Photochemistry

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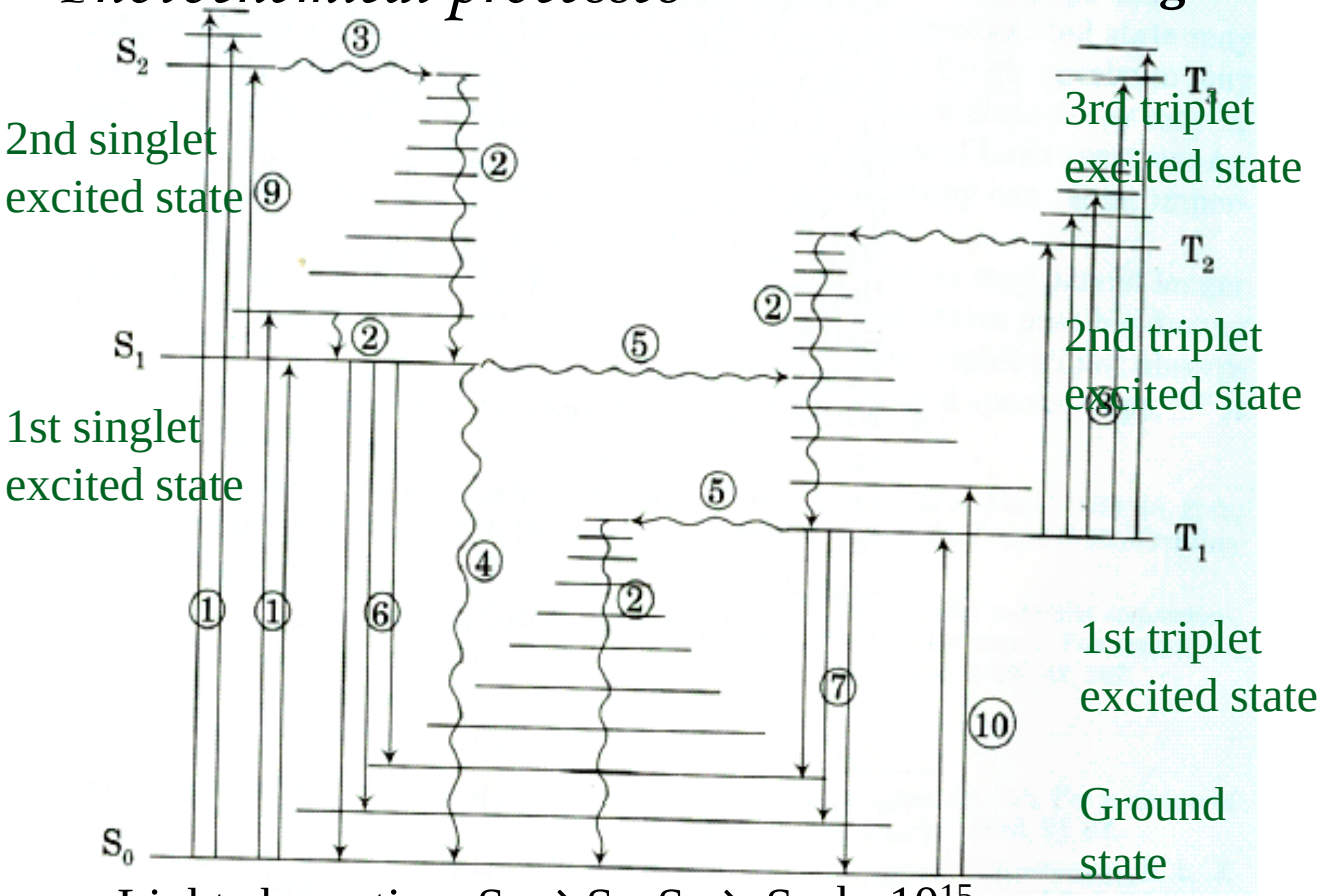
Photochemistry

Photochemical processes

Jablonski diagram



1. Light absorption: $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$ $k \sim 10^{15}$
2. Vibrational Relaxation: $k \sim 10^{12}$/s, from high ν to low ν
3. Internal Conversion: to lower electronic state of same multiplicity ($k > 10^{10}$/s)
4. Radiationless Decay: $S_1 \rightarrow S_0$, no emission, $k < 10^6$/s
5. Intersystem Crossing: $k \approx 10^6 \sim 10^{10}$ /s, depends on molecules. (carbonyl fast; alkene slow)
6. Fluorescence: $S_1 \rightarrow S_0$, with emission. $k \approx 10^6 - 10^9$.
7. Phosphorescene: $T_1 \rightarrow S_0$ with emission. $k \approx 10^{-2} - 10^4$
8. Triplet – Triplet Absorption
9. Singlet – Singlet Absorption
10. Singlet – Triplet Absorption

Photophysical Processes

- S_0(ground st.) of $H_2C{=}O$:

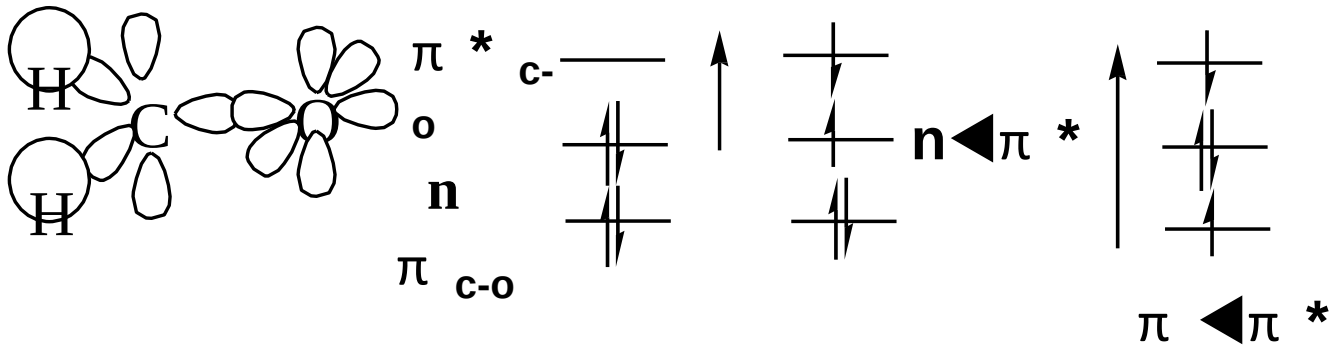
– $[(1S_O)^2(1S_C)^2(2S_O)^2(\sigma_{C\text{-}H})^2\,(\sigma'_{C\text{-}H})^2\,(\sigma_{C\text{-}O})^2](\pi_{C\text{-}O})^2\,(n_O)^2$

- S_1(1st exc.state):

– $[(1S_O)^2(1S_C)^2(2S_O)^2(\sigma_{C\text{-}H})^2\,(\sigma'_{C\text{-}H})^2\,(\sigma_{C\text{-}O})^2](\pi_{C\text{-}O})^2\,(n_O)(\pi^*_{C\text{-}O})$

- S_2(2nd exc.state):

– $[(1S_O)^2(1S_C)^2(2S_O)^2(\sigma_{C\text{-}H})^2\,(\sigma'_{C\text{-}H})^2\,(\sigma_{C\text{-}O})^2](\pi_{C\text{-}O})\,(n_O)^2(\pi^*_{C\text{-}O})$



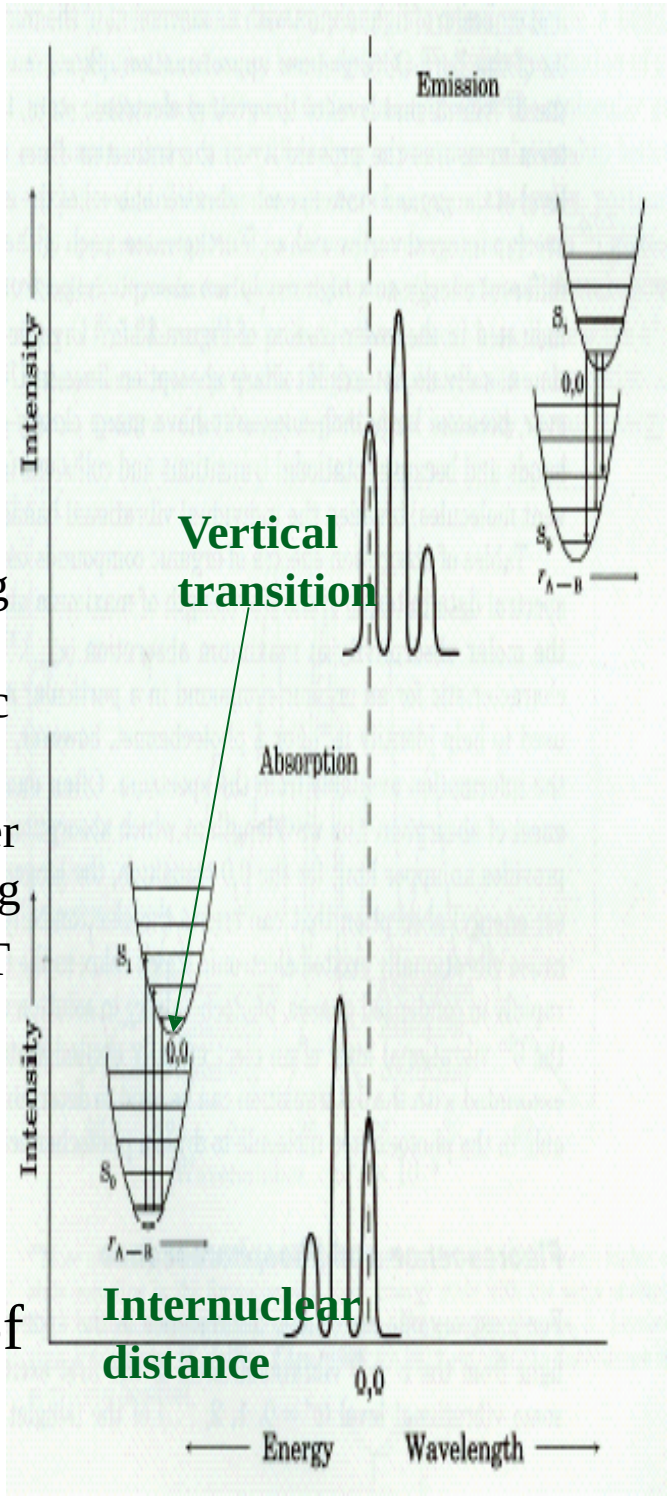
UV Absorption and Emission

- Factors determining radiative transition:
  1. Symmetry of electronic state (ini. final state)
  2. Multiplicity of the spin

❷Spin-orbit interaction (allows different spin transition mixing due to the mixing of magnetic moment of e^- and the magnetic moment of the nucleus)

- ◆Heavy atom effect: higher rate of intersystem crossing
- ◆Greater mixing if S and T are closer in energy, example carbonyl cpds.

3. Frank-Condon term, determined by overlap of nuclear coordinate of init. and final state



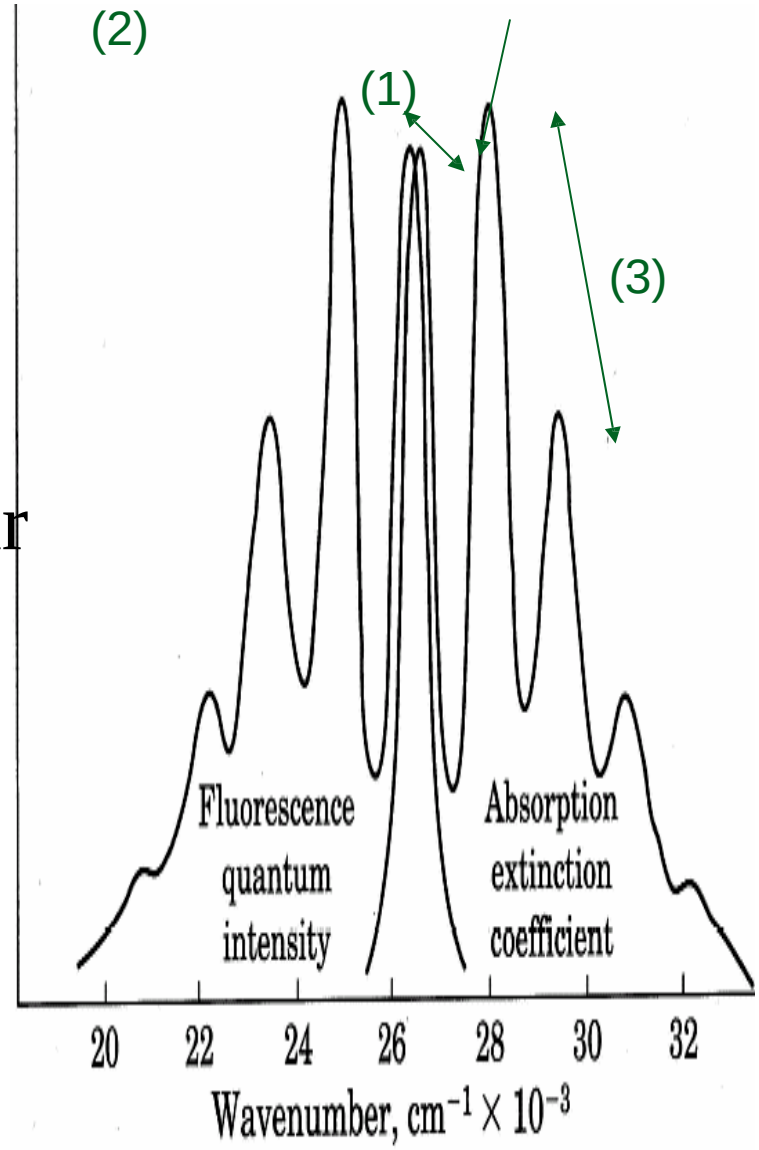
Frank-Condon Principle

- At the instant of excitation, only electrons are reorganized, the heavier nuclei retain the ground state geometry
- The excited state has similar molecular geometry as ground state

(1): Vib. energy diff. of S_0

(2): (0,0) transition

(3): Vib energy diff. of S_1



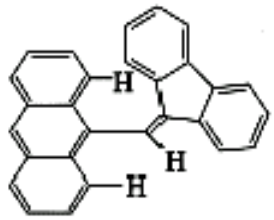
Anthrcene

Fluorescence

- The excited state

  geometry quite different from ground state geometry => large Stokes shift

  (anti-Stokes shift: the fluorescence is at shorter wavelength)



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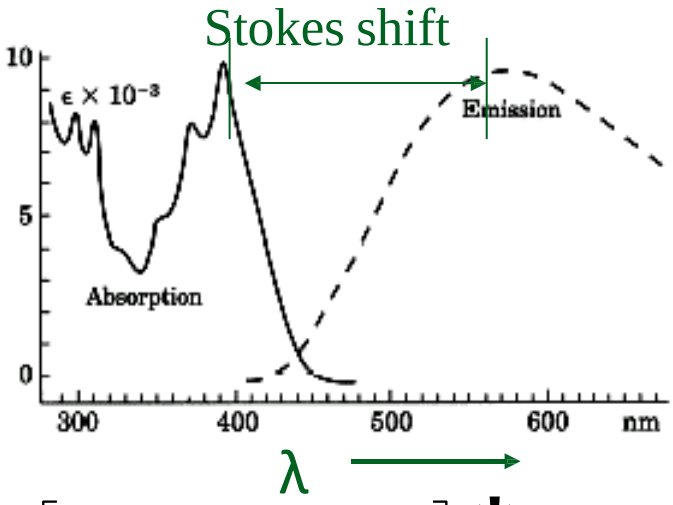
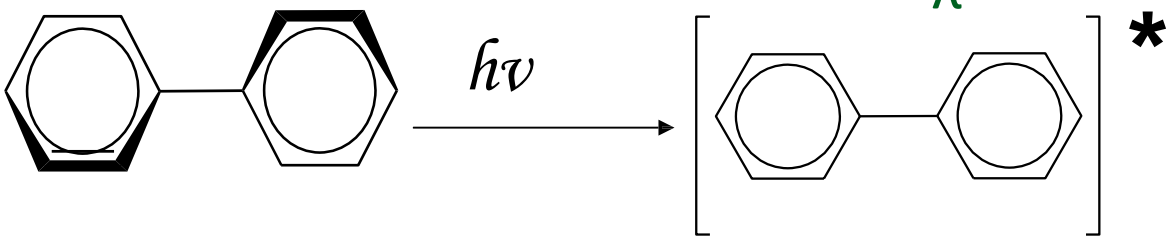
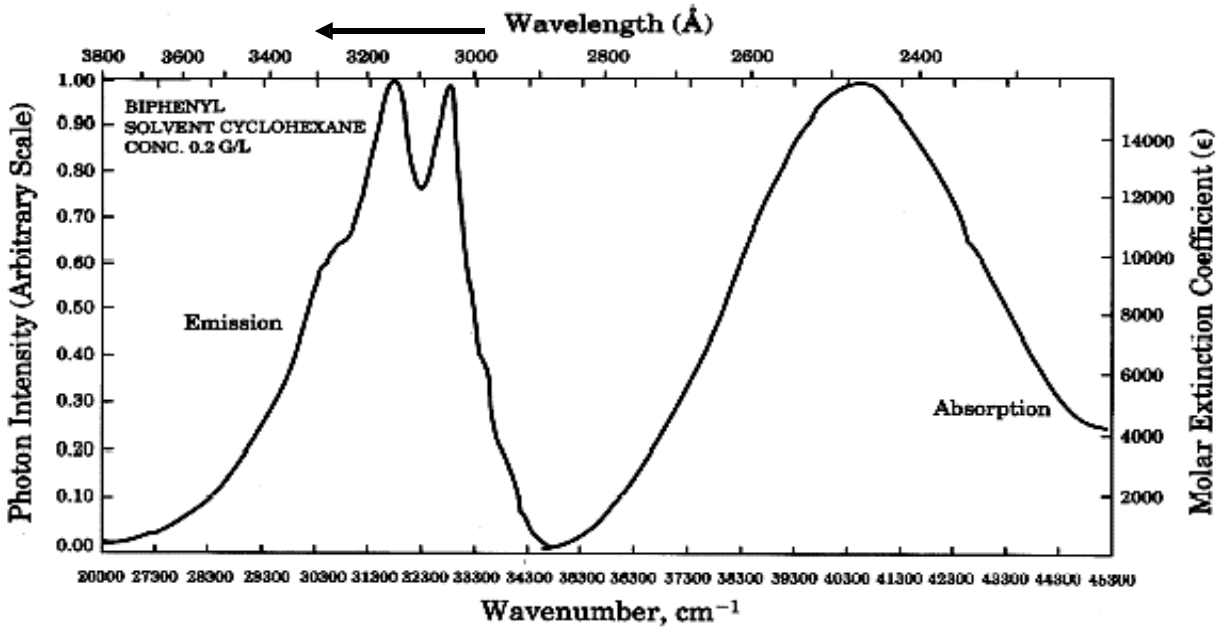




planar geometry



Measurement of Absorption

- Beer-Lambert Law: $\log \frac{I_o}{I_t} = \epsilon c\, d$

  =A (absorbance) I_0: incident light

  I_t: transmitted light

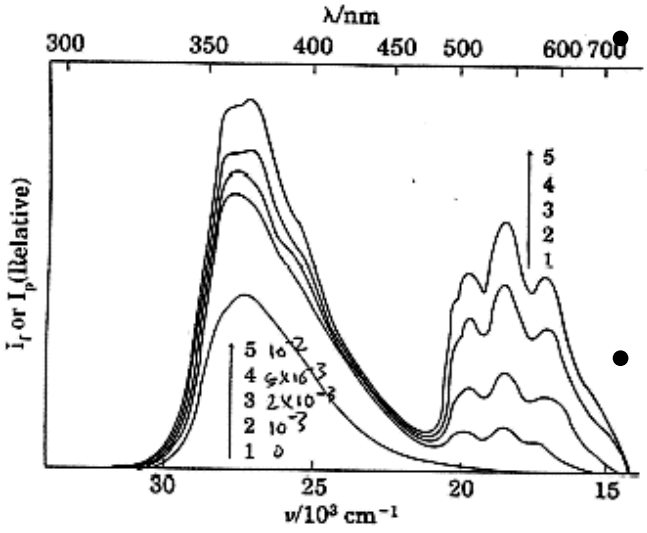
  ϵ: extinction coefficient c: concentration

  d: light path length

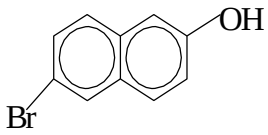
  •Quantum yield of emission:

$$\Phi_f = \frac{\#\ of\ \ photon\ emitted\ \ from\ S_1}{\#\ of\ \ photon\ absorbed}$$

Phosphorescence

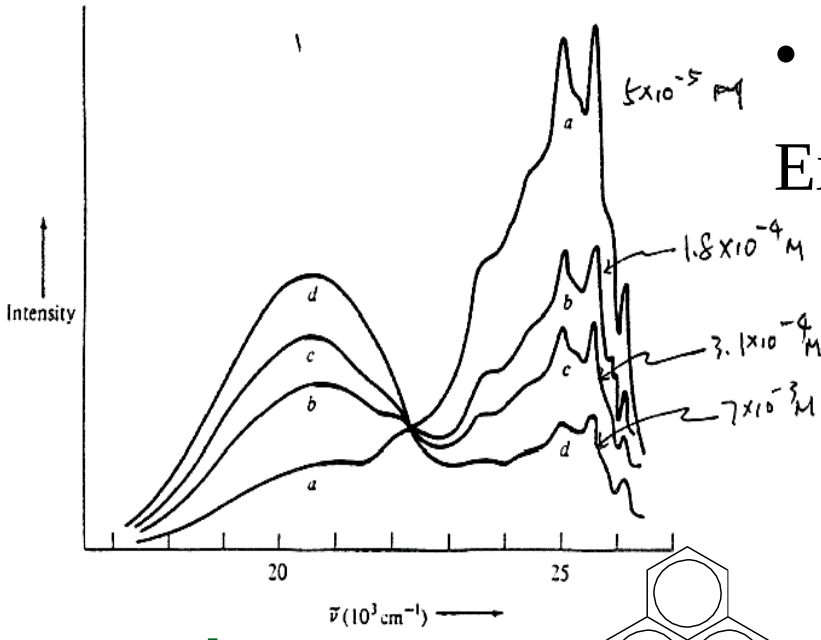


- Much reduced due to diffusional quenching with ground state species or O_2
- Observed in fixed matrix, such as liquid N2 temperature or surrounded by a host



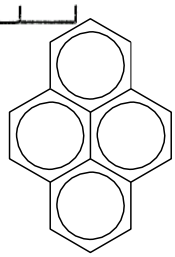
In aqueous solution with α -CD

Concentration –Dependent Fluorescence



- Excimer formation

Excimer: A complex formed between an excited molecule with a ground state molecule of same compound

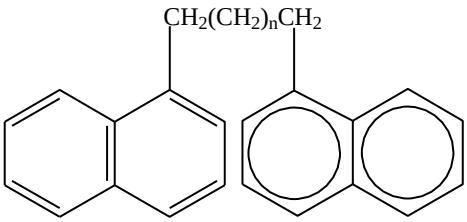


In heptane

A*A ⟶ AA*

Geometric Requirement of Excimer Formation

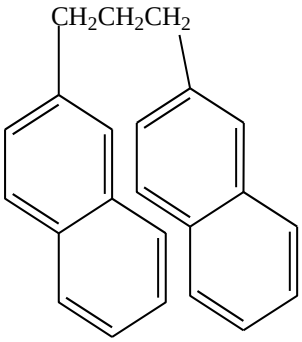
- The molecular plane can stack together with interplanar distance less than 3.5 Å.



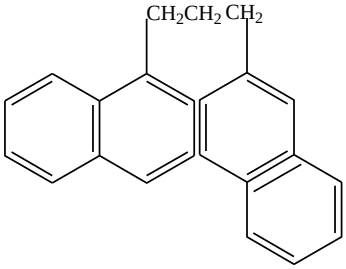
n=0 no overlap of ring

n=1 excimer formation

n=2 strain of chain

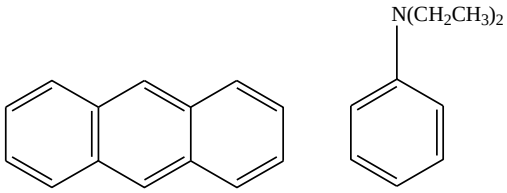


Excimer formation

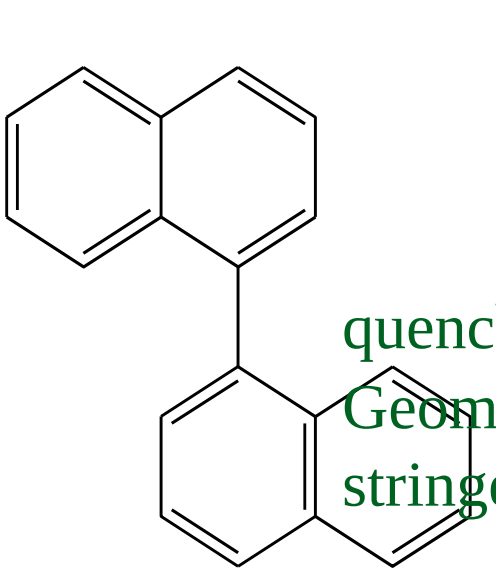


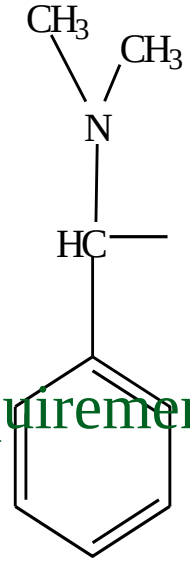
Partial overlap of ring plane

- Exciplex: complex formed between an excited molecule with a ground state molecule of dissimilar molecule
- A*B ⟷ AB* can give exciplex emission or quench emission



aromatics / amine
aromatics/conjugate olefin





Fluorescence quencher

quench by
Geometric requirement less stringent

Energy Transfer and Electron Transfer

- Pathways $\mathcal{D}^{\star}+\mathcal{A} \rightarrow \mathcal{D}+\mathcal{A}^{\star}$

1) Radiative energy transfer

♋ D* →D+ $h\nu$

♋ A+$h\nu$ →A* The rate depends on

♍ The quantum yield of emission by D* (Φ^{D}_{e})

♎ The concentration of (the # of) A in light path

♏ The light absorbing ability of A (extinction coefficient)

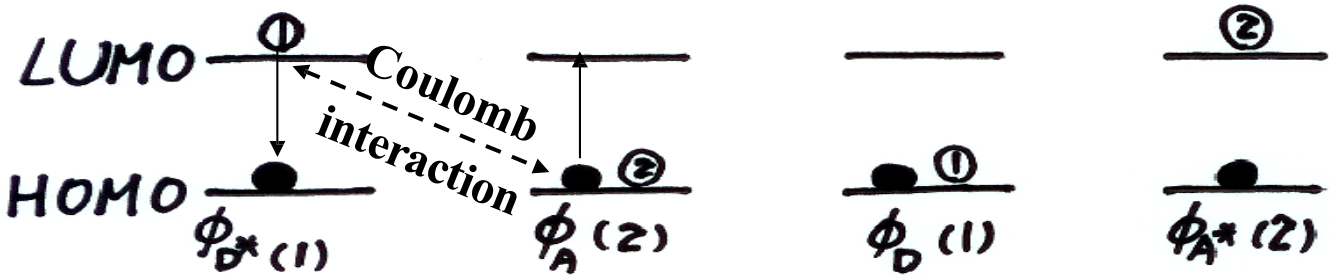
♐ The overlap of emission spectrum of D* and absorption of A (spectral overlap integral)

2) Förster energy transfer

–Long range (D*-A distance up to 100 Å)

–No radiation involved

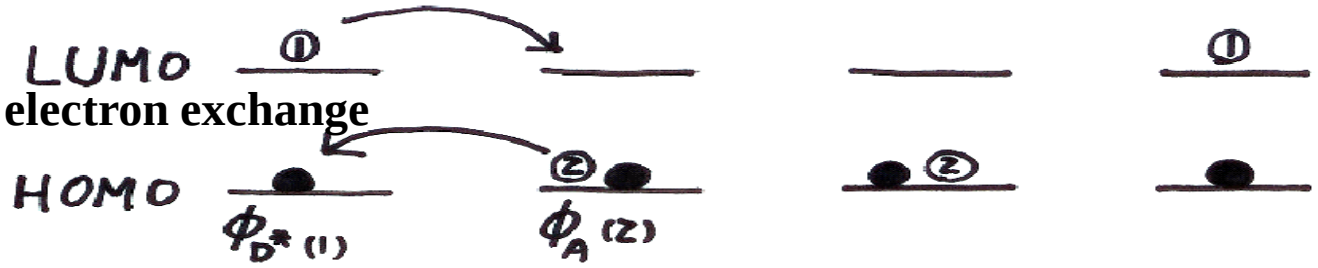
–The dipole-dipole interaction of D* and A



•An interaction at a distance via electromagnetic field, induce a dipole oscillation in A by D*.

•Efficient transfer requires a good overlap of emission of D* with absorption of A.

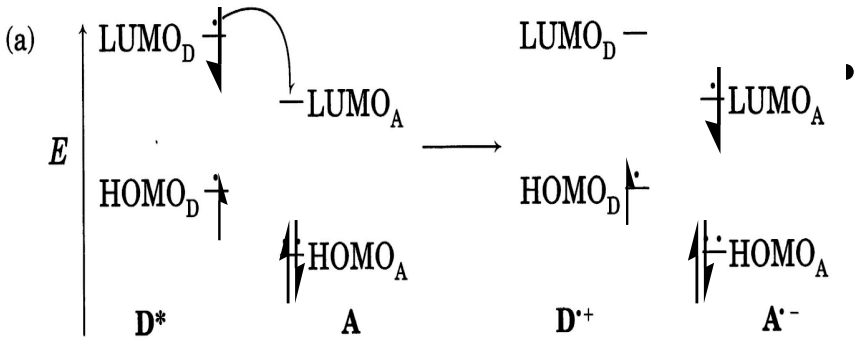
3) Collisional energy transfer (Dexter energy transfer): exchange of electron between the donor and acceptor

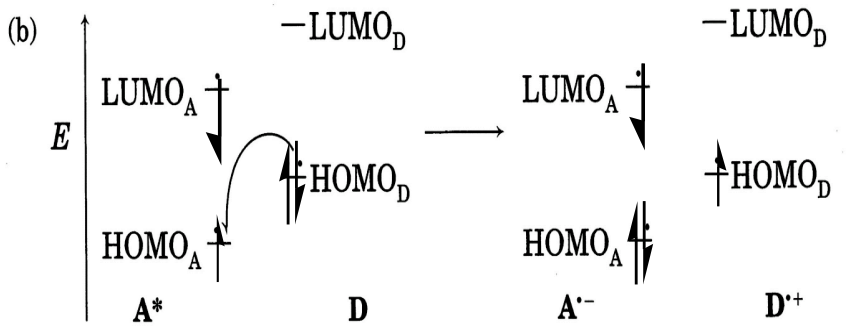


The exchange of electron via overlap of electron clouds require physical contact between the interacting partners.

- Spectral overlap integral also required
- This process allows triplet state to be generated
  $D^* + A_0 \rightarrow D_0 + A^*$
- A short-ranged interaction

Electron Transfer



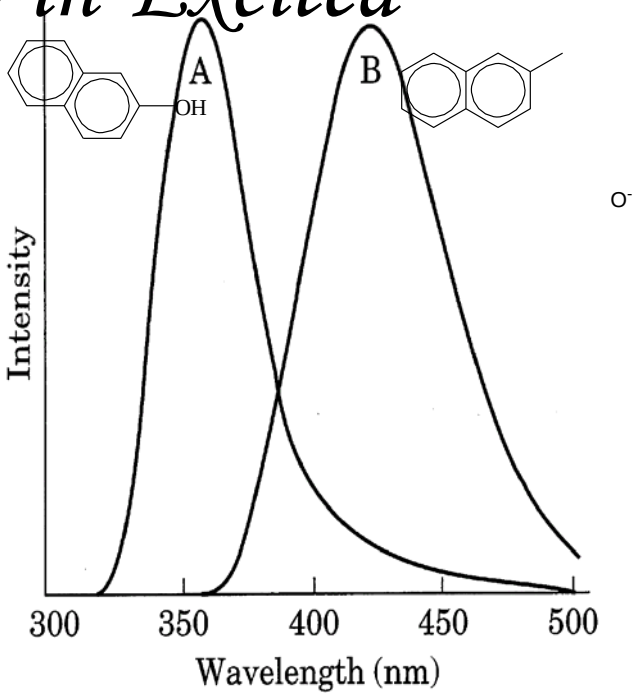


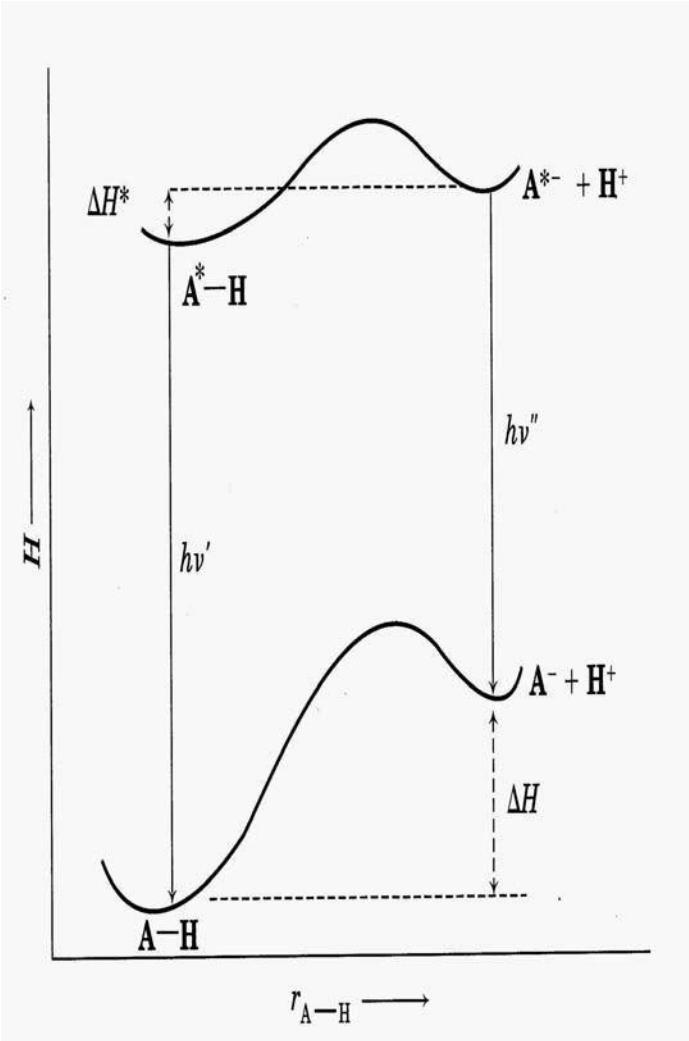
The photo excited state is a better donor (lower oxid. potential) as well as a better acceptor (lower reductive potential) relative to ground state

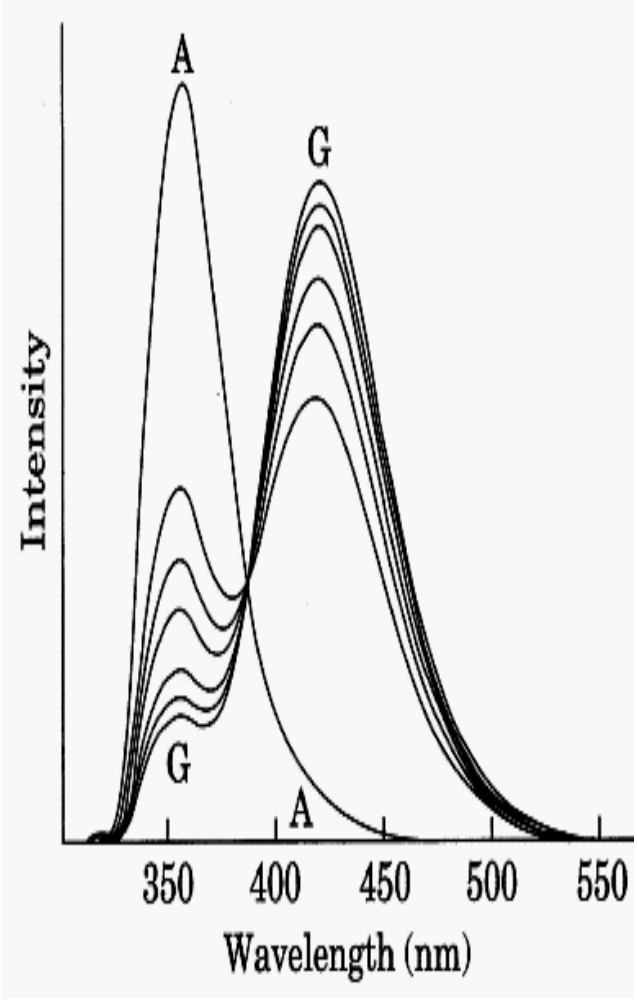
Acidity and Basicity in Excited States

- $A\text{-}H \rightleftharpoons A^- + H^+$
- $[A\text{-}H]^* \rightleftharpoons [A^-]^* + H^+$

($h\nu$ connects the ground-state pair to the excited-state pair)







- $\Delta H^* + h\nu' = \Delta H + h\nu''$

$\Delta H^* - \Delta H = +h\nu'' - h\nu' \approx \Delta G^* - \Delta G$

– (if $\Delta S^* \approx \Delta S$ for ionization)

– $\Delta G = 2.303RTpK$

– $pK^* - pK = \frac{\Delta G^* - \Delta G}{2.303RT} \approx \frac{h\nu'' - h\nu'}{2.303RT}$

Table 12.3 Acidity constants of ground and excited states. (Except as noted, data are from reference 80.)

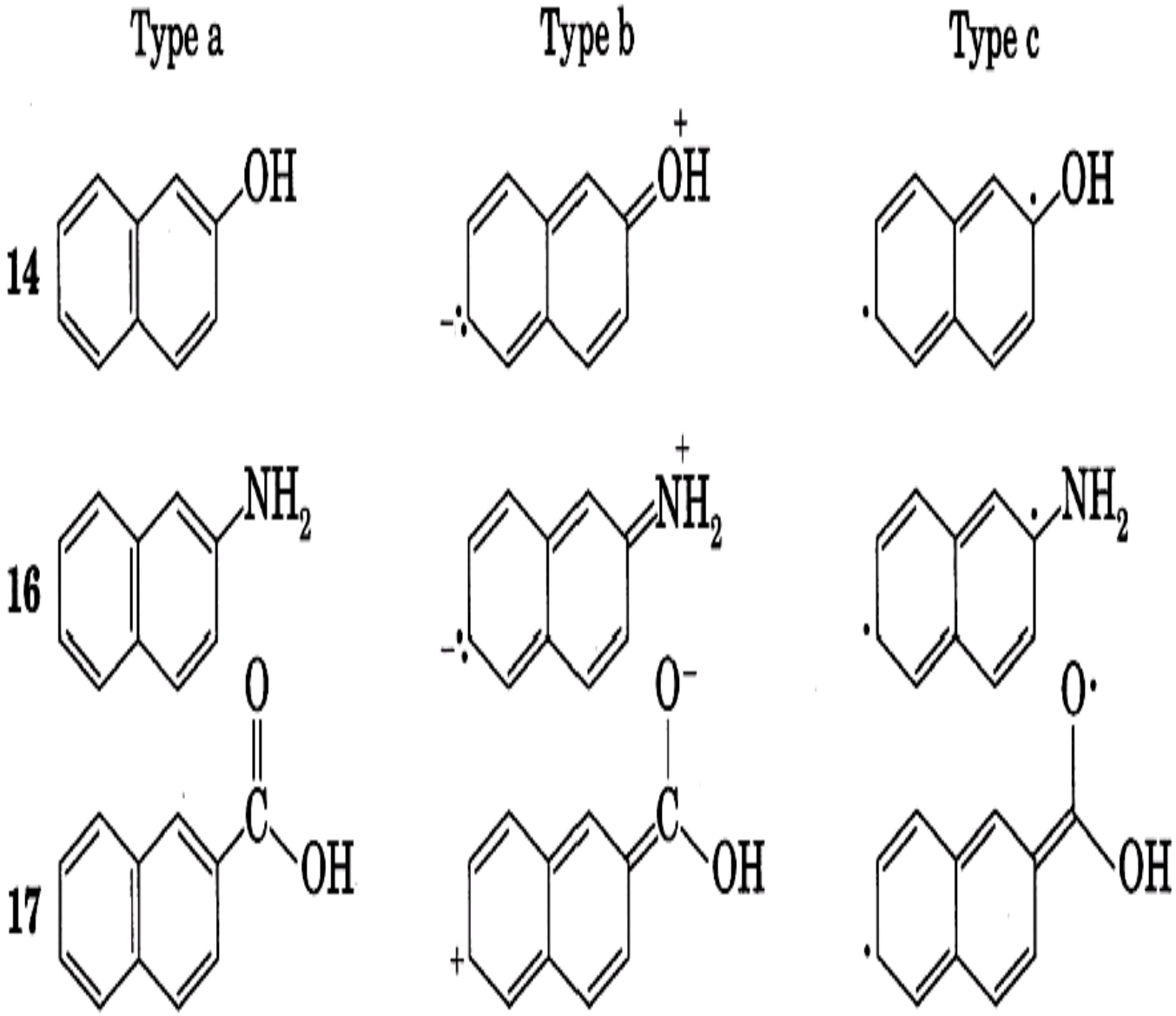
Compound	Reaction	p*K* (S_0)	p*K* (S_1)	p*K* (T_1)
Naphthalene[a]	protonation	−4.0	11.7	−2.5
2-Naphthol	deprotonation	9.5	(1) → 3.1	7.7 to 8.1
2-Naphthoic acid	deprotonation	4.2	(2) → 8.2[b]	4.0[c]
2-Naphthylamine	protonation	4.1	(3) → −2.0	3.1 to 3.3

[a]Vander Donckt, E.; Lietaer, D.; Nasielski, J. *Bull. soc. chim. Belges* **1970**, *79*, 283.
[b]Kovi, P. J.; Schulman, S. G. *Anal. Chim. Acta* **1973**, *63*, 39.
[c]Reference 81.

(1):more acidic

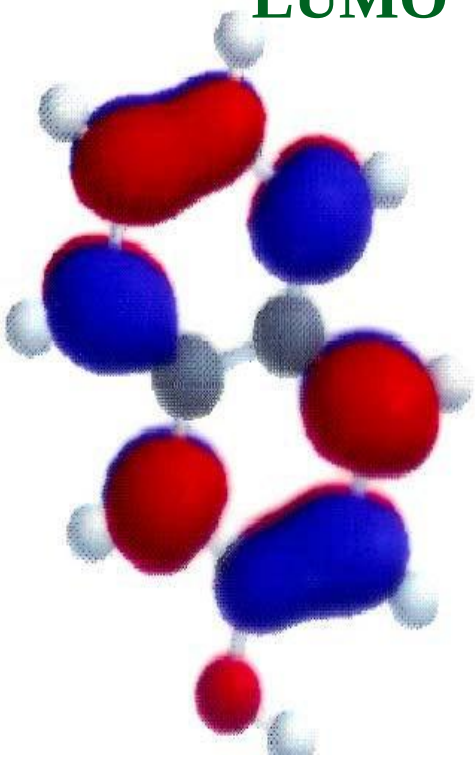
(2):less acidic

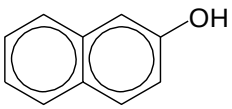
(3):more acidic



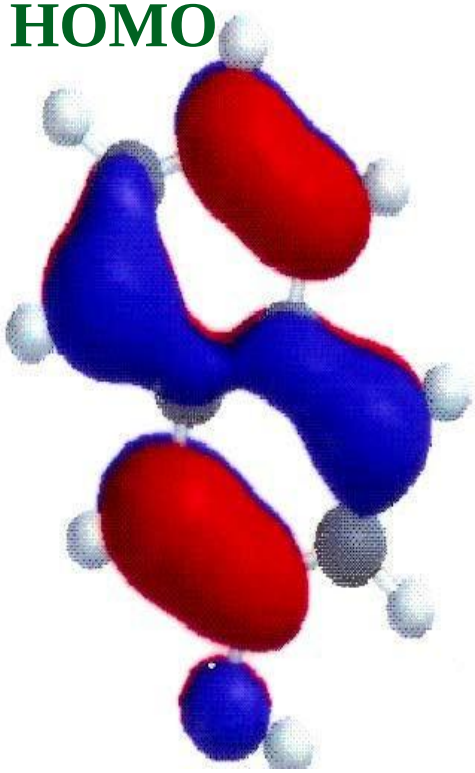
When photochem. excited, electron from HOMO ⟶ LUMO, and change the e^- density

LUMO

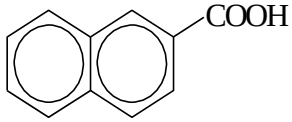




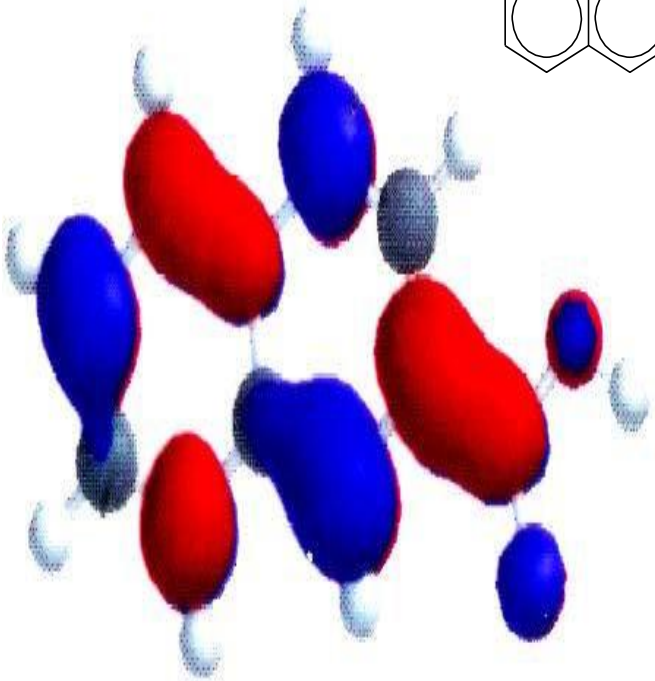
HOMO

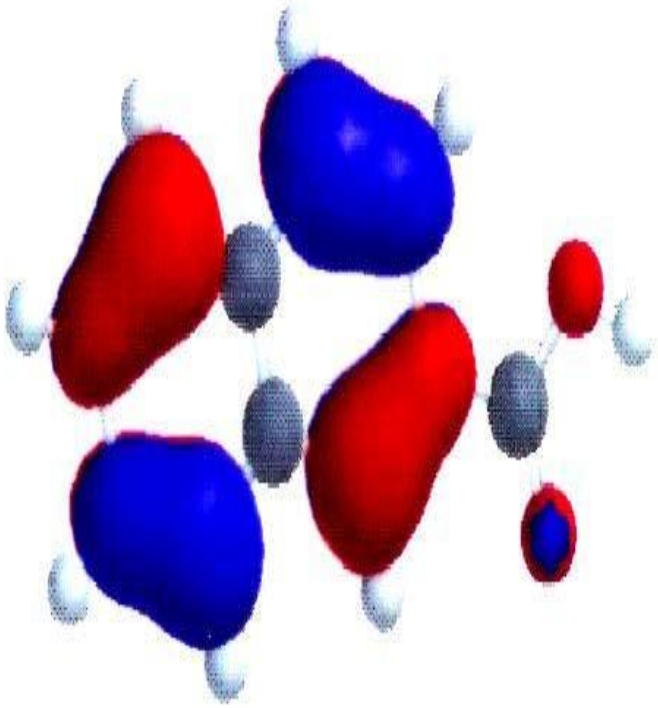


LUMO

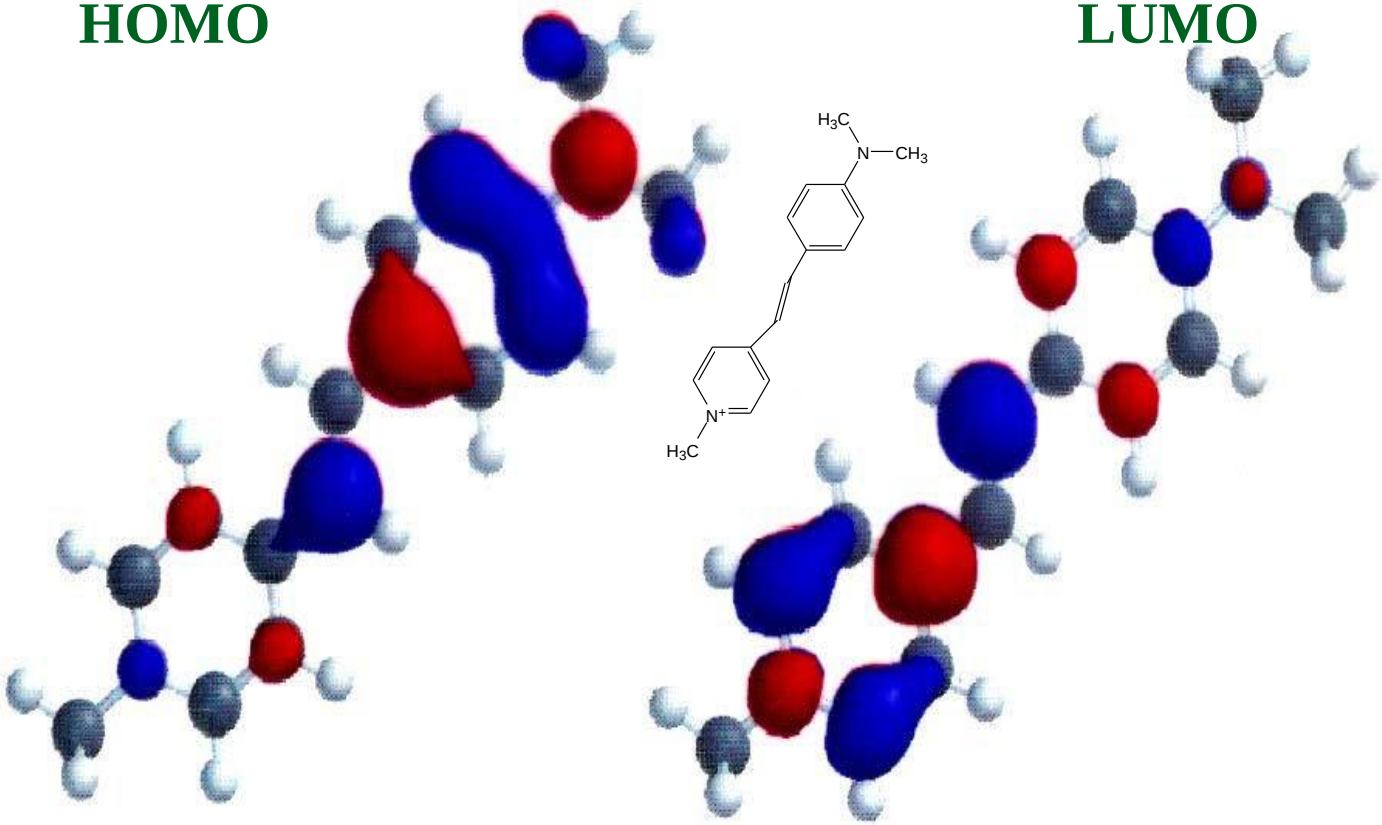


HOMO

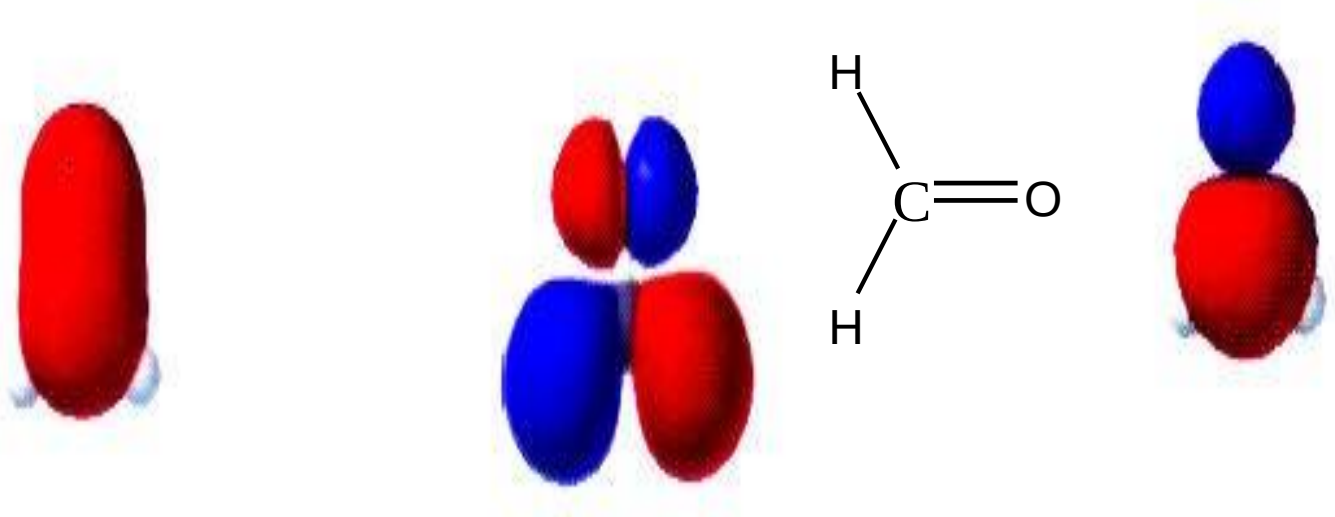




HOMO **LUMO**



π *n* π*



Bond angle, Dipole moments of Excited state

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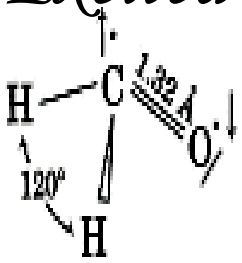
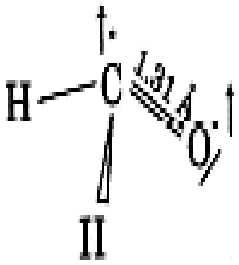


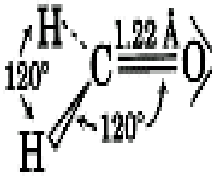
Table 12.4 Physical properties of formaldehyde excited states. (Data from references 89, 90, and 91.)

Property/State	S_0	S_1	T_1
Geometry	planar	pyramidal	pyramidal
Δ (nonplanarity)	0°	20°	35°
C=O length	1.22 Å	1.32 Å	1.31 Å
ν C=O stretch	1746 cm^{-1}	1182 cm^{-1}	1251 cm^{-1}
<HCH	120°	122°	
Dipole moment	2.3 D	1.5 D	1.3 D

S_1 $\mu = 1.5$ D, $E \cong 84$ kcal/mol^{-1}

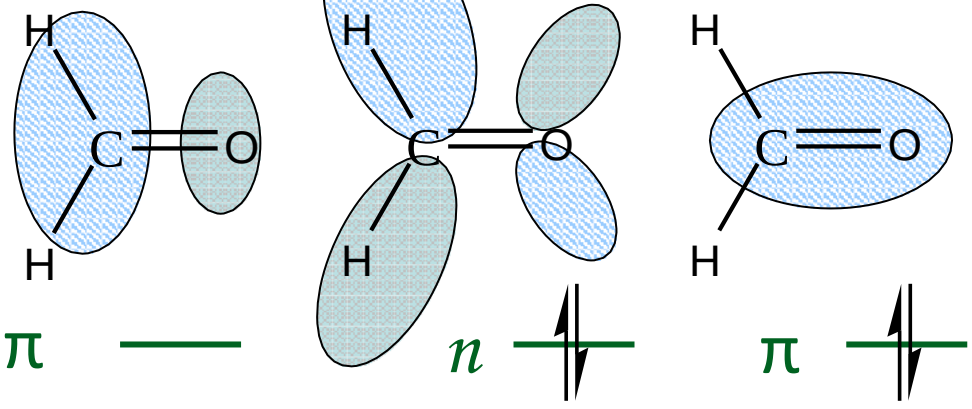


T_1 $\mu = 1.3$ D, $E \cong 76$ kcal/mol^{-1}

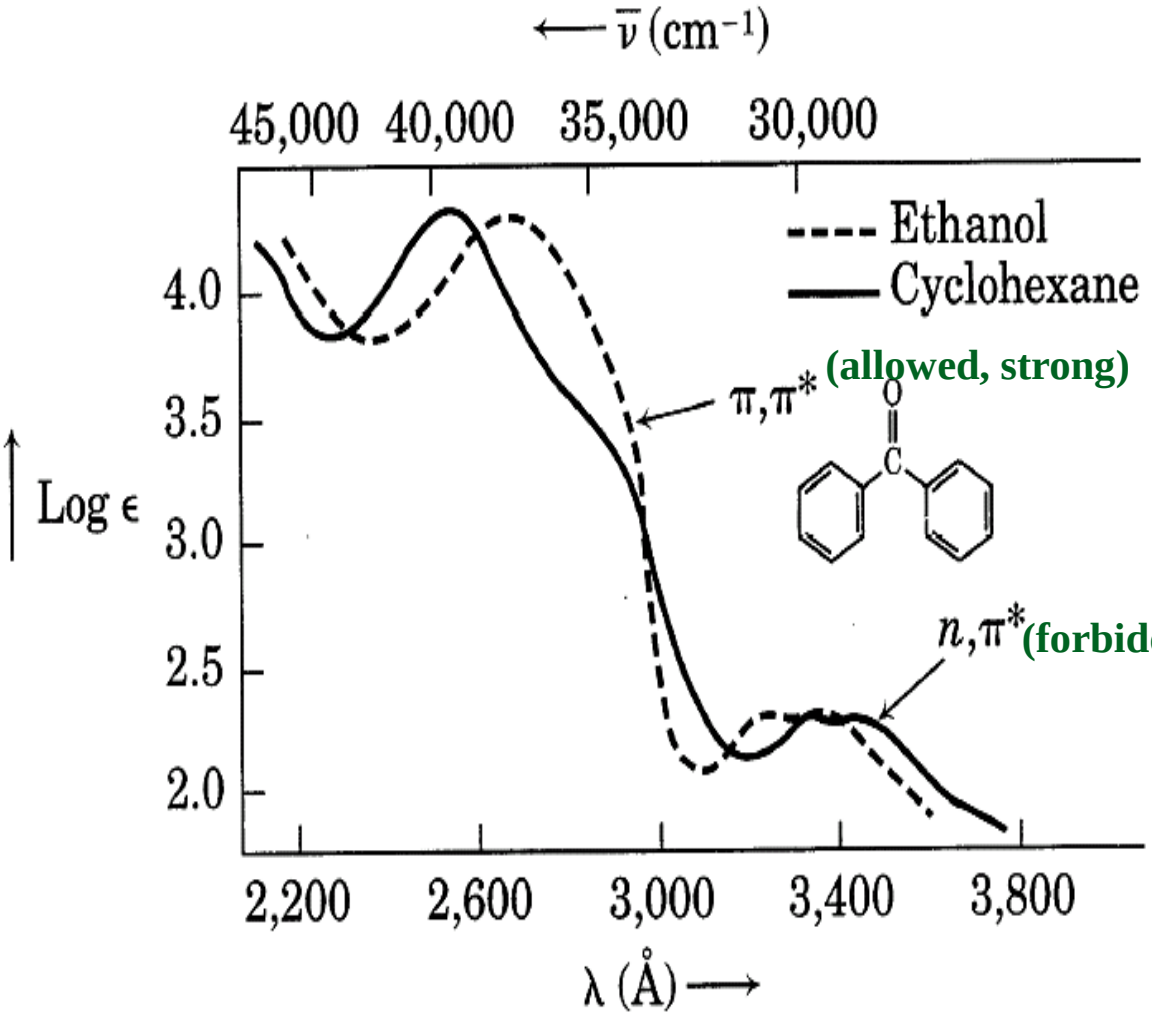


S_0 $\mu = 2.3$ D, $E \equiv 0$ kcal/mol^{-1}

LUMO **HOMO**

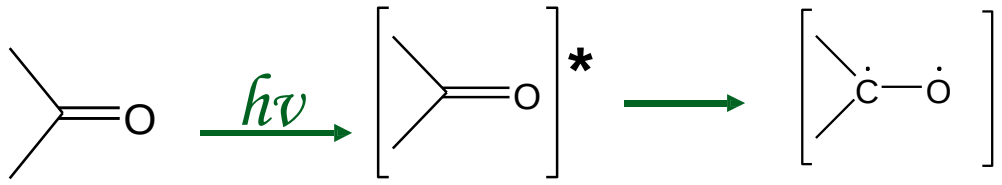


π* — *n* — π



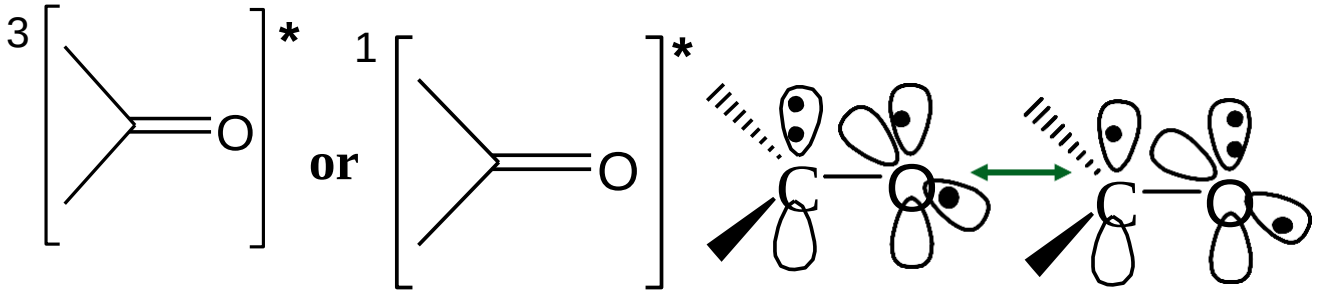
- $S_0 \rightarrow S_1$ (n-π*) excited state less polar than the ground state
  - hypsochromic (blue) shift with polar solvent
- $S_0 \rightarrow S_2$ (π- π*) excited state more polar than the ground state
  - bathochromic (red) shift with polar solvent

Photochemical Reactions of Carbonyl Compounds

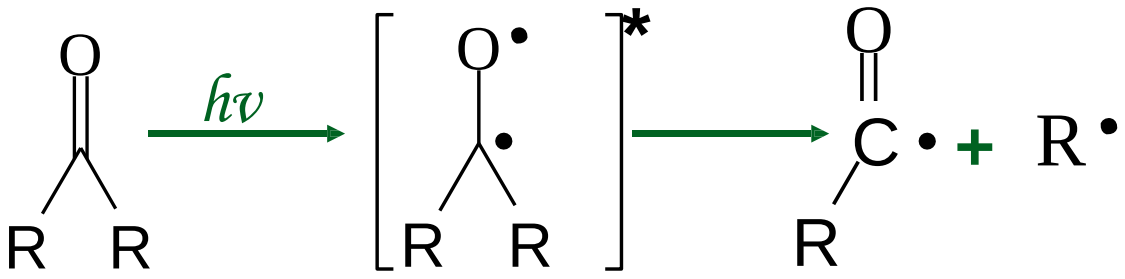


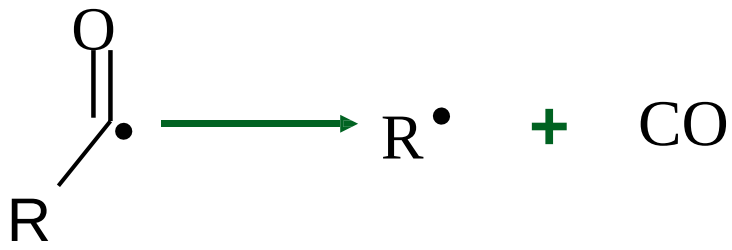
Sat'd Ketone

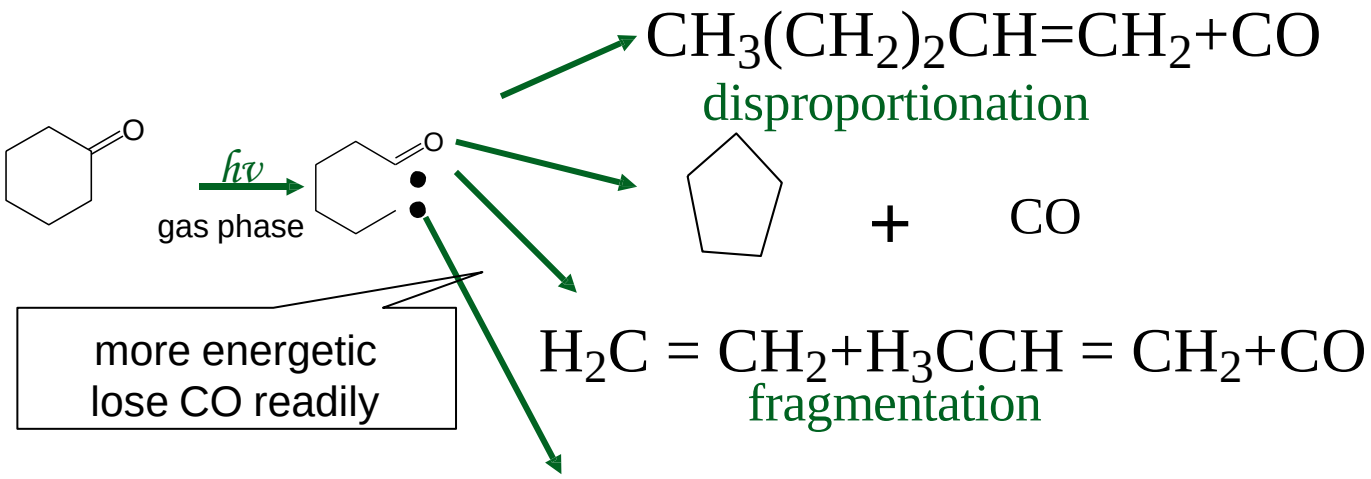
n → π *



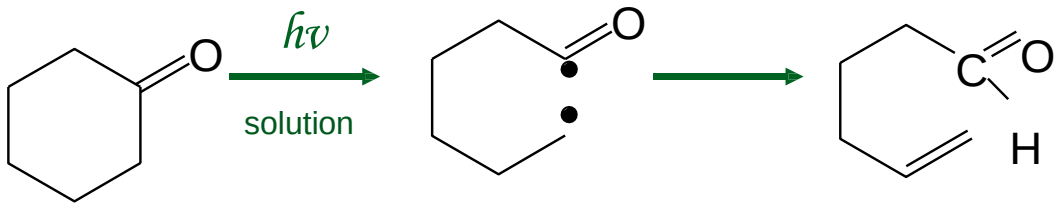
Norrish Type I Cleavage (α - cleavage)



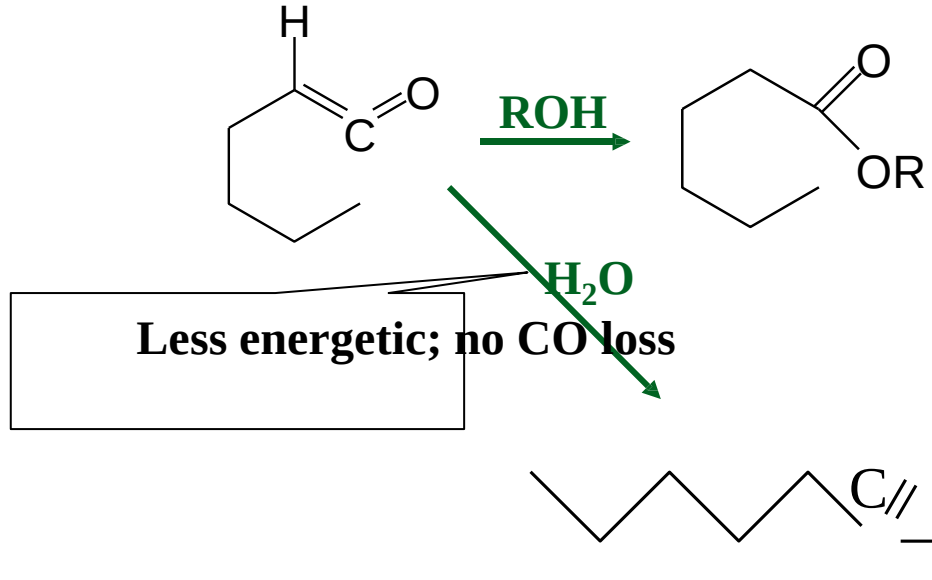




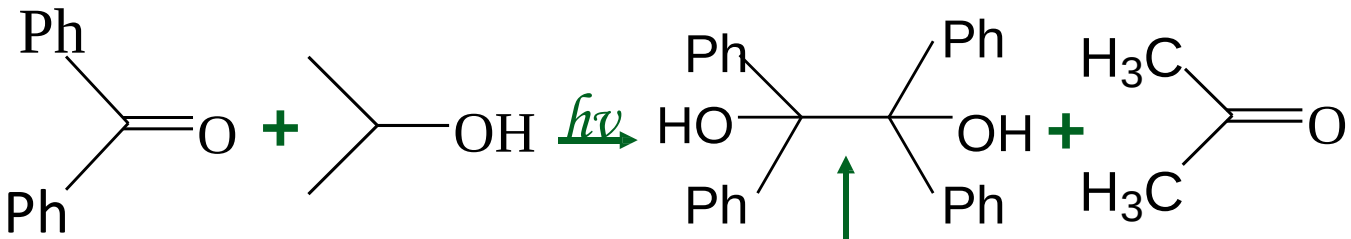
$S_1 \rightarrow T_1$ at vibrationally excited state of T_1



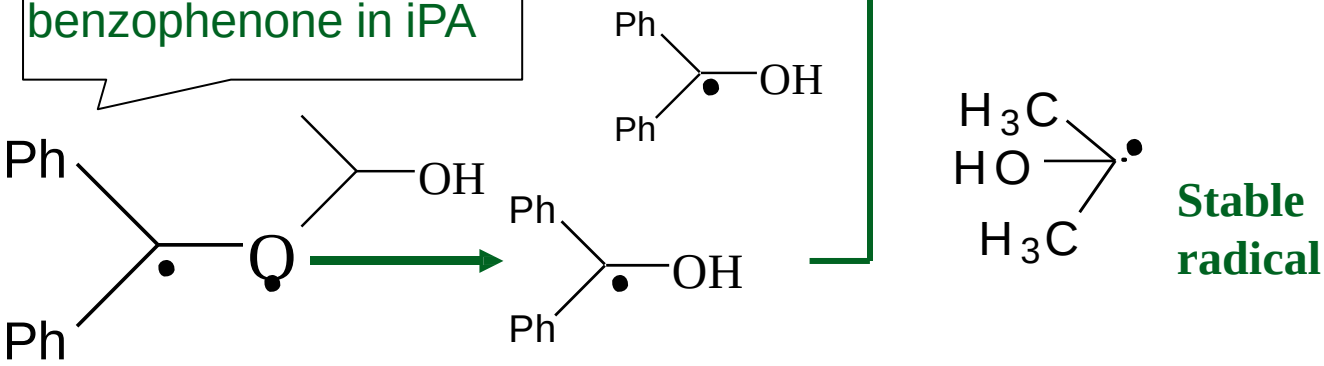
Ketene



Hydrogen Abstraction Reaction

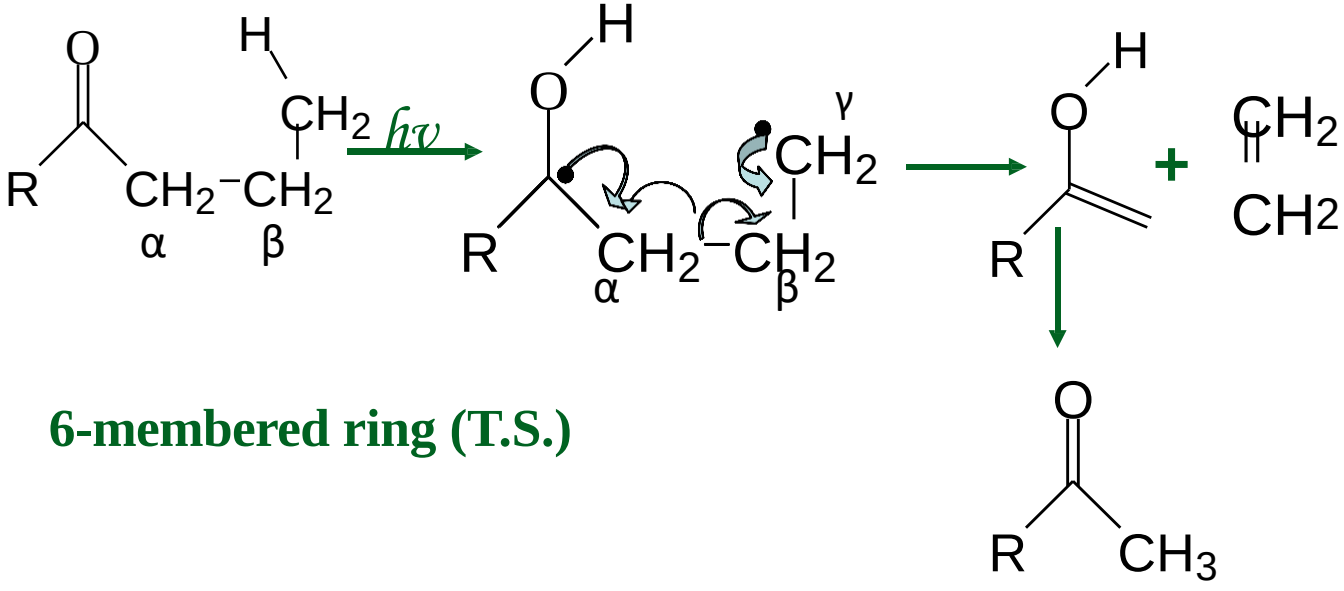


Photoreduction of benzophenone in iPA

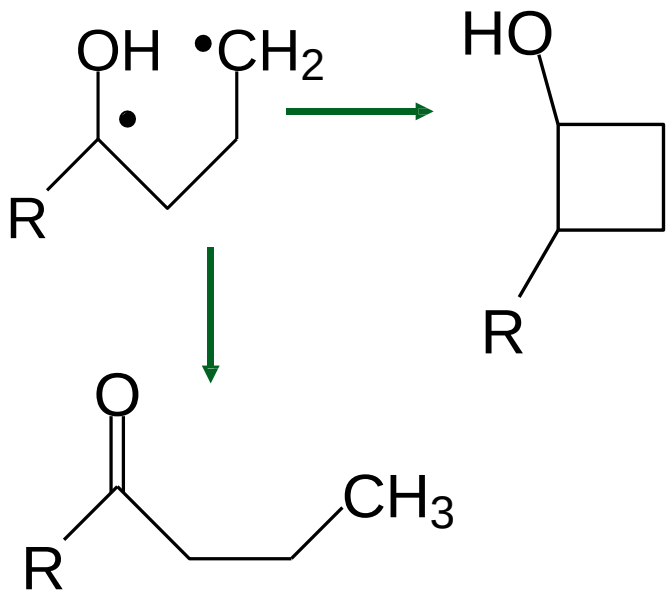


Stable radical

Norrish Type II Cleavage(β -Cleavage)

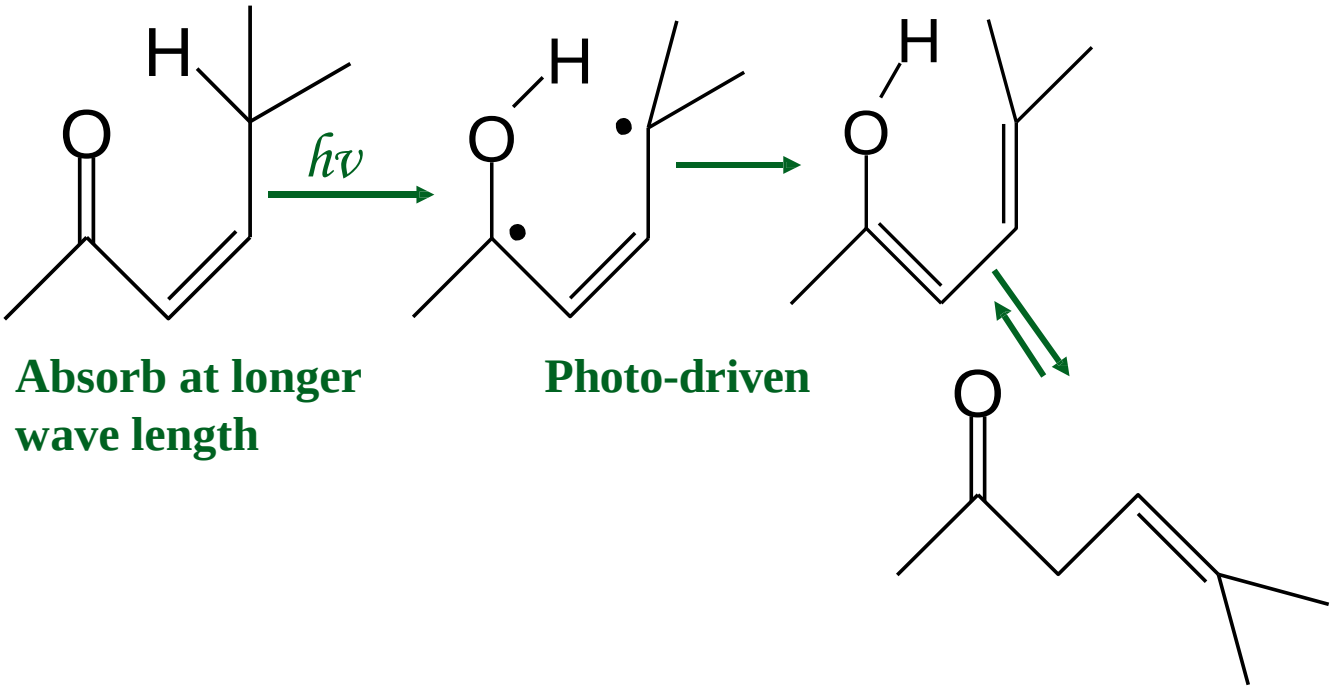


6-membered ring (T.S.)



If the S.M. is retrieved, the γcarbon may loose stereochem. (if chiral), so not exactly the same original S.M.

α -β unsaturated ketone

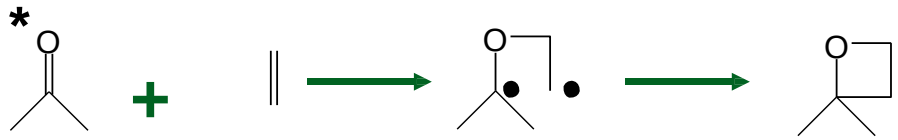


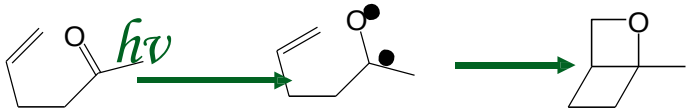
Absorb at longer wave length

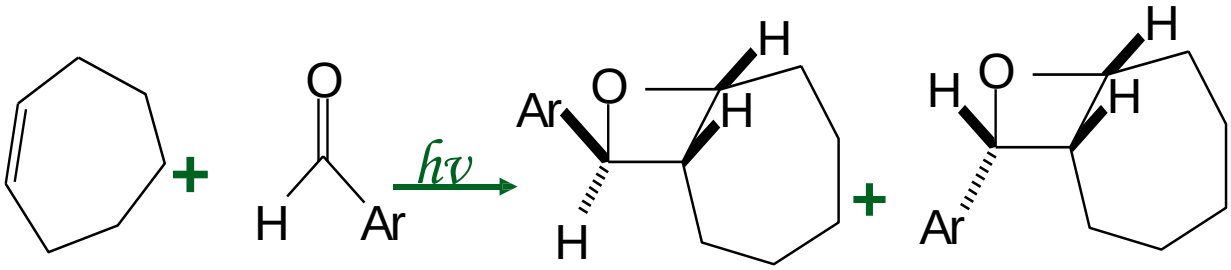
Photo-driven

De-conjugated absorb at shorter wave length

Oxetene Formation (Paterno-Buchi Reaction)

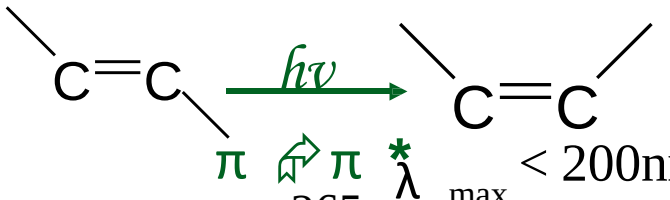




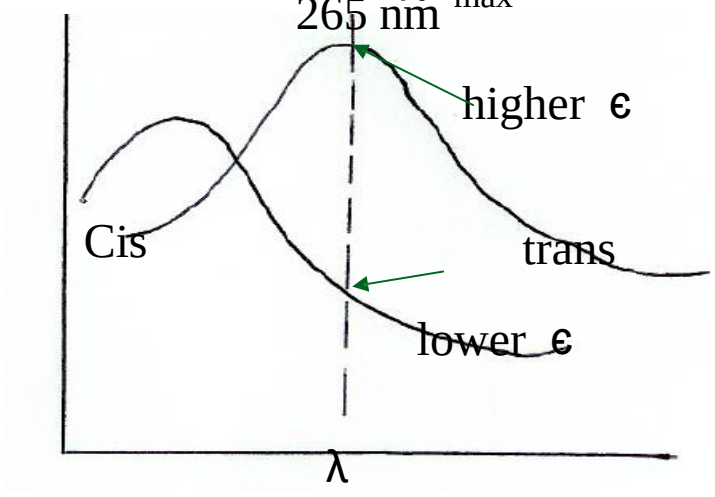


Photochemical Reactions of Alkene and Dienes

- Isomerization

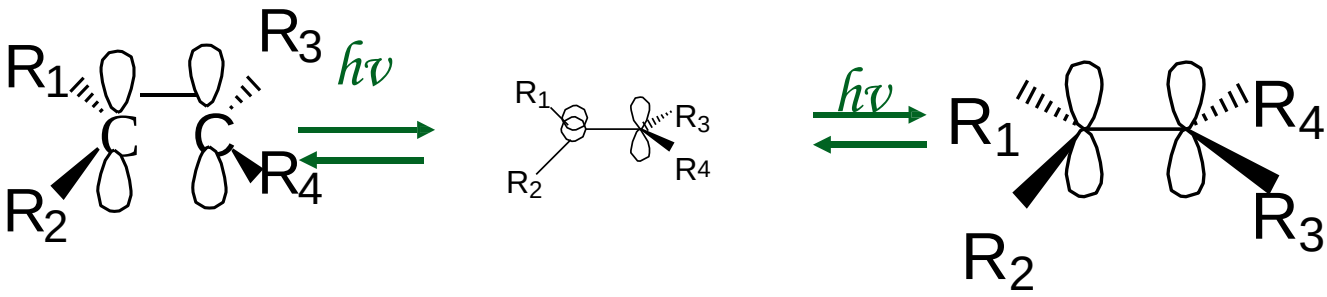


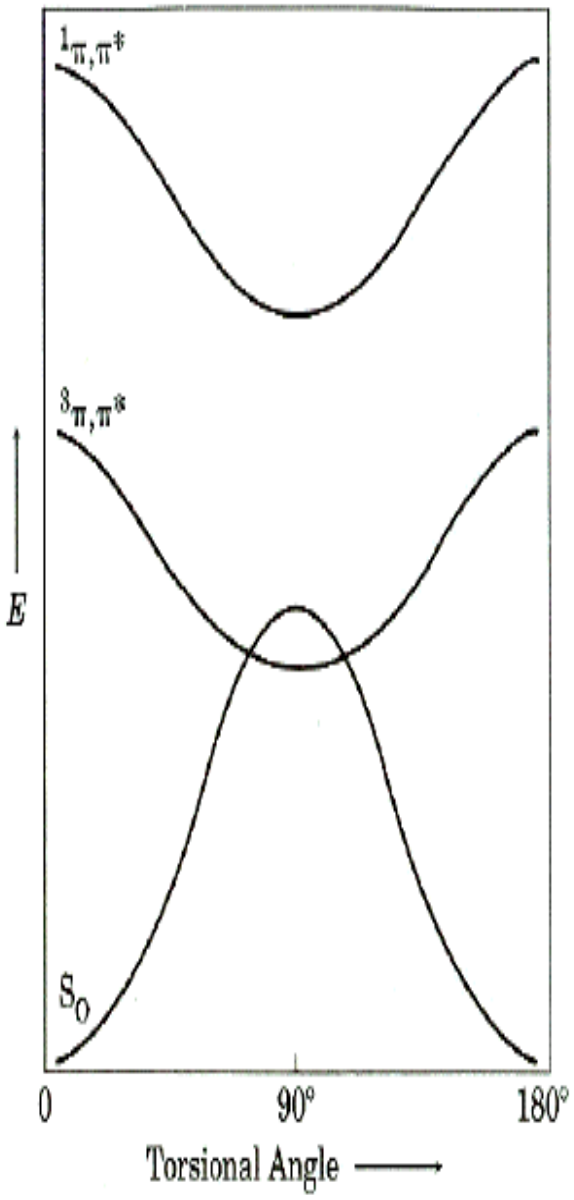
λ_{max} < 200nm



1. Trans compound has longer absorption wavelength
2. Both cis and trans give the same excited state species

=> twisted geometry with 90° rotation of p-orbital relative to each other





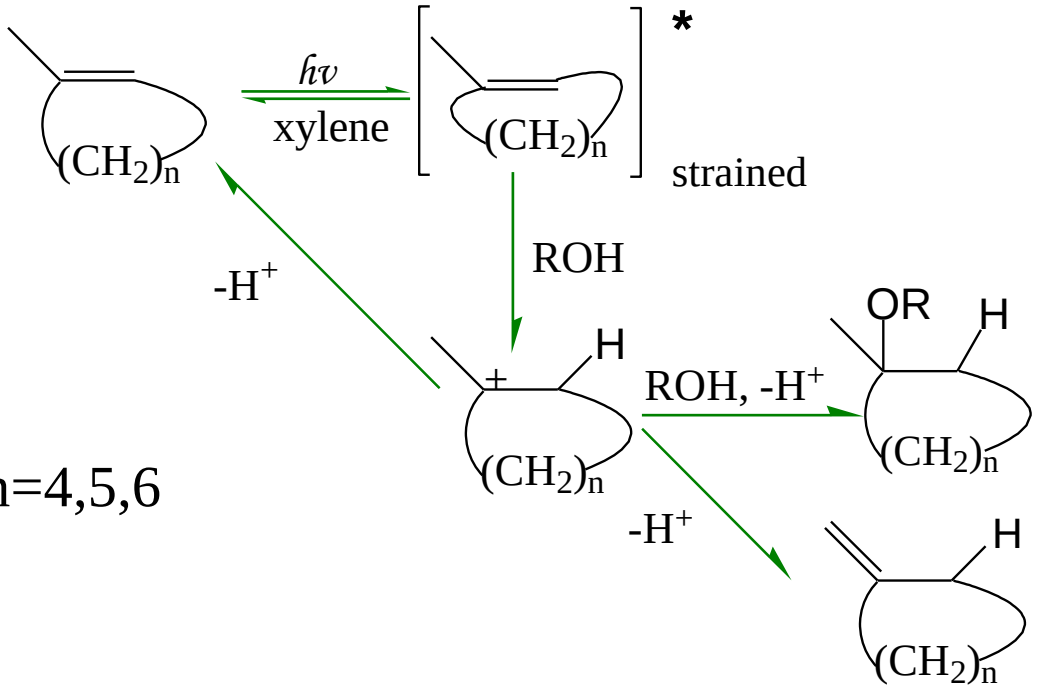
3

A photostationary state will be reached from either side (cis◀ photostationary state; trans◀ photostationary state)

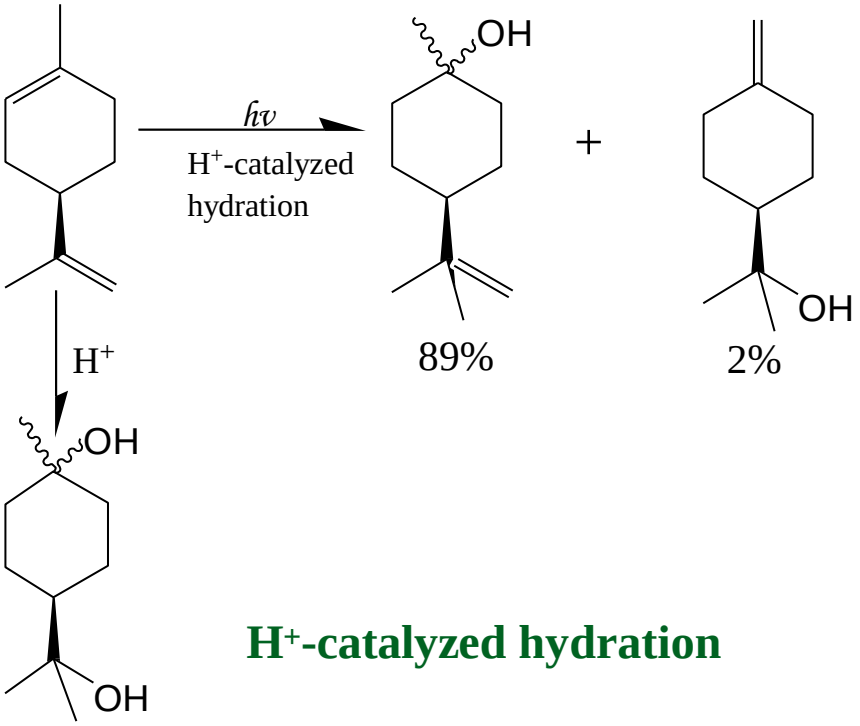
$$\left[\underline{C}\right]_{pss} = \frac{\varepsilon_t}{\varepsilon_c} \bullet \frac{k_c}{k_t}$$

k_c=formation constant of cis from the excited twisted state

k_t =formation constant of trans from the excited twisted state

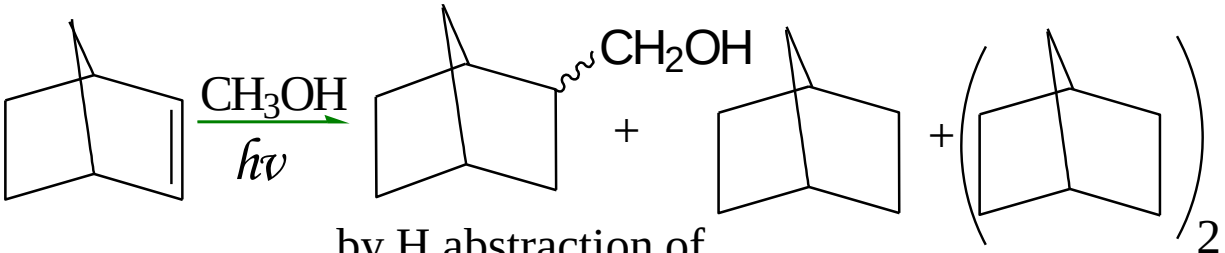


For n=4,5,6



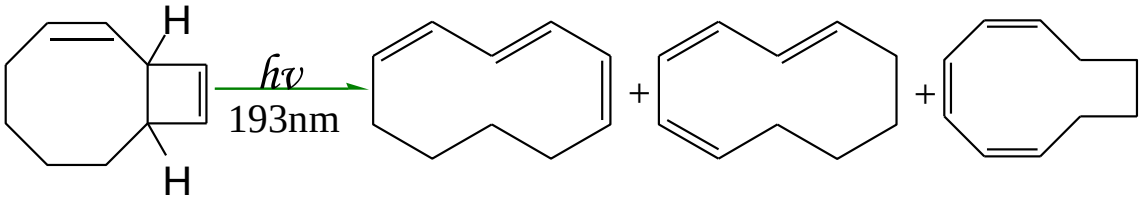
H⁺-catalyzed hydration

For cyclopentene, the cis-trans isomerization doesn't occur.



by H abstraction of the diradical species

The photochemically allowed reaction by symmetry rule may be only one of many reaction pathways



~~thermally allowed~~

Symmetry-allowed dis. rot. product

other mechanism

Thank you