Ultravioleta e Visível

~1900 – Max Planck e Albert Einstein

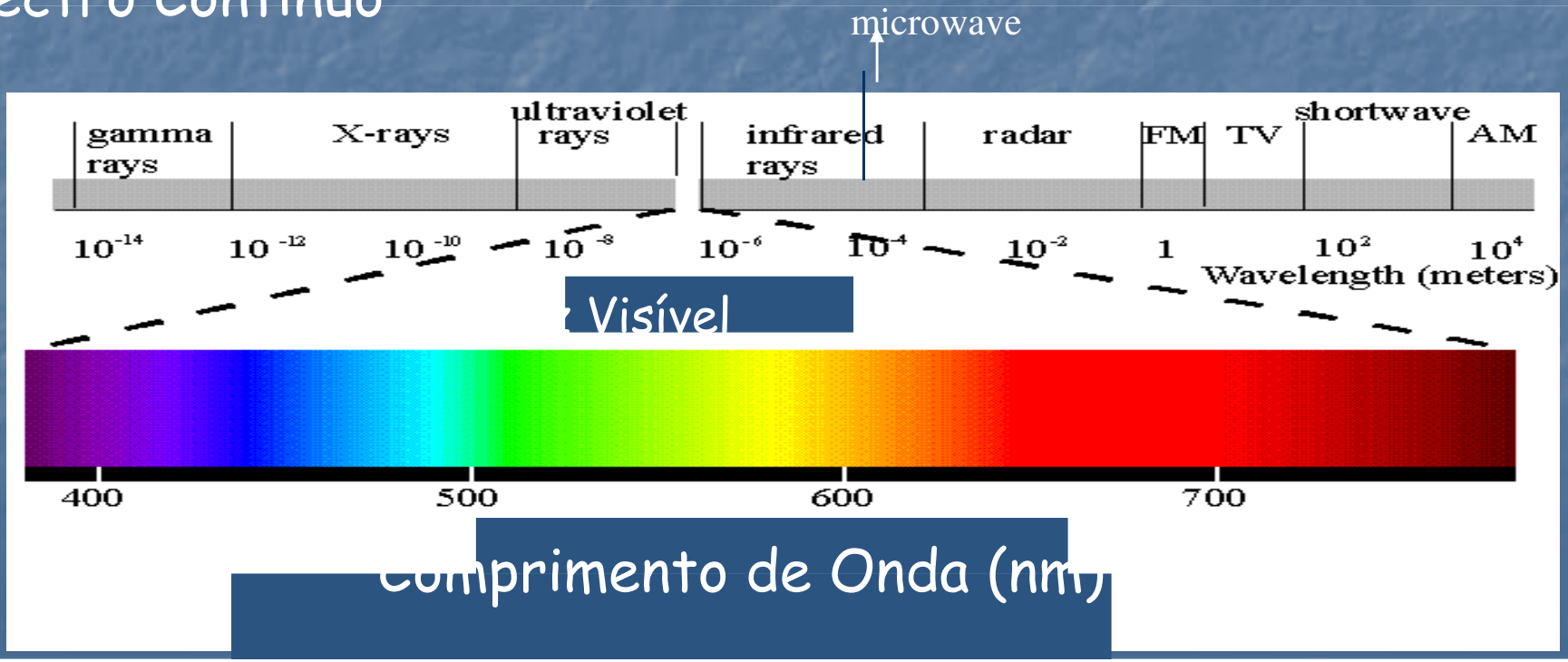
$$E_{fóton} = h\upsilon$$

h = constante de Planck = $6{,}63 \times 10^{-34}$ Js

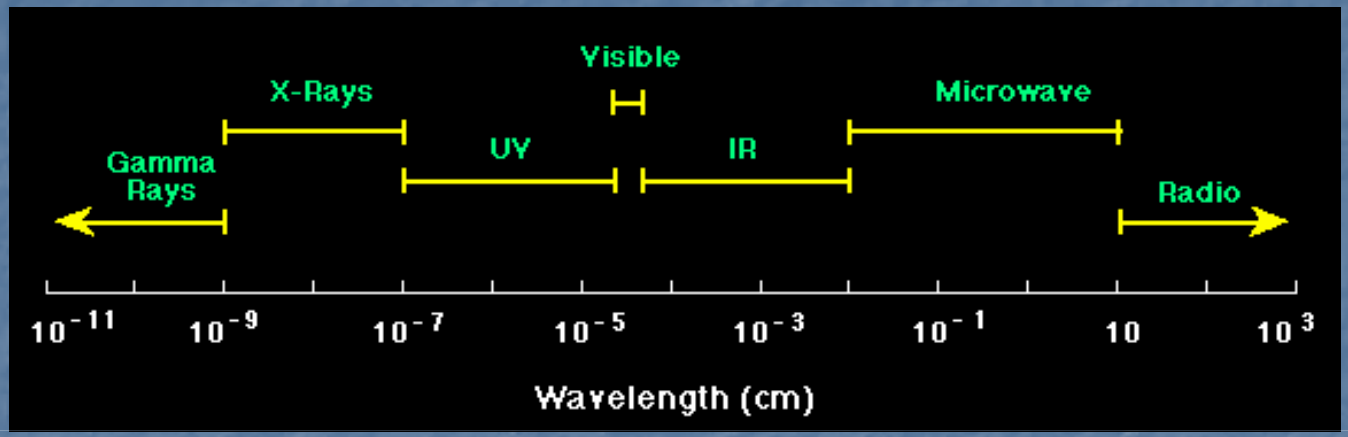
Se, $c = \lambda \upsilon$, então:

$$E_{fóton} = h \frac{c}{\lambda}$$

Espectro Contínuo

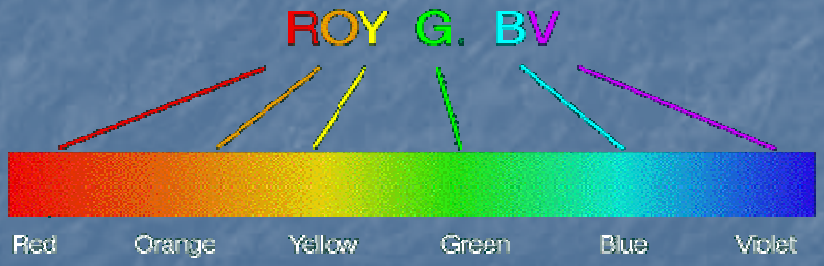


A luz visível, os raios gamas e as microondas são todas manifestação do mesmo fenômeno de radiação eletromagnética, apenas possuem diferentes comprimentos de onda.

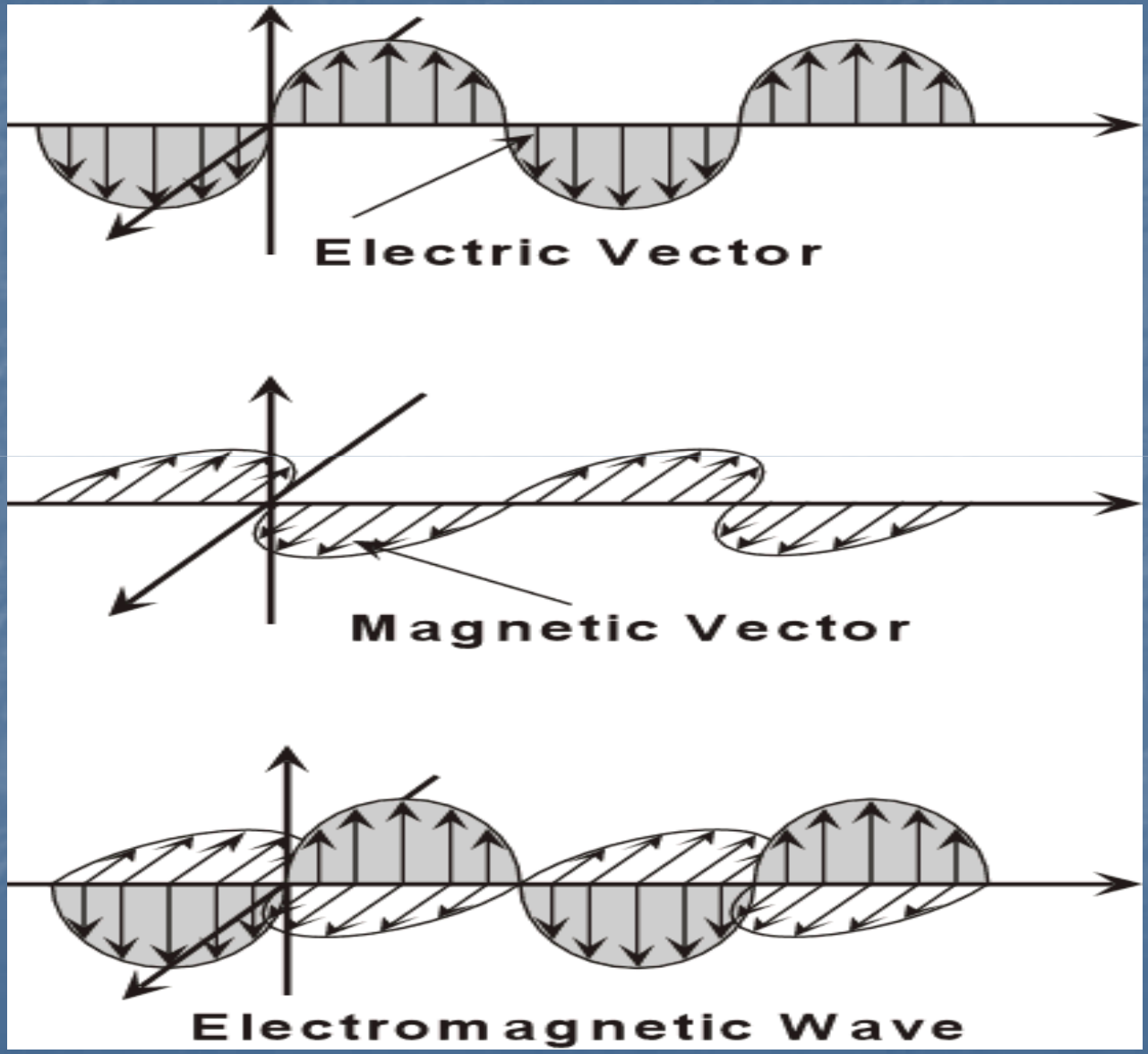


O olho humano só é sensível à radiações luminosas cujos comprimentos de onda se situem entre 4.000 e 8.000 Å - *Visível*.

O espectro visível pode ser subdividido de acordo com a cor, com vermelho nos comprimentos de onda longos e violeta para os comprimentos de onda mais curtos.



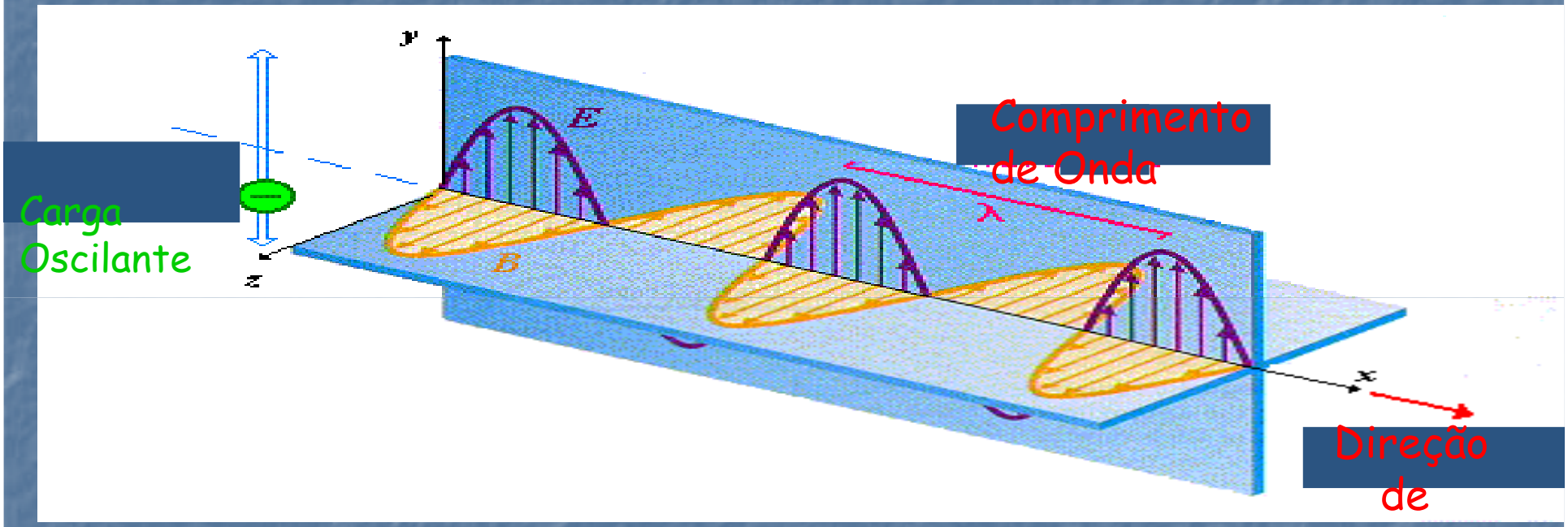
Representação de uma Onda Eletromagnética



Comprimento de onda

Frequência

$c = \lambda \upsilon$



C ⟹ Velocidade da onda no vácuo

$C = 300.000$ Km/s

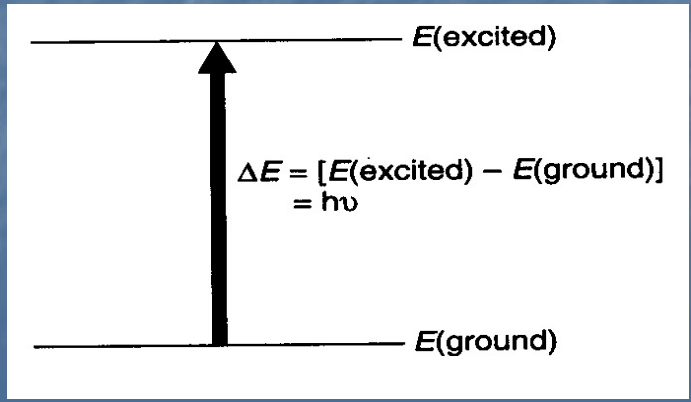
λ ⟹ m ou nm

υ ⟹ Hz = ciclos/s = s^{-1}

Types of Energy Transitions in Each Region of the Electromagnetic Spectrum

Region of Spectrum	Energy Transitions
X-rays	Bond breaking
Ultraviolet/visible	Electronic **200-400 nm**
Infrared	Vibrational
Microwave	Rotational
Radiofrequencies	Nuclear spin (nuclear magnetic resonance) Electronic spin (electron spin resonance)

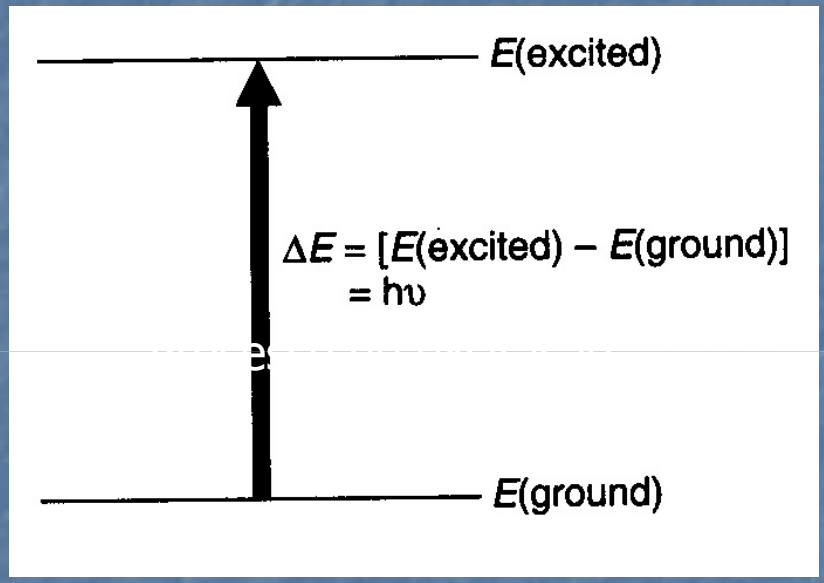
O processo de excitação



Processo de excitação

- Quando radiação contínua passa através de um material transparente, uma porção de radiação pode ser absorvida
- Como resultado da absorção de energia, átomos ou moléculas passam de um estado de baixa energia (estado fundamental) para um estado de mais alta energia (estado excitado)

Processo de excitação



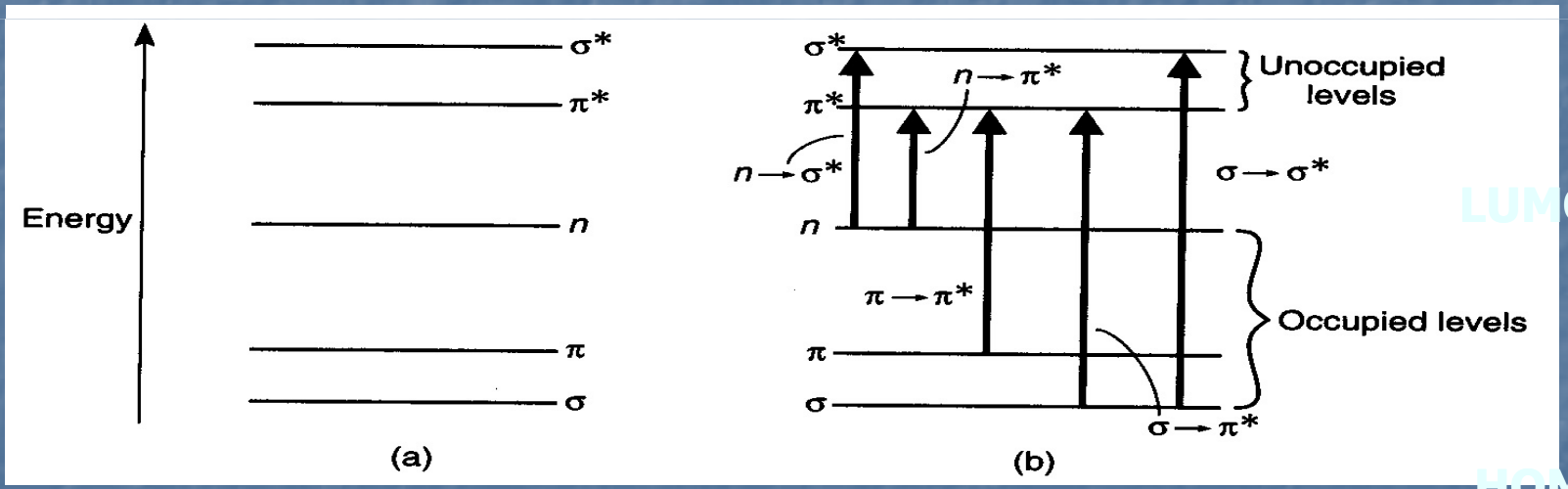
- O processo de excitação é quantizado: a energia da radiação eletromag. absorvida é exatamente igual à diferença de energia entre os 2 estados
- A transição eletrônica envolvida é entre estados eletrônicos de energia

Processo de excitação

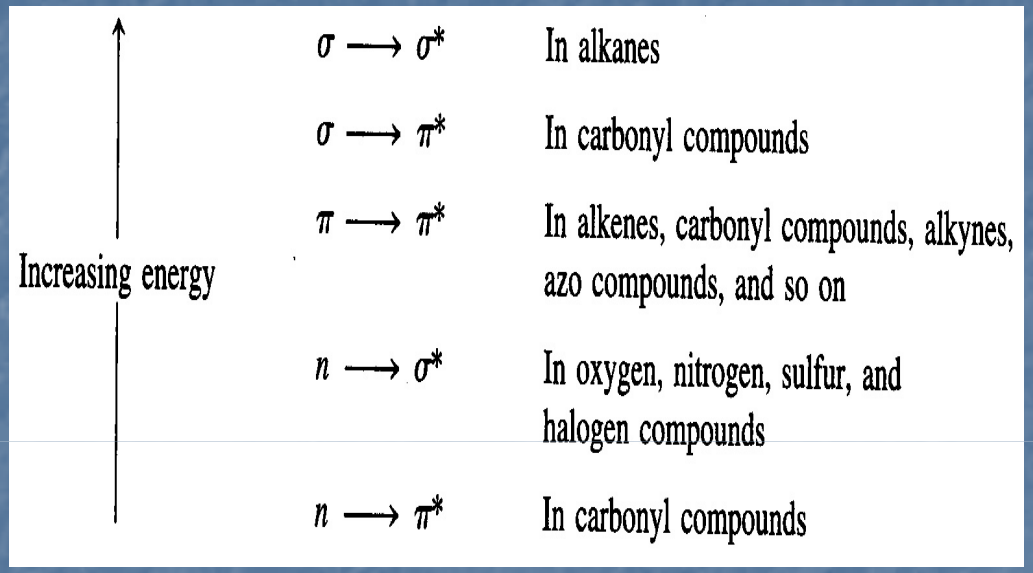
- Quando uma molécula absorve energia, um elétron é promovido de um orbital ocupado para um orbital desocupado de mais alta energia
- A transição mais provável é do orbital HOMO para o LUMO
- ΔE entre níveis eletrônicos na maioria das moléculas variam entre 125 e 650 kJ/mol

Processo de excitação

- A transição mais provável é do orbital HOMO para o LUMO



Transições mais importantes



- Nem todas as transições possíveis são observadas (regras de seleção)
- Algumas são proibidas (n $\rightarrow \pi^*$), porém observadas

Lei de Beer-Lambert

- Quanto maior o número de moléculas capazes de absorverem luz com um dado λ, maior a extensão da absorção de luz

$$A = \log I_0/I = \varepsilon \times C \times l \quad \text{ou} \quad \varepsilon = \frac{A}{C \times l}$$

A = absorbância

I_0 = intensidade da luz incidente na cela

I = intensidade da luz que sai pela cela

c = concentração molar do soluto

l = comprimento da cela

ε = absortividade molar (propriedade da molécula)

Lei de Beer-Lambert

- ε = absorbância com c = 1,0 M e l = 1,0 cm
- É característica de um composto a determinado λ

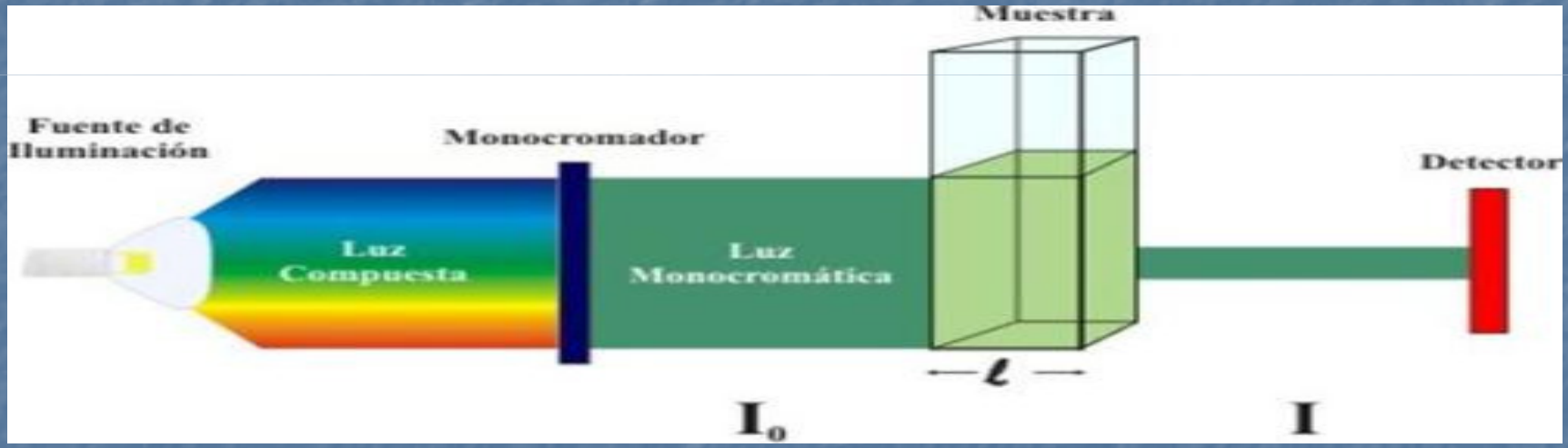
Ex: UV da acetona em hexano

$\lambda_{máx}$ 187 nm (ε = 900, hexano)
$\lambda_{máx}$ 270 nm (ε = 15, hexano)

Através da lei de Beer-Lambert, podemos determinar a concentração de uma solução

Espectrofotômetro de UV/Vis

- Consiste de uma fonte de luz, um monocromador e um detector



- Fontes de luz: lâmpada de D (UV) ou W (Vis)

Espectrofotômetro de UV/Vis

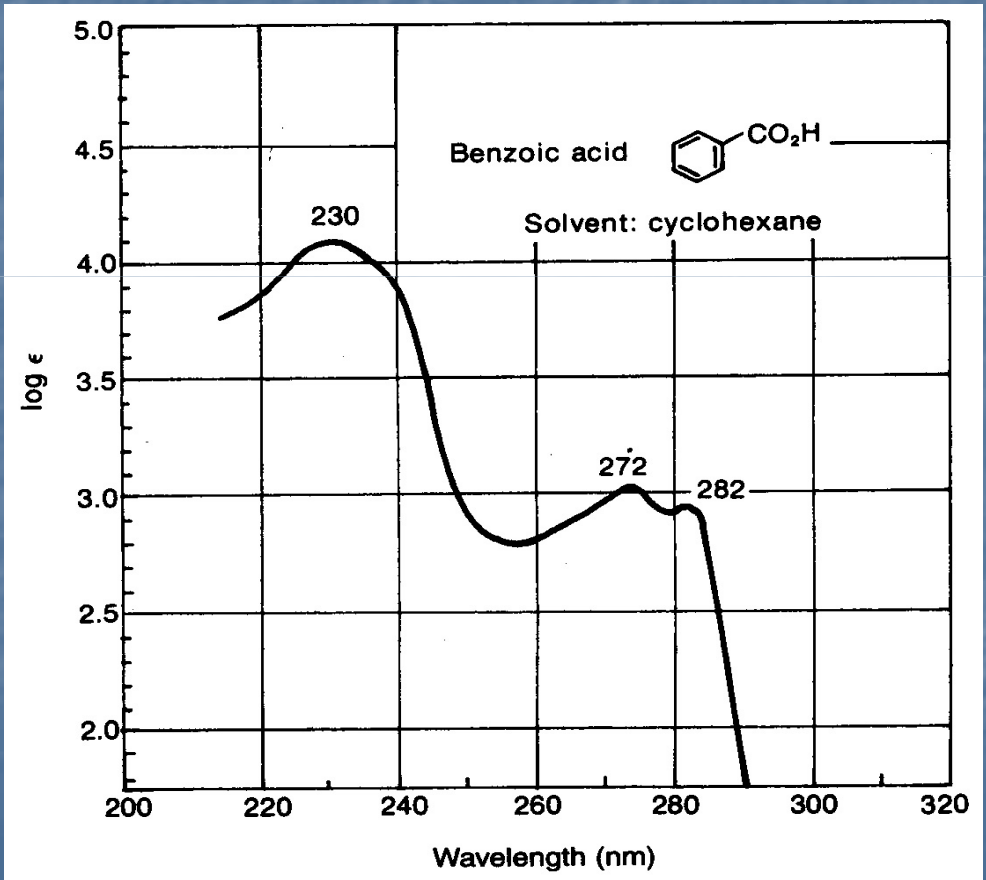
- Monocromador: rede de difração que espalha o feixe de luz em seus comprimentos de onda correspondentes
- Um sistema de fendas foca o λ desejado na cela com a amostra
- A luz que passa pela cela atinge o detector que detecta a intensidade da luz transmitida (I)

Espectrofotômetro de UV/Vis

- O detector é geralmente um tubo fotomultiplicador ou um fotodiodo
- Em um instrumento de duplo feixe, a luz é dividida em 2 feixes: amostra e referência
- Celas de vidro ou de quartzo são usadas para absorções no Vis, enquanto que apenas as de quartzo podem ser usadas no UV

Espectros

- Geralmente plotados como A vs λ e então replotados como log ε vs λ



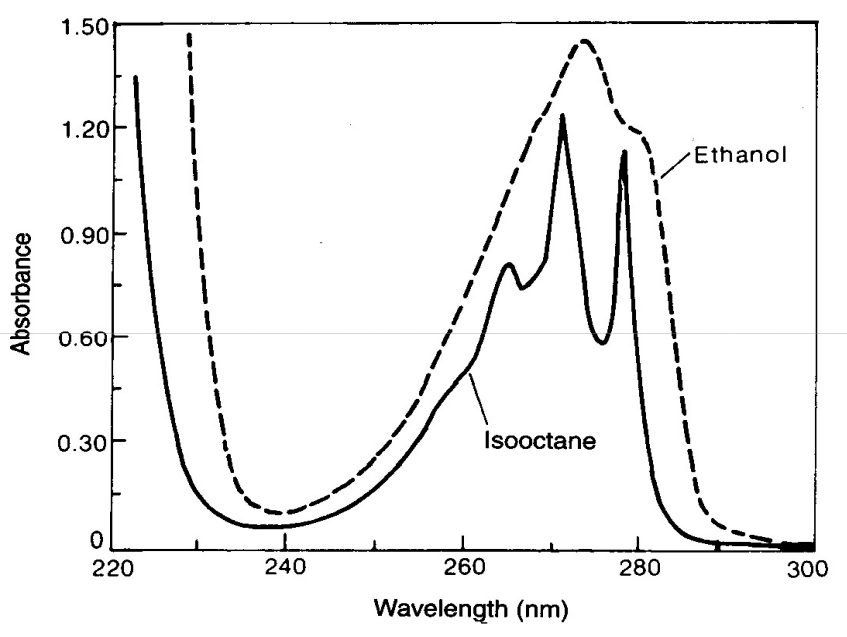
λ_{max} = 230 nm	log ε = 4.2
272	3.1
282	2.9

Absorções de alta intensidade apresentam ε > 10^4

Solventes

- Primeiro critério: não absorver radiação UV na mesma região que o analito
- Mais usados: H_2O, EtOH 95% e hexano
- Segundo critério: polaridade. Alteração da resolução do espectro por ligações de H com solvente
- Terceiro critério: habilidade de influenciar o λ da luz UV que será absorvida (estabilização do est. fund. ou do excitado)
- Solv. polares deslocam $n \rightarrow \pi^*$ para λ mais baixo e $\pi \rightarrow \pi^*$ para λ mais alto

Efeito do solvente



Espectro de fenol em etanol e iso-octano

Regiões de transparência

Solvent Cutoffs

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

Solvent Shifts on the $n \rightarrow \pi^*$ Transition of Acetone

Solvent	H_2O	CH_3OH	C_2H_5OH	$CHCl_3$	C_6H_{14}
λ_{max} **(nm)**	264.5	270	272	277	279

Solventes polares deslocam as transições $\pi \rightarrow \pi^*$

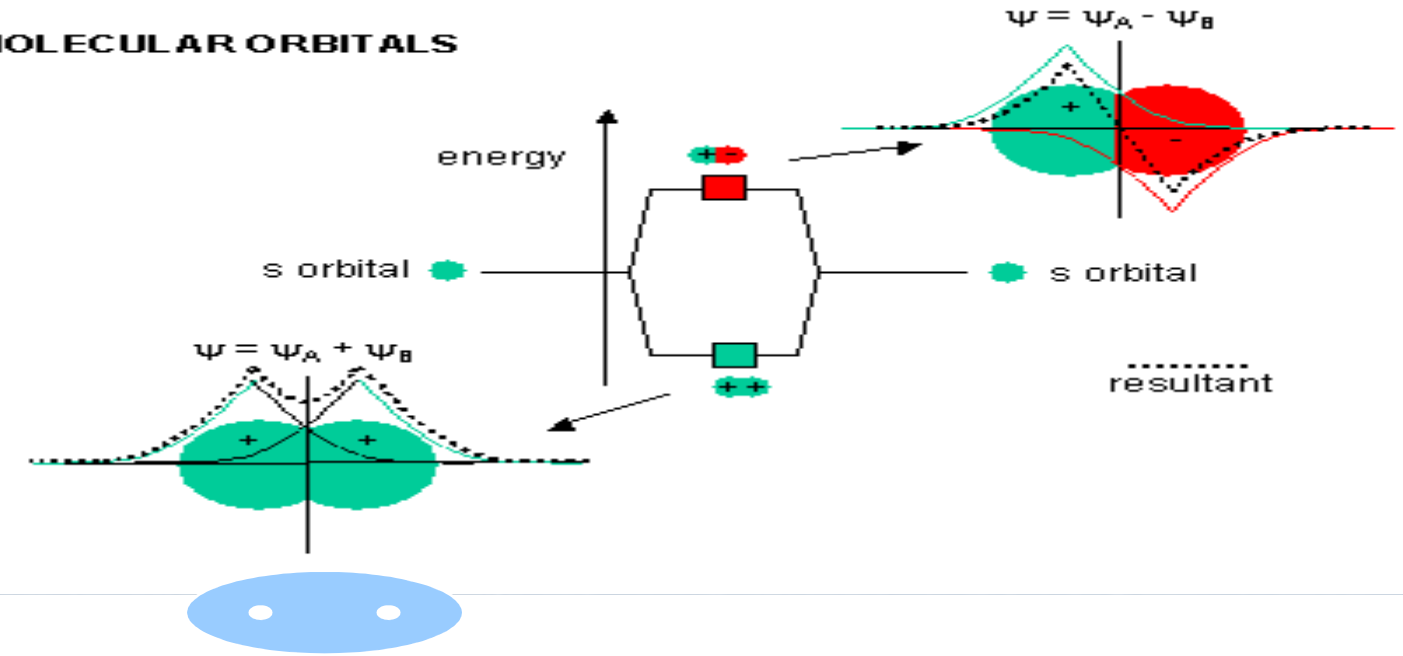
Teoria dos Orbitais Moleculares (TOM)

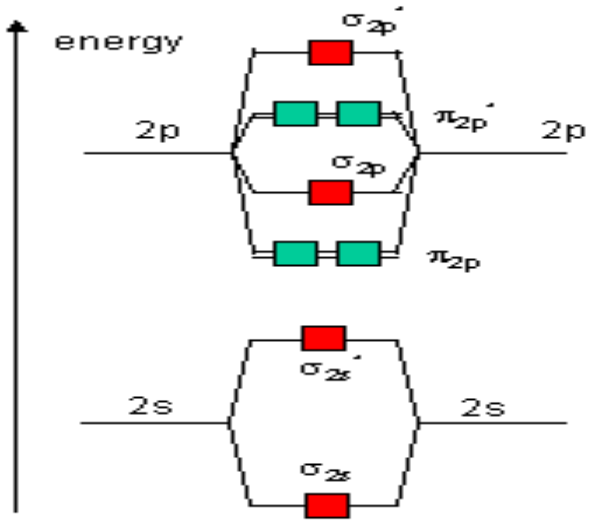
A TOM descreve a formação da ligação química como uma combinação linear matemática de orbitais atômicos (= funções de onda) para formar orbitais moleculares (OM).

Os OM resultantes dessa combinação linear de orbitais atômicos são também funções matemáticas que representam regiões no espaço, as quais podem ou não abranger a molécula inteira, com energias específicas, onde há uma alta probabilidade de se encontrar os elétrons.

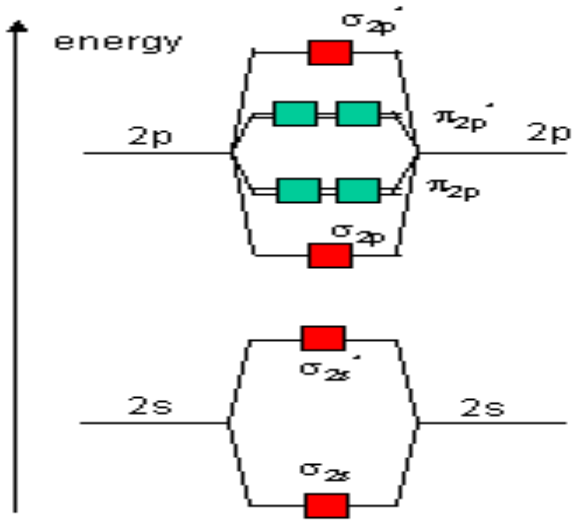
Portanto, cada OM possui uma determinada forma e energia, e pode ser ocupado por no máximo 2 elétrons com spins opostos. A Regra de Hund e o Princípio de Exclusão de Pauli são também válidos no preenchimento dos OM.

MOLECULAR ORBITALS

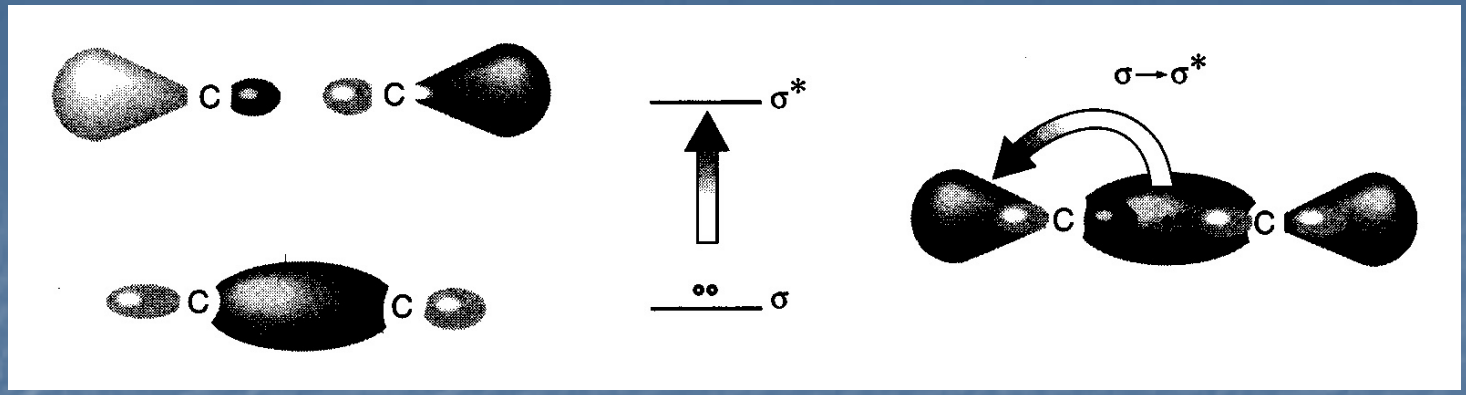




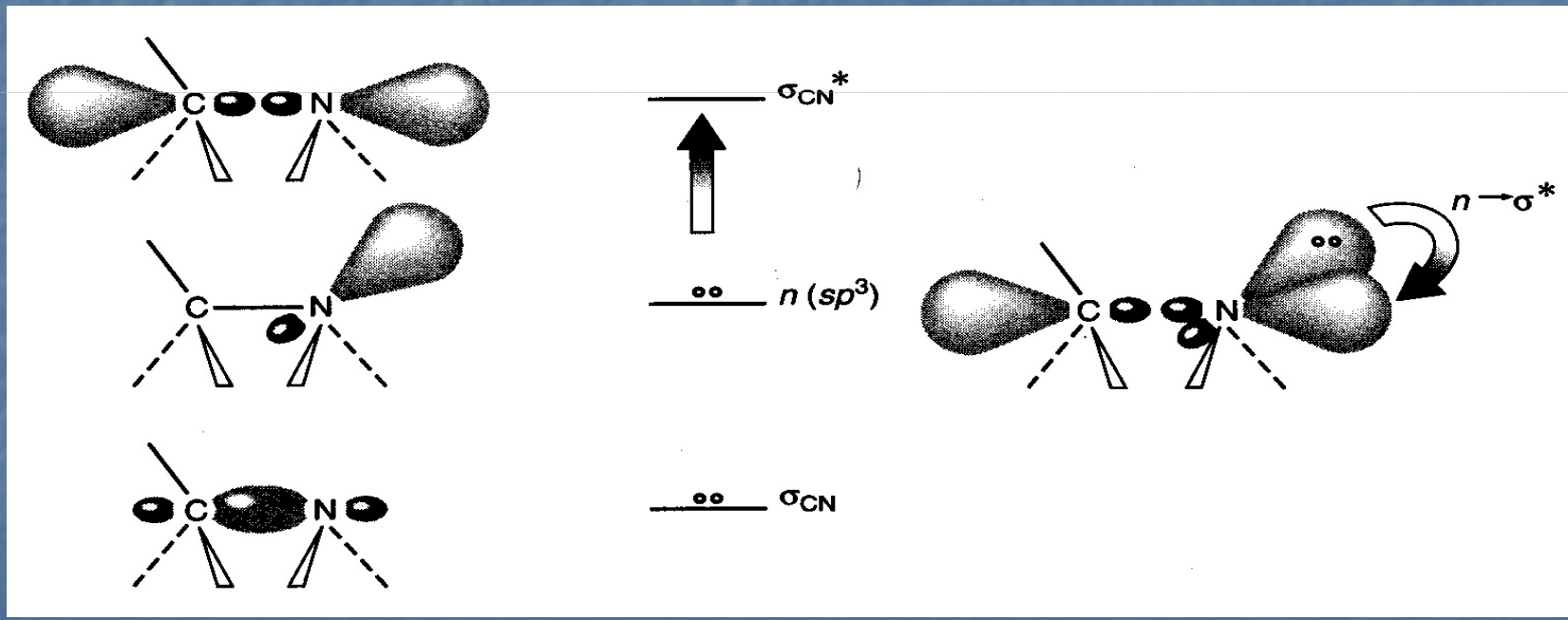
MO DIAGRAM: homonuclear diatomic
Molecules = Li_2 to N_2



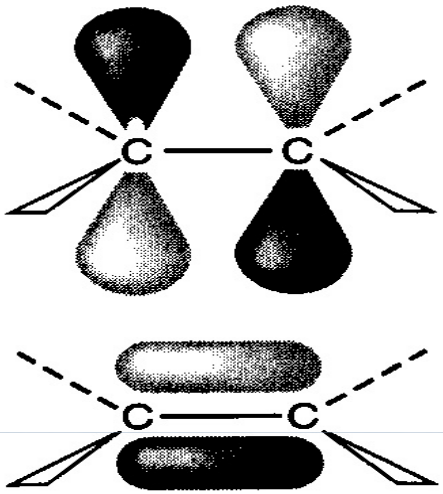
MO DIAGRAM: homonuclear diatomic
Molecules = O_2 to F_2

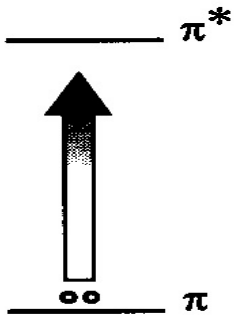


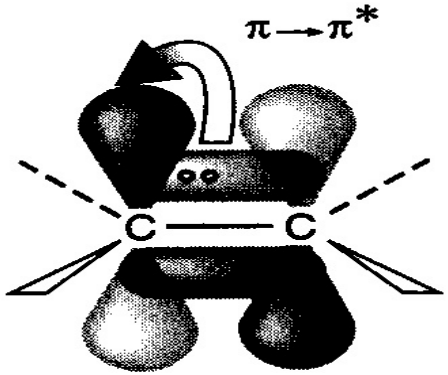
Transição σ → σ*



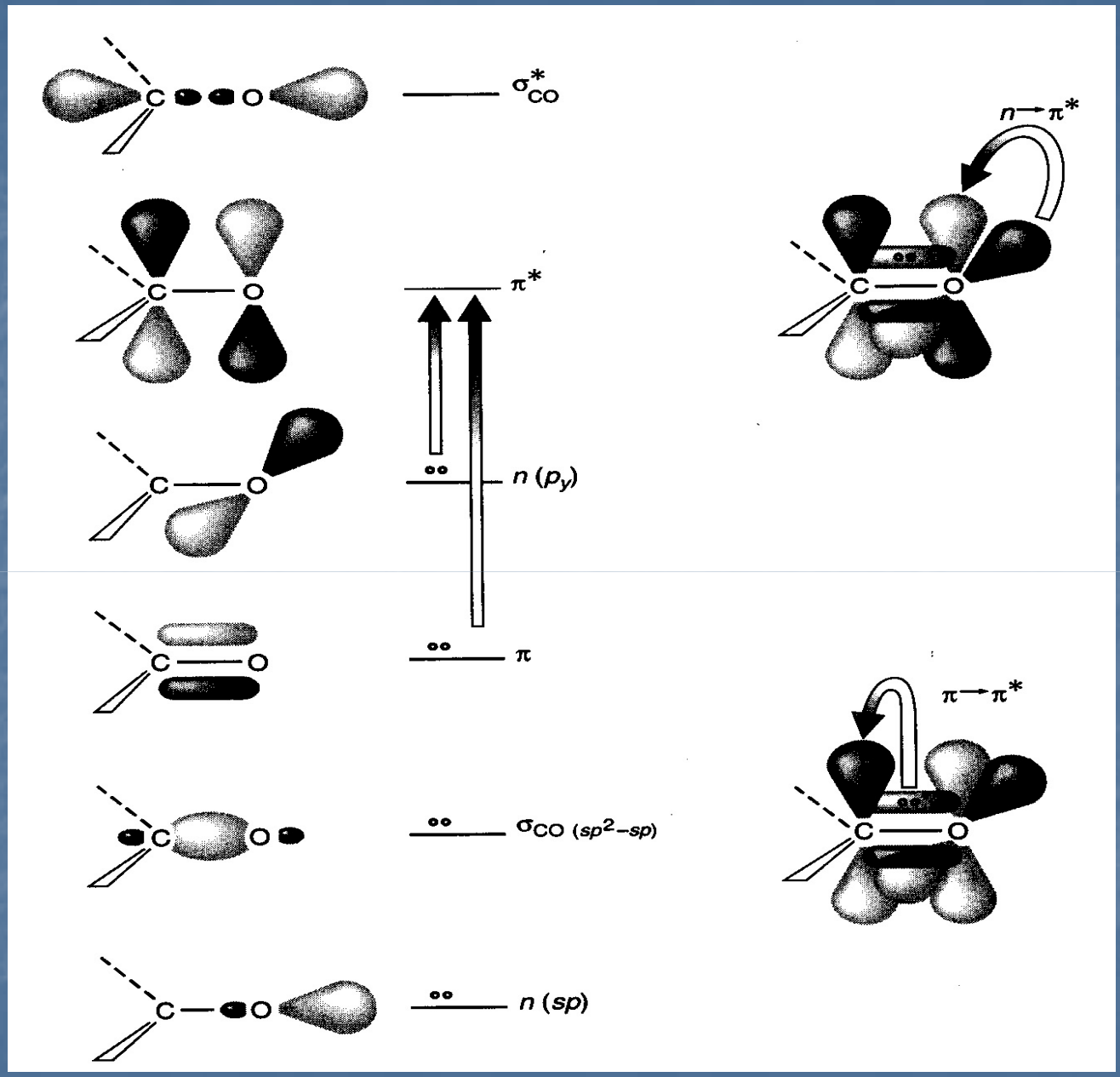
Transição n → σ*







Transição $\pi \rightarrow \pi^*$



Transições eletrônicas do grupo carbonila/acila

Termos usuais no UV-Vis

- Cromóforos: grupos covalentes insaturados
- Auxocromos: grupos que afetam os valores de ε e λ
- Deslocamento batocrômico: deslocamento para > λ
- Deslocamento hipsocrômico: deslocamento para < λ
- Efeito hipercrômico: um aumento em ε
- Efeito hipocrômico: uma diminuição em ε

Typical Absorptions of Simple Isolated Chromophores

Class	Transition	λ_{max} (nm)	log ϵ	Class	Transition	λ_{max} (nm)	log ϵ
R—OH	$n \rightarrow \sigma^*$	180	2.5	$R—NO_2$	$n \rightarrow \pi^*$	271	<1.0
R—O—R	$n \rightarrow \sigma^*$	180	3.5	R—CHO	$\pi \rightarrow \pi^*$	190	2.0
$R—NH_2$	$n \rightarrow \sigma^*$	190	3.5		$n \rightarrow \pi^*$	290	1.0
R—SH	$n \rightarrow \sigma^*$	210	3.0	R_2CO	$\pi \rightarrow \pi^*$	180	3.0
$R_2C{=}CR_2$	$\pi \rightarrow \pi^*$	175	3.0		$n \rightarrow \pi^*$	280	1.5
R—C≡C—R	$\pi \rightarrow \pi^*$	170	3.0	RCOOH	$n \rightarrow \pi^*$	205	1.5
R—C≡N	$n \rightarrow \pi^*$	160	<1.0	RCOOR′	$n \rightarrow \pi^*$	205	1.5
R—N=N—R	$n \rightarrow \pi^*$	340	<1.0	$RCONH_2$	$n \rightarrow \pi^*$	210	1.5

Efeito da conjugação

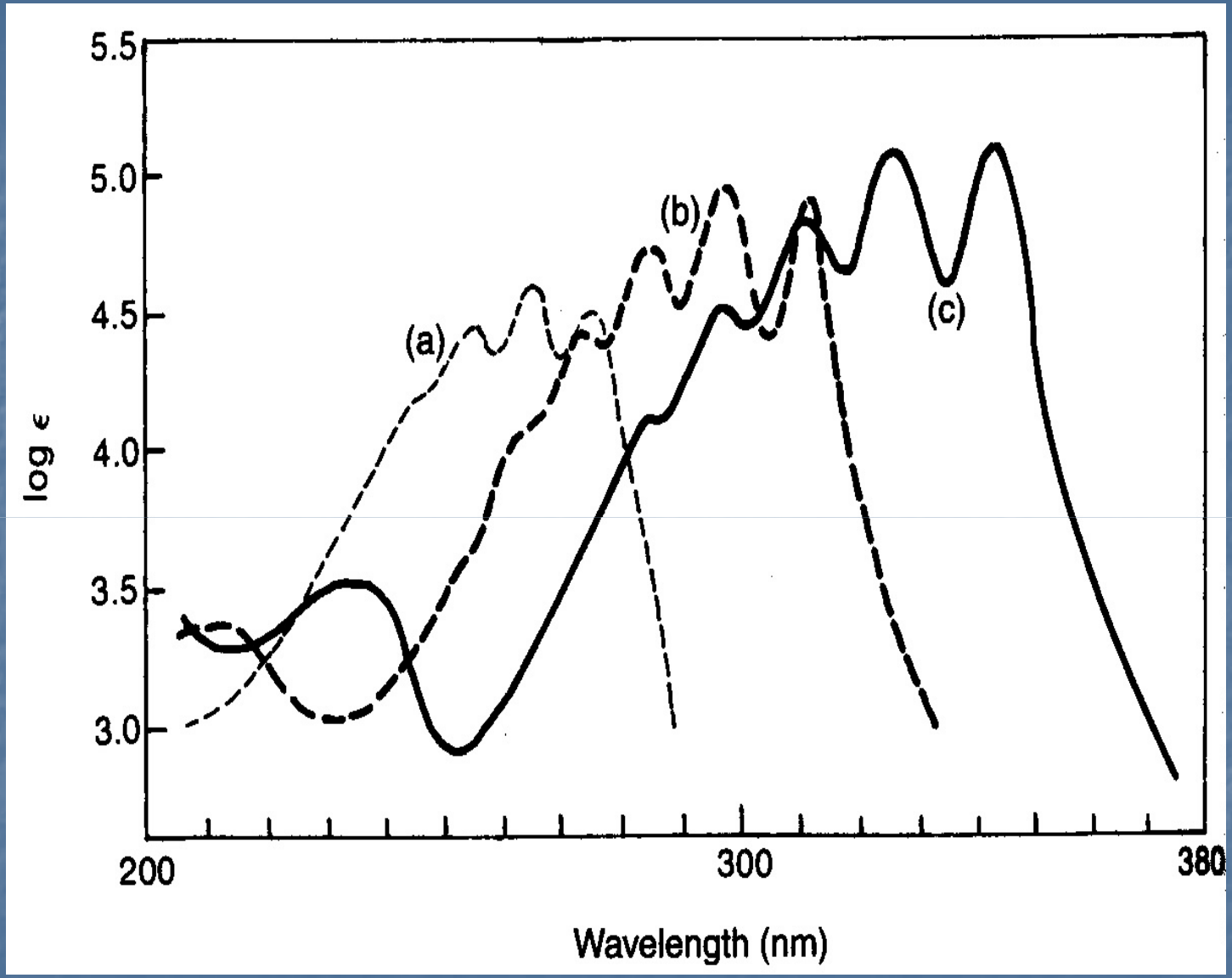
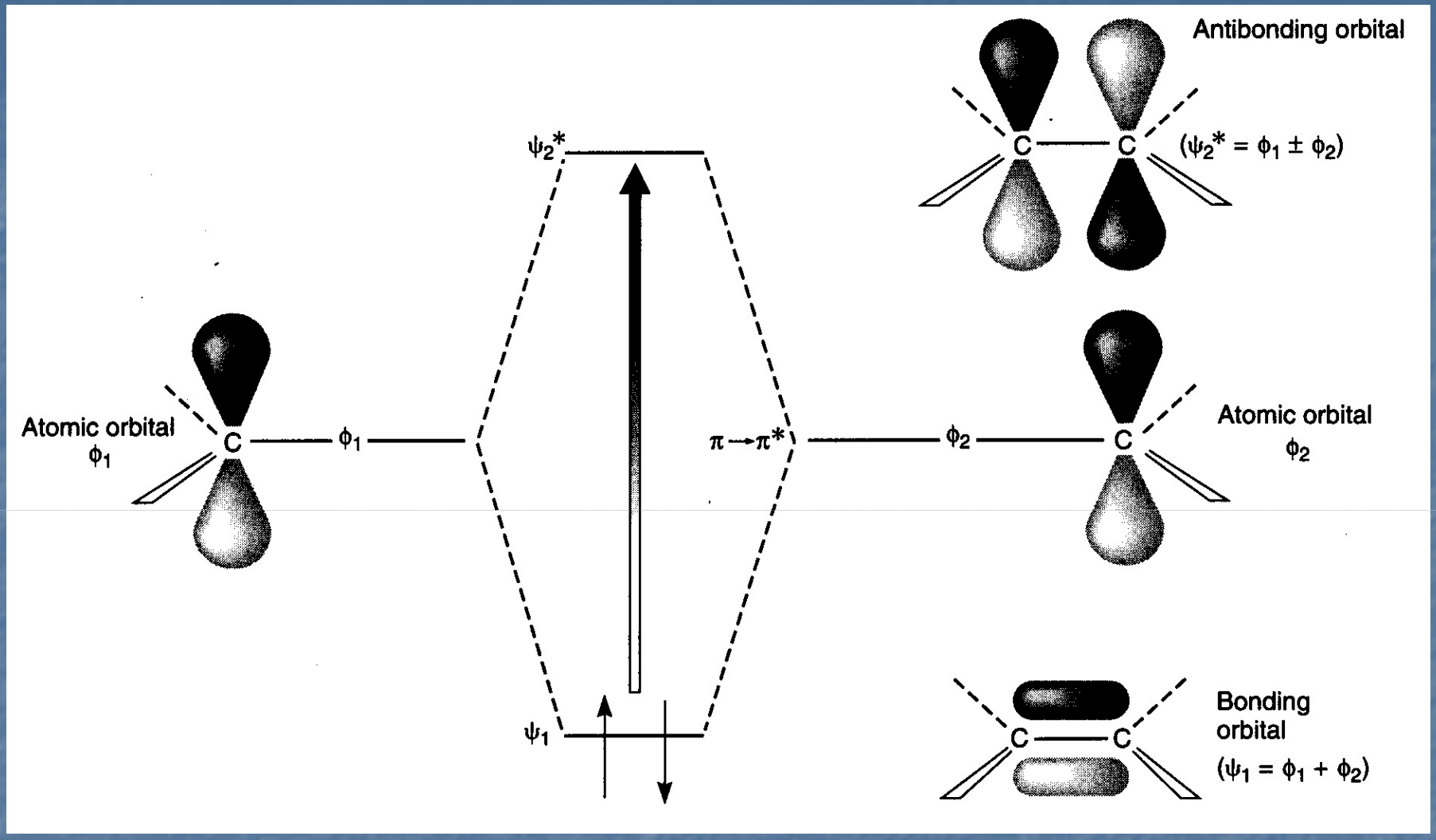


FIGURE 7.10 $CH_3—(CH=CH)_n—CH_3$ Ultraviolet spectra of dimethylpolyenes. (a) $n = 3$; (b) $n = 4$; (c) $n = 5$. (From Nayler, P., and M. C. Whiting, *J. Chem. Soc.* 1955: 3042.)

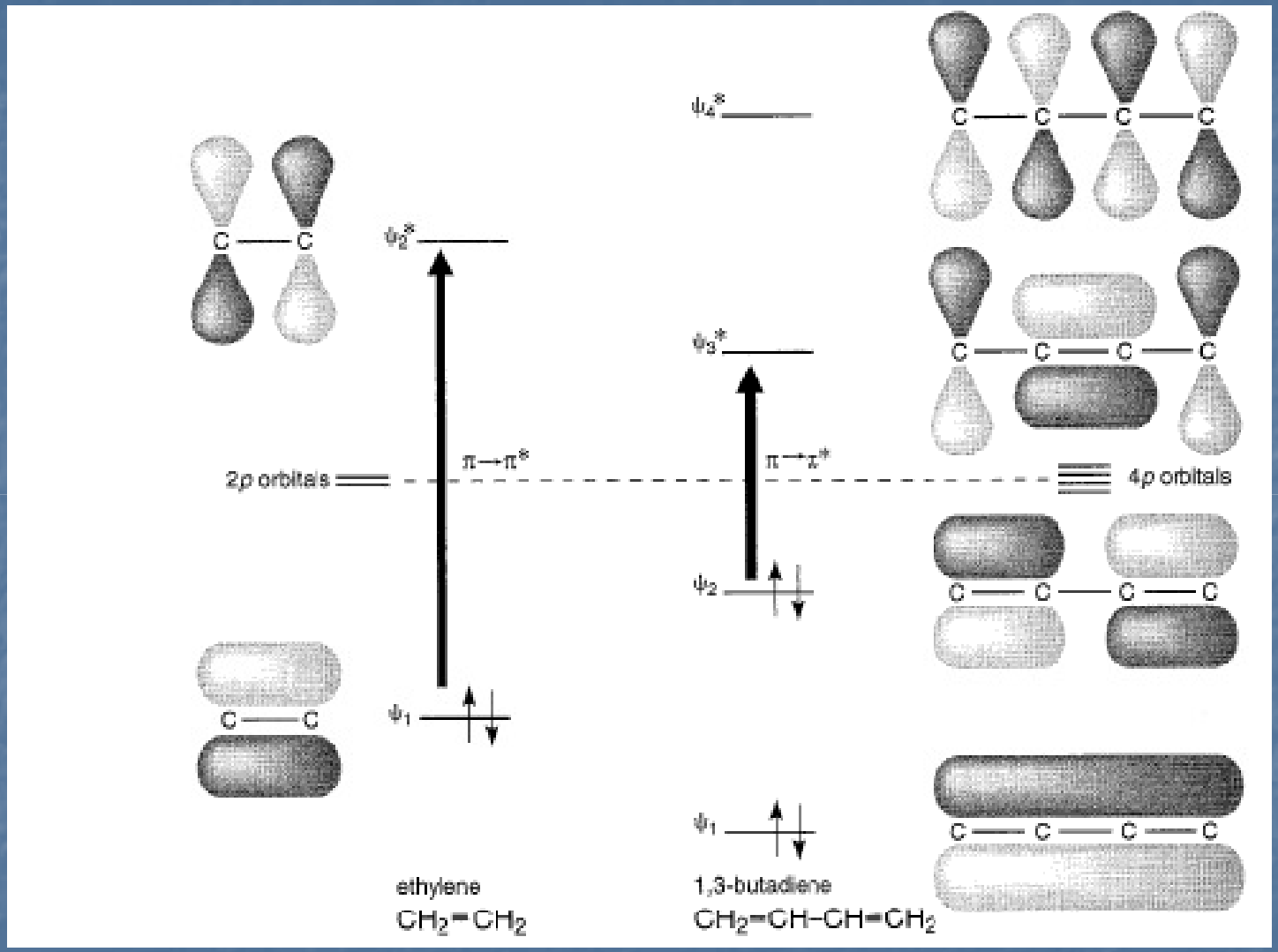
Effect of Conjugation on Electronic Transitions

		λ_{max} (nm)	ϵ
Alkenes			
Ethylene		175	15,000
1,3-Butadiene		217	21,000
1,3,5-Hexatriene		258	35,000
β-Carotene (11 double bonds)		465	125,000
Ketones			
Acetone	$\pi \rightarrow \pi^*$	189	900
	$n \rightarrow \pi^*$	280	12
3-Buten-2-one	$\pi \rightarrow \pi^*$	213	7,100
	$n \rightarrow \pi^*$	320	27

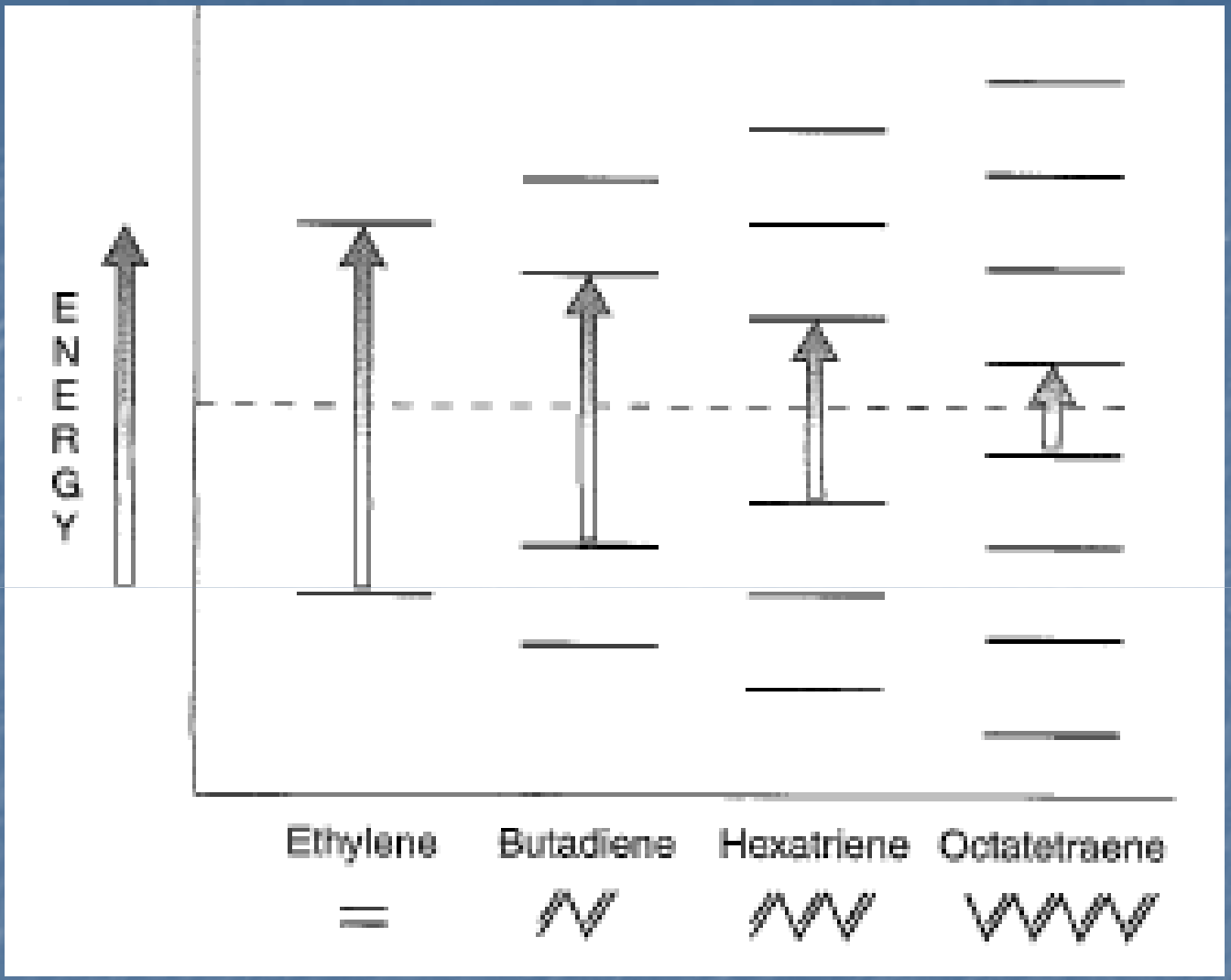


Formação do orbital molecular do etileno

Um aumento na conjugação diminui a energia necessária para a excitação eletrônica

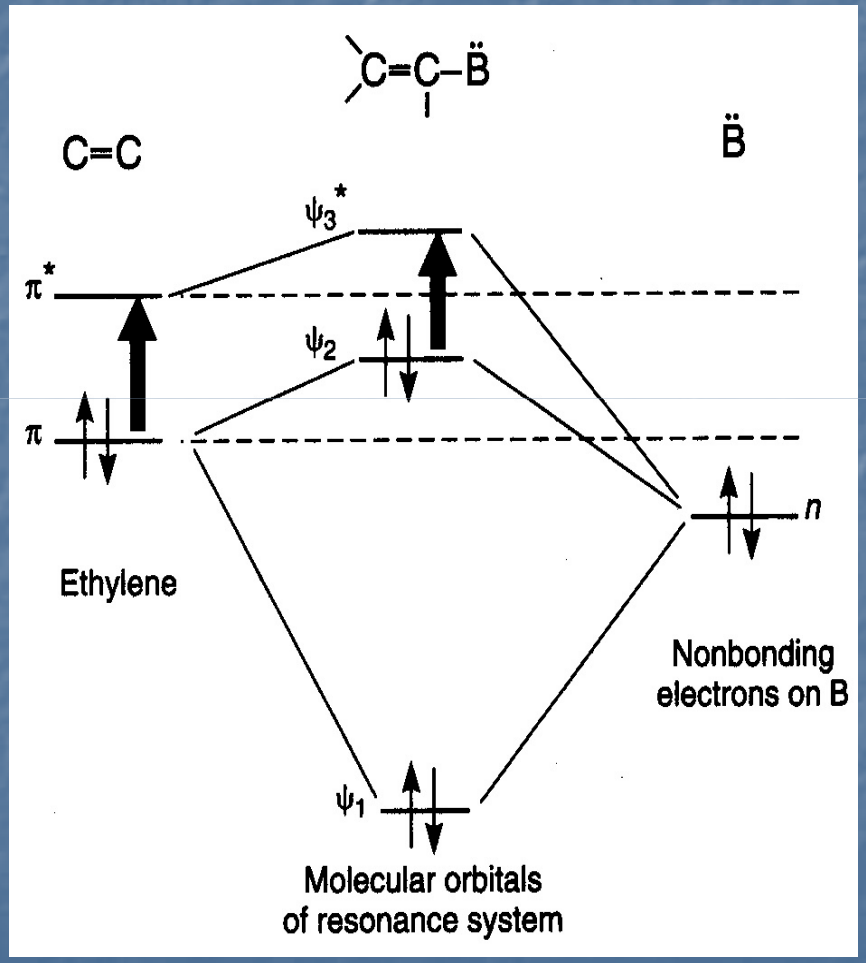


Níveis energéticos dos orbitais moleculares e a energia de $\pi \rightarrow \pi^*$ no etileno e 1,3-butadieno

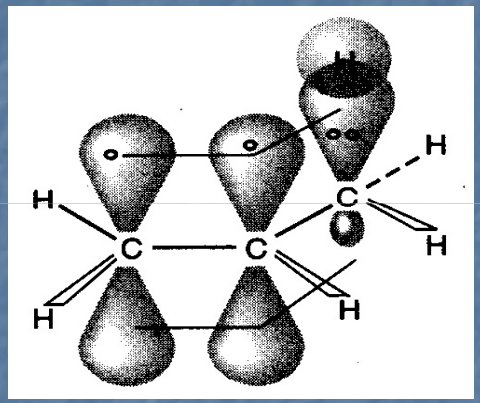


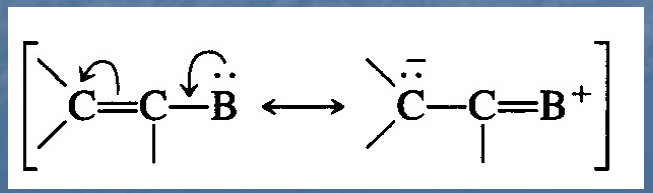
Transições $\pi \rightarrow \pi^*$ em alquenos/polienos

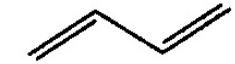
Interação do sistema π com o grupo auxocromo



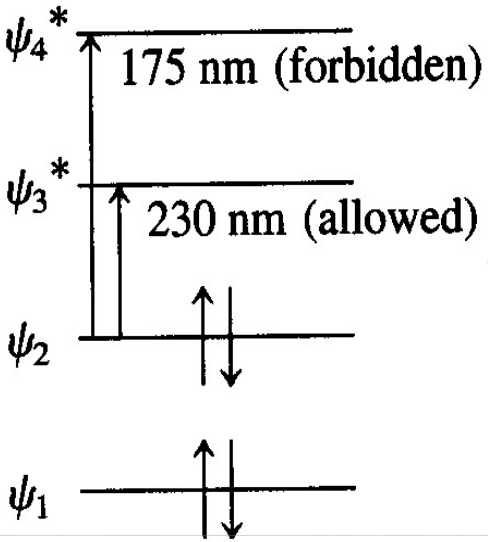
Hiperconjugação



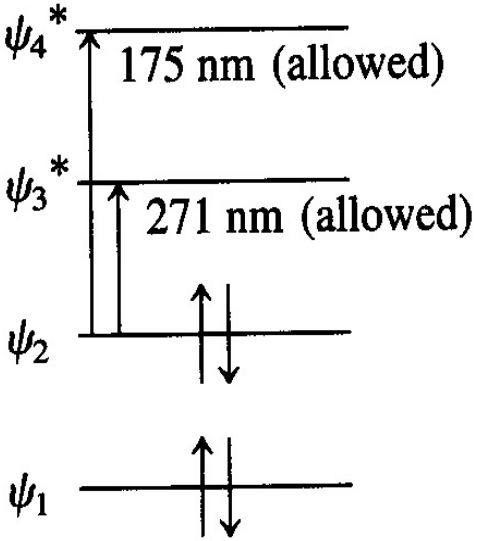


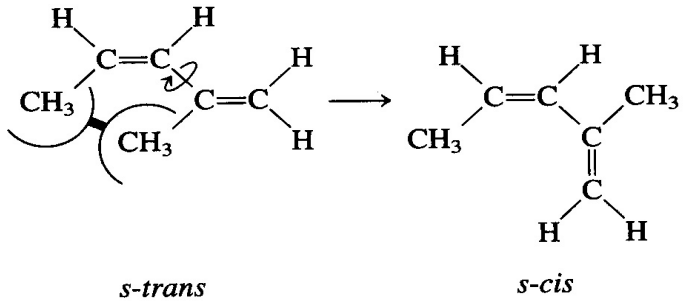


s-trans conformation



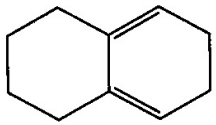
s-cis conformation



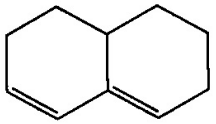


s-trans *s-cis*

Regras de Woodward-Fieser para dienos



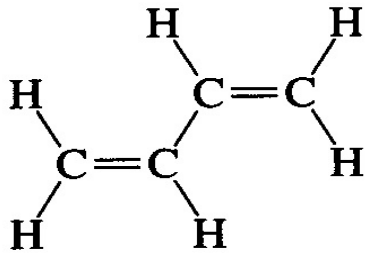
Homoannular diene (cisoid or *s-cis*)
Less intense, ϵ = 5,000–15,000
λ longer (273 nm)



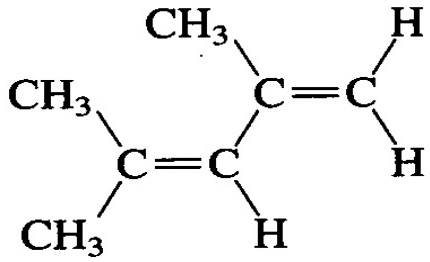
Heteroannular diene (transoid or *s-trans*)
More intense, ϵ = 12,000–28,000
λ shorter (234 nm)

Empirical Rules for Dienes

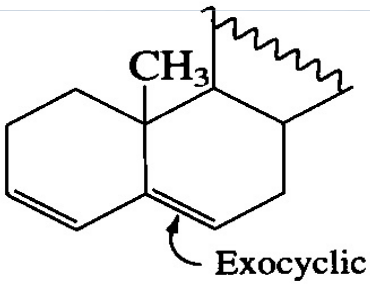
	Homoannular (cisoid)	Heteroannular (transoid)
Parent	$\lambda = 253$ nm	$\lambda = 214$ nm
Increments for:		
Double-bond-extending conjugation	30	30
Alkyl substituent or ring residue	5	5
Exocyclic double bond	5	5
Polar groupings:		
—$OCOCH_3$	0	0
—OR	6	6
—Cl, —Br	5	5
—NR_2	60	60



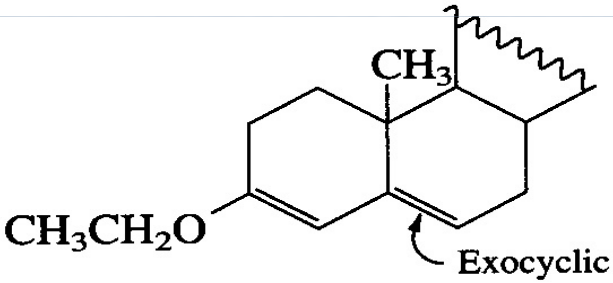
Transoid:	214 nm
Observed:	217 nm



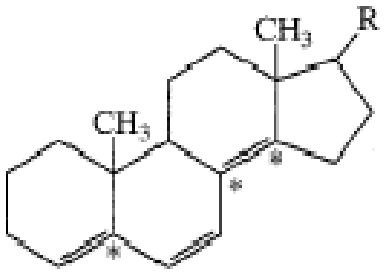
Transoid:	214 nm
Alkyl groups: $3 \times 5 =$	15
	229 nm
Observed:	228 nm



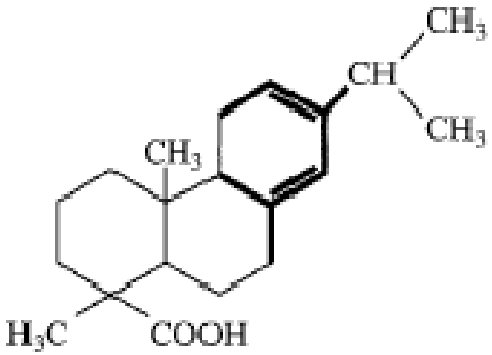
Transoid:	214 nm
Ring residues: $3 \times 5 =$	15
Exocyclic double bond:	5
	234 nm
Observed:	235 nm



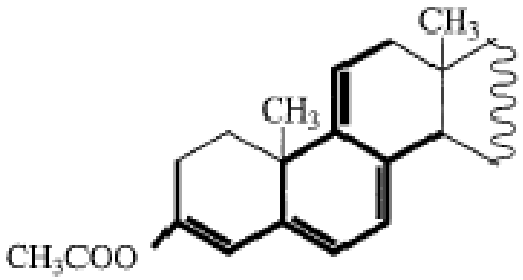
Transoid:	214 nm
Ring residues: $3 \times 5 =$	15
Exocyclic double bond:	5
—OR:	6
	240 nm
Observed:	241 nm



Three exocyclic double bonds = 3 × 5 = 15 nm

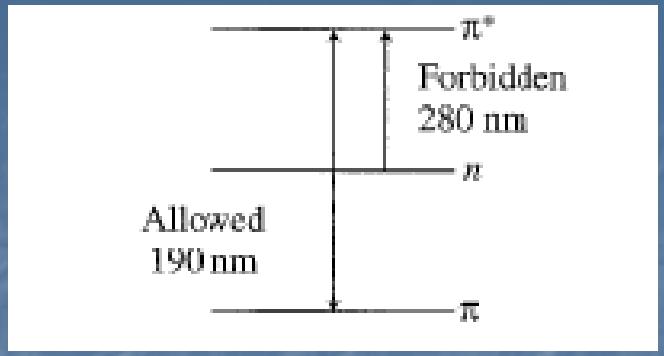


Cisoid:	253 nm
Alkyl substituent:	5
Ring residues: 3 × 5 =	15
Exocyclic double bond:	5
	278 nm
Observed:	275 nm



Cisoid:	253 nm
Ring residues: 5 × 5 =	25
Double-bond-extending conjugation: 2 × 30 =	60
Exocyclic double bond: 3 × 5 =	15
CH_3COO—:	0
	353 nm
Observed:	355 nm

Carbonilas/acilas e enonas



HYPSOCHROMIC EFFECTS OF LONE-PAIR AUXOCHROMES ON THE $n \rightarrow \pi^*$ TRANSITION OF A CARBONYL GROUP

	λ_{max}	ε_{max}	Solvent
$CH_3-C(=O)-H$	293 nm	12	Hexane
$CH_3-C(=O)-CH_3$	279	15	Hexane
$CH_3-C(=O)-Cl$	235	53	Hexane
$CH_3-C(=O)-NH_2$	214	—	Water
$CH_3-C(=O)-OCH_2CH_3$	204	60	Water
$CH_3-C(=O)-OH$	204	41	Ethanol

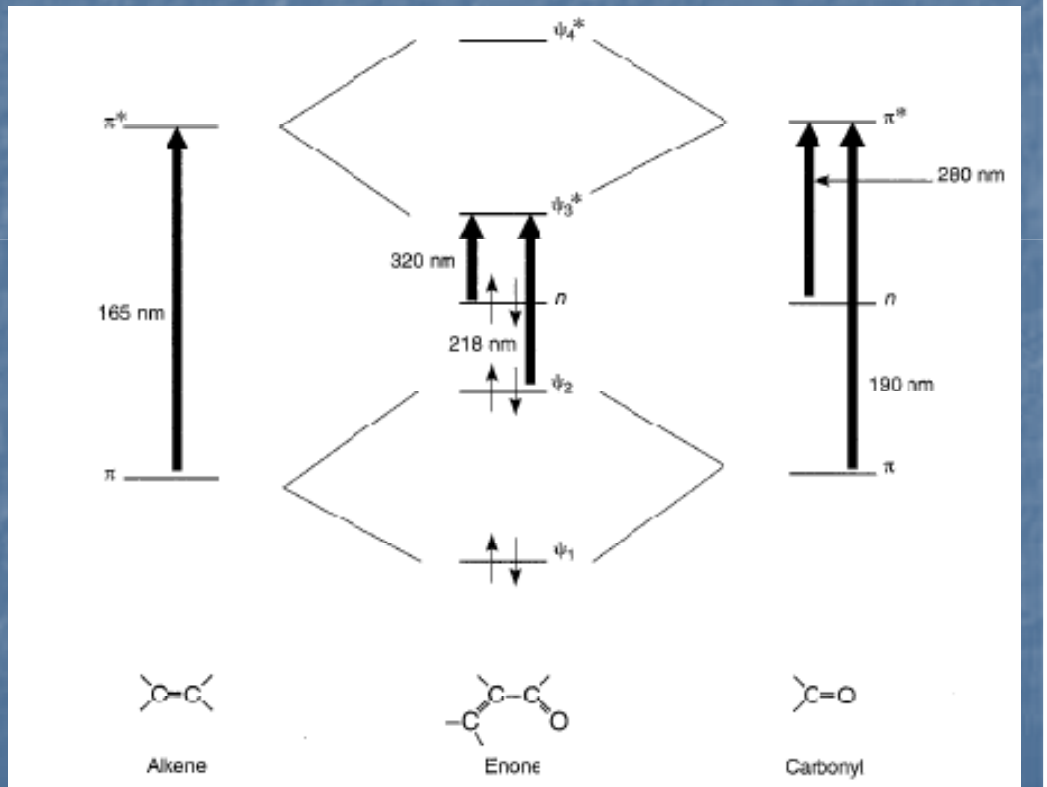
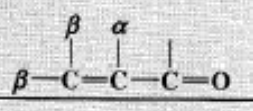
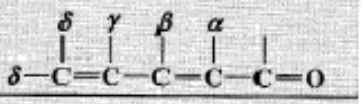


FIGURE 7.16 The orbitals of an enone system compared to those of the noninteracting chromophores.

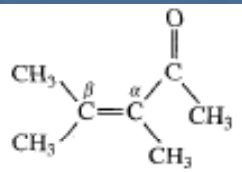
Regras de Woodward para enonas

EMPIRICAL RULES FOR ENONES

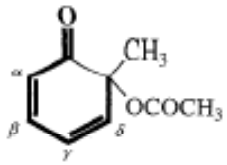




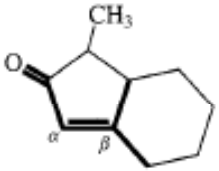
Base values:		
Six-membered ring or acyclic parent enone		= 215 nm
Five-membered ring parent enone		= 202 nm
Acyclic dienone		= 245 nm
Increments for:		
Double-bond-extending conjugation		30
Alkyl group or ring residue	α	10
	β	12
	γ and higher	18
Polar groupings:		
–OH	α	35
	β	30
	δ	50
$-OCOCH_3$	α,β,δ	6
$-OCH_3$	α	35
	β	30
	γ	17
	δ	31
–Cl	α	15
	β	12
–Br	α	25
	β	30
NR_2	β	95
Exocyclic double bond		5
Homocyclic diene component		39
Solvent correction		Variable
λ_{max}^{EtOH} (calc) = Total		



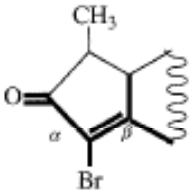
Acyclic enone:	215 nm
α-CH_3:	10
β-CH_3: $2 \times 12 =$	24
	249 nm
Observed:	249 nm



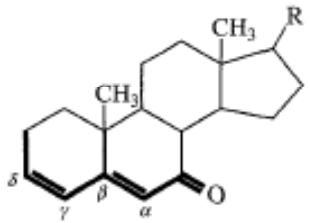
Six-membered enone:	215 nm
Double-bond-extending conjugation:	30
Homocyclic diene:	39
δ-Ring residue:	18
	302 nm
Observed:	300 nm



Five-membered enone:	202 nm
β-Ring residue: $2 \times 12 =$	24
Exocyclic double-bond:	5
	231 nm
Observed:	226 nm

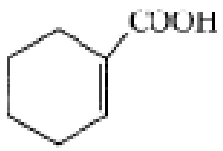
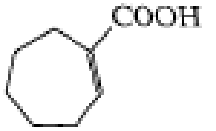


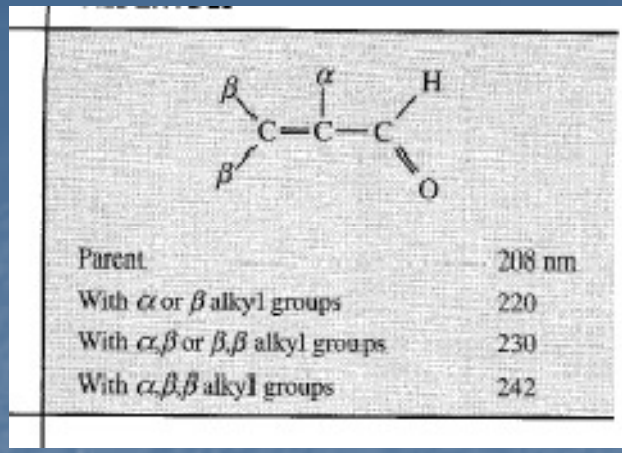
Five-membered enone:	202 nm
α-Br:	25
β-Ring residue: $2 \times 12 =$	24
Exocyclic double bond:	5
	256 nm
Observed:	251 nm



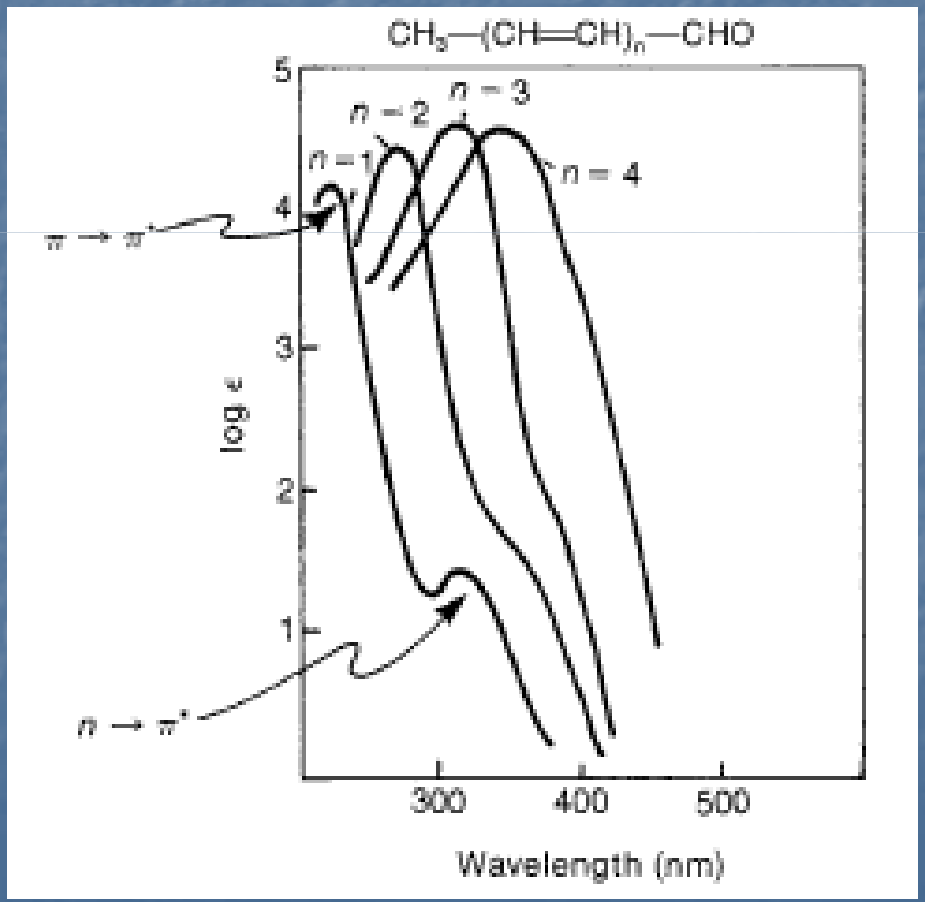
Six-membered enone:	215 nm
Double-bond-extending conjugation:	30
β-Ring residue:	12
δ-Ring residue:	18
Exocyclic double-bond:	5
	280 nm
Observed:	280 nm

Aldeídos, ácidos e ésteres α,β-insaturados

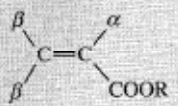
	α,β-dialkyl	217 nm calc.
	Double bond is in a six-membered ring, adds nothing	217 nm obs.
	α,β-dialkyl	217 nm
	Double bond is in a seven-membered ring	+ 5
		222 nm calc.
		222 nm obs.

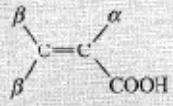


Parent	208 nm
With α or β alkyl groups	220
With α,β or β,β alkyl groups	230
With α,β,β alkyl groups	242

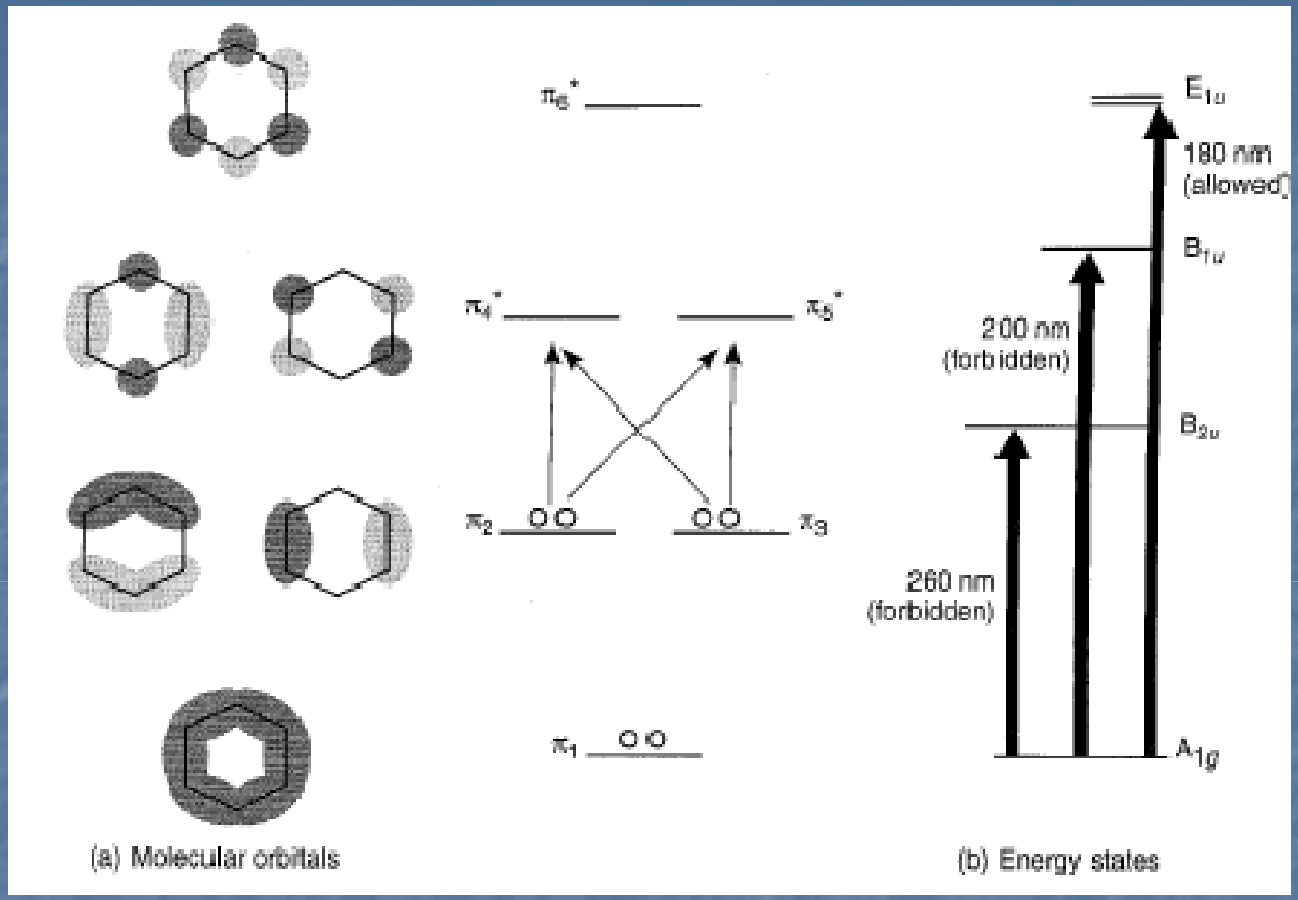


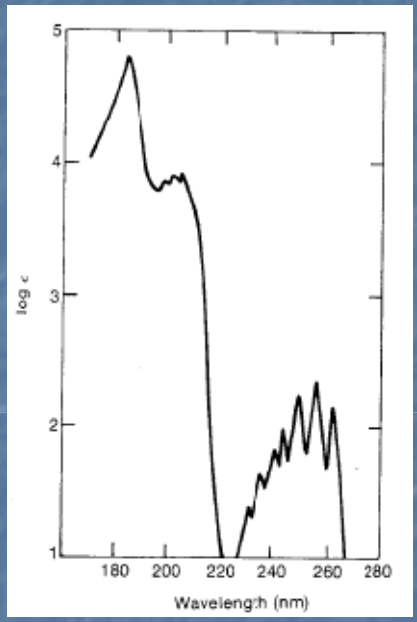
Base values for:





With α or β alkyl group	208 nm
With α,β or β,β alkyl groups	217
With α,β,β alkyl groups	225
For an exocyclic α,β double bond	Add 5 nm
For an endocyclic α,β double bond in a five- or seven-membered ring	Add 5 nm

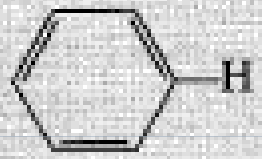




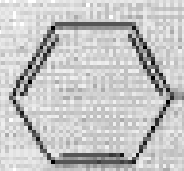
Espectro do benzeno

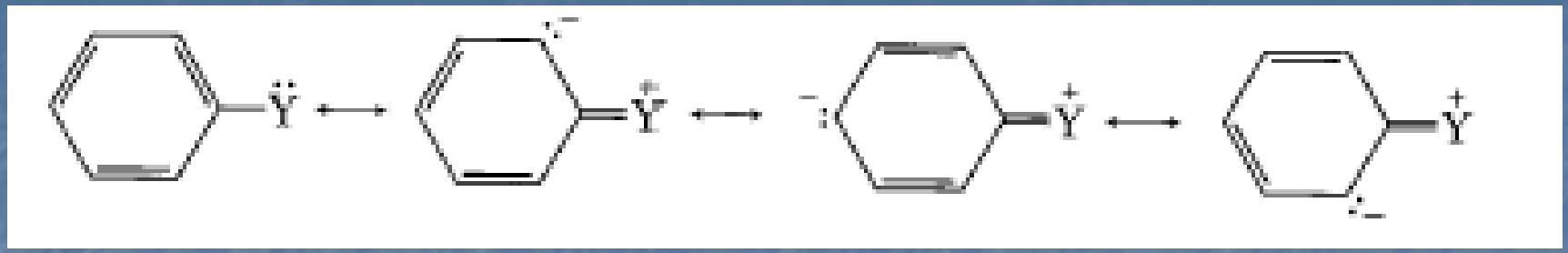
- **Orbitais moleculares e**
- **estados de energia para o benzeno**

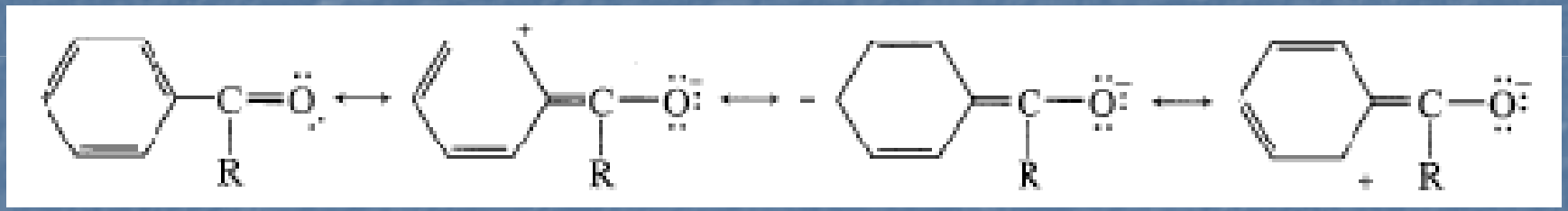
pH EFFECTS ON ABSORPTION BANDS

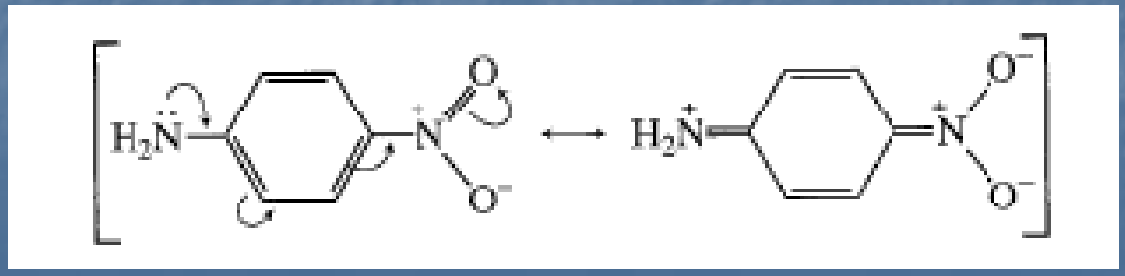
Substituent	Primary		Secondary	
	λ(nm)	ε	λ(nm)	ε
	203.5	7,400	254	204
$-OH$	210.5	6,200	270	1,450
$-O^-$	235	9,400	287	2,600
$-NH_2$	230	8,600	280	1,430
$-NH_3^+$	203	7,500	254	169
$-COOH$	230	11,600	273	970
$-COO^-$	224	8,700	268	560

ULTRAVIOLET MAXIMA FOR VARIOUS AROMATIC COMPOUNDS

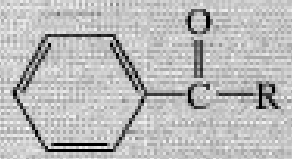
Substituent		Primary λ(nm)	Primary ε	Secondary λ(nm)	Secondary ε
	—H	203.5	7,400	254	204
Electron-releasing substituents	$-CH_3$	206.5	7,000	261	225
	—Cl	209.5	7,400	263.5	190
	—Br	210	7,900	261	192
	—OH	210.5	6,200	270	1,450
	$-OCH_3$	217	6,400	269	1,480
	$-NH_2$	230	8,600	280	1,430
Electron-withdrawing substituents	—CN	224	13,000	271	1,000
	—COOH	230	11,600	273	970
	$-COCH_3$	245.5	9,800		
	—CHO	249.5	11,400		
	$-NO_2$	268.5	7,800		



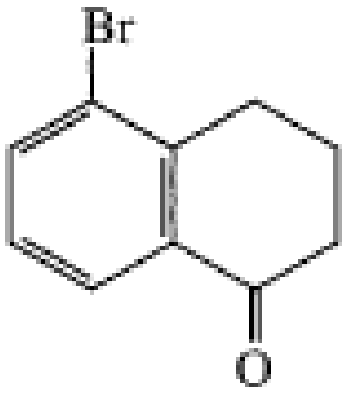




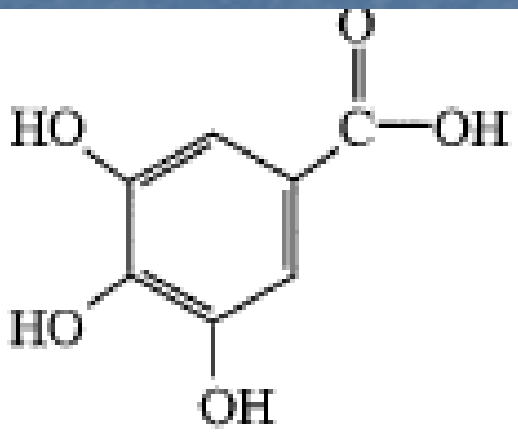
EMPIRICAL RULES FOR BENZOYL DERIVATIVES

Parent chromophore: 

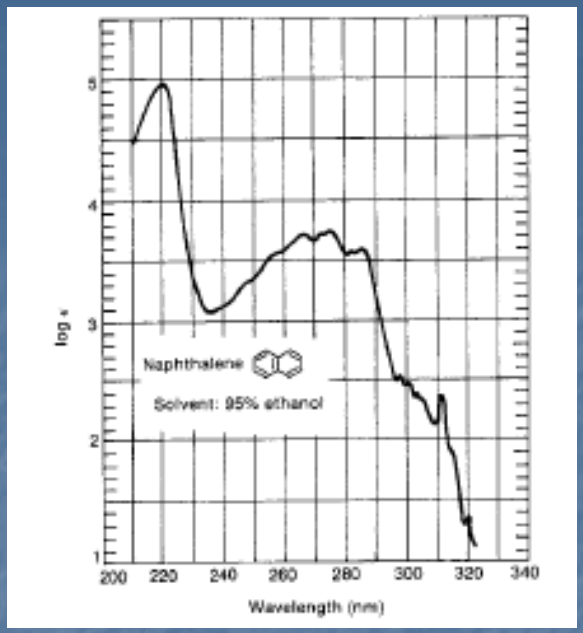
R = alkyl or ring residue		246
R = H		250
R = OH or OAlkyl		230
Increment for each substituent:		
—Alkyl or ring residue	*o*, *m*	3
	p	10
—OH, —OCH_3, or —OAlkyl	*o*, *m*	7
	p	25
—O^-	*o*	11
	m	20
	p	78
—Cl	*o*, *m*	0
	p	10
—Br	*o*, *m*	2
	p	15
—NH_2	*o*, *m*	13
	p	58
—$NHCOCH_3$	*o*, *m*	20
	p	45
—$NHCH_3$	*p*	73
—$N(CH_3)_2$	*o*, *m*	20
	p	85

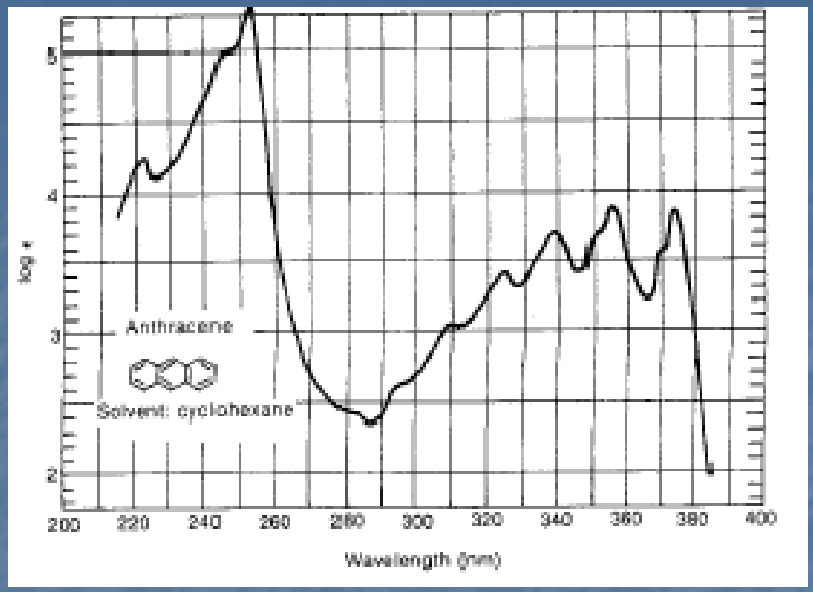


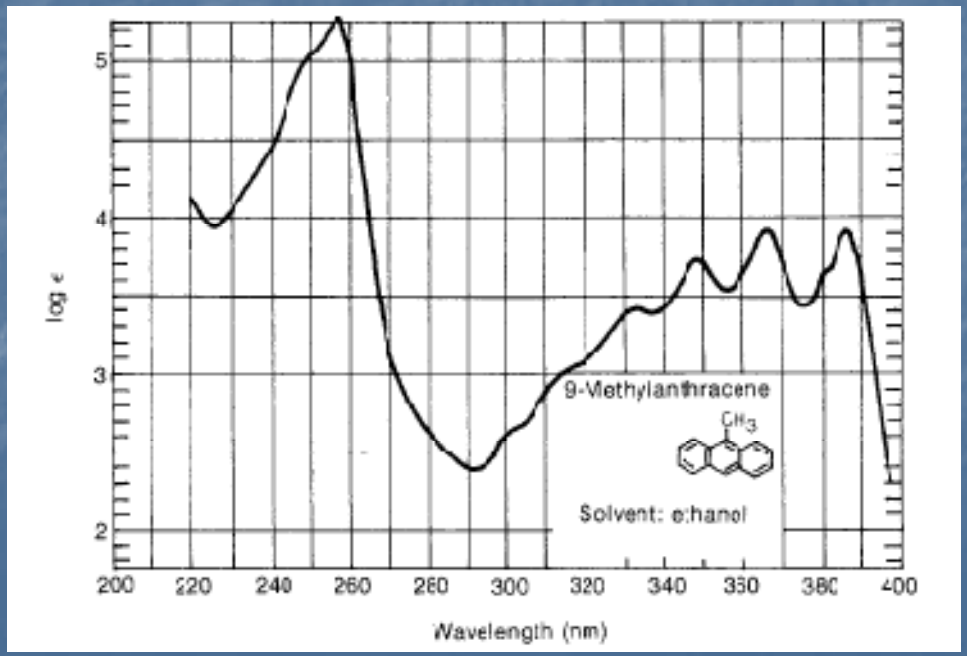
Parent chromophore:	246 nm
o-Ring residue:	3
m-Br:	2
	251 nm
Observed:	253 nm

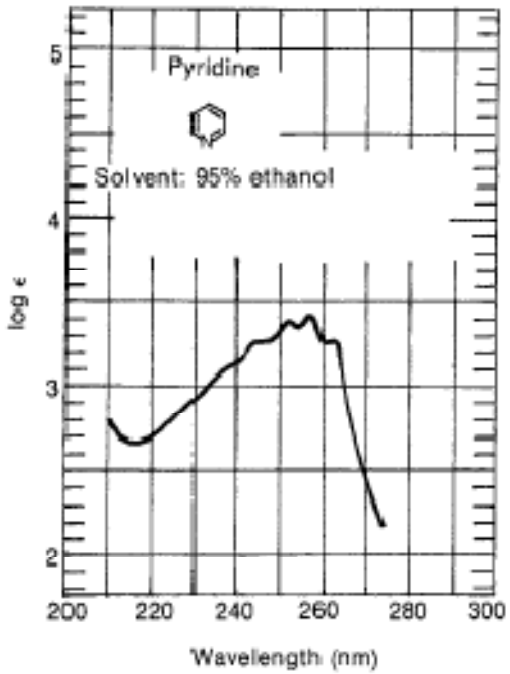


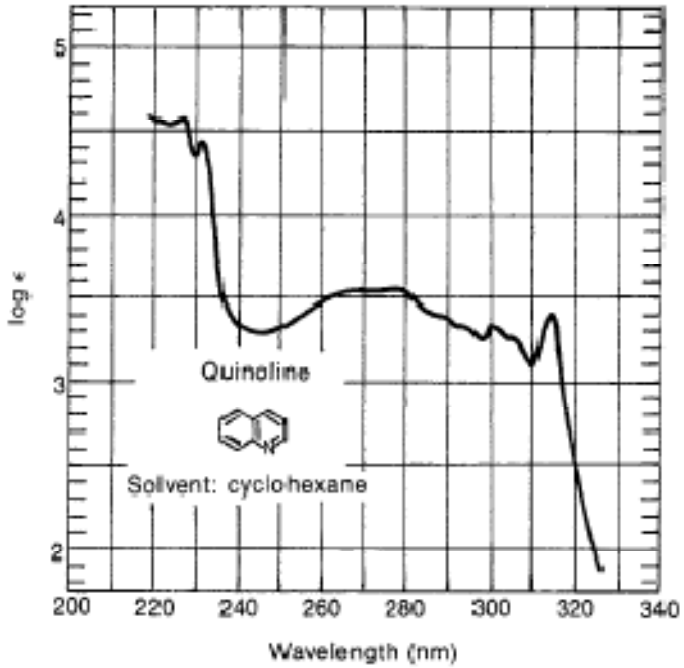
Parent chromophore:	230 nm
m-OH: 2 × 7 =	14
p-OH:	25
	269 nm
Observed:	270 nm

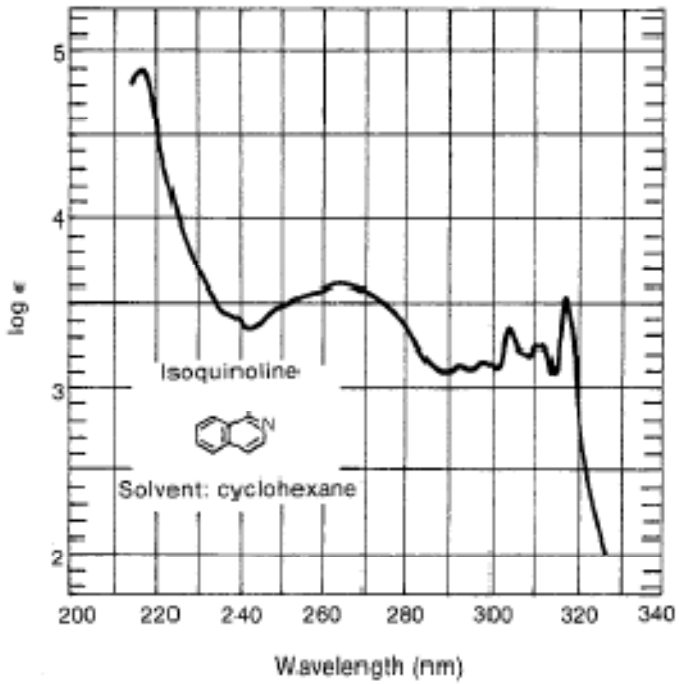

log ε
Naphthalene
Solvent: 95% ethanol
Wavelength (nm)


log ε
Anthracene
Solvent: cyclohexane
Wavelength (nm)


log ε
9-Methylanthracene
CH3
Solvent: ethanol
Wavelength (nm)

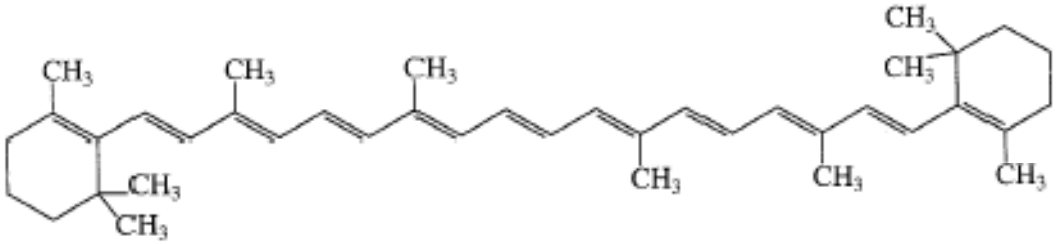

Pyridine
Solvent: 95% ethanol
log ε
5
4
3
2
200
220
240
260
280
300
Wavelength (nm)


Quinoline
Solvent: cyclohexane
log ε
5
4
3
2
200
220
240
260
280
300
320
340
Wavelength (nm)

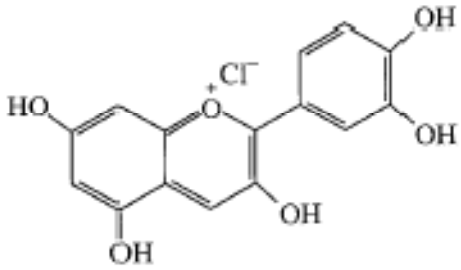

Isoquinoline
Solvent: cyclohexane
log ε
5
4
3
2
200
220
240
260
280
300
320
340
Wavelength (nm)

RELATIONSHIP BETWEEN THE COLOR OF LIGHT ABSORBED BY A COMPOUND AND THE OBSERVED COLOR OF THE COMPOUND

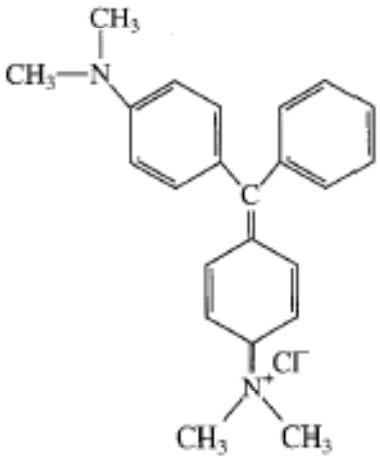
Color of Light Absorbed	Wavelength of Light Absorbed (nm)	Observed Color
Violet	400	Yellow
Blue	450	Orange
Blue-green	500	Red
Yellow-green	530	Red-violet
Yellow	550	Violet
Orange-red	600	Blue-green
Red	700	Green



β-Carotene (a carotenoid, which is a class of plant pigments)
$\lambda_{max} = 452$ nm



Cyanidin chloride (an anthocyanin, another class of plant pigments)
$\lambda_{max} = 545$ nm



Malachite green (a triphenylmethane dye)
$\lambda_{max} = 617$ nm