

Chapter 2

Photoinduced Energy and Electron Transfer Processes

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Abstract This chapter introduces the supramolecular photochemistry, i.e. photochemistry applied to supramolecular systems, and discusses the thermodynamic and kinetic aspects of photoinduced energy and electron transfer processes both between molecules and within supramolecular systems. In the case of electron transfer processes, Marcus theory is presented as well as quantum mechanical theory. For energy transfer processes, coulombic and exchange mechanisms are illustrated and the role of the bridge in supramolecular structures is discussed.

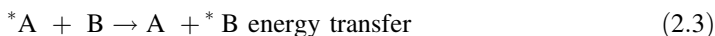
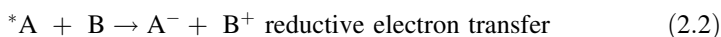
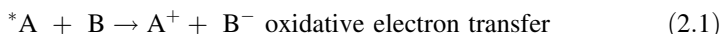
2.1 Bimolecular Processes

2.1.1 General Considerations

As we have seen in Sect. 1.6.5, each intramolecular decay step of an excited molecule is characterized by its own rate constant and each excited state is characterized by its *lifetime*, given by (1.8). In fluid solution, when the intramolecular deactivation processes are not too fast, i.e. when the lifetime of the excited state is sufficiently long, an excited molecule *A may have a chance to encounter a molecule of another solute, B. In such a case, some specific interaction can occur leading to the deactivation of the excited state by second order kinetic processes.

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The two most important types of interactions in an encounter are those leading to electron or energy transfer:



Bimolecular electron and energy transfer processes are important because they can be used (i) to quench an electronically excited state, i.e. to prevent its luminescence and/or reactivity, and (ii) to sensitize other species, for example to cause chemical changes of, or luminescence from, species that do not absorb light.

Simple kinetic arguments (vide infra, [Sect. 2.1.3](#)) show that only the excited states that live longer than ca. 10^{-9} s may have a chance to be involved in encounters with other solute molecules. Usually, in the case of metal complexes only the lowest excited state satisfies this requirement.

A point that must be stressed is that an electronically excited state is a species with quite different properties compared with those of the ground state molecule. Therefore, both the thermodynamic and kinetic aspects of photoinduced energy and electron transfer reactions must be carefully examined.

2.1.2 Thermodynamic Aspects

In condensed phases, vibrational relaxation is a very fast process (10^{-12} – 10^{-13} s) so that the electronically excited states involved in bimolecular processes are thermally equilibrated species ([Sect. 1.6.1](#)). This means that these reactions can be dealt with in the same way as any other chemical reaction, i.e. by using thermodynamic and kinetic arguments.

For a thermodynamic treatment of reactions involving excited states, we need to define the free energy difference between the excited and ground state of a molecule:

$$\Delta G(^*A, A) = \Delta H(^*A, A) - T\Delta S(^*A, A) \quad (2.4)$$

The readily available quantity for an excited state is its zero-zero energy $E^{00}(^*A, A)$, i.e. the energy difference between the ground and the excited state, both taken at their zero vibrational levels ([Fig. 1.9](#)). In the condensed phase at 1 atm, $\Delta H \approx \Delta E$, where ΔE is the internal (spectroscopic) energy. At 0 K, $\Delta E = NE^{00}(^*A, A)$. This is also approximately true at room temperature if the vibrational partition functions of the two states are not very different. As far as the entropy term is concerned, it can receive three different contributions due to: (i) a change in dipole moment with consequent change in solvation; (ii) changes in the internal degrees of freedom; (iii) changes in orbital and spin degeneracy. This last

contribution is the only one which can be straightforwardly calculated, but unfortunately it is also the least important in most cases. For a change in multiplicity from singlet to triplet it amounts to 0.03 eV at 298 K, which means that it can usually be neglected if one considers the experimental uncertainties that affect the other quantities involved in these calculations. The entropy contribution due to changes in dipole moment can be calculated if the change in dipole moment in going from the ground to the excited state is known. Finally, the contribution of changes of internal degrees of freedom is difficult to evaluate.

Changes in size, shape and solvation of an excited state with respect to the ground state cause a shift (Stokes shift) between absorption and emission (Sect. 1.6.2). When the Stokes shift is small (often a necessary condition to have a sufficiently long lived excited state), the changes in shape, size, and solvation are also small and the entropy term in (2.4) may be neglected. In such a case, the standard free energy difference between the ground and the excited state can be approximated as

$$\Delta G^0(*A, A) \approx NE^{00}(*A, A) \quad (2.5)$$

and the free energy changes of energy and electron transfer reactions can readily be obtained. An energy transfer process (2.3) will be thermodynamically allowed when $E^{00}(*A, A) > E^{00}(*B, B)$. As far as the electron transfer processes (2.1) and (2.2) are concerned, within the approximation described above the redox potentials for the excited state couples may be calculated from the standard potentials of the ground state couples and the one-electron potential corresponding to the zero-zero spectroscopic energy (i.e. the E^{00} value in eV):

$$E^0(A^+/*A) = E^0(A^+/A) - E^{00} \quad (2.6)$$

$$E^0(*A/A^-) = E^0(A/A^-) + E^{00} \quad (2.7)$$

The free energy change of a photoinduced redox process can then be readily calculated from the redox potentials, as is usually done for “normal” (i.e. ground state) redox reactions.

It should be noted that, as shown quantitatively by (2.6) and (2.7), an *excited state is both a stronger reductant and a stronger oxidant than the ground state* because of its extra energy content. Whether or not the excited state is a powerful oxidant and/or reductant depends, of course, on the redox potentials of the ground state.

2.1.3 Kinetic Aspects of Bimolecular Processes

Leaving aside for the moment a detailed treatment of the rate of photoinduced energy- and electron transfer (Sects. 2.3 and 2.5), we will briefly recall here some fundamental kinetic aspects of bimolecular processes involving excited states.

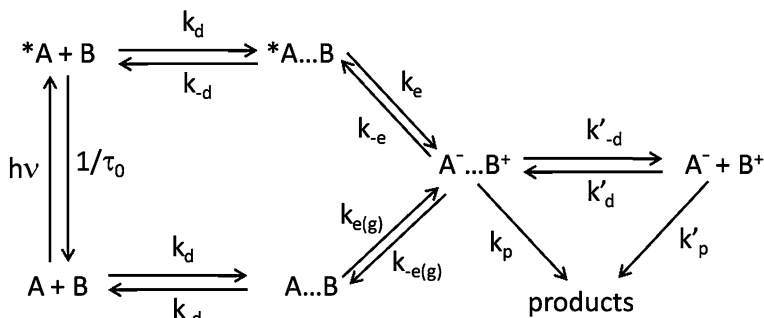


Fig. 2.1 Kinetic mechanism for photoinduced electron transfer reactions

For processes requiring diffusion and formation of encounters, we can use the Stern–Volmer model which assumes statistical mixing of $*A$ and B . The simplest case is that of a species $*A$ that decays via some intramolecular paths and, in fluid solution, can encounter a quencher B . The excited state lifetimes in the absence (τ_0) and in the presence (τ) of the quencher B are given by (2.8) and (2.9), where k_q is the bimolecular constant of the quenching process.

$$\tau_0 = 1/(k_r + k_{nr} + k_p) \quad (2.8)$$

$$\tau = 1/(k_r + k_{nr} + k_p + k_q[B]) \quad (2.9)$$

Dividing (2.8) by (2.9), yields the well-known Stern–Volmer Eq. 2.10

$$\tau_0/\tau = 1 + k_q\tau_0[B] \quad (2.10)$$

that can be used to obtain k_q when τ_0 is known. Since the maximum value of k_q is of the order of $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ (diffusion limit) and $[B]$ can hardly be $>10^{-2} \text{ M}$, it is clear that it is difficult to observe bimolecular processes in the case of excited states with lifetime $\leq 10^{-9} \text{ s}$.

The rate constant k_q of the bimolecular quenching process is, of course, controlled by several factors. In order to elucidate these factors, a detailed reaction mechanism must be considered. Since both electron transfer and exchange energy transfer are collisional processes, the same kinetic formalism may be used in both cases. Taking as an example a reductive excited state electron transfer process (2.2), the reaction rate can be discussed on the basis of the mechanism shown in the scheme of Fig. 2.1, where k_d , k_{-d} , k'_d , and k'_{-d} are rate constants for formation and dissociation of the outer-sphere encounter complex, k_e and k_{-e} are unimolecular rate constants for the electron transfer step involving the excited state, and $k_{e(g)}$ and $k_{-e(g)}$ are the corresponding rate constants for the ground state electron transfer step. A simple steady state treatment [1] shows that the experimental rate constant of (2.2) can be expressed as a function of the rate constants of the various steps by (2.11),

$$k_{\text{exp}} = \frac{k_d}{1 + \frac{k_{-d}}{k_e} + \frac{k_{-d}k_{-e}}{k_x k_e}} \quad (2.11)$$

where k_x may often be replaced by k'_{-d} (for more details, see [2]). In a classical approach, k_{-e}/k_e is given by $\exp(-\Delta G^0/RT)$, where ΔG^0 is the standard free energy change of the electron transfer step. An analogous expression holds for bimolecular energy transfer.

The key step of the process is, of course, the unimolecular electron–(or energy–) transfer step (k_e). Before going into more details (Sect. 2.2.3), it is important to extend our discussion to photoinduced energy and electron transfer processes in supramolecular systems where *A does not need to diffuse to encounter B, but is already more or less close to B because A and B are linked together.

2.2 Supramolecular Photochemistry

2.2.1 Definition of a Supramolecular System

From a functional viewpoint the distinction between what is molecular and what is supramolecular can be based on the degree of inter-component electronic interactions [3]. This concept is illustrated, for example, in Fig. 2.2. In the case of a photon stimulation, a system $A \sim B$, consisting of two units (\sim indicates any type of “bond” that keeps the units together), can be defined a supramolecular species if light absorption leads to excited states that are substantially localized on either A or B, or causes an electron transfer from A to B (or viceversa). By contrast, when the excited states are substantially delocalized on the entire system, the species can be better considered as a large molecule. Similarly (Fig. 2.2), oxidation and reduction of a supramolecular species can substantially be described as oxidation and reduction of specific units, whereas oxidation and reduction of a large molecule leads to species where the hole or the electron are delocalized on the entire system. In more general terms, when the interaction energy between units is small compared to the other relevant energy parameters, a system can be considered a supramolecular species, regardless of the nature of the bonds that link the units. It should be noted that the properties of each component of a supramolecular species, i.e. of an assembly of weakly interacting molecular components, can be known from the study of the isolated components or of suitable model compounds.

A peculiar aspect of photoinduced energy and electron transfer in supramolecular systems is that the relative positions and distances between the excited state *A and the quencher B can be preorganized so as to control the rate of the process (vide infra).

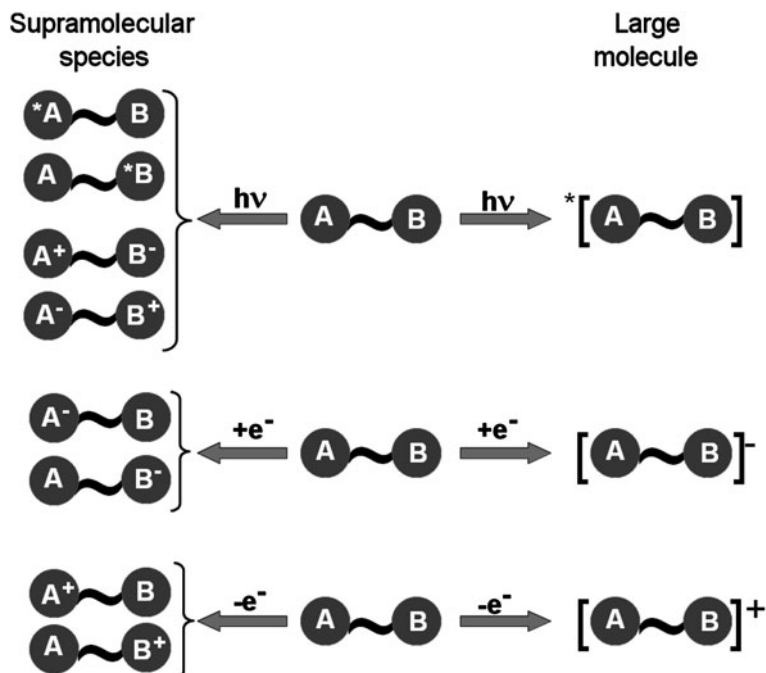
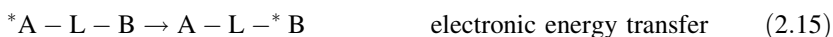
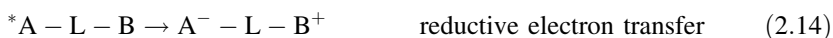
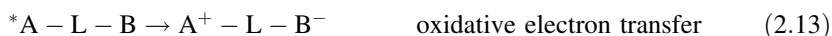


Fig. 2.2 Schematic representation of the difference between a supramolecular system and a large molecule based on the effects caused by a photon or an electron input. For more details, see text

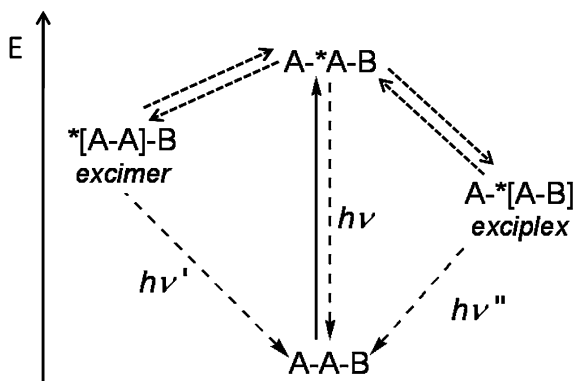
2.2.2 Photoinduced Energy and Electron Transfer in Supramolecular Systems

For simplicity, we consider the case of an $A-L-B$ supramolecular system, where A is the light-absorbing molecular unit (2.12), B is the other molecular unit involved with A in the light induced processes, and L is a connecting unit (often called bridge). In such a system, electron and energy transfer processes can be described as follows:

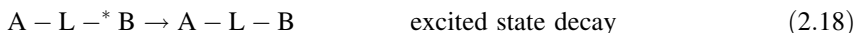


In the absence of chemical complications (e.g. fast decomposition of the oxidized and/or reduced species), photoinduced electron transfer processes are followed by spontaneous back-electron transfer reactions that regenerate the

Fig. 2.3 Schematic representation of excimer and exciplex formation



starting ground state system (2.16 and 2.17), and photoinduced energy transfer is followed by radiative and/or non-radiative deactivation of the excited acceptor (2.18):



Since in supramolecular systems electron- and energy transfer processes are no longer limited by diffusion, they take place by first order kinetics and in suitably designed supramolecular systems they can involve even very short lived excited states. The reactions described by (2.13–2.15) correspond to the key step (first order rate constant k_e , Fig. 2.1) occurring in the analogous bimolecular reactions (2.1–2.3) taking place in the encounters formed by diffusion. The parameters affecting the rates of such unimolecular reactions will be discussed in Sects. 2.3 and 2.5.

2.2.3 Excimers and Exciplexes

In most cases, the interaction between excited and ground state components in a supramolecular system, and even more so in an encounter, is weak. When the interaction is strong, new chemical species, which are called excimers (from excited dimers) or exciplexes (from excited complexes), depending on whether the two interacting units have the same or different chemical nature. The scheme shown in Fig. 2.3 refers to a supramolecular system, but it holds true also for species in an encounter complex. It is important to notice that excimer and exciplex formation are reversible processes and that both excimers and exciplexes sometimes can give luminescence. Compared with the “monomer” emission, the

emission of an excimer or exciplex is always displaced to lower energy (longer wavelengths) and usually corresponds to a broad and rather weak band.

Excimers are usually obtained when an excited state of an aromatic molecule interacts with the ground state of a molecule of the same type. For example, between excited and ground state of anthracene units. Exciplexes are obtained when an electron donor (acceptor) excited state interacts with an electron acceptor (donor) ground state molecule, for example, between excited states of aromatic molecules (electron acceptors) and amines (electron donors).

It may also happen that in an encounter or a supramolecular structure there is a non negligible electronic interaction between adjacent chromophoric units already in the ground state. In such a case, the absorption spectrum of the species may substantially differ from the sum of the absorption spectra of the component units. When the units have the same chemical nature, the interaction leads to formation of dimers. When the two units are different, the interaction is usually charge-transfer in nature with formation of charge-transfer complexes. Excitation of a dimer leads to an excited state that is substantially the same as the corresponding excimer, and excitation of a charge-transfer ground state complex leads to an excited state that is substantially the same as that of the corresponding exciplex.

2.3 Electron Transfer Processes

From a kinetic viewpoint, electron transfer processes involving excited states, as well as those involving ground state molecules, can be dealt with in the frame of the Marcus theory [4] and of the successive, more sophisticated theoretical models [5]. The only difference between electron transfer processes involving excited state instead of ground state molecules is that in the first case, in the calculation of the free energy change, the redox potential of the excited state couple has to be used (2.6 and 2.7).

2.3.1 Marcus Theory

In an absolute rate formalism (Marcus model [4]), potential energy curves of an electron transfer reaction for the initial (i) and final (f) states of the system are represented by parabolic functions (Fig. 2.4). The rate constant for an electron transfer process can be expressed as

$$k_{\text{el}} = v_N \kappa_{\text{el}} \exp\left(-\frac{\Delta G^\ddagger}{RT}\right) \quad (2.19)$$

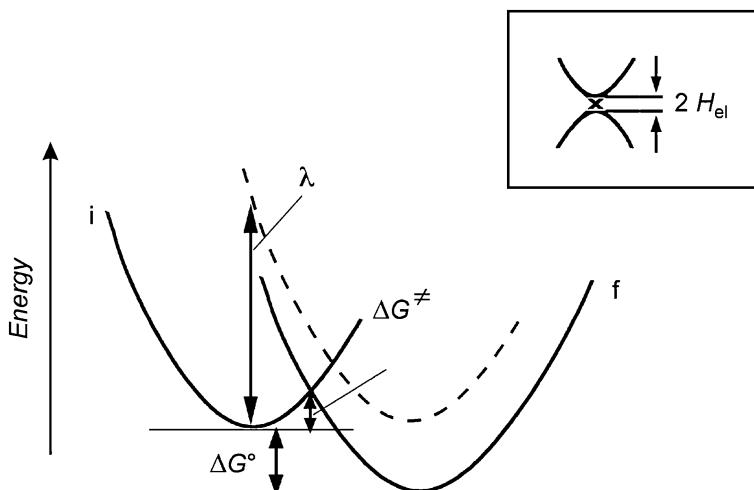


Fig. 2.4 Profile of the potential energy curves of an electron transfer reaction: *i* and *f* indicate the initial and final states of the system. The dashed curve indicates the final state for a self-exchange (isoergonic) process

where ν_N is the average nuclear frequency factor, κ_{el} is the electronic transmission coefficient, and ΔG^\ddagger is the free activation energy. This last term can be expressed by the Marcus quadratic relationship

$$\Delta G^\ddagger = \frac{1}{4\lambda} (\Delta G^0 + \lambda)^2 \quad (2.20)$$

where ΔG^0 is the standard free energy change of the reaction and λ is the nuclear reorganizational energy (Fig. 2.4).

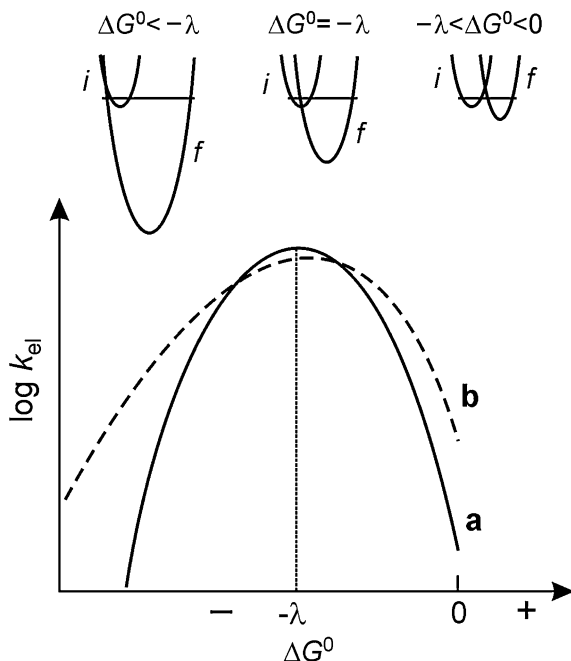
Equations 2.19 and 2.20 predict that for a homogeneous series of reactions (i.e. for reactions having the same λ and k_{el} values) a $\ln k_{el}$ versus ΔG^0 plot is a bell-shaped curve (Fig. 2.5, solid line) involving:

- a normal regime for small driving forces ($-\lambda < \Delta G^0 < 0$) in which the process is thermally activated and $\ln k_{el}$ increases with increasing driving force;
- an activationless regime ($-\lambda \approx \Delta G^0$) in which a change in the driving force does not cause large changes in the reaction rate;
- an “inverted” regime for strongly exergonic processes ($-\lambda > \Delta G^0$) in which $\ln k_{el}$ decreases with increasing driving force [3].

The reorganizational energy λ can be expressed as the sum of two independent contributions corresponding to the reorganization of the “inner” (bond lengths and angles within the two reaction partners) and “outer” (solvent reorientation around the reacting pair) nuclear modes:

$$\lambda = \lambda_i + \lambda_o \quad (2.21)$$

Fig. 2.5 Free energy dependence of electron transfer rate (i , initial state; f , final state) according to Marcus (a) and quantum mechanical (b) treatments. The three kinetic regimes (normal, activationless, and “inverted”) are shown schematically in terms of Marcus parabolae



The outer reorganizational energy, which is often the predominant term in electron transfer processes, can be estimated, to a first approximation, by the expression

$$\lambda_o = e^2 \left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s} \right) \left(\frac{1}{2r_A} + \frac{1}{2r_B} - \frac{1}{r_{AB}} \right) \quad (2.22)$$

where e is the electronic charge, ε_{op} and ε_s are the optical and static dielectric constants of the solvent, r_A and r_B are the radii of the reactants, and r_{AB} is the inter reactant center-to-center distance. Equation 2.22 shows that λ_o is particularly large for reactions in polar solvents between reaction partners which are separated by a large distance.

The electronic transmission coefficient k_{el} is related to the probability of crossing at the intersection region (Fig. 2.4). It can be expressed by (2.23)

$$k_{el} = \frac{2[1 - \exp(-v_{el}/2v_N)]}{2 - \exp(-v_{el}/2v_N)} \quad (2.23)$$

where

$$v_{el} = \frac{2(H^{el})^2}{h} \left(\frac{\pi^3}{\lambda RT} \right)^{1/2} \quad (2.24)$$

and H^{el} is the matrix element for electronic interaction (Fig. 2.4, inset).

If H^{el} is large, $v_{\text{el}} \gg v_{\text{N}}$, $k_{\text{el}} = 1$ and

$$k_{\text{el}} = v_{\text{N}} \exp\left(\frac{-\Delta G^\ddagger}{RT}\right) \quad \text{adiabatic limit} \quad (2.25)$$

If H^{el} is small, $v_{\text{el}} \ll v_{\text{N}}$, $k_{\text{el}} = v_{\text{el}}/v_{\text{N}}$ and

$$k_{\text{el}} = v_{\text{el}} \exp\left(\frac{-\Delta G^\ddagger}{RT}\right) \quad \text{non - adiabatic limit} \quad (2.26)$$

Under the latter condition, k_{el} is proportional to $(H^{\text{el}})^2$. The value of H^{el} depends on the overlap between the electronic wavefunctions of the donor and acceptor groups, which decreases exponentially with donor–acceptor distance. It should be noticed that the amount of electronic interaction required to promote photoinduced electron transfer is very small in a common chemical sense. In fact, by substituting reasonable numbers for the parameters in (2.26), it can be easily verified that, for an activationless reaction, H^{el} values of a few wavenumbers are sufficient to give rates in the sub-nanosecond time scale, while a few hundred wavenumbers may be sufficient to reach the limiting adiabatic regime (2.25).

As discussed in Sect. 2.6, it can be expected that the connecting unit L (2.12–2.15) plays an important role in governing the electronic interaction between distant partners.

2.3.2 Quantum Mechanical Theory

From a quantum mechanical viewpoint, both the photoinduced and back-electron transfer processes can be viewed as radiationless transitions between different, weakly interacting electronic states of the A–L–B supermolecule (Fig. 2.6). The rate constant of such processes is given by an appropriate Fermi “golden rule” expression:

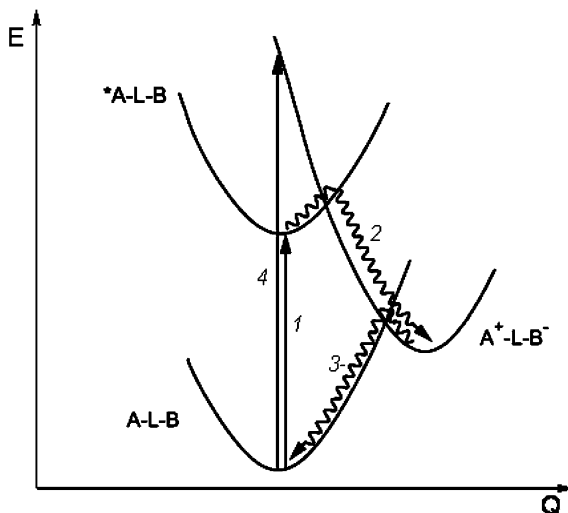
$$k_{\text{el}} = \frac{4\pi^2}{h} (H^{\text{el}})^2 \text{FC}^{\text{el}} \quad (2.27)$$

where the electronic H^{el} and nuclear FC^{el} factors are obtained from the electronic coupling and the Franck–Condon density of states, respectively. In the absence of any intervening medium (through-space mechanism), the electronic factor decreases exponentially with increasing distance:

$$H^{\text{el}} = H^{\text{el}}(0) \exp\left[-\frac{\beta^{\text{el}}}{2}(r_{\text{AB}} - r_0)\right] \quad (2.28)$$

where r_{AB} is the donor–acceptor distance, $H^{\text{el}}(0)$ is the interaction at the “contact” distance r_0 , and β^{el} is an appropriate attenuation parameter. The 1/2 factor arises

Fig. 2.6 Electron transfer processes in a supramolecular system: (1) photoexcitation; (2) photoinduced electron transfer; (3) thermal back-electron transfer; (4) optical electron transfer



because originally β^{el} was defined as the exponential attenuation parameter for rate constant rather than for electronic coupling, (2.29):

$$k_{\text{el}} \propto \exp(-\beta^{\text{el}} r_{\text{AB}}) \quad (2.29)$$

For donor–acceptor components separated by vacuum, β^{el} is estimated to be in the range $2\text{--}5 \text{ \AA}^{-1}$.

When donor and acceptor are separated by “matter” (in our case, the bridge L) the electron transfer process can be mediated by the bridge. If the electron is temporarily localized on the bridge, an intermediate is produced and the process is said to take place by a sequential or “hopping” mechanism (Sect. 2.6). Alternatively, the electronic coupling can be mediated by mixing the initial and final states of the system with virtual, high energy electron transfer states involving the intervening medium (superexchange mechanism), as illustrated in Fig. 2.7.

The FC^{el} term of (2.27) is a thermally averaged Franck–Condon factor connecting the initial and final states. It contains a sum of overlap integrals between the nuclear wave functions of initial and final states of the same energy. Both inner and outer (solvent) vibrational modes are included. The general expression of FC^{el} is quite complicated. It can be shown that in the high temperature limit ($h\nu < k_{\text{B}}T$), an approximation sufficiently accurate for many room temperature processes, the nuclear factor takes the simple form:

$$\text{FC}^{\text{el}} = \left(\frac{1}{4\pi\lambda k_{\text{B}}T} \right)^{1/2} \exp \left[-\frac{(\Delta G^0 + \lambda)^2}{4\lambda k_{\text{B}}T} \right] \quad (2.30)$$

where λ is the sum of the inner (λ_i) and outer (λ_o) reorganizational energies. The exponential term of (2.30) is the same as that predicted by the classical Marcus model based on parabolic energy curves for initial and final states. Indeed, also the

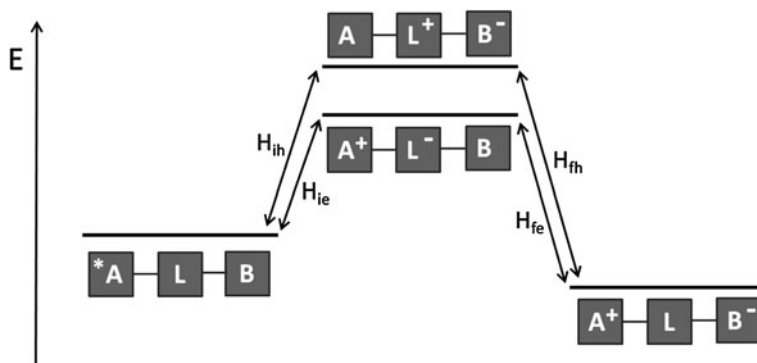


Fig. 2.7 State diagram illustrating superexchange interaction between an excited state electron donor (*A) and an electron acceptor (B) through a bridge (L)

quantum mechanical model contains the important prediction of three distinct kinetic regimes, depending on the driving force of the electron transfer process (Fig. 2.5). The quantum mechanical model, however, predicts a practically linear, rather than a parabolic, decrease of $\ln k_{\text{el}}$ with increasing driving force in the inverted region (Fig. 2.5, *dashed line*).

2.4 Optical Electron Transfer

The above discussion makes it clear that reactants and products of an electron transfer process are intertwined by a ground/excited state relationship. For example, for nuclear coordinates that correspond to the equilibrium geometry of the reactants, as shown in Fig. 2.6, A⁺-L-B⁻ is an electronically excited state of A-L-B. Therefore, optical transitions connecting the two states are possible, as indicated by arrow 4 in Fig. 2.6.

The Hush theory [6] correlates the parameters that are involved in the corresponding thermal electron transfer process by means of (2.31–2.33)

$$E_{\text{op}} = \lambda + \Delta G^0 \quad (2.31)$$

$$\Delta \bar{\nu}_{1/2} = 48.06(E_{\text{op}} - \Delta G^0)^{1/2} \quad (2.32)$$

$$\epsilon_{\text{max}} \Delta \bar{\nu}_{1/2} = (H^{\text{el}})^2 \frac{r^2}{4.20 \times 10^{-4} E_{\text{op}}} \quad (2.33)$$

where E_{op} , $\Delta \bar{\nu}_{1/2}$ (both in cm^{-1}), and ϵ_{max} are the energy, halfwidth, and maximum intensity of the electron transfer band, and r (in \AA) the center-to-center distance. As shown by (2.31–2.33), the energy depends on both reorganizational energy and thermodynamics, the halfwidth reflects the reorganizational energy, and the intensity

of the transition is mainly related to the magnitude of the electronic coupling between the two redox centers. In principle, therefore, important kinetic information on a thermal electron transfer process may be obtained from the study of the corresponding optical transition. In practice, due to the dependence of the intensity on H^{el} , optical electron transfer bands may only be observed in systems with relatively strong inter-component electronic coupling [e.g. for H^{el} values of 10, 100, and 1000 cm^{-1} , ε_{max} values of 0.2, 20, and 2000 $\text{M}^{-1} \text{cm}^{-1}$, respectively, $\Delta\bar{\nu}_{1/2} = 4000 \text{ cm}^{-1}$ and $r = 7\text{\AA}$ are obtained from (2.33) by using $E_{\text{op}} = 15000 \text{ cm}^{-1}$]. By recalling what is said at the end of Sect. 2.3.1, it is clear that weakly coupled systems may undergo relatively fast electron transfer processes without exhibiting appreciably intense optical electron transfer transitions. More details on optical electron transfer and related topics (i.e. mixed valence metal complexes) can be found in the literature [7].

2.5 Energy Transfer Processes

The thermodynamic ability of an excited state to intervene in energy transfer processes is related to its zero-zero spectroscopic energy, E^{00} . From a kinetic viewpoint, bimolecular energy transfer processes involving encounters can formally be treated using a Marcus type approach, i.e. by equations like (2.19) and (2.20), with $\Delta G^0 = E_{\text{A}}^{00} - E_{\text{B}}^{00}$ and $\lambda \sim \lambda_i$ [8].

Energy transfer, particularly in supramolecular systems, can be viewed as a radiationless transition between two “localized”, electronically excited states (2.15). Therefore, the rate constant can be again obtained by an appropriate “golden rule” expression:

$$k_{\text{en}} = \frac{4\pi^2}{h} (H^{\text{en}})^2 \text{FC}^{\text{en}} \quad (2.34)$$

where H^{en} is the electronic coupling between the two excited states inter-converted by the energy transfer process and FC^{en} is an appropriate Franck–Condon factor. As for electron transfer, the Franck–Condon factor can be cast either in classical or quantum mechanical terms. Classically, it accounts for the combined effects of energy gradient and nuclear reorganization on the rate constant. In quantum mechanical terms, the FC factor is a thermally averaged sum of vibrational overlap integrals. Experimental information on this term can be obtained from the overlap integral between the emission spectrum of the donor and the absorption spectrum of the acceptor.

The electronic factor H^{en} is a two-electron matrix element involving the HOMO and LUMO of the energy-donor and energy-acceptor components. By following standard arguments [5], this factor can be split into two additive terms, a *coulombic* term and an *exchange* term. The two terms depend differently on the parameters of the system (spin of ground and excited states, donor–acceptor

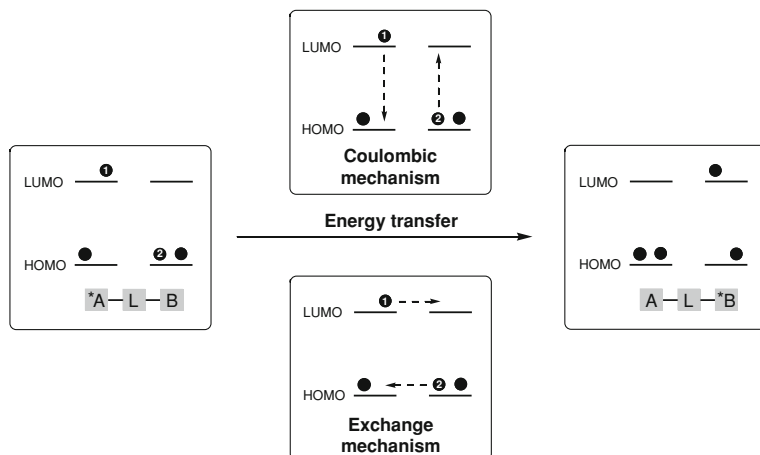


Fig. 2.8 Pictorial representation of the coulombic and exchange energy transfer mechanisms

distance, etc.). Because each of them can become predominant depending on the specific system and experimental conditions, two different mechanisms can occur, whose orbital aspects are schematically represented in Fig. 2.8.

2.5.1 Coulombic Mechanism

The coulombic (also called resonance, Förster-type [9, 10], or through-space) mechanism is a long-range mechanism that does not require physical contact between donor and acceptor. It can be shown that the most important term within the coulombic interaction is the dipole–dipole term [9, 10], that obeys the same selection rules as the corresponding electric dipole transitions of the two partners ($*A \rightarrow A$ and $B \rightarrow *B$, Fig. 2.8). Coulombic energy transfer is therefore expected to be efficient in systems in which the radiative transitions connecting the ground and the excited state of each partner have high oscillator strength. The rate constant for the dipole–dipole coulombic energy transfer can be expressed as a function of the spectroscopic and photophysical properties of the two molecular components and their distance.

$$k_{\text{en}}^{\text{F}} = \frac{9000 \ln 10}{128\pi^5 N} \frac{K^2 \Phi}{n^4 r_{\text{AB}}^6 \tau} J_{\text{F}} = 8.8 \times 10^{-25} \frac{K^2 \Phi}{n^4 r_{\text{AB}}^6 \tau} J_{\text{F}} \quad (2.35)$$

$$J_{\text{F}} = \frac{\int \frac{F(\bar{\nu})\varepsilon(\bar{\nu})}{\bar{\nu}^4} d\bar{\nu}}{\int F(\bar{\nu}) d\bar{\nu}} \quad (2.36)$$

where K is an orientation factor which takes into account the directional nature of the dipole–dipole interaction ($K^2 = 2/3$ for random orientation), Φ and τ are, respectively, the luminescence quantum yield and lifetime of the donor, n is the solvent refractive index, r_{AB} is the distance (in Å) between donor and acceptor, and J_F is the Förster overlap integral between the luminescence spectrum of the donor, $F(\bar{\nu})$, and the absorption spectrum of the acceptor, $\varepsilon(\bar{\nu})$, on an energy scale (cm^{-1}). With good spectral overlap integral and appropriate photophysical properties, the $1/r_{AB}^6$ distance dependence enables energy transfer to occur efficiently over distances substantially exceeding the molecular diameters. The typical example of an efficient coulombic mechanism is that of singlet–singlet energy transfer between large aromatic molecules, a process used by Nature in the antenna systems of the photosynthetic apparatus [11].

2.5.2 Exchange Mechanism

The rate constant for the exchange (also called Dexter-type [12]) mechanism can be expressed by:

$$k_{\text{en}}^{\text{D}} = \frac{4\pi^2}{h} (H^{\text{en}})^2 J_{\text{D}} \quad (2.37)$$

where the electronic term H^{en} is obtained from the electronic coupling between donor and acceptor, exponentially dependent on distance:

$$H^{\text{en}} = H^{\text{en}}(0) \exp\left[-\frac{\beta^{\text{en}}}{2}(r_{AB} - r_0)\right] \quad (2.38)$$

The nuclear factor J_{D} is the Dexter overlap integral between the emission spectrum of the donor and the absorption spectrum of the acceptor:

$$J_{\text{D}} = \frac{\int F(\bar{\nu})\varepsilon(\bar{\nu})d\bar{\nu}}{\int F(\bar{\nu})d\bar{\nu} \int \varepsilon(\bar{\nu})d\bar{\nu}} \quad (2.39)$$

The exchange interaction can be regarded (Fig. 2.8) as a double electron transfer process, one-electron moving from the LUMO of the excited donor to the LUMO of the acceptor, and the other from the acceptor HOMO to the donor HOMO. This important insight is illustrated in Fig. 2.9, from which it is clear that the attenuation factor β^{en} for exchange energy transfer should be approximately equal to the sum of the attenuation factors for two separated electron transfer processes, i.e. β^{el} for electron transfer between the LUMO of the donor and acceptor (2.29), and β^{ht} for the electron transfer between the HOMO (superscript ht denotes for hole transfer from the donor to the acceptor).

The spin selection rules for this type of mechanism arise from the need to obey spin conservation in the reacting pair as a whole. This enables the exchange

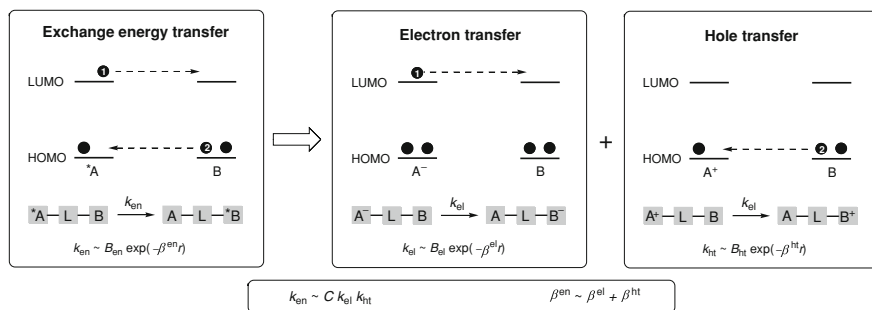
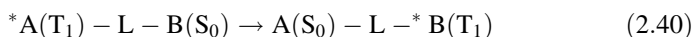


Fig. 2.9 Analysis of the exchange energy transfer mechanism in terms of electron- and hole transfer processes. The relationships between the rate constants and the attenuation factors of the three processes are also shown

mechanism to be operative in many instances in which the excited states involved are spin forbidden in the usual spectroscopic sense. Thus, the typical example of an efficient exchange mechanism is that of triplet-triplet energy transfer:



Exchange energy transfer from the lowest spin forbidden excited state is expected to be the rule for metal complexes [13].

Although the exchange mechanism was originally formulated in terms of direct overlap between donor and acceptor orbitals, it is clear that it can be extended to coupling mediated by the intervening medium (i.e. the connecting bridge), as discussed above for electron transfer processes (hopping and super exchange mechanisms).

2.6 The Role of the Bridge in Supramolecular Systems

The discussion above underlines the important role played by the connecting units (bridges) in mediation of electron- and energy transfer processes between donor and acceptor components in supramolecular structures [3]. As a colloquial way of emphasizing this role, it has become customary to consider bridges as “molecular wires” and to talk of their “conducting” properties. It should be remarked, however, that in the super exchange mechanism the bridge levels are always much higher in energy than those of donor and acceptor (Fig. 2.7), so the electron tunnels in a single step from donor to acceptor. Electron- and energy transfer processes through such bridges are, therefore, not comparable with electron transfer in macroscopic systems where the electron really moves along the wire. In some cases, however, the energy level of the bridge is so low that it becomes intermediate between the initial and final states. As a consequence, electron or energy hopping occurs and the bridge is directly involved in the process.

When such a hopping-type mechanism is operative, very small distance dependence of the rate constants is expected [3].

Finally, when there is complete mixing among the donor/bridge/acceptor orbitals (large coupling limit) the bridge essentially acts as an incoherent molecular wire, as happens for conjugated conducting polymers, and the system is expected to behave according to an ohmic regime where the distance dependence of the rate varies inversely with bridge length.

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