

UV-VIS (electron spectroscopy)**Introduction**

Spectral Region:

Vacuum UV: 190–100 nm

UV: 400–190 nm

Visible: 400–800 nm

Electron excitation – transitions of valence electrons

To detect the presence of **the conjugated hydrocarbons****Beer's Law**

$$A = \log (1/T) = \log (I_0/I) = \epsilon \cdot c \cdot b$$

A: absorbance or optical density

 ϵ : molar absorptivity or extinction coefficient

c: concentration in mole/L

b: path length of sample cell in cm unit

Peak intensity $\sim \epsilon$: molar absorptivity [L/(mole·cm)]Transition probability ($10^0 \sim 10^4$) $\epsilon > 10^4$ very strong, $\epsilon < 10^3$ weak (forbidden)

Additive rules in Beer's law

$$A_{\text{total}} = b(\epsilon_1 \cdot c_1 + \epsilon_2 \cdot c_2)$$

Exceptions of Beer's law

1. complex formation with solvents (hydrogen bonding)
2. fluorescent compound
3. acid-base equilibrium – isobestic point (λ whose A does not change with pH)

(1) Sample Handling

① UV cell

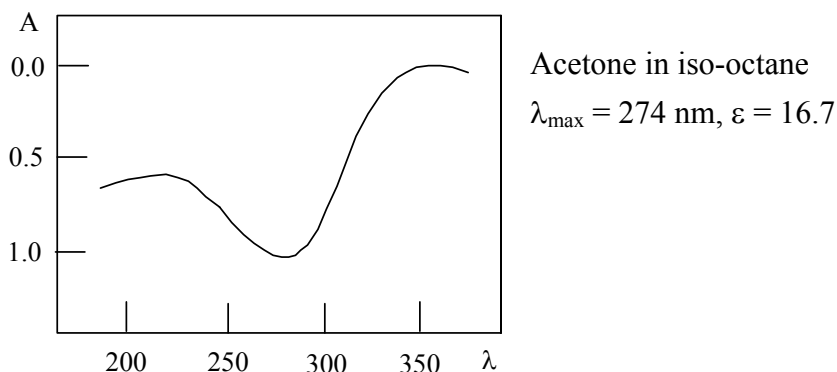
Quartz cell ($\lambda > 210$ nm) or fused silica, tridymite, cristoballite

Cell length: 1 cm; requires 3 mL of solution

② Solvents (high purity spectral grade)

solvent	cut off	solvent	cut off
Hexane	187	CCl ₄	245
CHCl ₃	223	CH ₂ Cl ₂	215
EtOH (95%)	198	MeOH	198
H ₂ O	197	dioxane	215
iso-octane	195		

(2) Presentation of Spectra



Sample presentation:

Calculate a concentration for the expected ϵ .

Most accurate measurement can be carried out at the Absorbance $A \approx 1.0$

Alkyl-substituted unconjugated carbonyl compounds $\epsilon \approx 12$

$$c = A / \epsilon \cdot b = 1.0 / [12 \text{ (L/mol}\cdot\text{cm)} \times 1.0 \text{ (cm)}] = 0.0833 \text{ mole/L}$$

For acetone (MW 58),

$$0.0833 \text{ mole/L} = 0.0833 \text{ (mole/L)} \times 58 \text{ (g/mole)} = 4.83 \text{ (g/L)} = \mathbf{0.120 \text{ g/25 mL}}$$

Observed value

$$\lambda_{\max} = \mathbf{274 \text{ nm}}, \epsilon = A/c \cdot b = \mathbf{1.391} / [0.0833 \text{ (mole/L)} \times 1 \text{ (cm)}] = \mathbf{16.7 \text{ L/(mole}\cdot\text{cm)}}$$

(3) Spectrometer Design

Light source: hydrogen discharge tube

Continuous band 160~360 nm

Incandescent sources > 360 nm

Detector: photomultiplier tube

(4) Vocabulary

Terms for spectral phenomena

Chromophore: Functional group that absorbs UV light ($C=C, C=O, NO_2$) – unsaturated groups

Bathochromic Shift: Red shift (to longer wavelength or lower energy)

Auxochrome: Auxiliary functional group that interacts with a chromophore causing bathochromic shift (OH, NH_2, Cl) – saturated group with nonbonded electrons.

Hypsochromic Shift: Blue shift (to shorter wavelength or higher energy)

Hyperchromic Effect: Enhancement in ϵ .

Hypochromic Effect: Decrease in ϵ .

(5) Transitions in UV spectroscopy

$\pi \rightarrow \pi^*$ (K band)

$\sigma \rightarrow \sigma^*$ $\lambda < 150$ nm

$n \rightarrow \pi^*$ (R band) } forbidden, $\epsilon = 100 \sim 3000$

$n \rightarrow \sigma^*$ }

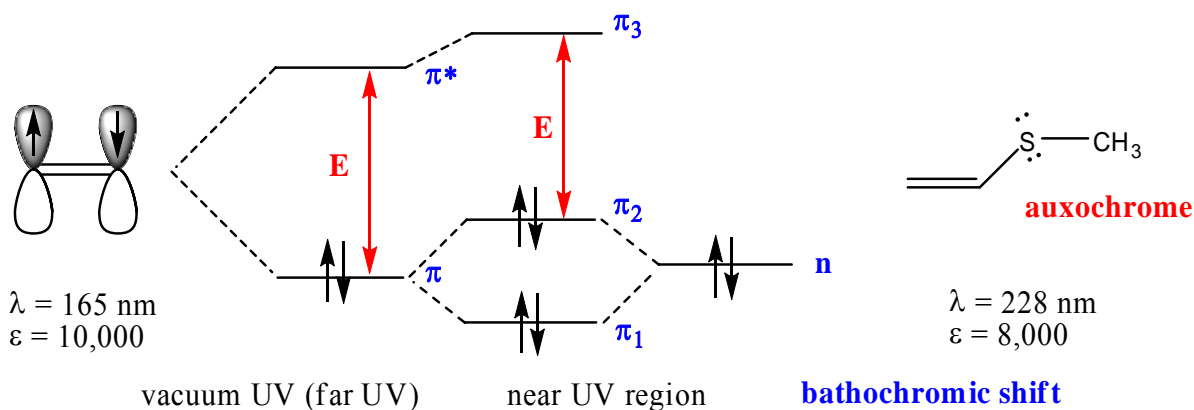
n from hetero atoms: O, N, S, X

$n \rightarrow \sigma^*$

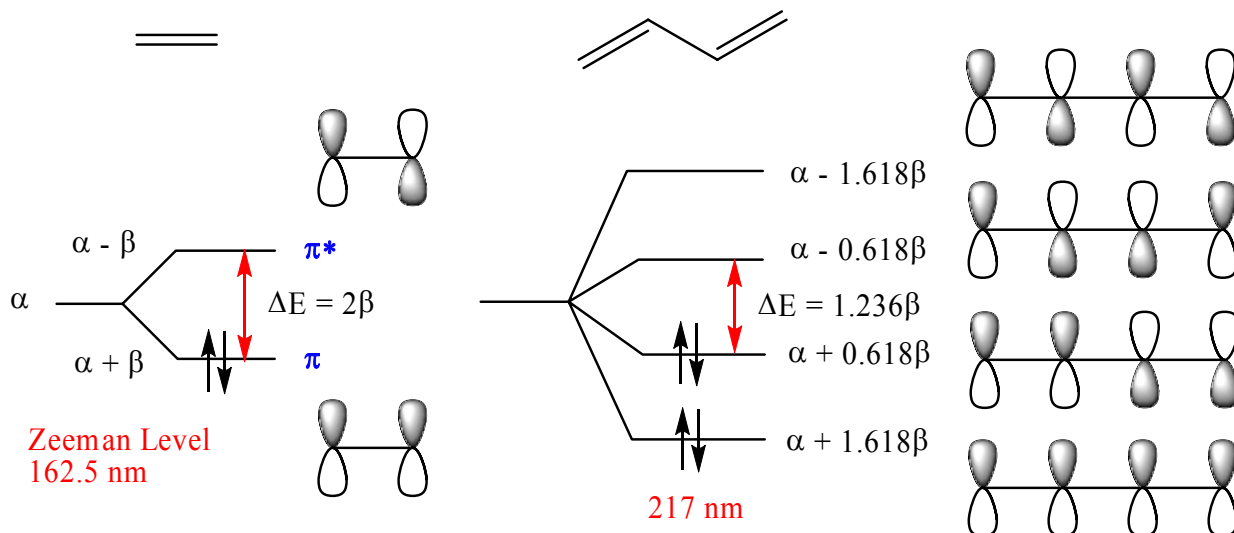
Compound	λ_{max} (ϵ)	Compound	λ_{max} (ϵ)
CH ₃ OH	177 nm (200)	CH ₃ Cl	173 nm (200)
Bu ₂ S	210, 229 (1,200)	nPr-Br	208 (300)
C ₆ H ₁₁ SH	224 (126)	CH ₃ I	259 (400)
Me ₃ N	199 (3,950)		

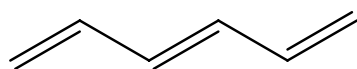
(6) The Ethylene Chromophore

$\left\{ \begin{array}{l} n \rightarrow \sigma^* \\ \pi \rightarrow \pi^* \\ n \rightarrow \pi^* \end{array} \right.$



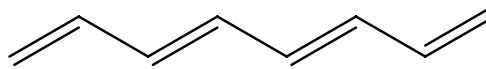
(7) Absorptions in Dienes (Based on Simple Huckel MO Theory)





$$\Delta E = 0.890\beta$$

251 nm



$$\Delta E = 0.695\beta$$

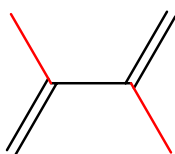
304 nm

(8) Woodward's Rules for Dienes

<Empirical Rules>

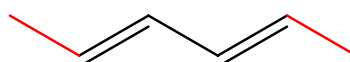
Base: Conjugated Diene \rightarrow 217 nm

- ① add 5 nm for each alkyl substituent
- ② add 5 nm for each exocyclic double bond



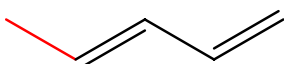
$$\text{Cal. } 217 + 5 \times 2 = 227 \text{ nm}$$

Obs. 226 nm



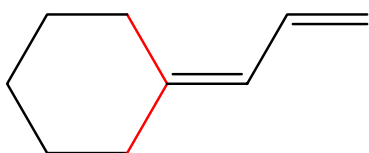
$$\text{Cal. } 217 + 5 \times 2 = 227 \text{ nm}$$

Obs. 227 nm



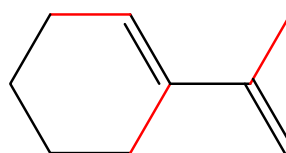
$$\text{Cal. } 217 + 5 = 222 \text{ nm}$$

Obs. 223.5 nm



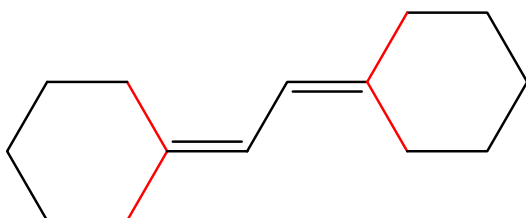
$$\text{Cal. } 217 + 5 \times 2 + 5 = 232 \text{ nm}$$

Obs. 236.5 nm



$$\text{Cal. } 217 + 5 \times 3 = 232 \text{ nm}$$

Obs. 235 nm

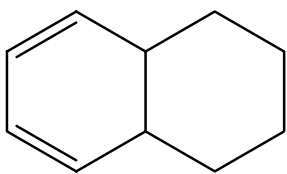


$$\text{Cal. } 217 + 4 \times 5 + 5 \times 2 = 247 \text{ nm}$$

Obs. 248 nm

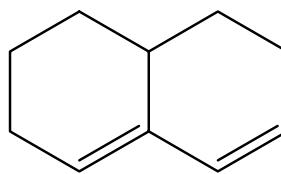
(9) Woodward and Fieser Rules for Cyclic Conjugated System

Base: conjugated cyclic dienes (steroid systems)



Homo-annular diene

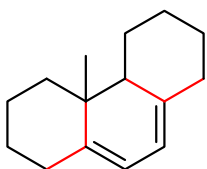
253 nm



Hetero-annular diene

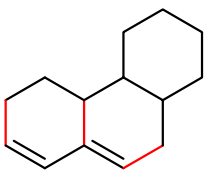
214 nm

- ① Add 5 for each alkyl group of ring residue
- ② Add 30 for each additional double bond in conjugation
- ③ Add 5 for each exocyclic double bond
- ④ Polar groups
OAc (+0), OR (+6), SR (+30), Cl, Br (+5), NR₂ (+60)



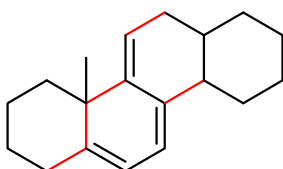
Cal. $253 + 5 \times 4 + 5 \times 2 = 283$

Obs. 282, $\epsilon = 11,900$



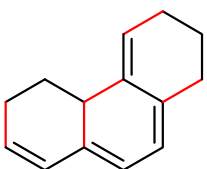
Cal. $214 + 5 \times 3 + 5 = 234$

Obs. 234, $\epsilon = 20,000$



Cal. $253 + 30 + 5 \times 5 + 5 \times 3 = 323$

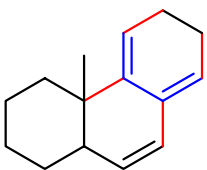
Obs. 324, $\epsilon = 11,800$



Cal. $253 + 30 \times 2 + 5 \times 5 + 5 \times 3 = 353$

Obs. 355

Cross-conjugation

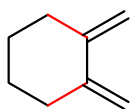


Cal. $253 + 5 \times 4 + 5 \times 2 = 283$

Obs. 285, $\epsilon = 9,100$

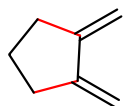
<Exceptions>

Strained Molecules – Away from coplanar



$$\text{Cal. } 217 + 5 \times 2 + 5 \times 2 = 237$$

$$\text{Obs. } 220, \epsilon = 10,050$$



$$\text{Cal. } 217 + 5 \times 2 + 5 \times 2 = 237$$

$$\text{Obs. } 243$$

The above rules work reasonably well for the conjugated polyenes containing four carbon-carbon double bonds or less.

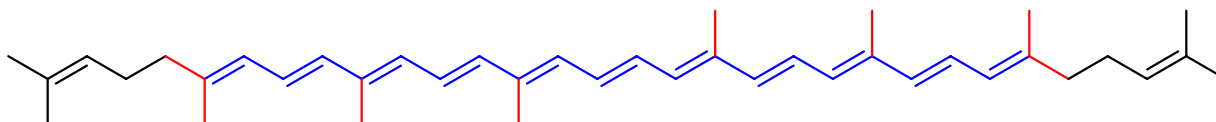
For polyenes containing more than four carbon-carbon double bonds →

Fieser–Kuhn rule

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

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

- n: number of conjugated carbon-carbon 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 in the conjugated system

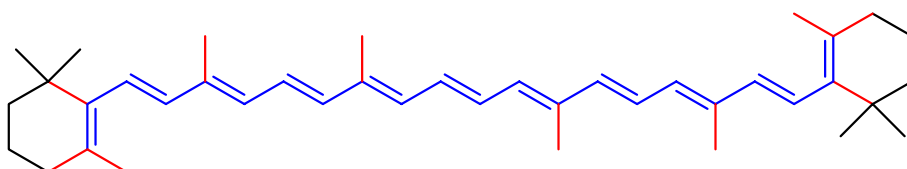
Lycopene

$$\lambda_{\text{max}}(\text{cal}) = 114 + 5 \times 8 + 11 \times (48.0 - 1.7 \times 11) = 476 \text{ nm}$$

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

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

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

β-Carotene

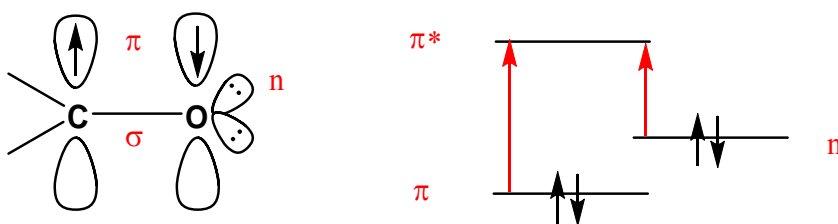
$$\lambda_{\text{max}}(\text{cal}) = 114 + 5 \times 10 + 11 \times (48.0 - 1.7 \times 11) - 16.5 \times 2 = 453.3 \text{ nm}$$

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

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

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

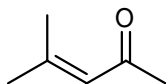
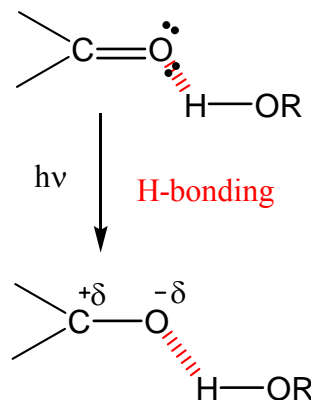
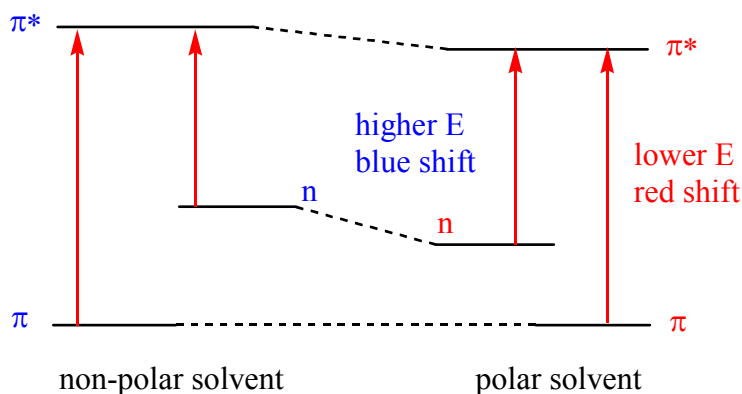
(10) Absorption of Carbonyl Groups



K band: $\pi \rightarrow \pi^*$ (150 nm)

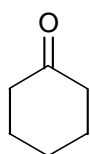
R band: $n \rightarrow \pi^*$ (lower E, 279 nm; forbidden $\epsilon = 10 \sim 1,000$)

Solvent Effect
Solvent polarity



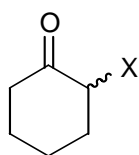
solvent	$\pi \rightarrow \pi^*$	ϵ	$n \rightarrow \pi^*$	ϵ
Hexane	229.5	12,600	327	97.5
Diethyl ether	230	12,600	326	96
EtOH	237	12,600	315	78
MeOH	238	10,700	312	74
H ₂ O	244.5	10,000	305	50

$n \rightarrow \pi^*$ Transition (R band)



$\lambda_{\max} = 285 \text{ nm}$ $\epsilon_{\max} = 14$ (hexane)

Effect of Halogen Substitution



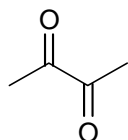
X	eq	ax
Cl	-7	+22
Br	-5	+28
OH	-12	+17
OAc	-5	+10

 α -Diketones and α -Ketoaldehydes $n \rightarrow \pi^*$ Transition (R band)

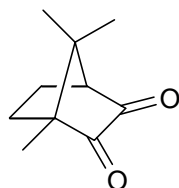
Angle dependent

$\phi = 0 \sim 10^\circ \quad \lambda_{\max} = 488 \text{ nm}$

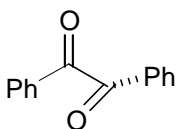
$\phi = 90^\circ \quad \lambda_{\max} = 370 \text{ nm}$

1) biacetyl (s-trans conformation) $\phi = 180^\circ$ 

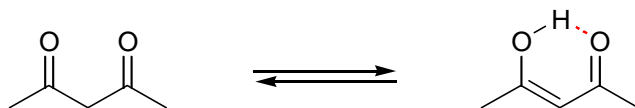
$\lambda_{\max} = 450 \text{ nm} \quad \epsilon = 10$

2) bicyclo[2.2.1]heptane $\phi = 10^\circ$ 

$\lambda_{\max} = 488 \text{ nm} \quad \epsilon = 17$

3) $\phi = 90^\circ$ 

$\lambda_{\max} = 370 \text{ nm} \quad \epsilon = 40$

 β -Diketones $\pi \rightarrow \pi^*$ (K band)15% in H₂O

91~92% in vapor phase

or in non-polar solvent

$\lambda_{\max} (\text{H}_2\text{O}) = 274 \text{ nm},$

$\epsilon_{\max} = 2,050$

$\lambda_{\max} (\text{iso-octane}) = 272 \text{ nm},$

$\epsilon_{\max} = 12,000$

(11) Prediction of $\pi \rightarrow \pi^*$ Transitions in α,β -Unsaturated Ketones**Woodward & Fieser****For enones**K band: 215~250 nm ($\epsilon_{\max} = 10,000\sim 20,000$)

R band: 310~330 nm (weak)

Parent

α,β -unsaturated ketone	215
Five-membered cyclic α,β -unsaturated ketone	202
α,β -unsaturated aldehydes	210
α,β -unsaturated carboxylic acids and esters	195

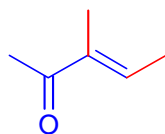
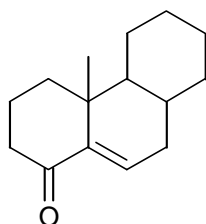
Substituents

Carbon substituent at α	add 10
Carbon substituent at β	add 12
Carbon substituent at γ and δ	add 18
Exocyclic double bond	add 5
Double bond extending conjugation	add 30

Substituents	α	β	γ	δ
OH	+35	+30		+50
OAc	+6	+6		+6
OMe	+35	+30	+17	+31
SR		+85		
Cl	+15	+12		
Br	+25	+30		
NR ₂		+95		

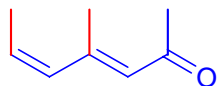
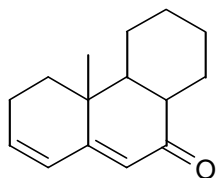
Solvent corrections

Alcohol	0	Hexane	-11	CHCl ₃	-1
water	+8	Ether	-7	dioxane	-5

Examples

$$215 + 10 + 12 + 5 = 242$$

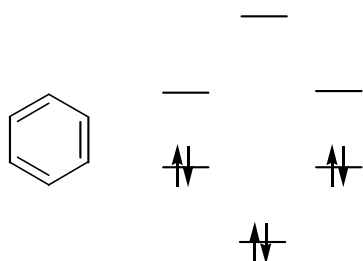
Observed: 240



$$215 + 30 + 12 + 18 + 5 = 280$$

Observed: 280

(12) Aromatic Compounds



Benzene Bands ($\pi \rightarrow \pi^*$ Transition)

184 nm (ϵ_{\max} : 68,000)	204 nm (ϵ_{\max} : 8,800)	254 nm (ϵ_{\max} : 250)
E_1	E_2	B
	K	B

Substitution on the benzene ring produces a **bathochromic shift** of the B and the E bands.

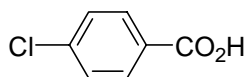
Benzenoid	E_2 band	B band	Benzenoid	E_2 band	B band
	204 (8,800)	254 (250)		211 (6,200)	258 (1,450)
	208 (7,900)	262 (260)		236 (10,000)	269 (700)
	210 (7,500)	257 (170)		217 (6,400)	269 (700)
	210 (7,500)	257 (170)		251 (14,000)	299 (2,100)
	230 (7,000)	280 (1,400)		252 (10,000)	280 (1,000) 330 (140)
	244 (15,000)	280 (1,500)		240 (13,000)	278 (1,100)
	230 (10,000)	270 (800)		224 (13,000)	271 (1,000)
	217 (6,700)	264 (977)	PhSOPh	232 (14,000)	262 (2,400)

Bathochromic shift of toluene is caused by the hyperconjugation of a σ C-H bond participating in resonance with the benzene ring

(13) Disubstituted Benzenes

1) Without resonance interactions

Additive effect



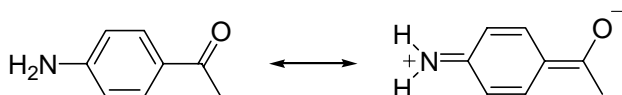
Calculated: $230 + (210 - 204) = 236 \text{ nm}$

Observed: 242 nm

2) With resonance interactions

One releasing/the other withdrawing \rightarrow **greater bathochromic effect**

Resonance Effect



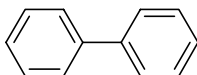
Calculated: $240 + (230 - 204) = 266 \text{ nm}$

Observed: 322 nm

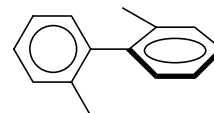
(14) Resonance Interactions between Aromatic Rings



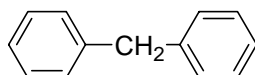
$\lambda_{\text{max}} = 204, \epsilon = 7,900$



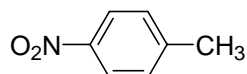
$\lambda_{\text{max}} = 252, \epsilon = 19,000$ (K band)



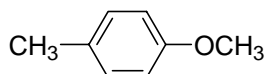
$\lambda_{\text{max}} = 270, \epsilon = 800$ (B band)



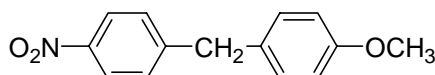
$\lambda_{\text{max}} = 262, \epsilon = 5,000$



$\lambda_{\text{max}} = 274, \epsilon = 9,490$



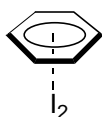
$\lambda_{\text{max}} = 277, \epsilon = 2,190$
 $\lambda_{\text{max}} = 285.5, \epsilon = 1,786$



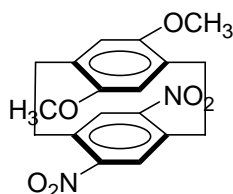
$\lambda_{\text{max}} = 280, \epsilon = 24,400$
 $\lambda_{\text{max}} = 287, \epsilon = 26,800$

(15) Charge Transfer Complexes

Donation of electrons from one set of orbital through space to another set



$\lambda_{\text{max}} = 290, \epsilon = 150,000$



$\lambda = 332, \epsilon = 3,965$
 $\lambda = 275, \epsilon = 802$
 $\lambda = 468, \epsilon = 414$