small barrier on the S1 pathway to CICO(2A') and Cl(2P) and the subsequent decomposition of CICO(2A') to CO(1Σ) + Cl(2P). The present electronic structure calculations give an evidence that the photo-induced Cl2CO dissociation to CO(1Σ) and 2Cl(2P) is a concerted and adiabatic process. The direct ab initio molecular dynamics simulations have been performed to probe photodissociation dynamics of Cl2CO at 230 nm. The intramolecular energy transfer is very fast (~260 fs), and the C-Cl bond cleavages were observed to occur within less than 100 fs. The photo-initiated dissociation of Cl2CO is the synchronous concerted three-body process and the sequential dissociation is ruled out.
Chapter 5

Wave-length dependent photodissociation of benzoic acid

As the simplest member of the aromatic carboxylic acid family, benzoic acid (C\textsubscript{6}H\textsubscript{5}COOH) has been extensively investigated in the past many decades. Most of the previous studies focused on its electronic structure, spectra, and H-bond character in the dimer.\textsuperscript{140-144} It is well known that the photodissociation of benzoic acid and the other carboxylic acids in UV plays an important role in atmospheric, combustion, and interstellar chemistry.\textsuperscript{145-153} Recently, theoretical studies\textsuperscript{154-158} reported three reaction channels of benzoic acid:

\[
\begin{align*}
\text{C}_6\text{H}_5\text{COOH} & \longrightarrow \text{C}_6\text{H}_6 + \text{CO}_2 \quad (1) \\
& \longrightarrow \text{C}_6\text{H}_5\text{CO} + \text{OH} \quad (2) \\
& \longrightarrow \text{C}_6\text{H}_5 + \text{COOH} \quad (3)
\end{align*}
\]

Following these theoretical studies, Yin and co-workers had performed experimental investigation of the C\textsubscript{6}H\textsubscript{5}COOH photodissociation by LIF technique at 266 nm\textsuperscript{159} and 280-295 nm\textsuperscript{160} with focus on the detection of OH fragment. The T\textsubscript{2} state was found to be dominant to produce OH fragment from the C\textsubscript{6}H\textsubscript{5}COOH photodissociation at 266 nm. We have performed a combined CAS(14,12)/CASPT2 calculation with large basis set to explore the photo-induced C-OH bond fission. A summary is given in this chapter and the detailed results can be found in the published paper 3.

![Schematic structure and atomic labels of C\textsubscript{6}H\textsubscript{5}COOH.](image)

**Figure 5-1** The schematic structure and atomic labels of C\textsubscript{6}H\textsubscript{5}COOH. Reprinted with permission from American Chemical Society.

5.1 The S\textsubscript{0} geometry and T\textsubscript{v} values

The C\textsubscript{6}H\textsubscript{5}COOH molecule in the ground state has two stable conformers, which are of planar structures with different relative positions of OH and C=O groups. The optimized structure is schematically shown in Figure 5-1 and the key bond parameters
are listed in Table 5-1 at the CAS(14,12)/ANO-RCC-VDZP level. On the basis of the optimized structure of C₆H₅COOH in the ground state, the vertical excitation energies (Tₖ) to the S₁-A", S₂-A', S₃-A', T₁-A', and T₂-A" states are calculated with the MS-CASPT2/CAS(14,12) method, which are listed in Table 5-1.

**Table 5-1:** The selected geometric parameters (in Å and degree) from the present CAS(14,12)/ANO-RCC-VDZP (level a) and previous CAS(10,8)/cc-pVDZ (level b from Ref. 19) optimizations. TS-S₁ and TS-T₂ are the transition states on the S₁ and T₂ potential energy surfaces, respectively. S₆/S₂ and T₀/Sₒ are the crossing points between S₁ and S₂ states, and T₂ and S₂ states, respectively. β: the H₅-O₁₄-C₁₂-O₁₄ dihedral angle. Tᵥ: the vertical excitation energies (eV).

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<th>C1-C12</th>
<th>C12-O13</th>
<th>C12-O14</th>
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<td>1.438</td>
<td>1.369</td>
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### 5.2 The potential energy profiles of the C-OH fissions in the low-lying electronic states

The main purpose of the present study is to explore the C-OH bond fission upon photo-excitation of benzoic acid at 266 nm (4.66 eV),¹⁵⁹,¹⁶⁰ which can reach doorway state (S₂-A') at most. The S₀-A', S₁-A", T₁-A', and T₂-A" states are lower than the S₂-A' state in energy, as can be seen from Table 5-1. The T₁ state is of the $^1\pi\pi^*$ character, which is localized in the aromatic ring and is unreactive with respect to the alpha bond fission. Thus, the potential energies of the S₀-A', S₁-A", S₂-A', T₂-A", and T₃-A' states were calculated as a function of the C-OH distance, and shown in Figure 5-2. When the C-O distance is changed from 1.3 to 5.0 Å with a step-size of 0.2 Å, all the remaining degrees of freedom were optimized at the CAS(14,12) level. Then the single-point energies were calculated with the CASPT2 method. In this way,
the potential energy profiles were obtained in Figure 5-2. From the calculated potential energy profiles, it can be seen that $S_2$-$A'$ and $T_3$-$A'$ give the dissociation products of $\text{C}_6\text{H}_5\text{CO}^+$ + OH in excited state, whereas the $S_0$-$A'$, $S_1$-$A''$, and $T_2$-$A''$ states are dissociated into the ground-state radicals of $\text{C}_6\text{H}_5\text{CO}$ and OH. The crossing points between $S_2$ and $S_1$ ($S_2/S_1$), $S_2$ and $T_2$ ($S_2/T_2$) and $S_1$ and $T_2$ ($S_1/T_2$) are located and the selected bond parameters are listed in Table 5-1.

![Figure 5-2](image)

**Figure 5-2** The CASPT2//CASSCF calculated potential energy profiles of the low-lying electronic states along the coordinate of the OH group leaving under $C_s$ symmetry. The inset is the profiles of the $S_1$ and $T_2$ states. The marked values in the inset were the relative energies (kcal/mol) relative to the $S_0$ minimum, which were corrected by zero-point energy on the corresponding fully optimized geometries. Reprinted with permission from American Chemical Society.

On the basis of the CAS(14,12)/CAS(14,12)/ANO-RCC-VDZP optimized structures for the $S_0$, $S_1$, $S_2$, $T_1$ and $T_2$ states, the adiabatic excited energies ($T_0$) were calculated with the CASPT2// CAS(14,12)/CAS(14,12)/ANO-RCC-VDZP method. The obtained results are in good agreement with the experimental values available. The saddle-point structures of TS-$S_1$ and TS-$T_2$ were optimized located and their selected bond parameters were listed in Table 5-1. Frequency analyses reveal that they are the
real transition states on the reaction pathways.

The S\textsubscript{2} state is the doorway state upon photoexcitation of benzonic acid at 266–294 nm. But S\textsubscript{2} is a bound state and can dissociate into the ground-state products through S\textsubscript{1} or T\textsubscript{2} as a result of the internal conversion (IC) or intersystem crossing (ISC). In this case, the crossing points of S\textsubscript{2}/S\textsubscript{1} and S\textsubscript{2}/T\textsubscript{2} control dissociation mechanism. Since the S\textsubscript{2}→S\textsubscript{1} IC is much easier than the S\textsubscript{2}→T\textsubscript{2} ISC process, the S\textsubscript{1} C–O bond cleavage might be a dominant channel for the C\textsubscript{6}H\textsubscript{5}COOH photodissociation at 266–284 nm. Once the S\textsubscript{1} state is populated, C\textsubscript{6}H\textsubscript{5}COOH can decay to the T\textsubscript{2} state due to a high barrier on the S\textsubscript{1} pathway. From the above discussion, it can be concluded that the S\textsubscript{1} and T\textsubscript{2} C–O bond cleavages are a pair of competition pathways for the C\textsubscript{6}H\textsubscript{5}COOH photodissociation at 266–284 nm.
Chapter 6

Generation of tropospheric OH radical from NO$_2$ and H$_2$O

Hydroxyl radicals are highly reactive molecule with very short lifetime, which play an important role in atmospheric photochemistry.$^{161-166}$ For example, the hydroxyl radical can function as the "detergent" of the troposphere and it controls the concentrations of man-made gaseous pollutants. The oxidation reaction of the OH radical with carbon monoxide mediates the eliminating of CO, producing carbon dioxide in atmosphere. Hydroxyl radical plays an important role in eliminating some greenhouse gasses like methane and ozone.$^{167-171}$ The product of radical HO$_2$ arising from the OH reaction chain can undergo further decomposition and eventually is recycled to OH.$^{171}$ The radicals OH and HO$_2$ are collectively known as HO$_x$ that is the heart of the photochemistry of the troposphere.$^{172-176}$

The photolysis of ozone by UV irradiation in the presence of water vapour is accepted as a primary generation mechanism of tropospheric OH radicals.$^{177-180}$ Recently, Sinha and his coworkers investigated the reaction of excited-state nitrogen dioxide with water and found that its is another important source of tropospheric hydroxyl radicals.$^{181,182}$ Irradiation of NO$_2$ at 420 nm or longer wavelength initiates the photochemistry of efficiency of OH formation in the presence of water vapor. The formed HONO can undergo further photo-decomposition into the OH radicals. Although numerous studies were reported on photochemistry of nitrogen dioxide and its reaction with water, quantitative understanding of its photo-reaction mechanism has not been achieved up to now. We have performed a combined CASSCF/CASPT2 calculation to elucidate how OH radical is generated in the troposphere from NO$_2$ and H$_2$O. A summary is given in this chapter and the detailed results can be found in the published paper 2.

6.1 The active space

The CASSCF method was employed to optimize structures of the critical points (minima and conical intersections) in three lowest-lying electronic states ($^2\!\!A_1$, $^2\!\!B_1$ and $^2\!\!B_2$). It is well known that choice of the active space is a critical step for the CASSCF calculations. I would like to give some comments on how to select the active orbitals in the following. As shown in Figure 6-1, three $\Pi$ orbitals delocalized in the NO$_2$ molecule, $\pi_{\text{ONO}}^0$, $\pi_{\text{ONO}}^1$, and $\pi_{\text{ONO}}^2$, which have zero, one and two nodes respectively, should be included in the active space. In addition, three non-bonding orbitals localized on oxygen and nitrogen atoms ($n_O^0$, $n_O^1$, $n_N^2$) are included in the active space,
due to their important contribution to the n→π* excited states. To account for the reaction of hydrogen abstraction, the O-H σ and σ* orbitals and non-bonding orbital of water O atom (σ_{O-H(W)}*, σ_{O-H(W)}*, n_{O(W)}) are added into the active space. Finally, the active space is composed of 13 active electrons in 9 active orbitals for the CASSCF calculation, referred to as CAS(13,9) hereafter.

![Orbitals](image)

Figure 6-1 The active orbitals used for the CASSCF calculations.

6.2 The critical structures involved

Figure 6-2 shows the structures of minima and conical intersections for NO₂ and its complex with water (NO₂-H₂O), along with the CASSCF/6-31G** optimized key bond parameters. The NO₂ molecule in the ground state (X̂ 2A₁) has a C₂ᵥ symmetry with the N-O bond length of 1.171 Å and the O-N-O angle of 133.9° at the CAS(9,6)/6-31G** level of theory. The optimized X̂ 2A₁ bond parameters are quantitatively consistent with those measured experimentally. The CAS(9,6) calculated wave functions indicate that the unpaired electron is populated in the non-bonding orbital of n_N, while the two three-center π orbitals (π_{ONO}^0 and π_{ONO}^1) with zero and one node are doubly occupied for NO₂ in the ground state. It is evident that there is a three-center-four-electrons π bond in the ground state of NO₂ rather than a three-center-three-electrons π bond. The electron spin resonance spectroscopy provides the strong evidence that the unpaired electron is distributed in nonbonding orbital rather than π orbitals. For the NO₂-H₂O complex in the ground state (X̂ 2A₁), the H-bond distance is 2.410 Å at the CAS(13,9)/6-31G** level of theory. The short H-bond distance predicts existence of a strong H-bond in the complex. However,
formation of the NO$_2$-H$_2$O complex has a little influence on the intramolecular bond parameters of NO$_2$ and H$_2$O, which are not given in Figure 6-2.

The $\tilde{A}^1B_2$ and $\tilde{B}^2B_1$ excited states were optimized at the CAS(9,6)/6-31G** level for NO$_2$ and at the CAS(13,9)/6-31G** level for NO$_2$-H$_2$O. The $\tilde{A}^2B_2$ state originates from one electron transition from $n_N$ to $n_O$ orbital. The formation of lone pair around N atom increases mutual interaction between nonbonding electrons and bonding electrons resulting in smaller O-N-O angle of 102.9 ° in $\tilde{A}^2B_2$ in comparison with 133.9 ° in $\tilde{X}^2A_1$. Meanwhile, the N-O bond lengths are also slightly elongated by ~ 0.071 Å due to increased interaction. The optimized $\tilde{A}^2B_2$ structure was confirmed to be the first-order saddle point for NO$_2$. But it is a true minimum-energy structure for the NO$_2$-H$_2$O complex. The H-bond interaction is stronger in the $\tilde{A}^2B_2$ state than that in the $\tilde{X}^2A_1$ state, which is supported by the fact that the H-bond distance is shorter in $\tilde{A}^2B_2$ than that in $\tilde{X}^2A_1$. The strong H-bond interaction changes the property of the $\tilde{A}^2B_2$ structure from the saddle point to the minimum point.

![Figure 6-2](image.png)

**Figure 6-2** The CASCF/6-31G** optimized structures of critical points for NO$_2$ and NO$_2$-H$_2$O, along with key bond parameters (angle in ° and distance in Å).

The $\tilde{B}^2B_1$ state of NO$_2$ adopts a linear geometry with $D_{sh}$ symmetry and the unpaired electron is excited from $n_N$ to the anti-bonding orbital of $\pi^2_{ONO}$ in the $\tilde{X}^2A_1 \rightarrow \tilde{B}^2B_1$ transition. The nature of this state is not changed upon formation of the NO$_2$-H$_2$O complex. The intersection structures among the $\tilde{X}^2A_1$, $\tilde{A}^2B_2$, and $\tilde{B}^2B_1$ states have been determined by the CASSCF optimizations for NO$_2$ and its complex with H$_2$O, which are referred to as CI($^2A_1$/$^2B_2$), CI($^2A_1$/$^2B_1$), and CI($^2B_1$/$^2B_1$) in line with the related electronic states. It should be pointed out that the CI($^2A_1$/$^2B_1$) intersection and the $\tilde{B}^2B_1$ minimum-energy structures are not distinguishable for the NO$_2$-H$_2$O complex.

### 6.3 The photophysical processes after irradiation at ~410 nm

Photophysical processes for NO$_2$ were illustrated in Figure 6-3, which is based on the CAS(9,6)/CASPT2 computed potential energy profiles. The relative energies of key structures are summarized in Table 6-1. Photoexcitation at ~ 410nm (70.7
kcal-mol\(^{-1}\)) vertically promote NO\(_2\) molecule to the Frank-Condon (FC) point of the \(\tilde{B}^2\text{B}_1\) surface with the O-N-O angle of 133.9°. As pointed out before, the O-N-O angle is 180° at the \(\tilde{B}^2\text{B}_1\) minimum. There is a large intrinsic driving force in the direction of the O-N-O bending mode, resulting in a fast relaxation from the FC structure (the O-N-O angle of 133.9°) to the \(\tilde{B}^2\text{B}_1\) minimum (the O-N-O angle of 180.0°). Since the energy difference between \(^2\text{B}_1\) and \(^2\text{A}_1\) at the linear geometry is only 1.0 kcal/mol for NO\(_2\), which indicates that NO\(_2\) evolves to the CI(\(^2\text{A}_1/\tilde{B}_1\)) intersection region very easily. Then the CI(\(^2\text{A}_1/\tilde{B}_1\)) intersection functions as an efficient nonadiabatic funnel, leading NO\(_2\) to the ground state (\(X^2\text{A}_1\)).

**Table 6-1** The relative energies of the key structures in the low-lying states (\(A_1, B_1, B_2\)) calculated at the CAS(9,6)//CASPT2 level.

<table>
<thead>
<tr>
<th>Angle O2-N1-O3</th>
<th>States</th>
<th>Relative Energies (kcal-mol(^{-1}))</th>
<th>Angle O2-N1-O3</th>
<th>States</th>
<th>Relative Energies (kcal-mol(^{-1}))</th>
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<td>B(_1)</td>
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<td>B(_1)</td>
<td></td>
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<td>B(_2)</td>
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<td>B(_2)</td>
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<td>95.4</td>
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<tr>
<td>105° CI((^2\text{A}_1/\tilde{B}_2))</td>
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<td>A(_1)</td>
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<td>7.4</td>
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<tr>
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<td>B(_2)</td>
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<td>182.9</td>
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</table>

In addition to the nonadiabatic funnel along an increase of the O-N-O angle, a decrease of the angle can drive NO\(_2\) at the \(^2\text{B}_1\) FC structure to the ground state, which involves two intersection points of CI(\(^2\text{B}_2/\tilde{B}_1\)) and CI(\(^2\text{B}_2/\tilde{A}_1\)). From the FC structure of the \(\tilde{B}^2\text{B}_1\) state, the NO\(_2\) molecule firstly relaxes to the CI(\(^2\text{B}_2/\tilde{B}_1\)) point, which is very close to the FC point of \(\tilde{B}^2\text{B}_1\) in structure. The nonadiabatic funnel to the \(^2\text{B}_2\) state via CI(\(^2\text{B}_2/\tilde{B}_1\)) proceeds with high efficiency. Ultimately the system returns to the ground state through the CI(\(^2\text{B}_2/\tilde{A}_1\)) intersection. Double-exponential
components of fluorescence have been observed experimentally,\textsuperscript{188-192} which could be well interpreted by present two decay channels along the increasing and decreasing of the O-N-O angle.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6-3.png}
\caption{The photophysical processes for NO\textsubscript{2} on the basis of CAS(9,6)//CASPT2 computed results. Reprinted with permission from American Chemical Society.}
\end{figure}

6.4 The hydrogen abstraction reaction between NO\textsubscript{2} and H\textsubscript{2}O

It can be expected that the NO\textsubscript{2}-H\textsubscript{2}O complex is formed before the hydrogen abstraction reaction take place. In principle, the abstraction reaction proceeds either in the ground state or in the excited states. Since a high barrier exists on the excited-state pathway and radiationless transition from an excited state to the ground state is an ultrafast process, the abstraction reaction takes place along the ground-state pathway.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6-4.png}
\caption{Schematic mechanism of the hydrogen abstraction between NO\textsubscript{2} and H\textsubscript{2}O after photo-excitation at 410 nm. Reprinted with permission from American Chemical Society.}
\end{figure}

The CAS(13,9)/6-31G** optimized structures of critical points are given in
Figure 6-2 for NO$_2$-H$_2$O complex in the low-lying electronic states. The possible photophysical processes and the hydrogen abstraction reaction are shown in Figure 6-4. The formation of NO$_2$-H$_2$O complex leads to all critical structures in C$_1$ symmetry. For convenience of discussion, irreducible representation in $C_2v$ group is still used for the NO$_2$-H$_2$O complex hereafter. A very sharp barrier connects the reactant of the NO$_2$-H$_2$O complex ($\tilde{X}$ $^2$A$_1$) and product of HONO($\tilde{X}$) + OH in the ground state. With respect to zero level of NO$_2$-H$_2$O ($\tilde{X}$ $^2$A$_1$) minimum, the barrier of the hydrogen abstraction is 51.6 kcal-mol$^{-1}$ at the CAS(13,9)/6-31G**//CASPT2 level of theory, which is decreased to 41.6 kcal-mol$^{-1}$ at the B3LYP/6-31G** level. A barrier of 40.0-50.0 kcal-mol$^{-1}$ is really high for thermal reaction in the ground state. This indicates that the zeroth-order $|n_1, n_2, n_3 = 0\rangle$ vibrational level can not functions as an efficient reaction precursor state to trigger the hydrogen abstraction. Herein, $n_1$, $n_2$, and $n_3$ are numbers of quanta in the symmetric stretching, bending, and asymmetric stretching modes, respectively. After photo-excitation at ~410 nm, the NO$_2$-H$_2$O complex is populated in the excited state. Once decaying to the ground state, the complex is left with sufficient internal energies to overcome the barrier on the pathway from NO$_2$-H$_2$O($\tilde{X}$ $^2$A$_1$) to HONO($\tilde{X}$) + OH.

6.5 Conclusion

To get insights into how to generate hydroxyl radical from NO$_2$ and H$_2$O in troposphere, the photo-induced physical and chemical processes for NO$_2$ and its complex with H$_2$O have been mapped by using multiconfigurational perturbation theory and density functional theory. The surface-intersections were found to dominate the photophysical processes upon irradiation of NO$_2$ by ~410 nm light source in troposphere and further control the generation of OH radical by means of hydrogen abstraction. We contribute an in-depth understanding on how hydroxyl radical is generated from NO$_2$ and H$_2$O in troposphere upon photo-initiated by 410 nm light source.
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