Electronic Excitation Energy Transfer

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Part 1: An experimental approach

Energy Collection, Transport, and Trapping by Supramolecular Organization of Dyes in Hexagonal Zeolite Nano Crystals

Part 2: Theoretical concepts

Förster Energy Transfer Theory

Förster Energy Transfer Theory

Förster theory

1 Weak interaction between donor and acceptor molecules

2 J-aggregates and H-aggregates

3 Energy transfer between weakly interacting donor and acceptor molecules

4 Förster energy transfer radius R_0

5 Selection rules

6 Examples of spectral overlap and Förster radius

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Förster Energy Transfer

In order for excitation energy transfer to occur between an electronically excited molecule D* and an acceptor A some interaction between D* and A is required.

EnT can take place if A possesses transitions which are isoenergetic with transitions of D*.

Model:

The energy separations between 2 vibrational states v,v+1 and v',v'+1 of D* and of A are the same and ΔE is twice this separation.

The following **r**esonance **e**nergy **t**ransfer processes, RET, can take place:

D*(0') + A(0) → D(2) + A*(0')

D*(0') + A(0) → D(1) + A*(1')

D*(0') + A(0) → D(0) + A*(2')
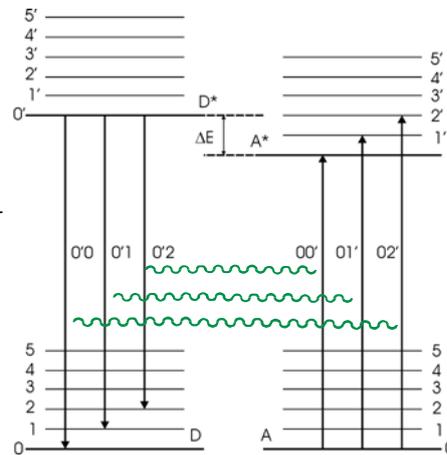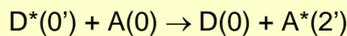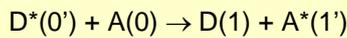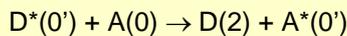
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RET can result from different interaction mechanisms.

Ψ_i :   Electronic wave function for the initial excited state (D excited but not A)
Ψ_f :   Electronic wave function for the final excited state (A excited but not D)

$$\Psi_i = \frac{1}{\sqrt{2}}\left(\Psi_{D^*}(1)\Psi_A(2) - \Psi_{D^*}(2)\Psi_A(1)\right)$$

$$\Psi_f = \frac{1}{\sqrt{2}}\left(\Psi_D(1)\Psi_{A^*}(2) - \Psi_D(2)\Psi_{A^*}(1)\right)$$

Interaction H' between the initial and the final state:

$$\beta = \langle\Psi_i|H'|\Psi_f\rangle$$

$$\beta = \left\langle \frac{1}{\sqrt{2}}\left(\Psi_{D^*}(1)\Psi_A(2) - \Psi_{D^*}(2)\Psi_A(1)\right)\middle| H' \middle| \frac{1}{\sqrt{2}}\left(\Psi_D(1)\Psi_{A^*}(2) - \Psi_D(2)\Psi_{A^*}(1)\right)\right\rangle$$

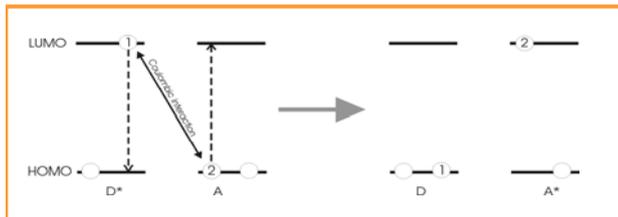$$\langle\Psi_{D^*}(1)\Psi_A(2)|H'|\Psi_D(1)\Psi_{A^*}(2)\rangle \quad = \beta_C$$

$$\langle\Psi_{D^*}(1)\Psi_A(2)|H'|\Psi_D(2)\Psi_{A^*}(1)\rangle \quad = \beta_{ex}$$

$$\beta = \beta_C - \beta_{ex}$$

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Electronic Excitation Energy Transfer
   Part 2

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The Coulomb and the exchange interactions lead to two different EnT mechanisms

The Coulomb interaction β_C describes a situation in which the initially excited electron on D returns to the ground state, while an electron on A is simultaneously promoted to the excited state.

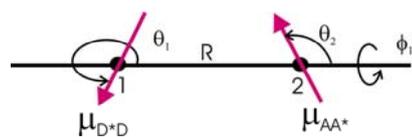β_C

The exchange interaction β_{ex} describes a situation which can be understood as an exchange of two electrons on D* and A.

β_{ex}

The wave functions of D and A must overlap for $\beta_{ex} \neq 0$; short range interaction. [5]

The **Coulomb term** can be expanded into a sum of terms (multipole-multipole exp.

First dominant term: dipole-dipole interaction between the transition dipole
moments μ_D and μ_A for the transitions D*→D and A→A*

Therefore the perturbation H'$_C$ can be expressed as:

$$H'_C = \frac{e^2}{4\pi\varepsilon_0 n^2}\frac{1}{R_{DA}{}^3}\,l_{D^*}l_A\kappa_{D^*A}$$

$$\kappa_{D^*A} = \left(\sin\theta_1\sin\theta_2\cos\phi_{12} - 2\cos\theta_1\cos\theta_2\right)$$

See: Dipole-dipole interaction and the orientation factor κ.

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Electronic Excitation Energy Transfer
   Part 2

1 Weak interaction between donor and acceptor molecules

In order for EnT to occur some interaction between D* and A is needee.

Strong interaction: the electronic spectra of a mixture of donors and acceptors are different from those of their diluted solutions.

Weak interaction: the electronic spectrum of a mixture of donors and acceptors is a superposition of the spectra of the diluted solutions.

Medium and   exciton theory
strong interaction: molecular orbital theory

Weak interaction: we follow the arguments given by
Th. Förster *Annalen der Physik*, 6. (2), (1948) 55-75.

To calculate the rate constant k_{EnT} of EnT between an D* and A,
we must calculate the product $(\beta_{D*A})^2 \rho_{D*A}$, according to **Fermi's golden rule**.

$$k_{EnT} = \frac{2\pi}{\hbar} \beta_{D*A}{}^2 \rho_{(D*A,DA*)}$$

Only the Coulomb term plays a role for weak interactions. The exchange term requires orbital overlap between the D* and A, which causes larger interaction.

$$\beta_{D*A} = \beta_C = \langle \Psi_i | H'_C | \Psi_f \rangle$$

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Only the Coulomb term plays a role for weak interactions, since the exchange term requires orbital overlap between the D* and A, which causes larger interaction.

$$\Psi_i = \Psi_{D*}\Psi_A$$
$$\Psi_f = \Psi_D\Psi_{A*}$$

$$H'_C = \frac{e^2}{4\pi\varepsilon_0 n^2} \frac{\kappa_{D*A}}{R_{DA}{}^3} l_D l_A$$

l_D and l_A = coordinates of the electrons belonging to D and A

$$\beta_{D*A} = \langle \Psi_i | H'_C | \Psi_f \rangle$$

$$\beta_{D*A} = \frac{1}{4\pi\varepsilon_0 n^2} \frac{\kappa_{D*A}}{R_{DA}{}^3} |\langle \Psi_{D*} | e l_D | \Psi_D \rangle||\langle \Psi_A | e l_A | \Psi_{A*} \rangle|$$
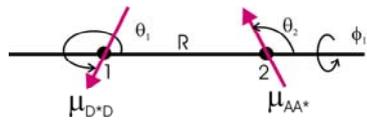
electronic transition $\mathbf{\mu}_{D*D}$ $\mathbf{\mu}_{AA*}$
moments

$$\beta_{D*A} = \frac{1}{4\pi\varepsilon_0 n^2} \frac{\kappa_{D*A}}{R_{DA}{}^3} |\mathbf{\mu}_{D*D}||\mathbf{\mu}_{AA*}|$$
$$k_{EnT} = \frac{2\pi}{\hbar} \beta_{D*A}{}^2 \rho_{(D*A,DA*)}$$

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$$\beta_{D^*A} = \frac{1}{4\pi\varepsilon_0 n^2} \frac{\kappa_{D^*A}}{R_{DA}^3} \left|\mathbf{\mu}_{D^*D}\right|\left|\mathbf{\mu}_{AA^*}\right|$$

This equation not only forms a basis for describing the rate of electronic EnT.

It also gives information about the influence of this interaction on the electronic states of D* and A.

Before continuing we therefore shortly discuss **J- and H-aggregates**, which are observed if the interaction is sufficiently strong.

This is necessary to make clear under what conditions arguments given later have a chance to be valid.

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2 J-aggregates and H-aggregates (Scheibe 1932)

Pair of molecules A_i and A_k at a distance R.
R is so large that the interaction in the electronic ground state is negligibly small.

Electronically excited states: $A^*_i \ldots A_k$ resp. $A_i \ldots A^*_k$

Negligible overlap of the wave functions between (A^*_i and A_k) and (A_i and A^*_k).

This does not necessarily mean that the interaction between the electronically excited states $A^*_i \ldots A_k$ and $A_i \ldots A^*_k$ is so weak that the splitting of these states is negligible.

Ground state: $\Psi_{A_i A_k} = \Psi_{A_i}\Psi_{A_k}$ Energy E_0

Excited state: $\Psi_{A_i A_k^*} = \Psi_{A_i}\Psi_{A_k^*}$ Energy E_1

Excited state: $\Psi_{A_i^* A_k} = \Psi_{A_i^*}\Psi_{A_k}$ Energy E_1

H'_C caused by the electronic transition dipole moments.

The excited state is described by a linear combination of $\Psi_{A_i A_k^*}$ and $\Psi_{A_i^* A_k}$

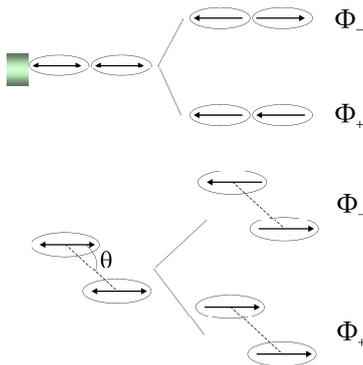$\Phi(c_1,c_2) = c_1\Psi_{A_i^* A_k} + c_2\Psi_{A_i A_k^*}$

$\langle\Phi(c_1,c_2)|H|\Phi(c_1,c_2)\rangle = \varepsilon\langle\Phi(c_1,c_2)|\Phi(c_1,c_2)\rangle$ $\langle\Psi_{A_i^* A_k}|\Psi_{A_i A_k^*}\rangle = 0$

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    Part 2

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$$\Phi(c_1, c_2) = c_1 \Psi_{A_i^* A_k} + c_2 \Psi_{A_i A_k^*}$$

The excitation is collective or delocalized.

$$\begin{vmatrix} h_{11} - \varepsilon & h_{12} \\ h_{21} & h_{22} - \varepsilon \end{vmatrix} = 0 \qquad \begin{array}{l} \varepsilon_+ = E_1 + \beta_C \\ \varepsilon_- = E_1 - \beta_C \end{array}$$

$$\Phi_+ = \frac{1}{\sqrt{2}} \left(\Psi_{A_i^* A_k} + \Psi_{A_i A_k^*} \right) \qquad \text{symmetric}$$

$$\Phi_- = \frac{1}{\sqrt{2}} \left(\Psi_{A_i^* A_k} - \Psi_{A_i A_k^*} \right) \qquad \text{antisymmetric}$$

$$\beta_C = \frac{1}{4\pi\varepsilon_0 n^2} \frac{\kappa_{A^* A}}{R_{DA}^3} \left| \mu_{AA^*} \right|^2$$

In both stationary states Φ_+ and Φ_- the excitation is on both molecules i and k.

Phase relation of the wave functions which describe the interaction between $A^*_i \ldots A_k$ and $A_i \ldots A^*_k$ caused by μ_{AA^*} ($\kappa = \pm 2$).

The node corresponding to the minus sign in Φ_- is an excitation node (not an electron orbital node).

At an excitation node, the phase relation between the transition moments of the respective molecular centres change phase.

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$$\begin{vmatrix} h_{11} - \varepsilon & h_{12} \\ h_{21} & h_{22} - \varepsilon \end{vmatrix} = 0 \qquad \begin{array}{l} \varepsilon_+ = E_1 + \beta_C \\ \varepsilon_- = E_1 - \beta_C \end{array}$$

$$\Phi_+ = \frac{1}{\sqrt{2}} \left(\Psi_{A_i^* A_k} + \Psi_{A_i A_k^*} \right)$$

$$\Phi_- = \frac{1}{\sqrt{2}} \left(\Psi_{A_i^* A_k} - \Psi_{A_i A_k^*} \right)$$

Exciton splitting caused by the interaction of the configurations due to the electronic transition dipole moments.
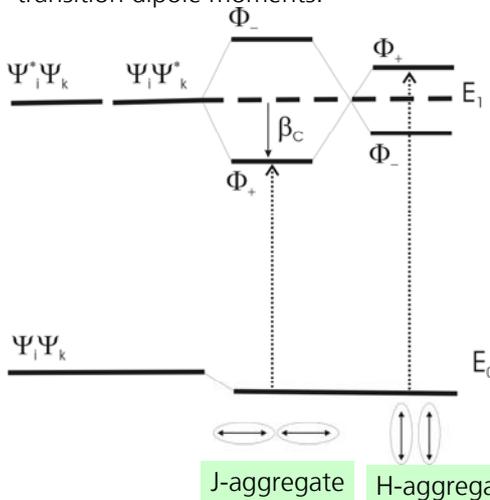
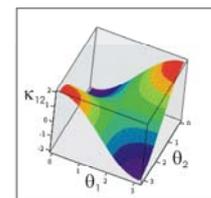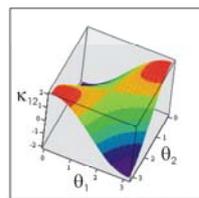In both stationary states Φ_+ and Φ_- the excitation is on both molecules.

β_C depends on the relative orientation of the transition dipole moments described by $\kappa_{A^* A}$.

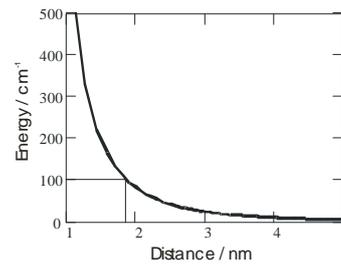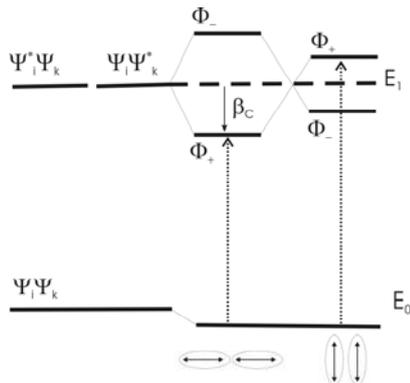$$\kappa_{A^* A} = \left(\sin\theta_1 \sin\theta_2 \cos\phi_{12} - 2\cos\theta_1 \cos\theta_2 \right)$$

J-aggregate   H-aggregate

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Magnitude of the splitting ($\phi_{12} = 0$ and $\theta_1 = \theta_2$)

$$\beta_C = \frac{1}{4\pi\varepsilon_0 n^2}\frac{\left|\mathbf{\mu}_{AA^*}\right|^2}{R_{DA}^{\,3}}\left(1-3\cos^2(\theta)\right)$$

$$f = \frac{8\pi c m_e}{3he^2}\bar{\nu}\left|\mathbf{\mu}_{AA^*}\right|^2$$

Selection rules for the transition moment: $(A_i\ldots A_k) \rightarrow [(A^*_i\ldots A_k)\leftrightarrow(A_i\ldots A^*_k)]$:
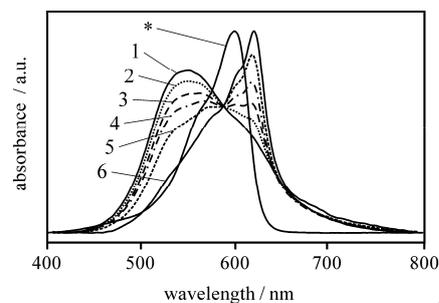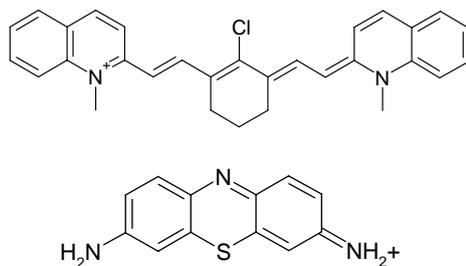
$$M_+ = \left\langle \Psi_i\Psi_k \left| \hat{\mu}_i + \hat{\mu}_k \right| \Phi_+ \right\rangle$$

$$M_- = \left\langle \Psi_i\Psi_k \left| \hat{\mu}_i + \hat{\mu}_k \right| \Phi_- \right\rangle$$

$$M_- = \frac{1}{\sqrt{2}}\left(\mu_{A_i^*A_k} - \mu_{A_iA_k^*}\right)$$

$$M_+ = \frac{1}{\sqrt{2}}\left(\mu_{A_i^*A_k} + \mu_{A_iA_k^*}\right)$$
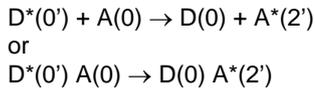
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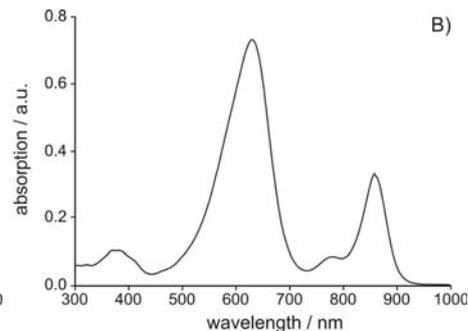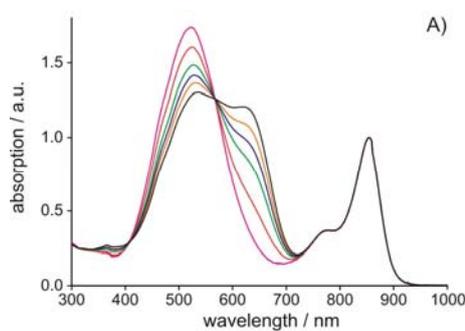
3 EnT between weakly interacting donor and acceptor molecules

$$\beta_{D^*A} = \frac{1}{4\pi\varepsilon_0 n^2} \frac{\kappa_{D^*A}}{R_{DA}{}^3} |\mu_{D^*D}||\mu_{AA^*}| \qquad k_{EnT} = \frac{2\pi}{\hbar}\beta^2 \rho_{(D^*A,DA^*)}$$

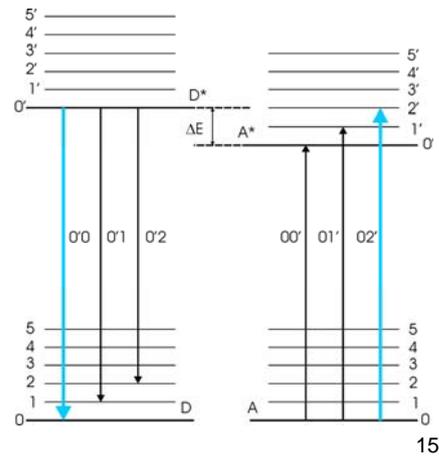EnT rate constant between 2 levels which are in resonance.

D*(0') + A(0) → D(0) + A*(2')
or
D*(0') A(0) → D(0) A*(2')

$$k_{EnT(0',0;0,2')} = \frac{2\pi}{\hbar}\beta_{D^*A}{}^2 \rho_{(0',0;0,2')}$$
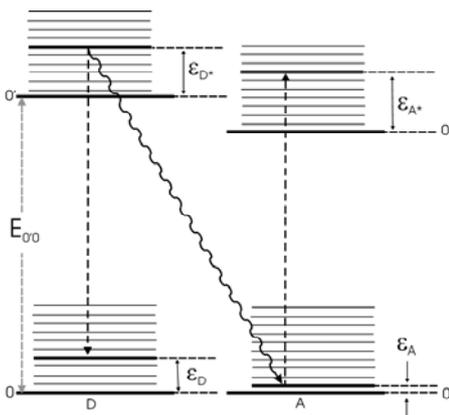
To find all transitions D*A→D A*
we must sum over all states
which are in resonance.
States of the donor: (d',δ)
States of the acceptor: (α,a')

$$k_{EnT(d',\delta;\alpha,a')} = \frac{2\pi}{\hbar}\beta_{D^*A}{}^2 \rho_{(d',\delta;\alpha,a')}$$

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Since EnT can be very fast, it is not sufficient to consider only the lowest v-state of D*.

We must sum over all iso-energetic
situations.

$$k_{EnT} = \sum k_{EnT(d',\delta;\alpha,a')}$$

Spectra in condensed phase are usually
broadened due to solute solvent
interactions and lattice vibrations.

The initial (i) and the final (f) levels of
D*…A and D…A* are not well
defined.

We may therefore express the density of states ρ_E within on a continuous energy range.

Normalized functions **$S_D(E_{D^*})$** and **$S_A(E_A)$**.
$S_D(E_{D^*})$ = probability that (isolated) D* emits photons of energy E_{D^*}.
$S_A(E_A)$ = probability that A absorbs photons of energy E_A.

$$\int_{E_Y} S_Y(E_Y)dE_Y = 1$$

$S_D(E_{D^*})$ and $S_A(E_A)$ reflect the shape of the luminescence spectrum of D* and of the absorption spectrum of A, respectively.

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Resonance condition:

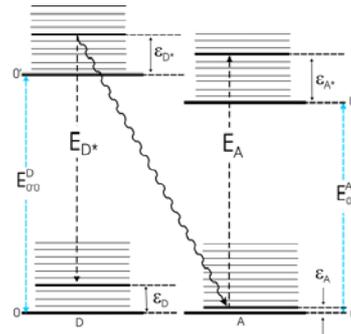$$E_{D^*} = E_{0'0}^D + \varepsilon_{D^*} - \varepsilon_D \qquad E_{res} = \int E_{D^*}\delta(E_{D^*} - E_A)dE_{D^*}$$

$$E_A = E_{0'0}^A + \varepsilon_{A^*} - \varepsilon_A$$

Rate constant for $D^* + A \rightarrow D + A^*$ EnT:

$$k_{EnT} = \frac{2\pi}{\hbar} \int_{E_{D^*}} \int_{E_A} \beta_{D^*A}^2 S_D(E_{D^*}) S_A(E_A) \delta(E_{D^*} - E_A) \, dE_{D^*}dE_A$$

Inserting β_{D^*A}:

$$k_{EnT} = \frac{2\pi}{\hbar} \left(\frac{\kappa'_{D^*A}}{R_{DA}^3} \right)^2 \iint_{E_{D^*},E_A} |\mathbf{\mu}_{D^*D}|^2 S_D(E_{D^*}) |\mathbf{\mu}_{AA^*}|^2 S_A(E_A)\delta(E_{D^*} - E_A) \, dE_{D^*}dE_A$$

Evaluation of this integral on a purely theoretical basis is often not possible.

Instead of integrating over E we integrate over the frequency ν.

$$k_{EnT} = \frac{1}{\hbar^2} \left(\frac{\kappa'_{D^*A}}{R_{DA}^3} \right)^2 \iint_{v_{D^*},v_A} |\mathbf{\mu}_{D^*D}|^2 S_D(v_{D^*}) |\mathbf{\mu}_{AA^*}|^2 S_A(v_A)\delta(v_{D^*} - v_A) \, dv_{D^*}dv_A$$

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Connection between electronic transition moments and the Einstein coefficients

$$k_{EnT} = \frac{1}{\hbar^2} \left(\frac{1}{R_{DA}^3} \frac{\kappa_{D^*A}}{4\pi\varepsilon_0 n^2} \right)^2 \iint_{v_{D^*},v_A} |\mathbf{\mu}_{D^*D}|^2 S_D(v_{D^*}) |\mathbf{\mu}_{AA^*}|^2 S_A(v_A)\delta(v_{D^*} - v_A) \, dv_{D^*}dv_A$$

Some lengthy calculations result in:

$$\left(\mathbf{\mu}_{D^*D} \right)^2 = \frac{c_0^3}{v_{D^*}^3} \frac{3\hbar}{32\pi^3} \frac{4\pi\varepsilon_0}{n} \frac{1}{\tau_{D^*}^0} \qquad \left(\mathbf{\mu}_{AA^*} \right)^2 S_A(v_A) = \frac{3\hbar}{4\pi^2} 4\pi\varepsilon_0 n c_0 \frac{10^3 \ln(10)}{N_L} \frac{\varepsilon_A(v_A)}{v_A}$$

Inserting this and keeping in mind that:

$$\int_{v_{D^*}} v_{D^*}\delta(v_{D^*} - v_A)dv_{D^*} = v_A \qquad v = \bar{v} c_0$$

$$k_{EnT} = \frac{9000\ln(10)}{128\pi^5 N_L} \frac{\kappa_{D^*A}^2}{n^4 R_{DA}^6} \frac{\phi_{D^*}}{\tau_{D^*}} \int_{\bar{v}} S_D(\bar{v}) \frac{\varepsilon_A(\bar{v})}{\bar{v}^4} d\bar{v} \qquad J_{\bar{v}D^*A} = \int_{\bar{v}} S_D(\bar{v}) \frac{\varepsilon_A(\bar{v})}{\bar{v}^4} d\bar{v}$$

$$k_{EnT} = \frac{9000\ln(10)}{128\pi^5 N_L} \frac{\kappa_{D^*A}^2}{n^4 R_{DA}^6} \frac{\phi_{D^*}}{\tau_{D^*}} J_{\bar{v}D^*A}$$

Spectral overlap integral

$[J] = [cm^3 M^{-1}]$, $k_{EnT} = ns^{-1}$

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    Part 2

4 Förster energy transfer radius R_0

Luminescence rate of D*:
$$\frac{d\rho_{D^*}}{dt} = -\frac{1}{\tau_{D^*}}\rho_{D^*}$$

Energy transfer rate:
$$\frac{d\rho_{D^*}}{dt} = -k_{EnT}\rho_{D^*}$$

At a specific D*….A distance, the rate at which D* emits light is equal to the rate at which it transfers its excitation energy A. At this distance R_0 we can write:

$$\frac{1}{\tau_{D^*}} = k_{EnT}$$

Inserting k_{EnT} and solving for R_0:

$$R_0^{\,6} = \frac{9000\ln(10)}{128\pi^5 N_L}\frac{\kappa_{D^*A}^{\,2}}{n^4}\phi_{D^*}J_{\bar{\nu}D^*A}$$

From this we find the Förster radius R_0 for electronic excitation energy transfer.

$$R_0 = \sqrt[6]{\frac{9000\ln(10)}{128\pi^5 N_L}\frac{\kappa_{D^*A}^{\,2}}{n^4}\phi_{D^*}J_{\bar{\nu}D^*A}}$$

R_0 is equal to the donor- acceptor distance at which the probability for energy transfer is equal to 0.5.

Distance dependence of the energy transfer rate constant:
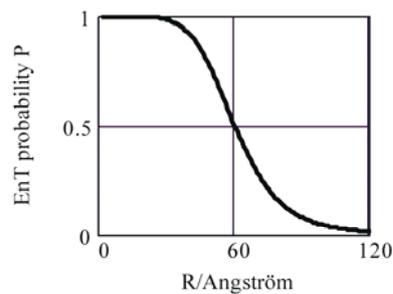$$k_{EnT} = \frac{1}{\tau_{D^*}}\left(\frac{R_0}{R}\right)^6$$

Luminescence rate of D*:
$$\left(\overline{\frac{d\rho}{dt}}\right)_{\text{fluorescence of D*}} = -\frac{1}{\tau_{D^*}}\rho_{D^*}$$

Energy transfer rate:
$$\left(\overline{\frac{d\rho}{dt}}\right)_{\text{energy transfer}} = -k_{EnT}\rho_{D^*}$$

Probability P for EnT:
$$P = \frac{\left(\overline{\dfrac{d\rho}{dt}}\right)_{\text{energy transfer}}}{\left(\overline{\dfrac{d\rho}{dt}}\right)_{\text{fluorescence}} + \left(\overline{\dfrac{d\rho}{dt}}\right)_{\text{energy transfer}}} \times \frac{\dfrac{1}{\left(\overline{\dfrac{d\rho}{dt}}\right)_{\text{energy transfer}}}}{\dfrac{1}{\left(\overline{\dfrac{d\rho}{dt}}\right)_{\text{energy transfer}}}}$$

$$k_{EnT} = \frac{1}{\tau_{D^*}}\left(\frac{R_0}{R}\right)^6$$

$$P = \frac{1}{1 + \left(R/R_0\right)^6}$$
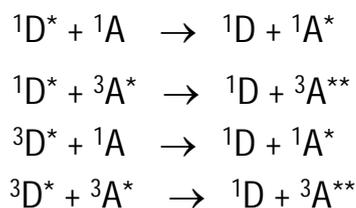

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5 Selection rules

The are no strict selection rules for Förster energy transfer. We can, nevertheless, get a good idea by considering the following proportionality:

$$k_{EnT} \propto \frac{1}{\tau_{D^*}^0} \int_v S_D(v) \frac{\varepsilon_A(v)}{v^4} dv$$

This means that the EnT rate constant depends on the extinction coefficient of the acceptor.

If a forbidden transition of the acceptor is involved, the energy transfer rate is small.

$$^1D^* + {}^1A \quad \rightarrow \quad {}^1D + {}^1A^*$$

$$^1D^* + {}^3A^* \quad \rightarrow \quad {}^1D + {}^3A^{**}$$

$$^3D^* + {}^1A \quad \rightarrow \quad {}^1D + {}^1A^*$$

$$^3D^* + {}^3A^* \quad \rightarrow \quad {}^1D + {}^3A^{**}$$

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6 Examples for spectral overlap and Förster radius

$$J_{D^*A} = \int_{\bar{v}} S_D(\bar{v}) \frac{\varepsilon_A(\bar{v})}{\bar{v}^4} d\bar{v}$$

$$R_0 = \left(\frac{9000\ln(10)}{128\pi^5 N_A} J_{D^*A} \frac{\phi_{D^*}\kappa^2}{n^4} \right)^{1/6}$$

Examples for dyes in zeolite L:
(n = 1.4)

$J_{py,py} = 1.1 \times 10^{-13}$ cm^{3}M^{-1}

$R_0(\kappa^2 = 2/3) = 5.1$ nm

$R_0(\kappa^2 = 4) = 6.8$ nm

$J_{ox,ox} = 4.4\ldots \times 10^{-13}$ cm^{3}M^{-1}

$R_0(\kappa^2 = 2/3) = 6.4$ nm

$R_0(\kappa^2 = 4) = 8.6$ nm

$J_{py,ox} = 2.3 \times 10^{-13}$ cm^{3}M^{-1}

$R_0(\kappa^2 = 2/3) = 5.7$ nm

$R_0(\kappa^2 = 4) = 7.7$ nm

Py$^+$ Ox$^+$

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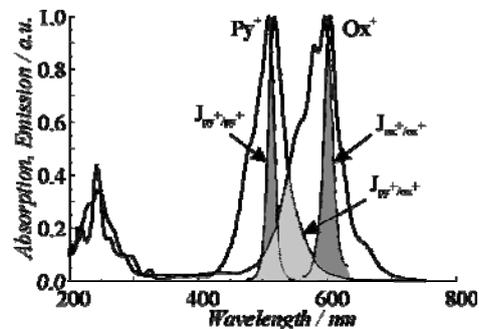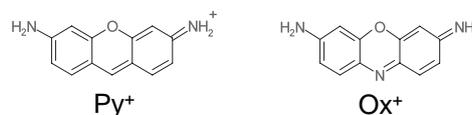
Electronic Excitation Energy Transfer
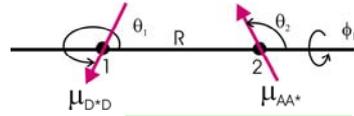Part 2

$$J_{D^*A} = \int_{\bar{v}} S_D(\bar{v}) \frac{\varepsilon_A(\bar{v})}{\bar{v}^4} d\bar{v}$$

$$R_0 = \sqrt[6]{\frac{9000\ln(10)}{128\pi^5 N_L} \frac{\kappa_{D^*A}^2}{n^4} \phi_{D^*} J_{\bar{v} D^*A}}$$

$$k_{EnT} = \frac{1}{\tau_{D^*}} \left(\frac{R_0}{R}\right)^6$$

Dyes	J / cm³M⁻¹	κ^2	R_0 / Å	τ_{D^*} /ns	k_{EnT} / ps⁻¹ R=R₀	R=1.5nm
Ox⁺ / Ox⁺	4.4×10^{-13}	2/3 4	64 86	3.2	3.1×10^{-4}	1.9 11
Py⁺ / Py⁺	1.1×10^{-13}	2/3	51 68	3	3.3×10^{-4}	0.5 2.9
Py⁺ / Ox⁺	2.3×10^{-13}	4	57 77	3	3.3×10^{-4}	1.0 6.0
Ox1 / Ox1		2/3 4	73 98	3.2	3.1×10^{-4}	4.1 24
					$= 2.4\times10^{13}$ s⁻¹	

Connection between electronic transition moments and the Einstein coefficients:

$$B_{D^*D} = \frac{2\pi}{3\hbar^2} \frac{1}{4\pi\varepsilon_0} \frac{1}{n^2} (\mu_{D^*D})^2 \qquad A_{D^*D} = 8\pi \frac{h v_{D^*}^3}{c_0^3} n^3 B_{D^*D}$$

The dimension of B_{DD^*} is:
$$[B_{D^*D}] = \frac{1}{(J\cdot s)^2} \frac{1}{J^{-1}C^2 m^{-1}} (C\cdot m)^2 = \frac{m^3}{J\cdot s^2}$$

We check the dimension of A_{D^*D}:
$$[A_{D^*D}] = \frac{J\cdot s\cdot(s^{-1})^3}{(m\cdot s^{-1})^3} \frac{m^3}{J\cdot s^2} = \frac{1}{s}$$

$$A_{D^*D} = \frac{v_{D^*}^3}{c_0^3} \frac{32\pi^3}{3\hbar} \frac{n}{4\pi\varepsilon_0} (\mu_{D^*D})^2 \qquad A_{D^*D} \frac{c_0^3}{v_{D^*}^3} \frac{3\hbar}{32\pi^3} \frac{4\pi\varepsilon_0}{n} = (\mu_{D^*D})^2$$

Since $A_{D^*D} = \frac{1}{\tau_{D^*}^0}$ we obtain:
$$(\mu_{D^*D})^2 = \frac{c_0^3}{v_{D^*}^3} \frac{3\hbar}{32\pi^3} \frac{4\pi\varepsilon_0}{n} \frac{1}{\tau_{D^*}^0}$$

$$B_{AA^*} = \frac{2\pi}{3\hbar^2} \frac{1}{4\pi\varepsilon_0} \frac{1}{n^2} (\mu_{AA^*})^2 \qquad (\mu_{AA^*})^2 = \frac{3\hbar^2}{2\pi} 4\pi\varepsilon_0 n^2 B_{AA^*}$$

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Connection between electronic transition moments and the Einstein coefficients:

$$B_{AA^*} = \frac{2\pi}{3\hbar^2} \frac{1}{4\pi\varepsilon_0} \frac{1}{n^2} \left(\mu_{AA^*}\right)^2 \qquad \left(\mu_{AA^*}\right)^2 = \frac{3\hbar^2}{2\pi} 4\pi\varepsilon_0 n^2 B_{AA^*}$$

We now relate the Einstein coefficient weighted with the shape of the absorption spectrum to the molar extinction coefficient $e_A(n)$ (see Appendix 8.2):

$$B_{AA^*} S_A(\nu_A) = \frac{10^3 \ln(10)}{hN_L} \frac{c_0}{n} \frac{\varepsilon_A(\nu_A)}{\nu_A}$$

The extinction coefficient $\varepsilon_A(n)$ is usually given in $M^{-1}cm^{-1} = Lmol^{-1}cm^{-1}$. Using this we find:

$$\text{Dimension of the right side} = \frac{1}{J \cdot s \cdot mol^{-1}} m \cdot s^{-1} \frac{L \cdot mol^{-1} \cdot cm^{-1}}{s^{-1}} = \frac{1}{J \cdot s} m \cdot 10^{-3} \frac{m^3}{L} L \frac{1}{10^{-2} \frac{m}{cm} cm} = \frac{m^3}{J \cdot s} 10^{-1}$$

This is correct since the dimension of $S_A(n_A)$ is s:

From this we find:

$$\left(\mu_{AA^*}\right)^2 S_A(\nu_A) = \frac{3\hbar}{4\pi^2} 4\pi\varepsilon_0 n c_0 \frac{10^3 \ln(10)}{N_L} \frac{\varepsilon_A(\nu_A)}{\nu_A}$$

Note that the factor 10^3 depends on the dimension used for $\varepsilon_A(\nu)$.

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