Graduate Core Course I (891G):

Physical / Organic Chemistry

Problem Set # 1

① UV/Vis Spectroscopy of Conjugated Alkenes:

Particle in a Box Model

(a) molecule 1,3,5-hexatriene

6-π electrons are there in the system.

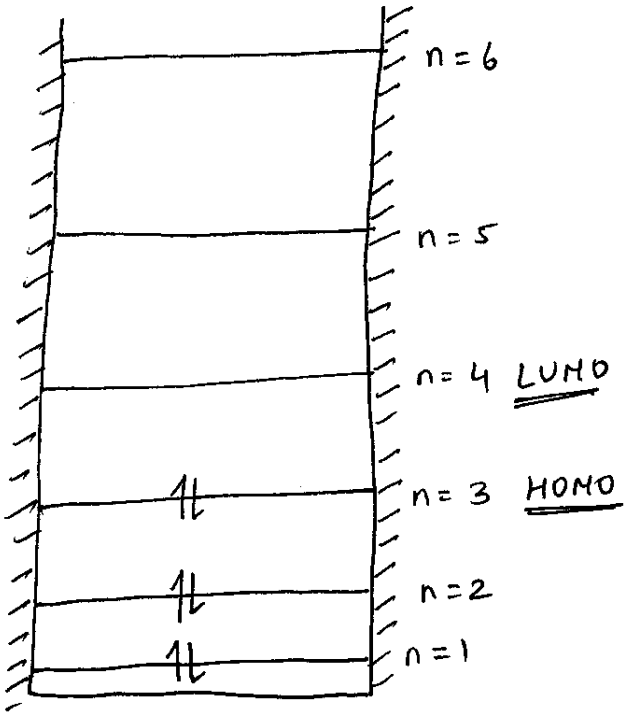
Assuming, Carbon-Carbon bondlength of 1.4 Å,

Length of the box, $L = 1.4 \times 6 = 8.4$ Å

(b) Schematic picture of the first 6 quantized energy levels with each carbon in the conjugated system contributing 1-π electron.

According to Pauli's exclusion principle, we fill the energy levels with electrons.

(2 electrons, one spin up '↑' and one spin down '↓' per energy level)



(c) Energy levels, $E_n = \varepsilon n^2 = \left(h^2/8 m_e L^2 \right) n^2$

$h = 6.6 \times 10^{-34}$ J.S

m_e = electron mass

n = quantum number (1, 2, 3 ....)

HOMO → LUMO transition in the system given is

$n = 3 \longrightarrow n = 4$

$$\therefore \quad \Delta E = (4)^2 \left(h^2/8 m_e L^2 \right) - (3)^2 \left(h^2/8 m_e L^2 \right)$$

In atomic units $h = 2\pi\hbar = 2\pi \quad (\because \hbar = 1)$

$m_e = 1$

$1 A^\circ = \frac{1}{0.53} a_0$ (Bohr Radius)

$$\therefore \quad L = 8.4 A^\circ = 15.849 \, a_0$$

$$\Delta E = (16 - 9) \left((2\pi)^2 / (8 \times (15.849^2)) \right) \text{ a.u}$$

$$= 0.1375 \text{ Hartree}$$

$$\Delta E \left(\text{in kJ/mol} \right) = 0.1375 \times 627 = 86.23 \text{ kcal/mol}$$

(d) $\Delta E = hc/\lambda$ Fundamental formula of Spectroscopy.

λ – absorption wavelength, c – speed of light = 137 a.u

$$\Delta E = 0.1375 \text{ Hartree} = \frac{2\pi\hbar c}{\lambda}$$

$$\therefore \quad \lambda = \frac{2\pi \times 137}{0.1375} = 6260.33 \, a_0 = (6260.33 \times 0.53) A^\circ$$

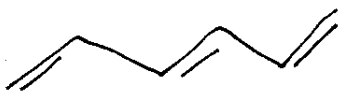
$$= 331.8 \text{ nm} \simeq 332 \text{ nm}.$$

Experimental value of $\lambda = 268\,nm$.

The λ that we get using the particle in a box model is ~ 30% greater than the λ obtained from experiment. This is due to the fact that we do not include the Coulombic potential [(nucleus - electron attraction) and (electron-electron repulsion)] and therefore lack the corrugation in the Potential energy levels. [Assumption that $V(x) = 0$ inside the box causes most error].

(e) Extra Credit Problem:

Consider Linear conjugated alkenes with '2k' carbons and hence 'k' double bonds

Eg.  1,3,5 - hexatriene has $k = 3 \Rightarrow (2k = 6)$ carbons

The formula,

$$\lambda = (260\,nm)\, k^2/(2k+1) \approx 130\,nm\,(k)$$

Suggests that adding a double bond to the conjugated chain increases the wavelength by 130nm.

Naively, if we analyze the variation of E_n with respect to chain length, L,

$$L = (\text{bond length} \times 2k)$$

$$\text{Hence } E_n = \frac{n^2 h^2}{8m\,(\text{bond length})^2 \times (2k)^2}$$

Hence we might expect

$$\lambda \propto k^2$$

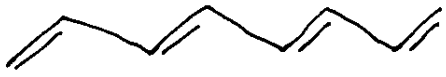
The physical origin of this linear relationship ⇒ between the chain length and HOMO → LUMO absorption wavelength can be explained as follows:

Consider $k = 3$

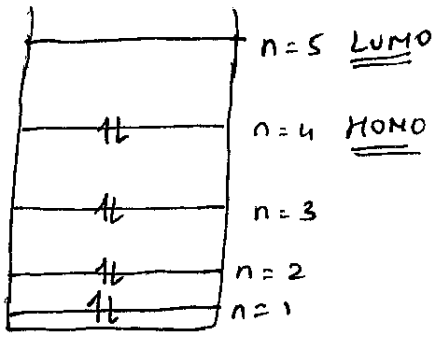
$$\Delta E = (4^2 - 3^2)\left(\frac{h^2}{8m(1.4 \times 6)}\right)$$

$n = 4$ LUMO
$n = 3$ HOMO
$L = (1.4 \times 6)\,A^\circ$

$k = 4$



$$\Delta E = (5^2 - 4^2)\left(\frac{h^2}{8m(1.4 \times 8)}\right)$$



Illy for $k = 5$

$n = 6 \rightarrow$ LUMO

$n = 5 \rightarrow$ HOMO

$$\therefore \quad \Delta E = (6^2 - 5^2)\left(\frac{h^2}{8m(1.4 \times 10)}\right)$$

Generalizing

$$\Delta E = ((k+1)^2 - k^2)\left[h^2 / (8m(1.4 \times (2k))^2)\right]$$

$$= (k^2 + 2k + 1 - k^2)\left[h^2 / (8m(2.8)^2 k^2)\right]$$

$$= \frac{(2k+1)}{k^2}\left(\frac{(2\pi)^2}{8(2.8/0.53)^2}\right) \text{ a.u}$$

$$\therefore \quad \lambda = hc/\Delta E = \frac{2\pi \times 137 \times 8(2.8/0.53)^2}{(2\pi)^2}\,\frac{k^2}{(2k+1)}$$

$$\lambda = 4868.5 \text{ a.u} \quad \frac{k^2}{(2k+1)}$$

$$= \left(\frac{4868.5 \times 0.53}{10}\right) \text{nm} \quad \frac{k^2}{(2k+1)}$$

$$\lambda \approx (260)\,\text{nm} \quad k^2/2k+1$$

when $2k >> 1$

$$\lambda \approx (260\,\text{nm}) \quad (k^2/2k)$$

$$\approx 130\,\text{nm}\,(k)$$

So eventhough due to the increase in chain length, we might expect $\lambda \propto k^2$, the HOMO – LUMO gap is also affected due to the increase in 'k' and hence the number of electrons in the system which contributes to the term $2k+1$, hence $\lambda \propto (k^2/2k+1)$ and $\lambda \approx \propto k$ when $2k >> 1$.