Probability of Electron Transfer Rate Constant at Nanoscale Metal/Molecule Interface System

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Abstract

Devices Nano technology largely rely on metal/liquid interfaces, whose most important electronic transferring parameter are the probability of rate constant, reorganization energy and temperature. The probability of electron transport rate constant in Au/TCNQ molecule interface system has been calculated and the transmission through interface is examined.

A theoretical study according to the quantum system have been adapted to study the electron transfer cross Au and TCNQ molecule system. Rate constant of electron transfer are calculated based on the quantum expression and depending on the calculation of the reorganization energy, coupling coefficient, and temperature.

A Mat lab program has been used to calculate the reorganization energy, and rate constant of electron transfer by solving the suitable formulas. Our results data show that the probability of the rate constant for electron transfer \( \Phi_{\text{ET}} \) increases with the increasing of the coupling coefficient and temperature, and decreasing of the reorganization energy \( E_{\text{ho}} \).

Key word : Probability of Electron Transfer, Rate Constant, Nano scale Metal/Molecule

Introduction

Electron transfer reactions represent a simple process which occurs in donor-acceptor system molecules. The transfer of a single electron from an atom or a molecule to another is considered to be the most elementary reactions [1]. Electron transfer is one of the most important reactions in physical chemistry and biophysics involves an oxidation of donor state \( |D\rangle \) and reduction of an acceptor state \( |A\rangle \).

The electron transfer reaction could be as fast as 1(PecoSec)¹ and as slow as 1Year¹, depending on reactions environmental conditions. An electron transfer reaction may occur between an electrode and molecule [2]. Electron transport at the Nano scale is remarkably essential to many processes in nature and is therefore an important subject in scientific disciplines such as biophysics, and physical chemistry, and physics [3]. Rudolph Marcus described electron transfer between two states, a model which was the basis for the classical theory of electron transfer. Later, this model was extended to describe electron transfer from a single donating state to a continuum of accepting state[4]. Electron transfer at molecule-metal interfaces is of interest to many research fields. Examples include, among others, photo catalysis surface photochemistry, dye-sensitized solar cells (DSSCs), organic semiconductor-based photovoltaic, and Nano scale optoelectronics based on a single molecule or a small group of molecules [5].

In addition to the fundamental importance understanding ET dynamics at the molecule Nano particle interface is also crucial to the development of many Nano particle based devices such as molecular [6]. In particular the position of molecular energy levels relative to the metal energy level and the size of the electron binding energy are of key importance for the change transfer across the organic-metal interface [5]. The field of electron transfer has been greatly advanced by the detailed analytical theory in the past half century ago depending on the standards Marcus theory and also by the introduction of new technology, such as photochemical initiation [7].

Research in the field of nanotechnology is fueled by the possibility of tailoring the fundamental properties of materials with simplification of processing and assembly of devices. The change in properties arises from quantum confinement effects, where the properties of a material become size dependent [8]. Nano scale materials that have been widely investigated for their properties and application include: 0-dimensional system (0-D) of nanoparticles (NPs), 1-D system of Nano rods and nanotubes, biological polymers like deoxyribonucleic acid (DNA) and proteins, thin polymer films, polyelectrolyte's (PE), Nano composites, and organic-inorganic hybrid structures [8].

The ability to control the particle size and morphology of nanoparticles is of crucial importance nowadays both from a fundamental and industrial point of view, considering the tremendous amount of high-technology applications of nanostructured material devices such as dye-sensitized solar cells, displays and smart windows, chemical, gas and biosensors, lithium batteries, and super capacitors [9]. In this paper a theoretical description and studied of probability rate constant for electron transfer at Au/7,7,8,8-tetracyanoquinodimethaneTCNQ molecule interface Nanoscale.
system and will be evaluated theoretically the rate constant for this transfer of electrons depending on the reorganization energy and coupling matrix element coefficient.

**Theory**

For electron transfer between the localized quantum states, we can introduce the donor state vector \( | \phi_d \rangle \) and acceptor state vector \( | \phi_a \rangle \) in Hilbert space at quantum system. We can adapt Anderson Hamiltonian to describe the electron transfer dynamics across molecules of liquid to metals system that is illustrated in Figure (1)[10].

![Energy interface diagram of the molecule liquid/metal interface at both sides of the TCNQ/Cu (100) interface][1]

The net rate of electron transfer in Eq.(5) with integral calculation in Eq.(6) is given by.

\[
\mathcal{R}_{ET} = \frac{2\pi}{\hbar} \left| \langle \phi_d | \mathcal{H}_{DA} | \phi_a \rangle \right|^2 \int D(E) F(E) \delta(E_m - E_a) dE \tag{1}
\]

Where \( \left| \langle \phi_d | \mathcal{H}_{DA} | \phi_a \rangle \right|^2 \) is the coupling matrix element. \( D(E) \) is the density of state and \( F(E) = \left( 1 + \exp \left( \frac{E - \mu}{kT} \right) \right)^{-1} \) is the Fermi-Dirac probability distribution relative to the chemical potential of the electrons in the electron metal-liquid interface and that given by [78]. The density of state \( D(E) \) is given by [12].

\[
D(E) = \frac{1}{(2\pi)^2} \frac{1}{\sqrt{E_{\text{max}} - E}} \exp \left( - \frac{E}{2kT} \right) \tag{2}
\]

By substituting Eq.(2) in Eq.(1) the rate constant for ET can be written as:

\[
\mathcal{R}_{ET} = \frac{2\pi}{\hbar} \left[ \int D(E) \left| \langle \phi_d | \mathcal{H}_{DA} | \phi_a \rangle \right|^2 \delta(E_m - E_a) dE \right] \tag{3}
\]

Where the \( \left( \left| \langle \phi_d | \mathcal{H}_{DA} | \phi_a \rangle \right|^2 \right) \) is an averaged coupling electronic matrix elements square of all the electronic states which are given by [13].

\[
\left( \left| \langle \phi_d | \mathcal{H}_{DA} | \phi_a \rangle \right|^2 \right) = \pi kT \sum \left| \langle \phi_d | \mathcal{H}_{DA} | \phi_a \rangle \right|^2 \delta(E_m - E_a). \tag{4}
\]

Inserting Eq.(4) in Eq.(3), results:

\[
\mathcal{R}_{ET} = \frac{2\pi}{\hbar} \left[ \int D(E) \left| \langle \phi_d | \mathcal{H}_{DA} | \phi_a \rangle \right|^2 \delta(E_m - E_a) dE \right] = \frac{2\pi}{\hbar} \left[ \int D(E) \left| \langle \phi_d | \mathcal{H}_{DA} | \phi_a \rangle \right|^2 \delta(E_m - E_a) dE \right] \tag{5}
\]

By evaluated the integral in Eq.(5) the result integral

\[
\int_{-\infty}^{\infty} \frac{dE}{\exp \frac{E}{kT} + \exp \frac{E}{2kT}} = \frac{\pi kT}{2} \int_{-\infty}^{\infty} \frac{dE}{\exp \frac{E}{kT} + \exp \frac{E}{2kT}} = \frac{(\pi kT)^2}{4} \tag{6}
\]

The net rate of electron transfer in Eq.(5) with integral calculation in Eq.(6) is given by.
The reorganization energy, $E_{\text{reorg}}$, and density ical dielectric constant values of the solvent, $n$ is the refractive index of the solvent. The reorganization energy due to electron transfer reaction for a redox active at metal electrode interface is given by 

$$E_{\text{reorg}} = \frac{1}{2\pi \varepsilon_0 \varepsilon_r f'(n, \varepsilon)} \left( \frac{1}{n^2} - \frac{1}{\varepsilon} \right)$$

(8)

Where $Q$ is the electron charge, $\varepsilon_0$ is the vacuum permittivity, $D$ is the distance between the complex and electrode, $R$ is the radius of the molecule and $f'(n, \varepsilon)$ is the polarity function that given by

$$f'(n, \varepsilon) = \left( \frac{1}{n^2} - \frac{1}{\varepsilon} \right)$$

(9)

Where $\varepsilon$ is the static dielectric constant of the solvent, $n$ is the refractive index of the solvent.

The radius of the molecule can be estimated from the apparent molar volume using spherical approach [15].

$$R = \left( \frac{M}{2\pi N_p} \right)^{1/3}$$

(10)

Where $M$ is the molecular weight, $N$ is Avogadro's number, and $\rho$ is the mass density.

Results

A theoretical model based on the quantum system using to study the probability of transfer across metal molecule Nanoscale system. The transition rates $R_{\text{ET}}(\frac{1}{2\pi})$ at Au/TCNQ system is calculated using quantum transport formalism in Eq.(6) due to the reorganization energy $E_{\text{reorg}}$, the coupling matrix elements coefficient $T_{\text{ET}}$, for metal and molecule state, and temperature respectively. Amore important parameters effect on the probability of transfer at metal/molecule interface such that, the reorganization energy $E_{\text{reorg}}$ (eV), that’s must be evaluation radius for Au metal, and 7,7,8,8-tetracyanoquinodimethaneTCNQ molecule liquid from Eq.(10) by inserting the values of Avogadro's constant $N = 6.02 \times 10^{23}$ mol$^{-1}$, molecular weight $M=204.19$ g/mol[16], and density $\rho = 1.359$ g/cm$^3$[17] for 7,7,8,8-tetracyanoquinodimethaneTCNQ molecule and $\rho = 19.3$ g/cm$^3$ for Au metal [18]. In Eq.(6), we can estimate the values of radii for metals and TCNQ molecule respectively. Reorganization energies for Au/ TCNQ molecule liquid interface can be calculated according to Eq.(8) and Eq.(9) ,with the values of the static dielectric constant $\varepsilon$, and optical dielectric constant $\varepsilon_\infty$ ,for solvents from Table (1), and radii estimation of the Au metal and TCNQ molecule ,result are tabulated in Table(2).

### Table(1) :Common properties of organic solvent[17].

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Refractive index[17]</th>
<th>Dielectric constant[17]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>1.3265</td>
<td>32.70</td>
</tr>
<tr>
<td>Acetunitnile</td>
<td>1.3416</td>
<td>37.50</td>
</tr>
<tr>
<td>Ethylenimine</td>
<td>1.4123</td>
<td>18.30</td>
</tr>
<tr>
<td>Formicacid</td>
<td>1.3694</td>
<td>58.50</td>
</tr>
<tr>
<td>Propionitnile</td>
<td>1.3636</td>
<td>27.20</td>
</tr>
<tr>
<td>Ethyleneolamine</td>
<td>1.4513</td>
<td>12.90</td>
</tr>
<tr>
<td>Propanol-1</td>
<td>1.3837</td>
<td>20.33</td>
</tr>
<tr>
<td>Benzen</td>
<td>1.5011</td>
<td>2.28</td>
</tr>
<tr>
<td>Dimethylsulfoxidl</td>
<td>1.4773</td>
<td>46.68</td>
</tr>
<tr>
<td>Vale-onirile</td>
<td>1.3991</td>
<td>19.71</td>
</tr>
</tbody>
</table>
Table (2): Our results of the reorganization energy $E_{\text{met}}^{\text{liq}}$ (eV) for electron transfer at Cu/ TCNQ molecule interface system.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$f(n, \varphi)$</th>
<th>Refractive index$^{[17]}$</th>
<th>Dielectric constant$^{[17]}$</th>
<th>Reorganization energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>0.5377</td>
<td>1.3265</td>
<td>32.70</td>
<td>0.627253882932577</td>
</tr>
<tr>
<td>Acetunitnile</td>
<td>0.5289</td>
<td>1.3416</td>
<td>37.50</td>
<td>0.616981167307094</td>
</tr>
<tr>
<td>Ethyleneimine</td>
<td>0.4467</td>
<td>1.4123</td>
<td>18.30</td>
<td>0.521082404658469</td>
</tr>
<tr>
<td>Formicacid</td>
<td>0.5161</td>
<td>1.3694</td>
<td>58.50</td>
<td>0.602101158733898</td>
</tr>
<tr>
<td>Propionitnile</td>
<td>0.5010</td>
<td>1.3636</td>
<td>27.20</td>
<td>0.584458456514570</td>
</tr>
<tr>
<td>Ethyleneolamine</td>
<td>0.3972</td>
<td>1.4513</td>
<td>12.90</td>
<td>0.463390481490933</td>
</tr>
<tr>
<td>Propanol-1</td>
<td>0.4731</td>
<td>1.3837</td>
<td>20.33</td>
<td>0.551872835445298</td>
</tr>
<tr>
<td>Dimethyloxidol</td>
<td>0.4367</td>
<td>1.4773</td>
<td>46.68</td>
<td>0.509503481151695</td>
</tr>
<tr>
<td>Vale-onirile</td>
<td>0.4601</td>
<td>1.3991</td>
<td>19.71</td>
<td>0.536729641861015</td>
</tr>
</tbody>
</table>

For next, we can calculate the electron transfer rate constant for Cu / TCNQ molecule liquid interface system using Eq. (3) with a Matlab program and substituting the reorganization energies data from table (2). The matrix element coupling coefficient $H_{\text{DA}}(0)$ = 0.01115, 0.01177, 0.01239, and 0.01363 eV$^{[18]}$, and temperature is taken depending on experimental $T = 250,300$, and $350K$ results have been summarized in table(3).

Discussion

The probability of electron transfer rate constant $R_{\text{ET}}(\text{Sec}^{-1})$ in Eq. (6) indicates that the transition of electron rate constant $R_{\text{ET}}(\text{Sec}^{-1})$ increases with the increasing of the coupling coefficient $|H_{\text{DA}}(E)|$ (eV) and temperature $(k)$, and decreasing of the reorganization energy $E_{\text{met}}^{\text{liq}}$ (eV). Due to this model, the transition of electron has occurred by tunneling region at the overlap of the wave functions for the acceptor metal state and donor molecule state. Probability of electron transport $R_{\text{ET}}(\text{Sec}^{-1})$ by the tunneling due to the interface created between metal and molecule in Au/TCNQ system.

First of all the calculation of electron transfer parameters requires us to define a theoretical model which describes the behavior of electron transfer we must evaluation the reorganization energy $E_{\text{met}}^{\text{liq}}$ (eV), it is effected on the probabilities of rate constant $R_{\text{ET}}(\text{Sec}^{-1})$ at metal/molecule system and the most important parameter that enables us to calculation the other parameters and the rate constant of electron transfer for the Nano scale metal/molecule system. It is calculated according to continuum classical theory. On the other hand, the simplicity and different physical nature for metal, and molecule interface appear to predict correctly the typical order of magnitude values observed for the reorganization energies $E_{\text{met}}^{\text{liq}}$ (eV) and rate constant $R_{\text{ET}}(\text{Sec}^{-1})$ of electron transfer with solvent. Results of the reorganization energy in table (2) for Au/TCNQ system is effected by polarity parameter for the solvent molecules. The reorganization energy $E_{\text{met}}^{\text{liq}}$ (eV) is large for large polarity function and vice versa. This indicates that the reorganization energy $E_{\text{met}}^{\text{liq}}$ (eV) is a function for the polarity of the solvent.

Consequently, interface effects compete with the metals properties gave us good image about scenario of potential barrier at interface. The interface interactions of electron transfer at Nano scale metal/molecule system should be effected by the properties of polarity for the Nano scale molecules solvent, since these molecules have static dielectric constant and optical dielectric constant properties. Taking into account information of polarity from investigations of the reorganization energy by classical continuum model.

However the most important factor in the probability rate expression is the transmission matrix element coefficient $|H_{\text{DA}}(E)|$ (eV) that has been used to study the two type of electron transfer adiabatic and non-adiabatic. The coefficient matrix element $|H_{\text{DA}}(E)|$ (eV) of the electron transfer reaction process is proportional to the square of the electronic matrix element $H_{\text{DA}}$ (eV). The coupling matrix element coefficient $H_{\text{DA}}(0)$ (eV) has controlled the mechanism of electron transfer between the metal and molecule system. The electronic properties of molecules are...
markedly affected by the proximity of metal surfaces, depending on the strength of the metal–organic molecules interaction [19].

Electronic coupling evidently reflects that the capability to transfer electron is determined by the alignment of the levels state of molecules with respect to the metal Fermi energy. Hence, the coupling coefficient of matrix element $\mathcal{H}_{2a}(0)$ (eV) has been used in the range from (0.000111- 0.000186) eV depending on the typical results of experimental data [20]. As expected, the data results according to our theoretical models give a good idea for the behavior of transition for electron in the non-scale limit. On the other hand result of our data show the interaction of electron in Nano scale devices Au/molecule systems is Nano-adiabatic, that view from results of the coupling coefficient $\mathcal{H}_{2a}(0)$ (eV) of matrix element between metal and molecule state.

Rate constant of electron becomes small when the coupling coefficient matrix element between metal and molecules system will be weak that shown from data in table (3). The present data for the probability of electron transfer that occurs in a metal/molecule system with least polar solvents like Au/molecule with Ethyleneolamine that have polarity function $f(\mu, e) = 0.3972$ compared to more polar solvent such that Methanol that have polarity function $f(\mu, e) = 0.5377$. The reorganization energy $E_{\text{met}}^{\text{h}q}$ (eV) is large for more polarity function solvents and small for less polarity function solvents. This indicates that the transfer of electron is more probable in metal/molecule system have less polarity parameter. Not ably the electron transfer in system have large dielectric constant are stronger than system have small dielectric constant solvent.

The data of the reorganization energy $E_{\text{met}}^{\text{h}q}$ (eV) that’s evaluated are fitting with the experimental values of $E_{\text{met}}^{\text{h}q}$ (eV) = 0.303312 to 0.72577 for Au/molecule interface [1]. The transition constant $\mathcal{H}_{\text{ET}}(\text{Sec}^{-1})$ results are large for Au/molecule with less polar. This indicates that there is Au metal is more reactive towards molecules for less polar system than more polar system and ET reaction occurs activity with less polar solvents. Data in table (3) and Eq.(6) of the rate constant for electron transfer show that the rate is a function of the temperature and increasing temperature make more electron to transfer.

Furthermore, the reorganization energy $E_{\text{met}}^{\text{h}q}$ (eV) temperature and the coupling coefficient energy are the bases of electron transfer in Cu/TCNQ system. Data of rate constant depending on these parameters enable to understand the idea of the behavior of electron transfer in metal/molecule.

Conclusions

Probability of rate constant for electron transfer in Nano scale devices system have been studied theoretically depending on quantum picture. A theoretical model for electron transfer rate constant derived depending on a continuum level state assume for metal and molecule in donor-acceptor system and satisfied model by Hilbert space. Probability of transfer at Au/TCNQ interface Nano scale system depending on the reorganization energy, temperature and the coupling coefficient.

According to the present results that have been discussed above several conclusions can be mentioned.

1- A model that is derived depending on experimental consideration successfully to describe the behavior of electron which transition across interface in Au/TCNQ system and provides a perfect evidence for studying the probability at Nano scale system.

2- The rate constant of electron transfer at Au/TCNQ system results have enabled us to elaborate and tested the system and have its advantage to use or not in many applied physical through calculation of the probability of electron transition.

3- Reorganization energy $E_{\text{met}}^{\text{h}q}$ (eV) of the electron transfer should be effected on the quantum transport probabilities of rate constant $\mathcal{H}_{\text{ET}}(\text{Sec}^{-1})$ at Au/TCNQ system and the rate constant $\mathcal{H}_{\text{ET}}(\text{Sec}^{-1})$ are large for system with lest polarity function and increases with decreases of the reorganization energy.

4- The use of different solvents has been clearly shown to influence on the probability of electron transfer. All these results are very important to address future investigations in the Nano scale field.

5- The rate of probability of transition increases with increases of the temperature, this indicates, increasing temperature drive more electrons to cross the tunneling at interface at the metal/molecule system.

Reference