

# Chapter 2

## Energy Transfer Review

In this chapter, we discuss the basic concepts of excitation energy transfer, making the distinction between *radiative* and *nonradiative*, and giving a brief overview on the classical and quantum mechanical description of energy transfer [1].

### 2.1 Introduction

Excitation energy transfer of an excited state energy of the donor ( $D$ ) to the ground state of the acceptor ( $A$ ) is possible provided that the emission spectrum of the donor partially overlaps the absorption spectrum of the acceptor. This is a very important process, which occurs in a variety of situations. Excitation energy transfer can be grouped into *heterotransfer* versus *homotransfer* and *radiative* versus *nonradiative* transfer.

Energy transfer from an excited donor ( $D^*$ ) to another that is chemically different, ground acceptor  $A$ , is called *heterotransfer*.



If the donor and the acceptor are identical, then the energy transfer is *homotransfer*.



In homotransfer, excitation transport or energy migration can occur. In such case, the process of energy transfer repeats itself such that the excitation migrates over several molecules.

In *radiative transfer*, a photon emitted by the donor is absorbed by the acceptor, whereas *nonradiative transfer* occurs without emission of “real” photons; it is mediated by the so-called “virtual” photons. In the following we briefly discuss the classical and quantum mechanical description for the energy transfer.

## 2.2 Classical Description of Energy Transfer

In classical terms, the electronic energy transfer between the donor and the acceptor is viewed as the interaction of two oscillating electric dipoles. The donor’s dipole is initially in oscillation, and the acceptor’s dipole is initially at rest. Because of the resonance condition, the excitation is transferred from the first dipole to the second one.

The electric field of a dipole oscillating in vacuum is given by

$$\mathbf{E}(r, t) = \frac{p(t')}{4\pi\epsilon_0} \left\{ [3(\mathbf{n} \cdot \mathbf{d})\mathbf{n} - \mathbf{d}] \left( \frac{1}{r^3} - \frac{ik}{r^2} \right) + [(\mathbf{n} \cdot \mathbf{d})\mathbf{n} - \mathbf{d}] \frac{k^2}{r} \right\} \quad (2.3)$$

where  $p(t) = p_0 \cos(\omega t)$  is the time-dependent electric dipole moment, with amplitude  $p_0$ ,  $t' = t - r/c$ ,  $\mathbf{n}$  and  $\mathbf{d}$  are the unit vectors in the donor to acceptor direction and the donor’s dipole moment, respectively,  $k = \omega/c$  and  $r$  is the distance from the dipole [2]. The distance dependence of the electric field defines two different zones: (1) for  $r \ll \lambda$  (near zone) the  $r^{-3}$  term dominates, and the angular dependence is identical to that of a static dipole, with transversal and longitudinal components; and (2) for  $r \gg \lambda$  (radiative or far zone, also known as wave zone), the  $r^{-1}$  term dominates, the electric field is always perpendicular to  $\mathbf{n}$  (transversal field), and the radiation corresponds to a spherical wave.

The power radiated by the dipole is [2]

$$P^0 = \frac{p_0^2 \omega^4}{12\pi\epsilon_0 c^3} \quad (2.4)$$

For simplicity, the acceptor can be considered as a passive absorber characterized by an absorption cross-section. Therefore, the power it absorbs, when placed at a distance  $r$  from the dipole is

$$P' = \frac{1}{2} c \epsilon_0 E_0^2 \sigma \quad (2.5)$$

where  $\sigma$  is the acceptor’s cross-section and  $E_0^2$  is the amplitude of the dipole’s electric field given by (2.3). After orientation averaging,  $E_0^2$  takes the form of

$$E_0^2 = 2 \left( \frac{P_0}{4\pi\epsilon_0} \right)^2 \left( \frac{k^4}{3r^2} + \frac{k^2}{3r^4} + \frac{1}{r^6} \right) \quad (2.6)$$

Substitution of (2.6) into (2.5) gives

$$P' = \frac{\sigma}{4\pi r^2} \left[ 1 + \left( \frac{\tilde{\lambda}}{r} \right)^2 + 3 \left( \frac{\tilde{\lambda}}{r} \right)^4 \right] P^0 \quad (2.7)$$

where  $\tilde{\lambda} = \lambda/(2\pi)$  For large distances  $r \gg \lambda$ , (2.7) reduces to

$$P' = \frac{\sigma}{4\pi r^2} P^0 \quad (2.8)$$

This equation has a simple geometric interpretation and corresponds to the radiative transfer. Equation (2.8) implies that the power emitted by the donor in the presence of an acceptor is

$$P = \left\{ 1 + \frac{\sigma}{4\pi r^2} \left[ \left( \frac{\tilde{\lambda}}{r} \right)^2 + 3 \left( \frac{\tilde{\lambda}}{r} \right)^4 \right] \right\} P^0 \quad (2.9)$$

When the acceptor is located in the near zone  $r \gg \lambda$ ,  $P$  exceeds  $P^0$ . The reason for this lies in Eq. (2.3), which allows us to see that energy is stored in the near field. Energy periodically flows out of the source and returns without being lost. This energy does not appear in the net radiative balance, which only accounts for the small amount of energy leaked as radiation. When an acceptor is located in the near zone, the donor decay rate increases because the acceptor feeds on energy temporarily deposited in the field by the donor.

On the other hand, from Eq. (2.7), the absorbed power of the acceptor, when it is in the near zone, is

$$P' = \frac{3\sigma}{64\pi^5} \left( \frac{\lambda^4}{r^6} \right) P^0 \quad (2.10)$$

This equation can be written in terms of the transfer rates  $k_T$  and the radiative rate  $k_r$ , by dividing both sides by  $h\nu$ , and relating  $\sigma$  to the molar absorption coefficient  $\epsilon_A$ , which gives

$$k_T = k_r \left( \frac{3 \ln 10 \epsilon_A \lambda^4}{64\pi^5 N_A n^4} \right) \frac{1}{r^6} \quad (2.11)$$

where  $N_A$  is the Avogadro's number and  $n$  is the medium refractive index, which is assumed to be non-absorbing.  $k_r = Q_D/\tau_0$ , here  $\tau_0$  is the donor's lifetime in the absence of acceptors and  $Q_D$  is the donor's quantum yield. Moreover, if we assume a spectral distribution for the emission wavelength, then Eq. (2.11) becomes

$$k_T = \frac{1}{\tau_0} \left( \frac{Q_D^3 \ln 10}{64\pi^5 N_A n^4} \right) \left( \frac{1}{r^6} \right) \int_0^\infty F_D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda = \frac{1}{\tau_0} \left( \frac{R_0}{r} \right)^6 \quad (2.12)$$

where  $R_0$  is the Förster radius, named after Theodor Förster, who first derived Eq. (2.12) from quantum mechanical [3] and classical [4] treatments of the dipole-dipole interaction of the donor and acceptor.

### 2.3 Quantum Mechanical Description of Energy Transfer

The quantum mechanical treatment of the energy transfer considers that only two electrons are involved in the D-A transition, one from the donor and one from the acceptor. In such case, the properly anti-symmetrized wave-functions for the initial excited state  $\Psi_i$  (D excited, A unexcited) and the final excited state  $\Psi_f$  (D unexcited, A excited) can be written as

$$\begin{aligned} \Psi_i &= \frac{1}{\sqrt{2}} [\Psi_{D^*}(1)\Psi_A(2) - \Psi_{D^*}(2)\Psi_A(1)] \\ \Psi_f &= \frac{1}{\sqrt{2}} [\Psi_D(1)\Psi_{A^*}(2) - \Psi_D(2)\Psi_{A^*}(1)] \end{aligned} \quad (2.13)$$

where the number 1 and 2 refer to the two electrons involved.

The interaction matrix element describing the coupling between the initial and final state is given by

$$U = \langle \Psi_i | \hat{V} | \Psi_f \rangle \quad (2.14)$$

where  $\hat{V}$  is the perturbation part of the total Hamiltonian  $\hat{H} = \hat{H}_D + \hat{H}_A + \hat{V}$ .  $U$  can be written as a sum of two terms

$$U = \langle \Psi_{D^*}(1)\Psi_A(2) | \hat{V} | \Psi_D(1)\Psi_{A^*}(2) \rangle - \langle \Psi_{D^*}(1)\Psi_A(2) | \hat{V} | \Psi_D(2)\Psi_{A^*}(1) \rangle \quad (2.15)$$

The first term in Eq. (2.15) is called the *Coulombic term*,  $U_C$ , where the initially excited electron on D returns the ground state while an electron on A is simultaneously promoted to the excited state. The second term in (2.15) is called the *exchange term*,  $U_{ex}$ , here there is an exchange of electrons on D and A. The exchange interaction is a quantum mechanical effect arising from the symmetry properties of the wave-functions with respect to the exchange of spin and space coordinates of two electrons.

The Coulombic term can be expanded into a sum of multipole-multipole terms, however, it is generally approximated by the first predominant term representing the dipole-dipole interaction between the transition dipoles moments  $\mathbf{M}_D$  and  $\mathbf{M}_A$  of the

transitions  $D \rightarrow D^*$  and  $A \rightarrow A^*$ . It is worth mentioning that the squares of the transition dipole moments are proportional to the oscillator strengths of these transitions. Thus, the Coulombic term can be written as

$$U_{d-d} = \frac{\mathbf{M}_D \cdot \mathbf{M}_A}{r^3} - \frac{(\mathbf{M}_A \cdot \mathbf{r})(\mathbf{M}_D \cdot \mathbf{r})}{r^5} \quad (2.16)$$

where  $r$  is the donor-acceptor separation distance. This expression can be simplified into

$$U_{d-d} = 5.04 \frac{|\mathbf{M}_D||\mathbf{M}_A|}{r^3} (\cos \theta_{DA} - 3 \cos \theta_D \cos \theta_A) \quad (2.17)$$

$U_{d-d}$  is expressed in  $\text{cm}^{-1}$ , the transition moments in Debye units, and  $r$  in nanometers.  $\theta_{DA}$  is the angle between the two transition moments and  $\theta_D$  and  $\theta_A$  are the angles between each transition moment and the vector connecting them. Note that 1 *Debye* unit is equal to  $3.33 \times 10^{-30}$  C m.

The dipole approximation is valid only for point-like dipoles, i.e., when the D-A separation is much larger than the donor and acceptor dimensions. At the short distances or when the dipole moments are large, higher multipole terms should be included in the calculations.

The exchange term represents the electrostatic interaction between the charge clouds. The transfer occurs via the overlap of the electron clouds and requires physical contact between the donor and the acceptor. The interaction is short range because the electron density decays exponentially outside the boundaries. For two electrons separated by the distance  $r_{12}$  in the D-A pair, the space part of the exchange interaction can be written as

$$U_{ex} = \left\langle \Phi_{D^*}(1)\Phi_A(2) \left| \frac{e^2}{r_{12}} \right| \Phi_D(2)\Phi_{A^*}(1) \right\rangle \quad (2.18)$$

where  $\Phi_D$  and  $\Phi_A$  are the contributions of the spatial wave-functions to the total wave-function  $\Psi_D$  and  $\Psi_A$  that include the spin functions. The spin selection rules (Wigner's rule) for allowed energy transfer are obtained by integration over the spin coordinates.

The transfer rate  $k_T$  is given by the *Fermi's Golden rule*

$$k_T = \frac{2\pi}{\hbar} |U|^2 \rho \quad (2.19)$$

where  $\rho$  is a measure of the density of the interacting initial and final states, as determined by *Franck-Gordon* factors, and is related to the overlap integral between the emission spectrum of the donor and the absorption spectrum of the acceptor.

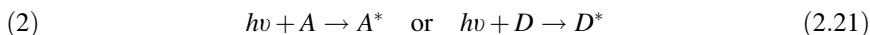
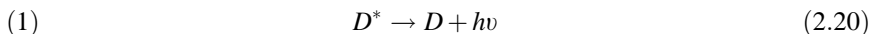
The Förster rate constant for the energy transfer in the case of long-range dipole-dipole interaction is obtained by substituting Eq. (2.17) into Eq. (2.19), whereas the Dexter rate constant for the short-range exchange interaction is obtained by substituting Eq. (2.18) into Eq. (2.19).

## 2.4 Radiative and Nonradiative Energy Transfer

Radiative energy transfer corresponds to the absorption of a photon, by the acceptor, upon emission by the donor and it is observed when the average distance between the donor and the acceptor is larger than the emitted photon wavelength. Such transfer does not require any interaction between D-A pairs, but it depends on the spectral overlap and the concentration. On the other hand, nonradiative energy transfer occurs at subwavelength distances and without the emission of a photon; and it is the result of the short- and long-range interactions between D-A pair. For instance, nonradiative energy transfer by the dipole-dipole interaction can extend over distances up to nearly 20 nm. Such kind of transfer provides a tool for determining separations of a few nm between D-A pair.

### 2.4.1 Radiative Energy Transfer

Radiative energy transfer is a two-step process where a photon emitted by the donor is absorbed by the acceptor.



This process is usually called trivial transfer because of the simplicity of the phenomenon; however the quantitative description is complicated because it depends on the sample's size and its configuration with respect to excitation and observation.

The fraction  $f$  of photons emitted by the donor and absorbed by the acceptor is given by

$$f = \frac{1}{Q_D} \int_0^{\infty} I_D(\lambda) \left[ 1 - 10^{-\varepsilon_A(\lambda)C_A l} \right] d\lambda \quad (2.22)$$

where  $C_A$  is the molar concentration of acceptors,  $Q_D$  is the donor's quantum yield in the absence of acceptor,  $l$  is the thickness of the sample,  $\varepsilon_A(\lambda)$  is the molar

absorption coefficient of the acceptor, and  $I_D(\lambda)$  is the donor emission intensity with the normalization condition

$$Q_D = \int_0^{\infty} I_D(\lambda) d\lambda \quad (2.23)$$

If the optical density is not too large,  $f$  can be approximated by

$$f = \frac{2.3}{Q_D} C_A l \int_0^{\infty} I_D(\lambda) \varepsilon_A(\lambda) d\lambda \quad (2.24)$$

where the integral represents the overlap between the donor emission spectrum and the acceptor absorption spectrum.

### 2.4.2 Nonradiative Energy Transfer

Nonradiative energy transfer requires interaction between the donor and the acceptor. It can occur if the emission spectrum of the donor overlaps the absorption spectrum of the acceptor so that several vibronic transitions between the donor and the acceptor, with the same energy at the donor and acceptor side, couple and thus are in resonance. This type of transfer is called resonance energy transfer (RET).

There are different types of interaction that are involved in resonance energy transfer. These interactions may be Coulombic and/or due to intermolecular orbital overlap. The Coulombic interactions consist of the long-range dipole-dipole interactions (Förster's mechanism) and short-range multipolar interactions. The interaction due to intermolecular orbital overlap, which includes electron exchange (Dexter's mechanism) and charge resonance interactions, are short range. It is worth mentioning that for the singlet-singlet energy transfer ( $^1D^* + ^1A \rightarrow ^1D + ^1A^*$ ), all types of interactions are involved, whereas the triplet-triplet energy transfer ( $^3D^* + ^1A \rightarrow ^1D + ^3A^*$ ) is due to only the orbital overlap. For allowed transition between the D-A pair, the Coulomb interaction is predominant, even at short distances. For forbidden transition between the D-A, the exchange mechanism is dominant. The interaction distance range for the exchange mechanism is usually less than 1 nm; and for the Coulombic mechanism, it is usually less than 20 nm.

There are three main classes of coupling, depending on the relative values of the interaction energy ( $U$ ), the electronic difference between  $D^*$  and  $A^*$  ( $\Delta E$ ), the absorption bandwidth ( $\Delta w$ ), and the vibronic bandwidth ( $\Delta \varepsilon$ ).

- (1) *Strong Coupling* ( $U \gg \Delta E, U \gg \Delta w, \Delta \varepsilon$ ): In this case, the Coulombic term  $U_C$  is much larger than the width of the individual transition  $D \rightarrow D^*$  and  $A \rightarrow A^*$ . Thus, all the vibronic subtransitions in the D-A pair are in resonance

with one another. Here, the transfer energy is faster than the nuclear vibrations and vibrational relaxation ( $\sim 10^{-12}$  s). The excitation energy is delocalized over the two components oscillating back and forth between the D and A. This type of energy transfer is a coherent process and is described in the frame of exciton theory. Strong coupled systems are characterized by large differences between their absorption spectra and those of their components. For a two-component system, two new absorption bands are observed due to transitions of the in-phase and out-of-phase combinations of the locally excited states. These two transitions are separated in energy by  $2|U|$ . The transfer rate for strongly coupled system is

$$k_T \approx \frac{4|U|}{h} \quad (2.25)$$

When  $U$  is approximated by the dipole-dipole interaction, the distance dependence of  $U$  and, therefore,  $k_T$  are  $r^{-3}$ .

- (2) *Weak Coupling* ( $U \gg \Delta E, \Delta w \gg U \gg \Delta \epsilon$ ): In this case, the interaction is much lower than the absorption bandwidth but larger than the width of an isolated vibronic level. Here, the vibronic excitation is considered as delocalized so that the system can be described in terms of stationary vibronic exciton states. This kind of system is characterized by minor alterations of the absorption spectrum.

The transfer rate is

$$k_T \approx \frac{4|U|S_{vw}^2}{h} \quad (2.26)$$

where  $S_{vw}$  is the vibrational overlap integral of the intramolecular transition  $v \leftrightarrow w$ . This is the transfer rate between an excited molecule with vibrational quantum number  $v$  and an unexcited one with quantum number  $w$ . Here, the transfer rate is fast compared to the vibrational relaxation but slower than the nuclear motions. Here,  $S_{vw} < 1$ , thus the transfer rate is slower than in the case of strong coupling.

- (3) *Very Weak Coupling* ( $U \ll \Delta \epsilon \ll \Delta w$ ): The interaction energy is much lower than the vibronic bandwidth. Thus, the vibrational relaxation occurs before the transfer takes place. This kind of interaction does not alter the absorption spectra. The transfer rate is given by

$$k_T \approx \frac{4\pi^2 |US_{vw}^2|^2}{h\Delta \epsilon} \quad (2.27)$$

Here, the transfer rate depends on the square of the interaction energy as compared to the previous cases. Thus, for dipole-dipole interactions, the distance dependence is  $r^{-6}$  instead of  $r^{-3}$  for the preceding cases.



In Chap. 3 we are discussing the main feature of Förster type nonradiative energy transfer, which corresponds to the very weak coupling case. Also, in the following Chapters we will only discuss the case of very weak coupling.

## References

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