광화학과 응용

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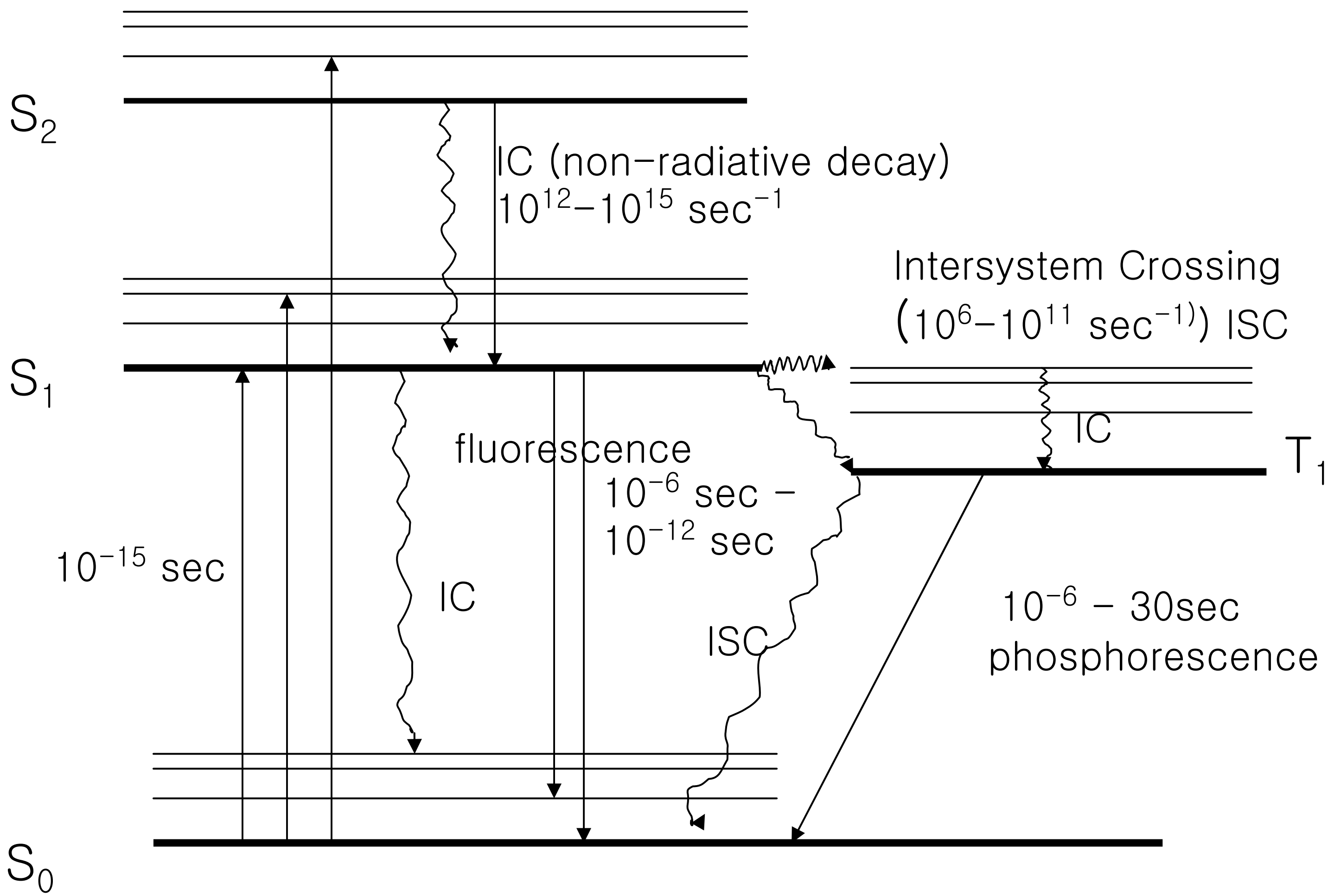
Introduction

- 1. Excited states and the groud state
- An electron can move from the groud-state energy level of a molecule to a higher level (i.e., an unoccupied orbital of higher energy) if proper energy is supplied.
- Light of any wavelength is associated with an energy value given by $E = h\nu$, where ν is the frequency of the light (i.e., ν = velocity of light c divided by the wavelength) and h is Planck's constant.
- Since the energy levels of a molecule are quantized, the amount of energy required to raise an electron in a given molecule from one level to a higher one is a fixed quantity. Therefore, only light with exactly the frequency corresponding to this amount of energy will cause the electron to move to the higher level.
- Normally this energy depends mostly on the nature of the two orbitals involved and much less on the rest of the molecule. Therefore, a simple functional group such as the C=C double bond always causes absorption in the same general area. A group that causes absorption is called a *chromophore*.

Introduction

- Jablonski Diagram



Introduction

- 2. Singlet and triplet states
- In most organic molecules, all electrons in the ground state are paired, with each member of a pair possessing opposite spin as demanded by the Pauli principle.
- When one of a pair of electrons is promoted to an orbital of higher energy, the two electrons no longer share an orbital, and the promoted electron may, in principle, have the same spin as its former partner or the opposite spin.
- A molecule in which two unpaired electrons have the same spin is called a *triplet (T)*, while one in which all spins are paired is a *singlet (S)*.
- The lowest-energy excited state is called S_1, the next S_2, etc., and triplet states are similarly labeled T_1, T_2, T_3, etc.
- Therefore, S_0 indicates the ground state. In most cases promotions from the S_0 state to any T states are improbable (these are called "forbidden"transitions).
- Thus it can be stated that in most molecules only singlet-singlet promotions take place.

- 2. Singlet and triplet states
- Minimum energy to excite organic molecules
- – Electronic transition (30-40 Kcal/mol, 700-800nm) : visible range 중에서
  – inorganic materials 200nm 정도의 energy

Energy (kcal/mole) = 2.86 X 10^{4} / λ (nm)

700nm 40 kcal/mole
200nm 140 kcal/mole

유기분자에서 가장 낮은 결합에너지 : 약 35kcal/mole (O-O 결합)
250 nm (114kcal/mole)이면 모든 결합을 다 끊는가?
- selectivity (localized on specific bond)

Introduction

- Reaction dynamics
- Rate constant =A exp –(Ea/RT) = A 10 –(Ea/0.0046T)
- A: probability factor – frequency

max = $10^{12} \sim 10^{15}$ sec^{-1} Unimolecular reactions

min = $10^{6} \sim 10^{8}$ sec^{-1} Bimolecular reactions

- Ea = exothermic (2 ~ 3 kcal/mol ~ 40kcal/mol (Photorxn 에선가능)

  – endothermic

몇 분 정도에 진행되는 반응 : 20 ~ 30 kcal/mol

광화학 반응

A= 10^{13} sec^{-1} Ea = 6kcal/mol -> rate = $10^{8} \sim 10^{9}$ sec^{-1}

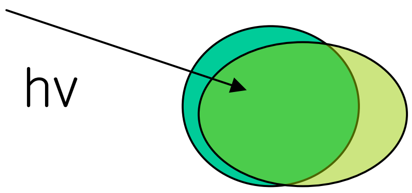
Unimolecular reactions

A= 10^{8} sec^{-1} Ea = 6kcal/mol -> rate = $10^{3} \sim 10^{4}$ sec^{-1}

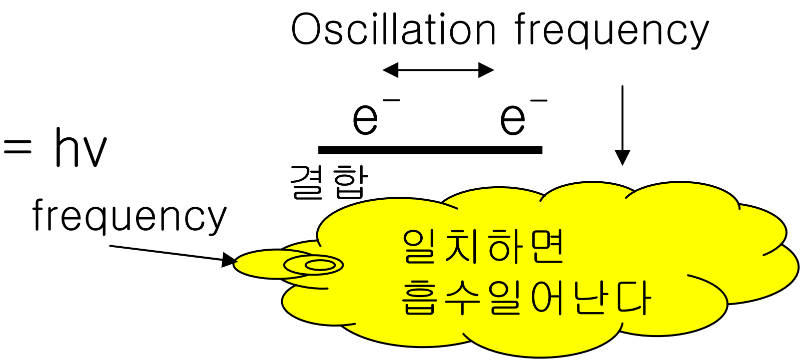
Bimolecular reactions

msec life time 이므로 다른 과정으로 빠르게 진행된다.

- Absorption and Emission of Light



E = hv



- $H_0 \Psi_i = E \Psi_i$
- Oscillation frequency of electrons : $10^{15} \sim 10^{16}\ sec^{-1}$

200~700 nm photon oscillation에 해당

- $(H_0 + H') \Psi(x,t) = E \Psi(x,t)$

$\psi(x,t) = \Sigma\, a_f(t)\, \Psi_k$ [$a_f(t)$: time dependent term]

$[a_f(t)]^2 = (3\pi^3/2h^2) < \Psi_i \,|\, \mu \,|\, \Psi_f > 2\, \rho(\nu_{if})\, t$

t : time of irradiation, ρ = radiation density at ν_{if}

μ : transition moment (dipole moment operator $e\, \Sigma\, r_j$)

Radiation Density & Frequency

- E total = nhν

hν

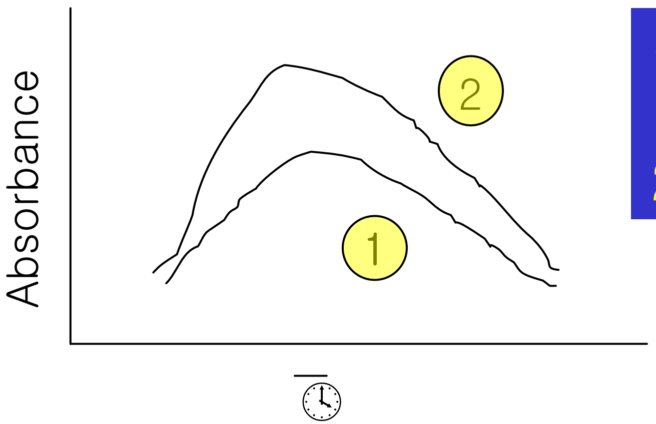
Density 크다 -> n 값이 크고 빛을 많이 또는 오래쪼인다.

강한 빛 -> ν 값이 크고 빛의 파장이 짧다.

Probability and Absorption Spectra

$$f = [8 \pi^2 \nu_{if} m_e < \psi_i | \mu | \psi_f >^2] \; / \; 3 h e^2$$

$$\approx 4.3 \times 10{-}9 \int \varepsilon \, d\bar{\nu}$$



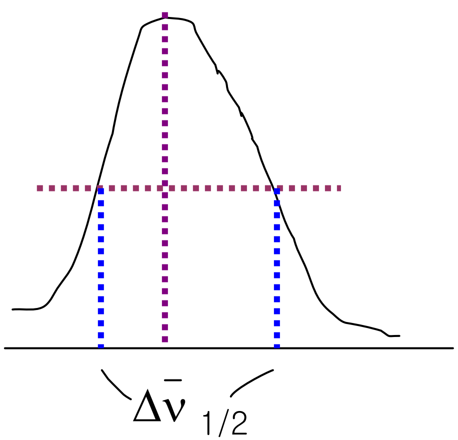
같은 몰농도의 용액에서 absorbance가 다른 경우: final state에 도달할 확률은 2같은 경우가 크다

Selection Rule (빛의 흡수)

- $E = h\nu$: 양자화 되어있다.
- Transition moment ≠ 0 이어야 한다.
- F 는 $< \psi_i | \mu | \psi_f >^2$에 비례 한다. 즉 $< er >^2$ 에 비례 한다.

$\int \varepsilon \, d\bar{\nu} = \varepsilon_{max} \, \Delta\bar{\nu}$ |

Half bandwidth



ex) ε_{max} = 5 X 10^4 at 20,000cm^{-1} (500nm)

$\Delta\bar{\nu}_{1/2}$ = 5000cm^{-1}

f = (ε_{max} $\Delta\nu_{1/2}$) / 2.5 X 10^8

= (5 X 10^4) X (5 X 10^3)/ 2.5 X 10^8

= 1

transition이 매우 잘 된다.

Ex) 🖫❐ $>^2$

= (5 X 10^4) X (5 X 10^3)/

(2.5 X 10^{19} X 2 X 10^4)

= 5 X 10^{-16}

따라서 r = 2.2 X 10^{-8} cm

🖫❐ $>^2$ ~ [ε_{max} $\Delta\bar{\nu}_{1/2}$] / 2.5 X 10^{19} $\bar{\nu}$

(unit cm^2)

Radiative lifetime

- $\tau = 10^{-4} / \varepsilon_{max}$

Ex) $\varepsilon_{max} = 10^{5}$ L mol^{-1} cm $^{-1}$

$\tau = 10^{-9}$ sec = 1 nsec

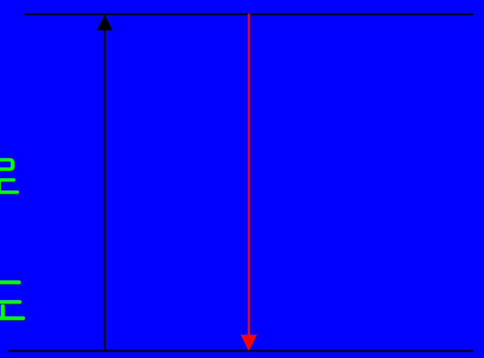
(실제 값과 다르다. 다른 과정으로 deactivation가능하기 때문에)

$\tau = 1/\{ \&_{f} + (\&_{r} + \&_{isc} + \&_{rl} + \cdots) \}$

따라서 τ 는 $1/\&_{f}$ 보다 작다.

$< \psi_{i} | \mu | \psi_{f} >^{2}$ 이므로

◷ 잘되면 ◷ 도 잘됨

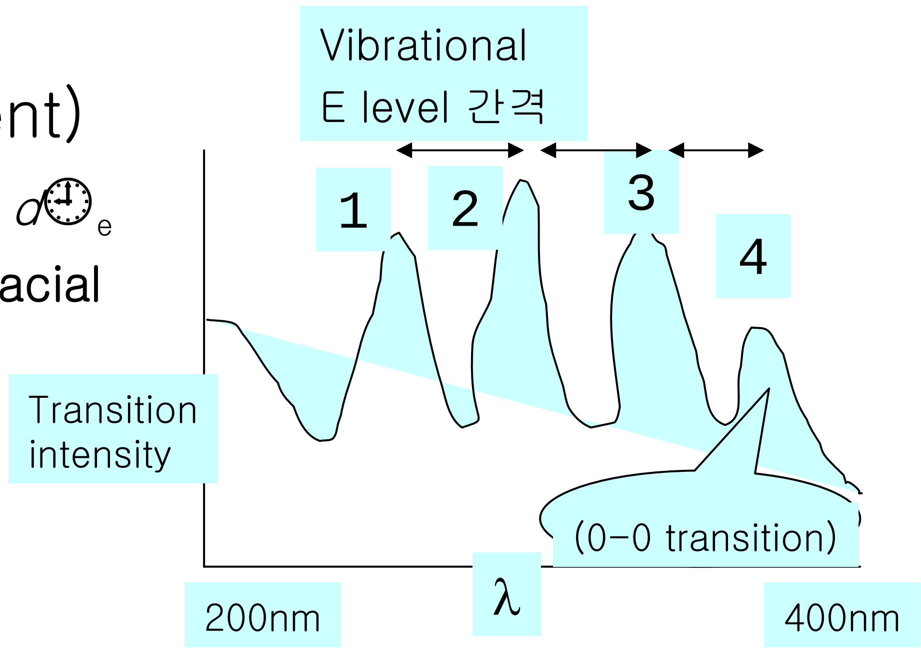


Total Transition Moment

- $< \psi_i \,|\, \mu \,|\, \psi_f >$: transition moment
- Ψ_{hv} = total wave function = (θ : nuclear wave function)
- (ϕ : electronic wave function)
- Absorption의 경우 electronic motion이 중요
- ϕ = ψ s
- TM (total transition moment)

$$= \int \theta_i \theta_f \, d\tau_N \int s_i s_f \, d\tau_S \int \psi_i \mu \psi_f \, d\tau_e$$

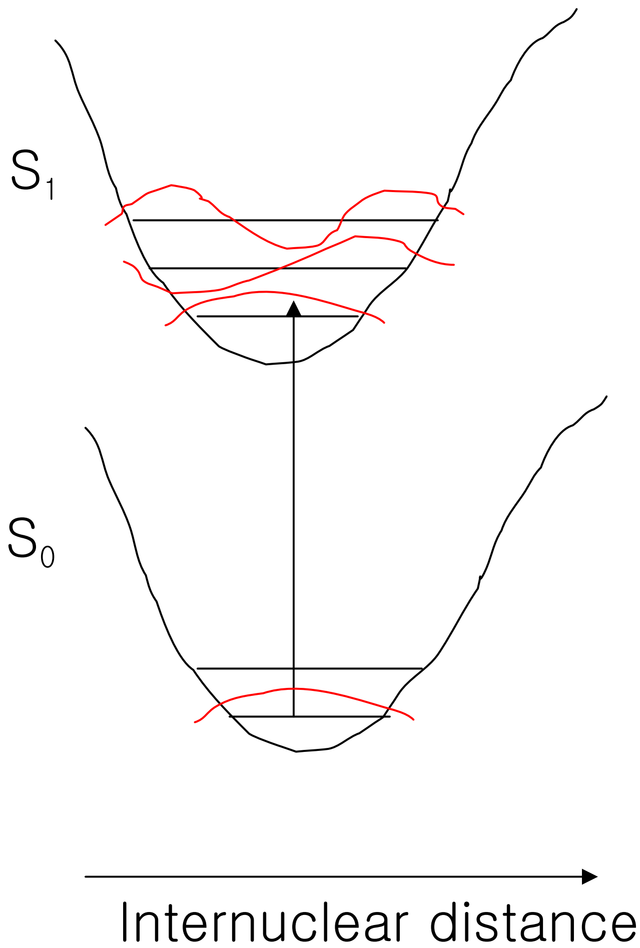
nuclear spin electron spacial

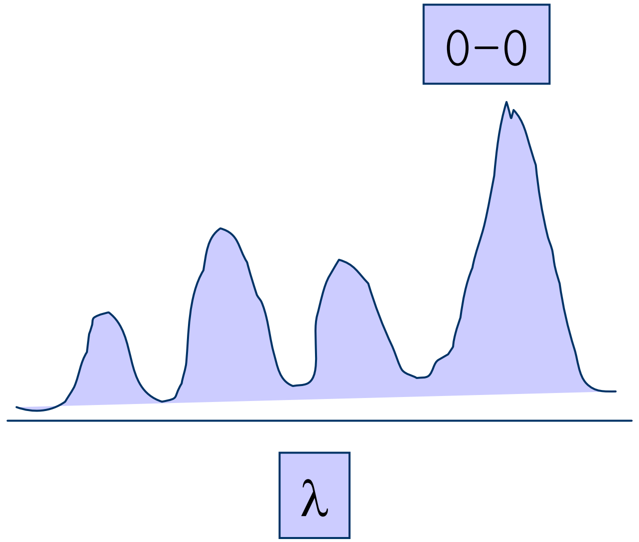


(0–0 transition)
ground v=0 level에서
excited state v=0 level로의 transition
=> Lowest energy transition

W/O geometry change

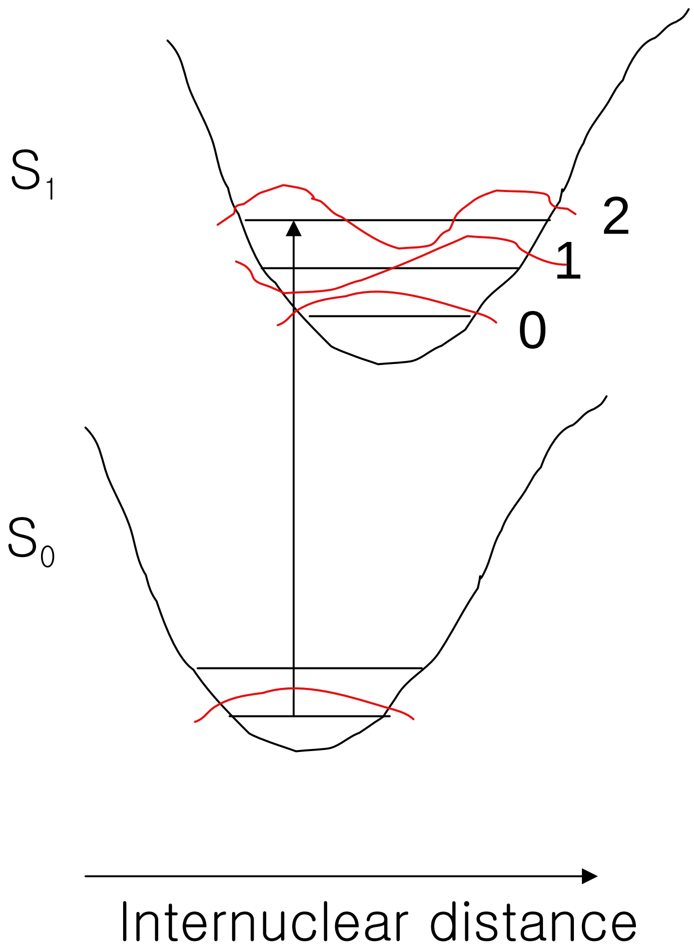
- $<\psi_i|\mu|\psi_f>$:(0–0 transition)이 가장 잘 일어난다.

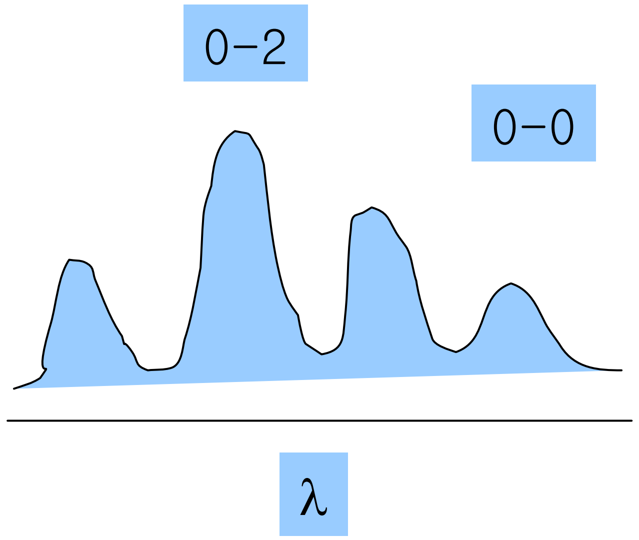




W/ geometry change

- $\langle \psi_i | \mu | \psi_f \rangle$:(0–0 transition) 아닌 것 중에서 잘 전이.

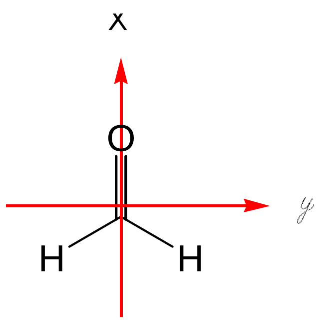




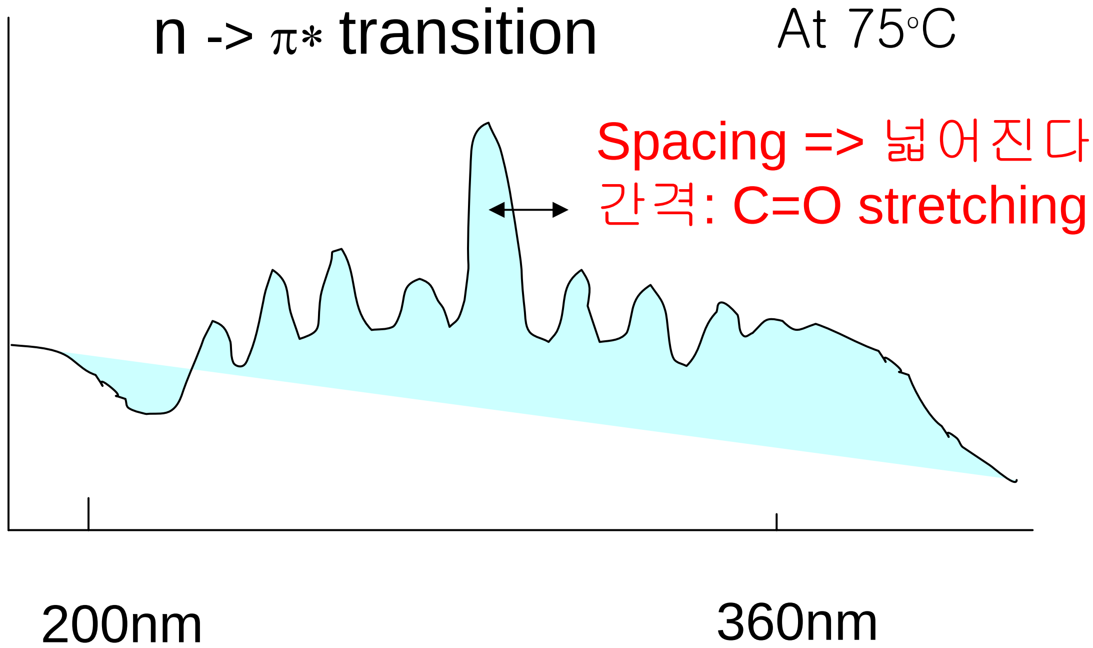
Introduction

- Types of excitation.
- For most orgainc molecules four types of electronic excitation need to be considered. They are listed below in the order of decreasing energy.
- 1. $\sigma \rightarrow \sigma^*$. Alkanes, which have no *n* or electrons, can be excited only in this way (*n* = one in an unshared pair).
  2. $n \rightarrow \sigma^*$. Alcohols, amines, ethers, etc. can also be excited in this manner.
- 3. $\pi \rightarrow \pi^*$. This pathway is open to alkenes as well as to aldehydes, carboxylic esters, etc.
- 4. $n \rightarrow \pi^*$. Aldehydes, ketones, carboxylic esters, etc. can undergo this promotion as well as the other three.
- In general, the more conjugation in a molecule, the more the absorption is displaced toward higher wavelengths.
- Examples of chromophores in the visible or uv are C=O, N=N, Ph and NO_2. Groups such as Cl, OH and NH_2 generally shift the bands of chromophores such as Ph to a longer wavelength (through resonance).

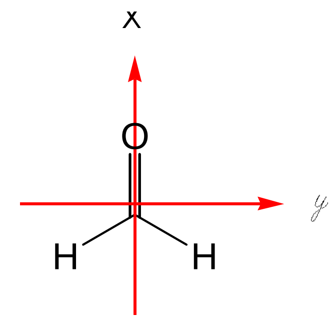
- Electronic Excitation of Formaldehyde

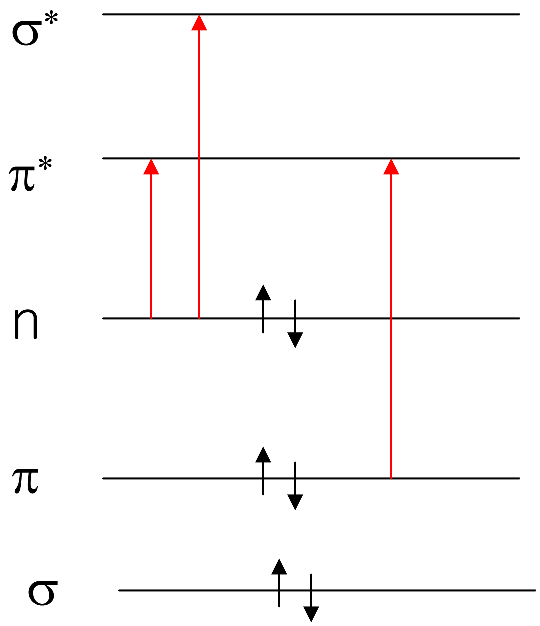


Vapor
At 75°C



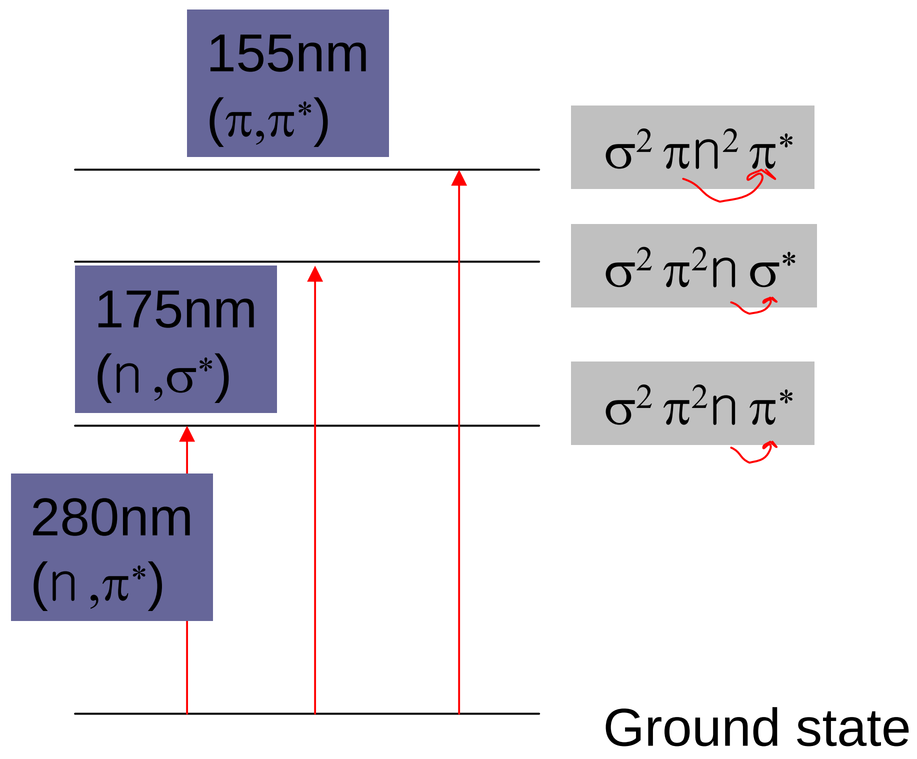
- Electronic Excitation of Formaldehyde



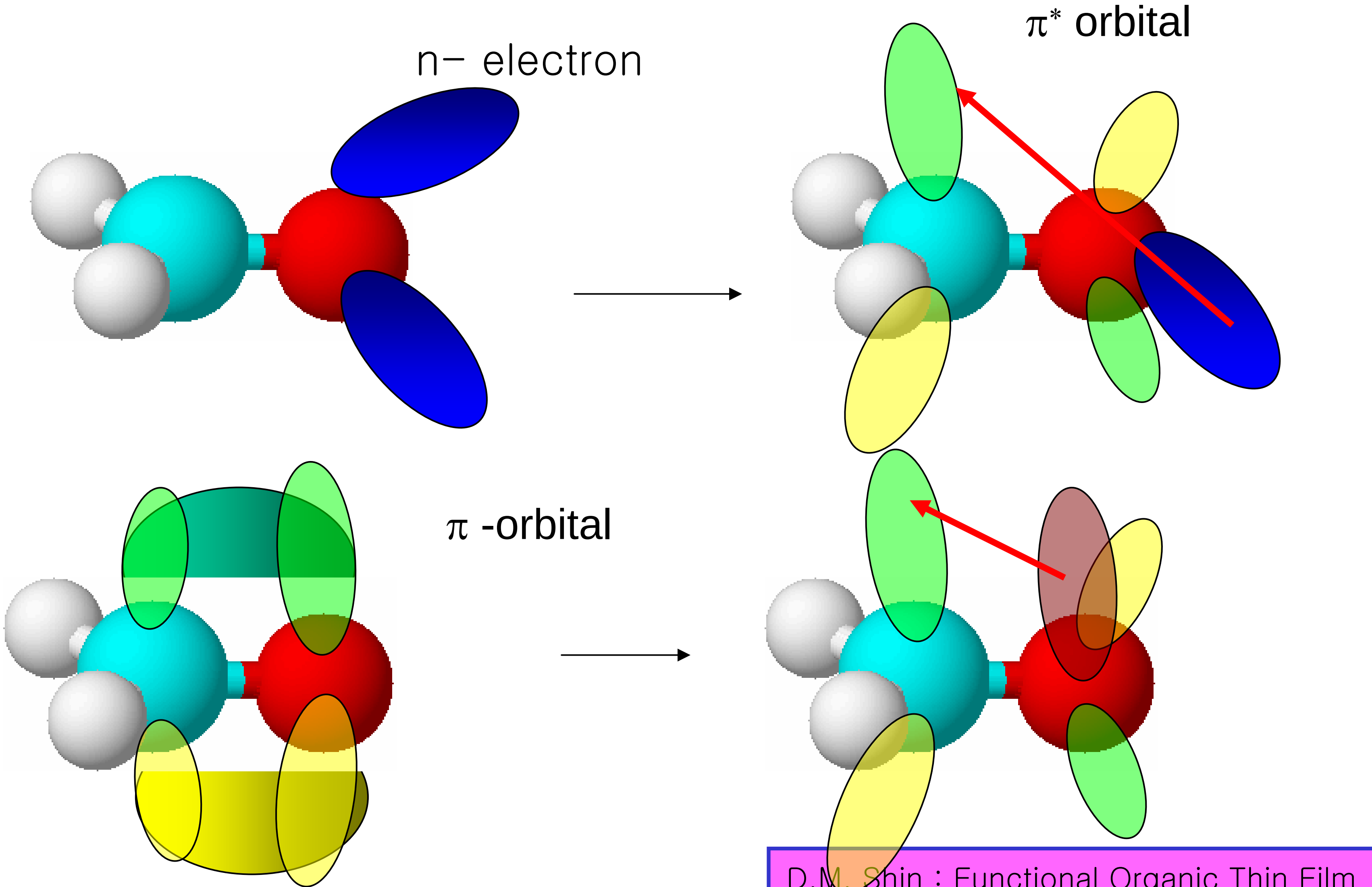


$\sigma^2 \pi^2 n^2$

Ground state configuration



- Visualization of (n ,π*) and (π,π*) : formaldehyde



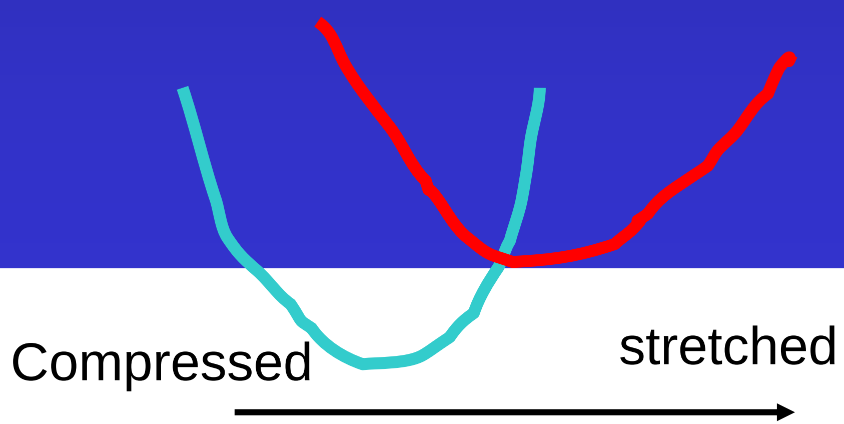
Introduction– Types of Transition

- Energy difference

- $E(n,\pi^*) < E(\pi,\pi^*)$; redistribution energy

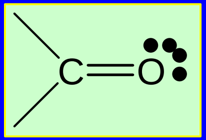
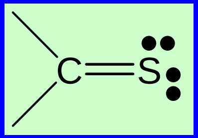
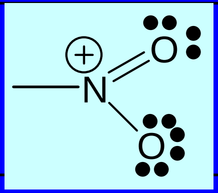
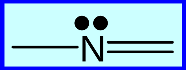
- => n-orbital의 electron이 π-orbital의 electron 보다 덜 holding 되어 있다
  즉 떼어내기 쉽다. : low energy transition

- 두개의 transition 모두 C=O의 결합길이가 늘어난다. π^* -character 때문



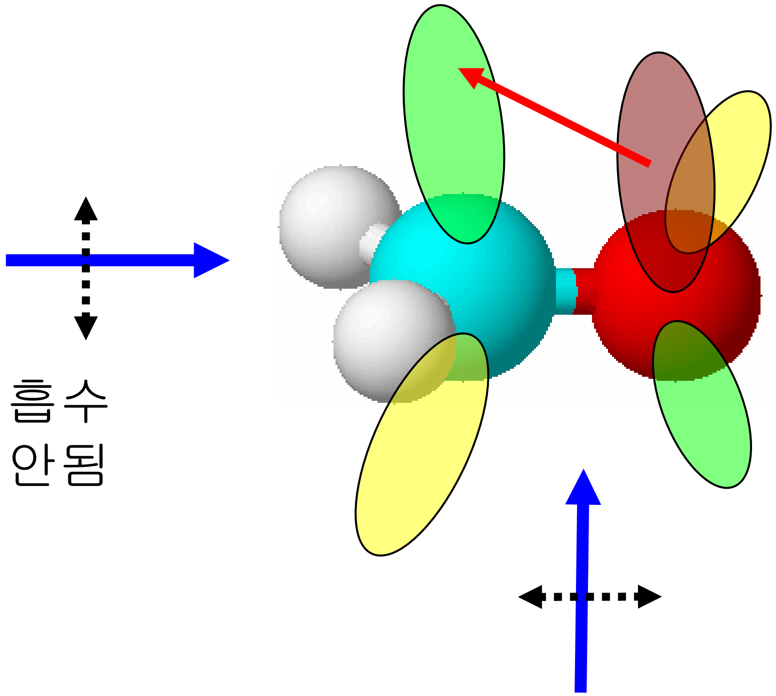
Introduction– Types of Transition

◇ n,π^* 예

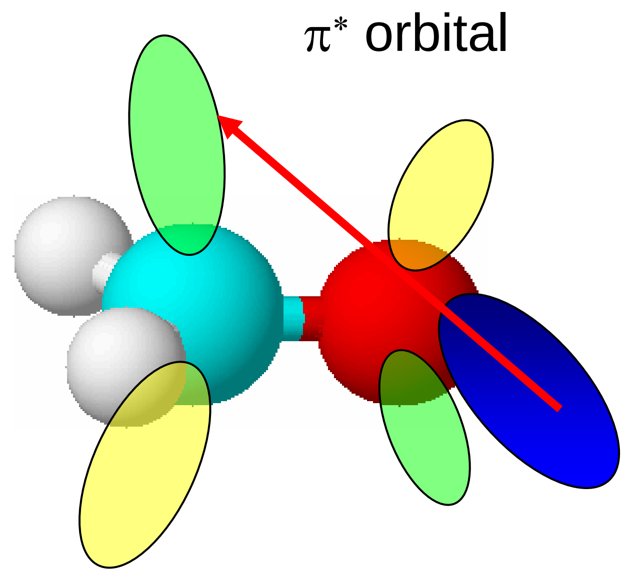
		λ_{max}
	Acetone	279nm
	Thioacetamide	318nm
	Nitromethane	270nm
	pyridine	290nm

Introduction– Types of Transition

- 흡광도 차이 (n ,π^*) and (π,π^*) : formaldehyde



In-plane polarization
같은 축에서 분자내 전자 배치의 변화



Out-of-plane polarization
분자의 π plane에 수직으로 흡수 – 모든 방향의 vector 성분 갖고 있다.

- TM = $= \int \pi^* \mu n \tau = < \pi^* | \mu \; | n >$

$$= < 2p_z \left| \rightarrow (x), \uparrow (y), \underset{\leftarrow}{\nearrow} (z) \right| 2s >$$

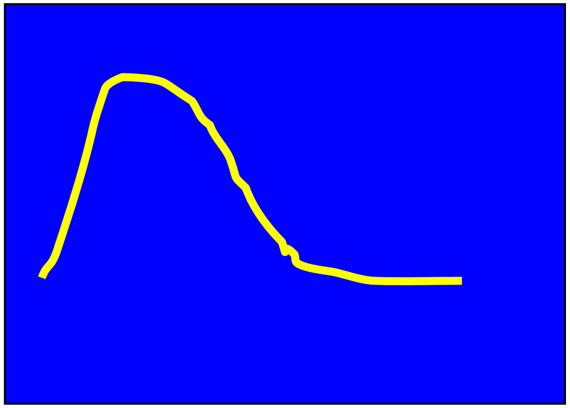
- Z방향으로 된 것 만이 0이 아니다.

- Transition은 가능하나, 적분 값이 적다 (symmetry forbidden).

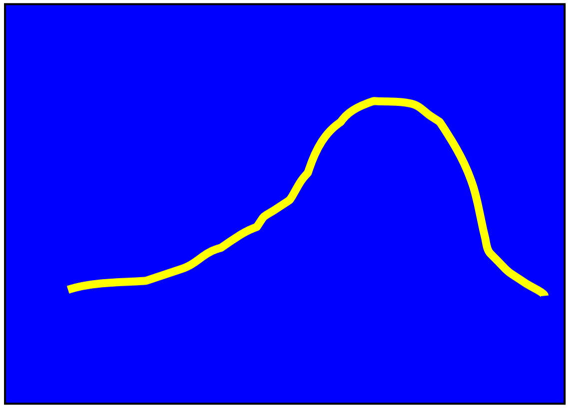
- $(\pi, \pi*)$transition

⇒ Absorption 이 크다, transition Intensity 크다.

⇒ Cyclic Oscillator   Linear Oscillator



λ



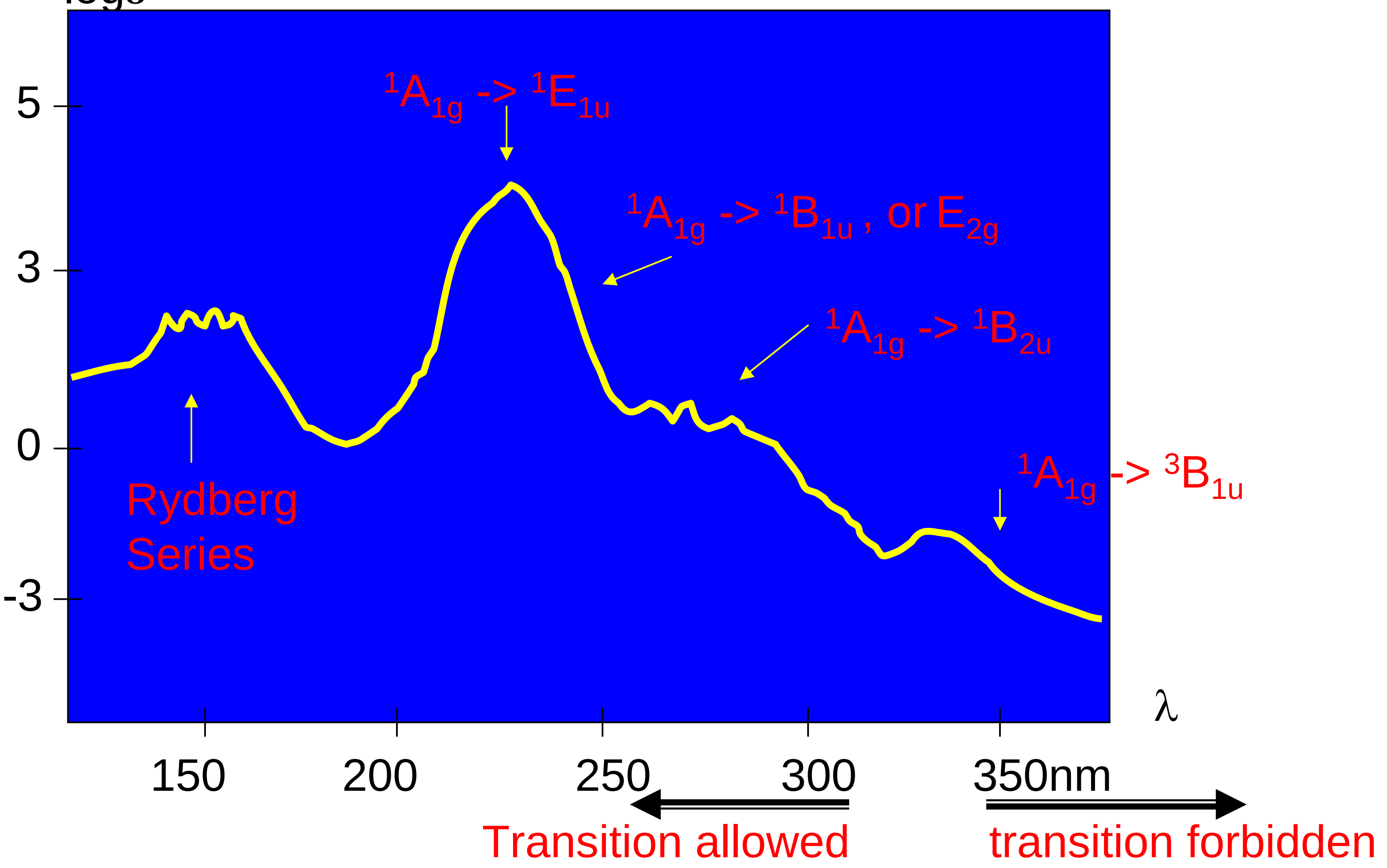
λ

Cyclized 되면서 전자 안정화
전자가 잘 hold되어 있다.
Transition Energy 가 크다.

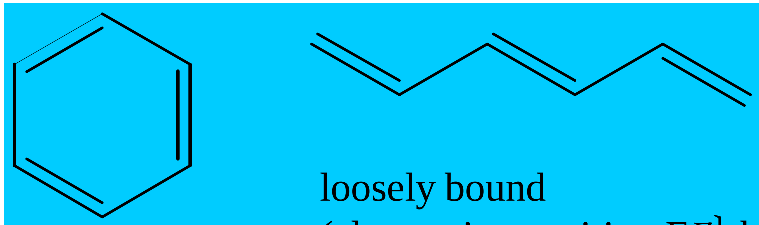
전자가 느슨하게 bind
Transition Energy 적게 든다.

- benzene 의 transition
- logε

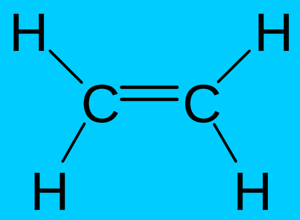
Characteristic cyclic oscillator



- benzene 과 hexatriene

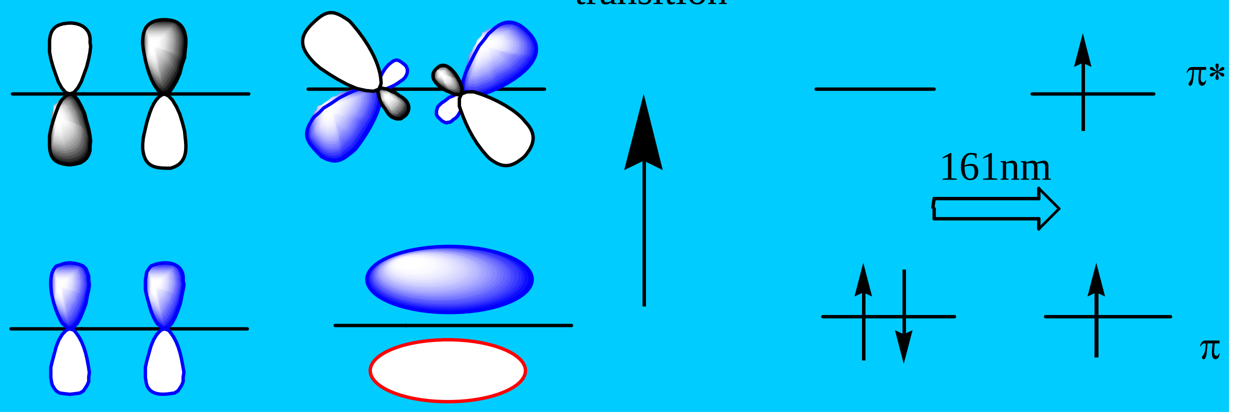


loosely bound
(electronic transition E가 benzene보다 작다.)



ethene

transition



Introduction– Molecular Orbitals

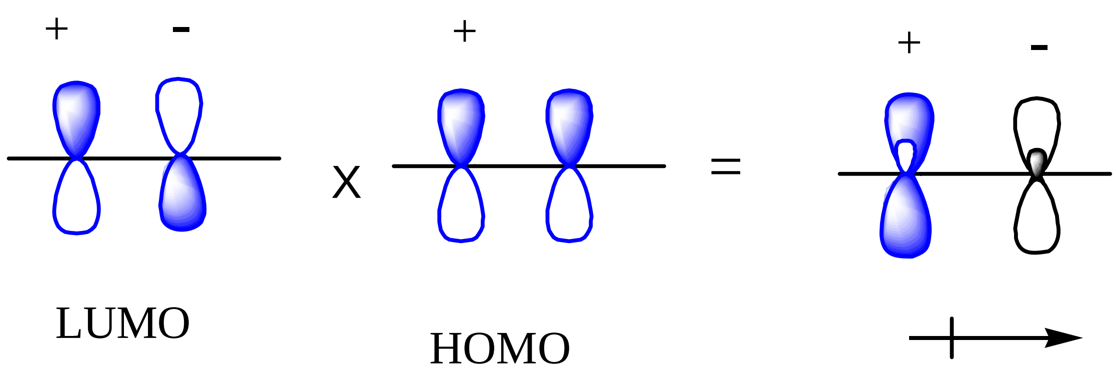
- Transition Moment

$$TM = <\varphi_i|\mu|\varphi_f>^2$$

□ μ: dipole moment operator : odd function

$$<odd|odd|odd> = \int(odd) = 0$$

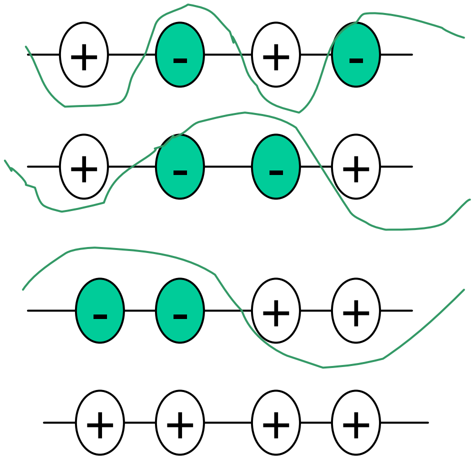
$$<even|odd|odd> = \int(even) \neq 0$$



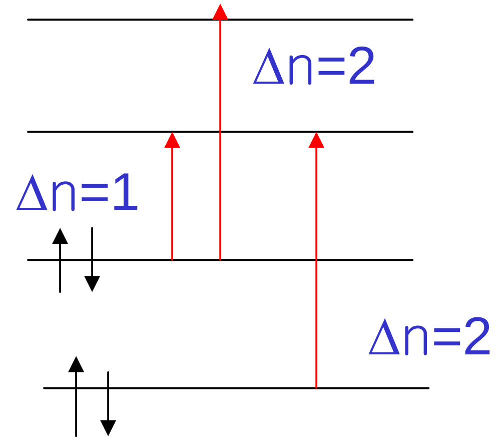
C 축을 따라 electronic transition
따라서: allowed transition

Introduction– Molecular Orbitals

- Butadiene



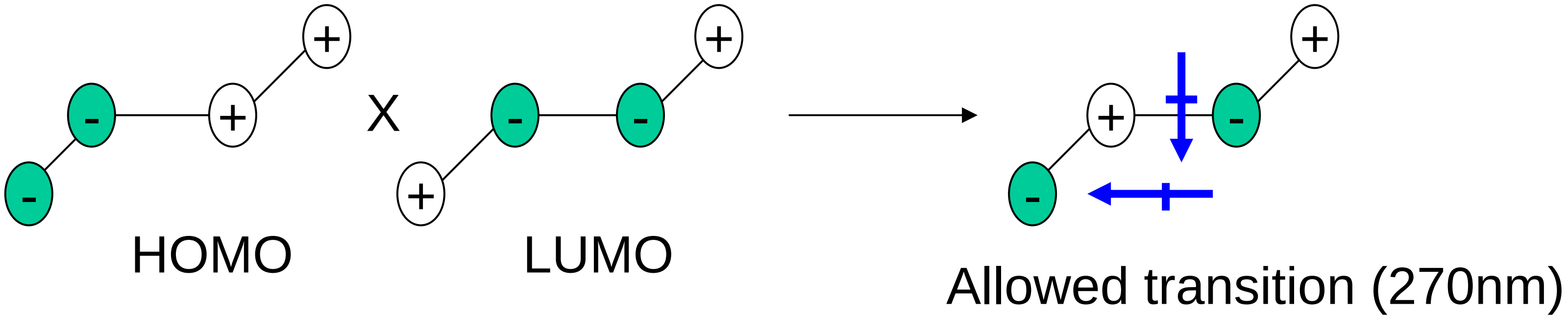
- π_4
- π_3
- π_2
- π_1



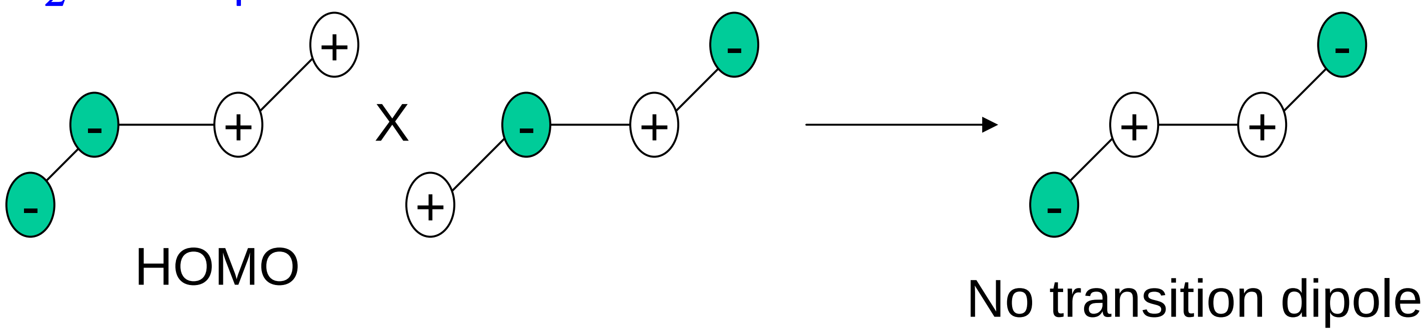
- $\pi_2 \rightarrow \pi_3$
- $\pi_2 \rightarrow \pi_4$
- $\pi_1 \rightarrow \pi_3$

- Butadiene

$\pi_2 \rightarrow \pi_3$

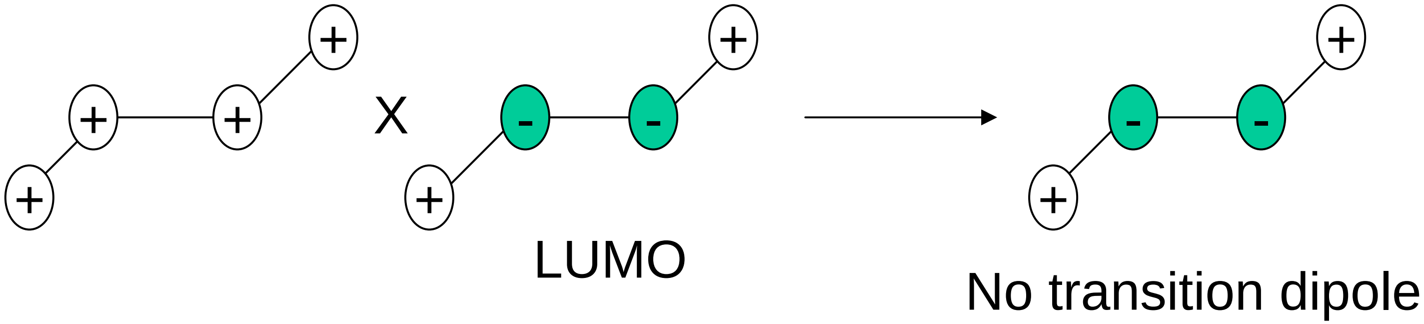


$\pi_2 \rightarrow \pi_4$



- Butadiene

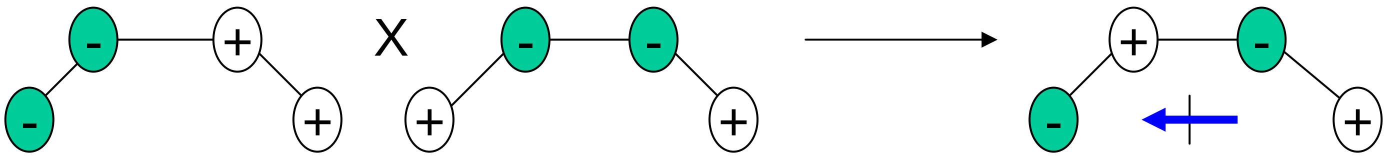
π_1 –> π_3



그러나 분자가 **vibration**과 **rotation** 을 하므로 **forbidden transition** 이라도 약간의 **transition**은 일어날 수 있다.

- *S–cis*–Butadiene 은 어떤 결과를 만드는가?

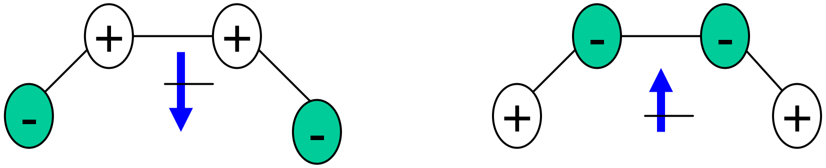
$\pi_2 \rightarrow \pi_3$



HOMO LUMO

Allowed transition (270nm)

175nm (100nm blue shift)

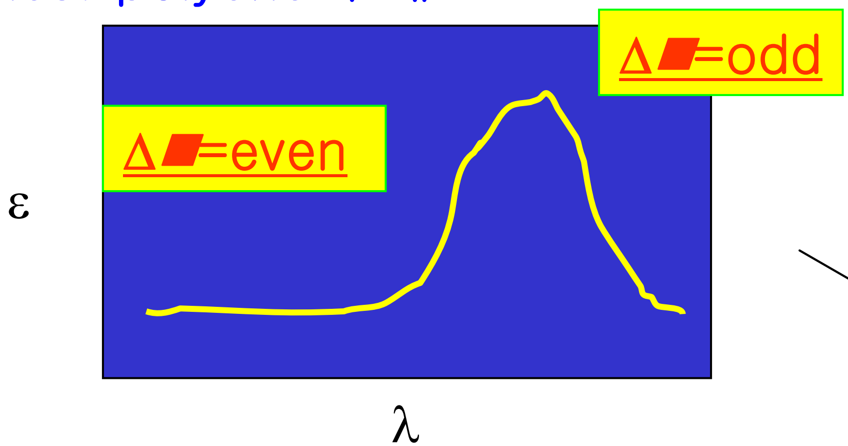


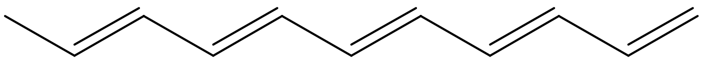
All Allowed transitions

$\pi_2 \rightarrow \pi_4$ $\pi_1 \rightarrow \pi_3$

□ Δ■=odd 인 경우 : low energy transition

- Linear polyene의 예





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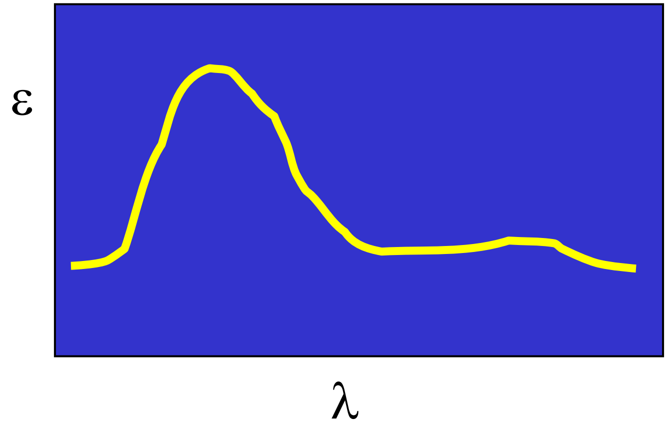

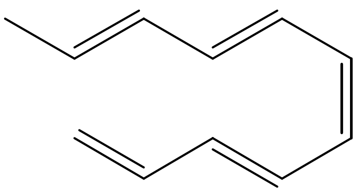

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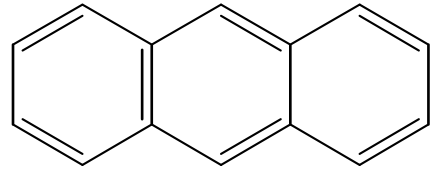
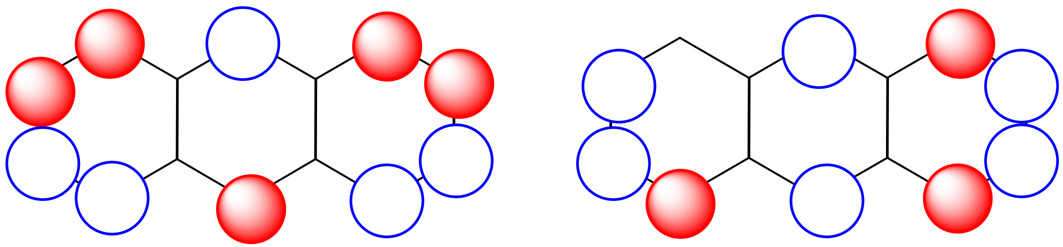
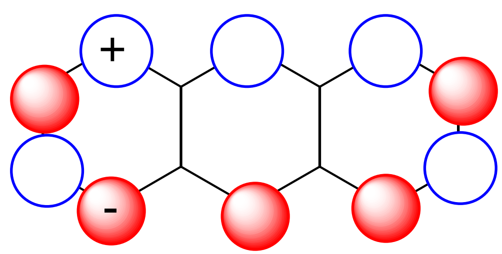




HOMO φ_{34} LUMO φ_{33}

⇩



→ 이 방향은 작다.

↓ 이 방향의 Transition 이 크다.

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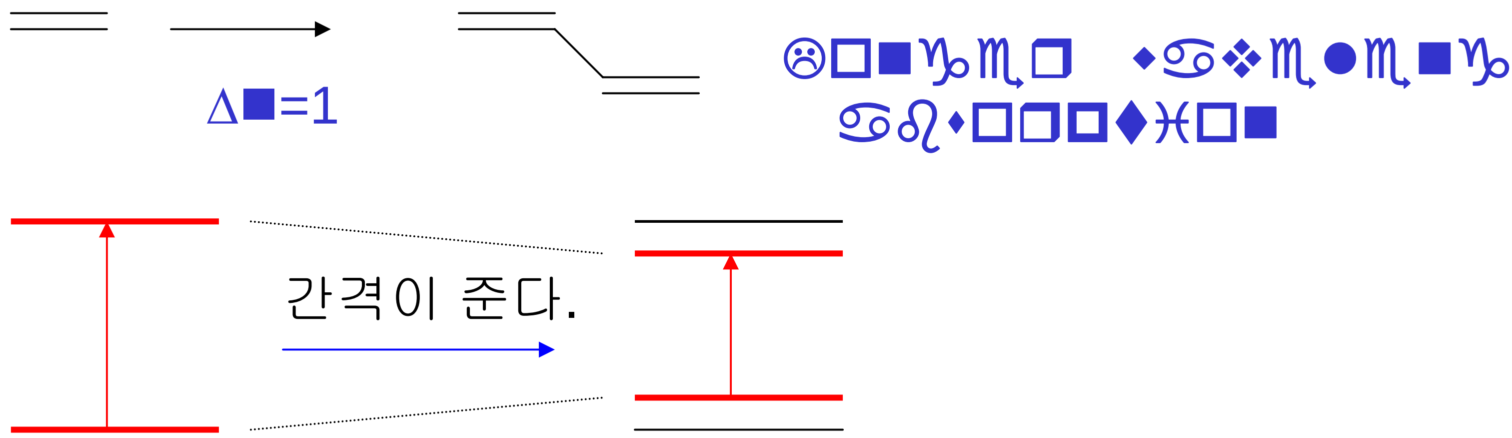

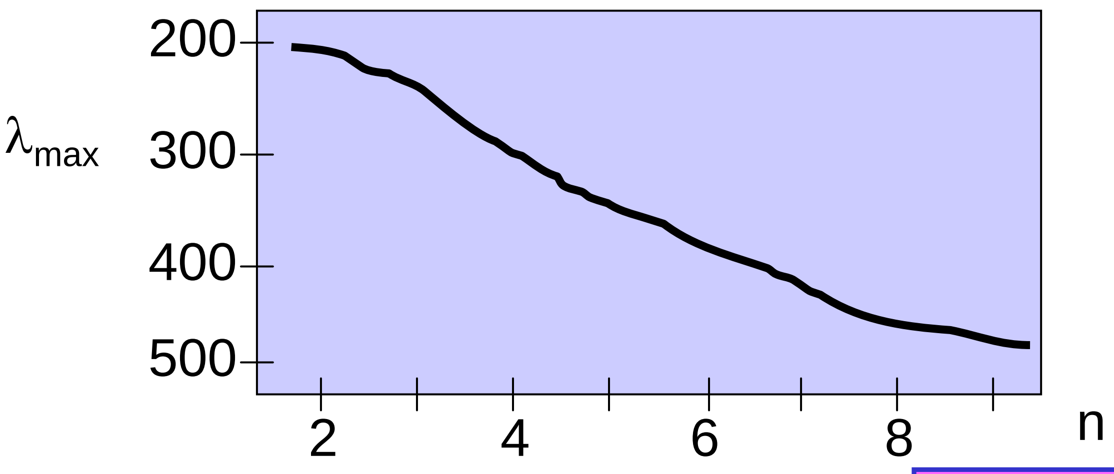

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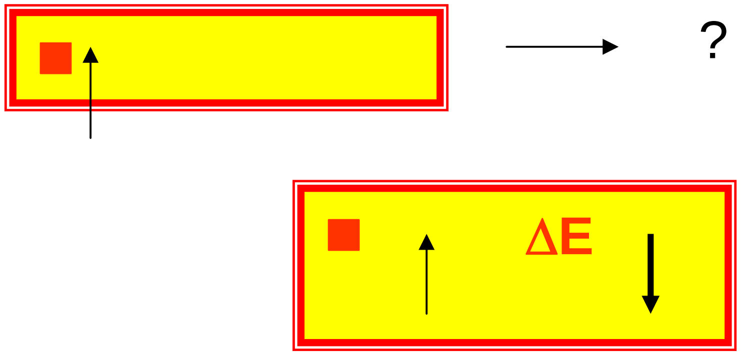
Huckel의 근사치

$$E_r = \alpha + 2\beta \cos\frac{r\pi}{2n+1}$$

α= coulomb integral

β= resonance integral

$$\Delta E = E_{n+1} - E_n$$
$$= -4\beta \sin\frac{\pi}{4n+2}$$



(n,π*) 와 (π, π*)의 비교

	(n,π*)	(π, π*)
• λ	200~600nm	100 ~ 1000nm
• ε_{max}	10~ 1000	1000 ~ 10^5 (전이 잘 일어남)
• Polarization	out-of- plane (in-plane도 있다. vibronic coupling인 경우)	in-plane
• Vibrational stretching	C=O, C=N, C=S등 (용액에서는 잘 안보임)	C-C, C-H 등
• Solvent Effects	polarity 🕒 -> blue shift protonation -> disappear	polarity 🕒 -> red shift no protonation effects
• Conjugation	small red shift	large red shift

(n,π*) 와 (π, π*)의 비교

	(n,π*)	(π, π*)
• τ_F^0	10^{-7} ~10^{-5} sec	10^{-9} sec (transition쉽다)
• Φ_F	0	0 ~ 1 (형광이 강한 편이다)
• τ_P^0	0.01sec (잘일어남)	1 ~10 sec (allowed 아님).
• Φ_P	0.05 ~ 1	0 ~ 0.05
• Heavy atom effects	negative	large positive effects (spin-orbit coupling)
• μ^*	smaller than ground s.	Larger
• photoreactions	H-atom abstraction	isomerization rearrangement, condensation
ΔE_{ST} • (Singlet-triplet energy difference)	small (<10kcal/mol)	large (>20kcal/mol)

Quantum Yields

$$\Phi_{product} = \frac{\#\text{ of moles of product formed}}{\#\text{ of einstein(photon) of radiation absorbed}}$$

Chemical reaction인 경우 Φ>1 일 수 있으나,

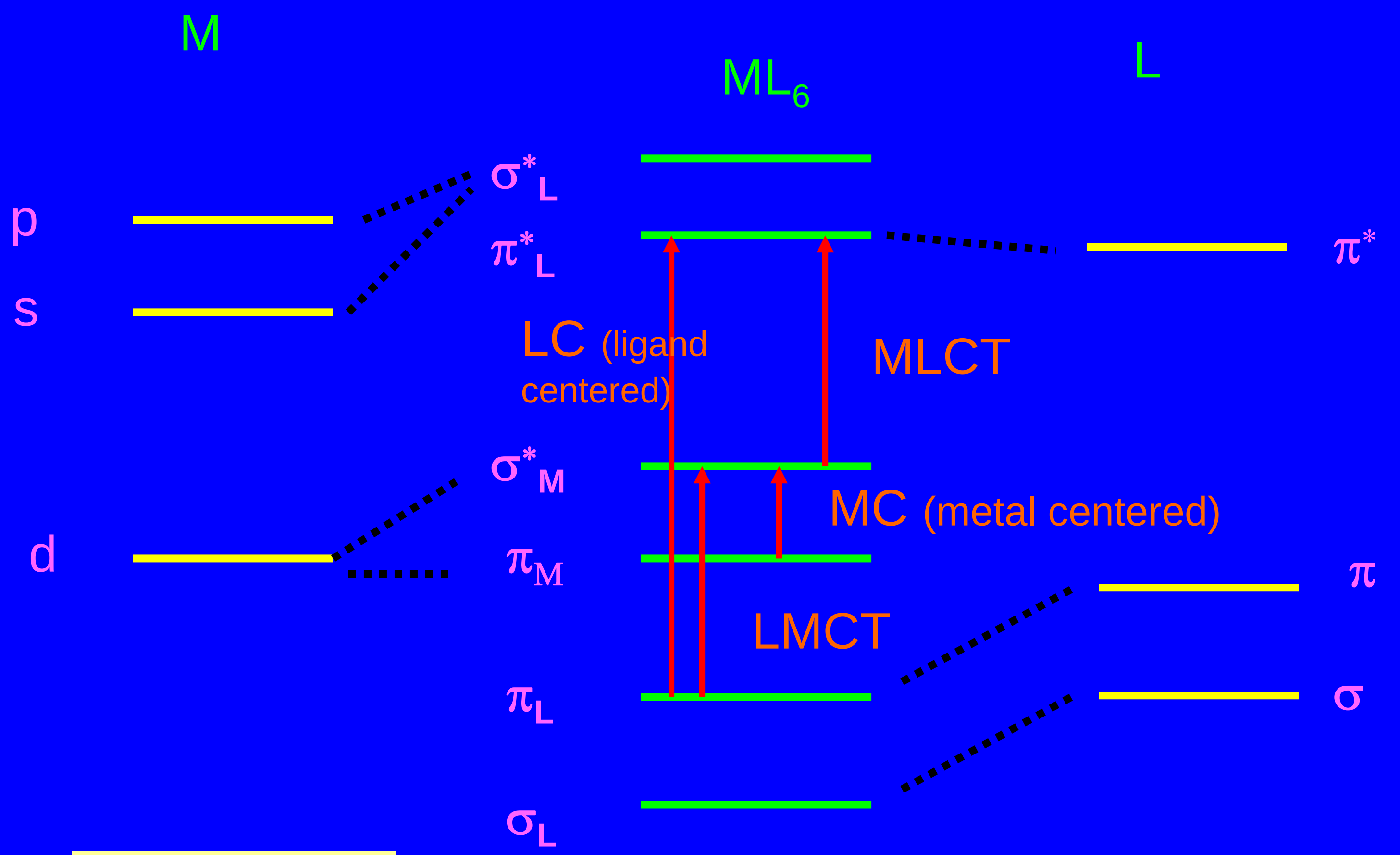
대부분 Φ<1

문? 어떤 경우에 Φ>1 일 수 있겠는가?

Photo-initiated radical chain reaction,

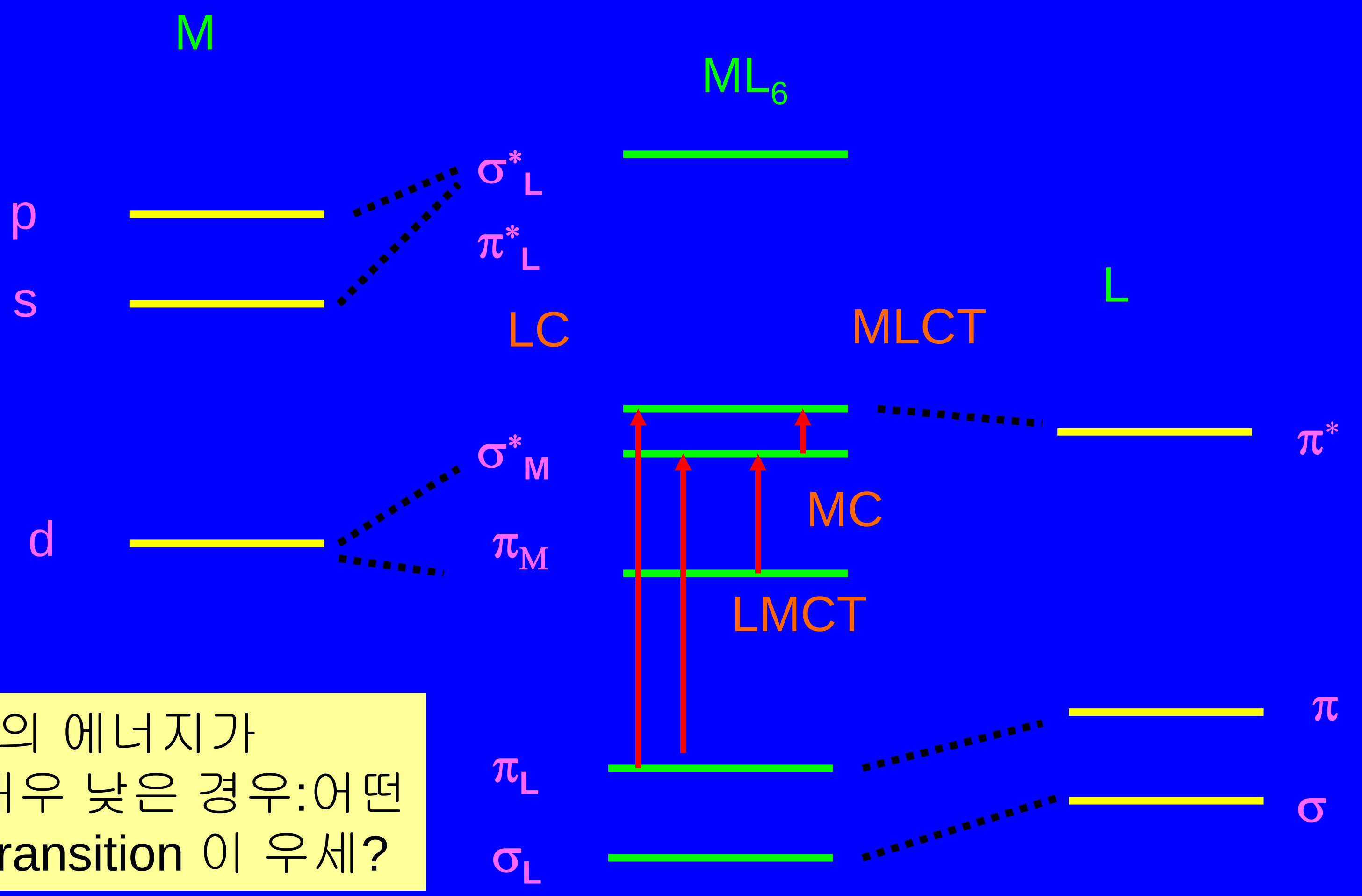
photo-dissociation to form two identical products.

Transitions in metal complexes



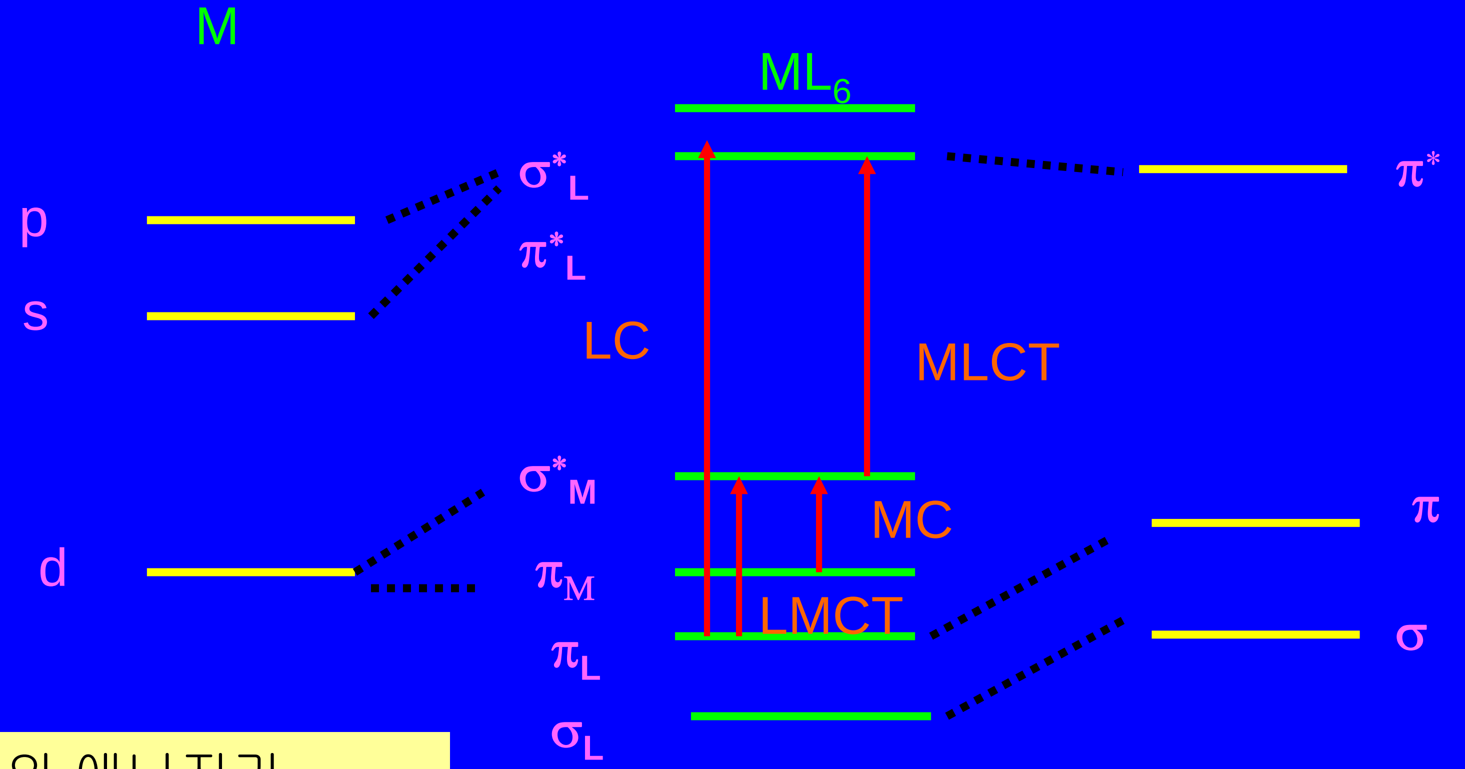
$MC(t_{2g} \rightarrow e_g)$

Transitions in metal complexes – extreme case



L의 에너지가
매우 낮은 경우:어떤
transition 이 우세?

Transitions in metal complexes



L의 에너지가 매우높은 경우:어떤 transition 이 우세?