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Theoretical Study of the Transfer Rate Constant for Electron at Metal /Liquid Interface.

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Abstract

A quantum transport in Cu/ TCNQ molecule liquid interface, the influence of reorganization energy coupling matrix element, and temperature are studied. For the tunneling transport description, reorganization energy and rate constant of electron transfer of Cu/ TCNQ molecule liquid interface system are calculated and the transmission through interface are examined. A theoretical model based on the quantum system is depending to study the transfer across Cu and TCNQ molecule. While on the interface system, classical reorganization energy equation using to evaluate the electrons energy to reorientation before transfer, the transition rates are calculated using quantum transport formalism. Our results data show that the rate constant $\Re_{ET}$increases with the increasing of the coupling coefficient and temperature, and decreasing of the reorganization energy $E_{\mathrm{met}}^{\mathrm{liq}}$.

Keywords: Theoretical study for transfer rate constant, electron transfer, metal/liquid interface.

دراسة نظرية لثابت معدل الانتقال الالكتروني عند سطح معدن /سائل

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الخلاصة

لنظام الانتقال الكمي عبر سطح Cu/ TCNQ وجزيئة سائل تم دراسة تاثير طاقة اعادة التنظيم وعناصر مصفوفة الازدواج و درجة الحرارة . كما تم وصف الانتقال على اساس الانتقال النفقي و طاقة اعادة التنظيم ومعدل الانتقال الالكتروني عبر نظام سطح معدن /سائلCu/ TCNQ إضافة الى اعتماد انموذج نظري وفقا لنظام كمي لدراسة الانتقال الالكتروني عبر سطح نظام Cu /TCNQ.بينما على سطح النظام استعملت المعادلة الكلاسيكية لطاقة اعادة التنظيم لتقييم طاقة اعادة التنظيم للإلكترونات قبل النقل ومعدلات النقل حسبت باستعمال صيغة انتقال كمية. نتائجنا اظهرت ان ثابت الانتقال للإلكترونات يتزايد بزيادة معامل الازدواج ودرجة الحرارة وبتناقص طاقة اعادة الالتحام لنظام معدن – جزيئة سائل.

الكلمات المفتاحية: دراسة نظرية لثابت معدل الانتقال، الانتقال الالكتروني، وصلة معدن–جزيئة

1- Introduction

Electron transfer (ET) 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 chemical and biological reactions. In general, reactions which involve the transfer of an electron are called redox reactions [1]. In this reaction an electron is transferred from an electron donor state $|\varphi_{\mathrm{D}}\rangle$ to an electron acceptor state$|\varphi_{\mathrm{A}}\rangle$, and a result a charge separated state is created consisting of the radical cat ion of the donor $|\varphi_{\mathrm{D}}{}^{+}\rangle$ and the radical anion of the acceptor$|\varphi_A{}^-\rangle$[2], that may be written in formula .

$$|\varphi_D\rangle + |\varphi_A\rangle \rightarrow |\varphi_D{}^+\rangle + |\varphi_A{}^-\rangle \qquad \dots\dots\dots (1)$$

The excitation, which renders well defined redox potential difference between two interacting species, facilitates transfer of an electron to generate radical ions . Electron transfer (ET) from a metal donor state to an acceptor molecule state is one of the simplest conceivable reactions, as chemical bonds are neither formed nor broken. Electron such charge transfer reactions are of vital importance to a variety of processes in physics, chemistry and biology. For example, homogeneous electron transfer is the primary step in photosynthesis, and various chemical reaction [3].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 nanoscale optoelectronics based on a single molecule or a small group of molecules. Although this is focuses on molecule-metal interfaces [4]. 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 [5]. Since the seminal work predicting dynamical of ET reaction in the early 1980's, a great deal of theoretical effort has gone into clarifying the dynamics of the electron transfer. 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 important for the change transfer across the organic-metal interface [6]. 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]. In this paper a theoretical description and studied of electron transfer at Cu/7,7,8,8-tetracyanoquinodimethaneTCNQ molecule liquid interface and will be calculated theoretically the rate constant for this transfer of electrons depending on the results of reorganization energy and coupling matrix element coefficient.

2- Mathematical model

For electron transfer between the localized quantum states for the donor state vector $|\psi_D^{et}\rangle$ and acceptor state vector $|\psi_A^{et}\rangle$ on solution side perturbs the energy between the electrode of metal and molecule liquid in solution and electron can tunnel to the acceptor state as shown in figure (1).

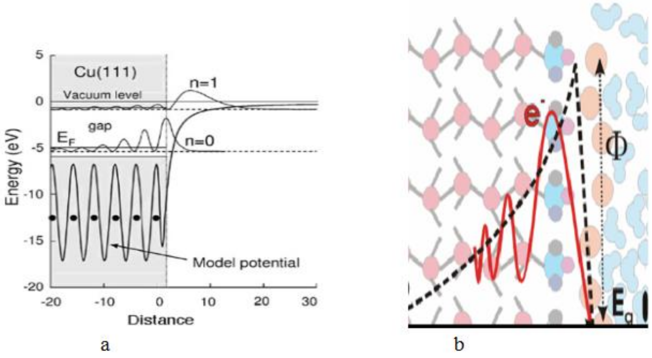


Figure (2-12): Schematic illustration of (a) model potential of electron transfer at band probability at the Cu /liquid[8],and (b) tunneling process[9].

Near equilibrium, the exchange of electrons occurs mainly near the Fermi level, but a reduced species can denote an electron to any empty level on the metal . The probability of the electron transfer from a discrete metal donor state to continuum molecule liquid acceptor state have been given by [10].

$$\Re_{ET} = \frac{2\pi}{\hbar}\int_{-\infty}^{\infty}|\mathcal{H}_{DA}(E)|^2(4\pi E_{met}^{liq}k_BT)^{\frac{-1}{2}} exp\frac{-(E_{met}^{liq}+\Delta V)^2}{4E_{met}^{liq}k_BT}F_{(E)}\delta(E_m-E_n)dE \qquad (1)$$

where ħ is the Planck constant divided to 2π, $|\mathcal{H}_{DA}(E)|^2$ is the coupling coefficient between the electronic state of the metal and the molecule of liquid ,E_{met}^{liq} is the reorganization energy ,k_B is the Boltzmann constant , T is absolute temperature ,and $F_{(E)}$ is the Fermi-Dirac probability distribution of the electrons in the electron metal-liquid interface and given by [11].

$$F_{(E)} = (1 + exp^{\frac{E}{k_BT}})^{-1} \qquad (2)$$

At the interface of metal/liquid system the probability of electron transfer rate constant can be evaluated by substituting Eq.(2) in Eq.(1),and solvent the integration Eq.(1) ,results[12].

$$\Re_{ET} = \frac{2\pi}{\hbar}(4\pi E_{met}^{liq}k_BT)^{\frac{-1}{2}} \exp - \frac{E_{met}^{liq}}{4k_BT}|\overline{\mathcal{H}_{DA}(0)}|^2\Bigg[[1 - \frac{1}{4E_{met}^{liq}k_BT}\left(\frac{(\pi k_BT)^2}{4}\right) + \frac{1}{32E_{met}^{liq}{}^2k_B{}^2T^2}\left(\frac{5(\pi k_BT)^4}{16}\right) - \frac{1}{384E_{met}^{liq}{}^3k_B{}^3T^3}\left(\frac{61(\pi k_BT)^6}{64}\right)\dots\dots\dots\dots + \frac{1}{n!\left(4E_{met}^{liq}k_BT\right)^n}(\propto (\pi k_BT)^{2n})\Bigg] \qquad (3)$$

The reorganization energy E_{met}^{liq} due to the electron transfer reaction for metal/liquid interface is given by [13].

$$E_{met}^{liq} = \frac{e^2}{8\pi\varepsilon_o} f(n,\varepsilon)(\frac{1}{R} - \frac{1}{2D}) \quad (4)$$

where e is the electron charge, ε o 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 $f(n,\varepsilon)$ that given by.

$$f(n,\varepsilon) = (\frac{1}{n^2} - \frac{1}{\varepsilon}) \quad (5)$$

Where ε 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 [14].

$$R = (\frac{3M}{4\pi N\rho})^{\frac{1}{3}} \quad (6)$$

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

3- Results and discussion

Theoretical description and studied of electron transfer at donor–acceptor system pending on many important parameter are dependent on many parameters such that; transfer rate constant $\Re_{ET}$, reorganization energy E_{met}^{liq}, and electronic coupling coefficient $\mathcal{H}_{DA}(0)$.

To known the behavior of electron across interface Cu/ Molecule liquid ,we can evaluated the rate of electron transfer $\Re_{ET}$depending on calculation of the reorganization energy$E_{met}^{liq}(eV)$ and the values of the coupling coefficients $\mathcal{H}_{DA}(0)$for metal and molecule liquid .

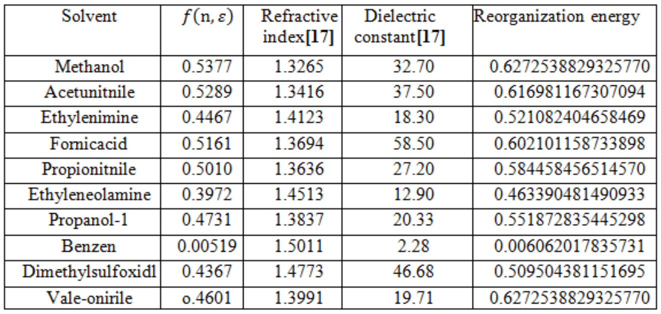
One of the calculation of the reorganization energy$E_{met}^{liq}(eV)$,that's must be estimation radius for Cu metal ,and 7,7,8,8-tetracyanoquinodimethaneTCNQ molecule liquid from Eq.(6) by inserting the values of Avogadro's constant $N = 6.02 \times 10^{23} \frac{Molecule}{mol}$,molecular weight M=204.19 g/mole[15], and density $\rho = 1.358\ g/cm^3$[16] for 7,7,8,8-tetracyanoquinodimethaneTCNQ molecule and M =$63.546 g.mol^{-1}$, and ρ = for$8.92 g.cm^{-3}$ for Cu metal [17] in Eq.(6), we can estimate the values of radii for metals and TCNQ molecule respectively.

Reorganization energies for Cu/ TCNQ molecule liquid interface can be calculated according to Eq.(4) and Eq.(5) ,with the values of the static dielectric constant ε , and optical dielectric constantϵ_{op} ,for solvents from Table (1), and radii estimation of the Cu metal and TCNQ molecule ,result are tabulated in Table(2).

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

Solvent	Refractive index[17]	Dielectric constant[17]
Methanol	1.3265	32.70
Acetunitnile	1.3416	37.50
Ethylenimine	1.4123	18.30
Fornicacid	1.3694	58.50
Propionitnile	1.3636	27.20
Ethyleneolamine	1.4513	12.90
Propanol-1	1.3837	20.33
Benzen	1.5011	2.28
Dimethylsulfoxidl	1.4773	46.68
Vale-onirile	1.3991	19.71

Table(2): The reorganization energy $E_{met}^{liq}(eV)$ for electron transfer at Cu/ TCNQ molecule interface system.



Solvent	$f(n,\varepsilon)$	Refractive index[17]	Dielectric constant[17]	Reorganization energy
Methanol	0.5377	1.3265	32.70	0.6272538829325770
Acetunitnile	0.5289	1.3416	37.50	0.616981167307094
Ethylenimine	0.4467	1.4123	18.30	0.521082404658469
Fomicacid	0.5161	1.3694	58.50	0.602101158733898
Propionitnile	0.5010	1.3636	27.20	0.584458456514570
Ethyleneolamine	0.3972	1.4513	12.90	0.463390481490933
Propanol-1	0.4731	1.3837	20.33	0.551872835445298
Benzen	0.00519	1.5011	2.28	0.006062017835731
Dimethylsulfoxidl	0.4367	1.4773	46.68	0.509504381151695
Vale-onirile	o.4601	1.3991	19.71	0.6272538829325770

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) , and the matrix element coupling coefficient $\mathcal{H}_{DA}(0) = 0.01115, 0.01177, 0.01239$,and 0.01363eV [18], and temperature is taken depending on experimental T= 250,300 ,and 350K ,results have been summarized in Table(3).

Table(3):Data of the rate constant calculation for electron transfer at Cu / TCNQ molecule liquid interface with variety coupling coefficient H_DA (0) ,at T= 250,300 ,and 350K.

Solvent	Rate constant $\mathfrak{R}_{ET}$(Sec^{-1}) at $\mathcal{H}_{DA}(0) = 0.01115$ eV			Rate constant $\mathfrak{R}_{ET}$(Sec^{-1}) at $\mathcal{H}_{DA}(0) = 0.01177$eV			Rate constant $\mathfrak{R}_{ET}$(Sec^{-1}) at $\mathcal{H}_{DA}(0) = 0.01239$ eV			Rate constant $\mathfrak{R}_{ET}$(Sec^{-1}) at $\mathcal{H}_{DA}(0) = 0.01363$eV		
	T=250	T=300	T=350	T=250	T=300	T=350	T=250	T=300	T=350	T=250	T=300	T=350
	$\times 10^8$	$\times 10^9$	$\times 10^9$	$\times 10^8$	$\times 10^9$	$\times 10^9$	$\times \mathbf{10^8}$	$\times 10^9$	$\times 10^9$	$\times 10^8$	$\times 10^9$	$\times 10^9$
Methanol	3.3405	1.2242	3.1296	3.7224	1.3641	3.4873	4.1249	1.5116	3.8644	4.9918	1.8294	4.6766
Acetunitnile	3.7307	1.3402	3.3778	4.1571	1.4934	3.7639	4.6066	1.6549	4.1709	5.5748	2.0028	5.0475
Ethylenimine	10.379	3.0963	6.8320	11.565	3.4502	7.6129	12.816	3.8233	8.4360	15.510	4.6269	1.0209
Fomicacid	4.3769	1.5277	3.7717	4.8772	1.7023	4.2028	5.4045	1.8864	4.6573	6.5405	2.2829	5.6361
Propionitnile	5.2873	1.7835	4.2967	5.8917	1.9873	4.7879	6.5287	2.2022	5.3056	7.9009	2.6651	6.4207
Ethyleneolamine	19.045	5.0798	1.0345	21.222	5.6604	11.528	23.517	6.2725	12.774	28.460	7.5908	1.5459
Propanol-1	7.4859	2.3705	5.4587	8.3415	2.6415	6.0827	9.2435	2.9271	6.7404	11.186	3.5423	8.1571
Benzen	43357.0	8454.8	14808	48312	9421.2	16500	53536	10439	1828.5	64788	12634	22128
Dimethylsulfoxidl	11.7311	3.4218	7.4298	13.072	3.8129	8.2790	14.485	4.2252	9.1742	17.530	5.1132	11.102
Vale-onirile	8.79319	2.7039	6.0971	9.7982	3.0130	6.7940	10.857	3.3388	7.5286	13.139	4.0405	9.1110

Our results show that the rate constant $\mathfrak{R}_{ET}$increases with the increasing of the coupling coefficient and temperature, and decreasing of the reorganization energy E_{met}^{liq} . A quantum transport in Cu/ TCNQ molecule liquid interface and the influence of reorganization energy coupling matrix element ,and temperature are studied. Transfer of electron across Cu/ TCNQ interface system had been studied depending on quantum transport theory . Many parameters influence of these transfer such that: the reorganization energy ,coupling matrix element ,and temperature are studied . Probability of electron transport $\mathfrak{R}_{ET}(\mathrm{Sec}^{-1})$ by the tunneling due to the interface created between metal and molecule in Cu/ TCNQ system depends on the reorganization energy E_{met}^{liq}(eV), temperature and the coupling coefficient $|\mathcal{H}_{DA}(E)|$(eV) . Reorganization energy E_{met}^{liq}(eV) of the electron transfer should be effected on the probabilities of rate constant $\mathfrak{R}_{ET}(\mathrm{Sec}^{-1})$at metal/molecule system. It is evaluated the electrons energy to reorientation before transfer depending on classical reorganization energy equation for Marcus under the physical concepts such as a refractive index, and static dielectric constant for donor/ acceptor system. Results of the reorganization energy in Table(2) for Cu/ TCNQ system is be effected by polarity parameter for the solvent molecules. The reorganization energy E_{met}^{liq}(eV) is large for large polarity function and vice versa, this indicates that the reorganization energyE_{met}^{liq}(eV) is a function for the polarity of the solvent. On the other hand the rate constant $\mathfrak{R}_{ET}(\mathrm{Sec}^{-1})$values are large for system with lest polarity function and increases with decreases of the reorganization energy, this indicates that Benzen, Ethyleneolamine ,and Dimethylsulfoxidl are more reactive towards Cu/ TCNQ system than others solvents and electron transfer occur activity with less polarity solvents. Next the controlling of the probability to transfer of electron is the coupling coefficient matrix element $|\mathcal{H}_{DA}(E)|$(eV), that describe the overlapping between of the wave functions for both Cu and TCNQ state ,that's taken in the range $\mathcal{H}_{DA}(0) = 0.01115 , 0.01177, 0.01239$,and 0.01363eV [18] for metal/molecule system depending on the experimental data .At interface between metal and molecule , the wave functions for metal and molecule overlapping and electron can be transfer due tunneling . However ,if the electron tunneling occurs, the initial and final electronic states should have approximated equal energies that happen under the considering continuum of electronic states for the metal/molecule system interfaces .These electronic states are brought into resonance by fluctuations of polar medium surrounding metal and molecule system and this resonance is the transition state of electron transfer reaction. From Table(3),we can show that , the rate constant of electron in Cu/ TCNQ system is increasing with increasing the coupling coefficient and vice versa . Also ,we can find from data in Table (3) , the rate is increasing with increases of the temperature ,this indicate that increasing temperature drive more electrons to cross the tunneling at interface of the Cu/ TCNQ system. Data in Table (3) and Eq.(3) 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$E_{met}^{liq}(eV)$,temperature and the coupling coefficient energy are the base 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.

4- Conclusions

In summary the quantum transport probability in Cu/ TCNQ system depending on the reorganization energy $E_{met}^{liq}(eV)$, temperature(K) , and the coupling coefficient $|\mathcal{H}_{DA}(E)|(eV)$ .Reorganization energy $E_{met}^{liq}(eV)$ of the electron transfer should be effected on the probabilities of rate constant $\mathfrak{R}_{ET}(Sec^{-1})$at Cu/ TCNQ system. The rate constant $\mathfrak{R}_{ET}(Sec^{-1})$ are large for system with lest polarity function and increases with decreases of the reorganization. Probability to transfer of electron depends on the coupling coefficient scale of the overlapping between the wave functions for both Cu and TCNQ states that limited the transfer across tunneling created between Cu and TCNQ . Rate constant $\mathfrak{R}_{ET}$increases with the increasing of the coupling coefficient . The rate is increased with increases of the temperature ,this indicate that the increasing temperature drive more electrons to cross the tunneling at interface of the Cu/ TCNQ system.

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