Lecture # 17
Physical Chemistry
for Life Scientists
National Tsing-Hua
University
May 25, 2001

The Quantum Mechanics of Interacting Chromophores

Let begin with a dimer of non-interacting monomers

→ Monomer

For simplicity, take a 2-level system

a ——— ϵ_a , ϕ_a

o ——— ϵ_o , ϕ_o

where ϕ_o, ϕ_a, ϵ_o, ϵ_a are eigenfunctions and energies of one-chromophore Hamiltonian

i.e., $\hat{h}\,\phi_o = \epsilon_o \phi_o$

$\hat{h}\,\phi_a = \epsilon_a \phi_a$

→ Dimer

$\hat{H} = \hat{h}_1 + \hat{h}_2$ non-interacting chromophores

For non-interacting chromophores, Hamiltonian for dimer is just sum of one-chromophore hamiltonians.

∴ wavefn for dimer just products of one-chromophore eigenfunctions

Ground State

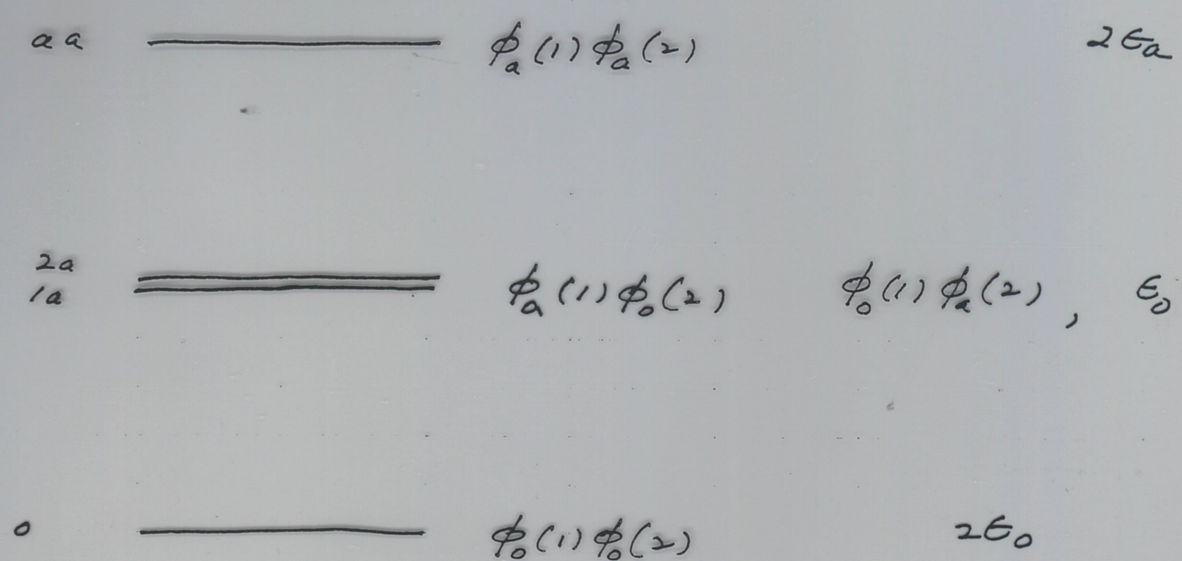
$$\Psi_0 = \phi_0(1)\,\phi_0(2) \qquad W = 2\epsilon_0$$

Excited States

$$\Psi_{1a} = \phi_a(1)\,\phi_0(2) \qquad W = \epsilon_0 + \epsilon_a$$

$$\Psi_{2a} = \phi_0(1)\,\phi_a(2) \qquad W = \epsilon_0 + \epsilon_a$$

$$\Psi_{aa} = \phi_a(1)\,\phi_a(2) \qquad W = 2\epsilon_a$$



Transitions

Only $0 \rightarrow 1a$ or $2a$ allowed!

Dipole operator of dimer $= \vec{\mu}_1 + \vec{\mu}_2$

So dipole strength for $0 \rightarrow 1a$ transition

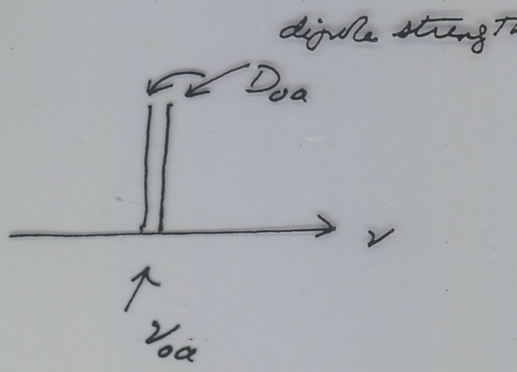
$$= \left| \int \Psi_0^* (\vec{\mu}_1 + \vec{\mu}_2) \Psi_{1a} \, d\tau \right|^2$$

$$= \left| \int \phi_0^*(1) \, \phi_0^*(2) \, (\vec{\mu}_1 + \vec{\mu}_2) \, \phi_a(1) \, \phi_0(2) \, d\tau \right|^2$$

$$= \left| \int \phi_0^*(1) \, \vec{\mu}_1 \, \phi_a(1) \, d\tau \right|^2 = D_{0a} \text{ for monomer}$$

Same result for $0 \rightarrow 2a$ transition.

Spectrum



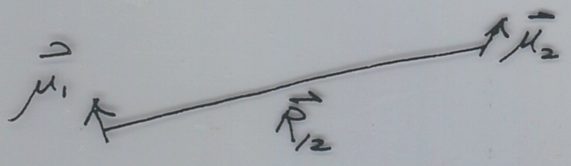
A dimer of interacting monomers

Now $\hat{H}_{\text{dimer}} = \hat{h}_1 + \hat{h}_2 + \hat{V}$

where V describes interaction between monomers

most important interaction is electric dipole-dipole interaction

$$V = \frac{\vec{\mu}_1 \cdot \vec{\mu}_2}{R_{12}^3} - \frac{3(\vec{\mu}_1 \cdot \vec{R}_{12})(\vec{R}_{12} \cdot \vec{\mu}_2)}{R_{12}^5}$$



Ground state

$$\Psi_0 = \phi_0(1)\,\phi_0(2) \quad , \quad W = 2\epsilon_0$$

Excited states

$$\rightarrow \quad \Psi_{A+} = \frac{1}{\sqrt{2}}(\Psi_{1a} + \Psi_{2a}) \quad , \quad W = \epsilon_0 + \epsilon_a + V_{12}$$

where $V_{12} = \int \phi_a(1)\,\phi_0(2)\,\hat{V}\,\phi_0(1)\,\phi_a(2)\,d\tau$

$$= \left(\int \phi_a^*(1)\,\vec{\mu}_1\,\phi_0(1)\,d\tau\right) \cdot \left(\int \phi_0^*(2)\,\vec{\mu}_2\,\phi_a(2)\,d\tau\right) / R_{12}^3$$

$$- \frac{\left(3\int \phi_a^*(1)\,\vec{\mu}_1\,\phi_0(1)\,d\tau \cdot \vec{R}_{12}\right)\left(\vec{R}_{12} \cdot \int \phi_0(2)^*\,\vec{\mu}_2\,\phi_a(2)\,d\tau\right)}{R_{12}^5}$$

$$\rightarrow \quad \Psi_{A-} = \frac{1}{\sqrt{2}}(\Psi_{1a} - \Psi_{2a}) \quad , \quad W = \epsilon_0 + \epsilon_a - V_{12}$$

Allowed transitions

Frequencies

$0 \longrightarrow A^+$: $\quad \nu_+ = \nu_{0a} + (V_{12}/h)$

$0 \longrightarrow A^-$: $\quad \nu_- = \nu_{0a} - (V_{12}/h)$

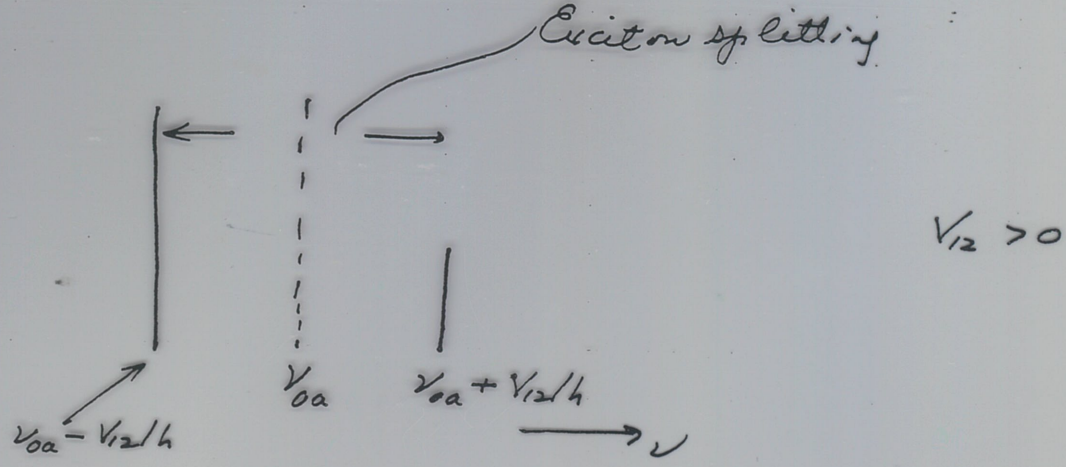
Dipole Strengths

$0 \longrightarrow A^+$: $\quad D_{0a} + D_{0a}\cos\theta = D_{0\rightarrow A^+}$

$0 \longrightarrow A^-$: $\quad D_{0a} - D_{0a}\cos\theta = D_{0\rightarrow A^-}$

where θ is the angle between the transition dipoles involved in the individual electronic absorption of monomer 1 and monomer 2

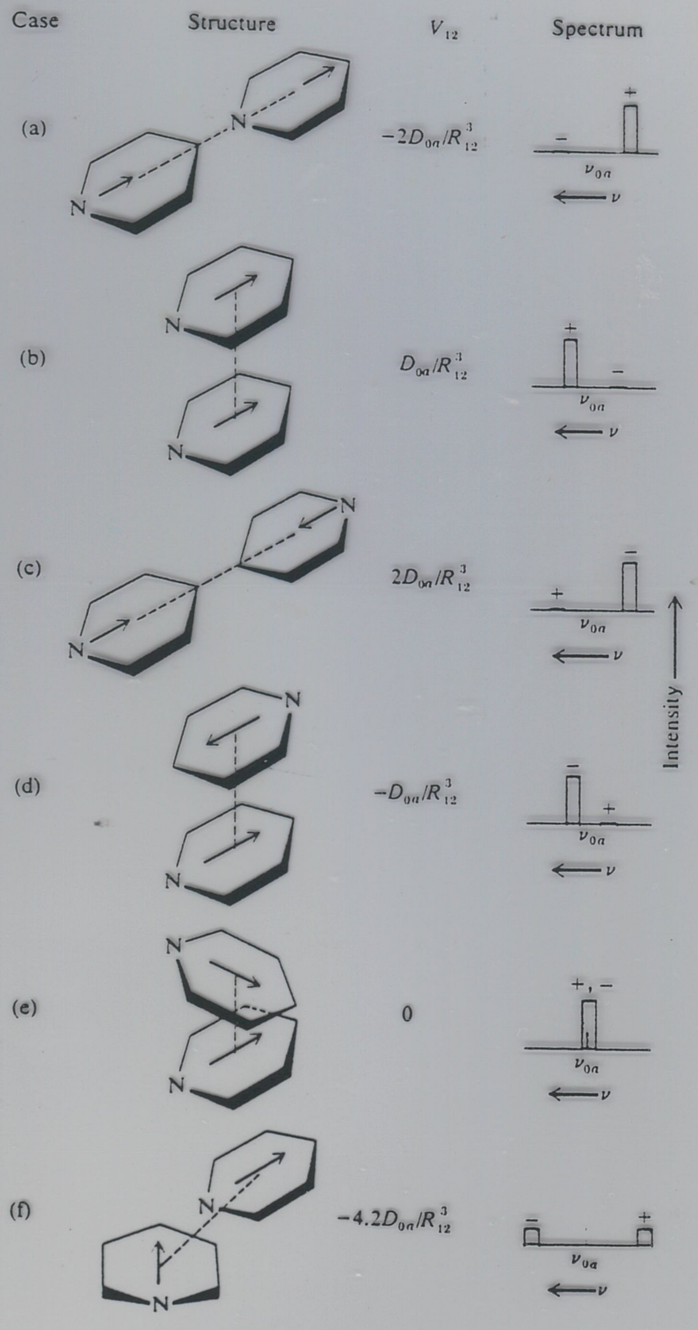
Spectrum



above splitting is called **exciton splitting** and interaction is usually referred to as **exciton interaction**

Note that $D_{0\to A^+} + D_{0\to A^-} = 2D_{0a}$

Typical situations



$\theta = 90°$

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An important example

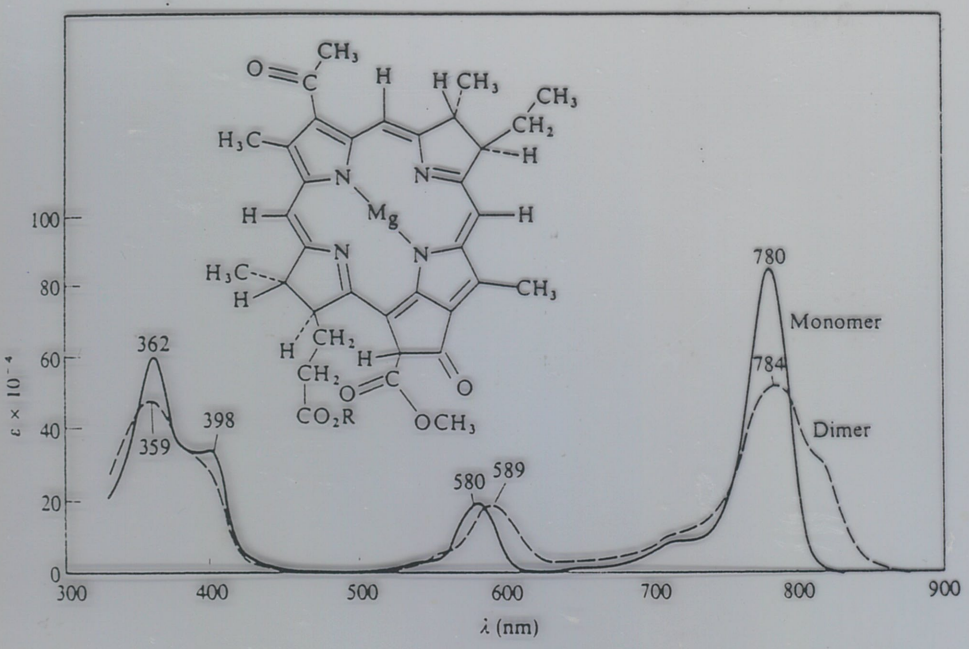


Figure 7-19

Monomer and dimer spectra for solutions of bacteriochlorophyll. A pronounced splitting of the longest-wavelength band in the dimer is visible. [After K. Sauer, J. R. L. Smith, and A. J. Schultz, *J. Am. Chem. Soc.* 88:2681 (1966).]

Hypochromism

In the above treatment, $D_{0\to A^+} + D_{0\to A^-} = 2D_{0a}$

So the intensity (total) expected for an exciton band same as if exciton interaction did not occur. ← This is only true when a 2-level system is considered, as was done here. In practice, $\hat{V}$ mixes all the states of the aggregate system, and the dipole strength for the first

excitation is less than $2D_{0a}$ for the monomer, i.e., it has less intensity (less color). This is called the hypochromic effect. Typically, hypochromic effects are of the order of 10% - 50%.

Example base-stacking in nucleic acids

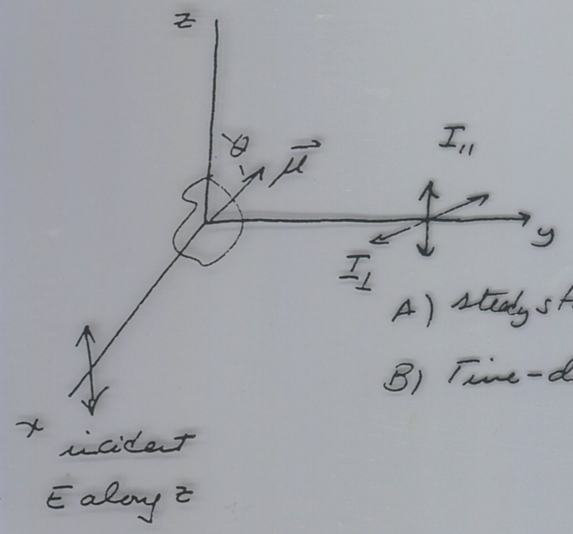
Note that strength of hypochromism $\propto \frac{1}{R_{1,2}^3}$ of interacting chromophores.

See OD change during melting or denaturation of DNA.

Transition dipoles of chromophores

Polarization of Fluorescence Emission

If plane-polarized light is used to excite a fluorescent system, linearly polarized components of the emission are detected.



not ⟷ along y because light is a transverse wave.

A) steady state if continuous excitation

B) Time-domain if pulse

$I_{\parallel}$, $I_{\perp}$ = ?

Suppose excite chromophore into excited state emitting radiation

1) Crystal or oriented chromophores

Probability that chromophores will be excited is proportional to $(\vec{\mu} \cdot \vec{E})^2$ [redacted]

Because $\vec{E}$ is parallel to z-axis, probability is $\cos^2\theta$

To calculate fluorescence polarization, we note that

Probability that chromophore will emit with E emission along z or $\parallel$ axis $\propto \cos^2\theta$

Probability that chromophores will emit with Emission along $\parallel$ or $\perp$ axis $\propto \sin^2\theta \cos^2\phi$

$\therefore \quad I_\parallel \propto \cos^4\theta$

$I_\perp \propto \sin^2\theta \cos^2\phi \cos^2\theta$

2) rigid, isotropic sample on a glass

Chromophores randomly oriented.

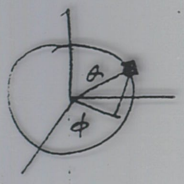
Probability that a particular chromophore will be excited $\propto (\mu \cdot E)^2 = \cos^2\theta$

$\therefore$ molecules or chromophores with transition dipoles near the z-axis will be preferentially excited. This is called the principle of photoselection.

Fraction of chromophores excited oriented at θ to $\theta + d\theta$ ~~[illegible]~~ $\phi \to \phi + d\phi$

$$W(\theta,\phi)\, d\theta\, d\phi \propto \cos^2\theta \underbrace{\sin\theta\, d\theta\, d\phi}$$

fraction of chromophores oriented at angles θ to $\theta + d\theta$, ϕ to $\phi + d\phi$



Proportionality constant = reciprocal of

$$\int_0^{\pi} \int_0^{2\pi} \cos^2\theta \sin\theta\, d\theta\, d\phi$$

$$= 2\pi \int_0^{\pi} \cos^2\theta \sin\theta\, d\theta = 2\pi \int_{\theta=0}^{\theta=\pi} \cos^2\theta\, d(\cos\theta) \quad (-1)$$

$$(-1)$$

$$(+1)$$

$$= -2\pi \int_1^{-1} \frac{x^3}{3} = -2\pi \left(-\frac{1}{3} - \frac{1}{3}\right) = \frac{4\pi}{3}$$

$$\therefore W(\theta,\phi)\, d\theta\, d\phi = \frac{3}{4\pi} \cos^2\theta \sin\theta\, d\theta\, d\phi$$

Hence distribution of excited chromophores anisotropic.

Because distribution of excited chromophore anisotropic, resulting fluorescence also will be anisotropic.

If the same electronic transition that absorbed does the emission ($S_a \to S_b$ followed by $S_b \to S_a$)

then probability that emission will occur polarized along z axis is $\propto |\vec{\mu}\cdot\hat{k}|^2$ $\hat{k}$ unit vector along z

$$\propto \cos^2\theta$$

Probability that emission will occur polarized along x-axis $\propto |\vec{\mu}\cdot\hat{i}|^2 \propto \sin^2\theta \cos^2\phi$

$$\therefore I_{\parallel} \propto \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \cos^2\theta\, W(\theta,\phi)$$

$$= \frac{3}{4\pi} \underbrace{\int_0^{2\pi} d\phi}_{2\pi} \int_0^{\pi} \cos^2\theta \cos^2\theta \sin\theta\, d\theta$$

$$= \frac{3}{2} \int_0^{\pi} \cos^4\theta \sin\theta\, d\theta$$

$$= \frac{3}{2}\left(-\frac{\cos^5\theta}{5}\right)\Big|_0^{\pi} = \frac{3}{5}$$

$$I_\perp \propto \int_0^{2\pi} \int_0^{\pi} \cos^2\theta \sin\theta \sin^2\theta \cos^2\phi \, d\theta \, d\phi \left(\frac{3}{4\pi}\right)$$

$$= \frac{1}{5}$$

To express anisotropy of emitted radiation or fluorescence, two quantities have been introduced into field

$$\text{Polarization} \equiv P = \frac{(I_{\parallel} - I_\perp)}{I_{\parallel} + I_\perp}$$

$$\text{Anisotropy} \equiv A = \frac{I_{\parallel} - I_\perp}{I_{\parallel} + 2I_\perp}$$

So for glass (rigid)

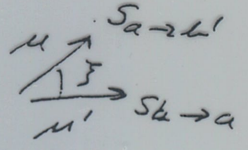
$$P = \frac{3/5 - 1/5}{3/5 + 1/5} = \frac{2}{5} \times \frac{5}{4} = \frac{1}{2}$$

Steady state values

$$A = \frac{\frac{3}{5} - \frac{1}{5}}{\frac{3}{5} + \frac{2}{5}} = \frac{2}{5}$$

These are maximal values of polarization and anisotropy

If exciting transition dipole and emitting dipole do not coincide, such as when chromophore is excited to a higher singlet (excited) and emits from 1st excited single, and if the two transition dipoles make a angle of ζ with respect to each other



$$P_0 = \frac{(3\cos^2\zeta - 1)}{\cos^2\zeta + 3}$$

$$A_0 = \frac{(3\cos^2\zeta - 1)}{5}$$

↑ limiting value for rigid glass

3) Solution

If chromophore can tumble fast enough to randomize orientation during lifetime of excited state, by time emission occurs, all memory of the original photoselection is lost, and $I_{\parallel} = I_{\perp}$

$$P = 0$$
$$A = 0.$$

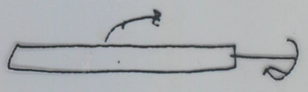
Molecular Motion

Examine the effects of molecular motion a touch more closely.
Must look into real time response or time decay
Complicated problem

Types of motions

a) isotropic unrestricted
b) anisotropic unrestricted } during τ_F 10^{-8} — 100 ps
c) restricted motion

small molecules, particularly spherical ones 

small prolate or oblate molecules 

big rigid molecules or small chromophores covalently attached to or embedded in hydrophobic / hydrophilic pocket

a), b) $A, P \to 0$

c) $A, P \neq 0$

Treat only simplest case

a chromophore undergoing isotropic Brownian rotation diffusion; i.e., a chromophore that obeys rotational diffusion equation

$$\frac{\partial W(\theta,\phi,t)}{\partial t} = D_{rot} \nabla^2 W(\theta,\phi,t)$$

$W(\theta, \phi, t) \equiv$ probability that any molecule has a particular orientation at time t

where $D_{rot} = \dfrac{kT}{f_{rot}} = \dfrac{kT}{6 V_h \eta}$

$V_h \equiv$ hydrated or solvated molecule.

B.C. $W(\theta, \phi, 0)$ immediately following excitation $= \left(\frac{3}{4\pi}\right) \cos^2\theta \sin\theta$

Now, the population of excited singlets produced at time 0 decays with time as follows

$$W(\theta, \phi, t)\, e^{-t/\tau_F}$$

If ξ is the angle between absorbing + emitting dipole

Then

$$I_{\substack{\parallel \\ \perp}} = \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \; P_{\substack{\parallel \\ \perp}}(\theta, \phi, \xi)\, W(\theta, \phi, t)\, e^{-t/\tau_F}$$

$$I_\parallel = \left[\left(\frac{1}{3}\right) + \left(\frac{4}{15}\right) e^{-6 D_{rot} t \left(3\cos^2\xi - 1\right)/2}\right] e^{-t/\tau_F}$$

$$I_\perp = \left[\left(\frac{1}{3}\right) - \left(\frac{2}{15}\right) e^{-6 D_{rot} t \left(3\cos^2\xi - 1\right)/2}\right] e^{-t/\tau_F}$$

decay as a sum of two exponentials

τ_F, $\boxed{\dfrac{1}{6 D_{rot}} = \tau_c = \dfrac{V_h \eta}{kT} = \dfrac{4\pi a^3 \eta}{3kT}}$

Nonpolarized emission decays as single exponential

$$A(t) = \left(\frac{2}{5}\right) e^{-t/\tau_c} \left[\left(3\cos^2\zeta - 1\right)/2\right]$$

If now we average $\bar{I}_{\parallel}$ or $\bar{I}_{\perp}$ on $A(t)$ over lifetime of emitting state

$$\bar{I}_{\substack{\parallel \\ \perp}} = \tau_F^{-1} \int_0^{\infty} I_{\substack{\parallel \\ \perp}}(t)\, dt$$

$$\bar{P} = \frac{\bar{I}_{\parallel} - \bar{I}_{\perp}}{\bar{I}_{\parallel} + \bar{I}_{\perp}} = \frac{3}{1 + 10\left(1 + \tau_F/\tau_c\right)\left(3\cos^2\zeta - 1\right)^{-1}}$$

Steady state or average polarization

$$\bar{A} = \frac{\bar{I}_{\parallel} - \bar{I}_{\perp}}{\bar{I}_{\parallel} + 2\bar{I}_{\perp}} = \frac{3\cos^2\zeta - 1}{5\left(1 + \tau_i/\tau_c\right)}$$

Now if η/Γ sufficiently high that chromophore is unable to rotate during time life of excited state i.e., $\tau_F/\tau_c \to 0$,

$$\bar{P}_0 = \frac{3}{1 + 10\left(3\cos^2\zeta - 1\right)^{-1}} = \frac{3\cos^2\zeta - 1}{\cos^2\zeta + 3}$$

$$\bar{A}_0 = \frac{3\cos^2\zeta - 1}{5}$$

} same as limiting steady state polarization and anisotropy

Other limit — long lifetime

$\frac{\tau_F}{\tau_c}$ large

$$\bar{P} = \frac{3(3\cos^2\xi - 1)}{10\left(\tau_F/\tau_c\right)} = \frac{\tau_c}{\tau_F}\left(\frac{3}{10}\right)\left(3\cos^2\xi - 1\right)$$

$$\longrightarrow 0$$

$$\bar{A} = \frac{1}{5}\frac{3\cos^2\xi - 1}{}\left(\frac{\tau_c}{\tau_F}\right) \longrightarrow 0$$