CHAPTER I

INTRODUCTION

1.1 Background

Understanding of the excited-state proton/hydrogen-atom transfer (ESPT/HT) reaction is a fundamental piece of knowledge in chemistry and biochemistry [1-2]. The ESPT/HT reaction, a subclass of proton transfer (PT) or hydrogen-atom transfer (HT) reaction, has been intensively studied due to its practical uses in many applications, particularly fluorescent probes [3-7], laser dyes [8-9], photostabilizers [10], and light-emitting devices [11-12]. Most of the PT and HT take place in molecules having bifunctional groups (proton donor and acceptor) [13-17] in which these molecules can form intramolecular hydrogen bonds between two functional groups.

The excited-state intramolecular proton/hydrogen atom transfer (ESIntraPT/HT) reactions can spontaneously occur in some molecules such as *o*-hydroxy Schiff base molecules [18-21], for example, 2-(iminomethyl)phenol and its derivatives. The appropriate position of proton donor and acceptor is the most important point of PT/HT reactions. However, the ESIntraPT/HT reaction cannot spontaneously occur in some molecules because the proton donor is positioned too far from the acceptor [15]. Thus, the solvents will be needed to trigger the excited-state intermolecular proton/hydrogen atom transfer (ESInterPT/HT) reactions. In presence of solvent assistance, formation of strong hydrogen bonds along the hydrogen-bonded network can reduce the reaction barrier and induce intermolecular multiple-PT/HT reaction to take place after the photoexcitation. Simple model compounds of certain molecules with appropriate protic solvents show this kind of ESInterPT/HT processes, for instance, 1*H*-pyrrolo[3,2-*h*]quinoline (PQ) [15,17,22-24], 7-hydroxquinoline (7HQ) [25-27], and 7-azaindole (7AI) [13,16,28-30].

1.2 Excited-state proton/hydrogen atom transfer (ESPT/HT) reactions

The ESPT/HT process is a fundamental reaction which plays an important role in chemistry and biochemistry [1-2]. The ESPT/HT reaction or sometime called a phototautomerization (a reversible transformation process between two forms of molecules by adsorption of light) is studied in many applications, for example, a model for hydrogen bonding in DNA bases and fluorescence emitting mechanism of green fluorescence markers in fluorescent probe [7]. Typically, this type of the PT/HT process occurs along the hydrogen-bonded network.

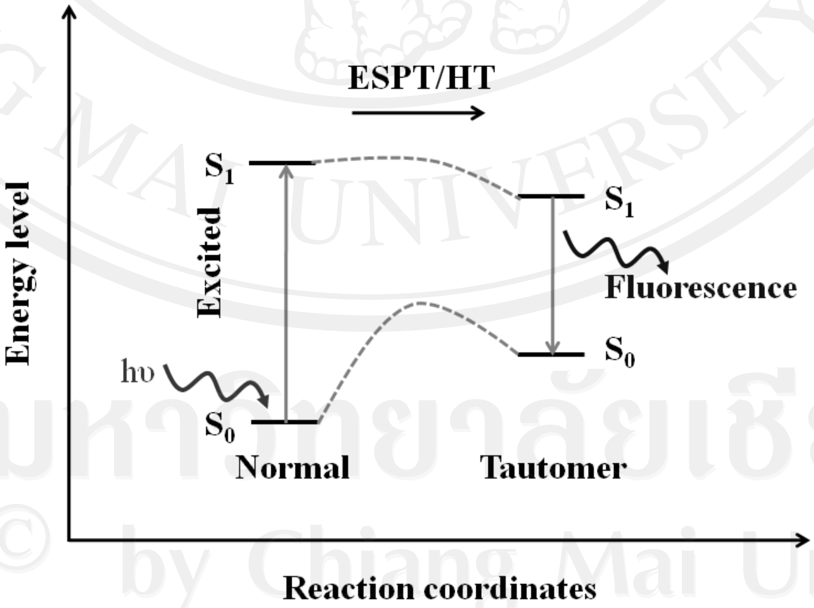


Figure 1.1 Scheme of the excited-state proton/hydrogen atom transfer (ESPT/HT) reaction

From Figure 1.1, normal form is quite stable in the ground state. It cannot transform into tautomer spontaneously because of high reaction barrier. In photoexcitation process, however, the tautomer easily occurs because it has energy lower than its normal form in existence of low barrier or barrierless [13-17]. The reactions taking place can be divided into two types: intermolecular or intramolecular PT/HT. In addition, the intermolecular PT/HT reaction occurs by proton/hydrogen atom transfer between the same molecules (7-azaindole dimer) or assisted molecules (solvent-assisted molecules) and the intramolecular PT/HT reaction occurs by proton/hydrogen atom migration within its molecule without any help from other molecules.

1.2.1 Excited-state intermolecular proton/hydrogen atom transfer (ESInterPT/HT) reactions

Previous reports [29,31] of the molecules and hydrogen-bonded clusters provided insight into the intermolecular multiple-PT/HT process along the hydrogen-bonded network. A simple model compound of certain molecules with specific solvents show this kind of property such as 7-azaindole (7AI) and 1*H*-pyrrolo[3,2-*h*]quinoline (PQ). The 7AI molecule, a part of DNA bases in a model compound, is an important bicyclic aza-aromatic molecule that can form hydrogen bonds with solvent molecules forming cluster. The hydrogen bonds between donating proton from five-membered ring of the pyrrole and accepting proton on six-membered ring of the pyridine are formed. Tautomerization of the 7AI with solvent clusters accompanying the ESInterPT/HT reaction has been both experimentally and theoretically studied [32-33]. The 7AI with solvent molecules such as water, ammonia, and alcohol (ethanol and methanol) are served as a prototype of the ESInterPT/HT processes which have been intensively studied by many groups [13,33-34].

Gordon and coworkers [13,29] studied on the $7AI(H_2O)_{n=1-2}$ clusters where subscript n indicates number of water molecules in the cluster that showed an asynchronous HT time less than 50 fs after photoexcitation process using quantum mechanics/molecular mechanics (QM/MM) molecular dynamics. Their results showed equilibrium geometries and relative CASSCF energies of normal and tautomers in the ground (S_0) and excited state (S_1) that a tautomer is higher energetic than a normal form in the ground state. But in photoexcitation process, the tautomer easily occurs because it has energy less than its normal form. However, some models used in this simulation did not cover a dynamics property such as reaction probability or the energy distribution of the products from the simulations.

Sakota *et al.* [31,35-36] also experimentally investigated the $7AI(MeOH)_{n=1-3}$ clusters which were small enough to be studied in supersonic jet with laser spectroscopy. Their experimental studies based on dispersed fluorescence and resonance-enhanced multiphoton ionization spectra were observed and found that $7AI(MeOH)_2$ cluster could undergo an excited-state triple-proton/hydrogen atom transfer (ESTPT/HT) process. The reaction reveals the importance of dynamics on methanol-assisted PT and shows a remarkable feature of the ESTPT/HT reaction in the $7AI(MeOH)_2$ cluster. This remarkable feature is the nature of the reaction mechanism changes from vibrational-mode specific fashion with increasing the internal energy. Thus, the 7AI with methanol cluster is an interesting model for studying mechanism pathways in quantum dynamics simulations of the ESInterPT/HT reaction.

1.2.2 Excited-state intramolecular proton/hydrogen atom transfer (ESIntraPT/HT) reactions

Aromatic Schiff bases [21,37-38] are among the most studied compounds in the photochemistry because of their photochromic properties and structural varieties. For example, the best known and most widely studied photochromic Schiff base is salicylideneaniline (SA) [39]. This molecule is the earliest example of a system concerning about intramolecular PT/HT reaction. In Schiff base molecule, the photochromic investigation likely arises from the ESIntraPT/HT reaction. For more information of the PT/HT reaction, the development of ultrafast spectroscopic techniques has allowed not only a direct observation of PT/HT dynamics but also in several molecular systems. A Schiff base molecule such as 2-(iminomethyl)phenol is the most important compound in photochemistry. 2-(iminomethyl)phenol, the hydrogen atom of hydroxy group in the aromatic ring forming hydrogen bond to the nitrogen atom in the imine group which gives enol-keto tautomerization, is investigated for a model system of the intramolecular PT/HT process in biological systems [18]. 2-(iminomethyl)phenol and its derivatives are of interest due to the existence of O–H···N and O···H–N types of hydrogen bonds. In addition, the ESIntraPT/HT reactions taking place in 2-(iminomethyl)phenol and its derivatives are computationally affordable for theoretical study because of its simple reaction and small molecule for the molecular dynamics simulation on the excited state [19-20]. Furthermore, substituent effects showed that steric modification or increased acidity on an aromatic ring resulted in shortening and strengthening of the intramolecular hydrogen bond. Moreover, the steric effect of a bulky substituent could bring about shortening of O–H···N hydrogen bridge [18,20].

1.3 Molecular property

1.3.1 Fluorescence

There are two types of emissions of photons on excited state: fluorescence and phosphorescence. These types are very important in light-emitting devices. Their emission of photons produces different color of light. In this work, only fluorescence emission will be studied.

When a molecule absorbs photons, the energy goes to its electrons. They will be excited from ground state into excited state with no changing of electron spin. Then, they will emit energy called fluorescence and fall down into the lower state which is our interest in this research. If the spin changes from singlet to triple state, the relaxation time will take longer than fluorescence called phosphorescence [40].

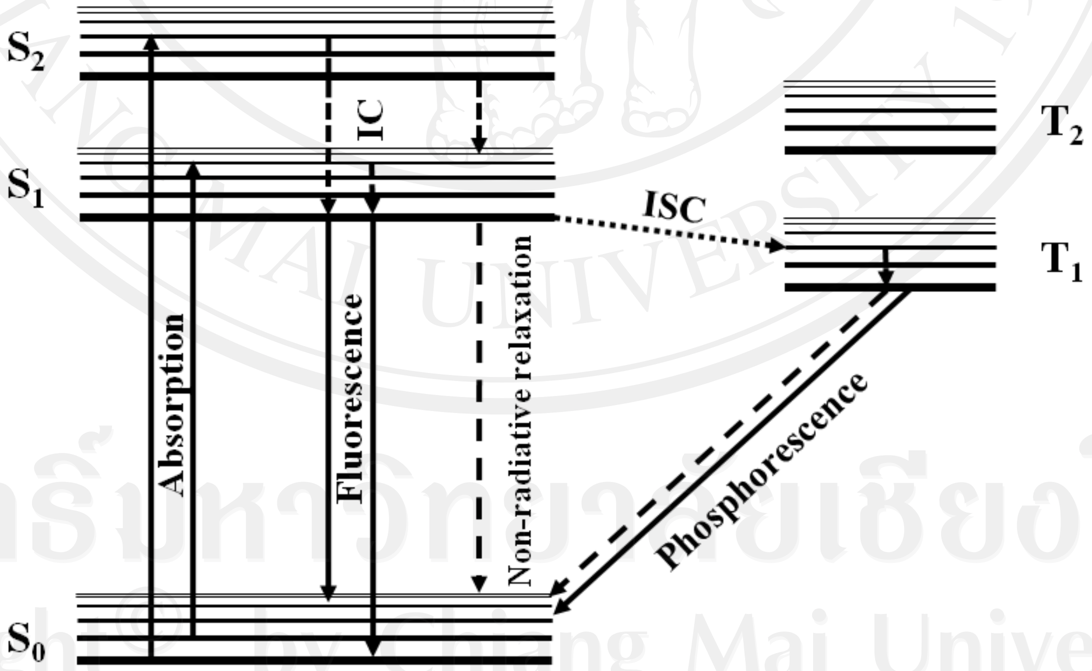


Figure 1.2 Jablonski diagram

From Figure 1.2, Jablonski diagram shows the energy levels of each state indicated its spin multiplicity. The lowest lines represent the ground state, S_0, of the atom or molecule. The higher lines (S_1 and S_2) represent excited singlet states. Whereas, the other lines (T_1 and T_2) represent excited triplet states. In a diatomic or polyatomic molecule, one or several series of vibrational and rotational states (quantized) are superimposed on each electronic state. The absorption lines (or bands) are represented by arrows directed upwards and the emission lines or bands by arrows directed downwards. The energy of the quanta of emission or absorption is proportional to the lengths of the arrows. An atom or molecule can absorb only energy into S_1 and S_2, then, it can release energy represented by downward arrows, leading from S_2 to a lower energy state S_1. It should be noted that energy absorption is very fast (10^{-15} fs). A radiationless process from S_2 to S_1 way in which a transition can occur by energy loss to surrounding molecules called internal conversion (IC) and vibrational relaxation of the excited molecule within 10^{-14}-10^{-11} s. Emission of photons from S_1 to S_0 state called fluorescence (10^{-9}-10^{-7} s) is found at higher wavelengths (low energy) than the absorption spectrum because it losses some energy in excited state due to the relaxation of electron and it does not change the spin multiplicity. The gap or the energy between the maximum of the first absorption band and the maximum of fluorescence is known as Stoke rule. In addition, there is some energy emission that is not fluorescence called non-radiative relaxation. However, a radiationless process involving a transition between two electronic states with different spin multiplicity, or intersystem crossing (ISC), possibly occurs. The radiative decay from an excited triplet state (T_1) back to ground state (S_0) is known as phosphorescence (10^{-3}-10^{2} s) [41].

1.3.2 Franck-Condon principle

Classically, the Franck–Condon principle is the approximation that an electronic transition is most likely to occur without changes in the positions of the nuclei in the molecular entity and its environment. According to the Born-Oppenheimer approximation, the electrons are much lighter than those of nuclei so the motion of electrons is very rapid compared to the motion of nuclei [42].

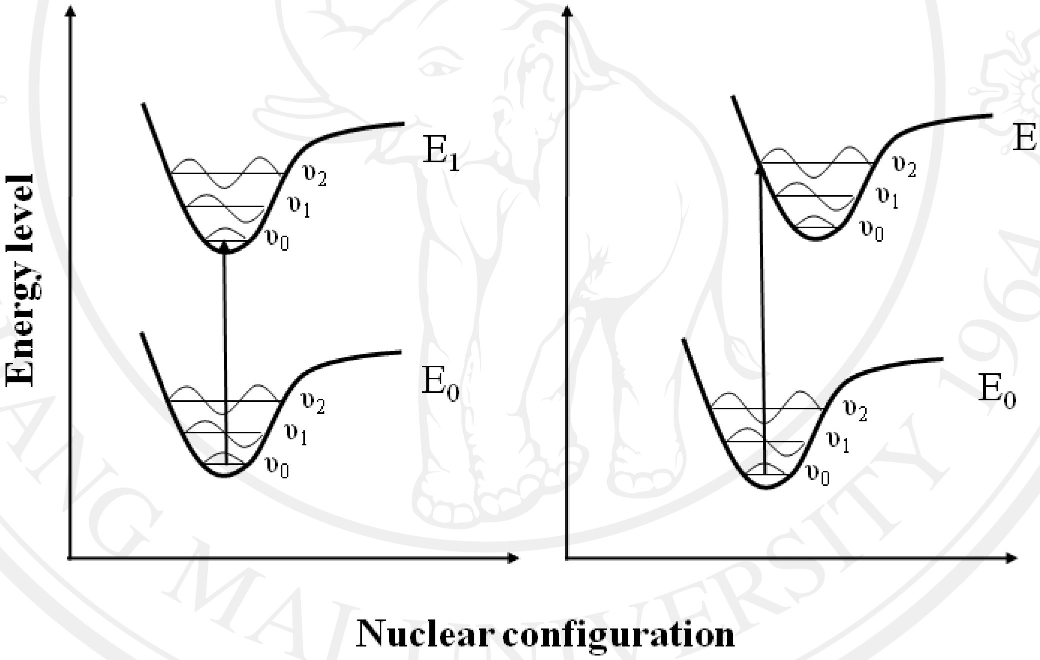


Figure 1.3 Potential energy diagrams of vertical excitation [41]

The resulting state is called a Franck–Condon state and the transition involved a vertical transition (Figure 1.3). Since electronic transitions are very fast compared with nuclear motions, vibrational levels are favored when they correspond to a minimal change in the nuclear coordinates. The electronic transition can be 0-1, 0-2, or arbitrary state depending on the vibrational energy.

1.4 Computational chemistry

1.4.1 Schrödinger equation

Quantum mechanics (QM) is a correct mathematical description of the behavior of electrons especially in chemistry. Theoretically, QM can be used to predict any property of an individual atom or molecule exactly. Practically, however, the QM equations have been solved exactly for one electron systems only.

There are many descriptions in QM concepts of the motions of particles; one describes the system using a wavefunction, □. The wavefunction for an interested system governed by a Hamiltonian, $\hat{H}$ is determined by the Schrödinger equation since it is the basis for most computational chemistry methods [43].

$$\hat{H}\Psi = E\Psi \tag{1.1}$$

The wavefunction is found by solving the Schrödinger equation for the system. The Schrödinger equation (1.1) represents a description of a molecular system in terms of a wavefunction (□), Hamiltonian operator ($\hat{H}$), and the total energy (E).

The Schrödinger equation can be solved exactly only for atoms or molecule containing one electron. For this reason, the numerical methods that allow us to approximate wavefunction have been employed to describe in theoretical approximations such as *ab initio* methods, simiempirical methods, density functional theory, and etc.

1.4.2 Born-Oppenheimer approximation

The complete nonrelativistic Hamiltonian of a molecule as a sum of kinetic and potential energy terms [44]:

$$\hat{H} = -\frac{\hbar^2}{2m}\sum_i \nabla_i{}^2 - \sum_A \frac{\hbar^2}{2M_A}\nabla_A{}^2 - \sum_{A,i}\frac{Z_A e^2}{4\pi\varepsilon_0 r_{iA}} + \sum_{A>B}\frac{Z_A Z_B e^2}{4\pi\varepsilon_0 R_{AB}} + \sum_{i>j}\frac{e^2}{4\pi\varepsilon_0 r_{ij}} \quad (1.2)$$

where Z_A and Z_B are the nuclear charges, M_A is the mass of nucleus A, m is the mass of the electron, R_{AB} is the distance between nuclei A and B, r_{ij} is the distance between electrons i and j, r_{iA} is the distance between election i and nuclei A, ε_0 is the permittivity of free space, and $\hbar$ is the Plank constant. The compact formula could be represented as

$$\hat{H} = T_N(R) + T_e(r) + V_{eN}(r,R) + V_{NN}(R) + V_{ee}(r) \quad (1.3)$$

where $T_N(R)$ = kinetic energy of the nuclei

$T_e(r)$ = kinetic energy of the electrons

$V_{eN}(r,R)$ = electron-nuclei attractive Coulomb potential

$V_{NN}(R)$ = nuclear-nuclear repulsive Coulomb potential and

$V_{ee}(r)$ = electron-electron repulsive Coulomb potential

Born-Oppenheimer approximation is the assumption that the electronic motion and the nuclear motion in molecules can be separated. The electronic motion should be the same as if the nuclei are fixed. It notes that the nuclear motion is so much slower than that of electron or the nuclei are very much more massive than the electrons. Thus, leaving $V_{NN}(R)$ out of the electronic Schrödinger equation leads to a similar equation,

$$\hat{H}_{electron} = T_e(r) + V_{eN}(r,R) + V_{ee}(r) \tag{1.4}$$

such that

$$\hat{H}_{electron}\Psi(r;R) = E_{electron}\Psi_{electron}(r;R) \tag{1.5}$$

For most chemical applications, it is a good approximation to assume that the Schrödinger equation can be parametrically separated into a product of electronic and nuclear parts. This leads to an exact solution can be obtained by using an expansion of the form

$$\Psi(r,R) = \psi(r;R)\chi(R) \tag{1.6}$$

where ψ is a wavefunction associated with solving the electron part of the Schrödinger equation for fixed nuclear coordinates, and χ is a wavefunction associated with nuclear motion.

1.4.3 *Ab initio* method

1.4.3.1 Hartree-Fock approximation

The *ab initio* term originated from Latin means “from the beginning”. The mathematical approximations are derived from only theoretical principle in order to find an approximate solution with no in conclusion of experimental data [43,45].

The well-known type of *ab initio* calculation is Hartree-Fock (HF) approximation. The HF calculation starts with an initial guess for the orbital coefficients, usually using a semiempirical method. This function is used to calculate energy and a new set of orbital coefficients, which can then be used to obtain a new set, and so on. This procedure continues iteratively until the energy and orbital coefficient remain constant from one iteration to the next or convergence called a self-consistent field (SCF) [43,45].

There are several ways in which we can proceed with the derivation of the HF equations. The traditional one is to look for an eigenvalue equation for the HF orbitals:

$$\hat{h}^F \psi_i = \varepsilon_i \psi_i \tag{1.7}$$

where the HF operator $\hat{h}^F$ depends only on the coordinates of any one of the electrons, but allows for the averaging over their interactions.

There are *n* doubly occupied molecular orbitals, and the number of electrons is 2*n* because we have allocated α and β spin electron. Generally, Hartree model, the many-electron wavefunction was written as a straightforward product of one-electron orbital ψ_A and ψ_B. From Fock's contribution to the field, it shows as a Slater determinant which is satisfied by the Pauli principle. For an *N*-electron system, the spin-orbital, $\chi_1(x_1)$, where x_1 denotes the position and spin of the singular electron the Slater determinant is defined as

$$\Psi(x_1, x_2, ..., x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(x_1) & \chi_2(x_1) & \dots & \chi_N(x_1) \\ \chi_1(x_2) & \chi_2(x_2) & \dots & \chi_N(x_2) \\ \dots & \dots & \dots & \dots \\ \chi_1(x_1) & \chi_2(x_N) & \dots & \chi_N(x_N) \end{vmatrix} \tag{1.8}$$

The linear combination of Hartree products for the two-particle case can clearly be seen as identical with the Slater determinant for $N = 2$. A single Slater determinant is used as an approximation to the electronic wavefunction in Hartree-Fock theory. In more accurate theories, for example, configuration interaction (CI) and multireference configuration self-consistency field (MCSCF), a linear combination of Slater determinants is needed [45].

1.4.3.2 Coupled cluster

Coupled cluster (CC) calculations are similar to configuration interaction (CI) calculations in that the wavefunction is a linear combination of many determinants. The CI calculation wavefunction is a multiple-determinant wavefunciton conducted by starting with the HF wavefunciton and making new determinant by promoting electron from the occupied to unoccupied orbitals. This CI calculation can be very accurate, but the cost of computing is very high (N^8 time complexity). However, the means of choosing the determinants in a coupled cluster calculation is more complex than the choice of determinants in a CI. For CC expansion, it is included perturbation. It gives variational energies as long as the excitations. The CC results are a bit more accurate than the equivalent size CI calculation results [43].

The resolution-of-the-identity (RI) with second-order approximate coupled-cluster model, RI-CC2 is a module for the calculation of excitation energies and response properties at a correlated *ab initio* level, in particular the CC2. All calculations employ RI approximation for the electron repulsion integrals needed for the correlation treatment and the description of excitation processes. All functionalities are implemented for closed-shell restricted HF and open-shell unrestricted HF reference wavefunctions. However, RI with the algebraic diagrammatic construction through second order, RI-ADC(2), is paid attention in 7-azaindole system and is used in the calculations [46-47].

In addition, the performance of the second-order methods for excitation energies is concerned in many systems. The approximation of CC2 is been used to solve the excitation energies corrected through second-order in the fluctuation potential, the Jacobian becomes

$$A^{CC2} = \left(\frac{\left\langle {}^{a}_{i} \right| ([\hat{H} + [\hat{H}, T_2]), \tau^{c}_{k}] \left| HF \right\rangle}{\left\langle {}^{ab}_{ij} \right| [\hat{H}, \tau^{c}_{k}] \left| HF \right\rangle} \middle| \frac{\left\langle {}^{a}_{i} \right| [\hat{H}, \tau^{cd}_{kl}] \left| HF \right\rangle}{\left\langle {}^{ab}_{ij} \right| [F, \tau^{cd}_{kl}] \left| HF \right\rangle} \right) \tag{1.9}$$

where F is the usual Fock operator and $\hat{H} = \exp(-T_1)H \exp(T_1)$, i.e., a Hamiltonian similarly transformed with the exponential function of the single replacement part of the cluster operator $T=T_1+T_2$. Here and in the following indices i, j, k, … are used for orbitals which are occupied in the reference determinant $\left| HF \right\rangle$ and indices a, b, c, … are used for virtual orbitals. τ^{c}_{k} and τ^{cd}_{kl} denote, respectively, single and double replacement operators.

The secular used in ADC(2) is the symmetric or, in the some case, the Hermitian part of that for the iterative variant of the doubles correlation to CI singles, CIS(D_∞) in equation 1.10.

$$A^{CIS(D_\infty)} = \left(\frac{\left\langle {}^{a}_{i} \right| ([H + [H, T_2^{(1)}]), \tau^{c}_{k}] \left| HF \right\rangle}{\left\langle {}^{ab}_{ij} \right| [H, \tau^{c}_{k}] \left| HF \right\rangle} \middle| \frac{\left\langle {}^{a}_{i} \right| [H, \tau^{cd}_{kl}] \left| HF \right\rangle}{\left\langle {}^{ab}_{ij} \right| [F, \tau^{cd}_{kl}] \left| HF \right\rangle} \right) \tag{1.10}$$

so that

$$A^{ADC(2)} = \frac{1}{2}(A^{CIS(D_\infty)} + (A^{CIS(D_\infty)})^*) \tag{1.11}$$

The above relations between CC2, CIS(D_∞), and ADC(2) provide a simple recipe to implement the latter two methods in an existing CC2 program: for CIS(D_∞), the only modification required is that the converged CC2 ground-state amplitudes are replaced by those form first-order perturbation theory. For ADC(2), in addition, the contributions of $[\hat{H}, T_2^{(1)}]$ to the singles-singles block have to be symmetrized.

1.4.4 Density functional theory

Density functional theory (DFT) is one of the most widely used methods based on electron density. This method has become popular in recent years because it is less computational requirement than other methods with similar accuracy such as second order Møller–Plesset perturbation (MP2). The general theoretical framework of DFT was originated by the Hohenberg and Kohn theorem. However, in practical applications, Kohn and Sham developed the theory formulated a method similar in structure of HF method [41].

1.4.4.1 Honnenberg-Kohn theorems

Instead of solving the problem using single electron wavefunction, this method uses one function which represents the entire electron density of the molecule represented as $\rho(r)$. Electronic energy of electron density is represented as

$$E[\rho] = E_T[\rho] + E_V[\rho] + E_U[\rho] \tag{1.12}$$

where $E_T[\rho]$ is kinetic energy, $E_V[\rho]$ is potential energy, and $E_U[\rho]$ is external perturbation and Coulombic repulsive force between pairs of electrons.

1.4.4.2 Kohn-Sham equations

A density functional is used to obtain the energy for the electron density. The advantage of using electron density is that integrals for Coulombic repulsion need to be done only over the electron density which is a three-dimensional function (N^3).

The exact ground-state electron density is given by

$$\rho(r) = \sum_{i=1}^{n} \left|\psi_i(r)\right|^2 \tag{1.13}$$

We can write in simple form as

$$E[\rho] = E_T[\rho] + E_V[\rho] + E_{xc}[\rho] \tag{1.14}$$

where the sum is overall energy of the occupied Kohn-Sham orbitals, the first term in the equation 1.14 represent the kinetic energy of the electrons; the second term is potential energy including electron-nucleus attraction and Coulomb repulsive interaction between electrons; and last term is the exchange-correlation energy of the system. E_{xc} term, which is often split the exchange-correlation term into a sum of one part for exchange effects and one part for correlation effects, must be the functional of the electron density.

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho] \tag{1.15}$$

Therefore, exchange-correlation potential, V_{xc} can be presented as the functional derivatives of the exchange-correlation energy:

$$V_{xc}[\rho] = \frac{\delta E_{xc}[\rho]}{\delta \rho} \tag{1.16}$$

1.4.4.3 Hybrid three parameters of Beck and Lee-Yang-Parr correlation functional (B3LYP)

The purpose of including this complex mathematical function (functional) is to suggest the hybrid nature of the mathematics. It notes that various approximations– local density approximation (LDA), Hartree-Fock (HF), Becke-1988 (B88), Lee-Yang-Parr 1988 (LYP88), and Vosko,Wilks, Nusair 1980 (VWN80) – are part of this hybrid functional:

$$E^{XC}_{hybrid}[\rho] = C_{HF} E^{XC}_{HF} + C_{DFT} E^{XC}_{DFT} \tag{1.17}$$

From three parameters of Beck and Lee-Yang-Parr correlation functional (B3LYP), it has been reported that it could give a good results on the organic molecules with various experiments. The hybrid models B3LYP method is expressed in equation:

$$E^{XC}_{B3LYP}[\rho] = E^{X}_{LDA} + c_0 (E^{X}_{HF} - E^{X}_{LDA}) + c_X \Delta E^{C}_{B88} + E^{C}_{VWN3} + c(CE^{C}_{LYP} - E^{C}_{VWN3} \tag{1.18}$$

where HF exchange, E^{X}_{HF}. Local density approximation, E^{X}_{LDA}. Gradient-corrected exchange, E^{C}_{B88}. Lee, Yang, and Parr correlation, E^{C}_{LYP}.

1.4.4.4 Time-dependent density functional theory (TD-DFT)

Time-dependent density functional theory (TDDFT) [48] is the generalization of stationary DFT to time-dependent potentials and electron densities, $\rho(r,t)$. In the vast majority of cases, such as the calculation of photo absorption spectra for fixed nuclei, the electric field constitutes a small perturbation which can be treated using linear response theory. This has to be distinguished from directly solving the time-dependent Kohn-Sham equations in the time domain, i.e. dynamically propagating orbitals and nuclei. TDDFT is a very popular tool for electronic excitation energies and oscillator strength. It is a powerful tool in studying photochemistry because its computation cost is not expensive.

The excited-state electron density is given by Runge-Gross theorem as

$$\rho(r,t) = \sum_{i=1}^{n} \left|\psi_i(r,t)\right|^2 \tag{1.19}$$

Therefore, exchange-correlation potential, V_{xc} can be presented as the functional derivatives of the exchange-correlation energy:

$$V_{xc}[\rho] = \left.\frac{\delta A_{xc}[\rho]}{\delta\rho}\right|_{\rho=\rho(r,t)} \tag{1.20}$$

From excitation energy, the procedure starts with the construction of many-particle starts with good symmetry, $\square_i$, by taking a finite superposition of states

$$\Psi_i = \sum_{\alpha} c_{i\alpha}\Phi_{\alpha} \tag{1.21}$$

where Φ_α is Slater determinants of Kohn-Sham orbitals, and the coefficients $c_{i\alpha}$ is determined form group theory. Simply, we can express the determinants as linear combinations of the many-body wavefuntions

$$\Phi_\beta = \sum_j a_{\beta j} \Psi_j \tag{1.22}$$

By taking the expectation value of the Hamiltonian in the state Φ_β we reach here

$$\left\langle \Phi_\alpha \left| \hat{H} \right| \Phi_\beta \right\rangle = \sum_j \left| a_{\beta j} \right|^2 E_j \tag{1.23}$$

where E_j is the energy of the many-body state Ψ_j and Φ_β is built from n Kohn-Sham orbitals.

The next technique, called ensemble DFT, makes use of fractional occupation numbers. Ensemble DFT evolves around the concept of an ensemble. In the simplest case it consists of a mixture of the ground state, Ψ_1, and the first excited state, Ψ_2, described by the density matrix,

$$\hat{D} = (1-\omega)\left| \Psi_1 \right\rangle \left\langle \Psi_1 \right| + \omega \left| \Psi_2 \right\rangle \left\langle \Psi_2 \right| \tag{1.24}$$

where the weight, ω, is between 0 and 1/2 (in this last case the ensemble is called "equiensemble". We can further define the ensemble energy and density

$$E(\omega) = (1-\omega)E_1 + \omega E_2 \tag{1.25}$$

$$\rho_{\omega}(r) = (1-\omega)\rho_1(r) + \omega\rho_2(r) \tag{1.26}$$

at $\omega = 0$, the ensemble energy clearly reduces to the ground-state energy. Using the ensemble density it is possible to construct a DFT, i.e. to prove a Hohenberg-Kohn theorem and construct a Kohn-Sham scheme. To calculate the energies from ensemble DFT we can follow two paths. The first involves obtaining the ground-stat energy and the ensemble energy for some fixed ω, from which the excitation energy E_1-E_2 trivially follows

$$E_2 - E_1 = \frac{E(\omega) + E(0)}{\omega}\,. \tag{1.27}$$

The second path is obtained by taking the derivatives of equation 1.24

$$\frac{dE(\omega)}{d\omega} = E_2 - E_1\,. \tag{1.28}$$

It is then possible to prove

$$E_2 - E_1 = \varepsilon_{\omega}^{N+1} - \varepsilon_{\omega}^{N} + \left.\frac{\partial E_{xc}(\omega)}{\partial \omega}\right|_{\rho=\rho_{\omega}}\,. \tag{1.29}$$

1.4.5 Adiabatic dynamics [49]

The basic problem in dynamics simulations of molecules is to solve the time-dependent Schrödinger equation (TDSE) for the complete molecular system,

$$\left(i\hbar\frac{\partial}{\partial t}-\hat{H}\right)\Psi(r,R,t)=0 \tag{1.30}$$

where $\hat{H}$ is the Hamiltonian and □ is the wavefunction depending on t, on the nuclear coordinates, R, and on the electronic coordinates, r, of the whole system.

The nuclear motion can be described using Born-Oppenheimer expansion

$$\Psi(r,R,t)=\sum_i \psi_i(r;R)\chi_i(R,t) \tag{1.31}$$

where ψ_i is a electronic wavefunction and χ_i is a nuclear wavefunction in equation (1.30) for electronic state i.

$$F_{kj}^{m}(R)\equiv\left\langle\psi_k\middle|\nabla_m\middle|\psi_j\right\rangle_r \tag{1.32}$$

where F_k is the electronic wavefunction.

In equation 1.32, each quantity with superscript c was approximated by its value at a single nuclear configuration, R^c, which is given by the Newton's equations for each nucleus m

$$\frac{d^2R_m^c}{dt^2}-\frac{F_m^c}{M_m}=0. \tag{1.33}$$

For this reason, we should impose a series of approximations to perform the simulations. In this approximation, the TDSE is reduced to a set of first-order differential equation for the amplitudes c_k of each electronic state k:

$$i\hbar \frac{dc_k}{dt} + \sum_j (- V_k^c \delta_{kj} + i\hbar F_{kj}^c . v^c) c_j = 0, \text{ (adiabatic)} \qquad (1.34)$$

In this equation, V_k is the potential energy surface for state k, v is the nuclear velocity and F_{kj} is the nonadiabatic coupling vector between the states k and j.

1.4.5.1 Initial conditions

In order to integrate the Newton's equations for the nuclei, an ensemble of initial conditions needs to be prepared. Normally, this problem is approached by building a phase space distribution in the electronic ground state and then projecting it onto the electronic excited states. The ground state distribution can be prepared either by a ground state trajectory simulation or from a probabilistic sampling. In addition, the quantum nature of typical distributions like that given by the Wigner function, the two sets may differ substantially.

1.4.5.2 Wigner distributions

Assuming a quadratic approximation for the ground-state potential energy surface around the minimum, the $3N_{at}-6$ internal coordinates can be described in terms of normal modes Q and the nuclear wavefunction can be approximated as that of a quantum harmonic oscillator. The classical phase space distribution can be approximated by a Wigner distribution

$$P_W(Q^i, P^i) = (\pi\hbar)^{-1} \int d\eta \chi_{HO}^0 (Q^i + \eta)^* \chi_{HO}^0 (Q^i - \eta) e^{2i\eta P^i/\hbar}, \qquad (1.35)$$

where χ_{HO}^{0} is the quantum harmonic oscillator wavefunction for the ground vibrational state and P^{i} is the momentum associated with the normal coordinate Q^{i}.

$$P_W(Q^i, P^i) = (\pi\hbar)^{-1}\exp(-\mu^i\omega_{OH}^i Q^{i2}/\hbar)\exp(-P^{i2}/(\mu^i\omega_{OH}^i\hbar)), \qquad (1.36)$$

where μ^i and ω_{OH}^i are, respectively, the reduced mass, the harmonic frequency and the equilibrium, distance of normal mode *i*.

To sample coordinates and momentum, independent random values are assigned to P^{i} and Q^{i}, then, the acceptance of the pair is evaluated according to the probability given by equation 1.36. To solve the problem, the equation 1.35 can be written as

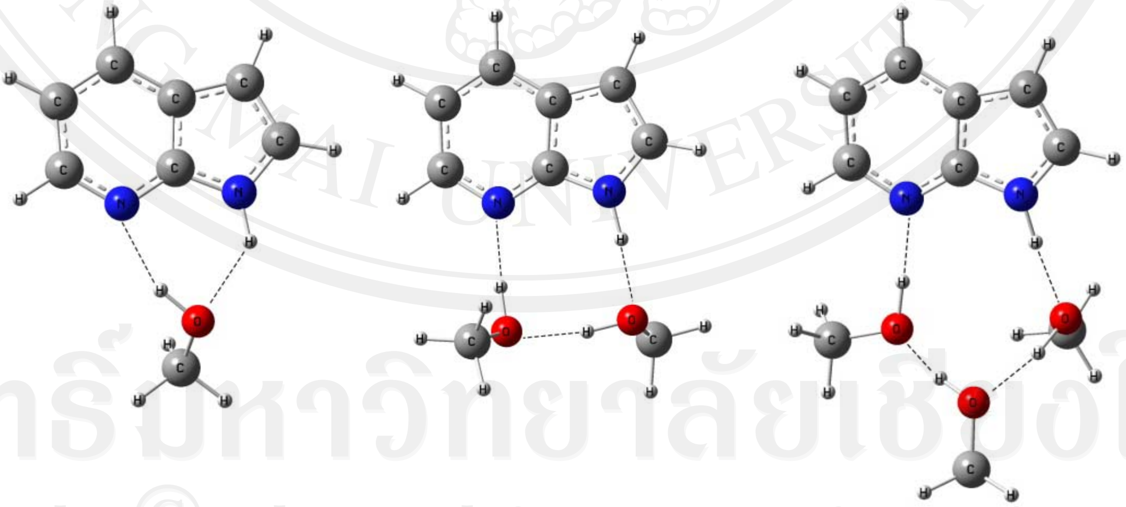
$$P_W(Q^i, P^i) = \left|\chi_{OH}^{0}(Q^i)\right|^2\left|\xi_{OH}^{0}(P^i)\right|^2, \qquad (1.37)$$

where ξ_{OH}^{i} is the harmonic oscillator wavefunction in the momentum respresentation. Even though equation 1.37 is valid for the ground vibrational level, it motivated to write an analogous quasi-Wigner distribution for the excited vibrational states

$$P_{QW}(Q^i, P^i) = \left|\chi_{OH}^{n}(Q^i)\right|^2\left|\xi_{OH}^{n}(P^i)\right|^2. \qquad (1.38)$$

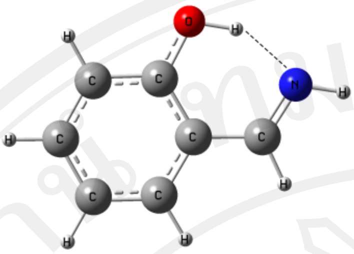
1.5 Objectives

In this work, the computational investigations of interested systems: 7AI with methanol or 7AI(MeOH)$_n$ (when n=1-3) clusters and 2-(iminomethyl)phenol derivatives as shown in Figure 1.4 will be prepared and used to perform computational details in both ground-state optimizations and excited-state dynamics simulations. Prior to dynamics simulations, ground-state optimizations in the gas phase will be used to carry out for detailed information of static calculations. In the first-excited state, S$_1$, on-the-fly dynamics simulations will be employed to obtain the ESInterPT/HT reactions for 7AI(MeOH)$_{n=1\text{-}3}$ clusters and the ESIntraPT/HT reactions for 2-(iminomethyl)phenol derivatives. In 7AI(MeOH)$_{n=1\text{-}3}$ clusters, cluster-size effects of methanol added in the complexes will be studied. Similarly in 2-(iminomethyl)phenol derivatives, substituent effects in a phenol ring will be also examined.

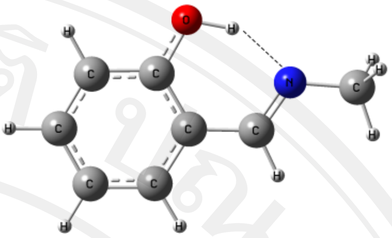


7AI(MeOH)$_1$ 7AI(MeOH)$_2$ 7AI(MeOH)$_3$

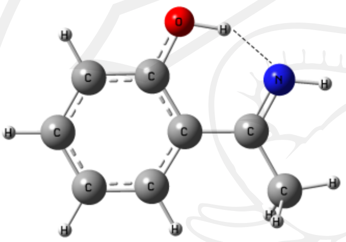
Figure 1.4 Geometries of 7AI(MeOH)$_n$ (n=1-3) and 2-(iminomethyl)phenol derivatives



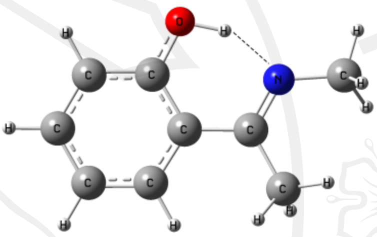
2-(Iminomethyl)phenol
(IMP)



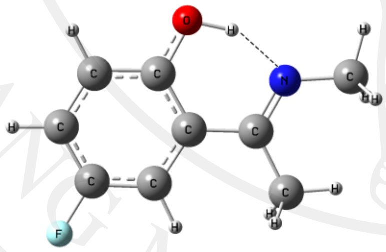
2-(*N*-Methyliminomethyl)phenol
(MIMP)



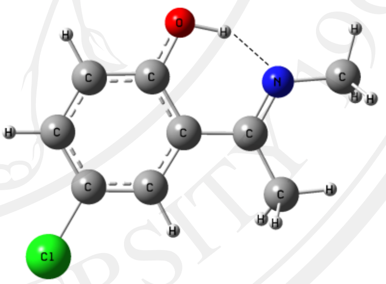
2-(α-Iminoethyl)phenol
(IEP)



2-(*N*-Methyl-α-iminoethyl)phenol
(MIEP)



2-(*N*-Methyl-α-iminoethyl)-4-fluorophenol
(MIEFP)



2-(*N*-Methyl-α-iminoethyl)-4-chlorophenol
(MIECP)

Figure 1.4 (continued) Geometries of $7AI(MeOH)_n$ (n=1-3) and 2-(iminomethyl)phenol derivatives

Finally, excited-state analysis will be investigated to determine time evolution, vertical excitations and reaction pathways in which the ESPT occurs through $S_{\pi\pi^*}$ state whereas ESHT occurs through $S_{\pi\sigma^*}$ state in photoexcitation.