ATOMS, MOLECULES & RESEARCH
QUANTUM MECHANICS - SPRING - WEEK 7

Chapter 13

① $\lambda = 10^{3}\ cm \qquad E = \dfrac{hc}{\lambda} = \dfrac{(6.626\times10^{-34}\ Js)(2.99\times10^{10}\ cm\,s^{-1})}{10^{3}\ cm}$

$E = 1.9812\times10^{-26}\ J = kT$

$T = \dfrac{1.9812\times10^{-26}\ J}{1.381\times10^{-23}\ J\,K^{-1}} = \underline{\underline{1.4346\times10^{-3}\ K}}$

Note: $T = \dfrac{hc}{\lambda k}$

when $\lambda = 10^{-1}\ cm \qquad T = \dfrac{(6.626\times10^{-34}\ Js)(2.99\times10^{10}\ cm\,s^{-1})}{(10^{-1}\ cm)(1.381\times10^{-23}\ J\,K^{-1})}$

$= \underline{\underline{14.34\ K}}$

when $\lambda = 10^{-3}\ cm \qquad T = \underline{\underline{1434.6\ K}}$

when $\lambda = 10^{-5}\ cm \qquad T = \underline{\underline{143{,}460\ K}}$

② $40\ \dfrac{kJ}{mol} \times \dfrac{10^{3}\ J}{kJ} \times \dfrac{1}{(6.626\times10^{-34}\ Js)(2.99\times10^{8}\ m\,s^{-1})}$

$= \dfrac{2.019\times10^{29}\ m^{-1}}{mol} \times \dfrac{mol}{6.02\times10^{23}} \times \dfrac{10^{-9}\ m}{nm} =$

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

$$\lambda = \frac{(6.626 \times 10^{-34}\, Js)(2.99 \times 10^{8}\, ms^{-1})}{40 \times 10^{3}\, J\, mol^{-1}} \times \frac{6.02 \times 10^{23}}{mol} \times \frac{10^{9}\, nm}{m}$$

$$= \underline{\underline{2981.7\, nm}}$$

$$\frac{1}{\lambda} = \frac{1}{2981.7\, nm} \cdot \frac{nm}{10^{-7}\, cm} = \underline{\underline{3353.8\, cm^{-1}}}$$

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

(3) $E = kT = (1.381 \times 10^{-23}\, J\, K^{-1})(298.15\, K) = 4.117 \times 10^{-21}\, J$

$$E = \frac{hc}{\lambda} \qquad \frac{1}{\lambda} = \frac{E}{hc} = \frac{4.117 \times 10^{-21}\, J}{(6.626 \times 10^{-34}\, JS)(2.99 \times 10^{8}\, ms^{-1})}$$

$$\frac{1}{\lambda} = 20,782.9\, m^{-1} = \underline{\underline{207.8\, cm^{-1}}}$$

$$\lambda = \frac{1}{207.8\, cm^{-1}} = \underline{\underline{4.81 \times 10^{-3}\, cm}}$$

(5) $$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{(2)(35)}{(2+35)}\, amu \times \frac{1.661 \times 10^{-27}\, kg}{1\, amu}$$

$$\mu = \underline{\underline{3.142 \times 10^{-27}\, kg}}$$

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

$$= \underline{\underline{5.108 \times 10^{-47}\, kg\, m^2}}$$

(8)

——— $J=1 \quad E_1 = 2B$

——— $J=0 \quad E_0 = 0$

$\therefore \; E_1 - E_0 = 2B \qquad\qquad B = \dfrac{h}{8\pi^2 I C}$

$I = \mu R^2 = 5.108 \times 10^{-47}\ \text{kg m}^2$

$$B = \frac{6.626\times10^{-34}\ \text{J s}}{8\pi^2\left(5.108\times10^{-47}\ \text{kg m}^2\right)\left(2.99\times10^{8}\ \text{m s}^{-1}\right)} \times \frac{\text{m}}{10^2\ \text{cm}}$$

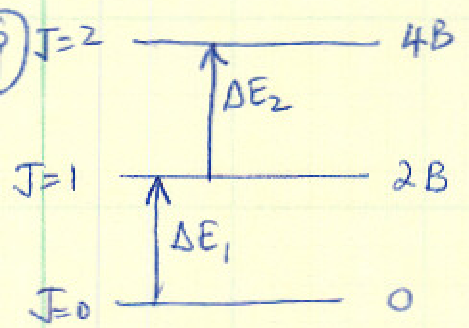
$B = 5.495\ \text{cm}^{-1}$

$\therefore \Delta E = 2B = \underline{\underline{10.99\ \text{cm}^{-1}}}$

$\cancel{\Delta E = \frac{hc}{\lambda} \qquad \frac{1}{\lambda} = \frac{\Delta E}{hc} = 10.99\ \text{cm}^{-1}}$

$\dfrac{1}{\lambda} = 10.99\ \text{cm}^{-1} \qquad \lambda = \dfrac{1}{10.99\ \text{cm}^{-1}} = \underline{\underline{9.09 \times 10^{-2}\ \text{cm}}}$

(9)



Let the excited state rotational quant. # = J'
ground state rot. quantum # = J''

$E' = B\,J'(J'+1) \qquad\qquad$ But $J' = J'' + 1$

$E'' = B\,J''(J''+1)$

$\therefore E' = B\left(J''+1\right)\left(J''+2\right)$

$$\Delta E = E' - E'' = B(J''+1)[J''+2 - J'']$$

$$\Delta E = 2B(J''+1)$$

when $J''=0$ $\quad \Delta E = 2B(0+1) = 2B = 2\left(\frac{h}{8\pi^2 I c}\right)$

$$\Delta E = 2B = 3.863\,cm^{-1} \Rightarrow \frac{h}{4\pi^2 I c} = 3.863\,cm^{-1} \quad (1)$$

when $J''=1$ $\quad \Delta E = 2B(1+1) = 4B = 4\left(\frac{h}{8\pi^2 I c}\right)$

$$= \frac{h}{2\pi^2 I c} = 7.725\,cm^{-1} \quad (2)$$

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

$\frac{J\,s}{cm^{-1}}$

$$(1) \Rightarrow I = \frac{h}{4\pi^2 c\,(3.863\,cm^{-1})} = \quad \times 10^{-4}\,kg\,m^{+2}$$

$$I = 1.453 \times 10^{-46}\,kg\,m^2 = \mu R_e^2$$

$$\mu = \frac{m_1 m_2}{(m_1+m_2)} = \frac{(12)(16)}{(12+16)}\,amu \times \frac{1.661\times10^{-27}\,kg}{1\,amu}$$

$$= 1.1389 \times 10^{-26}\,kg$$

$$I = \mu R_e^2 \Rightarrow R_e^2 = \frac{I}{\mu} = \frac{1.453\times10^{-46}\,kg\,m^2}{1.1389\times10^{-26}\,kg}$$

$$R_e^2 = 1.276 \times 10^{-20}\,m^2$$

$$R_e = 1.129 \times 10^{-10}\,m \times \frac{10^{10}\,\mathring{A}}{m} = \underline{\underline{1.129\,\mathring{A}}}$$

The next two lines will be from

$J''=2 \rightarrow J'=3$ and $J''=3 \rightarrow J'=4$

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$\Delta E = 2B(J''+1)$

for $J''=2 \rightarrow J'=3$ $\quad \Delta E = 2B(3) = 6B$

$\Delta E = (3.863\ cm^{-1})\,3 = \underline{\underline{11.59\ cm^{-1}}}$

for $J''=3 \rightarrow J'=4$ $\quad \Delta E = 2B(3+1) = 2B(4)$

$= (3.863\ cm^{-1})\,4$

$= \underline{\underline{15.452\ cm^{-1}}}$

(10) $\underline{\underline{\text{for } {}^{13}C\,{}^{16}O}}$ $\quad \mu = \dfrac{(13)(16)}{(13+16)}\ amu \times \dfrac{1.661\times10^{-27}\ kg}{1\ amu}$

29 $\quad \mu = 1.191\times10^{-26}\ kg$

$I = \mu R_e^2 = (1.191\times10^{-26}\ kg)(1.129\times10^{-10}\ m)^2$

$= 1.518\times10^{-46}\ kg\,m^2$

$B = \dfrac{h}{8\pi^2 I c} = \dfrac{6.626\times10^{-34}\ Js}{8(\pi)^2(1.518\times10^{-46}\ kg\,m^2)(2.99\times10^{10}\ cm\,s^{-1})}$

$= 1.848\ cm^{-1}$

first transition $\Delta E = 2B = \underline{\underline{3.697\ cm^{-1}}}$

$\underline{\underline{{}^{13}C\,{}^{17}O}}$ $\quad \mu = \dfrac{(13)(17)}{(13+17)} \times \dfrac{1.661\times10^{-27}}{1}\ kg$

30 $\quad \mu = 1.186\times10^{-26}\ kg$

$$I = (1.186 \times 10^{-26} kg)(1.129 \times 10^{-10} m)^2 = 1.512 \times 10^{-46} kgm^2$$

$B = 1.857 cm^{-1}$

first transition $\Delta E = 2B = \underline{\underline{3.713 cm^{-1}}}$

$\underline{\underline{^{12}C\,^{17}O}}$ $\mu = \dfrac{(12)(17)}{(12+17)} \dfrac{1.661 \times 10^{-27}}{1} kg$

$= 1.168 \times 10^{-26} kg$

$$I = (1.168 \times 10^{-26} kg)(1.129 \times 10^{-10} m)^2 = 1.489 \times 10^{-46} kgm^2$$

$B = 1.885 cm^{-1}$

first transition $\Delta E = 2B = \underline{\underline{3.769 cm^{-1}}}$

For $^{12}C\,^{16}O$ using problem #9

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

(11) $\Delta \tilde{\nu} = 2B = 12.8 cm^{-1}$

$B = 6.4 cm^{-1} = \dfrac{h}{8\pi^2 I C}$

$$I = \frac{h}{8\pi^2 C (6.4 cm^{-1})} = \frac{6.626 \times 10^{-34} Js}{8\pi^2 (2.99 \times 10^{10} cm s^{-1})(6.4 cm^{-1})}$$

$$I = \underline{\underline{4.52 \times 10^{-47} kgm^2}}$$

$I = \mu R_e^2$ $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$

for HI $\mu = \frac{(1)(127)\,\text{amu}}{(1+127)} \times \frac{1.661 \times 10^{-27}\,\text{kg}}{1\,\text{amu}}$

$$\mu = 1.648 \times 10^{-27}\,\text{kg}$$

$$R_e^2 = \frac{I}{\mu} = \frac{4.52 \times 10^{-47}\,\text{kg m}^2}{1.648 \times 10^{-27}\,\text{kg}} = 2.743 \times 10^{-20}\,\text{m}^2$$

$$R_e = 1.656 \times 10^{-10}\,\text{m} \times \frac{10^{10}\,\text{Å}}{1\,\text{m}} = \underline{\underline{1.656\,\text{Å}}}$$

(12) at 300K

$$N_i \propto g_i\, e^{-E_i/kT}$$

$$N_j \propto g_j\, e^{-E_j/kT}$$

		deg. $= 2J+1$	energy $BJ(J+1)$
$J=1$	———	3	$2B$
$J=0$	———	1	0

$$\frac{N_i}{N_j} = \frac{g_i}{g_j}\, e^{-(E_i - E_j)/kT}$$

$J=0$ population in N_j $\quad g_j = 2J+1 = 1$

$J=1$ — " — is $N_i \rightarrow g_i = 2J+1 = 3$

$$\frac{N_{J=1}}{N_{J=0}} = \frac{f_1}{f_0} = \frac{3\, e^{-[2B-0]hc/kT}}{1}$$

$$\frac{f_1}{f_0} = 3\, e^{-2Bhc/kT}$$ if B is in cm^{-1} units.

B for $H^{35}Cl$ = $10.5934\,\text{cm}^{-1}$ from Table 13.4 of text

$$\frac{f_1}{f_0} = 3\, e^{-2(10.5934\,\mathrm{cm^{-1}})(6.626\times10^{-34}\,\mathrm{Js})(2.99\times10^{10}\,\mathrm{cm\,s^{-1}})/(1.381\times10^{-23}\,\mathrm{JK^{-1}})(300\,\mathrm{K})}$$

$$= \underline{\underline{2.71}}$$

at 1000 K $$\frac{f_1}{f_0} = 3\, e^{-2(10.5934\,\mathrm{cm^{-1}})(6.626\times10^{-34}\,\mathrm{Js})(2.99\times10^{10}\,\mathrm{cm\,s^{-1}})/(1.381\times10^{-23}\,\mathrm{JK^{-1}})(1000\,\mathrm{K})}$$

$$= \underline{\underline{2.910}}$$

at $\underline{\underline{300\,\mathrm{K}}}$ $$\frac{N_{J=2}}{N_{J=0}} = \frac{f_2}{f_0} = \frac{5}{1}\, e^{-(6B-0)hc/kT}$$

$$\frac{f_2}{f_0} = 5\, e^{-6(10.5934\,\mathrm{cm^{-1}})(6.626\times10^{-34}\,\mathrm{Js})(2.99\times10^{10}\,\mathrm{cm\,s^{-1}})/(1.381\times10^{-23}\,\mathrm{JK^{-1}})(300\,\mathrm{K})}$$

$$= \underline{\underline{3.689}}$$

at 1000 K $$\frac{f_2}{f_1} = \underline{\underline{4.564}}$$

$\underline{\underline{\text{at } 300\,\mathrm{K}}}$ $$\frac{N_{J=3}}{N_{J=0}} = \frac{f_3}{f_0} = \frac{7}{1}\, e^{-(12B-0)hc/kT}$$

$$\frac{f_3}{f_0} = \underline{\underline{3.811}}$$

at $\underline{\underline{1000\,\mathrm{K}}}$ $$\frac{f_3}{f_0} = \underline{\underline{5.833}}$$