

1.3. Energy transfer

Absorption of a photon by a molecule results in an electronically excited state. This absorbed energy after a short time is released by the emission of a photon, so called luminescence. Depending on the nature of the excited and the ground state, luminescence is separated into fluorescence and phosphorescence. Fluorescence is observed if the emission occurs from an excited singlet state ($S_1 \rightarrow S_0$), whereas phosphorescence results from a transition of an excited triplet state to the singlet ground state ($T_1 \rightarrow S_0$). Molecules in an excited state may undergo alternative photochemical processes such as internal conversion, intersystem crossing and vibrational relaxation.

In *figure 9* the absorption and emission of light is illustrated by a Jablonski diagram. S_0 , S_1 and S_2 represent the ground, first and second electronically excited states respectively. Each of these electronic states show a complete range of vibrationally excited levels indicated by 0, 1 and 2.

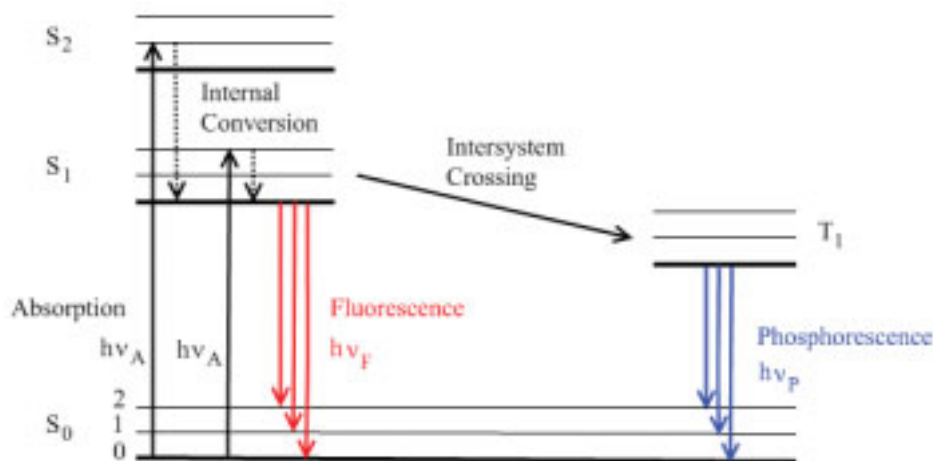


Figure 9: Jablonski diagram.

Following light absorption and subsequent excitation, a rapid relaxation to the lowest vibrational level of S_1 occurs within 10^{-12} s. Since the lifetime of fluorescence is near 10^{-8} s, internal conversion is usually completed before luminescence occurs. Thus, fluorescence emission principally results from the lowest energy vibrational state of S_1 and therefore the energy of emission is typically less than that of absorption, a so called Stoke shift. Return to the ground state usually populates higher excited vibrational ground state levels, which is the reason that the emission spectra appears typically as a mirror image of the absorption spectrum of $S_0 \rightarrow S_1$ as can be seen for perylene in *figure 10*. Born-Oppenheimer approximation states that electronic excitation does not greatly affect the nuclear geometry and therefore the spacing of the vibrational energy levels of the excited and the ground state are similar. Consequently, we observe comparable vibrational structures in the absorption and emission spectra.

Alternatively molecules from the S_1 state can undergo a spin conversion to the first triplet state T_1 (intersystem crossing, *figure 9*), which is a radiationless transition. Phosphorescence is the spin

forbidden transition from $T_1 \rightarrow S_0$ and requires population of the triplet state prior to emission and thus has an increased lifetime over fluorescence of $> 10^{-4}$ s.

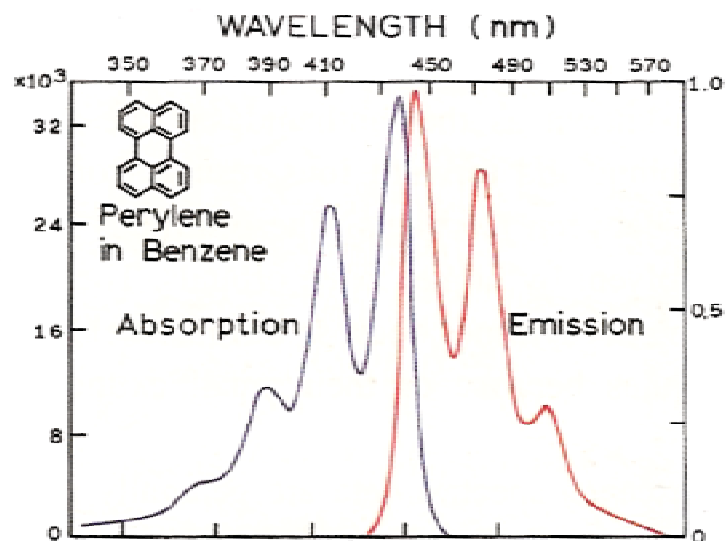


Figure 10: Absorption (purple line) and emission (red line) spectra of perylene.²¹

Further, if the lifetime of an excited molecule is reduced by another molecule, we speak from quenching. Usual bimolecular quenching processes are: collision, electron transfer or energy transfer (D = donor and A = acceptor):



According to a simplified picture of molecular orbitals, electron and energy transfer can be described by occupied and unoccupied orbitals of donor and acceptor levels.²² An electron transfer quenching mechanism involves only one electron which is transferred from an occupied orbital of a donor to an unoccupied orbital of an acceptor, resulting in a radical ion pair, also known as charge-transfer complex (*figure 11*).

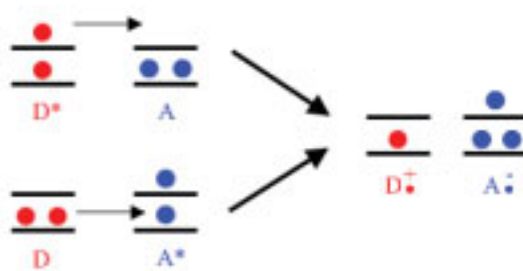
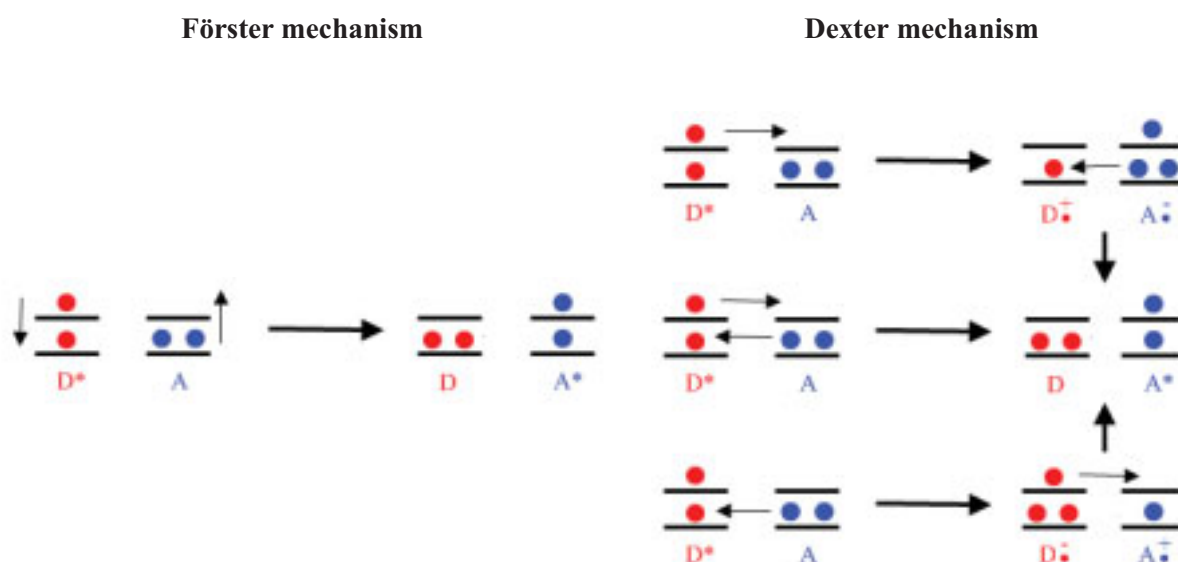


Figure 11: Quenching by electron transfer leads to charge-transfer complex formation (orbital overlap is required).²²

In 1946 Theodor Förster discovered the physical process which now bears his name, where the energy of an excited chromophore (donor) was transferred to an acceptor molecule at a distance of 1.5 to 10 nm.^{23,24} Actually this energy transfer is the result of a long range dipole-dipole interaction between donor and acceptor (“transmitter-antenna mechanism” *figure 12*) and occurs without the appearance of a photon. Therefore the F in a resonance energy transfer mechanism (FRET) should stand for “Förster” in acknowledgement of its discoverer and not for “Fluorescence”, which is misleading.²⁵ Another possible pathway for an energy transfer mechanism is a double electron exchange as proposed by Dexter (*figure 12*). For electron transfer as well as energy transfer by electron exchange (Dexter mechanism) to occur, an orbital overlap is required and therefore their distances are generally limited to less than 10 Å. In contrast, no such orbital overlap is involved in a dipole-dipole energy transfer mechanism and therefore this energy transfer can still be effective over larger distances and has been used to probe the structure of biological macromolecules.



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| <ul style="list-style-type: none"> - long distances ($r = 10\text{-}100 \text{ \AA}$). - spectral overlap of the emission spectra from the donor with the absorption spectra from the acceptor is necessary. - coulombic dipole-dipole interaction. | <ul style="list-style-type: none"> - short distances ($r = 5\text{-}10 \text{ \AA}$). - overlap of orbitals necessary. - electron exchange and usually collision of the molecules is needed. |
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Figure 12: Energy transfer mechanism according to Förster and Dexter.²²