

Introduction to Electron Transfer

by

René M. Williams

Adapted from: “*Fullerenes as Electron Accepting Components in Supramolecular and Covalently Linked Electron Transfer Systems*”.

PhD Thesis, Amsterdam **1996**, René Marcel Williams.

Promotor: Prof. Dr. Jan W. Verhoeven

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Since my “intro to et” appeared on the web (ten years ago) I have been meeting people in the most unexpected places that appeared to have read it and I know people that use it for teaching to their students, so I thought I put it back on the web, as the old server died. I realized some things were missing (e.g. the bell curve) so I improved it and updated some refs.

It should be suited for anyone starting in the “electron transfer field”, from synthetic people that want to know more about what will be studied on their compounds, to biophysicist who wants to read a “physical organic chemist’s view on electron transfer theory”. For hard-core physicist this view may be very “organic” but that could help them in interdisciplinary projects. Even the “experts” may find some new perspectives (I know at least one has). I am still looking for a picture of the Closs-Miller data fitted classic and semi-classical.

It starts from the simplest D-A scheme, but also covers the difference between nuclear tunneling and electron tunneling, and tries to project Frank-Condon excitation onto the FCWD and correlate it (visually) with the electron density flow.

So use it as you like... as a handout for teaching, for new PhD’s starting in a group... if you use the pictures or material separately in other (web)-publications please mention the above source.

René

“It is an excellent basic physico-chemical description of generalized electron transfer, and includes a very good exposure to the Marcus theory and the equations.”

Larry Orr and Govindjee

Photosynthesis Research 68: 1-28, 2001.

<http://www.life.uiuc.edu/govindjee/photoweb/>

<http://photoscience.la.asu.edu/photosyn/photoweb/>

<https://netfiles.uiuc.edu/slhee/www/korean/academic.htm>

This process can make its cycle endlessly back and forth, with the net effect being a transfer of twenty electrons from our universe to theirs per each nucleus cycled. Both sides can gain energy from what is, in effect, an Inter-Universe Electron Pump.

Isaac Asimov, The gods themselves

Electron transfer

1. Introduction

Photoinduced electron transfer is one of the most pivotal processes in photosynthesis, photo-imaging, organic reaction mechanisms and optoelectronic devices. Studying this process in well-defined artificial systems may lead to further insight into the first events of the biological processes that are responsible for a major part of the energy on earth. Not only is the energy in all “food and feed” on earth derived from the light induced conversion of carbon dioxide and water into carbohydrates, also all the energy in fossil fuels like oil, natural gas and coal was initially fixed by phototrophic organisms.

Light induced electron transfer is a process in which an electron is transferred from an electron donating species (D) to an electron accepting species (A). Prior to electron transfer one of the components is excited with light:

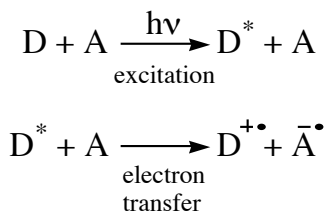


Fig. 1. *Excitation of a donor followed by electron transfer.*

By this simple sequence, light energy is converted into electrochemical energy. Subsequent to the electron transfer a charge transfer state is created, which is a dipolar species, consisting of the radical cation of the donor ($\text{D}^{+\bullet}$) and the radical anion of the acceptor ($\text{A}^{-\bullet}$).

The charge transfer state created can undergo many different processes. In the photosynthetic reaction center (after the energy transfer from the light harvesting system to the special pair) a first electron transfer from the special pair (SP) to the pheophytin P (in 3 ps) is followed by a second electron transfer from the $\text{P}^{-\bullet}$ to ubiquinone Q_A (in 200 ps). Next, the electron is transferred from Q_A to a second quinone Q_B (in 100 μs).

Thus, the first electron transfer is followed by two consecutive steps. In the final state chemistry takes over: Q_B takes up two protons (after two electron transfer cycles) and leaves its site, traverses the membrane in which the system is embedded and releases its protons again. Thus a proton coupled electron transfer process is accomplished, by which light-energy is converted into an

electrochemical proton gradient, by which the biological synthesis of energy rich molecules like ATP (adenosine triphosphate) is driven.

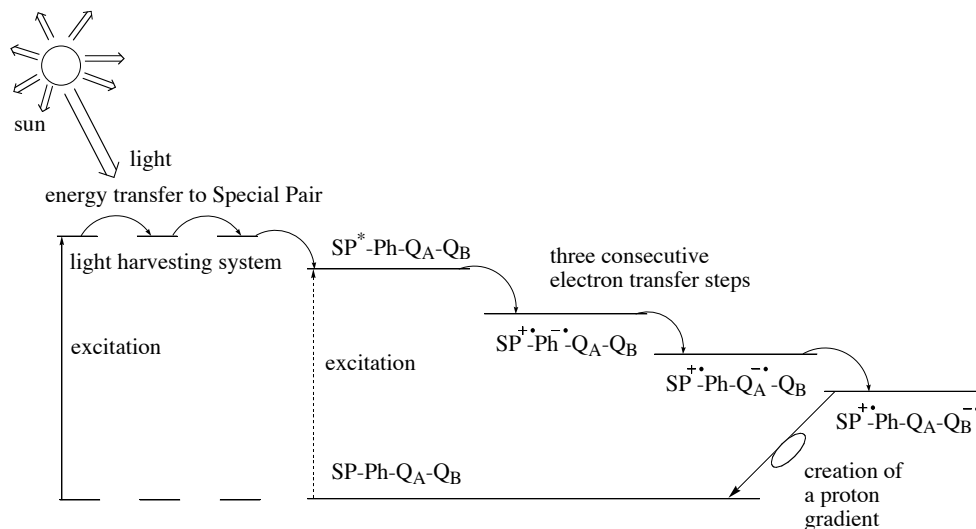


Fig. 2. Representation of the first events in photosynthesis. Light harvesting, followed by energy transfer to the special pair, and subsequently by three electron transfer steps. The charge separated state is used to create a transmembrane proton gradient.

In a more trivial process, the taking of a photograph, the first step also is light induced electron transfer. The charge transfer state is now trapped by imperfections in the silver halide crystals and development leads to the generation of metallic silver clusters. Many other reactions exist in which electron transfer is followed by the formation or breaking of bonds or the trapping of a charge transfer state, followed by further chemical reactions.

Another process that can follow charge separation (or forward electron transfer) is simply charge recombination (or back electron transfer) leading to the initial state. This is in fact a very common process, which is often the fate of a charge transfer state.

This charge recombination can occur by a dark (non-radiative) process, but there exist many systems in which the charge transfer state undergoes a radiative charge recombination. The wavelength of the emission of this process (often called charge transfer fluorescence or, more accurately, charge recombination fluorescence) is very dependent on the environment of the dipolar charge transfer state. A polar environment stabilizes this state and thus lowers its

energy and thereby shifts the emission to the red. These types of systems can be used as a polarity (and mobility) probe.

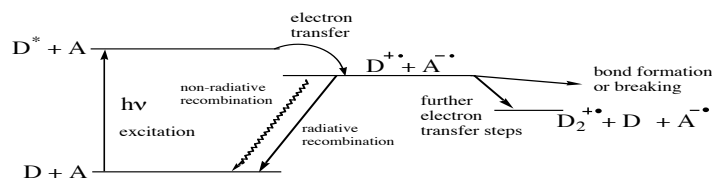


Fig. 3. Representation of the several possibilities that a charge separated state can undergo.

Also in silicon-based solar cells electron transfer from an n-type silicon to a p-type silicon layer is the first process after light excitation. In organic solar cells this process occurs between two solid layers consisting of electron donating and electron accepting molecules, respectively. In a photocopying machine light is used to create a charge transfer state in a solid, which is thereby converted into a conducting material (a photoconductor). Thus the charges put on a certain area, that attract the black toner, can leak away at places where the solid state photoconductor is created by electron transfer, and at the places not reached by light the toner sticks and can be transferred to paper.

It thus is clear that electron transfer is part of life itself and is routinely encountered in daily life.

2. History of electron transfer

The first electron transfer reactions that were studied were self-exchange electron transfer reactions of inorganic ions in aqueous solution. The intervalence absorption of metal complexes in solution and isotope effects were used. The understanding of organic charge transfer complexes ¹ started in the late 1940's, early 1950's with the reports of Benesi and Hildebrand (1949), who observed new absorption bands in solutions of aromatic hydrocarbons and iodine and the idea of partial charge transfer in the ground-state of Brackman ². The Mulliken model (1952) for electron- donor acceptor complexes, and the discovery of excimer formation by Förster and Kaspar in 1954 were essential steps that have led to the extensive developments in the field of electron- donor acceptor systems in the last decades.

Early examples of a donor and acceptor that are covalently linked were reported by Verhoeven and co-workers in 1969 ³. Linking donor and acceptor to each other by covalent bonding has proved to be an important step towards a better

understanding of the electron transfer process. Studies on photoinduced intramolecular electron transfer in covalently linked donor-bridge-acceptor compounds that incorporate a hydrocarbon bridge of e.g. the steroid ⁴, cyclohexyl ⁵, or norbornylogous ⁶ type, to link two chromophores, have been numerous during the past decades. Thus, a lot of information about this process, regarding distance dependence, symmetry effects, influence of the bridge configuration and the energetics has been obtained. The predictions made in the 1960's by Nobel price winner R.A. Marcus regarding the *Marcus inverted region* (see section 3) were first confirmed by this type of donor-bridge-acceptor systems. These studies have also shown that photoinduced intramolecular charge separation can be accomplished in systems in which donor and acceptor are spaced upto 15 Å by a saturated hydrocarbon bridge. This bridge not only establishes exact inter chromophore distance, it also is strongly involved in the electronic coupling between donor and acceptor, that is required for photoinduced electron transfer. Mixing of the σ and σ^* orbitals of the bridge with the donor and acceptor π orbitals, results in a mixing of the electronic wave functions of the latter two, resulting in electronic coupling.

The electron accepting properties of fullerenes in photoinduced electron transfer, combined with the many methods of functionalization of fullerenes, indicate that they are very well suited for the study of bridge mediated photoinduced electron transfer.

The functionalization of fullerenes with electron donating moieties may further lead to the development of advanced materials with new optical and opto-magnetic properties. One of the means to elucidate the properties of these materials is to investigate their photophysical properties in solution, to determine whether a charge transfer state can be populated by photoinduced (or optical) electron transfer.

3. Theory and experiment

A photoinduced electron transfer from D to A results in the formation of a charge separated state which consists of the corresponding radical cation and anion, and the process is in direct competition with the radiative and nonradiative processes that are present in the excited state of A (or D). Electron transfer can be regarded as an extra deactivation path of the locally excited (singlet) state that can exist next to internal conversion (ic), inter system crossing (isc) to the triplet manifold (both iso-energetic) and emission (f).

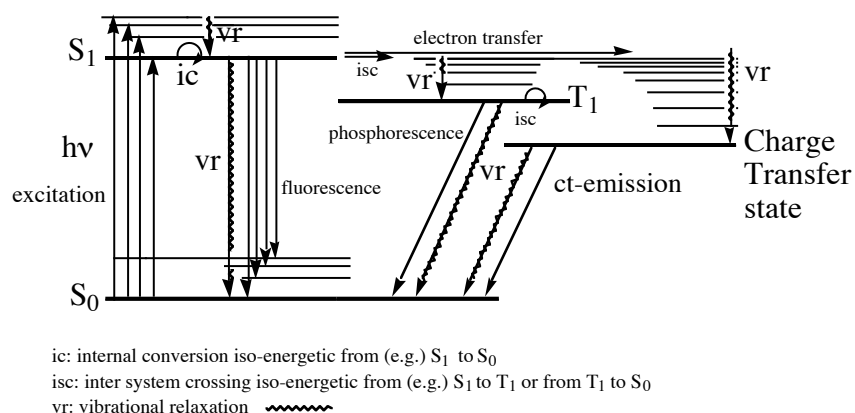


Fig. 4. *Jablonski diagram that includes electron transfer as one of decay pathways of the first excited singlet state.*

Thus the occurrence of electron transfer should diminish both the emission quantum yield and lifetime. There are, however, other mechanisms that can be responsible for fluorescence quenching: e.g. energy transfer, proton transfer, hydrogen bonding and the external heavy atom effect. Only by careful examination of the experimental conditions, and chosen variations thereof, we can establish the cause of fluorescence quenching.

Energy transfer can only proceed from a state of a certain multiplicity to a state with a lower energy with the same multiplicity. Thus, from the absorption and emission characteristics it can be predicted whether energy transfer is possible. Proton transfer can be a highly efficient and fast non-radiative decay channel, i.e. an intramolecular vibrational relaxation (e.g. ortho-hydroxybenzophenone). The presence of hydrogen bonds can also introduce a non-radiative deactivation path, i.e. many compounds do not fluoresce in protic solvents. The heavy atom effect is caused by enhanced spin orbit coupling, which is more efficient in heavier atoms, by which the rate of inter system crossing is enhanced and thus the lifetime of the excited singlet state is reduced.

Electron transfer depends on the redox properties of the donor acceptor couple together with the excitation energy. In polar solvents it can be said that the Gibbs free energy change for charge separation (ΔG_{CS}), is given by $\Delta G_{CS} = e(E_{OX}(D) - E_{red}(A)) - E_{00}$. (the “polar driving force” P). In other words, the energy put into the system by excitation (E_{00}) should be more than the energy it costs to oxidize the donor and to reduce the acceptor (see Weller).

3.1. Rate of electron transfer

The fluorescence quantum yield (Φ_{ref}) and the fluorescence lifetime (τ_{ref}) of a certain (reference) species can be described, using the rates (k) of the processes (f, ic and isc see figure 4) by:

$$\Phi_{ref} = \frac{k_f}{k_f + k_{ic} + k_{isc}} \quad \tau_{ref} = \frac{1}{k_f + k_{ic} + k_{isc}}$$

If we now introduce an extra deactivation path by for instance making an electron transfer energetically favorable (by e.g. change of solvent), these expressions become:

$$\Phi_f = \frac{k_f}{k_f + k_{ic} + k_{isc} + k_{cs}} \quad \tau_f = \frac{1}{k_f + k_{ic} + k_{isc} + k_{cs}}$$

The lifetime and quantum yield of the excited state in the absence of electron transfer can be regarded to be the reference value, and we can thus determine the charge separation rates (k_{CS}) with the following equations:

$$k_{CS} = 1/\tau_f - 1/\tau_{ref} \quad k_{CS} = (\Phi_{ref}/\Phi_f - 1)/\tau_{ref}$$

The rate parameters regarding charge separation and charge recombination processes can also be probed by using the radical cation and anion absorptions, resolved in time, i.e. the absorption of the excited state by using (laser) flash photolysis. Also other techniques such as time resolved microwave conductivity, photoacoustic calorimetry, resonance Raman, electron spin resonance, chemically induced nuclear polarization (CIDNP) and time resolved infra red spectroscopy can give information regarding this process.

3.2 Marcus and Weller

A theoretical description of the energetics and rates of the electron transfer process is formulated in a Marcus-Weller type analysis:

An estimate of the driving force for photoinduced charge separation ($-\Delta G_{CS}$) in a solvent with dielectric constant ϵ_s can be made using the standard Weller-type approach^{7, 6}.

$$\Delta G_{CS} = \underbrace{e(E_{OX}(D) - E_{red}(A))}_{P} - \underbrace{E_{00}}_{C} - \underbrace{e^2/4\pi\epsilon_0 \epsilon_s R_c - e^2/8\pi\epsilon_0 (1/r^+ + 1/r^-)(1/\epsilon_{EC} - 1/\epsilon_s)}_{S}$$

This requires, in addition to the donor and acceptor redox potentials ($E_{OX}(D)$ and $E_{red}(A)$ [in e.g. V vs SCE in a solvent with dielectric constant ϵ_{EC}]; e denotes the elementary charge)[#] and the singlet or triplet state energy [in eV] ($^1E_{00}$ and $^3E_{00}$; using the $^3E_{00}$ can give estimates for the energetics of the electron transfer process starting from the triplet state [together this makes up P , the polar driving force]), knowledge about the center to center distance (R_c [in Å]) and of the effective ionic-radii of the donor and acceptor radical cation and anion (r^+ respectively r^- [in Å])).

[#] Note that $e^2/4\pi\epsilon_0 = 14.4 \text{ eV Å}$; multiplying with e converts V into eV; if $\epsilon_{EC} = \epsilon_s$ the last solvation term (S) of the equation is zero; second term (C) is coulombic attraction of ions.

For R_c a value can be estimated using molecular modeling. The r^+ and r^- values can be calculated from the apparent molar volumes, using a spherical approach.

$$4/3 \pi r^3 = M/N\rho$$

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

Furthermore values for the barrier to charge separation ($\Delta G^\#$) can be estimated via the classical Marcus equation.

$$\Delta G^\# = (\Delta G + \lambda)^2 / 4\lambda \quad \text{with} \quad \lambda = \lambda_i + \lambda_s$$

For the estimation of the solvent reorganization term (λ_s) the Born-Hush approach can be used:

$$\lambda_s = e^2/4\pi\epsilon_0 (1/r - 1/R_c)(1/n^2 - 1/\epsilon_s)$$

and the internal reorganization energy (λ_i) can be estimated using the charge transfer absorption maximum and the charge transfer emission maximum in a non-polar solvent (where $\lambda_s \approx 0$) of the electron donor-acceptor system studied (or one that shows great resemblance to the system). The energy difference between these two maxima equals $2\lambda_i$. Values range from 0.2 to 0.7 eV. An estimate of the Gibbs free energy change for charge recombination ($\Delta G_{cr} = -\Delta G_{cs} - {}^1E_{00}$) can also be given.

By using the harmonic approximation together with the quantities described above the Marcus equation was derived. (it took 25 years to prove a theory [Closs & Miller, 1988] that was derived with high school mathematics! *There is still hope for you!*). The relation between these quantities and the parabola is given below.

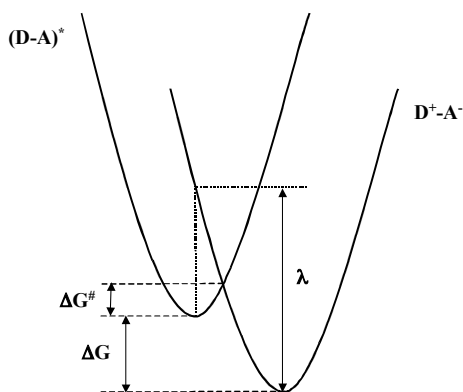


Fig. 5. Representation of the potential energy curves used in electron transfer theory. The barrier to charge separation (ΔG^\ddagger), the overall Gibbs free energy change (ΔG) and the total reorganization energy (λ) are indicated (from Kaletas, B. K. Thesis 2004).

3.3 Marcus inverted region

The Marcus theory implies that barrierless electron transfer can occur if $\lambda = -\Delta G_{cs}$. This is called the optimal region. If $\lambda > -\Delta G_{cs}$ the electron transfer rate increases with larger driving forces. However, in the so-called Marcus inverted region, if $\lambda < -\Delta G_{cs}$, the rate *decreases* with larger driving forces. This is counter-intuitive. The barrier is very *thin* in the inverted region. This facilitates nuclear tunneling and thus, in processes in the inverted region (charge recombination is often an inverted region process) the observed rates are higher than expected from the classical Marcus theory (see later).

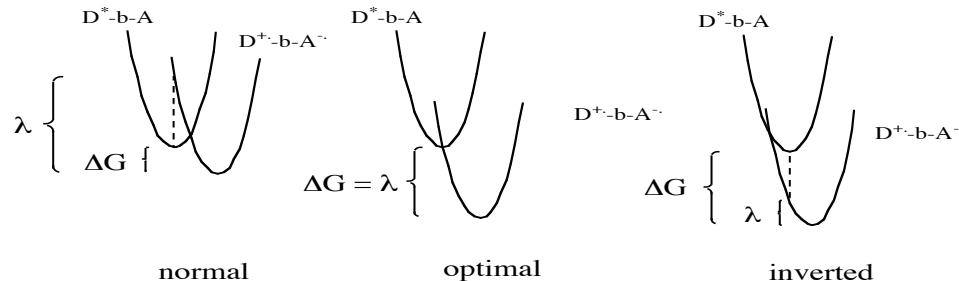


Fig. 6. The different regions in the Marcus theory of electron transfer, together with the representations of the Gibbs free energy change, and the reorganization energy.

The reorganization energy (λ) is the energy needed to distort the product state and its surroundings to reach the equilibrium configuration of the reactant state (i.e. while staying in the potential energy well of the product state; the point to which the product state has to be distorted is denoted with the dashed line in figure 6).

When the barrier is known and the electronic coupling (V) between donor and acceptor is weak, the rate of charge separation can be obtained using the non-adiabatic expression for electron transfer processes⁸ given by eqn. :

$$k_{cs} = \frac{2\pi^{3/2}}{h\sqrt{\lambda k_B T}} (V)^2 \exp\left[\frac{-\Delta G_{cs}^\#}{k_B T}\right]$$

Here, the electronic coupling matrix element (V) and the reorganization energy (λ) together with the Boltzman constant (k_B) Planck's constant (h) and the temperature (T) determine the pre-exponential factor.

Apart from this, the rate equation is very similar to the well known Arrhenius equation:

$$k = (A) \exp \left[\frac{-\Delta G_{cs}^{\#}}{k_B T} \right]$$

in which A is the pre-exponential factor. Reactions are non-adiabatic if the coupling matrix element V is smaller than $k_B T$ ($\sim 200 \text{ cm}^{-1}$ at room temperature). Because V in general diminishes exponentially with distance (like any orbital), the distance dependence of the rate of electron transfer can be described by

$$k_{cs} = k_0 \times e^{-\beta R_e}$$

in which β (attenuation factor) is a constant, scaling the distance dependence, and R_e is the edge to edge distance between donor and acceptor. k_0 is the rate at close contact ($\sim 10^{13} \text{ s}^{-1}$).

The medium between donor and acceptor strongly influences the rate of the electron transfer process, through (solvation and) the value of β . If donor and acceptor are separated by vacuum, the interaction (*through space interaction*) is much less ($\beta \approx 2.8$ to 3.8) than when a protein ($\beta \approx 1.4$) or a solvent (*through solvent coupling*) like benzene is the medium ($\beta \approx 1$). If donor and acceptor are linked by a saturated hydrocarbon bridge the interaction (*through σ -bond coupling*) can be rather strong ($\beta \approx 0.5$ to 0.8), and if a hypothetical graphitic bridge (or a recently applied poly-para-phenylene-vinylene π -bridge; Wasielewski, 1998) would be the intervening medium, the interaction would be so strong that rates of charge separation and recombination would be vibrationally limited at any distance ($\beta \approx 0$). But if the energy level of the bridge becomes too low it can work as a trap for the electron and the transfer stops (now the electron localizes on the bridge). The through bond interaction between D and A is an interaction between the electronic orbitals of D and A, and the orbitals of the bridge. Thus the (*cis-trans*)-configuration of the bridge, the angles between aromatic units (in *through π -bond coupling*) and the presence of orbital coefficients at the *interaction points* of D and A are of crucial importance.

It is generally believed that the k_{cs} is a time independent rate constant. However, there are models that predict non-exponential electron transfer kinetics⁹, in which the electron transfer rate would change in time (i.e. be time dependent). This implies an electron transfer rate that decreases in time, after the excitation. This aspect may explain why the determination of time-resolved fluorescence quenching of a locally excited state by intramolecular electron transfer often fails to give one exponential decay component only.

3.4 How is the electron transferred from D to A?

One of the questions that arises when electron transfer processes are studied, is: how are we supposed to view the actual transfer of the electron. What happens. In oral discussions electrons are often said to be jumping from D to A, to hop around or to be injected into an acceptor. It has to be realized that when we speak of electrons we have to consider the fact that we can only speak of the probability to find the electron in a certain area.

Electron transfer in a system consisting of D and A, connected by a bridge (b), in which D has the lowest excitation energy is visualized in figure 7A and B. In figure 7A three positions on the potential energy curves representing the excited state (D^*-b-A) and the charge separated state ($D^{+·}-b-A^{-·}$) are denoted with numbers (①, ②, ③). In the figure 7B, these three positions are described in further detail.

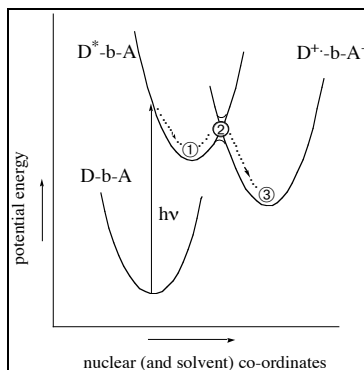


Fig. 7A. Three positions on the potential energy surface representing the excited state and the charge separated state of a donor-bridge-acceptor system (ground state is also shown).

① Upon excitation of D we get to a situation (D^*-b-A) that we can describe with a potential energy curve by making use of the harmonic approximation. An electron is promoted from a low-lying state to a state in which most of the electron probability density is located on D. However, as electronic coupling is present, there also is a very small chance of finding the electron on the acceptor site. After excitation, relaxation leads to the bottom of the first potential energy well and the barrier can be reached.

② Having reached the barrier, two things can happen: crossing to the product state, or remaining on the initial state. At this point, at the top of the barrier, there is a 50 % change of finding the electron on the acceptor site: the orbital that is inherently linked with this situation has 50 % electron probability density on the donor site and 50 % electron probability density on the acceptor site (this

is often described as the situation where the electron is formally transferred as we now are present on the potential energy curve of the product).

③ A crossing, going from the top of the barrier to the bottom of the potential energy well of the product state, leads to an orbital coefficient evolution which implies a reduction of electron probability density on the donor site and an increase of electron probability density on the acceptor site.

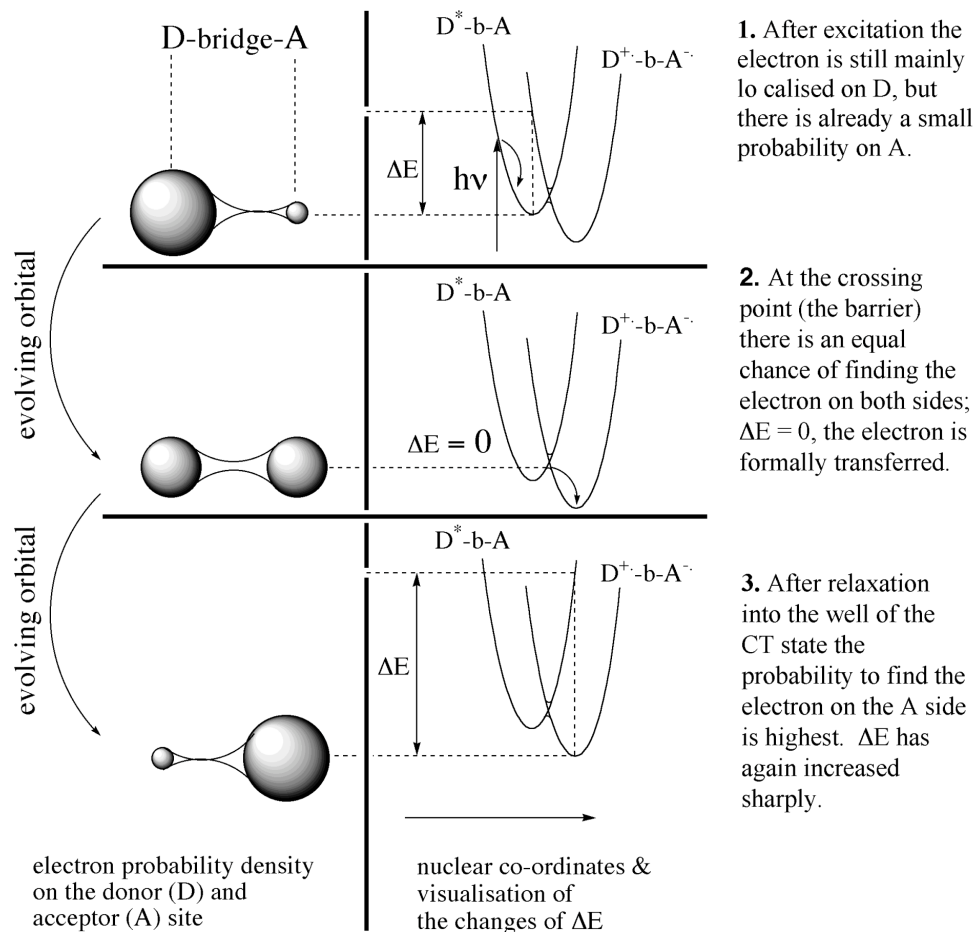


Fig. 7B. This figure gives a representation of several aspects that occur during electron transfer. On the left, the electron probability density (also referred to as electronic position) at the donor site and at the acceptor site and the evolution of the electron density during the process is displayed. On the right, the two parabola represent the initial reactant state and the final product state. As the process proceeds the position on the potential energy surface changes, and thereby the energy gap between the two states becomes smaller, until the barrier is reached, to increase again in the final state of the process (adapted from Marcus and Sutin)¹⁰.

Thus, now we can visualize the events that occur between excitation and product formation: a travel across a potential energy surface (which involves nuclear and solvent reorganization), accompanied by an evolution of electron probability density on the donor and acceptor site.

During these events we can see that the energy gap ΔE (the energy difference between the initial and the final state at a certain nuclear co-ordinate) changes drastically. In going to the top of the barrier it decreases to become zero at the top (now the mixing between the two states is strongest (!), like in an orbital interaction diagram). Descending into the D^+-b-A^- potential energy curve ΔE increases again.

The electron transfer rate can thus be viewed as the time it takes for the wave function (or the time dependent Schrödinger equation) to evolve from one zero-order state to another. This time becomes longer if the electronic coupling between the two states becomes weaker.

It has to be noted that the electron density is never highest on the bridge, i.e. the electron does not localize on the bridge.

Besides photoinduced electron transfer the process called *optical* electron transfer also exists. In this process the charge transfer state is directly populated by excitation (in the charge transfer absorption band). The speed of this process obviously can not be measured, as it takes place during excitation.

3.5 Marcus inverted region and Frank-Condon factors

Frank-Condon excitation is often described as the absence of the change of the nuclear coordinates upon excitation (because the nuclei are so much more massive than the electrons, an electronic transition takes place very much faster than the nuclei can respond), but in the quantum chemical description of the Franck-Condon principle, the molecule undergoes a transition to the upper vibrational state that most closely resembles the vibrational wavefunction of the vibrational ground state of the lower electronic state (*Physical Chemistry Atkins*,).

In the figure on the right, the system is excited with white light and the corresponding spectrum is shown vertically. The wavefunction drawn in black has highest overlap with that of the ground state level. In this case the Frank-Condon factors are

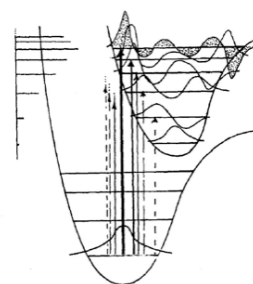


Fig. 8. Frank-Condon excitation with white light (spectrum on the left). Biggest overlap with wave-function in black.

related to the Einstein coefficients (and the extinction coefficients). The Franck-Condon factor is simply the overlap matrix element between vibrational nuclear states. In case only one wavelength is used, the wavefunction of the lowest vibrational level of the ground state shown here would be “projected” onto one vibrational wavefunction of the higher electronic state.

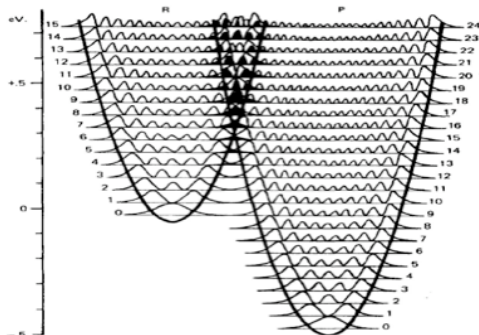
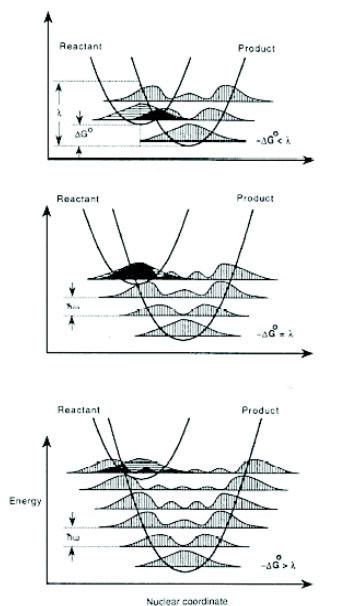


Fig. 9. *Overlap (in black) of the vibrational wavefunctions of two states.*

In the electron transfer process that occurs after Frank-Condon excitation of a donor-acceptor system, the direct overlap of the vibrational wavefunctions (see left, in black) of the initial and the final state plays a role. The two curves represent the local excited state and the charge transfer state and together with figure 8 can be projected onto figure 7A. Electron transfer that is described by nuclear tunneling is related to this overlap. So if we want to understand the influence of the Frank-Condon factors in relation to the Marcus theory we have to project this view onto figure 7A and think how the amount of vibrational overlap changes if we lower the final state to the optimal region and then further down to the inverted region.



In the Marcus inverted region a similar “travel” occurs as depicted in figure 7B: from the bottom of the initial state, over the top of the *thin* barrier to the product state, when viewed in a classic way. However, if we would draw in the vibrational wavefunctions of the two interacting states we could see that because the barrier is thin, the overlap of these wavefunctions is larger than expected on the basis of the height of the barrier in the inverted region. So the barrier does not have to be overcome, but more nuclear tunneling through

Fig. 10. *Changes of the vibrational overlap in the three regions (Dutton 1992).*

the barrier occurs (remember the “particle in a box” from your first year quantum, if the barrier is thin, the wave comes more out of the box). The change of this vibrational wavefunction overlap with increase of the driving force is smaller in the inverted region than in the normal region. This is why in the dependence of the electron transfer rate on the driving force in the inverted region is less steep than in the normal region (the relative amount of tunneling in the inverted region is more constant). We need a quantum-chemical variant of the Marcus equation to describe the observed rates.

The influence of the overlap of the vibrational wavefunctions is called “the Frank Condon factor in electron transfer”.

Figure 10 is a representation of the change of the overlap (black) of the vibrational wavefunctions in the normal (top), optimal (middle) and inverted region (bottom). See Dutton 1992 for more insight.

We said before that the electron transfer that is described by nuclear tunneling is related to this overlap. Because nuclear tunneling is almost independent of temperature this means that we can discriminate this process by looking at temperature dependence of the electron transfer process. If the transfer still works at very low temperature this part is due to nuclear tunneling. *Electron* tunneling applies to any electron transfer. This is because there is always a barrier between the electronic “particle in a box” description of donor and of acceptor.

Also the “Energy gap law” is due to the change of overlap of vibrational wavefunctions of two states with respect to the change in their energy difference (see *Modern Molecular Photochemistry* by N.J. Turro).

3.6 The bell-shaped Marcus curve

Rudolph A. Marcus received the Nobel price, at least partly, because he developed a counter intuitive theory that describes that a process becomes slower if you increase the driving force (I am sure the rest of his work was also a reason). If you start with two iso-energetic parabola (e.g. self-exchange reactions of (inorganic) complexes) and move the product state down (increase the driving force) the rate will increase until you get to the optimal region and as you go down further the rate will decrease (this is what the Marcus equation implies). Closs and Miller were the first to show this by using a series of covalent donor-bridge-acceptor compounds and studying the rate of the charge shift reaction with pulse radiolysis (Marcus send them Valentines card when he

saw the paper!). You pump an electron on the biphenyl and look with probe light at the rate with which it disappears.

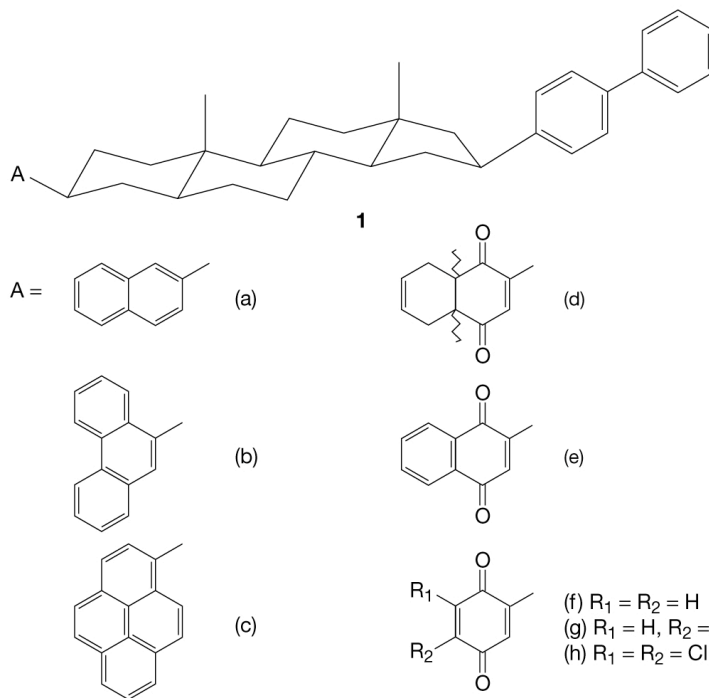


Fig. 11. The series of compounds studied by Closs and Miller. A steroid-skeleton that is substituted with a biphenyl on one side and an electron acceptor on the other side. The acceptor strength increases from (a) to (h). The dichloro-quinone (h) is the strongest acceptor.

If we now plot the driving force that you can calculate with a Weller-type analysis versus the rate that was measured, you get the bell shaped Marcus curve. The top of the curve is the Marcus optimal region (corresponding to barrierless electron transfer), the right side of the curve is the inverted region.

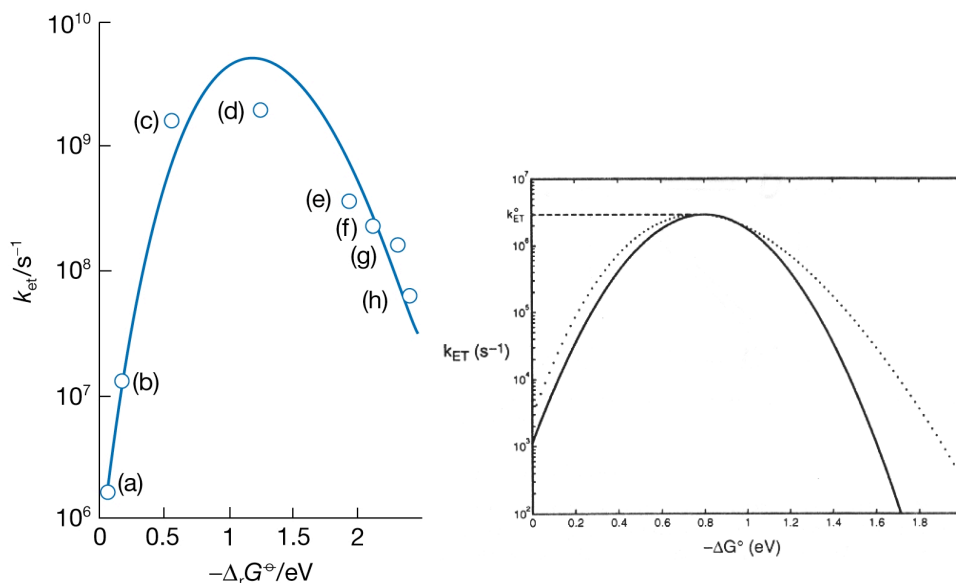


Fig. 12. *Left: the electron transfer rate of the different compounds studied by Closs and Miller as a function of the driving force of the reaction. The data and the fit by using the semi-classic Marcus equation are shown. Right: The difference in shape of the classical (solid) and the semi-classical (dotted) Marcus equation (from www.life.uiuc.edu/crofts/bioph354/lect19.html).*

Since then, this phenomenon has been observed many times and it turned out that the classic Marcus equation works wonderfully well in the normal and optimal region but that in the inverted region the rates are higher than expected. Quantum chemical vibrational effects start playing a role and the semi-classical (semi-quantum chemical) Marcus equation has to be used.

When we combine the non-adiabatic expression for electron transfer (page 9) with the Marcus equation (for the barrier, page 7) we get the classical Marcus expression for electron transfer:

$$k_{cs} = \frac{2\pi^{3/2}}{h\sqrt{\lambda k_B T}} (V)^2 \exp\left[\frac{-(\Delta G + \lambda)^2 / 4\lambda}{k_B T}\right]$$

With the help of Fermi's Golden Rule it is possible to introduce the Frank-Condon Weighted Density of states (FCWD), that equates the overlap of the vibrational wavefunctions that was described above. The FCWD depends on the internal reorganization λ_i along an intramolecular high frequency vibrational mode ν_i .

The low frequency solvent reorganization is still treated in a classical way. This then leads to the semi-classical Marcus expression for the rate of electron transfer (developed by Jortner):

$$k_{cs} = \frac{2\pi^{3/2}}{h\sqrt{\lambda_s k_B T}} (V)^2 \sum_{m=0}^{\infty} \frac{e^{-S} S^m}{m!} \exp\left[-\frac{(\lambda_s + \Delta G_{cs} + m h \nu_i)^2}{4\lambda_s k_B T}\right]$$

with the electron-vibronic (phonon) coupling $S = \lambda_i/h\nu_i$. Here ν_i is the average skeletal (IR)-vibration (in general between 300 and 2300 cm^{-1}). The “ Σ ” term indicates a summation over all “m” levels.

Marcus has proven that this equation reduces to the classical in the high temperature limit.

Models based on parabola are wonderful (and easy to draw), but some people may say that Lennard-Jones potential are a much more accurate description. Actually, we should look at the concepts of the Marcus theory and project them on a three- (or multi)- dimensional potential energy surface where the pathways that the wave-packets take depend on the exact structure of the mountainous surface (and how hot the wave-packets are). Modern calculation methods can do that and in this field “conical intersections” between the upper and lower state are a hot topic (a sort of funnel between two states). The representations of the electron transfer theory made here are two-dimensional planes cut out of this three-dimensional surface. An example of a 3-D-surface of two intersecting “3D-parabola” is given here.

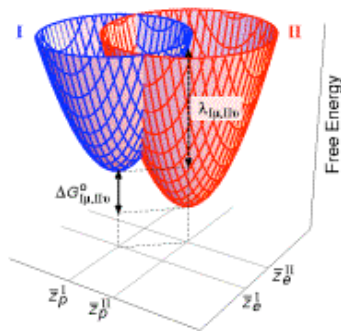


Fig. 13. Representation of two intersecting “3D-parabolic surfaces”. The “real” potential energy surface will be less smooth and more mountainous. Taken from: <http://research.chem.psu.edu/shsgroup/research.html>

3.7. Frontier Molecular Orbital description

From the previous sections it is obvious that certain orbitals of the electron transfer system are of crucial importance for the occurrence of the charge transfer.

A simple frontier molecular orbital (FMO) description of photoinduced electron transfer in a D/A system, in which the acceptor has the lowest excited state is given in Figure 14.

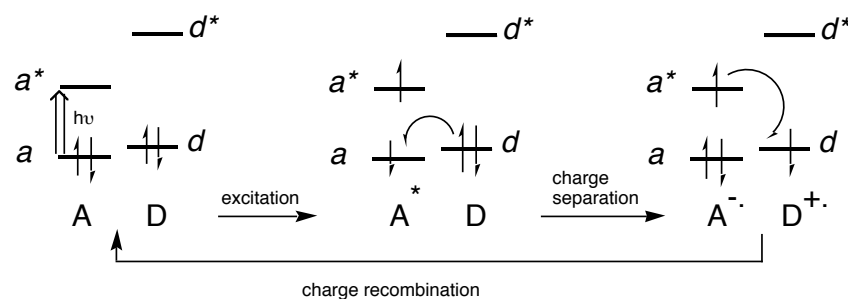


Fig. 14. FMO representation of charge separation and charge recombination following local excitation of the acceptor in a D/A system.

The HOMOs and LUMOs of D and A are labelled d , d^* and a , a^* , respectively. Local acceptor excitation ($a \rightarrow a^*$) is followed by electron transfer involving orbital interactions between d and a , while charge recombination involves interactions between a^* and d . The FMO description is undoubtedly an oversimplification, which may, for example, neglect important interactions between charge-transfer configurations and locally excited configurations¹¹. Nevertheless, it is a useful starting point for identifying important orbital interactions that contribute to the electronic coupling matrix elements involved in the photoinduced charge separation step, following local acceptor excitation (i.e. V^* is related to d/a interaction), and in the subsequent thermal charge recombination step (i.e. V is related to a^*/d interaction).

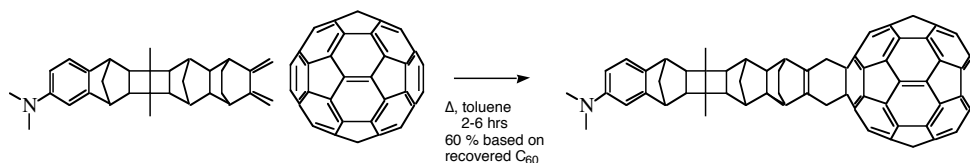


Fig. 15. Diels-Alder reaction with C₆₀ to obtain C₆₀[11]DMA.

The MOs a , a^* and d of $C_{60}[11]DMA^{12}$ are shown in Figures 16-18. These were obtained from AM1 calculations. Although the frontier orbitals are mainly localized on D or on A, it turns out that the highest occupied orbital of A (i.e. a) is extensively delocalized into the bridge and tailing out all the way into the donor domain (see Figure 16). Importantly, such delocalization into the bridge is found to a much lesser extent for a^* (see Figure 17) and for d (see Figure 18).

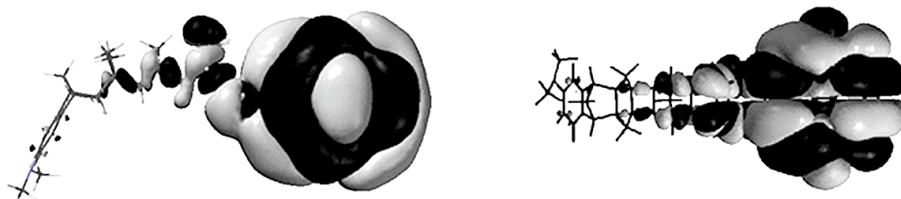


Fig. 16. Visualization of orbital a of the donor-bridge-fullerene(acceptor) system in 'side' (left) and 'top'(right) view, obtained from AM1 calculations, using a value of $0.001 \text{ electrons/au}^3$.

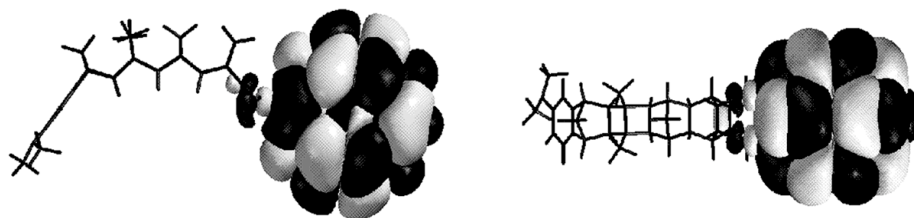


Fig. 17. Visualization of orbital a^* of the donor-bridge-fullerene(acceptor) system in 'side' (left) and 'top'(right) view, obtained from AM1 calculations, using a value of $0.001 \text{ electrons/au}^3$.

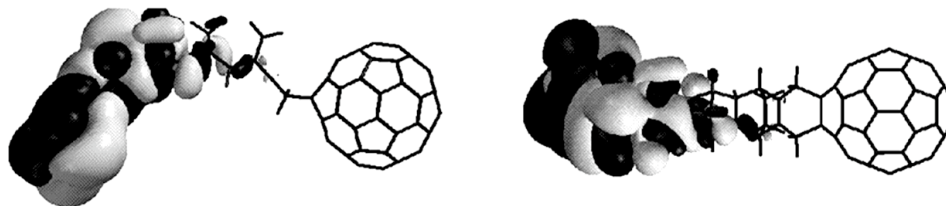


Fig. 18. Visualization of d of the donor-bridge-fullerene(acceptor) system in 'side' (left) and 'top'(right) view, obtained from AM1 calculations, using a value of $0.001 \text{ electrons/au}^3$.

As mentioned, the charge separation involves an interaction between the orbitals a and d , while charge recombination involves interactions between a^* and d . If

we now “project” orbital ***a*** onto orbital ***d***, and compare this to the “projection” of ***a**** and ***d*** we get a view of the difference in the electronic coupling (orbital overlap) that determines the rate of charge separation (***a*** and ***d***) and the electronic coupling that determines the rate of charge recombination (***a**** and ***d***). Clearly the former is much larger. Interestingly, experimental observations show that the ratio between the rates of charge separation and charge recombination for this system is in fact more than three orders of magnitude ($k_{CS}/k_{CR} = 1400$). As the equation described on page 9 expresses the relation between the electronic coupling and the rate, this is in perfect agreement.

Furthermore, we can now relate the left side of figure 7B to a “real” chemical structure with π -orbitals and we can have a better vision of how the electron density “flows” from one orbital to the other, through the small overlap. Figure 16 also is a very nice visualization of “*through bond interaction*” as the π -orbital (filled HOMO ***a***) of the fullerene extends strongly into the saturated hydrocarbon bridge and the orbital coefficients on different sigma bonds can actually be seen. This exemplifies that the way in which two units are connected (the medium in between) together with the manner in which the π -orbitals of these units couple to the bridge determine the extent of interaction between the two groups. If for example a chromophore has an orbital node (with coefficients of zero) at the attachment point of the bridge, this has the effect that the interaction is much less than expected on forehand. Imides often have a node on the nitrogen. The fullerene however has a high electron density at the attachments points of the bridge and its HOMO also has a very special symmetry (symmetric with respect to the plane of the bridge). This allows for strong coupling with the bridge.

The experimental results, together with semi-empirical MO calculations indicate that the special symmetry properties of the fullerene π -system may cause it to enter into very strong electronic coupling with the hydrocarbon bridge to allow fast photoinduced charge separation, while at the same time the electronic coupling relevant for charge recombination remains small.

Epilogue

I remember doing a late night low temperature emission experiment (in methyl-THF/ethyliodide!) with a student named Stijn Berkhout, during my PhD, who suddenly asked me: “So how is the electron transferred from donor to acceptor”? (the experiment actually ended up in JACS ‘95). This was the first time I started contemplating on how to describe this process in an understandable way. Many papers and books are either too extensive or too complicated (e.g. read ref. 10, 11), so my aim here was to keep concise and keep all the important details but make the concepts more easy to understand for non-experts.

Any comments (both positive and negative) are welcome as I now hope to keep this information available and updated (the server that contained the original crashed) . If you find any mistakes or missing information let me know.

I am contemplating on making something similar about energy transfer, and about the practical determination of electron transfer rates, beta's, hopping, tunneling, superexchange, solvent effects, some exercises, web-tools to use the equations used in this piece (like the Photonic Number Cruncher; what happened to the on-line Weller analysis?). How about an interactive version of figure 7B that is connected to changeable Weller-data and calculates and shows the Frank-Condon factor? Any Java-experts reading this?

René

4 References

This is not an extensive reference list, but contains some “classic” papers (ref. 5 to 8 and 10) and useful books for further reading. A few new (post 1996) general references have been added.

Sources of pictures: section 3.5 (Frank-Condon section): found on the web in a .ppt-talk of “Jean-Marie André “, must be scanned from Baggot or another book (Google: search (exact?): “overlap of vibrational wavefunctions”); F-C and Marcus: Dutton’s paper; section 3.6: Atkins, P.J. *Physical Chemistry*-downloadable from website.

All other pictures were made by myself (or the source is indicated).

New general references: (listed from short papers to extensive books or series)

Moser, C., J.M. Keske, K. Warncke, R.S. Farid and P.L. Dutton; *Nature* **1992** 355, 796-802. (tunneling in plants)

Davis, W. B.; Svec, W. A.; Ratner, M. A.; Wasielewski, M. R.; *Nature* **1998** 396, 60-63. (wire behaviour)

Williams, R. M.; Zwier, J. M.; Verhoeven, J. W. *J. Am. Chem. Soc.* **1995**, 117, 4093-4099. (application of Weller and Marcus to a D-A system. λ_s values are not correct, see my chapter 4 for corrected values)

Sautter, A.; Kaletas, B. K.; Schmid, D. G.; Dobrawa, R.; Zimine, M.; Jung, G.; van Stokkum, I. H. M.; De Cola, L.; Williams, R. M.; Würthner, F. *J. Am. Chem. Soc.*; **2005** 127(18) 6719-6729. (a recent example)

Paddon-Row, M.; “Electron and Energy Transfer” in *Stimulating Concepts in Chemistry*, Vögtle, F.; Stoddart J. F.; Shibasaki, M. (Eds), Wiley, **2000**. (very nice, the whole book)

Kuznetsov, A. M.; Ulstrup, J.; *Electron Transfer in Chemistry and Biology: An Introduction to the Theory*, Wiley, **1998**. (very physical)

Balzani, V. (Ed.) *Electron transfer in chemistry* (vol 1- 5). Wiley-VCH **2001**. (five books)

Atkins, P.; de Paula, J. *Physical Chemistry* 7-th edition chapter 29 (Marcus has made it to study-books!).

The old general references (from the 1996 version, short to extensive)

Closs, G.L.; Miller, J.R. *Science* **1988**, 240, 440. (a classic paper)

Marcus, R.A. *Angew. Chem. Int. Ed. Engl.* **1993**, 32, 1111 (Nobel Lecture).

Wasielewski, M.R. *Chem. Rev.* **1992**, 92, 435. (with loads of examples)

Kavarnos, G.J. "*Fundamentals of Photoinduced Electron Transfer*" VCH Publishers Inc **1993**. (rather compact)

Fox, M.A.; Chanon, M. "*Photoinduced Electron Transfer*" Elsevier Science Publishers **1988**. (four volumes).

Parts of this Chapter were also published in:

Williams, R. M.; Braslavsky, S. E.; "Triggering of Photomovement - Molecular Basis" in *Photomovement* Häder, D.-P. and Lebert, M. (Eds.); Elsevier Science B.V.: Amsterdam, Comprehensive Series in Photosciences, **2001**; Vol. 1, pp 15-50.

A few interesting elaborate websites of great photo-chemists working on electron transfer:

<http://photoscience.la.asu.edu/photosyn/faculty/gust/index.htm>

http://www.ups.upenn.edu/biocbiop/local_pages/dutton_lab.html

<http://www.chem.northwestern.edu/~wasielew/wazmain.html>

<http://turmac13.chem.columbia.edu/>

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