

3. Energy transfer EnT

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Atoms, molecules, clusters, and solids can exist in many different states in which they have the possibility to exchange energy.

Translational energy T

Rotational energy R

Vibrational energy V

Electronic excitation energy E

The possibility to exchange any kind of energy between atoms and molecules is responsible for the very short lifetime of excited rotational and vibrational states of molecules in the gas phase at medium and at high pressure and especially also in condensed phase.

Green plants benefit from the possibility to transfer electronic excitation energy. They have developed very sophisticated tools for trapping and transporting electronic excitation energy in their antenna system.

In molecular crystals and in some polymers which contain the right type and arrangement of chromophores energy quanta can be transported as „bound electron-hole packages“ over large distances.

The mechanism responsible for the energy transfer depends on the kind of interaction which determines the transfer probability.

Mechanical contact (impact)	T-T R-R V-V E-E	T-R T-V R-V (V-E)
Overlap of the electronic wave functions	E-E	Exchange mechanism
Near field interaction	E-E	Dipole-Dipole mechanism etc.
Large distances	Free photons	Electromagnetic radiation field

3.1 Transfer of vibrational, rotational, and translational energy

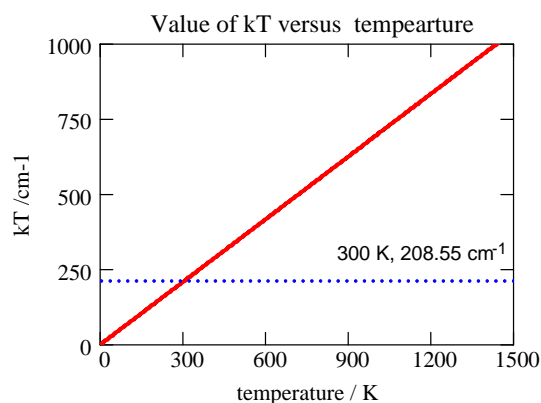
The equilibrium of molecules in the gas-phase is characterized by a constant (time independent) fraction n_i of molecules in each possible energy state ε_i .

$$\text{Boltzmann: } \frac{n_i}{N} = g_i \frac{e^{-\varepsilon_i/kT}}{Q(T)}$$

$$\text{Sum of states: } Q(T) = \sum_i g_i e^{-\varepsilon_i/kT}$$

The comparison of kT with ε_i shows above what temperature a state i starts to be occupied:

$$\varepsilon_i \approx kT \quad e^{-1} \approx 0.37$$

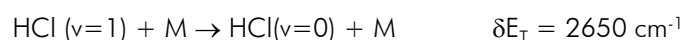


In absence of chemical reactions, thermal equilibrium is established by exchange of

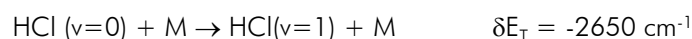
$$\left. \begin{array}{l} \text{translational} - T \\ \text{rotational} - R \\ \text{vibrational} - V \\ \text{electronic} - E \end{array} \right\} \text{energy}$$

Example: a vibrationally excited HCl molecule ($v = 0, 1, 2, \dots$) collides with a molecule M and transforms its vibrational energy into translational energy of the two colliding partners.

V \rightarrow T transformation



T \rightarrow V transformation

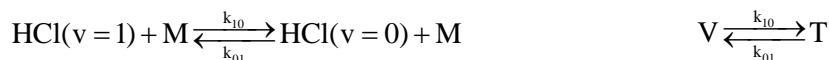


3 kinds of collisions:

$\left. \begin{array}{l} \text{elastic } e \\ \text{inelastic } i \\ \text{reactive } r \end{array} \right\} \text{collisions}$	$\left\{ \begin{array}{l} - \text{only exchange of translational energy} \\ - \text{energy transfer (different kinds of energy)} \\ - \text{chemical reactions} \end{array} \right.$
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These processes can be observed by means of relaxation methods:

Example: HCl is in a highly diluted environment of molecules M in gas phase.



n = number density of the buffer gas M

n_0 = number density of HCl($v=0$)

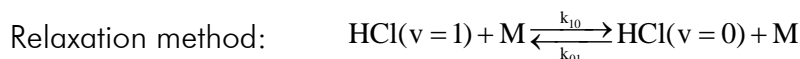
n_1 = number density of HCl($v=1$)

$$-\frac{dn_0}{dt} = \frac{dn_1}{dt} = -k_{10}nn_1 + k_{01}nn_0$$

k_{10} is the rate constant for the V-T process which depletes the population in the $v=1$ state and k_{01} is that for the reverse T-V process which populates the $v=1$ state.

At equilibrium there is no change in the populations: $-\frac{dn_0}{dt} = \frac{dn_1}{dt} = 0$

$$\frac{k_{01}}{k_{10}} = \left(\frac{n_1}{n_0} \right)_{\text{eq}} = e^{-(\epsilon_1 - \epsilon_0)/kT} = e^{-h\nu/kT}$$



When the system is suddenly displaced from equilibrium (e.g. by a pulse of light of frequency ν), the population of HCl in the $v=1$ state will temporarily increase from its equilibrium value $(n_1)_{\text{eq}}$ to $(n_1)_{\text{eq}} + \Delta n_1$. The population of the $v=0$ state will decrease by the corresponding amount.

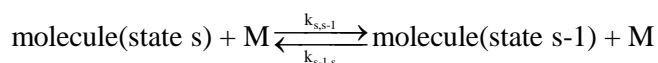
$$n_i = (n_i)_{\text{eq}} + \Delta n_i \quad \text{V} \xrightleftharpoons[k_{01}]{k_{10}} \text{T}$$

$$\frac{dn_1}{dt} = \frac{d}{dt} \left[(n_1)_{\text{eq}} + \Delta n_1 \right] = \frac{d\Delta n_1}{dt} = -k_{10} n_{\text{M}} \left[(n_1)_{\text{eq}} + \Delta n_1 \right] + k_{01} n_{\text{M}} \left[(n_1)_{\text{eq}} - \Delta n_1 \right]$$

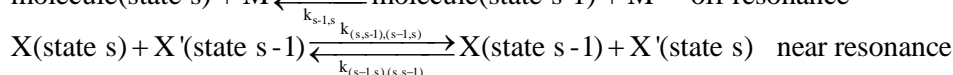
$$\frac{dn_1}{dt} = -(k_{10} + k_{01}) n_{\text{M}} \Delta n_1 = -\Delta n_1 \frac{1}{\tau}$$

Relaxation time: $\tau = \frac{1}{n_{\text{M}}(k_{10} + k_{01})}$

Since the number density n of the inert buffer gas is proportional to its pressure, the result of bulk relaxation studies are often given in terms of the product $p\tau$ (bar s).



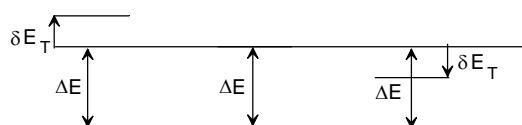
Overview of relaxation times



Process	Relaxation time $p\tau$ (bar s).
$\text{V} \rightleftharpoons \text{V}$	10^{-8} near resonant
$\text{V} \rightleftharpoons \text{R}$	10^{-6}
$\text{V} \rightleftharpoons \text{T}$	10^{-4}
$\text{R} \rightleftharpoons \text{R}$	10^{-10} near resonant
$\text{R} \rightleftharpoons \text{T}$	10^{-8}

We observe that e.g. the off-resonance processes V—T and V—R are much less efficient than the near resonance transitions R—R and V—V. As a rule we can state that a large translational energy defect is an indication of an inefficient transfer process.

Energy gap rule: τ increases with increasing energy gap $|\delta E_{\text{T}}|$.

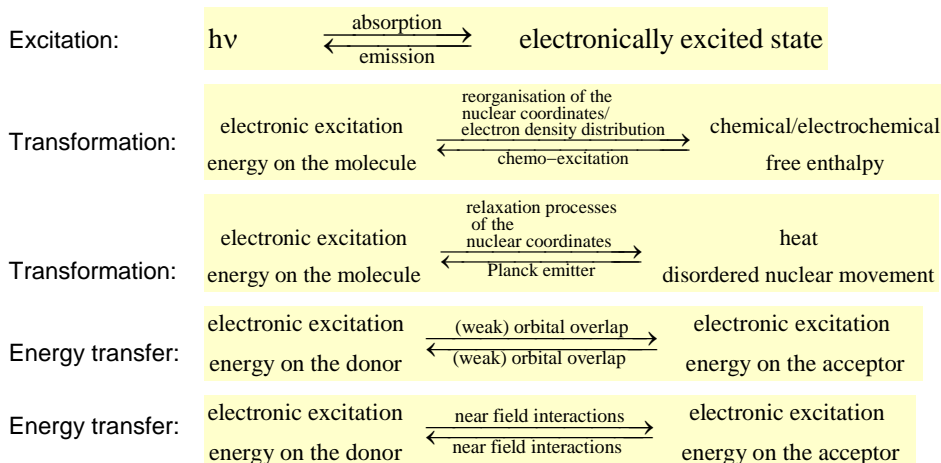


3.2 Transfer of electronic excitation energy

2 fundamentally different kinds of electronic excitation energy transfer:

(a) energy transfer process during which free photons appear.

(b) energy transfer process during which **no** free photons appear.



An energy transfer process during which free photons appear is sometimes also referred to as „trivial“ transfer process.

It is useful to distinguish between cases where the interaction energy between D^* and A of a ($D^* \dots A$) pair is so small, that it can be neglected for most purposes, and cases where this interaction energy is large.

D and A can be individual molecules in the gas phase, in a solution or in a solid matrix. They can, however also be connected by e.g. a hydrocarbon chain which can be regarded as being inert with respect to the electronic states of A and B of interest.

1.) The interaction energy between D and A is small in the electronic ground state ($D \dots A$) and also in the electronically excited states ($D^* \dots A$) and ($D \dots A^*$).

The molecules behave in any state as individuals which, however, can communicate with each other via electromagnetic interactions, e.g. via a dipole-dipole interaction.

2.) The interaction energy between D and A is negligible in the electronic ground state ($D \dots A$). It is important, however, in the electronically excited states ($D^* \dots A$), ($D \dots A^*$), so that a non negligible splitting of the energy states occurs.

The electronically excited state can no longer be described by one of the two configurations ($D^* \dots A$) and ($D \dots A^*$). We speak about excimers (excited dimers) or exciplexes (excited complexes). The electronically excited states are described by means of exciton theory.

3.) The interaction energy between D and A is large.

($D \dots A$) is a complex, e.g. a charge transfer complex.

3.3 Very weak interaction, a semiclassical approach

The interaction of molecules with light is described by means of a semiclassical approach, similar as it has been used by Hans Kuhn; see e.g. Principles of Physical Chemistry, H. Kuhn and H.-D. Försterling, Wiley 2000)

We describe systems in which the interaction energy between D and A is small in the electronic ground state (D.....A) as well as in the electronically excited states (D*.....A) and (D.....A*).

radiant power

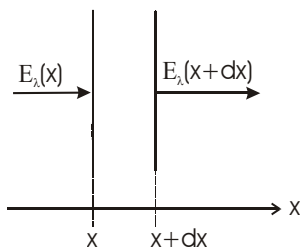
$$\Phi \quad \text{Watt}$$

irradiance (intensity)

$$E = \frac{d\Phi}{dA} \quad \text{Watt/m}^2$$

spectral irradiance (intensity)

$$E_\lambda = \frac{dE}{d\lambda} \quad \text{W/(m}^2\text{nm)} \quad E_\lambda = \frac{dE}{d\lambda} \quad \text{W/(m}^2\text{cm}^{-1})$$



$$dE_\lambda = E_\lambda(x) - E_\lambda(x + dx)$$

c = concentration in mol/L

$$dE_\lambda = -\sigma_\lambda c E_\lambda(x) dx$$

σ_λ = absorption cross section

$$E_\lambda(d) = E_\lambda(0) 10^{-\epsilon_{M,\lambda} c d}$$

$$\epsilon_{M,\lambda} = \sigma_\lambda \log_{10} e$$

$$a(\lambda) = \frac{E_\lambda(0) - E_\lambda(d)}{E_\lambda(0)} = 1 - 10^{-\epsilon_{M,\lambda} c d}$$

$$\epsilon_{M,\lambda} = -\frac{1}{\ln(10) c} \frac{1}{E_\lambda} \frac{dE_\lambda}{dx}$$

Absorption probability between the positions of the source of emission and the absorption = $a(\lambda)$.

dE_λ is the decrease of intensity caused by the absorbing molecules within a volume $dV = A dx$.

A is the cross section of the illuminated volume.

Number of absorbing molecules in this volume: $dN = \frac{N}{V} dV = \frac{n N_A}{V} dV = N_A c A dx$

Each molecule absorbs the energy $d\epsilon$ of the electromagnetic radiation per time interval dt :

$$dE_\lambda = - \left(\frac{d\epsilon_\lambda}{dt} \right) dN = - \left(\frac{d\epsilon_\lambda}{dt} \right) \cdot N_A c dx$$

The intensity of the incoming light can be expressed by the square of the amplitude F_0 of the field strength of the electromagnetic wave:

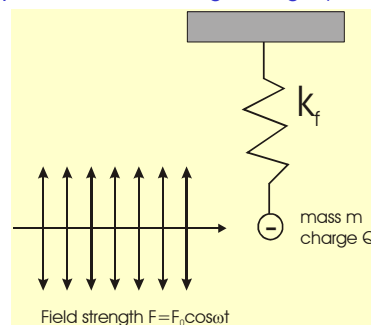
$$E_\lambda = \frac{1}{2} c_0 \epsilon_0 (F_0^\lambda)^2 \quad \text{(Molecules are small with respect to the wavelength of light.)}$$

c_0 = vacuum light velocity

ϵ_0 = vacuum dielectric constant

$$\epsilon_{M,\lambda} = - \frac{1}{\ln(10) c} \frac{1}{E_\lambda} \frac{dE_\lambda}{dx} = \frac{2 N_A}{\ln(10) c_0 \epsilon_0} \frac{1}{(F_0^\lambda)^2} \left(\frac{d\epsilon_\lambda}{dt} \right)$$

To calculate the extinction coefficient $\epsilon_{M,\lambda}$ we describe the molecule as classical oscillator of charge Q and mass m, which vibrates at frequency $\nu_0 = \frac{\Delta E}{h}$.



We first calculate the mean power $\left(\frac{d\varepsilon_{\lambda}}{dt}\right)$ for an isotropic damped classical oscillator of mass m and charge Q .

The deflection ξ of the charge is described by the following differential equation:

$$m \frac{d^2\xi}{dt^2} = -k_f \xi - \rho \frac{d\xi}{dt} + QF_0 \cos \omega t$$

ρ = damping constant
 k_f = force constant

$$\xi = \frac{QF_0}{m} \frac{1}{\sqrt{(\omega_0^2 - \omega^2)^2 + \rho^2 \omega^2 / m^2}} \cos(\omega t + \alpha)$$

$$\frac{d\xi}{dt} = -\frac{QF_0}{m} \frac{\omega}{\sqrt{(\omega_0^2 - \omega^2)^2 + \rho^2 \omega^2 / m^2}} \sin(\omega t + \alpha)$$

$\omega = 2\pi\nu$, ν is the frequency of the electric field of the light.

The energy $d\varepsilon$, absorbed by the oscillator in the time interval dt , is equal to the product of the damping force $\rho d\xi/dt$ and the change of elongation $d\xi$ divided by the time interval dt :

$$\frac{d\varepsilon}{dt} = \rho \left(\frac{d\xi}{dt}\right)^2$$

Averaging $\sin^2(\omega t + \alpha)$ over t :

$$\frac{d\varepsilon}{dt} = \rho \frac{Q^2 F_0^2}{m^2} \frac{\omega^2}{(\omega_0^2 - \omega^2)^2 + \rho^2 \omega^2 / m^2} \sin^2(\omega t + \alpha)$$

$$\left(\frac{d\varepsilon}{dt}\right) = \rho \frac{Q^2 F_0^2}{m^2} \frac{1}{2} \frac{\omega^2}{(\omega_0^2 - \omega^2)^2 + \rho^2 \omega^2 / m^2}$$

$$\varepsilon_{M,\lambda} = \frac{2N_A}{\ln(10)c_0\varepsilon_0} \left(\frac{d\varepsilon_{\lambda}}{dt}\right) \frac{1}{(F_0^2)^2}$$

$$\varepsilon_{M,\lambda} = \frac{2N_A}{\ln(10)c_0\varepsilon_0} \rho \frac{Q^2}{m^2} \frac{1}{2} \frac{\omega^2}{(\omega_0^2 - \omega^2)^2 + \rho^2 \omega^2 / m^2}$$

Hence, we find for the extinction coefficient:

$$\left(\frac{d\varepsilon_{\lambda}}{dt}\right) = \frac{\ln(10)c_0\varepsilon_0}{2N_A} \varepsilon_{M,\lambda} F_0^2$$

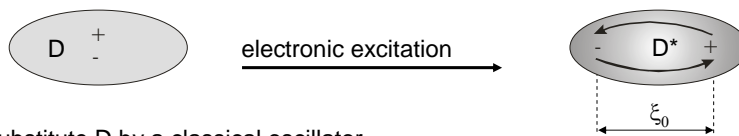
$$g = \frac{\ln(10)c_0\varepsilon_0}{2N_A}$$

$$\left(\frac{d\varepsilon_{\lambda}}{dt}\right) = g \varepsilon_{M,\lambda} F_0^2$$

3.3.1 Dipole-dipole interaction

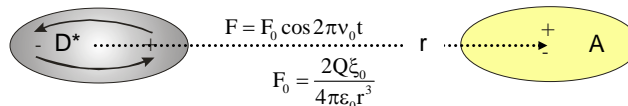
We investigate an electronically excited molecule D^* (energy donor), located at a distance r of a molecule A (acceptor). The electronic transition moments for the emission of D^* and for the absorption of A are assumed to be on the same axis aligned along r .

The size of the molecules is assumed to be small with respect to the wavelength of light.



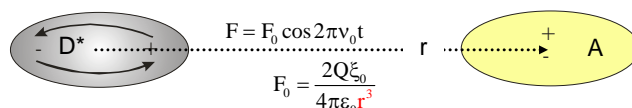
We substitute D by a classical oscillator

of frequency ν_0 of mass m of charge Q of amplitude ξ_0 and of energy $E = \frac{1}{2} k_f \xi_0^2$



The electric field which acts on the acceptor A is equal to the Coulomb field F of the oscillators (donors) D^* .

r is assumed to be much smaller than the wavelength $\lambda = c_0/\nu_0$ of light, but large with respect to the size of the molecules A and D (point-dipole approximation).



The mean power $\left(\frac{d\varepsilon}{dt}\right)$ absorbed by the acceptor A, is equal to the molar extinction coefficient $\varepsilon_{A,\bar{\lambda}}$, at energy $\bar{\lambda}$, and it is proportional to the square of the field strength F_0 of the donors at the position of the acceptors:

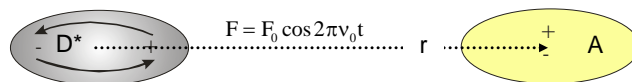
$$\left(\frac{d\varepsilon}{dt}\right)_{\text{Energy transfer}} = g\varepsilon_{A,\bar{\lambda}}F_0^2 \quad \text{where} \quad g = 3 \frac{\ln(10)c_0\varepsilon_0}{2N_A} \quad F_0 = \frac{2Q\xi_0}{4\pi\varepsilon_0 r^3}$$

The factor 3 takes into account that we have assumed the transition moments of the acceptors to be parallel to the field F . (Published decadic molar absorption coefficients usually refer to a statistic isotropic distribution in space.)

$$\left(\frac{d\varepsilon}{dt}\right)_{\text{energy transfer}} = g\varepsilon_{A,\bar{\lambda}} \left(\frac{2Q\xi_0}{4\pi\varepsilon_0 r^3}\right)^2 = g\varepsilon_{A,\bar{\lambda}} \frac{4Q^2}{16\pi^2\varepsilon_0^2} \frac{\xi_0^2}{r^6}$$

The mean electromagnetic power emitted by the oscillator D^* corresponds to that of a "Hertz dipole" and can be expressed as follows:

$$\left(\frac{d\varepsilon}{dt}\right)_{\text{fluorescence of } D^*} = \frac{1}{4\pi\varepsilon_0} \frac{\omega_0^4 Q^2}{3c_0^3} \xi_0^2 = \frac{4Q^2\pi^3\nu_0^4}{3\varepsilon_0 c_0^3} \xi_0^2$$



$$\left(\frac{d\varepsilon}{dt}\right)_{\text{fluorescence of } D^*} = \frac{4Q^2\pi^3\nu_0^4}{3\varepsilon_0 c_0^3} \xi_0^2$$

$$\left(\frac{d\varepsilon}{dt}\right)_{\text{Energy transfer}} = g\varepsilon_{A,\bar{\lambda}} \frac{4Q^2}{16\pi^2\varepsilon_0^2} \frac{\xi_0^2}{r^6}$$

At a specific $D^* \dots A$ distance $r = R_0$, the portion of light which D^* emits as fluorescence is equal to the portion that jumps via energy transfer to A. Hence, we can write:

$$\left(\frac{d\varepsilon}{dt}\right)_{\text{fluorescence of } D^*} = \left(\frac{d\varepsilon}{dt}\right)_{\text{energy transfer}}$$

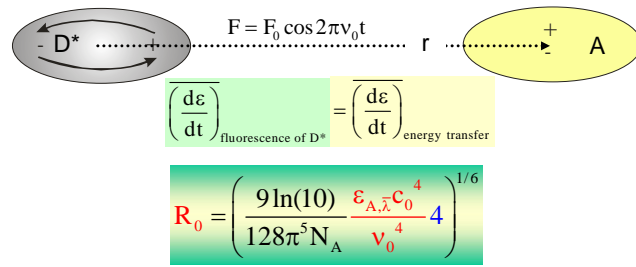
$$\frac{4Q^2\pi^3\nu_0^4}{3\varepsilon_0 c_0^3} \xi_0^2 = g\varepsilon_{A,\bar{\lambda}} \frac{4Q^2}{16\pi^2\varepsilon_0^2} \frac{\xi_0^2}{R_0^6}$$

$$g = 3 \frac{\ln(10)c_0\varepsilon_0}{2N_A}$$

Solving for R_0 :

$$R_0^6 = \frac{3g\varepsilon_{A,\bar{\lambda}}c_0^3}{16\pi^5\varepsilon_0\nu_0^4} \quad \text{or} \quad R_0^6 = \left(\frac{9\varepsilon_{A,\bar{\lambda}}\ln(10)c_0^4}{128\pi^5N_A\nu_0^4}4\right)$$

These equations hold for donors which – in absence of acceptors – do fluoresce with a quantum yield $\phi=1$, at a refractive index of the environment $n=1$, and for parallel arrangement of the transition moments of D^* and A.



The fluorescence quantum yield of D*, ϕ_{D^*} , is in general smaller than 1, the refractive index n of the environment is larger than 1 and the orientation is different.

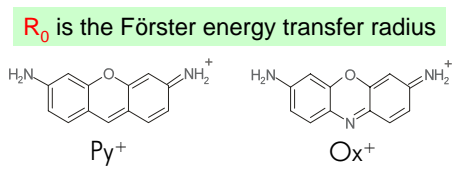
For the general case the factor 4 must be substituted by: $\frac{\phi_{D^*} \kappa^2}{n^4}$

In general molecules do not show line spectra because of many line broadening interactions. Hence, the resonance condition is fulfilled in the whole range of spectral overlap between donor emission and acceptor absorption.

Therefore, the resonance factor $\frac{\epsilon_{A,\lambda} c_0^4}{\nu_0^4}$ must be substituted by the integral J over the range of spectral overlap.

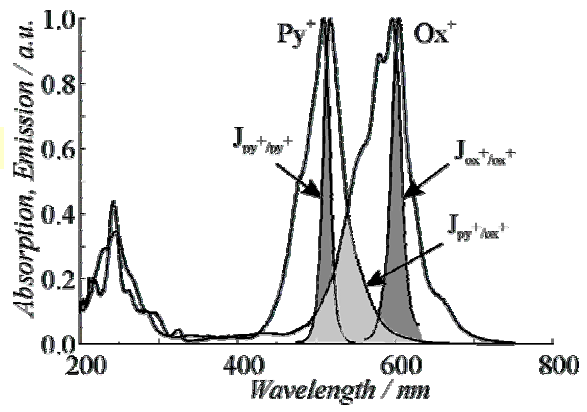
Expressing the spectral overlap in cm^3M^{-1} we get: $R_0 = \left(\frac{9000 \ln(10)}{128 \pi^5 N_A} J \frac{\phi_{D^*} \kappa^2}{n^4} \right)^{1/6}$

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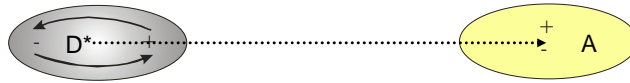


Examples for dyes in zeolite L:
spectral overlap J
and Förster Radius ($n = 1.4$)

- $J_{py,py} = 1.1 \times 10^{-13} \text{ cm}^3\text{M}^{-1}$
- $R_0(\kappa^2=2/3) = 5.1 \text{ nm}$
- $R_0(\kappa^2=4) = 6.8 \text{ nm}$
- $J_{ox,ox} = 4.4 \dots \times 10^{-13} \text{ cm}^3\text{M}^{-1}$
- $R_0(\kappa^2=2/3) = 6.4 \text{ nm}$
- $R_0(\kappa^2=4) = 8.6 \text{ nm}$
- $J_{py,ox} = 2.3 \times 10^{-13} \text{ cm}^3\text{M}^{-1}$
- $R_0(\kappa^2=2/3) = 5.7 \text{ nm}$
- $R_0(\kappa^2=4) = 7.7 \text{ nm}$



3.3.2 Summary



$$\left(\frac{d\varepsilon}{dt}\right)_{\text{fluorescence of } D^*} = \frac{4Q^2\pi^3\nu_0^4}{3\varepsilon_0c_0^3}\xi_0^2$$

$$\left(\frac{d\varepsilon}{dt}\right)_{\text{energy transfer}} = g\varepsilon_{A,\lambda} \frac{4Q^2}{16\pi^2\varepsilon_0^2} \frac{\xi_0^2}{r^6}$$

$$R_0^6 = \frac{g}{\varepsilon_0} \frac{3\varepsilon_{A,\lambda}c_0^3}{16\pi^3\nu_0^4}$$

The probability P for energy transfer is:

$$P = \frac{\left(\frac{d\varepsilon}{dt}\right)_{\text{energy transfer}}}{\left(\frac{d\varepsilon}{dt}\right)_{\text{fluorescence}} + \left(\frac{d\varepsilon}{dt}\right)_{\text{energy transfer}}} \quad \text{canceling} \quad \left(\frac{d\varepsilon}{dt}\right)_{\text{energy transfer}}$$

$$C = \frac{\left(\frac{d\varepsilon}{dt}\right)_{\text{fluorescence}}}{\left(\frac{d\varepsilon}{dt}\right)_{\text{energy transfer}}}$$

$$P = \frac{1}{C+1}$$

$$C = \frac{4Q^2\pi^3\nu_0^4}{3\varepsilon_0c_0^3}\xi_0^2 \frac{16\pi^2\varepsilon_0^2}{g\varepsilon_{A,\lambda}4Q^2\xi_0^2} r^6 = \frac{\varepsilon_0}{g} \frac{16\pi^3\nu_0^4}{3\varepsilon_{A,\lambda}c_0^3} r^6$$

$$\frac{\varepsilon_0}{g} \frac{16\pi^3\nu_0^4}{3\varepsilon_{A,\lambda}c_0^3} = \frac{1}{R_0^6}$$

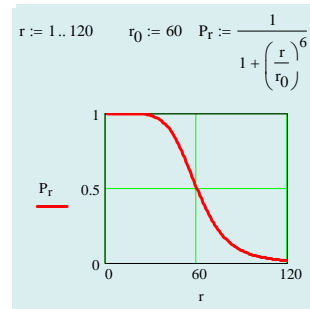
Hence:

$$C = \left(\frac{r}{R_0}\right)^6$$

$$P = \frac{1}{1 + (r/R_0)^6}$$

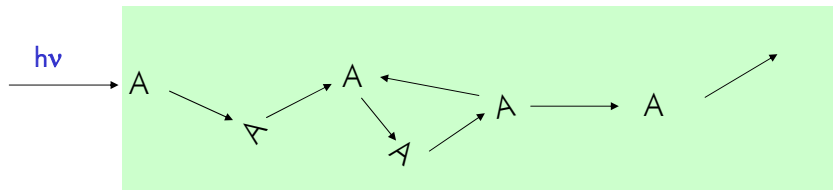
R_0 is equal to the donor- acceptor distance at which the probability for energy transfer is equal to 0.5.

A typical good value for R_0 is in the order of 6 nm.



3.3.3 Energy migration

We consider a set of noninteracting molecules A. If one of them is excited to become A^* , energy transfer to a neighboring A can take place. This process is repeated until the excitation energy is captured by a trap or lost by e.g. luminescence or radiationless decay.



Energy transfer between the same kind of molecules is called **energy migration**.

An important quality of this energy migration is, that it can not be observed by just measuring the luminescence decay of A^* , as we shall discuss now..

A molecule A is excited electronically at time $t = 0$ by absorption of a photon.

$\rho_A(t)$ is the probability that A is in the excited state at time t .

At $t = 0$ we have:

$$\rho_A(0) = 1$$

Decay of the excitation probability:

$$\frac{d\rho_A}{dt} = -\frac{1}{\tau}\rho_A$$

Solving this equation gives:

$$\rho_A(t) = \rho_A(0)e^{-\frac{t}{\tau}}$$

τ is the decay time (mean lifetime).

τ^0 is the natural lifetime, which corresponds to the lifetime in the absence of other relaxation processes.

If all decay processes which result in deactivation of A^* to the ground state are of first order with the decay constants k_i , we can write:

$$\tau = \frac{1}{\sum_i k_i} \quad \text{and} \quad \tau^0 = \frac{1}{k^0}$$

The luminescence yield ϕ_L can be expressed as follows:
$$\phi_L = \frac{1}{\tau^0} \int_0^\infty \rho_A(t) dt = \frac{\tau}{\tau^0}$$

We number the alike molecules A with the indices k and j .

If there is a possibility for a radiationless transition $A_k^* \rightarrow A_j$ then the decrease of A_k^* is proportional to the probability ρ_{A_k} that A_k is in the excited state. There is an equal increase of the excitation probability ρ_{A_j} of A_j .

Considering these processes between all molecules, we can write:

$$\frac{d\rho_{A_k}}{dt} = \sum_j \bar{F}_{kj}(\rho_{A_j} - \rho_{A_k}) - \frac{1}{\tau}\rho_{A_k} \quad \text{Since we are studying alike molecules, we have:} \quad \bar{F}_{kj} = \bar{F}_{jk}$$

Emission and energy transfer take place in parallel (at the same time). This formulation is different from the mechanism of self-absorption and reemission which are consecutive processes.

This means that the decay of excitation probability $\frac{1}{\tau}\rho_{A_k}(t)$ is accompanied by a balancing - out of the excitation probability among the individual molecules.

Considering not only the molecule A_k but the behavior of an ensemble we must sum over all cases:

$$\sum_k \frac{d\rho_{A_k}}{dt} = \sum_k \left(\sum_j \bar{F}_{kj}(\rho_{A_j} - \rho_{A_k}) - \frac{1}{\tau}\rho_{A_k} \right) = -\sum_k \frac{1}{\tau}\rho_{A_k}$$

The double sum cancels: $\sum_k \left(\sum_j \bar{F}_{kj}(\rho_{A_j} - \rho_{A_k}) \right) = 0$ because \bar{F}_{ki} is equal to \bar{F}_{jk} .

From this, we find:

$$\sum_k \frac{d\rho_{A_k}}{dt} = -\frac{1}{\tau} \sum_k \rho_{A_k}$$

Inserting $\rho_{A_k}(t) = \rho_{A_k}(0)e^{-t/\tau}$ leads to the following expression for the luminescence

intensity which is observed after excitation of an ensemble of molecules A:

$$\sum_k \frac{d\rho_{A_k}}{dt} = -\frac{1}{\tau} \sum_k \rho_{A_k}(0)e^{-t/\tau} = -\frac{1}{\tau} e^{-t/\tau} \sum_k \rho_{A_k}(0)$$

Solving this differential equation we find that the sum of the excitation probabilities for the individual molecules is:

$$\sum_k \rho_{A_k}(t) = e^{-t/\tau} \sum_k \rho_{A_k}(0)$$

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

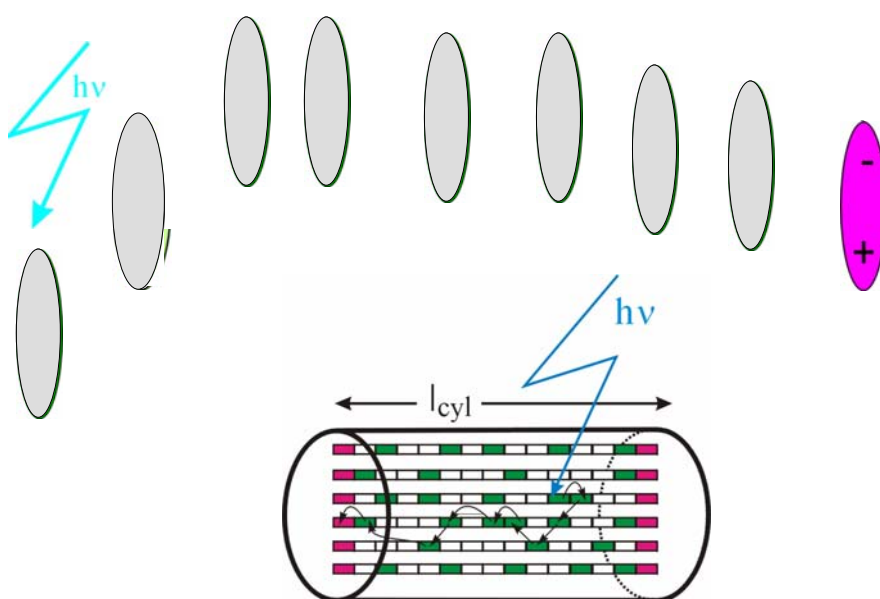
This means that on average the decay of luminescence of the ensemble is not affected. Hence, energy migration is not observed in a simple luminescence decay measurement.

This rises the question: [How can migration of excitation energy be observed?](#)

There are several possibilities. One of them is based on the fact, that under many conditions, excitation energy migration causes a change of the polarization of the emitted light. This can be observed in stationary and in time resolved luminescence experiments.

Another possibility is to add luminescent traps at well defined positions in space.

Visualization of migration of electronic excitation energy

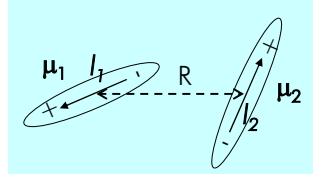


3.3.4 Comment on the dipole-dipole interaction and on the orientation factor κ

The interaction energy V_{Di-Di} between two dipoles $\mu_1=l_1q$ and $\mu_2=l_2q$ can be expressed as follows (μ_1 and μ_2 are vectors):

$$V_{Di-Di} = \frac{1}{4\pi\epsilon_0} \frac{\mu_1 \cdot \mu_2 - 3(\mathbf{n} \cdot \mu_1)(\mathbf{n} \cdot \mu_2)}{R^3}$$

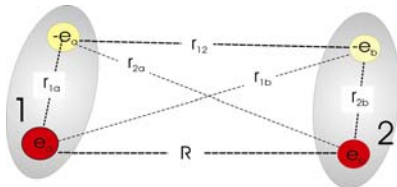
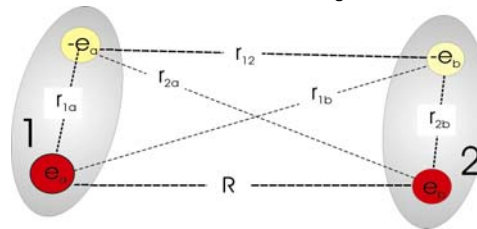
$$4\pi\epsilon_0 = 1.11265 \cdot 10^{-10} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$$



\mathbf{n} is a unit vector in direction of \mathbf{R} . The dipole-dipole interaction is often the first term in a Taylor's series expansion of the electrostatic interaction between two neutral molecules.

It is often desirable to express the interaction energy V_{Di-Di} between two dipoles in polar coordinates. It is convenient to introduce the factor κ in order to describe the angle dependence $V_{Di-Di} = V_{Di-Di}(R, \theta_1, \theta_2, \phi_{12})$.

To do this, it is useful to investigate the following situation: We assume two fixed positive charges e_a and e_b at distance R , each of them compensated by a negative charge $-e_a$ and $-e_b$.



Then the potential energy is:

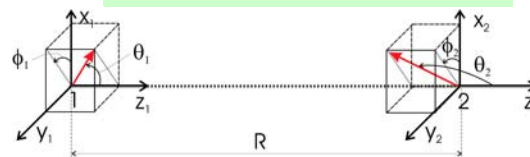
$$V = \left\{ e_a e_b \left(\frac{1}{R} + \frac{1}{r_{12}} - \frac{1}{r_{1b}} - \frac{1}{r_{2a}} \right) - \frac{e_a^2}{r_{1a}} - \frac{e_b^2}{r_{2b}} \right\} \frac{1}{4\pi\epsilon_0}$$

The first four terms in this expression represent the mutual interaction of two dipoles and it is convenient to derive an approximate expression for this interaction by assuming that R is constant (hence, R changes only slowly with respect to the movements of the electrons) and that the distances between e_a and $-e_a$, and also between e_b and $-e_b$, are very short with respect to the distance R between the objects 1 and 2 ($R \gg r_{1a}$ and $R \gg r_{2b}$). It also means, that the term indicated in blue color is of constant value and does not depend on R and, hence, also not on r_{12} , r_{2a} and r_{1b} . **This is the condition for a dipole-dipole interaction.**

From this follows, that the interaction energy V_{dd} between two dipoles can be expressed as:

$$V_{dd} = \frac{e_a e_b}{4\pi\epsilon_0} \left(\frac{1}{R} + \frac{1}{r_{12}} - \frac{1}{r_{1b}} - \frac{1}{r_{2a}} \right)$$

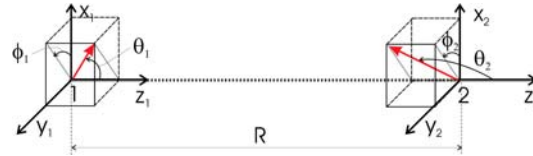
This expression can be expanded in a series along the indicated Cartesian coordinates:



$$V_{dd} = \frac{e_a e_b}{4\pi\epsilon_0} \frac{1}{R^3} (x_1 x_2 + y_1 y_2 - 2z_1 z_2) + \text{Terms in } R^{-4} + \dots$$

Neglecting higher terms, we get:

$$V_{dd} = \frac{e_a e_b}{4\pi\epsilon_0} \frac{1}{R^3} (x_1 x_2 + y_1 y_2 - 2z_1 z_2)$$



This equation is equivalent to:
$$V_{Di-Di} = \frac{1}{4\pi\epsilon_0} \frac{\mu_1 \mu_2 - 3(n\mu_1)(n\mu_2)}{R^3}$$

We now express the dependence of V_{dd} on the coordinates $(R, \theta_1, \theta_2, \phi_{12})$:

$$\begin{aligned} z_1 &= l_1 \cos(\theta_1) & z_2 &= l_2 \cos(\theta_2) \\ x_1 &= l_1 \sin(\theta_1) \cos(\phi_1) & x_2 &= l_2 \sin(\theta_2) \cos(\phi_2) \\ y_1 &= l_1 \sin(\theta_1) \sin(\phi_1) & y_2 &= l_2 \sin(\theta_2) \sin(\phi_2) \end{aligned}$$

$$x_1 x_2 + y_1 y_2 - 2z_1 z_2 = l_1 l_2 \{ \sin(\theta_1) \sin(\theta_2) [\cos(\phi_1) \cos(\phi_2) + \sin(\phi_1) \sin(\phi_2)] - 2 \cos(\theta_1) \cos(\theta_2) \}$$

$$\cos(\phi_1 - \phi_2)$$

$$\cos\phi_{12} = \cos(\phi_1 - \phi_2)$$

$$V_{dd} = \frac{e_a e_b}{4\pi\epsilon_0} \frac{l_1 l_2}{R^3} (\sin \theta_1 \sin \theta_2 \cos \phi_{12} - 2 \cos \theta_1 \cos \theta_2) = \frac{e_a e_b}{4\pi\epsilon_0} \frac{l_1 l_2}{R^3} \kappa_{12}$$



$$V_{dd} = \frac{e_a e_b}{4\pi\epsilon_0} \frac{l_1 l_2}{R^3} \kappa_{12}$$

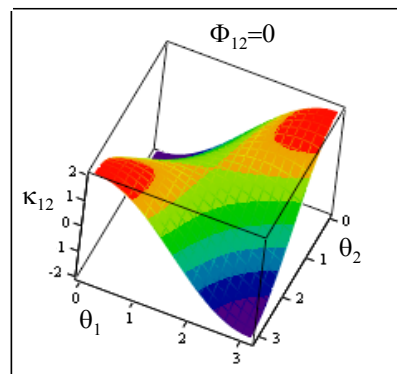
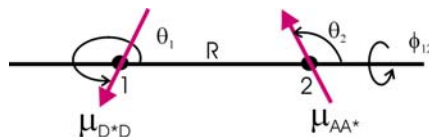
$$\kappa_{12} = (\sin \theta_1 \sin \theta_2 \cos \phi_{12} - 2 \cos \theta_1 \cos \theta_2)$$



Hence, κ_{12} is an orientation factor which describes the dependence of the dipole-dipole interaction energy $V_{dd} = V_{dd}(R, \theta_1, \theta_2, \phi_{12})$ on the relative orientation of the two dipoles with respect to each other.

It is often more convenient to set the origin of the coordinate system in the middle of the dipoles and to use the following equivalent picture.

Some values for $\kappa(\theta_1, \theta_2, \phi_{12} = 0)$:



3.4 Förster Theory

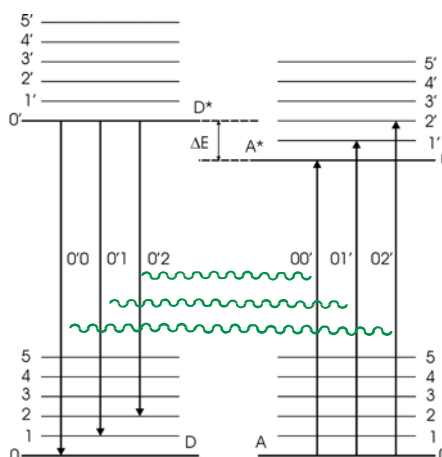
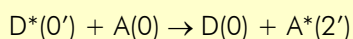
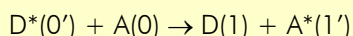
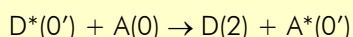


In order to occur, excitation energy transfer between an electronically excited molecule D^* and an acceptor A requires some interaction between the excited and the unexcited molecules.

Energy transfer can take place if the acceptor molecule possesses transitions which are isoenergetic with transitions of the excited donor molecule.

Transitions of this kind are resonance transitions (RET=resonance energy transfer).

Example: We assume, that the energy separations between two vibrational states $v, v+1$ and $v', v'+1$ of the donor and of the acceptor are the same and that ΔE is twice this separation. This is shown in the figure where also the meaning of the numbers $0, 1, \dots, 0', 1', \dots$ is explained. In this case, the following RET processes can take place:



Transfer of electronic excitation energy can result from different interaction mechanisms.

Considering that only two electrons are involved in a transition, one on D and one on A , the properly antisymmetrized electronic wave functions for the initial excited state Ψ_i (D excited but not A) and the final excited state Ψ_f (A excited but not D) are:

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

The numbers 1 and 2 refer to the two electrons involved.

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

The interaction term between the initial and the final state can be expressed as:

$$\beta = \langle \Psi_i | H' | \Psi_f \rangle \quad H' \text{ is the perturbation part of the Hamiltonian: } \hat{H} = \hat{H}_D + \hat{H}_A + H'$$

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

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

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

Hence, β can be written as a sum of two terms:

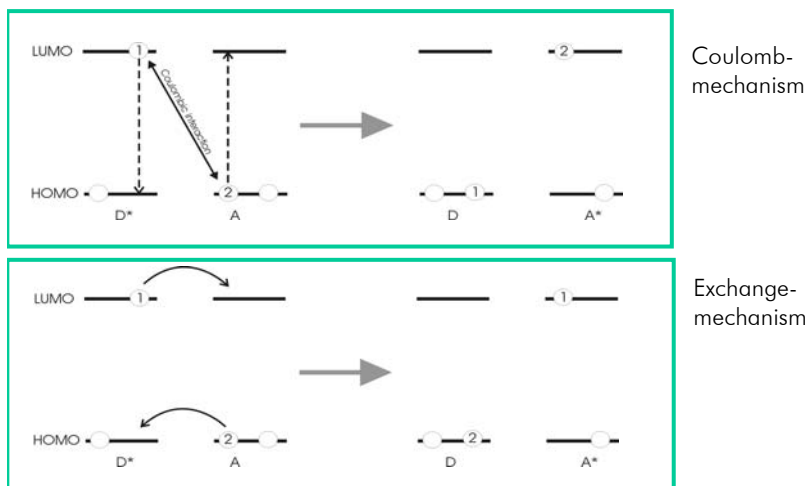
$$\beta = \beta_C - \beta_{ex}$$



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

β_{ex} is the exchange term. It describes a situation which can be understood as an exchange of two electrons on D and A.

The Coulomb and the exchange interactions lead to two distinctly different energy transfer mechanisms which we can draw as follows.



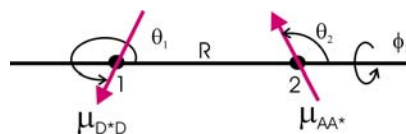
The **Coulomb term** can be expanded into a sum of terms (multipole-multipole series).



The first dominant term is the dipole-dipole interaction term between the transition dipole moments μ_D and μ_A of D and A (for the transitions $D^* \rightarrow D$ and $A \rightarrow A^*$) in an environment of refractive index n. Therefore the perturbation H'_C can be expressed as:

$$H'_C = \frac{e^2}{4\pi\epsilon_0 n^2} \frac{1}{R_{DA}^3} I_D I_A \kappa_{12}$$

$$\kappa_{12} = (\sin \theta_1 \sin \theta_2 \cos \phi_{12} - 2 \cos \theta_1 \cos \theta_2)$$

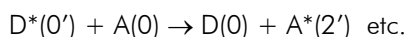
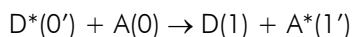
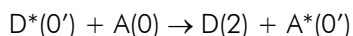


The exchange term represents the electrostatic interaction between the charged clouds. The transfer occurs via overlap of the electron clouds and requires physical contact between D and A. This means that the wave functions of D and A must overlap. This interaction is short range.

For two electrons separated by a distance r_{12} in the pair D...A, the perturbation H'_{ex} is: $H'_{ex} = \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{12}}$

The energy transfer rate constant k_{EnT} for electronic excitation energy of the type:

(We abbreviate energy transfer with the EnT in order to distinguish from electron transfer, which is often abbreviated as ET.)

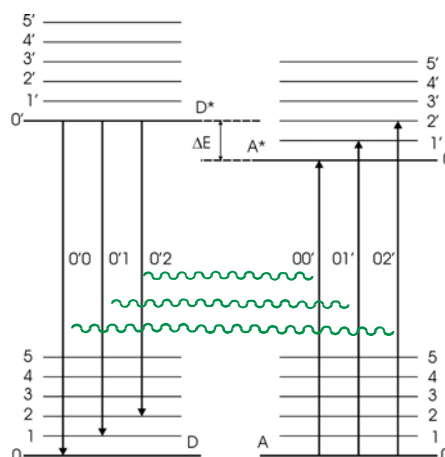


can be expressed by means of Fermi's golden rule:

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

where ρ is a measure of the density of the interacting initial $D^* \dots A$ and final $D \dots A^*$ states.

It is related to the overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor.



3.4.1 Weak interaction between donor and acceptor molecules

In order to occur, excitation energy transfer requires some interaction between excited and unexcited molecules.

If this interaction is sufficiently strong, the electronic spectra of a mixture of donors and acceptors will be different from electronic spectra of e.g. sufficiently diluted solutions of donors and acceptors.

If this interaction is weak, e.g. in the order of 10 cm^{-1} or less, the electronic spectrum of a mixture of donors and acceptors will be a superposition of the spectra of sufficiently diluted solutions of the donors and of the acceptors separately.

While the medium and strong interaction cases are best discussed within the exciton theory and within the molecular orbital theory, respectively, the weak interaction case can be best understood by following the arguments given by Th. Förster in his original paper which appeared in *Annalen der Physik*, 6. Folge, Band 2 (1948) p. 55-75. This paper is, however, not easy to read and I have therefore tried to present the arguments in a more comprehensive way.

In order to calculate the rate constant k_{EnT} , which describes how fast an excitation energy transfer occurs between an electronically excited donor D^* and an acceptor A , we must calculate the product $(\beta_{D^*A})^2 \rho_{D^*A}$, according to Fermi's golden rule.

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

We now consider only situations for which the exchange term can be neglected. This means that we concentrate on cases for which only the Coulomb term is of relevance.

The wave functions for the initial (i) and the final (f) states and the perturbation Hamiltonian H' can therefore be expressed as:

$$\Psi_i = \Psi_{D^*} \Psi_A$$

$$\Psi_f = \Psi_D \Psi_{A^*}$$

$$H'_C = \frac{e^2}{4\pi\epsilon_0 n^2} \frac{1}{R_{DA}^3} l_D l_A \kappa_{12}$$



l_D and l_A are the coordinates of the electrons belonging to the D and A, respectively.

Inserting this in $\beta_C = \langle \Psi_i | H' | \Psi_f \rangle$ we can write:

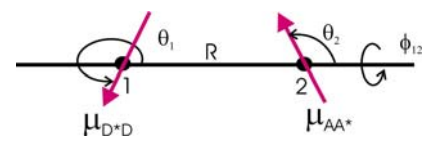
$$\beta_{D^*A} = \frac{1}{4\pi\epsilon_0 n^2} \frac{1}{R_{DA}^3} \langle \Psi_{D^*} | e l_D | \Psi_D \rangle \langle \Psi_A | e l_A | \Psi_{A^*} \rangle$$

The two matrix elements are equal to the electronic transition moments μ_{D^*D} and μ_{AA^*} :

$$\mu_{D^*D} = \langle \Psi_{D^*} | e l_D | \Psi_D \rangle$$

$$\mu_{AA^*} = \langle \Psi_A | e l_A | \Psi_{A^*} \rangle$$

$$\beta_{D^*A} = \frac{1}{4\pi\epsilon_0 n^2} \frac{1}{R_{DA}^3} |\mu_{D^*D}| |\mu_{AA^*}| \kappa_{12}$$



Using the definition of κ_{12} , we have introduced before, and writing: $\kappa'_{D^*A} = \frac{\kappa_{D^*A}}{4\pi\epsilon_0 n^2}$ we obtain:

$$\beta_{D^*A} = \frac{\kappa'_{D^*A}}{R_{DA}^3} |\mu_{D^*D}| |\mu_{AA^*}|$$

This means that the rate constant of e.g. a transition $D^*(0') + A(0) \rightarrow D(0) + A^*(2')$, which we can also express as $D^*(0') A(0) \rightarrow D(0) A^*(2')$, is:

$$k_{EnT}(0',0;0,2') = \frac{2\pi}{\hbar} \beta_{D^*A}^2 \rho(0',0;0,2')$$

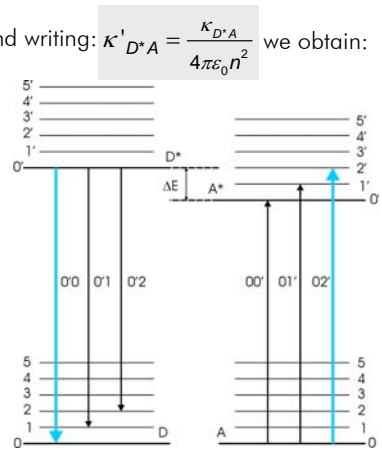
This formula describes the energy transfer rate constant between two selected levels which are in resonance.

In order to find all transitions which take place between D^* and A, $D^*A \rightarrow D A^*$, we must sum over all states which are in resonance.

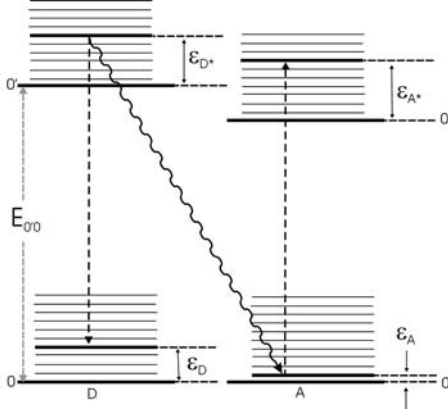
We are interested in condensed phase. Hence, rotational levels play no role.

Denoting the states of the donor as (d',δ) and those of the acceptor with (α,a') the transfer rate constant can be expressed as follows:

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



Since energy transfer can be very fast, it is not sufficient to consider only the lowest vibrational state of the donor.



We must sum over **all** iso-energetic situations. This means that we must sum over all donor and acceptor states which are in resonance.

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

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

Hence, the initial (i) and the final (f) levels of $D^* \dots A$ and $D \dots A^*$ are not well defined.

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

We introduce the normalized functions $S_D(E_{D^*})$ and $S_A(E_A)$. $S_D(E_{D^*})$ expresses the probability that (isolated) D^* emits photons of energy E_{D^*} . $S_A(E_A)$ is the 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.

The resonance condition can be expressed as follows:

$$E_{D^*} = E_{0'0}^D + \epsilon_{D^*} - \epsilon_D \quad E_{res} = \int E_{D^*} \delta(E_{D^*} - E_A) dE_{D^*}$$

$$E_A = E_{0'0}^A + \epsilon_{A^*} - \epsilon_A$$

The rate constant for the EnT $D^* + A \rightarrow D + A^*$ can be expressed as integral over the resonant energy range:

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

Inserting β_{D^*A} , we get:

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

Evaluation of this integral on a purely theoretical basis is often not possible and, fortunately, also not necessary. We now show that the transition moments times the distribution functions can be substituted by the lifetime and the shape of the luminescence spectrum of the donor D^* and by the absorption spectrum of the acceptor A.

Instead of integrating over the energy E we integrate over the frequency ν . Since $E = h\nu$, dE must be substituted by $h d\nu$. We also substitute E_{D^*} and E_A by ν_{D^*} and ν_A , respectively:

$$k_{EnT} = \frac{1}{\hbar^2} \left(\frac{\kappa'_{D^*A}}{R_{DA}^3} \right)^2 \iint_{\nu_{D^*}, \nu_A} |\mu_{D^*D}|^2 S_D(\nu_{D^*}) |\mu_{AA^*}|^2 S_A(\nu_A) \delta(\nu_{D^*} - \nu_A) d\nu_{D^*} d\nu_A$$



Connection between electronic transition moments and the Einstein coefficients:



$$B_{D^*D} = \frac{2\pi}{3\hbar^2} \frac{1}{4\pi\epsilon_0} \frac{1}{n^2} (\mu_{D^*D})^2$$

$$A_{D^*D} = 8\pi \frac{h\nu_{D^*}^3}{c_0^3} n^3 B_{D^*D}$$

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

$$A_{D^*D} = \frac{\nu_{D^*}^3}{c_0^3} \frac{32\pi^3}{3\hbar} \frac{n}{4\pi\epsilon_0} (\mu_{D^*D})^2 \quad A_{D^*D} \frac{c_0^3}{\nu_{D^*}^3} \frac{3\hbar}{32\pi^3} \frac{4\pi\epsilon_0}{n} = (\mu_{D^*D})^2$$

Since $A_{D^*D} = \frac{1}{\tau_{D^*}^0}$ we obtain:

$$(\mu_{D^*D})^2 = \frac{c_0^3}{\nu_{D^*}^3} \frac{3\hbar}{32\pi^3} \frac{4\pi\epsilon_0}{n} \frac{1}{\tau_{D^*}^0}$$

$$B_{AA^*} = \frac{2\pi}{3\hbar^2} \frac{1}{4\pi\epsilon_0} \frac{1}{n^2} (\mu_{AA^*})^2$$

$$(\mu_{AA^*})^2 = \frac{3\hbar^2}{2\pi} 4\pi\epsilon_0 n^2 B_{AA^*}$$

Connection between electronic transition moments and the Einstein coefficients:



$$B_{AA^*} = \frac{2\pi}{3\hbar^2} \frac{1}{4\pi\epsilon_0} \frac{1}{n^2} (\mu_{AA^*})^2$$

$$(\mu_{AA^*})^2 = \frac{3\hbar^2}{2\pi} 4\pi\epsilon_0 n^2 B_{AA^*}$$

We now relate the Einstein coefficient weighted with the shape of the absorption spectrum to the molar extinction coefficient $\epsilon_A(\nu)$ (see e.g. S.J. Strickler, R.A. Berg, J. Chem. Phys. 37 (1962) 814), Förster, Fluoreszenz Organischer Verbindungen, Vandenbock&Ruprecht Göttingen, 1951)

$$B_{AA^*} S_A(\nu_A) = \frac{10^3 \ln(10) c_0}{h N_L} \frac{\epsilon_A(\nu_A)}{n \nu_A}$$

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

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

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

From this we find: $(\mu_{AA^*})^2 S_A(\nu_A) = \frac{3\hbar}{4\pi^2} 4\pi\epsilon_0 n c_0 \frac{10^3 \ln(10)}{N_L} \frac{\epsilon_A(\nu_A)}{\nu_A}$

Please note that the factor 10^3 depends on the dimension used for $\epsilon_A(\nu)$.

$$k_{EnT} = \frac{1}{\hbar^2} \left(\frac{\kappa'_{D^*A}}{R_{DA}^3} \right)^2 \iint_{\nu_{D^*}, \nu_A} |\mu_{D^*D}|^2 S_D(\nu_{D^*}) |\mu_{AA^*}|^2 S_A(\nu_A) \delta(\nu_{D^*} - \nu_A) d\nu_{D^*} d\nu_A$$



$$(\mu_{D^*D})^2 = \frac{c_0^3}{\nu_{D^*}^3} \frac{3\hbar}{32\pi^3} \frac{4\pi\epsilon_0}{n} \frac{1}{\tau_{D^*}^0}$$

$$(\mu_{AA^*})^2 S_A(\nu_A) = \frac{3\hbar}{4\pi^2} 4\pi\epsilon_0 n c_0 \frac{10^3 \ln(10)}{N_L} \frac{\epsilon_A(\nu_A)}{\nu_A}$$

$$Q = \frac{1}{\hbar^2} \left(\frac{\kappa'_{D^*A}}{R_{DA}^3} \right)^2 |\mu_{D^*D}|^2 S_D(\nu_{D^*}) |\mu_{AA^*}|^2 S_A(\nu_A)$$

$$Q = \frac{1}{\hbar^2} \left(\frac{1}{R_{DA}^3} \frac{\kappa_{D^*A}}{4\pi\epsilon_0 n^2} \right)^2 \frac{c_0^3}{\nu_{D^*}^3} \frac{3\hbar}{32\pi^3} \frac{4\pi\epsilon_0}{n} \frac{1}{\tau_{D^*}^0} S_D(\nu_{D^*}) \frac{3\hbar}{4\pi^2} 4\pi\epsilon_0 n c_0 \frac{10^3 \ln(10)}{N_L} \frac{\epsilon_A(\nu_A)}{\nu_A}$$

$$Q = \frac{10^3 \ln(10)}{N_L} \frac{9c_0^4}{128\pi^5} \frac{1}{\tau_{D^*}^0} \frac{\kappa_{D^*A}^2}{n^4 R_{DA}^6} S_D(\nu_{D^*}) \frac{\epsilon_A(\nu_A)}{\nu_{D^*}^3 \nu_A} \quad fc = \frac{9000 \ln(10)}{128\pi^5 N_L}$$

Inserting this result and keeping in mind that we can set:

$$\int_{\nu_{D^*}} \nu_{D^*} \delta(\nu_{D^*} - \nu_A) d\nu_{D^*} = \nu_A$$

$$k_{EnT} = \frac{9000 \ln(10)}{128\pi^5 N_L} c_0^4 \frac{\kappa_{D^*A}^2}{n^4 R_{DA}^6} \frac{1}{\tau_{D^*}^0} \int_{\nu} S_D(\nu) \frac{\epsilon_A(\nu)}{\nu^4} d\nu \quad \nu = \bar{\nu} c_0$$



The dimension of $S(\nu)$ is equal to that of ν^{-1} . Hence, expressing the spectral overlap integral in wave numbers, and using $\tau_{D^*} = \phi_{D^*} \tau_{D^*}^0$, we get:

$$k_{EnT} = \frac{9000 \ln(10)}{128\pi^5 N_L} \frac{\kappa_{D^*A}^2}{n^4 R_{DA}^6} \frac{\phi_{D^*}}{\tau_{D^*}^0} \int_{\bar{\nu}} S_D(\bar{\nu}) \frac{\epsilon_A(\bar{\nu})}{\bar{\nu}^4} d\bar{\nu}$$

The spectral overlap integral is usually abbreviated with the symbol J :

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

The above formula is correct if the dimension of $[J]$ is chosen to be $\text{cm}^6 \text{mole}^{-1}$. For chemists the more natural way to choose the dimension of the spectral overlap integral is: $[J] = [\text{cm}^3 \text{M}^{-1}]$, $[M] = [\text{mol L}^{-1}]$. The formula for the rate constant k_{EnT} for energy transfer must then be expressed as follows:

$$k_{EnT} = \frac{9 \ln(10)}{128\pi^5 N_L} \frac{\kappa_{D^*A}^2}{n^4 R_{DA}^6} \frac{\phi_{D^*}}{\tau_{D^*}^0} J_{\bar{\nu} D^* A}$$

3.4.2 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 $D^* \dots A$ 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 :
$$R_0^6 = fc \frac{\kappa_{D^*A}^2}{n^4} \phi_{D^*} J_{\nu D^*A}$$

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

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

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^* : $\left(\frac{d\rho}{dt} \right)_{\text{fluorescence of } D^*}$

Energy transfer rate: $\left(\frac{d\rho}{dt} \right)_{\text{energy transfer}}$

The probability P for energy transfer is:
$$P = \frac{\left(\frac{d\rho}{dt} \right)_{\text{energy transfer}}}{\left(\frac{d\rho}{dt} \right)_{\text{fluorescence}} + \left(\frac{d\rho}{dt} \right)_{\text{energy transfer}}} \quad \text{cancelling } \left(\frac{d\rho}{dt} \right)_{\text{energy transfer}}$$

$$C = \frac{\left(\frac{d\rho}{dt} \right)_{\text{fluorescence}}}{\left(\frac{d\rho}{dt} \right)_{\text{energy transfer}}}$$

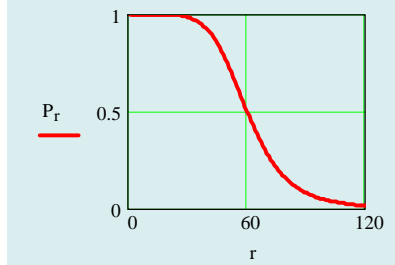
$$P = \frac{1}{C + 1}$$

$r := 1..120 \quad r_0 := 60 \quad P_r := \frac{1}{1 + \left(\frac{r}{r_0} \right)^6}$

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

$$C = \left(\frac{R}{R_0} \right)^6$$

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

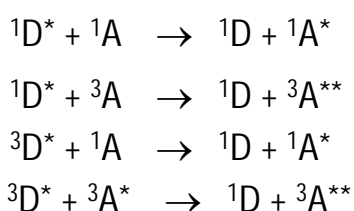


3.4.3 Dipole-dipole mechanism: selection rules

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

$$k_{ENT} \propto \frac{1}{\tau_{D^*}} \int S_D(\nu) \frac{\epsilon_A(\nu)}{\nu^4} d\nu$$

This means that the energy transfer depends on the extinction coefficient of the acceptor. If a forbidden transition of the acceptor is involved, the energy transfer rate is small. If the natural lifetime of the acceptor is large, the rate constant is scaled, correspondingly. Hence, the following energy transfer processes are examples of processes which can be regarded as being Förster energy transfer processes.



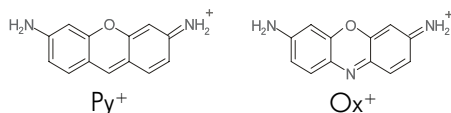
3.4.4 Examples for spectral overlap and Förster radius

The spectral overlap J_{D^*A} between the emission of an electronically excited molecule D^* and a molecule A is defined as:

$$J_{D^*A} = \int S_D(\bar{\nu}) \frac{\epsilon_A(\bar{\nu})}{\bar{\nu}^4} d\bar{\nu}$$

Knowing the spectral overlap integral, we can calculate the Förster EnT radius R_0 :

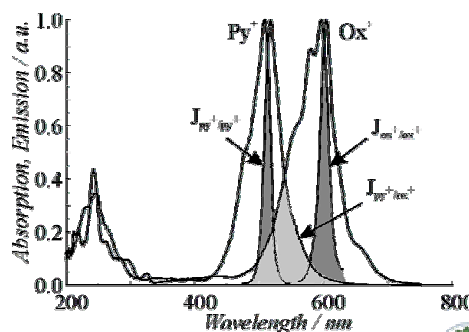
$$R_0 = \left(\frac{9000 \ln(10)}{128 \pi^5 N_A} J_{D^*A} \frac{\phi_{D^*} \kappa^2}{n^4} \right)^{1/6}$$



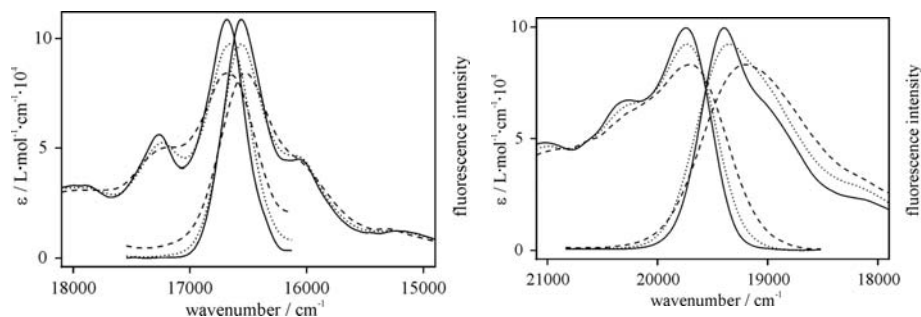
$$J_{PyOx} = 2.4 \times 10^{-13} \text{ cm}^3 \text{ M}^{-1}$$

Using the values for the fluorescence yield of the donor ($\phi = 1$), the refractive index of the medium ($n = 1.34$) and the orientation factor $\kappa^2 = 2/3$, we find the following value for the Förster Radius:

$$R_0 = 6 \text{ nm}$$

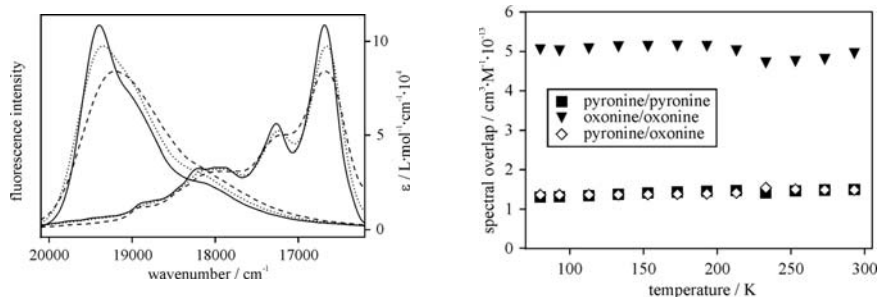


The spectral overlap integral and hence also the Förster radius and the energy transfer rate constant are sometimes thought to decrease with decreasing temperature. This is, however not generally correct as it depends on the way the shape of the spectra change with changing temperature.



Fluorescence and excitation spectra of Py⁺-zeolite L (left) and Ox⁺-zeolite L (right) at 80 K (solid), 193 K (dotted) and 293 K (dashed), illustrating the development of the spectral overlap of the two molecules. The fluorescence spectra have been scaled to the same height as the corresponding excitation spectra.

Data from: Solid State Sciences 2 (2000, 421).



Left: Fluorescence and excitation spectra of Py⁺, Ox⁺- zeolite L at 80 K (solid), 193 K (dotted) and 293 K (dashed), illustrating the development of the spectral overlap between the fluorescence spectrum Py⁺ with the absorption spectrum of Ox⁺, in zeolite L. The fluorescence spectra have been scaled to the same height as the corresponding excitation spectra.

Right: Temperature dependence of the spectral overlap of the investigated donor/acceptor pairs in the channels of zeolite L.





3.4.5 Calculating the spectral overlap from experimental data

MathCad-Program for calculation of the spectral overlap integral and the critical distance.

Part A. Calculation of the absorption and emission spectra (which were measured as a function of wavelength) as a function of wavenumber.

Note: It is easier, to work with the absorption spectrum than to work with the excitation spectrum, because in the Förster-equation the spectral overlap integral is a function of the extinction coefficient, and the extinction coefficient is proportional to the absorption intensity.

Reading the spectra:

```

Abswl := READPRN("AbsOrSol.prm")      Emwl := READPRN("EmPySol.prm")
LastAbs := length(Abswl^(0))          LastEm := length(Emwl^(0))
x := 0, 1, ..., LastAbs - 1            y := 0, 1, ..., LastEm - 1
    
```

The read ASCII-files of the specific spectra are translated into matrix-variables. The content of the ASCII-files has to be in the same configuration as the calculating program, otherwise an error occurs. Now we can start the calculation. It has to be taken into account that besides the wavelength, the fluorescence intensity also has to be calculated in comparison to the absorption intensity:

$$I_{\text{Emission}}(\text{wave number}) = \epsilon \cdot I_{\text{Absorption}}(\lambda)$$

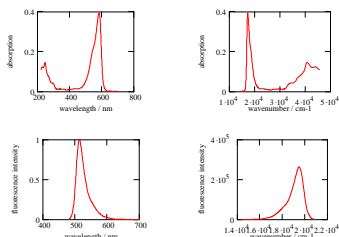
```

YEmwly := Abswl_{x,1}                YEmwly := Emwl_{y,1} (Emwl_{y,0})^2
XAbswly := 10^7 / Abswl_{x,0}          XEmwly := 10^7 / Emwl_{y,0}
    
```

The Y-vectors represent the measured (absorption) and the calculated (fluorescence) intensities of the specific spectrum. The X-vectors represent the wavenumbers, calculated from the wavelengths of the data.

```

Abswn := augment(XAbswly, (YAbswly))  Emwn := augment(reverse(XEmwly), reverse(YEmwly))
    
```



The X- and Y-vectors, which are coupled, have to be put in a matrix-variable, so that the calculated spectra can be plot. This happens with the function "augment".

Note: In part B an interpolation is executed on the data which are put in the matrices. For that it is necessary that the elements in the X-vector are ordered increasingly. This means that the elements in the X- and Y-vectors of the emission have to be reversed.

Part B. Calculation of the overlap integral of the calculated spectra of part A.

To calculate the overlap integral, we have to read the files with data that are coupled to the emission and absorption to work with.

```

LastEm := length(Emwl^(0))          x := 0, 1, ..., LastEm - 1
LastAbs := length(Abswl^(0))        y := 0, 1, ..., LastAbs - 1
    
```

$Abswl^{(1)} := Abswl^{(0)} - \min(Abswl^{(1)})$ <1> of the matrix-variable Abs refers to the second column of the matrix, which contains the measured intensities of the absorption spectrum. With this command a baseline correction for the absorption measurement is executed.

$$\epsilon := 4.67 \cdot 10^{-6}$$

$$l_{\text{cm}} := 1$$

The concentration of the sample solution given ϵ and the length of the light ray given l_{cm} are needed to find out the extinction coefficient.

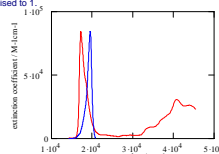
$$Abswl^{(1)} := \frac{Abswl^{(0)}}{\epsilon \cdot l_{\text{cm}}}$$

Calculation of the absorption intensity in the extinction coefficient.

$$Emwl^{(1)} := Emwl^{(0)} \cdot \left(\frac{\max(Abswl^{(1)})}{\max(Emwl^{(1)})} \right)$$

Scaling of the fluorescence to the extinction coefficient.

This scaling allows a better picture of the overlap between the absorption and the fluorescence spectra. For the calculation of the spectral overlap integral however the fluorescence spectrum has to be normalised to 1.



The spectra now have to be interpolated at the same wavenumbers. The Interp-function generates a function by making linear interpolation between every 2 datapoints.

For the calculation of the interpolated spectra the wavenumber range has to be set for the absorption and the emission:

```

absfirst := Abswn_{0,0}                emfirst := Emwn_{0,0}
abslast := Abswn_{LastAbs-1,0}        emlast := Emwn_{LastEm-1,0}
    
```

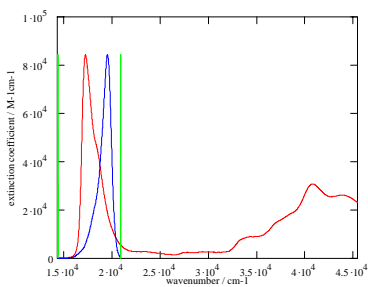
```

v_ab := absfirst, absfirst + 10, ., abslast    v_em := emfirst, emfirst + 10, ., emlast
    
```

```

Absint(v_ab) := Interp(Abswn^(0), Abswn^(1), v_ab)    Emiin(v_em) := Interp(Emwn^(0), Emwn^(1), v_em)
    
```

Now, let's look at the spectrum calculated by interpolation:



Spectral overlap

Integration: Next, the integration range [a,b] for the overlap surface has to be defined. In principle [a,b] equals the range in wavenumbers of the overlap region. Mostly, the overlap region is defined by the first absorption data and the last emission data. **Be sure that both interpolated functions have data points in the integration range. This can be checked in the graph above. If this is not the case, then the integration range has to be adjusted!**

$$a := \text{absfirst} \quad b := \text{emlast} \quad F_{\text{tot}} := \int_{\text{emfirst}}^{\text{emlast}} \text{Emiin}(v_{\text{em}}) dv_{\text{em}}$$

For the calculation of the overlap integral j, the fluorescence has to be normalized at integral = 1.

$$j := \frac{1}{F_{\text{tot}}} \int_a^b \text{Emiin}(v_{\text{em}}) \cdot \frac{\text{Absint}(v_{\text{em}})}{v_{\text{em}}} dv_{\text{em}} \quad j = 2.41 \times 10^{-13} \text{ L.cm}^3/\text{mol}$$

$$\text{When } L \text{ is calculated in cm}^3: \quad j_{\text{overl}} := j \cdot 10^3 \quad j_{\text{overl}} = 2.41 \times 10^{-10} \text{ cm}^6/\text{mol}$$

The calculation of the overlap integral is finished. We can also calculate the critical distance. For that, we need information on the quantum yield of fluorescence of the donor ϕ_D , the refraction index n in the specific solvent and the orientation factor κ^2 . N_A is the Avogadro-number.

$$N_A = 6.022 \cdot 10^{23} \text{ 1/mol} \quad \phi := 1 \quad n := 1.34 \quad \kappa^2 := \frac{2}{3} \quad \kappa^2 \text{ for isotropic conditions is } 2/3.$$

$$R_0 := \left(j_{\text{overl}} \frac{9 \cdot \ln(10) \cdot \phi \cdot \kappa^2}{128 \cdot \pi^5 \cdot n^4 \cdot N_A} \right)^{\frac{1}{6}} \quad R_0 = 5.937 \times 10^{-7} \text{ cm} \quad R_0 := R_0 \cdot 10^8 \quad R_0 = 59.365 \text{ Angstrom}$$

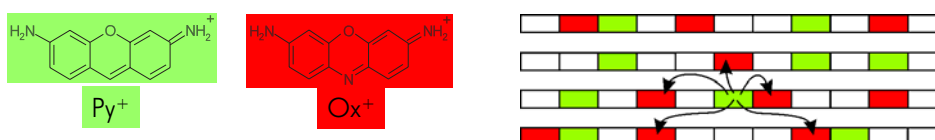
The mathcad programs
 OverlapintegralsOL.mcd and
 OverlapintegralLAYER.mcd can
 be downloaded at:
<http://www.dcb.unibe.ch/groups/calzaferri/start.html>
 (Computational Chemistry)

3.4.6 A demonstration experiment for Förster Energy Transfer

An interesting situation could be created if we could keep the ratio of the donor and the acceptor concentration constant but increasing both mean distance. This is usually not possible to realize over a sufficiently large concentration range because of quenching phenomena. However, using zeolite L as host it is possible to realize Experiments over a sufficiently large concentration range.

Dye loaded zeolite materials do not meet the conditions imposed by this theory completely, because of substantial anisotropy, as we shall discuss in chapter 5. But At the moment we assume that the theory is applicably 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 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 Φ_F^D and of the acceptor Φ_F^A under stationary conditions is therefore:

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

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

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

or

