ADVANCED CHEMISTRY

QUANTUM MECHANICS – SPRING – WEEK 8

Chapter 13

(30)

molecule	total # of degrees of freedom	translational	rotational	vibrational
(a) Ne	3	3	0	0
(b) N_2	6	3	2	1
(c) CO_2	9	3	2	4
(d) CH_2O	12	3	3	6

(31) (a) ν_4 and ν_5 are doubly degenerate because these two inplane modes have out-of-plane counterparts that are degenerate with ν_4 and ν_5.

(b) ν_3, $\cancel{\nu_4}$, ν_5 (c) cannot do this yet but the answer is ν_1, ν_2, ν_4

(34) $N_j \propto e^{-E_j/kT}$ (no degeneracy)

$$N_0 \propto e^{-E_0/kT} \qquad \frac{N_1}{N_0} = e^{-(E_1-E_0)/kT}$$

$$N_1 \propto e^{-E_1/kT} \qquad \frac{N_1}{N_0} = e^{-ch\tilde{\nu}/kT}$$

(34) Using Equation 13.73 from text

$$N_v = \left(1 - e^{-h\nu/kT}\right) e^{-vh\nu/kT}$$

When $v = 0$

$$N_0 = \left(1 - e^{-h\nu/kT}\right) e^{0} = 1 - e^{-h\nu/kT}$$

$$\frac{h\nu}{kT} = \frac{hc\tilde{\nu}}{kT} = \frac{(6.626\times10^{-34}\,\mathrm{J\,s})(2.998\times10^{10}\,\mathrm{cm\,s^{-1}})(559.7\,\mathrm{cm^{-1}})}{(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})(1000\,\mathrm{K})}$$

$$= 0.8051 \qquad e^{-h\nu/kT} = 0.447$$

$$N_0 = 1 - 0.447 = \underline{\underline{0.553}}$$

when $v = 1$

$$N_1 = \left(1 - e^{-h\nu/kT}\right) e^{-h\nu/kT}$$

$$= (0.553)(0.447) = \underline{\underline{0.247}}$$

When $V = 2$

$$N_2 = \left(1 - e^{-h\nu/kT}\right) e^{-2h\nu/kT}$$

$$= (0.553)\, e^{-2(0.8051)} = \underline{\underline{0.111}}$$

When $V = 3$

$$N_3 = \left(1 - e^{-h\nu/kT}\right) e^{-3h\nu/kT} = (0.553)\, e^{-3(0.8051)}$$

$$= \underline{\underline{0.049}}$$

(60) HBr $\nu = 2645\ cm^{-1}$ $2B = 16.9\ cm^{-1}$

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

$$\frac{\nu_{DBr}}{\nu_{HBr}} = \sqrt{\frac{\mu_{HBr}}{\mu_{DBr}}} = \sqrt{\frac{\left(\frac{1\times 80}{81}\right)}{\left(\frac{2\times 80}{82}\right)}} = 0.7115$$

$$\nu_{DBr} = (2645\ cm^{-1})(0.7115) = \underline{\underline{1881\ cm^{-1}}}$$

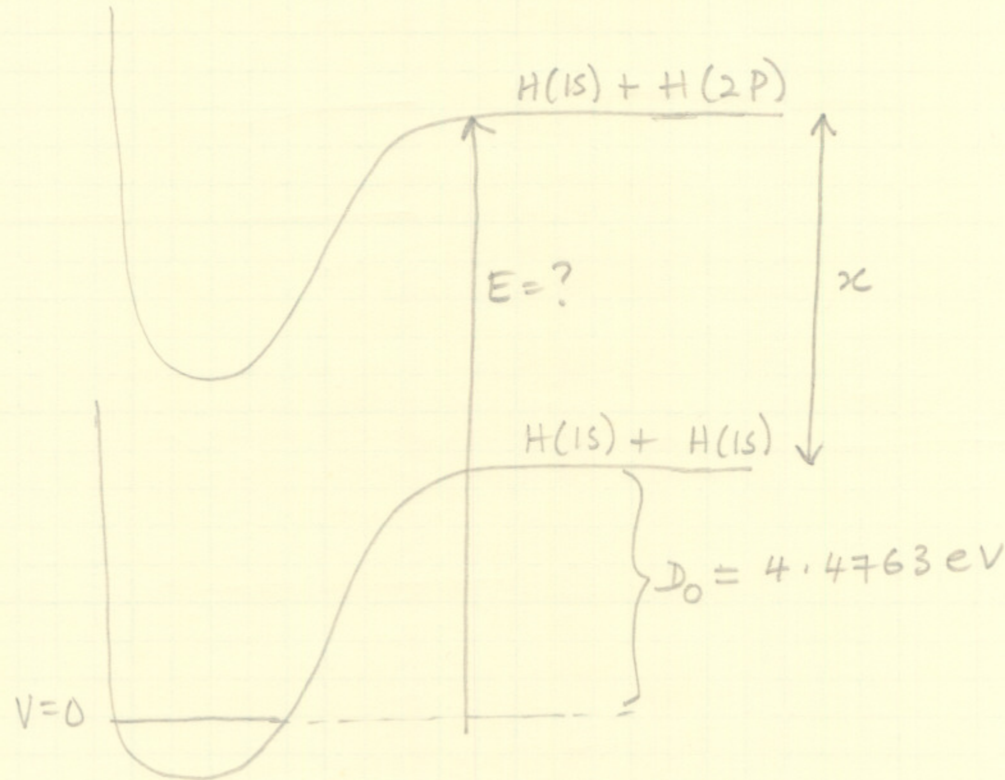
$$B \propto \frac{1}{I} \propto \frac{1}{\mu R^2}$$

$$\frac{B_{DBr}}{B_{HBr}} = \frac{\mu_{HBr}}{\mu_{DBr}} = \frac{\left(\frac{80}{81}\right)}{\left(\frac{160}{82}\right)} = 0.506$$

$$B_{DBr} = (8.45\ cm^{-1})(0.506) = 4.28\ cm^{-1}$$

Space between lines $= 2B = \underline{\underline{8.55\ cm^{-1}}}$

Chapter 14



x = energy difference between H(2P) and H(1S)

Energy of a H atom $E_n = -13.6\,\text{eV}\left(\frac{Z^2}{n^2}\right)$

energy of H(1S) $= E_1 = -13.6\,\text{eV}\left(\frac{1}{1}\right) = -13.6\,\text{eV}$

energy of H(2P) $= E_2 = -13.6\,\text{eV}\left(\frac{1}{4}\right) = \frac{-13.6}{4}\,\text{eV}$

$$x = E_2 - E_1 = -13.6\,\text{eV}\left(\frac{1}{4} - 1\right) = 10.2\,\text{eV}$$

$$E = x + D_0 = 10.2\,\text{eV} + 4.4763\,\text{eV}$$

$$= 14.6763\,\text{eV}$$

If H_2 is dissociated by photons with 15 eV, the excess energy = 15 eV − 14.6763 eV = 0.3237 eV

This energy is the kinetic energy of the two H atoms being ejected.

$$\text{Kinetic energy of 2 atoms} = 2\left(\frac{1}{2}mv^2\right) = 0.3237\ eV$$

$$v^2 = \frac{2 \times 0.3237\,eV}{2 \times m} \times \frac{1.602 \times 10^{-19}\,J}{eV}$$

$$= \left(\frac{0.3237\ eV}{1.008\ g \cdot mol^{-1}}\right) \times \left(\frac{1.602 \times 10^{-19}\,J}{eV}\right)\left(\frac{6.02 \times 10^{23}}{mol}\right)$$

$$= \frac{6.1939 \times 10^{4}}{2}\ \frac{J}{g} \times \frac{10^3\,g}{kg} = 6.1939 \times 10^{7}\ m^2 s^{-2}$$

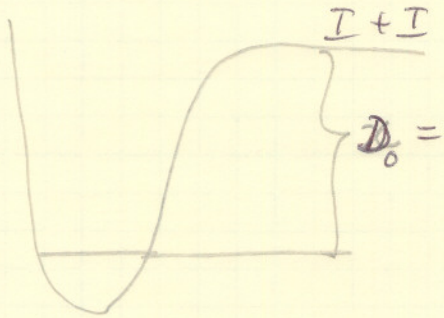
$$mv^2 = 0.3237\ eV \qquad m = 1.008\ g/mol$$

$$v^2 = \frac{0.3237\,eV}{1.008\ g\ mol^{-1}} \times \left(\frac{1.602 \times 10^{-19}\,J}{eV}\right)\left(\frac{10^3\,g}{kg}\right) \times \left(\frac{6.02 \times 10^{23}}{mol}\right)$$

$$= 3.0969 \times 10^{7}\ m^2 s^{-2}$$

$$v = \underline{\underline{5.57 \times 10^{3}\ m s^{-1}}}$$

(4)



$D_0 = 1.5423$ eV

kinetic energy of one I atom $= \frac{1}{2} m v^2$

$= \frac{1}{2}(126.904 \times 10^{-3}\ \text{kg mol}^{-1})(10^3\ \text{m s}^{-1})^2$

kinetic energy of two I atoms $= (126.904 \times 10^{-3}\ \text{kg mol}^{-1})(10^6\ \text{m}^2\ \text{s}^{-2})$

$= \dfrac{126.904 \times 10^3\ \text{kg m}^2\ \text{s}^{-2}\ \text{mol}^{-1}}{6.02 \times 10^{23}\ /\text{mol}}$

$= 2.108 \times 10^{-19}\ \text{J} \times \left(\dfrac{1\ \text{eV}}{1.602 \times 10^{-19}\ \text{J}}\right)$

$= 1.316$ eV

Energy of the required photon $= D_0 +$ kinetic energy of the two I atoms

$= (1.5423 + 1.316)$ eV $= 2.858$ eV

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

$= \dfrac{(6.626 \times 10^{-34}\ \text{J s})(2.998 \times 10^{8}\ \text{m s}^{-1})}{(2.858\ \text{eV})} \times \left(\dfrac{\text{eV}}{1.602 \times 10^{-19}\ \text{J}}\right)$

$= 4.338 \times 10^{-7}$ m $=$ $\underline{\underline{433.8\ \text{nm}}}$

~~8~~ 20

$$\text{Energy of photon} = \frac{hc}{\lambda} = \frac{(6.626\times10^{-34}\,Js)(2.998\times10^{8}\,ms^{-1})}{(58.43\times10^{-9}\,m)}$$

$$= \cancel{3.3998\times10^{-18}\,J}$$

$$= 3.3998\times10^{-18}\,J \times \left(\frac{eV}{1.602\times10^{-19}\,J}\right)$$

$$= 21.22\ eV$$

K.E. of the Ar atom $= 21.22\,eV - 15.755\,eV$
$= 5.47\,eV$

K.E of Kr atom $= 21.22\,eV - 13.966\,eV$
$= 7.26\,eV$

K.E of Xe atom $= 21.22 - 12.130)\,eV$
$= 9.09\,eV$

Ar atom

$$\frac{1}{2}mv^2 = 5.47\,eV$$

$$V^2 = \frac{2\,(5.47\,eV)}{39.948\times10^{-3}\,kg\,mol^{-1}} \times \left(\frac{1.602\times10^{-19}\,J}{eV}\right) \times \left(\frac{6.02\times10^{23}}{mol}\right)$$

$$V = \cancel{5139.14}\ 5139.14\ ms^{-1} = \underline{\underline{5.14\,kms^{-1}}}$$

Kr atom

$$V^2 = \frac{2\,(7.26\,eV)}{83.80\times10^{-3}\,kg\,mol^{-1}} \times \left(\frac{1.602\times10^{-19}\,J}{eV}\right) \times \left(\frac{6.02\times10^{23}}{mol}\right)$$

Xe atom

$$v^2 = \frac{2(9.09\,eV)}{131.29\times10^{-3}\,kg\,mol^{-1}} \times \left(\frac{1.602\times10^{-19}\,J}{eV}\right)\times\left(\frac{6.02\times10^{23}}{mol}\right)$$

$$V = 3654.35\ m s^{-1} = \underline{\underline{3.7\ km\,s^{-1}}}$$

(27) $B\ {}^3\Sigma_u^- \longleftarrow X\ {}^3\Sigma_g^-$ of O_2 is $\approx$ 6 eV from Fig. 14.1 (the lowest energy vibrational band) = longest wavelength

$$\cancel{6\,eV \times \left(\frac{1.602\times10^{-19}\,J}{eV}\right)\times\left(\frac{2.998\times10^{8}\,ms^{-1}}{6.626\times10^{-34}\,Js}\right)}$$

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

$$\lambda = \frac{(6.626\times10^{-34}\,Js)(2.99\times10^{8}\,ms^{-1})}{(6\,eV)} \times \left(\frac{1\,eV}{1.602\times10^{-19}\,J}\right)$$

$$= 2.06\times10^{-7}\ m = \underline{\underline{206\ nm}}$$