Photophysics in Condensed Media
Energy Migration

Dong-Myung Shin
Hongik University
Department of Chemical Engineering

Energy Transfer

- Energy Transfer
  - between different species
- Energy migration
  - group of same species
- Intermolecular
  - between separate species
- Intramolecular
  - b/w different groups in the same molecule

Energy Transfer

- Radiative Energy Transfer

  - absorption of photon emitted from donor

  - very long range

- Non-radiative Energy Transfer

  -Coulombic (dipole-dipole) interaction

  (~20-60 A) long range

  - Electron Exchange

  (~6-15 A) short range

Energy Transfer – radiative

- Radiative Energy Migration

$$^1M_A^* \rightarrow {}^1M_A + h\nu_M \quad ; \quad {}^1M_B + h\nu_M \rightarrow {}^1M_B^*$$

- Singlet–singlet

- Triplet–triplet migration?

  일반적으로는 무시 : triplet absorption이 작다.

Energy Transfer – Radiative

- Radiative Energy transfer

$$^1M_A^* \rightarrow {}^1M_A + h\nu_M \quad ; \quad {}^1Y + h\nu_M \rightarrow {}^1Y^*$$

singlet - singlet

$$^3M_A^* \rightarrow {}^1M_A + h\nu_p \quad ; \quad {}^1Y + h\nu_p \rightarrow {}^1Y^*$$

triplet - singlet

- Singlet–triplet, Triplet–triplet migration?

  일반적으로는 무시 : triplet absorption이 작다.

Energy Transfer – Collisional

- Collisional migration due to excimer formation

$$^1M_A^* + {}^1M_B \leftrightarrows {}^1\mathrm{D}_{\mathrm{AB}}^* \rightarrow {}^1M_A + {}^1M_B^*$$

singlet - singlet

$$^3M_A^* + {}^1M_B \leftrightarrows {}^3\mathrm{D}_{\mathrm{AB}}^* \rightarrow {}^1M_A + {}^3M_B^*$$

triplet - triplet

- Exciplex formation and dissociation

$$^1M_A^* + {}^1Y \leftrightarrows {}^1(\mathrm{MY})^* \rightarrow {}^1M_A + {}^1Y^*$$

singlet - singlet

$$^3M_A^* + {}^1Y \leftrightarrows {}^3(\mathrm{MY})^* \rightarrow {}^1M_A + {}^3Y^*$$

triplet - triplet

Energy Transfer – Electron Exchange

- Short-lived excimer intermediate

$$^1M_A^* + {}^1M_B \rightarrow {}^1M_A + {}^1M_B^*$$

singlet - singlet

$$^3M_A^* + {}^1M_B \rightarrow {}^1M_A + {}^3M_B^*$$

triplet - triplet

- Short-lived Exciplex formation and dissociation

$$^1M_A^* + {}^1Y \rightarrow {}^1M_A + {}^1Y^*$$

singlet - singlet

$$^3M_A^* + {}^1Y \rightarrow {}^1M_A + {}^3Y^*$$

triplet - triplet

Collisional P.와는 rigid Matrix에서 collisional Process가 불가능하면 Electron exchange로 해석

Energy Transfer – Coulombic interaction

- Radiationless migration

  Dipole-dipole, multipole-multipole interactions

$$^1M_A^* + {}^1M_B \rightarrow {}^1M_A + {}^1M_B^*$$

singlet - singlet

- Raiationtionless transfer

$$^1M_A^* + {}^1Y \rightarrow {}^1M_A + {}^1Y^*$$

singlet - singlet

$$^3M_A^* + {}^1Y \rightarrow {}^1M_A + {}^3Y^*$$

triplet - triplet

Radiative transfer와 유사하다.
Absorption-emission spectrum의
Overlab이 기여.

Energy Transfer – Triplet+triplet

$$^3M^* + {}^3M^* \rightarrow {}^1M + {}^1M^*$$

$$^3M^* + {}^3M^* \rightarrow {}^1D^*$$

$$^3M^* + {}^3M^* \rightarrow {}^1M + {}^3M^{**}$$

Triplet의 lifetime이 길기 때문에 가

- Solution에서는 excimer 형성으로 가능
- Rigid matrix에서는 electron exchange로 가능
- 다음 process들은 exciplex 형성 또는 electron exchange로 가능

$$^3M^* + {}^3Y^* \rightarrow {}^1M + {}^3Y^{**}$$

$$^3M^* + {}^3O_2 \rightarrow {}^1M + {}^1O_2^*$$

$$^3M^* + {}^3Y^* \rightarrow {}^1M + {}^1Y^*$$

2차 여기상태로의 전이가 allowed transition이므로 radiative, dipole-dipole interaction으로도 가능

Energy Transfer – Singlet+triplet

$$^1M^* + {}^3M^* \rightarrow {}^1M + {}^3M^{**}$$

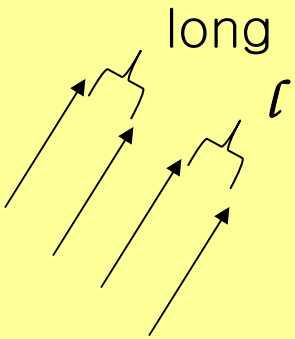
$$^1M^* + {}^3Y^* \rightarrow {}^1M + {}^3Y^{**}$$

Triplet의 lifetime이 길기 때문에 가능

- 전이가 allowed transition이므로 radiative, dipole-dipole interaction으로도 가능
- Spin conservation도 됨으로, collisional 또는 electron-exchange로도 가능

Condensed Media

- Oriented Gas

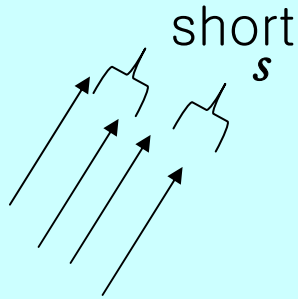


- E

— — — —

Iso-energy

- Condensed Phase



ΔW:interaction energy
-Coulombic interaction
- Electron-exchange interaction

Lifetime against migration

- $\Delta\tau \sim h/\Delta W$
- (Uncertainty principle)

- Crystal 내에 에너지 분포
- Exciton states of the crystal.

Davydov

- Crystal 에서 translationally inequivalent molecules
- (Two molecules per unit cell)

□ φ_a φ_b for two molecules:

$$\varphi_\alpha = \frac{1}{\sqrt{2}}(\varphi_a + \varphi_b)$$

$$\varphi_\alpha = \frac{1}{\sqrt{2}}(\varphi_a - \varphi_b)$$

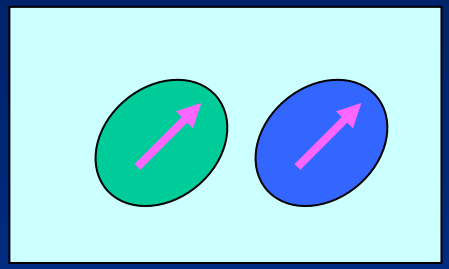
Two groups

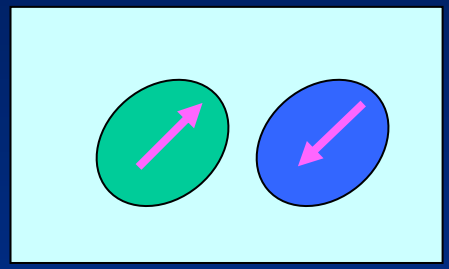
- Translationally equivalent : 결정에서 규칙성 있다
- Inequivalent : 간격 배향 등이 다름

Theory of Exciton States of aromatic crystals

분자 한 개에 대하여 한가지 transition moment ($\vec{m}$) 존재

Exciton states α, β 에 대하여





ΔE

두개의 에너지 차이

Two groups

이 interaction이 dipole-dipole interaction이며

$$\Delta E \propto \frac{\rho_2 m^2}{r^3}$$

(orientation factor)

r : intermolecular distance

Theory of Exciton States of aromatic crystals

- unit cell에 두개의 분자가 존재하면 결정상태에서 두개의 exciton states 존재
- 이때 $\Delta E \propto \frac{\rho_2 m^2}{r^3}$ => Davydov splitting factor
- => interaction E of molecules

- Transition은 crystal의 symmetry axis에 수평으로 형성
- 두 transition의 비는 두 polarization 비로 설명할 수 있다.

Theory of Exciton States of aromatic crystals

- $$E_e = E_0 + A \pm B$$

- E_e : transition E of exciton states
- E_o : transition E of isolated molecules
- A : spectral shift parameter

  {environmental effects=solvent shift (polarization of environment) + exiton shift (interaction with translationally equivalent molecules):

  +, – 모두 가능}

- $\Delta E = 2B$: Davydov splitting factor
- interaction with translationally inequivalent molecules

Exciton States of benzene

- *Benzene과 같이 unit cell에 4개의 분자가 있는 경우나 더 많이 있는 경우*

$$E_e = E_0 + A + B_j$$

- *B_j: Unit cell에서 jth factor group*

Magnitude of Davydov splitting factor

$$\propto \vec{m}$$

- Allowed e dipole β(^1A– $^1B_{a,b}$) : 2B ~ 20000cm^{-1}
- Anthracene p(^1A – ^1L_a) : 2B ~ 200cm^{-1}
- naphthalene p(^1A – ^1L_b) : 2B ~ 200cm^{-1}
- Anthracene, naphthalene (^1A – ^3L_a) : 2B ~ 10cm^{-1}

- 각 vibronic state에 대한 transition은 각 vibronic trnasition moment에 비례

□ ΔE 측정과 계산의 어려움

- Crystal strains
- Defects
- Surface effects

Benzene Crystal

4 moclecules/cell -> 4 Davydov components
(1 forbidden)

□ $\alpha(^1A - {}^1L_b)$ $\varepsilon_{max} = 250$

- The Davydov splitting of 0-0 band: $2B=45cm^{-1}$
- Crystal: Octupole-Octupole interaction이 계산치 보다 10배 정도 강하게 보인다.

□ Crystal field mixing of exciton states with ion-pair state of crystal □

- S.A.Rice and J. Jortner, Physics and Chemistry of the Organic Solid State, Vol 3, pp199 (Ed.D. Fox, M.M. Labes and A. Weissberger) Interscience, New York, 1967

Naphthalene Crystal

2 moclecules/cell -> 2 Davydov components

Weak $\alpha(^1A - {}^1L_b)$ $\varepsilon_{max} = 270$

- The Davydov splitting of 0-0 band: 2B=150 cm^{-1}
- Octupole-Octupole interaction (Craig and Walmsley)
- Crystal field mixing (S.A.Rice and J. Jortner)
- $p(^1A - {}^1L_a)$: 2B ~ 320 cm^{-1}
- $\beta(^1A - {}^1B_b)$: 2B ~ 10,000 cm^{-1}
- Dipole-dipole interaction으로는 너무 큰 값

  -> higher multipole interaction 필요
- Crystal field mixing 으로 어느정도 설명

Anthracene Crystal

- Low energy absorption

  Medium p($^1A - {}^1L_a$) : 2B ~ 200 cm^{-1}

  ε_{max} = 8500

  Polarized along short axis

- Strong β($^1A - {}^1B_b$) : 2B ~ 16,000 cm^{-1}

  ε_{max} = 220000

  Polarized along long axis

Davydov Model

Weak coupling model

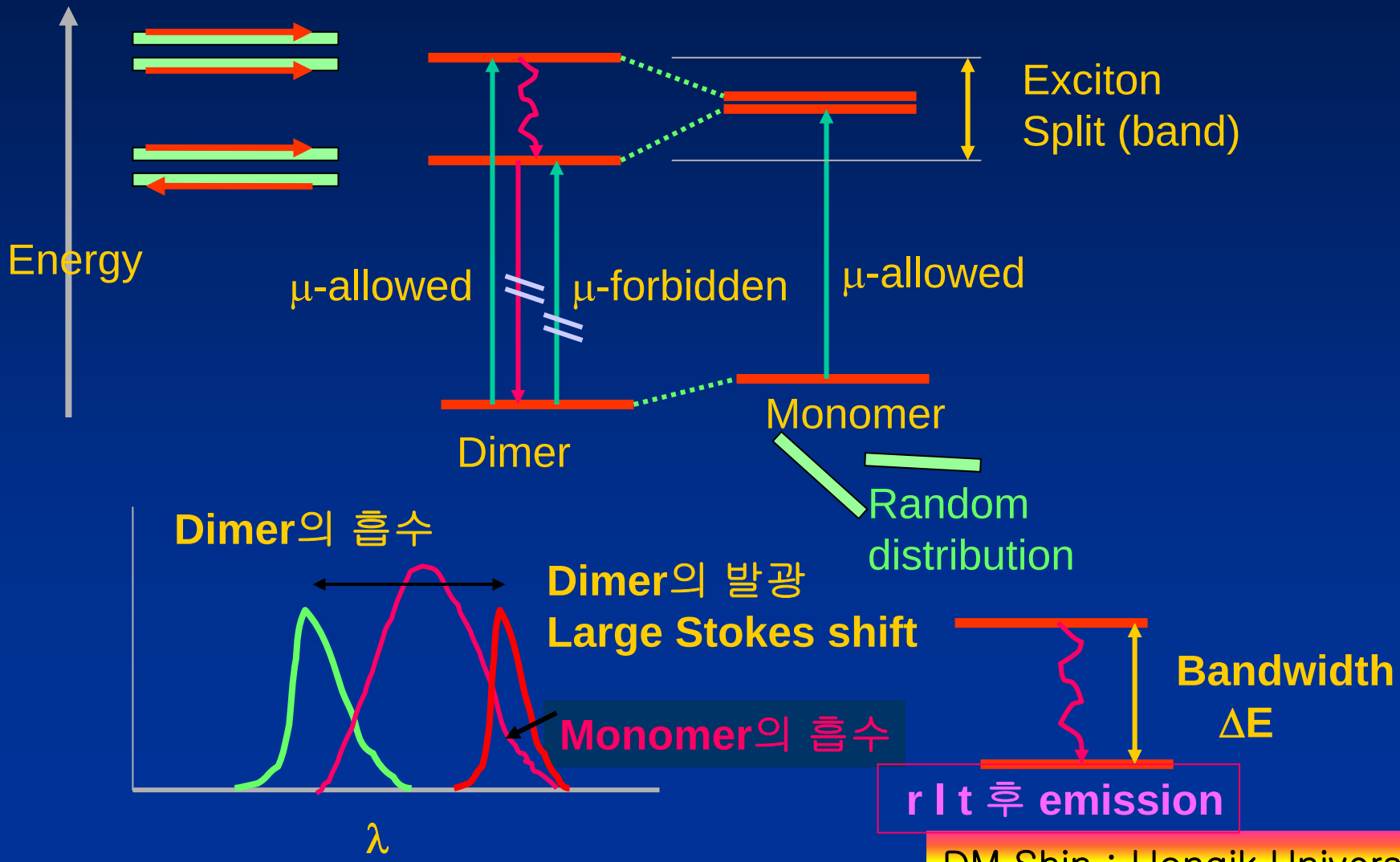
⇒Medium to strong transition에 대해서는 변형 필요

⇒분자 모양

⇒Retardation potential등 고려

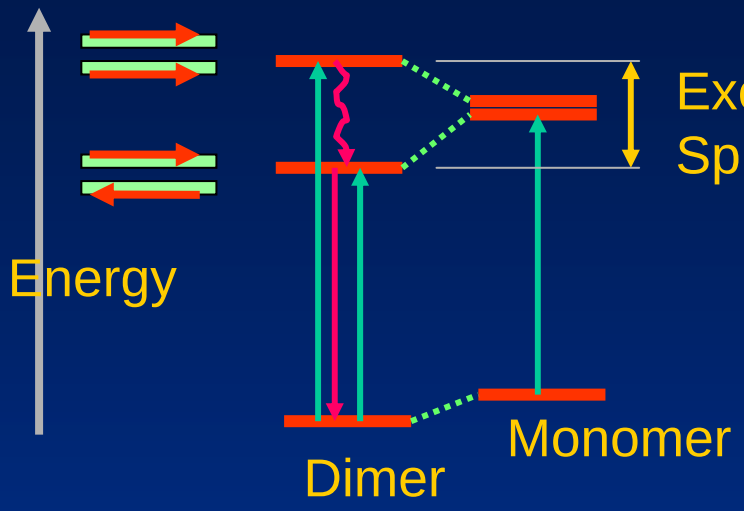
Exciton Interaction

- Sandwitch Type (Card Packed) : Blue shift



Exciton Interaction

- Sandwitch Type (Card Packed) : Blue shift



$$\Psi_{in-phase} = \frac{1}{\sqrt{2}}(\varphi_1^* \varphi_2 + \varphi_1 \varphi_2^*)$$

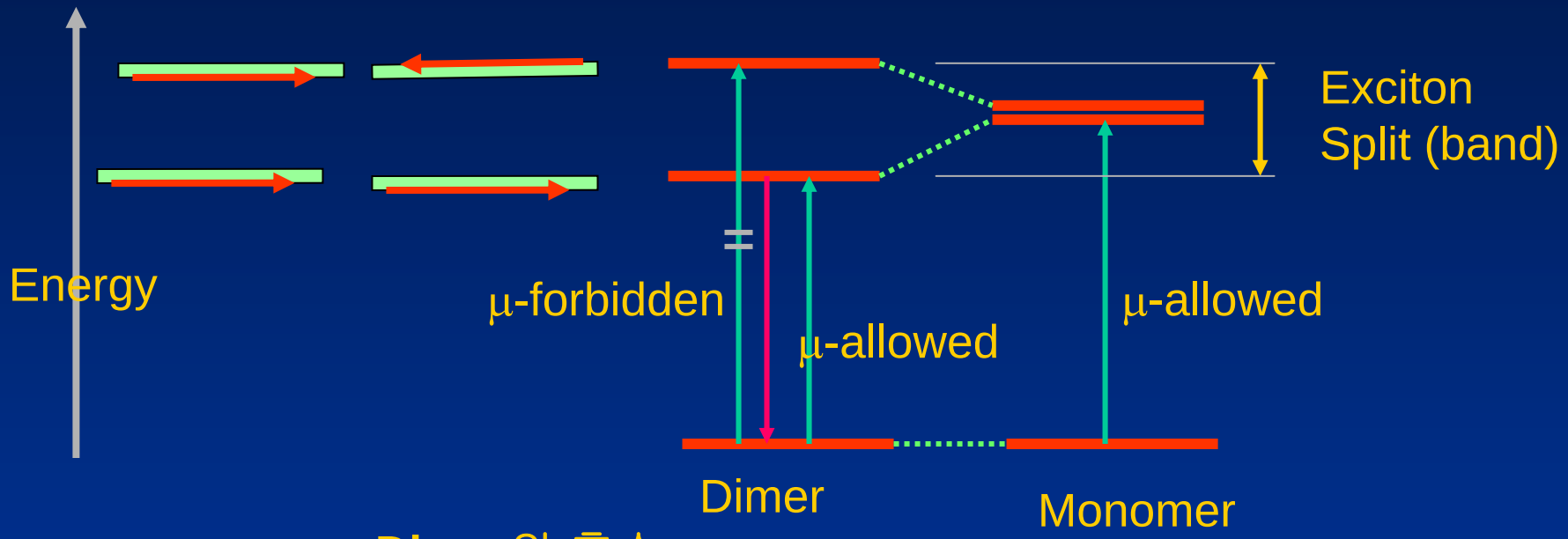
$$\Psi_{out\ of\ phase} = \frac{1}{\sqrt{2}}(\varphi_1^* \varphi_2 - \varphi_1 \varphi_2^*)$$

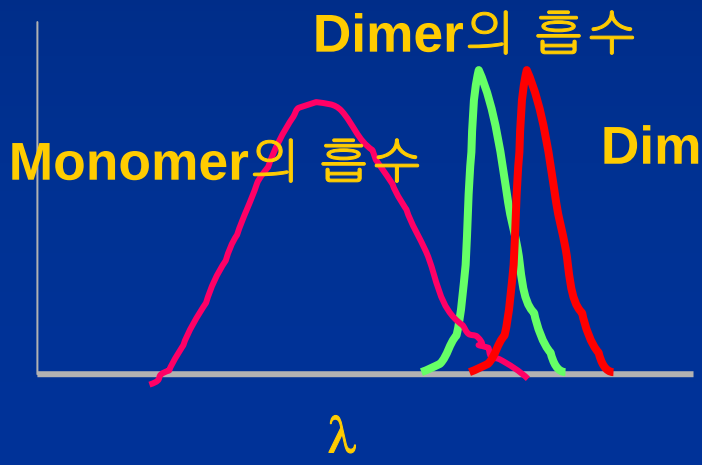
$$E_{exciton} = \frac{-(\vec{\mu}_1)(\vec{\mu}_2)}{R_{12}^3} = -\frac{-(\vec{\mu})^2}{R_{12}^3}$$

$$\Delta E_{exciton} = 2\left|E_{exciton}\right|$$

Exciton Interaction

- Linear Type : Red Shift

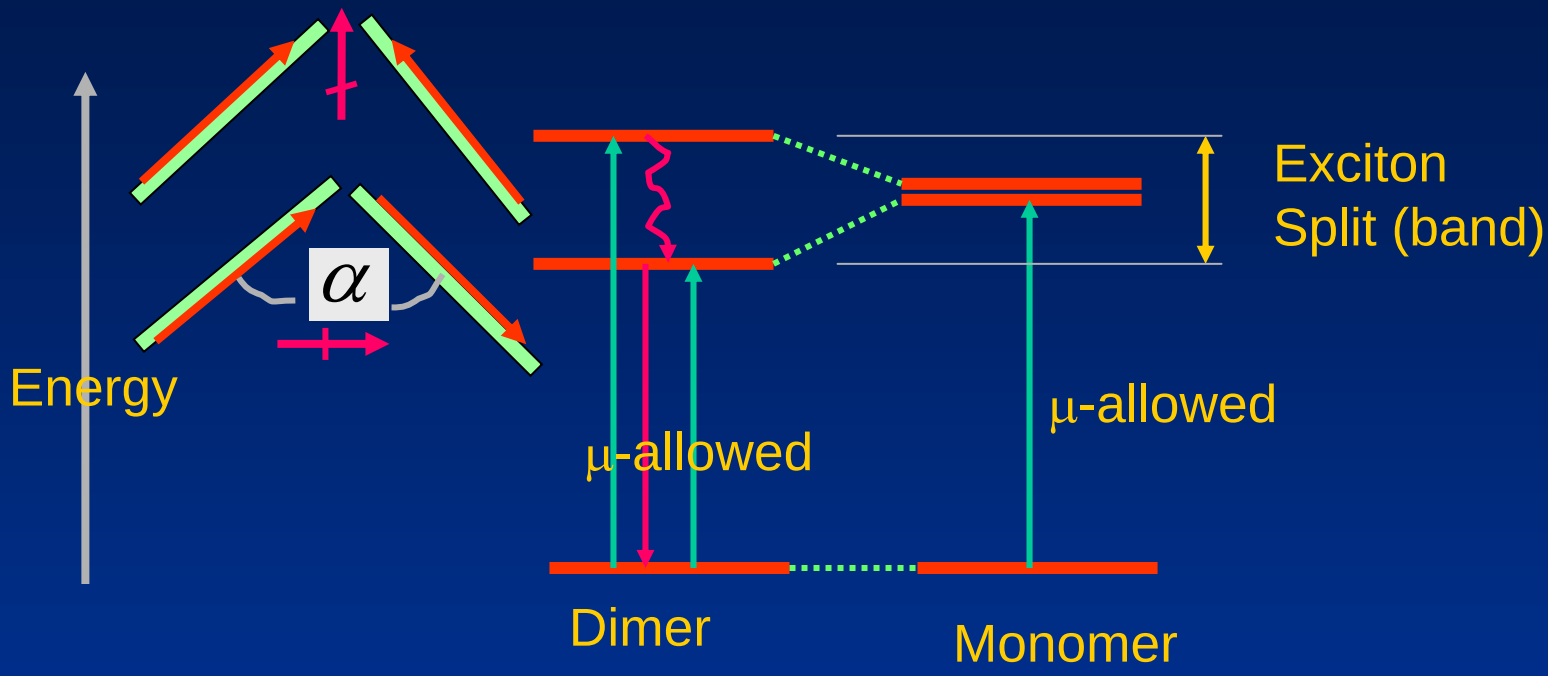




Dimer의 emission : small Stokes shift

Exciton Interaction

- Oblique Type :



$$\Delta E_{exciton} = 2\frac{|\vec{\mu}|^2}{R_{12}^3}(\cos\alpha + 3\cos^2\alpha)$$

Singlet Exciton Migration – Models

$^1M^*$ in crystal : migrate

- Exciton band model

⇒Exiton-phonon scattering 작고

⇒Mean free path of the coherent exciton 클 때 적용

Hopping Model

⇒위와 반대 경우 적용

⇒ $^1M^*$ localized molecular state

⇒ Random walk

Singlet Exciton Migration – Models

$^1M^*$ in crystal : migrate

- Exciton band model

⇒Excited lifetime 이 crystal properties에 따라 결정

⇒Low temperature에서는 Mean free path of the coherent exciton 클 때가 있다.

Hopping Model

⇒분자의 여기상태 성질이 중요

⇒상온에서는 이 모델을 대부분 적용

Singlet Exciton Migration –Hopping Models

- Exciton jump frequency

$$M_1^* \leftrightarrow M_2 \longrightarrow M_1 \leftrightarrow M_2^*$$

$$k'_{mig} = k_{mig}\left[{}^1M\right]$$

K_{mig} : *rate const. of* $^1M^*$ *exciton migration*

$^1M^*$ 가 ^1Y에 의하여 energy를 잃을 확률 p

Singlet Exciton Migration –Hopping Models

- Rate of $^1M^* - ^1Y$ energy transfer:

$$k_{YM}[^1Y] = pk_{mig}[^1Y] = pk'_{mig}c_Y$$

$$c_Y = \frac{[^1Y]}{[^1M]}, k_M = \frac{1}{\tau_M}, \sigma_{YM} = \frac{k_{YM}[^1M]}{k_M}$$

$$k'_{mig} = \frac{\sigma_{YM}k_M}{p} = (\sigma_{YM})_{\max}k_M$$

$$\text{maximum value of } \sigma_{YM}, \text{lifetime} => k'_{mig}$$

- $k'_{mig} \sim 6.7 \times 10^{12}\ sec^{-1}$ (tetracene in anthracene crystal)

□ $\Delta w \sim h\,k'_{mig} \sim 220\ cm^{-1} \sim 2B$

- $\tau_M \uparrow$ ⇨ $k_M \downarrow$ $\sigma_{YM} \uparrow$ (상대적 크기가 비교된다)

(주의 σ_{YM} 의 크기는 τ_M 이 클수록 작게 계산될 수 있다.
예로 naphthalene crystal의 경우 =82nsec -> σ_{YM} 세배 더 크다.)

Mean Singlet Exiciton Migration Length (L)

- r.m.s. displacement in a time τ_M .
- $$L = \sqrt{2\Lambda\tau_M}$$
- Λ : exciton migration coefficient
- Isotropic medium 에서는 3차원으로 계산

$$L = \sqrt{6\Lambda\tau_M}$$

- L 값의 범위 0.3 ~ 0.01 μm (for aromatic crystals)
- Naphthalene, anthracene, phenanthrene τ_M = 10~80 nsec)

- How about polycrystals? Amorphous?

Mean Singlet Exiciton Migration Length (L)

- Benzene crystal의 경우
- Singlet lifetime에서 10^5 hopping
  으로 10^5 X 2A (mean dist.)= 2 X 10^5 A
- Triplet의 경우 10^{11} hopping : 2 X 10^{11} A

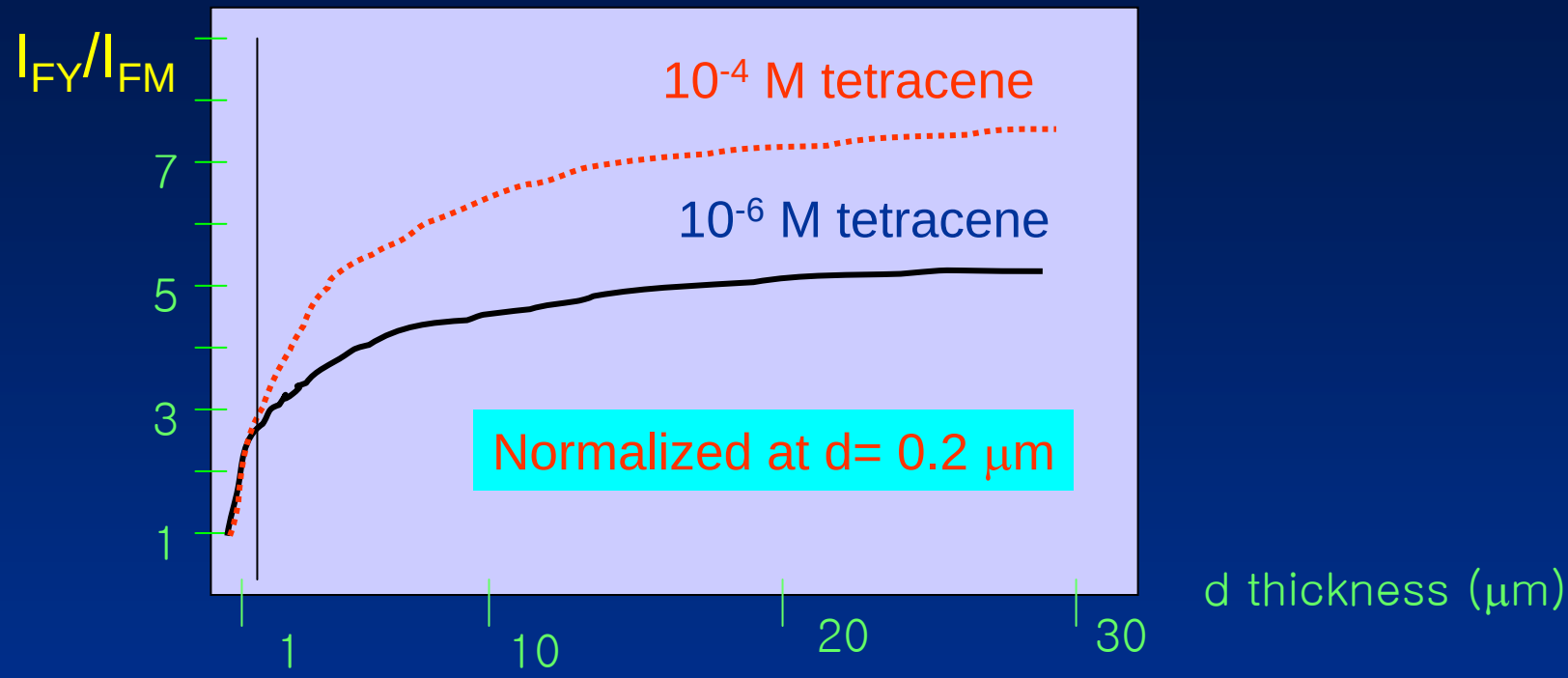
- 실제로 이렇게 멀리 갈 수 있는가?

Exiciton Traps

- Low energy traps
  => Emission site로 작용
- High energy traps
- => defects 형성
- => τ_M 및 σ_{YM} 감소
- $c_Y = \frac{[^1Y]}{[^1M]}$ 의허용범위는? 경우에 따라서 다를 수 있으나 ->
- Solution study에 따르면
- $c_Y << 2 \times 10^{-5}$M radiative transfer 우세
- $c_Y > 2 \times 10^{-5}$M : $(\tau_M)_Y$ ↓ radiationless transfer 생기면서 host fl. 와 경쟁

Layer Thickness Effects

- Tetracene (Y) in anthracene (M)



- [Y] ↑ I_{FY} ↑ I_{FM} ↓ 그러므로 I_{FY}/I_{FM} ↑

□ Thin sample과 thick sample 차이가 있다.

Thin : I_{FY}/I_{FM} 가 작고 농도에 거의 무관

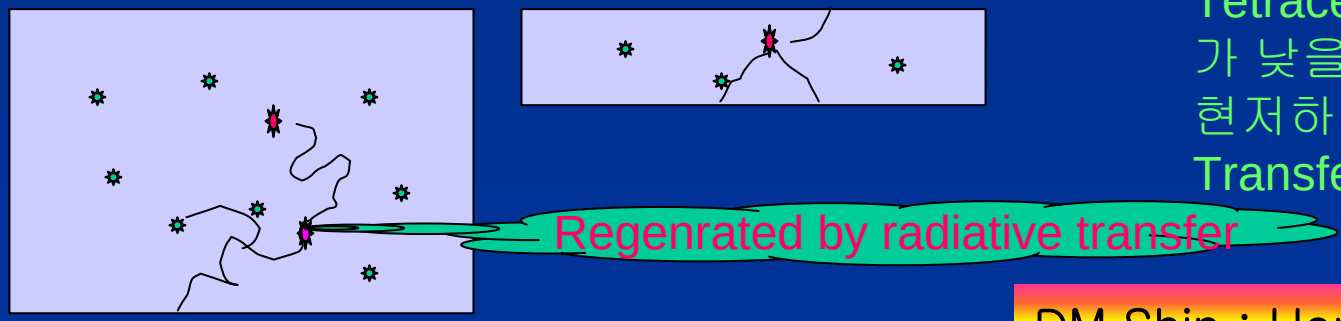
Thick: I_{FY}/I_{FM} 가 일정 **Y** 농도에 비례

Layer Thickness Effects

- Thin Sample의 경우
- surface defects가 tetracene의 exciton 과 효율적으로 경쟁

- Thick Sample의 경우
- Radiative migration이 중요해 진다.
- 물질에 따라서 base material의 self-absorption으로
  => exciton 다시 형성 => effective lifetime ↑
  => migration length ↑

*tetracene의 농도는 일정하고 surface 면적은 큰 차이 없다.



Tetracene의 농도가 낮을 수록 더욱 현저하다. Radiative Transfer 많아 지기때문

Layer Thickness Effects

- Doping 실험에서 고려해 봐야 한다!
- $$(f_{YM})_a = \frac{k_{YM}[^1Y]}{k_{FM}(1-a_{MM}) + k_{IM} + k_{YM}[^1Y]}$$

  a_{MM} : *effect* of finite self-absorption

  $k_{FM}(1-a_{MM})$: 음의값이다. M*재생하기때문.

  $\therefore (f_{YM})_a > f_{YM}$
- 실예: anthracene crystal

  few μm thick : 10 nsec

  few mm thick : ~30 nsec

  small crystal ; ~ 3 nsec

  (surface defects or oxidation)

Base material이 self-absorption이 없으면 이런 문제 없다.