ADVANCED CHEMISTRY

QUANTUM MECHANICS - SPRING - WEEK 5

Chapter 11

(15) $\psi_1 = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4$ no nodes

$\psi_2 = c_1\phi_1 + c_2\phi_2 - c_3\phi_3 - c_4\phi_4$ one node

$\psi_2 = c_1\phi_1 - c_2\phi_2 - c_3\phi_3 + c_4\phi_4$ two nodes

$\psi_4 = c_1\phi_1 - c_2\phi_2 + c_3\phi_3 - c_4\phi_4$ three nodes.

(17) 1,3 butadiene

using fig. 11.21

π electron energy $= 2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta)$

$= 4\alpha + 4.472\beta$

$\left.\begin{array}{l}\pi \text{ electron energy of} \\ \text{two ethylene molecules}\end{array}\right\} = 2\left[2(\alpha+\beta)\right] = 4\alpha + 4\beta$

$\therefore$ delocalization energy $= 4\alpha + 4.472\beta - (4\alpha + 4\beta)$

$= \underline{0.472\beta}$

benzene using fig 11.22

π electron energy $= 2(\alpha+2\beta) + 4(\alpha+\beta) = 6\alpha + 8\beta$

$\left.\begin{array}{l}\pi \text{ electron energy} \\ \text{of 3 ethylene molecules}\end{array}\right\} = 3\left[2(\alpha+\beta)\right] = 6\alpha + 6\beta$

delocalization energy $= 6\alpha + 8\beta - (6\alpha + 6\beta) = \underline{2\beta}$

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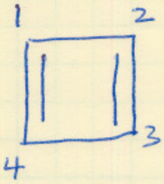


Secular ~~equa~~ determinant

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

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

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

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

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

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

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

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

$$- \left[(1-0) - x(0-x) + (0-1)\right] = 0$$

$$x\left[x^3 - x - x\right] - \left[x^2 - 1 + 1\right] - \left[1 + x^2 - 1\right] = 0$$

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

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

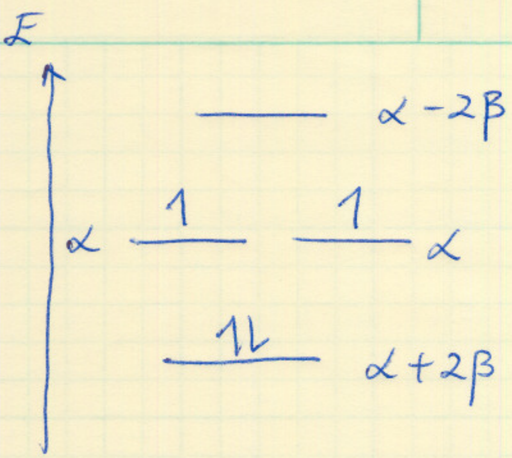
$$x^2(x+2)(x-2) = 0$$

$$\Rightarrow x = 0, 0, -2, +2$$

When $x=0$ $\quad \dfrac{\alpha - E}{\beta} = 0 \Rightarrow \underline{E = \alpha, \alpha}$

When $x = -2$ $\quad \dfrac{\alpha - E}{\beta} = -2 \Rightarrow \underline{E = \alpha + 2\beta}$

When $x = +2$ $\quad \dfrac{\alpha - E}{\beta} = 2 \Rightarrow E = \underline{\alpha - 2\beta}$



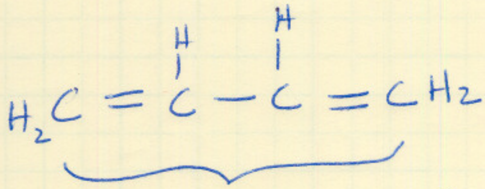
π electron energy $= 2(\alpha+2\beta) + \alpha + \alpha$

$= 4\alpha + 4\beta$

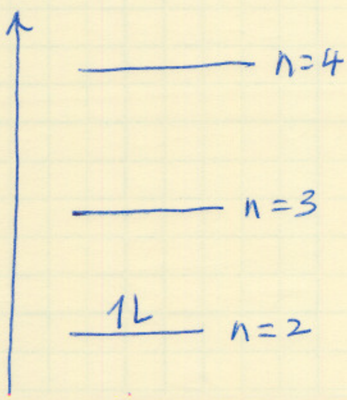
energy of two ethylenes $= 2[2(\alpha+\beta)] = 4\alpha + 4\beta$

delocalization energy $= 4\alpha+4\beta - (4\alpha+4\beta) = 0$

There is no π electron stabilization due to delocalization

(28)  butadiene

length $= (4-1)\,150\,\text{pm} = 450\,\text{pm}$ 4 π electrons



using the particle in a box model $E_n = \dfrac{n^2 h^2}{8ml^2}$

Electron configurations in the ground state 2 electrons in $n=1$
2 electrons in $n=2$

Excitation energy (ΔE) $= E_3 - E_2$

~~[illegible]~~

$$= \frac{3^2 h^2}{8ml^2} - \frac{2^2 h^2}{8ml^2}$$

$$= \frac{5h^2}{8ml^2}$$

m = mass of an $\bar{e}$

l = 450 pm.

$$= \frac{5(6.626\times10^{-34}\ \mathrm{J\,s})^2}{8(9.109\times10^{-31}\ \mathrm{kg})(450\times10^{-12}\ \mathrm{m})^2}$$

$$= \underline{\underline{1.4876\times10^{-18}\ \mathrm{J}}}$$

$$\frac{J^2 s^2}{kg\ m^2}$$

$$\frac{J\,(\cancel{kg}\,m^2 \cancel{s^{-2}})\,\cancel{s^2}}{\cancel{kg}\ \cancel{m^2}}$$

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

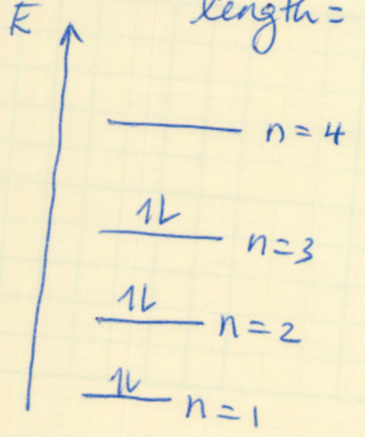
$$\lambda = \frac{(6.626\times10^{-34}\ \mathrm{J\,s})(2.998\times10^{8}\ \mathrm{m\,s^{-1}})}{(1.4876\times10^{-18}\ \mathrm{J})}$$

$$= 1.33535\times10^{-7}\ \mathrm{m} \times \left(\frac{10^9\ \mathrm{nm}}{\mathrm{m}}\right)$$

$$= \underline{\underline{133.535\ \mathrm{nm}}}$$

$$\underbrace{H_2C=CH-CH=CH-CH=CH_2}$$ hexatriene

length = $(6-1)$ 150 pm = 750 pm = l 6 π electrons



Ground state

2 electrons each in $n=1$, $n=2$ and $n=3$

First excited state

2 electrons each in $n=1$, $n=2$

1 electron each in $n=3$, $n=4$

excitation energy $= E_4 - E_3$

$$= \frac{4^2 h^2}{8ml^2} - \frac{3^2 h^2}{8ml^2} = \frac{7h^2}{8ml^2}$$

$$= \frac{7(6.626 \times 10^{-34}\ \mathrm{Js})^2}{8(9.109 \times 10^{-31}\ \mathrm{kg})(750 \times 10^{-12}\ \mathrm{m})^2}$$

$$= \underline{\underline{7.4975 \times 10^{-19}\ \mathrm{J}}}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34}\ \mathrm{Js})(2.998 \times 10^{8}\ \mathrm{ms^{-1}})}{(7.4975 \times 10^{-19}\ \mathrm{J})}$$

$$= 2.6495 \times 10^{-7}\ \mathrm{m} = \underline{\underline{264.95\ \mathrm{nm}}}$$

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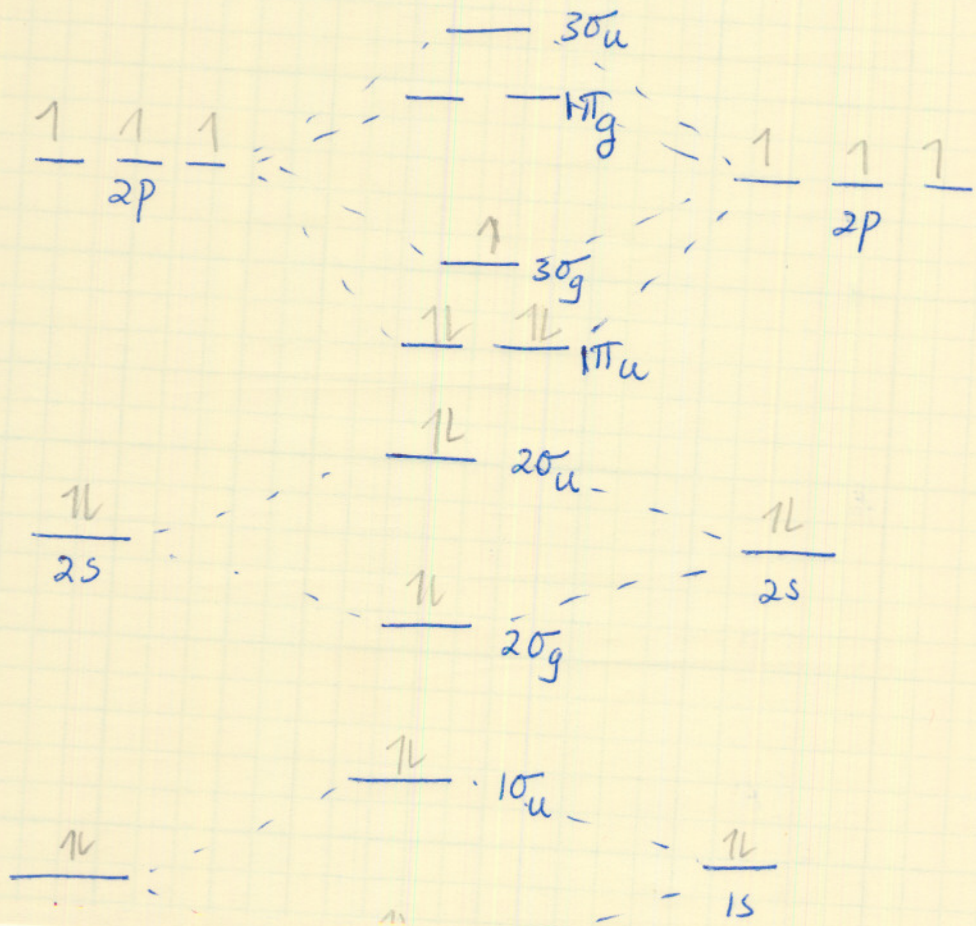


Li_2^+ $(1\sigma_g)^2 (1\sigma_u)^2 (2\sigma_g)^1$ bond order $= \frac{1}{2}(3-2) = \underline{\underline{0.5}}$

Be_2^+ $(1\sigma_g)^2 (1\sigma_u)^2 (2\sigma_g)^2 (2\sigma_u)^1$ bond order $= \frac{1}{2}(4-3) = \underline{\underline{0.5}}$

B_2^+ $(1\sigma_g)^2 (1\sigma_u)^2 (2\sigma_g)^2 (2\sigma_u^2) (1\pi_u)^1$ b.o. $= \frac{1}{2}(5-4) = \underline{\underline{0.5}}$

N_2^+ $(1\sigma_g)^2 (1\sigma_u)^2 (2\sigma_g)^2 (2\sigma_u)^2 (1\pi_u)^4 (3\sigma_g)^1$

bond order $= \frac{1}{2}(9-4) = \underline{\underline{2.5}}$

Chapter 12

① C_{2v} ② C_{3v} ③ D_{4h} ④ C_2 ⑤ D_{3h}

Chapter 13

②

$$\frac{40\ kJ}{mol} \times \frac{mol}{6.02\times10^{23}} \times \frac{10^3\ J}{kJ} \times \frac{eV}{1.602\times10^{-19}\ J} = \underline{\underline{0.415\ eV}}$$

$$\frac{400\ kJ}{mol} \times \frac{mol}{6.02\times10^{23}} \times \frac{10^3\ J}{kJ} \times \frac{eV}{1.602\times10^{-19}\ J} = \underline{\underline{4.15\ eV}}$$

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

$$\lambda_1 = \frac{(6.626\times10^{-34}\ Js)(2.998\times10^{8}\ ms^{-1})}{(0.415\ eV)} \left(\frac{eV}{1.602\times10^{-19}\ J}\right) = 2.988\times10^{-6}\ m$$

$$= 2.988\times10^{3}\ nm = \underline{\underline{2988\ nm}}$$

$$\lambda_2 = \frac{(6.626\times10^{-34}\,Js)(2.998\times10^{8}\,m\,s^{-1})}{(4.15\,eV)}\left(\frac{eV}{1.602\times10^{-19}\,J}\right)$$

$$= 2.988\times10^{-7}\,m = 2.988\times10^{2}\,nm = \underline{\underline{298.8\,nm}}$$

$$\tilde{\nu}_1 = \frac{1}{2.988\times10^{-6}\,m} = 3.347\times10^{5}\,m^{-1} = \underline{\underline{3.347\times10^{3}\,cm^{-1}}}$$

$$\tilde{\nu}_2 = \frac{1}{2.988\times10^{-7}\,m} = 3.347\times10^{6}\,m^{-1}\times\left(\frac{m}{100\,cm}\right) = \underline{\underline{3.347\times10^{4}\,cm^{-1}}}$$

5 $^{2}D^{35}Cl$ $\quad \mu = \left(\frac{2\times35}{2+35}\right)amu \times \left(\frac{1.661\times10^{-27}\,kg}{1\,amu}\right)$

$$= \underline{\underline{3.142\times10^{-27}\,kg}}$$

$$I = \mu R_e^2 = (3.142\times10^{-27}\,kg)\left(127.5\,pm\times\frac{10^{-12}\,m}{pm}\right)^2$$

$$\underline{\underline{I = 5.108\times10^{-47}\,kg\,m^2}}$$

7 The gross selection rule - molecules <u>must</u> have a permanent dipole moment. Only the following molecules will therefore have a pure rotational spectrum.

HBr, CH_3CH_2OH, H_2O,

(8)

E

$J=1 \qquad E_J = BJ(J+1) = 2B \qquad E_1 = 2B$

$J=0 \qquad E_J = J(J+1)B = 0 \qquad E_0 = 0$

$$\Delta E = E_1 - E_0 = 2B$$

$$B = \frac{h}{8\pi^2 I c} \qquad I = 5.108 \times 10^{-47}\ \text{kg m}^2 \ (\text{Problem } 5)$$

$$B = \frac{6.626 \times 10^{-34}\ \text{Js}}{8\pi^2 (5.108 \times 10^{-47}\ \text{kg m}^2)(2.998 \times 10^{10}\ \text{cm s}^{-1})}$$

$$= 5.479\ \text{cm}^{-1}$$

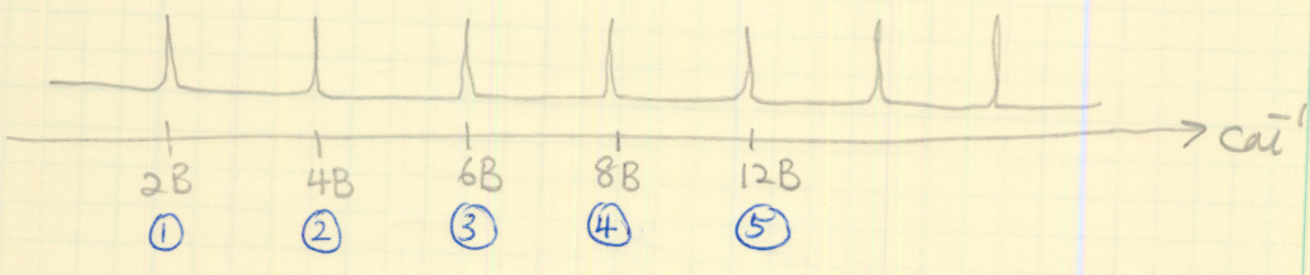
$$\Delta E = (5.479\ \text{cm}^{-1})2 = \underline{\underline{10.959\ \text{cm}^{-1}}}$$

$$\cancel{\Delta E = \frac{hc}{\lambda} \qquad \lambda = \frac{hc}{\Delta E} = (6.626 \times 10^{-34}\ \text{Js})(2.99 \times 10^{8}\ \text{ms}^{-1})}$$

$$\tilde{\nu} = 10.959\ \text{cm}^{-1} \qquad \frac{1}{\lambda} = 10.959\ \text{cm}^{-1}$$

$$\lambda = \frac{1}{10.959\ \text{cm}^{-1}} = \underline{\underline{9.124 \times 10^{-2}\ \text{cm}}}$$

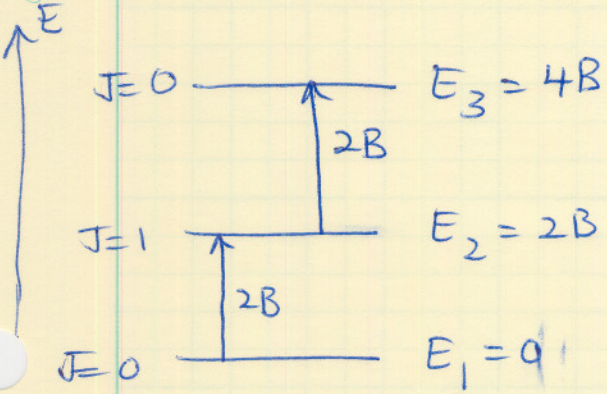
(9) The pure rotational spectrum of a diatomic molecule looks like the following.



from this is easy to note that the frequency of peak ② = 2(freq. of peak ①) also these are the only two peaks that have such a relationship.

$\therefore$ $3.863\ cm^{-1}$ is $J=0 \rightarrow J=1$ transition

$7.725\ cm^{-1}$ is $J=1 \rightarrow J=2$ transition



$$\Rightarrow \quad 2B = 3.863\ cm^{-1}$$

$$B = 1.9315\ cm^{-1}$$

$$B = \frac{h}{8\pi^2 I c}$$

$$I = \frac{h}{8\pi^2 B c} = \frac{6.626 \times 10^{-34}\ J\,s}{8\pi^2 (1.9315\ cm^{-1})(2.998 \times 10^{10}\ cm\,s^{-1})}$$

$$I = 1.449 \times 10^{-46}\ J\,s^2 = 1.449 \times 10^{-46}\ kg\,m^2$$

For $^{12}C^{16}O$ $\quad \mu = \left(\frac{12 \times 16}{12+16}\right) amu \times \left(\frac{1.661 \times 10^{-27}\ kg}{1\,amu}\right)$

$$= 1.139 \times 10^{-26}\ kg$$

$$I = \mu R^2 \Rightarrow R^2 = \frac{I}{\mu} = \frac{1.449 \times 10^{-46}\ kg\,m^2}{1.139 \times 10^{-26}\ kg}$$

$$R^2 = 1.272 \times 10^{-20}\ m^2$$

$$R = 1.128 \times 10^{-10}\ m = 1.128\ \mathring{A}$$

The third line occurs at $6B = \underline{\underline{11.589\ cm^{-1}}}$

The fourth line occurs at $8B = \underline{\underline{15.452\ cm^{-1}}}$

(10) $\underline{^{13}C\,^{16}O}$ $\mu = \left(\frac{13 \times 16}{13+16}\right) amu \times \left(\frac{1.661 \times 10^{-27}\ kg}{amu}\right) = 1.191 \times 10^{-26}\ kg$

$I = \mu R^2 = 1.191 \times 10^{-26}\ kg\ (1.272 \times 10^{-20}\ m^2)$

$= 1.515 \times 10^{-46}\ kg\ m^2$

$$B = \frac{h}{8\pi^2 I c} = \frac{6.626 \times 10^{-34}\ JS}{8\pi^2 (1.515 \times 10^{-46}\ kg\,m^2)(2.998 \times 10^{10}\ cm\ s^{-1})}$$

$B = 1.847\ cm^{-1}$

first rotational transition ($J=0 \rightarrow J=1$) is at $2B$ $\Big\} = \underline{\underline{3.694\ cm^{-1}}}$

$\underline{\underline{^{13}C\,^{17}O}}$ $\mu = \left(\frac{13 \times 17}{13+17}\right) amu \times \left(\frac{1.661 \times 10^{-27}\ kg}{amu}\right) = 1.224 \times 10^{-26}\ kg$

$I = \mu R^2 = (1.224 \times 10^{-26}\ kg)(1.272 \times 10^{-20}\ m^2) = 1.556 \times 10^{-46}\ kg\,m^2$

$$B = \frac{6.626 \times 10^{-34}\ JS}{8\pi^2 (1.556 \times 10^{-46}\ kg\,m^2)(2.998 \times 10^{10}\ cm\ s^{-1})}$$

$= 1.798\ cm^{-1}$

First transition is at $2B = \underline{\underline{3.597\ cm^{-1}}}$

$^{12}C\,^{17}O$ $\mu = \left(\frac{12\times17}{12+17}\,amu\right)\times\left(\frac{1.661\times10^{-27}\,kg}{amu}\right) = 1.168\times10^{-26}\,kg$

$I = \mu R^2 = (1.168\times10^{-26}\,kg)(1.272\times10^{-20}\,m^2) = 1.486\times10^{-46}\,kg\,m^2$

$$B = \frac{6.626\times10^{-34}\,JS}{8\pi^2(1.486\times10^{-46})\,kg\,m^2\,(2.998\times10^{10}\,cm\,s^{-1})}$$

$= 1.883\,cm^{-1}$

First transition is at $2B = \underline{\underline{3.767\,cm^{-1}}}$

(11) Since the equally spaced lines are separated by $(\Delta\tilde{\nu}) \cdot 2B$;

$2B = 12.8\,cm^{-1} \Rightarrow B = 6.4\,cm^{-1}$

$B = \frac{h}{8\pi^2 IC}$ $\quad I = \frac{h}{8\pi^2 BC}$

$$I = \frac{6.626\times10^{-34}\,JS}{8\pi^2(6.4\,cm^{-1})(2.998\times10^{10}\,cm\,s^{-1})}$$

$= \underline{\underline{4.374\times10^{-47}\,kg\,m^2}}$

$\mu = \left(\frac{1\times127}{1+127}\right)amu\left(\frac{1.661\times10^{-27}\,kg}{amu}\right)$

$= 1.648\times10^{-27}\,kg$ $\quad I = \mu R^2$

$10^{-47}\,kg\,m^2$ $\quad -20$

$$R = 1.629 \times 10^{-10}\ m = \underline{\underline{1.629\ \text{Å}}}$$

(12) $J=2$ ——— $E_2 = 6B$ $\quad N_2 = 5\, e^{-E_2/kT} = 5\, e^{-6Bhc/kT}$

$J=1$ ——— $E_1 = 2B$ $\quad N_1 = 3\, e^{-E_1/kT} = 3\, e^{-2Bhc/kT}$

$J=0$ ——— $E_0 = 0$ $\quad N_0 = 1\, e^{-E_0/kT} = 1$

for $^1H^{35}Cl$ $\quad B = 10.5934\ cm^{-1}$ (Table 13.4 of text)

$$\frac{F_1}{F_0} = \frac{3\, e^{-2Bhc/kT}}{1} \cancel{\approx 3Be^{-2}}$$

$$= 3\, e^{-2(10.5934\, cm^{-1})(6.626\times10^{-34}\, Js)(2.998\times10^{10}\, cm\, s^{-1})/kT}$$

$$\frac{F_1}{F_0} = 3\, e^{-4.209\times10^{-22}\, J/(1.381\times10^{-23}\, J K^{-1})T}$$

$$\frac{F_1}{F_0} = 3\, e^{-30.476/T (K^{-1})}$$

at 300 K $\quad \frac{F_1}{F_0} = 3\, e^{-30.476/(300K)K^{-1}} = \underline{\underline{2.710}}$

at 1000 K $\quad \frac{F_1}{F_0} = 3\, e^{-30.476/(1000K)K^{-1}} = \underline{\underline{2.9010}}$

$$\frac{F_2}{F_0} = \frac{5\,e^{-6Bhc/kT}}{1}$$

$$\frac{F_2}{F_0} = 5\,e^{-6(10.5934\,cm^{-1})(6.626\times10^{-34}\,Js)(2.998\times10^{10}\,cm\,s^{-1})/(1.381\times10^{-23}\,JK^{-1})T}$$

$$= 5\,e^{-9.143\times10^{1}/T(K^{-1})}$$

at 300K $\frac{F_2}{F_1} = 5\,e^{-91.43/(300K)\,K^{-1}} = \underline{\underline{3.686}}$

at 1000K $\frac{F_2}{F_1} = 5\,e^{-91.43/(1000K)K^{-1}} = \underline{\underline{4.563}}$

For $J = 3$ $N_3 = 7\,e^{-12Bhc/kT}$

$$\frac{F_3}{F_0} = \frac{7\,e^{-12Bhc/kT}}{1}$$

$$= 7\,e^{-12(10.5934\,cm^{-1})(6.626\times10^{-34}\,Js)(2.998\times10^{10}\,cm\,s^{-1})/(1.381\times10^{-23}\,JK^{-1})T}$$

$$= 7\,e^{-182.85/(K^{-1})T}$$

at 300K $\frac{F_3}{F_0} = \underline{\underline{3.805}}$

at 1000K $\frac{F_3}{F_0} = \underline{\underline{5.830}}$