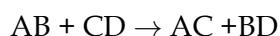


Introduction

Understanding the motion of constituent atoms in molecules and mechanisms of chemical reactions lies at the heart of chemistry which addresses the most fundamental questions: Why chemical reactions occur? How the constituent atoms in reacting molecule(s) evolve in time as the chemical transformation occurs? Answers to these questions is essential since they have a profound influence on all aspects of life. *Chemical kinetics* [Steinfeld *et al.*, 1989] describes the rates of transformation from reactants to products. It is based on chemical intuition and experimental observations and calculates the rates of reactions using appropriate rate laws. At the macroscopic level, the celebrated Transition State Theory (TST), Rice-Ramsperger-Kassel-Marcus (RRKM) theory and Collision Theory were used to find the rates of reactions. Although these statistical rate theories consider the molecular nature of the reactants and the energy distribution in molecules to some extent, they do not provide a detailed atomistic picture and the dynamics of the reacting molecular system. In the last few decades, the subject of *Molecular Reaction Dynamics* [Steinfeld *et al.*, 1989; Levine, 2009] have gained a lot of attention. Reaction dynamics is the study of motion of atoms at the microscopic level which describes the elementary aspects of a chemical reaction. It is also concerned with the individual quantum states of the reactant(s) and the product(s). Study of reaction dynamics deepens our understanding of molecular systems at the atomic scale and shows how the macroscopic thermal rate constant $k(T)$, obtained from chemical kinetics, arises as average of the state-to-state rate constants which are related to the individual quantum states of reactants and products. Statistical rate theories give rate constants by averaging out the details. To extract microscopic properties such as energy dependent cross sections, rate constants, and atomic level mechanisms, it is necessary to design a theoretical model (such as a molecular dynamics simulation) or an experiment (such as molecular beam and laser based experiments) [Herschbach, 1987; Lee, 1987; Polanyi, 1987] and with the help of these sophisticated techniques, state-to-state properties can be estimated and can be related to conventional experimental observations. Atomic level classical trajectory simulation methods are state-of-the-art modeling techniques to unfold the atomistic and microscopic insights of chemical reactions [Henriksen and Hansen, 2018; Levine *et al.*, 1988; Foresman and Frish, 1996]. The technique complements the experiments and provides microscopic information about how the system evolves in time and hints clues to what external parameters can be used to control the reactions. Such detailed studies on microscopic properties also enables one to derive rate laws and determine rate constants from time evolved molecular properties. A great advantage of doing computer simulations is that experimental conditions which are difficult to setup in a laboratory can be successfully modeled using appropriately designed simulations. In the present thesis, a few important reactions relevant to atmospheric and prebiotic chemistry were investigated in detail using electronic structure theory calculations and classical dynamics simulations. In the literature, there are several examples where an accurately performed dynamics simulation has provided insights about mechanisms and other properties which otherwise cannot be established from conventional experiments. For example, identification of *roaming* mechanism in formaldehyde [Townsend *et al.*, 2004] and *roundabout* mechanism in S_N2 reactions [Mikosch *et al.*, 2008] were established via dynamics simulations.

1.1 REACTION DYNAMICS IN GAS-PHASE

In a chemical reaction, reactants are converted into products by breaking and making of bonds.



The reaction path may involve formation of intermediate species, transition states, and various elementary steps. An elementary step in a reaction is one which cannot be broken down further into smaller steps. These elementary steps form the reaction mechanism of a reaction and determining the mechanism is important to completely understand a chemical reaction. Such a detailed understanding is required for not only to provide correct interpretation of the experimental spectra but also to achieve a chemist's long standing goal of mode selective chemistry [Gruebele, 2003; Gruebele and Wolynes, 2004]. A unimolecular reaction involves a single reactant and it may be excited by optical or thermal processes or by collision with an inert atom or a molecule. A bimolecular reaction involves collision between two molecules. Typically, bimolecular reactions in the gas phase are of the ion-molecule type as neutral-neutral reactions involve large barriers in the gas phase [Henriksen and Hansen, 2018]. A great advantage of studying gas-phase dynamics is that it provides a solvent-free environment and enables the study of elementary reactions without much interference from the surroundings. Energetics of several reactions are much lower such that the solvation energies are larger and studying the condensed phase dynamics may not provide the required details. There are several experimental techniques available today to perform gas phase dynamics studies. For example, pump-probe techniques, mass analyzed threshold ionization (MATI), resonance-enhanced multi-photon ionization (REMPI), pulsed field ionization, ion-beam mass spectrometry and kinetic energy photo-electron spectroscopy are some of the widely used techniques today [Hudgens *et al.*, 1983; Rose *et al.*, 1987; Zhu and Johnson, 1991; Yang *et al.*, 1995; Weibel *et al.*, 2003; Ashfold *et al.*, 2006]. In the present work, state-of-the-art electronic structure theory calculations and dynamics simulation methods were used to study gas phase atomic level reaction dynamics of select reactions.

1.2 ELECTRONIC STRUCTURE CALCULATIONS

Electronic structure theory calculations are used to study detailed energy profiles and time independent molecular properties of a system such as equilibrium geometry, energy, normal mode vibrational frequencies of stable and transient species, dipole moment, etc. Typically, time independent Schrödinger equation is solved in an electronic structure calculation [Helgaker *et al.*, 2014]. There are four main approaches used in computational chemistry to describe the electronic structure of molecules: *ab initio* methods, semi-empirical methods, density-functional methods, and molecular mechanics methods. *Ab initio* and semi-empirical methods are wave function based approaches whereas density functional theory is based on electron densities. *Ab initio* methods [Ben-Nun and Martínez, 2002] use exact Hamiltonian to solve the Schrödinger's equation under various approximations. The most popular *ab initio* methods are Hartree-Fock (HF) [Roothaan, 1951; Pople and Beveridge, 1970], Møller-Plesset (MP) perturbation [Cremer, 2011] and couple-cluster (CC) [Bartlett, 1981] theories. *Ab initio* methods use adequate approximations in the selected method to solve the Schrödinger equation using an appropriate basis set. Semi-empirical methods [Thiel, 2014; Segal, 2012; Purcell and Singer, 1967] are quantum-mechanical but use a much simpler Hamiltonian than the exact Hamiltonian and adjust the parameters in the Hamiltonian to achieve the results of *ab initio* calculations or experimental data. However, due to the empirical nature of these methods, they are limited by accuracy but can be applied to larger systems such as proteins. Molecular mechanics [Engler *et al.*, 1973] is not a quantum mechanical method. It is based on the laws of classical physics and considers molecules as composed of balls

and springs. This is typically used for studying large systems under conditions where the quantum effects are minimal. Another approach is the density functional theory (DFT) [Becke, 2014] which uses electron density (ρ) instead of molecular wave function (ψ) to calculate ground state molecular properties of a system. Among the above mentioned methods, DFT is one of the most popular and versatile methods available to do electronic structure calculations in today's computational chemistry world. Computational time for DFT calculations is comparable to Hartree-Fock method and the accuracy can be close to higher level ab initio methods.

Molecular Schrödinger equation

The time-independent Schrödinger equation is the fundamental equation of quantum mechanics [Rota, 1977]. The wavefunctions and energies can be obtained by solving the Schrödinger equation

$$\hat{H}\psi(\vec{r}, \vec{R}) = E\psi(\vec{r}, \vec{R}) \quad (1.1)$$

where \hat{H} is the Hamiltonian operator and it is the sum of kinetic energy and potential energy of the system ($\hat{H} = \hat{T} + \hat{V}$), ψ is the many-particle wave function, \vec{r} and \vec{R} are the electronic and nuclear coordinates, respectively, and E is the total energy of the system. The non-relativistic Hamiltonian for a system is given below.

$$\hat{H} = -\frac{\hbar}{2m} \sum_i \nabla_i^2 - \sum_A \frac{\hbar^2}{2M_A} \nabla_A^2 - \sum_{A,i} \frac{Z_A e^2}{4\pi\epsilon_0 r_{Ai}} + \sum_{A>B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{AB}} + \sum_{i>j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} \quad (1.2)$$

$$\hat{H} = \hat{T}_e(r) + \hat{T}_N(R) + \hat{V}_{eN}(r, R) + \hat{V}_{NN}(R) + \hat{V}_{ee}(r) \quad (1.3)$$

In the above equations, subscripts (i, j) and (A, B) are used for electrons and nuclei, respectively. ∇_i^2 and ∇_A^2 denote the Laplacian operators. M_A and Z_A are the mass and atomic number of nucleus A , respectively, and m is the electron mass. \hat{T}_N and \hat{T}_e are the kinetic energy operators of nuclei and electrons, respectively. \hat{V}_{eN} , \hat{V}_{NN} , and \hat{V}_{ee} are the electron-nuclei attraction, nucleus-nucleus repulsions, and electron-electron repulsions, respectively. Beyond Hydrogenic species, Schrödinger's equation becomes non-separable and several approximations [Langhoff *et al.*, 1966; Born and Oppenheimer, 1927; Millam *et al.*, 1999] are made to find solutions. The first approximation is the Born-Oppenheimer approximation.

Born-Oppenheimer Approximation

Born-Oppenheimer approximation (BOA) [Born and Oppenheimer, 1927] proposed by Max Born and Robert Oppenheimer separates the electronic and nuclear motion to simplify the many-body problem. As nuclei are heavier than electrons they move on different time scales. During nuclear motion, electrons will rearrange themselves instantaneously and the electronic quantum state remains unchanged and because of this reason, BOA is also known as *adiabatic approximation*. By making BOA, kinetic energy operator of nuclei is dropped from the Hamiltonian operator and the total wavefunction becomes

$$\psi(\vec{r}, \vec{R}) = \psi_{el}(\vec{r}; \vec{R}) \psi_N(\vec{R}) \quad (1.4)$$

Here, $\psi_{el}(\vec{r}; \vec{R})$ is the electronic wavefunction which depends only parametrically on the nuclear coordinates and $\psi_N(\vec{R})$ is the wavefunction for nuclear motion. The Hamiltonian operator can be written as

$$\hat{H} = \hat{H}_{el} + \hat{V}_{NN} + \hat{T}_N \quad (1.5)$$

where the first term (\hat{H}_{el}) denotes the purely electronic Hamiltonian, the second term (\hat{V}_{NN}) the internuclear repulsion, and \hat{T}_N is kinetic energy operator of nuclei. For a given nuclear configuration, the electronic Schrödinger equation is given by:

$$\hat{H}_{el} \psi_{el}(\vec{r}; \vec{R}) = E_{el} \psi_{el}(\vec{r}; \vec{R}) \quad (1.6)$$

Here, \hat{H}_{el} is the purely electronic Hamiltonian containing \hat{T}_{el} , \hat{V}_{ee} and \hat{V}_{eN} only. The energy E_{el} is the electronic energy. Adding the internuclear repulsion (\hat{V}_{NN}) to electronic energy gives the potential energy $U(\vec{R})$.

$$U(\vec{R}) = E_{el} + \hat{V}_{NN} \quad (1.7)$$

Thus, BOA provides a way of separating the nuclear and electronic motion. For fixed nuclear configurations, electronic Schrödinger equation can be solved and the potential energy $U(\vec{R})$ can be obtained as a function of nuclear coordinates. Plot of $U(\vec{R})$ as a function of nuclear coordinates leads to the concept of *potential energy surface* (PES) which is central to understand chemical reactivity. Determining the properties of PES is the primary goal of doing electronic structure calculations.

Density Functional Theory

DFT is primarily used for performing electronic structure calculations in the present work and the principles of DFT are briefly mentioned here. DFT differs from wavefunction based methods in that the electron density is the central quantity. For a system containing n electrons, the wavefunction depends on all the $3n$ coordinates of the electrons but the electron density depends only on three Cartesian coordinates of the system. This aspect enormously simplifies the DFT methods in applicability. Detailed discussions on DFT can be found in a number of textbooks [R. G. and Yang, 1989; Dreizler and Gross, 2012] and excellent review articles [Parr, 1983; Ziegler, 1991; Geerlings *et al.*, 2003; Jones and Gunnarsson, 1989] available in the literature. DFT is based on two theorems. In 1964, Kohn and Hohenberg [Hohenberg and Kohn, 1964; Kohn and Sham, 1965] proposed two theorems in which they proved that the energy obtained from the Schrödinger equation is a functional of the electron density. These are applicable to non-degenerate ground state only. The first theorem states that *the ground-state electron density (ρ_0) of a molecule with a non-degenerate ground state uniquely determines the ground-state energy, wave function, and other properties.*

$$E_0 = E_0[\rho_0] \quad (1.8)$$

By this theorem, knowing the electron probability density, all the ground state properties of a molecule can be calculated. The second theorem states that *true ground state electron density*

(ρ_0) minimizes the functional that gives the ground state energy of the system (E_0). It was proved that the energy of the ground state can be obtained using a variational approach and the density which minimizes the total energy is the exact ground state electron density. The exact density functional is not known and the success of a DFT approach depends on how the functional is approximated. There is a list of functionals with different levels of approximations are available in the literature and excellent review articles on modern DFT methods has been published [Becke, 1993; Lee *et al.*, 1988; Perdew *et al.*, 1996; Vosko *et al.*, 1980]. The most appropriate DFT functional for the dynamics calculations is selected by comparison of the reaction energetics calculated using different DFT functionals with benchmark wavefunction based calculations such as a CCSD(T) method. The level of electronic structure theory will be chosen by optimizing the required accuracy and the computational cost. DFT methods provide an affordable way to achieve sufficient accuracy in limited computational time. In the present work, on-the-fly direct classical trajectory simulations were performed which require a large number of single point electronic structure calculations. For this purpose, DFT is an excellent choice and has been used extensively in this thesis.

1.3 CLASSICAL TRAJECTORY SIMULATIONS

Potential energy surface (PES) is time independent and the features of PES such as energies and minimum energy paths provide some information about a reaction. Only the dynamics i.e., time dependent nuclear motion provide a complete picture of the reaction. Due to the quantum mechanical nature of atoms and molecules, time dependent Schrödinger equation must be solved for dynamics. Modeling the nuclear motion using time dependent Schrödinger equation is called *quantum dynamics* and is employed for smaller systems only due to computational complexities [Kosloff, 1994; Marx and Hutter, 2000]. Quantum dynamics simulation is accurate and the results are comparable to experiments [Blatt, 1967] but it is computationally unfavorable even for smaller molecules to perform full quantum dynamics calculations [Sinanoglu, 1964]. On the other hand, classical mechanics provides an affordable way to model dynamics of chemical reactions and this method is called *classical dynamics* [Sutmann, 2002]. Dynamics calculations, irrespective of quantum or classical, provide a complete picture of a reaction event as reactants proceed to form products. The method of choice depends on the nature of the system under investigation and the properties of interest [Lubich, 2008]. Classical dynamics simulations have been used to study chemical reactions for the past several decades and the advantages and limitations of using classical mechanics are known [Baer and Hase, 1996; Lourderaj *et al.*, 2008b; Paranjothy *et al.*, 2013]. Some phenomena such as zero point energy (ZPE) [Guo *et al.*, 1996], tunneling [Thorner *et al.*, 1967] and resonances [Pratihari *et al.*, 2017] are purely quantum effects and cannot be modeled using classical equations. Unphysical flow of ZPE into the reaction coordinate is less probable in smaller molecules and faster processes. However, ZPE effects are non-negligible for large molecules and on longer timescales. This unphysical flow of ZPE may alter the estimated reaction rate constants and the deviations from true rate constants may be large [Schatz, 1983]. When quantum effects are unimportant, classical simulations have ability to predict dynamics correctly comparable to experimental measurements. Initial conditions for the classical trajectories may be selected to mimic quantum states of reactant molecules but the time evolution of the trajectories are controlled by the classical equations of motion.

Classical trajectory simulations have been used to investigate various problems including reaction mechanisms, intramolecular vibrational energy flow, intermolecular collisional energy transfer, conformational changes, molecular motions under external parameters, gas-surface collisions, transitions between adiabatic surfaces (surface hopping), unimolecular and bimolecular reactions [Baer and Hase, 1996; Lourderaj *et al.*, 2008b; Paranjothy *et al.*, 2013; Bunker, 1962; Blais and Bunker, 1962; Karplus *et al.*, 1965; Bosio and Hase, 1997; Lu and Hase, 1988; Preston and Tully, 1971]. In a classical trajectory simulation, the time evolution of the atoms of a system is simulated

by solving classical equations of motion [Bunker, 2012] and an ensemble of classical trajectories are required. The classical equations of motion are either Newton's equations

$$-\frac{\delta V(q_i)}{\delta q_i} = m_i \frac{d^2 q_i}{dt^2} \quad (1.9)$$

or Hamilton equations

$$\frac{\delta q_i}{\delta t} = \frac{H(q_i, p_i)}{\delta p_i} \quad (1.10)$$

$$\frac{\delta p_i}{\delta t} = -\frac{H(q_i, p_i)}{\delta q_i} \quad (1.11)$$

where the Hamiltonian $[H(q_i, p_i)]$ is the total energy of a system i.e. the sum of the kinetic $[T(p_i)]$ and potential $[V(q_i)]$ energy. The index i represents atom indices and q_i are coordinates and p_i are momenta.

$$H(q_i, p_i) = T(p_i) + V(q_i) \quad (1.12)$$

The potential energy function $V(q_i)$ of the system is required for solving either Newton's or Hamilton's equations of motion. The traditional way to compute potentials $V(q_i)$ and its gradients $\delta V(q_i)/\delta q_i$ required to perform classical dynamics simulation is constructing analytic potential energy functions using model potentials such as Lennard-Jones potentials, London-Eyring-Polanyi-Sato (LEPS) function [Steinfeld *et al.*, 1989] and other analytical functions. These analytical functions are generated by fitting experimental data and/or quantum chemistry calculations. Using these analytical potential energy functions, large molecular systems can be modeled because they are computationally not expensive. However, they are limited by accuracy due to the parametric nature of the potential functions. One of the known problems with this approach is that higher order mode-mode couplings are neglected.

Another approach to do classical trajectory simulations is *direct dynamics* which is used from the early 1990s. In this method, classical trajectories are integrated *on-the-fly* and the required potential energies $V(q_i)$ and its derivatives $\delta V(q_i)/\delta q_i$ with respect to the atom's coordinates (also the second derivatives known as Hessian) are directly computed from a quantum mechanical electronic structure theory and avoids the need for analytic potential energy functions. With the advancement in computer speeds and well written algorithms, direct dynamics simulation is suitable to study the atomistic dynamics of chemical reactions. In direct dynamics, there is no need of analytic potential energy functions for the numerical integration of classical equations of motion and at each integration step, time-independent Schrödinger equation is solved. Single point energy calculations for fixed nuclear coordinates are performed and updated at each time step [Thompson, 1998] which makes computational time higher for trajectory integrations. For numerical integration of the trajectories, Hamilton's Eq. (1.10) are preferred as being first-order ordinary differential equations, they minimize the computational time. Direct dynamics provides accurate results within the limits of the electronic structure theory as it uses exact Hamiltonian.

Direct dynamics is computationally very expensive and applicable to medium sized molecules. Using analytic potentials, thousands of trajectories can be generated but in direct dynamics, number of trajectories that can be generated is limited. For a successful direct dynamics simulation, an appropriate electronic structure theory is needed balancing computational cost and accuracy. The first direct dynamics study using the CNDO semi-empirical method was performed by Wang and Karplus to study the $\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_4$ reaction [Wang and Karplus, 1973]. Several years later, the first *ab initio* direct dynamics using HF/STO-3G theory was reported by Leforestier for the study of $\text{H}^- + \text{CH}_4 \rightarrow \text{CH}_4 + \text{H}^-$ $\text{S}_{\text{N}}2$ reaction [Leforestier, 1978].

Two broad approaches are available in the literature for performing direct dynamics simulations. The first is Born-Oppenheimer (BO) direct dynamics [Sun and Hase, 2003; Wang and Karplus, 1973] in which the Born-Oppenheimer approximation is used to separate the electronic and nuclear coordinates. The other approach is Car-Parinello (CP) direct dynamics [Marx and Hutter, 2000; Car and Parrinello, 1985] in which the electronic and nuclear coordinates are propagated simultaneously. The two approaches have their own advantages and limitations. In the CP approach, within the DFT framework, the wavefunction is propagated by introducing fictitious electronic mass parameter μ . It was assumed earlier that CP approach is more efficient as it does not require the optimization of the wave function at each integration step. Later, it was realized that the reoptimization of CP wavefunction is required at each integration step to avoid the coupling between nuclear and electronic degrees of freedom which increases the computational time. In order to obtain accurate results in the CP approach, one needs to choose a small value of μ , which decreases the computational efficiency significantly. On increasing μ , the computational cost is decreased but this reduces accuracy. Computationally, both the approaches have comparable cost, but the BO method assures correct classical direct dynamics results. In the present work, BO method is used to simulate classical trajectories to study the dynamics of interesting reactions.

1.4 ORGANIZATION OF THESIS

Direct dynamics simulations play an important role in modeling chemical reactions and used to explore the atomistic dynamics and energy transfers. The advancements in this field in the past few decades are noteworthy. In the present thesis, direct dynamics simulations were used to study unimolecular decompositions for (bio)organic reactions and mass spectrometry fragmentation dynamics.

Chapter 2 provides description of the fundamental principles and techniques of electronic structure calculations and direct dynamics simulations that have been used in the present study.

In Chapter 3, the decomposition pathways of formamide (NH_2CHO) in the electronic ground state were investigated using electronic structure calculations and direct chemical dynamics simulations at three different energies using B3LYP/aug-cc-pVDZ theory. This was inspired by previous work done by Nguyen et al. [Nguyen *et al.*, 2011] to explore the unimolecular dissociation of formamide in the gas phase. This molecule is the simplest molecule containing an amide functional group and serves as a model to study protein chemistry.

In Chapter 4, the investigation of gas phase dissociation chemistry of formyl halides HXCO ($X = \text{F}, \text{Cl}, \text{Br}, \text{and I}$) were undertaken using electronic structure theory, classical chemical dynamics simulations, and Rice-Ramsperger-Kassel-Marcus (RRKM) rate constant calculations. This work was motivated by the important role of formyl halides in atmospheric and combustion chemistry. Dissociation products of formyl halides are known to play an important role in the ozone depletion.

In Chapter 5, gas phase dissociation of glycolaldehyde anion are reported. The study

was performed to model a recently reported collision induced dissociation (CID) experiment on the same molecule to investigate the retro formose reaction. Trajectories were launched with two different deprotonated forms of glycolaldehyde anion for a range of collision energies. The simulations were performed under CID conditions. Reverse formose reaction was observed primarily from the high energy isomer.

Chapter 6 summarizes the research work carried out in the thesis and provides possible future extensions of the work.

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