

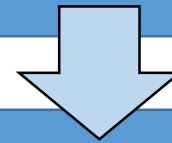
T1 - ENERGIA DAS ORBITAIS π DE POLIENOS CONJUGADOS

Objetivo:

Aplicar **modelo da partícula numa caixa de potencial nulo a 1D**
e o tratamento **dual onda-corpúsculo (quantização E)**



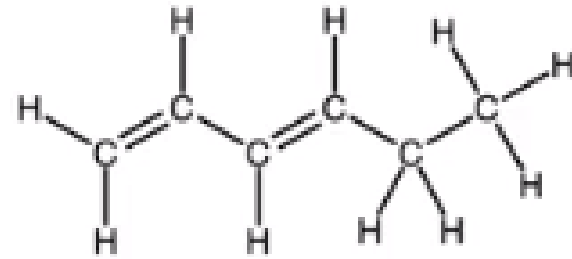
para prever **transições eletrônicas**



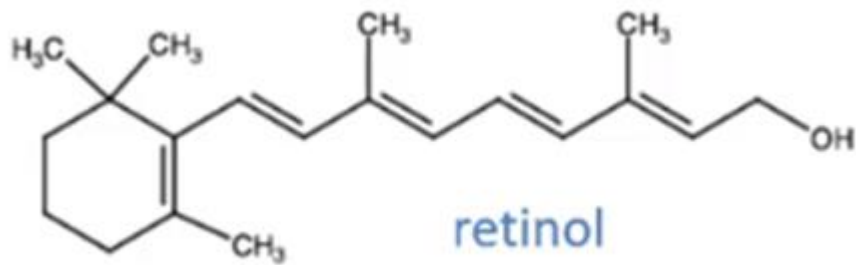
de **elétrões deslocalizados** em **polienos conjugados**

Polienos: hidrocarbonetos com diversas ligações C=C (insaturados)

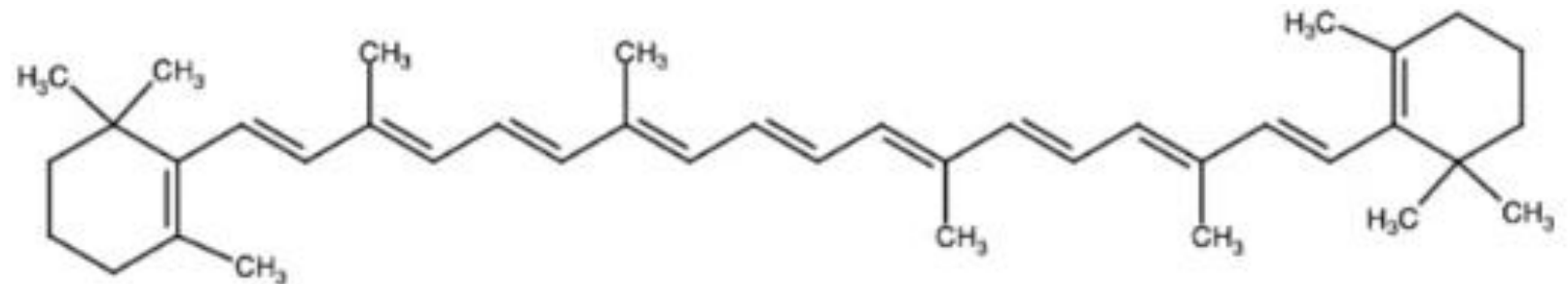
Conjugados: C=C alternam com C-C



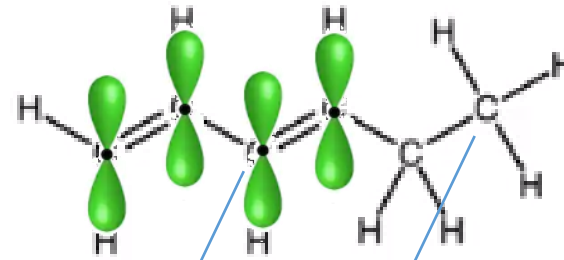
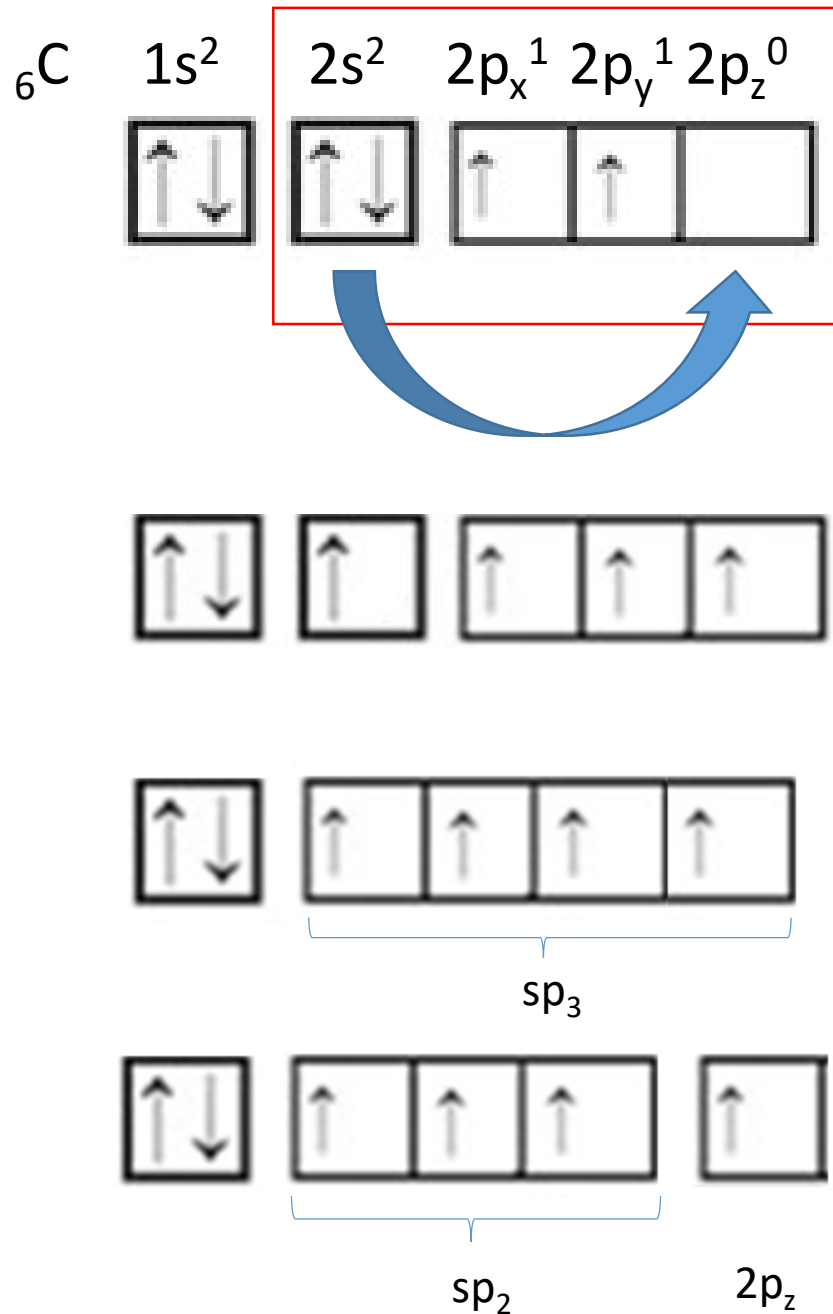
1,3-hexadieno (trans)



retinol



β -caroteno

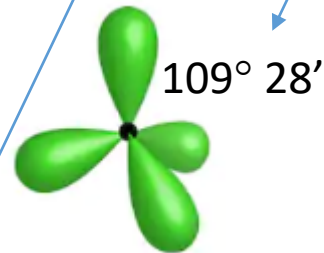


1,3-hexadieno (trans)

orbitais $2p_z$ coalescem lateralmente

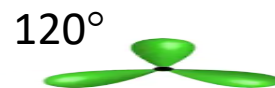


Sistema de orbitais π deslocalizado



4 orbitais híbridas sp_3

4 ligações σ



3 orbitais híbridas sp_2

3 ligações σ



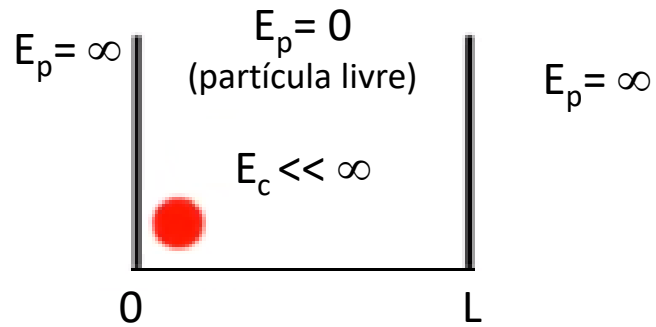
1 orbitais $2p_z$

1 ligação π

e^- π deslocalizados

Dualidade onda-corpúsculo

Modelo do partícula livre numa caixa 1D



$$L = (N+1) d_{cc}$$

n° lig CC
(simples/duplas)

dist. média lig CC
(141 pm)

e^- pode comportar-se como **onda**

Eq. Schrödinger

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} + E_p \psi(x) = E \psi(x)$$

Soluções da **Eq. Schrödinger**

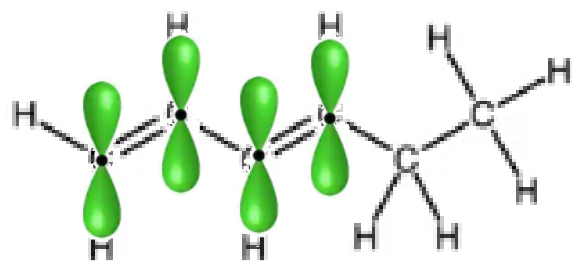
$$E_m = \frac{m^2 \hbar^2}{8mL^2}$$

Energia

$$\psi_m(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{m\pi x}{L}\right)$$

Função
de onda

$$m = 1, 2, \dots$$



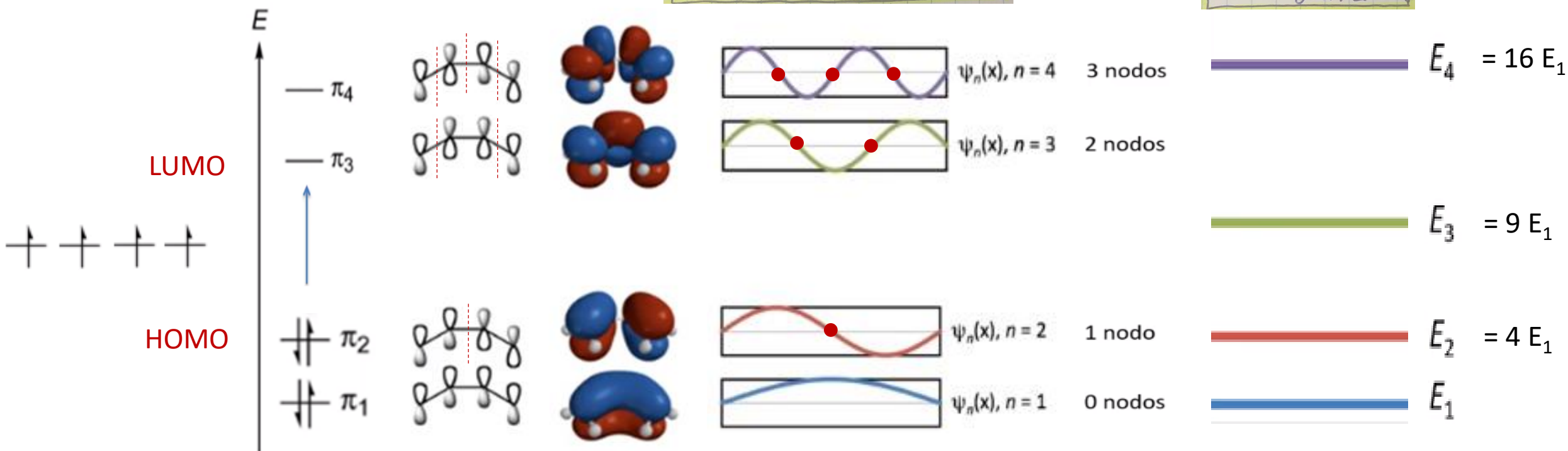
1,3-hexadieno (trans)

TOM-CLOA

4 OA $p_z \Rightarrow$ 4 OM π

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

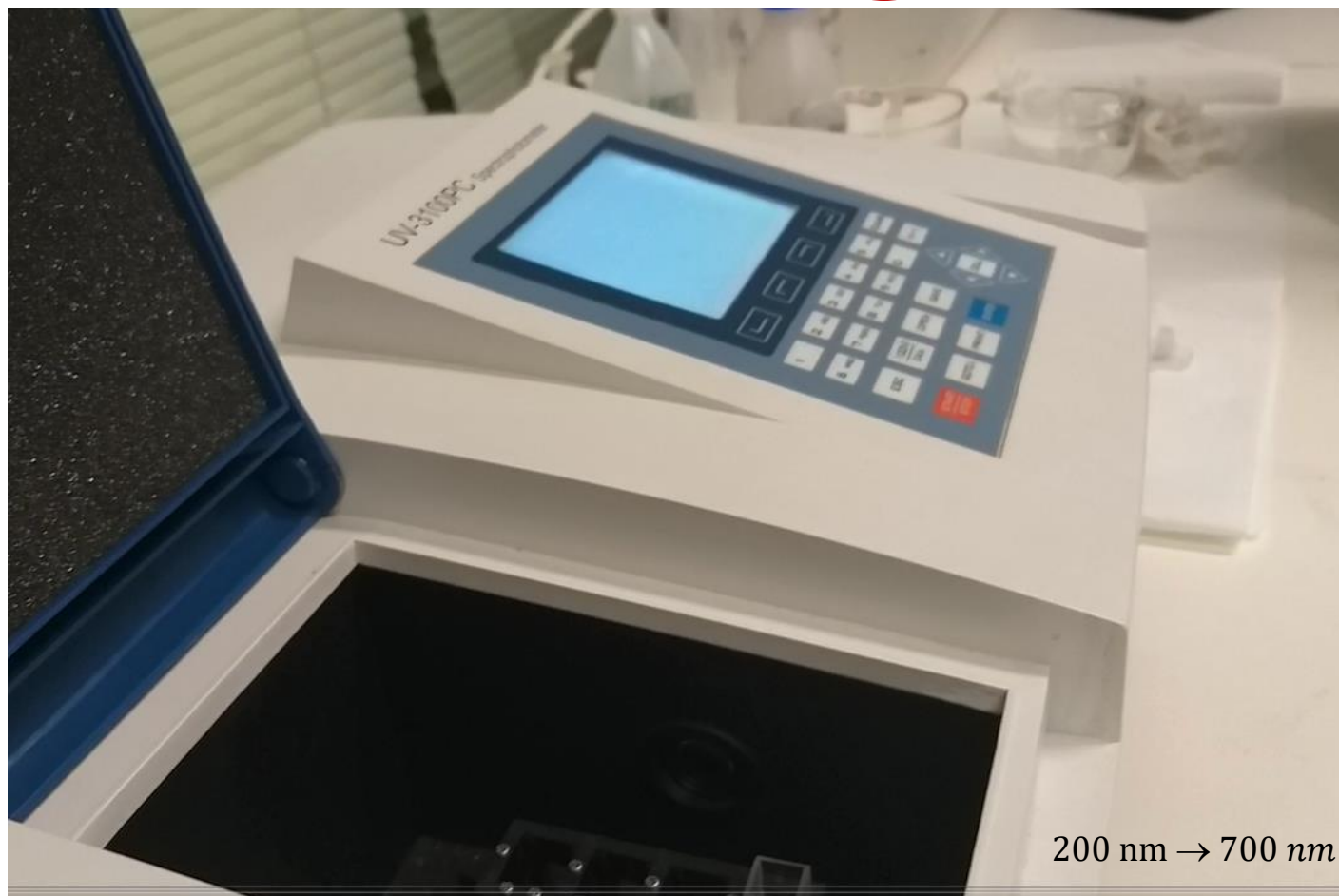
$$E_n = \frac{n^2 h^2}{8 m L^2}$$



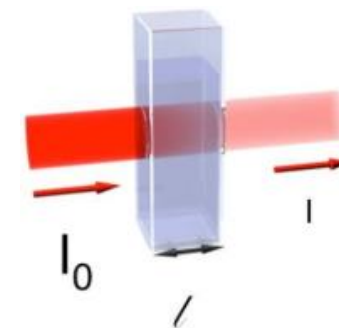
Transição *Eni* → *Enf*

Transição HOMO → LUMO
(menor energia)

$$\Delta E = h\nu = h \frac{c}{\lambda}$$
$$\Delta E_{\min} \Rightarrow \lambda_{\max}$$



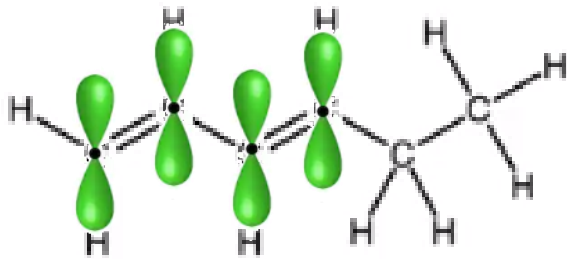
n-hexano
+
composto



$$T = \frac{I_0}{I}$$

$$A = \log_{10} \frac{1}{T}$$





1,3-hexadieno (trans)

λ_{max} teórico

4 OA $p_z \Rightarrow$ 4 OM π (2 lig e 2 anti lig) 141 pm

Transição $n = 2 \rightarrow n = 3$

$L = (3+1) d_{\text{cc}}$

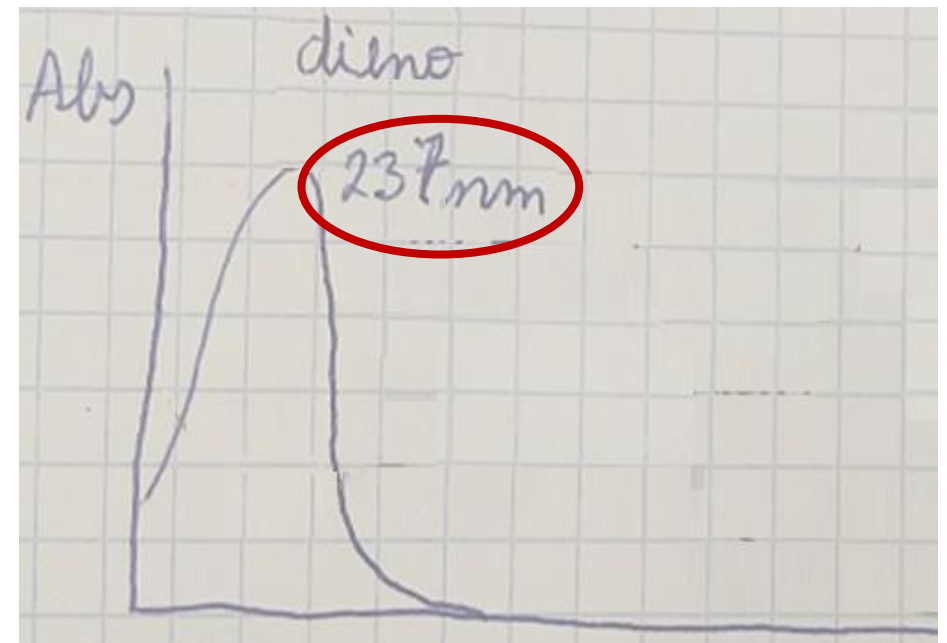
$$\Delta E_{n_i \rightarrow n_f} = (n_f^2 - n_i^2) \frac{h^2}{8 \times m \times L^2}$$

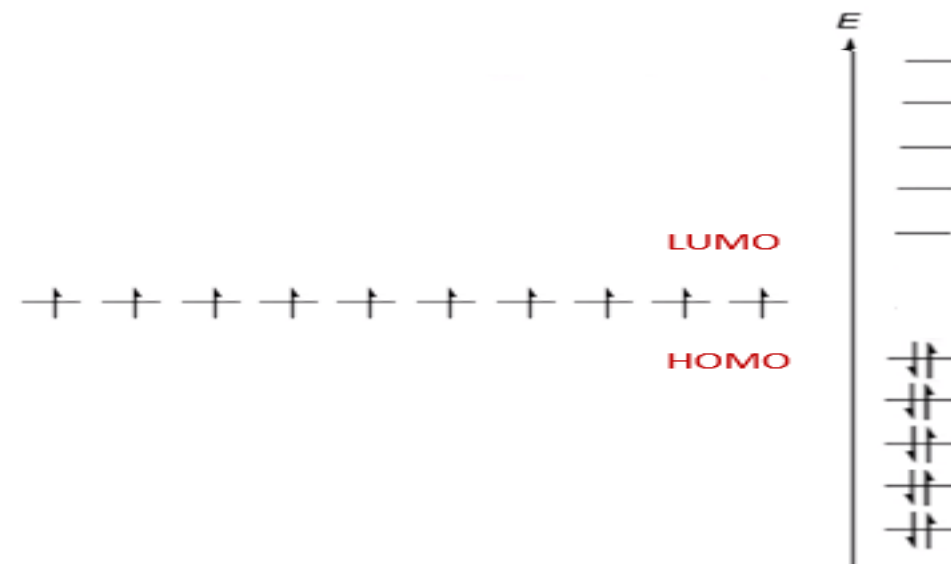
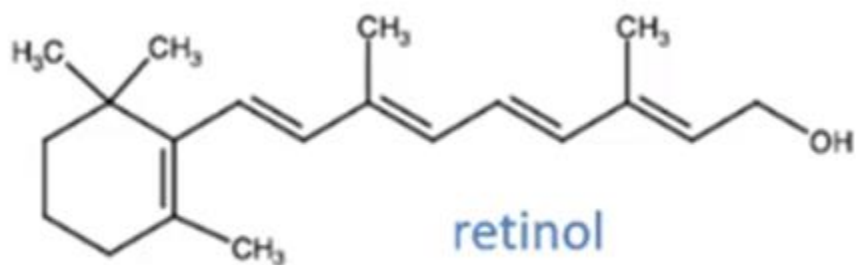
$$\Delta E_{2 \rightarrow 3} = (3^2 - 2^2) \frac{(6,626 \times 10^{-34})^2}{8 \times 9,109 \times 10^{-31} \times (4 \times 1,41 \times 10^{-10})^2} = 9,47 \times 10^{-19} \text{ J}$$

$$\Delta E = h \frac{c}{\lambda} \quad 9,47 \times 10^{-19} = 6,626 \times 10^{-34} \frac{2,998 \times 10^8}{\lambda}$$

$$\lambda_{\text{max}} = 2,097 \times 10^{-7} \text{ m} = 209,7 \text{ nm}$$

λ_{max} experimental





λ_{max} teórico

10 OA $p_z \Rightarrow$ 10 OM π (5 lig e 5 anti lig) 141 pm

Transição $n = 5 \rightarrow n = 6$

$$L = (9+1) d_{cc}$$

$$E_n = \frac{n^2 h^2}{8 m L^2}$$

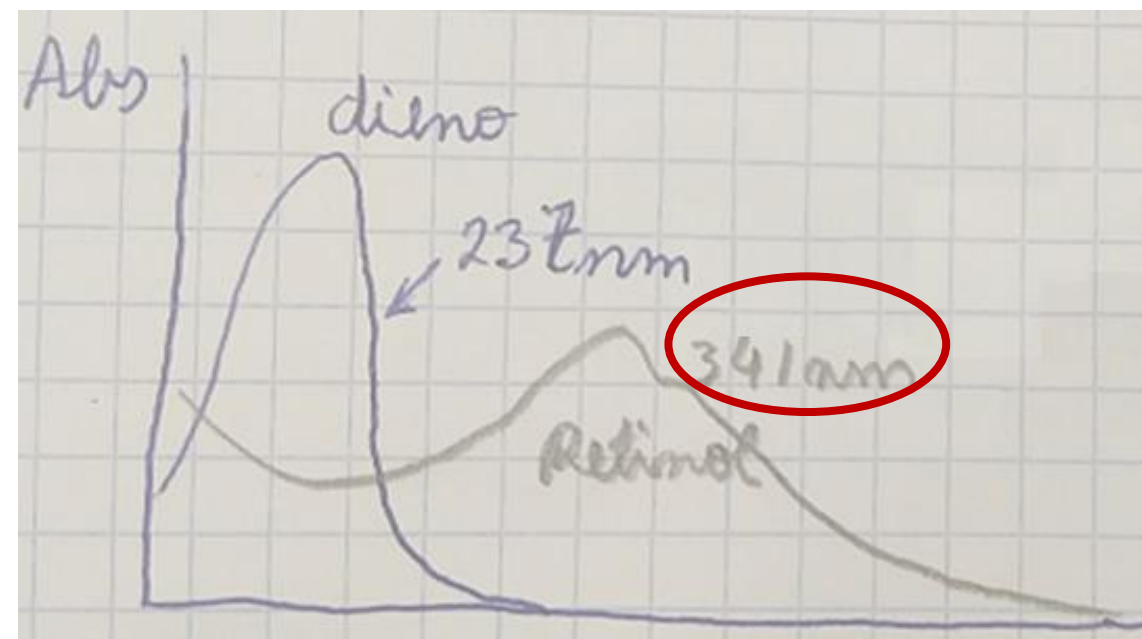
$$\Delta E_{ni \rightarrow nf} = (nf^2 - ni^2) \frac{h^2}{8 m L^2}$$

$$\Delta E_{5 \rightarrow 6} = 3.33 \times 10^{-19} \text{ J}$$

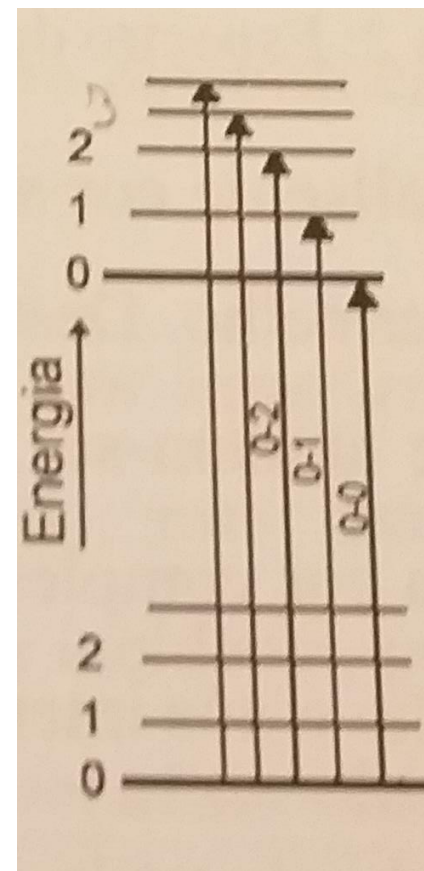
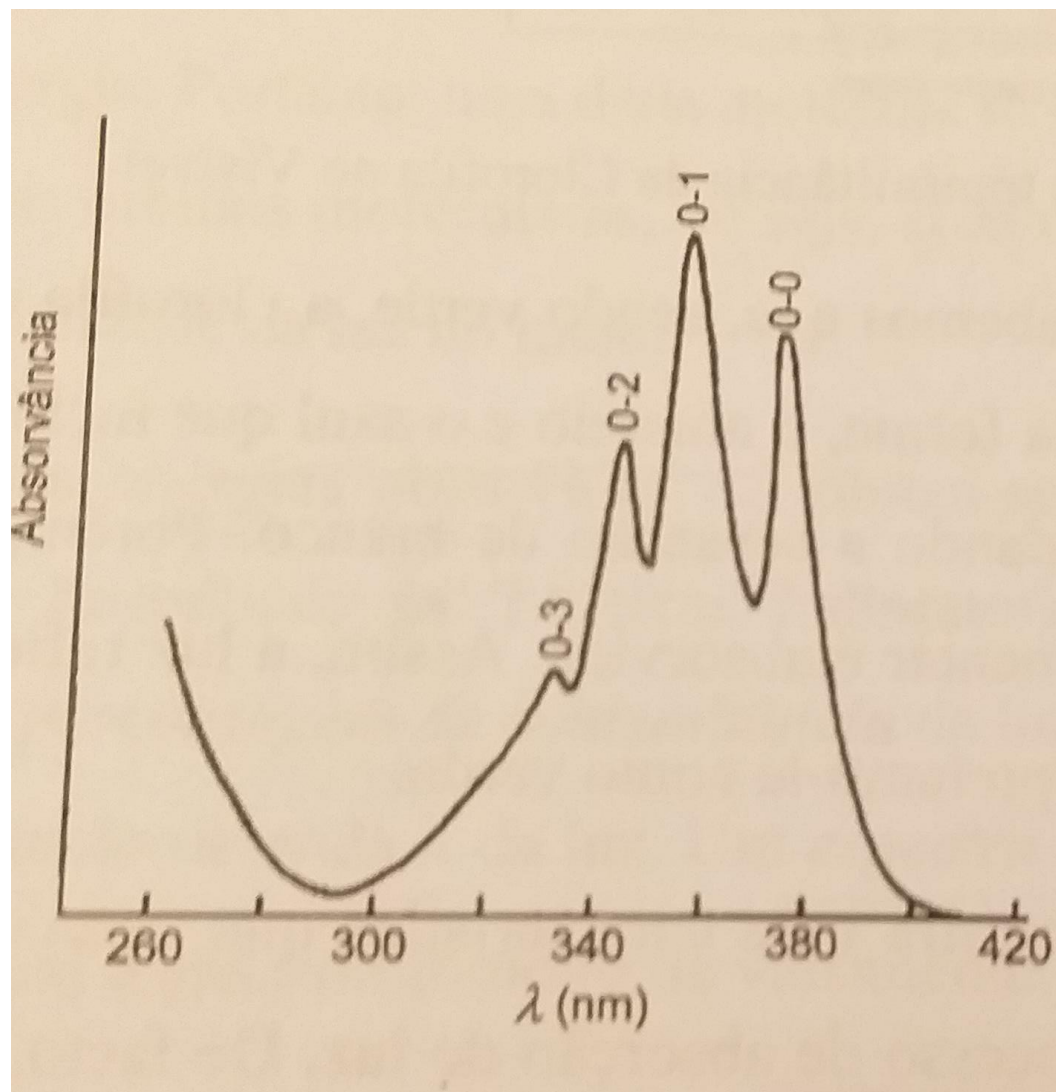
$$\Delta E = h \frac{c}{\lambda}$$

$$\lambda_{\text{max}} = 5,95 \times 10^{-7} \text{ m} = 595,9 \text{ nm}$$

λ_{max} experimental

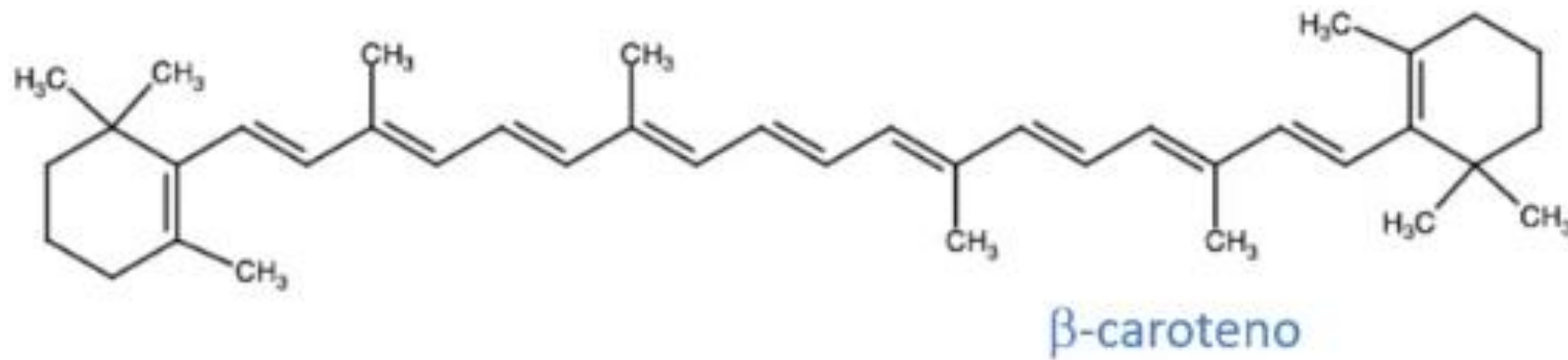


Diversas bandas



Estado excitado:
diferentes estados
vibracionais/rotacionais

Estado fundamental:
a molécula está no
modo de vibração de
menor E



λ_{\max} teórico

22 OA $p_z \Rightarrow$ 22 OM π (11 lig e 11 anti lig)

Transição $n = 11 \rightarrow n = 12$

$L = (21+1) d_{cc}$

141 pm

$$E_m = \frac{m^2 h^2}{8 m L^2}$$

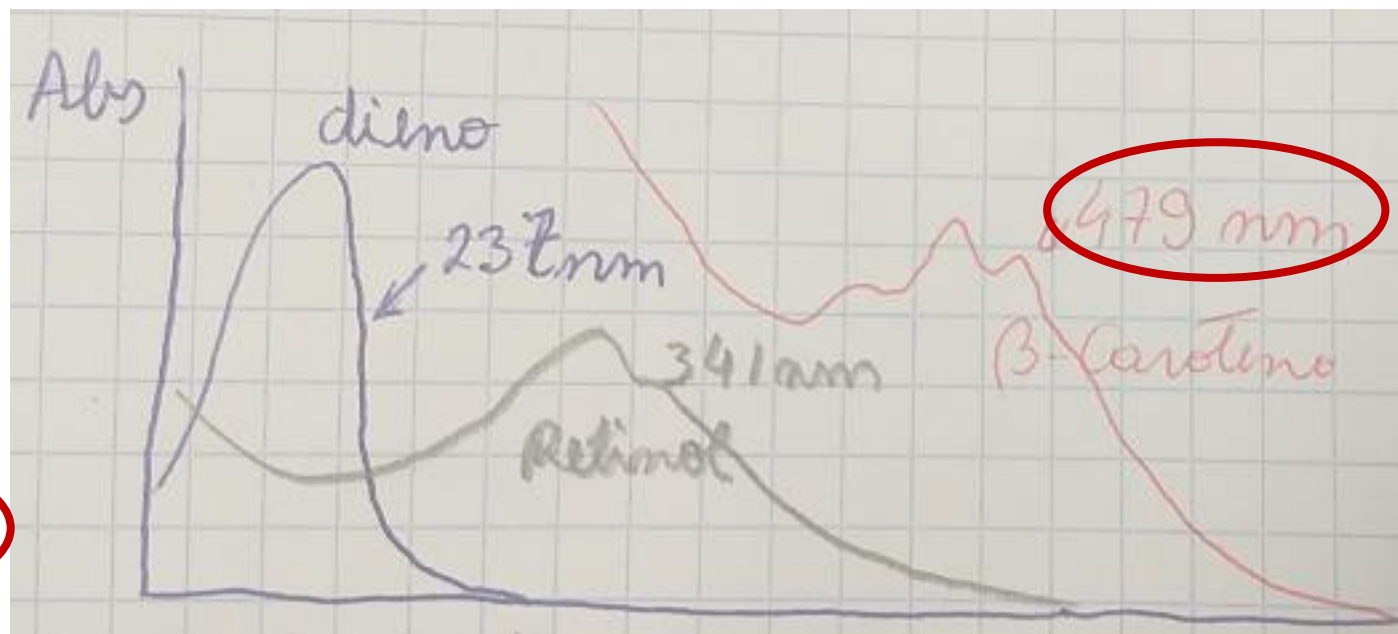
$$\Delta E_{ni \rightarrow nf} = (nf^2 - ni^2) \frac{h^2}{8 \times m \times L^2}$$

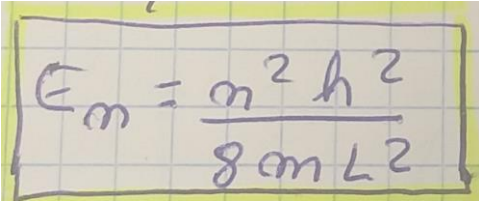
$$\Delta E_{11 \rightarrow 12} = 1,440 \times 10^{-19} J$$

$$\Delta E = h \frac{c}{\lambda}$$

$$\lambda_{\max} = 1,3795 \times 10^{-6} m = 1379,5 \text{ nm}$$

λ_{\max} experimental





$$E_m = \frac{m^2 h^2}{8 m L^2}$$

- $E_{min \neq 0} = E_1 = \frac{h^2}{8 m L^2}$

$$E = E_{cin} + E_p = E_{cin} \neq 0$$

0

$$\Rightarrow v \neq 0$$

Partícula em movimento

Não é possível saber simultaneamente x e p

(Princ. Incert. Heisenberg)

- $\downarrow m \text{ e } \downarrow L \Rightarrow \Delta E_{ni \rightarrow nf} = (nf^2 - ni^2) \frac{h^2}{8 m L^2}$

Maior a separação de níveis de Energia (ΔE)

$\uparrow m \text{ e } \uparrow L$ Partículas macroscópicas \Rightarrow níveis de E próximos (contínuo de E)

Composto	$\lambda_{\text{máx}}$ teórico	$\lambda_{\text{máx}}$ exp	IDifl (%)
1,3, hexadieno	209,7	237	13.0
retinol	595,9	341	42.8
β -caroteno	1379,5	479	65.3

Assumimos **modelo do e- livre** ($E_p=0$)

Eq. Schrödinger monoelétrica

Não considera

Repulsões $e^- - e^-$
Atração e^- - Núcleo