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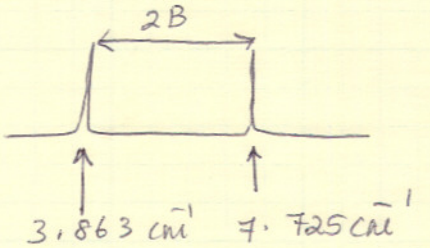
ATOMS, MOLECULES & REACTIONS

HW sheet   Final HW ~~Final~~ WEEK 9 - Wednesday

⑨



$$2B = (7.725 - 3.863)\ cm^{-1}$$

$$= 3.862\ cm^{-1}$$

$$B = 1.931\ cm^{-1}$$

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

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

$$I = \frac{6.626 \times 10^{-34}\ J\,s}{8\pi^2 (1.931\ cm^{-1})(2.99 \times 10^{10}\ cm\ s^{-1})}$$

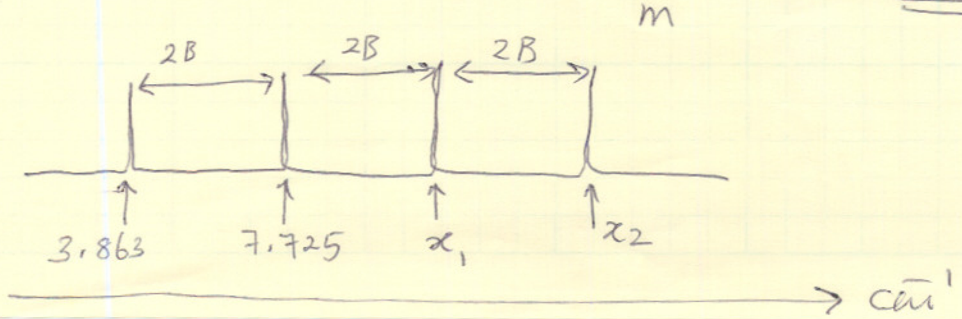
$$I = 1.4535 \times 10^{-46}\ kg\,m^2 = \mu R^2$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \left(\frac{12 \times 16}{12 + 16}\right) amu \cdot \left(\frac{1.673 \times 10^{-27}\ kg}{amu}\right)$$

$$= 1.1472 \times 10^{-26}\ kg$$

$$R^2 = \frac{I}{\mu} = \frac{1.4535 \times 10^{-46}\ kg\,m^2}{1.1472 \times 10^{-26}\ kg} = 1.266998 \times 10^{-20}\ m^2$$

$$R = 1.1256 \times 10^{-10}\ m \times \frac{10^9\ nm}{m} = \underline{\underline{0.11256\ nm}}$$



b

$$x_1 = (7.725 + 2B)\ \text{cm}^{-1}$$

$$= (7.725 + 3.862)\ \text{cm}^{-1} = \underline{\underline{11.587\ \text{cm}^{-1}}}$$

$$x_2 = 7.725 + 4B = \underline{\underline{15.449\ \text{cm}^{-1}}}$$

(10) $\underline{\underline{{}^{13}C\,{}^{16}O}}$

$$\mu = \left(\frac{13 \times 16}{13 + 16}\right) \text{amu} \times \left(\frac{1.673 \times 10^{-27}\ \text{kg}}{\text{amu}}\right)$$

$$\mu = 1.1999 \times 10^{-26}\ \text{kg}$$

$$I = \mu R^2 = \left(1.1999 \times 10^{-26}\ \text{kg}\right)\left(1.1256 \times 10^{-10}\ \text{m}\right)^2$$

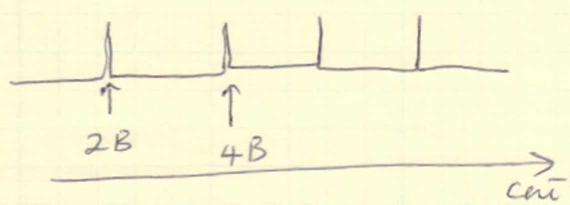
$$= 1.5202 \times 10^{-46}\ \text{kg m}^2$$

$$\frac{\text{kg m}^2 \cancel{\text{s}^{-2}}\ \cancel{\text{s}}}{\text{kg m}^2\ \text{m s}^{-1}}$$

$$B = \frac{h}{8\pi^2 I c} = \frac{6.626 \times 10^{-34}\ \text{J s}}{8\pi^2\left(1.5202 \times 10^{-46}\ \text{kg m}^2\right)\left(2.99 \times 10^{8}\ \text{m s}^{-1}\right)}$$

$$= 190.349\ \text{m}^{-1} \times \left(\frac{\text{m}}{100\ \text{cm}}\right)$$

$$B = 1.9035\ \text{cm}^{-1}$$



$$2B = \underline{\underline{3.807\ \text{cm}^{-1}}}$$

position~~s~~ of the first ~~two~~ rotational line~~s~~ for ${}^{13}C\,{}^{16}O$

C

All the other molecules are isotopes of $^{13}C^{16}O$.

For two isotopes with reduced masses μ_1 and μ_2 (with same bond length R)

$$B_1 = \frac{h}{8\pi^2 \mu_1 R^2 c} \qquad B_2 = \frac{h}{8\pi^2 \mu_2 R^2 c}$$

$$\frac{B_1}{B_2} = \frac{\mu_2}{\mu_1}$$

$$\mu \text{ of } {}^{13}C^{17}O = \left(\frac{13 \times 17}{13+17}\right) \text{amu} = 7.3667 \text{ amu}$$

$$\mu \text{ of } {}^{13}C^{16}O = \left(\frac{13 \times 16}{13+16}\right) \text{amu} = 7.1724 \text{ amu}$$

$$\frac{B \text{ of } {}^{13}C^{17}O}{B \text{ of } {}^{13}C^{16}O} = \frac{7.1724 \text{ amu}}{7.3667 \text{ amu}} = 0.9736$$

$$B \text{ of } {}^{13}C^{17}O = (0.9736)(1.9035 \text{ cm}^{-1}) = 1.8533 \text{ cm}^{-1}$$

First rotational line $= 2B = \underline{\underline{3.7066 \text{ cm}^{-1}}}$

$$^{12}C^{17}O \text{ reduced mass} = \left(\frac{12 \times 17}{12+17}\right) \text{amu} = 7.0345 \text{ amu}$$

$$\frac{B \text{ of } {}^{12}C^{17}O}{B \text{ of } {}^{13}C^{16}O} = \frac{7.1724 \text{ amu}}{7.0345 \text{ amu}} = 1.01961$$

d

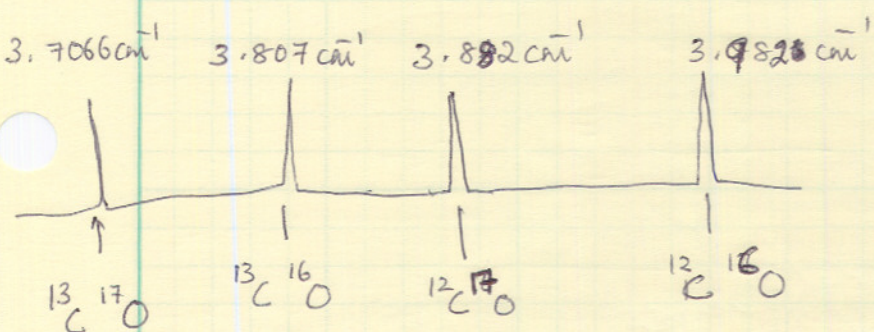
B of $^{12}C\,^{17}O = 1.01961\,(1.9035\ cm^{-1}) = 1.9408\ cm^{-1}$

first rotational line $= 2B =$ $\underline{\underline{3.8816\ cm^{-1}}}$

<u>$^{12}C\ ^{16}O$</u> $\quad \mu = \left(\dfrac{12 \times 16}{12 + 16}\right)$ amu $= 6.857$ amu

B of $^{12}C\,^{16}O$ (~~from problem~~) $= 1.991\ cm^{-1}$

$2B =$ first rotational line $=$ $\underline{\underline{3.982\ cm^{-1}}}$



f

$$\frac{F_2}{F_0} = 5\,e^{-6(10.5934\,cm^{-1})hc/kT} = 5\,e^{-91.183\,K/T}$$

<u>at 300 K</u> $\frac{F_2}{F_0} = 5\,e^{-91.183\,K/300\,K} = \underline{\underline{3.6895}}$

<u>at 1000 K</u> $\frac{F_2}{F_0} = 5\,e^{-91.183\,K/1000\,K} = \underline{\underline{4.564}}$

$$\frac{F_3}{F_0} = \frac{g_3\,e^{-E_3/kT}}{g_0\,e^{-E_0/kT}} = 7\,e^{-12B/kT}$$

$$\frac{F_3}{F_0} = 7\,e^{-12(10.5934\,cm^{-1})hc/kT} = 7\,e^{-182.3667\,K/T}$$

<u>at 300 K</u> $\frac{F_3}{F_0} = 7\,e^{-182.3667\,K/300\,K} = \underline{\underline{3.8115}}$

<u>at 1000 K</u> $\frac{F_3}{F_0} = 7\,e^{-182.3667\,K/1000\,K} = \underline{\underline{5.8331}}$

(19) fundamental band $v''=0 \quad v'=1$

$$E_{v''} = \left(v''+\tfrac{1}{2}\right)h\nu = \tfrac{1}{2}h\nu \qquad E_{v'} = \left(v'+\tfrac{1}{2}\right)h\nu = \tfrac{3}{2}h\nu$$

Energy of the fundamental band $= E_{v'} - E_{v''} = h\nu$

in cm^{-1} units $= \frac{h\nu}{hc} = \frac{\nu}{c}$

e

(12) $F_0 = g_0 e^{-E_0/kT} / \text{constant}$ $\boxed{g = (2J+1)}$

$F_1 = g_1 e^{-E_1/kT} / \text{constant}$ $F_2 = g_2 e^{-E_2/kT} / \text{Const}$

$$\frac{F_1}{F_0} = \frac{g_1 e^{-E_1/kT}}{g_0 e^{-E_0/kT}} = \frac{3 e^{-E_1/kT}}{e^{-E_0/kT}}$$

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

$$\frac{F_1}{F_0} = 3 e^{(-E_1 + E_0)/kT}$$

$E_J = BJ(J+1)$ $E_0 = 0$ $E_1 = 2B$

$$\frac{F_1}{F_0} = 3 e^{-2B/kT}$$ B_e for $H^{35}Cl = 10.5934 \text{ cm}^{-1}$

$$= 3 e^{[-2(10.5934 \text{ cm}^{-1}) hc]/kT}$$

$$\frac{F_1}{F_0} = 3 e^{-30.3945 K/T}$$

at 300 K $\frac{F_1}{F_0} = 3 e^{-30.3945K/300K} = \underline{\underline{2.711}}$

at 1000 K $\frac{F_1}{F_0} = 3 e^{-30.3945 K/1000K} = \underline{\underline{2.9101}}$

$$\frac{F_2}{F_0} = \frac{g_2 e^{-E_2/kT}}{g_0 e^{-E_0/kT}} = 5 e^{(-E_2+E_0)/kT}$$

$E_2 = 6B$ $\therefore \frac{F_2}{F_0} = 5 e^{-6B/kT}$

h

$\tilde{\nu}_{\cancel{D^{35}}}$ $\mu_{D^{35}Cl} = \dfrac{2 \times 35}{2+35}$ amu $= 1.89189$ amu

$\mu_{D^{37}Cl} = \dfrac{2 \times 37}{2+37}$ amu $= 1.89744$ amu

$$\frac{\tilde{\nu}_{D^{35}Cl}}{\tilde{\nu}_{H^{35}Cl}} = \sqrt{\frac{0.972222 \text{ amu}}{1.89189 \text{ amu}}} = 0.71581$$

$$\tilde{\nu}_{D^{35}Cl} = (0.71581)(2998.9967 \text{ cm}^{-1}) = \underline{\underline{2146.7188 \text{ cm}^{-1}}}$$

$$\frac{\tilde{\nu}_{D^{37}Cl}}{\tilde{\nu}_{D^{35}Cl}} = \sqrt{\frac{1.89189 \text{ amu}}{1.89744 \text{ amu}}} = 0.99854$$

$$\tilde{\nu}_{D^{37}HCl} = 0.99854\,(2146.7188 \text{ cm}^{-1})$$

$$= \underline{\underline{2143.5769 \text{ cm}^{-1}}}$$

$\left.\begin{array}{l}\text{seperation of bands} \\ \text{between } D^{35}Cl \text{ and } D^{37}Cl\end{array}\right\} = (2146.7188 - 2143.5769)\text{ cm}^{-1}$

$= \underline{\underline{3.1419 \text{ cm}^{-1}}}$

For $H^{35}Cl$ $\quad \nu = 8.967 \times 10^{+13}\ s^{-1}$

$\cancel{\therefore \bar{\nu} = 5.9415 \times 10^{-12}\ \Omega}$

$\therefore \tilde{\nu} = \dfrac{\nu}{c} = 2998.9967\ cm^{-1}$ ← fundamental band.

$$\tilde{\nu}_1 = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu_1}} \qquad \tilde{\nu}_2 = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu_2}}$$

where $\tilde{\nu}_1$ and $\tilde{\nu}_2$ are wavenumbers for 2 isotopes.

$$\therefore \frac{\tilde{\nu}_1}{\tilde{\nu}_2} = \sqrt{\frac{\mu_2}{\mu_1}} \qquad \mu_{H^{35}Cl} = \frac{1 \times 35}{1+35}\ amu = 0.972222\ amu$$

$$\mu_{H^{37}Cl} = \frac{1 \times 37}{1+37} = 0.973684\ amu$$

$$\frac{\tilde{\nu}_{H^{37}Cl}}{\tilde{\nu}_{H^{35}Cl}} = \sqrt{\frac{0.972222\ amu}{0.973684\ amu}} = 0.9992489$$

$$\tilde{\nu}_{H^{37}Cl} = (0.9992489)(2998.9967\ cm^{-1}) = \underline{\underline{2996.7440\ cm^{-1}}}$$

$$\left.\begin{array}{l}\therefore \text{seperation of bands} \\ \text{between } H^{35}Cl \text{ and } H^{37}Cl\end{array}\right\} = 2998.9967 - 2996.7440\ cm^{-1} = \underline{\underline{2.25269\ cm^{-1}}}$$

(i)

(26)

$R(0) = 2906.25 \quad J''=0 \quad J'=1$

$R(1) = 2925.78 \quad J''=1 \quad J'=2$

$R(2) = 2944.89 \quad J''=2 \quad J'=3$

$v''=0$

$v'=1$

$\cancel{\tilde{\nu}_0 = B_{v'} J'(J'+1) - B_{v''} J''(J''+1)}$

$$\tilde{\nu}_0 = \omega_e(v'-v'') - \omega_e x_e\left[\left(v'+\tfrac{1}{2}\right)^2 - \left(v''+\tfrac{1}{2}\right)^2\right]$$

$$= \omega_e(1) - \omega_e x_e\left[\left(\tfrac{3}{2}\right)^2 - \left(\tfrac{1}{2}\right)^2\right]$$

$$\tilde{\nu}_0 = \omega_e - 2\omega_e x_e$$

For the fundamental band

$$\tilde{\nu}_R = \tilde{\nu}_0 + (B_1 - B_0)J''^2 + (3B_1 - B_0)J'' + 2B_1$$

$\therefore$ $$R(0) = \tilde{\nu}_0 + (B_1 - B_0)(0)^2 + (3B_1 - B_0)(0) + 2B_1$$

$$R(0) = \tilde{\nu}_0 + 2B_1 = 2906.25\ \text{cm}^{-1} \text{ —— } (1)$$

$$R(1) = \tilde{\nu}_0 + (B_1 - B_0)(1)^2 + (3B_1 - B_0)(1) + 2B_1$$

$$= \tilde{\nu}_0 + \underline{B_1} - B_0 + \underline{3B_1} - B_0 + \underline{2B_1}$$

$$2925.78\ \text{cm}^{-1} = \tilde{\nu}_0 + 6B_1 - 2B_0 \text{ —— } (2)$$

$$R(2) = \tilde{\nu}_0 + (B_1 - B_0)(4) + (3B_1 - B_0)(2) + 2B_1$$

$$= \tilde{\nu}_0 + 4B_1 - 4B_0 + 6B_1 - 2B_0 + 2B_1$$

$$2944.89\ \text{cm}^{-1} = \tilde{\nu}_0 + 12B_1 - 6B_0 \text{ —— } (3)$$

$$③ - ① \Rightarrow \quad 38.64\ \text{cm}^{-1} = 10B_1 - 6B_0 \quad — ⑤$$

$$④ \times 3 \Rightarrow \quad 58.59\ \text{cm}^{-1} = 12B_1 - 6B_0 \quad — ⑥$$

$$⑥ - ⑤ \Rightarrow \quad 19.95\ \text{cm}^{-1} = 2B_1$$

$$\underline{\underline{B_{v'} = B_1 = 9.975\ \text{cm}^{-1}}}$$

$$④ \Rightarrow \quad 2B_0 = 4B_1 - 19.53\ \text{cm}^{-1} = 20.37\ \text{cm}^{-1}$$

$$\underline{\underline{B_{v''} = B_0 = 10.185\ \text{cm}^{-1}}}$$

$$① \Rightarrow \quad \cancel{R(0)} \quad \tilde{\nu}_0 + 2B_1 = 2906.25\ \text{cm}^{-1}$$

$$\tilde{\nu}_0 = 2906.25 - 2B_1 = \underline{\underline{2886.05\ \text{cm}^{-1}}}$$

$$B_v = B_e - \alpha_e\left(v + \tfrac{1}{2}\right)$$

$\underline{v=1}$ $$B_1 = B_e - \frac{3}{2}\alpha_e \quad — ⑦$$

$v=0$ $$B_0 = B_e - \frac{1}{2}\alpha_e \quad — ⑧$$

$$⑧ - ⑦ \Rightarrow \quad B_0 - B_1 = \alpha_e = (10.185 - 9.975)\ \text{cm}^{-1}$$

$$\underline{\underline{\alpha_e = 0.210\ \text{cm}^{-1}}}$$

k

Substitute in (8)

$$B_0 = B_e - \frac{1}{2}\alpha_e$$

$$B_e = B_0 + \frac{1}{2}\alpha_e = \left[10.185 + \frac{1}{2}(0.210)\right] cm^{-1}$$

$$\underline{\underline{B_e = 10.290\ cm^{-1}}}$$

(29) (a) SO_2 (bent) $N = 3$

$3N-6 = 9-6 = \underline{\underline{3}}$

(b) H_2O_2 (bent) $N = 4$ $3N-6 = \underline{\underline{6}}$

(c) $HC\equiv CH$ (linear) $N=4$ $3N-5 = \underline{\underline{7}}$

(d) C_6H_6 $N = 12$ $3N-6 = \underline{\underline{12}}$

(30)

			translational	rotational	vibrational
	(a)	Ne	3	0	0
$N\equiv N$	(b)	N_2	3	2	1
$O=C=O$	(c)	CO_2	3	2	4
$H_2C=O$	(d)	CH_2O	3	3	6

l

(45) $2B = 3.8626\ cm^{-1}$

$$B = 1.9313\ cm^{-1} = \frac{h}{8\pi^2 \mu R^2 c}$$

$$\mu = \frac{12 \times 16}{12 + 16}\ amu = 6.85714\ amu$$

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

$$= \frac{6.626 \times 10^{-34}\ JS\ \left[(1 amu)/1.673 \times 10^{-27}\ kg\right]}{8(\pi^2)(6.85714 amu)(1.9313\ cm^{-1})(2.99 \times 10^{10}\ cm\ s^{-1})}$$

$$R^2 = 1.26678 \times 10^{-20}\ m^2$$

$$R = 1.1255 \times 10^{-10}\ m \times \frac{10^9\ nm}{m} = \underline{\underline{0.1126\ nm}}$$

(60) <u>HBr</u> $\tilde{\nu}_{1-0} = 2645\ cm^{-1}$ $2B = 16.9\ cm^{-1}$

$B = 8.45\ cm^{-1}$

for isotopes $\dfrac{\tilde{\nu}_1}{\tilde{\nu}_2} = \sqrt{\dfrac{\mu_2}{\mu_1}}$

$$\mu_{HBr} = \left(\frac{1 \times 79.9}{1 + 79.9}\right) amu = 0.9876\ amu$$

$$\mu_{DBr} = \left(\frac{2 \times 79.9}{2 + 79.9}\right) amu = 1.9512\ amu$$

m

$$\frac{\tilde{\nu}_{DBr}}{\tilde{\nu}_{HBr}} = \sqrt{\frac{0.9876\ \text{amu}}{1.9512\ \text{amu}}} = 0.7114$$

$$\tilde{\nu}_{DBr} = 1881.78\ \text{cm}^{-1} = \underline{\underline{1882\ \text{cm}^{-1}}}$$

$$B_1 = \frac{h}{8\pi^2 \mu_1 R^2 c} \qquad B_2 = \frac{h}{8\pi^2 \mu_2 R^2 c}$$

$$\frac{B_2}{B_1} = \frac{\mu_1}{\mu_2}$$

$$\frac{B_{DBr}}{B_{HBr}} = \frac{0.9876\ \text{amu}}{1.9512\ \text{amu}} = 0.5062$$

$$B_{DBr} = \underline{\underline{4.28\ \text{cm}^{-1}}}$$

(63) NNO (linear) $N = 3$

$3N - 5 = \underline{\underline{4}}$ = vibrational degrees of freedom

$\left.\begin{array}{l}3 \text{ translational} \\ 2 \text{ rotational}\end{array}\right\}$ degrees of freedom

NH_3 (non-linear) $N = 4$

$3N - 6 = 6$ vibrational degrees of freedom

$\left.\begin{array}{l}3 \text{ translational} \\ 3 \text{ rotational}\end{array}\right\}$ degrees of freedom