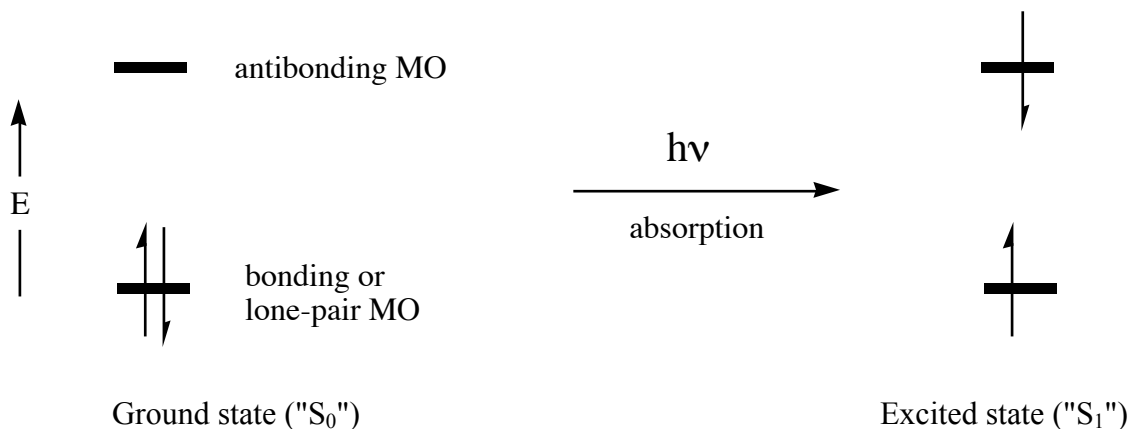


## Lecture outline

### Ultraviolet-visible (UV-vis) Spectroscopy

Absorption of UV or visible light causes *electronic excitation* — promotion of one electron from a filled to an empty molecular orbital (MO)



The energy of the light must match what?

Let's digress briefly into *photophysics* and *photochemistry*.... With the molecule now in the excited state several things can happen:

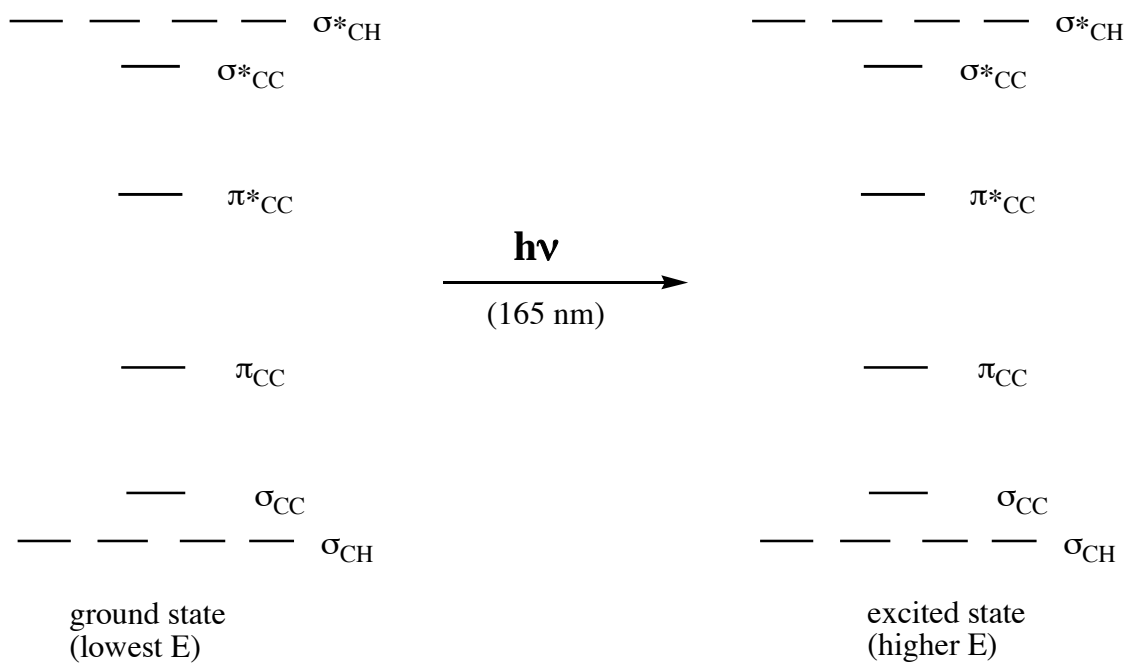
- 1 The electron can fall back down into the bonding orbital (usually within a few ns) and release energy in one of two ways:
- 2 An electron in either of the orbitals can flip its spin to make an excited triplet state ( $T_1$ ).  $T_1$  can then return to the ground state ( $S_0$ ) and release energy in one of two ways:
- 3 Photochemistry can originate from either  $S_1$  or from  $T_1$ .  
Stereoisomerizations, bond cleavages, rearrangements, etc
- 4 The excitation energy can be transferred to another molecule
- 5 An electron can be transferred — from the high-E orbital to another molecule, or from another molecule to the low-E orbital

First, a short refresher on visible and UV light is in order...

Recall what we learned about how atomic orbitals are paired up to make molecular orbitals —

MOs of ethylene,  $\text{H}_2\text{C}=\text{CH}_2$

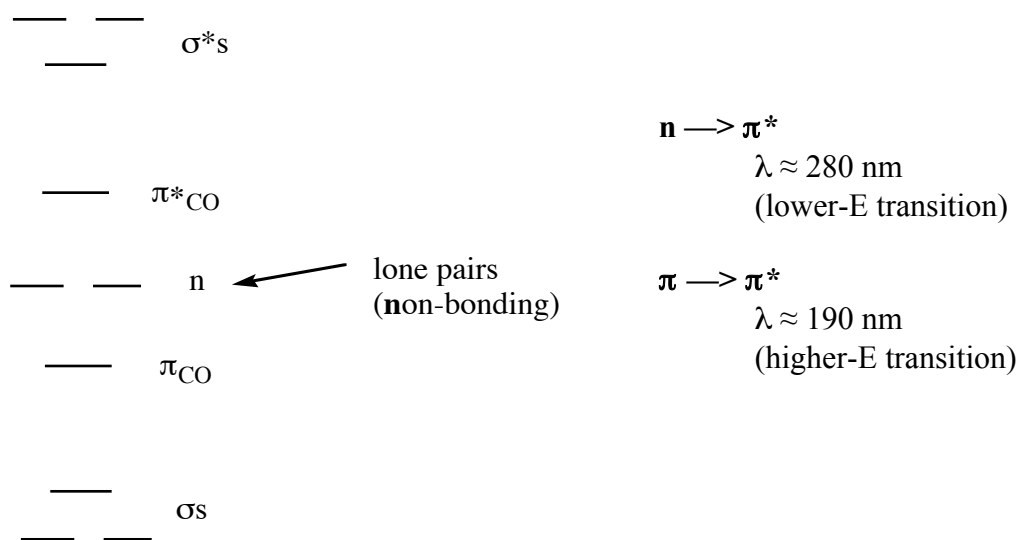
(complete this diagram by filling in the valence electrons)



— transitions involving  $\sigma$  and  $\sigma^*$  orbitals of CC and CH bonds are much higher in energy and are usually not studied.

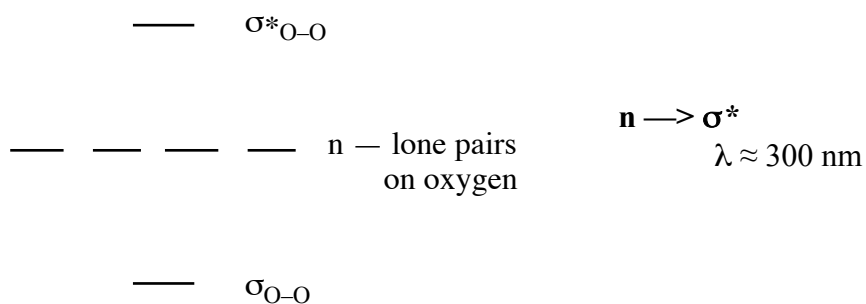
— in general, it is not possible to depict an excited state with a simple Lewis structure. Ethylene is an exception. Think about how the  $\pi$ -bond order changes as a result of promotion of an electron from  $\pi$  to  $\pi^*$ , and draw the Lewis structure for the excited state

H<sub>2</sub>C=O displays two low-E transitions in the UV.



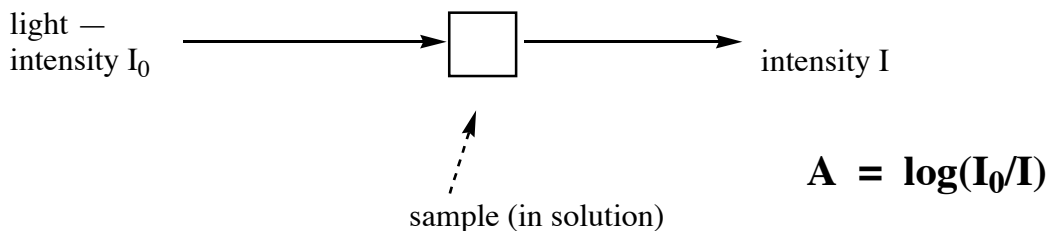
Molecules with weak  $\sigma$ -bonds, like peroxides and halogen molecules ( $X_2$ ) absorb UV and/or visible light and do photochemistry — specifically, they undergo homolytic cleavage of the weak  $\sigma$ -bond, initiated by an  $n \rightarrow \sigma^*$  transition.

e.g., R–O–O–R (a dialkyl peroxide) has an unusually high-E  $\sigma$  and a low-E  $\sigma^*$  MO —



Why does this excitation cause the O–O bond to break?

UV-vis spectrum — absorbance vs  $\lambda$  (typically 200 - 800 nm)



Beer's law —

$$\epsilon = A / c b$$

$A$  = absorbance

$b$  = path length (in cm)

$c$  = concentration (in M)

$\epsilon$  = *extinction coefficient* (or "molar absorptivity")

(units  $M^{-1} cm^{-1}$ )

intrinsic intensity of absorption —

related to probability that light of the correct

$\lambda$  will be absorbed by a particular molecule,

which is related to the electronic transition

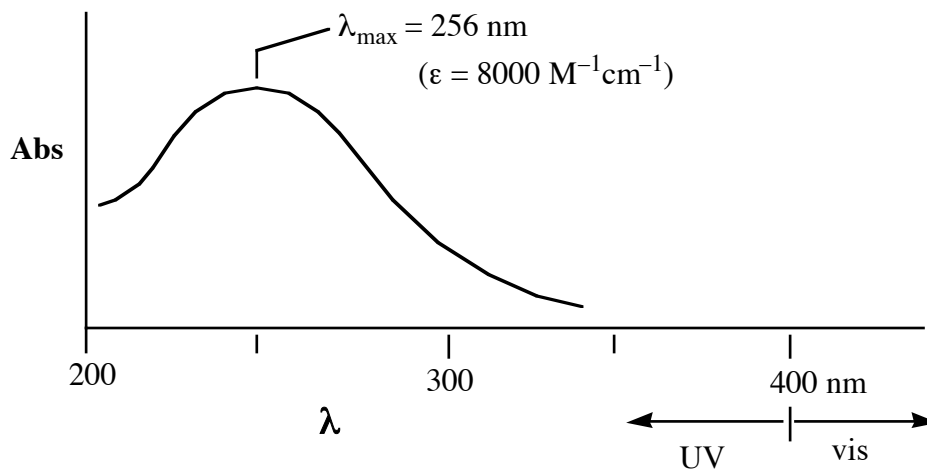
probability

e.g.,

$\pi \rightarrow \pi^*$   $\epsilon \approx 10,000 M^{-1} cm^{-1}$  (relatively intense)

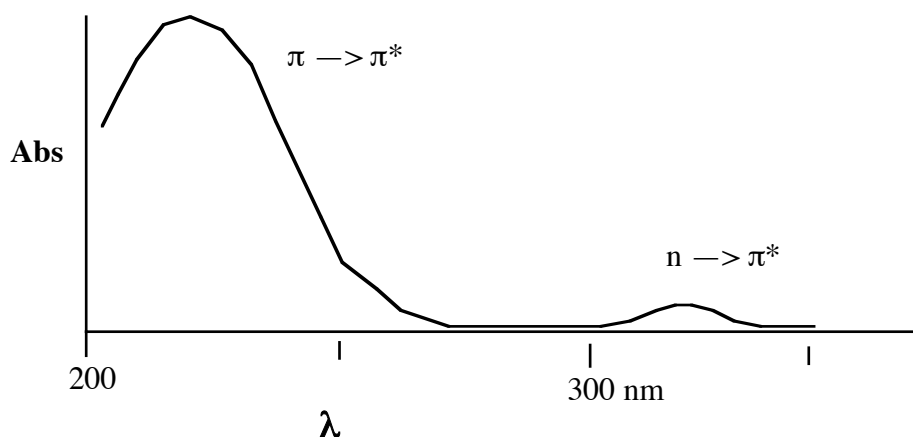
$n \rightarrow \pi^*$   $\epsilon \approx 100 M^{-1} cm^{-1}$  (relatively weak)

Here's the UV-vis spectrum of 1,3-cyclohexadiene in hexane...



Q: Snrzzzzzzzz..... A: Thrilling, ain't it?

Though many UV-vis spectra are featureless blobs, we often see more than one transition, e.g., the spectrum of a conjugated ketone might look like this...



... and in some cases, we see vibrational structure within a transition — several separate, evenly spaced peaks instead of a featureless lump — these come from coupling of the electronic transition with *vibrations* of the excited state.

Q: Now *that's* cool. A: Totally.

Remember that absorption wavelength (usually reported as  $\lambda_{\text{max}}$ ) depends on the  $\Delta E$  between filled and empty MOs. The longest- $\lambda$  (lowest-E) transitions are generally the most important and interesting. The longest- $\lambda$  one is from the **h**ighest **o**ccupied MO (HOMO) to the **l**owest **u**noccupied MO (LUMO).

Factors affecting  $\lambda_{\text{max}}$  for the lowest-E transition(s) —

1. Nature of the **chromophore** — the light-absorbing portion of the molecule
  
2. Type of transition