CSO202—Atoms, Molecules & Photons

Homework – 2

Solutions

1.(a) Complete the following table for electromagnetic waves in vacuum (Plank's constant, $h = 6.62 \times 10^{-34}$ Js; velocity of light, $c = 3 \times 10^8 m/sec$):

$\lambda_{\square}(\mu m)$	$\nu_{\square}(Hz)$	$E(eV)$	Wavenumber(cm⁻¹)	Spectral region
0.6	5x10¹⁴	2.0664	16667	Visible
74.95	4×10^{12}	0.0165	133.08	Microwave
0.09116	3.29x10¹⁵	13.6	109691.36	Ultraviolet
2.48	1.2x10¹⁴	0.5	4000	Near-Infrared

1.(b) Now redo this table below but assume that the medium has an index of refraction n=1.5 (this is pretty close to correct for glass at visible frequencies, and for coaxial cables at radiofrequencies).

$\lambda_\square(\mu m)$	$v_\square(Hz)$	$E(eV)$	Wavenumber(cm⁻¹)	Spectral region
0.6	7.5x10¹⁴	3.1017	25017	Ultraviolet
50	4×10^{12}	0.0165	133.08	Microwave
0.06077	3.29x10¹⁵	13.6	109691.36	Ultraviolet
1.65	1.2x10¹⁴	0.5	4000	Near-Infrared

1.(c) Based on your answers to a & b, which are the preferred units to use & why?

Values that are directly proportional to the measurable terms of Energy dictate the spectral region of the Electromagnetic radiation. Since Wavelength of light is dependent on the refractive index, it cannot be considered as the preferred unit. The rest of the three units are directly proportional to the Energy and can be considered as the preferred units to use.

2. Consider the vibrational motion of HI. Since Iodine is very heavy, assume it is stationary and the hydrogen atom undergoes harmonic motion. With force constant $k = 317$ N.m^{-1}. What is the fundamental vibration frequency v_0? How much error has resulted because of neglecting the motion of I ?   What is v_0 if H is replaced by D?

Ans.   For HI, since I(127) is very heavy compared to H(1), ignore its motion.

Given, force constant $k = 317$ N.m^{-1}.

$$v_0 = \frac{1}{2\pi}\sqrt{\frac{k}{m_H}} \cong \frac{1}{2\pi}\sqrt{\frac{317}{1.67\times10^{-27}}} \approx 6.93 \times 10^{13} s^{-1} = 2311.3 \ cm^{-1}$$

Now, if we do not neglect motion of I then we would use reduced mass :

$$\mu = \frac{m_H m_I}{m_H + m_I} \cong \frac{127}{128} \approx 9.92\times10^{-1} \approx 1.657\times10^{-27} kg$$

$\therefore$
$$v \approx \frac{1}{2\pi}\sqrt{\frac{317}{1.657\times10^{-27}}} \approx 6.96\times10^{13} s^{-1} \approx \underline{2320.4 \ cm^{-1}}$$

$\therefore$
$$error \approx \frac{2320.4 - 2311.3}{2320.4}\times100 \approx \underline{0.4\%} \qquad \text{(fairly small)}$$

(But with high resolution spectroscopy, error of $9 cm^{-1}$ is quite large !
      Experimental value $\approx 2309 cm^{-1}$)

For   DI   : $v_0 = \frac{1}{\sqrt{2}}\times2311.3 \ cm^{-1} \approx \underline{1634.3 \ cm^{-1}}$

3. The wavenumber of the $j = 1 \leftarrow j = 0$ rotational transitions for $^1H^{35}Cl$ and $^2H^{35}Cl$ are 20.8784 and 10.7840 cm^{-1} respectively. Accurate atomic masses are 1.007825 and 2.0140 for ^1H and ^2H respectively. The mass of ^{35}Cl is 35.96885. Based on this information alone, can you conclude that the bond lengths are the same or different in the two molecules?

Ans.   Given wavenumber of the $j = 1 \leftarrow j = 0$ transitions for $^1H^{35}Cl$ and $^2H^{35}Cl$ are 20.8784 and 10.7840 cm^{-1} respectively.

$$m\left(^1H\right)=1.007825 \; amu \quad ; \quad m\left(^2H\right)=2.0140 \; amu \; ; \qquad m\left(^{35}Cl\right)=34.96885 \; amu.$$

$$\therefore \qquad \mu\left(^1H^{35}Cl\right)=\frac{(1.007825)\,(34.96885)}{(34.96885+1.007825)}\cong 0.97959 \; amu.$$

$$\& \qquad \mu\left(^2H^{35}Cl\right)=\frac{(2.0140)\,(34.96885)}{(34.96885+2.0140)}\approx 1.90432 \; amu.$$

We know that the transition wavenumber $=2\tilde{B}=\dfrac{2h}{8\pi^2 cI}=\dfrac{h}{4\pi^2 c\mu R_e^2}$

$$\therefore \qquad \text{For,} \quad ^1H^{35}Cl \; : \quad \frac{h}{4\pi^2 c\mu R_e^2}=20.8781$$

$$\Rightarrow \qquad R_e\left(^1H^{35}Cl\right)=\left\{\frac{6.63\times10^{-34}\,Js}{4\pi^2\left(2.998\times10^{10}\,cms^{-1}\right)\left(20.8781cm^{-1}\right)\left(0.97959\,amu\right)}\right\}^{\frac{1}{2}}$$

$$\approx 1.2807\times10^{-10}\,m \approx \underline{128.07\,pm}$$

Similarly, $\quad R_e\left(^2H^{35}Cl\right)=1.2780\times10^{-10}\,m\approx\underline{127.80\,pm}$

Yes, we can distinguish.

4. Calculate the proportion of HI molecules in their ground, first, and second excited vibrational states at 298 K. On substituting H with D would you expect a larger proportion of DI in the first excited state as compared to the case of HI? (Fundamental Frequency of vibration of HI = 2230 cm⁻¹.)

Ans. In the simple Harmonic Oscillator model of the HI molecule, we have an infinite number of equally spaced non-degenerate energy-levels, and the corresponding partition function, q can be calculated as follows:

$$q=\sum_v e^{-E_v/k_B T} \qquad \text{since } g_i=1.$$

where, $E_v = \left(v + \dfrac{1}{2}\right) hc\tilde{v}$ & $\tilde{v}$ is the Fundamental Frequency of vibration of HI ($=2230\text{cm}^{-1}$), such that $\tilde{v} = \sqrt{\dfrac{k}{\mu}}$ with k as the spring constant and μ is the reduced mass of HI.

We expect the partition function to increase from 1 at $T = 0$ and approach infinity as $T \to \infty$.

$$q = 1 + e^{-\frac{hc\tilde{v}}{k_B T}} + e^{-\frac{2hc\tilde{v}}{k_B T}} + \ldots = 1 + e^{-\frac{hc\tilde{v}}{k_B T}} + \left(e^{-\frac{hc\tilde{v}}{k_B T}}\right)^2 + \ldots = \frac{1}{1 - e^{-\frac{hc\tilde{v}}{k_B T}}}$$

Thus, population in the vth level can be calculated as :

$$p_v = \frac{N_v}{N} = e^{-\frac{vhc\tilde{v}}{k_B T}}\left(1 - e^{-\frac{hc\tilde{v}}{k_B T}}\right) \qquad \left[\because N_v = \frac{e^{-E_v/k_B T}}{q}\right]$$

Now, $\dfrac{hc\tilde{v}}{k_B T} = \dfrac{6.6\times10^{-34}\text{Js}\times3\times10^{10}\text{cm}/s\times2230\text{ cm}^{-1}}{1.38\times10^{-23}\text{JK}^{-1}\times(273+25)\text{K}} = 10.74$

$\therefore p_v = e^{-v\times10.74}\left(1 - e^{-10.74}\right) = 2.17\times10^{-5}\times e^{-v\times10.74}$

Thus, for $v = 0$, 1 & 2, the respective populations are :

$p_0 \approx 1; \quad p_1 = 2.17\times10^{-5}; \quad p_2 = 4.69\times10^{-10}.$

Also, as stated before, since $\tilde{v} = \sqrt{\dfrac{k}{\mu}}$, as we go from HI to DI (reduced mass increases), $\tilde{v}_0$ decreases (considering no change in the force constant k) and so does $\dfrac{hc\tilde{v}}{k_B T}$ implying that a larger proportion of DI in the first excited state as compared to the case of HI.

Specifically, using these arguments for DI, we can calculate $\tilde{v} = 1583\text{cm}^{-1}$ and the corresponding $\dfrac{hc\tilde{v}}{k_B T} = 7.62$, which implies that the corresponding first excited state population for DI is : $p_1 = 4.9\times10^{-4}$ ...An order of magnitude more than HI !!

5. Use the collision theory of gas phase reactions to calculate the theoretical value of the second–order rate constant for the reaction $H_2(g) + I_2(g) \rightarrow 2HI\ (g)$ at 650 K, assuming that it is elementary bimolecular. The collision cross section is 0.36 nm^{-1}, the reduced mass is 3.32×10^{-27} kg, and the activation energy is 171 kJ.mol^{-1}.

From collision theory, second order rate constant for the given equation can written as:

$$k_2 = \pi\sigma_{AB}^2 \sqrt{\frac{8k_BT}{\pi\mu}} N_o e^{-E_a/RT} = \sigma\sqrt{\frac{8k_BT}{\pi\mu}} N_o e^{-E_a/RT} \qquad [\because \text{cross-section}, \sigma = \pi\sigma_{AB}^2]$$

$$= 0.36 \times 10^{-18} m^2 \times \sqrt{\frac{8 \times 1.38 \times 10^{-23} JK^{-1} \times 298K}{\pi \times \left(\frac{2 \times 254}{2+254}\right) \times 1.66 \times 10^{-27} kg}} \times 6.023 \times 10^{23} mol^{-1} \times e^{-\frac{171000 J.mol^{-1}}{8.31 J K^{-1} mol^{-1} \times 298K}}$$

$$= 3.867 \times 10^8 \times e^{-69.05} m^3 K^{-1} mole^{-1} = 4 \times 10^{-22} m^3 s^{-1} mol^{-1} = 4 \times 10^{-16} lit.s^{-1} mol^{-1}$$