Investigating of Charge Transfer in Cu/ F8 Using Donor-Acceptor Model due Quantum Transition

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Abstract. In this paper, we study and investigate a simple donor-acceptor model for charge transfer formation using a quantum transition theory. The transfer parameters which enhanced the charge transfer and the rate of the charge transfer have been calculated. Then, we study the net charge transfer through interface of Cu/F8 contact devices and evaluate all transfer coefficients. The charge transfer rate of transfer processes is found to be dominated in the low orientation free energy and increased a little in decreased potential at interface comparison to the high potential at interface. The increased transition energy results in increasing the orientation of Cu to F8. The transfer in the system was more active when the system has large driving force energy and caused fast transfer from the donor to the acceptor and the charge transfer rate dependent on potential and solvents effect.

Keywords: Charge Transfer, Cu/ F8, orientation energy

1. Introduction
The charge transfer at level energy of a molecule has been played a basic role in different areas of physics, chemistry, material science, and biology [1]. Charge transfer was important fundamental process in electronics devices. The charge transfers from the molecule to the solid cross potential at interface. This transfer changes the electronic distribution by rearrangement of molecules and atoms [2]. In recent years, more attention of the charge transfer at interface between two different materials. Field of charge transfer in materials introduced more knowledge to understand and characterize the mechanisms of charge transition through interfaces such that molecule/semiconductor, molecule/molecule and molecule/metal interfaces [3]. The basic concept for describing the electronic transfer in solid contact with liquid has defined by the classical charge transfer theory that introduced by Marcus R. A. in 1992, it's still an actively field research after more than 60 years ago and developed by Rudolph Marcus, Levich, Dogonadeze and Gerischer [4]. The interface of contact organic active with metallic is very an importance to investigated and study electron transfer and determined the efficiency of the metal/ molecule through study the orbital levels of dye alignment with Fermi levels for metal [5]. The characteristic of electronic transfer at metal contact with the organic molecule are depending on the alignment of energy levels of electrons at molecule and the bands levels at metal [6]. In this research the theoretical system Cu/ F8 device include study the charge
transfer and determine the rate of the charge transfer. For Cu/ F8 system, the transition energy, potential and current electronic transfer will be present.

2. Theory
The non-adiabatic rate of electron transfer is [7].

\[ k_{nd} = \frac{2\pi}{\hbar} |R_c|^2 WFC \]  

(1)

Where \( \hbar \) is the \( \frac{\hbar}{2\pi} \), \( h \) is Blank constant, \( R_c \) is the resonance coupling of electronic term and WFC is the Franck–Condon weight. However, the Franck–Condon weight \( WFC = \delta(E_{\beta f} - E_{\alpha g}) \), the non-adiabatic rate with summed over all probability of vibrational quantum levels can be written as.

\[ k_{nd} = \frac{2\pi}{\hbar} \sum g(E) |\langle \hat{R}_c \rangle|^2 \delta(E_f - E_i) \]  

(2)

\( g(E) \) is the distribution of electronic density of state and given by Fermi density of state [8].

\[ g(E) = \frac{1}{1 + e^{\frac{E - E_F}{kT}}} \]  

(3)

Where \( E = E_i - E_f \). Inserting Eq.(3) in Eq.(2)

\[ k_{nd} = \frac{2\pi}{\hbar} \sum \frac{1}{1 + e^{\frac{E - E_F}{kT}}} |\langle \hat{R}_c \rangle|^2 \delta(E_f - E_i) \]  

(4)

Introduce the total density \( D_{(E)} \) for all states of system

\[ k_{nd} = \frac{2\pi}{\hbar} \sum \frac{1}{1 + e^{\frac{E - E_F}{kT}}} |\langle \hat{R}_c \rangle|^2 D_{(E)} \delta(E_f - E_i) \]  

(5)

However, the activity density of metal-molecule system is equivalent to \( \delta(E_f - E_i) \), then Eq.(5) can be written.

\[ k_{nd} = \frac{2\pi}{\hbar} \sum \frac{1}{1 + e^{\frac{E - E_F}{kT}}} |\langle \hat{R}_c \rangle|^2 D_{(E)} \rho_a(E) \]  

(6)

Then, active density of states for charge transition interaction is [9]

\[ \rho_a(E) = \rho_M(E) = \frac{l_M}{d_M^{2/3}(\frac{6\pi}{\hbar})^{2/3}} \]  

(7)

here \( l_M \) is the length coupling and \( d_M(\frac{cm}{atom}) \) is average diameter in lattice for metal. Thus, Eq.(7) and Eq.(6) lead to.

\[ k_{nd} = \frac{2\pi}{\hbar} \sum \frac{1}{1 + e^{\frac{E - E_F}{kT}}} |\langle \hat{R}_c \rangle|^2 D_{(E)} \rho_M(E) \frac{l_M}{d_M^{2/3}(\frac{6\pi}{\hbar})^{2/3}} \]  

(8)

Due to Drude theory, the density of metal states per electron concentration is [10].

\[ \rho_M(E) = \frac{1}{2E_F} \]  

(9)

Where \( E_F \) is the Fermi energy. Substituting Eq.(9) in Eq.(8) results

\[ k_{nd} = \frac{2\pi}{\hbar} \sum \frac{1}{1 + e^{\frac{E - E_F}{kT}}} |\langle \hat{R}_c \rangle|^2 D_{(E)} \left( \frac{3}{2E_F} \right) \frac{l_M}{d_M^{2/3}(\frac{6\pi}{\hbar})^{2/3}} \]  

(10)

the density of state given [11].

\[ D_{(E)} = \frac{1}{4\pi l_k T} \frac{e^{-(l - \Delta E)^2}}{4l_k T} \]  

(11)

For all electrons in the donor-acceptor interface, we inserting Eq.(11) in Eq.(10) and integrated the results.

\[ k_{nd} = \frac{2\pi}{\hbar} \sqrt{\frac{3}{4\pi l_k T}} \frac{l_M}{d_M^{2/3}(\frac{6\pi}{\hbar})^{2/3}} \int_{-\infty}^{\infty} |\langle \hat{R}_c \rangle|^2 \frac{e^{-(l - \Delta E)^2}}{4l_k T} dE \]  

(12)

Where the \( \Delta E^0 = E_f - E_I \). The potential at interface of system is.

\[ \Delta U = \frac{(E_f - E_I + \Gamma)^2}{4\Gamma} \]  

(13)

The Fermi factors can be simply
\[
\frac{1}{k} = e^{-\frac{E}{kT}} \quad (14)
\]

Inserting Eq.(14) in Eq.(13)

\[
k_{nd} = \frac{2\pi}{h} \sqrt{\frac{1}{4\pi\hbar k_{B}T}} \left( \frac{3}{2E_{F}} \right) \frac{l_{M}}{d_{M}^{2/3}} e^{\frac{-(\tau_{I}+\Delta\delta)^2}{4k_{B}T}} \int_{-\infty}^{\infty} \langle \hat{R}_{C} \rangle^{2} e^{-\frac{E}{k_{B}T} + \frac{E}{2k_{B}T}} dE \quad (15)
\]

The \( e^{-\frac{E}{k_{B}T}} \) can be expand to

\[
e^{-\frac{E}{k_{B}T}} = 1 - \frac{E}{2k_{B}T} + \frac{1}{2!} \left( \frac{E}{2k_{B}T} \right)^{2} \ldots \ldots \ldots + \frac{1}{n!} \left( \frac{E}{2k_{B}T} \right)^{n} \quad (16)
\]

Then Eq.(15) with Eq.(16) reduced to

\[
k_{nd} = \frac{2\pi}{h} \sqrt{\frac{1}{4\pi\hbar k_{B}T}} \left( \frac{3}{2E_{F}} \right) \frac{l_{M}}{d_{M}^{2/3}} e^{\frac{-(\tau_{I}+\Delta\delta)^2}{4k_{B}T}} \int_{-\infty}^{\infty} \langle \hat{R}_{C} \rangle^{2} e^{E_{F}} \left[ 1 - \frac{1}{2!} \left( \frac{E}{2k_{B}T} \right) \right] dE \quad (17)
\]

The Eq.(17) simply to

\[
k_{nd} = \frac{2\pi}{h} \sqrt{\frac{1}{4\pi\hbar k_{B}T}} \left( \frac{3}{2E_{F}} \right) \frac{l_{M}}{d_{M}^{2/3}} e^{\frac{-(\tau_{I}+\Delta\delta)^2}{4k_{B}T}} \int_{-\infty}^{\infty} \langle \hat{R}_{C} \rangle^{2} \left[ \int_{-\infty}^{\infty} E dE \right] e^{E_{F}} dE \quad (18)
\]

We solved term by term to get

\[
k_{nd} = \frac{2\pi}{h} \sqrt{\frac{1}{4\pi\hbar k_{B}T}} \left( \frac{3}{2E_{F}} \right) \frac{l_{M}}{d_{M}^{2/3}} e^{\frac{-(\tau_{I}+\Delta\delta)^2}{4k_{B}T}} \left[ \pi k_{B}T + \frac{1}{2!} \left( \frac{E}{2k_{B}T} \right)^{2} (\tau k_{B}T)^{3} + \frac{4}{4!} \left( \frac{E}{2k_{B}T} \right)^{4} (\tau k_{B}T)^{5} \right] \quad (19)
\]

The electronic transfer rate per electronic density of metal \( N(E_{F}) \)

\[
K_{nd} = \frac{k_{nd}}{N(E_{F})} \quad (20)
\]

Inserting Eq.(20) in Eq.(19) and taken two term approximation

\[
k_{nd} = \frac{2\pi}{N_{M}(E_{F})} \sqrt{\frac{1}{4\pi\hbar k_{B}T}} \left( \frac{3}{2E_{F}} \right) \frac{l_{M}}{d_{M}^{2/3}} e^{\frac{-(\tau_{I}+\Delta\delta)^2}{4k_{B}T}} \left[ \pi k_{B}T + \frac{1}{2!} \left( \frac{E}{2k_{B}T} \right)^{2} (\tau k_{B}T)^{3} \right] \quad (21)
\]

The transfer energy \( \Gamma(\varepsilon V) \) for charge transfer processes is given by [12].

\[
\Gamma(\varepsilon V) = \frac{q^{2}}{8\varepsilon_{0}c} \left[ 1 - \frac{1}{2} \left( \frac{\varepsilon_{r}}{\varepsilon_{r} - 1} \right) \right] \quad (22)
\]

where \( q \) is charge electron, \( \varepsilon_{0} \) is the permittivity of vacuum ,\( \varepsilon \) and \( n \) are the dielectric constant and refractive index of solvent, \( r \) is the distance between dye and metal, \( R \) is the radius of dye can be estimated from the approach [13].

\[
R = \left( \frac{3M}{4\pi N_{D}} \right)^{1/2} \quad (23)
\]

where the molecular weight is \( M \) , Avogadro’s number is \( N \) and \( \rho \) is the density of material. The driving force energy for charge transfer from donor state to an acceptor state when photons incident on the system is given by

\[
\Delta E = E_{in} - \Gamma(\varepsilon V) \quad (24)
\]

Where \( E_{in} = h \frac{c}{\lambda} \) incident energy by light, \( c \) is speed of light and wavelength \( \lambda \)
3. Results

Based on the theory of charge transfer, we calculate the charge transfer rate in Cu/F8 device according to transfer energy, Fermi energy, ionization energy, coupling constant and potential at interface for two materials. The transfer energy in Eq (22) refers to effect of solvent, molecule and metal. The charge transfer rate in Cu/F8 device has been studied and calculated using theoretical model for identical state of electrons. The rate expression in Eq. (21) is theoretical tools for study the mechanism and behavior of charge transfer. In general, Eq. (22) could be used to evaluation the transition energy for the system using MATLAB program. The radii of F8 and Cu are estimated using Eq. (23) with inserting the molecular weight M, and mass density for materials (F8 and Cu) from the table (1) in Eq.(23) with Avogadro's constant $N = 6.02 \times 10^{23}$ Molecule $mol^{-1}$, the results of radii are show in Table (1) and (2).

### Table 1. Physical properties of Cu.

| Properties          | Cu metal [14] |
|---------------------|---------------|
| Molecular weight g/mol | 63.546        |
| Mass Density (g/cm$^3$) | 8.96          |
| Boiling Point (K)    | 2840          |
| Atomic Radius (Å)    | 1.28          |
| Lattice Structure    | Face-Centered Cubic |
| Lattice constant(Å)  | 3.610         |
| Radius (Å)           | 1.28          |
| Work function        | 4.61 ± 0.04   |
| Melting point (°C)   | 1357.77       |
| Fermi energy (eV)    | 7.0           |

### Table 2. The properties of F8 molecule dye.

| F8                  |
|---------------------|
| CAS                 | 19456-48-5      |
| Molecular Formula   | (C$_{29}$H$_{41}$)$_n$ |
| Molar Mas g/mol     | 114,050         |
| Density g/cm$^3$    | 1.564           |
| Radius cm           | $5.181 \times 10^{-8}$ |
| Index of Refraction | 1.736           |
| Melting point °C    | 250.4           |
| Ionization energy(eV)| 5.8             |
| HOMO (eV)           | 5.9eV           |
| LUMO(eV)            | 3.3eV           |
| Vapor Pressure(mmHg at 25°C)| 0.00508 |
| Name                | Poly(9,9-di-n-octylfluorenyl-2,7-diyl) (F8) |

Transition energy $\Gamma$(eV) for charge transfer processes has been calculated using Eq. (22) with MATLAB program. Its inserting the radii $R$ for F8 molecule and the distance $D(m)=R(Cu)+R(F8)$ from table (1) and (2) and the dielectric constants and refractive index for the solvents from the table (3), results are shown in the table (3) for Cu/F8.
According to theory, the rate of charge transfer has evaluated using Eq.(21) with different solvents using MATLAB with all parameters of charge transfer processes the transition energy from table (3).
taken Fermi energy, ionization energy, and taken coupling \( \left( R_e \right)^2 = \text{2.25, 2.5, 2.75, 3.0, 3.25, 3.5, and 3.75} \times 10^{-2} \text{ eV/ state} \) [16], results of the calculation of current are listed in table (6) for Cu/F8.

| Solvent type            | The charge transition rate constant \( x10^{-24} \) | Strength coupling \( \left( R_e \right) \times 10^{-2} \text{ eV/ state} |
|------------------------|--------------------------------------------------|-------------------------------------------------|
| 1-bromooctane          | 2.99E-13                                         | 2.5    | 3.75 | 5.27E-13 | 6.25E-13 | 7.24E-13 | 8.32E-13 |
| 2-methylpyridin        | 2.75E-07                                         | 3.4E-07| 4.11E-07 | 4.9E-07 | 5.75E-07 | 6.66E-07 | 7.65E-07 |
| 2-Hexanone             | 0.021558                                         | 0.026615 | 0.032205 | 0.038326 | 0.04498 | 0.052166 | 0.059885 |
| Acetone                | 2.027632                                         | 2.50325 | 3.028932 | 3.60468 | 4.230492 | 4.90637 | 5.632312 |
| Bezonitrile            | 0.000134                                         | 0.000166 | 0.000201 | 0.000239 | 0.000281 | 0.000325 | 0.000374 |
| Propanonitrile         | 3.734418                                         | 4.610393 | 5.578575 | 6.638966 | 7.791564 | 9.03637 | 10.37338 |
| Nitrobenzene           | 0.001839                                         | 0.002271 | 0.002748 | 0.00327 | 0.003838 | 0.004451 | 0.005109 |
| 1,2-ethanediol         | 0.186316                                         | 0.23002 | 0.278324 | 0.331228 | 0.388733 | 0.450838 | 0.517544 |
| dimethylsulfoxide      | 0.519366                                         | 0.641193 | 0.775843 | 0.923317 | 1.083615 | 1.256737 | 1.442683 |

### 4. Discussion

Understanding and calculated of charge transition rate at the interface of Cu/F8 is an important key prerequisite for investigated and studied the electronic properties of the Cu/F8 devices. However, the characterize of the mechanisms and charge transfer rates needs to understand the transition energy, energy level alignment, potential, driving force and electronic strength coupling between Cu metal and F8 molecule. This indicate that transition energy is the scale parameters of charge transfer processes. The transition energy in table (3) indicate that the system with Propanonitrile solvent has transition energy 0.402805 eV while the system with 1-bromooctane solvent has transition energy 0.21983 eV, this indicate the system with Propanonitrile is less active to charge transfer compare with other solvents. The gap between the transition energy of solvents between the top solvent and bottom solvent are in range (0.21983 eV to 0.402805 eV), the system with low transition energy enhances more transfer compare with large transition energy because low transition energy acting to forming charge transfer states fastly compare with large transition energy and lead to driving more charge cross from donor to acceptor state. To date, the potential and transition energy of charge transfer interaction between metal and molecules are used to study device structure hasn’t been properly characterized. Unlike the driving force energy fore system in table (4) with 1-bromooctane solvent in range 3.9134 to 1.3301eV comparing with Propanonitrile solvent in range 3.7304 to 1.1471eV order, when the driving force energy is large that’s indicate the charge will transfer cross interface, there is mean the charge transfer rate is large and potential is small. The Cu/F8 system with solvents fall into two categories, low polarity solvent and high polarity solvents.

Table (5) show the potential energy and transition energy for Cu/F8 devices with solvents, the system has small potential 0.695464 with Propanonitrile and high potential 2.4569 with 1-bromooctane solvents, this indicate the potential states formed at interface by the \( \pi^* \) orbitals similar in chromophore types forcedly with solvents has low polarity function. This lead to assume that charge transfer happened as well as from the donor state to acceptor state when potential is low, that shown in table (6). Additionally, the charge transfer increased due to increase the electronic coupling of transition interactions to be observed.

### 5. Conclusions

The calculation of rate gives details on the charge transfer dynamics cross interface. Theoretical calculation of charge transfer rate has described in this account and became a good tool to examine the system before made any devices through recent theoretical calculation of charge transfer rate. Transition energy, driving force with potential are of particular value for limited the slow or fast charge transfer processes through different of individual events dynamical polarity, such as the low
and large transition energy, large transfer for system has more driving force energy from the donor to acceptor, potential dependent of the quantum charge transfer rates, and solvents effect. The theoretical description of the charge transfer at interface created an intuitive scenario that appeals to Cu/F8 devices and gives a clear understanding of the effects of charge transfer characteristic on charge transfer rate, the structure of devices, electrical properties, and charge transfer interactions that occur cross interface.

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