

Chapter 3

Förster-Type Nonradiative Energy Transfer Models

In this chapter, we present and discuss models for describing Förster-type nonradiative energy transfer (NRET). In the first part, we explain the main features of Förster-type NRET. In the second part, we give a brief description of another process of NRET, Dexter-type energy transfer or charge transfer. This section is reprinted (adapted) with permission of Ref. [1]. Copyright 2014 Laser and Photonics Reviews (John Wiley and Sons).

3.1 Nonradiative Energy Transfer

Energy transfer from excited donor to unexcited acceptor is a common phenomenon that occurs in nature. The excitation processes involved in energy transfer can be either radiative, or nonradiative, or both. For radiative energy transfer, a photon is emitted by an excited donor and this photon is absorbed by an unexcited acceptor. In the case of nonradiative energy transfer (NRET), energy is transmitted from the excited donor to the unexcited acceptor by a process or processes where no photon is emitted by the excited donor. This nonradiative character of the process ensures a high efficiency of NRET. One of the most important examples of nonradiative energy transfer is fluorescence resonance energy transfer, which is also known as a Förster-type resonance energy transfer (FRET). FRET is an electrodynamic phenomenon and is the result of long-range dipole-dipole interactions between the donor and the acceptor. The rate of energy transfer depends on the extent of spectral overlap of the emission spectrum of the donor with the absorption spectrum of the acceptor, the quantum yield of the donor, the relative orientation of the donor and acceptor transition dipoles, and the spatial distance between the donor and the acceptor.

The process of energy transfer can be described as a transition between two states:



where D^* (D) is the donor in the excited (ground) state, A (A^*) is the acceptor in the ground (excited) state, and k_T is the rate of resonance energy transfer (RET) between the donor and acceptor pair. In this process, the donor absorbs an external photon leaving it in an excited state. Then, the donor transfers its excited energy, via a nonradiative process, to the acceptor leaving it in an excited state.

Förster was the first to describe this process correctly [2–4]. Förster derived an expression for the resonance energy transfer and the formulation of the FRET rate and efficiency has been described in detail in various textbooks and reviews [5, 6]. From Förster's theory, the rate of energy transfer from the donor to the acceptor $k_T(r)$ is given by [6]

$$k_T(r) = \frac{1}{\tau_D} \left(\frac{R_0}{r} \right)^6 \quad (3.2)$$

where τ_D is the decay time of the donor in the absence of an acceptor, R_0 is the Förster radius, and r is the donor-to-acceptor distance. Looking at (3.2), the rate of energy transfer depends strongly on the distance and is proportional to r^{-6} . In addition, the rate of transfer is equal to the decay rate of the donor $1/\tau_D$ when r is equal to R_0 , and the resulting transfer efficiency is 50 %. From this observation, we define the Förster radius as the distance at which FRET is 50 % efficient, which typically ranges from 1 to 10 nm. At this distance ($r = R_0$), the donor emission decreases to half its intensity in the absence of acceptors.

In a more detailed study of FRET [6, 7], the rate of transfer for a single donor and a single acceptor separated by a distance r can be written as

$$k_T(r) = \frac{Q_D \kappa^2}{\tau_D r^6} \left(\frac{9000(\ln 10)}{128\pi^5 N_A n^4} \right) \int_0^\infty F_D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda \quad (3.3)$$

where Q_D is the quantum yield of the donor in the absence of acceptors, n is the refractive index of the medium, N_A is Avogadro's number, r is the distance between the donor and the acceptor, and τ_D is the lifetime of the donor in the absence of acceptors. The term κ^2 is the factor describing the relative orientation of the transition dipoles of the donor and the acceptor in space. κ^2 is taken $2/3$ for dynamic random averaging of the donor and the acceptor. $F_D(\lambda)$ is the normalized fluorescence intensity of the donor in the wavelength range λ to $\lambda + \Delta\lambda$ with the total intensity (area under the curve) normalized to unity. $\varepsilon_A(\lambda)$ is the extinction coefficient of the acceptor at λ , which is typically in units of $M^{-1} \text{ cm}^{-1}$.

The overlap integral $J(\lambda)$ expresses the degree of spectral overlap between the donor emission and the acceptor absorption:

$$J(\lambda) = \int_0^{\infty} F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda \quad (3.4)$$

$$J(\lambda) = \frac{\int_0^{\infty} F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda}{\int_0^{\infty} F_D(\lambda) d\lambda} \quad (3.5)$$

$F_D(\lambda)$ is dimensionless. In calculating $J(\lambda)$ one should use the corrected emission spectrum with its area normalized to unity, or normalize the calculated value of $J(\lambda)$ by the area. The most common units of $J(\lambda)$ are: (1) M^{-1}cm^3 , if $\varepsilon_A(\lambda)$ is expressed in units of $\text{M}^{-1}\text{cm}^{-1}$ and λ is taken in centimeters, and (2) $\text{M}^{-1}\text{cm}^{-1}\text{nm}^4$, if $\varepsilon_A(\lambda)$ is expressed in units of $\text{M}^{-1}\text{cm}^{-1}$ and λ is in nanometers ($M = \frac{\text{mol}}{\text{L}}$).

For practical reasons it is easier to think in terms of the spatial distance rather than transfer rate. Thus, (3.2) is then expressed in terms of the Förster radius R_0 . From (3.2) and (3.3) one obtains:

$$R_0^6 = \left(\frac{9000(\ln 10)Q_D\kappa^2}{128\pi^5 N_A n^4} \right) \int_0^{\infty} F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda \quad (3.6)$$

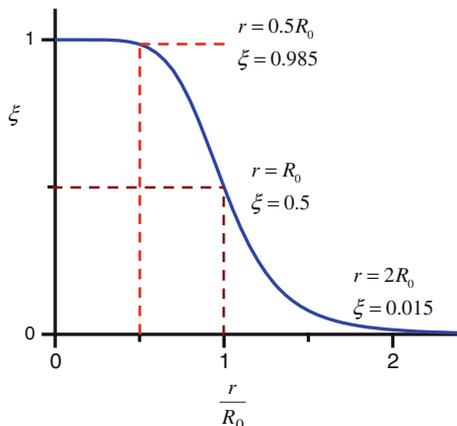
This expression allows to calculate the Förster radius from the spectral properties of the donor and the acceptor and the donor quantum yield. The efficiency of energy transfer (ξ) is the fraction of photons absorbed by the donor of which excitation energy is transferred to the acceptor. This fraction is given by

$$\xi = \frac{k_T(r)}{\tau_D^{-1} + k_T(r)} \quad (3.7)$$

which is the ratio of the transfer rate to the total decay rate of the donor in the presence of the acceptor. From (3.7), we can observe: (1) when the transfer rate is much faster than the decay rate, the energy transfer is efficient; and (2) when the transfer rate is slower than the decay rate, the energy transfer is inefficient because only a little transfer occurs during the excited state lifetime.

The efficiency of energy transfer can be written as a function of the distance by substituting (3.2) into (3.7).

Fig. 3.1 Energy transfer efficiency (ξ) versus distance normalized with respect to R_0 . R_0 is the Förster radius



$$\xi = \frac{R_0^6}{R_0^6 + r^6} \quad (3.8)$$

This equation clearly shows that the transfer efficiency is strongly dependent on the distance when the D-A distance is near to R_0 (Fig. 3.1). The efficiency quickly increases to unity as the D-A distance decreases below R_0 . Conversely, the efficiency quickly diminishes if r is greater than R_0 . Note that when $r = 2R_0$, the transfer efficiency is 1.5 %, and when $r = 0.5R_0$, the transfer efficiency is 98.5 %.

FRET is a highly distance sensitive process owing to the inverse sixth power (r^{-6}) dependence of the separation distance in the case of point-to-point dipole coupling. Therefore, FRET was first used as a nanoscale ruler [8]. FRET distance dependency is altered for different acceptor geometries. For example, small molecules and 3D-confined quantum dot (QD) acceptors are considered to be infinitesimal transition dipoles, which lead to the classical r^{-6} dependence in the case of a single-donor-to-a-single-acceptor. On the other hand, 2D confined quantum wire (NW) and 1D confined quantum well (QW) acceptors lead to distance dependencies that vary with r^{-5} and r^{-4} , respectively [9, 10]. Basically, quantum confinement of the acceptor modifies the distance dependency of the FRET. Furthermore, different assemblies of the acceptors can also alter the distance dependence, as in the case where a 2D-like assembly of QDs (i.e., a monolayer of QDs on a QW donor) act as a 1D-confined structure, which consequently results in the distance dependence having the form of r^{-4} similar to QWs [9, 10]. Note that the confinement of the donor (i.e., the dimensionality of the donor) tailors the effective dielectric constant [10], which is discussed in Chap. 6 of the 2nd brief of the series.

FRET has been widely exploited in various application areas of molecular biology for sensing, labelling, nanoscale distance measurements and understanding of the molecular-level interactions. For these biological systems, typically in

solution, point-to-point like interaction is effective, and, thus, r^{-6} dependence is commonly valid. Recently, FRET has been shown to be useful for optoelectronic technologies towards the purpose of creating highly efficient lighting and solar energy-harvesting systems. For this aim, exciton energy transfer in the QD-, NW-, and QW-based nanostructures can be employed to improve and control the photonic properties for light-generation and -harvesting systems. In these systems, with dimensionality of particles systems and their assemblies, one has to be careful about the distance dependence. In the following chapters, we will describe the theory of FRET in extended nanostructures (assemblies).

To sum up, here we briefly discussed FRET beyond the dipole-dipole approximation. In the case of multipole Coulomb interaction, such as dipole-quadrupole and quadrupole-quadrupole interaction, the FRET rates become proportional to r^{-8} and r^{-10} , respectively [11]. As can be seen, the energy transfer rate becomes increasingly more dependent on distance, becoming more spatially sensitive. In addition, the interaction range becomes shorter. Therefore, the dominant term is the dipole-dipole interaction term, and higher other poles may be considered for larger QDs and/or when the donor and the acceptor are in very close proximity.

3.2 Dexter Energy Transfer, Charge Transfer, Exciton Diffusion and Dissociation

Dexter-type energy transfer [12], which is also known as the charge (electron) exchange energy transfer, relies on the wavefunction overlap of the electronic states between different molecules in the near field. Dexter energy transfer is a short-range energy transfer unlike FRET, which is known to be a long-range energy transfer owing to the working distances that are on the order of 10 nm. Dexter energy transfer is only effective for the donor-acceptor separations that are typically on the order of 1 nm or shorter. Dexter energy transfer can also occur between non-emissive electronic states of the materials, such as spin-forbidden triplet states, whereas it is currently believed that these excitons cannot be transferred via FRET because they have negligible oscillator strengths [13]. These exchange mechanisms are based on the Wigner spin conservation rule; thus, the spin-allowed processes are: (1) singlet-singlet energy transfer:



and (2) triplet-triple energy transfer:



Dexter energy transfer has exponential distance dependence as compared to the $k_T \propto r^{-3} - r^{-6}$ distance dependencies in the long-range FRET processes [14]. Dexter energy transfer can be written as

$$k_{Dexter} = \frac{2\pi}{h} KJ' \exp(-2r/L) \quad (3.9)$$

$$k_{Dexter} = k_0 \exp\left[\frac{2(r - R_C)}{L}\right] \quad (3.10)$$

where J' is the integral overlap

$$J' = \int_0^{\infty} F_D(\lambda) \varepsilon_A(\lambda) d\lambda \quad (3.11)$$

with the normalization condition

$$\int_0^{\infty} F_D(\lambda) d\lambda = \int_0^{\infty} \varepsilon_A(\lambda) d\lambda = 1 \quad (3.12)$$

and R_C is the distance of the closest approach (collisional radius) and L is the average Bohr radius. K is a constant that is not related to any spectroscopic data. Please note that J' in (3.11) is different than J in (3.4).

Another important excitonic process is exciton diffusion. The exciton diffuses in a material in the broadened density of states of the same material; this process is called energy migration. Exciton diffusion has been widely studied for the organic semiconductors in the search for materials with large diffusion lengths to increase the probability of charge separation at the donor-acceptor hetero-interfaces in organic solar cells [15]. In addition to organic materials, exciton diffusion is crucial in bulk and quantum-confined semiconductor structures i.e., QWs, NWs, and QDs assemblies. Excitons can be transported in these quantum-confined materials; however, these systems should be well understood and controlled because defects can trap the diffusing excitons such that the emission efficiencies significantly reduce due to the increase of nonradiative recombination channels of the excitons. This picture is also valid for organic semiconductors.

Exciton dissociation is the separation of the bound electron-hole pairs into free carriers. This dissociation is a central step for excitonic solar cells [16] (bulk-heterojunction [17] and dye-sensitised [18]) because the generation of free charge carriers is required to realise the photovoltaic operation. In excitonic solar cells, dissociation of the excitons is facilitated by the interfaces that have type-II band alignments to physically break the excitons into free charges. The resistance

against the disassociating of excitons in terms of energy is called the exciton binding energy. Materials with larger exciton binding energy have more stable excitons because it is difficult to overcome this large Coulomb energy between the electron-hole pairs.

Lately, excitonic processes such as multi-exciton generation (MEG), Auger recombination and exciton-exciton annihilation have been studied in the quantum-confined semiconductors. Multi-exciton generation, also dubbed carrier multiplication, is the generation of multi-excitons upon the absorption of a high-energy photon $h\nu \geq 2 \times E_{Gap}$. It has been shown that semiconductor QDs can be very efficient in terms of converting higher-energy photons into multi-excitons [19, 20]. Related to the multi-exciton phenomena, Auger recombination becomes severe because excitons are spatially very close to each other. In Auger recombination, the energy of the recombining exciton is transferred to another already excited charge carrier in the material such that this charge is excited into higher energy states (i.e., hot carrier). This hot carrier quickly thermalizes to the respective band edge by losing its energy to the phonon vibrations; therefore, Auger recombination can significantly decrease the multi-exciton operation in the quantum-confined structures [21].

3.3 Selection Rules for Energy Transfer

In this section we summarize the processes that are allowed under the dipole-dipole and exchange mechanisms.

3.3.1 Dipole-Dipole Mechanism

- ${}^1D^* + {}^1A \rightarrow {}^1D + {}^1A^*$: Singlet-Singlet Energy Transfer.
- ${}^1D^* + {}^3A^* \rightarrow {}^1D + {}^3A^{**}$: Higher Triplet Energy Transfer. This type of transfer requires overlap of the fluorescence spectrum of the donor and the T-T absorption spectrum of the acceptor. In this case, both donor and acceptor are in the excited states, but FRET formalism remains valid, with a few adaptations.
- ${}^3D^* + {}^1A \rightarrow {}^1D + {}^1A^*$: Triplet-Singlet Energy Transfer. This type of transfer leads to phosphorescence quenching of the donor.
- ${}^3D^* + {}^3A^* \rightarrow {}^1D + {}^1A^{**}$: Higher Triplet Energy Transfer. This type of transfer requires overlap of the phosphorescence spectrum of D^* and the T-T absorption spectrum of A. The donor and acceptor are both in excited states.

3.3.2 Exchange Mechanism

- ${}^1D^* + {}^1A \rightarrow {}^1D + {}^1A^*$: Singlet-Singlet Energy Transfer.
- ${}^3D^* + {}^1A \rightarrow {}^1D + {}^3A^*$: Triplet-Triplet Energy Transfer. This type of transfer is possible because the exchange mechanism does not imply transition moments of the donor and acceptor.
- ${}^3D^* + {}^3A^* \rightarrow {}^1D + {}^1A^*$: Triplet-Triplet Annihilation. This type of transfer part of the energy resulting from the annihilation allows one of the two partner to return to the singlet state from which fluorescence is emitted, but with a delay determined by the triplet state lifetime.

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