CHAPTER 1

Introduction

1.1 Background of excited-state proton/hydrogen atom transfer reaction

The excited state proton/hydrogen atom transfer (ESPT/HT) reactions play important role in chemical reactions and biological system [1–5] such as enol–keto tautomerizations [6], proton transport via membrane-spanning proteins [7, 8], and proton relay systems in enzymes [8]. Moreover, the ESPT/HT reaction or sometimes called a phototautomerization (a reversible transformation process between two forms of molecules by absorption 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 [9-11]. This type of the PT/HT process occurs along the hydrogen-bonded network. The ESPT/HT bonded network can be formed by heteroaromatic molecules containing both hydrogen-bonding donor and hydrogen-bonding acceptor groups.

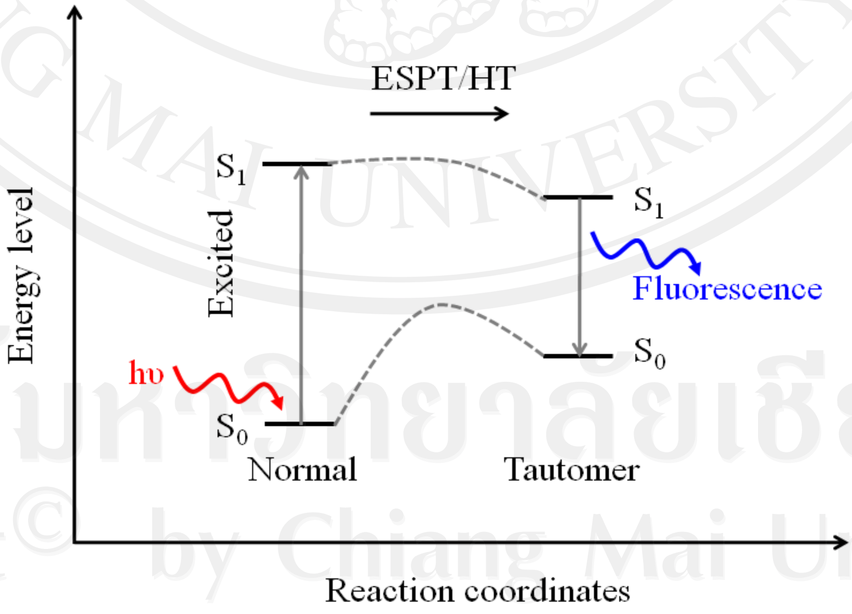

Figure 1.1 Scheme of the excited-state proton/hydrogen atom transfer reaction

From Figure 1.1, a normal form is quite stable in the ground state. It cannot transform into a tautomer spontaneously because of high barrier of reaction. In photoexcitation process, however, the tautomer easily occurs because it has a lower barrier height than the normal form [12-15]. The reactions can be divided into two types, which are intermolecular or intramolecular PT/HT. The intermolecular PT/HT reaction occurs via a proton or a hydrogen atom transfer between the same molecules (dimer) or through the assisted molecules (solvent-assisted molecules). For instance, a simple model compound of certain molecules with specific solvents show this kind of property such as 1*H*-pyrrolo[3,2-*h*]quinoline (PQ) [14-18], 7-hydroxquinoline (7HQ) [19-24], and 7-azaindole (7AI) [25-52]. Whereas, the intramolecular PT/HT reaction occurs by proton/hydrogen atom transfer within molecule without any help from other molecules.

1.2 Molecular 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 light called fluorescence and go down into the lower state which is our interest in this research. If the spin changes from singlet to triplet state and then emits light, the radiation time will take longer than fluorescence called phosphorescence [53].

From Figure 1.2, Jablonski diagram shows the energy levels of each state indicating its spin multiplicity. The lower 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).

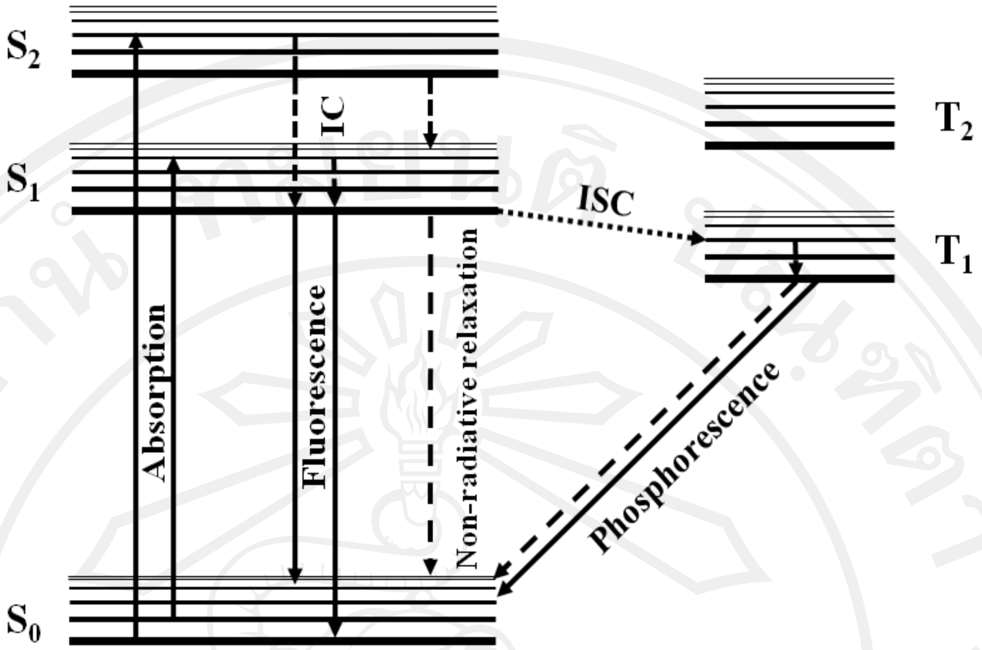

Figure 1.2 Jablonski diagram

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 longer 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) [54].

1.3 7-Azaindole (7AI)

The 7AI molecule (Figure 1.3), a part of DNA bases as a model compound, is an important bicyclic aza-aromatic molecule consisting of pyrrole (proton donor) and pyridine (proton acceptor) rings that can form hydrogen bonds with solvent molecules forming cluster. The normal form becomes unstable with respect to the tautomer form

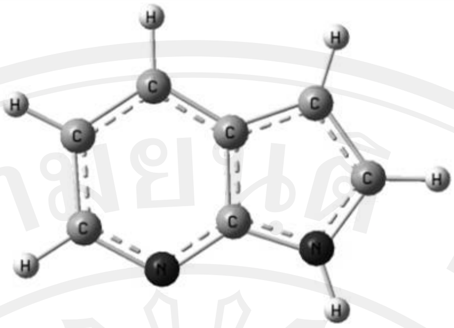

Figure 1.3 7AI structure

in the S_1 state. Tautomerization of the 7AI with solvent clusters such as water, ammonia, and alcohol accompanying the ESInterPT/HT reaction has been both experimentally and theoretically studied [25-52].

Most of theoretical reports have paid much attention to 7AI molecule because of its simple structure. It has been employed as a model compound to reveal a key reaction for chemical mutagenesis of DNA base pairs [47, 50]. The 7AI with solvent clusters, which have been extensively studied in solvents such as ammonia, water, and alcohol (especially ethanol and methanol), are prototypes for understanding the ESInterPT/HT reactions as illustrated in Figure 1.4.

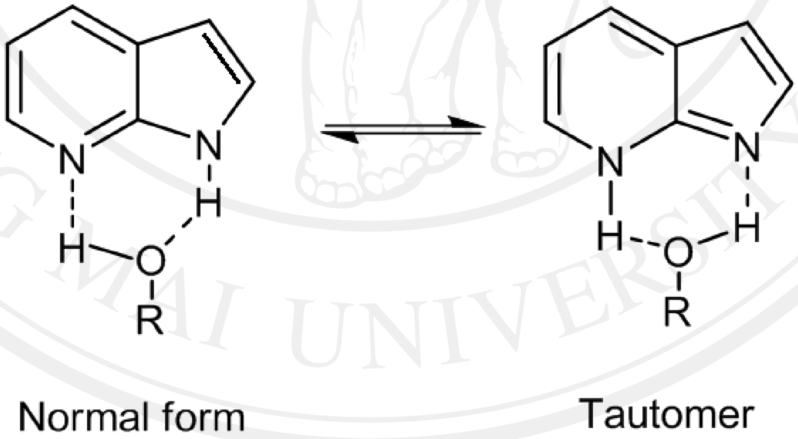

Figure 1.4 Scheme of intermolecular PT/HT reaction of 7-azaindole with alcohol

In addition, theoretical calculations of model compounds consisting of 7AI and solvents can be employed to clarify mechanistic aspects of the reaction. Dynamics simulations can be employed to explore this challenging system to understand the ESPT/HT mechanism. Most of the PT and HT reactions occur in molecules having bifunctional groups (proton donor and acceptor) via hydrogen-bonded network between two functional groups. However, the excited-state intramolecular PT/HT reaction cannot spontaneously occur in some molecules because the proton donor is positioned too far from the acceptor. In such situations, solvent molecules may trigger the ESPT/HT reactions. In presence of solvent assistance, formation of strong hydrogen bonds along the hydrogen-bonded network can reduce the barrier high of reaction and induce intermolecular multiple PT/HT reaction to occur after the photoexcitation.

1.4 Theoretical background of computational chemistry

Quantum mechanics (QM) was established since twenty centuries for explanation effort of electron movement around nucleus. QM is fundamental knowledge for study molecule or atom structure to understand the natural of them which are explain the microscopic phenomena and interaction between atoms. QM is employed in all branches of chemistry. In physical chemistry, thermodynamic and kinetic properties of gases are calculated with statistical mechanics. Organic chemists use it to observe reaction processes by stimulating reaction mechanism, which suitable models provide deep understanding along reaction. Moreover, some specific catalysts and drug are also designable by computational chemistry to calculate their barrier height energy and binding energy of model such as the reaction of enzyme-substrate complex.

When we focus on consideration of QM concept, chemical reaction occurs via electron interaction so theoreticians transform this reaction to mathematical equation. In general, by solving Schrödinger’s equation both atomic and molecular properties can be obtained. However, the exact solution to Schrödinger’s equation cannot be solved analytically due to the electron correlation. So, numerical methods have been used to approximate the solution such as *ab initio*, semi-empirical methods, density functional theory, coupled cluster, and etc.

1.4.1 Schrödinger equation

QM is a mathematical function that describes microscopic phenomena such as the behavior of electron. Erwin Schrödinger and Werner Heisenberg individually developed this new quantum theory in 1925. QM can be used to predict the property of an individual atom or molecule exactly. However, this method is mathematically equivalent and the Schrödinger equation can solve the exact solution for one electron system only.

The wave function is found by solving the Schrödinger equation (1.1), it usually describes on wave function (Ψ), Hamiltonian operator ($\hat{H}$), and the total energy (E). Normally, Ψ is function reported atomic or molecular system. $\hat{H}$ is defined as eigenfunction. Ψ is taken by $\hat{H}$ to give solution as eigenvalue, E.

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

1.4.2 Born-Oppenheimer approximation

The complete nonrelativistic Hamiltonian operator (1.2) includes sum of kinetic and potential energy terms of both nucleus and electron motions [55]:

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

where Z_A and Z_B define at 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 electron i and nuclei A, ε_0 is the permittivity of free space, and $\hbar$ is the Plank constant. Note that it is impossible to obtain solution without reduces some variants except one electron case. The compact formula (1.3) can be represented as

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

where $T_N(R)$ and $T_e(r)$ is the kinetic energy of nuclei and electron, respectively, $V_{eN}(r,R)$ is electron-nuclei attractive Coulomb potential, and $V_{NN}(R)$ and $V_{ee}(r)$ are repulsive Coulomb potential of nuclear-nuclear and electron-electron, respectively.

From the complex equation, it is too complicated to get the solution because there are many variables. The estimated solution to Schrödinger equation can be obtained by using Born-Oppenheimer approximation (BOA). BOA considers nuclear and electron motions separately because the electron is too much lighter than the nucleus. Consequently, the electron can move much faster than the nuclei or the nucleus is fixed while the electron moves. Therefore, leaving $V_{NN}(R)$ and $T_N(R)$ out of the electronic Schrödinger equation leads to only electron motion form (1.4)

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

Such that

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

Schrödinger equation with separated electronic and nuclear parts is easier to be solved. The simple Schrödinger electron equation part is given in equation (1.5). Thus, Ψ can be set at multiple between wave function of electron part ψ and wave function of nuclear part χ as equation (1.6)

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

The BOA is accepted but it cannot be used for all cases. The boundary of solving equation is limited only to hydrogen atom or some molecules with the help of numerical methods. *Ab initio* method, one of numerical methods, is progressive process assigned matrix to estimate more than one electron system that will be discussed in next section.

1.4.3 *Ab initio* method

Ab initio is Latin term meaning *"from the beginning"*, combined from the word *ab* which means *"from"* and *initio* that means *"beginning"*. It originates from Schrödinger equation supported by an appropriately approximated theory. A calculation of eigenvalue is done when a basis set is put into the operator. The results of eigenvalue are more accurate when we choose more accurate levels and big basis sets.

1) Hatree-Fock approximation

The well-known type of *ab initio* calculation is Hatree-Fock (HF) approximation. This approximation starts by guessing initial orbital coefficient (c_a) which is combined with wavefunction of electron (χ_a). The linear-combination of χ_a, and c_a is called combination of molecular orbital (φ). To calculate energy (ε_i) and new set of orbital coefficient values, substitution of ψ_i continuously iterates until these answer is constant. This procedure is known as a self-consistent field (SCF). Mathematically, Schrödinger equation can be rewritten by changing Hamiltonian operator to be Fock operator ($\hat{h}^F$) as equation (1.7) by

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

The appropriated method applied by matrix procedure is transformation molecular orbital function intro Slater's determinant showed in equation (1.8).

Due to electron has spin itself (α or β spin) on Pauli principle, the modified molecular orbital is multiple of φ and spin function. In N-electron system, the Slater determinant is defined as a single matrix.

$$\Psi(1,2,\ldots,N)=\frac{1}{\sqrt{N!}}\begin{vmatrix}\varphi_1\alpha(1)\varphi_1\beta(1) & \varphi_2\alpha(2)\varphi_2\beta(1) & \ldots & \varphi_N\alpha(N)\varphi_N\beta(1)\\ \varphi_1\alpha(1)\varphi_1\beta(2) & \varphi_2\alpha(2)\varphi_2\beta(2) & \ldots & \varphi_N\alpha(N)\varphi_N\beta(2)\\ \ldots & \ldots & \ldots & \ldots\\ \varphi_1\alpha(1)\varphi_1\beta(N) & \varphi_2\alpha(2)\varphi_2\beta(N) & \ldots & \varphi_N\alpha(N)\varphi_N\beta(N)\end{vmatrix} \tag{1.8}$$

Although HF approach can solve Schrödinger equation, solution which lack of electron-electron correlation is not exactly true. There are more accurate theories that using mixing with exited-states functions such as Møller-Plesset perturbation theory, configuration interaction and coupled cluster theory.

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 wavefunction conducted by starting with the HF wavefunction and making new determinant by promoting electron from 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 energy as long as the excitations. The CC results are a bit more accurate than the equivalent size CI calculation results [56].

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 used in 7-azaindole system which is a main interest of this thesis. This method has been employed in our previous calculations [57-58].

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

$$A^{CC2} = \left(\begin{array}{c|c} \dfrac{\left\langle {}_{i}^{a} \middle| [(\hat{H} + [\hat{H}, T_2]), \tau_k^c] \middle| HF \right\rangle}{\left\langle {}_{ij}^{ab} \middle| [\hat{H}, \tau_k^c] \middle| HF \right\rangle} & \dfrac{\left\langle {}_{i}^{a} \middle| [\hat{H}, \tau_{kl}^{cd}] \middle| HF \right\rangle}{\left\langle {}_{ij}^{ab} \middle| [F, \tau_{kl}^{cd}] \middle| HF \right\rangle} \end{array} \right) \tag{1.9}$$

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_k^c and τ_{kl}^{cd} denote, respectively, single and double replacement operators.

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

$$A^{CIS(D_\alpha)} = \left(\begin{array}{c|c} \dfrac{\left\langle {}_{i}^{a} \middle| [(H + [H, T_2^{(1)}]), \tau_k^c] \middle| HF \right\rangle}{\left\langle {}_{ij}^{ab} \middle| [H, \tau_k^c] \middle| HF \right\rangle} & \dfrac{\left\langle {}_{i}^{a} \middle| [H, \tau_{kl}^{cd}] \middle| HF \right\rangle}{\left\langle {}_{ij}^{ab} \middle| [F, \tau_{kl}^{cd}] \middle| HF \right\rangle} \end{array} \right) \tag{1.10}$$

So that

$$A^{ACD(2)} = \frac{1}{2}\left(A^{CIS(D_\alpha)} + (A^{CIS(D_\alpha)})* \right) \tag{1.11}$$

The above relations between CC2, CIS(D_α), and ADC(2) provide a simple recipe to implement the latter two methods in an existing CC2 program: for CIS(D_α), 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 Adiabatic dynamics

The basic problem in dynamics simulations of molecules is to solve the time-dependent Schrödinger equation (TDSE) [59] for the complete molecular system,

$$\left(i\hbar \frac{\partial}{\partial t} - \hat{H} \right) \Psi(r, R, t) = 0 \tag{1.12}$$

where $\hat{H}$ is the Hamiltonian and Ψ 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

$$\Psi(r, R, t) = \sum_i \psi_i(r; R) \chi_i(R, t) \tag{1.13}$$

where ψ_i is a electronic wavefunction and χ_i is a nuclear wavefunction in equation (1.12) for electronic state i.

$$F_{kj}^{m}(R) \equiv \left\langle \psi_k \middle| \nabla_m \middle| \psi_j \right\rangle_r \tag{1.14}$$

where F_k is the electronic wavefunction.

In equation 1.14, 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

$$\frac{d^2 R_m^c}{dt^2} - \frac{F_m^c}{M_m} = 0 \tag{1.15}$$

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:

$$i\hbar \frac{dc_k}{dt} + \sum_j (-V_k^c \delta_{kj} + i\hbar F_{kj}^c . v^c) c_j = 0, \text{ (adiabatic)} \tag{1.16}$$

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) 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.

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

$$P_W(Q^i,P^i)=(\pi\hbar)^{-1}\int d\eta\,\chi_{HO}^{0}(Q^i+\eta)^{*}\chi_{HO}^{0}(Q^i-\eta)e^{2i\eta P^i/\hbar}, \qquad (1.17)$$

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.

$$P_W(Q^i,P^i)=(\pi\hbar)^{-1}\exp(-\mu^i\omega_{OH}^{i}Q^{i2}/\hbar)\exp(-P^{i2}/(\mu^i\omega_{OH}^{i}\hbar)), \qquad (1.18)$$

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 1.18. To solve the problem, the equation 1.17 can be written as

$$P_W(Q^i,P^i)=\left|\chi_{OH}^{0}(Q^i)\right|^2\left|\xi_{OH}^{0}(P^i)\right|^2, \qquad (1.19)$$

where ξ_{OH}^{i} is the harmonic oscillator wavefunction in the momentum representation. Even though equation 1.19 is valid for the ground vibrational level, it is motivated to write an analogous quasi-Wigner distribution for the excited vibrational states

$$P_{QW}(Q^i,P^i)=\left|\chi_{OH}^{n}(Q^i)\right|^2\left|\xi_{OH}^{n}(P^i)\right|^2. \qquad (1.20)$$

1.5 Objectives

In this study, we will study the ESInterPT/HT reactions in the gas phase occurring through the solvent-assisted molecules on the hydrogen-bonded cyclic network of 7AI with water (7AI(W)$_n$ when n=1-5), ammonia (7AI(A)$_n$ when n=1-3) and mixed ammonia-water (7AI(AW)$_n$ when n=2-3) clusters. These systems are interesting because of their simple reactions and small structures. Most previous reports [36-38] did not give any important dynamics properties of the systems in molecular level such as reaction pathway, reaction probability, solvent effects, and time evolution of the

ESPT/HT process. Thus, our theoretical study using dynamics simulation in the first excited state in the gas phase will provide the detailed information that cannot be obtained from the experimental results or previous theoretical reports.