11 Mechanisms of Energy Transfer

The energy transfer processes could be classified as follows: (a) The energy transfer could be a short-range (distances of several Angstroms) and a long-range (distances up to several tens of Angstroms). In short distances the electronic clouds of the donor and acceptor are sufficiently overlapped. In long distances the overlap is small. The smaller is the donor-acceptor distance, the more efficient is the energy transfer. (b) The energy transfer is occurred due to strong or weak interactions. Under strong interactions between the donor in the ground state and the acceptor the absorption spectra are modified. Under weak interactions the absorption spectra are changed insignificantly. Usually, interaction between the excited donor and the acceptor is strong. (c) The energy transfer could be singlet-singlet, triplet-triplet, singlet-triplet, and triplet-singlet, depending on the spin state of the donor and acceptor. (d) The energy transfer could be «hot» and «cold». If the rate constant of the transfer is not less than that of the vibrational relaxation in the donor, this is a hot transfer. If the rate constant is less, the transfer is a cold. When transfer is hot, the sensitized and individual lifetimes are equal taking into account the rate constant of vibrational relaxation of the donor. When energy transfer is cold, the lifetime of sensitized acceptor emission is approximately equal to the sum of acceptor own lifetime and the donor lifetime. (e) The energy transfer could be direct and reverse. If the electronic excitation transferred to the acceptor returns to the donor, this is a reverse transfer. (f) The energy transfer could be of Coulomb or exchange nature. (g) The energy transfer could be total (resonant) and fractional (non-resonant). If a quantum of energy is transferred from the donor as a whole, this is a total transfer induced by resonance between electronic levels of the acceptor and the excited donor. If only a part of the energy is transferred, this is a fractional transfer.

The main features of resonance energy transfer are: (a) the intensity and quantum yield of the donor luminescence is decreased in the presence of the acceptor; (b) the donor lifetime is decreased (it often accompanied by a non-exponential decay); (c) the shape of the donor emission spectrum remains unchanged in the course of quenching (if the donor luminescence is spectral homogeneous); (d) sensitized acceptor luminescence is developed, if the acceptor is able to fluoresce or phosphoresce; (e) a correlation between the intensity of sensitized acceptor and quenched donor luminescence should be observed; (f) the acceptor luminescence is depolarized (it may be not occur in the case of rigid fixation of parallely oriented chromophores); (g) in the excitation spectrum of the acceptor the intensity of the donor band is proportional to the transfer efficiency; (h) the efficiency of the energy transfer sharply depends on the donor-acceptor distance.

N. L. Vekshin, *Photonics of Biopolymers*  
© Springer-Verlag Berlin Heidelberg 2002
The resonance energy transfer in any biopolymer can be recognized with a set of all above features. One or two features are usually not enough to prove the resonant transfer, since each separate feature could be observed also in other processes. For instance, quenching of donor luminescence may be related not only to the transfer of energy of electronic excitation, but also to deactivation, electron transfer, etc.; shortening of the lifetime and non-exponential decay are observed in dynamic quenching as well; the emission spectrum could remain unchanged during screening and deactivation, etc.; acceptor luminescence may enhance due to reabsorption of donor emission; in thin layers the effect of volume reabsorption is possible; etc. To determine the efficiency of the resonant transfer in a certain system, all mentioned effects should be taken into account.

The energy transfer efficiency \( E \) is a ratio between the amount of quanta of electronic excitation which are transferred to the acceptor and the amount of photons absorbed by the donor. \( E \) is frequently calculated through the donor fluorescence intensity or lifetime in the presence and absence of acceptor, \( F \) or \( \tau \) and \( F_0 \) or \( \tau_0 \), respectively:

\[
E = \frac{F_0 - F}{F_0} \quad \text{(11.1)}
\]

\[
E = \frac{\tau_0 - \tau}{\tau_0} \quad \text{(11.2)}
\]

These formulae are suitable when quenching of the donor emission is caused only by electronic energy transfer. However, the acceptor molecule may quench not only by accepting of electronic excitation, but also by (a) direct deactivation (change a quantum of electronic excitation of the donor to a lot of vibrational quanta in acceptor); (b) electron transfer, (c) exciplex formation, etc.

### 11.1 Inductive-Resonance Model

Assume that the donor and acceptor are separated by a rather large distance so that their electronic absorption spectra are not deformed, i.e. the interaction is weak, and the electronic energy levels are not shifted. Assume also that the acceptor has an absorption band overlapping with the donor luminescence, i.e. the acceptor and the excited donor have a number of levels of equal or close energies. Thus, the effect of "resonance" is possible between the equal levels. This effect is similar to the mechanical resonance that is occurred between two pendula. The energy "flows" from one pendulum to the other. One quantum-mechanical oscillator induces a transition in the other. Therefore, a nonradiative transfer of excitation energy from the donor to the acceptor is feasible. Based on such approach, Forster developed a quantum-mechanical theory [147, 149, 265].

On the basis of perturbation theory Forster used the known equation for the probability of transitions between two states in terms of the quantum-mechanics (the "golden rule" [257, 266, 267]):

\[
P = \frac{2\pi}{\hbar} |\langle H \rangle|^2 \rho
\]

(11.3)