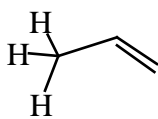
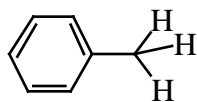
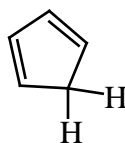


**Back to acidity and basicity:**

ca 35



ca 35



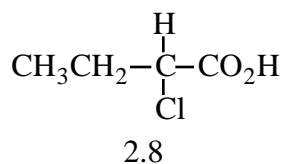
ca 16

Critical point: in the allyl structures (and in the carboxylate example), the negative charge is distributed equally at both of the terminal atoms and not at all at the central carbon. That means when the anion is quenched by addition of water, a proton can return to either end (but not the middle carbon)

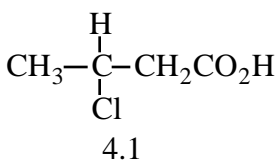
## Phenols

## Inductive effects on the acidity of carboxylic acids:

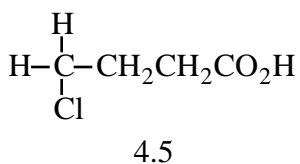
|                                   |                                    |                                    |                                   |
|-----------------------------------|------------------------------------|------------------------------------|-----------------------------------|
| $\text{CH}_3\text{-CO}_2\text{H}$ | $\text{FCH}_2\text{-CO}_2\text{H}$ | $\text{F}_2\text{CH-CO}_2\text{H}$ | $\text{CF}_3\text{-CO}_2\text{H}$ |
| pK <sub>a</sub> 4.8               | 2.7                                | 1.2                                | 0.2                               |



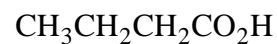
2.8



4.1



4.5



4.8

Summary: resonance and inductive effects rationalize acidity of organic compounds.  
inductive effects depend on electronegativity of attached or nearby atoms  
resonance effects depend on delocalization and stability of contributing structures

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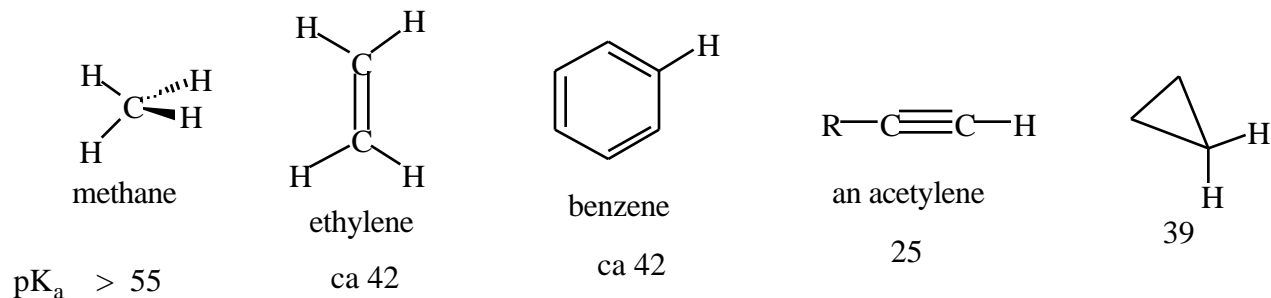
2

One more factor:

Especially in considering the acidity of hydrocarbons:  $\text{CH}_4$   $[\text{:CH}_3]^- + \text{H}^+$

Consider the stability of the orbital in which the electron pair of the anion resides

### HYBRIDIZATION: "s character" effects



### Now: BASICITY

Lewis base: Capable of donating a pair of electrons to a Lewis acid (or  $\text{H}^+$ )

More readily donated--stronger base

less strongly held---more readily donated

Occupying higher energy MO--less strongly held

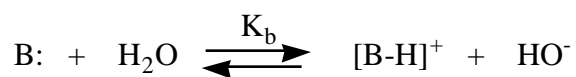


Measure basicity:

(a) related to  $\text{pK}_a$  of the conjugate acid (higher  $\text{pK}_a$  = stronger base)

i.e.,  $\text{pK}_a$  of  $[\text{H-B}]$  relates to the base strength of  $\text{:B}^-$ .

(b) can define  $\text{pK}_b$  which relates directly to base strength in water



$$\text{p}K_b = 14 - \text{p}K_{a(\text{BH})}$$

$$K_b = \frac{[\text{B-H}]^+ [\text{HO}^-]}{[\text{B:}] [\text{H}_2\text{O}]} = \left( \frac{[\text{B-H}]^+}{[\text{B:}] [\text{H}^+]} \right) \left( \frac{[\text{HO}^-] [\text{H}^+]}{[\text{H}_2\text{O}]} \right)^3$$

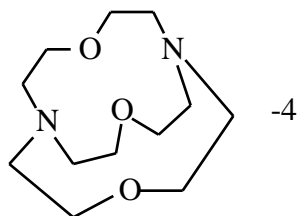
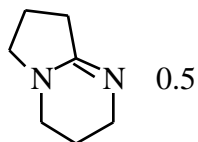
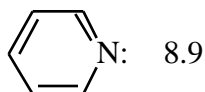
$$= \left( \frac{1}{K_{a(\text{BH})}} \right) \left( K_{a(\text{H}_2\text{O})} \right)$$

Amines are the most common organic bases:

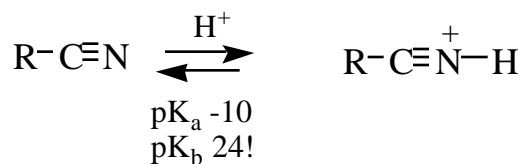
Data:  $\text{p}K_b$

$\text{:NH}_3$  4.7

$(\text{CH}_3)\text{NH}_2$  3.4

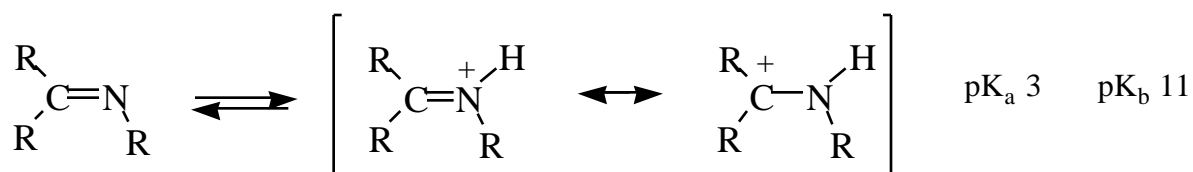


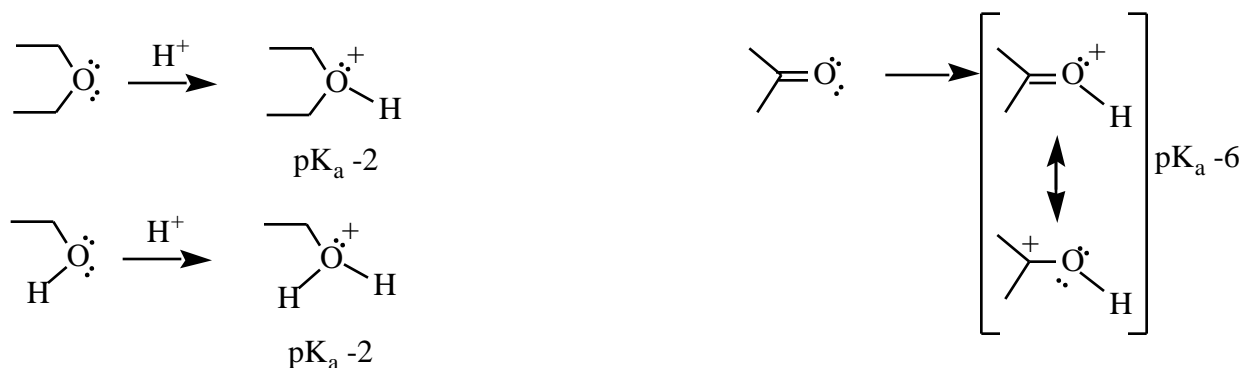
**Hybridization effects:** *extreme in nitriles*



**sp** hybridization,  
non-bonding electrons tightly held: weak base

*intermediate in imines:*  $\text{sp}^2$  hybridization



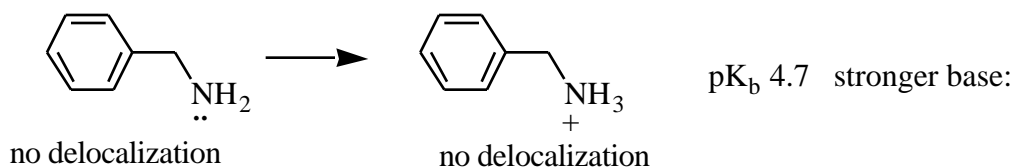
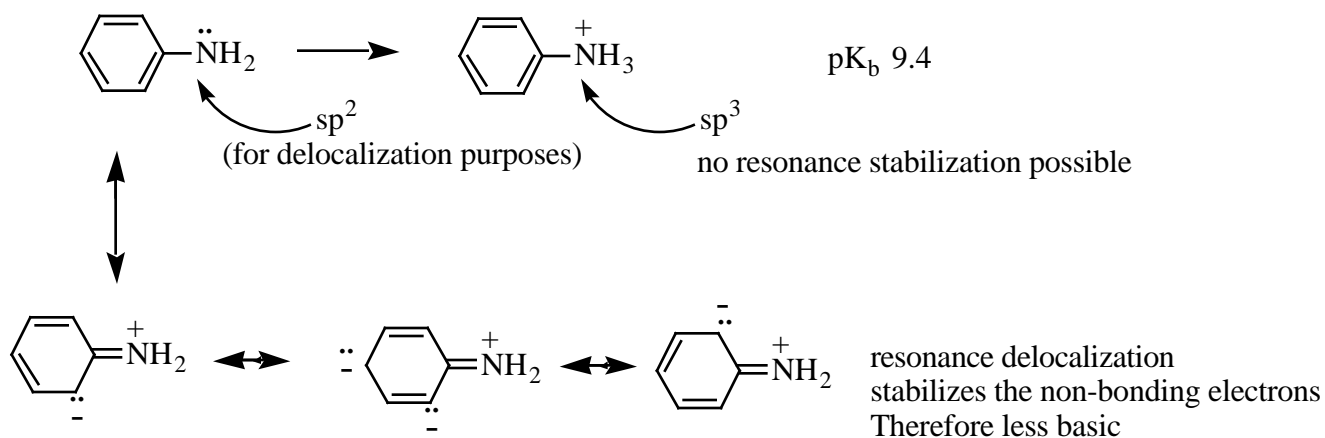


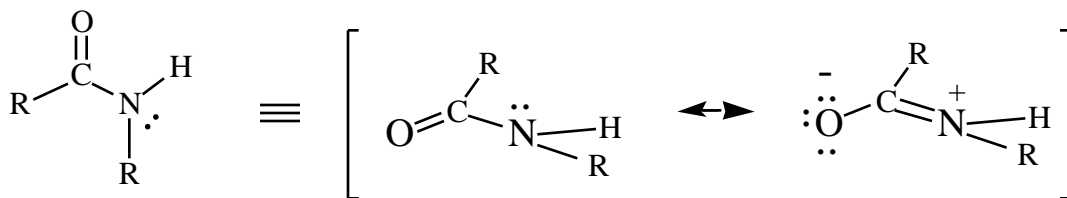
Reasons for the differences in  $pK_a$  not simple--solvent effects, ambiguous hybridization, etc.

Most important conclusion is that the oxygen in an ether, alcohol, or carbonyl group can serve as a (very) weak base. This will be important in considering reactions of these groups.

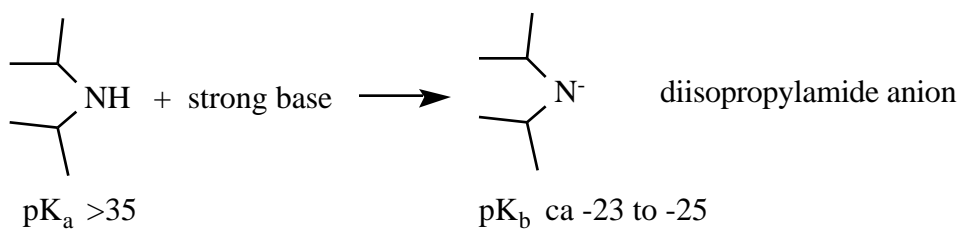
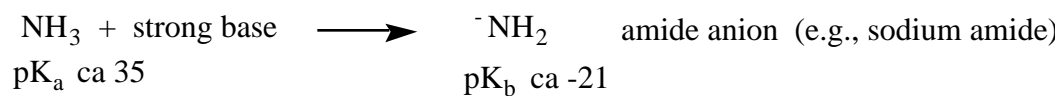
### Special cases:

#### a. aniline derivatives



**b. amides**

relatively non-basic

 $\text{pK}_a$  ca 0 to -1 $\text{pK}_b$  ca 14-15**c. Nitrogen anions:****e.g., lithium diisopropyl amide, LDA**

Ultraviolet spectroscopy;

Infrared spectroscopy;

Nuclear magnetic resonance spectroscopy

General basis of spectroscopy:

Shine light at a collection of molecules      monitor response  
interpret in terms of molecular structure

Analogy with photography; measure reflection, monitor with dyes which change color depending on wavelength (color) and intensity of light reflected.

Spectroscopy: usually measure absorption of light energy, monitor change in intensity of light as passes through sample.

Different structure features (functional groups, pi bonds) cause absorption of different wavelengths of the light beam.

Interpretation:

- a. quantum mechanics
- b. empirical correlations--study many known structures, develop correlations or patterns.

Molecules can absorb (or emit) radiant energy in quanta of photons

$E = nh$        $E$  = energy of light being absorbed  
                  $n$  = integer (# of quanta)  
                  $h$  = Planck's constant  
                 = frequency of light waves

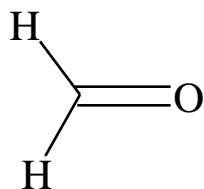
$h$  = energy of one quanta

Consider ELECTRONIC EXCITATION:

Light is absorbed and an **electron** moves from one orbital to a higher energy orbital.

The energy transferred,  $h$ , must exactly match the energy gap between orbitals.

What energies are we talking about? Consider formaldehyde (a fairly complicated case)

**Orbitals:**

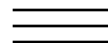
2 (1s) atomic orbitals on C,O

2 C-H and 2 C-H \*

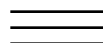
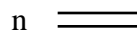
1 C-O and 1 C-O \*

1 C-O and 1 C-O \*

2 n-type on O



Total of 12 orbitals, 8 are filled



Energy can be absorbed to promote an electron to a higher, empty (or half filled) orbital.

Possible combination: n

n

70-150 Kcal/mol  
convenient range>150 Kcal/mol  
possible, but not commonWhat type of radiation for 70-150 Kcal/mol. Recall:  $E = hc/\lambda$ 

150 kcal/mol = 195 nm (wavelength, ) longer wavelength, lower energy per photon

|              |   |                    |   |                |   |                 |   |                  |
|--------------|---|--------------------|---|----------------|---|-----------------|---|------------------|
| <b>X-ray</b> | / | <b>ultraviolet</b> | / | <b>visible</b> | / | <b>infrared</b> | / | <b>microwave</b> |
| 100 nm       |   | 400 nm             |   | 800 nm         |   | 25000 nm        |   | 25 mm            |
|              |   | 70 kcal/mol        |   |                |   |                 |   | 1 kcal/mol       |

Practical cut-off: **vacuum UV** / **UV**

180 nm

160 kcal/mol

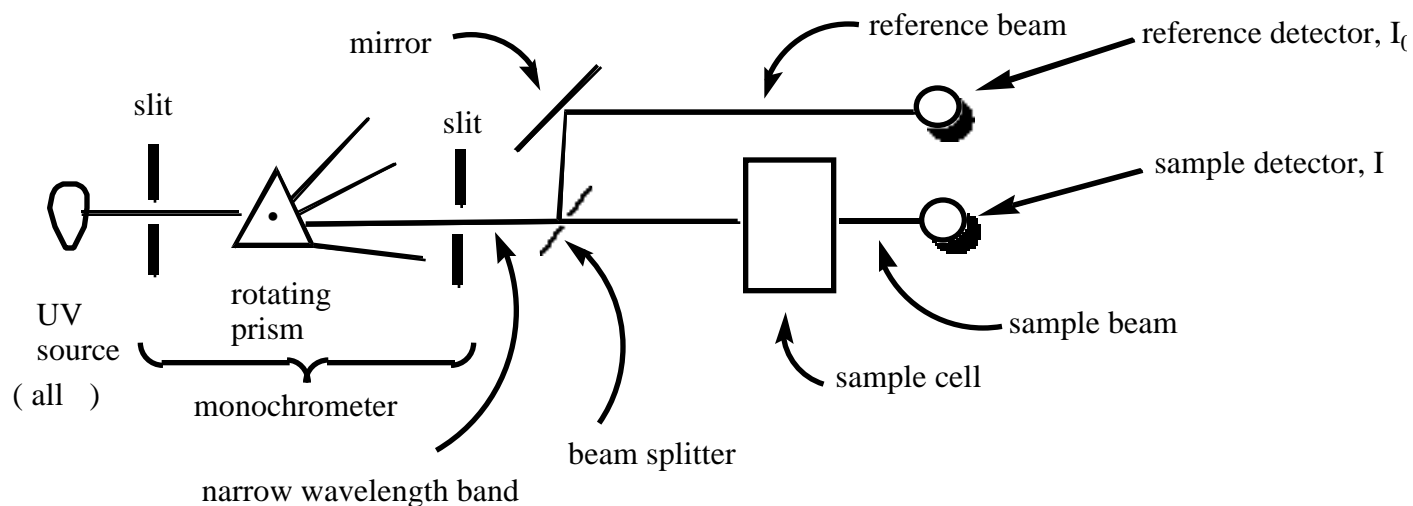
So for organic structure analysis, convenient to use light of  $\lambda = 180-400 \text{ nm}$  (ultraviolet)

8

$$E = 160-70 \text{ Kcal/mol}$$

$n$  only (others too high energy jump)

Mechanics:



### Experiment:

systematically change  $\lambda$  by rotating the prism, allow light of different  $\lambda$  to pass through the sample.

Measure  $I$ , the intensity of transmitted light. Compare with incident intensity (before sample; reference beam)

Calculate:  $A = \log_{10} (I/I_0) = \epsilon c d$   $\epsilon$  = extinction coefficient (characteristic of molecule)

$d$  = path length of sample cell in cm

$c$  = concentration of sample in moles/L

depends on overlap of orbitals involved in the electron jump:  $\epsilon$  good overlap, high (1000-10,000)

$n$  poor overlap, low (10-100)

Can use for quantitative purposes: for pure compound, get  $\epsilon$ .

if know  $\epsilon$ , can measure amount ( $c$ ) of cpn in a solution (measure  $A$ ,  $d$ )

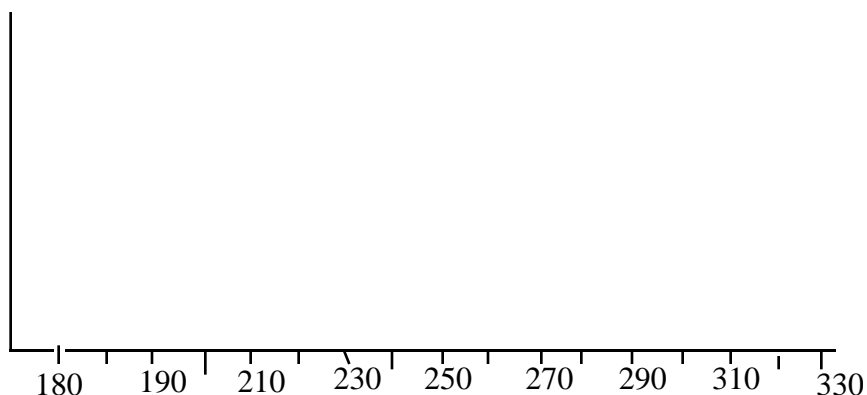


Consider the UV spectrum of ethylene:

two observations:

$$\lambda_{\text{max}} = 180 \text{ nm} \quad = 12,000$$

peak is broad. Why?



Each electronic state has a collection of vibrational states associated with it.

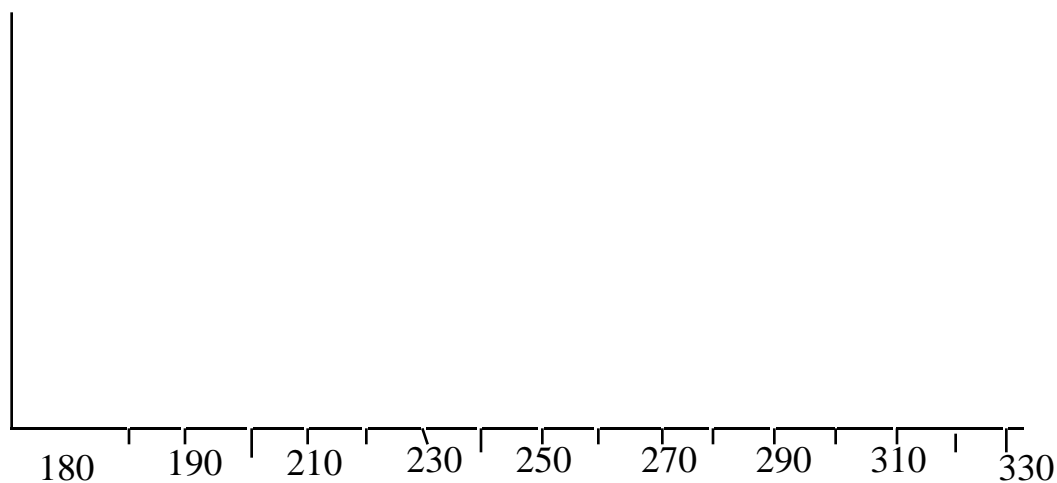
In promoting the electron, can arrive at several different vibrational levels of higher state.

The absorption is an envelope of all excitations,

$E_0$   $E_1$  (at various vibrational levels).

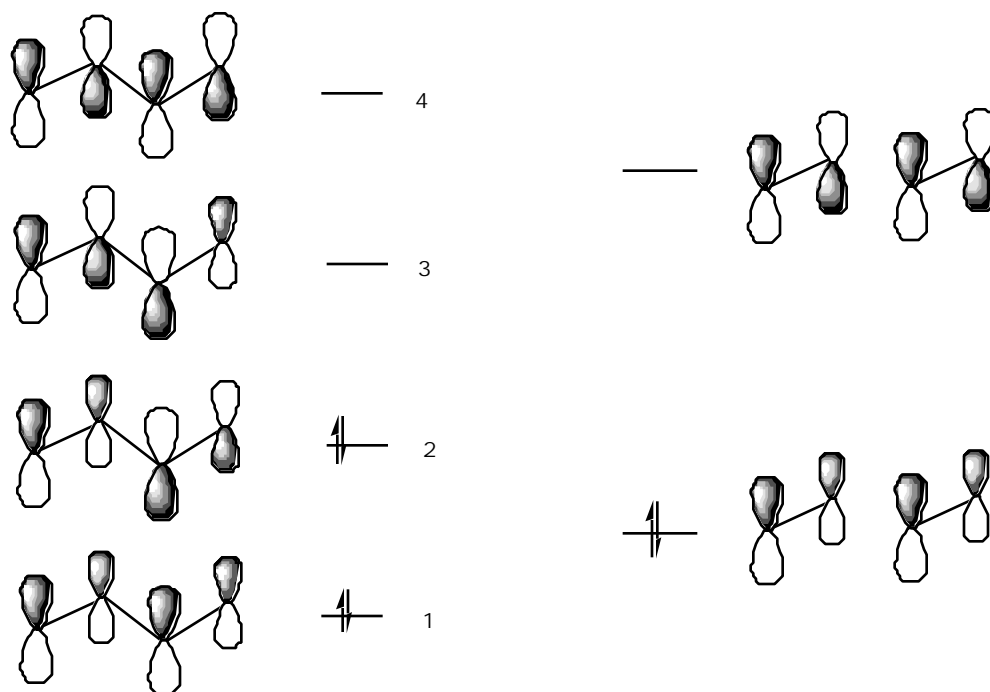
Can observe vibrational "fine structure":

Consider the UV spectrum of ethylene at "high resolution"

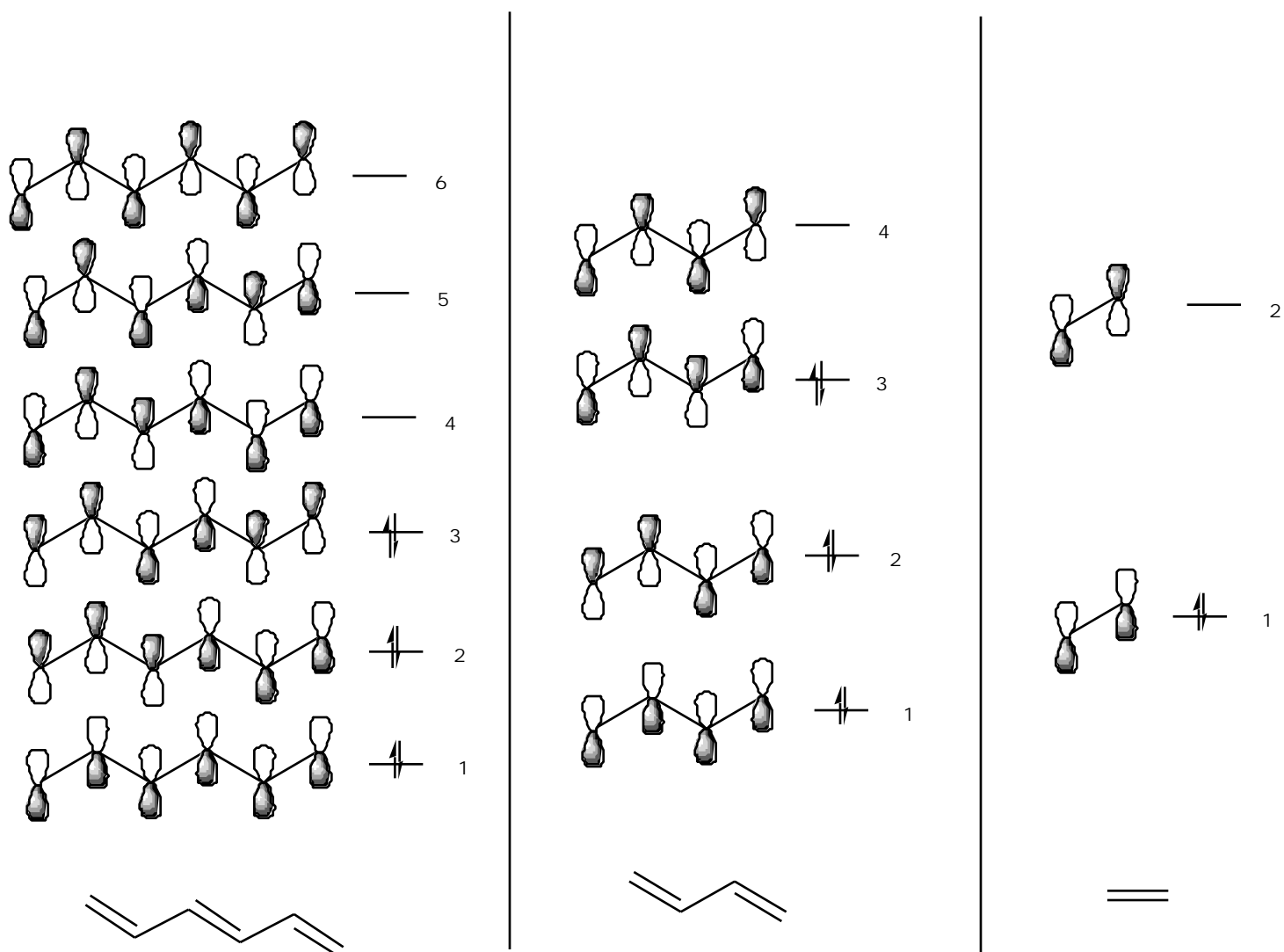


Record  $\lambda_{\text{max}}$ . For simple spectra, characterize the molecule by  $\lambda_{\text{max}}$  at longest (lowest energy)

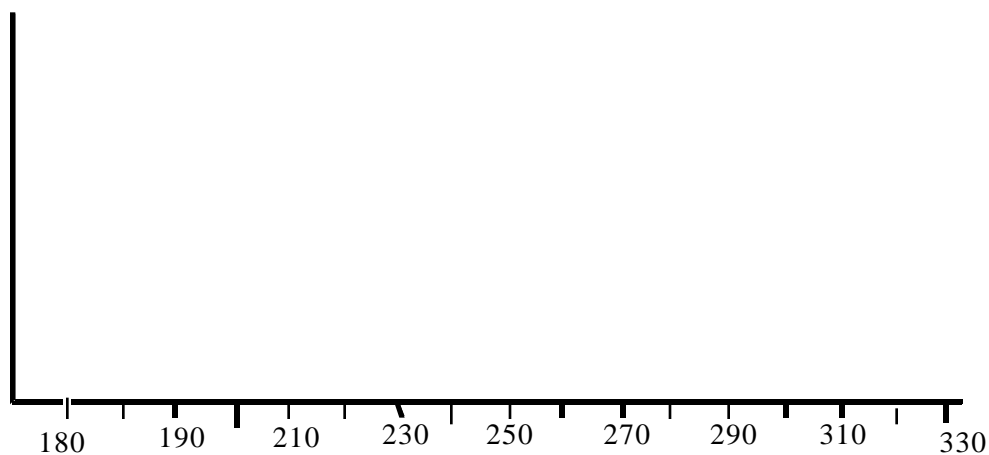
Now: consider 1,3-butadiene. Predict the UV spectrum. Two ethylenes? Same  $\lambda_{\text{max}}$ , twice the ? No.



Consider 1,3,5-hexatriene: 6 p orbitals give 6 MOs



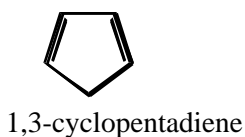
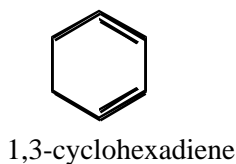
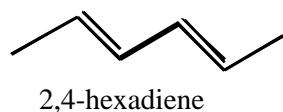
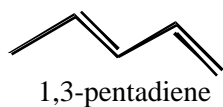
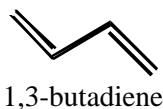
Lowest energy gap between filled and unfilled is  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  smaller compared to 1,3-butadiene lowest energy  $\lambda_{\text{max}}$  is 268 nm



$\pi$  bonds OR  $n$  electrons on or adjacent to an atom participating in a  $\pi$  bond MUST be present in order to see a UV absorption. Sigma bonds lead to a too-high energy gap to the nearest antibonding orbital, and cannot be excited with radiation of energy corresponding to wavelengths above 180 nm.

Additional conjugation (additional  $\pi$  bond) leads to an incremental decrease for the energy gap between the highest filled orbital and the lowest empty orbital, and a corresponding increase in  $\lambda_{\text{max}}$ .

Substituent effects:



In a typical ketone, the MO distribution has a high lying  $\pi$  orbital and a still higher energy set of non-bonding electrons (highest filled orbitals).

The  $\pi^*$  is still the lowest empty orbital, as in ethylene, but now the  $n \rightarrow \pi^*$  transition is the lowest energy, longest wavelength, absorption

There are then two maxima, a strong one for the  $\pi \rightarrow \pi^*$  and a weaker one for  $n \rightarrow \pi^*$ .

UV spectroscopy is a detector of  $\pi$  bonds; no  $\pi$  bonds--no UV absorption

position of  $\lambda_{\text{max}}$  for longest  $\lambda_{\text{max}}$  number of interacting p orbitals

intensity: low =  $n \rightarrow \pi^*$  high =  $\pi \rightarrow \pi^*$

