Problem set 1

(1) $\lambda_1 = 350\,nm = 350\times10^{-9}\,m = 350\times10^{-7}\,cm$

$\bar{\nu} = \frac{1}{\lambda} \Rightarrow \bar{\nu} = \frac{1}{350\times10^{-7}\,cm} = 28571.4\,cm^{-1}$

$(1\,eV = 8065.6\,cm^{-1})$

$\Rightarrow \frac{28571.4\,cm^{-1}}{8065\,cm^{-1}/eV} = 3.54\,eV$

$\lambda_2 = 750\,nm = 750\times10^{-7}\,cm$

$\bar{\nu} = \frac{1}{750\times10^{-7}\,cm} = 13,333.3\,cm^{-1}$

$\Rightarrow 1.65\,eV$

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(2) $\nu = 1\,GHz = 1\times10^{9}\,Hz$

$\nu = \frac{c}{\lambda} \Rightarrow \lambda = \frac{c}{\nu} = \frac{2.997\times10^{10}\,cm.s^{-1}}{1\times10^{9}\,s^{-1}} = 29.99\,cm$

$\nu = 100\,GHz \Rightarrow \lambda = \frac{2.997\times10^{10}\,cm.s^{-1}}{100\times10^{9}\,s^{-1}} = 0.29\,cm$

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(3) $\nu = 4.6\,GHz = 4.6\times10^{9}\,s^{-1}$

$E_1 = h\nu = 6.626\times10^{-34}\,J.s \times 4.6\times10^{9}\,s^{-1} = 30.48\times10^{-25}\,J$

For one mole of photons: $\Rightarrow 30.48\times10^{-25}\,J \times 6.023\times10^{23}$

$E = 183.58\times10^{-2} = 1.84\,J/mole$

For $\bar{\nu} = 37000\,cm^{-1}$ $E = hc\bar{\nu} = 6.626\times10^{-34}\,J.s \times 2.997\times10^{10}\,cm.s^{-1} \times 37000\,cm^{-1}$

$= 7.34\times10^{-19}\,J$

For one mole of photons: $7.34\times10^{-19}\,J \times 6.023\times10^{23}$

$= 4.43\times10^{5}\,J/mole$

(4) Reduced mass of $^{12}C\,^{1}H$

$$\mu = \frac{m_C \cdot m_H}{m_C + m_H}$$

where m_C and m_H are masses of C and H atoms respectively, in kg.

If M_C and M_H are relative atomic masses,

then mass of carbon atom $m_C = \left(\frac{M_C}{N} \times 10^{-3}\right)$

mass of Hydrogen atom $m_H = \left(\frac{M_H}{N} \times 10^{-3}\right)$.

$$\mu = \frac{\left(\frac{M_C}{N} \times 10^{-3}\right)\left(\frac{M_H}{N} \times 10^{-3}\right)}{\left[\left(\frac{M_C}{N} \times 10^{-3}\right) + \left(\frac{M_H}{N} \times 10^{-3}\right)\right]}$$

$$= \frac{10^{-3}}{N}\left[\frac{M_C \cdot M_H}{M_C + M_H}\right]$$

For $^{12}C\,^{1}H$: $\mu = \frac{10^{-3}}{N}\left(\frac{12 \times 1}{12+1}\right) = 1.5326 \times 10^{-27}$ kg

$^{13}C\,^{1}H$: $\mu = \frac{10^{-3}}{N}\left(\frac{13 \times 1}{13+1}\right) = 1.5417 \times 10^{-27}$ kg

$^{12}C\,^{2}H$: $\mu = \frac{10^{-3}}{N}\left(\frac{12 \times 2}{12+2}\right) = 2.8462 \times 10^{-27}$ kg.

Note: Replacing ^{1}H with ^{2}H changes 'μ' more drastically than replacing ^{12}C with ^{13}C.

Light atom replacement is therefore more effective!

(5) $B = \dfrac{h}{8\pi^2 I c}$

$= \dfrac{h}{8\pi^2 \mu r^2 c}$

$r = 1.1199\,\text{Å}$
$= 1.1199\times10^{-10}\,m$

For $^{12}C^1H$: $B = \dfrac{6.626\times10^{-34}\,J.s}{8\times\pi^2\times(1.5326\times10^{-27}\,kg)\times(1.1199\times10^{-10}\,m)^2\times(2.997\times10^{+10}\,cm\,s^{-1})}$

$= 14.57\,cm^{-1}$

For $^{13}C^1H$: $B = 14.48\,cm^{-1}$

For $^{12}C^2H$: $B = 7.84\,cm^{-1}$

Note light atom effect on 'B'

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(6) Spacing between rotational lines in

$^{12}C^1H$: $2\times B = 2\times14.57 =$ ~~29~~ $\underline{29.14\,cm^{-1}}$

$^{13}C^1H$ = $2\times B = 2\times14.48 =$ $\underline{28.96\,cm^{-1}}$

$^{12}C^2H$ -- $2\times B = 2\times7.84 =$ $\underline{15.68\,cm^{-1}}$

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(7) $\mu_{I_2} = \dfrac{10^{-3}}{N}\left(\dfrac{127\cdot127}{127+127}\right)$

$= 1.054\times10^{-25}\,kg$

$M_I = 127$

$[r = 2.6663\,\text{Å}$
$= 2.6663\times10^{-10}\,m]$

$B = \dfrac{h}{8\pi^2\mu r^2} = \dfrac{6.626\times10^{-34}\,J.s}{8\times\pi^2\times1.054\times10^{-25}\,kg\times(2.6663\times10^{-10}\,m)^2\times2.997\times10^{10}\,cm\,s^{-1}}$

$= .037\,cm^{-1}$

Spacing is $2B = 2\times.037\,cm^{-1} = .074\,cm^{-1}$!!
Too close to be resolved!

(8) $\mu_{HgH} = 1.652 \times 10^{-27}$ kg

$\mu_{H_2} = \cancel{7}\ 8.302 \times 10^{-28}$ kg

$\mu_{Li_2} = $ ~~[illegible] kg.~~ 5.811×10^{-27} kg

Li_2 has the largest reduced mass (more than HgH!) and H_2 has the smallest.

The line spacings in Li_2 will be the ~~largest~~ smallest and those in H_2 will be the ~~smallest~~ largest.

(But can you see rotational spectra of Li_2 and H_2 !?).

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(9) H_2 : $\mu = 0$: No ~~[illegible]~~ pure rotational spectra.

HCl : $\mu \neq 0$ Pure rotational spectra observed

$^1H^2H$: $\mu \neq 0$! Pure rotational spectra observed!

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(10) $B = 1.929$ (1^{st} experiment) $\mu_{CO} = 1.138 \times 10^{-26}$ kg

$$= \frac{h}{8\pi^2 I c} = \frac{h}{8\pi^2 \mu r^2 c}.$$

$$r^2 = \frac{h}{8\pi^2 \mu c B} = \frac{6.626 \times 10^{-34}\ Js}{8 \times \pi^2 \times 1.138 \times 10^{-26}\ kg \times 2.997 \times 10^{10}\ cm\,s^{-1} \times 1.929\ cm^{-1}}$$

$= 1.2756 \times 10^{-20}\ m^2$

$r = 1.129\ \mathring{A}$

For $B = 3.858\ cm^{-1}$, a similar calculation will give

$r = 0.7986\ \mathring{A}$. This is a very short bond length. Hence value of $B = 3.858\ cm^{-1}$ is <u>incorrect</u>