Decay from the Excited State

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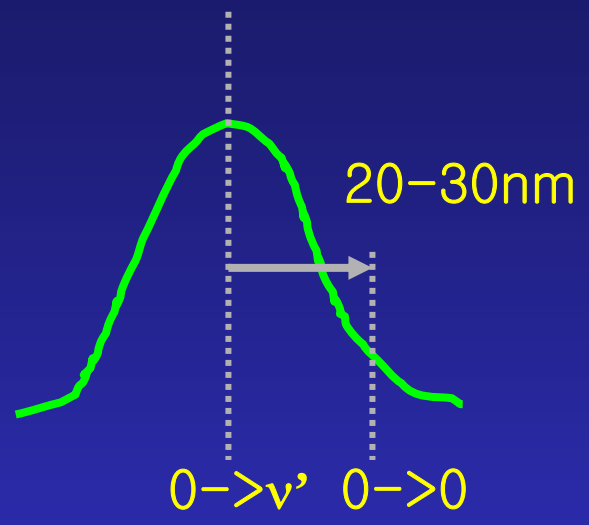
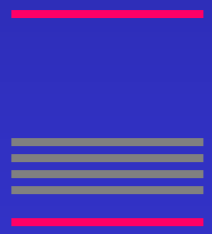
- Vibrational relaxation ~ Internal conversion



IR 영역이 된다. -> thermal relaxation이 되면서 electromagnetic radiation으로 나올 수 있다.

그러나: 실제로는 나오지 않는다.

Radiation probability $B_{ul} \propto \nu^3$



E 간격이 작아서 ν^3 의 값이 너무 작다.

따라서 excited 된 후 radiationless decay가 가장 빨리 일어난다.

- What Could affect IC?

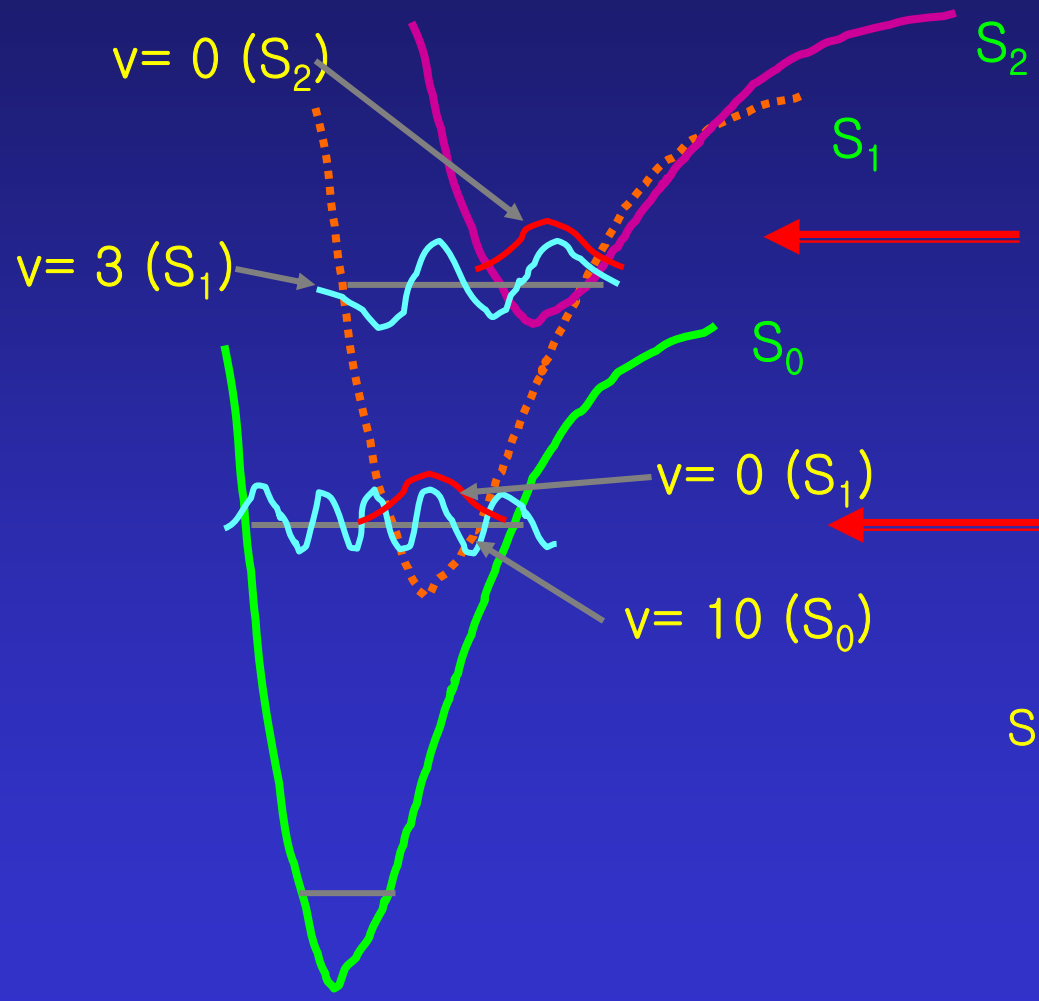
1. Franck-Condon Factor (F)
2. Vibronic coupling (Electronic Matrix Element) (β_{el})
3. Density of states (ρ)

: overlap of many density of state increases F

Fermi's Golden Rule (for radiationless transition)

$$k_{RLT} = \frac{4\pi^2}{n} F \beta_{el} \rho$$

- Franck-Condon Factor (F)
- Radiationless transitions b/w "Matching" Surface

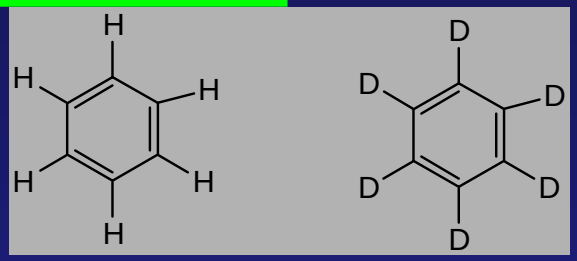


Large Franck-Condon Factor

$$\langle \chi S_1 | \chi S_2 \rangle \rightarrow \text{"large"}$$
$$\therefore k_{IC} \rightarrow \text{"}fast\text{"}$$

$$\langle \chi S_0 | \chi S_1 \rangle \rightarrow \sim 0$$
$$\therefore k_{IC} \rightarrow \text{"}slow\text{"}$$

Small Franck-Condon Factor



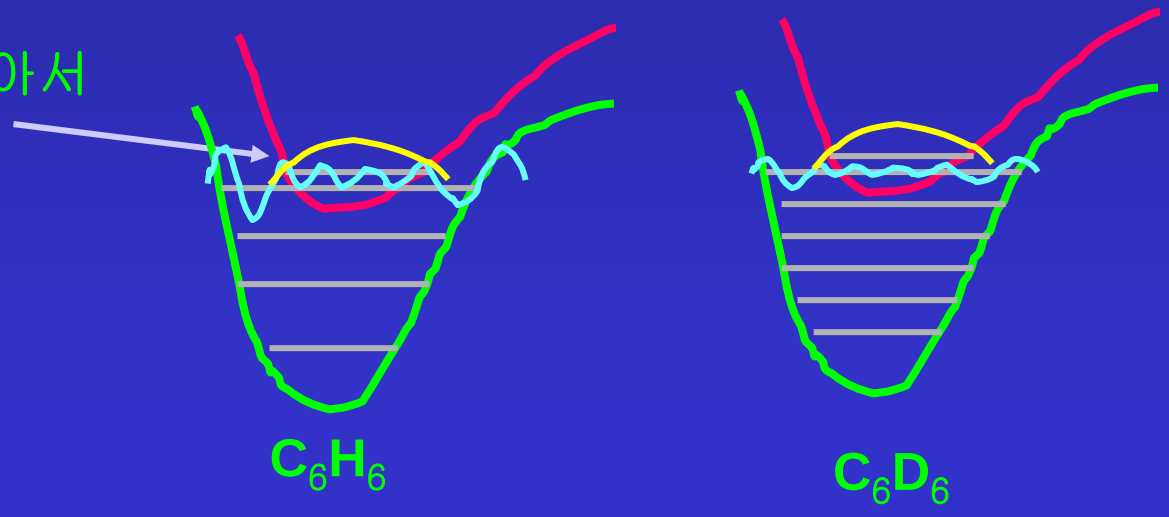
- Franck-Condon Factor (F)
- Benzene and benzene-d_6
- Fluorescence quantum yield of benzene-d_6 is higher.
- Benzene decays faster.
- Why?

$$\Phi_F(H_6) < \Phi_F(D_6)$$

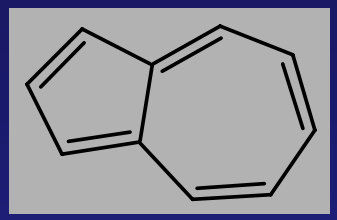
$$\tau_P(H_6) = 6\,\text{sec}, \tau_P(d_6) = 12\,\text{sec}$$

C-H vibration frequency : 3000cm^{-1}
C-D vibration frequency : 2200cm^{-1}

Wave ftn overlap 이 많아서
F 값이 크고,
k_{RLT}가 크며
Φ_F가 작다.



- Azulene

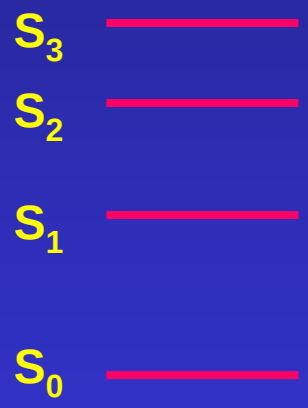


$$\Phi_F(S_2 \rightarrow S_0) \approx 0.03$$

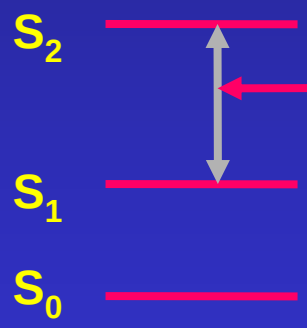
$$k_{ic}(S_2 \rightarrow S_1) \approx 7X10^8 \text{ sec}^{-1}$$

$$k_{ic}(S_1 \rightarrow S_0) \approx 10^{12} \text{ sec}^{-1}$$

Exceptionally fast: Why?



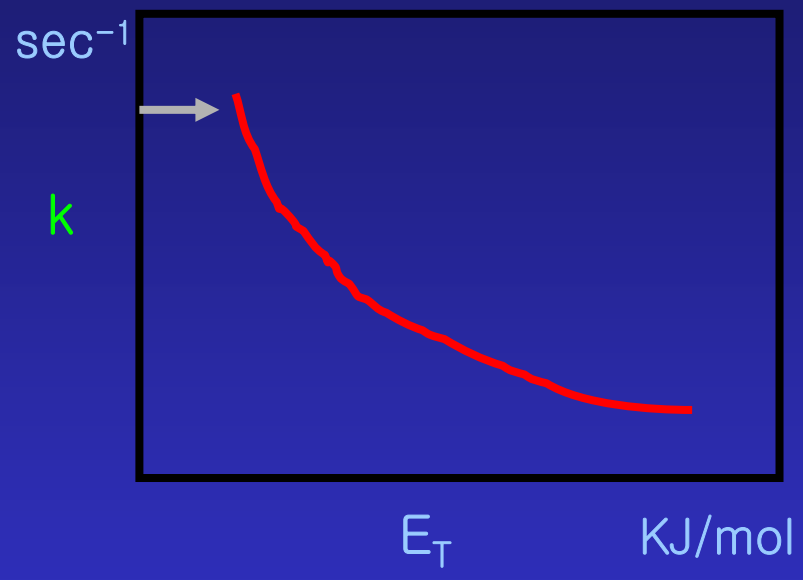
일반적인 **energy** 간격

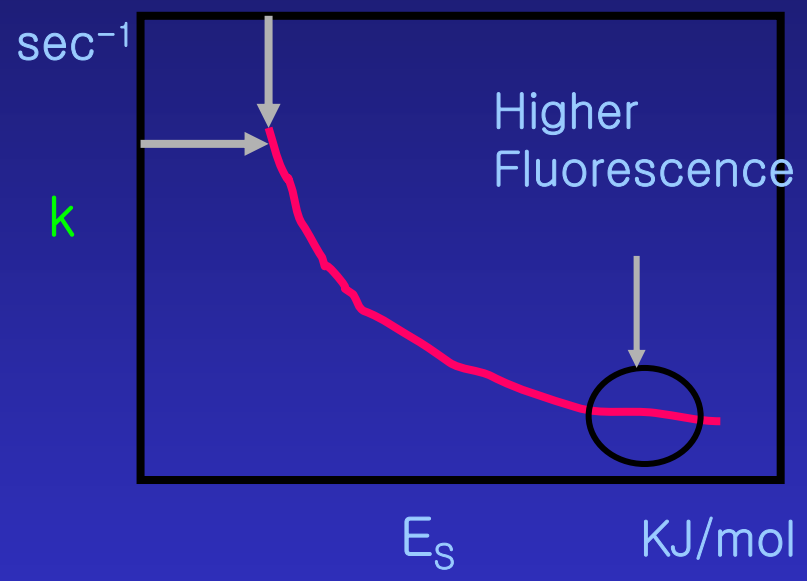


Azulene의 경우

energy간격 **= 40 kcal /mole** 로 유난히 크다.
=> F가 작고
=> k_{ic}가 작게 된다.

- Energy Gap and rate of RLT
- Aromatic hydrocarbon의 경우





- 두 state 사이의 orbital overlap이 클수록 F 가 크다. 에너지 gap 이 작을수록 overlap이 크다.

- **SO coupling ; Vibronic coupling (β_{el})**

$$\beta_{elec}^{SO} = \langle \psi | H_{SO} | \psi \rangle$$

H_{SO} has three components R_x, R_y, R_z.

- **When ψ is p_x, p_x X p_x = symmetric.**
- **p_x H_{SO} p_x = antisymmetric => β_e =0. Transition is forbidden.**

- **El Sayed's Rule**

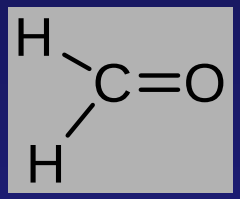
Intersystem crossing

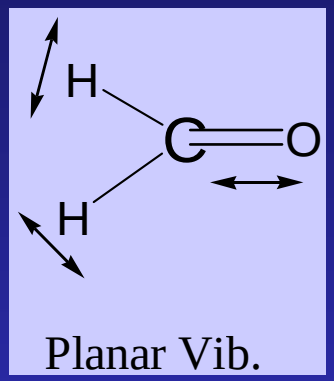
allowed	$^1(n,\pi^*) \longleftrightarrow {}^3(\pi,\pi^*)$	$^3(n,\pi^*) \longleftrightarrow {}^1(\pi,\pi^*)$
forbidden	$^1(n,\pi^*) \longleftrightarrow {}^3(n,\pi^*)$	$^3(\pi,\pi^*) \longleftrightarrow {}^1(\pi,\pi^*)$

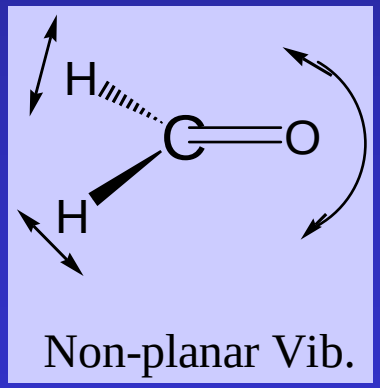
Φ~10^{-2} ~10^{-3}

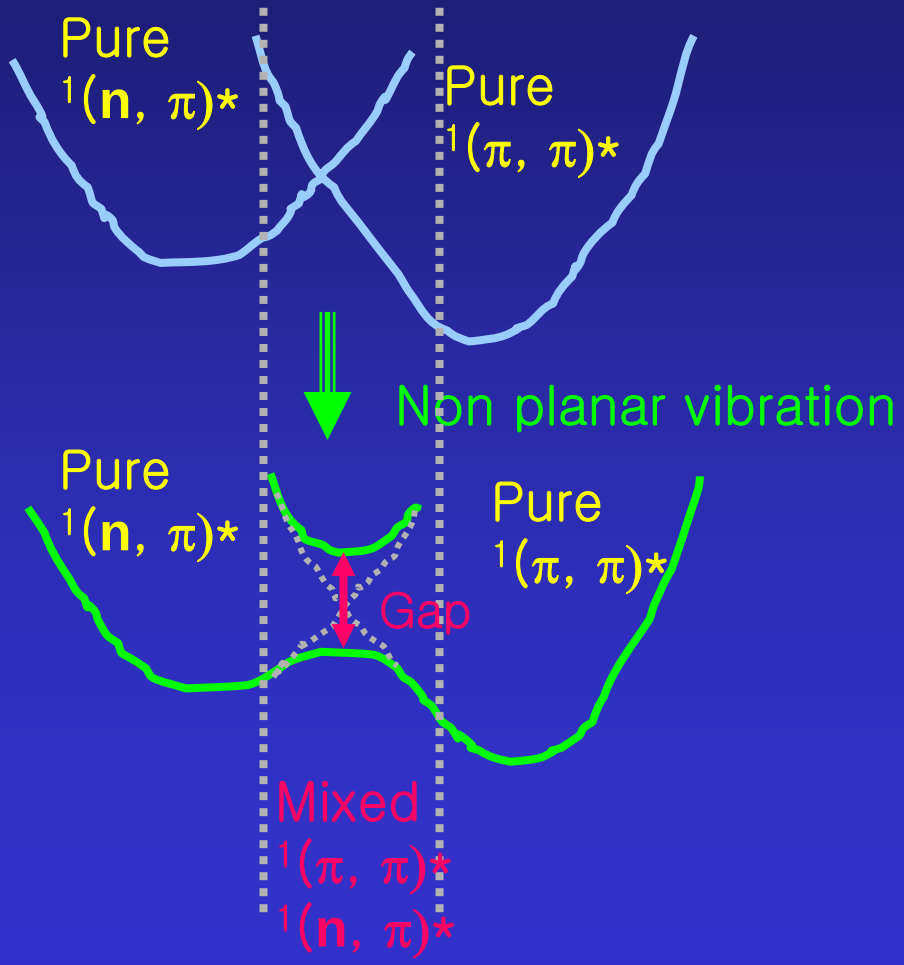
Forbidden에 해당되는 것은 같은 두개의 ft.
따라서 두개 곱하면 symmetric,
여기에 Hso 곱하면 antisym. 이므로 forbidden

- **SO coupling ; Vibronic coupling (β_{el})**
- $(\pi, \pi)^*$, $(\mathbf{n}, \pi)^*$ mixed

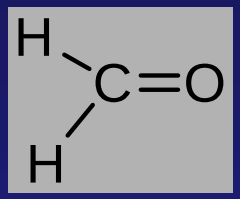


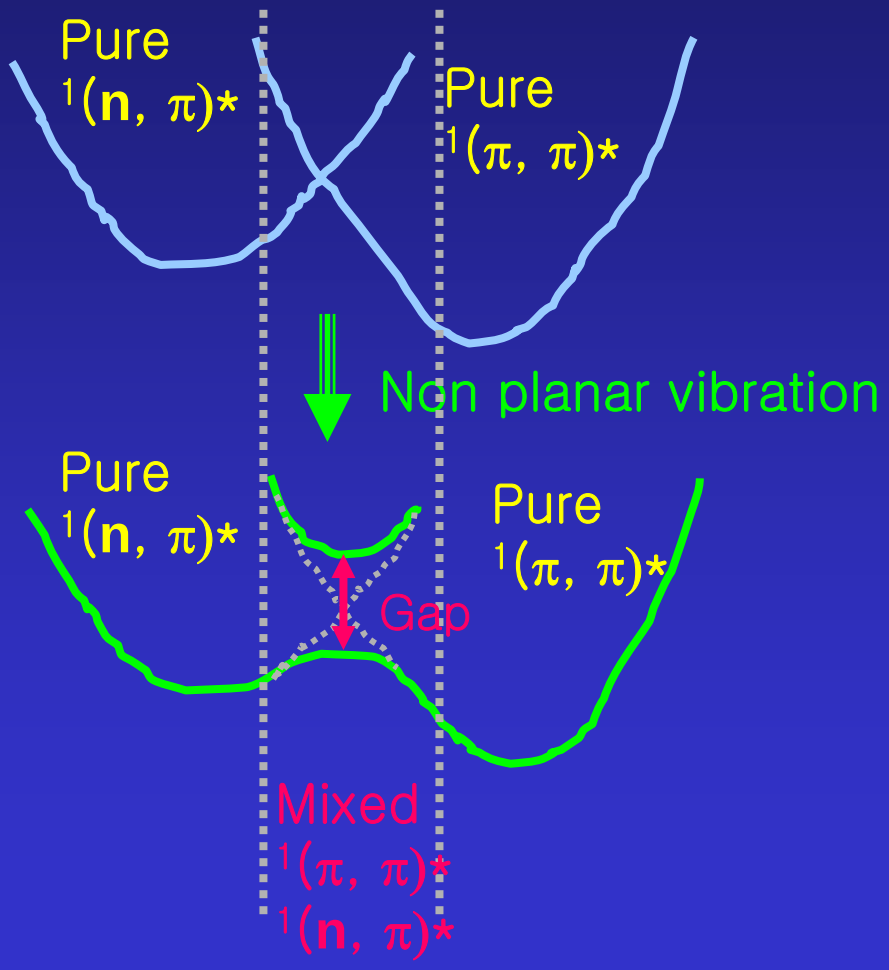






- **SO coupling ; Vibronic coupling (β_{el})**
- **(π, π)*, (n, π)*** mixed





Gap=0 : No mixing

Small gap: vibration energy 가 electronic coupling과 유사 따라서 둘 사이의 관계에 따라 떨어지는 방향이 다르다.

Large gap: electronic coupling 즉 mixing. Gap 영역에서의 vertical Transition이 어려워 진다. 즉 위로 일단 올라가면 radiationless transition 이 느려진다.

- **SO coupling ; Vibronic coupling (β_{el})**

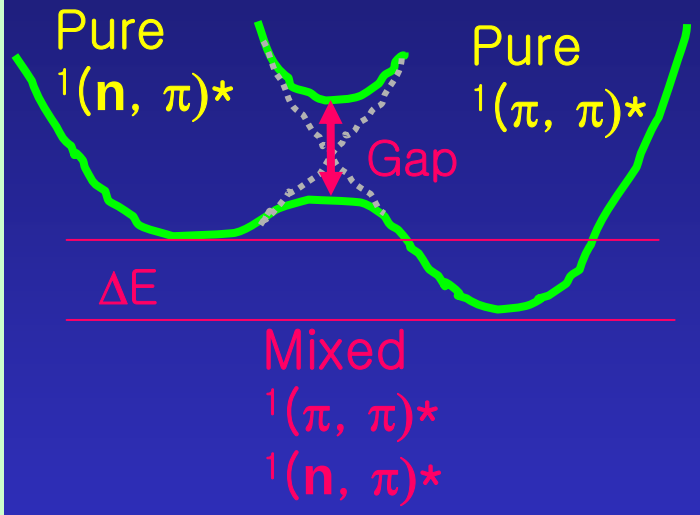
$$\varphi(S_1) = \varphi(n,\pi^*) + \lambda\varphi(\pi,\pi^*)$$

λ : mixing coefficient.

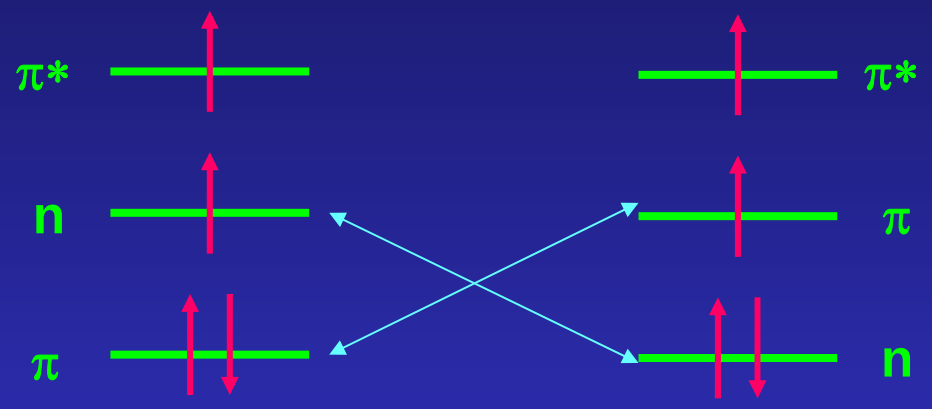
$$\lambda = \left|\frac{\langle \varphi_a | H_{vib} | \varphi_b \rangle}{E_a - E_b}\right| \quad : \quad \frac{\text{matrix element}}{\text{energy separation}}$$

$$S_1 = n\pi^* + \left|\frac{\langle n\pi^* | H_{vib} | \pi\pi^* \rangle}{E_{\pi\pi^*} - E_{n\pi^*}}\right| \pi\pi^*$$

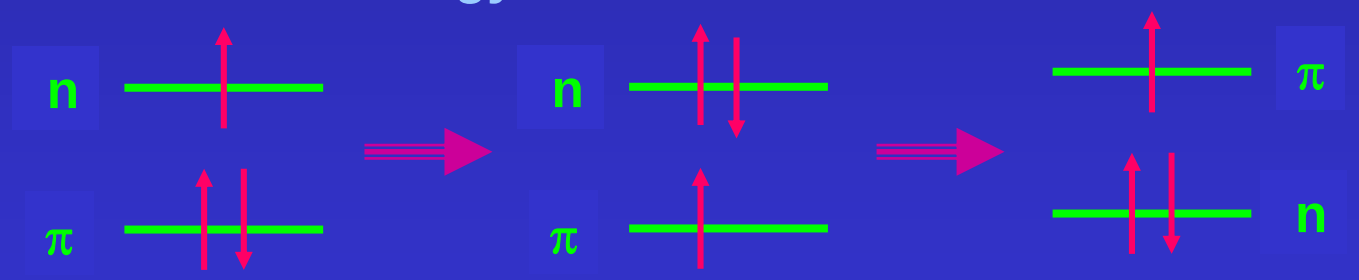
$$\langle n\pi^* | H | \pi\pi^* \rangle \sim \langle n | H | \pi \rangle \neq 0 : \text{non-planar vib.}$$



- **SO coupling ; Vibronic coupling (β_{el})**



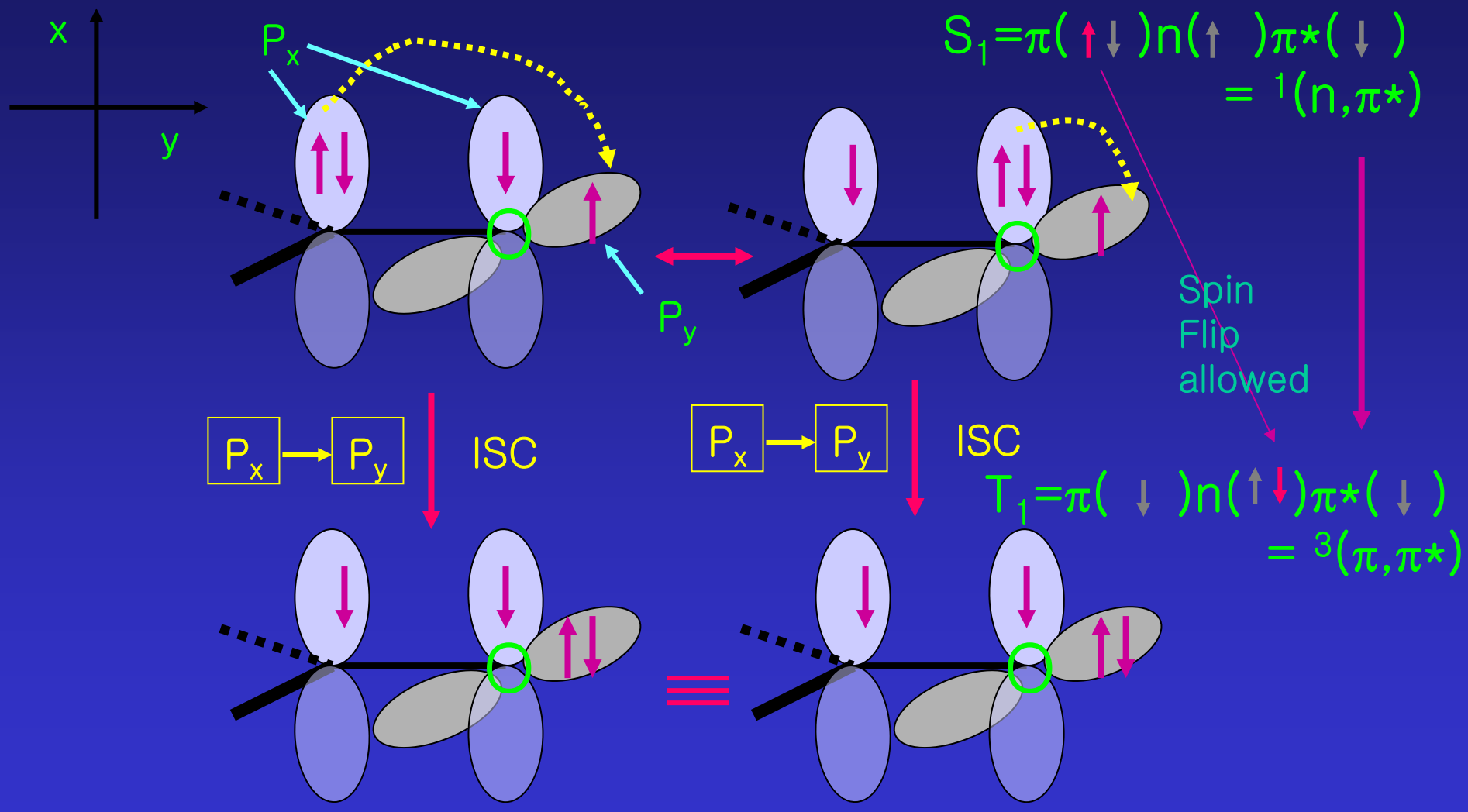
Vibration에 의해서
Energy level이 바뀜



전자가 위로 올라감

Energy적으로 불안해 져서
Vibration을 이용하여 낮아짐

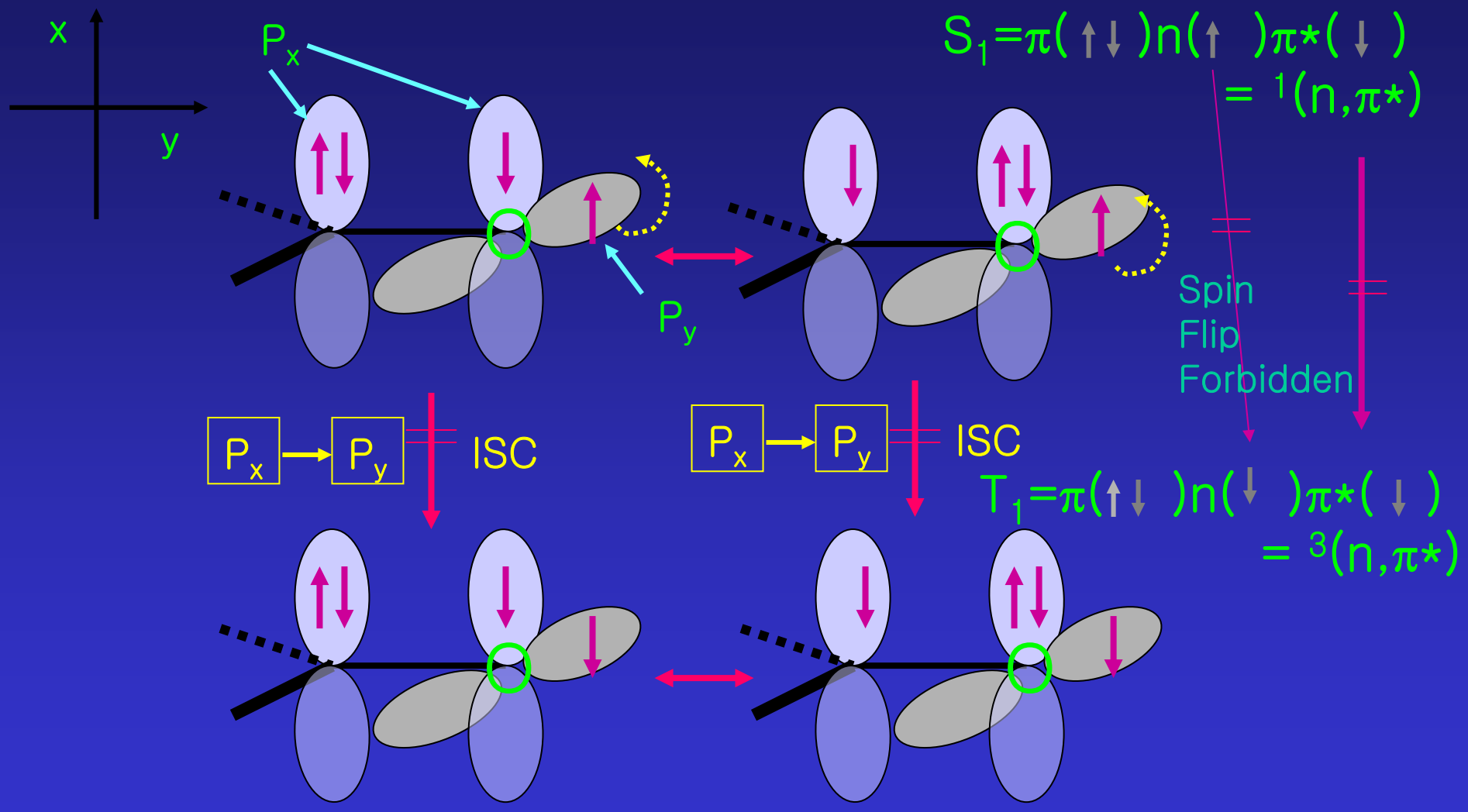
- Visual Presentation of S.O. Coupling



Spin과 Orbital이 coupling 되는
Process라서 spin-flip 이 allowed

이쪽이 더 잘 일어난다.

- Visual Presentation of S.O. Coupling



Decays from Excited States : Spin-Orbit Coupling

- 다음 carbonyl 화합물의 isc rate를 비교해 보자.

•k_{ST} ~10^{11}–10^{10} sec^{-1}

fast

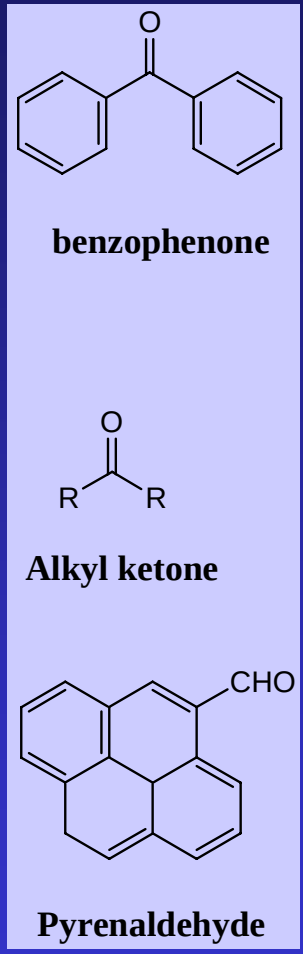
•k_{ST} ~ 10^{9}– 10^{8} sec^{-1}

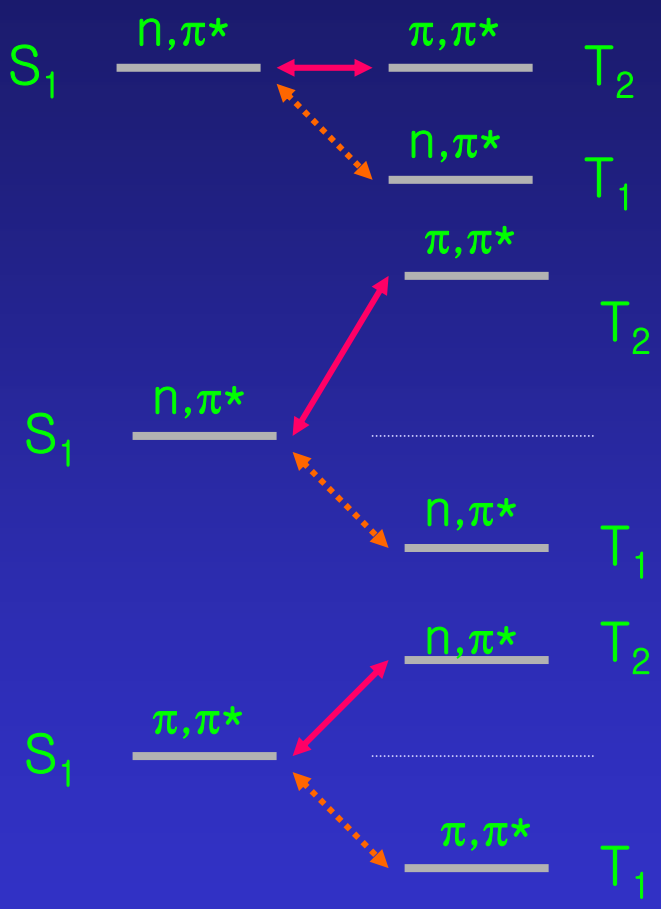
intermediate

•k_{ST} ~ 10^{7}– 10^{6} sec^{-1}

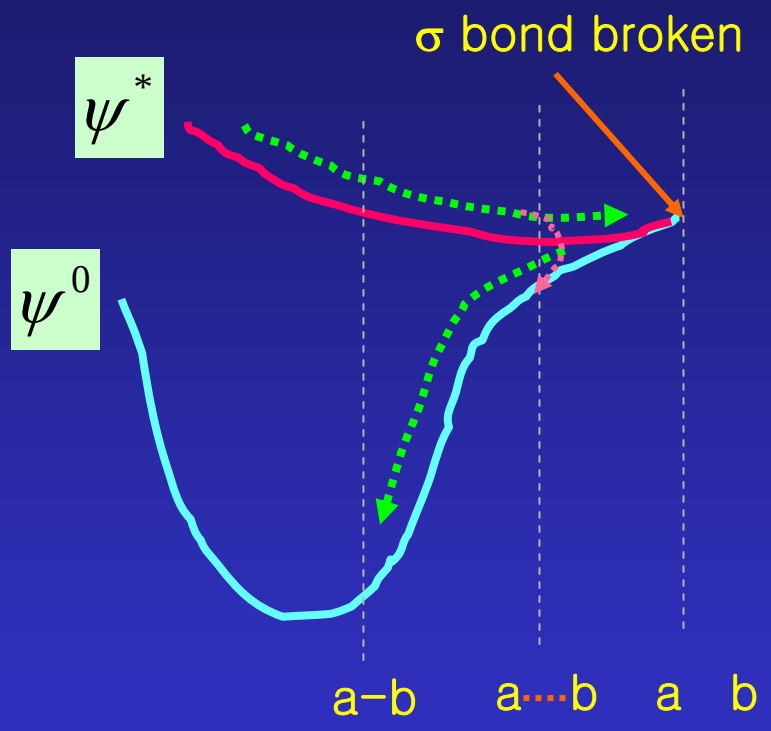
slow

(out-of-plane bending 이 적다.)

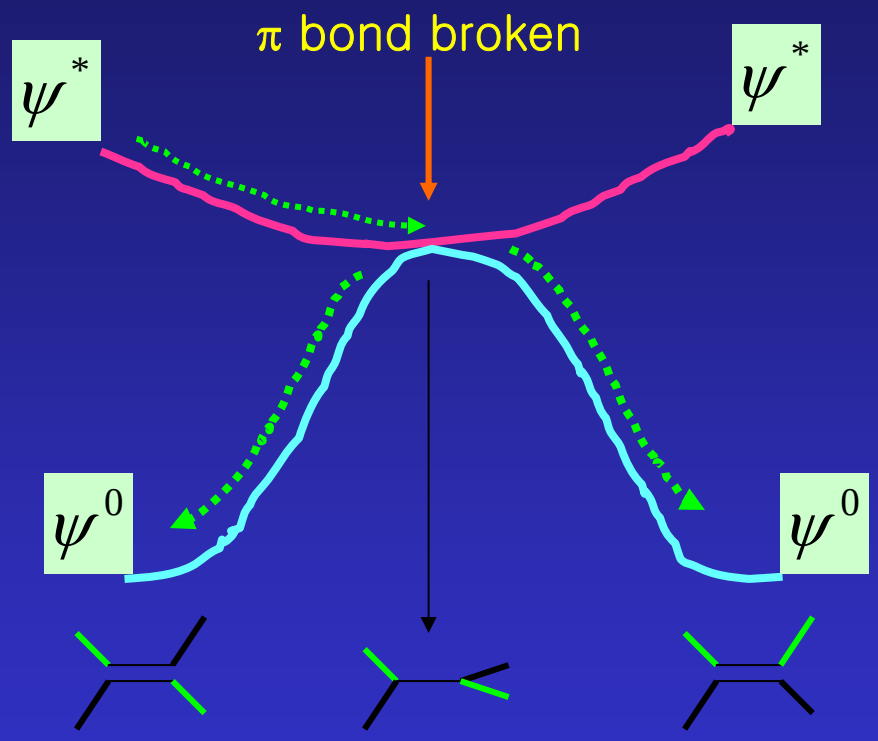




- Structural Effects

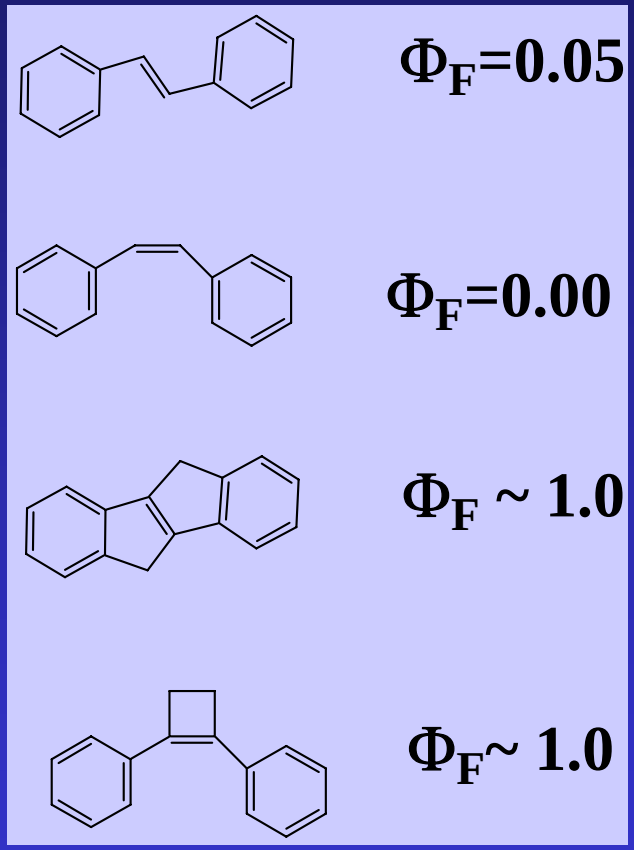


stretching a σ bond



twisting a π bond

- Structural Effect
- 아래와 같은 형광 효율을 갖는 이유를 알아보자.

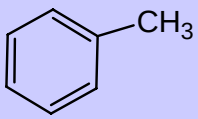


Steric interactions b/w the phenyl groups of cis-stilbene : rapid r l t by twisting. trans-Stilbene can also twist about the C=C bond in S_1.

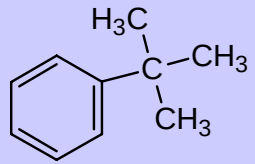
The other two molecules: twisting motion is severely hindered by structural constraints.

이외에도 온도를 낮추거나, 주변의 환경을 조정하여 분자들이 움직이지 못하게 하면 형광의 양을 크게 증가할 수 있다.

- Structural Effect
- 아래와 같은 형광 효율을 갖는 이유를 알아보자.



$k_{IC} \sim 10^7\ sec^{-1}$



$k_{IC} \sim 10^8\ sec^{-1}$

Ph-C의 길이가 tert-butyl benzene의 경우 매우 길어서 loose한 bolt 와 같은 형태로 쉽게 열에너지로 전환되면서 기저상태로 떨어지게 된다.

77 K 에서 Φ_P (toluene) ~1.0 . 이고 Φ_P (tert-butyl benzene) ~0.0 인 것도 같은 이유에서 이다.

- Intersystem Crossing
- $S_1 \longrightarrow T_1\ (T_n)$
- $k_{isc} \longrightarrow 10^6 \sim 10^{11}\ sec^{-1}$

Aromatic hydrocarbon

Molecules containing "heavy atom"

- Intersystem Crossing

compounds	k_{isc}	ΔE_{ST}	
Naphthalene	10^6	30	
Anthracene	10^8	2-3	
Pyrene	10^6	30	
9-acetoanthracene	$\sim 10^{10}$	~5	
9,10-dibromoanthracene	$\sim 10^8$	30	$^1\pi\pi^* \rightarrow {}^3\pi\pi^*$
Benzophenone	10^{11}	5	$^1n\pi^* \rightarrow {}^3\pi\pi^*$
acetone	$5X10^8$	5	$^1n\pi^* \rightarrow {}^3n\pi^*$

- ΔE_{ST} 작아지면 k_{isc} 증가
- Nonbonding electron 있는 경우와 없는 경우에 차이가 있다.
- Heavy atom effect: 9,10-dibromoanthracene ΔE_{ST}=30임에도 10^8으로 2 order 증가
- Benzophenone 과 acetone 의 경우 allowed tr. 과 forbidden tr. 차이

Film

- ISC internal heavy atom effects:

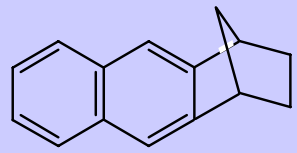
	k_F	k_{isc}	k_{TS}	Φ_P
naphthalene	10^6	10^6	10^{-1}	0.05
1-fluoronaphthalene	10^6	10^6	10^{-1}	0.06
1-chloronaphthalene	10^6	10^8	10	0.54
1-bromonaphthalene	10^6	10^8	50	0.55
Perylene	$2x10^8$	10^7	Φ_F =0.98	
3-bromoperylene	$2x10^8$	$<10^8$	Φ_F =0.98	

- Naphthalene : k_{isc} k_{TS} (T 에서 S로 , 인광등) Φ_P 모두 증가

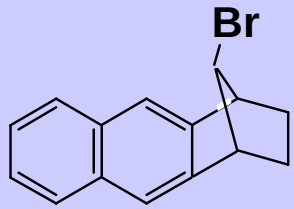
- Perylene : bromo 로 치환 했음에도 인광이 없다. ???이유는???

- 2 order 정도는 차이가 나야 heavy atom effect가 있다. 이경우는 형과의 속도가 isc속도보다 빨라서 영향이 없다.

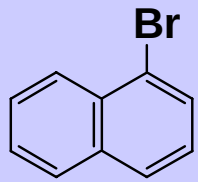
- ISC external heavy atom effects:



$k_{isc} = 2 \times 10^6$



$k_{isc} = 300 \times 10^6$



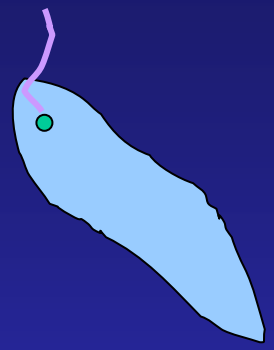
$k_{isc} = 500 \times 10^6$

- Benzene의 흡수 spectrum

L_a L_b 는 변화하지 않고 S_0 -> T_1 만 증가 시킬 수 있는가?

- EtI를 첨가하면 spin orbit coupling 의하여 inetersystem crossing 증가

- ISC external heavy atom effects: Euglena
- 빛을 따라 움직인다.



- Flavin : photo receptor (빛을 감지한다.)

0.01 molar KI 를 첨가하였더니 빛을 따라가는 움직임이 감소?

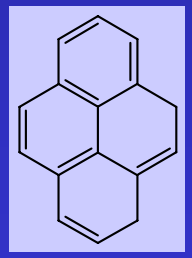
- singlet excited state가 KI에 의하여 quenching 되었다.

- 모든 경우 heavy atom effect가 있는 것이 아니다! carotein 의 singlet 은 kic =10^{14}이므로 k_{isc} 가 일어날 수 없다. 즉 KI의 효과가 없다.

- ISC external heavy atom effects:
- 영향을 미치는 물질들:
- 산소, Xe, organic halide, organometallic

- 산소의 경우 (10^{-2}~ 10^{-3} mol in solution)
- $k = k_{isc} + k_q [O_2]$

- $K_q = 10^{10} \sim 10^{9}\ M^{-1}\ sec^{-1}$ (diffusion controlled rxn)
- $k_{isc} = \sim 10^{10}$ 이면 산소의 영향이 거의 없다.
- $k_{isc} = \sim 10^{6}$ 이면 산소의 영향 많이 받는다.

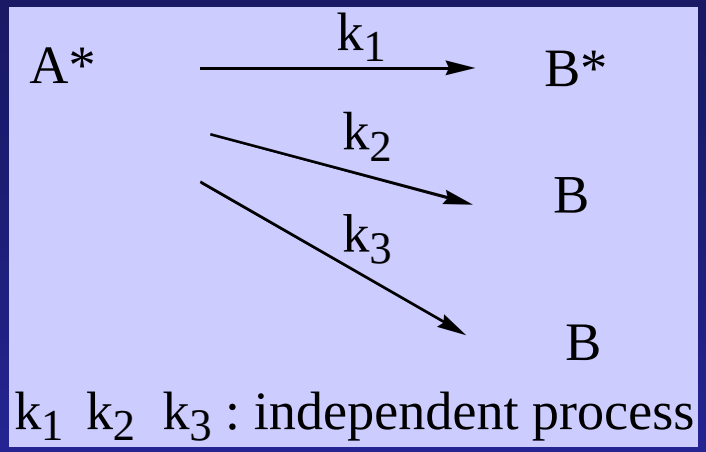


$K = 10^7$ w/o O_2
$\Phi_{isc} \sim 0.3$

→ $k_{isc} < k_q [O_2]$

산소의 영향이 크다.

- Kinetics



$$\frac{d[A^*]}{dt} = -[A^*](k_1 + k_2 + k_3) = -\sum k[A^*]$$

$$\frac{d[A^*]}{[A^*]} = -\sum k dt$$

$$[A^*] = [A^*]_o e^{-\sum kt}$$

$$\tau = \frac{1}{\sum k}$$

- Kinetics

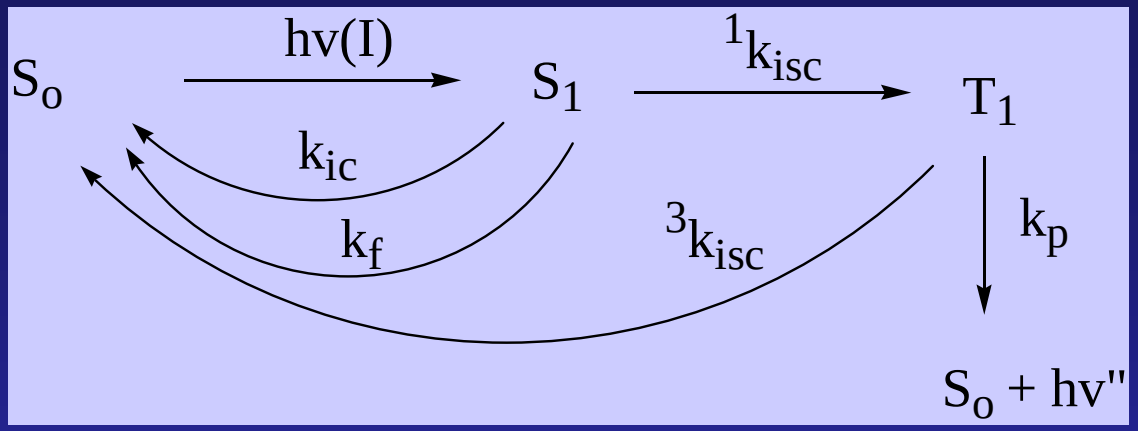
$$\tau_f = \frac{1}{k_F^o + {}^1k_{isc} + k_{ic}}$$

$$\tau_p = \frac{1}{k_P^o + {}^3k_{isc}}$$

$${}^1k_{isc} : \text{singlet} \rightarrow \text{triplet}$$

$${}^3k_{isc} : \text{triplet} \rightarrow \text{singlet}$$

- Kinetics



I : *rate* of absorption of photons

$$[I] = [S_1]\sum {}^1k \quad : \quad \sum {}^1k = k_{ic} + k_f + {}^1k_{isc}$$

$$\Phi_f = \frac{\textit{rate} \text{ of emission by } S_1}{\textit{rate} \text{ of absorption of photons by } S_o}$$

$$= \frac{k_f[S_1]}{I_a} = \frac{k_f}{\sum {}^1k}$$

$$[S_1] = \frac{I_a}{k_{isc} + k_{ic} + k_f}$$

- Kinetics

$$\tau_f = \frac{1}{\sum {}^1k} \text{ 이므로 } \Phi_f = k_f \tau_f$$

$$\Phi_{ic} = k_{ic}\tau_f \quad , \quad \Phi_{isc} = k_{isc}\tau_f$$

- Kinetics

$$ {}^{1}k_{isc}[S_1] = {}^{3}k_{isc}[T_1] + k_p[T_1] $$

$$ [T_1] = \frac{{}^{1}k_{isc}[S_1]}{{}^{3}k_{isc} + k_p} $$

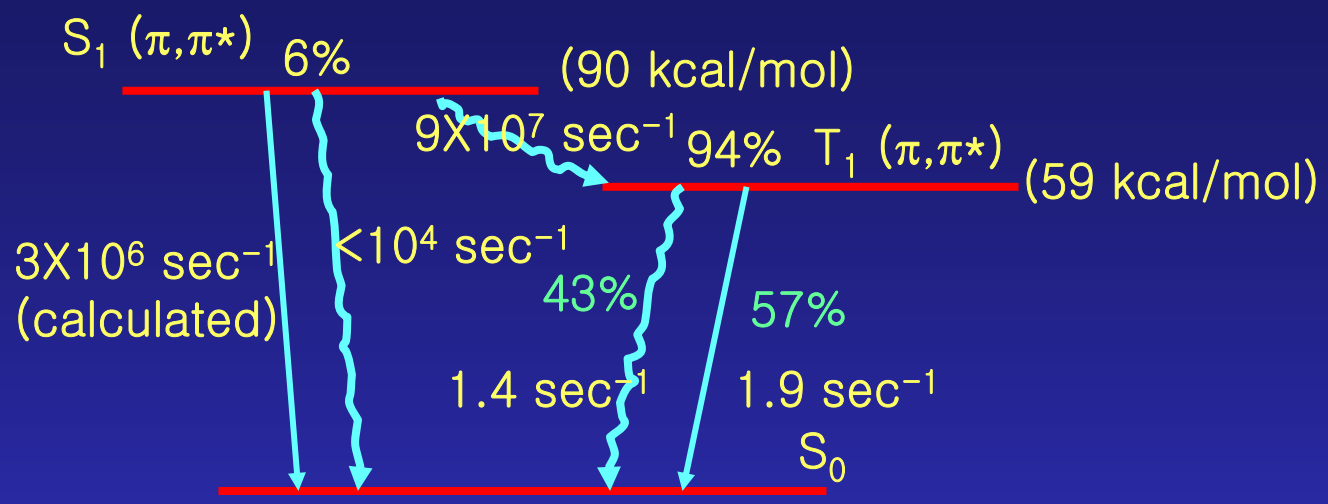
$$ \Phi_p = {}^{1}\Phi_{isc} \frac{k_p}{k_p + {}^{3}k_{isc}} = {}^{1}\Phi_{isc}\tau_p k_p $$

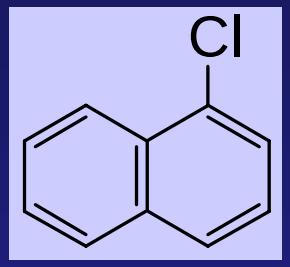
설명

$$ \Phi_p = \frac{k_p[T_1]}{I_a} = \frac{k_p \dfrac{k_{isc}}{{}^{1}k_{isc} + k_p} \dfrac{I_a}{{}^{1}k_{isc} + k_f + k_{ic}}}{I_a} $$

$$ = \underbrace{\frac{1}{({}^{1}k_{isc} + k_p)}}_{\tau_p} k_p \underbrace{\frac{k_{isc}}{({}^{1}k_{isc} + k_f + k_{ic})}}_{\Phi_{isc}} $$

- Kinetics





설명

Φ_f=0.06 Φ_p=0.54

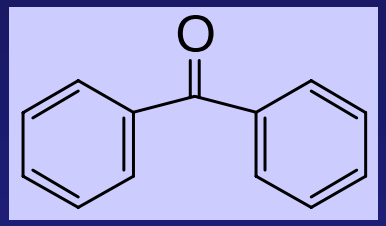
ΔE_{ST} = 31 Kcal/mol 상당히 커서 일반적인 aromatic hydrocarbon 과 일치

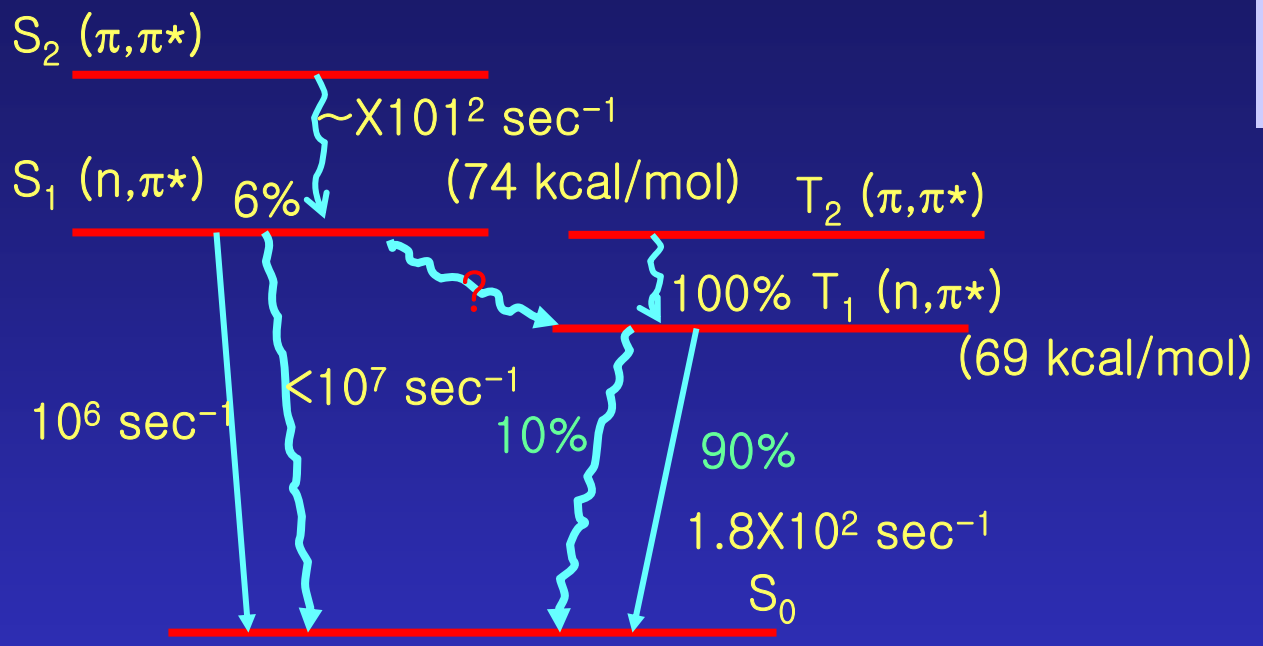
Cl 치환기로 인해 조금 빨라지나 느린 편이다.

그러나) 형광으로 떨어지는 속도가 상당히 느리고, internal conversion rate 도 느려서 상대적으로 isc가 잘 일어난다.

$\Phi_f + \Phi_p$=0.6 이므로 나머지는 빛이 안 나오는 isc (T_1 -> S_o)

- Kinetics –home work

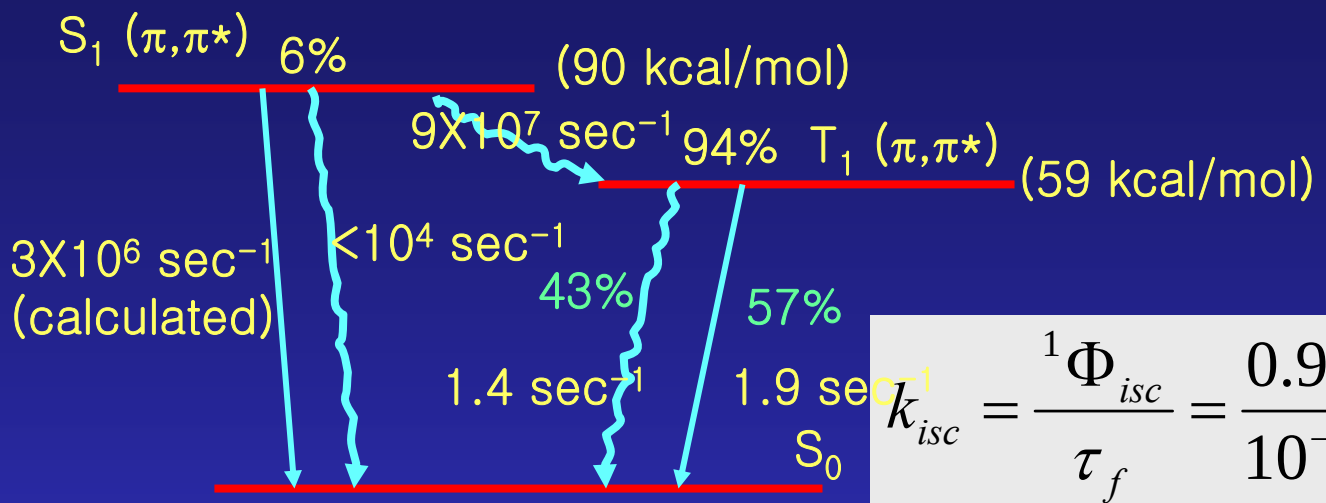


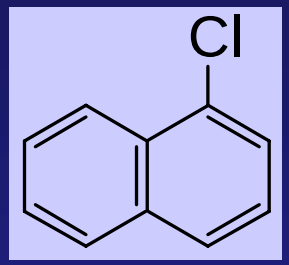


$\Phi_f < 10^{-4}$ $\tau_S \sim 10^{-11}$ $\tau_T = 6 \times 10^{-3}$

$^1k_{isc}$, $^3K_{isc}$,k_f 를 구해 보아라.

- Kinetics





$^1K_{isc}$, $^3K_{isc}$,k_f 를 구해 보아라.

$$k_{isc} = \frac{^1\Phi_{isc}}{\tau_f} = \frac{0.94}{10^{-8}} = 9.4\times10^7\ \mathrm{sec}^{-1}$$

$$^3\Phi_{isc} = {}^1\Phi_{isc}\tau_p\ {}^3k_{isc}$$ 이므로

$$^3k_{isc} = \frac{^3\Phi_{isc}}{^1\Phi_{isc}\tau_p} = \frac{0.4}{0.94\times0.3} = 1.4\,\mathrm{sec}^{-1}$$

$$:\ 0.4 = 0.94\times0.43,\ \ 0.3 = 1/(1.4+1.9).$$

$$k_f = \frac{^3\Phi_f}{\tau_f} = \frac{0.06}{10^{-8}} = 6\times10^6\ \mathrm{sec}^{-1}$$

- 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

$$^1D^* + A \rightarrow {}^1D + {}^1A^* \quad \text{Singlet - Singlet ET}$$ (spin conserved)

$$^3D^* + A \rightarrow {}^1D + {}^3A^* \quad \text{Triplet - Triplet ET}$$ (spin conserved)

$$^3D^* + {}^3A_0 \rightarrow {}^1D + {}^3A_n^* \quad \text{Triplet - Triplet ET}$$

$$^3D^* + A \rightarrow {}^1D + {}^1A^* \quad \text{Triplet - Singlet ET}$$

$$^3D^* + {}^3A_0 \rightarrow {}^1D + {}^1A^* \quad \text{Triplet - Singlet ET}$$ (singlet Oxygen 형성) (spin conserved)

$$^3D^* + A \rightarrow {}^1D + {}^1A^* \quad \text{Triplet - Singlet ET}$$

이 경우 triplet lifetime 이 길어서 Process를 가능하게 한다.

Triplet – triplet annihilation도 같은 이유로 가능하다. ~ 40 A 까지 in cellulose acetate film

- Trivial 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

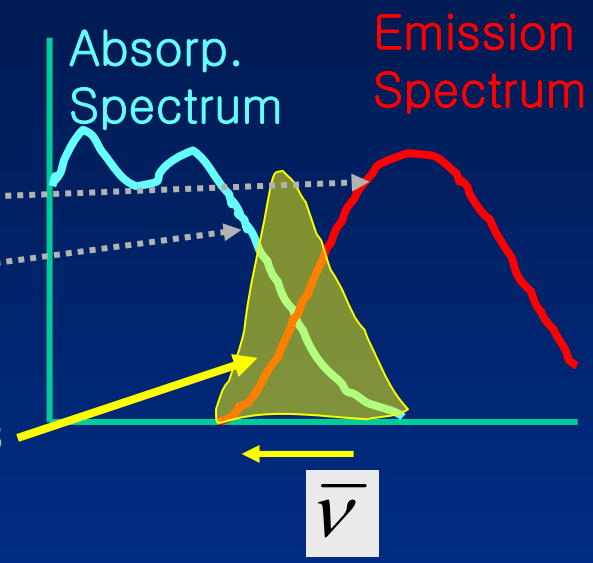
- Singlet–triplet, Triplet–triplet migration?

  일반적으로는 무시 : triplet absorption이 작다.

- Trivial Radiative Energy Transfer

$$P_{r.t.} \propto \frac{[A]l}{\theta_E} \int_0^\infty F_D(\bar{\nu})\varepsilon_A(\bar{\nu})d\bar{\nu}$$

: overelap of D and A species



$[A]$: # of acceptor molecules in the path of the emitted photon.

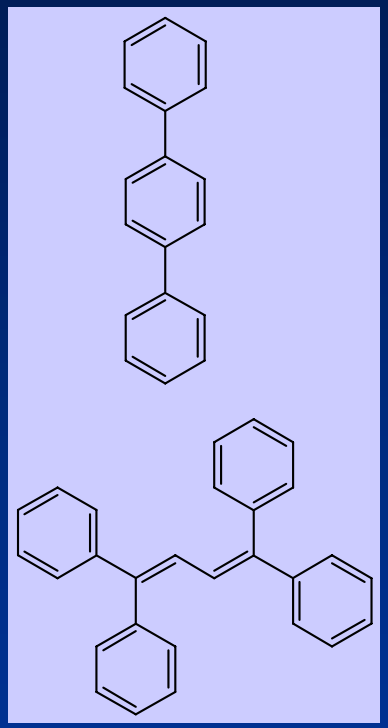
l : path length.

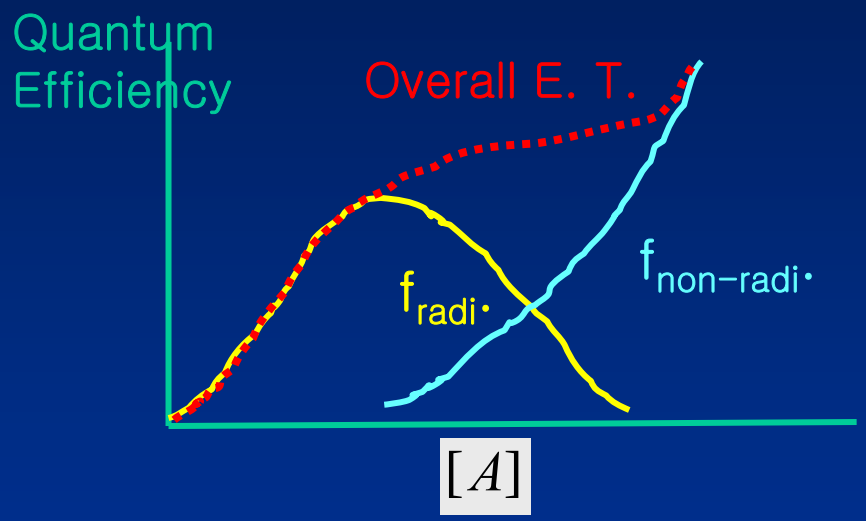
θ_E : Quantum efficiency of emission by donor.

- Energy transfer experiment 1:
- Donor의 농도는 일정하게 하게, acceptor의 농도를 바꿔가며 실험.

Donor

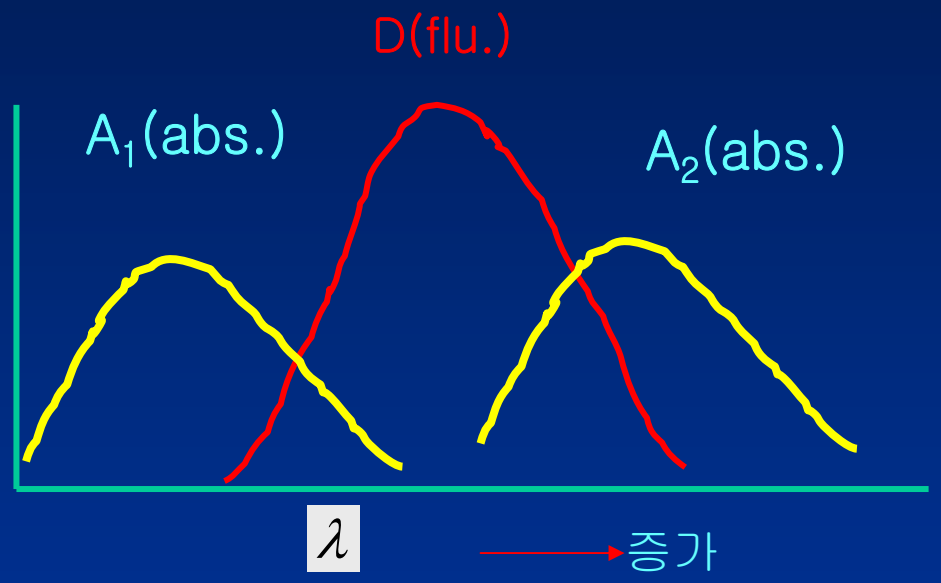
Acceptor





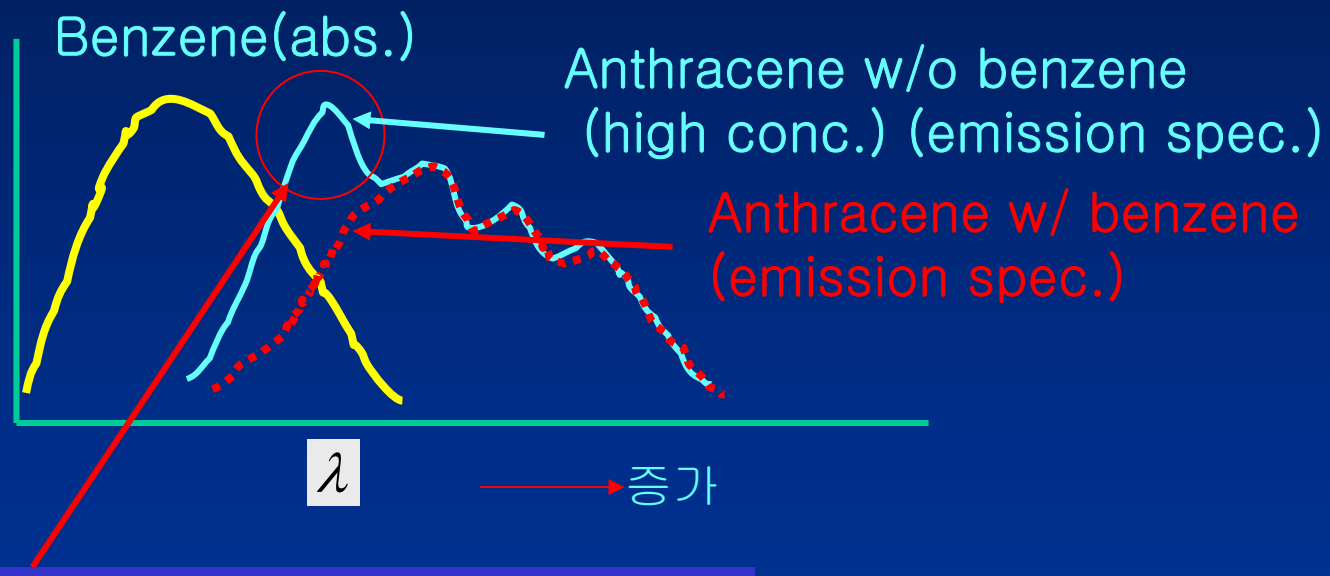
1. Radiative transfer는 spectrum overlap으로만 가능
2. Non-radiative trans. 은 어느 정도 가까운 거리에서 가능 (농도에 의존 (농도가 높아야 가능)

- Acceptor의 위치에 따른 E. T.
- 어느 것에 ET 가능한가?



모두 다 ET 가능. Overlap만 되면 된다.

- Spectrum of D&A mixture
- D의 spectrum 변화



Energy transfer 에 의해 peak이 보이지 않는다.

Decays from Excited States : Energy Transfer – non-radiative

- Collisional Process

D* A

⇩

(D* + A) ⟷ (D + A*)

isoenergetic

φ_i φ_f

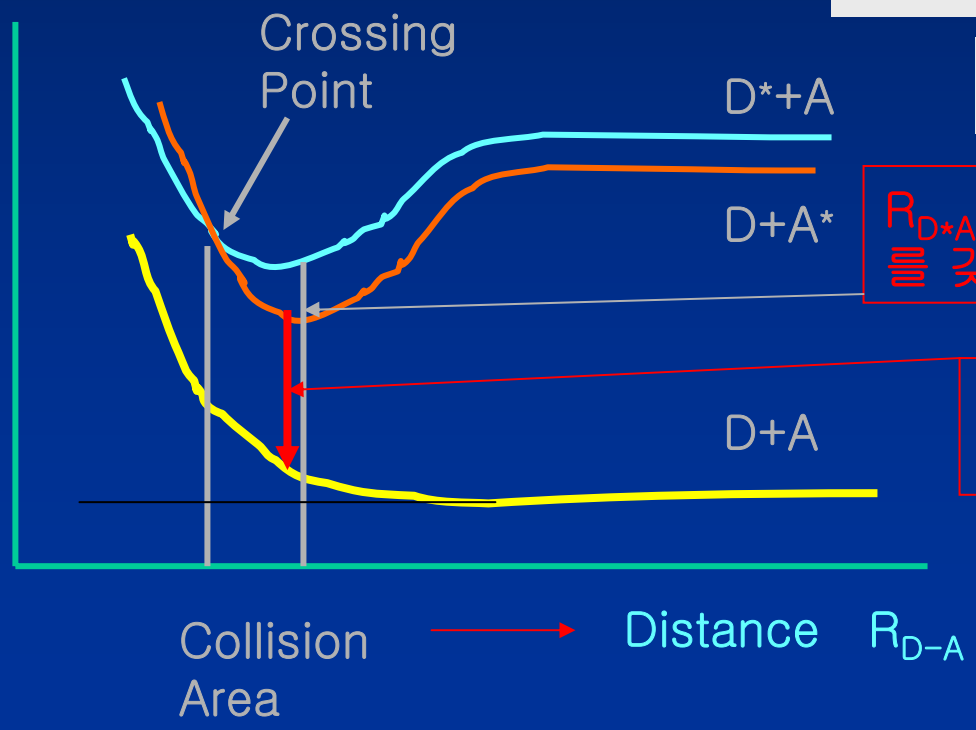
- Perturbation 이 두 state를 오가게 한다.

- 두 상태의 energy transfer 확률 p 는

$$P \propto \rho \left\langle \varphi_i \middle| H' \middle| \varphi_f \right\rangle^2$$

$$H' \approx \frac{e^2}{r_{12}}$$

ρ : Density of isoenergetic state



R_{D*A} 가 5Å는 되어야 충분한 속도를 갖는다.

$$k_{D^* \to A} \propto e^{-2R_{D^*A}}$$

Exciplex fluorescence는 broad 하고 낮은 Energy.

Decays from Excited States : Energy Transfer – non-radiative

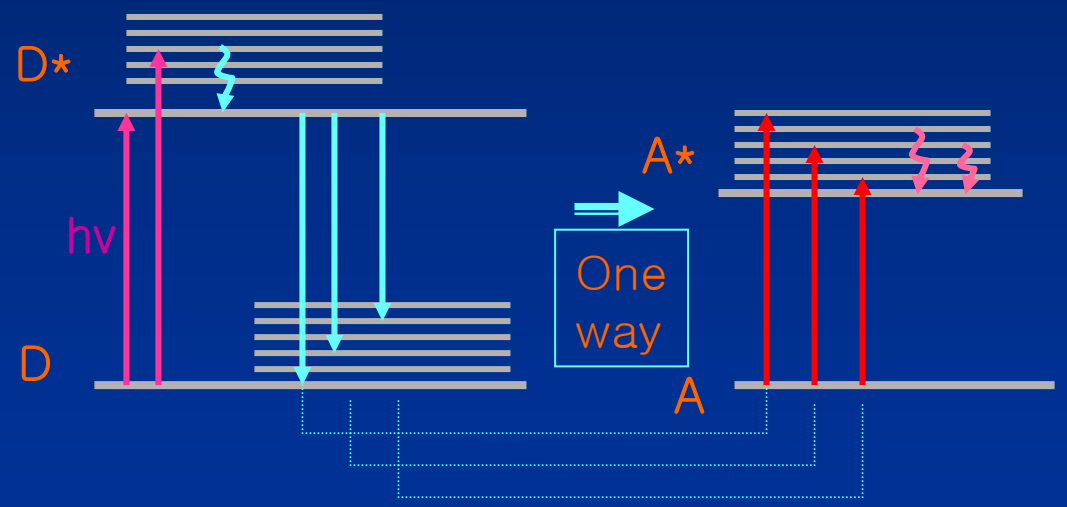
- P가 매우 클때는 $k_{energy\ transfer}$가 매우 크다.
  - $\left(D^* + A \right) \longleftrightarrow \left(D + A^* \right)$ 를 매우 빨리 오간다.
  - Excitation이 더 이상 localize 안된다.

- D와 A를 섞어 찍은 absorption spectrum과 D abs. Spec. + A abs. Spec. 이 같은가?

  D+A의 흡수 spec.은 energy transfer에 의하여 D abs. Spec. + A abs. Spec. 이 같을 수 없다.

Decays from Excited States : Energy Transfer – non-radiative

- $K_{\text{Energy Trans}} < k_{\text{vibrational relaxation}}$ 인 경우
  - D* undergo energy transfer from its bottom vibrational level, A* 형성 후 빨리 bottom level로 가서
  - $\left(D^* + A \right) \longleftrightarrow \left(D + A^* \right)$ 이 degeneracy 가 쉽게 깨지고,
  - Energy transfer가 한 방향으로 진행된다.



Coupled degenerate non-radiative transitions

이와 같은 matching 이 유기분자에서 가능한 것은?

많은 vibrational, rotational sub-level 이 존재하기 때문이다.

- Rate const. Of energy transfer:
- 앞의 그림과 같은 coupling 이 많을 수록 overlap이 많다.

$$J_{D*A} \equiv \text{spectral overlap intergral}$$
$$= \int \mathrm{I_F}(\bar{\nu})\varepsilon_A(\bar{\nu})d\bar{\nu}$$

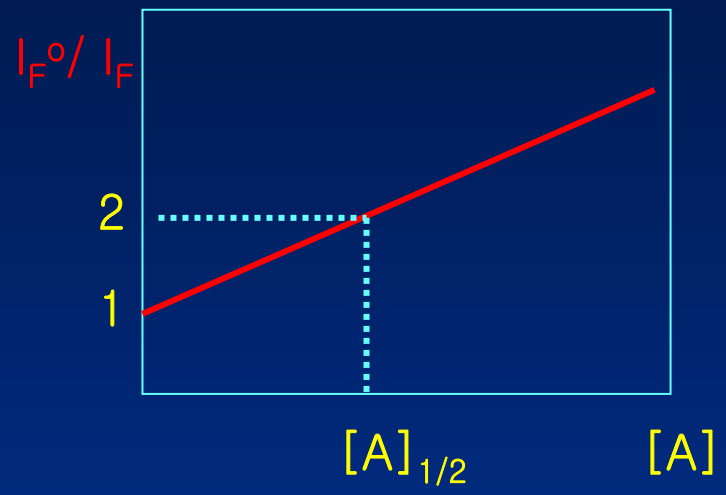
$$k_{D*A} = \frac{9000\,(\ln 10)k^2\Phi_D}{128\pi^4 n^4 N\tau_D}\left(\frac{1}{R^6}\right)\int_0^\infty I_F(\bar{\nu})\varepsilon_A(\bar{\nu})\frac{1}{\bar{\nu}^4}d\bar{\nu}$$
$$= \frac{1}{\tau_D}\left(\frac{R_0}{R}\right)^6$$

Radiative lifetime

R : donor-acceptor average distance
R_o : critical distance = R at 50% transfer efficiency

R 이 –6승에 비례함은 D-A 거리를 공유결합으로 조절하여 비례관계 구했다.

- R_0 구하는 방법



$$R_0^{\,6} = \frac{9000\,(\ln 10)k^2\Phi_D}{128\pi^4 n^4 N\bar{\nu}^4}\underbrace{\int_0^\infty I_F(\bar{\nu})\varepsilon_A(\bar{\nu})d\bar{\nu}}_{J_{D*A}}$$

$$R_0 = \frac{7.35}{\sqrt[3]{[A]_{1/2}}}$$

- Critical Distance의 예

이 경우 energy transfer는 solvent viscosity에 무관
10-4 M 이하에서는 D---A가 만나야 하므로 viscosity 관계된다.

Energy Transfer – Collisional

- Collisional migration due to excimer–exciplex formation

$$^1D^* + {}^1A \leftrightarrows {}^1\mathrm{D}A^* \rightarrow {}^1D + {}^1A^*$$

singlet - singlet

$$^3D^* + {}^1A \leftrightarrows {}^3\mathrm{DA}^* \rightarrow {}^1D + {}^3A^*$$

triplet - triplet

D=A : excimer

Energy Transfer – Electron Exchange

$$^1D^* + {}^1A \rightarrow {}^1D + {}^1A^*$$

singlet - singlet

Spin conservation
Dipole-allowed
efficient

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

triplet - triplet

Spin conservation
Dipole forbidden
moderate

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

triplet - singlet

Spin forbidden
Dipole allowed
Moderate
^{1}A의 lifetime은 ^{3}D의 lifetime 에 의하여 결정된다.

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

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

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

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

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

Energy Transfer – Singlet+triplet

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

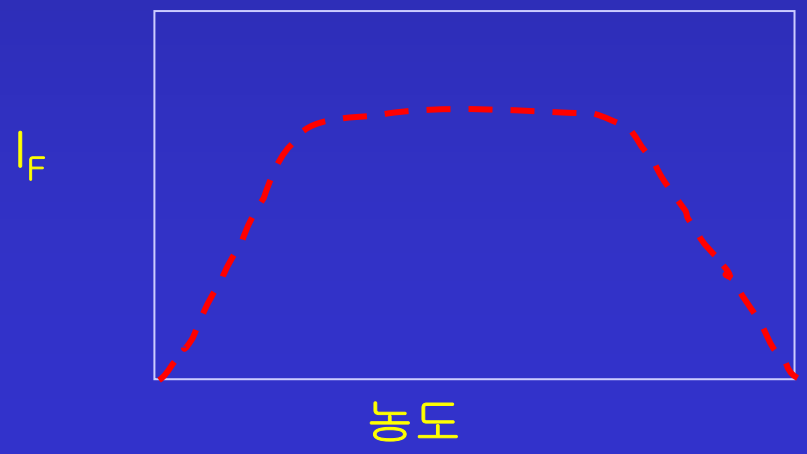
$$^1M^* + {}^3Y^* \rightarrow {}^1M + {}^3Y^{**}$$

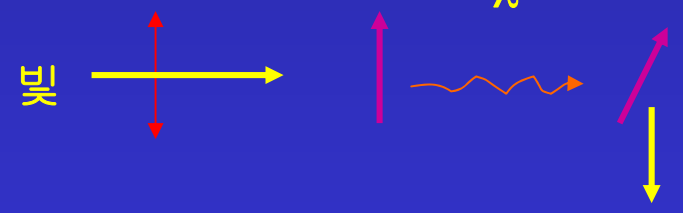
Spin conservation
Dipole allowed
Fast
S-T fusion

» Triplet의 lifetime이 길기 때문에 가능

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

- Energy Transfer – Chlorophyll



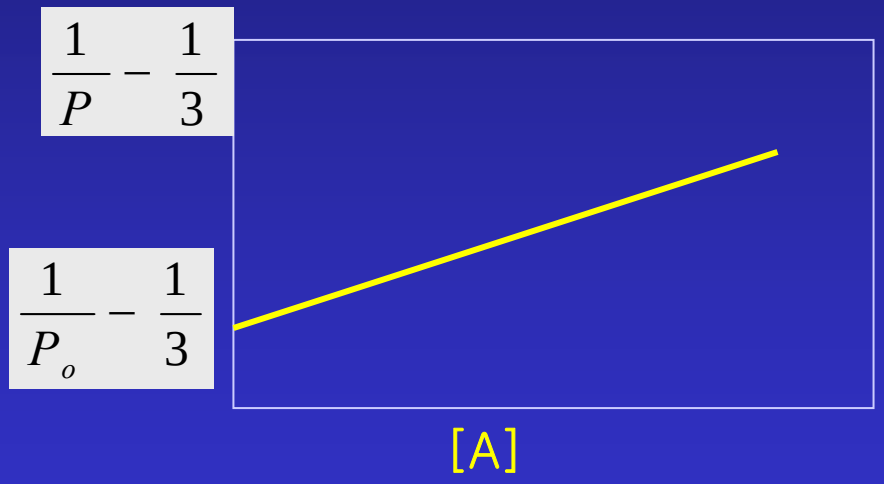


농도가 높아 질수록 Energy transfer 에 의해 depolarization 이 크다.

- Energy Transfer – Chlorophyll

$$\frac{1}{P}-\frac{1}{3}=(\frac{1}{P_o}-\frac{1}{3})[1+\frac{4\pi NR_o^6[A]}{15(2a)^3}\times 10^{-3}]$$

- a: molecular radius (cm) 를 구할 수 있다.



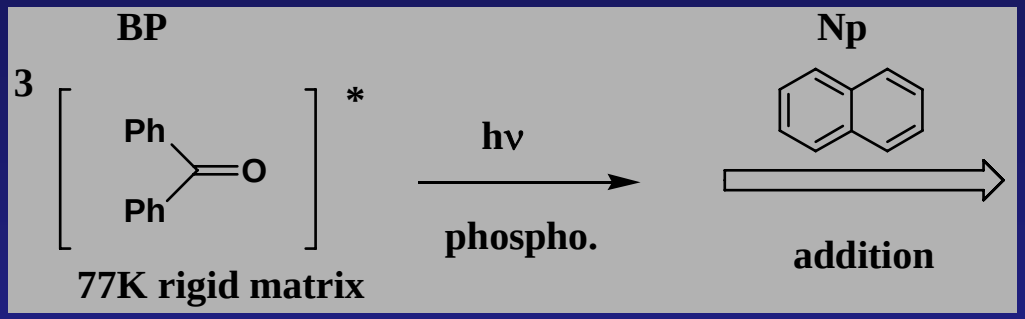
Energy transfer에 의해 농도가 높아질수록 depolarization 이 크다.

- Energy Transfer

parameter	Radiative	Exciton	Foster	e – exchange
Volume up	+	0	0	0
Viscosity up	0	+	0	–
Temp. down	0	+	?(o,+)	–
Lifetime (D*)	0	–	–	–
D* Lum. Spectrum 변화	yes	slightly	no	no
A absop. 변화	no	slightly	no	no
Conc. range	>0.5M	>0.1 M	10^{-4} ~0.1	10^{-4} ~0.1

0 : no effects
+ : increase – : decrease

- Energy Transfer
- Terenin & Ermolaev



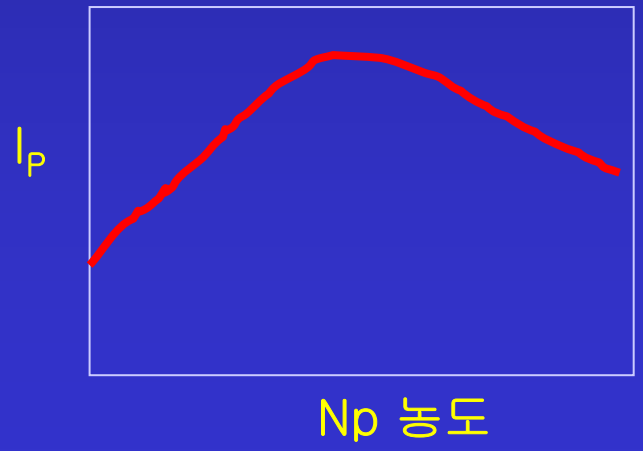
- Addition of Np
- Reduction in benzophenone(BP) phosphorescence.
- New phos. Peak of Np.

- $^1BP \xrightarrow{isc} {}^3BP \xrightarrow{Np\ (S_o)} BP\ (S_o) + {}^3NP$

$\downarrow$ hν'

- Diffusion is rate-limiting: $k_{ET}\eta$ 는 여러 용매에서 일정한 값

Np를 많이 넣으면 Np의 phosphorescence 증가하다 감소한다. Why?

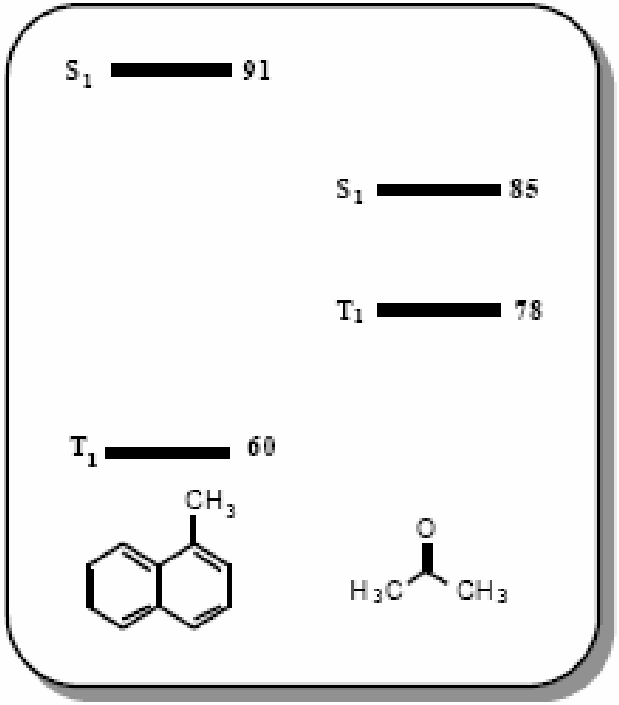


$$^3Np^* + {}^3Np^* \longrightarrow {}^1Np^* \quad {}^1Np$$

Triplet-Triplet annihilation

- Energy Transfer – energy diagram

Energy transfer in the ketone naphthalene system



Approximate energies given in kcal/mol

$$N \xrightarrow{h\nu} {}^1N^*$$

$${}^1N^* + K \longrightarrow N + {}^1K^*$$

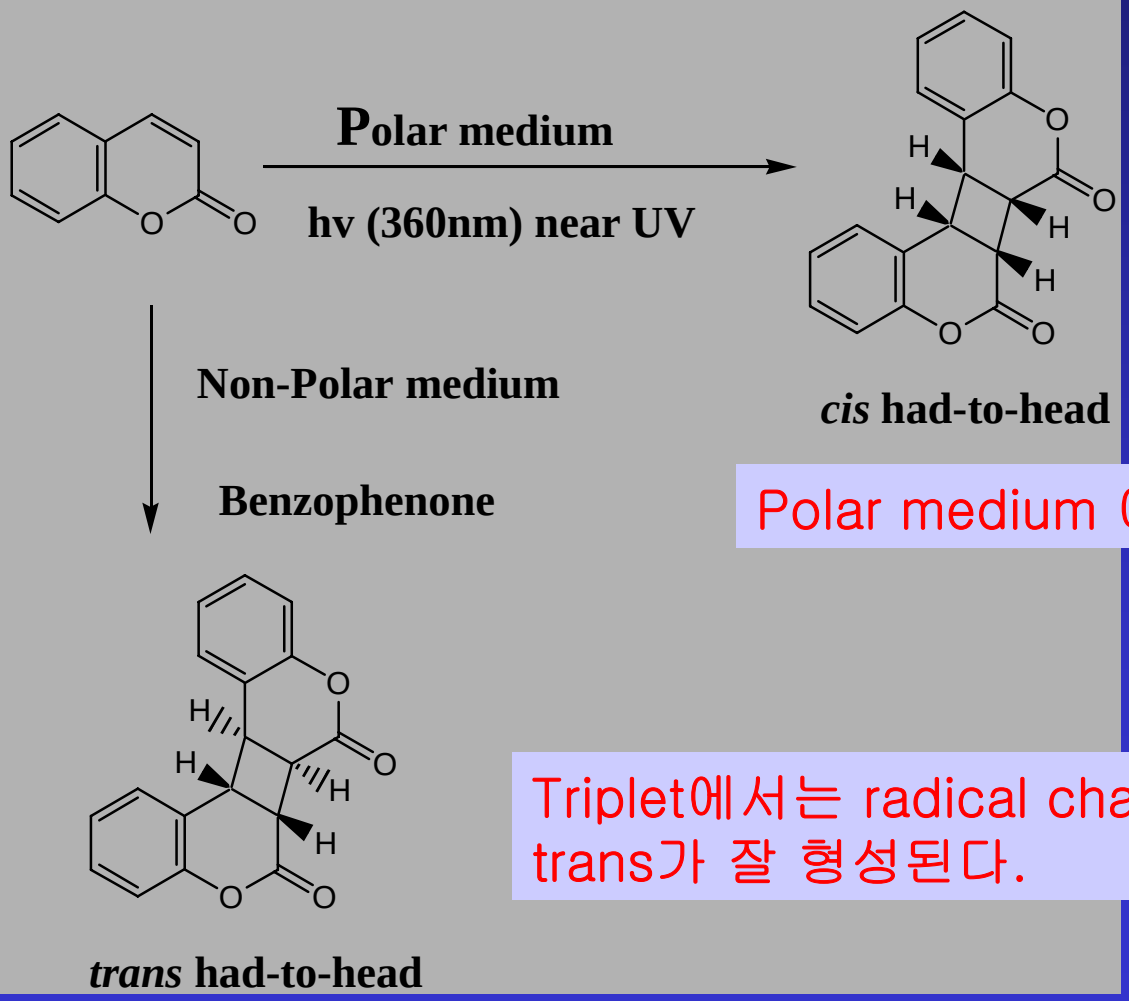
$${}^1K^* \longrightarrow {}^3K^*$$

$${}^3K^* + N \longrightarrow K + {}^3N^*$$

The consequence of this exchange is assisted intersystem crossing in naphthalene.

It also provides a way of 'isolating' the singlet chemistry of carbonyl compounds

- Coumarin
- Polar medium : cis & head-to-head dimer formed
- Non-polar medium : w/ BP (일정량, 350 nm) : trans & head-to-head dimer.



Polar medium 에서는 excimer 형성 잘된다.

Triplet에서는 radical character 때문에 trans가 잘 형성된다.