NITheCS Mini-School on "Modelling Optical Spectra"

Lecture 2: Coupled molecular dipoles:

Molecular excitons & Förster interactions

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Outline of the 4 lectures

1. Basic principles of electronic spectroscopy
2. Coupled molecular dipoles: Molecular excitons & Förster interactions
3.
   - Linear & nonlinear spectroscopy
4.
   - EET in the strong-coupling limit

Dr. Towan Nöthling

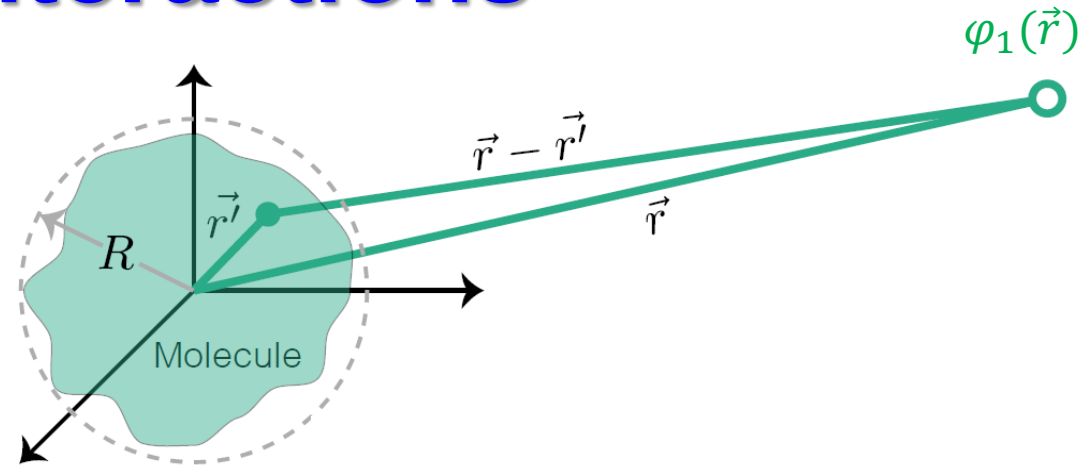
Outline of this lecture

1. Intermolecular interactions
2. The excitonically coupled dimer
3. H- and J-aggregates
4. Förster resonance energy transfer (FRET)

Intermolecular interactions

Consider a molecule's electron cloud with a continuous volume charge density $\rho(\vec{r}')$, generating an electrostatic scalar potential at $\vec{r}$:

$$\varphi(\vec{r}) = \frac{1}{4\pi\epsilon_0}\int_V \frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}d\tau'$$



The corresponding electric field is $\vec{E} = -\vec{\nabla}\varphi(\vec{r})$

If $|\vec{r}| \gg R$ we can do Taylor series expansion about $\vec{r}' = 0$

$$\frac{1}{|\vec{r}-\vec{r}'|} = \frac{1}{r} - (\vec{r}'\cdot\nabla)\frac{1}{r} + \frac{1}{2}(\vec{r}'\cdot\nabla)^2\frac{1}{r} - \ldots$$

We can thus expand $\varphi(\vec{r})$ into multipole moments:

$$\varphi(\vec{r}) = \frac{1}{4\pi\epsilon_0}\left[\frac{q}{r} + \frac{\vec{\mu}\cdot\vec{r}}{r^3} + \frac{1}{2}\frac{\vec{r}\cdot\mathbf{Q}\cdot\vec{r}}{r^5} + \ldots\right]$$

Multipole moments of a charge distribution

Electric monopole: $q = \int_V \rho(\vec{r})\,d\tau$

Electric dipole: $\vec{\mu} = \int_V \vec{r}\rho(\vec{r})\,d\tau,$

Electric quadrupole: $Q_{i,j} = \int_V (3r_i r_j - r^2\delta_{i,j})\rho(\vec{r})\,d\tau,$

Intermolecular interactions

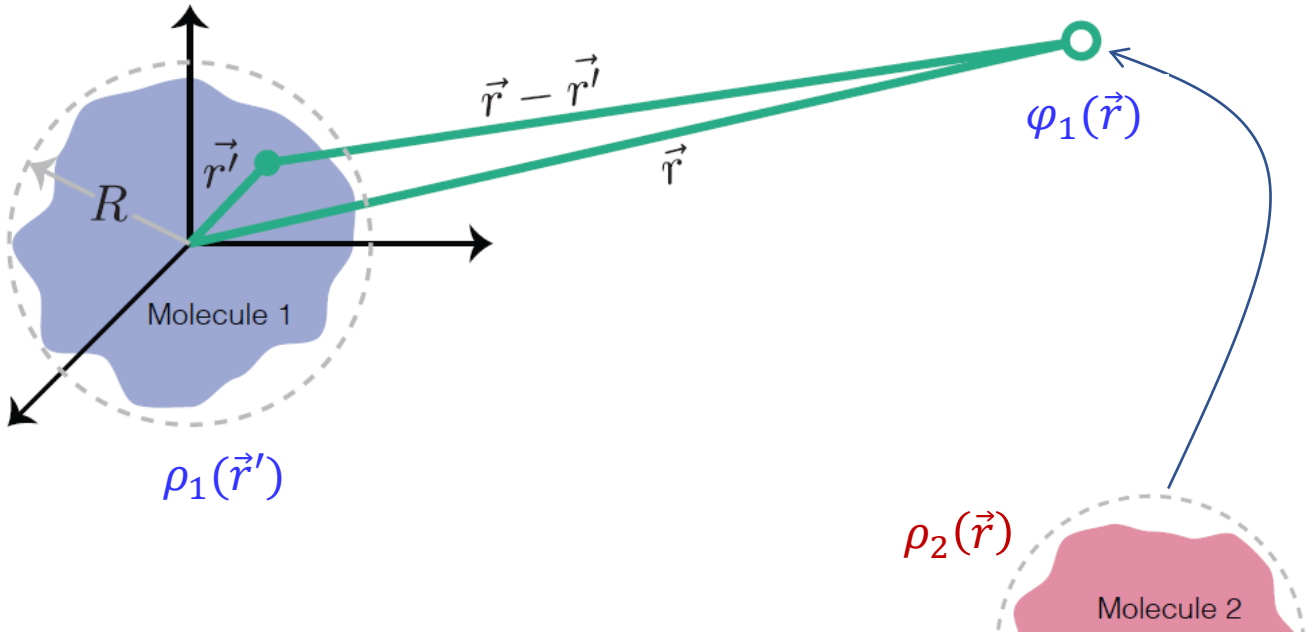
Now place molecule 2 with charge density $\rho_2(\vec{r})$ at $\vec{r}$.

Since molecule 1 generates an electrostatic scalar potential $\varphi_1(\vec{r})$ at this position, $\varphi_1(\vec{r})$ and $\rho_2(\vec{r})$ interact with a potential energy of

$$V(\vec{r}) = \int_V \rho_2(\vec{r})\varphi_1(\vec{r})\, d\tau$$

But due to ρ_2, molecule 2 also generates an electrostatic scalar potential, φ_2.
Molecule 1's centre-of-mass is at $-\vec{r}$ with respect to molecule 2, i.e., we must consider $\rho_1(\vec{r}' - \vec{r})$ interacting with $\varphi_2(\vec{r}' - \vec{r})$ with potential energy

$$V(\vec{r}' - \vec{r}) = \int_V \rho_1(\vec{r}' - \vec{r})\varphi_2(\vec{r}' - \vec{r})\, d\tau$$



The total (electrostatic) potential energy is then:

$$V_{12}(\vec{r}) = \frac{1}{4\pi\varepsilon}\left[\frac{q_1 q_2}{r} + \frac{q_1(\vec{\mu}_2 \cdot \hat{r}) - q_2(\vec{\mu}_1 \cdot \hat{r})}{r^2} + \frac{\vec{\mu}_1 \cdot \vec{\mu}_2 - 3(\vec{\mu}_1 \cdot \hat{r})(\vec{\mu}_2 \cdot \hat{r})}{r^3} + \sum_{\alpha,\beta=1}^{3} \hat{r}_\alpha \hat{r}_\beta \left(q_1 Q_{2,\alpha\beta} + q_2 Q_{1,\alpha\beta}\right)\frac{1}{2r^3} + \cdots\right]$$

Intermolecular interactions

For charge distributions $\rho_1(\vec{r})$ and $\rho_2(\vec{r})$: $V_{Coulomb} = \frac{1}{4\pi\varepsilon}\iint \frac{\rho_1(\vec{r})\rho_2(\vec{r}')}{|\vec{r}-\vec{r}'|} d\tau\, d\tau'$

For each molecule we can calculate the following:

Total charge $q_i = \int \rho_i(\vec{r}) d\tau$

Dipole moment $\vec{\mu}_i = \int (\vec{r}-\vec{r}_i)\rho_i(\vec{r}) d\tau$

Quadrupole tensor $Q_{i,\alpha\beta} = \int \left[3(\vec{r}-\vec{r}_i)_\alpha(\vec{r}-\vec{r}_i)_\beta - \delta_{\alpha\beta}(\vec{r}-\vec{r}_i)^2\right]\rho_i(\vec{r}) d\tau$

etc.

$$V_{12}(\vec{r}) = \frac{1}{4\pi\varepsilon}\left[\frac{q_1 q_2}{r} + \frac{q_1(\vec{\mu}_2\cdot\hat{r}) - q_2(\vec{\mu}_1\cdot\hat{r})}{r^2} + \frac{\vec{\mu}_1\cdot\vec{\mu}_2 - 3(\vec{\mu}_1\cdot\hat{r})(\vec{\mu}_2\cdot\hat{r})}{r^3} + \sum_{\alpha,\beta=1}^{3}\hat{r}_\alpha\hat{r}_\beta\left(q_1 Q_{2,\alpha\beta} + q_2 Q_{1,\alpha\beta}\right)\frac{1}{2r^3} + \cdots\right]$$

$\vec{\mu} \to \vec{\mu}_{nk} \equiv \langle k|\hat{\vec{\mu}}|n\rangle$

Dipole-dipole approximation for uncharged molecules:

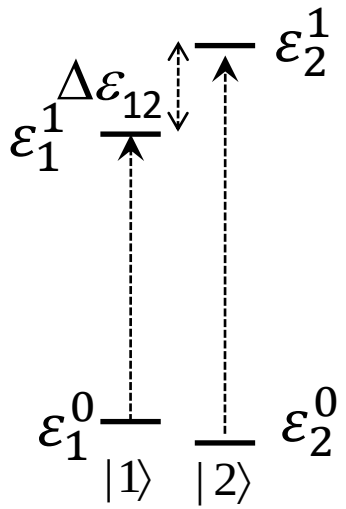
$$V_{12} = \frac{1}{4\pi\varepsilon}\langle\phi_1^1\phi_2^0|\frac{\vec{\boldsymbol{\mu}}_1\cdot\vec{\boldsymbol{\mu}}_2 - 3(\vec{\boldsymbol{\mu}}_1\cdot\hat{\boldsymbol{r}})(\vec{\boldsymbol{\mu}}_2\cdot\hat{\boldsymbol{r}})}{r^3}|\phi_1^0\phi_2^1\rangle = \frac{1}{4\pi\varepsilon}\frac{\vec{\boldsymbol{\mu}}_1^{01}\cdot\vec{\boldsymbol{\mu}}_2^{01} - 3(\vec{\boldsymbol{\mu}}_1^{01}\cdot\hat{\boldsymbol{r}})(\vec{\boldsymbol{\mu}}_2^{01}\cdot\hat{\boldsymbol{r}})}{r^3}$$

The excitonically coupled dimer

Consider two spatially separated, interacting molecular dipoles.

Each molecule has its own set of electronic states and energy levels, which, in the absence of the interaction, are governed by $\hat{H}_n \varphi_n^i = \varepsilon_n^i \varphi_n^i \quad (n = 1, 2)$

Consider the simplest case (a two-level system): $i = 0, 1$



Ground-state wavefunction: $\psi^0 = \varphi_1^0 \varphi_2^0$

Ground-state energy:

$$E^0 = \left\langle \varphi_1^0 \varphi_2^0 \middle| \hat{\mathrm{H}}_1 + \hat{\mathrm{H}}_2 + \hat{\mathrm{V}} \middle| \varphi_1^0 \varphi_2^0 \right\rangle$$

$$= \varepsilon_1^0 + \varepsilon_2^0 + \left\langle \varphi_1^0 \varphi_2^0 \middle| \hat{\mathrm{V}} \middle| \varphi_1^0 \varphi_2^0 \right\rangle$$

$$= \varepsilon_1^0 + \varepsilon_2^0 + V_{00}$$

Excited-state wavefunction: $\psi^f = c_1 \varphi_1^1 \varphi_2^0 + c_2 \varphi_1^0 \varphi_2^1$

Excited dimer SE: $\left(\hat{\mathrm{H}}_1 + \hat{\mathrm{H}}_2 + \hat{\mathrm{V}}\right) \psi^f = E^f \psi^f$

This can be solved through time-independent degenerate PT.

The excitonically coupled dimer

Non-trivial solutions require: $\begin{vmatrix} \varepsilon_1^1 + \varepsilon_2^0 + V_{11} - E^f & V_{12} \\ V_{21} & \varepsilon_1^0 + \varepsilon_2^1 + V_{22} - E^f \end{vmatrix} = 0$

where $V_{11} = \langle \varphi_1^1 \varphi_2^0 | \hat{V} | \varphi_1^1 \varphi_2^0 \rangle$

$V_{22} = \langle \varphi_1^0 \varphi_2^1 | \hat{V} | \varphi_1^0 \varphi_2^1 \rangle$

$V_{12} = \langle \varphi_1^0 \varphi_2^1 | \hat{V} | \varphi_1^1 \varphi_2^0 \rangle$

$V_{21} = \langle \varphi_1^1 \varphi_2^0 | \hat{V} | \varphi_1^0 \varphi_2^1 \rangle$

Or with $|\varphi_a\rangle = |\varphi_1^1 \varphi_2^0\rangle$ and $|\varphi_b\rangle = |\varphi_1^0 \varphi_2^1\rangle$, $W_{ab} = \langle \varphi_b | \hat{H}' | \varphi_a \rangle$

resonance interaction terms

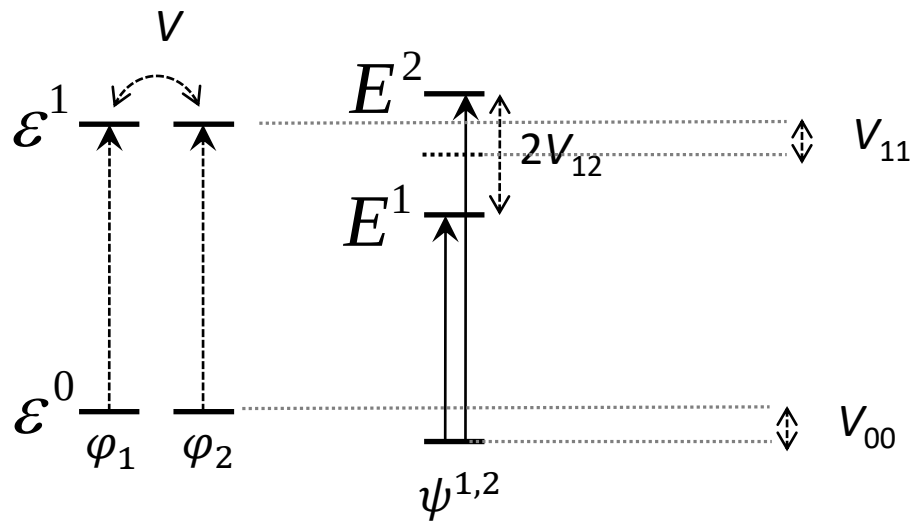
Identical molecules: with $\varepsilon_1^0 = \varepsilon_2^0 = 0$, $\varepsilon_1^1 = \varepsilon_2^1 = \varepsilon^1$, $V_{12} = V_{21}$, and $V_{11} = V_{22}$

Then $\left(\varepsilon^1 + V_{11} - E^f\right)^2 = V_{12}^2$

Hence, $E^{1,2} = \varepsilon^1 + V_{11} \pm V_{12}$

$$\psi^{1,2} = \frac{1}{\sqrt{2}}\left(\varphi_1^1 \varphi_2^0 \pm \varphi_1^0 \varphi_2^1\right)$$

$$= \frac{1}{\sqrt{2}}\left(|e_1 g_2\rangle \pm |g_1 e_2\rangle\right)$$



The excitonically coupled dimer: optical transitions

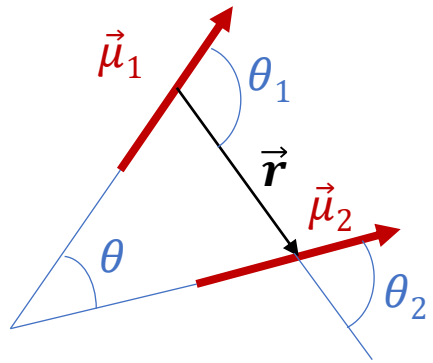
Transition dipole moment: $\vec{\mu}^{01} \equiv \langle \varphi_1^1 | \hat{\vec{\mu}} | \varphi_1^0 \rangle$

Dipole strength $D_{01} = \left|\vec{\mu}^{01}\right|^2 = 1.01 \cdot 10^{-61} \int_{band} \frac{\varepsilon(\omega)}{\omega} d\omega \quad (\mathrm{Cm})^2$

Excitonic transitions (and hence dipole strengths) depend on the structure of the dimer.

For isoenergetic molecules:

$$D^{1,2} = \left\langle \psi^{1,2} \right|_{\mu} \hat{\mu}_1 + \hat{\mu}_2 \left| \varphi_1^0 \varphi_2^0 \right\rangle^2 = D_{01}\left(1 \pm \cos\theta\right)$$



Example: For anti-parallel dipoles, $\cos\theta = -1$

$D^1 = 0$: no absorption occurs to the 1st level

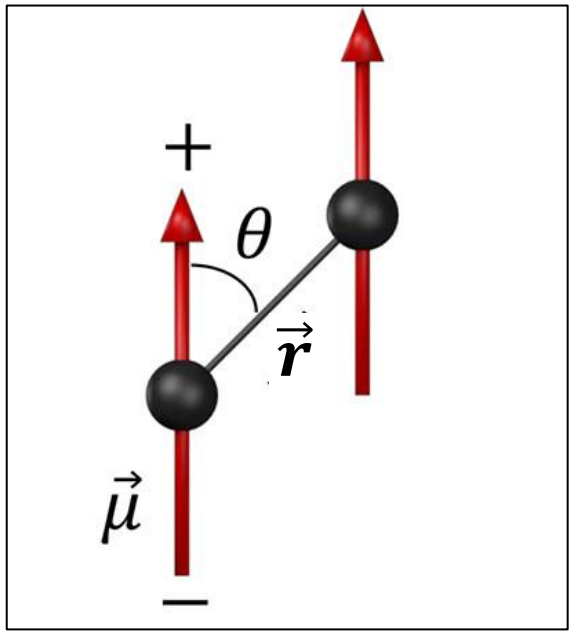
$D^2 = 2D_{01}$: all oscillator strength is accumulated in transition to the 2nd level

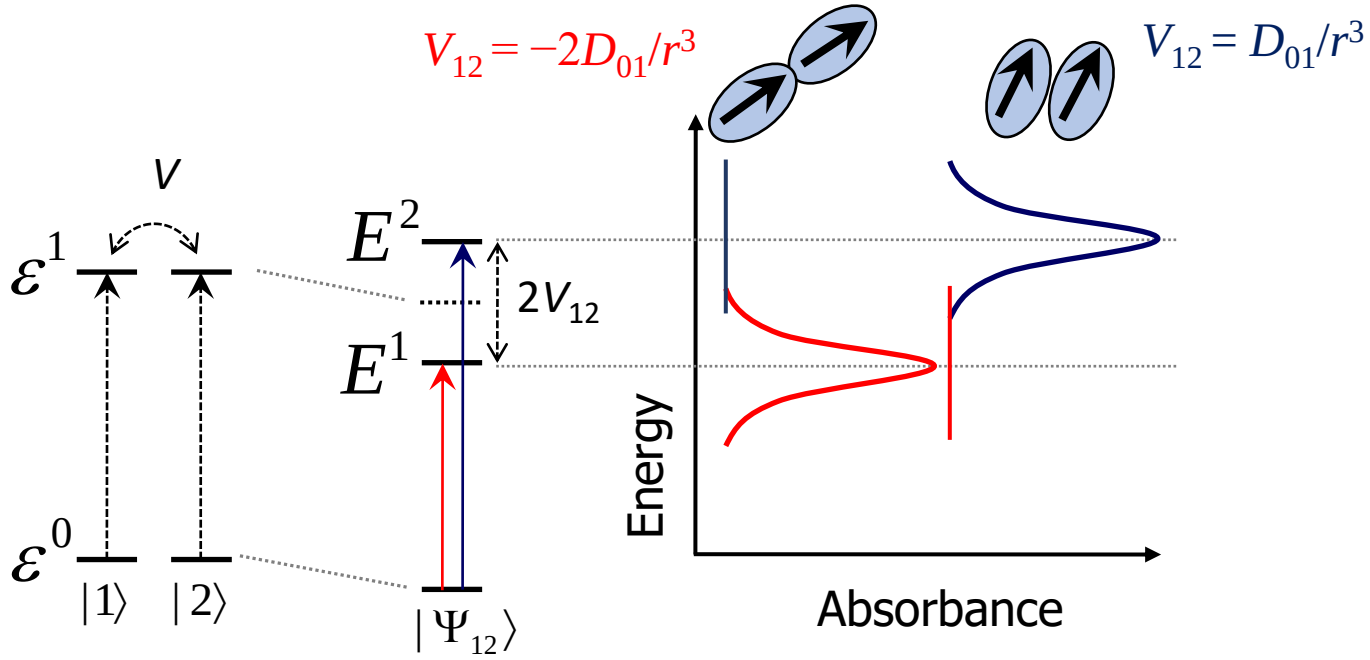
Excitonically coupled dimer: parallel dipoles

Dipole-dipole approximation for uncharged molecules:

$$V_{12} = \frac{1}{4\pi\varepsilon}\langle\phi_1^1\phi_2^0|\frac{\vec{\mu}_1\cdot\vec{\mu}_2 - 3(\vec{\mu}_1\cdot\hat{r})(\vec{\mu}_2\cdot\hat{r})}{r^3}|\phi_1^0\phi_2^1\rangle = \frac{1}{4\pi\varepsilon}\frac{\vec{\mu}_1^{01}\cdot\vec{\mu}_2^{01} - 3(\vec{\mu}_1^{01}\cdot\hat{r})(\vec{\mu}_2^{01}\cdot\hat{r})}{r^3}$$

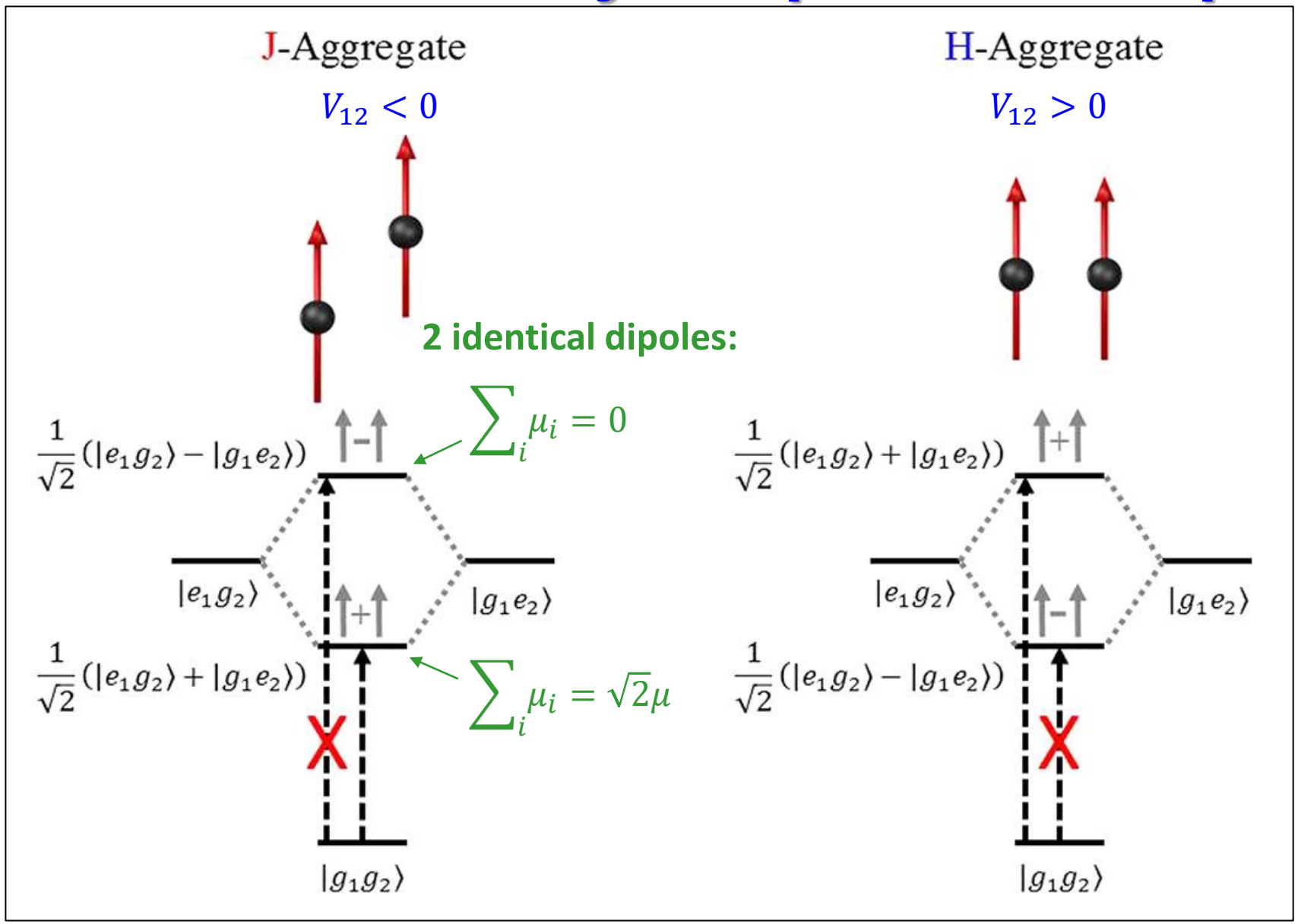
For parallel, identical dipoles, $V_{12} = \frac{\mu^2}{4\pi\varepsilon}\frac{1-3\cos^2\theta}{r^3}$

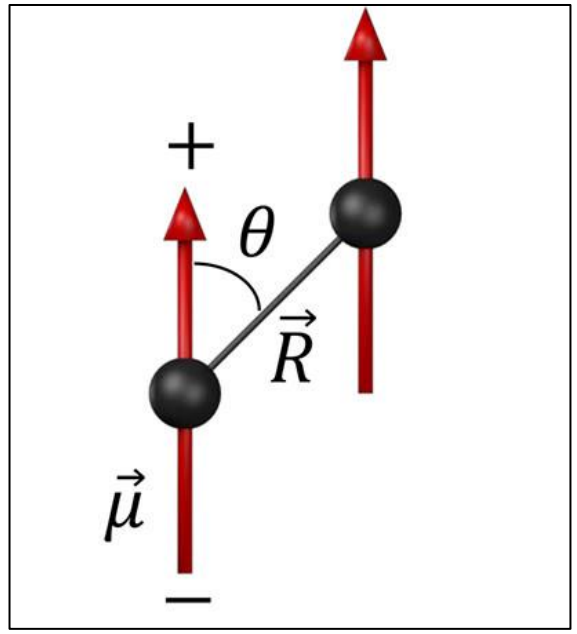




Hestand & Spano, *Chem. Rev.* 2018, 118, 15, 7069-7163

Excitonically coupled dimer: parallel dipoles





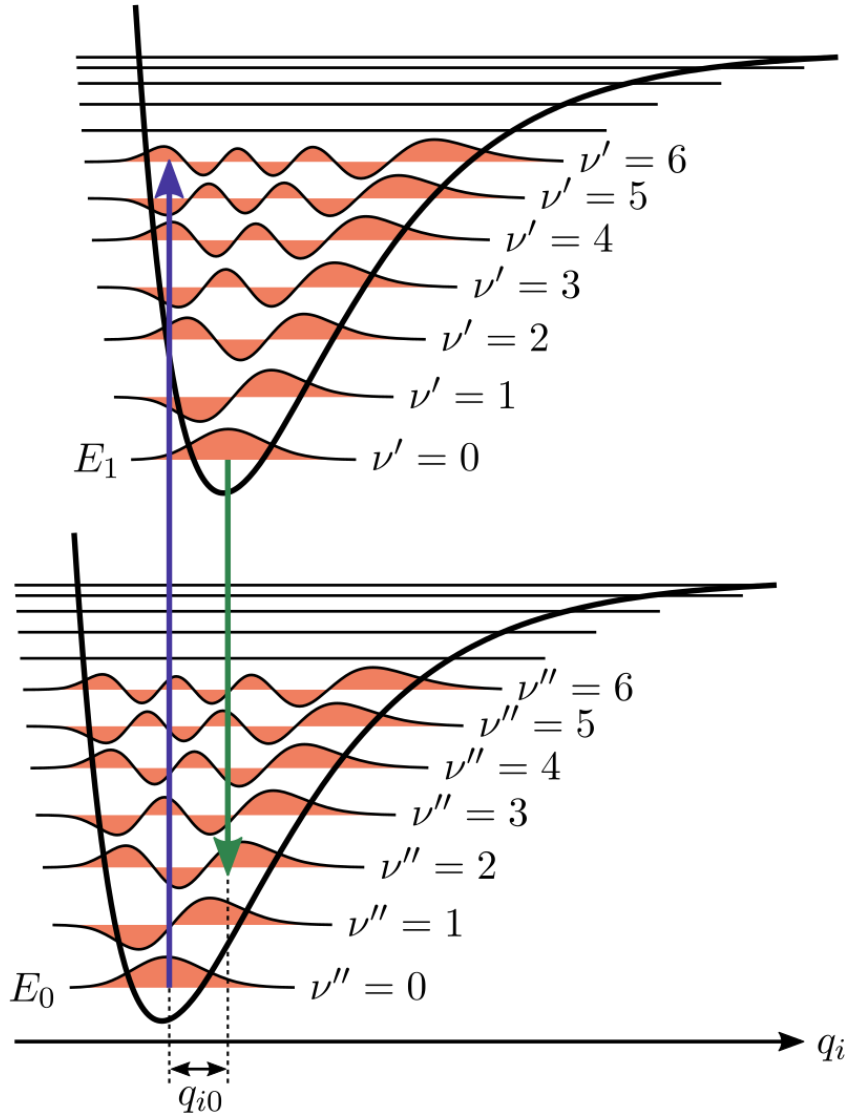
$$V_{12} = \frac{\mu^2}{4\pi\varepsilon}\frac{1-3\cos^2\theta}{r^3}$$

J-aggregate: $\theta < \theta_M$
H-aggregate: $\theta_M < \theta < \pi/2$
$\theta_M = 54.7°$

Hestand & Spano, *Chem. Rev.* 2018, 118, 15, 7069-7163

Franck-Condon principle

$$\vec{\mu}_{if} = \langle e_f \upsilon_f \sigma_f | \hat{\vec{\mu}} | e_i \upsilon_i \sigma_i \rangle = -e \sum_i \langle e_f | \vec{r}_i | e_i \rangle \langle \upsilon_f | \upsilon_i \rangle \langle \sigma_f | \sigma_i \rangle$$



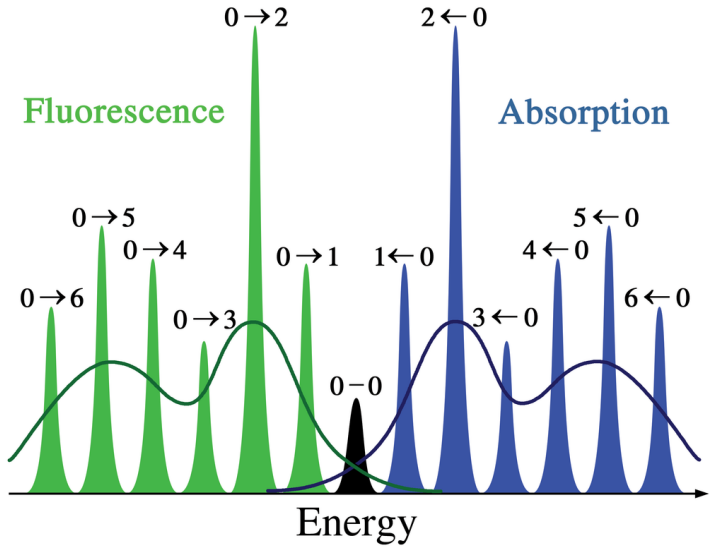
Transition probability dictated by:

FC factor $S^2 = |\langle \upsilon_f | \upsilon_i \rangle|^2$

Symmetry
1. Laporte's orbital selection rules
2. Phase relation between multiple dipoles

Spin selection rules: multiplicity

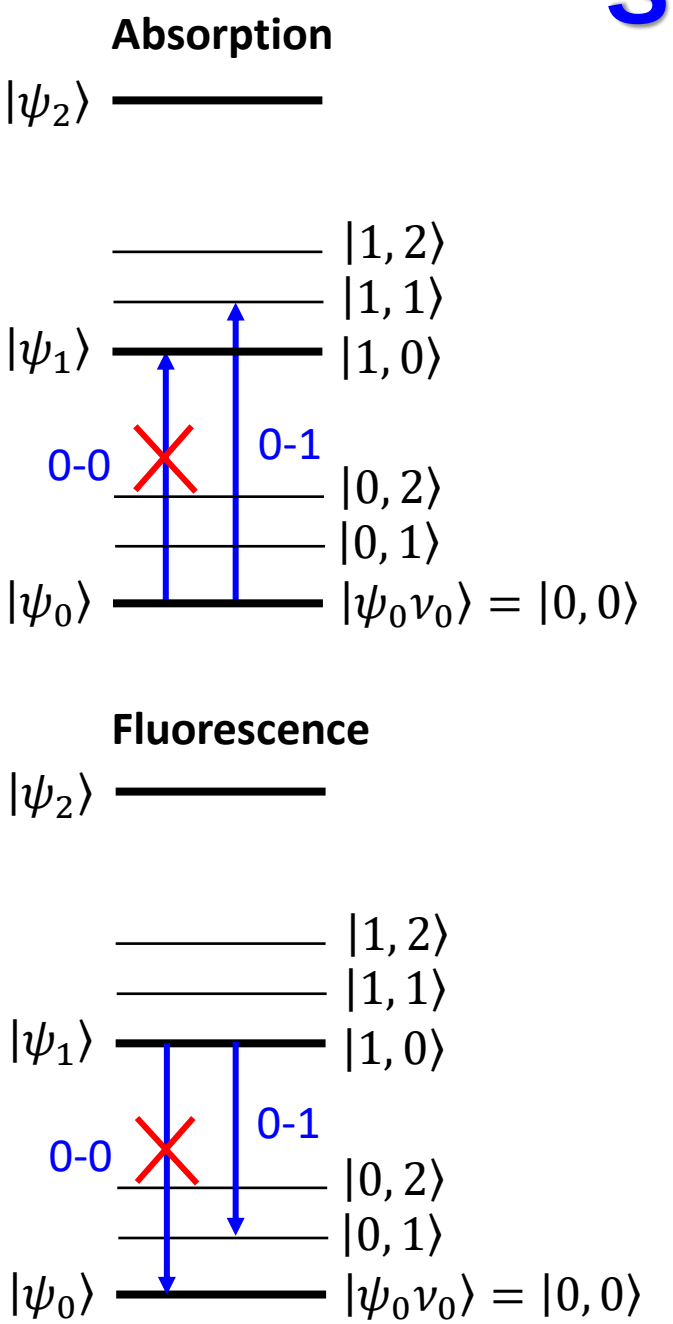
Can be broken by perturbations



Mark M. Somoza, https://commons.wikimedia.org/wiki/File:Franck_Condon_Diagram.svg

Mark M. Somoza, https://commons.wikimedia.org/wiki/File:Vibration-fluor-abs.png

Symmetry-breaking perturbations



For H-aggregates: $\langle\psi_1|\vec{r}_i|\psi_0\rangle = 0$

1. Structural disorder
   I_{0-0} increases with temperature

2. Mixing with $|\psi_2\rangle$
   0-1 side-band + blue-shift

Huang-Rhys factor: $S = \dfrac{I_{01}}{I_{00}}$

The same perturbations apply to fluorescence, with the effect of disorder strongly enhanced because of Kasha's rule.

Determine aggregation types:

1. Temperature-dependent abs./fluorescence spectral evolution
2. Fluorescence lifetime
3. Fluorescence quantum yield

Franck–Condon analysis of PL spectra

S : Huang-Rhys factor
E_P: Phonon energy
Γ : Gaussian lineshape

J-aggregates: $$I_J(h\omega) \propto (n\hbar\omega)^3 e^{-S}\left[\sum_{m=0}\frac{S^m}{m!}\Gamma(\hbar\omega - E_o + mE_P)\right]$$

Franck–Condon analysis of PL spectra

S : Huang-Rhys factor
E_P: Phonon energy
Γ : Gaussian lineshape
α : Exciton coherence number

J-aggregates: $$I_J(h\omega) \propto (n\hbar\omega)^3 e^{-S}\left[\sum_{m=0}\frac{S^m}{m!}\Gamma(\hbar\omega - E_o + mE_P)\right]$$

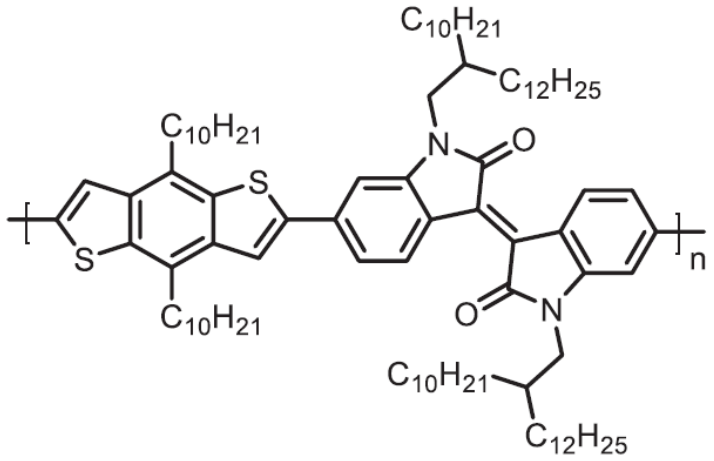
H-aggregates: $$I_H(h\omega) \propto (n\hbar\omega)^3 e^{-S}\left[\alpha\Gamma(\hbar\omega - E_o) + \sum_{m=1}\frac{S^m}{m!}\Gamma(\hbar\omega - E_o + mE_P)\right]$$

$$\propto = \begin{cases} 0, & \text{no disorder } (\mathrm{T} = 0\ \mathrm{K}) \Rightarrow \text{exciton delocalisation} \\ 1, & \text{completely disordered (high T)} \Rightarrow \text{exciton localisation} \end{cases}$$

→ spectral line-broadening + blue-shift
→ spectral line-narrowing + red-shift

Determining molecular aggregation types

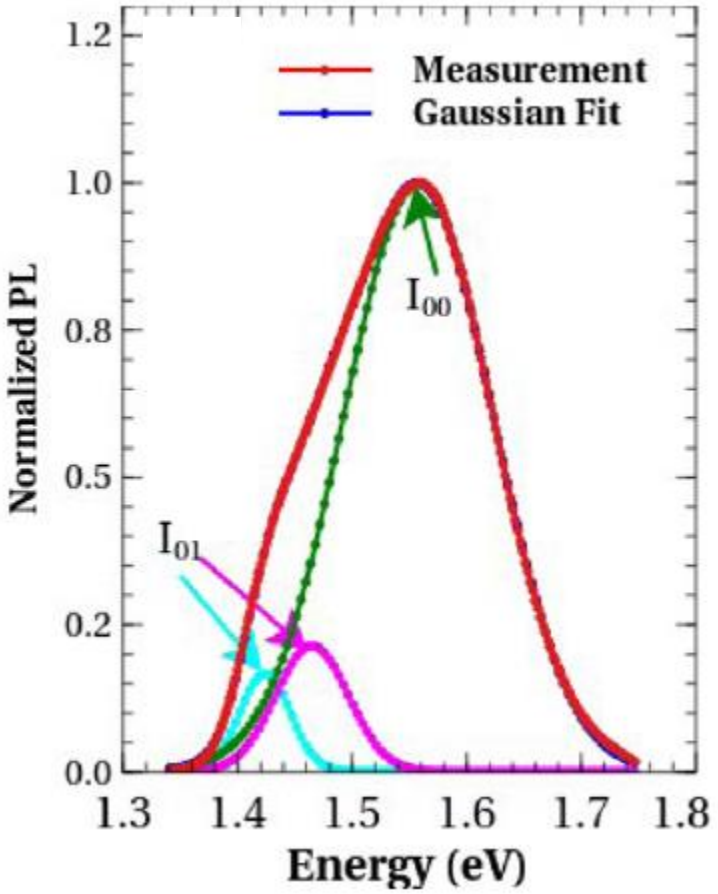
1. Temperature-dependent PL spectral evolution
2. PL lifetime
3. PL quantum yield

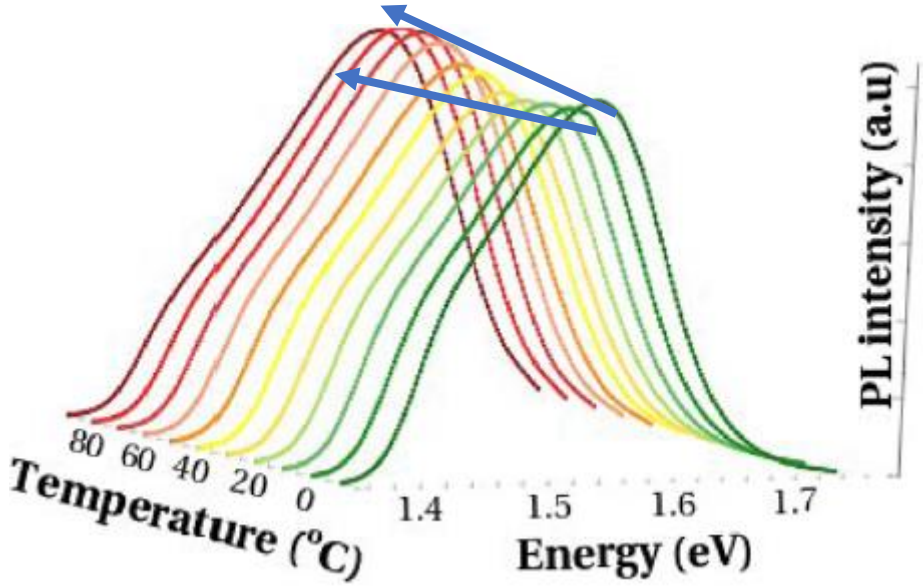


benzodithiophene–isoindigo copolymer

E Asmare, FG Hone, W Mammo, TPJ Krüger, NA Tegegne, *J Chem Phys* **159**, 034901 (2023)

Temperature-dependent PL spectral evolution



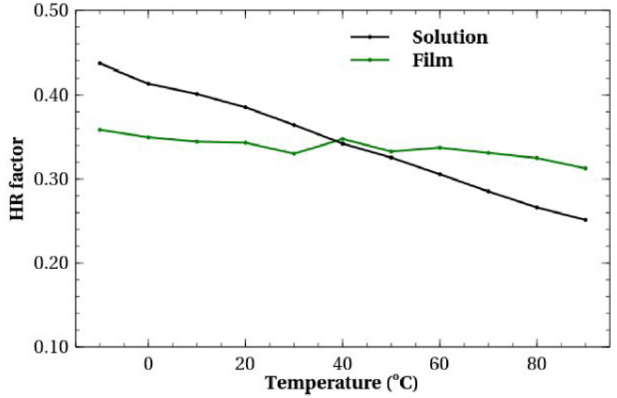


$$S = \frac{I_{01}}{I_{00}}$$

1a. Intensity increase ⟹ H-aggregates

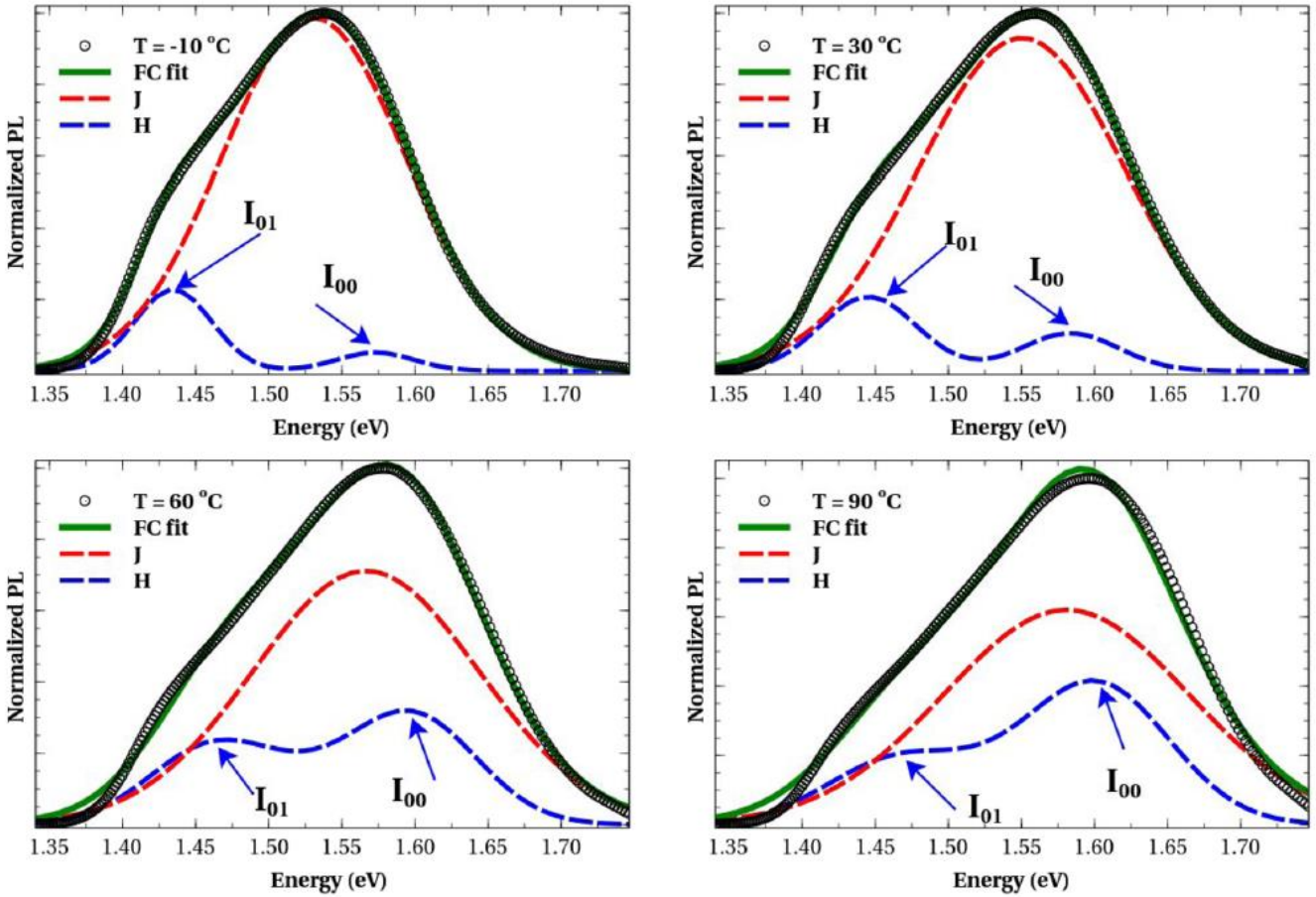
1b. S decreases ⟹ H-aggregates

2. Red-shift ⟹ H-aggregates



E Asmare, FG Hone, W Mammo, TPJ Krüger, NA Tegegne, *J Chem Phys* **159**, 034901 (2023)

Franck–Condon analysis of PL spectra



J-aggregates

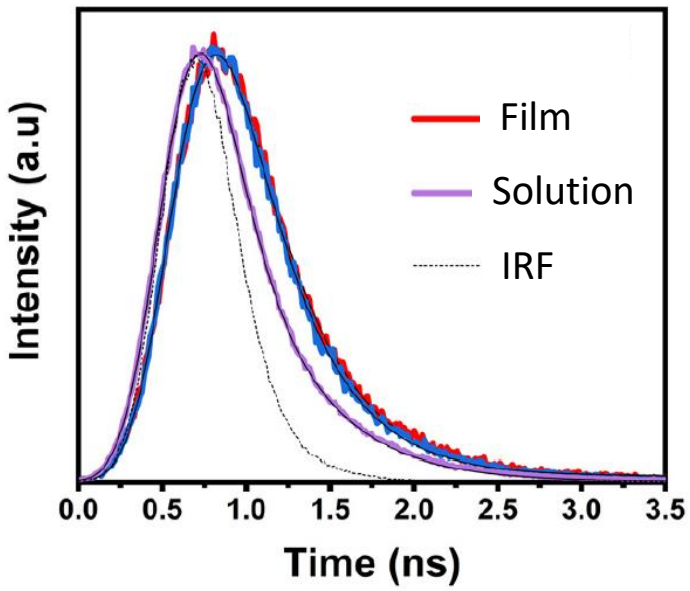
$$I_J(h\omega) \propto (n\hbar\omega)^3 e^{-S}\left[\sum_{m=0}\frac{S^m}{m!}\Gamma(\hbar\omega - E_o + mE_P)\right]$$

H-aggregates

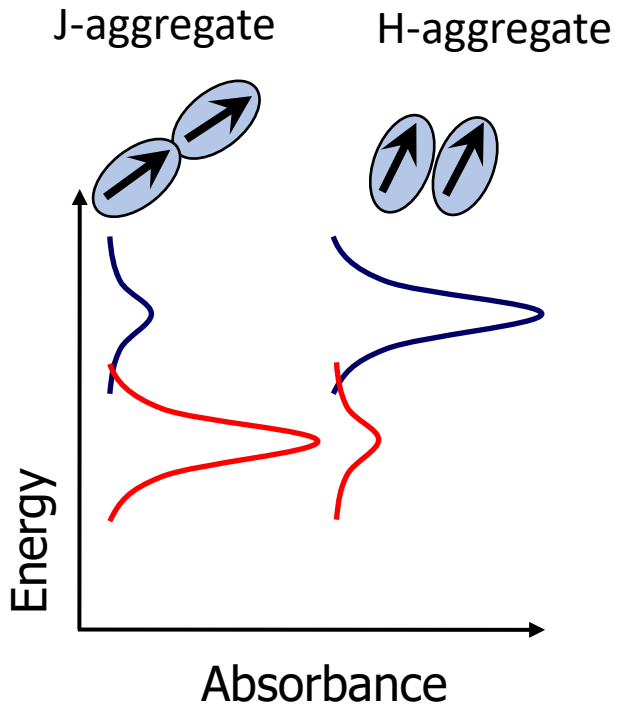
$$I_H(h\omega) \propto (n\hbar\omega)^3 e^{-S}\left[\begin{array}{c}\alpha\Gamma(\hbar\omega - E_o) + \\ \sum_{m=1}\frac{S^m}{m!}\Gamma(\hbar\omega - E_o + mE_P)\end{array}\right]$$

E Asmare, FG Hone, W Mammo, TPJ Krüger, NA Tegegne, *J Chem Phys* **159**, 034901 (2023)

PL lifetime and yield



$$IRF \otimes (A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2})$$



Sample	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	Avg. τ (ns)
Solution	0,3	66	1,0	34	0,57
Film	0,3	50	1,1	50	0,70

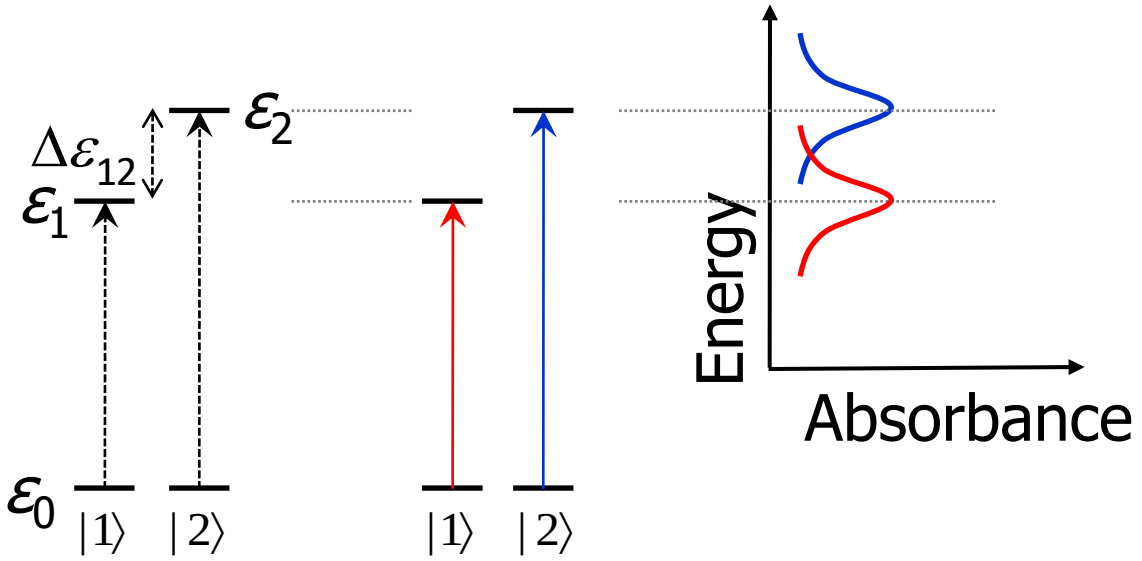
QY ~ 22%

Asmare et al. *J Chem Phys* **159**, 034901 (2023)
Asmare et al. *submitted*

Weak intermolecular coupling

$$V_{12} \ll \Delta\varepsilon_{12} \text{ or } V_{12} \ll V_{el-ph}$$

Excited-state wavefunction: $\psi^f = c_1\varphi_1^1\varphi_2^0 + c_2\varphi_1^0\varphi_2^1 = \varphi_1^1\varphi_2^0 + \varphi_1^0\varphi_2^1$



Förster regime: Localised excited states

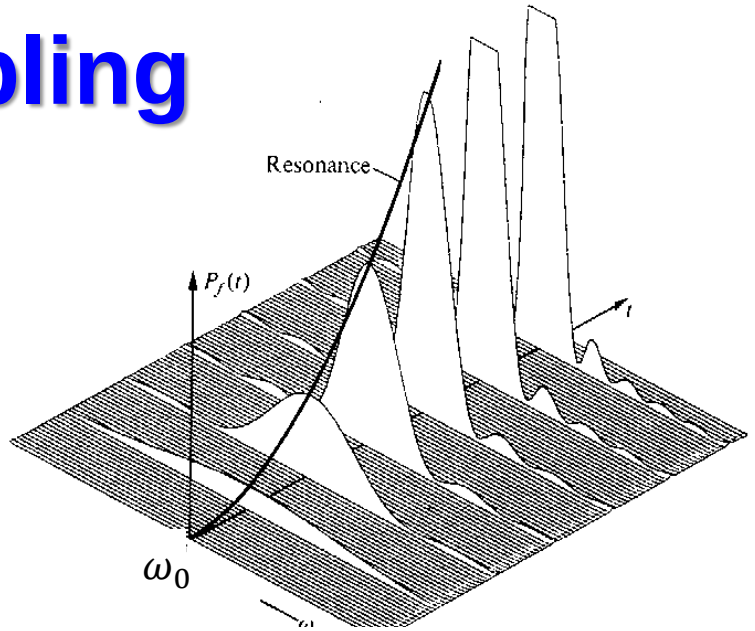
Excitation energy transfer b.m.o. resonance hopping

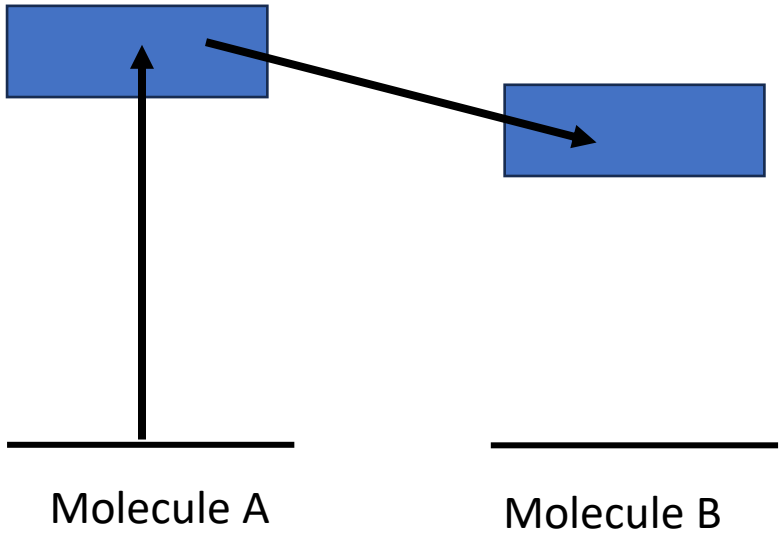
Weak intermolecular coupling

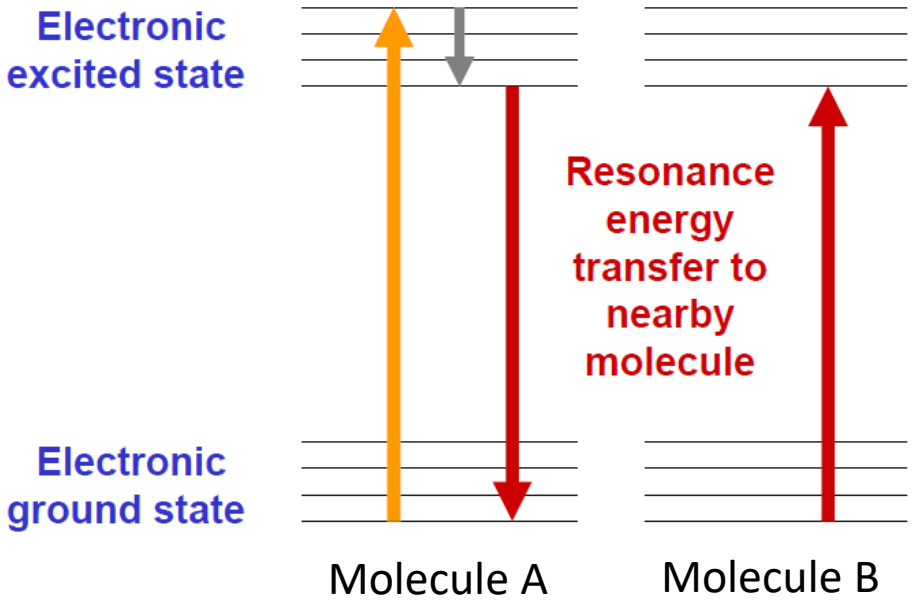
$V_{12} = \langle \varphi_1^0 \varphi_2^1 | V | \varphi_1^1 \varphi_2^0 \rangle$ implies EET.

Timescale of EET?

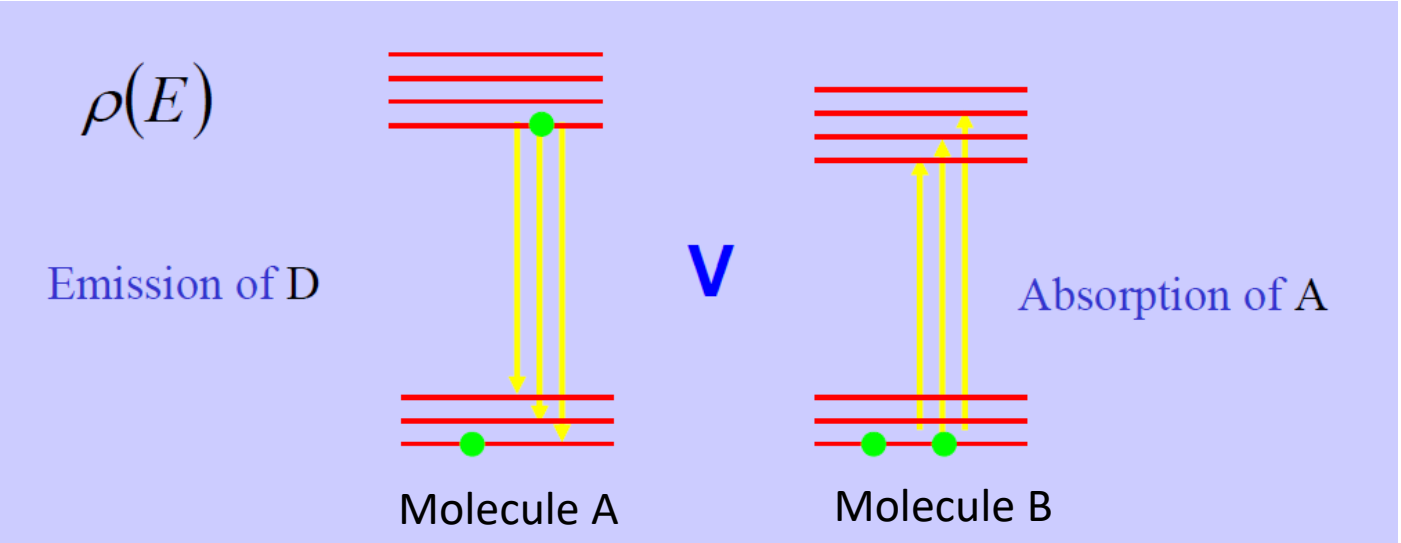
$$P_{A\to B}(t) = |c_B(t)|^2 \approx \frac{|V_{12}|^2}{\hbar^2} \frac{\sin^2 \frac{1}{2}(\omega_0 - \omega)t}{(\omega_0 - \omega)^2}$$







Density of states



Density of states $\rho(E)$ = number of simultaneous emission-absorption combinations that conserve the energy.

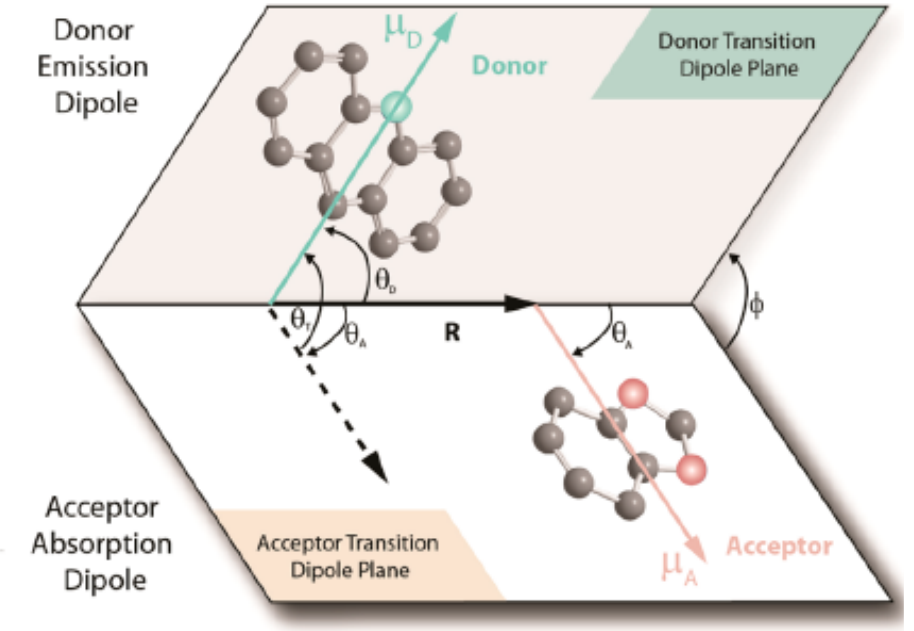
I.e., number of combinations of D*A and DA* that are available for exchange of the excitation energy and that conserve the energy.

Förster resonance energy transfer

$$P_{A\to B}(t) \approx \int_{E_B-\frac{\Delta E}{2}}^{E_B+\frac{\Delta E}{2}} \frac{|V_{12}|^2}{\hbar^2} \frac{\sin^2 \frac{1}{2}(\omega_0-\omega)t}{(\omega_0-\omega)^2}\, \rho(E)dE$$

$$\approx \frac{\pi}{2\hbar}|V_{12}|^2 \rho(E) t$$

$$k_{A\to B} = \frac{dP_{A\to B}}{dt} \approx \frac{\pi}{2\hbar}|V_{12}|^2\rho(E) \qquad \text{Fermi's golden rule}$$



Mirkovic et al. *Chem. Rev.* 2017, 117, 249−293

If we include also off-resonance transitions and switch to donor-acceptor notation, then

$$k_{DA} \approx \frac{2\pi}{\hbar} V_{DA}^2\, \rho(E) = \frac{4\pi^2}{h} V_{DA}^2\, \rho(E)$$

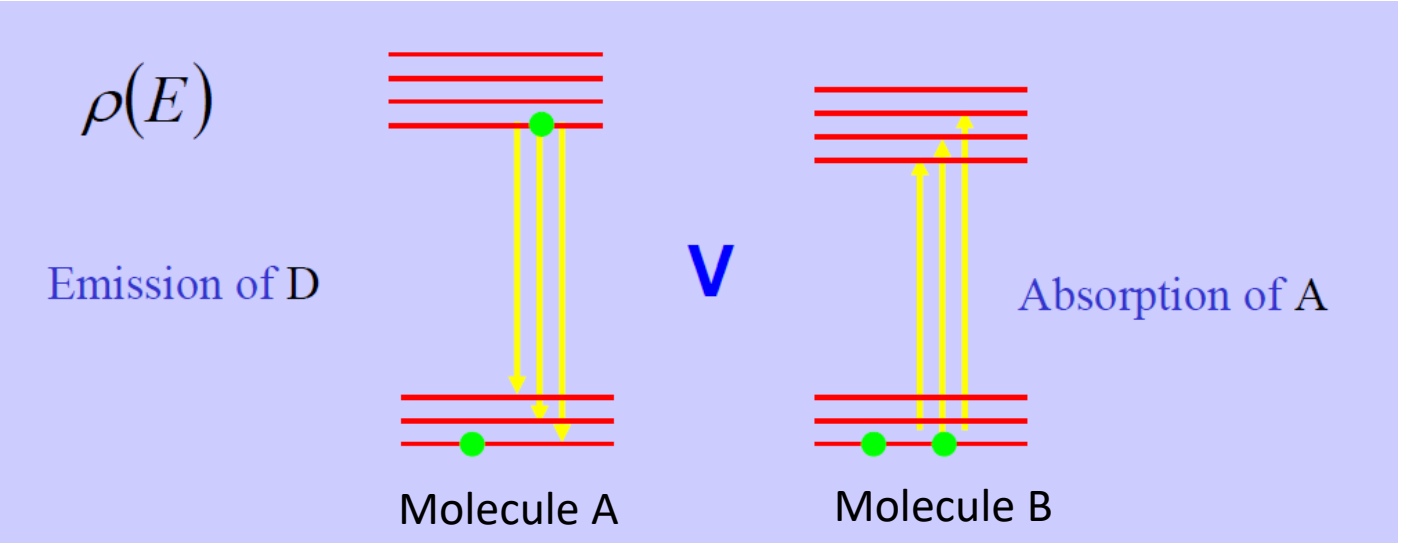
The coupling matrix element is given by the dipole-dipole coupling

$$V_{\text{dip-dip}}(\vec{R}) = f^2 \frac{\mu_D \mu_A}{\epsilon_r} \frac{1}{R^3} \kappa \qquad \text{(in Gaussian units)}$$

with f the Lorentz factor and $\kappa = \cos\theta_T - 3\cos\theta_D \cos\theta_A$ the orientation factor

This gives $V_{DA}^2 = f^4 \kappa^2 \frac{\mu_D^2 \mu_A^2}{\epsilon_r^2} \frac{1}{R^6}$

Density of states



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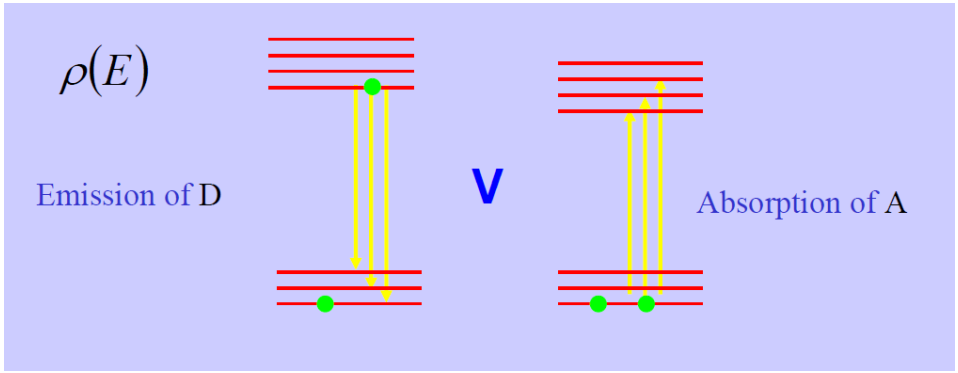
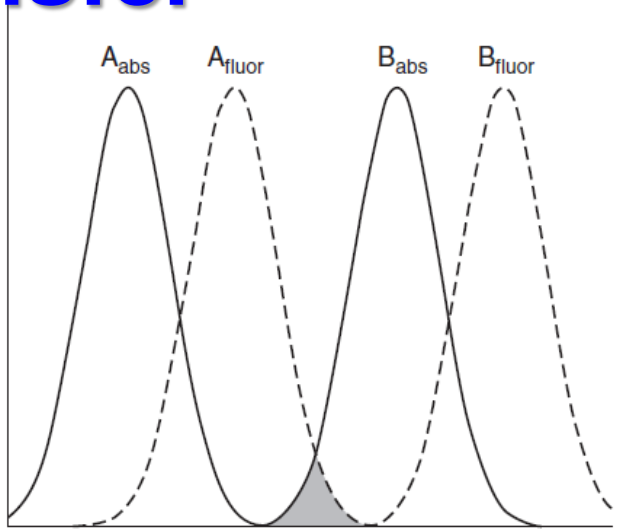
Förster resonance energy transfer





The spectral overlap that determines $\rho(E)$ is proportional to $\int F_D(\nu)\varepsilon_A(\nu)d\nu$

with $F_D(\nu) = A_{21}\int e^{-E_D/kT}S_D^2 dE_D$

$$= \frac{64\pi^4\nu^3}{3hc^3}\mu_D^2\int e^{-E_D/kT}S_D^2 dE_D \quad \text{(Gaussian units)}$$

$$F_D(n) = f^2 n\, F_D(vac)$$

Franck-Condon factor: $S_D^2 = |\langle v_f|v_i\rangle|^2 = |\langle v_{E_D-h\nu}|v_{E_D}\rangle|^2$

$S_A^2 = |\langle v_f|v_i\rangle|^2 = |\langle v_{E_A+h\nu}|v_{E_A}\rangle|^2$

and $\varepsilon_A(\nu) = \frac{8\pi^3 N_A}{3000\ln 10\, hc}\mu_A^2\int e^{-E_A/kT}S_A^2 dE_A$ (Gaussian units)

$$\varepsilon_A(n) = \frac{f^2}{n}\varepsilon_A(vac)$$

$k_{DA} \approx \frac{4\pi^2}{h}V_{DA}^2\,\rho(E)$, with $V_{DA}^2 = f^4\kappa^2\frac{\mu_D^2\mu_A^2}{\epsilon_r^2}\frac{1}{R^6}$

$$B_{12} = \frac{4\pi^2}{3\hbar^2}|\vec{\mu}_{12}|^2 = \frac{4\pi^2}{3\hbar^2}\mu_A^2$$

$$= \frac{c}{\hbar\omega_0}\int\sigma(\omega)d\omega$$

$$\varepsilon(\omega_0) = \frac{N_A}{\ln 10}\sigma(\omega_0)$$

$$\omega_0 = 2\pi\nu$$

The Förster equation

$$k_{DA} \approx k_r^D \left(\frac{R_0}{R}\right)^6$$

Rate of Förster resonance energy transfer (FRET)

with

$$R_0^6 = 8.8 \cdot 10^{17} \cdot \frac{\kappa^2}{n^4} \cdot \int \frac{\varepsilon_A(\tilde{\nu}) \cdot F_D(\tilde{\nu})}{\tilde{\nu}^4} d\tilde{\nu}$$

(*R* is in nm and $\tilde{\nu}$ is in cm^{-1})

$$k_r^D = \frac{64\pi^4 \nu^3}{3hc^3} f^2 n$$

(radiative rate)

k_{DA} depends strongly on:

1. Relative dipole orientation
2. Spectral overlap
3. Inter-dipole distance

This is incoherent energy transfer: Phase information is lost when integrating over whole spectral band of the acceptor to get Fermi's golden rule.

Coherent energy transfer: next two lectures

What we have learned

1. Intermolecular interactions
2. The excitonically coupled dimer
3. H- and J-aggregates
4. Förster resonance energy transfer (FRET)

Next lectures

1. Basic principles of electronic spectroscopy
2. Coupled molecular dipoles: Molecular excitons & Förster interactions
3.
   - Linear & nonlinear spectroscopy
4.
   - EET in the strong-coupling limit

Dr. Towan Nöthling

NITheCS Mini-School on "Modelling Optical Spectra"

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