UV Spectroscopy:

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
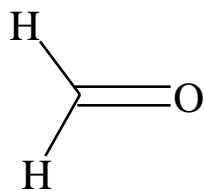   = frequency of light waves

    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.

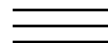What energies are we talking about? Consider formaldehyde (a fairly complicated case)

H
‖
C=O
/
H

Orbitals:
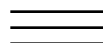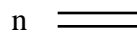
2 (1s) atomic orbitals on C,O

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

n ═══

───

═══

s ══

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

Possible combination: n   n

70-150 Kcal/mol   >150 Kcal/mol
convenient range   possible, but not common

What type of radiation for 70-150 Kcal/mol.   Recall: = c/   E = h

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

X-ray   /   **ultraviolet**   /   **visible**   /   **infrared**   /   **microwave**
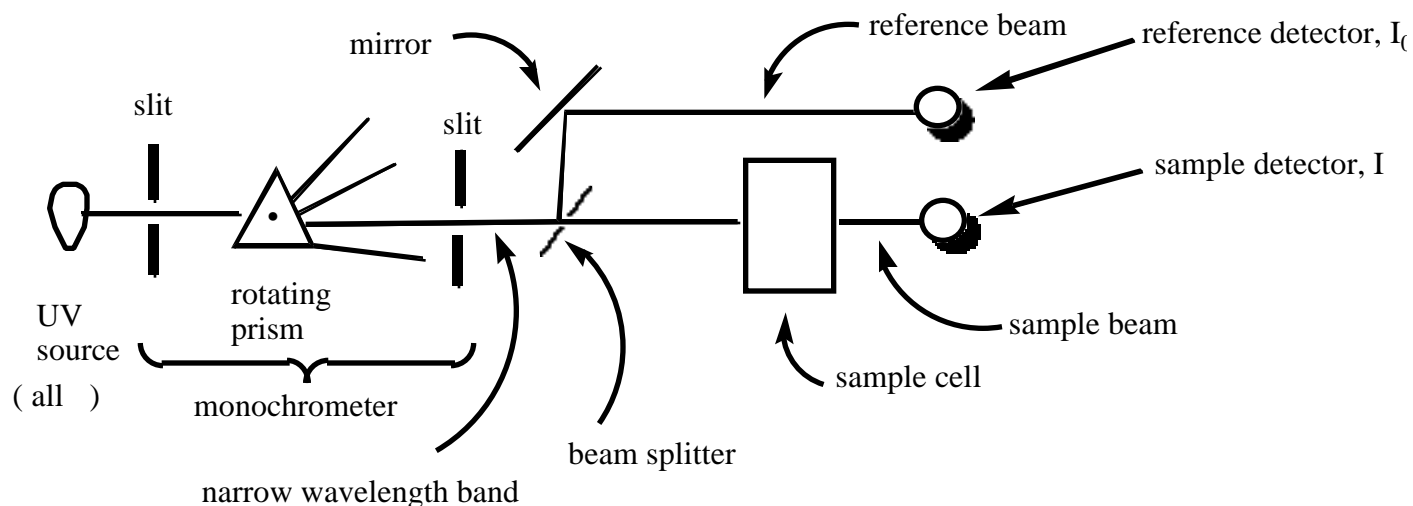100 nm   400 nm   800 nm   25000 nm   25 mm
                                70 kcal/mol   1 kcal/mol

Practical cut-off: **vacuum UV   /   UV**
                                      180 nm
                                      160 kcal/mol

So for organic structure analysis, convenient to use light of   = 180-400 nm (ultraviolet)
                                                                          E = 160-70 Kcal/mol

            n   only (others too high energy jump)

Mechanics:

Experiment:

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

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

Calculate: $A = \log_{10}(I/I_O) = \quad dc \qquad$ = 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: $\qquad$ good overlap, high   (1000-10,000)

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

Can use for quantitative purposes: for pure compound, get .

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

Consider the UV spectrum of ethylene:

two observations:

$_{max}$ = 180 nm $\quad$ = 12,000
peak is broad. Why?
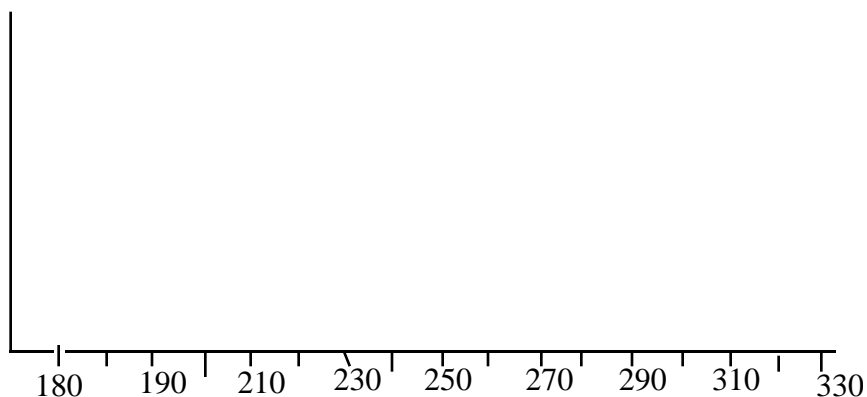
Each electronic state has a collection of vibrational states associated with it.
In promoting the electron, can arrive at several different vibrational levels of higher state.
The absorption is an envelope of all excitations, $E_O \quad E_1$ (at various vibrational levels).
Can observe vibrational "fine structure":

Consider the UV spectrum of ethylene at "high resolution"

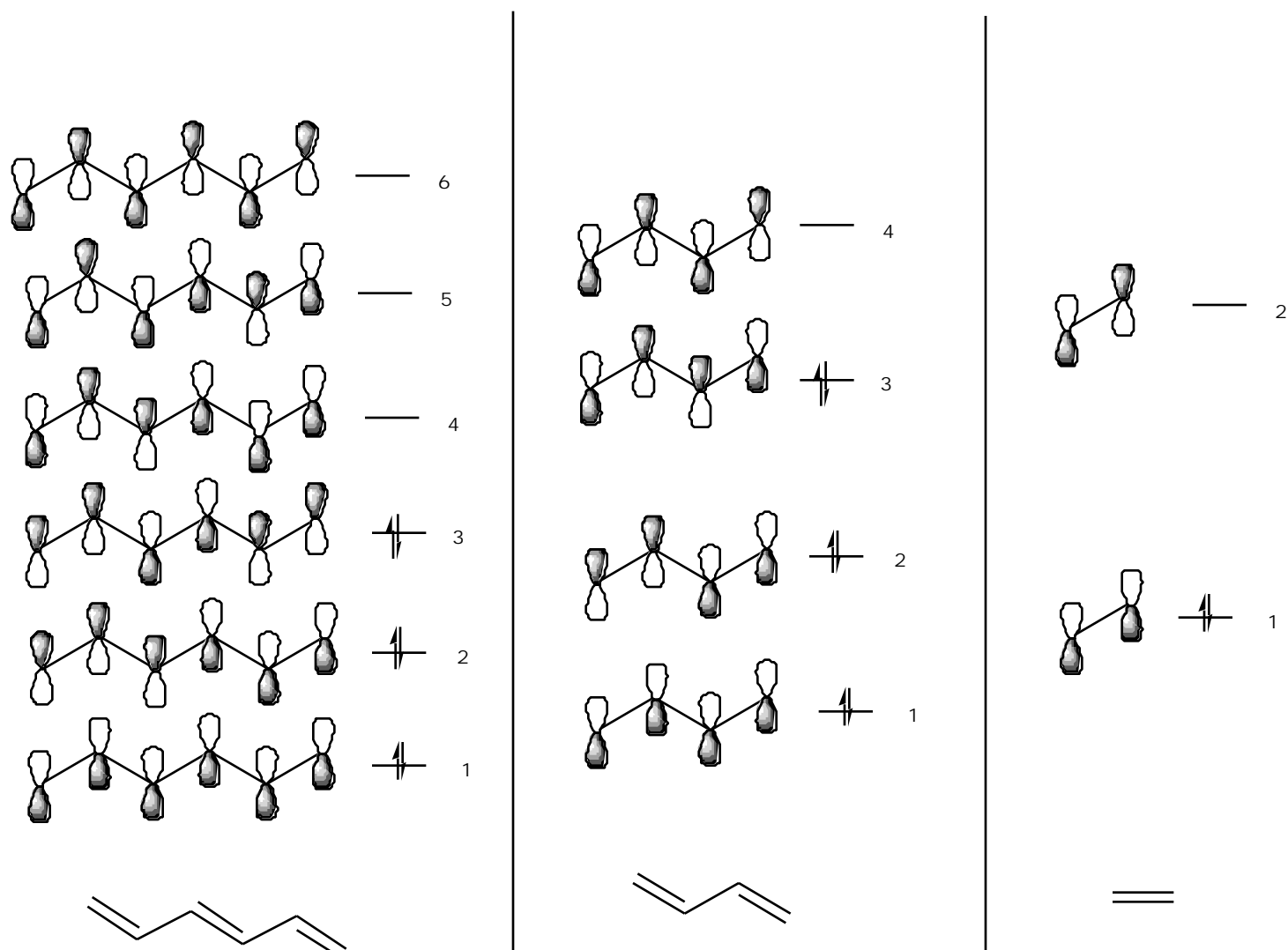|								
180	190	210	230	250	270	290	310	330
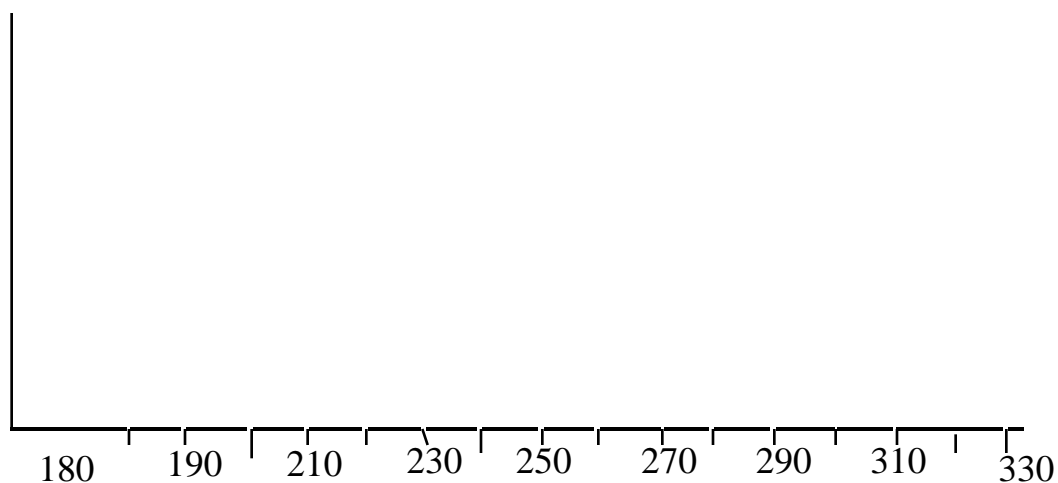
Record λ for $_{max}$. For simple spectra, characterize the molecule by ϵ and λ_{max} at longest λ (lowest energy). For complete description, assign λ_{max} and ϵ to each significant maximum

Now: consider 1,3-butadiene. Predict the UV spectrum. Two ethylenes? Same λ_{max}, twice the ϵ? No.
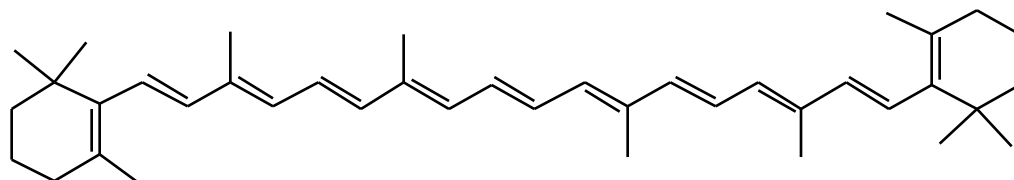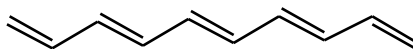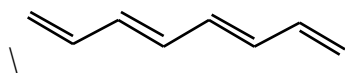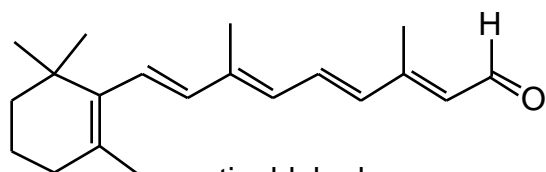
180 190 210 230 250 270 290 310 330
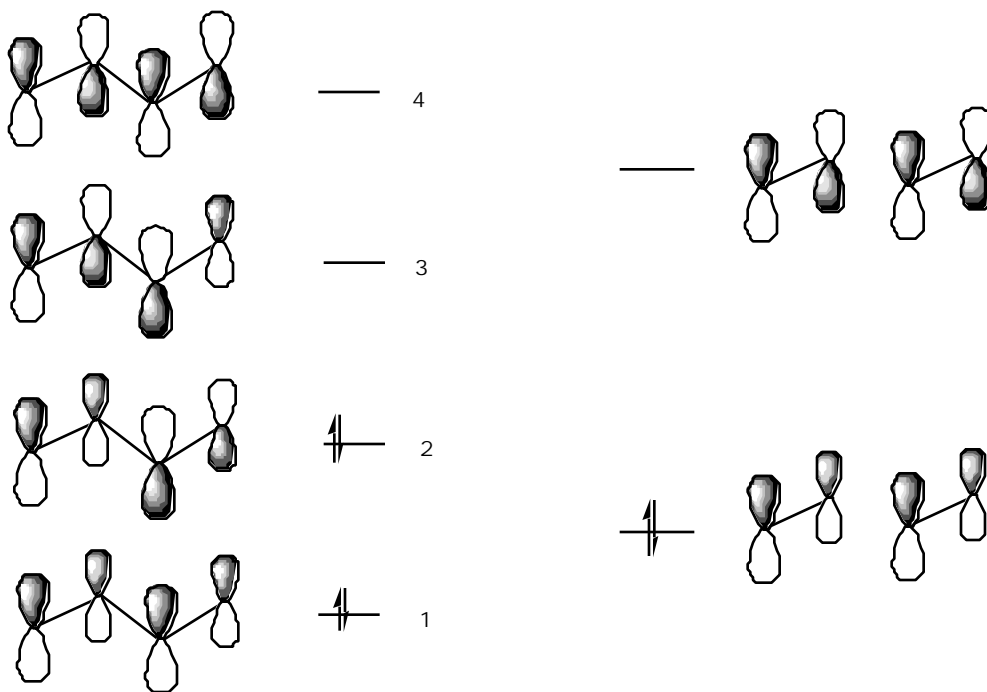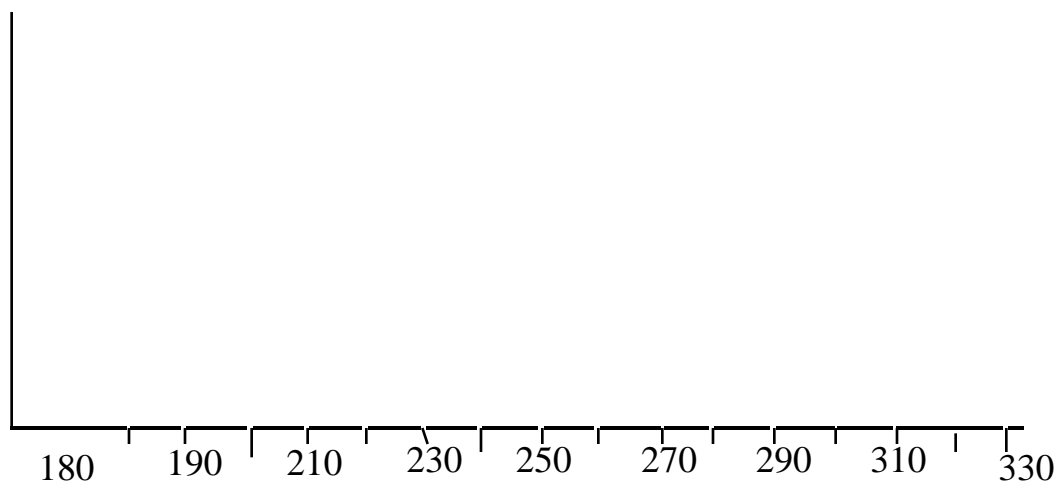
Consider 1,3,5-hexatriene: 6 p orbitals give 6 MOs

— 6

— 5

— 4

⫴ 3

⫴ 2

⫴ 1

— 4

⫴ 3

⫴ 2

⫴ 1

— 2

⫴ 1
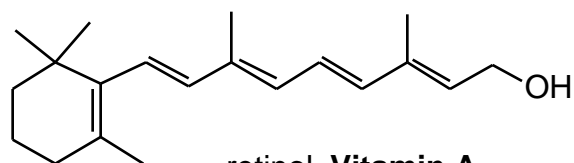
Lowest energy gap between filled and
         unfilled is   3 and   4
         smaller compared to 1,3-butadiene
         lowest energy $_{max}$ is 268 nm
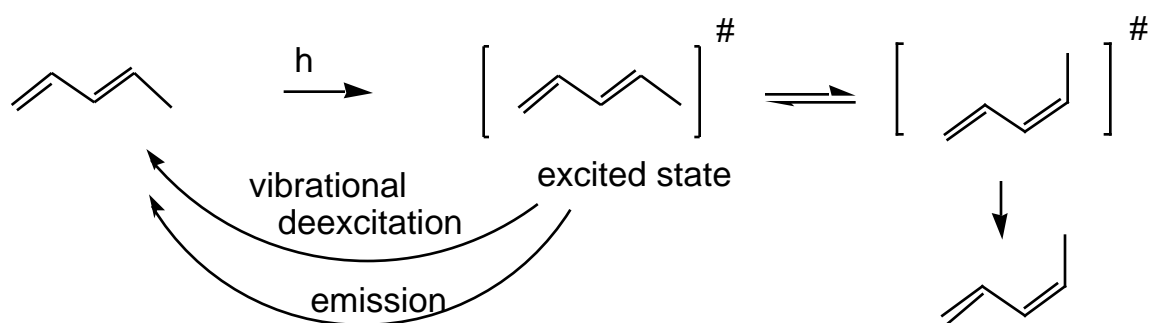
β–carotene λ_{max} 453, 483

retinaldehyde

retinol **Vitamin A**

What actually happens to the molecule after absorption of the photon: PHOTOCHEMISTRY

hν

excited state

vibrational
deexcitation

emission

Photoisomerization of *trans* to *cis* 1,3-pentadiene

7

all trans retinal

cis-retinal

opsin

H₂N—

rhodopsin

=N—

h

opsin

H₂N—

+