Chapter 3

Excitation Energy Transfer

3.1   Introduction

we will discuss the electronic excitation energy transfer (EET) between two molecules according to the general scheme

$$\mathrm{D}^* + \mathrm{A} \longrightarrow \mathrm{D} + \mathrm{A}^*$$

the excitation energy donor is labeled by D and the excitation energy acceptor by A; the starting point is a situation where the donor molecule has been excited (D^*), for instance, by means of an external laser pulse, and the acceptor molecule is in its ground state (A); then the Coulomb interaction between these molecules leads to a reaction where the donor molecule is de–excited and the electrostatic energy is transferred to the acceptor molecule which is excited;
since the de–excitation of the donor molecule reminds on the process of spontaneous photon emission (fluorescence) the describe process of EET is often also named *fluorescence resonance energy transfer* (FRET, the term "resonance" reminds on the need that the energy of the initial EET state should coincide with the energy of the final state);

the product state can be also reached via an electron exchange between the donor and the acceptor molecule; the electron in the LUMO of the D moves to the LUMO of the A and the hole in the HOMO of the D is filled by an electron of the HOMO of the A; this process requires electronic wave function overlap between the D and the A, while the former mentioned process (without electron exchange) may take place even if both molecules are spatially well separated;

if the coupling responsible for EET becomes sufficiently large the state $|D^*A\rangle$ which corresponds to the initial state of the EET and the state $|DA^*\rangle$ which describes the result of the EET may form an quantum mechanical superposition state

$$|\phi\rangle = c_1|D^*A\rangle + c_2|DA^*\rangle$$

if generalized to an arbitrary set of molecules this state is known as the *Frenkel exciton*; to distinguish the Frenkel exciton from other types of excitons it can be considered as an electron hole pair with both particles staying at the same molecule (the missing single electron in the HOMO of an excited molecule is considered as the hole);

Frenkel excitons are encountered in associated and non–covalently bound complexes;

examples are molecular crystals of aromatic compounds such as benzene or naphthalene, for instance, and rare gases in the solid phase; another important class of systems forming Frenkel excitons are dye aggregates (for instance, isocyanine or pseudo–isocyanine); upon aggregation which occurs in solution or in thin solid films, the dyes form rod–like arrangements consisting of several hundreds of molecules; in the last two decades also biological *chromophore complexes* attracted broad interest; the light–harvesting complex of natural photosynthetic antenna systems represents one of the most fascinating examples where the concept of Frenkel excitons could be applied; of actual interest are also hybrid systems where molecules have been attached to semi-conducting (or metallic) nano particles (quantum dots); EET is now possible between the nano particle and the molecule;

the theoretical and experimental investigation of the behavior of excitons in molecular aggregates has a long tradition; early theoretical contributions by T. Förster and D. L. Dexter were based on an incoherent rate equation approach; the variety of phenomena highlighted in recent discussions ranges from cooperative radiative decay (superradiance) and disorder–induced localization to nonlinear effects like exciton annihilation and two–exciton state formation;

the case opposite to the Frenkel exciton, where electron and hole are separated by a distance much larger than the spacing between neighboring molecules, is called *Wannier–Mott exciton*; it occurs in systems with strong binding forces between constituent molecules or atoms such as covalently bound semiconductors; frequently, also an intermediate form, the *charge transfer exciton*, is discussed; here electrons and holes reside on molecules which are not too far apart, this type of exciton appears if the wave functions of the involved molecules are sufficiently overlapping, as is necessary for an electron transfer reaction; charge transfer excitons can be found, for example, in polymeric chains formed by silicon compounds (polysilanes);

we will focus on the description of Frenkel excitons in molecular aggregates; the term "aggregate" is used to characterize a molecular system which consists, at least, of some hundred non–covalently bound molecules; occasionally, we will also use the term chromophore complex or supra–molecular complex;

the initial state relevant for the transfer process is often created by means of an external laser pulse resonant to the respective $S_0 \rightarrow S_1$ transitions; in general, this state is a superposition of eigenstates of the molecular system including the mutual Coulomb interaction, i.e., it may contain contributions of all monomers; in terms of the corresponding wave functions this implies a delocalization over the whole aggregate (provided that the wavelength of the exciting light is large compared to the aggregate size); the degree of delocalization and the type of motion initiated by the external field depends crucially on the interaction between the exciton system with environmental DOF such as intramolecular nuclear motions; the ratio between the characteristic times of intramolecular (vibrational) relaxation and intermolecular transitions decides on the particular way the EET proceeds; two limiting cases can be distinguish; if the intramolecular relaxation is fast (compared with the intermolecular transitions) then the excitation remains localized and the EET is named *incoherent*; in the contrary case the excitation may move as a delocalized state through the aggregate, i.e. the EET is a *coherent* transfer

3.2 Förster Theory of Incoherent Exciton Transfer

to deal with the main reference case we will consider the regime of incoherent transfer where a localized excitation jumps from molecule to molecule; this can be achieved by the rate equation for the state occupation probabilities, $P_m(t)$ describing the presence of a single excitation at molecule m;
the rate equations read

$$\frac{\partial}{\partial t}P_m(t) = -\sum_n \left(k_{m \to n} P_m(t) - k_{n \to m} P_n(t) \right)$$

to calculate the transition rates we introduce two molecules one emitting the excitation energy (the donor) and one accepting the energy (the acceptor); the adiabatic wave functions for both molecules ($m = D, A$) read:

$$\Psi_{maM}(r_m; R_m) = \varphi_{ma}(r_m; R_m)\chi_{maM}(R_m)$$

the expression includes the electronic wave functions φ_{ma} and the vibrational one χ_{maM}, where $a = g, e$ (S_0, S_1); M denotes the set of vibrational quantum numbers; r_m are the electronic coordinates; the R_m comprise the intramolecular nuclear coordinates;
the $S_0 \to S_1$ transition energies are given by $E_{meM} - E_{mgN}$; accordingly the transfer rate follows as

$$k_{D \to A} = \frac{2\pi}{\hbar} \sum_{M_D, N_D} \sum_{M_A, N_A} f_{DeM_D}\ f_{AgN_A}$$

$$\times \left| \langle \Psi_{DeM_D}, \Psi_{AgN_A} | V_{DA} | \Psi_{AeM_A}, \Psi_{DgN_D} \rangle \right|^2$$

$$\times \delta(E_{DeM_D} + E_{AgN_A} - E_{AeM_A} - E_{DgN_D})$$

the coupling potential V_{DA} covers the complete Coulomb interaction between the D and the A molecule; it separates into electronic and nuclear contributions

$$V_{DA} = V_{DA}^{(\text{el}-\text{el})} + V_{DA}^{(\text{el}-\text{nuc})} + V_{DA}^{(\text{nuc}-\text{el})} + V_{DA}^{(\text{nuc}-\text{nuc})}$$

we first consider $V_{DA}^{(\text{el}-\text{el})}$; the Coulomb interaction is written in terms of the electronic coordinates related to the center of masses, $\mathbf{X}_D$ and $\mathbf{X}_A$, of the two molecules

$$V_{DA}^{(\text{el}-\text{el})} = \sum_{j,k} \frac{e^2}{|\mathbf{X}_{DA} + \mathbf{r}_j(D) - \mathbf{r}_k(A)|}$$

we have introduced the intermolecular distance $\mathbf{X}_{DA} = \mathbf{X}_D - \mathbf{X}_A$, and $\mathbf{r}_j(D)$ ($\mathbf{r}_k(A)$) denotes the coordinates of the jth (kth) electron at molecular excitation energy donor (acceptor);
the electron–nuclei coupling reads (nuclear coordinates are also related to the center of masses)

$$V_{DA}^{(\text{el}-\text{nuc})} = -\sum_{j,n} \frac{e Z_n e}{|\mathbf{X}_{DA} + \mathbf{r}_j(D) - \mathbf{R}_n(A)|}$$

there also exist a second form with electronic and nuclear coordinates interchanged;
the nuclei–nuclei coupling takes the form

$$V_{DA}^{(\text{nuc}-\text{nuc})} = \sum_{m,n} \frac{Z_m e Z_n e}{|\mathbf{X}_{DA} + \mathbf{R}_m(D) - \mathbf{R}_n(A)|}$$

we compute the coupling matrix elements

$$\langle \Psi_{DeM_D}, \Psi_{AgN_A} | V_{DA} | \Psi_{AeM_A}, \Psi_{DgN_D} \rangle =$$

$$\langle \chi_{DeM_D} \varphi_{De}, \chi_{AgN_A} \varphi_{Ag} | V_{DA}^{(el-el)} + V_{DA}^{(el-nuc)} + V_{DA}^{(nuc-el)} + V_{DA}^{(nuc-nuc)} | \chi_{AeM_A} \varphi_{Ae}, \chi_{DgN_D} \varphi_{Dg} \rangle$$

$$= \langle \chi_{DeM_D} | \chi_{DgN_D} \rangle \langle \chi_{AgN_A} | \chi_{AeM_A} \rangle \times \langle \varphi_{De}, \varphi_{Ag} | V_{DA}^{(el-el)} | \varphi_{Ae}, \varphi_{Dg} \rangle$$

it results a pure electronic coupling matrix element; the other contributions vanish because of the orthonormalization of the electronic wave functions; for example, when considering the matrix element of the electron–nuclear coupling $V_{DA}^{(el-nuc)}$, the electronic overlap expression $\langle \varphi_{Ag} | \varphi_{Ae} \rangle$ appears which vanishes (in a similar way the matrix elements with $V_{DA}^{(nuc-el)}$ and $V_{DA}^{(nuc-nuc)}$ do not contribute);
the pure electronic matrix element is written as

$$J_{DA} = \langle \varphi_{De}, \varphi_{Ag} | V_{DA}^{(el-el)} | \varphi_{Ae}, \varphi_{Dg} \rangle$$

$$\equiv \sum_{j,k} \int dr_D dr_A \varphi_{De}^*(r_D) \varphi_{Ag}^*(r_A) \frac{e^2}{|\mathbf{X}_{DA} + \mathbf{r}_j(D) - \mathbf{r}_k(A)|} \varphi_{Ae}(r_A) \varphi_{Dg}(r_D)$$

since the electronic wave functions are anti–symmetric with respect to an interchange of the electronic coordinates we may introduce formal charge densities and express the matrix element by an integration with respect to a single electron coordinate of the D–molecule as well as of the A–molecule; we, first, note

$$\rho_{Deg}(\mathbf{r}_D) = e N_e \int dr_D \delta(\mathbf{r}_D - \mathbf{r}_1(D)) \varphi_{De}^*(r_D) \varphi_{Dg}(r_D)$$

this density is known as the *transition density* (relating the electronic ground–state to the first excited state); in the same way one may introduce $\rho_{Aeg}(\mathbf{r}_A)$; it results a rather simplified expression for the matrix element

$$J_{DA} = \int d\mathbf{r}_D^3 d\mathbf{r}_A^3 \frac{\rho_{Deg}(\mathbf{r}_D) \rho_{Aeg}^*(\mathbf{r}_A)}{|\mathbf{X}_{DA} + \mathbf{r}_D - \mathbf{r}_A|}$$

it corresponds to the standard expression of electrostatics, however, the meaning of the charge densities is completely quantum mechanically

3.2.1 Dipole–Dipole Coupling

if the two molecules interacting with each other are sufficiently far a part (no overlap of the wave functions) we may remove the short–range contribution to the intermolecular Coulomb interaction; this is achieved by employing a multi-pole expansion;
the multi-pole expansion in powers of $|\mathbf{r}_D - \mathbf{r}_A|/|\mathbf{X}_{AD}|$ is performed up to the second–order term; since $\mathbf{r}_D$ and $\mathbf{r}_A$ are defined with respect to the center of masses, in the present case $|\mathbf{r}_D - \mathbf{r}_A|$ can be considered to be small compared with $|\mathbf{X}_{AD}|$;
we abbreviate $\mathbf{X}_{DA} = \mathbf{X}$ and $\mathbf{r}_D - \mathbf{r}_A = \mathbf{r}$ and obtain

$$\frac{1}{|\mathbf{X} + \mathbf{r}|} \approx \frac{1}{|\mathbf{X}|} + \mathbf{r}\nabla_{\mathbf{x}}\frac{1}{|\mathbf{X}|} + \frac{1}{2}(\mathbf{r}\nabla_{\mathbf{x}})(\mathbf{r}\nabla_{\mathbf{x}})\frac{1}{|\mathbf{X}|}$$

the derivatives read in detail

$$\mathbf{r}\nabla_{\mathbf{x}}\frac{1}{|\mathbf{X}|} = -\frac{\mathbf{r}\mathbf{X}}{|\mathbf{X}|^3}$$

and

$$(\mathbf{r}\nabla_\mathbf{X})(\mathbf{r}\nabla_\mathbf{X})\frac{1}{|\mathbf{X}|} = -\frac{\mathbf{r}^2}{|\mathbf{X}|^3} + \frac{3(\mathbf{rX})^2}{|\mathbf{X}|^5}$$

if we insert the obtained approximation into the matrix element it follows

$$J_{DA} = \int d\mathbf{r}_D^3 d\mathbf{r}_A^3 \rho_{Aeg}^*(\mathbf{r}_A)\rho_{Deg}(\mathbf{r}_D)$$

$$\left(\frac{1}{|\mathbf{X}_{DA}|} - \frac{[\mathbf{r}_D - \mathbf{r}_A]\mathbf{X}_{DA}}{|\mathbf{X}_{DA}|^3} - \frac{1}{2}\frac{[\mathbf{r}_D - \mathbf{r}_A]^2}{|\mathbf{X}_{\mathbf{DA}}|^3} + \frac{3}{2}\frac{([\mathbf{r}_D - \mathbf{r}_A]\mathbf{X}_{DA})^2}{|\mathbf{X}_{DA}|^5}\right)$$

we immediately see that the zeroth– and first–order terms do not contribute since $\int d^3\mathbf{r}_m\rho_{meg}(\mathbf{r}_m) = 0$ (the wave functions have been assumed to be orthogonal to each other); there only remains

$$J_{DA} = \int d\mathbf{r}_D^3 d\mathbf{r}_A^3 \rho_{Aeg}^*(\mathbf{r}_A)\rho_{Deg}(\mathbf{r}_D)\left(\frac{\mathbf{r}_D\mathbf{r}_A}{|\mathbf{X}_{\mathbf{DA}}|^3} - \frac{3([\mathbf{r}_D\mathbf{X}_{DA}][\mathbf{r}_A\mathbf{X}_{DA}]}{|\mathbf{X}_{DA}|^5}\right)$$

we note the definition of transition dipole matrix elements ($m = D, A$)

$$\mathbf{d}_{meg} \equiv \mathbf{d}_m = \langle\varphi_{me}|\sum_j e\mathbf{r}_j(m)|\varphi_{mg}\rangle \equiv \int d\mathbf{r}_m^3 \mathbf{r}_m\rho_{meg}(\mathbf{r}_m)$$

we may write for the matrix element

$$J_{DA} = \frac{\mathbf{d}_D\mathbf{d}_A^*}{|\mathbf{X}_{DA}|^3} - 3\frac{[\mathbf{d}_D\mathbf{X}_{DA}][\mathbf{d}_A^*\mathbf{X}_{DA}]}{|\mathbf{X}_{DA}|^5}$$

it is often abbreviated as

$$J_{DA}(\mathbf{X}_{DA}) = \kappa_{DA}\frac{|\mathbf{d}_D||\mathbf{d}_A^*|}{|\mathbf{X}_{DA}|^3}$$

we introduced an orientational factor defined as

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

where $\mathbf{n}_m$ and $\mathbf{e}_{DA}$ are the unit vectors pointing in the directions of the transition dipole moment $\mathbf{d}_m$, and the distance vector $\mathbf{X}_{DA}$, respectively;
this finally gives the matrix element of intra–molecular Coulomb interaction in dipole–dipole approximation as:

$$\langle\Psi_{DeM_D}, \Psi_{AgN_A}|V_{DA}|\Psi_{AeM_A}, \Psi_{DgN_D}\rangle = J_{DA}\langle\chi_{DeM_D}|\chi_{DgN_D}\rangle\langle\chi_{AgN_A}|\chi_{AeM_A}\rangle$$

3.2.2 The Rate Expression

it is obvious that the process of excitation energy transfer can formally be viewed as the combined process of optical recombination at the donor and simultaneous optical absorption at the acceptor; the Förster approach is built upon this analogy; therefore we rewrite the delta function in k_{DA} as

$$\delta(E_{DeM_D}+E_{AgN_A}-E_{AeM_A}-E_{DgN_D}) = \int dE\, \delta(E_{DeM_D}-E_{DgN_D}-E)\times\delta(E+E_{AgN_A}-E_{AeM_A})$$

the first delta function on the right–hand side accounts for the donor emission; the energy, $E = \hbar\omega$, which is set free in this process is used to excite the acceptor; it follows for the overall rate

$$k_{D\to A} = \frac{2\pi}{\hbar} \sum_{M_D, N_D} \sum_{M_A, N_A} f_{DeM_D} \, f_{AgN_A}$$

$$|J_{DA}|^2 |\langle \chi_{DeM_D} | \chi_{DgN_D} \rangle|^2 |\langle \chi_{AgN_A} | \chi_{AeM_A} \rangle|^2$$

$$\times \int_0^\infty dE \, \delta(E_{DeM_D} - E_{DgN_D} - E) \times \delta(E + E_{AgN_A} - E_{AeM_A})$$

we may introduce the combined density of states of donor de–excitation

$$\mathcal{D}_D(E) = \sum_{M_D, N_D} f_{DeM_D} |\langle \chi_{DeM_D} | \chi_{DgN_D} \rangle|^2 \delta(E_{DeM_D} - E_{DgN_D} - E)$$

and acceptor excitation

$$\mathcal{D}_A(E) = \sum_{M_A, N_A} f_{AgN_A} |\langle \chi_{AgN_A} | \chi_{AeM_A} \rangle|^2 \delta(E + E_{AgN_A} - E_{AeM_A})$$

it gives the overall EET rate as

$$k_{D\to A} = \frac{2\pi}{\hbar} |J_{DA}|^2 \int dE \, \mathcal{D}_D(E) \mathcal{D}_A(E)$$

we specify the donor acceptor Coulomb interaction by introducing the approximation of a dipole–dipole coupling

$$k_{D\to A} = \frac{2\pi}{\hbar} \frac{\kappa_{DA}^2}{X_{DA}^6} \int_0^\infty dE \, |d_D|^2 \mathcal{D}_D(E) \times |d_A|^2 \mathcal{D}_A(E)$$

at the final step of our derivation we note the definition of emission and absorption spectra of molecular systems
accordingly, the donor emission spectrum (valid for a single molecule but averaged with respect to many emission processes) is given by

$$I_D(\omega) = \frac{4\omega^3}{3c^3} |d_D|^2 \mathcal{D}_D(E)$$

it is defined in such a way to give the inverse radiation life–time as

$$\frac{1}{\tau_{\mathrm{rad}}^{(D)}} = \int_0^\infty d\omega I_D(\omega)$$

the acceptor absorption coefficient (of an ensemble of molecules with volume density n_{mol}) reads

$$\alpha_A(\omega) = \frac{4\pi^2 \omega n_{\mathrm{mol}}}{3c} |\mathbf{d}_A|^2 \mathcal{D}_A(E)$$

we obtain the Förster formula which expresses the energy transfer rate in terms of the spectral overlap between the monomeric emission and absorption characteristics:

$$k_{D \to A} = \frac{2\pi}{\hbar} \frac{\kappa_{DA}^2}{X_{DA}^6} \int_0^\infty dE \frac{3c^3}{4\omega^3} I_D(\omega) \frac{3c}{4\pi^2 \omega n_{\mathrm{mol}}} \alpha_A(\omega)$$

$$= \frac{9c^4 \kappa_{DA}^2}{8\pi n_{\mathrm{mol}} X_{DA}^6} \int_0^\infty \frac{d\omega}{\omega^4} I_D(\omega) \alpha_A(\omega)$$

the rate decreases with the sixth power of the distance between the monomers
the distance, R_{F}, for which the transfer rate is equal to the radiative decay rate of the donor,

$$k_{D \to A}(R_{\mathrm{F}}) = \frac{1}{\tau_{\mathrm{rad}}^{(D)}} = \int_0^\infty d\omega I_D(\omega)$$

is called the *Förster radius*;
in terms of the Förster radius the transfer rate is

$$k_{D \to A} = \frac{1}{\tau_{\mathrm{rad}}^{(D)}} \left(\frac{R_{\mathrm{F}}}{X_{DA}} \right)^6$$

the absolute value of the Förster rate is determined by the donor emission rate and the acceptor absorption coefficient;

3.2.3 An Alternative Derivation of the Excitation Energy Transfer Rate

we give a somewhat more general description; therefore we introduce electronic states of the two molecules interacting with each other (the dimer) as $|m\rangle$ ($m = D, A$); they count the molecule in the excited state and are simply defined as

$$|D\rangle = |\varphi_{De}\varphi_{Ag}\rangle$$

$$|A\rangle = |\varphi_{Dg}\varphi_{Ae}\rangle$$

next the zero order Hamiltonian for the dimer is introduced

$$H_0 = \sum_m \left(T_{\mathrm{nuc}} + U_m(q) \right) |m\rangle\langle m|$$

with the common PES $U_D = U_{De} + U_{Ag}$ and $U_A = U_{Dg} + U_{Ae}$; as in the foregoing section the donor as well as the acceptor molecule have their own set of vibrational coordinates the Coulombic inter–molecular coupling defines the perturbation

$$\hat{V} = \sum_{mn} J_{mn} |m\rangle\langle n|$$

the respective transition rate can be written as

$$k_{D \to A} = \frac{2\pi}{\hbar} |J_{DA}|^2 \mathcal{D}_{DA}(\omega_{DA})$$

here, we introduced the combined density of states $\mathcal{D}_{DA}$ for the transition

$$\mathcal{D}_{DA} = \frac{1}{2\pi\hbar} \int dt \, \mathrm{tr}_{\mathrm{vib}}\{\hat{R}_D \hat{U}_D^+(t) \hat{U}_A(t)\}$$

the $\hat{U}_m(t)$ denote the time–evolution operator describing nuclear motions of the whole dimer if molecule m is excited;
the vibrational equilibrium statistical operator takes the following form:

$$\hat{R}_D = \hat{R}_{De} \hat{R}_{Ag}$$

in a similar manner the time–evolution operator is obtained as

$$\hat{U}_D(t) = \hat{U}_{De}(t) \hat{U}_{Ag}(t)$$

and

$$\hat{U}_A(t) = \hat{U}_{Dg}(t) \hat{U}_{Ae}(t)$$

as a result the trace expression reads

$$\mathrm{tr}_{\mathrm{vib}}\{\hat{R}_D \hat{U}_D^+(t) \hat{U}_A(t)\} = \mathrm{tr}_D\{\hat{R}_{De} \hat{U}_{De}^+(t) \hat{U}_{Dg}(t)\} \mathrm{tr}_A\{\hat{R}_{Ag} \hat{U}_{Ag}^+(t) \hat{U}_{Ae}(t)\}$$

$\mathrm{tr}_D\{...\}$ denotes the trace expression with respect to the donor molecule vibrational coordinates and $\mathrm{tr}_A\{...\}$ the trace related to the acceptor coordinates;, the separation became possible since both molecules posses their own set of vibrational coordinates; the following formulas may be formulated by the donor and acceptor combined DOS; however, it is more appropriate to define correlation functions for the de–excitation of the donor

$$C_{De\to g}(t) = \mathrm{tr}_D\{\hat{R}_{De} U_{De}^+(t) U_{Dg}(t)\}$$

and the excitation of the acceptor

$$C_{Ag\to e}(t) = \mathrm{tr}_A\{\hat{R}_{Ag} U_{Ag}^+(t) U_{Ae}(t)\}$$

the the combined density of states defining the rate can be written as

$$\mathcal{D}_{DA} = \frac{1}{2\pi\hbar} \int dt \, C_{De\to g}(t) C_{Ag\to e}(t)$$

if the correlation functions are replaced by their Fourier–transforms it follows

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

Correlation Functions for the Case of Harmonic Vibrational Motion

if the vibrational dynamics in the donor as well as in the acceptor are harmonic the above introduced correlation functions can be drastically specified (as already demonstrated when dealing with electron transfer reactions)
to simplify the notation we drop the donor and acceptor index for a moment and introduce a correlation function $C_{a\to b}(t)$ which refers to the donor de–excitation ($a = e$, $b = g$) or the acceptor excitation ($a = g$, $b = e$); it reads

$$C_{a\to b}(t) = \exp\left(i\omega_{ab}t - G(0) + G(t)\right)$$

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we introduced the transition frequencies (difference of the minima of the PES related to the donor or the acceptor)

$$\omega_{ab} = (U_a^{(0)} - U_b^{(0)})/\hbar$$

and the so–called line shape function

$$G(t) = \int\limits_0^\infty d\omega \ \left[(1 + n(\omega))e^{-i\omega t} + n(\omega)e^{i\omega t}\right] J(\omega)$$

the spectral density reads

$$J(\omega) = \sum_\xi \big(g_e(\xi) - g_g(\xi)\big)^2 \delta(\omega - \omega_\xi)$$

we can use the spectral density to write the Stokes shift as

$$S = 2\hbar \int\limits_0^\infty d\omega \ \omega J(\omega)$$

let us separate the function $G(t)$ into its real and imaginary part

$$G(t) = G_1(t) - iG_2(t)$$

where

$$G_1(t) = \int\limits_0^\infty d\omega \ \cos(\omega t)[1 + 2n(\omega)]J(\omega)$$

and

$$G_2(t) = \int\limits_0^\infty d\omega \ \sin(\omega t)J(\omega)$$

according to this separation of $G(t)$ the Fourier–transformed correlation function reads

$$C_{a \to b}(\omega) = \int dt \ \exp\left\{i\left[(\omega + \omega_{ab})t - G_2(t)\right] + G_1(t) - G_1(0)\right\}$$

the imaginary part of $G(t)$ introduces a shift of the electronic transition frequency ω_{ab}, whereas the real part leads to an exponential decay
one example for J is the so–called Debye spectral density

$$\omega J(\omega) = \Theta(\omega)\frac{S}{\pi\hbar}\frac{\omega_{\mathrm{D}}}{\omega^2 + \omega_{\mathrm{D}}^2}$$

it is related to the dynamics in a polar solvent;
in order to discuss the resulting $C_{a \to b}$ we may introduce two time scales; first we have the time scale for vibrational motion characterized by

$$T_{\mathrm{vib}} \approx 1/\omega_{\mathrm{D}}$$

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the second time scale is related to the strength of the coupling between electronic and nuclear motions and can be interpreted as the time scale for fluctuations of the electronic energy gap

$$T_{\text{fluc}} = \hbar/\sqrt{k_{\text{B}}TS}$$

we can distinguish two limits:

Slow nuclear motion

we suppose that $T_{\text{vib}} \gg T_{\text{fluc}}$; one obtains

$$C_{a\to b}^{(\text{slow})}(t) = \exp\left(i(\omega_{ab} - S/2\hbar)t - k_{\text{B}}TSt^2/2\hbar^2\right)$$

and after Fourier–transformation

$$C_{a\to b}^{(\text{slow})}(\omega) = \sqrt{2\pi}T_{\text{fluc}}\exp\left\{-\frac{1}{2}\left(T_{\text{fluc}}[\omega + \omega_{ab} - S/2\hbar]\right)^2\right\}$$

$$\equiv \sqrt{\frac{2\pi\hbar^2}{k_{\text{B}}TS}}\exp\left\{-\frac{\left(\hbar[\omega + \omega_{ab}] - S/2\right)^2}{2k_{\text{B}}TS}\right\}$$

this case is known as the limit of *inhomogeneous broadening*, where the time scale for nuclear motion is such that the nuclei can be considered to be frozen; it results, for example, in a Gaussian absorption line shape centered around the vertical Franck–Condon transition $\omega = \omega_{eg} + S/2$

Fast nuclear motion

here, $T_{\text{vib}} \ll T_{\text{fluc}}$ and the absorption line shape follows as a Lorentzian ($\tau = T_{\text{fluc}}^2/T_{\text{vib}}$)

$$C_{a\to b}^{(\text{fast})}(t) = \exp\left(i\omega_{ab}t - |t|/\tau\right)$$

and a Fourier–transformation results in

$$C_{a\to b}^{(\text{fast})}(\omega) = \frac{2/\tau}{(\omega + \omega_{ab})^2 + 1/\tau^2}$$

this is the limit of *homogeneous broadening*; note that the absorption is now centered at the electronic transition frequency and the Stokes shift does not appear; it can be rationalized by the fact that the nuclear motion is so fast that only the electronic transition which is averaged with respect to the nuclear dynamics is detected in the experiment; finally, we point out that the transition between the limits of inhomogeneous and homogeneous broadening can be observed upon changing the temperature; while at low temperature the nuclear motions are frozen and the line shape is Gaussian, at higher temperature it becomes Lorentzian; this phenomenon is also known as *motional line narrowing*;

Rate Expressions in Two Limiting Cases

while a computation of the correlation functions is best carried out in the time domain an interpretation should be given in terms of released and absorbed excitation energy, i.e. in the frequency domain; therefore, we quote again the Fourier–transformed single molecule correlation functions now specified for the donor and the acceptor and first for slow nuclear motion

$$C_{De\to g}^{(\text{slow})}(-\omega) = \sqrt{\frac{2\pi\hbar^2}{k_{\text{B}}TS_D}}\exp\left\{-\frac{\left(\hbar[\omega - \omega_{Deg}] + S_D/2\right)^2}{2k_{\text{B}}TS_D}\right\}$$

$$C_{Ag\to e}^{(\text{slow})}(\omega) = \sqrt{\frac{2\pi\hbar^2}{k_{\mathrm{B}}TS_A}} \exp\left\{ -\frac{\left(\hbar[\omega - \omega_{Aeg}] - S_A/2\right)^2}{2k_{\mathrm{B}}TS_A} \right\}$$

we distinguished between donor and acceptor transition frequencies and Stokes–shifts the correlation function for the fast nuclear motion read

$$C_{De\to g}^{(\text{fast})}(-\omega) = \frac{2/\tau_D}{(\omega - \omega_{Deg})^2 + 1/\tau_D^2}$$

and

$$C_{Ag\to e}^{(\text{fast})}(\omega) = \frac{2/\tau_A}{(\omega - \omega_{Aeg})^2 + 1/\tau_A^2}$$

next we present for both cases the combined DOS for the donor acceptor EET; the case of slow nuclear motion leads to ($\omega_{DA} = \omega_{Deg} - \omega_{Aeg}$, $S_{DA} = S_D + S_A$)

$$\mathcal{D}_{DA}^{(\text{slow})} = \frac{1}{\sqrt{2\pi k_{\mathrm{B}}TS_{DA}}} \exp\left\{ -\frac{\left(\hbar\omega_{DA} - S_{DA}/2\right)^2}{2k_{\mathrm{B}}TS_{DA}} \right\} .$$

in the case of fast nuclear motion we arrive at

$$\mathcal{D}_{DA}^{(\text{fast})} = \frac{1}{\pi\hbar} \frac{\gamma_{DA}}{\omega_{DA}^2 + \gamma_{DA}^2}$$

with

$$\gamma_{DA} = 1/\tau_D + 1/\tau_A$$