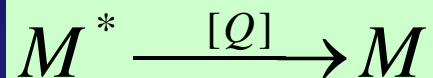


Quenching of Excited States

홍익대학교
신동명

- Quenchers



- Q : Oxygen, Metals (Heavy, transition metals), solvents

- Oxygen 제거: 질소 또는 헬륨으로 degassing (용매가 날라가서 농도가 바뀔 수 있기 때문에 천천히 해야 한다.)

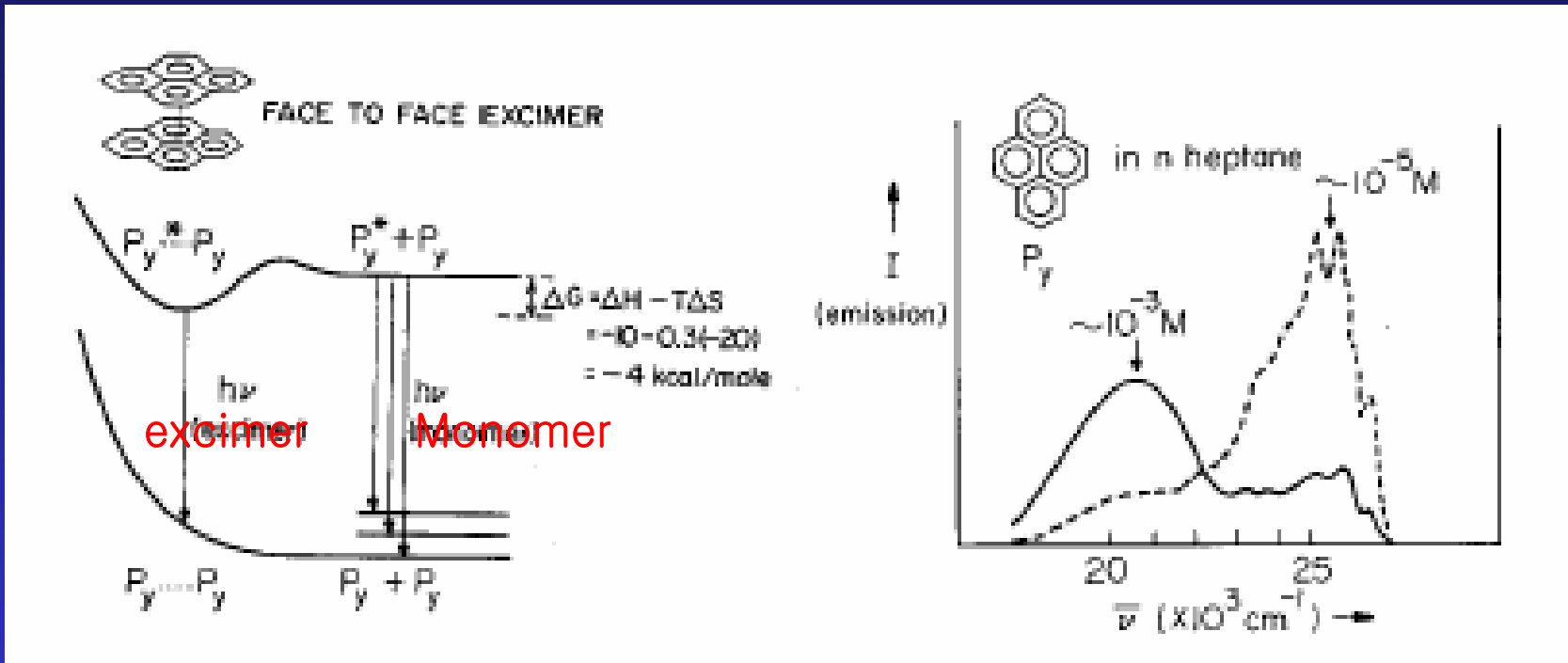
10^{-2} M 에 $k_q [O_2] = 10^{10} \times 10^{-4} = 10^6$ Copper tubing 또는 Tygon tube
사용 : 여기상태의 life time이 긴 경우

에는 사용할 수 없다.

- Freeze-pump-thaw : 10^{-5} Torr (3번 반복)

Quenching of Excited States: Excimer & Exciplex

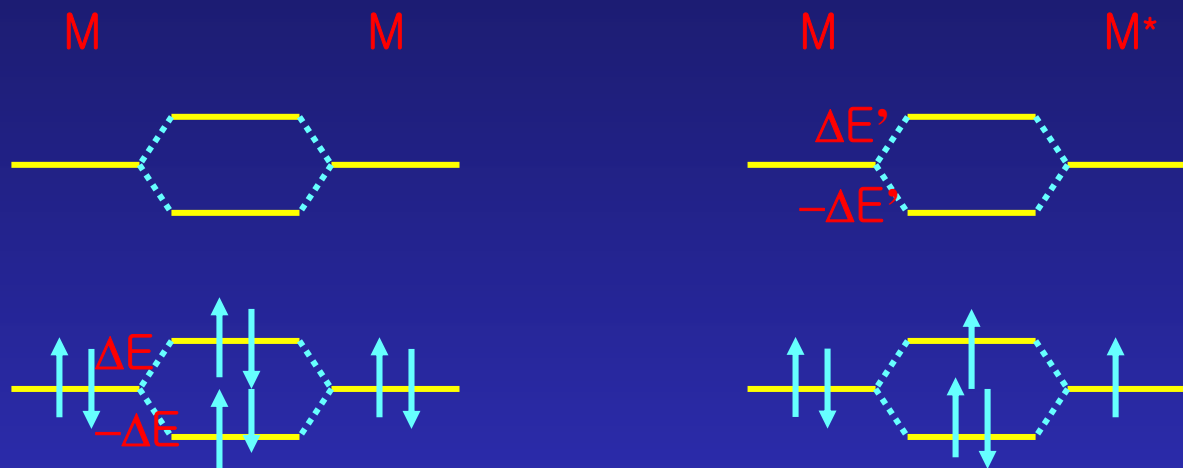
- Excimer



Two identical molecules:
EXCited diMER \Rightarrow EXCIMER

Two different molecules:
EXCited comPLEX \Rightarrow EXCIPLEX

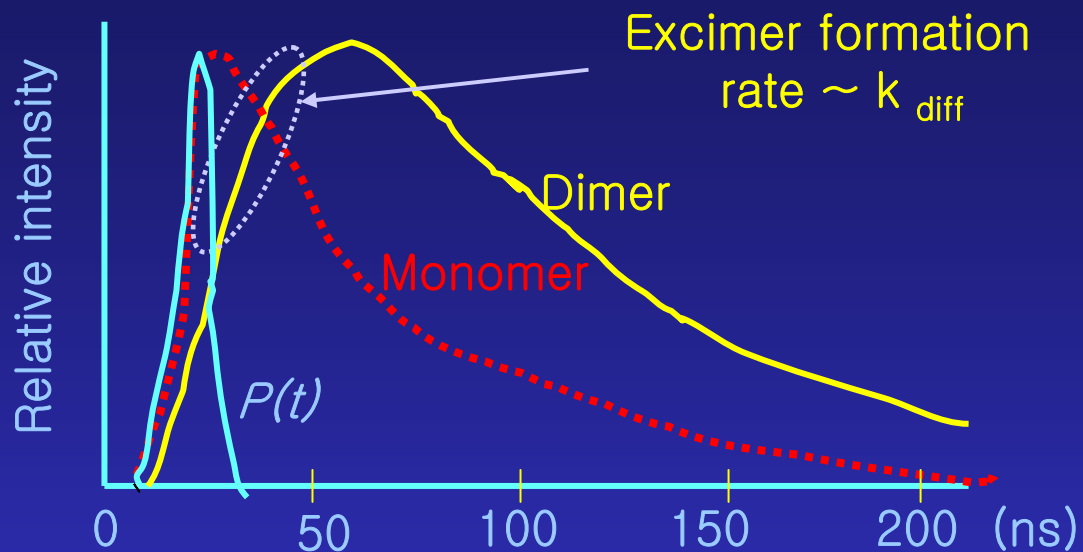
- Excimer



- Unbound state : $\Delta E_T = 0$
- Bound state : $\Delta E_T = -(\Delta E + \Delta E')$

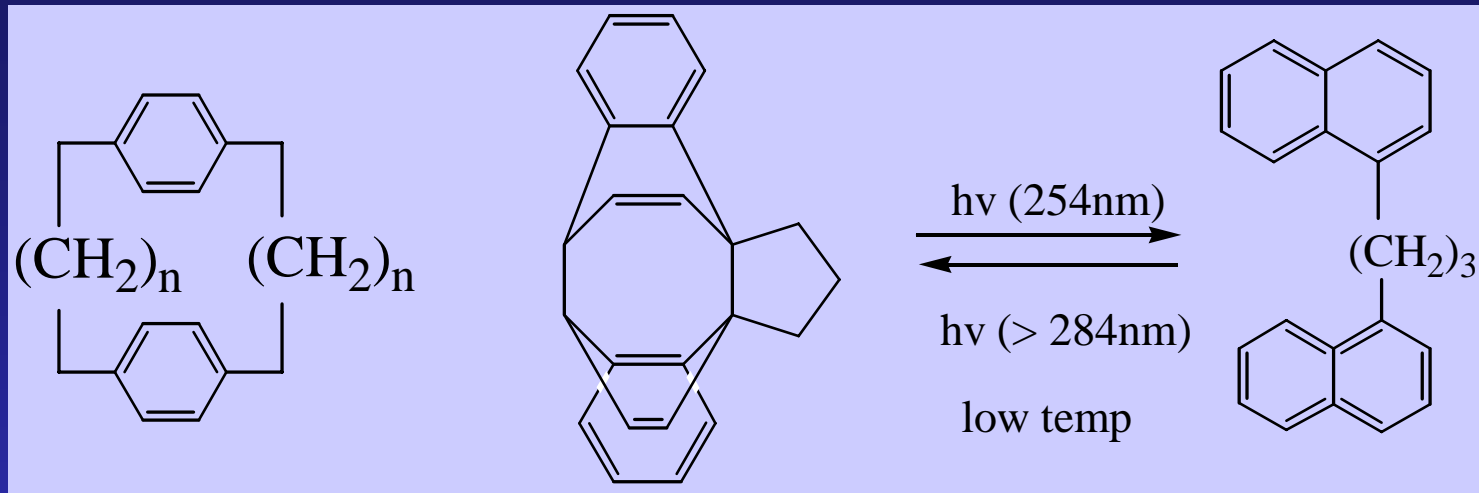
Temperature dependence of emission으로 ΔE_T 또는 ΔH 를 계산
 $\Delta E \sim 40$ KJ/mole (10 kcal/mol) $\Delta S \sim 80$ JK⁻¹ (20 cal K⁻¹) for
 strongly bound rigid structure molecules

- Excimer formation – fl. Decay curve



Pyrene(5×10^{-3} M) in cyclohexane.

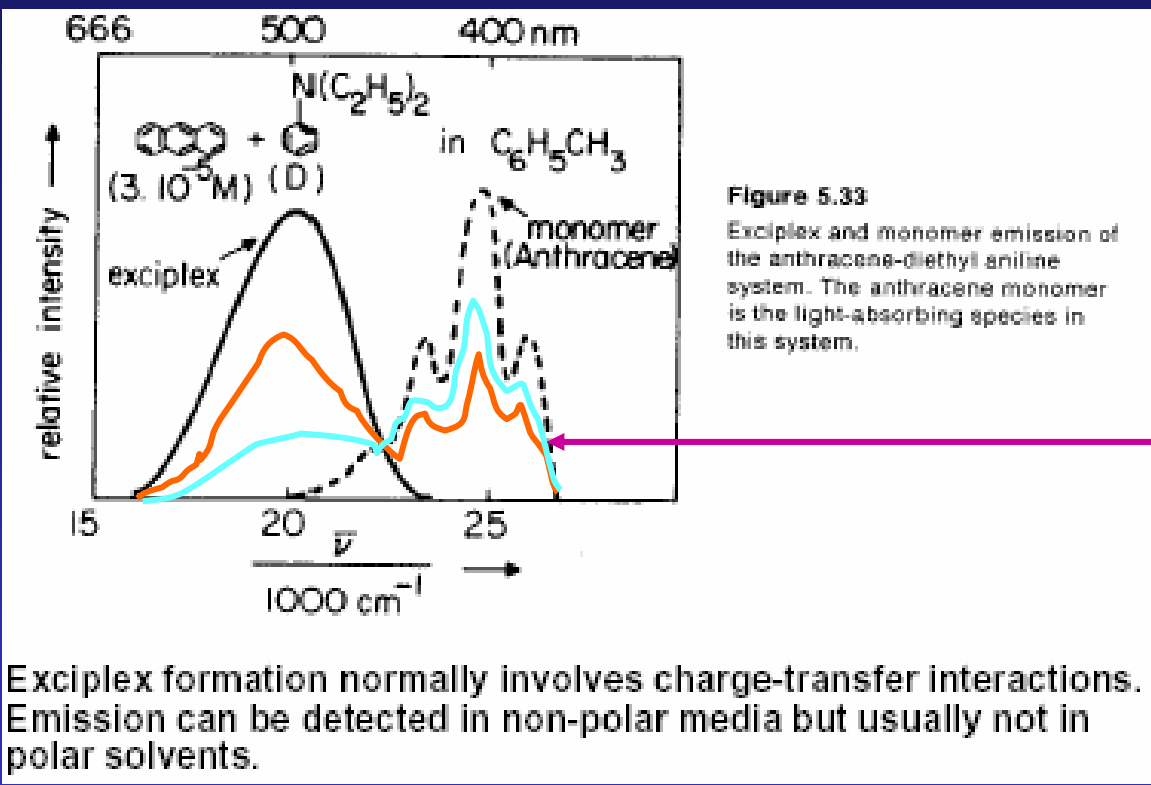
- Excimer formation



$(n=4)3.73\text{\AA}$
 Alkyl benzene의
 absorption spec.
 Excimer fl 보임.

이 물질이
 naphthalene 의 .
 Excimer fl 보임.

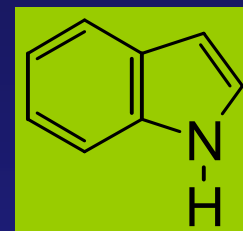
- Exciplex formation



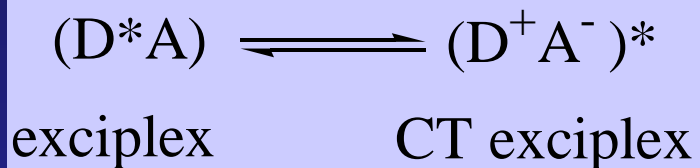
농도에 따라서 isosbestic point를 갖으면서 spectrum이 변한다.

Exciplex는 dipolar 한 성격때문에 용매의 극성이 증가하면 red shift 한다. Excimer 는 0 dipole moment이다.

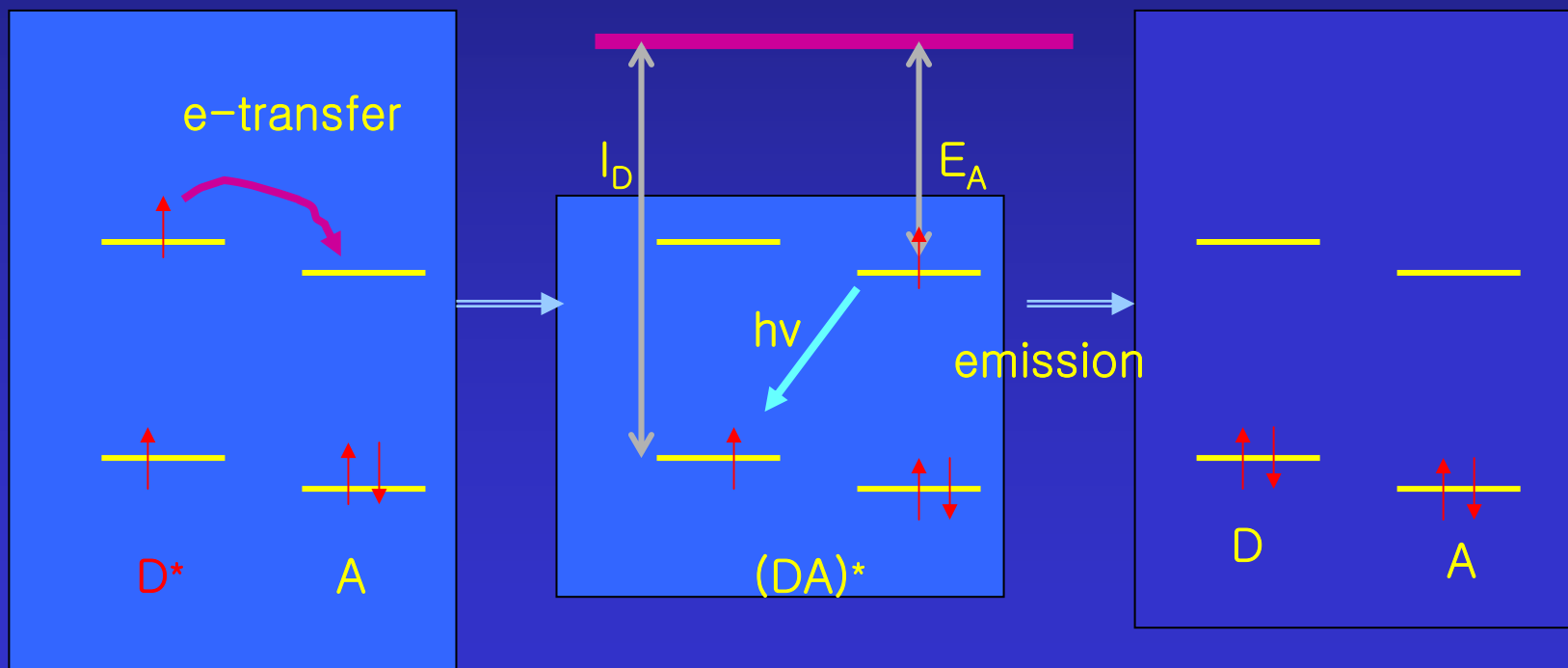
- Exciplex formation f/b electron transfer



Eg. Indole + TCNE



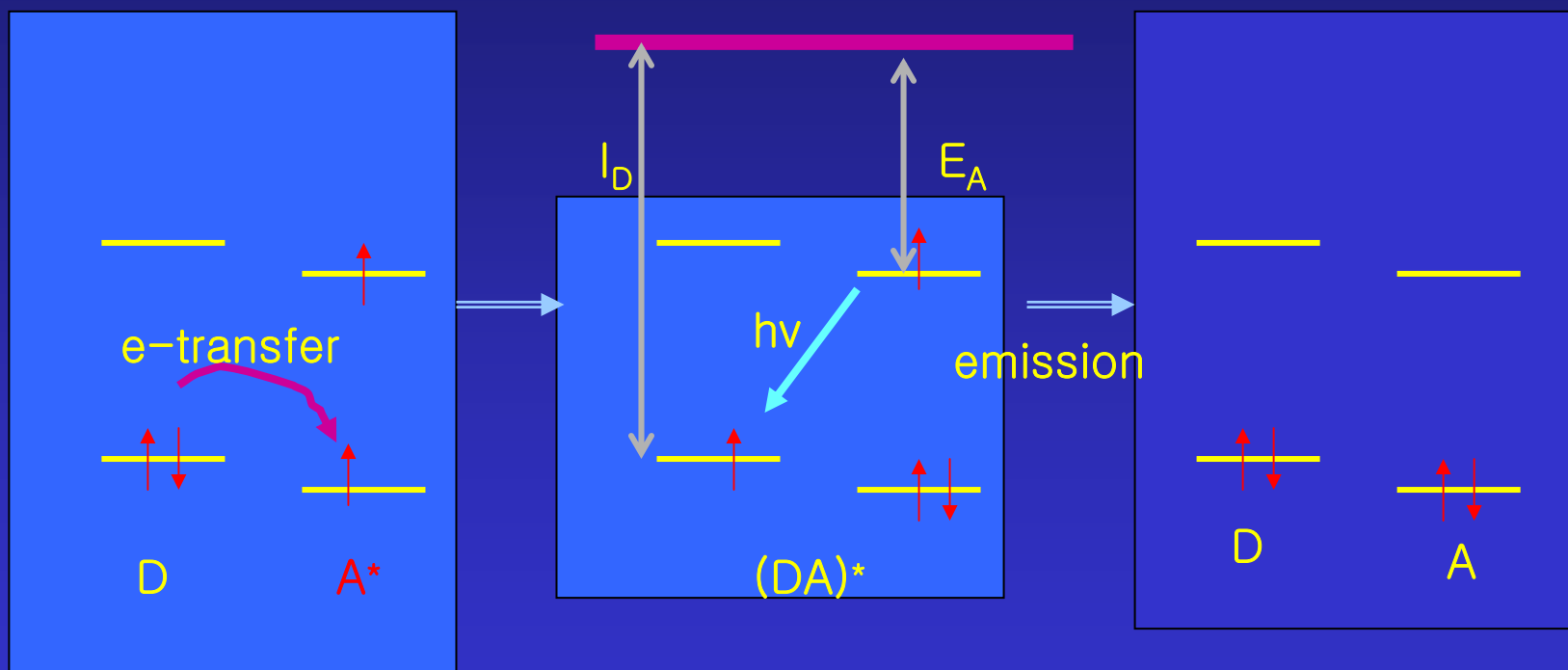
Exciplex formation – Donor excited



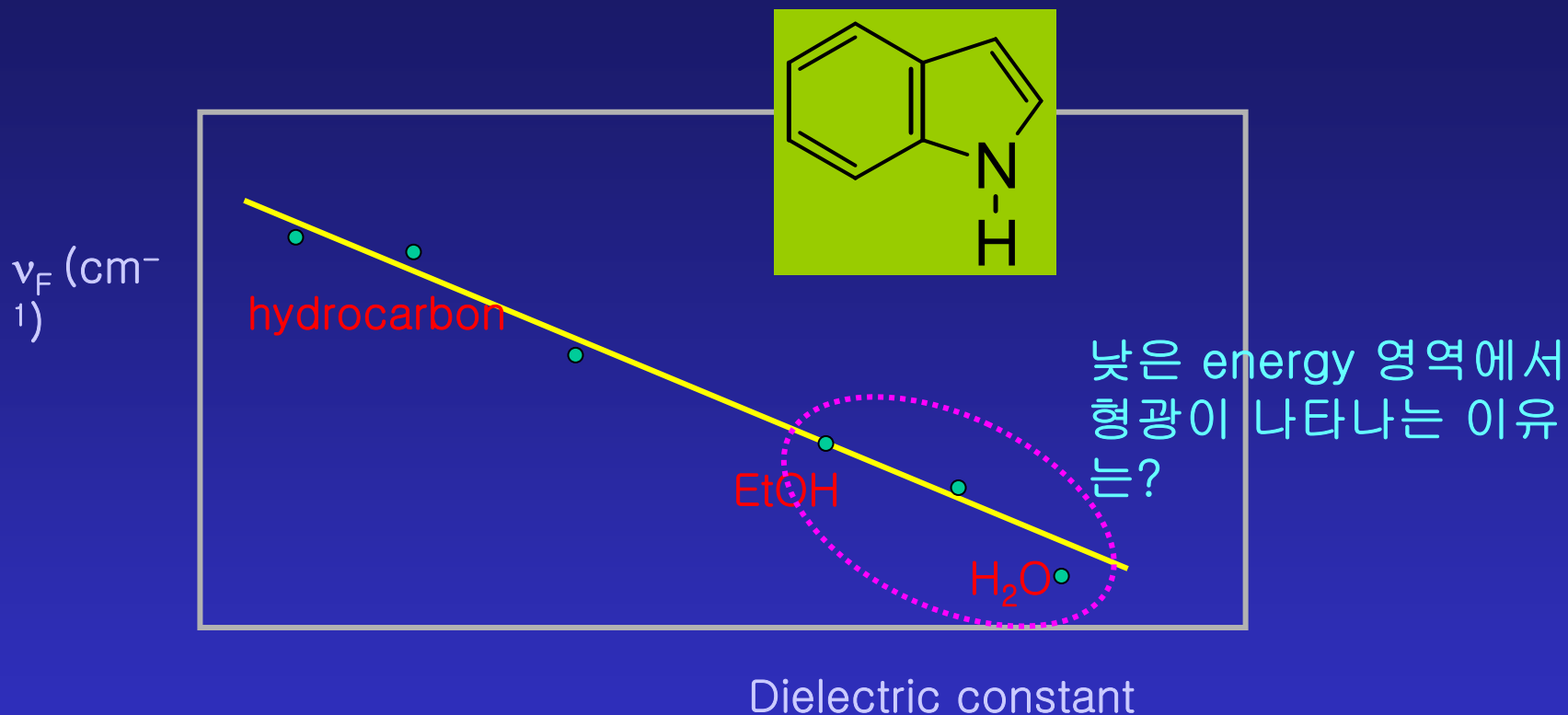
How about acceptor excited?

- Exciplex formation f/b electron transfer

Exciplex formation – acceptor excited

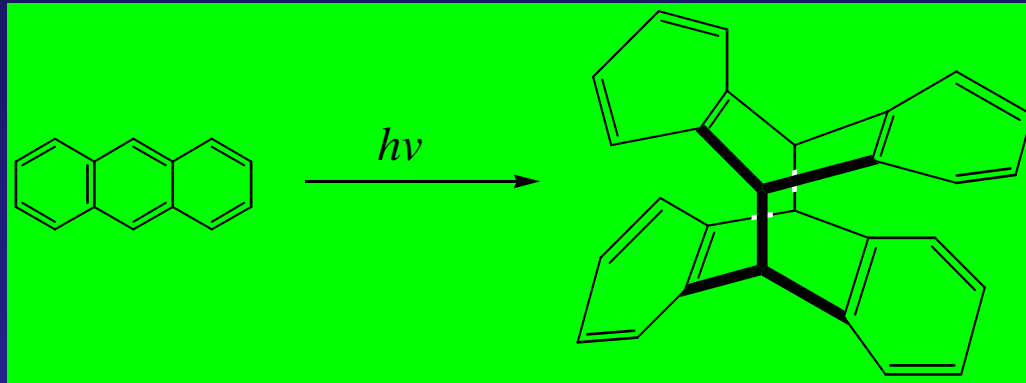


- 예1



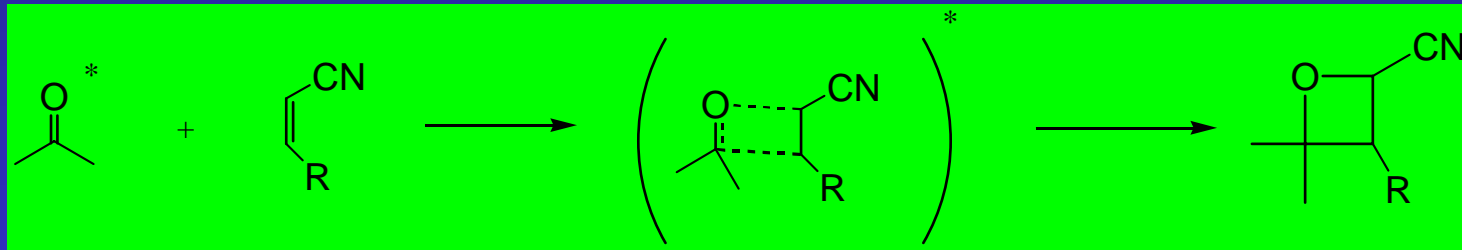
용매와 1:1 complex 형성한다. Exciplex 의 극성으로 인해 낮은 energy 영역에서 형광이 나타난다.

- 예2



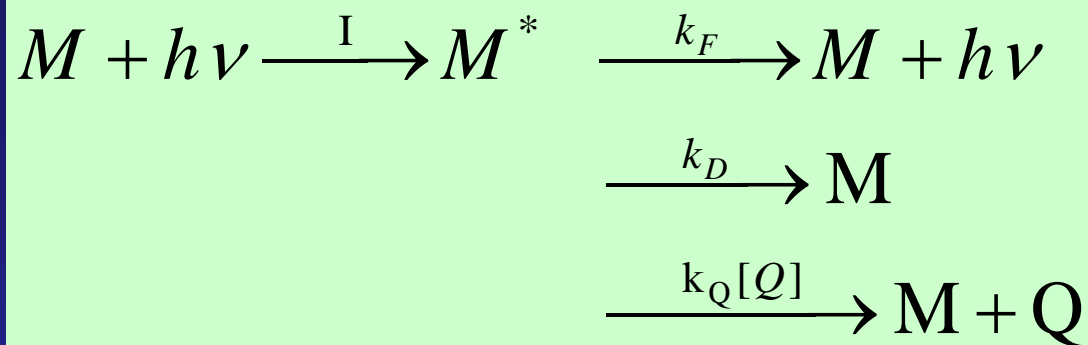
-

- 예3



- 예4 : Triplet – Triplet annihilation

- Kinetics

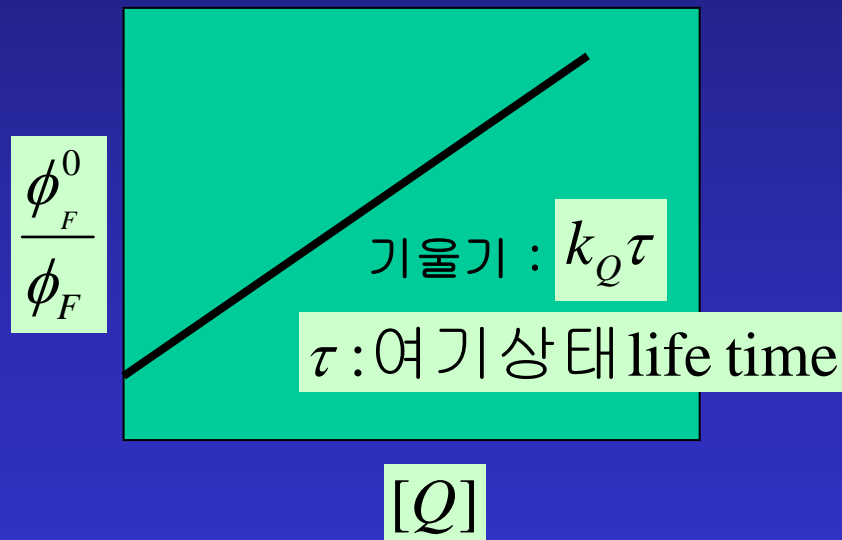


$$I = [M^*](k_F + k_D + k_Q[Q])$$

$$\phi_F = \frac{k_F[M^*]}{I} = \frac{k_F}{k_F + k_D + k_Q[Q]}$$

$$\phi_F^0 = \frac{k_F}{k_F + k_D}$$

$$\frac{\phi_F^0}{\phi_F} = 1 + \frac{k_Q}{k_F + k_D}[Q] = 1 + k_Q\tau[Q]$$

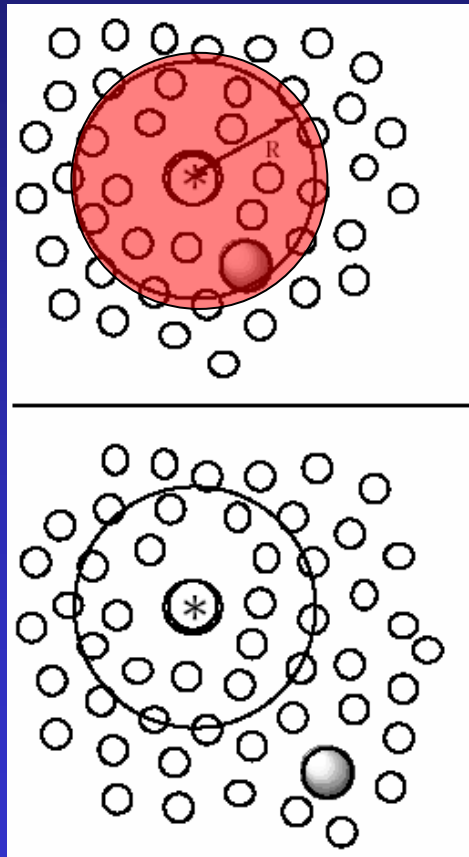


k_Q : 많은 경우 diffusion controlled rate이다.

$10^9 \sim 10^{10} L^{-1}mol \cdot sec^{-1}$ (용매에 따라 다름)

- Perrin Model – Static quenching
- The Perrin model assumes:
 - (a) The donor and acceptor **cannot undergo displacements** in space during the lifetime of D^* .
 - (b) There exists a volume in space - or more precisely a "**quenching sphere**" - about D^* whose radius is R and if a quencher molecule is within this quenching sphere, then D^* is deactivated with unit efficiency.
 - (c) If a quencher molecule is outside of the quenching sphere, it does not quench D^* at all.

• Perrin Model

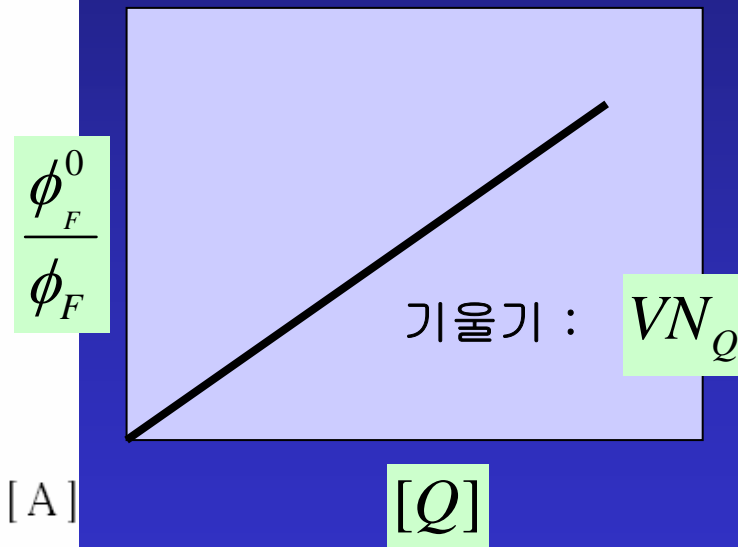
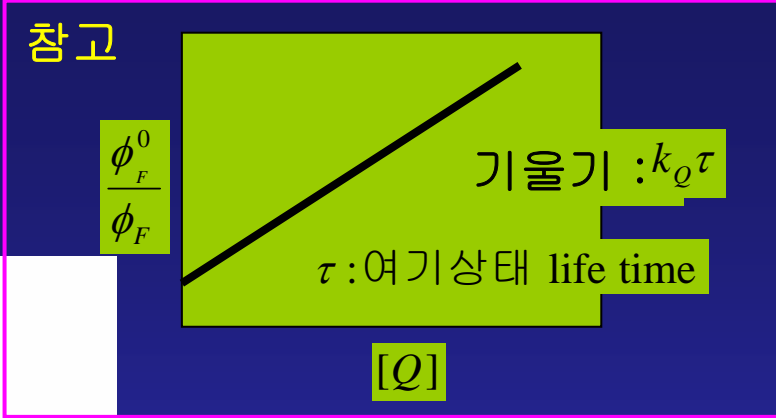


(a) $\phi = 0$

(b) $\phi = 1$

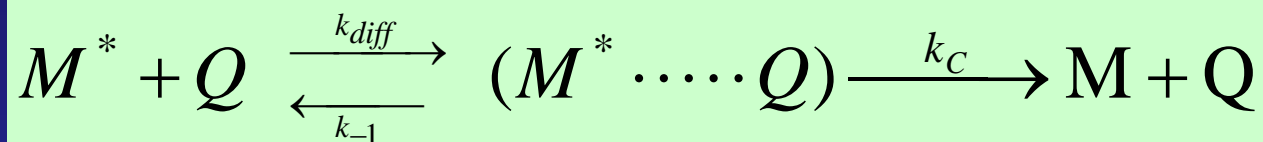
	= D*
	= A Q
	solvent

(b) $\ln (\phi^{\circ} / \phi) = V N_A [A]$



Life time에 관계 없고
농도에 비례

- Kinetics



encounter complex or exciplex

$$\begin{aligned} k_{diff} [M^*][Q] &= k_{-1} [M^* \cdots Q] + k_c [M^* \cdots Q] \\ &= (k_{-1} + k_c) [M^* \cdots Q] \end{aligned}$$

$k_{-1} + k_c$: *quenching* rate const. within the complex

- Kinetics

rate of quenching

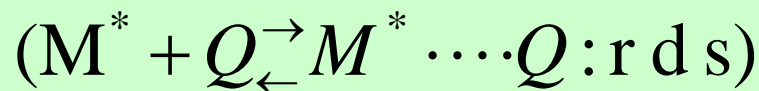
$$= k_C [M^* \cdots Q]$$

$$= k_C \frac{k_{diff}}{k_{-1} + k_C} [M^*][Q]$$

$$k_Q(\text{observed}) = \frac{k_C k_{diff}}{k_{-1} + k_C}$$

- $k_{-1} \ll k_C : k_Q = k_{diff}$

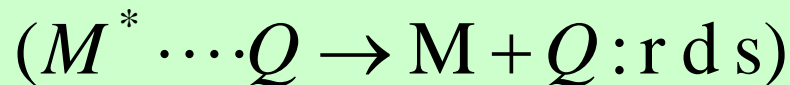
solvent의 영향이 크다



- $k_{-1} \gg k_C : \text{weak quencher}$

Independent of sol. viscosity

$$k_Q = \frac{k_{diff} \cdot k_C}{k_{-1}} = k_C \cdot K$$



- $k_{-1} \approx k_C : k_Q \text{는 } k_{diff} \text{ 보다는}$

작다.

- Diffusion
- 1, 2, 3 모두 k_{diff} 와 관계가 있다.

$$k_{diff} = \frac{8RT}{3000\eta} \quad (1 \cdot \text{mol}^{-1} \cdot \text{sec}^{-1})$$

η : viscosity (in poise)

solvent와 solute의 크기 차이가 작을 때:

이식으론 원래값보다 작다. 실제론

$$k_{diff} = \frac{8RT}{2000\eta} \quad (\text{modified})$$

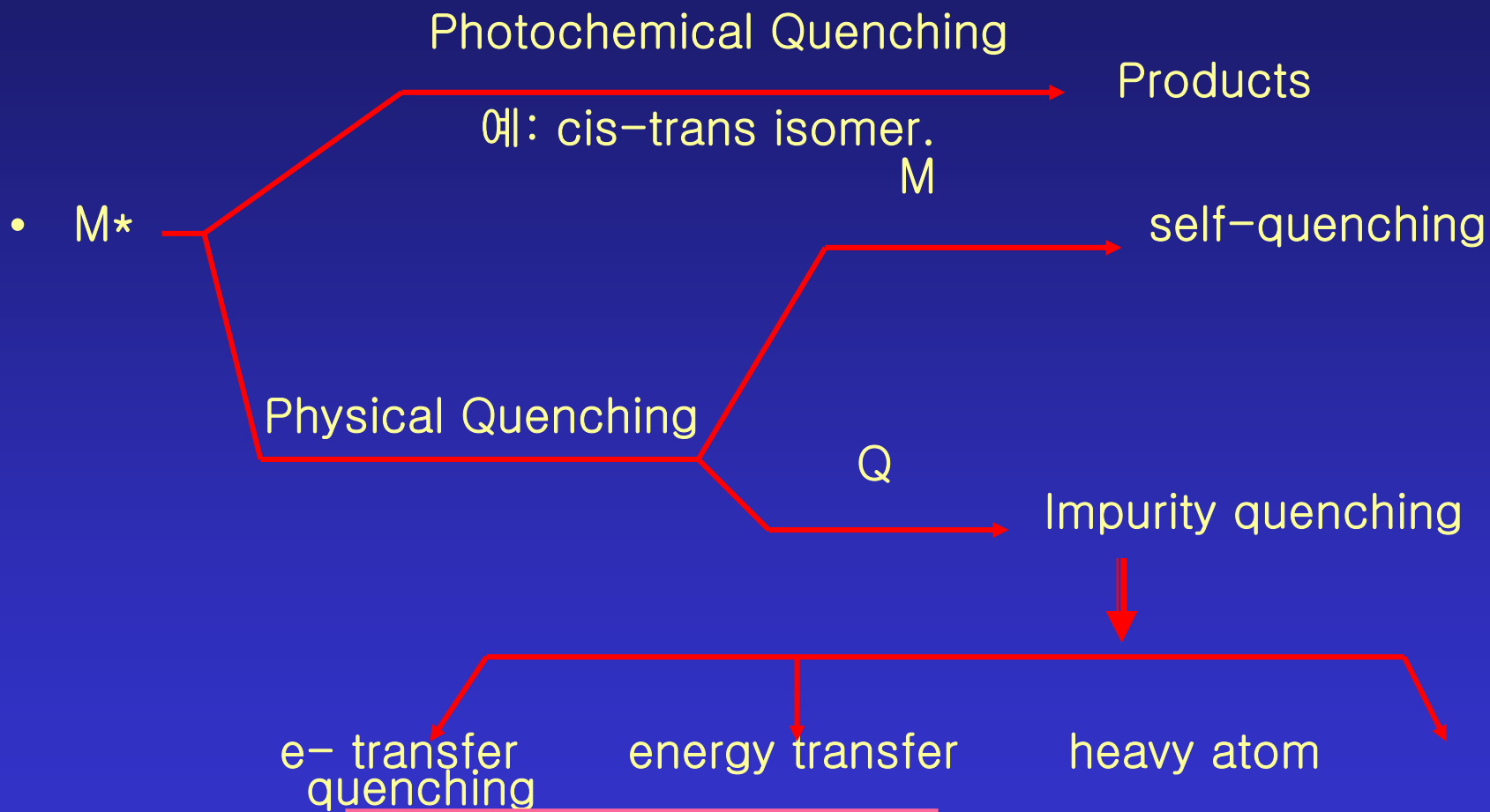
분자모양이 hard sphere이어야 한다.

이에 적용 안 되는 것은

모양이 구형이 아닌 경우

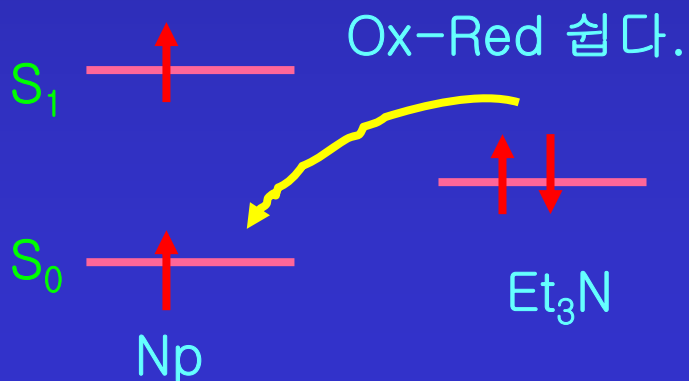
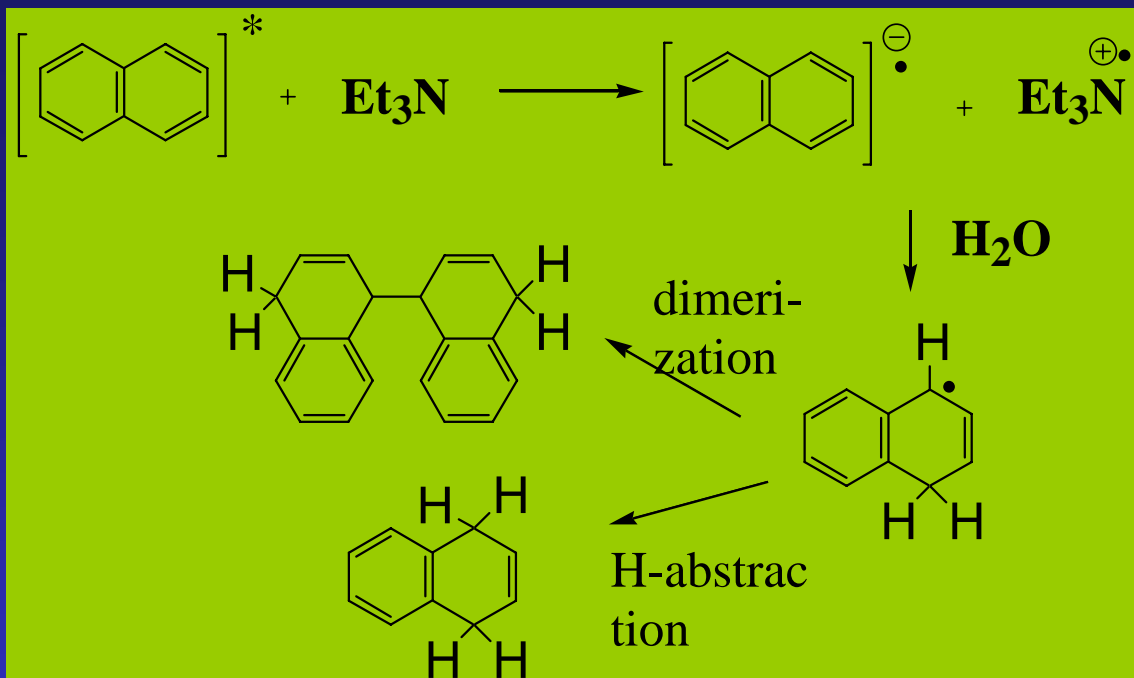
Solvent 와 solute의 size 차이가 많이 나는 경우

• Quenching Processes and Quenching Mechanisms



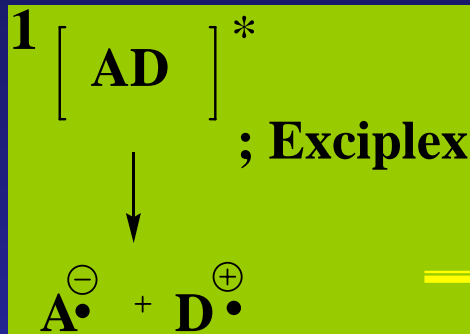
(구분이 어렵다. 산화환원 전위 등이 뒷받침 되면 가능)

• Electron Transfer



=> e-transfer에 의하여 전하가 생성되어 극성 물질이 생성되어, 용매 polarity 효과가 크다.

- Electron Transfer



⇒ Polar solvents에서 형성이 잘 된다.

Polar solvents에서는 안정화되기 때문에 쉽게 떨어져 나간다.

Non-polar solvent에서는 exciplex 형태로 남아 있으려 한다.

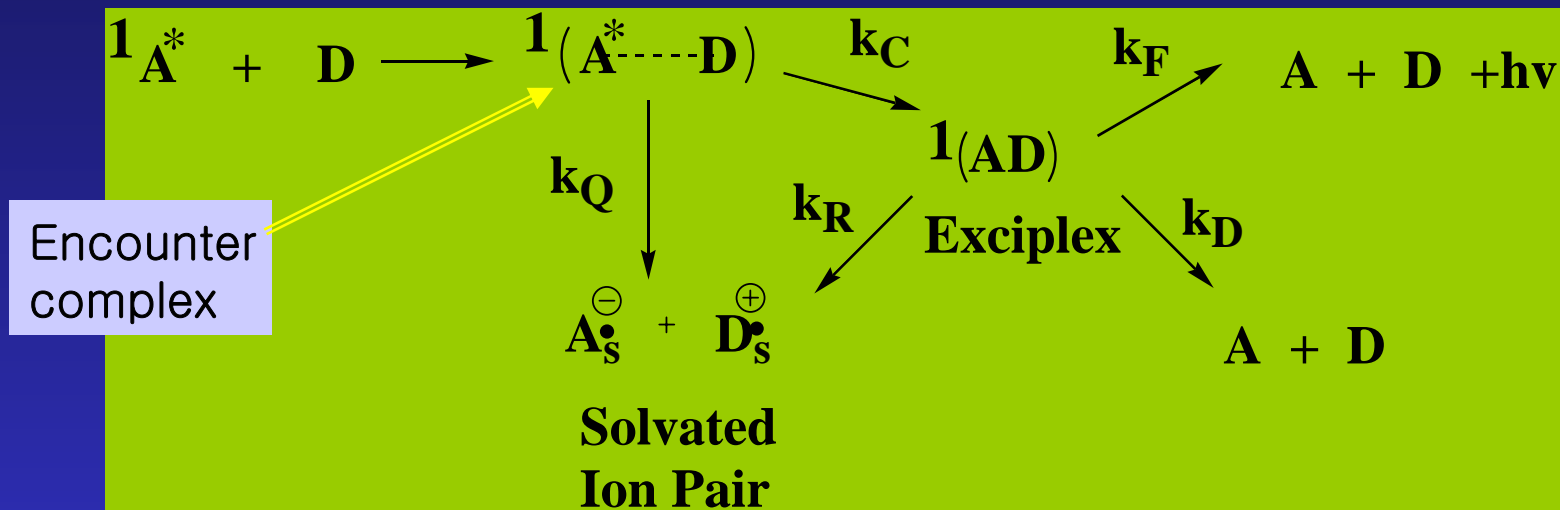
Solvent Polarity를 증가시키면:

Exciplex fl. 감소 (charged species 로 전환된다.)

Fl. Lifetime 감소

Fl. Lifetime의 감소 폭이 fl. Intensity 감소 폭 보다 적다. Why?

- **Electron Transfer**
- Fl. Lifetime의 감소 폭이 fl. Intensity 감소 폭 보다 적다. Why?



Fl. Lifetime: exciplex에서 k_D , k_R process로 감소

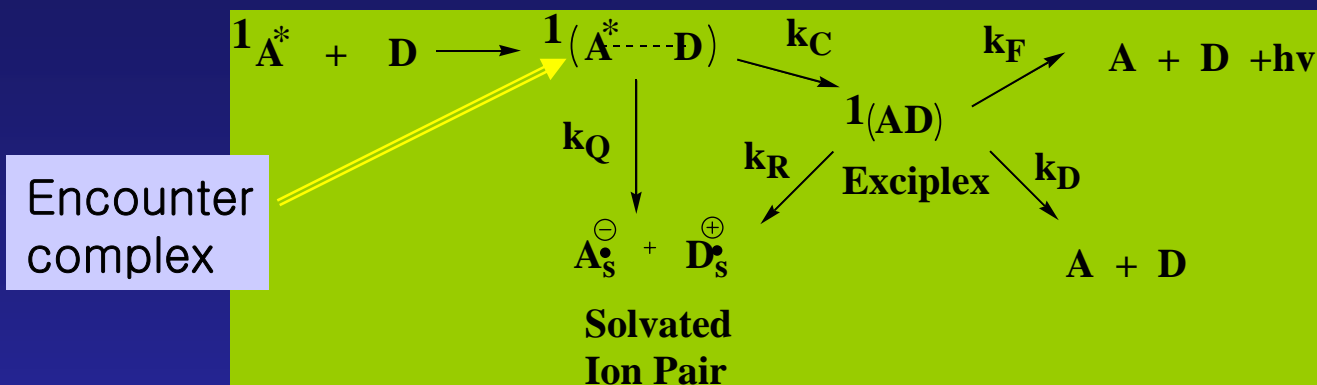
Fl. Intensity: k_D , k_R process로 감소 + encounter complex에서 k_Q 로

ion pair까지 가는 process 까지 있다.

Solvent polarity $\uparrow \rightarrow k_Q, k_R \uparrow$
 k_C : independent

Quenching of Excited States: Quenching Process and Mechanism

- Fl. Lifetime의 감소 폭이 fl. Intensity 감소 폭 보다 적다. Why?



$$exciplex \text{ lifetime} = \tau_F = \frac{1}{k_F + k_R + k_D}$$

$$\text{Quantum Yields} = \Phi_F = \left(\frac{\text{probability of exciplex formation}}{\text{exciplex formation}} \right) \times \frac{k_F}{k_F + k_R + k_D}$$

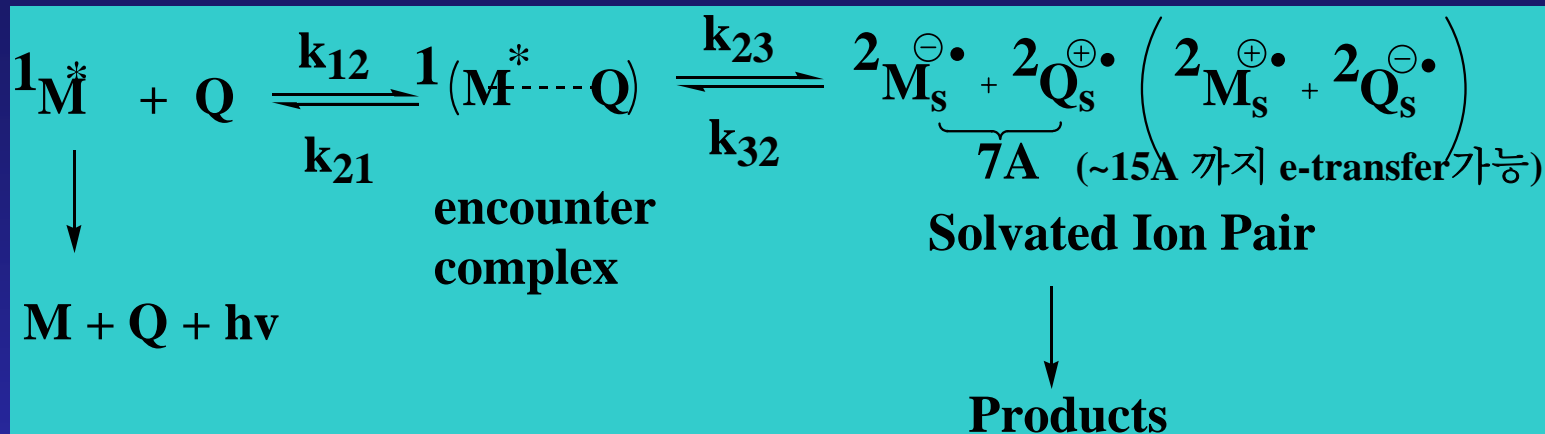
$$= \frac{k_C}{k_C + k_Q} k_F \tau_F$$

Solvent polarity \uparrow

$\Rightarrow k_Q \uparrow$

$\Rightarrow \Phi_F \downarrow$

- Rehm and Weller



$$\Delta G_{23} = E(D / D^+) - E(A^- / A) - \frac{e^2}{\epsilon a} - \Delta E_{00}$$

$E(D / D^+)$: ionization potential

$E(A^- / A)$: electron affinity

$\frac{e^2}{\epsilon a}$: Coulombic E. energy released by

bringing the ions to within the encounter distance "a", ϵ : dielectric const. of medium

ΔE_{00} : electronic excitation E.

- $$\Delta G_{23} = 2E(D / D^+) - E(A^- / A) - \frac{e^2}{\epsilon a} - \Delta E_{00}$$

E

$$k_Q = \frac{2.0 \times 10^{10}}{1 + 0.25 \left[\exp(\Delta G_{23} / RT) + \exp(\Delta G_{23}^* / RT) \right]}$$

ΔG_{23}^* : Encounter complx. 에서 sip 형성에 필요한 activation Energy.

$$\Delta G_{23}^\ddagger = \frac{(\lambda + \Delta G_{23})^2}{4\lambda}$$

$$\lambda = \lambda_i + \lambda_o$$

λ_i : Inner sphere recognition term (donor acceptor 사이의 through bond electron transfer에서 orientation 과 같은 것에 의하여 결정)

λ_o : Outer sphere recognition term

$$\lambda_o = e^2 \left(\frac{1}{2r_1} + \frac{1}{2r_2} - \frac{1}{d} \right) \left(\frac{1}{n^2} - \frac{1}{D} \right)$$

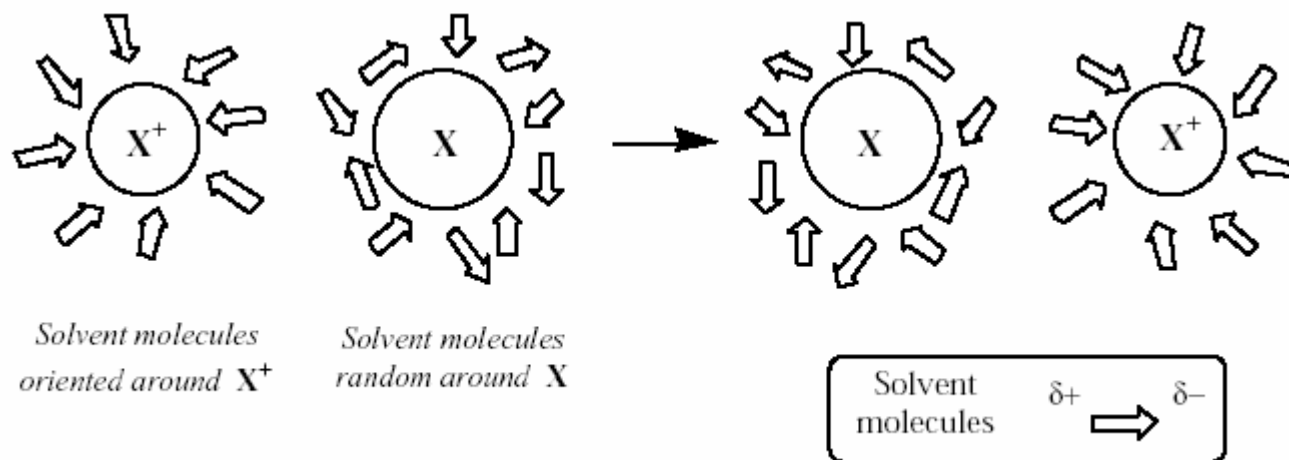
d : D-A 사이의 거리

n : 용매의 Optical dielectric const.

D : Static dielectric const.

- Inner and Outer change

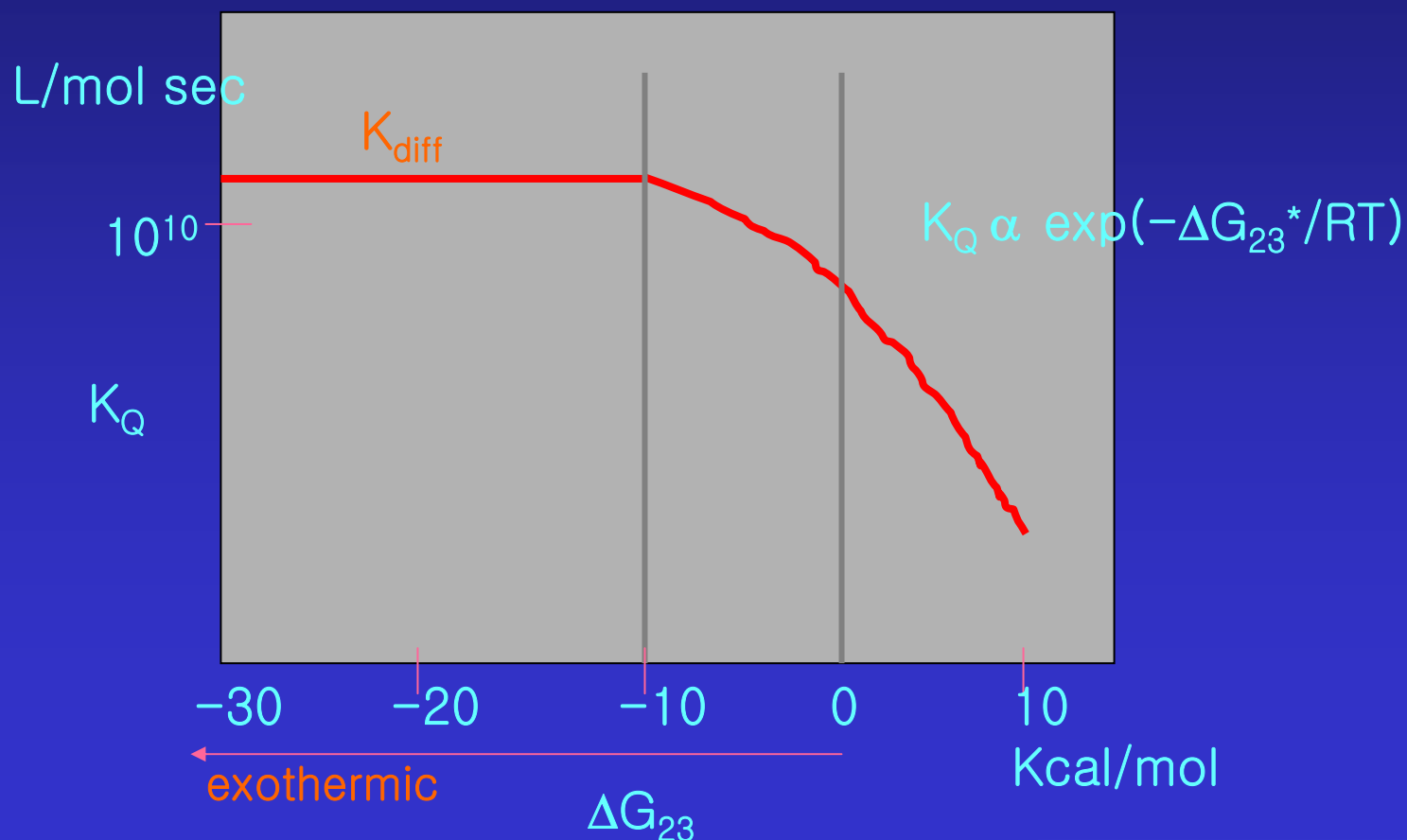
Visualization of the inner (note size change) and outer (note solvent reorganization) changes



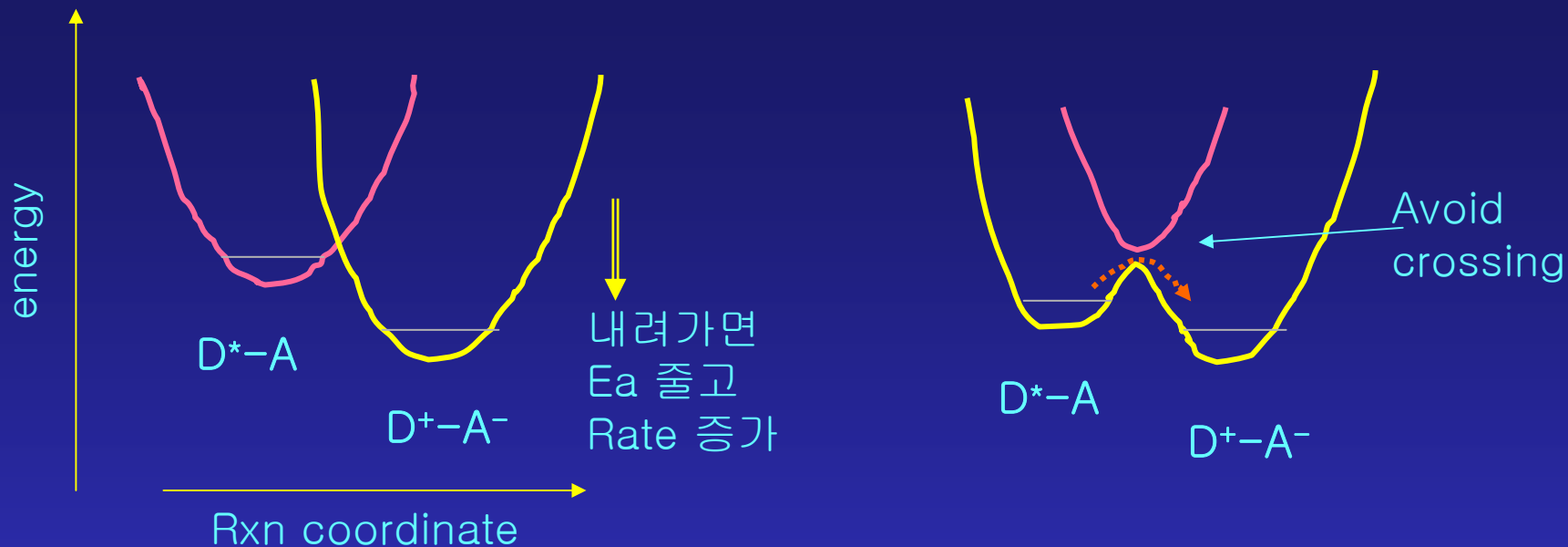
Quenching of Excited States: Free Energy of Electron Transfer

- Rehm and Weller Eq.

$$k_Q = \frac{2.0 \times 10^{10}}{1 + 0.25 \left[\exp(\Delta G_{23} / RT) + \exp(\Delta G_{23}^* / RT) \right]}$$



Quenching of Excited States: Free Energy of Electron Transfer



$$k_{et} = A \exp\left(\frac{-\Delta G^\ddagger}{RT}\right)$$

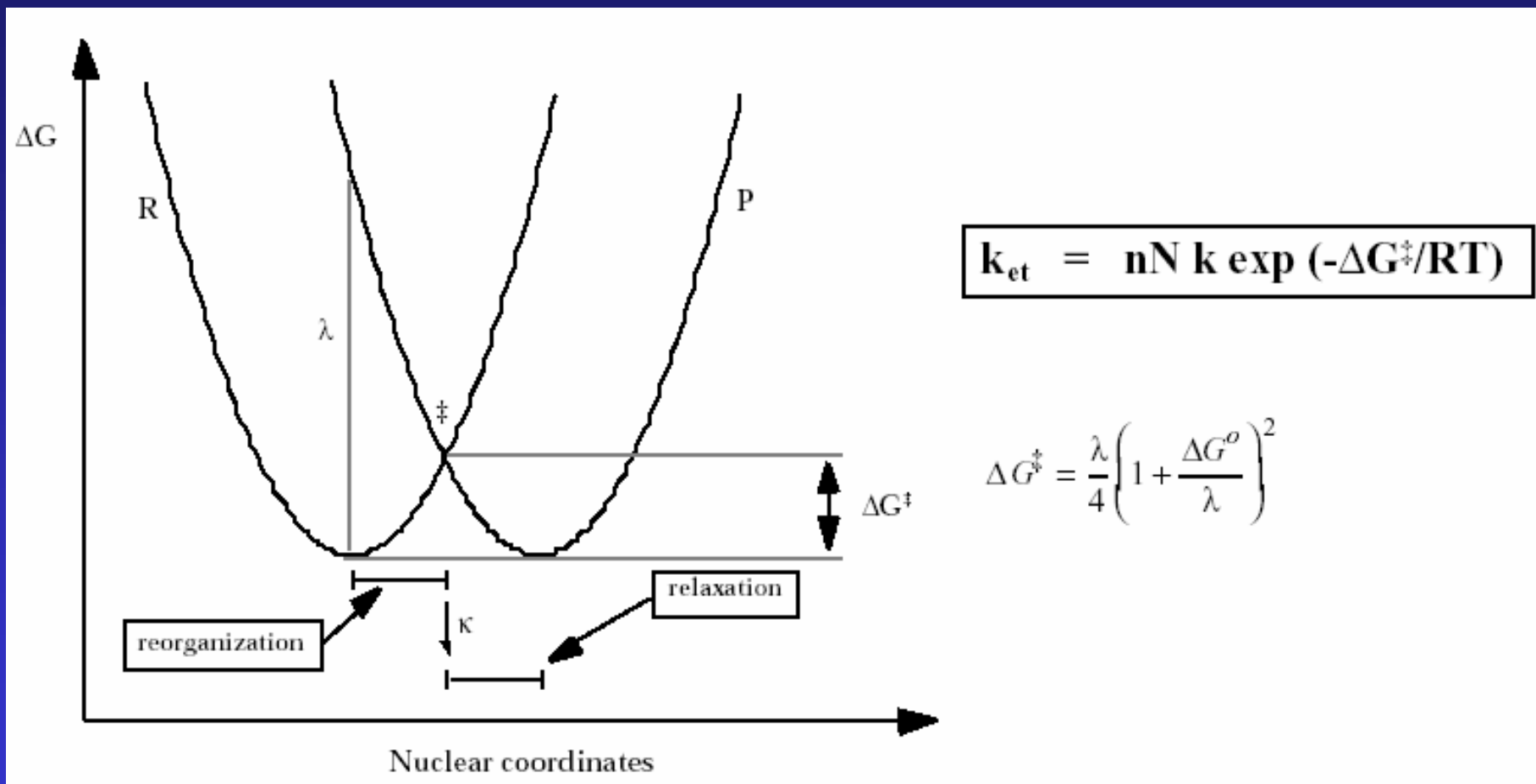
$$\Delta G^\ddagger = \frac{(\Delta G_0 + \lambda)^2}{4\lambda}$$

옆식에서

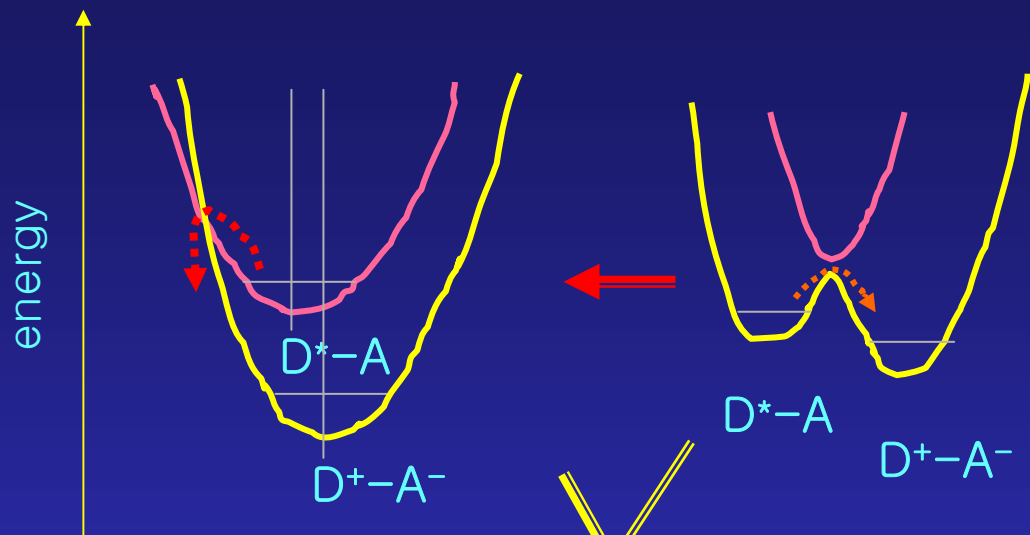
ΔG_0 이 -로 많아 지게 되면 ΔG^\ddagger 이 더 커지게 된다.

이것의 의미는?

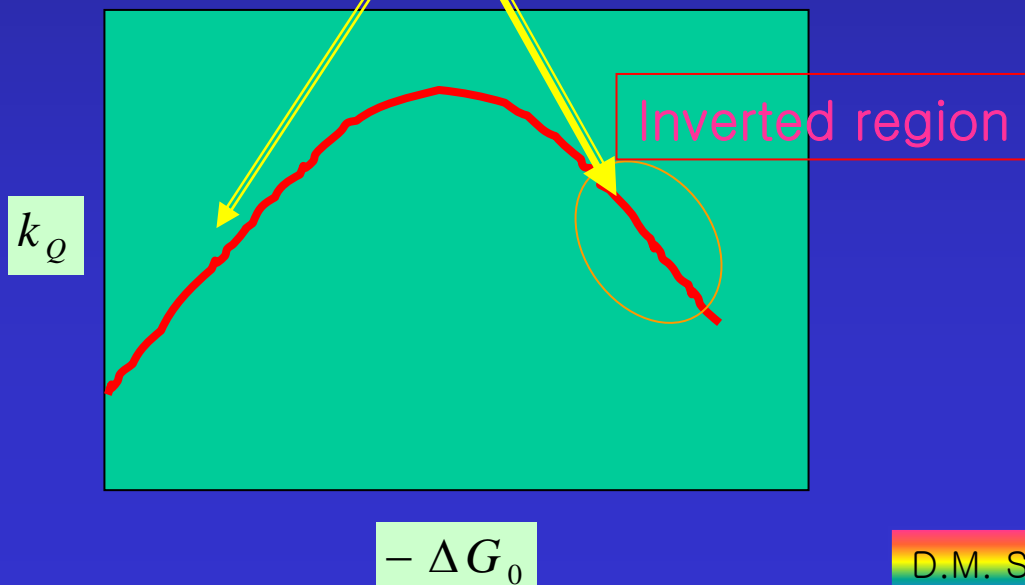
- Potential energy description of an electron transfer reaction with $\Delta G = 0$



Quenching of Excited States: Free Energy of Electron Transfer



Reaction coordinate
에 변화가 적은 경우

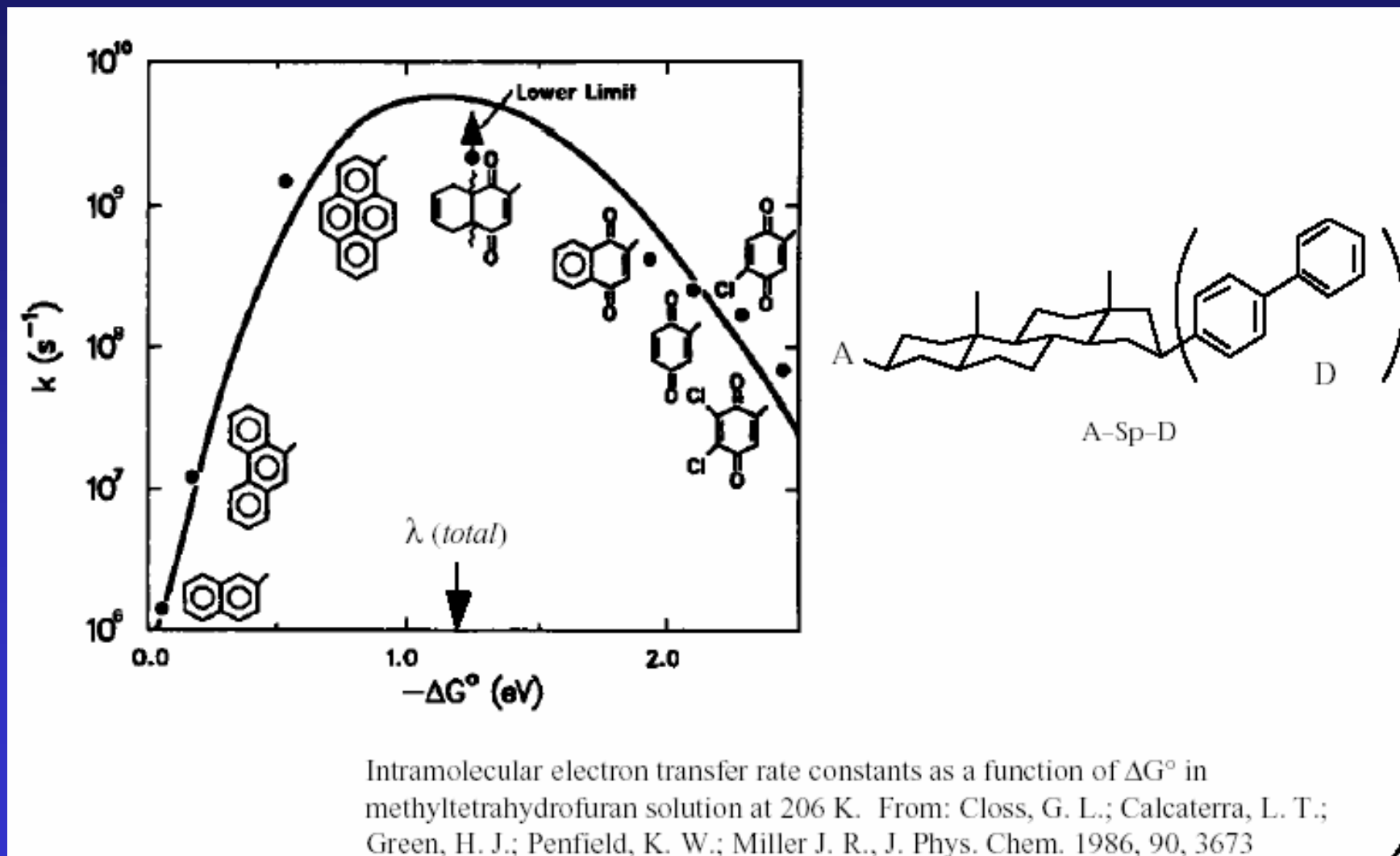


ΔG_0 이 -로 많아 지게
되면 ΔG^\ddagger 이 더 커지게
된다.
이것의 의미는?

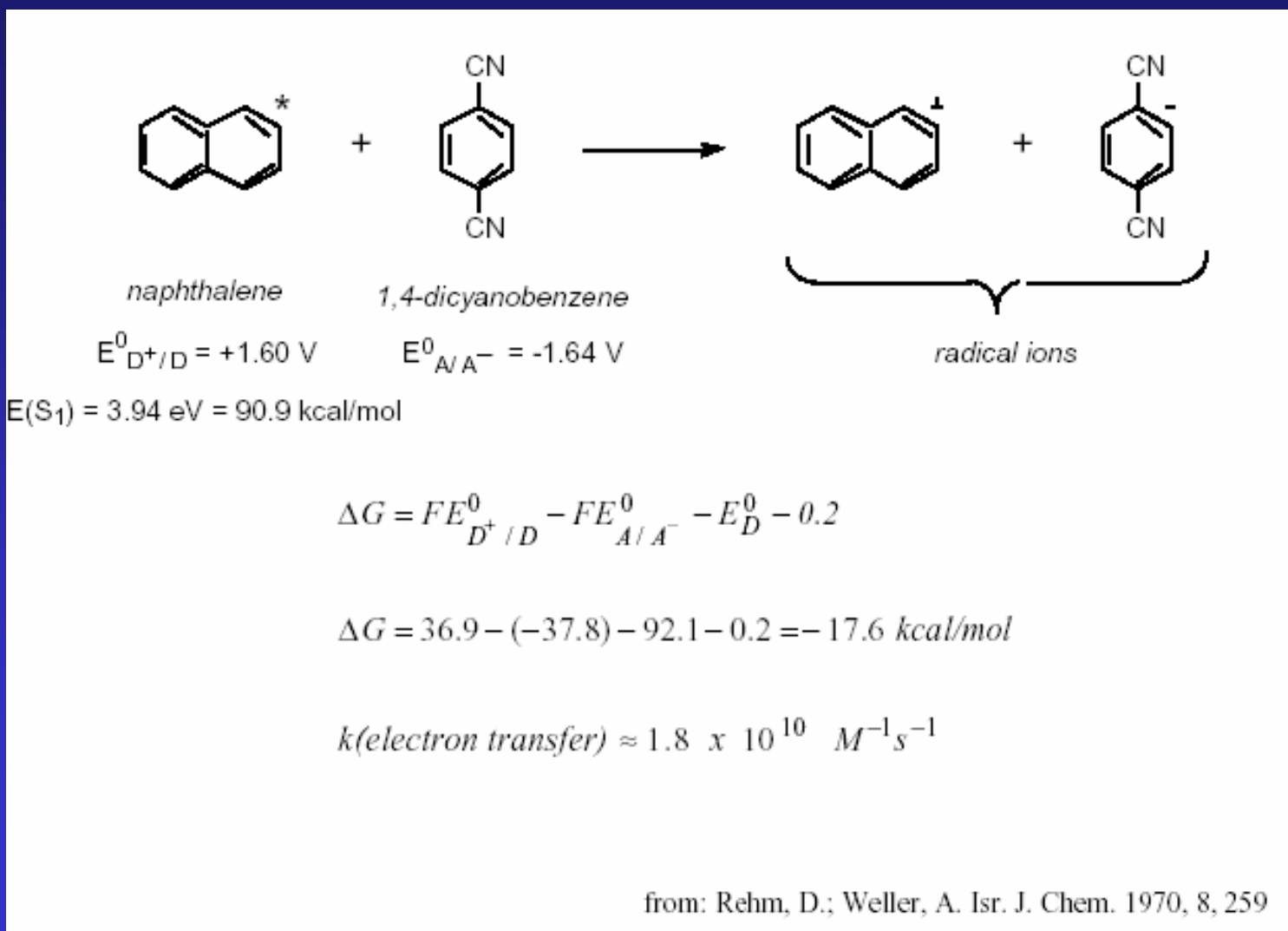
$$k_{et} = A \exp\left(\frac{-\Delta G^\ddagger}{RT}\right)$$

$$\Delta G^\ddagger = \frac{(\Delta G_0 + \lambda)^2}{4\lambda}$$

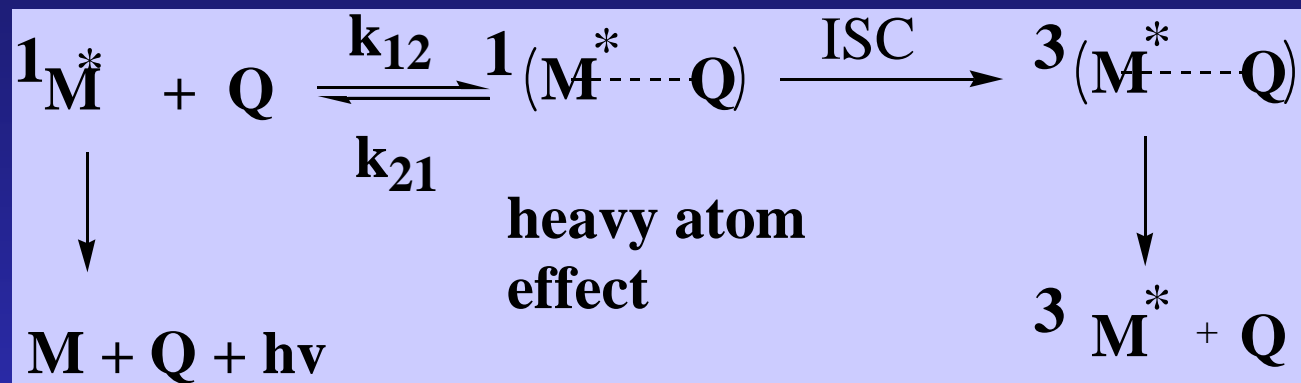
- Inverted region**



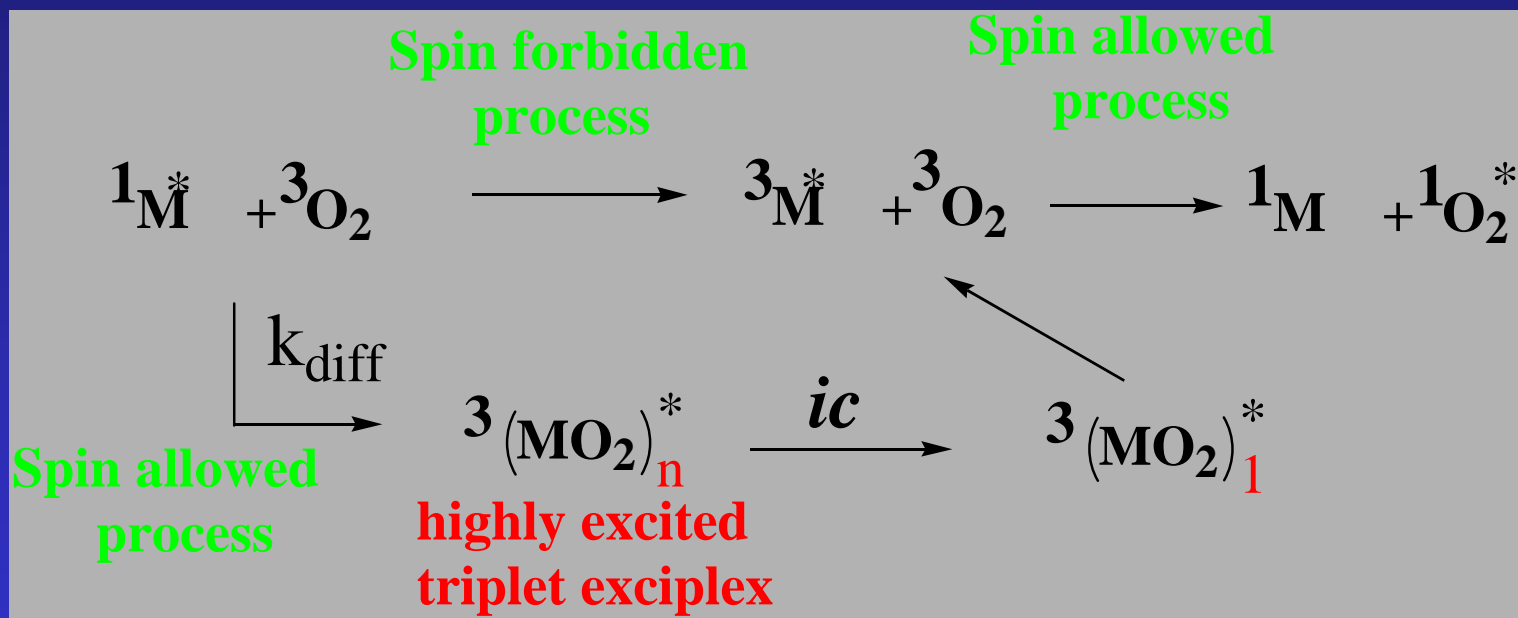
- Thermodynamics and Kinetics

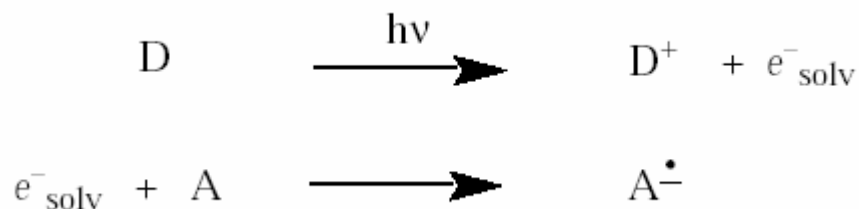


- Heavy atom effects
- Exciplex 형성 때 heavy atom이 isc 증가 시킨다.



- Oxygen quenching effects
- Diffusion에 의해 highly excited triplet exciplex 형성한 다음 singlet oxygen까지 형성한다.





Electron trapping rate constants

Substrate	k ($10^9 \text{ M}^{-1} \text{ s}^{-1}$)	Substrate	k ($10^9 \text{ M}^{-1} \text{ s}^{-1}$)
	<i>Inorganic</i>		<i>Olefins</i>
Oxygen	20	styrene	3.0
N ₂ O	9.0	tetracyanoethylene	15
Cu ²⁺	39	butadiene	8.0
	<i>Aromatic</i>		<i>Ketones</i>
benzene	0.01	acetone	7.0
anisole	0.003	acetophenone	28
benzonitrile	19	benzophenone	28
naphthalene	5.0		

- **Electron Exchange mechanisms**

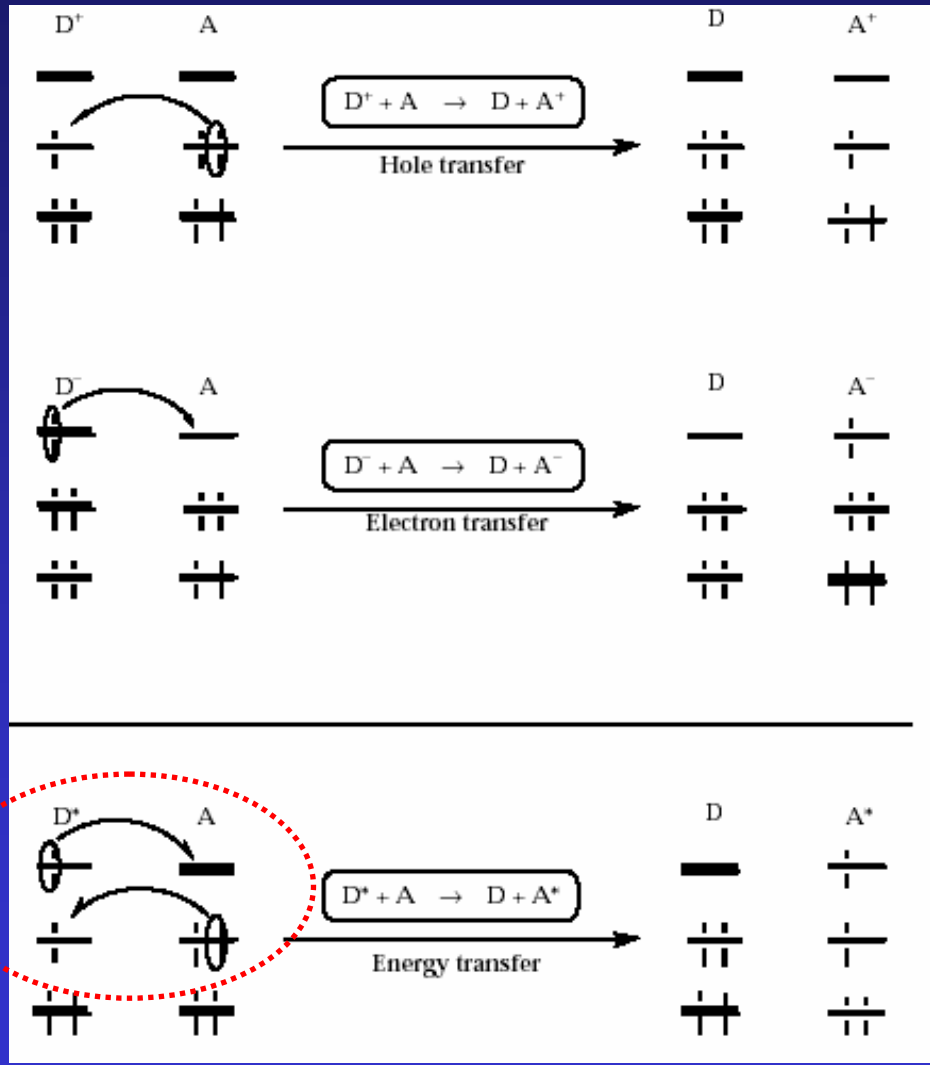
- Energy transfer in some cases
 - always in the case of triplet-triplet energy transfer
- Triplet-triplet annihilation
- Charge transfer
- Charge translocation

- A theory of energy transfer by electron exchange was worked out by Dexter:
- $k_{ET}(\text{exchange}) = KJ \exp(-2 r_{DA}/L)$
- K is related to specific orbital interactions.
- J is the normalized spectral overlap integral, where normalized means that both the emission intensity (I_D) and extinction coefficient (ϵ_A) have been normalized to unit area on the wave number scale.
- J , by being normalized does not depend on the actual magnitude of ϵ_A .
- r_{DA} is the donor-acceptor separation relative to their van der Waals radii, L .
- By being defined in this manner r_{DA} corresponds to the edge-to-edge separation

- **Förster (Coulombic) vs. Dexter (exchange)**
- The rate of dipole-induced energy transfer decreases as R^{-6} whereas the rate of exchange-induced transfer decreases as $\exp^{-(2r/L)}$. This means that $k_{ET}(\text{exchange})$ drops to negligibly small values (relative to the donor lifetime) as the intermolecular (edge-to-edge) distance increases more than on the order of one or two molecular diameters (5-10Å).
- The rate of dipole-induced transfer depends on the oscillator strength of the $D^* \rightarrow D$ and $A \rightarrow A^*$ radiative transitions, but the rate of the exchange-induced transfer is independent of the oscillator strength of the $D^* \rightarrow D$ and $A \rightarrow A^*$ transitions.
- The efficiency of energy transfer (fraction of transfers per donor lifetime $\sim k_{ET}/k_D$) by the dipole mechanism depends mainly on the oscillator strength of the $A \rightarrow A^*$ transition (since a smaller oscillator strength for $D^* \rightarrow D$ is compensated by a slower radiative rate constant), whereas the efficiency of energy transfer by the exchange interaction cannot be directly related an experimental quantity.

Quenching of Excited States: Electron transfer 와 energy transfer

- 왜 두 process를 동시에 고려하는가?



두 process
같이 일어난다.