Luz: ondas e fótons

natureza ambivalente

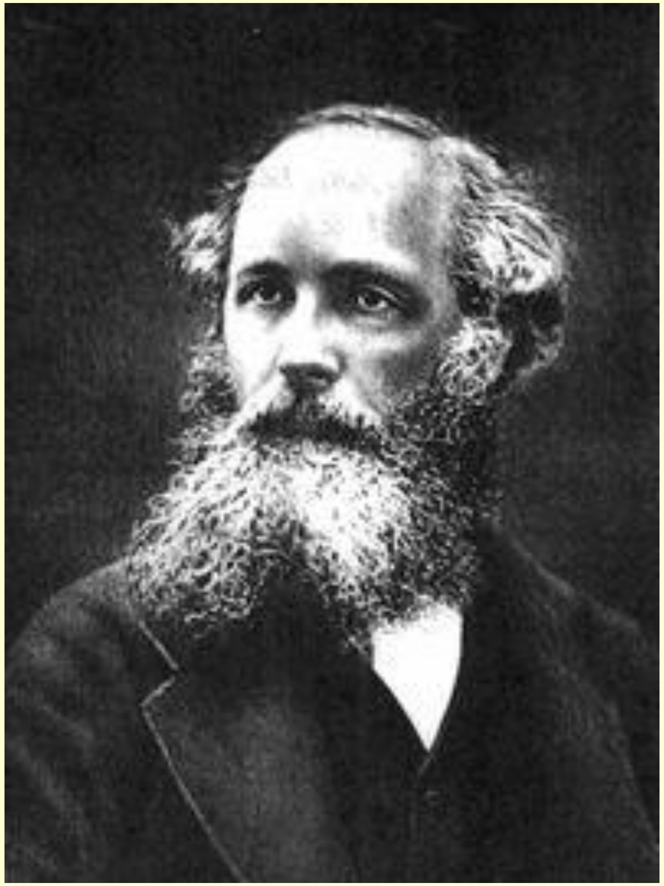
propriedades descritas por dois modelos (necessários para criar um retrato mais completo da natureza da luz):

$\Rightarrow$ modelo da onda eletromagnética (XIX) que descreve a luz como uma transferência de energia **contínua** através do espaço, que se dá pela combinação de ondas de **campos elétricos e magnéticos**.

$\Rightarrow$ modelo da eletrodinâmica quântica que descreve a luz em termos de partículas elementares sem massa (**fótons**), que podem ser imaginadas como **pulsos localizados** de energia.

modelos complementares, embora pareçam contraditórios

A natureza da luz: modelo ondulatório



Ondas eletromagnéticas
James Clerk Maxwell
(1831 – 1879)

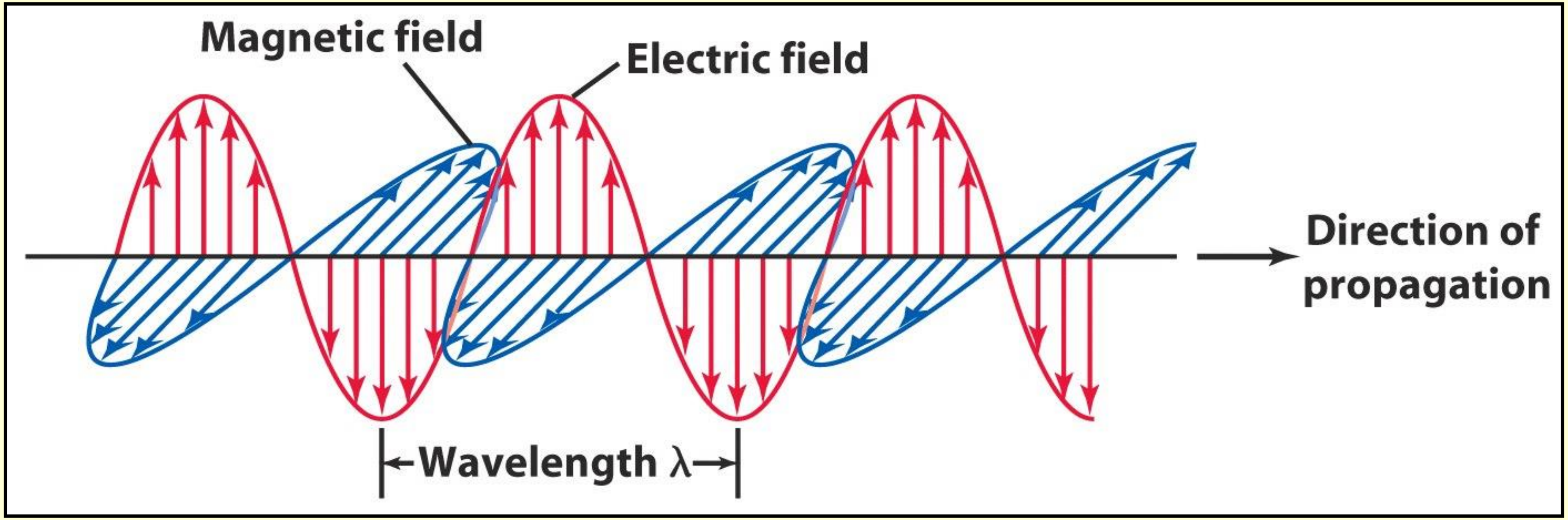
calculou que as ondas se propagariam a velocidades muito próximas à da velocidade da luz: inferiu que a luz poderia ser compreendida como ondas eletromagnéticas transversais em um meio hipotético ("eter").

afirmou que a luz correspondia a uma pequena parte do espectro de ondas eletromagnéticas existentes.

Hertz confirmou isso posteriormente (1888), por meio do descobrimento das ondas de rádio.

A natureza da luz: modelo ondulatório

- No século XIX (~1860), **James Clerk Maxwell**, físico e matemático escocês descreveu as propriedades elétricas e magnéticas básicas através de quatro equações, demonstrando que as forças elétricas e magnéticas podem ser encaradas como dois aspectos de um mesmo fernômeno. Hoje, esse fenômeno é designado por **eletromagnetismo**.



Maxwell's Law on Electromagnetism

- **Electricity according to Gauss**
  - relates electricity to electric charge
- **Faraday's Law**
  - relates electric fields to magnetic fields
- **Magnetism according to Gauss**
  - relates magnetism to electricity
- **Ampere-Maxwell Law**
  - relates magnetic field to electricity

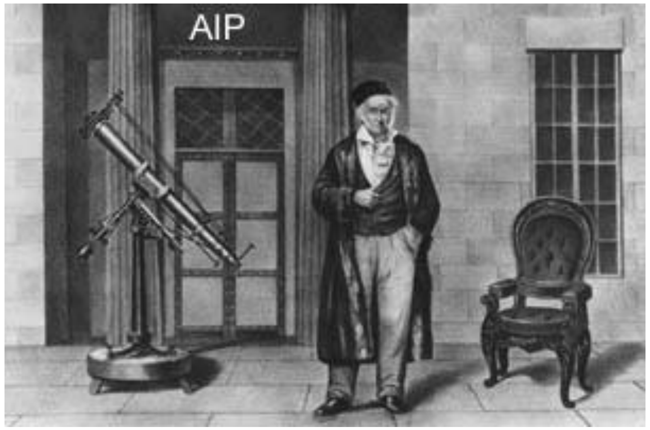
$$\nabla \bullet E = \frac{1}{\varepsilon_0} \rho$$

$$\nabla \times E = -\frac{\partial B}{\partial t}$$

$$\nabla \bullet B = 0$$

$$\nabla \times B = \mu_0 J + \mu_0 \varepsilon_0 \frac{\partial E}{\partial t}$$

Don't worry about notation here



A natureza da luz: modelo ondulatório

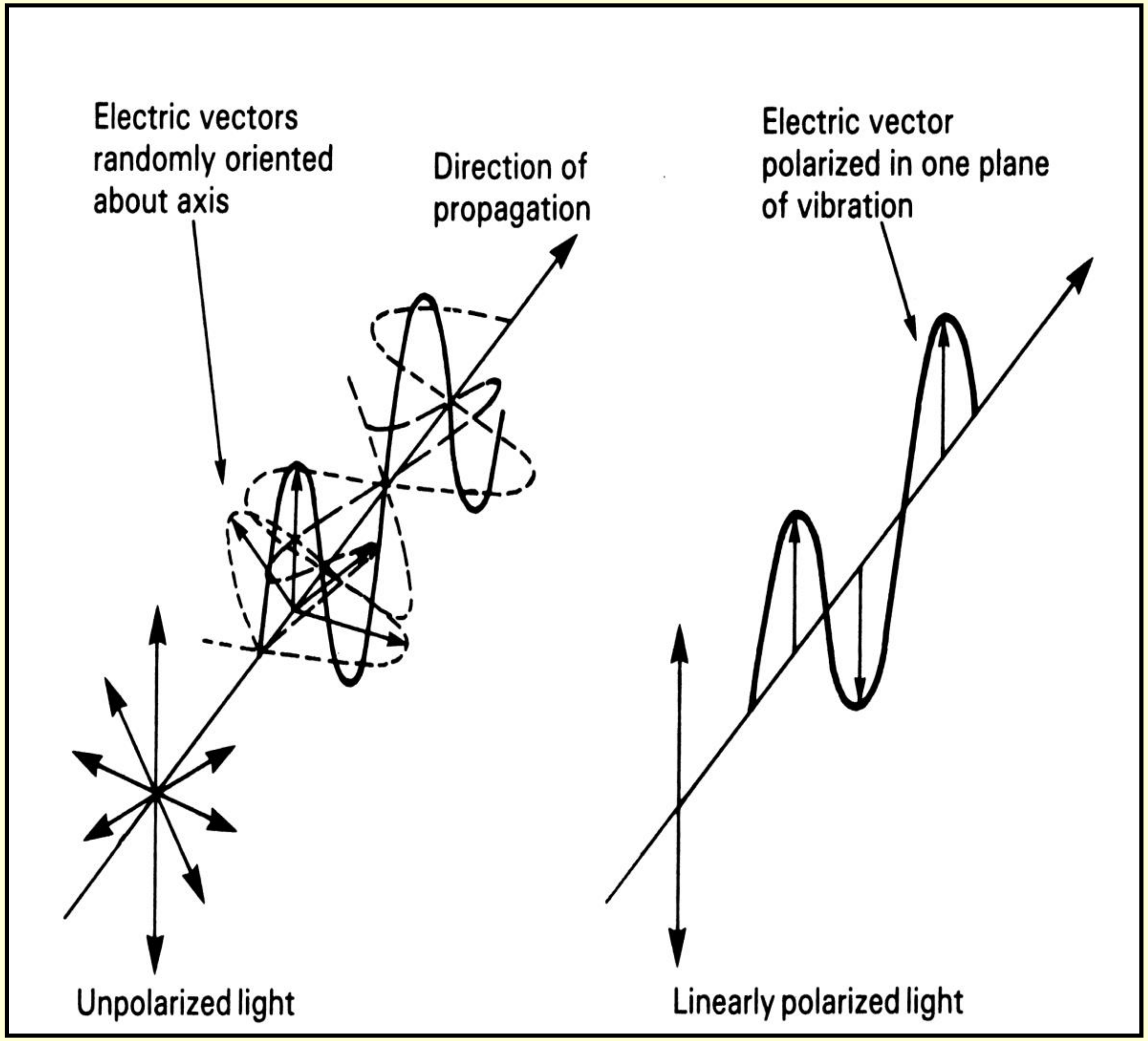
- descreve a propagação da luz
- contribui para explicar fenômenos como:

♦ **radiação do corpo negro** (catástrofe do ultra-violeta)
♦ **difração**
♦ **interferência**
♦ **polarização**

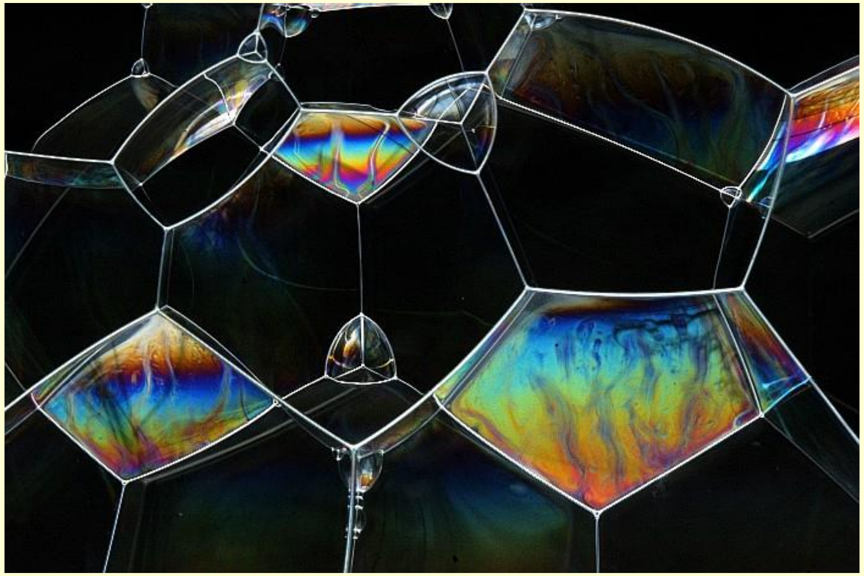
Difração da luz

Difração da luz

A natureza da luz: modelo ondulatório



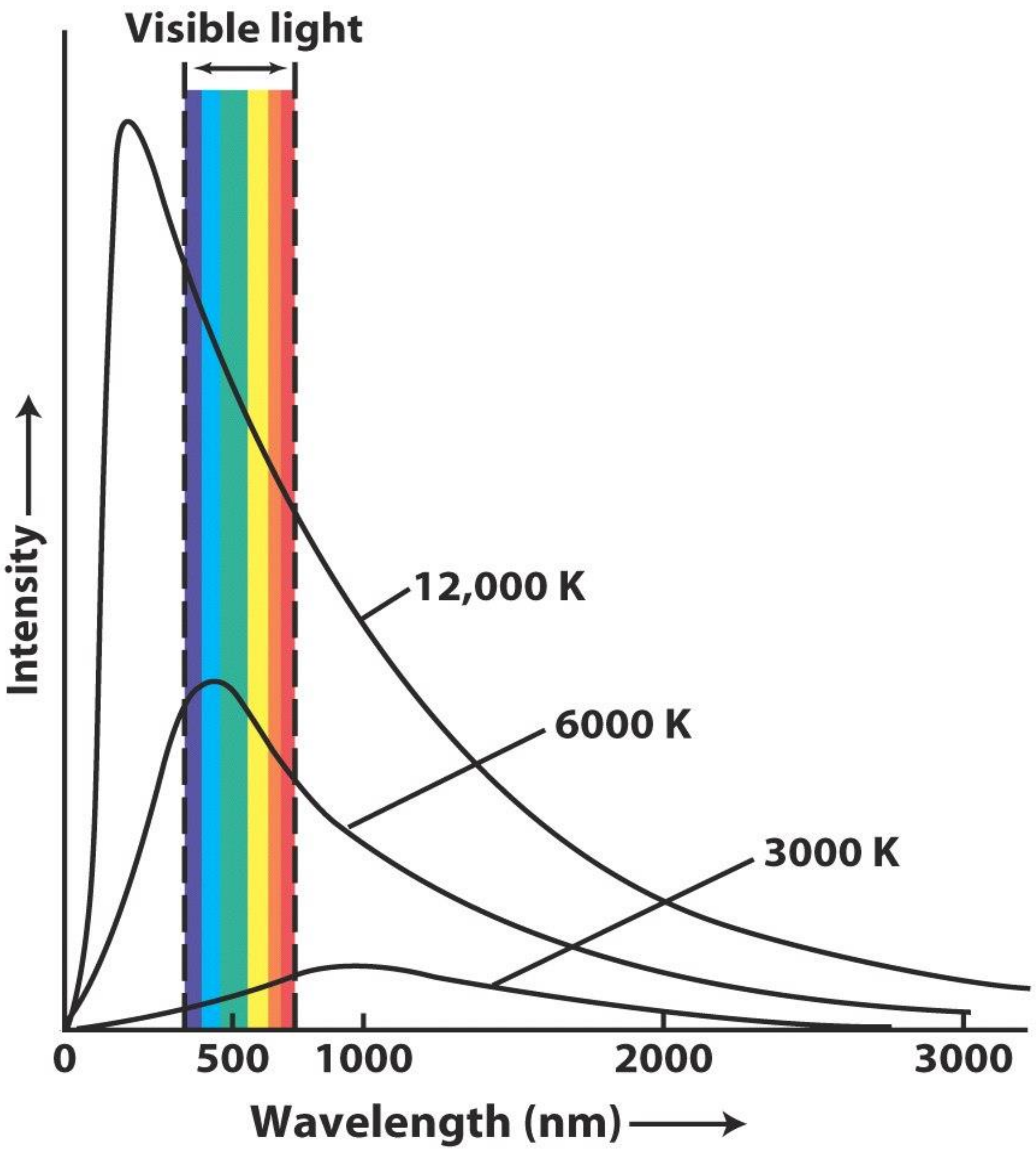
Luz polarizada

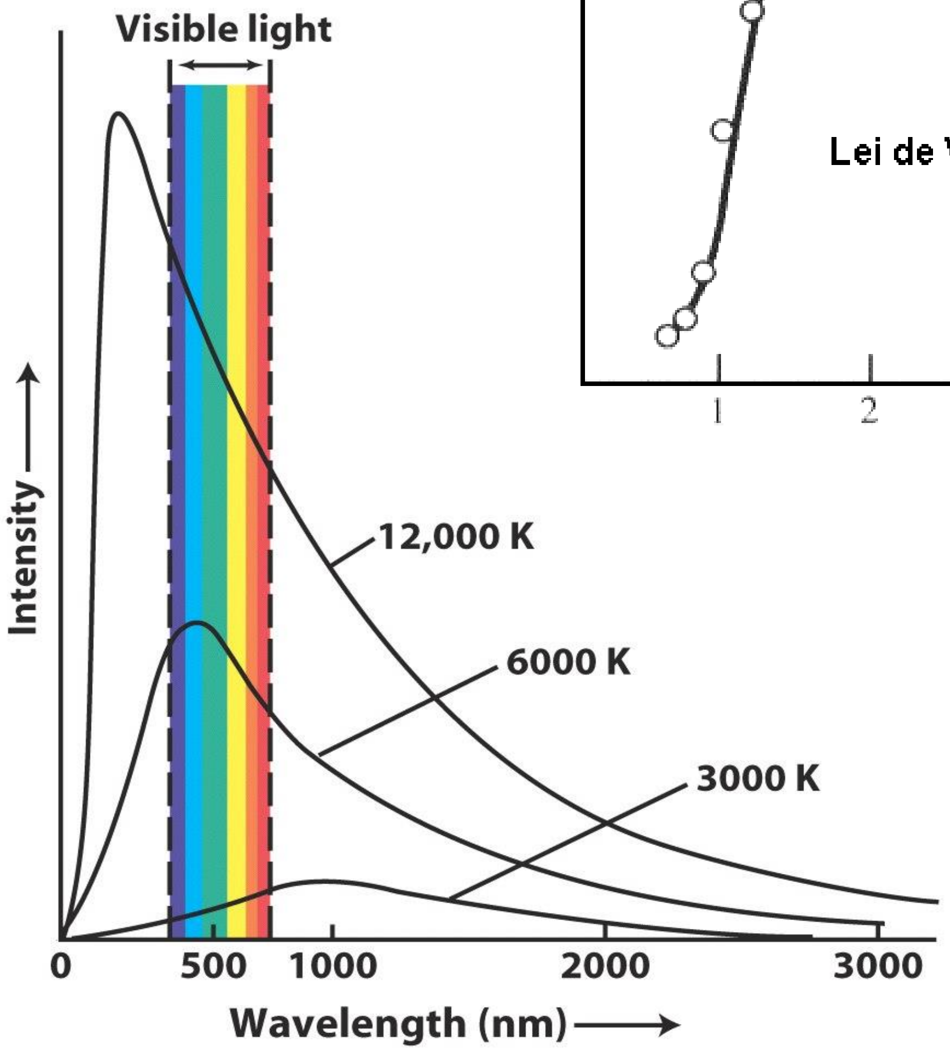


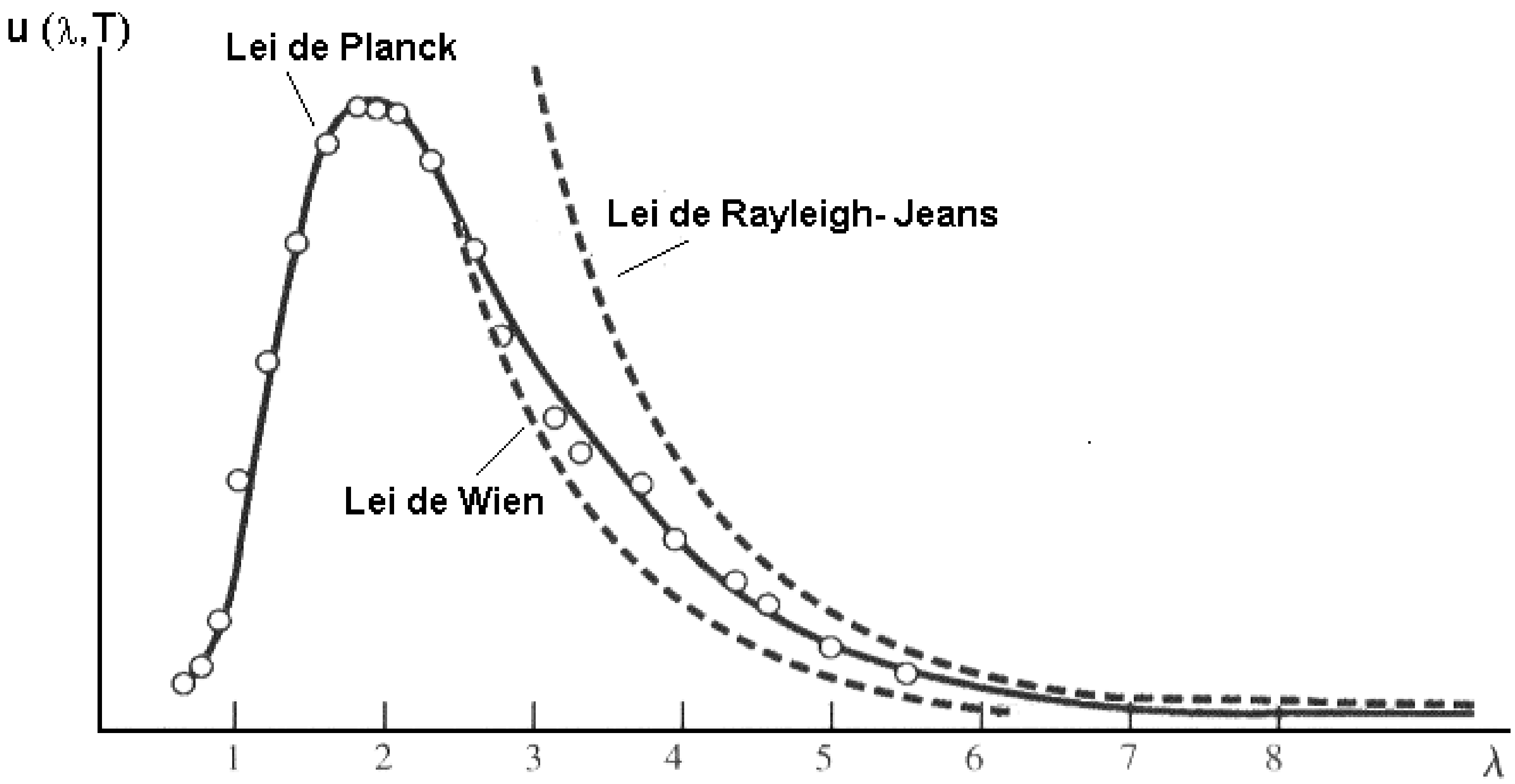
Padrões de interferência da luz

Blackbody

- A blackbody is a hypothetical object that is a perfect absorber of electromagnetic radiation at all wavelengths
- Stars closely approximate the behavior of blackbodies, as do other hot, dense objects
- The intensities of radiation emitted at various wavelengths by a blackbody at a given temperature are shown by a blackbody curve







catástrofe do ultra-violeta

corpo negro

A natureza da luz: modelo eletrodinâmico quântico (fóton)

- necessário para descrever interações entre a luz e a matéria.

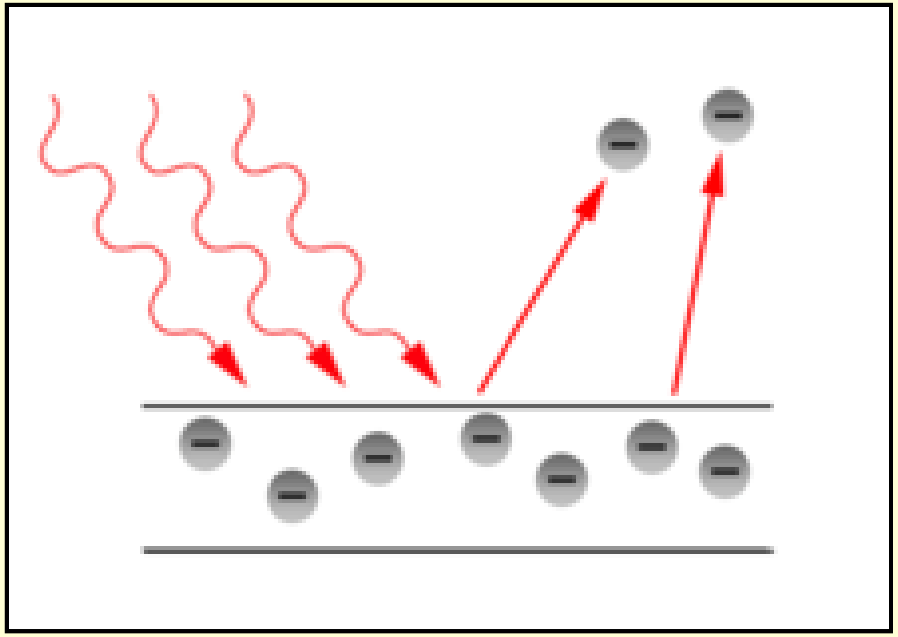
- contribui para a descrição da emissão e absorção de luz pelos materiais.

- **Albert Einstein (1905)** : "*On a Heuristic Viewpoint Concerning the Production and Transformation of Light*".

- Nobel: 1921.

A natureza da luz: modelo eletrodinâmico quântico (fóton)

- Einstein admitiu que a luz era constituída por pacotes discretos de energia.
- descrição matemática: absorção de fótons (ou quanta) de luz.
- interação entre a luz e os elétrons da substância.



Efeito fotoelétrico

A luz tem propriedades similares às de partículas

- a energia das ondas de luz se apresenta em pacotes discretos, chamados de quanta de luz ou fótons.
- para luz de freqüência *f*, a energia de cada fóton é **E = h*f***, onde h é a constante de Planck

Photon Energy

$$E = h\,v$$

$$E = \frac{hc}{\lambda}$$

- **Planck's law** relates the energy of a photon to its frequency or wavelength

  E = energy of a photon
  h = Planck's constant
  c = speed of light
  λ = wavelength of light
  v = frequency of light

- The value of the constant h in this equation, called *Planck's constant,* has been shown in laboratory experiments to be

  $h = 6.625 \times 10^{-34}$ J s

A natureza da luz: modelo eletrodinâmico quântico (fóton)

- **Controvérsia:** contradição com a teoria ondulatória da luz que advém naturalmente das equações de Maxwell para o comportamento eletromagnético e. mais genericamente. À idéia de que a energia nos sistemas físicos é infinitamente divisível.

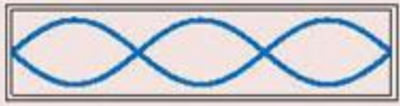
GENERAL PRINCIPLES

Light has particle-like properties

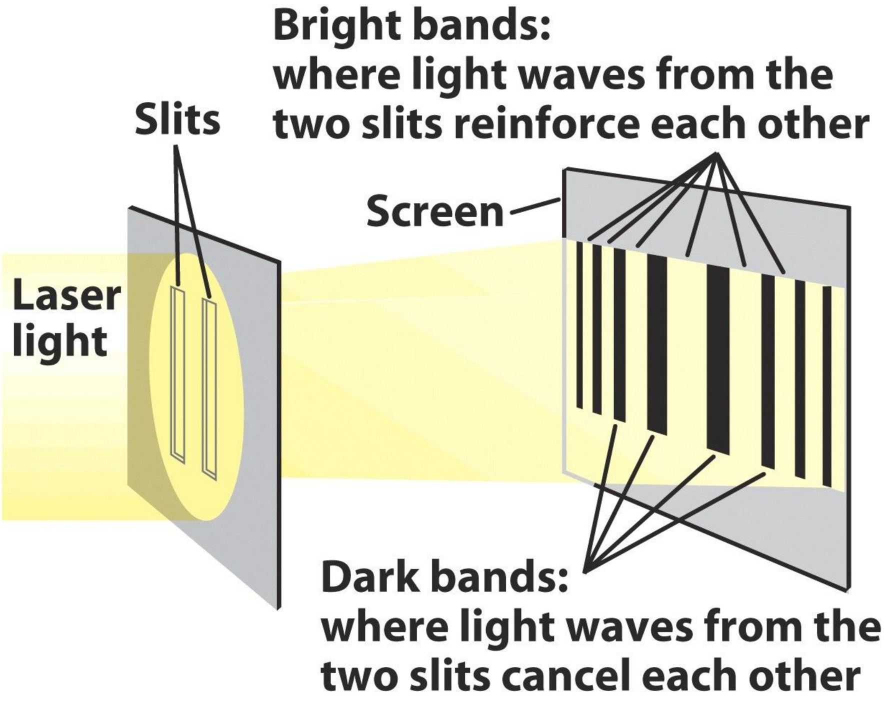
- The energy of a light wave comes in discrete packets called light quanta or photons.
- For light of frequency f, the energy of each photon is $E = hf$, where h is **Planck's constant.**
- For a light wave that delivers power P, photons arrive at rate R such that $P = Rhf$.
- Photons are "particle-like" but are not classical particles.

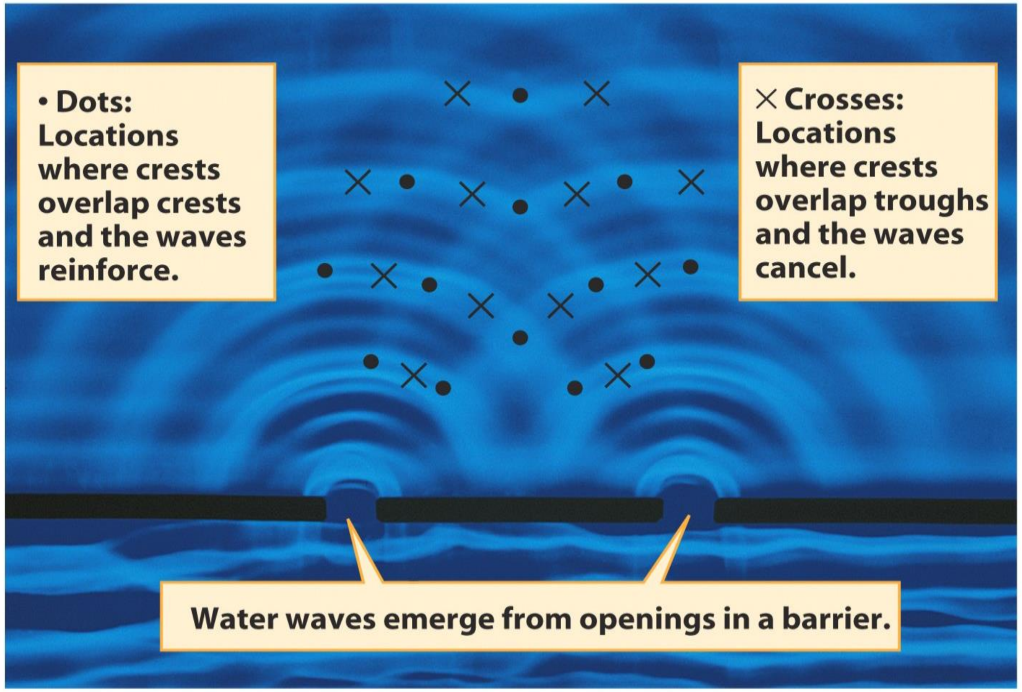
Matter has wave-like properties

- The **de Broglie wavelength** of a "particle" of mass m is $\lambda = h/mv$.
- The wave-like nature of matter is seen in the interference patterns of electrons, neutrons, and entire atoms.
- When a particle is confined, it sets up a de Broglie standing wave. The fact that standing waves have only certain allowed wavelengths leads to the conclusion that a confined particle has only certain allowed energies. That is, energy is quantized.



Light has properties of both waves and particles

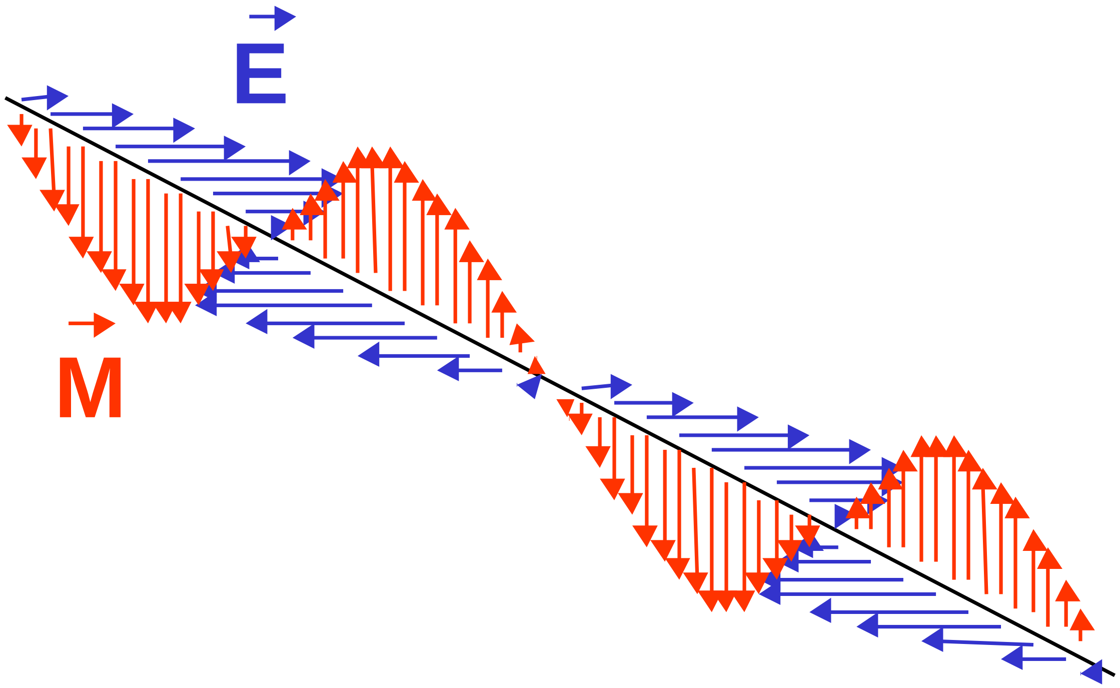




- Einstein thought light was in the form of little packets of energy called photons and subsequent experiments with blackbody radiation indicate it has particle-like properties
- Young's Double-Slit Experiment indicated light behaved as a wave
- Light has a dual personality; it behaves as a stream of particle like photons, but each photon has wavelike properties

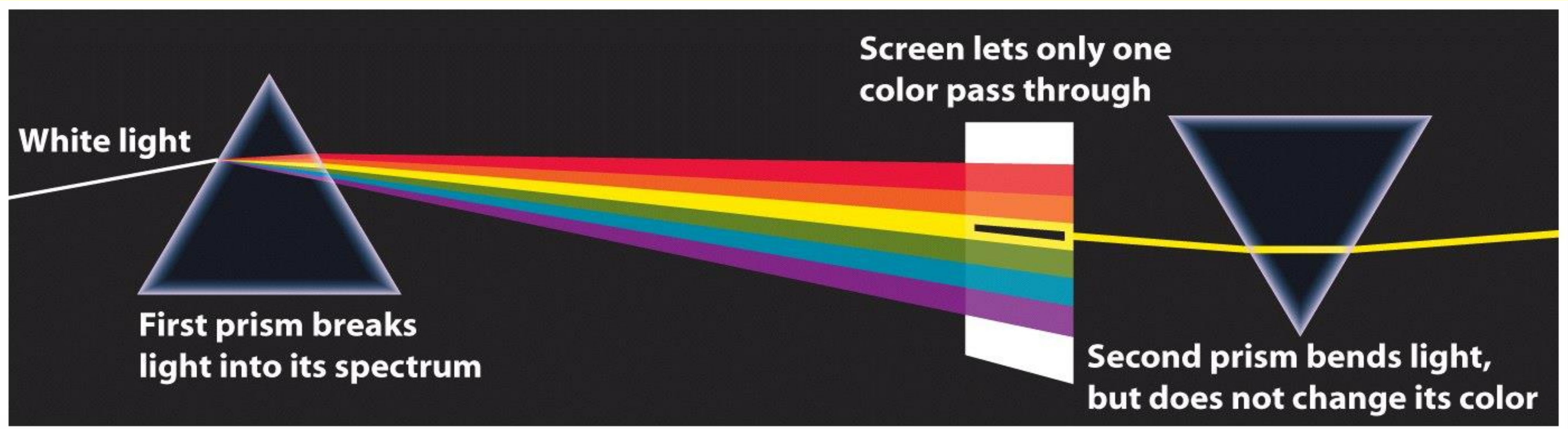
Espectroscopia na região do UV-Visível

Espectroscopia: estudo das interações da radiação eletromagnética com a matéria.



Modelo ondulatório de **Maxwell**

Comprimento de onda e freqüência



Relação entre frequência e comprimento de onda de uma onda eletromagnética:

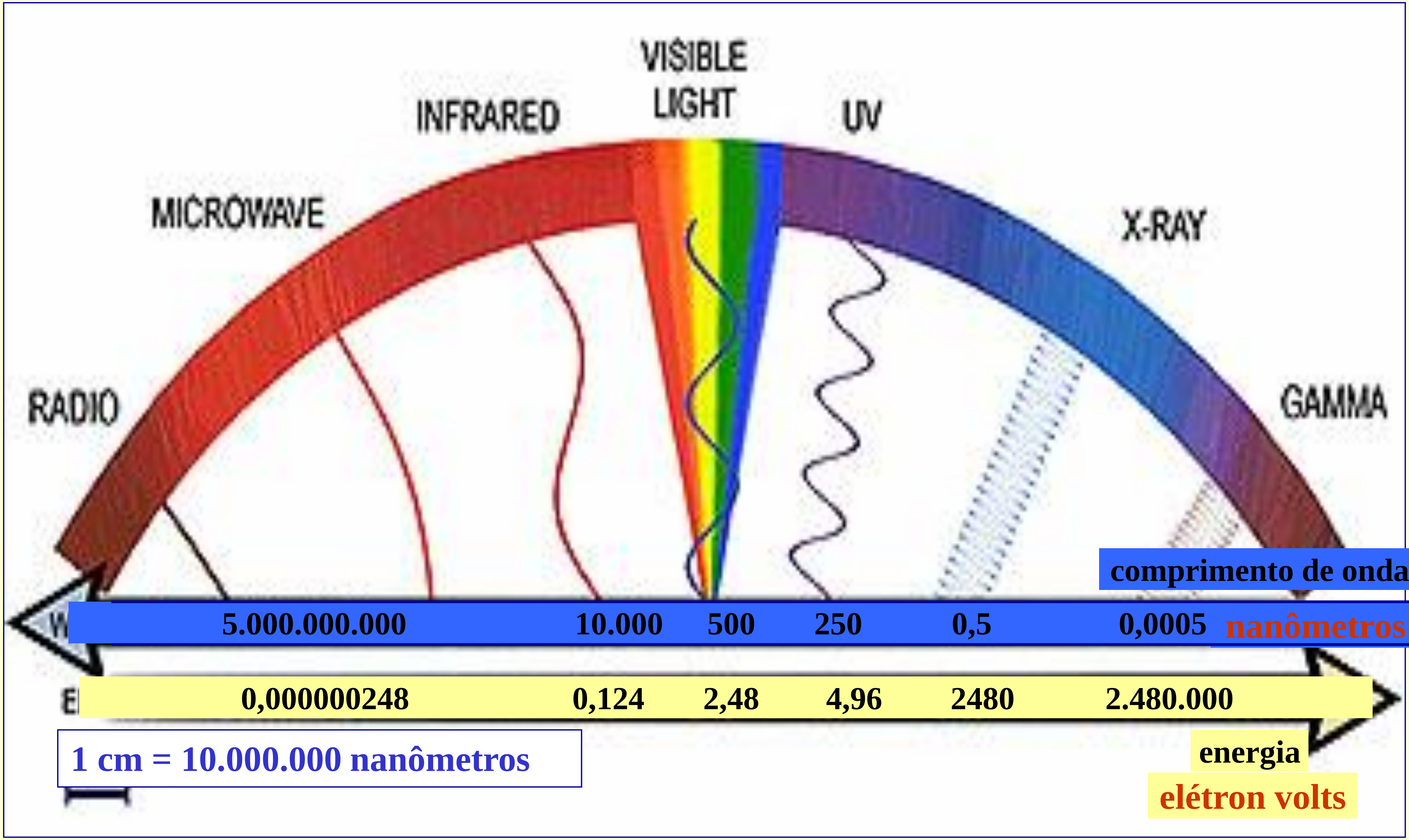
$$\nu = \frac{c}{\lambda}$$

n = freqüência de uma onda eletromagnética (em Hz)

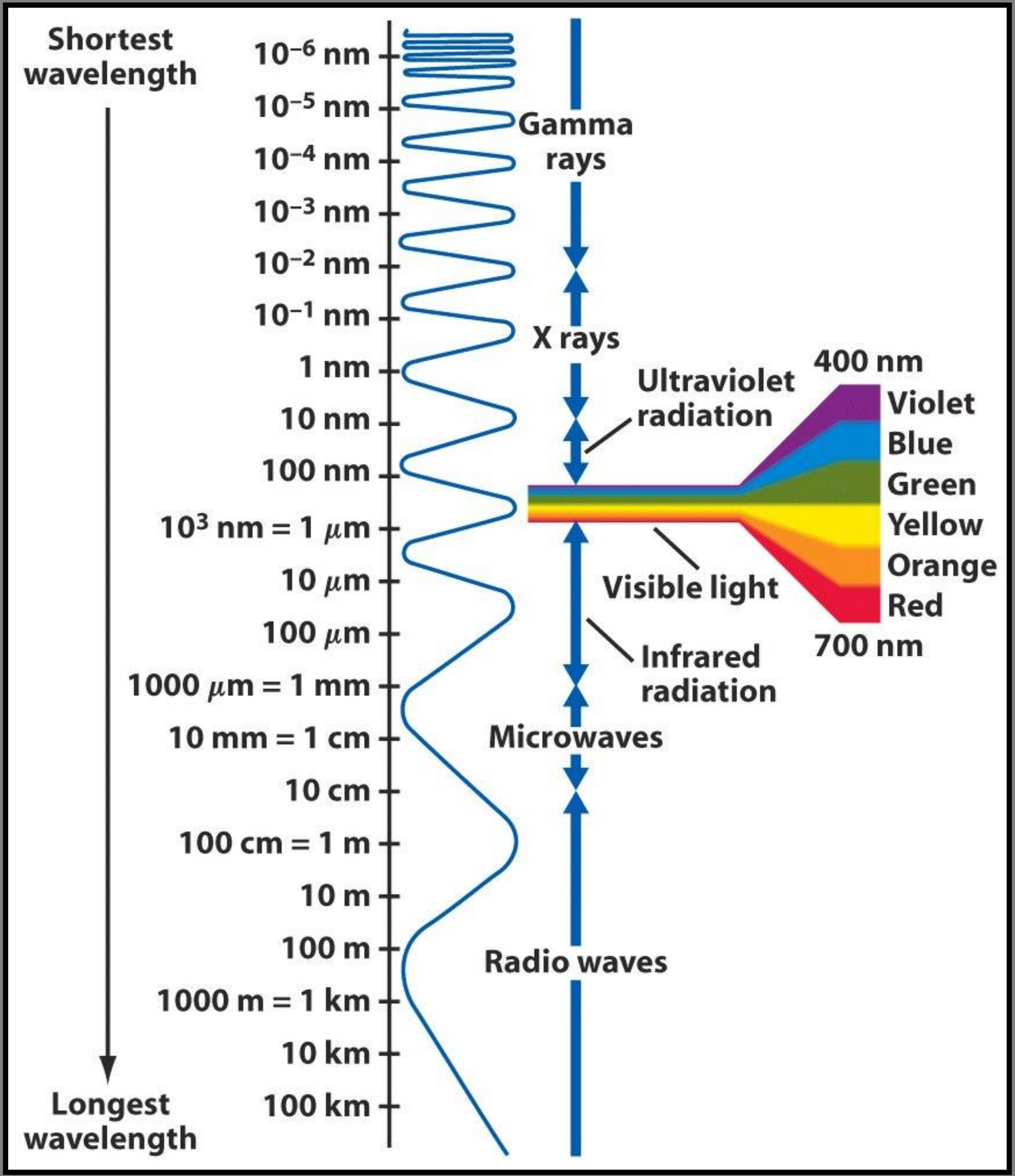
c = velocidade da luz = 3×10^{8} m s^{-1}

l = comprimento de onda da onda (em metros)

Espectro eletromagnético

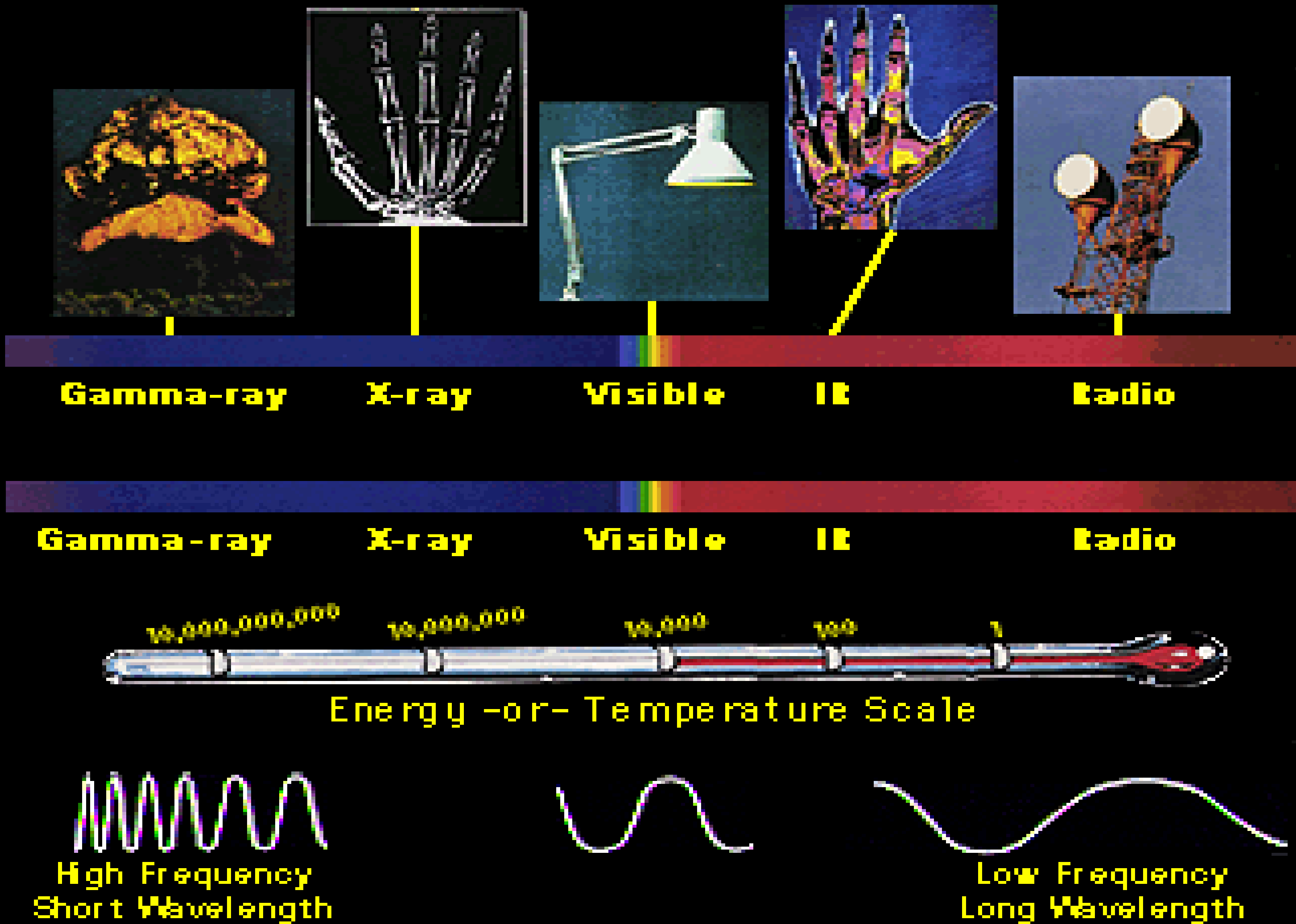


Espectro eletromagnético



- light is also called **electromagnetic radiation**
- Visible light falls in the 400 to 700 nm range
- Stars, galaxies and other objects emit light in all wavelengths

Espectro eletromagnético



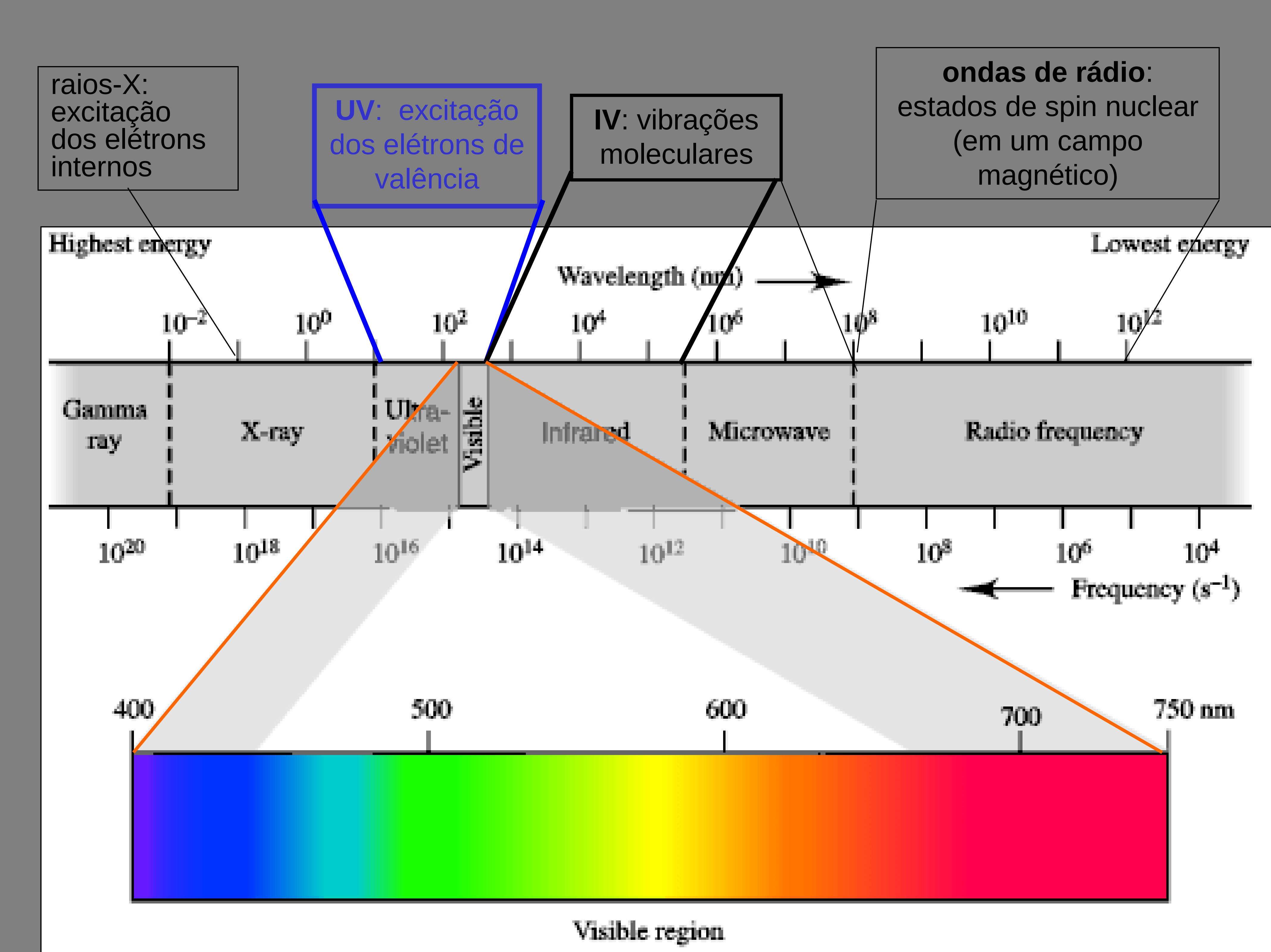
Definições

- E = energia (Joule, erg)
- c = velocidade da luz (constante)
- λ = comprimento de onda
- h = constante de Planck
- ν = "nu" = frequência (Hz)
- nm = 10^{-9} m
- Å = angstrom = 10^{-10} m

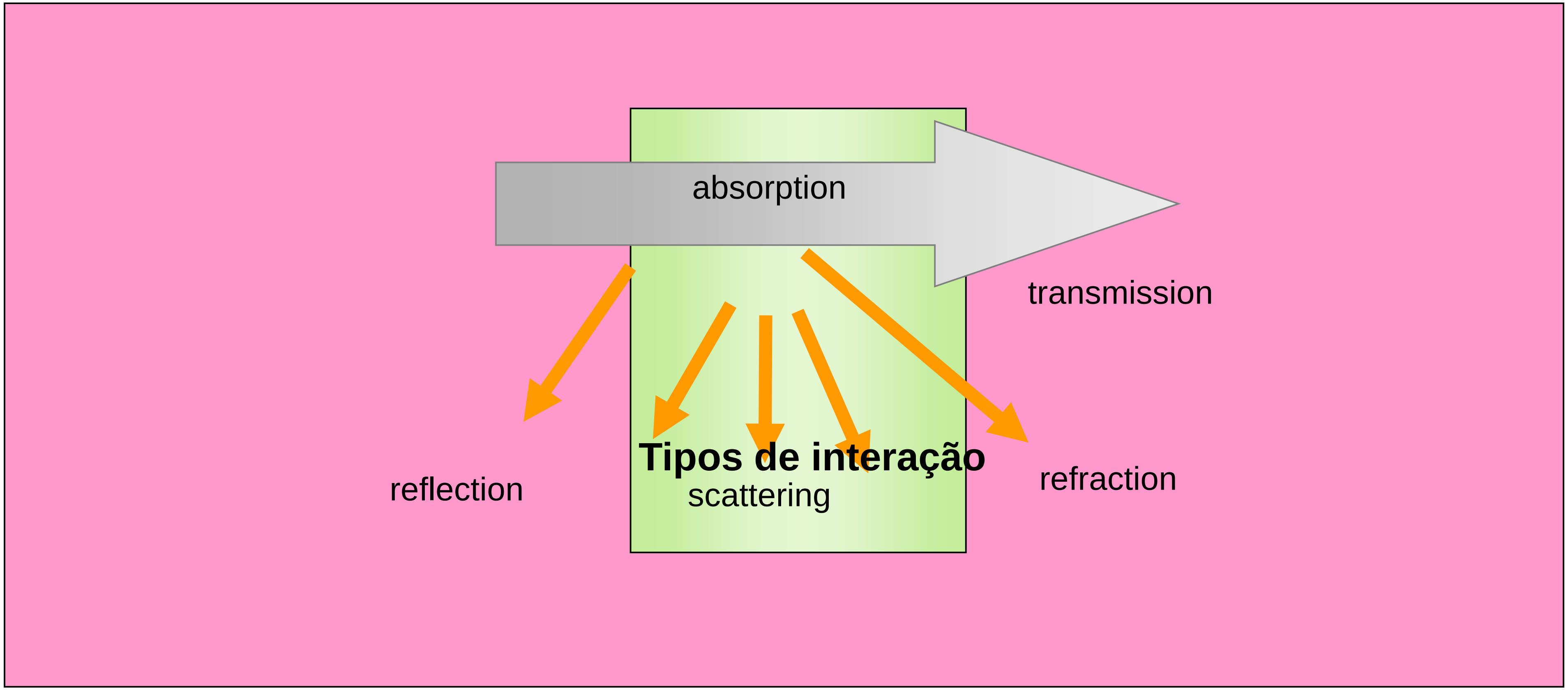
Fórmulas-chave

- E = hν
- h = 6,626 x 10^{-34} J s
- ν = frequência em Hz; E = energia

- λ = c/ν
- c = 3,0 x 10^{8} m/s
- λ = comprimento de onda
- ν = frequência em Hz

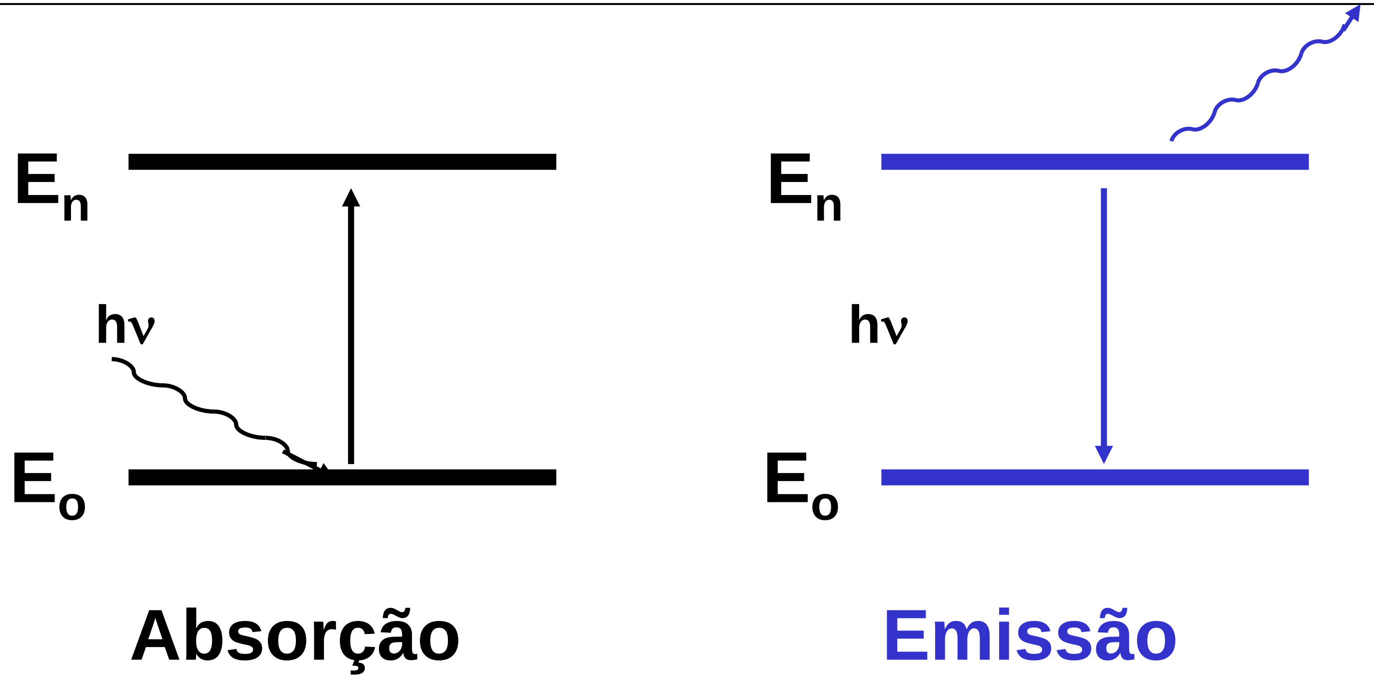

raios-X: excitação dos elétrons internos
UV: excitação dos elétrons de valência
IV: vibrações moleculares
ondas de rádio: estados de spin nuclear (em um campo magnético)
Highest energy
Lowest energy
Wavelength (nm)
10^-2
10^0
10^2
10^4
10^6
10^8
10^10
10^12
Gamma ray
X-ray
Ultra-violet
Visible
Infrared
Microwave
Radio frequency
10^20
10^18
10^16
10^14
10^12
10^10
10^8
10^6
10^4
Frequency (s^-1)
400
500
600
700
750 nm
Visible region

Interação da radiação eletromagnética com a matéria



- revelam diferentes propriedades da matéria
- o emprego de radiações de diferentes freqüências permite a obtenção de diferentes tipos de informação

- Absorção - EM energy transferred to absorbing molecule (transition from low energy to high energy state)
- Emissão - EM energy transferred from emitting molecule to space (transition from high energy to low energy state)



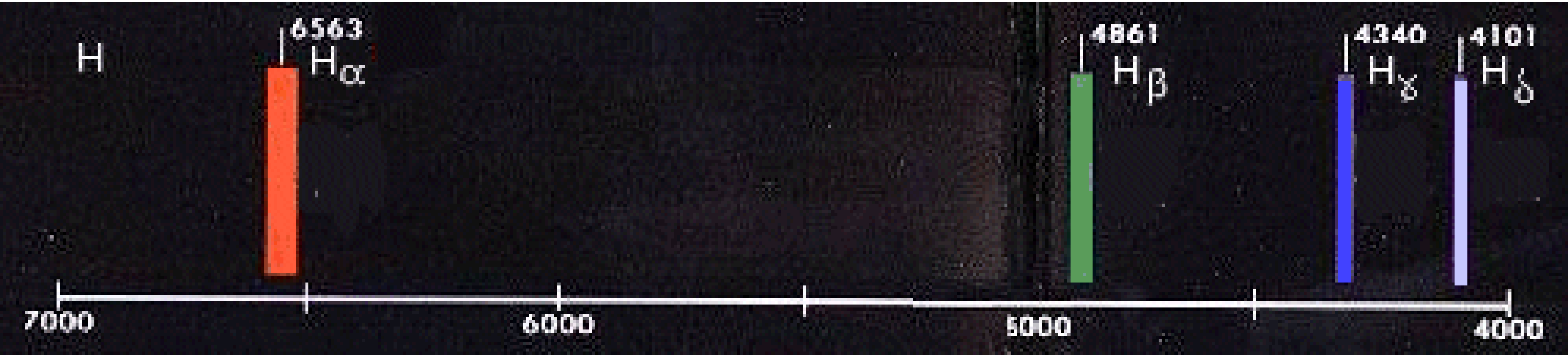
Redirecionamento da luz sem transferência de energia

Espalhamento (scattering)

Reflexão

Refração

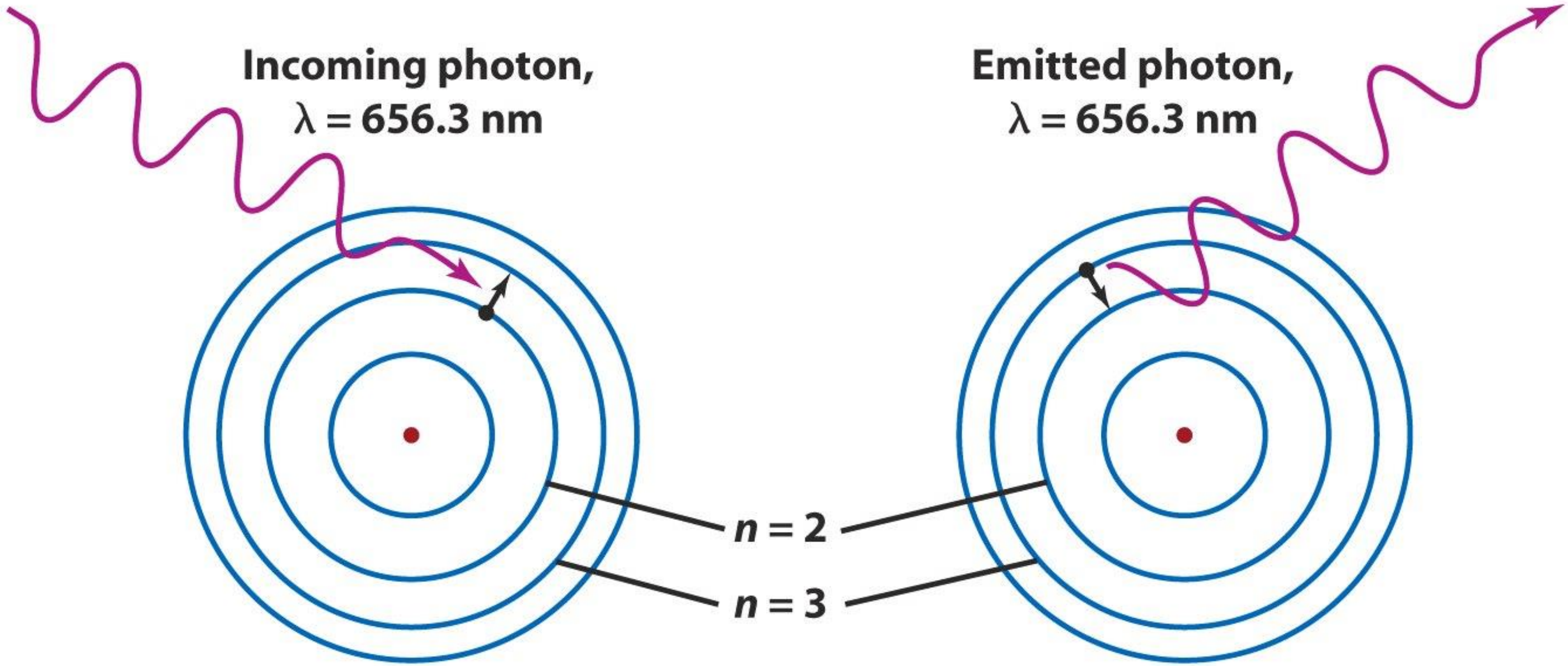
Espectros atômicos



Freqüências discretas: linhas espectrais

COR	NOME	λ (em Angstroms)	n
VERMELHO	H_α	6563	3
VERDE	H_β	4858	4
AZUL	H_γ	4340	5
VIOLETA	H_δ	4101	6

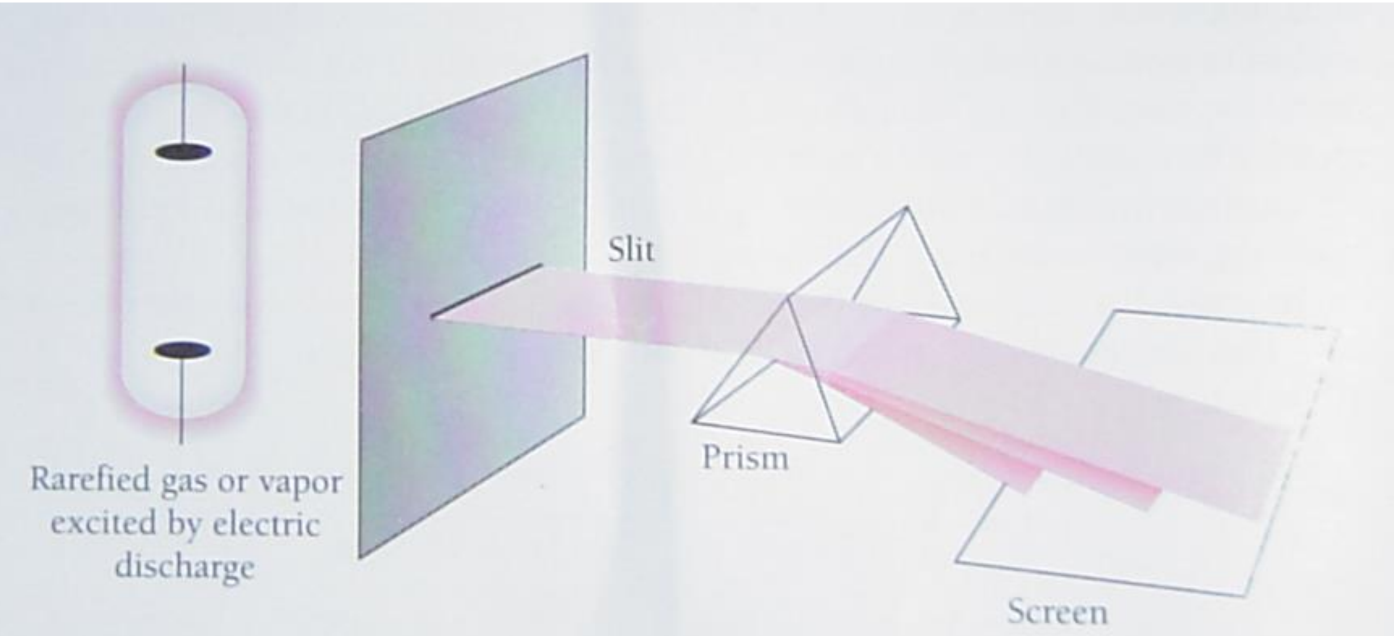
Hydrogen alpha (Hα) line

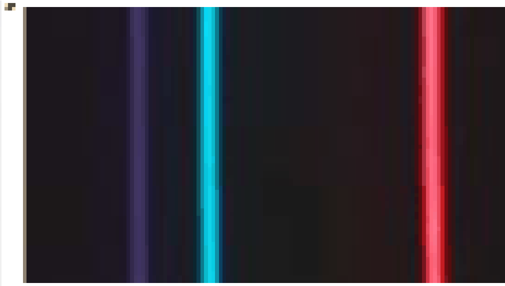


(a) Atom absorbs a 656.3-nm photon; absorbed energy causes electron to jump from the $n = 2$ orbit up to the $n = 3$ orbit

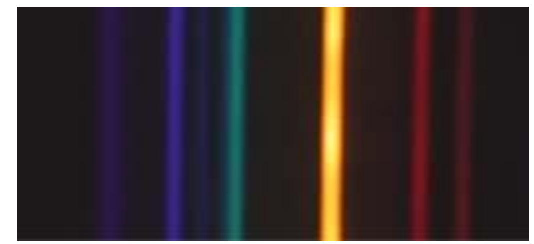
(b) Electron falls from the $n = 3$ orbit to the $n = 2$ orbit; energy lost by atom goes into emitting a 656.3-nm photon

atomic spectra (emission)





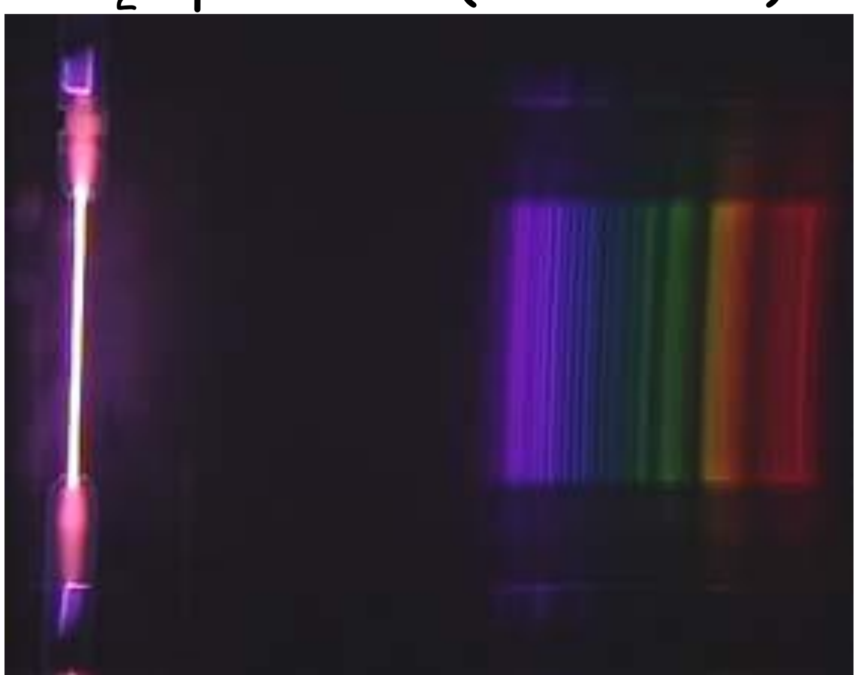
H_2



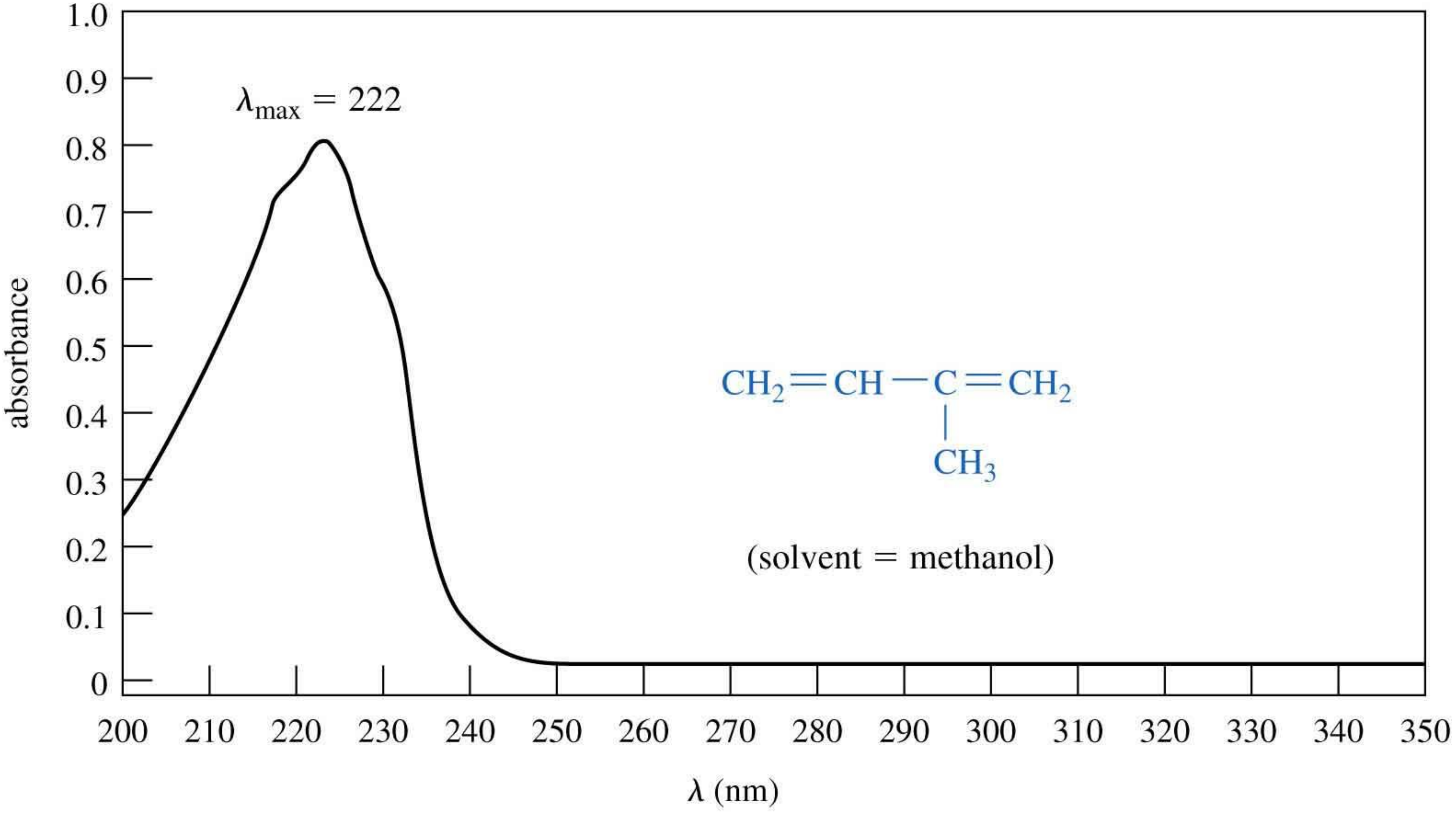
He

Ne

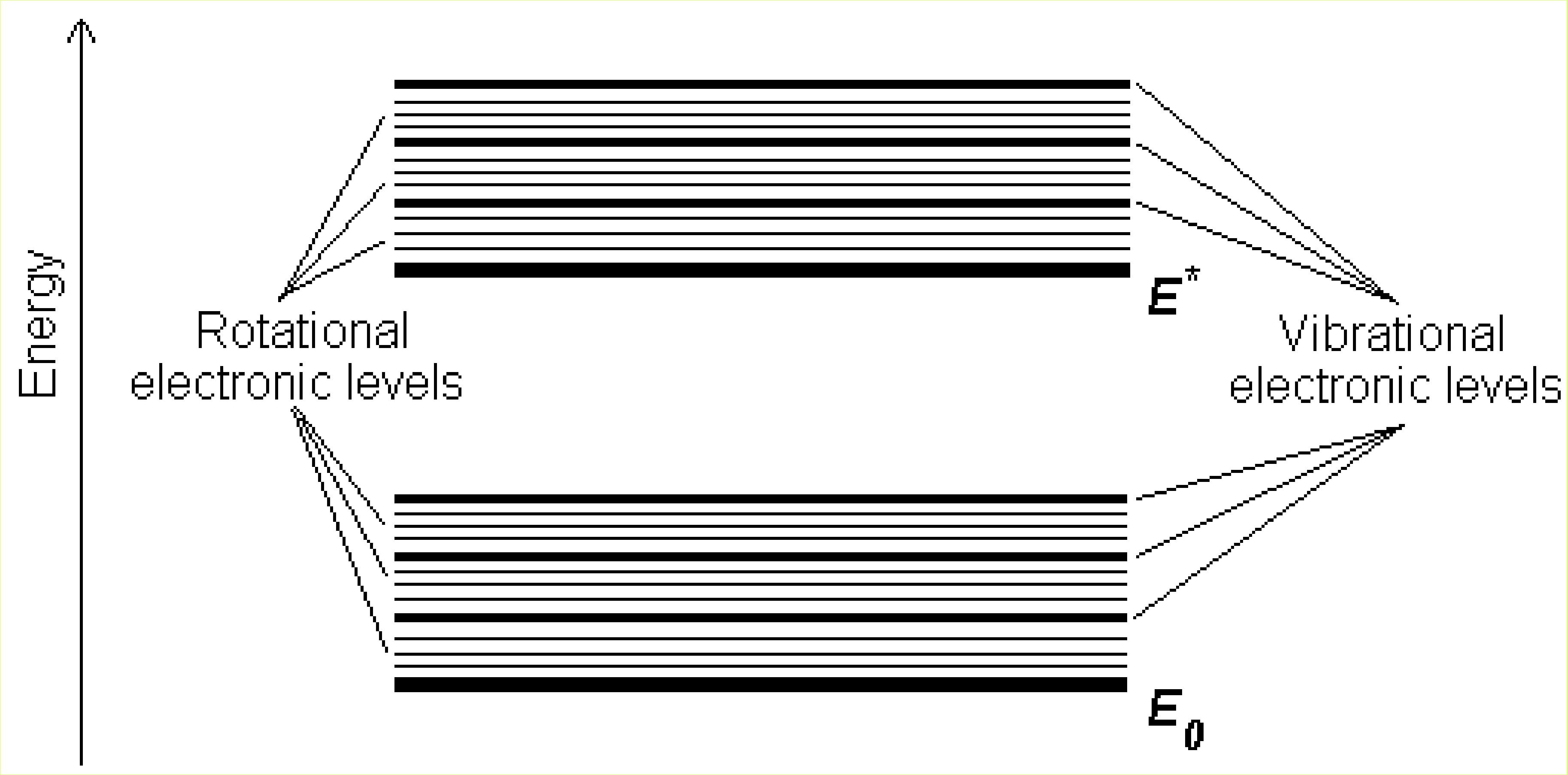
N_2 spectrum (with tube)



UV Spectrum of Isoprene



A cada nível de energia eletrônica (configuração) estão associados vários níveis de energia vibracional.



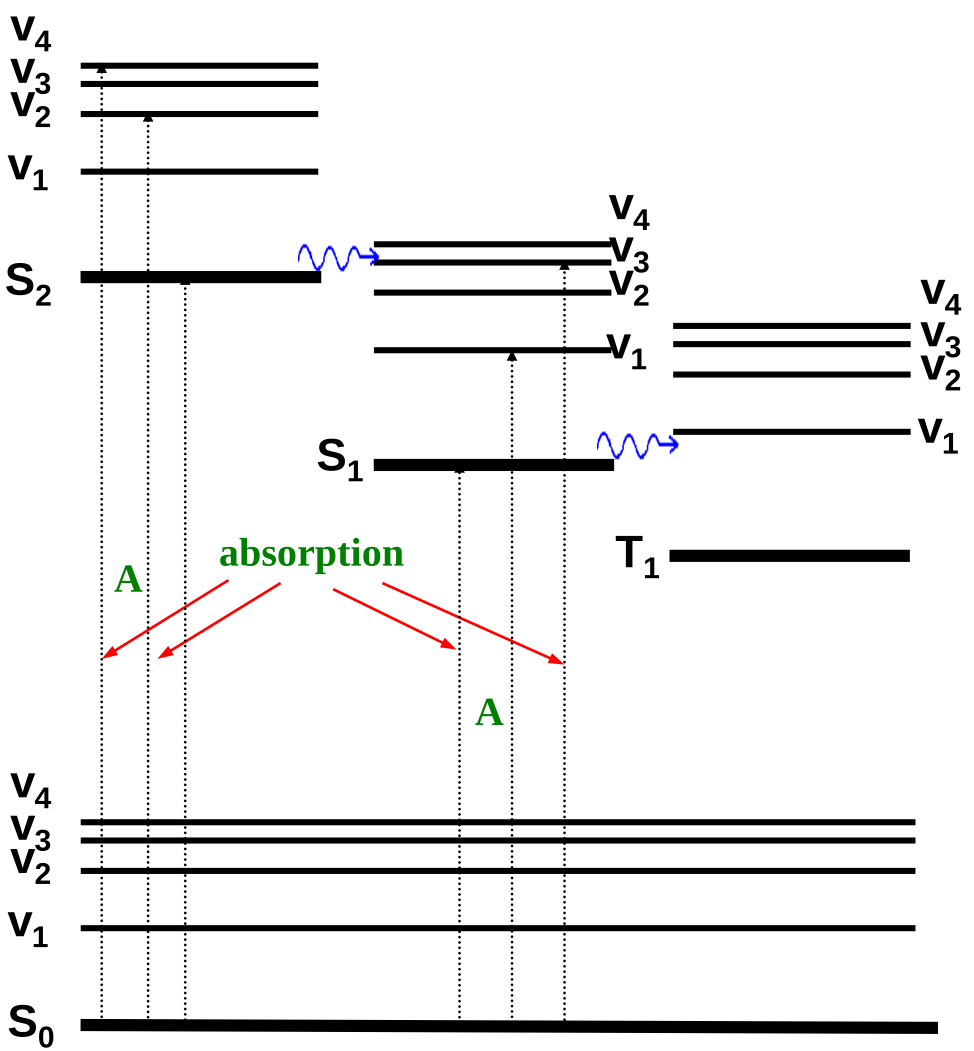
Molecular Spectra

- **Excitation of a molecule** (Process A)

to excite a molecule from **$S_{0,v1}$ to $S_{2,v2}$**, e.m.r with wavenumber *v'* must be used

The values of energy levels vary with the (molecule of) substance.

$$hcv' = E_{S_{2,v2}} - E_{S_{0,v1}}$$



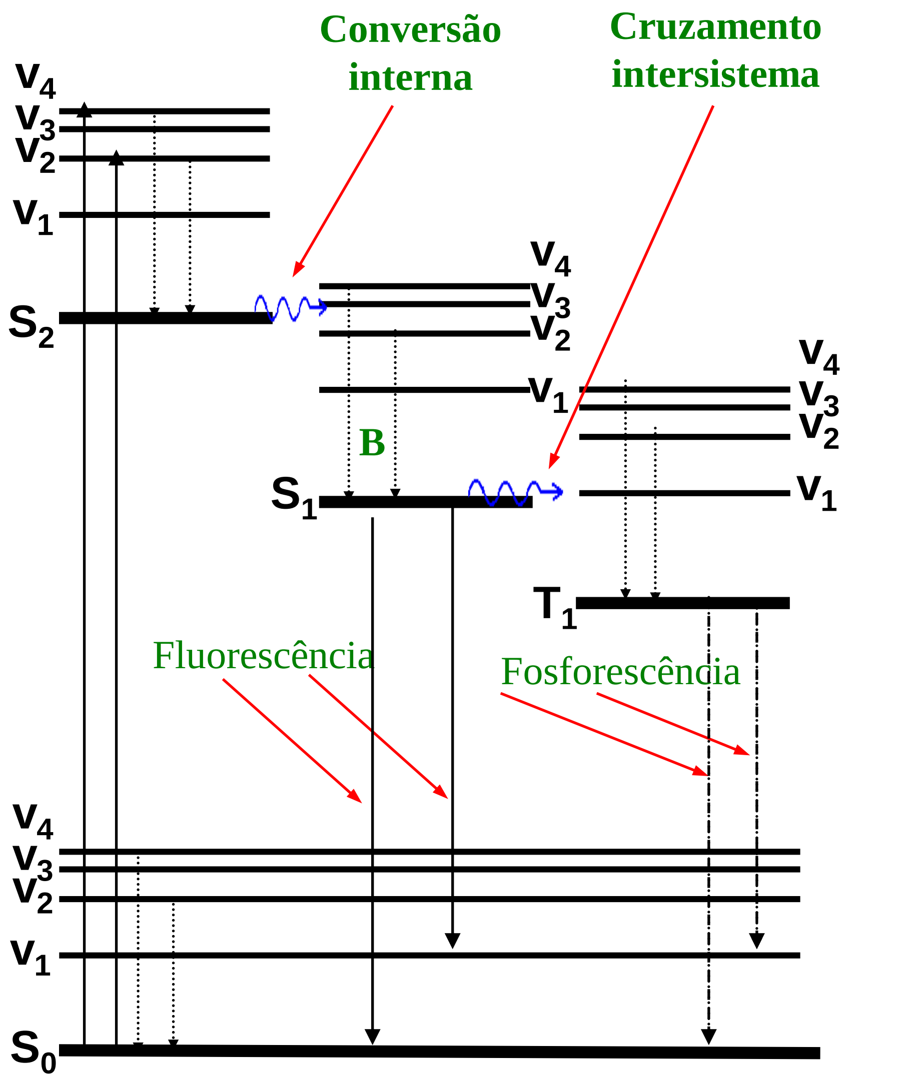
Molecular Spectra: Energy change of excited molecules

Energia dissipada como calor

- **–when changing from a sub-state to the parental state occurs within the same state**
- **– transfer its remaining E to other chemical species by collision**
- **– undergoing *internal transition* within the same mode of the excited state**
- **– undergoing *intersystem crossing* to a triplet sublevel of the excited state**

–*Fluorescence* - emitting photons when falling back to the ground state

–*Phosphorescence* - Radiating E from triplet to ground state



Jablonsky diagram

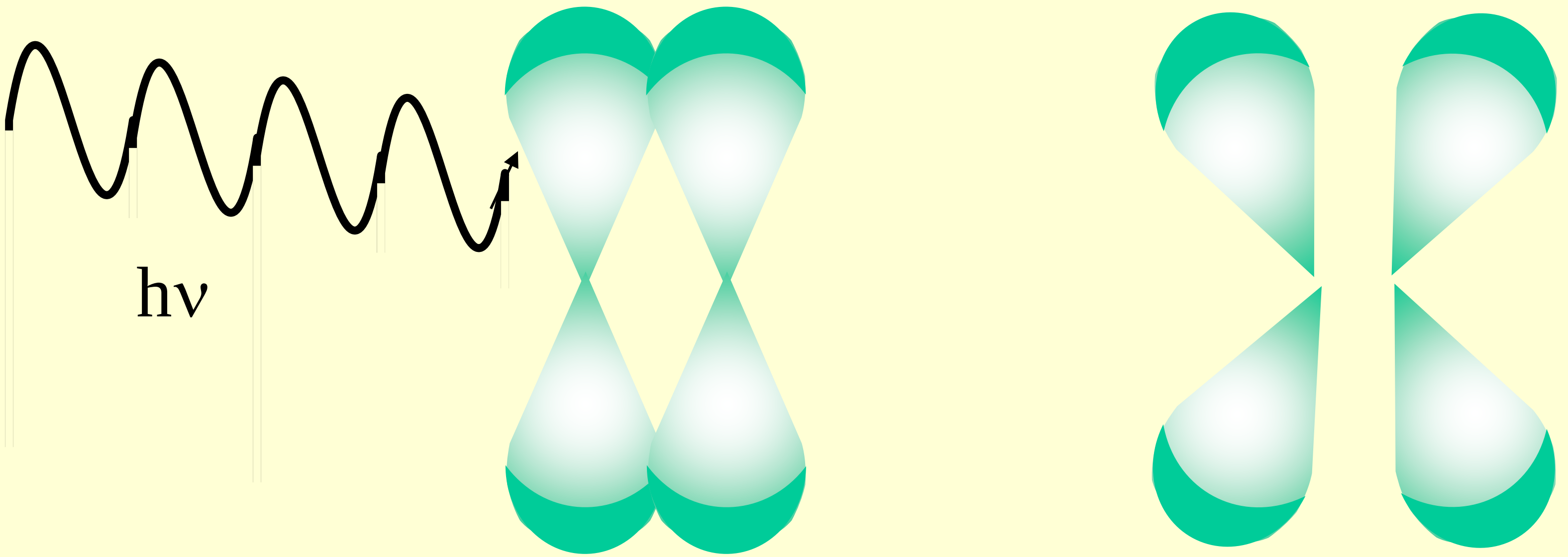
Atomic Spectra & Molecular Spectra

- **Comparison of atomic and molecular spectra**

	Atomic spectra	Molecular spectra
Adsorption spectra	Yes	Yes
Emission spectra	Yes	Yes
Energy required for excitation	high	low
Change of energy level related to	change of e^-'s orbital	change of vibration states
Spectral region	UV	mainly visible
Relative complexity of spectra	simple	complex

- **Quantum mechanics is the basis of atomic & molecular spectra**
  - The transitional, rotational and vibrational modes of motion of objects of atomic / molecular level are well-explained.

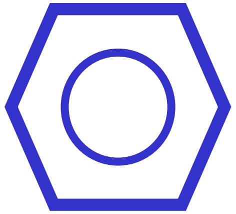
Atividade no UV



π   π*

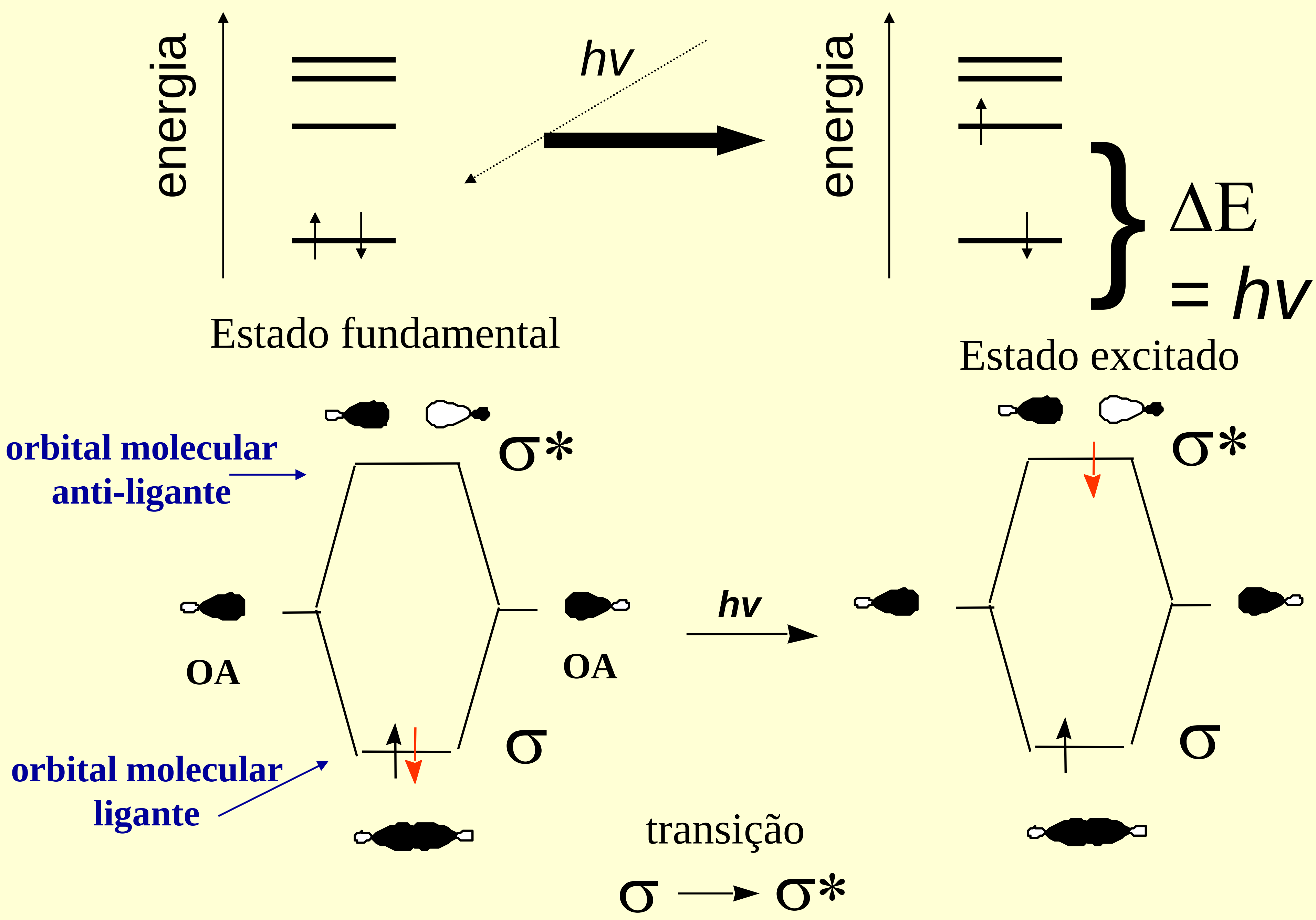
UV Activity

- Needs chromophores
- C=C, C=O, N=N, NO_2,



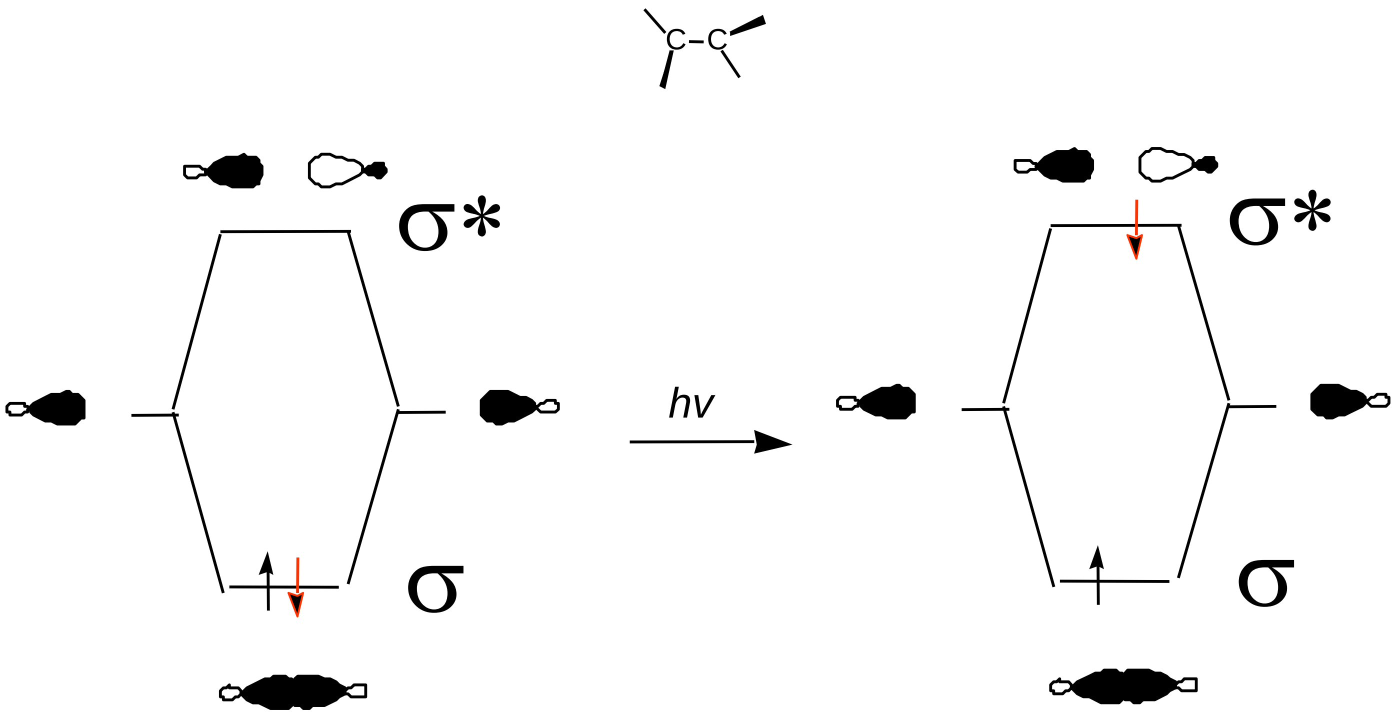
- π -> π* and n -> π* transitions
- napthoquinones, anthocyanins
- Non-absorbers…
  - long chain aliphatics
  - alcohols, ethers, non-conjugated mols.

Os níveis eletrônicos de energia das moléculas são quantizados

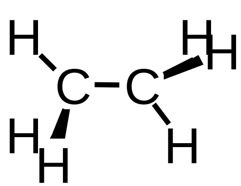


Ultraviolet Spectroscopy

- 200-400 nm photons excite electrons from a π bonding orbital to a π^* antibonding orbital.
- Conjugated dienes have MO's that are closer in energy.
- A compound that has a longer chain of conjugated double bonds absorbs light at a longer wavelength.

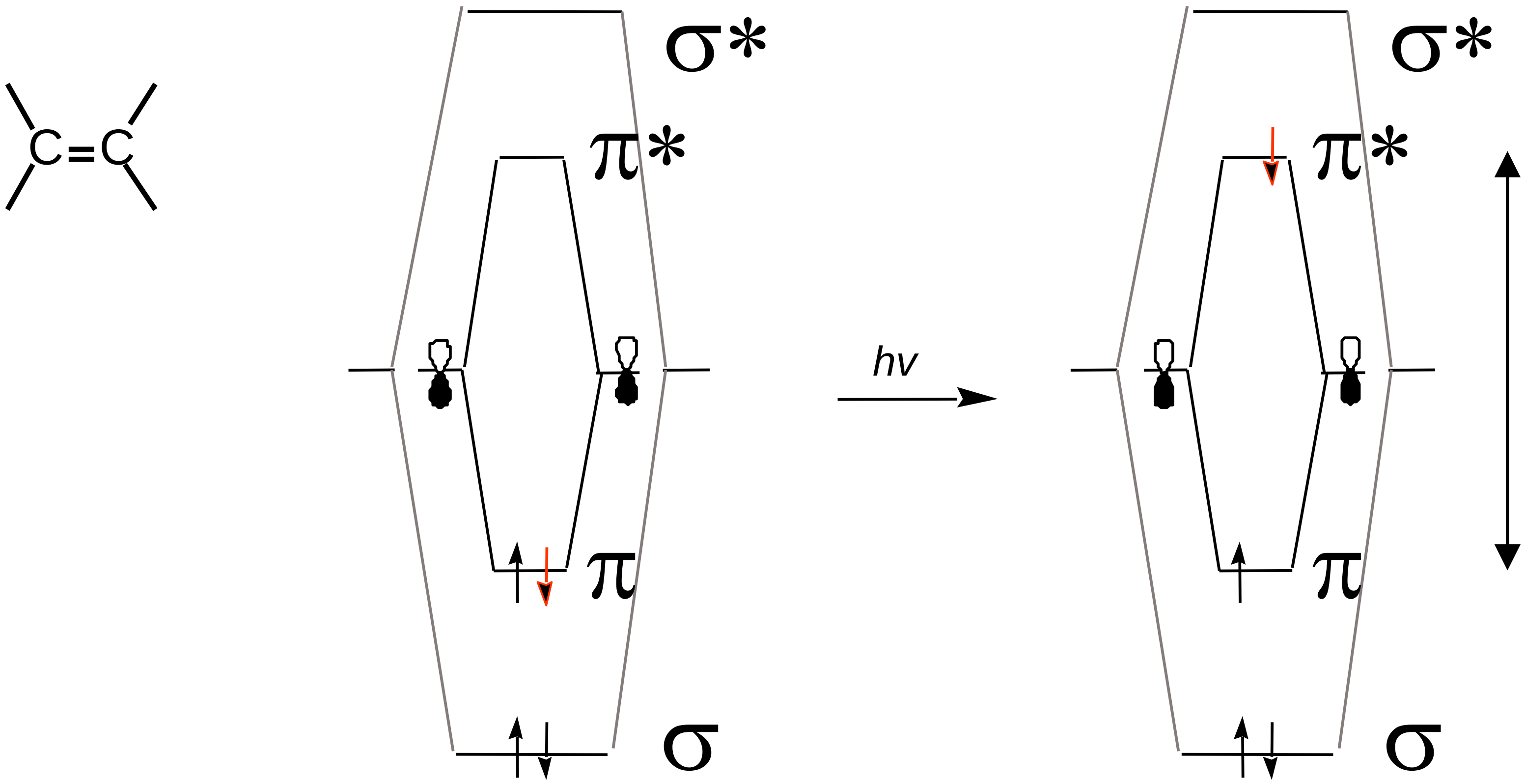


$\sigma \longrightarrow \sigma^*$



λ_{max} = 135 nm   (a high energy transition)

Absorptions having λ_{max} < 200 nm are difficult to observe because everything (including quartz glass and air) absorbs in this spectral region.

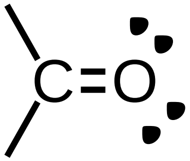


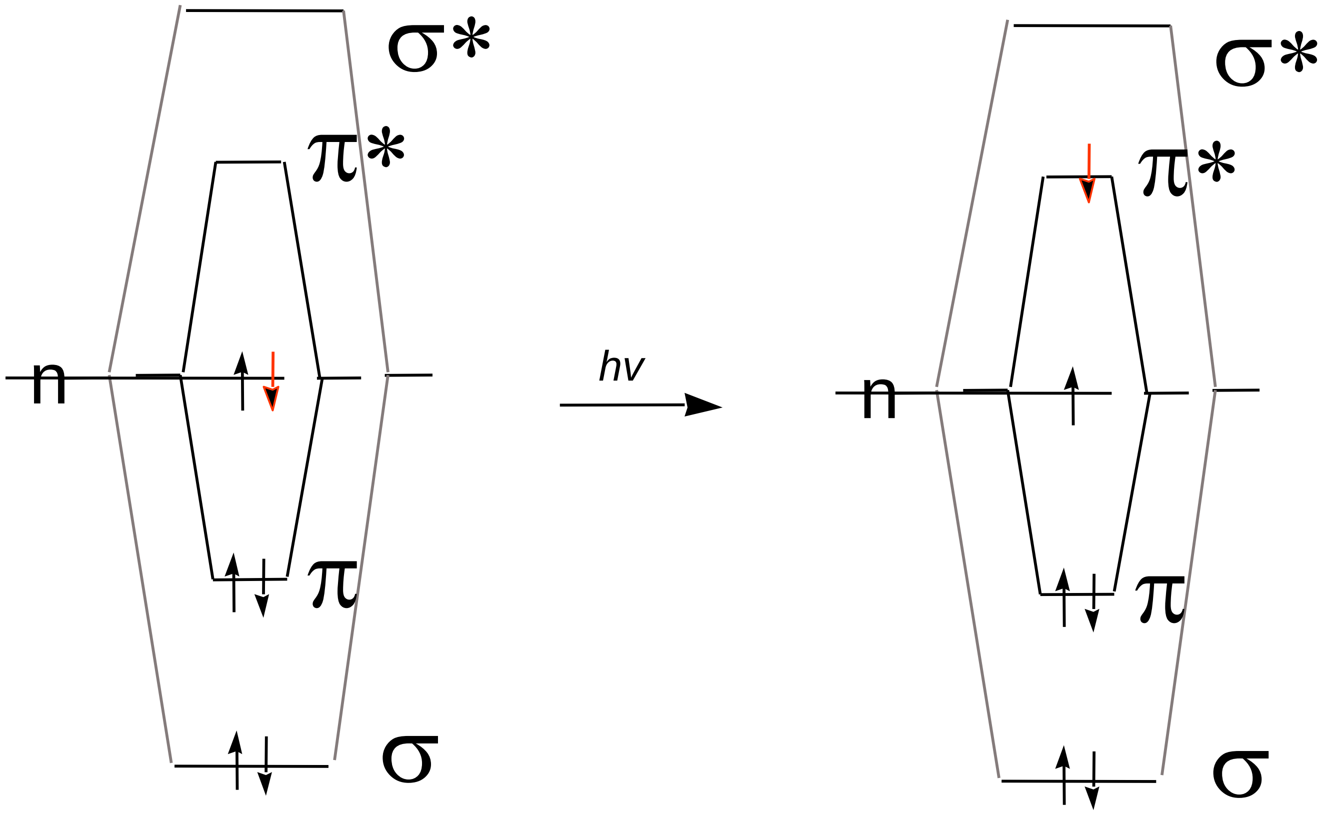
$\Delta E = h\nu$
$= hc/\lambda$

$\pi \longrightarrow \pi^*$

Example: ethylene absorbs at longer wavelengths:

λ_{max} = 165 nm ε= 10,000



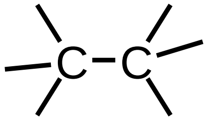


n $\longrightarrow$ π*

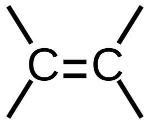
The n to pi* transition is at even lower wavelengths but is not as strong as pi to pi* transitions. It is said to be “forbidden.”

Acetone: n–σ* λ_{max} = 188 nm ; ε= 1860

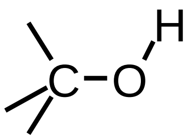
n–π* λ_{max} = 279 nm ; ε= 15



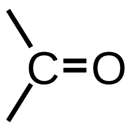
σ –> σ* 135 nm



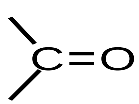
π –> π* 165 nm

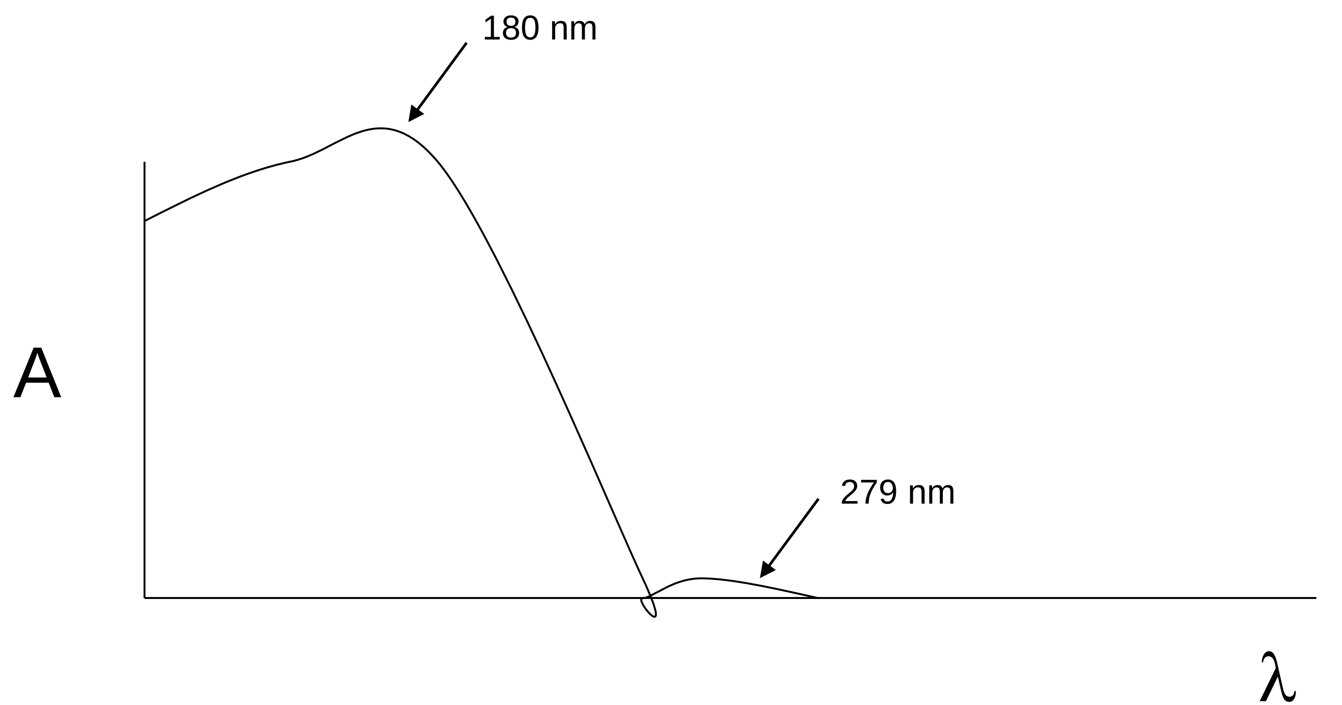


n –> σ* 183 nm weak

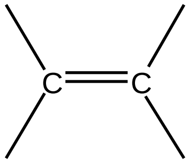


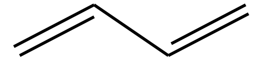
π –> π* 150 nm
n –> σ* 188 nm
n –> π* 279 nm weak

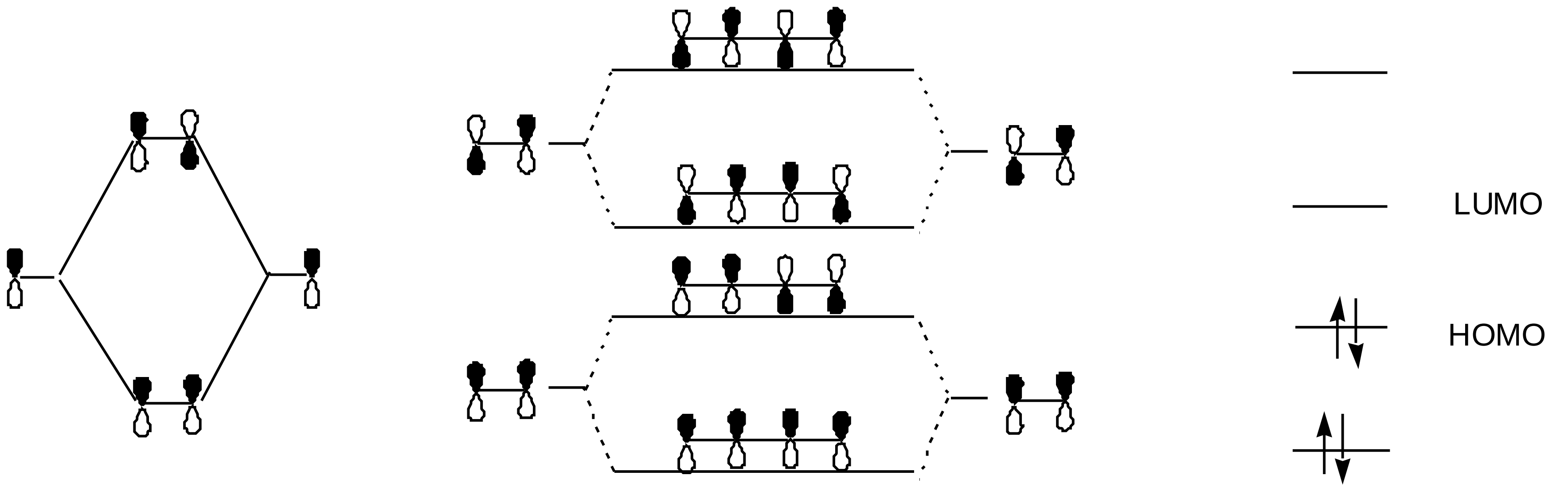




Conjugated systems:







Preferred transition is between Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO).

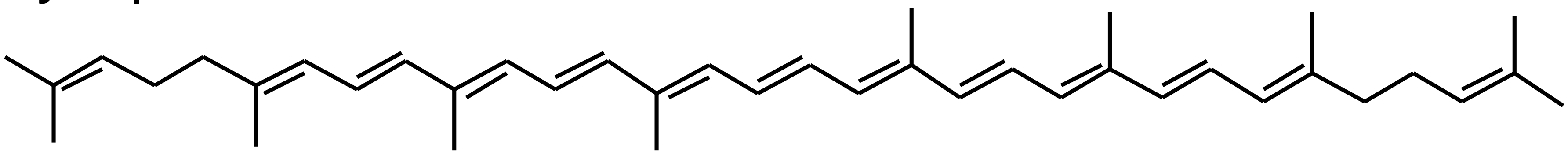
Note: Additional conjugation (double bonds) lowers the HOMO-LUMO energy gap:

Example:

1,3 butadiene: λ_{max} = 217 nm ; ε= 21,000

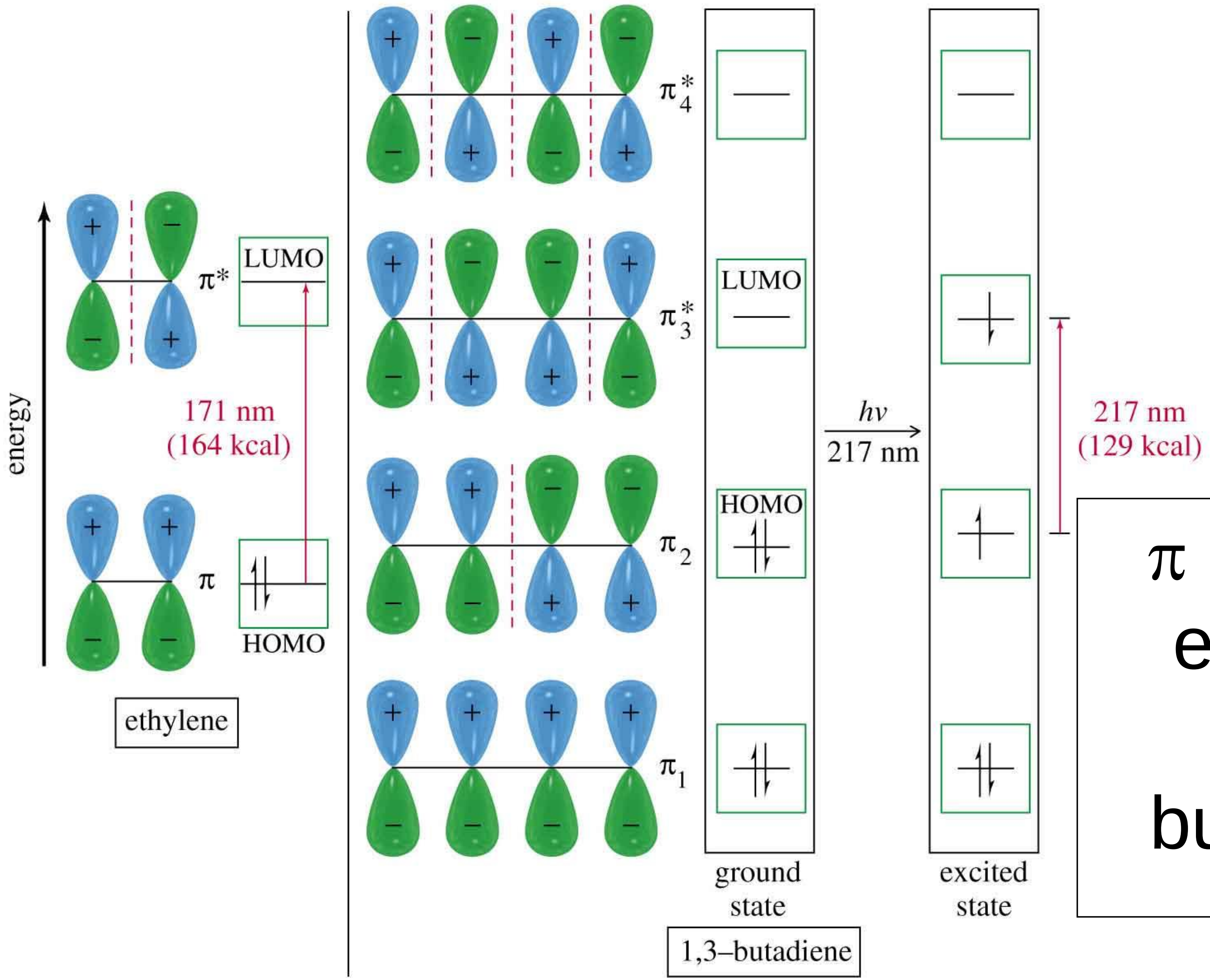
1,3,5-hexatriene λ_{max} = 258 nm ; ε= 35,000

Lycopene:



λ_{max} = 114 + 5(8) + 11*(48.0-1.7*11) = 476 nm

λ_{max}(Actual) = 474.

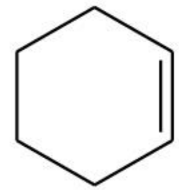


π → π* for ethylene and butadiene

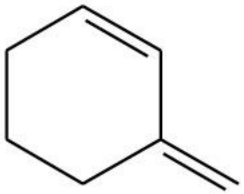
=>

TABLE 15-2 Ultraviolet Absorption Maxima of Some Representative Molecules

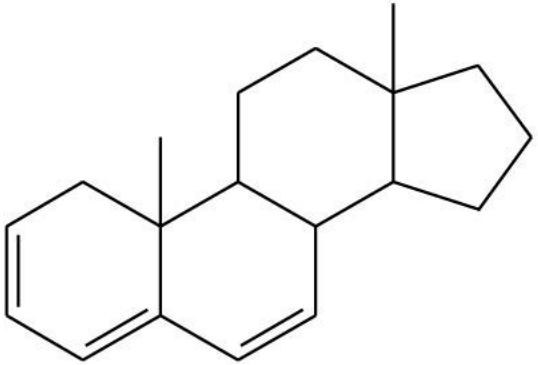
Isolated

	$CH_2{=}CH_2$		
	ethylene	cyclohexene	1,4-hexadiene
λ_{max}:	171 nm	182 nm	180 nm

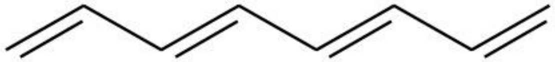
Conjugated dienes

				
	1,3-butadiene	2,4-hexadiene	1,3-cyclohexadiene	3-methylenecyclohexene
λ_{max}:	217 nm	227 nm	256 nm	232 nm

Conjugated trienes

		
	1,3,5-hexatriene	a steroid triene
λ_{max}:	258 nm	304 nm

Conjugated tetraene


1,3,5,7-octatetraene
290 nm

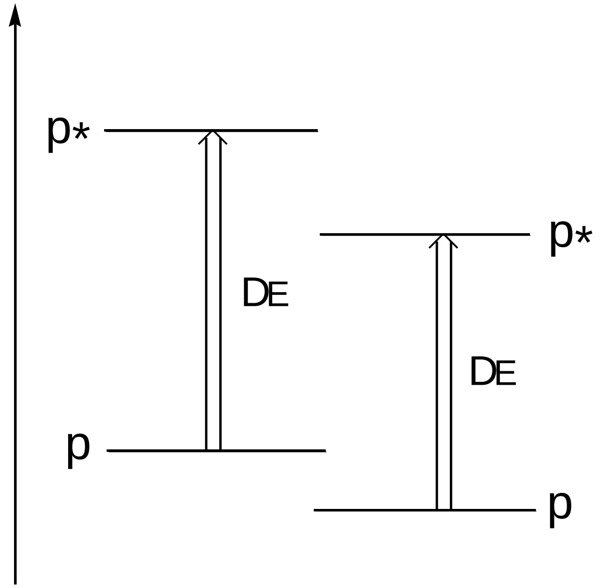
Aumento da polaridade do solvente:

deslocamento do máximo da banda de absorção para o vermelho (isto é para comprimemntos de onda maiores): energias menores.

Modelo:

π* é mais estabilizado do que π pelo aumento da polaridade do solvente.

Conseqüência:



Aumento da polaridade do solvente:

deslocamento do máximo da banda de absorção π, π^* para o vermelho (isto é para comprimentos de onda maiores): *energias menores*.

deslocamento do máximo da banda de absorção n, π^* para o azul (isto é para comprimentos de onda menores): *energias maiores*.

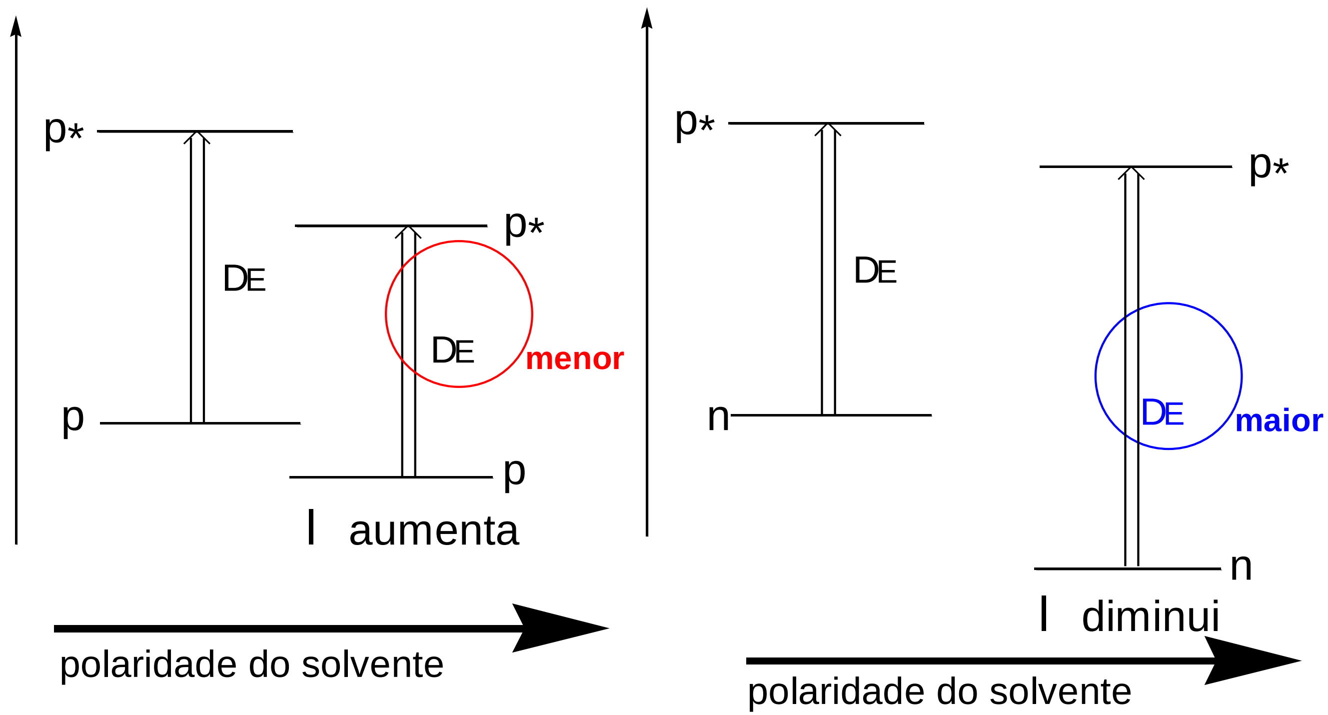
Modelo: como

π^* é mais estabilizado do que π

n é mais estabilizado do que π^*

transição $\pi \rightarrow \pi^*$ — transição n $\rightarrow \pi^*$

deslocamento batocrômico — deslocamento hipsocrômico



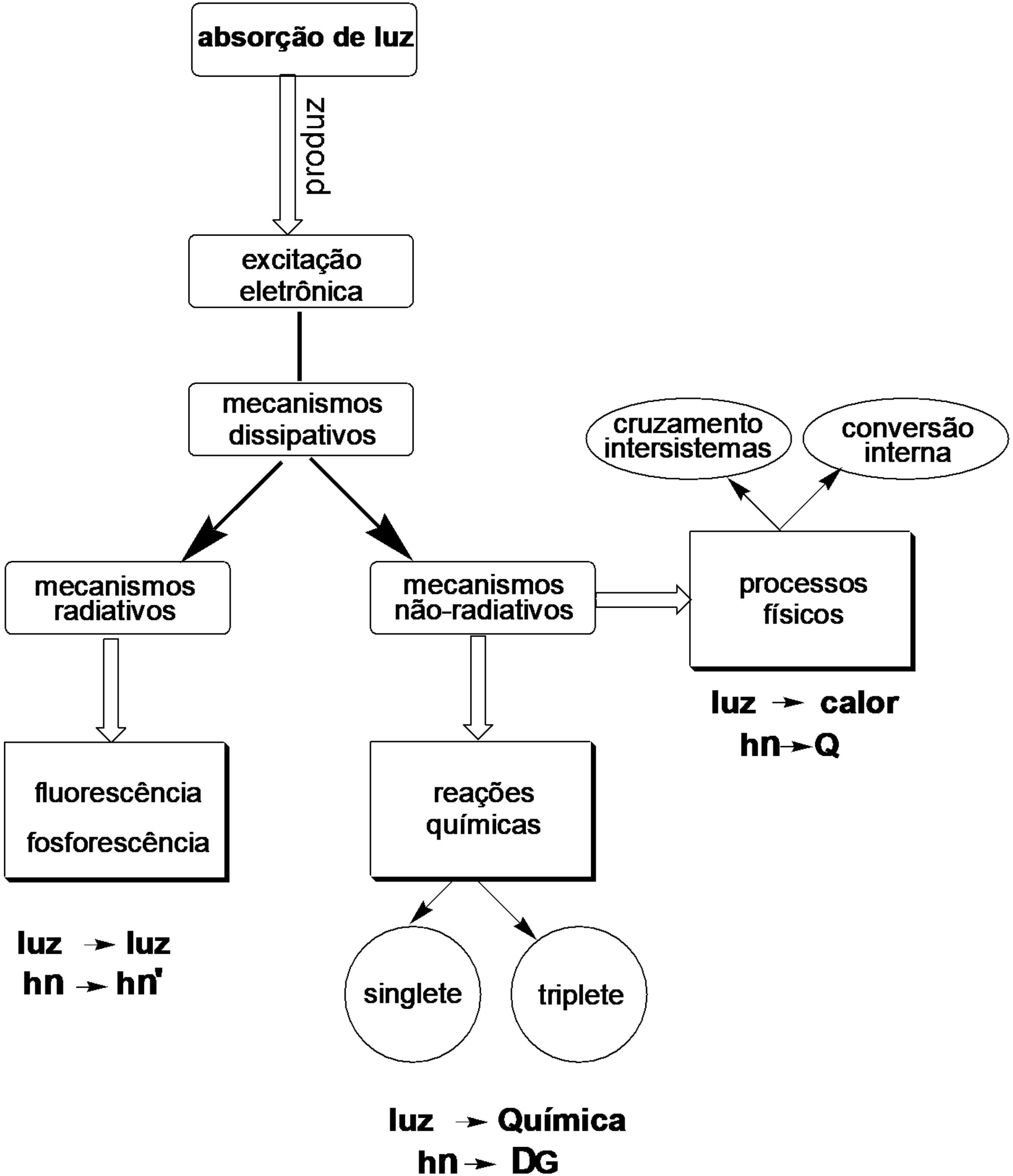
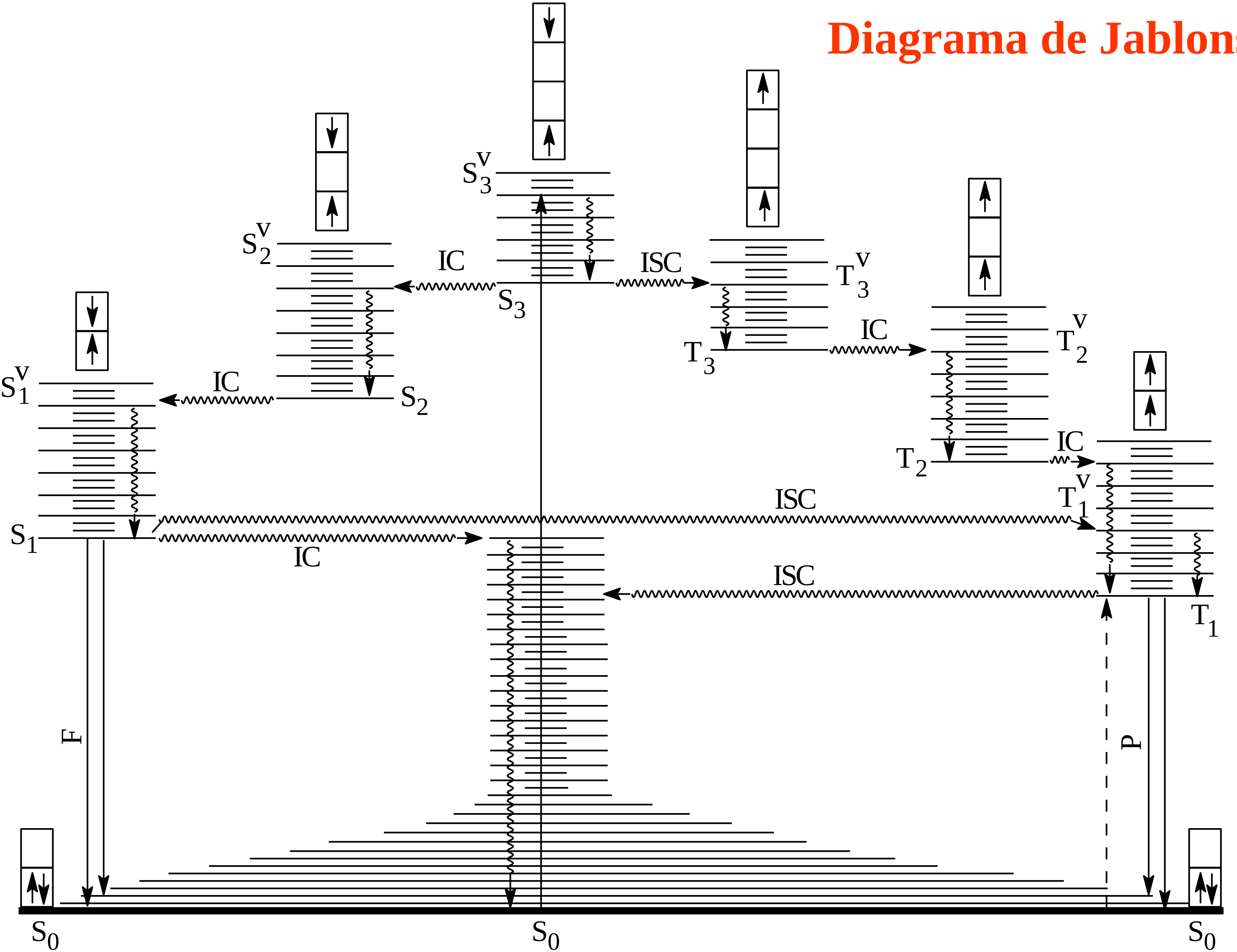

absorção de luz
produz
excitação eletrônica
mecanismos dissipativos
mecanismos radiativos
mecanismos não-radiativos
processos físicos
cruzamento intersistemas
conversão interna
fluorescência
fosforescência
reações químicas
singlete
triplete
luz → calor
hn→Q
luz → luz
hn → hn'
luz → Química
hn → DG

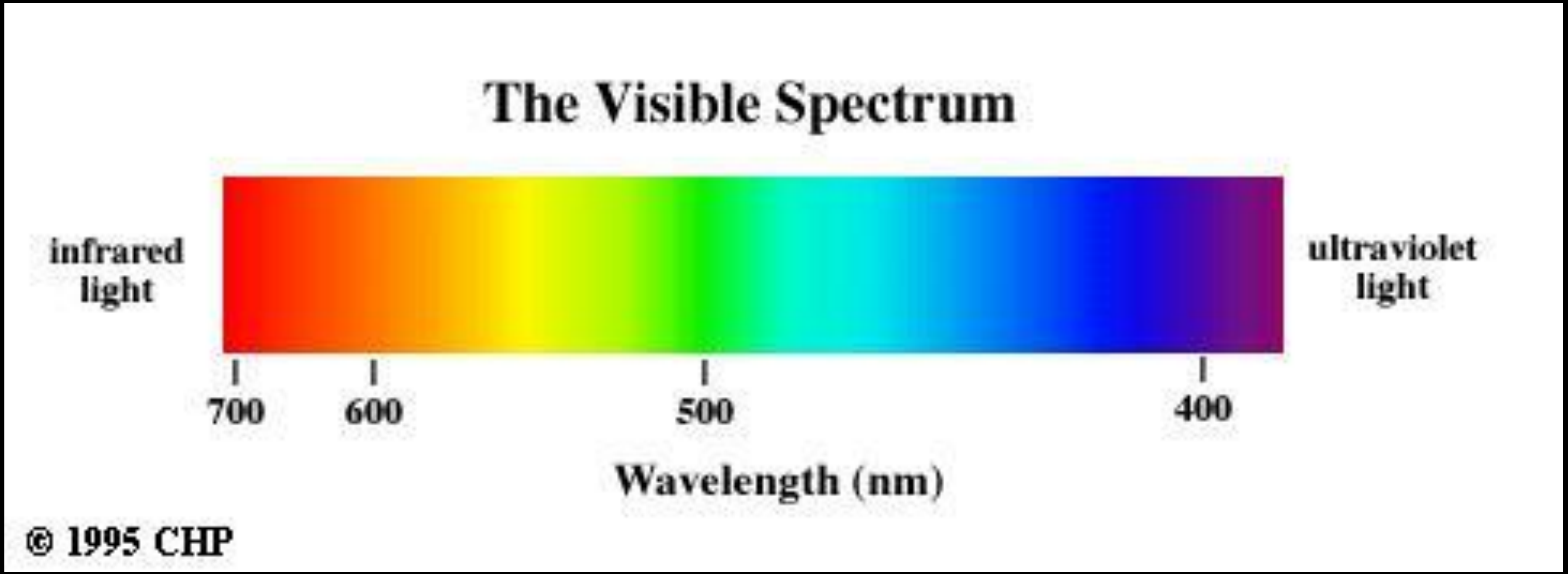
Tabela 1: Energia de um mol de fóton, nas regiões do visível e do ultra-violeta:

	$\frac{\lambda}{nm}$	$\frac{\nu}{cm^{-1}}$	$\frac{E}{kJ}$	$\frac{E}{kcal mol^{-1}}$	$\frac{E}{eV}$
Ultravioleta	200	50000	598	142,9	6,20
Violeta	400	25000	299	71,4	3,10
Azul	450	22222	266	63,5	2,76
Verde	590	20000	239	57,1	2,48
Amarelo	570	17544	209	49,9	2,16
Laranja	500	16949	203	48,5	2,0
Vermelho	620	16129	192	45,9	2,10
	750	13333	159	38,0	1,60

Diagrama de Jablonski



Luz Visível

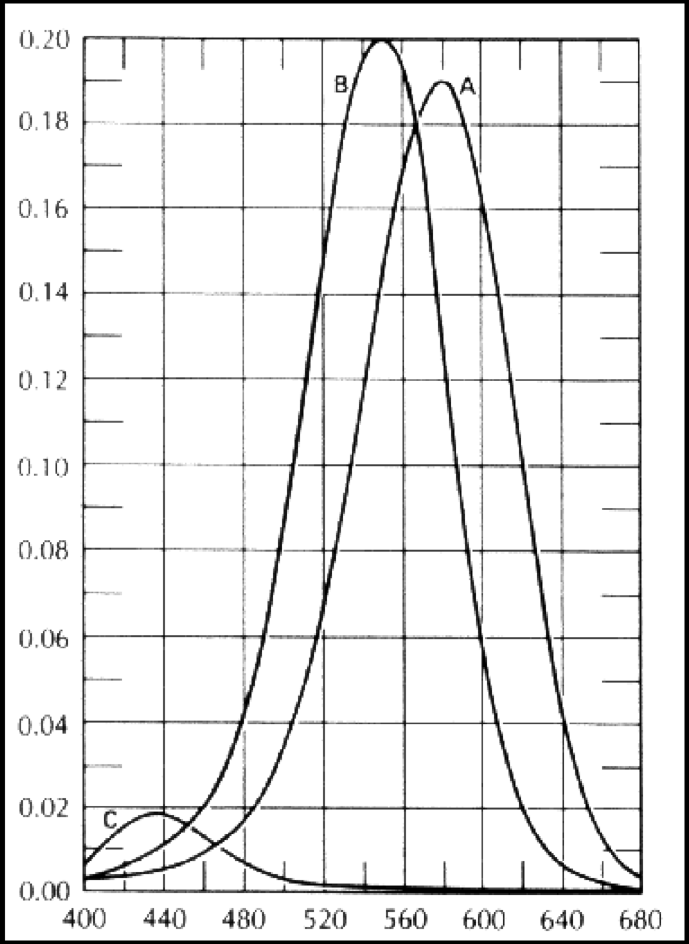


The Visible Spectrum
infrared light
ultraviolet light
700
600
500
400
Wavelength (nm)
© 1995 CHP

Luz Visível

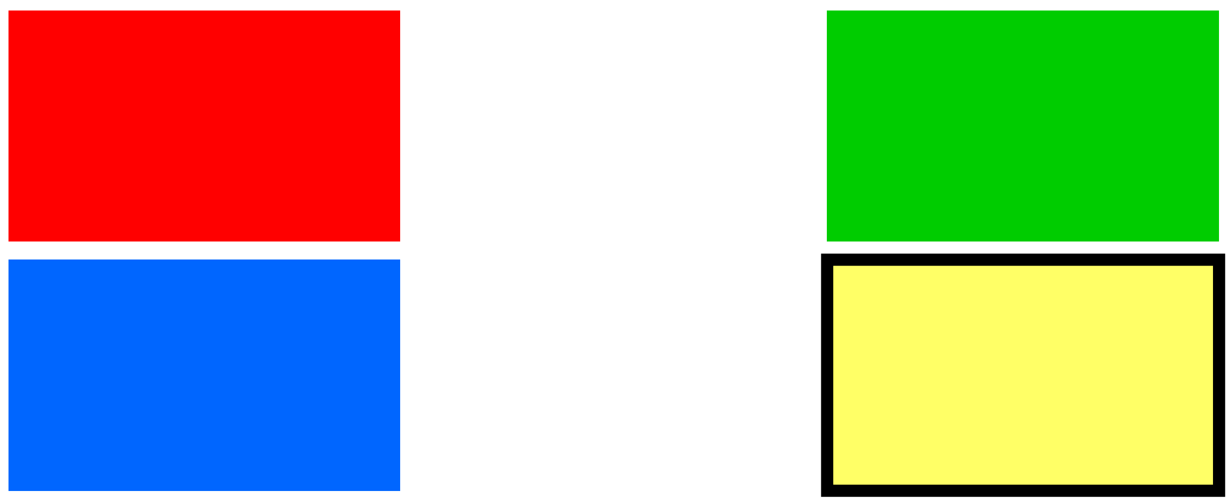
Red	**R**	**700 nm**
Orange	**O**	**650 nm**
Yellow	**Y**	**600 nm**
Green	**G**	**550 nm**
Blue	**B**	**500 nm**
Indigo	**I**	**450 nm**
Violet	**V**	**400 nm**

Absorção na região do visível: cor

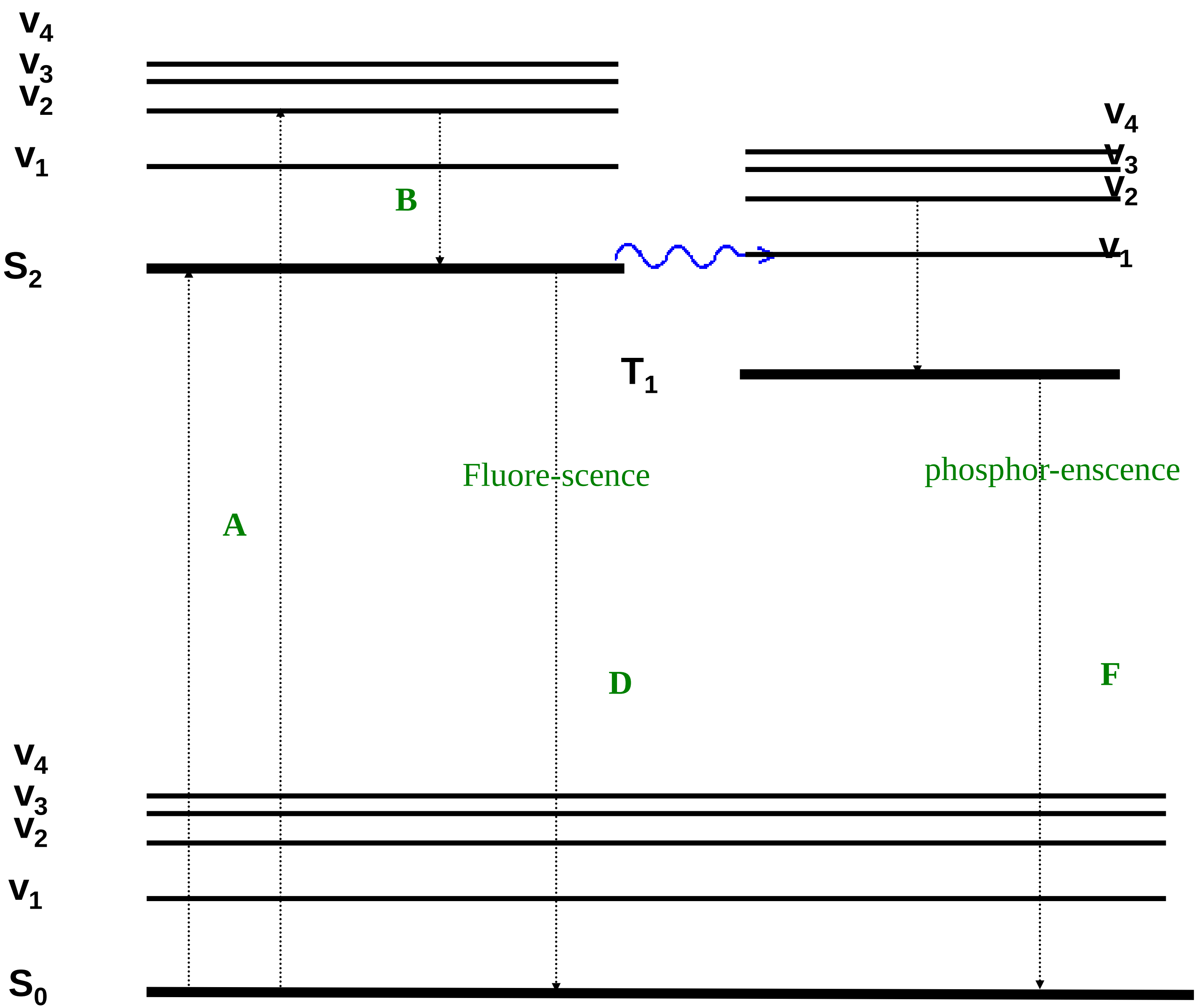


Complementary Colours

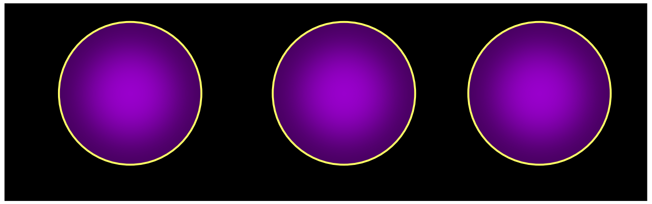
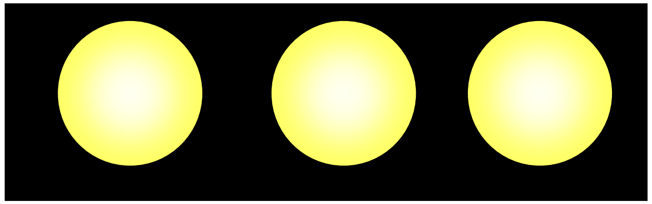
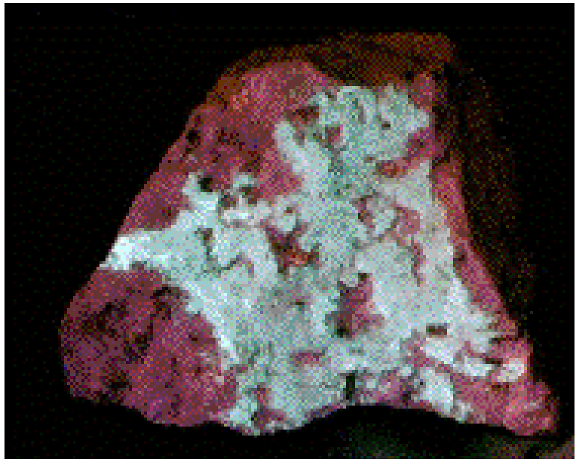
Absorbed **Observed**



Espectros de emissão



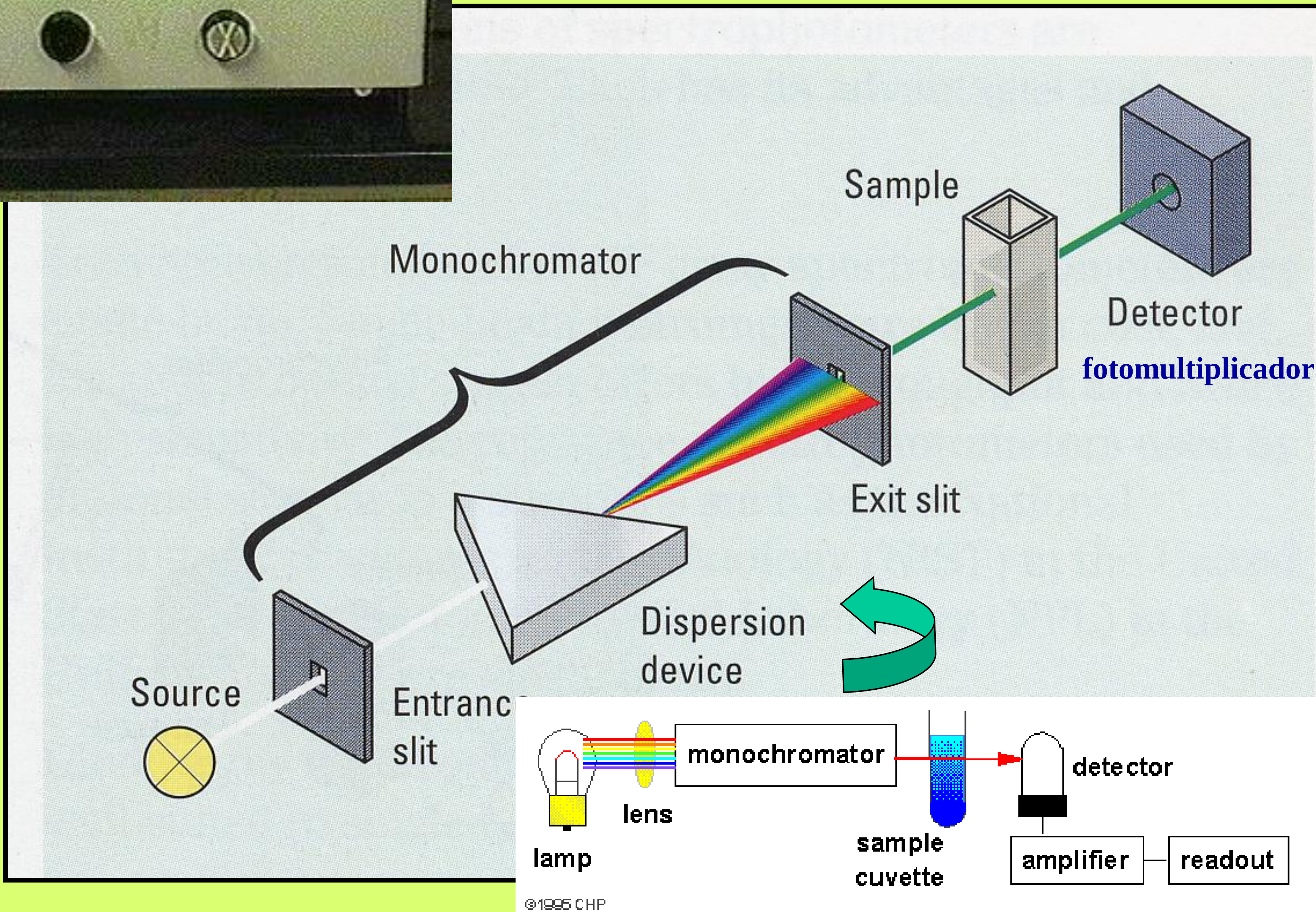
Fluorescence (Emission)

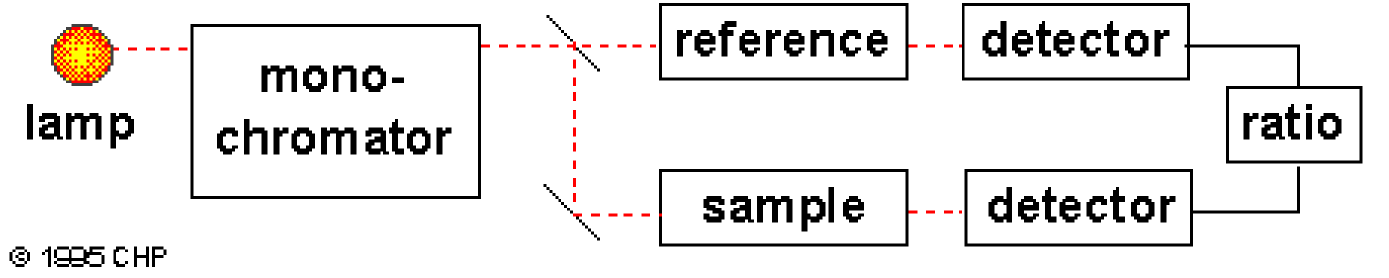

Obtaining a UV Spectrum

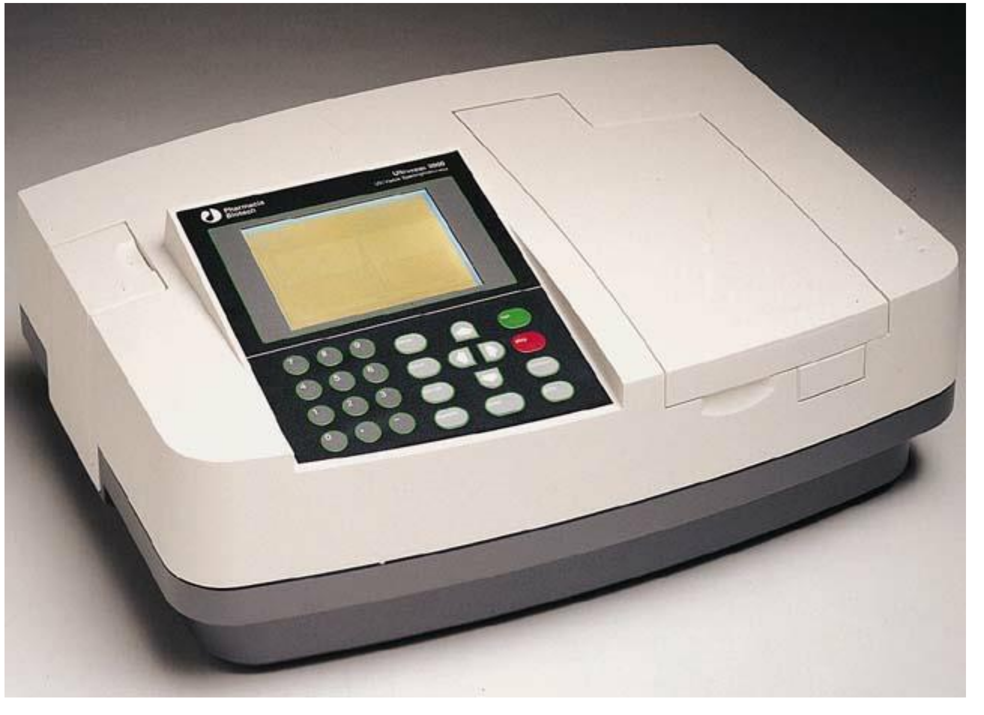
- The spectrometer measures the intensity of a reference beam through solvent only ($\boldsymbol{I}_r$) and the intensity of a beam through a solution of the sample ($\boldsymbol{I}_s$).
- Absorbance is the log of the ratio $\frac{I_s}{I_r}$
- Graph is absorbance vs. wavelength.

Esquema de um espectrômetro de UV-vis convencional

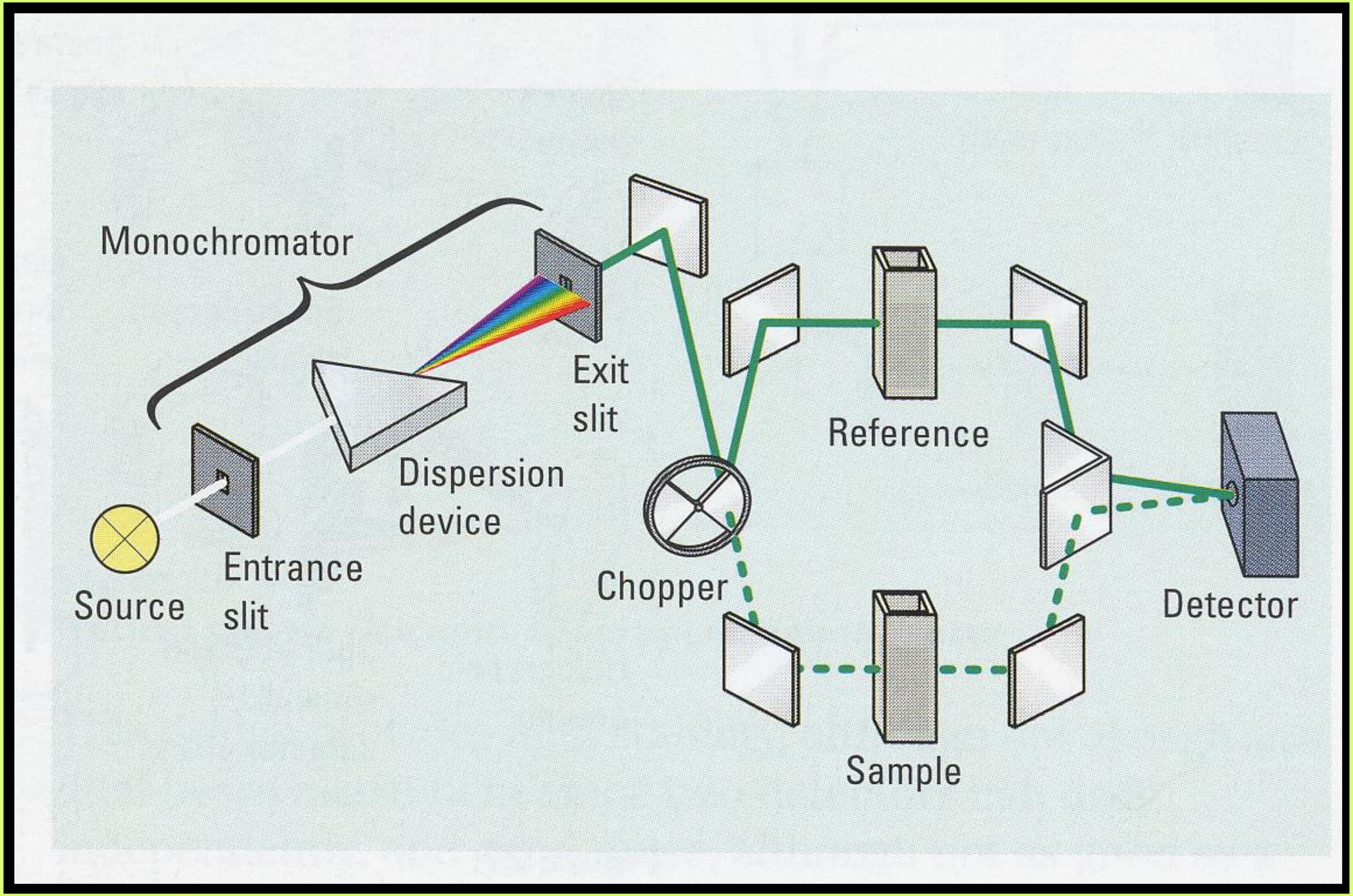


Dual Beam Spectrophotometer



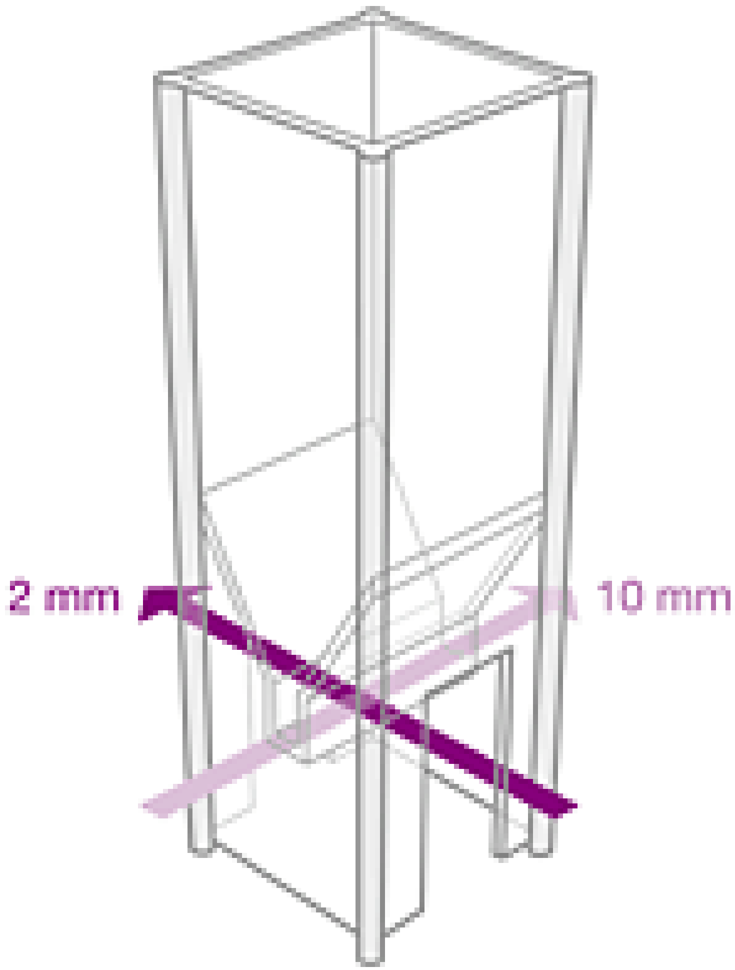


Esquema de um espectrômetro de UV-vis de duplo feixe

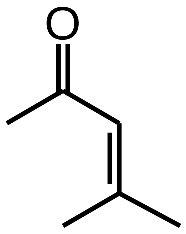


Cuvettes (sample holder)

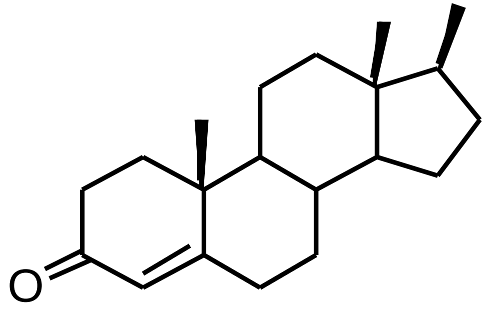
- Polystyrene
  - 340-800 nm
- Methacrylate
  - 280-800 nm
- Glass
  - 350-1000 nm
- Suprasil Quartz
  - 160-2500 nm



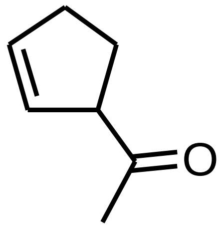
Similar structures have similar UV spectra:



λ_{max} = 238, 305 nm



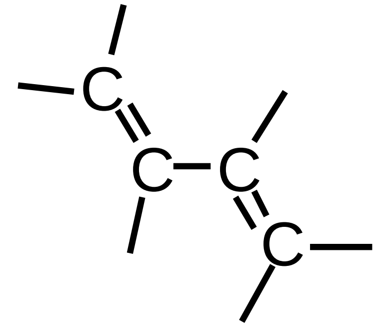
λ_{max} = 240, 311 nm



λ_{max} = 173, 192 nm

Woodward-Fieser Rules for Dienes

	Homoannular	Heteroannular
Parent	λ=253 nm	λ=214 nm
		=217 (acyclic)



Increments for:

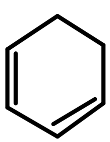
Double bond extending conjugation

+30

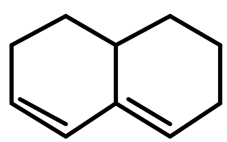
Alkyl substituent or ring residue	+5
Exocyclic double bond	+5

Polar groupings:

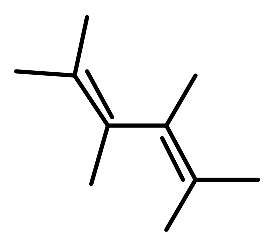
-OC(O)CH_3	+0
-OR	+6
-Cl, -Br	+5
-NR_2	+60
-SR	+30



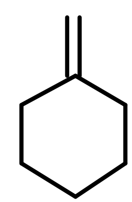
Homoannular



heteroannular



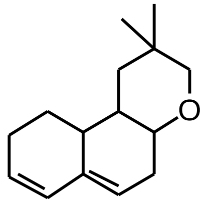
acyclic



exocyclic

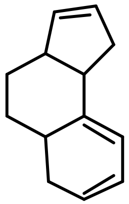
For more than 4 conjugated double bonds:

λ_{max} = 114 + 5(# of alkyl groups) + n(48.0-1.7n)



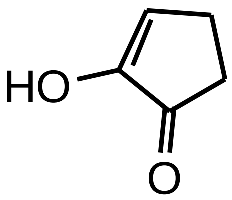
Parent:	214 (heteroannular)
3 alkyls	+15 (3x5)
	+5 (exocyclic)
TOTAL	234 nm

(Actual = 235 nm)

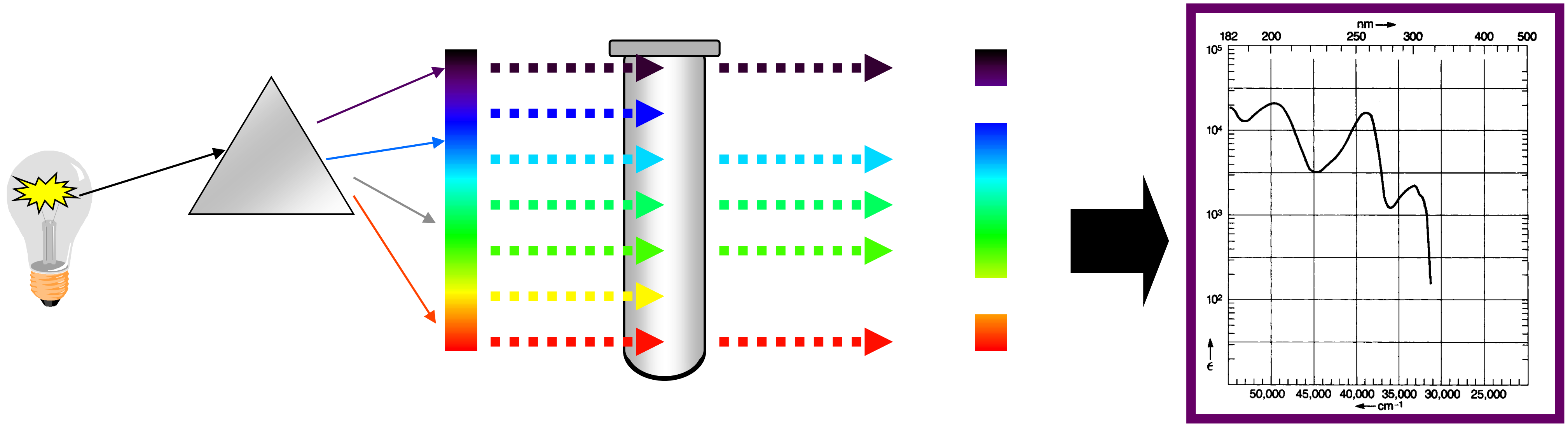


Parent:	253 (homoannular)
3 alkyls	+15 (3x5)
	+5 (exocyclic)
TOTAL	273 nm

(Actual = 275 nm)



Parent:	202 (5-member ring ketone)
	+35 (alpha hydroxyl)
	+12 (beta alkyl - note part of ring)
Total:	249



The wavelength and amount of light that a compound absorbs depends on its molecular structure and the concentration of the compound used.

The concentration dependence follows Beer's Law.

$$\mathbf{A=\varepsilon bc}$$

Where A is absorbance (no units, since *A = log10 P0 / P*)

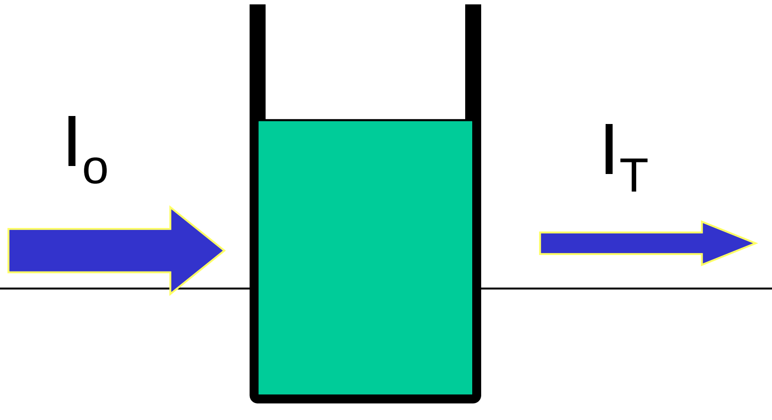
ε is the molar absorbtivity with units of L mol-1 cm-1

b is the path length of the sample - that is, the path length of the cuvette in which the sample is contained (typically in cm).

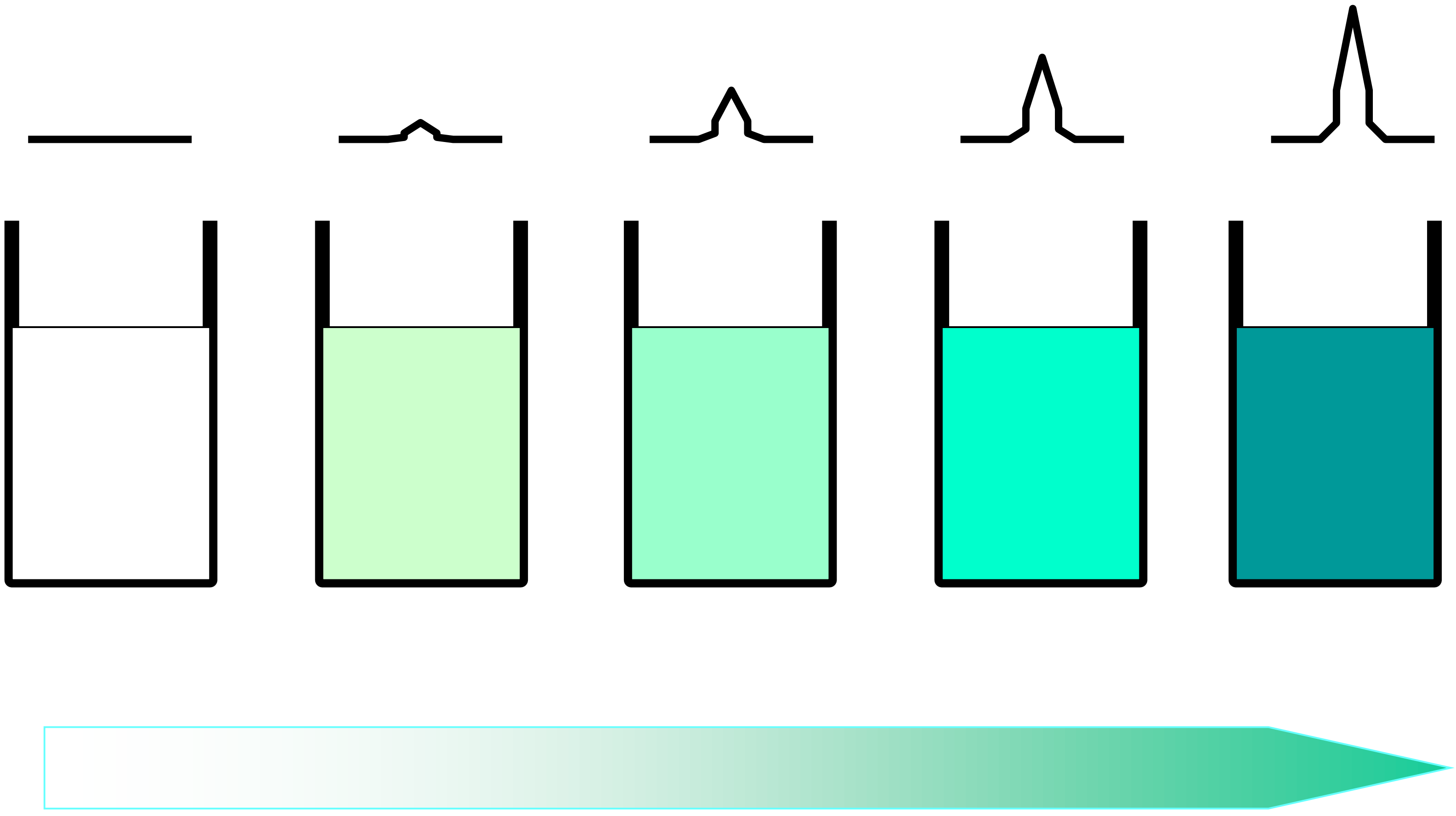
c is the concentration of the compound in solution, expressed in mol L-1

Definitions

- I_o = intensity of light through blank
- I_T = intensity of light through sample
- Absorption = $I_o - I_T$
- Transmittance = I_T/I_o
- Absorbance = $\log(I_o/I_T)$

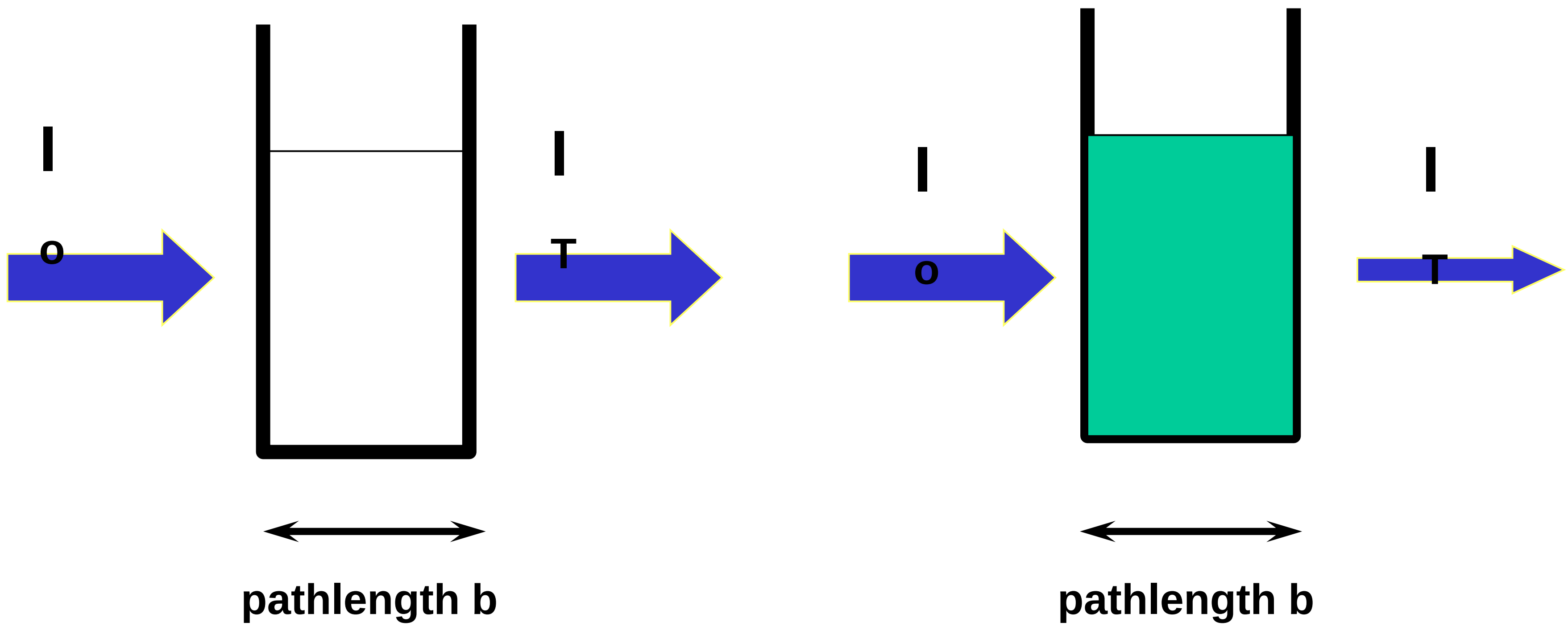


Absorbance & Beer's Law

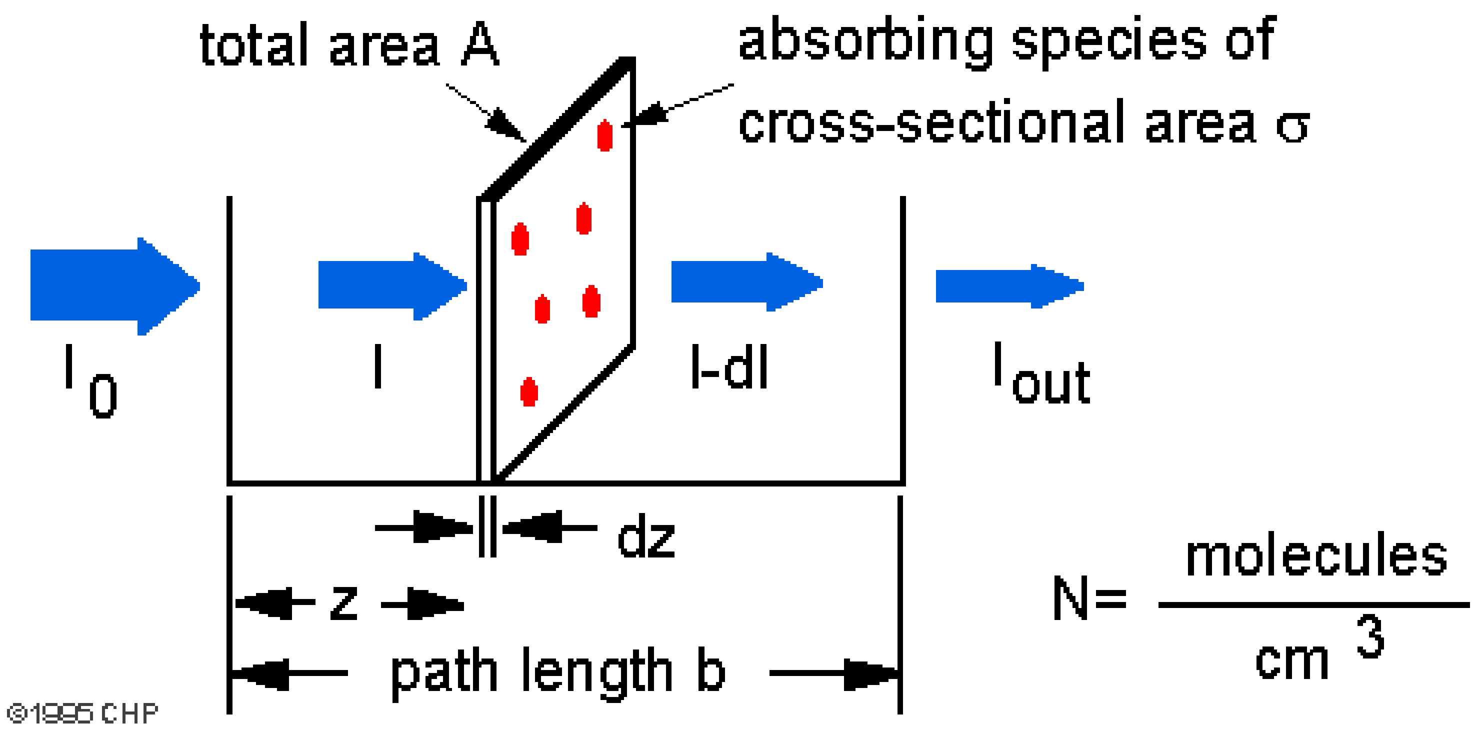


Increasing absorbance

Beer's Law

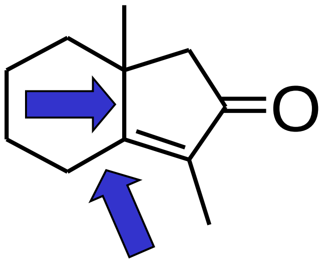


Beer's Law



Absorbance = Cεl

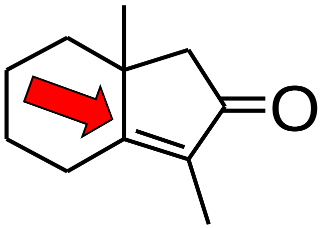
UV-Vis problems



α,β-unsaturated ketone
Table 7.12

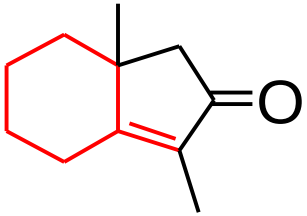
Base value:	202 nm
α-alkyl group	10 nm
Two β-alkyl groups	24 nm

UV-Vis problems

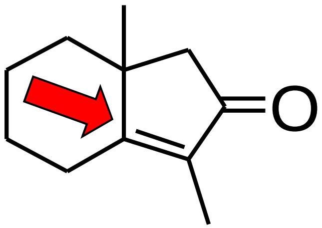


α,β-unsaturated
ketone
Table 7.12

Base value:	202 nm
α-alkyl group	10 nm
Two β-alkyl groups	24 nm
exocyclic double bond	5 nm



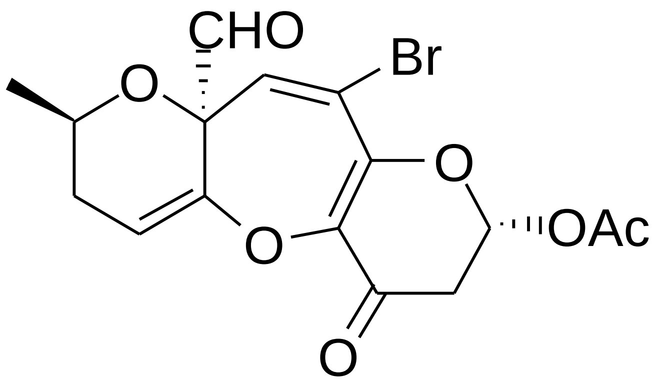
UV-Vis problems



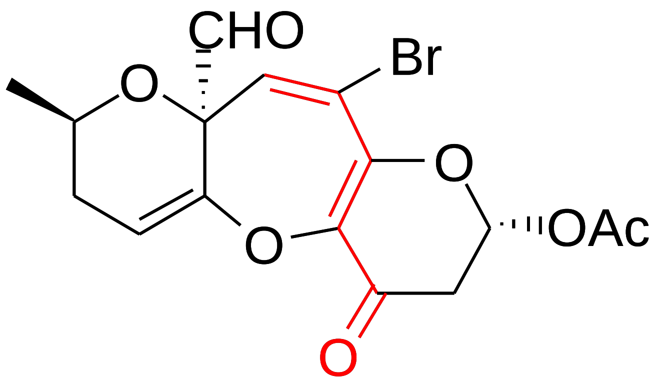
α,β-unsaturated ketone
Table 7.12

Base value:	202 nm
α-alkyl group	10 nm
Two β-alkyl groups	24 nm
exocyclic double bond	5 nm
	241 nm

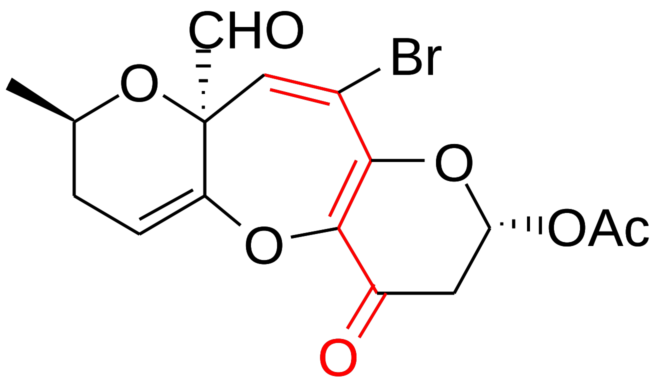
UV-Vis problems



UV-Vis problems



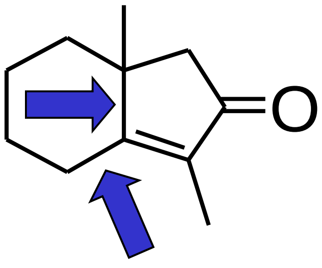
UV-Vis problems



α,β-unsaturated
ketone
Table 7.12

Base value: 215 nm

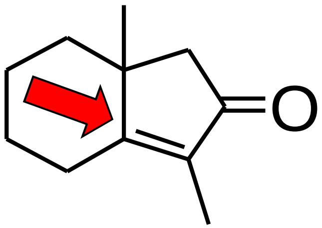
UV-Vis problems



α,β-unsaturated
ketone
Table 7.12

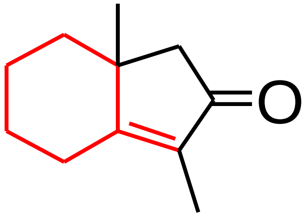
Base value:	202 nm
α-alkyl group	10 nm
Two β-alkyl groups	24 nm

UV-Vis problems

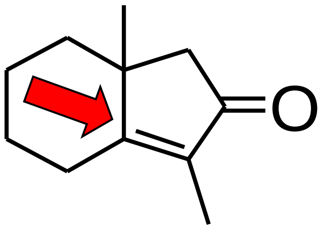


α,β-unsaturated
ketone
Table 7.12

Base value:	202 nm
α-alkyl group	10 nm
Two β-alkyl groups	24 nm
exocyclic double bond	5 nm



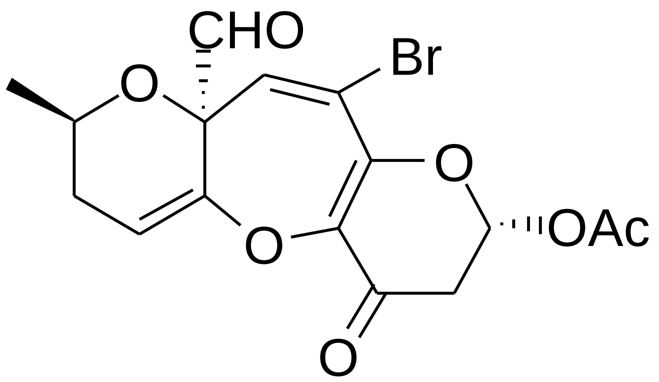
UV-Vis problems



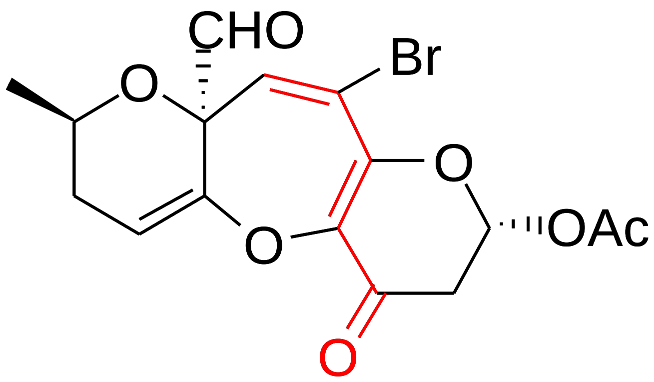
α,β-unsaturated
ketone
Table 7.12

Base value:	202 nm
α-alkyl group	10 nm
Two β-alkyl groups	24 nm
exocyclic double bond	5 nm
	241 nm

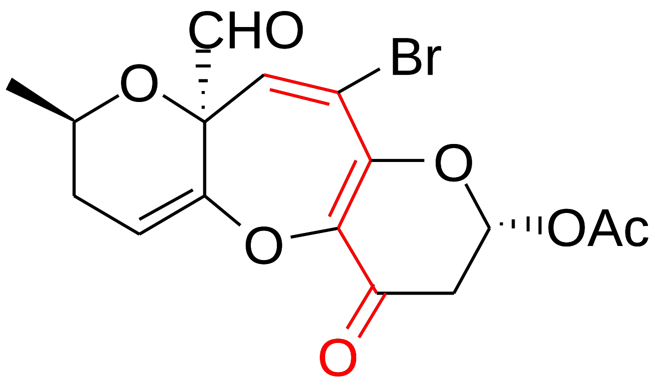
UV-Vis problems



UV-Vis problems



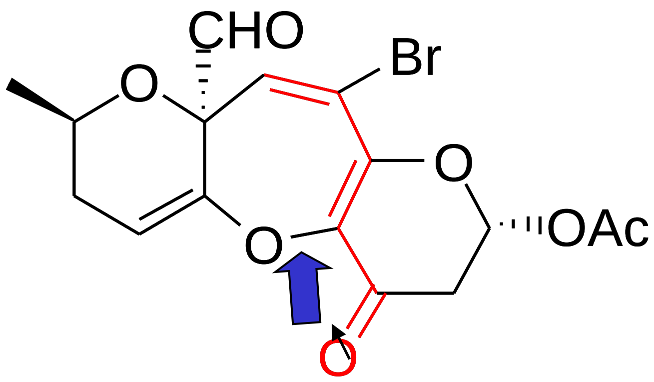
UV-Vis problems



α,β-unsaturated
ketone
Table 7.12

Base value: 215 nm

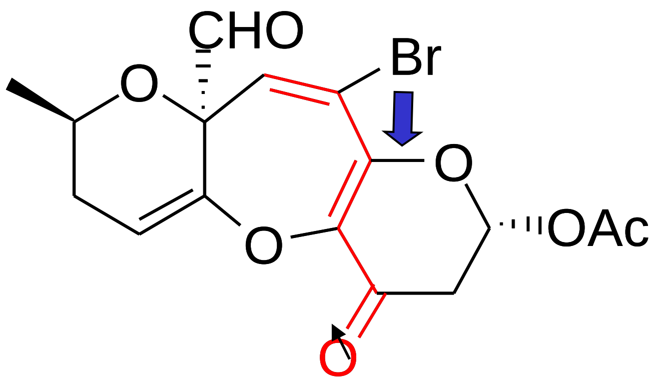
UV-Vis problems



α,β-unsaturated ketone
Table 7.12

Base value:	215 nm
α-alkoxy (OMe)	35 nm

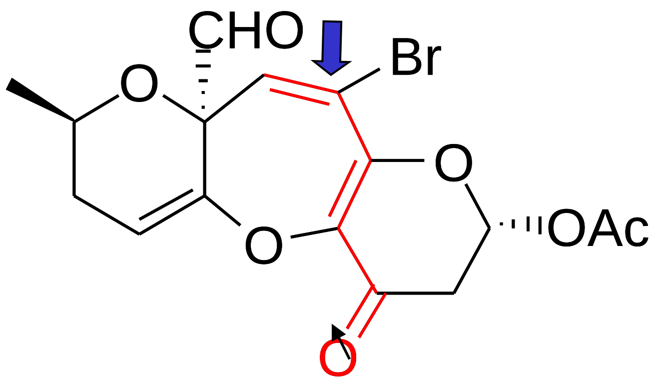
UV-Vis problems



α,β-unsaturated
ketone
Table 7.12

Base value:	215 nm
α-alkoxy (OMe)	35 nm
β-alkoxy (OMe)	30 nm

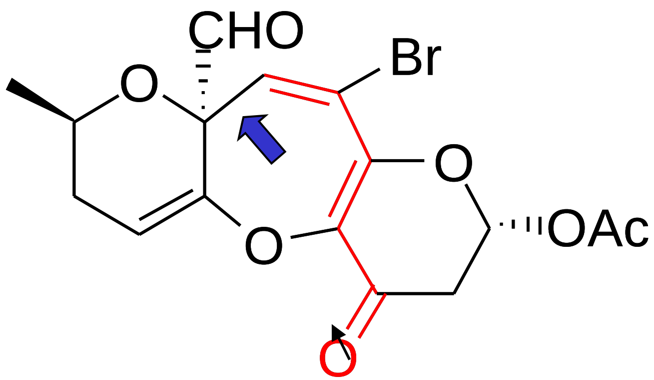
UV-Vis problems



α,β-unsaturated ketone
Table 7.12

Base value:	215 nm
α-alkoxy (OMe)	35 nm
β-alkoxy (OMe)	30 nm
Double bond	
Extending conj	30 nm

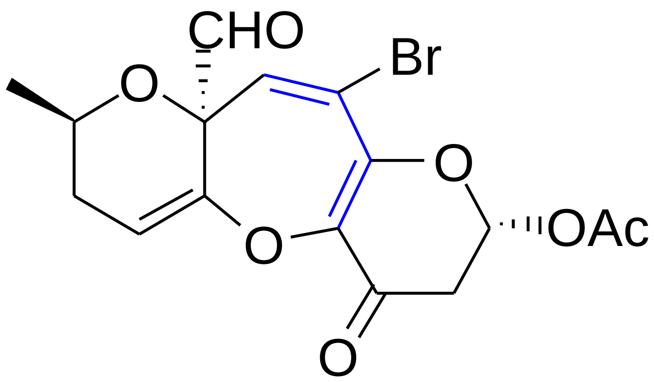
UV-Vis problems



α,β-unsaturated ketone
Table 7.12

Base value:	215 nm
α-alkoxy (OMe)	35 nm
β-alkoxy (OMe)	30 nm
Double bond	
Extending conj	30 nm
>γ alkyl group	18 nm

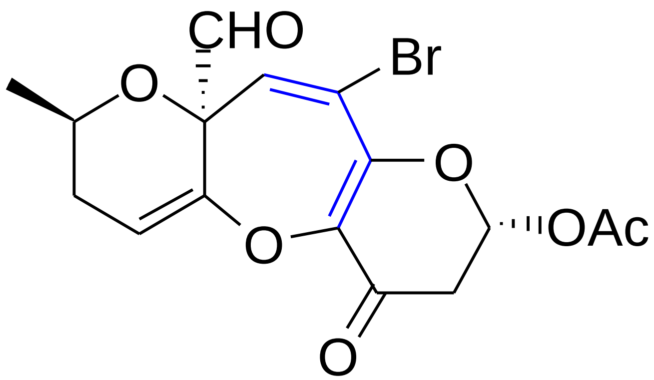
UV-Vis problems



α,β-unsaturated
ketone
Table 7.12

Base value:	215 nm	
α-alkoxy (OMe)	35 nm	
β-alkoxy (OMe)	30 nm	
Double bond extending conj		30 nm
>γ alkyl group		18 nm
Homodiene	39 nm	

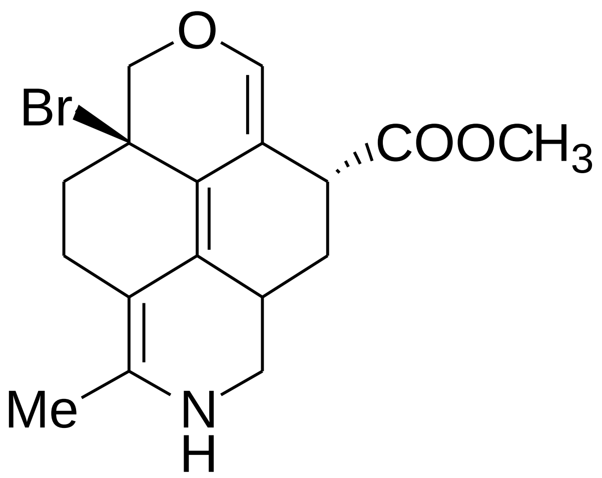
UV-Vis problems



α,β-unsaturated
ketone
Table 7.12

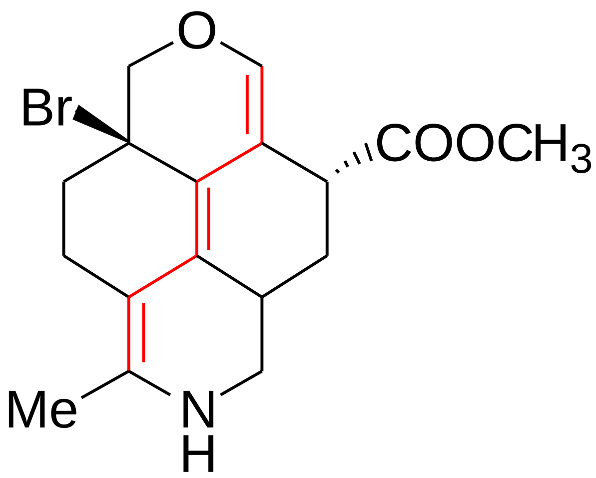
Base value:	215 nm	
α-alkoxy (OMe)	35 nm	
β-alkoxy (OMe)	30 nm	
Double bond		
extending conj		30 nm
>γ alkyl group		18 nm
Homodiene	39 nm	
	367 nm	

UV-Vis problems



triene
Table 7.5

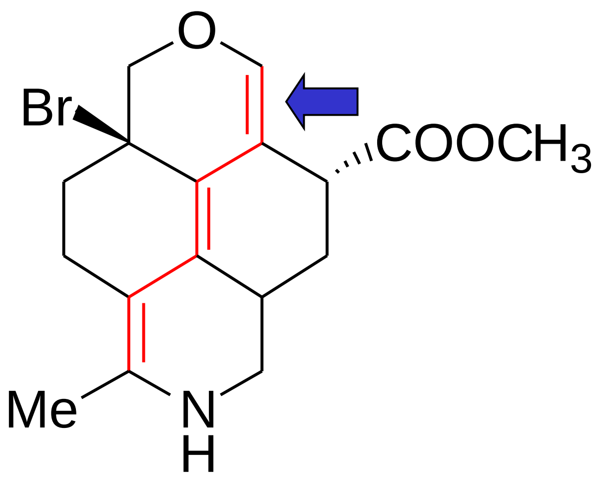
UV-Vis problems



triene
Table 7.5

Base value (heteroannular diene): 214 nm

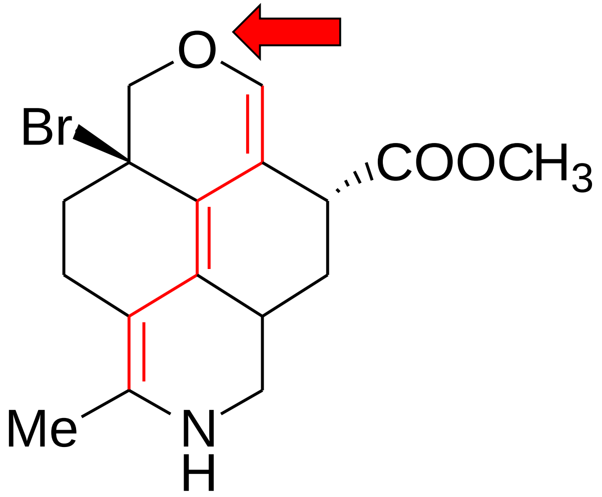
UV-Vis problems



triene
Table 7.5

Base value (heteroannular diene):	214 nm
Double bond extending conjugation	30 nm

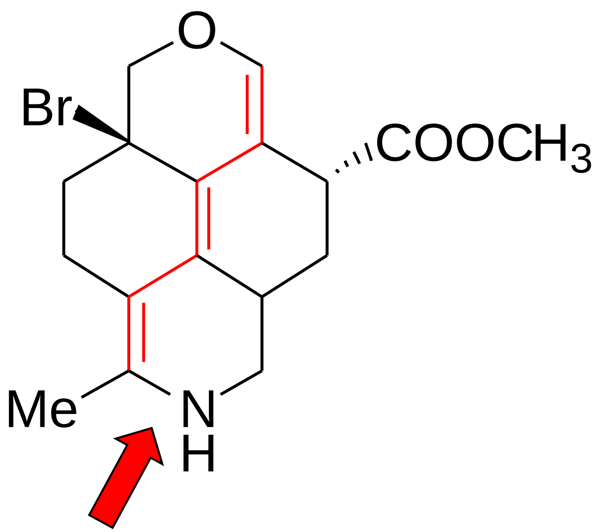
UV-Vis problems



triene
Table 7.5

Base value (heteroannular diene):	214 nm
Double bond extending conjugation	30 nm
Oalk group	6 nm

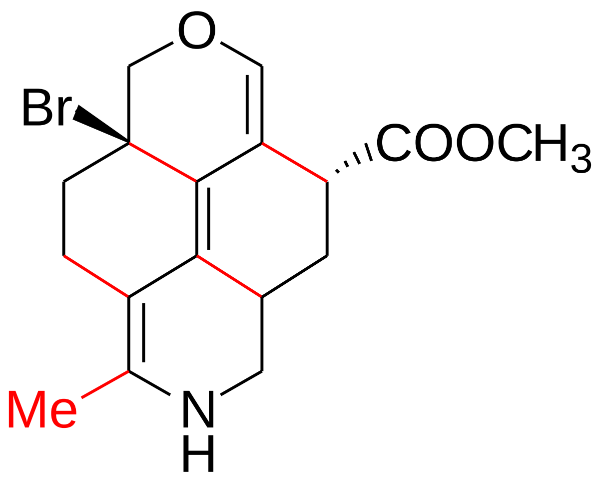
UV-Vis problems



triene
Table 7.5

Base value (heteroannular diene):	214 nm
Double bond extending conjugation	30 nm
Oalk group	6 nm
N(Alk)2	60 nm

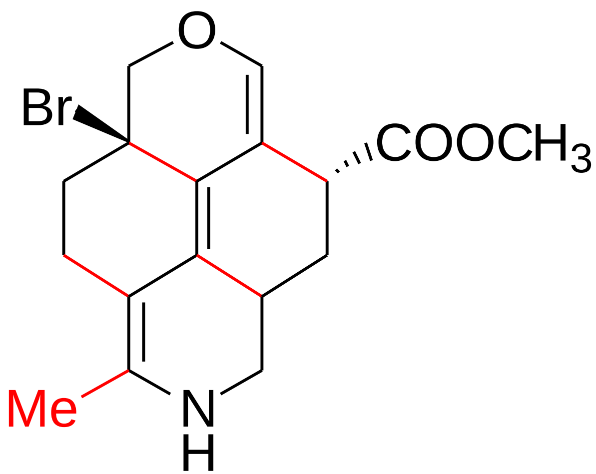
UV-Vis problems



triene
Table 7.5

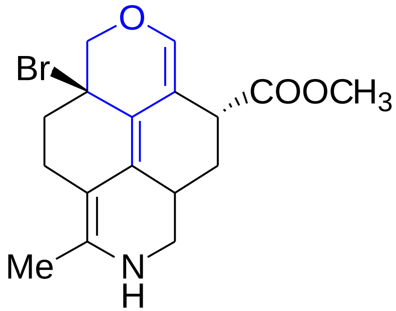
Base value (heteroannular diene):	214 nm
Double bond extending conjugation	30 nm
Oalk group	6 nm
N(Alk)2	60 nm
5 alkyl residues	25 nm

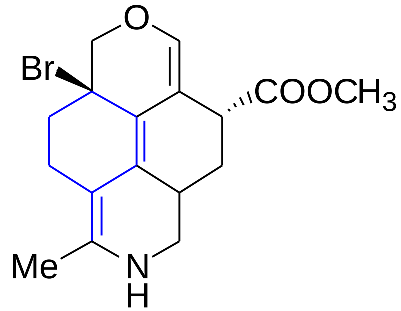
UV-Vis problems

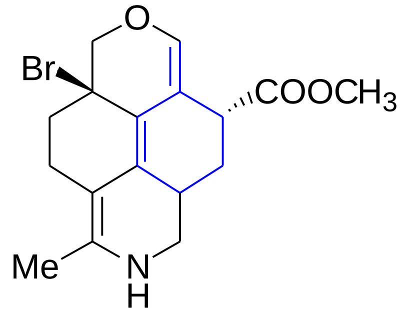


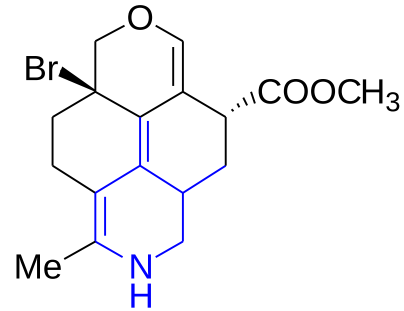
triene
Table 7.5

Base value (heteroannular diene):	214 nm
Double bond extending conjugation	30 nm
Oalk group	6 nm
N(Alk)2	60 nm
5 alkyl residues	25 nm
4 exocyclic double bonds	20 nm

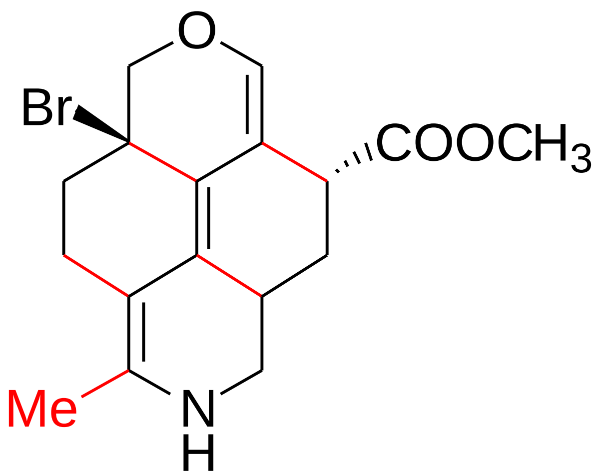








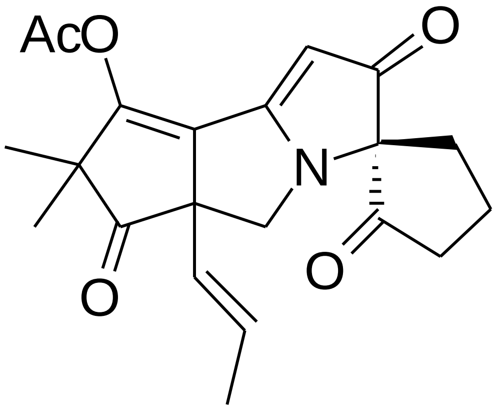
UV-Vis problems



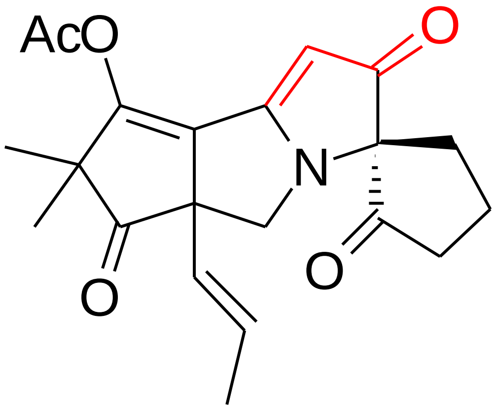
triene
Table 7.5

Base value (heteroannular diene):	214 nm
Double bond extending conjugation	30 nm
Oalk group	6 nm
N(Alk)2	60 nm
5 alkyl residues	25 nm
4 exocyclic double bonds	20 nm
	355 nm

UV-Vis problems



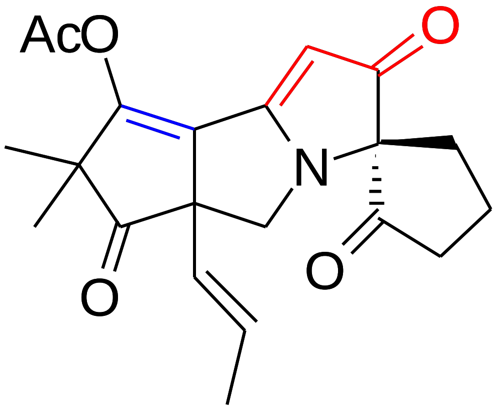
UV-Vis problems



α,β-unsaturated
ketone
Table 7.12

Base value: 202 nm

UV-Vis problems

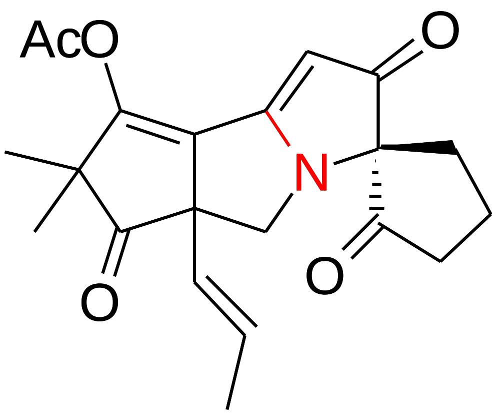


α,β-unsaturated
ketone
Table 7.12

Base value: 202 nm

Extended conjugation 30 nm

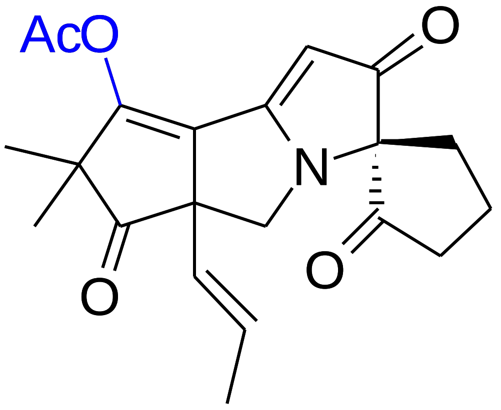
UV-Vis problems



α,β-unsaturated
ketone
Table 7.12

Base value:	202 nm	
Extended conjugation		30 nm
β-NR_2	95 nm	

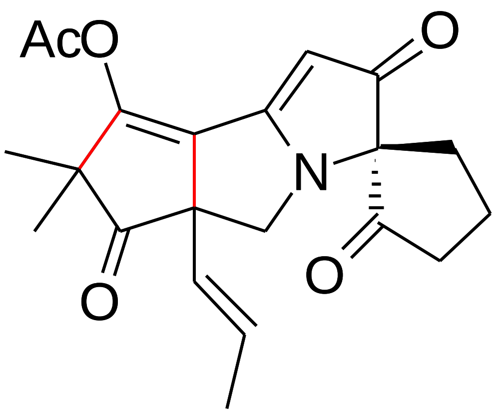
UV-Vis problems



α,β-unsaturated
ketone
Table 7.12

Base value:	202 nm
Extended conjugation	30 nm
β-NR_2	95 nm
δ-OAc	6 nm

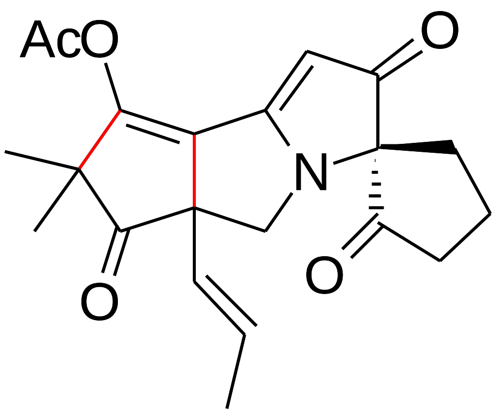
UV-Vis problems



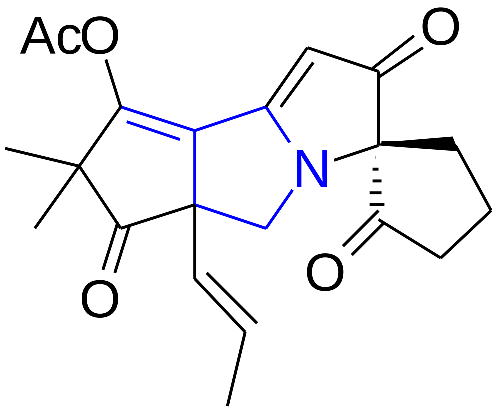
α,β-unsaturated
ketone
Table 7.12

Base value:	202 nm
Extended conjugation	30 nm
β-NR_2	95 nm
δ-OAc	6 nm
2 γ and higher alkyls	36 nm

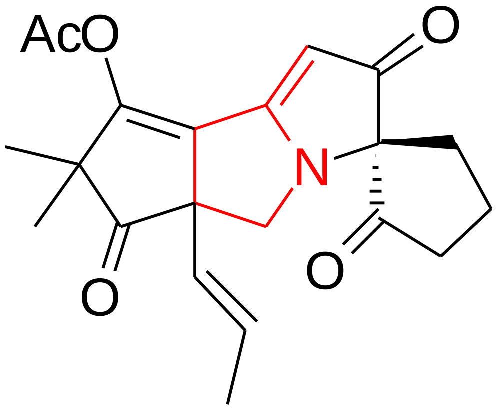
UV-Vis problems



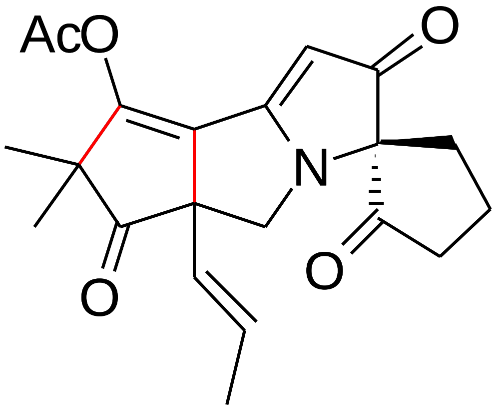
α,β-unsaturated
ketone
Table 7.12



Base value:	202 nm	
Extended conjugation		30 nm
β-NR_2	95 nm	
δ-OAc	6 nm	
2 γ and higher alkyls		36 nm
Two exocyclic olefins		10 nm



UV-Vis problems



α,β-unsaturated
ketone
Table 7.12

Base value:	202 nm
Extended conjugation	30 nm
β-NR_2	95 nm
δ-OAc	6 nm
2 γ and higher alkyls	36 nm
Two exocyclic olefins	10 nm
	379 nm

Types of Light Spectroscopy

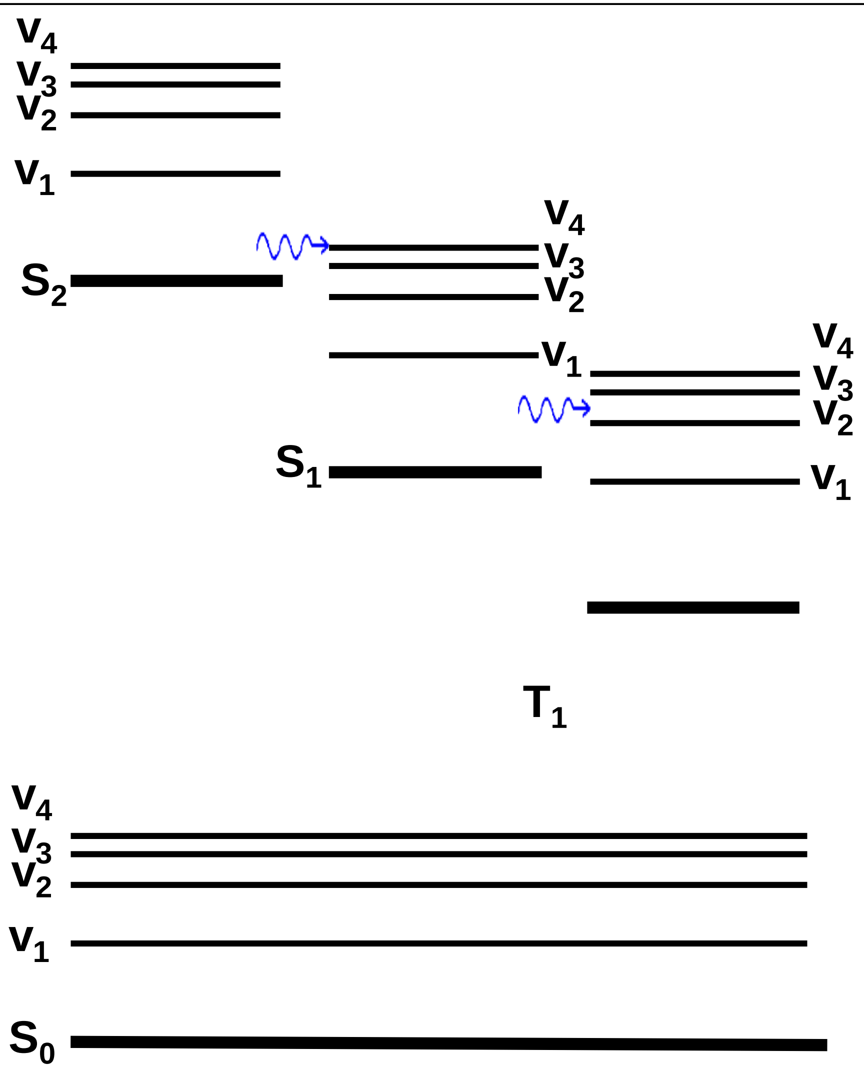
- Absorption spectroscopy
  - Measures amount of light absorbed
  - Most common, non-destructive
  - Concentration, pH measures, purity, ID
- Atomic emission spectroscopy
  - Measures light emitted from burned sub.
  - Elemental analysis
- Luminescence (Luminol)

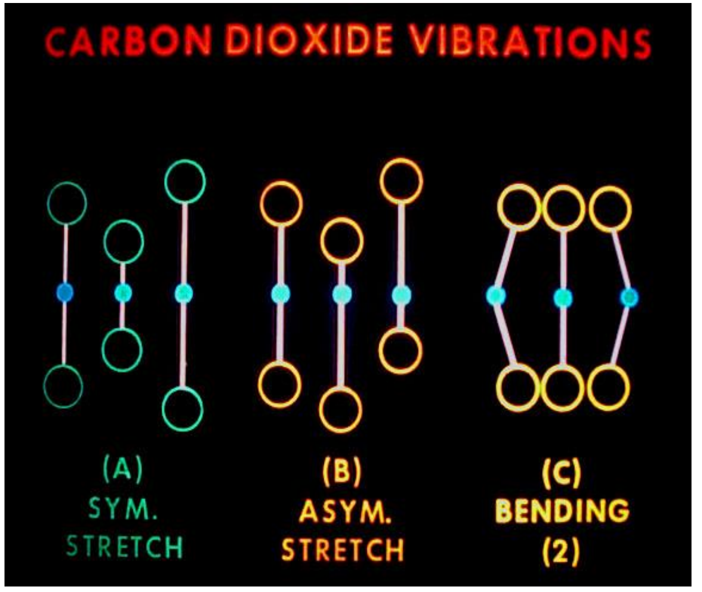
Types of Light Spectroscopy

- Fluorescence spectroscopy
  - Things fluoresce when they emit at higher λ than what they absorb
  - Measure solvent interactions, distances
- Circular Dichroism spectroscopy
  - Absorption of circular polarized light
  - Chiral compound identification
- Transmission spect. (colorimetry)

Molecular Spectra

- Molecules are vibrating and rotating all the time.
- Molecules are normally at their ground state (S_0)





UV vs. IR vs. NMR

- UV has broad peaks relative to IR & NMR
- UV has less information than IR & NMR
- UV spectra are easier to collect
- UV spectra are faster to collect
- UV spectrometers are cheaper
- UV spectra require only nanograms of material or chemicals

Practical Applications

- Pharmacy Practice
  - Ultraquin (psoriasis med. Needs UV. Act.
  - Pregnancy tests (colorimetric assays)
  - Blood glucose tests, Bilichek
  - ELISA's
- Pharmaceutics
  - pH titrations, purity measurement
  - concentration measurement

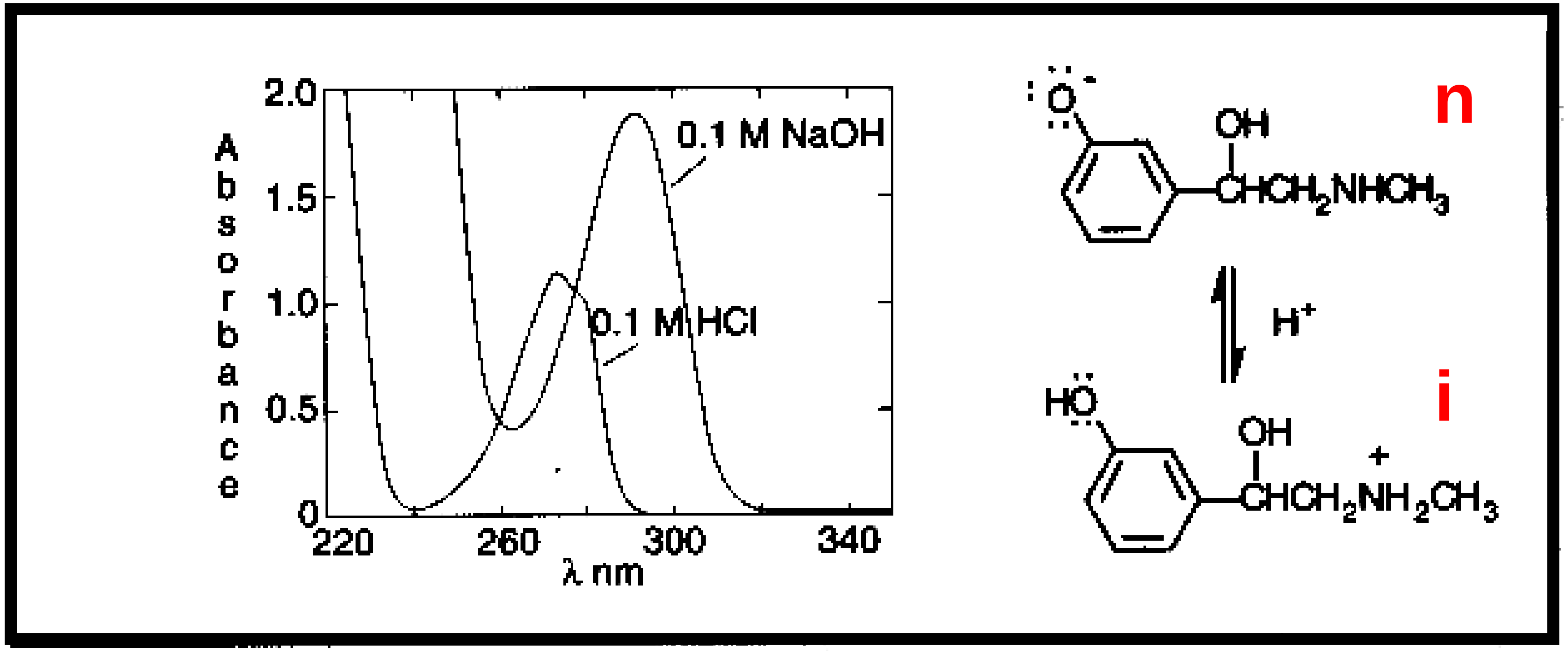
Practical Applications

- Medicinal Chemistry
  - compound ID (steroids, nucleosides)
  - monitoring isomerization, chirality
- Pharmaceutical Biotechnology
  - concentration/purity measurements
  - monitoring conformation of protein drugs
- Pharmacokinetics/Med. Chem.
  - HPLC monitoring and purification

Pharmaceutical Apps.

- On Line Analysis of Vitamin A and Coloring Dyes for the Pharmaceutical Industry
- Determination of Urinary Total Protein Output
- Analysis of total barbiturates
- Comparison of two physical light blocking agents for sunscreen lotions
- Determination of acetylsalicylic acid in aspirin using Total Fluorescence Spectroscopy
- Automated determination of the uniformity of dosage in Quinine Sulfate tablets using a Fibre Optics Autosampler
- Determining Cytochrome P450 by UV-Vis Spectrophotometry
- Light Transmittance of Plastic Pharmaceutical Containers

pKa Measurement with UV



Titration of Phenylephrine

$$pKa = pH + \log \frac{A_i - A}{A - A_n}$$