

Electron Transfer At Metal/Molecule Interface

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Abstract

Theoretically description of the electron transfer of the electron transfer of met/mol has been investigated in this work according to the quantum theory. By using a model that is derived depending on the first order perturbation theory, the rate constant at met/mol interface can be calculated with the calculated reorganization energy. The reorganization energy that is evaluated according to the outer sphere model is based on the electstatistics potential of the molecular donor and acceptor. The molecular parameters introduced in this model are the molecular weight, mass, density, and radius of molecule have been evaluated according to the apparent molar volume using spherical approach.

The theoretical results are obtained according to our model of rate constant for electron transfer, a corresponding with the experimental data for some qualilative metal/molecule interface some qualitative of the experimental studies .

Key word : Electron transfer, Metal/Molecule interface

Introduction

Electron transfer (ET) from a metal donor to an acceptor molecule state is one of the simplest conceivable reactions, as chemical bonds are neither formed nor broken. Such charge transfer reactions are of vital importance to a variety of processes in physics, chemistry and biology. For example, homogeneous ET is the primary step in photosynthesis, and various chemical reactions. Electron transfer at molecule–solid interfaces, on the other hand, plays an important role in technologically highly relevant fields [1]. Electronic transport has been a central issue of physical research during the last century. Tremendous amounts of materials have been investigated, for instance metals [2]. Electron transfer processes through molecular systems have attracted much attention over the past fifty years [3]. Now a days , the field of organic electronics has reached the point where several applications are routinely available for use. Others are close to be commerce lited , while others are in a design or testing phase for unique application including nano scale technologies [4]. Electron transfer at the metal/molecule interface is important for technological application such as bio catalysis, electrochemistry, photodiodes, solar energy conversion, and more recently, molecular electronics [5]. The traditional experimental approach for studying these processes is based on measuring the electron transfer in D – A super molecular systems between electron donor and acceptor A unit that are covalently liked through molecular. In many instances electron transfer reaction takes place near interface are part of the interface being the solvent and the other part being a more or less solid such as a metal [6]. Electron transfer processes have been studied extensively in donor – acceptor system and in the last decade at an electrode interface through an electrochemical approach. Rudolph Marcus described electron transfer between two stats, a model which was the basis for his 1992 Nobel prize [7].

Latter, this model was extended to describe Electron transfer from a single donating state to a continuum of accepting state. Understanding transport across the interface between the active organic molecule and the metallic electrode has proved particular challenging, especially in the single molecule limit [8].

In this paper, a theoretical calculation of rate constant for electron transfer in Metal/Molecule interface system is given depending on the reorganization energy ,and the coupling matrix element coefficient.

Theory

A theoretical model formulation for charge transfer in metal /molecule interface utilized is based on the first order perturbation theory and quantum mechanic theory. The state of donor and acceptor system is given by the time dependent wave function [9].

$$\varphi_{(r,t)} = \sum_0^{\infty} C_K(t) \langle \varphi_{n(r)} \rangle e^{-\frac{iE_n t}{\hbar}} \dots\dots\dots (1)$$

The Hamiltonian model for our system consists of three parts [10].

$$\hat{H}_{\text{met-mol}} = \hat{H}_{\text{met}} + \hat{H}_{\text{mol}} + \hat{U}_{\text{met/mol}} \dots\dots\dots (2)$$

The Hamiltonian operator of the metal/molecules system $\hat{H}_{\text{met-mol}}$ satisfies the Schrodinger equation $i\hbar \frac{\partial}{\partial t} |\varphi_{(r,t)} \rangle = \hat{H}_{\text{met-mol}} |\varphi_{(r,t)} \rangle$ [11].

The probability of the rate electron transfer from donor state to acceptor state per unit time is the rate constant that is given by [12].

$$K_{\text{ET}} = \frac{W_{\text{DA}}}{t} = \frac{2\pi}{\hbar} |H_{\text{DA}}(E)|^2 \delta(E_A - E_D) \dots\dots\dots (3)$$

Then the probability of electron transfer rate constant equation [3], also can be expressed in term of density of state $\rho(E - E_A - E_D)$.

$$K_{\text{ET}} = \frac{2\pi}{\hbar} |H_{\text{DA}}(E)|^2 \rho(E) \dots\dots\dots (4)$$

Where the integral delta function is $\int_{-\infty}^{\infty} \rho(E - E_0) \delta(E - E_0) dE = \rho(E_0)$ [13].

The system density operator ρ by the definition can be expressed in the form [14].

$$\rho(E) = \frac{e^{-\frac{(E_0 + \Delta G)}{4E_{mol}^{met} k_B T}}}{(4E_{mol}^{met} k_B T)^{1/2}} \dots \dots \dots (5)$$

Where ΔG is the free energy difference between the acceptor and the donor and E_0 is the energy of reorganization .The rate constant for electron transfer from a metal to a reactant at the interface is given by [15].

$$K_{ET} = \frac{2\pi}{\hbar} \int_0^\infty |H_{DA}(t)|^2 \frac{1}{(4E_{mol}^{met} k_B T)^{1/2}} F(E) e^{-\frac{(E_0 + \Delta G)^2}{4E_{mol}^{met} k_B T}} dE \dots \dots \dots (6)$$

Where $F(E)$ is the Fermi-Dirac distribution with E measured relative to the chemical potential of the electrons $F(E) = \frac{1}{1 + \exp \frac{E - E_F}{k_B T}}$ [16].

The expansion of $H_{DA}(E)$ is given by.

$$H_{DA}(E) = a_0 V_0 + a E + \dots \approx |V_0|^2 (1 + a E + b E^2 + \dots) \dots \dots \dots (7)$$

The integration of equation [6], with expansion in equation [7], can be written as.

$$K_{ET} = \frac{2\pi}{\hbar} \frac{e^{-\frac{E_{mol}^{met}}{4k_B T}}}{\sqrt{4\pi E_{mol}^{met} k_B T}} \int_{-\infty}^{+\infty} |H_{DA}(E)|^2 \frac{(1 + E^2 + E^4 + \dots)}{2(e^{2k_B T} + e^{-2k_B T})} e^{-\frac{-E^2 + F(E, \eta)}{4E_{mol}^{met} k_B T}} dE \dots \dots \dots (8)$$

Where $F(E, \eta) = 2(E_{mol}^{met} - E)\eta - e^2 \eta^2$, the result of solvent integral equation[8]

$$K_{ET} = \frac{2\pi}{\hbar} \frac{e^{-\frac{E_{mol}^{met}}{4k_B T}}}{\sqrt{4\pi k_B T}} |H_{DA}|^2 \left[\pi k_B T - \frac{\pi^3 k_B^3 T^3}{16 E_{mol}^{met}} + \frac{5\pi^5 k_B^5 T^5}{522 (E_{mol}^{met})^2} - \dots \right] \dots \dots \dots (9)$$

Using the first and second term that.

$$K_{ET} \cong \frac{2\pi}{\hbar} \frac{e^{-\frac{\lambda}{4k_B T}}}{\sqrt{4\pi k_B T}} |H_{DA}|^2 \left[\pi k_B T - \frac{\pi^3 k_B^3 T^3}{16 E_{mol}^{met}} \right] \dots \dots \dots (10)$$

Where \hbar is the planks constant, k_B is the Boltzmann' s constant, T the temperature , $|H_{DA}|$ is the coupling coefficient between two state system and E_{mol}^{met} is the free energy.

The reorganization energy for charge transfer at metal /molecule system a notification of Marcus theory exist which takes into account the electrostatic interaction between the metal and molecule is given by [17].

$$E_{mol}^{met} = \frac{q^2}{8\pi\epsilon_0} \left(\frac{1}{D} - \frac{1}{2R} \right) \left(\frac{1}{n^2} - \frac{1}{\epsilon} \right) \dots \dots \dots (11)$$

Where ϵ_0 is the vacuum permittivity , ϵ is the static dielectric constant of the solvent , n is the refractive index of the solvent , R is the distance between center to center , and D is the radius of the molecules.

The radii of molecules can be estimated from the apparent molar volume using spherical approach [18].

$$D = \left(\frac{3M}{4\pi N_A \rho} \right)^{\frac{1}{3}} \dots \dots \dots (12)$$

Where M is the molecular weight, N_A is the Avogadro's number, and ρ is the mass density.

Results

First-order perturbation theory and quantum theory treatment have been used to study the transitions of electron at metal/molecule system.

One of the important parameters for calculation and study of the rate constant of electron transfer at metal/molecule interface is the reorganization energies E_{mol}^{met} (eV).

It can be evaluated theoretically using equation [11], the first steps to calculate the reorganization energies E_{mol}^{met} (eV) involved which estimated the radii for donor metals and acceptor molecules using spherical approach equation [12], inserting the values of Avogadro's

construes $N = 6.02 \times 10^{23} \frac{\text{Molecule}}{\text{mol}}$, molecular weight M , and density mass ρ for all metals and molecules from tables (1) to (2) in equation [12], we can estimate the values of radii for metals and variety of molecules, results of calculation are listed in the table (2).

Next we can calculate the reorganization energy for metal / molecule system for Au metals donor, and (4-aminothiophenol), (3,4,10-perylenetetracarboxylic diimide), Pentacene, and naphthalene an acceptor molecules by substituting in equation [11], the values of acceptor radius D , dielectric constant ϵ optical dielectric constant ϵ_{op} for solvents from table (2) and assume the distance $R = D_D + D_A$ between center to center for donor and acceptor, knowing that $\frac{e^2}{8\pi\epsilon} = 7.2 \text{ eV}$, results of reorganization energy have been summarized in table (3).

Next, we calculated the rate constant of electron transfer at metal / molecule depending on Eq. [10], Inserting the results of the reorganization energy from table (3), and take the coupling coefficient $(91) \text{ cm}^{-1}$ [20]. Results are summarized in table (4)

Discussion

As depending on quantum theory, a first-order perturbation theory and quantum theory treatment have been used to study the transitions of electron at metal/molecule system.

The most important factor that limited the values of rate constant at metal/molecule system is the reorganization energy of electron transfer.

It is calculated according to continuum classical theory. These theoretical approaches are modeled in the sense that their physical concepts such as a refractive index, and static dielectric constant for donor acceptor system are determined.

Table (3) shows that the reorganization energy values for metal / molecule system increase with the increase of the dielectric constant for the solvent lead to decrease in rate compared with system having small reorganization energy, because the system has small value of reorganization energy more orient to transfer of electron.

On the other hand there is an increase in the refractive index for solvent leads to decrease in the reorganization energies for all metal / molecule systems.

The interactions of electron transfer should be affected by properties of organic solvent molecules, since these molecules have polarity parameter $[\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s}]$ which gives a less defined, the small polarity function results to decrease the reorganization energy and increase in rate of charge for system that shows a comparison between table(3), and table(4) for rate constant.

The more range dielectric constant for acceptor reduces the reorientation of the donor metal about acceptor molecule needed more energy. It has been observed from table (3) that when the refractive index of acceptor molecule is large leads to small energy to reorganize for system and large rate of transfer see table (4). Also, then in spite of these facts, the results showed in table (4) are depending on the active radii for both donor and acceptor respectively this means the rate dependence on distant.

Also, table (4) shows that when the solvent is more polar leads to have large value of the reorganization energy and small rate transfer, this is because of the type of solvents has large dielectric constant and small refractive index that is shown for 2,2,2-trifluoroethano solvent have $(\epsilon \approx 26.726)$ and refractive index $n = 1.2907$ have polarity range value of (0.5628) , and the reorganization energy are ranged $E_{mol}^{met}(\text{eV}) = 0.77748$, 0.565626 , 0.583684 , and 0.770667 eV for the Au/naphthalene, Au/3,4,10,perylene tetracarboxylic diimide, Au/pentacene, and Au/4,aminothiophenol interface system and rate $K_{ET} = 1.92 \times 10^{11}$, 2.25×10^{11} , 2.22×10^{11} , 1.93×10^{11}

On the other hand the xylene liquid has small polarity ≈ 0.0259 , this indicates that xylene have small dielectric constant 2.3879 and large refractive index 1.4995 , results to small

reorganization energy and large rate constant (8.88×10^{11} , 1.04×10^{12} , 1.02×10^{12} , 8.92×10^{11}) that are shown in table(4). That leads to opinion the reorganization energies are the key of the probability of electron transfer at metal / molecule interface.

Our results show a good agreement with experimental data ($7 \times 10^{11} - 4 \times 10^{12} \text{ sec}^{-1}$) [21].

Conclusions

In this study, we have investigated the electron transfer at metal/molecule interface system depending on quantum theory. The reorganization energy has been calculated depending on the semi classical continuum dielectric model based on classical electron transfer theory.

It can be concluded that electron transfer at metal/molecules interface system depends on the polarity from depending on both dielectric constant, and optical properties (refractive index).

Our results of the reorganization energy calculation indicate that electron transfer is more probable happen in the metal/molecules system have large polarity. It can be concluded that the metal/molecule with solvent system has large dielectric constant, leads to large reorganization energies for electron transfer, and the transitions involve more energy to happen. Also the increases of refractive index lead to small reorganization energy depending on the optical properties of solvent. Consequently the system has large E_0 refers that system has less electron reaction media than other system has small reorganization energy.

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Table No.(1): Properties and calculated radii of molecule[11]

Molecule	Molecule weight g. mol ⁻¹ [11]	density g. cm ⁻³ [11]	Radii calculated (A)
Pentacene	278.36	1.3	4.39534
Nphthalene	128.17	1.14	3.54594
3,4,10,perylene tetracarboxyl eicdiimide	390.35	1.68	4.51668
4-aminothiophenol	125.19	1.2	3.4586

Table No.(2): Properties of organic solvent[19]

Solvent type	Refraction index (n)	Dielectric constant (ε)
1,1,1-trichloroethane	1.4379	7.0826
Dichloroethane	1.4448	10.125
Hexanol	1.4178	12.51
Pentanol	1.4101	15.13
Butanol	1.3993	17.332
Nitropropane	1.4018	23.73
Trifluoroethanol	1.2907	26.726
Acetonitrile	1.3442	35.688
Dimethylsulfoxide	1.4170	46.826
formic acid	1.3714	51.1
N-methylformamide(E/Z mixture)	1.4319	181.56
Formamide	1.4472	108.94
Water	1.3328	78.355
xylene (mixture)	1.4995	2.3879
Dibromoethane	1.5387	4.9313

Table No.(3): Theoretical results of the reorganization energy for electron transfer at metal/ molecule interface system.

Solvent	Au/ nphthalene	Au/3,4,10,peryl enetetra carbox yleidii mide	Au/pentacene	Au/4,aminothiop henol
xylene(mixture)	0.035863	0.026091	0.026924	0.035549
Dibromoethane	0.303312	0.220663	0.227708	0.300654
1,1,1-trichloroethane	0.47306	0.344157	0.355144	0.468914
1,2- dichloroethane	0.525296	0.38216	0.39436	0.520694
1- hexanol	0.576749	0.419592	0.432987	0.571695
Pentanol	0.603394	0.438977	0.452991	0.598107
1- butanol	0.625758	0.455247	0.46978	0.620275
1- nitropropane	0.644732	0.46905	0.484024	0.639082
2,2,2- trifluoroethanol	0.77748	0.565626	0.583684	0.770667
Acetonitrile	0.72577	0.528007	0.544863	0.71941
Dimethylsulfoxide	0.658443	0.479025	0.494318	0.652673
formic acid	0.70742	0.514657	0.531086	0.701221
Water	0.75998	0.552895	0.570546	0.753321
Formamide	0.64685	0.470591	0.485614	0.641182
N-methylformamide (E/Z mixture)	0.666091	0.484589	0.500059	0.660254

Table No.(4) : Our theoretical results of electron transfer rate constant for metal/ moIecul interface system with variety solvent at the coupling coefficient H= 91 cm⁻¹

Solvent	Rate of electron transfer K _{ET} (sec ⁻¹)			
	Au/nephthalen	Au/3,4,10,pe rylenetetrac arboxyleicdi imide	Au/pentacene	Au/4- aminothiop henol
xylene(mixture)	8.88 ×10 ¹¹	1.04×10 ¹²	1.02×10 ¹²	8.92×10 ¹¹
Dibromoethane	3.08 ×10 ¹¹	3.61×10 ¹¹	3.55×10 ¹¹	3.09×10 ¹¹
1,1,1-trichloroethane	2.46 ×10 ¹¹	2.89×10 ¹¹	2.84×10 ¹¹	2.47×10 ¹¹
1,2- dichloroethane	2.34 ×10 ¹¹	2.74×10 ¹¹	2.7×10 ¹¹	2.35×10 ¹¹
1- hexanol	2.23×10 ¹¹	2.61×10 ¹¹	2.57×10 ¹¹	2.24×10 ¹¹
Pentanol	2.18 ×10 ¹¹	2.56×10 ¹¹	2.52×10 ¹¹	2.19×10 ¹¹
1- butanol	2.14 ×10 ¹¹	2.51×10 ¹¹	2.47×10 ¹¹	2.15×10 ¹¹
1- nitropropane	2.11 ×10 ¹¹	2.47×10 ¹¹	2.43×10 ¹¹	2.12×10 ¹¹
2,2,2- trifluoroethanol	1.92 ×10 ¹¹	2.25×10 ¹¹	2.22×10 ¹¹	1.93×10 ¹¹
Acetonitrile	1.99 ×10 ¹¹	2.33×10 ¹¹	2.29×10 ¹¹	1.99×10 ¹¹
Dimethylsulfoxide	2.09 ×10 ¹¹	2.45×10 ¹¹	2.41×10 ¹¹	2.09×10 ¹¹
formic acid	2.01 ×10 ¹¹	2.36×10 ¹¹	2.32×10 ¹¹	2.02×10 ¹¹
Water	1.94 ×10 ¹¹	2.28×10 ¹¹	2.24×10 ¹¹	1.95×10 ¹¹
Formamide	2.1 ×10 ¹¹	2.47×10 ¹¹	2.43×10 ¹¹	2.11×10 ¹¹
N-methylformamide	2.07×10 ¹¹	2.43×10 ¹¹	2.39×10 ¹¹	2.08×10 ¹¹

الانتقال الالكتروني لسطح معدن / جزيئة

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الخلاصة

انتقال الإلكترون في سطح معدن / جزيئة وصف نظريا تبعا" لنظرية الكم. الانموذج المشتق بالاعتماد على التقريب الاول لنظرية الاضطراب استعمل لحساب ثابت المعدل لسطح المعدن / جزيئة مع حساب الطاقة لإعادة التنظيم. طاقة اعادة التنظيم حسبت تبعا لانموذج الكروي الخارجي على اساس الجهد الكهروستاتيكي للجزيئات المانحة والمستقبلة. المعاملات الجزيئية التي أدخلت في هذا الانموذج هي الوزن الجزيئي والكثافة الكتلية، ونصف قطرها الجزيئي الذي حسب تبعا لحجم المولاري باستخدام التقريب كروي. النتائج النظرية المستحصلة وفقا لانموذج ثابت معدل الانتقال الالكتروني كانت متوافقه مقارنة مع النتائج العملية لبعض سطوح معدن/ جزيئة لدراسات تجريبية.

الكلمات المفتاحية: الانتقال الالكتروني، سطح معدن / جزيئة