

Marcus Theory for Electron Transfer a short introduction

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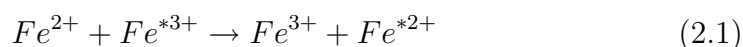
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1 Intro

Electron transfer (ET) is one of the most important chemical process in nature and it plays a central role in many biological, physical and chemical (both organic and inorganic) systems. In nature ET occurs in photosynthetic reaction center where transfer of electrons is used to create charge imbalance across a membrane, originating a proton pumping mechanism to produce ATP. In chemical system, ET at the metal surface with oxygen is responsible of the corrosion. Solid state electronics depends on the control of the ET in semiconductors and the new area of molecular electronics depends critically on the understanding and the control of the transfer of electrons in and between molecules. Figure 1 shows some fields related to the ET.

2 History and Concepts

The main contribute to the ET theory comes from Marcus, Nobel for the chemistry in the 1992, which has given a first formulation of the theory in 1956[1]. Early experiments in the electron transfer field were on “isotopic exchange reactions” (self-exchange reactions) and later “cross reactions”. Equation 2.1 shows a typical self exchange process, where the asterisk denote a radioactive isotope.



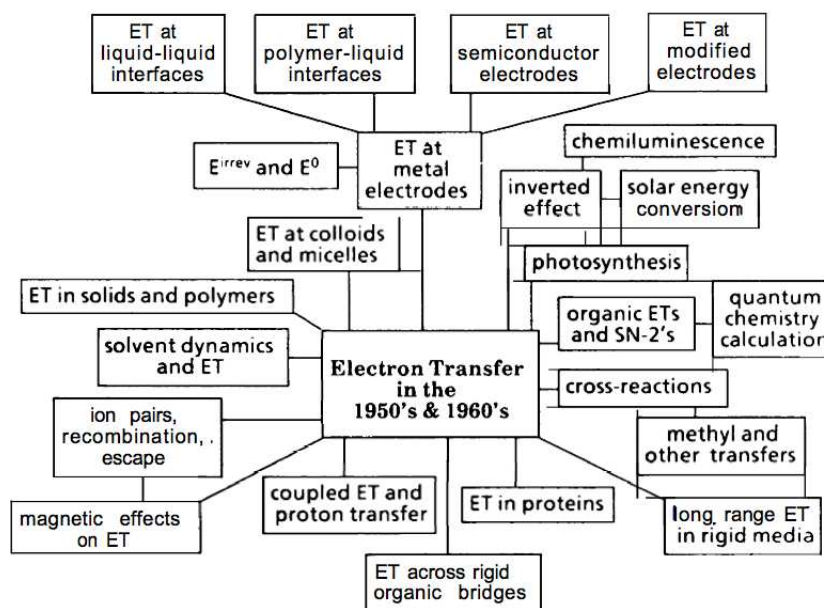


Figure 1.1: Examples of topics in the electron transfer field.

These experiments originate by the huge amount of radioactive isotopes available after the Second World War and by the introduction of new instrumentation which permitted to study the rates of rapid chemical reactions such the electron transfer. Before 1940s only slow electrochemical reactions, such as the discharge of an H_3O^+ ion at an electrode to form H_2 , had been investigated extensively.

For Marcus the inspiration to develop his theory was a paper of Bill Libby in which Franck-Condon principle was used to explain why reactions, as in eq. 2.1, between pairs of small cations in aqueous solution are relatively slow with respect the same electron transfer reactions involving larger ions, such as $Fe(CN)_6^{4-}$. In contrast with the classical chemical reaction (eq. 2) in simple electron transfer reactions no chemical bonds are broken or formed, so a different picture is needed for the reaction-rate for electron transfer.



2.1 Frank-Condon principle applied to Electron Transfer

In his paper in 1952 Libby noted that when an electron transfer from one reacting ion or molecule to another, the two new ions or molecules formed

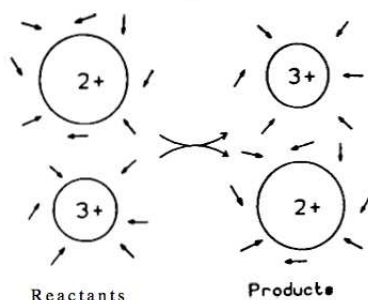


Figure 2.1: Typical nuclear configurations for reactants, products and surrounding solvent molecules in reaction 2.1. The longer M-OH₂ bond length in the state +2 is indicated schematically by the larger ionic radius.

are in the wrong environment of the solvent molecules since the nuclei do not have time to move during the fast electron jump. Looking at the electron transfer reaction 2.1, after the electron jump the Fe²⁺ ion would be formed in some configuration of the many nearby dipolar solvent molecules that was appropriate to the original Fe³⁺ ion. This introduces a “solvation energy barrier” for the process (Figure 2.1). The “solvation energy barrier” is not the only mechanism playing an important role in the electron transfer reaction rate: the self exchange reaction 2.3 involves big ions but the experimental rate for the reaction is really slow, in contrast to the picture of a ET governed by the “solvation energy barrier”.



The missing ingredient to explain the slow rate of the reaction 2.3 is the fact that there is a dramatic difference in the equilibrium Co-N bond length in the 3+ and 2+ ions so that each ion would be formed in a very “foreign” configuration of the vibrational coordinates. It is clear then that electron transfer implies changing in the chemical structure of the reactants.

To understand how the Franck-Condon principle is used, it is better to recall its classical definition in spectroscopy: *an electronic transition is most likely to occur without changes in the positions of the nuclei in the molecular entity and its environment. The resulting state is called a Franck-Condon state, and the transition involved, a vertical transition.* As electronic transitions, electron transfers are instantaneous compared to the motion of the nuclei of the molecules or ions involved in the process and of the orientation of the molecules in the medium (e.g. solvent molecules). The foreign environment for the new electronic state after the electronic jump can be seen as an energetic barrier for the ET process.

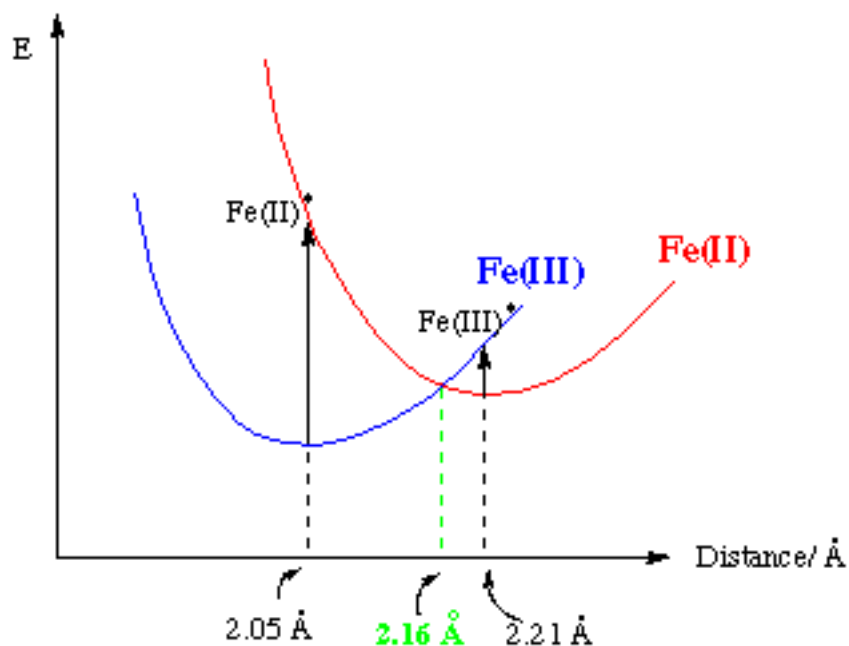
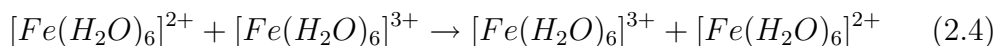


Figure 2.2: Potential energy surface for the reactants and the products

2.2 The Marcus Correction

The idea of Libby turns out to be incorrect, or incomplete, because for reactions occurring in the dark the energy is not conserved: the ions would be formed in the wrong high-energy environment, but the only way such a non conserving event could happen would be by absorption of light (vertical transition) and not in the dark. To clarify let's consider the energy transfer reaction 2.4.



Here the Fe-O equilibrium distance in the ion Fe(II) is 2.21Å while is 2.05Å for the ion Fe(III). Scheme 2.2 shows the potential energy surfaces for the reactants and the products: If the electron transfer takes place at their equilibrium positions, then we would have compressed Fe(II) ion and a stretched Fe(III) ion. These are in vibrational excited states and would release energy: if the ET occurs in dark, then the energy is not conserved. Thus the reagents must match their energies before electron transfer can occur. In the limit of weak electron interactions between the reactants both the Franck-Condon principle (vertical transition) and energy conservation must be satisfied. Fluctuations had to occur in the various nuclear coordinations as well as in the orientation coordinates of the solvent molecules and in any other coordi-

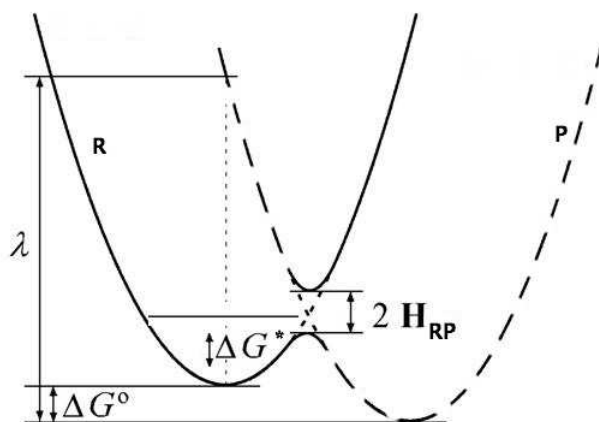


Figure 2.3: Potential energy surface for the reactants and the products

nates whose most probable distribution for the products differs from that of the reactants. With such fluctuations, values of the coordinates (i.e. **reaction coordinates**) could be reached which satisfy both the Franck-Condon and energy conservation conditions so to permit ET to occur in the dark.

2.3 Potential energy surfaces: adiabatic and non-adiabatic process

The potential energy of the system is a function of the translational, rotational and vibrational coordinates of the reacting species and of the molecules of the surrounding medium. A profile of the potential energy surface is given in figure 2.3. The abscissa, a line drawn in the many-dimensional coordinates space introduced before, represents any concerted motion (fluctuation) leading from any spatial configuration (on all atoms) that is suited to the electronic structure of the reactants to one suited to that for the products. Surface R denotes the potential energy profile when the reacting species have the electronic structure of the reactants, while surface P corresponds to their having the electronic structure of the products. If the distance between the reactants is sufficiently small there is the usual splitting of the two surfaces at their intersection. If the electronic interaction is very weak the splitting at the intersection of the two surfaces is negligible. In the first case the system will always remain on the lowest surface as it moves from left to right in figure 2.3. Thus the system has moved from the R to the P surface adiabatically. On the other hand, if the splitting is negligible, a system initially on

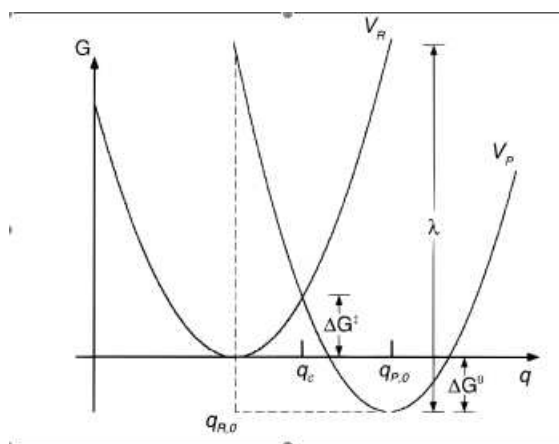


Figure 3.1: Potential energy surface for the reactants and the products

the surface R will tend to remain on R as it passes to the right across the intersection. The probability that as a result of this nuclear motion the system ends up on surface P is calculated by treating this motion non-adiabatically. Please note that the potential curves can be approximate to a parabola.

2.4 Classical and semi-classical ET

Considering figure 2.3, it should be noted that the system can undergo this electron transfer either by surmounting the barrier if it has enough energy (classical) or by tunneling (semi-classical). If nuclear tunneling is unimportant, the rate of the ET reaction is simply the rate of crossing the barrier top times its relative population. The top of the barrier is then the activation energy for the electron transfer.

3 Classical electron transfer theory

The free energy barrier, ΔG^* (figure 3) is the difference between the crossing point (for diabatic process) and the bottom of the reactant free energy parabola. If the entropy changes are ignored, the free energy becomes energy or potential energy. Referring to figure 3 the barrier top occurs at the crossing (position q_c) and is given by the conditions 3.1.

$$V_R(q_c) = V_P(q_c) \quad (3.1)$$

In the approximation of parabolic potential energy, the condition 3.1 can be rewritten in terms of the position of the minima for the potential energy of

the reactants and the products, q_R and q_P respectively.

$$\frac{1}{2}f(q_c - q_R)^2 = \Delta G^0 + \frac{1}{2}(q_c - q_P)^2 \quad (3.2)$$

We can solve for the crossing the previous equation obtaining

$$q_c = \frac{\Delta G^0}{f} \frac{1}{(q_c - q_P)} + (q_P + q_R)^2 \quad (3.3)$$

A fundamental physical quantity is the reorganization energy, λ which can be defined as

$$\lambda = \frac{1}{2}f(q_R - q_P)^2 \quad (3.4)$$

This energy increases with increasing the separation between the minima corresponding to the initial and final state and with increasing the stiffness or force constant f .

The potential energy barrier is thus given by:

$$\Delta G^* = G_R(q_c) - G_R(q_R) = V_R(q_c) - V_R(q_r) = \frac{1}{2}f(q_c - q_R)^2 \quad (3.5)$$

Substituting for q_c the expression in eq 3.3

$$\Delta G^* = \frac{\lambda}{4} \left[1 + \frac{\Delta G^0}{\lambda} \right]^2 \quad (3.6)$$

This express the barrier height or the free energy activation for crossing two adiabatic curves in terms of the overall free energy of reaction ΔG^0 and the reorganization energy λ . The expression for the rate constant k_{et} of the reaction is given from the standard Arrhenius relationship in eq 3.7.

$$k_{et} = A \exp \left[\frac{-\Delta G^*}{K_B T} \right] \quad (3.7)$$

The prefactor A in equation 3.7 depends on the nature of the electron transfer reaction (e.g., bimolecular or intramolecular). ΔG^0 is the standard free energy for the reactions (and equals to zero for a self-exchange reaction) and λ is a “*reorganization term*” composed of solvational (λ_0) and vibrational (λ_i) components:

$$\lambda = \lambda_0 + \lambda_i \quad (3.8)$$

The standard estimation for solvational energy in eq 3.9 was obtained by Marcus by using a model in which reactants and products were modeled as spheres and the solvent as a dielectric continuum.

$$\lambda_0 = (\Delta e)^2 \left[\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{R} \right] \left[\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right] \quad (3.9)$$

Here a_1 , a_2 , R , ϵ_∞ and ϵ_0 are respectively the radii of the donor and acceptor in the Marcus' two spheres model, the distance between the centers of the donor and acceptor spheres and the optical and static dielectric constants. Δe is the amount of charge transferred. The difference in the inverse dielectric constants relates to the fact that nuclear degrees of freedom cannot readjust instantaneously to the motion of the electrons and thus contribute to the barrier. This is a manifestation of the Born-Oppenheimer separation. The vibrational contribute to the reorganization energy λ_i is given by the equation 3.10.

$$\lambda_i = \sum_l \lambda_{i,l} = \frac{1}{2} \sum_l f_l (\Delta q_{e,l})^2 \quad (3.10)$$

Here, the summation is over the coupled intramolecular vibrations. The contribution of the l th normal mode to the reorganization energy is given in terms of its constant force f_l and the change in equilibrium positions between the reactants and the products, $\Delta q_{e,l} = q_{P,e} - q_{R,e}$. As mentioned above, in case of self-exchange reactions the driving force $-\Delta G^0$ vanishes and equation 3.7 becomes:

$$k_{et}(\Delta G^0 = 0) = A \exp\left[\frac{-\lambda}{K_B T}\right] \quad (3.11)$$

and the activation free energy for self-exchange ET is simply one-fourth of the reorganization energy.

A more extensive mathematical treatment can be found in the paper of Newton.[3]

4 The semi-classical formulation

The equations 3.7 and 3.11 completely characterize the electron transfer reaction in terms of three quantities: the prefactor A , the free energy ΔG^0 and the reorganization energy λ . On the other way, the theory as presented before shows some limits, and the most important is probably the temperature dependence. Equation 3.7, in fact, predicts a vanishing electron transfer rate constant at zero temperature, in contrast with experiments (Figure 4). This and other problems arise from the classical assumption that the energy barrier must be crossed (overcome) while, in reality, it exists the possibility to have tunneling through the barrier. A semi-classical approach has been addressed by a number of workers to include quantum effects into the classical Marcus theory. Experimental results in figure 4 shows that the predictions of eq. 3.7 are verified at high temperature, where the electron transfer is an activated process. Relation 4.1 provides a guide to which modes l coupled

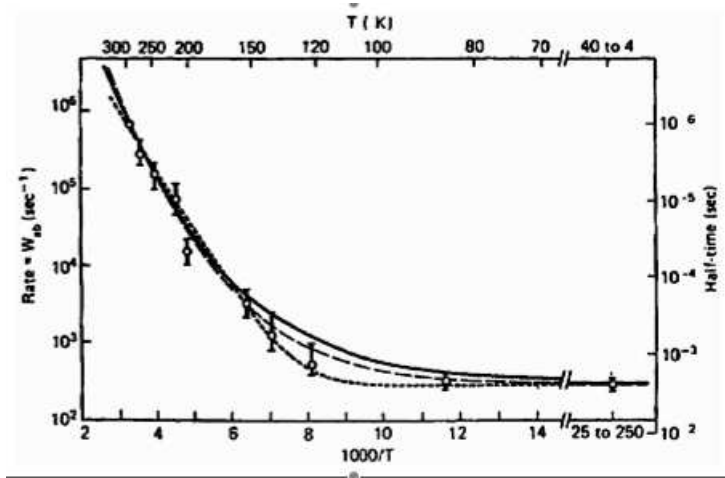


Figure 4.1: Comparison of theories with data on *C. vinosum* cytochrome oxidation. Data are points and various theoretical models yield the curves. Note the nonvanishing rate constant at low temperature.

to electron transfer must be treated as quantum mechanical and which can be assumed classical.

$$\begin{aligned} \frac{\hbar\omega_l}{K_bT} &\gg 1 && \text{quantum} \\ \frac{\hbar\omega_l}{K_bT} &\ll 1 && \text{classical} \end{aligned} \quad (4.1)$$

The necessity to introduce quantum effects become clear introducing the harmonic oscillator vibrational energy levels within the potential curves of figure 2.3, as shown in figure 4. As shown there, tunneling can occur between the ground level in the reactant potential and the ninth vibrational level in the product curve. The extent to which tunneling plays a role depends on the extent of the vibrational overlap between the initial and the final states. The rate constant for electron transfer, from the Fermi's golden rule of perturbation theory with the full Hamiltonian of the system, gives the ET rate constant K_{ET} as in eq. 4.2.

$$k_{ET} = \frac{2\pi}{\hbar} |\langle R | H | P \rangle|^2 |\langle r_{vib} | p_{vib} \rangle|^2 \delta(E_R - E_P) \quad (4.2)$$

$$= \frac{2\pi}{\hbar} |\langle R | H | P \rangle|^2 |\langle r_{vib} | p_{vib} \rangle| \rho(E_P) \quad (4.3)$$

$$= \frac{2\pi}{\hbar} |\langle R | H | P \rangle|^2 (DFWC) \quad (4.4)$$

$$= \frac{2\pi}{\hbar} H_{RP} (DFWC) \quad (4.5)$$

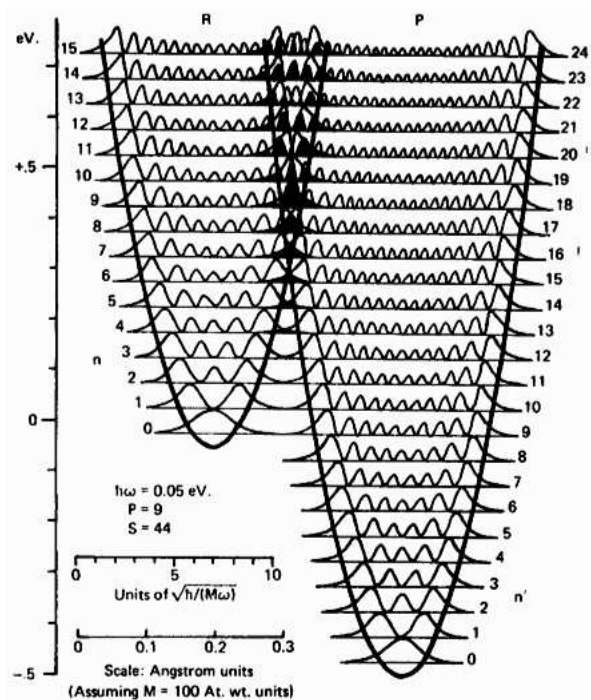


Figure 4.2: Schematic one-dimensional representation of the intersection between reactant and product vibrational levels. Here the splitting at the crossing is not shown and the optimal overlap of the $\nu = 0$ initial vibrational level is with the $\nu' = 9$ product level.

Here the electron transfer rate constant is given first in terms of isolated levels for the reactant and product, then in terms of density of states, $\rho(E_P)$ of the product, and finally in terms of density of states weighted Franck-Condon factor (DWFC). H_{RP} is the electronic matrix element that mixes the donor and acceptor states. The states $|r_{vib}\rangle$ and $|p_{vib}\rangle$ are vibrational states of reactant and product respectively. H is the Hamiltonian for the entire system, and the matrix elements in eq. 4.2 and 4.3 are averaged over the full Hamiltonian of the system.

In the case of non-adiabatic ET, with the Condon approximation this formulation is correct, while for adiabatic ET a more general prefactor is required. We focus now on the case of non-adiabatic ET.

Using the polaron model, each electronic state is coupled with a number of vibration, treated as harmonic oscillators with separation of nuclear and electronic coordinates assumed (i.e. in Born-Oppenheimer approximation regime). Under these conditions, the Hamiltonian for the system can be written as:

$$\begin{aligned}
H = & |R\rangle\langle R| \left[E_R^0 + \frac{1}{2} \sum_l f_l (q_l - q_{R,l})^2 \right] + \\
& |P\rangle\langle P| \left[E_P^0 + \frac{1}{2} \sum_l f_l (q_l - q_{P,l})^2 \right] + \\
& (|R\rangle\langle P| + |P\rangle\langle R|) H_{RP}
\end{aligned} \tag{4.6}$$

Here, the first term in braces is the energy represented by the left parabola of figure 4, and the second set of braces is the same energy term for the right potential. E_R^0 and E_P^0 are respectively the energy origin for these states and are characterized by the force constant f_l for the l th mode, whose displacement origin is $q_{R,L}$ and $q_{P,l}$ in the reactants and products respectively.

This Hamiltonian is called polaron models and consists in two electronic states coupled with a number of vibrational levels, which can be either classical or quantum mechanical, according to relation 4.1. In addition to the classical solvent motion, one can specify one coupled vibration characterized by frequency ω and equilibrium displacement Δq_e , then is possible to define the intramolecular reorganization energy for this mode as

$$\lambda_i = \left(\frac{f}{2}\right)(\Delta q_e)^2 \tag{4.7}$$

This can be related to a related adimensional quantity: the electron vibrational coupling constant, or Huang-Rhys factor as define in eq. 4.8.

$$S = \frac{\lambda_i}{\hbar\omega} \tag{4.8}$$

The generalization of equations 3.7 for non-adiabatic ET for one coupled mode in the quantum mechanical limits is then:

$$k_{ET} = \frac{2\pi}{\hbar} H_{RP}^2 \left(\frac{1}{4\pi\lambda_0 K_B T} \right)^{1/2} (FC) \quad (4.9)$$

where FC is the Franck-Condon factor

$$(FC) = \sum_{\nu'} \exp(-S) \frac{S^{\nu'}}{\nu'!} \exp \left[\frac{-(\lambda_0 + \nu'\hbar\omega + \Delta G^0)^2}{4\lambda_0 K_B T} \right] \quad (4.10)$$

The term in front the FC factor is the frequency of electron transfer in the absence of barrier and contains H_{RP} and the classical density of states. The FC factor consists of the sum over all possible vibrational overlap integrals between the initial vibrational level ν and the final level. ν' . Each individual ν' represents a separate $\nu = 0 \rightarrow \nu'$ reaction channel. Each separated exponential term in the sum is the population of molecules having the required energy to undergo electron transfer with energy conservation through channel $\nu = 0 \rightarrow \nu'$. The sum is dominated by those channels for which $|\Delta G^0| \sim \lambda_0 + \nu'\hbar\omega$, so there is a close energy match between the energy released (ΔG^0) and the sum of the reorganization energy and the initial product vibrational energy ($\nu'\hbar\omega$).

A more complete treatment of the semi-classical ET theory can be found in papers [2] and [4].

5 Applications

6 References

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