Theoretical Photochemistry WiSe 2017/18 – Exercise 11

Fluorescence Resonance Energy Transfer.
Consider the process of excitation energy transfer between an initially excited donor molecule (D) and an acceptor molecule (A). According to Fermi's golden rule, the rate of energy transfer is given as

$$k_{\mathrm{DA}} = \frac{2\pi}{\hbar} \sum_{N,M} \sum_{S,T} P^N_{\mathrm{D}^*} P^M_{\mathrm{A}} \left| \left\langle \Psi^N_{\mathrm{D}^*} \Psi^M_{\mathrm{A}} \left| \hat{V} \right| \Psi^S_{\mathrm{D}} \Psi^T_{\mathrm{A}^*} \right\rangle \right|^2 \delta \left(E^N_{\mathrm{D}^*} + E^M_{\mathrm{A}} - E^S_{\mathrm{D}} - E^T_{\mathrm{A}^*} \right) , \tag{1}$$

where

- Ψ^K_α, with $\alpha = \mathrm{D}, \mathrm{D}^*, \mathrm{A}, \mathrm{A}^*$ is an electronic-vibrational wavefunction for either the donor or the acceptor, $\Psi^K_\alpha = \psi_\alpha(\mathbf{r})\chi_{\alpha,K}(\mathbf{Q})$. For example, $\Psi^N_{\mathrm{D}^*} = \psi_{\mathrm{D}^*}\chi^N_{\mathrm{D}^*}$.
- P^K_α is the initial population of the state Ψ^K_α.
- $\hat{V}$ is the Coulomb interaction operator,

$$\hat{V} = \frac{1}{2} \sum_{jk} \frac{e^2}{|\mathbf{R}_{\mathrm{DA}} + \mathbf{r}_{D,j} - \mathbf{r}_{A,k}|} , \tag{2}$$

  where $\mathbf{R}_{\mathrm{DA}}$ represents the distance between the centers of mass of the donor and the acceptor and $\mathbf{r}_{D,j}$ and $\mathbf{r}_{A,k}$ denote the coordinates of the j-th electron of D and the k-th electron of A.

For large values of $|\mathbf{R}_{\mathrm{DA}}|$ the Coulomb potential can be approximated as a dipole-dipole interaction,

$$\begin{aligned} \left\langle \psi_{\mathrm{D}^*}\psi_{\mathrm{A}} \left| \hat{V} \right| \psi_{\mathrm{D}}\psi_{\mathrm{A}^*} \right\rangle &= \left\langle \psi_{\mathrm{D}^*}\psi_{\mathrm{A}} \left| \frac{\hat{\mu}_{\mathrm{D}} \cdot \hat{\mu}_{\mathrm{A}}}{|\mathbf{R}_{\mathrm{DA}}|^3} - 3\frac{(\mathbf{R}_{\mathrm{DA}} \cdot \hat{\mu}_{\mathrm{D}})(\mathbf{R}_{\mathrm{DA}} \cdot \hat{\mu}_{\mathrm{A}})}{|\mathbf{R}_{\mathrm{DA}}|^5} \right| \psi_{\mathrm{D}}\psi_{\mathrm{A}^*} \right\rangle \\ &= \kappa_{\mathrm{DA}} \frac{|\left\langle \psi_{\mathrm{D}^*} \left| \hat{\mu}_{\mathrm{D}} \right| \psi_{\mathrm{D}} \right\rangle| \, |\left\langle \psi_{\mathrm{A}} \left| \hat{\mu}_{\mathrm{A}} \right| \psi_{\mathrm{A}^*} \right\rangle|}{|\mathbf{R}_{\mathrm{DA}}|^3} \\ &= \kappa_{\mathrm{DA}} \frac{|\mathbf{d}_{\mathrm{D}}||\mathbf{d}_{\mathrm{A}}|}{|\mathbf{R}_{\mathrm{DA}}|^3} \end{aligned} \tag{3}$$

- Using the identity

$$\int_{-\infty}^{+\infty} \hbar \mathrm{d}\omega \delta \left(E^N_{\mathrm{D}^*} - E^S_{\mathrm{D}} - \hbar\omega \right) \delta \left(E^M_{\mathrm{A}} - E^T_{\mathrm{A}^*} + \hbar\omega \right) \tag{4}$$

express the energy transfer rate of Eq. (1) in terms of the donor fluorescence spectrum,

$$I_{\mathrm{D}}(\omega) = \frac{4\omega^3}{3\hbar c^3}|\mathbf{d}_{\mathrm{D}}|^2 \sum_N \sum_S P^N_{\mathrm{D}^*} \left|\langle \chi^N_{\mathrm{D}^*} | \chi^S_{\mathrm{D}} \rangle\right|^2 \delta\left(E^N_{\mathrm{D}^*} - E^S_{\mathrm{D}} - \hbar\omega\right) \quad (5)$$

and the acceptor absorption spectrum

$$\alpha_{\mathrm{A}}(\omega) = \frac{4\pi^2\omega}{3c}|\mathbf{d}_{\mathrm{A}}|^2 \sum_M \sum_T P^M_{\mathrm{A}} \left|\langle \chi^M_{\mathrm{A}} | \chi^T_{\mathrm{A}^*} \rangle\right|^2 \delta\left(E^M_{\mathrm{A}} - E^T_{\mathrm{A}^*} + \hbar\omega\right) \ . \quad (6)$$

- Derive an expression for the orientational factor κ_{DA} of Eq. (3). (*Hint:* Express the vectors $\mathbf{R}_{\mathrm{DA}}$, $\mathbf{d}_{\mathrm{D}} = \langle \psi_{\mathrm{D}^*} | \hat{\mu}_{\mathrm{D}} | \psi_{\mathrm{D}} \rangle$ and $\mathbf{d}_{\mathrm{A}} = \langle \psi_{\mathrm{A}} | \hat{\mu}_{\mathrm{A}} | \psi_{\mathrm{A}^*} \rangle$ in polar coordinates, aligning the z axis with $\mathbf{R}_{\mathrm{DA}}$)

- What is the value of κ^2_{DA}: (i) When $\mathbf{d}_{\mathrm{D}}$ and $\mathbf{d}_{\mathrm{A}}$ are orthogonal? (ii) When $\mathbf{d}_{\mathrm{D}}$, $\mathbf{d}_{\mathrm{A}}$ and $\mathbf{R}_{\mathrm{DA}}$ are all parallel? (iii) When $\mathbf{d}_{\mathrm{D}}$ and $\mathbf{d}_{\mathrm{A}}$ are parallel but orthogonal to $\mathbf{R}_{\mathrm{DA}}$?