

## 5. Dynamics of energy transfer phenomena

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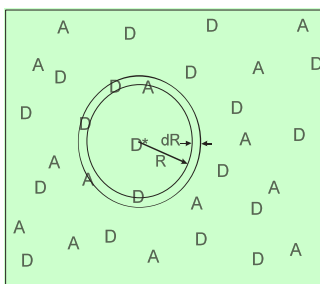
#### 5.1 Introduction

This chapter is under construction and, hence, incomplete.

Additional information can be found in the publications mentioned in section 5.3

### 5.2 Luminescence intensity dynamics in homogeneous systems

Energy transfer in a rigid environment (Th. Förster, *Z. Naturforschung* 4a (1949) 321)



We assume that  $N_D$  molecules D (donor) and  $N_{ac}$  molecules A (acceptor) are randomly distributed in a large volume, so that effects due to the border of the rigid system can be neglected. The molecules D and A are assumed to be at fixed positions. This means that they cannot move around. A is assumed to absorb at lower energy than D, so that energy transfer can occur from  $D^*$  to A but not in the reverse direction.

The donor is in its electronically excited state  $D^*$  at time  $t = 0$ . It relaxes to the ground state D within a mean time  $\tau_{D^*}$  via radiative and radiationless processes, in absence of molecules A.

Any acceptor molecule  $A_i$ , at distance  $R_i$  from  $D^*$ , gives an additional channel for relaxation, the rate constant of which is  $k_{EnT}(i)$ :

$$k_{EnT}(i) = \frac{1}{\tau_{D^*}} \left( \frac{R_0}{R_i} \right)^6, \text{ where } R_i \text{ is the distance between } D^* \text{ and } A_i.$$

The same is true for energy transfer not only to  $A_i$  but to any of the  $N_{ac}$  acceptor molecules. From this we find that the decrease of excitation probability of  $D^*$  can be expressed as follows:

$$-\frac{d\rho_{D^*}}{dt} = (k_F + k_{IC})\rho_{D^*} + \left( \sum_{i=1}^{N_{ac}} k_{EnT}(i) \right) \rho_{D^*} \quad (k_F + k_{IC}) = \frac{1}{\tau_{D^*}} \text{ This means that we have } N_{ac} + 1 \text{ independent deactivation channels.}$$

$$\rho_{D^*} = \exp \left[ - \left( (k_F + k_{IC}) + \sum_{i=1}^{N_{ac}} k_{EnT}(i) \right) t \right]$$

This means that the excitation probability of  $D^*$  decays exponentially. This can also be expressed as follows:

$$(k_F + k_{IC}) + \sum_{i=1}^{N_{ac}} k_{EnT}(i) = \frac{1}{\tau_{D^*}} + \frac{1}{\tau_{D^*}} \sum_{i=1}^{N_{ac}} \left( \frac{R_0}{R_i} \right)^6 \quad \rho_{D^*} = e^{-t/\tau_{D^*}} \prod_{i=1}^{N_{ac}} \exp \left( - \left( \frac{R_0}{R_i} \right)^6 \frac{t}{\tau_{D^*}} \right)$$

Apart from „single molecule experiments“ we do not observe the decay of a single molecule  $D^*$ , but that of a large number of statistically distributed molecules which have acceptor molecules at statistically distributed distances  $R_i$ .  $P(R_i)dR_i$  is the probability that a given acceptor  $A_i$  is located in the environment of an electronically excited  $D^*$  at distance between  $R_i$  and  $R_i + dR_i$ . Then the decrease of the mean excitation energy  $\langle \rho_{D^*}(t) \rangle$  is:

$$\langle \rho_{D^*}(t) \rangle = e^{-t/\tau_{D^*}} \prod_{i=1}^{N_{ac}} \int_0^{R_v} \exp \left( - \left( \frac{R_0}{R_i} \right)^6 \frac{t}{\tau_{D^*}} \right) P(R_i) dR_i$$

We use the following abbreviation:  $J_i(t) = \int_0^{R_v} \exp \left( - \left( \frac{R_0}{R_i} \right)^6 \frac{t}{\tau_{D^*}} \right) P(R_i) dR_i$

$$\langle \rho_{D^*}(t) \rangle = e^{-t/\tau_{D^*}} \prod_{i=1}^{N_{ac}} J_i(t)$$

We now assume that the electronically excited  $D^*$  is in the center of a sphere with radius  $R_v$  and volume  $V$ .

$$V = \frac{4\pi}{3} R_v^3 \quad \text{We further assume a uniform statistical distribution of donors and acceptors in space, which means: } P(\mathbf{R})d\mathbf{R} = \frac{dV}{V} = \frac{4\pi R^2}{V} d\mathbf{R}$$

This distribution is for all acceptors  $A_i$  the same. Hence, we have:  $J(t) = J_i(t)$  what leads to:

$$\langle \rho_{D^*}(t) \rangle = e^{-t/\tau_{D^*}} J(t)^{N_{ac}}$$

$$J(t) = \frac{4\pi}{V} \int_0^{R_V} \left[ \exp\left(-\left(\frac{R_0}{R}\right)^6 \frac{t}{\tau_{D^*}}\right) \right] R^2 dR \quad x = \left(\frac{R_0}{R}\right)^6 \frac{t}{\tau_{D^*}} \quad J(t) = \frac{4\pi}{V} \int_0^{R_V} [\exp(-x)] R^2 dR$$

$$x_V = \left(\frac{R_0}{R_V}\right)^6 \frac{t}{\tau_{D^*}} \quad x_V \ll 1, \text{ because } R_V \ll R_0 \Rightarrow V = \frac{4\pi}{3} R_V^3$$

$$J(t) = \frac{-1}{2} \sqrt{x_V} \int_{\infty}^{x_V} [\exp(-x)] \frac{dx}{\sqrt{x^3}} \quad J(t) = \frac{1}{2} \sqrt{x_V} \int_{x_V}^{\infty} [\exp(-x)] \frac{dx}{\sqrt{x^3}}$$

$$\int_{x_V}^{\infty} [\exp(-x)] \frac{dx}{\sqrt{x^3}} = \int_{x_V}^{\infty} e^{-x} \cdot x^{-\frac{3}{2}} dx \rightarrow -2\pi^{\frac{1}{2}} + \frac{1}{x_V^{\frac{1}{2}}} + 2 + 2\pi^{\frac{1}{2}} \operatorname{erf}\left(\frac{1}{x_V^{\frac{1}{2}}}\right) \cdot x_V^{\frac{1}{2}} \cdot \exp(x_V) \cdot \exp(-x_V)$$

rearrangement:  $2(-\sqrt{\pi} + \sqrt{x_V} \exp(-x_V) + \sqrt{\pi} \operatorname{erf}(\sqrt{x_V}))$

Using this we find:

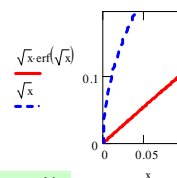


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$$J(t) = \sqrt{x_V} \left( \frac{e^{-x_V}}{\sqrt{x_V}} - \sqrt{\pi} [1 - \operatorname{erf}(\sqrt{x_V})] \right)$$

This gives for  $x \ll 1$  the following result:

$$J(t) = 1 - \sqrt{\pi x_V}$$



Inserting this in:

$$\langle \rho_{D^*}(t) \rangle = e^{-t/\tau_{D^*}} J(t)^{N_A} \text{ gives: } \langle \rho_{D^*}(t) \rangle = e^{-t/\tau_{D^*}} (1 - \sqrt{\pi x_V})^{N_A}$$

$$\langle \rho_{D^*}(t) \rangle = e^{-t/\tau_{D^*}} (1 - \sqrt{\pi x_V})^{N_{ac}}$$

We develop this equation for the limiting value  $N_{ac} \rightarrow \infty$ . This is reasonable since we assume that the total number of molecules in the volume V is large.

$$\langle \rho_{D^*}(t) \rangle = e^{-t/\tau_{D^*}} (1 - \sqrt{\pi x_V})^{N_{ac}} \xrightarrow{N_{ac} \rightarrow \infty} \langle \rho_{D^*}(t) \rangle = e^{-t/\tau_{D^*} - N_{ac} \sqrt{\pi x_V}}$$

$$x_V = \left(\frac{R_0}{R_V}\right)^6 \frac{t}{\tau_{D^*}} \quad \langle \rho_{D^*}(t) \rangle = e^{-t/\tau_{D^*} - \sqrt{\pi} N_A \left(\frac{R_0}{R_V}\right)^3 \sqrt{\frac{t}{\tau_{D^*}}}}$$

Using the following definition for  $\gamma$ :

$$\gamma = \frac{\sqrt{\pi}}{2} c_A \frac{4\pi}{3} R_0^3 \quad \text{we get:}$$

$$\langle \rho_{D^*}(t) \rangle = e^{-\frac{t}{\tau_{D^*}} - 2\gamma \sqrt{\frac{t}{\tau_{D^*}}}}$$

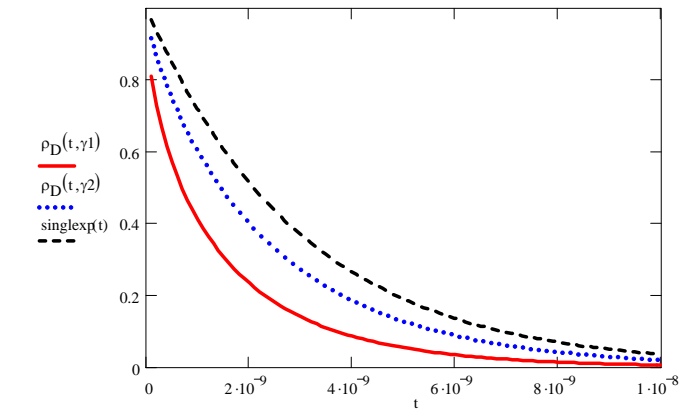
$c_A \frac{4\pi}{3} R_0^3$  is the average number of acceptor molecules in a sphere of radius  $R_0$ .

$c_0 := \frac{3}{2\sqrt{\pi}} \frac{1}{N_L R_0^3}$  represents the critical concentration of acceptor molecules.

Hence,  $\gamma$  can be expressed as ratio between the actual concentration of acceptor molecules and the critical concentration  $c_0$ :  $\gamma = \frac{c_A}{c_0}$

We observe that, despite of the fact that each excited donor molecule  $D^*$  decays strictly according to a mono-exponential law, the mean decay of an ensemble of donor molecules is not single exponential, but becomes faster with an increasing value for  $\gamma$ . We illustrate this in the following picture:.

$$\begin{aligned}
 N_L &:= 6.022 \cdot 10^{23} \cdot \text{mol}^{-1} & \text{nm} &:= 10^{-9} \text{m} & \text{ns} &:= 10^{-9} \text{s} & t &:= 0.1 \text{ns}, 0.2 \text{ns} \dots 10 \text{ns} & R_0 &:= 6 \text{nm} & \tau_D &:= 3 \text{ns} \\
 c_{A1} &:= 10^{-3} \frac{\text{mol}}{\text{L}} & c_{A2} &:= 10^{-3.5} \frac{\text{mol}}{\text{L}} & \gamma_1 &:= \frac{\sqrt{\pi}}{2} \cdot c_{A1} \cdot N_L \cdot \frac{4 \cdot \pi}{3} \cdot R_0^3 & \gamma_2 &:= \frac{\sqrt{\pi}}{2} \cdot c_{A2} \cdot N_L \cdot \frac{4 \cdot \pi}{3} \cdot R_0^3 \\
 \rho_D(t, \gamma) &:= e^{-\frac{t}{\tau_D} - 2 \cdot \gamma \cdot \sqrt{\frac{t}{\tau_D}}} & \text{singlexp}(t) &:= e^{-\frac{t}{\tau_D}} & \gamma_1 &= 0.483 & \gamma_2 &= 0.153
 \end{aligned}$$



Comparison of the fluorescence decay of an electronically excited donor molecule D\* in absence and in presence of acceptor molecules for a Förster radius of 60 Å.

We wonder about the intensity of the emission of the donor at constant donor concentration but varying acceptor concentration which we express by means of the parameter  $\gamma$ . This can be done by investigating the fluorescence yield as a function of  $\gamma$ , for otherwise constant conditions.

The fluorescence yield  $\phi_{D^*}$  of the donor is proportional to the integral, with the proportionality constant C, over the whole time range from  $t = 0$  to  $t = \infty$ . We compare  $\phi_{D^*}$  with the luminescence yield in absence of acceptors  $\phi_{D^*}^0$ .

$$\phi_{D^*} = C \int_0^\infty e^{-\frac{t}{\tau_{D^*}} - 2\gamma \sqrt{\frac{t}{\tau_{D^*}}}} dt \quad \phi_{D^*}^0 = C \int_0^\infty e^{-\frac{t}{\tau_{D^*}}} dt = C \tau_{D^*} \quad \frac{\phi_{D^*}}{\phi_{D^*}^0}(\gamma) = \frac{1}{\tau_{D^*}} \int_0^\infty e^{-\frac{t}{\tau_{D^*}} - 2\gamma \sqrt{\frac{t}{\tau_{D^*}}}} dt$$

We substitute:  $s = \frac{t}{\tau_{D^*}}$ ,  $ds = \frac{dt}{\tau_{D^*}}$  and  $f(\gamma) = \frac{\phi_{D^*}}{\phi_{D^*}^0}(\gamma)$

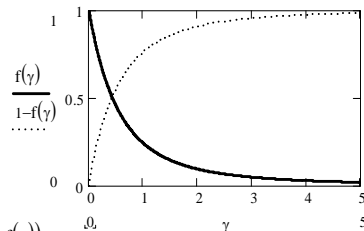
$$\int_0^\infty e^{-s - 2\gamma \sqrt{s}} ds \rightarrow -\gamma \cdot \pi^{\frac{1}{2}} \cdot \exp(\gamma^2) + 1 + \gamma \cdot \pi^{\frac{1}{2}} \cdot \exp(\gamma^2) \cdot \text{erf}(\gamma)$$

$$-\gamma \cdot \pi^{\frac{1}{2}} \cdot \exp(\gamma^2) + 1 + \gamma \cdot \pi^{\frac{1}{2}} \cdot \exp(\gamma^2) \cdot \text{erf}(\gamma)$$

$$\gamma \cdot \sqrt{\pi} \cdot \exp(\gamma^2) \cdot (-1 + \text{erf}(\gamma)) + 1 \quad 1 - [\gamma \cdot \sqrt{\pi} \cdot \exp(\gamma^2) \cdot (1 - \text{erf}(\gamma))]$$

$$\gamma := 0, 0.001 \dots 10$$

$$f(\gamma) := 1 - \gamma \cdot \sqrt{\pi} \cdot \exp(\gamma^2) \cdot (1 - \text{erf}(\gamma))$$



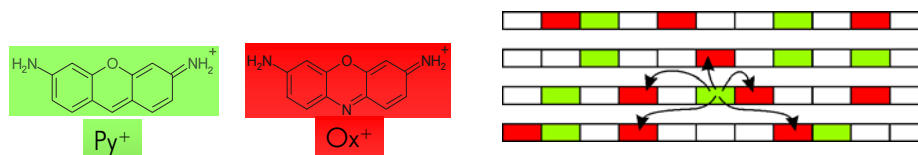
We find that the fluorescence quantum yield of the donor decreases fast under these conditions. That of the acceptor increases accordingly.

### 5.2.1 A demonstration experiment

An alternative situation could be created if we could keep the ratio of the donor and the acceptor concentration constant but increasing the mean distance between them. This is usually not possible to realize over a sufficiently large concentration range because of quenching phenomena. However, using zeolite L we have been able to realize such experiments.

Dye loaded zeolite materials do not meet the conditions imposed by this theory completely, because of substantial anisotropy. But, at the moment we assume that the theory is applicable without any restriction. Hence, we describe the following experiments accordingly.

The two molecules pyronine  $Py^+$  and oxonine  $Ox^+$  can be inserted into the channels of zeolite L at about the same rate so that zeolite nanocrystals containing a random mixture of these strongly luminescent donor ( $Py^+$ ) and acceptor molecules can be prepared.



Left: Scheme of a few channels of a zeolite L crystal containing acceptor A (red rectangles) and donor D (green rectangles) molecules. Each rectangle marks a site which can be occupied by a dye molecules. Right: Main processes taking place after excitation of a donor:  $k_{EnT}$  is the energy transfer rate constant,  $k_F^A$  and  $k_F^D$  are the fluorescence rate constants.

Taking into account radiationless processes, namely internal conversion  $k_{IC}$ , intersystem crossing  $k_{ISC}$ , and bimolecular quenching  $k_Q[Q]$  with a quencher Q, the time dependent concentrations of the donor D and the acceptor A in the excited state  $S_1$ ,  $[D_{S_1}]$  and  $[A_{S_1}]$ , can be expressed as follows, where  $i_{abs}$  is the number of photons absorbed per unit time.

$$\frac{d[D_{S_1}]}{dt} = [D_{S_1}] \sum_d k_d^D \quad \frac{d[A_{S_1}]}{dt} = k_{EnT} [D_{S_1}] - [A_{S_1}] \sum_d k_d^A$$

The fluorescence quantum yield of the donor  $\Phi_F^D$  and of the acceptor  $\Phi_F^A$  under stationary conditions is therefore:

$$\phi_F^D = \frac{k_F^D}{\sum_d k_d^D} \quad \phi_F^A = \frac{k_{Ent}}{\sum_d k_d^D} \frac{k_F^A}{\sum_a k_a^A}$$

A quantity we can measure with good accuracy, even in a heterogeneous system, is the ratio between the two fluorescence quantum yields  $\Phi_F^D$  and  $\Phi_F^A$ . This ratio is equal to the ratio of the corresponding luminescence intensities  $I_F^D$  and  $I_F^A$

$$\frac{\phi_F^A}{\phi_F^D} = k_{Ent} \frac{k_F^A}{k_F^D \sum_a k_a^A} \quad \frac{I_F^A}{I_F^D} = k_{Ent} \frac{k_F^A}{k_F^D \sum_a k_a^A} = k_{Ent} \tau_{D^*}^0 \phi_F^A \quad \frac{I_F^A}{I_F^D} = C p_A$$

According to the results we have derived in chapter 3.4.1 the energy transfer constant  $k_{Ent}$  can be expressed as:

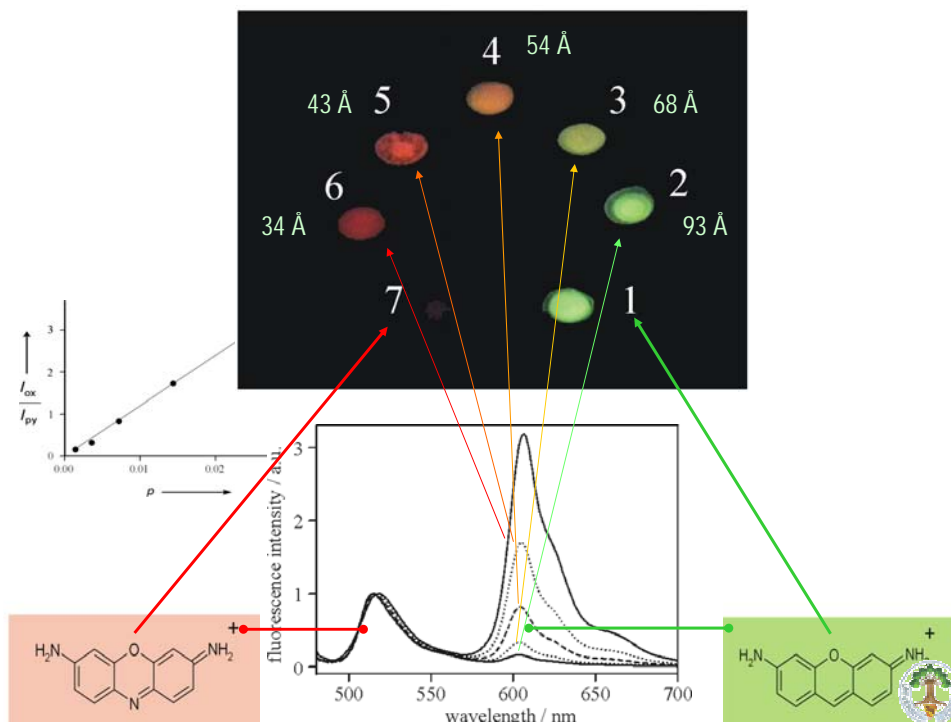
$$k_{Ent} = fc \frac{k_{D^*A}^2}{n^4 R_{DA}^6} \frac{\phi_{D^*}}{\tau_{D^*}} J_{\bar{\nu}D^*A} \quad \langle k_{Ent} \rangle = \frac{fc}{n^4} \frac{\phi_{D^*}}{\tau_{D^*}} J_{\bar{\nu}D^*A} G_{D^*A} p_A \quad G_{D^*A} = \left\langle \frac{k_{D^*A}^2}{R_{DA}^6} \right\rangle$$

$$fc = \frac{9 \ln(10)}{128 \pi^5 N_L} \quad [J_{\bar{\nu}D^*A}] = cm^3 M^{-1}$$

$p_A$  is the occupation probability of the sites of the zeolite with acceptor molecules.

Hence the constant C is given by:

$$C = \phi_F^A \frac{fc}{n^4} J_{\bar{\nu}D^*A} G_{D^*A} \quad \langle k_{Ent} \rangle = \frac{\phi_{D^*}}{\tau_{D^*}} \frac{C}{\phi_F^A} p_A$$



$$\frac{I_F^A}{I_F^D} = C\rho_A \quad \langle k_{EnT} \rangle = \frac{\phi_{D^*}}{\tau_{D^*}} \frac{C}{\phi_F^A}$$

$$C=250 \quad \frac{\phi_{D^*}}{\phi_F^A} \cong 1 \quad \tau_{D^*} \cong 2.5 \text{ ns}$$

$$\langle k_{EnT} \rangle = \frac{125}{2.5 \cdot 10^{-9} \text{ s}} = 10^{11} \text{ s}^{-1}$$

### 5.2.2 Data analysis of EnT phenomena in homogeneous media

A) Steady state measurements (see e.g. B. Valeur, Molecular Fluorescence, Wiley-VCH, 2002)

*Decrease in donor fluorescence:*

Transfer from the donor D to an acceptor A causes the quantum yield of the donor to decrease. The transfer efficiency  $\Phi_{EnT}$  (probability for energy transfer) is given by:

$$\Phi_{EnT} = 1 - \frac{\Phi_D}{\Phi_D^0} \quad \Phi_{EnT} = \frac{1}{1 + (R/R_0)^6}$$

where  $\Phi_D$  and  $\Phi_D^0$  are the donor fluorescence quantum yield in absence and presence of acceptors respectively.

Because only the relative quantum yields need to be determined, a single observation wavelength is sufficient and the latter is selected so that there is no emission from the acceptor. If this condition can be fulfilled, the above equation can be expressed in terms of absorbance at the excitation wavelength  $\lambda_D$  and the fluorescence intensities of the donor at  $\lambda_D^{em}$  in the absence and presence of acceptors, where  $A(\lambda_D)$  is the sum of the absorption of the donor and of the acceptor at wavelength  $\lambda_D$  :

$$\Phi_T = 1 - \frac{A(\lambda_D) I_D(\lambda_D, \lambda_D^{em})}{A_D(\lambda_D) I_D^0(\lambda_D, \lambda_D^{em})} \quad (A1) \quad A(\lambda_D) = A_D(\lambda_D) + A_A(\lambda_D)$$

Attention should be paid to inner filter effects caused by absorption of the acceptor at emission wavelength of the donor. Corrections might be necessary in some cases.

Comparison between the absorption spectrum and the excitation spectrum

The corrected excitation spectrum, observed at the emission wavelength  $\lambda_A^{em}$ , is described by

$$I_A(\lambda, \lambda_A^{em}) = C [A_A(\lambda) + A_D(\lambda)\Phi_T] \quad \text{where } C \text{ is a constant (instrumental factor).}$$

In the case of quantitative energy transfer ( $\Phi_{EnT} = 1$ ) the excitation spectrum is equal to the absorption spectrum, which is equal to the sum of the absorption spectrum of the acceptor plus the absorption spectrum of the donor.

But for any value of  $\Phi_{EnT} < 1$ , the excitation band corresponding to the donor is relatively lower than the absorption band.

The comparison of the absorption and excitation spectra can be done at two wavelengths  $\lambda_D$  and  $\lambda_A$ . If there is no absorption of the donor at  $\lambda_A$ , we get the following two equations:

$$\frac{I_A(\lambda_A, \lambda_A^{em})}{A_A(\lambda)} = C\Phi_A \qquad \frac{I_A(\lambda_D, \lambda_A^{em})}{A_A(\lambda_D)} = C \frac{\Phi_A [A_A(\lambda_D) + A_D(\lambda_D)\Phi_T]}{A_A(\lambda_D)}$$

The ratio of these two equations yields:

$$\Phi_{EnT} = \frac{A_A(\lambda_A)}{A_D(\lambda_D)} \left[ \frac{I_A(\lambda_D, \lambda_A^{em})}{I_A(\lambda_A, \lambda_A^{em})} - \frac{A_A(\lambda_D)}{A_A(\lambda_A)} \right] \quad (A2)$$

Enhancement of acceptor fluorescence:

The fluorescence intensity of the acceptor is enhanced in the presence of energy transfer. Comparison with the intensity  $I^0$  in absence of energy transfer provides the transfer efficiency  $\Phi_{EnT}$ :

$$\Phi_{EnT} = \frac{A_A(\lambda_D)}{A_D(\lambda_D)} \left[ \frac{I_A(\lambda_D, \lambda_A^{em})}{I_A^0(\lambda_D, \lambda_A^{em})} - 1 \right] \quad (A3)$$

In many cases the value of  $A_A(\lambda_D)$  can be too small to be measured accurately.

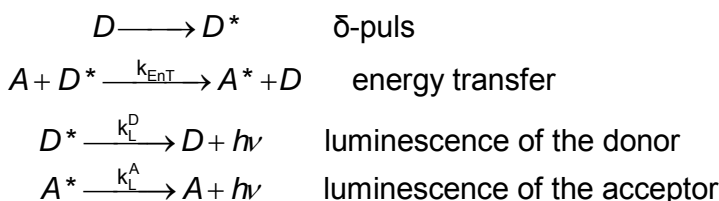
Equation (A.1) appears to allow the most straightforward determination of the efficiency of energy transfer,  $\Phi_{EnT}$ . However, it cannot be used in the case of very low quantum yields. Furthermore, quenching of the donor by the acceptor may occur. This can be checked by comparing the values obtained for  $\Phi_{EnT}$  by using (A.2) or (A.3). Time resolved measurements provide an additional independent source of information.



## B) Time resolved measurements

We first discuss the most simple cases where donors and acceptors can be regarded as being statistically distributed in a homogeneous way. We shall later investigate supra-molecularly organized systems for which the following arguments may not apply.

We assume, that the following reaction scheme applies:

*Decay of the donor luminescence*

If the fluorescence decay of the donor following pulse excitation is a single exponential, the measurement of the decay in presence ( $\tau_D$ ) and in absence ( $\tau_D^0$ ) of transfer is a straightforward method to determine the EnT transfer rate constant, the transfer efficiency and the donor-acceptor distance:

$$\frac{1}{\tau_D} = \frac{1}{\tau_D^0} + k_{\text{EnT}} \quad \Phi_{\text{EnT}} = 1 - \frac{\tau_D}{\tau_D^0} \quad \Phi_{\text{EnT}} = \frac{1}{1 + (R/R_0)^6} \quad R = \frac{R_0}{\left(\frac{\tau_D^0}{\tau_D} - 1\right)^{1/6}}$$

We now assume that the decay is a multi exponential in the absence of acceptors, because of some in-homogeneity of the microenvironment:

$$i_D(t) = \sum_J \alpha_J e^{-t/\tau_J}$$

In this case, if the donor fluorescence is not too far from a single exponential, the EnT transfer efficiency can be calculated by using the following average decay times in absence and presence of acceptors:

$$\langle \tau \rangle = \frac{\sum_J \alpha_J \tau_J}{\sum_J \alpha_J} \quad \Phi_{\text{EnT}} = 1 - \frac{\langle \tau_D \rangle}{\langle \tau_D^0 \rangle}$$

Note that for the calculation of the EnT transfer efficiency, it is incorrect to use the intensity-averaged decay time

$$\langle \tau \rangle = \frac{\sum_J \alpha_J \tau_J^2}{\sum_J \alpha_J \tau_J}$$

because such an integrated intensity is not relevant to a dynamic process like energy transfer. In fact, the signal measured at a certain time after excitation is proportional to the number of donor molecules still excited at that time and able to transfer their energy to an acceptor molecule; therefore the amplitude average should be used.

### Increase of the acceptor luminescence

The transfer rate can also be determined from the increase in the acceptor fluorescence following pulse excitation of the donor. The change in excited acceptor concentration obeys in the simplest case the following differential equations:

$$\frac{d[A^*]}{dt} = k_{EnT} [D^*] - \frac{1}{\tau_A^0} [A^*]$$

$$\frac{d[D^*]}{dt} = - \left( k_{EnT} + \frac{1}{\tau_D^0} \right) [D^*]$$

The solution of these equations, with the initial conditions  $[D^*](t=0) = [D^*]_0$ , is:

$$[A^*] = \left\{ \frac{[D^*]_0 k_{EnT}}{1/\tau_D - 1/\tau_A^0} + [A^*]_0 \right\} e^{-t/\tau_A^0} - \frac{[D^*]_0 k_{EnT}}{1/\tau_D - 1/\tau_A^0} e^{-t/\tau_D}$$

which simplifies, if no acceptors are directly excited with the pulse:

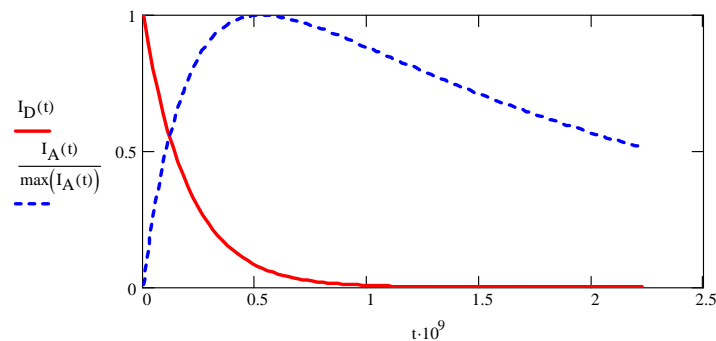
$$[A^*] = \frac{[D^*]_0 k_{EnT}}{1/\tau_D - 1/\tau_A^0} \left\{ e^{-t/\tau_A^0} - e^{-t/\tau_D} \right\}$$

$$\frac{[A^*]}{[D^*]_0} = \left\{ \frac{k_{EnT}}{1/\tau_D - 1/\tau_A^0} + \frac{[A^*]_0}{[D^*]_0} \right\} e^{-t/\tau_A^0} - \frac{k_{EnT}}{1/\tau_D - 1/\tau_A^0} e^{-t/\tau_D}$$

$$k_D := .5 \cdot 10^9 \cdot s^{-1} \quad k_A := .9 \cdot k_D \quad k_{EnT} := 10 \cdot k_A \quad A_D := .99 \quad I_0 := 1$$

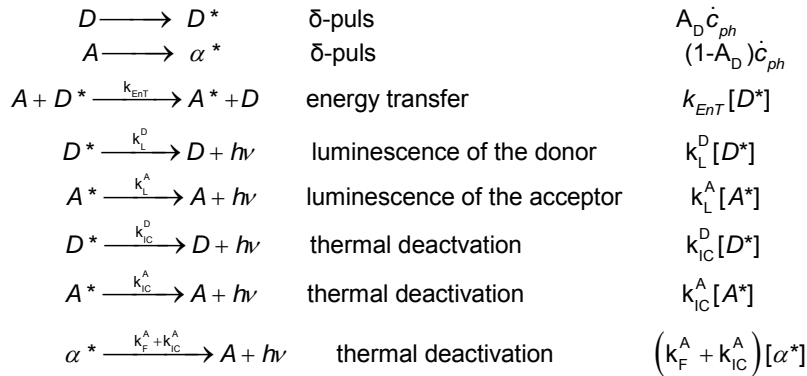
$$\tau_D := \frac{1}{k_D + k_{EnT}} \quad \tau_A := \frac{1}{k_A} \quad \kappa := 1 - \frac{k_D}{k_{EnT}} \quad \tau_{\text{max}} := 0.100 \quad \tau_T := \frac{T}{100} \cdot \tau_A$$

$$I_D(t) := I_0 \cdot e^{-\frac{t}{\tau_D}} \quad I_A(t) := \left( \frac{1}{\kappa} + \frac{1 - A_D}{A_D} \right) \cdot e^{-\frac{t}{\tau_A}} - \frac{1}{\kappa} \cdot e^{-\frac{t}{\tau_D}} \quad \kappa = 0.889$$



### C) Increase of the acceptor luminescence, a detailed derivation of the formula

We include the possibility of direct excitation of the acceptors at the excitation wavelength and we name the directly excited acceptors A not as A\* but as  $\alpha^*$  because this facilitates the calculations. The kinetic parameters of A\* and of  $\alpha^*$  are the same, however.



$$\frac{d[D^*]}{dt} = A_D \dot{c}_{ph} - (k_{EnT} + k_L^D + k_{IC}^D) [D^*]$$

$$\frac{d[A^*]}{dt} = k_{EnT} [D^*] - (k_L^A + k_{IC}^A) [A^*] \quad \frac{d[\alpha^*]}{dt} = (1 - A_D) \dot{c}_{ph} - (k_L^A + k_{IC}^A) [\alpha^*]$$

Considering a  $\delta$ -puls excitation, the terms:  $A_D \dot{c}_{ph}$  and  $(1 - A_D) \dot{c}_{ph}$  can be substituted by the initial conditions:  $[D^*]_0 = [D^*](t=0)$  and  $[A^*]_0 = [A^*](t=0)$

Using  $k^D = k_L^D + k_{IC}^D$  and  $k^A = k_L^A + k_{IC}^A$  we can write:

$$\frac{d[D^*]}{dt} = [D^*]_0 - (k_T + k^D) [D^*]$$

$$\frac{d[A^*]}{dt} = k_{EnT} [D^*] - k^A [A^*]$$

$$\frac{d[\alpha^*]}{dt} = [\alpha^*]_0 - k^A [\alpha^*]$$

The solution of the equation for  $[D^*]$  is trivial and the equation for  $\alpha^*$  can be solved independently because energy migration among the excited acceptors does not influence the decay of  $\alpha^*$ .

$$[D^*](t) = [D^*]_0 e^{-(k_{EnT} + k^D)t} \quad \frac{[\alpha^*]_0}{[D^*]_0} = \frac{1 - A_D}{A_D}$$

$$[\alpha^*](t) = [\alpha^*]_0 e^{-k^A t}$$

What remains is to find the solution for  $[A^*]$ . Inserting  $[D^*](t)$  we find:

$$\frac{d[A^*]}{dt} = k_{EnT} [D^*]_0 e^{-(k_{EnT} + k^D)t} - k^A [A^*]$$

This is an inhomogeneous, linear differential equation of the type:  $\frac{dy}{dt} + ay = be^{-ct}$

The solution of this equation is:  $y(t) = \frac{b}{a - c} (e^{-ct} - e^{-at})$

$$a = k_A, b = k_{EnT} [D^*]_0, c = (k_{EnT} + k^D) \quad [A^*](t) = \frac{k_{EnT} [D^*]_0}{k_A - (k_{EnT} + k^D)} (e^{-(k_{EnT} + k^D)t} - e^{-k_A t})$$

Some technical details.

$$i_D(t) = i_D^0 e^{-(k_{EnT} + k^D)t} \quad i_A(t) = i_{A^*}(t) + i_{\alpha^*}(t)$$

$$i'_{A^*}(t) = \frac{k_{EnT} [D^*]_0}{k_A - (k_{EnT} + k^D)} \left( e^{-(k_{EnT} + k^D)t} - e^{-k_A t} \right) + [\alpha^*]_0 e^{-k_A t}$$

$$i_A(t) = \frac{k_{EnT}}{k_A - (k_{EnT} + k^D)} \left( e^{-(k_{EnT} + k^D)t} - e^{-k_A t} \right) + \frac{1 - A_D}{A_D} e^{-k_A t}$$

$$i_A(t) = \frac{k_{EnT}}{k_A - (k_{EnT} + k^D)} e^{-(k_{EnT} + k^D)t} + \left( \frac{1 - A_D}{A_D} - \frac{k_{EnT}}{k_A - (k_{EnT} + k^D)} \right) e^{-k_A t}$$

$$i_A(t) = \left( \frac{1 - A_D}{A_D} + \kappa \right) e^{-k_A t} - \kappa e^{-(k_{EnT} + k^D)t}$$

$$\kappa = \frac{k_{EnT}}{k_A - (k_{EnT} + k^D)}$$

Solution of:  $\frac{dy}{dt} + ay = be^{-ct}$       $a, b$  and  $c$  are positive numbers with dimension,  $s^{-1}$ ,  $mol/s$  and  $s^{-1}$ , respectively.

Solution of the homogeneous equation:  $\frac{dy}{dt} + ay = 0$       $y_h = y_0 e^{-at}$

Particulate solution:  $\frac{dy}{dt} = 0$       $y = \frac{b}{a} e^{-ct}$      From this we guess, that the following is a particulate solution:  $y_p = \alpha \frac{b}{a} e^{-ct}$

Inserting into the original equation leads to:  $-c\alpha \frac{b}{a} e^{-ct} + a\alpha \frac{b}{a} e^{-ct} = be^{-ct}$

$$-c\alpha \frac{1}{a} + \alpha = 1 \quad \left( -c \frac{1}{a} + 1 \right) \alpha = 1 \quad \alpha = \frac{a}{(a - c)} \quad y_p = \frac{b}{(a - c)} e^{-ct}$$

Solution:  $y = y_p + qy_h = \frac{b}{(a - c)} e^{-ct} + qy_0 e^{-at}$

$y(t=0) = 0$ , because  $[A^*](t=0) = 0$ , hence:  $0 = \frac{b}{(a - c)} e^{-c \cdot 0} + qy_0 e^{-a \cdot 0}$

$$qy_0 = \frac{b}{(c - a)}$$

$$y = \frac{b}{(a - c)} (e^{-ct} - e^{-at})$$

### 5.3 Time resolved measurements in organized systems

**Organization** implies transfer of a signal in a specific way to a specific place.

In this chapter I refer to some of our publications.

#### 5.3.1 Selected systems

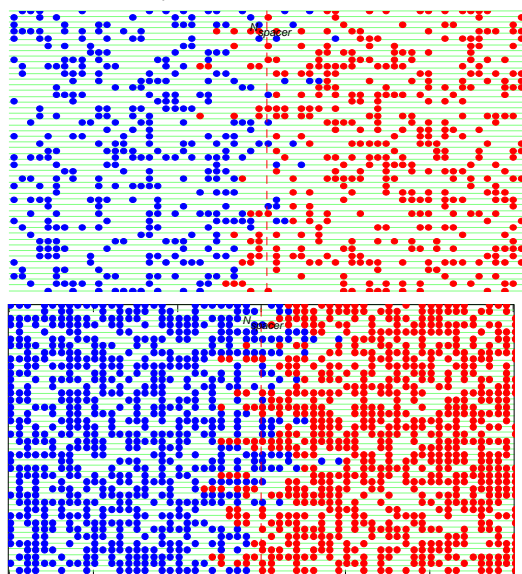
Electronic Excitation Energy Migration in a Photonic Dye-Zeolite Antenna  
Mikalai Yatskou, Michel Pfenniger, Marc Meyer, Stefan Huber, Gion Calzaferri  
*ChemPhysChem*, **2003**, 4, 2003, 567-587.

Energy Transfer from Dye-Zeolite L Antenna Crystals to Bulk Silicon  
Stefan Huber, Gion Calzaferri  
*ChemPhysChem* **2004**, 5, 239-242.

Injecting Electronic Excitation Energy Into an Artificial Antenna System by a  $\text{Ru}^{2+}$  Complex  
Olivia Bossart, Luisa De Cola, Steve Welter, and Gion Calzaferri  
*Chem. Eur. J.* **2004**, in press

#### 5.3.2 Distribution of the chromophores in a host-guest material

Electronic Excitation Energy Migration in a Photonic Dye-Zeolite Antenna  
Mikalai Yatskou, Michel Pfenniger, Marc Meyer, Stefan Huber, Gion Calzaferri  
*ChemPhysChem*, **2003**, 4, 2003, 567-587.



A Monte Carlo based Mathcad program  
*MC-Distribution.mcd*  
will be provided  
(must first be translated from  
German to English).

### 5.3.3 Markow chain treatment of EnT a host-guest material

Transfer of electronic excitation energy between dye molecules in the channels of zeolite L

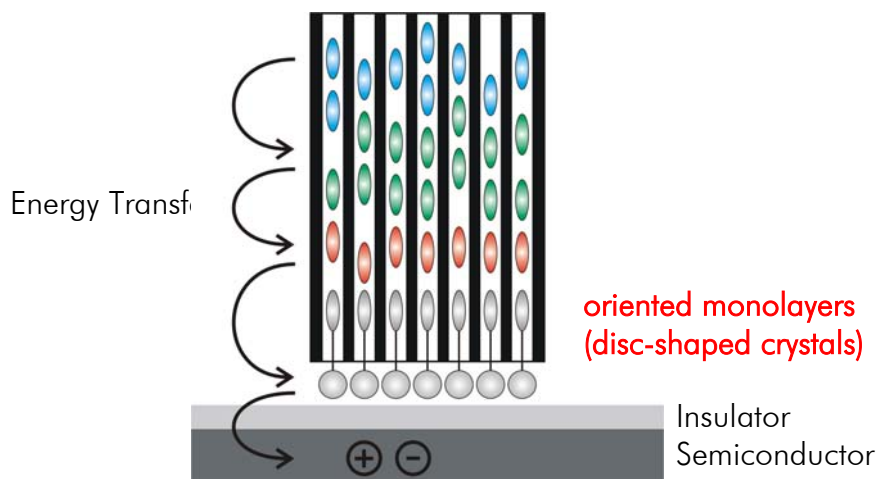
Niklaus Gfeller, Silke Megelski and Gion Calzaferri  
*J. Phys. Chem. B.* **104** (1998) 2433-2436.

A Mathcad program *Makow EnToneD.mcd*  
 will be provided (must first be translated from German to English).

### 5.4 3-dimensional, 2-dimensional, and 1-dimensional EnT

Claudia Minkoski, Gion Calzaferri, in preparation

#### Photonic Antenna



The theory for describing such photonic antenna systems is under construction.