Chap. 12 Photochemistry

Photochemical processes

Jablonski diagram

S_2

2nd singlet
excited state ⑨

S_1

1st singlet
excited state

Ground state

S_0

T_3
3rd triplet
excited state

T_2
2nd triplet
excited state

T_1
1st triplet
excited state
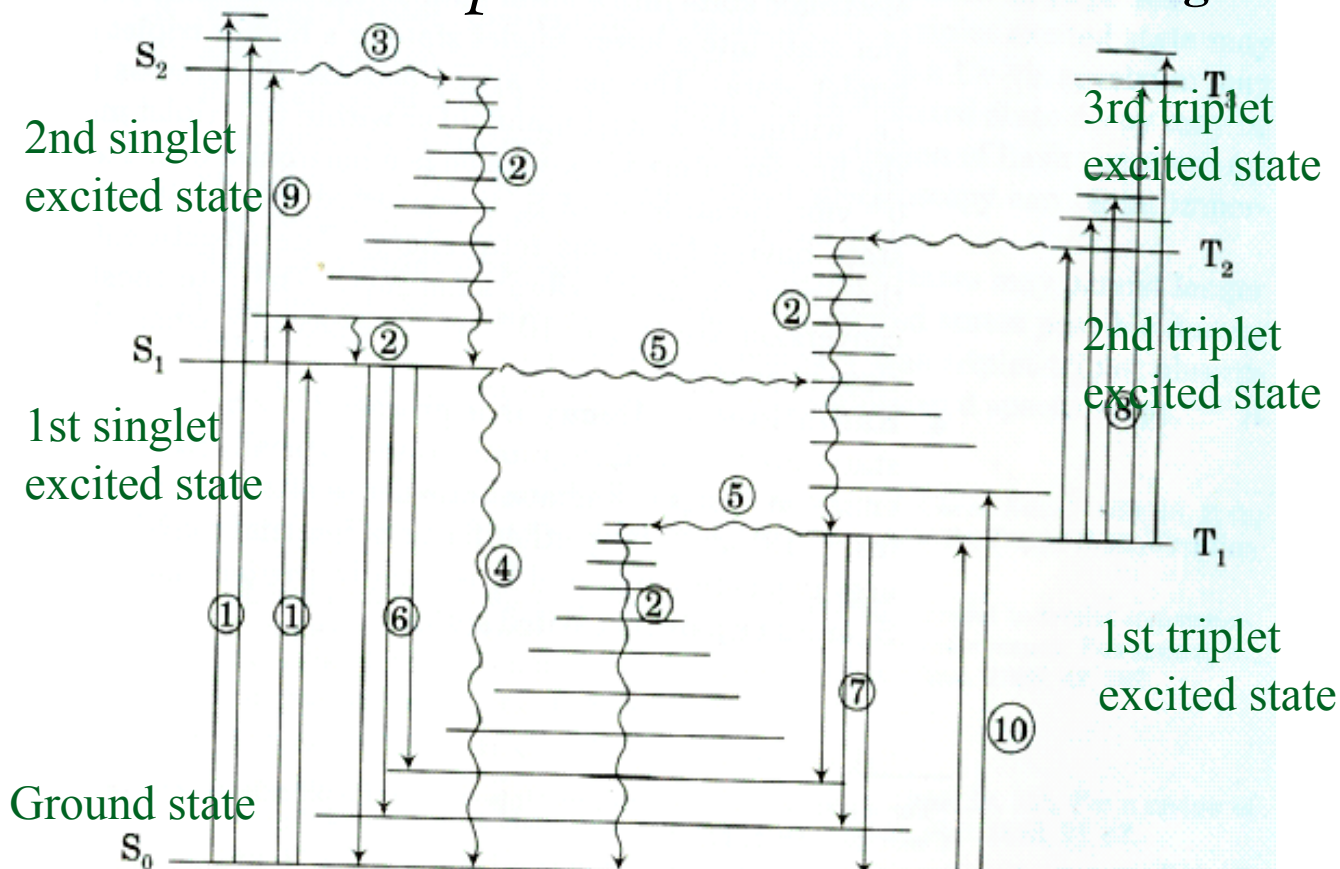
1. Light absorption: $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$ k~10^{15}
2. Vibrational Relaxation: k~10^{12}/s, from high ν to low ν
3. Internal Conversion: to lower electronic state of same multiplicity (k>10^{10}/s)
4. Radiationless Decay: $S_1 \rightarrow S_0$, no emission, k<10^6/s
5. Intersystem 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 $H_2C=O$:
  - $[(1S_O)^2(1S_C)^2(2S_O)^2(\sigma_{C-H})^2(\sigma'_{C-H})^2$
    $(\sigma_{C-O})^2](\pi_{C-O})^2(n_O)^2$
- S_1(1st exc.state):
  - $[(1S_O)^2(1S_C)^2(2S_O)^2(\sigma_{C-H})^2(\sigma'_{C-H})^2$
    $(\sigma_{C-O})^2](\pi_{C-O})^2(n_O)(\pi*_{C-O})$
- S_2(2nd exc.state):
  - $[(1S_O)^2(1S_C)^2(2S_O)^2(\sigma_{C-H})^2(\sigma'_{C-H})^2$
    $(\sigma_{C-O})^2](\pi_{C-O})(n_O)^2(\pi*_{C-O})$

$\pi*_{c-o}$ n π_{c-o} $n \rightarrow \pi*$ $\pi \rightarrow \pi*$
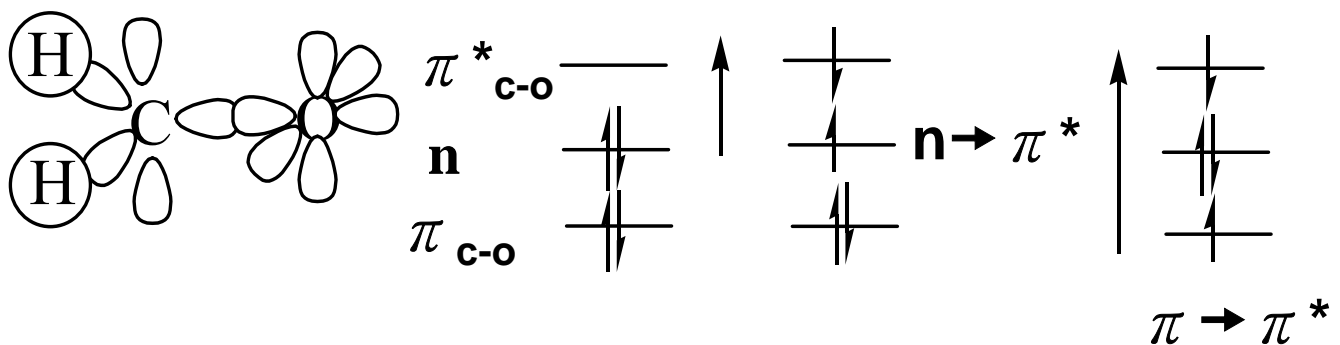
UV Absorption and Emission

- Factors determining radiative transition:

  1. Symmetry of electronic state (ini. final state)

  2. Multiplicity of the spin

     ♦ Spin-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
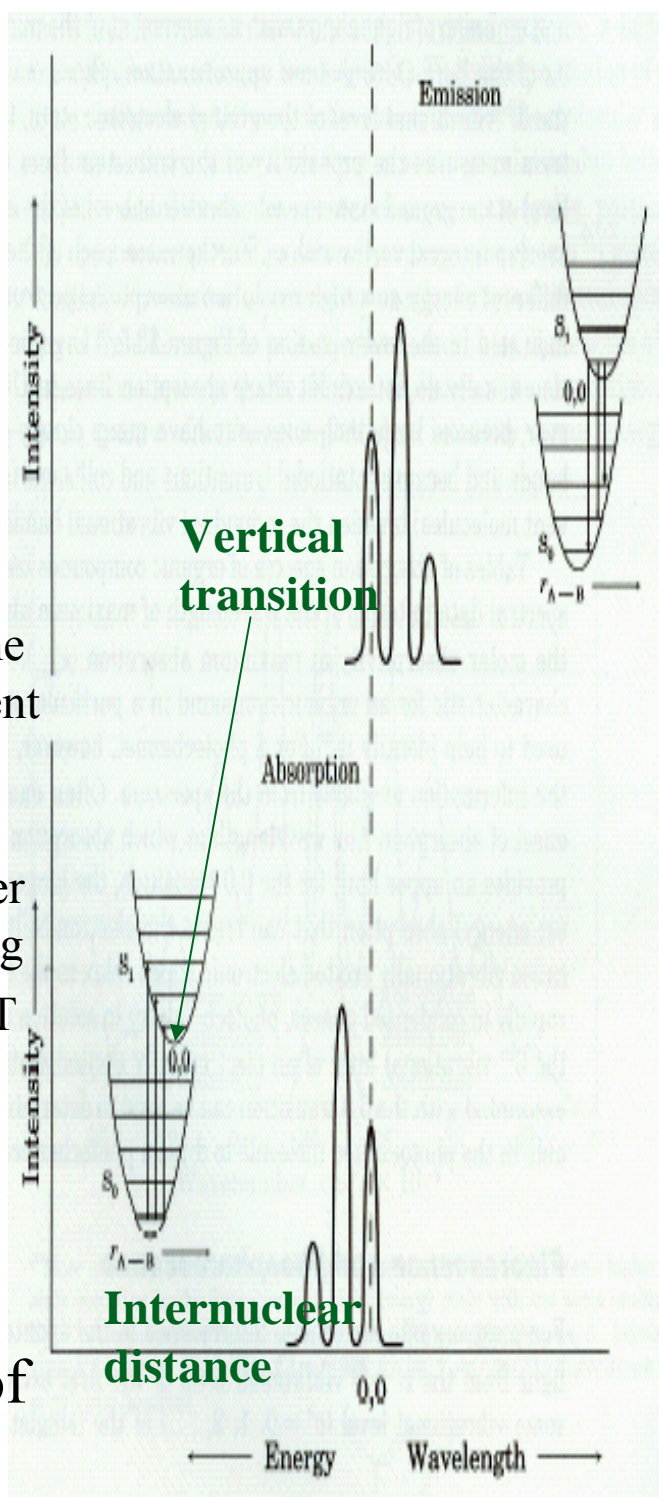
Frank-Condon Principle

- 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

(2)

(1)

(3)

Fluorescence
quantum
intensity

Absorption
extinction
coefficient

20   22   24   26   28   30   32

Wavenumber, $cm^{-1} \times 10^{-3}$

Anthrcene
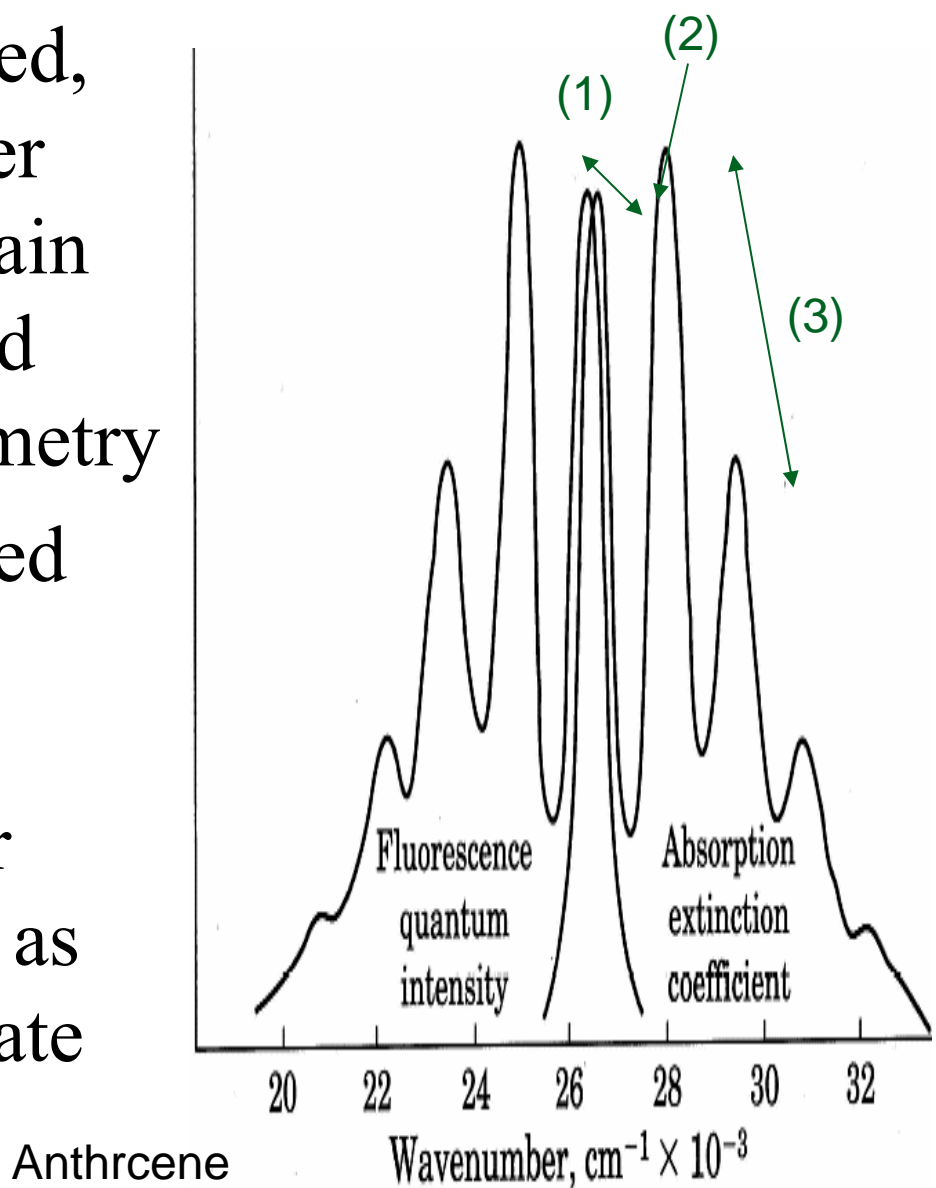
Fluorescence

- The excited state geometry quite different from ground state geometry => large Stokes shift

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

planar geometry

BIPHENYL
SOLVENT CYCLOHEXANE
CONC. 0.2 G/L
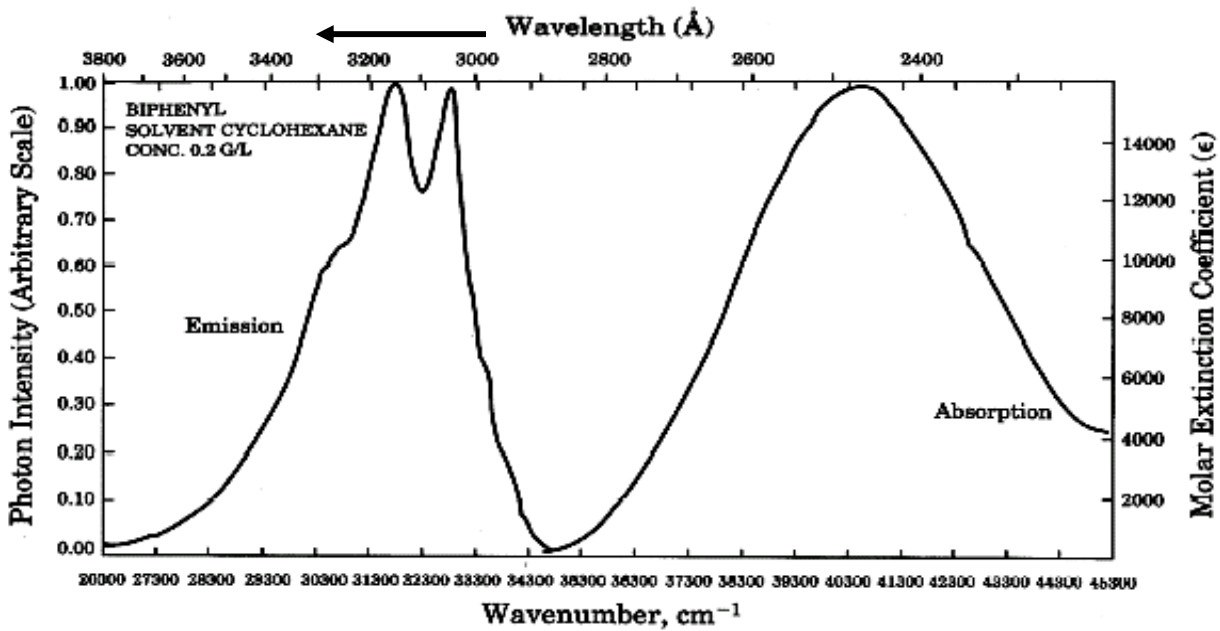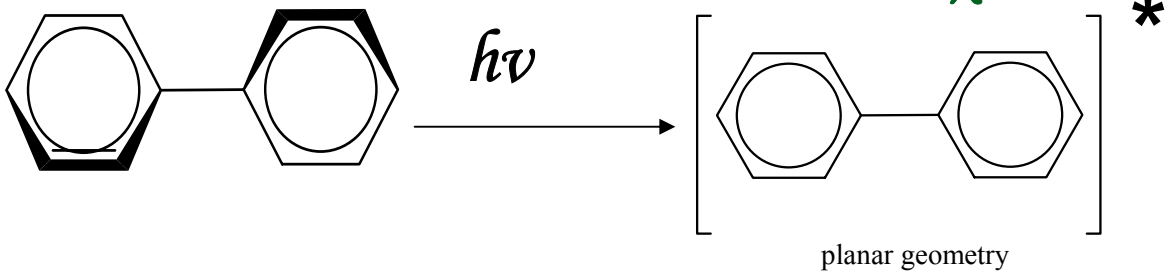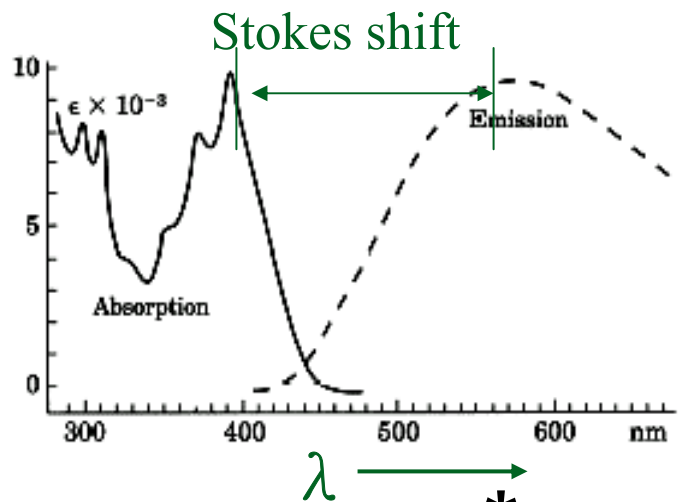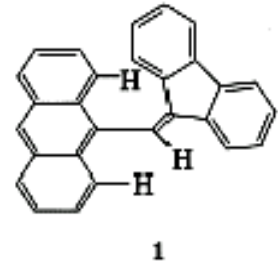
Measurement of Absorption

- Beer-Lambert Law: $\log \dfrac{I_o}{I_t} = \varepsilon c\, d$ = 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
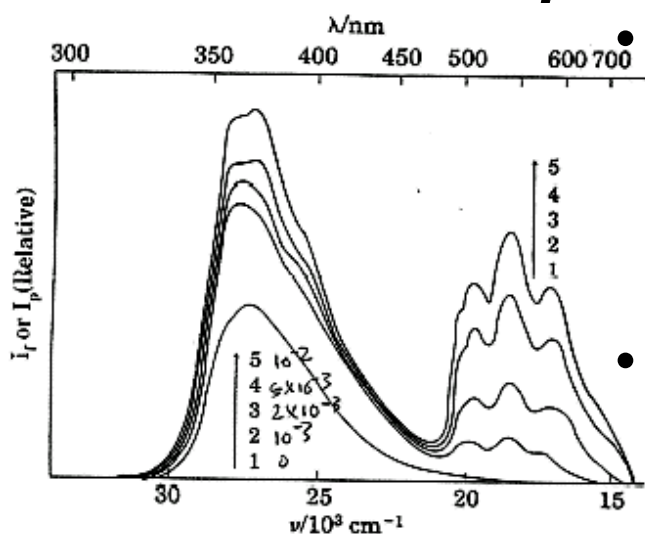
- Much reduced due to diffusional quenching with ground state species or O_2

- Observed in fixed matrix, such as liquid N2 temperature or surrounded by a host
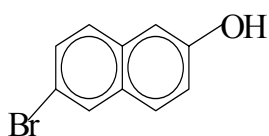
In aqueous solution with α-CD

Concentration –Dependent Fluorescence
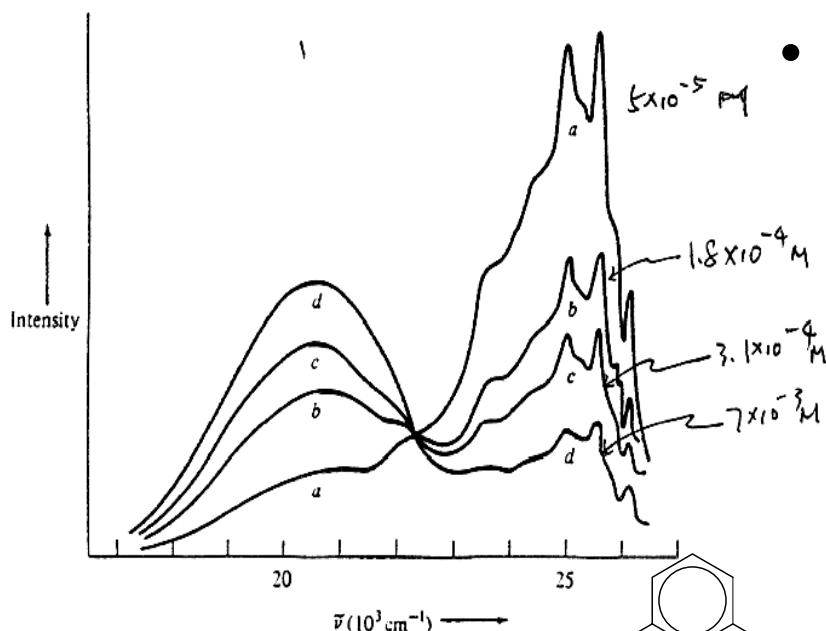
- Excimer formation

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

In heptane

A*A ———→ AA*
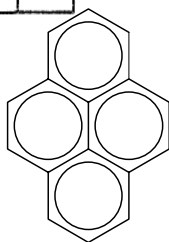
Geometric Requirement of Excimer Formation

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

CH$_2$(CH$_2$)$_n$CH$_2$
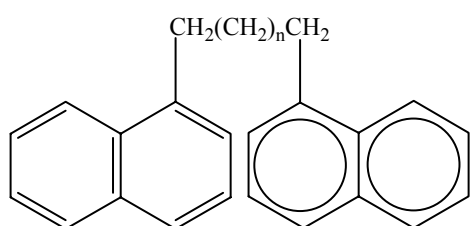
n=0 no overlap of ring

n=1 excimer formation

n=2 strain of chain

CH$_2$CH$_2$CH$_2$

CH$_2$CH$_2$CH$_2$
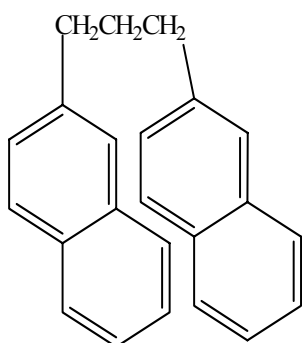
Excimer formation
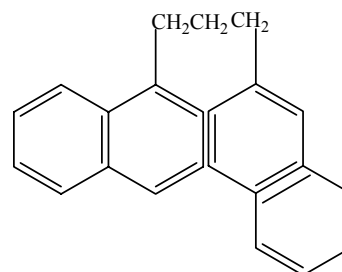
Partial overlap of ring plane

- Exciplex: complex formed between an excited molecule with a ground state molecule of dissimilar molecule
- $A^*B \longleftrightarrow AB^*$ can give exciplex emission or quench emission
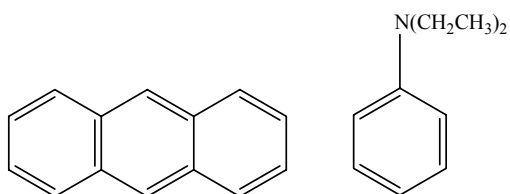
aromatics / amine
aromatics/conjugate olefin

quench by

Fluorescence quencher

Geometric requirement less stringent
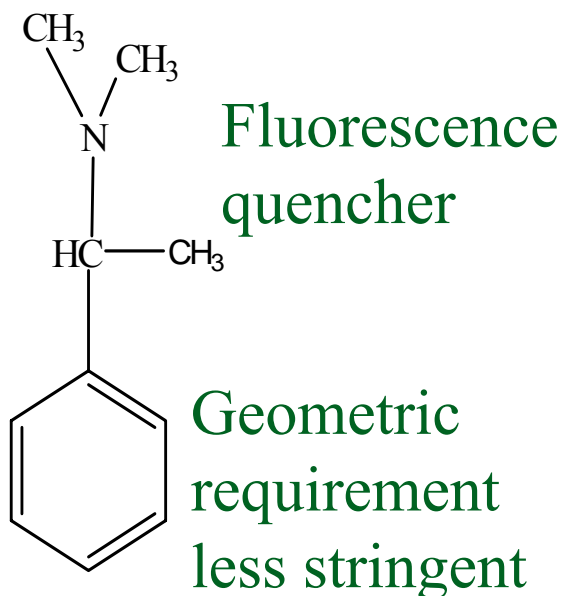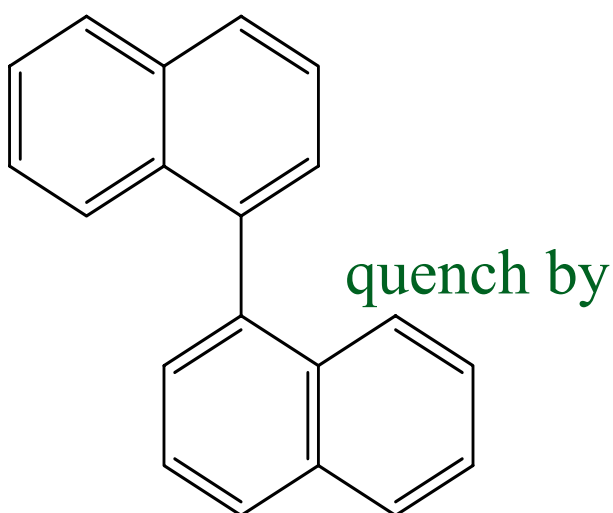
Energy Transfer and Electron Transfer

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

   1)   Radiative energy transfer

      ☙ $D^* \rightarrow D+ \hbar v$

      ☙ $A+\hbar v \rightarrow A^*$
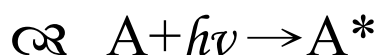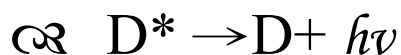
The rate depends on

   ①   The quantum yield of emission by D* (Φ^D_e)

   ②   The concentration of (the # of) A in light path

   ③   The light absorbing ability of A (extinction coefficient)

   ④   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
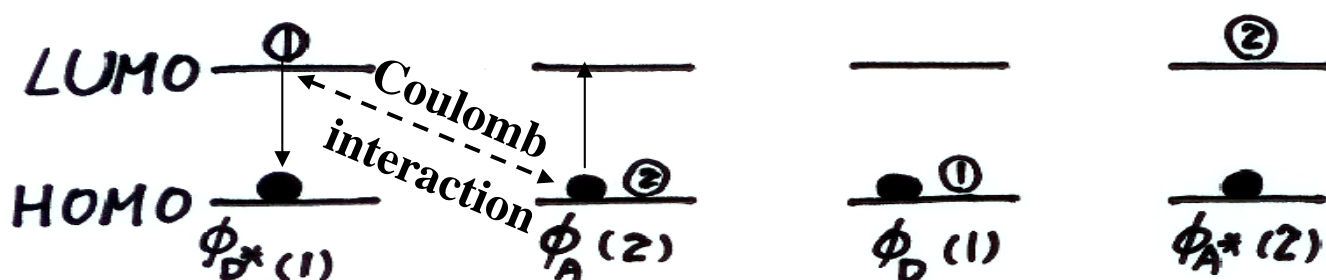
•An interaction at a distance via electromagnetic field, induce a dipole oscillation in A by D*.

•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
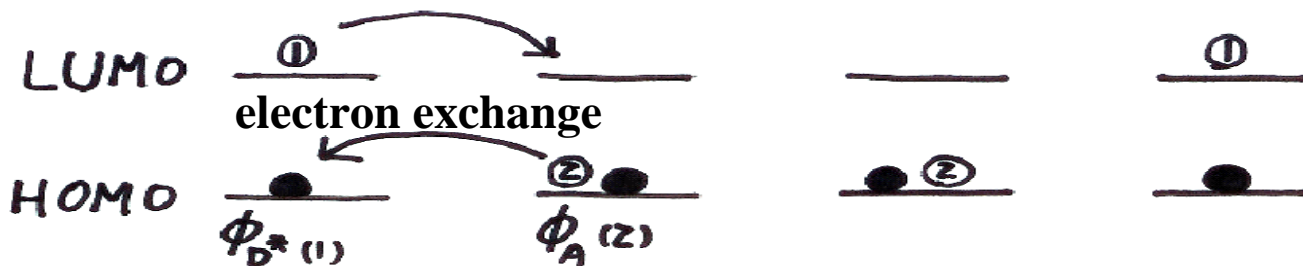
electron exchange

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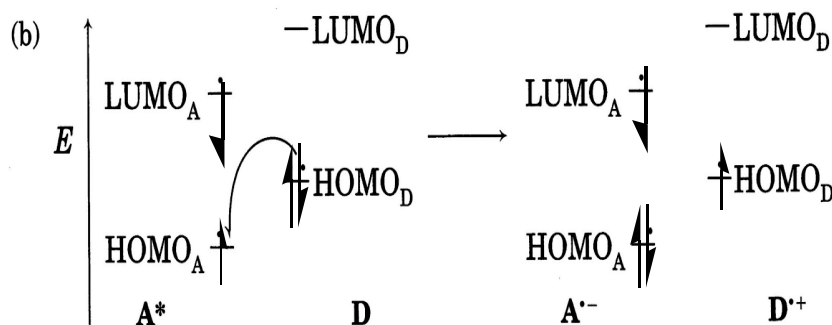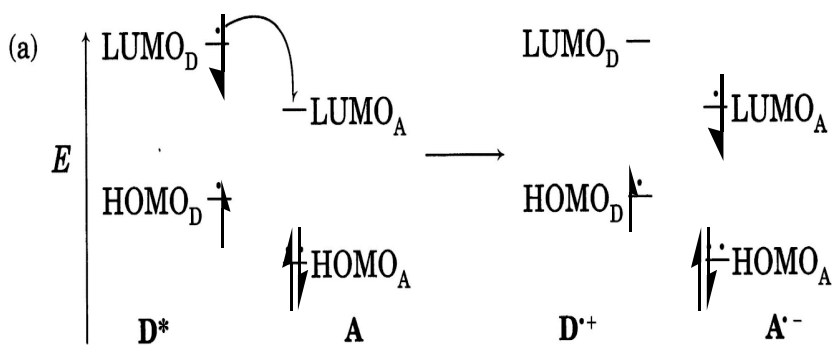
- The photo excited state is a better donor (lower oxid. potential) as well as a better acceptor (lower reductive potential) relative to ground state

Acidity and Basicity in Excited States

- $A\text{-}H \rightleftharpoons A^- + H^+$

  $\downarrow hv$

- $[A\text{-}H]^* \rightleftharpoons [A^-]^* + H^+$
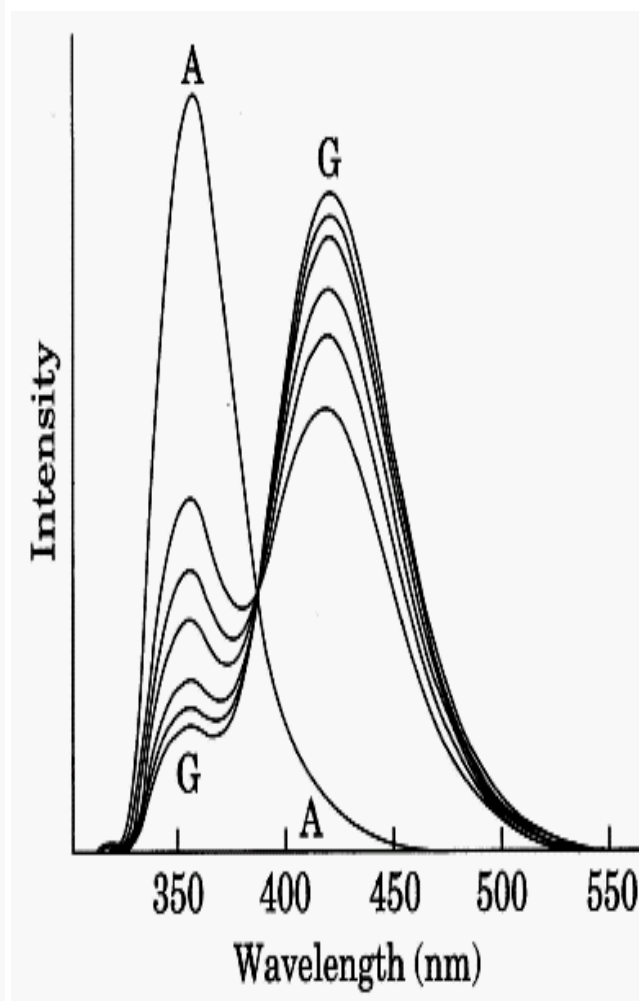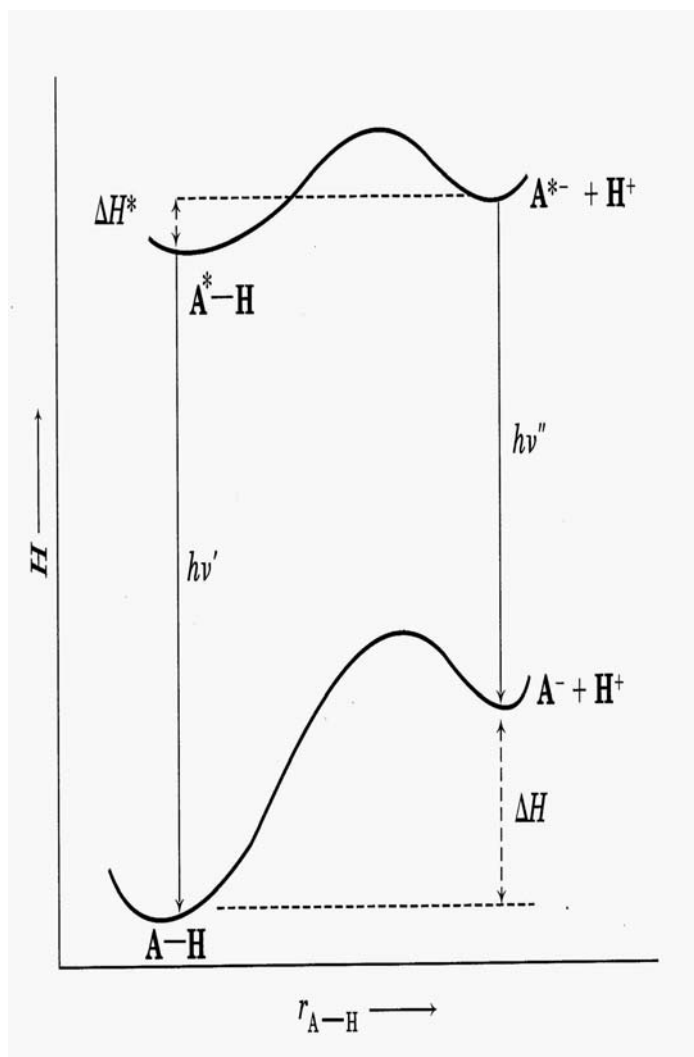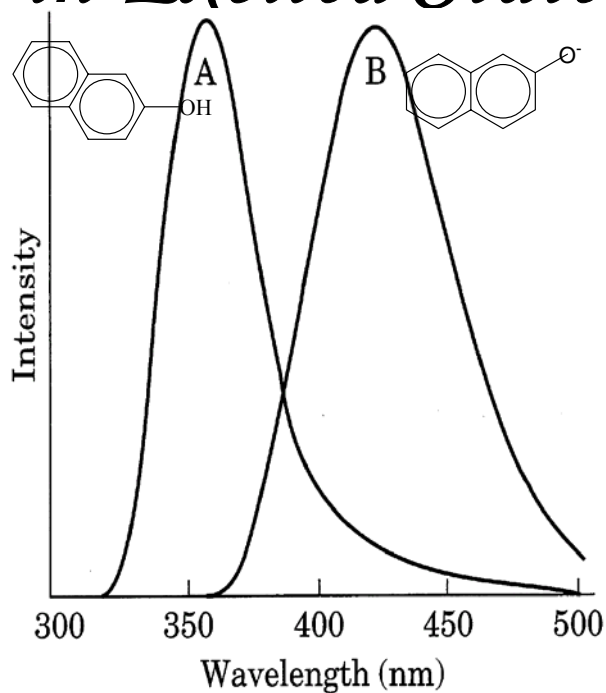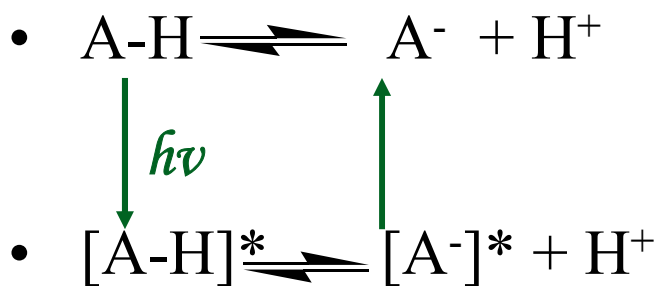
- $\Delta H^* + h\nu' = \Delta H + h\nu''$
- $\Delta H^* - \Delta H = +h\nu'' - h\nu' \approx \Delta G^* - \Delta G$
  - (if $\Delta S^* \approx \Delta S$ for ionization)
  - $\Delta G = 2.303RTpK$
  - $pK^* - pK = \dfrac{\Delta G^* - \Delta G}{2.303RT} \approx \dfrac{h\nu'' - h\nu'}{2.303RT}$

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

Compound	Reaction	pK (S$_0$)	pK (S$_1$)	pK (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

	Type a	Type b	Type c
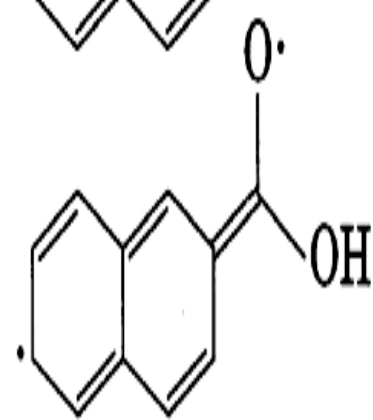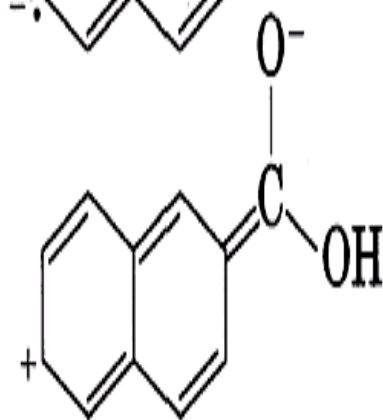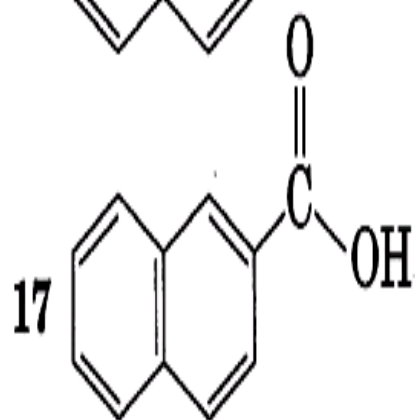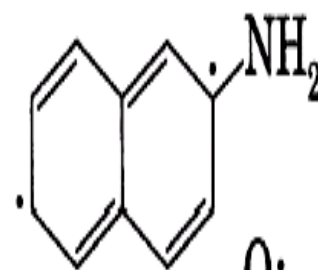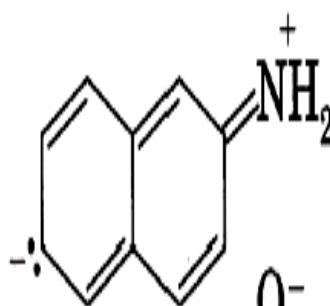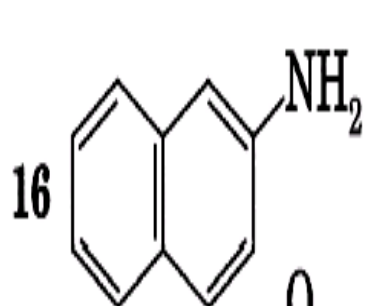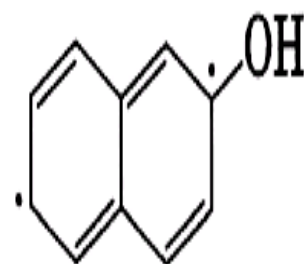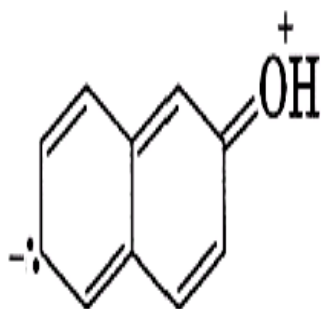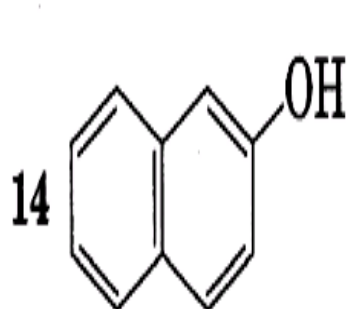
When photochem. excited, electron from
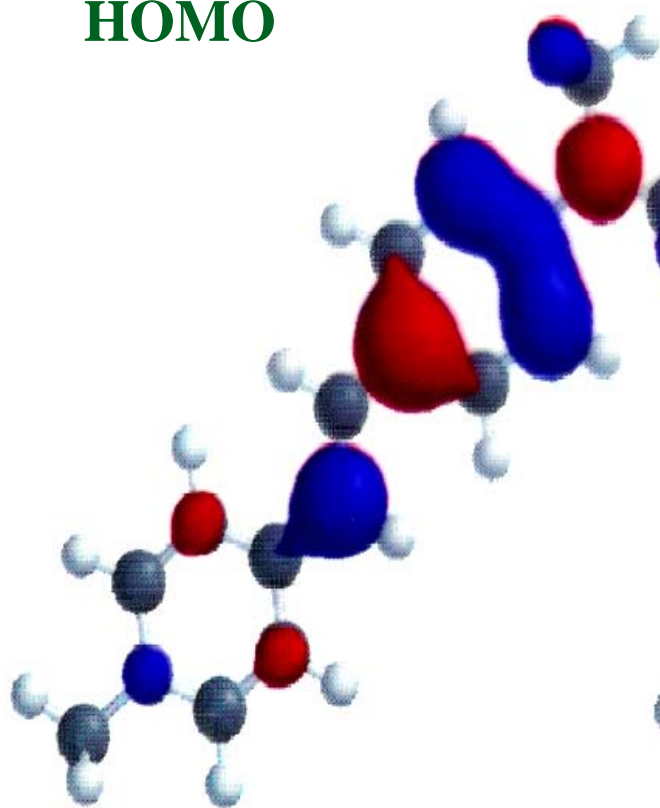HOMO ⟶ LUMO, and change the e⁻ density
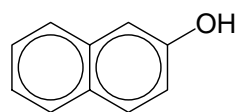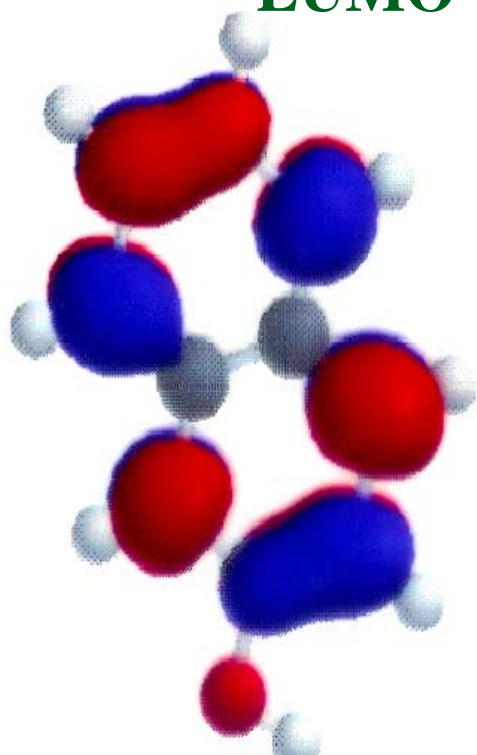
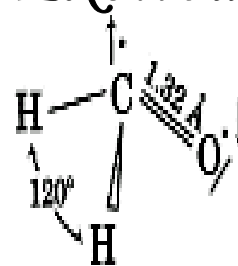LUMO   HOMO
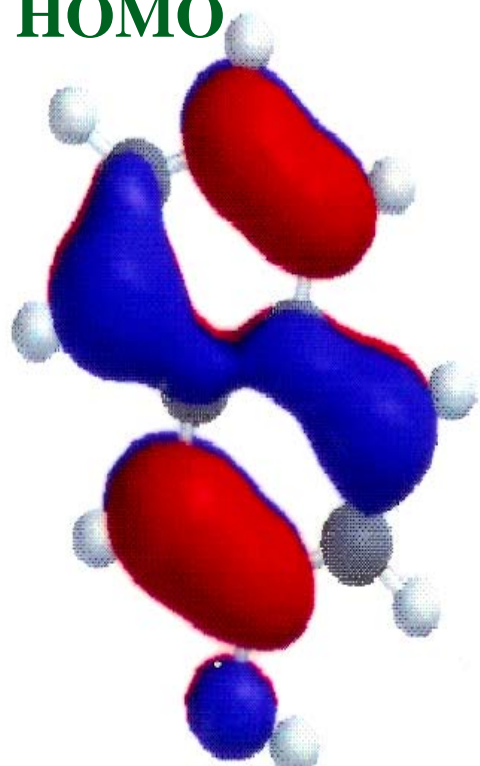
LUMO   HOMO

HOMO

LUMO

π

n

π *
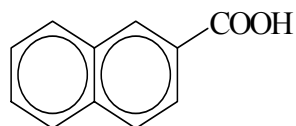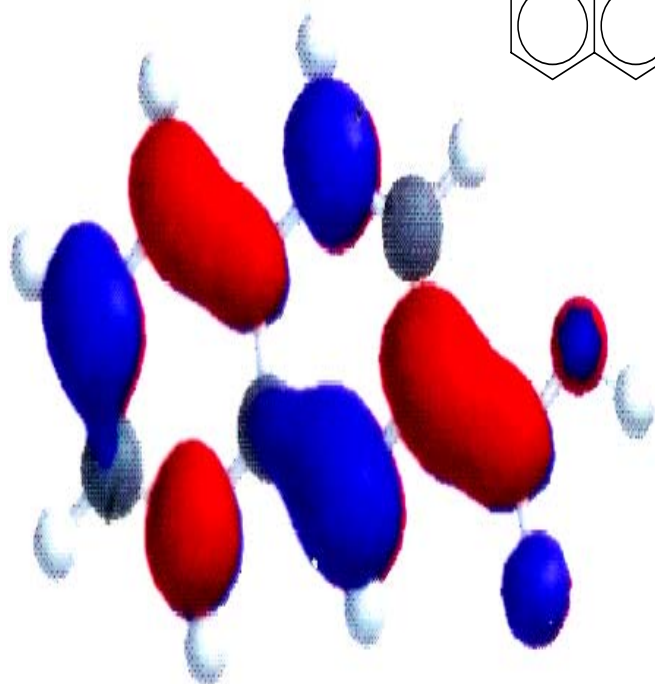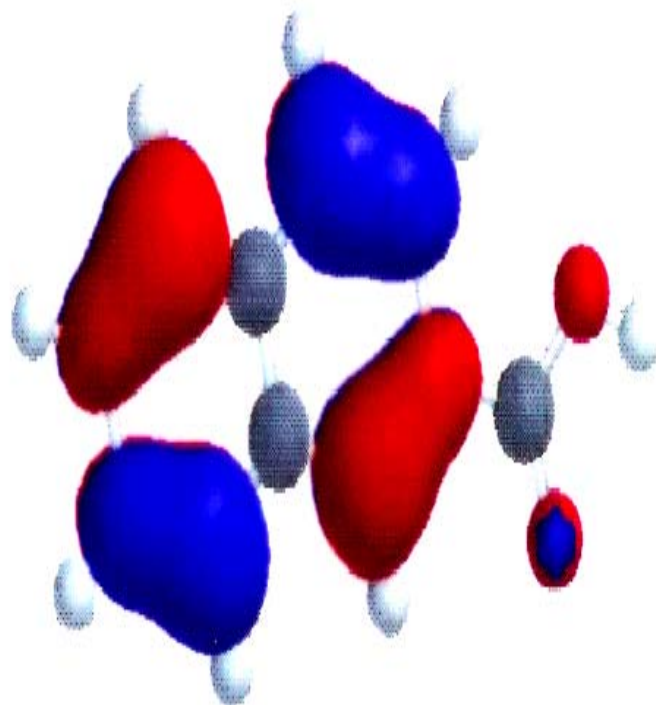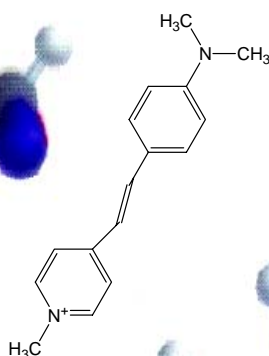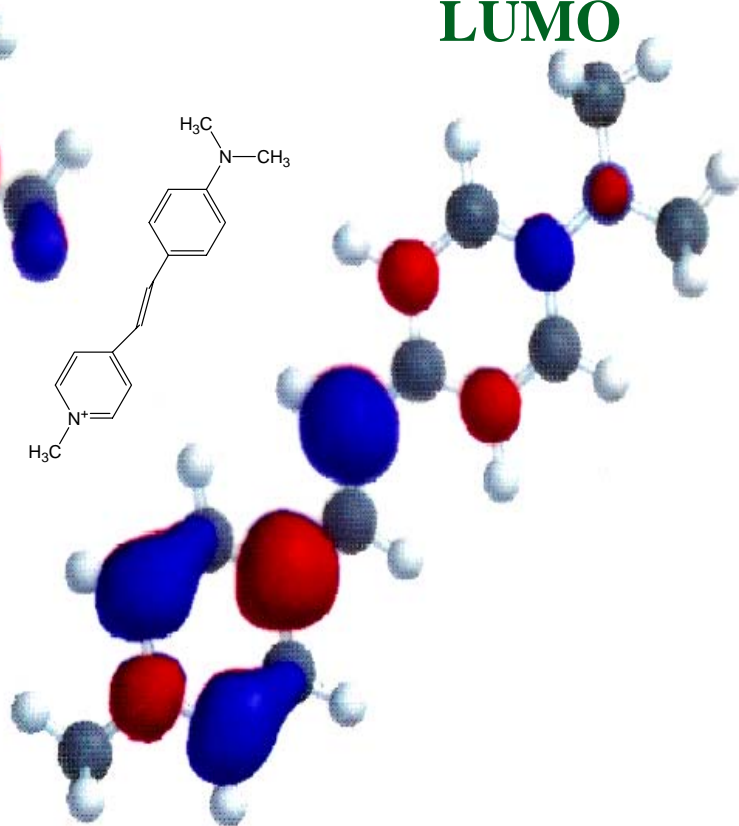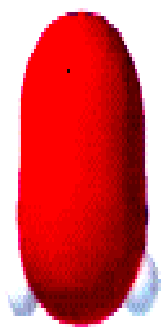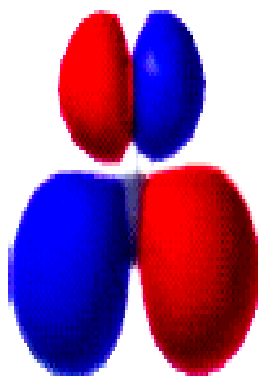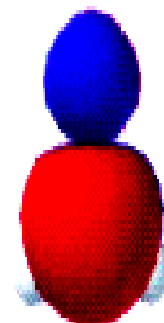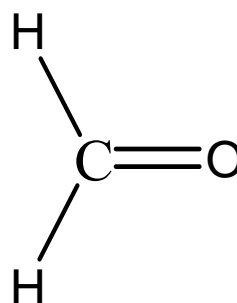
Bond angle, Dipole moments of Excited state

hv

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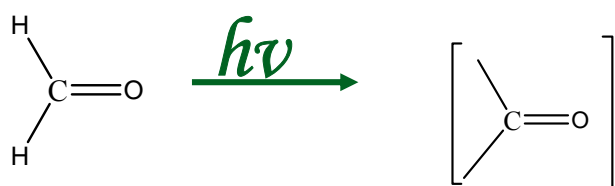
S_1 $\mu = 1.5\,D$
$E \doteq 84\ kcal/mol^{-1}$

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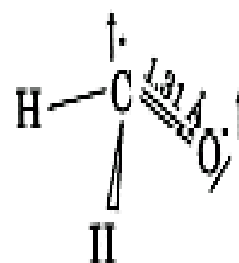
T_1 $\mu = 1.3\,D$
$E \doteq 76\ kcal/mol^{-1}$
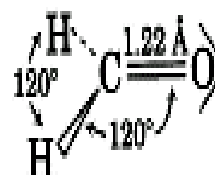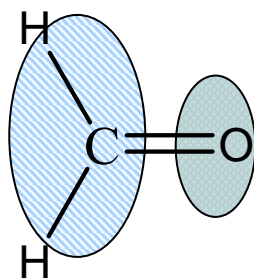

S_0 $\mu = 2.3\,D$
$E \equiv 0\ kcal/mol^{-1}$

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

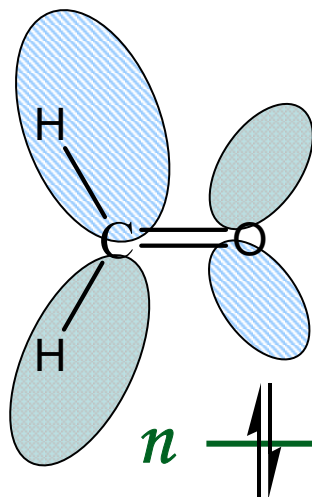| Property/State	S_0	S_1	T_1
Geometry	planar	pyramidal	pyramidal
Δ (nonplanarity)	0°	20°	35°
C=O length	1.22 Å	1.32 Å	1.31 Å
ν C=O stretch	1746 cm^{-1}	1182 cm^{-1}	1251 cm^{-1}
<HCH	120°	122°	
Dipole moment	2.3 D	1.5 D	1.3 D

LUMO   **HOMO**

$\pi^* $ —— n ⇅ π ⇅
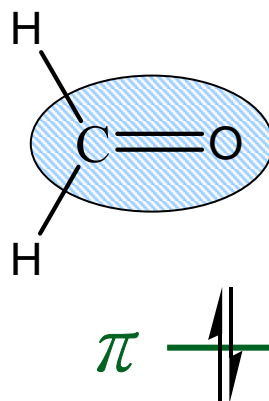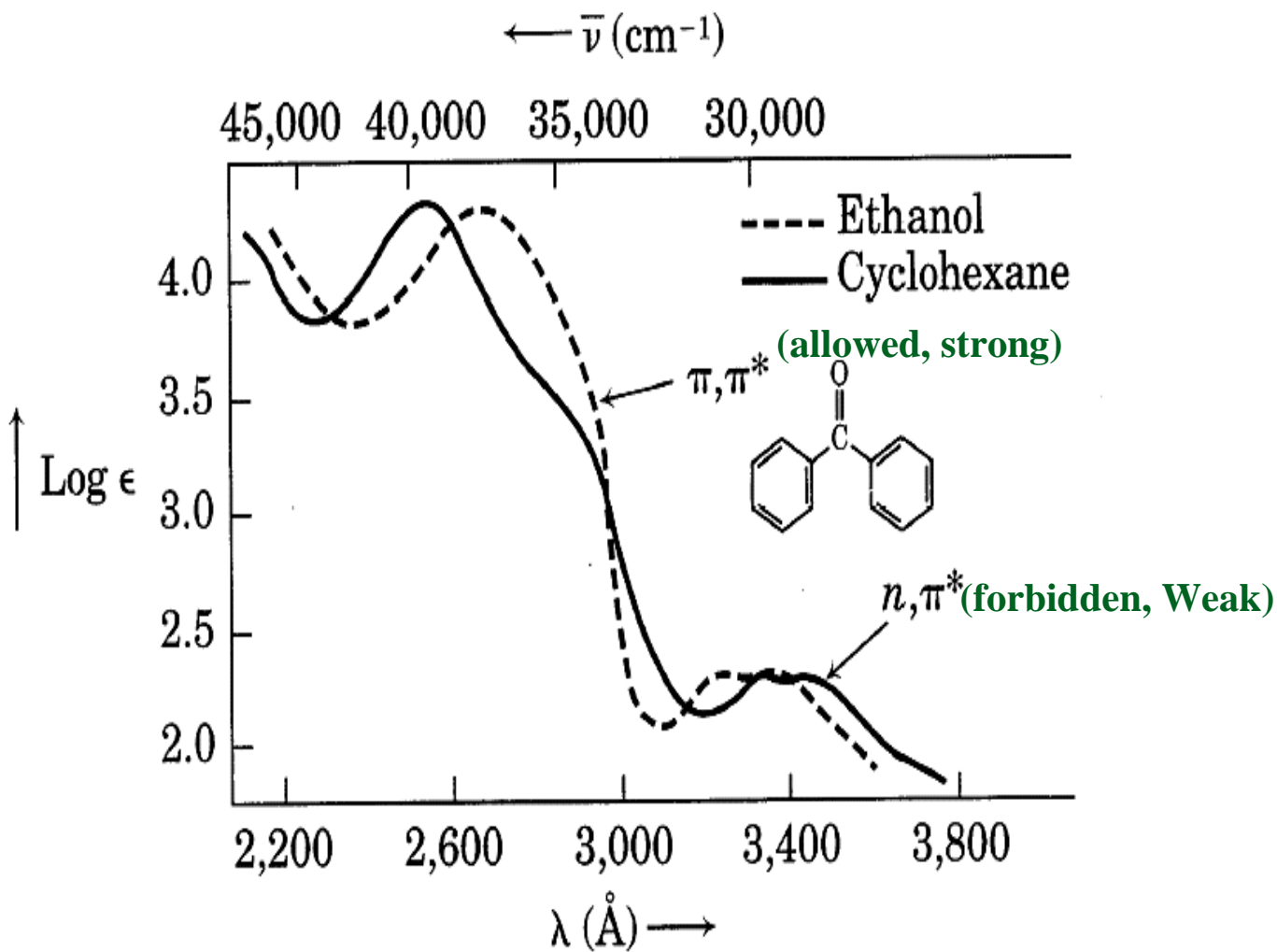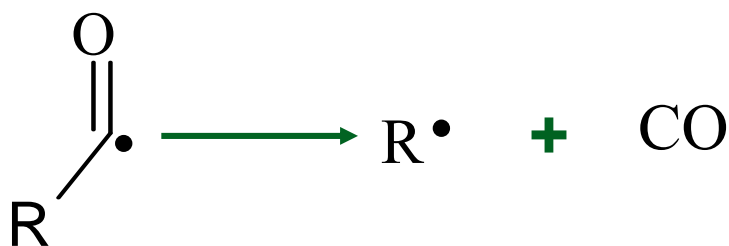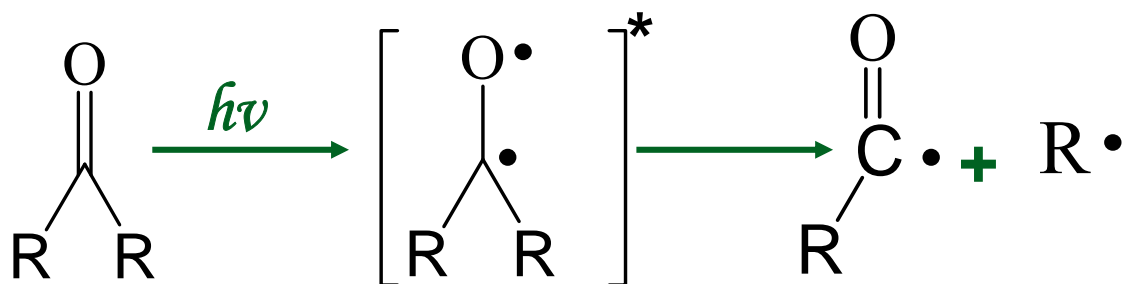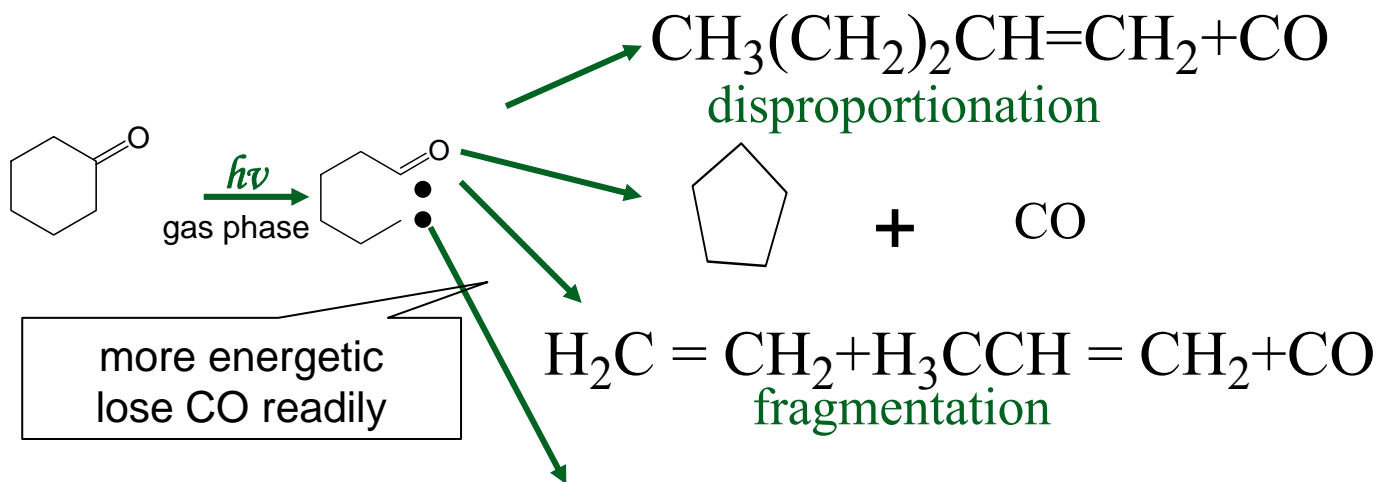
- S$_0$→S$_1$ (n- π *) excited state less polar than the ground state
  - hypsochromic (blue) shift with polar solvent
- S$_0$→S$_2$ (π - π *) excited state more polar than the ground state
  - bathochromic (red) shift with polar solvent

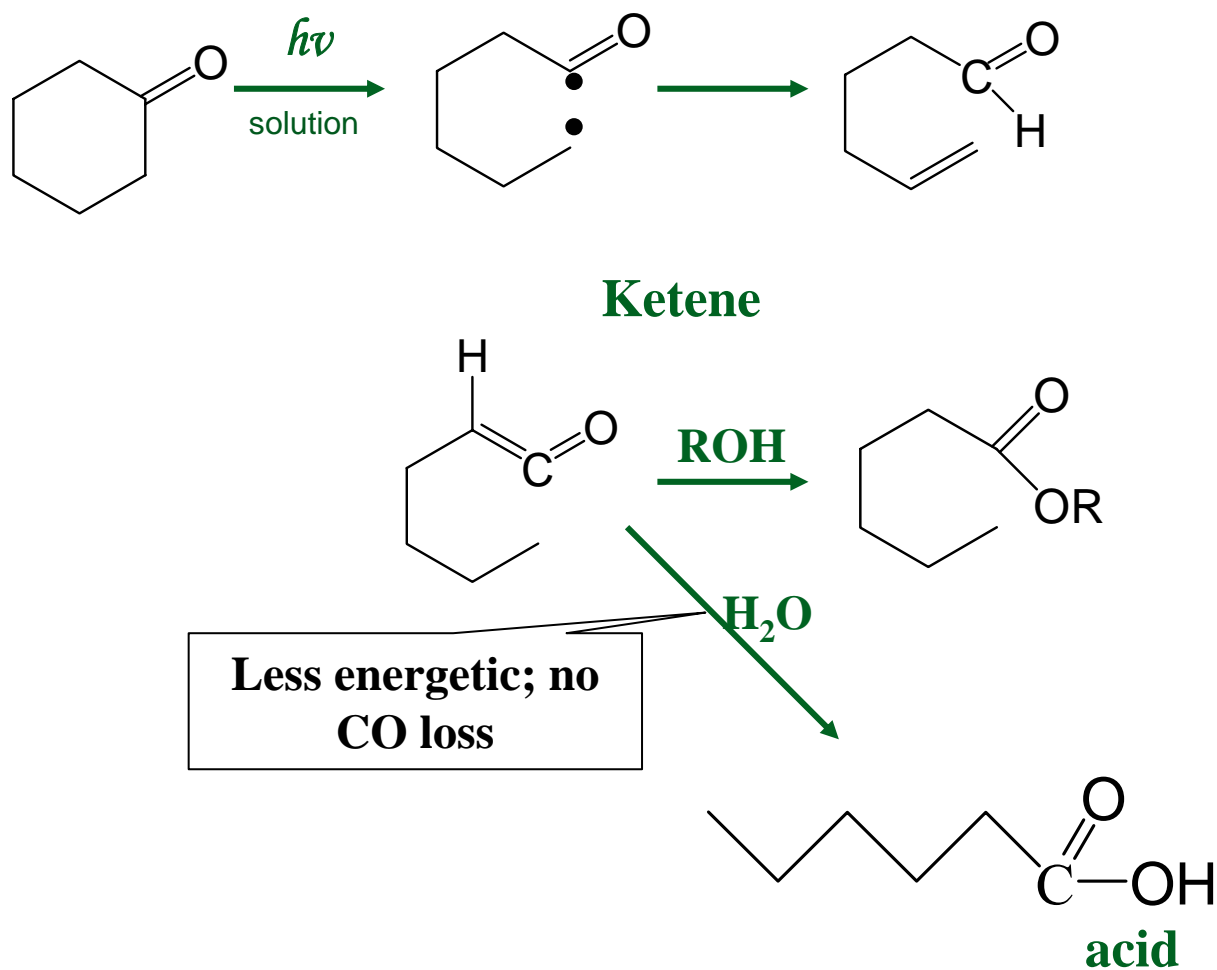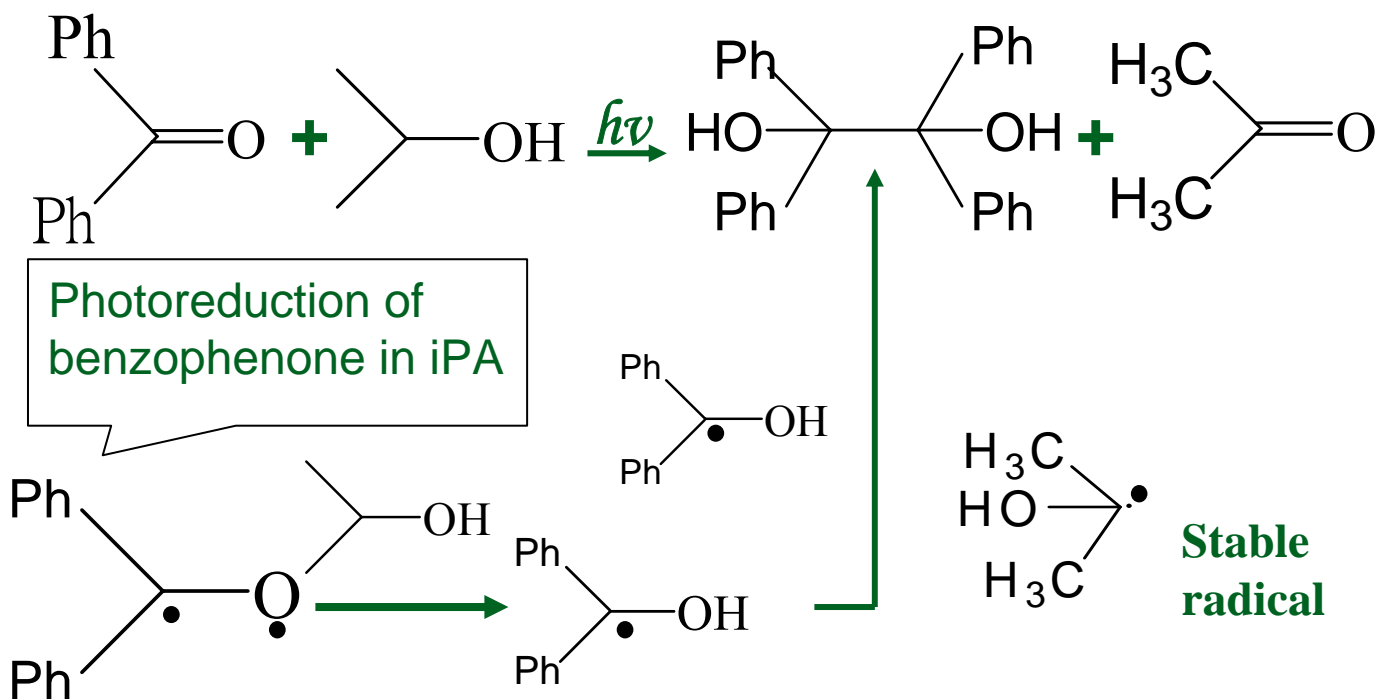# Photochemical Reactions of Carbonyl Compounds

Sat'd Ketone $n \rightarrow \pi^*$ diradical character

Norrish Type I Cleavage (α - cleavage)

$$CH_3(CH_2)_2CH{=}CH_2{+}CO$$

disproportionation

hv

gas phase

more energetic
lose CO readily

+   CO

$$H_2C = CH_2{+}H_3CCH = CH_2{+}CO$$

fragmentation
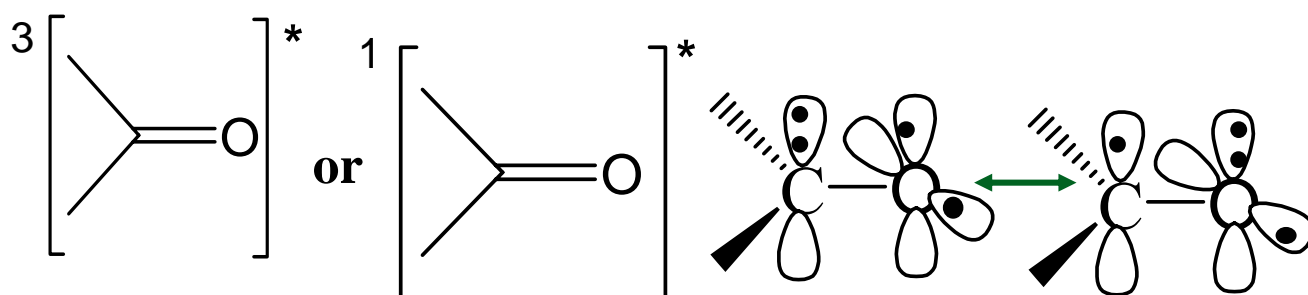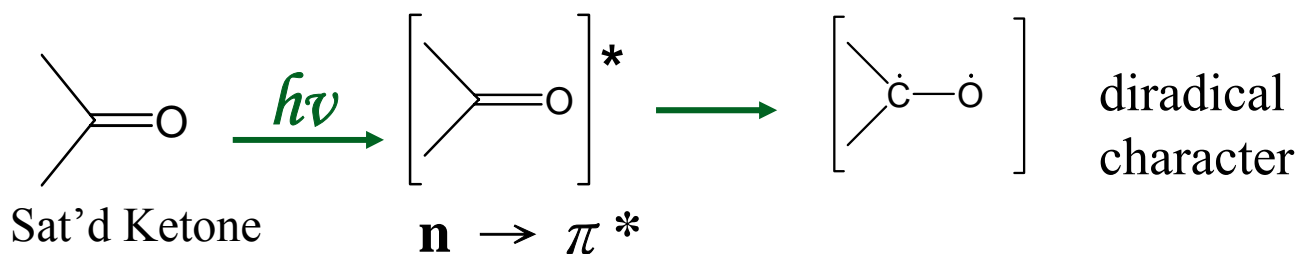
$$H_2C{=}CH(CH_2)_3CHO$$

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

hv

solution

Ketene

ROH

Less energetic; no
CO loss

H_2O

acid

Hydrogen Abstraction Reaction

Photoreduction of benzophenone in iPA

Stable radical

Norrish Type II Cleavage(β -Cleavage)

6-membered ring (T.S.)
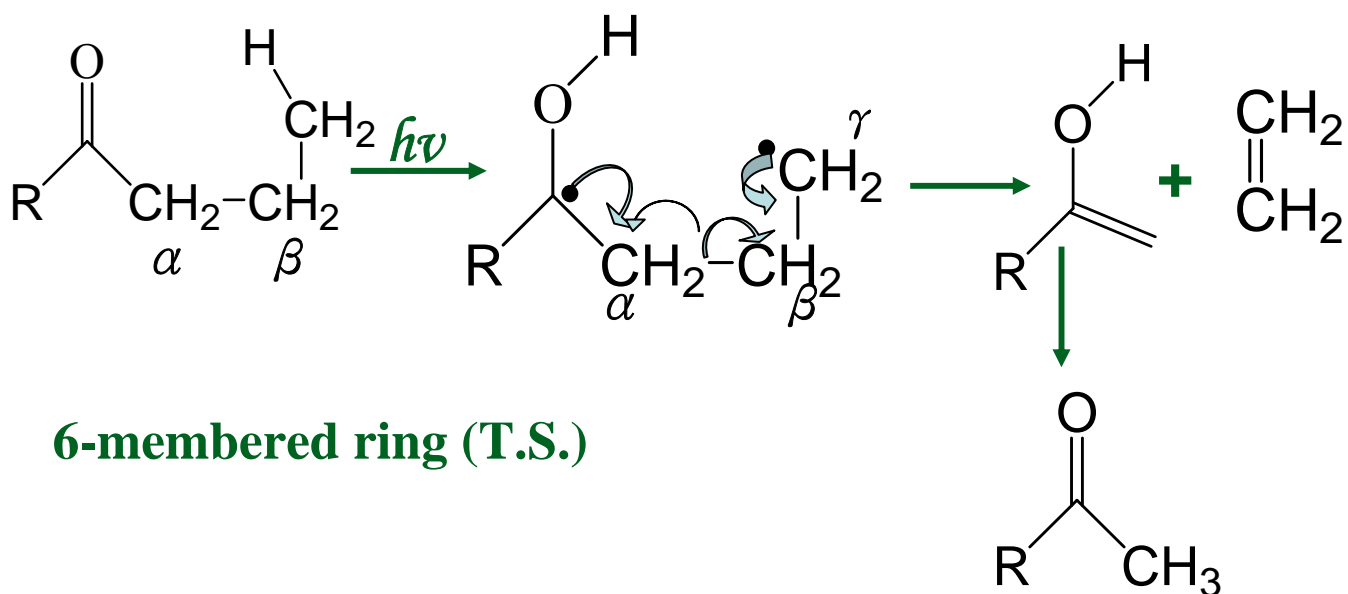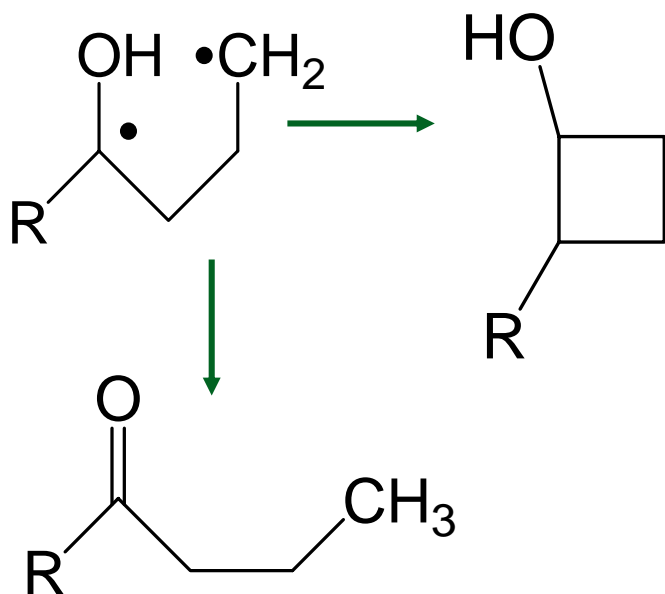
If the S.M. is retrieved, the γ carbon may loose stereochem. (if chiral), so not exactly the same original S.M.
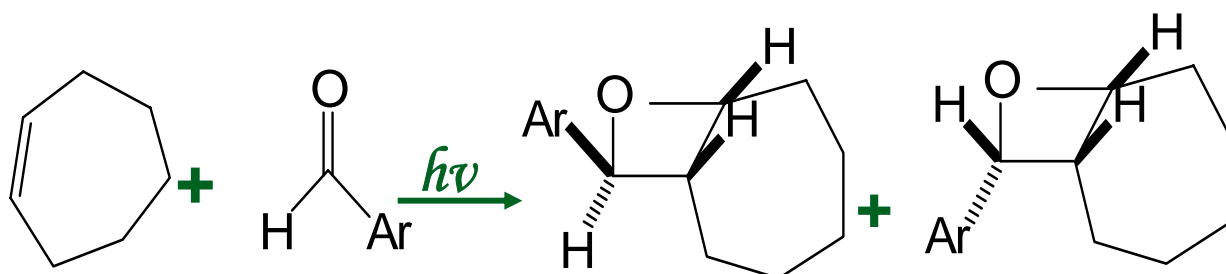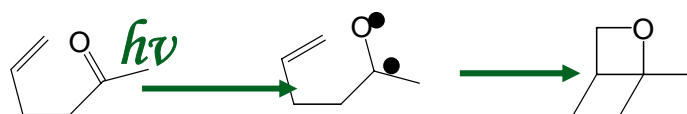
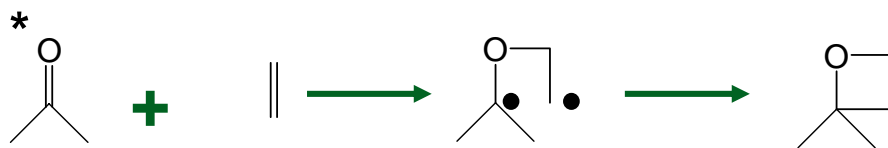α - β unsaturated ketone
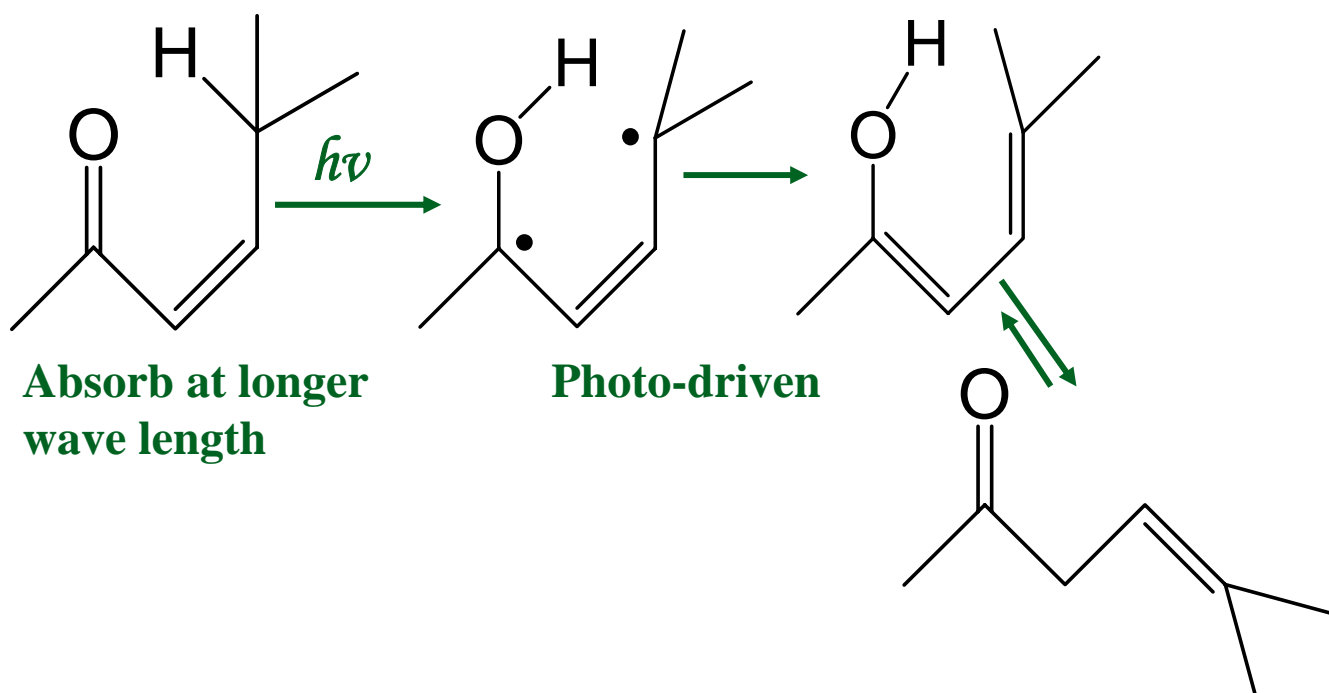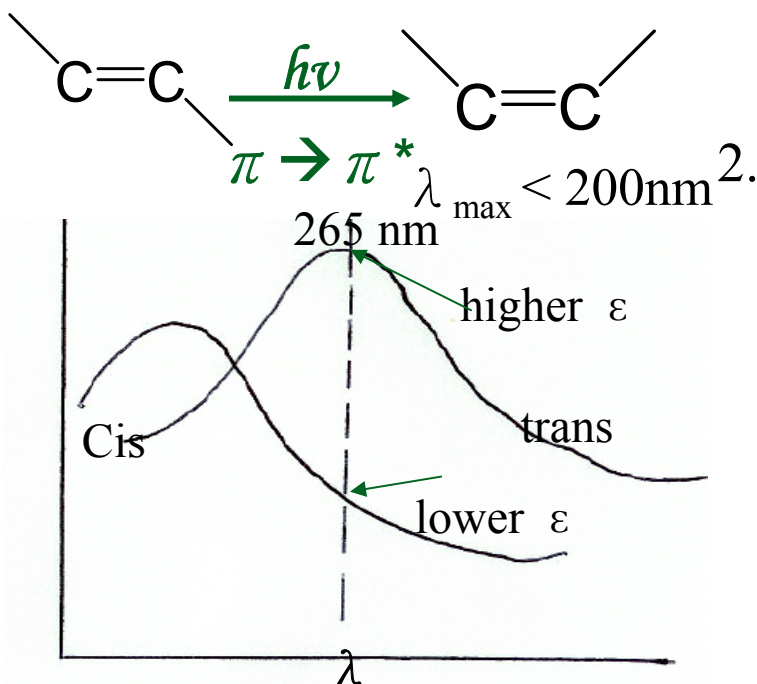

Absorb at longer wave length

Photo-driven

De-conjugated absorb at shorter wave length
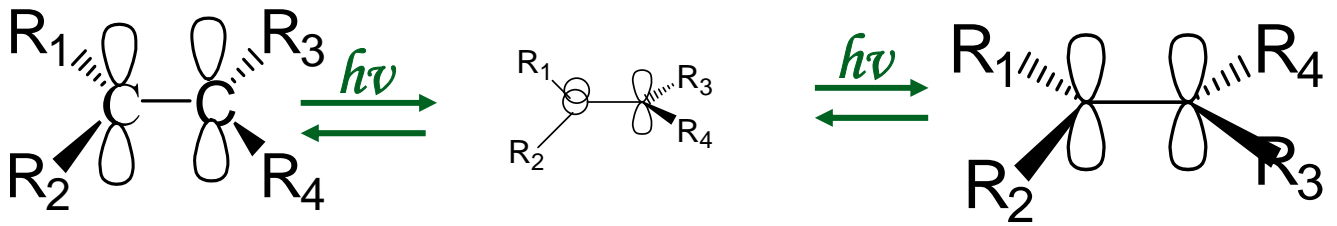
Oxetene Formation (Paterno-Buchi Reaction)

Photochemical Reactions of Alkene and Dienes

- Isomerization

$$\pi \rightarrow \pi^* \quad \lambda_{max} < 200nm$$

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
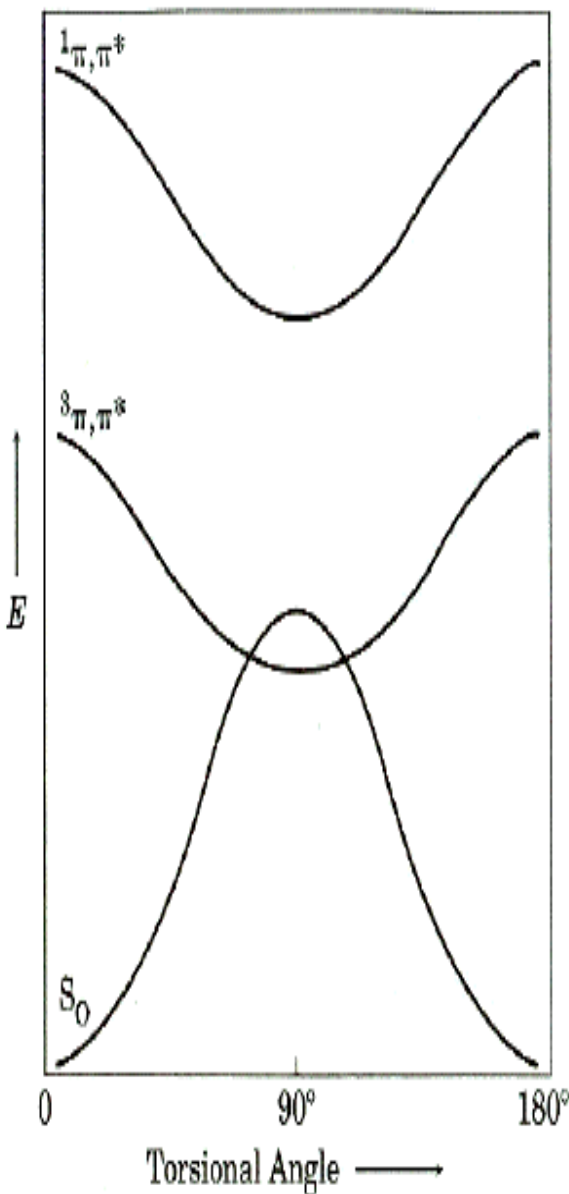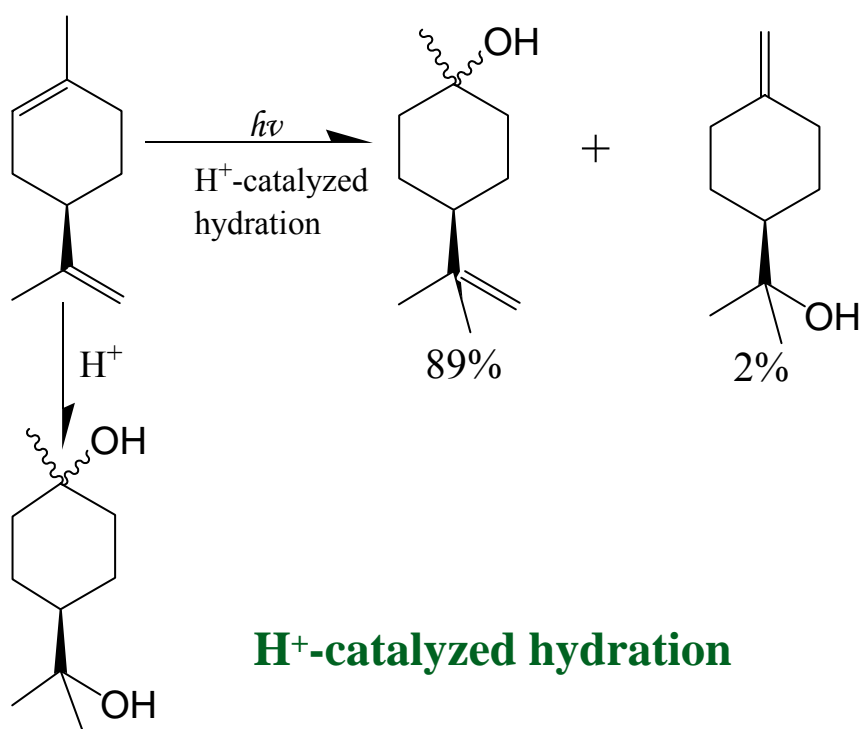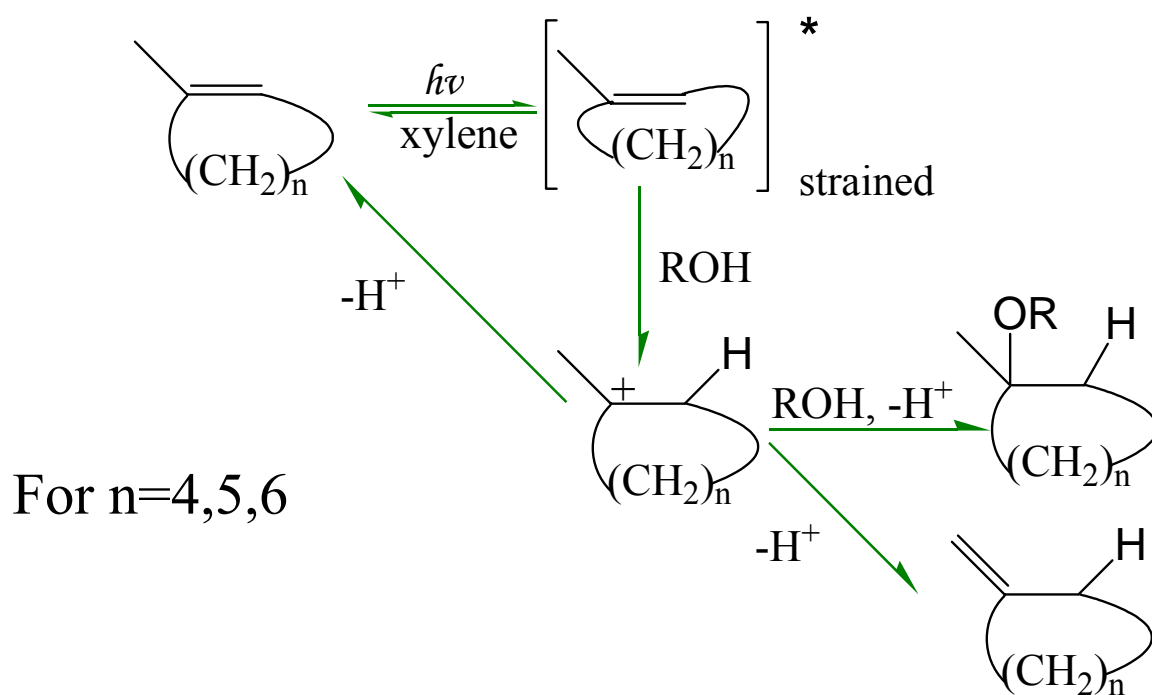
3

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

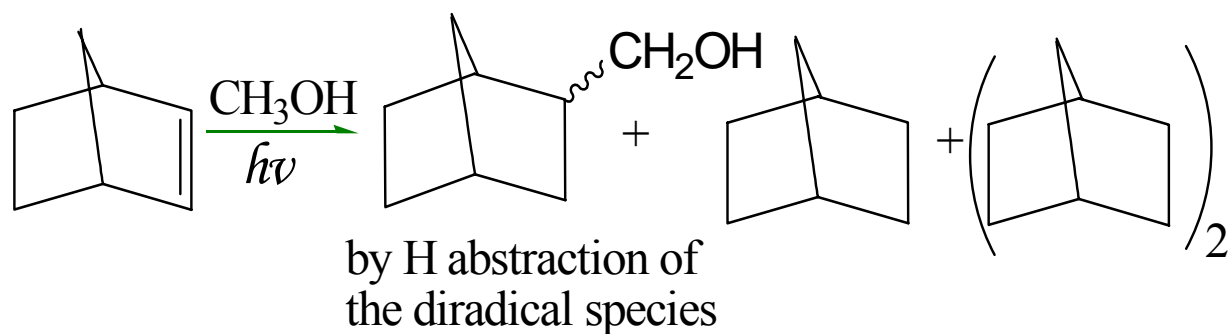$$\frac{[C]_{pss}}{[T]_{pss}} = \frac{\varepsilon_t}{\varepsilon_c} \bullet \frac{k_c}{k_t}$$

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

other mechanism

Symmetry-allowed
dis. rot. product