SPECTROSCOPY

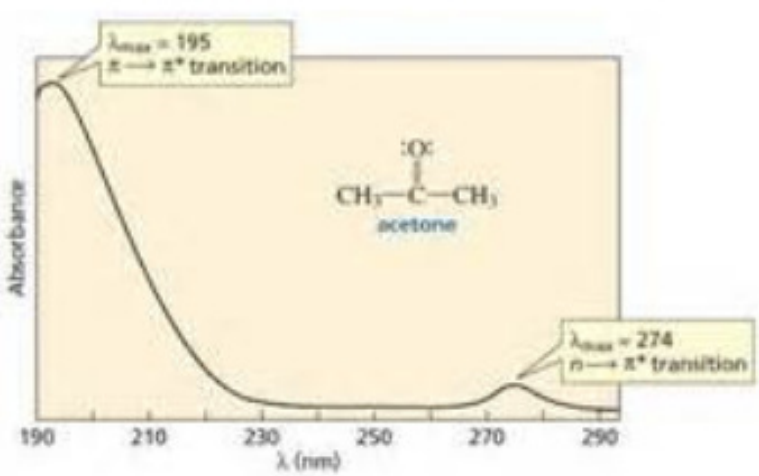
What is spectroscopy?

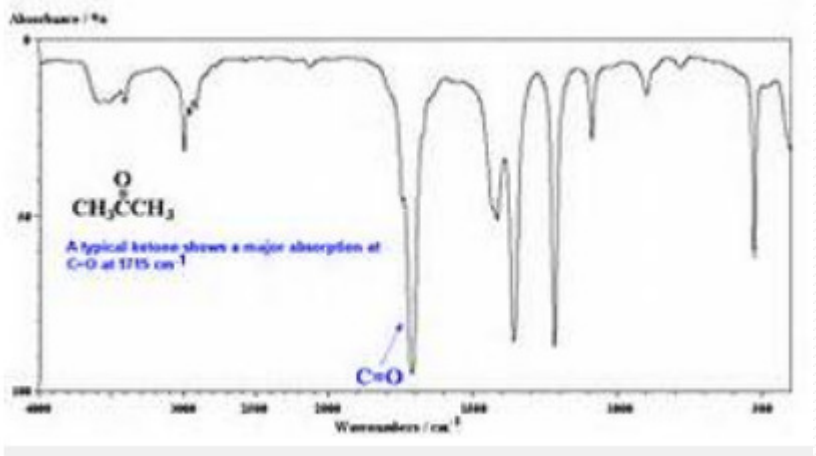
Studying the properties of matter through its interaction with different frequency components of the electromagnetic spectrum.

Latin: "spectron"—ghost or spirit
Greek: "σκοπειν"—to see

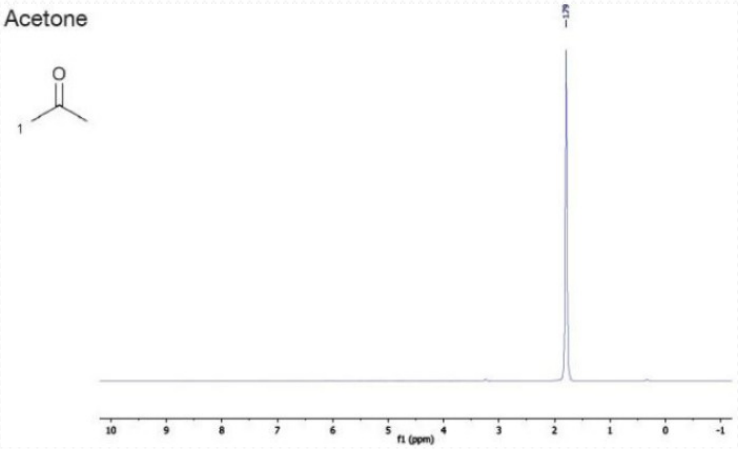
With light, you aren't looking directly at the molecule—the matter—but its "ghost." You observe the light's interaction with different degrees of freedom of the molecule. Each type of spectroscopy—different light frequency—gives a different picture → ***the spectrum***.

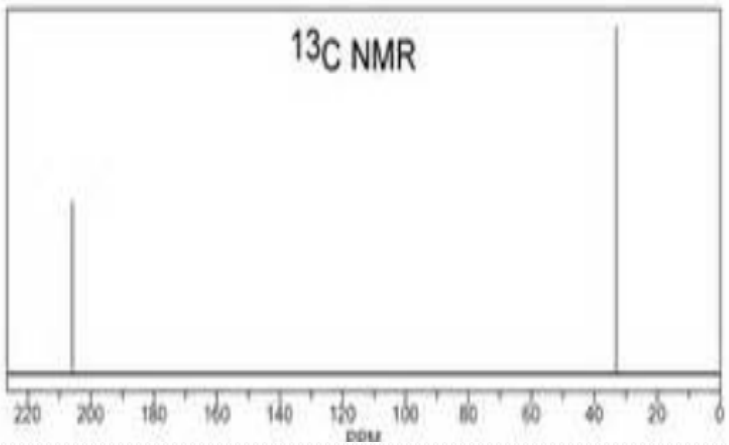
Spectroscopy is a general methodology that can be adapted in many ways to extract the information you need (energies of electronic, vibrational, rotational states, structure and symmetry of molecules, dynamic information).

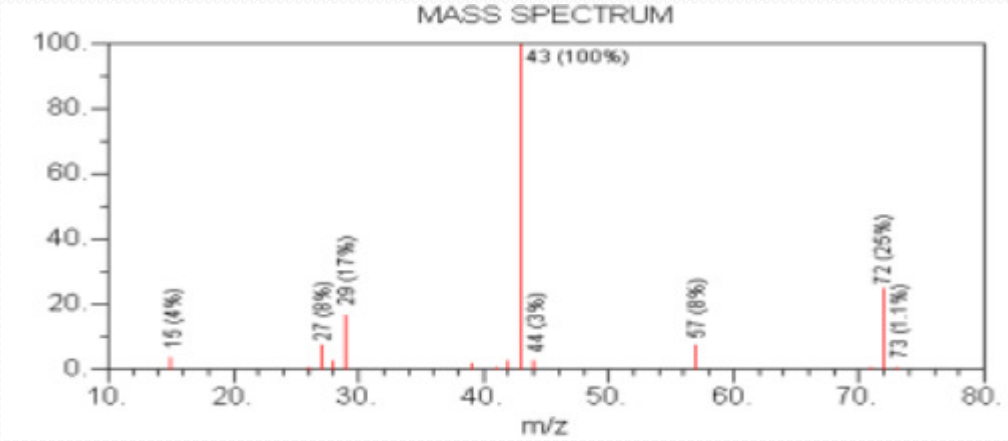

λmax = 195
π ⟶ π* transition
:O:
CH3—C—CH3
acetone
λmax = 274
n ⟶ π* transition
Absorbance
190
210
230
250
270
290
λ (nm)


CH3CCH3
A typical ketone shows a major absorption at C=O at 1715 cm-1
C=O
Wavenumbers / cm-1

Acetone


O
1
f1 (ppm)

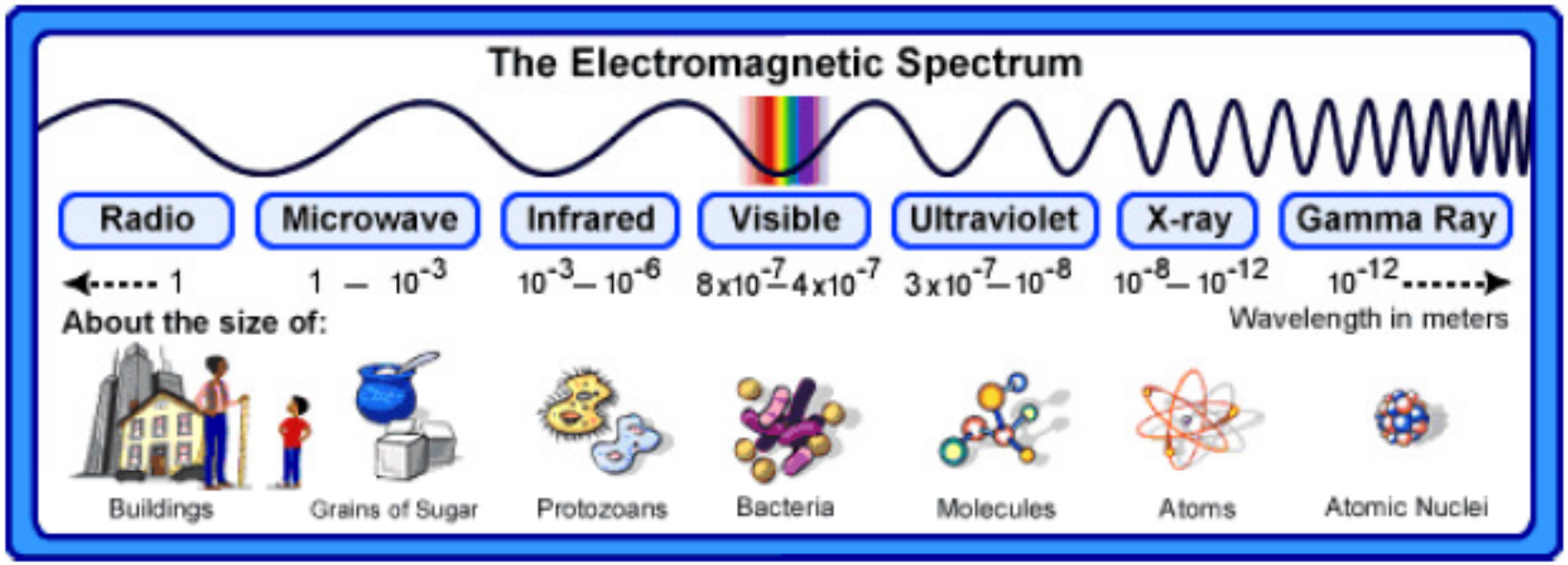

13C NMR


MASS SPECTRUM
43 (100%)
15 (4%)
27 (8%)
29 (17%)
44 (3%)
57 (8%)
72 (25%)
73 (1.1%)
m/z

Goals:

- Understand how light interacts with matter and how you can use this to *quantitatively* understand your sample.
- Understand spectroscopy the way you understand other common tools of measurement like the watch or the ruler.
- See that *spectroscopy is a set of tools that you can put together in different ways to understand systems* → solve chemical problems.

The Electromagnetic Spectrum



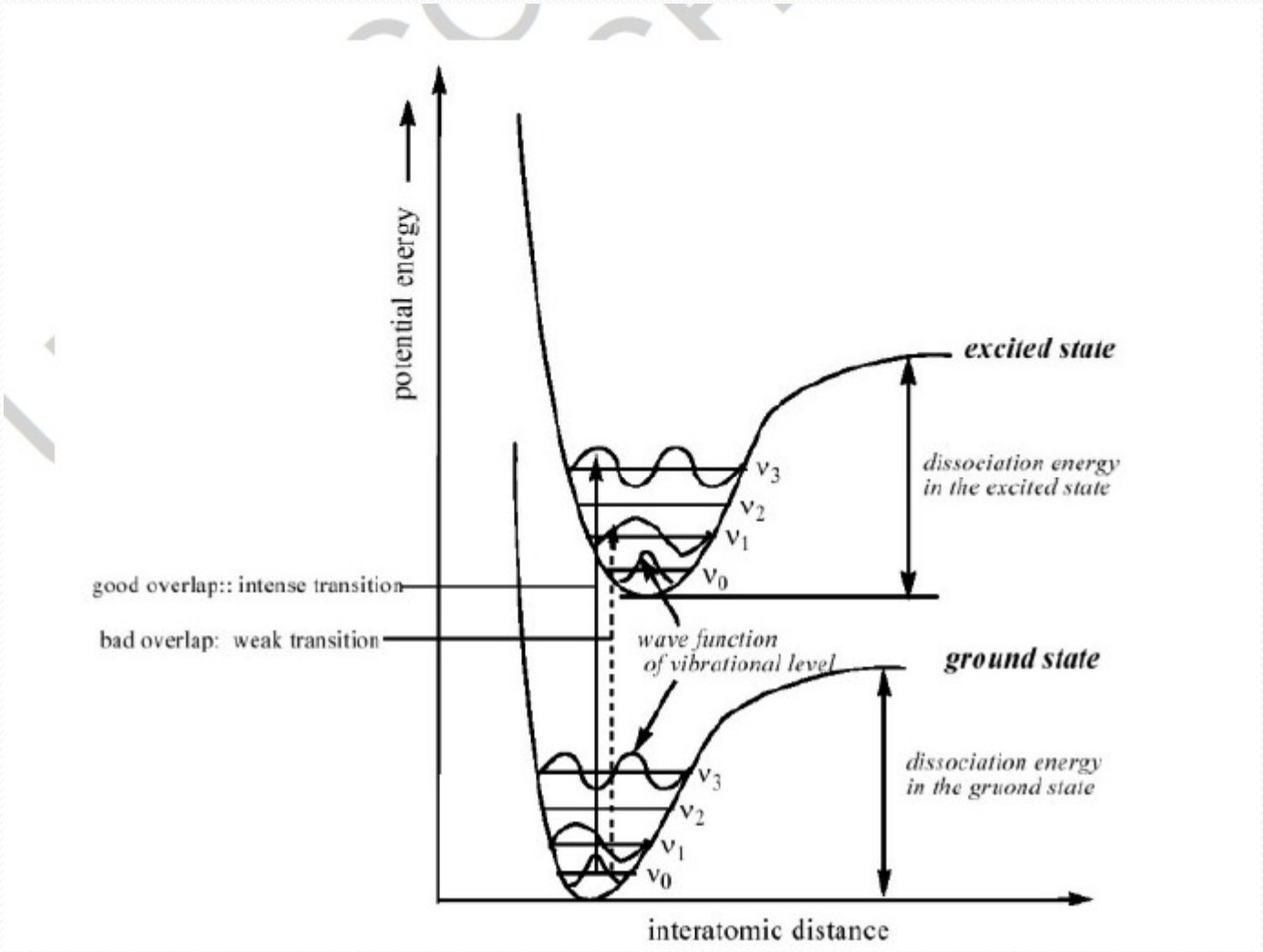
- Units used for photon energies and wavelengths:
  - 1 eV = 8065.54 cm^{-1} = 96.4853 kJ/mol = 23.0605 kcal/mol = 11604.4 K
  - 1 Å = 0.1 nm = 10^{-10} m; micron = 10^{-6} m = 1000 nm
- Solve in class: Calculate the energy, frequency, and wavenumber of a green photon (λ = 530 nm).

$$\lambda = \frac{c}{\nu}$$

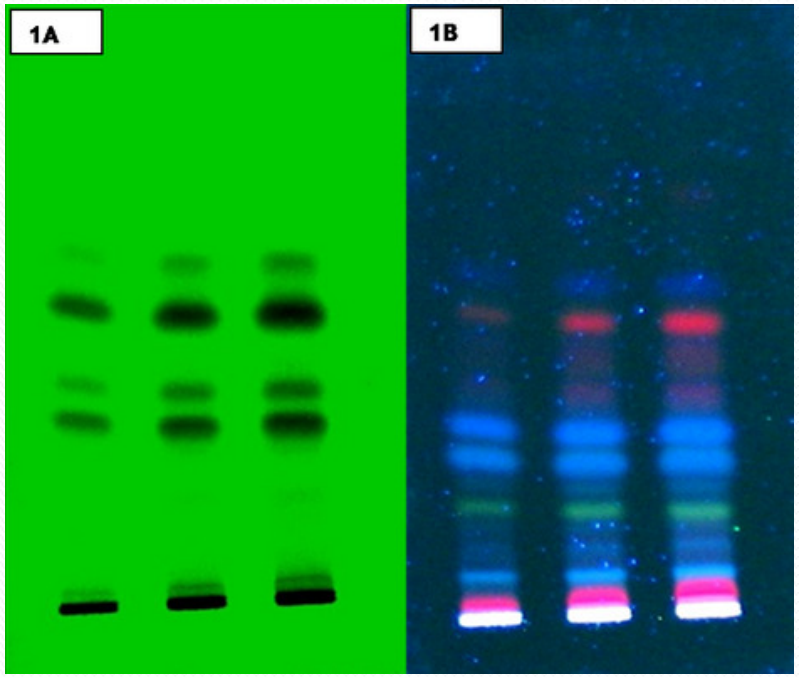
$$E = h\nu$$

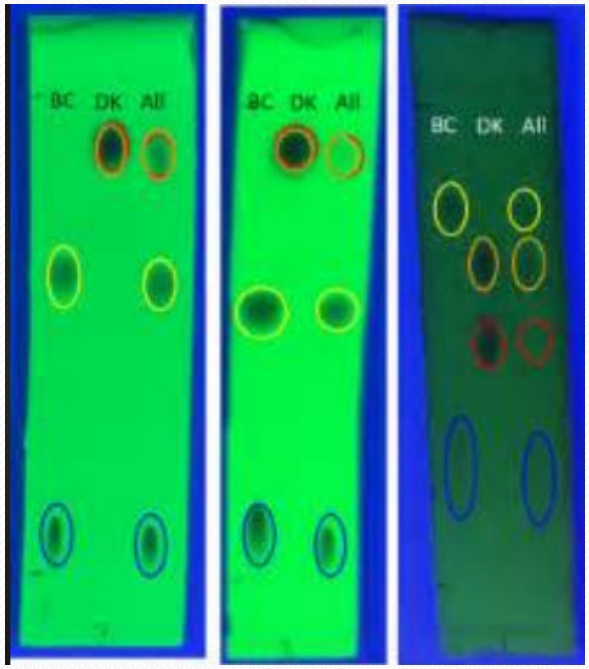
$$\bar{\nu} = \frac{1}{\lambda}$$

(wavenumber)

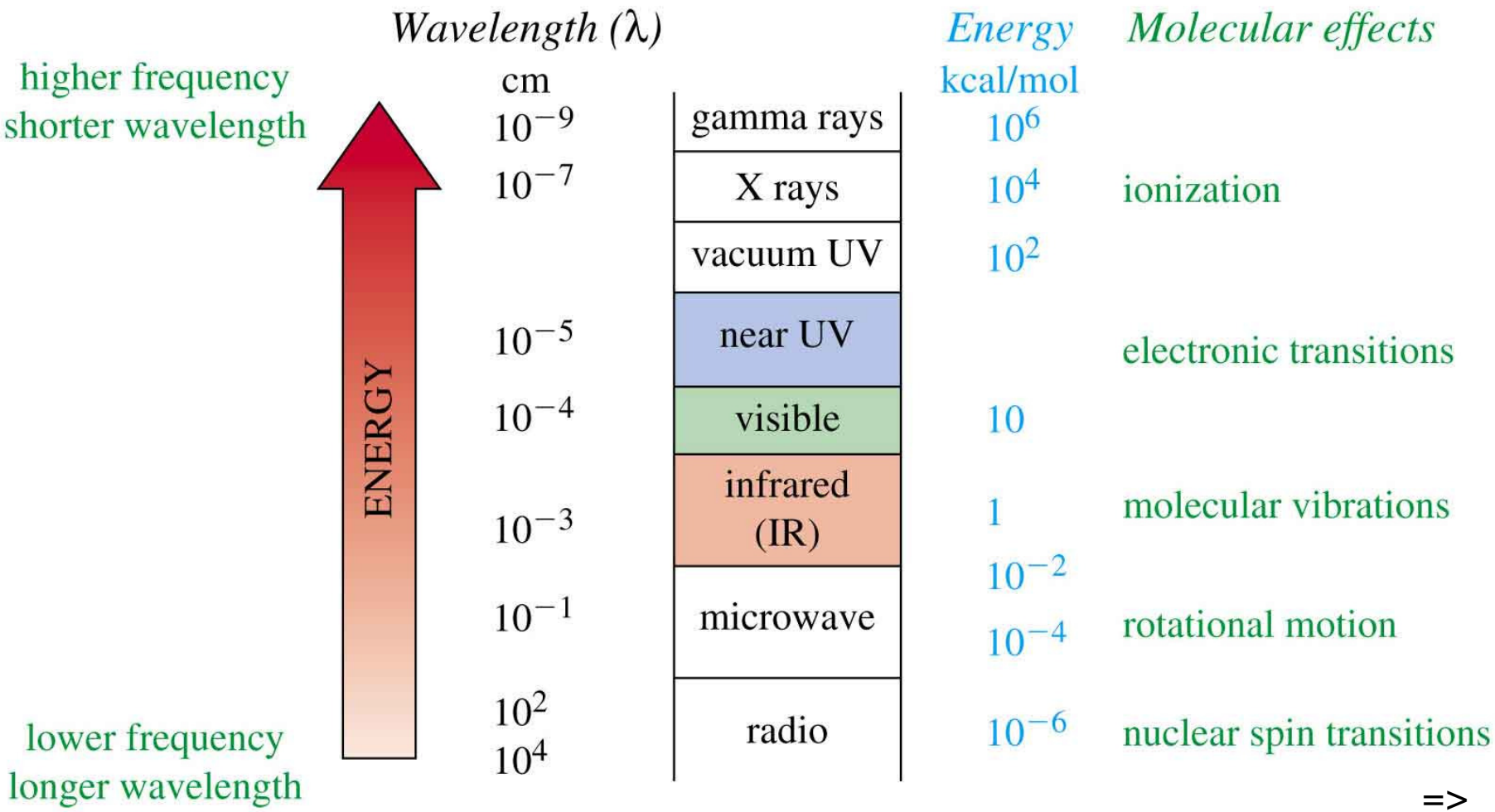

potential energy
excited state
dissociation energy
in the excited state
ν_3
ν_2
ν_1
ν_0
good overlap:: intense transition
bad overlap: weak transition
wave function
of vibrational level
ground state
dissociation energy
in the gruond state
ν_3
ν_2
ν_1
ν_0
interatomic distance

USEFUL APPLICATIONS





The Spectrum and Molecular Effects



=>

Ultraviolet and Visible Spectroscopy

UV region:180-400 nm
Vis region 400-780 nm

UV /Vis spectroscopy provides information about compounds with conjugated double bond.

This is also called electronic spectra because they have the right amount of energy to cause electronic transition from one orbital to another of higher energy

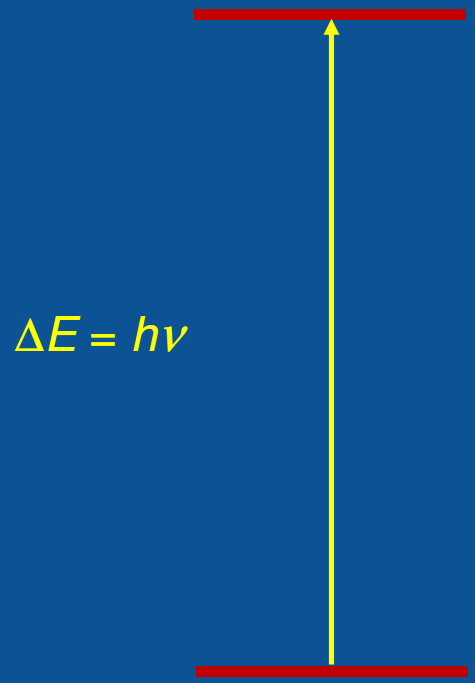
If it absorb UV light, a UV spectrum is obtained and if it absorb low energy visible light a Visible spectrum is obtained.

The energy states:

Ground state: **All the electrons are in the lowest energy molecular orbital(s).**

Excited state: **With the absorption of light of appropriate wavelength the electron is promoted to a higher energy molecular orbital.**

Transitions between electron energy states



gaps between electron energy levels are greater than those between vibrational levels

gap corresponds to wavelengths between 200 and 800 nm

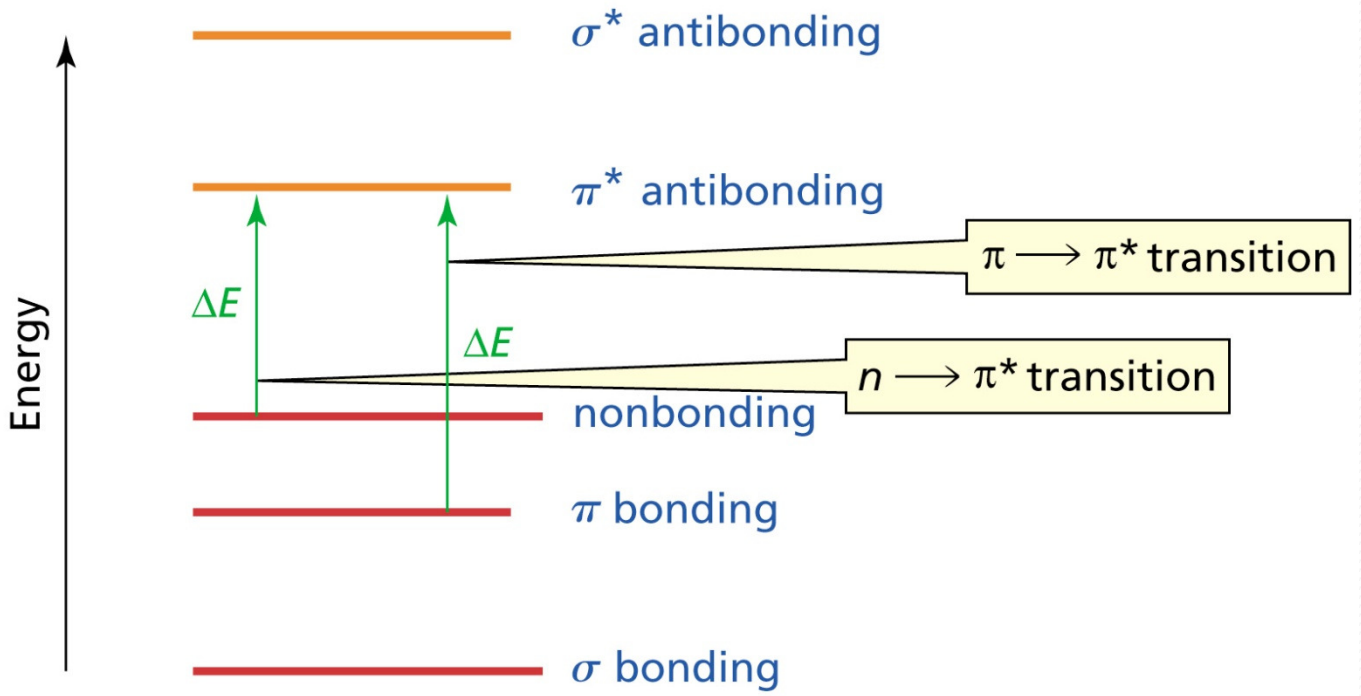
Conventions in UV-VIS

X-axis is wavelength in nm (high energy at left, low energy at right)

λ_{max} is the wavelength of maximum absorption and is related to electronic makeup of a molecule especially π electron system

Y axis is a measure of absorption of electromagnetic radiation expressed as Absorbance or molar absorptivity (ε)

UV and Visible light cause only two kinds of electronic transitions

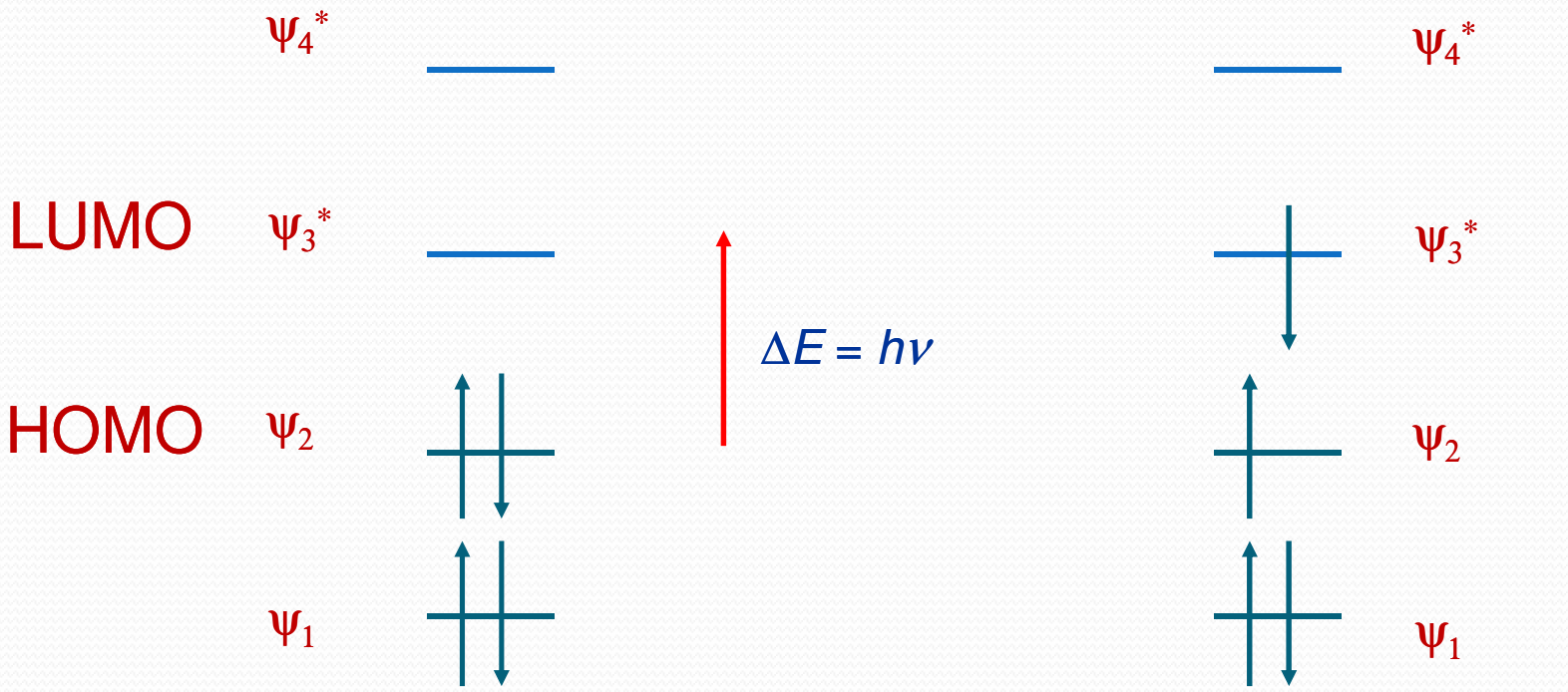


- **Only organic compounds with π electrons can absorb energy in the UV/Visible region**

- **A visible spectrum is obtained if visible light is absorbed**

- **A UV spectrum is obtained if UV light is absorbed**

$\pi \rightarrow \pi^*$ Transition in cis,trans-1,3-cyclooctadiene



Most stable π-electron configuration

π-Electron configuration of excited state

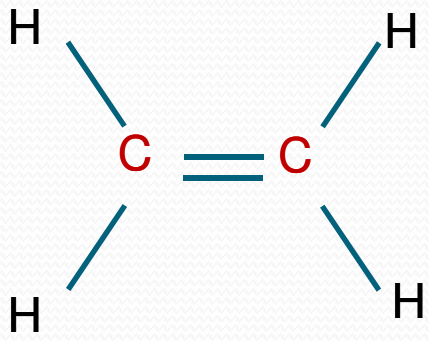
$\pi \rightarrow \pi^*$ Transition in Alkenes

HOMO-LUMO energy gap is affected by substituents on double bond

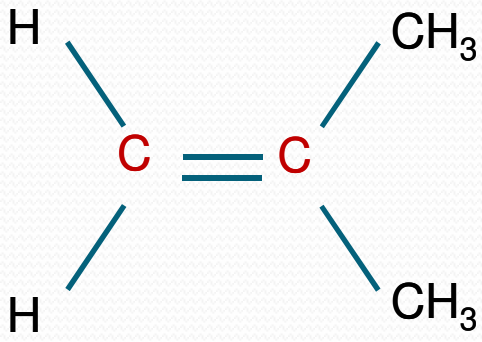
as HOMO-LUMO energy difference decreases (smaller ΔE), λ_{max} shifts to longer wavelengths

Substituent Effects

Methyl groups on double bond cause λ_{max} to shift to longer wavelengths



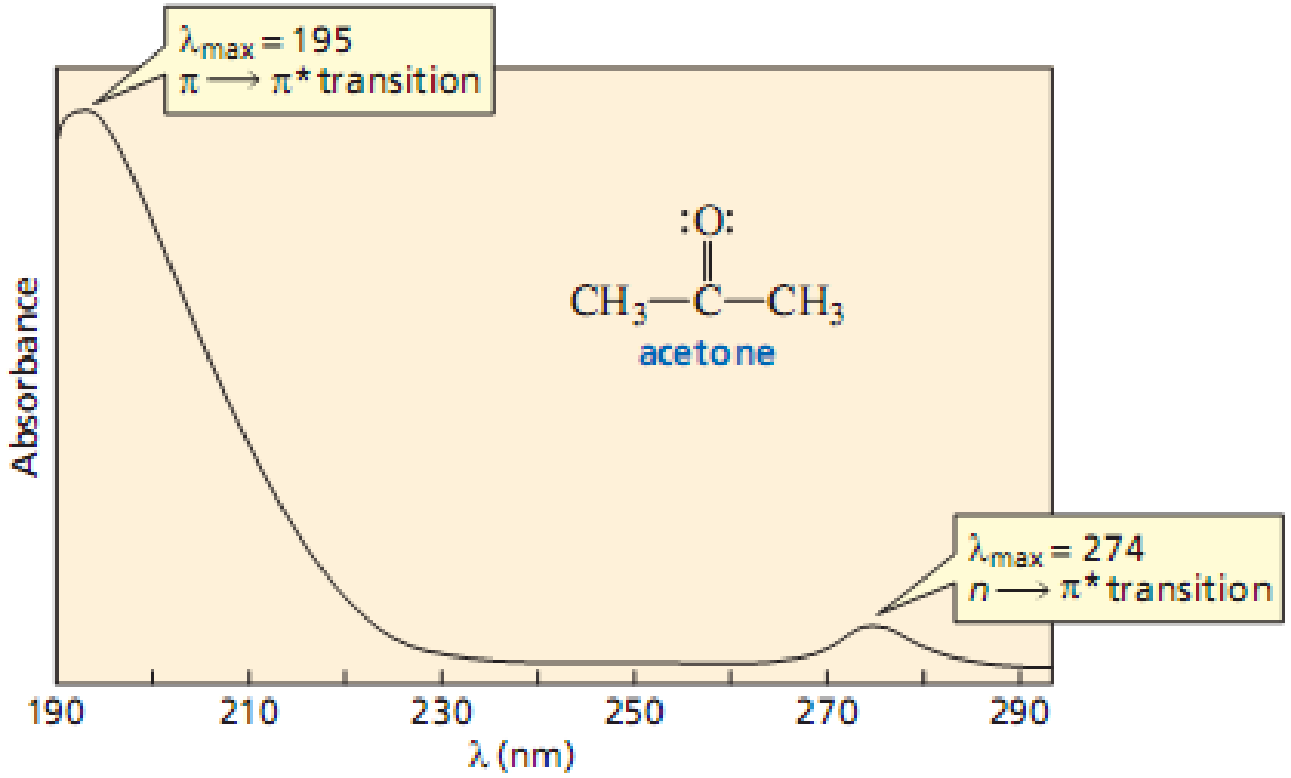
λ_{max} 170 nm



λ_{max} 188 nm

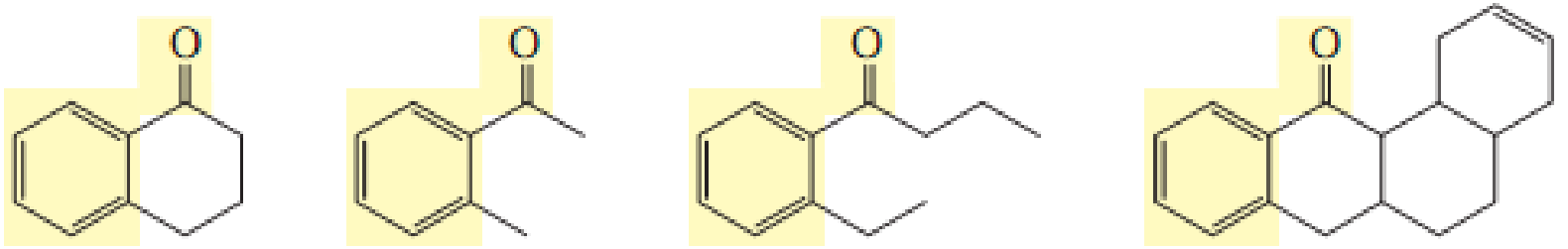
This means that *only organic compounds with π electrons can produce UV/Vis spectra.*

Electronic spectra of Acetone

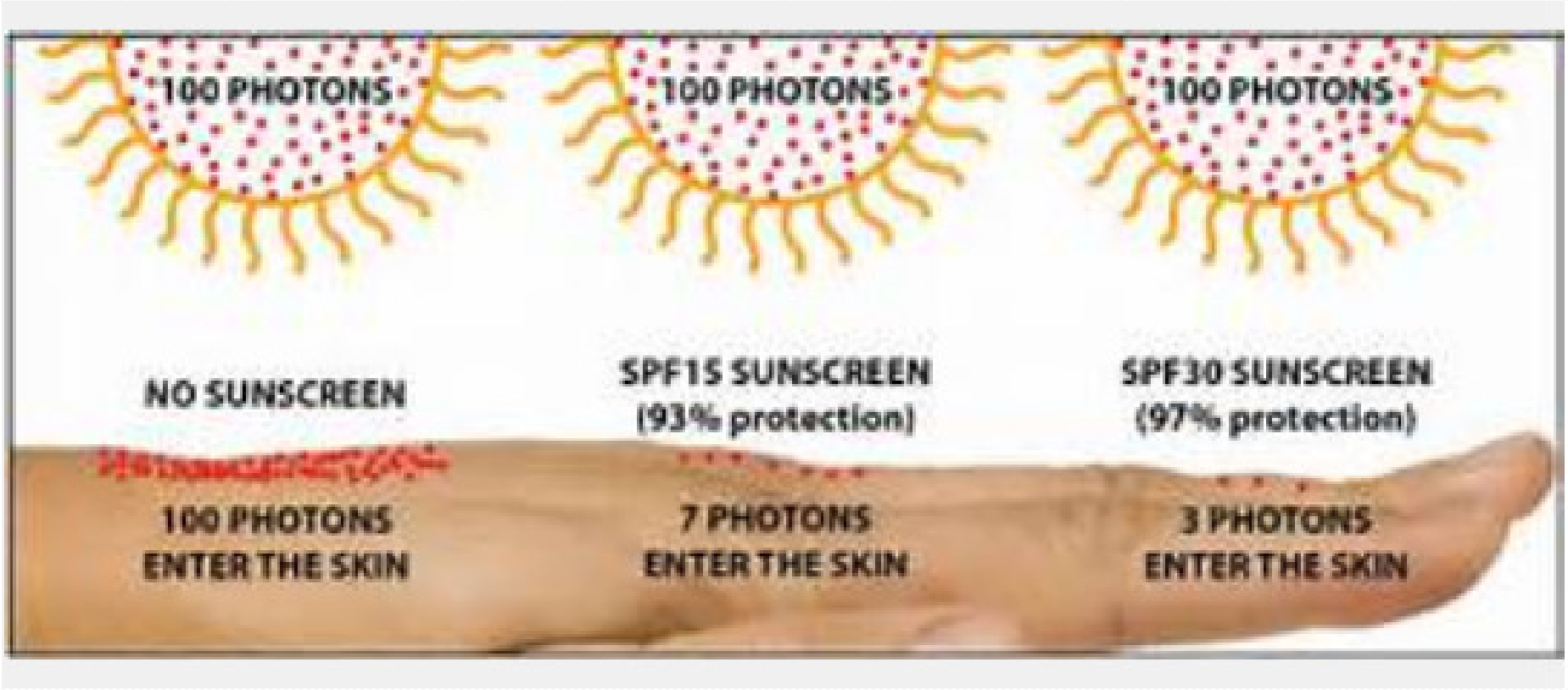


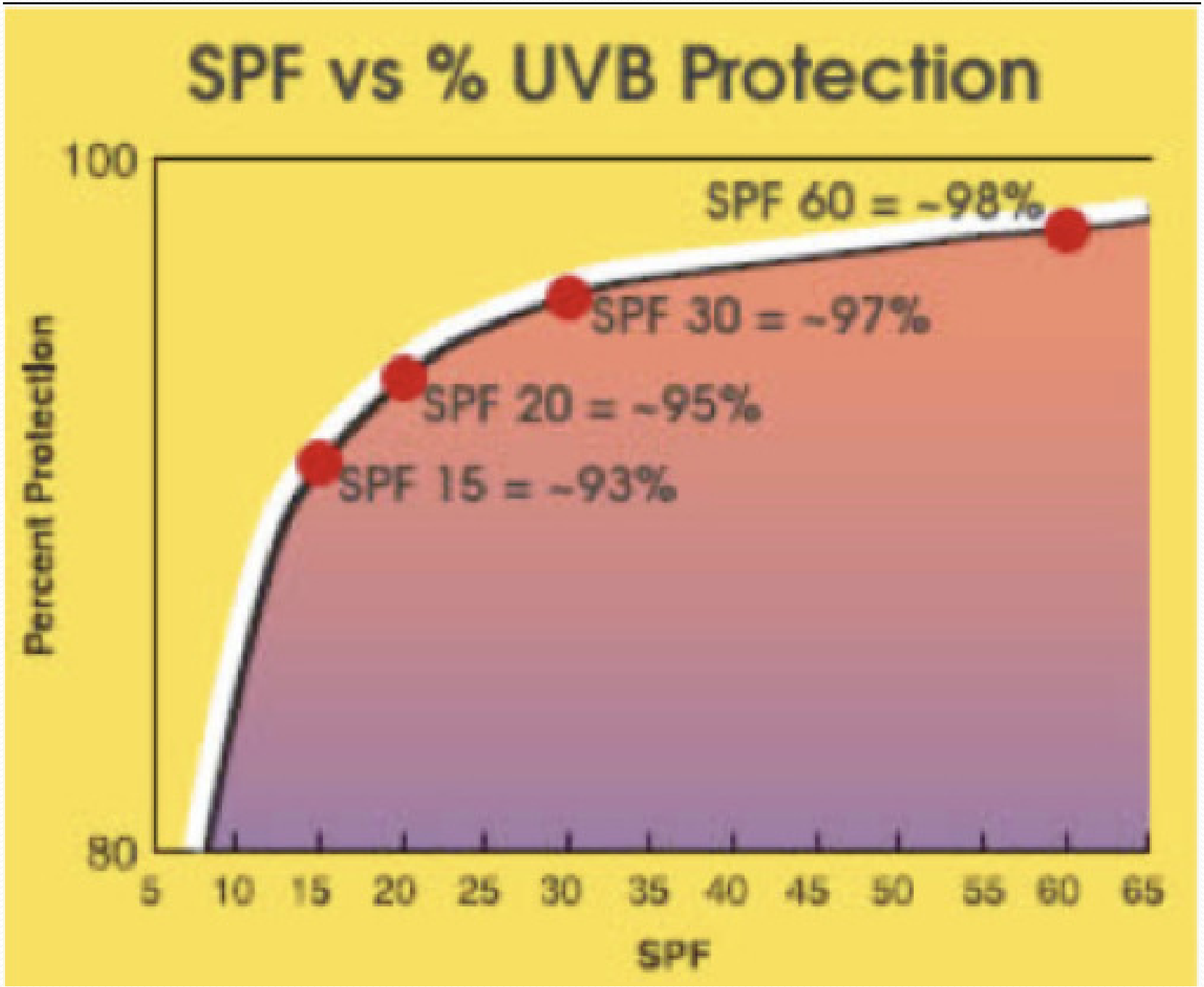
The λ_{max} (stated as "lambda max") is the wavelength corresponding to the highest point (maximum absorbance) of the absorption band. For the $\pi \rightarrow \pi^*$ transition, $\lambda_{max} = 195$ nm; for the $n \rightarrow \pi^*$ transition, $\lambda_{max} = 274$ nm.

A **chromophore** is that part of a molecule that absorbs UV or visible light. The carbonyl group is the chromophore of acetone. The following four compounds all have the same chromophore, so they all have approximately the same λ_{max}.




Eucerin
Sun Protection
50+
SUN CREME
VISAGE • GEZICHT
Peau sèche
Droge huid


100 PHOTONS
100 PHOTONS
100 PHOTONS
NO SUNSCREEN
SPF15 SUNSCREEN
(93% protection)
SPF30 SUNSCREEN
(97% protection)
100 PHOTONS
ENTER THE SKIN
7 PHOTONS
ENTER THE SKIN
3 PHOTONS
ENTER THE SKIN


SPF vs % UVB Protection
100
80
Percent Protection
SPF 60 = ~98%
SPF 30 = ~97%
SPF 20 = ~95%
SPF 15 = ~93%
5 10 15 20 25 30 35 40 45 50 55 60 65
SPF

SPF SELECTION GUIDE

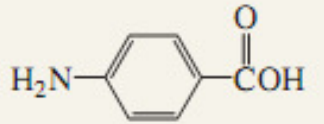
Reapply at least every 2 hours or as directed on package to help ensure adequate protection.

ULTRAVIOLET LIGHT AND SUNSCREENS

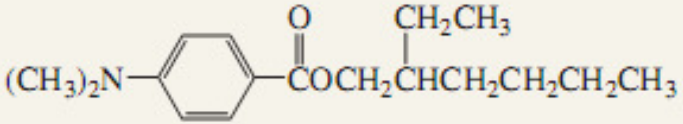
Exposure to ultraviolet light stimulates specialized cells in the skin to produce a black pigment known as melanin, which causes the skin to look tan. Melanin absorbs UV light, so it protects our bodies from the harmful effects of the sun. If more UV light reaches the skin than the melanin can absorb, the light will burn the skin and can cause photochemical reactions that can result in skin cancer (Section 29.6). UV-A is the lowest-energy UV light (315 to 400 nm) and does the least biological damage. Fortunately, most of the more dangerous, higher-energy UV light, UV-B (290 to 315 nm) and UV-C (180 to 290 nm), is filtered out by the ozone layer in the stratosphere. That is why there is such great concern about the apparent thinning of the ozone layer (Section 9.9).

Applying a sunscreen can protect skin against UV light. Some sunscreens contain an inorganic component, such as zinc oxide, that reflects the light as it reaches the skin. Others contain a compound that absorbs UV light. PABA was the first commercially available UV-absorbing sunscreen. PABA absorbs UV-B light, but is not very soluble in oily skin lotions. Less polar compounds, such as Padimate O, are now commonly used. Recent research has shown that sunscreens that absorb only UV-B light do not give adequate protection against skin cancer; both UV-A and UV-B protection are needed. Giv Tan F absorbs both UV-B and UV-A light, so it gives better protection.

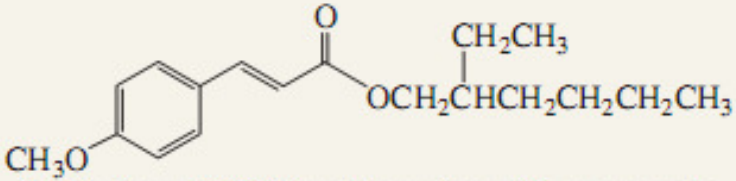
The amount of protection provided by a particular sunscreen is indicated by its SPF (sun protection factor). The higher the SPF, the greater is the protection.



para-aminobenzoic acid
PABA



2-ethylhexyl 4-(dimethylamino)benzoate
Padimate O



2-ethylhexyl (*E*)-3-(4-methoxyphenyl)-2-propenoate
Giv Tan F

8.10 The Beer–Lambert Law

Wilhelm Beer and Johann Lambert independently proposed that at a given wavelength, the absorbance of a sample depends on the amount of absorbing species that the light encounters as it passes through a solution of the sample. In other words, absorbance depends on both the concentration of the sample and the length of the light path through the sample. The relationship among absorbance, concentration, and length of the light path is known as the **Beer–Lambert law** and is given by

$$A = clε$$

A = absorbance of the sample = $\log \frac{I_0}{I}$

I_0 = intensity of the radiation entering the sample

I = intensity of the radiation emerging from the sample

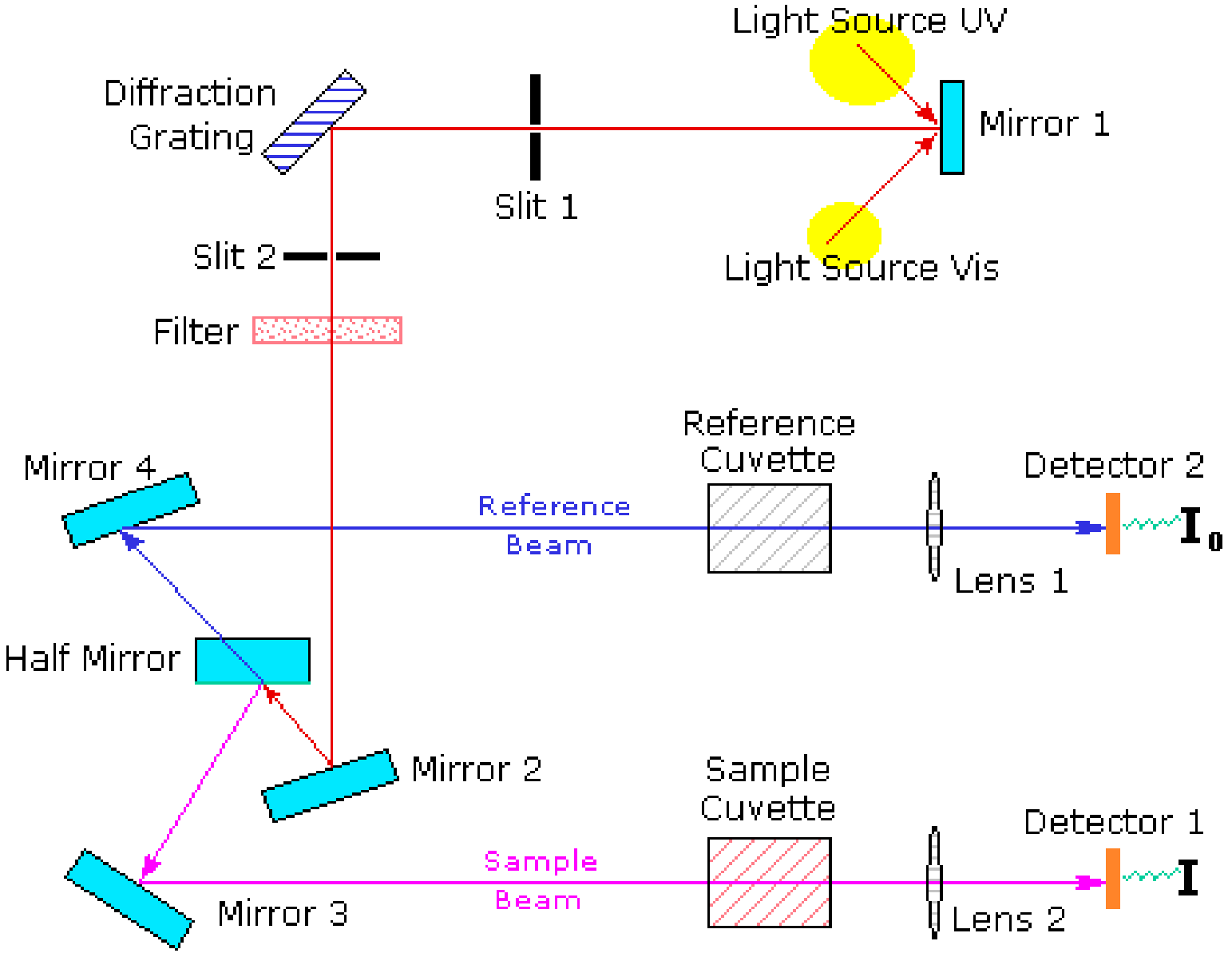
c = concentration of the sample, in moles/liter

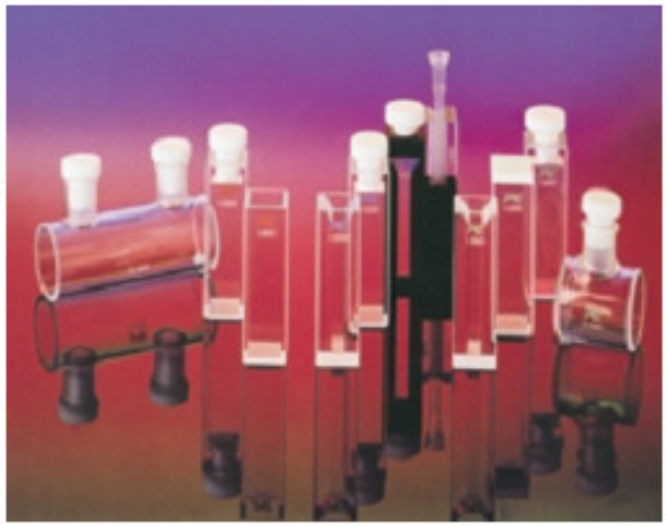
l = length of the light path through the sample, in centimeters

ε = molar absorptivity (liter mol^{-1} cm^{-1})

The **molar absorptivity** (formerly called the extinction coefficient) of a compound is a constant that is characteristic of the compound at a particular wavelength. It is the absorbance that would be observed for a 1.00 M solution in a cell with a 1.00-cm path length. The molar absorptivity of acetone, for example, is 9000 at 195 nm and 13.6 at 274 nm. The solvent in which the sample is dissolved when the spectrum is taken is re-

UV-Visible spectrophotometer


Light Source UV
Diffraction Grating
Slit 1
Mirror 1
Slit 2
Light Source Vis
Filter
Reference Cuvette
Mirror 4
Detector 2
Reference Beam
I_0
Lens 1
Half Mirror
Mirror 2
Sample Cuvette
Detector 1
Sample Beam
I
Mirror 3
Lens 2



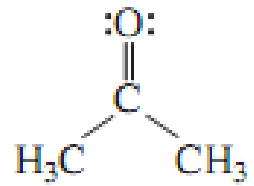
▲ Cells used in UV/Vis spectroscopy.

In order to obtain a UV or visible spectrum, the solution is placed in a cell. Most cells have 1-cm path lengths. Either glass or quartz cells can be used for visible spectra, but quartz cells must be used for UV spectra because glass absorbs UV light.

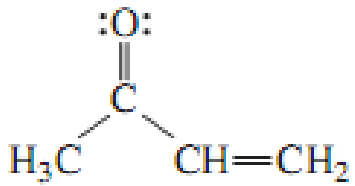
A solution of 4-methyl-3-penten-2-one in ethanol shows an absorbance of 0.52 at 236 nm in a cell with a 1-cm light path. Its molar absorptivity in ethanol at that wavelength is 12,600. What is the concentration of the compound?

8.11 Effect of Conjugation on λ_{max}

The $n \longrightarrow \pi^*$ transition for methyl vinyl ketone is at 324 nm, and the $\pi \longrightarrow \pi^*$ transition is at 219 nm. Both λ_{max} values are at longer wavelengths than the corresponding λ_{max} values of acetone because methyl vinyl ketone has two conjugated double bonds.



acetone

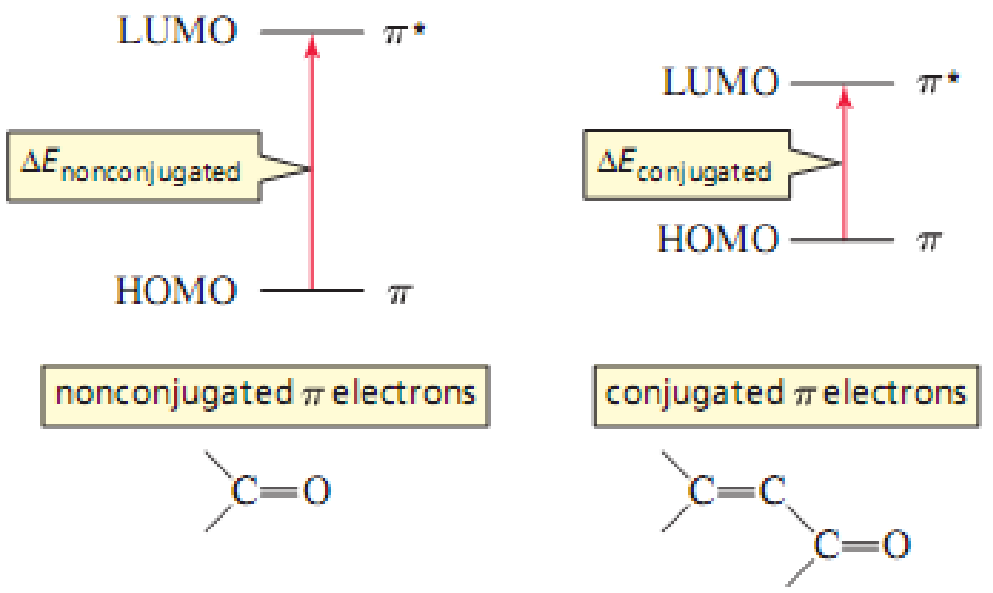


methyl vinyl ketone

$n \longrightarrow \pi^*$ λ_{max} = 274 nm (ε_{max} = 13.6) λ_{max} = 331 nm (ε_{max} = 25)

$\pi \longrightarrow \pi^*$ λ_{max} = 195 nm (ε_{max} = 9000) λ_{max} = 203 nm (ε_{max} = 9600)

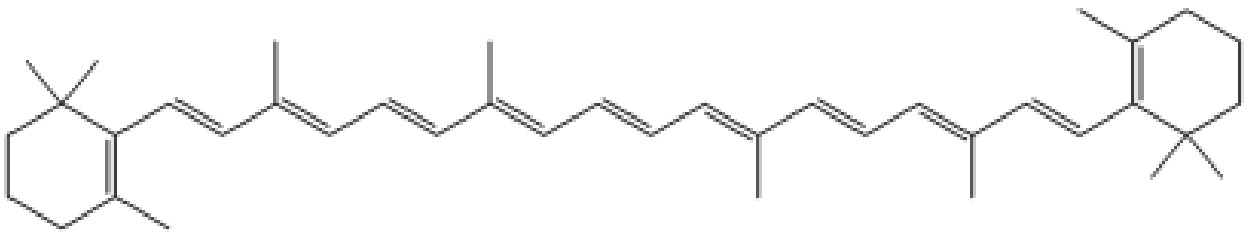
Conjugation raises the energy of the HOMO and lowers the energy of the LUMO.



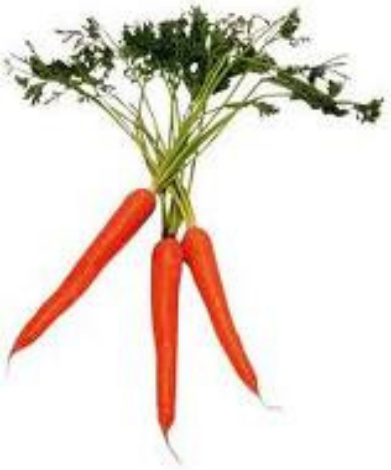
Both the λ_{max} and ε increase as the number of conjugated double bonds increases

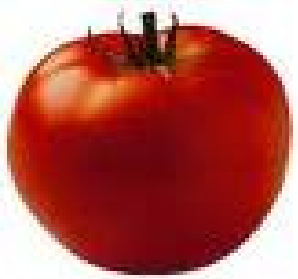
Table 8.3 Values of λ_{max} and ε for Ethylene and Conjugated Dienes

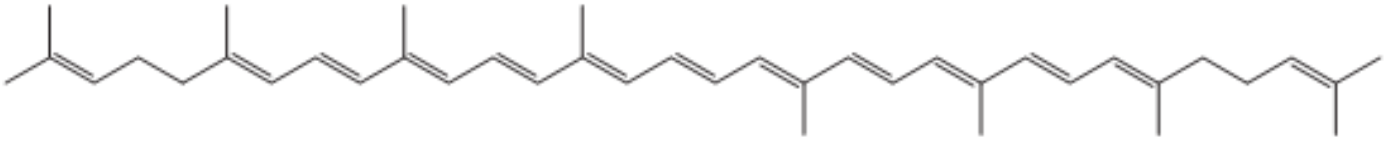
Compound	λ_{max} (nm)	ε
$H_2C{=}CH_2$	165	15,000
	217	21,000
	256	50,000
	290	85,000
	334	125,000
	364	138,000



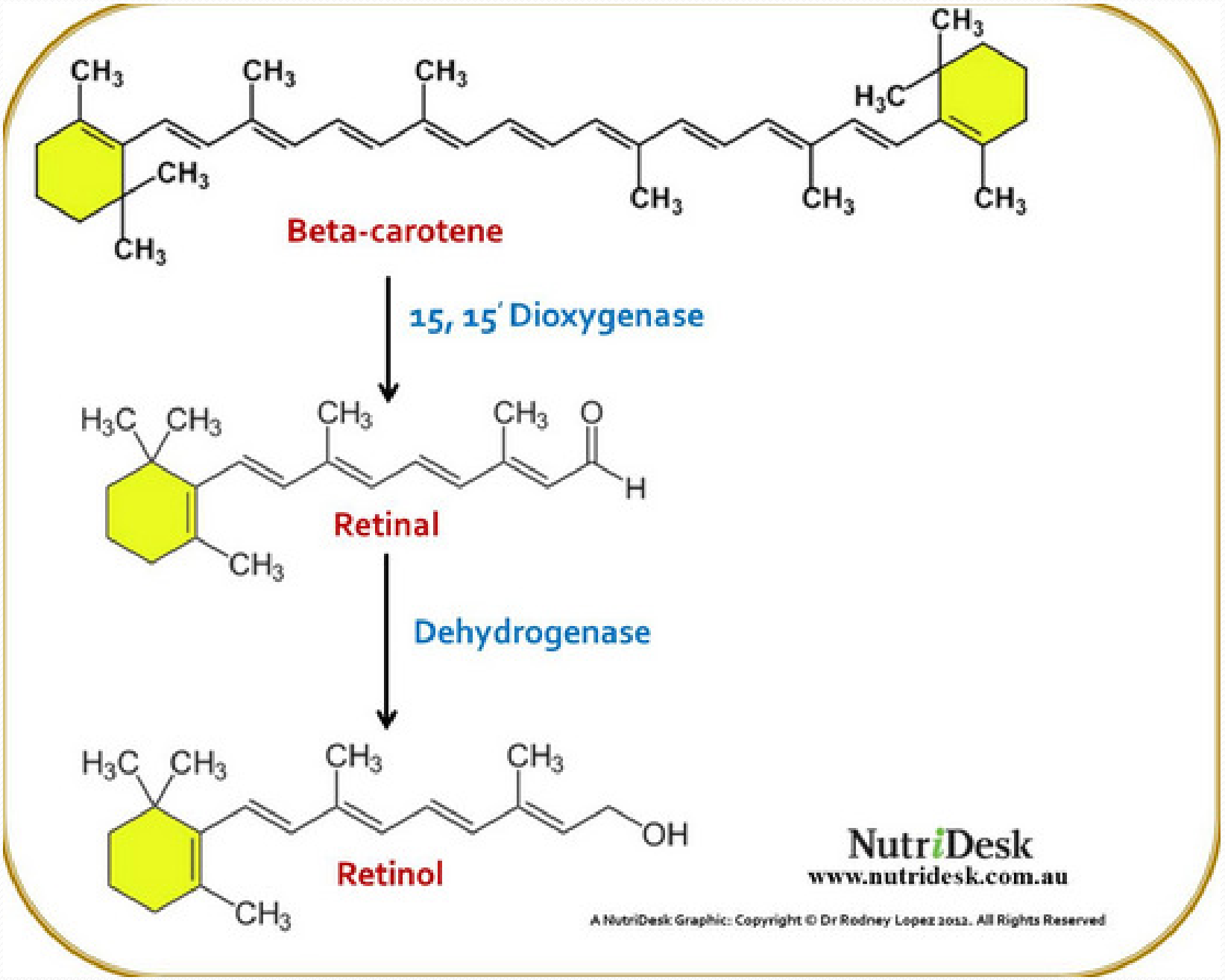
β-carotene
λ_{max} = 455 nm







lycopene
λ_{max} = 474 nm



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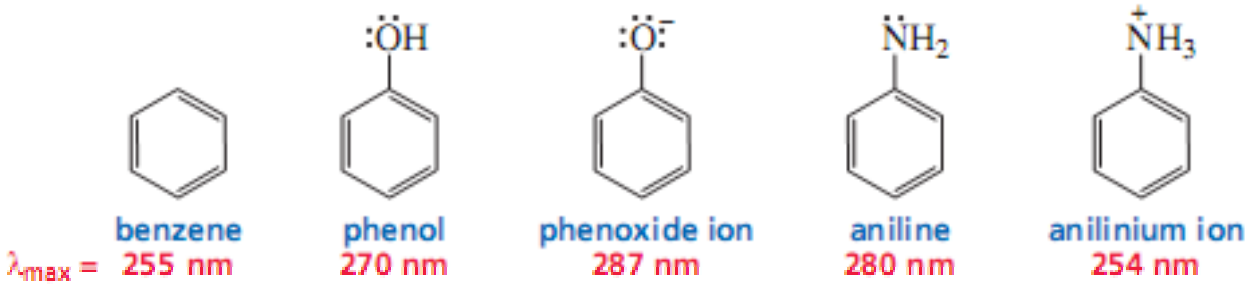
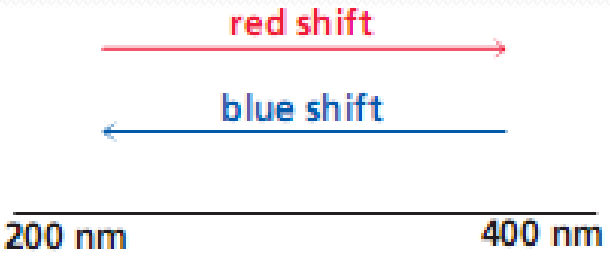
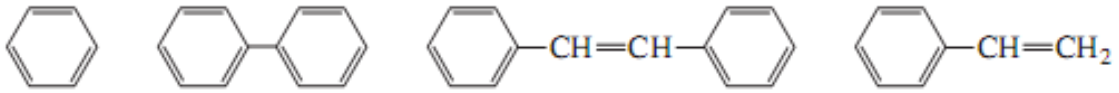
An **auxochrome** is a substituent that when attached to a chromophore, alters the λ_{max} and the intensity of the absorption, usually increasing both; OH and NH_2 groups are auxochromes. The lone-pair electrons on oxygen and nitrogen are available for interaction with the π electron cloud of the benzene ring, and such an interaction increases λ_{max}. Because the anilinium ion does not have an auxochrome, its λ_{max} is similar to that of benzene.





PROBLEM 22◆

Rank the compounds in order of decreasing λ_{max}:



Application of UV/Vis Spectroscopy

- **Measure the rates of a reaction rates**

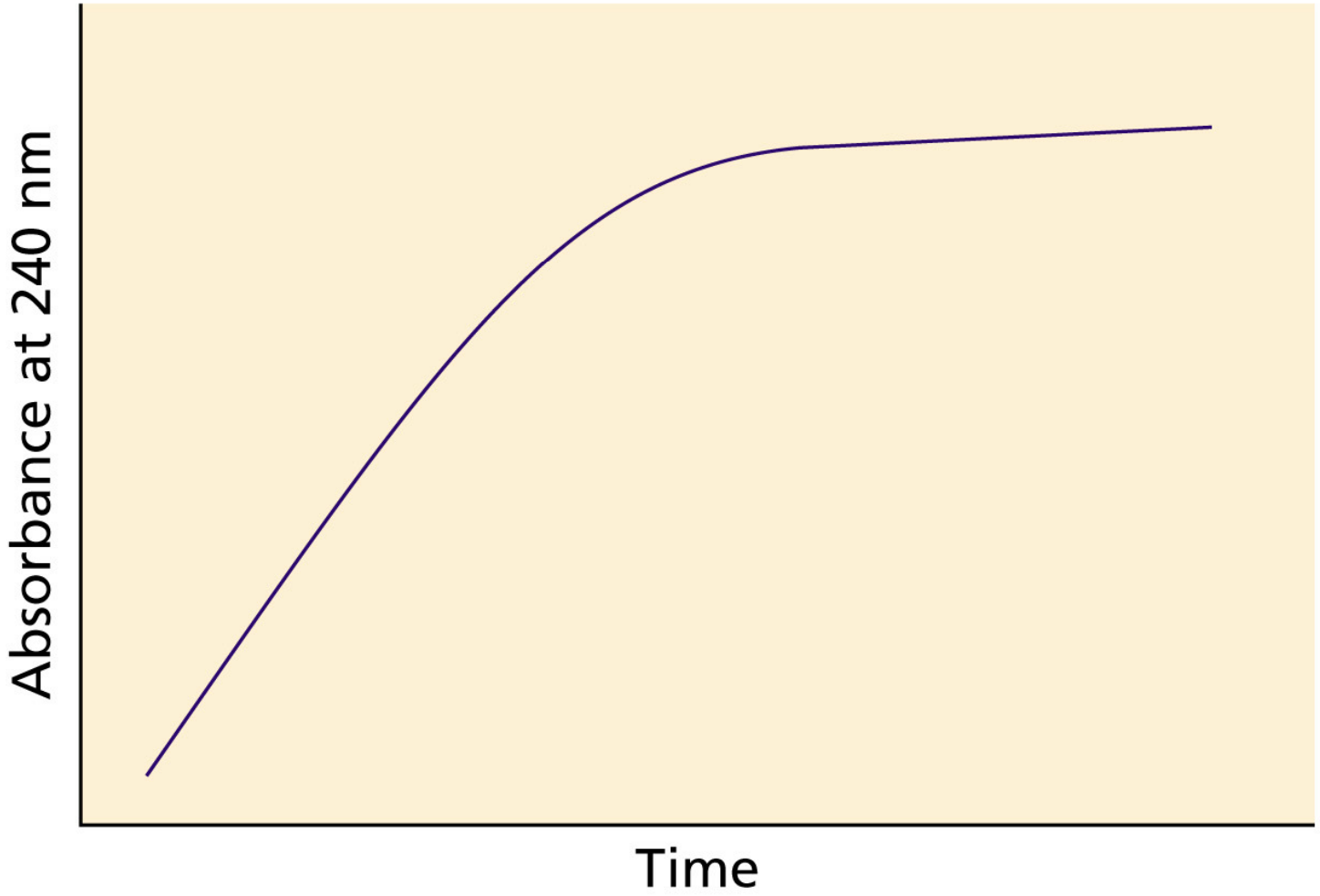
- **Determine the pK_a of a compound**

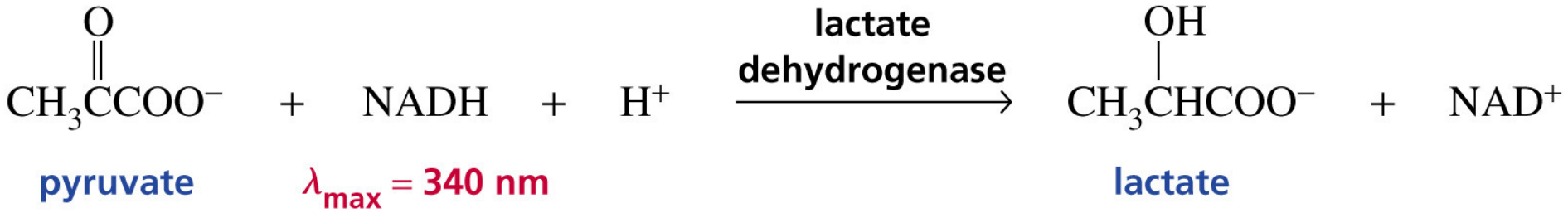
- **Estimate the nucleotide composition of DNA**

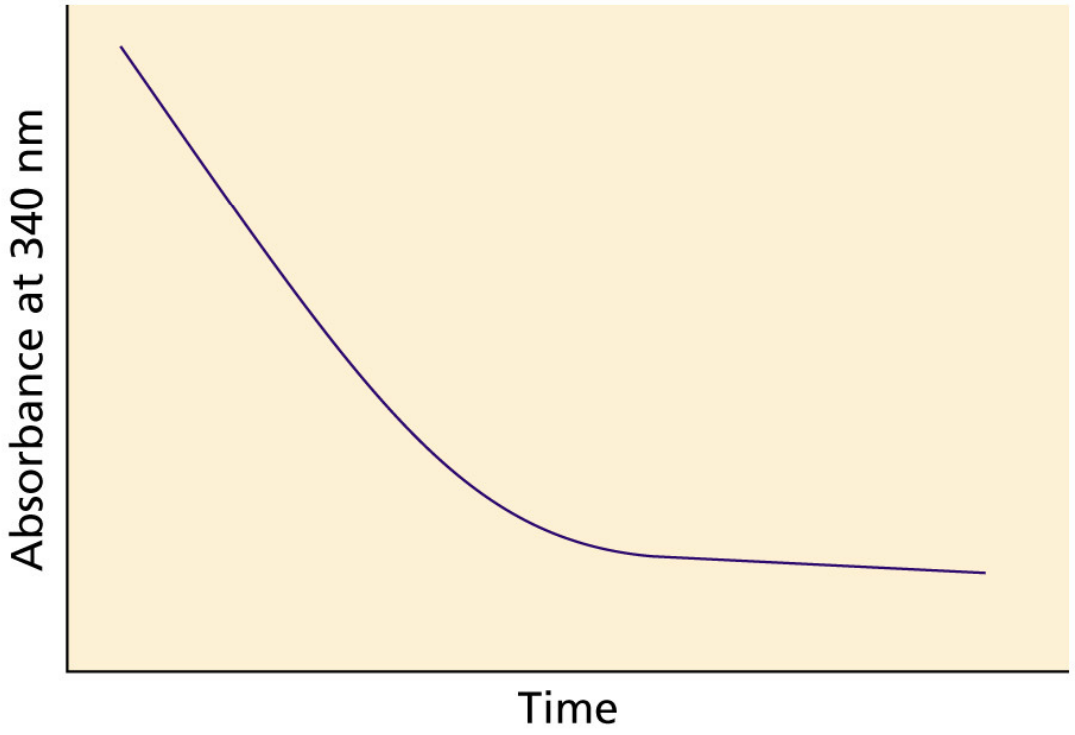
$$CH_3CH_2NO_2 + HO^- \rightleftharpoons CH_3\bar{C}HNO_2 + H_2O$$

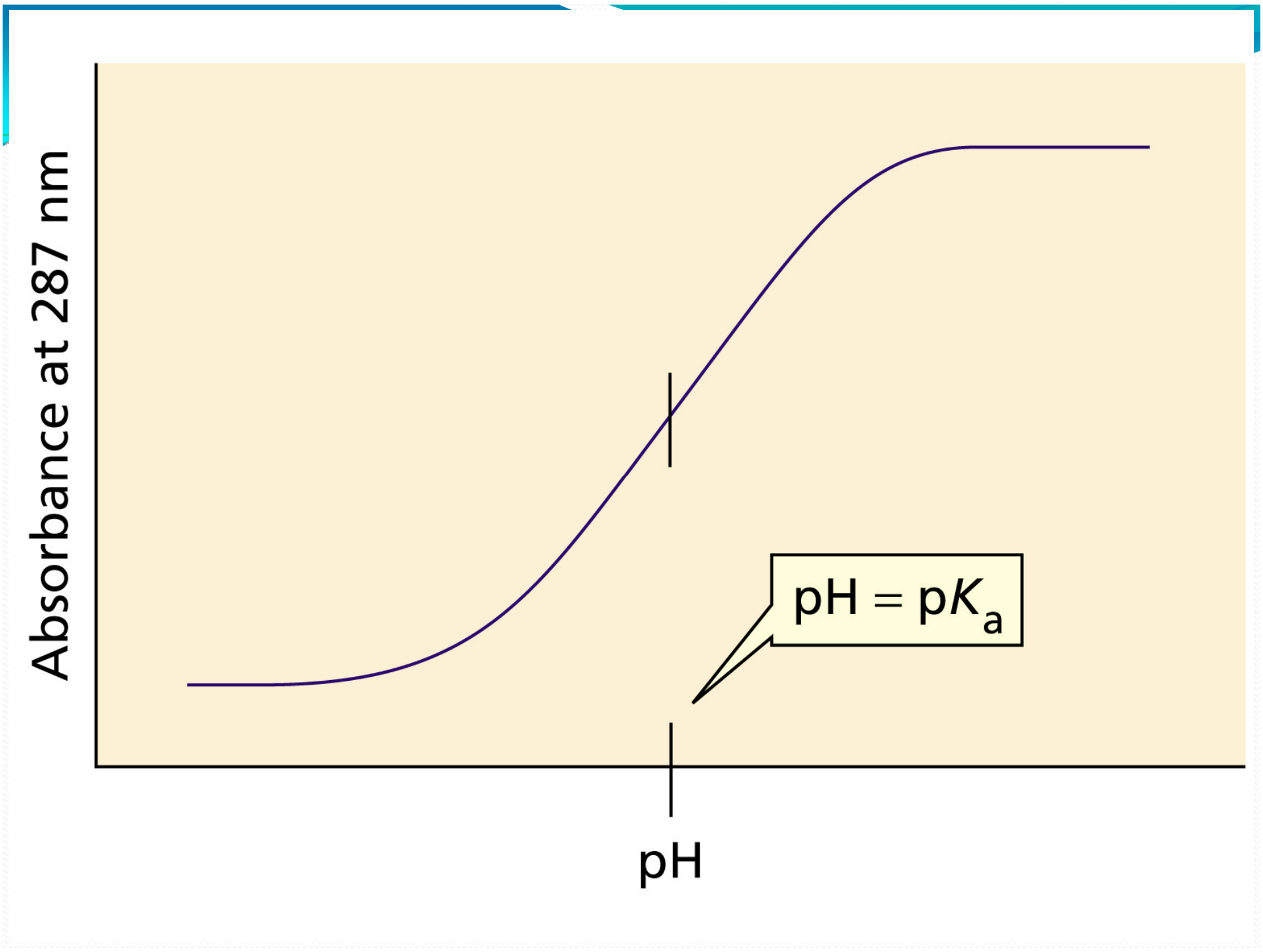
nitroethane — **nitroethane anion**

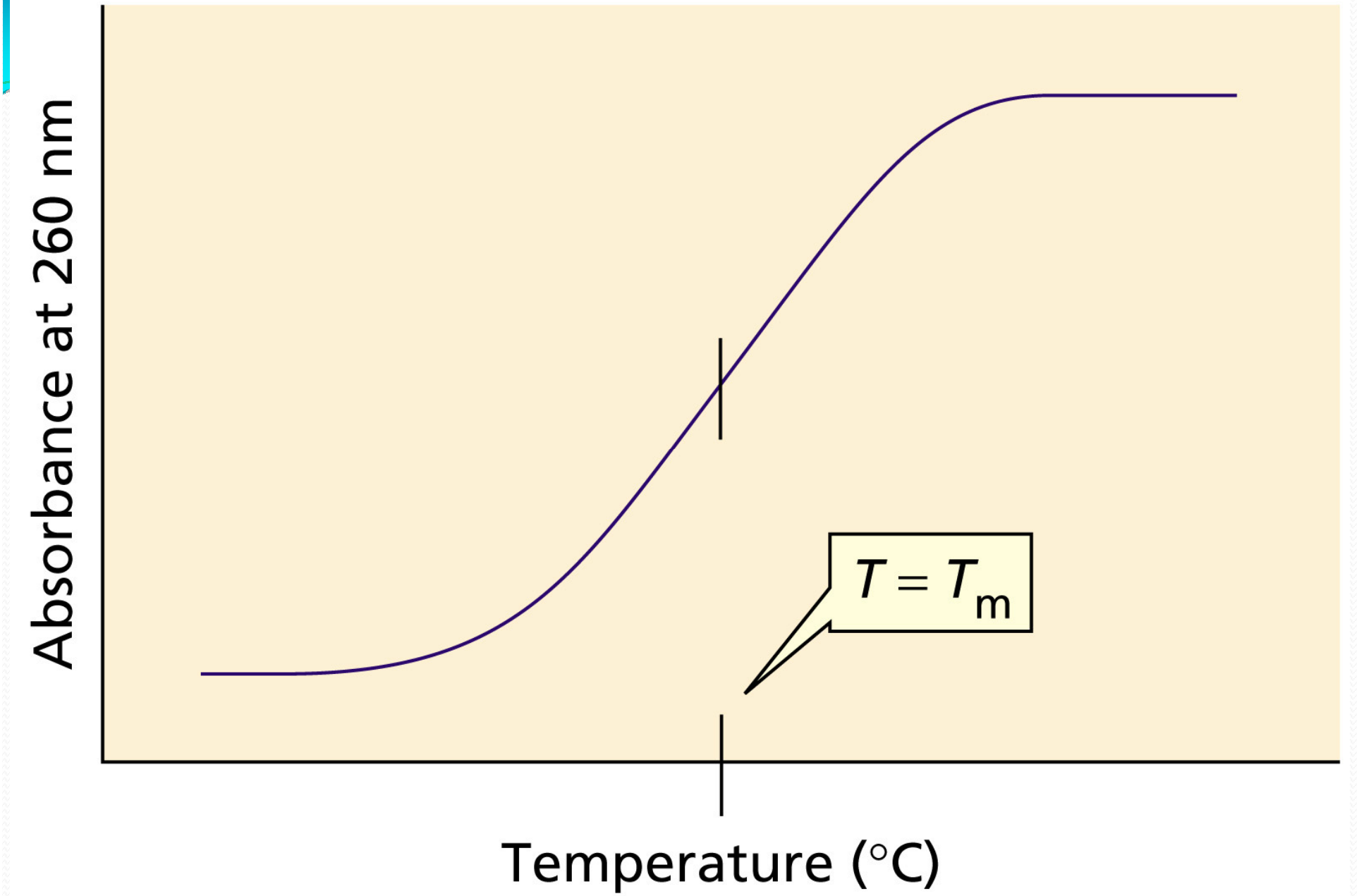
$\lambda_{max} = 240$ nm




lactate
dehydrogenase
pyruvate
λ_{max} = 340 nm
lactate


Absorbance at 340 nm
Time


Absorbance at 287 nm
pH = pK$_a$
pH

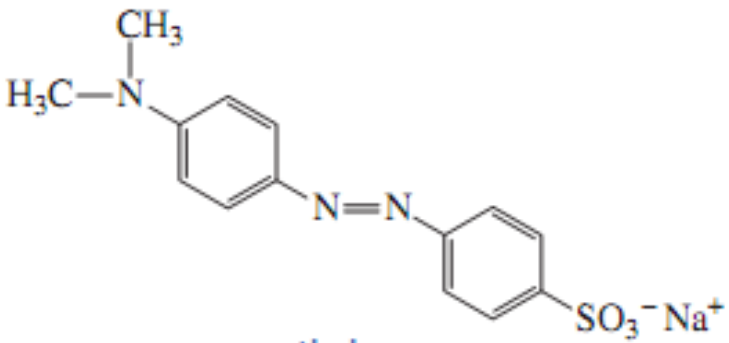

Absorbance at 260 nm
$T = T_m$
Temperature (°C)

The Visible Spectrum and Color

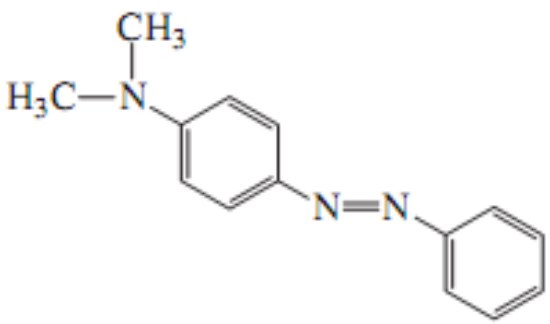
Table 8.4 Dependence of the Color Observed on the Wavelength of Light Absorbed

Wavelengths absorbed (nm)	Observed color
380–460	yellow
380–500	orange
440–560	red
480–610	purple
540–650	blue
380–420 and 610–700	green

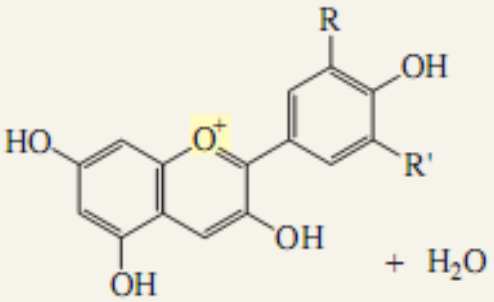
Optical Brightener



methyl orange
an azobenzene

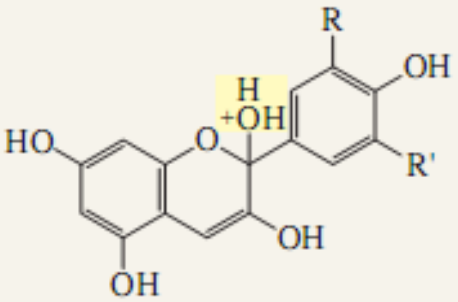


butter yellow
an azobenzene



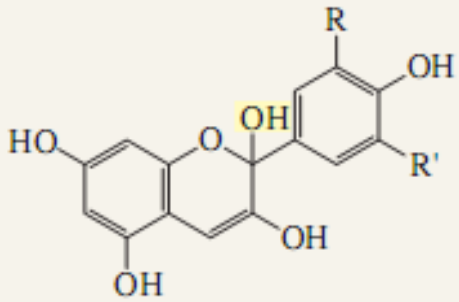
+ H_2O

anthocyanin
(three rings are conjugated)
red, blue, or purple



(conjugation is disrupted)
colorless

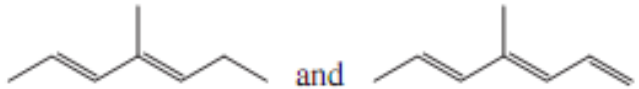
H_2O
H_3O^+



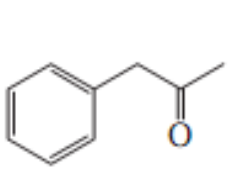
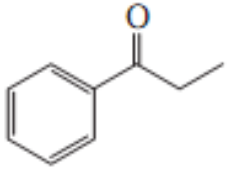
(conjugation is disrupted)
colorless

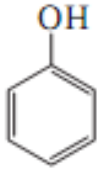
R = H, OH, or OCH_3
R' = H, OH, or OCH_3

39. How could one use UV spectroscopy to distinguish between the compounds in each of the following pairs?

a.  and

b. $CH_2{=}CHCH{=}CHCH{=}CH_2$ and $CH_2{=}CHCH{=}CHC(=O)CH_3$

c.  and 

d.  and