ADVANCED CHEMISTRY

QUANTUM MECHANICS – SPRING – WEEK 7

Chapter 13

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

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

When $J=0$

$2906.25\ cm^{-1} = \tilde{\nu}_0 + 2B_1$ —— ①

When $J=1$

$2925.78\ cm^{-1} = \tilde{\nu}_0 + 2B_1 + (3B_1 - B_0) + (B_1 - B_0)$

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

When $J=2$

$2944.89\ cm^{-1} = \tilde{\nu}_0 + 2B_1 + (3B_1 - B_0)2 + (B_1 - B_0)4$

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

② – ③

$(2925.78 - 2944.89)\ cm^{-1} = 4B_0 - 6B_1$

$19.11 = 6B_1 - 4B_0$

$9.555 = 3B_1 - 2B_0$ —— ④

① – ②

$(2906.25 - 2925.78)\ cm^{-1} = -4B_1 + 2B_0$

$-19.53 = -4B_1 + 2B_0$

$19.53 = 4B_1 - 2B_0$ —— ⑤

⑤ − ④ $\quad 9.975\ cm^{-1} = B_1$

Substitute in ④ $\quad 9.555\ cm^{-1} = 3(9.975\ cm^{-1}) - 2B_0$

$B_0 = 10.185\ cm^{-1}$

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

$v=1 \quad B_1 = B_e - \alpha_e\left(\tfrac{3}{2}\right)$ —— ⑥

$v=0 \quad B_0 = B_e - \alpha_e\left(\tfrac{1}{2}\right)$ — ⑦

⑦ − ⑥ $\quad B_0 - B_1 = \alpha_e\left[-\tfrac{1}{2} + \tfrac{3}{2}\right]$

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

Substite α_e in ⑥

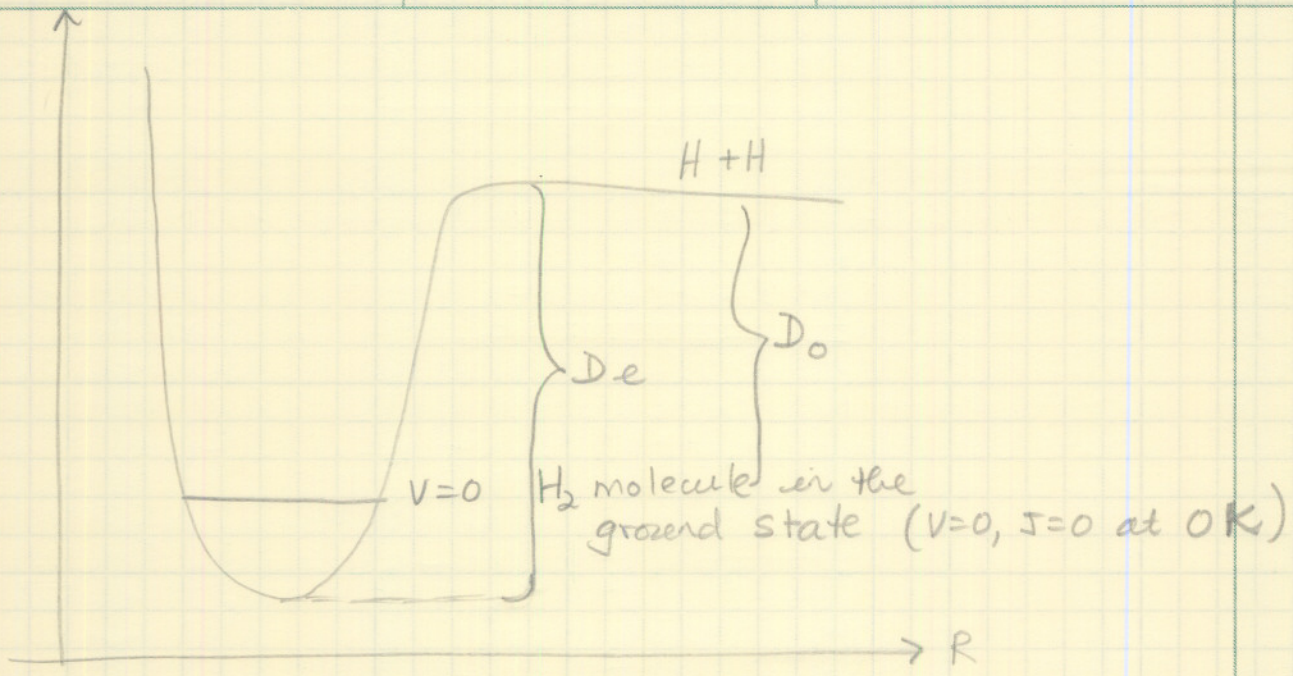
$9.975\ cm^{-1} = B_e - 0.210\left(\tfrac{3}{2}\right)$

$B_e = 10.29\ cm^{-1}$

↳ Using ① $\quad 2906.25\ cm^{-1} = \tilde{\nu}_0 + 2(9.975\ cm^{-1})$

$\tilde{\nu}_0 = 2886.30\ cm^{-1}$

(27)



$$D_e = 4.7483\ eV = 458.135\ kJ\,mol^{-1}$$

D_e = D_0 + energy of V=0 state at J=0

$$= D_0 + \left[\left(V+\tfrac{1}{2}\right)\omega_e - \left(V+\tfrac{1}{2}\right)^2 \omega_e x_e \text{ at } V=0\right]$$

$$= D_0 + \left[\tfrac{1}{2}\omega_e - \tfrac{1}{4}\omega_e x_e\right]$$

$$D_0 = D_e - \left(\tfrac{1}{2}\omega_e - \tfrac{1}{4}\omega_e x_e\right)$$

From Table 13.4

$$\tfrac{1}{2}\omega_e - \tfrac{1}{4}\omega_e x_e = \left[\tfrac{1}{2}(4401.21) - \tfrac{1}{4}(121.34)\right] cm^{-1}$$

$$= 2170.27\ cm^{-1}\left[2.998\times10^{10}\ cm\,s^{-1} \times 6.626\times10^{-34}\ J\,s\right]$$

$$= 4.3112\times10^{-20}\ J \times \frac{10^{-3}\ kJ}{J} \times \frac{6.02\times10^{23}}{mol}$$

$$= 25.9533\ kJ\,mol^{-1}$$

$$D_0 = D_e - 25.9533\ kJ\,mol^{-1} = 432.1817\ kJ\,mol^{-1}$$

D_0 = bond dissociation energy of H_2

$$H_2(g) \longrightarrow 2H(g) \quad \Delta H = 432.1817 \text{ kJ/mol}$$

$$\therefore \frac{1}{2} H_2(g) \longrightarrow H(g) \quad \Delta H = \frac{1}{2}(432.1817 \text{ kJ/mol})$$

$$= 216.09 \text{ kJ/mol}$$

This is the formation reaction for H(g)

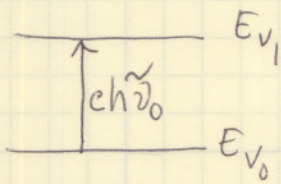
$$\Delta H_f [H(g) \text{ at } 0K] = \underline{216.09 \text{ kJ/mol}}$$

(57) $N_i \propto g_i e^{-E_i/kT}$ for vibrational levels $g_i = 1$

$$N_1 \propto e^{-E_{V_1}/kT}$$

$$N_0 \propto e^{-E_{V_0}/kT}$$

$$\frac{N_1}{N_0} = \frac{e^{(-E_{V_1} + E_{V_0})/kT}}{} = e^{-(E_{V_1} - E_{V_0})/kT}$$



For $H^{35}Cl$ $\tilde{\nu}_0 = 2990 \text{ cm}^{-1}$

$$E_{V_1} - E_{V_0} = (2990 \text{ cm}^{-1})(2.998 \times 10^{10} \text{ cm s}^{-1}) \times 6.626 \times 10^{-34} \text{ J s}$$

$$= 5.939 \times 10^{-20} \text{ J}$$

$$\frac{N_1}{N_0} = e^{-5.939 \times 10^{-20} \text{ J} / (1.381 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})}$$

$$= 5.94 \times 10^{-7}$$

For $^{127}I_2$ $E_{v_1} - E_{v_0} = (213\ cm^{-1})(2.998 \times 10^{10}\ cm\,s^{-1})(6.626 \times 10^{-34}\ J\,s)$

$= 4.231 \times 10^{-21}\ J$

$- 4.231 \times 10^{-21}\ J / (1.381 \times 10^{-23}\ J\,K^{-1})(300\ K)$

$\frac{N_1}{N_0} = e$

$= \underline{\underline{0.360}}$

(59) $R(0) = 2101.60\ cm^{-1}$

$R(1) = 2111.94\ cm^{-1}$

$R(2) = 2122.05\ cm^{-1}$

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

$\tilde{\nu}_R(0) = 2101.60\ cm^{-1} = \tilde{\nu}_0 + 2B_1$ —— ①

$\tilde{\nu}_R(1) = 2111.94\ cm^{-1} = \tilde{\nu}_0 + 2B_1 + (3B_1 - B_0)1 + (B_1 - B_0)1^2$

$2111.94\ cm^{-1} = \tilde{\nu}_0 + 6B_1 - 2B_0$ —— ②

$\tilde{\nu}_R(2) = 2122.05\ cm^{-1} = \tilde{\nu}_0 + 2B_1 + (3B_1 - B_0)2 + (B_1 - B_0)4$

$2122.05\ cm^{-1} = \tilde{\nu}_0 + 12B_1 - 6B_0$ —— ③

③ − ② $10.11\ cm^{-1} = 6B_1 - 4B_0$

$5.055\ cm^{-1} = 3B_1 - 2B_0$ —— ⑤

② − ① $10.34\ cm^{-1} = 4B_1 - 2B_0$ —— ⑥

Substituting in ⑤

$$5.055\ cm^{-1} = 3(5.285\ cm^{-1}) - 2B_0$$

$$B_0 = 5.40\ cm^{-1}$$

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

$v=1$ $\quad B_1 = B_e - \alpha_e\left(\tfrac{3}{2}\right)$ — ⑦

$v=0$ $\quad B_0 = B_e - \alpha_e\left(\tfrac{1}{2}\right)$ — ⑧

⑧ − ⑦ ⇒ $B_0 - B_1 = \alpha_e\left[\tfrac{3}{2} - \tfrac{1}{2}\right] = \alpha_e$

$$\alpha_e = 0.115\ cm^{-1}$$

⑦ ⇒ $B_e = B_1 + \tfrac{3}{2}\alpha_e = 5.458\ cm^{-1}$

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

For $^2H^{35}Cl$

$$\mu = \frac{2\times 35}{2+35}\ amu$$

$$= 1.8919\ amu$$

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

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

$$R_e^2 = \frac{6.626 \times 10^{-34}\ J\,s}{8\pi^2 (3.142 \times 10^{-27}\ kg)(5.458\ cm^{-1})(2.998 \times 10^{10}\ cm\,s^{-1})}$$

$$= 1.632 \times 10^{-20}\ m^2$$

$$R_e = 1.278 \times 10^{-10}\ m \times \frac{10^{12}\ pm}{m} = \underline{\underline{127.75\ pm}}$$

For $^1H^{35}Cl$ $R_e = \underline{\underline{127.455\ pm}}$

(I am not as concerned with the accuracy of t answers as much as I am with the proce of getting to the answers).