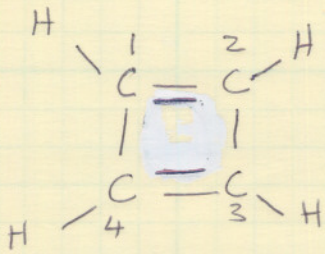
ATOMS, MOLECULES & REACTIONS

QUANTUM MECHANICS, SPRING, WEEK 8 HW

HW sheet

(27)



$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & H_{13}-ES_{13} & H_{14}-ES_{14} \\ H_{21}-ES_{21} & H_{22}-ES_{22} & H_{23}-ES_{23} & H_{24}-ES_{24} \\ H_{31}-ES_{31} & H_{32}-ES_{32} & H_{33}-ES_{33} & H_{34}-ES_{34} \\ H_{41}-ES_{41} & H_{42}-ES_{42} & H_{43}-ES_{43} & H_{44}-ES_{44} \end{vmatrix} = 0$$

$$\begin{vmatrix} \alpha-E & \beta & 0 & \beta \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ \beta & 0 & \beta & \alpha-E \end{vmatrix} = 0$$

Divide by β

$$\begin{vmatrix} \frac{\alpha-E}{\beta} & 1 & 0 & 1 \\ 1 & \frac{\alpha-E}{\beta} & 1 & 0 \\ 0 & 1 & \frac{\alpha-E}{\beta} & 1 \\ 1 & 0 & 1 & \frac{\alpha-E}{\beta} \end{vmatrix} = 0$$

Let $\frac{\alpha-E}{\beta} = x$

$$\begin{vmatrix} x & 1 & 0 & 1 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 1 & 0 & 1 & x \end{vmatrix} = 0$$

$$x \begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} - 1 \begin{vmatrix} 1 & 1 & 0 \\ 0 & x & 1 \\ 1 & 1 & x \end{vmatrix} - \begin{vmatrix} 1 & x & 1 \\ 0 & 1 & x \\ 1 & 0 & 1 \end{vmatrix} = 0$$

$$x\left\{ x\left[x^2-1\right] - \left[x-0\right] \right\} - \left\{ (x^2-1) - (0-1) \right\} -$$

$$\left\{ 1 - x(0-x) + (0-1) \right\} = 0$$

$$x\left\{ x^3 - x - x \right\} - \left\{ x^2 \cancel{-1} \cancel{+1} \right\} - \left\{ \cancel{1} + x^2 \cancel{-1} \right\} = 0$$

$$x^4 - 2x^2 - x^2 - x^2 = 0 \Rightarrow x^4 - 4x^2 = 0$$

$$x^2 \left(x^2 - 4 \right) = 0$$

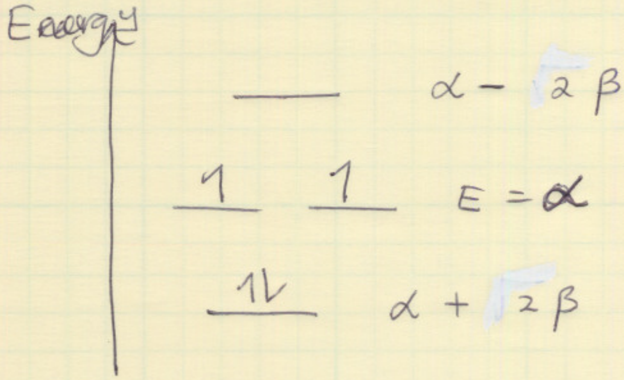
$$x^2 = 0 \qquad x^2 - 4 = 0$$

$$x = 0,\ 0 \qquad x^2 = 4 \qquad x = \pm 2$$

$$\frac{\alpha - E}{\beta} = x = 0 \Rightarrow E = \alpha,\ \alpha$$

$$\frac{\alpha - E}{\beta} = x = 2 \Rightarrow E = \alpha - 2\beta$$

$$\frac{\alpha - E}{\beta} = -\sqrt{2} \Rightarrow E = \alpha + \sqrt{2}\beta$$



π electron energy $= 2(\alpha + 2\beta) + (\alpha + \alpha)$

$$= \underline{\underline{4\alpha + 4\beta}}$$

energy of ethylene $= 2(\alpha + \beta) = 2\alpha + 2\beta$
(2 π electron system)

energy of a 4π electron system $= 2$(ethylene) $\Big\} = 4\alpha + 4\beta$

∴ There is no extra π-electron stabilization in C_4H_4

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① $\lambda = 10^{3}$ cm $\qquad E = \dfrac{hc}{\lambda} = kT$

$$T = \frac{hc}{\lambda k} = \frac{(6.626\times10^{-34}\ \mathrm{J\,s})(2.99\times10^{8}\ \mathrm{cm\,s^{-1}})}{1.381\times10^{-23}\ \mathrm{J\,K^{-1}}}\cdot\left(\frac{1}{\lambda}\right)$$

$$T = 1.4346\times10^{-2}\ \mathrm{cm\,K^{+1}}\left(\frac{1}{\lambda}\right)$$

$\lambda = 10^{3}$ cm $\qquad T = 1.4346\times10^{-2}\ \mathrm{cm\,K}\left(\dfrac{1}{10^{3}\ \mathrm{cm}}\right)$

$$= \underline{\underline{1.435\times10^{-5}\ \mathrm{K}}}$$

$\lambda = 10^{-1}$ cm $\qquad T = 1.435\times10^{-2}\ \mathrm{cm\,K}\left(\dfrac{1}{10^{-1}\ \mathrm{cm}}\right)$

$$= 1.435\times10^{-1}\ \mathrm{K}$$

$\lambda = 10^{-3}$ cm $\qquad T = 1.435\times10^{-2}\ \mathrm{cm\,K}\left(\dfrac{1}{10^{-3}\ \mathrm{cm}}\right) = \underline{\underline{14.35\ \mathrm{K}}}$

$\lambda = 10^{-5}$ cm $\qquad T = 1.435\times10^{-2}\ \mathrm{cm\,K}\left(\dfrac{1}{10^{-5}\ \mathrm{cm}}\right) = \underline{\underline{1.435\times10^{3}\ \mathrm{K}}}$

(2) $E = \frac{hc}{\lambda}$ $\lambda = \frac{hc}{E}$

$E = 40\ kJ\ mol^{-1}$

$$\lambda = \frac{(6.626 \times 10^{-34}\ Js)(2.99 \times 10^{10}\ cm\ s^{-1})}{40\ kJ\ mol^{-1}} \cdot \frac{6.02 \times 10^{23}}{mol} \times \frac{kJ}{10^{3}\ J}$$

$$= 2.9817 \times 10^{-4}\ cm \times \frac{m}{100\ cm} \times \frac{10^{9}\ nm}{m}$$

$$\lambda = \underline{\underline{2981.67\ nm}}$$

$$\frac{1}{\lambda} = \frac{1}{2.9817 \times 10^{-4}\ cm} = \underline{\underline{3353.79\ cm^{-1}}}$$

$$\frac{40\ kJ}{mol} \times \frac{mol}{6.02 \times 10^{23}} \times \frac{10^{3}\ J}{kJ} \times \frac{eV}{1.602 \times 10^{-19}\ J}$$

$$= \underline{\underline{0.415\ eV}}$$

$E = 400\ kJ\ mol^{-1}$

$$\lambda = \frac{(6.626 \times 10^{-34}\ Js)(2.99 \times 10^{10}\ cm\ s^{-1})}{400\ kJ\ mol^{-1}} \cdot \frac{6.02 \times 10^{23}}{mol} \cdot \frac{kJ}{10^{3}\ J}$$

$$= \underline{\underline{298.17\ nm}}$$

$$\frac{1}{\lambda} = \frac{1}{298.17\ nm} \times \frac{10^{7}\ nm}{cm} = \underline{\underline{33,537.9\ cm^{-1}}}$$

$$\frac{400\ kJ}{mol} \times \frac{mol}{6.02 \times 10^{23}} \times \frac{10^{3}\ J}{kJ} \times \frac{eV}{1.602 \times 10^{-19}\ J} = \underline{\underline{4.148\ eV}}$$

③ kT at $25°C = (1.381 \times 10^{-23}\ J K^{-1})(298.15 K)$

$= 4.1175 \times 10^{-21}\ J$

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

$\frac{1}{\lambda} = \frac{E}{hc} = \frac{4.1175 \times 10^{-21}\ J}{(6.626 \times 10^{-34}\ Js)(2.99 \times 10^{10}\ cm\ s^{-1})}$

$= \underline{\underline{207.83\ cm^{-1}}}$

$\lambda = \frac{1}{207.83\ cm^{-1}} = \underline{\underline{4.812 \times 10^{-3}\ cm}}$

⑤ $D^{35}Cl$ $\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{(2)(35)}{2+35}$ amu

$= 1.8919$ amu or 1.8919 g/mol

$= 1.8919 \text{ amu} \times \frac{1.673 \times 10^{-27}\ kg}{amu}$

$= \underline{\underline{3.165 \times 10^{-27}\ kg}}$

$I_e = \mu R_e^2 = (3.165 \times 10^{-27}\ kg)\left[(127.5\ pm)\left(\frac{m}{10^{12}\ pm}\right)\right]^2$

$= \underline{\underline{5.145 \times 10^{-47}\ kg\,m^2}}$

(8) $F(J) = B\,J(J+1)$

$\frac{kg\,m^2 s^{-2}\,s}{kg\,m^2 \;\; m\,s^{-1}}$

$F(0) = 0 \qquad F(1) = 2B$

$\Delta F = F(1) - F(0) = 2B$.

$$B = \frac{h}{8\pi^2 I C} = \frac{6.626 \times 10^{-34}\ J\,s}{8\pi^2 (5.145 \times 10^{-47}\ kg\,m^2)(2.99 \times 10^{8}\ m\,s^{-1})}$$

(use I from problem #5)

$$B = 562.44\ m^{-1} \times \frac{m}{100\ cm} = 5.6244\ cm^{-1}$$

$$\Delta F = 2(5.6244\ cm^{-1}) = \underline{\underline{11.2489\ cm^{-1}}}$$

$$\lambda = \frac{1}{11.2489\ cm^{-1}} = 0.088898\ cm$$

$$= \underline{\underline{8.8898 \times 10^{-2}\ cm}}$$