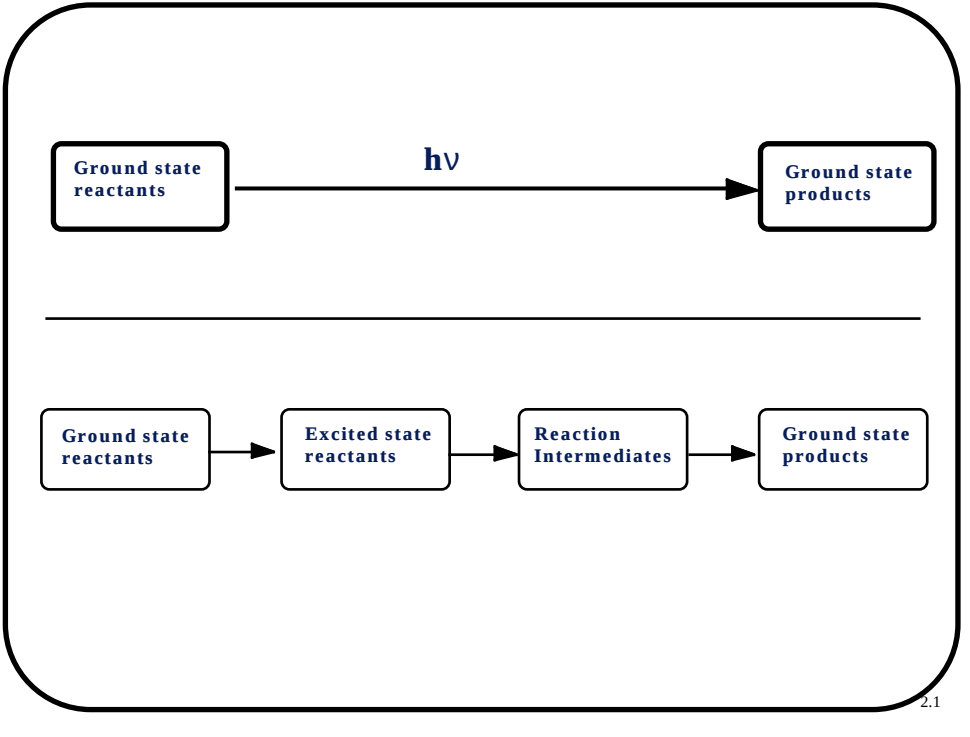
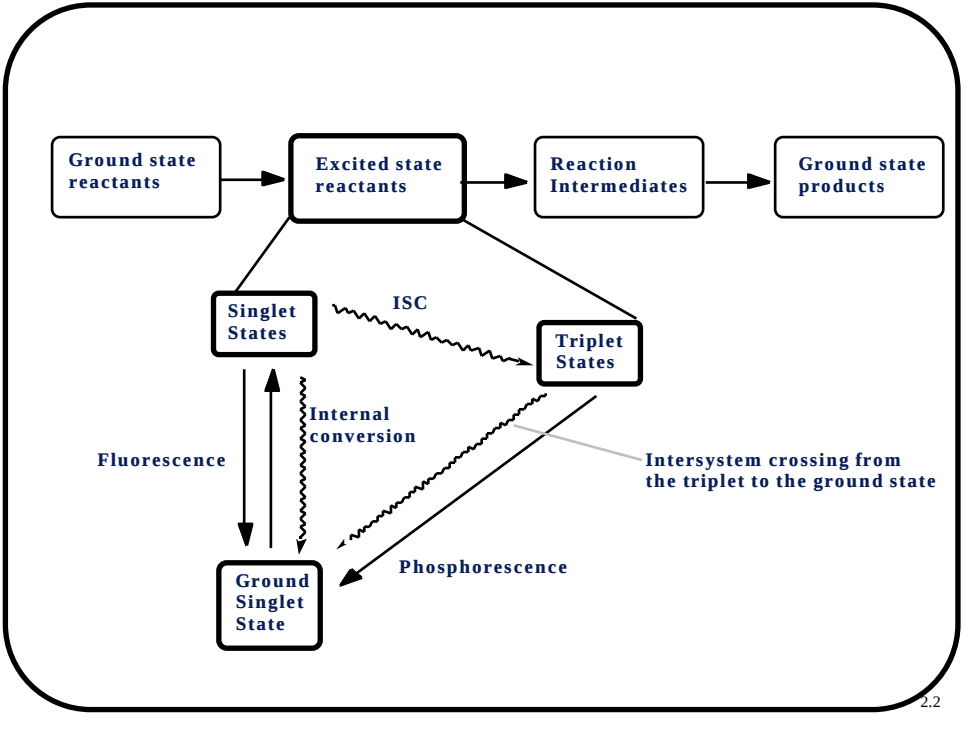
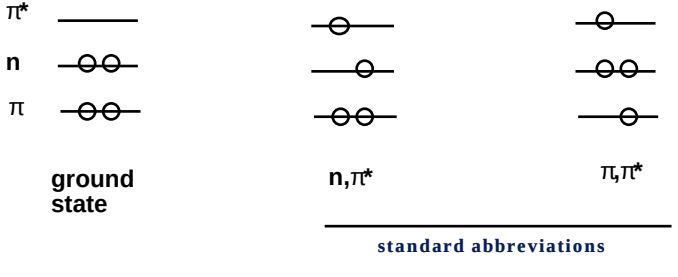

Ground state reactants
hν
Ground state products
Ground state reactants
Excited state reactants
Reaction Intermediates
Ground state products


Ground state reactants
Excited state reactants
Reaction Intermediates
Ground state products
Singlet States
ISC
Triplet States
Internal conversion
Fluorescence
Intersystem crossing from the triplet to the ground state
Phosphorescence
Ground Singlet State

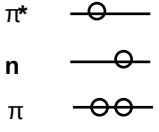
Transitions in formaldehyde

$$\Psi(CH_2{=}O) = (1s_O)^2(1s_C)^2(2s_O)^2(\sigma_{CH})^2(\sigma'_{CH})^2(\sigma_{CO})^2$$
$$(\pi_{CO})^2(n_O)^2(\pi^*_{CO})^0$$

Transitions at relatively low (UV/Vis) energies involve: $(\pi_{CO})^2(n_O)^2(\pi^*_{CO})^0$

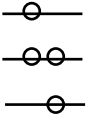


Excited state properties determined by type of excitation



n,π*

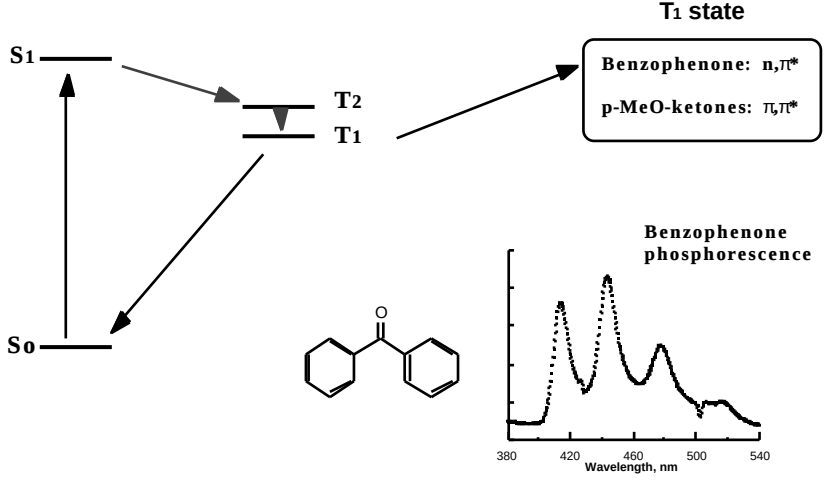
Half-filled orbital localized on oxygen: species resembles an alkoxy radical



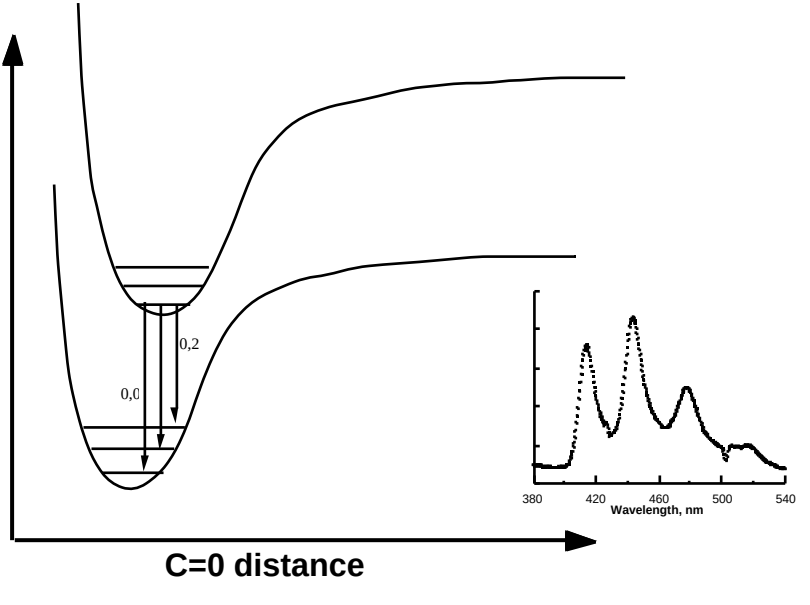
π,π*

Transitions involve only the π system, no free radical properties expected. In aromatic ketones the aryl π system is usually involved

Basics of carbonyl photochemistry



Vibrational structure in benzophenone phosphorescence



Frank-Condon Principle

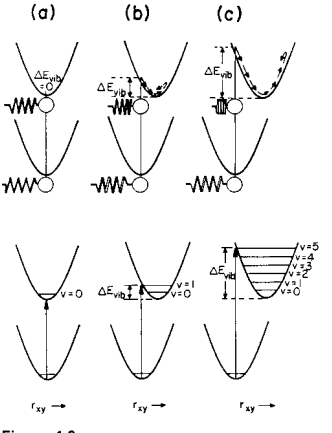


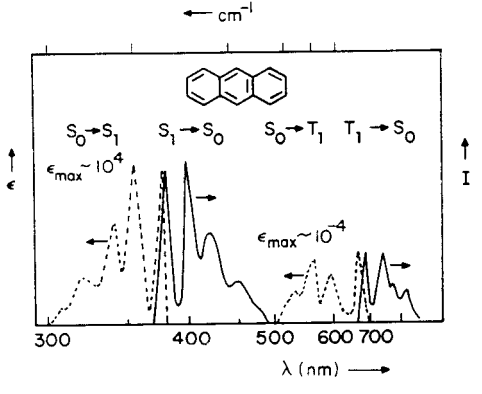
Figure 4.9

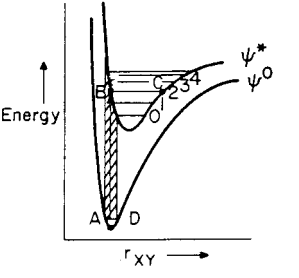
from N.J. Turro, "Modern Molecular Photochemistry", 1978

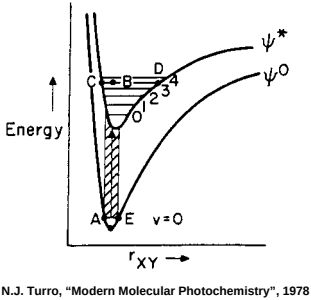
A mechanical analogue to the Frank-Condon principle for radiative transitions. The motion of a point representing the motion of the vibrating atoms is shown as a sequence of arrows. These arrows represent the motion of a representative point on the curve.

Electronic transitions occur sufficiently fast that only "vertical" transitions are of importance. The nuclei are *frozen* as the transition takes place.

Absorption and emission properties of anthracene

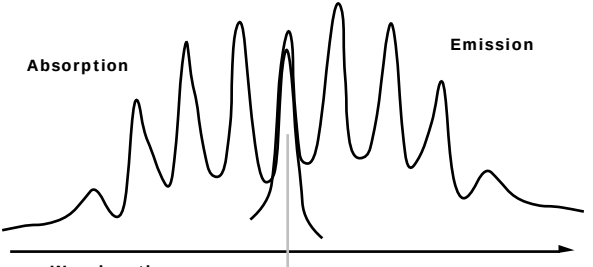






Which is the right set of potential energy curves for this system?

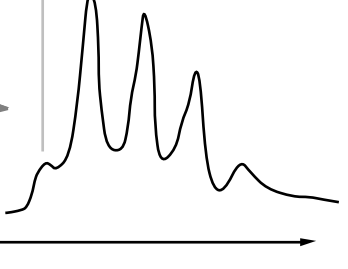
from N.J. Turro, "Modern Molecular Photochemistry", 1978

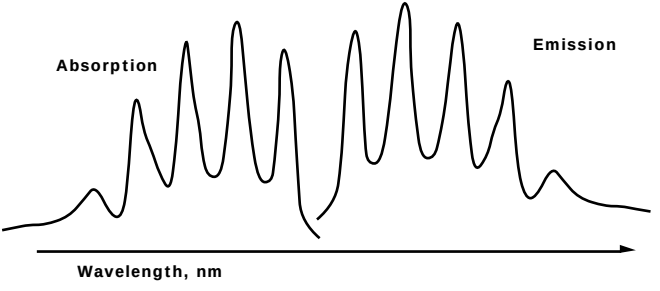


The 0,0 emission band is very small or totally absent.

Origin of the problem ?

Implications in terms of Frank-Condon effects ?





Which is the right set of potential energy curves ?

Vibrational separation determined by type of atoms and of bonds involved

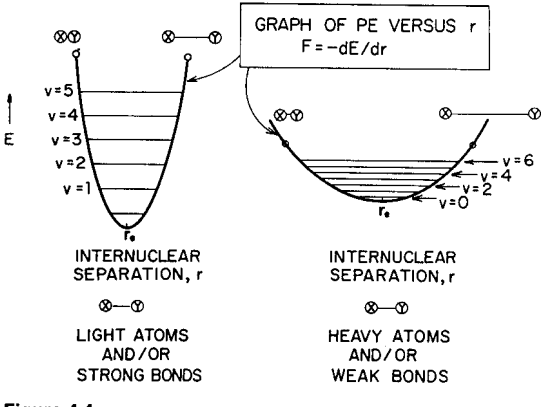
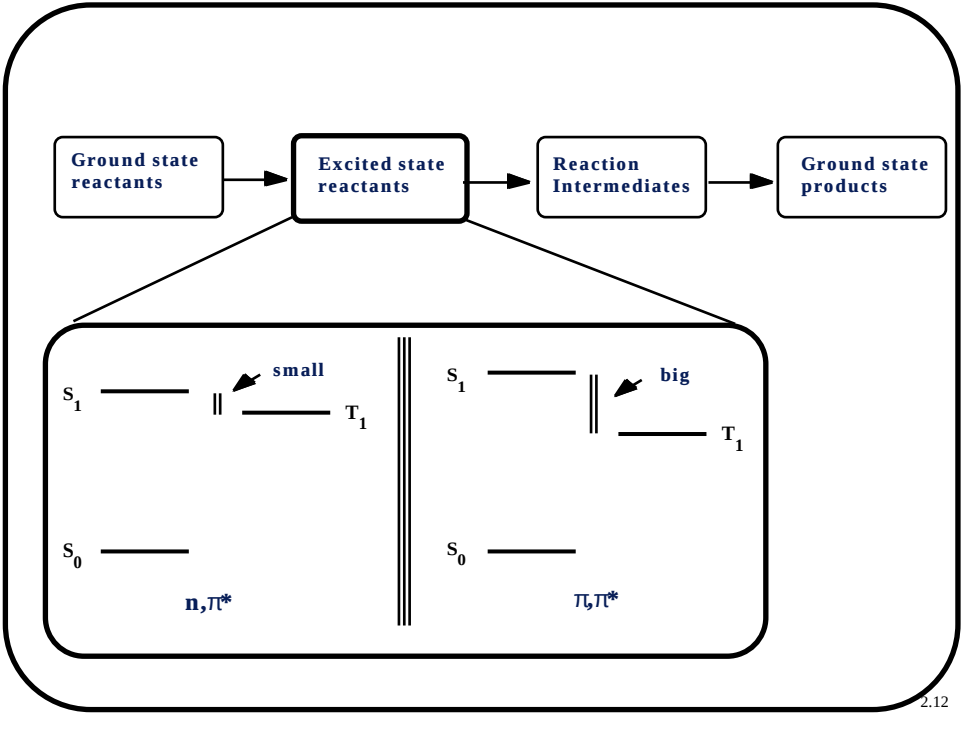


Figure 4.4

Comparison of vibrational spacings for a strong bond (or light atoms) to those for a weak bond (or heavy atoms).

from N.J. Turro, "Modern Molecular Photochemistry", 1978


Ground state reactants
Excited state reactants
Reaction Intermediates
Ground state products
small
S1
T1
S0
n,π*
big
S1
T1
S0
π,π*

Singlet-triplet splitting for states with the same electronic configuration

$E(S_0) = 0$

$E(S_1) = E(n,\pi^*) + K(n,\pi^*) + J(n,\pi^*)$

$E(T_1) = E(n,\pi^*) + K(n,\pi^*) - J(n,\pi^*)$

$$\Delta E_{ST} = 2J(n,\pi^*) > 0$$

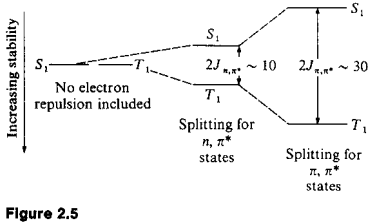
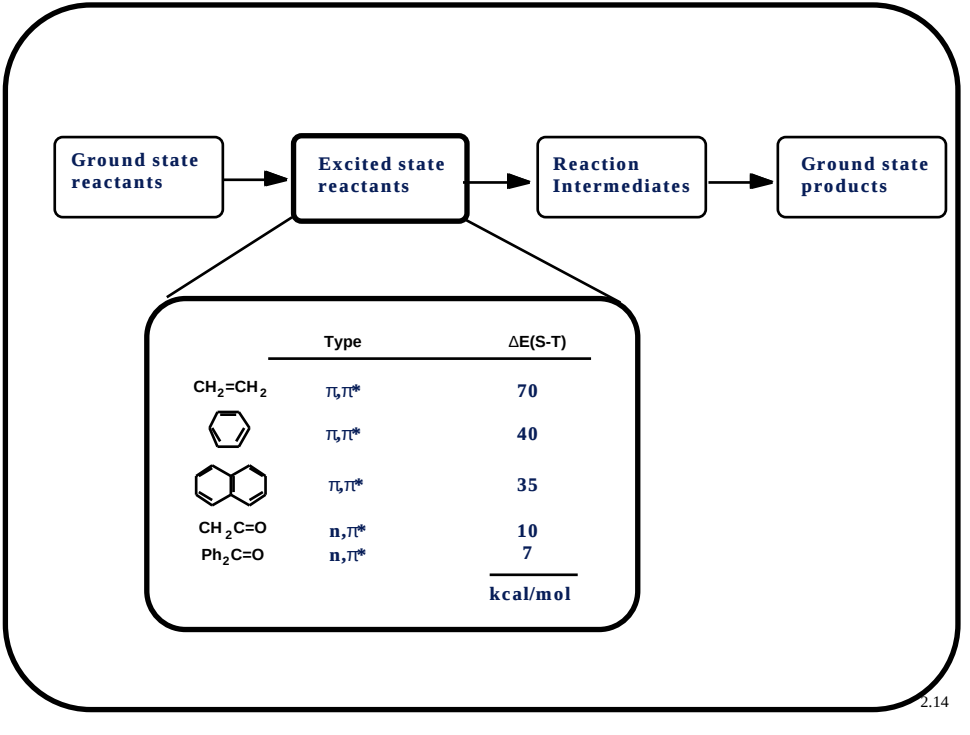
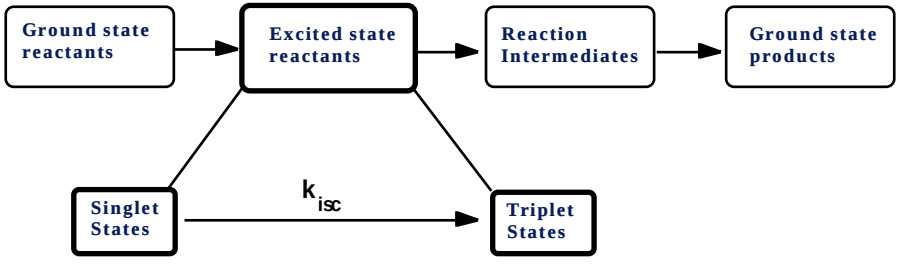


Figure 2.5

Singlet-triplet separation for n, π^* and π, π^* states. Energies in kcal/mole.

from N.J. Turro, "Modern Molecular Photochemistry", 1978


Ground state reactants
Excited state reactants
Reaction Intermediates
Ground state products
Type
ΔE(S-T)
CH2=CH2
π,π*
70
π,π*
40
π,π*
35
CH2C=O
n,π*
10
Ph2C=O
n,π*
7
kcal/mol



Intersystem crossing from the first excited singlet state to the lowest triplet state

Intersystem crossing

Assisted by spin-orbit coupling (SOC)

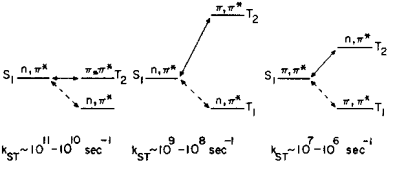
BEST WHEN involving px → py jump
localized on a single atom

El Sayed Rules

n,π* ↔ n,π* Forbidden

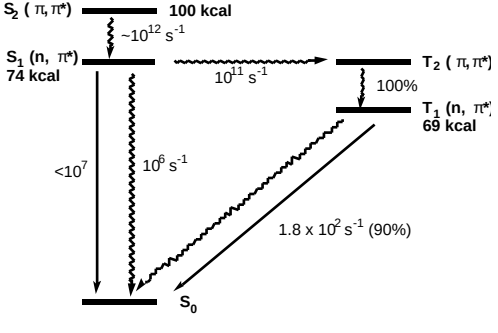
n,π* ↔ π,π* 'Allowed'

π,π* ↔ π,π* Forbidden

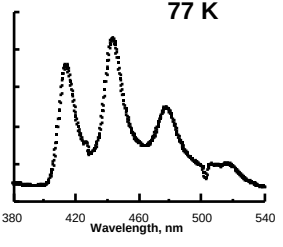


from N.J. Turro, "Modern Molecular Photochemistry", 1978

More on benzophenone



Jablonski diagram at 77 K



Room T

Aspects of an introduction to photochemistry