

## 6 Photon-Mediated Long Range Excitation Energy Transfer

Förster theory of excitation energy transfer (EET) between molecules is based on the overlap of the donor emission spectrum and the acceptor absorption spectrum;

this suggests an interpretation of the transfer as a process where a photon is emitted by the donor and afterwards absorbed by the acceptor;

however, the use of the donor-acceptor Coulomb interaction  $V_{DA}$  to compute the rate indicates that the Förster transfer cannot be viewed as a *photon-mediated* EET process;

therefore, a theory of EET is formulated, which is based on the general electromagnetic interaction between the donor and the acceptor;

## 6.1 The Basic Model

we briefly review some basics of matter radiation interaction;

within Coulomb gauge the vector potential  $\mathbf{A}$  represents a transversal field which couples to the molecular system via the so-called minimal coupling Hamiltonian where the momenta of the charged particle are replaced by  $\mathbf{p}_j - \mathbf{A}(\mathbf{r}_j)q_j/c$ ;

the full electromagnetic interaction among electrons and nuclei is mediated by the short-ranged instantaneous Coulomb interaction and the long-ranged retarded exchange of transversal photons; it is advisable to move from the minimal coupling Hamiltonian to the so-called multipolar Hamiltonian by applying a canonical transformation (Power-Zienau transformation)

the transformation becomes much easier if one can restrict the description of donor and acceptor to their transition dipole moments  $\mathbf{d}_D$  and  $\mathbf{d}_A$ , respectively;

the complete electromagnetic interaction is reduced to an interaction between transition-dipoles and can be accounted for by the *dipolar coupling Hamiltonian*:

$$H_{\text{int}} = \sum_{m=D,A} \sum_{\lambda,\mathbf{k}} (\mathbf{g}_{\lambda\mathbf{k}}(\mathbf{X}_m) \hat{a}_{\lambda\mathbf{k}} + \text{H.c.}) (\mathbf{d}_m |\varphi_{me}\rangle \langle \varphi_{mg}| + \text{H.c.}) .$$

the coupling constant entering this expression takes the form

$$\mathbf{g}_{\lambda\mathbf{k}}(\mathbf{x}) = i \sqrt{\frac{2\pi\hbar\omega_{\mathbf{k}}}{L^3}} e^{i\mathbf{k}\mathbf{x}} \mathbf{n}_{\lambda\mathbf{k}} .$$

the model is completed by fixing the Hamiltonian of the donor-acceptor complex

$$H_{\text{agg}} = \mathcal{H}_0|0\rangle\langle 0| + \sum_{m=D,A} \mathcal{H}_m|m\rangle\langle m| + \mathcal{H}_{DA}|DA\rangle\langle DA| .$$

the ground-state is  $|0\rangle$  with Hamiltonian  $\mathcal{H}_0 = H_{Dg} + H_{Ag}$ ;

singly excited states are  $|m = D, A\rangle$  with Hamiltonians  $\mathcal{H}_D = H_{De} + H_{Ag}$  and  $\mathcal{H}_A = H_{Dg} + H_{Ae}$ ;

simultaneous excitation of both molecules describes  $|DA\rangle$  and the related Hamiltonian is  $\mathcal{H}_{DA} = H_{De} + H_{Ae}$

## 6.2 Preparatory Considerations of the Rate

now, the rate represents a fourth-order transition rate including intermediate states;  
the transition is of two-step character:

donor de-excitation does not directly lead to an acceptor excitation but first sets free a photon  
in a second step the photon is absorbed by the acceptor moving the latter into its excited state  
when calculating the rate we will also meet the counter intuitive two-step transition where photon emission and acceptor excitation takes place before donor de-excitation (formally such an additional process appears since the molecule-photon coupling comprises simultaneous photon creation and annihilation);

in the following we will make use of the fact that reproducing the Förster rate of EET in a particular limit, we can concentrate on the Liouville space pathway of type I;

the rate of *photon-mediated* EET takes the form (dropping the Liouville space pathway index I)

$$k_{D \rightarrow A}^{(\text{pm})} = 2\text{Re} \int_0^{\infty} dt_3 dt_2 dt_1 C_{AD}(t_3, t_2, t_1)$$

to calculate the correlation function we identify the statistical operator of state 1 with  $\hat{W}_D$  describing the excited donor and the absence of any photon (photon vacuum  $|\text{vac}\rangle$ );

it takes the form  $\hat{W}_D = \hat{R}_D |D\rangle \langle D| \times |\text{vac}\rangle \langle \text{vac}|$ , where  $\hat{R}_D = \hat{R}_{De} \hat{R}_{Ag}$

the state 3 corresponds to the final state of the transition with the unexcited donor, the excited acceptor and again the photon vacuum;

we obtain

$$C_{AD}(t_3, t_2, t_1) = \frac{1}{\hbar^4} \text{tr}_{\text{vib}} \{ \langle A | \langle \text{vac} | U(t_3 + t_2) H_{\text{int}} U(t_1) H_{\text{int}} \hat{W}_D U^+(t_1 + t_2) H_{\text{int}} U^+(t_3) H_{\text{int}} | \text{vac} \rangle | A \rangle \}$$

the included electron-photon matrix element separates into two matrix elements

$$\langle A | \langle \text{vac} | U(t_3 + t_2) H_{\text{int}} U(t_1) H_{\text{int}} | \text{vac} \rangle | D \rangle = U_A(t_3 + t_2) \langle A | \langle \text{vac} | U_{\text{phot}}(t_3 + t_2) H_{\text{int}} U_{\text{agg}}(t_1) U_{\text{phot}}(t_1) H_{\text{int}} | \text{vac} \rangle | D \rangle$$

the transition from the excited donor state to the excited acceptor state (from the right to the left part of the matrix element) may proceed in two ways: via the unexcited donor-acceptor pair as well as via the state of a simultaneous donor-acceptor excitation;

therefore, we may replace  $U_{\text{agg}}(t_1)$  by  $U_0(t_1)|0\rangle\langle 0| + U_{DA}(t_1)|DA\rangle\langle DA|$ ;

when calculating the photon-state matrix element one meets the photon correlation function (the hat reminds on the tensorial character of this function; note also  $\mathbf{X}_{AD} = \mathbf{X}_A - \mathbf{X}_D$ ):

$$\begin{aligned} \hat{C}_{\text{phot}}(\mathbf{X}_{AD}, t) &= \langle \text{vac} | \sum_{\lambda, \mathbf{k}} (\mathbf{g}_{\lambda \mathbf{k}}(\mathbf{X}_A) a_{\lambda \mathbf{k}} + \text{H.c.}) U_{\text{phot}}(t) \sum_{\kappa, \mathbf{q}} (\mathbf{g}_{\kappa \mathbf{q}}(\mathbf{X}_D) a_{\kappa \mathbf{q}} + \text{H.c.}) | \text{vac} \rangle \\ &= \frac{2\pi\hbar}{V} \sum_{\lambda, \mathbf{k}} \mathbf{n}_{\lambda \mathbf{k}} \otimes \mathbf{n}_{\lambda \mathbf{k}} \omega_{\mathbf{k}} e^{i(\mathbf{k}\mathbf{x} - \omega_{\mathbf{k}}t)} \end{aligned}$$

accordingly we may write

$$\langle A | \langle \text{vac} | U(t_3 + t_2) H_{\text{int}} U(t_1) H_{\text{int}} | \text{vac} \rangle | D \rangle = U_A(t_3 + t_2) \left( U_0(t_1) + U_{DA}(t_3 + t_2) \right) [\mathbf{d}_A \hat{C}_{\text{phot}}(\mathbf{X}_{AD}, t_1) \mathbf{d}_D^*]$$

in the same way we arrive at (note the negative time argument in the photon correlation function which is caused by the appearance of  $U_{\text{phot}}^+$ )

$$\langle D | \langle \text{vac} | U^+(t_1 + t_2) H_{\text{int}} U^+(t_3) H_{\text{int}} | \text{vac} \rangle | A \rangle = U_D^+(t_1 + t_2) \left( U_0^+(t_3) + U_{DA}^+(t_3) \right) [\mathbf{d}_D \hat{C}_{\text{phot}}(\mathbf{X}_{DA}, -t_3) \mathbf{d}_A^*]$$

one ends up with four new correlation functions;

the expression  $\text{tr}_{\text{vib}} \{ \hat{R}_D U_D^+(t_1 + t_2) U_0^+(t_3) U_A(t_3 + t_2) U_0(t_1) \}$  corresponds to the EET process with the unexcited donor-acceptor pair as the intermediate state;

being aware of the separate vibrational coordinates for the donor and the acceptor this three-time correlation function factorizes into  $C_{De \rightarrow g}(t_1 + t_2) C_{Ag \rightarrow e}(t_3 + t_2)$ ;

in contrast, the correlation function  $\text{tr}_{\text{vib}} \{ \hat{R}_D U_D^+(t_1 + t_2) U_{AD}^+(t_3) U_A(t_3 + t_2) U_{DA}(t_1) \}$  results from the presence of the doubly excited pair as an intermediate state

it reduces to  $C_{De \rightarrow g}(t_2 + t_3) C_{Ag \rightarrow e}(t_1 + t_2)$ ;

the interference of both transition paths leads to two mixed (interference) terms;

we finally arrive at (the mixed contributions are at the second and third position of the right-hand side)

$$C_{AD}(t_1, t_2, t_3) = \frac{|d_D d_A|^2}{\hbar^4} \left( C_{De \rightarrow g}(t_1 + t_2) C_{Ag \rightarrow e}(t_3 + t_2) + C_{De \rightarrow g}(t_1 + t_2 + t_3) C_{Ag \rightarrow e}(t_2) + C_{De \rightarrow g}(t_2) C_{Ag \rightarrow e}(t_1 + t_2 + t_3) + C_{De \rightarrow g}(t_2 + t_3) C_{Ag \rightarrow e}(t_1 + t_2) \right) \times [\mathbf{n}_A \hat{C}_{\text{phot}}(\mathbf{X}_{AD}, t_1) \mathbf{n}_D] [\mathbf{n}_D \hat{C}_{\text{phot}}(\mathbf{X}_{DA}, -t_3) \mathbf{n}_A]$$

### 6.3 Photon Correlation Functions

we analyze the photon correlation function with the focus on its Fourier-transformed version (with respect to its time-argument);

to carry out the  $\lambda\mathbf{k}$ -summation we first note that  $\sum_{\lambda} \mathbf{n}_{\lambda\mathbf{k}} \otimes \mathbf{n}_{\lambda\mathbf{k}} = 1 - \mathbf{k} \otimes \mathbf{k}/|\mathbf{k}|^2$

secondly,  $\mathbf{k}$ -vectors inside the  $\mathbf{k}$ -summation are replaced by the action of the nabla-operator outside;

we get

$$\hat{C}_{\text{phot}}(\mathbf{x}, t) = [-\nabla^2 + \nabla \otimes \nabla] \zeta_{\text{phot}}(x, t)$$

the newly introduced function  $\zeta_{\text{phot}}$  only depends on  $x = |\mathbf{x}|$  and reads (note  $k = |\mathbf{k}|$ , the change to a  $\mathbf{k}$ -integration, and the introduction of spherical coordinates):

$$\zeta_{\text{phot}}(x, t) = \frac{\hbar c}{4\pi^2} \int \frac{d^3\mathbf{k}}{|\mathbf{k}|} e^{i(\mathbf{k}\mathbf{x} - \omega_{\mathbf{k}}t)} = \frac{\hbar c}{\pi} \int_0^{\infty} dk \frac{\sin(kx)}{x} e^{-ickt}$$

the Fourier-transform simply follows as ( $\theta(\omega)$  is the unit step function)

$$\zeta_{\text{phot}}(x, \omega) = \theta(\omega) 2\hbar \frac{\sin(\omega x/c)}{x}$$

calculating the photon-mediated EET rate we also need the retarded correlation function

$$\hat{C}_{\text{phot}}^{(\text{ret})}(\mathbf{x}, t) = \theta(t) \hat{C}_{\text{phot}}(\mathbf{x}, t)$$

a Fourier transformation leads to (be also aware of  $\hat{C}_{\text{phot}}(\mathbf{x}, t) = \hat{C}_{\text{phot}}^*(\mathbf{x}, -t)$ )

$$\hat{C}_{\text{phot}}^{(\text{ret})}(\mathbf{x}, \omega) = - \int \frac{d\bar{\omega}}{2\pi i} \frac{\hat{C}_{\text{phot}}(\mathbf{x}, \bar{\omega})}{\omega - \bar{\omega} + i\varepsilon}$$

in order to derive a concrete expression for  $\hat{C}_{\text{phot}}^{(\text{ret})}(\mathbf{x}, \omega)$  one may directly compute the Fourier-transform of  $\zeta_{\text{phot}}^{(\text{ret})}(x, t) = \theta(t)\zeta_{\text{phot}}(x, t)$  at positive and negative frequency arguments ending up with expressions, which include the integral cosine and sine function;

to arrive at the rate of photon-mediated EET we only need the combination of the retarded photon correlation function at positive and negative frequencies;

this combination can be calculated by adding both parts but also directly without a separate determination at positive and negative frequencies;

in any case, one arrives at the following simple form (note the introduction of  $K = \omega/c$ )

$$\frac{1}{\hbar} (\zeta_{\text{phot}}^{(\text{ret})}(x, \omega) + \zeta_{\text{phot}}^{(\text{ret})}(x, -\omega)) = (\theta(\omega) - \theta(-\omega)) \frac{\sin(Kx)}{x} - i \frac{\cos(Kx)}{x}$$



## 6.4 Rate of Photon-Mediated EET

it is advisable to introduce Fourier-transformed molecular correlation functions  $C_{De \rightarrow g}$  and  $C_{Ag \rightarrow e}$  as well as Fourier-transformed retarded photon correlation function  $\hat{C}^{(\text{ret})}$ :

$$k_{D \rightarrow A}^{(\text{pm})} = \frac{|d_D d_A|^2}{\hbar^4} \int \frac{d\omega d\bar{\omega}}{(2\pi)^2} C_{De \rightarrow g}(-\omega) \left\{ \frac{-i}{\omega - \bar{\omega} - i\varepsilon} \right. \\ \times \left( [\mathbf{n}_D \hat{C}_{\text{phot}}^{(\text{ret})*}(\mathbf{X}_{DA}, \omega) \mathbf{n}_A] + [\mathbf{n}_D \hat{C}_{\text{phot}}^{(\text{ret})*}(\mathbf{X}_{DA}, -\bar{\omega}) \mathbf{n}_A] \right) \\ \left. \times \left( [\mathbf{n}_A \hat{C}_{\text{phot}}^{(\text{ret})}(\mathbf{X}_{AD}, \bar{\omega}) \mathbf{n}_D] + [[\mathbf{n}_A \hat{C}_{\text{phot}}^{(\text{ret})}(\mathbf{X}_{AD}, -\omega) \mathbf{n}_D] + \text{c.c.}] \right) C_{Ag \rightarrow e}(\bar{\omega}) \right.$$

the retarded photon correlation functions are responsible for mediating the EET;

the combination of the part proportional to  $\hat{C}^{(\text{ret})*}(\mathbf{X}_{DA}, \omega)$  with that proportional to  $\hat{C}^{(\text{ret})}(\mathbf{X}_{AD}, \bar{\omega})$  corresponds to the intuitive photon-mediated transfer process shown as pathway “a”;

the total rate follows via the inclusion of pathway “b” and a mixture of both;

the expression simplifies considerable if we note that the photon correlation function changes only slightly across the frequency range where  $C_{De \rightarrow g}(\omega)$  and  $C_{Ag \rightarrow e}(\omega)$  deviate from zero; characterizing this range by a mean frequency  $\omega_0$  we obtain ( $X_{DA} = |\mathbf{X}_{DA}|$ )

$$k_{D \rightarrow A}^{(\text{pm})} = \frac{2\pi}{\hbar} |d_D d_A|^2 |\mathcal{A}(x_{DA}, \omega_0)|^2 \mathcal{D}_{DA}$$

the combined density of states  $\mathcal{D}_{DA}$  takes the form

$$\mathcal{D}_{DA} = \frac{1}{2\pi\hbar} \int dt C_{De \rightarrow g}(t) C_{Ag \rightarrow e}(t) \equiv \frac{1}{(2\pi)^2\hbar} \int d\omega C_{De \rightarrow g}(-\omega) C_{Ag \rightarrow e}(\omega)$$

with the correlation function of donor de-excitation

$$C_{De \rightarrow g}(t) = \text{tr}_D \{ \hat{R}_{De} \hat{U}_{De}^+(t) \hat{U}_{Dg}(t) \} ,$$

and the correlation function of acceptor excitation

$$C_{Ag \rightarrow e}(t) = \text{tr}_A \{ \hat{R}_{Ag} \hat{U}_{Ag}^+(t) \hat{U}_{Ae}(t) \} .$$

the newly defined function  $\mathcal{A}$  (photon transition amplitude) is determined by the retarded correlation functions;

it can be expressed by  $\zeta_{\text{phot}}^{(\text{ret})}$  introduced earlier

$$\begin{aligned} \mathcal{A}(x_{DA}, \omega_0) &= \frac{1}{\hbar} \left( - [\mathbf{n}_D \mathbf{n}_A] \nabla^2 + [\mathbf{n}_D \nabla] [\mathbf{n}_A \nabla] \right) \left( \zeta_{\text{phot}}^{(\text{ret})}(X_{DA}, \omega_0) + \zeta_{\text{phot}}^{(\text{ret})}(X_{DA}, -\omega_0) \right) . \\ &= K_0^3 \left[ \frac{\kappa_{DA}}{(K_0 X_{DA})^2} - \frac{i\bar{\kappa}_{DA}}{K_0 X_{DA}} + \frac{i\kappa_{DA}}{(K_0 X_{DA})^3} \right] e^{iK_0 X_{DA}} \end{aligned}$$

note the introduction of  $K_0 = \omega_0/c$ , which determines the inverse wavelength of the exchanged photon;

the orientation factors read

$$\kappa_{DA} = [\mathbf{n}_D \mathbf{n}_A] - 3[\mathbf{n}_D \mathbf{e}_{DA}][\mathbf{n}_A \mathbf{e}_{DA}]$$

and

$$\bar{\kappa}_{DA} = [\mathbf{n}_D \mathbf{n}_A] - [\mathbf{n}_D \mathbf{e}_{DA}][\mathbf{n}_A \mathbf{e}_{DA}]$$

if  $K_0 X_{DA} \ll 1$ , i.e. if the donor-acceptor distance is much smaller than the photon wavelength, the rate  $k_{D \rightarrow A}^{(pm)}$  reduces to the Förster type expression; it depends on  $1/X_{DA}^6$ ;  
in the present context one may state that Förster type EET is dominated by a *virtual photon exchange*;

in the contrary case the rate accounts for real photon emission by the donor and photon absorption by the acceptor (here it decreases with the inverse square of the donor-acceptor distance).  
if one ignores the counter-intuitive photon-mediated process (pathway “b”) the transition amplitude also includes sine and cosine functions;

in particular, one cannot reproduce the Förster type rate for short DA-distances;  
this has to be expected since the energy-time uncertainty works most effectively at short distances, i.e. at short “photon flight times” (strong contribution by the counter-intuitive process);  
interestingly, the elaborated combination of the two transition pathways reproduces the simple picture of a Coulomb interaction between the donor and the acceptor;

to estimate the rate of photon-mediated EET we use

$$k_{D \rightarrow A}^{(\text{pm})} = \frac{2\pi}{\hbar} |d_D d_A|^2 \left( \frac{\kappa_{DA}^2}{X_{DA}^6} + \frac{K_0^2 \kappa_{DA} (\kappa_{DA} - 2\bar{\kappa}_{DA})}{X_{DA}^4} + \frac{K_0^4 \bar{\kappa}_{DA}^2}{X_{DA}^2} \right) \mathcal{D}_{DA}$$

the acceptor molecule has been chosen to be identical to the donor  $\hbar\omega_D = \hbar\omega_A = \hbar\omega_0$  (the transition dipole moments are perpendicular to the line connecting the donor and the acceptor, i.e.  $\kappa_{DA} = \bar{\kappa}_{DA} = 1$ );

for distances less than 20 nm the photon-mediated transfer agrees completely with the Förster rate and any dependence on the choice of  $\hbar\omega_0$  vanishes;

the extreme smallness of the Förster rate for the largest distance of 500 nm is compensated when using the general rate due to photon mediated transfer;

its distance dependence is dominated by  $1/X_{DA}^2$ -term and it is increased according to the fourth power of  $\omega_0$ ;

such a behavior indicates that the EET appears mainly as a photon emission by the donor and a subsequent photon absorption by the acceptor (this view of a real photon exchange just confirms that the rate becomes proportional to  $\omega_0^4/X_{DA}^2$ );