

Problem set 1

① $\lambda_1 = 350 \text{ nm} = 350 \times 10^{-9} \text{ m} = 350 \times 10^{-7} \text{ cm}$

$$\bar{\nu} = \frac{1}{\lambda} \Rightarrow \bar{\nu} = \frac{1}{350 \times 10^{-7} \text{ cm}} = 28571.4 \text{ cm}^{-1}$$

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

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

$$\lambda_2 = 750 \text{ nm} = 750 \times 10^{-7} \text{ cm}$$

$$\bar{\nu} = \frac{1}{750 \times 10^{-7} \text{ cm}} = 13333.3 \text{ cm}^{-1}$$

$$\Rightarrow 1.65 \text{ eV}$$

② $\nu = 1 \text{ GHz} = 1 \times 10^9 \text{ Hz}$

$$\nu = \frac{c}{\lambda} \Rightarrow \lambda = \frac{c}{\nu} = \frac{2.997 \times 10^{10} \text{ cm} \cdot \text{s}^{-1}}{1 \times 10^9 \text{ s}^{-1}} = 29.99 \text{ cm}$$

$$\nu = 100 \text{ GHz} \Rightarrow \lambda = \frac{2.997 \times 10^{10} \text{ cm} \cdot \text{s}^{-1}}{100 \times 10^9 \text{ s}^{-1}} = 0.29 \text{ cm}$$

③ $\nu = 4.6 \text{ GHz} = 4.6 \times 10^9 \text{ s}^{-1}$

$$E_i = h\nu = 6.626 \times 10^{-34} \text{ J} \cdot \text{s} \times 4.6 \times 10^9 \text{ s}^{-1} = 30.48 \times 10^{-25} \text{ J}$$

$$\text{For one mole of photons: } \Rightarrow 30.48 \times 10^{-25} \text{ J} \times 6.023 \times 10^{23}$$

$$E = 183.58 \times 10^{-2} = 1.84 \text{ J/mole}$$

$$\text{For } \bar{\nu} = 37000 \text{ cm}^{-1} \quad E = hc\bar{\nu} = 6.626 \times 10^{-34} \text{ J} \cdot \text{s} \times \frac{2.997 \times 10^{10} \text{ cm} \cdot \text{s}^{-1}}{37000 \text{ cm}^{-1}} \times 37000 \text{ cm}^{-1} \\ = 7.34 \times 10^{-19} \text{ J}$$

$$\text{For one mole of photons: } 7.34 \times 10^{-19} \text{ J} \times 6.023 \times 10^{23} \\ = 4.43 \times 10^5 \text{ J/mole}$$

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Reduced mass of $^{12}\text{C}^1\text{H}$

$$\mu = \frac{m_{\text{C}} \cdot m_{\text{H}}}{m_{\text{C}} + m_{\text{H}}}$$

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,

$$\begin{aligned} \text{then mass of carbon [atom]} \quad m_{\text{C}} &= \left(\frac{M_{\text{C}}}{N} \times 10^{-3} \right) \\ \text{mass of hydrogen [atom]} \quad m_{\text{H}} &= \left(\frac{M_{\text{H}}}{N} \times 10^{-3} \right), \end{aligned}$$

$$\mu = \frac{\left(\frac{M_{\text{C}}}{N} \times 10^{-3} \right) \left(\frac{M_{\text{H}}}{N} \times 10^{-3} \right)}{\left[\left(\frac{M_{\text{C}}}{N} \times 10^{-3} \right) + \left(\frac{M_{\text{H}}}{N} \times 10^{-3} \right) \right]}$$

$$= \frac{10^{-3}}{N} \left[\frac{M_{\text{C}} \cdot M_{\text{H}}}{M_{\text{C}} + M_{\text{H}}} \right]$$

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

 $^{13}\text{C}^1\text{H}$

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

 $^{12}\text{C}^2\text{H}$

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

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

Light atom replacement is therefore more effective!

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

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

$$r = 1.199 \text{ \AA}$$

$$= 1.199 \times 10^{-10} \text{ m}$$

For $^{12}\text{C}^1\text{H}$: $B = \frac{6.626 \times 10^{-34} \text{ J}\cdot\text{s}}{8 \times \pi^2 \times (1.5326 \times 10^{-27} \text{ kg}) \times (1.199 \times 10^{-10} \text{ m})^2 \times (2.997 \times 10^{10} \text{ cm s}^{-1})}$

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

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

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

Note light atom effect on 'B'

⑥ Spacing ^{between} rotational lines in

$^{12}\text{C}^1\text{H}$: $2 \times B = 2 \times 14.57 = \underline{29.14 \text{ cm}^{-1}}$

$^{13}\text{C}^1\text{H}$: $2 \times B = 2 \times 14.48 = \underline{28.96 \text{ cm}^{-1}}$

$^{12}\text{C}^2\text{H}$: $2 \times B = 2 \times 7.84 = \underline{15.68 \text{ cm}^{-1}}$

⑦ $M_{I_2} = \frac{10^{-3}}{N} \left(\frac{127 \cdot 127}{127+127} \right)$

$$= 1.054 \times 10^{-25} \text{ kg}$$

$M_I = 127$

$$\left[r = 2.6663 \text{ \AA} \right]$$

$$= 2.6663 \times 10^{-10} \text{ m}$$

$$B = \frac{h}{8\pi^2 \mu r^2} = \frac{6.626 \times 10^{-34} \text{ J}\cdot\text{s}}{8 \times \pi^2 \times 1.054 \times 10^{-25} \text{ kg} \times (2.6663 \times 10^{-10} \text{ m})^2 \times 2.997 \times 10^{10} \text{ cm s}^{-1}}$$

$$= 0.037 \text{ cm}^{-1}$$

Spacing is $2B = 2 \times 0.037 \text{ cm}^{-1} = 0.074 \text{ cm}^{-1} !!$
Too close to be resolved!

$$\textcircled{8} \quad \mu_{\text{H}_2\text{H}} = 1.652 \times 10^{-27} \text{ kg}$$

$$\mu_{\text{H}_2} = 8.302 \times 10^{-28} \text{ kg}$$

$$\mu_{\text{Li}_2} = \text{~~approx } 10^{-27} \text{ kg}~~, 5.811 \times 10^{-27} \text{ kg}$$

Li_2 has the largest reduced mass (more than H_2H !) 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 !?)

$\textcircled{9} \quad \text{H}_2 : \mu = 0 : \text{No pure rotational spectra.}$

$\text{HCl} : \mu \neq 0 \quad \text{Pure rotational spectra observed}$

$^1\text{H}^2\text{H} : \mu \neq 0! \quad \text{Pure rotational spectra observed!}$

$\textcircled{10} \quad B = 1.929 \text{ (1st experiment)}$

$$\mu_{\text{CO}} = 1.138 \times 10^{-26} \text{ kg}$$

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

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

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

$$r = 1.129 \text{ \AA}$$

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

$r = 0.7986 \text{ \AA}$, This is a very short bond length.

Hence value of $B = 3.858 \text{ cm}^{-1}$ is incorrect