

1.1 CHEMICAL REACTION DYNAMICS

Why do chemical reactions occur, how to predict the behavior of a chemical system, and how to control a reaction are the primary motivations why study of *chemical reaction dynamics* is pursued. A chemical reaction may involve several elementary steps before leading to the formation of the final product(s). To understand a reaction completely, every elementary step must be completely characterized. Reaction dynamics is concerned with the atomic level changes that occur as a function of time in the molecule(s) during a chemical transformation. Detailed understanding of the elementary steps associated with a reaction may give clues to how to control the reaction using external parameters. Investigating the time-dependent motion of constituent atoms as reactant(s) form products is the central theme of chemical reaction dynamics[Crim, 2008]. In chemical kinetics[Laidler, 2008], one calculates the rate of reactions which is averaged over that of elementary reactions and this rate constant gives macroscopic view of the chemical changes. Celebrated reaction rate theories such as transition state theory (TST) and Rice-Ramsperger-Kassel-Marcus (RRKM) theory allow us to find the rates of reactions. These theories are statistical in nature and ignore the inherent dynamics associated with the reactions. Chemical kinetics is about bulk reaction rates at thermal equilibrium[Levine, 2009] and this viewpoint does not provide a full description of the chemical process. At the microscopic level, state-to-state kinetics associated with individual quantum states are considered with well defined rotational, vibrational, and translational energies associated with reactants and products[Levine, 2009]. Such detailed investigations are needed to achieve the long standing aspiration of a chemist - *mode selective chemistry*[Zewail, 1994]. Goals of the dynamics studies[Levine, 2009] are concerned with detailed description of the reagent approach and the collision process, exchange of energy among the reacting species, and the breaking and forming of bonds resulting in the final products via different mechanisms. Experiments like crossed molecular beam techniques probe a chemical reaction at the microscopic level and provide view of reactions with unprecedented detail[Herschbach, 1987; Lee, 1987; Polanyi, 1987]. Theoretically, quantum mechanics and classical mechanics provide models to study chemical reactions[Levine, 1987]. Creating appropriate reaction conditions experimentally is a highly challenging task. On the other hand, setting the conditions computationally is relatively less difficult with proper models and simulation conditions for a reaction. This is one of the advantages of chemical dynamics simulations. Performing complete quantum mechanical dynamics simulations is computationally challenging[Hase *et al.*, 2003] and for several decades, classical trajectory simulations have been used to study reaction mechanisms, energy flow pathways, product branching ratio, etc.[Carrascosa *et al.*, 2017; Guo, 2012] Parallel computational techniques and sophisticated algorithms have made it possible today to generate classical trajectories on an *ab initio* potential surface - a method known as *direct Dynamics*[Sun and Hase, 2003] which has been extensively used in the present work to study important reactions.

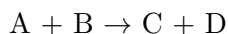
1.2 REACTIONS IN GAS PHASE

Gas phase studies play an important role in combustion chemistry, astrophysics, and atmospheric chemistry[Stolow, 2003]. Electronic structure calculations are performed in the gas

phase to construct the potential energy surface (PES) associated with different electronic states of molecules. PES can be used to study reaction mechanisms but dynamics studies are needed[Xie and Hase, 2016; Lahankar *et al.*, 2006; Stavros and Verlet, 2016] for a complete understanding of the atomic level mechanisms and for the successful interpretation of the experimental spectra. Presence of solvent in a reaction has thermodynamic and steric effects and the presence of a solvent may change the outcome of a reaction in comparison to the reactions in the gas phase[Otto *et al.*, 2012]. In a gas phase reaction, reacting molecules and the motion of constituent atoms are not hindered due to the absence of solvent medium and hence the required energy for the reaction is the activation energy of the reaction. Gas phase reaction dynamics studies are also performed to understand how the energy flows within a molecule i.e., establishing the timescales and mechanisms of intramolecular vibrational energy redistribution (IVR) occurring in a molecule[Nesbitt and Field, 1996]. In a unimolecular gas phase reaction,



energy flows intramolecularly and the activated molecule may dissociate or undergo isomerization reaction. Activation of the molecule may occur via chemical activation, photoactivation or via collision with an inert species[Baer and Hase, 1996]. In a gas phase unimolecular reaction, the internal energy must be greater than the activation energy of the dissociation or isomerization reaction. In a bimolecular gas phase reaction,



energy flows inter-molecular i.e., one molecule transfers energy to the other molecule during the collision process. Bimolecular collision reactions in the gas phase are primarily ion-molecule type reactions. Such reactions require minimum or no activation energy and they are mostly exothermic reactions[Gronert, 2001; Carrascosa *et al.*, 2017]. On the other hand, gas phase reactions involving neutral reagents have large activation energies and lower rate constants[Smith, 2015].

Owing to the technological advancements, there are several experimental and theoretical developments that have happened and most advanced methods are available to study gas phase reaction dynamics. Experimental techniques such as kinetic energy photo-electron mass spectrometry, ion-beam mass spectrometry, pulsed-field ionization technique, pump-probe techniques, resonance enhanced multi photon ionization (REMPI), mass analyzed threshold ionization (MATI) are some methods available today to investigate gas phase reaction dynamics[Weibel *et al.*, 2003; Ashfold *et al.*, 2006; Zhu and Johnson, 1991; Yang *et al.*, 1995; Hudgens *et al.*, 1983; Rose *et al.*, 1987]. *Ab initio* molecular dynamics simulations of energized clusters like $\text{CO}_2 \cdot (\text{H}_2\text{O})_6^-$ are used to elucidate the nature of the network deformations that mediate intracuster electron capture[Breen *et al.*, 2012]. Understanding of the structure and dynamics of the lowest lying singlet excited state of the diplatinum complex $[\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4]_4$ photocatalyst by performing potential energy surface calculations and BornOppenheimer molecular dynamics simulations in the gas phase and in water[Levi *et al.*, 2018]. Direct molecular dynamics simulations have been carried out to understand the relaxation dynamics of photoexcited charge-transfer-to-solvent (CTTS) states for the $\text{I}^-(\text{H}_2\text{O})_6$ cluster and the subsequent excess electron stabilization dynamics by solvent molecules[Takayanagi and Takahashi, 2006]. The dynamics of the $\text{O}(^3\text{P}) + \text{HCl}$ reaction at hyperthermal collision energies were investigated using the quasiclassical trajectory method[Camden and Schatz, 2006]. The stationary point geometries and frequencies on the lowest singlet potential energy surface for the CH_3OH system are calculated using the complete-active-space self-consistent-field method. The energetics are refined using a restricted internally contracted multireference configuration interaction (MRCI) method[Yu and Muckerman, 2004]. Theoretically, quantum mechanics and classical mechanics provide models to study chemical reactions[Levine, 1987]. Theoretically, *ab initio* and density functional electronic

structure methods have been well developed and they can be used to study the potential energy surface, various reaction paths, global and local minima, transition states, and associated normal mode frequencies. Predictions from PES calculations can be compared with experimental data to establish structures and energetics and also can be used to propose reaction mechanisms. However, to get a complete atomic level understanding of the reaction, the time-independent PES predictions are not sufficient and the dynamics of the system must be investigated.

1.3 ELECTRONIC STRUCTURE CALCULATIONS

A molecule is composed of atoms and the forces binding the atoms are responsible for chemical reactions. A chemical reaction is the process of making and breaking of bonds and a rearrangement of electrons. To find out the electronic energy and structure, electronic Schrödinger equation, under the Born-Oppenheimer approximation [Levine *et al.*, 2009], must be solved. Properties such as equilibrium geometries, dipole moments, normal mode vibrational frequencies, etc., can also be determined from electronic structure calculations. These calculations can be performed using *ab initio* methods, semi-empirical methods, density functional methods or molecular mechanics methods. In *ab initio* or first principles methods, exact molecular Hamiltonian is used [Ben-Nun and Martínez, 2002] with no parameterization. Most commonly used *ab initio* methods are Hartree-Fock (HF), [Roothaan, 1951; Pople and Beveridge, 1970], Møller-Plesset (MP) perturbation theory, [Cremer, 2011] and couple-cluster (CC) [Bartlett, 1981] methods. By making several approximations, the electronic Schrödinger equation is solved by using an appropriate basis set. Semi-empirical methods use simpler, parameterized Hamiltonians rather than the exact one [Thiel, 2014; Purcell and Singer, 1967; Segal, 2012] and Hückel’s molecular orbital theory is an example of a semi-empirical method. Molecular mechanics methods [Engler *et al.*, 1973] are not quantum mechanical. They are classical and view molecules as composed of balls and springs and energy and other properties are determined by solving the classical equations. These methods are computationally feasible for large molecules such as polymers and proteins. On the other hand, *ab initio* methods are computationally expensive and are applicable to small to medium sized molecules. A very good alternate to first principles method is density functional theory (DFT) [Mardirossian and Head-Gordon, 2017; Yu *et al.*, 2016; Burke, 2012]. DFT is formulated in terms of electronic density ρ rather than the wavefunction. ρ is a function of 3 spatial coordinates rather than the wavefunction which depends on $3n$ coordinates, where n is the number of electrons. Computational time for the DFT methods is comparable to that of HF method but the accuracy is comparable to higher level post-HF methods. DFT has become a versatile tool in electronic structure calculations and is very popular and used extensively.

1.3.1 Born-Oppenheimer Approximation

Time-independent properties of a system such as structure and energetics can be determined by solving the time-independent Schrödinger equation

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

where $\psi(r, R)$ is the wavefunction of the system; r and R are the electronic and nuclear coordinates, respectively. The Hamiltonian operator of a molecule is given by

$$\hat{H} = -\frac{\hbar^2}{2} \sum_{\alpha} \frac{1}{m_{\alpha}} \nabla_{\alpha}^2 - \frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_{\alpha} \sum_{\beta > \alpha} \frac{Z_{\alpha} Z_{\beta} e^2}{4\pi\epsilon_0 r_{\alpha\beta}} - \sum_{\alpha} \sum_i \frac{Z_{\alpha} e^2}{4\pi\epsilon_0 r_{i\alpha}} + \sum_j \sum_{i > j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} \quad (1.2)$$

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

where α and β are used to designate nuclei and i and j correspond to electrons. $\hat{T}_N(R)$, $\hat{T}_e(r)$, $\hat{V}_{NN}(R)$, $\hat{V}_{eN}(r, R)$, and $\hat{V}_{ee}(r)$ correspond to nuclear kinetic energy, electronic kinetic energy,

internuclear repulsions, electron-nuclear attractions, and interelectronic repulsions. One of the first approximations made to solve the molecular Schrödinger equation is the Born-Oppenheimer approximation [Levine *et al.*, 2009] which states that nuclei are much heavier than electrons and hence they can be assumed to be static in the time scale of the motion of electrons. By invoking such an adiabatic approximation, the nuclear kinetic energy term can be dropped from the molecular Hamiltonian. Further, the internuclear repulsion term becomes a parameter because of the fixed nuclear coordinates. Hence, the Hamiltonian for the electronic motion becomes

$$\hat{H}_{el} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_\alpha \sum_i \frac{Z_\alpha e^2}{4\pi\epsilon_0 r_{i\alpha}} + \sum_j \sum_{i>j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} \quad (1.4)$$

The corresponding electronic Schrödinger equation is

$$\hat{H}_{el}\psi_{el} = E_{el}\psi_{el} \quad (1.5)$$

Electronic wavefunction ψ_{el} depends parametrically on the nuclear coordinates i.e., $\psi_{el}(r; R)$. Adding the internuclear repulsion energy to the purely electronic energy E_{el} gives the potential energy $U(R)$

$$U(R) = E_{el} + \hat{V}_{NN}(R) \quad (1.6)$$

To construct the PES of a system, the electronic Schrödinger equation is solved at fixed nuclear coordinates i.e., $U(R)$ is determined for a range of fixed values of R .

1.3.2 Density Functional Theory

DFT is formulated in terms of the electron density ρ rather than the multi-dimensional wavefunction $\psi(r, R)$. It is not only extremely difficult to obtain correct $\psi(r, R)$ for a multi-electron system but also it is difficult to obtain direct physical significance from $\psi(r, R)$. DFT is based on two theorems proposed by Hohenberg and Kohn [Hohenberg and Kohn, 1964; Kohn and Sham, 1965]. The first theorem states that the electronic density uniquely determines the energy and other properties of a non-degenerate ground state of a system.

$$E_0 = E_0[\rho_0] \quad (1.7)$$

where E_0 and ρ_0 are the non-degenerate ground state energy and electronic density, respectively. The second Hohenberg-Kohn theorem states that the true ground state density determines the true ground state energy and any other density leads to energy greater than the true energy. This variational principle may be stated as

$$E_0[\rho_0] \leq E_v[\rho_v] \quad (1.8)$$

where ρ_v is electronic charge density not equal to the true density ρ_0 . Kohn and Sham used the theorems and formulated the practical usage of DFT [Kohn and Sham, 1965]. A variety of commercial functionals have been developed based on several further approximations [Mahler *et al.*, 2017]. Computational time requirements for DFT methods is comparable to self-consistent field method but the accuracy can be tuned to that of advanced *ab initio* methods. DFT is used as an electronic structure theory tool in several branches of chemistry ranging from synthetic organic chemistry, coordination chemistry, bio-inorganic chemistry to materials science [Curtarolo *et al.*, 2013]. For instance, significant developments in the field of catalysis design [Grimme *et al.*, 2012] and development of Li battery materials [Mo *et al.*, 2011] are recent examples of successful applications of DFT. Due to the computational flexibility associated with the DFT methods, they are also the most popular choice for *ab initio* molecular dynamics simulations [Fattebert and Gygi, 2002; Marsalek and Markland, 2016]. In the work presented in the thesis, DFT methods were used to perform electronic structure calculations and direct chemical dynamics simulations.

1.4 DIRECT DYNAMICS

In order to understand the complete reaction dynamics of a system, the time-dependent nuclear Schrödinger equation must be solved. Such a *quantum dynamics* approach is highly accurate[Kosloff, 1994; Marx and Hutter, 2000] and the predictions from such simulations are directly comparable to experiments[Blatt, 1967]. For example, Masgrau et al.[Masgrau *et al.*, 2006] have established the dominant role of proton tunneling in enzyme catalyzed reactions using quantum dynamics calculations. One of the most popular quantum dynamics methods known in the literature is the multi-configuration time-dependent Hartree (MCTDH) method[Beck *et al.*, 2000; Schröder *et al.*, 2011; Schröder and Meyer, 2014]. Quantum dynamics methods are computationally very expensive and they are usually limited to few atom systems only. As an alternative, classical dynamics methods[Porter, 1974] have been used to study chemical processes for the past several decades. In such a "classical trajectory" approach, classical equations of motion are time propagated[Bunker, 1962; Blais and Bunker, 1962]. An ensemble of initial conditions, chosen to mimic an experiment or to model the predictions of a statistical rate theory such as TST[Laidler, 2008] or RRKM theory[Steinfeld *et al.*, 1999] are time propagated using Newton's equation of motion

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

or Hamilton's equations of motion

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

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

Here, q_i and p_i are the generalized coordinates and momenta, respectively, and $H(q_i, p_i)$ is the Hamiltonian of the system. Classical trajectory methods have been used to study unimolecular and bimolecular reactions[Pfeifle *et al.*, 2018; Czak and Bowman, 2011; Chen *et al.*, 2009; Godara *et al.*, 2017], intramolecular energy flow dynamics in polyatomic molecules[Semparithi and Keshavamurthy, 2006], reactions at heterogeneous interfaces[Khoo *et al.*, 2020], etc. One of the well known limitations of classical trajectory methods is that purely quantum effects such as zero-point energy and tunneling cannot be modeled using purely classical techniques[Paranjothy *et al.*, 2013b]. Despite these limitations, classical trajectory methods are widely used to study reaction dynamics and several new features have been discovered using these methods. For example, the *roaming* atom pathway in formaldehyde decomposition[Lahankar *et al.*, 2006] and the *roundabout* mechanism associated with S_N2 reactions[Mikosch *et al.*, 2008] are discovered using classical trajectory methods.

Accuracy of classical trajectory simulations depends primarily on the quality of potentials $V(q_i)$ and gradients $\partial V(q_i)/\partial q_i$ required for the time propagation of classical equations of motion. Conventionally, analytic potential energy functions such as harmonic oscillator and Morse oscillator models and non-bonded interaction potential functions such as Lennard-Jones potentials are used[Leach and Leach, 2001]. Such an approach has been used for the study of several chemical processes on large scale systems such as proteins, etc. However, this method is limited by accuracy due to the analytic nature of the potential energy functions. Also, development of an analytic potential energy surface for a polyatomic molecule is a challenging, if not impossible, task. Due to the developments in computing power in the past couple of decades, another approach has been developed to perform the classical trajectory simulations. In this approach, trajectory integrations are performed using potentials and gradients computed directly from an electronic structure theory in an 'on-the-fly' manner. Such a technique is called *direct dynamics*[Pratihari *et al.*, 2017] and it avoids the tedious process of fitting and storing analytic PES of a system. On the other hand, direct dynamics is computationally expensive due to the requirement of large number of electronic structure calculations to generate trajectories. Using the direct dynamics

approach, earliest calculations were performed by Karplus et al., [Wang and Karplus, 1973] and Leforestier [Leforestier, 1978]. Two approaches have been developed for performing direct dynamics simulations. The first one is the Car-Parrinello molecular dynamics (CPMD) method [Car and Parrinello, 1985; Rana and Chandra, 2013] in which explicit electronic structure calculations are avoided by introducing a fictitious classical motion for the electronic wavefunction. The other approach is the Born-Oppenheimer molecular dynamics (BOMD) [Paranjothy *et al.*, 2013b] in which single-point electronic structure calculations are performed at each integration step. Computational time requirements for both approaches are almost same. In the present thesis work, BOMD approach was used to study reaction dynamics. There are several studies reported in the literature which utilized the BOMD approach to establish reaction mechanisms, unimolecular and intramolecular dynamics, etc. [Yang *et al.*, 2011; Pfeifle *et al.*, 2018; Godara *et al.*, 2020; Gahlaut and Paranjothy, 2020; Sharma *et al.*, 2015].

1.5 PRESENT WORK AND ORGANIZATION OF THESIS

Electronic structure calculations and direct dynamics simulations were used to study unimolecular and bimolecular dynamics of select reactions in the present work. In Chapter 2, theoretical methods and algorithms used in the thesis are described. Bimolecular collision dynamics of $\text{H}_3^+ + \text{CO} \rightarrow \text{HCO}^+/\text{HOC}^+ + \text{H}_2$ reaction is presented in Chapter 3. This proton transfer reaction is a cornerstone reaction happening in the interstellar media. Ionic reaction products, formyl (HCO^+) and isoformyl (HOC^+) cation, are known to initiate several reaction networks leading to the formation of complex organic molecules in space. This reaction was studied using chemical dynamics simulations at the density functional PBE0/aug-cc-pVDZ level of theory to model a recently reported velocity map imaging studies of the same reaction [Carrascosa *et al.*, 2016]. Internal energy and product scattering angle distributions were computed from simulations and compared with experiments. Simulation results were in qualitative agreement with experiments and interesting dynamical features observed. In Chapter 4, unimolecular dissociation dynamics of γ -ketohydroperoxide (KHP) is presented. KHP is an important reagent in synthetic chemistry and its decomposition plays an important role in tropospheric chemistry. Experimental studies of KHP are limited due to its enhanced reactivity. Automated reaction discovery methods have been used to study the unimolecular reaction pathways of KHP [Suleimanov and Green, 2015; Grambow *et al.*, 2018]. In the present study, direct dynamics simulations at the B3LYP/6-31+G* level of theory was used to investigate the dissociation pathways of KHP. Out of the numerous pathways reported previously, three dissociation channels were identified to be dominant. An important finding in the present work is that the Korcek decomposition of KHP, which was proposed earlier to be preferred dissociation path of KHP, was not observed in the high temperature simulations reported here. Chapter 5 presents the thermal dissociation chemistry of thiophene in the gas phase. Thiophene and its derivatives are present in shale oil and their removal from the fuel is a challenging process [Vasiliou *et al.*, 2017]. The thermal decomposition of parent thiophene molecule was investigated to establish atomic level dissociation mechanisms. Chapter 6 summarizes the thesis work and future perspectives are discussed.