

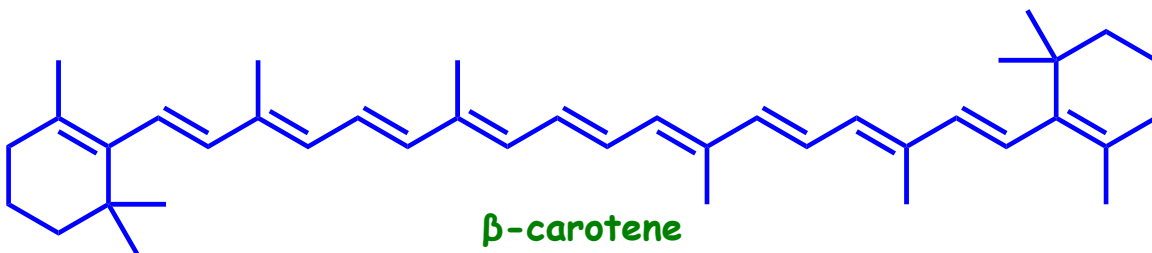


# Ultraviolet Spectroscopy



# Ultraviolet Spectroscopy

- UV light can be absorbed by molecules to excite higher energy (most loosely bound) electrons from lower energy states to higher states.
- Such transitions can be studied extensively to understand the binding energy of the corresponding electrons undergoing transition.
- Since  $\pi$ -electrons are most loosely bound in an organic molecule, UV spectroscopy yields a lot of information about the degree of unsaturation in a molecule.
- When the wavelength of the transition exceeds the UV range, based on the same principle, even the colours of molecules can be explained on the basis of absorption of visible light.



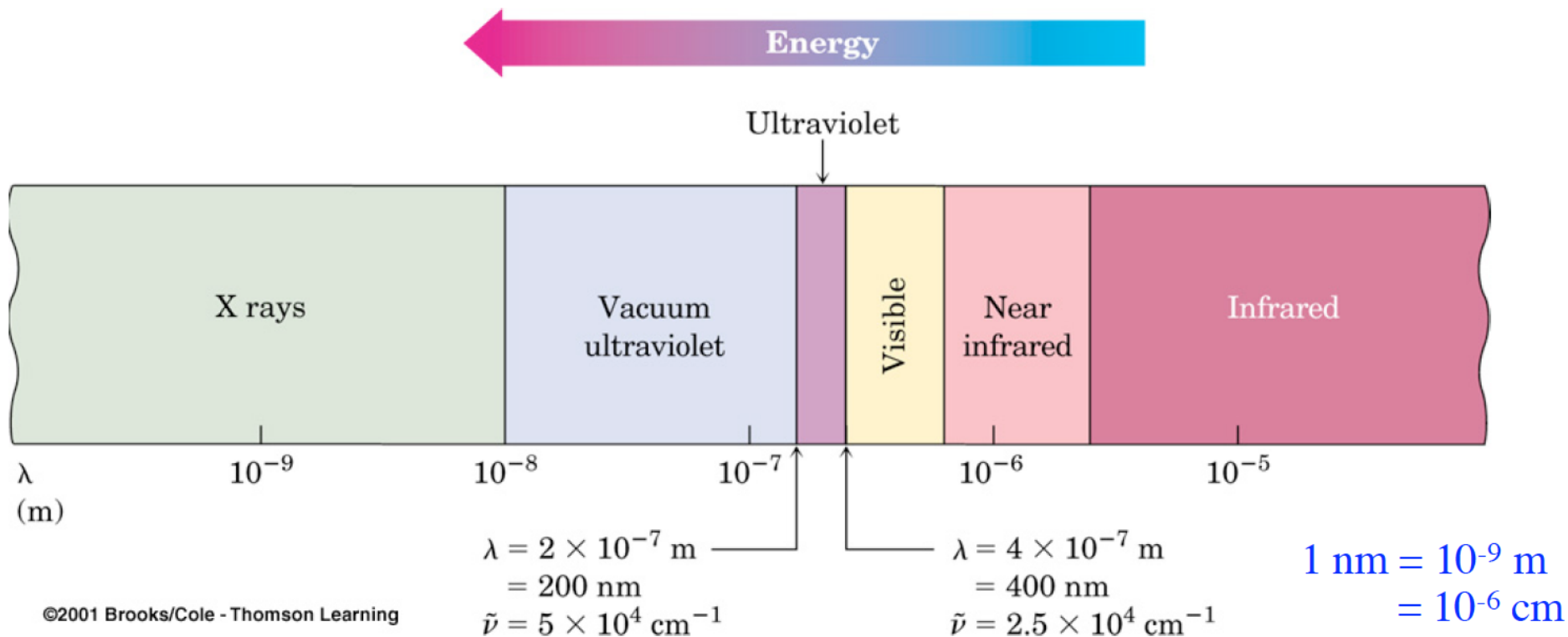
$\beta$ -carotene  
 $\lambda_{\max} = 452 \text{ nm}$



1,3-butadiene  
 $\lambda_{\max} = 217 \text{ nm}$



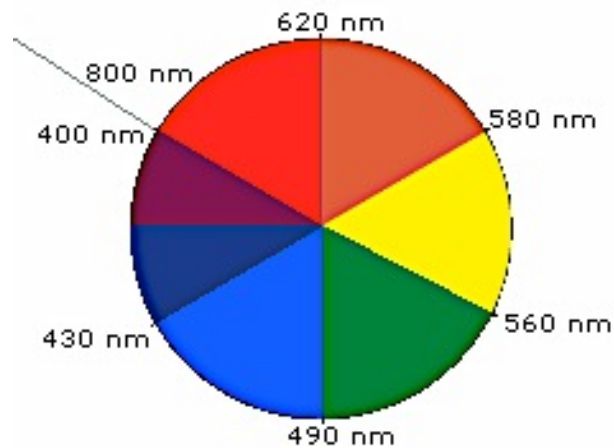
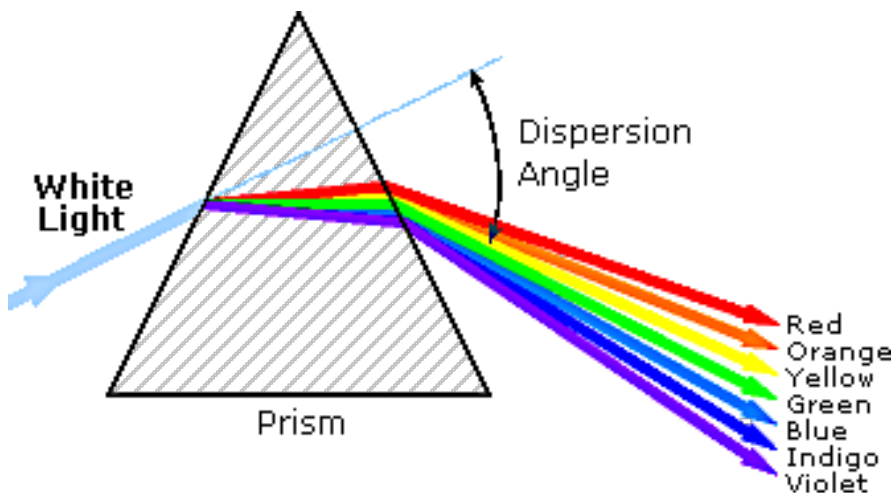
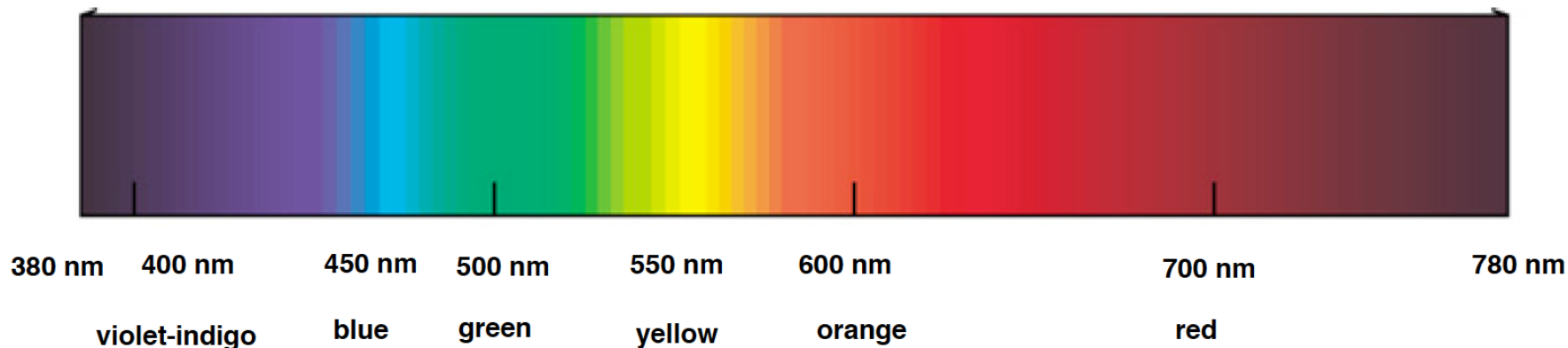
# Electromagnetic Spectrum



Energy is proportional to frequency  
Frequency is inversely proportional wavelength

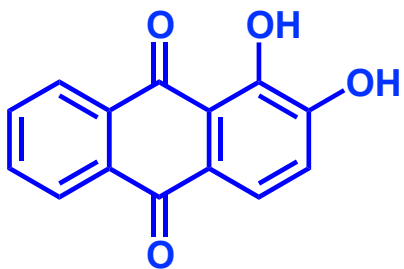


# The Visible Spectrum

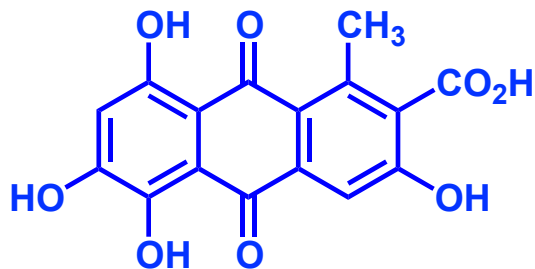




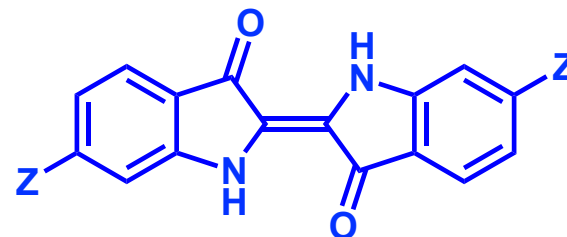
# Some Natural Organic Pigments



**Alizarin**

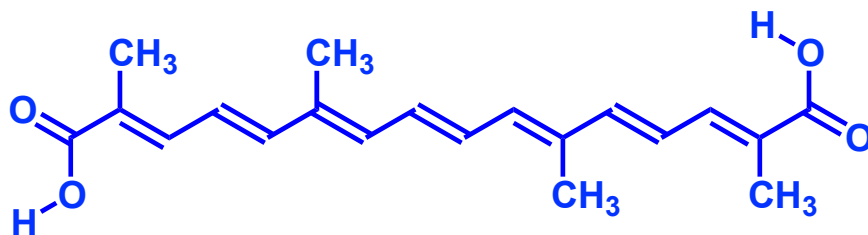


**Kermesic Acid**

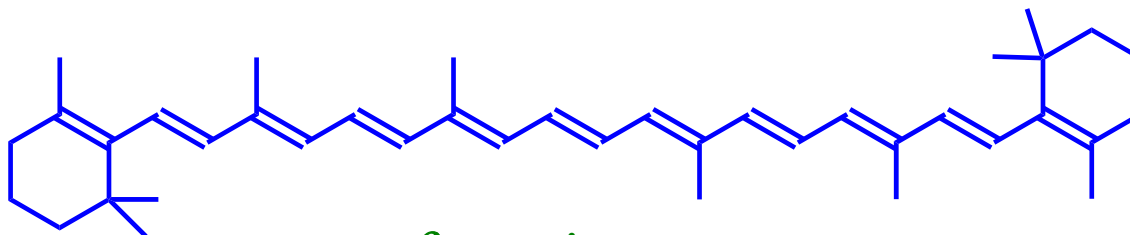


**Z=H, Indigo**

**Z=Br Punicin/Tyrian Purple**



**Crocetin**

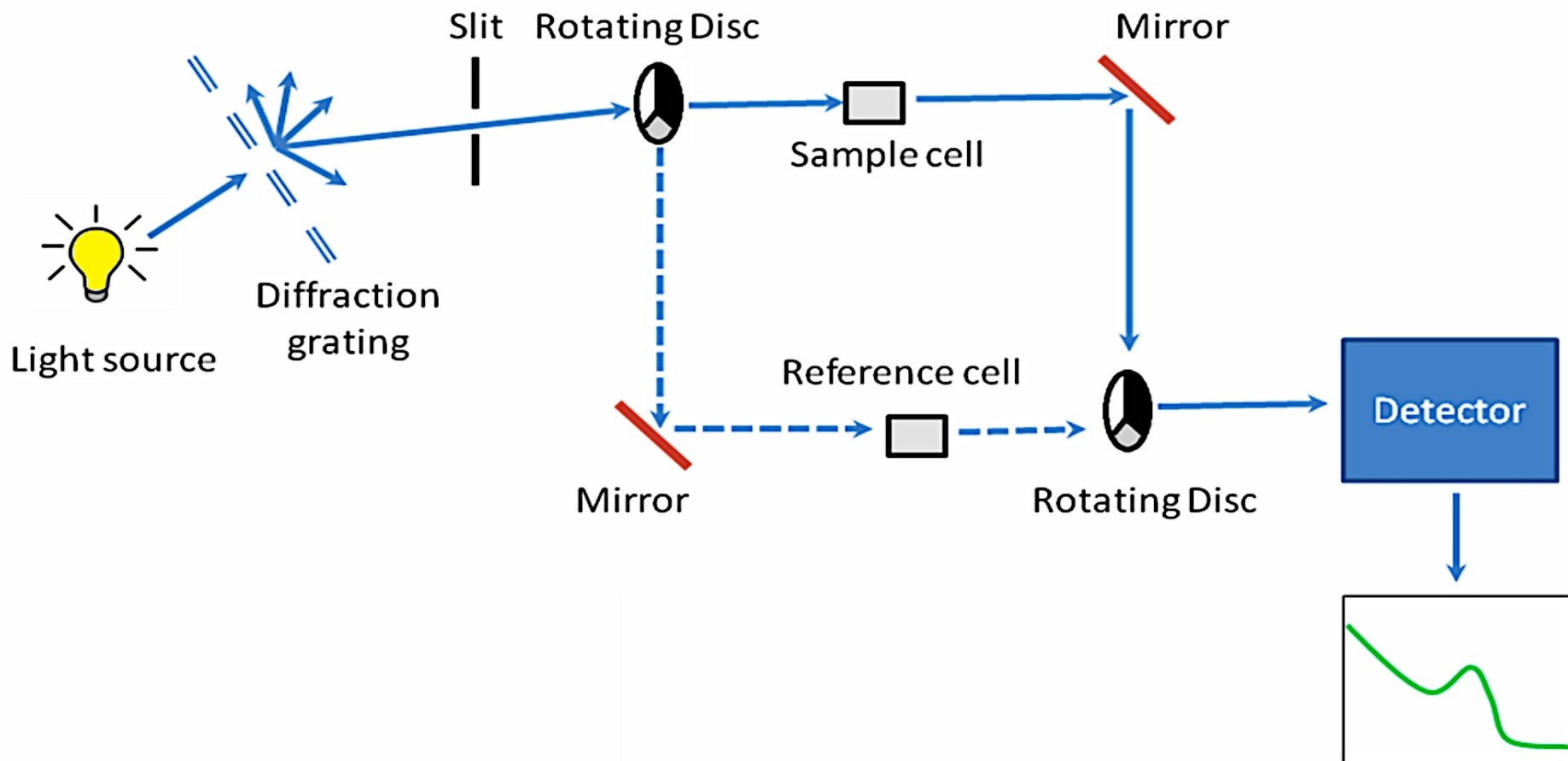


**$\beta$ -carotene  
(from carrots)**



# Instrumentation

## Double Beam UV Spectrometer:



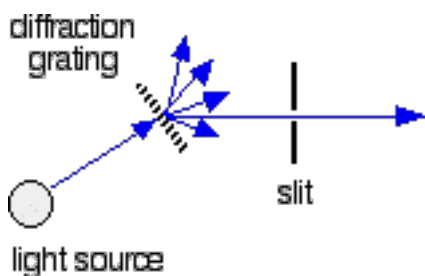


# Double Beam UV Spectrometer

## Light Source:

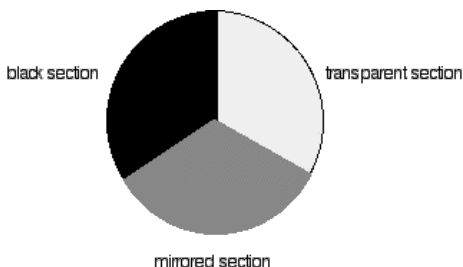
- Combined sources used to cover a range of 200-800 nm
- Deuterium lamp for UV range
- Tungsten/halogen for visible range

## Diffraction Grating & The Slit:



- Diffraction grating splits lights to its component colors like a prism
- Slit allows to pass only a narrow range of wavelengths to the rotating disk

## Rotating Disks:



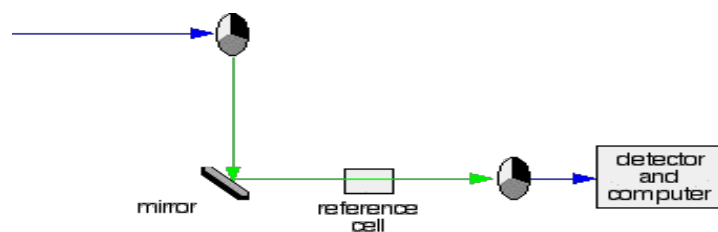
- Rotating disks are made of different number of segments



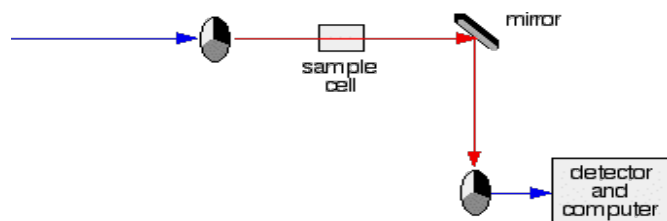
# Double Beam UV Spectrometer

## Rotating Disks:

- If light hits the mirrored section, it bounces back to a mirror. The reflected light meets the transparent section of the second disk and passes through it to the detector.



- If light hits the transparent section, it will pass through and be bounced by a mirror onto a second rotating disk. Light meets the mirrored section of the second disk and bounces onto the detector.







# Double Beam UV Spectrometer

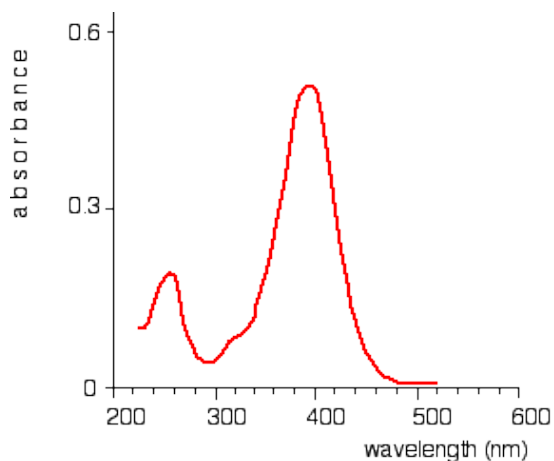
## Sample & Reference Cells:



- Small rectangular glass/quartz containers.
- Designed in such a manner that light has to travel 1 cm through the contents.

## Detector & Computer:

- Detector converts light to current. The greater is the intensity of light, the higher is the current.
- An absorbance (A) could be written as-



$$A = \log_{10} \frac{I_0}{I}$$

Intensity of light passing through reference cell =  $I_0$

Intensity of light passing through sample =  $I$



# Principle Behind UV Spectrometers

## Lambert-Beer's Law:

$$\log_{10} \frac{I_0}{I} = \epsilon l c$$

Greek letter, epsilon

↓

concentration of solution  
(mol dm<sup>-3</sup>) ←

↑

length of solution the light  
passes through (cm)

- Molar absorptivity = Absorbance of 1 mol dm<sup>-3</sup> solution if cell length = 1 cm.

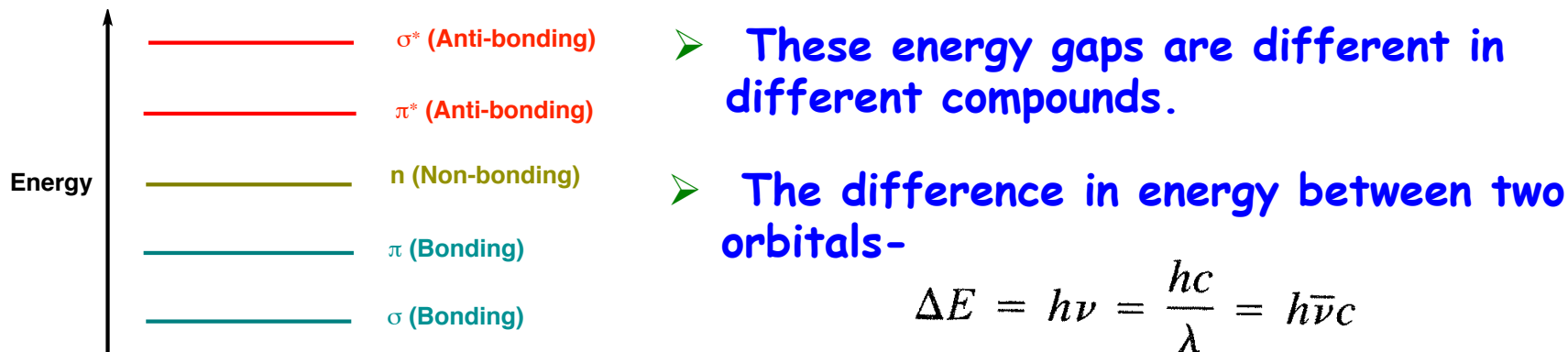
$$A = \log_{10} \frac{I_0}{I} = \epsilon l c$$

- The intensity of an absorption band in UV is expressed as the "molar absorptivity" at maximum absorption  $\epsilon_{max}$ .



# Principle Behind UV Spectrometers

## Relative Energies of Various Orbitals:



- When light passes through a compound, some of its energy promotes an electron from one of the bonding or non-bonding orbitals to one of the anti-bonding orbitals.
- The frequency (or wavelength) of absorption depends on the energy gaps between those two energy levels.

$$\Delta E = h\nu = \frac{hc}{\lambda}$$

$$c = \lambda\nu$$

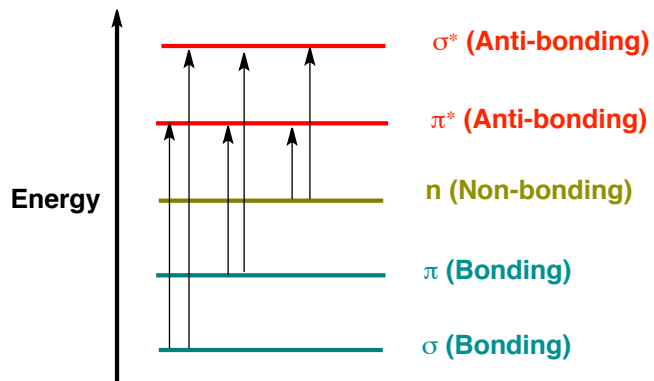
speed of light

wavelength

frequency (Greek letter, nu)



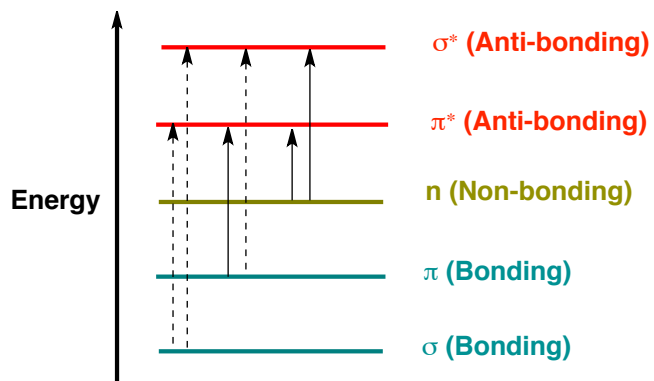
# Electronic Transitions



➤ The higher is the energy gap, the lower is the wavelength of the light absorbed.

➤ Bigger jumps requires more energy, so absorb light with a shorter wavelength.

➤ Not all electronic transitions are allowed. Certain restrictions should be considered for electronic transitions, called "selection rules"



(1) The spin quantum number of an electron should not change during the electronic transition.

(2) The transition between two orbitals should be symmetry allowed.

➤ Any transition that violates these rules are called "forbidden transition". Most common "forbidden transition" is  $n \rightarrow \pi^*$ .



# Electronic Transitions

## Important Electronic Transitions:

- From  $\pi$  (bonding) orbital to  $\pi^*$  (anti-bonding) orbital ( $\pi \rightarrow \pi^*$ ).
- From  $n$  (non-bonding) orbital to  $\pi^*$  (anti-bonding) orbital ( $n \rightarrow \pi^*$ ).
- From  $n$  (non-bonding) orbital to  $\sigma^*$  (anti-bonding) orbital ( $n \rightarrow \sigma^*$ ).
- **In Alkanes:**
  - $\sigma \rightarrow \sigma^*$  or  $n \rightarrow \sigma^*$
  - Usually weak absorptions

## Absorption Characteristics of $n \rightarrow \pi^*$

Compound	$\lambda_{\max}$	$\epsilon_{\max}$	Solvent
Methanol	177	200	Hexane
1-Hexanethiol	224 (s)	126	Cyclohexane
Trimethylamine	199	3950	Hexane
<i>N</i> -methylpiperidine	213	1600	Ether
Diethyl ether	188	1995	Gas phase
Methyl chloride	173	200	Hexane
Methyl iodide	259	400	Hexane



# Electronic Transitions

## ➤ In Alkenes:

In unconjugated alkenes  $\pi \rightarrow \pi^*$  transition takes place around 170 -190 nm.

### Absorption Data for Conjugated Alkenes ( $\pi \rightarrow \pi^*$ )

Compound	$\lambda_{\max}$	$\epsilon_{\max}$	Solvent
1,3-Butadiene	217	21,000	Hexane
2,3-Dimethyl-1,3-butadiene	226	21,400	Cyclohexane
1,3,5-Hexatriene	253	50,000	Isooctane
	263	52,000	
	274	50,000	
1,3-Cyclohexadiene	256	8,000	Hexane
1,3-Cyclopentadiene	239	3,400	Hexane

➤ In Carbonyls:  $\pi \rightarrow \pi^*$  around 190 nm ( $\epsilon = 900$ ) &  $n \rightarrow \pi^*$  around 280 nm ( $\epsilon = 15$ ).

Since  $n \rightarrow \pi^*$  transition is a symmetry forbidden transition, intensity of this transition is much lower than other allowed transitions.



# Other Examples

Chromophore	Example	Excitation	$\lambda_{\max}$	$\epsilon_{\max}$	Solvent	
$C=C$	Ethene	$\pi \rightarrow \pi^*$	165 nm	15,000	hexane	
$C\equiv C$	1-Hexyne	$\pi \rightarrow \pi^*$	173 nm	10,000	hexane	
$C=O$	Ethanal	$n \rightarrow \pi^*$	290 nm	15	hexane	
		$\pi \rightarrow \pi^*$	180 nm	10,000	hexane	
$N=O$	Nitromethane	$n \rightarrow \pi^*$	275 nm	17	ethanol	
		$\pi \rightarrow \pi^*$	200 nm	5,000	ethanol	
$C-X$	$X=Br$	Methyl bromide	$n \rightarrow \sigma^*$	205 nm	200	hexane
	$X=I$	Methyl Iodide	$n \rightarrow \sigma^*$	255 nm	360	hexane



# Conventions & Terminologies

## ➤ Chromophore:

A covalently unsaturated group responsible for electronic absorption (e.g.,  $C=C$ ,  $C=O$ , esters, amides,  $-NO_2$  etc.).

## ➤ Auxochrome:

A saturated group with non-bonded electrons which, when attached to a chromophore, alters both the wavelength and the intensity of the absorption (e.g.,  $-OH$ ,  $-NH_2$ ,  $-NR_2$ ,  $-SH$  etc.)

## ➤ Bathochromic Shift:

The shift of absorption to a longer wavelength (also known as "red shift").

## ➤ Hypsochromic Shift:

The shift of absorption to a shorter wavelength (also known as "blue shift").

➤ **Hyperchromic Effect:** An increase in absorption intensity.

➤ **Hypochromic Effect:** A decrease in absorption intensity.



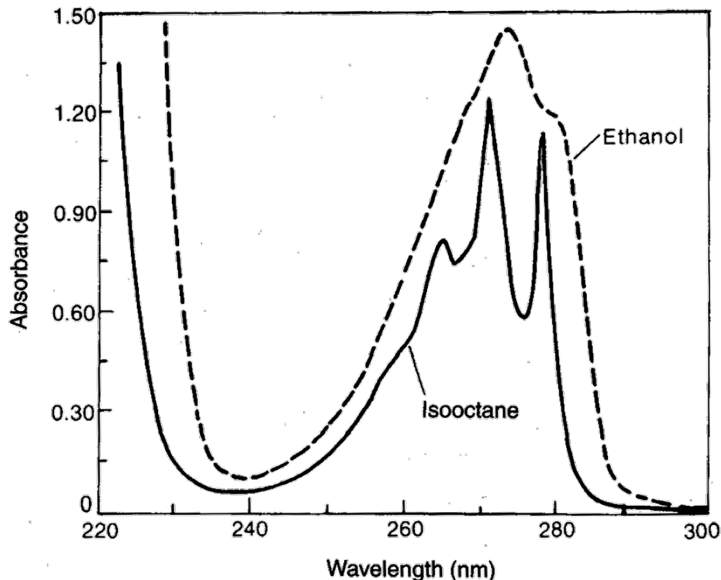


# Solvents & Solutions

- Solvents should not absorb UV-radiation within same range as the substance.

Acetonitrile	190 nm	<i>n</i> -Hexane	201 nm
Chloroform	240 nm	Methanol	205 nm
Cyclohexane	195 nm	Isooctane	195 nm
1,4-Dioxane	215 nm	Water	190 nm
95% Ethanol	205 nm	Trimethyl phosphate	210 nm

- A strong absorbing solvent allows very little amount of light to pass through the sample.



UV spectra of phenol in ethanol and isooctane.

- Non-polar solvents do not form H-bond with solute, so “fine structure” is often observed.
- Polar solvents form solute-solvent complexes through H-bonding, hence, “fine structure” may disappear.

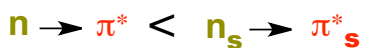
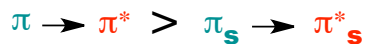
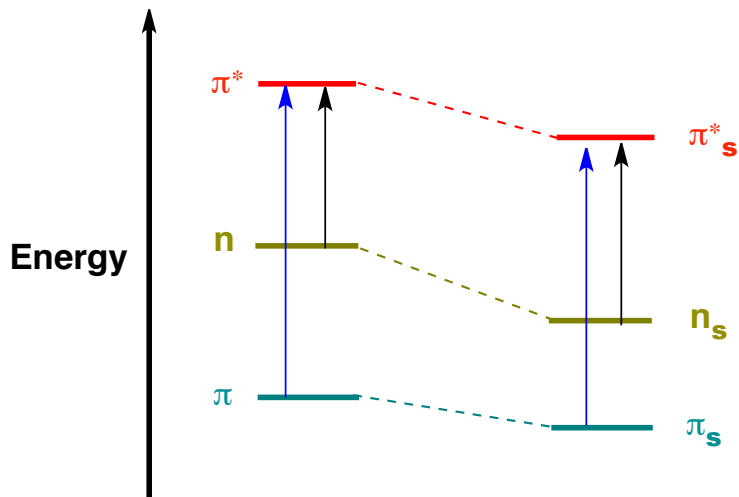


# Solvents & Solutions

## Solvent Effects:

The position and intensity of an absorption band may shift if the spectrum was recorded in different solvents.

- Conjugated dienes and aromatic hydrocarbons experience very less "solvent effect".
- $\alpha,\beta$ -Unsaturated carbonyls show two different shifts in bands for changing solvents from non-polar to a polar protic one.

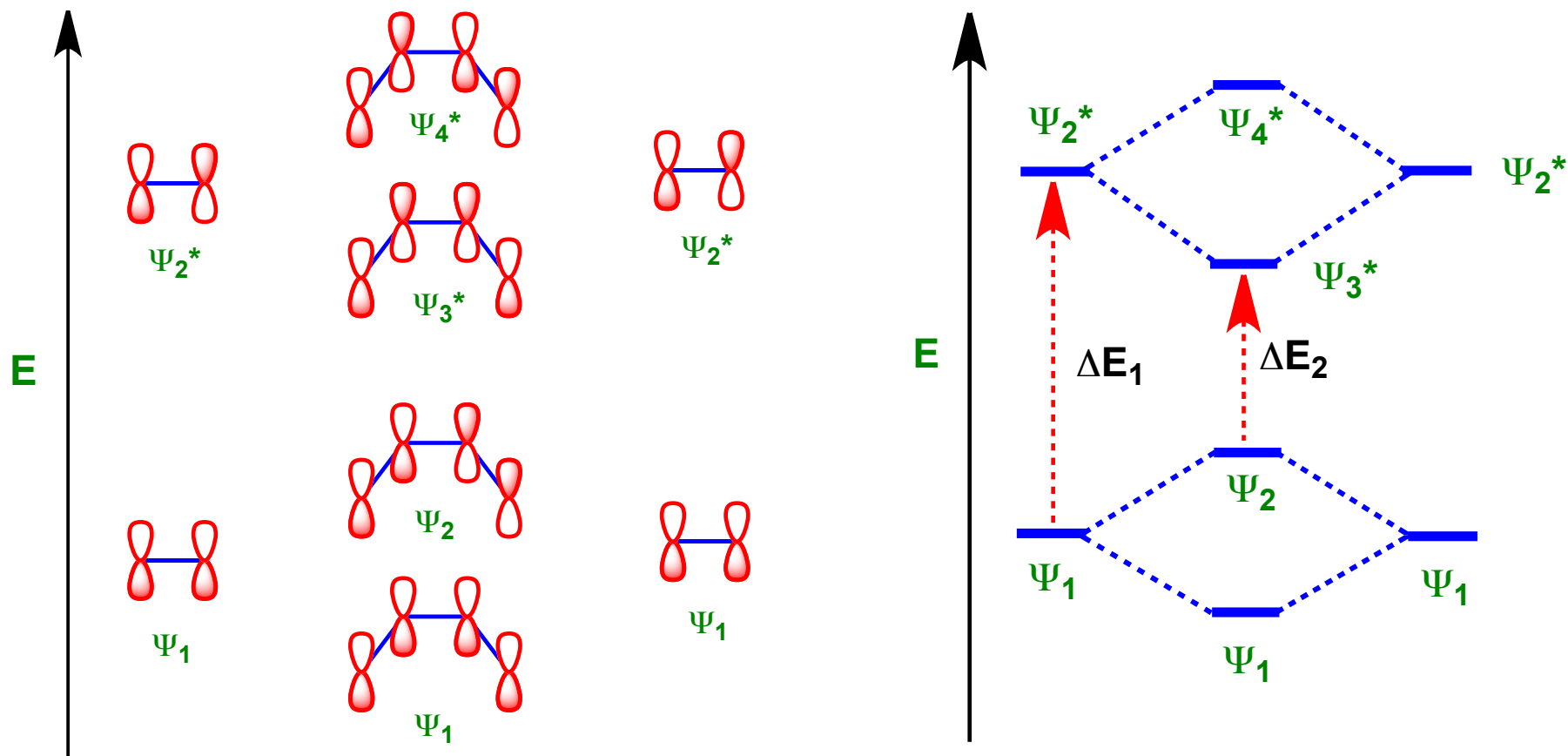


- $\pi \rightarrow \pi^*$  band moves to longer wavelength,  $n \rightarrow \pi^*$  band moves to shorter wavelength.

- $\pi^*$  orbitals get stabilized (due to more polarity) by solvation than  $\pi$  orbitals.  $n$  orbitals get stabilized mainly by H-bonding.

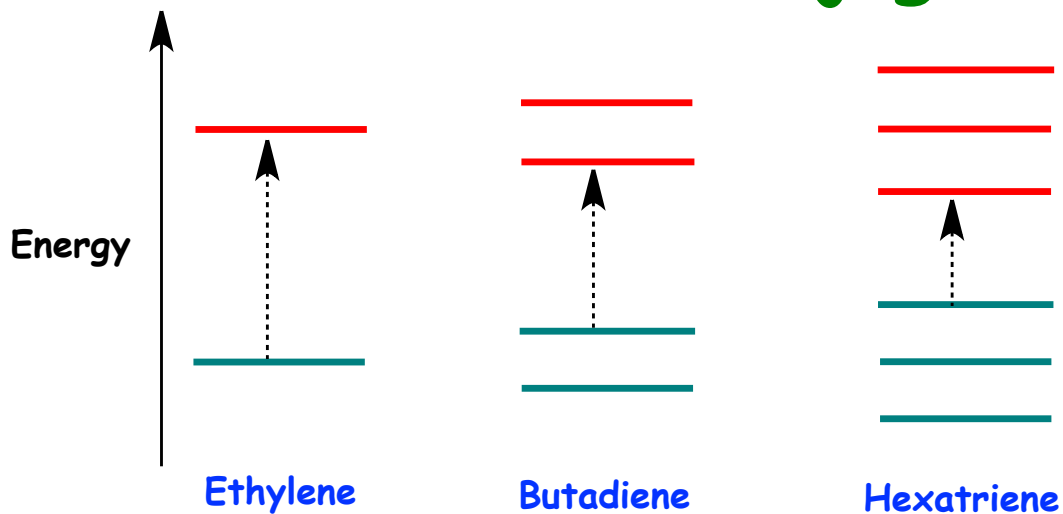


# Effect of Conjugation





# Effect of Conjugation



## Molecule

Ethylene

1,3-butadiene

1,3,5-hexatriene

$\beta$ -Carotene

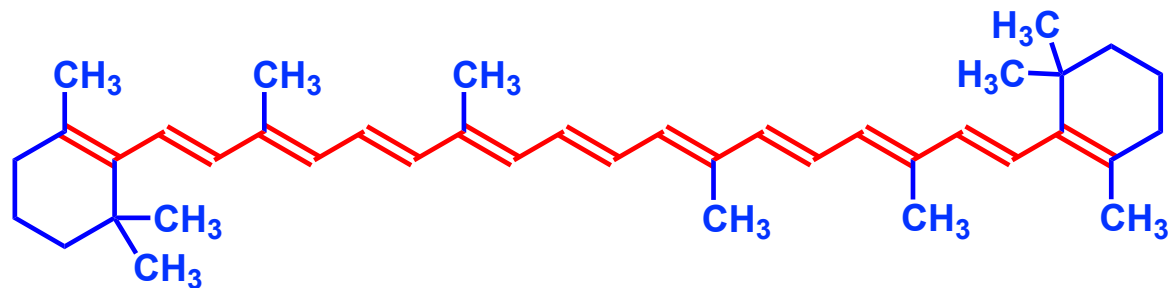
## $\lambda_{\max}$ (nm)

165

217

258

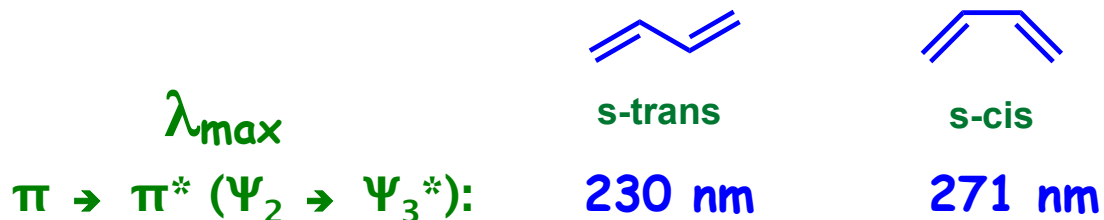
470



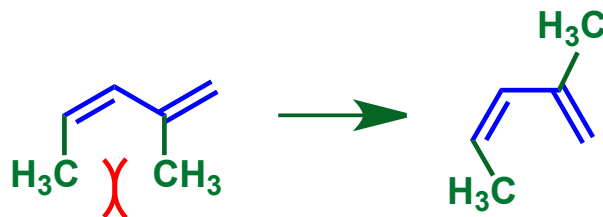


# Effect of Conjugation

## Effect of s-cis & s-trans Conformers:



- Probably repulsion between terminal lobes of  $\Psi_2$  increases energy of HOMO ( $\Psi_2$ ) in s-cis form. Hence, less energy (ie. Higher wavelength) is required for  $\Psi_2 \rightarrow \Psi_3^*$  transition.



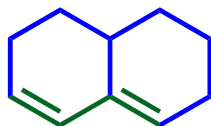
- Substitution may force a molecule to take s-cis form, therefore, absorbs energy from a longer wavelength (shows a red shift) than usual s-trans conformer.



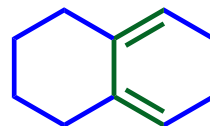
# Effect of Conjugation

- In cyclic system a double bond is forced to stay in s-cis (Cisoid) form, therefore, shows a red shift with a drop in intensity.

## Homoannular & Heteroannular Dienes:



$$\lambda_{\max} = 234 \text{ nm}$$
$$\epsilon_{\max} = 12000-28000$$



$$\lambda_{\max} = 273 \text{ nm}$$
$$\epsilon_{\max} = 5000-15000$$



# Woodward-Fieser Rules for Diene

- Woodward (1941) predicted  $\lambda_{\max}$  values only for the lowest energy transition ( $\pi \rightarrow \pi^*$ ) from HOMO to LUMO.

## Base values:

- Base value for an unsubstituted, conjugated, acyclic or heteroannular diene 214 nm
- Base value for an unsubstituted, conjugated, homoannular diene 253 nm

## Increments for:

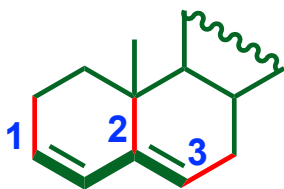
- Each extra double bonds in conjugation + 30 nm
- Exocyclic double bond (effect is two fold if the bond is exocyclic to two rings) + 5 nm

## Substituent effect:

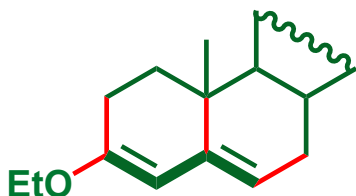
- A. -OCOR or -OCOAr + 0 nm
- B. Simple alkyl substituents or ring residue + 5 nm
- C. Halogen (-Cl, -Br) + 5 nm
- D. OR (R=Alkyl) + 6 nm
- E. SR (R=Alkyl) + 30 nm
- F. NR<sub>2</sub> (R=Alkyl) + 60 nm



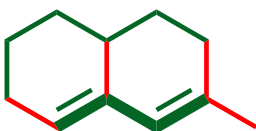
# Woodward-Fieser Rules for Diene



Transoid (base):	214 nm
3 ring residues :	+15
1 exocyclic C=C:	+ 5
Total:	<hr/> 234 nm
Observed:	235 nm



Transoid (base):	214 nm
3 ring residues:	+15
1 exocyclic C=C:	+ 5
-OR:	+ 6
Total:	<hr/> 240 nm
Observed:	241 nm

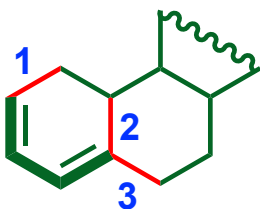


Transoid (base):	214 nm
3 Ring residues:	+15
1 Alkyl substituent:	+ 5
1 Exocyclic C=C:	+ 5
Total:	<hr/> 239 nm

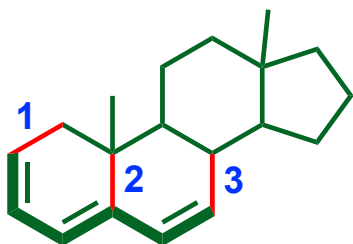




# Woodward-Fieser Rules for Diene



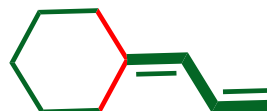
Cisoid (base):	253 nm
3 ring residues:	+15
1 exocyclic C=C:	+ 5
Total:	<hr/> 273 nm
Observed:	275 nm



Cisoid (base):	253 nm
3 Ring residues:	+15
1 Exocyclic C=C:	+ 5
Double-bond Extending Conjugation:	+30
Total:	<hr/> 303 nm
Observed:	304 nm



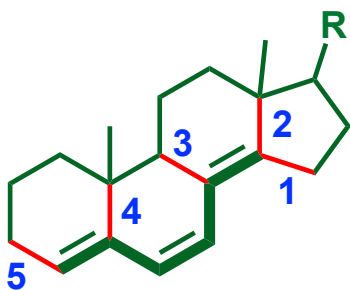
Base value:	214 nm
2 Ring residue	+10
Exocyclic C=C:	+ 5
Total:	<hr/> 229 nm
Observed:	230 nm



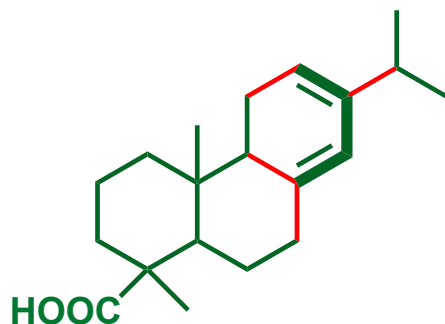
Base value:	214 nm
2 Ring residue:	+10
Exocyclic C=C:	+ 5
Total	<hr/> 229 nm
Observed:	236 nm



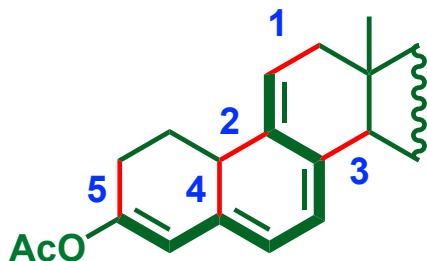
# Woodward-Fieser Rules for Diene



Transoid (base):	214 nm
5 ring residues:	+25
1 DEC:	+30
3 exocyclic C=C	+15
Total:	<hr/> 284 nm
Observed:	283 nm



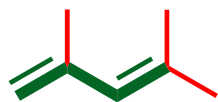
Cisoid (base):	253 nm
3 ring residues:	+15
1 Alkyl subs:	+5
1 exocyclic C=C	+5
Total:	<hr/> 278 nm
Observed:	275 nm



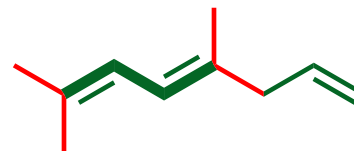
Cisoid (base):	253 nm
5 ring residues:	+25
2 DEC:	+60
3 exocyclic C=C	+15
Total:	<hr/> 353 nm
Observed:	355 nm



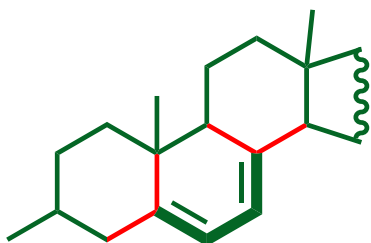
# Woodward-Fieser Rules for Diene



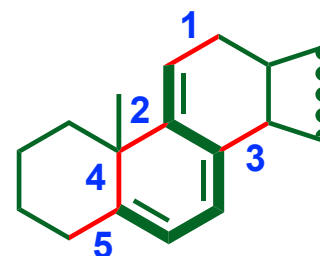
Base value:	214 nm
3 Alkyl grs:	<u>+15</u>
Total:	229 nm
Observed:	232 nm



Base value:	214 nm
4 Alkyl grs:	<u>+20</u>
Total:	234 nm
Observed:	235 nm



Base value:	253 nm
4 Ring residues:	+20
2 Exocyclic C=C:	<u>+10</u>
Total:	283 nm
Observed:	282 nm



Base value:	253 nm
5 Ring residues:	+25
3 Exocyclic C=C:	+15
DEC:	<u>+30</u>
Total	323 nm
Observed:	325 nm



# Woodward-Fieser Rule for Enones

## Rules of Enone & Dienone Absorption

### Base values:

➤ Acyclic $\alpha,\beta$ -unsaturated ketones	215 nm
➤ 6-membered cyclic $\alpha,\beta$ -unsaturated ketones	215 nm
➤ 5-membered cyclic $\alpha,\beta$ -unsaturated ketones	202 nm
➤ $\alpha,\beta$ -unsaturated aldehydes	210 nm
➤ $\alpha,\beta$ -unsaturated carboxylic acid & esters	195 nm

### Increments for:

Double bond extending conjugation (DEC):	+30
Exocyclic double bond:	+ 5
Homodiene component:	+39



# Woodward-Fieser Rule for Enones

*Increments for:*

Alkyl group/ring residue:  $\alpha$  +10

$\beta$  +12

$\gamma$  & higher +18

Polar groups: -OH:  $\alpha$  +35

$\beta$  +30

$\delta$  +50

-OAc:  $\alpha, \beta, \gamma$  + 6

-OMe:  $\alpha$  +35

$\beta$  +30

$\gamma$  +17

$\delta$  +31

-SAlk:  $\beta$  +85

-Cl:  $\alpha$  +15

$\beta$  +12

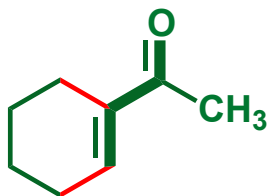
-Br:  $\alpha$  +25

$\beta$  +30

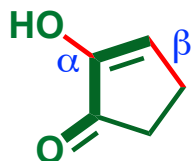
-NR<sub>2</sub>:  $\beta$  +95



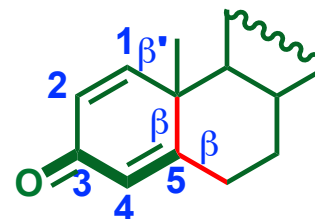
# Woodward-Fieser Rule for Enones



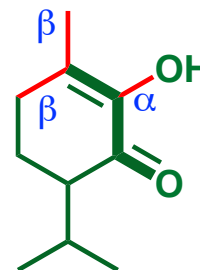
Base value:	215 nm
$\alpha$ substituent:	+10
$\beta$ substituent:	+12
Total:	237 nm
Observed:	232 nm



Base value:	202 nm
$\beta$ substituent:	+12
$\alpha$ -OH:	+35
Total:	249 nm
Observed:	247 nm



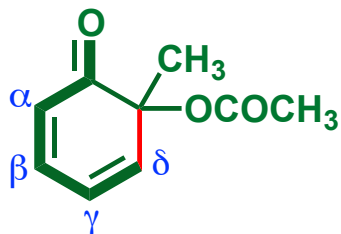
$\Delta^{4,5}$ system (base):	215 nm
2 $\beta$ substituents:	+24
1 exocyclic C=C:	+5
Total:	244 nm
Observed:	245 nm



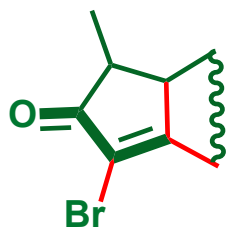
Base value:	215 nm
2 $\beta$ substituents:	+24
$\alpha$ -OH:	+35
Total:	274 nm
Observed:	270 nm



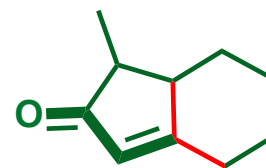
# Woodward-Fieser Rule for Enones



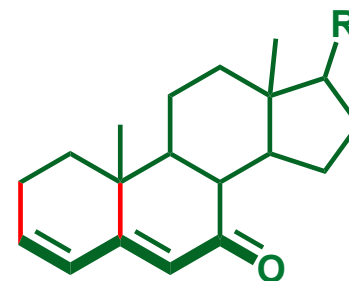
Base value:	215 nm
1 DEC:	+30
Homocyclic diene:	+39
$\delta$ ring residue:	+18
Total:	302 nm
Observed:	300 nm



Base value:	202 nm
1 $\alpha$ -Br:	+25
2 $\beta$ -ring residue:	+24
Exocyclic C=C:	+5
Total:	256 nm
Observed:	251 nm



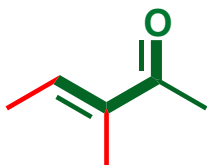
Base value:	202 nm
Exocyclic C=C:	+5
2 $\beta$ -ring residues:	+24
Total:	231 nm
Observed:	226 nm



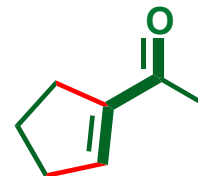
Base value:	215 nm
1 DEC:	+30
$\beta$ -ring residue:	+12
$\delta$ ring residue:	+18
2 Exocyclic C=C:	+5
Total:	280 nm
Observed:	280 nm



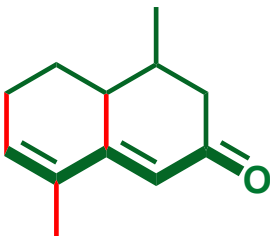
# Woodward-Fieser Rule for Enones



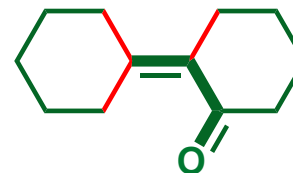
Base value:	215 nm
$\alpha$ alkyl substituent:	+10
$\beta$ alkyl substituent:	+12
Total:	<u>237 nm</u>



Base value:	215 nm
$\alpha$ alkyl:	+10
$\beta$ alkyl:	+12
Total:	<u>237 nm</u>



Base value:	215 nm
1 DEC:	+30
Exocyclic C=C:	+5
$\beta$ -alkyl substituent:	+12
$\gamma$ -alkyl substituent:	+18
$\delta$ -alkyl substituent:	+18
Total:	<u>298 nm</u>



Base value:	215 nm
1 $\alpha$ -alkyl:	+10
2 $\beta$ -alkyl:	+24
2 Exocyclic C=C:	+10
Total:	<u>259 nm</u>





# Aromatic Compounds

Parent chromophore: Ar = C<sub>6</sub>H<sub>5</sub>

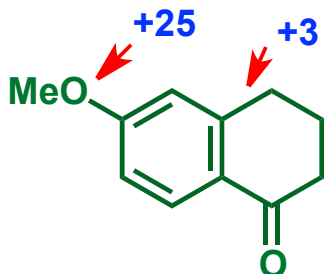
Ar-CO-R	246 nm
Ar-CHO	250 nm
Ar-COOH or Ar-COOR	230 nm

## *Increment for each substituent on Ar:*

Alkyl or ring residue	<i>o, m</i>	+ 3 nm
	<i>p</i>	+ 10 nm
OH, OCH <sub>3</sub> , OAlk	<i>o, m</i>	+ 7 nm
	<i>p</i>	+ 25 nm
NH <sub>2</sub>	<i>o, m</i>	+ 13 nm
	<i>p</i>	+ 58 nm
NHCOCH <sub>3</sub>	<i>o, m</i>	+ 20 nm
	<i>p</i>	+ 45 nm
NHMe	<i>p</i>	+ 73 nm
	NMe <sub>2</sub>	<i>o, m</i>
<i>p</i>		+ 85 nm
Cl	<i>o, m</i>	+ 0 nm
	<i>p</i>	+ 10 nm
Br	<i>o, m</i>	+ 2 nm
	<i>p</i>	+ 15 nm

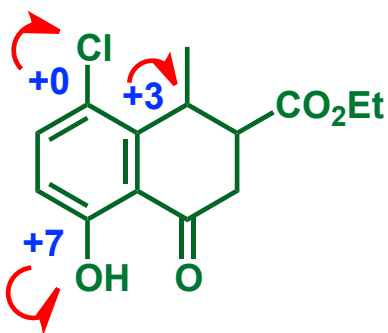


# Aromatic Compounds



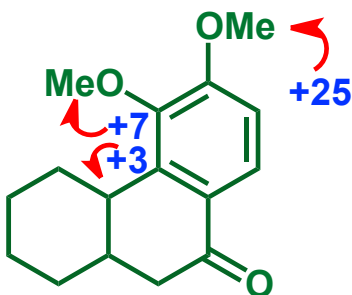
$$\begin{aligned}\text{Calc } \lambda_{\text{max}}^{\text{EtOH}} &= 246 \text{ (parent chromophore)} + 3 \text{ (o-ring residue)} + 25 \text{ (p-OMe)} \\ &= 274 \text{ nm}\end{aligned}$$

$$\text{Obs } \lambda_{\text{max}}^{\text{EtOH}} = 276 \text{ nm}$$



$$\begin{aligned}\text{Calc } \lambda_{\text{max}}^{\text{EtOH}} &= 246 + 3 \text{ (o-ring residue)} + 7 \text{ (o-OH)} \\ &= 256 \text{ nm}\end{aligned}$$

$$\text{Obs } \lambda_{\text{max}}^{\text{EtOH}} = 257 \text{ nm}$$



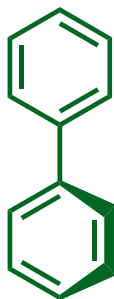
$$\text{Calc } \lambda_{\text{max}}^{\text{EtOH}} = 246 + 25 + 7 + 3 = 281 \text{ nm}$$

$$\text{Obs } \lambda_{\text{max}}^{\text{EtOH}} = 278 \text{ nm}$$



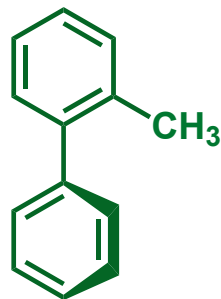
# Violations of Woodward Rules

## Biphenyls:



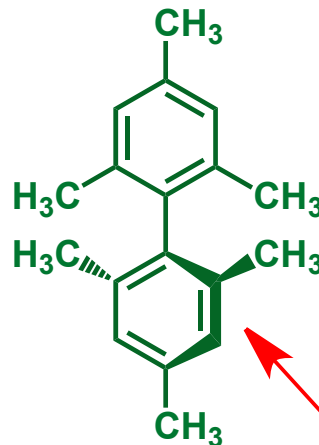
250 nm

Not planar  
45 °C angle

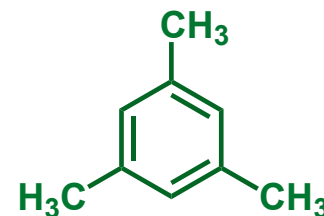


237 nm

Substitutions cause loss of co-planarity of orbitals.  
Loss of overlap, blue shift with reduced intensity.



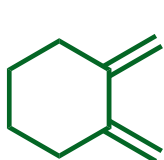
266 nm



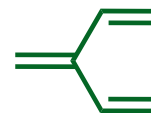
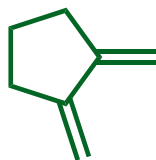


# Steric Inhibition of Resonance

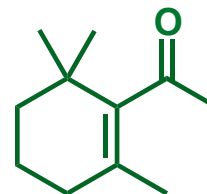
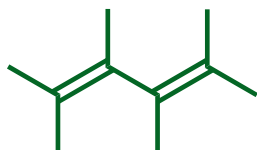
- (1) In alkenes, trans isomers exhibit absorption at longer wavelength and high intensity.
- (2) Woodward rules are applicable only if there is no strain around chromophore.



Ring strain



Cross conjugation



Steric inhibition of resonance

- (3) If calculated and experimental values of  $\lambda_{\max}$  do not match, one can say that the molecule must have some strain.
- (4) Thus UV can be used indirectly to determine if the molecule has any strain.



# Fieser-Kuhn rules for Conjugated Polyenes

$$\lambda_{\max} = 114 + 5M + n(48.0 - 1.7n) - 16.5R_{\text{endo}} - 10R_{\text{exo}}$$

$$\epsilon_{\max} = (1.74 \times 10^4)n$$

Where  $n$  = number of conjugated double bonds

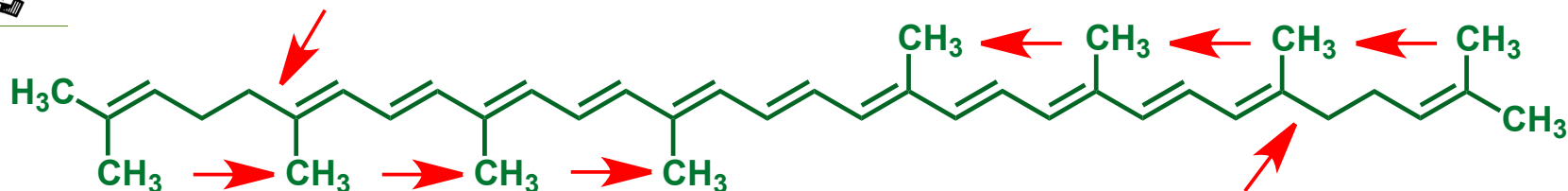
$M$  = number of alkyl or alkyl like substituents on the conjugated system

$R_{\text{endo}}$  = number of rings with endocyclic double bonds in the conjugated system

$R_{\text{exo}}$  = number of rings with exocyclic double bonds



# Lycopene



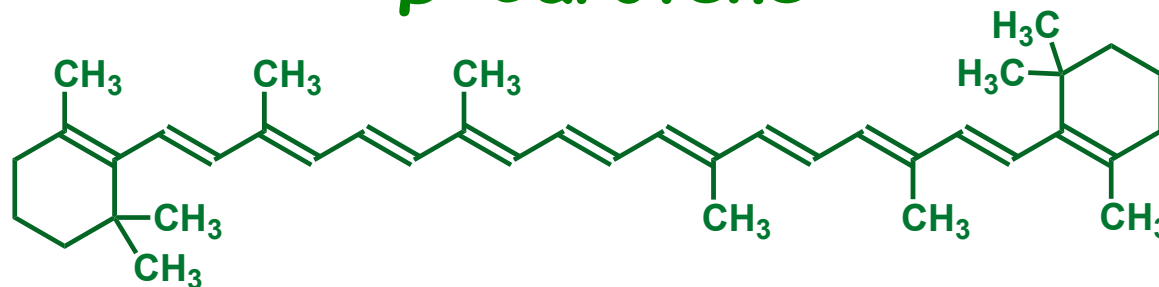
$$\lambda_{\max}^{\text{calc}} = 114 + 5(8) + 11[48.0 - 1.7(11)] - 0 - 0$$
$$= 476 \text{ nm}$$

$$\lambda_{\max}^{\text{obs}} = 474 \text{ nm (hexane)}$$

$$\epsilon_{\max}^{\text{cal}} = 1.74 \times 10^4(11) = 19.1 \times 10^4$$

$$\epsilon_{\max}^{\text{obs}} = 18.6 \times 10^4 \text{ (hexane)}$$

# $\beta$ -Carotene



$$\lambda_{\max}^{\text{calc}} = 453.3 \text{ nm}$$

$$\lambda_{\max}^{\text{obs}} = 452 \text{ nm (hexane)}$$

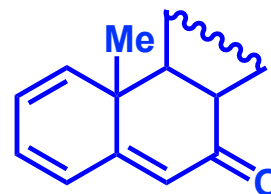
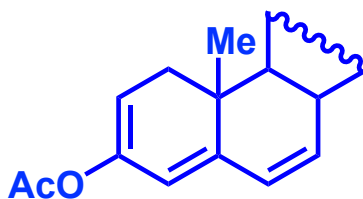
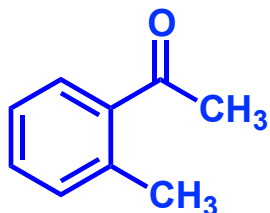
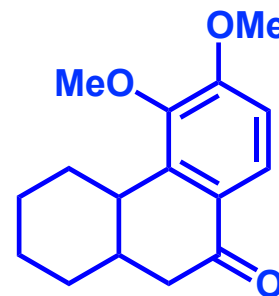
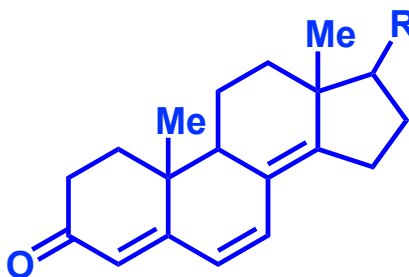
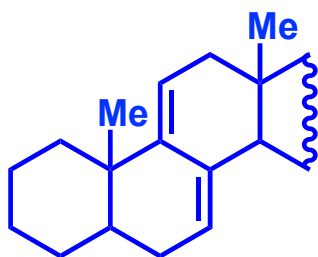
$$\epsilon_{\max}^{\text{cal}} = 19.1 \times 10^4$$

$$\epsilon_{\max}^{\text{obs}} = 15.2 \times 10^4$$

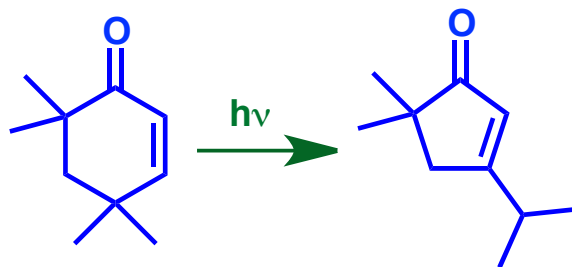


# Home Work

Predict  $\lambda_{\max}$  values of the following compounds using Woodward-Fieser rules:



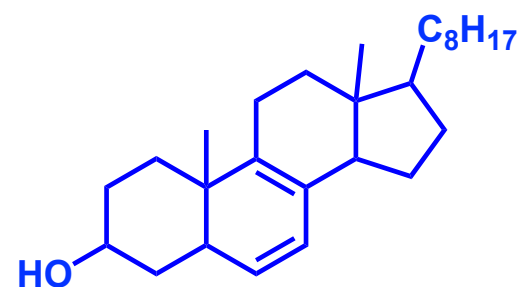
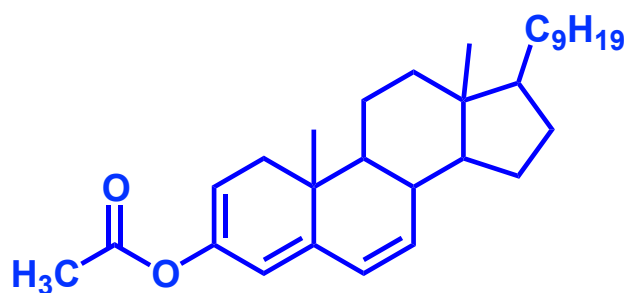
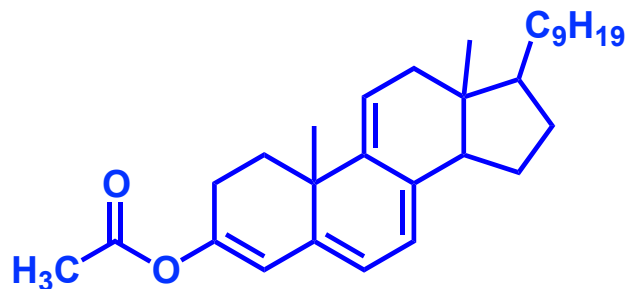
Is it possible to use UV spectroscopy as a tool to predict the course of this reaction ?





# Home Work

Match three steroid structures shown below to the following values for  $\lambda_{\max}^{\text{hexane}}$ : Compound A, 275 nm; B, 304 nm, and C, 356 nm.



Partial hydrogenation of the triene shown below results in two compounds, D and E, both of molecular formula  $C_{10}H_{14}$ . Compound D shows a  $\lambda_{\max}^{\text{hexane}} = 235$  nm and E, 275 nm. Assign the structures.

