Theoretical Discussion of Electron Transport Rate Constant at TCNQ / Ge and TiO₂ System

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Abstract. We have been studying and estimation the electronic transport constant at TCNQ / Ge and TiO₂ interface by means of tunneling potential (TP), transport energy reorientation (TER), driving transition energy DTE and coupling coefficient constant. A simple quantum model for the transition processes was adapted to estimation and analysis depending on the quantum state for donor state |α_D> and acceptor state |α_A> and assuming continuum levels of the system. Evaluation results were performed for the surfaces of Ge and TiO₂ as best as for multilayer TCNQ. The results show an electronic transfer feature for electronic TCNQ density of states and a semiconductor behavior. The electronic rate constant result for both systems shows a good tool to election system in applied devices. All these results indicate the

1. Introduction
Charge transition reaction were fundamental steps processes in more biophysical and physical chemistry and study of condensing phase of electron transfer field in molecular electronics. Where its development of charge transfer theory by Marcus [1]. Electronics are such an elementary particles that mobile in molecular devices and movement at condensed phases due to fluctuations and/or external electromagnetic excitation [2]. Nonadiabatic charge transfer in molecular electronic via quantum mechanical tunneling was characteristic of processing limited from photosynthesis to conduction at molecular wires [3]. The special type of molecular have electronic properties was a multidisciplinary and active research area to study a fundamental process, such that charge transfer .The low-cost and molecular-sized make us to using, molecular electronic in much-applied research [4]. Marcus R was one famous scientist that provided to describe the transfer depending simple theory. Depending on the Marcus assumption of charge transfer reactions, there are a simple relation the rate reaction and the system fundamental quantities [5]. The exploitation of charge transfer reaction processes to construct more technological devices had already been proposing and needed to understand the transfer mechanism theoretically [6].The important challenging against the scientists today was developing the scale of molecular systems that could be controlling and signals processes, besides to producing more applied devices such as rectifiers, wires, transistors, memories and optoelectronic triggering switches [7]. On the other hand, the charge transfers at semiconductor surfaces include many important applications such that photoelectrolysis, photocatalysis, quantum confinement devices, waste processing, and solar cells [8].
The aims of this paper are to study and discuss the electronic transfer interaction at the molecule/semiconductor interface according to simple quantum model to gate result an expression enables us to evaluate the transfer rate flow of electrons through molecule/semiconductor systems. Wing the last numbered section of the paper.

2. Theory
The consideration of quantum theory assumes that the two wave function of system donor and acceptor are satisfied a linear function in the Hilbert space. The assume two wave function are $|\psi_D>\,$, and $|\psi_A>\,$ which refers to the electronic donor and acceptor state function and given by [9].

$$|\psi_D(\epsilon)\rangle = \frac{e^{-\frac{\epsilon^2}{2\theta^2}}}{(2\theta^2)^{\frac{1}{4}}} H_\ell(\frac{\epsilon}{\sqrt{2\theta}})$$

$$|\psi_A(\epsilon)\rangle = \frac{1}{(2\theta^2)^{\frac{1}{4}}} H_\ell(\frac{\epsilon}{\sqrt{2\theta}})$$

Here $\epsilon$ is the effective transition energy, $\theta = \sqrt{2\Delta k_B T}$. $H_\ell$ is Hermite polynomial. According to Schrödinger assumption the distribution function $\rho(t)$ for the electron transfer system. Maybe written due to Neuman ‘as in equation (3)’ [10].

$$\frac{d}{dt} \rho(\epsilon,t) = \dot{\rho}(\epsilon,t) \equiv H\rho(\epsilon,t)$$

The Hamiltonian operators of the system can be written as [11].

$$\hat{H} = \hat{H}_{EL} + \hat{H}_{VIB} + \hat{H}_{INT}$$

Where $\hat{H}_{EL}$ is the electronics Hamiltonian, $\hat{H}_{VIB}$ is the Hamiltonian for the classical dynamics oscillators and $\hat{H}_{INT}$ is the interaction between the electronic and the vibrational. According to the classical-quantum treatment [12], the density of electron transfer reduces to rate $\Pi(\epsilon,t)$ according to.

$$\Pi(\epsilon,t) = \frac{d}{dt} \rho(\epsilon,t) = H\rho(\epsilon,t) = (\epsilon + i\xi)\rho(\epsilon,t)$$

Where $\rho$, and $\xi$ are the relaxation dynamics and for the electronic transition between two states and Eq. (6) lead to results.

$$\dot{\rho}_{aa}(\epsilon,t) = H_{aa}\rho_{aa} + i\hat{T}(\rho_{ab} - \rho_{ba})$$

$$\dot{\rho}_{bb}(\epsilon,t) = H_{bb}\rho_{bb} - i\hat{T}(\rho_{ab} - \rho_{ba})$$

$$\dot{\rho}_{ab}(\epsilon,t) = H_{ab}\rho_{ab} - i\omega_{ab}\rho_{ab} + i\frac{\hat{T}}{\hbar}(\rho_{aa} - \rho_{bb})$$

$$\dot{\rho}_{ba}(\epsilon,t) = H_{ba}\rho_{ba} + i\omega_{ab}\rho_{ba} - i\frac{\hat{T}}{\hbar}(\rho_{aa} - \rho_{bb})$$

Where $\hat{T}$ is the coupling coefficient, $\omega_{12}$ is the differences frequency between two free energies $U_1(E)$, and $U_2(E)$ given by[13].

$$\hbar \omega_{12} = U_1(E) - U_2(E) = \Delta + E_o$$

For non-adiabatic limit of electron transfer Eq. (6-C) and (6-D) in time domain solution

$$\rho_{ab}(\epsilon,t) = \rho_{ba}(\epsilon,t) = i\hat{T} \int_0^t dt \int_{-\infty}^{\infty} d\epsilon_o G_{ab}(\epsilon,\tau|\epsilon_o) [\rho_{aa}(\epsilon_o, t + \tau) - \rho_{bb}(\epsilon_o, t + \tau)]$$

The operator of green function $G_{ab}$ is.

$$G_{ab}(\epsilon,\tau|\epsilon_o) = \langle \epsilon|e^{(H_{21} + i\omega_{12})t}|\epsilon_o\rangle$$

Substitute ‘equation (8)’ in ‘equation (6-A) and ‘equation (6-B), to results.
\[
\frac{d}{dt} \rho_{\mu}(\epsilon, t) = L_{\mu} \rho_{\mu}(\epsilon, t) - \frac{2\pi}{h} |\vec{T}|^2 R e \int_{-\infty}^{\infty} d\epsilon_o \int_{0}^{\infty} d\tau G_{12}(\epsilon, \tau|E_o) [\rho_{\mu}(E_o, t-\tau) - \rho_{\mu}(E_o, t-\tau)]
\]

(10)

for non adiabatic electron transfer is given by:

\[
\Pi(\epsilon, t) = \frac{2\pi}{h} |\vec{T}|^2 R e \int_{-\infty}^{\infty} d\epsilon_o \int_{0}^{\infty} d\tau G_{12}(\epsilon, \tau|E_o) [\rho_{aa}(\epsilon_o, t-\tau) - \rho_{bb}(\epsilon_o, t-\tau)]
\]

(11)

Then result of evaluation Eq. (11) is:

\[
\Pi(\epsilon, t) = \frac{2\pi}{h} (4\Delta k_B T)^{-\frac{1}{2}} \exp \left[\frac{\Delta}{4 k_B T} \left(1 - \frac{1}{4 k_B T} \left(\frac{(\pi k_B T)^2}{4} + \frac{1}{32 k_B T^2} \left(\frac{5(\pi k_B T)^4}{16}\right)\right)\right)\right]
\]

(12)

The reorientation transition energy \(\Delta(eV)\) for electronic transition is [14]:

\[
\Delta(n, \epsilon) = \frac{(\Delta e)^2}{8\pi\epsilon_0} \left[f(n, \epsilon) \left(\frac{1}{R} - \frac{1}{2\rho}\right)\right]
\]

(13)

Here \(f(n, \epsilon)\) is the polarity of system \(f(n, \epsilon) = \left(\frac{1}{n^2} - \frac{1}{\epsilon^2}\right)\), \(n\) and \(\epsilon\) are the optical and statistical dielectric constant, \(\Delta e = e_D - e_A\) the difference in electron charge of donor and acceptor, \(R\) is molecule radius, and \(D\) is the distance between semiconductor and molecule. The radii of the molecule could be evaluation using [15].

\[
R = \left(\frac{3M}{4\pi N\rho}\right)^{\frac{1}{3}}
\]

(14)

Where \(M\) is the molecular weight, \(N\) is Avogadro’s number, and \(\rho\) is the mass density.

3. Result and Discussion:

A theoretical discussion of electronic transport according to the quantum system that assumes depending on the experimental system to understanding the mechanism of charge transfer at the molecule /semiconductor interface. A two quantum state \(|\psi_D(\epsilon)\rangle\), and \(|\psi_A(\epsilon)\rangle\) for donor and acceptor system and the transfer of electrons via the interface of the system. The evaluation of the rate of electronic flow has been performed for TCNQ molecule with Ge and TiO2 semiconductor. It was evaluated using expression Eq. (12) due to the transition energy \(\Delta(n, \epsilon)(eV)\), the electronic coupling coefficient \(\tilde{T}\) for molecule and semiconductor state at room temperature. The rate expression indicates the behavior of electronic transfer through interface molecule/semiconductor. The mechanisms of electronic transfer at molecule/semiconductor system have been the discussion from evaluated flow rate and all transfer coefficient, one can be evaluated the transition energy \(\Delta(n, \epsilon)(eV)\) depending on the continuum model. To evaluate the transition energy, it could be estimated the radii of TCNQ molecule using expression Eq. (14) and substituting Avogadro’s constant \(N = 6.02 \times 10^{23}\) Molecule mol\(^{-1}\), molecular weight \(M = 204.19\) [16], and density masses \(\rho = 1.358\) [17], in Eq. (14), we can evaluate the values of radii for the molecule is 3.906109457.

Next, it can be calculating with inserting the transition energy radii and optical and dielectric constant from Table 1 using Eq. (13) with a Mat lab program and substituting. Results are listed in tables (2,3).

| Properties               | Ge[18] | TiO\(_2\) [19] |
|--------------------------|--------|----------------|
| Atomic weight            | 72.60  | 79.866         |
| Crystal structure        | Diamond | Tetragonal rutile |

Table 1. Properties of Ge and TiO\(_2\) semiconductor.
Density (g/cm$^3$) 5.3267 4.23 [19]
Refractive index 4.0 2.609[19]
Dielectric Constant 16.0 15.10 [20]
Radius(Å) 1.7547 1.95612

| Solvent              | $f(n, \varepsilon)$ | Refractive Index [21] | Dielectric constant [21] | Transition energy |
|----------------------|----------------------|-----------------------|--------------------------|------------------|
| Acetunitnile         | 0.5289               | 1.3416                | 37.50                    | 0.567            |
| Propionitnile        | 0.5010               | 1.3636                | 27.20                    | 0.564            |
| Ethyleneolamine      | 0.3972               | 1.4513                | 12.90                    | 0.456            |
| Propanol-1           | 0.4731               | 1.3837                | 20.33                    | 0.534            |
| Dimethylsulfoxidl    | 0.4367               | 1.4773                | 46.68                    | 0.487            |

Table 2. Data of transition energy $E_{met}^{liq} (eV)$ for electron transfer at TCNQ/Ge system.

| Solvent          | $f(n, \varepsilon)$ | Refractive Index [21] | Dielectric constant [21] | Transition energy |
|------------------|----------------------|-----------------------|--------------------------|------------------|
| Acetunitnile     | 0.5289               | 1.3416                | 37.50                    | 0.567            |
| Propionitnile    | 0.5010               | 1.3636                | 27.20                    | 0.564            |
| Ethyleneolamine  | 0.3972               | 1.4513                | 12.90                    | 0.456            |
| Propanol-1       | 0.4731               | 1.3837                | 20.33                    | 0.534            |
| Dimethylsulfoxidl| 0.4367               | 1.4773                | 46.68                    | 0.487            |

Table 3. Data of transition energy $E_{met}^{liq} (eV)$ for electron transfer at TCNQ/TiO$_2$ system.

The coupling strength $\bar{T}$ between molecule level state and conduction band of semiconductor system is estimation using a typical result from experimental data 0.4, 0.45, 0.5, and 0.55)cm$^{-1}$ depending on literature data in ref. [20] and exchange to $\bar{T} = 0.01115, 0.01177, 0.01239$, and 0.01363eV using transform parameter [20]. However, it has been evaluated the transition rate of electron transfer $\Xi_{el}$ for TCNQ/Ge, and TCNQ/TiO$_2$ systems using Eq.(12) with the result of transition energy $\Gamma(n, \varepsilon)$, and coupling strength $\bar{T}$. The electronic rate constant of electron transition from Eq. (12) using A MATLAB program .results are shown in tables (4,5).

| Solvent              | $f(n, \varepsilon)$ | Refractive index [21] | Dielectric constant [21] | Transition energy |
|----------------------|----------------------|-----------------------|--------------------------|------------------|
| Acetunitnile         | 0.5289               | 1.3416                | 37.50                    | 0.567            |
| Propionitnile        | 0.5010               | 1.3636                | 27.20                    | 0.564            |
| Ethyleneolamine      | 0.3972               | 1.4513                | 12.90                    | 0.456            |
| Propanol-1           | 0.4731               | 1.3837                | 20.33                    | 0.534            |
| Dimethylsulfoxidl    | 0.4367               | 1.4773                | 46.68                    | 0.487            |

Table 4. Theoretical data of electronic rate constant $\Pi(\varepsilon, t)$ (Sec$^{-1}$) at (TCNQ)/Ge system.
Table 5. Theoretical data of electronic rate constant $\Pi(\epsilon, t)$ (Sec$^{-1}$) at (TCNQ)/ TiO$_2$ system.

| solvent          | $T$ (eV) | $0.01115$ | $0.0117$ | $0.01239$ | $0.01280$ | $0.01363$ |
|-----------------|---------|-----------|----------|-----------|-----------|-----------|
| Acetunitnile    | 7       | 1.43      | 1.56     | 1.75      | 1.98      | 2.21      |
| Propionitnile   |         | 1.75      | 1.86     | 1.95      | 2.43      | 2.74      |
| Ethyleneolamine |         | 1.87      | 2.18     | 2.42      | 2.87      | 3.41      |
| Propanol-1      |         | 5.86      | 5.96     | 6.47      | 7.89      | 8.49      |
| Dimethylsulfoxid |        | 2.88      | 3.21     | 3.54      | 3.83      | 4.17      |

Analytical of results according to quantum theory indicates that a high potential barrier formed at the interface of molecule and semiconductor and the potential depending on nature of the material. A simple quantum model of donor acceptor are adapted to discussion transfer of electronic flow via interface according to the wave functions for the acceptor and donor electronic state levels at molecule and conduction band. The important factor that limited the transfer via potential is the coupling strength between donor and acceptor state. Data results in the table (4,5), show that the transfer increases when increases of coupling strength , this indicate the more of electron are cross interface and have energy large than potential and vice versa.

Another parameter effect on transfer rate is transition energy at molecule/semiconductor system. It is evaluated depending on continuum theory to approaches results of experimental data. Transfer energy is modeled depending on physical concepts such as optical and static dielectric constant for donor acceptor and solvent system. The fluctuation of polar media helped to reorientation system to transfer and find the system has large transfer flow when having large transition energy ,this means the system has large transition energy make more electron transfer cross interface because have large energy to drive cross potential at interface that showing from tables (2,3) and tables(4,5)and vice versa.

Tables (2,3) show that the transition energy increase with increasing the solvent dielectric constant and decreasing in rate compared with the system has small the solvent dielectric constant because the system has a small value of transition energy make orient system to transfer of electron. However, it is an increase the solvent refractive index refers to decrease in transition energies for systems. The flow charge proportional due to polarity function $f(n, \epsilon)$, and the system have small polarity results to decreasing transition energy and increases flow charge that showing in the table (4,5) for two system.

Apparentely, it may be explained the transfer more electron in (TCNQ)/ TiO$_2$ system indicate this system have transition energy can drive more electronic to transfer potential and have rate larger than TCNQ)/Ge.

4. Conclusions
In this paper, it has been discussing the electronic rate at molecule / semiconductor interface system according on the simple quantum model. The transition energy has been estimated according to assume levels of all system are a continuum.

We concluded that electronic rate at interface system depends on transition energy, coupling strength, and polarity media.

The transition energy evaluation indicates that electronic rate flow is most probably in the system have large polarity.
Consequently, the system (TCNQ)/TiO$_2$ have electronic rate transition large than TCNQ)/Ge, this indicates the physical properties of two semiconductors.

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