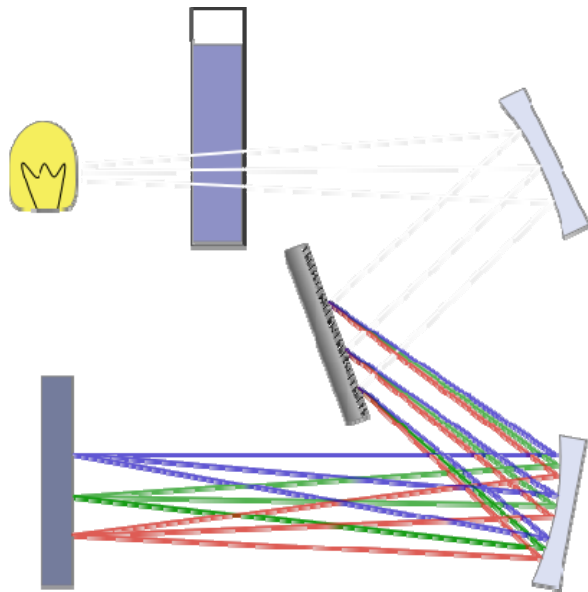


UV-vis Absorption (Extinction) Spectroscopy



Single-Beam or Double-Beam

Fixed λ or Dispersive

Common:

Source – Tungsten Halogen Lamp (360-2000 nm)

Sample – Liquid In Cuvette

Dispersion – Spectrograph w/ Diffraction Grating

Detector – CCD

Beer's Law: $A = \epsilon bc$

Assumptions

TABLE 3-1

Assumptions of the absorption law

1. The incident radiation is monochromatic.
 2. The absorbers (molecules, atoms, ions, etc.) act independently of each other.
 3. The incident radiation consists of parallel rays, perpendicular to the surface of the absorbing medium.
 4. The pathlength traversed is uniform over the cross section of the beam. (All rays traverse an equal distance of the absorbing medium.)
 5. The absorbing medium is homogeneous and does not scatter the radiation.
 6. The incident flux is not large enough to cause saturation effects. (Lasers can cause such effects, as discussed in Chapters 11 and 15.)
-

Apparent Deviations from Beer's Law

Non-Zero Intercept

Improper blank
measurement or
correction.

Instrumental drift.

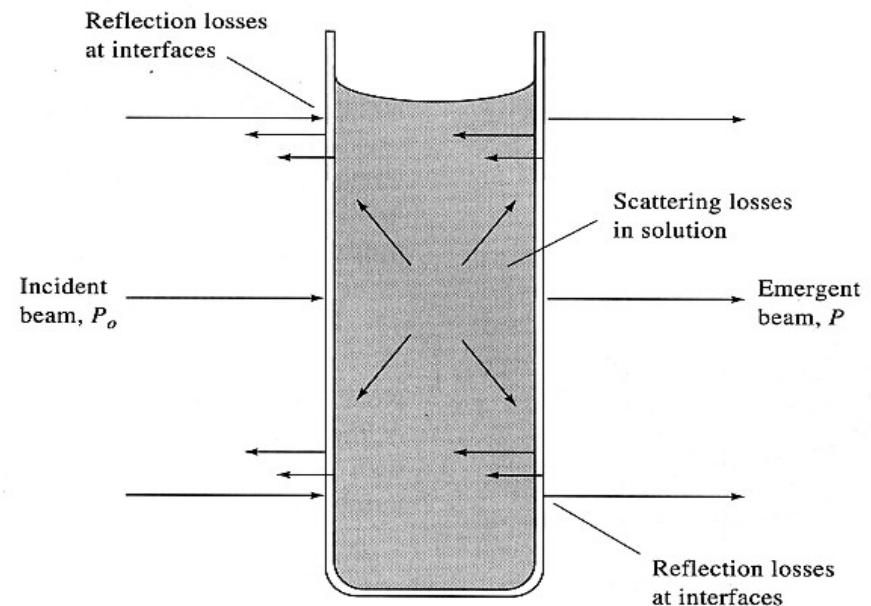


Figure 13-1 Reflection and scattering losses.

Apparent Deviations from Beer's Law

Non-Linear Calibration Plot

Chemical Equilibrium – if multiple chemical forms of analyte exist and only one absorbs

Other Chemical Effects – solute/solvent interactions, solute/solute interactions, H bonding at high concentrations

Using Polychromatic Radiation – non-optimum wavelengths are still transmitted and detected

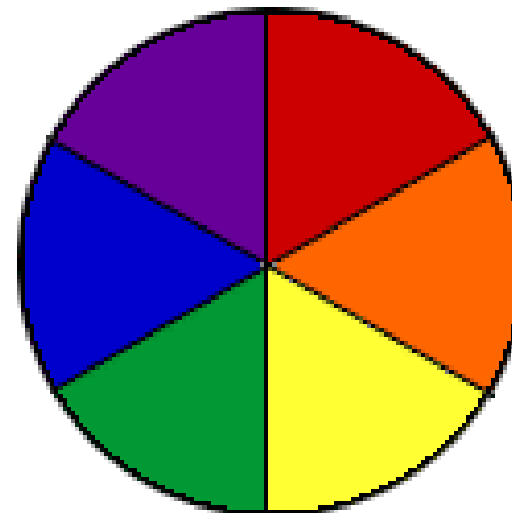
Stray Light – causes measured transmittance to be larger than it should be

Absorbed/Emitted Colors

8.1

Correlation between Wavelength of Absorbed Radiation and Observed Color

Absorbed light		Observed (transmitted) color
Wavelength [nm]	Corresponding color	
400	violet	yellow-green
425	indigo blue	yellow
450	blue	orange
490	blue-green	red
510	green	purple
530	yellow-green	violet
550	yellow	indigo blue
590	orange	blue
640	red	blue-green
730	purple	green



Chromophores

Often transitions are localized in specific bonds or functional groups within a molecule.

Group will have a characteristic λ_{\max} and ϵ .

Molecular structure or environment can influence λ_{\max} and ϵ .

Shift to longer λ \rightarrow bathochromic (red) shift.

Shift to shorter λ \rightarrow hypsochromic (blue) shift.

Increase in ϵ \rightarrow hyperchromic effect.

Decrease in ϵ \rightarrow hypochromic effect.

What effect does conjugation usually have?

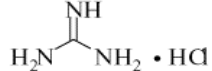
hyperchromic effect / bathochromic shift

Characteristic Electronic Transitions

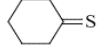
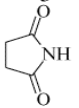
8.2

UV/Vis Absorption of Simple Chromophores

L mol⁻¹ cm⁻¹

Chromophore	Compound	Transition	λ_{\max}	ϵ_{\max}	Solvent
C-H	CH ₄	$\sigma \rightarrow \sigma^*$	122	strong	gas
C-C	CH ₃ -CH ₃	$\sigma \rightarrow \sigma^*$	135	strong	gas
C=C	CH ₂ =CH ₂	$\pi \rightarrow \pi^*$	162	15000	heptane
	(CH ₃) ₂ C=C(CH ₃) ₂	$\pi \rightarrow \pi^*$	196	11500	heptane
C=C=C	CH ₂ =C=CH ₂		170	4000	
			227	630	
C≡C	CH≡CH		173	6000	gas
	<i>n</i> -C ₅ H ₁₁ -C≡C-CH ₃		178	10000	hexane
			196	2000	
			222	160	
C-Cl	CH ₃ Cl	$n \rightarrow \sigma^*$	173	200	hexane
C-Br	<i>n</i> -C ₃ H ₇ Br	$n \rightarrow \sigma^*$	208	300	hexane
C-I	CH ₃ I	$n \rightarrow \sigma^*$	259	400	hexane
C-O	CH ₃ OH	$n \rightarrow \sigma^*$	177	200	hexane
	CH ₃ OCH ₃	$n \rightarrow \sigma^*$	184	2500	gas
C-N	(C ₂ H ₅) ₂ NH	$n \rightarrow \sigma^*$	193	2500	hexane
	(CH ₃) ₃ N	$n \rightarrow \sigma^*$	199	4000	hexane
C=N			265	15	water
	(CH ₃) ₂ C=NOH		193	2000	ethanol
	(CH ₃) ₂ C=NONa		265	200	ethanol

Characteristic Electronic Transitions

Chromophore	Compound	Transition	λ_{\max}	ϵ_{\max} ← Solvent	$\text{L mol}^{-1} \text{cm}^{-1}$
N=N	$\text{CH}_3\text{-}\bar{\text{N}}\text{=N-CH}_3$		340	16	ethanol
N=O	$(\text{CH}_3)_3\text{C-NO}$		300	100	ether
	$(\text{CH}_3)_3\text{C-NO}_2$		665	20	
	$(\text{CH}_3)_3\text{C-NO}_2$		276	27	ethanol
	$n\text{-C}_4\text{H}_9\text{-O-NO}$		218	1050	ethanol
			313–384	20–40	ethanol
	$\text{C}_2\text{H}_5\text{-O-NO}_2$		260	15	ethanol
C≡N	CH_3CN		<190		
X=Y=Z	$\text{C}_2\text{H}_5\text{-N=C=S}$		250	1200	hexane
	$\text{C}_2\text{H}_5\text{-N=C=N-C}_2\text{H}_5$		230	4000	
			270	25	
C-S	CH_3SH	$n \rightarrow \sigma^*$	195	1800	gas
		$n \rightarrow \sigma^*$	235	180	
	$\text{C}_2\text{H}_5\text{-S-C}_2\text{H}_5$	$n \rightarrow \sigma^*$	194	4500	gas
		$n \rightarrow \sigma^*$	225	1800	
	$\text{C}_2\text{H}_5\text{-S-S-C}_2\text{H}_5$	$n \rightarrow \sigma^*$	194	5500	hexane
		$n \rightarrow \sigma^*$	250	380	
C=S	$(\text{CH}_3)_2\text{C=S}$		460	weak	
			495	weak	ethanol
C=O	$(\text{CH}_3)_2\text{C=O}$	$n \rightarrow \sigma^*$	166	16000	gas
		$\pi \rightarrow \pi^*$	189	900	hexane
		$n \rightarrow \pi^*$	279	15	hexane
	CH_3COOH	$n \rightarrow \pi^*$	200	50	gas
	CH_3COONa	$n \rightarrow \pi^*$	210	150	water
	$\text{CH}_3\text{COOC}_2\text{H}_5$	$n \rightarrow \pi^*$	210	50	gas
	CH_3CONH_2	$n \rightarrow \pi^*$	220	63	water
			191	15200	CH_3CN
C=C=O	$(\text{C}_2\text{H}_5)_2\text{C=C=O}$		227	360	
			375	20	

Auxophore

Does not absorb

Induces a bathochromic shift and hyperchromic effect when conjugated to a chromophore (e.g. -OH, -Br, -NH₂).

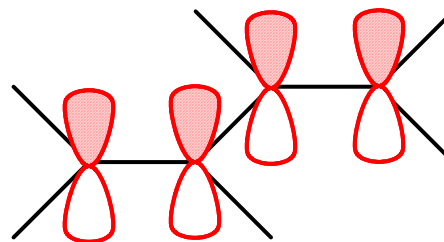
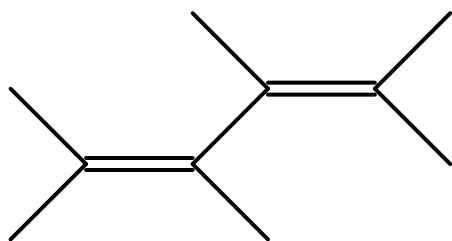
Solvent Effects

Hypsochromic shift in $n \rightarrow \pi^*$ transitions as solvent polarity increases. Solvation stabilizes the nonbonding pair.

Bathochromic shift in $\pi \rightarrow \pi^*$ transitions as solvent polarity increases. Solvation stabilizes π^* , which is often more polar than π .

Conjugated Alkenes

Woodward-Fieser Rules

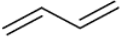
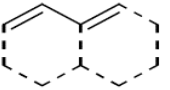

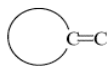


Solvent correction

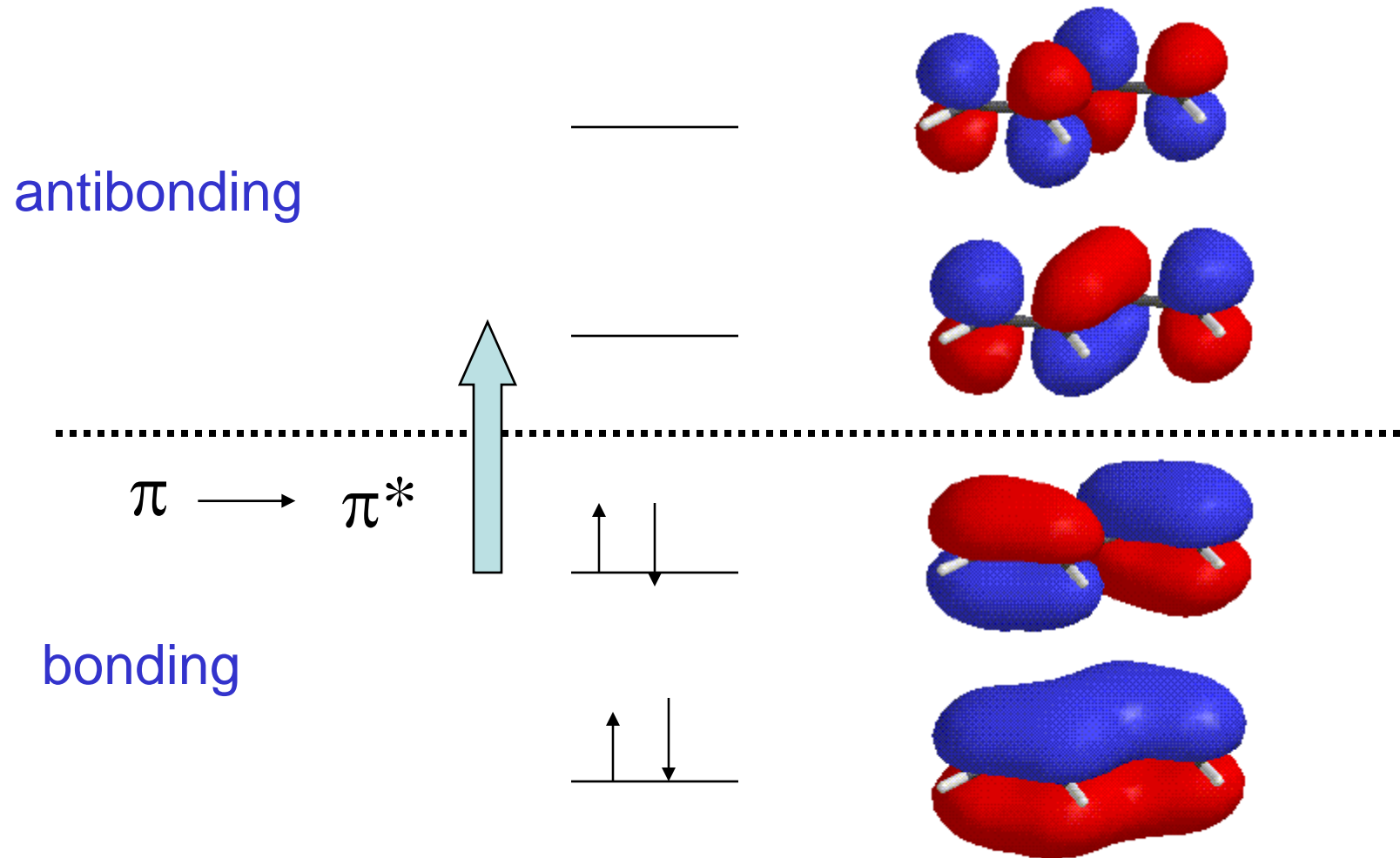
8.3.1 UV Absorption of Dienes and Polyenes

The π - π^* transition of conjugated double bonds is above ≈ 200 nm with typical intensities of the order of $\log \epsilon \approx 4$. Its position can be estimated with the Woodward-Fieser rule. For cross-conjugated systems, the value for the chromophore absorbing at the longest wavelength must be calculated.

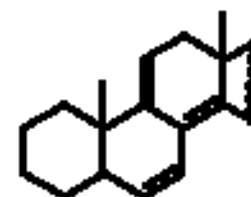
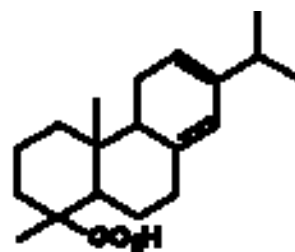
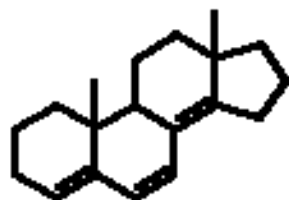
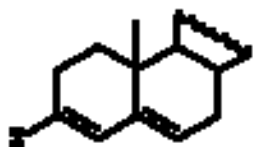
Woodward-Fieser rule for estimating the position of the π - π^* transition (λ_{max} in nm)

Parent system		acyclic	217
		heteroannular	214
		homoannular	253
Increments	for each additional conjugated double bond		+30
	for each exocyclic double bond 		+5
	for each substituent		
		C-substituent	+5
		Cl	+5
		Br	+5
		O-alkyl	+6
		OCOCH ₃	0
		N(alkyl) ₂	+60
		S-alkyl	+30
		Solvent correction	≈ 0

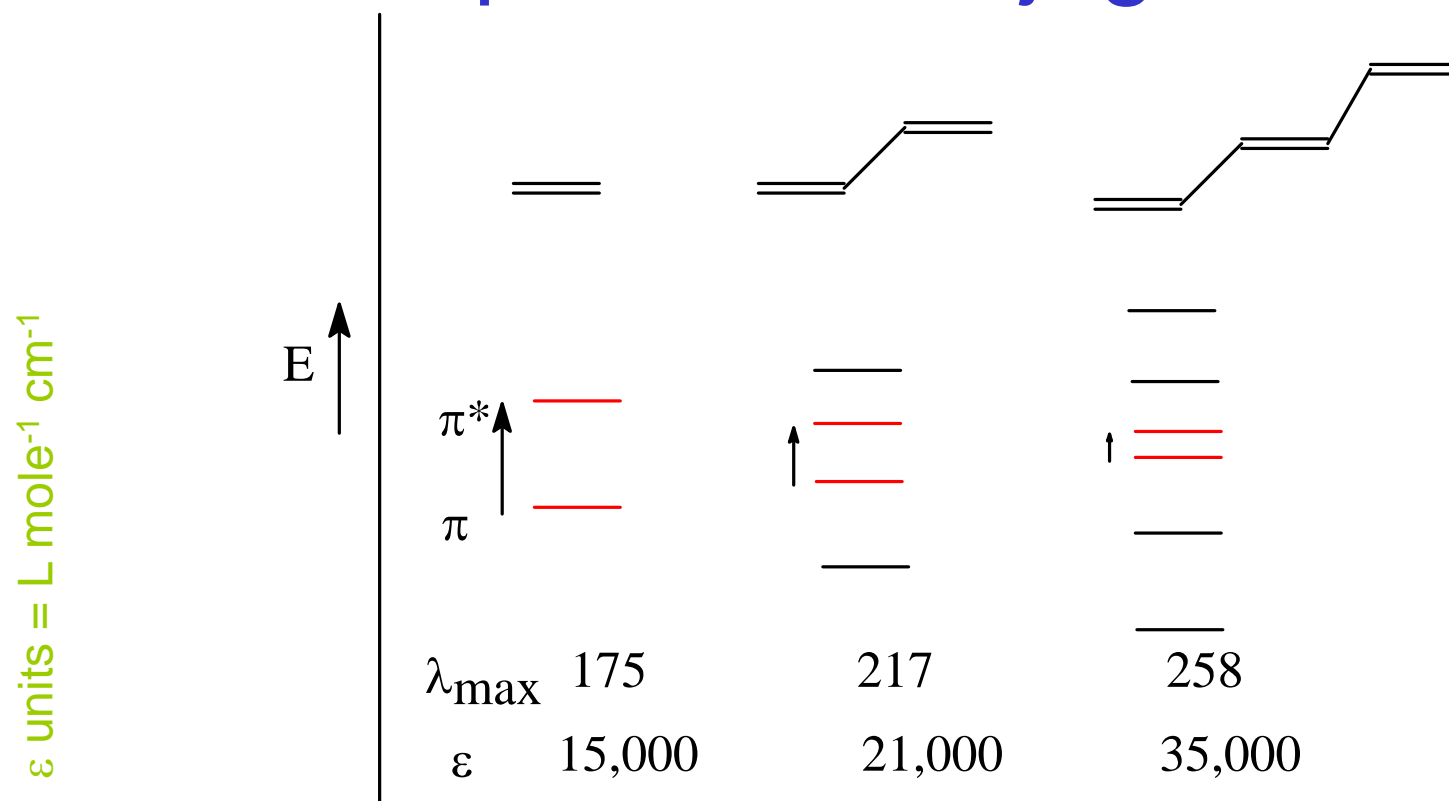
1,3-butadiene



Conjugated Dienes

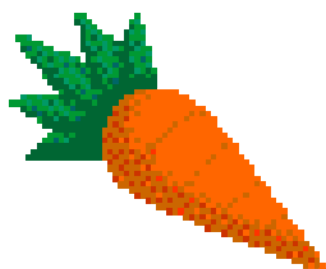


UV Absorption of Conjugated Alkenes

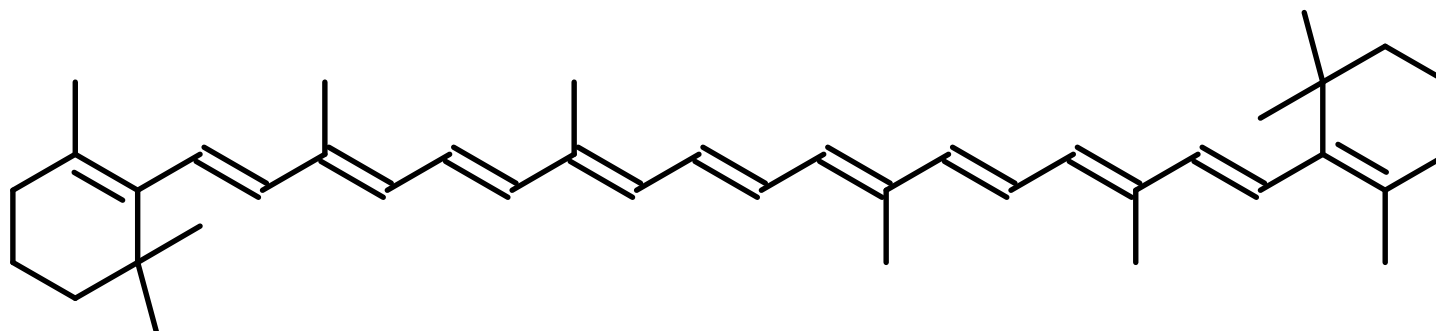
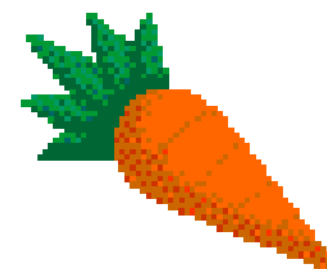


Increasing conjugation gives:

- longer wavelength absorption
- more intense absorption

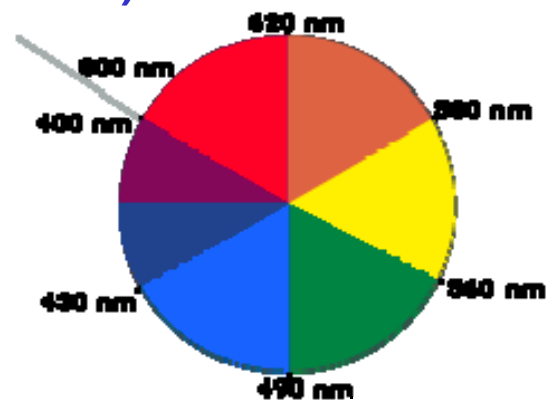


β -Carotene



11 double bonds

$$\lambda_{\max} = 460 \text{ nm } (\epsilon = 139,000)$$



Fieser-Kuhn Rules

Systems with More than 4 Double Bonds

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

n = number of conjugated double bonds

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

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

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

Are you getting the concept?

Calculate the absorption maximum for lycopene:

