

Introduction

Chemical reactions, the inter-conversion of matter, comprise transfer of electrons or protons or transfer of group of nuclei and electrons between molecules. These processes are significant to many aspects of life in the sense that they determine the function and development of biological and chemical systems. Essentially, a chemical reaction is a collision process at the atomic level[Levine, 2009]. A complete description of a chemical reaction requires characterizing reactants, products, intermediates, transition states, and all the reaction pathways and mechanisms along with the corresponding energetics. The mechanism of a chemical reaction may depend on reaction parameters such as temperature (energy), solvent medium, etc. Chemical reaction dynamics is concerned with obtaining a detailed picture of the changes which occur during a reaction at the fundamental level[Levine, 2009]. The objective of a chemist is to understand what really happens to the atoms in the regions of closest approach during a reaction. In this respect, molecular reaction dynamics lies at the center of chemistry.

1.1 REACTION DYNAMICS IN GAS PHASE

The objective of this thesis is to study unimolecular reaction dynamics in the gas-phase using theoretical methods. A few important gas phase dissociation reactions relevant in atmospheric and combustion chemistry were taken as examples. Computational chemistry can be defined as the theoretical study of chemical reactions using the laws of quantum, classical, and statistical mechanics[Simons, 2003]. Electronic structure theory is used to study detailed energy profiles of a reaction and dynamics is the study of nuclear motion as a function of time. Studying the dynamics of a chemical reaction in the gas phase provides mechanistic details in the absence of solvent influence[Baer *et al.*, 1996]. Understanding the atomic level dynamics of a reaction is important in order to exercise control over the reaction which may possibly lead to mode selective chemistry[Gruebele and Wolynes, 2004] and also to invent new chemistry. In a unimolecular reaction, decomposition of a polyatomic molecule in the gas phase occurs resulting in fragments.



Sufficient amount of internal energy, higher than the activation barrier, is required for the molecule to dissociate. This activation can occur via thermal or photochemical activation[Baer *et al.*, 1996]. Bimolecular reactions in the gas phase are mainly ion-molecule reactions where an ion and a neutral species react to give products. Neutral-neutral reactions in the gas phase are rare and usually occur with large reaction barriers.



Physical chemists are keen to identify progression in chemical reactivity of reactions and relate the trends with molecular parameters. A great advantage of studying gas-phase chemistry

is that it provides a solvent-free environment to observe reactions and in determining quantitative properties of the species involved in the reaction[Chabynyc *et al.*, 1998]. Further, gas phase reactions are easier to model at a high level of electronic structure theory since fewer number of interactions has to be taken into consideration. A solvent medium can affect chemical reaction mechanism and reaction rates. The solvent effect is significant in ion-molecule reactions due to the electrostatic interactions of the polar reactants with the solvent. The solvation energies of reactants in solution can be so large that the relation between intrinsic reactivity and energy profiles becomes difficult to understand in solution. Hence, gas-phase techniques are widely used for studying various type of chemical reactions. These techniques have turned into a very important tool to investigate the reactivity and properties of the non-polar interior of biological molecules such as proteins and DNA and also in the study of supramolecular chemistry[Lundegaard and Jensen, 1999; Kurinovich and Lee, 2000; Schalley, 2000]. Since gas-phase studies do not consider solute-solvent interactions, these techniques are well suited to study reaction energetics, product energy distributions, rates and mechanisms of chemical reactions, and also explicit solvent effects by using the microsolvation technique[Naz *et al.*, 2018; Gronert, 2001]. Results of these studies can be analyzed and compared with condensed-phase experiments, which provide a means of identifying the inherent behavior of a solvent medium in a reaction. Several experimental techniques have been developed to study the dynamics of gas phase reactions such as resonance-enhanced multi-photon ionization (REMPI), ion beam mass spectrometry, and mass analyzed threshold ionization (MATI), pulsed-field ionization, and kinetic energy photo-electron spectroscopy. Several excellent reviews are available in the literature discussing the recent advancements in gas phase experimental techniques[Hudgens *et al.*, 1983; Weibel *et al.*, 2003; Zhu and Johnson, 1991; Yang *et al.*, 1995; Rose *et al.*, 1987; Ashfold *et al.*, 2006]. Among the theoretical methods, *ab initio*[Friesner, 2005; Ben-Nun and Martínez, 2002] electronic structure theory has advanced to an extent to compute structures, energies, and vibrational frequencies of transient and stable species which are directly comparable to experimental data. In the present thesis, select unimolecular reactions are studied using electronic structure theory calculations and direct classical trajectory methods which are described below.

1.2 ELECTRONIC STRUCTURE THEORY

Objectives of performing electronic structure calculations (ESCs) is to determine molecular properties such as optimized geometry, energy, dipole moment, normal mode vibrational frequencies, etc. These can be performed using *ab initio* (first principles), semi-empirical, density functional or molecular mechanics methods. In the *ab initio* method,[Ben-Nun and Martínez, 2002] time independent Schrödinger wave equation is solved to calculate the wavefunction of a molecule. The *ab initio* methods use exact Hamiltonian to predict molecular properties. Beyond Hydrogen-like species, Schrödinger equation is not solvable due to inter-electronic repulsions. Examples of *ab initio* wave function based methods are Møller-Plesset perturbation theory[Cremer, 2011], coupled-cluster methods[Bartlett, 1981] and configuration interaction[Roos *et al.*, 1980] (CI) methods.

Semi-empirical methods[Thiel, 2014; Segal, 2012; Purcell and Singer, 1967] are based on parameterized Hamiltonians. In Hartree-Fock calculations a large number of electron-electron integrals need to be calculated. Whereas, in semi-empirical method, these many electrons integrals and the products of all basis functions on different atoms are reduced, that reduces the computational cost. To compensate for these reduced calculations, parametrization is used to represent the remaining integrals. There are a few semi-empirical approximations namely neglect of diatomic differential overlap (NDDO), MNDO[Dewar and Thiel, 1977], AM1[Dewar *et al.*, 1985], PM3[Stewart, 1991] etc., where parametrization is required to represent the integrals. These semi-empirical methods has been modified over the years by using specific reaction parameters (SRPs)[Gonzalez-Lafont *et al.*, 1991]. Parameterization is performed using experimental quantities

such as enthalpy and other physical properties, and hence the accuracy of semi-empirical methods depends on the accuracy of fitting the experimental data. These methods are useful for large molecular systems such as proteins and also widely employed in computational materials chemistry. Molecular-mechanics[Engler *et al.*, 1973] is a classical mechanical method and models the atoms and chemical bonds as balls and springs, respectively. Classical analytical potential functions are used to model bond stretching, bending, etc. These methods are widely used in molecular dynamics simulations. Another approach is QM/MM (Quantum Mechanics/Molecular Mechanics) wherein the important regions are modeled using quantum mechanics and the rest using classical force fields[Friesner, 2005; Murphy *et al.*, 2000].

Mean-field electronic structure approaches namely Hartree– Fock (HF), semi-empirical molecular orbital theory and Kohn–Sham density functional theory, are widely used methods for large systems. But these methods do not describe long-range electronic correlation effects, also known as vDW and London dispersion interactions. Hence these methods cannot be used to define the interactions between atoms and molecules where non-bonded interactions are present. Capturing these effects is mandatory for systems which involves large or condensed phase medium. To remove such errors dispersion corrected mean field electronic structure methods are widely used[Grimme *et al.*, 2016; Rinaldi *et al.*, 1986]. These methods mostly incorporates the scheme classified as: by using non-local density-based corrections, and semi-classical treatment of dispersion, effective one-electron potentials.

Today, the most practical way of doing electronic structure calculations is based on density functional methods (DFT)[Becke, 2014]. Computational time for DFT is comparable to Hartree-Fock methods and the accuracy can be close to higher level *ab initio* methods. In DFT, electron density (ρ) is used to calculate the ground state properties of a system based on theorems proposed by Hohenberg and Kohn[Hohenberg and Kohn, 1964; Kohn and Sham, 1965]. The molecular wavefunction of a system is not calculated in DFT. In this thesis, DFT is primarily used for electronic structure calculations and direct dynamics simulations.

1.2.1 Molecular Schrödinger equation

The Schrödinger equation is the fundamental equation of quantum mechanics. It describes the evolution of wavefunction of a physical system over time. Time-independent non-relativistic Schrödinger equation for a molecule containing N number of nuclei and n electrons can be written as:

$$\hat{H}\psi(\vec{r}, \vec{R}) = E\psi(\vec{r}, \vec{R}) \quad (1.3)$$

Here, the wavefunction of a molecule is given by $\psi(\vec{r}, \vec{R})$ and the total energy is obtained by solving the above Schrödinger equation and \vec{r} and \vec{R} represent the electronic and nuclear coordinates, respectively. If the nuclei and electrons are assumed as point masses and ignore spin-orbit and other relativistic terms, the non-relativistic molecular Hamiltonian can be written as

$$\hat{H}(\vec{r}, \vec{R}) \equiv \hat{T}_e(\vec{r}) + \hat{T}_N(\vec{R}) + \hat{V}_{eN}(\vec{r}, \vec{R}) + \hat{V}_{NN}(\vec{R}) + \hat{V}_{ee}(\vec{r}) \quad (1.4)$$

Here, \hat{T}_e, \hat{T}_N are the electronic and nuclear kinetic energy operators, respectively.

$$\hat{T}_e = \sum_i \left(\frac{-1}{2m_e} \right) \nabla_i^2 \quad (1.5)$$

$$\hat{T}_N = \sum_\alpha \left(\frac{-1}{2m_\alpha} \right) \nabla_\alpha^2 \quad (1.6)$$

The symbol m_e and m_α denote the masses of electron and nuclei, respectively. \hat{V}_{eN} , \hat{V}_{NN} , and \hat{V}_{ee} are the electron-nuclei attraction, nuclear-nuclear repulsion, and electron-electron repulsion operators, respectively.

$$\hat{V}_{eN} = - \sum_\alpha \sum_i \left(\frac{e^2}{r_{\alpha i}} \right) \quad (1.7)$$

$$\hat{V}_{NN} = \sum_\alpha \sum_{\beta > \alpha} \left(\frac{e^2}{r_{\alpha\beta}} \right) \quad (1.8)$$

$$\hat{V}_{ee} = \sum_j \sum_{i > j} \left(\frac{e^2}{r_{ij}} \right) \quad (1.9)$$

where α, β refer to nuclei and i and j refer to electrons. Unfortunately, the exact solution of Schrödinger equation containing more than one electron can not be obtained due to the involvement of correlation terms. Thus various approximate methods are being used for solving the equations. The most fundamental approximation used in electronic structure calculations is the Born-Oppenheimer approximation which leads to potential energy surface.

Born-Oppenheimer Approximation

Born-Oppenheimer (or adiabatic) approximation[Born and Oppenheimer, 1927] states that due to the much heavier mass of nuclei in comparison to electrons, nuclei can be treated as stationary compared to the motion of electrons. In other words, the change in nuclear configuration is insignificant in the time scale of electronic motions. This adiabatic separation of electronic and nuclear motion leads to potential energy surface. By invoking this approximation, the nuclear kinetic energy in the Hamiltonian can be ignored and the total wavefunction can be written as

$$\psi(\vec{r}, \vec{R}) = \psi_{el}(\vec{r}; \vec{R}) \chi(\vec{R}) \quad (1.10)$$

$\psi_{el}(\vec{r}; \vec{R})$ is the electronic wavefunction wherein the semicolon (;) indicates that electronic wave function is parametrically dependent upon the nuclei coordinates and $\chi(\vec{R})$ is the wavefunction associated with nuclear motion. Thus by ignoring nuclear kinetic energy operator the Hamiltonian becomes:

$$\hat{H} = \hat{H}_{el} + \hat{V}_{NN} \quad (1.11)$$

Here, \hat{H}_{el} , \hat{V}_{NN} , and \hat{T}_N are purely electronic Hamiltonian, nuclear-nuclear repulsion, and nuclear kinetic energy operators, respectively. The electronic energy can be obtained by solving the electronic Schrödinger equation,

$$(\hat{T}_e + \hat{V}_{eN} + \hat{V}_{ee})\psi_{el}(\vec{r}; \vec{R}) = E_{el}\psi_{el}(\vec{r}; \vec{R}) \quad (1.12)$$

The potential energy $U(\vec{R})$ can be obtained by adding nuclear-nuclear repulsion energy to the electronic energy.

$$U(\vec{R}) = V_{NN}(\vec{R}) + E_{el}$$

In electronic structure calculations, $U(\vec{R})$ is calculated by solving the electronic Schrödinger equation for fixed nuclear configurations. In order to determine the potential energy surface of a system, electronic Schrödinger equation is solved for a range of fixed nuclear coordinates.

Hohenberg-Kohn Theorem

Density functional theory (DFT) was primarily used to perform the electronic structure calculations and direct dynamics simulations reported in the present work. DFT is based on two theorems which are briefly mentioned here. The first theorem states that the non-degenerate ground state wavefunction of a system is a unique functional of the ground-state electron probability density. In principle, all the ground state properties of a molecule can be computed if the electron probability density is known.

$$E_0 = E_0[\rho_0] \quad (1.13)$$

Here, E_0 is the ground state energy and ρ_0 is the ground state electron density. The second theorem states that the true ground state electron density minimizes the functional for the energy. The true ground state energy is a global minimum value, which corresponds to the system's exact ground-state density i.e., for any trial density function which is not the same as exact density, $\rho_{tr}(r)$ which satisfies $\rho_{tr}(r)dr = n$ and $\rho_{tr}(r) \geq 0$ for all r , ground state energy is

$$E_0[\rho_{tr}] \geq E_0 \quad (1.14)$$

Since the exact density functional is unknown, the success of a DFT approach depends on how the functional is approximated. There are several functionals available in the literature and excellent review articles on modern DFT methods has been published[Mardirossian and Head-Gordon, 2017; Goerigk *et al.*, 2017; Yu *et al.*, 2016; Burke, 2012; Mardirossian and Head-Gordon, 2016]. The most appropriate DFT functional for the dynamical calculations is selected by comparison of the reaction energy profiles, computed using different DFT functionals with some gold standard wave function based calculations such as a CCSD(T) method. The DFT

methods provide a good alternate to wavefunction based methods and they are computationally efficient. In the present work, direct classical trajectory simulations were performed which require a huge number of single point electronic structure calculations to be carried out. For this purpose, DFT is an excellent choice and has been used extensively in the present work. In the next section, the methodology of classical trajectory simulations is discussed.

1.3 CLASSICAL TRAJECTORY SIMULATIONS

Molecular reaction dynamics is concerned with studying the atomic level changes that occur during a chemical reaction. These changes depend on the reaction and system parameters and determine the mechanism and rate of reactions. The time evolution of the atoms - the dynamics - can be investigated using classical[Sutmann, 2002] or quantum[Kosloff, 1994] mechanics. Studying the dynamics using quantum mechanics, the quantum dynamics,[Kosloff, 1994; Marx and Hutter, 2000] is accurate and it's predictions are directly comparable to experimental measurements. However, the computational complexities increase exponentially with increase in the number of electrons in a system. Both time-independent and time-dependent Schrödinger equations become intractable for large systems and quantum dynamics is limited to only molecules with fewer light atoms[Sinanoglu, 1964]. On the other hand, starting as early as 1960's, classical equations of motion were used to study the dynamics of chemical reactions[Sutmann, 2002] and such a 'classical trajectory' approach is used in the present work.

In a classical trajectory simulation, appropriately selected initial conditions modeling experiments, are time propagated using classical equations of motion. Earlier classical trajectory studies were focused on unimolecular and bimolecular reaction dynamics, intermolecular collisional energy transfer, and intra-molecular energy flow dynamics. Later the studies were extended to larger systems including gas-surface collisions and heterogeneous reactions. Advantages and limitations of using a classical dynamics approach for studying chemical reactions are well known[Henriksen and Hansen, 2018; Levine, 1987; Foresman and Frish, 1996]. In classical trajectory simulations,[Bunker, 2012] an ensemble of initial conditions are time propagated by integrating either Hamilton's equations of motion,

$$\frac{\partial H}{\partial p_i} = \frac{dq_i}{dt}, \quad \frac{\partial H}{\partial q_i} = -\frac{dp_i}{dt} \quad (1.15)$$

where

$$H(q_i, p_i) = T(p_i) + V(q_i) \quad (1.16)$$

or Newton's equation of motion

$$m_i \frac{d^2 q_i}{dt^2} = -\frac{\partial V(q_i)}{\partial q_i} \quad (1.17)$$

Here, $T(p_i)$ is the kinetic energy term and $V(q_i)$ is the potential energy term and $H(q_i, p_i)$ is the classical Hamiltonian of the system. Classical Hamiltonian is equal to the sum of both kinetic and potential energies, here p_i and q_i are the momenta and position coordinates, respectively. Some of the well known limitations of classical trajectory simulations is that phenomena such as zero-point energy flow[Guo *et al.*, 1996] and tunneling[Thornber *et al.*, 1967] cannot be properly modeled.

Though in the past five decades, a significant growth in the area of experimental gas-phase chemical dynamics has been achieved and our understanding of the chemical processes has reached to a good extent, there is a lot of places where understanding has to be improved. Experiments such as ion-imaging, crossed-beam methods, velocity map imaging, optical pump-probe[Lin *et al.*, 2003; Lui and Hegmann, 2001; Williamson and Zewail, 1993] techniques provide useful dynamical information of chemical reactions via product translational energy distributions, internal energy distributions, scattering angle dependencies on collision energies, product branching ratios, etc. These quantities can be computed from accurately performed classical trajectory simulations[Yan *et al.*, 2008; Naz *et al.*, 2018] and this method serves as an excellent alternate to quantum dynamics studies. The conventional classical trajectory simulation involves using analytic mathematical functions to model the potential energy surface of a molecule[Hay, 1993]. The fitting of the analytic functions are based on experimental data and *ab initio* calculations. An example for analytic function is the well known London-Eyring-Polanyi-Sato (LEPS) potential for a triatomic system[Kafri and Berry, 1977; Jaffe and Anderson, 1971]. Though using analytic potential energy functions significantly reduces computational time of generating classical trajectories, they are limited by accuracy. Further, generating accurate analytic potential energy functions for polyatomic molecules is an extremely difficult task, if not impossible. Another approach to generate accurate classical trajectories is that the potentials and gradients required for the trajectory integration can be obtained directly from an electronic structure theory calculation. This method is known as *direct dynamics*[Sun and Hase, 2003; Paranjothy *et al.*, 2013]. The trajectories generated using the direct dynamics method are unadulterated and accurate to the level of selected electronic structure theory. The time independent electronic Schrödinger equation is solved at each integration step to obtain the potentials and gradients. This method, of course, is computationally expensive due to the large number of *on-the-fly* single point calculations performed during the trajectory integration. For example, if a classical trajectory is run for 2 ps with an integration step-size of 1 fs, 2000 single point electronic structure calculations are needed to generate one trajectory. To generate statistically meaningful results, large number of classical trajectories are required which increases the computational time enormously. Owing to high speed computers and parallel programming algorithms, the direct dynamics method has become a valuable simulation tool to study atomic level reaction dynamics. It is important to note here is that the simulations performed for several systems are true within the time frame and initial conditions provided, it may vary at different environment. The direct dynamics method described here is called Born-Oppenheimer direct dynamics because explicitly Born-Oppenheimer approximation is invoked and the electronic and nuclear motions are separated adiabatically. There is another approach for performing direct dynamics called Car-Parrinello (CP) method[Car and Parrinello, 1985]. In the CP approach, the electronic and nuclear motions are treated together. This method explicitly includes the propagation of electronic wavefunction using fictitious electronic degrees of freedom with arbitrary masses within the framework of density functional theory whereas in Born-Oppenheimer direct dynamics approach, nuclear motions and electronic wavefunctions are treated separately.

In the present thesis work, ground state dynamics simulations were performed by using Born-Oppenheimer direct dynamics approach to study unimolecular reaction dynamics of select systems. In ground state (Born-Oppenheimer) dynamics nuclear motion is studied only over the PES for which nuclear and electronic motion are separable (on adiabatic surface). But for the systems where several coupled electronic states are present Born-Oppenheimer approximation does not work. Thus, one cannot treat the nuclear and electronic motions separately due to the chance of electronic transitions between different electronic states. For such systems non adiabatic molecular dynamics method[Ben-Nun and Martinez, 1998] is used where the nuclear motion studied over several PESs.

In the next Chapter, a brief description of methods and techniques used to study the

gas-phase unimolecular reaction mechanisms are given. In Chapter 3, unimolecular dissociation dynamics of 3-oxetanone molecule is presented. This molecule is important in synthetic chemistry and its dissociation chemistry was investigated using electronic structure theory, Born-Oppenheimer direct dynamics simulations and Rice-Ramsperger-Kassel-Marcus (RRKM) theory rate constant calculations. The results were compared with experiments and a new, previously unknown, reaction pathway was identified.

In Chapter 4, the unimolecular decomposition of various Halons (Halomethanes) viz., CF_2Cl_2 , CF_2Br_2 , CHBr_3 , and CH_2BrCl were presented. The dissociation of these molecules are important in atmospheric chemistry due to their role in stratospheric ozone depletion [Bennett and Wiesner, 1992; Bennett *et al.*, 1993]. These molecules can dissociate via radical and molecular pathways and it is important to understand the branching ratio of these pathways. Their dissociation chemistry was studied using direct dynamics method and new reaction mechanisms were identified. The simulations showed that, for the dissociation of halons, *roaming* [Suits, 2008] is an important reaction pathway and iso-halons (isomers involving halogen-halogen bond) play a crucial role in the reaction dynamics.

In Chapter 5, a dynamics perspective on the effect of different substituents on the Curtius rearrangement reaction is presented. The Curtius rearrangement product, isocyanates, is a significant intermediate and works as a starting material for several organic synthetic reactions [Chen and Shen, 2008; Balewski *et al.*, 1985; Paquette and Horton, 1968]. In the Curtius reaction, elimination of N_2 from carbonyl azides $\text{R}(\text{CO})\text{N}_3$ occurs to form isocyanates RNCO . Two competing mechanisms viz., step-wise and concerted are known for this reaction. It is generally accepted that the concerted mechanism is obeyed under thermal reaction conditions and both mechanisms are preferred under photochemical conditions. In the present work, the effect of substituents viz., $\text{R}=\text{F}$ and CH_3 were investigated under thermal conditions. These substituents are similar in size but have differing electronic effects in the local environment. Direct dynamics simulations show that the mechanism was dependent on the nature of the substituent under similar reaction conditions. Finally, a summary is provided in Chapter 6.

...