Solved Numericals

(Electronic Spectroscopy)

Q-1 Calculate $\pi - \pi^*$ transition wavelength for ethylene, given C=C bond length is 134 pm.

Ans: $\Delta E = E_{\frac{N}{2}+1} - E_{\frac{N}{2}}$

$$= \frac{\left(\frac{N}{2}+1\right)^2 h^2}{8 m_e a^2} - \frac{\left(\frac{N}{2}\right)^2 h^2}{8 m_e a^2}$$

$$= \frac{h^2 (N+1)}{8 m_e a^2} \quad -(1)$$

m_e = mass of electron = 9.1×10^{-31} kg -(2)

a = length of molecules (as per Free Electron Model)

$= (N - 1 + \frac{1}{2} + \frac{1}{2}) l$ (half C-C bond is added on both sides)

$= (N) l$ -(3) $\quad l = 134$ pm -(5)

$N = 2$ -(4)

using values of (2), (3), (4) & (5) in (1)

$$\Delta E = \frac{(6.6 \times 10^{-34}\ Js)^2 (2+1)}{8 \times 9.1 \times 10^{-31}\ kg \times ((2) \times 134 \times 10^{-12}\ m)^2} \quad -(6)$$

$1 J = 1 kg\ m^2\ s^{-2}$

$\Delta E = h\nu = h\frac{c}{\lambda}$ -(7)

$c = 3 \times 10^8\ m s^{-1}$ (speed of light)

Using (7.) & (8) in (6.)

$$\frac{6.6\times10^{-34}\,Js \times 3\times10^{8}\,ms^{-1}}{\lambda} = \frac{(6.6\times10^{-34}\,Js)^2\times 3}{8\times 9.1\times10^{-31}\,kg \times (2\times134\times10^{-12}\,m)^2}$$

$$\lambda = \frac{3\times10^{8}\,ms^{-1}\times 8\times 9.1\times10^{-31}\,kg\times(2\times134\times10^{-12}\,m)^2}{3\times6.6\times10^{-34}\,Js}$$

$$= \frac{\cancel{35294313.6}\ 15686361.6\times10^{-24+8-31}\ m^2\, ms^{-1}\, kg}{19.8\times10^{-34}\ kg\, m^2 s^{-2}\, s} \qquad (1J = 1\,kg\,m^2 s^{-2})$$

$$= \cancel{1782541.09}\ 792240.485\times10^{-24+8-31+34}\ m$$

$$\cancel{=178.2\times10^{-9}\,m} \qquad = 79.2\times10^{-9}\,m$$

$$\cancel{=178.2\,nm} \qquad = 79.2\,nm$$

Q-2 Calculate $\pi-\pi^*$ transition wavelength for (I) 1,3-butadiene & (II) 1,3,5-hexatriene. Assume average bond length of 140 pm.

Ans: $\Delta E = \frac{h^2(N+1)}{8m_e a^2} = h\nu = \frac{hc}{\lambda}$ $\therefore \lambda = \frac{hc\,8m_e a^2}{h^2(N+1)}$

$$\lambda = \frac{c\,8m_e(N+1)^2 l^2}{h(N+1)}$$

~~N=4~~ $m_e = 9.1\times10^{-31}\,kg$

$h = 6.6\times10^{-34}\,Js$

$l = 140\,pm = 140\times10^{-12}\,m$

$c = 3\times10^{8}\,ms^{-1}$

(I) $N=4$, $\lambda =$ ~~540.4 nm~~ 207.5 nm

(II) $N=6$, $\lambda =$ ~~1059.3 nm~~ ~~454 nm~~ 333.5 nm